Elsevier Editorial System(tm) for Carbohydrate Polymers

Manuscript Draft

Manuscript Number: CARBPOL-D-18-00415R1

Title: Thermal conductivity, structure and mechanical properties of konjac glucomannan/starch based aerogel strengthened by wheat straw

Article Type: Research Paper

Keywords: konjac glucomannan; thermal insulation aerogel; wheat straw; starch; pore size distribution; mechanical property.

Corresponding Author: Professor Fatang Jiang, PhD

Corresponding Author's Institution: Hubei University of Technology

First Author: Yixin Wang

Order of Authors: Yixin Wang; Kao Wu; Man Xiao; Saffa B Riffat; Yuehong Su; Fatang Jiang, PhD

Abstract: This study presents the preparation and property characterization of a konjac glucomannan (KGM)/starch based aerogel as a thermal insulation material. Wheat straw powders (a kind of agricultural waste) and starch are used to enhance aerogel physical properties such as mechanical strength and pore size distribution. Aerogel samples were made using environmentally friendly sol-gel and freeze drying methods. Results show that starch addition could strengthen the mechanical strength of aerogel significantly, and wheat straw addition could decrease aerogel pore size due to its special micron-cavity structure, with appropriate gelatin addition as the stabilizer. The aerogel formula was optimized to achieve lowest thermal conductivity and good thermal stability. Within the experimental range, aerogel with the optimized formula had a thermal conductivity 0.04641 Wm-1K-1, a compression modulus 67.5 kPa and an elasticity 0.27. The results demonstrate the high potential of KGM/starch based aerogels enhanced with wheat straw and starch for application in thermal insulation.

Thermal conductivity, structure and mechanical properties of konjac glucomannan/starch based aerogel strengthened by wheat straw

Yixin Wang[1,2], Kao Wu[1,2], Man Xiao[1,2], Saffa B.Riffat[3], Yuehong Su[3]* and Fatang Jiang[1,2,3]*

[1]Glyn O. Philips Hydrocolloid Research Centre at HUT, Hubei University of Technology, Wuhan 430068, China;

[2]School of Bioengineering and Food Science, Hubei University of Technology, Wuhan 430068, China;

[3]Department of Architecture and Built Environment, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Abstract:

This study presents the preparation and property characterization of a konjac glucomannan (KGM)/starch based aerogel as a thermal insulation material. Wheat straw powders (a kind of agricultural waste) and starch are used to enhance aerogel physical properties such as mechanical strength and pore size distribution. Aerogel samples were made using environmentally friendly sol–gel and freeze drying methods. Results show that starch addition could strengthen the mechanical strength of aerogel significantly, and wheat straw addition could decrease aerogel pore size due to its special micron-cavity structure, with appropriate gelatin addition as the stabilizer. The aerogel formula was optimized to achieve lowest thermal conductivity and good thermal stability. Within the experimental range, aerogel with the optimized formula had a thermal conductivity 0.04641 $Wm^{-1}K^{-1}$, a compression modulus 67.5 kPa and an elasticity 0.27. The results demonstrate the high potential of KGM/starch based aerogels enhanced with wheat straw and starch for application in thermal insulation.

Keywords: konjac glucomannan; thermal insulation aerogel; wheat straw; starch; pore size distribution; mechanical property.

Highlights:

1. Four natural raw materials were used for KGM/starch based aerogel preparation

2. KGM/starch based aerogel preparation via an energy efficient freeze drying method.

3. Starch was used to increase the mechanical strength of KGM/starch based aerogels.

4. Wheat straw can improve thermal insulation by affecting pore structure.

5. Thermal insulation mechanism of KGM/starch based aerogel was discussed.

1. Introduction

Although people's living standards have been greatly improved with rapid economic growth, the energy consuming level becomes much higher, raising considerable social concerns about energy crisis and environmental problems. Currently energy conservation and environmental protection have received growing attentions. To reduce CO_2 emissions, numbers of low-energy buildings and passive houses have been built in German (Beck, Heinemann, Reidinger, & Fricke, 2004).On the other hand, a large amount of energy is used for space heating and air conditioning, especially in extremely hot and cold climate regions, and the real estate has great potential for energy saving by rational use of resources. According to this, the European Union has set a goal for reductions in energy use and flue gas emissions (Ramírez-Villegas, Eriksson, & Olofsson, 2016). Therefore, energy conservation policy can be enforced and implemented by the development of thermal insulation materials.

Commonly, thermal insulation materials are composed of organic polymers, such as polyurethane foam, polystyrene foam, glass wool, etc. Polyurethane foam can be divided into two categories: flexible polyurethane foam and rigid polyurethane foam (Septevani, Evans, Chaleat, Martin, & Annamalai, 2015), and is often used as thermal insulation materials in the building envelop and domestic refrigerators (Janik, Sienkiewicz, & Kucinska-Lipka, 2014). However, the production of polyurethane foam relies on the unsustainable petroleum sources, as its two main components are isocyanates and polyether. Moreover, the widely use of polyurethane has produced considerable amount of wastes, and these wastes usually go into landfill, which need quite long time to be degraded. Possessing extremely low density and large surface area, aerogel was invented by Kistler in 1931 (Kistler, 1931) and has also been used as insulation material, e.g. in space suit and aerospace detector (Randall, Meador, & Jana, 2011; Sabri, Marchetta, Faysal, Brock, & Roan, 2014). The heat transfer mechanism of aerogel is explained by the combination of heat conduction in solid backbone and gaseous phase and thermal radiation between the interior surfaces (Lee & Cunnington, 2012; Lu, Caps, Fricke, Alviso, & Pekala, 1995). The effective total thermal conductivity can be expressed as the solid thermal conductivity of the solid backbone, the effective thermal conductivity of the gaseous phase, and the radiative heat exchange (Lee, Lee, Yim, Sun, & Yoo, 2002; Lu et al., 1995). Currently, most aerogel materials are prepared from inorganic or petrochemical-based feedstock, such as silica aerogels and resorcinol-formaldehyde aerogels (Mikkonen, Parikka, Ghafar, & Tenkanen, 2013). However, the degradation time of these aerogels can be quite long in nature and thus may cause harm to the environment. Therefore, alternative new, green and sustainable polysaccharide-based aerogels have attracted a lot of interests from researchers (Robitzer, Renzo, & Quignard, 2011).

As a renewable, sustainable, non-toxic material, polysaccharides including cellulose (Thakur & Voicu, 2016), hemicellulose, marine polysaccharides, starch (Miculescu et al., 2017), etc. have in common the ability to form gels in the presence of water or with other cross-linking agents (He, Sui, He, & Li, 2015), and polysaccharide aerogels with different physical, thermal, optical and acoustical properties (Wang, Chen, Kuang, Jiang, & Yan, 2017) can be obtained by drying these gels through two commonly used drying methods, supercritical drying and freezing drying. Protecting structures from collapsing, the latter method, also known as lyophilization, is a low-cost and convenient method preferred by industry consisting of moving frozen water from a frozen sample by sublimation under vacuum. There have been a number of reports on the preparation of polymer materials through freeze-drying process from aqueous mixtures due to the safety and low cost (Wang, Alhassan, Yang, & Schiraldi, 2013), e.g. nanocellulose aerogel (Nemoto, Saito, & Isogai, 2015), biobased poly (furfuryl alcohol) and clay aerogel (Wang, Sun, Long, Wang, & Schiraldi, 2016), alginate nanocomposite aerogels (Ke et al., 2016).

Konjac glucomannan (KGM) is an abundant, nontoxic polysaccharide found in the tuber of amorphophallus konjac plant. KGM is composed of glucose and mannose linked by β-1, 4 glycosidic bonds at 1:1.5–1:1.6 molar ratio, with 5–10% acetyl substitution (Davé & Mccarthy, 1997), and has high viscous property (30,000 mPa·s, 1%, w/v) and high molecular weight (6.8×10^5~9×10^6 Da) (Crosby, 2002). It can be a good skeleton material for aerogel preparation based on our previous research (Ni et al., 2016; Wang et al., 2017) . Wheat is cultivated in over 115 nations in the world, producing a huge amount of straw as a byproduct. Wheat straw is usually treated by incineration, causing serious air pollution to the environment. However, with its special cavity structure, wheat straw can be also used as thermal insulation materials

(Beck et al., 2004; Palumbo, Avellaneda, & Lacasta, 2015). Gelatin and starch as degradable natural materials can also be used for aerogel preparation (Chang, Chen, & Jiao, 2010; García-González, Uy, Alnaief, & Smirnova, 2012; Kenar, Eller, Felker, Jackson, & Fanta, 2014; Wang, J. et al., 2016). Appropriate combination of different polymers could contribute to significant improvements on material properties (Corobea et al., 2016). According to previous research (Chen et al., 2017; Ni et al., 2016; Wang et al., 2017), the pore structure and mechanical property of KGM-based aerogels can vary a lot with different composition and formulae. Therefore, this study aims to investigate the relationship between thermal insulation property and pore structure of KGM/starch based aerogels enhanced with wheat straw and gelatin. The impact of aerogel components on the mechanical property, thermal stability, density, porosity of KGM/starch based aerogels was also studied. This research can contribute to the development of biodegradable thermal insulation materials.

