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ORIGINAL RESEARCH

Mechanical performance and thermal stability of polyvinyl alcohol–cellulose aerogels by freeze drying

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Abstract Polyvinyl alcohol (PVA)/cellulose nanofibers (CNFs)/Gelatin hybrid organic aerogels were synthesized using a facile and environmentally friendly freeze-drying method. The biobased gelatin acted as a cross-linking agent and combined PVA and CNFs tightly by hydrogen bonds. The composites were characterized and analyzed by various techniques including uniaxial compression test, scanning electron microscopy, as well as thermal conductivity analysis and TGA–DTG analyses. The mechanical properties were strengthened significantly with the introduction of a small amount of gelatin. The modulus of PVA/CNF/G3 was 1.65 MPa, nearly eightfold of the PVA/CNF aerogel and 91 times higher than the neat CNF aerogel. Microstructure analyses revealed the three-dimensional network of the aerogels. The composites also possess good thermal stability, low density, and low thermal conductivity. Therefore they have broad prospects in the field of thermal insulation.

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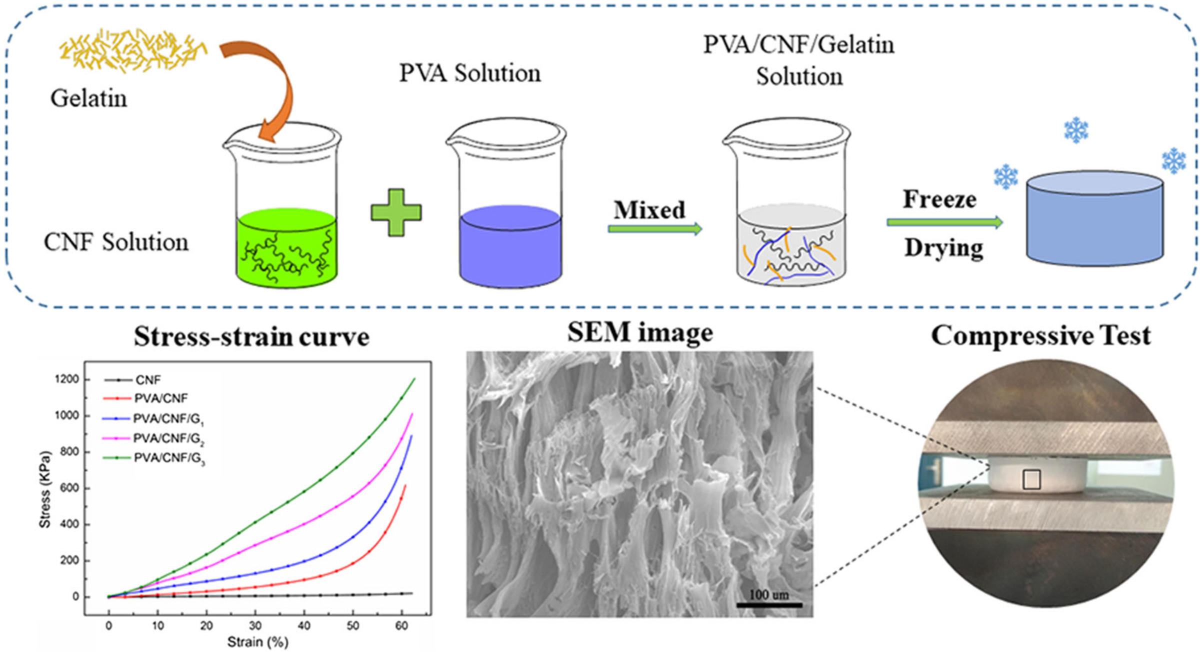
Graphical abstract



Keywords Polyvinyl alcohol · Cellulose nanofibers · Gelatin · Aerogel · Mechanical properties

Introduction

Aerogels are excellent materials prepared by replacing the solvent by air with almost 95% air and 5% network structure. Aerogels were first reported by Kistler (1931), using silicon alkoxides as precursors, followed by sol–gel method and supercritical drying technique. With the development of ambient pressure drying, aerogels have become industrialized and commercialized. Silica aerogels are typical representatives of nanostructured materials with attractive characteristics, such as ultralow density, high specific surface area, low thermal conductivity and high porosity (Li et al. 2016; Rao et al. 2007; Wei et al. 2007). Therefore, they attracted wide attention in various fields, like thermal insulation, aviation, catalyst supports, biomedical engineering and automobiles (Amonette and Matyáš 2017; Maleki et al. 2014; Yun et al. 2014). In spite of these excellent properties, inorganic aerogels (silica aerogel) generally exhibit low strength, fragility and inherent brittleness, which seriously limit the practical application. Deng et al. (1998) investigated the mechanical strength of silica aerogels with the density of 0.112 g/cm^3 of only 0.018 MPa. On the other hand, surface modification will use lots of hazardous organic solvent which is not environmentally friendly (Pan et al. 2017). Organic aerogels derived from biocompatible and renewable materials aroused a growing interest. Organic polymer aerogels also exhibit high fracture toughness.

