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Hygro-mechanical coupling and multiscale swelling coefficients assessment of flax yarns and flax / epoxy composites

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Abstract

This paper proposes to assess, in a multi-scale experimental approach, the hygroscopic expansion coefficients of flax yarns in radial direction and of flax fibre reinforced composites in the three directions (longitudinal, transverse and out of plane). Results show a significant flax yarn radial swelling coefficient ($\beta_r = 1.06$) and a composite highly anisotropic swelling behaviour ($\beta_L = -0.02$; $\beta_T = 0.13$; $\beta_{T'} = 0.85$). An analysis of conditioning until saturation at different relative humidities shows the dramatic effect of water content on the composite tensile behaviour. The evolutions of tangent modulus with respect to stress indicate the existence of two types of behaviour depending on water content within the material. As water content increases, the behaviour becomes predominantly plastic and a rigidification phenomenon is highlighted.

Keywords: A. Biocomposite; Natural fibres; B. Mechanical properties; D. Moisture.

1. Introduction

The demand for bio-based materials in semi-structural and structural applications is constantly growing to conform to new environmental policies. Among them, plant fibre reinforced composites (PFRC) are attractive due to their relatively low densities and low environmental impact. Plant fibres appear to be suitable as reinforcing materials for polymers [1–4]. The durability of plant fibres when subjected to changing environments (relative humidity, temperature) is nevertheless a major issue.

The service life of PFRC could be strongly affected by exposure to moisture. Flax fibres and their associated products (yarns, fabrics and Flax Fibre Reinforced Composites (FFRC)) are characterised by a high affinity to water molecules. This hydrophilicity is mainly attributed to the flax fibre chemical composition and structure [5,6]. Flax fibres are considered as biocomposites constituted of cellulose

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microfibrils held together by a matrix of hemicellulose and lignin [7–9]. It is the capacity of the molecular sites of the polymer to establish Hydrogen bonds with the water molecules that controls, in a way, the diffusion phenomenon [10]. Amorphous cellulose and hemicellulose are the principal contributors to the moisture absorption, due to their open structure containing hydroxyl (OH) and acetyl (C_2H_3O) groups [11]. In addition, water absorption in plant fibres could be due to capillary effects by the lumen for instance [12,13].

In literature, studies focus on influence of water absorption by immersion on the mechanical properties of PFRC [14–21]. Most of them indicated the decrease of PFRC performance with water absorption. Nevertheless, these experimental conditions do not match the use conditions of those materials. Few studies focus on studying the effect of humid atmospheres on hygroscopic and mechanical behaviours of FFRC. Recently, Abida et al. [22] showed a strong influence of water content on flax yarn fabric behaviour when exposed to a humid atmosphere. This behaviour modification can be explained by the physical and / or chemical modifications within the reinforcement [23–26]. The effect of water uptake on the surface properties of natural fibres such as flax and hemp is studied by Bismarck et al. [27].

Water absorption by flax fibres causes a dimensional change. The ratio of length variation of a sample to its mass variation (due to water absorption) is defined as the hygroscopic expansion coefficient, also known as the swelling coefficient β. Le Duigou et al. [25] showed that the residual stresses at the fibre / matrix interface are strongly influenced by the hygroscopic expansions and therefore this β coefficient. Stuart et al. developed a modified Washburn equation (MWE) that takes into account swelling of flax and viscose fibres [28]. It was proven that wicking and swelling mechanisms of flax fibres with lumen and viscose fibres with no lumen are different. In order to model FFRC behaviour with consideration of hygro-mechanical coupling, this coefficient needs to be identified.

In a multi-scale experimental approach, the present study proposes to investigate the influence of water absorption on the hygroscopic and mechanical behaviours of flax yarns and composites reinforced with a quasi-unidirectional flax yarn fabric. The water absorption of flax yarn and flax UD fabric is studied, in order to analyse the reinforcement with the same microstructure as in composite. Firstly, a direct method for determining the hygroscopic expansion coefficients of flax yarns and composites reinforced with a quasi-unidirectional fabric of flax yarns is proposed. The method consists in sorption isotherm coupled

with swelling measurements. The effect of water content on mechanical behaviour of flax/epoxy composite is then investigated.

2. Materials and methods

2.1. Materials

2.1.1. Quasi-unidirectional flax reinforcement

The studied material is a quasi-unidirectional flax fabric FUD 180 supplied by LINEO NV Company (Figure 1). This flax fabric is characterised by a basic weight of 180 $g \cdot m^{-2}$. The abbreviation FUD corresponds to quasi-unidirectional reinforcement. The associated number is the theoretical basic weight of the fabric. On our sample batch, a basic weight of 207 ± 0.5 $g \cdot m^{-2}$ is measured on two different random samples of 1 m^2 surface each. This fabric is constituted of twisted yarns. As shown in Figure 1, few yarns in weft direction are used to facilitate the fabric handling. A density of 1.52 is measured on the quasi-UD flax fabric using a Helium pycnometer called Pycnomatic Evo from Thermo-Scientific. The value obtained is in accordance with those obtained by Amiri et al. [29] and Legall et al. [30]. The technical data of flax fabric are given in Table 1. The filling rate is the orthogonal projection of the fabric divided by the total area. It is determined theoretically using the flax density, the yarn metric number and the pick count. The balancing coefficient K_G is defined as the warp pick count divided by the total pick count. This fabric is characterised by a pre-treatment of epoxy based sizing which justifies the choice of the matrix described in the next section.

2.1.2. Epoxy matrix

The matrix used for the elaboration of the composite laminates is a mixture of an epoxy resin developed by Hunstman and commercialised under the name Araldite LY1564 and a hardener developed by the same company and commercialised under the name Aradur 3487. As mentioned above, the resin was chosen for compatibility reasons with the flax fabric reinforcement. It is characterised by low toxicity and a good performance / cost ratio. The viscosity of the Araldite LY1564 resin at room temperature (T=25°C) is between 10 and 20 mPa.s and its density is between 1.1 and 1.2 $g.cm^{-3}$. The viscosity of the hardener Aradur 3487 at T=25 °C is between 30 and 70 mPa.s and its density is between 0.98 and 1 $g.cm^{-3}$. An optimum weight ratio of 34 : 100 is proposed by the manufacturer. Based on this ratio of the masses of the two constituents, the density of the matrix is around 1.14 $g.cm^{-3}$. This resin has been developed and

adapted for contact moulding. Due to its low viscosity, impregnation and fibre / matrix adhesion is improved.

