# Moisture sorption and swelling of flax fibre and flax fibre composites

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**ABSTRACT**

This study evaluates the influence of moisture sorption on the properties of flax fibres and their composites. The radial swelling of both the elementary and technical flax fibres at a wide range of relative humidity (RH) values is determined. Moreover, the effects of moisture sorption on both the thickness swelling and flexural properties of flax/polyester and flax/epoxy composites are evaluated. Park's model is used to define the fibre moisture sorption curve. The model suggests that the moisture is first sorbed on hydrophilic fibre surfaces or microcavities until specific sites within the fibre reach saturation and later, the moisture forms aggregates at high RH. Flax elementary fibres have a lower radial swelling coefficient when compared to technical fibres, with radial swelling coefficients of $\beta_r$ = 1.2 and 1.9, respectively. At the composite level, flax/polyester and flax/epoxy systems have approximately the same thickness swelling coefficients, $\beta_t$ = 0.5 and 0.6, respectively, over the RH range, 11–97%. This behaviour could be explained by the constraining effect of the resins on flax fibres due to higher stiffness of matrix and probably due to resin penetrating the fibre lumen. Flexural properties of longitudinal and transverse fibre-oriented flax/polyester and flax/epoxy composites conditioned at different RH, and tested in fully dry condition, decreased as RH increased beyond 54%, likely due to moisture swelling which induced damage. This study provides new insights into the moisture sorption and dimensional changes of both the elementary and technical flax fibres and their composites and also the effects of moisture on the flexural properties of the composites.

**Keywords:** A. Fibres, A. Polymer-matrix composites, D. Mechanical testing, E. Thermosetting resin, F. Moisture

## 1. Introduction

The applications of natural fibre composites have been limited due to their lower moisture durability when compared to synthetic fibre composites, especially in outdoor conditions with high moisture exposure. Due to the presence of hydroxyl and other polar groups, natural fibres and their composites swell in the presence of moisture [1]. This hygro-expansion phenomenon of fibres inside their composites, which includes both the swelling and shrinking, has been suggested to prevent their use at a large scale in composite materials [2].

The mechanism of moisture sorption in hydrophilic fibre materials is a complex process because it involves a continuous change of the structure of the fibre due to swelling [3]. To give a better insight into the swelling mechanisms in a fibre, most studies focus on the swelling and water sorption of the three main fibre components: cellulose, hemicellulose, and lignin. Cellulose is a highly crystalline material and is thus less affected by water than lignin and hemicellulose [4]. In addition, the cellulose polymers' orientation within the cell wall makes natural fibres exhibit a strong anisotropic swelling, wherein the longitudinal swelling is significantly lower than in the transverse direction [5,6].

Flax fibres have good mechanical properties such as high specific modulus, making the fibres a good candidate as reinforcement materials for composite applications [7]. However, the fibre's strong hydrophilic behaviour which leads to a high level of moisture sorption [8] and large swelling deformation [9,10] is often considered as a limitation for biocomposites. Flax has been investigated at the elementary (single plant cell) and technical (bundle of elementary fibres) fibre levels to determine the mechanical and moisture sorption properties of the fibres [11] for their use in composites.

Direct measurement of the swelling of individual natural fibres is difficult to perform due to the small dimensions and irregular shape of the fibres [6]. For example, flax technical fibres are about 60–140 cm long with a diameter of only 40–80 µm [11], while flax elementary fibres are only a few cm long and have diameters between 10–20 µm [12]. Therefore, some studies in the literature highlight the importance of accurately measuring the swelling of natural fibres. Direct measurement of dimensional changes of natural fibres has been studied using x-ray micro-computed tomography (XµCT) for wood fibre [6], environmental scanning electron microscopy (ESEM) for flax elementary fibres [10] and flax technical fibres [13], and optical microscopy for flax elementary fibre [14]. The swelling or shrinking of wood and cellulosic fibres such as flax is normally quantified by the swelling/ shrinkage coefficient (β) which can be defined as the strain induced by a variation of 1% moisture content (MC) [5]. Some of the values reported for flax elementary and technical fibres are 1.14 [10] and 1.06 [15], respectively.

The swelling of flax fibres due to moisture sorption produces stress on the matrix material around the fibres, leading to microcracks in the composites [1]. In addition, the drying of composites that have sorbed water results in fibre shrinkage causing fibre/matrix debonding [1,16], which leads to the deterioration of the composites' mechanical properties and dimensional stability [10]. In literature, several authors have studied the effects of moisture sorption on flax fibre composites. Moisture sorption of flax/epoxy induces a significant change in the shape of the tensile stress-strain curve, a decrease in dynamic elastic modulus and a large increase in damping ratio [17]. Both Young's modulus and strength of flax/epoxy decrease with moisture sorption [18]. For flax/polyester composite, an increase in moisture uptake causes thickness swelling and reduction in the flexural properties of the composite [19].

In order to study the durability of natural fibre composites, it is thus relevant to understand water interactions occurring in plant fibres alone and the influence of water on their properties [2]. In this study, the influence of moisture sorption on the swelling of individual technical and elementary flax fibres and their composites is investigated. The radial swelling of both the elementary and technical flax fibres at a wide range of relative humidity (RH) values is determined. Factors that influence the accuracy of the fibre swelling test method and procedure are identified and discussed. Moreover, the effects of moisture sorption on both the thickness swelling and flexural properties of flax/polyester and flax/epoxy composites are evaluated. Understanding the influence of moisture sorption on the properties of flax fibres and their composites is of great interest as it provides information to improve the moisture durability of composites and their production processes for practical applications.

## 2. Materials and methods

### *2.1 Materials*

Long unidirectional (UD) flax fibre (Flax Tape 200, Lineo) with an areal weight of 200 g/m$^2$ and 400 mm width is used as received in this study. No treatment is performed on the fibre surface. Unsaturated polyester resin (Synolite 1967-N-1, DSM) with peroxide curing agent (Butanox M-50, Nouryon), accelerator (Nouryact CF-32, Nouryon) and an inhibitor (NLC-10, Nouryon) are used for the preparation of the matrix. The proportions of the materials were 1 wt.% for both the curing agent and accelerator and 0.6 wt.% for the inhibitor. The other matrix used in the study was epoxy resin (Epikote 828 LV) with Vestamin® IPD hardener from Evonik with a weight ratio of 100:23.

### *2.2 Composite plate preparation*

UD composites are made using the vacuum-assisted resin infusion technique. Composites (dried flax fibre/polyester and dried flax fibre/epoxy) with dimensions 300 mm × 300 mm and a targeted fibre volume fraction ($V_f$) of 35% were prepared. The $V_f$ was determined using the following formula:

$$V_f = \frac{nA_f}{\rho_f t} \quad (1)$$

where n, $A_f$, $\rho_f$, and t are the number of fibre layers (5 layers), areal weight of the fibres (g/cm$^2$), flax fibre density (1.45 g/cm$^3$) and laminate thickness (cm), respectively.

