Carbohydrate Polymers 81 (2010) 541–544

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Manufacture and properties of cellulose/O-hydroxyethyl chitosan blend fibers

Xianlin Xu[a], Xupin Zhuang[a], Bowen Cheng[b,*], Jing Xu[a], Guoqiang Long[c], Huiqin Zhang[c]

[a] School of Textile, Tianjin Polytechnic University, Tianjin 300160, China
[b] Tianjin Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, China
[c] Chengdu Huaming Cellophune Co. Ltd., Chengdu 610304, China

ARTICLE INFO

Article history:
Received 11 February 2010
Received in revised form 26 February 2010
Accepted 2 March 2010
Available online 18 March 2010

Keywords:
O-Hydroxyethyl chitosan
Cellulose
Antimicrobial fiber
Viscose rayon

ABSTRACT

Cellulose/O-hydroxyethyl chitosan fibers (CHCFs) were manufactured by blending O-hydroxyethyl chitosan (HECS) xanthate with cellulose xanthate for spinning via the viscose process. The fibers were characterized by transmission electron microscope (TEM) and thermal gravimetric analysis (TGA). TEM photographs showed that HECS was mixed homogeneously with cellulose and oriented along the fiber direction. TGA results suggested that the decomposition temperature increased and the decomposition rate slowed down with HECS addition in the fiber. The physical, mechanical properties and antimicrobial activity against *Escherichia coli* (*E. coli*) were measured. Although the addition of HECS slightly reduced the dry and wet strength, the mechanical properties of the fibers are close to that of viscose rayon and CHCFs could fit the following textile processing. CHCFs exhibited good moisture absorption, antistatic property and antibacterial activities against *E. coli*.

1. Introduction

Chitosan, a copolymer of glucosamine and N-acetylglucosamine units linked by 1-4 glucosidic bonds, is the second abundant natural polymer found in a wide range such as crustaceans, fungi, and insects. Chitosan has found applications in many fields for its excellent properties such as biocompatibility, biodegradability, nontoxicity, and adsorption properties (Jayakumar et al., 2010; Muzzarelli, 2009; Odaci, Timur, & Telefoncu, 2009; Wang, Chi, & Tang, 2008; Zhu & Jiang, 2009). Its antimicrobial activity is of great interest. Chitosan inhibits the growth of a wide variety of bacteria and fungi with several advantages over other types of disinfectants because of its high antibacterial activity, broad spectra of activity, high killing rate, and low toxicity toward mammalian cells (Kim, Choi, Chun, & Choi, 1997). And also many derivatives were synthesized to obtain stronger antimicrobial activity (Jin, Wang, & Bai, 2009; Runarsson et al., 2007; Wu et al., 2006; Yang, Chou, & Li, 2005).

Chitosan and its derivatives are currently being used as an antibacterial agent for cellulose fiber, polyester fiber, alginate fiber and others (Fan et al., 2006; Gao & Cranston, 2008; Hu, Jou, & Yang, 2002; Jou et al., 2007; Knill et al., 2004; Li, Liu, Zhuang, Guan, & Yao, 2002). Because of the antimicrobial activity and little skin reaction over a wide range of biomedical investigation, chitosan and its derivatives can be applied in the next-to-skin fabrics. Cellulose fibers are people's favorite undergarment materials due to its comfortableness and the safety to human body. Currently, cellulose fibers are mainly manufactured using viscose process and lyocell process. Despite the inborn pollution in viscose process, viscose rayon is still an important man-made fiber and many researches about cellulose/chitosan fibers are focused on this process. Seo developed an antibacterial modified viscose fiber under the trademark CHITOPOLY which is produced by introduction into a viscose doped in the solid particles of chitosan and by spinning using polynosic viscose fiber technology (Seo, 1990), Guan and co-workers added chitosan emulsion into viscose with N,O-carboxymethyl chitosan to improve their compatibility (Li et al., 2002), Nousiainen et al. mixed gelatinous microcrystalline chitosan (MCCh) water dispersion with viscose and investigated the effects of aqueous MCCh gel concentration and additives on the spinnability of hybrid cellulose/chitosan fibers and their properties (Nousiainen et al., 2000). Chitosan was in the form of microparticles in the above fibers and the difficulties during the manufacture are concerned with aggregation of microcrystalline chitosan particles or solid particles, blocking of filtration fabrics or spinnerets and inhomogenity distribution in the fiber structure, which all affect the fiber properties and behaviors. To make the distribution more homogeneous, chitosan, microcrystalline chitosan or chitin was xanthated by the reaction with carbon disulfide and blend with viscose dope (He, Ma, & Sun, 2009; Pang, He, & Wang, 2003; Yoshikawa et al., 1998). In this method, the spinning dope is easily homogenized. But it requires the use of several complicated operations in the xanthogenation reaction.

