AN EXPERIMENTAL STUDY ON SWELLING OF CELLULOSE NANO-FIBER FILMS IN EPOXY RESINS AND WATER

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ABSTRACT

The current breed of natural-fiber based polymer composites, because of their biobased and possibly biodegradable nature, offer an alternative as a 'green' material available for automotive and other engineering applications. However such composites suffer from the drawback of low strength and fatigue properties compared to the carbon- or glass-fiber based polymer composites. Cellulose nanofibers (CNFs) are a new type of nanofibers made purely from cellulose molecules and have very high mechanical properties compared to other natural fibers, even approaching that of inorganic reinforcing fibers. However, there remain several hurdles in the use of CNF films for the production of polymer composites through the liquid composite molding technologies. One such problem is the swelling of these films during the manufacturing of such composites. In this study, we have microscopically studied the swelling of CNF films when they come in contact with three different liquids: water, epoxy, and bio-based epoxy. It was observed that the swelling rate was very high in the beginning but decreased subsequently. The swelling process was seen to be complete within two minutes for all the three liquids. The highest and lowest swelling of CNF films were observed for water and bioepoxy, respectively.

1. INTRODUCTION

Polymer composites are one of the most important high-tech materials of recent times. Such composites, which result from combining plastics with reinforcements, such as glass or carbon fibers, are lightweight, strong, stiff, and corrosion-resistant. As a result, polymer composites are increasingly used in several engineering sectors, such as aerospace, automotive, civil construction and sports equipment manufacturing. Growing environmental awareness worldwide also has increased interest in using environmentally benign materials in engineering. Since the 1990s, natural fiber composites have emerged as an alternative to glass-reinforced polymer composites [Brosius, 2006]. Natural fiber composites, such as those made from hemp fiber-epoxy, flax fiber-polypropylene, and china reed-polypropylene, are particularly attractive in the automotive industries because of their lower cost and lower density, which lead to lower-weight components [Joshi et al., 2004].

Other advantages of natural fiber composites over traditional composites are economic viability, reduced tool wear in machining operations, enhanced energy recovery, reduced dermal and respiratory irritation, and biodegradability (these advantages have been verified by several lifecycle assessment studies conducted with these fibers [Joshi et al., 2004]). According to

Directive 2000/53/EC, the European Community requests member countries to reuse and recover at least 95% of the weight for all end-of-life vehicles by 2015 [Euro, 2000]. Thus, car companies such as Diamler-Chrysler have created programs to make their vehicles 95% recyclable with the help of natural fiber composites. For example, Diamler-Chrysler found that using natural fibers in an engine and transmission casing reduces weight by 10%, lowers the energy needed for production by 80%, and keeps the cost 5% lower than the comparable fiberglass-reinforced component. Consequently, the application of natural fiber composites of both thermoplastic and thermoset types is increasing in the automobile sector, with average annual growth rates of between 10 to 15% [Brosius, 2006]. Natural fibers composites, because of their attractive properties, have begun to replace glass or carbon fiber composites in secondary structural applications such as door panels, package trays, and trunk liners in vehicles.

Cellulose nanofibers (CNFs) are one class of natural fibers that have resulted in structures with remarkable mechanical properties [Saito et al., 2009; Henriksson et al., 2008]. Films or "nanopaper" of cellulose nanofibers have recently been proclaimed to be the strongest man-made, cellulose-based material [Lindström and Ankerfors, 2009]. However, the full reinforcing potential of these materials has yet to be realized partly because of issues related to manufacturing processes. Cellulose nanofibers have only recently begun receiving serious consideration as a reinforcement material partly because the energy requirements for breaking down cellulose fibers in nanofibers were prohibitively high until recently [Siró and Plackett, 2010]. Recent advances in chemical and mechanical technologies have drastically reduced the energy requirements for producing cellulose nanofibers [Lindström and Ankerfors, 2009]. However, there are still several problems remained unsolved in using the cellulose nanofibers in the form of films for composite materials.

Liquid composite molding (LCM) process is a versatile process for making polymer composites in which mats of fibrous reinforcement are wetted with the matrix resin either through injection or vaccuum suction using a mold. Such a technology has several variants including resin transfer molding (RTM) and vacuum-assisted RTM (VARTM). Numerical simulation of mold-filling in LCM molds is regularly conducted to optimize mold designs. Accuracy of such simulations depends on capturing all aspects of resin flow through packed fibers in an LCM mold [Tan and Pillai, 2009, Tan and Pillai, 2010].

