

# Production of Textile Fibers from Zein and a Soy Protein-Zein Blend<sup>1</sup>

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## ABSTRACT

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Zein fibers were successfully prepared by a wet-spinning technique from a zein suspension formulated with 15% zein, 60% water, 22% 0.4*N* sodium hydroxide, and 3% urea by weight. Tenacities were measured with an Instron machine, and flexibility was determined by noting the smallest diameter rod around which a fiber could be looped without breaking. After spinning, the tenacity of the zein fibers was improved by modification with several agents: acetic anhydride for acetylation, glutaraldehyde, and dialcohols for cross-linking and physical stretching. The tenacity and flexibility of the fibers were measured at 11, 65, and 100% rh. Untreated fibers had tenacities of 3.41, 2.65, and 0.17 g/tex at 11, 65,

and 100% rh, respectively. A combination of chemical treatments (20% glutaraldehyde and 95% acetic anhydride) and 115% stretching increased tenacities to 6.89, 6.56, and 1.17 g/tex at 11, 65, and 100% rh, respectively. Control zein fibers had flexibilities of 5 and 2.5 mm at 11 and 65% rh, respectively, whereas the treated fibers had flexibilities of 1.5 mm at both humidities. Extrusion of zein fibers was not successful. Zein-soy protein mixture could be extruded, but properties of wet-spun fibers of zein-soy blends were not much improved over those of soy protein alone. The tenacity of blended soy protein-zein fibers was greater than that of soy protein fibers at 11% rh.

Recent interest in the production of protein-based textile fibers has been prompted by the uncertain and high prices for petroleum used to make synthetic fibers, a concern for environmental safety, and a search for new markets for agricultural commodities. In the 1930's and 40's, proteins from corn, soybean, milk, and peanuts were used to manufacture fibers. Corn Products Refining Company applied for a patent for zein fibers (Swallen 1939), and the Virginia Carolina Chemical Corporation produced a zein fiber called Vicara in 1948 by a process similar to the production of rayon (Croston et al 1945). The fibers reportedly had weak wet strength, good elongation, excellent elastic recovery, a texture not unlike wool, and excellent resistance to heat (Veatch 1941).

Soybeans were also used for fibers because of their high protein content (40%) and relatively low cost. The Ford Motor Company obtained two patents for the manufacture of soybean fiber in 1945 (Boyer et al 1945a,b). Lack of wet strength was considered a serious defect of the soy fibers (Hartsuch 1950).

Corn contains an average of 8% protein; zein is the primary protein at 4–5%. Zein is classified as a prolamin and is insoluble in water, absolute ethanol, and other neutral solvents, but it is soluble in 70–80% ethanol, isopropanol, and dilute alkalis and acids. Zein has an elongated globular shape and contains large proportions of glutamine, proline, leucine, and alanine (Wilson 1987). Zein is relatively nonpolar, is able to form films and filaments (Reiners et al 1973, Rubens 1990), and is currently used as a coating agent in pharmaceutical and food applications.

The amino acid composition of soy protein is more heterogeneous than that of zein. The proteins are more polar than zein and are soluble in water and dilute salt solutions. Huang et al (1995) reexamined the production of textile fibers from soy protein by the wet-spinning methods described in the early literature (Croston et al 1945) and attempted to produce improved fibers by extrusion and by chemical treatment of the extruded fibers. The strongest soy fibers produced had tenacities less than those of wool and acetate fibers and had low tenacities in moist conditions.

Decreasing moisture absorption by the soy fibers increased tenacity, so possibly, use of a more nonpolar protein such as zein would result in improved fibers.

The objectives of this study were: 1) to characterize the coagulating properties of zein, 2) to produce and evaluate wet-spun fibers of zein, 3) to improve the properties of wet-spun zein fibers and extruded soy fibers, and 4) to produce and evaluate extruded fibers of a soy protein-zein blend.

## MATERIALS AND METHODS

### Reagents

Commercial zein (regular grade F 4000) with a protein content of 88–96% and 8% moisture content was obtained from Freeman Industrial, Inc. (Tuckahoe, NY). Soy protein isolate (ARPRO 1100) was obtained from Archer Daniels Midland Co. (Decatur, IL). Glutaraldehyde, 1,3-propanediol, 1,3-butanediol and 1,5-pentanediol (Aldrich Chemical Co., Milwaukee, WI), dimethylformamide, dimethylsulfoxide, and 1,4-benzoquinone (Sigma Chemical Co., St. Louis, MO) and acetic anhydride, urea, and other common reagents (Fisher Scientific, Pittsburgh, PA) were purchased.

