

Optimization and Photocatalytic Performance of Gels Based on Modified Cellulose

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Abstract

Two kinds of cellulose-based gels were prepared by introducing chitosan, citric acid and epichlorohydrin, β -cyclodextrin and butyl titanate on the basis of optimized cellulose matrix. Comparison of performance properties were swelling and photocatalysis. The results show that different amounts of butyl titanate, the amount of cross-linking agent chlorochloropropane and the ratio of citric acid are closely related to the formation, properties, stability and photocatalytic properties of hydrogel. The optimum preparation conditions for obtaining a gel with good photocatalytic properties and maintaining excellent strength and swelling properties were: butyl titanate 0.4 mL, epichlorohydrin 1.5 mL, chitosan 0.5 g, β -cyclodextrin 0.5 g and dried at 70 °C for 10 h.

Keywords

Modified cellulose; Chitosan; Butyl titanate; Hydrogel; Photocatalysis.

1. INTRODUCTION

In order to meet the needs of human social life and ease the tension in the shortage of resources, a new type of natural or modified in a photocatalytic degradation of polymer synthetic polymer as the substrate of hydrogel become popular area of study, with water solubility and biocompatibility of the cellulose hydrogel is becoming a hot point of attention at home and abroad. Through the starch cellulose [1,2], natural polymer hydrocoagulants prepared by sodium alginate [3], chitosan [4] and their derivatives have attracted wide attention in the fields of medicine, pharmacy, agriculture, forestry, horticulture, environmental governance and bioengineering [5-7].

Carboxyl methyl cellulose (CMC), also known as modified cellulose, is one of the most widely used cellulose raw materials at present. It is cheap, non-toxic and has good biocompatibility, degradation and hydroscopicity. CMC is a kind of stabilizing and dispersing agent. As a result, it has been widely used in the production of food, medicine, daily chemical, petroleum and other fields [8]. Hydrogel is a new functional polymer material with three-dimensional network. The structure was formed by moderate physical or chemical crosslinking of water-soluble polymer with water as the dispersion medium [9].

So far, wound dressing in personal hygiene products is drug carrier from several aspects, such as water treatment hydrogel has been widely used butyl titanate can provide rapid crosslinking reaction, improving the performance of polyester lacquer and used for preparation of high temperature resistant coatings. At the same time of crosslinking reaction, butyl titanate can improve the adhesive properties of polymer and improve the printing ink adhesion of system

Butyl titanate is also a common raw material for the preparation of nano-sized titanium dioxide by sol-gel method. Due to its severe hydrolysis, ethanol glacial acetic acid diethanolamine is often added to slow down the hydrolysis rate. Tetrabutyl titanate hydrolyzes with water in the medium to generate $Ti(OH)_4$, and the dispersed phase is the $Ti(OH)_4$ generated epichlorohydrin is an organic compound with moderate toxicity and potential carcinogenic risk, while citric acid is a relatively inexpensive and pollution-free organic polycarboxylic acid. Studies have shown that only part of the carboxylic group in the cross-linking reaction of citric acid is esterified with the hydroxyl group on the cellulose molecular chain in the gel [10-12].

This test raw materials for the modification of polymer materials carboxymethyl cellulose, butyl titanate solution was introduced to achieve the purpose of photocatalytic degradation, with epoxy chloropropane and citric acid, chitosan as crosslinking agent, the preparation of hydrogels with chemical crosslinking method and performance testing. The performance, mainly carries on the swelling performance test, infrared spectrum analysis and light catalytic effect were investigated. And the best preparation process was determined.

2. EXPERIMENT

2.1. Preparation of Matrix

According to the $H_2O: NaOH: Urea=200 :15.1 :8$, the raw material was set in 250 mL clean beaker, prepared into NaOH/Urea (11:4) solution system, under the condition of stirring 0.2 g nano SiO_2 . The mixture was dispersed in the solution system, stirred vigorously for 6 h at room temperature by magnetic stirrers, and further dispersed by ultrasound for 0.5 h to prevent more bubbles in the later experimental samples. After the mixture was evenly dispersed, the mixture was put into the refrigerator for 12h, removed from the refrigerator and thawed at room temperature, then 3 wt. % (7 g) of carboxymethyl cellulose was slowly added to the solution under the condition of stirring, and then stood overnight until completely dissolved. After completely dissolved cellulose, stood overnight for use. The composition ratio of each sample matrix was shown in Table 3.

