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Improved process for the production of cellulose sulfate using sulfuric acid/ethanol solution

Guo Chen*, Bin Zhang, Jun Zhao, Hongwen Chen

Department of Biotechnology and Bioengineering, Huaqiao University, Xiamen 361021, PR China

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ABSTRACT

An improved process for production of cellulose sulfate (CS) was developed by using sulfuric acid/ethanol solution as sulfonating agent and Na_2SO_4 as water absorbent. The FTIR, SEM and TG analysis were used to characterize the CS prepared. The total degree of substitution and viscosity of the product solution (2%, w/v) were ranging from 0.28 to 0.77 and from 115 to 907 mPa s, respectively, by changing the process parameters such as the amount of Na_2SO_4, the reaction time, the temperature, the sulfuric acid/alcohol ratio and liquid/solid ratio. The results indicated that the product with DS (0.28–0.77) and $\eta_{2\%}$ (115–907) mPa s could be produced by using this improved process and more cellulose sulfate could be produced when cellulose was sulfonated for 3–4 h at −2 °C in sulfuric acid/ethanol (1.4–1.6) solution with addition of 0.8 g Na_2SO_4. The ^{13}C NMR indicated that the sulfate group of CS produced using sulfuric acid/ethanol solution was at *C*6 position.

1. Introduction

Cellulose sulfate (CS) is the derivative of cellulose with the hydroxyl groups (position 2, 3 and 6) in cellulose anhydroglucose unit (AGU) substituted by sulfate groups in partially or completely. Water-soluble cellulose sulfate (CS) is the material of choice for several medical and biotechnological applications because it is biocompatible and biodegradable (Xie, Wang, & Yao, 2009; Zhu, Lin, & Yao, 2010). Moreover, CS has great potential in broad-spectrum microbicides (Friend, 2010), drug delivery system (Wang, Xie, Chen, & Yao, 2010), anticoagulant agent (Wang, Li, Zheng, Normakhamatov, & Guo, 2007) and thickener (Yang, Ling, & Qu, 1988). It can also be used with polycation of poly-dimethyldiallyl-ammonium-chloride (PDMDAAC) or chitosan to prepare novel polyelectrolyte complex (PELC) membranes for salt rejection and vapor permeation (Chen, Yao, Fang, & Peng, 2007; Li & Yao, 2009), or microcapsules for the immobilization of micro-organisms (Liu, Ren, & Yao, 2010), enzymes (Vikartovska et al., 2007), and animal cells etc. (Stiegler et al., 2007).

At present, the preparation of NaCS primary includes homogeneous and heterogeneous processes. In traditional homogeneous process, the mixture N_2O_4/N,N-dimethylformamide (DMF) formed nitrite ester groups, and subsequently substituted by sulfate groups using SO_3 or chlorosulfonic acid as sulfonating agents (Schuldt, Wagenknecht, & Richter, 2002). It was not environment-friendly because of toxic solvent used. In a newly developed homogeneous process, cellulose was dissolved in ionic liquids, and then sulfonated by SO_3-pyridine complex. CS with DS ranging from 0.14 to 1.46 was prepared in BMIMCl/DMF (Gericke et al., 2009a, 2009b; Gericke et al., 2009). In heterogeneous process, CS was prepared in a mixture of isopropylalcohol and sulfuric acid as shown in Eq. (1) (Yao, 1999, 2000). The typical DS of CS was about 0.7. Compared to the homogeneous process, heterogeneous method is a direct cellulose sulfonating process. Although the acidic reaction conditions led to significant chain degradation and the various distribution of substituents, the simple and safe process without toxic reagents was an appealing process for industrial preparation of CS.

Propanol, which was used as the diluent in traditional heterogeneous processes, can decrease the carbonization of cellulose by decreasing the concentration of sulfuric acid. However, it is a low toxicity reagent with intense irritant smell, and will do harm to the human body and the environment. To overcome the problems of propanol, the cheap ethanol is used to replace the propanol in this work. Ethanol is the homologue of propanol, and is a non-toxic reagent. In addition, it is very easy to recycle by distillation. Hence, it is an ideal substitute of propanol in the heterogeneous process. The molecular weight is a very important characteristic of CS which affects the solubility, viscosity and antimicrobial. The serious degradation of cellulose, which results in the sharp decrease of product molecular weight, is another problem of the heterogeneous processes. In the reaction system, the hydrolysis of cellulose is due to the water produced in the esterification of alcohol with sulfuric acid and the cellulose sulfonating. Anhydrous Na_2SO_4 often used for the dehydration of organic solvents. Anhydrous sodium sulfate

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* Corresponding author. Tel.: +86 592 6166135.
E-mail addresses: chenguo@hqu.edu.cn, guochen1212@gmail.com (G. Chen).

