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ORIGINAL PAPER

The effects of physical and chemical interactions in the formation of cellulose aerogels

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Abstract Aerogels are low density materials which are produced from wet gels, and find a variety of potential uses. The relative importance of shape/geometry and self-association of the starting materials for the production of aerogels is studied herein. Aerogels were produced from microcrystalline cellulose (MCC) and its functionalized analog, carboxymethyl cellulose (CMC). With increasing functionalization, CMC gains the potential for self-association, differentiating itself from MCC. The present study explores the preparation of aerogels from MCC and CMC, comparing performance with and without significant self-association potential, and more broadly evaluating the production of low density structural materials from renewable cellulose. It was observed that the self-association present in CMC substantially increases aerogel mechanical properties when compared those of non-interactive MCC. Aspect ratio is proposed to also be an import parameter in the structure–property relationship for these materials.

Keywords Aerogel · Structure · Cellulose · Self association

Introduction

As low density, and highly porous materials, inorganic and organic aerogels are widely studied for their structures, properties, and applications [1]. First reported by Kistler, silica aerogels were produced by replacing the liquid in solution of silica gel by air, producing a highly porous solid structure [2]. Useful drying methods for aerogel production include supercritical drying, ambient-pressure,

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and freeze-drying [3]. Supercritical drying is probably the most commonly used method at the present time for aerogel production; this process can remove the synthesis solvent from the wet gel without collapsing its solid state structure [4]. The potential commercial applications which are under development for aerogels include catalyst supports, insulators, capacitors, sensors, and particle detectors [5, 6].

Naturally occurring polymers are attractive candidates for the development of new materials for environmental/sustainability reasons. Aerogels made from alginate, chitosan, and cellulose have been studied; these renewable materials are biocompatible, and have potential uses in drug delivery, agriculture, foods, and the pharmaceutical industry [7–9]. A fundamental understanding of the formation of such bio-based aerogels has not been reported to date.

Cellulose is the most abundant polymer from nature; much is known about its structure and properties [10]. Because of the syndiotactic structure of its constituent anhydroglucose units, cellulose is a linear polymer composed of glucose units linked by β-1,4-linkages [10]. Two general applications of cellulose are for structural materials (textiles, wood, and paper) and for its chemical conversion into other useful materials [11]. Microcrystalline cellulose (MCC) is a highly crystalline, naturally occurring polymer which can be extracted from alpha cellulose by strong acid hydrolysis, reducing its degree of polymerization to 200–300 [12]. MCC is a white, free-flowing powder, which is odorless, tasteless, free from inorganic contaminants, and insoluble in water [13]. When treated with water, MCC swells and can be readily dispersed [14]. Moreover, the molecules of MCC swell causing the expansion of the crystallites [13]. With its excellent properties of solid flowability, compressibility, biocompatibility, and binding capability, MCC has been widely used as an additive for direct compression such as medical tablets, and also used as fillers and binder [13, 15]. Solid MCC compacts well under relatively low pressure to create tablets which are hard and stable, but will disintegrate when wet [16].

Chemical modification of cellulose allows for variations of its mechanical and chemical properties. Carboxymethyl cellulose (CMC) is one of the best-known derivatives of cellulose [16, 17]. Non-toxic, renewable, biodegradable and modifiable, CMC is used as a raw material for industrial and biomedical application including paper, paint, food, and pharmaceuticals [18]. The determination of substitution of the functional group per unit of cellulose can be determined and quantified by the degree of substitution (DS) typically ranging from 0 to 3 [14]. With increasing functionalization, CMC gains the potential for self-association, differentiating itself from MCC. The present study explores the preparation of aerogels from MCC and CMC, comparing performance with and without significant self-association potential, and more broadly evaluating the production of low density structural materials from renewable cellulose. While a number of synthetic and bio-based polymers have been previously converted into aerogels via cryoprocessing, to the best of our knowledge, this is the first report of the use of cellulose as the matrix polymer in such a process.

Experimental

MCC, Lattice NT®, NT-100, obtained from FMC Corporation was used as received to produce CMC and to prepare MCC aerogels. All other reagents were obtained from Fisher Scientific Company, and used as received.

CMC was prepared by a chemical modification procedure adapted from the preparation of carboxymethylated chitosan [19]. 5.0 g MCC was dispersed in 200 mL isopropanol then 12.5 mL of 10 M NaOH was added dropwise. The temperature of the solution was then increased to 60 °C for 30 min and 0.7 g monochloroacetic acid was added. After approximately 3 h, CMC was obtained; the solids were filtered and dried at 60 °C in vacuo.