A mould, consisting of a top and a bottom plate and two spacers, was used to produce a composite with a thickness of 2 mm. A vacuum of 0.6 bar was applied to the infusion process that is performed at ambient temperature. The matrix was cured at room temperature for 24 h followed by post-curing in an oven at 70 °C for 12 h for the case of the flax/polyester system. The flax/epoxy system was cured on a hot plate at 70 °C for 4 h and post cured at 150 °C for 1 h in a hot press using 15 bar pressure. The laminates are cut into smaller pieces (60 mm x 12.7 mm) using a band saw to prepare samples for both physical and mechanical tests. Then, the sides of the samples are ground using a grinding machine with 300 and 800 grit size abrasive papers. Both in longitudinal and transverse fibre orientations, the edges of all samples have not been coated to accelerate composites' moisture sorption and swelling. The void contents of flax/polyester and flax/epoxy composites are 0.4% and 0.2%, respectively calculated using SEM and the ImageJ software. At least 20 images with a magnification of x 350 were taken from each sample to represent the composite's average void content.

*2.3 Sorption test*

The static gravimetric method is used to determine the equilibrium moisture content (EMC) of fibre and composite samples. Seven desiccators with different saturated salt solutions are used to maintain RH values of 11%, 33%, 54%, 75%, 84%, 94% and 97% at constant temperature (23 °C). After oven drying at 80 °C for 7 days, 6 samples of each material (fibres, polyester/flax and epoxy/flax composite) are placed into the desiccators simultaneously and allowed to attain equilibrium. The reason for choosing the drying temperature of 80 °C instead of the standard temperature for oven-drying plant fibres (105 °C) was to prevent a significant drop in both fibre and composite's strength due to the decrease in fibres interfacial bonding [20].

The weights of the samples were measured on an analytical balance (sensitivity ± 0.0001 g). The changes in the weight of the fibre samples were determined every two days until the equilibrium was reached (approximately after 10 days). For composite samples, the weight is measured every week for the first three weeks and after every two days until the equilibrium is reached (approximately 29 days). Equilibrium was judged to have been attained when the weight of the sample after two successive measurements remained apparently constant so that the difference between two successive weighing is lower than 0.1% [21]. The moisture sorption $M_t$ at saturation is calculated as follows:

$$M_t(\%) = \left(\frac{W_t - W_o}{W_o}\right) x\ 100 \qquad (2)$$

where $W_t$ and $W_o$ are the weights of the sample after moisture exposure and the weight of the dry material before moisture exposure, respectively.

*2.4 Material swelling*

The radial swelling of both the elementary and technical flax fibres is determined in this study. Technical fibres are directly obtained from the flax preform (Flax Tape 200), while elementary fibres are separated from the technical fibres by manual extraction. Elementary fibres are peeled off from the technical fibres using tweezers. Fibre swelling measurement in the radial direction is performed using a goniometer (OCA 50, DataPhysics). The resolution of the images is 1.0 µm/pixel. The RH is controlled by a humidity generator and controller (HGC 30, DataPhysics) in the RH range 5–90%. The fibre diameter was measured every minute for each RH value at the same point along the sample until it reaches the equilibrium fibre swelling, normally within a 10-min period. The measurements have been performed at ambient temperature over the full RH range. The initial dimension of the fibre is obtained after oven-drying at 80 °C for 3 h and by placing the fibre in a desiccator containing silica gel (~0% RH) for at least 24 h until it is used for the swelling measurement.

It should be noted that the preparation and the process of fibre swelling measurement are difficult and time-consuming due to the irregularities in the fibre size and shape, due to the instability of fibres, and the splitting of technical fibre at high humidity. Therefore, samples with irregularities that led to measuring errors are excluded. Fig. 1 shows some 'acceptable' and 'unacceptable' examples of fibre samples used for swelling measurements. 'Acceptable' fibre samples (Fig. 1a) have a uniform diameter while 'unacceptable' samples (Fig. 1b) have an irregular diameter or show fibre splitting. For each RH, a total of 6 single technical and 6 elementary flax fibres are subjected to swelling measurement. Thus, one single elementary or technical fibre is measured at a time.

(Insert Figure 1)

A sample is mounted in a holder which prevents fibre twisting and sagging, particularly at high RH when the fibre has sorbed ample amounts of moisture (Fig. 2). Both ends of the fibre are fixed with an adhesive tape, which held the fibre in place even at high RH. The use of slots in the holder helped the fibre to remain in a stable position (see Fig. 2). Fibre swelling is measured along the length of the fibre exposed in the gaps of the sample holder since the tape or the sample holder itself could constrain the radial swelling in areas in contact. The total length of the fibre being observed is limited to 2 mm of the fibre throughout the swelling test. The technical fibres used in the study are limited to a range of 40–50 microns in diameter, and elementary fibres are approximately between 10–20 microns, to avoid errors encountered in the study like uneven diameter and fibre splitting. Only the swelling of the fibre in the radial direction is measured in this study which is of engineering relevance for dimensional instability caused by swelling of composite material during moisture uptake [6].

(Insert Figure 2)

For direct single fibre swelling measurement, it is vital to ensure that the same profile view of the fibre is observed throughout the measurement to avoid misreading the change in diameter from measuring the dimension of a different position. Some of the common errors encountered in the study are the twisting or movement of the fibre and splitting of technical fibres at high RH (Fig. 3). Twisting is shown in Fig. 3a, wherein the nodes of the fibre change their position during the swelling measurement. Splitting of technical fibres starts at around 70% RH, producing gaps between fibres as presented in Fig. 3b. Damage during fibre extraction, such as separation of elementary fibre from the technical fibre, is common due to the mechanical forces employed during extraction [22]. Therefore, during swelling measurement at high humidity levels, the middle lamella is in some cases already broken allowing the easy access of water molecules in between the elementary fibre interface, producing the separation of the elementary fibres due to swelling. Further work is required to understand the mechanism of flax fibre splitting when exposed to high humidity, but it can be hypothesised that fibre splitting is restricted when the fibre is embedded in matrix material. In any case, fibres showing splitting were discarded and not used in this study. For precise measurement of the fibre swelling, images and videos of the samples were recorded to watch closely if swelling measurements were always performed at the same position of the fibre.

(Insert Figure 3)

Since the radial swelling varies along the length of the fibre, the swelling is measured throughout the whole length of the fibre and then the mean radial swelling is recorded. This is performed using the poly-area command of Matlab software (Fig. 4). To determine the mean diameter of the fibre along its length, the images of both the technical and elementary fibres subjected to different RH are put together in one image (Fig. 4a, d). The images are thresholded to form a binary image, and then the area and diameter of each fibre are calculated. The mean diameter of the fibre at a specific RH is calculated by dividing the total surface area of the fibre by the total length of the fibre. The radial swelling (T) at saturation is calculated as follows:

$$T(\%) = \frac{(T_f - T_o)}{T_o} \ x \ 100 \qquad (3)$$

where $T_f$ and $T_o$ are the mean diameter of the sample after moisture exposure and the diameter of the dry material before moisture exposure, respectively.

(Insert Figure 4)

Swelling in the thickness direction of the composites is measured on 60 mm × 12.7 mm samples using a Mitutoyo digital micrometre with a precision of ± 0.001 mm. Three measurements are performed along the length of each specimen and the average values are recorded.

*2.5 Flexural test*

Longitudinal and transverse unidirectional composites are tested according to ASTM D790 standard on a 60 mm × 12.7 mm sample, with a test span of 32 mm. Flexural tests of the composites are performed using a universal testing machine (Instron 5567) with a 1 kN load cell and cross-head speed of 0.85 mm/min. All tests on samples are performed after drying the samples at 80 °C for 7 days to accentuate the possible damage due to swelling and subsequent shrinkage of the fibres. Samples are no longer than 15 min out of the oven before testing. During this period, the temperature of the samples returns to room temperature, while the MC is assumed to be nearly unchanged.

