Ageing of autoclaved epoxy/flax composites: effects on water absorption, porosity and flexural behaviour

Júlio César dos Santos[a], Lívia Ávila de Oliveira[a], Túlio Hallak Panzera[a, b], Chrystel D L Remillat[b], Ian Farrow[b], Vincent Placet[c], Fabrizio Scarpa[b]

[a] Centre for Innovation and Technology in Composite Materials – CIT[e]C, Federal University of São João del Rei-UFSJ, 36307352 São João del Rei, Brazil.

[b] Bristol Composites Institute (ACCIS), University of Bristol, BS8 1TR Bristol, UK.

[c] Université Bourgogne Franche-Comté, FEMTO-ST Institute, CNRS/UFC/ENSMM/UTBM, Department of Applied Mechanics, 25000 Besançon, France.

Abstract

This work investigates the effects of ageing on autoclaved composites made with unidirectional prepreg epoxy and flax tape in environments with 50% and 100% of relative humidity. A Design of Experiment (DoE) has been used first to determine the effect of the ageing time (0, 2, 4, 6, 8 and 16 days), type of bending (3-point and 4-point bending) and fibre orientation (longitudinal and transverse) on the water absorption and flexural properties of 50% saturated composites. A second experiment at 100% humidity has been also performed to further characterise the composites and to identify the equivalent ageing time that provides the mechanical behaviour of the 50% humidity samples after sixteen days. The water absorption and apparent porosity levels increase progressively with the ageing time, in particular for the case of transverse laminates; these features compromise the flexural properties of the composites. The laminates subjected to 4-point bending showed increased water absorption levels and improved flexural properties compared to the samples under 3-point bending. The flexural properties of flax composites at 50% humidity after 16 days are equivalent to those shown by composites immersed in water for less than one day.

Keywords: flax composite; prepreg, ageing process; fibre orientation; flexural properties; water absorption; apparent porosity.

1. Introduction

Flax (*Linum usitatissimum*) is one of the most widely used types of biofibres for textile applications, the latter dating back to 5000 BC [1, 2]. Linen fabric represents a strong traditional niche among high quality household textiles, such as bedding, furnishing fabrics and interior decoration accessories [2]. In recent years, the use of flax fibres as reinforcement in composite materials has attracted the attention of the research community due to biodegradability, renewable aspects, low cost, low density and good mechanical performance [3-6]. The most promising applications of these composites are in the transport industries because of the lightweight characteristics, high specific strength and stiffness required in those domains [7, 8].

Due to their high hydrophilicity, the use of plant fibre composites in humid or outdoor environments requires however a thorough evaluation to assess the impact on the mechanical behaviour [8, 9]. Since the thermosetting polymer is less hydrophilic than natural fibres, water absorption is mainly governed by the characteristics of the fibres, and this aspect plays an important role in the ageing of biocomposites [10-13]. Swelling, plasticizing and hydrolysis due to water absorption result in physical damage to the polymeric matrix. Interfacial damage between fibres and matrix and delamination of the layers are also present, and all these factors contribute to reduce the overall mechanical performance of the composites [12].

Several studies have shown that biocomposites feature a reduced stiffness and strength in humid environments. Scida *et al.* [14] evaluated the influence of hygrothermal ageing on the mechanical performance and damage behaviour of quasi-unidirectional flax-fibre reinforced epoxy composites. The tensile properties were clearly affected by hygrothermal ageing, with an overall significant reduction, in particular for the Young's modulus. The reduction in terms of stiffness and strength was explained by the reorientation of the flax microfibrils and the plasticizing effect of the water on the matrix. Yan *et al.* [15] evaluated the effect of water, seawater and alkaline (5% NaOH) solution ageing on the mechanical properties of flax fabric/epoxy composites used for civil engineering applications. All the ageing procedures used have led to a noticeable degradation of the tensile/flexural properties. Alkaline ageing was the most damaging, followed by the ones provided by seawater and water. Fiore *et al.* [16] have investigated the wettability and the dynamic mechanical properties of flax and flax/basalt reinforced composites subjected to long-term ageing under critical environmental conditions. The results showed that the storage modulus of the two types of composites decreased after 15 days of ageing, mainly due to the progressive damage to the resin/fibre interface that induces formation of cracks. The hydrophilic nature of the fibres (with resultant water uptake) and the poor fibre-matrix bonding were also other significant factors that contributed to the reduction of the mechanical performance. Regazzi *et al.* [17] examined the influence of thermohydro-mechanical-based ageing on the elastic behaviour of flax/poly (lactic acid) composites. The results confirmed that the ageing temperature in wet conditions led to a loss of the elastic properties. In addition, the combination of mechanical loading with water immersion generated in a strong synergistic effect on the stiffness loss. Berges *et al.* [18] studied the effect of moisture absorption on the mechanical properties of unidirectional flax fibre-reinforced epoxy composites through quasi-static, fatigue and vibration tests. The results revealed that the water vapour sorption promoted a significant change in the shape of the tensile stress-strain curve, a decrease in the dynamic elastic modulus of about 20% and a great increase in damping ratio of 50%. Contrary to all expectations, water saturation does not degrade the monotonic tensile strength of flax-epoxy composites and leads to an increase in fatigue strength over a large number of cycles. Jeannin *et al.* [19] investigated the influence of hydrothermal ageing on the fatigue behaviour of the unidirectional flax-epoxy laminated composite, implementing fatigue tests in a water bath. The results showed that hydrothermal ageing, while inducing a decrease in stiffness and strength, leads to an improvement in fatigue resistance. The maximum stress level for an expected lifetime of 5.3×10^6 cycles is comparable to one of the unaged specimens. Despite the high sensitivity of the composite to water, its resistance to ageing under very severe conditions is good. Cheour *et al.* [20] have evaluated the effect of water ageing on the mechanical and damping properties in quasi-unidirectional flax fibre reinforced epoxy composites. The results showed that the water uptake induces a decrease in flexural modulus and an increase of the loss factors in comparison with the ageing time. Shen *et al.* [21] have investigated the effect of the manufacturing and environment temperatures and water absorption on the low-velocity impact response and damage mechanisms of flax fibre reinforced epoxy plastic laminates at the onset of damage. The results showed that excessive temperature can cause chemical decomposition and structural damage to the flax fibres, resulting in a serious reduction of the impact damage threshold and of the resistance to damage. Shen *et al*. also observed that a small amount of water absorption can slightly improve the damage threshold load and the damage resistance, while more water uptake causes severe degradation at the composite interface and structural damage of the flax fibre, reducing the impact performance of flax fibre reinforced composites. Moudood *et al.* [22] have evaluated the durability and the mechanical performance of flax/bio-epoxy composites exposed to different environmental conditions. The results showed that exposure to warm and humid environments slightly reduced the mechanical properties of the bio-composites. Almost no detrimental effects were however observed regarding the performance of the composites after freeze/thaw cycles. The authors suggested that flax/bio epoxy composites can therefore be used in most environmental conditions, excluding underwater applications that cause severe damage to the materials properties. Recently, Koolen *et al.* [23] investigated the development of damage in epoxy composites reinforced with unidirectional flax fibres during the hygroscopic cycle by inserting an elastomeric silicone in the fibre/matrix interphase. Hygroscopic cycling was performed by varying the relative humidity between 25 and 80% at 80 °C. The results showed that the degradation of the mechanical properties can be attributed to the fibre–matrix debonding and the cohesive failure within the fibre bundles. Contrary to the hypothesis, the insertion of the silicone interphase led to an accelerated decrease of the transverse strength. Chaudhary *et al.* [24] studied the properties of hybrid jute/flax epoxy composites in dry and one-year water aged condition; those composites were subjected to tensile, flexural, impact and hardness tests. The experimental findings showed reductions of 37.8% and 43.2% in tensile strength and modulus; 33.6% and 45.1% in flexural strength and modulus. The hardness and the impact resistance however decreased by only 2.1% and 4.3% respectively, compared to the dry composites. Cheng *et al.* [25] investigated the durability of carbon/flax fibre reinforced polypropylene composites exposed to water immersion ageing at 60 °C until saturation. The inclusion of carbon fibres reduced the water absorption and improved the mechanical properties of the composites when compared to pure flax/polypropylene composites. The carbon/flax interface is however vulnerable to both hygrothermal attack and delamination, reducing the tensile and flexural properties of the laminates while increasing the tensile failure strain due to plasticization. Wang and Petru [26] studied the effect of natural and accelerated ageing on the flexural properties of flax fibre reinforced polymer composites. Natural ageing was carried out under daily temperature and humidity and lasted 180 days, while accelerated ageing was carried out at 60°C, with 100% relative humidity. Although both ageing tests have shown a decrease in mechanical properties, they generated different degradation effects on the properties of composites, since only limited ageing factors (temperature and humidity) are considered. Natural ageing is on the opposite caused by a combination of various environmental factors, such as rainwater, ultraviolet rays, oxygen and ozone. Panzera *et al.* [27] investigated the tensile, flexure and impact properties of autoclaved UD and cross-ply flax fibre composites impregnated with fire retardant epoxy polymer, following the recommendations for aerospace applications, as a previous study to the current work.

