

Effect of Chitosan on Properties of Modified Cellulose-Based Gels

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Abstract: In order to obtain a modified cellulose-based hydrogel with excellent properties, this experiment determined the superior process of gel preparation by controlling single factor conditions. The nano-SiO₂ was dispersed in a NaOH/urea liquid-containing system, and modified cellulose (CMC) was added under refrigeration to prepare a cellulose matrix. The cross-linking agent epichlorohydrin was added to the matrix to crosslink the hydroxyl groups of the cellulose to construct a cellulose chemical gel, and the gel was subjected to mechanical, infrared, swelling and the like. The effects of matrix stirring time, matrix freezing, chitosan and cross-linking agent on the formation, properties and stability of hydrogel were investigated. The results showed that a certain amount of nano-SiO₂ was dispersed in the NaOH/urea liquid system, stirred for 6 h, the cellulose was dissolved under freezing conditions, 2 mL cross-linking agent and 1 g chitosan was added at 60 °C. After drying for 6 h, the prepared gel has the best performance.

Keywords: modified cellulose; NaOH/urea solution; chitosan; hydrogel; Aerogel.

INTRODUCTION

The shortage of renewable energy and non-renewable energy are both. The form of crisis that began to face a shortage has led to an increasingly debilitating environment that is closely related to us. However, it is worthy of attention that in order to meet the needs of human social life and alleviate the shortage of resources, the biodegradable new natural or modified polymer synthetic polymeric adhesive has become a hot research field.

Water-soluble and biocompatible cellulose-based hydrogels have become the focus of attention at home and abroad and have been widely used [1-4].

The natural high molecular polymer hydrogel prepared by the derivative organism such as starch cellulose has the characteristics of water solubility and biocompatibility. Therefore, it has attracted wide attention in many fields such as medicine, biological environment management, and bioengineering. The raw material of this experiment is modified high molecular weight carboxymethyl cellulose, with epichlorohydrin and chitosan as crosslinkers [5-8]. The hydrogel was prepared by chemical crosslinking and tested for performance. The performance of the study is mainly carried out by mechanical and infrared tests, swelling tests, to select the best preparation process.

Cellulose, considered being the main source of chemicals and future energy, has always been the most abundant natural polymer compound in storage. At present, environmental and energy issues are becoming

more and more prominent in China, and environmentally friendly materials have become the unremitting pursuit of researchers in various fields in China. Cellulose has many advantages such as low cost, easy availability, non-toxicity, and environmental friendliness. It plays an important role in solving environmental problems and energy problems, and has received extensive attention. As the most abundant natural polymer on the planet, cellulose is recyclable, biodegradable, and biocompatible, with many attractive properties and extensive chemical modification capabilities. Therefore, cellulose is considered to be a sustainable raw material for energy and chemical industry in the future. To this end, exploring the dissolution of new "green" solvents such as cellulose and the "green" process of building materials is the key to developing and utilizing the resources of these natural polymer compounds. However, the solubility problem of cellulose affects the reactivity of cellulose to some extent, and the low solubility leads to the decrease of reactivity, which is a hindrance to the wide

application of cellulose. For this reason, modified cellulose has emerged.

Carboxyl methyl cellulose (CMC) is also known as modified cellulose. It is a kind of derivative which is the most used, the widest range, the low price, the non-toxic, the good biocompatibility, the degradability and the hygroscopicity of the cellulose raw materials. The morphology of CMC is a white fibrous or granular powder, odorless, tasteless, hygroscopic, insoluble in organic solvents, and soluble in hot water to form a transparent solution. CMC has properties such as stabilizers, dispersants, binders, emulsifiers, thickeners, and suspending agents, sizing agents, etc., so it is obtained in the production of food, medicine, daily chemicals, petroleum, paper, textile, construction and other fields. Widely used.

