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The production of textile fibers from soy proteins

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The production of textile fibers from soy proteins

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INTRODUCTION

The soybean, *Glycine max*, an annual legume originally from Asia, is one of the most important crops grown in the United States today (Ensminger et al., 1983). Approximately 55 million tons of soybeans were grown in the United States in 1990, and of these soybeans, 60% were crushed to produce oil and meal (Myers, 1993). The protein of soybean meal has an excellent amino acid composition, and it is estimated that 98% of it is used in animal feeds (Waldroup and Smith, 1989). The remaining 2% are used in foods and industrial products such as paper coating, wood-working glues and plastics (Myers, 1992). Industrial uses for soy proteins are being advocated to increase the value of soy protein and to decrease the dependence of soybean producers on animal feed markets. The production of textile fibers is an example of an industrial use.

Textile fibers from soy proteins were first investigated by Japanese scientists in 1940. In the United States, soy protein fibers were first introduced and patented by Boyer (1940 and 1947). During the 1940's, several patents were issued to cover wet spinning of soy fibers. The process included the extraction of oil to obtain an oil-free meal, extraction of proteins from the meal with alkali, dispersion of the alkaline proteins, fiber formation by passage through a spinnerette into an acid coagulating bath and post-spinning treatments. However, these soy textile fibers lacked good functional characteristics and were never produced commercially in the United States. The Japanese reportedly produced about 450 thousand kg of soy protein fibers (Johnson et al., 1992). After World War II, petroleum became the major source of synthetic textile fibers, because of its low cost and unique functional properties, and research on agriculturally-based fibers was discontinued. Recent concerns about pollution and the availability of petroleum have rekindled an interest in agricultural raw materials.

The objectives of this study were 1) to reexamine the wet-spinning process and attempt to apply extrusion technology to the production of textile fibers from soy protein, 2) to

understand the factors limiting the functional properties of soy protein fibers and 3) to attempt to improve the properties of these fibers by chemical modification.

LITERATURE REVIEW

I. Textile Fibers

The term "textile" was originally used to define a woven fabric and the processes involved in weaving (Needles, 1986). A fiber is defined as a flexible, macroscopically homogeneous body having a high ratio of length to width and a small cross section (Gioello, 1982).

Textile fibers normally are divided into two main classes: natural fibers and manufactured fibers (Figure 1). Natural fibers are materials that can be harvested from nature, such as cotton, flax, silk and wool; manufactured fibers are created by technology.

The ingredients of manufactured fibers are formed into long chain polymers, extruded, twisted or spun as fibers, and processed into yarns. The manufactured fibers are divided into two groups: regenerated and synthetic fibers. Regenerated fibers refer to those made from cellulosic materials such as wood and cotton linters. Textile scientists also refer to the fibers made from proteins such as those from corn or milk as "regenerated", although these are not really regenerated. Synthetic fibers are manufactured completely from synthetic chemicals produced from substances such as petroleum, coal, nitrogen, hydrogen and carbon (Gioello, 1982).

II. Polymers

A polymer is a large molecule consisting of repeating small and simple chemical units. The repetition can be linear, branched or interconnected to form three-dimensional networks. The repeat unit of the polymer is usually equivalent, or nearly equivalent, to the monomer or starting material (Billmeyer, 1984).

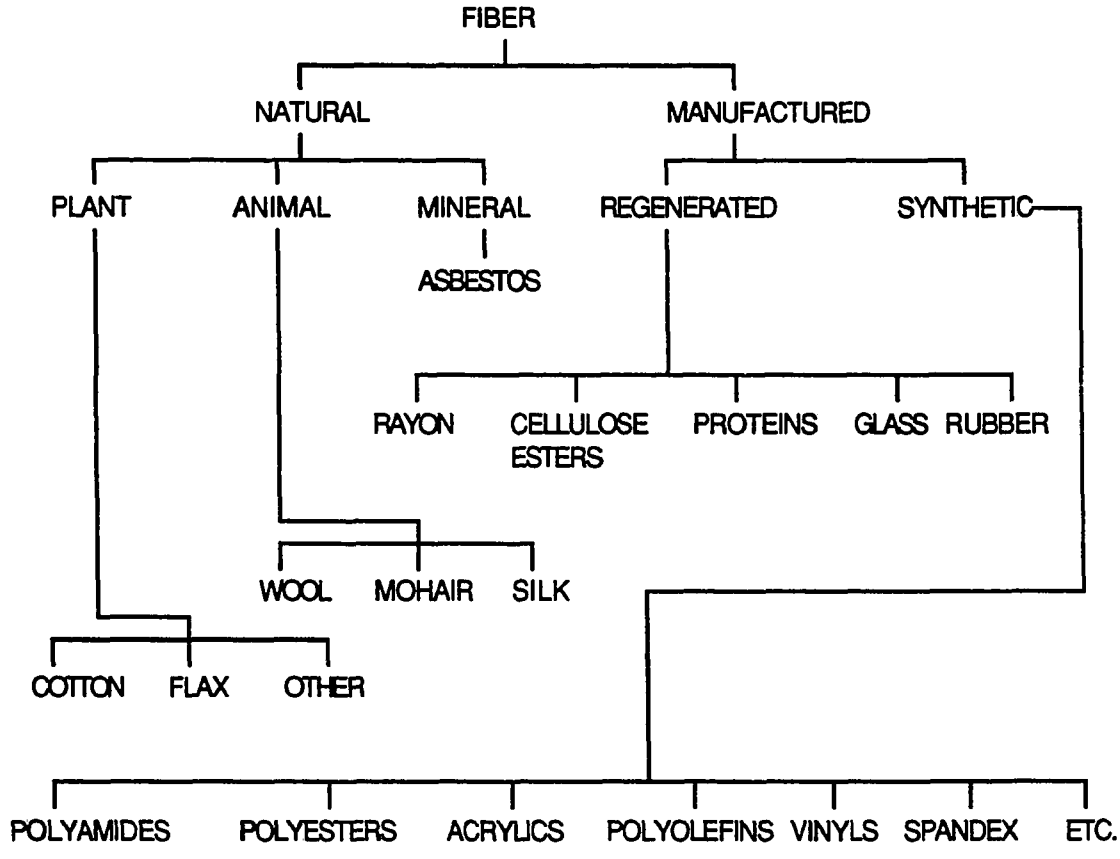


Figure 1. Classification of natural and manufactured fibers (Needles, 1986).

Various types of bonding are important in polymeric materials. Bonds can be divided into primary or covalent and secondary types. Hydrogen bonding, dipole interaction, van der Waals forces and ionic bonding are collectively defined as secondary forces (Rosen, 1982). Polymer molecules generally are tied together by covalent bonds, while the separate molecules, or segments of the same molecule, are attracted to each other by secondary forces (Rodriguez, 1989; Pauling, 1960).

III. Manufacture of Fibers

The basic structural requirements for a biopolymer such as a protein, to be fiber-forming, are a high molecular weight (greater than 10,000), a long linear chain length, a high degree of linear symmetry, the presence of few bulky side chains and a high degree of polarity (Hartman, 1978).

The fiber-forming ingredients of manufactured fibers are extruded, twisted or spun to form yarns. The three most common processes for producing manufactured fibers are dry spinning, wet spinning and melt spinning.

Dry-spinning processes have been used for producing acetate, acrylic, modacrylic, triacetate and vinyon fibers (Gioello, 1982). Figure 2 illustrates a dry-spinning process.

Wet-spinning processes have been used to spin soy protein fibers. Wet-spinning apparatus includes a compressor, a pressure vessel, a metering pump, a candle filter, a coagulating bath, a flat-surfaced reel, a precuring bath, stretching reels, a stretching bath and a dryer (Croston et al., 1945). The protein for wet-spinning was extracted from soy meal with dilute alkaline solutions, precipitated from solution with acid and salts, washed, redissolved in an alkaline solution, aged and spun into an acid bath (Hartman, 1978).

The melt-spinning processes have been used for producing nylon, polyester, olefin, aramid and glass fibers (Gioello, 1982). The fiber-forming substance is melted for extrusion and hardened by cooling in cool air or by quenching with cool water. Modern extrusion combines the technologies of dry- and melt-spinning processes. Extruders are designed to operate at high temperatures and pressures. In order to obtain products within defined specifications, process conditions must be controlled within acceptable and achievable limits (Yacu, 1990; Linko et al., 1983). Variables in an extrusion process can be classified as independent or dependent. The independent variables are 1) feed ingredient composition,

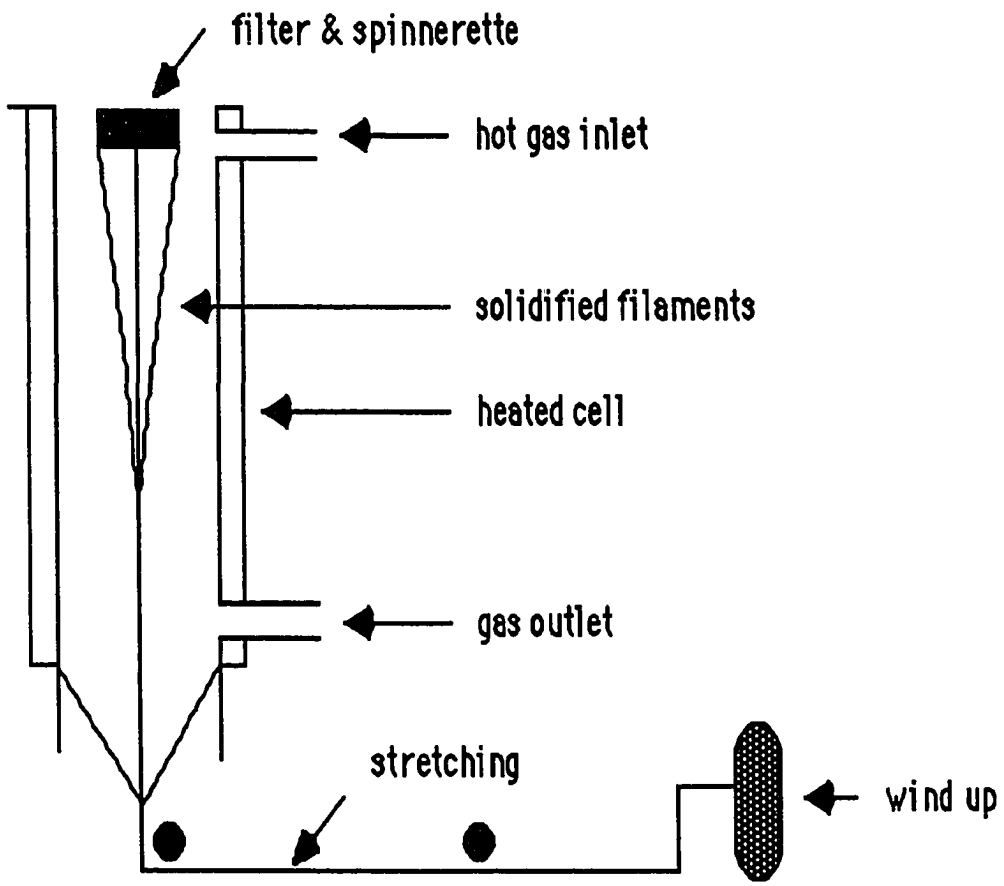


Figure 2. The design of dry spinning (Gioello, 1982).

including particle size, temperature, mixing conditions and feed rate; 2) extruder design, including barrel and screw configuration and die design; and 3) extruder operating conditions, including screw speed, barrel temperature profile and cutter speed. The dependent variables include 1) material viscosity, temperature and pressure; 2) residence time and mixing profiles; 3) power consumption; and 4) extruded product properties. The last factor is the most important (Yacu, 1984).

IV. Fiber Properties

Primary properties

The criteria that are essential for formation, fabrication and assembly of fibers into textile substrates have been considered by the textile and polymer industry. The primary properties necessary for a polymeric material to yield an adequate fiber are: fiber length to width ratio, fiber uniformity, fiber strength and flexibility, fiber extensibility and elasticity and fiber cohesiveness (Needles, 1986).