*2.6 Composite microstructure*

The composite cross section surface (perpendicular to the fibre direction) was analysed by scanning electron microscope (SEM) (Philips XL-30 FEG). The composite samples were coated with a 5 nm platinum layer before the imaging and then examined using 10 kV acceleration voltage. Specimens that were used for surface analysis of composites were prepared by sanding and polishing. Moreover, the cross section of flax fibres exposed from the fracture surface of composites in transverse fibre orientations is also evaluated using SEM.

## 3. Results and discussion

### *3.1 Equilibrium moisture sorption and desorption isotherm*

The equilibrium moisture sorption and desorption plotted against the water activity for technical flax fibres, flax/polyester and flax/epoxy composites are presented in Fig. 5. Water activity ($a_w$) is the ratio of the vapour pressure of water in equilibrium with the material to the saturated vapour pressure of pure water at the same temperature [23]. The $a_w$ value is equivalent to the equilibrium RH divided by 100. The graphs are constructed so that the MC of samples after oven-drying at 80 °C for 7 days is shown as zero moisture sorption. All samples reached an equilibrium state at each moisture interval. The results showed that moisture sorption of the fibres and composites varied as the humidity was changed over the whole water activity range, exhibiting a curve with a sigmoid or S-shape, which is typical for cellulosic-based materials and can be generalised to many hydrophilic materials [24–26]. The equilibrium moisture isotherms for all the samples show a distinct hysteresis between sorption and desorption, indicating structural changes of the fibres [3] and likewise of the composites, caused by the interaction with water. The difference between the sorption and desorption mechanisms of composites can be explained by the swelling of the fibre forming microcracks at the fibre/matrix interface [1] and the plasticising effects of sorbed water which influence the fibre, resin, and interface simultaneously [27].

(Insert Figure 5)

Water sorption isotherm equations are useful for predicting water sorption properties of cellulosic materials and provide some insight into the interaction between water molecules and cellulosic compounds [23]. Given the behaviour of the flax fibre sorption curve, the sorption isotherm of flax fibre can be described using Park's model [28] according to the following formula:

$$M_t = \frac{A_L * b_L * a_w}{1 + b_L * a_w} + k_H * a_w + K_a * {a_w}^{n_a} \tag{4}$$

with $M_t$: equilibrium MC for specific water activity ($a_w$) $A_L$: Langmuir capacity constant, $b_L$: Langmuir affinity constant, $k_H$: Henry's solubility constant, $K_a$: Equilibrium constant for clustering reaction, $n_a$: mean number of water molecules per cluster.

Table 1 shows the sorption parameters of Park's model fitted to the experimental data along with the correlation coefficient ($R^2$) and the mean relative percentage deviation modulus (E). The model presented $R^2$ close to unity and a small E value, indicating good fit to experimental data. The fitted curve of moisture sorption for flax fibres from the Park model is presented in Fig. 5a. The contribution of each parameter is different in the specific range of $a_w$ corresponding to the three sorption mechanisms of the Park model: Langmuir sorption, Henry's law and water clustering. The Langmuir's terms, $A_L$ and $b_L$ which are of influence at a low $a_w$ ($a_w < 0.1$) are physically observed when a monolayer of water molecules (or bonded water) is adsorbed on specific sites at the fibre surface or in microcavities. For flax fibres, such specific sites exist at the periphery of the fibre bundles wherein the main components are pectins [25,26]. Henry's solubility, $k_H$, defines the slope of the isotherm in the range $0.1 < a_w < 0.5$ and shows the sorption of polylayer water (or free water) that occurs when saturation of specific sites is reached. The values $K_a$ and $n_a$ could be linked to the equilibrium state corresponding to the aggregate formation at $a_w > 0.5$. It is assumed that the sorbed water can cause swelling of the fibres and that water molecules link together to form clusters [2]. However, it should be noted that using this model, the information about the mechanisms of water sorption in flax fibres is a rough estimate. Flax fibres are composite structures with highly heterogeneous composition so that the actual sorption mechanisms are more complex to be interpreted [26].

(Insert Table 1)

As shown in Fig. 5a, technical flax fibre sorbs 22.1% of moisture at $a_w = 0.97$ confirming the results of previous studies on the moisture sorption of flax fibres [7,29]. The moisture sorption of flax/polyester is higher compared to flax/epoxy composite throughout the whole $a_w$ range (Fig. 5b). Flax/polyester and flax/epoxy sorb 7.8% and 6.5% of moisture, respectively at $a_w = 0.97$. In literature, it has been reported that the amount of moisture sorption is influenced by the nature of the fibre and matrix materials, fibre/matrix interface and the mechanical properties of composites [1,30]. The epoxy resin forms a stronger interface with flax fibres than polyester resin [30], and it is better in obtaining a more covered area so that it exhibits lesser porosities at the interface. These characteristics result in lower moisture sorption of flax/epoxy composites. This is supported by the transverse flexural strength results presented in Fig. 10c. To understand the contribution of moisture sorption within the material, a moisture sorption test was also conducted on pure resins. Both polyester and epoxy resins reach moisture sorption of only 0.7% at $a_w$ = 0.97. Therefore, it is plausible that the fibres' moisture sorption is the main contributor to the total moisture sorption of the composite. The increase of composite moisture sorption at high $a_w$ can be associated with similar behaviour of the fibres. Moreover, the reduction in the moisture sorption of the fibre when embedded in resins can be roughly estimated by using the rule of mixtures:

$$\alpha_c = \alpha_f w_f + \alpha_m \cdot (1 - w_f) \tag{4}$$

where $\alpha_c$, $\alpha_f$, $w_f$, and $\alpha_m$ are the predicted moisture sorption of composite, moisture sorption of fibre, the weight fraction of fibre, and moisture sorption of resin respectively. The estimated weight fraction of the fibre is 40% when using the polyester and epoxy resin density of 1.16 g/cm$^3$ and the flax fibre density of 1.45 g/cm$^3$. Then, at $a_w$ = 0.97, a decrease of 17% and 32% in moisture sorption are observed for fibres embedded in polyester and epoxy resins, respectively compared to free fibres. Therefore, the results show that moisture sorption is reduced by embedding the fibres in the resin.

*3.2 Equilibrium swelling*

For direct measurement of single fibre swelling, the complexity of the procedure comes from maintaining the same profile view of the camera and to detect if no fibre twisting and splitting occur. Photographic images can determine when such irregularities could lead to measurement errors. A good sample in Fig. 6 shows visible fibre nodes that stay in the same position along the fibre length with no fibre twisting or splitting.

(Insert Figure 6)

The swelling of both fibres and composites plotted against RH and MC are presented in Fig. 7. The radial swelling results plotted for both the elementary and technical flax fibres and thickness swelling of composites after various moisture exposure times are presented in Fig. 7a and 7b, respectively. Samples were all exposed until full saturation. The maximum humidity value used in the study for measuring the swelling of fibres is 90% RH which is the maximum RH limit of the used humidity generator. The results show that swelling of the fibres and composites increases as the RH increases. The swelling of elementary and technical fibres is 15.5% and 24.9%, respectively, while for flax/polyester and flax/epoxy composites the values are approximately 2.7% and 2.5%, respectively at 90% RH.