A hydrogel is a novel functional polymer material having a three-dimensional network structure formed by water-soluble polymer having a network cross-linked structure and having a moderate physical or chemical cross-linking, which is a chemical bond. The crosslinked network formed by hydrogen bonding, van der Waals force or physical entanglement is insoluble in water, but can absorb a large amount of hydrophilic polymer material which is highly swollen and maintains a fixed shape. So far, hydrogels have been widely used in personal hygiene products, wound dressings, drug carriers, contact lenses, water treatment, tissue engineering, etc., such as hydrogel hydrating masks in daily life, hydrogel pain relief stickers [9].

The formation principle of a hydrogel is that a water-soluble or hydrophilic polymer can form a hydrogel by chemical crosslinking or physical crosslinking. The preparation of hydrogel materials according to the cross-linking method can be divided into three methods: chemical, physical and radiation crosslinking. Chemical cross-linking refers to the formation of a network structure by the action of a covalent bond. The gel only hydrates and swells

without dissolution, and is permanent, called a true gel. The physical cross-linking is formed under physical action, but such gel heating causes the gel to disappear and is a pseudo-gel that can be called a reversible gel. Radiation crosslinking is a method in which a polymer is crosslinked by electron beam irradiation to form a substance ubiquitous in the natural biological world and then obtained from the bio-functionality of this natural rain molecule and its own compatibility and widely concerned in various fields, such as sex and microbial engineering, chemical processing, daily makeup, even thousands of water treatment, toxic gold rot extraction and effective gold rot recycling, biochemical and biomedical engineering. Significant progress has been made in applied research in many fields [10].

In this paper, CMC was used as the matrix, and then the performance of the modified gel was compared with or without chitosan. The mechanical strength of the modified gel was tested by water absorption test and Fourier transforms infrared spectroscopy (FTIR).

EXPERIMENTAL METHODS

Preparation of matrix

According to the ratio of H₂O: NaOH: Urea=200 g:15.1 g:8 g, the corresponding raw materials were weighed and placed in a 250 mL beaker to prepare 11 wt.% NaOH/urea 4 wt.% alkali/urea. In a solution system, a certain amount of nano-SiO₂ is dispersed in a solution system under stirring for 6 h, and then vigorously stirred at room temperature for several hours and further ultrasonically dispersed for 0.5 h, uniformly dispersed, and then the mixed solution is placed in a refrigerator. It was frozen at medium (-5 °C) for 5 h, taken out from the refrigerator and thawed at room temperature to dissolve cellulose. After thawing, low temperature was applied, and 3 wt. % (7 g) of carboxymethylcellulose was slowly added to the solution under stirring, and allowed to stand overnight for use. The composition ratio of each sample matrix is shown in Table 1.

Table-1: The ratio of each sample matrix

No.	H ₂ O (g)	NaOH (g)	Nano-SiO ₂ (g)
1	200.16	15.11	0.20
2	200.65	15.11	0.20
3	200.12	15.12	0.20
4	200.16	15.18	0.20

Preparation of hydrogel

Screening of crosslinker dosage

Adding a certain amount of cross-linking agent epichlorohydrin (20 mL solution to 1 mL) to the matrix, stirring at room temperature for 2 h, chemically cross-link was in an oven at 60 °C for 2 h. The hydrogel was rinsed with ionized water to remove alkali, urea and

unreacted crosslinker from the hydrogel. The prepared hydrogel samples were marked and placed in a petri dish and wrapped with plastic wrap and marked, placed in a dry and cool place for use.

The No. 2 was selected and weighed into three parts. 20 g each in a 50 mL beaker, adding 1 mL, 2 mL, 3 mL of cross-linking agent epichlorohydrin, and stirring

slowly at room temperature for 2 h. avoid stirring too fast to generate bubbles. After ultra-sonication, put it into a constant temperature incubator at 60 °C for 6 hours, and then take it out. After cooling, we took it out of the beaker, observed the morphology of the hydrogel and do the mechanical test, and then used deionized water. Repeating the cleaning, we removed excess alkali and cross-linking agent, putted in a petri dish and wrapped it with plastic wrap and mark it.