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was added to the heterogeneous reaction system to timely remove the water generated, which did not introduce new impurity ions into system.

In this paper, an improved heterogeneous process was studied. CS was prepared by using the mixture of sulfuric acid/ethanol as sulfonating agent with addition of Na_2SO_4 as water absorbent. The FTIR was used to determine the groups of the product. The effect of process parameters on Ds (total degrees of substitution), $\eta_{2\%}$ (the kinematic viscosity of the 2% CS aqueous solutions), Y (yield) and X (percent conversion of cellulose) were evaluated as well.

2. Materials and methods

2.1. Materials

Native cotton with a cellulose content of 87–90% was purchased from Qipan Quilt Factory(Xiamen). Sulfuric acid (98%, pure), ethanol (>99.7%, pure) and anhydrous sodium sulfate were obtained from Sinopharm (China) Chemical Reagent Co., Ltd., sodium hydroxide was from Xilong (Shantou) Chemical Factory Co., Ltd., and deionized water was prepared in our laboratory. All other chemicals and reagents were analytical grade and used as received.

2.2. Process for the preparation of NaCS

NaCS was prepared by process of heterogeneous reaction. First, the cool down ethanol (4 °C) was dropped slowly into the sulfuric acid of −10 °C under slight stirring to reach completely mixing. A series of reaction solution with different molar ratio of sulfuric acid/ethanol (A/E = 1, 1.2, 1.4, 1.6, 1.8, 2 mol/mol) were prepared. And then, anhydrous sodium sulfate was added into a beaker containing 100 ml reaction solution with different sulfuric acid/ethanol molar ratio. Cotton as cellulose material was immersed in the reaction solution, which was sulfated at designed low temperature for a designed duration. The reaction solution was separated from solid sulfated cellulose by filtration and washed out with ethanol 90% at −10 °C. Afterwards, the product was solved in deionized water with vigorous stirring over a period of 30 min, and the PH value of the product solution was adjusted to 9.0 using 2 M sodium hydroxide solution. Finally, the NaCS solution was obtained by removing the insoluble residue through vacuum filtration, and the soluble NaCS was precipitated by industrial alcohol (95%). The NaCS was lyophilized to obtain the dry product.

A single factor method was used to investigate the preparation of NaCS with sulfuric acid and ethanol as sulfonating agent. The amount of sodium sulfate (0, 0.4, 0.8, 1.2, 1.6, 2.0 g/l reagent), the time of sulfation (2, 3, 4, 5 h), the reaction temperature (−4 °C, −2 °C, 0 °C, 2 °C), the sulfuric acid/ethanol molar ratio (A/E = 1, 1.2, 1.4, 1.6, 1.8, 2, 2.2 mol/mol) and the liquid/solid ratio (L/S = 20, 25, 30, 35, 40 g/g) were investigated, respectively.

2.3. Yield

The yield of product (Y) was determined as following: 5 ml (V_2) of product solution before sediment using ethanol was placed in a weighing bottle, and then dried to a constant weight at 105 °C in a vacuum oven. Afterwards, it was weighed (m_2). The yield was calculated according to Eq. (1):

$$Y = \frac{(m_2 - m_1) \times V_1/V_2}{M} \times 100 \qquad (1)$$

where m_1 is the initial weight of the empty bottle, V_1 is the total volume of product solution and M is the weight of the initial cellulose.

2.4. Conversion ratio of cellulose

The insoluble cellulose was collected and washed during the preparation of cellulose sulfate. Then it was dried to a constant weight at 105 °C, and weighed (m). The cellulose conversion ratio (X) was calculated according to Eq. (2):

$$X = \frac{M - m}{M} \times 100\% \qquad (2)$$

where M is the weight of the initial cellulose.

2.5. Kinematic viscosity

The kinematic viscosity of cellulose sulfate solutions (2%, w/v) was measured at 20 °C with Rotational Viscometer (NDJ-5S, Shanghai Fangrui Instrument Co., Ltd.).

2.6. Total degree of substitution

The contents of carbon (C%) and sulfur (S%) were determined by Elemental Analyzer Euro Vector EA3000 (Italy), and the total degree of substitution (DS) was calculated according to Eq. (3):

$$\mathrm{DS} = \frac{\mathrm{S}\%/32}{\mathrm{C}\%/72} \qquad (3)$$

2.7. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the cellulose and product prepared were recorded on an instrument (Shimadzu FTIR 8400S) in the wavenumber range of 4000–400 cm^{-1} with step size of 4 cm^{-1}. The samples were ground into powder by a fiber microtome and then blended with KBr followed by pressing the mixture into ultra-thin pellets.