Fiber length to width ratio

Fibers generally are separated into filament and staple fibers according to their lengths. Filament fibers such as polyester are long continuous fiber strands of indefinite length, usually measured in yards or meters. Staple fibers such as cotton and wool range in length from 1.9 cm to 45.7 cm. All natural fibers except silk are staple. The manufactured fibers and silk can be made into staple form by cutting or breaking the filament or filament tow into short lengths (Hollen et al., 1979). The width of the fiber (the diameter of the cross section) must be much less than the overall length of the fiber. Usually the fiber diameter should be no more than 1/100 of the length of the fiber, referred to as a high length-to-width ratio in staple fibers (Joseph, 1988; Needles, 1986).

Fiber uniformity

Only fibers uniform in shape and size are processed into yarns and fabrics. Without sufficient uniformity of dimensions, formation of the yarn might be impossible or may result in a yarn that is weak, rough and irregular in size and shape and unsuitable for textile usage (Needles, 1986).

Fiber strength and flexibility

The strength of a single fiber is called fiber tenacity, which is defined as the force per unit linear density necessary to break a sample of that fiber. The breaking tenacity of a fiber may be expressed in grams per denier (g/d) or grams per tex (g/tex). Both denier and tex are units of linear density (mass per unit of fiber length) and are defined as the number of grams of fibers measuring 9000 meters and 1000 meters, respectively. In the International System of Measurement Units, referred to as SI, the appropriate length unit for tenacity is kilometer (km) of breaking length or Newton per tex (N/tex), and is equivalent to g/tex (Needles, 1986).

Strength, or tenacity, of fibers varies among the different generic classes and within specific fiber types. A single fiber strength of 5 g/d is necessary for most textile applications. However, some common fibers with lower strengths than 5 g/d are acceptable and used in the textile industry (Joseph, 1988).

To make fibers into yarns and fabrics, the fibers must be pliable or flexible. Flexibility permits freedom of movement and the ability to shape fabrics. Fibers of different types vary in their degree of flexibility. The flexibility of fibers is directly related to the flexibility of the textile product; therefore, fabric adaptation to the end use and fabric durability are important and closely related to evaluating fibers for specific uses (Joseph, 1988).

Fiber extensibility and elasticity

An individual fiber must be able to undergo slight extensions in length (less than 5%) without fiber breakage and be able to recover almost completely following slight fiber deformation. In other words, the extension deformation of the fiber must be nearly elastic. These properties are important because the individual fibers in textiles are often subjected to sudden stresses and the textile must be able to give and recover without significant overall deformation of the textile (Needles, 1986).

Fiber cohesiveness

Cohesiveness can best be described as the ability of fibers to stick together during fiber-arranging or yarn-manufacturing, a process especially important for staple fibers. The cohesiveness of fibers may be due to the contour of the cross-sectional shape, or may result from the surface, or skin, structure of the fibers. The spinning quality of a fiber influences characteristics such as yarn fineness, fabric thickness, snagging, pilling, texture, appearance and fabric or textile product durability. Without adequate cohesiveness, fibers would not hold together properly in yarns and/or fabrics (Joseph, 1988).

Secondary properties

The secondary fiber properties that increase fiber value and desirability, but are not necessary to make a fiber, include moisture absorbency, fiber resiliency, abrasion resistance, density, luster, chemical resistance and thermal characteristics (Needles, 1986).

Moisture regain

The moisture absorbency of fibers usually is expressed as moisture regain and has a great effect on fiber properties. Most fibers tend to absorb moisture when in contact with a humid atmosphere. The amount of water absorbed by the textile fiber will depend on the chemical and physical structures and properties of the fiber, as well as the temperature and humidity of the surroundings. The percentage absorption of water vapor by a dry fiber is often expressed as its moisture regain. The regain is determined by weighing a dry fiber, then placing it in a room set to standard temperature and humidity (21° ± 1° C and 65% ± 2% relative humidity), allowing the fiber to come to equilibrium, and calculating the percentage of regain of the fiber by the equation listed as follow (Needles, 1986). Percentage regain = (Conditioned weight - Dry weight) x 100% / Dry weight.

Fibers vary greatly in their moisture regain. Hydrophobic fibers have moisture regains near zero and hydrophilic fibers like cotton, rayon and wool have regains as high as 15% at 21°C and 65% relative humidity. Fibers with high regains are easier to process, finish and dye in aqueous solutions, but they dry more slowly. The low regain found for many manufactured fibers makes them quick drying, a distinct advantage in certain applications (Needles, 1986).

V. Protein Regenerated Fibers

Regenerated protein fibers are characterized by the presence of free amino acids and carboxylic acid groups, which can bind internally to form salt linkages. Such linkages are electrovalent, not covalent, and are easily broken. Regenerated protein fibers lack cross-linkages, and are sensitive to dilute alkali (Moncrieff, 1975).

Azlon fibers, such as Vicara and Aralac, were manufactured from regenerated naturally-occurring proteins. Theoretically, any protein-containing substance might serve as a starting material. The protein might be extracted, dissolved in a suitable solvent, and extruded into a coagulating bath by techniques similar those used in the production of rayon.

Protein as a raw material for making textile fibers should be available in adequate quantity and inexpensive. Four proteins that might meet these criteria are milk casein, zein from corn and the proteins of soybeans and peanuts. However, only casein fiber has become a commercially important product (Cook, 1964; Hartsuch, 1950; Anonymous, 1989).

The first "regenerated" protein fiber was patented and developed in Italy in 1935 by Faretti, who used cow's milk casein as the raw material. This fiber was called "Lanital" (Hartsuch, 1950). Casein fiber was made by extracting the casein from skim milk, dissolving it in dilute alkali and extruding it into an acid bath, where it coagulated and was hardened and treated with formaldehyde. This fiber was manufactured in the United States under the name Aralac in the 1940's. Another casein fiber called Chinon was made by the Japanese in 1970.

Chinon was a copolymer of 30% casein and 70% acrylic and was described as a fiber that was "silkier" than silk (Anonymous, 1989).

Ardil fibers were made from peanut protein. There is about 25% protein content in peanuts. The peanut fibers were first spun at Ardeer, Scotland in 1938 and, after World War II were manufactured at Dumfries until 1957 when production was suspended. The manufacture included grinding blanched peanuts and extracting the oils. The oil-free meal was extracted with dilute alkali and precipitated with acid to give a protein called Ardein. The Ardein was redissolved in dilute caustic soda, and spun into a bath containing 2% sulfuric acid and 15% sodium sulfate (Moncrieff, 1975; Cook, 1964).

A commercially "regenerated" protein fiber from zein was sold under the name Vicara. Zein was extracted from corn gluten meal with 70% isopropyl alcohol, and the alcohol was evaporated to leave a yellow powder. The procedure for the manufacture of Vicara was generally similar to that for producing rayon. This included extruding a solution through a spinnerette into a coagulating bath followed by suitable treatments with acetic anhydride or other agents (Croston et al., 1945). This fiber reportedly had weak wet strength, good elongation, excellent elastic recovery, a texture unlike wool and excellent resistance to heat (Hartsuch, 1950).

Because of their increasing production in the 1930's, soybeans offered the cheapest and most abundant source of vegetable protein in the world. Soybeans were attractive as a raw material for producing fibers because of their high protein content (40%) compared with peanuts (25%) and corn (10%). In 1937, the Ford Motor Company became interested in commercial uses for soybean. Boyer obtained two basic patents for the manufacture of soybean fiber in 1945 and assigned them to Ford. It was reported that the softness of this fiber was similar to that of sheep's wool (Bergen, 1939).

The properties of various protein fibers were summarized by Moncrieff (1975). The tenacity of casein fibers was 1.1 g/d dry and 0.6 g/d wet. Elongation of casein fibers were

50% dry and 65% wet. The dry tenacity and dry elongation at break of peanut fibers were 0.8 g/d and 50% respectively. Zein fibers had a tenacity of about 1.2 g/d dry and 0.75 g/d wet; elongation at break was 32% dry and 35% wet. Moisture regain of zein fibers was about 10%. Soy protein fibers had a tenacity of 0.8 g/d dry but only 0.25 g/d wet. Lack of wet strength was considered as a serious defect of soy fibers. Elongation at break of soy protein fibers was about 50%; moisture regain was 11%.

In general, regenerated protein fibers tend to be weak. The molecules are not aligned with precision and regularity to form crystalline regions in the fiber, and do not hold tightly together to provide the tensile strength characteristic of fibers with crystalline structures (Cook, 1964). The most attractive feature of protein fibers was the abundance and low cost of the raw material.

The production of protein regenerated fibers ceased when less expensive petroleum-based fibers such as polyester and nylon became available. In 1990, petroleum prices had increased to almost 21 times over the 1940 price. Conversely, the price of soybean protein had increased only 6.5-fold from 1940 to 1990. Thus, soybeans could be a very competitive raw material for fibers in the textile industry (Agricultural Statistics Board, 1990; Monthly Energy Review, 1991).

VI. Molecular Structures of Proteins

Proteins are made up of 20 or so amino acids. Amino acids consist of at least one primary amino group ($-NH_2$) and one carboxyl group (-COOH). Protein structure has generally been described in terms of primary, secondary, tertiary and quaternary structures. The primary structure is simply the sequence of amino acids and the locations of disulfide bridges. Secondary structure refers to the steric relationship of amino acid residues in the linear sequence. In other words, secondary structure is the conformation of successive

adjacent amino acids residues in a polypeptide chain to form an α-helix, a ß-pleated sheet or a collagen helix. Tertiary structure refers to long-range steric relationships of the amino acid residues that are farther apart in the linear sequence. Proteins that contain more than one polypeptide chain can display an additional level of structural organization, quaternary structure, which refers to the way polypeptide chains are packed together (Stryer, 1981; Lehninger, 1982).

The major types of chemical bonding affecting various protein structures are listed in Table 1. The properties of each type are summarized in Table 2.

There are two types covalent bonds linking the amino acids in proteins: peptide bonds and disulfide bonds. The main covalent bonds are the peptide bonds between the amino acid residues and the disulfide bonds which are cross-linked intermolecular or intramolecular structures of proteins.

Intramolecular disulfide bonds are important in stabilizing the tertiary structure of proteins and imparting molecular rigidity. In general, proteins containing disulfide bonds tend

Table 1. Major chemical bonding and interactions in proteins

Structure	Chemical bonding and interaction
Primary structure	Covalent bond (peptide bond)
Secondary structure	Hydrogen bond, electrostatic and dipole interactions
Tertiary structure	Hydrogen bond, electrostatic and dipole interactions, hydrophobic association, van der Waals and disulfide bonds
Quaternary structure	Hydrogen bond, hydrophobic interactions, ionic interaction, and disulfide cross-linking

Table 2. The protein-protein linkages and interactions[a]

Type	Energy (kJ/mol)	Interaction distance (Å)	Functional groups involved	Disrupting solvents
Covalent bonding	330-380	1-2	cystine S-S	reducing agents
Hydrogen bonding	8-40	2-3	amide, NH··OC; hydroxyl; phenol, OH··OC;	urea, guanidine hydrochloride, detergents or heat
Hydrophobic interactions	4-12	3-5	amino acid residues with aliphatic or aromatic side chains	detergents, organic solvents
Electrostatic interactions	42-84	2-3	carboxyl (COO^-), amino (NH_3^+), etc.	salt solutions, high or low pH
Van der Waals	1-9		permanent, induced and instantaneous dipoles	

[a] Adapted from Cheftel et al. (1985).

to be more heat stable and show higher enthalpies of denaturation than proteins without disulfide bonds (Kinsella et al., 1985).