Introduction of Chitosan (Chitin-CS)

0.5 g chitosan was weighed and dissolved in 5 g of deionized water to prepare a 5 wt. % polyvinyl alcohol solution. Put in a water bath until completely dissolved, then add 20 g matrix (the same substrate as the above substrate), add 2 mL cross-linking agent epichlorohydrin, stir slowly at room temperature for 2 h at a constant rate to avoid stirring too fast. The bubbles were ultra-sonicated and placed in a constant temperature incubator at 60 °C for 6 h. After removal, they were taken out from the beaker after cooling. The morphology of the hydrogel was observed and mechanically tested, and then repeatedly washed with deionized water to remove excess. The alkali and cross-linking agent are placed in an evaporating dish and wrapped with plastic wrap and marked. They are baked in a 60° drying oven until they are dry and separated into dry shapes for related swelling and infrared testing.

Freeze drying

Freeze-drying is divided into three stages of freezing-sublimation-re-drying. The prepared hydrogel was frozen in a refrigerator at -70 °C for 24 h or placed in liquid nitrogen for 5 minutes to completely freeze the hydrogel, placed in a freeze dryer that had been lowered to -30 °C, and freeze-dried. During the period, the temperature is around -50 °C, the vacuum is about 0.5 mBar, freeze-dried for 24 h, then taken out, placed in a sealed bag and marked. Leave the test for use.

Performance test

Mechanical test and morphology characterization

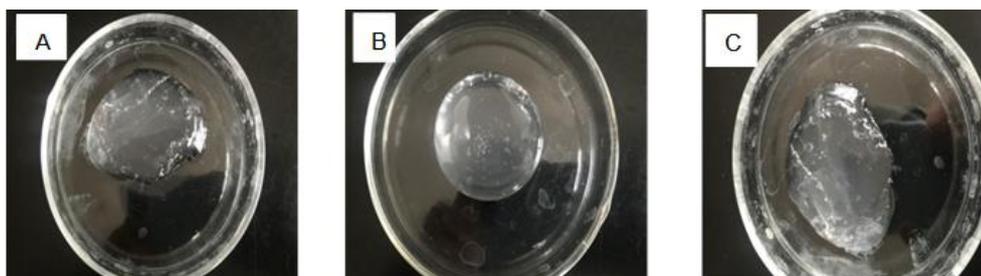


Fig-1: The morphology of hydrogels with different crosslinkers (A: 1 mL; B: 2 mL; C: 3 mL)

After drying for 2 h, the excess cross-linking agent still existed. If the water droplets are distributed inside and on the surface of the hydrogel, affecting the

A 50 g weight was placed over the prepared hydrogel sample, and its deformation state and resilience were observed to judge its strength and toughness. Analyze and judge the pros and cons of hydrogel by means of macroscopic observation.

Swelling performance test

The freeze-dried hydrogel sample was cut into 1.0 cm × 1.0 cm samples, and the dried hydrogel sample dry weight (Md) was weighed separately, and then added with sufficient deionized water at room temperature. After soaking, remove the excess water on the surface of the gel with filter paper every 1 h, weigh it with an electronic balance, test 6 sets of data (M_{sw}) for each sample, and calculate the water absorption rate of the gel by formula (1).

$$\text{Water absorption rate: } (M_{sw}/M_d) \times 100\% \quad (1)$$

Fourier transforms infrared spectroscopy (FTIR)

A certain amount of the freeze-dried hydrogel sample and KBr powder were placed in an agate mortar, mixed and ground, and then compressed, and subjected to FTIR infrared spectrum scanning to obtain an infrared spectrum of the sample. The scanning wavelength range is 500~4000 cm⁻¹.

