Properties of Fibers Produced from Soy Protein Isolate by Extrusion and Wet-Spinning

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ABSTRACT: Fibers were produced from soy protein isolate by both wet-spinning and extrusion. In the wet-spinning process, aged, alkaline protein solution was forced through a spinnerette into an acid coagulating bath. In the extrusion process, a twin-screw extruder forced a protein isolate–water mixture through a die. The physical properties of the fibers were measured at various water activities. The fibers produced by both methods were brittle and lacked tensile strength (tenacity). The addition of glycerol reduced brittleness in extruded fibers. Zinc and calcium ions decreased the brittleness of wet-spun fibers. The tenacity of soy fibers was significantly improved by post-spinning treatments, including acetic anhydride, acetaldehyde, glyoxal, glutaraldehyde, a combination of glutaraldehyde and acetic anhydride, and stretching. The best extruded fibers were produced with a mixture of 45% soy protein, 15% glycerol, and 40% water, finished with a combination of glutaraldehyde and acetic anhydride and then stretched to 150% their original lengths. The best wet-spun fibers were produced with a 19.61% soy protein suspension at pH 12.1; coagulated in a 4% hydrochloric acid solution that contained 3.3% sodium chloride, 3.3% zinc chloride, and 3.3% calcium chloride; and followed by treatment with 25% glutaraldehyde and stretching to 170% their original lengths.

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KEY WORDS: Chemical modification, cross-linking, elongation, extrusion, fibers, flexibility, soy isolate, tenacity, wet-spinning.

The possibility of producing fibers from soy protein was first investigated in the 1930s and 1940s by Kajita and Inoue (1–3) in Japan and by Boyer (4) in the United States. Subsequently, the Ford Motor Co. (Detroit, MI) sponsored studies on the wet-spinning of soy protein to produce textile fibers (5–12). These studies were mostly empirical, and soy fibers were never produced commercially. Little information is available about the properties of the soy fibers that were produced, but they were reported to lack wet strength and to have inconsistent quality. In the late 1940s the introduction of inexpensive, petroleum-based textile fibers with good physical properties discouraged further exploration of fibers spun from plant and animal protein.

Recently, however, several factors have rekindled interest in textile fibers produced from agricultural raw materials. These factors are (i) the slow degradation of discarded petroleum-based fibers and the resulting environmental damage, (ii) the increased price of petroleum and concern about its future availability, and (iii) the possibility that plant protein can be modified by molecular genetic techniques to enhance its properties in specific applications.

Our study was undertaken for the following reasons: (i) to reexamine the production of fibers from soy protein by wet-spinning and to attempt production by extrusion, (ii) to examine the properties of these fibers, (iii) to observe the effect on fiber properties of protein modification and the addition of plasticizers and cross-linking agents, and (iv) to generate a theory of the factors that affect the fibers' properties to guide further explorations.

MATERIALS AND METHODS

Chemicals and reagents. Soy protein isolate (SPI) (ARPRO 1100), alkali-extracted, acid-precipitated at its isoelectric point, and tunnel-dried to 7% moisture, was obtained from Archer Daniels Midland Co. (Decatur, IL). Glutaraldehyde (25%) was purchased from Aldrich Chemical Co. (Milwaukee, WI); glyoxal (40%) from Fluka Chemika-Biochemiks (Ronkonkoma, NY). Other reagents were purchased from Fisher Scientific (Pittsburgh, PA).

Extrusion. To select soy protein mixtures suitable for extrusion spinning, ARPRO 1100 was mixed with water and/or glycerol in a heavy-duty Kitchen Aid mixer (Kitchen Aid Portable Appliances, St. Joseph, MI) at 70 rpm for 10 min. After equilibration at room temperature for 24 h, the mixtures were placed in a Brabender Plastic-Corder PL2000 with a half-size, roller-style mixer-measuring head (C.W. Brabender Instruments, Inc., South Hackensack, NJ) at 110°C and mixed at 20 rpm. As the temperatures of the mixtures rose during a 15-min heating time, the maximum and minimum torques and the temperatures at which they occurred were noted.

In a typical extrusion, ARPRO 1100, glycerol, and water (45:15:40) were mixed with a Kitchen Aid mixer at 70 rpm for 10 min. After equilibration at room temperature for 24 h, the mixture was extruded with a twin-screw Brabender Plastic-Corder PL2000 at 96°C and 20 rpm through a die that con-

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tained eight 368-μm openings (Engineering Research Institute, Iowa State University, Ames, IA).

Wet-spinning. To evaluate mixtures for wet-spinning, ARPRO 1100, and water mixtures, adjusted to various pH values with sodium hydroxide, were blended 30–120 min with a Kitchen Aid mixer at 70 rpm. Viscosities were measured with a Brookfield Synchro-Lectric Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA) at 0, 1, and 2 d.

The typical spinning mixture contained 750 g ARPRO 1100, 410 g 10% sodium hydroxide, and 2.665 L water and was aged 24 h. Preliminary tests were conducted by placing a sample of the alkaline protein mixture in a 10-mL syringe with a 26-gauge needle and injecting it in a 4% hydrochloric acid solution.

