Synthesis and characterization of highly porous cellulose aerogels for textiles applications

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In this paper we present the synthesis and properties of ultra-light and porous cellulose aerogels in different forms: monoliths and fine spun fibers. The cellulose aerogel monoliths and fibers are prepared by dissolving microcrystalline cellulose (0.5-6 wt. %) in a hydrated calciumthiocyanate salt melt-Ca(SCN)$_2$.4H$_2$O at 110°C upon cooling the solution gels around 80°C. Washing the wet gels and regeneration of the cellulose in an ethanol bath followed by drying in an autoclave yields aerogels. The envelope densities of the samples were determined as in the range between 10-140 g/L. The microstructure was viewed with a SEM. The microstructure can be described as an open porous nano-felt with pore size ranging from 10 to 100 nm and fiber diameters of around 10-20 nm. The specific surface area and pore size distribution with nitrogen adsorption were measured with a surface area of 150-230 m^2/g. Furthermore compression tests were performed. The mechanical behavior is typical for a porous material: after onset of deformation there is a long plateau at almost constant stress. The aerogels exhibit a Poisson ratio of around zero.

Introduction

Cellulose is one of the most important natural biopolymers. Cellulose is hydrophilic, and is insoluble in water and most organic solvents. It has a complex crystalline and amorphous morphology [1]. Cellulose has fascinating properties. It is biocompatible, renewable, and biologically degradable and it has many hydroxyl groups allowing network formation by hydrogen bonds as well as chemical reactions [2].

Cellulose aerogels are solid multifunctional materials with a sponge-like porous network. They exhibit a high surface area and porosity, low thermal conductivity and low mass densities. Kistler produced a variety of aerogels from different materials, such as silica, alumina, rubber and even cellulose derivatives [2-4]. Aerogels are mainly prepared by sol-gel chemistry. Cellulose aerogels can be prepared by dissolving cellulose in suitable media, such as salt melt hydrates and ionic liquids, followed by washing and regeneration and then they can be dried by using special techniques like supercritical or freeze drying in order to preserve their solid network [2, 3, 5-7]. Several methods are described in the literature to synthesize cellulose aerogels [2, 3, 8-10]. This paper mainly focuses on synthesis of monoliths and fibers forms of cellulose aerogels based on the work of Jin and co-workers [9] and our previous works [2, 5, 11].

Experimental

a. Chemicals

All chemicals have been used without further purification. The chemicals used are calciumthiocyanate-Ca(SCN)$_2$.4H$_2$O as salt melt hydrate, with a purity of 95 % and commercial cellulose fibres (medium), both from Sigma-Aldrich, product numbers 520144 and C6288. Cellulose fibers dried in oven at 105°C before use. Absolute ethanol was used for washing and regeneration step and CO$_2$ has a purity of 99.9 % and used as received.

