Moisture induced hygroscopic and mechanical properties of hemp reinforced biocomposite.

Requile S., Le Duigou A., Bourmaud A. and Baley C.

University Bretagne Sud, IRDL, Polymer and Composites, UMR CNRS 6027, 56100 Lorient, France
Email: samuel.requile@univ-ubs.fr,

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Abstract
Biocomposites reinforced with hemp fibres present a high potential for valorisation in new industrial applications due to their intrinsic mechanical characteristics. To reach certain markets, it is unavoidable to validate their behaviour and durability in humid and water environments. This article aims to provide a better insight into the effect of vapour water, ranging from 9% to 98% Relative Humidity (RH), on the evolution of the tensile properties of hemp/epoxy unidirectional biocomposites. The influence of reinforcement morphology is also studied using individualized hemp fibres from retting process. The evolution of water uptake and dimensional variations are found to be correlated with the water activity and dependant on fibre division. The use of Park model enables the understanding of water sorption mechanism predominantly governed by the distribution of the fibre for a water activity between 0.1 and 0.8. In addition, the evolution of mechanical properties, evaluated using tensile tests and SEM observations, evidence that above a water uptake of 3%, a dramatic decrease in stiffness of more than 50%.

1. Introduction

The current ecological trend is leading to an interesting alternative for the development of composite materials using cellulosic fibres as reinforcements such as hemp, flax or jute fibres. These plant-derived fibres are potential competitors of glass fibres due to their abundances, renewable character and good specific mechanical properties. Hemp fibre reinforcements present a potential for valorization in new and demanding structural applications. However, the development of high performance composites requires an advanced knowledge of their mechanical behaviour in various environments. From observations, and as a consequence of the nature of their applications, biocomposite structures are often subjected to humid environments during their lifetime.
They interact with humid environments because of the hydrophilic properties of the natural fibre reinforcements mainly explained by their complex multi-scale structure and biochemical composition [1]. The fibre cell wall rich in amorphous polysaccharides such as hemicellulose (~15%) and pectin (~6%) [2] leads to an important amount of available hydroxyl groups responsible for water sorption [3]. Water diffusion occurs by the penetration of water in the form of vapor water creating bonds with the fibre cell wall (monolayer water) and through micro-capillaries (polylayer water) in a continuous and dynamic process. Besides the composite mass gain, water sorption in natural fibres has been identified by Lee et al. [4] as the main contributor of their anisotropic swelling.
The important water sorption and anisotropic swelling of hemp fibres associated to the hydrophobic nature of a polymer matrix leads to fully or partially reversible consequences on the performances of biocomposite. Several authors have shown the impact of increasing moisture sorption in composites, inducing an alteration of the material mechanical properties described by physico-chemical processes: differential swelling, internal stress, fibre/matrix interface degradation, hydrolysis and plasticizing [5], [6]. Most of the work in literature deals with the influence of water sorption on the hygroscopic and

mechanical properties of biocomposites in water. However, a significant lack of information on the effect of a wide range of Relative Humidity (RH) on the performances of biocomposites in humid environments is existant.
The present study aims to evaluate the influence of water vapor on the hygroscopic and tensile properties of hemp/epoxy unidirectional biocomposites. As a first step, the water uptake of biocomposites is measured. In addition, swelling measurements across environments with varying relative humidity from 9% to 98% are also performed. A second topic completes this study by investigating the effect of retting degree on both hygroscopic and composite tensile performances. For this purpose, experiments are carried out on biocomposites using hemp fibres showing different retting degrees and thus different reinforcement aspect ratio.

2. Materials and Methods

2.1. Materials

Hemp fibres (Cannabis Sativa L., cultivars “Fedora 17”) were supplied by “Fibre Recherche Développement”, in Troyes, France. They were extracted using a mechanical process that includes breaking and scutching of the straws. Non-retted and retted fibres were extracted from straws harvested in Bar-sur-Aube. Non-retted straws were directly kept in controlled environment after harvesting to prevent retting whereas retted straws were laid out for field retting for 37 days. The thermoset resin was an epoxy system consisting of a DGEBA resin (AXSON Epolam 2020) and an aliphatic amine hardener at a weight ratio of 100:34.
Fibres were extracted and aligned to form a unidirectional bundle of around 1.25 g and 10 cm in length before being impregnated with epoxy resin. This laboratory protocol reduces fibre misalignment and enables a control of the fiber fraction. The impregnated fibres were placed in an aluminum mold of 6 x 2 mm² section open at each end to evacuate the excess of resin. The specimens were then cured with a temperature cycle of 3h at 40 ° C, 2h at 60 ° C then 2h at 80 ° C and finally 4h at 100 ° C.

