Effect of Chitosan and Citric Acid on Properties of Hydrogels based on Modified Cellulose

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Abstract

In order to obtain modified cellulose-based hydrogel with excellent properties, the better process of gel preparation was determined by controlling the single factor condition. A cellulose matrix was prepared by dispersing Nano-SiO2 in NaOH/urea liquid system and adding modified cellulose (CMC) under freezing conditions. In the matrix, crosslinking agent epoxy chloropropane was added to cross the hydroxyl group of cellulose to construct cellulose chemical gel, and the gel was tested for mechanics, infrared, swelling and so on. The results showed that in a certain amount of nano-SiO2 dispersed in the NaOH/urea liquid system, stirring 6 h, dissolving cellulose under freezing conditions, adding 2 mL crosslinking agent, adding 1g chitosan, drying 6 h under 60 ℃ conditions to improve, replacing 2 mL epoxy chloropropane with 1.5 mL epichlorohydrin, 0.5 g chitosan and 0.5 g citric acid. The preparation of gel performance is the best.

Keywords

Modified Cellulose; NaOH/Urea Solution System; Hydrogel; Citric Acid.

1. Introduction

In order to meet the needs of human social life and alleviate the tension of resource shortage, the synthesis of new natural or modified biodegradable polymers has become a hot research field. Cellulose based hydrogels with water solubility and biocompatibility have become the focus of attention at home and abroad and have been widely used [1]. Through its derivatives creatures such as starch cellulose preparation of natural polymer hydrogel has the characteristics of the water solubility and biocompatibility. Cellulose, considered as a major chemical source and future energy source, has always been the most abundant natural polymer compound.

Carboxymethyl cellulose (CMC) is currently cellulose raw materials in the most amount, the most wide range, low price, non-toxic, has good biocompatibility, degradation and hygroscopicity of a derivative[2,3]. Cellulose has many advantages such as cheap, easy to obtain, non-toxic, good renewability and environmental friendliness. It plays an important role in solving environmental and energy problems and has received wide attention. As the most abundant natural polymer on earth, cellulose has attractive properties and strong chemical modification ability, whether it is renewable or other biological properties [4-6]. Therefore, cellulose is considered as a sustainable feedstock for future energy chemicals. However, the solubility of cellulose affects the reactivity of cellulose to a

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certain extent, and the low solubility leads to the decline of reactivity, which becomes the obstacle to the wide application of cellulose, so modified cellulose comes into being[7,8].

Citric acid its alias folic acid, is a kind of organic acids in colorless crystals, play an important role in the nature, the molecular structure contains a molecular crystal water, taste is odourless, but there is a strong acid, water soluble for its property of natural harmless so widely used in industry, food industry, cosmetic industry and other industry fields Environmental governance in medicine, biology, biological engineering, and many other areas caused widespread concern[9,10].

This experiment materials for modification of polymer carboxymethyl cellulose, epoxy chloropropane and citric acid as crosslinking agent were chosen. The preparation of hydrogels with chemical crosslinking method and performance testing in this study the main mechanics and infrared test performance, swelling test, and to choose the best preparation technology. In this paper, sodium carboxymethyl cellulose was used as the matrix and citric acid was used to improve its performance. The improved gel was tested for mechanical strength, infrared spectrum analysis and water absorption performance, and the best ratio and technological process were obtained, which provided a certain theoretical basis for environmental protection green aerogel.

2. Materials and Methods

2.1 Preparation of Matrix

According to the H2O: NaOH: Urea (200:15:8) of the corresponding raw materials, placed in 250 mL beaker, prepared into alkali/Urea solution system (NaOH/Urea=1:4), under the condition of stirring a certain amount of nano SiO2 dispersed in the solution system. Then, the mixture was stirred vigorously for several hours at room temperature and further dispersed by ultrasound for 0.5 h. After the mixture was evenly dispersed, the mixture was put into the refrigerator (-5°C) and frozen for 6 h. After being removed from the refrigerator, the mixture was thawed at room temperature and used to dissolve cellulose. After thawing at low temperature, 3 wt% (7 g) carboxymethyl cellulose was slowly added to the solution under stirring condition and left overnight for later use.

2.2 Preparation of Hydrogel

2.2.1 Introduction of Chitosan (CS)

0.5 g chitosan was weighed and dissolved in 5 g deionized water to prepare a 5wt% polyvinyl alcohol solution. Add 20 g of matrix (the same matrix as the above matrix), add 2 mL of crosslinker epichlorohydrin, and stir it slowly at a constant speed at room temperature for 2 h to avoid bubbles caused by too fast stirring. After ultrasound, put it in a constant temperature incubator at 60 ℃ and dry it for 12 h before taking it out. Let cool and remove from beaker to get chitosan gel.