b. Preparation of cellulose aerogel

The preparation procedure of cellulose aerogels is shown in Figure 1. Aerogels have been produced using a standard sol-gel routine. Certain amount of calciumthiocyanate tetrahydrate is filled into a beaker. Cellulose fibers are added in different amounts (0.5-6 wt. %) and deionized water. This mixture is heated while stirring at 110°C. Dissolution of cellulose takes 10-30 min depending on cellulose concentration. When the solution becomes transparent and homogeneous the cellulose is completely dissolved. The homogeneous viscous solution is transferred to appropriate molds. Gel formation was realized while slow cooling to room temperature. To avoid crystallization the gel samples are covered with a few drops of ethanol. After gelation ethanol was added into each mold and gels were washed and regenerated in to get rid of the calciumthiocyanate salt. Washing is performed in a soxhlet apparatus for 3 days. Residual salt traces in the gel body were determined with 1 % iron (III) nitrate solution. The iron ion (Fe^{3+}) is yellowish colored and the thiocyanate ion (SCN$^-$) is colorless; however, the ion that forms from their combination, the FeSCN^{2+} ion, is colored a dark red-brown (almost blood red in color).
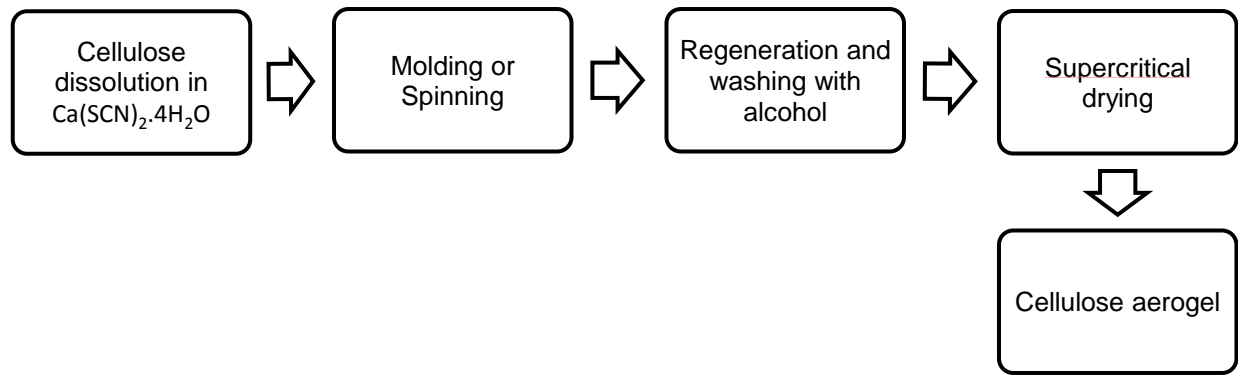
Figure 1: Preparation procedure of cellulose aerogels

c. Supercritical drying (scCO₂)

c.   Supercritical drying (scCO$_2$)

Drying with CO_2 in supercritical conditions is done within an autoclave developed at DLR.

d.   Characterization

The envelope density of the aerogels was determined by using the GeoPyc 1360 Envelope Density Analyzer. Thermal conductivity measurements were done using the Hot Disk TPS 2500S system. The specific surface area of aerogels was examined with BET method from the nitrogen adsorption in a Tristar II 3020 Surface Area Analyzer from Micromeritics. The microstructure was view by a scanning electron microscopy (SEM) with MERLIN by Carl Zeiss Microscopy. Compression tests were performed using a table top testing machine from Chatillon, TCD200-SS with a compression rate of 1 mm/min.

Results and Discussions

The aerogel monoliths shown in Figure 2 are white and tough. Figure 3 shows the density of aerogels with varying cellulose content. The density varies between 10-140 g/L with cellulose concentrations varying between 0.5-6 wt. %. There is a linear relation between density and cellulose concentration. The linear relation between aerogel density and cellulose concentration agrees well with our previous work [5]. The density of aerogel (   ) is determined by the density of pore free, massive cellulose and the volume fraction of cellulose in the aerogel. The volume fraction is related to the concentration of cellulose in the salt hydrate melt (, measured in weight percent, and the density of the salt melt hydrate (   ) which is given by
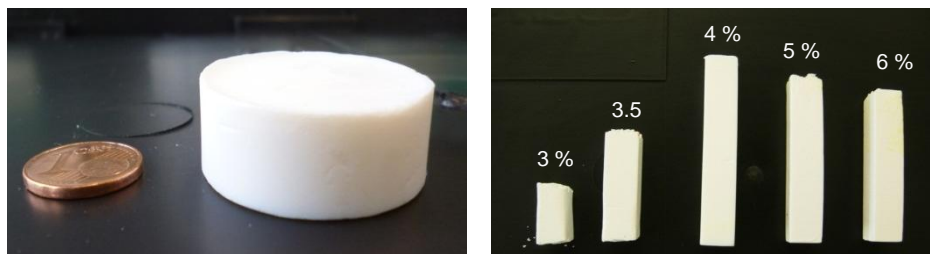

Figure 2: View of cellulose aerogels with different cellulose contents and in different shapes.

