

Research Letter

Ultralight-Weight Cellulose Aerogels from NBnMO-Stabilized Lyocell Dopes

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Cellulose aerogels are intriguing new materials produced by supercritical drying of regenerated cellulose obtained by solvent exchange of solid Lyocell moldings. From *N*-methylmorpholine-*N*-oxide solutions with cellulose contents between 1 and 12%, dimensionally stable cellulose bodies are produced, in which the solution structure of the cellulose is largely preserved and transferred into the solid state. The specific density and surface of the obtained aerogels range from 0.05 to 0.26 g/cm³ and from 172 to 284 m²/g, respectively, depending on the cellulose content of the Lyocell dopes and regeneration procedure. A reliable extraction and drying procedure using supercritical carbon dioxide, the advantageous use of NBnMO as stabilizer for the Lyocell dopes, and selected physical properties of the materials is communicated.

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1. INTRODUCTION

Aerogels are highly porous, very lightweight materials that consist of only about 1–15% of solid material [1, 2] having usually a very large specific surface. Even though aerogels are still being produced mainly from silica, they can also be derived from metal oxides, carbon, or special synthetic polymers [3, 4]. Aerogels are built of nanoparticles, linked to each other forming chains and stable three-dimensional networks, the interchain distances typically being in the order of 10–100 nm. Due to these structural features, aerogels have been mainly investigated as thermal insulators [5], supercapacitors, storing media for gases, especially for fuel cells [6], or as scavengers for even smallest space dust particles [7].

Cellulose aerogels are intriguing materials as they feature properties similar to their inorganic counterparts, with the additional advantages and characteristics of the regrowing biopolymer cellulose. While common silica aerogels are generally produced by sol-gel processes, this technology is not applicable to cellulose aerogels, as the initially precipitated porous cellulose structures immediately collapse upon contact with protic media and conventional drying. Cellulose-

derived aerogels have been produced by Tan et al. in 2001 [8] and Fischer et al. some time later [9]. Both approaches started from cellulose acetate additionally cross-linked by polyisocyanates and required complex gelation procedures besides long gelation times of around seven days. In 2004, Jin et al. [10] were the first to use cellulose in the nonderivatized form; their approach produced film-like material of less than 1 mm thickness. Innerlohinger et al. [11] and our group [12] applied also nonderivatized cellulose for aerogel production, but employed the procedure of directly dissolving the cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) as it is commercially used for the production of Lyocell fibers. Although dimensionally stable cellulosic bodies were obtained with this approach, the regeneration procedure was hitherto rather lengthy and somewhat erratic with regard to the quality of the products, that is, the size and stability of the desired micropore structure and the chemical purity. Cross-linking agents or polar protic solvents involved in the extraction so far were shown to be unsuitable. Additionally, propyl gallate as the stabilizer used [13, 14] and its colored oxidation and degradation products could not be removed tracelessly by the extraction procedure.

2. EXPERIMENTAL

Scanning electron microscopy was performed on a Phillips XL 30 ESEM (Environmental Scanning Electron Microscope). The samples were sputtered with gold and mapped at an acceleration voltage of 10 kV. Using this setup, a 2000-fold magnification was possible.

Specific surface and porosity of the cellulose aerogels were calculated from the BET isotherms obtained from N_2 -adsorption/desorption experiments at 77 K using a Micrometrics ASAP 2020 analyzer.

2.1. Preparation of the cellulose solutions and regeneration of the cellulose

N-methylmorpholine-*N*-oxide monohydrate containing 1 wt% of *N*-benzyl-morpholine-*N*-oxide (NBnMO) was heated to 100°C in a glass vial until a clear melt was obtained. Cellulose corresponding to a final content of 3%, 5%, 10%, and 12%, respectively, related to NMMO was then added under stirring with mechanical shear force until a clear, viscous melt was obtained. At cellulose concentrations above 10%, the temperature was increased to 120°C, care should be taken not to exceed 130°C solution temperature due to the instability of NMMO. The cellulose dope was poured into the desired form by molds and cooled to room temperature. NMMO/cellulose moldings were regenerated by adding ethanol or DMSO or mixtures of both (or 10 ml of H₂O for comparison) in an end-over-end-mixer for 24 hours. Then the regeneration was repeated with another 10 ml of the corresponding solvent for another 24 hours. In the case of regeneration with H₂O, the water in the tube was replaced with ethanol (10 ml). In order to avoid the presence of any water during supercritical drying, the solvent exchange step was repeated 3 times.

