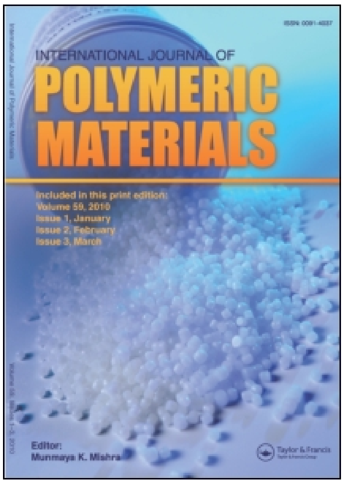

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Optimization of a process for carboxymethyl cellulose (CMC) preparation in mixed solvents

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OPTIMIZATION OF A PROCESS FOR CARBOXYMETHYL CELLULOSE (CMC) PREPARATION IN MIXED SOLVENTS

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A benzene–ethanol–water mixture was investigated as the solvent medium in synthesizing carboxymethyl cellulose (CMC). The process of carboxymethylation was optimized to produce CMC with DS > I.0, solution viscosity about 1500 mpa·s, and with uniform distribution of substituents. It is possible to scale up this process by using a kneading machine.

Keywords: carboxymethyl cellulose (CMC), degree of substitution (DS), uniform substituents

INTRODUCTION

Carboxymethyl cellulose (CMC) is an important cellulose derivative that possesses many attractive properties, such as emulsification, filming, inspissation, suspension, and bind, etc. Therefore, CMC has been widely used in many industrial areas such as textile finishing, food, medicine, dyeing, electrical elements, and papermaking, etc. Recent research [1] also found its application as a new heterobifunctional ligand carrier for affinity precipitation of proteins. Physical and chemical properties of CMC are mainly determined by the degree of substitution (DS), distribution of substituents and degree of polymerization. Among these

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properties, the DS and homogeneity of substituent distribution along CMC chains have greater influence on the solubility, shearing stability and rheological behavior of CMC solution and its stability against temperature and low molecular additives [2]. The preparation of CMC has been studied for many years since 1910's [3] and was industrialized in the 1940s. However, due to the crystalline structure in the cellulose, preparations of CMC with high DS, high solution viscosity and homogeneous distribution are quite difficult. Recent report [4] shows that a maximum DS of 0.68 was obtained with isopropyl alcohol as the solvent medium. Our previous research [5–7] indicates that CMC produced in the benzene–ethanol–water solvent medium could achieve a high DS and uniform distribution of substituents along CMC chains.

In the present work, CMC with high DS, high solution viscosity and homogeneous distribution of substituents was achieved by using a mixed solvent (benzene–ethanol–water) to destroy and transform the internal crystalline structure in cellulose. The easy scaled-up experimental equipment, kneading machine, was used and several reaction conditions were optimized.

EXPERIMENTAL

Preparation of CMC

100 g cotton linters and 320 g mixture of benzene and 95% ethanol were added to a horizontal kneading machine. Stirred and scissored at room temperature (25°C) for 5 minutes, followed by adding NaOH solution. At least 30 minutes later, monochloroacetic acid was added. The reaction proceeded at 50–60°C for at least 15 minutes and was terminated by dropping acetic acid until pH 7–8. The product was washed with 80% methanol until Cl^- could not be detected by $AgNO_3$ solution. White powder was obtained after drying and crushing.

Analysis of DS and Solution Viscosity

The DS of the prepared CMC was determined by standard method [8]. CMC sample was washed several times with ethanol to remove salts. After firing at high temperature, the organic substances of CMC were removed while sodium oxide remained. The quantity of Na^+ of the remainder could be determined by titration, and the average DS of CMC was calculated.

$$DS = \frac{0.162A}{1 - 0.058A}$$

where A is the equivalent weight of alkali required per gram of sample.

The viscosity of 2%(wt) CMC water solution was obtained by rotational viscometer at room temperature and used as the characteristic viscosity parameter of CMC.