The slope of Figure 3 should agree with the density of the salt hydrate melt. It should be noticed that Jin and co-workers did not observe the linear relation between density of the aerogels and cellulose concentration. Innerlohinger et al. [3] observed a similar relation as we did, but first their data extrapolate at zero cellulose content not to zero but a finite value and second they observe a saturation at higher contents, which shows that their dissolution medium is not effective enough to separate all nanofibrils. This relation also shows that our aerogels are free from salt traces.
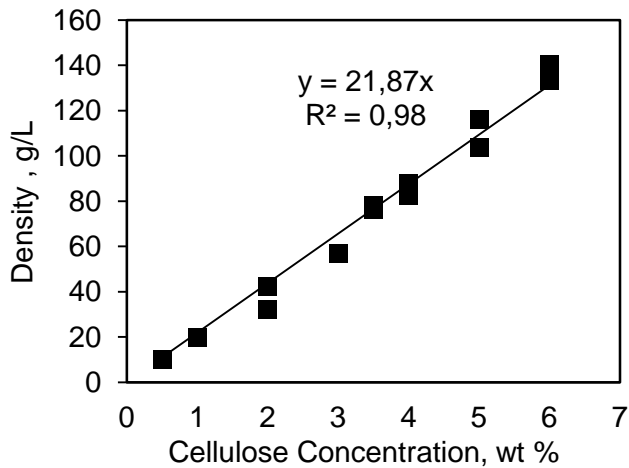
Figure 3: Envelope density of cellulose aerogels aged in ethanol

The porosity of the cellulose aerogels was measured with nitrogen gas adsorption analysis and the results are shown in Figure 4. The BET specific surface areas of cellulose aerogels is between 150-230 m^2/g as observed also by other authors [8, 9]. The isotherms can be categorized as an IUPAC type IV with a hysteresis loop in the range of 0.5–1 P/P_0, indicating the presence of meso- and macro-porous structures [12, 13]. Hoepfner et al. [5] reported a mathematical model on BET surface area of cellulose aerogels (0.5-3 % wt.). The mass specific surface area should be independent of the cellulose concentration. In this study we observed that for higher than 4 % wt. cellulose there is a slight decrease in specific surface area. In the model of Hoepfner this would indicate that the number density of nanofibril nodes increases leading to a decrease in specific surface area.

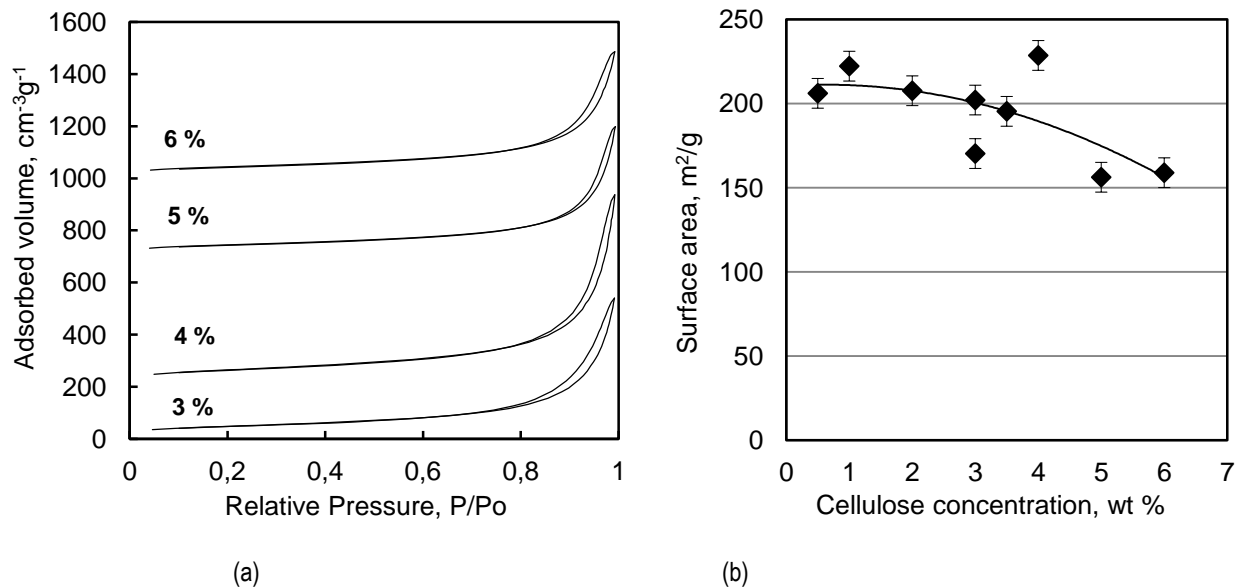(a)   (b)

Figure 4: (a) Nitrogen adsorption-desorption isotherms and (b) BET surface areas of cellulose aerogels.

