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Effects of Crosslinking Agents on the Properties of Butyl Titanate/Cellulose Composite Membrane

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Abstract **Original Research Article**

In order to obtain cellulose matrix composite films with excellent strength and adsorbability, butyl titanate/cellulose matrix composite films were prepared from cellulose and butyl titanate. 2 ml butyl titanate was mixed into cellulose matrix, the properties of the composite films prepared by different crosslinking agents and their dosage and ratio were studied by means of the corresponding mechanical properties test. The results show that the addition of butyl titanate and the use of citric acid solution as crosslinking agent increase the deformation rate of the composite film. It increased tensile strength with the membrane more elastic.

Keywords: Modified cellulose; Butyl titanate; Film; Crosslinking agent.

INTRODUCTION

With the development of economy and the progress of science and technology, environmental pollution is becoming more and more serious, and renewable resources will be exhausted. With the globalization of economy and trade, the problem of environmental pollution is becoming international day by day. The transboundary movement of hazardous wastes is the outstanding manifestation of the problem in the whole world, and the problem of environmental pollution is becoming more and more internationalized with the globalization of economy and trade, and the transboundary movement of hazardous wastes is the outstanding manifestation in this respect. Environmental pollution will cause direct damage and impact on the ecosystem, environmental problems have attracted much attention. Therefore, the search for biodegradable natural polymer materials has attracted much attention from all walks of life [1]. It is a hot topic [2] for modern membrane scientists to use biodegradable natural polymer materials instead of nonrenewable resources to fabricate membrane materials.

Cellulose is one of the most abundant natural macromolecule compounds in nature. It has a wide range of sources and is considered to be the main source of energy and chemical industry in the future. At present, environmental problems and energy problems are becoming more and more prominent in our country, and environmental friendly materials have become the goal that researchers in various fields pursue unremittingly. Cellulose has many advantages, such as cheap, easy to get, non-toxic, good regeneration, environmental friendly and so on. It plays an important role in solving environmental and energy problems. As the most abundant natural polymer on earth, cellulose is renewable, biodegradable, biocompatible, many attractive properties, and a wide range of chemical modification ability. Therefore, cellulose is considered as a sustainable raw material for the future energy chemical industry. Carboxymethyl cellulose (Carboxyl methyl cellulose, CMC) is also called modified cellulose [3]. CMC is one of the most widely used, inexpensive, non-toxic, biocompatible, biodegradable and hygroscopic derivatives in cellulose [4]. The morphology of CMC is a white fibrous or granular powder, with good biocompatibility, degradation and hygroscopicity. CMC has the properties of stabilizers, dispersants, adhesives, emulsifiers, thickeners, suspensions, sizing agents, etc., so in food, medicine, and so on, CMC has the properties of stabilizers, dispersants, adhesives, emulsifiers, thickeners, suspensions, sizing agents, etc. Daily chemical, petroleum, papermaking, textile, architecture and other fields of production have been widely used. The most important is its excellent film-forming and biodegradability, which is widely used [5].

Butyl titanate (Tetra-n-butyl Titanate) is also known as tetrabutyl titanate. It is colorless to light yellow liquid, flammable, low toxic, glass-like solid below -55℃, except ketones,dissolved in most organic solutions, rapidly absorb moisture and decompose in the air, have very high chemical activity to water.

During the crosslinking reaction, butyl titanate can improve the adhesion of the polymer and the adhesion of the system. Butyl titanate can cross-link the fiber membrane by solgel method, improve the water resistance of the fiber and realize the high dispersion of the fiber on the surface of the fiber membrane, and obtain the crosslinking modified composite fiber membrane [6]. Cellulose, as a kind of biodegradable renewable resource, has attracted great attention in many countries. The preparation, properties and application of cellulose based membrane materials have broad prospects. Using carboxymethyl cellulose as raw material, adding butyl titanate and combining with different cross-linking agents, the environmental protection film material [7] with excellent biodegradability was obtained.

In this experiment, carboxymethyl cellulose was used as the matrix, butyl titanate and different cross-linking agents were added to improve the crosslinking, then the film was prepared, and the mechanical test, infrared analysis, water absorption test and so on were carried out on the cross-linked composite membrane. The best cross-linking agent and its optimum proportion and technology were obtained. It provides a theoretical reference for the preparation of biodegradable environmental protection film materials.