Recently the authors of this paper have been investigating the possibility of using CNF films as reinforcements for the LCM processes in order to create high-quality CNF-based natural-fiber composites. However swelling of CNF films on coming in contact with resins and liquids poses new challenge as far as numerical modeling of resin flow in an LCM mold packed with such sheets is concerned.

Previous research establishes the presence of cellulose in natural fibers as one of the main causes of swelling of such fibers during LCM processing [Masoodi and Pillai, 2011]. Understanding of swelling rate in natural fibers is important for developing resin-flow physics employed in LCM simulations during the processing of natural-fiber composites [Masoodi et al., 2009; Languri et al., 2010]. In this paper, the swelling of CNF sheets was experimentally studied in three different test liquids: 1) water, 2) a traditional epoxy (thermosetting) resin, 3) a bio-based epoxy (thermosetting) resin. The aim was to investigate how fast the CNF sheets swell in these liquids and also obtain some information about the relative swelling-rates and thickness growth that may happen during the processing of green composites made from cellulose nanofibers.

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

a) Epoxy   b) Bioepoxy

Figure 2: Different resins used in the swelling tests

2. EXPERIMENTATION

2.1 Test Materials

We used cellulose nanofiber (CNF) sheets or films produced at USDA Forest Product Laboratory in Madison WI for this study. Figure 1 shows a sample of such a clear film made out of cellulose nanofibers. Cellulose nanofibers were prepared according to a procedure described by Saito and Isogai (2006). Fully bleached Kraft Eucalyptus fibers were oxidized with sodium hypochlorite using tetramethylpiperidine-1-oxy radical (TEMPO) sodium bromide as catalysts. The TEMPO-mediated oxidation was carried out at pH 10 and 25 °C for three hours. The fibers were then thoroughly washed and refined in a disk refiner with a gap of approximately 200 μm. The coarse fibers were separated by centrifuging at 12,000g, and the nanofiber dispersion was concentrated to 1% using ultrafiltration. A final clarification step was performed in which the

nanofiber dispersed was passed once through an M-110EH-30 Microfluidizer (Microfluidics, Newton, MA) with 200- and 87-μm in series.

Films or sheets of cellulose nanofibers fibers were formed by ultafiltration of fiber slurries using a 142 mm Millipore ultrafiltration apparatus with polytetrafluoroethylene (PTFE) membranes with 0.1 micrometer pore sizes (Millipore JVWP14225). Filter paper was placed below the ultrafiltration membranes to provide support. Fiber slurries of approximately 0.2% (wt) were added to the ultrafiltration apparatus to make sheets with a target weight of 1.0 g. After de-watering, individual films were blotted and placed between filter and blotter papers. The films and blotter papers were placed between caul plates with a pressure of approximately 2-3 psi and put in an oven at 50 °C for approximately three days.

As mentioned before, we used three different liquids to induce swelling in CNF films: 1) water, 2) conventional epoxy (thermosetting) resin, 3) bio-based epoxy (thermosetting) resin. Tap water was used as one of the test liquids for reference, since we expected to have large swelling of CNF films in water due to the large expansion of cellulose on coming in contact with water. The conventional epoxy resin used in the present study is System 2000 epoxy resin from Fibre Glast Development Corporation (See Figure 2a). The bio-based epoxy resin is Super Sap 100/1000, which is a two-part liquid epoxy system designed by Entropy Bio-Resins Company (see Figure 2b). Unlike traditional epoxies that are composed primarily of petroleum-based materials, Super Sap 100/1000 is claimed to be up to 75% bio-based. In this paper, the terms 'water' refers to tap water,'epoxy' refers to System 2000 epoxy resin, and 'bioepoxy' refers to Super Sap 100/1000 epoxy rein.

