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ORIGINAL ARTICLE

The effect of freezing speed and hydrogel concentration on the microstructure and compressive performance of bamboo-based cellulose aerogel

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Abstract Cellulose aerogel is a kind of ultra-light solid material which resulting from natural cellulose materials, and its performance is highly related to its structure. In this study, we prepared cellulose aerogels with different densities by regulating the concentration of microfibrillated cellulose (MFC) hydrogel using bamboo parenchymal cells as a starting material. The effects of the freezing speed and hydrogel concentration on the microstructure and compression performance of the resultant aerogels were investigated. The results demonstrated that higher freezing speed can inhibit the aggregation of MFC, resulting in aerogel with higher porosity. Conversely, increasing hydrogel concentration facilitated the aggregation of MFC, generating a distinct conversion from a looser fibril network structure (low density) to a more compact sheet-like structure (high density). Moreover, the results showed an expected positive correlation between the density of the aerogel and its compression performance, both in compression modulus and energy absorption.

Keywords Bamboo · Hydrogel · Aerogel · Microstructure · Compression performance

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Introduction

Aerogel is a kind of ultra-light solid material with exceptionally high porosity. It is prepared by replacement of a solvent in a hydrogel by air without significantly altering the network structure in the hydrogel state. Aerogel was first reported by Kistler in 1931 [1], attracting great interest worldwide ever since due to the fact that it combines low density, low thermal conductivity and dielectric permittivity, with high specific surface area and excellent shock absorption [2–4]. When cellulose aerogel is used instead of silica or synthetic polymers as a skeleton material, it has also shown to produce materials with comparatively high strength and ductility [5–7]. Therefore, it has great potential for applications where biocompatibility and biodegradability are especially required [8].

Within this field, the preparation of cellulose aerogels using microfibrillated cellulose (MFC) as the skeleton material is of high interest to academics and industry. Herein, the MFC is defined as a string-like material formed by laterally packing cellulose microfibrils with hydrogen bonding, which have outstanding mechanical properties, high capacity to build up an entangled network structure, and many other excellent features [9]. Furthermore, MFC is classified as a non-toxic material, derived from renewable sources without adverse effect on the human health or the environment [10].

Several mechanical methods have already been used to fabricate MFC, including high-pressure homogenization, grinding, cryocrushing and ultrasonication [11]. Among these methods, ultrasonication is considered to be very promising, because of the relative ease of the procedure and its ability to break cellulose interfibrillar hydrogen bonds and, ultimately, extract nanofibrils from plant cell walls [12, 13].

The performance of cellulose aerogel materials is mainly determined by their hierarchical structure, which, in turn, is predominantly dependent on the drying procedure adopted and the hydrogel concentration. In the past, supercritical drying has been widely used to transform a hydrogel into an aerogel, but this requires large investments and is costly [14]. Therefore, freeze-drying is becoming an increasingly preferred option, owing to its simplicity and the comparable performance and controlled structure of aerogels produced using this method [15]. Several studies have been performed to investigate the morphological characteristics and mechanical properties of cellulose aerogels. Previous research has shown that by varying the freeze-drying conditions, along with MFC hydrogel concentration, one can tailor the microstructure of cellulose aerogels based on the MFC network [10, 16] and their mechanical properties [8].

Bamboo, one of the world's fastest growing plants, is used to produce a wide spectrum of industrial products in China. Therefore, China already produces a very large quantity of bamboo processing residue today, which means that finding new ways to use these residues in high value-added applications is a major priority. In a previous study, we have already demonstrated that these residues contain a high proportion of parenchymal cells. It has been proved that fibrillation to produce MFC should be less energy demanding due to the parenchymal cells having a thinner cell wall and a larger diameter compared to fibers [17, 18]. In the present study, the prepared MFC was used to prepare cellulose aerogels with variable porosity. The primary aim of the study was to confirm the effect of freezing speed on the microstructure of aerogels and to further tune the microstructure and compressive behavior of aerogel by altering the density of these aerogels. Through the process, we hoped to observe that aerogels with a variety of structure can be tailored for different applications based on a wide range of densities.

