Formaldehyde-Free Zein Fiber—Preparation and Investigation

YIQI YANG,[1,*] LIMING WANG,[2] and SHIQI LI[2]

[1]Institute of Textile Technology, Charlottesville, Virginia 22903, and [2]University of Illinois, Urbana, Illinois, 61801

SYNOPSIS

A novel dry-spinning method for the preparation of zein fiber without using formaldehyde is presented. The fiber thus obtained had good stability to boiling aqueous acetic acid solution with breaking tenacity and elongation of 1.0 g/d and 30%, respectively. Citric acid and butanetetracarboxylic acid were used as nonformaldehyde crosslinking agents for the preparation of zein fiber successfully. Using polycarboxylic acids have advantages such as no toxicity and low sensitivity to the variation of processing conditions over formaldehyde-containing stabilizers. The effects of crosslinking before and after stretching on improvement of fiber properties were discussed. Fiber morphological structure was also examined by means of wide angle x-ray diffraction and sonic velocity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Natural protein fibers such as wool and silk have excellent performance properties, due, in part, to their unique chemical and morphological structure. However, natural protein fibers are not easy to produce. Therefore, the preparation of protein fibers from other sources such as plants and milk has long been investigated since the late 19th century. Among the regenerated protein fibers, those from milk, soybean, and corn were the major ones studied.[1-11] To our knowledge, the earliest patents of the regenerated protein fibers from zein, the corn protein, belonged to Swallen[12] and Meigs[13] 55 years ago. Due to the impact of synthetic fibers since the late 1950s, the investigation and production of regenerated protein fibers were gradually discontinued because of economical as well as technical reasons.

Although synthetic fibers have many advantages over natural and regenerated fibers in durability, easy-care property, and energy consumption during textile processing and laundering, they can hardly meet the increasing demand for comfortability from consumers. Another disadvantage of synthetic fibers is their poor environmental degradability. Although environmentally degradable textile polymers and recycling processes are more and more studied,[14] there is still a long way to go before obtaining an economic approach to produce environmentally degradable synthetic fibers or to satisfactorily recycle the used fibers for textile industry. Comfortability and environmental degradability of cellulose and proteins allow them to have a growing market in textiles.

Currently, the main regenerated fiber is rayon. Raw materials for rayon production have come from wood feedstocks, which are basically the coniferous or softwood species of the western and southern parts of the U.S. According to the National Research Council,[15] it is predicted that there will be a shortage of wood fibers in the U.S. and many other countries by the year 2000. This is not only a problem to cellulose industries, but also poses a threat to the environment. In addition, rayon production is a relatively complex process, generating wastes containing caustic soda, carbon disulfide, sulfuric acid, or sodium and zinc sulfates. Hence, it is beneficial to continue the research on regenerated protein fibers.

As proteins are easily extractable from corn kernels, zein fiber is from the annually renewable biomass with a large production and low price. The properties of zein fiber are close to that of other protein fibers, such as wool, with high resiliency,

* To whom correspondence should be addressed.

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absorbency, elongation, and excellent dyeability. It could be a promising textile fiber.

Zein fiber was mainly produced by the wet-spinning technology. The proteins were first dissolved in sodium hydroxide solution. The polymer strands, extruded from such a spinning dope, were hardened through an acidic coagulation bath. After that, the fibers were drawn, heat treated, and crosslinked with formaldehyde to be the product. The wet-spinning technologies of zein fiber were discussed comprehensively by Gillespie in 1956.[16]

The technology investigated in this work uses a dry-spinning method with nonformaldehyde crosslinking agents as an additive to the spinning dope for the improvement of fiber properties. The nonformaldehyde crosslinking agents used are polycarboxylic acids such as citric acid (CA) and butanetetracarboxylic acid (BTCA). The zein fiber thus obtained has advantages of simplified technological process and no pollution over the wet-spinning methods reported previously. The stretching characteristics of the zein fiber with the consideration of the effect of crosslinking agent discussed in this work is helpful for the study of the protein structure.