RESULTS AND DISCUSSION

Effect of the amount of cross-linking agent on the mechanics and morphology of hydrogel

Since there was no other quantitative analysis method of mechanical properties, the mechanical properties of the gel can only be judged by qualitative macroscopic methods, but it is not so easy to be broken in use. Value. The amount of crosslinker affects the morphology of the hydrogel and its strength. As shown in Fig. 1 to Fig. 2, it can be seen from the Fig. that the hydrogel prepared by adding 1 mL of cross-linking agent showed fluidity after drying for 2 h, and was not formed by cooling. The hydrogel prepared by adding 3 mL of cross-linking agent was stirred for 2 h, and the oil-like substance was distributed in the mixed solution. The main reason was that the cross-linking agent was dispersed therein.

morphology, strength and network structure of the hydrogel, and thus affecting the performance of the hydrogel, as shown in the mechanical test chart shown

in Fig. 2, add 1 mL and 3 mL The hydrogel of the crosslinker is very poor in mechanical properties and is not as strong as the hydrogel with 2 mL of crosslinker. The hydrogel prepared by adding 2 mL of cross-linking agent can be seen from macroscopic morphology

observation and qualitative mechanical test. The hydrogel prepared by adding 2 mL of cross-linking agent was formed and stable after drying for 2 h. Has a certain strength, elasticity and transparency.

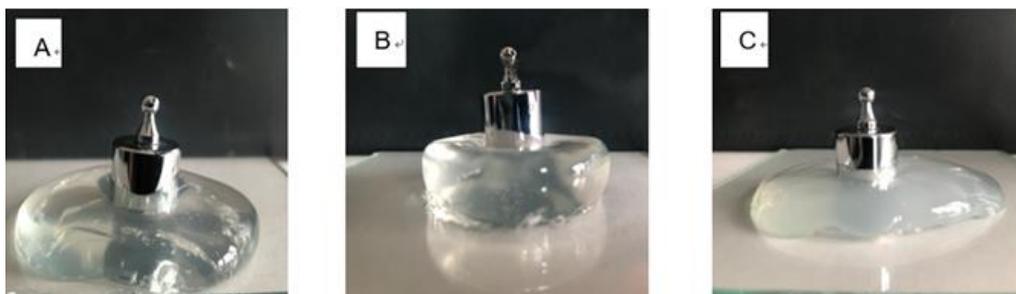


Fig-2: The mechanical properties of hydrogel with different amounts of crosslinker (A: 1 mL; B: 2 mL; C: 3 mL)

Too high or low cross-linking agents affect the morphology of the hydrogel and its strength [11]. Therefore, the content of the cross-linking agent plays an important role in the preparation of the hydrogel, which directly affects the cross-linking density of the hydrogel network. When the amount of the cross-linking agent was too low, the hydrogel formed was unstable and soluble. The gel network also experiences the flow out of the network; when the dosage is too high, the excess cross-linking agent was distributed in the hydrogel to affect the hydrogel network structure, affecting the morphology and strength of the hydrogel [12]. Therefore, the more the cross-linking agent was better. From the observation of the gel morphology, the shape, strength, toughness and transparency of the gel at 2 mL of cross-linking agent are the best.

In summary, in order to prepare a hydrogel with excellent strength and toughness, the optimum dosage of the crosslinking agent is 2 mL.

Effects of chitosan introduction

Analysis of mechanics and morphology

The introduction of other materials had a certain influence on the formation and stability of the hydrogel. It can be seen from Fig. 3 that the hydrogel prepared by adding chitosan was dried after being dried for 6 hours, and the shape was stable after being taken out. No deformation, quickly removing the original shape after removing the weight. Without the chitosan added to the prepared hydrogel, the gel was in a relatively stable state after drying for 6 hours, and the inside of the gel was trapped when the weight is placed, causing the hydrogel to be damaged. Therefore, the hydrogel made of chitosan had higher stability, better strength and toughness, and more energy and time. We could clearly see the difference after lyophilization.

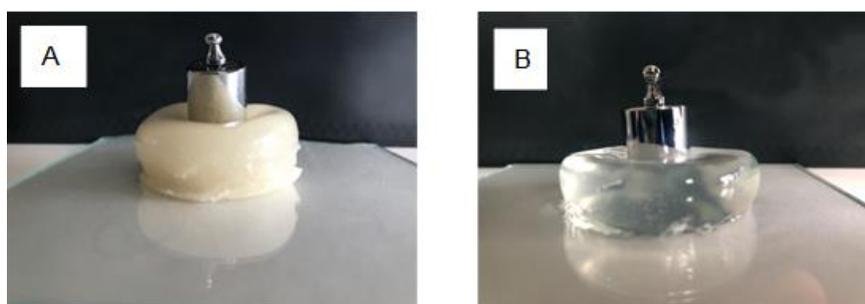


Fig-3: Mechanical effects of chitosan on hydrogels (A: hydrogel with chitosan; B: hydrogel without chitosan)

