An Environment-Friendly Thermal Insulation Material from Cellulose and Plasma Modification

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ABSTRACT: Cellulose aerogels were prepared by combining the NaOH/thiourea/H_2O solvent system and the freeze-drying technology. Hydrophobic aerogels were obtained with the cold plasma modification technology. The results showed that cellulose aerogel had good heat insulation performance, while the main factors affecting thermal conductivity were density and porosity. Thermal conductivity decreased with the decrease of density and the increase of porosity. It could be as low as 0.029 W/(m K). Cellulose aerogel adsorbed moisture easily. The moisture adsorption had a significant influence on the heat insulation performance of aerogel. After conducting hydrophobic modification using CCl_4 as plasma, cellulose aerogel was changed from hydrophilic to hydrophobic and water contact angle was as high as 102°. Hydrophobic modification did not affect the heat insulation performance of aerogel. This work provided a foundation for the possibility of applying cellulose aerogels in the insulating material field. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3652–3658, 2013

INTRODUCTION

Aerogel is a kind of material prepared by replacing the liquid solvent in a gel by air without substantially altering the network structure or the volume of the gel body.[1,2] Due to the unique pore structure, it has many special properties, such as low density,[3] high porosity,[4,5] specific surface area,[6] nanosize pore space,[7] low acoustic impedance,[8] and low thermal conductivity.[9] For these important properties, aerogel materials have many great potential applications. Cellulose aerogel materials possess features of traditional aerogels,[10,11] at the same time they have their own excellent specificity. The preparation of aerogels made from cellulose derivatives needs complicated and non-controllable chemical crosslinking process; however aerogels prepared by unmodified cellulose avoids these processes,[12] which is essential for aerogels from cellulose derivatives.

At low temperatures, the NaOH/thiourea/H_2O system rapidly dissolves cellulose ($M_w \leq 1.2 \times 10^5$) and transparent solution can be obtained. Solution state can be maintained for quite a long time.[13] Novel cellulose silk,[14] membrane,[15] chromatographic column fillers,[16,17] composite materials, and cellulose derivative[18,19] were successfully prepared with this solution. However, there is still lack of systematic study about heat insulation performance of cellulose aerogel. Cellulose aerogel is rich in hydrophilic groups and has specific surface area and porous

structure, which make it easy to adsorb water vapor in the air. Thus its original heat insulation performance is damaged. The defect of moisture adsorption is a general problem in the application of aerogels. But there are few reports about hydrophobic modification of polysaccharide aerogels.[20] Many studies about hydrophobization of cellulose[21,22] and cellulose derivatives[23–25] can be found, whereas the reports about hydrophobization of cellulose aerogel don't have much at all. Cold plasma modification technology is an effective surface modification technology, and is developing fast.[26–29] Using the method of gas ionization produced plasmas. Plasmas contain large numbers of active particles, such as excited atoms and molecules, electrons, ionics, and free radicals. These active particles bring about chemical and physical reaction on the surface of material. With this technology, the surface of organic material can be modified from hydrophilic to hydrophobic. Thereby the physicochemical property of surface can be improved without any influence on the basic performance.[30,31]

In this article, cellulose aerogels were prepared by the freeze-drying method with the NaOH/thiourea/H_2O system as solvent. The relationship between cellulose aerogels structure and heat insulation performance was investigated. The influence of hygroscopicity on heat insulation performance was analyzed further. Hydrophobic modification was attempted with cold plasma

modification technology using CCl_4 as plasma. The modifying effect was investigated and the heat insulation performance of aerogels was analyzed before and after modification.

EXPERIMENTAL

Materials

Cellulose (cotton linter) provided by Hubei Chemical Fiber Co., Ltd, and the α-cellulose content was more than 95%. The cellulose was used without being further purified. M_η was measured to be 1.01×10^5 with cadoxen as the solvent at 25°C by using viscometer according to $[\eta] = 3.85 \times 10^{-2} \, M_w^{\,0.76} (\text{mL g}^{-1})$.[32] Sodium hydroxide (NaOH), thiourea (CH_4N_2S), ethanol absolute, and carbon tetrachloride (CCl_4) were purchased from Tianjin Beilian Fine Chemicals Co., Ltd., Guangzhou Xilong Chemical Co., Ltd., Shanghai Green Food Additive Co., Ltd., and Tianjin Hongyan Chemical Reagents Factory, respectively. All chemical reagents were of analytical grade and directly used unless otherwise mentioned.