2.2. Supercritical drying to produce cellulose aerogels

Supercritical drying was performed on a laboratory scale high-pressure apparatus. The wet (ethanol or DMSO), regenerated cellulose was placed into an autoclave (Alltech Grom GmbH, Germany) which was filled with the respective solvent in order to prevent uncontrolled drying. The filled autoclave was placed into an oven kept at 40°C throughout, controlled by a Julabo LC4 controller. After 30 minutes of equilibration, the system was pressurized to 150 bars. Liquid CO₂, heated up to the required temperature before entering the drying autoclave, was introduced using an HPLC-pump (miniPump, TSP Thermal Separation Products, USA). After 1 hour, the outlet valve was opened and the autoclave was flushed with CO₂ for 5 hours at constant pressure. The CO₂ delivery was stopped and the autoclave was depressurized slowly.

3. RESULTS AND DISCUSSION

For practical purposes and in order to obtain stable gel objects, the starting materials for the subsequent gelation procedure should be compact, solid bodies. This basically limits

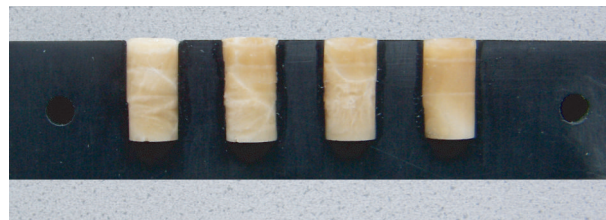


FIGURE 1: Example casting mould for the production of cylindrical stable bodies made from Lyocell dope, for subsequent regeneration and supercritical drying.

the choice of cellulose to *N*-methylmorpholine-*N*-oxide and to salt melts, which both afford cellulose solutions which are solid at ambient conditions and become tractable at elevated temperatures. The hydrated salt melts [15] were excluded for three reasons: they dissolve only rather low amounts of cellulose (up to about 3%), they are limited to relatively low-molecular weight celluloses, and they cause heavy degradation of the solute upon dissolution and further handling, that is considerable decrease of the molecular weight. NMMO was evidently superior with regard to these three points. However, it is well known as well that NMMO is a relatively strong oxidant, and cellulose solutions in NMMO tend to be unstable. This instability may be manifested in a relatively “harmless” way by introduction of oxidized groups and discoloration of the melt, but it might also result in spontaneous and noncontrollable blasts or “exothermic events” [14, 16]. Lyocell dopes stabilized with *N*-benzylmorpholine-*N*-oxide (NBnMO) [17, 18] can be safely handled, and cast into moulds at temperatures above 90°C. NBnMO acts as a sacrificial substrate, its detailed action mechanism have been published previously [18], which is removed tracelessly along with its by-products by the later extraction/drying procedure, in contrast to the commonly used propyl gallate which leaves behind difficult-to-remove chromophores on the cellulose matrix. After cooling to room temperature, the dope solidifies and can be removed from the moulds (Figure 1).

After shaping and solidification of the Lyocell dope, the solvent NMMO including the stabilizer has to be removed quantitatively by extracting the moldings with appropriate solvents. The quality of the interconnected, open-pored network of solid cellulose aerogels is an important criterion for most aerogel applications. Hence, special caution must be exercised when extracting and drying the solid Lyocell moldings since both steps can easily cause collapsing of micro- and, partially, macrostructures.

One option to avoid pore collapsing of the regenerated gel would be lyophilization where the moist sample is flash-frozen and the solvent is removed subsequently by sublimation. However, this method has not been employed due to its drawback that some degradation products of NMMO, the stabilizers (NBnMO, propyl gallate), as well as most of their by-products cannot be removed by freeze-drying.

