

Cellulose nanofiber aerogel production and applications

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Abstract

Aerogels are highly porous solids formed by replacing the liquid in a gel by air, without changing the original structure. The present cellulose aerogels are made by sublimating the water from a colloidal suspension of cellulose nanofibers. The nanofibers form three-dimensional networks, crosslinked by hydrogen bonds bridging the surface hydroxyl groups and also by mechanical entanglements between nanofibers. Although the studies on aerogels from cellulose nanofiber hydrogels by freeze drying reported so far had produced small samples, improved cooling techniques that produces larger

samples were attempted and the obtained cellulose nanofiber aerogels were impregnated with epoxy resin to fabricate composites. The highly porous structure allowed complete impregnation of resin and translucent composites were produced. The modulus of composites was increased in relation to neat epoxy, but due to high brittleness the ultimate strength was decreased. This is likely caused by nanofiber agglomerations of uneven pore sizes acting as stress concentrators. The evaluation of the mechanical properties of composites serves as an indirect way to assess the quality of the aerogels produced.

Keywords:

cellulose, aerogel, nanofiber, composite

Introduction

Cellulose is the most abundant polysaccharide on Earth and is the main constituent of the structural framework of the fiber cell wall of higher plants. Plant fibers are composites comprised of thin cellulose nanofibers embedded in a matrix of hemicelluloses and lignin. These nanofibers have lateral dimensions of a few nanometers, with remarkable mechanical properties of 138 GPa¹ in tensile modulus and a strength estimated to be beyond 2 GPa. These values are similar to those of aramid fibers. Cellulose nanofibers can be extracted from plant fibers by a variety of methods², each of them delivering a

distinct cellulose morphology at nanoscale. These nanofibers are able to mutually connect by hydrogen bonds, in the same way as cellulose microfibrils are interconnected in ordinary paper. During fabrication, an aqueous fiber suspension is dewatered and during drying, the capillary forces of the intervening water being evaporated draws the fibers together, bridging them by hydrogen bonds. In the case of nanofibers, the greater number of exposed hydroxyl groups available for bonding due to the nanoscale morphology, produces much enhanced bonding forces. This percolated nanostructured paper is significantly stronger than common paper, and thus can be used as the reinforcing phase in high-strength composites³. Besides strong papers, other lower density materials can be made from cellulose nanofibers by controlling the number of nanofiber interconnecting hydrogen bonds through adequate drying methods.

One of the cellulose-based low density materials, possessing highly porous structures are known as cellulose aerogels. Aerogels are porous materials of interconnected nanostructure made from gels by replacing the liquid by gas, resulting in extremely low density solids. Such structures have low density, high specific surface area and low thermal conductivity. Materials with porosity at micro- and nano- scale made of renewable resources like cellulose have potential applications in medical, cosmetic, and pharmaceutical fields that requires biocompatibility and biodegradability, in addition to environmentally friendly packaging and insulating materials⁴.

Some early methods to produce cellulose aerogels consisted in dissolving cellulose by suitable chemical compounds followed by precipitation and subsequent supercritical drying or freeze drying to avoid collapsing the porous structure ⁵. More recent methods rely on aqueous suspensions of cellulose nanofibers, replacing the water by air through sublimation, in a process that averts the use of chemicals. In these methods, the starting material consists of a cellulose nanofiber gel, in which the water is frozen and sublimated rather than evaporated, since the action of capillary forces during evaporation would collapse the porous structure. The first report of such class of aerogels by Paakko et al. ⁶ described the fabrication from cellulose nanofiber hydrogels by freeze drying upon quick freezing by liquid propane at -180°C. The mechanical integrity after drying is accomplished by a percolated web-like nanostructured cellulose connected by hydrogen bonds and mutual entanglements. The cellulose nanofibers were produced by a unique method of enzymatic pre-treatment and mechanical fibrillation by a microfluidizer ⁷. Sehaqui et al. ⁸ produced tough aerogels using similar cellulose nanofibers, by freezing the suspensions with liquid nitrogen and freeze-drying. The density was tailored by changing the nanofiber concentration in the initial suspensions, resulting in structures with mechanical properties superior to other hybrid materials such as clay aerogel/ cellulose whisker nanocomposites, epoxy/clay aerogels, polymer/clay/nanotube aerogels, and polymer/silica aerogels at comparable densities.

