CELLULOSE NANOFIBER AEROGELS AS PREFORMS IN VACUUM INFUSION

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Introduction

There is a growing interest in finding renewable alternatives to the more commonly used reinforcement materials in composites. One widely studied candidate is cellulose nanofibers (CNFs). They are nanoscale cellulosic fibers with many favorable properties such as high modulus and strength and low density [1]. The raw material for CNFs is widely available since they are processed from cellulose, the most abundant organic polymer on Earth present in cell walls of plants.

One method to utilize CNFs in composites is to use them to make paper-like sheets, often called nanopapers, and then use the sheets as preforms in composite preparation. Strong composites have been prepared by impregnating cellulose nanopapers with thermosetting resins [2]. However, the fiber network in nanopapers is very dense, with nanoscale porosity, and is thus very difficult to infuse with a polymer. The porosity can be increased with various solvent exchange methods [3] but to make the impregnation easier, it is necessary also to be able to increase the pore size.

A promising way to achieve this is to use freeze casting (also called ice templating or unidirectional freezing) as a means to prepare porous and low-density CNF networks called aerogels [4]. In freeze casting, a CNF water suspension is placed inside a mould and gradually frozen through the bottom of the mould. During the process, ice crystals are formed that grow vertically from the bottom to the top and push the CNFs into the spaces between the crystals. The ice can then be sublimated from the sample in a freeze dryer with the aid of vacuum. This leads to a self-standing foam-like material with a unidirectionally aligned and porous CNF structure resembling a honeycomb (Figure 1). The pore size is in the micrometer scale and can be varied by varying the freezing rate, with slower freezing leading to larger pores. An idealized pore has a hexagonal cross section due to the hexagonal geometry of ice crystals but the actual shape varies as can be seen in Figure 1 b.

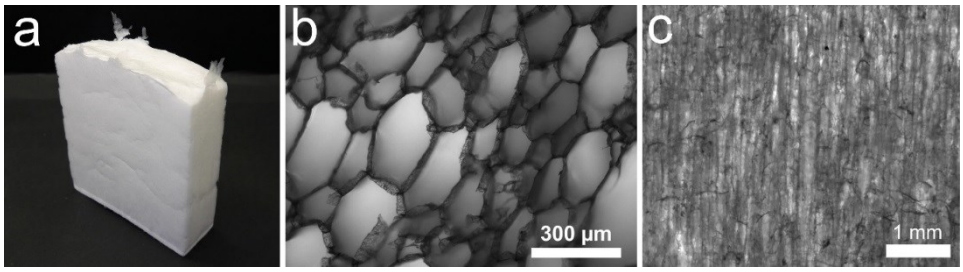

Figure 1: *CNF aerogels. (a) A photograph of a typical CNF aerogel specimen. Optical microscope images of (b) horizontal (perpendicular to the freezing direction) and (c) vertical (parallel to the freezing direction) cross sections of the aerogel inner structure.*

Vacuum infusion of cellulose nanofiber aerogels

We have developed a processing method that utilizes CNF aerogels as preforms in conventional vacuum infusion process [5]. The porous structure of the aerogel is filled with a low viscosity thermosetting resin, such as epoxy, to obtain a composite material with CNFs as the reinforcement phase (Figure 2). The processing route closely resembles the ones used for glass or carbon fiber composites, the greatest difference being the nanometer scale of the fibrous raw material and the continuous and monolithic nature of the preform structure in our method. The capability of CNFs to self-assemble due to intermolecular hydrogen bonding, and thus to form strong paper-like structures, plays a major role in determining the properties of such a three-dimensional architecture.

The CNFs used in the aerogels are prepared from bleached softwood kraft pulp by mechanical grinding, during which the shear forces of the grinding stones fibrillate the larger cellulose fibers into nanofibers. The resulting CNF water suspensions are then either diluted or concentrated to a desired consistency and frozen in a Teflon mould that has a copper bottom plate. The bottom plate material has been chosen to maximize the heat transfer between the suspension and the freezing source. The freezing sources used include liquid nitrogen and a dry ice/acetone solution, out of which liquid nitrogen has proven to be more convenient and has been used exclusively after the initial experiments. The freezing rate of the CNF suspension can be controlled with a PID controller and a heating element that have been attached to the freezing system. This process, as already mentioned, then results in an aerogel with a structure consisting of adjacent micrometer scale pores separated by sheet-like CNF walls. The aerogel structure can be filled by infusing the pores with a thermosetting resin (Figure 2 b).

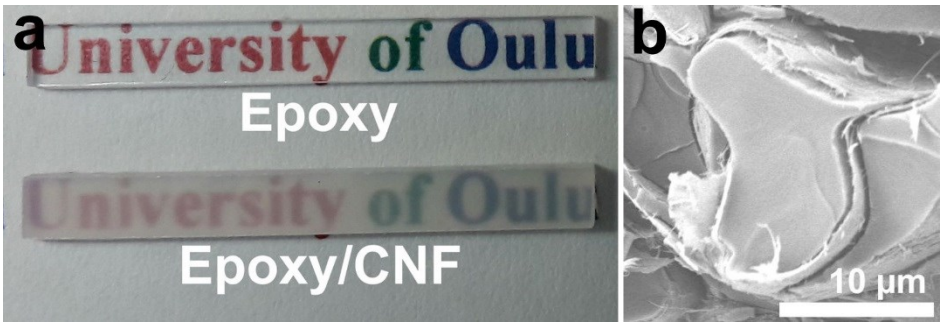

Figure 2: *Epoxy/CNF composites. (a) A photograph showing 25 mm long epoxy/CNF composite and neat epoxy specimens. (b) An FE-SEM image of a horizontal (perpendicular to the aerogel freezing direction) fracture surface of a composite specimen revealing a resin-filled aerogel pore. The composite sample shown in the figure has a fiber content of approximately 12 wt%.* **(***Please note that the resin-filled pore shown in (b) has a smaller diameter than the ones seen in Figure 1 b, as the aerogel used in this particular composite sample was frozen without controlling the freezing rate, resulting in a fast freezing and thus a smaller average pore size.)*

The method has proven to be a promising way of utilizing the strong network-forming tendency of cellulosic nanoparticles in composite materials. The CNF aerogels endure the forces caused by both the compaction and the flow of the resin during the infusion process. The resulting composite materials have also shown significantly improved mechanical properties when compared to neat epoxy resin. Measurements are underway to determine the permeability of the material at various degrees of compaction and to reveal the relationship between the infusion time and the processing conditions, such as the temperature of the resin and the vacuum pressure applied to the infusion system. In addition, the influence of using coupling agents, such as various silane-based chemicals, on the infusion process itself and on the properties of the resulting composites is being studied.

Acknowledgements

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