

Dissolution and Regeneration of Cellulose and Chitosan in Molten Salt Hydrate

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Abstract. The energy and environmental problems caused by current fossil resources are becoming more and more serious, and the development of renewable and sustainable materials has become a research hotspot. Chitosan and cellulose, as the two most abundant biomasses in nature, have the advantages of being non-toxic, harmless, and environmentally friendly. However, due to their high crystallinity, it is difficult to dissolve in water and common organic solvents. Molten salt hydrate has been discovered as a cost-effective and non-derivative solvent system for dissolving biomass. In this paper, the dissolution and regeneration of microcrystalline cellulose and chitosan in the molten salt system to prepare gel materials is investigated using lithium bromide molten salt as an example. First dissolve cellulose and chitosan, the total mass is unchanged according to the mixing ratio of the two are divided into multiple groups, dissolved in a mass fraction of 60% lithium bromide solution at 140°C into a hydrogel, gradient regeneration in water-ethanol-tert-butanol, to produce aerogel composites, the molten salt rotary evaporation back to use. Characterization tests show that the material has uniform distribution of nanoscale pores, pore size of about 50nm, porosity of 97.53%, strain 50% range can withstand up to 0.4MPa. 6mm thickness of the sample can be insulated at 150°C for up to 2h or more, the degree of adsorption of 2500mg/L copper sulfate solution reaches 22115.4mg/g. It has excellent thermal insulation and adsorption performance and has a wide range of application prospects in environmental protection, biomedical and other fields.

Keywords: Cellulose; chitosan; molten salt hydrate; lithium bromide; composite materials.

1. Introduction

Cellulose is a macromolecular polysaccharide whose molecular chain is composed of a single D-glucose unit through a β -1,4-glycosidic bond. Cellulose is the main component of plant cell wall, which widely exists in nature, and through photosynthesis can produce more than one hundred billion tons of natural cellulose per year [1]. Chitosan is another biomass obtained by N-deacetylation of chitin and is the only naturally positively charged alkaline polysaccharide in nature. Although cellulose has the advantages of easy degradation and high strength, it has poor antimicrobial properties and low adsorption. Chitosan is well known for its excellent antibacterial properties and its heavy metal adsorption ability, but it has the disadvantages of poor mechanical strength. The development of hybrid materials can synthesize the advantages making the material performance more superior and more widely used. However, due to the strong hydrogen bonding network structure, both are difficult to dissolve in water and general organic solvents therefore the search for efficient co-solvent system has become the key [2].

Chitosan is structurally similar to cellulose, and both have good affinity, which provides a basis for the preparation of their mixtures. The size of the components is reduced by physical means such as grinding, shaking and centrifugation, and the well-mixed product is of high purity and relatively simple to post-treat. The mechanical properties of cellulose chitosan composites prepared by this method are greatly enhanced and are good bio-tissue materials and bio-fillers [3]. Aerogels, hydrogels, membranes and fibers can be developed by chemical method. Chitosan coatings, films or nanoparticles are prepared on cellulose matrices, and the products prepared can be used in packaging, chemical and medical applications with good biocompatibility and antimicrobial properties [4].

The concept of molten salt hydrates (MSHs) was first defined as a solution in which the molar ratio of water to salt in the system is close to the maximum hydrated cation coordination number by German scientists Steffen Fischer and Heike Leipner in 2000 [5]. Molten salt hydrates have become

an excellent performing biomass solvent system due to a variety of excellent physicochemical properties such as stable performance, no structural deformation at high temperatures, low vapor pressure and low viscosity. The recovery of inorganic salts, the main component of molten salt hydrates, is simple and can be achieved by evaporation and concentration of water for recycling and reuse. Some molten salt hydrates have been discovered to dissolve cellulose, such as $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{ZnBr}_2 \cdot 4\text{H}_2\text{O}$, and $\text{LiI} \cdot 2\text{H}_2\text{O}$. Comparative studies by scholars have found that the solubility of several typical molten salts on cellulose varies greatly, such as ZnCl_2 solution mass fraction of 65% or more to have a solubility effect on cellulose and zinc chloride tetrahydrate solution at 80°C cellulose solubility is very low (<5 wt.%) [6]; $\text{ZnBr}_2 \cdot 4\text{H}_2\text{O}$ dissolution ability is stronger than that of zinc chloride at 80°C can be dissolved for 10min to significantly reduce the cellulose polymerization [7].

