Blend Films of *O*-Carboxymethyl Chitosan and Cellulose in *N*-methylmorpholine-*N*-oxide Monohydrate

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ABSTRACT: To introduce *N*-methylmorpholine-*N*-oxide (NMMO) process to prepare antibacterial lyocell fiber, the blend films of *O*-carboxymethyl chitosan (O-CMCS) and cellulose were prepared. O-CMCS in aqueous suspension with particles having a surface mean diameter of 2.24 μm was blended with cellulose in NMMO hydrate. The blend films with different O-CMCS content were prepared with the blend solutions. SEM confirmed that O-CMCS remained within the cellulose film in the particle. The mechanical properties of the blend films show little increased value when O-CMCS was less 5%; however, it decreased sharply when O-CMCS was over 8%. Thus, the optimum O-CMCS content may give a good combination of antibacterial action and mechanical properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4601–4605, 2006

Key words: *O*-carboxymethyl chitosan; cellulose; *N*-methylmorpholine-*N*-oxide; polyblend; antibacterial activities

INTRODUCTION

Chitosan as a linear natural polyaminosaccharide is the second most abundant regrowing organic material with outstanding properties and a variety of useful applications.[1–4] In the recent decades, chitosan has attracted considerable interest due to its antibacterial and antifungal activities with a broad spectra, high killing rate, and low toxicity to mammalian cells,[5] and it is being used as an antibacterial agent for fiber, food, and other applications.[6] On the other hand, poor solubility of chitosan in some common solvents, e.g., water, alkali, and organic solvents, limits its applications. To overcome this problem, chemical modification of chitosan is required and lots of derivatives have been synthesized. Among these, *O*-carboxymethyl chitosan (O-CMCS), which is a kind of derivative introducing a $-CH_2COOH$ group at C-6 position, shows stronger antibacterial activities and better solubility than chitosan.[7]

Having a molecular structure similar to that of cellulose, chitosan and its derivatives were mixed with cellulose to prepare antibacterial materials. In our previous work, a kind of antibacterial rayon fiber containing 1 ~ 3 wt % chitosan or O-CMCS was prepared, and this fiber exhibited excellent antibacterial activity and mechanical properties.[8–10] Pertti et al. manufactured another fiber by mixing microcrystalline chitosan with cellulose xhanthate alkaline.[11] All these works were carried out through the viscose process, which is based on a metastable cellulose derivative (cellulose xanthogenate). The process is accompanied, however, by environmental hazardous byproducts (CS_2, H_2S, heavy metals).

Correspondingly, lyocell process is a new method, producing cellulose fibers from its direct solvents, e.g., LiCl/*N*,*N*-dimethylacetamide (DMAc), *N*-methylmorpholine-*N*-oxide (NMMO) hydrate. To introduce this environment friendly process in the manufacture of antibacterial cellulose fiber, a series of attempts were carried out by our research group. The blend films of O-CMCS with cellulose were prepared from LiCl/DMAc solution and phase behavior was studied in our previous work.[7] In fact, lyocell process using NMMO hydrate has ripened technically nowadays, and the works focusing on this process are with remarkable significance. In the present work, the blend films of O-CMCS and cellulose were prepared by mixing O-CMCS aqueous suspension in NMMO process. The structure, miscibility, and mechanical properties of the blends were investigated. Also, the antibacterial activity of the film against *E. coli* was examined.

EXPERIMENTAL

Materials

Chitosan was supplied by Zhejiang Ao-Xing Biotechnology (Zhejiang, China). The molecular weight was

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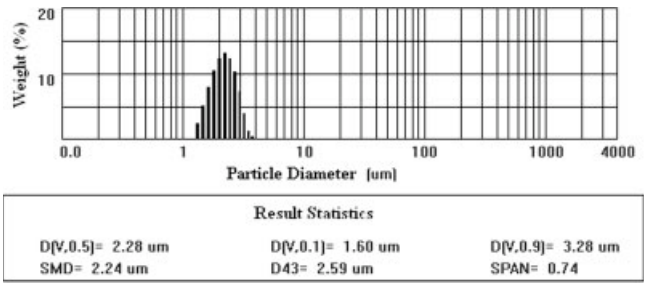

Figure 1 O-CMCS particles' sizes distribution in aqueous suspension.

