Study on Microstructures of Complex Plant Polysaccharides Aerogels and Their Effects on Porosity

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Abstract—The microstructure of polysaccharide aerogels is a key factor affecting porosity, and directly determines the efficiency of its application as filter rod material. Scanning electron microscopy was used to observe the effects of different amounts of starch on the microstructure of the complex plant polysaccharide aerogels. The experimental results showed that the aerogel samples showed a complete and homogeneous three-dimensional network structure. With the increase of starch content, the pore size became smaller and the pore structure on the hole wall became smaller. After adding starch, the concentration of the system increased, that is, the solute in the unit volume increased, the moisture content decreased, and the air replaced the water in the gel after freeze drying, resulting in the increase of the density of the aerogel and the decrease of porosity. All aerogels showed a trend of increasing filtration efficiency with increasing particle size. The filtration performance of aerogels with different starch content was tested by using the comprehensive performance test bed of filter media. The test results showed that the capture of filter material was mainly through inertial collision. When the particle size was bigger, the greater the inertia, the greater the possibility of particle contamination being captured, so the higher the filtration efficiency.

1. INTRODUCTION
Aerogel is a kind of material with high specific surface area, high porosity and light weight[1,2]. It is widely used in packaging materials, thermal insulation materials, adsorption materials and other fields[3]. The source of plant polysaccharides is extensive, degradable and harmless to human body. It is an ideal material for preparing aerogels. Raw materials include cellulose, hemicellulose, starch and so on[4,5].

The plant polysaccharide aerogel not only has the characteristics of gas gel, light porous, high specific surface area and low density, but also has biodegradability and special chemical functions[6,7]. When used as adsorption material, plant polysaccharide aerogel avoids the disadvantages of traditional adsorbent, such as high cost, unfriendly environment and limited source, and also has good adsorption effect because of its microstructure.
2. EXPERIMENTAL
Jsm6390lv scanning electron microscope (SEM) of Japan Electronics Co., Ltd. was used to observe the micro morphology of the filter rod before and after degradation, and to investigate the damage of biodegradation on the micro structure of the filter rod. The dry filter rods before and after degradation were cut into small pieces with the length × width × height of 5 × 5 × 1 mm with stainless steel blades, then fixed on the stainless steel round table sample table with conductive adhesive, sprayed gold on the surface of the sample under the protection of argon to make it have the conductivity, and then the microstructure of the filter rods was observed with scanning electron microscope under the accelerating voltage of 5 kV.

The porosity of aerogels was measured by drainage method, as shown in Fig. 1. N-hexane as the test liquid was applied, and the aerogel sample was immersed in the hexane as volume \( V_1 \) for 5 min, the volume of aerogel impregnated with hexane + hexane was \( V_2 \), the aerogels impregnated with hexane were removed, the remaining hexane volume was \( V_3 \). Each test was repeated for 5 times, and the porosity was calculated by the following formula:

\[
\varepsilon (%) = \frac{(V_1 - V_3)}{(V_2 - V_3)} \times 100
\]

![Figure 1. Schematic diagram for determining porosity of aerogel by drainage method](image)

3. RESULTS & DISCUSSIONS
The SEM images of magnifying 50 times and magnifying 200 times were shown in Figure 2. It can be seen from the diagram that all aerogel samples present a complete and homogeneous three-dimensional network structure. When the initial content of KGM is the same as that of gelatin, the microstructure of aerogels will change with the addition of starch. In particular, with the increase of starch content, the pore size becomes smaller and the pore structure on the hole wall becomes smaller. When the starch content is 2-4%, the pore size is smaller, also the distribution is more uniform and the structure is more compact. This is because KGM, gelatin and starch molecular chains are hydrated and interpenetrated respectively in the system. In the process of freezing, the growth of ice crystal will squeeze solute molecules into the gap of ice crystal, and form a film outside the ice crystal. When the concentration is higher, the thicker the film is, the more complete the film is, the smaller the ice crystal is, and the hole wall left after freeze-drying is more complete.

