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Heat insulation performance, mechanics and hydrophobic modification of cellulose–SiO_2 composite aerogels

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ABSTRACT

Cellulose–SiO_2 composite hydrogel was prepared by combining the NaOH/thiourea/H_2O solvent system and the immersion method with controlling the hydrolysis–fasculation rate of tetraethyl orthosilicate (TEOS). The hydrophobic composite aerogels were obtained through the freeze-drying technology and the cold plasma modification technology. Composite SiO_2 could obviously reduce the thermal conductivity of cellulose aerogel. The thermal conductivity could be as low as 0.026 W/(mK). The thermal insulation mechanism of the aerogel material was discussed. Composite SiO_2 reduced hydrophilicity of cellulose aerogel, but environmental humidity had a significant influence on heat insulation performance. After hydrophobic modification using CCl_4 as plasma was conducted, the surface of composite aerogel was changed from hydrophilic to hydrophobic and water contact angle was as high as 132°. The modified composite aerogel still kept good heat insulation performance. This work provided a foundation for the possibility of applying cellulose–SiO_2 composite aerogel in the insulating material field.

1. 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 (Kistler, 1931, 1932). As the new third-generation material, cellulose aerogel possesses features of traditional aerogel (Fischer, Rigacci, Pirard, Berthon-Fabry, & Achard, 2006; Hoepfner, Ratke, & Milow, 2008), at the same time it has its own excellent specificity. Therefore, cellulose aerogel has received great concern (Cai, Kimura, Wada, Kuga, & Zhang, 2008; Gavillon & Budtova, 2008; Innerlohinger, Weber, & Kraft, 2006; Khare et al., 2007; Phisalaphong, Suwanmajo, & Sangtherapitikul, 2008).

At present, SiO_2 composite materials are becoming the focus of study in the field of inorganic particulate/organic hybrid materials (Ray & Bousmina, 2005). Due to the quantum tunneling effect, the volume effect of SiO_2 and the action of swimming permeability of cellulose, SiO_2 particulars can penetrate into near the π-bond of cellulose, and the electron cloud occurs to interlapping. The composite SiO_2 improves the heat endurance, resistance to wear, toughness, hydrophobicity. However, there is still lack of systematic study about the heat insulation performance of cellulose–SiO_2 composite aerogel. Cellulose aerogel is rich in hydrophilic groups and has relatively big specific surface area (Liebner et al., 2009) 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 hydrophilicity is a general problem in the application of aerogels. After adsorpting moisture in the air, silica aerogel will be broken into small pieces (Dou, Xu, Cui, & Qian, 2010), and the performances of thermology and phonics are reduced, with the result that the application has been greatly limited (Wang, Lin, Zhang, Yan, & Liu, 2011). Many reports are concerned about the hydrophobic modification of silica aerogels (Kwon, Choi, Kang, & Baek 2000; Valerie, Thomas, & Dale, 2001). But there are few reports about hydrophobic modification of polysaccharide aerogels (Cheng, Lu, Zhang, Shi, & Cao, 2012). Surface modification of porous aerogel materials is a research hotspot. Cold plasma modification technology is an effective surface modification technology, and is developing fast (Sahin, Manolache, Young, & Denes, 2002; Teare et al., 2002; Teshima, Sugimura, Inoue, Takai, & Takano, 2004; Zhang et al., 2002). Plasmas are produced by using the method of gas ionization, and contain large numbers of active particles, such as excited atoms and molecules, electrons, ions and free radicals. These active particles result chemical and physical reaction on the surface of materials and the surface of organic matter can be modified from hydrophilic to hydrophobic. The physicochemical property of material surface can be improved without any influence on the basic performance (Lens, 1997; Thoms, Gladwin, & Robert, 2000).

In this paper, the NaOH/Thiourea/H_2O solvent system was selected. Cellulose–SiO_2 composite hydrogel was prepared by the immersion method with controlling the hydrolysis–fasculation

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rate of TEOS through acid–base catalysis. The hydrophobic composite aerogel was obtained with the freeze-drying technology and the cold plasma modification technology. The relationship between the structure and heat insulation performance of composite aerogel was investigated. The influence of SiO_2 on the performance was discussed.

2. Experimental

2.1. 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 $[\eta] = 3.85 \times 10^{-2} M_w^{0.76}$ (mL/g) (Brown & Wiskston, 1965). Tetraethyl orthosilicate (TEOS), nitric acid and ammonia were purchased from Guangzhou Chemical Reagents Factory. Sodium hydroxide (NaOH), thiourea (CH_4N_2S), ethanol absolute (EtOH), 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.