2.7×10^5 and the degree of deacetylation was 0.91. Cellulose was supplied by Tianjin Rayon Factory (Tianjin, China), whose degree of polymerization was 612. *N*-methylmorpholine-*N*-oxide (NMMO) aqueous solution (50 wt %) was purchased from BASF, Germany.

Preparation of O-CMCS aqueous suspension

O-carboxymethyl chitosan (O-CMCS) was synthesized following the process described by Muzzarelli.[12] O-CMCS aqueous suspension was prepared by adding NMMO aqueous solution into O-CMCS solution to precipitate it out. A concentrating process was followed to make the content of O-CMCS equal to 40 wt %. Finally, the O-CMCS aqueous suspension was gained after being treated using an ultrasonic processor (VC 130, Sonics and Materials, USA) for 10 min at 130 W. A laser particle sizer III (Tianjin University Modern Optics Institute, Tianjin, China) was used to get the size distribution of O-CMCS particles.

Preparation of O-CMCS/cellulose blend solutions

Cellulose was dissolved in NMMO monohydrate as described by Loubinoux[13] with a cellulose concentration of 15 wt %. To get O-CMCS/cellulose blend solutions, a given amount of O-CMCS suspension was mixed with NMMO aqueous solution before the dissolving process. Considering its following application, the solutions contained 2–8 wt % O-CMCS in relation to the content of cellulose.

Preparation of O-CMCS/cellulose blend films

The films were shaped in a mold at a stable temperature of 80°C, and deionized water was used as coagulation bath. The resultant films were washed three times to ensure complete coagulation and removal of NMMO. The thickness of the films was controlled to about 250 μm.

Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Mattson IR spectrometer. The morphology of the surfaces of blend films was observed by a Philips SL-30 scanning electron microscope (SEM). Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DTA1700 differential scanning calorimeter. Samples were examined at a heating rate of 10°C/min under a nitrogen stream in the temperature range of 0–380°C. Changes in the crystalline state were obtained by a Rigaku Denki D/MAX 1200 diffractometer, which employed Cu Kα X-radiation between a 2θ angle of 8°–40°. Mechanical tests were performed by a M350-20KN Testometric. The gauge length was 20 mm, and the crosshead speed was 10 mm/min.

Antibacterial assessment

The Shaking Flask test method was applied for determining the antibacterial activity.[14] *E. coli* 8099 was selected as a test bacteria.

RESULTS AND DISCUSSION

The change of the sizes of O-CMCS particles

Although O-CMCS has better water-solubility, it cannot be dissolved in NMMO hydrate. The described precipitation method was applied to get O-CMCS aqueous suspensions with small sized particles. The size distribution of O-CMCS particles in the suspension was examined. The results show that surface mean diameter is equal to 2.24 μm and volume mean diameter (D43) is equal to 2.59 μm. The data indicate that the particles are with a narrow size distribution (ca. SPAN 0.74) and 90% particles are below 3.28 μm (Fig. 1).

Because the cellulose solution in NMMO hydrate has a higher melting temperature (above 75°C), SEM was employed to observe O-CMCS particles in O-CMCS/cellulose solutions (shown in Fig. 2). O-CMCS particles were observed in the mixture and

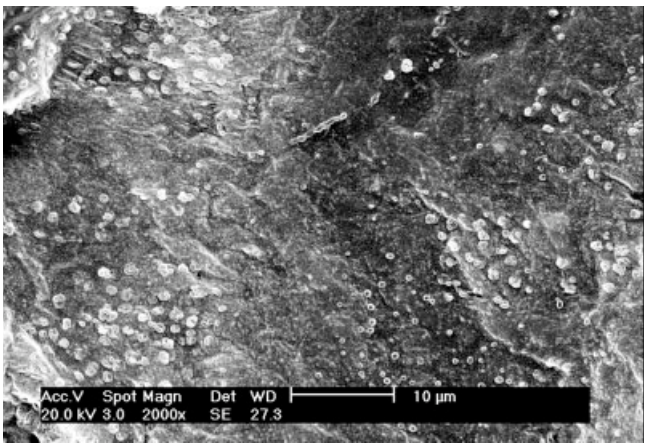

Figure 2 SEM photograph of O-CMCS/cellulose solution.