Preparation of Cellulose Hydrogels and Aerogels

In the first step, cellulose was rinsed with distilled water and ethanol absolute repeatedly. Then dry it and add it into the NaOH/thiourea/H_2O solution (the percentage of cellulose weight: 2–5%, the percentage of NaOH weight: 9.5%, the percentage of thiourea weight: 4.5%) and the swollen cellulose-dispersing solution was obtained. The cellulose-dispersing solution was injected into a mold and stirred by 750 rpm to disperse cellulose homogeneously. Then the solution was frozen for 24 h. After that the solution was thawed at room temperature and the hydrogel was obtained. The hydrogel was rinsed with distilled water repeatedly. Finally, bulk cellulose aerogels were obtained through a FreeZone Plus 2.5L Cascade Console Freeze Dry System (Labconco Co.).

Hydrophobic Modification with the Cold Plasma Treatment

The prepared cellulose aerogels were modified by HD-1A plasma modification processor provided by Chinese Academy of Sciences. The plasma excitation uses glow discharge and the variable power was from 0 to 250 W. After cellulose aerogel was on specimen holder, the reaction chamber of processor was evacuated. When the degree of vacuum was down to the lowest point, CCl_4 was filled into the reaction chamber at a rate of 0.9 mL/min. When the degree of vacuum kept a constant value, adjust the power to a required value, the discharge system was then started. Adjust the adapter until reflection power reached the lowest value, then discharge under required power and time. Finally hydrophobic cellulose aerogels were obtained.

Characterization

Aerogel Density Assay. Dry the regular geometrical shaped aerogel for 6 h at the temperature of 60°C, weigh it and record as m_0. Volume "length × width × height" of the aerogel was measured by a digital caliper and recorded as V. Then measure digital information of the aerogel for three times and takes the average value. The density (ρ) was calculated by:

$$\rho = \frac{m_0}{V}$$

Estimation of Porosity. Porosity is an important parameter to the structure of aerogel. Dry the sample for 6 hours at the temperature of 60°C, weigh it and record as m_1. Put the sample in a container and the sample was completely immersed with ethanol. Then put the container in a vacuum drying oven and vacuumize it until no bubble spilled out of the sample. Take out the container and weigh the container, record as m_2. Then take out the sample from container and weight the container with the residual ethanol, record as m_3. Porosity of the sample was calculated according to the following formula:

$$\text{porosity}(\%) = \frac{m_2 - m_3 - m_1}{m_2 - m_3} \times 100\%$$

Estimation of Moisture Adsorption. Moisture adsorption is the capacity of materials to hold water molecules from the surrounding environment. This capacity is determined by chemical composition and micro-structure of materials. As water molecules enter into materials, thermal conductivity increases with the amount of physically adsorbed water. Thus, moisture adsorption has an influence on insulating materials. Moisture adsorption of aerogels is represented by hygroscopicity. After dry in vacuum for 24 h at 60°C, weigh the sample as m_0. Then put the sample in a constant temperature and humidity chamber, adjust the humidness and keep it constant for 24 h, weigh and record as m_1. Hygroscopicity was calculated by the following formula:

$$\text{hygroscopicity} = \frac{m_1 - m_0}{m_0} \times 100\%$$

Measurement of Thermal Conductivity. Thermal conductivity is usually used to estimate the heat insulation performance of insulating materials. In order to investigate the heat insulating efficiency of cellulose aerogels, their thermal conductivity was performed using conductometer (model: DZDR-PL) of Nanjing Dazhan Institute of Electrome Chanical Technology. Thermal conductivity was measured by the guarded hot plate apparatus. Cellulose materials are stable in normal and low temperature environment ($-20°C$ to $300°C$). In the application of thermal insulation field, cellulose aerogel can be used as insulating materials in normal and low temperature environment. In the experiment, the temperature of hot plate was set at 50°C and the temperature of cold plate was set at $-15°C$. All of the samples were dried at 60°C before the measurement was performed.

Measurement of Contact Angle. Water contact angles (drop, volume 10 μL) were performed using a HARKE Contact Angle Meter with a color CCD camera (×20 objective). The results were calculated according to the acquired photos with a direct angle measurement on its own software (HARK-SOFT).