Conductimetric titration [20] was used to determine the DS of carboxymethyl groups. 0.5 g CMC was dissolved in 500 mL deionized water. 0.1 M HCl was added to the solution until a pH of 3 was achieved, then the solution was titrated using 0.5 M NaOH. The plateau region in the plot of consumed NaOH solution (mL) versus conductivity (μS/cm) was used to calculate the DS.

For the production of aerogels, CMC was dissolved in water at the desired level of solids, whereas MCC required dispersion in by sonicating at 60 °C for 4 h. These solutions and dispersions were taken into cylindrical molds, frozen in a solid carbon dioxide/methanol bath, and dried in a Virtis Advantage EL-85 freeze drier, using the methodology previously reported for a range of polymers [21].

The aerogels were cut into 2.00-mm thick disks for compressive testing (Instron Model 5565 universal tester equipped with a 1 kN load cell, at head speed of 1 mm/min). Values reported are the average and standard deviations from five tests. Imaging was performed on Pd-coated samples using Philips XL-30 Environmental Scanning Electron Microscope.

Results and discussion

CMC was obtained from the two-phase derivatization of MCC as shown in Fig. 1. The DS in CMC samples were then determined using conductrimetric titration, Fig. 2 [22].

The DS of CMC batched produced in this study ranged from 0.22 to 0.36, as is shown in Table 1. Because the derivatization of cellulose is a heterogeneous reaction, the resulting DS was dependent upon the reaction time, the speed/concentration of reagent addition, and the effectiveness of mixing. Approximately one hydroxyl group was substituted every four repeat units of cellulose under the reaction conditions employed therein. The literature suggests that the carboxymethyl

$$C_6H_9O_4\text{-}OH + NaOH \rightarrow C_6H_9O_4\text{-}O^- \, Na^+ \qquad (1)$$

$$C_6H_9O_4\text{-}ONa + ClCH_2COOH \rightarrow C_6H_9O_4\text{-}OCH_2COOH + NaCl \qquad (2)$$

Fig. 1 Derivatization of MCC to produce CMC

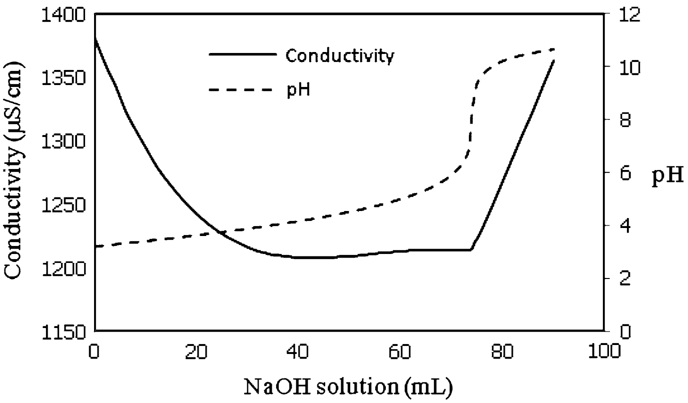


Fig. 2 A typical conductimetric titration for DS measurement

Table 1 Degree of carboxymethyl substitution in experimental CMC batches

CMC	DS
1	0.28
2	0.22
3	0.36
4	0.28
5	0.36
6	0.25

substitution can take place at any of the hydroxyl group positions in cellulose, typically distributed 40% at 3C, 40% at 6C, and 20% at 2C [22].

Aerogels were successfully produced from both MCC and CMC, using a freeze drying process that we have discussed previously [6, 21, 23] (Lamison K, Gawryla MD Schiraldi DA, unpublished results). This process relies on exclusion of solids from the formation of ice crystals as the aqueous solvent is frozen; the excluded solids are rejected to the grain boundaries of impinged ice crystals, producing micron-scale layers which are typically separated by ca. 100 micron galleries, producing highly porous solids when the frozen water (or other solvent) is removed by sublimation. Densities of the MCC and CMC aerogels produced in this manner are shown in Table 2, range from 0.05 to 0.11 g/cm^3, and as expected are proportional to the level of solids present in solution/suspension prior to freezing [23].