In this study, a similar protocol was adopted, with the exception that we used commercially available nanofibers in dilute aqueous suspension. These nanofibers are produced by a high pressure homogenizing method^{9,10} as follows. A pulp fiber slurry, the raw material of ordinary paper, is mechanically treated by several passes through a disk refiner up to the point when the fibers cell wall is broken down into bundles of nanofibers. Subsequently, the slurry is introduced in a device called high-pressure homogenizer, in which it is pumped at high-pressure through a spring-loaded valve that reciprocates opening and closing in succession. The fibers are accelerated through a tiny slit colliding against an impact ring, subjected to a sudden pressure drop and expansion. The slurry is passed several times through the valve, and the combination of impact, shear, and pressure drop fibrillates the fibril bundles into tiny nanofibers. However, as the process is exclusively mechanical, the morphology is not as homogeneous as the one obtained by enzymatic treatment and microfluidizer described above. The diameter of fibrils has a broad distribution, ranging from tens of nanometers to a few micrometers. Nonetheless this morphology is readily available and is intended to be used in food, cosmetics, and medical products.

This study aimed to produce large cellulose nanofiber aerogels by a more accessible method, avoiding the use of liquid nitrogen as refrigerant, thus lowering the cost and still being environmentally friendly. The dispersion of nanofibers in water and the freezing method were carefully selected to obtain homogeneous structures throughout

the aerogel, as differences in cooling speed along the parts of bigger samples produce different pore sizes. The best aerogels obtained had a web-like structure of interconnected cellulose fibrils similar to bacterial cellulose. The optimized protocol enabled the fabrication of large samples of about 12 cm in diameter that were impregnated with epoxy resin to produce composites. Even though the mechanical properties of the composites were not good, they were intended as a means to assess the quality of the aerogels produced.

Experimental

Materials

Cellulose nanofibers consisted of a commercially available morphology, trade name Celish KY-100G (Daicel Corporation, Japan) consisting of a 10 wt% fibril content slurry. Epoxy resin NEOPOL 8250LP (Japan U-PICA Company, Ltd., Japan) and curing agent methyl ethyl ketone peroxide were used to fabricate composites.

Equipment

To obtain the cellulose nanofiber aqueous suspensions, dispersion was accomplished by a household blender Vitamix TNC 5200 (Vitamix Corporation, USA) or by a magnetic stirrer HS-1D (AS ONE Kabushiki Kaisha, Japan). Ethylene glycol-based antifreeze and an ultra-low temperature freezer Sanyo MDF-C8V (Sanyo Electric Co. Ltd., Japan)

were used to freeze the nanofiber suspensions. A desk top type freeze dryer Eyela FDU-1200 (Tokyo Rikakikai Co., Ltd., Japan) was employed for freeze drying.

Cellulose nanofiber aerogel fabrication

The cellulose nanofiber suspension was prepared by diluting the Celish slurry to 1 wt% fibril concentration, and the dispersion was accomplished by a domestic blender for 1 hour or by a magnetic stirrer for 6 days without temperature monitoring. Suspensions were frozen with liquid nitrogen or by placing in an ultra-low temperature freezer at -50°C. Different combinations of dispersion/freezing, depicted in Table 1, were tested to determine the optimal condition.