The wet-spinning apparatus (Fig. 1) consisted of a pressure vessel, filter, pump, and coagulating bath. Air pressure (4.14×10^5 N/m^2) moved the alkaline protein mixtures through the 25- to 30-μm filter (Ronningen-Petter, Protage, MI). A Zenith pump with a QM-SY 1416 digital speed controller (Parker Hannifin Co., Waltham, MA) forced the filtered mixtures through a spinnerette (Engineering Research Institute, Iowa State University) with 386-μm openings into a 90 × 13 × 12-cm coagulating bath. A Posiflo II Pump (Gelman Sciences, Ann Arbor, MI) circulated acid solution in the coagulating bath. The individual wet-spun fibers were dried on waxed paper.

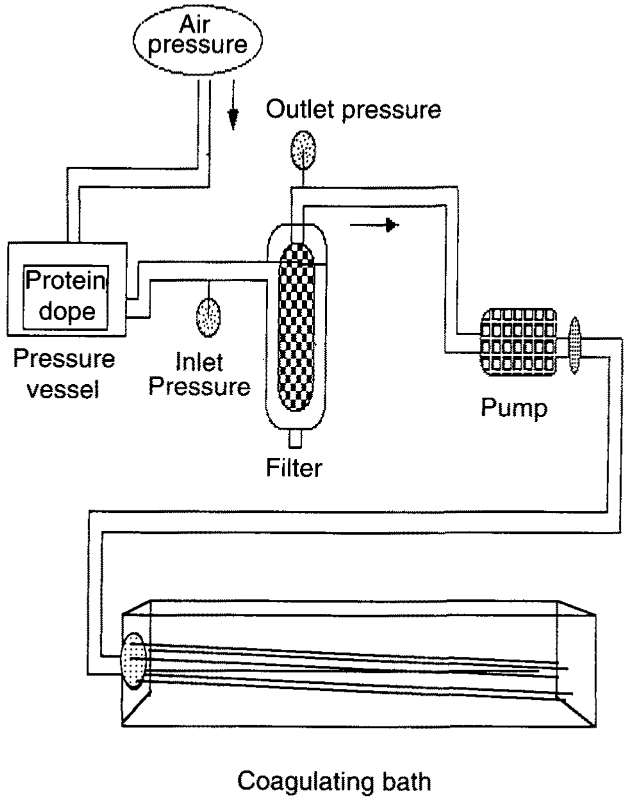

FIG. 1. Schematic drawing of the wet-spinning process.

Post-spinning modification of fibers. Fibers (10 g) were modified by the following procedures: (i) heated in 100 mL acetic anhydride/acetic acid 9:1, 7:3, or 1:1 (vol/vol) at 85°C for 30 min; (ii) soaked in 100 mL 10, 15, 20, or 25% acetaldehyde (vol/vol) at room temperature for 30 min; and (iii) soaked in 100 mL 10, 15, 20, or 25% glyoxal or glutaraldehyde (vol/vol) at pH 3.5 at room temperature for 30 min. To test the effect of stretching, fibers treated with 25% glutaraldehyde were stretched to a percentage of their original length under the same conditions used to measure elongation.

Testing of fiber properties. Fiber linear density (tex) was measured by weighing six 20-cm fibers and multiplying the average weight in grams by 5,000. Fibers were air-dried for 24 h after spinning or treatments and stored for 72 h in desiccators over saturated aqueous lithium chloride for water activity (a_w) 0.11 and over sodium nitrite for a_w 0.65 (13). Wet fibers (a_w 1.0) were prepared by soaking for 15 min in a 0.1% solution of detergent according to the American Society for Testing and Materials (ASTM) (14). The Instron Universal Testing Machine (Instron Corp., Canton, MA) Model 4500 with a 100 N load cell and pneumatic-action grips (No. 2712-002) was used to measure tensile strength (breaking tenacity in g/tex) and elongation (percentage of increase in the original length) of single fibers. Each test was replicated six times with a stretching rate of 5 cm/min. The initial test length of the fibers was 10 cm.

Fiber flexibility was determined (six replicates) by looping fibers three times around a set of glass rods with diameters 1.5, 2, 2.5, 3, 3.5, 4, 5, 11, 16, 21, 25, 34, and 45 mm. The diameters of the smallest glass rods that could be looped successfully without breaking the fiber was recorded as a measure of fiber flexibility. Flexibility tests were run at a_w 0.11 and 0.65. At a_w 1.0, all fibers were flexible enough to be looped around the smallest rod.

To determine moisture uptake, fibers were dried in a 100°C oven for 24 h; 1 g dried fibers was equilibrated over water and salt solutions at a_w 0.11 and 0.65 (13) for 72 h, and water absorption was measured by weighing.

To determine titratable groups, fibers were stirred for 30 min in 100 times their weight of water, dried in 100°C oven for 24 h, and stored in a desiccator overnight. A 5-g sample was ground to powder, suspended in 200 mL water with stirring for 30 min, and titrated with 0.1 N sodium hydroxide or hydrochloric acid between pH 3 and 11.