Under compression testing (Table 2, Figs. 3, 4), the moduli of MCC aerogels significantly increased with increasing solid concentration (5–10% solids). CMC aerogels exhibited not only a similar modulus/solids concentration trend, but also exhibited considerably higher moduli than were observed with MCC aerogels. Density versus modulus results for the MCC aerogels produced in this study are shown in Fig. 5. The graph presents 3 three sections: moduli around 20, 50, and 150 kPa at density 0.06, 0.09, and 0.11 g/mm^3, respectively. This plot shows the

Table 2 Properties of MCC and CMC aerogels

% Solids used	Density (g/cm^3)		Modulus (kPa)	
	Average	SD	Average	SD
MCC				
5.0	0.056	0.004	17	8
5.5	0.064	0.004	15	9
6.0	0.063	0.003	60	55
7.5	0.093	0.009	50	13
10.0	0.106	0.012	120	54
CMC				
5.0	0.062	0.010	830	344
6.0	0.073	0.004	1200	530
7.5	0.090	0.011	1033	340
10.0	0.120	0.012	3442	1649

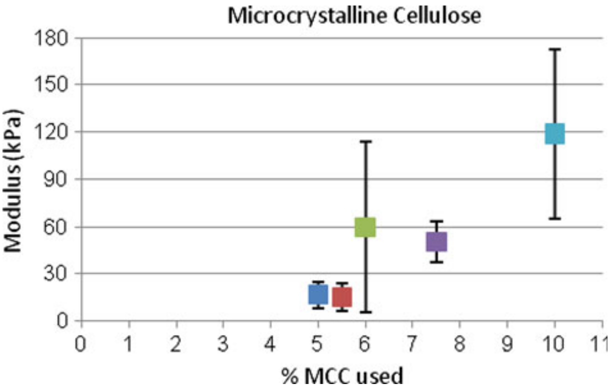


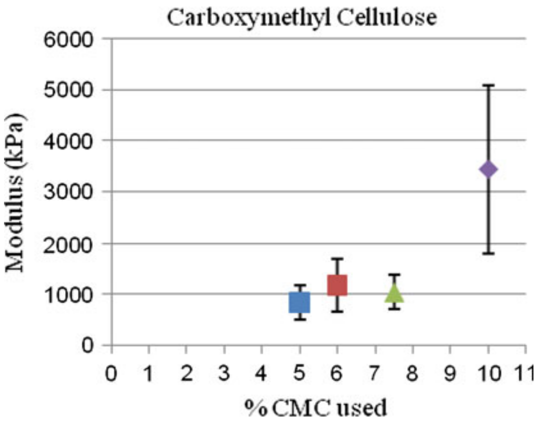
Fig. 3 Modulus of MCC aerogels at various percent solids

scatter distribution of the data while confirming that modulus generally increases with density for these materials.

A similar plot for the CMC aerogels (Fig. 6a) shows no trend between modulus and density. It can be assumed that increasing the density of CMC aerogels might or might not improve the modulus of the aerogels. The DS could potentially have an effect on the modulus of aerogels, but DS is not homogeneous through entire cellulosic particles, so wide distribution of data is expected. The plot DS versus modulus of 5 and 6% (Fig. 6b) of CMC aerogels suggests that even though the average DS (Table 1) of each batch of CMC is different, no real effect on modulus is obtained.

Investigated by ESEM, MCC aerogels show isotropic structures, while lamellar structures are found in CMC aerogels, as shown in Fig. 7. Ice growth and the structure of the MCC and CMC are factors of the formation of aerogels. Three-

Fig. 4 Modulus of CMC aerogels at various percent solids



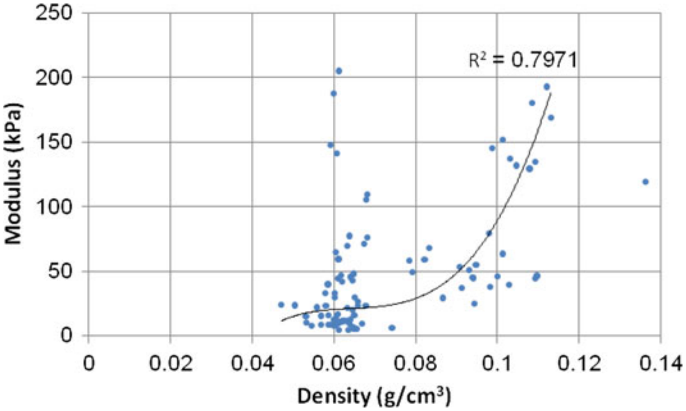


Fig. 5 Density versus modulus of MCC aerogels

dimensional random structures of MCC aerogels also contain occasional defects caused by swelling, agglomeration, and dispersion of the MCC. By sonicating in high temperature, cellulose particles were swelled, allowing water to penetrate into the crystalline cellulose by disrupting hydrogen bonds [13] and reducing intermolecular interaction between particles. Differences in size of, and in numbers of hydrogen bonds within MCC particles likely led to varying degrees of hydroscopic particle swelling. Agglomeration and dispersion of the swollen particles also can lead to defects within MCC aerogel structures.