2.2.2 Introduction of Citric Acid

4 parts of the above-mentioned matrix were taken, 2 mL epichlorohydrin in the chitosan gel was reduced to 1.5 mL epichlorohydrin, and 0.5g chitosan was added to the four parts of the matrix to introduce 0.5g, 1 g, 1.5g and 2 g citric acid. After drying in the oven, only the gel with 0.5g citric acid was found to have the best performance. Reduce the toxicity of epichlorohydrin and get better performance gel. After obtaining the citrate gel, observe the morphology of the hydrogel and do mechanical tests. Put the hydrogel into the evaporation dish, wrap it with plastic wrap and mark it. Bake it in a drying oven at 60° until it becomes dry without moisture.

2.3 Preparation of Aerogel

Freeze-drying can be divided into three stages: freeze-sublimation-redrying. The prepared hydrogel was frozen in the refrigerator at -70 ℃ for 24 h or in liquid nitrogen for 5 min to make the hydrogel completely frozen. Then, the hydrogel was put into the freeze dryer which had been reduced to -30 ℃. During the freeze drying period, the temperature was about -50 ℃ and the vacuum degree was about 0.1mbar. Place in a sealed bag and mark. Leave it for testing.

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2.4 Mechanical Properties and Morphological Characterization

Put 50 g weight on the top of the prepared hydrogel sample, observe its deformation state and resilience, and judge its strength and toughness. The advantages and disadvantages of hydrogels were analyzed and judged by macroscopic observation.

2.5 Swelling Performance

The swelling performance of hydrogels was tested by grametry. The freeze-dried aerogel samples were cut into 1.0cmx1.0cm size samples, and the weight of each cut aerogel sample (Wd) was weighed, and then soaked in sufficient amount of deionized water at room temperature every 10min The soaked sample was taken out with tweezers, and the moisture on the surface of the sample was absorbed with filter paper. After that, it was weighed with electronic balance (Wt). Six groups of data were tested for each sample, and the swelling rate of aerogel was calculated by recording and using the following formula (1), and the line chart of swelling rate was drawn.

$$SR = (Wt - Wd) / Wd \quad (1)$$

3. Results and Discussion

3.1 Effect of Chitosan on Mechanical and Morphological Characterization of gels

The introduction of other materials has a certain impact on the molding and stability of hydrogels. The hydrogels were made by adding chitosan are formed after drying for 6 h, and the shape is stable after removal. There was no deformation after placing the weight, and the original shape was quickly restored after removing the weight. The hydrogel made without chitosan was in a relatively stable state when it was dried for 6 h. When the weight was placed, it fell into the gel interior, resulting in the damage of the hydrogel. Therefore, the hydrogel made by adding chitosan is more stable, strong and tough, and saves energy and time.

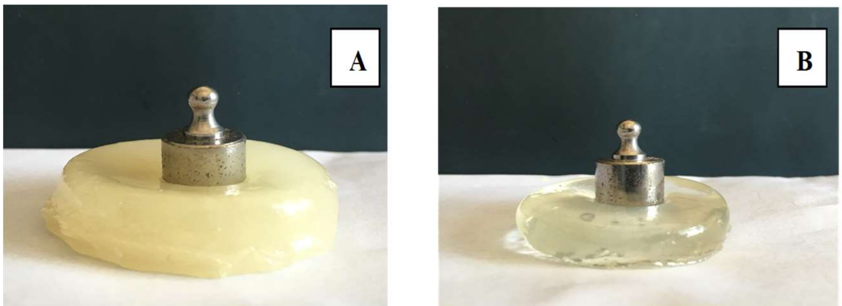

Figure 1. Mechanical effects of chitosan on gels (A: gels with chitosan; B: gel without chitosan)

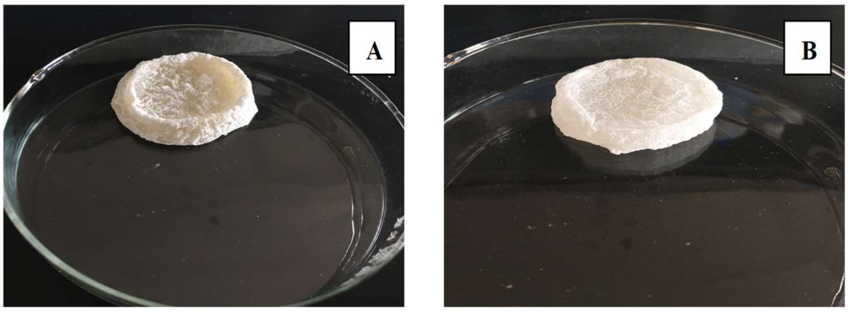

Figure 2. Mechanical effects of chitosan on aerogels (A: aerogels with chitosan; B: aerogel without chitosan)

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It can be seen in Figure 2 that gel A with chitosan is in the freeze-dried aerogel state, while gel B without chitosan forms A membrane state on its surface. The reason is that there is no internal cross-linking in the gel[8]. It can be seen that the addition of chitosan increased the cross-linking effect. Hydrogels with a high degree of chitosan association usually have a high degree of deformation ability, and the chemical cross-linking network structure of chitosan hydrogels tends to be perfect.