### Preparation of Wet-Spinning Suspension

Modifications of the procedure described by Croston et al (1945) were used. Zein was thoroughly wetted with ice cold water (0.15 g zein/mL of water) in a heavy-duty Kitchen Aid mixer (Kitchen Aid Portable Appliances, St. Joseph, MO), and additional cold water was added to attain a smooth suspension of 1:4 zein to water. Dilute (0.4*N*) sodium hydroxide (22%) and solid urea (3%) were added. A mixer speed of 70 rpm was maintained throughout the process. After mixing, the suspensions were aged at room temperature for 10 hr before spinning.

Viscosity of suspensions was measured with a viscometer (Synchro-Lectric, Brookfield Engineering Laboratories, Inc., Stoughton, MA).

### Wet-Spinning Technique

A wet-spinning technique was developed by Huang (1994) at Iowa State University based on the work of Croston et al (1945). The equipment consisted of a pressure vessel, a filter, a pump, and a 12-L coagulating bath. Air pressure (60 psi) flowing into the pressure vessel forced protein suspensions through a 25–35  $\mu$ m filter (Ronningen-Peter, Portage, MI), which removed particulate

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contaminants. A high-viscosity Zenith pump with a QM-SY 1416 digital speed controller (Parfer Hannifin Co., Waltham, MA) was used to force the zein dope through the 368- $\mu$ m spinnerette and into a coagulating bath. The pressure vessel, acid bath, and spinnerette were designed at Iowa State University. A Posiflo II pump (Gelman Science, Ann Arbor, MI) was used to circulate the solution in a coagulating bath. Various coagulating baths were used to test the effects of the pH and acid type on zein fiber characteristics. The coagulating bath contained hydrochloric acid (pH 1.0, 1.5, or 2.0), acetic acid (pH 2.5), or an acetic acid and sodium acetate buffer (pH 3.0, 3.5, 4.0, or 4.5).

### Extrusion Technique

A Brabender Plastic-Corder PL2000 (C.W. Brabender Instruments, Inc., South Hackensack, NJ) with a twin-screw extruder was used to produce protein fibers. The temperature and screw speed of the extruder were 90°C and 15 rpm, respectively, for zein and 96°C and 20 rpm, respectively, for soy. The exit die had eight 368- $\mu$ m diameter openings. Zein was mixed with water and glycerol or with organic solvents (1,3-propanediol, 1,3-butanediol, or 1,5-pentanediol) in a mixer at 70 rpm for 10 min before extrusion. The weight ratio was 45:40:15 for water, glycerol, and solvent.

Soy fibers were successfully extruded from a mixture of 45% protein, 15% glycerol, and 40% water (Huang et al 1995). Soy protein was also mixed with water, glycerol, and 1,5-pentanediol or 1,3-butanediol as solvents in the weight ratio of 45:40:15.

Blends of protein mixtures were prepared by mixing different proportions (80:20, 70:30, and 60:40) of soy protein and zein with water and glycerol in the weight ratio of 45:40:15. All mixtures were equilibrated for 24 hr before extrusion.

### Modification of Wet-Spun Zein Fibers

For modification by acetylation and cross-linking with glutaraldehyde, wet-spun zein fibers (500 g) were modified by soaking at room temperature for 30 min in 200 mL of 100% acetic anhydride, 95% acetic anhydride-5% acetic acid, 90% acetic anhydride-5% acetic acid-5% sodium acetate, 95% acetic anhydride-5% sodium acetate, or 5, 10, 15, 20, 25, 30, or 40% glutaraldehyde solutions (w/w). After treatment, fibers were washed in water, air-dried, and stored in desiccators at various water activities before evaluation.

To stretch wet-spun zein fibers, 500 mg of fibers were soaked in 2 L of water at room temperature for 30 min and stretched to 110, 115, or 120% of their original length with the Instron universal testing machine (UTM, model 4500, Instron Corp., Canton, MA) fitted with a 100-N load cell and pneumatic-action grips (No. 2712-002). The stretching rate was 2 cm/min, and the initial distance between the two grips was 10 cm.

