CAPILLARY PRESSURE ESTIMATION FOR DIFFERENT FIBROUS REINFORCEMENT/LIQUID COUPLES; APPLICATION TO LIQUID COMPOSITE MOLDING

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ABSTRACT

This work presents recent developments on the influence of capillarity during impregnation of a fibrous preform for LCM processes. In order to evaluate preform impregnation, saturated and unsaturated permeability tests are commonly carried out. This work highlights the influence of capillary effects during impregnation, considering the effect of liquid, fabric and fiber volume fraction choice. In order to take into account those capillary effects, a definition of capillary pressure was introduced. Tests of capillary wicking were performed and models accounting of swelling for natural fabrics were developed. Results on capillary pressure estimation are relevant for a better understanding of impregnation during LCM processes and they could be inserted into numerical models of voids prediction.

1 INTRODUCTION

An overview of recent studies carried out on capillary effects during Liquid Composite Molding (LCM) processes and on how to consider them is here presented. During LCM processes, the fibrous preform is impregnated by the action of a pressure gradient or a constant fluid flow. Viscous and capillary effects are known to occur during impregnation or dynamic wetting of the preform by the liquid resin (thermoset or thermoplastic). Impregnation phenomena are usually estimated defining homogeneous equivalent parameters at the scale of the preform like saturated and unsaturated permeabilities [1]. However, those parameters are defined by empirical laws, like Darcy law, considering only viscous effects in saturated flow. Capillary forces play also a role during flow that need to be identified. More specifically, capillary effects have to be considered in physical and numerical models for an accurate prediction of voids formation and local interfacial defects during LCM processes [2]. To achieve this objective, a homogeneous equivalent parameter representative of capillary effects is introduced: the capillary pressure [3]. Theory to estimate the capillary pressure and all experimental factors allowing the determination of this parameter will be detailed here. Different kinds of reinforcements, with some of them changing morphology during flow, will be considered. Validity range of these methods, as a function of the different parameters (like liquid viscosity and surface tension), will be defined and capillary pressure thresholds will be finally identified experimentally.

2 THEORY

2.1 Capillary Wicking And Associated Pressure

In order to consider only the effect of capillarity during impregnation of a fibrous preform, the experience of capillary wicking is considered. The aim is here to analyze a spontaneous impregnation. That is to say: capillary effects are the only ones driving the flow in preforms.

Fibrous preforms can be considered as porous media, which are idealized as tortuous capillary tubes network. The capillary rise in a tube is well described by the Washburn equation, which has been extended for porous media packed in a cylindrical column of radius *R*. Then, Washburn equation for porous media describes capillary wicking in fibrous preforms [3]. According to this approach, neglecting the gravity effects, the mass gain (*m*) during wicking is a function of time (*t*) depending on an apparent advancing contact angle θ_a (representative of the homogeneous equivalent medium), liquid properties (density ρ, viscosity η and surface tension γ_L) and the morphology of the medium (mean capillary radius $\bar{r}$, tortuosity, and fiber volume fraction), as follows:

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

where ε is the porosity of medium, *c* is a factor inversely proportional to the tortuosity. It is important to highlight some points of this theory:

(1) This approach is used to determine the morphology of porous medium using a totally wetting liquid, and particularly the geometric factor ($c\bar{r}$), assuming that the morphology of medium does not change during the spontaneous impregnation;

(2) This approach is also used to determine the equivalent mean advancing contact angle θ_a. This parameter is not actually an angle but a parameter representative of the liquid/solid couple interaction during the spontaneous impregnation.

