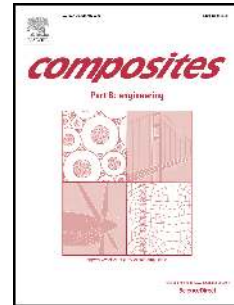


# Accepted Manuscript

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PII: S1359-8368(18)34239-2

DOI: <https://doi.org/10.1016/j.compositesb.2019.05.032>

Reference: JCOMB 6821

To appear in: *Composites Part B*

Received Date: 6 December 2018

Revised Date: 14 March 2019

Accepted Date: 5 May 2019

Please cite this article as: Moudood A, Rahman A, Khanlou HM, Hall W, Öchsner A, Francucci G, Environmental effects on the durability and the mechanical performance of flax fiber/bio-epoxy composites, *Composites Part B* (2019), doi: <https://doi.org/10.1016/j.compositesb.2019.05.032>.

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## Environmental effects on the durability and the mechanical performance of flax fiber/bio-epoxy composites

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### Abstract

The growing usage of bio-composite materials in different engineering applications demands a thorough understanding of their performance during their service. Extreme environmental conditions, such as warm, humid, and freezing environments, among others, can degrade the mechanical properties of the bio-composites when they are exposed to harsh environmental conditions. In addition, the use of these composites in underwater applications can also shorten their life cycle. In this work, the durability and mechanical performance (tensile and flexural behavior) of flax/bio-epoxy composites exposed to different environmental conditions were evaluated. These conditions were chosen to replicate those found outdoors that can affect the durability of these materials: water immersion, warm humid environment and freeze-thaw conditions. Moisture and water absorption behavior were evaluated and the water content (or exposure time) was related to the physical changes and mechanical properties. Results show that the mechanical properties of flax/bio-epoxy composites are clearly degraded by water ageing when they are compared to the “as manufactured” composites. The tensile strength and modulus is decreased approximately by 9% and 57%, respectively for water saturated (immersed in water until saturation) samples compared to as manufactured samples. On contrary, this reduction rate is only 0.8% and 3%,

respectively in case of humidity saturated (exposed to humid environment until saturation) samples. Furthermore, water incurred more severe effects on the flexural properties of the composites, since their flexural strength and modulus is decreased by 64% and 70%, respectively, as compared to as manufactured samples. It was found, however, that these properties can be partially regained after drying the water aged composites. Warm humid environments and freezing-thawing cycles have very little effect on the bio-composites.

**Keywords:** A. Flax fiber composites; B. Physical properties; C. Mechanical testing; E. Vacuum infusion.

## 1. Introduction

The environment is a major global concern nowadays due to the increasing rate of greenhouse gas emissions. Traditional metals, metal-based alloys or synthetic materials are usually responsible for emitting carbon dioxide (CO<sub>2</sub>) gas during their processing and usage. In this context, researchers are interested in environment-friendly materials, such as bio-composites, and consider these as a possible replacement of metal and metal-based alloys or synthetic fiber composites. Bio-composites possess satisfactory mechanical properties, and are inexpensive, lightweight and structurally efficient materials [1]. Alternatively, high-performance composites, where synthetic fibers, such as glass and carbon fibers are used, have a wide range of applicability from household to aerospace industries. However, recycling problem and their dependency on large volumes of fossil fuels for processing, generate environmental hazards on earth.

The natural fiber composites are potentially environmentally superior to synthetic fiber i.e., glass reinforced composites in most applications, as the specific properties of the natural fiber composites are higher than those of glass in certain circumstances. Several mechanical properties of natural fiber composites could be compared with glass fiber composites. In addition, natural fiber composites are also the best choice for commercial purposes [2-4].

Therefore, different interior parts and accessories are manufactured by natural fiber reinforced bio-composites in the production industries, especially in automotive, construction and packaging industries [5]. However, bio-composites are mainly used for indoor applications due to their low durability and immediate degradation problem in the harsh and humid environment during outdoor usage. The lignocellulosic chemical composition and microstructure of the vegetable fibers are responsible for moisture absorption from the surrounding environment. This behavior causes weakening of the fiber-matrix bonding which might result in lower mechanical properties and poor dimensional stability. The highly hydrophilic nature of vegetable fibers and the moisture sensitivity of their composites are the main disadvantages in applying these composites for exterior usage [6, 7]. Therefore, it is important to consider the moisture absorption behavior of the bio-composites in moist and humid environments for their potential applications.

The temperature and humidity of the surrounding environment and nature of the fiber used in the composites influence the water and moisture absorption behavior of the bio-composites. The water molecules spread within the composites via the moisture diffusion mechanism inside the matrix. In general, the diffusion behavior of the polymeric composites is differentiated as Fickian, pseudo-Fickian and non-Fickian. For example, Assarar et al. [8] concluded that the water absorption behavior of the flax fiber reinforced epoxy composites, was Fickian at room temperature, and absorbed 13.5% moisture at saturation level. Different studies [8, 9] have stated that water diffusion is mainly assisted by three main mechanisms. Firstly, as defects generate into the matrix, such as cracks and pores and diffusion of water molecules occur inside the micro gaps and pores. The second cause of water diffusion is due to the capillary transport of water molecules along the fiber/matrix interface. Finally, the micro-cracks are transported to the matrix due to the fiber swelling. The moisture absorption behavior of the natural fiber composites has been studied by many researchers. For example, the water absorption behavior of flax fiber composites was compared with jute fiber

composites indicating that jute composites absorbed more moisture content (MC) than the flax fiber bio-composites. The saturated moisture contents were 9.61% for flax and 14.41% for jute bio-composites after forty days of water immersion at room temperature [10]. Berges et al. [11] reported on the moisture absorption trend of unidirectional (UD) flax fiber-reinforced epoxy laminates. They found that the diffusion kinetics of UD flax/epoxy composites follow a one-dimensional Fickian behavior when exposed to hygrothermal conditioning at 70°C and 85% relative humidity (RH). Chilali et al. [12] also compared the water uptake behavior of the flax fiber reinforced thermoplastic and thermosetting composites when they are immersed under water for different time durations. The water absorption tendency was found to be the same for two different conditions of the flax composites. The amount of absorbed water increased linearly at the beginning, but the absorption slowed down as the saturation level was reached. However, flax composites with a thermosetting resin (epoxy) absorbed more water than the composites with the thermoplastic resin (acrylic).