Statistical analyses. The properties of the fibers were analyzed by studying the variance (15), and differences among individual treatments were determined by a least significant difference (LSD) test at a 5% level of significance.

RESULTS AND DISCUSSION

Spinning formulations. Table 1 gives the viscoelastic properties of soy and water mixtures observed in the mixing/measuring apparatus. When soy protein was heated with water, the viscosity increased with temperature up to a transition temperature and then decreased. In producing fibers by extru-

TABLE 1
Transition Temperatures and Viscosity of ARPRO™ 1100 and Water Mixtures at Various Moisture Contents

Moisture (%)	Temperature (°C) at maximum torque	Maximum torque (M-Newtons)	Temperature (°C) at minimum torque	Minimum torque (M-Newtons)
30	92.5^a	20.27^a	99.5^a	14.14^a
35	87.5^b	12.78^b	97.5^b	4.23^b
40	78.5^c	10.39^c	96.0^b	3.76^c

$^{a-c}$Values in each column with same superscripts are not significantly different ($P > 0.05$).

sion, it was important to keep the viscosity within the design limits of the extruder and to avoid temperatures above the boiling point of water so that the fibers would not puff as they exited from the extruder. A moisture level above 30% was required to achieve torques within the design limit of the extruder. The mixing torque decreased with moisture percentage, and the transition temperature decreased as moisture content increased. Fibers produced from mixtures with low moisture percentages were tough and inelastic when dried, but when the moisture during extrusion exceeded 40%, the fibers became sticky, weak, and irregular and were difficult to extrude.

Various die sizes were tested to see how fine a fiber could be made by extrusion. Generally, a die with openings 386 μm or larger could be operated without plugging.

The changes in viscosity of wet-spinning mixtures with time and sodium hydroxide concentration are given in Table 2. The viscosity of the mixtures increased with protein concentration and pH up to 11. The viscosity of mixtures at pH 10 and 11 reached a maximum in one day. The protein molecules in the alkaline solutions seemed to slowly rearrange themselves and form aggregates with greater viscosities. In choosing mixtures for producing fibers by wet-spinning, the primary considerations were viscosity and the fragility of the fibers produced. Viscosities greater than 150 poise made wet-spinning through 386-μm openings extremely difficult. The fragility of the freshly-spun fibers required the use of the greatest concentration of protein and the maximum possible viscosity. Fiber formation by syringe injection indicated that mixtures containing about 20% protein at a pH higher than 10 merited further study because these had the maximum usable protein concentration and viscosity. Table 3 shows the viscosity of batches, containing 19.6% protein and approximately 79% moisture, that were adjusted to pH values between 10.45 and 12.77 with sodium hydroxide. Alkali concentration and storage time significantly affected viscosity. The pH of all solutions declined slightly with time. The mixtures with initial pH values of 11.38 and 12.08 had the greatest viscosities and exhibited the most increase in viscosity after aging 24 h. After testing fiber formation from the day-old mixtures by syringe injection, formulation B (see Table 3) was chosen as the most suitable for wet-spinning. Formulation A gave fibers that floated on the surface of the coagulation bath. Formulations C and D were inconveniently viscous, and E and F released copious amounts of ammonia. The release of ammonia presumably comes from the loss of amine and amide groups by the protein and may account for the gradual decrease in viscosity that occurs with these solutions.

Formulation B could be spun through spinnerettes as small as 36 μm, but, for ease of handling and comparison with extruded fibers, a 386-μm spinnerette was selected. Wet-spun fibers that coagulated in a bath containing only acid were extremely fragile.

Effect of moisture and plasticizers on fiber properties. Tables 4 and 5 show the effects of humidity, polyols, and inorganic salts on the fiber properties. Freshly produced fibers

TABLE 2
Viscosity of Soy Protein–Water–Sodium Hydroxide Mixtures at Various pH Values Concentrations, and Aging Times

	Viscosity (poise)		
Protein (%)	pH 9	pH 10	pH 11
After mixing			
15	8.5^c	7.8^c	13.5^c
20	63.2^b	25.2^b	52.0^b
25	187.0^a	157.0^a	181.0^a
One day			
15	7.5^c	8.5^c	16.0^c
20	41.5^b	73.5^b	149.0^b
25	182.0^a	585.0^a	653.0^a
Two days			
15	7.0^c	7.5^c	10.5^c
20	36.4^b	65.0^b	99.0^b
25	172.0^a	475.0^a	570.0^a

$^{a-c}$Values within each column with the same superscript are not significantly different ($P > 0.05$).