EXPERIMENTAL

Spinning Apparatus

The spinning apparatus used in this work for the dry spinning of zein fiber was shown in Figure 1. The degassed spinning dope was loaded into the spinning tank (3), which had a water jacket to adjust the spinning temperature. The force required to squeeze the spinning solution was from the nitrogen pressure supplied by the nitrogen cylinder (1) and was kept constant by the pressure buffering system (2). The spinning dope was extruded through a filter and the single hole spinnerette (4) at the bottom of the spinning tank (3), which could move longitudinally along the winding drum (5). The winding drum (5) was a cylinder with a diameter of 30 inches and a very smooth surface coated with chromium. Its winding speed was controlled by an adjustable DC motor.

Preparation of Spinning Dope

Zein powder used in this work was Regular F-4000 from Freeman Industries of Tuckahoe, NY, with an average molecular weight of 35,000. Zein has many di- and tri-component solvents.[17] In this work, aqueous isopropanol and ethanol solutions were selected with the consideration of dry spinnability, price, toxicity, and recycling convenience. The alcohol concentrations examined were 90, 85, 80, 75, 70, 65, 60, 55, and 50% based on the total weight of the solvent. The spinning dope was prepared by first dissolving the crosslinking agent and the catalyst into water then in the required alcohol solution. The zein powder was added into that solution to 30, 35, 40, and up to 45% of the total weight of the spinning dope. The zein powder could quickly wet, swell, and dissolve. The solution thus prepared was filtrated, deaerated, and ripened for spinning.

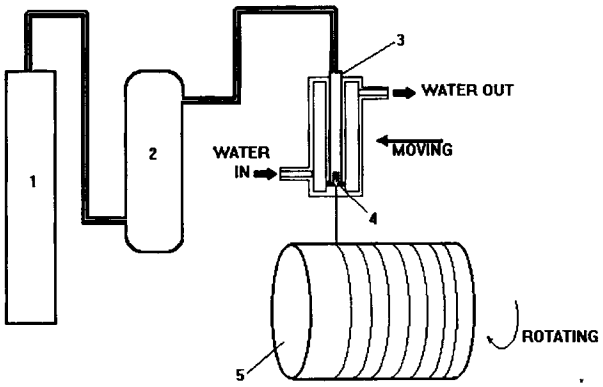

Figure 1 Schematic diagram of the spinning apparatus. 1: Nitrogen cylinder; 2: pressure buffering system; 3: spinning tank; 4: filter and single hole spinnerette; 5: winding drum.

For the spinning dopes using formaldehyde as the crosslinking agent, the addition of formaldehyde was 1 or 3% on the weight of zein with 50% of NH_4Cl or 50% of $MgCl_2$ as the catalyst based on the weight of HCHO. For those using CA and BTCA as crosslinking agents, the addition of the polycarboxylic acid was 6% based on the weight of zein with 3.3% $NaH_2PO_2 \cdot H_2O$ based on the weight of zein as the crosslinking catalyst. CA, BTCA, and $NaH_2PO_2 \cdot H_2O$ were from EM Science of Gibbstown, NJ, Aldrich Chemical of Milwaukee, WI, and Sigma Chemical of St. Louis, MO, respectively.

Fiber Spinning and Aftertreatment

The spinning solution was first filtered, deaerated, and ripened for 24 to 48 h. Then it was added to the spinning tank. The spinnerettes used in this work had diameters of 0.1 and 0.3 mm, with a length-to-width ratio (L/D) of 2:1. Spinning temperature was controlled by adjusting the water temperature in the jacket of the tank through a water bath. The spinning dope was extruded out through the spinnerette by the pressure of nitrogen in the range of 20 to 60

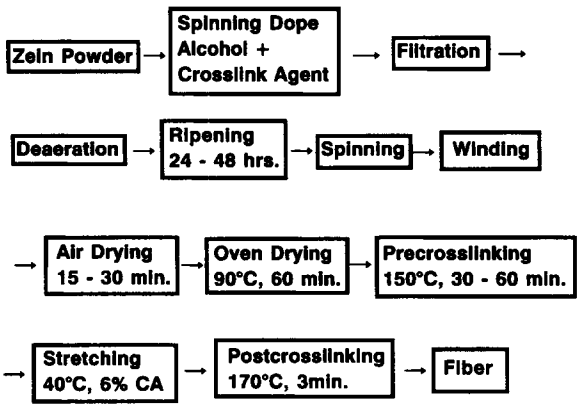

Figure 2 Flow chart of fiber spinning and aftertreatment.

psi. The very fine stream of the liquid passed through the spinnerette first contacted with the air and then was wound onto the winding drum with a linear winding speed of 100 m/min. Due to the lack of a drying system with conventional dry spinning equipment, fiber wound onto the drum was required to stay there for 15 to 30 min for air drying before being taken off.

