Fabrication and Characterization of Zein/Viscose Textibe Fibers

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ABSTRACT: Azlons are increasingly concerned for their excellent performance properties and biodegradation. A kind of novel azlon, zein/viscose textibe fibers, were fabricated by wet-spinning of zein and cellulose sulfonate blended solution. Some parameters that determine the fabrication process were optimized. The structure and properties of zein/viscose fibers were characterized, and compared with those of common viscose fibers. Dry breaking tenacity of zein/viscose fibers was 2.02 CN/dtex, whereas dry breaking elongation was 16.6%. Mechanical properties of zein/viscose fibers were a little better than common viscose fibers. The moisture regain rate of zein/viscose fibers was 14.1%, similar to that of viscose fibers. From the microstructure of zein/viscose fiber, viscose acted as framework and zein was accreted to viscose. The content of protein was 14.48% in zein/viscose fibers. The basic chains of zein and viscose were not changed by blended spinning, so the fibers had advantages of both zein and viscose. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3364–3370, 2010

Key words: corn; zein; viscose; fiber; cellulose; wet-spinning

INTRODUCTION

Natural protein fibers such as wool and silk have excellent performances, such as good absorption of moisture and comfortability. However, natural protein fibers have a high-price, because of the limited resources. Although synthetic fibers have many advantages over natural and regenerated fibers on mechanical properties and prices, they cannot meet the increasing demands of consumers for poor comfortability and degradability. Therefore, the fabrication of azlons from other sources such as plants and milk has attracted considerable interest, since the late 19th century. Some azlons were fabricated by chemical modification of natural proteins, whereas others were fabricated by blended spinning with some materials. Blended fibers usually have advantages of each blended material.

Zein comprises 45–50% of the protein in corn, which can be extracted from corn endosperm.[1] In whole corn, zein occurs as a heterogeneous mixture of disulfide-linked aggregates having a weight average molecular weight of 44,000 Da.[2] Peptides of zein have some health functions, such as blood pressure reduction,[3–5] antioxidation,[6] and accelerating alcohol metabolism.[7,8] Zein has the ability to form fibers, but mechanical properties of natural zein fibers are too poor to be as for textile function. Many researches on zein-based textile fibers have been done, since the early 1900s.[9–13] These zein-based textile fibers were prepared by chemical modification to zein, but they were not produced in industry, because of poor performance and high-cost. In 1950s, zein-based textile fibers[14] were sold under the brand name *Vicara* for clothing purposes and for stuffing furniture. But they withdrew from the market because of the high-price. Since 1990s, there have been some researches on zein-based textile fibers again,[15–20] and there have also been some researches on zein nanofibrous membranes by electrospinning.[21–26] But there are no research on blended spinning of zein and other materials to fabricate textile fibers reported by far.

Viscose fibers are regenerated fibers, which are moisture absorbent, breathable, comfortable to wear, and easily dyed in different vivid colors. Moreover, they have a low-price and good biodegradation. Viscose fibers have many hydroxyl groups that can easily graft and cross-link with other groups, so viscose can be easily blended spun with other materials.

If zein and viscose can be used to fabricate fibers by blended spinning, the regenerated fibers thus obtained may own the advantages of both zein and viscose, such as comfortability and health care of zein and good mechanical propertites of viscose.

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Moreover, as zein and cellulose sulfonate have a low-price and can be easily obtained from biomass, the blended fibers have a low-cost and are renewable. Therefore, in this article, zein and viscose were used to fabricate novel zein/viscose textibe fibers by blended wet-spinning. The structure and properties of zein/viscose fibers were characterized to evaluate performances of the fibers.

EXPERIMENTAL

Materials and reagents

Zein was extracted from corn gluten meal by 75% (v/v) ethanol with pH 11∼12 (using NaOH to adjust pH) at 50°C for 2 h. After adjusting pH of the extraction to 5∼6, distill most ethanol by rotary evaporator, centrifugate the remains to obtain zein precipitation, and dry the zein precipitation. Cellulose sulfonate, which was the precursor of viscose, was obtained from Baoding Swan Co., (China). Viscose fibers were also obtained from Baoding Swan Co., (China). Other reagents were all analytically pure and produced in China.

