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Abstract

The use of vegetal fibers to reinforce polymeric matrix composites is challenging and goes with questions of durability issues, especially when exposed to damp conditions. The aim of this study is to quantify, up to 1 year, the impact of humidification/drying cycles, i.e. 3.5 days at 90% HR and 3.5 days at 40% HR, both at 55°C, on the longitudinal mechanical properties of a unidirectional flax/epoxy composite. Then, by a multi-scale analysis, the objective is to identify the causes of mechanical properties evolutions. According to the results of this study, a cyclic hygrothermal ageing induces irreversible degradations of fibers (matrix-embedded or not) and interfaces within the composite. Indeed fiber/fiber and fiber/matrix debondings have been observed by morphological analyses and a loss of fibers hydrophilic components has been highlighted by chemical and microstructural characterizations. A plasticization of flax fibers has also been shown during this kind of ageing. All these modifications induce a drop of composite's moduli after the first cycles of exposure and a decrease of ultimate tensile stress and strain after long time exposure. But these mechanical properties evolutions are much lower than the values found in the

literature. Decreases of about -10% for the modulus and about -14% for the ultimate tensile stress have been recorded after 1 year of exposure and 52 cycles of ageing. Thus, this study highlighted that a well manufactured flax/epoxy composite is resistant to a cyclic hygrothermal ageing. These results are therefore promising for the development of this type of bio-based materials on a larger scale.

Keywords:
- Flax fibers
- Biocomposite
- Ageing
- Hygrothermal effect
- Mechanical properties

1. Introduction

In the current environmental awareness, innovative solutions have been studied to reduce the environmental impact of composites materials. Vegetal fibers are increasingly used as reinforcement instead of synthetic ones. Among these fibers, flax fibers have a low density, around 1.5 (Amiri et al., 2017; Baley, 2002) and associated with thermosets matrix, obtained composites can reach good mechanical properties. (Berges et al., 2016; Cadu et al., 2018; Poilâne et al., 2014). However, like many materials, they are subject to ageing and their properties can be altered when exposed to service conditions, such as moisture, temperature or ultra-violet rays (Azwa et al., 2013).

The study of bio-based composites ageing is essential to make sure of the durability of this kind of materials. In the literature, most studies have been performed by immerging composites for several months in water or sea water, from room temperature to 100°C (Assarar et al., 2011; Dhakal et al., 2007; A. Le Duigou et al., 2014; Le Duigou et al., 2015; Li and Xue, 2016; Yan and Chouw, 2015). For flax-epoxy composites, this kind of ageing induces a change in the shape of tensile curve of the composites and noticeable variations of mechanical properties (Li and Xue, 2016). In these composites, the amount of absorbed moisture is greater for flax fibers than for used thermosetting resins. For example, the quantity of absorbed water for immersed saturated materials is between 1.25 and 2.75% for pure epoxy and between 7 and 9% for unidirectional composite with a fiber volume fraction of 37%, depending on the water temperature from 23 to 60°C (Li and Xue, 2016). Temperature seems to impact the kinetic and the saturation value of moisture water absorption. Composites' water absorption is furthermore proportional to their fiber contents (Assarar

et al., 2011; Dhakal et al., 2007). The more hydrophilic behavior of flax fibers compared to matrix induces a differential swelling effect leading to localized stresses in the interfaces zones. It can irreversibly deform the matrix and damage the cohesion between fibers and matrix (Azwa et al., 2013). Micro-cracks can appear in the matrix around swollen fibers promoting water transport through the interface. Water soluble substances (pectin and hemicellulose) can also be leached and accentuate the interfacial strength reduction (Li and Xue, 2016). Newman (Newman, 2009) has observed that the interfacial debonding is emphasized by cycled exposure to immersion and dry conditions, due to the differential kinetics of water sorption and swelling between the fibers and the matrix.

Thus, the influence of composites immersion has been widely studied. However, depending on the intended use, immersion ageing might not be realistic, involving phenomena that would not be activated when the material is not repeatedly exposed to liquid water. A few studies have been carried out on hygrothermal ageing of flax/epoxy composites (Berges et al., 2016; Scida et al., 2013). It has been observed that exposure of this kind of composites to high relative humidity (85% or 90% RH) induces a modulus decrease of around 33% after three days and about 55% after 38 days. Scida et al. (Scida et al., 2013) noted a lower reduction for the ultimate tensile strength (about 12%) while no evolution has been observed by Berges et al. (Berges et al., 2016). In both studies, authors attribute observed evolutions to the plasticization of both matrix and fibers by absorbed water. It should be noted that tests have been performed on water vapor saturated materials and it is not possible to distinguish if the decrease of mechanical properties is related to the reversible phenomenon such as plasticization or irreversible phenomenon such as hydrolysis. Moreover, these studies did not focus on cycled exposures to humid/dry conditions and induced multi-scale mechanisms still have to be studied.