2. Experiments

2.1 Materials

KGM was supplied by Licheng Biological Technology Co., Ltd. (Wuhan, China). Potato starch was purchased from Wuhan Lin He Ji Food Co., Ltd. (Wuhan, China). Gelatin was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Raw wheat straw was obtained from Local farmers in Wuhan. After being cut to small segments and washed more than 5 times, raw wheat straw was completely dried in an oven at 90 °C. The dried straw segments was mechanically milled into particles by a cereal pulverizer. Wheat straw powder were sieved through a 160 mesh

Tyler screen (pore size 94 μm) before being used.

2.2 KGM/starch based aerogel preparation.

The preparation of KGM/starch based aerogels was based on an invention patent of Licheng Biological Technology in China (Jiang, 2013) as illustrated in Fig. 1. Gelatin (0-1.5%, w/v) was first dissolved in double-distilled water (100 mL) in a water bath at 90 °C. Then KGM (0.5-1.5%, w/v), potato starch (1.0-3.0%, w/v) and wheat straw powder (0.5-1.5%, w/v) were gradually added and mixed homogenously with the stirring speed 600 rpm for 1 h to obtain the mixed sol. Subsequently the sol was injected into a cylindrical 6 well cell culture cluster (diameter 34.8 mm and height 18 mm) and put into a 4 °C refrigerator for aging and molding for 2 h, before immediately frozen in an ultra low temperature freezer (DW-FL262, Rowsen, China) at -25 °C for 10 h. The frozen sample was dried in a freeze dryer (Modulyod-230, Thermo Electron Corporation, USA) at -55 °C under a vacuum of 1 Pa for approximately 24 h, and the aerogel (34.8 mm in diameter and about 10 mm in height) was formed and obtained. All aerogel samples were coded in the form of K0S0G0WS0 (K, S, G, WS represents konjac glucomannan, potato starch, gelatin, wheat straw, respectively), and the number after K, S, G, WS indicates the weight volume percent of composition in the original sol. Prior to tests, all samples were stored in a dryer with silica gel beads and dried for 6 h at 60 °C in an oven.

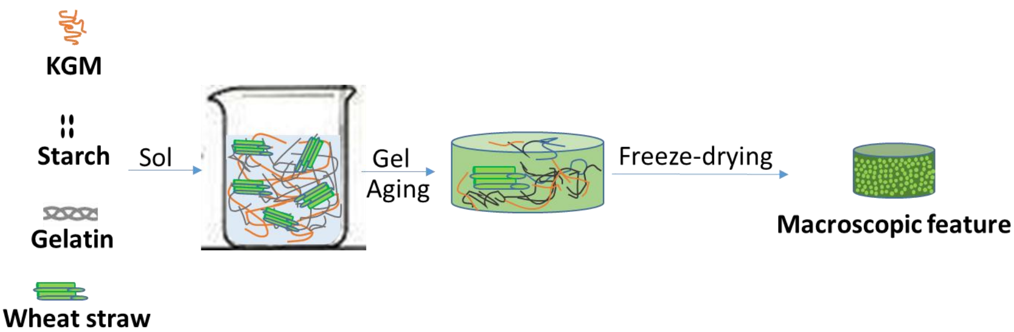


Fig. 1. Schematic procedure of preparing KGM/starch based aerogels

2.3 Characterization of KGM/starch based aerogels

2.3.1 Dry density

The dry density (ρ) was calculated by the following equation:

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

Where m_0 is the dry weight of aerogel, V is the volume of the aerogel samples

2.3.2 Estimation of porosity

Porosity is an important structure parameter of KGM/starch based aerogel, and porosity of aerogels was estimated according to Shi et al. (2013). Aerogel sample was weighed first (m_0), then completely immersed in ethanol in a container and weighted in total (m_1). The container was then put in a vacuum drying oven and vacuumized until no air bubble coming out of the sample. After taking out the sample from the container, the container with the residual ethanol was weighed (m_2). The porosity of the sample can be calculated as below:

$$\text{Porosity (\%)} = \frac{\textit{Weight of ethanol in sample}}{\textit{Total weight of sample and ethanol}} = \frac{m_1 - m_2 - m_0}{m_1 - m_2} \times 100\%$$

2.3.3 Morphology, microstructure and pore size distribution of KGM/starch based aerogels

The morphology and microstructure of KGM/starch based aerogels were observed using SEM (JSM6390LV, JEOL, Tokyo, Japan). Prior to test, aerogel samples were cut into 5 mm*5 mm*1 mm cubical pieces using a sharp razor blade. The cut surface of samples were coated with gold particles (Bio-Rad type SC 502, JEOL Ltd, Japan) by sputtering for 60 s, before observed at magnification of 50×, 150×, 500×, 1000× using an accelerated voltage of 30 kV. Image Pro Plus software (Media Cybernetics Inc, Maryland, America) was used to evaluate the pore size distribution of the KGM/starch based aerogels based on 6 representative SEM images.

2.3.4 Texture profile analysis

The mechanical property of samples were tested by Texture analyzer (TA.XT Plus, Stable Micro Systems, Surrey, UK) equipped with a 30 kg load cell and a discoidal probe (d=100 mm, compression platen Model No. 10585) through double compression tests. The test compression rate and ratio were 60 mm/min and 30%, respectively, and the trigger force was set to 1.00 N in auto mode. The compressive strength of specimens is defined as the maximum stress during the test. Sress (σ) was calculated by the following standard equations:

$$\sigma = \frac{F}{S_0}$$

where F is the force (in N) applied on the sample surface, S_0 in mm^2, the initial cross-sectional area of the sample.

2.3.5 Thermal conductivity measurement

Thermal conductivity of samples were measured at room temperature using a Thermal

Conductivity Analyzer (HOT DISK TPS2500, Uppsala, Sweden). The senor (polyimide senor d=9.868 mm, Model No. 8563) are squeezed between two KGM/starch based aerogel specimens. The equipment was put on a stable and flat table with a heat shield. The core of the apparatus is a double spiral of thin nickel wire (Gustafsson, 1991), which acts as the heat source controlling the temperature of the senor. An orthogonal design experiment was applied to investigate optimization of the aerogel formula to minimize thermal conductivity. 4 factors (KGM, gelatin, starch, wheat straw) and 3 levels (component concentration level) were selected according to previous results.

2.3.6 Thermogravimetric analysis (TGA)

TGA was carried out to determine the thermostability by weight loss in relation to temperature with a Netzsch TG 209 (Netzsch, Selb, Germany). The samples were pulverized into granules by a pulverizer. With the nitrogen flow rate 20 mL/min, the specimen was heated from 25 °C to 600 °C at heating rate 20 °C /min, and weight loss curve was recorded.

2.4 Statistical analysis

All tests were performed at least in triplicate. Origin Pro 8 SR4 v8.0951 (OriginLab, MA, USA) was used for figure drawing and linear regression analysis. SPSS (version 19, Endicott, NY, USA) was used for Pearson correlation analysis among porosity, density, and thermal conductivity of aerogels.

3. Results and discussion

3.1 Impact of starch on mechanical property of KGM-based aerogels

Generally, aerogels with higher compressive stress and elasticity are suggested for practical applications. Representative stress-strain curves (strain 0-30%) for the effect of starch concentration on the compressive strength are shown in Fig. 2. The KGM-based aerogels had elasticity between 0.248 and 0.384. With starch concentration 1%, the compressive strength of aerogel was improved slightly, and starting from 2%, the compressive strength aerogel samples began to have significant increase with the increase of starch concentration. The starch addition as the filler can significantly improve the mechanical strength of the aerogels. There are two different molecular components in starch, *i.e.*, amylose and amylopectin. Amylopectin (molecular weight ≈ 10^8Da) contains a significantly higher branch density than amylose (approximately 1% branch density, molecular weight ≈ 10^4 to 10^6 Da). Amylopectin is the major component in potato starch, and its branched structure could endow the structural rigidity of starch, compared with KGM molecules which are mostly linear chains without branches. Thus, starch presence could increase the mechanical properties of KGM-based aerogel samples. To be more specific, compared with K1S0G0WS0, starch addition of 1%, 2%, 3%, 4% can bring improvement of stress by 161%, 956%, 1505%, 2788%, respectively.