The environmental degradation problem of bio-composites is a critical issue that must be considered for their potential use in engineering applications. Scida et al. [13] found that the tensile properties of the flax composites are influenced by hygrothermal ageing. At 90% RH and 20°C, the reduction of Young's modulus was 33% for the first 3 days and reduced by 55% after 38 days. Environmental degradation of the flax bio-composites was studied by testing the interfacial strength of a single flax fiber/epoxy micro-composite. The shear strength of the composites was reduced by 60% after 135 hours when immersed under water. The interfacial strength decreased due to the swelling of the fibers at the fiber-matrix interface. In addition, polysaccharides (pectin and hemicellulose) present at the middle lamella of the fiber, act as matrix materials which cover the cellulose microfibrils within the fiber. These polysaccharides contain high polar components which accelerate the generation of hydrogen bonds with the absorbed water [6]. Assarar et al. [8] also reported poor fiber-

matrix interface of the water absorbed composites after analyzing their acoustic emission test results.

Moudood et al. [14] reported the effects of moisture present in the fibers prior to manufacturing flax-epoxy bio-composites. Composite panels, manufactured with flax fibers taken from 70% and 95% RH environments, showed severe warpage. The fiber-matrix interface became weaker due to the high moisture content in the fibers and porosity was increased in the microstructure of the composites. Although the fiber-matrix interface was affected, the optimum tensile strength was found in composites made with 50% RH conditioned fabrics and, below and above that value, the tensile strength of the composites decreased. They indicated that the water molecules in the fibers plasticized and deformed, which increased the strain at break and resulted in the decreased Young's modulus.

Over the years, researchers have developed different methods to reduce moisture absorption tendency of the bio-based fibers which are also responsible to reduce the moisture absorption effects of the natural and cellulosic fiber reinforced composites. Pothan and Thomas [15] studied the hybridization and chemical modification effects on banana fiber reinforced polyester composites. They found that banana/polyester composites absorbed less water when these composites were hybridized with glass fibers and water uptake was inversely proportional with the increase of glass fiber content. They further showed that water uptake was minimum for the silane treated banana fiber reinforced composites. Similar results were found by Dhakal et al. [16], when flax/epoxy composites were hybridized with carbon fibers, then the moisture absorption rate was 85% less than the UD flax/epoxy composites and 65% less than the cross-ply (CP) flax/epoxy composites. Both the tensile and flexural properties were increased more than 50% for the flax fiber composites hybridized with carbon fibers than the UD and CP flax/epoxy composites. In a different study [17], surface modification of the flax fibers with vinyltrimethoxy silane (VTMO) and maleic anhydride-polypropylene (MAPP) was investigated where polypropylene (PP) was used as the matrix

material to manufacture the composites. They reported that untreated flax/PP composites absorbed 38% more water than the silane and MAPP treated composites. All the tensile, flexural, and impact properties of the treated flax/PP composites were higher than the untreated composites. Increased mechanical property indicated that chemical covalent bond strongly connected the flax fibers and PP matrices and therefore, superior compatibility was found by the MAPP treatment. These above explained methods are just a few examples of the available means to reduce hydrophilicity of vegetable fibers and their composites. However, many manufacturers of composite parts utilize raw untreated fiber fabrics as reinforcements for many reasons (costs, complexity of the usage of chemical treatments, etc.), and therefore the study of the durability and performance of raw flax fiber based composites is still of great interest.

The acceptance of natural fiber reinforced composites for useful engineering applications is dependent on their durability. Flax fiber reinforced composites could be exposed to a range of harsh environments such as humidity, basic, acid and alkaline solutions, temperature, freeze-thaw, thermal cycles, UV rays, etc. in practical applications [18]. Therefore, it is significant to study the durability and performance of flax fiber reinforced composites for their proper selection in practice. This article deals with the effects of water saturation (WS), humidity saturation (HS) and freeze-thaw (F/T) cycling on the physical and mechanical properties of the flax/bio-epoxy composites. The water saturated and completely dried (WSD) and water saturated and freeze-thaw (WSF/T) samples are manufactured and tested to understand the feasibility of using the bio-composites in different environments. The mechanical properties are also compared to the “as manufactured (AM)” composites. Finally, degradation of the bio-composites is discussed with enhanced exposure time.

## **2. Experimental procedure**

### 2.1. Materials

The unidirectional (UD) flax fiber fabrics (FlaxPLY UD, 180 gm/m<sup>2</sup>) were procured from Lineo, France and a bio-epoxy resin (Greenpoxy 56, Sicomin) was used. Up to 56% of the molecular structure of this bio-epoxy resin has been extracted from plant origin. A multi-purpose hardener (series SD 8605) was used, leading to a total of 37% of bio-based content in the mixture. TR 102 regular wax (TR industries, USA) was used to free the mold surface from impurities.