Experimental

Materials

Bamboo (*Phyllostachys pubescens*) processing residues purchased from a flooring company, Yiyang Taohuajiang Bamboo Industry Development Co., Ltd, China, were used to prepare MFC. It is estimated that parenchymal cells make up nearly 80 % of bamboo processing residue weight [17]. These residues were ground into bamboo powder and then passed through a 200-mesh screener (aperture of 75 μm) to separate bamboo parenchymal cells. After removing dust and impurities by hot-water extraction, bamboo parenchymal cells were then chemically purified to obtain pure cellulose, with lignin removed using acidified sodium chlorite, followed by hemicellulose removal with potassium hydroxide [19]. After purification, the pure cellulose was soaked in distilled water (concentration: ~0.5 % in mass, Fig. 1a) and then treated 50 min by an ultrasonic generator (JY99-IIND, Ningbo Science Biotechnology Co., Ltd., China) set at 19.5–20.5 kHz in frequency at 540 W to isolate fibrils (Fig. 1b) [20].

Aerogels preparation

A 1 wt% MFC hydrogel was prepared from the 0.5 wt% MFC hydrogel by vacuum filtration and three groups of 120 ml MFC hydrogel were then transferred into three glass flasks (140 mm in height and 95 mm in diameter) and frozen (freezing stage) at different speeds. The first one was performed at ca. −196 °C in liquid nitrogen for 30 min, the second one at −80 °C in an ultra-low-temperature freezer for 12 h and the last one at −20 °C in an ordinary freezer for 24 h. Then the frozen samples were freeze-dried (sublimation stage) in a lyophilizer (FreeZone plus 6L, Labconco Corp., Kansas, MO, USA) at a temperature of −85 °C. All samples were kept frozen under a vacuum of 0.06 mPa for 48 h.

Four concentrations of MFC hydrogel (i.e., 0.05, 0.1, 0.2 and 1.0 wt%) were prepared to investigate the effect of hydrogel concentration on the microstructure and compressive properties of the resultant MFC aerogels. The concentration of MFC hydrogel was adjusted from the original hydrogel with the addition of distilled water. Hydrogel (30 mL) samples of targeted concentration were poured into glass flasks (115 mm in height and 30 mm in diameter). They were then frozen using liquid nitrogen and freeze-dried in the lyophilizer under the above-mentioned conditions. The freeze-dried aerogels were stored in a desiccator containing silica gel until further characterization was conducted.

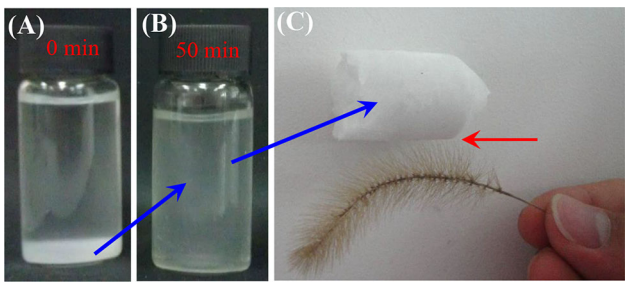

Fig. 1 Photography of bamboo processing residue suspension (**a**) and MFC hydrogel with a concentration of 0.5 wt% (**b**) after ultrasonic treatment for 50 min and its corresponding ultra-light aerogel were put on dog tail grass (**c**)

Density and porosity measurement

The bulk density of the aerogel was measured as the ratio of its weight to its volume. Porosity (P) was estimated from the density of the cellulose aerogel (d_a) by taking 1.6 g/cm^3 as the density of crystalline cellulose (d_n) using Eq. (1):

$$P\ (\%) = \left(1 - \frac{d_a}{d_n}\right) \times 100\ \% \quad (1)$$

Microstructure observation

Prior to the microstructural analysis, all samples were dried overnight in a desiccator containing silica gel. The microstructure of the MFC aerogel samples was observed by an environmental scanning electron microscope (FE-SEM, XL30, FEI, USA) at an accelerating voltage of 7.0 kV. Before the FE-SEM observation, samples were sputter-coated with a layer of platinum under a vacuum for 90 s (Leica EM SCD 005, Germany). The measurement of the fibril widths was conducted with image analysis software (Image-Pro Plus 6.0).