2.2. Specimens manufacturing

2.2.1. Flax yarns

The behaviour of elementary yarns constituting the flax reinforcement fabric is studied. Flax yarns are randomly extracted from the quasi-unidirectional flax fabric. The latter are handled very carefully in order to avoid their damage (untwisting of the yarn, partial rupture…). At least 30 specimens per water content are tested. An average length of 150 mm is chosen for flax yarn specimens. Yarn identification is performed by giving each sample a number so that it can be distinguished during conditioning and mechanical testing.

2.2.2. Flax fabric

Hygroscopic behaviour of quasi-unidirectional flax fabric reinforcement specimens is studied. Specimens of 80×25 mm^2 are cut randomly in the flax yarn fabric roll. Like flax yarns, flax fabric specimens are carefully handled in order to avoid their damage. At least 5 specimens are examined per relative humidity. The reproducibility of these tests is considered satisfactory.

2.2.3. Epoxy resin

For pure resin plates manufacturing, the two constituents of the matrix (resin and hardener) are mixed in accordance with the mass proportions recommended by the manufacturer, the mixture is degassed for 30 min under vacuum in order to eliminate the air bubbles introduced during mixing. The resin is then casted and left to rest for 2 hours in order to allow the elimination of any air bubbles introduced during casting. The same thermal cycle as that of the composite laminates is respected, namely curing for 2 hours at 100 °C.

2.2.4. Composites

The composite laminates are manufactured following a two-step process. It consists of a hand lay-up of successive plies process (8 plies) followed by a curing by thermocompression. During the draping and impregnation phase (hand lay-up), the reinforcements are positioned so as to ensure the same orientation of the warp yarns of all the plies. This unidirectional stratification is respected during the fabrication of all plates required for this study. Prior to stratification, flax fabric bands of 330×250 mm^2 are firstly cut and then dried at 110 °C for 1 hour to evaporate water molecules and promote resin impregnation. At the end

of the impregnation, a pressure of 7.1 ± 0.5 bar is applied on the composite laminates for 2 hours at room temperature to ensure the penetration and impregnation of the resin within the plies. The impregnated samples are then cured at 100 °C for 2 hours under pressure to respect the curing cycle of the resin (manufacturer recommendation).

The fibre volume fraction obtained is 55 % and the porosity volume fraction is between 2.5% and 3.5%.

2.3. Conditioning and monitoring protocol

2.3.1. Conditioning

After manufacturing, the specimens need to be dried in order to eliminate water molecules. Drying times up to 72 hours at 103 °C were previously investigated and no significant change in the lost mass was found after 24 hours which explains the drying time. Furthermore, all materials are dried at the same temperature (103 °C) and duration of 24 hours in order to have initially the same reference state. After drying, they are weighed and conditioned in an enclosed chamber at constant and regulated relative humidity (RH) according the standard ISO 483. The use of a saturated saline solution in a closed enclosure at constant temperature provides an atmosphere with constant RH. The saturated saline solutions are prepared from mineral salts. Four chambers with constant RH each are set up and kept in a room at 20 ±1 °C. Table 2 represents the aqueous saturated saline solutions used and the RH that each one of them provides. More details about the conditioning protocol are provided in [22]. Some samples were immersed in water at T = 20 °C in order to reach higher water content at saturation. The latter conditioning is supposed to be an atmosphere with a relative humidity of 100 %. All samples were conditioned until water uptake stabilisation.

2.3.2. Gravimetric measurements

Flax yarn specimen weight after drying is around 10 mg depending on their length. Flax / epoxy composite specimens weigh around 10 g, and they are weighed on a 10^{-4} g precision balance (Mettler Toledo). Water content in composite specimens is estimated assuming that all water molecules are evaporated and using the Equation (1).

$$water\ content\ (wc)\ (\%) = \frac{m_{saturation} - m_{dried}}{m_{dried}} \times 100 \quad (1)$$

where m_{dried} and $m_{saturation}$ are the weight of the dry sample before conditioning and the weight at saturation of sample after exposure respectively.

2.3.3. Hygroscopic strain

An optical method which consists of using a profile projector equipped with a camera is referred to in order to measure the apparent diameter of the flax yarns. The measurements are carried out using a Baty Venture 2512CN machine with a precision of 1µm. The thickness of the projected profile is measured at locations previously identified to ensure that measurements are always performed at the same locations before and after conditioning. The cylindrical section of yarns was checked by performing measurements in two orthogonal directions at each point. Therefore, the profile thickness is assimilated to an apparent diameter, which makes it possible to assess the average swelling strain for each test specimen (by computing the average of the swelling ratio of each section). At least 10 measurements of the apparent diameter are made on each yarn.

For composite specimen, hygroscopic strain is measured in the three directions (ε_x, ε_y, ε_z).

Measurements in the out of plane direction (ε_z) are conducted using a digital micrometre of 1 µm precision. For the other directions (ε_x, ε_y), a digital calliper of 10 µm precision is used for measurements.

2.4. Characterisation of mechanical properties

A servo-hydraulic machine INSTRON 8801 equipped with a force cell of 100 kN is used to perform monotonic tensile tests on composite specimens. The strain is measured with an axial extensometer with a gauge length of 50 mm. The test speed is set at 2 mm·min^{-1} so as to have a strain rate of the order of 10^{-4} s^{-1}, which is the standard strain rate for quasi-static tests. The warp yarns are aligned with the loading direction. In order to verify the repeatability and reproducibility, at least 3 samples of each configuration of the material are tested. Mechanical tests are carried out on dry samples as well on samples immersed in water or conditioned at various RH until water uptake stabilisation.

3. Results and discussions

3.1. Multiscale three-dimensional sorption

Contrary to 1D sorption where the edges of samples are sealed in order to force water molecules to diffuse in one specific direction (generally in the out of plane direction), in three-dimensional sorption no such preparation is needed. Thus, water molecules can penetrate and diffuse in the material through the 3 directions.