### 2.2. Preparation of Composite samples

Moisture content in flax fibers changes with laboratory conditions (temperature and humidity). The temperature and humidity of the storage room was controlled and set to 20°C and 55% RH respectively, and the equilibrium moisture content of the flax fibers under these conditions is roughly 6%. However, in order to obtain composite samples with identical moisture content in the fibers, a drying step prior to manufacturing was performed. Ten layers of fabrics (300 mm × 300 mm) were dried in the oven for 4 h at 60°C, then placed on the mold (a flat aluminum plate), and the stacking sequence was [0<sub>10</sub>] (all ten layers at the same orientation, obtaining unidirectional composites). The vacuum infusion set up was prepared and the vacuum bag was completely sealed to the mold (Fig.1). Full vacuum (vacuum level reached was -100 kPa) was applied, and the stack of flax fabrics was dried in the oven for another 3 h under full vacuum at 45°C. The resin was infused 15 minutes after the mold was withdrawn from the oven, allowing the system to cool down and reach the laboratory temperature. This procedure allowed to manufacture composite samples having a negligible moisture content in the fibers.

All composites were cured under full vacuum at room temperature for 24 h and then post cured for 8 h at 60°C. The test samples were cut from the panels by means of a laser cutter device to the required shape and dimensions given by the standards used for the mechanical characterization.



The average thickness of the as manufactured composite samples was 2.5 mm. The void content of the AM composites was negligible, as shown in Fig 1. c and the adhesion between fibers and matrix was very good, as shown in the SEM image (Fig.1. d). The volumetric fiber content in the composites was 50%, estimated with Eq. (1), where: n is the number of fabric layers,  $\delta$  is the areal weight of the fabrics (180 g/cm<sup>2</sup>),  $\rho$  is the flax fibers density (1.45 g/cm<sup>3</sup>) and t is the panel thickness (cm).

$$\text{Fiber volume fraction} = (n \delta) / (\rho t) \quad (1)$$

**Fig. 1.** (a) Schematic diagram to process flax/bio-epoxy composite by vacuum infusion, (b) Composite plate manufactured by vacuum infusion method and flexural and tensile samples, (c) Optical micrograph of the “as manufactured” composites, (d) SEM image of the fiber-matrix interphase of AM composites.

### 2.3. Weathering tests

#### 2.3.1. Water absorption tests

Water absorption was measured by immersing the test samples into the distilled water at room temperature. The specimens were withdrawn from the water and wiped dry to remove the surface moisture before the weight and thickness measurements. Then the samples were weighed periodically using an analytical scale accurate to 100  $\mu$ g. To calculate the correct thickness, the sample thickness was measured at three different positions and finally, the average thickness was determined. After collecting the specimen weight and immersion time data, the relative water absorption (WA) was calculated using Eq. (2):

$$M_r(t) = \frac{W_t - W_0}{W_0} \times 100 \quad (2)$$

Where,  $M_r(t)$  is the relative WA of the specimen at each time t,  $W_t$  is the specimen weight at each time,  $W_0$  is the initial specimen weight. The WA tests were stopped after 30 days.

One set of the WS samples were completely dried (WSD) to estimate the residual properties of samples that have been fully saturated but dried afterwards. The drying process was performed in a dehydrating oven at 40°C for three days (until no changes in the weight were observed). This drying cycle (low temperature-long time) was chosen to avoid possible damage to the mechanical properties of the bio-composite at higher temperatures.

### *2.3.2. Humidity tests*

The tensile and flexural test specimens from each batch were conditioned in a climate chamber (CH700 V, Angelantoni) at 75% RH and 45°C. These specimens were periodically removed from the chamber to measure the weight and dimensional changes at certain periods of time. After 30 days, weighing of the samples was terminated as the weight reached at saturation point or in other words, the weight gain due to moisture absorption was nearly constant.

### *2.3.3. Freeze/Thaw (F/T) cycling tests*

The composite samples were exposed to F/T weathering tests. F/T cycling was done according to the ASTM D7031-04 standard recommendations. In the weathering test, two types of F/T cycling were considered. For the first type, F/T cycling was performed on the as manufactured (AM) specimens for 1, 5 and 10 cycles. One complete F/T cycle for AM specimens consists of two stages: at first, the samples were placed in a freezer for 24 h at a temperature of -18°C. Next, the samples were removed from the freezer and allowing them to thaw at room temperature for another 24 h. For the second type, water saturated (WS) samples were subjected to 1, 5 and 10 F/T cycles. One complete F/T cycle for WS specimens consists of two stages: the water saturated samples were kept inside the freezer for 24 h and then they were thawed in water at room temperature so that the water content remained in the samples at the saturation level. The mechanical performance of the materials under freezing process at

the most favourable condition (AM samples) and the most unfavourable condition (WS samples), where maximum moisture content existed in the microstructure was determined by this type of tests.

#### *2.4. Mechanical properties characterization*

##### *2.4.1. Tensile testing*

The tensile test was carried out using an Instron 3367 testing machine (serial no. 68296) according to ASTM D3039/D3039 M. Test specimens were cut by a laser cutter from the composite plates (parallel to the fiber direction). The test specimen dimensions were  $250 \times 15 \times 2.5$  mm. The crosshead displacement rate was set at 2 mm/min. The tensile modulus was calculated over the axial strain range of 1000-3000 microstrain. All strength and modulus values were calculated by taking the average of five samples for each weathering condition.

##### *2.4.2. Flexural testing*

ASTM D790-03 standard was followed for the flexural test using the same Instron 3367 testing machine. Calculations of flexural strength and modulus were performed according to the recommendations provided by the same standard. The test specimen dimensions were  $80 \times 12.7 \times 2.5$  mm. Three-point bending tests were performed where the test span was taken as 60 mm and the crosshead displacement rate was set at 2.4 mm/min. Five samples were tested for each weathering condition and the average value for each property was reported.

