AN EXPERIMENTAL ESTIMATION OF LIQUID ABSORPTION COEFFICIENT FOR CELLULOSE NANO-FIBER FILMS

A. Javadi[1], K.M. Pillai[1] and R. Sabo[2]

[1]Laboratory for Flow and Transport Studies in Porous Media, Dept. of Mechanical Engineering, University of Wisconsin-Milwaukee, 3200 N. Cramer St., Milwaukee, WI 53211, USA.

[2]USDA, Forest Products Laboratory, One Gifford Pinchot Dr., Madison, WI 53726, USA.

ABSTRACT

While making polymer composites from natural fibers using the liquid composites molding (LCM) process, the fibrous porous medium inside the LCM mold undergoes swelling and porosity reduction as a result of enlargement of natural fibers due to liquid absorption. The preforms made from plant-derived cellulose nanofibers (CNF) have a potential for creating higher-quality and bio-based green composites. The absorption coefficient, *b*, plays a very important role in the modified continuity equation that is proposed for such swelling media for conducting LCM mold-filling simulations. Past research has shown that an ad-hoc value of unity for *b* is quite good for modeling flows in LCM molds packed with natural fibers. In this paper, a simple dipping experiment is proposed to estimate b directly using a microbalance. The final results indicate that *b* is indeed one for CNF preforms as measured with water as the wetting liquid.

1. INTRODUCTION

The usage of glass, carbon or kevlar fibers for providing reinforcement in polymer composites has been increasing for the past few decades. Due to several disadvantages associated with such composites including adverse environmental impact, difficult recycling, and high amount of energy needed for processing and recycling, there has been a trend of using natural fibers such as flax, kenaf and jute as reinforcement in polymer composites [1]. Natural fibers are preferred since they are biobased and biodegradable. However, the usage of natural fibers in polymer composites has some drawbacks including lower mechanical properties, degradation due to moisture absorption, and inconsistent reinforcement properties due to natural variability in fibers [2].

Cellulose nanofibers (CNFs), a new type of nanoscale fibers made of cellulose molecules and derived from plant sources, have very high mechanical properties compared to the natural or inorganic reinforcing fibers. Recent reduction in costs of producing CNFs due to the development of new chemistry-based processing methods [3, 4] has made it possible to use such fibers as reinforcement for nanocomposites. However, the CNF based nanocomposites remain confined to labs since there remain several hurdles in scaling-up their production [5]. A research collaboration between USDA Forest Products Laboratory at Madison, WI and University of

Wisconsin-Milwaukee has been investigating the possibility of producing scalable CNF based composites through the use of CNF as reinforcement in liquid composites molding processes [6]. Preliminary wetting tests with various liquids have indicated that CNF sheets [Figure 1] absorb liquid and swell at a rapid pace [7].

Figure 1: Transparent CNF film produced at USDA Forest Product Laboratory, Madison, WI.

2. MODELING RESIN FLOW IN SWELLING, LIQUID ABSORBING POROUS MEDIUM

For modeling single-phase flows in swelling porous media [1], the Darcy's law can be still considered to be valid:

$$< V > = -\frac{K}{\mu} \nabla < P >^{f} \tag{1}$$

Here $< V >$ is the phase average velocity, K is the porous-medium permeability, μ is the resin viscosity, and $< P >^{f}$ is the intrinsic phase average pressure. Unlike the non-swelling porous media formed by glass or carbon fibers, the permeability of a porous medium formed by CNF will be a function of both time and space due to swelling of solid matrix as a result of liquid absorption. Borrowing from the flow model for liquid flows in liquid-absorbing, swelling porous medium formed by paper [8] or natural fibers [9], the continuity equation for flow in porous media made from CNF reinforcement can be described as

$$\nabla . < V > = -S - \frac{\partial \varepsilon}{\partial t} \tag{2}$$

where S is the liquid absorption rate and $\boldsymbol{\varepsilon}$ is the porosity. In contrast to the traditional continuity equation $\nabla . < V > = 0$ employed by non-swelling glass or carbon fibers in rigid-mold LCM processes, Eqn. 2 has S as the sink term and $-\ \partial\varepsilon/\partial t$ as the source term (note that this term is positive since the porosity reduces with time in a swelling porous medium). A detailed derivation Eqn. (2) using the respected volume averaging method is presented in [9]. So the resin will either decelerate or accelerate depending upon whether the right hand side of Eqn. 2 is negative or positive, respectively.