Table 1. Cellulose nanofiber suspension preparation and freezing conditions

Sample	Dispersion method (time)	Freezing method	Pre-freezing temp.
1	Blender (1h)	Freezer (-50°C)	Room temp.
2	Blender (1h)	Liquid nitrogen	Room temp.
3	Blender (1h)	Liquid nitrogen	0.3°C
4	Blender (1h)	Antifreeze (-50°C)	0.3°C
5	Magnetic stirrer (6 days)	Liquid nitrogen	0.3°C
6	Magnetic stirrer (6 days)	Antifreeze (-50°C)	0.3°C

Scanning electron microscopy

The microstructural morphology was observed by a field emission electron microscope Hitachi S-4700 (Hitachi High-Technologies Corporation, Japan). Samples were sputter-coated with platinum to avoid charging.

Results and discussion

To ensure a good dispersion of the cellulose nanofibers in the aqueous suspensions, two dispersion methods were attempted. The suspensions were agitated by a household blender in order to accomplish faster dispersions, whereas a magnetic stirrer was used for slower agitation. The dispersion of suspended nanofibers accomplished by a blender apparently delivered poorer aerogels than those obtained by slow stirring for several days. The difference between dispersions accomplished by blender versus stirrer is not obvious since the blender treatment may be possibly contributing to fibrillate the thicker fibril bundles in the original commercial nanofiber. Thus, the blender agitation would result in a cellulose morphology different from the original one. But a long and gentle agitation seems to be more appropriate as a way to attain good dispersion as reported by Takagi and Asano ¹¹, and the stress-strain curves of tensile test of the resulting composites (Fig. 8) show a slightly tougher composite when nanofibers were dispersed with the magnetic stirrer.

The freezing stage is considered to be the critical step that influences the aerogel structure the most. The cooling speed should be maintained constant throughout the sample to ensure the formation of evenly sized ice grains. These grains will generate the tiny cavities of the aerogel when water is sublimated. Concomitantly, the nanofibers at the interstices of the ice grains should be percolated so that they will be connected by hydrogen bonds to enable the physical integrity of the aerogel. The first attempt corresponding to Sample 1 in Table 1, was by directly placing the nanofiber suspension container inside a freezer set at -50°C . The obtained aerogel had pores big enough to be observed by visual inspection, probably as a consequence of slow cooling speed. Hence, in order to speed up cooling, freezing was performed dipping the cellulose nanofiber suspension container in liquid nitrogen, and subsequently freeze dried (Sample 2, Table 1). The fast cooling from ambient temperature down to liquid nitrogen temperature resulted in aerogels that broke into pieces upon demolding, as shown in Fig. 1. For the next trial, to achieve a faster cooling rate, the suspension was first brought to temperature just above the freezing point of water, and frozen by liquid nitrogen (Samples 3 and 5, Table 1). The aerogels still had not enough mechanical integrity and presented big cracks along the sample (Fig. 2). It was observed that during freezing, when the container with the suspension is put in contact with liquid nitrogen, the latter boils at the interface with the container and forms a gas layer that hinders heat transfer. Despite the extremely low temperature of liquid nitrogen, the phase change at -196°C

showed to be a disadvantage as a way to effectively cool down the sample from a much higher temperature.

As the phenomenon described above is difficult to avoid, a different freezing protocol was then adopted. After pre-cooling to near water freezing temperature, the container with the nanofiber suspension was dipped in an antifreeze liquid previously cooled down to a temperature of -50°C by placing it inside a freezer. As the antifreeze acts as a heat conductor, the cooling rate of the sample is faster than if it was just placed in the freezer. By this cooling method, integral pieces of cellulose nanofiber aerogel larger than 10 cm in diameter were obtained (Fig. 3), and when combined with a slow dispersion of nanofibers by a magnetic stirrer, a significantly improved microstructure was obtained (Fig. 4). The observed nanofibers are similar to the morphology of the original Celish depicted in Fig. 5, indicating that the nanofibers did not collapse, and were kept individualized.



Figure 1. Aerogel prepared from cellulose nanofiber suspension frozen by liquid nitrogen from ambient temperature.