### Modification of Extruded Soy Fibers

Extruded soy fibers (1 g) were soaked in 1,4-benzoquinone solution (89% water, 9.5% ethanol, and 1.5% 1,4-benzoquinone), dimethylformamide solution (60% water, 10% ethanol, and 30% dimethylformamide), or dimethylsulfoxide solution (60% water, 10% ethanol, and 30% dimethylsulfoxide) at room temperature for 30 min.

### Evaluation of Wet-Spun and Extruded Fibers

Fibers were air-dried for 24 hr after spinning or modification and stored in desiccators with 11 or 65% rh for 72 hr before testing (ASTM 1991). Humidities of 11 and 65% were produced by using saturated salt solutions of lithium chloride and sodium nitrite, respectively. Fiber properties were tested in a wet condition (100% rh) by soaking them in a dilute detergent (ASTM 1991). Water absorption by the fibers (moisture regain) was measured by weighing the dried and conditioned fibers. Fibers were dried in an oven at 110°C for 24 hr.

The tenacity and initial modulus of the fibers were measured by the UTM described previously. The rate of strain was 5 cm/min for a 10-cm length of test fiber. Fiber tex is the unit of linear density or the weight in grams of 1,000 m of fiber. Tenacity, the maximum force applied to break a single fiber, is expressed as g/tex. Modulus (the ratio of the change in stress to the change in strain and expressed as g/tex) was obtained from the slope of the initial straight portion of a stress-strain curve.

Fiber flexibility was measured by the ability of fibers to be looped three times around glass rods of various diameters without breaking at 11 and 65% rh at room temperature. The smaller the diameter of the glass rod, the better was the flexibility of the fiber. The diameters of the glass rods were 1.5–34 mm.

Wet-spun zein fibers coagulated in a pH 2.5 acetic acid bath were used as control fibers. Fibers finished with chemical or physical treatments, soy fibers, and soy protein-zein blended fibers were compared with zein control fibers. Analysis of variance was used to test for effect of the treatments on individual fibers within a batch (SAS Institute, Cary, NC). Six fibers of each treatment were tested at each humidity. When *F*-values were significant, mean differences were compared by using a least significant difference (LSD) test at a probability level of 0.05.

## RESULTS AND DISCUSSION

### Optimization of Wet-Spinning

The most desirable viscosity for the spinning dispersions of zein or soy protein was “at the incipient gel stage when the protein mass slowly flowed together when cut” (Croston et al 1945). Such dispersions had the greatest amount of solids that could be

TABLE I  
Properties of Zein Fibers Coagulated at Various pH Levels and Tested after Equilibrating to 11, 65, and 100% rh<sup>a</sup>

Treatment	HCl				CH <sub>3</sub> COOH	CH <sub>3</sub> COOH and CH <sub>3</sub> COONa		
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
11% rh								
Tenacity (g/tex)	0.93 ± 0.21h	1.21 ± 0.19g	1.78 ± 0.70d	3.41 ± 0.26a	2.12 ± 0.34b	1.92 ± 0.31c	1.50 ± 0.37e	1.35 ± 0.27f
Modulus (g/tex)	382 ± 76b	397 ± 86a	306 ± 98c	261 ± 19d	213 ± 12e	221 ± 19e	189 ± 21f	156 ± 12g
Moisture regain (wt %)	1.25 ± 0.12c	1.23 ± 0.21c	1.24 ± 0.19c	0.84 ± 0.07d	1.57 ± 0.19a	1.31 ± 0.21b	1.51 ± 0.49a	1.49 ± 0.36a
Flexibility (mm)	21	16	11	5	11	11	21	21
65% rh								
Tenacity (g/tex)	1.13 ± 0.14f	1.46 ± 0.19e	2.02 ± 0.58c	2.65 ± 0.51a	2.46 ± 0.18b	2.09 ± 0.61c	1.62 ± 0.31d	0.94 ± 0.12g
Modulus (g/tex)	132 ± 61e	147 ± 81d	176 ± 98b	216 ± 43a	179 ± 21b	169 ± 45c	178 ± 26b	132 ± 16e
Moisture regain (wt %)	7.25 ± 0.23c	7.38 ± 0.61c	7.01 ± 0.54d	7.07 ± 0.45d	8.35 ± 0.46ab	8.56 ± 0.30ab	8.00 ± 0.48b	8.94 ± 0.17a
Flexibility (mm)	5	4	4	2.5	3	3	4	4
100% rh								
Tenacity (g/tex)	0.09 ± 0.01d	0.15 ± 0.02b	0.13 ± 0.03bc	0.17 ± 0.01a	0.11 ± 0.01c	0.14 ± 0.01b	0.14 ± 0.02b	0.10 ± 0.01c
Modulus (g/tex)	6.7 ± 1.1d	6.8 ± 2.9d	8.9 ± 3.7c	12.0 ± 5.0a	9.0 ± 3.9c	9.5 ± 8.2b	9.4 ± 6.9b	9.0 ± 2.8c
Moisture regain (wt %)	23.2 ± 1.9c	22.9 ± 3.3d	26.1 ± 2.9b	22.0 ± 0.5d	28.9 ± 1.8a	26.8 ± 3.9b	26.9 ± 2.76b	28.3 ± 1.8a