Fabrication of zein/viscose fibers

Preparation of blended spinning solution

The spinning solution was prepared by dissolving zein in 4.0% NaOH and blended with cellulose sulfonate solution. The final spinning solution contained 1.0% (w/w) zein, 8.2% (w/w) cellulose sulfonate, and 5.8% (w/w) NaOH. The solution was filtrated, deaerated, and ripened for spinning. The maturity index was measured by Hottenroth number method,[27] whereas the viscosity was measured by a falling ball viscometer.

Wet-spinning of zein/viscose fibers and aftertreatment

Viscose-type wet-spinning apparatus was used in the fabrication of zein/viscose fibers. The fibers was 133.3 dtex/30f with a linear winding speed of 81 m/min.

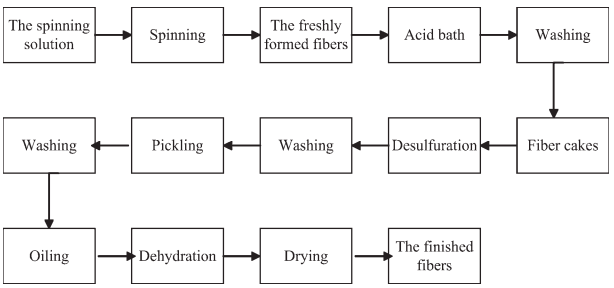

Figure 1 The fabrication process of zein/viscose fibers.

The contents of acid bath were as follows: 132.0 g/L H_2SO_4, 265.0 g/L Na_2SO_4, and 10.0 g/L $ZnSO_4$, with a temperature of 52°C.

The process of fabrication was shown in Figure 1.

Table I Shows the parameters of aftertreatment.

Oiling rate was measured by gravimetric method.[27]

Characterization of zein/viscose fibers

Structure and morphology of zein/viscose fibers

The appearance and color of zein/viscose fibers were investigated by naked eyes, whereas the diameter of zein/viscose fibers was measured by optical microscope (OLYMPUS BX41). The structure and morphology of zein/viscose fibers and common viscose fibers were investigated by a field emission scanning electron microscope (JEOL JSM-6700F) after gold coating.

Zein/viscose fibers and viscose fibers were soaked in 5, 10, and 30% (w/v) NaOH, respectively for 2 h to remove zein, to investigate the distribution of zein in zein/viscose fibers. The remains were washed by water and dried at room temperature before investigated by a scanning electron microscope (SEM) after gold coating.

Mechanical properties of zein/viscose fibers

The breaking tenacity and elongation of zein/viscose fibers were measured by a single-yarn strength

TABLE I
The Parameters of Aftertreatment

	Concentration (g/L)	Temperature (°C)	Time (min)
Desulfuration (by Na_2SO_4)	5	80 ± 1	120
Pickling (by HCl)	5.2 ± 0.2	Room temperature	40
Oiling (by Viscose-type oiling agent)	1.6 ± 0.2	42 ± 1	40
The first water washing		70 ± 1	40
The second water washing		40 ± 1	40
The third water washing		35 ± 1	40
Drying			
The first drying		80 ± 2°C	24 h
The second drying		70 ± 2°C	24 h

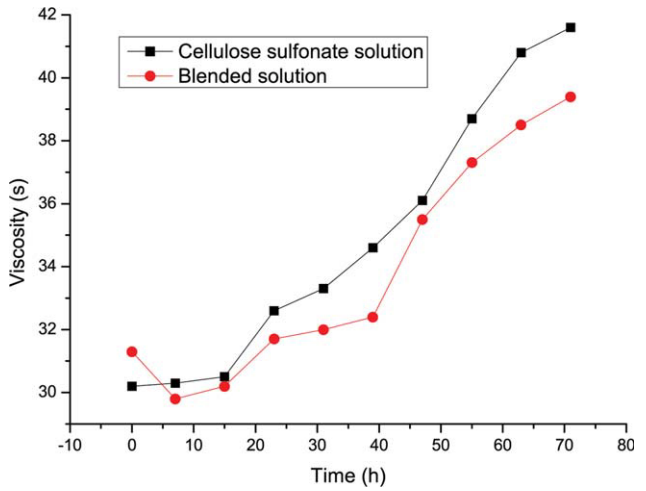

Figure 2 The viscosity of blended solution and cellulose sulfonate solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tester, according to the method of National Standard of China (GB/T13758-92).[28] Iodimetry method[28] was used to measure the amount of residual sulfur. Moisture regain rate was measured by gravimetric method, which was calculated as follows:

$$\text{Moisture regain rate} = (\text{Wet weight} - \text{Dry weight})/\text{Dry weight}$$

Wet weight was measured at temperature of 20°C and humidity of 65%.

