

Preparation and Characterization of Chitosan/Poly(vinyl alcohol) Blend Fibers

HUA ZHENG,¹ YUMIN DU,¹ JIAHUI YU,¹ RONGHUA HUANG,¹ LINA ZHANG²

¹ Department of Environmental Science, Wuhan University, Wuhan 430072, People's Republic of China

² Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

Received 27 March 2000; accepted 5 September 2000

ABSTRACT: Chitosan and poly(vinyl alcohol) blend fibers were prepared by spinning their solution through a viscose-type spinneret at 25°C into a coagulating bath containing aqueous NaOH and ethanol. The influence of coagulation solution composition on the spinning performance was discussed, and the intermolecular interactions of blend fibers were studied by infrared analysis (IR), X-ray diffraction (XRD), and scanning electron micrograph (SEM) and by measurements of mechanical properties and water-retention properties. The results demonstrated that the water-retention properties and mechanical properties of the blend fibers increase due to the presence of PVA in the chitosan substrate, and the mechanical strength of the blends is also related to PVA content and the degree of deacetylation of chitosan. The best mechanical strength values of the blend fibers, 1.82 cN/d (dry state) and 0.81 cN/d (wet state), were obtained when PVA content was 20 wt % and the degree of deacetylation of chitosan was 90.2%. The strength of the blend fibers, especially wet tenacity could be improved further by crosslinking with glutaraldehyde. The water-retention values (WRV) of the blend fibers were between 170 and 241%, obviously higher than pure chitosan fiber (120%). The structure analysis indicated that there are strong interaction and good miscibility between chitosan and poly(vinyl alcohol) molecular resulted from intermolecular hydrogen bonds. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2558–2565, 2001

Key words: chitosan; poly(vinyl alcohol); blend fibers; miscibility; mechanical properties; water-retention properties

INTRODUCTION

Chitin, a (1 → 4)-linked N-acetamido-2-deoxy-β-D-glucan, is the second most abundant form of organic resource found in nature next to cellulose, and is present in marine invertebrates, insects, fungi, and yeasts.¹ Chitosan is the fully or partially deacetylated form of chitin. These biopoly-

mers have good biocompatibility,^{2,3} biodegradation^{3,4} and various biofunctionalities including antithrombotic, homeostatic, immunity enhancing, and wound healing.^{5,6} Therefore, many attempts have been made to produce new biofunctional materials from chitin and chitosan in cotton, films, nonwoven fabric, sponge, and gel forms.⁵

Owing to a high molecular weight, chitosan forms viscous solutions in dilute aqueous acetic acid that can be used to spin fibers. Its fiber forming properties have been investigated by several workers.^{7–9} The primary deficiencies of chi-

Correspondence to: Y. Du (duyumin@wku.edu.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 29977014

Journal of Applied Polymer Science, Vol. 80, 2558–2565 (2001)
© 2001 John Wiley & Sons, Inc.

tosan fibers are their poor wet strength. Several methods have been developed to improve the tensile strength of chitosan fibers such as crosslinked chitosan fiber with epichlorhydrin⁸ and chitosan derivative fibers.^{10–12}

Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, biocompatible, and biodegradable synthetic polymer, which is widely used in biochemical and biomedical applications.¹³ PVA has good fiber-forming, highly hydrophilic properties, and its fibers have been commercialized since the 1950s, and are used in textiles as a silk substitute.¹⁴ Poly(vinyl alcohol) and polysaccharides are unique in that both types of fiber are usually spun, coagulated, oriented, and crosslinked under essentially similar conditions.

It is well known that blending is an effective and convenient method to improve the performance of polymer materials. The tensile strength of chitosan fibers may also be improved by mixed-component spinning solutions with other water-soluble polymers. Thus, in the present study, bi-component fibers were prepared from chitosan and poly(vinyl alcohol), and crosslinked with glutaraldehyde in varying concentrations. The morphological structure and miscibility of the blend fibers were studied with the aids of infrared spectra (IR), scanning electron micrograph (SEM), and X-ray diffraction (XRD). The mechanical properties and water-retention values of blends were also measured with regard to the different proportions of the two components.