<sup>a</sup> Values within each row (for each rh level) with same letters are not significantly different (*P* > 0.05).

pumped through the spinnerettes. This required a high viscosity of 6,000–8,000 cps. The viscosity of zein suspensions increased with zein percentage and aging time and decreased with increases in water content, sodium hydroxide, and urea. A formulation of 15% zein, 60% water, 22% 0.4*N* sodium hydroxide, and 3% urea (pH 12.4) had a viscosity of 6,500 cps after 10 hr of aging and was satisfactory for spinnerette operation. This compares with a 19.6% soy protein dispersion at pH 10.9 and 9,459 cps by Huang et al (1995) for wet-spinning.

Zein fibers coagulated in a pH 2.5 acid bath had greater tenacity, less moisture regain, and greater flexibility than did fibers coagulated at other pH levels at all humidities (Table I). The modulus decreased with decreasing pH for zein fibers coagulated in a HCl bath. The least moisture regain at pH 2.5 may reflect a minimum in ionizable protein groups and osmotic values. This minimal fiber hydration resulted in maximum tenacity and, as the humidity of the testing conditions increased, decreased fiber tenacity. These tenacities were considerably better than the best wet-spun soy protein fiber prepared by Huang et al (1995). Flexibilities were comparable for the zein and soy fibers. Flexibility increased with increased fiber hydration. Presumably, this is due to hydrogen bonds between protein molecules being replaced by hydrogen bonds between protein and water, resulting in weaker but more flexible fibers. Water-soaked fibers were so flexible that they could be wrapped around rods of the smallest diameter and even be knotted.

### Modification of Wet-Spun Zein Fibers

The tenacity of zein fibers treated with 95% acetic anhydride-5% acetic acid at pH 3.5 was greater than the tenacity of fibers given other acetic anhydride treatments (Table II). The tenacity of zein fibers exceeded those of extruded soy fibers treated with acetic anhydride (Huang et al 1995), but the increase in tenacity caused by the acetic anhydride was much less for zein than for soy fibers probably because zein contains fewer polar groups to be blocked by the acetic anhydride. Addition of sodium acetate to buffer the reaction at higher pH levels did not improve the tenacity. Acetic acid promoted swelling of zein fibers and access by acetic anhydride, but a high concentration of acetic acid was undesirable because the acetylated zein fibers became too swollen and weak to be withdrawn from the modifying solutions. Five percent acetic acid solution was a good compromise, allowing penetration into the fibers but preserving their strength. The 95% acetic anhydride-5% acetic acid treatment also resulted in fibers with the highest modulus. As with soy fiber (Huang et al 1995), the acetic anhydride treatments suppressed moisture regain of zein fibers at 11 and 65% rh, but this effect was not as evident in wet fibers. There was little correlation between tenacity and moisture regain except in wet fibers.