3.2 Effect of Chitosan on Swelling Property of Aerogels

As can be seen from Figure 3, joining of the preparation of chitosan and did not join two gels at 6 h after immersing obvious difference, especially to join the chitosan hydrogel soaking. The whole process is very stable, shape in good condition, no any broken phenomenon inside the water gel. The network structure change is not even the same. Chitosan introduction will not affect the performance of the hydrogel.

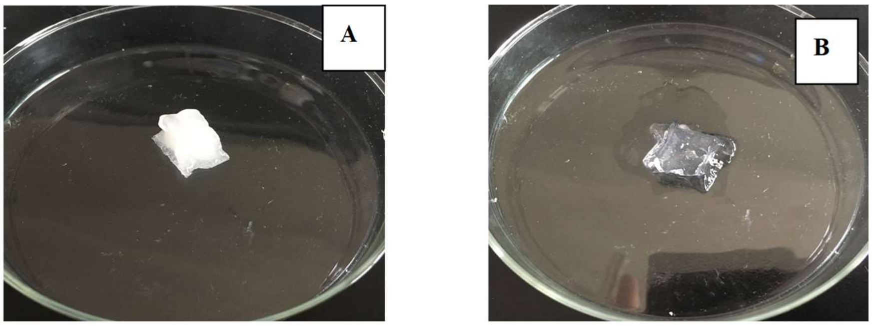

Figure 3. The swelling state of aerogels at 6 h (A: aerogels with chitosan; B: aerogel without chitosan)

However, the hydrogel without other substances has no original shape and structure after soaking for 6h. The structure does not change in application is the basis for maintaining the performance. The stability of the structure is crucial to the performance of a substance. As can be seen from the Figure 4, the bibulous rate of gels with chitosan is higher than that of the gels without chitosan, but we've learned from Figure 4 that gels with chitosan swelling with immersion time lengthen even not broken apart. In conclusion, the hydrogel prepared by adding chitosan has the best mechanical properties, swelling properties and stability.

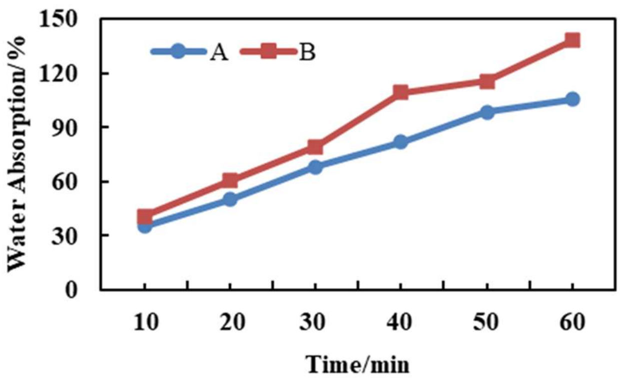

Figure 4. The 6 h water absorption rate of gels with different introductions (A: gels with chitosan; B: gel without chitosan)

3.3 Effect of Citric Acid on Mechanical and Morphological Characterization of Gels

2 mL epichlorohydrin crosslinker was added into the chitosan gel. however, due to its molecular properties, epichlorohydrin has certain microtoxicity, which leads to the toxicity of the gel in the production and manufacturing process. In order to reduce the dosage of epichlorohydrin crosslinking

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agent, 2 g epichlorohydrin was changed to 1.5 g epichlorohydrin and 0.5 g citric acid. But it did not change the dose of chitosan. The gel forming effect is better when the quantity of epichlorohydrin is reduced and citric acid is added after drying as shown in Figure 5. And it takes less time to dry.