O-Hydroxyethyl chitosan (HECS) is a partially hydroxyethyl-substituted chitosan derivative on C6 position (Wan, Creber,

* Corresponding author. Tel.: +86 22 24528353; fax: +86 22 24528287.
E-mail address: bowen15@tjpu.edu.cn (B.W. Cheng).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.03.011

Peppley, & Bui, 2004). HECS has a good reaction performance and often acts as mesosome to synthesize other derivatives (Ronghua, Yumin, & Jianhong, 2003; Zhao et al., 2008). The objective of this study was to develop a new antibacterial cellulose fiber containing chitosan derivative by spinning the mixture of xanthate ester of O-hydroxyethyl chitosan and cellulose via viscose process. The principal properties and structure of the cellulose/O-hydroxyethyl chitosan fibers (CHCFs) were investigated.

2. Experimental

2.1. 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-Hydroxyethyl chitosan was prepared by the reaction of alkaline chitosan with 2-chloroethanol (Wan et al., 2004) and the degree of substitution (DS) was 14.4%. 2-Chloroethanol was analytical reagent and used as received. Other materials such as carbon disulfide, sodium hydroxide, sulfuric acid, sodium sulfate, and zinc sulfate are of industrial grade. *E. coli* (8099) was provided by school of biology science, NanKai University, Tianjin, China.

2.2. Preparation of spinning solutions

HECS xanthate ester was obtained as follows: a certain amount of HECS powder was mixed with 42 wt% sodium hydroxide solution at room temperature and stirred for 120 min in the ratio of 1:20 (w/v). Then the redundant sodium hydroxide solution was compressed to control the weight of the alkaline HECS that was four to five times the original HECS weight. The alkaline HECS was added into the reaction kettle with some water and the solid content was between 20 wt% and 25 wt%, then an amount of carbon disulfide was added at 15 °C under stirring. The reaction was kept for about 120 min reaction in the same conditions and an orange-like stable solution of HECS xanthate was obtained. After being filtered, 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.

2.3. Spinning of cellulose/HECS blend fiber

The spinning 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 spinneret adopted was 0.06 mm. The spinning velocity was 50 m min^{-1}. Spinneret draw ratio was 1.2–1.25 fold and the usual post-treatments such as washing with water and acid, bleach, oiling and dry were operated as viscose rayon process.

The spun cellulose/O-hydroxyethyl chitosan blend fibers were noted as CHCFs-3, CHCFs-4 and CHCFs-6 with HECS content of 3.1 wt%, 4.5 wt% and 6.2 wt%, respectively. The HECS content in the fibers was calculated by the original weight of HECS and cellulose in the blended spinning solutions.

2.4. Measurements

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.

Table 1
The corresponding temperature of different mass remaining determined in TGA.

Mass remaining (%)	95	90	80	50	35
Viscose rayon	47.5	112.9	290.4	323.8	335.1
CHCFs-3	43.0	175.2	292.7	328.1	339.1
CHCFs-4	44.1	202.0	293.0	329.7	340.4
CHCFs-6	44.3	201.4	294.0	329.7	341.0

Thermal gravimetric analysis (TGA) was performed with an instrument of NETZSCH TG 209. Each sample was run under nitrogen atmosphere at a scanning rate of 5 °C min^{-1} from 20 °C to 350 °C.