2.2. Humidity controlled experiments

Samples were first oven-dried at 105°C for 15h to remove free and bonded water molecules [7]. Composites were placed in 4 climatic chambers for storage with monitored relative humidity, 9%, 33%, 75% and 98% using saturated salt solutions at a constant temperature or 23°C each. A continuous air flow within the chamber allowed homogeneous environment conditions. To characterize the samples, they were periodically removed from the chambers to be weighed and swealing measurements were performed.

2.3. Characterization of mechanical properties

The tensile properties of biocomposites with hemp fibre orientation set at 0° were measured using a 5566 Instron testing machine at controlled temperature (23°C) with a crosshead speed of 1 mm/min. Mechanical tests were performed on dry and wet samples that had reached their saturation time. A 10kN force sensor was used to measure the load and an axial extensometer with a nominal length of 25 mm (L_0) was used to measure the strain.

2.4. Scanning electron microscope observation

The samples were sputter-coated with a thin layer of gold in an Edwards Sputter Coater, and analyzed with a Jeol JSM 6460LV scanning electron microscope at 20 kV accelerating voltage.

3. Results and Discussions

3.1. Sorption isotherms: water vapor

The water vapor sorption experimental results at 23°C for hemp/epoxy unidirectional biocomposites are reported in figure 1. Water uptake (M_t) is measured from samples stored under different relative humidity corresponding to an activity of water (a_{water}) ranging from 0.09 to 0.98. The obtained isotherm shows a sigmoidal shape categorized in the BET sorption mode classification. This profile distributed in three distinct regions is generally obtained when observing water sorption in hydrophilic cellulosic compounds and to a larger extend in natural fibre composites [8]. The isotherm corresponds to the addition of Langmuir and Henry sorption followed by the formation of water molecule clusters. Given their behaviour, sorption isotherms can be well fitted by Park mathematical model (Figure 1a) given by the following formula [9]:

$$M_t = \frac{A_L \cdot b_L \cdot a_{water}}{1 + b_L \cdot a_{water}} + k_H \cdot a_{water} + K_a \cdot {a_{water}}^{n_a} \quad (1)$$

With (M_t) equilibrium moisture content for a specific water activity a_{water}; (A_L) Langmuir capacity constant; (b_L) Langmuir affinity constant; (k_H) Henry solubility constant; (K_a) Equilibrium constant for clustering reaction; (n_a) number of water molecules per cluster.
The contribution of each parameter is different in the specific range of water activity. However, it is to be noted that these models only give a simplified interpretation of the phenomenon occurring in the real system in continuous evolution. At low water activity (a_{water}<0.1) Langmuir terms A_L and b_L have a predominant effect. In the present case, because of a lack of numerous experimental data points for water activity below 0.1, Langmuir model and parameters were not taken into consideration. In the second region (0.1<a_{water}<0.7), Henry's coefficient k_H defines the slope of the isotherm. Finally, K_a and n are linked to the aggregate formation in the last region (a_{water}>0.7). The different Park parameters obtained from hemp/epoxy composites sorption isotherms are given in table 1. The observation of the regression coefficient R^2 indicates the consistency of Park model with the experimental sorption isotherms.

Table 1. Sorption parameters of Park model for hemp/epoxy composites

	Langmuir		**Henry**	**Clustering**		
	A_L	**b_L**	**k_H**	**K_a**	**n**	**R^2**
Hemp/epoxy composite	0.051	0.001	1.90	7.385	5.769	0.99
Retted hemp/epoxy composite	0.100	0.100	2.28	5.916	4.862	0.99

Depending on water activity (related to the storage relative humidity by a_{water} =RH/100), three different sorption mechanisms arise: Langmuir model is physically observed when sorption occurs on specific sites or micro cavities. A monolayer of water molecules is then adsorbed on hydroxyl groups at the fibre surface and is defined as free water. When saturation of specific sites is reached, new sorption sites are created. The resulting polylayer water, or free water, absorption will lead to diffusion of water in the free volume network and is responsible for capillarity mechanisms. This behaviour leads to a quasi-linear relation between water uptake and water activity and is representative of Henry type isotherm. Finally, clustering of water molecules linked to capillarity phenomenon induces an important increase in water uptake.

