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CONSIDERATION OF THE DUAL SCALE OF PORE SIZE IN WICKING – VALIDATION ON CARBON REINFORCEMENTS AND APPLICATION TO THE SWELLING OF BIO-BASED REINFORCEMENTS

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ABSTRACT

In Liquid Composite Moulding (LCM) process, capillary phenomena occur during impregnation of a fibrous reinforcement. Capillary wicking in a fibrous medium is described by the Washburn's equation and then can be modelled through the Darcy's law where the driving force can be described as a capillary pressure. In case of natural fibres, Washburn's model is not sufficient to describe wicking because of water absorption that causes fibre swelling during liquid imbibition. In this study, a new model is proposed, taking into account the effect of fibre swelling at two scales: elementary fibres and yarns. These effects have been modelled and a modified approach of Washburn's theory has been developed to predict capillary wicking in fabric undergoing swelling in liquids.

1 INTRODUCTION

Liquid Composite Moulding (LCM) processes are well-known and low cost processes to manufacture composite parts in automotive industry. Nevertheless, the problem of void formation due to air entrapment during processes is still common and of primary importance. Void minimization in composites manufactured by LCM calls for an improved understanding of local wetting mechanisms to predict void formation in composite parts, and to develop models for fibrous preforms filling.

Moreover, due to environmental impact, the use of natural fibres as reinforcements in composite materials has significantly increased. Natural fibres have interesting mechanical and damping properties, low density, and sustainability. In some cases, *e.g.* flax fibres, the specific modulus is comparable or even higher to glass fibres [1]. However, there are some limitations on natural fibres such as intrinsic hydrophilic character, low thermal stability, large variability of properties in geometry and chemical composition [2]. During LCM process, the hydrophilicity of natural fibre and the hydrophobicity of resin can result in issues of impregnation, inducing a significant amount of voids in the final products [3]. Furthermore, this hydrophilic character also implies moisture sorption. Only few studies focused on capillary rise methods to evaluate the water sensitivity on different fibres such as hemp, flax [4–7]. Those effects have to be considered to allow manufacturing of bio-based composites with no porosity and an adequate fibre volume fraction by LCM processes.

Fibrous reinforcements are porous media, and they can be ideally considered as a capillary tube network. Hence, wicking in those media can be described by the Washburn's theory [8], where the medium porosity is considered as constant, *e.g.* with synthetic fabrics, during wicking. However, it is not the case for natural fibres because the fibres swell during wicking, especially with polar liquids, leading to change in medium porosity. Therefore, the swelling of natural fibres should be taken into account during wicking to adapt the Washburn's equation.

Medium porosity is defined as spaces between fibres. Depending on scales, such spaces can be considered as between tows, yarns, fibre bundles, and elementary fibres [3,9,10]. The aim of the present work is to predict capillary wicking in natural fibres undergoing swelling. The effects on

wicking were evaluated at two scales: elementary fibres and yarns. Wicking tests were carried out with tensiometer in the warp direction of quasi-unidirectional carbon and flax fabrics. Wicking parameters determined in carbon fabrics were used as reference for predicting wicking parameters in flax fibres. Moreover, the swelling behaviour of flax fibres in water were characterized at both scales, *e.g.* elementary fibres and yarns, as input information to evaluate a new model of wicking.

2 THEORY

The spontaneous impregnation of fibrous reinforcements inserted in a cylindrical sample holder of radius R , by a liquid (wicking) can be described through the modified Washburn's equation [11]:

$$m^2(t) = \left[\frac{(c\bar{r})\varepsilon^2(\pi R^2)^2}{2} \right] \frac{\rho^2 \gamma_L \cos \theta_a}{\eta} t \quad (1)$$

where c is a parameter taking into account tortuosity, \bar{r} is a mean porous radius, ε the porosity is $1-V_f$ (V_f the fibre volume fraction, so the porosity is defined as the space between yarns and elementary fibres). The squared-brackets term is related to both morphology and configuration of the porous medium. The other parameters express the effect of interactions between liquid and fabric during wicking (through ρ , η , and γ_L that are respectively the density, viscosity, and surface tension of liquid, and an apparent advancing contact angle θ_a).