The sensitivity of this kind of bio-based composites to water is partially inherited from flax fibers. Indeed, it has already been shown that the water content inside flax fibers has a major impact on their mechanical properties and on those of their composites (Baley et al., 2012). Moreover, as these fibers exchange water molecules very easily, modifying their environment conditions can significantly modify their properties (Stamboulis et al., 2001). Thus, one explanation of mechanical properties modification is that differential swelling may occur inside cell-wall layers, induced by the differences in hydrophilic constituents' (i.e. cellulose, pectin and hemicellulose) volumetric variations while drying or wetting, causing the development of stresses and structural damages within fiber (Baley et al., 2012; Le Duigou et al., 2015; Roudier, 2012). In some cases, cracks can be observed, initiated in the lumen area (Le Duigou et al., 2015). Absorbed water also plays a role of plasticizer in the fiber, breaking the initial secondary bonds within hydrophilic

constituents (Girault et al., 1997). In a general way, drying (Baley et al., 2012, 2005) or moistening fibers (Roudier, 2012) reduces their ultimate tensile strength. Moistening fibers can also reduce their modulus.

In this study, the influence of hygrothermal ageing on a flax based composite's properties has been investigated. The selected ageing process was composed of humidification/drying cycles with a temperature chosen to accelerate phenomena without inducing thermal alteration of the materials. Fibers have also been submitted to the same ageing and studied to understand the origins of composite's properties evolutions. Tensile tests have been performed to characterize mechanical properties of materials i.e. fibers' samples and composites, while multi-scale analyses: DVS, SEM, XRD, FTIR and Van Soest method, allowed to obtain explanations on mechanical properties evolutions at short and long time of exposure.

2. Materials and methods

2.1. Materials

The flax fibers (*Linum usitatissimum*) used in this study are in the form of pure unidirectional reinforcements FlaxTape™ 110 produced by Lineo©. We measured an areal weight of 96 $g.m^{-2}$ and a density of 1.45 for fibers (Cadu et al., 2018). Fibers plies were cut from the roller to be conditioned and aged. Fibers' samples were composed of several bundles and were cut from plies, with a width of 5.0 ± 0.5 mm, a gauge length of 150 ± 0.5 mm and have a thickness of 0.20 ± 0.03 mm. They were weighed, and then steel tabs were glued using Loctite® to perform tensile tests. The measured mass of samples is 140 ± 18 mg.

The matrix used is a DGEBA epoxy resin (SR 8500) with an amine hardener (SZ 8525) produced by Sicomin©. We measured the following properties for the unfilled thermoset: σ_{max} = 59 ± 4.54 MPa; E = 2.65 ± 0.10 GPa; ε_{max} = 2.54 ± 0.44 %. 12 plies unidirectional composites have been produced by thermocompression using a dedicated manufacturing process detailed in a previous study (Cadu et al., 2018). The curing was composed of two steps: a first one at 40 °C for 15 minutes and a second one at 80°C for an hour, during both steps a 3 bars pressure was applied. The samples then underwent a 2-hour post-curing at 80°C.

By weighing method, fiber volume fraction has been measured to be around 47% and void content around 2.5%. Unidirectional tensile specimens have been prepared according to geometry 4 from ISO 527 standard, their dimensions are 250 ± 0.5 mm long, 25 ± 0.5 mm wide and 1.8 ± 0.1 mm thick. The edges

of the composite's samples have been coated just before the post-curing step with the same resin used for the manufacture.

2.2. Ageing Method

Ageing method has been designed to stimulate the differential swelling effect inside the composite material with humid and dry steps. The ageing temperature has been chosen to 55°C. This temperature has been chosen to accelerate the ageing mechanisms induced by water. It also limits the micro-organisms development which is optimal around 30°C (Gradeci et al., 2017). Moreover, it does not activate the melting of fibers waxes that we measured around 60°C by differential scanning calorimetry, in accordance with the literature values (Athukorala et al., 2009). To avoid dew point and liquid water appearance on our materials during ageing, temperature and humidity are progressively increased after the first insertion of samples in the climatic chamber. Then, humidity ramps of 2 hours were used between humid and dry steps. Samples have been submitted to cyclic ageing at 55°C ± 1°C in a climatic chamber (CTS® C-20/200). As presented on Figure 1, a cycle is composed of humidification for 3.5 days at 90 ± 1% RH and drying for 3.5 days at 40 ± 1% RH. We chose these durations to perform a complete cycle in a week. Tested ageing durations are defined in Table 1.

2.3. Characterization Methods

Samples' preparation before characterizations: Aged samples are extracted from the climatic chamber after the "dry" (40% RH) step of the ageing method. All, aged and unaged, fibers' samples and composites specimens have been conditioned at 23 ± 1°C and 50 ± 1% RH for 7 days in a climatic chamber (CTS® CP+10/600) before characterizations. This stage is performed to get the materials in the same hydric state (Cadu et al., 2018).

Dynamic Vapor Sorption (DVS) measures were used to investigate the water uptake of samples using a SMS DVS-Advantage. The DVS is able to provide highly accurate mass changes in humid environments. Samples are small balls for flax fibers and square specimens of about 1 cm for composite and resin. Analyzes were performed at 25°C and composed of a humid step (3.5 days at 90%RH) and a dry step (3.5 days at 40%RH).

