

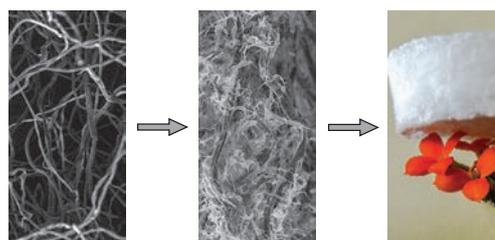
Dimensionally stable aerogels from cellulose mechanically treated to a moderate microfibrillar degree

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Cotton was subjected to moderate treatment using combined grinding and freeze-thawing to transfer initial fibers into microfibrillated cellulose (MFC) form without preliminary chemical oxidation. The following freeze-drying of solutions of dispersed MFC resulted in cellulosic aerogels with low density ($0.02\text{--}0.07\text{ g cm}^{-3}$) and sharply increased mechanical strength and dimensional stability both in dried and wet states.



Cellulose is most abundant, being at the first place among biopolymers, renewable and inexpensive.^{1–4} As all polysaccharides, it is biodegradable and biocompatible.^{5,6} Dried cellulosic fibers have high values of elastic modulus and toughness but their hardness drops by a factor of about 100 in water.⁷ When being dried back, cotton wool, for example, forms stiff solid mass that was mentioned in the first work on the preparation of aerogels in 1931.⁸ As being immersed in water, they did not hold their shape, shrinking irreversibly. A problem of dimensionally stable cellulose aerogels is still of current importance.^{9–11}

It is known that paper made of cellulose pulps after its mechanical treatment (beating) possesses increased tensile strength and stiffness.^{3,12–14} The effect was related to the defibrillation usually called fibrillation of cellulosic fibers. Upon very intense mechanical treatment by a high-pressure milk homogenizer, an unstable aqueous dispersion of kraft pulp was transferred into a translucent gel-like state¹⁵ due to disintegration of initial fibers into micro/nanofibrils to afford microfibrillated cellulose (MFC). The latter is also called the nanofibrillated cellulose and nanocellulose because of the fibril diameter in the nanometer range.

The MFC, when being admixed, provided a significant improvement of the mechanical and consumption properties of paper.^{3,16} The demonstration of this effect was ideally suited for preparing aerogels.¹⁷ Characteristic features of these materials are very low density and high porosity. Cellulose used for their fabrication has advantages over inorganic materials (like silica), providing the aerogel flexibility and less brittleness.^{17,18} Furthermore, the cellulosic fibrils can be functionalized *via* mineralization¹⁹ or well-developed reactions of the carbohydrate chemistry.

Common method of MFC preparation includes a very intense mechanical treatment.¹⁵ For example, in ref. 20 aerogels were prepared after 40 grinding cycles. It needs large energy consumption, which is notably increased with the each treatment. To facilitate the disintegration, cellulose is initially pre-treated. Its oxidation by sulfuric acid or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)^{16,18,21} as well as enzymatic hydrolysis by endoglucanases¹⁷ are applied. The disadvantage of these pretreatments is a decreased molecular weight of polysaccharide and, as a result, deteriorated mechanical properties.

Here, the MFC was prepared without chemical treatment using combination of grinding and freeze-thawing, which allowed us to reduce the number of cycles. Cellulose aerogels fabricated from this MFC are dimensionally stable in wet state and solutions that offers a means of their treatment for modification and functionalization. The structure and mechanical properties of the obtained MFC have been studied.

A piece cut from one of aerogels prepared from the MFC with the thickness of a little more than 10 mm is shown in Figure 1(a).[†] Obviously, it is rather homogeneous. Figure 1(b) presents a picture of aerogel which we attempted to make from non-MFC. A problem was with the preparation of an initial solution with homogeneously dispersed cellulosic fibers. They associated in clots which could be separated into the individual fibers only by hands, however they were clotting again when being placed in a solution. Upon immersion in water, this aerogel did not hold its shape, disintegrating into clots and some fibers. In contrast to this, samples prepared from MFC were stable [Figure 1(c)]. Some small swelling was observed because of absorbing water. When being wetted by restricted amount of water, aerogels shrank for 10–20%.

Aerogelic materials prepared from MFC had very low density varied from 0.02 to 0.07 g cm^{−3} depending on the MFC concentration in the initial solution. The BET surface area was around 100 m² g^{−1}. Figure 1(d) shows a sample with the density of 0.03 g cm^{−3} placed on flowers, which is so light that petals of flowers are almost not bent.

The microfibrillation brought about a sharp increase in the mechanical strength of aerogels, which was examined by the

[†] Pure cotton-wool without fluorescent additives bought in a local pharmacy was washed by acetone, chopped into pieces (5–6 mm), mechanically treated by the Laboratory High-Speed Rotor Mill/Grinder CIT-FW100 (Coll-Ibt Tech) in combination with freeze-thawing 5 times, dispersed in deionized water, frozen and subjected to common freeze drier using the Laboratory Freeze Dryer Stellar (Millrock). The morphology of aerogels was examined by the scanning electron microscopy (EVO-40, Carl Zeiss). Their surface was covered by platinum layer. Mechanical compression measurements were performed with a Haake Mars III rheometer (Thermo Scientific). Cell with plate-and-plate geometry was equipped with plates (30 mm in diameter) having serrated surface.