Thermal conductivity of cellulose aerogels varies linearly with cellulose concentration from 0.04 to 0.075 W/m.K at atmospheric pressure and room temperature (Figure 5). At zero cellulose concentration it extrapolates to almost the conductivity of air at rest (0.032 W/m.K). According to Faessel et al. [14] the conductivity of a random 3D cellulose fiber network is mainly determined by that of the solid skeleton. Since the pores are smaller than a micron, one can assume that diffusive heat transport via the gas phase is the other important contribution. The overall conductivity therefore can be described by the weighted addition of heat conduction through the gas phase and solid state conduction through the cellulose fibers. Therefore the thermal conductivity should vary linearly with the cellulose concentration.
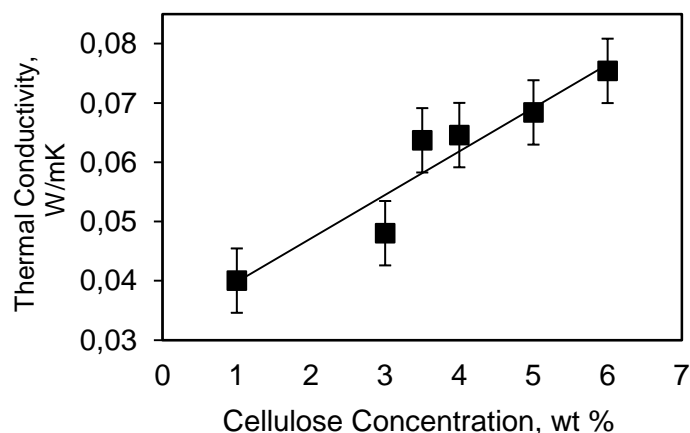
Figure 5: Thermal Conductivity values of cellulose aerogels at room temperature.

Figures 6 a, b and c show scanning electron microscopy (SEM) images of cellulose aerogel monoliths with different cellulose contents. In all cases investigated the cellulose fibrils exhibit a spongy mesh of fibers connected randomly in 3D. The fibrils have typical sizes of about 10-20 nm thickness. The pores have sizes up to a micron and are thus rather big compared to conventional aerogels.
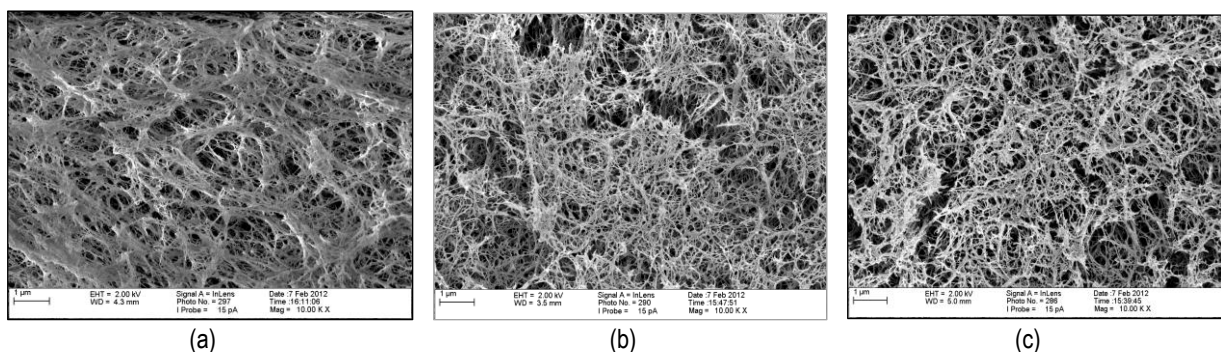

| (a) | (b) | (c) |

Figure 6: SEM images of cellulose aerogel monoliths (a) 4 % wt., (b) 5 % wt. and (c) 6 % wt. cellulose concentrations.