Tensile tests on composite materials have been performed at room temperature on a MTS Criterion C45, equipped with a 100kN load cell and a 50 mm gauge length mechanical extensometer. Test speed was set at 1mm/min. As previously mentioned, unidirectional 0° samples' dimensions complied with the ISO 527-4 standard. This standard recommends to calculate the Young's modulus in the 0.05% to 0.25% strain range. However, as it has been observed in other studies (Berges et al., 2016; Cadu et al., 2018; Poilâne et al., 2014), unidirectional flax fibers reinforced composites exhibit bilinear behavior in this strain range. Thus we used two modulus, calculated by linear regression, E_1 on the linear part before the inflection point and E_2 on the linear part just after this point as presented on the Figure 2, respectively the triangles and diamonds marks. Depending on ageing time and samples, inflection point was in a strain range of 0.12%-0.16%. For each sample, the strain range selected to calculate E_1 started from 0 and was taken as wide as possible to keep $R^2 > 0.99$ in the linear regression calculation. In the same way, the strain range selected for E_2 started as close as possible to the inflection point to end at 0.4%. For each ageing duration, 5 specimens were tested.

Tensile tests of fibers samples have been performed at room temperature on an Instron 5969 tensile machine equipped with a 2kN load cell. Test speed was set at 1 mm/min. Stiffness of samples was calculated in the linear strain range of the curve, from 0.05% to 0.3%. Apparent modulus and stress have been calculated using a rectangular section of 5mm width and 0.2mm thick. 40 samples were tested for each ageing duration.

Thermogravimetric analyses (TGA) have been performed in order to estimate water content for unaged composites and after 1 year of ageing, using a Netzsch STA 409 CD thermo-balance. Based on the study of Baley et al. (Baley et al., 2012), isothermal analyses are composed of a first step at 105°C for 14h and a second step at 150°C for 5h in one run.

Fourier-Transform Infrared Spectroscopy (FTIR spectroscopy) has been used to characterize the chemical evolution of the first few µm of flax fibers' bundles during the ageing cycles. The samples were analyzed on a Nicolet™ impact 380 spectrometer using the Attenuated Total Reflectance (ATR) method with a diamond Durascope fixture. For each measure, 32 scans have been performed, with a resolution of 4 cm^{-1} in a wave number range from 400 to 4000 cm^{-1}. Spectra were baseline-corrected and normalized using the peak at 1160 cm^{-1}. This peak is attributed to the C-O-C stretching asymmetric bridge of the

cellulose and is assumed not to evolve during ageing, as reported in previous studies (Célino et al., 2014; Colom et al., 2003; Zhang et al., 2003). For each ageing duration, 8 measures have been performed.

X-ray diffraction (XRD) analyzes have been used to check the evolution of fibers microstructure within bundles, especially the apparent crystallinity. A Philips PW 3830 diffractometer employing a CoKα1 (λ=1.79 Å) radiation was used. Samples were laid on silicon support and measures were performed on the 4-76° 2θ angle range. X-ray diffraction spectra of flax fibers presented 3 crystalline peaks and an amorphous halo. Gaussian functions have been used for the complete deconvolution of the signal using the Origin™ software. Thus, the apparent crystallinity is calculated from the ratio of the area of the 3 crystalline peaks to the total area including the amorphous fraction using the following equation:

$$C = 100.\frac{I_{cr\ peak1}+I_{cr\ peak2}+I_{cr\ peak3}}{I_{cr\ peak1}+I_{cr\ peak2}+I_{non-cr}+I_{cr\ peak3}} \quad (1)$$

Where: C is the apparent crystallinity (%), $I_{cr\ peakx}$ is the area under the crystalline peak n°x and $I_{non\text{-}cr}$ is the area under the non-crystalline peak of the diffraction pattern. The Figure 3 shows a typical X-ray diffraction spectrum of flax fibers. For each ageing duration, 4 measures have been performed.

Scanning electron microscope (SEM) observations of fibers and composite have been performed with a FEI XL 30 microscope equipped with an EDAX DX 4i microprobe. For fibers surfaces observations, samples were bonded on a 12 mm diameter carbon tape. For cross-sections observations, samples were embedded in ambient crosslinking epoxy matrix EpoFix© and polished with mirror finish using Struers© polishing machine. Ethanol has been used in place of water to reduce fibers' swelling and limit as much as possible the potential damages that may occur during polishing. All the specimens have been coated with a thin carbon layer to avoid charging.

The Van Soest method (AFNOR, 2013; Van Soest et al., 1991) has been used to determine the hemicellulose content in fibers' bundles dry matter, using a Fibretherm (Gerhardt©). The samples have been grinded but unlike all others characterizations, samples have also been dried before analyses. The analysis is composed of two hydrolyses. The first hydrolysis (NDF) is performed with a neutral detergent. During this step, proteins and pectines are extracted. The residue is then washed and dried. It contains the hemicellulose, the lignins and the cellulose. The second hydrolysis (ADF) is carried on this residue by an

acid solution, also followed by washings and drying. The second residue contains the lignins and the cellulose. Analyses have been performed on unaged samples and after 9, 26 and 52 weeks of ageing. Analyses have been performed 3 times for each of these durations. The hemicellulose content is expressed as a percentage of fibers' dry matter and calculated using the following equation:

$$NDF - ADF = hemicellulose\ content \quad (2)$$

Since the variability of mechanical properties for this kind of materials is not negligible, we used a statistic variance test (ANOVA) to determine if observed variations are significant or not. The significance of the variation between the average values will be noted S and is calculated with $S = \frac{F}{F_{crit}}$. F is calculated with the intergroup variance (variance considering all specimens) divided by the intragroup variance (mean value of the variances of the two groups of specimens) and F_{crit} is determined on a 95% safety Snedecor F-table. F and F_{crit} values are automatically calculated with Excel's ANOVA function. If S > 1, the null hypothesis of the ANOVA test is invalid, which means that the specimens do not belong to a single population. In other terms, if S > 1, observed variations between averages of two groups can be assumed as significant.