| No.  | Density(g/cm³) | Porosity(%) |
|------|---------------|-------------|
| K1G2S0 | 0.0350 ± 0.0007 | 97.96 ± 4.087 |
| K1G2S1 | 0.0467 ± 0.0021 | 94.15 ± 1.521 |
| K1G2S2 | 0.0589 ± 0.0014 | 84.85 ± 0.818 |
| K1G2S3 | 0.0696 ± 0.0041 | 68.95 ± 1.618 |
| K1G2S4 | 0.0789 ± 0.0004 | 57.05 ± 3.475 |

Porosity directly reflects the space occupation volume ratio of materials, indicating the compactness of materials. High porosity means low density. It can be seen from Table 1 that with the increase of starch content, the density of the material increases, from 0.035 to 0.0789 g/cm³, and the porosity of the gels decreases significantly at this time. This is because after adding starch, the concentration of the
system increases. The solute in the unit volume increases, and the moisture decreases. After freeze drying, the air takes the place of the water in the gel, resulting in the increase of the density of the aerogels and the decrease of porosity. This is consistent with the picture of SEM.

Figure 2. SEM picture of KGM/ gelatin / starch composite plant polysaccharide aerogel, (a, A) K1G2, (b, B) K1G2S1, (c, C) K1G2S2, (d, D) K1G2S3, (e, E) K1G2S4
Figure 3. (a) the filtration efficiency of composite aerogels for different particle sizes under different starch dosage; (b) filtration efficiency and filtration resistance of composite aerogels for 0.3 μm and above particles.

The filtration experimental results are shown in Figure 3. As shown in Fig. 3.a, all aerogels showed a trend of increasing filtration efficiency with increasing particle size. This is because when particle diameter of particles larger than 0.3μm is passed through filtration material, the capture of filter material is mainly through inertial collision. When the particle size is bigger, the greater the inertia, the greater the possibility of particle contamination being captured, so the higher the filtration efficiency. Figure 3.b shows the filtration efficiency and filtration resistance of aerogels for particulate matter of 0.3μm and above. It can be seen that with the increase of starch content from 0% to 4%, the filtration efficiency of aerogels for particulate matter also increases, but at the same time, filtration resistance also shows a significant upward trend. When the starch content is 1%, 2% and 3%, the filtration efficiency of aerogels is 49%, 59% and 77.97% respectively, and the drag resistance is 56 Pa, 116 Pa and 896 Pa respectively. When the starch content is 4%, the aerogel filtration efficiency is as high as 97.32%, and at this time the filtration resistance reaches the maximum, and the resistance value approaches the Pa. This is because when the starch content increases, the overall concentration of the system increases, the solute content in the unit volume increases, the pore size becomes smaller after freeze-drying, and the pore structure on the pore wall becomes smaller, which is consistent with the results of SEM and porosity test. When it is used for air filtration, the direct interception effect on particles is stronger, so the efficiency is higher, but at the same time, it also causes more obstacles to gas passing through, so that the filtration resistance is higher.

According to the above experimental results, it is considered that as a cigarette filter rod, suction resistance is an important index. When the starch content is 2%, the aerogel has less resistance, only 116 Pa, and has a 59% filtration efficiency, a porosity of 84.85%, a smaller pore size, a more uniform
distribution, a denser structure, and a certain compressive strength and elasticity. Cigarette filter material.

4. CONCLUSIONS
Aerogel samples showed a complete and homogeneous three-dimensional network structure. When the initial content of KGM is the same as that of gelatin, the microstructure of aerogels will change with the addition of starch. In particular, with the increase of starch content, the pore size becomes smaller and the pore structure on the hole wall becomes smaller. When the starch content is 2-4%, the pore size is smaller, the distribution is more uniform and the structure is more compact. Aerogels showed increased filtration efficiency with increasing particle size. The pore size is small, the distribution is uniform, the structure is compact, and has certain compressive strength and elasticity, the comprehensive performance is superior, so it is suitable for cigarette filter rod material.