TABLE 3
Viscosity at Various Aging Times and Initial pH of Soy Protein (19.61% by wt)–Water–Sodium Hydroxide Mixtures

Formulation	Initial pH	Viscosity (poise) Day 0	Day 1	Day 2	Day 3	Day 4
A	10.45	25.5^e	57.5^e	49.0^d	38.5^e	24.5^e
B	10.88	31.5^d	94.5^d	82.0^c	78.0^c	54.5^c
C	11.38	54.5^a	453.3^b	418.8^b	402.0^b	392.5^b
D	12.08	44.0^b	730.0^a	640.0^a	645.0^a	475.0^a
E	12.67	35.5^c	121.0^c	99.5^c	69.0^d	34.5^d
F	12.77	34.5^c	27.5^f	27.5^e	13.5^f	9.0^f

[a–f]Values within each column with the same superscript are not significantly different ($P > 0.05$).

were quite flexible, but, as the water they contained volatilized, both the extruded and wet-spun fibers became brittle. Flexibility could be restored by exposing the fibers to water or elevated humidity. Glycerol improved the flexibility of the fibers and, under some conditions, increased their tenacity and elongation. Sorbitol did little to enhance the fibers' properties. Replacing water with glycerol in soy protein mixtures increased the mixing torque and decreased transition temperatures (16). From these results, the formulation 45% ARPRO 1100, 15% glycerol, and 40% moisture was chosen as the basic mixture for preparing extruded soy fibers. Glycerol could not be used to improve wet-spun fibers because it was extracted from the fibers in the acid coagulating bath.

Table 5 shows that the addition of various inorganic salts to the extrusion mix increased the flexibility of the resulting fibers, but the salts also decreased fiber tenacity. For wet-spun fibers, the salts increased fiber tenacity enough so that fibers could be harvested and their properties measured at a_ws of 0.11 and 0.65. This was partly caused by the increased osmotic value of the coagulating bath, which tended to dehydrate the freshly spun fibers and increase their protein content, thus increasing their strength. If one assumes that the effect of sodium chloride is primarily osmotic, zinc ions increased fiber flexibility, and both zinc and calcium ions increased tenacity compared with sodium. Zinc and calcium ions are capable of complexing with amino acids, and the formation constants with glycine are greater for zinc than for calcium ($\log K_1$ 5.52, and 1.38; $\log K_2$ 9.96 and 0, respectively) (17). The greater constants indicate a stronger association.

Tables 4 and 5 also show that, as the water activity increased, the tenacity of the fibers decreased markedly, and their moisture content increased. The wet-spun fibers gained more moisture than the fibers extruded with inorganic salts. Presumably, as water activity increased, hydrogen bonds between protein molecules were replaced by hydrogen bonds between protein and water, thus decreasing tenacity and making it easier to move molecules with respect to each other. Polyvalent inorganic ions presumably interact with charged groups on the protein and facilitate the movement of charged protein molecules with respect to each other.

Chemical modification. Chemical modification of soy protein before fiber production (such as by acylation with anhy-

TABLE 4
Properties of Extruded Fibers When Glycerol and Sorbitol Were Used as Plasticizers

Treatment	Tenacity (g/tex)	Elongation at break %	Flexibility (mm)	wt% Moisture uptake[a]
a_w 0.11				
0% Glycerol	$1.49^{b,c}$	0.5^d	45	1.59^b
15% Glycerol	1.57^b	1.6^b	21	1.61^b
15% Sorbitol	0.38^d	0.7^d	45	1.20^c
7.5% Glycerol, 7.5% sorbitol	1.23^c	1.3^c	21	1.24^c
a_w 0.65				
0% Glycerol	0.31^c	0.6^c	2.5	9.99^e
15% Glycerol	0.56^b	73.4^b	2	14.32^b
15% Sorbitol	0.33^c	1.2^c	4	11.88^d
7.5% Glycerol, 7.5% sorbitol	0.54^b	8.5^c	2	13.07^c
a_w 1.00				
0% Glycerol	0.090^b	1.9^b	1.5	63.19^c
15% Glycerol	0.076^b	3.9^b	1.5	88.82^b
15% Sorbitol	—[f]	—	1.5	86.82^b
7.5% Glycerol, 7.5% sorbitol	—	—	1.5	87.59^b

[a]Uptake by oven-dried fibers.
[b–e]Values within each column and water activity (a_w) with the same superscript are not significantly different ($P > 0.05$). Data at each a_w were analyzed independently.
[f]— Values too low to determine.

TABLE 5
Properties of Fibers When Salts Were Used as Plasticizers[a]

