# Capillary wicking in flax fabrics - Effects of swelling in water

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In this study, wicking in flax fabrics was investigated through an experimental method coupled with Washburn theory. This method was previously shown effective for carbon fabrics (Pucci et al. [21]) to determine morphological characteristics and apparent advancing contact angles. For natural fibers, Washburn equation is not sufficient to describe wicking because of moisture sorption that causes fiber swelling during liquid imbibition. Some flax fabrics were submitted to a thermal treatment known to modify fibers chemistry. Wicking tests with water were performed on both fabrics at different fiber volume ratios. It was observed that wicking trend is very different for these two types of reinforcements: treated fabrics show typical linear trends described by Washburn equation, while untreated flax fabrics lose linearity during wicking. Sorption tests performed on elementary fibers proved that swelling is less significant for treated flax fibers. A model was proposed and was shown to describe properly wicking in natural fabrics undergoing swelling.

## 1. Introduction

Natural fibers are more and more considered as reinforcements in composite materials, but their chemical composition and morphology induce more complexities compared with synthetic fibers for manufacturing and durability of composite preforms [1–4]. It is well-known that many natural fibers have a hydrophilic character [5], making them difficult to wet with hydrophobic resins commonly used for Liquid Composite Moulding (LCM) processes. Moreover this hydrophilic character implies moisture sorption, decreasing mechanical performance. In literature, several studies focus on the kinetics of water sorption in different types of natural fibers, and propose some chemical treatments allowing to reduce those effects, but which can affect drastically the fiber mechanical properties [6–10]. Other few studies focus also on some capillary rise methods in order to evaluate the water uptake, but they only consider wicking in fiber plant straw fractions [11,12] or single technical fibers and bundles [13–15]. Those effects have to be

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considered to allow manufacturing of bio-based composites with no porosity and an adequate fiber volume fraction by LCM processes.

Generally wicking flow in a porous medium, and also in fiber arrangements, can be described by the Washburn theory [16], but it was proved that the conventional equation cannot describe wicking for natural fibers absorbing water [17–19]. Wicking depends on both the morphology of the porous medium (porosity $\epsilon$, tortuosity $\tau$...) and the interactions between the medium and the liquid (liquid surface tension $\gamma_L$ and an apparent advancing contact angle $\theta_a$) [20]. As natural fibers are sensitive to moisture sorption, they swell during wicking in water, causing changes in medium porosity, while the Washburn equation is verified when the morphology remains constant during wicking. Porosity is here referred to as spaces between fibers and tows, to be consistent with experimental methods based on the Washburn theory applied to synthetic fabrics [21], in order to determine some morphological parameters of fabrics porous media and wetting interactions. More precisely, a geometric product ($c\bar{r}$) taking into account the tortuosity and a mean porous radius and an apparent advancing contact angle ($\theta_a$) can be estimated. This method, which keeps the sample volume constant thanks to a sample holder with fixed dimensions [21], turns out to be relevant for the estimation of capillary parameters (such as capillary pressure $P_{cap}$) influencing resin flow during LCM processes for orthotropic fabrics. Those capillary parameters will be used in numerical models in order to predict accurately voids formation [22–24]. It is one aim for studying the spontaneous impregnation of fabrics [25–27]. In this field, works concerning natural reinforcements coupled with the phenomenon of fibers swelling are rare and focus on change in the permeability $K$ of porous media due to liquid sorption [28–30].

The main contribution of the present work is the prediction of capillary wicking in natural fiber fabrics undergoing swelling. A thermal treatment [31] that modifies surface chemistry making flax fibers more hydrophobic was applied here to fabrics. The effects on wicking were evaluated at the macro-scale of reinforcements. Wicking tests were then carried out in the warp direction of quasi-unidirectional untreated and treated fabrics at different fiber volume ratios thanks to a tensiometer, allowing to record the liquid mass as a function of wicking time. Results of experimental tests show a good accordance with the Washburn analytical model for treated fabrics, allowing to estimate both morphological characteristics of porous media and values of the apparent advancing contact angle $\theta_a$. For untreated flax fabrics, the typical Washburn trend was not found. Tests of swelling in water were then also performed for untreated and treated elementary fibers in order to evaluate swelling, and a model of wicking in a porous medium undergoing swelling was developed.

## 2. Theory

In this section the conventional Washburn equation formulated for fabrics is presented. During wicking with water for flax reinforcements, it is also necessary to include the effect of swelling. A semi-empirical model taking into account this phenomenon is then proposed. The change of fabric microstructure, particularly the diminution of both mean pore radius and porosity during wicking, were considered.

### 2.1. Washburn equation for fabrics

The Washburn equation describes capillary rise of a liquid in a tube, and by extension into a porous medium [16]. Eq.(1) defines the flow front position of a liquid over time $h(t)$ into a porous material packed in a column assuming a mean capillary radius referred to as $\bar{r}$, and a factor $c$ inversely related to the tortuous path of liquid in the equivalent capillary tube arrangement [21].

$$h^2(t) = \left[\frac{(c\bar{r})}{2}\right] \frac{\gamma_L \cos\theta_a}{\eta} t \tag{1}$$

$\theta_a$ is the apparent advancing contact angle, $\gamma_L$ and $\eta$ are respectively the liquid surface tension and viscosity.

This equation can be rearranged as a function of the squared mass gain in a cylindrical sample holder filled with a porous medium:

$$m^2(t) = \underbrace{\left[\frac{(c\bar{r})\epsilon^2(\pi R^2)^2}{2}\right]}_{C} \frac{\rho^2 \gamma_L \cos\theta_a}{\eta} t = C \frac{\rho^2 \gamma_L \cos\theta_a}{\eta} t \tag{2}$$

where $\epsilon$ is the relative porosity, $R$ the inner radius of the sample holder and $C$ a constant known as "geometric porous medium factor". It was proved that this equation fits experimental curves for synthetic fabrics [21].

### 2.2. Swelling model

During wicking in water, flax fibers swell under the effect of moisture sorption and then swelling has to be included in the Washburn equation describing capillary wicking. Swelling of fibers implies that the geometric product $c\bar{r}$ and the porosity $\epsilon$ in Eq.(2) are not constant and their variation has then to be expressed. Pores in the present study exclude lumens and only consider the spaces between fibers and tows. Indeed in first approach, lumens volume is considered as negligible compared to the volume between fibers and tows at the scale of fabrics. Swelling in water should cause a decrease over time of both porosity $\epsilon(t)$ and mean capillary radius $\bar{r}(t)$ since the sample volume is set by the sample holder [21]. The mean pore radius modification is mainly due to individual fibers swelling since the present study considers wicking in the warp direction of quasi-unidirectional fabrics. In this section we propose a semi-empirical model in which we express the variation of porosity against the geometric product, neglecting the modification of tortuosity.