On the other hand, Darcy law for a porous medium describes the flow over time depending on the pressure gradient, the liquid viscosity and the saturated permeability of medium *K*.
Considering a spontaneous imbibition in the medium, a capillary pressure P_{cap} was introduced in the Darcy pressure gradient and the Darcy law was rewritten as a function the mass gain over time, as follows:

$$m^2(t) = \frac{2K\varepsilon\rho^2(\pi R^2)^2 P_{cap}}{\eta}t \tag{2}$$

Then, an equivalence between Darcy (Equation 2) and Washburn (Equation 1) equations was made. This allowed to obtain a new expression of capillary pressure, as follows:

$$P_{cap} = (c\bar{r})\varepsilon\frac{\gamma_L cos\theta_a}{4K} \tag{3}$$

The advantage and the originality of this approach compared to ones in literature is that the estimated P_{cap} is a parameter representative of exclusively the capillary effects during impregnation of a fabric and it is obtained at the macroscopic scale of the equivalent homogeneous medium [3]. Parameters defined in the P_{cap} equation are determined experimentally. Specifically, the ($c\bar{r}$) and the $\theta_a$can be obtained from wicking tests and the fit of wicking curves with the Washburn equation. The saturated permeability can be measured thanks to a adapted permeability test and the application of Darcy law. Otherwise, permeability can be obtained by calculation using Gebart law and assuming a specific arrangement of fibers [4].

2.2 Models Accounting Swelling

As mentioned above, laws expressed in the previous section do not take into account the eventual modification of preform morphology during liquid impregnation. Indeed, swelling of fibers, for instance natural ones, occurs during impregnation with high polar liquids like water. This generates a reduction of the mean capillary radius and of porosity defined in the Washburn equation (Equation 1).

Firstly, a model to modify Washburn equation considering swelling during wicking was developed [5]. This means that the parameters related to the morphology of the porous medium in Equation 1 were replaced by a function of time *f(t)*, as follows:

$$m^2(t) = \left[\frac{f(t)(\pi R^2)^2}{2}\right]\frac{\rho^2\gamma_L cos\theta_a}{\eta}t \tag{4}$$

A linear law of pore shrinking depending of a swelling rate was defined (Equation 5) and an empirical law relating the mean pore radius to the fiber volume fraction (Equation 6) was used.

$$(c\bar{r})(t) = (c\bar{r}_{ini}) - at \quad (5)$$

$$\varepsilon(t) = (\varepsilon_{ini}) + b\,[(c\bar{r})(t) - (c\bar{r}_{ini}) \quad (6)$$

with a the swelling rate and b a parameter estimated experimentally.
It is important to make some remarks on the hypothesis of this modified Washburn law accounting swelling:

(1) The models suppose that the porous medium swells instantaneously with the wicking (meaning that the swelling time is equal to the wicking time (t) in the model.
(2) The porous medium is homogeneous with a mean porous radius and an associated swelling kinetic.

In order to improve approximation to the real case of used fabrics, an extension of this model considering a dual scale pore morphology of woven preforms (pores between and into the yarns as shown in Figure 1) was proposed [6]. Two mean capillary radii were then considered with the related swelling rates.

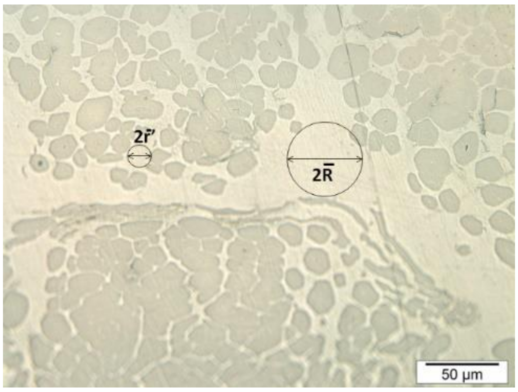

Figure 1: Optical observation of a flax/epoxy composite and definition of the smallest mean capillary radius between the elementary fibers ($\bar{r}$) and the largest mean capillary radius between the yarn ($\bar{R}$).

3 MATERIALS AND METHODS

3.1 Materials

Quasi-unidirectional carbon and flax fabrics were used. The first ones were provided by Hexcel (48580®), the second ones by Libeco (FLAXDRY UD 180®). Test fluids with known surface tension and viscosity were used in first approach: n-hexane and water. Then, wicking using more viscous fluids having different surface properties (silicon oils, polyethylene glycols and resins) were investigated.