### **3. Results and discussion**

#### *3.1. Moisture absorption and dimensional stability*

The main constituents of the plant fibers are cellulose, hemicellulose, pectin and lignin. Cellulose is the main constituent of the flax fiber. More than 75% of the total mass of the fiber contains cellulose. Celluloses consist of the hydroxyl (OH) groups which permit

moisture or water absorption by establishing hydrogen bonds with the water molecules. The water absorption of the cellulose micro fibrils depends on their crystallinity. Nakamura et al. [19] reported that the bound water volume in the cellulose decreases when the rate crystallinity increases and the moisture diffusion within cellulose occur mainly in the amorphous phase. Hemicellulose and lignin constitute the major part of the amorphous phase and act as the key participants to absorb and store moisture. Pectin is located at the middle lamella and the S<sub>2</sub> layer of the fiber structure. Pectin consists of highly polar carboxyl (COOH) groups which have the ability to generate hydrogen bonds with the absorbed water molecules. On the other hand, these fibers are particularly porous and have surfaces which can be vastly exchanged. Therefore, when the fibers are placed in a humid environment, they can absorb moisture and be stored inside the free volume of the structure. The saturated water and moisture content (MC) of the bio-epoxy matrix and flax/bio-epoxy composites exposed to different environmental conditions are illustrated in Fig 2. The water immersed samples clearly absorbed more water than the samples exposed to other environmental conditions.

**Fig. 2.** Moisture content absorbed by WS epoxy and flax/bio-epoxy composites at different environmental conditions: WS, humidity saturated (HS), freeze/thaw (F/T) environments.

Furthermore, Sgriccia et al. [20] reported that the saturated water absorption of the water immersed flax-epoxy composites (thickness 3 mm) was 17.2%. In this study, the WS composite samples absorbed slightly more than 11% water, whereas the other samples (HS, F/T and WS epoxy) absorbed less than 2.5% moisture after 21 days to reach an equilibrium state. Several studies [9, 21] reported that the moisture absorption rate increases with the increased fiber volume fraction in case of natural fiber (hemp and jute) reinforced composites, which makes sense due to the hydrophilic nature of these fibers. Constant fiber volume fraction was used for all samples during the experiments. Therefore, only the environmental conditions are the driving force for a different rate of water absorption. It is evident that

composites absorbed the highest MC when they were immersed in water. Although the HS samples were saturated within a high humidity environment (75% RH), still their absorption rate is much lower than the WS samples. The HS samples absorbed more than 70% less moisture than those of WS samples (Table 1).

### Table 1

Maximum moisture content absorption at different environmental conditions.

In F/T cyclic weathering, the composites absorbed a very little amount of MC. The maximum MC was only 1.8% even after 10 cycles in the F/T environment. Khanlou et al. [22] stated that the moisture exists in the environment could be condensed on the cold surface of the composites during the transformation of the freezing phase to the thawing phase. As a result, both dew and rainfall could wash away on the sample surface and eventually few moistures could also be absorbed. The bio-epoxy resin absorbed 1.55% of water at saturation level since it is derived from the plant sources [23]. It could be roughly estimated from the 11.18% of WS composites that around 9.63% of saturated water was absorbed by the flax fibers.

The physical changes of the bio-composite could also be evaluated by measuring the thickness of the samples periodically, to estimate the dimensional stability of these composites. The swelling thickness of the bio-composites in environmental conditions could be calculated by the following equation:

$$f_{Swelling}(t) = \frac{T_{f,t} - T_{f,0}}{T_{f,0}} \times 100 \quad (3)$$

Where,  $f_{swelling}(t)$  is the thickness swelling ratio,  $T_{f,t}$  is the bio-composite thickness exposed to the environment, and  $T_{f,0}$  is the AM bio-composite thickness.

### Table 2

Swelling rate of flax/bio-epoxy composite samples and WS bio-epoxy at WS, HS and F/T environments.

Table 2 illustrates the physical changes as measured from the thickness of the bio-composites and the bio-epoxy matrix under different environmental conditions until saturation reached over the time periods. The swelling thickness of the WS composite samples which were submerged under water is higher (almost 11%) than the swelling data of the other samples (HS, F/T and WS bio-epoxy). In other words, the pattern of swelling thickness curves has a similar trend to the MC absorption plots as shown in Fig 1. The hydrophilic nature of the flax fibers due to the cellulosic constituents in the fiber cell wall attracts water molecules and the cohesion of water molecules with cellulose micro-fibrils results in moisture generation inside the cell walls that causes swelling of the flax fibers, as well as the composite samples. It is evident that WS bio-epoxy resin swelled less than 0.5% since bio-epoxy has no lignocellulosic fibers in it. Masoodi and Pillai [21] reported this situation in their research. As the fibers swelled significantly higher than the bio-epoxy matrix, so the swelling of the fibers applies pressure on the resin materials within the fiber-matrix interface. As a result, stretching of the matrix materials takes place which incurs more spaces for the fiber swelling. This process proceeds until an opposing stress from the matrix material equalizes the applied stress of the fibers. As a consequence, microcracks in the fibers and at the fiber-matrix interfaces are generated. Dhakal et al. [9] reported that the water diffusion process inside the composites occurs through these micro-cracks and pores and the diffusion rate of the water molecules is enhanced by the capillary movement along the fiber-matrix interface. The water molecules are harmful to the interfaces which might cause debonding and eventually degrade the composite quality.

The HS and F/T samples swelled 3.5 and 1.9% respectively. This means that limited swelling occurred in these samples but even this amount of physical change might affect the

dimensional stability and the mechanical properties of the bio-composites which are explained in the following sections.

### 3.2. Analytical models

The water absorption behavior and diffusion kinetics in the composites are described by several analytical models. Fick's and Langmuir's models are widely used among them. As such, Chilali et al. [24] reported that water diffusion inside the natural fiber composites are generally described by the Fick's diffusion theory whereas the anomalous diffusion processes can be predicted by using Langmuir's model.