2.8. SEM

The microstructure of cellulose and CS prepared was observed with a JSM-6400 scanning electron microscope (JEOL, Ltd., Tokyo, Japan). The samples were placed in an oven at 80 °C for a few days for dehydration. The dehydrated samples were then evenly distributed on SEM specimen stubs with double-sided adhesive tape and coated with a 10 nm gold layer.

2.9. Thermogravimetric analysis (TGA)

Thermal analysis was carried out by recording TG curve on a Perkin-Elmer thermogravimetric analyses equipment. Approximately 2 mg of each sample was heated from 30 °C to 800 °C at a heating rate of 10 °C/min. All of the measurements were performed under a nitrogen atmosphere with a gas flow of 20 ml/min in order to prevent any thermoxidative degradation.

2.10. ^{13}C NMR spectroscopy analysis

The ^{13}C NMR spectra were recorded at RT on Bruker 500 Avance spectrometer (Bruker, Etlingen, Germany) with a frequency of 120 MHz, 90° pulse length, 0.865 acq. time and a relaxation delay of 1.5 s. The scans of up to 3000 were accumulated and D_2O was used for dissolving cellulose sulfates. The signal integrals of the ‘substituted’ and ‘non-substituted’ C-atoms were compared.

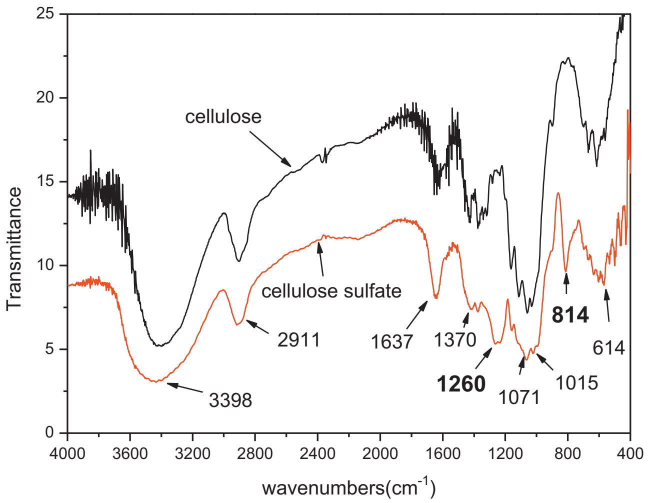


Fig. 1. FTIR spectra of cellulose and cellulose sulfate.

3. Results and discussion

3.1. Characteristics of cellulose sulfate

3.1.1. FTIR of cellulose sulfate

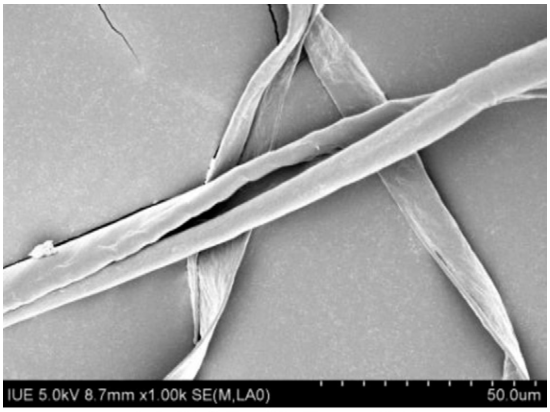
FTIR spectroscopy was used to confirm the structure of product prepared from the improved process. The IR spectra of native cellulose and CS prepared were shown in Fig. 1. The spectrum of native cellulose was in agreement with the study (Gumuskaya, Usta, & Kirci, 2003; Nazi, Malek, & Kotek, 2012; Qua, Hornsby, Sharma, & Lyons, 2011). The vibration band at 3398 cm^{-1} and 2911 cm^{-1} are assigned to the stretching of H-bonded OH groups and C—H stretching, respectively. The characteristic peak of the cellulose main structure was at 1637 cm^{-1}. The bending vibration at 1370 cm^{-1} belonged to the C—H deformation. The C—O stretching at C-3, C—C stretching and C—O stretching at C-6 was between 1060 cm^{-1} and 1073 cm^{-1}. In addition, the peak at 614 cm^{-1} related to the C—OH out-of-plane bending mode. Comparing the IR spectra of native cellulose and the product, there is no significant change at the main absorption bands of cellulose, such as 3398 cm^{-1}, 2911 cm^{-1} and 1637 cm^{-1} in the sulfonating process, which demonstrated that the product was the derivative of cellulose. However, two more peaks can be seen in the CS at 1260 cm^{-1} and 814 cm^{-1}, which belonged to S═O and C—O—S, respectively. Therefore, the product of this process was the cellulose sulfate.

