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Book Title	Nano and Biotech Based Materials for Energy Building Efficiency	
Series Title		
Chapter Title	Nanocellulose Aerogels as Thermal Insulation Materials	
Copyright Year	2016	
Copyright HolderName	Springer International Publishing Switzerland	
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Abstract

There is a high demand of energy consumption due to the increasing population, industrial expansion, and development plans. However, the increasing cost of energy and the negative impact on the environment by energy production plants have resulted in the need to find means to substantially reduce energy consumption. Buildings are one of the main factors contributing to the world energy consumption. About two-thirds of the total energy is used for buildings. It is essential to reduce energy consumption of buildings by finding more effective thermal insulation materials. Cellulose is a green, cheap, and abundant material with low thermal conductivity. Its combination with aerogel structure forms a novel and effective heat insulation material known as cellulose aerogel. Cellulose aerogels can be fabricated from bacterial cellulose, wood/paper pulps, or cellulosic wastes. The aerogels become water-repellent after being treated with silane reagents via a chemical vapor deposition (CVD) method. They show highly porous structures with good flexibility, high stability, and extremely low thermal conductivities. These characteristics make them promising for thermal insulation applications.

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Chapter 15
Nanocellulose Aerogels as Thermal Insulation Materials

Hai M. Duong and Son T. Nguyen

Abstract There is a high demand of energy consumption due to the increasing population, industrial expansion, and development plans. However, the increasing cost of energy and the negative impact on the environment by energy production plants have resulted in the need to find means to substantially reduce energy consumption. Buildings are one of the main factors contributing to the world energy consumption. About two-thirds of the total energy is used for buildings. It is essential to reduce energy consumption of buildings by finding more effective thermal insulation materials. Cellulose is a green, cheap, and abundant material with low thermal conductivity. Its combination with aerogel structure forms a novel and effective heat insulation material known as cellulose aerogel. Cellulose aerogels can be fabricated from bacterial cellulose, wood/paper pulps, or cellulosic wastes. The aerogels become water-repellent after being treated with silane reagents via a chemical vapor deposition (CVD) method. They show highly porous structures with good flexibility, high stability, and extremely low thermal conductivities. These characteristics make them promising for thermal insulation applications.

15.1 Introduction

Cellulose is one of the most common and abundant polymers on the planet. It is widely used in industry and normal life. Cellulose is a non-branched macromolecule containing ringed glucose molecules. Its repeat unit consists of two anhydroglucose rings linked together through oxygen covalently bonded to C1 of one glucose ring and C4 of the adjoining ring. This bond is known as the β 1–4 glucosidic bond. Intra- and interchain hydrogen bonding makes cellulose a relatively stable polymer (Cai et al. 2008; Cervin et al. 2012; Chang and Zhang 2011;

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F. Pacheco Torgal et al. (eds.), *Nano and Biotech Based Materials for Energy Building Efficiency*, DOI 10.1007/978-3-319-27505-5_15

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Kalia et al. 2011; Wicklein et al. 2015; Pour et al. 2015). Van der Waals and intermolecular hydrogen bonds promote parallel stacking of multiple cellulose chains forming elementary fibrils. These fibrils then aggregate to form larger microfibrils in the plant cell wall, which also aggregate into macroscopic fibers. These microfibrils have typically a diameter of about 10–30 nm and are made up of 30–100 cellulose molecules in extended chain conformation and provide mechanical strength to the fiber (Eichhorn et al. 2010; Mieck et al. 1994; Moon et al. 2011).

Cellulose fibers have many potential applications because of their advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, and good mechanical properties. Cellulose fibers can be classified according to their origin and grouped as follows: (1) leaf: abaca, pineapple, sisal, banana, etc.; (2) seed: cotton; bast: flax, hemp, etc.; (3) fruit: coir, kapok, etc.; (4) grass: bagasse, bamboo, etc.; and (5) stalk: straw (cereal) (Eichhorn et al. 2010; Kalia et al. 2011; Klemm et al. 2011; Mieck et al. 1994; Moon et al. 2011; Oshima et al. 2014). Commonly used plant fibers are cotton, jute, hemp, flax, ramie, sisal, coir, henequen, and kapok. Properties of cellulose fibers are affected by many factors such as variety, climate, harvest, maturity, retting degree, decortications, disintegration (mechanical, steam explosion treatment), fiber modification, textile, and technical processes (spinning and carding). Cellulose fibers with moduli up to 40 GPa can be separated from wood by chemical-pulping process. Such fibers can be further subdivided into microfibrils with elastic modulus of 70 GPa.

Cellulose nanofibers (CNFs) have a high potential to be used in many different areas such as reinforcement in development of nanocomposites. Many studies have been done on isolation and characterization of CNFs from various sources. Cellulose nanofibers can be extracted from the cell walls by simple mechanical methods or by a combination of both chemical and mechanical methods (Eichhorn et al. 2010; Kalia et al. 2011; Klemm et al. 2011; Mieck et al. 1994; Moon et al. 2011; Oshima et al. 2014). Cellulose nanofibers are extracted from the agricultural residues, wheat straw, and soy hulls, by a chemomechanical technique. The wheat straw nanofibers have diameters in the range of 10–80 nm and lengths of a few thousand nanometers. By comparison, the soy hull nanofibers have diameters of 20–120 nm and shorter lengths than the wheat straw nanofibers. Zimmermann et al. (2004) separated nanofibrillated cellulose at the greatest possible lengths and diameters below 100 nm from different starting cellulose materials by mechanical dispersion and high-pressure (up to 1500 bar) homogenization processes. The treatment resulted in nanoscaled fibril networks.