Glutaraldehyde is a bifunctional aldehyde and should cross-link proteins with the formation of  $\alpha$ -,  $\omega$ -schiff bases (Lundblad 1991). Glutaraldehyde could react with amino groups, which would sometimes be on separate molecules and cross-link them. Such

**TABLE II**  
Properties of Zein Fibers Finished with Various Concentrations of Acetic Anhydride for 30 min and Tested After Equilibrating to 11, 65, and 100% rh<sup>a</sup>

Treatment <sup>b</sup>	pH	Tenacity (g/tex)	Modulus (g/tex)	Moisture Regain (wt %)
11% rh				
Control		3.41 ± 0.26b	403 ± 54b	1.61 ± 0.16a
100:0:0	0.7	2.35 ± 0.21c	261 ± 19c	0.84 ± 0.07d
95:5:0	3.5	3.98 ± 0.12a	456 ± 18a	0.98 ± 0.06c
90:5:5	4.6	2.58 ± 0.32c	200 ± 24d	1.15 ± 0.28b
95:0:5	6.7	2.42 ± 0.16c	206 ± 5.1d	0.95 ± 0.01c
65% rh				
Control		2.65 ± 0.51b	216 ± 43b	7.07 ± 0.45a
100:0:0	0.7	2.04 ± 0.43c	183 ± 10c	5.85 ± 0.38c
95:5:0	3.5	3.12 ± 0.16a	268 ± 17a	6.87 ± 0.23ab
90:5:5	4.6	2.29 ± 0.04bc	166 ± 18c	6.92 ± 0.21a
95:0:5	6.7	2.09 ± 0.65c	172 ± 46c	6.45 ± 0.08b
100% rh				
Control		0.17 ± 0.01b	12 ± 5.0b	22.00 ± 0.51c
100:0:0	0.7	0.10 ± 0.01c	6 ± 2.1d	27.40 ± 5.12b
95:5:0	3.5	0.68 ± 0.04a	15 ± 2.8a	16.00 ± 0.48d
90:5:5	4.6	0.17 ± 0.04b	14 ± 6.1a	30.10 ± 4.82a
95:0:5	6.7	0.16 ± 0.01b	10 ± 0.4c	27.70 ± 3.42b

<sup>a</sup> Values within each column (for each rh level) with same letters are not significantly different ( $P > 0.05$ ).

<sup>b</sup> Solutions of acetic anhydride, acetic acid, and sodium acetate.

**TABLE III**  
Zein Fibers Finished with Various Concentrations of Glutaraldehyde for 30 min and Tested After Equilibrating to 11, 65, and 100% rh<sup>a</sup>

Treatment	Control	Glutaraldehyde (%)						
		5	10	15	20	25	30	40
11% rh								
Tenacity (g/tex)	3.41 ± 0.26b	1.96 ± 0.54d	2.16 ± 0.73c	2.21 ± 0.86c	4.53 ± 1.05a	1.76 ± 0.33e	1.64 ± 0.53e	1.46 ± 0.64f
Modulus (g/tex)	261 ± 19c	209 ± 39d	186 ± 60e	208 ± 37d	348 ± 51a	206 ± 41d	278 ± 84b	200 ± 17d
Moisture regain (wt %)	0.84 ± 0.07g	0.96 ± 0.41f	1.53 ± 0.31b	1.20 ± 0.03c	1.08 ± 0.17e	1.88 ± 0.27a	1.15 ± 0.37d	1.06 ± 0.21e
Flexibility (mm)	5	11	11	5	3.5	11	11	11
65% rh								
Tenacity (g/tex)	2.65 ± 0.51b	1.72 ± 0.33e	1.74 ± 0.80e	2.27 ± 0.29c	4.00 ± 0.62a	1.86 ± 0.45d	1.83 ± 0.19d	1.50 ± 0.29f
Modulus (g/tex)	216 ± 43b	136 ± 33f	154 ± 46e	178 ± 25c	288 ± 44a	157 ± 27e	169 ± 59d	155 ± 19e
Moisture regain (wt %)	7.07 ± 0.45e	7.21 ± 0.49d	7.63 ± 0.38b	7.67 ± 0.91b	4.89 ± 0.09f	7.39 ± 0.26c	7.01 ± 0.69e	7.88 ± 0.36a
Flexibility (mm)	2.5	3.5	3.5	3	2	3	3.5	3.5
100% rh								
Tenacity (g/tex)	0.17 ± 0.01f	0.34 ± 0.06e	0.43 ± 0.09d	0.50 ± 0.05c	0.78 ± 0.01a	0.55 ± 0.15b	0.50 ± 0.13c	0.10 ± 0.01g
Modulus (g/tex)	12 ± 5.0e	25 ± 4.1d	36 ± 9.3b	39 ± 5.8a	38 ± 9.6a	40 ± 4.2a	31 ± 8.8c	9 ± 2.8f
Moisture regain (wt %)	22.0 ± 0.51b	21.1 ± 1.57c	21.6 ± 1.39c	21.8 ± 1.12c	19.9 ± 0.45e	21.6 ± 1.51c	27.0 ± 4.3a	20.6 ± 1.83d

<sup>a</sup> Values within each row (for each rh level) with same letters are not significantly different ( $P > 0.05$ ).

cross-linking should be at a maximum when the number of reactive protein groups and glutaraldehyde are at a molar ratio of 2:1.