EXPERIMENTAL

Materials

A commercial crab shell chitosan (provided by Zhejiang Yuhan Ocean Biochemistry Co. Ltd.) was dissolved in aqueous 2 wt % acetic acid, filtered through a glass filter, and neutralized with aqueous 4 wt % NaOH. The precipitate was collected by filtration, and washed thoroughly with hot distilled water, ethanol, and acetone. The purified chitosan was obtained by drying under reduced pressure, whose degree of deacetylation (DD) was calculated to be 90.2% from the nitrogen content using the following equation¹⁵:

$$DD = 1 - [(W_C/W_N - 5.14)/1.72] \times 100\% \quad (1)$$

Where W_C/W_N is the ratio of carbon to nitrogen.

The limiting viscosity number ($[\eta]$) of the chitosan sample was measured by using a modified Ubbelohde viscometer, and the viscosity-average weight (M_η) was calculated to be 5.0×10^5 from the Mark-Houwink equation¹⁶:

$$[\eta] = KM_\eta^\alpha \quad (2)$$

Where $K = 6.589 \times 10^{-3} \text{ mL/g}$ $\alpha = 0.88$.

The other chitosan materials with the same molecular weight and different degrees of deacetylation, 84.5, 79.1, and 71.3%, respectively, were prepared by using the purified chitosan as raw material according to the methods described by Hirano et al.¹⁷

Poly(vinyl alcohol) (PVA) purchased from Shanghai Chemical Reagent Company, was used without further purification. The degree of polymerization of PVA was 1750 ± 50 , and the saponification degree was about 99.8%.

Glutaraldehyde and acetic acid (all chemical grade) were also the products of Shanghai Chemical Reagent Company.

Preparation of Blend Fibers

A 15 wt % poly(vinyl alcohol) aqueous solution was obtained by adding the required amount of PVA powder with stirring to the known volume of distilled water at 90°C. After cooling at room temperature, a certain amount of urea and a suitable weight of 4.5 wt % chitosan solution in 2 wt % acetic acid was added to the above solution of PVA. The mixed solutions were vigorously stirred at room temperature for an hour, and filtered through a 200 mesh filter cloth under pressure. The clear filtrate as a spinning solution was poured into the spinning tank, and degassed under diminished pressure for an hour. After that, the spinning solution was extruded at 25°C from a 30-hole (0.08-mm diameter) viscose-type spinneret into a coagulating bath containing an aqueous solution of NaOH and ethanol to form fibers. The as-spun fibers were washed and stretched (stretching ratio is 29%) in distilled water at 35°C, then air-dried to afford white fibers. According to the PVA contents of 10, 20, 30, 40, and 50 wt %, the blend fibers were labeled as CHPVA-1, CHPVA-2, CHPVA-3, CHPVA-4, and CHPVA-5, respectively. The pure chitosan fiber was coded as CH.

Preparation of Crosslinked Fibers

The following method was adapted to crosslink chitosan or chitosan/PVA blend fibers. A 200-cm

length of fiber was fixed as a single loop on a glass tube and placed in a large tube containing the known concentration of glutaraldehyde aqueous solution at 25°C, purged with nitrogen, and sealed. After 2 h, the fiber was taken out, washed repeatedly with distilled water to eliminate any unreacted glutaraldehyde, then dried naturally. The crosslinked chitosan or chitosan/PVA blend fibers were thus obtained.

Characterization of Fibers

FTIR spectra of PVA, chitosan and chitosan/PVA blend fibers were recorded with a Nicolet 17DSX FTIR Spectrometer. The fibers were cut into small pieces for preparation of KBr discs. The samples were made thin enough so to obey the Lambert-Beer Law. The morphological structure of the blend fibers were studied with Hitachi S-570 Scanning Electron Microscopy (SEM). Prior to examination, the blend fiber samples were fractured in liquid nitrogen, the sections of the fibers were coated with gold, then observed and photographed. X-ray diffraction patterns of fibers were recorded with a Rigaku Dmax-II X-ray diffractometer, using Nickel-filtered Cu K α radiation at 40 kV and 50 mA in the 2θ range of 5–40°. The crystallinities (X_c) of the fibers were estimated using a “cut and weigh” method by the equation¹⁸:

$$X_c = A_c / (A_a + A_c) \times 100\% \quad (3)$$

where A_a and A_c are the areas of amorphous crystal peaks, respectively.