Recent studies have shown that the trihydrate lithium bromide molten salt can dissolve polysaccharides at moderate temperatures. Li^+ is a small-sized, strongly polarized cation. At elevated temperatures the unsaturated coordinated lithium cation acts through electrostatic forces on the oxygen in the hydroxyl groups of cellulose to reconnect, destroying the inter- and intramolecular hydrogen bonding of cellulose, causing the dense crystalline structure of cellulose to be disrupted, which leads to cellulose wetting and solubilization [8]. The free bromide anion interacts with the hydrogen in the hydroxyl group and reduces the ability to reconstruct the hydrogen bonds between cellulose molecular chains. Some of the lithium cation hydration spheres penetrate the crystalline zone region of cellulose and promote the separation of cellulose molecular chains. When the cellulose solution in the Lithium bromide system is cooled to room temperature, a shape-fixed hydrogel is formed. LiBr is recycled by washing and the hydrogel is dried to obtain a regenerated cellulose aerogel [9]. However, the understanding of the process of cellulose regeneration from molten salt hydrates is still lacking. Therefore, a comprehensive study of the effect of regeneration solvents on the structure and properties of regenerated cellulose in lithium bromide trihydrate molten salts is essential.

2. Materials and Methods

2.1. Materials

All chemicals were of the highest purity available and were used without further purification. Microcrystalline cellulose with average particle size 50 μm and lithium bromide ($\geq 99\%$, w/w) were purchased from Aladdin Biochemical Technology (Shanghai, China). Chitosan ($\text{DD} \geq 95\%$), absolute ethanol (AR) and tert-butanol (AR) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Deionized (DI) water was used for all experiments.

2.2. Dissolution and regeneration process

Preparation of lithium bromide molten salt solution: Firstly, weigh the lithium bromide salt with the mass ratio of 3:2, deionized water was placed in a glass bottle, and then it was mechanically stirred continuously for 10 minutes at room temperature to obtain the clarified and transparent lithium bromide molten salt solution, and finally the prepared molten salt solution was sealed and stored for spare.

Cellulose and chitosan mixed dissolution: weighing the total mass of 1g, which microcrystalline cellulose and chitosan mass ratio of 10:0, 9:1, 8:2, 7:3, etc. of the solid to add 100 g mass fraction of 60% of the lithium bromide molten salt solution placed in a beaker, heated and stirred in a 140 °C oil bath for 20 min to get a clear and transparent solution. Pour into the mold while hot and ultrasonic discharge of air bubbles, the gel is rapidly molded at room temperature to obtain hydrogel.

Regeneration of cellulose mixed with chitosan: Water, ethanol and tert-butanol were selected as the regeneration solvents, and all regeneration solvents were used directly without further treatment. The obtained hydrogel was transferred into a beaker and the regeneration solvents were added sequentially, and the regenerated cellulose was filtered and washed until the conductivity of the filtrate was lower than 20 $\mu\text{S}/\text{cm}$. The purified regenerated cellulose was collected in a sealed bag and

then placed in the refrigerator for freezing. The freeze-dried aerogel was tested for properties and the molten salt was spun and reused.

3. Results and Discussion

3.1. Structural Characterization

Microcrystalline cellulose is a kind of white powder, chitosan raw material is a light-yellow powder, the configuration of the mass fraction of 60% of the lithium bromide molten salt solution is clarified and transparent, and the dissolution is carried out by heating in an oil bath at 140°C and kept at this temperature for 20 min until complete dissolution, followed by the formation of a clarified and transparent light-yellow solution. Poured into a cylindrical plastic tube mold, the solution solidified rapidly. It was found that with the increase of the proportion of chitosan, the gel molding time was substantially prolonged, and the molded hydrogel became soft and friable, and the yield was substantially reduced. It was also found that when only 1% (i.e., 1 g) of chitosan was added, it could not be completely dissolved, and bubbles still appeared in the solution. The regenerated hydrogel was put into the refrigerator to freeze and harden, and then put into the freeze dryer, with the increase of chitosan, the color of the aerogel tended to become yellow. The aerogels obtained were weighed and the yield, density and porosity were calculated shown in Table 1.

Table 1. Basic parameters of aerogel with different proportions

Sample/MCC:CS	Yield/%	Density/g·cm ⁻³	Porosity/%
10:0	73.8	0.04835	96.78
9:1	71.9	0.03760	97.37
8:2	94.0	0.03368	97.53
7:3	86.9	0.05440	95.83
4:6	57.3	0.10485	90.91

The microscopic morphology of microcrystalline cellulose and chitosan after dissolution and regeneration in molten lithium bromide was captured under scanning electron microscope (Fig. 1). Compared with the typical fibrous rough fiber surface structure exhibited by the raw materials, the regenerated aerogel materials all lost the original fibrous appearance and showed a brand-new microstructure, and the regenerated aerogel materials could be seen more obvious nanostructures. Taking the cellulose to chitosan mass ratio 8:2 sample as an example, the number of small pores on the gel surface can be seen to be large and dense under the 5μm scanning electron microscope and zoomed in at 1μm conditions found that the distribution of small pores is uniform. Microstructure photos taken at 500nm size, zoomed in on the local structure, and compared with the scale can be seen that the pore size reaches about 50nm, with a small pore size.