MATERIALS AND METHODS

Raw materials and reagents

The main reagents and raw materials used in this experiment are sodium hydroxide from Tianjin Ketong Chemical Reagents Co., Ltd., urea from Nachuan Biotechnology Studio, and carboxymethyl cellulose from Tianjin Komeo Chemical Reagents Co., Ltd. As well as from Aladdin reagent company epichlorohydrin, butyl titanate and nano-SiO_2 and so on. 1.2 Test instrument and equipment experiment are magnetic heating mixer produced by Rong Hua instrument Manufacturing Co., Ltd in Jintan City, Jiangsu Province, electric heating constant temperature bath pot, electrothermal constant temperature incubator and vacuum drying box produced by Shanghai Yiheng Scientific Instruments Co., Ltd. CNC ultrasonic cleaning machine from Kunshan ultrasonic instrument co., Ltd., freeze dryer from Beijing Holos technology co., Ltd, electronic balance from Changshu scale instrument co., Ltd.

Preparation of Matrix

Water (H_2O): sodium hydroxide (NaOH): urea (Urea) = 200 g:15.1 g:8 g, and placed in the beaker of 250 mL, the NaOH/ urea solution system was prepared. Add 0.2g nano-SiO_2, under stirring condition to stir at room temperature for several hours, then ultrasonic 0.5h to make it evenly dispersed, then put the mixed solution into the refrigerator (-5 ℃) for 5 hours, and then add the mixed solution to the refrigerator for 5 hours, and then add the mixture solution to the refrigerator for 5 hours. Remove from refrigerator and thaw at room temperature for dissolving cellulose [8]. After thawing, take advantage of the low temperature, 3 wt% (7 g) Carboxymethyl cellulose was slowly added to the solution under stirring conditions and stirred for the night, then 2 ml of butyl titanate was added and fully stirred [9,10]. The composition of the matrix is shown in Table 1.

Table-1: Proportion of raw material composition of matrix

H_2O	NaOH	Urea	Nano-SiO_2	CMC	Butyl titanate
200.15 g	15.0 g	8.01 g	0.21 g	7.0 1 g	2 ml

Preparation of Citric Acid Solution

Three beakers were used to weigh the corresponding raw materials in the proportion of microcrystalline cellulose (MFC): citric acid (CA): trisodium citrate (TSC) = 1 : 0.5 : 0.5、1 : 1 : 1、1 : 1.5 : 1.5Citric acid solution of 4 % concentration was prepared [11,12]. The matching data are shown in Table 2.

Table-2: proportion of citric acid solution

No.	MFC : CA : TSC
1	1 : 0.5 : 0.5
2	1 : 1 : 1
3	1 : 1.5 : 1.5

Preparation of Membrane with Citric Acid Solution as Crosslinker

Take 15 portions of 30 g butyl titanate matrix and place them in a 50 ml beaker numbered 1 / 15 and then mix 1 citric acid solution 1 ml,2 ml,3 ml,4 ml,5 ml into 1,2,3,4,5 beaker. No. 2 citric acid solution 1 ml,2 ml,3 ml,4 ml,5 ml was dripped into 6,7,8,9, and No. 10 beaker was mixed. Citric acid solution No. 3 was used to drop 1 ml,2 ml,3 ml,4 ml,5 ml into beaker No. 11,12,13,14,15. The mixture was mixed in beaker No. 15. The mixture of citric acid solution No. 3 was mixed into beaker No. 11, 12, 13, 14. After mixing thoroughly for 0.5 h, the film was coated on the glass plate and then dried at 50 ℃ in an electrothermal incubator [13]. After drying, the film was weighed and photographed. The dried membrane is carefully removed for storage and used for performance testing.

Preparation of Membranes with Epichlorohydrin as Crosslinker

Take 5 portions of 30 g butyl titanate matrix and place it in a 50 ml beaker labeled 16、17、18、19、20, then pour epichlorohydrin 1 ml,2 ml,3 ml,4 ml,5 ml into 16,17,18,19,20 beakers and mix well for 0.5 h, using epichlorohydrin (epichlorohydrin) to drip into 16, 17, 18, 19, 20 beakers. Then spread the film on the glass plate and put it in an electrothermal constant temperature incubator for drying at 50 ℃. After drying, weighing and photographing were carried out. The dried membrane is removed and stored for subsequent performance testing.