Compression test

For the compression test, the MFC aerogel materials were trimmed into cylindrical samples using curved tweezers (Dumont, Switzerland) with a diameter of 30 mm and a height of 30 mm. The compression tests were performed with a micro-mechanical testing machine (Instron 5848, USA), with a sensor attached to a 5 N load cell operated at the rate of 10 mm/min. The modulus of the aerogels was derived from the initial linear region of the stress–strain curves generated from the experiment. At least five samples were measured. In addition, the energy absorption was calculated by integrating the area under the stress–strain curve from 0 to 70 % of the strain.

Results and discussion

The effect of freezing speed on the microstructure of aerogel

At the freezing stage, the water in the MFC hydrogel is frozen into ice crystals with MFC trapped among them. The final cellulose aerogel is then formed when ice crystals are sublimated during the following drying step [15, 21]. Therefore, the freezing conditions are closely related to the microstructure properties of the final aerogel. MFC hydrogels frozen at three different temperatures, namely −196, −80 and −20 °C, resulted in aerogels with different macroscopic and microscopic microstructures. The aerogels frozen by liquid nitrogen exhibited a uniform and smooth surface (Fig. 2a), while the ones frozen at slower speeds presented rougher surfaces and even some streaks, where ice crystals had formed (Fig. 2d, g).

Using liquid nitrogen to rapidly freeze the MFC hydrogel was effective in preserving the high porous network structure, with the corresponding aerogels exhibiting a homogeneous three-dimensional network structure (Fig. 2b) that was composed of finer fibrils of about 10–100 nm in width (Fig. 2c). However, aerogels cooled at slower speeds using an ultra-low temperature freezer (−80 °C) and regular freezer (−20 °C) exhibited less porous structures. The aerogel frozen at −80 °C was composed of aggregated MFC bundles and less individualized MFC (Fig. 2f). Interestingly, MFC aggregates were also partially aligned parallel to the orientation of freezing direction at a lower magnification (Fig. 2e). This indicates that crystal structures formed in the freezing stage began to have a significant effect on the self-assembling of MFC via hydrogen bonding during the freezing process at slower speeds. When the MFC hydrogel was frozen under a slower speed, ice crystals gradually grew in the direction of freezing and trapped the MFC aggregates in the space between these growing ice crystals [15]. Moreover, a compact film-like structure was formed during the relatively slow freezing process at −20 °C (Fig. 2h, i). It was also clear that the isolated cellulose nanofibrils tend to aggregate spontaneously during the slower freezing process. This self-organizing phenomenon could be attributed to the strong hydrogen bonding that attracts isolated nanofibril together into larger-sized bundles or film-like structures [22]. The fast formation of ice crystals under rapid freezing reduced the possibility of this type of coalescence. Based on these results, liquid nitrogen was selected as the preferred approach of freezing for the preparation of cellulose aerogel with different densities.

The effect of density on the microstructure of aerogel

Ultra-light aerogels with white appearance had been successfully prepared from MFC hydrogel using bamboo parenchyma cells via freeze-drying using liquid nitrogen (Fig. 1c). Aerogels were prepared from various concentrations of MFC hydrogel to compare their microstructure with different densities. By altering the concentration of the MFC hydrogel from 0.05 to 1.0 wt%, the resulting densities changed from 0.5 to 10.19 mg/cm^3, and the porosities increased from 99.38 to 99.97 % (Table 1). Aerogel with a density as low as 0.50 mg/cm^3 could be successfully prepared from low concentration of MFC hydrogel. Furthermore, the aerogel with any target density in the above range can be easily prepared just through