Aerogels have been well known as highly porous solids that hold air within their pores. As a result, their lightness, low heat conductivity, and large surface area make them ideal for possible applications as heat insulators, particle filters, particle trappers, and catalyst supports (Innerlohinger et al. 2006; Gesser and Goswami 1989; Bheekhun et al. 2013; Bryning et al. 2007; Pierre and Pajonk 2002; Nguyen et al. 2012). The combination of aerogel structure and cellulose fibers forms cellulose aerogel, a new kind of aerogel, which is green, cheap, and abundant. Cellulose-based aerogels were developed during the 1950s by Stamm and coworkers (1950). However, little further development occurred until the 2000s.

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Most research efforts have been in aerogel processing and in some isolated cases the subsequent functionalization of the aerogel via coatings. The environmentally friendliness, low thermal conductivity (0.040–0.050 W/m K) of cellulose, and the highly porous aerogel structure facilitate the heat insulation property of cellulose aerogels and thus open a new chapter in thermal insulation (Baetens et al. 2011; Fan et al. 2014; Al-Homoud 2005; Briga-Sá et al. 2013; Jelle 2011). The total global aerogel market is forecast to grow at a very high rate of 19.3 % from 2012 to 2017 and reach global revenues of $332.2 million by 2017 (Nguyen et al. 2014). In particular, the thermal and acoustic insulation sector accounted for 82.3 % of all revenues in 2012 and shows the most potential growth with a five-year compound annual growth rate of 20.2 % from 2012 through 2017. Therefore, cellulose aerogels will have a very bright future in the global insulation market.

15.2 Advanced Cellulose Aerogels for Heat Insulation of Buildings

There have been several works on cellulose aerogels. Based on the cellulose source, cellulose aerogels can be synthesized from bacterial cellulose, wood/paper pulp, or wastes.

15.2.1 Cellulose Aerogels Prepared from Bacterial Cellulose

15.2.1.1 Fabrication Methods

Bacterial cellulose (BC) was first reported by Adrian Brown while working with *Bacterium aceti* in 1886 (cite from …). A solid mass is formed at the surface of vinegar fermentation medium and is commonly used in homemade vinegar production (Oshima et al. 2014; Cai et al. 2012; Sai et al. 2013, 2014; Pircher et al. 2014; Liebner et al. 2010). The constituent was later identified as cellulose, and the name *Bacterium xylinum* was assigned to the microorganism responsible for its synthesis. Since its discovery, several names were given to this bacterium including *Acetobacterium xylinum* and *Bacterium xylinodes*. It was later named as *Acetobacter xylinum* and became the official name according to the International Code of Nomenclature of Bacteria (Cannon and Anderson 1991; Yamanaka et al. 1989). Now, this Gram-negative, strictly aerobic bacteria are referred to as species *Gluconacetobacter xylinus.* Although BC can be produced from the species of genera *Achromobacter, Alcaligenes, Aerobacter, Agrobacterium, Azotobacter, Gluconacetobacter, Pseudomonas, Rhizobium, Sarcina, Dickeya, and Rhodobacter,* only *species from genus Gluconacetobacter* can produce cellulose at commercial levels.

BC is produced by acetic acid bacteria in both synthetic and non-synthetic media through partial oxidation of ethanol. As mentioned above, *Acetobacter xylinum* is the most studied and the most efficient BC producer that manages to assimilate various sugar sources such as glucose, sucrose, and coconut milk and yields high level of cellulose in liquid media. It needs to be given the optimal conditions in terms of temperature, oxygen supply, and nutrients to be able to synthesize cellulose (Liebner et al. 2010; Liang et al. 2015; Keshk 2014; Sai et al. 2014; Pircher et al. 2014). As a nutrient source, several growth media exist, one that is very common is a mixture introduced by Schramm and Hestrin in 1954, which consists of 20 g l^{-1} glucose, 5 g l^{-1} peptone, 5 g l^{-1} yeast extract, 1.15 g l^{-1} citric acid monohydrate, and 6.8 g l^{-1} Na_2HPO_4 12 H_2O (Hestrin and Schramm 1954). Process is active at pH 3–7 and at temperature between 25 and 30 °C. It was reported that almost 30 % of bacterial fermentation cost belongs to the cost of fermentation medium. High cost and low-yield production have limited the industrial production of BC and its commercial application (Liebner et al. 2010; Liang et al. 2015; Keshk 2014; Sai et al. 2014; Pircher et al. 2014). Therefore, it is important to look for a new cost-effective carbon source with shorter fermentation process for high-yield BC production. The BC hydrogel then undergoes a drying process to be converted to BC aerogel. To maintain the porous structure of the BC hydrogel, two drying ways are usually used: freeze drying and supercritical point drying. In the first method, the hydrogel is frozen by liquid nitrogen or a refrigerator, and then, the ice in the sample is removed by sublimation directly with vacuum. In the supercritical drying method, the BC hydrogel is subject to thorough solvent exchange with ethanol to form BC alcogel. Then, ethanol is replaced by liquid CO_2. After that, CO_2 is converted into the supercritical state and slowly released to ambient pressure. Unlike plant cellulose, BC does not require extra processing to remove unwanted impurities and contaminants such as lignin, pectin, and hemicellulose, thus being able to retain a greater degree of polymerization.