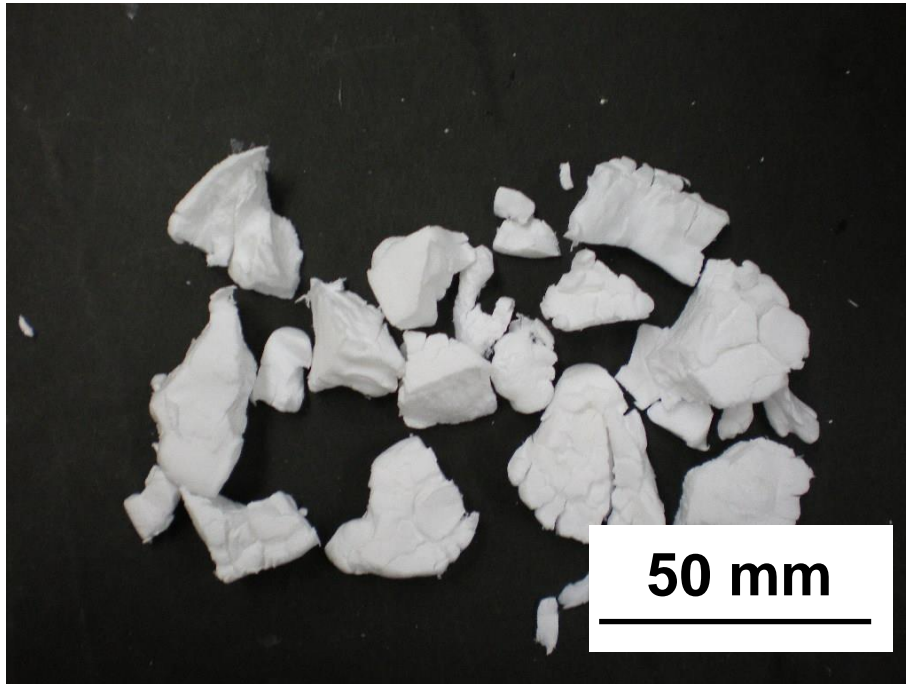


Figure 2. Aerogel prepared from cellulose nanofiber suspension frozen by liquid nitrogen from near water freezing point.

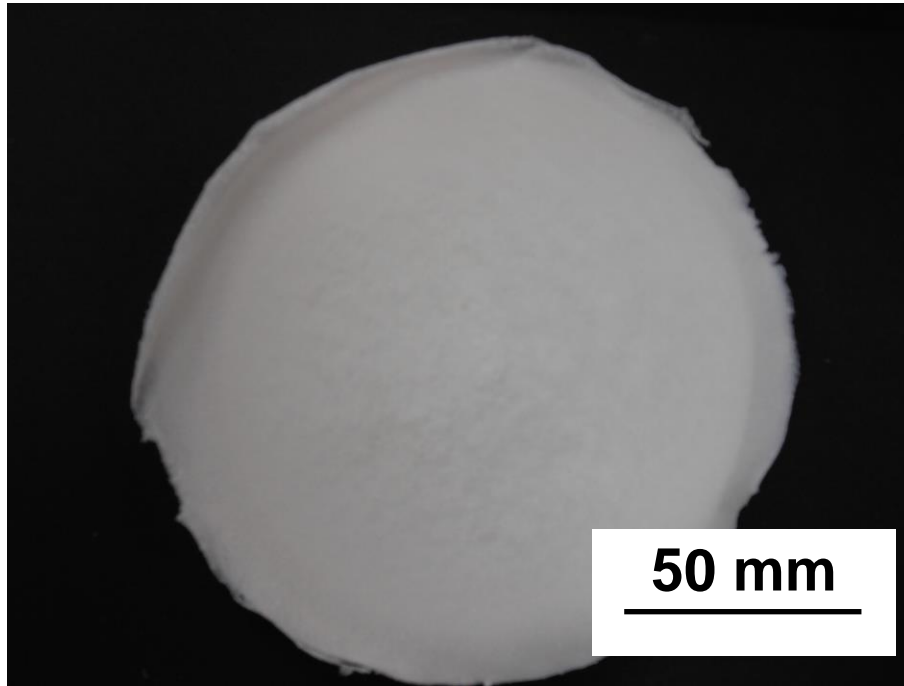


Figure 3. Aerogel prepared from cellulose nanofiber suspension frozen by antifreeze and ultra-low temperature freezer from near water freezing point.