Although several studies in open literature describe the effect of critical environments on the mechanical properties of flax reinforced composites, this work is the first to report about the interaction between the ageing time, type of bending loading (with related sample size) and fibre orientations, through a statistical design, of autoclaved composites made with a commercialised unidirectional prepreg flaxtape, and the influence provided on the water absorption capability, porosity and flexural properties of those composites, meeting the requirements of AC 25-853a [28] in terms of self-extinguishing at 50% RH (relative humidity).

Moreover, this work evaluates composites machined via a laser cutting process. Laser cutting reduces the presence of microstructural defects, stress concentrations, premature swelling due to the coolant, or any other uncontrolled geometric parameter that affects the responses.

2. Materials and Methods

2.1 Materials

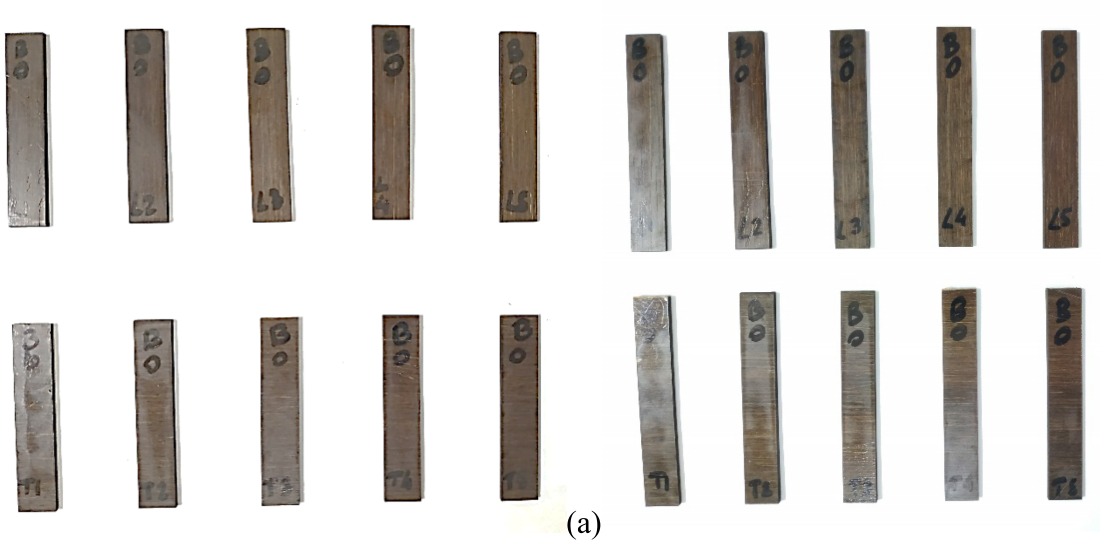
The unidirectional flax fibre reinforced composites are made of flax fibres pre-impregnated with fire-retardant epoxy polymer (XB 3515 GB - Huntsman), combined with Aradur 1571 BD and Accelerator 1573 BD. The prepreg flaxtape is supplied by EchoTechnilin-Lineo (France). The prepreg has a nominal 50% flax weight fraction, and the matrix/fibre volume fraction is estimated at 43/56%.

2.2 Fabrication process

The composites have been fabricated in two processes: hand lay-up followed by autoclave curing. Twelve prepreg flax plies have been laid up along the unidirectional orientation. Lay-up $[0]_{12}$ is autoclaved and cured at ~0.7 MPa (100 psi), with two dwell times of 100 minutes each at 80°C and 140°C. An aluminium plate is placed on the upper surface of the lay-up to obtain a surface finish similar to the one of the lower plane in contact with the tool plate. The aluminium plate also helps to obtain a final flat laminate. The final composites have an average thickness of 2.05 mm, corresponding to approximately 0.17 mm per layer.

2.3 Water saturation (50% and 100%)

A laser cutting machine has been used to obtain samples along the longitudinal and transverse directions with the required dimensions for the characterisation of the composites (Figure 1). The laser cutting avoids any swelling effect attributed to traditional coolant cutting and peripherical damages that may also affect the physical and mechanical properties of the composites. Prior to the ageing and the characterisation process, the samples have been weighed in a precision scale (0.001g) and placed in a climatic chamber (Solab climatic chamber SL - 206) for saturation during 2, 4, 8 and 16 days. The humidity and temperature inside the chamber were adjusted to 50 ± 5% and 21 ± 5°C, respectively, following the ASTM D5229/D5229M standard [29]; the sorption measurements have been however carried out here under a transient regime at each ageing time level, i.e., not corresponding to the water equilibrium state. Hundred percent humidity (100%RH) samples were immersed in water within the climatic chamber at 21 ± 5°C, for 2, 4 and 8 days. An additional immersion time level of 30 minutes is used to measure apparent porosity only. The results are compared with 50% saturated humidity samples for 16 days to identify the equivalent ageing time for a similar mechanical behaviour. This test has been performed with UD flax composite samples of 65 × 13 × 2 mm^3 and 80 × 13 × 2 mm^3 and oriented along the transverse and longitudinal fibre directions (Figure 1).



(a) (b)

Figure 1. Longitudinal and transverse (a) 3PB and (b) 4PB samples.

2.4 Physical and mechanical properties

2.4.1 Water absorption and apparent porosity

The water absorption and the apparent porosity are determined using the Archimedes principle. Water absorption is measured during every experimental condition considering the sample size (3PB, 4PB), the fibre orientation (longitudinal and transverse) and the ageing time (2, 4, 8 and 16 days at 50%RH and 2, 4 and 8 days at 100%RH). The apparent porosity is measured considering 3PB samples (longitudinal and transverse) saturated at 100%RH for 30 min, 2, 4 and 8 days.

Water absorption is measured according to the ASTM D570-98 standard [30], in which the relative weight uptake (M_t) of the specimens is calculated for each exposure time:

$$M_t = \frac{W_t - W_o}{W_o} x\ 100\% \quad (1)$$

where W_o is the weight of the dry specimen and W_t is the weight of the wet specimen at time t.

The apparent porosity P is expressed as a percentage of the volume of open pores to the exterior volume, and may be calculated according to Eq. 2, following the recommendations of the ASTM C1039-85 standard [31]:

$$P = \frac{W_t - W_o}{W_t - W_s}\ x\ 100\% \quad (2)$$

In (2), W_t, W_o and W_s are the weight of the wet specimen at the time t, the dry and suspended specimens, respectively.