RESULTS AND DISCUSSION

Effect of Solvents and Their Mixing Ratio

The effect of the ratio of solvents on the DS and solution viscosity is shown in Figure 1. The DS increases with the benzene content in the mixed solvent, and the viscosity increases to maximum value at $C_6H_6/C_2H_5OH(wt) = 1.0$. The role of the solvent in the carboxymethylation reaction is to provide accessibility of the etherifying reagent to the reaction centers of cellulose chains [9]. In this research, benzene mainly adjusts the polarity of the solvent system. The lower polarity was achieved with the increasing percentage of benzene, which tends to decrease the accessibility of solvents and NaOH to the cellulose chains. However, in lower polar solvents, the solvation of the Na^+ decreases which makes it easier for the hydrated Na^+ to access the cellulose chains and break the crystalline structure. This improved accessibility of the solvents and the etherifying reagent into cellulose increases the reaction rate, and thus increases the DS and solution viscosity of CMC. The viscosity of CMC solution decreases at high

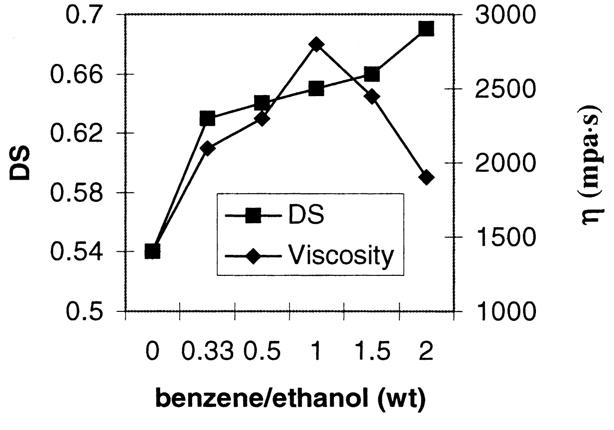

FIGURE 1 Effect of the ratio of the medium on DS and η. (Reaction conditions: Cellulose/solvents (wt) = 1:3.2, NaOH/AGU (mol) = 2:1 [AGU stands for anhydroglucose unit], $ClCH_2COOH$/AGU (mol) = 1:1, Alkalization time: 1 hour, Etherifying time: 1 hour).

C_6H_6/C_2H_5OH(wt) ratio because when more etherifying reagent permeates into the cellulose, the cellulose chains will break down and the resulting CMC has a smaller average molecular weight.

The microstructures of CMC produced with and without benzene are shown in Figures 2 and 3 respectively through Scanning Electron Micrograph. Although these two samples have the same DS (0.83), the crystalline structure in CMC synthesized with benzene was seriously destroyed and the CMC chains were obviously swelled by the solvents. This is a possible reason the benzene–ethanol–water medium could improve the DS and the uniformity of the distribution of the substituents. The NMR and X-ray diffraction results in our previous

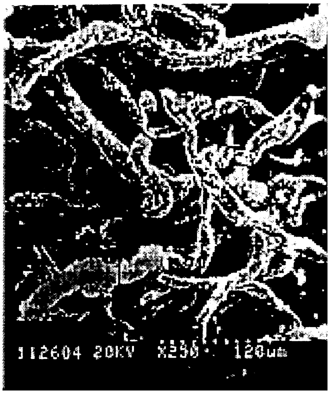

FIGURE 2 Scanning electron micrography of CMC produced with benzene.

FIGURE 3 Scanning electron micrography of CMC produced without benzene.

studies [5–7] indicate that the uniform distribution of the substituents could be achieved by using benzene–ethanol–water medium.

Effect of Alkali Concentration

Using benzene and 95% ethanol as the solvent medium, the effects of alkali concentration for steeping α-cellulose on the DS and solution viscosity were studied (Figure 4).