Nanocellulose based aerogels have attracted broad interest in scientific circles (Li et al. 2017). The combination of these characteristics makes the CNF based aerogels a prospective application in thermal insulation (Guo et al. 2018; Zheng et al. 2014). There are several methods available for making CNFs. The primary methods are high-pressure homogenization or mechanical milling (Pääkkö et al. 2007). Saito et al. (2007) used 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation to process raw materials, followed by mechanical treatment of the oxidized cellulose/water slurries, which reduced energy consumption and increased reaction rate. The cellulose nanofibers were fabricated based on TEMPO-mediated oxidation in our laboratory.

Despite the remarkable properties of CNF aerogels, the low strength, fragility and brittleness limited the further application. Crossing-linking is an effective way to increase the mechanical strength (Shang et al. 2015). Jiang and Hsieh (2017) made CNF aerogels with significantly improved compressive properties using a facile cross-linking approach. The hydrogels were solvent exchanged with acetone and then cross-linked with methylene diphenyl diisocyanate (MDI). Polyvinyl alcohol is a good organic binder in aerogel system because of it is water soluble and has a lot of hydroxyl bonds. Chen et al. (2014) fabricated strengthened poly(vinyl alcohol)/clay aerogel composites, exhibiting significantly increased compressive moduli compared to control materials. In order to further enhance the mechanical properties, we have also introduced biobased material, gelatin. Gelatin is an inexpensive material and is known for its biocompatibility and nontoxicity. It can be obtained from bones, skin and connective tissues, and has been widely used in food, pharmaceutical and cosmetic industries (Liu et al. 2010; Yang et al. 2007). Therefore, we applied a green way to prepare hybrid organic aerogel with nanocellulose as the base, PVA and gelatin might connect with nanocellulose through the amino and hydroxyl groups. In addition, CNF aerogels are usually dried by supercritical drying and freeze drying, in order to avoid collapse of network caused by capillary pressure. Supercritical drying is difficult to promote because it requires intensive energy and high-cost facility. So freeze drying is an easy and environmentally friendly method to produce CNF aerogels.

In the present study, PVA/CNF/Gelatin hybrid aerogels were synthesized via freeze drying. The density, morphology, thermal conductivity, mechanical properties and thermal stabilities were investigated. The composites endowed excellent characteristics and will have board prospects in the field of thermal insulation.

Experimental

Preparation of cellulose nanofibers (CNFs)

Cellulose nanofibers (CNFs) used in this study were prepared by TEMPO-mediated oxidation from wood pulp cellulose in accordance with the previous work reported by Saito et al. (2006). Bleached wood pulp fibers (1 g) were suspended in deionized water using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (0.1 mmol, Aladdin) and sodium bromide (1 mmol, Aladdin). A desired amount of sodium hypochlorite (NaClO) (1 mmol, Aladdin) was added to the cellulose slurry whilst stirred at room temperature. The PH of the reaction was adjusted to 10 and maintained at this value by adding 0.5 M NaOH until no more NaOH was consumed. The TEMPO-oxidized fibers were washed thoroughly with deionized water by filtration and stored refrigerated (4 °C) for further treatment.

The oxidized fibers were then dispersed in deionized water to a desired concentration, and fibrillation was conducted through a high pressure homogeniser. Finally, the cellulose nanofibers possess an average length of several microns and diameter of 3–4 nm.