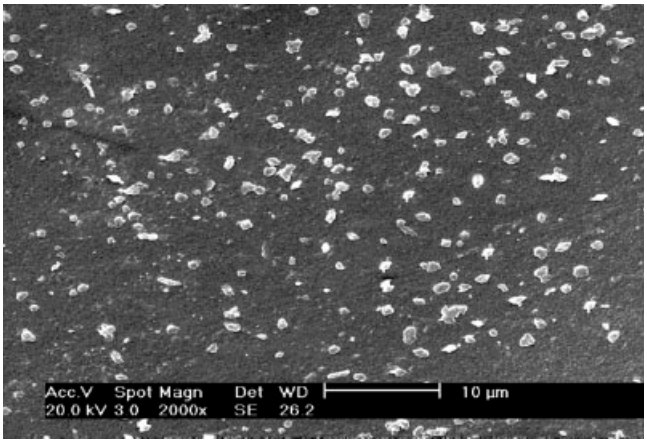

Figure 3 SEM photographs of the O-CMCS/cellulose blend film.

the particles were between 0.5 and 2.5 μm in size. It is seen that the mean particles size decreases slightly compared to that in the previous stage (in the suspension).

Figure 3 shows the SEM photograph of the O-CMCS/cellulose blend film. It displays a binary morphology, and O-CMCS is dispersed as particles in the consecutive phase of cellulose. Its sizes are between 0.1 and 2 μm, mostly less than 1.5 μm. From the above data, it is found that the mean size of O-CMCS particles decrease stepwise in the three sequence stages, which approves the affinity of the two polymers coming from their similar molecular structure.

Structure of O-CMCS/cellulose blends

The structure of the blend films was studied by FTIR spectroscopy (Fig. 4). The spectrum of cellulose shows its basic characteristic peaks at 1375 cm^{-1} peak, contributing to the C—O—H bond and a broad band around 3375 cm^{-1} to —OH. In the spectrum of O-CMCS, the appearance of C=O stretching vibration band at 1741 cm^{-1} and C—O stretching vibration band of the group $—CH_2—COOH$ at 1251 cm^{-1} indicated the existence of carboxymethyl group.[15] The existence of N—H stretching vibration band at 897 cm^{-1} and the appearance of 1629 cm^{-1} and 1521 cm^{-1} assigned to $—NH_3^+$ indicate the carboxymethyl groups to be on the —OH position. The IR spectra of blend films with different O-CMCS content are similar. Compared with the spectrum of O-CMCS, C=O stretching peak shifts to a higher frequency with the increasing O-CMCS content in the blend, which indicates the presence of the interaction between O-CMCS and cellulose. The presence of the adsorptions of $—NH_3^+$ ensures its antibacterial activity.

The X-ray diffraction patterns of O-CMCS and blend films were also studied. As shown in Figure 5, the cellulose film basically exhibits a diffraction pattern of cellulose II,[16] and O-CMCS was almost amorphous. For the blend films, the introduction of O-CMCS does not alter its crystal pattern, but the calculated crystallinity (χ_c) changes with the content of O-CMCS (Table I). The χ_c of the cellulose film is 74.9%, and it increases up to 75.3%, when the O-CMCS content is 5% but decreases to 74.1% with the O-CMCS content of 8%. It is suggested that the presence of a small quality of O-CMCS helps in the crystallization process, but obstructs the crystallization process when O-CMCS is excessive.

Thermal analysis

Polysaccharides usually have a strong affinity for water, and so all films underwent a quick scan from 0 to 150°C to eliminate free water in DSC analysis. The second scan spectra are listed in Figure 6. Two transitions of cellulose are observed at about 252.1 and 350.0°C and all blend films show similar results. The endothermic peaks at about 250°C are due to the melting of cellulose crystal region.[17] For the