#### 2.2.1. Empirical relationship of porosity modification

Modification of porosity $\epsilon(t)$ is related to the variation of the geometric product $c\bar{r}(t)$. In order to take into account this correlation in a model, it is here proposed to link both parameters through a linear relationship (Eq. (3)):

$$\epsilon(t) = \epsilon_{ini} + b\Delta(c\bar{r}) = \epsilon_{ini} + b\left[(c\bar{r})(t) - (c\bar{r})_{ini}\right] \tag{3}$$

where $\epsilon_{ini}$ and $(c\bar{r})_{ini}$ are respectively the porosity and the geometric product of the porous medium before wicking. Parameter $b$ is a coefficient describing how porosity changes along with the geometric product $c\bar{r}$. This relationship was verified experimentally, and coefficient $b$ was identified in Section 4.4. However with this preliminary assumption, the change of geometric product over time $c\bar{r}(t)$ has to be defined during wicking.

#### 2.2.2. Pore radius diminution

During wicking of water, the pore radius of natural fabric decreases because of swelling [28]. In literature, a linear change of this parameter over time was assumed [17–19]. Neglecting the effect of tortuosity, it is here considered that the geometric product varies also linearly over time from the initial value $(c\bar{r})_{ini}$ (determined experimentally through the Washburn equation) to a final lower value $(c\bar{r})_{fin}$. With a classical calculation of the pore radius based on a triangular packing of fibers, it is possible to define a relationship to identify the lower bound $(c\bar{r})_{fin}$:

$$(c\bar{r})_{ini} = G(c\bar{r})_{fin} \tag{4}$$

where $G$ is a parameter deriving from the hypothesis of triangular arrangement of fibers. It is expressed as follows:

$$G = \frac{\frac{R_{f,ini}}{\sqrt{2}}\sqrt{\frac{\epsilon_{ini}}{1-\epsilon_{ini}}}}{\frac{R_{f,fin}}{\sqrt{2}}\sqrt{\frac{\epsilon_{fin}}{1-\epsilon_{fin}}}} \tag{5}$$

where $R_{f,ini}$ refers to the initial radius of fibers and $R_{f,fin}$ to the maximal radius after swelling. It is important to note that if $G$ tends to 1, there is no modification of the geometric product and so the conventional Washburn equation still holds. Pore radius modification is assumed to decrease linearly over time from the initial value ($(c\bar{r})_{ini}$) to the one $(c\bar{r})_{fin}$ corresponding to maximal swelling defined by means of the ratio $G$. Eq. (6) describes the relation to calculate $(c\bar{r})$ [17–19]:

$$\text{if}\,(c\bar{r})(t) > (c\bar{r})_{fin} \quad (c\bar{r})(t) = (c\bar{r})_{ini} - at \tag{6}$$

$$\text{else} \quad (c\bar{r})(t) = (c\bar{r})_{fin} \tag{7}$$

where $a$ is the rate of the porous radius changes due to fiber swelling. This parameter have been found around $4\,.\,10^{-5}$ mm/s for some flax fibers in literature [19]. Eq. (7) defines the boundary condition for $c\bar{r}(t)$.

Fig. 1 presents the change in $c\bar{r}(t)$ along time for flax fabric with a fiber volume ratio of 35 %. The initial value $(c\bar{r})_{ini}$ is then determined experimentally (see Section 4.2 for experimental values of $c\bar{r}$).

### 2.2.3. Washburn relation with swelling

Feeding these proposed laws of porosity modification and of pore radius diminution (Sections 2.2.1 and 2.2.2) into the Washburn equation (Eq. (2)), it is possible to predict the loss of linearity due to fiber swelling during capillary wicking (Eq. (8)).

$$m^2(t) = \left[\frac{f(t)(\pi R^2)^2}{2}\right]\frac{\rho^2 \gamma_L \cos\theta_a}{\eta} t \tag{8}$$

$f(t)$ can then be expressed as follows:

$$\text{if}\,(c\bar{r})(t) > (c\bar{r})_{fin} \quad f(t) = [(c\bar{r})_{ini} - at]^3 + [(c\bar{r})_{ini} - at]^2\,[2\epsilon_{ini}b - 2(c\bar{r})_{ini}] + [(c\bar{r})_{ini} - at] \tag{9}$$

$$\text{else} \quad f(t) = (c\bar{r})_{fin}^3 + (c\bar{r})_{fin}^2\,[2\epsilon_{ini}b - 2(c\bar{r})_{ini}] + (c\bar{r})_{fin} \tag{10}$$

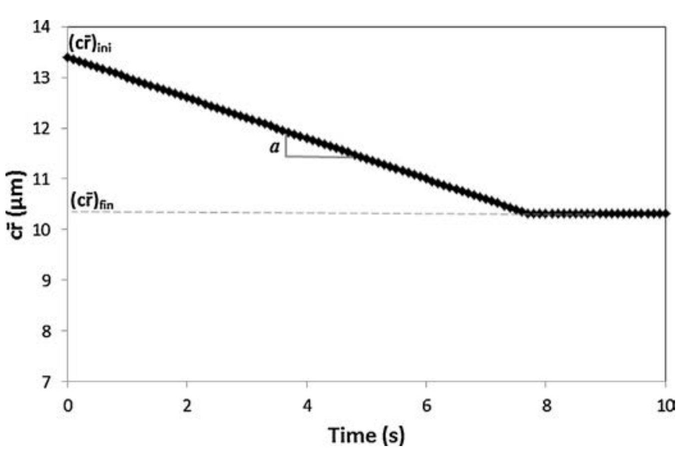


**Fig. 1.** Evolution of $(c\bar{r})$ along time for flax fabrics at $\nu_f = 35\%$.

This model considers two main assumptions. The first assumption is that the mass of liquid absorbed by the fiber can be neglected at the scale of the fabric. The second one is that the entire sample is beginning to swell when the wicking starts. It implies that the time scale for swelling is of the same order of the capillary wicking. It might be more realistic to assume a model involving either or both of two possibilities: (1) there could be a time delay between wetting and swelling; (2) the wetting and swelling happen progressively in the sample, so there are fully swollen and swelling areas throughout the experiment. The present model is a simplification and these approximations have to be tested. This was done in the results section.

## 3. Materials and methods

Tests performed in the present study have been designed to investigate capillary effects coupled with swelling during spontaneous infiltration of water in flax fabrics that were submitted, or not, to a thermal treatment. For this purpose, wicking tests were then carried out at the macro-scale of reinforcements, at three different values of fiber volume ratio ($\nu_f$) in the same fabric main direction. The complementary swelling tests were performed at the micro-scale on both types of elementary fibers.