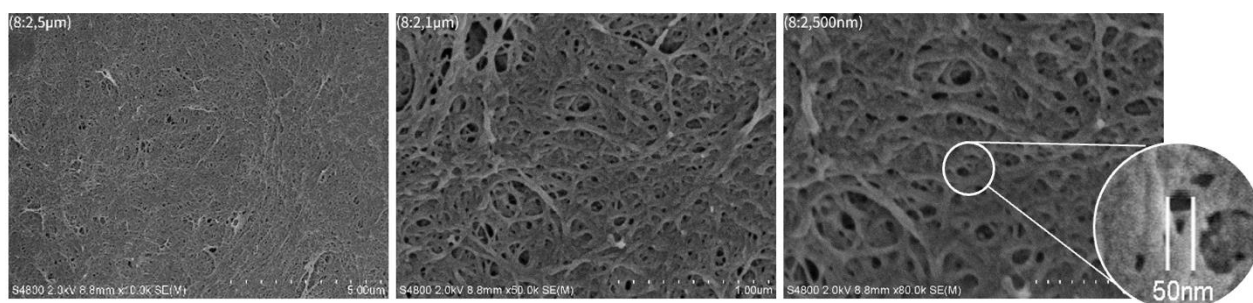


Fig. 1 5μm, 1 μm, 500 nm SEM image of aerogel materials (Picture credit: Original)

The infrared spectra of the regenerated materials with different ratios of microcrystalline cellulose and chitosan were examined by infrared analysis, and according to the resultant graphs, the infrared spectra of several ratios of regenerated aerogel materials did not produce new absorption peaks, which

indicates that no derivatization reaction occurred and no intermediate polymers were generated in the process of regeneration of two biomasses from dissolution with the solvent of the lithium bromide molten salt solution. However, the infrared spectra of the regenerated cellulose still showed some differences compared with those of the raw material, which was due to the reconstruction of the cellulose and chitosan molecular chains after the dissolution and regeneration process, and the crystalline structure was also changed after the treatment with the lithium bromide molten salt. It is known from past experience that the characteristic absorption peaks of cellulose exist roughly at wave numbers of 3700 cm^{-1} , 2900 cm^{-1} , 1163 cm^{-1} , and 897 cm^{-1} (Fig. 2). The peaks near 2900 cm^{-1} represent saturated hydrocarbon single bond (C-H) stretching vibrations, the peaks near 1163 cm^{-1} indicate pyranose ring skeleton (C-O-C) stretching vibrations, and the peaks near 897 cm^{-1} are cellulose structure stretching vibrations. 1 near the peaks are characteristic peaks of the β -D-glucose group in the cellulose structure [10]. Among them, the most obvious difference is the hydroxyl group stretching vibration band located near the wave number of $3700\text{--}3000\text{ cm}^{-1}$. The hydroxyl absorption peaks of regenerated cellulose are all shifted towards higher wave numbers, which implies that the number of intermolecular hydrogen bonds between cellulose molecules decreases after cellulose dissolution and regeneration. The results of infrared spectroscopy showed that although the intensity of some of the absorption peaks of microcrystalline cellulose and chitosan decreased or shifted to a certain extent after regeneration by dissolution of the molten salt, the infrared spectra of the regenerated material samples were basically the same as those of the raw materials and no new functional groups were generated, which once again demonstrated that the lithium bromide molten salt is the non-derivatization solvent system for cellulose, and this solvent can retain the nature of the cellulose itself, and is more favorable for the future applications. This solvent can better retain the properties of cellulose itself, which is more favorable for future applications.