3.1.2. SEM of cellulose sulfate

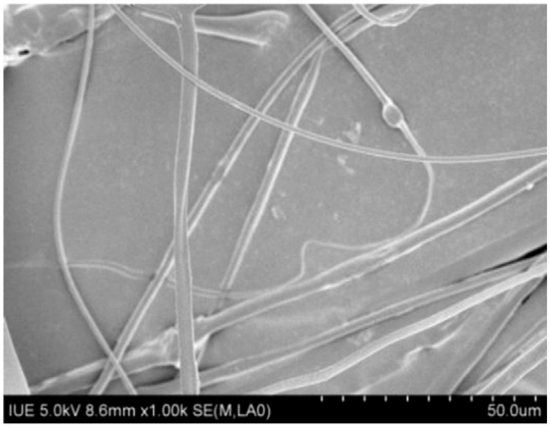
SEM photographs of native cotton cellulose and CS fiber were captured in Fig. 2(a and b). The surface topology of cellulose before and after sulfonating was found to be even, but the width of CS fiber decreased dramatically, compared with the cellulose untreated, which may be due to the amorphous region of cellulose destroyed by the acid hydrolysis.

3.1.3. Thermogravimetric analysis

The bond energy of cellulose will change after chemical modification of cellulose. The thermal stability was recorded by TGA and DTG analysis in Fig. 3. The CS had good thermal stability as cellulose, because there was no decomposition under 190 °C and the loss of gravity between 0 and 100 °C could be assigned to the water loss. The thermal decomposition temperature of CS was 242 °C, far lower than 325 °C of cellulose, which was caused by the ordered structure destroyed during the sulfonating. According to Fig. 3, a peak at 710 °C was the cleavage of —SO_3Na in cellulose sulfate, which further indicated the successful preparation of CS.



(a) Cellulose before sulfation



(b) Cellulose after sulfation for 3 hours

Fig. 2. SEM of cellulose before and after sulfation for 3 h (1000× times).

3.1.4. Characterization of substitution pattern

The pattern of sulfating in cellulose sulfates was analyzed via ^{13}C NMR spectroscopy. Fig. 4 shows the ^{13}C NMR spectrum of CS, and in the spectrum the chemical shifts of C1–C6 of cellulose were at 102.4, 73.9, 72.9, 78.4, 77.4 and 59.9 ppm, respectively (Wang et al., 2007). After the sulfating of cellulose, a new peak, of which the intension was almost equal to the peak of C6, was appeared at 66.1 ppm, which indicated that nearly half of the —OH groups at *C6* position were sulfated. In addition, the peaks of C1–C5 of cellulose in the spectrum were almost not change after sulfating, which indicated that the sulfating of —OH groups at C2 and C3 were rarely take place. Thus, the sulfate group of CS which produced using heterogeneous method in sulfuric acid/ethanol solution was at *C6* position.

3.2. The effects of conditions on CS preparation

3.2.1. Effect of Na_2SO_4

Anhydrous Na_2SO_4 used as the water absorbent could timely remove the water in the reaction. The influences of Na_2SO_4 on the Ds and $\eta_{2\%}$ of CS, yield (Y) and conversion ratio (X) were investigated under other condition of $t = 5$ h, $T = -5$°C, $A/E = 1.4$, and $L/S = 20$. It can be seen in Table 1 that the $\eta_{2\%}$ showed a sharp increase with the increasing amount of Na_2SO_4 and finally reached to the maximum of 400 Pa m s^{-1} at 0.8 g Na_2SO_4. The viscosity of CS primarily depends on the substitute and length of cellulose chain. That the DS of product was around 0.4 and varied slightly with the addition of Na_2SO_4, indicated that the addition of Na_2SO_4 had minor effect on sulfonating. Therefore, the molecular weight (Mw) of product increased with the addition of Na_2SO_4 in process,

Table 1
The effect of conditions on properties of CS and production yield.