Let us now present a modification of the continuity equation which has produced impressive results while modeling flows in swelling porous media, irrespective of whether it is the capillary-pressure driven wicking flow [8], or the injection-pressure driven flow in an RTM mold [9, 10]. Let v be the fiber volume fraction in our CNF based porous medium. Since S is the rate of liquid absorption by fibers and since dv / dt is directly related to the rate of increase of fiber volume, then S is anticipated to be proportional to dv/dt. As a first approximation, we assume S to be linearly proportional to dv/ dt, i.e.,

$$S = b\frac{dv}{dt} \tag{3}$$

where b is the *absorption coefficient* that is expected to fall in the range $0 < b < 1$. Note that $b = 0$ indicates zero absorption of liquid by the porous medium, while $b=1$ implies that the rate of increase in the volume of solid matrix is equal to the volumetric rate of liquid absorption by the matrix during the resin-flow process.

The assumption $b = 1$, i.e., the volume of liquid absorbed by the solid matrix in a given time period is equal to the increase in the matrix volume during the same period, has yielded impressive results while predicting the moving liquid-front location during wicking in a liquid-absorbing, swelling paper-like medium [8]. This same assumption proved effective even for predicting the pressure and flow-front location in fiber mats made from natural fibers such as jute that absorb liquid and swell during 1-D RTM mold-filling experiments [9, 10]. It is important to note that though the assumption $b = 1$ has proven to be effective, *it has not be established through a direct measurement of volume of liquid absorbed along with volume change in the solid matrix.* In this paper, an attempt will be made to directly estimate the absorption coefficient b using a microbalance available within a Tensiometer, also called DCA (Dynamic Contact-Angle Analyzer). To test the proposed methodology, water is used as the fluid instead of an actual resin.

3. THEORY: MEASURING THE ABSORPTION COEFFICIENT THROUGH A MICROBALANCE

A small rectangular CNF sheet is suspended from a hook attached to the microbalance. The reading of the microbalance gives the weight of the dry sheet. A container of water resting on the moving platform is raised to immerse the sheet (Figure 2). After this immersion, the microbalance reading is reduced as a result of the buoyancy force acting on the immersed sheet. As shown below through our derivation, the readings before and after the immersion can be used to estimate the values of the absorption coefficient.

The various forces acting on the submerged CNF sheet (Figure 3) follow the relation

$$T + F_b = W \tag{4}$$

where T is tension in the string suspending the sheet and which is read as the reading of the microbalance, W is the weight of the specimen along with that of the water absorbed by it. Note that the buoyant force, F_b, can be estimated as

$$F_b = \rho V g \tag{5}$$

where ρ is the density of water (= 998 kg/m^3), V is the volume of water displaced by the CNF sample (which is nothing but the sample volume), and g is the acceleration due to gravity (=9.8 m/s^2). The use of Eqns. (4) and (5) leads to the following relation at the initial time $t = 0$:

$$T_o + \rho V_o g = W_o \tag{6}$$

Here the subscript o signify the initial ($t = 0$) quantities.