2.2. Preparation of cellulose–SiO_2 composite aerogels

2.2.1. Preparation of cellulose hydrogel

Linter 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 mould and stirred by 750 rpm to disperse cellulose homogeneously. Then the solution was frozen at −18 °C for 24 h. Follow the solution was thawed at room temperature and the cellulose hydrogel was obtained. The hydrogel was rinsed with distilled water repeatedly.

2.2.2. Preparation of TEOS reaction solution

Mix TEOS, H_2O, ethanol absolute with stoichiometric ratio (TEOS/H_2O/EtOH mol ratio 1.0/3.4/8.5), adjust the pH = 3 with nitric acid (0.8 mol/L). In order to complete the hydrolysis of TEOS mixture, reflux condensation was taken for 90 min at 60 °C.

2.2.3. Preparation of cellulose–SiO_2 composite aerogels

Immerse cellulose hydrogel into TEOS reaction solution, and adjust the pH > 7 with ammonia (1.45 mol/L), then the reactant mixtures were sealed. After standing for 48 h, the hydrogel was rinsed with distilled water repeatedly. Finally, bulk cellulose–SiO_2 composite aerogel was obtained with a FreeZone Plus 2.5L Cascade Console Freeze Dry System (LABCONCO Co.). For all cellulose–SiO_2 composite aerogels, the concentration of cellulose was described with the percentage of weight in cellulose solution, the SiO_2 content was described with the percentage of weight in composite aerogel. For example, the 2% concentration of cellulose and the 9% SiO_2 content were recorded as 2%cellulose–9% SiO_2.

2.3. Hydrophobic modification with the cold plasma treatment

The prepared cellulose–SiO_2 composite 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 composite aerogel was on specimen holder, the reaction chamber of processor was evacuated. When the vacuum degree was down to the lowest point, CCl_4 was filled into the reactor at a rate of 0.9 mL min^{-1}. When the pressure kept a constant value, adjust the plasma power to a required value and started it. Adjust the adapter until reflection power reached the lowest value, then discharge under required power and time. Finally hydrophobic cellulose–SiO_2 composite aerogel was obtained.

2.4. Characterization

2.4.1. Aerogel density assay

Dry the regular geometric shaped composite aerogels for 6 h at the temperature of 60 °C, weigh it and record as m_0. Volume 'length × width × height' of the aerogels was measured by a digital caliper and recorded as V. Then measure digital information on the composite aerogels for 3 times and takes the average value. The density (ρ) was calculated by Eq. (1).

$$\rho = \frac{m_0}{V} \tag{1}$$

2.4.2. Estimation of porosity

Porosity is an important parameter to structure of composite aerogel. Dry the sample for 6 h 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 Eq. (2).

$$\text{porosity}\,(\%) = \frac{m_2 - m_3 - m_1}{m_2 - m_3} \times 100\% \tag{2}$$

2.4.3. Estimation of moisture adsorption

Moisture adsorption is the capacity of material to hold water molecules from the surrounding environment. This capacity is determined by chemical composition and micro-structure of materials. As water molecules entering into materials, thermal conductivity increases with the amount of physically adsorbed water. Thus, moisture adsorption has an influence on insulating materials. Moisture adsorption of composite aerogel is represented by hygroscopicity. After dry in vacuum for 24 h at 60 °C, weight the sample m_0. Then put the sample in a constant temperature and humidity chamber, adjust the humidness and keep it constant for 24 h, weight and record m_1. Hygroscopicity was calculated by Eq. (3).

$$\text{hygroscopicity} = \frac{m_1 - m_0}{m_0} \times 100\% \tag{3}$$

2.4.4. Measurement of SiO_2 content

The SiO_2 content of composite aerogel expressed the efficiency of polyreaction. After drying at 60 °C for 24 h and weighing the sample as m_1. The sample was ignited at 800 °C for 10 h by Electrical Resistance Furnace (model: YFX111012) of Shanghai Y-Feng Electrical Furnace Co., Ltd. Weight the residue as m_2. The rest component was SiO_2 after cellulose was burnt away. SiO_2 content was calculated by Eq. (4).