2.4.2 Flexural Properties

Longitudinal and transverse UD flax composites have been tested under three-point bending (3 PB) according to the ASTM D790-17 standard [32], while for the four-point bending (4 PB) one the ASTM D7264/D7264M-15 protocols has been followed [33]. The sizes of the samples for the two types of bending loading are $65 \times 13 \times 2$ mm^3 and $80 \times 13 \times 2$ mm^3, respectively, as shown in Figure 1. A load span of 32 mm and a support span of 64 mm were used for the four-point bending test, while a support span of 52 mm was used for the three-point bending test. The experiments have been performed using a Shimadzu AG-X Plus equipped with 100 kN load cell at 2 mm/min. Flexural strength and modulus have been determined based on ASTM recommendations [32, 33].

2.5 Statistical Design

A Full Factorial Design ($5^1 2^2$) has been used to identify the effects of the type of bending loading (3 and 4-point bending), the fibre orientation (longitudinal and transverse) and ageing time (0, 2, 4, 8 and 16 days) on the water absorption and the flexural properties of the composites at 50% of humidity. The 'bending type' factor also relates to the effect of the 'sample size (3PB and 4PB)' when the water absorption is evaluated. The Design results in 20 experimental conditions (ECs) (Table 1). Three specimens have been fabricated for each experimental condition in two different runs (replicate) to estimate the experimental error [36], totalling 120 specimens. The Minitab software v. 18 has been used to perform the Design of Experiment (DoE) and the Analysis of Variance (ANOVA). ANOVA is used to establish the statistical significance of the effects of factors and their interactions on physical and mechanical responses, considering a 95% confidence interval [36]. The interaction among factors occurs when the effect of one factor on a specific response depends on the level of other factors. The indicator of the significance of factors and interactions within the confidence interval is a $P \leq \alpha$. The parameter α (the so-called significance level, fixed at 0.05 in this study) represents the risk of stating that the effect of a factor (or interaction of factors) is significant when, in fact, it is not. The validity of ANOVA is based on the normality of the underlying probability distribution of the analysed data. The Anderson-Darling test is performed to verify this assumption. Given the construction of the Anderson-Darling hypothesis test, $P \geq 0.05$. Significant effects are interpreted through main or interaction plots. In addition to ANOVA, a statistical mean comparison test, such as Tukey, can be useful to compare the means between levels of the same factor. Tukey´s test attributes a letter to each mean; the means that do not share a letter are significantly different from each other [36].

Table 1. Full Factorial Design ($5^1 2^2$) for 50% moisture saturated samples.

E.C.	Bending Type	Fibre Orientation	Ageing Time (day)	E.C.	Bending Type	Fibre Orientation	Ageing Time (day)
1	3 PB	Longitudinal	0	11	4 PB	Longitudinal	0
2	3 PB	Longitudinal	2	12	4 PB	Longitudinal	2
3	3 PB	Longitudinal	4	13	4 PB	Longitudinal	4
4	3 PB	Longitudinal	8	14	4 PB	Longitudinal	8
5	3 PB	Longitudinal	16	15	4 PB	Longitudinal	16
6	3 PB	Transverse	0	16	4 PB	Transverse	0
7	3 PB	Transverse	2	17	4 PB	Transverse	2
8	3 PB	Transverse	4	18	4 PB	Transverse	4
9	3 PB	Transverse	8	19	4 PB	Transverse	8
10	3 PB	Transverse	16	20	4 PB	Transverse	16

3. Results

3.1 Experimental data

Table 2 presents the mean values and standard deviation of the responses obtained for 50% moisture saturated samples. As expected, increases in water absorption do compromise the bending properties of plant fibre composites. Similar trends of those shown in the current data can be also observed in other works from open literature focusing on the effects of ageing on the mechanical performance of flax composites [21, 22, 34]. According to Kollia *et al.* [35] for example, the flexural modulus and strength are significantly reduced after hydrothermal ageing due to the degrading effect of the water on the fibre-matrix bonding. Other causes of this degradation are the presence of excessive cracks in the matrix, swelling of the fibre-matrix interface, plasticization of the material, degradation of the cellulose structure (i.e., dissolution) and fibre sliding.

The data present in Table 2 will be better assessed in the statistical design described in the following section.

Table 2. Statistical descriptive for 50% moisture saturated samples.

E.C.	Water Absorption (%)		Flexural Strength (MPa)		Flexural Modulus (GPa)	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2

1	0.00	0.00	244.93 (±16.69)	250.08 (±34.96)	30.78 (±0.32)	30.38 (±0.94)
2	0.17 (±0.03)	0.13 (±0.02)	213.51 (±4.50)	215.71 (±19.86)	24.05 (±0.99)	24.16 (±1.65)
3	0.21 (±0.05)	0.22 (±0.07)	191.93 (±10.48)	192.77 (±22.29)	22.41 (±0.59)	22.18 (±1.43)
4	0.33 (±0.02)	0.33 (±0.08)	198.86 (±7.12)	196.93 (±22.64)	22.85 (±1.02)	22.83 (±1.22)
5	0.57 (±0.08)	0.45 (±0.09)	191.69 (±17.82)	195.22 (±1.84)	21.40 (±1.92)	21.69 (±0.22)
6	0.00	0.00	28.97 (±2.17)	30.04 (±3.42)	4.48 (±0.20)	4.36 (±0.18)
7	0.21 (±0.10)	0.22 (±0.10)	28.93 (±2.06)	29.69 (±0.86)	4.01 (±0.07)	3.91 (±0.25)
8	0.32 (±0.01)	0.41 (±0.04)	29.37 (±0.31)	28.89 (±1.17)	3.83 (±0.16)	3.80 (±0.24)
9	0.42 (±0.06)	0.50 (±0.07)	29.59 (±2.32)	30.16 (±1.92)	3.63 (±0.20)	3.71 (±0.02)
10	0.77 (±0.03)	0.71 (±0.08)	25.66 (±3.95)	25.40 (±1.55)	3.19 (±0.15)	3.27 (±0.06)
11	0.00	0.00	326.08 (±24.92)	324.05 (±17.32)	30.45 (±0.29)	30.02 (±1.59)
12	0.24 (±0.11)	0.25 (±0.11)	285.33 (±24.99)	284.81 (±12.27)	28.95 (±0.12)	28.73 (±2.07)
13	0.46 (±0.01)	0.40 (±0.08)	305.76 (±20.84)	302.38 (±29.84)	29.21 (±3.05)	28.76 (±2.18)
14	0.61 (±0.05)	0.68 (±0.16)	272.49 (±31.05)	269.83 (±22.31)	29.07 (±0.57)	28.85 (±3.01)
15	0.74 (±0.01)	0.69 (±0.13)	260.60 (±24.35)	258.06 (±26.35)	26.67 (±2.51)	26.52 (±1.06)
16	0.00	0.00	34.24 (±3.04)	35.38 (±2.73)	5.15 (±0.10)	5.20 (±0.24)
17	0.42 (±0.07)	0.38 (±0.01)	31.45 (±0.61)	31.30 (±1.79)	4.37 (±0.03)	4.44 (±0.63)
18	0.40 (±0.08)	0.35 (±0.01)	30.99 (±0.48)	29.44 (±0.96)	4.28 (±0.09)	4.28 (±0.12)
19	0.63 (±0.08)	0.60 (±0.03)	30.13 (±1.96)	30.69 (±2.88)	4.31 (±0.11)	4.33 (±0.15)
20	0.82 (±0.05)	0.83 (±0.02)	27.25 (±0.98)	29.63 (±3.07)	3.85 (±0.02)	3.83 (±0.18)

3.2 Statistical Design

Table 3 presents the DoE/ANOVA analysis for the 50% moisture saturated samples. All P-values are lower than 0.05, meaning that the main and the interaction effects are statistically significant within a 95% confidence level. This implies that change in the level of the factors produces a change in the response-variables [36]. The results are interpreted by using effect plots (Figures 2-7). The R^2-adj values, ranging from 98.03% to 99.98%, indicate high predictability models, since they are close to 100%. The ANOVA is validated by the Anderson-Darling normality test, showing P-values from 0.111 to 0.985. In this case, P-values ≥ 0.05 indicate that the data follow a normal distribution.