After being taken off the winding drum, the fiber was dried loosely at 90°C in an oven for 60 min. The temperature was raised to 150°C for the precrosslinking reaction for 30 to 60 min.

For those using formaldehyde as a precrosslinking agent, two different procedures were examined, i.e., adding HCHO into the spinning solution or into an additional precrosslinking bath. If the formaldehyde was used during the preparation of the spinning solution, no additional chemicals were used in the precrosslinking process. The process was shorter than the one with an additional precrosslinking bath. However, because of the high reactivity of HCHO, crosslinking reaction appeared during ripening stage, which caused spinning difficulties. Treating the fiber with HCHO after spinning, but before stretching, could avoid such disadvantages. The fiber, taken off from the winding drum, was immersed in a 5% formaldehyde solution for a certain amount of time and then stretched in 40°C water.

For the fibers using polycarboxylic acid as a precrosslinking agent, all chemicals were added in the spinning dope. Therefore, no additional chemicals were required during the precrosslinking reaction.

Crosslinking the fiber before stretching, so-called precrosslinking, improves the stretch effectiveness. To improve the thermal and chemical resistance of the fiber, an additional crosslinking reaction was used. That was called postcrosslinking, the reaction after drawing. After the precrosslinking reaction, the fiber was stretched in a 40°C water bath with 6% citric acid and 3.3% of $NaH_2PO_2 \cdot H_2O$. The fiber was then dried at 90°C for 5 min and cured at 170°C for 3 min for the postcrosslinking reaction. This whole process, spinning and aftertreatment, is summarized in Figure 2.

Test Methods

The stress–strain curves were obtained from an Instron Model TM machine according to ASTM D3822–93a.[18] The sonic velocity was measured by the Dynamic Modulus Tester PPM-5R from H. M. Morgan Co. of Norwood, MA. The sample length scanned was 10.16 cm. A wide-angle x-ray diffraction pattern of the fiber was obtained using a Philips (Norelco) x-ray generator equipped with a Statton camera.[19] Nickel filtered Cu K_α radiation (40 Kv, 10 mA) in transmission mode was used. The sample-to-film distance was 4.5 cm.

Three to eight specimens were used for each test. One standard deviation above and below the mean values was indicated in the tables and figures.

RESULTS AND DISCUSSION

Properties of the Fiber before the Precrosslinking Reaction

Without adding a crosslinking agent into the spinning dope for the precrosslinking reaction, fibers were very brittle, regardless of what concentrations of zein and alcohol were used. Fibers thus obtained could be stretched to as high as 2000% of its original length. But the fibers with such a high draw ratio were still very brittle. Table I lists the mechanical properties of a group of fibers with different draw ratios. The fiber was spun from the solution with 40% of zein in an 85% isopropanol aqueous solution. Both the breaking tenacity and elongation were very low. The breaking was due to brittle rupture, the

Table I The Mechanical Properties of Zein Fibers without Precrosslinking Treatment

Draw Ratio (%)	Breaking Tenacity (g/day)	Breaking Elongation (%)
0	0.38 ± 0.02	1.7 ± 0.4
800	0.39 ± 0.04	2.4 ± 0.6
1200	0.37 ± 0.12	2.0 ± 0.2