Regeneration of cellulose can be performed with different solvents. Water—as the solvent usually used for industrial production of Lyocell fibers or films [11,19,20]—will readily cause a far-reaching loss of the initially formed

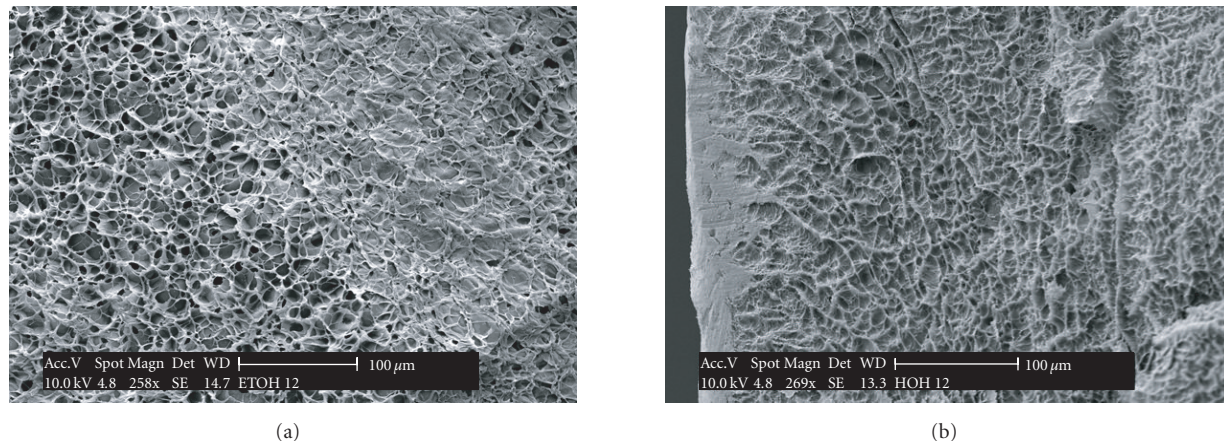


FIGURE 2: (a) ESEM pictures of cellulose aerogel, intact pore structure after ethanol regeneration and drying with supercritical CO_2 . (b) Partially collapsed pore structure after water regeneration, solvent exchange (ethanol,) and scCO_2 drying.

fine-porous, fragile cellulose solute structure simultaneous to its reorganization into the cellulose II polymorph, and requires, moreover, solvent exchange steps with solvents such as ethanol or acetone if subsequent drying of the regenerated gel with supercritical CO_2 (scCO_2) is envisaged. The regeneration with water and subsequent solvent exchange affected the pore structure of the cellulose gel to some extent (see Figure 2(b)). Thus, water/ethanol-regenerated aerogels had a distinct higher specific density of 0.09 g/m^3 after scCO_2 drying at 40°C and 100 bars compared to those cellulose bodies which were directly generated with ethanol (0.06 g/m^3) which is in accordance with previous reports [11].

DMSO is another interesting solvent for cellulose regeneration and subsequent supercritical drying since it is (1) dissolving NMMO, (2) well miscible with supercritical CO_2 , and (3) can be easily recovered under noncritical conditions. Utilization of ethanol or DMSO not only offers the advantage of a complete removal of the stabilizer (NBnMO, e.g.) and low-molecular oxidation products, but also preserves the fragile and interconnected fine-porous structure of the dry aerogel. As supercritical fluids show a continuous transition from a quasi-liquid state to a gaseous state without forming a meniscus, the solvent can be transported out of the gel without harming the pore structure by cohesion forces. An ESEM picture of an intact and faultless microporous structure of a cellulose aerogel which was regenerated with ethanol and dried with supercritical CO_2 is shown in Figure 2(a).

In order to demonstrate the superiority of supercritical drying, one gel sample was vacuum dried immediately after regeneration with ethanol instead of drying with supercritical CO_2 (Figure 3(a)). It was evident that the micropores were almost entirely collapsed after drying (Figure 3(a)) and hence, the fragile micro- and even macrostructure of this gel were largely destroyed. This effect is due to the forces occurring alongside a capillary pressure gradient at the pore walls adjacent to the solvent menisci and is most pronounced when water is used for regenerating the cellulose from NMMO moldings due to the high surface tension of water. In case of using supercritical CO_2 for removing the re-

generating solvent, such forces do not occur due to the lacking phase transition. Hence, the gel structure and the macroscopic dimension were much better retained during supercritical drying (Figure 3(b)), independently on the kind of solvent used for regeneration and solvent exchange, respectively. However, a certain volume reduction throughout the preparation process of the aerogel bodies was still observed even though it was significantly lower, and then reported by Innerlohinger et al. [11]. In the case of a 3% cellulose containing gel which was regenerated with ethanol, a remaining volume of 65–71% was measured whereas values of 25–55% were reported in the cited literature.