Non-covalent forces include electrostatic interactions, hydrophobic interactions, van der Waals interactions and hydrogen bonding. These non-covalent forces also affect protein conformation. Van der Waals forces are short-range forces whose strength is inversely proportional to approximately the sixth power of the distance between the molecules. Van der Waals forces frequently are attributed to polar interactions between induced dipoles in adjacent atoms and, therefore, are related to the polarizabilities of the molecules or atoms involved. The contribution of van der Waals interactions to the stability of protein structure has been clearly illustrated by the packing density of amino acid residues in the interior of globular proteins

(Ryan, 1975). The van der Waals force interactions are individually extremely weak and the lifetime of a molecule held together solely by van der Waals forces is limited by the collision frequency of the dimer. Therefore, the association energy is so small that on the average, every collision with any molecule will result in dissociation of the van der Waals interaction complex. Moreover, atoms involved in van der Waals interactions inside a folded protein would also interact with water molecules through van der Waals forces in the denatured and unfolded protein. The contribution of stability of the folded structure of protein is the difference between the energy of such interactions (Ryan, 1975).

Hydrogen bonds are stronger and more specific than van der Waals interactions. They can be considered an electrostatic (polar) interaction between a partial positive charge on a hydrogen atom and a partial negative charge on an electronegative acceptor atom. The stability of hydrogen bonds depends on the difference in free energy between protein-protein and protein-solvent hydrogen bonds. Since the donor and acceptor atoms found in proteins (e.g. N-H and O=C) are capable of hydrogen bonding with water, the net free energy of a hydrogen bond needs to be considered.

Electrostatic interactions between molecules containing opposite charges also affect functional properties. Amino acid residues in proteins such as aspartic and glutamic acids are negatively charged at neutral pH. At basic pH values, cysteine and tyrosine become negatively charged. Arginine, lysine and histidine usually are positively charged. The pK's of these groups vary considerably depending upon the local environment (Ryan, 1975).

Hydrophobic bonding is defined as "an interaction of molecules with each other which is stronger than the interaction of the separate molecules with water and which cannot be accounted for by covalent, electrostatic, hydrogen bond or charge transfer forces" (Jencks, 1969). It had been suggested by Ryan (1975) that hydrophobic interactions are the predominant forces stabilizing protein structure.

VII. Protein Fibers of Soybean, Silk and Wool

Soy proteins

Soybean (*Glycine max (L.) Merrill*) is a legume that originated in eastern Asia and is thought to have been derived from *Glycine ussuriensis* which grows wild throughout many parts of eastern Asia (Morse, 1950; Burnett, 1951; Pearson, 1984). Soybeans were introduced as an oilseed to Europe during the early 1900's, and the soybean processing industry became prominent in the United States in the mid-1920's. Since then, soybeans have become a major world source of edible oil and protein for animal feeds and food (Nielsen, 1985).

The amino acid composition of soybean meal is listed in Table 3. Soy protein consists of more than 20 amino acids which are distributed heterogeneously and unevenly. The essential amino acids in acid-precipitated soy protein are lower than those in the soybean meal (Smith and Circle, 1972).

Soy proteins consist of several individual proteins and protein aggregates with a broad range of molecular sizes. A typical ultracentrifuge pattern for water-extractable soy proteins includes four major fractions designated as 2S, 7S, 11S and 15S on the basis of their sedimentation rates (Nielsen, 1985). Wolf and Cowan (1975) reported the approximate amounts of each ultracentrifuge fraction in water-extractable soy proteins (Table 4).

The most important proteins in soybean are globulins. Globulins are insoluble near their isoelectric points (pI) but dissolve readily on addition of salts such as sodium or calcium chlorides. However, globulins dissolve in aqueous solutions in the absence of salt if the pH is above or below their pIs. Soy proteins have minimum solubility between pH 3.75 and 5.25, whereas their maximum solubility was at pH 1.5-2.5 and above pH 6.3 (Pearson, 1984). The insolubility of soybean proteins between pH 4 and 5 results from the pI of two major soybean storage proteins, glycinin and β-conglycinin, being in this pH range (Nielsen, 1985).

Table 3. Amino acid compositions of soybean meal fractions[a]

Amino acid	Whole meal	Acid-precipitated protein (g of amino acid/16g N)[b]	Whey protein
Arginine	8.42	9.00	6.64
Histidine	2.55	2.83	3.25
Lysine	6.86	5.72	8.66
Tyrosine	3.90	4.64	4.67
Tryptophan	1.28	1.01	1.28
Phenylalanine	5.01	5.94	4.46
Cysteine	1.58	1.00	1.82
Methionine	1.56	1.33	1.92
Serine	5.57	5.77	7.62
Threonine	4.31	3.76	6.18
Leucine	7.72	7.91	7.74
Isoleucine	5.10	5.03	5.06
Valine	5.38	5.18	6.19
Glutamic acid	21.00	23.40	15.64
Aspartic acid	12.01	12.87	14.08
Glycine	4.52	4.56	5.74
Alanine	4.51	4.48	6.16
Proline	6.28	6.55	6.66
Ammonia	2.05	2.20	1.53

[a] Adapted from Smith and Circle (1972).
[b] Data are based on weight percentage (g of amino acid/ 100 g of protein).

Table 4. Compositions in the ultracentrifuge fractions in water-extractable soybean proteins[a]

Sedimentation value (S_{w20})	Percentage (%)	Components	Molecular weights (daltons)
2S	22	Trypsin inhibitors	8,000- 21,500
		Cytochrome c	12,000
7S	37	Hemagglutinins	110,000
		Lipoxygenases	102,000
		ß-amylases	61,700
		7S globulin	180,000- 210,000
11S	31	11S globulin	350,000
15S	11	—	600,000

[a] Adapted from Wolf and Cowan (1975).

The predominant structural proteins are ß-conglycinin (7S) and glycinin (11S) in soybeans. ß-Conglycinin is a heterogeneous group of glycoproteins composed of varying combinations of three subunits [α' (MW = 58,000), α (MW = 57,000) and ß (MW = 42,000)]. These subunits have significant hydrophobic regions and a large negative charge and associate to form compactly folded trimers (Kinsella et al., 1985).

β-Conglycinin accounts for the major portion of the 7S fraction. The association-dissociation equilibria of its subunits are complex and respond to changes in ionic strength and pH. At neutral pH, β-conglycinin occurs mostly as a 7S fraction when the ionic strength is greater than 0.5, but it occurs as a 9.8S dimer at ionic strength less than 0.2. Both forms exist at intermediate ionic strengths (Thanh and Shibasaki, 1976, 1978a and b). When the ionic strength is less than 0.2, the 9.8S dimer is stable between pH 4.8 and 11, although

precipitation begins to occur as the isoelectric point is approached. Increased ionic strength reduces the extent of this precipitation, and the 9.8S dimer remains both stable and soluble at pH 1.0. In contrast, as the ionic strength decreases, slow, reversible dissociation of the 9.8S dimer into individual polypeptides occurs at pH below 3.0 (Nielsen, 1985).

Glycinin has a sedimentation coefficient of approximately 12 and a MW of approximately 350,000. The existence of a subunit structure is demonstrated by sodium dodecyl sulfate (SDS) gel electrophoresis. When sulfhydryl reducing agents are omitted during denaturation, six subunits of approximately 60,000 daltons pre-glycinin are obtained (Staswick, 1982). In the presence of sulfhydryl reductants, SDS electrophoresis resolves the complex into two classes of smaller polypeptides (Nielsen, 1985).

Glycinin is a large oligomeric protein of approximately 350,000 daltons. By using electron microscopy and X-ray scattering techniques, the quaternary structure of glycinin is revealed to be a pair of identical face-to-face hexamers, like facing doughnuts (Kinsella et al., 1985). Pearson (1984) suggested that these hexamers were made up of two monomers. The two monomers were termed either acidic or basic subunits according to their pIs. Nielsen (1985) proposed that acidic subunits had pIs of 4.6-5.4 and had apparent molecular MWs of approximately 40,000, whereas basic subunits had pIs of 8.0-8.5 and apparent MWs of approximately 20,000.

Utsumi and Kinsella (1985) reported that the structures of 7S, 11S and soy isolate proteins that occur in aqueous solution are three-dimensional networks that might involve hydrogen bonding, hydrophobic associations, ionic interaction and disulfide linkage. The possible molecular forces involved in the formation and maintenance of 11S, 7S globulin and soy isolate gels are summarized in Table 5.

Table 5. Possible molecular forces involved in formation and maintenance of the structural matrix of 7S, 11S and soy isolate gel[a]

Soy preparation	Possible molecular forces involved	
	Formation	Maintenance
7S	Hydrophobic interactions Hydrogen bonds	Hydrogen bonds
11S	Hydrophobic interactions Electrostatic interaction Disulfide bonds	Disulfide bonds Hydrogen bonds
Soy isolate	Hydrogen bonds Hydrophobic interactions	Disulfide bonds Hydrogen bonds

[a] Adapted from Utsumi and Kinsella (1985).

Changes of soy protein structures during fiber production

When the native globular soy proteins are dissolved in alkali, they unfold and dissociate into lower molecular weight units. The unfolding and dissociation were indicated by an increase in viscosity and a shift of the 2S, 7S, 11S and 15S proteins to 3S to 5S proteins (Kelley and Pressey, 1966). Kelley and Pressey (1966) also reported that alkali favored sulfhydryl-disulfide interactions. Therefore, when alkali soy protein dispersions were acidified, new disulfide bonds were formed which brought polypeptide chains closer together and favored hydrogen and ionic bonding. The wet spinning of soy protein dopes through a spinnerette also increased the alignment of fibers. Rosenfield and Hartman (1974) reported that fiber spinning was not a straightforward process; instead, other variations might be, for example, that the fibers be stretched to increase strength and elasticity and to decrease linear density.

The versatility of wet-spinning technology clearly indicated the possibility of producing engineered foods as well as textile fibers. Wet spinning technology has been applied in simulated and meat-like products, such as beef, ham, fish and chicken (Horan, 1974). A general review of wet spinning of soy protein in food applications was reported by Gutcho (1973).

Heating denatures moist soy proteins to produce gels (Wolf and Tamura, 1969). Protein gels are formed through intermolecular interactions that produce a continuous and rigid three-dimensional network (Nakamurs et al., 1984). The formation of protein gels is affected by pH, temperature, moisture and ionic strength (Circle et al., 1964; Catsimpoolas and Meyer, 1970). Specific studies on the thermal aggregation of soy proteins have shown that glycinin was dissociated into subunits at temperatures above 70°C (Catsimpoolas et al., 1970). The thermal aggregation of subunits was reduced at extreme pH values and at high ionic strengths. Maximum aggregation of glycinin occurred between pH 4 and 6, and involved ionic and hydrophobic bonds (Catsimpoolas et al., 1970). Damodaran and Kinsella (1982) reported that conglycinin prevented thermal aggregation of glycinin at temperatures below 80°C because of the formation of a soluble complex between subunits of conglycinin and the basic subunits of glycinin via electrostatic interactions.

Heat-induced interaction of soy proteins has been studied (Utsumi et al., 1984; German et al., 1982; Yamagishi et al., 1983). Heating caused dissociation of 7S and 11S globulins. The dissociated subunits of 7S and 11S globulins subsequently interacted with each other and formed soluble macro-complexes. However, heating 7S globulin alone did not cause precipitation (Yamagishi et al., 1983).

The pH and charge of soy proteins were highly correlated. Soy proteins exhibited minimal net charge at pI, and at the pI the attractive forces among protein molecules should be maximized (Ledward and Mitchell, 1988). A soy protein isolate prepared by isoelectric

precipitation yielded a tougher extrudate than did those prepared from isolates with pH values of 6.3-7.0 (Sheard et al., 1986).

Silk proteins

Raw silk consists of two proteins, fibroin and sericin. Fibroin contains 15 or 16 α-amino acids linked together to form a biopolymer. Sericin could be separated from fibroin by treating silk with various chemicals or by physical separation in heated aqueous soap solutions (Otterburn, 1977).

The most notable feature of the amino acid composition in fibroin is the presence of large quantities of chemically simple amino acids, such as glycine, alanine and serine. The amounts of cystine, methionine and acidic and basic charged amino acids are relatively small in silk fibroin, therefore, fibroin absorbs only a small amount of acid or alkali. The major polar groups in silk fiber come from the hydroxyl-containing amino acids -- serine, threonine and tyrosine (Otterburn, 1977).