Infrared absorption spectrum of zein/viscose fibers

Zein/viscose fibers and viscose fibers were first sheared into powers, and then their chemical bonds were measured by a fourier transform infrared spectrophotometer (SHIMADZU FTIR-8400S).

RESULT AND DISCUSSION

Some parameters in fabrication of zein/viscose fibers

Some properties of zein/celulose sulfonate blended solution

Zein solution should be blended with cellulose sulfonate solution, immediately after preparation, because it solidified easily when it was dissolved in NaOH solution and open to air. Compared with cellulose sulfonate solution, the blended solution had larger filtration resistance because zein and cellulose sulfonate grafted and cross-linked after blended, which increased the molecular weights of blended solution and increased the difficulty of spinning.

Spinnability of zein/viscose fibers most depended on the viscosity and maturity index of blended solution. Viscosity and maturity index of blended solution and cellulose sulfonate solution were measured at different time after blending, shown in Figures 2 and 3.

As shown in Figure 2, just after blending, the viscosity of blended solution was higher than cellulose sulfonate solution. But with time, the viscosity first decreased and then increased after 7 h, whereas the viscosity of cellulose sulfonate solution increased with time. After 7 h, the viscosity of blended solution was a little lower than that of cellulose sulfonate solution.

Larger viscosity increased the transport and filtration difficulty of blended solution, whereas lower viscosity decreased the spinnability. The viscosity of 32–40 s was the most optimized condition for fabrication of zein/viscose fibers.

According to Hottenroth number method, if the amount of NH_4Cl was smaller, the maturity index of blended solution was higher. As shown in Figure 3, the maturity index of both blended solution and cellulose sulfonate solution increased with time, whereas the maturity index of blended solution was a little higher than cellulose sulfonate solution all the time. Spinnability of zein/viscose fibers increased with the maturity index. But if the maturity index was too high, the fibers after spinning solidified easily, leading to the inhomogeneous structure of zein/viscose fibers, and the poor mechanical properties. The maturity index of 8.0–9.0 was the most optimized condition for fabrication of zein/viscose fibers.

Zein in the blended solution had some agglutination on standing. As illustrated in Figure 4, agglutination, 96 h after blending, were not obvious, compared with the one just after blending. There was

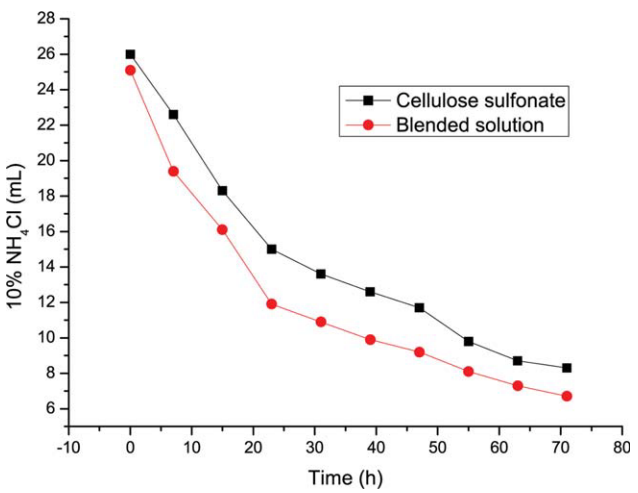

Figure 3 The maturity index of blended solution and cellulose sulfonate solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