PERFORMANCE TESTS

Determination of membrane strength

The tensile strength and deformation rate of butyl titanate/modified cellulose film were tested by the intelligent electronic tension tester of Jinan Languang Mechanical and Electrical Technology Co., Ltd. The long spline is the most commonly used type of specimen when the film is tested for tensile properties. When placing the specimen, it should be perpendicular to the fixture as far as possible, the specimen cannot be touched during the tensile test, and the tensile data should be carefully compared. The tensile strength of the film is an important index in the preparation of the film. According to the international measurement, the sample was prepared as a long spline with a test width of 15 mm, and a test length of 100 mm. The thickness of the film was measured at three points, the average value was taken, and the edges of the spline should be smooth. There are no gaps [14]. The tensile speed of the instrument is 25 mm/min. Record the machine reading, tensile strength σ, deformation rate ε. During the test, the distance between the clamps should be set to the standard distance of (100±5) mm, three times, and the average value should be taken.

Infrared Analysis of Film

Potassium bromide pressure plate transmission spectrometry is the most commonly used method for infrared spectrum analysis. Because KBr is not absorbed in infrared region, it is transparent, so KBr is the best carrier. Potassium bromide tablet method is simple to operate, suitable for solid powder samples. The chopped butyl titanate / cellulose film and potassium bromide solid were mixed and ground under the infrared lamp (generally 1 mg sample was added with 100 mg potassium bromide), the tablet was pressed, and then infrared scanning was carried out on the infrared instrument (Thermo Fisher Scientific). Scanning range is from 400~4000 cm^{-1}[15]. The ground powder should be as fine as possible to avoid scattering due to non-uniform particles. Grinding 5 minutes or so, press pressure of about15000 kg/cm^2, press time at least one minute. Grinding should be carried out under the infrared lamp, so that the powder is fully dried, and then pressed, otherwise it will absorb some water, there are water absorption peaks near 3300cm^{-1} and 1640cm^{-1}[16].

DISCUSSION AND ANALYSIS

After drying, the membrane of the substrate in the No. 3 beaker is the most complete and uniform, and the surface of the membrane is smoother, and the membrane has some elasticity and strength when stretched by hand. The membrane laid by the matrix in the No. 9 beaker is stretched by hand, although it has some elasticity and strength.

However, the forming of the film is not complete, and the thickness of the film is not uniform. The film formed by the matrix in other beakers is not ideal, and it is easy to break through by hand. The film of the matrix in the beaker labeled 17 is relatively complete with respect to 16 and 18, but the thickness is not very uniform and the surface of the membrane is not smooth either. Although the membrane is stretched by hand, it has some strength, but it is not elastic. From the mechanical data of the membrane, Look at the ratio of the substrate containing butyl titanate in No. 3 beaker to be MFC：CA：TSC=1：0.5：0.5. The mechanical test data of the membrane prepared by adding 3 ml citric acid solution as cross-linking agent is better than that of other citric acid solution with other proportion and amount of citric acid solution as cross-linking agent. From the infrared spectrum, there are obvious infrared peaks.

THE EFFECT OF CROSS-LINKING AGENT ON MECHANICAL PROPERTIES OF COMPOSITE FILM MATERIAL

Effect of Epichlorohydrin Content on Mechanical Properties

The mechanical test data of the film formed by adding epichlorohydrin as cross-linking agent can be found in Table 3. When the amount of epichlorohydrin (epichlorohydrin) is 1ml, the performance of the film is better than that of the other.

Table-3: Mechanical testing data of Butyl Titanate / Carboxymethyl Cellulose Composite Film with epichlorohydrin as Crosslinker

Epichlorohydrin content (mL)	Deformation rate (%)	Tensile strength (MPa)
1	42	1
2	4	2.76
3	17	0.79
4	15	0.58
5	12	0.32

With the increase of epichlorohydrin content, the elongation of the composite membrane decreases. When the dosage of 1ml was the highest, the elongation was the highest.

Effect of Ratio of Citric Acid Solution on Mechanical Properties

The mechanical test results of the film formed by adding citric acid solution as cross-linking agent are shown in Table 4 below. The performance of the membrane prepared by adding citric acid solution 3ml with no. 1 ratio is better than that prepared by adding other citric acid solution with other proportion and dosage.