The major amino acids in fibroin are glycine and aliphatic amino acids. Because of the presence of large quantities of glycine and amino acids with hydrocarbon side chains, rather than those with bulky aromatic or heterocyclic groups, close packing of polypeptide chains in the protein is possible. Consequently, hydrogen bonding plays an important role in the conformation and structure of the fibroin. They are few interchain polypeptide cross-links such as cystine (Otterburn, 1977).

Most raw silks possess ß-pleated sheet structures, although some α-helix, polyglycine II and collagen conformations also are present. The primary and secondary structures of fibroin have been resolved; however, the precise nature of the interactions between the polypeptide chains remains unclear. No evidence supports the existence of covalent bonding between polypeptide chains (Otterburn, 1977).

Wool proteins

Wool is mainly composed of proteins and is characterized by its high cystine content and birefringence. Wool gives an α-helical X-ray diffraction pattern that reverts to a ß type on stretching (Swift, 1977). X-ray diffraction suggests that wool microfibril might contain repeating units with a small fixed number of protein chains in a long helical structure (Speakman, 1983).

The hydrogen bonds in an α-helix are formed between carbonyl and secondary amino groups in adjacent turns of the coil. In the stretched ß form, the hydrogen bonds become intermolecular instead of intramolecular. Mechanical tension causes the rupture of the hydrogen bonds in the α-helix, a rupture shunt necessary to transform structure from the α to ß pleated form (Trotman, 1984).

In addition to hydrogen bonds, salt linkages between adjacent molecular chains are possible, where carboxyl and amino groups were situated opposite each other. Trotman (1984) indicated that salt linkages existed between pH 4 and 8, but would disappear in presence of excess hydrogen or hydroxyl ions. An unique feature of wool is the existence of disulfide linkages that have a profound effect on the mechanical properties of wool. These cross-linkages tended to strengthen the α helix and increased the amount of work needed to stretch the fibers into the ß configuration (Trotman, 1984). Little is known about the tertiary and quaternary structures of wool.

Comparison of soy, silk and wool proteins

The amino acid composition of soy protein is significantly different from those of wool and silk (Table 6). From the macroscopic view, the difference between wool or silk and soy proteins is that soy proteins are globular proteins and the others are fibrous proteins. On a molecular scale, major differences exist among their primary and secondary structures. There is considerable difference in amino acid composition between wool and silk. Silk consists

Table 6. Amino acid compositions of soy protein isolate, wool and silk[a]

Amino acid	Soy protein isolate[b]	Keratin (wool)[c]	Fibroin (silk)[d]
Arginine	9.0	9.9	1.0
Histidine	2.8	3.0	0.4
Lysine	5.7	0.9	0.6
Tyrosine	4.6	5.2	11.9
Tryptophan	1.0	1.9	0.9
Phenylalanine	5.9	3.7	1.3
Cysteine	1.0	12.8	0
Methionine	1.3	0.6	0
Serine	5.8	8.4	16.3
Threonine	3.8	6.6	1.4
Leucine	7.9	7.9	0.9
Isoleucine	5.0	3.8	1.1
Valine	5.2	5.5	3.3
Glutamic acid	23.4	14.5	1.9
Aspartic acid	12.9	6.9	2.2
Glycine	4.6	6.0	42.8
Alanine	4.5	3.9	33.5
Proline	6.6	6.7	0.5
Hydroxyproline	0	0	0
Hydroxylysine	0	0.2	0

[a] Data are based on weight percentage (g of amino acid/ 100g of protein).
[b] From Smith and Circle (1972).
[c] From Ward and Lundgren (1954).
[d] From Lucas et al. (1958).

mainly of four amino acids -- glycine, alanine, serine and tyrosine -- the first three of which have small R groups (-H, $-CH_3$ and $-CH_2OH$, respectively), whereas wool has a more heterogeneous mixture of amino acids. Wool contains a much higher proportion of cystine, indicating more possible cross-linkages through disulfide groups (Stevens, 1990). The predominant amino acid of soy protein isolate is glutamic acid. Acidic amino acids (glutamic acid and aspartic acid) of soy proteins are present in much higher amounts than in wool and silk. The sulfur-containing amino acids, cystine and methionine, are lower in soy protein isolate than in wool. Soy protein isolate has a higher average MW (300,000 daltons) compared with wool (40,000 - 80,000) and silk (33,000 - 84,000). The MW ranges of wool and silk are similar to each other. However, wool and silk molecules from individual animals can be quite different.

The relative absence of bulky side chain groups in silk possibly is responsible for its formation of the extended-chain β structure, whereas wool exhibits mostly an α-helical structure in its secondary structure. When stretched, wool forms an extended β-chain arrangement. In undenatured soy proteins, there is a combination of 5% α-helix, 35% β structure and 60% random coil (Kinsella et al., 1985). This might indicate that soy proteins have a more heterogeneous arrangement than wool and silk. The ß structure of silk makes its structure more linear and stronger than wool, but wool is more elastic than silk.

VIII. Chemical Modifications of Proteins

Although cereal and oilseed proteins may have various disadvantages in their functional properties when they are considered for non-food uses, a variety of reactions and treatments can be employed to modify proteins for specific end-uses. In general, chemical, physical or enzymatic treatments have been used. It might be expected that many treatments used to modify free amino acids side chains could result in the same modification when amino acids

were assembled in proteins; however, the reactivity of amino acids in proteins towards specific reagents often is significantly altered. This difference in reactivity is caused by steric effects and various bonding interactions (Simmonds and Orth, 1973).

The external environment also plays an important role in the structures of most proteins. Chemical modification changes the response of a protein to its environment, which might be the purpose of many modifications (Feeney, 1977). Chemical modifications used for altering the functional properties of soy proteins uses are listed in Table 7. Many of the side chain groups of amino acids in proteins are much more reactive than those in an isolated amino acid state.

Table 8 lists both the amino acid side chains that can be chemically modified by common reagents and the types of modifications that can be effected. The nucleophilicites of the amino and sulfhydryl groups make them particularly vulnerable to these reactions. Thus, the ε-amino group of lysine is a primary point to attack (Rhee and Kim, 1992).

The relative reactivity of a protein's side chains to a chemical reagent depends upon the properties of the side chain, the reagent and the environment. The ability of a reagent to physically approach a side chain depends upon the structure of the protein. In some cases, the chemical reagent is completely unable to approach a side chain that is tucked into a crevice or pocket or located in the interior of the protein. In other cases, the charges of other near amino acid residues have a profound effect on whether a particular chemical reagent approaches a particular group (Feeney, 1977).

Various chemical modifications to improve soy protein's properties for industrial applications have been reviewed (Meyer and Williams, 1977; Kinsella and Shetty, 1978). Chemical modification of proteins usually involves nucleophilic or reductive reactions of electron-rich amino groups. Reagents susceptible to nucleophilic attack might react with these groups, indicating a general lack of specificity. However, the groups' reactivity also

Table 7. Altered functional properties through chemical modification[a]

Reaction	Change in properties
Alkalis (pH > 10)	a. Increased dispersibility and solubility
sodium hydroxide, etc.	b. Increased resistance to aggregation (heat, etc.)
	c. Increased elasticity -- better fiber formation
Acetylation	a. Improved solubility in acidic foods
acetic anhydride	b. Increased solubility
succinic anhydride	c. Lower viscosity
	d. Increased tolerance to Ca^{++}
	e. More resistance to aggregation
Oxidation	
hydrogen peroxide (alkaline)	a. Reduced viscosity
choline	
peracid salts	
Reduction	
sulfite and related salts	a. Reduced viscosity in water dispersion
	b. Increased viscosity in salt solution
	c. Increased resistance to aggregation

[a] Adapted from Meyer and Williams (1977).

depended upon their accessibility, size of modifying agent and reaction conditions (Rhee and Kim, 1992).

Alkali

In alkaline solutions, proteins undergo denaturation, hydrolysis of peptide bonds, hydrolysis of amides (asparagine and glutamine), hydrolysis of arginine, destruction of amino acids, ß-elimination and racemization, formation of double bonds, formation of new amino

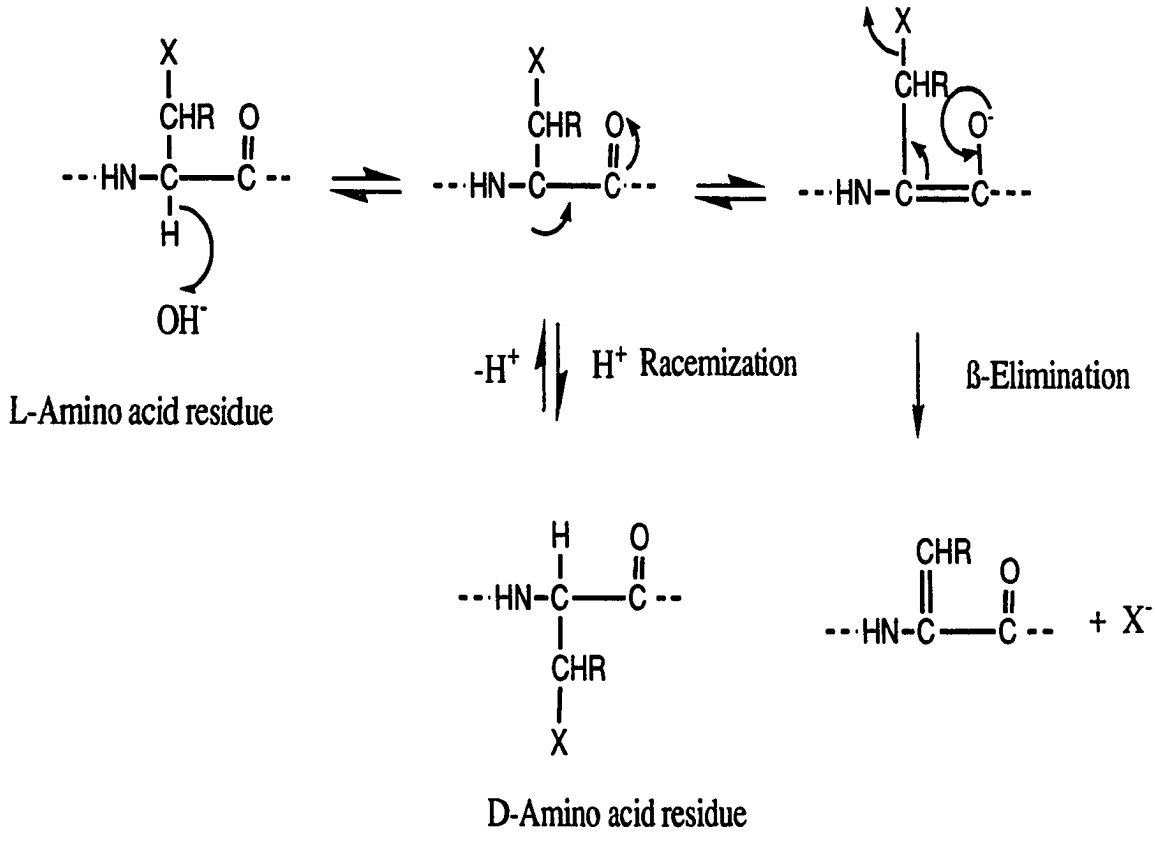
Table 8. Common amino acid side chains chemically modified[a]

Side chain	Commonly used modifications
Amino	Alkylation, acylation
Carboxyl	Esterification, amide formation
Disulfide	Reduction, oxidation
Imidazole	Oxidation, alkylation
Indole	Oxidation, alkylation
Phenolic	Acylation, electrophilic substitution
Sulfhydryl	Alkylation , oxidation
Thioether	Alkylation, oxidation
Guanidino	Condensation with dicarbonyls

[a] Adapted from Feeney (1977).

acids, splitting of disulfide bonds and formation of cross-linked products (Feeney, 1980; Whitaker, 1980).