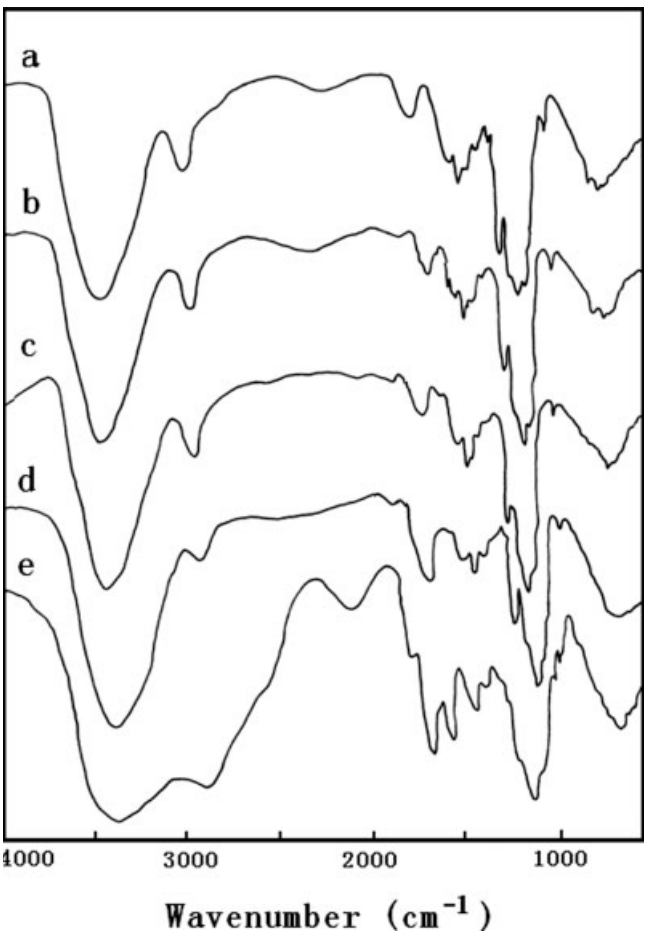

Figure 4 FTIR spectra of cellulose (a), O-CMCS (e), and blend films with different O-CMCS content: (b) 2%, (c) 5%, and (d) 8%

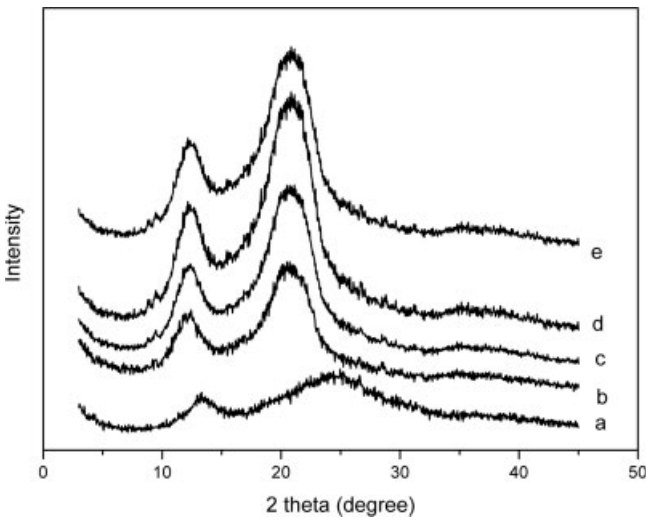

Figure 5 Wide-angle X-ray diffractions of O-CMCS (a) and blend films with different O-CMCS content: (b) 0%, (c) 2%, (d) 5%, and (e) 8%.

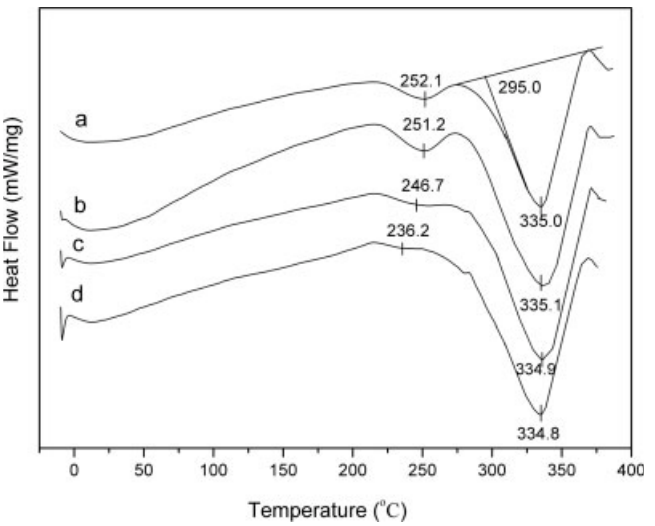

Figure 6 DSC thermograms of cellulose film (a) and blends with different O-CMCS content: (b) 2%, (c) 5%, and (d) 8%.

blend film with 2% O-CMCS, this peak temperature (T_{max}) is close to that of cellulose, but it goes down when the content of O-CMCS is over 5%. With regard to the results of X-ray diffraction, this decrease seems to be due to a decreased degree of crystallinity with the presence of O-CMCS.

The second wide endothermic peak of cellulose is connected with its decomposition at the onset temperature (T_o) of 295.0°C and T_{max} at 335.1°C. Compared with cellulose, the decomposition peaks of the blend films make no obvious shift.