Estimation of Structure and Morphology. The chemical structure of aerogels was investigated and compared with that of natural cellulose by Bruker FTIR spectrometer (model: TENSOR 27) with a resolution of 1 cm^{-1}.

Scanning electron microscopy (SEM) images of aerogel were obtained using a Hitachi S-3000N scanning electron microscope of Japan's Hitachi with an acceleration voltage of 5kV after 60 s metallization with Au.
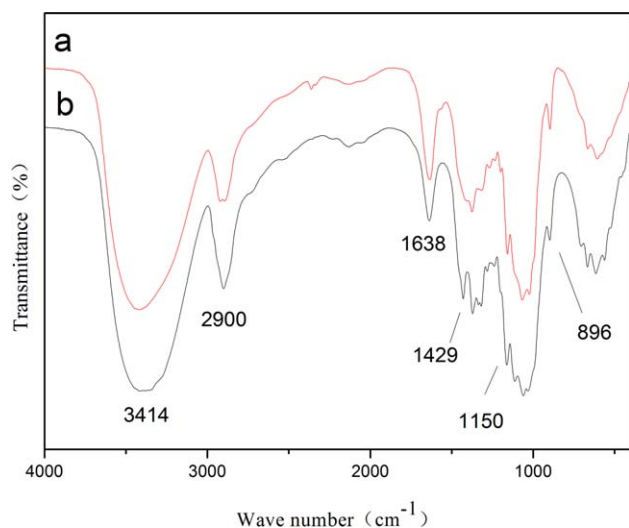
Figure 1. FTIR spectra of cellulose (a) and cellulose aerogel (b) with 5% cellulose concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Structure of Cellulose Aerogels

The infrared spectra of cellulose and cellulose aerogel are shown in Figure 1. The absorption peaks of the cellulose and cellulose aerogel were almost the same. Both of them had obvious characteristic absorption peaks of cellulose macromolecule, it indicated that cellulose was not derived during the course of dissolution. The course of dissolution was direct dissolution. The changes of infrared adsorption of cellulose aerogels showed that there was a phase transformation from cellulose I to cellulose II during the course of dissolution.

The SEM images of cellulose aerogel are shown in Figure 2. Cellulose aerogel had a support frame, which formed the three-dimensional network structure. Cellulose aerogel had a fine mechanical performance with the support frame (In this work, compressive strength of cellulose aerogels was 5.7–8.2 MPa). In the inner areas, the aerogel displayed a heterogeneous porous structure [Figure 2(a)], whereas compact pore structure was formed on the surface of the aerogel [Figure 2 (b)]. With the support frame and pore structure, aerogel had high porosity. The non-dissolved cellulose was present as circular fibers in the inner of aerogel [Figure 2(c)], and the areas of non-dissolved cellulose increased with the increase of cellulose concentration.

It was observed from the SEM images, during the process of cellulose forming aerogel, that the crosslinking between cellulose macromolecules made up the support space structure of aerogel, and the evaporation of water during the drying process led to the pore structure on the surface of the aerogel.