Table-4: Mechanical testing data of Butyl Titanate / Carboxymethyl Cellulose Composite membrane with citric Acid solution as Crosslinker

No.	Deformation rate (%)	Tensile strength (MPa)
1	43	1.69
2	42	1.55
3	68	2.28
4	55	1.86
5	46	0.63
6	38	1.87
7	19	1.38
8	65	1.41
9	38	1.02
10	26	1.00
11	18	1.76
12	20	1.79
13	28	2.01
14	12	1.01
15	6	0.5

The elongation and tensile strength of the membrane with different proportion of citric acid solution were significantly different, and the elongation of the membrane increased with the increase of citric acid solution ratio. When the ratio is higher than a certain ratio, the tensile rate decreases obviously. The tensile strength decreased with the increase of citric acid solution. When the amount of citric acid solution increased to a certain value, the tensile strength increased obviously. After increasing to a certain value, the tensile strength of citric acid solution continued to increase, and the tensile strength decreased obviously. It can be seen that the best elongation and tensile strength can be obtained by adding citric acid solution 3 ml.

In conclusion, the elongation of the film formed by adding epichlorohydrin is obviously lower than that of the film formed by adding citric acid solution. The best cross-linking agent for the film-forming of the matrix containing butyl titanate is citric acid solution with the ratio of No. 1 and the best dosage is 3ml.

Infrared Spectral Analysis

The infrared analysis results of the composite films added with butyl titanate are shown in Fig. 1. The characteristic peaks of the films formed by different citric acid solution ratios are obviously different. Some of them have characteristic peaks of -OH, -C-O, and citric acid solution is added to carboxymethyl cellulose. The characteristic peaks show that there exists characteristic peaks of ester carbonyl groups, which indicates that there is cross-linking reaction between hydroxyl groups and citric acid in cellulose molecules. The ester group is formed.

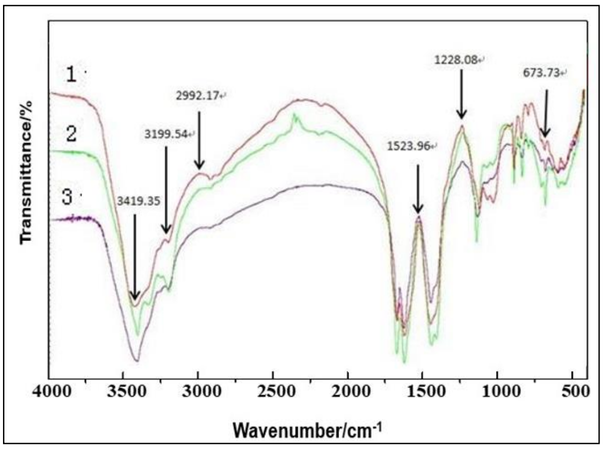

Fig-1: Infrared analysis of film

CONCLUSION

The composite membrane material with certain strength, butyl titanate can be blended with carboxymethyl cellulose and crosslinked with a certain proportion and amount of citric acid solution cross-linked with elastic composite membrane material. The best cross-linking agent for film formation was citric acid solution, and the optimum proportion of MFC:CA:TSC=1:0.5:0.5, was 3 ml. with the addition of butyl titanate as the film-forming agent. The elongation and tensile strength of the film formed by the addition of butyl titanate in the matrix were improved, and the performance of the film was better after the addition of butyl titanate. The optimum technological process of film formation is as follows: The urea solution system of NaOH/ was prepared with the ratio of H_2O: NaOH: Urea=200 g:15.1 g:8 g The mixture solution was frozen in refrigerator (-5 ℃) for 5 hour and thawed after adding 0.2 g nano-SiO_2,. Carboxymethyl cellulose of 3 wt% (7 g) was added to the solution and stirred for the whole night. Then 2 ml butyl titanate was added and fully stirred. A 4% citric acid solution was prepared by weighing the corresponding raw materials with the ratio of microcrystalline cellulose (MFC): citric acid (CA): trisodium citrate (TSC) = 1 : 0.5 : 0.5. The substrate containing 30 g of butyl titanate was dripped into citric acid solution of 3 ml, and the film was prepared.

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