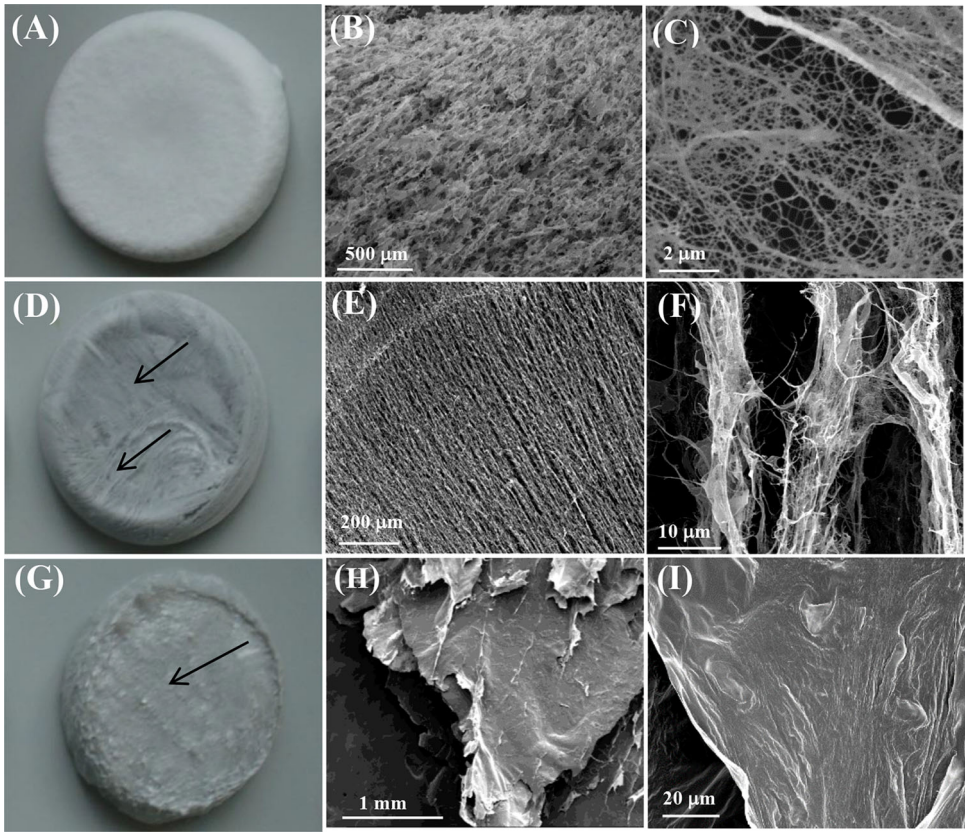

Fig. 2 Photography and SEM images of the aerogels by initial freezing at −196 °C (**a–c**), −80 °C (**d–f**) and −20 °C (**g–i**). *Arrows* show the streaks due to ice crystals

Table 1 Properties of aerogels made from MFC (microfibrillated cellulose) hydrogel of different concentrations

MFC concentration (wt%)	d_a (mg/cm^3)	P (%)
0.05	0.50	99.97
0.1	1.05	99.93
0.2	2.39	99.88
1.0	10.19	99.38

P porosity

simple controlling of the MFC hydrogel concentration. Aulin et al. [16] also found that the density and surface texture of aerogels could be tuned by selecting the concentration of the MFC hydrogel before freeze-drying.