3. Results and discussion

Multi-scale analyses have been carried out to characterize the materials and to identify the mechanisms occurring in the composite through ageing. The next section will present the evolution of mechanical properties.

3.1. Mechanical properties

Initial properties of unaged unidirectional composite samples have been measured by tensile tests on 7 specimens. They are the following: σ_{max} = 328 ± 23 MPa; E1 = 30.8 ± 0.8 GPa; E2 = 21.3 ± 0.5 GPa (Cadu et al., 2018). Composites specimens have then been exposed to hygrothermal cycles ageing up to one year and tensile tests were performed on all aged samples.

As shown on Figure 4 (a and b), the composite's ultimate tensile strength (σ_{max}) and deformation at break (ε_{max}) are stable up to 26 weeks of exposure. This is confirmed by the ANOVA test. A decrease of

ε_{max} of about 20% happened between 26 weeks and 52 weeks. On this period, a decrease of σ_{max} is also visible but is less significant, about 12%. Evolution of both moduli E_1 and E_2 starts earlier (Figure 4 c). Decrease occurred after the 1st week of exposure until the 4th. A decrease of respectively 8% and 12% is observed, then they stabilized up to 52 weeks. These decreases of moduli are much lower than values reported in the literature for non-cyclic hygrothermal exposures (where the decrease is already -33% after three days) (Berges et al., 2016; Scida et al., 2013). But in these literature studies, the edges of samples were not protected and mechanical tests were performed on water vapor saturated materials. The water saturation of the composite undoubtedly generates additional drops related to plasticization phenomena, as mentioned by authors. Moreover, in these studies void ratios of composite materials were between 6 and 9%. Using a weighing method inspired from ASTM D 3171 – 99, we measured a void content of approximately 2.5% by volume fraction in our material. In this regard, the lower impact of ageing might also be related to the lower porosity of our composite.

We investigated potential origins of the properties evolutions. In the longitudinal axis (0°), mechanical properties of the unidirectional composite are mainly controlled by fibers properties. To understand if the evolutions of composites properties directly came from a degradation of fibers properties, tensile tests have been performed on fibers' samples exposed to the same ageing conditions as composites.

Mechanical properties of flax fibers' samples are dispersed. Nevertheless, the 40 samples tested for each ageing duration allowed to be confident in observed tendencies. No evolution of three mechanical characteristics have been observed up to 4 weeks of exposure, as visible on Figure 5 . But unlike the composite, the ultimate tensile strength decreases of about 30% between the 9th and 13th weeks and then stabilized up to 52 weeks. The failure strain seems to increase slightly between the 4th and 9th weeks and then stabilized up to 26 weeks. A decrease seems to occur after 26 weeks. Regarding the modulus of fibers' samples, it decreases of about 40% between the 4th and the 13th weeks.

The Table 2 sums up the evolutions of composite and fibers' samples mechanical properties. The variations are expressed in percentage of initial value, for the unaged material. The shading also indicates if the variations are significant or not according to the ANOVA test. A black shading indicates a significant variation according to the ANOVA test ($S > 1$) with an amplitude higher than 20%. A dark grey shading indicates a significant variation according to the ANOVA test ($S > 1$) with an amplitude lower than 20%. Light gray indicates an almost significant variation ($S \approx 1$) with an amplitude higher than

10%. As shown in Table 2, it is noticeable that the evolutions of mechanical properties did not occur for the same ageing durations for composite's specimens and fibers' samples.

3.2. Impact of cyclic hygrothermal ageing on the composite's moduli

Comparing the evolutions of moduli through ageing, it appears that significant decreases occurred respectively until 4 weeks for the composite and from 9 weeks for fibers' samples. We could think that non-embedded fibers' modulus would be impacted before the composite's one. As this is not the case, fibers' samples tensile modulus could not be directly transposed to the composite. However, the solicitation mode of fibers is not exactly the same in bundles and in composites. Indeed, for fibers' bundles with gauge length longer than elementary fiber, Bos (Bos, 2004) assumed that the strain is mainly put on fiber/fiber interface, while the strain is mainly put on the elementary fiber in the case of composites. By tensile tests, we measured fibers' samples and composite's moduli between the values of flax fiber/fiber interfaces and those of elementary fibers taken from the literature (Table 3).

The evolution of fibers' samples tensile modulus indicates that this fiber/fiber interface, which is composed of water sensitive species (mainly pectin (Charlet and Béakou, 2011)), is not altered by ageing for the first 4 weeks. So it is reasonable to suppose that elementary fiber and highly crystalline cellulose are not damaged either. In the same way, we can suppose that the hemicellulose and the few pectins within the S2 layer, which are both responsible to the cohesion of cellulose micro-fibrils (Morvan et al., 2003), are no more degraded than in the surface. So, the variation of composite's modulus until 4 weeks cannot be directly explained by fibers' bundles evolutions.