### 3.1. Materials

#### 3.1.1. Untreated and treated flax fabrics

Tested materials are quasi-unidirectional flax fabrics (Fig. 2a) provided by Libeco (FLAXDRY UD 180®). The areal weight and the fiber specific mass are respectively 180 g/m$^2$ and 1.45 g/cm$^3$. With these woven characteristics, wicking test samples were prepared at three different fiber volume ratios ($\nu_f$ = 30, 35 and 40%) in order to study wicking in the warp direction of fabrics ($x$ in Fig. 2). Procedure to prepare samples used for wicking tests was validated previously for carbon fabrics and detailed in [21].

It is well-known that natural flax fibers have a hydrophilic character that make these reinforcements difficult to wet with mostly dispersive polymer resins [32,33]. A thermal treatment (220 °C for 2 h) in an inert atmosphere that has shown in a previous work [31] to modify the chemical composition and wettability of fiber surfaces, was carried out here on flax fabrics to evaluate its influence on swelling. This thermal treatment has the purpose of degrading the hemicelluloses, partially responsible for the hydrophilic character of flax fibers. In other words, the treatment aims to make fibers more hydrophobic. The free radicals generated by hemicelluloses cracking have been proved to modify pectins [31]. The characterization of surface energy modification is ongoing and will be presented

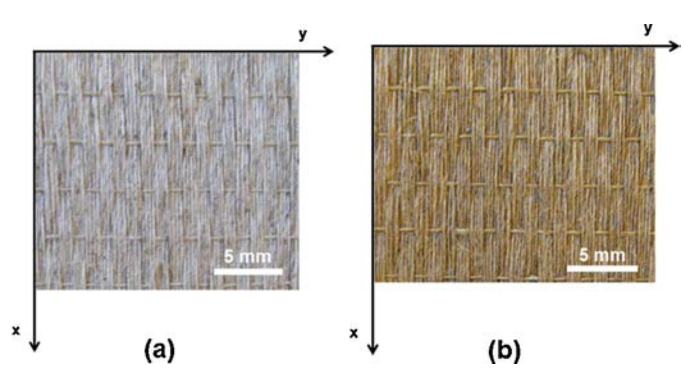


**Fig. 2.** Untreated (a) and treated (b) flax fiber reinforcements.

**Table 1**
Characteristics of test liquids at 20 °C [34].

| | $\eta$ (mPas) | $\rho$ (g/cm$^3$) | $\gamma_L^p$ (mN/m) | $\gamma_L^d$ (mN/m) | $\gamma_L$ (mN/m) |
|---|---|---|---|---|---|
| n-Hexane | 0.32 | 0.659 | 0.0 | 18.4 | 18.4 |
| Water | 1.00 | 0.998 | 51.0 | 21.8 | 72.8 |

in another paper. Flax fabrics after treatment are illustrated in Fig. 2b.

#### 3.1.2. Test liquids

Test liquids were n-Hexane and water. The first one was selected for its low and totally dispersive surface tension, making it suitable for determination of the initial non-swollen geometrical parameters of the fibrous medium ($c\bar{r}$). The second one was used to determine the apparent advancing contact angle and for swelling tests on elementary fibers. Table 1 presents the surface tensions $\gamma_L$, the polar $\gamma_L^p$ and dispersive $\gamma_L^d$ components, density $\rho$ and viscosity $\eta$ of test liquids, as found in literature [34].

### 3.2. Methods

#### 3.2.1. Wicking tests on fabrics

A DCAT11 tensiometer (DataPhysics Instrument GmbH, Fildestardt) was used to perform dynamic tests of capillary wicking on fabrics. This tensiometer is provided with an electronic microbalance (resolution of 10 µg) to which the tested solid is clamped. All tests were carried out under standardised conditions at 20 °C. The sample holder in which fibers were placed consists of a hollow cylinder with an inner radius $R$ of 6 mm and a height $H$ of 20 mm. A piston at the upper end and a screw cap at the lower end of the cylinder ensure compaction of fabrics and no change in the sample volume. It is thus possible to control the global volume fiber ratio $v_f$ from which the relative porosity $\epsilon = 1 - v_f$ can be calculated. A vessel filled with test liquid moves with a speed of 0.5 mm/s up to the detection of the sample holder and the mass gain over time is recorded. More details of sample preparation to perform wicking in $x$-direction and sample holder design were given in a previous work [21].

The conventional Washburn equation (Eq. (2)) can be adopted to fit experimental data of wicking if the square of mass gain recorded during tests has a linear trend. Knowing the linear square mass variation over time $m^2(t)$, the apparent wetting properties of the porous medium are easily derived from Eq. (2). More precisely, the geometric porous medium factor $C$ [$m^5$] and the geometric product $c\bar{r}$ [$m$] are determined using n-Hexane, a totally dispersive liquid for which the apparent advancing contact angle is supposed to be 0 degree. Then the apparent advancing contact angle $\theta_a$ is determined with another liquid. An example of Washburn linear fit obtained for flax fabrics at $v_f = 35\%$ with n-Hexane is shown in Fig. 3. With this dispersive liquid, the capillary rise is very quick and linearity is well achieved. Then the curve reaches an asymptotic equilibrium, given by the height of the sample itself. The equilibrium weight is due to the saturation of the porous medium by the test liquid. This test allows to obtain the morphological parameters of the porous reinforcement when it does not swell. It is thus possible to determine the geometric product $(c\bar{r})_{ini}$.

#### 3.2.2. Swelling tests on elementary flax fibers

Natural fibers are known to be sensitive to water sorption and swelling can affect significantly the measurement of mass gain during wicking. This is due to changes in morphology of the porous medium (porosity $\epsilon$ and geometric product ($c\bar{r}$)). However, modifying the wetting properties of flax fibers through a