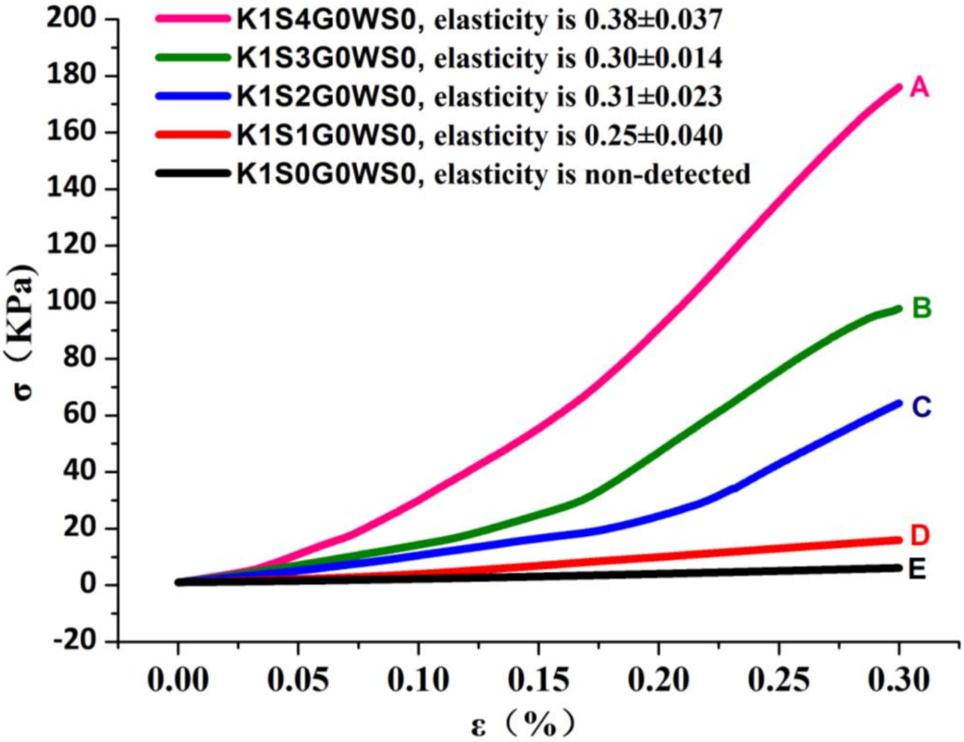
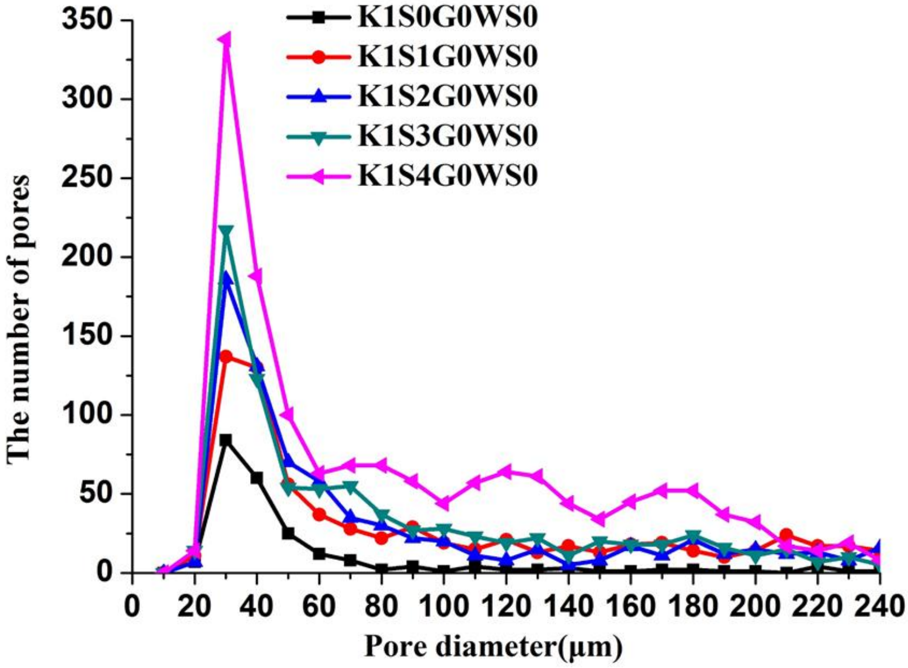


Fig. 2. Stress-strain curves for KGM-based aerogels with different starch concentration

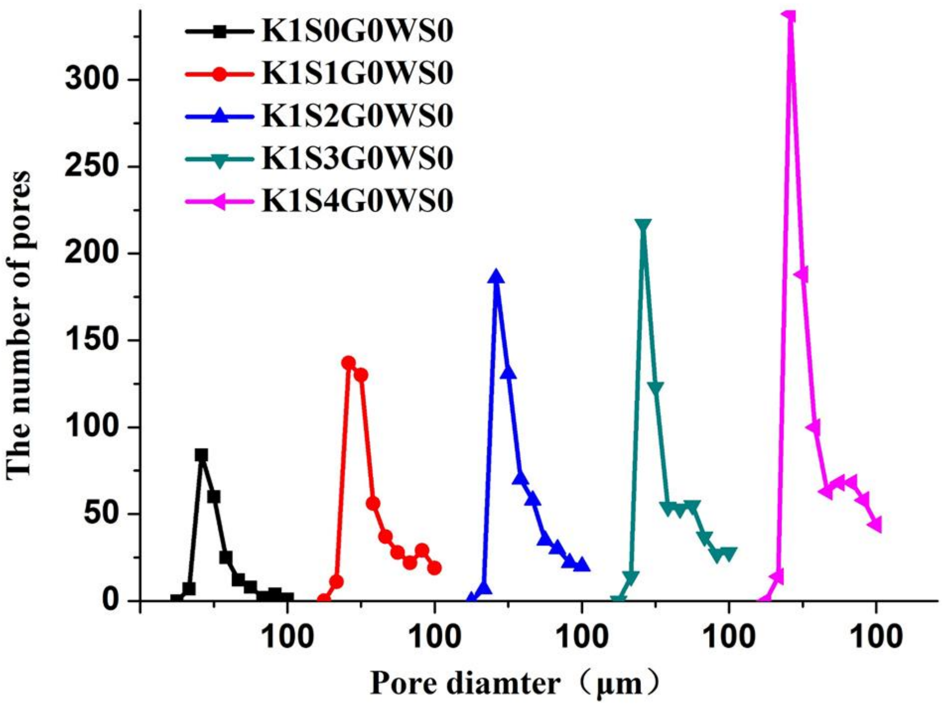
3.2 Impact of starch and wheat straw on the structure of KGM-based aerogels

Referring to our previous research (Ni et al., 2016), KGM-based aerogels pores are relatively big, spherical and uniform. With starch concentration increased from 0% to 4% (w/v), the sum numbers of pores in aerogel with pore sizes 10-50 μm were gradually increased (Fig. 3A, B). Moreover, a good linearity ($R^2 = 0.9240$) was observed between the sum number of pores and the starch concentration (Fig. 3C). This suggests that by varying starch concentration, the pore size of aerogels could be adjusted to desired value through a linear model. With increased starch concentration, the pore walls became thicker, and the pore channel size decreased. This would benefit formation of close pores in aerogels, improving thermal insulation property (Wang, Zhong, Wang, & Yu, 2006). However, too high starch concentration may lead to very high density of aerogels, and this does not benefit the thermal insulation capability. Therefore, starch concentration of 2% (w/v) was preliminarily selected in the following parts, as it could already significantly improve the compressive stress and pore size, compared with pure KGM aerogel (K1S0G0WS0).