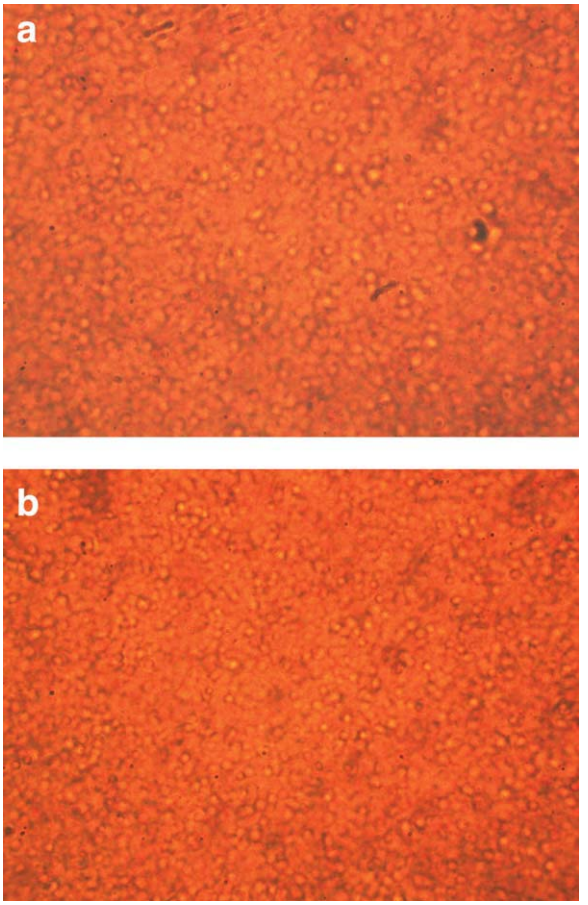

Figure 4 Morphology of blended solution observed by optical microscope. [Fig. 4(a) Just after blending × 400; Fig. 4(b) 96 h after blending × 400]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

still no floccule in the blended solution, 96 h after blending, so the unobvious agglutination of zein did not effect the spinnability.

Oiling rate of zein/viscose fibers

The fibers were oiled in our investigation to make them more comfortable, pliant, and flexible, and therefore, to reduce the friction and electrostatic effect of zein/viscose fibers and enhance cohesion. The oiling rate of zein/viscose fiber was 1.11%, higher than 0.81% of viscose fibers, indicating that zein/viscose fibers had a higher absorption than viscose fibers.

Some parameters of desulfuration and washing

Na_2SO_4 method was used in the process of desulfuration. If Na_2SO_4 was not supersaturated, zein in the fiber cakes would be washed away from the fibers to the desulfuration bath, which damaged the fibers. If pH was higher than 10, zein would also be washed away. So the follow components of desulfuration bath were adopted at the process of desulfuration: 380.0 g/L Na_2SO_4 and a certain concentration of NaOH with pH 10. As Na_2SO_4 was supersaturated at the condition of 380.0 g/L, insoluble crystals of Na_2SO_4 could cling to the fiber cakes. Washing with higher temperature should be used after desulfuration to wash away insoluble crystals of Na_2SO_4. So the temperature of washing, after desulfuration, was 70°C. In this condition, zein in the fiber cakes could not be washed away from the fibers, so there was no loss of protein in this process.

Characterization of zein/viscose fibers

Structure and morphology of zein/viscose fibers

The color of zein/viscose fibers was bright canary, whereas that of viscose fibers was bright white.