Assuming that tortuosity is not affected by liquid, the assumption for dual scale capillary radius is described in Eq. 2.

$$c\bar{r}_{ini} = c \left((1 - \phi_{yarn})\bar{R} + \phi_{yarn}\bar{r}' \right) \quad (2)$$

where \bar{R} is the largest mean radius (between yarns – Fig. 1), and \bar{r}' is the smallest mean capillary radius (between elementary fibres – Fig. 1). ϕ_{yarn} is thus the surface ratio of yarns for a section of the composite.

Considering the two different swelling rates of the elementary fibre (a) and the yarn (b) both estimated experimentally, Eq. 3 and Eq. 4 can be written to describe the evolution of the mean pore radius over time t .

$$c\bar{r}(t) = c \left((1 - \phi_{yarn})(\bar{R} - bt) + \phi_{yarn}(\bar{r}' - at) \right) \quad (3)$$

$$c\bar{r}(t) = c\bar{r}_{ini} - ct \left((1 - \phi_{yarn})b + \phi_{yarn}a \right) \quad (4)$$

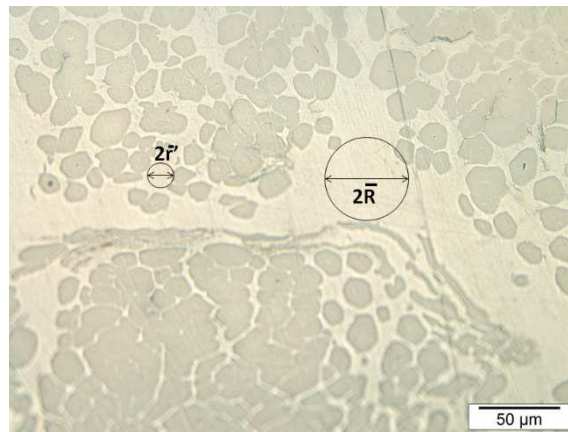


Figure1. Representation of the two-scale pore radii in an epoxy based composite reinforced by flax quasi-UD fabrics.

3 MATERIALS AND METHODS

Experiments were designed to investigate the capillary effects coupled with swelling during wicking of water in flax fabrics. Wicking test was first performed at the macro-scale of fabrics, with carbon fabrics in the warp direction and then with flax fabrics in the same direction. Swelling tests were then carried out at the micro-scale on yarns and elementary fibres.

3.1 Materials

Test reinforcements are quasi-unidirectional fabrics of carbon and flax. Carbon fabrics were provided by Hexcel with commercial designation 48580[®]. The fabrics contain 3% of glass yarns in volume, have areal weight of 541 g/m² and density of 1.8 g/cm³. Flax fabrics were supplied by Libeco with material code FLAXDRY UD 180[®]. Their areal weight and density are 180 g/m² and 1.45 g/cm³, respectively.

The cylindrical tube in which fibres were placed is made of poly(methyl methacrylate) polymer, it has an inner radius of 6 mm and a minimal height of 20 mm. The tube was cleaned with sulfochromic acid (50% of a saturated solution of potassium dichromate and 50% of concentrated sulfuric acid), rinsed with water and dried at ambient condition before testing.

N-hexane and distilled water were selected as reference liquids for this study. N-hexane is a totally wetting liquid, meaning that the advancing contact angle is supposed to be zero. This chemical is suitable for determination of initial non-swollen geometric parameter of the fibrous medium ($c\bar{r}$). Distilled water was used to determine the apparent advancing contact angle θ_a , and was also used for swelling tests on elementary fibres and yarns.