As shown in Fig. 7a and 7c, the radial swelling of technical and elementary fibres is not equal, wherein the technical fibre has higher radial swelling than elementary fibre. Some studies in literature measured the swelling of the elementary fibre, which brings into mind the possibility of using the swelling of technical fibres as a better alternative for predicting the overall thickness swelling of flax fibre in a composite. The middle lamella is mainly composed of pectin, which is highly hygroscopic. Since elementary fibres are joined by the middle lamella, moisture uptake is hence more pronounced in fibre bundles [2]. Therefore, the radial swelling of the elementary fibre may arrive at an underestimate and impractical measure since technical fibres are typically used for composite applications.

Fig. 7c shows the radial swelling of the fibres against MC values obtained by interpolation based on the measured swelling. Flax technical and elementary fibres have swelling coefficients in the radial direction, $\beta_r$ = 1.9 and 1.2, respectively over the RH range, 33–90%. The $\beta_r$ values are calculated from the slope of the swelling curve plotted against the MC [5]. The calculated value for elementary fibre is close to what is reported in the literature for flax elementary fibre, 1.14 [10] evaluated at 20–98% RH. In the case of flax technical fibres, the calculated $\beta_r$ is far from the value estimated in literature, which is 1.06 [15] and 0.63 [31] evaluated at 8–97% RH and 20–73% RH, respectively. Possible reasons for the differences in the measured $\beta_r$ of flax technical fibre could be the fibre materials and method used in the swelling measurement. In one study, the technical fibres used are twisted flax yarns [15]. While in the other study, the swelling of flax technical fibre was not directly measured; therefore, the $\beta_r$ was only estimated from the calculated cross-sectional hygro-expansion coefficient of the flax technical fibre [31]. Overall, the differences in the values of $\beta_r$ of flax technical fibre observed in this study and literature, besides the differences in RH ranges used in the methods, could be attributed to several factors such as fibre dimensions, treatment performed on the fibre material and the overall chemical composition of the fibre, which possibly influence the amount of swelling. A comparatively high deviation was also observed in the values obtained for the radial swelling of technical fibres compared to elementary fibres, shown in Fig. 7a and 7c, which could also support the differences in the measured $\beta_r$ of technical fibres. But an important factor is the observed swelling of the middle lamella at high humidity, which leads to higher fibre swelling (see Fig. 6).

Although flax/polyester has higher moisture sorption (see Fig. 5b) and thickness swelling than flax/epoxy at the given RH, the swelling coefficient in the thickness direction, $\beta_t$ of flax/polyester is somewhat lower than for flax/epoxy composite (Fig. 7d). Flax/polyester and flax/epoxy have $\beta_t = 0.5$ and 0.6, respectively over the RH range, 11–97%. The results emphasise that $\beta_t$ is basically constant and not influenced by the surrounding RH, in contrast to moisture sorption and thickness swelling of materials, which are strongly RH dependent. Unlike for the single fibre, the composite swelling coefficient is not difficult to measure experimentally. However, only one recent paper has reported the $\beta_t$ of flax/epoxy composite to the authors' best knowledge, which was 0.85, evaluated at 8–97% RH [15]. Normally, in literature, the effect of moisture sorption on natural fibre composites is commonly studied using water immersion tests. Therefore, the amounts of moisture sorption and swelling at different humidity values (both necessary input for the swelling coefficient) are not reported. Moreover, other studies showed that the swelling of composite varies non-linearly with MC. Therefore, the swelling coefficient is not reported. The deviation of the linear behaviour is possibly due to damage-induced sorption, which could have modified the sorption behaviour and water molecules localisation in hemp/epoxy [32] and flax/MAPP [33] materials.

The fact that the $\beta_t$ values for the composites are clearly smaller than 1 (taking into account effects of volume versus weight increase) is a clear indication that water can fill up spaces inside the composites such as porosity of fibres and matrix without causing a corresponding increase in the volume of the composite. Moisture sorption of fibre already started at $w_a = 0.1$ or 10% RH (see Fig. 5a), while radial swelling of both elementary and technical fibres only started at around 30% RH (see Fig. 7a). Thus, this suggests that the fibres first sorb water at the fibre surface or in microcavities as bound water described by Park's model, before they start to swell.

(Insert Figure 7)

The experimental results of both moisture sorption and thickness swelling of the composites are compared to the theoretical values predicted from the rule of mixtures. The predicted moisture sorption of composites, as well as the predicted thickness swelling of the composites, are calculated using Eqn. 4; however, in the latter case the volume fractions of both flax fibre and resins are used and also by replacing the moisture sorption parameters with the swelling values of technical or elementary fibre and the resin. The predicted moisture sorption and thickness swelling of both composites are calculated using the fibre volume fraction of 35% and the densities of flax fibre and the resins (Fig. 8). It can be observed that both results of moisture sorption against the RH (Fig. 8a) and thickness swelling against the MC (Fig. 8b) of the composites are not proportionate with the fibre weight and volume ratio respectively, wherein the predicted values are higher than experimental values. For example, the predicted moisture sorptions of flax/polyester and flax/epoxy composites are approximately 20% and 40%, respectively higher than the experimental values at 97% RH. A similar result is observed in literature with the moisture sorption of flax/epoxy [15] and flax/PP [29] but in contrast with hemp/PET composites [21]. Therefore, the types of materials used in composites could affect the applicability of the rules of mixtures in predicting the moisture sorption of composites [21]. In the current study, the difference between the experimental and predicted values could be attributed to the constraining effect of the resins on the flax fibres, which reduces their access to moisture and thereby the swelling; also, the stiffness of the matrix constrains the swelling fibre.

(Insert Figure 8)

An additional explanation could be related to resin penetrating the fibre lumen (central hole of elementary fibre) and thus reducing water sorption inside the lumen. Various authors have suggested this possibility [22,34,35]. It has been suggested that flax fibres could have permeable walls which would allow epoxy [34] and other likely candidates such as polyester resin with lesser viscosity than epoxy, to occupy the empty fibre lumens during impregnation. Penetration of resin into fibre lumens during the composite fabrication is possible due to the damage caused to the fibre during fibre processing [22]. In wood fibre, the occupation of the lumen by the resin limits the swelling of the fibre from the inside of the fibre, by filling in and limiting the opening of the lumen of the fibre [35]. The possibility of penetrating the flax lumen by the polyester resin used in this study during impregnation was revealed with the aid of SEM (Fig. 9). It can be seen that flax lumens were filled with polyester resin, as shown in Fig. 9a. During the SEM analysis, it was observed that only a reduced number of fibre lumens were not filled with the polyester resin. In general, almost all of the observed fibre lumens were filled with resin or have collapsed, either with some resin inside or without resin (see Fig. 9b). This supports previous findings in the literature that the resin inside the fibre lumen could reduce water sorption and swelling of the fibre in composites.

It is noticeable that the flax/polyester and flax/epoxy composites have almost identical predicted moisture sorption (Fig. 8a) and swelling (Fig. 8b). Applying the rule of mixtures shows that when the resins' moisture sorption and swelling are almost similar, the predicted sorption and swelling of their composites will also be similar. The composites' predicted swelling using either the swelling of elementary fibre or technical fibre is far from both composites' experimental values. In general, it can be observed that both the moisture sorption and swelling of the composites cannot be well-predicted using the rule of mixtures. Therefore, a new predictive equation would be welcome to account for the constraining effect of the resin on the fibre to make it more reflective of the actual thickness swelling of composites across varying RH, but this is beyond the scope of this paper.