$$SiO_2\ \text{content} = \frac{m_2}{m_1} \times 100\% \tag{4}$$

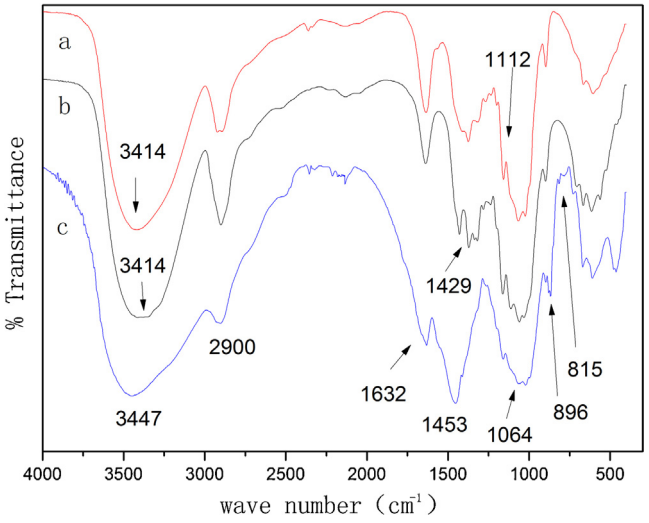

Fig. 1. FTIR spectra of cellulose (a), 5% cellulose aerogel (b) and 5% cellulose–11% SiO_2 composite aergel (c).

2.4.5. 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 composite aerogel, thermal conductivity was performed using Conductometer (model: DZDR-PL) of Nanjing Dazhan Institute of Electrome Chemical Technology. Thermal conductivity was measured by the guarded hot plate apparatus. Cellulose materials are stable in normal and low temperature environment (−20 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.

2.4.6. 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).

2.4.7. Estimation of structure and morphology

The chemical structure of composite aerogel was investigated and compared with 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 5 kV after 60 s metallisation with Au.

3. Results and discussion

3.1. Structure of cellulose–SiO_2 composite aerogels

The infrared spectra of cellulose (a), cellulose aerogel (b) and cellulose–SiO_2 composite aerogel (c) were shown in Fig. 1. The absorption peaks of cellulose, cellulose aerogel and cellulose–SiO_2 composite aerogel were almost the same. All of them had obvious characteristic absorption peaks of cellulose macromolecular, which indicated that cellulose did not derive during the course of dissolution. The course of dissolution was direct dissolution.

Cellulose is polyhydroxy compound, so it has the certain capacity of holding water (Sequeira and Evtuguin Dmitry, 2007). A weak absorption peak at 1632 cm^{-1} was the O—H bending vibration peak of trace impurity water absorbed by cellulose [as shown in Fig. 1(a)]. As compared with cellulose aerogel [Fig. 1(b)], the absorption peak of cellulose–SiO_2 composite aerogel [Fig. 1(c)] at 1632 cm^{-1} was weaker, it was indicated that the hydrophilicity of composite aerogel had been weakened. Near 1064 cm^{-1} was the stretching vibration peak of Si—O—Si, and the stretching vibration peak of C—O bond in cellulose was also at here. Although the molar extinction coefficient of stretching vibration peak of the C—O bond is lower than Si—O band about 4–5 orders of magnitude (Zunli, Zhongli, Hong, & Guiping, 2008), the stretching vibration peak of the C—O band here has been covered. In the meantime, the absorption peak of C—O—Si was also near here, the number of C—O—Si was responsibly less, and covered by the characteristic absorption peak of cellulose too. The stretching vibration peak of Si—O in the structure of Si—OH of composite aerogel [Fig. 1(c)] was near 815 cm^{-1}. It was indicated that SiO_2 was combined with cellulose.

In composite aerogel, it had a phase transformation from cellulose I to cellulose II during the course of cellulose dissolution (Ruan, Zhang, Mao, Zeng, & Li, 2004). It could be seen from the spectra, there was not an intense chemical action, and formed the absorption peak of C—Si—O which had been covered by the characteristic absorption peak of cellulose. However, the existence of the absorption peak of Si—O and Si—OH proved that it existed a combination of C—O—Si. So part of SiO_2 was deposited in the form of silica gels, and the other part of SiO_2 could interact with cellulose chain, this action may be caused by the covalent bond or hydrogen bond, or both.