Figure 3: Studying the swelling of CNF films under an optical microscope

2.2 Test Method

To test and measure the swelling rate of CNF films, the CNF film was cut into narrow strips and placed under an optical microscope to observe and record the changes of thickness of CNF film with time. To start swelling, a small drop of the test liquid was dropped on the film strips using a syringe and a needle. (The syringe was used for pumping the liquid while the needle was used for directing the liquid.) A camera attached to the microscope was used for recording a photo every five seconds. Later, by reviewing the photos, we were able to measure the CNF film thickness corresponding to time of each photo. Figure 3 shows the optical microscope and a photo of the film cross-section during swelling. We used CNF films with three different liquids, i.e., water, epoxy and bioepoxy. Figure 4 shows the test samples after completion of the swelling tests. As shown, we used five samples for each swelling liquid to ensure repeatability, which means that a total of 15 tests were conducted for the three test liquids.
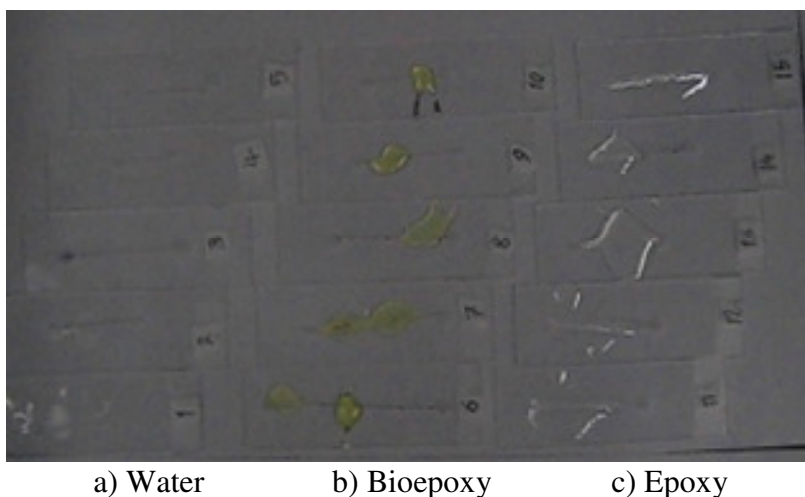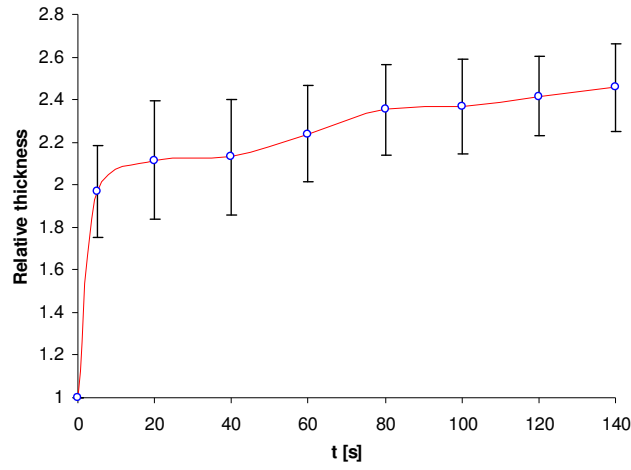

a) Water   b) Bioepoxy   c) Epoxy
Figure 4: Samples of CNF film slices after the swelling tests

3. RESULTS AND DISCUSSION

By definition, a solid is said to be swelling when: 1) its physical dimensions are increasing as a result of absorption, 2) it is still homogeneous at the microscopic level, 3) its molecular cohesion is decreasing but it is still strong enough to prevent rupture [Matanis et al., 1994]. It was also proven experimentally that all natural fibers swell significantly when exposed to organic liquids [Matanis et al., 1995]. The presence of cellulose molecules in natural fibers is one of the main reasons why all natural fibers swell [Masoodi and Pillai, 2011].

The main parameters that affect swelling of natural fibers as cellulose-based materials in liquids are: 1) Hydrogen bonding capability of the liquid, 2) molecular size (both weight and volume) of the liquid, 3) cohesive energy density of the liquid, 4) surface coating and treatment of the fibers, 5) density of the fibers, 6) ambient temperature, 7) crystallinity structure of the fibers, 8) basicity of the liquid, and 9) Steric effects [Masoodi and Pillai, 2011]. Cellulose nanofibers (CNF) as purely cellulose-based nanofibers should show a significantly higher swelling behavior compared to coarse fibers, especially with organic liquids.