(Insert Figure 9)

*3.3 Flexural test*

Fig. 10 shows the flexural properties of both longitudinal and transverse fibre-oriented composites conditioned at different RH. Flexural properties of composites were determined immediately after drying the samples at 80 °C for 7 days, so they were tested in the dry state. It is observed that samples in their as-produced condition, at 0% RH, have lower flexural properties than composites conditioned at 54% RH. The negative effects of drying on both the fibre (reduction of 44% on strength and 39% on failure strain) and composites (reduction of 36% on strength) as reported in literature [20] could be the reasons for the reduced properties of composites at 0% RH compared to 54% RH. In very dry state, many natural fibres tend to fail in a more brittle way, with lower strength; some plasticisation at standard humidity tends to improve the strength. Although the sample conditioned at 54% RH was also tested in fully dried state, due to hysteresis effects likely some more moisture remained inside this material and a higher strength was recorded. The small positive effect on modulus at 54% RH might also be related to this hysteresis effect. Compared to material conditioned at 0% RH, the more swollen material could have improved internal friction and stress transfer. The graphs in Fig. 10 generally show that the flexural properties of flax/epoxy are higher compared to flax/polyester composite.

Although the moisture sorption and swelling of the fibre are substantially reduced when embedded in resins, as shown in Fig. 8, the dimensional change of composites due to moisture sorption still contributes to its lower flexural properties, as will be discussed further on. Overall, the results showed that both composites' mean strength and modulus decreased as RH increased beyond 54%, both in longitudinal and transverse directions. Reductions of 10% and 15% in the longitudinal strength and modulus respectively are recorded for flax/epoxy while for flax/polyester, reductions of 11% and 12% in the longitudinal strength and modulus are observed respectively, when RH is increased from 54% to 97%. For the same increase in RH, the transverse strength and modulus of flax/epoxy are both reduced by 15%, while for flax/polyester, the transverse strength and modulus are reduced by 15% and 11% respectively. Therefore, after having been produced with fully dry fibres, just by exposing the composites to 1 'cycle' of high humidity and then going back to fully dried state, the composite properties already deteriorate substantially.

(Insert Figure 10)

The likely reason for the reduction in flexural properties of both composites subjected to high humidity conditions ( > 54% RH) is the plasticisation of both matrix and fibres, which weakens the fibre/matrix bonding resulting from moisture sorption [17,27]. Moreover, the flax fibres' swelling develops stress at the fibre/matrix interface regions, leading to microcracking at the interface and eventually in the degradation of the composites [1]. These effects are then accentuated when the composite is fully dried again and tested in dry condition. These possible mechanisms are confirmed by SEM observations of the surface of composite samples subjected at 97% RH (Fig. 11c, 11d), where composite structure appears degraded with several cracks caused by swelling and shrinking of the material. Note that the SEM also operates in a fully dry state (vacuum). Both composites show evidence of fibre/matrix debonding and technical fibre splitting.

(Insert Figure 11)

## 4. Conclusions

This study focuses on the determination of moisture sorption and swelling of elementary and technical fibres of flax and their composites at a wide range of RH values, and proposes a methodology for measuring radial deformation of individual fibres. Moreover, the effects of moisture sorption on flexural properties of composites are also determined. Park's model is used to define the fibre moisture sorption curve. The model suggests that the moisture is first sorbed on hydrophilic fibre surfaces or microcavities until specific sites within the fibre reach saturation and later, the moisture forms aggregates at high RH. Compared to elementary fibres, flax technical fibres exhibit a higher degree of swelling and a 60% higher radial swelling coefficient ($\beta_r$). Based on microscopic observation, the likely cause is the swelling of the middle lamella at high humidity.

The experimental results of both moisture sorption and thickness swelling of the composite are compared to the theoretical values predicted from rules of mixtures. Both results of moisture sorption and thickness swelling of the composite are not proportionate with the fibre weight and fibre volume ratio of the composite, wherein the predicted values are higher than experimental values. The experimental results highlight the constraining effect of the resin on the radial swelling of flax fibres due to moisture sorption and on the moisture sorption itself.

Flexural properties of both longitudinal and transverse fibre-oriented flax/epoxy and flax/polyester composites conditioned at different RH decreased ( up to 20% at 97% RH) as RH increased beyond 54% when tested in fully dry condition. This highlights the damage (fibre/matrix debonding and fibre splitting) that flax composites suffer when exposed to high humidity, likely due to the large difference in swelling between fibre and matrix, as evidenced in this study.

Overall, the results of this study provide new insights into the moisture sorption and dimensional changes of both the elementary and technical flax fibres and their composites and how moisture affects the flexural properties of composites. Future work will focus on extending this study in evaluating the effects of moisture sorption on other natural fibres used as reinforcement for composites, as well as on a more accurate modelling of the swelling phenomena. A closer look at the influence of moisture sorption on the properties of flax fibres and their composites reveals areas where the moisture durability and production processing of composites can be improved. This is in agreement with results from our previous publications [19, 36], which show that producing composites with pre-swollen fibres (non-dry) may lead to less damage in the composites when exposed to high humidity.

## 5. Acknowledgements

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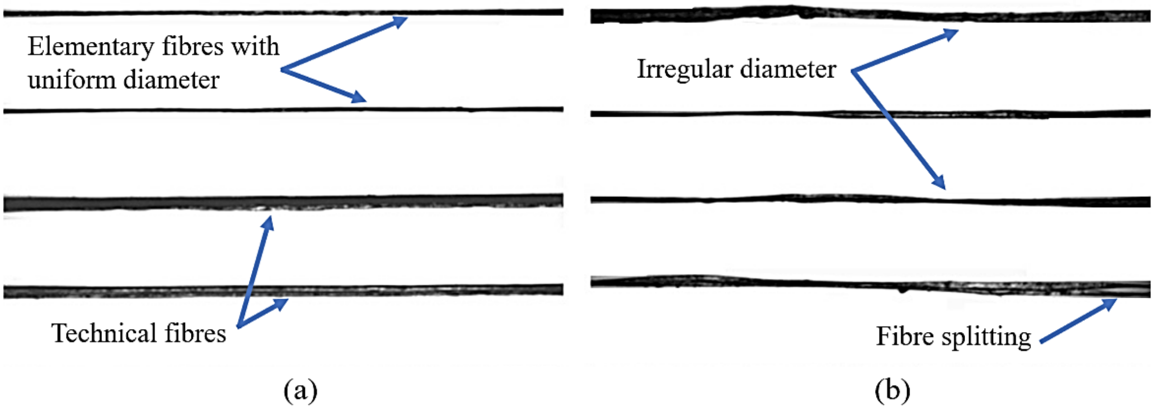


Fig. 1. Examples of 'acceptable' and 'unacceptable' fibre samples used for swelling measurement; (a) 'acceptable' elementary and technical fibres with roughly uniform diameters and (b) 'unacceptable' fibres with an irregular diameter and showing fibre splitting.