Figure 3a exhibits aerogel with a density of 0.5 mg/cm^3 had suffered an appreciable shrinkage, whereas the aerogels for the other three higher densities (1.05–10.19 mg/cm^3) retained their original shapes very well. The microstructure of the aerogel with different densities is shown in Fig. 3b–i. The aerogel with a density of 0.5 mg/cm^3 exhibited a highly porous network structure even after the large apparent shrinkage in volume (Fig. 3b). Furthermore, high-resolution SEM observations (Fig. 3c) revealed that this porous structure was built up with individual cellulose nanofibril without any visible aggregation. The high aspect ratio of the cellulose nanofibrils impart them with high flexibility to be interwoven and connected together by strong hydrogen bonds during the freeze-drying process, which resulted in this porous network structure [23]. When the aerogel density increased from 0.5 to 1.05 mg/cm^3, a hierarchical structure could be observed, which was noteworthy for the coexistence of individual fibrils and larger fibril bundles (Fig. 3d). These bundles were actually composed of fibrils with widths down to the nanoscale (Fig. 3e). A highly interconnected porous network of cellulose aerogel was also observed for aerogels with densities of 0.5 and 1.05 mg/cm^3, respectively. Both were suitable for cell culture scaffold applications as they can encourage cellular infiltration and allow the exchange of nutrients and metabolic waste [24].

Increasing the aerogel density from 1.05 to 2.39 mg/cm^3, the spontaneous aggregation of cellulose nanofibrils became predominant, with individual nanofibril rarely found (Fig. 3f). The layered structures formed at this density were further connected to each other under a relatively uniform honeycombed structure (Fig. 3g). Similar structural transformations with increasing densities from a network structure to a lamellar one have also been reported in other types of low-density aerogel materials [15, 17, 24]. The MFC aerogel with a density of 10.19 mg/cm^3 also exhibited a