To explain these evolutions of moduli, physico-chemical analyses were realized.

- Hydrophilic behavior of fibers and composite (unaged to 9 weeks of exposure)

First, to try to understand the composite's modulus decrease, we looked at the interactions between materials and water vapor. DVS analyzes have been performed on fibers' bundles, on resin and on composite's samples, as presented in

Table 4, on Figure 6, Figure 7 and Figure 8. A DVS measure is comparable to one ageing cycle with the same humid step of 3.5 days at 90% RH and dry step of 3.5 days at 40% RH. However, both were conducted at 25°C and may underestimate the phenomenon compared to 55°C used in ageing method. It is noticeable that water absorption kinetic is faster for unaged fiber's bundles than for the unaged

composite. Fibers' bundles could reach saturation in wet step and stabilization on dry step. Yet, for the unaged composite the stabilization did not occurred after 3.5 days, for the wet and the dry steps (Figure 6). Weight gain due to water, after the humid step, is also more important for fibers' bundles (9.1%) compared to the composite (3.7%). It is also noticeable that pure matrix absorbs almost no water (0.3%) compared to fibers' bundles and composite. As matrix is less hydrophilic than fibers this would lead to two effects. The matrix would reduce the water diffusion and prevent the fiber from swelling and shrinking freely in the composite. Moreover, DVS analyses tend to indicate that all the water absorbed by the unaged composite during humid step is not completely desorbed after the dry step. A small additional water quantity could stay in the material after the first weeks of ageing, even after a week conditioning. This would slightly participate to the composite's modulus decrease after first weeks of ageing. Moreover, absorbed water is totally desorbed for 9 weeks-aged composite (-0.2%) (Figure 8 and Table 4) and a slight rise of composite's modulus is observed between the 4^{th} and the 9^{th} weeks. These observations strengthen this hypothesis.

The DVS analyzes will also be discussed in the rest of the article.

- Morphological evolutions of the composite

To assess if other parameters could explain the composite modulus decrease observed from the 1^{st} week, we studied the cross-sections of composite. SEM observations have been performed in order to compare the evolution of interfaces areas within the composite material during ageing. Cross-sections of composite have been observed, before ageing and after 1 week (Figure 9). In certain specific area, poor cohesion between matrix and fibers can be observed, even for unaged composite (Figure 9 a). These defects, possibly caused by polishing, are especially located in areas of residual bark that seems to constitute a flaw for the good fibers/matrix cohesion. However, adhesion is good for the majority of fibers. Some differences have been observed on 1 week-aged composite. Additional cracks appear during this period within some fibers' bundles of the composite (Figure 9 b).

These cracks could be induced by the swelling and shrinking of flax fibers caused by humidity cycles. As previously mentioned and presented in Table 4, weight gains measured by DVS analyzes indicate that flax fibers absorb much more moisture than epoxy. The flax fiber radial swelling strain reaches more than 10% at 90% RH (le Duigou et al., 2017). However, in the composite, fibers volumetric variations are constrained and the fibers cannot swell

as much as they should because they are embedded in a matrix (Joffre et al., 2013; Le Duigou and Castro, 2016). The fibers' swelling induced by moisture absorption, during wet step, can therefore generate stresses. As a consequence, these stresses could induce modifications of the structural organization of fibers, which cannot swell freely. We may wonder if a fibers' micro-fibrillar angle variation could occur, and/or deformation of the matrix and interfaces degradation. The micro-fibrillar angle of fiber governs its stiffness (Baley, 2013; Bledzki and Gassan, 1999). A variation of this angle could impact the composite's moduli. This could explain observations made on Figure 4. During dry step, the fibers are constrained when they shrink, due to their cohesion with the matrix. If the fibers are not individualized and present in the form of bundles inside the composite, as in our case, cracks would preferentially appear more at the level of fiber/fiber interface than at the level of fiber/matrix interface. Indeed some authors reported that interfacial shear strength is about 4 times higher for flax/epoxy than flax/flax (Charlet and Béakou, 2011; Antoine Le Duigou et al., 2014) (respectively between 13.2 ± 3.2 MPa and 22.5 ± 1.5 MPa, depending on flax species, for flax/epoxy; and 2.9 ± 2.1 MPa for fiber/fiber). For few individualized fibers, cracks can appear between fibers and matrix, widening the imperfect interfaces or breaking it in weaker zones. This debonding phenomenon inside some fibers bundles in the composite could alter the stresses path. This would be an additional explanation to the reduction of modulus observed after the first few weeks of ageing.

So the composite modulus decrease observed until 4 weeks would result from a slight additional residual water within the material after ageing, associated with fiber/fiber debonding in composite's bundles.