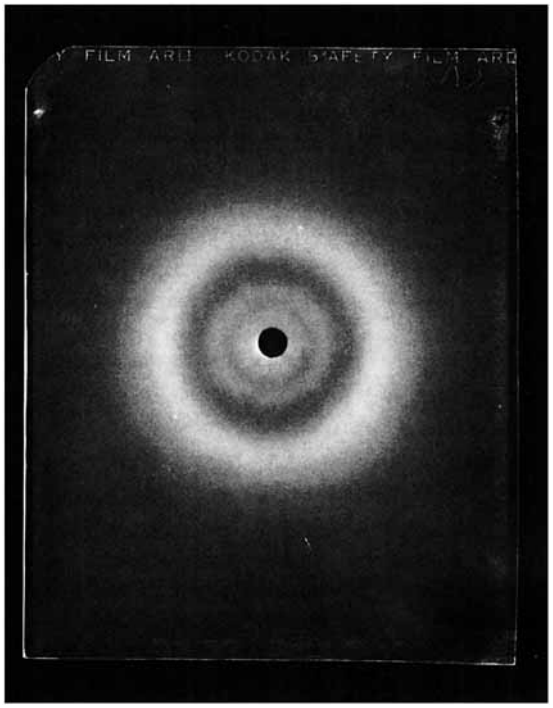

Figure 3 X-Ray diffraction diagram of the zein fiber with a draw ratio of 800% without crosslinking treatment.

fiber being brittle and weak. After 800% and 1200% stretching, notable improvement of strength and elongation still were not observed. This result was similar to what was reported by Jenkins et al.[20] Because of the brittleness of the fiber from dry spinning, previous reports were mainly focused on wet spinning. The x-ray diffraction pattern in Figure 3 shows no crystallization or notable orientation in the amorphous region of the fiber drawn 800%.

One explanation is that in the alcohol solution, zein protein molecules are not fully stretched. The folded polypeptides with large side groups prevents the molecules from getting close enough to each other to be aligned and form ordered structure after being extruded out of the spinnerette. Therefore, the stress–strain curve shows the typical brittle rupture and the fiber breaking tenacity and elongation were both low.

The major inter- and intramolecular forces in the zein fiber are hydrogen bondings, van der Waals forces, and ionic interactions. There are seldom disulfide linkages. Because of the longer intermolecular spaces, the forces between polypeptide chains are much weaker than that within the molecules. In 40°C water solution, these physical interactions between polypeptide chains were broken or weakened. But this condition is not strong enough to break the interactions within the molecules. Thus, during drawing, the main movement is the relative sliding between polypeptide chains. The polymers, which are not fully stretched or unfolded, do not have effective orientation. As a result, the fiber after drawing still had low breaking tenacity and elongation, and the breaking was still the brittle rupture. Based on the results, it is suitable to say that without precrosslinkage, the stretch of zein fiber is "ineffective drawing."

Formaldehyde Treated Fiber

To overcome the ineffective drawing, it is necessary to precrosslink the fiber before stretch. Two different precrosslinking reactions, treating the fiber in a formaldehyde solution after spinning but before stretching, and adding HCHO directly into the spinning solution, were examined.

Table II presents the mechanical properties of the zein fibers precrosslinked with formaldehyde in a 5% formaldehyde solution for a certain time after spinning and then stretched in 40°C water. The properties were tested for the fibers with a stretch of 50% of the maximum draw ratio. Table II shows the maximum draw ratio decreased with increasing treatment time in the formaldehyde solution. However, this precrosslinking reaction considerably improved the effect of drawing on the mechanical

Table II The Mechanical Properties of Zein Fibers Precrosslinked with 5% Formaldehyde in the Stretch Bath

Treating time (h)		0	0.5	1.0	2.0	5.0	20.0
Max. Draw Ratio (%)		> 2000	500	300	150	100	50
Breaking Tenacity (g/d)	BD[a]	0.38 ± 0.02	0.40 ± 0.02	0.38 ± 0.08	0.40 ± 0.08	0.42 ± 0.04	0.42 ± 0.02
	AD[b]	—	0.40 ± 0.02	0.63 ± 0.07	0.48 ± 0.07	0.35 ± 0.02	—
Breaking Elongation (%)	BD	1.7 ± 0.4	4.0 ± 2.7	4.0 ± 1.8	3.8 ± 2.3	4.0 ± 1.2	4.0 ± 1.7
	AD	—	7.8 ± 6.5	24.7 ± 11.1	32.7 ± 3.5	8.7 ± 4.6	—

[a] Before drawing.
[b] After drawing.

properties of the fiber. According to Table II, there was an optimum crosslinking condition in terms of the maximum improvement of tenacity and elongation of the fiber. For this study, it was approximately 1 to 2 h. The maximum improvement of tenacity was at 1 h. After drawing, the fiber breaking tenacity was increased from 0.38 g/d to 0.63 g/d, an increase of about 70%. The breaking elongation for that condition also considerably increased from 4.0% to 24.7%. The maximum breaking elongation was 32.7% after 2 h of HCHO treatment. Obviously, the formaldehyde crosslinkages caused the stretching to be effective on improving the mechanical properties of the zein fiber.