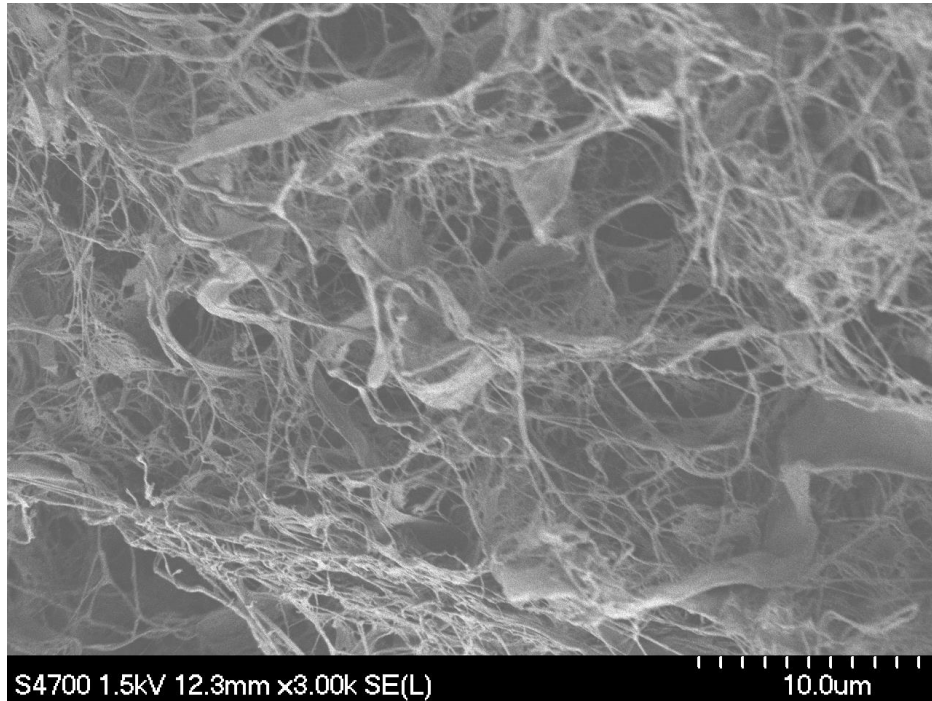


Figure 4. SEM image of aerogel prepared from cellulose nanofiber suspension frozen by antifreeze and ultra-low temperature freezer from near water freezing point.