a) Water
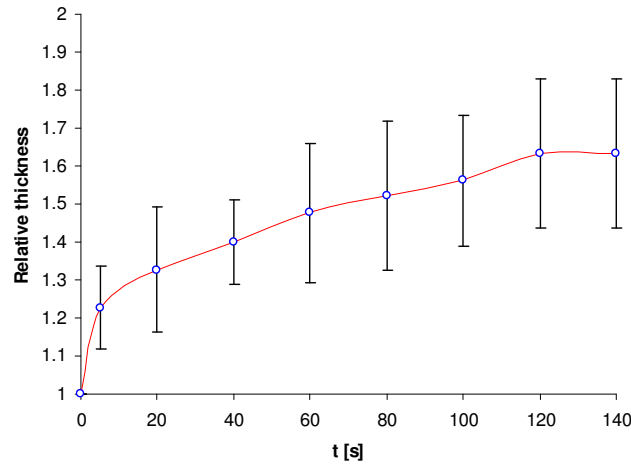
b) Bioepoxy
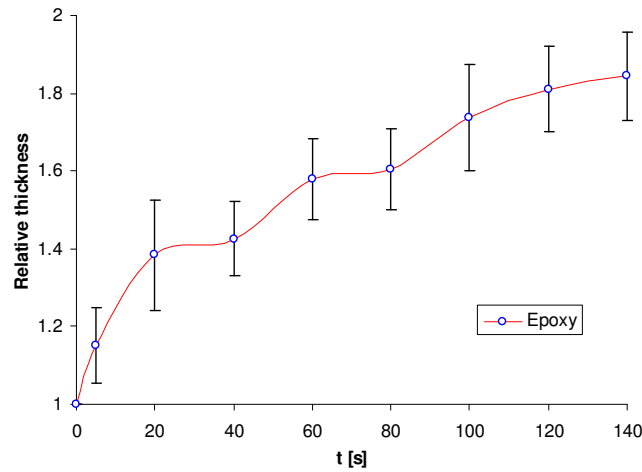
c) Epoxy

Figure 5: Evolution of relative thickness (=current thickness/original thickness) of CNF film slices in the three test liquids. (The error bars correspond to 95% confidence interval.)

The measured thickness of CNF film as a function of time is shown in Figures 5 to 7. We used relative thickness here to give a better view of the extent of swelling (and of swelling rate or thickness growing rate through the slopes of such plots) of CNF film. Relative thickness is defined as the ratio of the average current CNF-film thickness divided by the average initial, pre-swelling thickness of samples. Figures 5a to 5c show the plot of the average relative thickness for five test results against time for each test liquid. Figures 5 shows the repeatability of our test results as well: the scatter bars represent a confidence interval of 95%[1] [Wheeler and Ganji, 2003]. The smallness of these error bars allows us to infer that the repeatability of these results is very good.

Figure 6 plots the evolution of the average relative thickness as a function of time for the three different test liquids. It is clear that the CNF film swells the most in water as compared to the two epoxies. Through the slopes of the curves, a comparison of the relative swelling rates of the CNF film in the three test liquids can also be inferred. The swelling rate is very high for water and bioepoxy for the first five seconds. However the average increase rate is smaller at later times. In the case of epoxy, the swelling rate is high during the first 20 seconds and then there is a rather periodic decrease or increase of the swelling rate. The interesting behavior of bioepoxy is that the initial, linear swelling of the CNF film during the first five seconds is followed by swelling at a lower, almost-linear rate. An almost steady-state thickness is attained after about two minutes in all the three liquids; the relative thicknesses of the CNF film in water, epoxy, and bioepoxy are 2.42, 1.81, and 1.63, respectively.
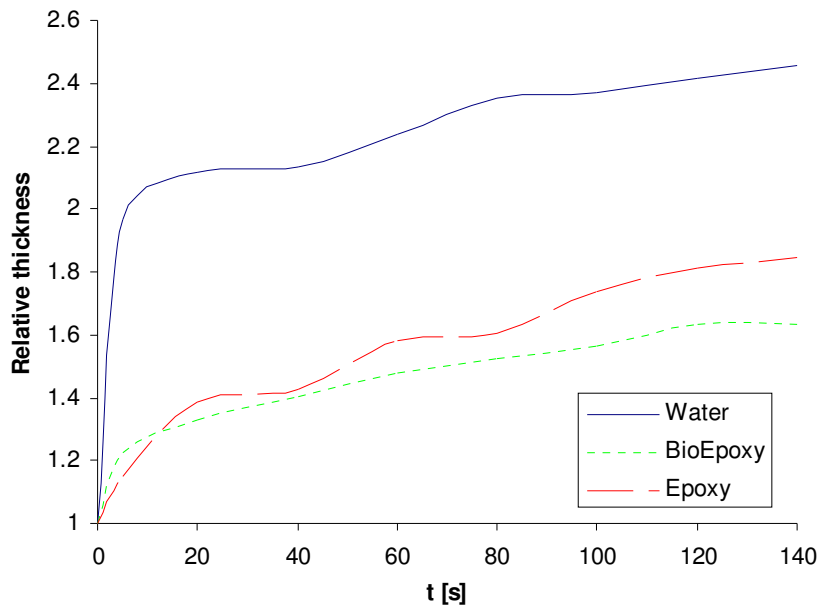

