

# Cellulose aerogels prepared from an aqueous zinc chloride salt hydrate melt



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## ABSTRACT

Monolithic cellulose aerogels are prepared using a salt hydrate melt based on cheap zinc chloride tetrahydrate ( $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ ) that can be washed out of the wet gel-body by using common solvents such as water, ethanol, isopropanol or acetone. Cellulose aerogels with concentrations of 1–5 wt.% cellulose were produced. These aerogels are characterized with respect to shrinkage, density and surface area as well as mechanical properties and micro-structure via SEM. Cellulose aerogels regenerated in acetone show a specific surface area of around  $340 \text{ m}^2 \text{ g}^{-1}$  being 60% higher than those regenerated in water. The onset of irreversible plastic deformation under compressive load is around 0.8 MPa for acetone-regenerated aerogels and thus a factor of two larger compared to ethanol regenerated ones. The Young's modulus depends almost linearly on the cellulose concentration which is observed for all regenerative fluids with the exception of water. The results achieved are presented in light of the polarity and ability of solvation of  $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$  in the regenerative fluids used.

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## 1. Introduction

Cellulose is the most abundant naturally occurring polymer. Due to its accessibility cellulosic materials have a promising future in several fields of application such as filter materials or in drug delivery (Valo et al., 2013). Polysaccharide based materials attract current research interests, measurable in the increasing numbers of publications during the last decade (Charreau, Foresti, & Vazquez, 2013).

Besides its renewability and biocompatibility cellulose offers the opportunity of functionalization by means of e.g. hydrophobization. Several solvents can be used to dissolve cellulose. Nevertheless, most of them are not as efficient as desired and therefore still represent an important topic in research and development. A well-arranged classification of cellulose solvents has been proposed by Heinze and Koschella (2005). In what follows, we focus on the class of non-derivatizing solvent systems based on aqueous media similar to previous works by Jin et al. or Hoepfner et al., who used aqueous calcium thiocyanate tetrahydrate ( $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ ) (Hoepfner, Ratke, & Milow, 2008; Jin, Nishiyama, Wada, & Kuga, 2004). The ability of concentrated zinc chloride salt hydrate melts to dissolve cellulose is well known and mentioned in several publications (Fischer, Leipner, Thümmeler, Brendler, & Peters, 2003; Heinze

& Koschella, 2005; Letters, 1932; Richards & Williams, 1969). It was first documented and patented by Th. Taylor in 1859 (Brit. Pat. No. 787) (Taylor, 1859). Many further patent applications were filed, most of them are focusing on the dissolution of cellulose and fibres thereof. Detailed studies on the complex formation between aqueous zinc chloride and D-glucopyranosides demonstrate the role of vicinal hydroxyl groups in the dissolution of cellulose. Williams et al. connected the swelling behaviour with the complex formation between the salt hydrate melt and the cellulose (Richards & Williams, 1969).

Basically, the preparation of aerogels is accompanied with low solid contents. Thus, the soluble amount of cellulose is not meant to exceed a volume fraction of approximately 10 wt.%, depending on the desired porosity. Cellulose aerogels have already been shown to possess a polymodal pore size distribution and to be build of a randomly arranged three dimensional network consisting of nano-sized fibrils. They can be tailored in their properties (Marjo, 2013). Different solvent-systems that are able to dissolve cellulose and produce cellulose aerogels are well described by several groups (Aaltonen & Jauhiainen, 2009; Fischer, Rigacci, Pirard, Berthon-Fabry, & Achard, 2006; Gavillon & Budtova, 2008; Innerlohinger, Weber, & Kraft, 2006; Liebner et al., 2009; Sescousse & Budtova, 2009; Sescousse, Gavillon, & Budtova, 2011; Wang, Liu, Matsumoto, & Kuga, 2012). To our knowledge there are neither publications on cellulose aerogels from aqueous zinc chloride salt hydrate melt reported, nor has the impact of the regeneration fluid on the properties of cellulose aerogels from this salt hydrate melt

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been investigated. For cellulose aerogels from ionic liquids and NaOH/water, however, work on regeneration kinetics was done by Gavillon and Budtova (2007). In case of other types of aerogels, for instance silica aerogels, a considerable impact on structure formation was observed (Omranpour & Motahari, 2013). Therefore, we investigated the influence of four regenerative fluids of distinguished polarity and as a consequence the varying ability of solvation of the salt including the impact on the resulting cellulose aerogels. The regenerative fluids used were water (H<sub>2</sub>O), ethanol (EtOH), 2-propanol (iPrOH) and acetone. Our studies look at effects on the density, the specific surface area, the mechanical properties as well as the micro-structural variety of cellulose aerogels prepared from an aqueous zinc chloride salt hydrate melt.

## 2. Experimental

### 2.1. Materials

All chemicals were used without further purification. Cellulose (microcrystalline, DP=211) was purchased by Sigma Aldrich and dried at 100 °C before use. Zinc chloride (minimum 98%) was acquired from Alfa Aesar. Deionized water with an electrical conductivity below 0.5 μS cm<sup>-1</sup> was used for preparation and regeneration of the cellulose gels. Other solvents used for regeneration of the solvogels were purchased by Th. Geyer and all in technical grade: acetone (98%), ethanol (96%), isopropanol (99%). The supercritical drying is carried out by an extraction autoclave with a pressure of 97 bar and a temperature of 55 °C using pure carbon dioxide (ECLASS 5.1).