3.3. Impact of cyclic hygrothermal ageing on the composite's tensile strength and strain

Comparing the evolutions of ultimate tensile strength through ageing in Table 2, it appears that significant decreases occurred around 52 weeks for the composite. We will now focus on the composite's ultimate tensile strength and strain decreases observed between 26 and 52 weeks of ageing. To explain the evolution of composite's tensile strength and strain during ageing, morphological analyses have been performed on composite's cross-sections. Cracks within composite do not appear to be significantly more numerous after 26 weeks (Figure 10 a) than after 1 week of exposure (Figure 9 b). After 52 weeks of ageing, additional cracks are visible in the composite. They are located around the edges of elementary fibers, whether individualized or in bundles (Figure 10 b). These more numerous debondings at fiber/matrix and fiber/fiber interfaces observed in 52 weeks aged composite are many defects induced by differential dimensional variation between fibers and matrix due to the ageing. This can explain the

decrease of composite's ultimate tensile strength and strain observed by tensile tests between 26 and 52 weeks (Figure 4). Moreover, these more numerous cracks facilitated diffusion of water molecules within the composite. We also noted this phenomenon by DVS analysis. We observed a faster sorption/desorption and the complete desorption of water on aged composites (Figure 8).

A slightly lower weight gain has also been measured for composites after ageing (Table 4). This phenomenon might be partially explained by a hornification mechanism of flax fibers within the composite (Fernandes Diniz et al., 2004; Gourier et al., 2014; le Duigou et al., 2017). If water is extracted from polysaccharides, above a certain level, hydrogen bonds that linked them together are broken and then rebuilt within polysaccharides. This results in a lower water sensitivity of fibers due to fewer available hydroxyl groups in hydrophilic components.

From another side, even if in the composite the fibers are slightly protected from water by the matrix, we can also suppose that the decrease of composite's ultimate tensile strength and strain between 26 and 52 weeks is partially due to similar mechanisms to those of fibers' samples. The reduction of fibers' samples mechanical properties measured by tensile tests between 5 and 13 weeks (Table 2) indicate that, mainly, fiber/fiber interfaces are weakening during this period. However, the fibers' bundles cohesion and the properties of the fiber/fiber interface originate from flax fibers surfaces chemical structure. So, we studied the multiscale evolution of fibers' bundles during ageing.

- Morphological evolutions of flax fiber's bundles

SEM observations of non-embedded fibers' surfaces have been realized for each ageing duration, to investigate the fibers evolution during ageing. Figure 11 presents these observations for (a) unaged bundles and (b) 52-week-aged bundles. No significant modification could be observed between unaged fibers and after 52 weeks of exposure. Cross-sections of the flax fibers' bundles have been observed too (Figure 11 c and d). No structural damage, such as cracks initiated in the lumen area has been observed after 52 weeks of ageing. In the composite, cracks in fibers are not observed either after ageing, unlike Le Duigou et al. (Le Duigou et al., 2015) did after immersion of composite in water.

- Microstructural evolutions of flax fibers' bundles

As no evolution of non-embedded fibers' surfaces has been observed by SEM, we used physicochemical analyses to study the evolutions of the first few µm of flax fibers' during ageing. XRD analyzes have

been performed in order to measure the influence of ageing on the microstructure of fibers in bundles. The Figure 12 shows the evolution of the apparent crystallinity of flax fibers through ageing.

The mean apparent crystallinity of unaged fibers is around 73.4 ± 0.6%. We observed that the apparent crystallinity slightly increases by about 2.5 points during ageing. This slight evolution could be due to a decrease in quantity of amorphous species in the fibers. Moreover, the variation of the apparent crystallinity becomes significant between the 4th and 9th weeks. This corresponds to the slight variation of fibers' samples failure strain (Figure 5) and to the period of fibers' samples modulus decrease (between the 4th and the 13th weeks). Moreover, the decrease of fibers' samples ultimate tensile strength occurs shortly afterwards (between the 9th and the 13th weeks). A modification of fiber microstructure by ageing would also be in accordance with the DVS analyses carried on non-embedded fibers. Indeed, after 9 weeks the weight gain (

Table 4 and Figure 7) of saturated fibers (7.1%) is 2 points lower than for unaged fibers (9.1%). As mentioned for composite, this lower weight gain might partially be due to a hornification mechanism of fibers. But this also tends to indicate a loss of some fibers' hydrophilic components. To support this hypothesis and identify the amorphous species involved in the apparent crystallinity modification, the first few µm of fibers' have also been analyzed by FTIR spectroscopy.

- Chemical evolutions of flax fibers' bundles

The Figure 13 shows the normalized IR spectra of fibers' bundles for different ageing durations. Up to 13 weeks, no evolution of chemical species in the first few µm of fibers' has been observed by FTIR. After 26 weeks of exposure, some variations could be observed with a decrease of the peak around 1735 cm^{-1}. This decrease is also more important after 52 weeks. This peak is attributed to the C=O stretching vibration of carboxylic acid in pectins or ester group in hemicelluloses (Célino et al., 2014). This diminution can be related to the peak around 1245 cm^{-1}. It is assigned to the C-O of acetyl in pectins or hemicelluloses. This tends to express a loss of these components. This is in agreement with XRD measurements because pectins and hemicellulose are amorphous. Moreover, the Van Soest method performed on fibers' samples dry matter indicates a loss of hemicellulose during ageing (Figure 14). So, this hygrothermal ageing induces a loss of some pectins but also some hemicellulose.