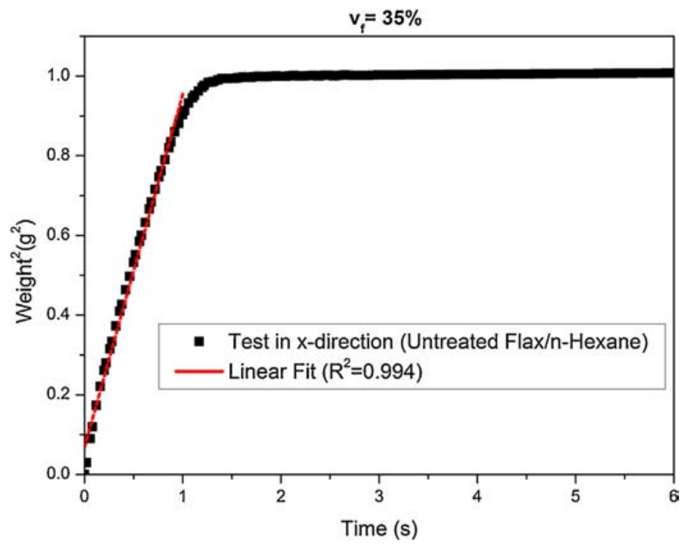


**Fig. 3.** Linear fit of a wicking test for flax fabrics at $v_f = 35\%$ with n-Hexane.

thermal treatment [31] might also have an effect on liquid sorption. In order to quantify those effects, swelling tests were carried out on untreated and treated elementary flax fibers. The experimental procedure used here is very similar to the one used by Nguyen et al. [35]. Fifteen elementary flax fibers were extracted from both treated and untreated yarns in dry conditions and maintained between two thin glass plates. A water drop was then instilled between plates and the liquid spreading along the fiber was observed with an optical microscope. The pixel size of pictures analyzed with this method is of 0.15 µm. The error associated to the methodology is assumed to be negligible compared to the variability of flax fiber diameter. Swelling was very quick for those fibers (around 5 s). Change in fiber diameter during sorption was measured through image analysis with the ImageJ software, as shown in Fig. 4. As the diameter of flax fibers is commonly largely variable, from a fiber to another but also along the same fiber [36], three measurements were performed for each fiber at the dry state and repeated in the wet state at the same position of fiber. The same distance from the edges of the picture along the fiber was considered and measurements were made perpendicularly to fiber axis. Therefore a "swelling ratio" $R_{sw}$ was calculated as:

$$R_{sw} = \frac{D_{f,fin}}{D_{f,ini}} \tag{11}$$

where $D_{f,ini}$ is the average fiber diameter (over three measurements) in dry conditions and $D_{f,fin}$ the average diameter after swelling.

## 4. Results and discussion

### 4.1. Determination of geometric factors at different fiber volume ratios

In order to obtain a value of capillary pressure $P_{cap}$ for flax fabrics in $x$-direction [21], the first parameter that has to be determined is the geometric product $c\bar{r}$. This product derives from the conventional Washburn equation that should fit linearly the experimental curves $m^2(t)$ (Eq. (2)). Therefore, to determine the geometric factor, five tests were carried out with n-Hexane on both untreated and treated flax fabrics at three different fiber volume ratios: 30%, 35% and 40%, following the procedure detailed in Section 3.2.1. Fig. 5 presents the square of mass gain versus time obtained for

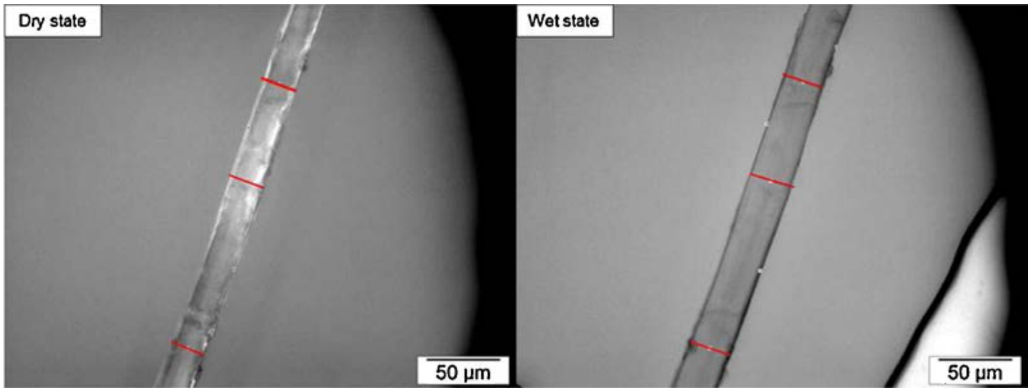


**Fig. 4.** Optical measurements of flax fiber diameter before and after water spreading.

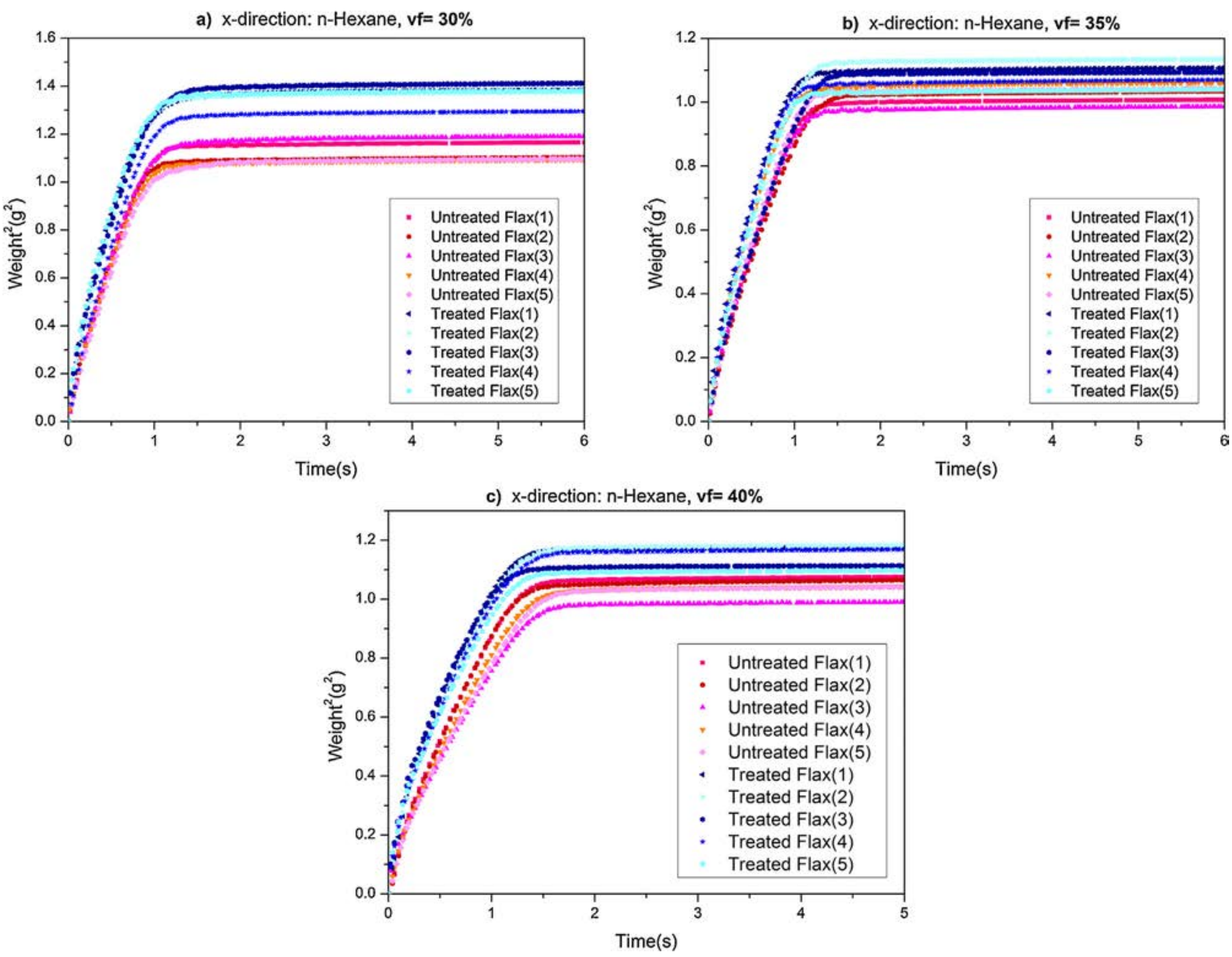


**Fig. 5.** Wicking curves in *x*-direction with n-Hexane for untreated and treated flax fabrics at different fiber volume ratios.

