Swelling of flax fibers: effect of a thermal treatment on their dimensional stability.

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Keywords: Natural fibers, swelling, wettability, Liquid Composite Molding

Abstract
This paper describes how flax fibers were submitted to a thermal treatment to modify their wettability and sensitivity to liquid sorption. The wettability of untreated and treated fibers was obtained by measuring contact angles between the fibers and two test liquids, water and diiodomethane. Contact angle measurements were performed in a tensiometer following a 2-step procedure. Fibers were first wetted by n-Hexane to obtain their wetted lengths. The weight of the meniscii between the test liquids in contact with the fibers were then used to calculate the contact angles via the Wilhelmy equation. However wetted lengths of flax fibers show a large variability which significantly complicates the contact angle analysis. In addition, since flax fibers are sensitive to liquid sorption, their diameters and thus wetted lengths were modified during experiments. In this study, combining an optical and a tensiometric methods, the swelling of fibers and thus the change in their wetted lengths was measured. It was found by both methods that the thermal treatment significantly reduces the swelling of flax fibers in water.

1. Introduction

Capillary phenomenon and wetting between fibers and resins have to be considered to understand and simulate properly the resin flow through porous preforms during LCM processes [1,2]. Flax fibers are usually considered as adequate bio-reinforcements for composites but their hydrophilic character makes them sensitive to moisture sorption and difficult to wet by hydrophobic resins [3].
In this work, a thermal treatment aiming at modifying the surface properties of flax fibers [4] has been applied to enhance their hydrophobicity, and thus ease their impregnation and decrease at the same time their sensitivity to water sorption. The wettability of untreated and treated fibers can be obtained by measuring contact angles between the fibers and two test liquids, water and diiodomethane. Contact angles can be determined via the Wilhelmy relation, once the wetted length and the weight of the menisus formed by the test liquid in contact with the fiber are known. However wetted lengths of flax fibers show a large variability which significantly complicates the contact angle analysis. In addition, since flax fibers are sensitive to liquid sorption, their diameters and thus the wetted lengths can be modified during the experiments [5,6]. This change in morphology has to be considered to evaluate properly the wettability of fibers (more precisely their surface energy and their dispersive and polar components) [7]. In this study, the swelling of fibers and thus the change in their wetted lengths was measured for untreated and treated elementary flax fibers by means of an optical and a tensiometric mehod for water and diiodomethane. Wetted lengths were measured before and after wetting with the test liquids to define their sensitivity to liquid sorption. The wetted lengths obtained after wetting with

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the test liquids have to be considered to derive reliable contact angle values. The results obtained not only illustrate the positive effect (reduced water and diiodomethane uptake) of the treatment on the dimensional stability of flax fibers, but also define a novel methodology to better assess the wettability of flax fibers and thus their surface energy.

2. Materials

2.1. Untreated (UF) and treated (TF) elementary flax fibers

Flax reinforcements were 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. In order to degrade hemicelluloses that are partly responsible for the hydrophilic character of the flax fibers, some fabrics were submitted to a thermal treatment at 220° C for 2h under an inert atmosphere to prevent fibre degradation. The treatment is able to crack hemicelluloses and produces free radicals inducing crosslinking in pectins [3]. Some elementary fibers were then extracted from fabrics to evaluate the wetted length before and after wetting by means of an optical and a tensiometric method.

2.2. Test liquids

Table 1 presents the liquid/vapor surface tensions γ_L , the polar γ_L^p and dispersive γ_L^d surface energy components, density ρ and viscosity η of test liquids used in this study[2]. n-Hexane was used for measurements of wetted lengths before (p_i) and after wetting (p_{sw}). Water and diiodomethane were then used to wet fibers.

Table 1. Characteristics of test liquids at 20°C [7].