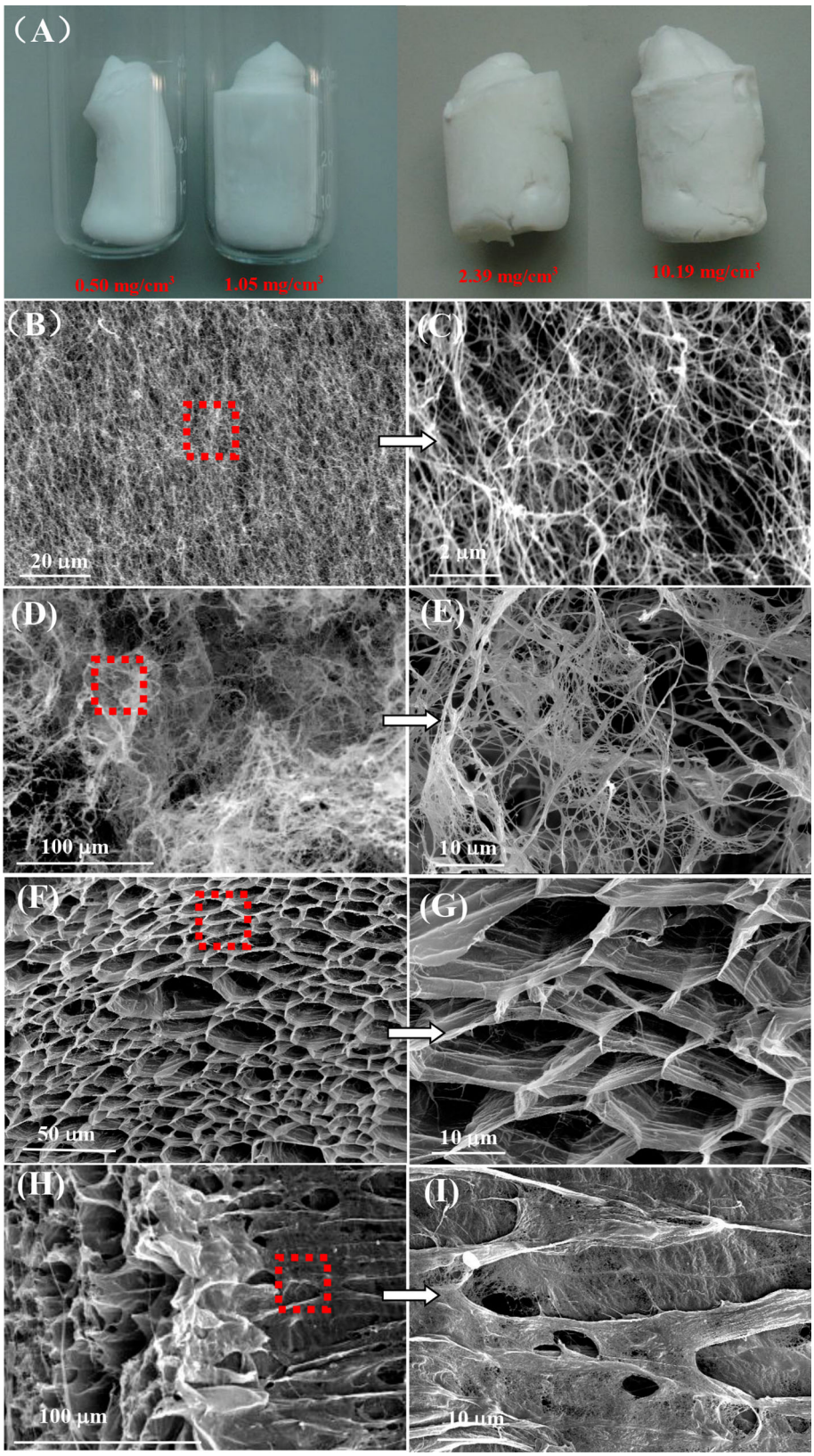

Fig. 3 Photography of aerogels with different density (**a**), SEM images of aerogel with density of 0.50 mg/cm^3 (**b**, **c**), 1.05 mg/cm^3 (**d**, **e**), 2.39 mg/cm^3(**f**, **g**) and 10.19 mg/cm^3 (**h**, **i**)

similar honeycombed structure, but with thicker layers and reduced cavities (Fig. 3h, i), thus indicating increased aggregation of MFC with rising density. In a word, density has a direct effect on the microstructure of the formed aerogel materials. Therefore, this can be tailored according to the target applications of the aerogel [25].

The effects of density on the compressive properties of MFC aerogels

Because the aerogels of 0.5 mg/cm^3 in density had suffered appreciable volume shrinkage, they were not suitable for the compressive test. The compressive stress–strain curves of the three other ultra-low-density MFC aerogels samples (1.05–10.19 mg/cm^3) are shown in Fig. 4a. The aerogels had excellent compressive ductility and could be deformed to a particularly high compressive strain of ca. 80 %. It is worth pointing out that the lowest density aerogel (1.05 mg/cm^3) was extremely ductile and could be deformed to ca. 95 %. The high ductility of aerogels is mainly correlated to their very porous structures and the fact that they contain sufficient amounts of flexible cellulose components [3, 23]. In contrast, inorganic aerogels, such as carbon and resorcinol–formaldehyde aerogels, are very brittle compared to their cellulose counterparts [26].

The compressive properties of aerogels have a strong dependence on density. For instance, a tenfold increase in yield stress was observed when the density was increased from 1.05 to 10.19 mg/cm^3, possibly because of the presence of a more solid sheet structure and tighter bonds between fibrils in the network. This hypothesis seems to be confirmed by the SEM images shown in Fig. 3. Interestingly, the aerogels with density of 1.05 and 2.39 mg/cm^3 presented a typical network structure and sheet-like structure, respectively, but their stress–strain curves were very similar. From Fig. 3, one could see that the layer structure of aerogels at 2.39 mg/cm^3 is much more tenuous when compared to the aerogels at 10.19 mg/cm^3. This explains why the former sheets are less rigid and can deform far more easily under compression.

Although all three stress–strain curves demonstrated a linear behavior up to large strains, the aerogels showed true elasticity (i.e., full recovery after deformation) only at small strains below 3 %. Sehaqui et al. have also reported similar results [25]. Therefore, the term "modulus" merely presented the slope of the stress–strain curves. As shown in Fig. 4b, the modulus of the MFC aerogels increased from 0.2 to 5.2 kPa when the density increased from 1.05 to 10.19 mg/cm^3. Therefore, the aerogels are more robust when they have a higher MFC content.