all tests. Capillary wicking up to the top of the sample holder was very quick (<2*s*) with the totally wetting liquid, at all three different fiber volume ratios of fabrics. Linearity was also observed for all experimental curves. This confirms the validity of the conventional Washburn equation for both types of woven fabrics (untreated and treated flax) with n-Hexane. Values of the geometric factor $c\bar{r}$ at the three different fiber volume ratios (30%, 35% and 40%) were then measured. It can be observed that the equilibrium weight is lower when the fiber volume ratio is higher. It was expected because the tensiometer measures the mass of liquid in the sample holder, that decreases if the void space is lower. The slight dispersion observed in equilibrium weight between the five tests in the same configuration is not an issue for our measurements, since only the slopes of the linear fit are relevant for calculation of geometric parameters.

Table 2 summarises the results of linear fitting with the correlation coefficient ($R^2$), and subsequently the determined geometric product $c\bar{r}$, for each test. Table 3 presents the mean results at different $v_f$ and for each type of reinforcements. One can verify

**Table 2**
Results of wicking tests in *x*-direction with n-Hexane at different fiber volume ratios.

| | $v_f = 30\%$ | | | $v_f = 35\%$ | | | $v_f = 40\%$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $m^2/t$ ($g^2/s$) | $R^2$ | $c\bar{r}$ (μm) | $m^2/t$ ($g^2/s$) | $R^2$ | $c\bar{r}$ (μm) | $m^2/t$ ($g^2/s$) | $R^2$ | $c\bar{r}$ (μm) |
| Untreated 1 | 1.181 | 0.996 | 14.5 | 0.927 | 0.994 | 13.1 | 0.810 | 0.999 | 13.5 |
| Untreated 2 | 1.218 | 0.995 | 14.9 | 0.852 | 0.995 | 12.1 | 0.827 | 0.999 | 13.8 |
| Untreated 3 | 1.231 | 0.996 | 15.1 | 0.899 | 0.994 | 12.7 | 0.629 | 0.999 | 10.5 |
| Untreated 4 | 1.131 | 0.995 | 13.8 | 1.094 | 0.991 | 15.5 | 0.719 | 0.999 | 12.0 |
| Untreated 5 | 1.080 | 0.996 | 13.2 | 0.960 | 0.994 | 13.6 | 0.682 | 0.999 | 11.3 |
| Treated 1 | 1.517 | 0.992 | 18.5 | 1.058 | 0.990 | 15.0 | 1.007 | 0.987 | 16.8 |
| Treated 2 | 1.432 | 0.994 | 17.5 | 0.998 | 0.994 | 14.1 | 0.935 | 0.990 | 15.6 |
| Treated 3 | 1.401 | 0.991 | 17.1 | 0.880 | 0.995 | 12.5 | 0.938 | 0.983 | 15.6 |
| Treated 4 | 1.330 | 0.997 | 16.3 | 1.062 | 0.992 | 15.1 | 0.899 | 0.989 | 15.0 |
| Treated 5 | 1.476 | 0.989 | 18.1 | 0.986 | 0.992 | 14.0 | 0.805 | 0.985 | 13.4 |

**Table 3**
Average results with standard deviations of calculated geometric factor in *x*-direction of fabrics at different fiber volume ratios.

| | $c\bar{r}$, $v_f$=30% (μm) | $c\bar{r}$, $v_f$=35% (μm) | $c\bar{r}$, $v_f$=40% (μm) |
|---|---|---|---|
| Untreated | 14.3 ± 0.8 | 13.4 ± 1.3 | 12.2 ± 1.4 |
| Treated | 17.5 ± 0.9 | 14.2 ± 1.0 | 15.3 ± 1.3 |

that values in *x*-direction for untreated and treated flax fabrics at $v_f = 40\%$ are of the same order than the ones found for carbon fabrics at the same $v_f$ ($c\bar{r}$ has been estimated at $12.1 \pm 1.5$ μm) [21]. This result shows that the direction of fibers at the macroscale of fabric affects predominantly the value of the geometric product, even if the morphologies of fibers and bundles are different. From Tables 2 and 3 a slight difference can be observed between untreated and treated flax reinforcements, indicating probably a decrease of the mean tortuosity at the scale of fabrics by treatment and/or a modification of fiber diameter. It is known that changes in fiber chemical composition cannot only alter capillary properties, but also the porous structure of natural fibers [15]. These tests can be used to express a relationship between fiber volume ratio $v_f$ (then also porosity $\epsilon = 1 - v_f$) and the geometric product $c\bar{r}$. This relation is important if fibers swell to determine the coefficient *b* from Eq. (3), as explained in Section 2.2.1.