Density and Porosity of Cellulose Aerogels

Density and porosity are important factors to the performance of aerogel materials. Using the freeze-drying technology, the volume shrinkage was 20.41%–28.36%. Under the condition of drying technology, cellulose aerogels had a relatively low density. Density of cellulose aerogels were in the range of 0.2–0.4 g/cm^3 in Figure 3(a). When the cellulose concentration was lower than 3%, density of aerogels reduced with the increase of cellulose concentration. Before the dissolving capacity of solvent reached the saturation point, cellulose was dissolved fully in the solvent, and the obtained aerogels were well-distributed and loose. When the cellulose concentration was 3%, the density reached the lowest point, 0.233 g/cm^3. That is because limited by the concentration of cellulose, 2% cellulose aerogels had less content of cellulose involved in forming the structure of aerogel, which caused the structure of aerogels incomplete. About 3% cellulose aerogel had relatively completed structure. As the cellulose concentration continued to increase, the density of the aerogels increased instead. The insoluble portion of cellulose increased with the increase of cellulose concentration. The insoluble portion made the aerogels dense and increased the density of aerogels. The relationship between the porosity of cellulose aerogels and cellulose concentration were discovered in Figure 3(b). The pore structure is predominantly controlled by the polymer concentration.[33] The higher the cellulose concentration was, the lower the mean porosity[34] was. For freeze-dried cellulose solutions of different cellulose concentrations had the same phenomenon.[7] The porosity of aerogels decreased with the increase of cellulose concentration. The increase of the number of polymer molecule per unit volume caused the increase of density of polymer network. That caused the probability of polymer nanocytes wound with each other increased accordingly. The polymer nanocytes composed of multiple polymer molecules. Therefore, relatively high polymer concentration was good for the association of polymer molecules during the forming process of hydrogel. It also made hydrogel easier to form small and uniform condensed phase and caused the decrease of porosity. Whereas cellulose concentration was 3%, porosity reached the highest point of 84.88%. In consideration of incompleted
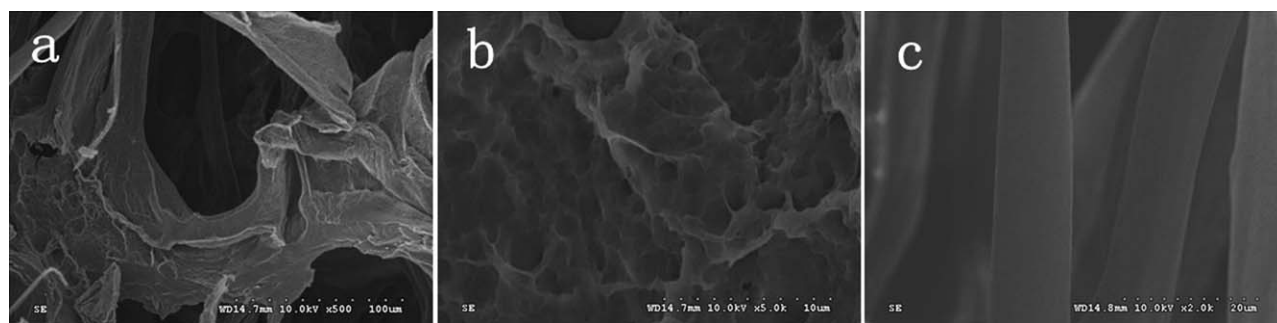

Figure 2. SEM images of cellulose aerogel with 5% cellulose concentration.
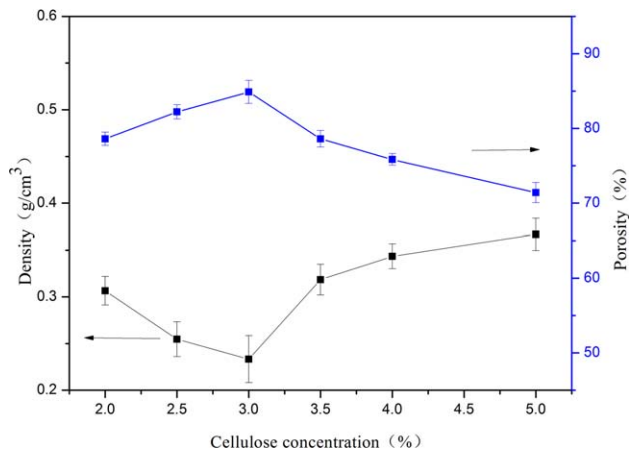
Figure 3. Effect of cellulose concentration on density and porosity of aerogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure of 2% cellulose aerogel, the density is lower than 3% cellulose aerogel, and the porosity is also lower. The decrease of the porosity was the direct reflection of the density increase of polymer network.

Heat insulation Performance of Cellulose Aerogels

Density and porosity are the main factors to influence the heat insulation property of materials.[35] Generally speaking, the thermal conductivity of dense solid has been always higher than that of still air. At normal temperatures, thermal conductivity increases with the increase of solid matter content in unit volume. The increase of porosity can reduce the mean free energy of phonon, and thus reduces the thermal conductivity of materials. As shown in Figure 4(a) the smaller the density was, the lower the thermal conductivity was. While the higher the porosity was, the lower the thermal conductivity was as shown in Figure 4(b). When density was 0.233 g/cm^3 and porosity was 84.88%, thermal conductivity reached the lowest point, 0.029 W/(m K). When porosity is higher, the heat transfer route increased, the heat transfer rate had greatly reduced. In the meantime, air molecules had a bigger motion space in aerogels.