A detailed comparative study of 3D sorption behaviour of composites and its constituents at different scales (flax fabric, elementary yarns that constitute the fabric and epoxy resin) is presented in Table 3. This study shows that water content within the materials is different from the relative humidity of the conditioning environment. A first study of the relationship between water content at saturation (WCS) and saturation time (ST) and RH of composite specimens shows their non-linear evolution with RH (Figure 2). Regardless of the relative humidity, the saturated water content of elementary flax yarns and flax fabrics is similar (Table 3). Therefore, the cavities between flax yarns within the fabric do not cause extra water absorption of the fabric due to capillarity effects. However, epoxy did not reach saturation after 45 weeks of conditioning. Furthermore, water content in epoxy resin remains low compared to the other studied materials. Thus, we can conclude that WCS of the composite is mainly governed by the flax absorption capacity. A classical law of mixtures based on the constituent moisture behaviour was applied to verify its reliability to obtain the experimental water content of the composite (Equation 2). According to the law of mixtures, the composite saturated water content is the average of the saturated water content of each constituent (flax fabric, epoxy and pores), weighted by its mass fraction. In this case, two hypotheses could be formulated. Either the pores are completely filled with water, which will lead to extra water absorption; or pores cannot be filled with water due to the presence of gas trapped in the voids. Under both assumptions, the computed composite water content at saturation is different from the experimentally measured one (Table 4). Hence, a classical law of mixtures based on the constituent moisture behaviour is not sufficient to explain the moisture absorption of the composite. The analysis should not only include the material behaviour (hygroscopic expansion of component) but also the structural effects (linked to the reinforcement microstructure). The reinforcement water absorption is not representative of the water absorption in the composite, due to extra phenomena in yarns and fabric (capillarity effects).

A comparison of saturation time of flax yarns and composites shows that the elementary yarns saturation time is lower than the composites, which could be attributed to the presence of epoxy that slows the diffusion of moisture in flax yarns.

$$wc^{composite} = wc^{flax} \cdot \upsilon_m^{flax} + wc^{epoxy} \cdot \upsilon_m^{epoxy} + \frac{\upsilon_v^{pore} \cdot \rho_{water}}{\rho^{composite}} \qquad (2)$$

Where wc is for water content, υ_m is the mass fraction, υ_v^{pore} is the volume fraction of pores occupied by water molecules, $\rho_{composite}$ is the composite density. The composite water content is assessed when the pores are completely filled with water ($\upsilon_v^{pore} = 3.5\%$) and when pores cannot be filled with water ($\upsilon_v^{pore} = 0\%$).

3.2. Swelling coefficients

3.2.1. Flax yarns

As a reminder, the absorption of water by the flax fibres causes their swelling, which is characterised by the hygroscopic expansion coefficient. This paper focus on estimating the radial swelling coefficient of single flax yarns, noted β_r. This parameter is very important to describe the hygro-mechanical coupling of composites as differential swellings of yarn and matrix could create interfacial stresses at the matrix / reinforcement interface and causing, thus, its damage. However, few studies in the literature are interested in the experimental assessment of this coefficient. Le Duigou et al. [25] measured this coefficient on flax fibres using SEM observations and theoretical water content obtained from the sorption isotherms of Hill [5]. However, studied composites are reinforced with a fabric constituted of flax yarns. Swelling mechanisms may be different (untwisting of yarns, etc.). Thus, determining the swelling coefficient of flax yarns is essential to understanding the swelling of FFRC composites. The evolution of the radial strain as a function of the water content is plotted in Figure 3. Each point of Figure 3 corresponds to the averages of the radial swelling and the water content obtained on at least 30 yarns, and the bars represent the observed variability.

The evolution of flax yarn radial swelling with water content appears to be linear. A high square of the linear correlation coefficient R is found (R^2=0.993). The linear correlation coefficient is an indicator that allows evaluation of the quality of a simple linear regression. It measures the fit between the model and the experimental data or how well the regression equation is adapted to describe the distribution of points. For the studied yarns, a coefficient $\beta_r = 1.06 \pm 0.039$ is measured. This value is higher than those conventionally admitted in the literature ($\beta_r = 0.6$) [31,32]. The swelling coefficient of flax yarn is similar to the one measured by Le Duigou et al. [25] on flax fibres ($\beta_r = 1.14$). In conclusion, the free radial swelling of flax yarns appears to be similar to that of flax fibres.

3.2.2. Composite

Water absorption in composite material causes a variation in its volume. A study of the relationship between hygroscopic strains and water content according to the 3 directions is carried out. The swelling coefficients β_L, β_T *and* $\beta_{T'}$ in the longitudinal, transverse and out of plane directions respectively are assessed (Figure 4 and Figure 5).

Even though the evolution of the transversal and longitudinal strains with water content may appear non-linear, a linear regression is considered in order to assess the swelling coefficients in both directions. The swelling coefficient is the slope of the linear curve of the hygroscopic strain with water content.

The longitudinal hygroscopic deformations (in the direction of the warp flax yarns) as a function of the water content of the FFRC are plotted in the Figure 4. The FFRC longitudinal swelling coefficient is hence negative ($\beta_L = -0.02 \pm 0.004$). That is to say, moisture absorption of FFRC induces a shrinkage in the direction of the warp yarns. Further works are required to understand the origin of the flax/epoxy composite longitudinal shrinkage due the water absorption. However, this particular behaviour could be explained by the microstructure of the reinforcement. This behaviour could arise from structural effects due to the reinforcement microstructure (yarns or fabrics) or material (elementary flax fibres). On the one hand, water absorption by the flax yarns could lead to a longitudinal shrinkage of elementary yarns. As mentioned in section 2.1 the fabric is constituted of twisted yarns. Water absorption causes radial swelling of yarns. Consequently, the yarn twisting angle could increase due to a spiral spring-like contraction (structural effect). On the other hand, water absorption could lead to elementary flax fibre shrinkage (material behaviour). It could also be explained by the significant radial swelling at high moisture content which could lead to a longitudinal shrinkage of yarns and hence a shrinkage of the composite. Additional measures are needed to confirm these assumptions.

The two transverse swelling behaviours are shown in Figure 5. In Figure 5(a), the out of plane hygroscopic strain referred to as transversal' ($\beta_{T'}$) is computed. The hygroscopic strain in the weft direction called transversal strain (β_T) is assessed in Figure 5(b).

The swelling coefficient in the out of plane direction is found to be $\beta_{T'} = 0.85 \pm 0.028$ (Figure 5(a)). This value is lower than that of the radial swelling of flax yarns ($\beta_r = 1.06 \pm 0.039$). This difference could be attributed to the presence of the epoxy which has lower hygroscopic coefficient ($\beta_{epoxy} = 0.6$) [33–35]

which may block the swelling of the yarns. This constraining effect has been modelled by Joffre et al. [36]. The swelling of flax yarns in the composite is therefore inferior to that of flax yarns that are free to deform. These differential swellings between yarns matrix are likely to induce interfacial stresses that can weaken the reinforcement / matrix interface in FFRC.

A ratio of 7 is measured between the weft and the out of plane swelling coefficients β_T and $\beta_{T'}$ (Figure 5). A swelling coefficient in the weft direction of $\beta_T = 0.13 \pm 0.019$ is assessed (Figure 5(b)). This dimensional stability could be explained by the presence of the few weft yarns that block the swelling in this direction. The swelling of the matrix and the radial swelling of the warp yarns should cause a higher swelling in the transverse direction. However, the assumed longitudinal behaviour of the flax yarns ($\beta_L < 0$) counterbalances the radial swelling and induces a dimensional stability of the composite in the direction of the weft yarns. This behaviour could also be the cause of internal stresses.