As an alternative precrosslinking method, 1 and 3% of formaldehyde on the weight of zein were added to the spinning solution. The results showed that the spinning dope with 3% HCHO had poor spinnability after a 48 h ripening. The spinnability of that with 1% HCHO was better. Properties of the fibers thus made with different draw ratios are presented in Table III. The treated fibers decreased their maximum draw ratios from more than 2000% to below 1000%. Because of the high reactivity, formaldehyde could crosslink polypeptide at ambient temperature. Therefore, even the samples without heat treatment decreased the maximum draw ratio to 1000%. With a more thorough crosslinking reaction at 90°C for 30 min, the maximum draw ratio was further decreased to 600%. Meanwhile, breaking tenacity and elongation of the fiber were improved. However, using this precrosslinking method, the breaking elongation varied considerably for those fibers having a certain draw ratio. This phenomenon will be discussed later.

Adding formaldehyde to spinning solutions for the precrosslinking reaction could improve stretch effectiveness. Fiber thus obtained was less brittle than those without crosslinkages. Formaldehyde could react with protein molecules at room temperature; thus, the reaction was very difficult to control. This was the reason for poor spinnability of the zein solution with 3% HCHO after a 48-h ripening. Furthermore, formaldehyde is toxic. Using formaldehyde is harmful to the operators and the environment. The free formaldehyde released from the fiber will also be harmful to the consumer later. Hence, using formaldehyde as a fiber crosslinking agent is not suitable.

Fiber Properties Using Polycarboxylic Acids as Crosslinking Agents in the Spinning Solution

Due to complaints involving formaldehyde containing crosslinking agents, nonformaldehyde multifunctional chemicals were widely explored in the textile durable press industry for the production of easy care cellulosic goods. Not long ago, it was reported[21-23] that polycarboxylic acids such as CA and BTCA could also be used for the durable crease resistant finishing of silk. This showed the possibility of using polycarboxylic acids as crosslinking agent for protein molecules. Based on that, these two acids were selected to precrosslink zein molecules using NaH_2PO_2 as the catalyst. The results presented in Table IV were of fibers with 6% CA or BTCA in the spinning solution and cured at 150°C for various time periods. The breaking tenacity and elongation data were of fibers stretched 100% less than the maximum draw ratio.

The increase of both breaking tenacity and elongation with the polycarboxylic acid treatment showed that CA and BTCA could crosslink with zein proteins. BTCA probably exhibited higher crosslinking activity than CA. The maximum draw ratio decreased with increasing curing time. After a 30-min curing followed by stretching, the tenacity of the zein fiber could be increased to approximately 1 g/d with a breaking elongation of 20% to 35%. The stretch was effective. Using this new crosslinking technology as the formaldehyde-free stabilization, the toxicity during production and consump-

Table III The Mechanical Properties of Zein Fibers Precrsslinked with 1% Formaldehyde in the Spinning Solution at Different Draw Ratio

Draw Ratio (%)		0	200	400	500	900
Uncured[a]	Tenacity (g/d)	0.40 ± 0.03	0.42 ± 0.03	0.51 ± 0.01	0.54 ± 0.05	0.49 ± 0.05
	Elongation (%)	3.6 ± 0.5	3.5 ± 0.1	96.0 ± 90.5	28.7 ± 27.2	68.0 ± 54.1
Cured[b]	Tenacity (g/d)	0.42 ± 0.07	0.59 ± 0.07	0.64 ± 0.07	—	—
	Elongation (%)	5.0 ± 0.8	65.7 ± 38.4	87.0 ± 13.1	—[c]	—[c]

[a] No heat treatment; maximum draw ratio = 1000%.
[b] Heat treatment at 90°C, 30 min; maximum draw ratio = 600%.
[c] Uneven breaking elongation from 3–110%.

tion was avoided. In the meantime, these chemicals would not react with proteins at ambient temperatures, so that the spinning process and quality were much easier to be controlled. Hence, polycarboxylic acid crosslinking technology is the better stabilization method for the manufacturing of zein fibers vs. conventional formaldehyde procedures.