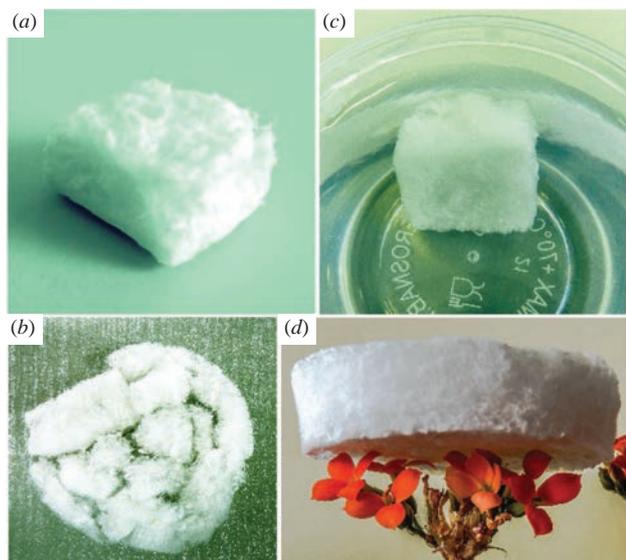


Figure 1 Photographs of (a) MFC aerogel, (b) aerogel prepared from cotton, (c) MFC aerogel placed in water and (d) MFC aerogel placed on flowers.

compression testing [Figure 2(a)]. The Young's modulus or modulus of elasticity found from the initial linear (elastic) region of the stress–strain curve was 15 kPa for the MFC aerogel and only 1.2 kPa for the cotton one. The difference in their mechanical strength exceeds an order of magnitude [Figure 2(b)]. After wetting, one may see a sharp drop in the mechanical strength of aerogel made from MFC. The Young's modulus for the wetted sample was 1.5 kPa that is at the level of untreated cotton.

To reveal the reasons for the substantial improvement of the mechanical properties and the dimensional stability of aerogels after the microfibrillation, we studied the samples by scanning electron microscopy (SEM) (Figure 3). Initial cotton consists of fibrils with smooth surface; there are contacts between them but their number is not so much [Figure 3(a)]. An image of MFC aerogel [Figure 3(b)] and its comparison with that of the cotton one demonstrate that the microfibrillation resulted in a substantial modification of cellulosic fibers. They are surrounded by vast majority of micro/nanofibrils like head of hair. These fibrils are entangled and attached together, numerous contacts serving as cross-links in the three-dimensional network. This gains an insight into the increased mechanical strength and dimensional stability of aerogels from MFC. For example, the addition of microfibrils like fibers in cellulosic aerogel [Figure 3(b)] in a polyvinyl alcohol matrix consisting of linear macromolecules led to a significant

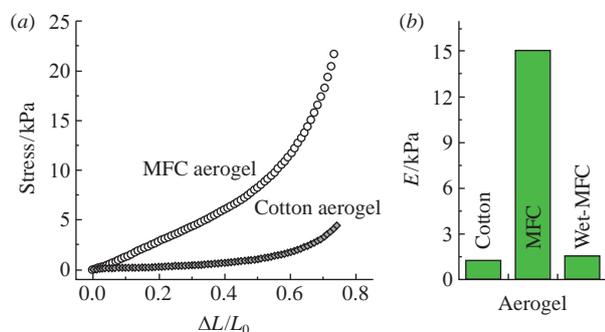


Figure 2 (a) Compressive stress vs. strain diagram for cotton and MFC aerogels. (b) Young's moduli of cotton and MFC (dry and wet) aerogels.

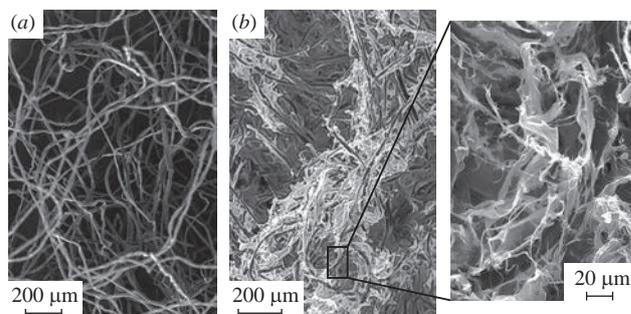


Figure 3 SEM images of (a) cotton aerogels and (b) MFC aerogels. Insert shows a magnified image of a part of MFC aerogel.

increase of stiffness.²² In an opposite model experiment, where stiff glass rods were added into paper,²³ the strength was reduced dramatically that was related to the decreased number of entanglements. Therefore, our observation of the tremendous growth of contacts between entangled micro/nanofibrils after the microfibrillation explains the sharply increased mechanical strength and dimensional stability.

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