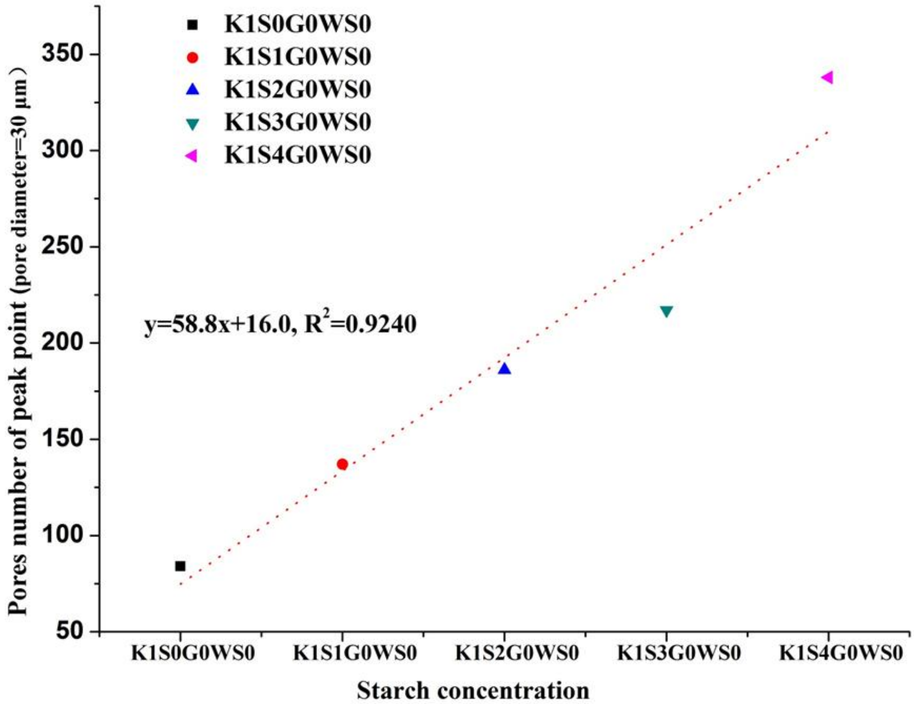
After wheat straw addition, the obtained KGM/starch based aerogels showed a greenish brown appearance with flat smooth parallel surface (Fig. 4a). Wheat straw has multi-cavities (Fig. 4b, c), and therefore with different wheat straw addition, the pore size distribution of KGM-based aerogels are adjusted, and thermal insulation properties can be changed. All KGM-based aerogels (Fig. 4d-i) had three-dimensional network structure. Without wheat straw addition, pores were almost round (Fig. 4d), and after wheat straw addition, the pores were smaller and their shapes was changed from polygons into irregular shape (Fig. 4e). This may be explained by that the wheat straw addition caused shape changes of ice crystal formed during freezing, which could affect the distribution of pore size, the shape and the connectivity of the porous network (Kiani & Sun, 2011). Besides, wheat straw can also provide many micron-scale pores due to their multi-cavities, and this was supported by the size distribution results of aerogel pores (Fig. 3D), as K1S2G0WS1.5 had much more numbers of smaller pores than K1S2G0WS0. Without wheat straw (K1S2G0WS0), the wave crest (10-50 μm) pores in aerogel was found to include only 48.83% of the total number (806) of pores, and when wheat straw was added, a slight spike (10-50 μm) appeared covering 66.98% of the total number (966) of aerogel pores. Therefore, with wheat straw addition, the pore size was significantly decreased **(Fig. 4)**.


K1S0G0WS0
K1S1G0WS0
K1S2G0WS0
K1S3G0WS0
K1S4G0WS0
The number of pores
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240
Pore diameter(μm)

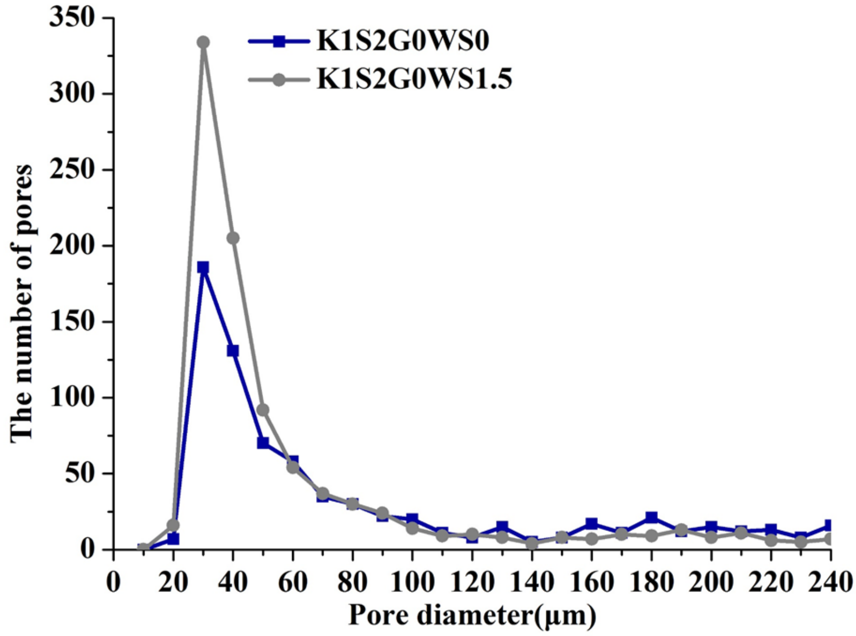
A


K1S0G0WS0
K1S1G0WS0
K1S2G0WS0
K1S3G0WS0
K1S4G0WS0
The number of pores
300
250
200
150
100
50
0
100 100 100 100 100
Pore diamter（μm）

B



C



D

Fig. 3. (A, B) Size distribution (A: 0-240 µm; B: 0-100µm) of KGM-based aerogels pores with different starch concentration; (C) Linear relationship between starch concentration and aerogel pore numbers at pore diameter 30 µm; (D) Size distribution of KGM-based aerogels pores with different wheat straw concentration

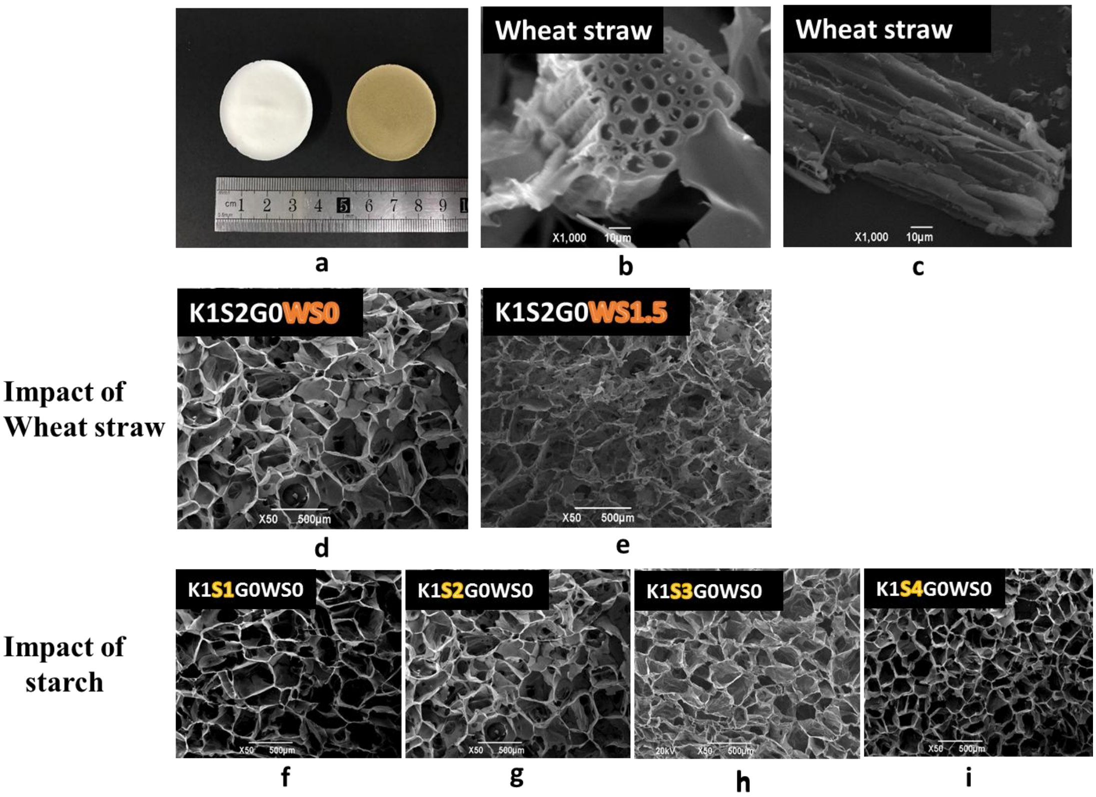


Fig. 4. Images of KGM-based aerogels with and without wheat straw (a), wheat straw (b, c) and SEM observations of KGM-based aerogels (d-i)

3.3 Thermal insulation property

3.3.1 General heat transfer analysis for KGM/starch based aerogels.

The effective total thermal conductivity can be expressed as the sum of solid thermal conductivity of the solid backbone, the effective thermal conductivity of the gaseous phase, and the radiative conductivity. For KGM/starch based aerogel, the heat transfer mechanism mainly include the solid conduction through the aerogel skeleton and the gas conduction in the pores. According to this, the thermal insulation property is related to the pores size distribution, pore shape, and pore walls. The solid backbone of aerogels were composed of different materials whose volume heat capacity, frequency-averaged mean free path of phonons and average phonons velocity are invariable. However, solid conduction correlates with density which can be changed by the concentration of raw materials, and the higher ρ, the higher solid heat conduction λ_s. Low-density porous materials can have superinsulation properties as a result of the air confined in their pores when the pore size is below the free mean path of air molecules. Therefore, smaller average pore size of KGM/starch based aerogel should be preferred in order to achieve lower thermal conductivity, and this can also reduce the occurrence of open pores, which will benefit restricting gaseous heat transfer.