Structure–Property Relation of Precrosslinked Zein Fiber

The stress–strain curves of the precrosslinked fiber changed gradually with fluctuating draw ratios. Figure 4 shows a set of stress–strain curves of CA precrosslinked samples with draw ratio from 0 to 400%. As shown, even after crosslinking reaction, the breaking tenacity and elongation of the fiber (curve a) was low and belonged to brittle rupture if it was not stretched. If the draw ratio was between 100 to 200%, the stress–strain curves showed an extremely unstable phenomenon. Breaking elongation varied from 5 to 120%. For those fibers with relatively high elongations, the stress appeared undulatory. Two of those examples are listed in Figure 4, with curve b having less than 10% elongation, whereas curve c has more than 110% elongation with unstable stress changes. If drawn more than 200%, the stress–strain curves of zein fibers belonged to typical stress–strain curves of manufactured fibers. These changes of the stress–strain properties with varying draw ratios are most likely due to the coil and/or folding structures of the zein molecules in the fiber after extrusion.

Zein proteins have a high content of nonionizable amino acid residues, such as glutamine, leucine, alanine, proline, serine, and phenylalanine,[24] which provide relatively strong intramolecular hydrophobic interactions. During fiber formation, the molecules were not stretched sufficiently. The precrosslinking was performed between and within the coiled and/or folded molecules. Without further stretching, the morphological structure of the fiber (a) was very similar to that before the crosslinking reaction. Therefore, the breaking still was brittle

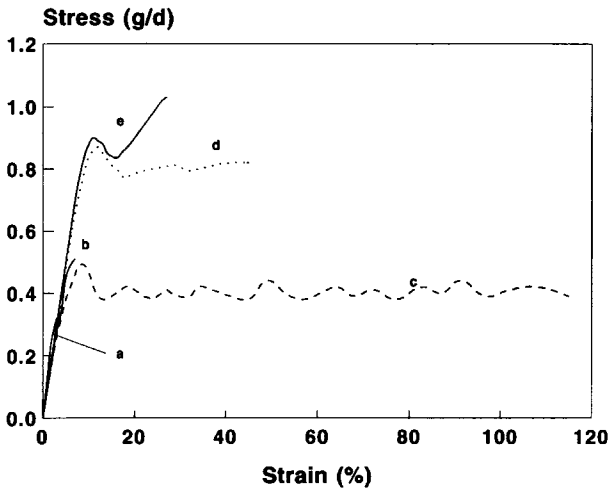

Figure 4 Stress–strain curves of zein fibers precrosslinked with CA and stretched to a different draw ratio. Draw ratio: a = 0%; b and c = 100–200%; d = 300%; e = 400%.

rupture. When the fiber was stretched in warm water, the physical bondings between and within the polypeptide chains were broken gradually. Because of the effect of crosslinkages, such stretching would not be limited to the relative sliding between folded molecules. Some of the irregularly aligned macromolecules were stretched and oriented along the fiber axis with drawing. With a low draw ratio, most of the folded molecules were not able to be stretched. Therefore, their stress–strain feature still belonged to brittle rupture with a slightly higher tenacity than the unstretched fiber due to some orientation alignment during drawing (e.g., curve b of Fig. 4). Another possible stress–strain phenomenon for fibers with low draw ratio is that shown by curve c. During straining, the folded molecules were gradually stretched, while the intermolecular connections were broken due to the relative movement between the polypeptides. The breaking of intermolecular bonds caused the decrease in stress, but the stretch of the folded molecules increased the stress of the fiber due to the improvement of the molecular orientation.