Treatment	Fiber process	Tenacity (g/tex)	Elongation at break %	Flexibility (mm)	wt% Moisture uptake[b]
a_w 0.11					
Control	Extruded	1.57^{c}	$1.6^{d,e}$	21.0	1.61^{c}
$ZnCl_2$ 4%	Extruded	1.12^{d}	2.1^{b}	5.0	1.37^{d}
$CaCl_2$ 4%	Extruded	0.81^{e}	1.3^{e}	11.0	1.36^{d}
$ZnCl_2$, $CaCl_2$ 2% each	Extruded	0.74^{e}	1.2^{e}	11.0	1.20^{e}
Na_2HPO_4 4%	Extruded	0.75^{e}	$1.8^{c,d}$	11.0	1.53^{c}
NaCl 10%	Wet-spun	0.68^{e}	0.5^{f}	45.0	1.06^{i}
$ZnCl_2$ 10%	Wet-spun	0.26^{i}	0.7^{f}	16.0	1.47^{h}
$CaCl_2$ 10%	Wet-spun	1.06^{e}	0.6^{f}	45.0	2.58^{f}
$ZnCl_2$–$CaCl_2$–NaCl 3.3% each	Wet-spun	1.84^{f}	0.5^{f}	45.0	1.61^{g}
a_w 0.65					
Control	Extruded	0.56^{c}	73.4^{c}	2.0	$14.32^{e,f}$
$ZnCl_2$ 4%	Extruded	$0.28^{d,e}$	19.1^{e}	1.5	$14.90^{d,e}$
$CaCl_2$ 4%	Extruded	0.25^{e}	60.1^{d}	1.5	$15.45^{c,d}$
$ZnCl_2$, $CaCl_2$ 2% each	Extruded	0.31^{d}	17.7^{e}	1.5	14.03^{f}
Na2HPO4 4%	Extruded	0.26^{e}	17.7^{e}	1.5	15.51^{c}
a_w 0.65					
NaCl 10%	Wet-spun	0.35^{g}	0.4^{g}	2.0	8.23^{i}
$ZnCl_2$ 10%	Wet-spun	0.25^{h}	1.5^{g}	1.5	12.6^{h}
$CaCl_2$ 10%	Wet-spun	0.06^{i}	5.9^{f}	1.5	30.08^{f}
$ZnCl_2$–$CaCl_2$–NaCl 3.3% each	Wet-spun	1.13^{f}	2.2^{g}	2.0	18.81^{g}
a_w 1.00					
Control	Extruded	0.076	3.9	1.5	88.82^{f}
$ZnCl_2$ 4%	Extruded	—[j]	—	1.5	$146.69^{c,d}$
$CaCl_2$ 4%	Extruded	—	—	1.5	150.48^{c}
$ZnCl_2$, $CaCl_2$ 2% each	Extruded	—	—	1.5	142.42^{d}
Na_2HPO_4 4%	Extruded	—	—	1.5	106.15^{e}
NaCl 10%	Wet-spun	—	—	1.5	83.15^{i}
$ZnCl_2$ 10%	Wet-spun	—	—	1.5	101.12^{h}
$CaCl_2$ 10%	Wet-spun	—	—	1.5	213.14^{f}
$ZnCl_2$–$CaCl_2$–NaCl 3.3% each	Wet-spun	—	—	1.5	198.19^{g}

[a] For extruded fibers, the inorganic ions were extruded with ARPRO 1100 (Archer Daniels Midland, Decatur, IL), glycerol, and water. For wet-spun fibers, the *inorganic ions were in the* coagulating bath.

[b] Uptake by oven-dried fibers.

[c–i] Values within each column and water activity (a_w) with the same letter are not significantly different ($P > 0.05$). Data for each a_w were analyzed independently.

[j] —Values too low to determine.

drides, esterification with alcohols, oxidations with hydrogen peroxide, and imine formation with aldehydes) did not succeed in improving the strength or flexibility of fibers (16). The physical properties of fibers, however, were significantly improved by post-spinning treatment with acetic anhydride and acetaldehyde, as shown in Table 6. Both reagents increased the tenacity of fibers at a_w 0.11 and increased elongation at a_w 1.0. Flexibility was improved by acetic anhydride at both a_w 0.11 and 0.65; with acetaldehyde flexibility, however, it was improved at a_w 0.11 and it decreased at a_w 0.65. The moisture absorption of both acetic anhydride- and acetaldehyde-finished fibers was significantly decreased, more so with acetic anhydride than with acetaldehyde. Derivatization with several concentrations of these reagents was tried, and the results are reported in Figure 2. The greatest increases in tenacity were obtained with the highest concentrations despite there being a large molar excess of reagent to reactive functional groups in the protein.

Titrations of the fibers given various treatments (Fig. 3) showed that the derivatized soy protein contained fewer titratable groups than did the control fibers ($P < 0.01$). Acetic anhydride would be expected to acetylate free amine and hydroxy groups on the protein. Acetaldehyde would be expected to form an imine bond with free amine groups. Both of these reagents would decrease the amine groups, which could be involved in ionic and hydrogen bonding, and replace them with less polar groups. Acetic anhydride-finished fibers were estimated to have about 46% of their titratable groups derivatized. Fibers, treated post-spinning with propionaldehyde and benzoic anhydride, were not improved as much as those treated with acetaldehyde and acetic anhydride (16). Formaldehyde was similar to acetaldehyde in its effects on a molar concentration basis (16) but was avoided because of its reputation as a carcinogen. Some researchers (18,19) have speculated that formaldehyde acts as a protein cross-linking agent, but, as Figure 2 shows, it is no more effective in in-

TABLE 6
Properties of Extruded Fibers Treated Post-Spinning with Chemical Reagents That React with Various Protein Functional Groups

Treatment	Tenacity (g/tex)	Elongation at break %	Flexibility (mm)	wt% Moisture uptake[a]
a_w 0.11				
Control	1.57[d]	1.6[d]	21.0	1.61[c]
Acetaldehyde (25%)	2.19[c]	0.9[e]	11.0	0.76[d]
Acetic anhydride[b]	2.31[c]	4.7[c]	2.0	0.77[d]
a_w 0.65				
Control	0.56[d]	73.4[c]	2.0	14.32[c]
Acetaldehyde (25%)	1.02[c]	0.8[d]	11.0	8.34[d]
Acetic anhydride[b]	1.07[c]	1.8[d]	1.5	5.52[e]
a_w 1.00				
Control	0.08[e]	3.9[e]	1.5	88.82[c]
Acetaldehyde (25%)	0.20[d]	31.1[d]	1.5	40.27[d]
Acetic anhydride[b]	0.58[c]	89.0[c]	1.5	16.61[e]

[a] By oven-dried fibers.