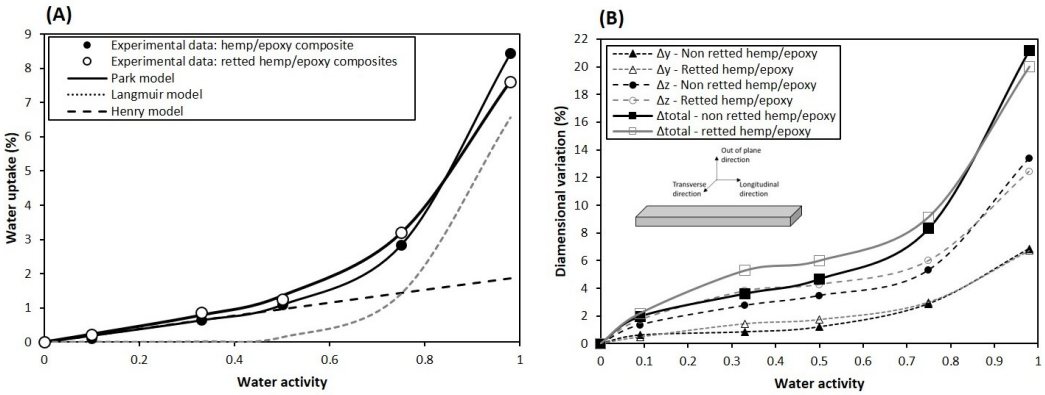

Figure 1. (A) Water vapor isotherm at 25° of non-retted and retted hemp/epoxy composites. Park model is used to fit experimental data and deconvoluted into Langmuir, Henry and clustering components. (B) Transverse swelling (Δy), out of plane swelling (Δz) and total swelling of non-retted and retted hemp/epoxy biocomposites over a range of water activity 0.09 and 0.98.

3.2 Influence of retting degree

The vapor sorption isotherms related to retted fibre bundles are presented in figure 1a in comparison to non-retted samples. Retting process does not influence the overall sorption behaviour of composites, although slight differences are observable in the water uptake at a given water activity. Data shows the influence of retting process on both Henry and clustering model resulting in a difference of water uptake between a water activity of 0.1 and 0.98. At this stage of the study it is not surprising to find a variation in moisture uptake related to retted samples. Indeed, this process plays an important role on the water sensitivity of natural fibres [10], [3].

The higher water sorption for retted samples between 0.1 and 0.8 is in agreement with the scanning electron microscopy images presented in figure 2. Important decohesion of fibres and reduction of surface roughness is observed between non-retted and retted hemp fibre bundles. Retting process results in degradation of the cementing substances present within fibre bundles and ensuring cohesion, leading to a modification of biochemistry and morphology. The alteration of the middle lamellae leads to reinforcement individualization which consequently is reflected by higher water molecule mobility and an increase in maximum water uptake at a given water activity. Hence, between $a_{water} = 0.1$ to $a_{water} = 0.8$, water uptake is governed predominantly (in addition to fibre surface/penetrant affinity) by the distribution of the reinforcement within the composite and more specifically by the ratio of the bundle perimeter and its surface area. This ratio being reduced when hemp bundles are individualized, accessibility of water molecules on specific sites is eased and biocomposites become less efficient in terms of moisture resistance. This implies a higher Henry solubility constant for retted composites (k_H=2.28) as compared to non-retted ones (k_H=1.90).

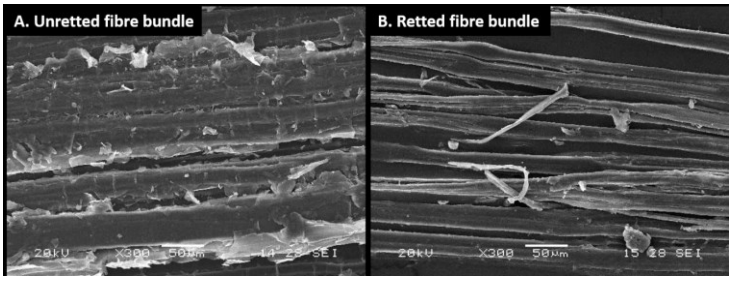

Figure 2. SEM microscope images of non-retted and retted hemp fibre bundle.

For water activity > 0.8 the tendency to form clusters, according to Park parameters (K_a and n), is also affected, resulting in a water uptake of 8.5% against 7.5% for non-retted and retted samples, respectively.