Alkali has long been used on proteins for such processes as the retting of wool and curing of collagen, but recently alkali treatments have received attention by the paper industry. Amino acids such as cystine, cysteine, serine, threonine, lysine and arginine can be lost during the alkaline treatment of proteins. Unlike arginine, loss of the other amino acids is not due to hydrolytic reaction but rather a ß-elimination reaction (Figure 3). Through ß-elimination and the addition of a thiol compound to the double bond to form a sulfhydryl group, the modified protein can be oxidized in air to form disulfide bridges (Rhee and Kim, 1992). ß-Elimination and the addition reactions are important in texturizing foods extruded from alkaline solution



X= H, OH, O-glycosyl, O-phosphoryl, -SH, SCH_2-R, aliphatic or aromatic residue;
R= H or CH_3.

Figure 3. The reaction of ß-elimination and racemization.

because ß-elimination changes the solubilities of proteins (Whitaker, 1980).

The treatment of soybean proteins with alkali improves solubility, increases adhesive properties and lowers viscosity. The alkali treatment of soy protein for industrial uses was done under more severe conditions such as higher temperature and higher pH than those in food uses (Meyer and Williams, 1977).

Acylation and acetylation

Acylation attaches an acyl group to amino groups of protein to form amide derivatives. Acetylation is an example of acylation. The acylation of soybean proteins with various acylhalides and anhydrides of low and high molecular weights were initially adopted for their effects on properties that were important in industrial applications, such as viscosity, adhesion, foaming and detergency. Meyer and Williams (1977) reported that various acyl groups altered the calcium sensitivity of proteins and their ability to associate and form aggregates. The predominant reaction was the acylation of the ε-amino acid group of the lysine residues.

Simonsky and Stanley (1982) reported that severe acetic anhydride modification of the charged groups on soy proteins markedly affected extrusion behavior. This treatment resulted in a great increase of the net negative charge on the proteins and significantly inhibited texture formation.

Acetylation changed the physical and chemical properties of soy proteins. One major effect was the dissociation of 11S fraction into small 7S and 2S components (Barman et al., 1977). This modification caused a 20% decrease in water-binding capacity, which was attributed to the cancellation of charged ε-amino group of lysine. The loss of the charged ε-amino group of lysine was also responsible for reducing the pI to pH 4 (Franzen, 1975). Three important changes in the physical properties of soy protein modified by mild acetylation were increased solubility, improved wettability and increased viscosity (Rhee and Kim 1992).

Acetylation of proteins also improved the properties of protein fibers. Atwood (1944) reported that the water-resistance of casein fiber (Aralac) was improved by acetylation. Evans et al. (1947) investigated the effect of acetylation on various properties of zein fibers and reported that zein fibers finished by acetylation had good resistance to boiling in alkaline solutions, but were mush less resistant to boiling in acid solutions.

Alkylation

A number of alkylating, arylating and related reagents had been used in studying the composition, structure and conformation of various soybean proteins and protein fractions. Formaldehyde was the most commonly used reagent.

The reaction between formaldehyde and protein has been widely studied, and many types of side chains, such as amino, amido, guanidino, sulfhydryl, phenolic, imidazole and indole, have been proposed as sites for mono or bifunctional reactions (Bjorksten, 1951; Fraenkel-Conrat and Olcott, 1948; Browes and Cater, 1966; Habeeb and Hiramoto, 1968; Meyer and Williams, 1977).

Soy proteins have been treated with formaldehyde and a variety of other aldehydes and ketones to produce insolubilized protein for adhesives, films, coatings and polymers. (Meyer and Williams, 1977). Croston et al. (1945) used formaldehyde to finish zein fibers to increase the water-resistance, improve the softness and boil-resistance, whiten and remove pigments and decrease dye uptake.

Other chemical modifications

Mild acid treatments have been described for the deamidation of proteins, but these have not been exploited in altering the functional properties of soy proteins (Meyer and Williams, 1977). Acid hydrolyzates of soy protein products have been used as flavoring agents in food (Meyer and Williams, 1977).

Cross-linked or network polymers have been produced by either addition or condensation reactions. The addition reaction begins with materials containing sufficient amounts of monomer or repeating unit. The condensation reaction creates cross-links between linear or branched molecules (Rosen, 1982; Stevens, 1990). Bifunctional aldehydes, acid chlorides and dianhydrides could be used as cross-linking reagents for proteins. They should produce covalent links between ε-amino groups of lysine or terminal α-amino groups. In the

case of bifunctional acid chlorides and anhydrides, other groups might also be involved. Bifunctional aldehydes are particularly useful cross-linking reagents because of their high reactivities and specificities. Glutaraldehyde has been shown to be very reactive towards the N-terminal amino groups of peptides as well as α-amino groups of amino acids (Bowes and Cater, 1966; Habeeb and Hiramoto, 1968).

Esterification of protein carboxyl groups can be achieved by nucleophilic attack by RO^- on the carbonyl carbon of the carboxylic acid residues, resulting in a displacement of OH by OR (Figure 4). Early in the 1950s, casein, gluten, gliadin and egg albumin were esterified with low molecular weight alcohols. These esterified proteins showed altered solubility behavior (Meyer and Williams, 1977). Esterification was applied to soy proteins to change their solubilities for industrial uses. However, partial carboxyl esterification for food uses has not been practiced because of the sensitivity of the esters to hydrolysis (Asquith and Leon, 1977).

Various patents and publications have suggested some treatments and changes in the spinning process to improve the properties of protein fibers. Kajita and Inoue (1940a) added lecithin before spinning to increase fiber strength. They also added sugar or tartaric acid to reduce the brittleness of the fibers (Kajita and Inoue, 1940b and 1941). Huppert (1942, 1943, and 1944) treated fibers with nitrous acid to prevent them from sticking together. He also modified fibers with alkyl sulfonates and coextruded them with a mixture of zein, cresol, chloroacetic acid, ammonium thiocyanate and formaldehyde to increase fiber strength and flexibility. Croston et al. (1945) strain-hardened fibers by stretching them up to 300%. This process was believed to align protein chains and encouraged interactions between groups on adjacent chains.

Soy protein spinning solutions are highly thixotropic, so handling them requires heavy duty mixers, pumps and filters (Boyer, 1978). Viscosity could be reduced by treating of the soy protein with pepsin (Huppert, 1945). Boyer et al. (1945a and b) reported an improved

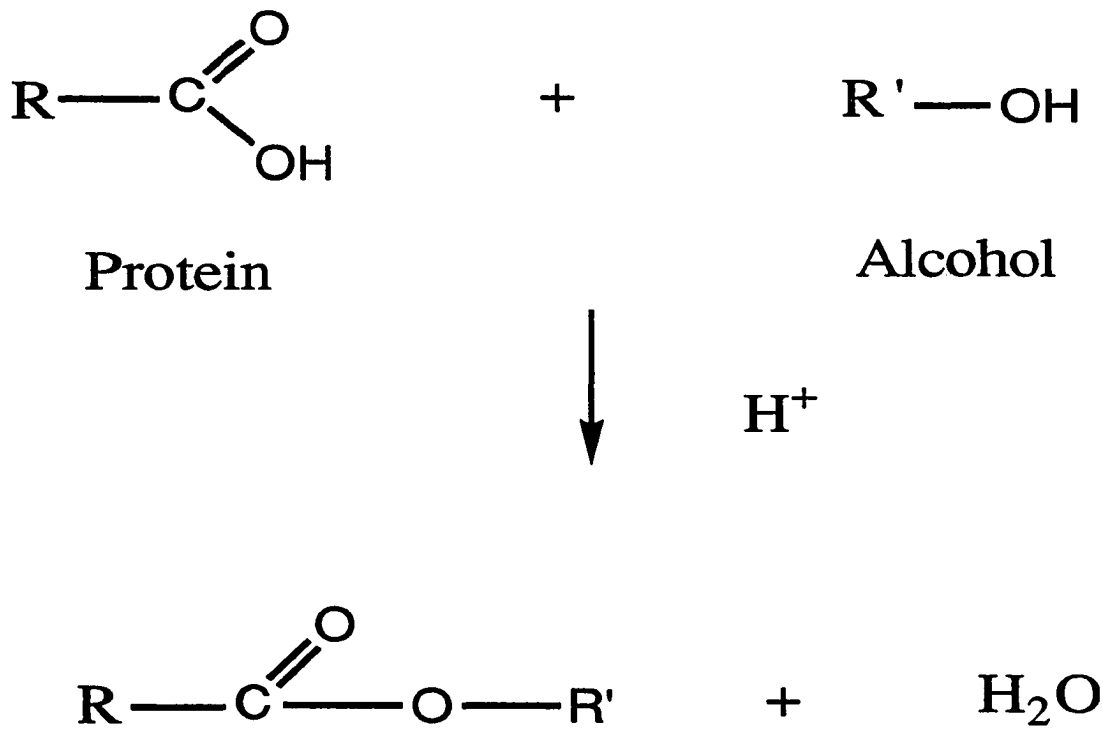


Figure 4. The esterification of protein with alcohol.

spinning solution by treating soy protein with carbon disulfide to form an xanthate.

MATERIALS AND METHODS

I. Materials

Several industrially available soy protein isolates including ARPRO 1100, 2100 and 2200 from Archer Daniels Midland Company (Decatur, IL) and PTI 500E and Super A from Ralston Purina Co, Protein Technologies International (St. Louis, MO) were investigated. After investigating the soy protein isolates, industrial soy protein isolate ARPRO 1100 was used to produce fibers. The protein was alkali-extracted, acid precipitated at its approximate isoelectric point and tunnel-dried to 7% moisture.

Chemicals and reagents

Glutaraldehyde (25%) and benzoic anhydride were purchased from Aldrich Chemical Company (Milwaukee, WI). Azelaic acid and glyoxal (40%) were purchased from Fluka Chemika-Biochemiks (Ronkonkoma, NY). Other common chemicals and reagents (certified A.C.S. grade) were purchased from Fisher Scientific (Pittsburgh, PA).

II. Methods

Testing of fiber properties

Linear density (tex) of fibers was measured by weighing one 20-cm single fiber and multiplying the weight in grams by 5,000. Six duplications of linear density of fibers were measured and averaged. The Instron Universal Testing Machine (UTM, model 4500) with a 100N load cell and pneumatic-action grips No. 2712-002 (Instron Corp., Canton, MA) was used to measure the fiber properties including tensile strength, elongation and modulus. The stretching rate was 5 cm/min and distance between the two grips was 10 cm.

Fibers for testing were air dried for 24 h after spinning or treatments, stored in desiccators with 11% or 65% relative humidity (RH) for 72 h before testing their properties according to recommended American Society for Testing and Materials (ASTM, 1991) methods. The fiber properties were tested in a wet condition according to ASTM (1991). Relative humidity (RH) conditions of 11% and 65% were maintained by using saturated aqueous lithium chloride and sodium nitrite solutions, respectively (Lubuza et al., 1976). Six replications fibers of each treatment were measured at 11% and 65% relative humidity and wet conditions.

Fiber flexibility was tested by the ability of six fibers to be looped three times around glass rods of various diameters (1.5, 2, 2.5, 3, 3.5, 4, 5, 11, 16, 21, 25, 34 and 45 mm) without breaking at 11% and 65% RH. The smaller the diameter of the glass rods that could be used successfully, the better the flexibility of the fibers.

Extrusion mixing-measuring

Soy proteins (ARPRO 1100) were mixed with water and/or glycerol by using a heavy-duty Kitchen Aid mixer (Kitchen Aid Portable Appliances, St. Joseph, MI) at #1 speed (70 rpm) for 10 min. All protein mixtures were equilibrated at room temperature for 24 h. A Brabender Plastic-Corder PL2000 and a half-size roller style mixer measuring head (C.W. Brabender Instruments, Inc., S. Hackensack, NJ) equipped with a computer were used to measure the maximum torque, temperature at maximum torque, minimum torque and temperature at minimum torque. The temperature and speed of the mixer were 110°C and 20 rpm, respectively, and the testing time was 15 min.

