Preparation and Properties of Viscose Rayon/O-carboxymethyl Chitosan Antibacterial Fibers

Youbo Di[1], Guoqiang Long[2], Huiqin Zhang[2], Qingshan Li[1]

[1]Yanshan University, Qinhuangdao, Hebei CHINA

[2] Chengdu Huaming Cellophune Co. Ltd., Chengdu CHINA

Correspondece to:
Youbo Di email: diyoubo@gmail.com

ABSTRACT

Antimicrobial viscose rayon/O-carboxymethyl chitosan fibers (VCMFs) were manufactured by spinning the mixture of O-carboxymethyl chitosan (O-CMCS) xanthate and cellulose xanthate via the viscose process. The structure, morphology and mechanical properties were investigated by infrared, scanning electron microscopy, transmission electron microscope and tensile test. The results show that the blend fibers of cellulose and O-CMCS were satisfactorily prepared and the two polymers were mixed homogeneously. VCMFs display striation along the fiber similar to those of viscose rayon fibers, and their mechanical properties are close to that of viscose rayon. With O-CMCS blended, VCMFs showed good moisture absorption and antibacterial activity against *E.coli*.

INTRODUCTION

Cellulose is the most abundant renewable resource and has been used as a raw material for making fibers with well-established technology for a long time [1]. Cellulose fiber is a favorite undergarment material and it is the most appropriately to be made into antibacterial next-to-skin fabrics due to its safety to human body and the comfort resulted from its high moisture-retentivity. Though new cellulose fiber processes using NMMO [2], ionic liquids [3] and NaOH/urea [4] as direct solvents are promising, the viscose process is still an important one, and the output of viscose is still increasing because of its excellent properties. In some application fields, antibacterial viscose rayon is required. But it is difficult to keep their properties for the most antibacterial agent because of the strong alkali and acid conditions throughout the whole process.

Chitosan, the deacylated product of the second natural polymer chitin, has been proved to be a good antibacterial material. Chitosan can inhibit the growth of a wide variety of bacteria and fungi with several advantages over other types of disinfectants, including higher antibacterial activity, broader spectra of activity, higher killing rate, and lower toxicity toward mammalian cells [5-9]. In an in vivo study, chitosan was proved inhibiting the growth of cells by preventing the transformation of DNA into RNA and suppress the metabolism of bacteria [10].

With similar molecular structure, it is believed there is good compatibility between chitosan and cellulose, and chitosan was attempted to be added into cellulose matrix to develop functional materials such as antibacterial viscose fiber [11, 12]. One method, chitosan microparticles less than 5μm in type of solid or emulsion was mixed with viscose to spin blend chitosan/cellulose fibers [13, 14]. However chitosan microparticles are liable to aggregate in the process and block the filtration fabrics or spinnerets, which affect the fiber structure and properties. Alternatevely, chitosan was xanthated by the reaction with carbon disulfide similar to viscose process and then blended with viscose dope to spin. In this method, the spinning dope is easily homogenized. But it requires high purity chitosan materials with less than 0.2wt% ash content to obtain the solution of chitosan xanthate ester with good filter property [15]. Some chitosan derivatives such as N-propylchitosan, hydroxyethylchitosan were attempted to get homogeneous spinning dope instead of chitosan [16, 17].

Carboxymethyl chitosan （CMCS） is an important derivative of chitosan and has unique chemical, physical and biological properties such as low toxicity, biocompatibility and good ability to form films, fibers and hydrogels[18]. CMCS is divided into O-carboxymethyl chitosan (O-CMCS), N-carboxymethyl chitosan (N-CMCS) and

N,O-carboxymethyl chitosan (N,O-CMCS) according to the substitution position. N,O-CMCS was reported to enhance the compatibility of cellulose and chitosan in viscose process [14]. O-CMCS has stronger antibacterial activity than chitosan [11]. Also, CMCS has good reaction performance and many derivatives were synthesized with CMCS as mesomer [19-22]. In this paper, O-CMCS xanthate ester was synthesized and blended with viscose to prepare antibacterial cellulose fibers. The structure and properties of the viscose rayon /O-carboxymethyl chitosan fibers (VCMFs) were investigated.