15.2.1.2 Morphology

Scanning electron micrographs (SEM) of BC aerogels (Fig. 15.1) reveal a hierarchical order of the open-porous network, which consists of a well-developed macropore system formed from disorderly dispersive 20–80 nm cellulose fibers. Apart from macropores, Liebner et al. (2010) found that BC aerogels also have a mesoporous substructure (Liebner et al. 2010). Nitrogen sorption experiments show that the mesopores considerably contribute to the total pore volume as the obtained isotherms are of type IV. The mesopore diameter is about 10 nm, and the surface area and pore volume are about 160–200 m^2 g^{-1} and 0.5 cm^3 g^{-1}, respectively. BC aerogels possess very low densities of around 6.7–8.3 mg cm^{-3}. Their porosity is about 99.6 %. X-ray diffraction (XRD) spectra of BC aerogels show three characteristic peaks centered at 14.78°, 16.98°, and 22.78°, corresponding to the typical $(1\bar{1}0)$, (110), and (020) planes of cellulose I, respectively.

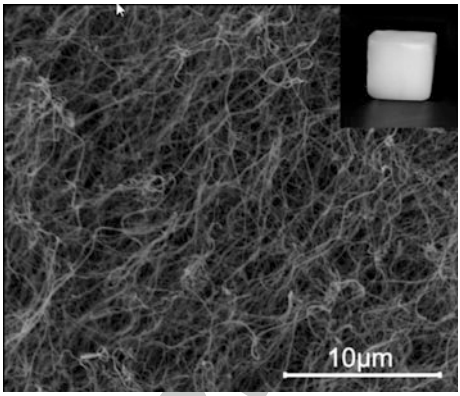

Fig. 15.1 BC aerogel (Pircher et al. 2014)

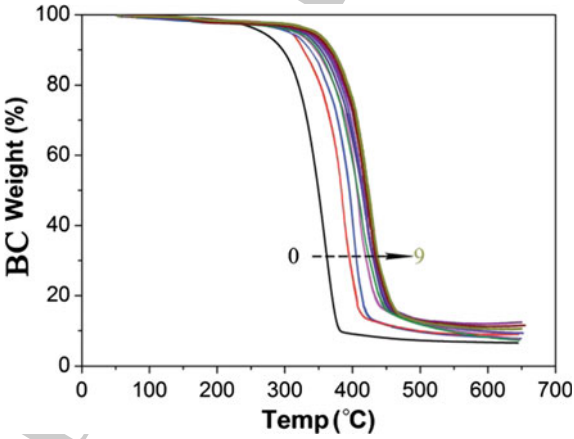

Fig. 15.2 TGA result of BC aerogels (Sai et al. 2014)

15.2.1.3 Thermal Properties

Thermogravimetric analysis (TGA) results (Fig. 15.2) show that BC aerogels start to decompose at 250 °C. They lose 5 % of their weight at 265 °C, 10 % of their weight at 290 °C, and completely degrade at about 380 °C. They exhibit an extremely low thermal conductivity of 0.0295 W m^{-1} K^{-1} (Sai et al. 2014), almost the same as that of silica aerogels, indicating that they are promising for thermal insulation applications.

15.2.1.4 Mechanical Properties

The BC aerogels have a 3D Web-like morphology formed from a large number of hydrogen bonds between the BC nanofibers. This makes them strong and flexible. Figure 15.3 shows compressive curves of BC aerogels. It was found that they

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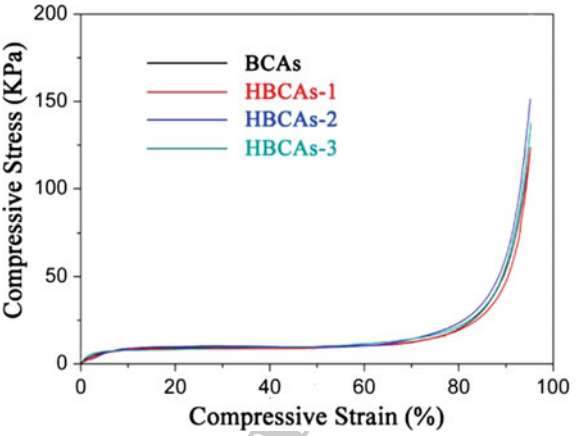

Fig. 15.3 Compressive curves of BC aerogels (Sai et al. 2015)

possess a compression modulus of 0.27 MPa in Sai et al.'s work (Sai et al. 2013). Pircher et al. (2014) found that BC aerogels have specific modulus values of 19–25 MPa $cm^3\ g^{-1}$, which are remarkably high compared to other porous materials. For example, for a polyurethane foam of a density of 90 mg cm^{-3}, a specific modulus of 7.8 MPa $cm^3\ g^{-1}$ was previously reported. A lower specific modulus of about 4 $cm^3\ g^{-1}$ was reported for silica aerogel.