Measurements of the FFRC swelling coefficients, among the three directions, highlight the strong anisotropy of the hygroscopic behaviour of these composites.

3.3. Hygro-mechanical properties of composites

In the following, it is more suitable to reason in terms of water content and not in terms of conditioning atmosphere. The reason for this is that, contrary to relative humidity which is an atmospheric property, the water content is an intrinsic property of the material.

3.3.1. Tensile behaviour of composites

Tensile behaviour of flax / epoxy composites with different water content is investigated. As shown in Figure 6, water content dramatically affects the tensile behaviour of FFRC. As a matter of fact, for water content $w_c < 4.9\%$, tensile curves are characterised by a linear elastic region followed by an apparent yield point. A change of slope involving both a rigidity decrease and the emergence of plasticity (in general, which includes viscoplasticity) is observed. This type of tensile curve was already observed by several authors [37–43].

As water content increases, the behaviour progressively changes. The apparent yield point is still noticeable on tensile curves at higher water content ($w_c \geq 4.9\%$) but an inflection point appears after the yield stress evoking an apparent rigidification of flax / epoxy composites. This behaviour was only observed in some favourable experimental conditions by Richard et al. [44] at low loading rates and by

Scida et al. [45] at high temperature. The explanation of this phenomenon is not well established and could be attributed to the reorientation of cellulose microfibrils in kink band areas, the spiral spring-like extension of cellulose microfibrils, and the shear-stress-induced crystallisation of the amorphous cellulose of the flax fibres [46].

3.3.2. Evolution of mechanical properties

In this section, the evolution of the mechanical properties of flax / epoxy composites is discussed. Primarily, the evolution of Young's modulus is studied. Then, a closer analysis of tangent modulus is presented. An investigation of the water content influence on the yield stress and on the appearance of the rigidification phenomenon is conducted in the last part of this section.

Young's modulus is computed in the first linear region of the tensile curve. A deformation between 10 % ($0.1\times\sigma_y$) and 90% of the yield stress ($0.9\times\sigma_y$) is set as the identification range. The yield stress is determined at the first slope change of tensile curves (Figure 6).

The evolution of Young's modulus with respect to water content appears to be non-linear and non-monotonic (Figure 7). As water content increases, Young's modulus increases up to a maximal value then drops. In fact, Young's modulus is divided by 2 when w_c increases from 0 to 10 %. However, the existence of an optimal water content ($0 \le w_c \le 2.4\%$), for which the Young's modulus is maximal, is highlighted.

A more detailed examination of the FFRC tensile curves is then conducted. The analysis of the tangent modulus is presented in Figure 8. Tangent modulus is computed via the derivative of the stress with respect to the deformation. The evolution of tangent modulus with stress confirms the high influence of water content on FFRC's mechanical behaviour as well as the highly non-linear behaviour of flax / epoxy composites. In fact, for low water content ($w_c \le 2.4\%$), tangent modulus remains constant to a stress level (yield stress) after which, rigidity decreases until failure. For high water content ($w_c \ge 4.9\%$), tangent modulus decreases to a stress level (referred to as rigidification stress in the following) then increases. The tangent modulus increases with stress at high water content highlights a rigidification phenomenon. Using the tangent modulus evolution curves (Figure 8), a quantitative study of the moisture content effect on yield stress and rigidification stress is carried out. Yield stress decreases with w_c in a non-linear way (Figure 9). A ratio of 5 when w_c increases from 0 to 10% is measured. Furthermore, for high w_c, yield

stress is very low, meaning that composite behaviour becomes predominantly plastic, more specifically viscoelastic-viscoplastic [47]. Water molecules could be considered as a plasticising agent for FFRC.

As mentioned above, for high w_c ($w_c \geq 4.9\%$), a rigidification phenomenon is observed for flax / epoxy composites. The evolution of the rigidification stress with water content is studied and given in Table 5. It is worthy of note that the rigidification stress is identified when tangent modulus is minimum. Water content increase lowers the rigidification stress. In fact, at a water content of 4.90 % the rigidification stress is 90 MPa and it drops sharply to 33 MPa when water content is 14.40 %. Rigidification phenomenon is still not well explained but is mostly linked to the rearrangement of microstructure of flax fibres. The rigidification stress drop indicates that the reorientation of cellulose microfibrils is enhanced with water absorption for high strains. The recent work conducted by Requile et al. on hemp / epoxy composites shows that, regardless of the conditioning atmosphere, the tangent modulus drops down to a minimum and then increases [48]. However, the constant tangent modulus at low water content observed on FFRC is not noted. The influence of water content on behaviour of hemp / epoxy composites is different to the behaviour of flax / epoxy composites. Plant fibre reinforced composite behaviour depends on the kind of fibres used as reinforcement.

4. Conclusion

An experimental method to assess the radial hygro-expansion coefficients of flax yarns β_r and flax / epoxy composites along the 3 main directions (β_L, β_T, $\beta_{T'}$) is developed. This work highlights the strong anisotropy of the studied composite. It shows that the radial hygro-expansion coefficient of flax yarns is $\beta_r = 1.06 \pm 0.039$ confirming that their radial swelling is similar to radial swelling of flax fibres ($\beta_f = 1.14$).

This study also reveals that a composite hygro-expansion coefficient in the out of plane direction ($\beta_{T'} = 0.85 \pm 0.028$) is smaller than the radial swelling coefficient of flax yarns. The differential swelling between the resin and the yarns blocks the swelling along the thickness.

Furthermore, measurements show a negative swelling coefficient of FFRC in the warp direction ($\beta_L = -0.02 \pm 0.004$) reflecting a longitudinal shrinkage when their water content increases. This behaviour could be attributed to the microstructure reinforcement. It could arise from structural effects due to the microstructure reinforcement (yarns or fabrics) or material (elementary flax fibres behaviour).

In fact, flax yarn twisting angle could increase due to a spiral spring-like contraction with water content increase. The latter could also cause a shrinkage of elementary fibres. Another explanation could be the significant radial swelling of flax yarns that could induce a longitudinal shrinkage of flax yarns.

A good dimensional stability in the weft direction is measured ($\beta_T = 0.13 \pm 0.019$). The swelling coefficients in the longitudinal and out of plane directions (β_L and $\beta_{T'}$) make it possible to explain the coefficient of hygro-expansion in the weft direction. Indeed, the negative longitudinal hygro-expansion coefficient of the weft yarns offsets the swelling of the warp yarns (radial) and the matrix.