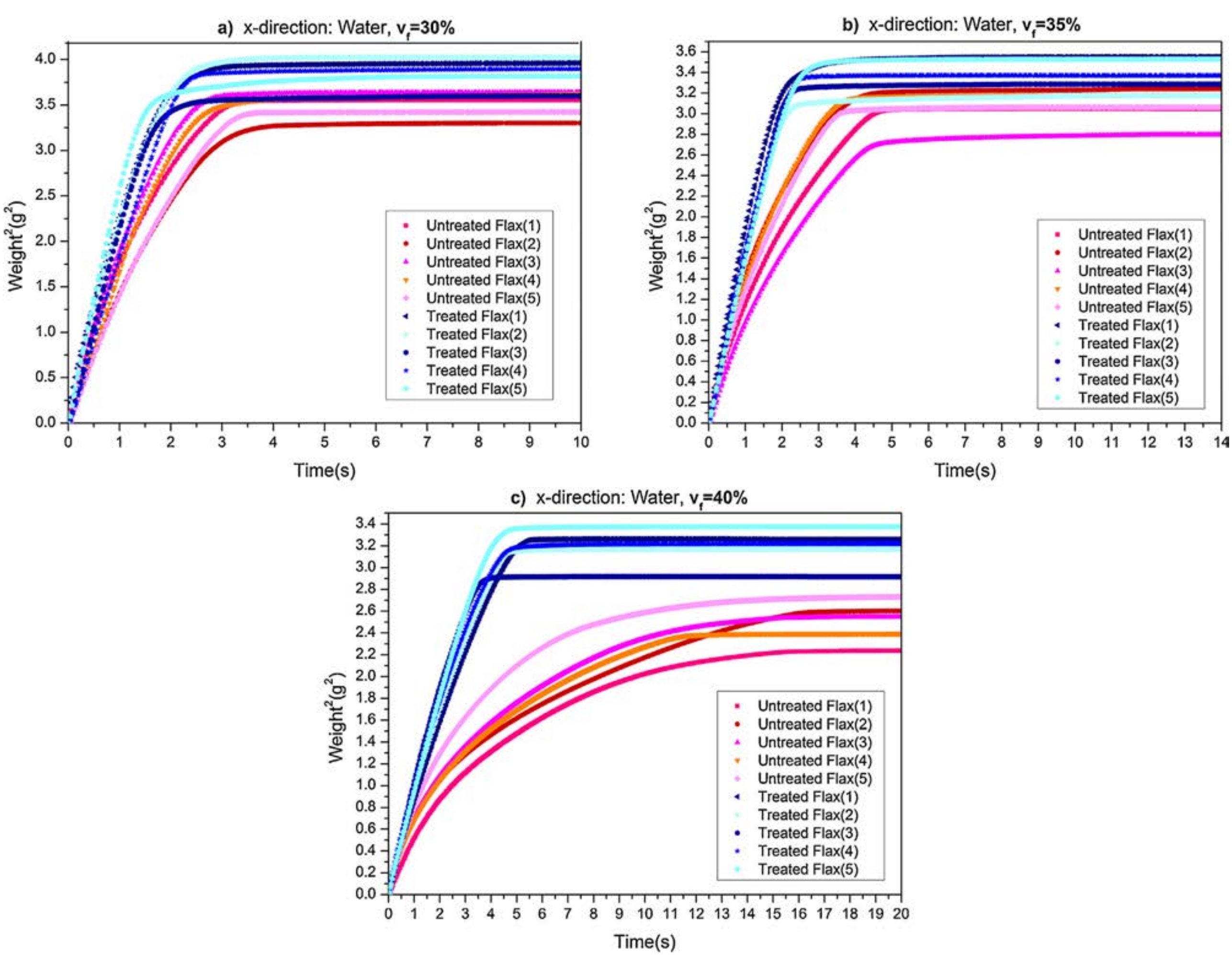


**Fig. 6.** Wicking curves in *x*-direction with water for untreated and treated flax fabrics at different fiber volume ratios.

**Table 4**
Results of wicking tests for treated flax fabrics in $x$-direction with water at different fiber volume ratios.

| | $\upsilon_f = 30\%$ | | | $\upsilon_f = 35\%$ | | | $\upsilon_f = 40\%$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $m^2/t$ ($g^2/s$) | $R^2$ | $\theta_a$ (°) | $m^2/t$ ($g^2/s$) | $R^2$ | $\theta_a$ (°) | $m^2/t$ ($g^2/s$) | $R^2$ | $\theta_a$ (°) |
| Treated 1 | 1.948 | 0.999 | 60.6 | 1.719 | 0.999 | 51.5 | 0.692 | 0.999 | 74.2 |
| Treated 2 | 1.954 | 0.999 | 60.5 | 1.484 | 0.997 | 57.5 | 0.729 | 0.999 | 73.3 |
| Treated 3 | 2.031 | 0.997 | 59.2 | 1.568 | 0.996 | 55.4 | 0.855 | 0.999 | 70.3 |
| Treated 4 | 1.830 | 0.995 | 62.6 | 1.530 | 0.999 | 56.4 | 0.761 | 0.999 | 72.5 |
| Treated 5 | 2.480 | 0.999 | 51.4 | 1.490 | 0.997 | 57.4 | 0.860 | 0.997 | 70.2 |

### 4.2. Determination of apparent advancing contact angles at different $\upsilon_f$

Similar tests, five for each type of fabrics, were then carried out with water for the three fiber volume ratios ($\upsilon_f = 30, 35, 40\%$), in order to determine an apparent advancing contact angle $\theta_a$. This parameter is required to estimate the capillary pressure $P_{cap}$ [21] thanks to the average geometric products $c\bar{r}$ determined earlier (Table 3). In this case, a relevant influence of treatment on flax reinforcements was observed on wicking (Fig. 6). It is clear that the linear fit of curves with the conventional Washburn equation is possible only for treated fabrics. Untreated reinforcements show a different trend. Differences in wicking are due to sensitivity to water that induces swelling in untreated flax fibers, while this effect is not relevant for treated fabrics that were found to be less hydrophilic [31]. As explained earlier, swelling of flax fibers causes an increase of fiber volume ratio (i.e. a decrease of porosity $\epsilon$ and of the mean pore radius $\bar{r}$) during wicking. This modification is not considered in conventional Washburn equation. Moreover, the swelling effect is higher when the fiber volume ratio increases: Fig. 6a–c shows that for untreated flax fabrics the loss of linearity is more significant, and the equilibrium weight is lower than for treated flax. It is also clear that difference between the equilibrium weights reached for untreated and treated fabrics is more significant when $\upsilon_f$ increases. Untreated flax fabrics do not show a linear trend and achieve the equilibrium weight more slowly, that is due to the decrease of pore radius as a result of swelling and the capillary rise rate, according to Washburn theory [16,15]. Those curves, and especially the equilibrium weight, prove that the mass gain due to water in fibers themselves (including both mass absorbed by fibers and liquid that is eventually in lumens) can be neglected compared to the pore radius modification, implying a diminution of the equilibrium weight. It is obvious that treated fibers lead to higher equilibrium weight. Since the morphology is the same and the fiber volume ratio is unchanged, it is reasonable to neglect the mass of water absorbed by untreated flax. To verify if this difference in wicking is actually due to swelling and if the assumption that treated fibers are less sensitive to humidity is valid, tests on elementary fibers were conducted (Section 4.3).

**Table 5**
Average results with standard deviations of calculated apparent advancing contact angle in $x$-direction at different fiber volume ratios.

| | $\theta_a, \upsilon_f = 30\%$ (°) | $\theta_a, \upsilon_f = 35\%$ (°) | $\theta_a, \upsilon_f = 40\%$ (°) |
|---|---|---|---|
| Treated | $58.9 \pm 4.3$ | $55.6 \pm 2.5$ | $72.1 \pm 1.8$ |

Values of $\theta_a$ were determined only for treated fabrics through the linear fit of experimental curves with the conventional Washburn equation (Eq. (2)), and presented in Table 4. It is important to note from Table 5 that values of $\theta_a$ are very similar at $\upsilon_f$ of 30% and 35%, while for a higher fiber compaction ($\upsilon_f = 40\%$) the apparent advancing angle $\theta_a$ increases significantly. The mean value of $\theta_a$ reported in Table 5 is quite similar to the one derived for carbon fabrics ($\theta_a$ was found to be $74.8 \pm 2.3°$ at $\upsilon_f = 40\%$ [21]), showing that effectively treated fabrics seem not to be affected by water sorption.