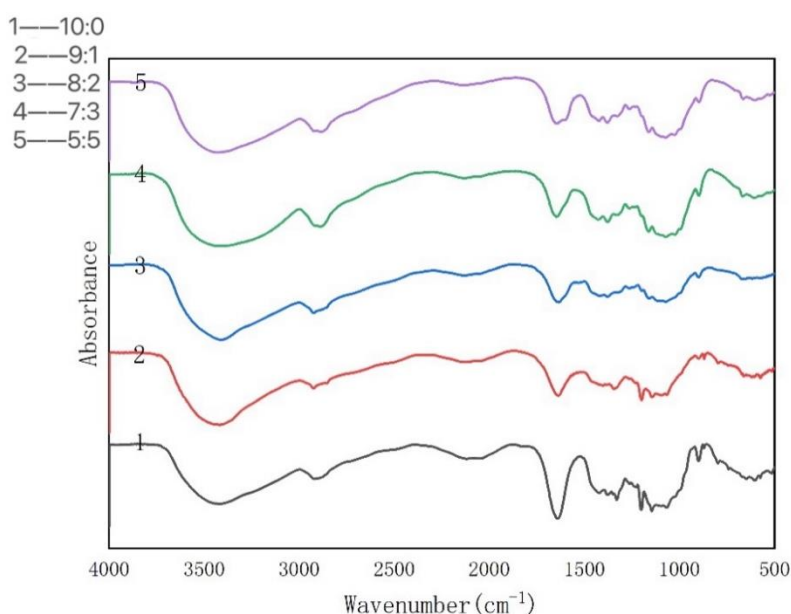


Fig. 2 Infrared spectra of aerogels mixed with different proportions (Picture credit: Original)

3.2. Mechanical Strength

From the molecular structure of chitosan, it can be seen that the six-membered rings in the main chain of chitosan molecule are difficult to undergo internal rotation and have a large number of intramolecular and intermolecular hydrogen bonding, extremely strong hydrogen bonding and structural characteristics have led to the rigidity of chitosan molecular chain is large. In this case, the strength of chitosan is still not high even though the C-atoms at 1,4 positions are connected by glycosidic bonds within the molecule. The mechanical strength of the blends was found to be somewhat improved by the addition of cellulose, as shown in Fig. 3, and the tests revealed that the mechanical strength was highest when the ratio of the two was 5:5. When the strain is 45%, it can

withstand the pressure up to 0.37 Mpa. cellulose obviously plays the role of reinforcing agent in this co-blended material, but the amount of cellulose added is not the only influencing factor, the mechanical strength of the material is also related to the contact area between cellulose and chitosan and the bonding situation. When the mass of cellulose was increased from 0.6 g to 0.7 g and the mass of chitosan was decreased from 0.4g to 0.3g, the actual contact area of the two did not increase, so the corresponding mechanical strengths measured by the two ratios did not have a large difference, and the curves obtained basically coincided. A continuous increase in the mass of cellulose would lead to a decrease in the infiltration effect of chitosan, a decrease in the bonding force at the interface, and a decreasing trend in strength [11].

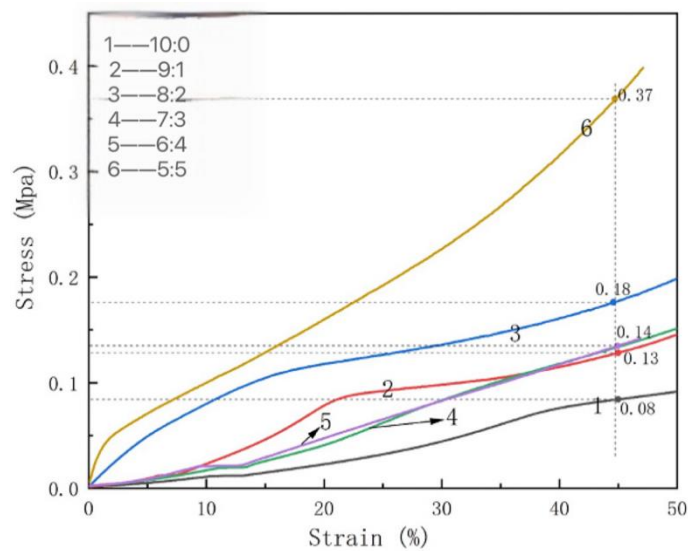


Fig. 3 Mechanical strength of aerogel materials (Picture credit: Original)

3.3. Thermal Insulation

The cellulose chitosan mixed aerogel material is placed on the heating plate at a constant temperature of 150 °C, and infrared photography is taken to get the temperature at the beginning and after 2 h as shown in the Fig. 4, according to the temperature bar, it can be seen that the temperature of the heating plate below the aerogel foam can reach 150 °C, but the temperature above the aerogel material can still be maintained at about 25 °C and the duration of the time can be up to 2 h and above. It can be concluded that because the aerogel reaches the nanostructure with small internal pore size and tight structure, which makes the heat not easy to be transferred, so the prepared material has excellent thermal insulation performance.