Tensile behaviour of flax / epoxy composites with different water content is investigated. The study points out the high non-linear behaviour of FFRC. At low water content ($w_c < 4.9\%$), the usual behaviour of FFRC is observed. Tensile curves exhibit a linear elastic region followed by an apparent yield point, which is still noticeable at higher water content ($w_c \geq 4.9\%$). An inflection point appears after the yield stress evoking an apparent rigidification of flax / epoxy composites for high w_c. This hygro-activated rigidification is related to the flax fibre microstructure rearrangement. The evolution of tangent modulus with respect to stress enhances the existence of the two types of behaviour (with or without rigidification). As water content increases, FFRC behaviour becomes predominantly plastic, more specifically viscoelastic-viscoplastic.

Declaration of conflicting interest

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References

1. Bledzki AK, Gassan J. Composites reinforced with cellulose based fibre. Prog Polym Sci 1999;24:221–74.

2. Van De Velde K, Kiekens P. Wettability of natural fibres used as reinforcement for composites. Die Angew Makromol Chemie 1999;272:87–93. doi:10.1002/(SICI)1522-9505(19991201)272:1<87::AID-APMC87>3.0.CO;2-Q.

3. Baley C. Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase. Compos - Part A Appl Sci Manuf 2002;33(7):939–948.

4. Misnon MI, Islam MM, Epaarachchi JA, Lau K tak. Potentiality of utilising natural textile materials for engineering composites applications. Mater Des 2014;59:359–368. doi:10.1016/j.matdes.2014.03.022.

5. Hill CAS, Nortin A, Newman G. The Water vapor sorption behavior of natural fibers. J Appl Polym Sci 2009;112:1524–1537.

6. Azwa ZN, Yousif BF, Manalo AC, Karunasena W. A review on the degradability of polymeric composites based on natural fibres. Mater Des 2013;47:424–442.

7. Jayaraman K. Manufacturing sisal-polypropylene composites with minimum fibre degradation. Compos Sci Technol 2003;63:367–374.

8. Baley C, Busnel F, Grohens Y, Sire O. Influence of chemical treatments on surface properties and adhesion of flax fibre-polyester resin. Compos Part A Appl Sci Manuf 2006;37:1626–1637.

9. John MJ, Thomas S. Biofibres and biocomposites. Carbohydr Polym 2008;71:343–364.

10. Célino A, Fréour S, Jacquemin F, Casari P. The hygroscopic behavior of plant fibers: a review. Front Chem 2014;1:1–12.

11. Fotouh A, Wolodko JD, Lipsett MG. Fatigue of natural fiber thermoplastic composites. Compos Part B Eng 2014;62:175–182. doi:10.1016/j.compositesb.2014.02.023.

12. Bessadok A, Marais S, Gouanvé F, Colasse L, Zimmerlin I, Roudesli S, et al. Effect of chemical treatments of Alfa (Stipa tenacissima) fibres on water-sorption properties. Compos Sci Technol 2007;67:685–697.

13. Morton WE, Hearle JWS. Physical Properties of Textile Fibres (Fourth Edition). In: Morton WE, Hearle JWS, editors. Woodhead Publ. Ser. Text., Woodhead Publishing; 2008.

14. Dhakal HN, Zhang ZY, Richardson MOW. Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. Compos Sci Technol 2007;67:1674–1683.

15. Assarar M, Scida D, El Mahi A, Poilâne C, Ayad R. Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax-fibres and glass-fibres. Mater Des 2011;32:788–795.

16. Christian SJ, Billington SL. Moisture diffusion and its impact on uniaxial tensile response of biobased composites. Compos Part B Eng 2012;43:2303–2312. doi:10.1016/j.compositesb.2011.11.063.

17. Alhuthali A, Low IM, Dong C. Characterisation of the water absorption, mechanical and thermal properties of recycled cellulose fibre reinforced vinyl-ester eco-nanocomposites. Compos Part B Eng 2012:2772–2781. doi:10.1016/j.compositesb.2012.04.038.

18. Le Duigou A, Bourmaud A, Davies P, Baley C. Long term immersion in natural seawater of Flax/PLA biocomposite. Ocean Eng 2014;90:140–148.

19. Mannberg P, Nyström B, Wallström L, Joffe R. Service life assessment and moisture influence on bio-based composites. J Mater Sci 2014;49:5265–5270. doi:10.1007/s10853-014-8211-6.

20. Kumar AP, Mohamed MN. A comparative analysis on tensile strength of dry and moisture absorbed hybrid kenaf/glass polymer composites. J Ind Text 2018;47:2050–2073. doi:10.1177/1528083717720203.

21. Sodoke FK, Toubal L, Laperrière L. Wetting/drying cyclic effects on mechanical and physicochemical properties of quasi-isotopic flax/epoxy composites. Polym Degrad Stab 2019:121–130. doi:10.1016/j.polymdegradstab.2019.01.014.

22. Abida M, Gehring F, Mars J, Vivet A, Dammak F, Haddar M. Effect of hygroscopy on non-impregnated quasi-unidirectional flax reinforcement behaviour. Ind Crops Prod 2019;128:315–322. doi:10.1016/j.indcrop.2018.11.008.

23. Alix S, Philippe E, Bessadok A, Lebrun L, Morvan C, Marais S. Effect of chemical treatments on water sorption and mechanical properties of flax fibres. Bioresour Technol 2009;100:4742–9. doi:10.1016/j.biortech.2009.04.067.

24. Placet V, Cissé O, Lamine Boubakar M. Influence of environmental relative humidity on the tensile and rotational behaviour of hemp fibres. J Mater Sci 2012;47:3435–3446.

25. Le Duigou A, Merotte J, Bourmaud A, Davies P, Belhouli K, Baley C. Hygroscopic expansion: A key point to describe natural fibre/polymer matrix interface bond strength. Compos Sci Technol 2017;151:228–233.

26. Péron M, Célino A, Castro M, Jacquemin F, Le Duigou A. Study of hygroscopic stresses in asymmetric biocomposite laminates. Compos Sci Technol 2019;169:7–15. doi:10.1016/j.compscitech.2018.10.027.

27. Bismarck A, Aranberri-Askargorta I, Springer J, Lampke T, Wielage B, Stamboulis A, et al. Surface characterization of flax, hemp and cellulose fibers; Surface properties and the water uptake behavior. Polym Compos 2002;23:872–894. doi:doi.org/10.1002/pc.10485.