[b] Acetic anhydride/acetic acid (9:1).

[c–e] Values within each column and water activity (a_w) with the same letter are not significantly different ($P > 0.05$). Data for each a_w were analyzed independently.

creasing tenacity than acetic anhydride, which is not a cross-linking agent.

A decrease in the capacity to form hydrogen and ionic bonds in the protein may account for the decrease in moisture-binding capacity of acetic-anhydride– and acetaldehyde-treated fibers. Replacement of hydrogen and ionic bonds with more nonpolar groups may increase tenacity by increasing nonpolar attractions between soy protein molecules.

Cross-linking. The effect of treatments with the dialdehydes glyoxal and glutaraldehyde on fiber properties is shown in Table 7. These difunctional reagents are believed to cause cross-linking. At a_w 0.11, the gains from the cross-linking reagents were not significantly greater than the effect of acetaldehyde, as shown in Table 6. At a_w 0.65 and 1.0; however, both glyoxal and glutaraldehyde treatments increased fiber tenacity more than did acetaldehyde alone. The cross-linking agents did not increase flexibility compared with the untreated control, but they also did not cause the decreased flexibility noted for acetaldehyde at a_w 0.65. Like acetaldehyde, the cross-linking agents decreased elongation at a_w 0.11 and 0.65, but at a_w 1.0, they greatly increased elongation. The gain of moisture was less for the cross-linked fibers than for those treated with acetaldehyde.

As with acetaldehyde and acetic anhydride, the effect of the cross-linking agents increased with the amounts used, and

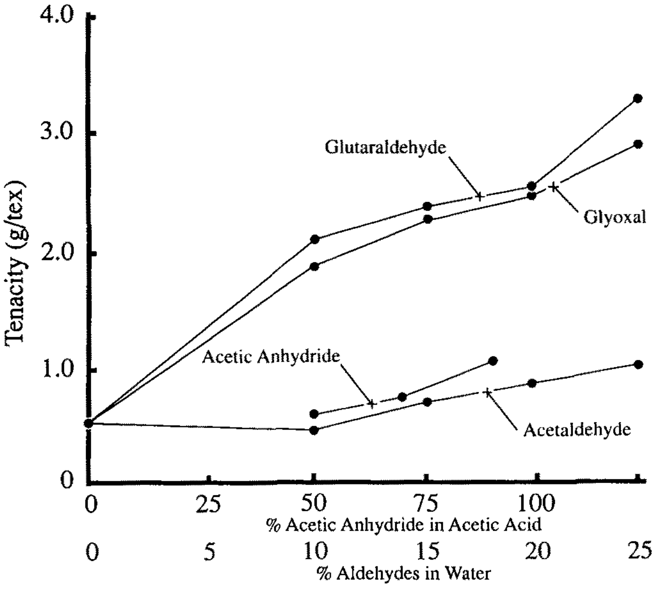

FIG. 2. Change in tenacity of extruded soy fibers at water activity 0.65 with the concentration (% by wt) of various chemical modification agents.

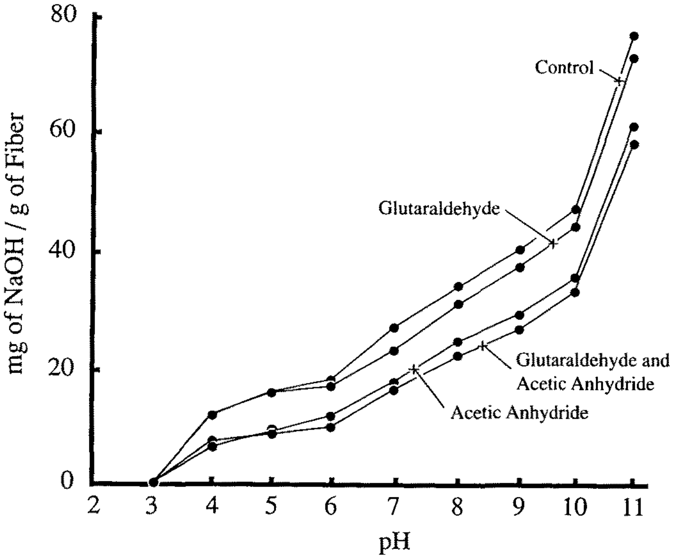

FIG. 3. Titration curves for soy protein fibers before and after treatment with agents capable of derivatizing various protein functional groups.