	η (mPas)	ρ (g/cm^3)	γ_L^p (mN/m)	γ_L^d (mN/m)	γ_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
Diiodomethane	2.76	3.325	0.0	50.8	50.8

3. Methods

3.1. Optical method for swelling tests

Natural fibers are sensitive to liquid sorption and fiber swelling can affect the measurement of contact angles. Moreover, modifying the wetting character of flax fibers through a thermal treatment might also have an effect on liquid sorption. This has never been evaluated. For these reasons, swelling tests were carried out on untreated and treated flax elementary fibers with water and diiodomethane.

Elementary flax fibers were extracted from treated and untreated fabrics in dry conditions and positioned between two thin glass plates. A water (or diiodomethane) drop was then deposited between the plates and the liquid spreading along the fiber was observed with an optical microscope. Change in fiber diameter during sorption was measured through image analysis with ImageJ (Figure 1) [6] and a swelling ratio R_{sw} was calculated as follow:

$$R_{sw} = \frac{D_f}{D_i} \quad (1)$$

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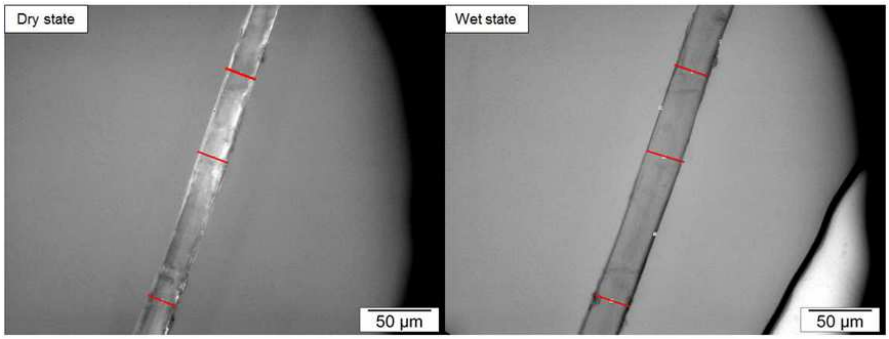

Figure 1. Optical measurements of elementary flax fiber diameter before (dry state) and after (wet state) water spreading.

Fifteen elementary fibers were extracted for each type of yarns (UF and TF) and liquid to test (water and diiodomethane). The experimental procedure is detailed more precisely in our previous work [6].

3.2. Tensiometric method for swelling tests

In order to evaluate reliable differences in wetting and swelling of untreated and treated flax (*UF* and *TF*) reinforcements, an analysis by means of a more accurate tensiometer at the microscale of some elementary fibers is mandatory. A Kruss K100 SF tensiometer with 0.1 µg weight resolution was used to perform wetted length tests on elementary fibers. Details of the procedure used to measure the wetted lengths are given in [7]. The tensiometer consists of a microbalance that measures the meniscus weight m (and then the capillary force F (mN/m)) of a liquid in contact with a fiber. A liquid vessel rises up at a speed of 1 *mm/min* and the fiber is then partially immersed into the liquid. The capillary force measured by the tensiometer is related to the wetted length via the Wilhelmy relation:

$$F = mg = \gamma_L p \cos\theta \tag{2}$$

where g (m/s^2) is the acceleration of gravity, p (m) the wetted length and θ (°) the contact angle. Assuming that n-Hexane is a totally wetting test liquid (θ=0°), the wetted length p can be determined. Sixteen UF elementary fibers and sixteen TF elementary fibers (8 for water and 8 for diiodomethane) were tested before and after wetting to evaluate the change of the fiber perimeter. After the first wetted length test, fibers were dipped into water (or diiodomethane) and the measurement of the wetted length after wetting was repeated. Figure 2 shows data recorded during the wetted length tests before and after wetting in water for an untreated elementary fiber. An average force over the immersion depth can be extrapolated from these data and wetted lengths before (p_i) and after (p_{sw}) wetting can be obtained through Equation 2. In Figure 2, the force recorded after wetting is higher, i. e. the fiber swells in water.