Mechanical properties of the fibers were measured using YG001A at the strain rate of 10 mm min^{-1} at room temperature. Moisture absorption was determined on dried samples kept at 20 °C and 65% R.H. for 2 days. A YG321 fiber specific resistance testing apparatus was used to test the antistatic property of the fibers.

Antibacterial properties of the fibers against *Escherichia coli* (*E. coli*) 8099 were determined with an initial culture cell level at 5.8×10^5 CFU mL^{-1}. 0.3 g of each fiber specimen was placed in a 250 mL Erlenmeyer flask in which 100 mL of culture was added. Bacterial culture without fiber was used as a control. The bacte-

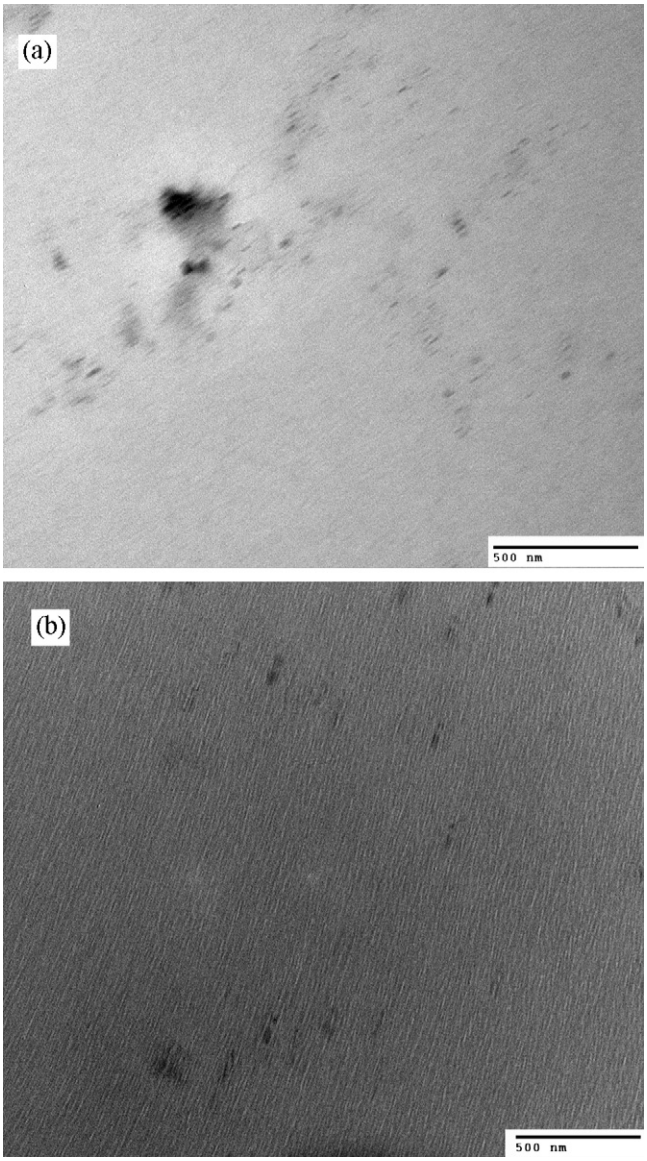

Fig. 1. TEM microscope photographs of CHCFs-3 (a.) and CHCFs-6 (b.).

Table 2
Properties of the cellulose/O-hydroxyethyl chitosan fibers and viscose rayon.

Fibers No.	Dry tensile strength (cN dtex^{-1})	Dry elongation at break (%)	Wet tensile strength (cN dtex^{-1})	Wet elongation at break (%)	Moisture absorption (%)	Mass specific resistance (Ω g cm^{-2})
Viscose rayon	3.06	19.0	2.70	17.9	13.01	4.7×10^8
CHCFs-3	3.04	21.2	2.66	19.4	13.23	4.3×10^8
CHCFs-4	3.01	22.5	2.61	21.2	13.40	4.2×10^8
CHCFs-6	2.97	22.9	2.55	24.5	13.55	4.0×10^8

rial suspensions were incubated at 25 °C for 12 h and the survival of *E. coli* was determined using the pour-plate method on nutrient agar medium. All measurements were performed with three replications.