Table 3. Analysis of variance (ANOVA) for 50% moisture saturated samples.

P-value ≤ 0.05				
Experimental Factors		Water Absorption (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)
Main Factors	Bending type (BT)	0.000	0.000	0.000
	Fibre orientation (FO)	0.000	0.000	0.000
	Ageing time (AT)	0.000	0.000	0.000

Interactions	BT x FO	0.003	0.000	0.000
	BT x AT	0.000	0.000	0.000
	FO x AT	0.002	0.000	0.000
	BT x FO x AT	0.004	0.000	0.000
	R^2-adj	98.03%	99.98%	99.98%
	Anderson Darling (P-value ≥ 0.05)	0.111	0.985	0.394

3.2.1 Water Absorption

Water absorption ranges from 0.13% (3 PB, longitudinal, 2 days) to 0.83% (4 PB, transverse, 16 days), as shown in Table 2. The main and interaction effect plots are visualized in Figures 2 and 3, respectively. The letters in the graphs represent the Tukey's comparison test, which displays the same group of letters for similar means (averages) with a 95% confidence interval.

An increase of 42% in water absorption is observed for the 4 PB samples (Figure 2a), which is attributed to the larger volume of the 4 PB samples (2080 mm^3) compared to the 3PB specimens (1690 mm^3). The transverse orientation of the fibres also contributes to the increase water absorption by 23% (Figure 2b) due to the greater number of fibre cross sections along the length of the sample and the shorter size along the width direction. This facilitates the percolation of the water along the fibre direction, as demonstrated by the diffusion coefficients determined in the works of Cheour *et al.* [20]. Although flax composites show a slight absorption of water after 16 days of ageing, a significant increase (176%) is noticed when the ageing times change from 2 to 16 days (Figure 2c). This could be attributed to a greater exposure of the sample to a constant humidity environment.

Figure 3 shows the interaction effect plot for mean water absorption. Figure 3a shows that the increase in water absorption by samples with transverse fibre orientation [90°] is larger for the 4PB samples (69%). This is an indicator of the interaction between the size of the sample and the architecture of the stacking sequence, i.e., a larger sample size increases the number of transverse fibres. The interaction between the type of bending loading and the ageing time (Figure 3b) shows a significant increase in water absorption (242%) between levels from day 2 to day 16. In addition, an increase of 77% is observed between the samples of 3PB and 4Pb. The interaction effect between fibre orientation and ageing time (Figure 3c) is quite similar to the previous one (Figure 3b), i.e. the sample size and the fibre direction factors similarly affect the water absorption of the flax laminates as a function of time.

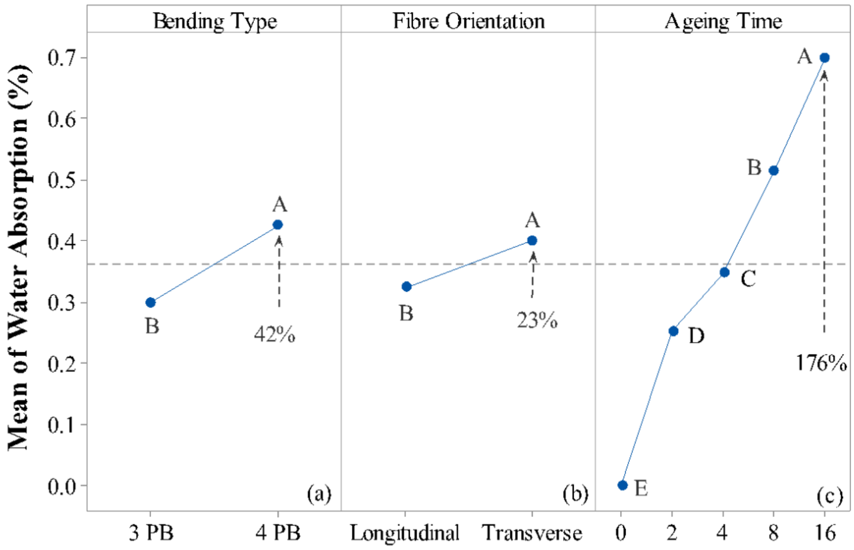


Figure 2. Main effect plot for the mean (average) water absorption.

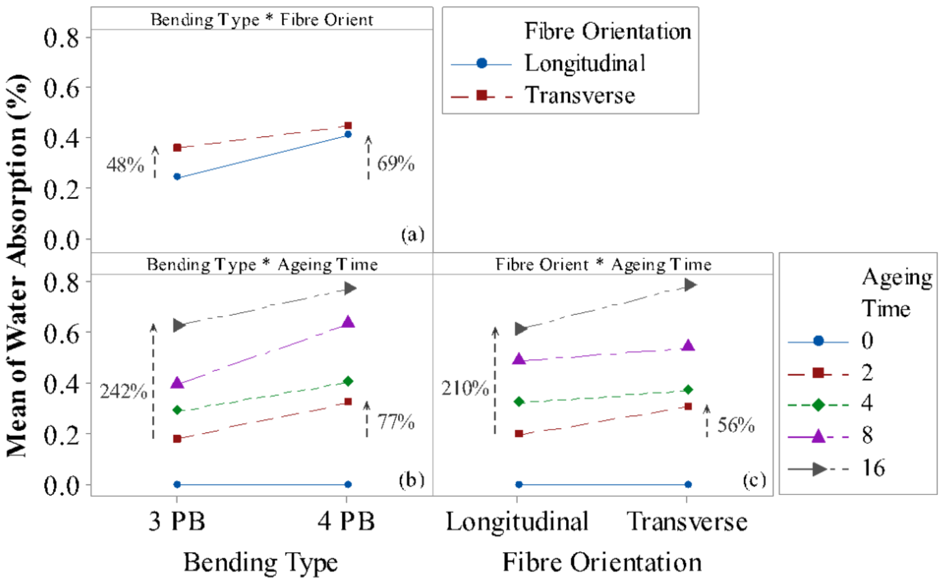


Figure 3. Third order interaction effect plot for the mean (average) water absorption levels.

3.2.2 Flexural properties

Typical behaviours of longitudinal and transverse samples under three- and four-point bending tests are shown in Figure 4. Although similar behaviour is observed between 3PB and 4PB samples, the 4PB test leads to higher maximum force values (Figure 4b). Flax composites tested in the longitudinal direction provide greater force than the transverse ones. Substantial reductions in force are achieved by water-saturated composites after 16 days at 50%RH. The effects of each factor on flexural strength and modulus will be assessed in sections 3.2.2.1 and 3.2.2.2.

Fracture modes of saturated samples under 3PB and 4PB loading are similar to those of pristine specimens. The cracks present in the longitudinal composites propagate along the diagonal direction (Figure 5a), while the transverse samples show cracks along the direction of the fibre orientation (Figure 5b).