The loss of some pectins and hemicelluloses in the first few µm of flax fibers' bundles after several weeks can explain the diminution of modulus and force at break observed for fibers' samples on Figure 5 a) and c). So evolutions of fibers' samples mechanical properties are related to a loss of hydrophilic amorphous

species (pectin and hemicellulose) responsible of the fiber/fiber cohesion, highlighted by XRD, DVS and FTIR analyses.

- Hydrophilic behavior of composite (up to 52 weeks of exposure)

To determine if, as previously supposed, the tensile strength and strain decreases are delayed effects of phenomena observed for fibers samples, the hydrophilic behavior of composite (up to 52 weeks of exposure) has been studied. First, water content within the composite has been measured by TGA analyses on samples taken right next to the ones used for DVS analyses. TGA analyses indicate that water content is almost the same for unaged composite (4.12 ± 0.72 %) and after 52 weeks of ageing (4.11 ± 0.41 %). On the one hand, considering composite's DVS analyses up to 52 weeks (Figure 8 and Table 4), we can notice that the composite weight gain (after the wet step) is 0.3 point lower after 9 weeks of exposure, compared with unaged. This could be attributed to a slight loss of some composite fibers' hydrophilic components within the first 9 weeks. This has been observed by XRD, ATR-FTIR and Van Soest method performed on non-embedded fibers: these hydrophilic components are a part of pectins and hemicellulose. On the other hand, the same weight gain measured for 9 and 52 weeks aged composites tends to indicate that fibers, within the composite, are no more affected by ageing between 9 weeks and 1 year. So, it excludes a delayed effect of fibers on composite's ultimate tensile strength and strain. However, it could be noted that water diffusion is faster (for sorption and desorption) between 9 and 52 weeks of exposure (Figure 8). This phenomenon is in accordance with more numerous cracks observed by SEM within the composite.

Considering these results, the decrease of composite's ultimate tensile strength and strain observed between 26 and 52 weeks, seems to be mainly due to the more numerous cracks and the fiber/matrix interfaces degradation within the material, highlighted by SEM. The hypothesis of a delayed effect of flax fiber and fiber/fiber interface alterations can be rule out because it take place for shorter exposure durations i.e. lower than 9 weeks.

The Figure 15 proposes a scenario of the hygrothermal ageing impact and of the mechanisms taking place within the composite from 1 week to 1 year of exposure. The state of the material is depicted after 1 week of conditioning at 23°C and 50%RH that followed an ageing of: a) unaged; b) 1week; c) 4 weeks; d) 9 weeks; e) 26 weeks and f) 52 weeks. The icons' schematically represent the quantity of the element

present in the material and the evolution is only given as a trend to qualitatively outline the modifications that take place in the material over time.

4. Conclusion

In this study, the influence of hygrothermal ageing on a flax based composite properties have been investigated, more precisely cyclic exposure to wet (90% HR) and dry (40% HR) conditions. The temperature has been chosen to accelerate the phenomena without inducing thermal alteration of the materials. Tensile tests on unidirectional composite have shown that its modulus is altered at short time (until 4 weeks), while its ultimate tensile strength and strain are impacted after long exposures (between 26 weeks and 52 weeks). Since the longitudinal mechanical properties mainly come from fibers, we submitted flax fibers' samples to the same ageing conditions as the composite to understand the origins of the composite's properties modifications. Tensile tests on fibers' samples indicated that evolution of properties occurred between the 4^{th} and the 13^{th} weeks, in a different period than composite. DVS, XRD and FTIR analyses have shown that evolutions of fibers' samples mechanical properties are related to a loss of hydrophilic amorphous species (pectin and hemicellulose) responsible for fiber/fiber cohesion. Moreover, analyses have shown that the fibers' behavior is not directly transposable to the composite. The SEM observations and DVS analyses on the composite tend to indicate that the composite's modulus decrease observed until 4 weeks would result from a slight additional residual water within the material after the first weeks of ageing, associated with fiber/fiber debondings in composite's bundles. Furthermore, the decrease of composite's ultimate tensile strength and strain observed between 26 and 52 weeks does not seem to come from a delayed effect of flax fibers and fiber/fiber interfaces alterations. Indeed, according to composite's DVS analyses, they take place for shorter exposure durations i.e. lower than 9 weeks. The composite's mechanical properties decrease is most likely due to the more numerous cracks and fiber/matrix interfaces degradation within the materials, highlighted by SEM.

Finally, this composite proved to be resistant to a realistic hygrothermal ageing. Decreases of about -10% of the moduli and about -14% of the ultimate tensile stress have been recorded after 1 year of exposure and 52 cycles of ageing. These results are promising for the development of this kind of bio-based materials.

This work was focused on the longitudinal behavior of the unidirectional composite, in a future study it could be interesting to investigate the transverse behavior of the composite and the contribution of the matrix to the composite's properties evolution through ageing.

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Declaration of interest: none

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608 **Figure captions:**

609 Figure 1: Hygrothermal ageing cycles.

610

611 Figure 2: Tensile behavior of the flax fiber reinforced composite on the 0% to 0.4% strain range. E_1

612 calculated on triangles area and E_2 calculated on diamonds area.

613

614 Figure 3: Typical X-ray diffractogram of flax fibers (in dark), the deconvolution's elementary peaks (in

615 green) and their sum (in red).