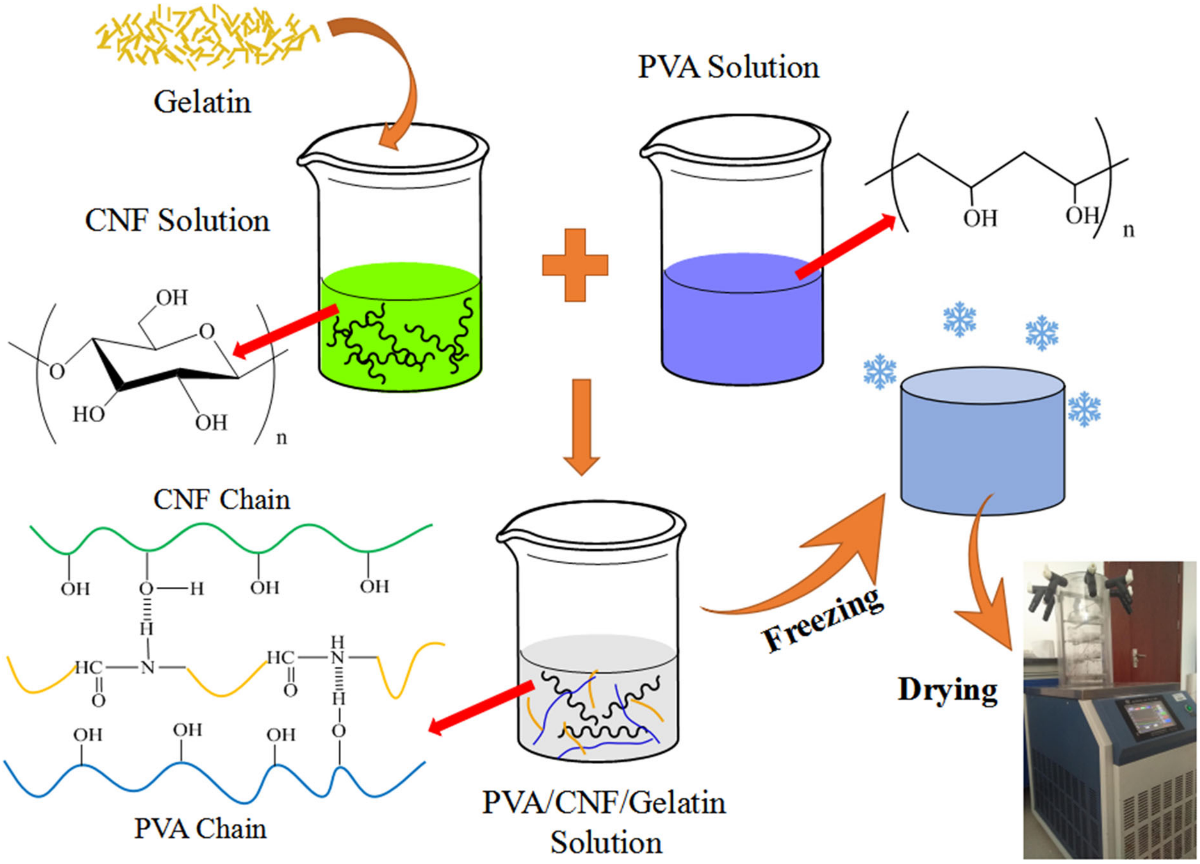
Preparation of cross-linked PVA/CNF/gelatin aerogels

The preparation process of aerogels is illustrated schematically in Scheme 1. Different amounts of gelatins (Sinopharm Chemical Reagent Co., Ltd, China) were mixed in the aforementioned CNF solution (25 g, 1 wt%) at a high speed of 10,000 rpm for 30 min. Simultaneously, 10 wt% poly(vinyl alcohol) (PVA) solution was prepared by adding 10 g of PVA (M_w = 31,000–50,000, 99% hydrolyzed, Sigma-Aldrich) in 100 ml deionized water at 90 °C for 8 h under mechanical agitation. Then the PVA solution was slowly added to the CNF/Gelatin suspension and stirred for 1 h. At the final refining step, the mixture was homogeneously dispersed with ultrasonic bath. The composition of hybrid aerogels was displayed in Table 1.

The resulting gels were poured in aluminum mold with the diameter of 46 mm and the height of the mixture was 20 mm. The samples were frozen in liquid nitrogen (− 190 °C) and then removed to the freeze dryer at the temperature of − 68 °C and pressure of 2 Pa for 2 days for the purpose of solvent sublimation. All the samples were stored in vacuum oven at 50 °C after freeze drying for further characterization. The samples CNF and PVA/CNF aerogels were prepared as control groups.

Characterization

The density of the aerogels was calculated based on their masses to volumes ratio. The masses and dimensions were measured by the electronic balance



Scheme 1 Schematic representation of the process to prepare the aerogels

Table 1 Overview of cross-linked aerogels with gelatin prepared by freeze drying

Samples	PVA (g)	CNF (g)	Gelatin (wt%)
CNF	0	50	–
PVA/CNF	25	25	–
PVA/CNF/G_1	25	25	1
PVA/CNF/G_2	25	25	2
PVA/CNF/G_3	25	25	3

(Sartorius SQP) and digital calipers respectively. Uniaxial compression test was performed using Electronic dynamic and static fatigue testing machine (E3000K8953, Instron) with a constant loading rate of 2 mm/min. Three specimens with the diameter of 46 mm were calculated for the test and the average results were reported. The microstructure of the aerogels was investigated by field emission scanning electron microscope (SEM, SIRION200, FEI). Fourier transform infrared spectroscopy (FTIR, Nicolet 8700, Thermo Fisher Scientific, USA) was studied to get the information about various chemical bonds of aerogels. The thermal stability of the aerogels was investigated by thermogravimetric analyzer (SDT Q600, TA). Thermal conductivity (λ) was measured using transient hot wire method (TC3000E, Xiaxi technology, China).