28. Stuart T, McCall RD, Sharma HSS, Lyons G. Modelling of wicking and moisture interactions of flax and viscose fibres. Carbohydr Polym 2015;123:359–368. doi:https://doi.org/10.1016/j.carbpol.2015.01.053.

29. Amiri A, Triplett Z, Moreira A, Brezinka N, Alcock M, Ulven CA. Standard density measurement method development for flax fiber. Ind Crops Prod 2017;96:196–202. doi:10.1016/j.indcrop.2016.11.060.

30. Le Gall M, Davies P, Martin N, Baley C. Recommended flax fibre density values for composite property predictions. Ind Crops Prod 2018;114:52–58. doi:10.1016/j.indcrop.2018.01.065.

31. Marklund E, Varna J. Modeling the hygroexpansion of aligned wood fiber composites. Compos Sci Technol 2009;69:1108–1114. doi:10.1016/j.compscitech.2009.02.006.

32. Srubar W V, Frank CW, Billington SL. Modeling the kinetics of water transport and hydroexpansion in a lignocellulose-reinforced bacterial copolyester. Polymer (Guildf) 2012;53:2152–2161. doi:10.1016/j.polymer.2012.03.036.

33. Loos AC, Springer GS. Curing of Epoxy Matrix Composites. J Compos Mater 1983;17:135–169. doi:10.1177/002199838301700204.

34. Agbossou A, Pastor J. Thermal stresses and thermal expansion coefficients ofn-layered fiber-reinforced composites. Compos Sci Technol 1997;57:249–260. doi:10.1016/S0266-3538(96)00137-6.

35. Lin YC. Investigation of the Moisture-Desorption Characteristics of Epoxy Resin. J Polym Res 2006;13:369–374.

36. Joffre T, Wernersson ELG, Miettinen A, Hendriks CLL, Gamstedt EK. Swelling of cellulose fibres in composite materials: Constraint effects of the surrounding matrix. Compos Sci Technol 2013;74:52–59. doi:10.1016/j.compscitech.2012.10.006.

37. Oksman K. High Quality Flax Fibre Composites Manufactured by the Resin Transfer Moulding Process. J Reinf Plast Compos 2001;20:621–627.

38. Hughes M, Carpenter J, Hill C. Deformation and fracture behaviour of flax fibre reinforced thermosetting polymer matrix composites. J Mater Sci 2007;42:2499–2511. doi:10.1007/s10853-006-1027-2.

39. Lebrun G, Couture A, Laperrière L. Tensile and impregnation behavior of unidirectional hemp/paper/epoxy and flax/paper/epoxy composites. Compos Struct 2013;103:151–160. doi:10.1016/j.compstruct.2013.04.028.

40. Poilâne C, Cherif ZE, Richard F, Vivet A, Ben Doudou B, Chen J. Polymer reinforced by flax fibres as a viscoelastoplastic material. Compos Struct 2014;112:100–112.

41. Yan L, Chouw N, Jayaraman K. Flax fibre and its composites - A review. Compos Part B Eng 2014;56:296–317.

42. Rubio-López A, Hoang T, Santiuste C. Constitutive model to predict the viscoplastic behaviour of natural fibres based composites. Compos Struct 2016;155:8–18.

43. Chilali A, Zouari W, Assarar M, Kebir H, Ayad R. Effect of water ageing on the load-unload cyclic behaviour of flax fibre-reinforced thermoplastic and thermosetting composites. Compos Struct 2018;183:309–319. doi:10.1016/j.compstruct.2017.03.077.

44. Richard F, Poilâne C, Yang H, Gehring F, Renner E. A viscoelastoplastic stiffening model for plant fibre unidirectional reinforced composite behaviour under monotonic and cyclic tensile loading. Compos Sci Technol 2018;167:396–403.

45. Scida D, Assarar M, Poilâne C, Ayad R. Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite. Compos Part B Eng 2013;48:51–58.

46. Placet V, Cissé O, Lamine Boubakar M. Nonlinear tensile behaviour of elementary hemp fibres. Part I: Investigation of the possible origins using repeated progressive loading with in situ microscopic observations. Compos Part A Appl Sci Manuf 2014;56:319–327.

47. Abida M. Comportement hygroscopique et couplage hygromécanique dans les composites lin / époxy: approche expérimentale multi-échelle et modélisation. PhD thesis, Normandy University, 2018.

48. Réquilé S, Le Duigou A, Bourmaud A, Baley C. Deeper insights into the moisture-induced hygroscopic and mechanical properties of hemp reinforced biocomposites. Compos Part A Appl Sci Manuf 2019;123:278–285. doi:10.1016/j.compositesa.2019.05.006.

Figures caption

Figure 1: quasi-unidirectional flax fabric (FUD180)

Figure 2: evolution of water content at saturation (WCS) and saturation time (ST) with RH of composite samples

Figure 3: radial swelling coefficient of flax yarns

Figure 4: composite swelling coefficient in the warp direction

Figure 5: assessment of the swelling coefficients of composites in the two transverse directions

(a) in the out of plane direction

(b) in the weft direction

Figure 6: stress-strain curves of composites at different water content

Figure 7: Young's modulus evolution with water content of flax / epoxy composites for fibre orientation $\theta=0°$

Figure 8: smoothed tangent modulus

Figure 9: yield stress evolution with water content

Tables

Table 1: details on flax fabric used (FUD180)

Warp		Weft		Balancing coefficient K_G	Filling rate (%)
Titration (mg/m)	Warp pick count (yarns/m)	Titration (mg/m)	weft pick count (yarns/m)		
48	4068	31	304	0.93	94

Table 2: relative humidities provided by each aqueous saturated saline solution

Aqueous saturated saline solution	**Relative humidity at 20°C**
Potassium hydroxide (KOH)	8 %
Potassium Carbonate (K_2CO_3)	45 %
Sodium Chloride (NaCl)	75 %
Potassium Sulphate (K_2SO_4)	97 %

Table 3: multiscale comparison of 3D sorption

Atmosphere	Elementary yarns		Flax fabric	Epoxy		Composite	
	Water content at saturation	Saturation time	Water content at saturation	Water content	Study time	Water content at saturation	Saturation time
RH = 8%	1.7%	98 h	1.5%	0.24%	26 w	0.63%	47 w
RH = 45%	4.6%	50 h	4.2%	1.2%	45 w	2.4%	38 w
RH = 75%	7.1%	36 h	7.0%	2.4%	45 w	4.9%	15 w
RH = 97%	10.9%	21 h	16%	3.8%	45 w	10.5%	10 w
RH = 100%	-	-	-	4.2%	45 w	14.4%	7 w

Table 4: law of mixtures (wc : water content at saturation, ν volumetric content)