Table 1. the ratio of raw material composition of sample

No.	H_2O/g	$NaOH/g$	$Urea/g$	nano- SiO_2	CMC
1	200.12	15.15	8.01	0.20	7.01
2	200.05	15.12	8.03	0.21	7.08
3	200.20	15.14	8.03	0.20	7.03

2.2. Preparation of Hydrogel

2.2.1 Screening of type and dosage ratio of crosslinking agent

The prepared cellulose matrix was selected into two groups with the same amount, and different gradients of crosslinkers were added. The A group was added with epichlorohydrin chitosan citric acid, and the B group was added with epichlorohydrin chitosan β -cyclodextrin. After several groups of experiments, according to the forming effect and mechanical effect of hydrogel after drying, it can be further judged that the hydrogel forming effect with the ratio of epichlorohydrin 1.5mL chitosan 0.5g, citrate 0.5g as cross-linking agent is the best, while epichlorohydrin 1.5mL chitosan 0.5g, β -cyclodextrin. The forming effect of hydrogel with 0.5g as crosslinker is relatively good.

2.2.2 Introduction of butyl titanate of hydrogel

Two groups of experiments were prepared, and three parallel experiments were prepared for each group. In the first group, 20g of cellulose matrix that had been weighed and prepared was

put into 12 small beakers respectively, and then 0.1ml, 0.2ml, 0.3ml, 0.4ml were added into each of the four beakers. For each concentration gradient of butyl titanate, three parallel experiments were performed. The amount of butyl titanate added in the second group and the number of parallel experiments were the same as those in the first group. After completion, different crosslinkers were added according to the determined optimal crosslinker ratio 0.5g, while in the other group, 1.5ml epichlorohydrin, 0.5g chitosan and 0.5g cyclodextrin were added and stirred slowly at a constant speed for 2 h at room temperature to avoid bubbles generated by stirring too fast. After removing bubbles by ultrasonic crushing for 30 min, the mixed gel was put into a 70 oven for drying for 10 h. After taking out, to be cooled from the beaker will have formed the hydrogel with tweezers out, observe the morphology of hydrogel and do mechanical tests. The above operations were repeated to observe the morphology of hydrogels, and all the prepared samples were repeatedly cleaned with deionized water. After washing the residual drugs on the surface of the prepared hydrogels, the samples were put into the Petri dish, wrapped with plastic wrap and marked, and then frozen in the refrigerator at -80°C for 24 h, take it out quickly and put it into the freeze dryer. After freeze drying, it will be made into aerogel, and relevant swelling test and infrared test were done to observe its performance.

2.3. Preparation of Aerogel

In this experiment, aerogel was prepared through three stages: freezing-sublimation-redrying, and the prepared hydrogel was frozen in the refrigerator of -80°C for 24 h to completely freeze the hydrogel. Then, the hydrogel was put into the freeze dryer which had been reduced to -50°C . During the freeze drying, the temperature was always around -50°C , and the vacuum degree was 0.1mbar. Take them out after 24 h freeze-drying, put them in a sealed bag and mark them, and place them in a dry and cool place for testing.

2.4. Swelling Performance of Aerogel

The swelling performance of hydrogels was tested by grametry. The freeze-dried aerogel samples were cut into $1.0\text{cm} \times 1.0\text{cm}$ size samples, and the weight of each cut aerogel sample (W_d) 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 (W_t). 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.

$$\text{SR} = (W_t - W_d) / W_d \quad (1)$$

2.5. Photocatalytic Degradation Performance of Aerogel

The aerogel sample cut into about 1 g was put into 50 mL of methyl orange solution with an initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, and then put into the dark place to allow the aerogel to fully swell in methyl orange solution for 1h, so that the methyl orange solution dye could be fully absorbed by aerogel. Using ultraviolet spectrophotometer to determine the initial absorbance of methyl orange solution C_0 , after being absorbed balance, placing the methyl orange solution of aerogel under the sunlight, photocatalytic degradation, in optical processing after reaching 4 h after the determination of methyl orange degradation of absorbance C_t , by the following formula (2) to calculate the degradation rate of methyl orange solution. Analyzing the data and with the corresponding conclusions, the absorbance was measured by UV spectrophotometer at a wavelength of 462 nm [12]. The degradation rate of methyl orange can be expressed as follows:

$$D = [(C_0 - C_t) / C_0] \times 100\% \quad (2)$$

3. RESULTS AND ANALYSIS

3.1. Analysis of Swelling Performance

To test the swelling rate of the freeze-dried aerogel samples. The above eight pieces of aerogel were cut off with a blade and weighed, and then 8 small beakers were respectively filled with 50 mL distilled water. The cut pieces of aerogel were put into the water, picked out with tweezers every 10 min and weighed. Record quality until there is no significant change in quality.