Results and discussion

Microstructure

Figure 1a–c show the microstructures of the freeze-dried CNF, PVA/CNF, and PVA/CNF/G_3 aerogels. As shown in Fig. 1a, the CNF aerogels exhibited a lamellar structure. This is because the weak connection between the celluloses leaded to the collapse of

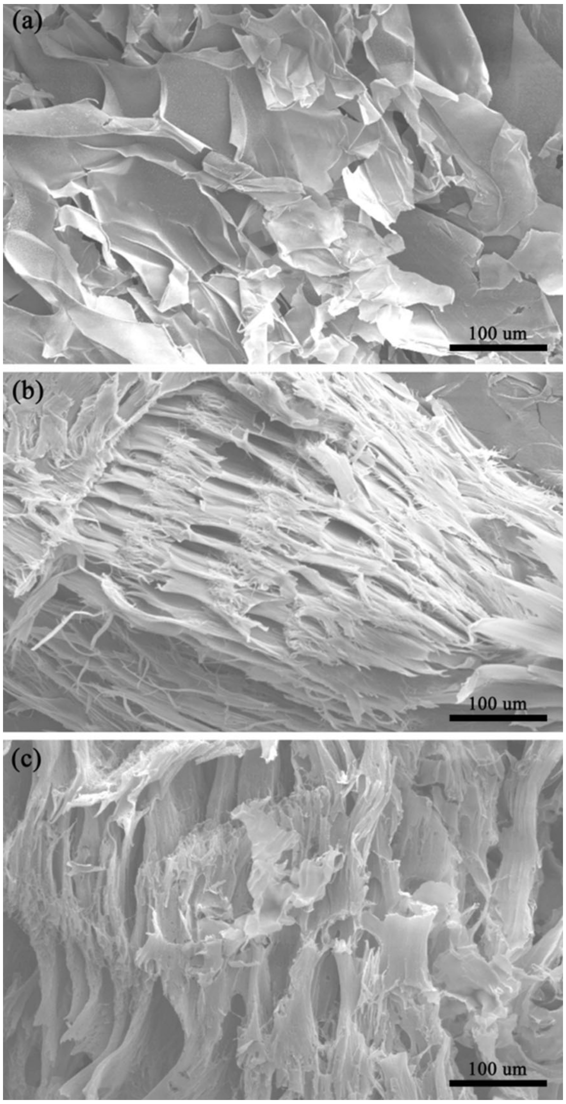


Fig. 1 SEM images of **a** CNF aerogel, **b** cross-linked PVA/CNF aerogel, **c** cross-linked PVA/CNF/G_3 aerogel

the 3D network during the sublimation of the ice crystals, so that a 2D sheet like structure was formed (Javadi et al. 2013). With the incorporation of PVA, the microstructure has changed significantly. Compared to the scattered connection of CNF aerogels, PVA/CNF aerogels jointed tightly followed the direction of ice growth (Lam et al. 2017). This might be caused by the bonding between PVA and CNF. For the PVA/CNF/G_3 aerogels, as shown in Fig. 1c, the morphology was converted to a more continuous, 3D-network structure.

FTIR analysis

The FTIR spectrum given in Fig. 2 indicates the information of chemical bonds between PVA, CNF and gelatin. For three spectra, a large peak from 3301 to 3310 cm^{-1} is attributed to the –OH stretching vibration of hydroxyl-group in CNF or the intermolecular bonding between PVA and CNF. For samples PVA/CNF and PVA/CNF/Gelatin, the adsorption peak at 1088 cm^{-1} is caused by the stretching vibrations of C–O bonds in PVA. Another characteristic peak of PVA is observed in the spectrum at 2918 cm^{-1} (asymmetric stretching vibrations of $–CH_2$ group) (Han et al. 2017). The peak at 1645 cm^{-1} is ascribed to the stretching of the C=O band (amide I) which indicates the presence of Gelatin in the PVA/CNF/Gelatin aerogel (Sadeghi et al. 2018). In addition, the faint peaks around 1544 cm^{-1} and 1237 cm^{-1} correspond to the amide II and amide III of gelatin, respectively (Wang et al. 2017).

Apparent density

Figure 3 shows the densities of cross-linked aerogels. It is well-known that cellulose nanofiber aerogel is an ultra-lightweight material (Liebner et al. 2010), the CNF aerogel without cross-linking exhibits extremely low density value of 0.024 g/cm^3 in the present work. But, the density of PVA/CNF aerogel increases to 0.057 g/cm^3. This is mainly due to the addition of PVA, which increases the amount of solid content. All the hybrid aerogels that introduced gelatin retained