#### 3.2.1. Fick's model

Fick's law can be expressed as the following equation when the composite sample has uniform initial distribution of thickness  $h$  and equal initial surface conditions [25]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 Dt}{h^2}\right] \quad (4)$$

Where  $M_t$  is the water uptake at time  $t$ ,  $M_\infty$  is the weight of water uptake when the sample is totally saturated,  $n$  is the summation index and  $D$  is the coefficient of diffusion in the composite.

Initially, absorption increases linearly with  $\sqrt{t}$ . Shen and Springer [26] simplified the above equation by identifying two cases. For  $\frac{M_t}{M_\infty} < 0.6$ , the equation reduces to:

$$\frac{M_t}{M_\infty} = \frac{4}{h} \sqrt{\frac{Dt}{\pi}} \quad (5)$$

In the second case, when  $\frac{M_t}{M_\infty} > 0.6$ , the equation related to absorption can be written as:

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3 \left(\frac{Dt}{h^2}\right)^{0.75}\right]$$

The average coefficient of diffusion,  $D$  can be calculated from Eq. (5) [9]:

$$D = \pi \left( \frac{kh}{4M_{\infty}} \right)^2 \quad (7)$$

Where  $k$  is the initial slope of a plot of the  $M_t$  versus  $\sqrt{t}$ . Due to finite dimensions of the composite samples, diffusion through the edges is also required to be considered. Therefore, corrected diffusion coefficient,  $D_c$  is calculated according to Eq. (8) for the rectangular composite samples:

$$D_c = D \left( 1 + \frac{h}{L} + \frac{h}{W} \right)^{-2} \quad (8)$$

Where  $L$  and  $W$  are the length and width of the samples.

Fig. 3 illustrates the comparison of experimental and analytical water absorption behavior of the flax/bio-epoxy composites and WS epoxy under different environmental conditions. Equations (5) and (6) of Fick's model are used to plot the solid curves which represent the theoretically predicted water absorption. Apart from the WS epoxy curve, the WS and HS composite samples clearly follow the Fickian diffusion behavior: linear rise found at the initial stage, absorption rate decreased afterwards and finally, saturation level reached with the steady state. These results are in good agreement with Assarar et al. [8]. The experimental data of the WS composite samples almost coincide with the Fickian theoretical model but the experimental data for the HS flax-epoxy composites diverged from the theoretical curve. In case of WS bio-epoxy, the experimental values coincide appropriately at the initial linear stage, but the data also diverge from the theoretical curve as time progresses. The coefficients of diffusion are summarized in Table 3. It is seen from the previous studies [9, 24] that fiber volume fraction plays an important role in diffusion coefficient measurement. The diffusion coefficient increases with the increased fiber volume fraction for hemp and flax fiber composites. In this study, constant fiber volume has been used to manufacture all the samples. Understandably, the WS composite samples contain higher



saturated water than the other two types and their diffusion coefficient is also higher than the WS bio-epoxy samples. As discussed previously, cellulose is mainly responsible for higher saturated water and diffusion coefficient during immersion tests. However, the diffusion coefficient of the HS composite samples is higher than those of WS samples. In the humidity test, samples were conditioned at 45°C and 75% RH, but the water immersion tests were performed under room temperature. Therefore, higher temperature and moisture might cause higher diffusion coefficient for the HS samples. Dhakal et al. [9] showed that the diffusion coefficient of the hemp fiber composites increases with elevated temperatures. Micro-cracks are formed after fiber swelling in the fiber-matrix interfaces of the HS composite samples due to high temperature and moisture in the environment. This formation might increase the diffusion of water molecules through micro-cracks in the interface which eventually helps to increase the diffusion coefficient.

**Fig. 3.** Water uptake curve obtained by experimental tests and analytical modelling for composites and WS epoxy matrix.

### Table 3

Diffusion coefficient and corrected diffusion coefficient with saturated water absorption data.

### 3.3. Effects on mechanical properties

#### 3.3.1. Tensile testing

A comparison of tensile strength, Young's modulus and tensile strain of the flax/bio-epoxy composite at different environmental conditions are displayed in Fig. 4. The AM samples have the highest ultimate tensile strength (360 MPa) and modulus (28.7 GPa). The tensile strength found in this work was similar to that one reported by Poilâne et al. [27] (357 MPa) for unidirectional (UD) flax-epoxy composites made by compression molding with prepregs, leading to a fiber volume content of 60%. Sawi et al. [28] also found similar values (307 MPa) for UD flax-epoxy composites made with prepregs by compression molding and autoclave. However, it should be noticed that these values for tensile strength fall in the upper

limit of the values reported in literature. As with synthetic fiber composites, the properties of natural fiber composites depend on many variables: the fibers, matrix, interphase and interface, void content (that is usually related to manufacturing methods), fiber volumetric content (also affected by the manufacturing procedure) and of course, the fabric architecture and stacking sequence. In addition, vegetables fibers have an inherent variability in properties, depending of the growth conditions of the plant, extraction methods used, moisture content in the fibers, among other factors. In our case, we manufactured UD composites by vacuum infusion which allowed us to obtain a fairly high fiber volume fraction of approximately 0.5 and very small void content. These factors, and the fact that our composites were tested in the direction of the fibers and all plies were oriented in that direction, led us to tensile strength values falling on the upper limit of the broad range of values reported in literature.