Twenty percent glutaraldehyde increased the tenacity of zein fibers at all humidities (Table III). This treatment also maximized the fiber modulus and minimized moisture regain, indicating some cross-linking. The increase in tenacity for zein fibers was not as great as that reported by Huang et al (1995) for soy fibers treated with 25% glutaraldehyde, but the treated zein fibers still exceeded the soy fibers in tenacity at all relative humidities.

Stretching to 115% with glutaraldehyde treatment resulted in the maximum fiber tenacity and flexibility at all humidities (Table IV). Stretching also increased zein fiber modulus. The stretching effect is attributed to increased interaction between molecules as the polypeptide chains are extended and aligned parallel to each other. Stretching fibers too much (120%) decreased tenacity because of fiber breakage. A combination of the treatments 20% glutaraldehyde, 95% acetic anhydride, and 115% stretching produced fibers with greater tenacity, modulus and flexibility values than other treatments (Table IV). Soy fibers were capable of greater stretching (150–170%) than zein fibers. Soy fibers treated with acetic anhydride and glutaraldehyde and stretched had tenacities of 9.11, 5.23, and 2.36 at 11, 65, and 100% rh, respectively (Huang et al 1995) compared to tenacities of 6.89,

6.56, and 1.17 at 11, 65, and 100% rh, respectively, for zein fibers (Table IV).

### Optimization of Extrusion

Although soy protein-water mixtures were readily extruded into fibers, poor solubility of zein in water and the high temperature requirements of zein extrusion made this impossible for zein fibers. Suspensions (1:4) of zein and 1,5-pentanediol, which boils at a temperature higher than water, resulted in weak fibers (1.62 g/tex at 11% rh).

It was possible to extrude 45% soy-zein mixtures dispersed in 40% water and 15% glycerol. The optimum soy protein-zein blended fiber was made from a suspension containing 80% soy protein and 20% zein in glycerol on the basis of total protein (Table V). The blend was generally comparable to the soy fiber in tenacity and inferior to the best wet-spun zein fiber in Table I. As the zein content in the blended suspensions increased, the fibers decreased in tenacity and became more brittle. Blended fibers had less moisture regain than soy fibers because zein contains fewer polar groups to absorb water.

### Modification of Extruded Fibers

The treatment of zein fibers with dimethylformamide and dimethylsulfoxide solutions for possible cross-linking caused the

**TABLE IV**  
Zein Fibers Finished with Various Treatments and Tested After Equilibrating to 11, 65, and 100% rh<sup>a</sup>