3.3.2 Thermal conductivity of KGM/starch based aerogels

Though wheat straw addition (1.5%, w/v) could improve aerogel pore size distributions, however, wheat straw subsidence occurred sometimes due to shear thinning phenomenon. As gelatin solution was found to convert into gel rapidly after the temperature was decreased to below 37 °C (Liu & Ma, 2009), it was further introduced to keep wheat straw from subsiding. We had designed a single-factor experimentto investigate the impact of gelatin on KGM-based aerogels, and the results indicated that higher gelatin addition would contribute to irregular macroscopic feature with more through-holes, which would lead to negative effect on thermal insulation (Fig. S1). However, a small number of gelatin can avoid the wheat straw from subsiding and can keep wheat straw evenly dispersive, and therefore a critical and small gelation addition would benefit the aerogel preparation.

Based on the above results and discussion, a L9 (3^4) orthogonal array test was performed to analyze the impact of different components and concentrations on the thermal conductivity and to obtain the optimized aerogel formula. Four factors (four different raw materials: KGM, starch, gelatin, and wheat straw) and three levels (three different concentration) were applied, and 9 different aerogel samples were selected (Table 1). Significant thermal conductivity differences were observed among different samples. K1.0S2.0G0WS1.5 showed the lowest thermal conductivity (0.04683 $Wm^{-1}K^{-1}$), and K1.5S2.0G1.0WS0.5 had the highest (0.05329$Wm^{-1}K^{-1}$). Based on the thermal conductivity values of the 9 designed samples, k and Range values were calculated and the results indicated the effect of raw material concentration on the thermal conductivity followed the order: gelatin > wheat straw > starch > KGM, according to the values of range. The optimized aerogel formula was therefore calculated to be K1S2G0.5WS1.5. To confirm this, we had prepared aerogel sample K1S2G0.5WS1.5, and its thermal conductivity was measured to be 0.04641$Wm^{-1}K^{-1}$, a little lower than K1S2G0WS1.5. Its compressive strength, elasticity were 80.5 kPa, 0.273, respectively. This thermal insulation orthogonal test result was also in accordance with the previous discussion in mechanical property section where 2 % (w/v) starch addition was preliminarily selected. With more starch concentration, the thickness of pore walls was increased and so was the solid phase heat conduction.

Porosity, density are important factors affecting thermal conductivity. The density and porosity of all samples are shown in Table 2. Pearson correlation analysis showed that density and porosity had strong negative relationship (Pearson coefficient= -0.799, $p<0.01$), and both of them did not have significant relationships with thermal conductivity ($p>0.05$). This was in agreement with most previous researchers who found that single relationship between thermal conductivity and porosity could hardly be established, because not only the volume pore fraction but also the other factors such as pore size, shape, density and orientation can impact thermal conductivity (Francl & Kingery, 1954). In the same time, the gaseous (λg) and the radiative (λr) conductivities reduce along with the density which relates to solid content, while the solid conductivity increase with the density (Lu et al., 1995). The thermal conductivity differences of KGM/starch based aerogels may have to be explained from the pore size and structure analysis.

From the samples listed in Table 1 and 2, we selected two aerogel samples with low thermal conductivity (K1S2G0WS1.5, K1S2G0.5WS1.5) and K1S2G0WS0 to analysis the impact of pore structure on thermal conductivity. Compared with K0.5S1G0WS0.5 which had lowest density, K1S2G0WS1.5 had smaller pores (Fig. 5), leading to lower values of λs and λg. K1S2G0WS1.5 may be composed of more closed pores with main pore size distribution about 30 μm. Compared with K1S2G0WS0, the pore wall surface of K1S2G0WS1.5 was unsmooth with some linear cavity structure which make the connectivity of the porous network more complex (Fig. 4e), due to the impact of wheat straw addition. Moreover, after adding wheat straw powder, gaseous flow path may have been changed to be more complicated leading to the lower thermal conductivity. Additionally, with many micron-scale pores, wheat straw addition could make aerogel pores (Fig. 5e, f) become more complicated which was good thermal insulation due to elongated heat transfer path. Compared with K1S2G0WS1.5, the optimized formula K1S2G0.5WS1.5 had only the differences of small amount of gelatin addition, and this resulted in further lower thermal conductivity. This may be explained by that wheat straw was more evenly distributed in K1S2G0.5WS1.5. Additionally, as air had low thermal conductivity (0.0267 $Wm^{-1}K^{-1}$), the higher porosity of K1S2G0.5WS1.5 may also contribute to its lowest thermal conductivity.

Table 1. Analysis of $L_9(3)^4$ test results

Sample code	KGM	Starch	Gelatin	Wheat straw	Thermal Conductivity
	(g/100mL)				(Mean ± SD)
K0.5S1.0G0WS0.5	0.5	1.0	0	0.5	0.05147±0.00050
K0.5S2.0G0.5WS1.0	0.5	2.0	0.5	1.0	0.04870 ± 0.00030
K0.5S3.0G1.0WS1.5	0.5	3.0	1.0	1.5	0.05275 ± 0.00066
K1.0S2.0G0WS1.5	1.0	2.0	0	1.5	0.04683 ± 0.00178
K1.0S3.0G0.5WS0.5	1.0	3.0	0.5	0.5	0.05166 ± 0.00012
K1.0S1.0G1.0WS1.0	1.0	1.0	1.0	1.0	0.05135 ± 0.00066
K1.5S3.0G0WS1.0	1.5	3.0	0	1.0	0.05163 ± 0.00012
K1.5S1.0G0.5WS1.5	1.5	1.0	0.5	1.5	0.04852 ± 0.00178
K1.5S2.0G1.0WS0.5	1.5	2.0	1.0	0.5	0.05329 ± 0.00017
k1	0.05098	0.05051	0.05004	0.05214	
k2	0.04995	0.04961	0.04957	0.05056	
k3	0.05114	0.05195	0.05246	0.04937	

Range	0.00120	0.00235	0.00290	0.00278	
Optimal level		G>WS>S>KGM			
Major factor	1%	2%	0.5%	1.5%	
Optimized formula		K1S2G0.5WS1.5			0.04641±0.00007

Range refers to the result of extreme analysis, Range = max {k1, k2, k3} – min {k1, k2, k3}. Where ki (i=1, 2, 3) represent the corresponding mean value of thermal conductivity at each level of concentration.

Table 2. Aerogels of different composition and their porosity and density testing results

Sample	Porosity (%)	Density(g/cm^{-3})
K0.5S1.0G0WS0.5	97.17±0.03	0.0201±0.0002
K0.5S2.0G0.5WS1.0	93.76±0.09	0.0410±0.0006
K0.5S3.0G1.0WS1.5	94.28±0.08	0.0524±0.0015
K1.0S2.0G0WS1.5	93.28±0.06	0.0409±0.0013
K1.0S3.0G0.5WS0.5	92.65±0.05	0.0506±0.0001
K1.0S1.0G1.0WS1.0	94.43±0.04	0.0358±0.0010
K1.5S3.0G0WS1.0	92.49±0.07	0.0471±0.0015
K1.5S1.0G0.5WS1.5	93.80±0.05	0.0392±0.0006
K1.5S2.0G1.0WS0.5	94.40±0.02	0.0437±0.0008
K1S2G0.5WS1.5(Optimized formula)	94.50±0.03	0.0433±0.0002