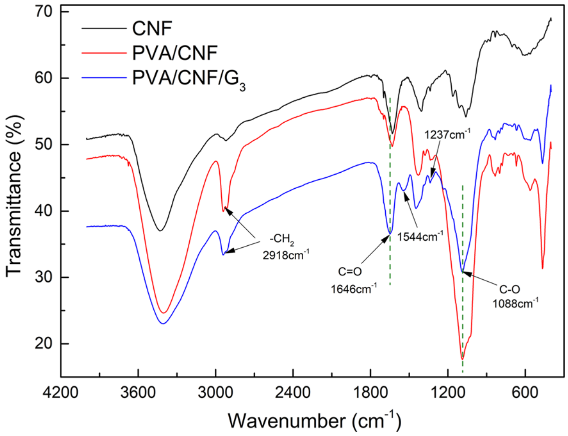


Fig. 2 FTIR spectrum of CNF, PVA/CNF and PVA/CNF/Gelatin aerogels

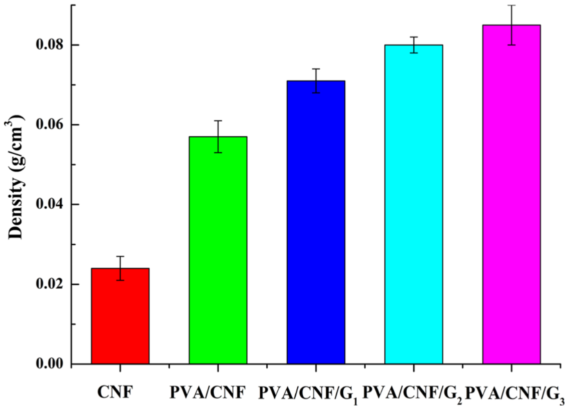


Fig. 3 The densities of the CNF, PVA/CNF and PVA/CNF/Gelatin aerogels

their shapes and did not exhibit significant volume shrinkage during the freeze drying process. Gelatin and PVA could combine tightly because of the good compatibility between them, which leads to an augment of the densities of rigid aerogel samples (Wang et al. 2017). In general, all of the densities still maintain at very low level.

Mechanical behavior

Figure 4 shows the photograph of typical uniaxial compression test of the samples. Figure 4A1, B1 represent the initial stage of the test of CNF aerogel and PVA/CNF/G$_3$ aerogel. Figure 4A2, B2, A3, B3 show the difference in the deformation of the CNF and PVA/CNF/G$_3$ aerogels under the same loading force. As can be seen from the comparison, CNF aerogel was easily compressed. On the contrary, the shape of PVA/CNF/G$_3$ aerogel does not change obviously under the same force. It can be seen initially that the composite exhibited high deformability and better mechanical strength with the addition of gelatin.

The compressive stress–strain curves of resulting aerogels are shown in Fig. 5. Each sample was compressed to 60% of its height. The slope of the linear elastic stage remains unchanged at a low strain and then the stress increased rapidly. Finally, the upward trend of stress rises sharply which is caused by cell collapse and densification of the aerogel structure. Table 2 summarizes the mechanical properties of the aerogels. The compression strength was obtained at 60% strain. For the CNF aerogel, the compressive strength was only 0.06 MPa. After being cross-linked by PVA, the compressive strength increases nearly 9.2 fold of that value. The strength of the composites was further enhanced by gelatin from 1.1 MPa of PVA/CNF/G$_3$ to 0.55 MPa of PVA/CNF.

The specific moduli in Table 2 were calculated based on the modulus to density ratio. The introduction of gelatin increases the specific modulus of PVA/CNF aerogel. Comparing PVA/CNF/G$_3$ with PVA/CNF, the specific modulus increased 5.3 fold, from the 3.68 to 19.6 m^2/s^2. The introduction of very little gelatin can dramatically enhance the compressive strength of aerogel. The result might be ascribed to the biobased gelatin by reinforcing the connection between PVA and CNF. The amino groups on the gelatin increases the hydrogen bonding on the surface of PVA and CNF.

Thermal conductivity and thermal stability

For the field of thermal insulation, thermal conductivity and thermal stability are two important parameters. The thermal conductivity of various aerogel samples is shown in Fig. 6. Compared with CNF aerogel, PVA/CNF aerogel endows greater heat insulating property with the ultralow thermal conductivity of 0.027 W/m K which is approach to that of silica aerogels. This may be due to the introduction of PVA might increase the mesoporous in the composites by increasing the crosslinking between cellulose and PVA. Although the density of the composites increases with the augment of gelatin, the thermal conductivity has little increase. The sample PVA/CNF/G$_3$ still has good thermal insulation properties with the maximum thermal conductivity of 0.037 W/m K.