It resulted in a relatively big mean free energy of the air molecules, and caused the decrease of thermal conductivity.

Thermal conductivity of aerogels increased with the increase of cellulose concentration in Figure 5. When cellulose concentration reached a certain amount, the amount of undissolved cellulose increased. And the absolute content of cellulose also increased. Thus heat conduction in solid and thermal conductivity increased accordingly. When the concentration of cellulose was 3%, thermal conductivity reached the lowest point. Compared with 2% cellulose aerogel, 3% cellulose aerogel had relatively completed structure, and had the lower density and the higher porosity. Thermal resistivity of open porous cellulose aerogel increased when its effective pore size decreases. The mean free motion path of air molecule is about in 70 nm.[36] Under the low density and high porosity conditions, the number of pores which met the size was increasing. In materials, thermal conduction through the small size of the connections between the particles made up the conduction path. When the pore's size was comparable to or smaller than the mean free path of the gas, the molecules of the latter collide more often with the molecules forming the solid part than among them. In fact, the gas molecules will tend to stick to the molecules of the solid part, virtually eliminating the thermal conductivity through the gas inside the material.

Cellulose aerogel which composed of solid phase (crystalloid and non-crystalloid) and gas phase (pore) is a kind of porous insulating materials. The heat transfer in aerogel can be divided into the heat conduction of solid phase and the heat conduction of gas phase.[37] The solid matrix of cellulose aerogels is formed by the interconnection of cellulose molecule clusters. The solid's heat transfer is mainly determined by the mean free path of phonon[38,39] in the structure unit of solid. During the course of dissolution, non-crystalline area and crystalline area are both opened. Thus the transfer space of phonon enlarges. At the same time, the size of solid particle also influences the density to a certain degree. Aerogel with relatively low density had quite small solid particle. So the mean phonon free path was reduced. Then thermal conductivity was decreased. At medium or low temperature, air molecules in random motion have different
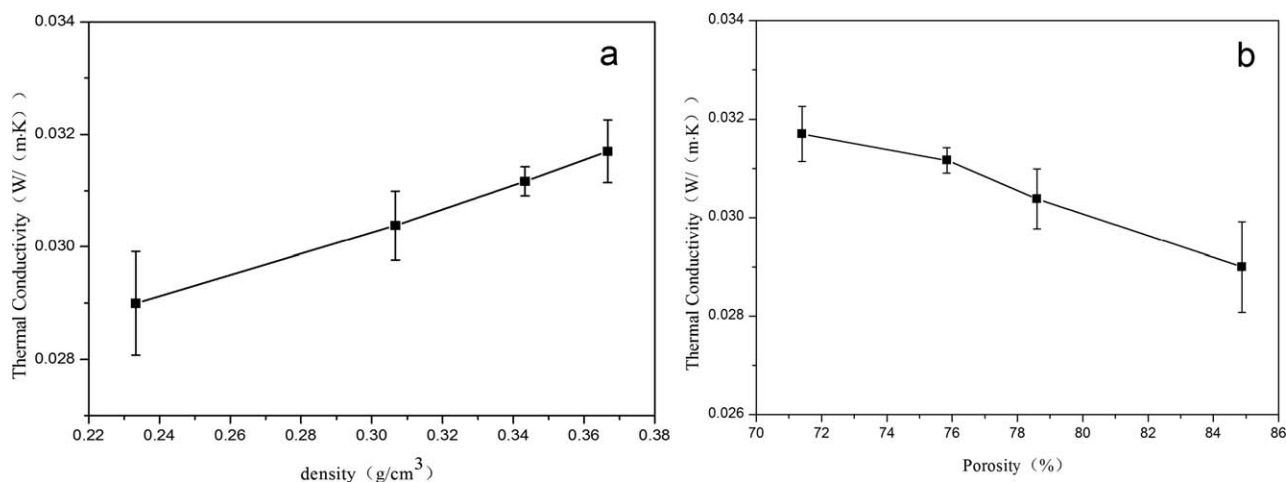