Measurements of Properties

The tensile strength (σ_b) and the breaking elongation (ε_b) of the fibers in dry and wet state, which was immersed in water for 3 h at room temperature, were determined on a YG001-A Fiber Electron Tensile Tester (The Weaving Meter Manufacture of Taicang, China), at room temperature and 50% relative humidity. All tests were performed on single filaments with a gauge length of 90 mm, and a crosshead speed of 20 mm/min was selected. The values quoted for each sample were average values of 40 samples. The water-retention values (WRV) of fibers were calculated as follows:

$$\text{WRV} = (W_1 - W_0) / W_0 \times 100\% \quad (4)$$

where W_0 denote the original weight (g) of fiber which was dried at 100°C until a constant weight

achieved, W_1 is the weight of fully swollen fiber that was centrifuged at 4000 rev/min for 10 min.

RESULTS AND DISCUSSION

Preparation of Chitosan/Poly(Vinyl Alcohol) Spinning Solution

The concentration of chitosan/poly(vinyl alcohol) spinning solution have important effects on the physical properties of the blend fibers. A better quality of fiber would be possible by applying higher concentration of spinning solution. PVA with 99.8% saponification degree was insoluble in cold water, but it dissolved completely in hot water at 90°C up to a concentration of 15 wt % with only stirring. After cooling at room temperature, the 15 wt % PVA solution was still clear and had a viscosity of about 450 poise, which was considered suitable for spinning strong and drawable fibers. The viscosity of 4.5 wt % chitosan solution was about 400 poise, and was considered appropriate for fiber spinning. However, a blend solution have good spinning quality and good spinning performance was not produced because of its very high viscosity. Addition of 1 wt % urea (a strong hydrogen bond breaker) can make the viscosity of the spinning solution decrease dramatically, making spinning successful.

Effect of Coagulation Solution Composition on Spinning Performance

The spinning trial of chitosan/poly(vinyl alcohol) blend fibers was carried out in a mixed coagulation solution of NaOH and ethanol. Table I shows the effects of coagulation solution composition on the spinning performance. The concentration of NaOH and the volume ratio of NaOH solution to ethanol are the important factors influencing the coagulation speed of the fibers. The concentration of NaOH solution was lower than 10 wt %, the rate of coagulation was very slow, and results in frequent filament breakage, so spinning performance cannot be proceeded smoothly. When the concentration of NaOH solution was higher than 10 wt %, and the volume ratio of NaOH solution to ethanol was between 70/30 and 50/50, the rate of coagulation was adequate, excellent spinning performance can be achieved. Therefore, in this study, 10 wt % NaOH solution and 50/50 volume ratio of NaOH solution to ethanol were selected for further spinning experiment.

Table I The Effect of Coagulation Solution Composition on the Spinning Performance

Concentration of NaOH %	Ratio of NaOH/Ethanol V/V	Temperature °C	Spinning Performance
5	90/10	25	Can proceed
5	70/30	25	Just proceed
5	50/50	25	Just proceed
5	30/70	25	Can not proceed
5	10/90	25	Can not proceed
10	90/10	25	Can proceed
10	70/30	25	Excellent
10	50/50	25	Excellent
10	30/70	25	Just proceed
10	10/90	25	Can not proceed

IR Spectra Analysis of Blend Fibers

The homopolymer solution and all the blend solution of chitosan and PVA were optically clear to the naked eye. They showed neither separation into two layers nor any precipitation, even after the solution was allowed to stand for more than 2 weeks at room temperature.

The infrared spectra of chitosan/PVA blend fibers with different composition are shown in Figure 1. The PVA fiber showed absorption bands at 2945, 1452, 1336, 1238, 1095 and 843 cm^{-1} , which are attributed to the $\nu_a(\text{CH}_2)$, $\delta(\text{CH}-\text{OH})$, $\delta(\text{CH}-\text{OH})$, $\omega(\text{CH})$, $\nu(\text{C}-\text{O})$, and $\nu(\text{C}-\text{C})$ resonance, respectively, in agreement with the literature data.¹⁹ The infrared spectrum of chitosan shows around 894 cm^{-1} and 1159 cm^{-1} peaks assigned saccharine structure²⁰ and a weaker amino characteristic peak at around 1597 cm^{-1} .²¹ The absorption peak at 1260 cm^{-1} is the absorption of $\delta(\text{O}-\text{H})$,²⁰ and the sharp band at 1381 cm^{-1} has been assigned to the CH_3 symmetrical deformation mode.²² Difference between infrared spectra of pure chitosan and chitosan/PVA blend fibers were: (1) the absorption band at about 3450 cm^{-1} concerned with $-\text{OH}$ and $-\text{NH}$ stretching vibrations²⁰ broadened and shifted obviously to a lower wave number with the increase of PVA in the blends, suggesting the formation of much hydrogen bonds between chitosan and PVA molecule. (2) The disappearance of crystallization sensitive bands of pure chitosan at 1098 cm^{-1} and 665 cm^{-1} in the blends,²¹ implying that an intermolecular interaction between PVA and chitosan disturbs the crystallization of chitosan in a blend state. These results were in agreement with Miya's IR analysis of PVA/chitosan blend films.²³