Table IV The Mechanical Properties of Zein Fibers with CA or BTCA for Different Curing Time

Curing Time (min)		0	10	20	30	45	60
CA	Max. Drawing (%)	> 2000	700	700	500	450	400
	Tenacity (g/d)	0.25 ± 0.03	0.48 ± 0.01	0.92 ± 0.19	1.02 ± 0.12	0.94 ± 0.13	0.84 ± 0.11
	Elongation (%)	2.0 ± 0.2	6.0 ± 1.0	14.0 ± 3.8	25.0 ± 7.9	31.0 ± 9.5	32.0 ± 7.5
BTCA	Max. Drawing (%)	> 2000	700	400	400	350	300
	Tenacity (g/d)	0.31 ± 0.01	0.40 ± 0.05	0.83 ± 0.05	0.92 ± 0.15	0.80 ± 0.07	0.68 ± 0.04
	Elongation (%)	1.8 ± 0.4	3.3 ± 0.8	23.0 ± 1.7	19.0 ± 10.9	18.0 ± 5.2	22.0 ± 4.9

Such opposite effects the stretching had on fiber morphology resulted in the zigzag shaped stress–strain curve.

When a relatively high draw ratio was used, the unfolded molecules were able to be orientated along the fiber axis. Therefore, the stress–strain curve showed the typical stress strengthening after the yield point, as indicated in curves d and e of Figure 4. The tenacity increased and elongation decreased with increasing draw ratio.

The effect of drawing on orientation of molecules in the fiber was studied through the sonic velocities of samples, which were precrosslinked with CA, with different draw ratios. Figure 5 showed that the sonic velocity rose linearly with increased draw ratio. Based on the linear regression, the sonic velocity at zero drawing could be calculated by extrapolating the curve to zero draw ratio, as indicated by C_u. For this case, C_u equaled to 1.91 km/s. C_u was used as the sonic velocity of the fiber with random orientation. According to Mosely,[25] fiber sonic orientation could be calculated from the following equation:

$$f_s = 1 - \frac{C_u^2}{C^2},$$

where f_s was the orientation factor representing the percentage of molecules that were orientated; C_u and C were sonic velocities of the fiber with zero and certain drawing, respectively. From the orientation factors of the fibers at different draw ratios and the corresponding breaking tenacities, the relationship between orientation of the polypeptides and fiber strength can be obtained in Figure 6. As expected,

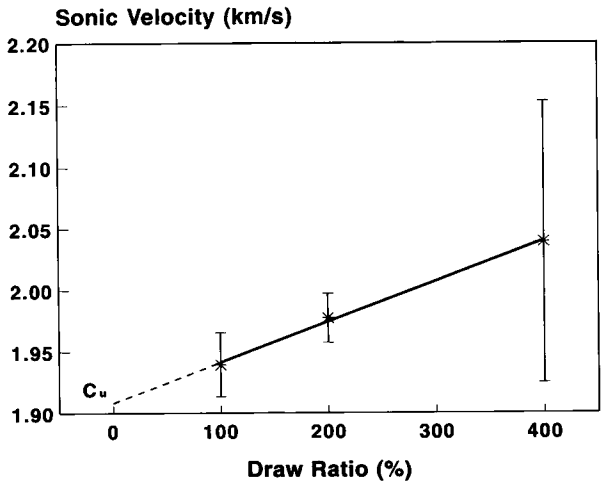

Figure 5 Effect of draw ratio on sonic velocity. C_u = sonic velocity of randomly oriented fiber.

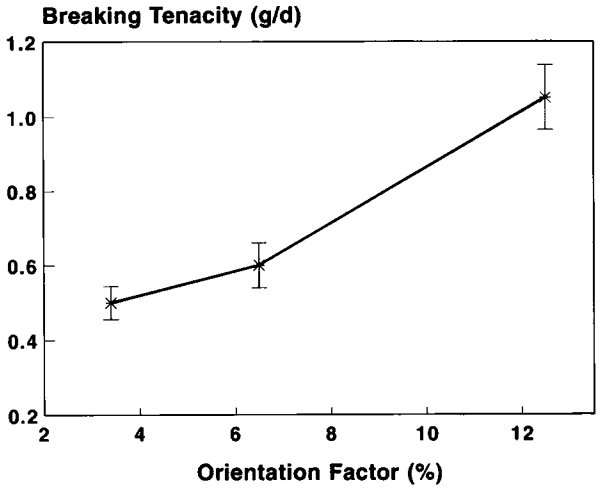

Figure 6 Relation between the sonic orientation factor and zein fiber breaking tenacity. The fiber was precrosslinked with CA.

the strength of the fiber increased with increasing molecular orientation within the fiber.