Figures 7 and 8 show the thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) results of PVA based aerogels. The hydrophilic composites with hydroxyl and amide bonds can easily absorb water in the air. So the negligible initial weight loss before 100 °C indicates the evaporation of water. Compared with PVA/CNF and PVA/CNF/Gelatin samples, the maximum decomposition temperature rose from 278 to 340 °C and the intensity of the peak weakened. This indicated that the introduction of gelatin can enhance the thermal stability of the aerogels and slow down the sharp decomposition of the PVA and CNF. It is because that the carbon layer formed by gelatin decomposition hinders the further

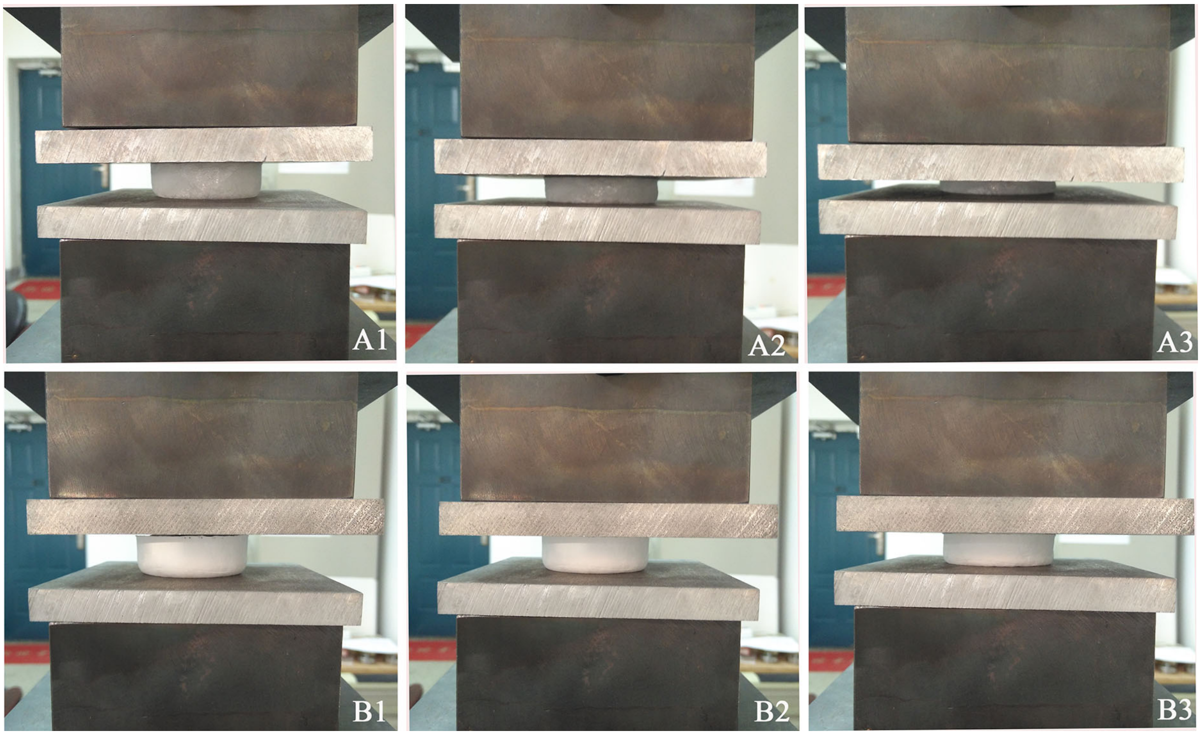


Fig. 4 Comparison of uniaxial compression test of the CNF aerogel (**A1**, **A2**, **A3**) and PVA/CNF/G_3 aerogel (**B1**, **B2**, **B3**)

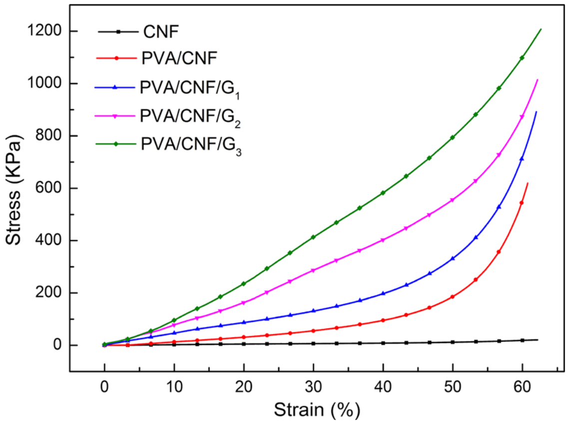


Fig. 5 Uniaxial compressive stress–strain curves of resulting aerogels

decomposition of PVA (He et al. 2018). In addition, there is a slight increase in thermal stability with the increase of gelatin, but the change is not significant.