TABLE 7
Properties of Fibers Treated Post-Spinning with the Cross-Linking Agents Glyoxal and Glutaraldehyde

Treatment	Fiber process	Tenacity (g/tex)	Elongation at break %	Flexibility (mm)	wt% Moisture uptake[a]
a_w 0.11					
Control	Extruded	$1.57^{c,d}$	1.6^{b}	21.0	1.61^{b}
Glyoxal (25%)	Extruded	$1.71^{c,d}$	$0.5^{c,d}$	16.0	0.90^{d}
Glutaraldehyde (25%)	Extruded	2.10^{c}	0.8^{c}	11.0	1.53^{b}
Glutaraldehyde (25%)	Wet-spun[e]	2.53^{b}	$0.7^{c,d}$	25.0	1.13^{c}
a_w 0.65					
Control	Extruded	0.56^{e}	73.4^{b}	2.0	14.32^{b}
Glyoxal (25%)	Extruded	2.85^{c}	3.8^{c}	2.0	6.72^{d}
Glutaraldehyde (25%)	Extruded	3.28^{b}	2.4^{c}	2.5	7.86^{c}
Glutaraldehyde (25%)	Wet-spun[f]	1.34^{d}	4.7^{c}	1.5	$7.43^{c,d}$
a_w 1.00					
Control	Extruded	0.08^{a}	3.9^{c}	1.5	88.82^{b}
Glyoxal (25%)	Extruded	$0.31^{b,c}$	82.1^{b}	1.5	25.12^{e}
Glutaraldehyde (25%)	Extruded	0.70^{b}	77.4^{b}	1.5	37.30^{c}
Glutaraldehyde (25%)	Wet-spun[f]	$0.38^{c,d}$	83.1^{b}	1.5	33.25^{d}

[a] By oven-dried fibers.

[b–e] Values within each column and water activity (a_w) with the same letter are not significantly different ($P > 0.05$). Data for each a_w were analyzed independently.

[f] Wet-spun into 3% $ZnCl_2$–3% $CaCl_2$–3% NaCl.

the molar amounts required were much greater than the moles of reactive groups on the protein (see Fig. 2). Much of the excess cross-linking agent could be washed out by soaking the fibers in water, but this decreased tenacity (16). Possibly the excess reagent drives the reaction with amine groups to completion, but the nonvolatile cross-linking agents remain in the unwashed fibers and may have a solvent-like effect on the ionization and hydrogen bonding of the protein molecules.

Titration curves (see Fig. 3) showed that reaction with cross-linking agents derivatized less of the titratable protein groups than did acetic anhydride or acetaldehyde. Possibly the cross-linking agents could not penetrate to some of the sites at which the acetaldehyde and acetic anhydride could react. The titrations suggested that fibers treated with glyoxal or glutaraldehyde had about 7 and 12%, respectively, of their titratable groups reacted.

Experiments to cross-link fibers with other reagents in post-spinning treatments were unsuccessful (16), probably because of solvent incompatibility, which might have prevented swelling and penetration of the reagent. Attempts to use cross-linking agents before spinning resulted in great increases of viscosity or gelation of the spinning solutions, which made their use impractical.

A combination of treatments with the cross-linking agent, glutaraldehyde, and the acetylating agent (acetic anhydride) had better results than either treatment alone (Tables 6 and 8). Experience showed that, to finish fibers with this combination of treatments, the fibers first should be reacted with glutaraldehyde and then with acetic anhydride. The combined treatments increased tenacity at every a_w and increased elongation at a_w 0.11 and 0.65, especially at the latter. Moisture absorption was reduced, and the titration curve (see Fig. 3) shows that the combined treatment resulted in the reaction of more titratable groups than did either treatment alone (12% with glutaraldehyde, 47% with acetic anhydride, and 53% with the combination). The order of reaction with the two reagents is necessary because, if the amine groups of the fibers were reacted first with acetic anhydride, they were not available for cross-linking with glutaraldehyde.

Stretching. Stretching significantly increased the tenacity of both extruded and wet-spun fibers (see Table 8). Stretching fibers to about 150% their original lengths gave the best results. Strain hardening of materials that are plastic under tensile stress is well known. During stretching, the protein molecules flow past each other, allowing attractive groups on adjoining molecules to interact. Also, protein molecules may become more linear as they flow so that they can interact with adjoining molecules at more points. When fibers were treated with glutaraldehyde and acetic anhydride and subsequently stretched, the fibers with the greatest tenacity in our study were produced (see Table 8).

The best extruded fibers were produced with a mixture of 45% soy protein, 15% glycerol, and 40% water; finished with a combination of glutaraldehyde and acetic anhydride; and then stretched to 150% their original lengths. The best wet-spun fibers were produced with a 19.61% soy protein suspension at pH 12.1; coagulated in a 4% HCl solution containing 3.3% sodium chloride, 3.3% zinc chloride, and 3.3% calcium chloride; followed by treatment with 25% glutaraldehyde; and then stretched to 170% their original lengths. The tenacities of our strongest extruded and wet-spun fibers are lower than wool (14 g/tex at a_w 0.65 and 9 g/tex at a_w 1.0) and acetate (10.8–12.6 g/tex at a_w 0.65 and 9–11.7 g/tex at a_w 1.0), which are the weakest fibers used in commercial textiles (20).