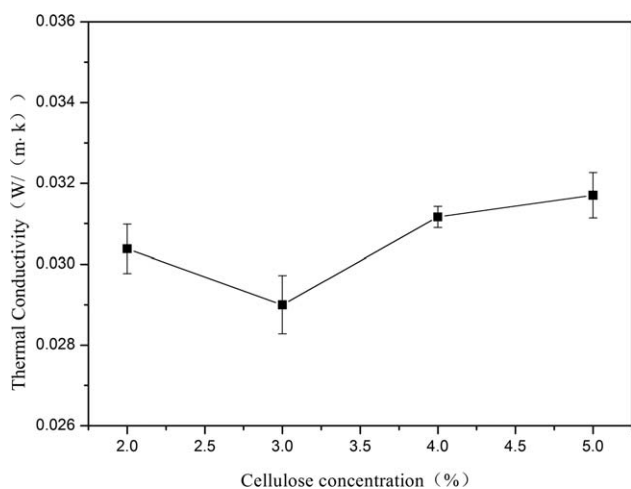**Figure 4.** Effect of density (a) and porosity (b) on thermal conductivity of aerogels.

Figure 5. Effect of cellulose concentration on thermal conductivity of aerogels.
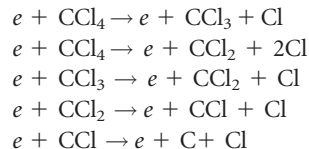
average kinetic energy in different areas.[40] When high energy molecules move from high to low temperature area, the energy is transmitted during the molecule collision process. Thus the heat conveyance is formed. Heat conveyance of a large quantity of molecules is expressed as macro heat conduction. The mean moving path of air molecule would influence the energy exchange of molecules on a certain infinitesimal surface in space,[36] and influences the heat insulation performance of the aerogels further. The low density and high porosity of cellulose aerogels made air molecule encounter vast scale circumvallation in the moving process. The efficiency of heat conduction reduced, which led to a relatively low thermal conductivity of the gas phase. Hence, because of low density and high porosity, cellulose aerogel had fine heat insulation performance.

Hydrophobic Modification of Cellulose Aerogels

Besides the relatively big specific surface area due to the porous structure, cellulose aerogel was also rich in hydroxyl. So it easily adsorbed water vapor in the air and gathered water on the

surface or in pores. Water has a much higher thermal conductivity than air (about 20 times).[41] If water molecules were adsorbed by cellulose aerogel, the thermal conductivity would increase, thus the heat insulation performance decreased. The relationship between hygroscopicity and air humidity are shown in Figure 6(a). The hygroscopicity always increased with the increase of humidity. Aerogel with 5% cellulose which had the lowest porosity had the smallest hygroscopicity. While aerogels with 3% cellulose whose structure was the loosest had the highest hygroscopicity. Therefore, in humid conditions, the loose structure led to high hygroscopicity. The relationship between the thermal conductivity of cellulose aerogels and air humidity is shown in Figure 6(b). With the increase of environmental humidity, the hygroscopicity of materials was rising. The thermal conductivity of aerogels increased with the increase of hygroscopicity. Compared with Figure 5, the thermal conductivity of aerogels in humid conditions increased significantly. Therefore, hygroscopicity had a great influence to heat insulation performance of cellulose aerogels.

In order to obtain the stable heat insulation performance, a practicable way was to improve the hydrophobicity of aerogels. Cold plasma modification technology was employed to modify the surface of aerogel from hydrophilic to hydrophobic with CCl_4 as plasma. The modification process mainly included chlorination. It was deduced that CCl_4 molecule was dissociated by electronic impact under the electrical discharge. The process of CCl_4 gas dissociation was the same as CF_4 dissociation.[42–44] The CCl_4 molecules are dissociated by electron collisions:

$$e + CCl_4 \rightarrow e + CCl_3 + Cl$$
$$e + CCl_4 \rightarrow e + CCl_2 + 2Cl$$
$$e + CCl_3 \rightarrow e + CCl_2 + Cl$$
$$e + CCl_2 \rightarrow e + CCl + Cl$$
$$e + CCl \rightarrow e + C + Cl$$