Table 2. Data of aerogel swelling

No.	Dry Weight/g	Weight after Water Absorption/g					
		10 min	20 min	30 min	40 min	50 min	60 min
A-1	0.72	1.32	1.47	1.79	1.89	2.08	2.08
A-2	1.01	1.30	1.45	1.76	1.91	1.95	2.00
A-3	1.15	1.57	1.77	2.08	2.09	2.13	2.17
A-4	0.82	1.33	1.57	1.64	1.70	1.74	1.83
B-1	1.07	1.47	1.74	1.87	1.99	2.17	2.20
B-2	0.95	1.26	1.61	1.64	1.80	1.96	2.08
B-3	0.83	1.11	1.29	1.46	1.59	1.84	2.00
B-4	0.92	1.21	1.32	1.48	1.62	1.87	2.02

According to Table 1, the swelling rate of aerogel was calculated by using the water absorption calculation formula, and the line chart of swelling rate was drawn, as shown in Figure 1.

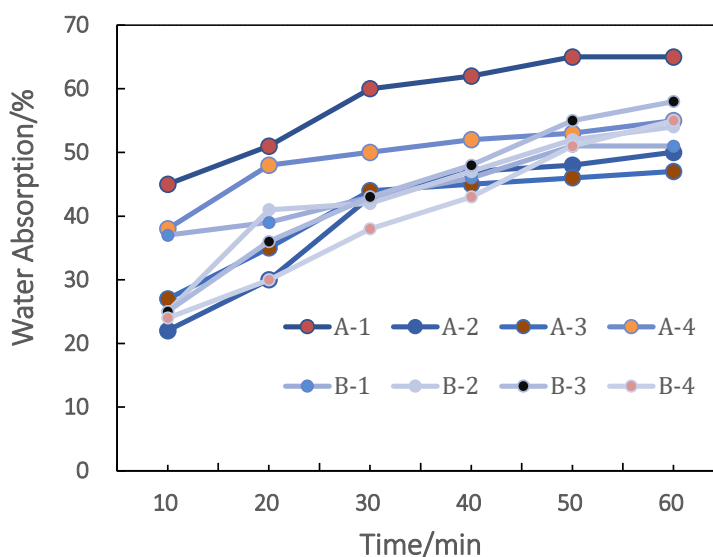


Figure 1. Change in swelling rate of aerogel

After 50 min, the swelling rate decreased significantly, showing a state of swelling equilibrium. The water absorption and swelling rate of aerogel can be roughly divided into three stages according to the figure. In the first stage, water molecules rapidly entered the gel within the first

30 min and formed hydrogen bonds with hydrophilic groups such as carboxyl hydroxyl group, which made the swelling rate increase rapidly. In the second stage, 30~50 min after the beginning, the expansion speed slows down and the swelling rate begins to slow down. In the third stage, after swelling for 50 min, the swelling rate gradually tended to be stable, with a small increase but little change, and reached swelling equilibrium.