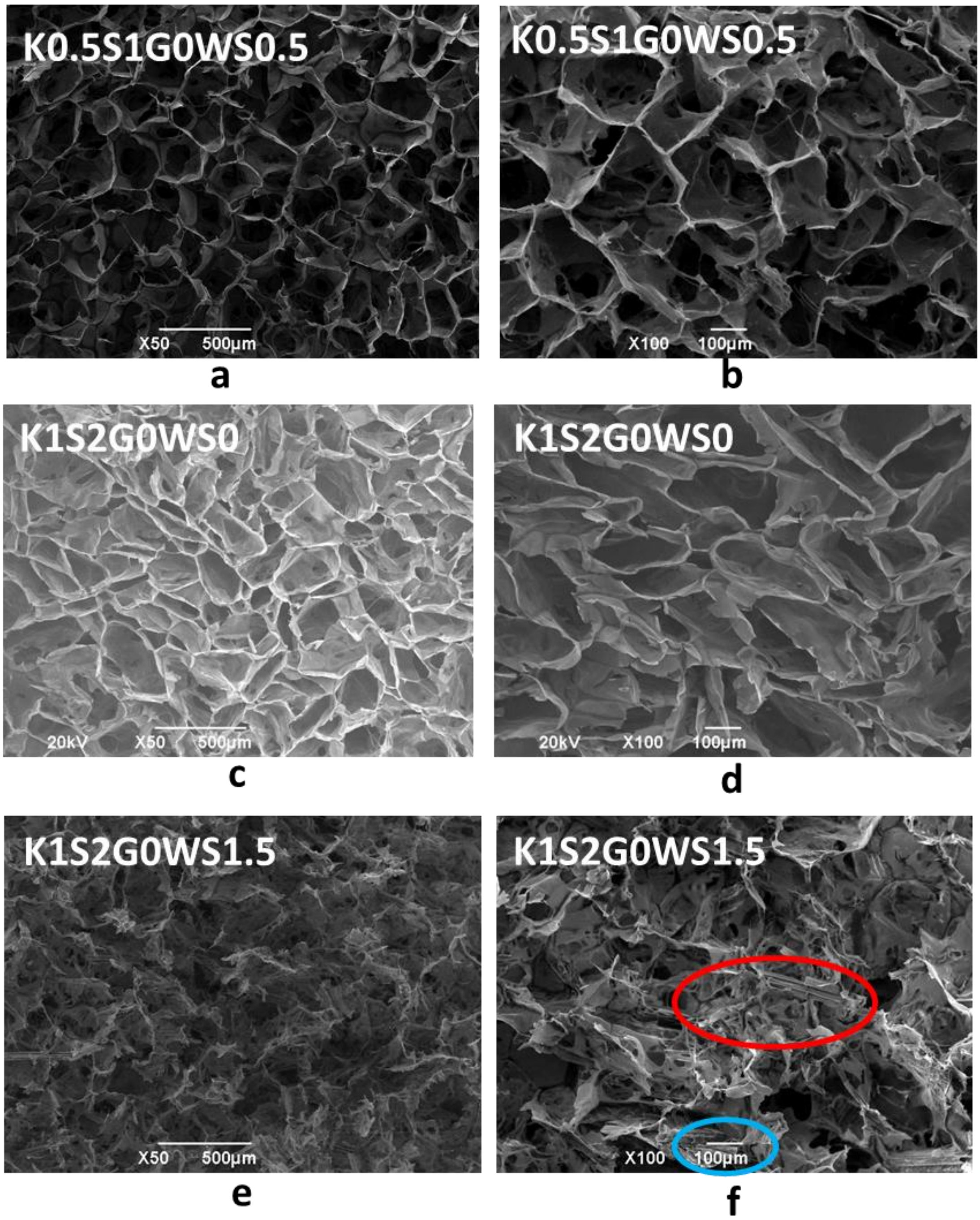
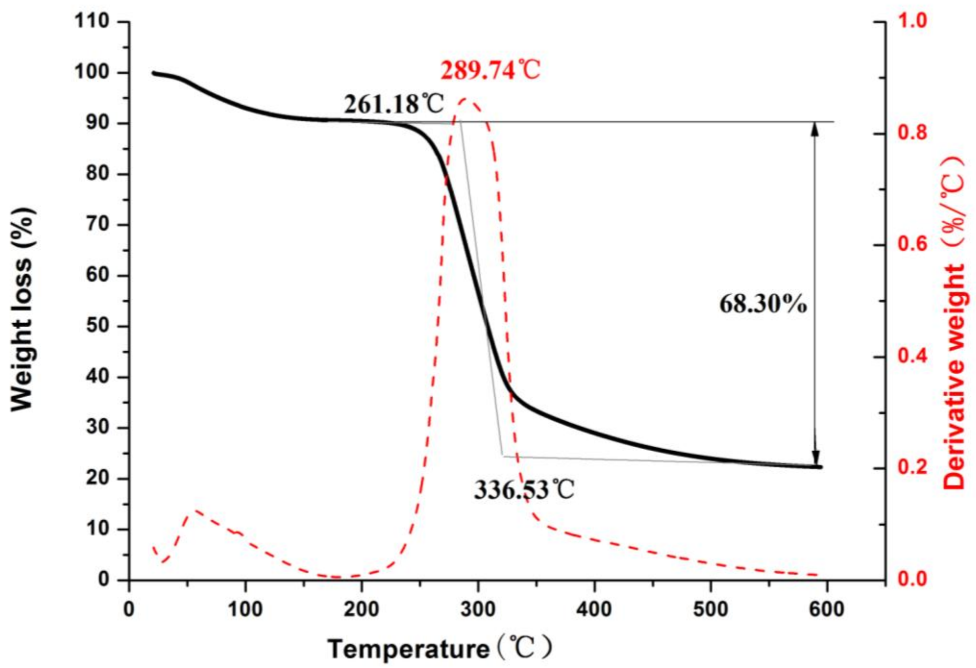


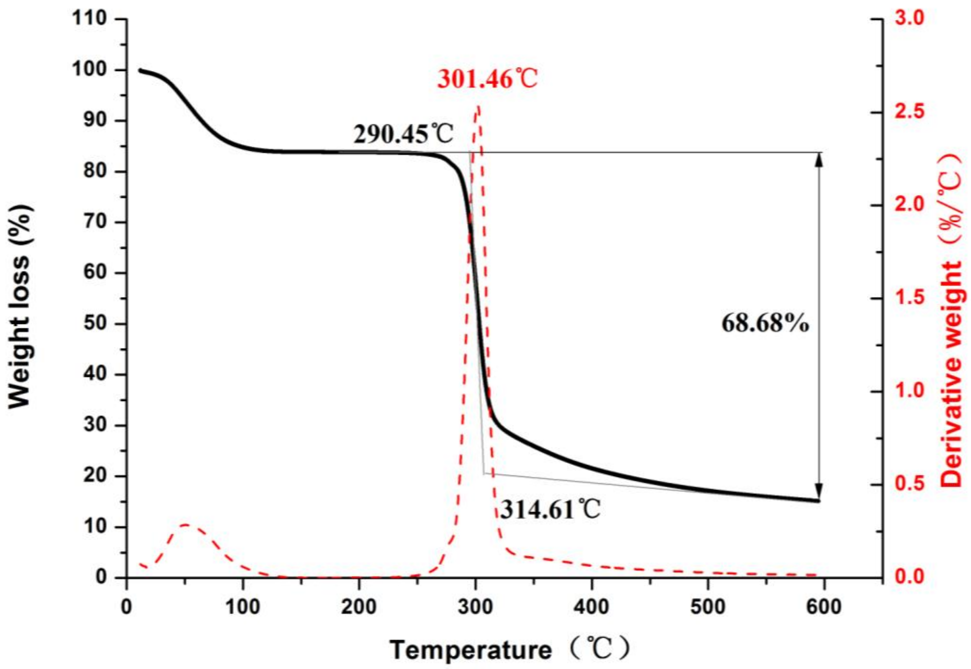
Fig. 5. SEM of Samples K0.5G0S1WS0.5 and K1S2 G0WS0 and SEM of Sample K1S2G0WS1.5 under different magnification 50X, 100X.