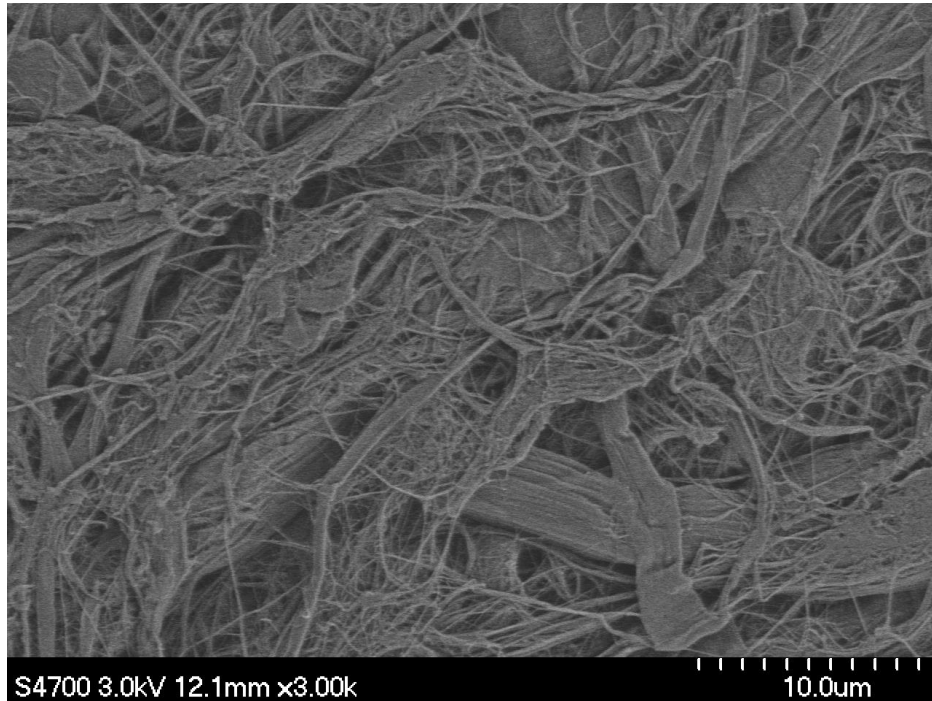


Figure 5. SEM image of commercial nanofiber morphology (Celish).

The obtained aerogels were used as reinforcing phase in composites produced by vacuum assisted resin transfer molding (VARTM). The aerogel was placed inside an evacuated chamber and epoxy resin mixed with hardener was pumped into. The aerogel was homogeneously impregnated as seen in Fig. 6, indicating that the aerogel pores were interconnected. The obtained composite is depicted in Fig. 7. The nanofiber content of composites was 8.5 wt% and after post curing, the composites were subjected to tensile test. The typical stress-strain curves are presented in Fig. 8. The tensile modulus of composites increased relative to neat resin, however, the tensile strength and

strain at fracture were drastically reduced, indicating the presence of nanofiber agglomerations or uneven pore sizes in the aerogel that acted as stress concentrators in the composites. As the observation by electron microscopy is confined to small portions of the aerogel, the detection of nanofiber agglomerations and pore size differences at a macroscopic level is limited. Fig. 9 shows a low magnification SEM image of the fracture surface of composites, where apparently smooth resin-rich spots can be seen (bigger pores of aerogel filled by resin) along fiber-rich portions. By evaluating the strength of composites obtained from the aerogels, it is possible to indirectly infer the presence of inhomogeneities in the whole structure.

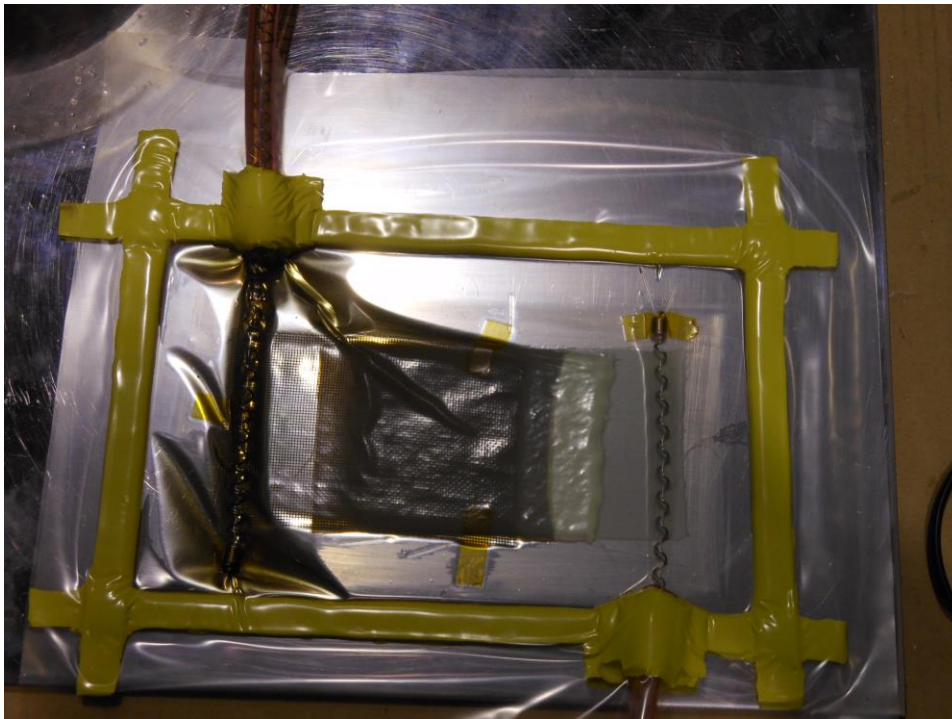


Figure 6. Cellulose nanofiber aerogel being impregnated with epoxy resin by VARTM.