3.3. Dimensional variation

In addition to the moisture diffusion phenomenon, a variation in the sample volume is also observed. This is explained by swelling of the material and characterized by a hygroscopic volume deformation. Sorption of water molecules in natural fibres leads to dimensional variation of the overall biocomposite [4]. At the fibre scale, water is absorbed in the cell wall causing anisotropic swelling. This behavior can be explained by the low orientation of microfibrils in the case of hemp fibres [11]. The water-capturing constituents are mainly pectins and hemicelluloses present in the amorphous region of the fibre. The swelling of this region is constrained by the high rigidity of the cellulose microfibrils, which opposes the dimensional variations in the direction of the fibre but does not impede them in the perpendicular plane. Swelling of the amorphous region is reflected by very weak swelling in the longitudinal direction as compared to transverse direction, this anisotropy is enhanced by low microfibrils orientation.
When constrained in a polymeric matrix, swelling of natural fibres are drastically reduced but still contribute significantly to the hygroscopic expansion of the composite [12]. Figure 4 shows the sigmoidal evolution of transverse (Δy) and out of plane (Δz) swelling of non-retted and retted hemp/epoxy biocomposites with increasing water activity. The longitudinal swelling is here neglected regarding the low microfibral angle of hemp fibres leading to important longitudinal stiffness.
Unlike the transverse isotropic swelling of fibres, orthotropic swelling is observed with large thickness variation for both composite samples and could be due to composites manufacturing. As stated in section 2.1., a compression force is applied during composite manufacturing before epoxy cross-linking in the out-of-plane direction (Δz) for thickness control. The process in represented in figure 5. During composite compression, excess resin tends to diffuse out of the mold through the open sides leaving a heterogeneous distribution of resin (Figure 5.B). Dimensional changes of samples when placed in various relative humidity environment are schematically represented in figure 5.C. Due to manufacturing process and the compression direction, compression stresses may appear and tend to relax with humidity leading to a more important swelling in the out-of-plane direction. Moreover, in the compression direction, the resin surface between fibress is decreased in comparison to the other directions. The swelling of the fibers, closer to each other, will therefore have a greater impact at the composite scale and lead to a higher swelling of the overall structure in this same direction.

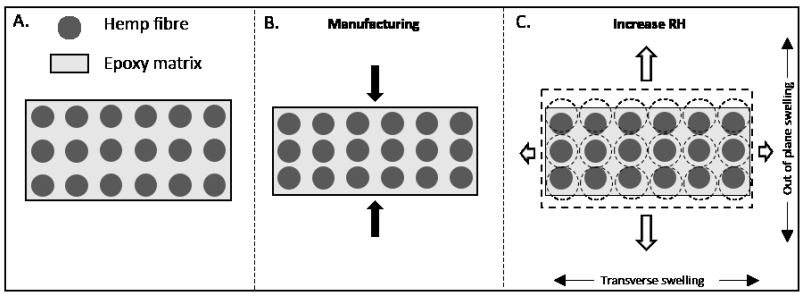

Figure 3. Schematic representation of dimensional variation of hemp/epoxy composite between initial state (A), after manufacturing (B) and after increasing the relative humidity.

Non-retted composites experience a slightly lower volume swelling as compared to retted samples for water activities ranging from 0.1 to 0.8. The differences in swelling between the samples may be explained by the specific fibre microstructure at the fibre bundle scale. The higher fibre division of retted hemp bundles leads to a more important swelling ability of the composite [13].

3.4. Tensile properties

3.4.1 Analysis of tensile behaviour

According to the previous results, the nature of the reinforcements plays an important role in the hygroscopic properties of biocomposites. It is clear that water sorption and structural anisotropy lead to reversible or partially reversible consequences in the mechanical properties of composites.
Figure 7 shows the evolution of tangent modulus as a function of applied strain for hemp/epoxy biocomposites after water saturation at relative humidity ranging from 9% to 98%. The tangent modulus evolution can be divided according to a range in deformation. Up to an applied strain of 0.4%, an important drop of stiffness of around 50% of the initial tangent modulus is noticeable. Tangent modulus then stabilizes before slightly increasing until failure of the material. As a result of the increase in water content, the tangent modulus of the material has a tendency to increase after 0.4% strain, reaching a maximum for high deformations. This effect is amplified with the increase of RH. Similar trend has previously been observed by Placet et al. (2012) [14] et the fibre scale. The evolution of composite stiffness reflects the non-linear behaviour of stress-strain curves of hemp/epoxy biocomposites associated to the intrinsic tensile behaviour of natural fibres. Indeed, natural fibres exhibit a non-linear behaviour attributed by many authors to the rearrangement of cellulose microfibrils which is hygro-activated with the increase in water content [15], [16].

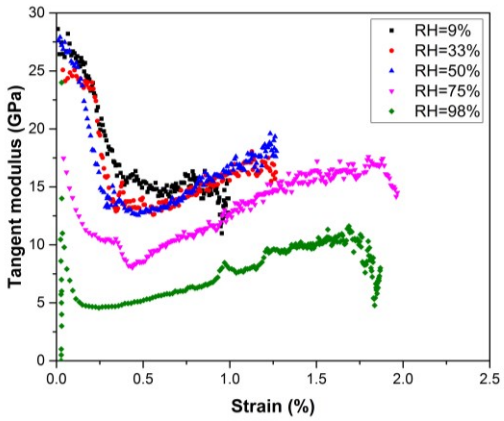

Figure 4. Evolution of tangent modulus with the longitudinal strain of hemp/epoxy UD composites saturated at different relative humidy: 9%, 33%, 50%, 75%, 98%.