The SEM images of cellulose–SiO_2 composite aerogel were showed in Fig. 2. Composite aerogel had a support frame, which formed the three-dimensional network structure [Fig. 2(a)]. While on the surface of the composite aerogel, there was a large number of compact pore structure [Fig. 2(c)]. Composite aerogel had high porosity with the support frame and pore structure. In composite aerogel, SiO_2 existed in two forms. One was the thin layer of silica aerogels which tiled on the surface of cellulose molecules [Fig. 2(b)]. The other was SiO_2 spherical particles whose diameter was 200–400 nm, SiO_2 particles were coated by cellulose molecules and inlaid in cellulose [Fig. 2(d)]. Composite aerogel had loose and porous network structure. The non-dissolved cellulose was present as circular fibers in the inner of composite aerogel [Fig. 2(e and f)], and the areas of non-dissolved cellulose increased with the increase of cellulose concentration. It was speculated from the SEM images, during the process of cellulose forming aerogel, the cross-linking between cellulose macromolecules made up the support space structure of composite aerogel, and the evaporation of water during the drying process led to the pore structure on the surface.

3.2. Heat insulation performance and mechanics of cellulose–SiO_2 composite aerogels

In order to analyze the effect of density and porosity on heat insulation performance, different density and porosity of composite aerogels were obtained by using variant SiO_2 content and cellulose concentration. Density and porosity of the resulting cellulose–SiO_2 composite aerogels with different SiO_2 content and cellulose concentration were shown in Table 1.

The relationship between porosity and SiO_2 content was shown in Fig. 3. As the SiO_2 content increased, the number of SiO_2 particles which filled up the pore of aerogel increased. It also made the thickness of silica aerogel layers increased. Thus the porosity reduced accordingly. The decrease of porosity was the direct reflection of the increase density of polymer network. Density and porosity are the main factors to influence the heat insulation