During the process, CCl_x radicals acted as functionalization agent, CCl_2 had the most density in plasmas. Relatively, chlorine atom played as the etching agent and had the least density in
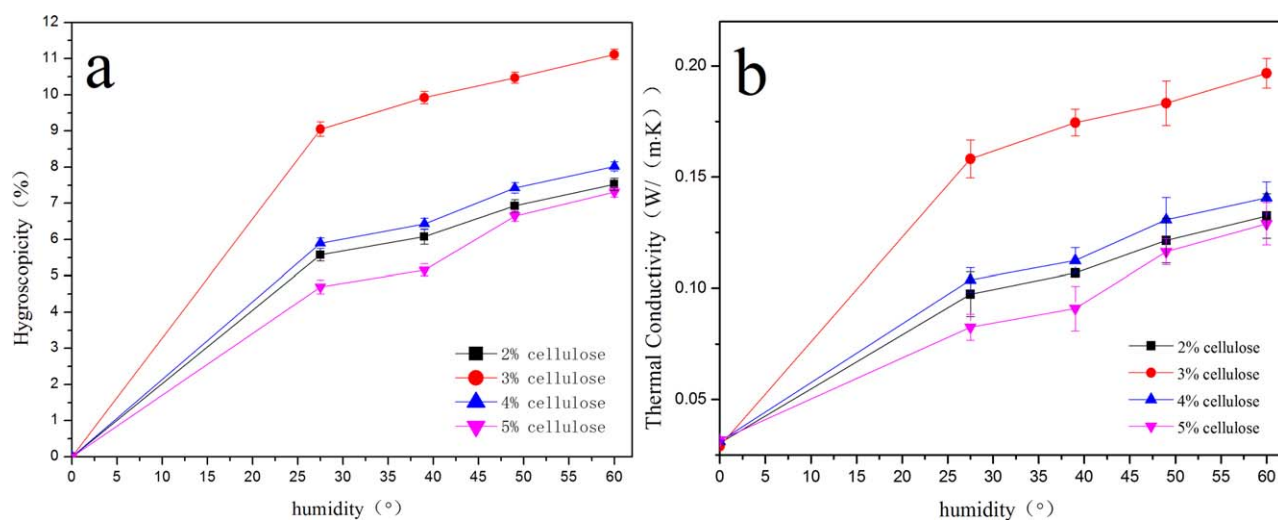

Figure 6. Effect of air humidity on hygroscopicity and thermal conductivity of aerogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
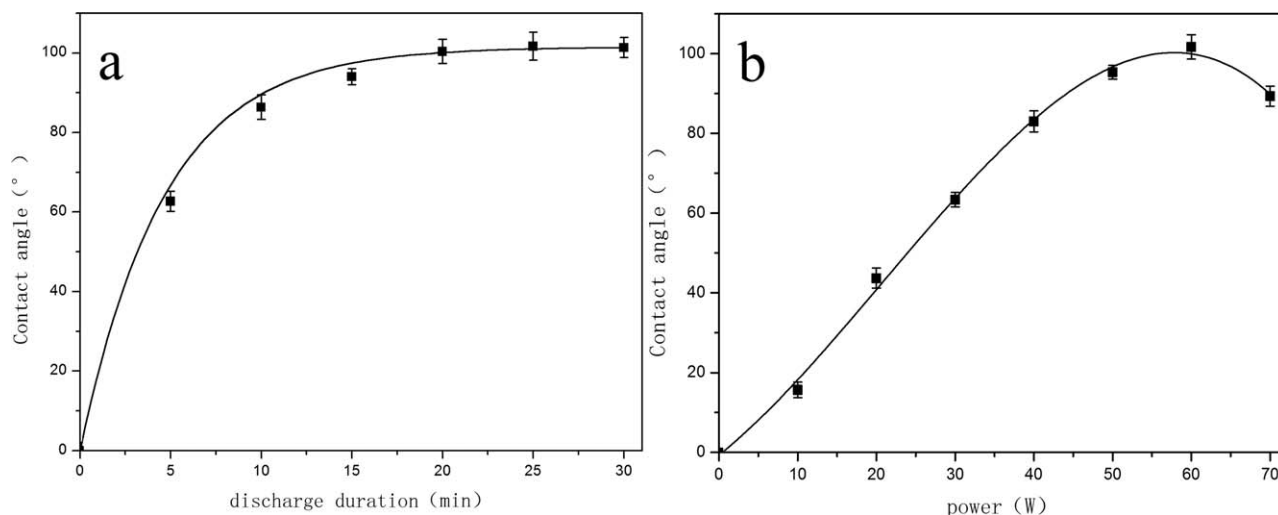
Figure 7. Effect of discharge duration and power on contact angle of cellulose aerogels with 5% cellulose concentration treated by the CCl_4 plasma.

plasmas.[43] When the discharge duration and power are taken as control factor, the dissociation conditions were observed.