X-Ray Analysis of Blend Fibers

Figure 2 presents the X-ray diffraction pattern of chitosan, PVA, and their blend fibers. The diffractogram of chitosan fiber consists of three major

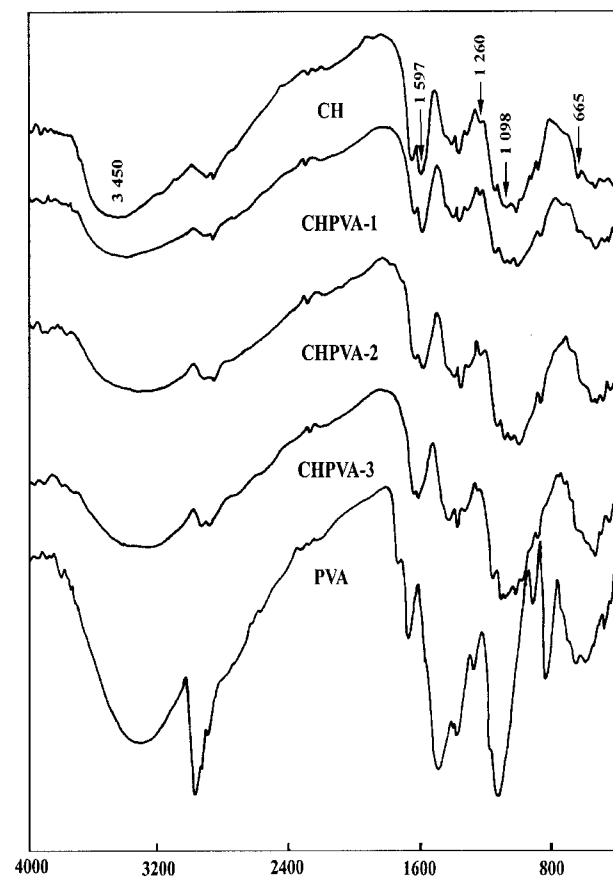


Figure 1 IR spectra of the fibers CH, CHPVA-1, CHPVA-2, CHPVA-3, and PVA.

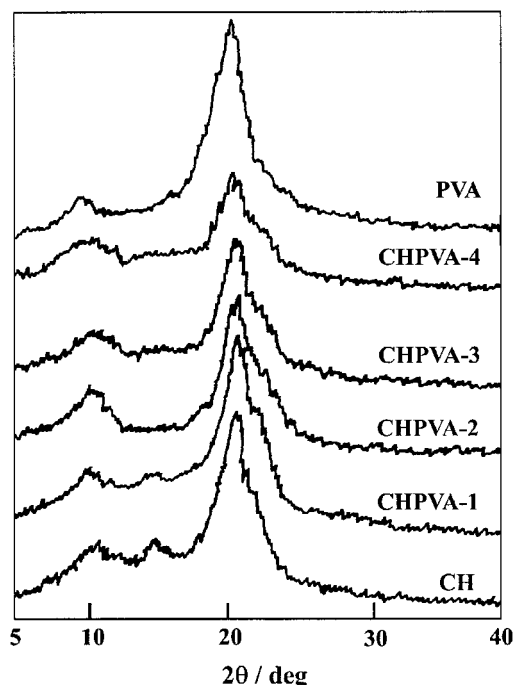


Figure 2 X-ray diffraction patterns of the fibers CH, CHPVA-1, CHPVA-2, CHPVA-3, CHPVA-4, and PVA.

