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Production of porous cellulose aerogel fibers by an extrusion process

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ABSTRACT

The preparation, production and properties of light weight, porous cellulose aerogels in the form of thin extruded fibers is compared to monolithic pieces. The cellulose aerogels were synthesized from microcrystalline cellulose in a hydrated calciumthiocyanate salt melt, which upon cooling forms a gel at around 80 °C. Twin screw extrusion experiments were performed systematically yielding thin and wet cellulose filaments. Washing and coagulation of the wet gels in ethanol was followed by supercritical drying with CO_2 yielding cellulose aerogel filaments. These were characterized with regard to envelope density, nitrogen adsorption-desorption (BET) analysis, thermal conductivity measurements, tensile and compression tests and scanning electron microscopy (SEM). The microstructure can be described as an open porous network of nano-fibrils with pore sizes ranging from 10 to 100 nm and fibril diameters of around 10 to 25 nm. The densities of supercritically dried (SCD) cellulose aerogels were in the range of 0.009–0.137 g/cm^3 and the BET specific surface areas (SSA$_{BET}$) were between 120 and 230 m^2/g. The cellulose aerogel possessed thermal conductivities from 0.04 to 0.075 W/m.K and compressive moduli up to 16.2 MPa. The tensile strength of aerogel filaments increases with the increasing cellulose amount in the spin dope. Extruded cellulose aerogel filaments show a dependency of their specific surface area on the extrusion temperature: the higher the spinning temperature the higher the surface area.

1. Introduction

Cellulose aerogels are multifunctional solid materials with low density, low thermal conductivity, large internal surface area and high porosity. Their structure can be described as a random three-dimensional network of cellulose fibrils of a few ten nanometers in diameter. They are promising materials for various applications such as nanostructured, bio-based materials for thermal insulators, insulation materials for the aerospace and aviation industry, storing media for gases in fuel cells, filter materials for extremely fine particles, drug delivery systems, drug coating purposes, hygiene products, highly functional fibers in textile and filtering applications were recently reviewed in [1,2]. Several methods are described in the literature to synthesize cellulose aerogels. These aerogels can be synthesized by dissolving cellulose in suitable media, such as sodium hydroxide [3–5], an aqueous alkali hydroxide/urea solution [6–8], salt hydrate melts [9–12], NMMO (*N*-Methylmorpholin-*N*-oxide) [3,13–15] or other ionic liquids [16–18]. Synthesis followed by washing, coagulation and finally drying by using special techniques, like supercritical or freeze drying in order to preserve their solid nano-porous network structure. The first cellulose aerogels were prepared by Tan et al. [19]. They used cellulose acetate as a starting material and de-esterified it. The cellulose ester was cross-linked in an acetone solution with toluene-2,4-di-isocyanate. Jin and co-workers [11] developed another technique to produce high-quality cellulose aerogels. They used a so-called salt-hydrate melt as a dissolving agent, being a mixture of water and $Ca(SCN)_2$ at a composition close to the coordination number of the salt cation ($Ca(SCN)_2 \cdot 4H_2O$). Their technique avoids the utilization of toxic isocyanates and allows in contrast to the method of Tan et al. [19] to use lower amounts of cellulose. The best structure preservation results have been obtained by supercritical CO_2 drying (SCD). Supercritically dried cellulose aerogels can present porosities as high as 99 % [12]. It is also possible to produce open porous and nano-structured cellulose aerogel fibers [20].

This paper mainly focuses on production and characterization of cellulose aerogel filaments or fibers, a term we synonymously use, based on the work of Jin et al. [11] and our previous works

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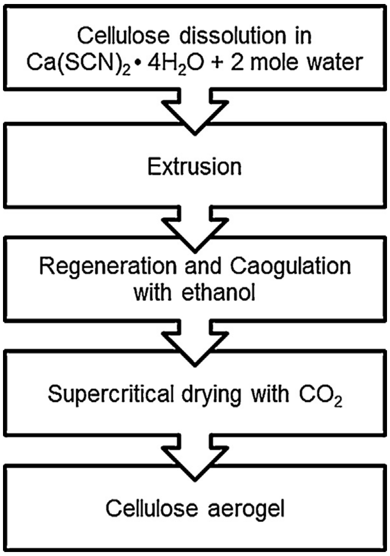

Fig. 1. Schematic diagram illustrating the preparation of cellulose aerogels.

[2,12,20] using supercritical CO_2 drying. The results are compared with those of cellulose aerogel monoliths.

2. Materials and methods

2.1. Materials

The chemicals used were calciumthiocyanate tetrahydrate ($Ca(SCN)_2 \cdot 4H_2O$) with a purity of 95% and cellulose fibers (medium) powder both from Sigma–Aldrich, product numbers 20,144 and C6288. The degree of polymerisation of cellulose used was determined by us as $DP_V = 211$ having a molecular weight of 32,998. The Cuoxam-method was used based on the change in viscosity of cellulose in Cuoxam solution [21]. The cellulose fiber powder was dried at 105 °C before use to get rid of adsorbed humidity. Ethanol (euro denatured 96%, TechniSolv.) from VWR Chemicals was used as received for washing and coagulation steps. Later on before the supercritical drying step, samples were washed with absolute ethanol (≥99,8 %, with ca. 1% MEK, Carl Roth). Carbon-dioxide (CO_2) with a purity of 99.9 % was used as received.