3. Results and discussion

3.1. TEM analysis

For the blend fibers, it is important to improve the uniformity of all components. The usual methods include reducing the size of additive particles or dissolving them in the same solvents. In the previous study, chitosan emulsion was prepared to reduce the size of chitosan particles and TEM was applied to analyse the distribution of chitosan in the fiber (Li et al., 2002). Chitosan was found dispersed uniformly in the fiber in the form of microparticles with the mean size ranging from 0.1 μm to 0.5 μm.

HECS xanthate ester can be easily mixed well with viscose by co-dissolving in sodium hydroxide solution. TEM photographs of CHCFs-3 and CHCFs-6 are shown in Fig. 1. In the microscope photographs, HECS stained with OsO_4 shows dark phase and cellulose shows bright phase. As a whole, Fig. 1 shows gray in different degrees with HECS content varied and no phase separation found. Some HECS accumulation spots are also found especially in Fig. 1(a.). Most of them are less than 20 nm and sometimes a lager one is up to 200 nm. It is believed that the accumulation spots will be decreased after further stirring. It is also found that heterogeneous spots were stretched and oriented along the direction of the fiber. This is helpful to enhance its mechanical strength.

3.2. TGA analysis

Thermal stability of the viscose rayon and antibacterial fibers were determined by TGA (Fig. 2). The four samples show the similar results. The mass loss below 100 °C is attributed to the free water which originated from the hygroscopicity of cellulose and HECS. The decomposition temperature of viscose rayons, CHCFs-3, CHCFs-4 and CHCFs-6 is 291.9 °C, 294.2 °C, 297.3 °C and 297.6 °C, respectively. Some mass changes and corresponding temperatures are listed in Table 1. The results suggested that the decomposition temperature increased and the decomposition rate slowed down with HECS addition in the fiber. The same phenomenon was found in the previous work, and the reason was explained as the good compatibility of two polymers (Li et al., 2002).

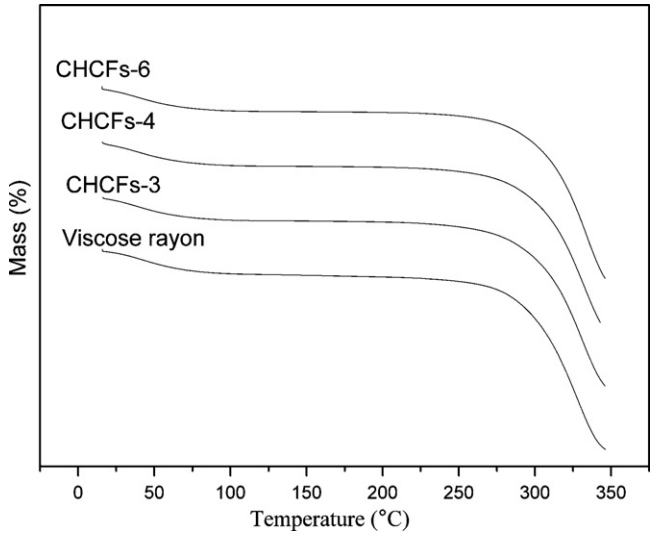

Fig. 2. TGA spectra of viscose rayon and CHCFs.

Table 3
The antibacterial activity of CHCFs against *E. coli*.

Fiber No.	*E. coli* reduction (log CFU mL^{-1})
CHCFs-3	1.93
CHCFs-4	2.02
CHCFs-6	2.05

3.3. Physical and mechanical properties

The mechanical properties of the blend fibers prepared are shown in Table 2. Although the addition of a small amount HECS may interfere with the orientation and crystallization of cellulose, the mechanical properties of the fibers are found close to those of viscose rayon. The strength and elongation of the CHCFs are slightly lower than those of the viscose rayon and all of these data are all fit the national criterion which indicates the fibers can meet the following textile processing.