The energy absorption of aerogels, characterizing the capacity of resistance to compression, was calculated by integrating the area under the stress–strain curve up to 70 % compression strain. An exponential rise of the energy absorption with an increase of densities is shown in Fig. 4c. Furthermore, the energy absorption of aerogels with a density 10.19 mg/cm^3 was very close to that found for the cellulose aerogel (29.6 kJ/m^3) at a density of 12 mg/cm^3 [8].

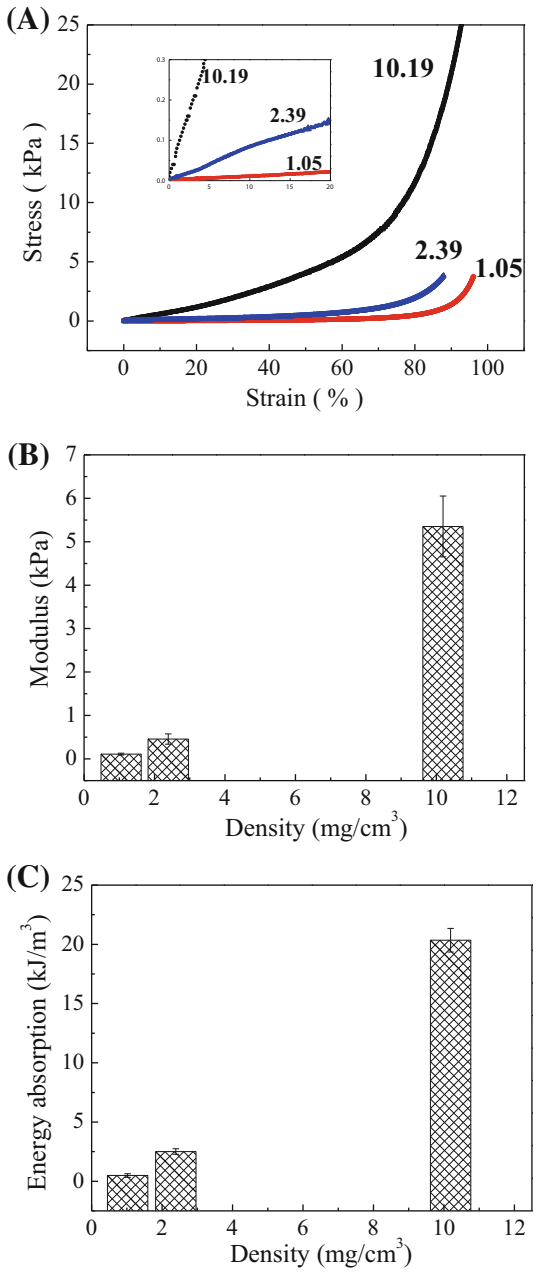

Fig. 4 Compressive stress–strain curves for aerogel of different densities at the same rate (**a**). Modules for aerogel of different density (**b**). Energy absorption for aerogel of different density (**c**)

Conclusion

MFC extracted from bamboo parenchymal cells was used to prepare aerogels, and the microstructure and compressive performance of aerogels were regulating the freezing speeds and MFC hydrogel concentration. MFC aerogels prepared under high freezing speeds using liquid nitrogen showed a typical three-dimensional network structure. Slowing down the freezing speed using an ultra-low freezer

or regular freezer led to an agglomeration of MFC, changing the structure from a cross-linked network to a film-like one. It was also observed that the microstructure and mechanical properties had a close relationship with the density of the aerogel. When densities were altered from 0.50 to 10.19 mg/cm^3, the present aerogels demonstrated a tunable structural transformation from a porous network structure to sheet-like one. Furthermore, energy absorption of the aerogels could vary by two orders of magnitude based on their density. Therefore, aerogels with different microstructure and mechanical properties can be easily designed to meet the requirements of various applications.

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