Atmosphere	Flax fabric		Epoxy		void	Composite	Computed water content of composite	
	wc	ν	wc	ν	ν	measured wc	no water in pores	pores are filled with water
RH = 8%	1.5%	0.55	0.24%	0.415	0.035	0.63%	1.01%	3.65%
RH = 45%	4.2%	0.55	1.20%	0.415	0.035	2.40%	3.05%	5.68%
RH = 75%	7.0%	0.55	2.40%	0.415	0.035	4.90%	5.23%	7.86%
RH = 97%	16%	0.55	3.80%	0.415	0.035	10.50%	11.39%	14.02%
RH = 100%	-	0.55	4.20%	0.415	0.035	14.40%	-	-

Table 5: rigidification stress evolution with water content

Water content (%)	0	0.63	2.4	4.9	10.5	14.4
Rigidification stress (MPa)	-	-	-	95	40	33

Figures

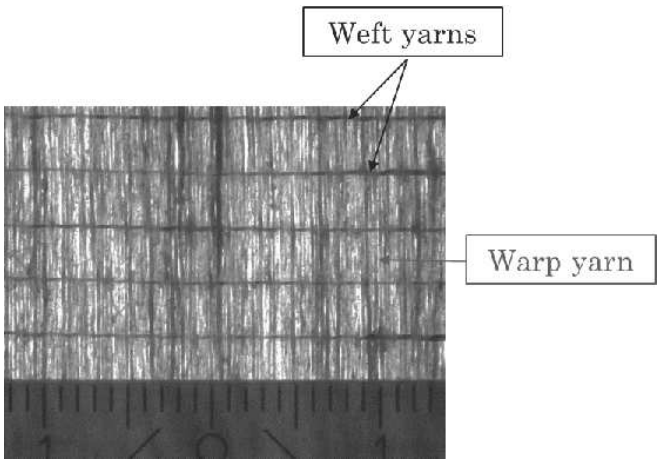


Figure 1: quasi-unidirectional flax fabric (FUD180)

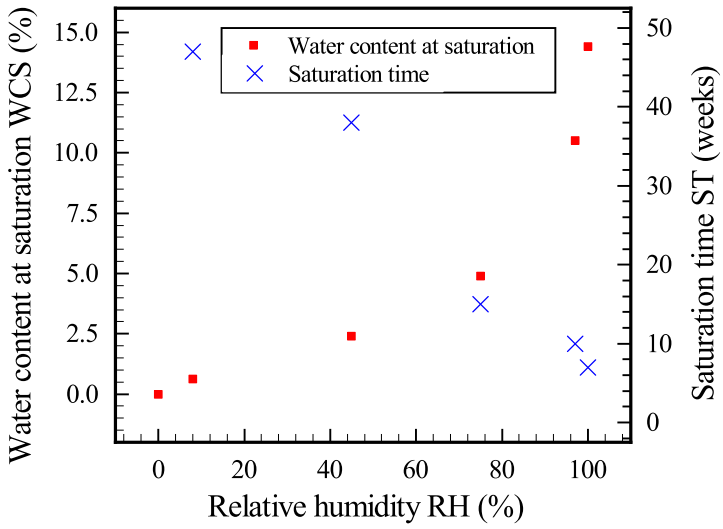


Figure 2: evolution of water content at saturation (WCS) and saturation time (ST) with RH of composite samples

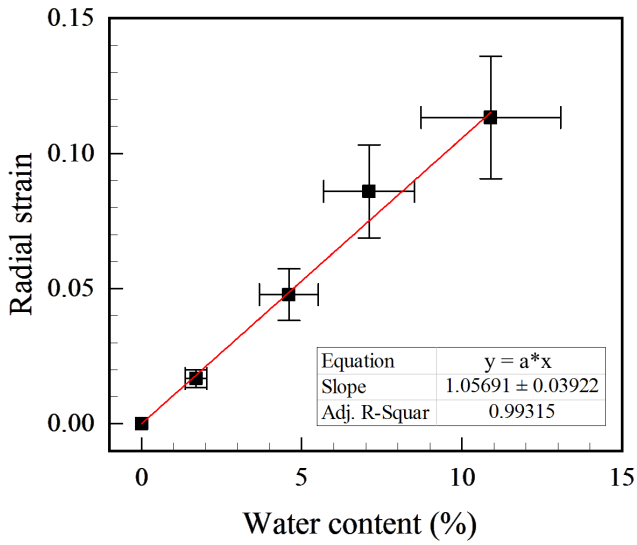


Figure 3: radial swelling coefficient of flax yarns

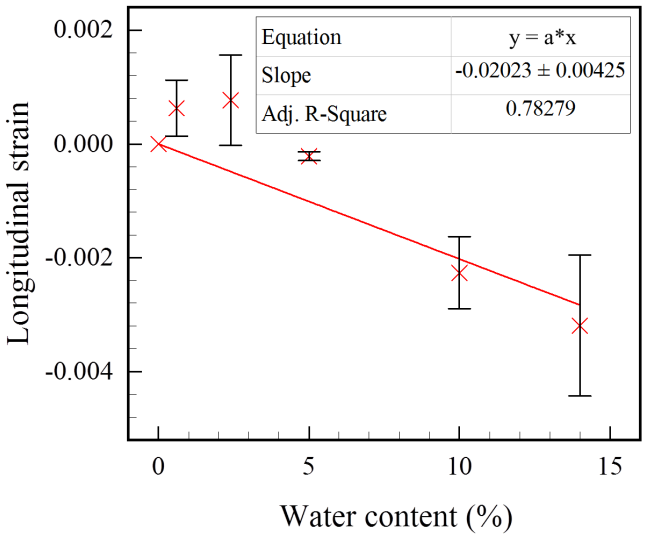
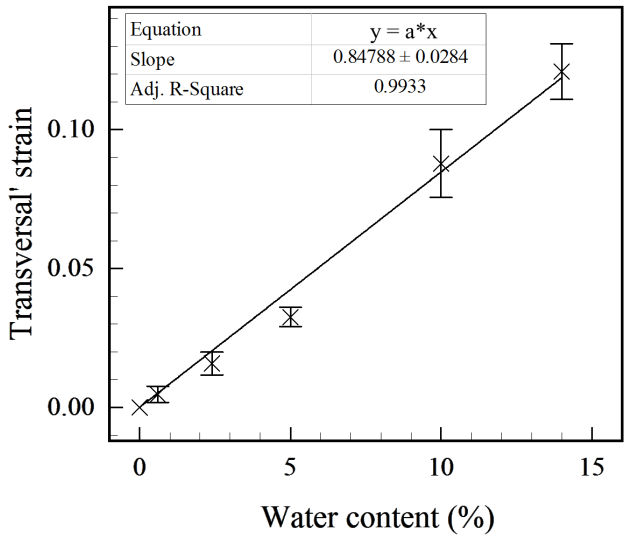
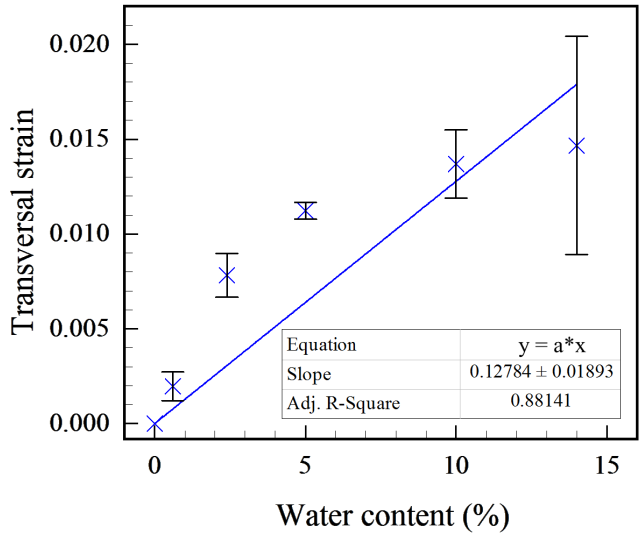