EXPERIMENTAL

Materials

Chitosan (viscosity-average molecular weight of 5.1×10^4 and deacetylation degree of 0.85) was supplied by Zhejiang Ao-Xing Biotechnology Co. Ltd., (Zhejiang province, P.R.China). Cellulose (degree of polymerization of 670) was supplied by Chengdu Huaming Cellophune Co. Ltd., (Sichuan province, P.R.China). O-carboxymethyl chitosan (O-CMCS) was synthesized by the reaction of carboxymethylation as follows: chitosan (15.0 g) and monochloroacetic acid (9.0 g) were added to 150 ml sodium hydroxide solution (42wt%). After being stirred 14 h at 0ºC, the pH of the mixture was adjusted to 1.0 using hydrochloric acid. Then, the product was filtrated and washed with methanol for several times, and then vacuum dried at 50ºC. The degree of substitution (DS) determined by pH titration was 56.8% [23]. Other materials such as carbon disulfide, sodium hydroxide, sulfuric acid, sodium sulfate, zinc sulfate are industrial grade. *Escherichia coli* (*E.coli*) 8099 was provided by school of biology science, NanKai University, Tianjin, China.

Preparation Of Spinning Solutions

O-CMCS xanthate ester was obtained as follows: a certain amount of O-CMCS powder was mixed up with 42wt% sodium hydroxide solution at room temperature and stirred for 120 min with the ratio of 1:20 (w/v). Then the redundant sodium hydroxide solution was compressed out to control the weight of the alkaline O-CMCS was four to five times the original weight. The alkaline O-CMCS was added into the tank reactor with some water and the solid content was between 20wt% to 25wt%, then an amount of carbon disulfide was added at 15°C under stirring. The reaction was kept for about 120 min reaction at 15°C until an orange-like stable solution of O-CMCS xanthate was obtained. After filtration, it was blended with cellulose xanthate solution with different mass ratio using a mechanical stirring. The blend solutions were homogeneous and had excellent filtering properties.

Spinning Of Antibacterial Viscose Rayon / O-CMCS Blend Fiber

The spinning process was performed on viscose fiber production facilities (Chengdu Huaming Cellophune Co. Ltd, Sichuan Province, China.). The blend spinning solution was found easy to spin. The usual coagulation bath for rayon fiber spinning was adopted. The diameter of the spineret adopted was 0.06 mm. The spinning velocity was about 50 $m\cdot min^{-1}$. Spinneret draw ratio was 1.2 to 1.25 fold and the usual post treatments such as washing with water and acid, bleach, oiling, dry and cut were operated as viscose rayon process and the stable fiber were obtained. The blend fibers were labeled as VCMF2, VCMF4 and VCMF6 in which O-CMCS content were 2.2 wt%, 4.8 wt% and 6.1wt%, respectively.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with a Mattson IR spectrometer. The surfaces morphology of the fibers was observed by a HITACHI SX-650 scanning electron microscope (SEM). Transmission electron microscope (TEM) observation was performed to investigate the morphology of the cross sectional area with a HITACHI H-7650 instrument. Ultrathin samples were dissected using a Leica ultramicrotome and stained with OsO_4. Mechanical properties of the fibers were measured using YG001A at the strain rate of 10 $mm\cdot min^{-1}$ at room temperature. Moisture absorption was determined on dried samples kept at 20ºC and 65% R.H. for 2 days.

Antibacterial properties of the fibers against *E.coli* were assessed by shaking flask test method as follows: a representative bacteria colony was picked off and placed in a nutrient broth (peptone 10 g, beef extract 3 g, NaCl 3 g in distilled water 1000ml; pH 7.0) and incubated at 37ºC for 24 h. Then the obtained fresh culture where bacteria cells grew luxuriantly was ready for antibacterial test. 0.2 mL of the fresh culture was inoculated to the medium (9.8 mL) containing viscose rayon or the blend fibers (0.1 g) and incubated in a shaking bed (150 rpm) at 37°C for 24 h. During incubation, turbidity of the medium was measured at 610 nm (by 756MC UV-VIS Spectrophotometer, Shanghai, China) for five times.

RESULTS AND DISCUSSION

Structure and Morphology

The FTIR spectra of O-CMCS and the blend fibers are shown in *Figure 1*. The spectrum of O-CMCS, the appearance of C=O stretching at 1734 cm^{-1} and C-O stretching of the group -CH_2-COOH at 1251 cm^{-1} indicated the existence of carboxymethyl group[23]. 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 spectra of VCMF2 and VCMF6 are similar. The appearance of absorption around 1631 cm^{-1} and 1518 cm^{-1} assigned to -NH_3^+ were also found in spectra of VCMF2 and VCMF6, which illustrate that the amino groups of O-CMCS were not affected during the fiber formation. Since the antibacterial activities of chitosan and O-CMCS are resulted from the –NH_3^+ on the molecular chain[18], the existence of –NH_3^+ ensured films to exhibit antibacterial activity.