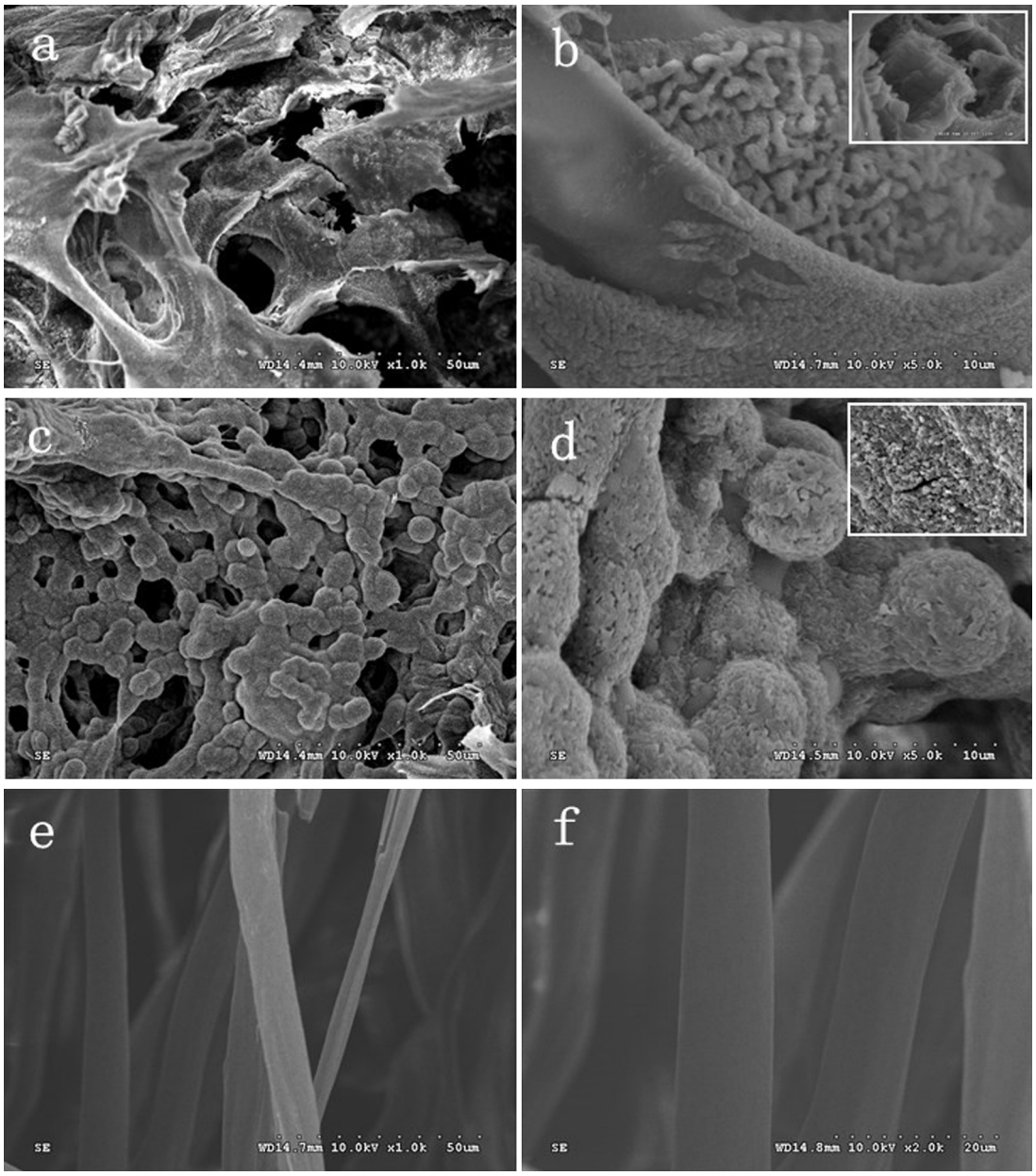

Fig. 2. SEM images of cross-section (a and b) and superficies (c and d) of 5% cellulose–11% SiO_2 composite aerogel.

performance of materials (Henning & Svensson, 1981). Generally speaking, the thermal conductivity of dense solid has been always higher than of still air. At normal temperatures, thermal conductivity increases with the increase of solid matter content in unit volume. As shown in Fig. 4(a), the smaller the density was, the lower the thermal conductivity was. The composite SiO_2 increased the density, however SiO_2 had very low density (Dorcheh & Abbasi, 2008), it had little effect on thermal conductivity. The higher the porosity was, the lower the thermal conductivity was as shown in Fig. 4(b). When density was 0.233 g/cm^3 and porosity was 75.97%, thermal conductivity reached the lowest point, 0.0257 W/(mK). When porosity is higher, the heat transfer route increased, the heat transfer rate had greatly reduced. The increase of porosity can reduce the mean free energy of phonon, and thus to reduce the thermal conductivity of materials. In the meantime, air molecular had a bigger motion space in composite aerogels. It resulted in a relatively big mean free energy, and causes the decrease of thermal conductivity.

Table 1
Density and porosity of the resulting cellulose–SiO_2 composite aerogels with different SiO_2 content and cellulose concentration.

Sample	CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8	CS9
Concentration of cellulose solution (%)	5	5	5	5	5	5	2	3	4
SiO_2 content (%)	9.95	10.85	13.66	14.14	14.26	16.25	7.25	8.76	12.36
Density (g/cm^3)	0.31	0.34	0.26	0.26	0.36	0.45	0.23	0.35	0.41
Porosity (%)	20.09	15.33	37.50	21.93	21.72	22.12	75.97	29.42	22.29

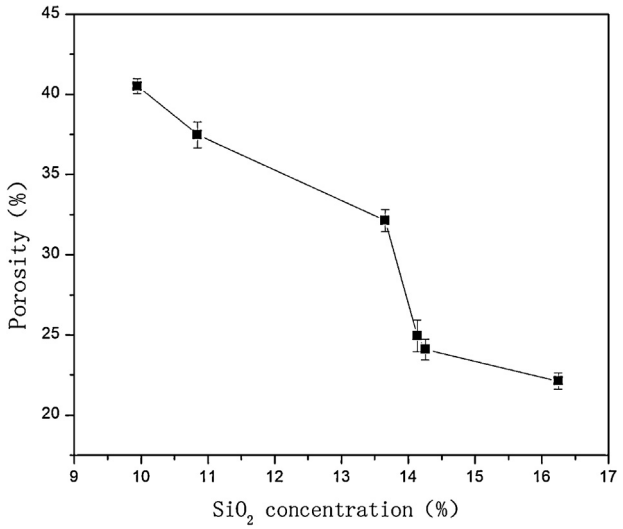

Fig. 3. Effect of SiO_2 concentration on porosity of composite aerogels at 5% cellulose concentration.