3.2 Methods

3.2.1. Wicking tests

The details of procedure was well described in the previous works [11,12]. Briefly, the amount of carbon and flax fabrics were determined to get a global 60% fibre volume fraction. These fabrics were then cut, rolled, and inserted into the cylindrical tube. Capillary wicking was performed with a tensiometer (DCAT11, DataPhysics Instrument GmbH, Filderstadt, Germany). The tube was clamped to the tensiometer and the vessel with test liquid moved with a speed of 0.5 mm/s up to the detection of the holder. The holder is linked to an electronic microbalance with a resolution of 10 μ g. The data was then recorded with the square of mass gain as a function of time.

3.2.2. Tomography

In order to evaluate the fabric internal structure in 3D, nanofocus X-ray computed tomography (nano-CT) was used. Measurements were performed with a Phoenix NanoTom S (GE Measurements and Control solutions, Wunstorf, Germany). The device was equipped with a tungsten target and the applied voltage and current were 100 kV and 100 μ A. After scanning, 3D images were reconstructed from the radiographs using Phoenix datos | x 2.5 reconstruction software. With an image analysis software – ImageJ –, the images were analysed to yield the pore volume percentage. Two flax fabrics were studied: dry condition and saturated wetting with water (Figure 2).

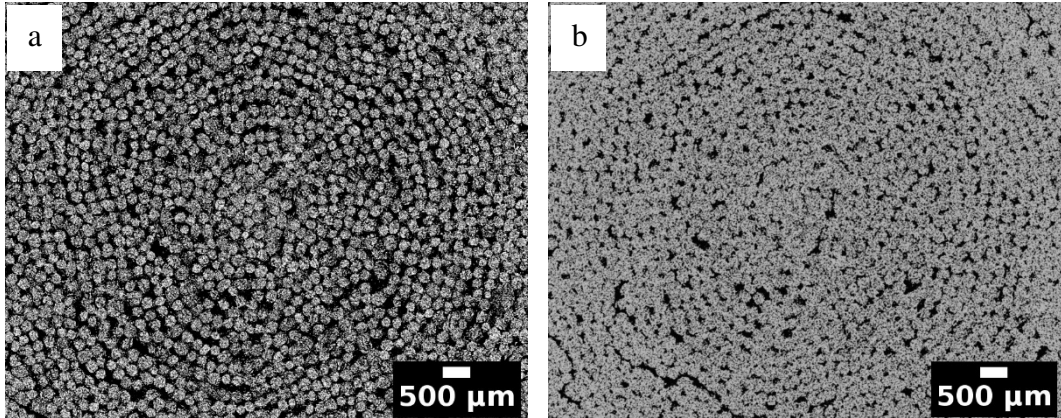


Figure 2. Nano-CT cross-sectional images of flax fibres within the cylindrical tube before (a) and after (b) swelling in water.

3.2.3. Swelling tests: optical method

In order to determine the swelling rate of flax fibres, *i.e.* elementary fibres and yarns, an optical microscopy (Laborlux 11 POLS, Leitz, Germany) equipped with a mon-CDD Leica DFC420 digital camera (resolution $1,728 \times 1,296$ pixels) and an image acquisition software Archimed® (Microvision Instruments, France) was used. Elementary fibres (extracted from yarns in dry condition) and yarns were positioned in a container made of two glass plates separated with double-sided tape. Distilled water was introduced by capillary forces between the two plates until the water filled the container and fibre swelling phenomenon occurred. The space between the two plates was sufficient for the fibres to freely float in water. Thanks to the camera, four to six images per second were recorded from the time of water introduction, until fibres reached a stabilized state of swelling. The ImageJ software was used to measure fibre diameter changing over time (assuming a circular section). Because diameter of elementary fibres and yarns vary along their length and largely change from one to another, diameters were measured at least five different positions (Fig. 3 and Fig. 4). It should be pointed out that in the case of flax yarns, diameter measurements were made more difficult due to fibrillation as seen in Fig. 4.