Acetic anhydride modification of soy proteins prior to extrusion

Two hundred grams of soy protein were reacted with 2 L of 0, 5, 7.5 and 12.5% of acetic anhydride-acetic acid (9: 1, v/v) in xylene, respectively, at 85°C for 30 min. The

modified soy protein was removed by filtration, washed with 500 mL of diethyl ether and 1 L of water and dried in an oven at 80°C for 48 h.

Acetaldehyde modification of soy proteins prior to extrusion

Two hundred grams of soy protein were reacted with 500 mL of 10% of acetaldehyde at room temperature for 30 min. The modified soy protein was removed by filtration, washed with 1 L of water, and dried in an oven at 80°C for 48 h.

Esterification

Two hundred grams of soy protein were subjected to azeotropic distillation with 500 mL of benzene to remove moisture. Seventy-five mL of ethylene glycol, butanol or propanol and 3.5 mL of sulfuric acid, were added and refluxing continued for an additional 4 h. The modified protein was washed with 1 L of water, centrifuged for 20 min at 4000xg and dried in an oven at 80°C for 48 h.

Extrusion of soy protein fibers

Protein mixtures were prepared by mixing soy protein, acetic-anhydride modified proteins or esterified proteins with glycerol and water in the weight ratio of 45: 15: 40 by using a Kitchen Aid mixer at #1 (70 rpm) speed for 10 min. Other formulations of protein mixtures were prepared by controlling the moisture at 40%. All protein mixtures were equilibrated at room temperature for 24 h before extrusion.

The Brabender Plastic-Corder PL2000 with a continuous twin screw mixer (C.W. Brabender Instruments, Inc., S. Hackensack, NJ) was used to produce soy protein fibers. The temperature and screw speed of extruder were 96°C and 20 rpm, respectively, and the exit die had eight 368-μ openings (Engineering Research Institute, Iowa State University, Ames, IA). Fibers were air-dried to about 12% moisture at room temperature.

Evaluation of soy protein "dopes" for wet-spinning process

Soy proteins were mixed with water to concentrations of 15, 20 and 25% by weight, respectively, by stirring for 30 min. Three hundred grams of protein-water solutions were adjusted to pH 9, 10 or 11, with 10% sodium hydroxide solution and stirred with a Kitchen Aid mixer at # 1 (70 rpm) speed. These protein "dopes" were aged for 0, 1 and 2 days, respectively, and their viscosities were measured with a Brookfield Synchro-Lectric Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA).

To determine the changes in pH and viscosity during the aging process, six preparations of soy protein-sodium hydroxide-water dopes (3825 g) were made. The protein was mixed with water for 30 min. Sodium hydroxide solutions of various strengths (0.98, 1.07, 1.20, 1.31, 1.48 and 1.61%) were added and the mixture was stirred with a Kitchen Aid mixer at # 1 (70 rpm) speed for 90 min. These protein "dopes" were aged for 0, 1, 2, 3 and 4 days, respectively, and the viscosities and pH's were determined periodically with a Brookfield Synchro-Lectric Viscometer and a pH meter.

Wet spinning of soy protein fibers

A 10-mL syringe with a 26 gauge (3/8") needle (Becton Dickinson & Co., Rutherford, NJ) was used to test soy protein dopes for fiber production by hand-injecting dopes into a 4% HCl coagulating solution. The protein dopes were selected and prepared by mixing 750 g of soy proteins , 410 g of 10% sodium hydroxide and 2.665 L of water. The mixtures were stirred with Kitchen Aid mixer at #1 (70 rpm) speed for 90 min and aged for one day before wet spinning.

The wet-spinning equipment consisted of a pressure vessel, a filter, a pump and a 12 L coagulating bath. Air pressure (4.14×10^5 N/m^2) flowing into the pressure vessel pushed protein dopes into the filter. The filter, which consisted of a polyester-dacron 25 to 30-μ fabric filter screen (Ronningen-Petter, Protage, MI), was used to remove particulate contaminants. A

high-viscosity Zenith pump with QM-SY 1416 digital speed controller (Parker Hannifin Co, Waltham, MA) was used to force the soy protein "dopes" through the spinnerette and into the coagulating bath (Figure 5). The pressure vessel, coagulation bath and 386-μ spinnerette were made by the Engineering Research Institute at Iowa State University. A Posiflo II Pump (Gelman Sciences, Ann Arbor, MI) was used to circulate acid solution in the coagulating bath.

The individual wet-spun fibers were dried on waxed paper for 24 h, stored in desiccators with 11% and 65% relative humidity (RH), respectively, for 72 h before further testing or treatments.

Treatment of finished fibers with acetic and benzoic anhydrides

The fibers extruded with glycerol (protein: glycerol: water = 45: 15: 40) were used for the following chemical finishing treatments. Soy fibers (10g) were heated in 100 mL of acetic anhydride-acetic acid at 85° C for 30 min. The acetic anhydride-acetic acid ratio was 9: 1, 7: 3, or 1: 1 (v/v). A benzoic anhydride-acetic acid treatment (9: 1, w/w) also was tested. Fibers made from acetic anhydride and acetaldehyde modified soy proteins and esterified soy proteins, were treated with acetic anhydride-acetic acid at 9: 1 (v/v).

Treatment of finished fibers with acetaldehyde

Ten grams of soy protein fibers were soaked in 100 mL of 10, 15, 20 or 25% acetaldehyde (v/v) at room temperature for 30 min.

Treatment of finished fibers with dianhydrides

Two moles of succinic acid, adipic acid and azelaic acid, respectively, were reacted with 4 moles of acetic anhydride at 120 ± 5° C for 4 h to form dianhydrides of the dicarboxylic acids. Dianhydride reagents were prepared at the concentrations of 0.16, 0.32, 0.64, 1.28 and 1.92M, respectively, in xylene. Acetic anhydride of concentrations that were of 2-fold greater

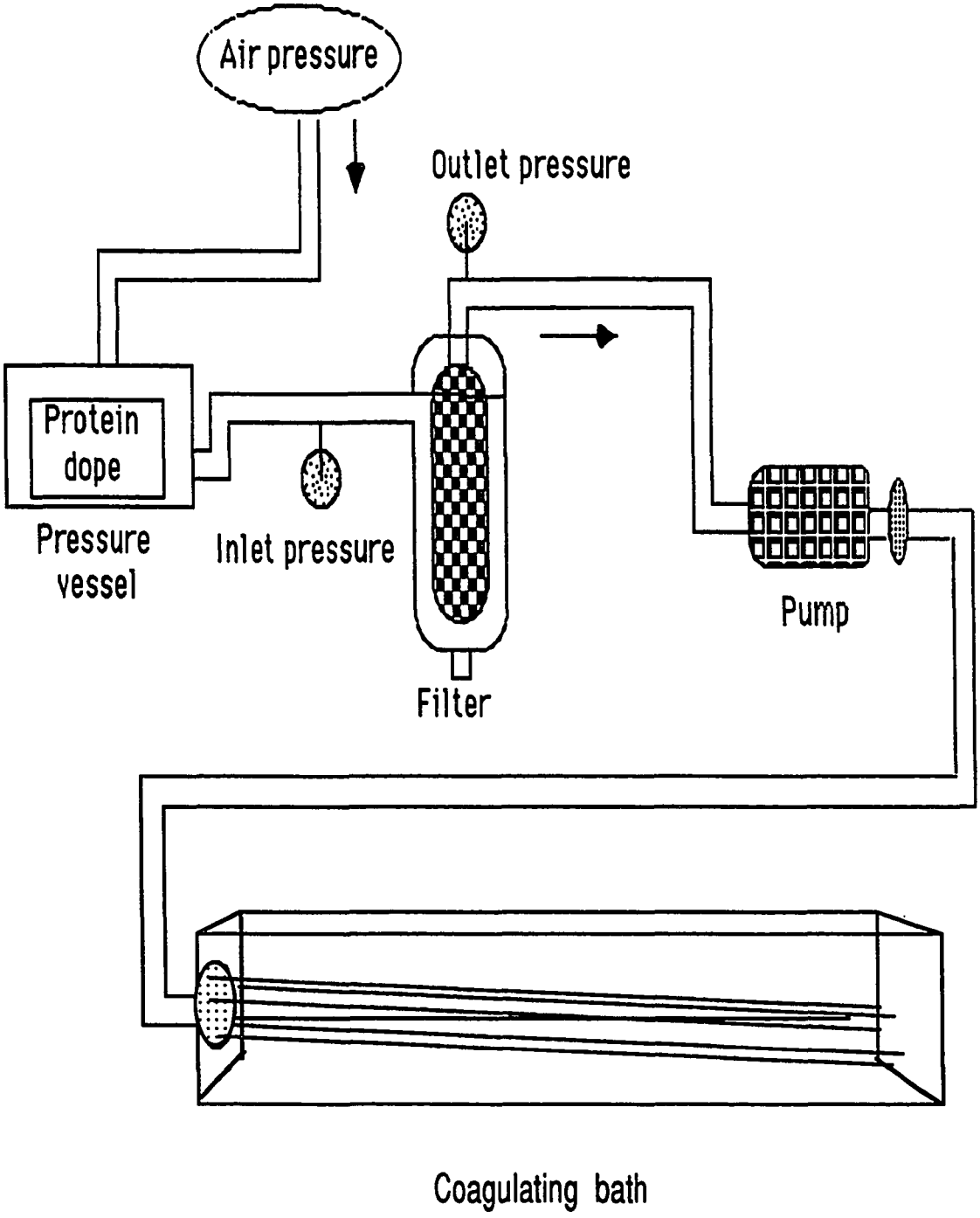


Figure 5. Set-up of wet-spinning process.

molarity than these concentrations was prepared in xylene as controls. Soy protein fibers (10g) were heated in 100 mL of the various reagents at 85°C for 30 min.

Treatment of finished fibers with glyoxal

Ten grams of soy protein fibers were soaked in 100 mL of 10, 15, 20 or 25% glyoxal (v/v) at pH 3.5 at room temperature for 30 min.

Treatment of finished fibers with glutaraldehyde

Extruded soy protein fibers (10g) were soaked in 100 mL of 10, 15, 20 or 25% glutaraldehyde (v/v) at pH 3.5 at room temperature for 30 min. The effects of pH, reaction time and temperature on soy protein fibers were also tested with 25% glutaraldehyde. The pH was adjusted to 1.5, 2.5, 3.0 or 3.5 with 2 N HCl and the reaction was carried out at room temperature for 30 min. At pH 3.5 and at room temperature, the effect of reaction times of 10, 20, 30, 45, 60, 75 and 90 min were tested. At pH 3.5 and for 30 min, the effect of reaction temperatures of room temperature, 50°, 70° and 90° C were tested. Extruded soy protein fibers treated with 25% glutaraldehyde at pH 3.5 at room temperature for 30 min were immediately subjected to stretching to 110, 130, 150 or 170% of their original lengths. Soy protein fibers treated with 25% glutaraldehyde at pH 3.5 at room temperature, 50°, 70° or 90°C for 30 min were immediately subjected to stretching to 150% of their original lengths.

Air-dried wet-spun soy protein fibers (10g) were soaked in 100 mL of 25% glutaraldehyde at room temperature for 30 min. These glutaraldehyde-treated wet-spun fibers were air-dried on waxed paper for 24 h and stored in desiccators with 11% and 65% RH for 72 h before testing.

Wet-spun fibers that had been coagulated in a 4% HCl solution containing 3.33% zinc chloride, 3.33% calcium chloride and 3.33% sodium chloride were air-dried and treated with

25% glutaraldehyde at room temperature for 30 min. Fibers were air-dried again, soaked in water for 15 min and immediately subjected to stretching to 170% of their original lengths.

Treatment of finished fibers with glutaraldehyde and acetic anhydride

Soy protein fibers (10g) were treated with 100 mL of 25% glutaraldehyde at pH 3.5 at room temperature for 30 min, then heated in 100 mL acetic anhydride-acetic acid solution (9: 1, v/v) at 85°C for 30 min. Treated fibers were immediately subjected to stretching to 130% or 150% of their original lengths.