As can be seen from Fig. 4, the gel A added with chitosan formed a dry aerogel state after freeze-drying, while the gel B to which no chitosan was added formed a state of the film. The reason for this was that no internal crosslinks are formed inside the gel [13]. It can be seen that the addition of chitosan increases the crosslinking effect. Hydrogels with a higher degree of chitosan combination usually have a certain degree of

deformation ability, and the chitosan hydrogel chemical cross-linking network structure tends to be perfect.

Analysis of swelling performance test

It can be seen from the swelling test chart of Fig. 5 that the two gels prepared by adding chitosan and not adding chitosan have obvious difference after soaking for 12 h, especially the hydrogel added with

chitosan in the whole soaking. The process was stable, the shape was intact. There was no breakage phenomenon, and the internal network structure of the

hydrogel changes little or even unchanged, and does not affect the performance of the hydrogel.

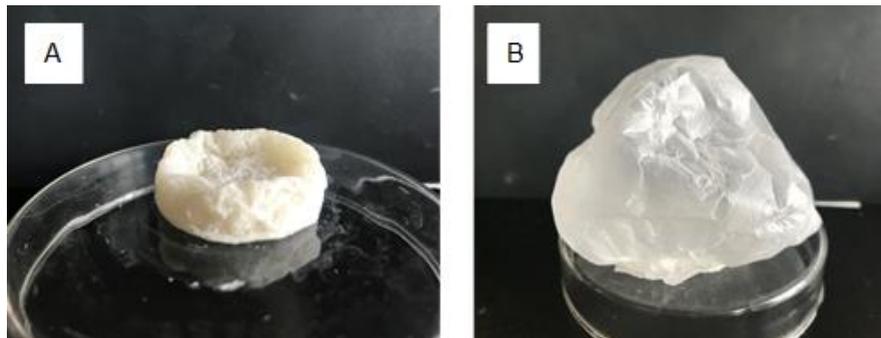


Fig-4: The morphology of aerogels (A: aerogel with chitosan; B: aerogel without chitosan)

Hydrogels that did not introduce other substances had no original shape and structure after soaking for 12 h, and the structure was not changed in

the application. Therefore, the stability of the structure is critical to the performance of the material.

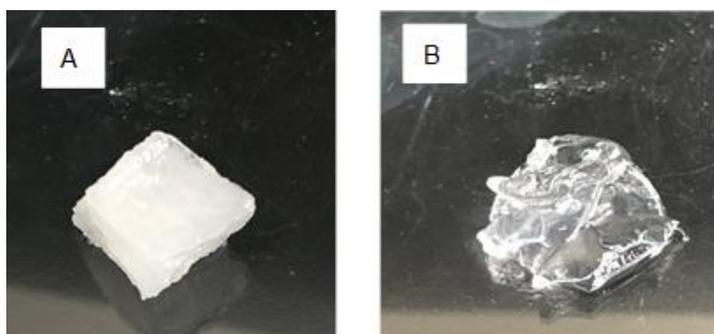


Fig-5: The morphology of aerogels after 12 h soaking (A: aerogel with chitosan; B: aerogel without chitosan)

It can be seen from the water absorption rate diagram of Fig. 6 that the water absorption rate of the non-added chitosan hydrogel is higher than that of the prepared hydrogel prepared by the addition of chitosan, but from Fig. 5, we know that the hydrogel is not added

with chitosan. The glue will swell or even break apart as the soaking time was lengthened. In summary, the hydrogel prepared by the addition of chitosan has the best mechanical properties, swelling properties and stability.