### 4.3. Measurements of swelling ratio

In order to assess the sensitivity to water sorption, fifteen tests of swelling were carried out on treated and untreated elementary flax fibers as described in Section 3.2.2. Three measurements of diameter were carried out on every fiber, in dry and wet conditions (Fig. 4), and for each fiber the mean swelling ratio was calculated with Eq. (11). Fig. 7 shows the results of swelling tests with water for untreated and treated fibers. The large variability of diameter (typical for elementary flax fibers [35,37]), and the large dispersion in swelling ratio can be clearly observed. However comparison between the two graphs in Fig. 7 shows that the treatment does not affect significantly the fiber morphology since the mean dry diameter of untreated flax was found to be $16.8 \pm 4.7$ μm, and $17.5 \pm 5.9$ μm for the treated ones. This is also consistent with results of wicking with n-Hexane (Fig. 2, Tables 2 and 3). Moreover the swelling of fibers and its dispersion is lower for treated fibers. The mean swelling ratio for untreated fibers is $1.27 \pm 0.13$ vs. $1.11 \pm 0.07$ for treated ones. This confirms that the treatment makes fibers less sensitive to water sorption and the swelling is less meaningful for those fibers. It can thus explain differences of wicking with water in untreated and treated fabrics.

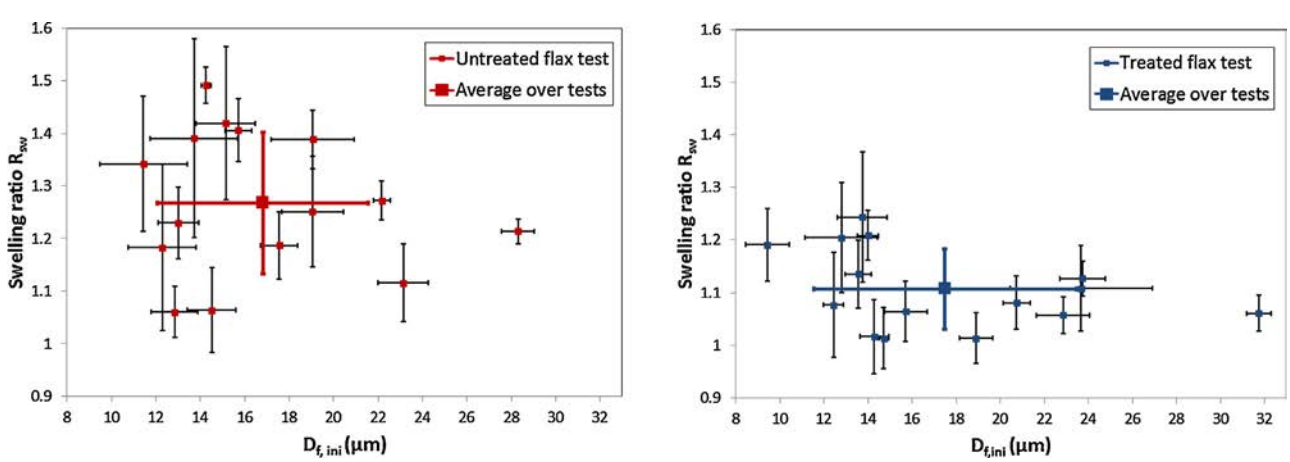


**Fig. 7.** Results of swelling ratio as a function of initial diameter for untreated and treated elementary flax fibers.

### 4.4. Comparison between experiments and model

Swelling of untreated flax fibers in water is sufficiently significant for the wicking curves not to be described by the conventional Washburn equation. The model proposed in Section 2.2 was applied to fit experimental data.

In order to determine how porosity $\epsilon$ varies as a function of the geometric product $c\bar{r}$ for untreated flax reinforcements, results of wicking tests with n-Hexane at the three different $v_f$ were used. More precisely, different values of porosity $\epsilon = 1 - v_f$ and the average results of $c\bar{r}$ in Table 3 for untreated flax fabrics were plotted to determine the coefficient $b$ of Eq. (3) and inserted into the proposed model of swelling (Eqs. (6)–(10)). Fig. 8 shows the plot of data obtained for untreated flax fabrics in Tab.3 and the linear fit to obtain coefficient $b$. Linearity of porosity $\epsilon$ over the geometric product $c\bar{r}$ is well-verified and $b$ was estimated at 0.0475 $\mu m^{-1}$. It is important to note that, as untreated flax fabrics swell during wicking, these values of geometric products have to be considered in the model as initial values, that is to say as $(c\bar{r})_{ini}$ in Eqs. (4) and (6). Moreover, to obtain values of $(c\bar{r})_{fin}$ for each fiber volume ratio, Eq. (4) was used supposing a value of $G = 1.3$, that is to say, in first approach, equivalent to the swelling ratio obtained from Section 4.3, neglecting the modification of tortuosity. Indeed, as a first approximation, if the fibers swell by 30%, the pore radius reduction will be assumed to be also 30%. Finally considering a swelling rate $a$ of $4 . 10^{-4}$ mm/s, it is thus possible to obtain the following fitting of experimental capillary wicking with ongoing swelling of flax fibers in water at the three fiber volume ratios (Fig. 9a–c). It is important to note that to fit those experimental data, only $\theta_a$ has been changed for each value of $v_f$ and of $(c\bar{r})_{ini}$. This tends to prove that it will be possible to identify apparent advancing contact angles with a similar model for porous media undergoing swelling. For $v_f = 40\%$, the advancing contact angle identified is of 75°, which is close to the