It was observed that both the degree of substitution and the solution viscosity increased by increasing sodium hydroxide concentration and reached a maximum, and thereafter declined with the alkali concentration. The carboxymethylation process involves two competing reactions that take place simultaneously [10]. The first reaction is between cellulose and monochloroacetic acid in the presence of alkali:

$$\begin{aligned} &\text{Cell-OH} + \text{ClCH}_2\text{COOH} + 2\text{NaOH} \\ &\quad \longrightarrow \text{Cell-OCH}_2\text{COONa} + \text{NaCl} + 2\text{H}_2\text{O} \end{aligned} \tag{1}$$

The second one is the reaction of sodium hydroxide with monochloroacetic acid to form sodium glycollate:

$$\text{ClCH}_2\text{COOH} + 2\text{NaOH} \longrightarrow \text{HOCH}_2\text{COONa} + \text{NaCl} + \text{H}_2\text{O} \tag{2}$$

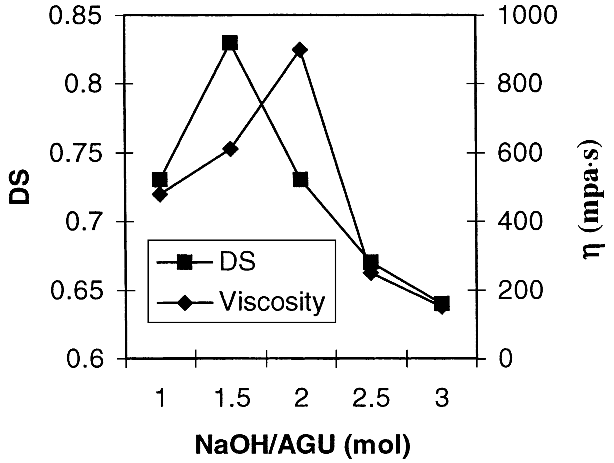

FIGURE 4 Effect of alkali concentration on DS and η. (Reaction conditions: Cellulose/solvents (wt) = 1:3.2, C_6H_6/C_2H_5OH(wt) = 1:3, $ClCH_2COOH$/AGU (mol) = 1:1, Alkalization time: 1 hour, Etherifying time: 1 hour).

The first reaction seems to prevail up to a certain NaOH concentration. Above this concentration, the second reaction predominates with the formation of a larger amount of sodium glycollate, which decreases the DS. A similar case was observed for the carboxymethylation of maize starch [11]. Also at higher concentration of sodium hydroxide, more cellulose chains were broken and the average molecular weight decreased, which decreases the solution viscosity of CMC after a certain NaOH concentration.

Effect of Alkalization Time

Experimental results (in Figure 5) show that the degree of substitution decreases with alkalization time and reaches a minimum value, thereafter increases. The viscosity data, however, show an opposite tendency that increases up to a certain alkalization time and then decreases.

X-ray diffraction results of alkali cellulose produced in different alkalization times are presented in Figure 6. This figure indicates that more crystalline structures were destroyed or transformed when the alkalization time was increased. The swelled cellulose chains during the alkalization process contribute to the increase of solution viscosity. However, if the alkalization time is so long that the cellulose

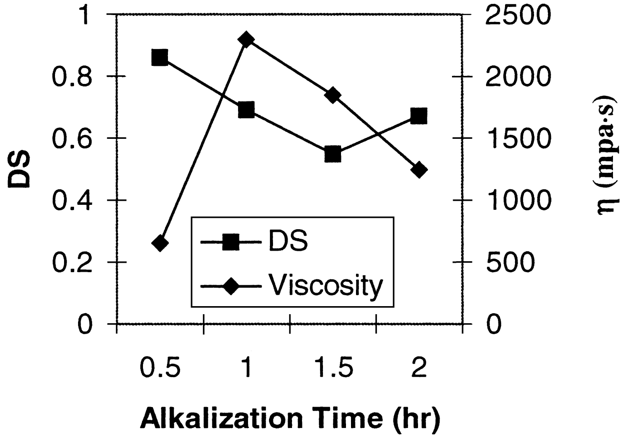

FIGURE 5 Effect of alkalization time on DS and η. (Reaction conditions: Cellulose/solvents (wt) = 1:3.2, C_6H_6/C_2H_5OH(wt) = 1:3, NaOH/AGU (mol) = 2:1, $ClCH_2COOH$/AGU (mol) = 1:1, Etherifying time: 1 hour).