15.2.2 Cellulose Aerogels Prepared from Wood/Paper Pulp

15.2.2.1 Fabrication Methods

Cai et al. (2008) fabricated cellulose aerogels from filter paper pulp, Whatman cellulose powder, cotton linter pulp, and tunicate cellulose. The solvent mixtures NaOH/urea/H_2O (7:12:81 w/w) and LiOH/urea/H_2O (4.6:15:80.4 w/w) were pre-cooled to −12 °C. Then, the desired amount of the cellulose sample was immediately dispersed into the solvent system under vigorous stirring for 10 min at ambient temperature to obtain a transparent cellulose solution (0.5–7 wt%). The cellulose solution was subjected to centrifugation at 5000 rpm for 10 min at 5 °C to remove air bubbles. The resulting solution was cast on a glass plate to give a 0.5-mm-thick layer and immersed into various coagulation baths for regeneration. The regeneration conditions were wt% H_2SO_4 aqueous solution at 0–60 °C for 5 min, ethanol–H_2O with different volume ratios at 20 °C for 2 h, methanol at 20 °C for 2 h, acetone at 20 °C for 2 h, isopropanol at 20 °C for 2 h, and tert-butanol at 20 °C for 2 h. The regenerated cellulose films were washed with excess deionized (DI) water to remove the residual chemical reagents. The cellulose hydrogels were then dried by supercritical drying or freeze-drying methods.

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Wang et al. (2012) pretreated microcrystalline cellulose, filter paper pulp, bleached sulfite pulp, cellulose I, and cellulose II (from beech wood holocellulose) with ethylene diamine (EDA) for 24 h at room temperature, and filtered and freeze-dried to get the cellulose-EDA complex. This complex was added into a 8 % LiCl/dimethyl sulfoxide (DMSO) solution. The mixture was stirred at room temperature for 24 h, followed by stirring at 75 °C for several hours to give clear solution. The cellulose solution was poured into a glass dish to form 1-mm-thick layer and immersed in ethanol for regeneration–gelation. The gel was thoroughly washed by ethanol, then by water to remove LiCl, DMSO, and EDA. The hydrogel was solvent-exchanged to ethanol and freeze-dried to form the final aerogel.

Instead of using NaOH/urea/H_2O, LiOH/urea/H_2O, or LiCl/DMSO solutions, Liebner et al. dissolved cellulose in a melting N-methylmorpholine-N-oxide (NMMO) and N-benzyl-morpholine-N-oxide (NBnMO) mixture (Liebner et al. 2007, 2008). 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 in an end-over-end mixer for 24 h. Then, the regeneration was repeated with another 10 ml of the corresponding solvent for another 24 h. Supercritical drying was used to convert the gel to aerogel.

Cellulose can also be dissolved in hydrophilic ionic liquids, such as 1-allyl-3-methylimidazolium chloride (AMImCl). In Li et al.'s work (2011), wood flour was mixed with AMImCl in a 500-mL beaker. The beaker was immersed in an oil bath at 80 °C under constant stirring for 4 h to form a brownish homogeneous mixture. The homogeneous viscous solution was transferred to appropriate molds and sealed individually. All samples underwent cyclic freeze–thaw (FT) treatment. The typical FT process is described as follows: The sample was frozen at −20 °C for 10 h; then, it was vacuum-thawed for 6 h to room temperature. After undergoing several FT cycles, all samples were immersed in the first coagulation bath with deionized water. The bath was replenished at least three times until no Cl^- was detected using $AgNO_3$ solution. The samples were then dried using supercritical drying with CO_2.

In Chen's group's research (Chen et al. 2011), wood fibers were dewaxed with a mixture of benzene and ethanol. Then, the lignin in the sample was removed using an acidified sodium chlorite solution at 75 °C for 1 h. Hemicellulose, residual starch, and pectin were removed by KOH treatment. Highly purified cellulose fibers were prepared by further treating the samples with a 1 wt% HCl solution at 80 °C for 2 h and thoroughly washing them with distilled water. Finally, about 100 ml of a solution containing purified cellulose fibers was placed in a common ultrasonic generator with a frequency of 19.5–20.5 kHz and equipped with a cylindrical titanium alloy probe tip 2.5 cm in diameter. The subsequent ultrasonication was conducted for 30 min at an output power of 1200 W, resulting in the cellulose hydrogels. The samples were then placed in a refrigerator at −18 °C for more than 24 h. Afterward, the samples were subjected to freeze-drying to allow frozen water in the materials to sublime directly from the solid phase to the gas phase.

15.2.2.2 Morphology

Cai et al. found that the cellulose aerogels fabricated from NaOH/urea or LiOH/urea had porosities of 73.9–98.0 % with Brunauer–Emmett–Teller (BET) surface areas of 260–495 m^2/g (Cai et al. 2008). For the NaOH/urea method, the porosity of the aerogels increased slightly from 85.5 to 88.7 % when increasing regeneration temperature (0–60 °C) in a regeneration bath of 5 wt% H_2SO_4. The LiOH/urea system exhibited a similar behavior. All the nitrogen adsorption/desorption isotherms obtained were of type IV (Fig. 15.4). BET surface area values of samples dried by water freeze-drying were smaller than those of samples dried with tert-butanol and CO_2. As shown in Fig. 15.5, the aerogels obtained by freeze-drying from water and tert-butanol showed differences in morphology between the surface and the inside (examined on cross sections). These aerogels had highly porous networks on the surface, consisting of fibrils less than 100 nm wide, but some parts of the sample obtained from water contained film-like structures spanning between the fibrils (Fig. 15.5b). These films could have resulted from the growth of relatively large ice crystals expelling fine fibrils of cellulose. This may be the cause of the small BET surface area value of the water freeze-dried material as compared with the other two samples. On the other hand, the inner parts of all the aerogel samples viewed on the cross sections displayed more uniform, nanometer-sized pore structures composed of fibrillar networks (Fig. 15.5d, h and l). The supercritical CO_2-dried material had a more homogenous structure, being the same on the surface and the cross section. These features confirm that supercritical CO_2 drying is the best method in preserving the liquid-swollen gel structure upon drying.