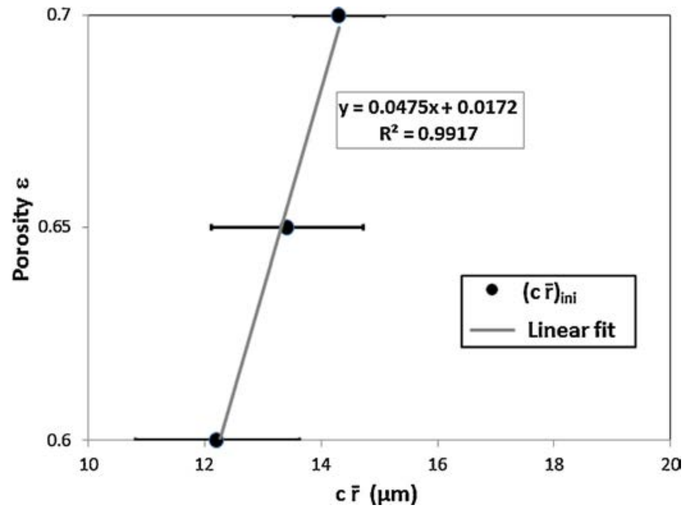


**Fig. 8.** Identification of parameter $b$ for flax fabrics (Eq. (3)).

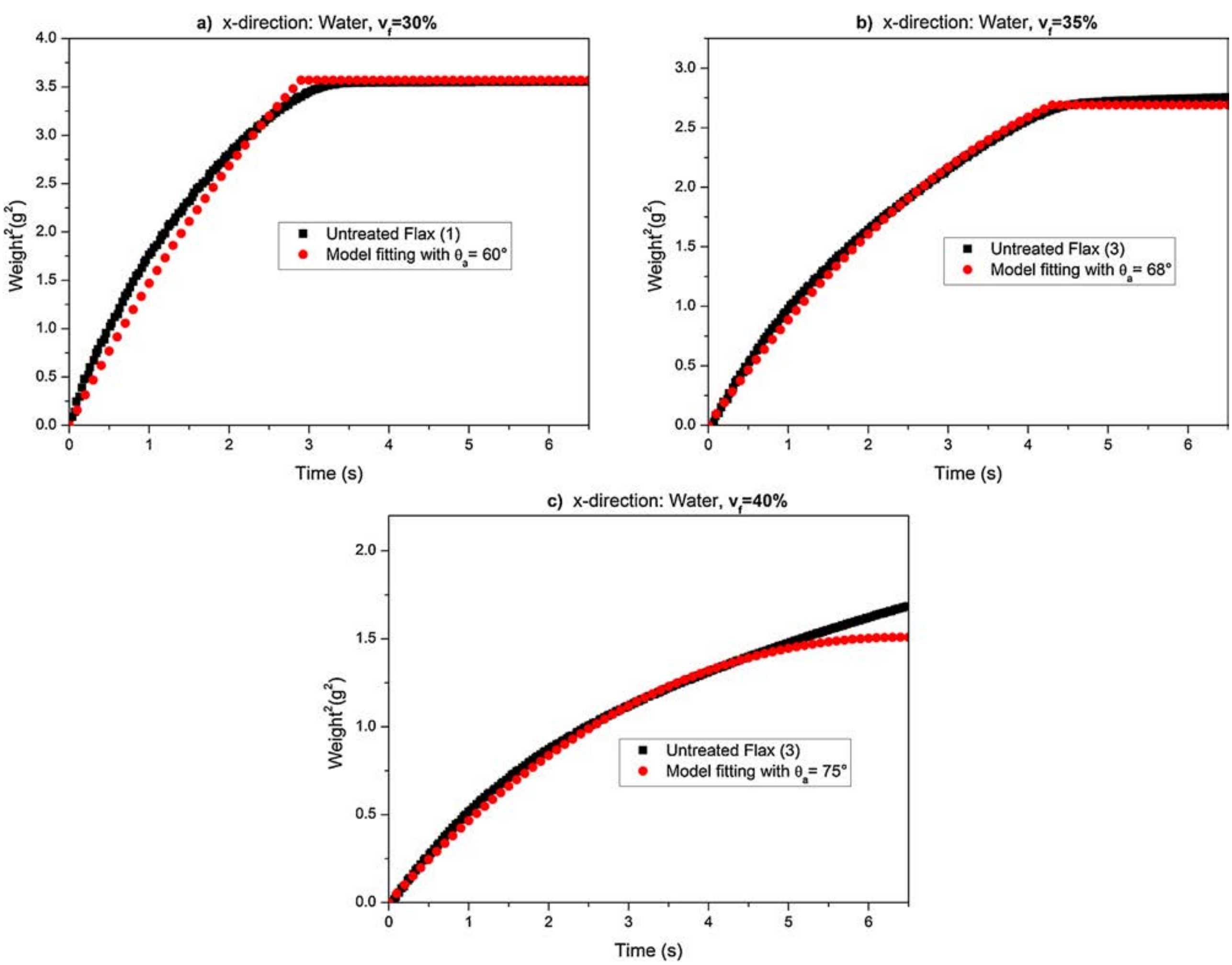


**Fig. 9.** Model fitting of experimental data for untreated flax fabrics with water at different fiber volume ratios.

one identified by the conventional technique on treated flax and on carbon fabrics at the same $v_f$. Fig. 9 shows that fitting of experimental data is good for $v_f = 30\%$ and well achieved for $v_f = 35\%$ with an equivalent advancing contact angle of respectively 60° and 68°, but also for the 5 first seconds of $v_f = 40\%$. We can thus assume that the model proposed here is valid in those conditions and that assumptions seem to be acceptable. At $v_f = 40\%$, as the fitting is very accurate for the 5 first seconds and predict a too drastic diminution of the wicking rate, the assumption considering that the entire sample is swelling from the beginning of wicking can be questioned. An evolution of this model to describe longer times of wicking, taking into account the different assumptions detailed in Section 2.2.2, will be presented in further works.

## 5. Conclusion

The aim of this work was to study wicking in natural flax fabrics, while the fibers undergo swelling. An experimental methodology was applied to natural fiber reinforcements in order to evaluate capillary rise and so the liquid mass gain in fabrics over time. Those methods, validated in previous studies, anticipate that the morphology of the medium remains constant during wicking, and then by means of the conventional Washburn equation, it is possible to determine the wetting properties of medium impregnated by a specific liquid. Flax fibers are sensitive to moisture sorption and the absorption of water causes fibers swelling, and subsequently a variation of porosity. The effects of mass gain with capillary wicking and the swelling of fibers due to water sorption are overlapping. Both phenomena have to be described in order to derive wetting properties of fibrous media.

For untreated flax fabrics, the typical Washburn linear trend was not found. Some tests of swelling in water were also performed on untreated and treated elementary fibers in order to quantify this effect. It was observed that the treatment does not modify significantly the morphology of elementary fibers, but effectively reduces their swelling. The thermal treatment decreases the sensitivity to water sorption of flax fibers. These results at the micro-scale are in agreement with those of wicking at the macro-scale of fabrics. Since the swelling phenomenon is relevant for flax fibers, a model describing wicking including swelling of natural fibers, was proposed. This model relates the modification of pore radius at the micro-scale of fibers to the modification of porosity at the scale of fabrics. This allowed to fit the loss of linearity in wicking of natural flax reinforcements. Evaluation of parameters relevant for capillary pressure estimation was made for treated flax and it has been shown that the model described here is suitable to represent experimental wicking for untreated fabrics. Further works will focus on removing assumptions that are limiting the model in its present form.

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