Hydroscopic by nature, cellulose would be expected to be surrounded by high concentrations of water. When an ice front is growing in aqueous MCC, ice crystals are created within swollen cellulose molecules. The voids in between the particles result from the low concentration regions among swollen MCC particles, the greater the distance between particles, the larger the voids produced in the aerogels. The aerogel properties presented in Table 2 show that the higher the concentration of solids, the smaller the voids found in the aerogels, in turn leading to the higher

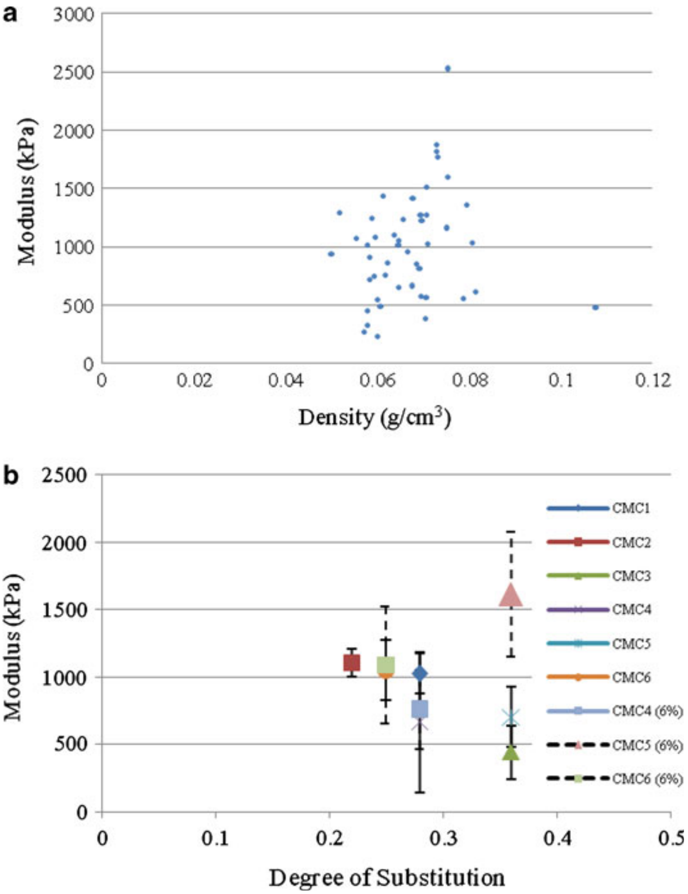


Fig. 6 (*Top*, **a**), Modulus versus density for MCC aerogels; (*bottom*, **b**), modulus versus degree of substitution for CMC

modulus of the MCC aerogels. The moduli of these aerogels demonstrate that MCC aerogels are more robust when higher solids content solids are used to produce freeze dried materials.

Not all the MCC, however, can disperse in water; the affinity of water cannot overcome the secondary bonding within some particles. Some level of non-dispersable MCC is inevitable and might affect the properties of the aerogels. The greater the MCC concentration in water, the greater the level of non-dispersed particles that can be expected. Agitation was therefore necessary in order to temporally disperse the swollen MCC. These dispersed particles can persist sufficiently long in the solution to allow for largely homogeneous freezing of the mixture. After freeze-drying, these MCC particles would be dispersed within the aerogels, and might even act as reinforcing fillers to enhance the strength of the structures, alternatively acting as defects which disrupt the geometric interaction of the swollen MCC.