Reaction condition					DS	$\eta_{2\%}$ (mPa s)	Yield (%)	Conv. ratio (%)
Na_2SO_4 (g/l)	Time (h)	Temp. (°C)	A/E (mol/mol)	L/S (g/g)				
0	5	−5	1.4	20	0.39 ± 0.02	218 ± 11	90.9 ± 4.5	81.2 ± 4.1
0.4					0.43 ± 0.02	200 ± 10	88.0 ± 4.3	76.4 ± 3.8
0.8					0.43 ± 0.02	668 ± 33	84.0 ± 4.1	80.6 ± 4.0
1.2					0.54 ± 0.02	453 ± 23	84.0 ± 4.2	80.6 ± 4.0
1.6					0.44 ± 0.02	424 ± 21	91.4 ± 4.4	80.6 ± 4.0
2					0.46 ± 0.02	437 ± 22	72.5 ± 3.6	71.4 ± 3.6
1.2	2	−5	1.4	20	0.29 ± 0.02	775 ± 39	52.0 ± 2.6	42.4 ± 2.1
	3				0.46 ± 0.02	907 ± 45	59.7 ± 3.0	50.2 ± 2.5
	4				0.50 ± 0.02	514 ± 26	79.8 ± 4.6	72.6 ± 3.6
	5				0.54 ± 0.02	453 ± 23	84.0 ± 4.2	80.6 ± 4.0
1.2	5	−4	1.4	20	0.54 ± 0.03	453 ± 23	84.0 ± 4.2	80.6 ± 4.0
		−2			0.72 ± 0.04	418 ± 21	97.0 ± 4.9	81.0 ± 4.0
		0			0.64 ± 0.03	367 ± 18	110.6 ± 5.8	94.4 ± 4.5
		2			0.77 ± 0.04	115 ± 6	99.2 ± 5.0	98.0 ± 4.9
1.2	5	−5	1.2	20	0.37 ± 0.02	516 ± 26	11.4 ± 0.6	6.8 ± 0.3
			1.4		0.54 ± 0.03	453 ± 23	84.0 ± 4.2	80.6 ± 4.0
			1.6		0.60 ± 0.03	397 ± 20	118.7 ± 6.0	95.4 ± 4.8
			1.8		0.62 ± 0.03	264 ± 13	123.6 ± 6.2	97.8 ± 4.8
1.2	5	−5	1.4	20	0.54 ± 0.03	453 ± 23	84.0 ± 4.2	80.6 ± 4.0
				25	0.63 ± 0.03	476 ± 24	99.2 ± 5.0	75.2 ± 3.8
				30	0.55 ± 0.03	404 ± 20	94.7 ± 4.7	71.8 ± 3.6
				35	0.59 ± 0.03	262 ± 13	101.8 ± 5.1	71.4 ± 3.6
				40	0.58 ± 0.03	257 ± 13	90.2 ± 4.5	70.0 ± 3.5

because the Na_2SO_4 could decrease the hydrolysis of cellulose chain by removing the water in the reaction system. From Table 1, the *Y* and *X* was about 90% and 80% respectively. This experiment indicated that the Na_2SO_4 influenced the reaction process by decreasing the hydrolysis of cellulose. According to Table 1, the addition of 0.8 g Na_2SO_4/l was optimum for the production of CS with highest molecular weight.

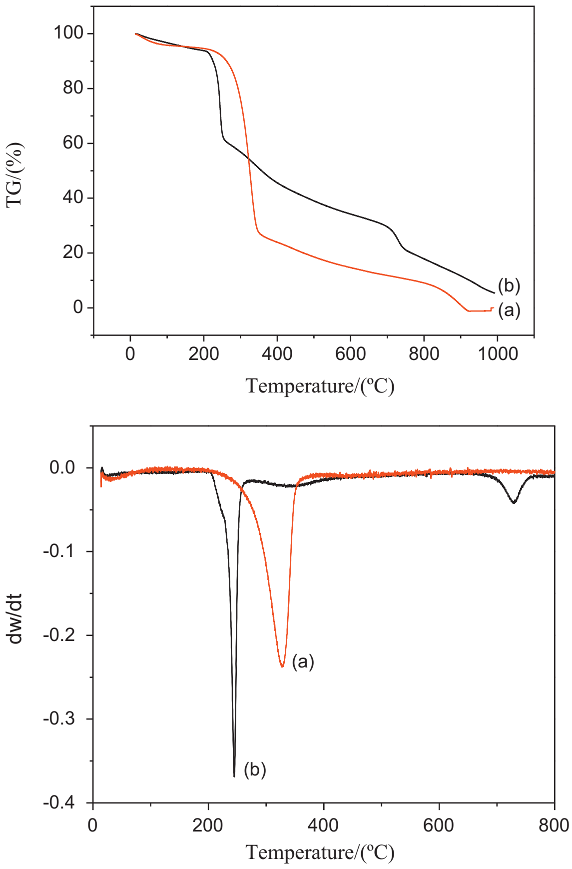


Fig. 3. TGA and DTG curves of (a) raw cellulose; (b) cellulose sulfate.