Moisture absorption and antistatic property are two important parameters for evaluating the comfortableness of the obtained textile. As we know, viscose rayon has an inborn good moisture absorption property. With large amount of –OH along the molecular chain, chitosan and its derivatives were also reported good hydrophilicity. The moisture absorption of CHCFs was tested and was found to be higher (13.22–13.55%) than that (13.01%) of viscose rayon. Viscose rayon has good antistatic property with the mass specific resistance of 4.7×10^8. The mass specific resistance of the CHCFs was lower than that of viscose rayon which suggests better performance in this aspect.

3.4. Antimicrobial property assessment

It is believed that the antimicrobial activity of chitosan is dependent on its amino group. Many derivatives of chitosan with stronger antimicrobial property were synthesized by modified its hydroxyl group on C_6 position of pyranose ring. In this study, HECS is also a hydroxylation derivative with high reactivity. The antimicrobial property of CHCFs and viscose rayon is shown in Table 3. After 12 h culture, even CHCFs-3 reduced the number of *E. coli* 1.93 log CFU mL^{-1} (ca. Table 3). The results show significant inhibitory effects against the growth of *E. coli* to varying extents.

4. Conclusions

O-Hydroxyethyl chitosan xanthate was synthesized and blended with cellulose xanthate in different ratios. Cellulose/O-

hydroxyethyl chitosan fibers were manufactured on viscose fiber production facilities. TEM microscope photographs showed that HECS dispersed uniformly along the oriented direction with a few of accumulation spots. TGA spectra showed that the decomposition temperature increased and the decomposition rate slowed down with HECS addition in the fiber. Although the addition of HECS slightly reduced the mechanical properties, the CHCFs could fit the national criterion and meet the following textile processing. The moisture absorption and antistatic property were enhanced with the addition of HECS. CHCFs exhibited significant antibacterial activities against *E. coli*.

Acknowledgements

The authors are grateful for the support of Tianjin College Science and Technology Development Fund under Grant 20060911.

References

Fan, L. H., Du, Y. M., Zhang, B. Z., Yang, J. H., Zhou, J. P., & Kennedy, J. F. (2006). Preparation and properties of alginate/carboxymethyl chitosan blend fibers. *Carbohydrate Polymers*, *65*(4), 447–452.

Gao, Y., & Cranston, R. (2008). Recent advances in antimicrobial treatments of textiles. *Textile Research Journal*, *78*(1), 60–72.

He, C. J., Ma, B. M., & Sun, J. F. (2009). The preparation and properties of cellulose/chitin blend filaments. *Journal of Applied Polymer Science*, 2777–2784.

Hu, S. G., Jou, C. H., & Yang, M. C. (2002). Surface grafting of polyester fiber with chitosan and the antibacterial activity of pathogenic bacteria. *Journal of Applied Polymer Science*, *86*(12), 2977–2983.

Jayakumar, R., Chennazhi, K. P., Muzzarelli, R., Tamura, H., Nair, S. V., & Selvamurugan, N. (2010). Chitosan conjugated DNA nanoparticles in gene therapy. *Carbohydrate Polymers*, *79*(1), 1–8.

Jin, X., Wang, J., & Bai, J. (2009). Synthesis and antibacterial activity of p-aminobenzoyl chitosan. *Journal of Wuhan University*, *55*(3), 305–309.

Jou, C. H., Yuan, L., Lin, S. M., Chou, W. L., Yu, D. G., & Yang, M. C. (2007). Biocompatibility and antibacterial activity of chitosan and hyaluronic acid immobilized polyester fibers. *Journal of Applied Polymer Science*, *104*(1), 220–225.

Kim, C. H., Choi, J. W., Chun, H. J., & Choi, K. S. (1997). Synthesis of chitosan derivatives with quaternary ammonium salt and their antibacterial activity. *Polymer Bulletin*, *38*, 387–393.