### 2.2. Characterization methods

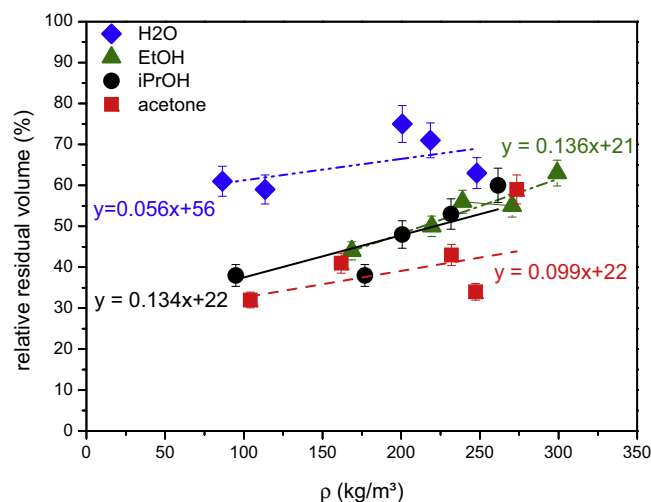
The resulting cellulose aerogels are characterized by their density gravimetrically, taking advantage of the well defined cylindrical shape. In case of 1 wt.% cellulose aerogel regenerated in water a Geopyc 1370 apparatus from Micromeritics was used to determine the envelope density (compression varied from 10 N up to 50 N then extrapolating to zero compression). A Tristar II 3020 apparatus (Micromeritics) was used to measure the surface area by the BET-method after degasing at 110 °C and vacuum (at 0.15 mbar) for 5 h. All measurements were conducted at least twice. In order to analyse the structure formation all samples were broken in liquid nitrogen then sputtered with gold to perform the structure analysis by SEM using a Merlin – Carl Zeiss Microscope (operated by 2 kV and 50 pA). The mechanical properties are determined in a compression test using a universal testing machine (Latzke, load cell of 5 kN and 1 mm min<sup>-1</sup>). Tested samples were cubic with edge lengths of about 10–12 mm.

## 3. Results and discussion

After drying the cellulose aerogels are of cylindrical shape, white in colour and apparently homogeneous. On visual examination the aerogels seem to get more robust with increasing cellulose content, they feel more stiff and are easier to handle than those with low cellulose content.

### 3.1. Shrinkage

The correlation of the shrinkage and the cellulose amount was already described by Innerlohinger et al. for cellulose aerogels prepared via dissolution of cellulose in N-methylmorpholin-N-oxide (NMMO) (Innerlohinger et al., 2006). They observed a lower shrinkage for samples with high cellulose concentrations. We have found a similar behaviour as shown in Fig. 1. All polysaccharide aerogels



**Fig. 1.** The relative residual volume of cellulose aerogels as a function of density. H<sub>2</sub>O-regenerated aerogels have smaller loss in volume than EtOH- and iPrOH-regenerated ones.

suffer from strong shrinkage even though the drying is carried out in supercritical carbon dioxide (scCO<sub>2</sub>) (Ganesan & Ratke, 2014). It has to be mentioned that washing itself causes shrinkage of these gels, as does the scCO<sub>2</sub> drying to some extent. The shrinkage is monitored volumetrically and displayed in the form of the relative residual volume after drying, see Fig. 1.

It shows that the slope of the shrinkage as a function of density depends on the regeneration fluid. For EtOH and iPrOH-regenerated aerogels the slopes are almost identical while H<sub>2</sub>O-regenerated aerogels show the lowest increase in relative residual volume with increasing density. The solubility of zinc chloride in the solvent used can be ordered in the following descending way: H<sub>2</sub>O > EtOH > iPrOH > acetone. The highest solubility is observed in water and in that row the lowest in acetone (Haynes, Lide, & Bruno, 2013). Exact solubility values are only found for H<sub>2</sub>O, namely 408 g/100 mL and EtOH with 76 g/100 mL (Haynes et al., 2013), while isopropanol is not mentioned at all. Thus, we determined the solubility of zinc chloride in isopropanol ourselves to be 73.7 ± 0.04 g/100 mL at room temperature (22 °C). And we find 52.6 ± 0.02 g of zinc chloride to be soluble in 100 mL of acetone (22 °C), which agrees well with above mentioned order of solubility. The removal of the salt from the wet gels is accompanied by a small volumetric loss. Obviously the polarity of the regeneration fluid is important and kinetic studies of this system are to be performed in the style of (Gavillon & Budtova, 2007; Sescousse et al., 2011). Immediately after gelation in cylindrically shaped boxes the cellulose gel is covered with the same volume of the regeneration fluid. Within 8–15 h the first washing step leads to minor shrinkage. At this point it is possible to transfer the wet gel into bigger boxes to allow the regenerative fluid to infiltrate the sample evenly from all sides. The volume ratio of gel-body to regenerative fluid was 1:10 for every solvent exchange. The total number of washings varied with the solubility of the salt in the regenerative fluid.

### 3.2. Density

The gravimetrically determined density ( $\rho_g$ ) is corrected by the volumetric shrinkage ( $\Delta V/V_0$ ) in order to get the envelope density without shrinkage ( $\rho_{e,corr}$ ) according to a relation given by Ganesan and Ratke (2014):

$$\rho_{e,corr} = \rho_g \left( 1 - \frac{\Delta V}{V_0} \right). \quad (1)$$

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