Thermal conductivity of both cellulose aerogels and cellulose–SiO_2 composite increased with the increase of cellulose concentration in Fig. 5. Limited by the solubility of cellulose in solvent, when the cellulose concentration reached a certain amount, the amount of non-dissolved cellulose increased and the absolute content of cellulose also increased. Thus thermal conduction in solid and the thermal conductivity increased accordingly. When the cellulose concentration was 3% in cellulose aerogels and was 2% in cellulose–SiO_2 composite aerogels, thermal conductivity reached the lowest point. That's because limited by the cellulose concentration, 2% cellulose aerogels had less cellulose involved in forming the structure of aerogel, which caused the structure of aerogel incomplete. 3% cellulose aerogel had relatively completed structure, and had lower density 0.233 g/cm^3 and higher porosity 84.88%. So 3% cellulose aerogel had the lowest thermal conductivity relative to others cellulose aerogels. Although there was the same problem in composite aerogel, 2% cellulose could not offer a complete structure, huge amounts of SiO_2 particles and silica aerogels filled up into aerogels, which provided an effective support to the stable structure of composite aerogel. And SiO_2 particles and silica aerogels had low density and low thermal conductivity (Schmidt & Schwertfeger, 1998), it resulted 2% cellulose had the lowest thermal conductivity. Fatherly, thermal conductivity of composite aerogel was lower than cellulose aerogel. On the one hand, because of low thermal conductivity of SiO_2, composite aerogels had a lower thermal conductivity. On the other hand, thermal resistivity of open porous composite aerogel increased when its effective pore size decreases. The mean free motion path of air molecule is about in 70 nm (Volz, 2006). After the SiO_2 composited, 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

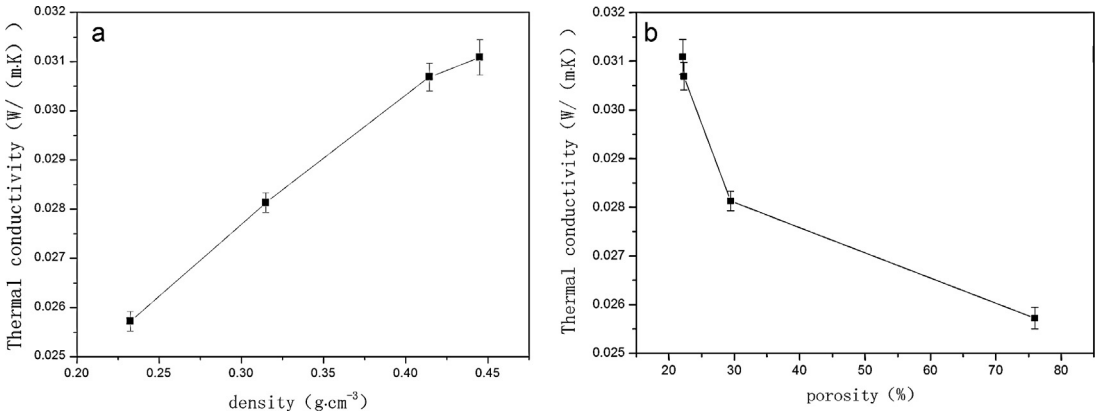

Fig. 4. Effect of density and porosity of CS7 on thermal conductivity of composite aerogels.

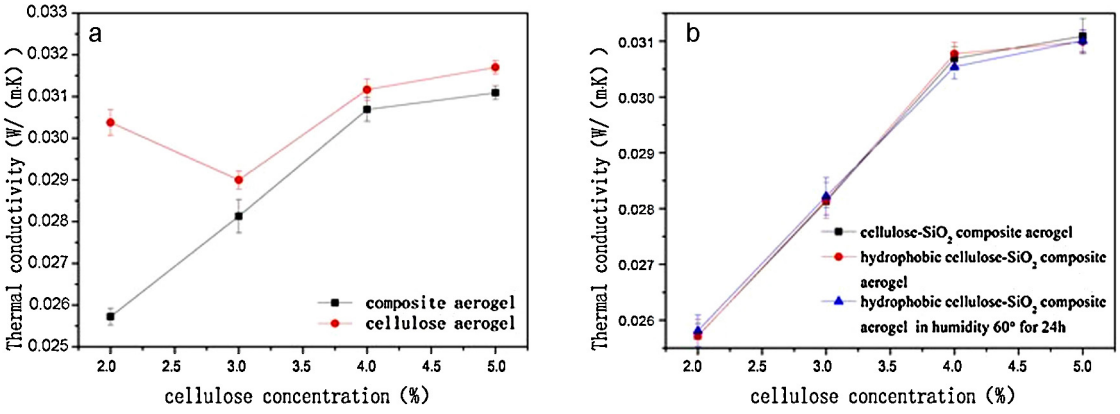

Fig. 5. Effect of cellulose concentration on thermal conductivity of CS7 and 5% cellulose aerogels.

conductivity through the gas inside the material. The internal pore size of composite aerogel reduced with the composition of SiO_2 while the number of pore less than 70 nm increased. Therefore, heat insulation performance of composite aerogel improved.