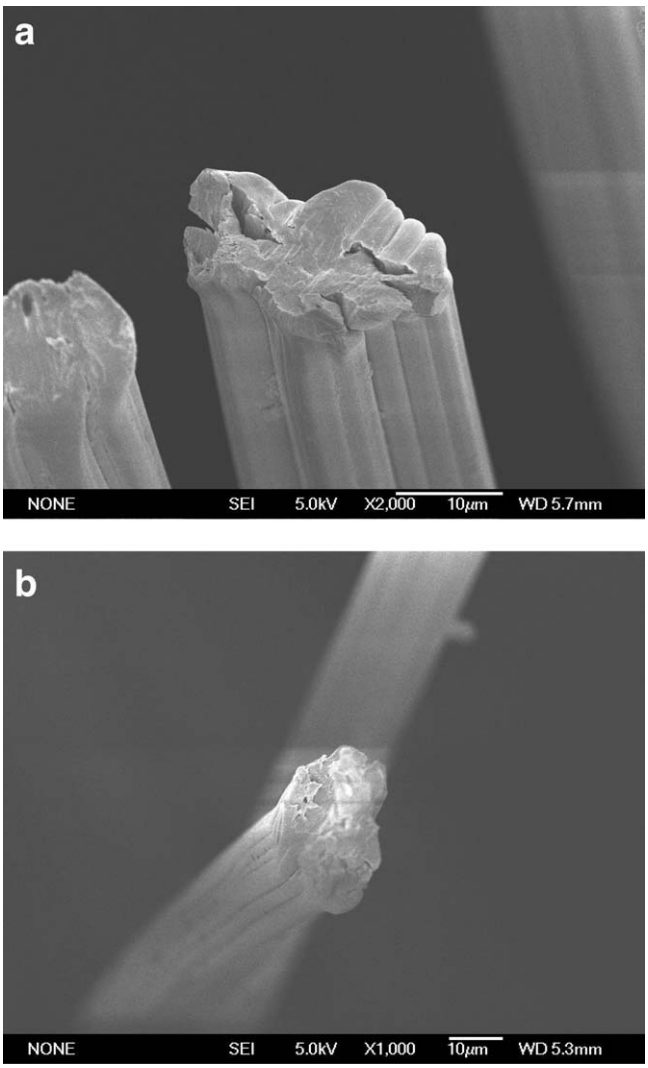

Figure 5 Zein/viscose fiber and viscose fiber observed by a SEM. [Fig. 5(a) Zein/viscose fiber ×2000; Fig. 5(b) Viscose fiber ×1000].

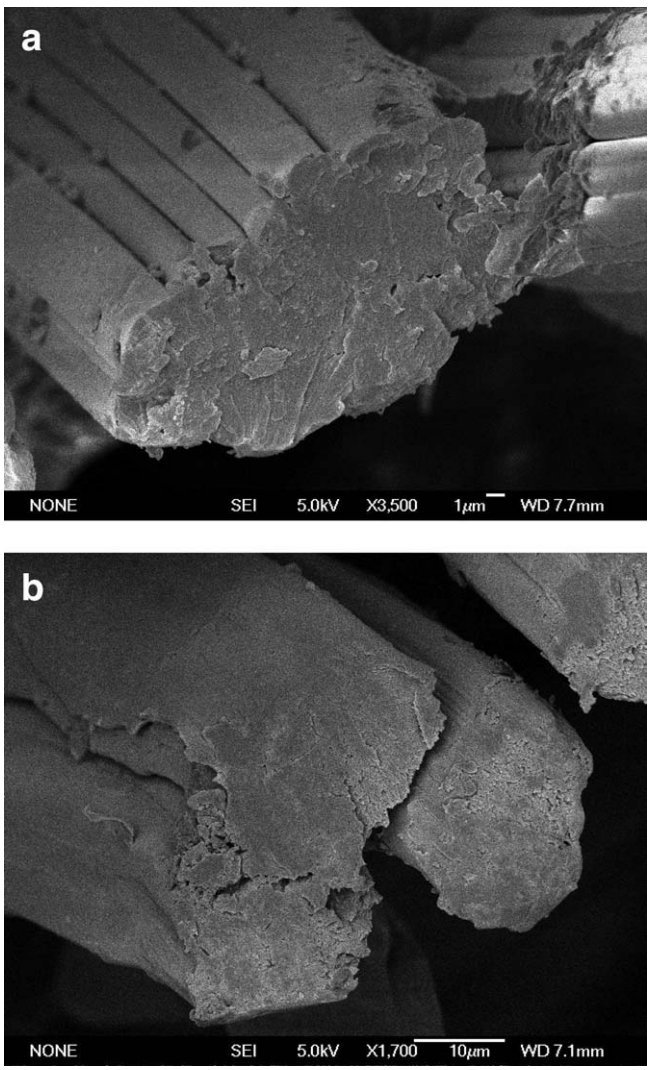

Figure 6 Zein/viscose fiber and viscose fiber handled with 5% NaOH observed by a SEM. [Fig. 6(a) Zein/viscose fiber ×3500; Fig. 6(b) Viscose fiber ×1700].

Zein/viscose fibers was more comfortable and pliant than viscose fibers. The diameter of zein/viscose fiber was about 1.5–2.0 μm.

From Figure 5(a) observed by a SEM, the structure of zein/viscose fiber was generally that of smooth and inelastic filaments like glass rods, similar to that of viscose fiber, shown in Figure 5(b). There were many grooves at vertical surface of zein/viscose fiber, so the cross section was irregular, which was also similar to viscose fiber.