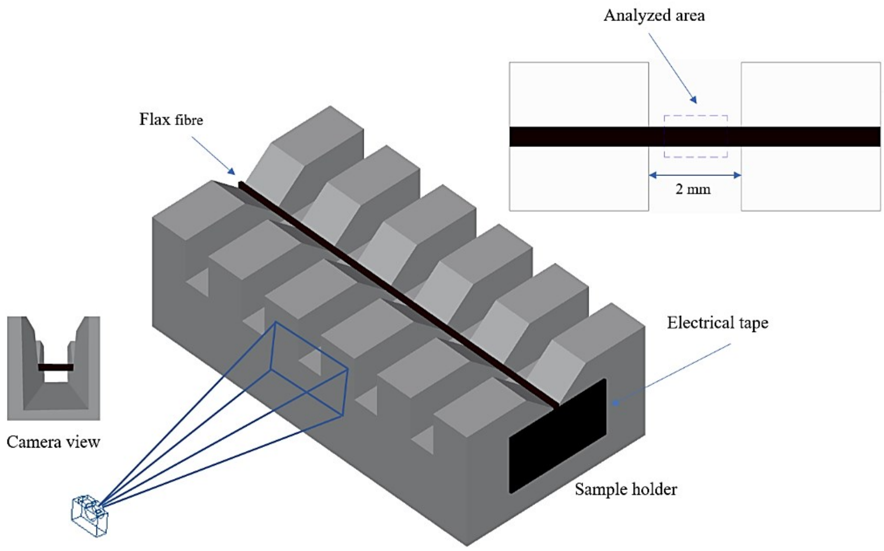


Fig.2. Schematic drawing showing the experimental setup. The length of the fibre being analysed is limited to 2 mm to prevent movement of the fibre. The sample holder has dimensions of 28 mm x 20 mm x 10 mm.

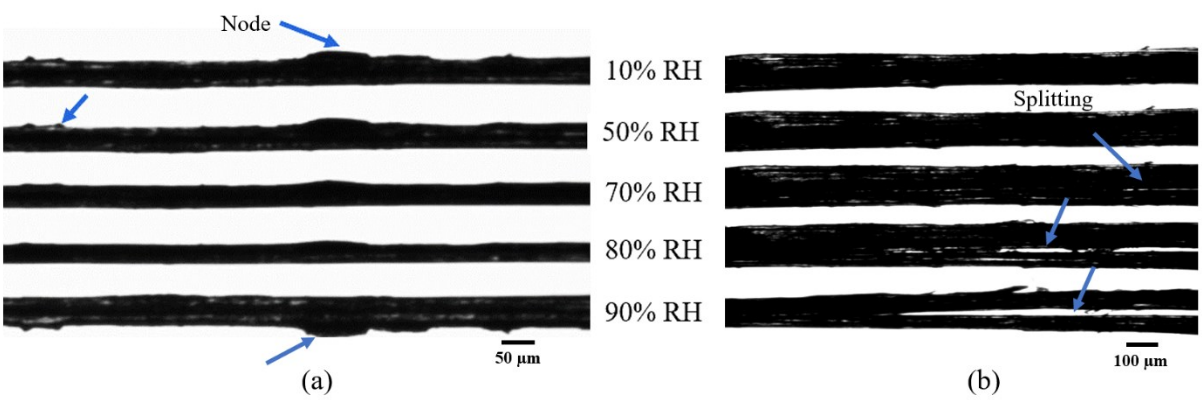


Fig. 3. Examples of errors encountered in technical fibre swelling measurement; (a) twisting or instability of fibre due to irregular shape and size of the fibre and (b) fibre splitting which starts around 70% RH.

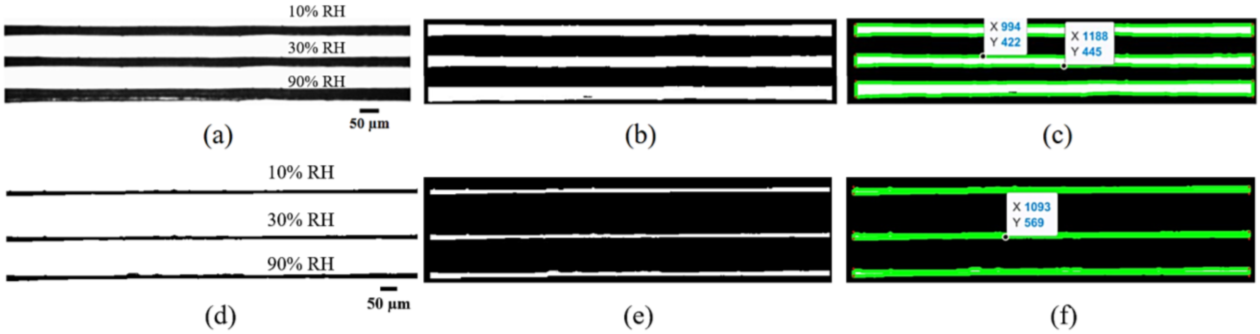


Fig. 4. Image processing using Matlab for the determination of the mean thickness of the technical (a,b,c) and elementary (d,e,f) fibres at each RH value; (a,d) images of the fibres at different RH before image processing, (b,e) after converting to a binary image and (c,f) after calculation of the area and average thickness of each fibre.

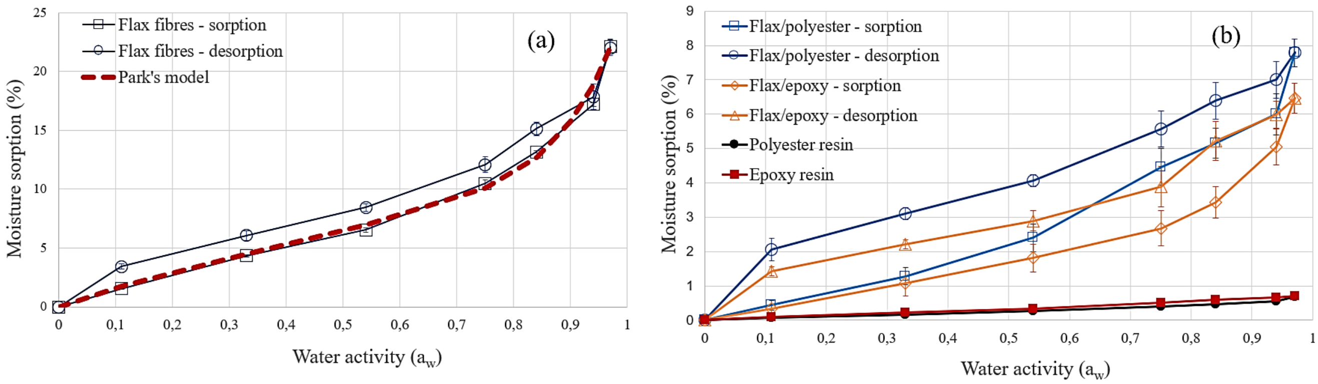


Fig.5. (a) Equilibrium sorption isotherm of technical flax fibres. Experimental sorption data are fitted to Park's model and (b) Equilibrium sorption isotherm for flax/polyester and flax/epoxy composites at 23 °C.