3.2 Experimental methods

Wicking tests were carried out using a DCAT11 tensiometer (Dataphysics). A cylindrical sample holder was used. Parameters set for tests and preparation of samples are more detailed in previous works. A preliminary study to validate the experimental protocol was carried out on the three main directions of the quasi-unidirectional carbon fabric with n-hexane and water at the same fiber volume fraction of 40% [3]. Then the direction of fiber (defined as x-direction) was considered and samples were prepared in order to obtain different fiber volume fractions (from 30 to 60%) [4].
From wicking curves and the linear fit with the Washburn equation, the geometric factor and the advancing contact angle for a specific solid/liquid couple were determined using Equation 1. An example of the linear fit of wicking curve is shown in Figure 2 for carbon fabric in x-direction (V_f = 40%) with water.
For flax fabrics, the modified Washburn equation accounting of swelling was considered. The non-linearity and the fit the wicking curve with the developed model is shown in Figure 3 for flax fabric in

x-direction (V_f = 40%) with water. Thanks to the developed models, equivalent mean contact angles were also determined for natural fabrics.

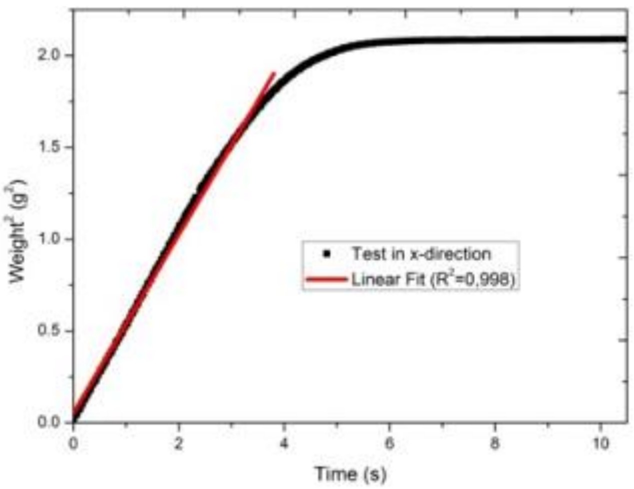

Figure 2: Wicking test in x-direction for carbon fabric (V_f = 40%) with water.

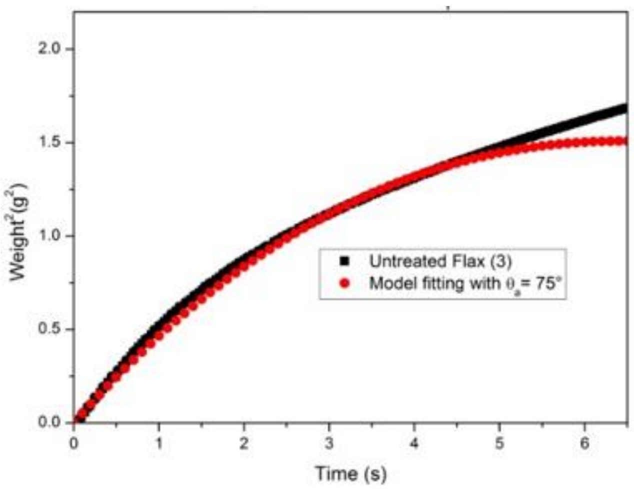

Figure 3: Wicking test in x-direction for carbon fabric (V_f = 40%) with water.

4 RESULTS

As a first result, it was obtained that all wicking curves with water for carbon fibers were linear as a function of time, according to Equation 1. For flax fabrics swelling in water, the non-linearity was always observed and this effect was more marked with the increase of the fiber volume faction [5].
As a second result, a comparison of the model accounting swelling and the model accounting the dual scale pore of swelling was made. It was found that the second model fits well experimental data for more long time of wicking than the previous one [6]. Moreover, the second model describes wicking for higher fiber volume fraction (up to Vf = 60%)
Using the adequate equations to describe the wicking for carbon and flax with n-hexane and water, the geometrical factor and the equivalent mean advancing contact angle were determined as a function of V_f. Results are reported in Table 1 [4].
It can be observed that the geometric factor decreases as the fiber volume fraction increases. This finding is expected since for a given tortuosity (fixed by the x-direction) the mean pore radius decreases. Moreover the equivalent mean advancing contact angle, accounting of liquid/solid interaction, decreases

as a function of the fiber volume fraction. The increase of V_f had a double effect: the impregnation kinetic was slower and the geometric factor decreased. Consequently, the dynamic contact angle decreased as V_f increased.