As shown in Figures 6–8, the surface of zein/viscose fiber was eroded more and more seriously with the concentration of NaOH, because zein can be dissolved in NaOH solution. The structure of viscose fiber was also distorted more and more seriously with the concentration of NaOH, but less obvious than that of zein/viscose fiber, showing that alkali could also affect the structure of viscose fiber. The inner structure of zein/viscose fiber was not eroded, indicating that zein was on the surface of zein/viscose fiber. After being eroded, the structure of zein/viscose fiber did not change much, indicating that viscose was framework and zein was attached to viscose. The grooves of both zein/viscose fiber and viscose fiber became shallower with the concentration of NaOH.

Mechanical properties of zein/viscose fibers

Table II shows the mechanical properties of zein/viscose fibers and viscose fibers. The mechanical properties data of viscose fibers were from National Standard of China.[28] As shown in Table II, the mechanical properties of zein/viscose fibers were better than superior level of viscose fibers except for slight deviation from linear density. Similar to viscose fibers, wet breaking tenacity of

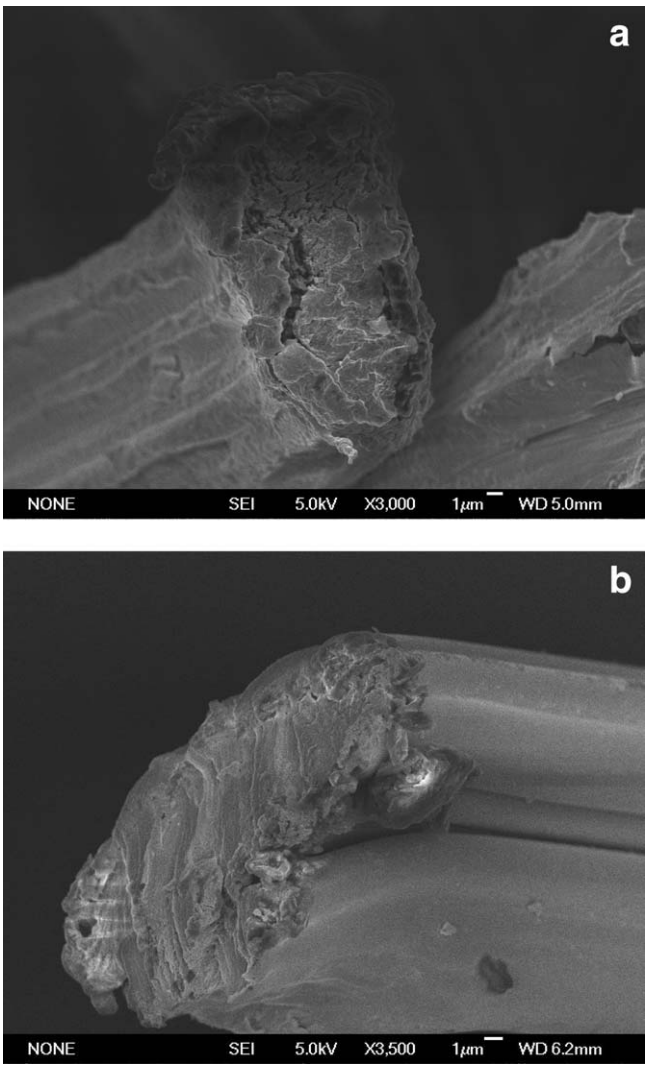

Figure 7 Zein/viscose fiber and viscose fiber handled with 10% NaOH observed by a SEM. [Fig. 7(a) ×3000; Fig. 7(b) ×3500].