The mechanical behavior of cellulose aerogel is determined by compression deformation test. Both Young's modulus and the 0.2 % offset compressive yield strength are given in Figure 7. Young's modulus varies between 1.7-13.5 MPa for cellulose aerogel monoliths for different cellulose content. The modulus of the cellulose aerogel with 6 % wt. cellulose is more than four orders of magnitude higher than that of silica aerogel [15] and about 50 times higher than that of the aerogel prepared from bacterial cellulose [16]. Typical stress-strain curves drawn under compression deformation and it shows three regimes; linear elasticity, plateau where collapsing of pores occurred and densifications. The stress-strain curve obtained is similar to an elastic-plastic foam structure which is explained in detailed in Gibson and Ashby [17]. In the literature [18] on aerogels Young's modulus scales with the density in form of a simple power law   , with a power n=1.8 – 3.6 for different aerogels like silica, carbon and resorcinol aerogels. The compressive yield strength behaves in the same way with is a power law   and m=2.3-3.1. Our findings for those values are n=1.3 and m=2.2, respectively. For random fibrous networks special models for the elasticity tensor are available, like those of Pan, Chen, Seo and Backer [19] which treat effects of the fiber elasticity itself and node or contact points. Their relation for cellulose fiber networks also yields a simple power law   , but it also states that Young's modulus should increase with decreasing fiber cross section *A*. Also Poisson's ratio of cellulose aerogels was investigated. Poisson's ratio is a measure of the change in lateral dimensions on elastically loading a material. The cellulose aerogels exhibit a Poisson ratio of zero.
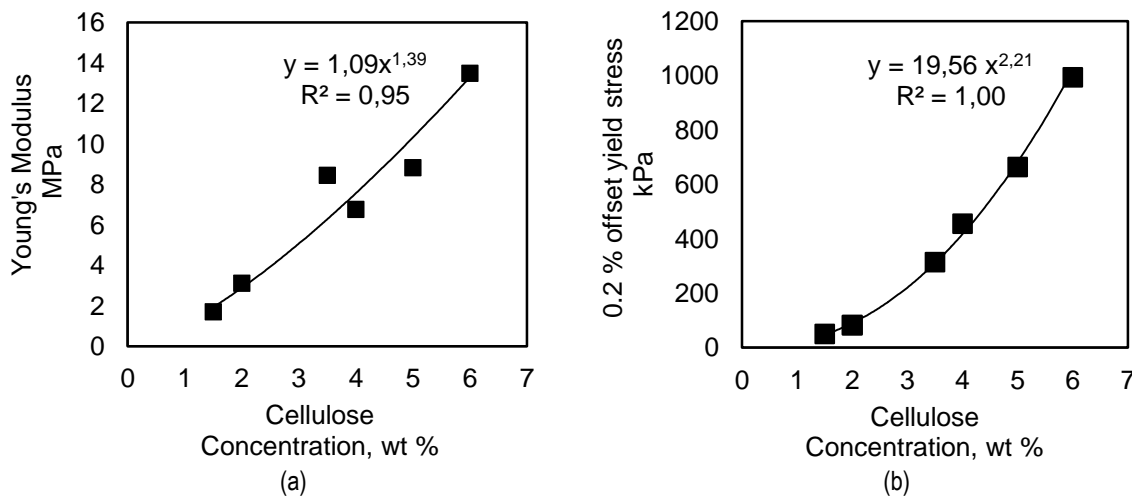
Figure 7: Young's Modulus E (a) and 0.2 % offset compressive yield strength (b) as a function of cellulose concentration for cellulose aerogel monoliths.

Conclusions

Cellulose aerogels were prepared via dissolving cellulose fibers in calciumthiocyanate salt hydrate melts, regeneration in ethanol and super critical CO_2 drying. It is possible to produce monolithic cellulose aerogels with low bulk densities (10-140 g/L). The cellulose aerogel's microstructure characterizations showed that cellulose aerogels had continuous 3D network with high specific surface area (150-230 m^2/g) and highly porous structure (98 %). In this work we could examine higher cellulose concentrations up to 6 % wt. Cellulose aerogels shown promising mechanical strength and thermal conductivity at atmospheric pressure. Young's modulus is up to 13.5 MPa and cellulose aerogels exhibit a Poisson ratio of around zero.

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