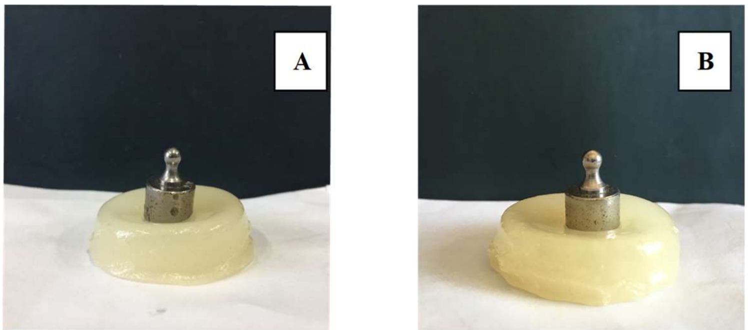

Figure 5. Mechanical effects of citric acid on hydrogels
(A: hydrogels with chitosan; B: hydrogels with citric acid)

As shown in Figure 6, the state of aerogel A with citric acid is basically the same as that B without citric acid. The reason is that both citric acid and epichlorohydrin play the role of cross-linking agent, and the reaction of citric acid with hydroxyl group in the matrix can also play the role of cross-linking. It can be seen that adding citric acid can replace part of the epichlorohydrin crosslinking.

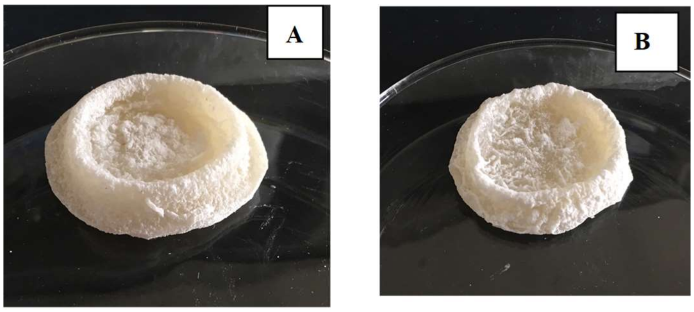

Figure 6. Mechanical effects of citric acid on aerogels
(A: aerogels with chitosan; B: aerogels with citric acid)

3.4 Effect of Citric Acid on Swelling Property of Aerogels

As can be seen from the swelling test chart in Figure 7, there is no significant difference between the two gels prepared with citric acid and without citric acid after soaking for 6 h. The stability, shape and internal network structure of the hydrogel in the soaking process of the gel with citric acid are better than those without citric acid.

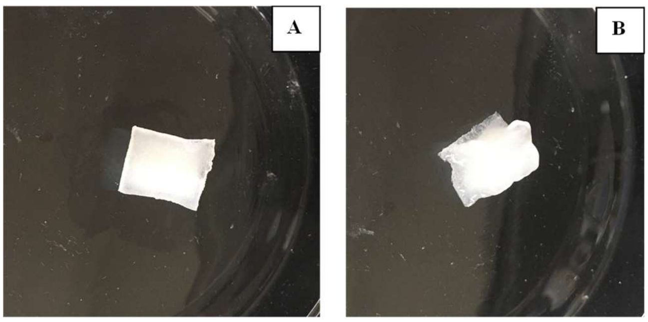

Figure 7. The swelling state of aerogels at 6 h
(A: aerogels with chitosan; B: aerogels with citric acid)

It can be seen from Figure 8 that the water absorption rate of the hydrogel with citric acid is higher than that of the hydrogel without citric acid. However, the performance of the hydrogel without citric acid is the same as that of the hydrogel with citric acid. In conclusion, the hydrogels prepared by adding citric acid maintain good mechanical properties and stability as shown in Figure 8.

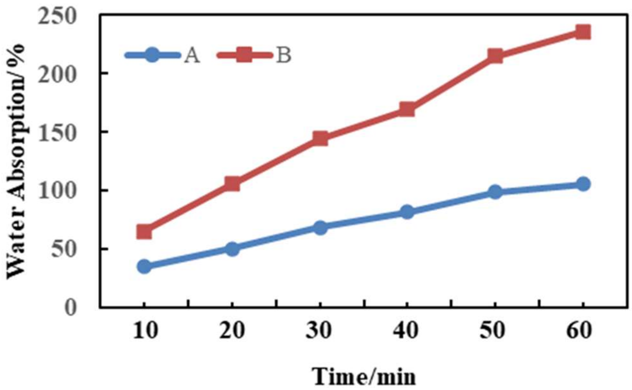

Figure 8. The 6 h water absorption rate of gels with different introductions (A: aerogels with chitosan; B: aerogels with citric acid)

4. Conclusion

In this study, the preparation process of hydrogel with excellent strength and swelling performance was obtained: the matrix was stirred for 6 h and frozen, the amount of nano-SiO2 (0.20 g) was dispersed in the alkali/urea solution system, 0.5g of chitosan, 1.5 mL of epichlorohydrin and 0.5g of citric acid were introduced, and the hydrogel was dried at 60 ℃ for 12 h.

Acknowledgments

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