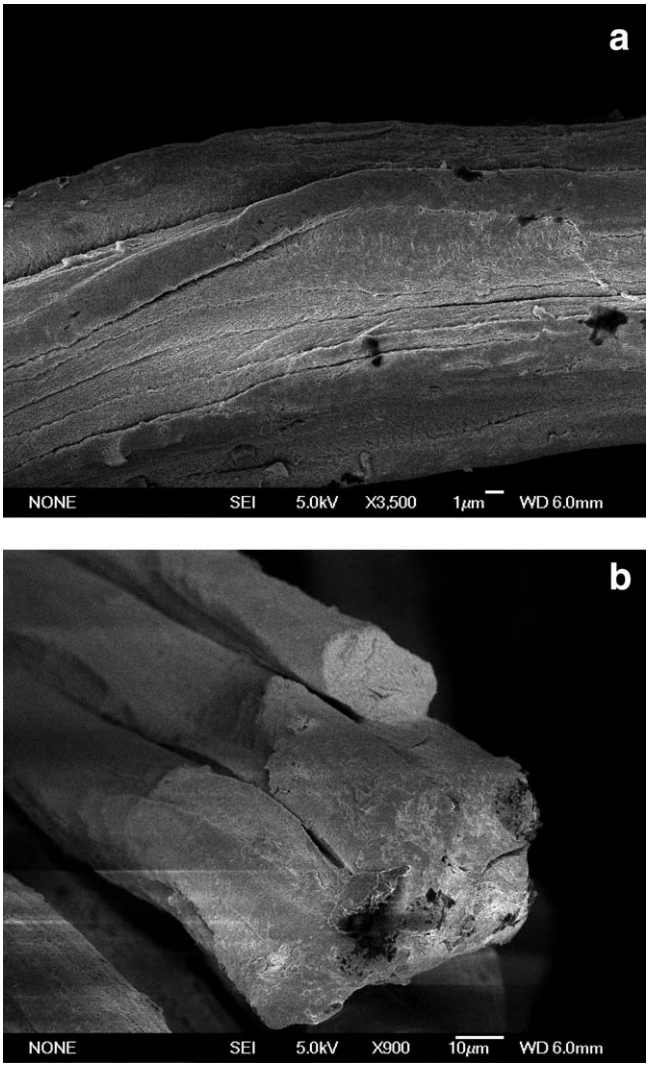

Figure 8 Zein/viscose fiber and viscose fiber handled with 30% NaOH observed by a SEM. [Fig. 8(a) ×3500; Fig. 8(b) ×900].

zein/viscose fibers was less than wet breaking tenacity, owing that water reduced the force among macromolecules.

The moisture regain rate of zein/viscose fibers was 14.1%, similar to that of viscose fibers (13.9%), which mean the moisture absorption of zein/viscose fibers was as good as viscose fibers.

Infrared absorption spectrum of zein/viscose fibers

As shown in Figure 9, the peak curves of zein/viscose fibers, viscose fibers, zein, and zein/viscose fibers handled with 30% NaOH were similar, which probably because both zein and viscose were macromolecules with many similar elements, such as C, H, and O and many similar chemical bonds. Moreover, zein extract had some impurities, such as xanthophylls, which might interfere in the infrared absorption spectrum of zein.

The infrared absorption spectrum of zein/viscose fibers showed the peaks at 3600 cm^{-1} from —OH bond, at 3100–3500 cm^{-1} from associated hydroxyl or —NH bond, at 2900 cm^{-1} from —CH or —CH_2 bond, at 2100 cm^{-1} might from C≡C bond, at 1637 cm^{-1} from C=C or acylamide bond, at 1541 cm^{-1} from acylamide bond, at 1521 cm^{-1} from C=C bond, at 1375 cm^{-1} from CH_3 bond, at 1320–1200 cm^{-1} from C=O bond, at 1250–1000 cm^{-1} from C—O bond, at 894 cm^{-1} from C—H bond and 671 cm^{-1} from —OH bond.

Zein, zein/viscose fibers and zein/viscose fibers handled with 30% NaOH had an extra peak at 1541 cm^{-1} from acylamide bond, which was the characteristic peak of protein. Acylamide bonds in zein/viscose fibers indicated the basic chains of protein were not changed by blended spinning, so zein/viscose fibers preserved the properties of zein. The peak 1541 cm^{-1} of zein/viscose fibers handled with 30% NaOH was weaker than zein/viscose fibers, probably because of partial removal of zein.

Both viscose and zein had many hydrogen bonds, so viscose and zein could be cross-linked with each other by hydrogen bonds through blended spinning.