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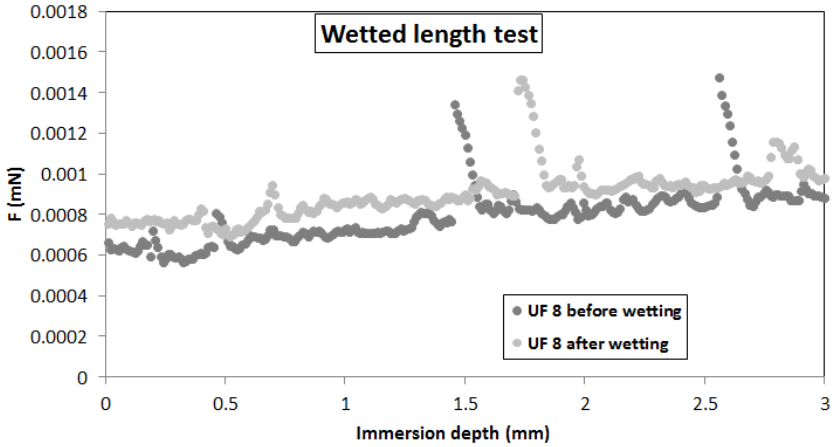

Figure 2. Wetted length test for an untreated elementary flax fiber, before and after wetting with water.

4. Results

4.1. Optical measurements

Fifteen tests of swelling in water and diiodomethane were carried out on treated and untreated single fibers as described in section 3.1. Table 2 shows the mean dry fiber diameter D_i and the mean swelling ratio R_{sw}. The heat treatment does not significantly modify the morphology of the fibers as the mean dry diameters of the UF and TF elementary fibers are similar. swelling of fibers in water and its dispersion is lower for TF, meaning that the treatment makes fibers less sensitive to water sorption. Results for diiodomethane seem to show a slight shrinkage of the fibers. Again the results obtained with the TF fibers are less scattered.

Table 2. Average values of initial diameter and swelling ratio for UF and TF fibers with water and diiodomethane obtained by the optical method.

	Water		Diiodo	
	D_i (µm)	R_{sw}	D_i (µm)	R_{sw}
Untreated Flax	16.8 ± 4.7	1.27 ± 0.13	15.8 ± 3.8	0.90 ± 0.08
Treated Flax	17.5 ± 5.9	1.11 ± 0.07	16.6 ± 3.8	0.94 ± 0.08

4.2. Tensiometric measurements

Wetted length tests were carried out before and after wetting in water and diiodomethane for UF and TF fibers with the tensiometer as explained in section 3.2. From the wetted lengths obtained before and after wetting (p_i and p_{sw}) fiber dry and wet diameters (D_i and D_f) can be determined and so the swelling ratio R_{sw}. Table 3 presents the average results of tests obtained with the tensiometric method, assuming that a fiber has a constant diameter and assuming cylindrical fibers (as in Table 2), which is justified for elementary fibers.

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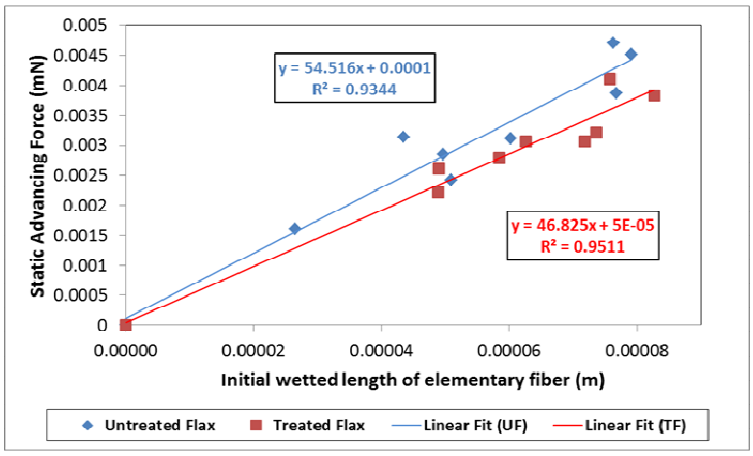
Table 3. Average values of initial diameter and swelling ratio for UF and TF fibers with water and diiodomethane obtained by the tensiometric method.