3.3. *Effect of reaction time*

In the process of cellulose sulfonating, some undesired reactions such as carbonization and hydrolysis often take place. However, the main undesired reactions were mutative at the different stage of reaction. The influences of reaction time on the DS and $\eta_{2\%}$ of CS, *Y* and *X* were studied under the condition of $Na_2SO_4 = 1.2$ g/l, $T = -5$°C, $A/E = 1.4$ and $L/S = 20$. As shown in Table 1, the time has significant influence on the preparation of CS. The DS and $\eta_{2\%}$ of product increased from 0.29 and 775 Pa m s^{-1} up to 0.46 and 907 Pa m s^{-1} respectively with the increasing of reaction time, because cellulose sulfonating was prime and rapid at initial. However, the increase of DS gradually mitigated and the $\eta_{2\%}$ exhibited a rapid decrease with the prolonged reaction time over 3 h, because the sulfonating rate slowed down and the hydrolysis rate increased due to the water produced in the process. From Table 1, the *Y* and *X* increased gradually from 52% and 42%g to 84% and 81%, respectively. The results indicated that the reaction time could affect the *Y*, *X*, DS and Mw of product thoroughly. The optimum reaction time was 4 h on comprehensive consideration of *Y*, *X*, DS and Mw of the product.

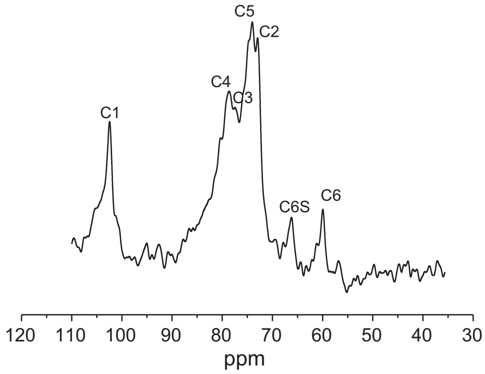


Fig. 4. ^{13}C NMR spectra of cellulose sulfate prepared.

3.4. Effect of reaction temperature

The acid treatment of cellulose is sensitive to the change of temperature. The influences of temperature on the DS and $\eta_{2\%}$ of CS, Y and X were investigated in the condition of $Na_2SO_4 = 1.2$ g/l, $t = 5$ h, $A/E = 1.4$, and $L/S = 20$. The effect of temperature on the reaction was significant as shown in Table 1. As the temperature increasing, the $\eta_{2\%}$ of product decreased sharply, and the DS increased except a slight decrease at the temperature from −2 °C to 0 °C. With the reaction proceeding, physical swelling (acid intrusive and destruct the crystal structure of cellulose) in the acid treatment of cellulose took place in the amorphous region of cellulose and aggravated by increasing temperature during cellulose sulfonating companied by hydrolysis. The swelling would destruct and expose the internal structure of cellulose chain to sulfuric acid, which increased the cellulose sulfonating. The swelling appearing in the crystalline region of cellulose caused severe damage of cellulose if the temperature elevated continuously, which resulted in the increase of DS and the sharp decrease of Mw with temperature as shown in Table 1. The Y increased sharply with temperature at the beginning, and then reached a maximum value. The X increased with the temperature increasing. The increase of Y and X primarily lied in that the high temperature promoted the reaction rate of cellulose sulfonating and hydrolysis, which increased the water-solubility of cellulose. The CS could not be precipitated if the cellulose chain was too short due to the excessive cellulose hydrolysis. The results indicated that −2 °C was the optimal temperature from the product performance and process cost.

3.5. Effect of sulfuric acid/ethanol

Ethanol was used as diluent to decrease the sulfuric acid concentration in the system, accordingly the carbonization was avoided and reduced greatly. However, the low concentration of sulfuric acid would retard the cellulose sulfonating. The influences of A/E (sulfuric acid/ethanol) on the Ds, $\eta_{2\%}$ of CS, Y and X were investigated under the conditions of $Na_2SO_4 = 1.2$ g/l, $t = 5$ h, $T = -5$ °C and $L/S = 20$. The A/E ratio of 1, 1.2, 1.4, 1.6 and 1.8 were chosen to investigated in Table 1. The CS hardly obtained at the A/E below 1.2. However, the DS of product, Y and X increased significantly and the $\eta_{2\%}$ decreased sharply with the increase of A/E from 1.2 to 1.8. It indicated that the cellulose sulfonating was affected by the concentration of sulfuric acid in the system and the suitable sulfuric acid concentration range was quite narrow. The cellulose sulfonating almost did not take place at the lower A/E according to the value of Y and X. However, the higher A/E would lead to serious damage of cellulose structure and hydrolysis of cellulose. Too much sulfuric acid would result in the carbonization. The dilution effect of ethanol on the sulfuric acid indicated that the optimal A/E was 1.4.