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REFERENCES
[1] Siracusa, V., Rocculi, P., Romani, S., et al. Trends in Food Sci. Tech., Vol. 19(2008), p.634
[2] Deng L., Kang X., Liu Y., et al. Food Hydrocolloids, Vol. 74(2018), p.324
[3] Wei X., Pang J., Zhang C., et al. Carbohydrate Polymers, Vol. 118(2015), p.119
[4] Wu K., Zhu Q., Qian H., et al. Food Hydrocolloids, Vol.79(2018), p.301
[5] Ni X., Chen W., Xiao M., et al. Inter. J. Bio. Macromolecules, Vol.92 (2016), p.423
[6] Xiao M., Wan L., Corke H., et al. Inter. J. Bio. Macromolecules, Vol.92 (2016), p.434
[7] Wang H., Zheng H., Zhan J.B., et al. (2019) IOP Conf. Ser.: Earth Environ. Sci., 310 032037
[8] Si X P, Zhang S J, Chen Y, et al. The Research Development of Cellulose Acetate Fiber and Cellulose Acetate Nanofiber Used as Filtering Materials[J]. Key Engineering Materials, 2015, 671: 279-284.
[9] Chattopadhyay S, Hatton T A, Rutledge G C. Aerosol filtration using electrospun cellulose acetate fibers[J]. Journal of Materials Science, 2016, 51(1): 204-217.
[10] Kulkarni P S, Patel S U, Patel S U, et al. Coalescence filtration performance of blended microglass and electrospun polypropylene fiber filter media[J]. Separation & Purification Technology, 2014, 124:1-8.
[11] Ma L C, Wang J N, Li L, et al. Preparation of PET/CTS Antibacterial Composites Nanofiber Membranes Used for Air Filter by Electrospinning[J]. Acta Polymerica Sinica, 2015(2): 221-227.
[12] Jiang Z, Wang X, Lv L H, et al. Immobilization of Hydroxyapatite Particles onto PET Filter Fabric via Heat Treatment[J]. Materials Science Forum, 2015, 814: 483-487.
[13] Brancher M, Franco D, De M L H.Photocatalytic Oxidation of H2S in gas phase over TiO2-coated glass fiber filter[J]. Environmental Technology, 2016, 37(22): 1-37.
[14] Okada T, Shimizu K, Yamakami T. An inorganic anionic polymer filter disc: direct crystallization of a layered silicate nanosheet on a glass fiber filter[J]. Rsc Advances, 2016, 6(31): 26130-26136.
[15] Gallego E, Roca F J, Perales J F, et al. Experimental evaluation of VOC removal efficiency of a coconut shell activated carbon filter for indoor air quality enhancement[J]. Building & Environment, 2013, 67(3): 14-25.
[16] Lim T H, Choi J R, Lim D Y, et al. Preparation of fiber based binder materials to enhance the gas adsorption efficiency of carbon air filter[J]. Journal of Nanoscience & Nanotechnology, 2015, 15(10): 8034-8041.
[17] Liang J, Cai Z, Li L, et al. Scalable and facile preparation of graphene aerogel for air purification[J]. Rsc Advances, 2014, 4(10):4843-4847.
[18] Xiong X, Ji N, Song C, et al. Preparation functionalized graphene aerogels as air cleaner filter[J]. Procedia Engineering, 2015, 121: 957-960.
[19] Rao H, Zhang Z, Tian Y. Preparation and high oxygen-enriching properties of cross-linking PDMS / Si O2 nanocomposite membranes for air purification[J]. Aiche Journal, 2013, 59(2): 650-655.
[20] Chin S F, Binti Romainor A N, Pang S C. Fabrication of hydrophobic and magnetic cellulose aerogel with high oil absorption capacity[J]. Materials Letters, 2014, 115: 241-243.
[21] Shi J, Lu L, Guo W, et al. On preparation, structure and performance of high porosity bulk cellulose aerogel[J]. Plastics Rubber & Composites, 2015, 44(1): 26-32.
[22] Bao M X, Xu S, Wang X, et al. Porous cellulose aerogels with high mechanical performance and their absorption behaviors[J]. Bioresources, 2016, 11(1): 8-20.
[23] García-González C A, Uy J J, Alnaief M, et al. Preparation of tailor-made starch-based aerogel microspheres by the emulsion-gelation method[J]. Carbohydrate Polymers, 2012, 88(4):1378-1386.
[24] Wang Z, Huang Y, Wang M, et al. Macroporous calcium alginate aerogel as sorbent for Pb2+ removal from water media[J]. Journal of Environmental Chemical Engineering, 2016, 4(3):3185-3192.