Figure 7. Cellulose nanofiber aerogel/epoxy composite.

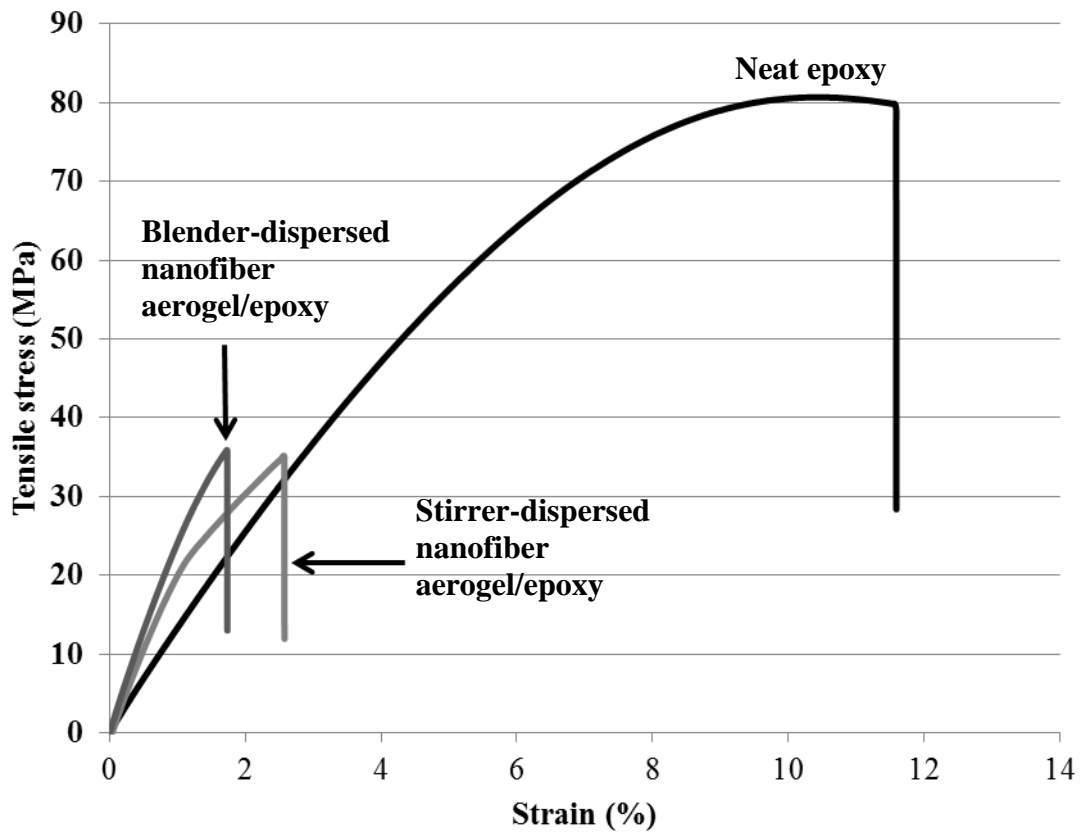


Figure 8. Tensile stress-strain curves of composites made by impregnating cellulose nanofiber aerogels with epoxy resin compared to the neat epoxy.