3.6. Effect of liquid/solid ratio

The high L/S ratio will lead to the waste of reagent, though it is efficient to improve the contact of sulfuric acid and cellulose by increasing the ratio of L/S. In order to make the rational utilization of reagent, the influences of L/S on the Ds and $\eta_{2\%}$ of CS, Y and X were investigated under the condition of $Na_2SO_4 = 1.2$ g, $t = 5$ h, $T = -5$ °C, and $A/E = 1.4$. The cotton could just be completely immersed by the reaction solution at the minimum L/S ratio of 20. From Table 1, the $\eta_{2\%}$ and DS increased with the increasing of L/S below 25, thereafter began decreasing. When the L/S was over 30 and 35, the DS and $\eta_{2\%}$ became steady, respectively. The cellulose and cellulose ester hydrolysis would take place at excess of liquid reagent in system, which would resulted in the decrease of DS and Mw. The influence of L/S on the reaction was less significant than that of the time and temperature. The experiment indicated that L/S ratio of 25 was optimal for the sulfonating process.

Cellulose can be esterified with inorganic sulfuric acid in the presence of 1-butanol, n-propanol or isopropyl, the degrading action of the sulfuric acid decreases and the product does not dissolve in the reaction liquor. In our research, the cheap and environmentally friendly reaction solution composed of sulfuric acid and ethanol was used. The product was green and no toxic agents were introduced in reaction. The CS with DS (0.28–0.77) and $\eta_{2\%}$ (115–907) mPa s could be obtained by regulating the reaction condition. The conversion of cellulose and the yield of CS was higher than that in sulfuric acid/n-propanol system. Yao (2000) used the reaction solution containing 31.5% sulfuric acid solution in n-propanol to produce the CS with linters/reaction solution (1/20, g/g) at −5 °C. The conversion ratio of linters was 50.6% and the yield of CS with a DS of 0.396 was 63.3%. A water-soluble cellulose sulfate ester with a DS of 0.392 was also obtained by Neetu Bhatt, Gupta, and Naithani (2008) at a reaction time of 60 min, a temperature 0 °C, a normality of 34.2 N aqueous sulfuric acid, 33% 1-butanol, and a quantity of aqueous sulfuric acid of 40 ml/g of a-cellulose. The viscosity of produced CS solution (2.0%, w/v) was 625 mPa s at a temperature of 25 °C.

4. Conclusion

In this study, the CS was successfully prepared by the improved heterogeneous process with sulfuric acid/ethanol solution as a novel sulfonating agent and anhydrous sodium sulfate as water absorbent. The improved process was more inexpensive and environmentally friendly, which could be applied to the scale production of CS instead of traditional sulfuric acid/N-propanol system. The CS prepared was characterized by FTIR, SEM and TGA. The DS and Kinematic viscosity ($\eta_{2\%}$) of the CS can be controlled in the range of 0.28–0.77 and 115–907 mPa s, respectively, by changing the reaction condition. The results indicated that the reaction time and temperature were both the primary factors in cellulose sulfating. The ratios of the sulfuric acid/ethanol and liquid/solid would affect the process prominently when they were changed within a narrow range. The optimum reaction condition was determined as following: 25 g liquid/g cotton, addition of 0.8 g Na_2SO_4/L reagent, 1.4–1.6 mole sulfuric acid/mole ethanol, reacting for 3–4 h, at the temperature of −2 °C. The 13C NMR indicated that the sulfate group of CS produced using sulfuric acid/ethanol solution was at *C*6 position.

Acknowledgements

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References

Chen, G., Yao, S. J., Fang, B. S., & Peng, Y. Q. (2007). Effect of additives on characteristics of polyelectrolyte complex membrane and exploration of related mechanism. *Acta Physico-Chimica Sinica*, *23*(9), 1415–1420.

Friend, D. R. (2010). Pharmaceutical development of microbicide drug products. *Pharmaceutical Development and Technology*, *15*(6), 562–581.