crystalline peaks at 2θ 10.5° , 15.4° , and 20.1° reported by Samuels et al.²⁴ The diffraction model of PVA shows two typical peaks at 2θ 10° and 19.8° .²⁵ If chitosan and PVA molecules have poor interaction or are without interaction in the blend fibers, each component has its own crystal region in the blend fibers, and X-ray diffraction patterns are expressed as simply mixed patterns of chitosan and PVA with the same ratios as those for mechanical blending. In fact, the diffraction intensities of chitosan at 15.4° decreased drastically with increasing the content of PVA in the blends, but the crystal intensities of chitosan/PVA blends increased as the amount of PVA increased. The

percent relative crystallinities of the blend fibers are 31.2, 34.7, 37.5, and 39.8%, corresponding to CHPVA-1, CHPVA-2, CHPVA-3, and CHPVA-4, respectively, greater than that of pure chitosan (30.2%) (Table II). Based upon these evidences, it can be further concluded that strong interaction occurred between chitosan and PVA molecule in the blends.

SEM Observations of Fibers

The sections of chitosan/PVA blend fibers were examined by scanning electron microscopy to verify the compatibility between chitosan and PVA molecules (Fig. 3). The sections of CHPVA-2 and CHPVA-4 showed a smooth and homogeneous morphology, suggesting high miscibility and blend homogeneity between chitosan and PVA at the composite ratio in the range of 9/1 ~ 5/5 by weight.

In view of IR, X-ray diffraction, and SEM analysis of chitosan/PVA blend fibers, it can be concluded that good miscibility was sustained by the hydrogen bonds and intermolecular interaction between chitosan and PVA in blend fibers.

Effect of PVA Content on Fiber Properties

The effect of PVA content on the tensile strength of the fibers in dry and wet states is shown in Figure 4 and Table II. The dry and wet tensile strengths of the blend fibers with PVA from 10 to 40% were higher than that of pure chitosan, and the maximum value was observed at 20% PVA content achieved 1.82 cN/d in the dry state and 0.81 cN/d in the wet state, respectively. The remarkable increase in tensile strength of this blend fiber indicates the presence of some interaction between cellulose and PVA molecules in the blend.

Table II The Properties of the Blend Fibers

Fiber No.	Chitosan/PVA (wt/wt)	Tensile Strength (cN/d) (Dry/Wet)	Breaking Elongation (%) (Dry/Wet)	WRV (%)
Chitosan	100/0	1.50/0.71	12.0/23.2	120
CHPVA-1	90/10	1.65/0.73	13.8/24.2	170
CHPVA-2	80/20	1.82/0.81	15.4/31.9	191
CHPVA-3	70/30	1.72/0.74	14.2/26.6	215
CHPVA-4	60/40	1.61/0.70	13.3/25.2	231
CHPVA-5	50/50	1.46/0.58	12.8/21.4	241