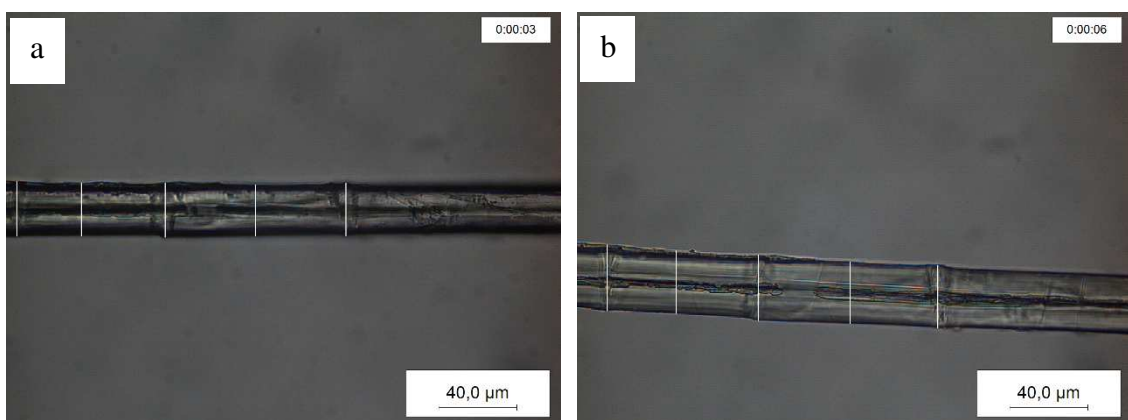


Figure 3. Optical measurements of diameters for an elementary flax fibre before (a) and after (b) swelling in distilled water.

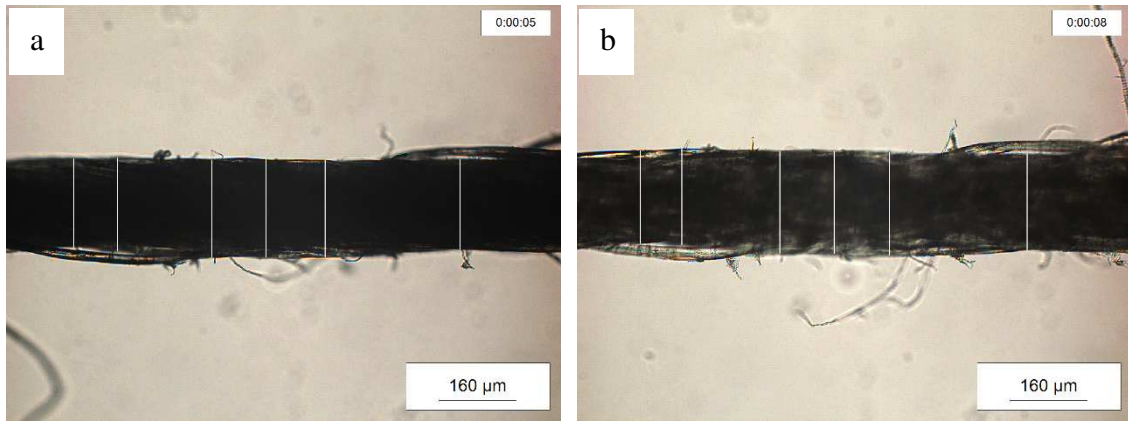


Figure 4. Optical measurements of diameters for a flax yarn before (a) and after (b) swelling in distilled water.

4 RESULTS AND DISCUSSION

4.1. Wicking in carbon fabrics

In order to obtain the geometric product $c\bar{r}$ in Eq. 1, at least five tests were carried out with n-Hexane on carbon fabrics at 60% fibre volume fraction, following the procedure detailed in Section 3.2.1. The evolution of square of mass gain as a function of time was monitored, as presented in Fig. 5a. The linearity confirms the validity of Washburn's equation with the totally wetting liquid for carbon fabrics. The equilibrium weight in this study at 60% V_f is lower than the one in the previous study at 40% V_f [11]. This is logical since the mass of liquid gaining inside the sample holder decreases with the void space available. The mean result of geometric product $c\bar{r}$ was calculated as $2.34 \pm 0.35 \mu\text{m}$.