3.4.2 Relationship between weigh gain and tensile properties

Reasoning in terms of water content rather than in relative humidity enables to quantify the evolution of tensile properties in proportion to the water absorbed in the samples. Figure 7a displays the evolution of tangent modulus, stress at break and strain at break for hemp/epoxy biocomposites as a function of water sorption in the humidity range of 9% to 98%. Each tested samples are represented in this figure. An important drop of the tangent modulus linked to the increase of water sorption in the sample is also shown. Samples stored in a dry environment (9%) show an average tangent modulus of 28.3 ± 4.8 GPa. The increase in water sorption, related to the increase in relative humidity leads to a continuous reduction the tangent modulus. A weight gain > 3% causes a decrease in stiffness of about 50%. For a higher water uptake (≈8 %) corresponding to a relative humidity of 98%, the stiffness reaches a value of 5.6 ± 1.3 GPa, slightly higher than pure epoxy. These results may be attributed to a

softening of the material leading to a general increase of the mobility of the molecular chains at the fibre, matrix and fibre/matrix interface, and consequently a decrease in composite stiffness.

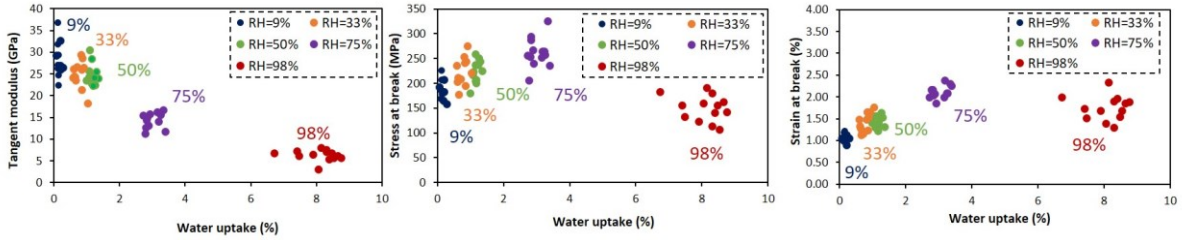

Figure 5. Evolution of the performances of hemp/epoxy composites as a function of water sorption.

Similar to composite stiffness, properties at break vary with moisture content. Both stress and strain at break shows optimal properties at around 3% water sorption, corresponding to samples stored at 75% RH. Figure 7b and c also show an increase of 35 % and 48 % between 9% RH and 75% RH for fracture stress and strain respectively. Beyond this water uptake in samples, properties at break are reduced. Explanation arise first from fibres scale. Indeed, increase in moisture content leads to plasticization favoring the realignment of cellulosic microfibrils, and improving fibre performances. Another hypothesis made for the evolution of composite performances concerns modification at the fibre/matrix interface level. As stated in section 3.3., water sorption of hemp fibre leads to more important radial swelling of the reinforcement as compared to the matrix itself. Compressive hygroscopic stresses will therefore be created at the fibre/matrix interface which could influence interfacial shear strength [17], [18].

4. Conclusion

Aimed at providing deeper insights in the effect of vapor and liquid water on hemp fibre reinforced epoxy biocomposites, this study has focused on the charactrization of their hygroscopic and mechanical behaviour. In order to evaluate the full potential of the use of hemp fibres in biocomposites, it is necessary to understand their behaviour and durability in humid environment. The results indicate that a modification of fibre division from retting leads to a variation of water molecule mobility and a change in hygroscopic behaviour. Unlike fibre, orthotropic swelling is observed with large thickness variation. Manufacturing step could be responsible of this phenomenon.
The increase of water activity leads to an important drop of the stiffness of the biocomposite from 3% water uptake. Both stress and strain at break show optimal properties at a water activity of 0.7 (≈3% water uptake in the material). These results are proposed to be related to the dominating hygroscopic swelling of hemp fibres and the related stress state improving the quality of the fibre/matrix interface.
The understanding of hygroscopic properties and induced mechanical properties of hemp/epoxy composites is today important for the development of new applications incorporating them. In order to continue is this field, extension of this work is to study the degradation of such materials for longer periods of time, analyses the diffusion processes related to the nature and the microstructure of the composites and the impact on composite performance.

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