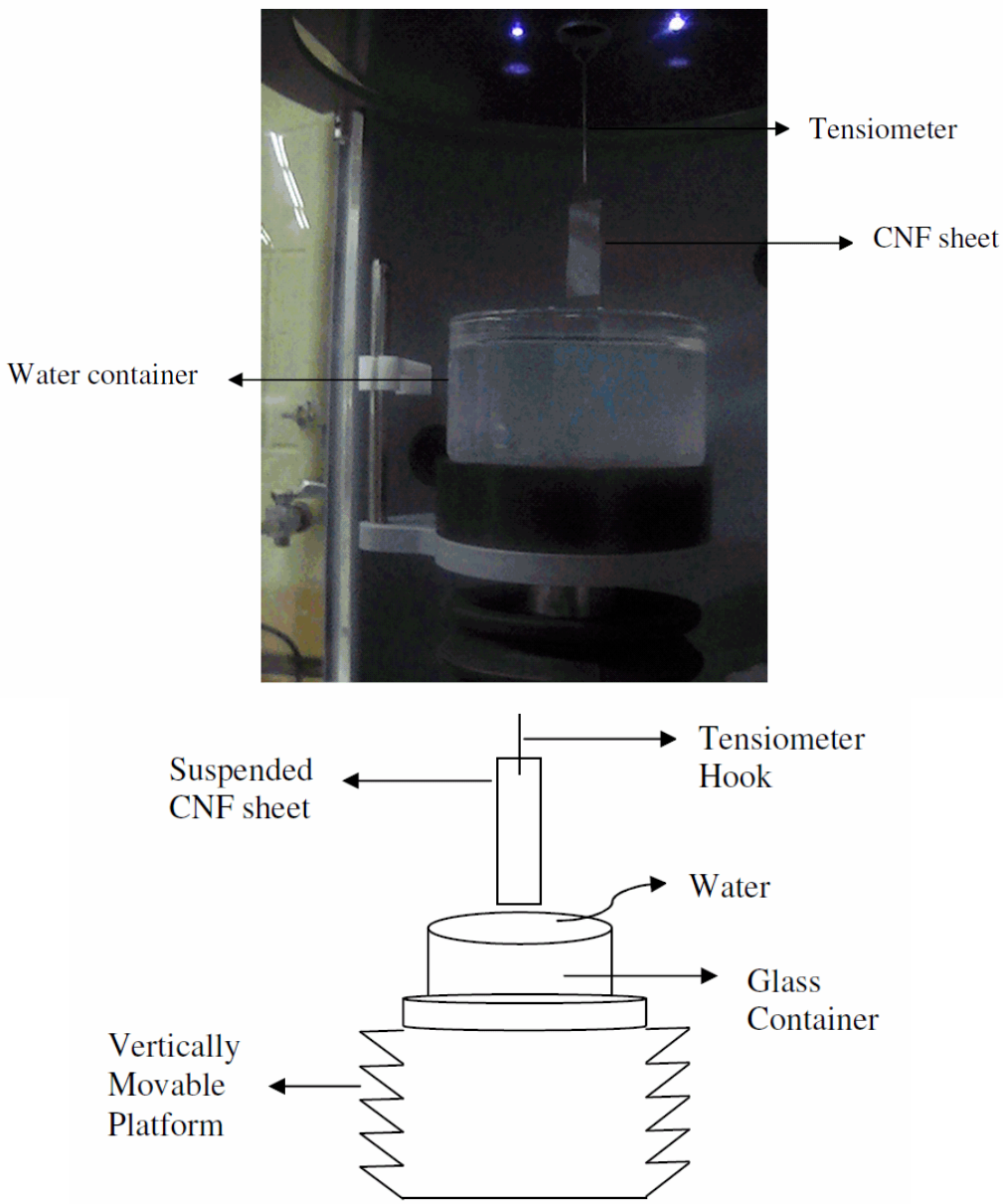

Figure 2: (Top) A photograph of the experimental setup used for estimating the absorption coefficient using the microbalance of tensiometer (DCA). (Bottom) A schematic of the setup showing the details.