After undergoing the plasma modification for a different modification time, the change of water contact angle on the aerogels surface is shown in Figure 7(a). Under 60 W treatment, after 10 min treating time, water contact angle increased from 0° to 90°. After the treating time kept for 15 min, the water contact angle was beyond than 90°, and the surface became hydrophobic. After treating time was beyond 20 min, no significant increase for the water contact angle was observed. Through the plasma modification, surface of cellulose aerogels changed from hydrophilic to hydrophobic successfully. When the discharge power was 60 W and modification time was 25 min, it had the largest contact angle 102°. When the discharge power increased from 0 W to 70 W with 25 min treating time, the change of water contact angle on the surface of aerogels is shown in Figure 7(b). When the discharge power increased from 0 W to 60 W,

water contact angle increased and the trend to hydrophobicity increased too. But as the discharge power increased to 70 W, water contact angle began to decrease. The possible reason was that when cellulose aerogels were under severe discharge conditions, sputtering or etching function took the leading role instead of chlorinated graft. It made the proportion of the carbon chlorine functional group decreased. The thermal conductivity of cellulose aerogels after hydrophobic modification was compared. As shown in Figure 8, the thermal conductivity had no significant change before and after modification. When the hydrophobic aerogels were maintained in humidity at 60° for 24 h, the thermal conductivity also had no significant change. But as compared with Figure 6(b), the thermal conductivity of unmodified aerogel was visibly growing. It indicated that the plasma modification had no effect on heat insulation performance of aerogels, the modification improved the heat insulation performance. It demonstrated that the plasma hydrophobic modification was just for modifying the hydrophobicity of aerogels surface, and wouldn't influence the properties of matrix aerogels. Hence, the plasma modification technology is an effective method to modify the surface properties of cellulose aerogel.
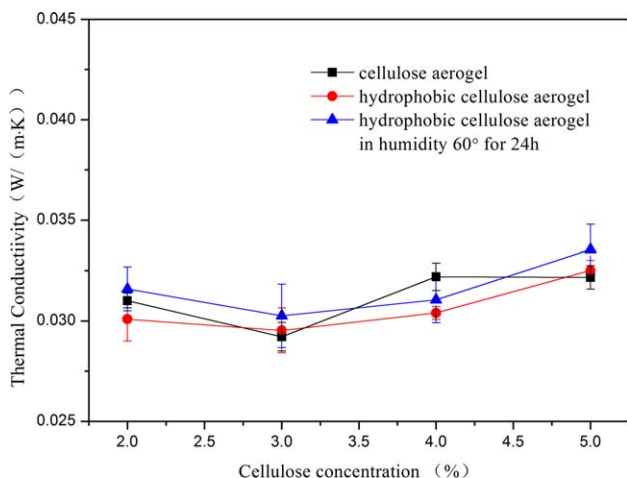
CONCLUSION

In this article, cellulose hydrogel and its bulk aerogels were successfully prepared by using NaOH/thiourea solvent system and freeze-drying method. The hydrophobic modification was carried out to aerogels by using the cold plasma modification technology. The obtained cellulose aerogel was cellulose II crystal phase, and formed a network structure. The cellulose aerogels had relatively low density with the density low to 0.233 g/cm^3 and relatively high porosity with the porosity up to 84.88%. These structural features made the cellulose aerogels having a good heat insulation performance. The thermal conductivity was as low as 0.029 W/(m K). Hygroscopicity of aerogels had a great influence on the heat insulation performance of the aerogels. The hydrophobic modification using CCl_4 as plasma turned the surface of cellulose aerogels from hydrophilic to hydrophobic,

Figure 8. Comparison of the thermal conductivity of cellulose aerogels before and after hydrophobic modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with a largest water contact angle of 102°. At the same time, the aerogels still kept good heat insulation performance.

This work avoids complicated and uncontrollable chemical crosslinking process, and provides effective simple method to prepare cellulose aerogel. The stable good heat insulation performance of cellulose aerogel provides a vast potential in medium and low temperature heat insulation material field.

ACKNOWLEDGMENTS

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