Gericke, M., Liebert, T., & Heinze, T. (2009a). Interaction of ionic liquids with polysaccharides, 8-synthesis of cellulose sulfates suitable for polyelectrolyte complex formation. *Macromolecular Bioscience*, *9*(4), 343–353.

Gericke, M., Liebert, T., & Heinze, T. (2009b). Polyelectrolyte synthesis and in situ complex formation in ionic liquids. *Journal of the American Chemical Society*, *131*(37), 13220.

Gericke, M., Schlufter, K., Liebert, T., Heinze, T., & Budtova, T. (2009). Rheological properties of cellulose/ionic liquid solutions: from dilute to concentrated states. *Biomacromolecules*, *10*(5), 1188–1194.

Gumuskaya, E., Usta, M., & Kirci, H. (2003). The effects of various pulping conditions on crystalline structure of cellulose in cotton linters. *Polymer Degradation and Stability*, *81*(3), 559–564.

Li, M. M., & Yao, S. J. (2009). Preparation of polyelectrolyte complex membranes based on sodium cellulose sulfate and poly(dimethyldiallylammonium chloride) and its permeability properties. *Journal of Applied Polymer Science*, *112*(1), 402–409.

Liu, J. F., Ren, Y. R., & Yao, S. J. (2010). Repeated-batch cultivation of encapsulated monascus purpureus by polyelectrolyte complex for natural pigment production. *Chinese Journal of Chemical Engineering*, *18*(6), 1013–1017.

Nazi, M., Malek, R. M. A., & Kotek, R. (2012). Modification of beta-cyclodextrin with itaconic acid and application of the new derivative to cotton fabrics. *Carbohydrate Polymers*, *88*(3), 950–958.

Neetu Bhatt, P. K., Gupta, & Naithani, S. (2008). Preparation of cellulose sulfate from a-cellulose isolated from lantana camara by the direct esterification method. *Journal of Applied Polymer Science*, *108*, 2895–2901.

Qua, E. H., Hornsby, P. R., Sharma, H. S. S., & Lyons, G. (2011). Preparation and characterisation of cellulose nanofibres. *Journal of Materials Science*, *46*(18), 6029–6045.

Schuldt, U., Wagenknecht, W., & Richter, A. (2002). Electrosorption of sodium cellulose sulfates with different substitution patterns. *Cellulose*, *9*(3/4), 271–282.

Stiegler, P. B., Stadlbauer, V., Schaffellner, S., Lackner, C., Iberer, F., & Tscheliessnlgg, K. (2007). Sodium cellulose sulfate (NaCS) as a novel method for microencapsulation of pancreatic cells. *Transplant International*, *20*, 168–168.

Vikartovska, A., Bucko, M., Mislovicova, D., Patoprsty, V., Lacik, I., & Gemeiner, P. (2007). Improvement of the stability of glucose oxidase via encapsulation in sodium alginate-cellulose sulfate-poly(methylene-co-guanidine) capsules. *Enzyme and Microbial Technology*, *41*(6/7), 748–755.

Wang, M. J., Xie, Y. L., Chen, Z. J., & Yao, S. J. (2010). Optimizing preparation of NaCS-chitosan complex to form a potential material for the colon-specific drug delivery system. *Journal of Applied Polymer Science*, *117*(5), 3001–3012.

Wang, Z. M., Li, L., Zheng, B. S., Normakhamatov, N., & Guo, S. Y. (2007). Preparation and anticoagulation activity of sodium cellulose sulfate. *International Journal of Biological Macromolecules*, *41*(4), 376–382.

Xie, Y. L., Wang, M. J., & Yao, S. J. (2009). Preparation and characterization of biocompatible microcapsules of sodium cellulose sulfate/chitosan by means of layer-by-layer self-assembly. *Langmuir*, *25*(16), 8999–9005.

Yang, K. X., Ling, X. Q., & Qu, T. Z. (1988). Influences of external salt on the solution viscosity of sodium-cellulose sulfate half-ester. *Acta Physico-Chimica Sinica*, *4*(5), 523–526.

Yao, S. J. (1999). Sulfation kinetics in the preparation of cellulose sulfate. *Chinese Journal of Chemical Engineering*, *7*(1), 47–55.

Yao, S. J. (2000). An improved process for the preparation of sodium cellulose sulphate. *Chemical Engineering Journal*, *78*(2–3), 199–204.

Zhu, L. Y., Lin, D. Q., & Yao, S. J. (2010). Biodegradation of polyelectrolyte complex films composed of chitosan and sodium cellulose sulfate as the controllable release carrier. *Carbohydrate Polymers*, *82*(2), 323–328.