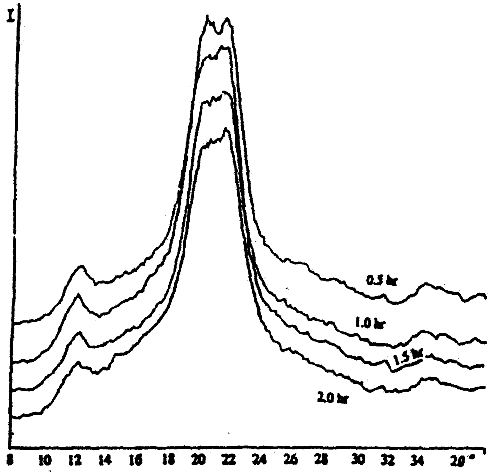

FIGURE 6 X-ray diffraction for alkali cellulose produced in different alkalization times.

chains are degraded, the viscosity of CMC solution will decrease eventually.

Although increasing alkalization time is beneficial for the formation of reaction centers, more water is also produced during this alkalization process, which will decrease the utilization efficiency of monochloroacetic acid and therefore decrease the degree of substitution. But if the alkalization time is extended further, more crystalline structure would be destroyed and more monochloroacetic acid molecules can diffuse into the alkali cellulose. Therefore, the degree of substitution increases after a certain alkalization time.

Effect of Monochloroacetic Acid Concentration

In order to keep the alkali environment in the reaction system, NaOH solution was added the second time with equivalent moles of etherifying reagent before the excess monochloroacetic acid was added. Experimental data show that the DS increases with the monochloroacetic acid concentration, while the solution viscosity decreases (Figure 7).

CMC samples produced in different concentrations of etherifying reagent were analyzed by X-ray diffraction and shown in Figure 8. When the monochloroacetic acid concentration is increased, especially when $ClCH_2COOH/AGU$ (mol)>1.0, the Cell-II structure is seriously

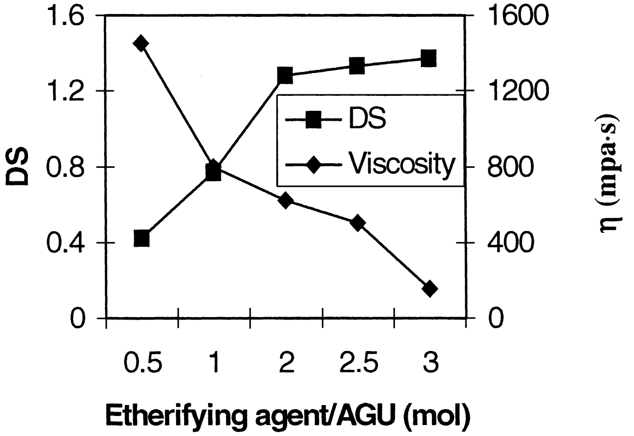

FIGURE 7 Effect of etherifying reagent concentration on DS and η. (Reaction conditions: Cellulose/solvents (wt) = 1:3.2, C_6H_6/C_2H_5OH(wt) = 1:3, NaOH/AGU (mol) = 2:1, Alkalization time: 1 hour, Etherifying time: 1 hour).

destroyed and almost becomes amorphous. This improves the diffusion efficiency of the etherifying reagent and therefore increases the degree of substitution. The solution viscosity decreases with increasing concentration of etherifying reagent because the added excess NaOH in this process obviously increases the alkali concentration and seriously degrades the cellulose chains.

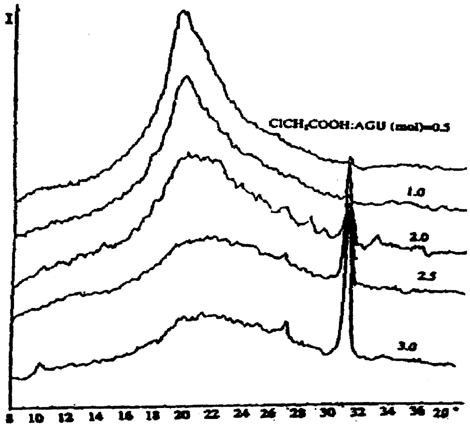

FIGURE 8 X-ray diffraction for CMC in different concentration of etherifying reagent.