Cellulose–SiO_2 composite aerogel is a kind of porous insulating materials composed of solid phase (crystalloid and non-crystalloid) and gas phase (pore). There is a lot of air molecule in the interstice of cellulose aerogels. The heat transfer in aerogels can be divided into solid phase heat conduction and gas phase heat conduction (Wang & Liu, 2010). The solid matrix of composite aerogels is formed by interconnection of cellulose molecule clusters. The solid heat transfer is mainly determined by the mean free path of phonon in solid structure unit. During the dissolution course of cellulose, noncrystalline area and crystalline area are both opened. Thus the transfer space of phonon (Chen, 2000; Zhou & Balandin, 2001) enlarges. At the same time, the size of solid particle also influences the density to a certain degree. Composite aerogels with relatively low density had quite small solid particle. So the mean phonon free path is reduced. Then thermal conductivity is decreased. At medium or low temperature, air molecules in random motion have different average kinetic energy in different areas (Zeng & Hunt, 1995). When the 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, and influences the heat insulation performance of composite aerogel further. The low density and high porosity of composite aerogel make air molecule encounter vast scale circum-vallation in the moving process. After SiO_2 composited, the number of pore less than 70 nm increased, so the flowability of gas reduced. It caused the gas phase heat conduction to reduce too. Thus the efficiency of heat conduction reduce, which lead to a relatively low thermal conductivity of gas phase. Therefore, because of low density and high porosity, cellulose–SiO_2 composite aerogel had fine heat insulation performance.

3.3. Hydrophobic modification of cellulose–SiO_2 composite aerogels

It reached a conclusion from FTIR spectra that the existence of SiO_2 could improve the hydrophobicity of composite aerogel to a certain degree. Besides the relatively big specific surface area and the porous structure, composite aerogel was 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; Yang & Tao, 1998). If water molecules were adsorbed by composite aerogel, thermal conductivity would increase, and thus the heat insulation performance decreased. As shown in Fig. 6, composite aerogels with 2% cellulose concentration, the hygroscopicity increased with the increase of humidity, while the thermal conductivity increased with the increase of humidity too. Compared with Fig. 5, the thermal conductivity of composite aerogels in humid conditions increased significantly. Therefore, heat insulation performance of composite aerogel was easy to be influenced by humidity of environment.

In order to obtain the stable heat insulation performance of composite aerogels, a practicable way was to improve the hydrophobicity of composite aerogels. Cold plasma modification technology was employed to modify the surface of the composite 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 (Bretagne, Epaillard, & Ricard, 1992; Chen, 2000; Fresnais, Chapel, & Poncin-Epaillard, 2006). The CCl_4 molecules are dissociated by electron collisions:

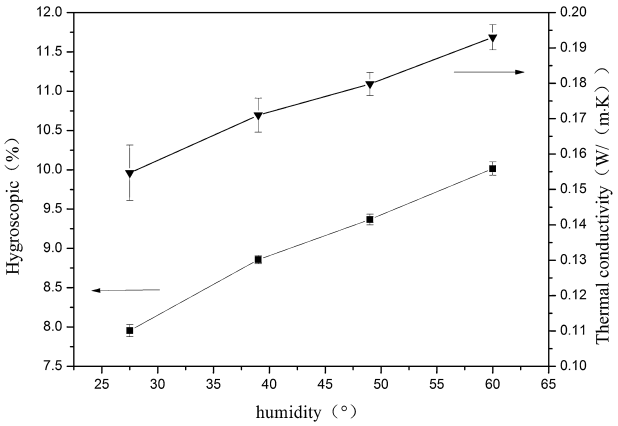

Fig. 6. Effect of air humidity on hygroscopicity rate and thermal conductivity of CS7.