For the cellulose aerogels synthesized with the LiCl/DMSO system, the surface of the aerogels showed somewhat collapsed structure; in contrast, the inside observed on fractured cross sections showed cellulose networks of unique structure. The bulk of aerogel was composed of long and fairly straight fibrils interconnected with one another to form three-dimensional networks with large interstitial spaces (Wang et al. 2012). The difference between the surface and inside is likely to result

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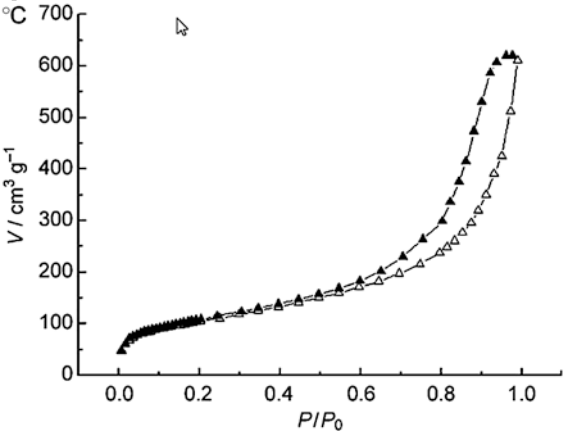

Fig. 15.4 Nitrogen adsorption/desorption isotherm of the cellulose aerogels (Cai et al. 2008)

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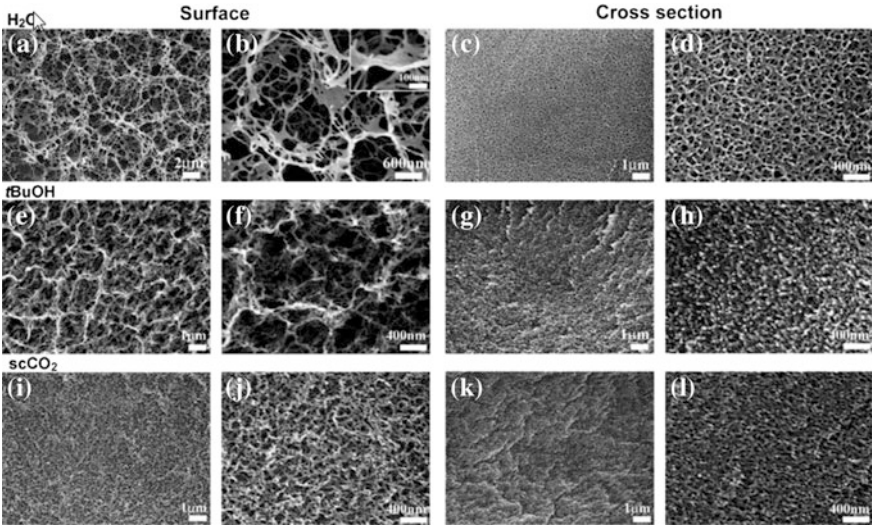

Fig. 15.5 SEM images of aerogels prepared from 4 wt% cellulose in aqueous LiOH/urea solution, regenerated with EtOH, and either freeze-dried from H_2O (**a**–**d**) or tBuOH (**e**–**h**) or dried from CO_2 (**i**–**l**) as indicated. (**a**), (**e**), (**i**) Low-magnification and (**b**), (**f**), (**j**) high-magnification images of the surface; (**c**), (**g**), (**k**) low-magnification and (**d**), (**h**), (**l**) high-magnification images of the cross sections of the aerogels. The inset in part (**b**) shows the SEM image of a tilted sample (Cai et al. 2008)

from the difference in regenerating condition; i.e., the surface was subjected to a drastic change in liquid composition, whereas the inside should have experienced gradual composition changes, leading to slow coagulation. XRD diagrams of the aerogels showed that the cellulose I structure was completely lost by dissolution–regeneration, and the pattern of aerogels was that of a poorly crystalline cellulose II. BET analysis of the aerogels gave surface area of around 200 $m^2\ g^{-1}$. The mesopore analysis by Barret–Joyner–Harrenda (BJH) method gave wide mesopore size distributions, mostly in the range of 10–100 nm. The average mesopore diameter of aerogels was 13–20 nm determined by the BJH method.

Cellulose aerogels produced by NMMO/NBnMO method displayed porous structures with specific density and surface area ranged 0.05–0.26 g cm^{-3} and 172–284 $m^2\ g^{-1}$, respectively, with increasing density at higher cellulose contents (Liebner et al. 2007, 2008). Among the tested regenerating solvents, ethanol gave the lowest specific densities upon supercritical drying at 40 °C and 100 bars and the highest retaining volume of about 70 %.