Effects of washing on soy protein fibers treated with dialdehyde

Soy protein fibers (10g) that had been treated with 25% glutaraldehyde (pH 3.5 and 30 min) or 25% glyoxal (pH 3.5 and 30 min) were washed with 4 L water for 30 min. The physical properties of these fibers were compared with those of soy protein fibers washed with 4 L of water for 30 min to remove glycerol and then treated with 25% glutaraldehyde or 25% glyoxal at pH 3.5 and room temperature for 30 min.

Soy protein fibers (5g) that had been dried in an 11% RH desiccator for one week were soaked in 50 mL of 10, 15, 20 and 25% glutaraldehyde or glyoxal at pH 3.5 at room temperature for 30 min. The fibers were wiped dry and the weight gain was measured. Fibers were air-dried for 48 h, then redried in an 11% RH desiccator for one week. The final weight was determined by weighing. The fibers were washed with 2 L water for 30 min, air-dried for 48 h, redried in an 11% RH desiccator for one week. The weight change was determined. These weight results were compared with those of similarly-treated fibers except that they were washed with 2 L of water for 30 min to remove glycerol before treatment with glutaraldehyde or glyoxal.

Moisture absorption of soy protein fibers

Soy protein fibers and acetic-anhydride-modified soy protein fibers were dried in a 100°C oven for 24 h. Dry fibers (1g) were equilibrated over salt solutions to yield 11, 23, 33, 54, 66, 76, 81, 93 or 100% RH for 72 h, and water absorption or loss was measured by weighing. The various relative humidities were produced by using saturated salt solutions of lithium chloride, potassium acetate, magnesium chloride, zinc nitrate, calcium nitrate, sodium nitrite, sodium chloride, ammonium sulfate, potassium nitrate and water, respectively (Lubuza et al., 1976).

Titration of soy protein fibers

Five grams of soy fibers were washed, filtered, dried in an oven at 100° C for 24 h, and stored in a desiccator overnight. The fibers were ground to powder, suspended in 200 mL of water with stirring for 30 min and titrated with 0.1 N sodium hydroxide or 0.1N HCl solutions from pH 3 to 11. The amounts of sodium hydroxide in mg/g fiber required to change the pH from 3 to 11 were plotted.

Microstructural analyses of soy protein fibers by scanning electron microscopy

The microstructures of soy fibers were revealed by scanning electron microscopy (SEM). Cross-sections of the fiber samples were cut, attached to specimen stubs, and coated with gold-palladium. The mounted specimens were examined with a JEOL JSM-35 SEM (JEOL Ltd., Tokyo, Japan). The surfaces of fibers were observed at an accelerating voltage of 25 kV and at a magnification of 1500 X. The cross-sections of fibers were observed under 15 kV and at 1500 X magnification.

Statistical analyses

As is typical for rheological measurements, there was a great deal of variance between test pieces for tenacity, elongation and modulus while there was little variation among duplicate batches of product from the extruder or wet spinning apparatus. Thus, when six batches of fibers were extruded and six fibers of each batch were analyzed under three humidities, an analysis of variance (Statistical Analysis System, 1992) showed no significant differences in batches, and variation between batches of fibers was much less than the variation between fibers within batches. For tenacity, the mean and standard deviation among fibers were 0.736 g/tex ± 0.005 while the standard deviation among fiber samples varied from 0.1 to 1.0. Therefore, six fibers per treatment were tested to reduce analytical variation, but as a general rule preparations were not duplicated.

Analysis of variance (SAS, 1992) was used to test for the effect of treatments on fiber properties and determine correlation coefficients. When F-values were significant, mean differences among treatments were compared by using a least significant difference (LSD) test at a probability level of 0.05.

Titrations, pH's and viscosities were measured in duplicate and mean differences were compared by an analysis of variance and LSD test.

Summary of chemical modification and treatments

Several chemical modification and treatments of soy proteins in extrusion and wet spinning are illustrated in Figure 6.

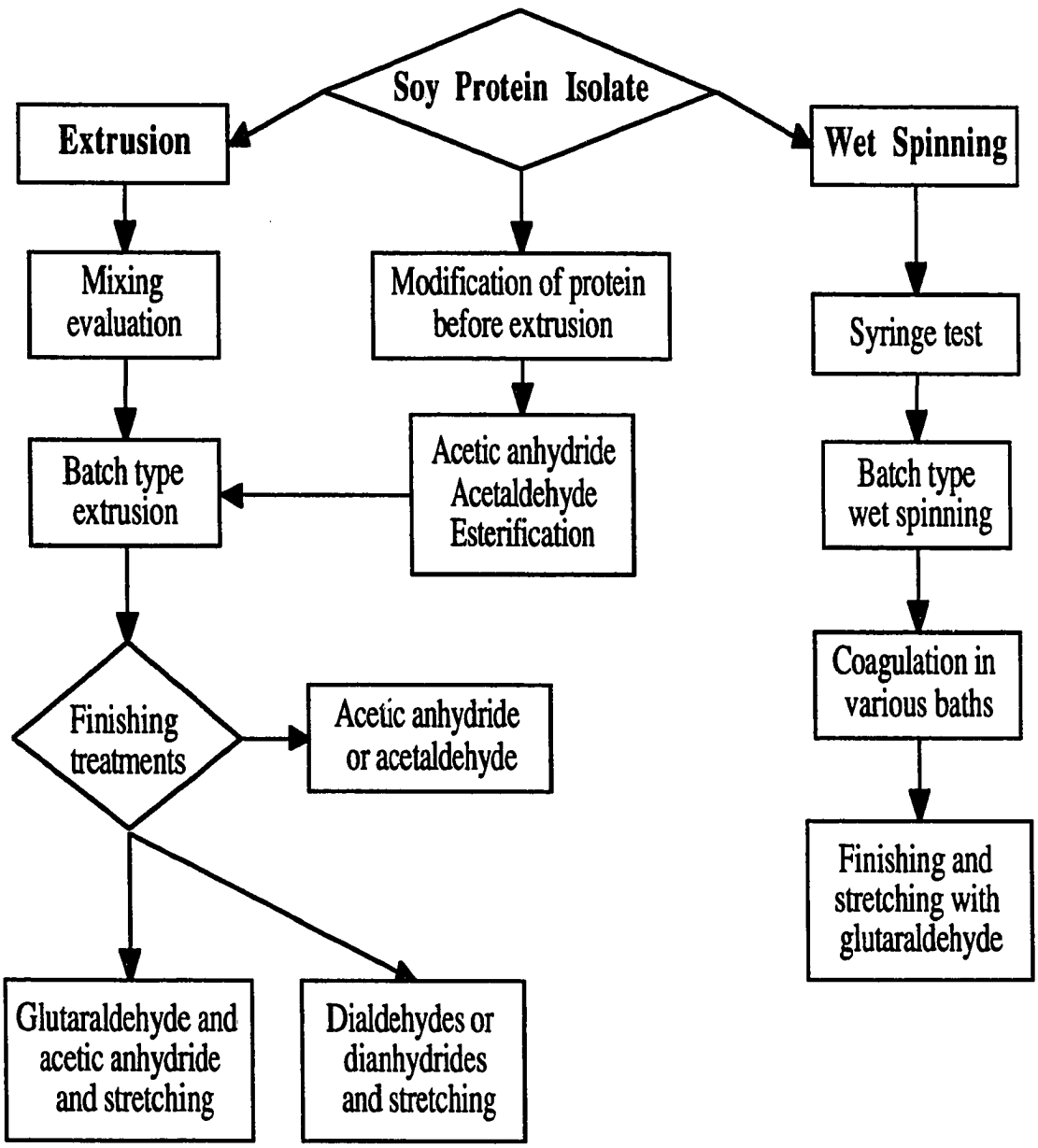


Figure 6. The procedures and chemical treatments of soy protein fibers in extrusion and wet spinning.

RESULTS AND DISCUSSION

I. Fiber Production Methods

Two processes were developed to manufacture fibers: extrusion and wet spinning. The wet-spinning technique was a redevelopment of the technology used in the 1930's and the 40's and was based on the description of Croston et al. (1945). A schematic of this apparatus is shown in Figure 5 in the materials and methods.

Mixing evaluations in preparation for extrusion

In order to operate both fiber-spinning processes, it was necessary to evaluate the viscoelastic properties of the solutions or mixtures that were to be spun. The effects of moisture content, temperature and additives on the viscoelastic properties were studied by a mixing evaluation. The soy protein mixture was mixed as the temperature was increased and the maximum and minimum torque were noted. Maximum torque was observed at the point when the protein mixture began "melting", and the minimum torque was observed at the point when the protein mixture "melted" and became homogeneous (Brabender, 1988). Torque is defined as the effectiveness of a force in producing rotation about an axis and is measured by the product of the force and the perpendicular distance from the line of action of the force to the axis of rotation (CRC, 1990).

When soy protein was heated with water at increasing temperatures, the protein gelled. The moisture content of such mixtures significantly changed their rheology during extrusion mixing. Mixing evaluations showed that a moisture content > 30% was required to maintain a consistency within the design limits of the extruder. The torque required to mix the soy protein gel decreased with increasing moisture content, and the "melting" temperatures decreased as moisture content increased (Table 9). There were significant differences among the moisture

Table 9. The changes of melting temperatures and viscosity of soy protein at various moisture contents

Moisture (%)	Temperature (°C) at maximum torque	Maximum torque (mg)	Temperature (°C) of minimum torque	Minimum torque (mg)
30	92.5 ± 0.7^{a}	2067 ± 49^{a}	99.5 ± 0.7^{a}	1442 ± 14^{a}
35	87.5 ± 0.7^{b}	1298 ± 8^{b}	97.5 ± 0.7^{b}	431 ± 16^{b}
40	78.5 ± 0.7^{c}	1060 ± 34^{c}	96.0 ± 0.0^{b}	383 ± 8^{c}
LSD	2.3	110	1.8	43

[a-c] Values with each column with same superscripts are not significantly different ($p>0.05$).

contents in the temperatures and torques ($p<0.01$). Experience showed that mixtures with lower moisture contents produced fibers that were tough and inelastic; however, when the moisture exceeded 40%, the fibers became very sticky, weak and irregular as well as being difficult to extrude. Extrusion temperatures > 100°C caused puffing of the fibers as they exited the extruder.

Effects of soy protein percentage, aging and pH on the viscosity of wet-spinning dopes

The viscosity of soy protein dope was an important index that needed to be considered before wet spinning fibers. Viscosities greater than 150 poise made wet spinning through small orifices extremely difficult. Table 10 shows the viscosities of soy protein dopes were affected by the concentration of soy protein and the pH ($p<0.01$).

The viscosity of soy protein dope increased as the concentration of protein increased. The viscosity of soy protein dope increased as pH increased from 9 to 11. After one day aging, the viscosity of dopes at pH 10 and 11 increased, but at two days, the viscosity

Table 10. The viscosity of soy protein dopes at various pHs, concentrations and aging times

Protein (%)	Viscosity (poise)		
	pH 9	pH 10	pH 11
After mixing			
15%	8.5 ± 0.7^{c}	7.8 ± 0.4^{c}	13.5 ± 0.7^{c}
20%	63.2 ± 1.1^{b}	25.2 ± 1.3^{b}	52.0 ± 1.4^{b}
25%	187.0 ± 1.4^{a}	157.0 ± 4.2^{a}	181.0 ± 1.4^{a}
LSD	3.6	6.3	6.7
One day aging			
15%	7.5 ± 0.7^{c}	8.5 ± 0.7^{c}	16.0 ± 1.4^{c}
20%	41.4 ± 2.0^{b}	73.5 ± 0.7^{b}	149.0 ± 1.4^{b}
25%	182.0 ± 2.8^{a}	585.0 ± 1.4^{a}	653.0 ± 9.9^{a}
LSD	6.5	3.2	49.5
Two days aging			
15%	7.0 ± 1.4^{c}	7.5 ± 0.7^{c}	10.5 ± 0.7^{c}
20%	36.4 ± 5.7^{b}	65.0 ± 1.4^{b}	99.0 ± 1.4^{b}
25%	172.0 ± 2.8^{a}	475.0 ± 4.2^{a}	570.0 ± 14.1^{a}
LSD	7.3	10.8	36.5

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

decreased at pH 10 and 11. Possibly, in strong alkaline conditions, protein association increased viscosity. Conversely, proteins possibly underwent hydrolysis with time, which would decrease viscosity. The viscosity of soy protein dope was greater at pH 9 than at 10 when fresh, and at pH 9, the viscosity decreased with aging. Possibly the proteins were not completely dissolved and dissociated at pH 9.