Effect of Etherifying Time

The degree of substitution increases with increasing etherifying time and the solution viscosity increases first up to a certain etherifying time and thereafter decreases (shown in Figure 9).

At the first half hour, with the increase of carboxymethylation time, plenty time was provided for the etherifying reagent to diffuse into the alkali cellulose and the utilization efficiency of monochloroacetic acid was increased, therefore the DS and solution viscosity increase with the etherifying time. However, with further extension of the etherifying time, $^-CH_2COONa$ groups already in the cellulose will repel the further diffusion of Na^+, OH^- and $ClCH_2COO^-$, which results in almost no change of the DS during this period. But the cellulose chains are destroyed and the average molecular weight of CMC decreases during this period, decreasing the solution viscosity. But in a longer etherifying time, more crystalline structure could be destroyed and the DS is expected to increase.

Optimization of Reaction Conditions

An ideal CMC product is one with high degree of substitution, high solution viscosity and uniform distribution of substituents. Based on the previous analysis of reaction conditions, an optimum process was generalized in an overall consideration: $C_6H_6/C_2H_5OH(wt) = 1:1$;

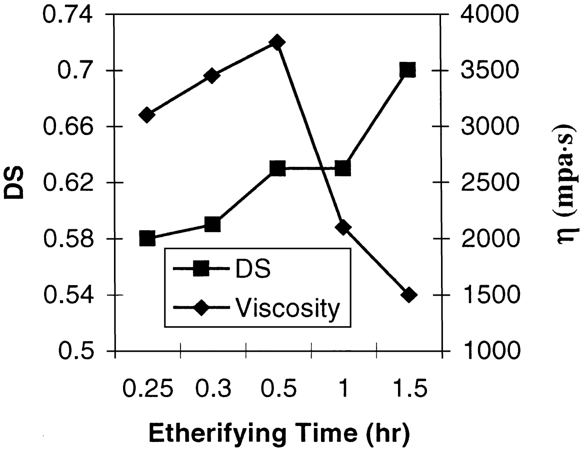

FIGURE 9 Effect of etherifying time on DS and η. (Reaction conditions: Cellulose/solvents (wt) = 1:3.2, $C_6H_6/C_2H_5OH(wt) = 1:3$, NaOH/AGU (mol) = 2:1, $ClCH_2COOH$/AGU (mol) = 1:1, Alkalization time: 1 hour).

TABLE 1 Stability of Synthesizing CMC at Optimum Conditions

No.	DS	Solution viscosity (η/mpa·s)	Percentage transmission (T/%)	Utilization efficiency of etherifying reagent (%)
1	0.95	1850	65.8	63.3
2	1.11	1400	71.6	74.0
3	1.00	1500	72.7	66.7

NaOH/AGU (mol) = 2:1; $ClCH_2COOH$/AGU (mol) = 1.5:1; alkalization time: 1 hour; and etherifying time: 0.5 hour, etc. At these optimum conditions, a CMC sample with DS = 1.10 and $\eta = 1500$ mpa·s was synthesized. In order to measure the stability of this optimum process, the same experiment was repeated three times. The results shown in Table 1 indicate that CMC with high DS and high solution viscosity can be achieved by this optimum process.

CONCLUSIONS

1. The benzene–ethanol–water solvent medium contributes to the formation of CMC with high DS, high solution viscosity and uniform distribution of substituents.
2. The effects of alkali concentration, time for alkalization process, etherifying reagent concentration and etherifying time were studied. The data were explained by analyzing the changes of microstructure.
3. An optimum process was determined for synthesizing CMC with DS > 1.0, solution viscosity about 1500 mpa·s, and with uniform distribution of substituents.
4. The scale-up of this process is possible by using a kneading machine.

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