Fabric	V_f (%)	$(c\bar{r})$ (µm)	θ_a(°)
Carbon	40	28.3 ± 2.4	82.7 ± 0.9
	50	13.0 ± 0.7	75.9 ± 1.5
	55	6.4 ± 0.8	68.7 ± 1.4
	60	2.3 ± 0.4	55.4 ± 3.8
	65	0.9 ± 0.1	56.5 ± 4.9
*Fl*ax	30	14.2 ± 0.8	87.0 ± 0.3
	35	13.4 ± 1.3	76.5 ± 0.4
	40	12.2 ± 1.4	76.5 ± 1.0
	50	5.7 ± 0.8	74.5 ± 7.7
	60	3.8 ± 0.4	68.3 ± 4.2

Table 1: Average wicking parameters of carbon and flax fabrics at different V_f.

Using these parameters, the capillary pressure was obtained. Firstly, it has been shown that, for a same volume fraction, the calculated capillary pressure had a different value along the main directions of the fabric [3]. The term capillary pressure is thus not the most appropriate and in numerical approach, the term of capillary stress has been introduced [7]. In addition, varying the fiber volume fraction and considering n-hexane as a test liquid, it can be seen on Figure 1 that a threshold appeared for carbon fibers. This threshold was shown by a no longer constant value of capillary pressure with a totally wetting liquid, n-hexane. For water, a maximum value can be identified. This might be linked to the viscous effects counterbalancing the capillary effects for this particular weaving and this particular fiber/fluid couple. Similar results were found for flax with n-hexane and with water and will be presented in the oral presentation [4]. Different fiber/liquid couples and proof of concept of morphological change correction by the semi-empirical model will also be presented.
At last, thanks to data with different fiber/liquid couples, limits of the Washburn theory will be defined, questioning the validity of Darcy law for some fiber/liquid couples under associated flow conditions.

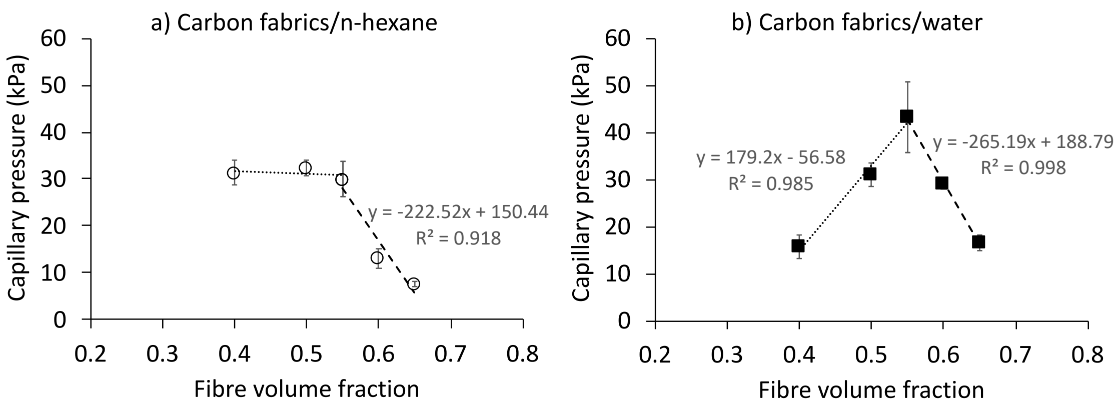

Figure 4: Capillary pressure for carbon fabrics/n-hexane (a) and carbon fabrics/water (b) at different fiber volume fractions

5 CONCLUSIONS

This work summarizes recent developments on the understanding of capillary effects during impregnation of preforms for LCM processes. Obtained results will be compared to approaches and data in literature and a critical analysis of used laws and their extension on the permeability determination will be made.

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