Mechanical properties of blend films

Tensile strength and elongation of the blend films in the dry state are given in Figure 7. The tensile strength of the cellulose film was 91.6 MPa, and the blend films showed little increase in value, when the O-CMCS content was below 5%, but it decreased sharply when the O-CMCS content was over 8%. But for elongation, the results show a continuous decrease with the content of O-CMCS increase, especially when O-CMCS was over 8%.

Antibacterial assessment

At present, the antibacterial function of amino-polysaccharides is acknowledged as generally coming from the group $—NH_2$ along the chains. So, the content of $—NH_2$ affects the antibacterial activity of chitosan derivatives. O-CMCS is proved to have stronger antibacterial activity than does chitosan.[14]

Figure 8 shows the plots of the optical density (OD) versus the culture time for the blend films against *E. coli*, measured by the Shaking Flask test method.

According to the test theory, the smaller the OD of the medium, the higher the antibacterial activity of the tested material.[14] Compared with the system containing cellulose film, OD of the system containing blend films are much lower, even O-CMCS content was only 1%, which shows satisfying antibacterial activities. Moreover, the antibacterial activities increase along with the increasing O-CMCS content.

On the basis of the results of the mechanical properties test, introduction of a small quantity of O-CMCS

TABLE I
The Crystallinity of Blend Films Calculated

O-CMCS content (%)	χ_c (%)
0	74.9
2	75.1
5	75.3
8	74.1

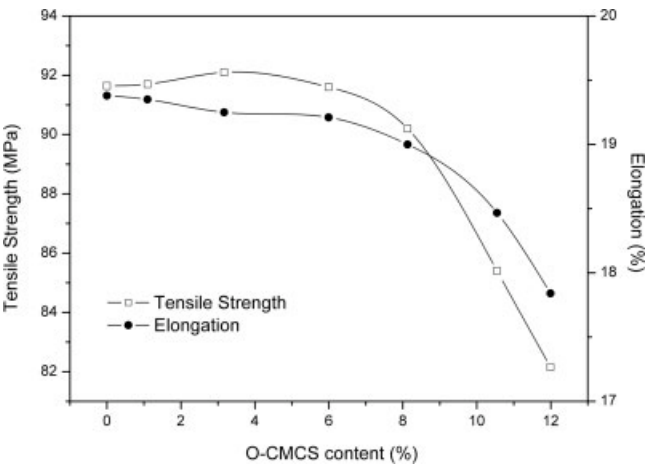

Figure 7 Mechanical properties of blend films with different O-CMCS content.

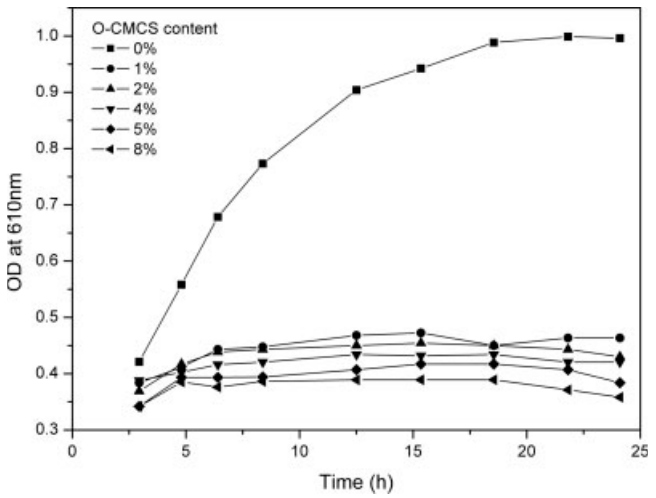

Figure 8 Antibacterial activities against *E. coli* of the blend films.

increased the tensile strength. The materials containing 1–5% O-CMCS prepared in this method possess good antibacterial activity with satisfying tensile strength and elongation.

CONCLUSIONS

A functional lyocell film with antibacterial activity could be prepared by introducing O-CMCS aqueous suspension to the cellulose solution in NMMO hydrate. The lyocell fibers containing 1–5 wt % O-CMCS show higher antibacterial activities and satisfying mechanical properties. Examination of films' morphology revealed that the introduced O-CMCS remained in blend films in particles less than 2 μm and O-CMCS less than 5% helps in the crystallization process. These results may be utilized in producing an antibacterial lyocell fiber, which is expected to find application in healthcare nonwoven fabric.

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