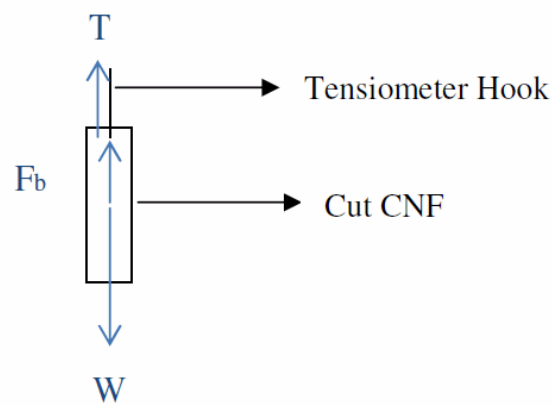

Figure 3: A Free Body Diagram depicting various forces on the CNF sheet hung with a hook in the microbalance while submerged in water.

Note that W_o is the weight of the CNF sample before it is submerged into water and was measured by a sensitive, two-digit electronic balance, while T_o is obtained from the microbalance. Since g and ρ are easily-determinable constants, we are able to estimate the initial sample volume, V_o , by using Eqn.6.

Since Eqn. 4 is a general equation valid at any given time, t, after the sample has been dipped into water, we can present it again as

$$T(t) + \rho V(t) g = W(t) \tag{7}$$

where $T(t)$ is the tension reading measure by the microbalance, and $W(t)$ is the CNF sample weight. ($W(t)$ after time t was obtained by taking the sample out from water, blowing air into it to shake-off the water sticking to it, and then using the electronic balance.)

On subtracting Eqn. (6) from Eqn. (7), we have

$$T(t) - T_o + \rho g (V(t) - V_o) = W(t) - W_o \tag{8}$$

By using the values of $T(t)$, T_o, $W(t)$, W_o, and V_o obtained from the previous equations, and employing the assumed values of ρ and g, we can calculate the current volume of the CNF sample, $V(t)$, from Eqn. 8.

Using $W_o = m_c g$, where m_c is the original (dry) mass of the CNF sample, and $W(t) = (m_c + m_w(t)) g$, where m_w is the mass of water absorbed by the sample since the start of the experiment, we obtain

$$V_w(t) = (W(t) - W_o)/\rho g \tag{9}$$

Thus we can calculate the volume of water absorbed by the CNF sample as a function of time during the course of the experiment.

Using Eqn. 3, we can set the definition of the absorption coefficient, b, as

$$b = \frac{\mathrm{S}}{\mathrm{dv/dt}} = \frac{\text{rate at which liquid volume is absorbed per unit porous-medium volume}}{\text{rate of change of fiber (solid-matrix) volume fraction}} \tag{10}$$

Now the fiber (solid-matrix created from CNF in an LCM mold) volume fraction can be defined as

$$v = \frac{V_f}{\mathrm{V}} \tag{11}$$

where V_f is the fiber volume within an REV (representative elementary volume) used for deriving macroscopic governing equations through the method of volume averaging [11]. $\mathrm{V_{REV}}$ is the REV volume that remains fixed with time. Taking the derivative of Eqn.11 with respect to time results in

$$\frac{\mathrm{d}v}{\mathrm{dt}} = \frac{1}{\mathrm{V_{REV}}} \frac{\mathrm{d}V_f}{\mathrm{dt}} \tag{12}$$

If we define the sink term of Eqns. 2 and 3 as the rate of depletion of water within an REV, then it can be expressed as

$$S = \frac{1}{\mathrm{V_{REV}}} \frac{d\,\mathrm{V_w}}{dt} \tag{13}$$

where $d\,\mathrm{V_w}$ is the differential reduction in the surrounding water volume due to absorption. On substituting Eqns. 12 and 13 in Eqn. 10, we get the definition of the absorption coefficient, b, as the ratio of the volume of water absorbed to the change in fiber or solid-matrix volume in a given differential time-interval:

$$b = \frac{d\,\mathrm{V_w}}{\mathrm{d\,V_f}} \tag{14}$$

The coefficient b as defined above is rather difficult to measure experimentally. Instead, we found it convenient to measure a quantity b' that is defined as