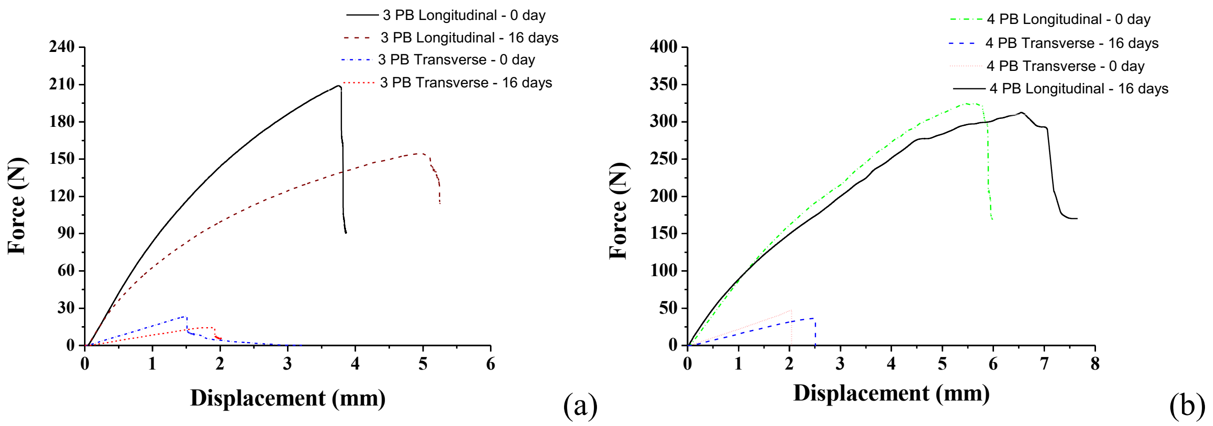


Figure 4. Typical bending behaviours of 3PB (a) and 4PB (b) samples.

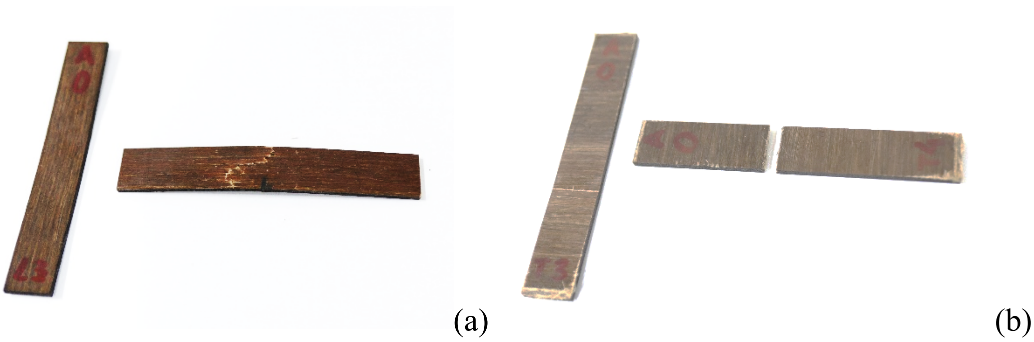


Figure 5. Examples of typical fracture modes in longitudinal (a) and transverse (b) samples.

3.2.2.1 Flexural Strength

Flexural strength ranges from 25.5 MPa (3 PB, Transverse, 16 days) to 325 MPa (3 PB, longitudinal, 0 day), as shown in Table 2. Figure 6 shows the effect plots for the main factors. Laminates tested under four-point bending show an increased strength (35%) compared to three-point bending samples (Figure 6a). The stress in the four-point bending loading is located between the two loading noses, which produces peak stresses over an extended region of the sample surface and thus more resistance to the applied load. On the other hand, the maximum stress, under three-point bending, is located under the loading roller, resulting in a non-uniform distributions and reduced stress elsewhere. Three-point bending also generates shear stress in the whole specimen, except on the vertical plane containing the central loading roller. In 4-

point bending, the shear stress is zero in the region between the two loading rollers and has a non-zero value outside this central region (out of the two loading noses). The shear stress direction is almost parallel to the applied loading direction throughout. The flexural strength of the UD longitudinal laminates is nearly 8-fold higher than the transverse composites (Figure 6b). Fibres oriented along the longitudinal direction, especially those under the neutral line, increase their flexural stress due to their improved mechanical performance under tensile loading [37]. A 20% reduction in strength is observed after 16 days of ageing (Figure 6c). No noticeable difference can be discerned between the mechanical performance related to the 2 and 4 days of ageing, as evidenced by the same group B provided by Tukey's comparison test.

There is no significant variation in strength between the transverse 3PB and 4PB samples. A 38% increase for the 4P laminates UD oriented is however evident (Figure 7a). Figure 7b reveals a similar strength increase when the ageing time is reduced for all the sample types. Figure 7c shows the interaction effect between fibre orientation and ageing time. A large reduction in strength over time is noted for longitudinal laminates, while no substantial change occurs for transverse samples. Although the transverse composites absorb more water (Figures 2b, 7a and 7c), their strength is however slightly affected by ageing. The tensile properties of the UD transverse laminates are known to be dominated by the matrix properties, and the polymer is less affected by water saturation.

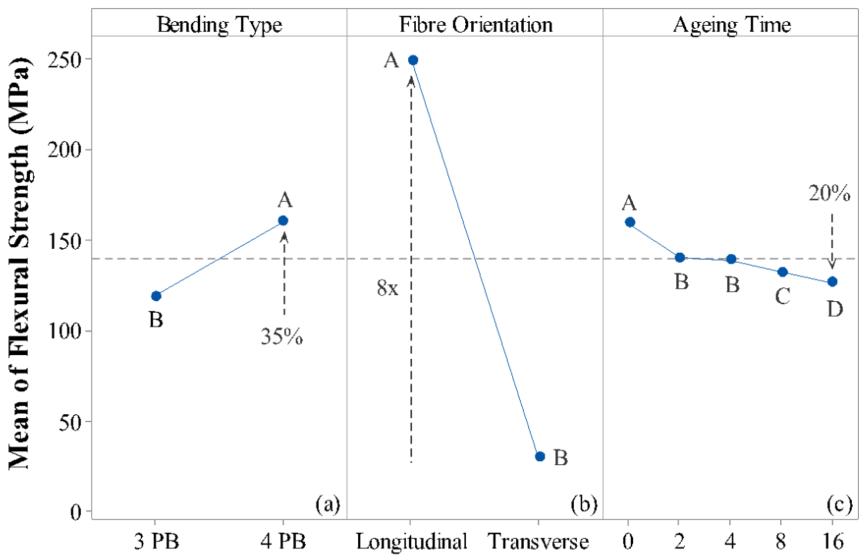


Figure 6. Main effect plot for the mean flexural strength.

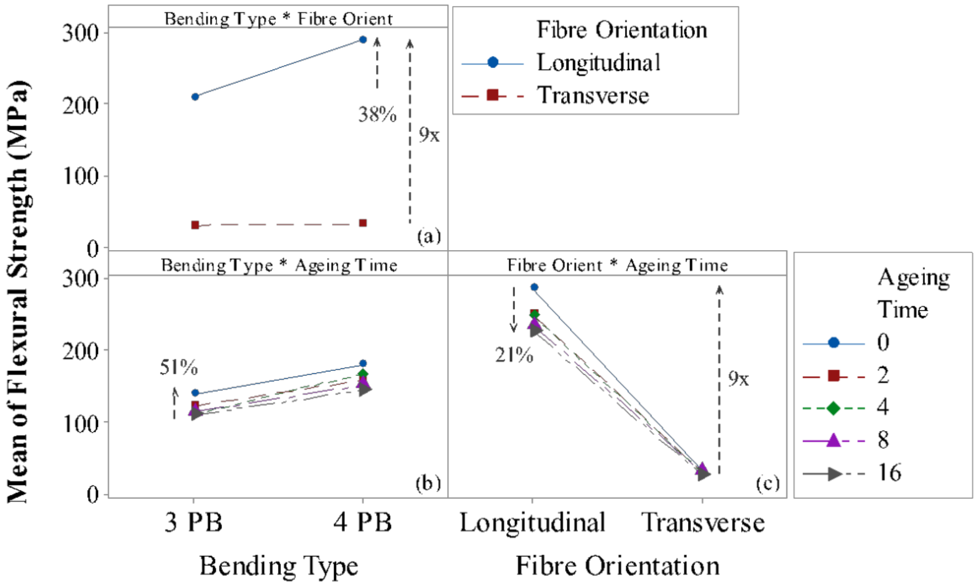


Figure 7. Third order interaction effect plot for the mean flexural strength.