In order to determine an apparent advancing contact angle θ_a , similar tests were performed with distilled water. The results of capillary wicking in water are presented in Fig. 5b. The linear slope was also observed and hence the Washburn's equation was applied. The advancing contact angle is calculated based on both the slope of the linear fit and the geometric product determined earlier. The mean value was obtained at $55.4^\circ \pm 3.8^\circ$.

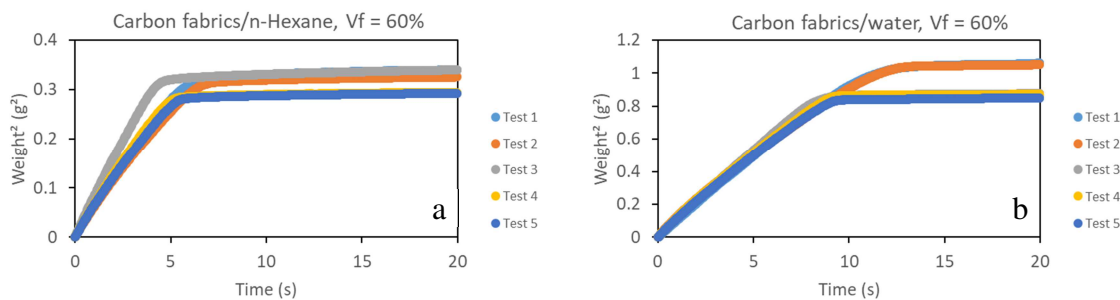


Figure 5. Wicking curves in warp direction of carbon fabrics with n-Hexane (a) and distilled water (b) at 60% fibre volume fraction.

4.2. Wicking in flax fabrics

Using a similar method to carbon fabrics, the geometric product $c\bar{r}$ was determined with capillary wicking of flax fibres with n-Hexane. Fig. 6a shows the results of wicking curves for five different

samples. The linearity was also observed, confirming the validity of Washburn's concept. A mean $c\bar{r}$ of $3.77 \pm 0.37 \mu\text{m}$ was obtained.

Regarding capillary wicking with water, the linearity only took place at the onset, for a few seconds, and then non-linear trends were observed with a large variation (Fig. 6b). In natural fibres, their chemical composition and diameter varying along their length lead to complex tortuosity of pore between the fibres (in both yarns and elementary fibres), influencing the capillary wicking behaviour [4,10,11]. As explained in the previous work [10], the swelling of flax fibres during wicking causes an increase of fibre volume fraction within the cylindrical tube, hence a decrease of porosity, and of the mean pore radius \bar{r} . As a result, the equilibrium weight is slowly achieved. It should be pointed out that the equilibrium weight could also be influenced by water sorption within the flax fibre cell walls.

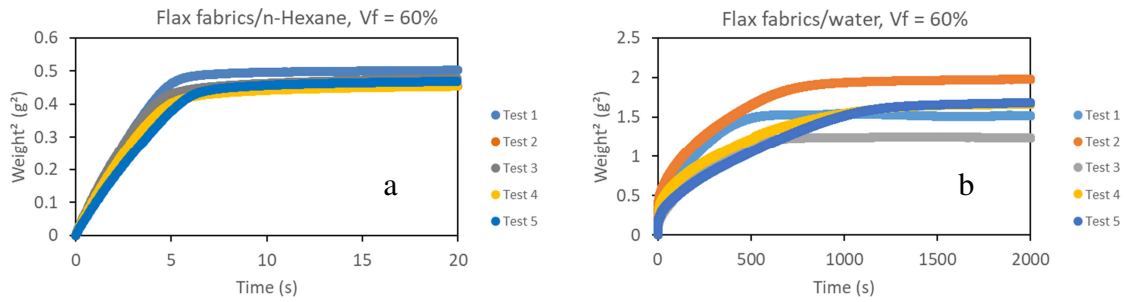


Figure 6. Wicking curves in warp direction of flax fabrics with n-Hexane (a) and distilled water (b) at 60% fibre volume fraction.