TABLE II
Mechanical Properties of Zein/Viscose Fibers and Viscose Fibers

			Viscose fibers			
	Unit	Zein/viscose fibers	Superior level product	Level 1 product	Level 2 product	Level 3 product
Linear density	dtex	129.9	–	–	–	–
Dry breaking tenacity	CN/dtex	2.02	≥1.52	≥1.47	≥1.42	≥1.37
Dry breaking elongation (%)	%	16.6	17.0~22.0	16.0~25.0	15.5~26.0	15.0~27.0
Variation coefficient of dry breaking Elongation	%	4.34	≤7.00	≤9.00	≤10.00	≤11.00
Wet breaking tenacity	CN/dtex	0.99	≥0.69	≥0.67	≥0.64	≥0.62
Deviation of linear density	%	−2.6	≤± 2.0	≤± 2.5	≤± 3.0	≤± 3.5
Variation coefficient of linear density	%	0.83	≤2.50	≤3.50	≤4.50	≤5.50
Variation coefficient of twist	%	9.05	≤13.00	≤16.00	≤19.00	≤22.00
Deviation of monofilament number	%	0.7	≤1.0	≤2.0	≤3.0	≤4.0
Residual sulfur	mg/100 g fibers	7.60	≤10.0	≤12.0	≤14.0	≤16.0

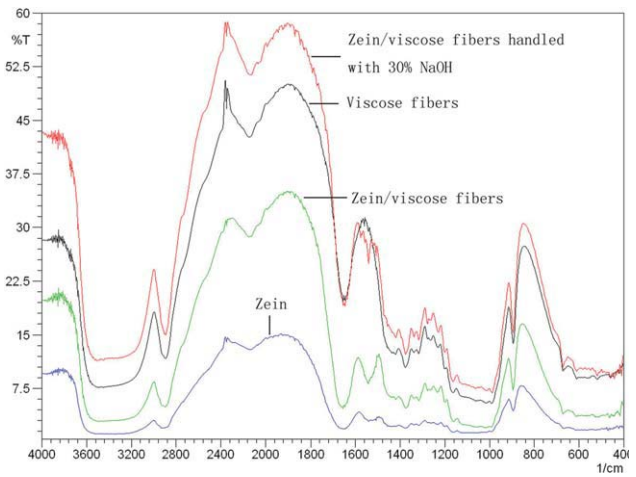

Figure 9 Infrared absorption spectrum of zein/viscose fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

But the force of hydrogen bonds was too weak to combine zein and viscose strongly. After blended spinning, zein in zein/viscose fibers was not easily washed away by water, so there were chemical bonds between zein and viscose. Viscose had many hydroxyl groups, which could easily graft with carboxyl groups, amino groups, hydroxyl groups, and sulphydryl groups in zein to form ester bonds, ether bonds, and so on. But the peaks of these new formed chemical bonds in infrared absorption spectrum could not been identified because zein and viscose contained the same chemical bonds (e.g. viscose contained ether bonds), or the peaks of some other bonds in zein and viscose interfered the identify of these new peaks. The grafting of hydroxyl groups in viscose did not influence the main chains of viscose, so zein/viscose fibers preserved the properties of viscose. The grafting of zein to viscose resulted in the increase of molecular weights, which was probably the reason on the superior mechanical properties of zein/viscose fibers than viscose fibers.

Protein analysis of zein/viscose fibers

The content of protein measured by Kjeldahl method in zein/viscose fibers was 14.48%, showing that component of viscose made up of most of the blended fibers.

Zein/viscose fibers might own the health care functions of zein peptides, because of the blended spinning did not change the basic chains of zein. So zein/viscose fibers may have some health functions of blood pressure reduction,[3–5] antioxidation,[6] accelerating alcohol metabolism,[7,8] and so on. The fabrics weaved by zein/viscose fibers could have higher comfortability than viscose fibers, as protein made the skin of human being feel comfortable.

CONCLUSION

The appropriate controls of some parameters made the fabrication of zein/viscose fibers successful, although larger resistance filtration of blended solution and easy removal of zein from fibers in desulfuration increased the difficult of fabrication. Zein/viscose fibers had advantages of both zein and viscose, such as health care and comfortability of zein, because the blended spinning did not change the basic chains of both zein and viscose. The grafting of zein to viscose resulted in the superior mechanical properties of zein/viscose fibers than viscose fibers. Moreover, as zein can be easily extracted from corn and viscose can be easily obtained from cellulose, zein/viscose fibers are from the annually renewable biomass with a large production and low-price. Comfortability and environmental degradability of cellulose and proteins allow zein/viscose fibers to have a growing market in textiles.

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