Figure 6: A comparison of the evolution of swelling in the CNF film in terms of the relative thickness when wetted by the three test liquids

Figure 7 shows, in terms of absolute thickness, the history of swelling of the CNF film for all the three test liquids. The measured average thickness of CNF films before the onset of

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[1] 95% confidence interval means that 95% of the times, the experimental values are expected to fall in the range.

swelling is 0.122 mm. After two minutes of growth discussed earlier, the average thickness increases to the final values of 0.295 mm, 0.221 mm, and 0.199 mm for water, epoxy, and bioepoxy, respectively.

In the end, we attempt a tentative explanation of the cause of disparities observed during swelling of the CNF film when exposed to the three liquids. In case of water, its small molecular size and its strong hydrogen bonding capability due to its polarity leads to a higher swelling of cellulose nanofibers in the film. The higher viscosity of the bioepoxy (reported by the manufacturer as 2000-4000cps at 25 °C) as compared to that of the petroleum based epoxy (reported as 1650 cps at 25 °C) may explain why the CNFs swelled less by the bioepoxy than the petroleum-based epoxy.
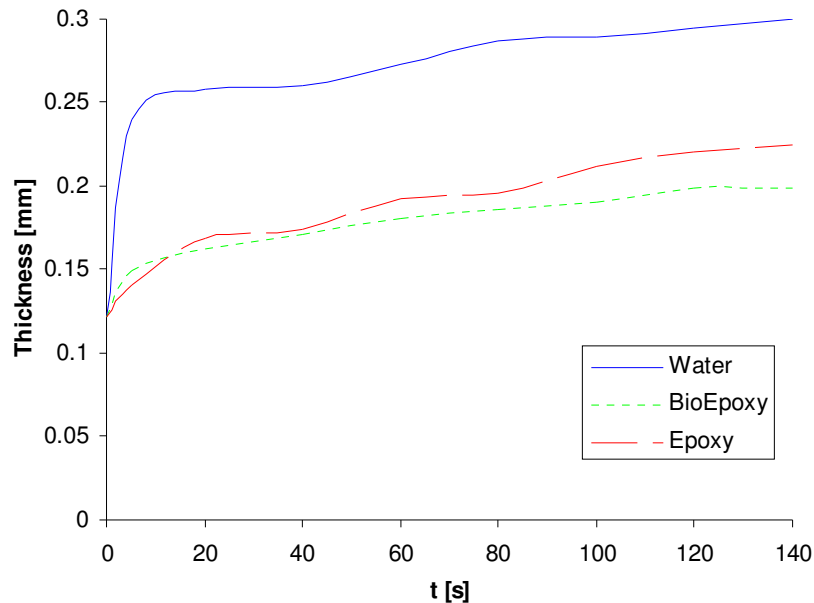

Figure 7: A comparison of the evolution of swelling in the CNF film in terms of the absolute thickness when wetted by the three test liquids

4. SUMMARY AND CONCLUSIONS

We have conducted an experimental study on swelling of CNF films made from cellulose nanofibers when exposed to three different liquids of water, epoxy, and bio-based epoxy. The swelling in films was observed and measured using an optical microscope. It observed that the swelling rate, very high at the beginning of the tests, reduces subsequently. The extent of swelling was observed to be highest for water, while it was the lowest for bioepoxy. The presence of hydrogen bounding and the small size of water molecules are the main reasons for higher swelling rate in water. The resulting data and graphs can be used for the prediction of porosity and permeability changes inside an LCM mold while conducting the mold-filling simulations.

5. REFERENCES

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