616

617 Figure 4: Evolution of tensile mechanical properties of flax/epoxy unidirectional composites depending

618 on ageing duration. a) Ultimate tensile stress, b) Ultimate tensile strain and c) E_1 and E_2 modulus. (The

619 error bars indicate the standard deviation).

620

621 Figure 5: Evolution of tensile mechanical properties of flax fibers' samples depending on ageing duration.

622 a) Apparent ultimate tensile stress, b) Ultimate tensile strain and c) Apparent modulus. (The error bars

623 indicate the standard deviation).

624

625 Figure 6: Weight variations of flax fibers and composite (unaged) measured by DVS.

626

627 Figure 7: Weight variations of fibers' samples: unaged, after 9 weeks ageing and after 52 weeks ageing;

628 measured by DVS analyses.

629

630 Figure 8: Weight variations of composites' samples: unaged, after 9 weeks ageing and after 52 weeks

631 ageing; measured by DVS analyses.

632

633 Figure 9: SEM observations of flax/epoxy composite, (a) unaged and (b) 1 week ageing. Arrows indicate

634 1) unperfected cohesion between residual bark and matrix and 2) fiber/fiber debonding.

635

636 Figure 10: SEM observations of flax/epoxy composite, (a) 26 weeks ageing and (b) 52 weeks ageing.

637 Arrows indicate 1) unperfected cohesion between residual bark and matrix, 2) fiber/fiber debonding and

638 3) fiber/matrix debonding.

Figure 11: SEM observations of flax fibers in the bundles, (a) unaged, (b) aged 52 weeks, (c) cross-section of unaged fibers' bundle and (d) cross-section of 52 weeks aged fibers' bundle.

Figure 12: Apparent crystallinity of flax fibers depending on ageing duration. (The error bars indicate the standard deviation).

Figure 13: FTIR spectra of flax fibers within bundles, unaged (1), aged 13 weeks (2), aged 26 weeks (3) and aged 52 weeks (4).

Figure 14: Evolution of hemicellulose content in the fibers' dry matter during ageing, determined by the Van Soest method.

Figure 15: Influence of hygrothermal ageing on flax/epoxy composite from 1 week to 1 year. The ageing conditions are the following: 55°C x [3.5 days at 90%RH + 3.5 days at 40%RH]. The state of the material is depicted after 1 week of conditioning at 23°C and 50%RH that followed an ageing of: a) unaged; b) 1week; c) 4 weeks; d) 9 weeks; e) 26 weeks and f) 52 weeks.

Tables:

Table 1 : Tested ageing durations for unidirectional composite's specimens and fibers' samples. * The mechanical properties of fibers' samples vary substantially between 2 and 6 months, so to get a more accurate idea of the timing when this evolution occurred, an additional ageing duration (3 months) has been added for fibers' samples.

	1 week	1 month	2 months	3 months	6 months	1 year
Unidirectional composite	x	x	x	*	x	x
Fibers' samples	x	x	x	x	x	x

Table 2: Evolution of composite and fibers' samples mechanical properties expressed in percentage of initial value and depending on ageing duration. The shading indicates the significance of these variations.

E	1 week	4 weeks	9 weeks	13 weeks	26 weeks	52 weeks
E1 Composite	-8.0	-16.7	-8.4	--	-10.4	-9.5
E2 Composite	-12.3	-16.3	-12.0	--	-15.0	-11.4
Fibers' samples	+0.9	+0.4	-13.6	-39.8	-43.1	-31.4
σ_{max}	1 week	4 weeks	9 weeks	13 weeks	26 weeks	52 weeks
Composite	+1.9	-5.3	+0.3	--	-2.2	-13.5
Fibers' samples	+1.8	+1.1	+0.8	-32.5	-31.8	-32.3
ε_f	1 week	4 weeks	9 weeks	13 weeks	26 weeks	52 weeks
Composite	+7.2	+17.6	+1.9	--	+0.1	-21
Fibers' samples	+0.1	+0.5	+14.2	+16.0	+14.7	-1.5
	x	: S >1 and var. >20%	x	: S >1	x	: S ≈1 and var. >10%

Table 3: Mechanical properties of flax fibers measured with a crosshead displacement rate of 1 mm/min.

	Strength (MPa)	Modulus (GPa)	T (°C)	RH (%)	Ref.
Elementary fiber	945 ± 200	52.5 ± 8.6	23	48	(Baley and Bourmaud, 2014)
Unidirectional composite (0°)	328 ± 23	30.8 ± 0.8	22	40	Present study
Fiber/Fiber interface	2.9 ± 2.1	$18.7\ 10^{-6} \pm 10.1\ 10^{-6}$	ambient		(Charlet and Béakou, 2011)

Table 4: Weight gain measured by DVS analyzes at 25°C.

	Weight gain	
	Humid step	Dry step
	3.5 days at 90% RH	3.5 days at 40% RH
Epoxy	0.3%	0.04%
Unaged flax fibers	9.1%	-0.2%
Flax fibers – 9 weeks ageing	7.6%	-0.4%
Flax fibers – 52 weeks ageing	7.4%	-0.3%
Unaged composite	3.7%	0.5%
Composite – 9 weeks ageing	3.4%	-0.2%
Composite – 52 weeks ageing	3.4%	-0.2%

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