3.2.2.2 Flexural Modulus

The flexural modulus ranges from 3.23 GPa (3 PB, Transverse, 16 days) to 30.58 GPa (4 PB, longitudinal, 0 day), as shown in Table 2. The main (Figure 8) and interaction (Figure 9) effects of the flexural modulus are similar to the flexural strength presented above. The highest flexural modulus value is provided by the 4PB samples (Figure 8a), and with the fibres longitudinally oriented (Figure 8b). A similar reduction in stiffness (22%) is obtained after 16 days of ageing. Samples after 4 and 8 days had however equivalent means (average) values, as also shown within the same group C.

The interaction effects reveal small variations between the 3PB and 4PB samples when transversely tested (Figure 9a), and also in pristine condition (Figure 9b). Similarly, to the flexural strength response, the stiffness of the transverse laminates is not affected by ageing (Figure 9c), since the mechanical performance is mainly dominated by the properties of the matrix.

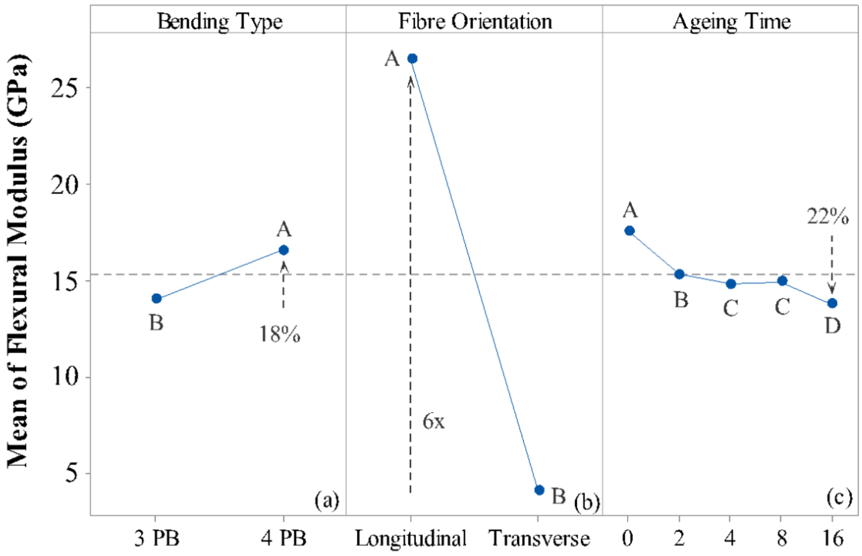


Figure 8. Main effect plot for the mean flexural modulus.

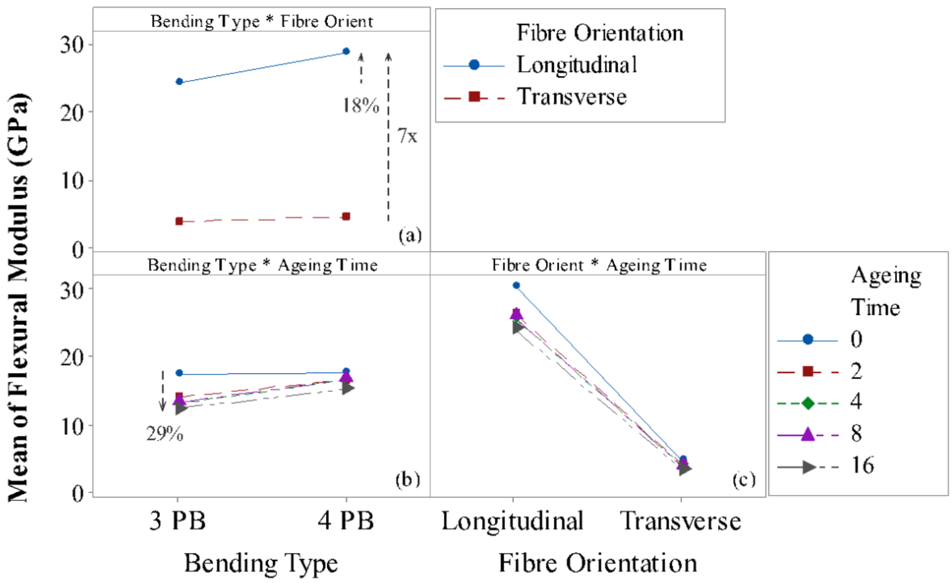


Figure 9. Third order interaction effect plot for the mean flexural modulus.

3.3 Fully saturated water environment

Flax laminate composites are tested after a fully saturated environment (100% humidity) and then compared with those saturated for 16 days at a humidity level of 50%. Results are presented in Table 4 and Figures 10-12. In general, the results presented here follow a trend similar to the one of the 50% saturated moisture samples, i.e. increases in water absorption and reduction of the flexural performance (3P and 4P bending) with ageing time and also along the transverse direction.

Table 4. Physical and mechanical results for 100% moisture saturated samples.

Bending Test	Fibre Orientation	Ageing Time (Days)	Water Absorption (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)
3 PB	Longitudinal	0	0.00	248.02 (±26.24)	30.19 (±1.16)
3 PB	Longitudinal	2	5.76 (±0.86)	130.83 (±9.86)	6.98 (±0.93)
3 PB	Longitudinal	4	8.97 (±1.00)	77.93 (±8.25)	5.67 (±0.39)
3 PB	Longitudinal	8	9.83 (±0.95)	64.59 (±10.79)	4.60 (±1.51)
3 PB	Transverse	0	0.00	28.64 (±2.85)	4.41 (±0.17)
3 PB	Transverse	2	8.62 (±0.14)	10.30 (±2.14)	0.56 (±0.03)
3 PB	Transverse	4	11.23 (±0.16)	7.53 (±0.41)	0.48 (±0.03)
3 PB	Transverse	8	11.68 (±0.15)	5.90 (±1.57)	0.44 (±0.10)
4 PB	Longitudinal	0	0.00	318.14 (±21.71)	30.75 (±10.71)
4 PB	Longitudinal	2	7.48 (±0.37)	149.81 (±11.35)	9.77 (±0.56)
4 PB	Longitudinal	4	12.96 (±0.63)	96.90 (±4.16)	6.41 (±1.11)
4 PB	Longitudinal	8	16.05 (±2.03)	65.47 (±11.73)	5.59 (±1.42)
4 PB	Transverse	0	0.00	34.07 (±2.68)	5.17 (±0.14)
4 PB	Transverse	2	10.95 (±0.24)	10.01 (±1.13)	0.55 (±0.04)
4 PB	Transverse	4	14.51 (±0.24)	9.64 (±0.67)	0.50 (±0.07)
4 PB	Transverse	8	15.32 (±0.25)	10.87 (±1.43)	0.60 (±0.05)

After eight days in a fully saturated environment, the water absorption increases by 30 and 25 times for the longitudinal 3PB and 4PB samples, respectively (Figure 10a). Similar behaviour is also observed in the transverse composites (Figure 10b). The water absorption levels are greater for the 4PB samples due to the increase in the fibre length, which raises the level of the permeability of the composites as described by Habibi *et al.* [38]. For the same surface density, composites manufactured with longer fibres possess therefore higher water absorption and porosity. A general trend towards equilibrium in water absorption is shown after 4 days for the 3PB fully (Group A) and 50% saturated samples, respectively (Figure 10). It is worth mentioning that the 4PB fully saturated samples do not reach such equilibrium after 4 days, as also revealed by the different Tukey letters (Group A, B); this can be attributed to their larger sample size affecting the water diffusion (Fick´s law). It is emphasised that the determination of the hygro-equilibrium state is not the scope of this work, and further investigations must be carried out to reach reliable conclusions.