$$e + CCl_4 \rightarrow e + CCl_3 + Cl$$

$$e + CCl_4 \rightarrow e + CCl_2 + 2Cl$$

$$e + CCl_3 \rightarrow e + CCl_2 + Cl$$

$$e + CCl_2 \rightarrow e + CCl + Cl$$

$$e + CCl \rightarrow e + C + Cl$$

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 plasmas. 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 composite aerogels surface was shown in Fig. 7(a). Under 50 W treatment, after 5 min treating time, water contact angle of composite aerogels increased from 0 to 83°. After the treating time kept for 10 min, the water contact angle was beyond than 90°, and the surface of composite aerogels became hydrophobic. After treating time was beyond 20 min, no significant increase for the water contact angle was observed. When the discharge power was 50 W and modification time was 25 min, it had the largest contact angle 132°. When the discharge power increased from 0 to 70 W with 25 min treating time the change of water contact angle on the surface of composite aerogels was shown in Fig. 7(b). When the discharge power increased from 0 to 50 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 composite 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 composite aerogels after hydrophobic modification was compared. As shown in Fig. 5(b), the thermal conductivity had no significant change before and after modification. When the hydrophobic composite aerogels were maintained in humidity 60° for 24 h, the thermal conductivity also had no significant change. But as compared with Fig. 6, the thermal conductivity of unmodified aerogel was visibly growing. It demonstrated that the plasma hydrophobic modification was just for improving the hydrophobility of composite aerogels surface, and would not influence heat insulation performance of composite aerogels. Hence, the plasma

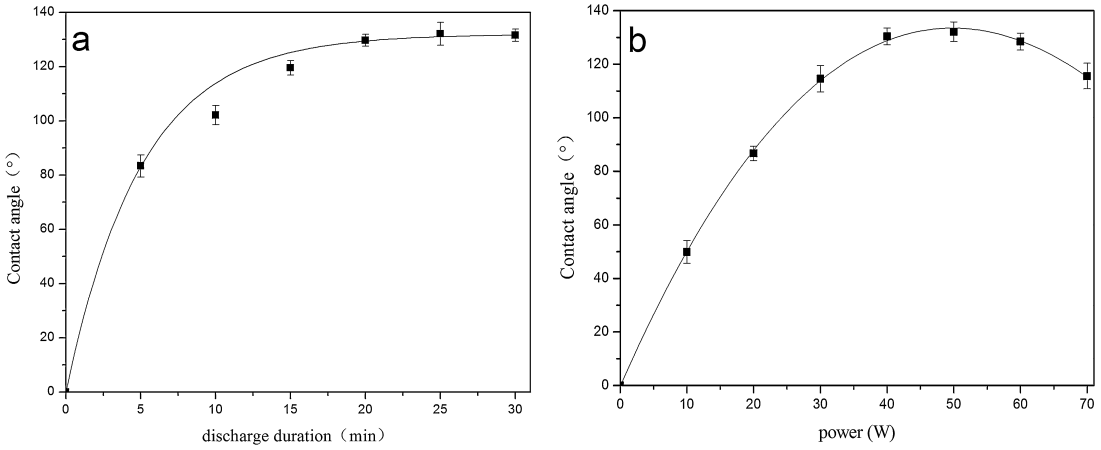

Fig. 7. Effect of discharge duration and discharge power on water contact angle of CS7 treated by the CCl_4 plasma.

modification technology is an effective method to modify the surface properties of cellulose–SiO_2 composite aerogel.

4. Conclusion

In this paper, through controlling the hydrolysis–fasculation reaction speed of TEOS, composite cellulose–SiO_2 aerogels were successfully prepared by using NaOH/thiourea solvent system and freeze-drying method. The result showed that composite aerogel was cellulose II crystal phase and the composition of SiO_2 could reduce the hydrophilicity. The SiO_2 was composited with cellulose in the form of SiO_2 particles and silica aerogel. A network structure was formed with high porosity. These structural features made the composite aerogels having a good heat insulation performance. Thermal conductivity decreased with the decrease of density and the increase of porosity. It could be as low as 0.026 W/(mK). After the composition of SiO_2, the heat insulation performance of composite aerogel was improved. But thermal conductivity was affected by the humidity of environment. With the cold plasma modification technology, the hydrophobic composite aerogel was obtained. The hydrophobic modification using CCl_4 as plasma turned the surface of composite aerogels from hydrophilic to hydrophobic successfully with a largest water contact angle of 132°. The composite aerogels still kept good heat insulation performance after the hydrophobic modification.

The thermal conductivity of the traditional porous thermal insulation materials, such as foam plastics, foam glass and calcium silicate material, is in the range of 0.030–0.047 W/(mK). Therefore, the stable good heat insulation performance of the cellulose–SiO_2 composite aerogel provides a vaster potential in heat insulation material field.

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