Treatment	Control	20% Glutaraldehyde	AA <sup>b</sup>	20% Glutaraldehyde			20% Glutaraldehyde + AA	
				110% ST <sup>c</sup>	115% ST	120% ST	0% ST	115% ST
11% rh								
Tenacity (g/tex)	3.41 ± 0.26f	4.53 ± 1.05d	3.98 ± 0.12e	4.57 ± 0.79d	5.50 ± 1.64b	4.23 ± 0.68d	5.04 ± 0.31c	6.89 ± 0.46a
Modulus (g/tex)	261 ± 19d	348 ± 51c	456 ± 18b	287 ± 29d	334 ± 27c	370 ± 39b	251 ± 31d	484 ± 48a
Moisture regain (wt %)	0.80 ± 0.07f	1.10 ± 0.17d	0.98 ± 0.06e	1.40 ± 0.09c	1.40 ± 0.01c	1.60 ± 0.15a	1.60 ± 0.11a	1.50 ± 0.26b
Flexibility (mm)	5	3.5	4	3	2.5	3	3	1.5
65% rh								
Tenacity (g/tex)	2.65 ± 0.51g	4.00 ± 0.62e	3.12 ± 0.16f	4.13 ± 0.86d	4.25 ± 0.27c	4.00 ± 0.96e	4.46 ± 0.16b	6.56 ± 0.92a
Modulus (g/tex)	216 ± 43f	288 ± 44d	268 ± 17e	304 ± 46d	369 ± 33b	285 ± 50d	354 ± 38c	375 ± 38a
Moisture regain (wt %)	7.10 ± 0.45a	4.90 ± 0.09f	6.89 ± 0.23b	6.00 ± 0.17c	5.41 ± 0.15d	5.02 ± 0.09e	5.52 ± 0.78d	5.04 ± 0.16e
Flexibility (mm)	2.5	2	3	2	1.5	2	1.5	1.5
100% rh								
Tenacity (g/tex)	0.17 ± 0.01g	0.78 ± 0.01de	0.68 ± 0.04f	0.79 ± 0.13d	0.90 ± 0.20b	0.75 ± 0.18e	0.83 ± 0.09c	1.17 ± 0.09a
Modulus (g/tex)	12 ± 5.0e	38 ± 1.0a	15 ± 2.8d	19 ± 2.6b	19 ± 4.5b	18 ± 8.1bc	17 ± 1.9c	17 ± 4.1c
Moisture regain (wt %)	22.00 ± 0.51a	19.90 ± 0.45b	16.00 ± 0.48c	21.40 ± 0.17a	20.90 ± 0.06a	21.60 ± 0.09a	20.90 ± 0.41 a	20.80 ± 0.61a

<sup>a</sup> Values within each row (for each rh level) with same letters are not significantly different ( $P > 0.05$ ).

<sup>b</sup> AA = 95% acetic anhydride and 5% acetic acid.

<sup>c</sup> ST = stretching.

**TABLE V**  
Extruded Soy Fibers, Wet-Spun Zein Fibers, Extruded Soy-Zein Blended Fibers<sup>a</sup> and Extruded Soy Fibers Treated with 1,4-Benzoquinone (BQ), Dimethylformamide (DMF), or Dimethylsulfoxide (DMSO) and Tested After Equilibrating to 11, 65, and 100% rh<sup>b</sup>

Treatment	Soy Fibers	Zein Fibers	Soy-Zein Blended Fibers			Treated Soy Fibers <sup>c</sup>		
			80:20	70:30	60:40	BQ	DMF	DMSO
11% rh								
Tenacity (g/tex)	1.54 ± 0.24f	1.62 ± 0.47e	1.70 ± 0.17d	0.19 ± 0.06g	0.21 ± 0.08g	3.54 ± 0.18a	3.22 ± 0.29b	2.65 ± 0.30c
Modulus (g/tex)	64 ± 10e	46 ± 11f	96 ± 14d	15 ± 5.6h	31 ± 5.5g	278 ± 26b	289 ± 42a	237 ± 73c
Moisture regain (wt %)	1.60 ± 0.05b	2.01 ± 0.12a	1.17 ± 0.11d	1.06 ± 0.21e	1.32 ± 0.18c	0.89 ± 0.10f	0.67 ± 0.12f	0.79 ± 0.48f
Flexibility (mm)	21	21	11	25	34	3	3	3
65% rh								
Tenacity (g/tex)	0.55 ± 0.12e	2.12 ± 0.62d	0.44 ± 0.04f	0.15 ± 0.03g	0.18 ± 0.04g	3.37 ± 0.08a	2.53 ± 0.12c	2.93 ± 0.02b
Modulus (g/tex)	22 ± 6d	152 ± 26c	17 ± 1e	7.1 ± 1f	14 ± 2e	280 ± 36a	183 ± 18b	190 ± 37b
Moisture regain (wt %)	13.1 ± 0.67a	8.01 ± 0.33d	9.83 ± 0.34c	11.3 ± 0.18b	11.2 ± 0.37b	8.20 ± 0.56d	6.78 ± 0.83e	9.83 ± 1.62c
Flexibility (mm)	2.5	11	1.5	2	3	1.5	1.5	1.5
100% rh								
Tenacity (g/tex)	0.076 ± 0.02d	0.01 ± 0.00f	0.072 ± 0.01e	0.015 ± 0.01f	0.011 ± 0.01f	0.53 ± 0.12a	0.43 ± 0.15b	0.31 ± 0.17c
Modulus (g/tex)	7.40 ± 3.0c	0.21 ± 0.1f	7.1 ± 1c	5.1 ± 2d	4.5 ± 1e	32 ± 6 a	23 ± 5b	22 ± 9b
Moisture regain (wt %)	88.10 ± 1.56a	26.40 ± 0.79d	87.20 ± 2.78a	83.80 ± 0.27a	89.70 ± 0.69a	37.90 ± 5.56b	30.60 ± 2.57 c	36.00 ± 2.57bc

<sup>a</sup> Protein, water, and glycerol (45:40:15).