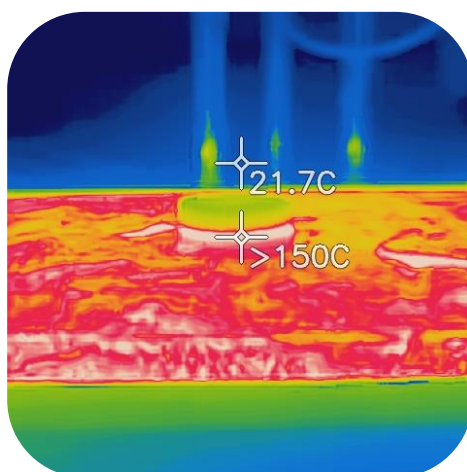


Fig. 4 Thermal image of aerogel on 150°C heating plate for 2h (Picture credit: Original)

3.4. Adsorption Capacity

Configure the concentration of 500 mg/L and 2500 mg/L copper sulfate solution, each concentration of the solution was taken 20mL in a beaker as a group, a total of two groups. Add pure microcrystalline cellulose aerogel and cellulose and chitosan ratio of 8:2 aerogel, respectively, heavy metal copper ion adsorption test, adsorption time of 24 h after each 10mL and diluted to 1ppm concentration below the use of ICP for the detection of the concentration of copper in the solution, the results obtained in Table 2, it can be seen that the addition of chitosan compared with the pure cellulose gel of the heavy metals in water copper ions have a more excellent adsorption effect.

Table 2. Part of aerogel adsorption capacity of heavy metal ion

Sample	Mass(g)	Conc.Cu ²⁺ /mg·L ⁻¹	Conc.Cu ²⁺ /mg·L ⁻¹ after 24h	Capacity/mg·g ⁻¹
MCC:CS	0.081	500	180.5	3944.4
10:0	0.124	2500	517.5	15987.9
MCC:CS	0.087	500	82.0	4804.6
8:2	0.091	2500	487.5	22115.4

As can be seen from the Table 2, the aerogel material mixed with chitosan compared to pure microcrystalline cellulose lyophilized aerogel for copper ion adsorption capacity has improved substantially, to the original 2500mg/L copper sulfate solution, for example, after adding chitosan, that is, 0.8g of cellulose and 0.2g of chitosan adsorption degree reached 22115.4mg/g is much larger than that of the material adsorption degree of only 1g of chitosan dissolution preparation. It can be proved that the material prepared by dissolving and regenerating cellulose and chitosan has a better adsorption capacity for heavy metals in water and can be applied in environmental protection scenarios such as water pollution treatment.

4. Conclusion

In this paper, the dissolution and regeneration behaviors of microcrystalline cellulose and chitosan in molten salt solvent systems, using lithium bromide molten salt as an example, are investigated. Fixing the total amount of cellulose and chitosan added for a certain amount, a series of gel materials mixed with different ratios were prepared by changing the proportional relationship between the two, and the materials were finally tested for relevant characterization. The following conclusions were obtained from the experiments:

- (1) The appearance of the gel material gradually turns yellow with the increase of chitosan content, and at the same time, the time consumed for gel molding is subsequently extended and soft.
- (2) The infrared spectra of the regenerated materials were generally consistent, except for a certain degree of downward shift in the intensity of some absorption peaks, suggesting that the lithium bromide molten salt is a non-derivatized solvent system for biomass dissolution.
- (3) Increasing cellulose content material mechanical properties are enhanced, but if the increase continues without a corresponding increase in chitosan, and can no longer be significantly enhanced on the contrary, there will be a decrease in strength phenomenon.
- (4) SEM images show that the regenerated gel internal pore size of only 50nm, and the distribution is more uniform, resulting in less easy to transfer heat, the gel has excellent thermal insulation properties.
- (5) Cellulose and chitosan mixed regeneration material for heavy metals in water has the ability to adsorb, to copper ions, for example, if the proportion of chitosan is increased to greatly improve the removal of heavy metals in the water for copper ions.

In this paper, only the dissolution regeneration of cellulose and chitosan mixed in lithium bromide molten salt solvent has been studied. It is determined that the material has excellent thermal insulation properties, can be used as aerospace thermal insulation materials; can adsorb heavy metal ions in water, in the direction of environmental protection and sewage treatment has significant application

prospects. However, further mass production and economic feasibility still need to be studied in the future. At the same time, the effects of different temperatures and pH on the dissolution and regeneration behavior of biomass can also be explored, and a comparison can be made to obtain a dissolution-efficient and more cost-effective molten salt system.

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