Both strength (328 MPa) and modulus (12.4 GPa) were reduced for the WS samples. The tensile stiffness of the WS samples was reduced by more than 50% than the AM samples, but the strength decreased by only 9%. Despite the fact that water causes fiber-matrix debonding and matrix microcracking degrades the interface and interphase, the swelling of the fibers increases the fiber-matrix friction. Therefore, the reduction rate of the tensile strength is much less than the Young's modulus of flax/bio-epoxy composites which was also explained by Munoz and Garcia [29]. The tensile strength of the WS samples was slightly decreased after drying but the WSD samples regained almost the same tensile modulus (28.5 GPa) of the AM samples. This confirms that the damage generated to the composites' microstructure by the water absorption process (fiber debonding, microcracks, etc.) is irreversible, as expected, and since fibers shrink, the strengthening effect caused by the fibers swelling and pushing onto the matrix disappears (which can explain the extra loss in tensile strength after drying). Newman [30] reported that fiber swelling occurred when composites are immersed under water and the matrix material around the fibers is stressed due to this fiber swelling. Some of the stresses are released during the molecular relaxation process of the matrix material. When

the fibers shrink during a drying stage, the matrix loses the bonding with the flax fibers and a gap is generated between the fibers and the matrix. In addition, fiber breakage, micropores and cracks on a fiber surface are generated due to the deterioration of the fiber-matrix interface. As a result, the strength of the composite is reduced [8, 13]. However, the softening and plasticization caused by water present in the material disappears almost completely when water is removed applying a drying stage [31].

HS samples exhibited a tensile strength and Young's modulus similar to those of the AM samples (365 MPa and 27.7 GPa), although HS samples contained around 2.5% MC. Apparently, the exposure to the humid environment did not have a significant detrimental effect on the performance of the composites.

The tensile strength decreased after the F/T tests but not substantially (9% after 10 cycles). The minor loss in strength could be associated with the small water absorption caused by water condensation on top of the specimens' surface. In the same way, Young's modulus did not change significantly either. Freezing and thawing water saturated samples did not cause any additional damage to the materials' properties. It was thought that the cyclic expansion-contraction of water present inside the microstructure could further damage the materials, but it was not the case. Either the water molecules were not grouped as free water able to form water crystals, or if that phenomenon did happen, the extra damage caused by F/T cycles was insignificant compared to the damage caused by immersion in water.

The tensile strain at break increased more than 50% for the WS samples in comparison to that of the AM and WSD samples. This can be explained by the softening and plasticizing effects of water on the vegetable fibers described by Stamboulis et al. [32]. The HS samples showed an intermediate strain at break value because the water content in those samples was lower than in the WS ones but higher than in the AM ones. Once again, freezing and thawing AM and WS materials did not affect the material behavior significantly (Table 4).

The tensile properties of the bio-epoxy matrix are shown in Fig. 5. Water molecules cause hydrolysis and plasticization of the matrix which degrades its mechanical properties. Interestingly, the loss in tensile strength is more significant for the neat matrix than for the composites, although the water uptake is much lower. This is consistent with the hypothesis given before, explaining the two opposite effects of water on the tensile strength of the composites. In the case of the neat matrix, the strengthening mechanism caused by fiber swelling against the matrix interface does not exist. As it was observed for the composites, the residual strength after drying the matrix was lower (about 9%) than the AM strength, suggesting that some permanent damage was caused by the hydrolysis. Young's modulus decreased due to plasticization and the drying stage was effective in restoring its original value. However, a decreasing trend was observed for the strain at break (Table 5), which could be related to the damage caused in the matrix by hydrolysis.

**Fig. 4.** Tensile behavior of flax/bio-epoxy composites at different environmental conditions.

**Table 4**

Tensile strain of the flax/bio-epoxy composites at different environmental conditions.

**Fig. 5.** Tensile behavior of the bio-epoxy matrix at different environmental conditions.

**Table 5**

Tensile strain of the bio-epoxy matrix exposed to different environments.

*3.3.2. Flexural testing*

The flexural properties of the flax/bio-epoxy composites are summarized in Fig. 6.

**Fig. 6.** Flexural behavior of flax/bio-epoxy composites at different environmental conditions.

The trends are similar to those observed for the tensile properties, with a couple of interesting differences:

- Water immersion did reduce substantially the flexural strength (64%). This could be associated with a premature failure caused by the degradation of the interface and interphase and the plasticization effect caused by water molecules. In the case of flexural testing, shear stresses can cause debonding of fiber-matrix interfaces and successive layers of the composite. On the compressed area of the cross section of the composite beam under 3-point bending, compressive stresses cause fibers and laminae buckling and reducing the effective loaded area, thus, increasing the stresses on the section. The severe loss in flexural modulus (almost 70%, see Fig. 6) of the material decreases significantly its resistance to buckling, magnifying this detrimental phenomenon.
- Drying the WS samples did restore most of their flexural strength (residual strength almost 90% of AM strength). This suggests that the previously described mechanisms are induced by water molecules present in the microstructure, so these phenomena must be intimately related to a plasticization effect, which causes a severe loss in flexural modulus reducing significantly the buckling resistance of the composite laminate.

Flexural properties of the bio-epoxy matrix exposed to different environmental conditions are illustrated in Fig. 7.

**Fig. 7.** Flexural properties of the bio-epoxy matrix at different environments.

#### 4. Conclusions

The applicability of the flax/bio-epoxy composite in engineering structures under different environmental conditions was focused in this study. An assessment of the durability of bio-composites was the main driving force of this research. This study could lead the research on environmental degradation problem of the flax/bio-epoxy composites to estimate the effects of exposure time on their properties. Flax/bio-epoxy composites were exposed to

different environmental conditions: water immersion, high humidity and freeze/thaw cycling. The overall performance of the bio-composites and the detrimental effects of the different exposure conditions were analyzed by the water and moisture absorption behavior, dimensional stability, and mechanical properties characterization (flexural and tensile). The water absorption trend was partially Fickian for the samples immersed in water at room temperature and these samples were the most affected and degraded. Exposing the composites to a warm and humid environment slightly reduced the mechanical properties of the bio-composites but this reduction was not significant. Almost no detrimental effects on the composites' performance were found for the freeze/thaw cycles on the bio-composites. The results obtained in this study suggest that flax/bio epoxy composites can be used in most environmental conditions, excluding underwater applications which cause severe damage to the properties of the material. If this type of material is accidentally immersed in water for a long period of time, drying the composites for up to three days will almost completely restore the flexural strength and modulus, and also Young's modulus, but the tensile strength will be reduced irreversibly.