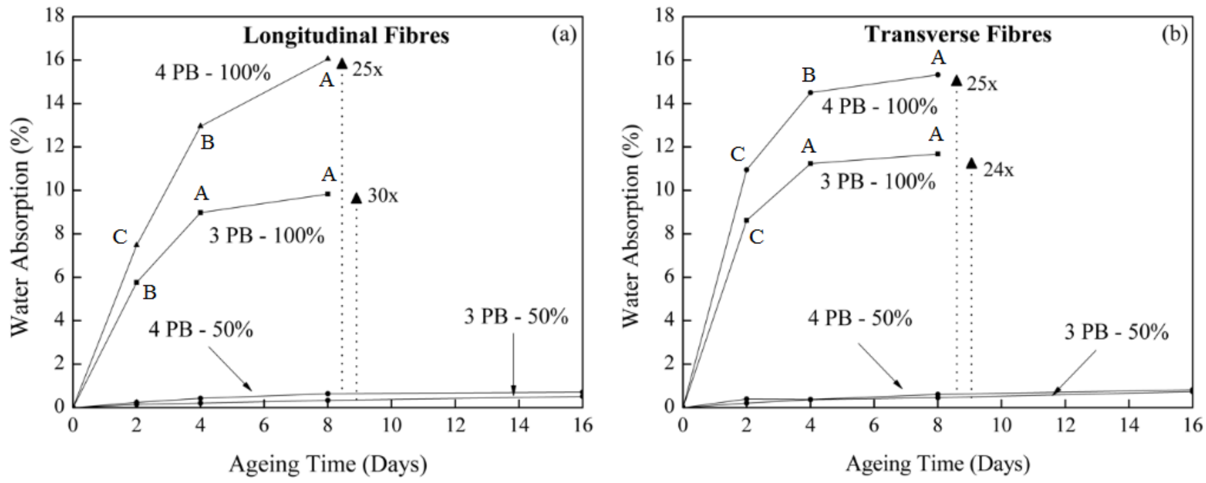


Figure 10. Water absorption at 50% and 100% humidity for (a) longitudinal and (b) transverse fibre composites.

Figure 11 shows the typical flexural behaviours of longitudinal and transverse 3PB (a) and 4PB (b) samples saturated at 50% and 100% for 8 days. 4PB samples reach a higher maximum force than 3PB samples. Substantial reductions in maximum force are achieved when the water saturation level increases from 50% to 100%. The effects of each factor on the flexural strength and modulus will be discussed in the following paragraphs.

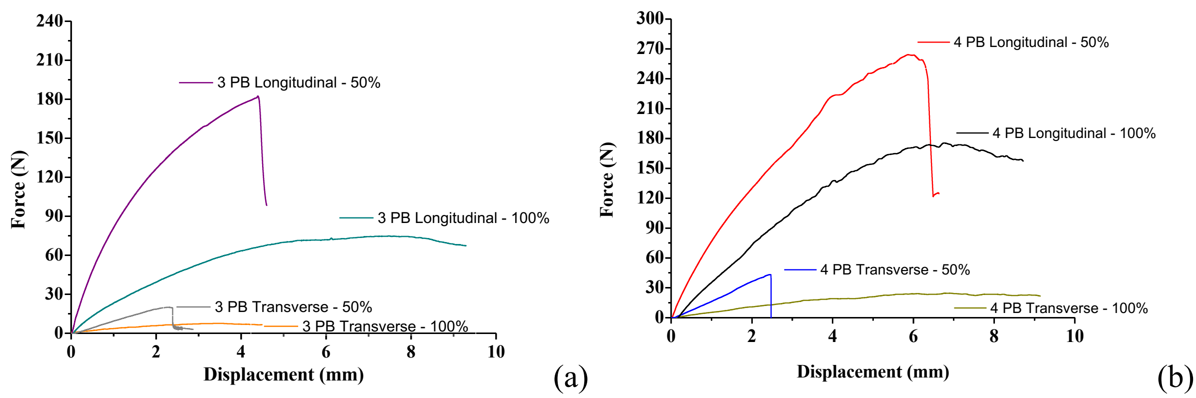


Figure 11. Typical flexural behaviour of 3PB (a) and 4PB (b) samples at 50% and 100% water saturation levels for 8 days.

Figures 12 and 13 show reductions in strength and stiffness over ageing and moisture levels for the longitudinal (a) and transverse (b) laminates. A drastic drop in strength is observed after 8 days in 3PB and 4PB samples saturated at 100% humidity. A slight variation in mechanical properties is found between the 3PB and 4PB samples saturated at 100% humidity compared to 50%. The laminates tested at four-point bending have however better mechanical properties. Samples saturated for 16 days at 50% humidity are equivalent to the ones with less than one day ageing at 100% humidity. Boris *et al.* [39] showed that the water diffusion coefficient increases with the relative humidity. The water diffusing within the composite material creates hydrogen bonds with the fibres, which can lead to the reduction of the interactions between fibres and matrix. Capillarity could provoke the flow of water molecules along the fibre/matrix interfaces, as well as a diffusion process through the bulk matrix. This water is bound to the network by hydrogen bonds breaking the existing bonds between the hydroxyl groups of the matrix chain [39]. This could result in interfacial debonding affecting the mechanical strength of the composite.

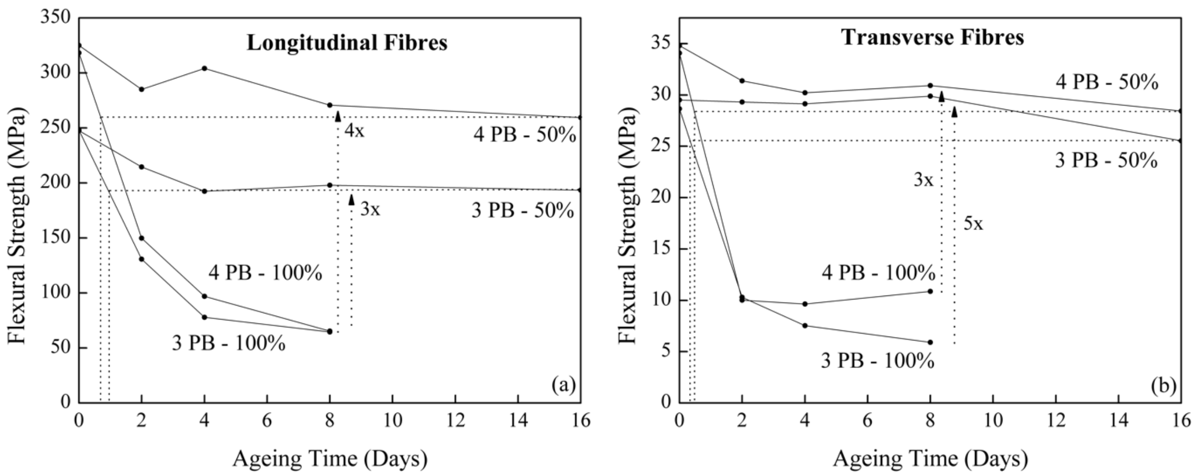


Figure 12. Flexural strength at 50% and 100% humidity for (a) longitudinal and (b) transverse fibre composites.