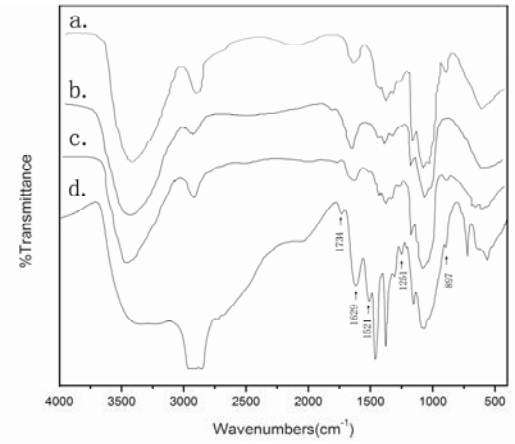
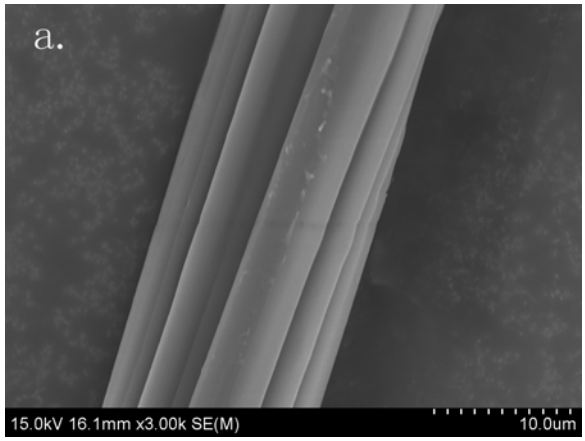


FIGURE 1. FTIR spectra of viscose rayon (a.), VCMF2 (b.), VCMF6 (c.) and O-CMCS(d.)

The SEM photographs of the selected fibers are shown in *Figure 2*. The surfaces of VCMF2 and VCMF6 showed homogeneous morphology. The fibers displayed striation along the fiber length as viscose rayon. Also some concave points were found on the surface. TEM was further used to characterize the miscibility of O-CMCS and cellulose. With stained by OsO_4, O-CMCS shows dark phase and cellulose shows bright in the blend. The selected TEM photo is shown in *Figure 3*. As a whole, the photograph shows homogenous gray and no phase separation is observed which suggest high miscibility between cellulose and O-CMCS. Obviously, the mixing effect using this method is better than microparticles adding method in which chitosan microparticles were embedded into cellulose matrix with the size more than 3 μm [13, 24].



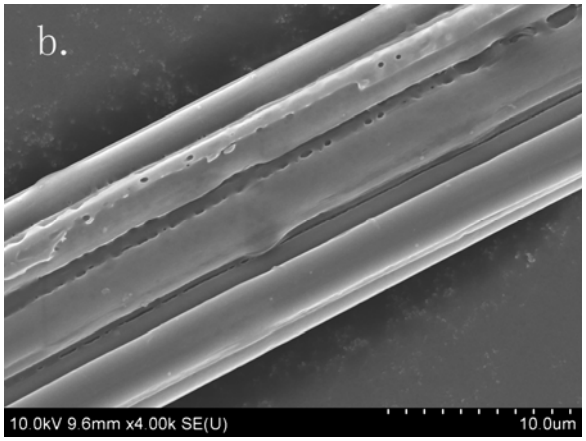


FIGURE 2. SEM microscope photographs of VCMF2 (a.) and VCMF6 (b.)

Physical and Mechanical Properties of Fibers

The effect of O-CMCS content on the tensile strength of fibers in dry and wet states is shown in *Table I*. The dry tensile strengths of the blend fibers were close to that of viscose rayon and the VCMF2 even no lower than that of viscose rayon. These results might be attributed to the good miscibility between the two polymers. The wet tensile strength decreased with the increase of O-CMCS content. Breaking elongation of the dry fibers of VCMF2, VCMF4, and VCMF6 were higher than that of viscose rayon, with the maximum value observed for VCMF6 having a 22.5% value. The alteration of breaking elongation in wet state expressed a tendency similar to that in the dry state.