In the ionic liquid method, the morphology of the aerogels was changed with the number of FT treatment cycles (Li et al. 2011). With one FT treatment, the aerogel showed a porous structure. The distribution of the pores became denser with the increase in the FT treatment cycles. However, the microporous structure disappeared, and a dense film-like structure, which was associated with common open-pore web structure, was observed from the samples after quintuplicate FT

treatment. The film-like structure rather than a network structure was observed for the samples after septuplicate and decuplicate FT treatment. The construction of cellulose fibril networks was ascribed to the formation of the ionic liquid crystal during the freezing process. Despite the influence of the wood/ionic liquid solution concentration on the density of the network, the frequency of crystallization was considered as the vital parameter to form the mesh structure.

Cellulose aerogels prepared via ultrasonication exhibited extremely low bulk densities in the range of 1.3×10^{-3}–17.0×10^{-3} g cm^{-3} (Chen et al. 2011) and porosities of 98.94–99.91 %. They had a 3D open-porous fibrillar network structure of continuous nanofibers (approximately 30–150 nm in width and several hundred microns long), indicating that the CNFs self-assembled via hydrogen bonding during the freeze-drying process, thus organizing them into long nanofibers and formation a porous network structure. The distribution of the pores became denser with the increase in the solid content of the hydrogels. Most of the microporous structure disappeared when the CNF content was higher than 0.5 %, and a dense 2D sheet-like structure, organized by small CNFs (around 20–30 nm wide and several microns long) with only a few aggregates, was observed.

15.2.2.3 Thermal Properties

Thermogravimetric analysis showed the degradation temperature of cellulose aerogels synthesized by the alkali/urea method was about 300–310 °C (Cai et al. 2012). The degradation point of the aerogels fabricated by the sonication method was in the range of 325–337 °C. This degradation point was much higher than that of original wood fibers (210 °C) (Chen et al. 2011). The cellulose aerogels showed a very low thermal conductivity of 0.025 W m^{-1} K^{-1}, which was slightly lower than that [0.0295 W m^{-1} K^{-1}, (Sai et al. 2014)] of BC aerogels (Cai et al. 2012).

15.2.2.4 Mechanical Properties

In Cai et al.'s work (Cai et al. 2012), the tensile modulus and strength of cellulose aerogels were determined as 72.0 and 12.4 MPa, respectively, which was much higher than the compression modulus, 0.27 MPa (Sai et al. 2013), of BC aerogels. Chen et al. found that their cellulose aerogels exhibited high flexibility and ductility because of the high aspect ratio, high crystallinity, high CNF mechanical properties, and an entangled 3D or 2D microstructure (Chen et al. 2011). As shown in Fig. 15.6a–c, an aerogel with approximate dimensions of $5.44 \times 5.44 \times 0.59$ cm^3 and a bulk density of 2.6×10^{-3} g cm^{-3} could be repeatedly bent without destroying its structural integrity. The compression property of the aerogels was also tested (Fig. 15.6d–f). A cylindrical aerogel with an approximate radius of 1.05 cm, a height of 1.67 cm, and density of 9.2×10^{-3} g cm^{-3} could be easily compressed by hand into a sheet about 0.09 cm thick without disintegrating. The obtained dense sheet with a bulk density of 0.17 g cm^{-3} could also be folded easily.

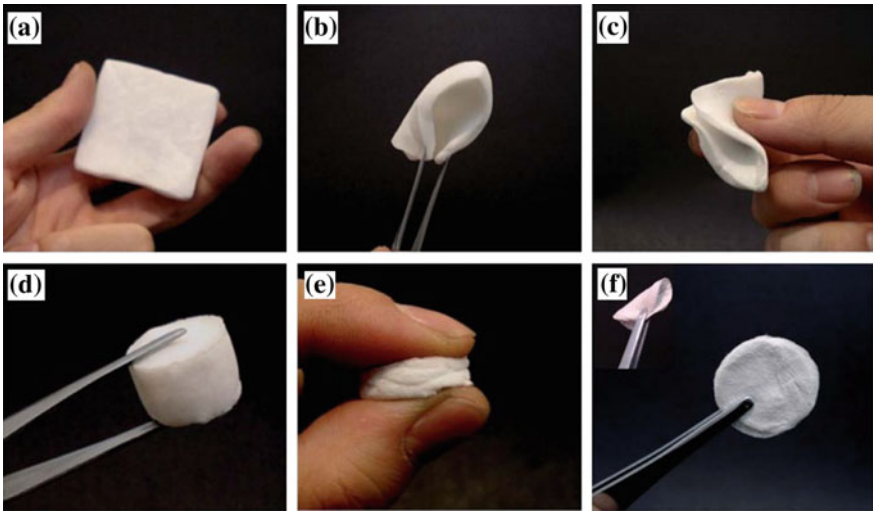

Fig. 15.6 A demonstration of the flexibility and deformability of the aerogels. **a–c** The aerogel with dimensions of about 5.44 × 5.44 × 0.59 cm^3 can be repeatedly bent as foldable as conventional paper. **d–f** Aerogel with a diameter of 2.10 cm and height of 1.67 cm can be compressed into a circuit sheet about 0.09 cm thick by hand; the obtained sheet can also be folded easily (Chen et al. 2011)

15.2.3 Cellulose Aerogels Prepared from Wastes

15.2.3.1 Fabrication Methods

In Nguyen et al.'s work (Nguyen et al. 2013, 2014), recycled cellulose fibers from paper waste were dispersed into a NaOH/urea solution by sonicating for 6 min. Thereafter, the solution was placed in refrigerator for more than 24 h to allow gelation of the solution. After the solution was frozen, it was then thawed at room temperature and then followed by immersing into ethanol (99 vol.%) for coagulation. After coagulation, solvent exchange was carried out by immersing the gel in DI water for 2 days. The sample was then frozen in a freezer at −18 °C for 12 h. After that, freeze drying is carried out for 2 days with a freeze dryer to obtain the desired aerogel.