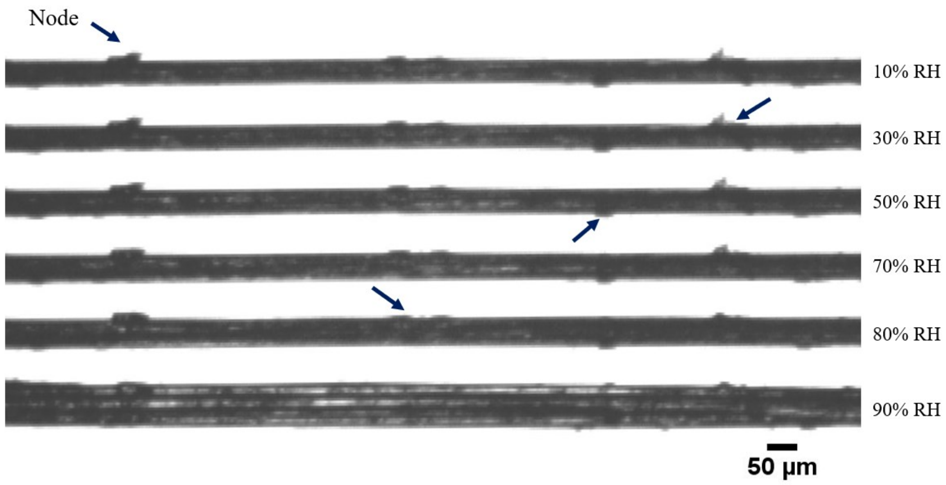


Fig. 6. Evolution of the thickness swelling of a single technical fibre. The nodes of the fibre stay in the same position throughout the swelling measurement.

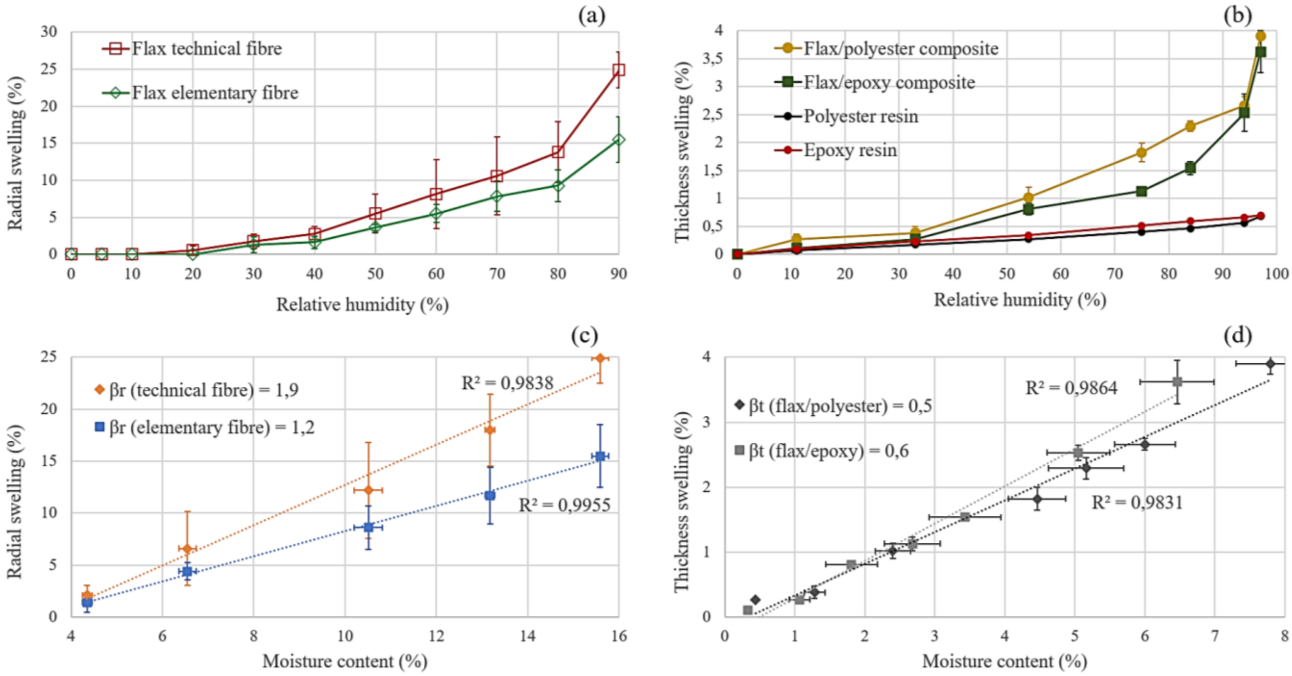


Fig. 7. Radial swelling of single technical and single elementary flax fibres and thickness swelling of the composites and resins as a function of relative humidity (a, b) and Fibres' measured radial swelling coefficient ($\beta_r$) and the thickness swelling coefficient ($\beta_t$) of the composites (c, d). The $\beta_r$/ $\beta_t$, which is initially measured at the beginning of the swelling, is equivalent to the slope of the linear curve of the swelling against the samples' moisture content values.

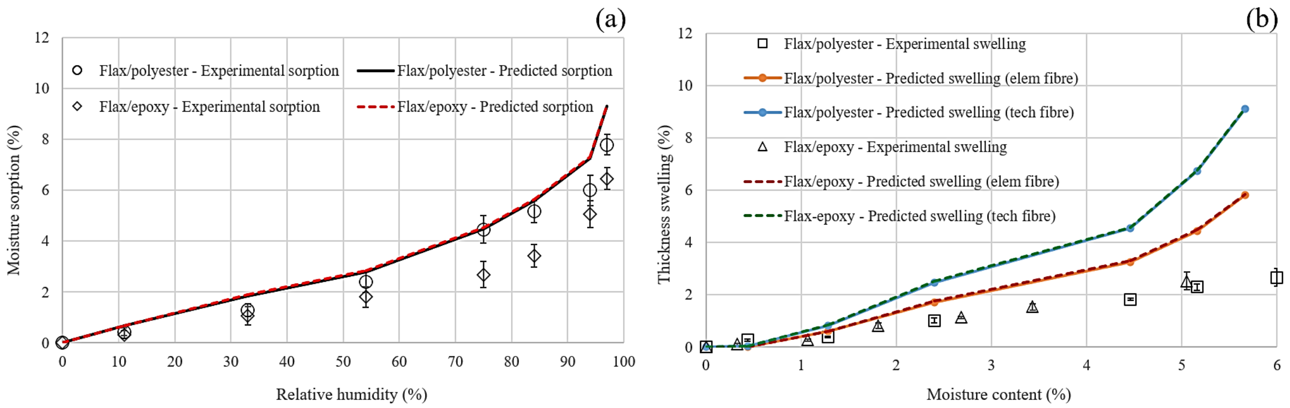


Fig. 8. Experimental and predicted moisture sorption against relative humidity (a) and thickness swelling against moisture content (b) of composites using the rule of mixtures.

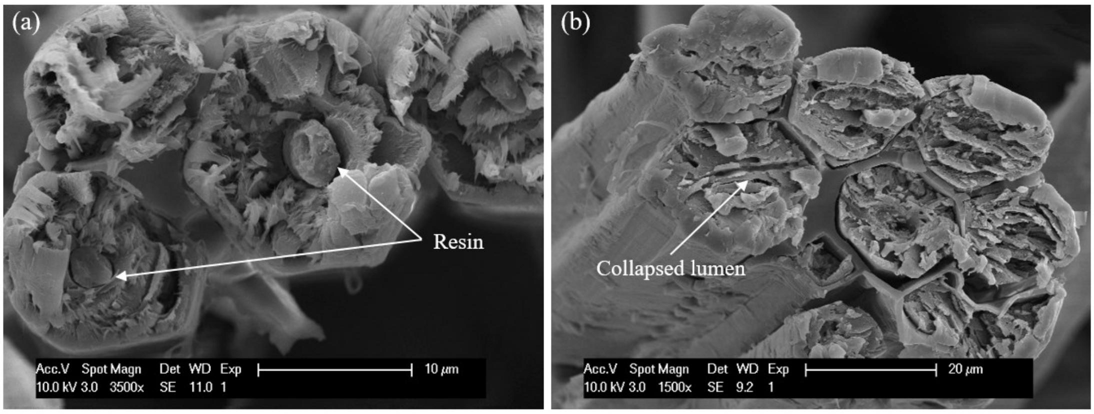


Fig. 9. SEM images of a flax/polyester composite fractured part; (a) showing fibre lumens filled with resin and (b) collapsed lumen which could either contain resin or not.