4. CONCLUSIONS

At temperatures of about $100\text{--}130^\circ\text{C}$, stable solutions of up to 12% cellulose in *N*-methylmorpholine-*N*-oxide were prepared using *N*-benzylmorpholine-*N*-oxide (1% rel. to cellulose) as the stabilizer. The viscous cellulose containing NMMO melts can be cast into moulds, shaped, and formed. Upon cooling to room temperature, solid bodies were obtained of which the shape was fully maintained during regeneration and supercritical drying.

With the obvious influence of the regenerating and scCO_2 drying conditions being topics of further investigations, we conclude that drying of regenerated cellulose bodies from solid NMMO dopes using supercritical CO_2 is a suitable method for producing dimensionally stable aerogels. The specific density and surface of the obtained aerogels ranged $0.05\text{--}0.26 \text{ g/cm}^3$ and $172\text{--}284 \text{ m}^2/\text{g}$, respectively, with increasing density at higher cellulose contents. Amongst the tested regenerating solvents, ethanol gives the lowest specific densities upon scCO_2 drying at 40°C and 100 bars and the highest retaining volume of about 70%.

With regard to the production of cellulose aerogels having a defined structure both in micro- and macroscale, the drying of the regenerated cellulose bodies is the limiting factor. After regenerating the cellulose with DMSO or ethanol/DMSO mixtures and subsequent drying of the

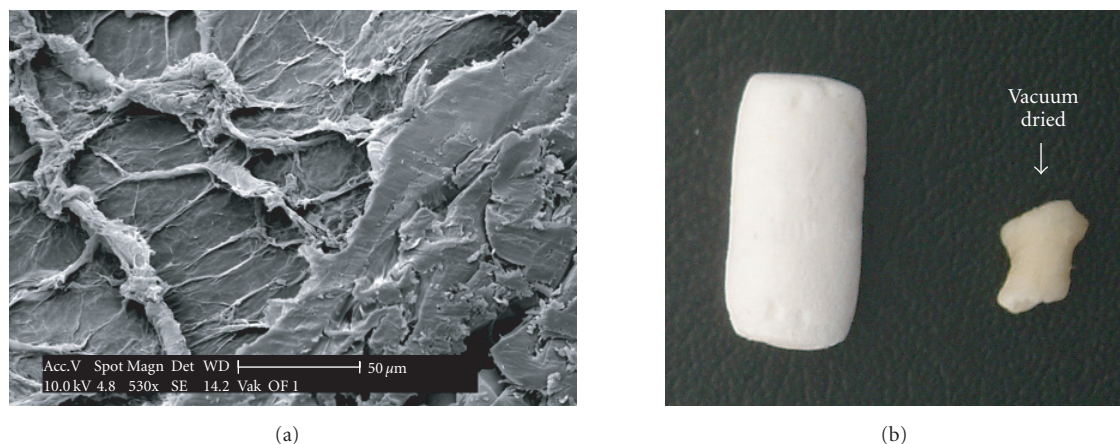
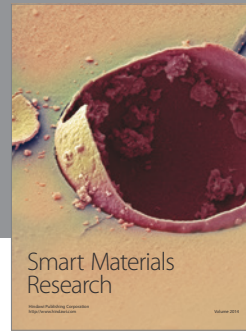


FIGURE 3: (a) ESEM picture of an ethanol-regenerated and vacuum-dried cellulose aerogel. (b) Macrostructures of cellulose aerogels regenerated with DMSO from a 3% cellulose containing NMMO dope after supercritical drying or conventional vacuum drying.

cellulose gels with supercritical CO_2 , the fragile, interconnecting fine-porous structure of the “dissolution state” is largely retained whereas conventional drying approaches fail. As the technology of supercritical drying has been explored only marginally for cellulose-based materials so far, further investigations into the influences of process parameters on the product properties are important. In future studies of our group, cellulose aerogels will be tested, for example, for drug delivery systems and drug coating purposes.

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