Knill, C. J., Kennedy, J. F., Mistry, J., Miraftab, M., Smart, G., Groocock, M. R., et al. (2004). Alginate fibres modified with unhydrolysed and hydrolysed chitosans for wound dressings. *Carbohydrate Polymers*, *55*(1), 65–76.

Li, Z., Liu, X. F., Zhuang, X. P., Guan, Y. L., & Yao, K. D. (2002). Manufacture and properties of chitosan/N,O-carboxymethylated chitosan/viscose rayon antibacterial fibers. *Journal of Applied Polymer Science*, *84*(11), 2049–2059.

Muzzarelli, R. (2009). Genipin-crosslinked chitosan hydrogels as biomedical and pharmaceutical aids. *Carbohydrate Polymers*, *77*(1), 1–9.

Nousiainen, P., Vehviläinen, M., Struszczyk, H., & Mäkinen, E. (2000). Functional hybrid fibers of cellulose/microcrystalline chitosan. I. Manufacture of viscose/microcrystalline chitosan fibers. *Journal of Applied Polymer Science*, *76*(12), 1725–1730.

Odaci, D., Timur, S., & Telefoncu, A. (2009). A microbial biosensor based on bacterial cells immobilized on chitosan matrix. *Bioelectrochemistry*, *75*(1), 77–82.

Pang, F. J., He, C. J., & Wang, Q. R. (2003). Preparation and properties of cellulose/chitin blend fiber. *Journal of Applied Polymer Science*, *90*(12), 3430–3436.

Ronghua, H., Yumin, D., & Jianhong, Y. (2003). Preparation and anticoagulant activity of carboxybutyrylated hydroxyethyl chitosan sulfates. *Carbohydrate Polymers*, *51*(4), 431–438.

Runarsson, O. V., Holappa, J., Nevalainen, T., Hjalmarsdottir, M., Jarvinen, T., Loftsson, T., et al. (2007). Antibacterial activity of methylated chitosan and chitooligomer derivatives: Synthesis and structure activity relationships. *European Polymer Journal*, *43*(6), 2660–2671.

Seo, H. (1990). *Sen'i Gakkaishi*, *46*(12), 564–569.

Wan, Y., Creber, K., Peppley, B., & Bui, V. T. (2004). Ionic conductivity and tensile properties of hydroxyethyl and hydroxypropyl chitosan membranes. *Journal of Polymer Science (B)*, *42*(8), 1379–1397.

Wang, X. M., Chi, N., & Tang, X. (2008). Preparation of estradiol chitosan nanoparticles for improving nasal absorption and brain targeting. *European Journal of Pharmaceutics and Biopharmaceutics*, *70*(3), 735–740.

Wu, Y. G., Wei, S., Zheng, Z., Zhou, L., Liu, B., Jiang, Z., et al. (2006). Structure of 6-O-carboxymethyl chitosan and its effects on bacterial resistance and healing promotin. *Chinese Journal of Biomedical Engineering*, *25*(5), 613–617.

Yang, T. C., Chou, C. C., & Li, C. F. (2005). Antibacterial activity of N-alkylated disaccharide chitosan derivatives. *International Journal of Food Microbiology*, *97*(3), 237–245.

Yoshikawa, M., Midorikawa, T., Otsuki, T., & Terashi, T. (1998). Process for producing articles of regenerated chitin-chitosan containing material and the resulting articles. *US Patent Office, Pat. No. 5 756 111*.

Zhao, Y. Q., Chen, J., Zeng, E., Hu, X. L., Liu, A. H., & Dong, Y. M. (2008). Synthesis and characterization of hydroxyethyl chitosan grafted by carboxyl ending DOVOB dendrimer: A novel liquid crystalline polymer. *Carbohydrate Polymers*, *74*(4), 828–833.

Zhu, H., & Jiang, R. (2009). Preparation of cross-linked chitosan film and its absorption behavior of acid scarlet dyeing. *Journal of Hebei University of Science and Technology*, *30*(1), 54–57.