Conclusions

Biobased PVA/CNF/Gelatin aerogels have been successfully synthesized with sustainable materials using a facile and environmentally friendly freeze-drying method. The microstructure, thermal conductivity, densities, thermal stability and mechanical properties of the hybrid organic aerogels with different amount of gelatin were systematically analyzed. The gelatin can be well-dispersed in the matrix forming three dimensional structures and act as a crosslinking material by hydrogen bonding. The density and thermal conductivity slightly increased as the increase of gelatin. The maximum thermal conductivity was 0.037 W/m K which still has good thermal insulation properties. In addition, the introduction of very little gelatin can dramatically enhance the compressive strength of aerogel. PVA/CNF/G_3 aerogel exhibited the highest compressive modulus 1.65 MPa, eightfold that of PVA/CNF aerogel. From the TGA and DTG results, the thermal stability was enhanced and the sharp decomposition rate slowed after adding the gelatin. Cheap biobased materials and excellent properties make the prepared aerogel have a broad prospect in

Table 2 Comparison of mechanical properties for the resulting samples

Samples	Density (g/cm^3)	Compression strength (MPa)	Modulus (MPa)	Specific modulus (m^2/s^2)
CNF	0.024 ± 0.003	0.06 ± 0.005	0.018 ± 0.003	0.75 ± 0.03
PVA/CNF	0.057 ± 0.004	0.55 ± 0.07	0.21 ± 0.01	3.68 ± 0.08
PVA/CNF/G$_1$	0.071 ± 0.003	0.71 ± 0.09	0.43 ± 0.03	6.06 ± 0.16
PVA/CNF/G$_2$	0.08 ± 0.002	0.88 ± 0.05	1.02 ± 0.08	12.8 ± 0.6
PVA/CNF/G$_3$	0.085 ± 0.005	1.1 ± 0.11	1.65 ± 0.06	19.6 ± 0.6

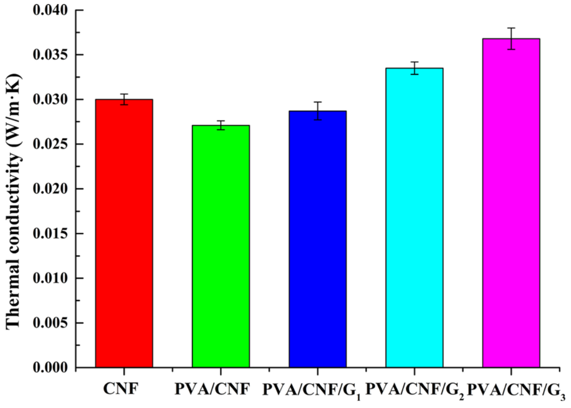


Fig. 6 Thermal conductivity of aerogel samples

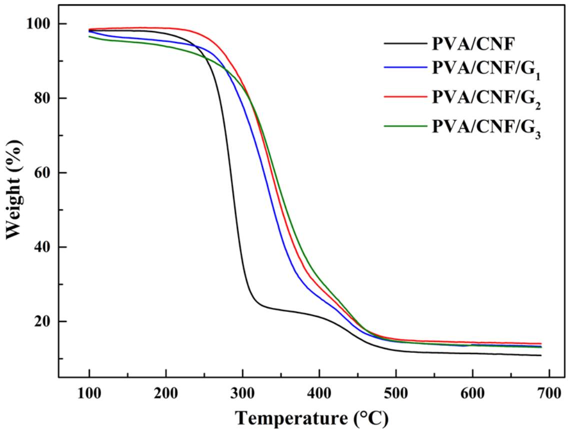


Fig. 7 TGA curves of PVA based aerogels under the nitrogen flow of 50 mL/min

thermal insulation field, such as external wall thermal insulation and pipe insulation. It can gradually develop from the laboratory to large-scale commercial production. In addition, we will continue to research other application such as biomedical.

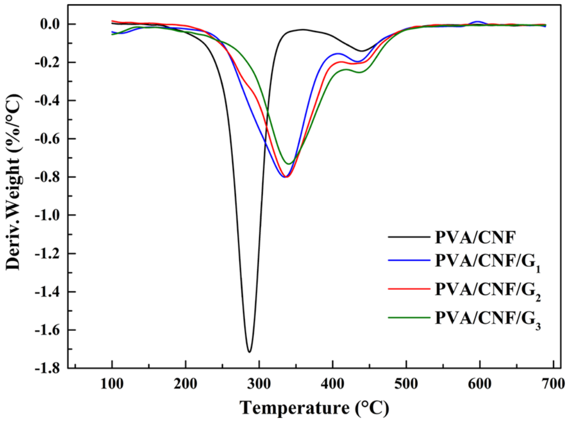


Fig. 8 DTG curves of PVA based aerogels under the nitrogen flow of 50 mL/min

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References

Amonette JE, Matyáš J (2017) Functionalized silica aerogels for gas-phase purification, sensing, and catalysis: a review. Microporous Mesoporous Mater 250:100–119

Chen HB, Liu B, Huang W, Wang JS, Zeng G, Wu WH, Schiraldi DA (2014) Fabrication and properties of irradiation-cross-linked poly(vinyl alcohol)/clay aerogel composites. ACS Appl Mater Interfaces 6:16227–16236. https://doi.org/10.1021/am504418w

Deng Z, Wang J, Wu A, Shen J, Zhou B (1998) High strength SiO_2 aerogel insulation1. J Non-Cryst Solids 225:101–104