	Water		Diiodo	
	D_i (µm)	R_{sw}	D_i (µm)	R_{sw}
U ntreated Flax	18.4 ± 5.9	0.95 ± 0.10	17.8 ± 3.6	0.95 ± 0.10
Treated Flax	20.8 ± 4.0	0.97 ± 0.03	21.5 ± 8.7	1.00 ± 0.03

One can observe that with water, the swelling ratio is different compared to the one obtained with the optical method. This is due to the methodology that is different (it is impossible to keep fibers immersed in water during measurements of wetted length with the tensiometer) and the fact that there is a large dispersion in the swelling and drying processes of flax fibers. Results obtained with diiodomethane are more in line with the swelling ratios shown in Table 2. Again, the treatment of fibers gives a better dimensional stability as TF always presents a swelling ratio closer to 1 and the dispersion is lower.

5. Discussion

The optical and tensiometric methodologies provided different swelling ratios due to differences in the way the measurements were implemented. However both methods show a higher dimensional stability of the treated flax fibers, evidenced by the values of the swelling ratios.
Taking into account swelling and then the effective wetted length after wetting in a liquid, is crucial to measure accurate contact angle values. Considering the Wilhelmy relation (Equation 2), varying the wetted length will affect the capillary force. If the contact angle remains constant, plotting the capillary force of a liquid in contact with a fiber as a function of the fiber wetted length should show a linear trend. Figure 3 presents plots of capillary forces with water for UF and TF fibers as a function of wetted length before (p_i) and after (p_{sw}) wetting (measured with the tensiometer). A linear fit of these points according to the Wilhelmy relation (Equation 2) is made and provides a unique contact angle value .
With water it can be observed in figure 3 that, even if fibers do not modify significantly their wetted length, values of slope for UF with the initial and the final wetted length are significantly different (indicating that it is relevant to consider swelling). Moreover, there seems to be a significant difference in slope between the untreated and treated flax fibres. This indicates that the thermal treatment has indeed modified the surface energy of the fibers, making them less hydrophilic.



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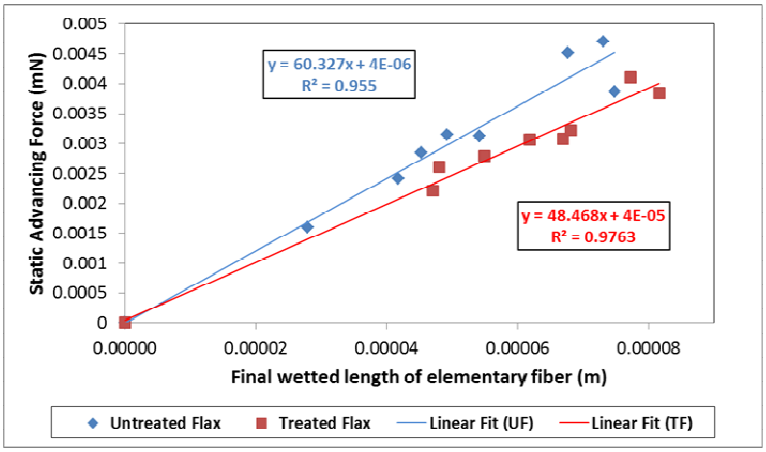

Figure 3. Plots of capillary force measured on the tensiometer for UF and TF elementary fibers with water as a function of the wetted length before and after wetting.

6. Conclusions

In this work swelling of untreated and heat treated flax fibers was characterised with optical and tensiometric methods. Swelling tests and the results obtained for untreated and treated elementary fibers were compared. Even if the two methods are very different, giving different results, they both evidence the higher dimensional stability of the treated fibers. The heat treatment makes fibers less sensitive to liquid sorption and then to swelling. Characterising the modification of fiber morphology due to swelling is of primary importance in order to determine reliable contact angle values and, thus, fiber surface energy.

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