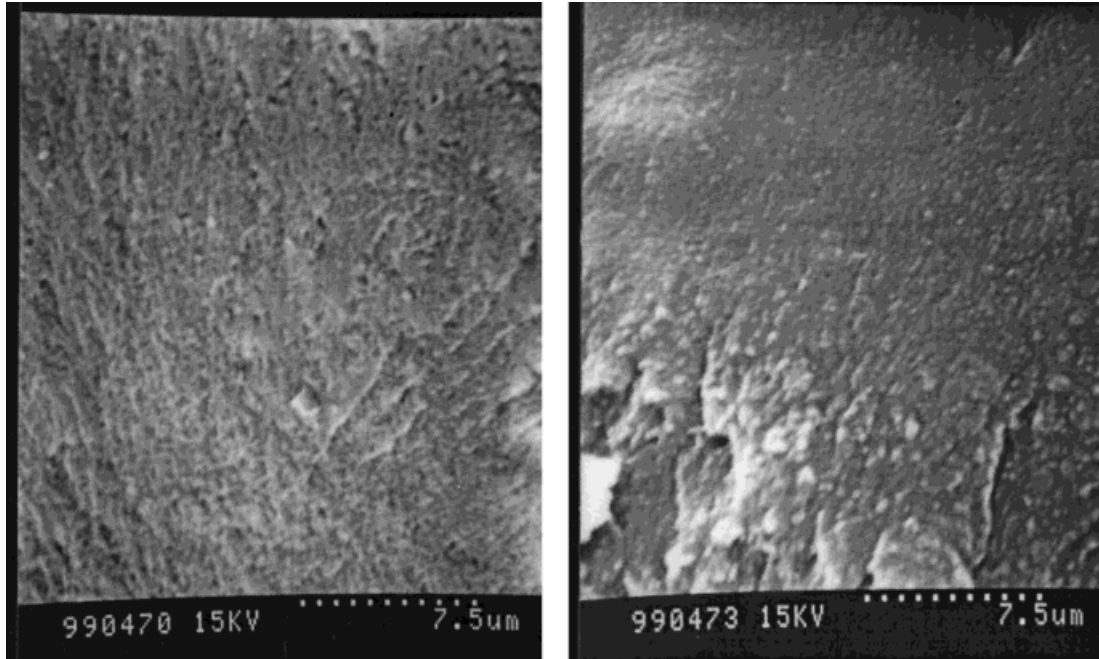
**A****B**

Figure 3 SEM of the sections of fiber CHPVA-2 (A) and CHPVA-4 (B).

Figure 5 shows the breaking elongation of the fibers in the dry and wet states. These elongation patterns corresponded well to the results in Figure 4.

The water-retention properties of the blend fibers are plotted in Figure 6 as a function of the weight content of PVA. Figure 6 shows that the water-retention values (WRV) of chitosan/PVA blends increase as the amount of PVA is raised,

but not linearly. The water-retention values (WRV) of the blends were in the ranges of 170–241%, obviously higher than that of pure chitosan fiber, which has the lowest values (120%) (Table II). The improvement in water-retention values owing to the hydrophilic nature of PVA could promise the wide application of chitosan/PVA blend fibers as biomedical dressings.

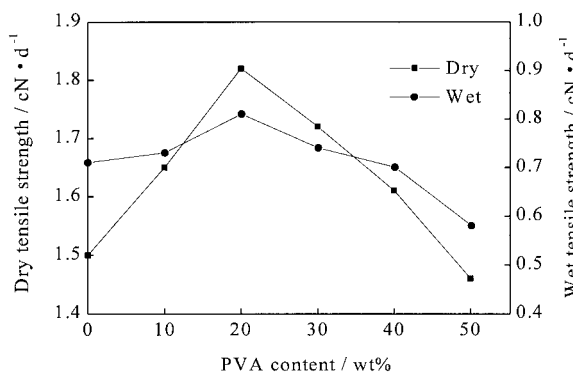


Figure 4 The effect of PVA content (wt %) on tensile strength of the fibers.

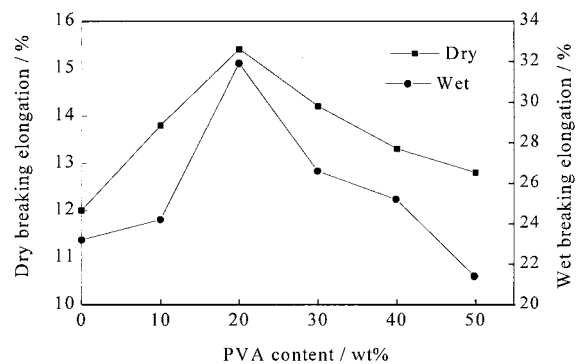


Figure 5 The effect of PVA content (wt %) on breaking elongation of the fibers.

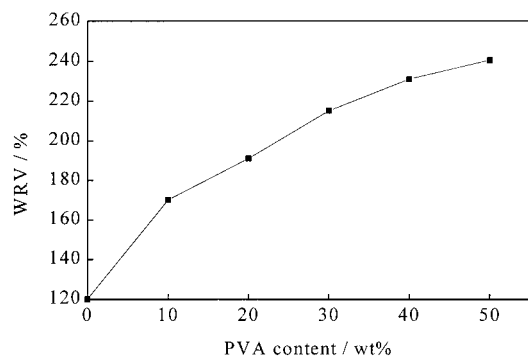


Figure 6 The effect of PVA content (wt %) on the WRV.