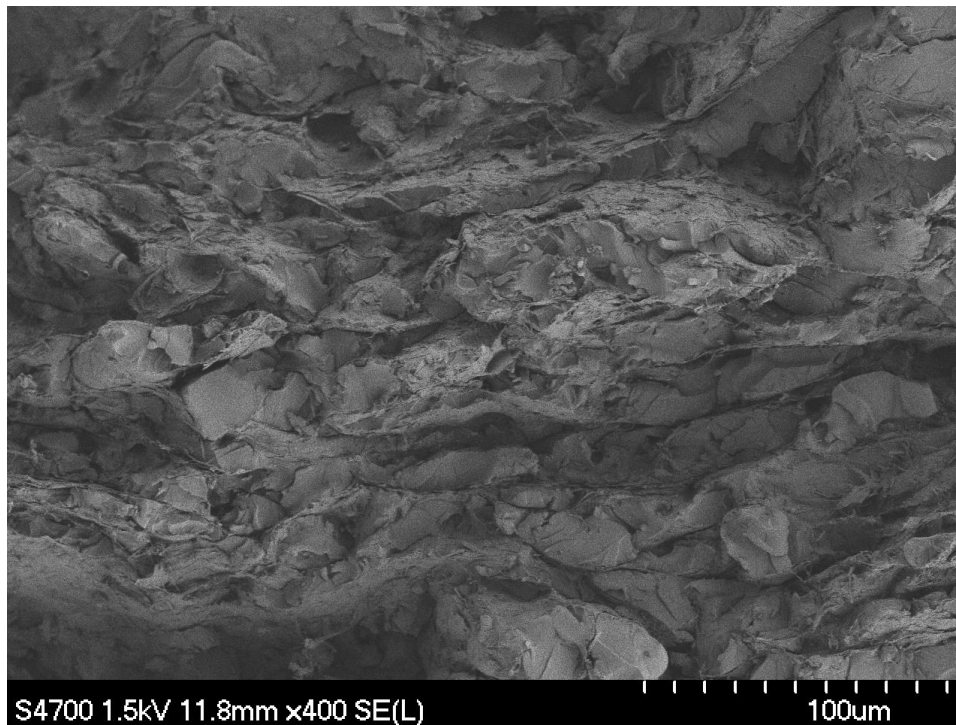


Figure 9. Fracture surface of the cellulose nanofiber aerogel/epoxy composite after subjecting it to tensile test.

The optimization of the aerogel preparation protocol is still under way, through improvements in the freezing stage to achieve faster and more uniform cooling rates. As the mechanical properties of the composites indicate, the structure of aerogels still contains irregularities as agglomerated nanofibers of uneven pore sizes. An adequately sealed container for the nanofiber suspension, enabling heat transfer through both top and bottom sides by complete immersion in the antifreeze liquid, would result in more homogeneous microstructures. Percolated networks of cellulose nanofibers in aerogels

are sought as potential reinforcing phase for composites as porosity allows easy impregnation with matrix resins and ensures good nanofiber dispersion, what is much more difficult by direct mixing or compounding.

The percolated structure formed by interconnected cellulose nanofibers by hydrogen bonds has the advantage of not requiring any kind of adhesives, making the aerogel made of pure cellulose. Due to the environmentally friendly process, which is based solely in water, and the porous structure made up of nanofibers, we are considering the use of these aerogels as high efficiency particulate air (HEPA) filter elements. The addition of chitosan nanofibers would give antibacterial property to the aerogel, giving an extra functionality to these filters.

Conclusion

In this study, cellulose nanofiber aerogels were obtained from commercially available nanofiber aqueous suspensions by sublimation of water by freeze drying. The aim was to produce cellulose aerogels by a simple and cost effective method to widen its potential applications, eventually finding use as composites framework or filtration media. The optimization of nanofiber dispersion and cooling rate enabled the fabrication of large aerogel samples. The use of antifreeze as a heat conductor to enhance cooling speed, in addition to a pre-cooling of the suspensions to near freezing point, produced aerogel samples with sufficient mechanical integrity and homogeneous structure of

networked cellulose nanofibers connected exclusively by hydrogen bonds. The use of water as the sole processing medium and the structure consisting of pure cellulose nanofibers make these aerogels suitable for possible applications in air filtration once improvements in pore size and nanofiber dispersion are realized.

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