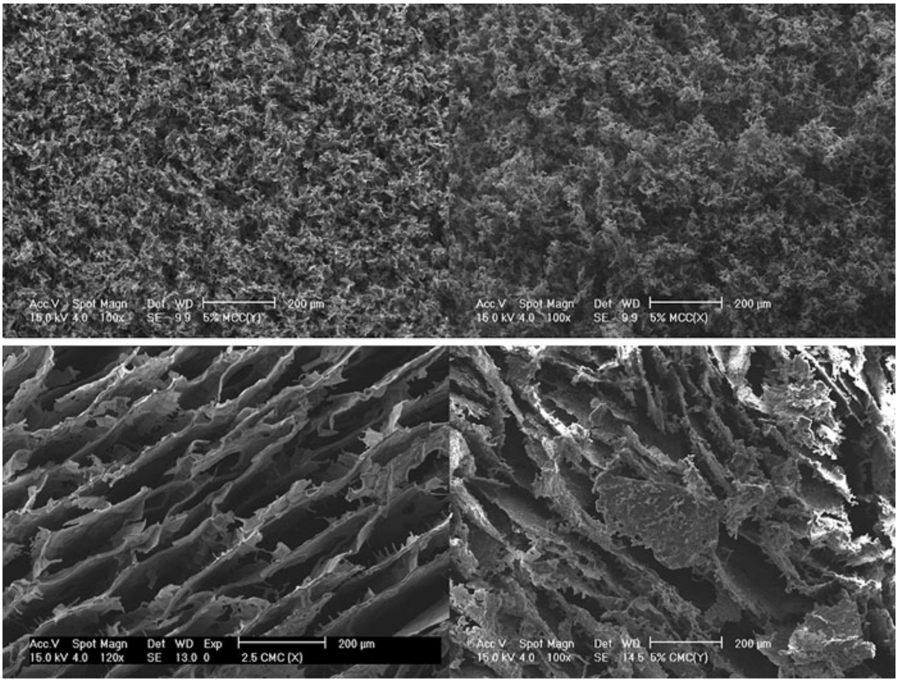


Fig. 7 Cross section of (*upper left*) 5% MCC aerogel parallel, and (*upper right*) perpendicular to a vial; (*bottom left*) 5% CMC aerogel parallel and (*bottom right*) perpendicular to a vial

CMC aerogels, on the other hand, have lamellar structures because their solubility in water and their inherent self-association. Ice front growth in the presence of CMC can simply push polymer chains aside as the freezing process progresses. With many ice fronts growing in the same direction, layers of ice and CMC are formed. The layered structures of the CMC aerogels are dependant upon the freezing direction. After the ice is removed, self-association via hydrogen bonding can stabilize layers of the CMC. Shrinkage after sublimation to form the aerogels is observed to be about 6% in the vertical and horizontal directions. From compression testing, it was confirmed that the moduli of CMC aerogels are higher than those of MCC aerogels. MCC aerogels show increasing trends in modulus when the densities of the aerogels increase whereas CMC aerogels do not show any such trend.

At 5 and 6% solids content, the moduli of CMC aerogels are approximately 50 and 20 times higher than those of the analogous MCC aerogels, respectively. We propose that chemical interactions of CMC–CMC, serve as strong bridges, enhancing the strength of the CMC aerogels. In contrast, MCC aerogels which are formed by sublimation of water around swelling (but not soluble) MCC retain largely particulate geometries due to a lack of the strong intermolecular attractions which are present in CMC. Unpublished results studying the structures of poly(vinyl alcohol) (PVOH) aerogels, show similar trends of aerogel strength as a function of structure, supporting the conclusions of the current work. Within PVOH aerogels, those composed of lamellar structures are stronger than those possessing isotropic structures (Lamison K, Gawryla MD Schiraldi DA, unpublished results). The results given in Fig. 6a, demonstrate that even though the density of the CMC aerogels are increased, they do not necessarily lead to higher moduli. The modulus of CMC aerogels hypothetically could be dependant on amounts of the intermolecular hydrogen bonds which act like bridges between molecules.

Gawryla et al. [24] also studied aerogels produced from cellulose whiskers, and found that at greater than 3 wt% of cellulose whiskers, aerogels from freeze-drying give isotropic structures. With its high aspect ratio, the moduli of cellulose whisker aerogels are higher than those of MCC in this project but still lower than those of CMC aerogels. Therefore, aspect ratio is likely another factor that affects to the properties of cellulose aerogels.

Conclusions

While both physical geometry and chemical self-association impact the formation of aerogels, chemical interactions are the key of the strength of these materials. Cellulosic aerogels present different structures and properties; microcrystalline (MCC) aerogels exhibit isotropic, three-dimensionally random structures, whereas by self-association CMC aerogels produce lamellar structures. Comparing under the modulus of these aerogels, the isotropic structure is weaker than that of the lamellar structure. The moduli of MCC aerogels also increase with increasing bulk density.

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