Moisture absorption is the ability of the fiber to absorb steam, which characterizes the comfortableness of the fabric made from fibers.

Viscose rayon is well known for its well moisture absorption. As a natural polysaccharide, chitosan and its derivatives were also reported good hydrophilicity. The moisture absorption of VCMF2, VCMF4 and VCMF6 were tested higher (13.38%-13.71%) than 13.01% of viscose rayon. As a whole, the blend fibers were characterized with good physical and mechanical properties.

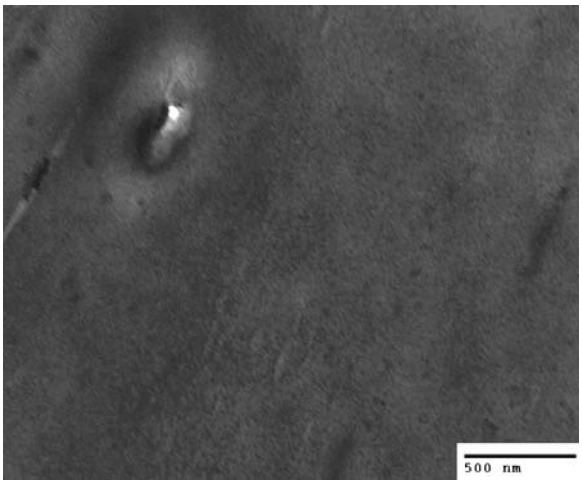


FIGURE 3. TEM microscope photographs of VCMF4.

TABLE I Properties of VCMFs and viscose rayon.

Fibers No.	Dry tensile strength ($cN \cdot dtex^{-1}$)	Dry elongation at break (%)	Wet tensile strength ($cN \cdot dtex^{-1}$)	Wet elongation at break (%)	Moisture absorption (%)
Viscose rayon	3.06	19.0	2.70	17.9	13.01
VCMF2	3.06	21.4	2.62	19.8	13.38
VCMF4	3.04	22.2	2.59	22.3	13.56
VCMF6	3.03	22.5	2.58	23.6	13.71

Antibacterial Property Assessment

The antibacterial activity of chitosan and its derivatives is a result of ionic interactions between the protonated amino groups of chitosan or its quaternized derivatives and the negatively charged surface of bacteria, which leads to loss of membrane permeability, cell leakage and cell death. In the present study, the antibacterial activity of the blend fibers against Gram negative bacteria *E.coli* was evaluated by shake-flask test. According to the test theory, the smaller the OD of the medium, the higher the antibacterial activity of the tested material is [25]. Compared with the medium containing viscose rayon and the control *Figure 4*, OD of the medium containing blend fibers are much lower, even O-CMCS content was only 2.2%, which shows satisfying antibacterial activities. Moreover, the antibacterial activities increase with the increasing O-CMCS content.

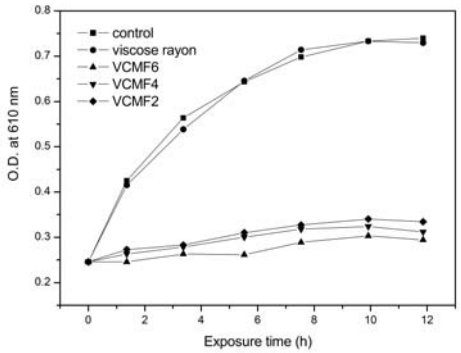


FIGURE 4. The antibacterial activity of VCMFs against *E. coli*

CONCLUSION

O-carboxymethyl chitosan was xanthated to prepare viscose rayon/O-carboxymethyl chitosan blend fibers by blending them with cellulose xanthate with different ratio. Cellulose and O-CMCS were mixed uniformly in microscopic scales. The fibers display striation along the fiber similar to those of viscose rayon fibers, and their mechanical properties are close to that of viscoserayon. With O-CMCS blended, VCMFs showed good moisture absorption and antimicrobial activity against *E.coli*.

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AUTHORS' ADDRESSES

Youbo Di,
Qingshan Li
Yanshan University
College of Materials Science & Engineeering
Qinhuangdao, Hebei 066004
CHINA

Guoqiang Long
Huiqin Zhang
Chengdu Huaming Cellophune Co. Ltd.
Research and Development Department
Sichuan, Chengdu 610304
CHINA