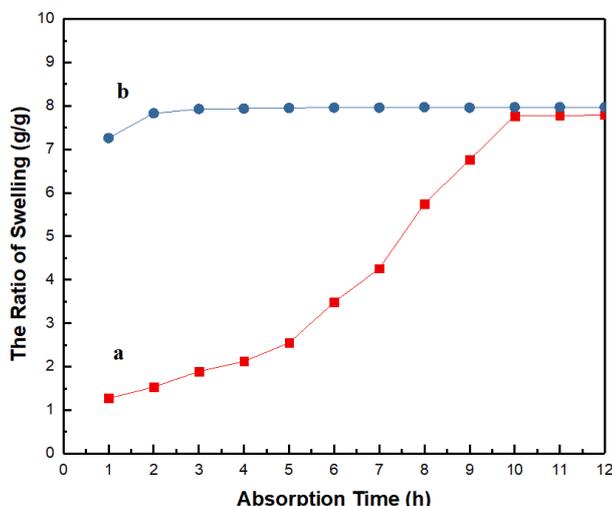


Fig-6: The ratio of swelling for aerogels with different introductions (a: chitosan added; b: without chitosan)

Infrared test analysis

Since chitosan itself can be degraded, and the method of degradation is various, and the cost is relatively low. Non-toxic, no side effects, no environmental pollution. New materials with biocompatibility and biodegradability can be developed through the action of cross-linking agents.

When the two polymers are compatible, there will be a significant interaction between the two molecules. From the infrared spectrum (Fig. 7), the stretching vibration peak of the -OH group was at 3415-3433 cm^{-1} for CMC [14]. The strength of the gel was weaker, and the stretching vibration peak of NOC was increased at 1047 cm^{-1} to 1050 cm^{-1} , indicating that the -OH group structure in chitosan was crosslinked with the carboxyl group in cellulose.

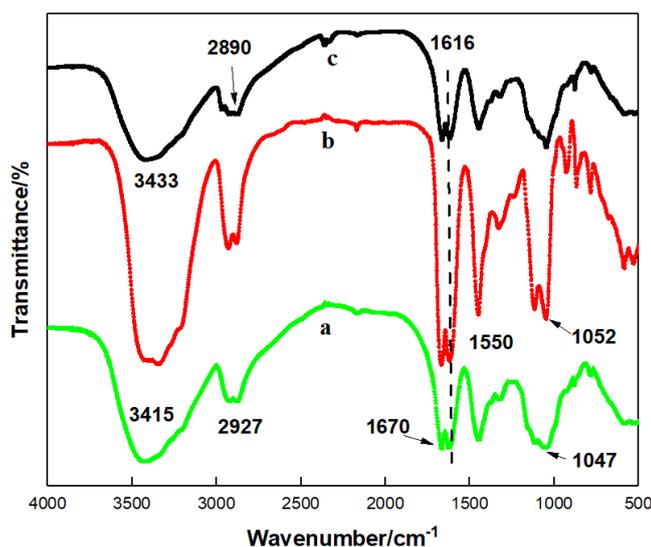


Fig-7: The FTIR spectrogram of gels and chitosan (a: chitosan added; b: without chitosan added; c: chitosan)

At the same time, the internal network structure of the gel was also enhanced, so that the mechanical properties were improved and the swelling property was also enhanced. Studies have shown that hydrogel toxicity is very low and even negligible in large systems. Similarly, excellent biocompatibility is an advantageous advantage of hydrogel itself. It has broad application prospects in drug release and tissue engineering. CS composite hydrogel is suitable for cartilage repair. The network structure of the alternative material and the equilibrium water content, CS enhances the interaction of water with the gel scaffold. The biocompatibility and degradation ability of the gel are optimized, which can be used as a model system for theoretical research in future theoretical research and practical operation.

CONCLUSION

In this study, a better preparation process of biodegradable hydrogel with good strength and good swelling performance was obtained: the substrate was stirred for 6 h and frozen, and the amount of nano-SiO₂ was dispersed in the alkali/urea solution system (0.20 g), 1 g chitosan and 2 mL cross-linking agent epichlorohydrin were introduced and dried at 60 °C for 6 h.

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