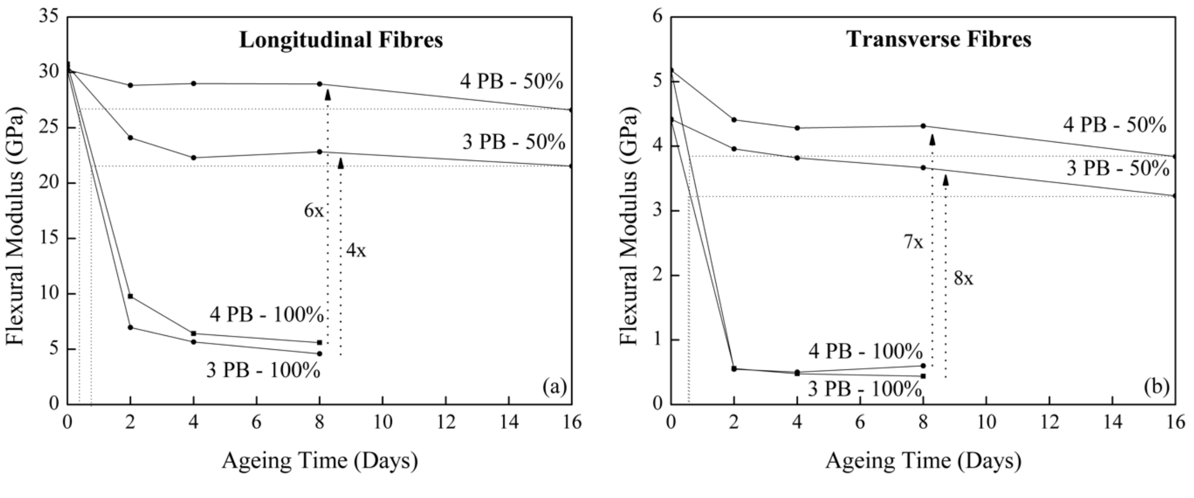


Figure 13. Flexural modulus at 50% and 100% humidity for (a) longitudinal and (b) transverse fibre composites.

Table 5 shows a comparison between the present results at 100% saturation with those obtained by Cheour *et al.* [20], who investigated the effect of the water ageing on the flexural modulus of composites reinforced with flax fibres. Although both studies show similar water absorption, the present work considers a transient sorption regime, while Cheour *et al* [20] performed the measurements in equilibrium state. In addition, the latter authors have investigated compacted flax composites made with a volume fraction of 35%, while the present study is related to a 43/56% epoxy/flax prepreg laminates manufactured with autoclave. The present work shows the presence of a larger flexural modulus only for dry composites (0 days); this is attributed to the larger amount of fibres along the loading direction (0°). In contrast, when the transverse matrix-dominated direction is considered (90°) the flexural modulus of the prepreg composites decreases due to its smaller matrix fraction (Table 5). The reduced flexural modulus featured by the prepreg flax composites compared to [20] after 4 days of ageing can be also attributed to the greater degradation due to the larger amount of fibres. The significant loss in modulus observed for the autoclaved prepreg epoxy/flax laminates and the composites shown in [20] may also be due to the different role that the interlaminar shear strength plays in the flexural behaviour of composites. The interlaminar shear strength in flexure is more dominant than in tensile failure; the compaction manufacturing process and lower fibre volume fraction in [20] can lead to different consolidation states between the plies and therefore generate different interlaminar shear strength in those composites compared to the case shown in this paper. As a consequence, the interlaminar shear strength could be more sensitive to the moisture sorption than in the case of the thermo-compressed specimens in [20]. The composites evaluated in the present work may also present heterogenous moisture contents due to the transient regime, in particular along the thickness of the specimens. This may lead to higher internal stresses and a consequent reduction of the stiffness and strength in the autoclaved samples.

Table 5. Comparison of the results for 100% RH.

	Fibre volume fraction	Water absorption (%)		Flexural Modulus (GPa)			
				0°		90°	
		0°	90°	0 days	4 days	0 days	4 days
Present work (prepreg)	56%	9.83	11.68	30.19	5.67	4.41	0.48

Cheour *et al.* [20]	35%	10.95	11.52	21.8	14.8	6.5	4.0

The apparent porosity ranges from 3.02 to 13.79% (Table 6). Figure 14 shows the apparent porosity results for UD flax composites (3PB samples) with up to 8 days of water saturation. Tukey´s test reveals that porosity levels for transverse and longitudinal samples are similar at 30 min (Group C) and 2 days (Group B) of saturation. Longitudinal samples have similar porosity levels at 2, 4 and 8 days, as indicated by the same letter group B. In contrast, the porosity of transverse samples increases up to 4 days, remaining constant after this period. A 52% variation is obtained between the transverse and longitudinal composites after 4 days of saturation. The water penetration is easier along the direction of the cross-section of the fibres [39, 40] because more porosity is present there than along their peripherical surface. Transverse prismatic samples feature a better percolation of water because of the presence of a larger number of fibres cross-sections, in comparison to the longitudinal samples. Mbou *et al.* [40] investigated the water diffusion from the pith of *Raffia vinifera* by Fick's second law. The diffusion coefficients decrease from the centre to the periphery in the radial position, while the water absorption increases from the periphery to the centre in the radial position. It is noteworthy that the microstructural characteristics of the transverse and longitudinal composites are the same, as also indicated by the equal apparent density (1.38±0.01 g/cm^3). However, the exposure of the fibre cross-sections facilitates the water diffusion along the length of fibres, leading to higher porosity values.

Table 6. Apparent porosity result for laminate composites under 100% humidity.

Fibre Orientation	Ageing Time	Apparent Porosity (%)
Longitudinal	30 min	3.36 (±0.36)
Longitudinal	2 days	7.24 (±0.97)
Longitudinal	4 days	9.05 (±1.02)
Longitudinal	8 days	8.89 (±0.83)
Transverse	30 min	3.02 (±0.58)
Transverse	2 days	8.36 (±0.78)
Transverse	4 days	13.79 (±0.28)
Transverse	8 days	13.49 (±1.28)

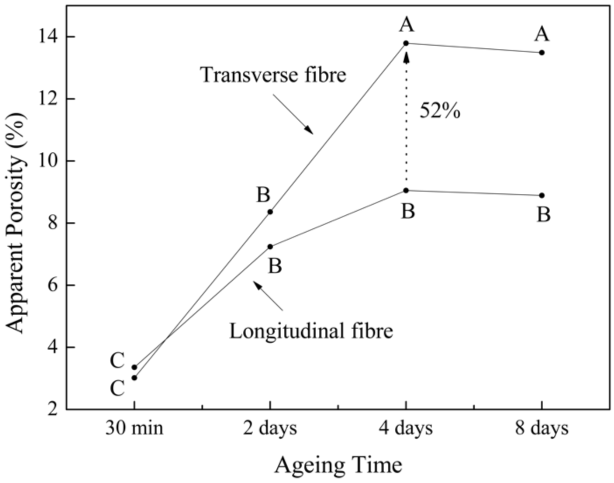


Figure 14. Apparent porosity for longitudinal and transverse fibre composites (3PB samples) under 100% humidity.

The increase in water absorption and porosity over time contribute to reduce the mechanical performance of the flax composites in a fully saturated environment. The reduction of the flexural properties is progressive until the fourth day and remains constant thereafter.

4. Conclusions

Unidirectional composites made with prepreg flaxtape have been here characterised to investigate the interaction between the ageing time, the type of bending loading and the fibre orientation and their influence on the water absorption, porosity and overall flexural properties. The main conclusions are described below:

i. The main factors (bending type, fibre direction and ageing time), as well as their interactions, affect all the responses related to the 50% humidity composites, as evidenced by ANOVA;

ii. Four-point bending test samples exhibit higher water absorption and flexural properties in the transient sorption regime, compared to three-point bending, being attributed to the dimensional effect of the sample;

iii. Longitudinal flax laminates lead to lower water absorption in the transient sorption regime, compared to the transverse ones, due to their lower cross-sectional exposure to moisture. The samples with $[0^{o}]_{12}$ architecture also show improved flexural properties, as the bending behaviour is strongly dominated by the tensile stress under the neutral line;

iv. The water absorption increases progressively with ageing time, compromising the flexural properties of the composites;

v. The flexural properties of the flax composites at 50% humidity for 16 days are equivalent to less than one day in a fully saturated environment;

vi. The water immersion time affects the apparent porosity of the flax composites, which increases until the fourth day, remaining constant thereafter.

Acknowledgement

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 744349 (SSUCHY project). JCdS, THP and LAdO are also grateful for the support provided by the Bristol Composites Institute, and the Brazilian Research Agencies CAPES and CNPq (PQ - 309885/2019-1) for the sandwich-doctoral and postdoctoral scholarships, respectively.

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