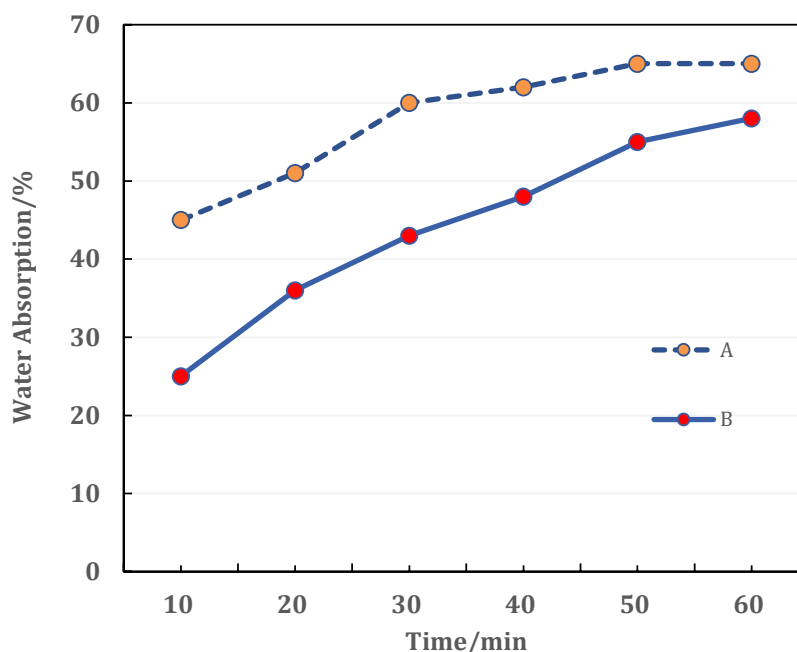


Figure 2. Line chart of optimal swelling rate of different crosslinkers

As shown in Figure 2, the aerogels with epichlorohydrin chitosan citric acid as the common cross-linking agent have a higher water absorption rate and a faster water absorption rate in the same time than those with epichlorohydrin chitosan β -cyclodextrin as the common cross-linking agent. In summary, epichlorohydrin chitosan has a higher water absorption rate. The aerogels prepared with citric acid as a common cross-linking agent have better swelling properties.

3.2. Analysis of Photocatalytic Degradation Performance

The aerogel samples selected for the photocatalytic test were consistent with those selected for the swelling test. The initial and degraded absorbance of methyl orange solution of each sample were measured by UV spectrophotometer at the maximum absorption wavelength of 462 nm, and the degradation rate of methyl orange was calculated and tabulated according to the obtained data, as shown in Table 3.

Table 3. Absorbance data of aerogel in photocatalytic degradation test

Samples	MO(C ₀)	C _t at different dosage of butyl titanate			
		0.1 mL	0.2 mL	0.3 mL	0.4 mL
A	2.083	0.587	0.461	0.438	0.438
B	3.983	0.584	0.521	0.516	0.501

In order to see the degradation rate of each sample more intuitively, according to the absorbance of methyl orange solution of each sample obtained in Table 3, equation (2) is used to calculate the degradation rate. As shown in the figure 3, in epichlorohydrin/citric acid/chitosan as a set of aerogel crosslinking agent, the degradation rate increased with the amount of butyl titanate, the phenomenon of declines after the first increases, maximum of 25% and another group to join epoxy chloropropane cross-linked chitosan beta cyclodextrin of aerogels as the grow in quantity of butyl titanate, presents the tendency of degradation rate increased gradually, the largest up to 30%.

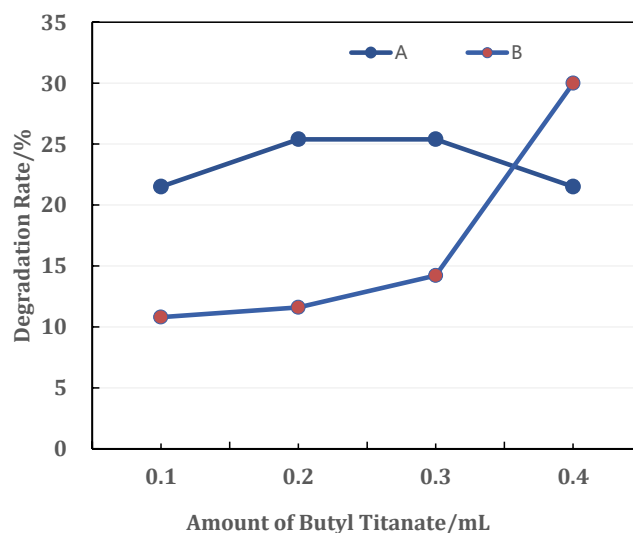


Figure 3. Effect of different amount of butyl titanate on degradation performance of aerogel

Figure 3 shows that using epoxy chloropropane/chitosan/citric acid as a crosslinking agent of aerogel with butyl titanate dosage increasing, the degradation of the first increases then decreases with epoxy chloropropane/chitosan/ β -cyclodextrin as crosslinking agent of aerogel with butyl titanate dosage increasing, the degradation rate increased gradually, and reached 0.4 mL in butyl titanate. In conclusion, adding 0.4 mL butyl titanate to the aerogels with epichlorohydrin/chitosan/ β -cyclodextrin as a common cross-linking agent has the best photocatalytic degradation performance.

4. CONCLUSION

The optimal preparation conditions of photocatalytic degradation gels with excellent strength and swelling performance were as follows: sample matrix was stirred for 6 h and frozen, 0.20 g nano-SiO₂ was added, 0.4 mL butyl titanate was introduced, and epichlorohydrin/chitosan/ β -cyclodextrin was used. The modified cellulose-based gel prepared under the optimum conditions of 0.5 g crosslinking agent and drying at 70 for 10 h. The gel has excellent strength, swelling performance and photocatalytic degradation performance.

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