$$b' = \mathrm{V}_w(t)\,/[V(t) - V_o] \tag{15}$$

which is the ratio of total volume of water absorbed by the CNF sample to change in the sample volume due to swelling. It turns out that, by taking the differential of Eqn. 15 and by conducting some algebraic manipulations, one can relate b to b' through the relation

$$b = [V(t) - V_o]\,\frac{d\,b'}{d\,V} + b' \tag{16}$$

In this paper, we intend to plot b' as a function of $[V(t) - V_o]$ such that the slope and value at any point of the curve will yield the value of b. (Note that $d\,b'/d\,V = d\,b'/d\,[V(t) - V_o]$.)

4. EXPERIMENTAL DETAILS AND DATA ANALYSIS

Samples were developed from the CNF sheets made at USDA forest product laboratory at Madison, WI [Figure 1]. The CNF sheet were cut in rectangular shape for the experiment. Tensiometer (DCA) was used for this purpose; the microbalance of the device was calibrated afresh at the start of these experiments. Note that the Tensiometer, which is designed to measure surface tension, was adapted suitably for our experiment—its inbuilt software that translates the microbalance measurements into surface tension values was manipulated to yield the force/weight values. A total of 11 CNF samples of varying sizes were used in our experiments. Each sample was subjected to a cyclical dipping process of 30 seconds time-period for 20 minutes. At the end of this period, it was observed that all CNF samples had reached their maximum-possible saturation states such that they were no longer absorbing any more water.

Then the final value of tension in the string, T(t), as well as the final weight of the specimen, W(t), were measured. Using Eqn. 8, the change in the volume of the CNF specimens, $V - V_o$, was estimated; using Eqn. 9, the volume of water absorbed by the CNF specimen, V_w, was evaluated. Using these two values, b' was estimated using Eqn. 15. Thus a total of eleven ordered pairs of the form (b', $[V(t) - V_o]$) were developed from the same number of CNF samples. (Table 1 lists details of five of these randomly-chosen samples.) These ordered pairs were then used to plot the graph shown in Figure 4 which then furnished the slope $d\,b'/d\,V$ or $d\,b'/d\,[V(t) - V_o]$ that was used in Eqn. 16 to get the final value of the absorption coefficient b.