Figure 4: composite swelling coefficient in the warp direction



(a) In the out of plane direction



(b) In the weft direction

Figure 5: assessment of the swelling coefficients of composites in the two transverse directions

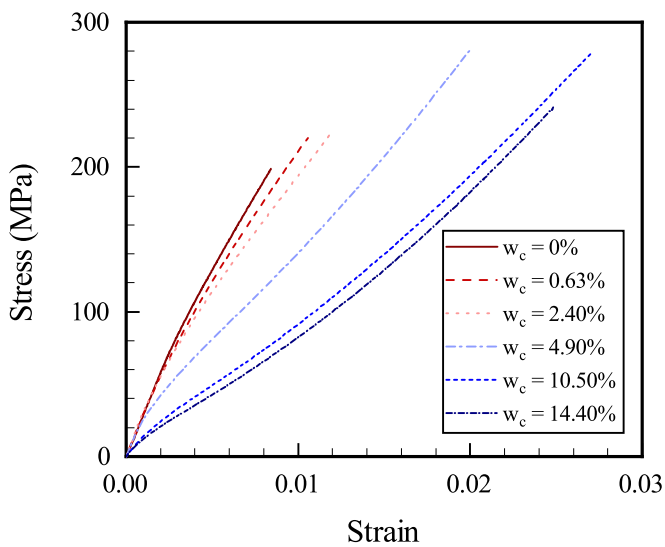


Figure 6: stress-strain curves of composites at different water content

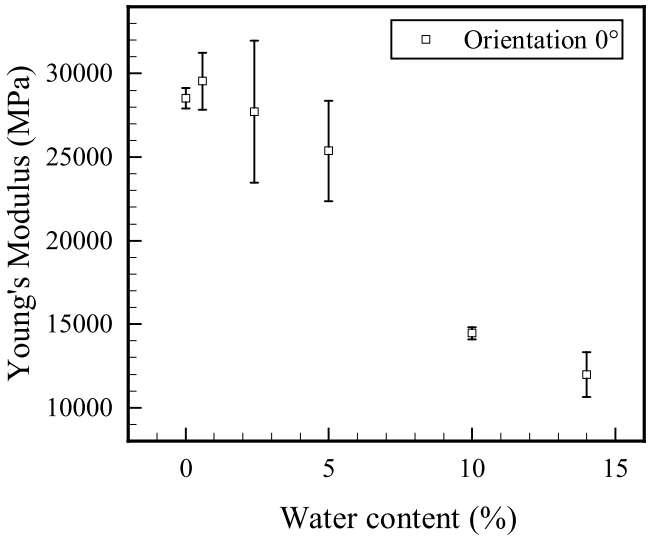


Figure 7: Young's modulus evolution with water content of flax / epoxy composites for fibre orientation θ=0°

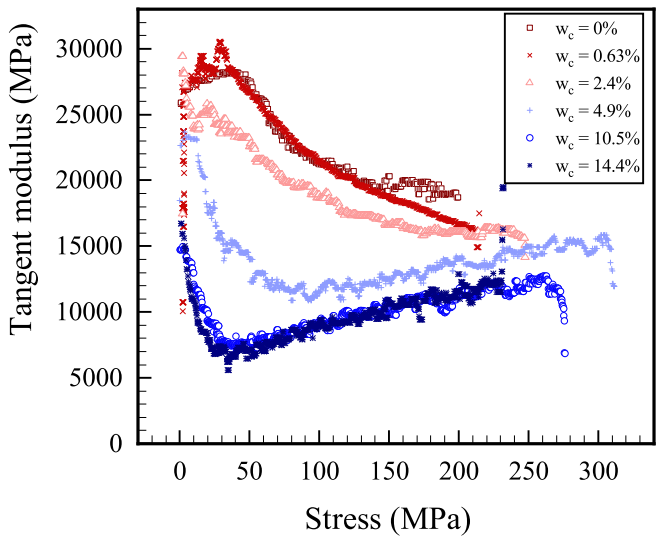


Figure 8: smoothed tangent modulus

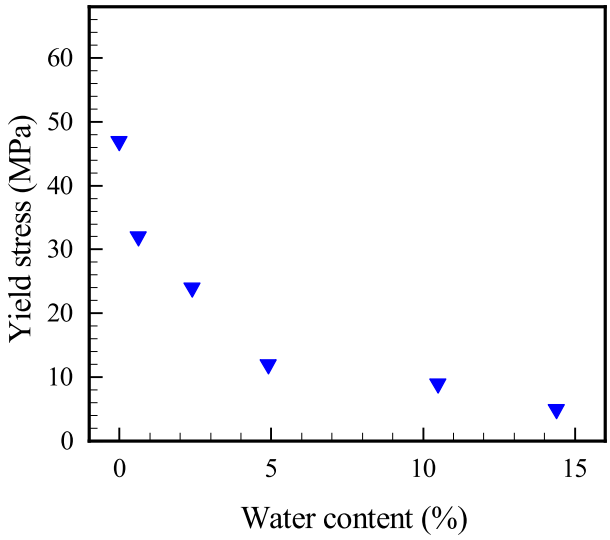


Figure 9: yield stress evolution with water content