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### **Figures Captions**

**Fig. 1.** (a) Schematic diagram to process flax/bio-epoxy composite by vacuum infusion, (b) Composite plate manufactured by vacuum infusion method and flexural and tensile samples, (c) Optical micrograph of the “as manufactured” composites, (d) SEM image of the fiber-matrix interphase of AM composites.

**Fig. 2.** Moisture content absorbed by WS epoxy and flax/bio-epoxy composites at different environmental conditions: WS, humidity saturated (HS), freeze/thaw (F/T) environments.

**Fig. 3.** Water uptake curve obtained by experimental tests and analytical modelling for composites and WS epoxy matrix.

**Fig. 4.** Tensile behavior of flax/bio-epoxy composites at different environmental conditions.

**Fig. 5.** Tensile behavior of the bio-epoxy matrix at different environmental conditions.

**Fig. 6.** Flexural behavior of flax/bio-epoxy composites at different environmental conditions.

**Fig. 7.** Flexural properties of the bio-epoxy matrix at different environments.

### **Tables captions**

#### **Table 1**

Maximum moisture content absorption at different environmental conditions.

#### **Table 2**

Swelling rate of flax/bio-epoxy composite samples and WS bio-epoxy at WS, HS and F/T environments.

#### **Table 3**

Diffusion coefficient and corrected diffusion coefficient with saturated water absorption data.

#### **Table 4**

Tensile strain of the flax/bio-epoxy composites at different environmental conditions.

#### **Table 5**

Tensile strain of the bio-epoxy matrix exposed to different environments.

**Table1**

Maximum moisture content absorption at different environmental conditions.

Materials	Maximum moisture content (%)		
	HS	WS	F/T cycle
Flax/bio-epoxy	2.57	11.18	1.84
Bio-epoxy	1.46	1.55	0.192

**Table 2**

Swelling rate of WS bio-epoxy and flax/bio-epoxy composite samples at WS, HS and F/T environments.

Days	Average thickness change, $f_{swelling}$ (%)			
	WS	Flax/bio-epoxy		WS bio-epoxy
		HS	F/T	
2	4.72	1.70	0.06	0.01
10	9.25	1.84	1.31	0.20
20	10.64	3.49	1.96	0.34
30	10.91	3.53		0.40

**Table 3**

Diffusion coefficient and corrected diffusion coefficient with saturated water absorption data.

Materials	$M_{\infty}$ (%)	$D \times 10^{-6}$ mm <sup>2</sup> /s	$D_c \times 10^{-6}$ mm <sup>2</sup> /s
WS flax/bio-epoxy	11.18	1.52	1.09
HS flax/bio-epoxy	2.57	2.17	1.56
WS bio-epoxy	1.55	0.39	0.28

**Table 4**

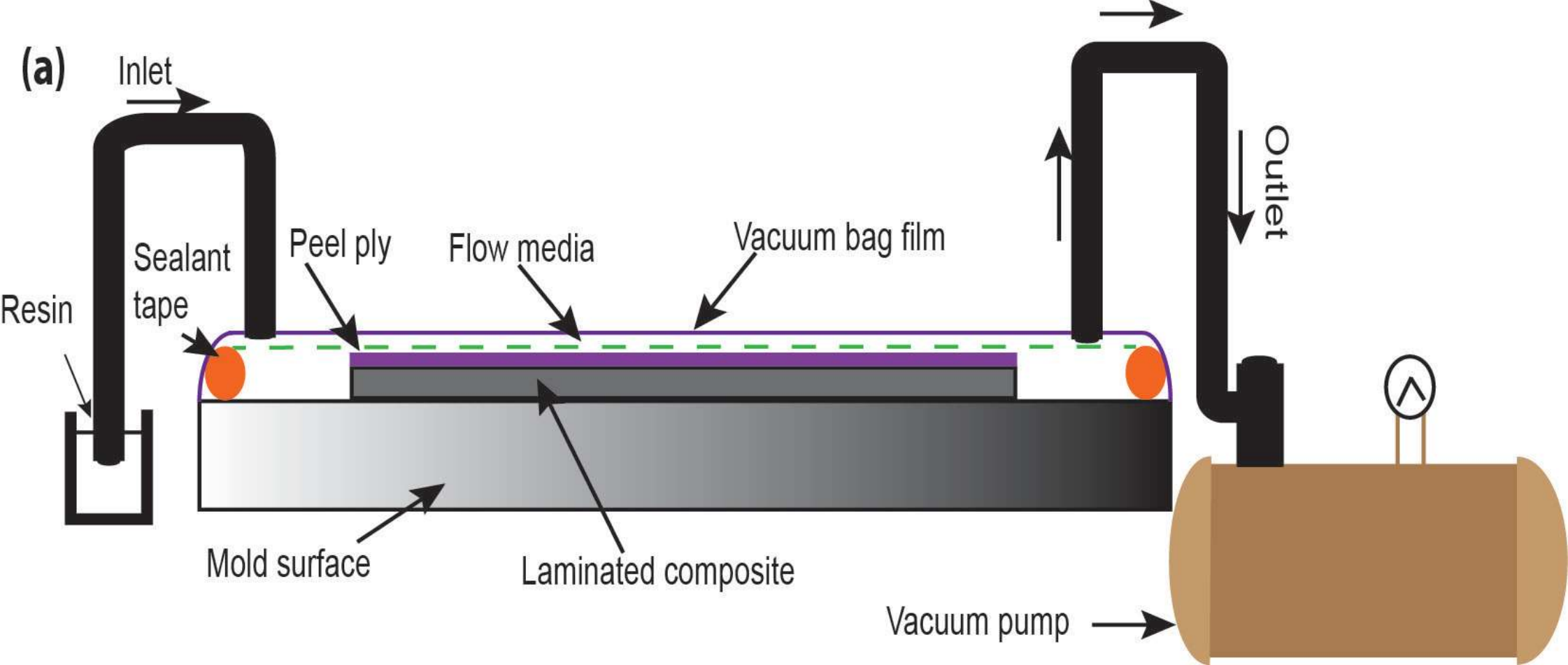
Tensile strain of the flax/bio-epoxy composites at different environmental conditions.