Effect of Chitosan with Different Degree of Deacetylation on Fiber Properties

To detect the degree of deacetylation of chitosan on the properties of blends, the chitosan and PVA blend fibers with 20 wt % PVA and 80 wt % chitosan with different degrees of deacetylation were prepared, their mechanical properties and water-retention values are listed in Table III. The tensile strengths in the dry or wet state and percent elongation at break decreased with the degree of deacetylation of chitosan decreased. Sixteen and 9% losses in the dry tensile strength and the wet tensile strength, respectively, are observed when the degree of deacetylation of chitosan in the blends is decreased from 90.2 to 71.3%. These losses are accompanied by a 20% decrease in the percent elongation at break in the dry or wet state. The decline of tensile strength in the blends is possible because the lower degree of deacetylation of chitosan has more side groups, which are detrimental to the formation of a neat structure between chitosan and PVA molecules and makes the crystallization degree lower. Details of this study will be reported elsewhere in the near future.

Table III The Effect of Degree of Deacetylation on the Properties of Blend Fibers

Degree of Deacetylation (%)	Tensile Strength (cN/d) (Dry/Wet)	Breaking Elongation (%) (Dry/Wet)	WRV (%)
90.2	1.82/0.81	15.4/31.9	191
84.5	1.71/0.77	14.7/28.3	190.3
79.1	1.65/0.76	14.1/27.5	189
71.3	1.52/0.74	12.4/25.8	185.4

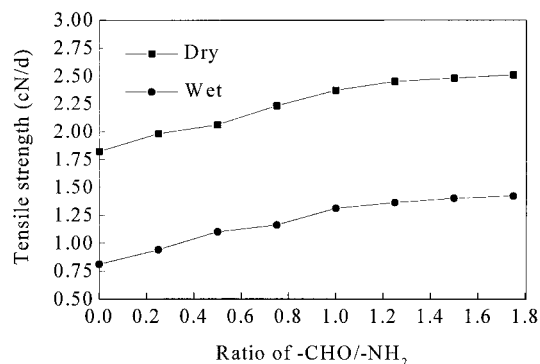


Figure 7 The effect of the ration of $-\text{CHO}/-\text{NH}_2$ on tensile strength of the crosslinked fibers.

The degree of deacetylation of chitosan also has an effect on the water-retention properties of the blends, but the influence is not obvious; only a 3% loss in water retention value is detected when the degree of deacetylation of chitosan in the blend is decreased from 90.2 to 71.3%.

Effect of Crosslinking on the Mechanical Properties of Blend Fibers

To examine the effect of crosslinking on the mechanical properties of blend fiber, the chitosan/PVA blend fibers composed of 20 wt % PVA and 80 wt % chitosan with a degree of deacetylation value of 90.2% was crosslinked with aqueous glutaraldehyde. The relationship of the tensile strength of crosslinked fiber in the dry or wet state to the ratio of $-\text{CHO}/-\text{NH}_2$ is shown in Figure 7 and Table IV. It is obvious that the tensile strength of the blend fiber, especially wet tensile strength, is improved by crosslinking.

Table IV The Effect of $-\text{CHO}/-\text{NH}_2$ Ratio on Fiber Properties

Ratio of $-\text{CHO}/-\text{NH}_2$	Tensile Strength (cN/d) (Dry/Wet)	Breaking Elongation (%) (Dry/Wet)
0	1.82/0.81	15.4/31.9
0.25	1.98/0.94	16.1/32.3
0.50	2.06/1.10	15.6/28.1
0.75	2.23/1.16	14.5/26.2
1.00	2.37/1.31	14.3/24.4
1.25	2.45/1.36	13.6/22.8
1.50	2.48/1.40	11.4/21.7
1.75	2.51/1.42	10.2/21.1

Thirty-eight and 75% increases in the dry tensile strength and the wet tensile strength, respectively, are examined when the —CHO/—NH₂ ratio is increase from 0 to 1.75. Moreover, the tensile strength increased rapidly with the increase of —CHO/—NH₂ ratio below 1.25. However, increasing the —CHO/—NH₂ ratio above 1.25 almost produce a further increase in the tensile strength of the crosslinked fiber.

Table IV also shows the results of the breaking elongation of the crosslinked blend fiber in the dry or wet state to the ratio of —CHO/—NH₂. Increasing the ratio of —CHO/—NH₂, a gradual decrease in the breaking elongation of the crosslinked fiber is observed, when the ration of —CHO/—NH₂ increases from 0 to 1.75, the breaking elongation of crosslinked fiber decreases about 34%.