<sup>b</sup> Values within each row (for each rh level) with same letters are not significantly different ( $P > 0.05$ ).

<sup>c</sup> DMF = 60% water, 10% ethanol, and 30% dimethylformamide; DMSO = 60% water, 10% ethanol, and 30% dimethylsulfoxide; BQ = 89% water, 9.5% ethanol, and 1.5% 1,4-benzoquinone.

fibers to disintegrate and dissolve. Zein fibers did not swell sufficiently in polar solvents to allow effective cross-linking within the fibers.

The tenacity, modulus, and flexibility of extruded soy fibers treated with 1,4-benzoquinone solution were improved compared with untreated soy fibers (Table V). 1,4-Benzoquinone is a good cross-linking agent for soy fibers, especially in wet conditions, because the cyclohexadiene ring can stabilize the cross-linked compounds by yielding a conjugated system. The tenacity and modulus of soy fibers were increased with treatments of dimethylformamide and dimethylsulfoxide solutions. Both solutions contained 60% water, which could supply enough water to swell soy fibers and allow the ethanol and 30% dimethylformamide or dimethylsulfoxide to enter the fibers. Dimethylformamide- and dimethylsulfoxide-treated soy fibers were more flexible than untreated soy fibers. Treatment of extruded soy fibers with glutaraldehyde, acetic anhydride, and stretching to 150% also improved tenacity (Huang et al 1995).

### CONCLUSIONS

Wet-spun zein fibers were successfully prepared by mixing 15% zein, 60% water, 22% dilute sodium hydroxide, and 3% urea and spinning into an acid bath of pH 2.5 acetic acid for 10 min. Optimum conditions for the suspension were pH 11.3–12.7 and viscosity of 6,000–8,000 cps after 10 hr of aging. The results confirm and extend the pioneering studies of Croston et al (1945).

Modification of wet-spun zein fibers by acetylation, cross-linking, or esterification to block the polar groups increased fiber tenacity. The tenacity of zein fibers was improved by treatment with 20% glutaraldehyde, 95% acetic anhydride at pH 3.5, dialcohols, and stretching to 115% of the original length. Wet-spun zein fibers finished with a combination of 20% glutaraldehyde, 95% acetic anhydride, and 115% stretching had the greatest tenacity of all treatments. Tenacity was 6.89 g/tex at 11% rh, 6.65 g/tex at 65% rh, and 1.17 g/tex in wet conditions compared with 6.43, 6.26, and 0.72 for treated and stretched wet-spun soy fibers tested at 11, 65, and 100% rh, respectively (Huang et al 1995). In comparison, tenacity values for wool fibers are 14 g/tex at 65% rh and 9 g/tex at 100% rh; tenacity values for acetate fibers are 10.8 to 12.6 g/tex at 65% rh and 9 to 11.7 g/tex at 100% rh (Joseph 1988).

Extruded soy fibers were improved by 1,4-benzoquinone treatment as a cross-linking agent, especially in wet conditions. The tenacity and flexibility of extruded soy fibers were improved by the plasticizing effect of dimethylformamide and dimethylsulfoxide treatments. However, treatment of extruded soy fibers with glutaraldehyde, acetic anhydride, and stretching resulted in greater

tenacity than treatment with 1,4-benzoquinone, dimethylformamide or dimethylsulfoxide (Huang et al 1995).

Improvements in protein fibers were made by chemical treatments and by stretching, but the major limitations of poor wet strength and limited flexibility in low-humidity conditions were not overcome. Extrusion was a more suitable process for soy protein fiber production than was zein because of soy protein's solubility in water and glycerol. Zein and soy proteins have the potential to be used as textile fibers because of their renewability and biodegradability. Because of the lower cost of soy protein, it has a greater potential for use as textile fibers than zein.

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