<b>Conditions</b>	<b>Elongation at break (%)</b>
AM	2.1 ± 0.05
WS	3.2 ± 0.07
WSD	1.9 ± 0.11
HS	2.5 ± 0.05
F/T-1 cycle	2.2 ± 0.13
F/T-5 cycle	2.1 ± 0.14
F/T-10 cycle	2.0 ± 0.06
WSF/T-1 cycle	3.1 ± 0.17
WSF/T-5 cycle	2.8 ± 0.25
WSF/T-10 cycle	2.9 ± 0.04

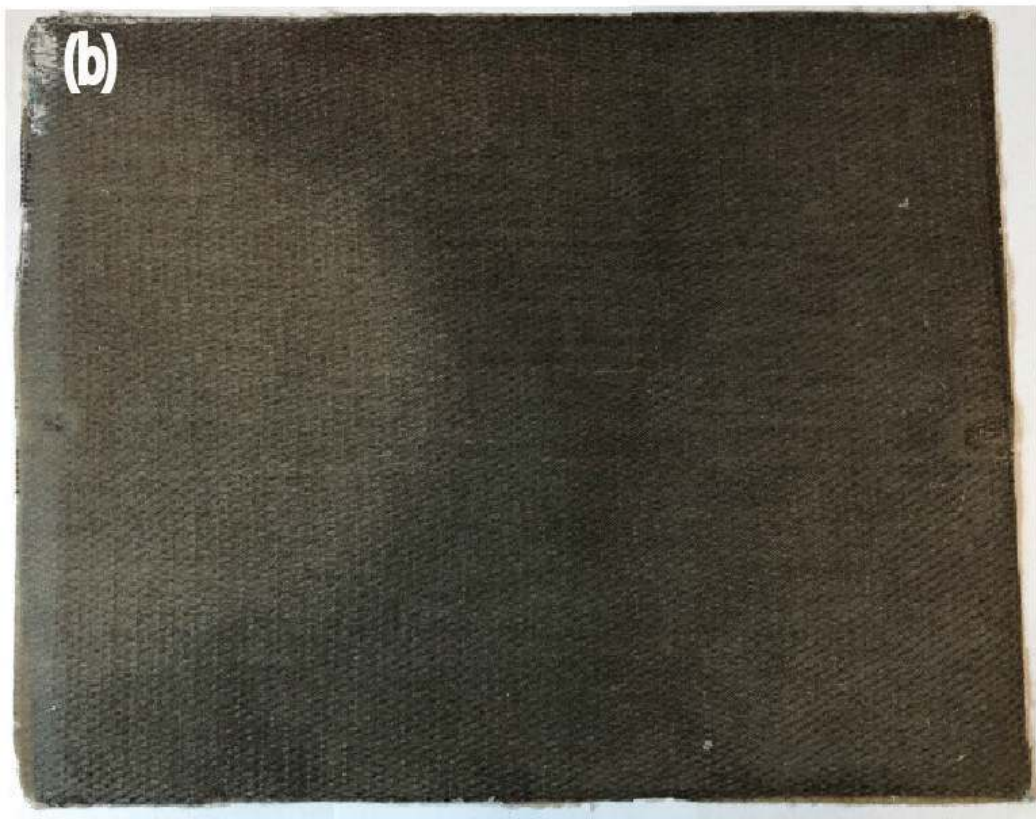
**Table 5**

Tensile strain of the bio-epoxy matrix exposed to different environments.

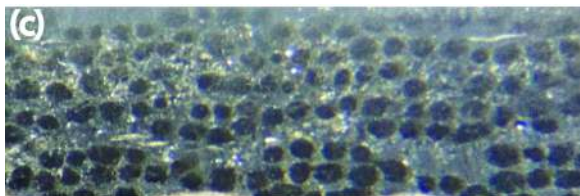
Conditions	Elongation at break (%)
AM	$3.80 \pm 0.07$
WS	$3.15 \pm 0.56$
WSD	$2.54 \pm 0.41$
HS	$2.34 \pm 0.48$
F/T- 10 cycle	$2.48 \pm 0.02$



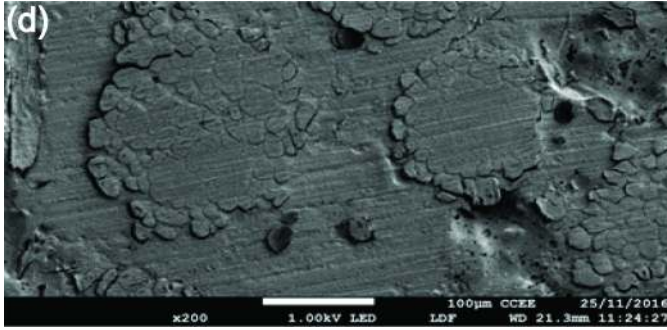
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