3.4 Thermogravimetric analysis

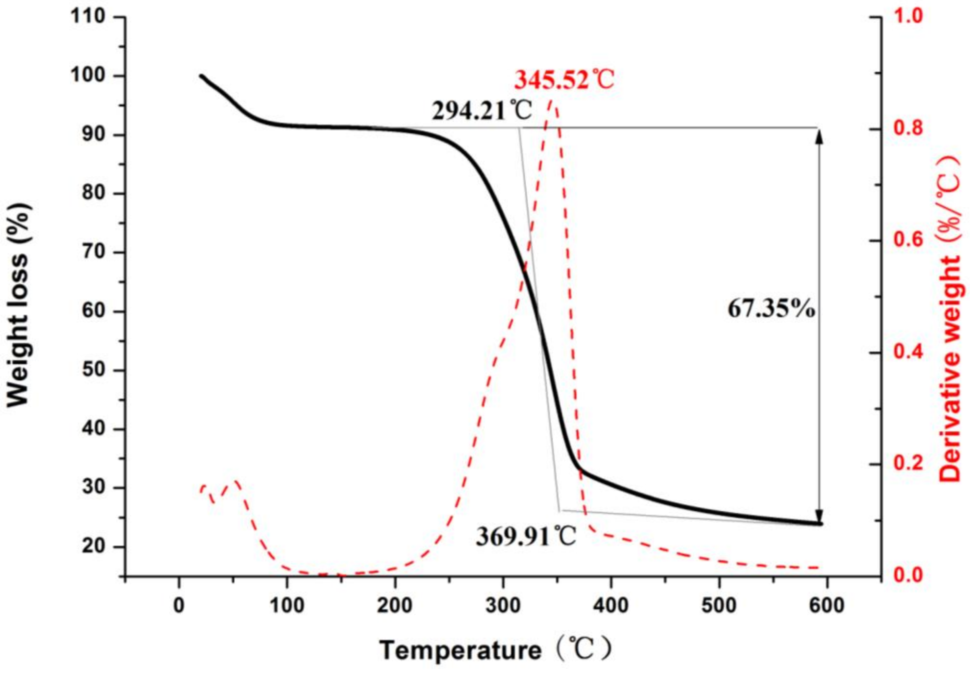
TG curves (**Fig. 6)** and detailed data in supplementary materials (**Table S1**) indicated that KGM/starch based aerogels were decomposed in two steps. The first stage of mass loss at around 100 °C in all samples corresponded to the dehydration, indicating some moisture was still present in samples. This may be caused by the porous structure and hydrophilic nature of KGM/starch based aerogels, which could adsorb moisture from the air. The second stage of mass loss should be accredited to the pyrolysis of polysaccharide and protein, reflecting thermal stability. All sample showed similar mass loss (≈68%) during the decomposition stage. As the framework material of aerogels, KGM had a decomposition temperature from 261.18 to 336.53 °C, lower than wheat straw, gelatin and starch. The mass loss stage for K1S2G0WS1.5 was from 272.62 to 344.38 °C, where around 70.90% weight was lost due to the degradation of the polysaccharide, protein and wheat straw. It can be seen that the thermal stability of KGM/starch based aerogel was between the properties of four pure components. At 302.98 °C, K1S2G0WS1.5 had the maximum thermal decomposition rate.



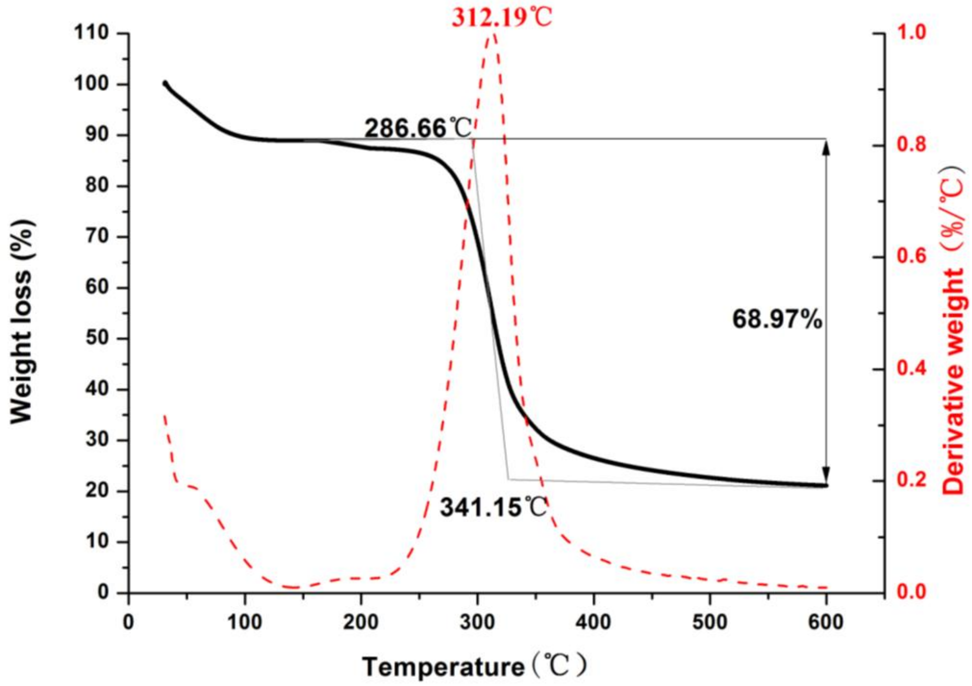
(a) KGM



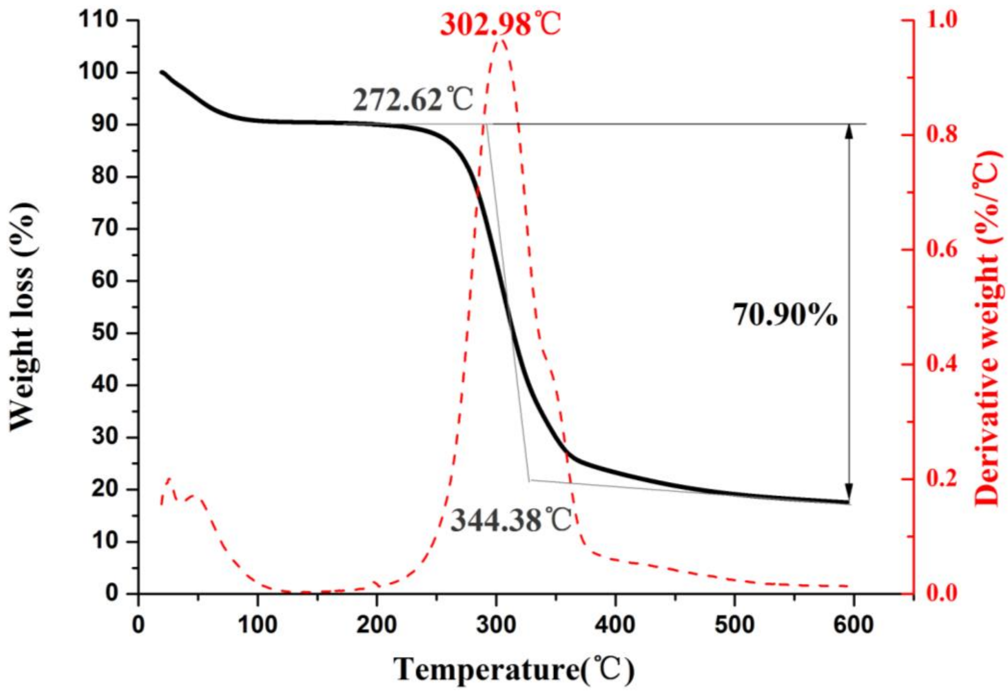
(b) Starch



(c) Wheat straw



(d) Gelatin



(e) K1S2G0WS1.5

Fig. 6. TGA of pure raw materials and KGM/starch based aerogel

4. Conclusions

KGM/starch based aerogels have been prepared via a convenient, energy-efficiency freeze drying method. The thermal conductivity of KGM/starch based aerogels has been determined to be 0.046-0.053 $Wm^{-1}K^{-1}$. The optimized KGM/starch based aerogel sample for thermal insulation was determined to be K1S2G0.5WS2, with its thermal conductivity 0.04641$Wm^{-1}K^{-1}$, density 0.043g/cm^{-3}, porosity 94.50±0.0291%, compressive strength 80.5kPa and elasticity 0.273. The effect of different aerogel components and their concentration on the mechanical property, porosity, density, insulation property, thermal stability, pore size distribution and structure of aerogels has been investigated. Starch can influence mechanical property, pore size, and pore wall thickness of aerogels. Wheat straw can strengthen the thermal insulation property of KGM/starch based aerogels due to the special cavity structure of wheat straw affecting aerogel pore structure and decreasing pore size. Small amount of gelatin addition is necessary to prevent wheat straw subsiding during aerogel preparation and can also improve thermal insulation property. Thermal decomposition properties of KGM/starch based aerogels fall between the values of their raw materials. This study presents a way to manufacture aerogel from natural polysaccharide materials with a satisfactory thermal insulation property.