Feng et al. dispersed recycled cellulose fibers and Kymene cross-linker in 30 ml DI water by sonicating for 10 min (Feng et al. 2015). The suspension was then placed in a refrigerator at −18 °C for more than 24 h to allow the gelation. The cellulose aerogel was obtained by freeze-drying the gel at −98 °C for 2 days using a freeze dryer. Thereafter, the cellulose aerogel was further cured at 120 °C for another 3 h to cross-link completely the Kymene molecules.

In Jin's work (Jin et al. 2015), waste newspaper (WNP) pieces were dispersed into 1-allyl-3-methyimidazolium chloride (AMImCl) in a 20-mL beaker. The beaker

was immediately immersed in an oil bath at 80 °C under vigorous stirring for 4 h to form a homogeneous mixture. Finally, a dark, amber-colored, viscous WNP suspension was obtained. The resultant WNP solution was completely cast in Teflon molds, took off air bubble in a vacuum oven, and then immediately coagulated in the water to obtain a regenerated cellulose hydrogel. It was washed with excess deionized water until the residual chemical reagents were absolutely removed. Then, the prepared hydrogels were freeze-drying in a vacuum freeze dryer at −50 °C for 48 h.

Li et al. used waste wheat straw powder to synthesize cellulose aerogels (Li et al. 2014). Wheat straw was first treated by a mixed solution of benzene/absolute ethanol (2:1 v/v) in a Soxhlet extractor at 90 °C for 6 h. Then, the treated sample was air-dried and treated with a 10 % $NaClO_2$ solution at 75 °C for 5 h. The next step was to collect the sample by filtration, wash it three times with DI water, and then immediately treat it with 2 % NaOH at 90 °C for 2 h. The product was again collected by filtration and washed three times with DI water before treating it with 1 % HCl at 80 °C for 2 h. Finally, the purified cellulose was collected by filtration, washed three times the deionized water, and dried at 60 °C for 24 h. The purified cellulose was added to a 10 % aqueous solution of NaOH/polyethylene glycol (PEG) (9:1 wt/wt) with magnetic stirring for 5 h to form a homogeneous solution. The solution was frozen for 12 h at −15 °C and then subsequently thawed at ambient temperature with vigorous stirring for 30 min. This process was repeated at least 3 times. The product was successively regenerated by 1 % HCl solution, DI water, and tert-butanol until the formation of an amber-like hydrogel. Finally, the resultant cellulose hydrogel samples were freeze-dried at −30 °C for 48 h.

15.2.3.2 Hydrophobic Coating Methods

As the cellulose aerogels developed in Sect. 2.3.1 were hydrophilic, the as-prepared cellulose aerogels were coated with a hydrophobic coating agent on their highly porous networks to form super-hydrophobic cellulose aerogels. Silane reagents such as methyltrimethoxy silane (MTMS) and trimethylchlorosilane (TMCS) were usually used as the coating agents via a CVD method (Feng et al. 2015; Jin et al. 2015; Li et al. 2014; Nguyen et al. 2013, 2014). The cellulose aerogel sample and an open glass vial containing MTMS/TMCS were placed in a big container. The container was then capped and heated at 70 °C for 3 or 12 h for the silanation reaction. Thereafter, the coated sample was placed in a vacuum oven to remove the excess coating reagent until the pressure reaches 0.03 mbar.

15.2.3.3 Environmental Stability

The MTMS-coated cellulose aerogels had super-hydrophobicity on both their external and internal surfaces. Large water contact angles of 153.5° and 150.8° were obtained, respectively, thus proving that the hydrophobic coating was

successfully covered the whole aerogel networks. The samples were then exposed in normal ambient atmosphere for five months. The water contact angles on the external surface and the cross section did not show any obvious change with time, confirming the excellent hydrophobicity stability of the MTMS-coated recycled cellulose aerogels (Feng et al. 2015).

15.2.3.4 Morphology Control

Figure 15.7 showed photographs and SEM images of the developed recycled cellulose aerogels (Feng et al. 2015; Nguyen et al. 2013; Nguyen et al. 2014). The recycled cellulose aerogels were formed via hydrogen bonding between the self-assembled cellulose fibers (Isobe et al. 2012). Besides, Kymene molecules could diffuse and react with the cellulose fiber surface to form the hydrogen bonding and also cross-linked with the surrounding Kymene molecules. The utilization of Kymene as a cross-linker combined the reinforcement and protection mechanisms (Nordell 2006) during the gelation process, which thus ensured the resultant aerogels with a robust structure and good flexibility. In contrast to the mesopores (2–50 nm) of the aerogels formed by the cellulose nanofibers, highly porous structures of the cellulose aerogels with macropores (>50 nm) could be clearly observed in SEM images of Fig. 15.7c–f. Their macropores were possibly caused by the larger size of the recycled cellulose fibers, obtained from the paper waste. Figure 15.7c, d shows the morphologies of the cellulose aerogels with cellulose concentrations of 0.25 and 1.00 wt%, respectively. The aerogel with the higher cellulose concentration (1.0 wt%) had a more compacted network and lower