Guo L, Chen Z, Lyu S, Fu F, Wang S (2018) Highly flexible cross-linked cellulose nanofibril sponge-like aerogels with improved mechanical property and enhanced flame retardancy. Carbohydr Polym 179:333–340

Han J et al (2017) Effects of nanocellulose on the structure and properties of poly(vinyl alcohol)–borax hybrid foams. Cellulose 24:4433–4448

He S, Huang Y, Chen G, Feng M, Dai H, Yuan B, Chen X (2018) Effect of heat treatment on hydrophobic silica aerogel. J Hazard Mater 362:294–302. https://doi.org/10.1016/j.jhazmat.2018.08.087

Javadi A et al (2013) Polyvinyl alcohol–cellulose nanofibrils-graphene oxide hybrid organic aerogels. ACS Appl Mater Interfaces 5:5969–5975

Jiang F, Hsieh Y-L (2017) Cellulose nanofibril aerogels: synergistic improvement of hydrophobicity, strength, and thermal stability via cross-linking with diisocyanate. ACS Appl Mater Interfaces 9:2825–2834

Kistler SS (1931) Coherent expanded aerogels and jellies. Nature 127:741

Lam NT, Chollakup R, Smitthipong W, Nimchua T, Sukyai P (2017) Utilizing cellulose from sugarcane bagasse mixed with poly(vinyl alcohol) for tissue engineering scaffold fabrication. Ind Crops Prod 100:183–197

Li Z, Gong L, Cheng X, He S, Li C, Zhang H (2016) Flexible silica aerogel composites strengthened with aramid fibers and their thermal behavior. Mater Des 99:349–355

Li Y, Wang B, Sui X, Xu H, Zhang L, Zhong Y, Mao Z (2017) Facile synthesis of microfibrillated cellulose/organosilicon/polydopamine composite sponges with flame retardant properties. Cellulose 24:3815–3823

Liebner F et al (2010) Aerogels from unaltered bacterial cellulose: application of $scCO_2$ drying for the preparation of shaped, ultra-lightweight cellulosic aerogels. Macromol Biosci 10:349–352

Liu Y, Geever LM, Kennedy JE, Higginbotham CL, Cahill PA, McGuinness GB (2010) Thermal behavior and mechanical properties of physically crosslinked PVA/Gelatin hydrogels. J Mech Behav Biomed Mater 3:203–209

Maleki H, Durães L, Portugal A (2014) Synthesis of lightweight polymer-reinforced silica aerogels with improved mechanical and thermal insulation properties for space applications. Microporous Mesoporous Mater 197:116–129

Pääkkö M et al (2007) Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. Biomacromol 8:1934–1941

Pan Y et al (2017) Low thermal-conductivity and high thermal stable silica aerogel based on MTMS/water–glass co-precursor prepared by freeze drying. Mater Des 113:246–253

Rao AP, Rao AV, Pajonk G (2007) Hydrophobic and physical properties of the ambient pressure dried silica aerogels with sodium silicate precursor using various surface modification agents. Appl Surf Sci 253:6032–6040

Sadeghi A, Pezeshki-Modaress M, Zandi M (2018) Electrospun polyvinyl alcohol/gelatin/chondroitin sulfate nanofibrous scaffold: fabrication and in vitro evaluation. Int J Biol Macromol 114:1248–1256

Saito T, Nishiyama Y, Putaux J-L, Vignon M, Isogai A (2006) Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. Biomacromol 7:1687–1691

Saito T, Kimura S, Nishiyama Y, Isogai A (2007) Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. Biomacromol 8:2485–2491

Shang K, Liao W, Wang J, Wang Y-T, Wang Y-Z, Schiraldi DA (2015) Nonflammable alginate nanocomposite aerogels prepared by a simple freeze-drying and post-cross-linking method. ACS Appl Mater Interfaces 8:643–650

Wang Y-T et al (2017) Green approach to improving the strength and flame retardancy of poly (vinyl alcohol)/clay aerogels: incorporating biobased gelatin. ACS Appl Mater Interfaces 9:42258–42265

Wei TY, Chang TF, Lu SY, Chang YC (2007) Preparation of monolithic silica aerogel of low thermal conductivity by ambient pressure drying. J Am Ceram Soc 90:2003–2007

Yang D, Li Y, Nie J (2007) Preparation of gelatin/PVA nanofibers and their potential application in controlled release of drugs. Carbohydr Polym 69:538–543

Yun S, Luo H, Gao Y (2014) Superhydrophobic silica aerogel microspheres from methyltrimethoxysilane: rapid synthesis via ambient pressure drying and excellent absorption properties. RSC Adv 4:4535–4542

Zheng Q, Cai Z, Gong S (2014) Green synthesis of polyvinyl alcohol (PVA)–cellulose nanofibril (CNF) hybrid aerogels and their use as superabsorbents. J Mater Chem A 2:3110–3118