Acknowledgement

This work is financially supported by the European Commission for the MARIE SKŁODOWSKA-CURIE individual Fellowship grant (project ID: 794680), National Natural Science Foundation of China (Grant No. 31671827) and the technology support program of Hubei Science and Technology Department (No. 2016ACA164)

References

Beck, A., Heinemann, U., Reidinger, M., & Fricke, J. (2004). Thermal transport in straw insulation. *Journal of Building Physics*, 27(27), 227-234.

Chang, X., Chen, D., & Jiao, X. (2010). Starch-derived carbon aerogels with high-performance for sorption of cationic dyes. *Polymer*, 51(16), 3801-3807.

Chen, X., Kuang, Y., Xiao, M., Wu, K., Yan, W., Jiang, F., & Huang, J. (2017). Study on adsorption of plant polysaccharide aerogels. *Science and Technology of Food Industry*, 38(11).

Corobea, M. C., Muhulet, O., Miculescu, F., Antoniac, I. V., Vuluga, Z., Florea, D., . . . Voicu, S. I. (2016). Novel nanocomposite membranes from cellulose acetate and clay‐silica nanowires. *Polymers for Advanced Technologies*, 27(12), 1586-1595.

Crosby, G. (2002). Managing healthy levels of blood glucose and cholesterol with konjac flour. *Special Publication- Roal Society of Chemistry*, 278, 338-341.

Davé, V., & McCarthy, S. P. (1997). Review of konjac glucomannan. *Journal of environmental polymer degradation*, 5(4), 237.

Francl, J., & Kingery, W. D. (1954). Thermal Conductivity: IX, Experimental investigation of effect of porosity on thermal conductivity. *Journal of the American Ceramic Society*, 37(2), 99-107.

García-González, C. A., Uy, J. J., Alnaief, M., & Smirnova, I. (2012). Preparation of tailor-made starch-based aerogel microspheres by the emulsion-gelation method. *Carbohydrate Polymers*, 88(4), 1378-1386.

Gustafsson, S. E. (1991). Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials. *Review of Scientific Instruments*, 62(3), 797-804.

He, F., Sui, C., He, X., & Li, M. (2015). Facile synthesis of strong alumina–cellulose aerogels by a freeze-drying method. *Materials Letters*, 152, 9-12.

Janik, H., Sienkiewicz, M., & Kucinska-Lipka, J. (2014). *9 - Polyurethanes*. In *Handbook of thermoset plastics (Third Edition)* (pp. 253-295). Boston: William Andrew Publishing

Jiang, F. (2013). Plant polysaccharide cigarette filter tip and preparation method thereof. (Pattern NO. 102423132). CN.

Ke, S., Wang, L., Wang, J., Wang, Y. T., Wang, Y. Z., & Schiraldi, D. A. (2016). Non-flammable alginate nanocomposite aerogels prepared by a simple freeze drying and post-crosslinking method. *ACS Applied Materials & Interfaces*, 8(1), 643.

Kenar, J. A., Eller, F. J., Felker, F. C., Jackson, M. A., & Fanta, G. F. (2014). Starch aerogel beads obtained from inclusion complexes prepared from high amylose starch and sodium palmitate. *Green Chemistry*, 16(4), 1921-1930.

Kiani, H., & Sun, D. W. (2011). Water crystallization and its importance to freezing of foods: A review. *Trends in Food Science & Technology*, 22(8), 407-426.

Kistler, S. S. (1931). Coherent expanded aerogels and jellies. *Nature*, 127, 741.

Lee, O. J., Lee, K. H., Yim, T. J., Sun, Y. K., & Yoo, K. P. (2002). Determination of mesopore size of aerogels from thermal conductivity measurements. *Journal of Non-Crystalline Solids*, 298(2–3), 287-292.

Lee, S., & Cunnington, G. R. (2012). Conduction and radiation heat transfer in high-porosity fiber thermal insulation. *Journal of Thermophysics & Heat Transfer*, 14(2), 121-136.

Liu, X., & Ma, P. X. (2009). Phase separation, pore structure, and properties of nanofibrous gelatin scaffolds. *Biomaterials*, 30(25), 4094.

Lu, X., Caps, R., Fricke, J., Alviso, C. T., & Pekala, R. W. (1995). Correlation between structure and thermal conductivity of organic aerogels. *Journal of Non-Crystalline Solids*, 188(3), 226-234.

Miculescu, F., Maidaniuc, A., Voicu, S. I., Thakur, V. K., Stan, G. E., & Ciocan, L. T. (2017). Progress in Hydroxyapatite–Starch Based Sustainable Biomaterials for Biomedical Bone Substitution Applications. *ACS Sustainable Chemistry & Engineering*, 5(10).

Mikkonen, K. S., Parikka, K., Ghafar, A., & Tenkanen, M. (2013). Prospects of polysaccharide aerogels as modern advanced food materials. *Trends in Food Science & Technology*, 34(2), 124-136.

Nemoto, J., Saito, T., & Isogai, A. (2015). Simple freeze-drying procedure for producing nanocellulose aerogel-containing, high-performance air filters. *Acs Applied Materials & Interfaces*, 7(35), 19809-19815.

Ni, X., Ke, F., Xiao, M., Wu, K., Kuang, Y., Corke, H., & Jiang, F. (2016). The control of ice crystal growth and effect on porous structure of konjac glucomannan-based aerogels. *International Journal of Biological Macromolecules*, 92, 1130-1135.

Palumbo, M., Avellaneda, J., & Lacasta, A. M. (2015). Availability of crop by-products in Spain: New raw materials for natural thermal insulation. *Resources Conservation & Recycling*, 99, 1-6.

Ramírez-Villegas, R., Eriksson, O., & Olofsson, T. (2016). Assessment of renovation measures for a dwelling area – Impacts on energy efficiency and building certification. *Building and Environment*, 97, 26-33.

Randall, J. P., Meador, M. A., & Jana, S. C. (2011). Tailoring mechanical properties of aerogels for aerospace applications. *ACS Applied Materials & Interfaces*, 3(3), 613.

Robitzer, M., Renzo, F. D., & Quignard, F. (2011). Natural materials with high surface area. Physisorption methods for the characterization of the texture and surface of polysaccharide aerogels. *Microporous & Mesoporous Materials*, 140(1–3), 9-16.

Sabri, F., Marchetta, J. G., Faysal, K. M. R., Brock, A., & Roan, E. (2014). Effect of aerogel aarticle concentration on mechanical behavior of impregnated RTV 655 compound material for aerospace applications. *Advances in Materials Science & Engineering*, 2014(14).

Septevani, A. A., Evans, D. A. C., Chaleat, C., Martin, D. J., & Annamalai, P. K. (2015). A systematic study substituting polyether polyol with palm kernel oil based polyester polyol in rigid polyurethane foam. *Industrial Crops and*

Products, 66, 16-26.
Shi, J., Lu, L., Guo, W., Zhang, J., & Cao, Y. (2013). Heat insulation performance, mechanics and hydrophobic modification of cellulose–SiO2 composite aerogels. *Carbohydrate Polymers*, 98(1), 282-289.
Thakur, V. K., & Voicu, S. I. (2016). Recent advances in cellulose and chitosan based membranes for water purification: A concise review. *Carbohydrate Polymers*, 146, 148-165.
Wang, J., Zhao, D., Shang, K., Wang, Y. T., Ye, D. D., Kang, A. H., Wang, Y. Z. (2016). Ultrasoft gelatin aerogels for oil contaminant removal. *Journal of Materials Chemistry A*, 4(24).
Wang, T., Sun, H., Long, J., Wang, Y., & Schiraldi, D. A. (2016). Biobased poly(furfuryl alcohol)/clay aerogel composite prepared by a freeze drying process. *Acs Sustainable Chemistry & Engineering*, 4(5).
Wang, X., Zhong, J., Wang, Y., & Yu, M. (2006). A study of the properties of carbon foam reinforced by clay. *Carbon*, 44(8), 1560-1564.
Wang, Y., Alhassan, S. M., Yang, V. H., & Schiraldi, D. A. (2013). Polyether-block-amide copolymer/clay films prepared via a freeze-drying method. *Composites Part B: Engineering*, 45(1), 625-630.
Wang, Y., Chen, X., Kuang, Y., Jiang, F., & Yan, W. (2017). Progress in application of polysaccharide aerogels. *Journal of Wuhan Institue of Technology*, 39(5), 443-449.
Wang, Y., Chen, X., Kuang, Y., Xiao, M., Su, Y., & Jiang, F. (2017). Microstructure and filtration performance of konjac glucomannan-based aerogels strengthened by wheat straw. *International Journal of Low-Carbon Technologies*.

Supplementary data
Click here to download Supplementary data: Supplementary material.docx

Graphical Abstract

Click here to download high resolution image