TABLE 8
Effect of Stretching on the Properties of Fibers Treated with 25% Glutaraldehyde or Glutaraldehyde and Acetic Anhydride (9:1)

Treatment	Production method	Tenacity (g/tex)	Elongation at break %	Flexibility (mm)	wt% Moisture uptake^{a}
a_w 0.11					
Control	Extruded	2.10^{f}	0.8^{e}	11.0	1.53^{b}
Stretched (150%)	Extruded	5.74^{d}	2.1^{d}	3.0	1.40^{b}
Control	Wet-spun^{h}	2.53^{f}	0.7^{e}	25.0	1.13^{c}
Stretched (170%)	Wet-spun^{h}	6.43^{c}	2.1^{d}	16.0	1.15^{c}
Ac$_2$O-treated^{i}	Extruded	3.50^{e}	8.8^{b}	2.0	1.42^{b}
Ac$_2$O-stretched^{i} (150%)	Extruded	9.11^{b}	5.7^{c}	2.0	1.50^{b}
a_w 0.65					
Control	Extruded	3.28^{e}	2.4^{d}	2.5	7.86^{b}
Stretched (150%)	Extruded	4.73^{d}	4.1^{d}	1.5	6.87^{c}
Control	Wet-spun^{h}	1.34^{g}	4.7^{c,d}	1.5	7.43^{b,c}
Stretched (170%)	Wet-spun^{h}	6.26^{b}	3.1^{d}	1.5	7.53^{b,c}
Ac$_2$O-treated^{i}	Extruded	2.79^{f}	31.0^{b}	1.5	7.99^{b}
Ac$_2$O-stretched^{i} (150%)	Extruded	5.23^{c}	9.2^{c}	1.5	8.22^{b}
a_w 1.00					
Control	Extruded	0.70^{d}	77.4^{b}	1.5	37.30^{b}
Stretched (150%)	Extruded	0.75^{d}	62.2^{c}	1.5	36.13^{b}
Control	Wet-spun^{h}	0.38^{e}	83.1^{b}	1.5	33.25^{c}
Stretched (170%)	Wet-spun^{h}	0.72^{d}	59.7^{c}	1.5	29.17^{d}
Ac$_2$O-treated^{i}	Extruded	1.16^{c}	58.5^{c}	1.5	16.55^{e}
Ac$_2$O-stretched^{i} (150%)	Extruded	2.36^{d}	39.3^{d}	1.5	17.00^{e}

[a] Uptake by over-dried fibers.

[b–g] Values within each column and water activity (a_w) with the same letter are not significantly different ($P > 0.05$). Data for each a_w were analyzed independently.

[h] Wet-spun into 3% $ZnCl_2$/3% $CaCl_2$/3% NaCl.

[i] Acetic anhydride/acetic acid (9:1).

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REFERENCES

1. Kajita, T., and R. Inoue, U.S. Patent 2,192,194 (1940).
2. Kajita, T., and R. Inoue, U.S. Patent 2,198,538 (1940).
3. Kajita, T., and R. Inoue, U.S. Patent 2,237,832 (1941).
4. Boyer, R.A., *Ind. Eng. Chem. 32*:1549 (1940).
5. Bergen, W., *Rayon Textile Monthly* 25:57 (1944).
6. Huppert, O., U.S. Patent 2,298,127 (1942).
7. Huppert, O., U.S. Patent 2,309,113 (1943).
8. Huppert, O., U.S. Patent 2,364,035 (1944).
9. Huppert, O., U.S. Patent 2,377,885 (1945).
10. Boyer, R.A., W.T. Atkinson, and C.F. Robinette, U.S. Patent 2,377,854 (1945).
11. Boyer, R.A., J. Crupi, and W.T. Atkinson, U.S. Patent 2,377,853 (1945).
12. Boyer, R.A., *Soybean Dig.*, June *12* (1947).
13. Lubuza, T.P., K. Acott, S.R. Tatini, R.Y. Lee, J. Fink, and W. McCall, *J. Food Sci. 41*:910 (1976).
14. *Annual Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia, 1991, Method D2101-91.
15. *SAS User's Guide, Basic*, SAS Institute, Inc., Cary, 1992.
16. Huang, H.C., The Production of Textile Fibers from Soy Proteins, Ph.D. Thesis, Iowa State University, Ames, 1994.
17. Dean, J.A., *Lange's Handbook of Chemistry*, 12th edn., McGraw-Hill Book Co., New York,1979.
18. Hartsuch, B.E. *Introduction to Textile Chemistry*, John Wiley & Sons, New York, 1950, pp. 360–373.
19. Ziegler, K., West German Patent 165-177 (1975).
20. Joseph, M.L., *Essentials of Textiles*, Holt, Reinhart and Winston, Inc., New York, 1988, p. 17.

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