Although the orientation increased with increasing draw ratio, the maximum orientation of CA precrosslinked fiber was only about 12% at the extreme drawing of 400%. This meant the molecules in the zein fiber were still highly disoriented. X-Ray diffraction diagrams of samples with different draw ratios were all very similar to Figure 3; no crystalline areas or notable orientation present. Thus, it could be concluded that with the help of a crosslinking agent, the drawing became effective, although improvement of fiber strength was limited. This was because the protein molecules were not fully extended in the spinning solution. The crosslinking treatment overcame the ineffective stretching due to the intermolecular crosslinkages, but meanwhile, it caused the crosslinkages within the folded polypeptides. This intramolecular crosslinkages prohibited the full stretch of the polymers during drawing. Therefore, the strength of the fiber was not able to be improved remarkably. For further improvement of the strength of zein fibers, the polymers must be fully unfolded in the spinning solution, so that the crosslinkages could be added, mainly between polypeptides. Thus, improved orientation and crystallization could occur in the fiber and fiber strength could be improved considerably.

Resistance to Boiling Water

A useful protein fiber must have certain resistance to boiling water in the acidic condition due to the requirement for wet processing. An example is acid

Table V The Mechanical Property Changes after the Postcrosslinking Reaction

Sample	Breaking	
	Tenacity (g/day)	Elongation (%)
Without Postcrosslinks	1.02 ± 0.04	28.0 ± 5.5
Postcrosslinked	1.06 ± 0.02	30.0 ± 2.9
Postcrosslinked* after Boiling Test	0.98 ± 0.07	42.0 ± 4.9

[a] Boiling test: 100°C aqueous acetic solution, pH 3.2, 20 min.

dyeing, one of the most widely used coloring techniques for protein fibers. The dyeing requires a low pH and high temperatures. Acidic conditions give fibers positively charged dye sites while high temperature improves the levelness and dye sorption. A test in boiling water with a pH of 3.2, adjusted by acetic acid, was used for the examination of fiber stability.

In such an environment, fibers without any crosslinking reactions dissolved immediately. After a precrosslinking reaction and drawing, the fiber did not dissolve in the boiling acidic aqueous solution but shrank remarkably. After 5 min at the boil, about 80% of the length due to the previous drawing was shrunk. If the precrosslinked fiber was drawn in a 40°C water bath with 6% CA and 3.3% $NaH_2PO_2 \cdot H_2O$, dried and then cured at 170°C for 3 min for the postcrosslinking treatment, the shrinkage in the boiling acid water could be effectively controlled. The shrinkage of the fiber thus treated was less than 10% after a 20-min boiling in such conditions. The changes in breaking tenacity and elongation of the postcrosslinked fibers are listed in Table V. After the acidic boiling test, the tenacity of the fiber decreased slightly with some increase in elongation. The fiber thus treated could endure conventional dyeing and finishing conditions.

CONCLUSIONS

A novel dry-spinning method of nonformaldehyde zein fiber was developed using CA or BTCA as crosslinking agents. The fiber was precrosslinked after spinning. The drawing was carried out in warm CA solution, followed by postcrosslinking. The fiber produced had a breaking tenacity of 1 g/d and a breaking elongation of about 30%. It had high resiliency, good boiling resistance, and excellent dyeability. Precrosslinking was very important to the improvement of drawing efficiency. CA and BTCA were successfully applied as nonformaldehyde crosslinking agents to substitute formaldehyde for the production of zein fiber, with advantages such as nontoxicity and easy control of spinning processes. Zein proteins have relatively more and larger side groups than ordinary textile proteins. The polypeptides in the initial fiber were not fully stretched, with many still folded. Therefore, the molecules could not have close contact with each other to be aligned regularly. Precrosslinking could remarkably improve the efficiency of drawing, increasing the orientation of the polymers in the fiber. However, the fiber obtained still had low orientation and lacked in crystalline region. Selecting other solvent systems for the full extension of polypeptides in the solution, making polyblends or multicomponent fibers to complement strength while keeping excellent absorbency, resiliency, and dyeability, may warrant future investigation.

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