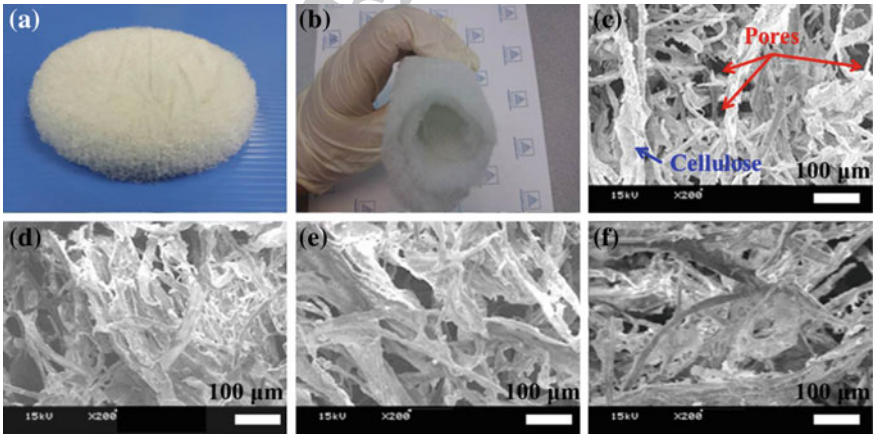

Fig. 15.7 **a** Super-hydrophobic recycled cellulose aerogel, **b** flexibility of the large-scale cellulose aerogel (38 × 38 × 1 cm) containing 0.60 wt% of the cellulose fibers, SEM images of the cellulose aerogels with different ratios of cellulose fibers (wt%) and kymene (μl): **c** 0.25:5, **d** 1.00:5, **e** 0.60:5 and **f** 0.60:20 (Feng et al. 2015)

porosity. However, an increase of Kymene from 5 to 20 μl did not significantly impact the aerogel structures as shown in Fig. 15.7e, f.

In Jin et al.'s study, the aerogels exhibited a highly open-porous structure (porosity ≈ 96.8 %) consisting of interconnected uniform cellulose fibers. The densities of the aerogels without and with silane modification were 0.020 and 0.029 g cm^{-3}, respectively (Jin et al. 2015). Li et al. found that the bulk densities of the samples increased with the enhanced cellulose concentrations (Li et al. 2014). The samples were referred as C1, C2, C4, and C8 with mass ratios of 1/100, 2/100, 4/100, and 8/100 cellulose to the NaOH/PEG solution. The bulk densities of C1, C2, C3, and C4 were 44.9, 56.7, 80.7, and 148.0 mg cm^{-3}, respectively. The pore configurations of C1 and C2 were dense, anfractuous, and multilayered, while the pore distributions of C3 and C4 were relatively uniform. Some larger sheet and blocky regions surrounding with pore structures were observed. This might be attributed to the existence of undissolved fractional cellulose at high concentrations. It was concluded that the concentration had a significant influence on the pore structures of the aerogels. Specific surface areas and mean pore diameters of the samples were in the ranges of 36.5–101 m^2 g^{-1} and 16.2–18.3 nm, respectively.

15.2.3.5 Thermal Properties

Thermal conductivity of the recycled cellulose aerogel was 0.032 W m^{-1} K^{-1} (Nguyen et al. 2014), which was comparable to those of good insulation materials such as silica aerogel (0.026 W m^{-1} K^{-1}), wool (0.03–0.04 W m^{-1} K^{-1}), and Aspen Aerogels products (0.021 W m^{-1} K^{-1}) (Sequeira et al. 2009; Nguyen et al. 2014). A TGA test was performed for the sample in air. There was a weight loss of 23 % in the temperature range of 25–230 °C due to the removal of absorbed water and some urea trace left in the sample. Then, a weight loss of 42 % occurred in the range of 230–330 °C due to the degradation and burning of the cellulose aerogel structure. There was small drop of the sample weight at 550–630 °C due to the oxidation of some stable local structures of the aerogel.

15.2.3.6 Mechanical Properties

As shown in Fig. 15.7b, the large-scale cellulose aerogel was easily bent or rolled without damaging its shape. The flexibility of the recycled cellulose aerogel was comparable to that of nanocellulose aerogels (Chen et al. 2011). A qualitative test was performed for the sample to investigate its mechanical strength by loading a 200 g weight on the sample for 1 h, 5 h, 1 day, and 5 days. No shape change of the aerogel was found after the test durations. Tensile and compression tests were performed for the aerogel samples. The yield and tensile strengths of the aerogel were 1080 and 1470 N/m^2, respectively, with a Young's modulus of 11 kPa (Nguyen et al. 2014).

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15.3 Conclusions and Future Perspectives

High energy consumption, climate changes, and the exhaust of fossil fuels require more sustainable and energy efficient construction solutions. In order to meet the demand of improved energy efficiency, the thermal insulation of building has an important role. As a result, it is essential to develop new insulation materials with low thermal conductivity for construction applications. Cellulose is a green, non-toxic, cheap, and abundant material. The combination of cellulose and aerogel structure has formed a novel and effective material for heat insulation. The extremely low thermal conductivity of 0.025–0.032 W m^{-1} K^{-1} and good flexibility of cellulose aerogels make them a promising material for building heat insulation. The thermal stability limitation of cellulose aerogels can be overcome by combining with fire retardants or other heat insulation materials such as flexible silica aerogels.

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