CONCLUSIONS

Chitosan and Poly(vinyl alcohol) blend fiber can be obtained by spinning their solution through a viscose-type spinnet at 25°C into a coagulation bath containing aqueous NaOH and ethanol. The addition of urea into spinning solution and the composition of coagulation solution have important influence on the spinning performance. The strong intermolecular interaction between chitosan and PVA molecule chain results in good miscibility. The introduction of PVA in the blend fiber can improve the tensile strength and water-retention properties of the blend fiber compared to pure chitosan fiber. The tensile strength of the blend fiber is also related to the degree of deacetylation of chitosan, and can be improved further by crosslinking with glutaraldehyde.

This work was financially supported by China Capital Group Co. Ltd., P. R. of China.

REFERENCES

1. Parisher, E.; Lombardi, D. *Chitin Sourcebook*; John Wiley & Sons: New York, 1989.
2. Hirano, S.; Seino, H.; Akiyama, Y.; Nonaka, I. In *Progress in Biomedical Polymer*; Gebelein, C. G.; Dunn, R. L., Eds.; Plenum Publishing Co.: New York, 1990, p. 283.
3. Shigemasa, Y.; Minami, S. In *Chitin/Chitosan, A Handbook of Chitin and Chitosan*. Gihodo Publishing Co., Japan Soc.: Tokyo, 1995, p. 178.
4. Muzzarelli, R. A. A. *Cell Mol Life Sci* 1997, 53, 137.
5. Hirano, S. *Biotechnol Annu Rev* 1996, 2, 237.
6. Shigemasa, Y.; Minami, S. *Biotechnol Genet Eng Rev* 1995, 13, 383.
7. Sakurai, K.; Miyata, M.; Takahashi, T. *Sen' Gakkaishi* 1990, 46, 79.
8. Wei, Y. C.; Hudson, S. M.; Mayer, J. M.; Kaplan, D. L. *J Polym Sci Polym Chem Ed* 1992, 30, 2187.
9. Tokura, S.; Nishimura, S.; Nishi, N.; Nakamura, K.; Hasegawa, O.; Sashiwa, H.; Sachiwa, H.; Seo, H. *Seni'Gakkaishi* 1987, 43, 288.
10. Tokura, S.; Nishi, N.; Somorin, O.; Noguchi, J. *Polym J* 1980, 12, 695.
11. Tokura, S.; Yoshida, J.; Nishi, N.; Hiraoki, T. *Polym J* 1982, 14, 527.
12. Delucca, G. V.; Kezar, H. K., III; Brien, J. P. O. U.S. pat 5(021), 207 (1991).
13. Rskukada, M.; Freddi, G.; Crighiton, J. S. *J Polym Sci Part B Polym Phys* 1994, 32, 243.
14. Sakurada, I. *Poly(vinyl alcohol) Fibers*; Marcel Dekker: New York, 1985.
15. Jin, X.; Stephen, P. M.; Richard, A. G.; David, C. K. *Macromolecules* 1996, 29, 3436.
16. Wei, W.; Shu, Q. B.; Wen, Q. *Acta Polym Sinica* 1992, 2, 202.
17. Hirano, S.; Ohe, Y.; Qno, H. *Carbohydr Res* 1976, 47, 315.
18. Klyg, H. P.; Alexander, L. E. *X-ray Diffraction Procedures for Poly-crystalline and Amorphous Material*; Wiley Interscience: New York, 1974.
19. Krimm, S.; Liang, C. Y. *J Polym Sci* 1956, 22, 227.
20. Pearson, F. F.; Marchessault, R. H.; Ciang, C. Y. *J Polym Sci* 1960, 43, 101.
21. Mima, S.; Miya, M.; Iwamoto, R. *J Appl Polym Sci* 1983, 28, 1909.
22. Sannan, T.; Lcurita, K.; Ogura, K. *Polymer* 1978, 19, 458.
23. Miya, M.; Iwamoto, R.; Mima, S. *J Polym Sci Polym Phys Ed* 1984, 22, 1149.
24. Samuels, R. J. *J Polym Sci Polym Phys Ed* 1981, 19, 1081.
25. Nishio, Y.; Johnmanley, R. St. *Macromolecules* 1988, 21, 1270.