4.3. Swelling measurements

Φ_{yarn} is considered as the surface ratio of yarns in the scale of composites, taking into account the largest mean radius between yarns \bar{R} and the smallest mean capillary radius between the elementary fibres \bar{r}^f . Based on the images in dry condition of flax fabrics obtained by nano-CT scan (Fig. 2a), the Φ_{yarn} was determined at 0.75.

As mentioned earlier, the elementary flax fibre and yarn diameter are not uniform. Table 1 shows an example of diameter distribution for an elementary flax fibre and for a yarn before wetting. After wetting of water, fibres have significantly swelled as clearly seen in Fig. 3 and Fig. 4. Thanks to ImageJ software, the diameter changing over time was measured. As a result, the mean swelling rates were found to be approximately $2.72 \mu\text{m/s}$ for an elementary fibre, and $5.18 \mu\text{m/s}$ for a yarn.

Table 1. The diameter distribution in an elementary flax fibre (Fig. 3a) and in a flax yarn (Fig. 4a) before wetting.

Samples	Position 1 (μm)	Position 2 (μm)	Position 3 (μm)	Position 4 (μm)	Position 5 (μm)	Position 6 (μm)
<i>Elementary fibre</i>	28.40	27.24	27.98	26.09	27.12	-
<i>Yarn</i>	181.93	188.21	200.33	201.65	200.33	185.62

4.4. Comparison between experiment and model

Capillary wicking is well described by conventional Washburn's equation. However, changes in the porous medium during wicking in case of natural fibres require a modification of the equation. Therefore, a new model proposed in Section 2 was applied to fit experimental data.

It is important to note that θ_a has been changed to fit the experimental data. As observed in Fig. 7, the trend was proved to fit the experimental data and hence the advancing contact angle was identified to the value of 53° . This value is closed to the one identified by the conventional technique on carbon fabrics at the same fibre volume fraction.

Moreover, the model is fitting well at the first two seconds of wicking. It has been shown in the previous work [10] that the effect of swelling is more significant at high fibre volume fraction. The model from previous work was fitting results at a V_f of 40% for four seconds, and was unable to fit data at a V_f of 60%. The present model fits data at 40% for six seconds and is able to predict the mass gain at 60% for two seconds.

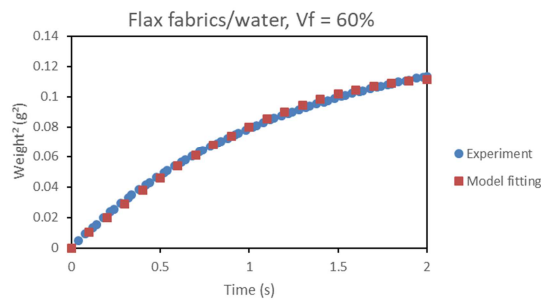


Figure 7. Model fitting of experimental data for flax fabrics with water at 60% fibre volume fraction.

5 CONCLUSIONS

Capillary wicking in natural fibres is important for LCM process. An experimental methodology was developed to evaluate capillary rise, taking into account the swelling of natural fibres. In the present work, such swelling was studied at two scales: elementary fibres and yarns. Wicking tests were performed on quasi-unidirectional carbon and flax fabrics. Carbon showed a linear trend following the Washburn's equation, while a non-linear trend was observed with flax fabrics. The capillary parameters obtained in carbon were used as reference inputs to evaluate a new model developed for wicking in flax fabrics. The model was shown to fit very accurately experimental data at the first two seconds, which is quite a short duration. A numerical implementation of this model allows to take into account the differential swelling of fibres depending on the time they were immersed in water. Fibres at the bottom of the sample tend to swell before the ones at the middle. This effect is, for now, not included in the model and can extend drastically its domain of validity.

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