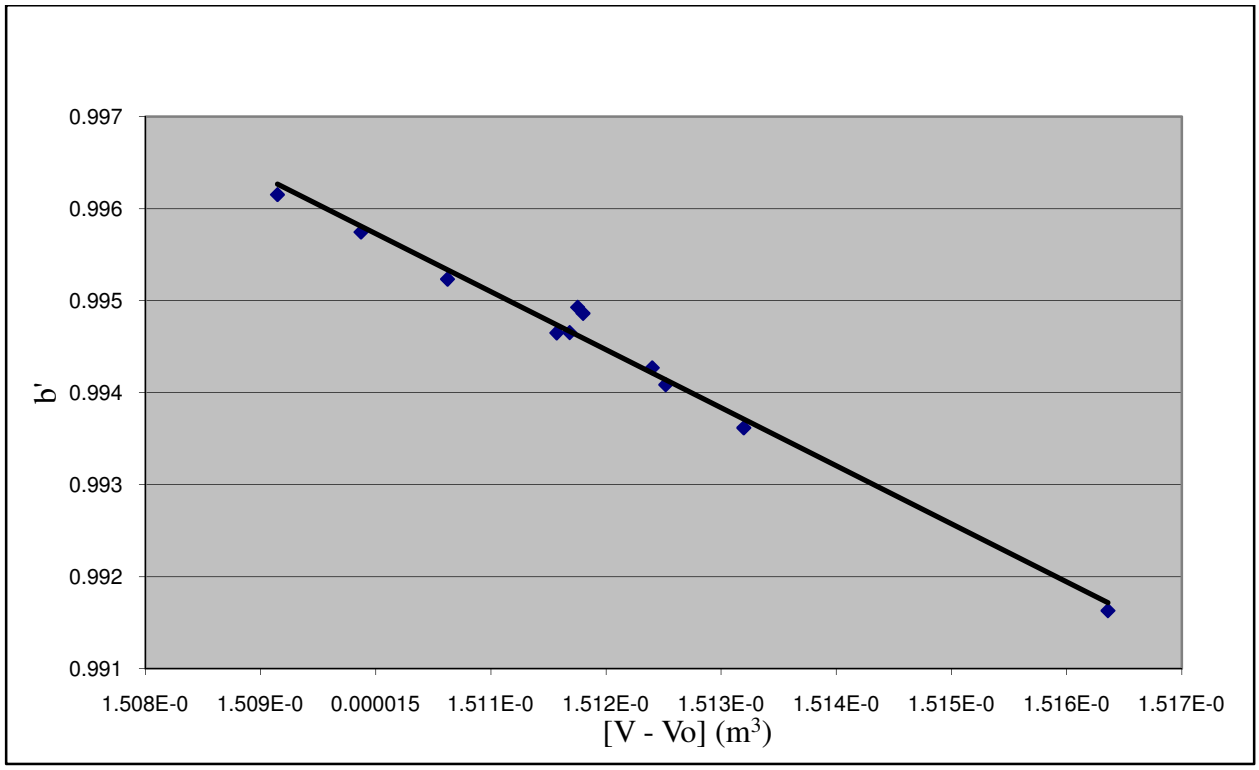

Figure 4: A plot b' as a function of $[V(t) - V_o]$ as observed for 11 different CNF samples.

CNF Sample Number	initial weight (mg)	Change in sample volume $[V - V_o]$ (m^3)	Volume of water absorbed by the sample (V_w)	b'
1	20.8	1.512E-05	1.5037E-05	0.994268362
2	31.8	1.51636E-05	1.504E-05	0.991626175
3	17.8	1.5132E-05	1.5035E-05	0993616028

4	18.7	1.51252E-05	1.5034E-05	0.995234051
5	21.1	1.51157E-05	1.5036E-05	0.994651994

Table 1: Some details of the experiments conducted with five randomly-chosen CNF samples out of a total of eleven.

5. RESULTS, CONCLUSIONS AND FUTURE WORK

The plot of Figure 4 furnished the final value b = 0.9942 that was an average of the b value obtained for each of the eleven samples using Eqn. 16. These b values were virtually indistinguishable from the b' estimated for the eleven samples. This close convergence clearly indicates that the liquid volume absorbed by samples and the corresponding changes in sample volumes, as indicated by Eqns. 14 and 15, are clearly equal. In other words, *change in the volume of CNF preforms during swelling is entirely due to the volume of water absorbed by it*. This implies that our earlier ad-hoc assumption of using b as unity for flow models in swelling porous media is correct at least for the CNF preforms.

We reiterate that the b' versus $[V(t) - V_o]$ plot, as shown in Figure 4, was done using $V - V_o$ or V_w values obtained after achieving a full saturation in CNF samples. Our attempts to get a similar plot in real time, after measuring these variables as a function of time, met with failure due to the rapid rate of swelling in CNF samples during the earlier part of the wetting process—the method of pulling out the sample from water, blowing air on it to shake-off the sticking liquid, and then measuring it using a weighing scale, is simply too slow to capture the fast changes happening in CNF during the dipping process. New techniques have to be developed to capture such changes in real time so that changes in the values of b as a function of time can also be studied.

The current work was based on using water for this preliminary study. In future, it would be instructive to measure b for the various resins used for making composites or for various test liquids used for studying flow and characterizing permeability.

It is also important to note that in a real LCM mold, the CNF solid matrix will be under compressive stress due to mold closure as well as liquid pressurization. New tests need to be developed to measure the absorption coefficient b under such conditions in order to check if the findings of the present paper are going to be valid for such in *in-situ* situations as well.

6. ACKNOWLEDGEMENTS

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