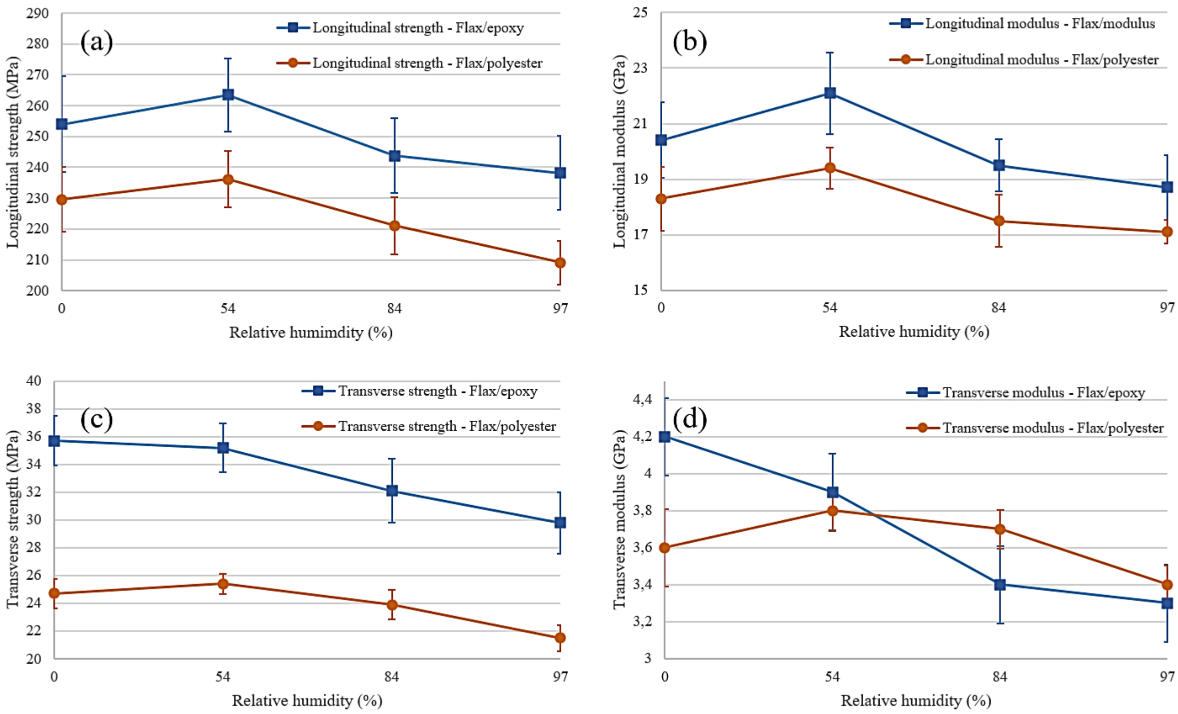


Fig. 10. Longitudinal and transverse flexural properties of composites conditioned at different RH; samples were subsequently tested in a fully dry state after oven drying.

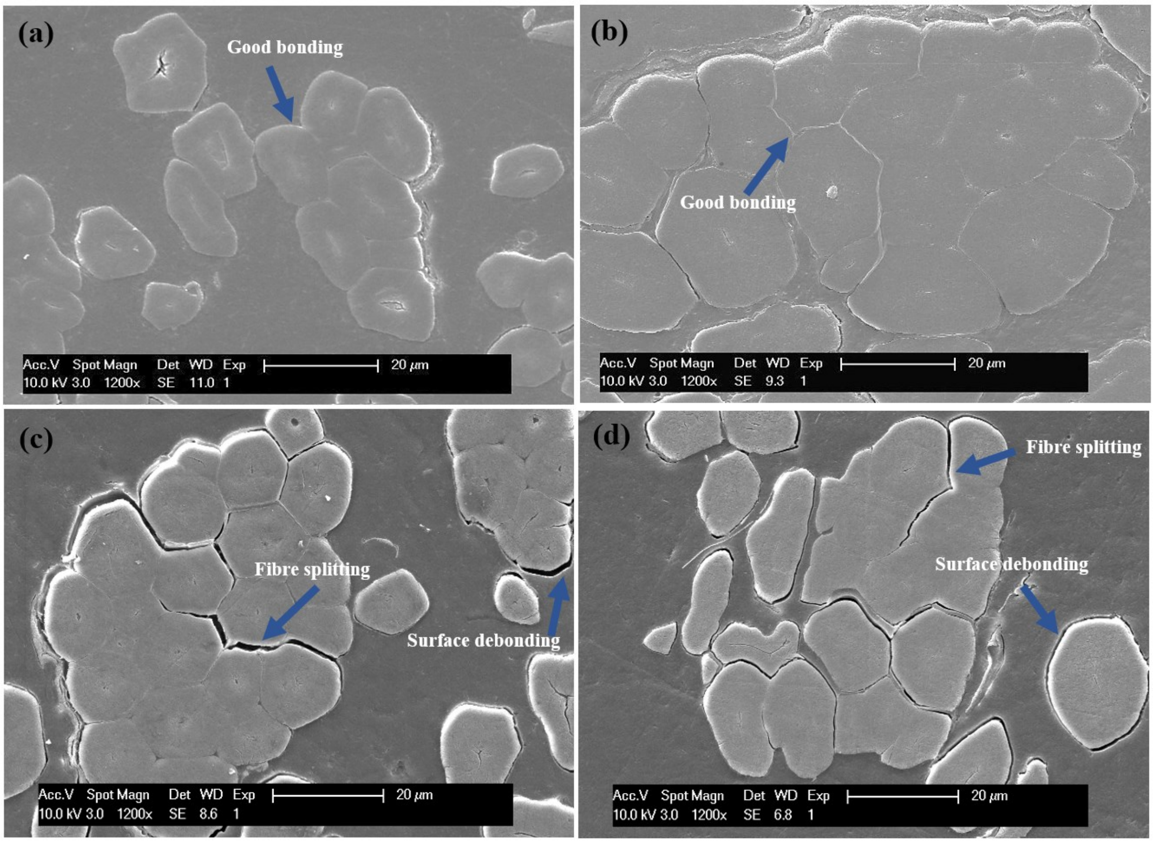


Fig. 11. SEM micrographs of composites before (a,b) and after (c,d) saturation at 97% RH and subsequent full drying: (a,c) flax/epoxy composite and (b,d) flax/polyester composite.

**List of Tables**

Table 1. Sorption parameters of Park's model determined from the water sorption isotherm of flax fibres.

| Park's model | | | | | | $R^2$ | E |
|---|---|---|---|---|---|---|---|
| Constants | $A_L$ | $b_L$ | $k_H$ | $K_a$ | $n_a$ | | |
| Flax fibre | 0.009 | 11 | 0.115 | 0.14 | 10.6 | 0.993 | 4.7 |