2.2. Preparation of cellulose wet gels

The preparation procedure of cellulose aerogels is summarized in Fig. 1. A certain amount (25 g) of calciumthiocyanate tetrahydrate was filled into a beaker, cellulose (0.14–1.74 g) was added in different amounts (0.5–6 wt.%) and two additional moles of deionized water (3,94 g) added finally. The amount of deionized water was calculated due to the coordination number of the cation, calcium(II), so that 6 H_2O molecules deliver the best composition of the dope. The turbid suspension is heated up to 110 °C while stirring. Dissolution of cellulose takes 10–30 min depending on the cellulose concentration and the final temperature. The larger the amount of cellulose the longer it takes to dissolve the cellulose in the salt hydrate melt. When the solution became homogeneous and transparent the cellulose was assumed to be completely dissolved. This was also supported by DP measurements. The DP remains constant up to 60 min and then decreases considerably. The homogeneous viscous solution was transferred to appropriate polypropylene molds for the production of monoliths, or to the twin-screw extrusion apparatus for fiber production. To avoid crystallization and the building of a solid cellulose skin at the surface of the samples, they were covered with ethanol. During cooling the viscosity rises and below 80 °C a stable gel is formed.

Table 1
Extrusion parameters.

Sample	Cellulose content (wt.%)	Extrusion conditions (temperature, twin screw rotation speed, nozzle hole diameter)
1	2	95 °C, 200 rpm, Ø 0.5 mm
2	3	93 °C, 200 rpm, Ø 0.5 mm
3	3	95 °C, 200 rpm, Ø 0.5 mm
	3	100 °C, 200 rpm, Ø 0.5 mm
4	3	105 °C, 100 rpm, Ø 1 mm
5	3	105 °C, 200 rpm, Ø 0.5 mm
6	3	115 °C, 250 rpm, Ø 0.5 mm
7	4	95 °C, 200 rpm, Ø 0.5 mm
8	4.5	95 °C, 200 rpm, Ø 0.5 mm
9	5	95 °C, 200 rpm, Ø 0.5 mm
10	6	110 °C, 50 rpm, Ø 1 mm

2.3. Production of cellulose aerogel fibers

Cellulose aerogel fiber production was conducted with a twin screw extrusion facility. After dissolving cellulose in the salt melt hydrate, the homogeneous viscous solution was transferred to a micro-extruder Xplore 15 (DSM, Geleen, Netherlands) for fiber production (Fig. 2). This instrument is utilized for formulation development and screening of polymer materials and polymer blends and polymer composites, and it is possible to produce fibers with it. The micro-compounder can process batch volumes up to 15 ml. The compounder gives the opportunity to select batch volumes of 3, 7 or 15 ml, via multiple recirculation channels. It is formed by a divisible, fluid tight mixing compartment containing two detachable, conical mixing screws to ensure a maximal homogenization (Fig. 2a and b). The main drive is continuously digitally variable. It allows for vertical force and rheological data measurement and constantly controls the pressure for film and fiber productions, by throughput control. The processing temperature can be controlled in separate barrel heating zones, which also enables to process with a temperature gradient over the barrel, or directly via an additional melt thermocouple. Residence time of the spin dope in the extruder can be varied via recirculation of the melt. No screw optimization is needed. Mixing and dispersion are superb, preventing agglomeration. Shear can be set by adjusting the temperature, rotation speed of the screws and gap between screw flank and barrel [22].

15 ml of viscous cellulose-salt melt hydrate solution were filled into the extruder by loading over a heated hopper in each experiment (Fig. 2c). The complete extruder apparatus was heated up to 250 °C. After reaching 250 °C and waiting for warming the hopper, the extruder was cooled down to reach the extrusion temperature for the experiments. Various extrusion parameters such as temperatures in the range of 95–115 °C, twin screw rotation speeds (50, 100 and 200 rpm) and diameters of the spinnerets (0.5 and 1 mm) were used (Table 1).

The extruded wet cellulose gel fibers were directly spun into an ethanol bath at room temperature. The gels were washed and coagulated within an ethanol bath to get rid of the calciumthiocyanate salts from the wet gel body. Washing was performed by using a Soxhlet apparatus for three days. It could be replaced with ion-exchange process for large scale implementation which we are also using currently to coagulate such gels within this lab scale process. Residual salt traces in the gel body were determined with conductometry until the conductivity of the washing solution is negligible low (<1 µS) and a spot test with 1% iron(III) nitrate solution is negative. The dry gels were also analyzed by EDX in a scanning electron microscope to check the salt melt hydrate content and to prove