Testing fiber formation by syringe injection indicated that about 20% protein and pH >10 gave soy protein dopes that merited further study. Batches containing 19.61% soy protein (weight 3825g) ~79% water and various amount of sodium hydroxide were prepared

(Table 11). Sodium hydroxide percentages and aging times significantly affected pH and viscosity ($p<0.01$) (Table 12). These results were similar to those observed in Table 9. The soy protein dopes had the greatest viscosities between pH 11.5 and 12 (Figure 7). It was possible that protein hydrolysis occurred more rapidly and produced ammonia at pH's > 12. After syringe injection testing, formulation B was chosen to be 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 ammonia copiously after one day.

The soy protein dope made from formulation B was tested and successfully spun through various sizes of spinnerettes including 1016, 368, 191 and 36 μ. For the handling of wet-spun fibers, a 368-μ spinnerette was selected to spin fibers.

II. Methods of Measurements of Fiber Properties

The fibers were characterized for selected physical properties such as breaking tenacity, elongation and initial modulus as measured by an Instron Universal Testing Machine. Breaking tenacity is the maximum force applied to rupture a single fiber and is expressed as g/tex. Tex is a unit of linear density (mass per unit of fiber length) and is defined as the weight in grams of a fiber measuring 1000 meters. Elongation is the maximum ratio of extension of a fiber to the unstrained length of the fiber expressed as a percentage. The modulus is the ratio of the change in stress to the change in strain and expressed as g/tex. Modulus is obtained from the slope of the initial straight portion of a stress-strain curve. A bending test was developed to measure flexibility of fibers to bending strains. The bending test measured the ability of fibers to be looped three times around glass rods of various diameters without breaking at 11% and 65% relative humidity (RH). Fibers were so flexible that they were able to bend freely after soaking in water. The smaller the diameter of the glass rod, the better the

Table 11. The formulations of soy protein dopes with constant percentages of protein and various percentages of sodium hydroxide and water

Composition (%) by wt.	Dope A	B	C	D	E	F
Protein	19.61	19.61	19.61	19.61	19.61	19.61
NaOH	0.98	1.07	1.20	1.31	1.48	1.61
Water	79.41	79.32	79.19	79.08	78.91	78.78

Table 12. The pH and viscosity of the soy protein dope formulas of Table 11 at various aging times

	pH				
Aging Time (Day) / Formulation	0	1	2	3	4
A	10.45±0.04^{f}	10.36±0.02^{f}	10.27±0.04^{f}	10.22±0.04^{f}	9.36±0.02^{f}
B	10.88±0.04^{e}	10.74±0.02^{e}	10.63±0.03^{e}	10.58±0.04^{e}	10.45±0.06^{e}
C	11.38±0.03^{d}	11.19±0.04^{d}	11.06±0.03^{d}	11.03±0.01^{d}	10.99±0.01^{d}
D	12.08±0.04^{c}	11.60±0.03^{c}	11.53±0.03^{c}	11.48±0.03^{c}	11.37±0.02^{c}
E	12.67±0.04^{b}	12.25±0.02^{b}	12.13±0.04^{b}	12.08±0.04^{b}	11.96±0.08^{b}
F	12.77±0.04^{a}	12.52±0.04^{a}	12.38±0.04^{a}	12.33±0.04^{a}	12.27±0.04^{a}
LSD	0.10	0.07	0.08	0.08	0.11
	Viscosity (Poise)				
Aging Time (Day) / Formulation	0	1	2	3	4
A	25.5 ± 0.7^{e}	57.5 ± 0.7^{e}	49.0 ± 1.4^{d}	38.5 ± 2.1^{e}	24.5 ± 0.7^{e}
B	31.5 ± 0.7^{d}	94.5 ± 2.1^{d}	82.0 ± 1.4^{c}	78.0 ± 1.4^{c}	54.5 ± 5.0^{c}
C	54.5 ± 2.1^{a}	453.3 ± 6.0^{b}	418.8 ± 12.4^{b}	402.0 ± 4.2^{b}	392.5 ± 3.5^{b}
D	44.0 ± 1.4^{b}	730.0 ±14.1^{a}	640.0 ± 7.1^{a}	645.0 ± 7.1^{a}	475.0 ± 7.1^{a}
E	35.5 ± 0.7^{c}	121.0 ± 1.4^{c}	99.5 ± 2.1^{c}	69.0 ± 1.4^{d}	34.5 ± 0.7^{d}
F	34.5 ± 0.7^{c}	27.5 ± 0.7^{f}	27.5 ± 0.7^{e}	13.5 ± 0.7^{f}	9.0 ± 1.4^{f}
LSD	2.9	9.8	18.9	8.8	9.5

$^{a-f}$ Values within each column with the same superscript are not significantly different ($p>0.05$).
A-F See Table 11.

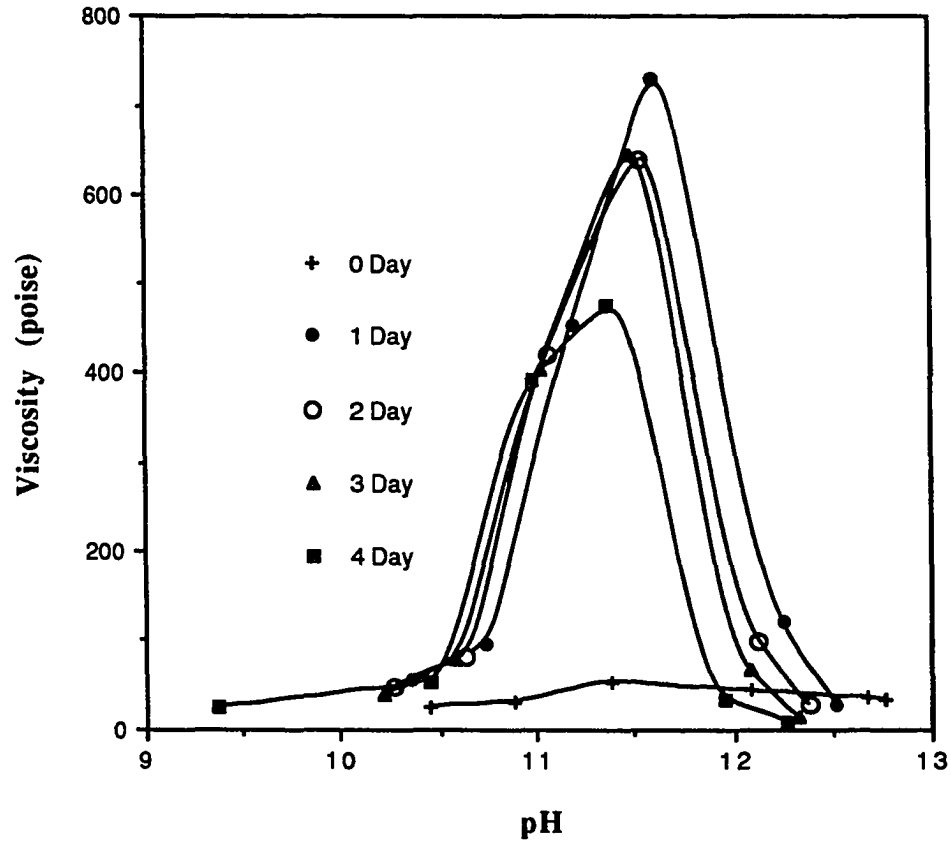


Figure 7. The relationships between viscosity and pH's of soy protein dopes at 0, 1, 2, 3 and 4 days of aging.

flexibility of the fibers. The moisture regain tested how much water the fibers could absorb at 11%, 65% or 100% relative humidity after being dried in an oven at 110 °C for 24 h. The moisture regain of fibers was affected by blocking polar groups, cross-linking, and the presence of plasticizers. Because soy protein has more than 50% of polar groups, the properties of soy protein fibers were very moisture dependent. Higher moisture regain usually indicated lower tenacity and better flexibility.

III. Comparison of Plasticizers in Extrusion and Wet Spinning

Plasticizers in extrusion

Water was an effective plasticizer for soy protein and made the resulting fibers flexible, but water was easily volatilized allowing the fibers to become brittle. In many of the preparations, water was partially replaced with glycerol since glycerol could also plasticize the protein and was not volatile. Replacing water with glycerol in soy protein mixtures increased the mixing torque of soy protein gels. The "melting" temperatures of protein mixtures decreased with increasing amount of glycerol (Figures 8 and 9). Adding glycerol to soy protein decreased the "melting" temperature to 95°C and avoided puffing of the extruded fibers. From these observations and mixing tests, the formulation of 45% soy proteins, 15% glycerol and 40% moisture was chosen as the basic mixture for use in preparing extruded soy fibers.

Various extrusion die sizes were tested to see how fine a fiber could be made by extrusion. Sizes 3969, 1588, 794 and 386 μ were tested by using 45% soy protein, 15% glycerol and 40% moisture. The 386-μ die was the finest die that we could make at Iowa State University. Generally a 386-μ die could be operated without the openings becoming blocked.

In order to decrease the brittleness of soy protein fibers, several plasticizers such as sorbitol and inorganic salts were also used in fiber extrusion in the formulations listed in Table 13.

The results are given in Tables 14 and 15. The tenacity was positively correlated with modulus ($r= 0.76$) and negatively correlated with linear density ($r= -0.45$) and moisture regain ($r= -0.61$). There were significant differences among the testing humidities and plasticizers in the measurements of tenacity, elongation, modulus, linear density and moisture regain ($p<0.01$).

The tenacities and moduli of soy fibers increased as the humidity of testing decreased. The linear density of soy fibers increased as the humidity of testing increased. These

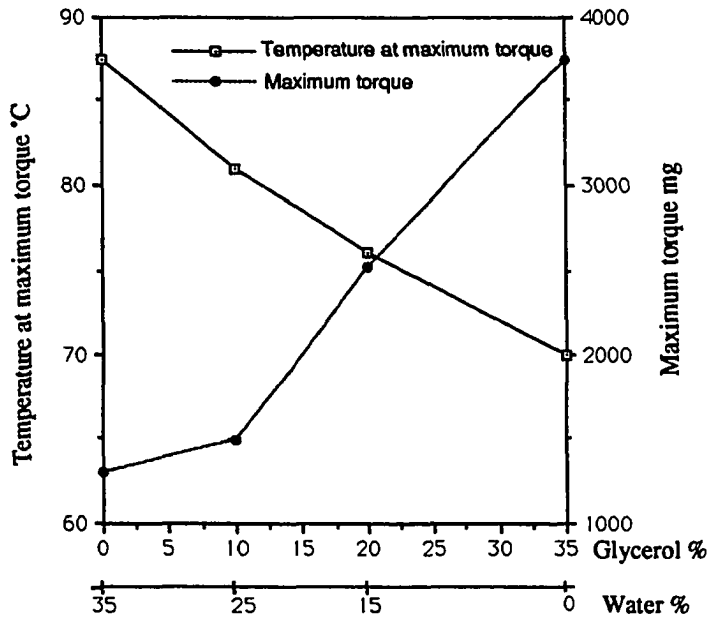


Figure 8. The relataionships among glycerol-water content, temperature at maximum torque and maximum torque in mixing evaluations.

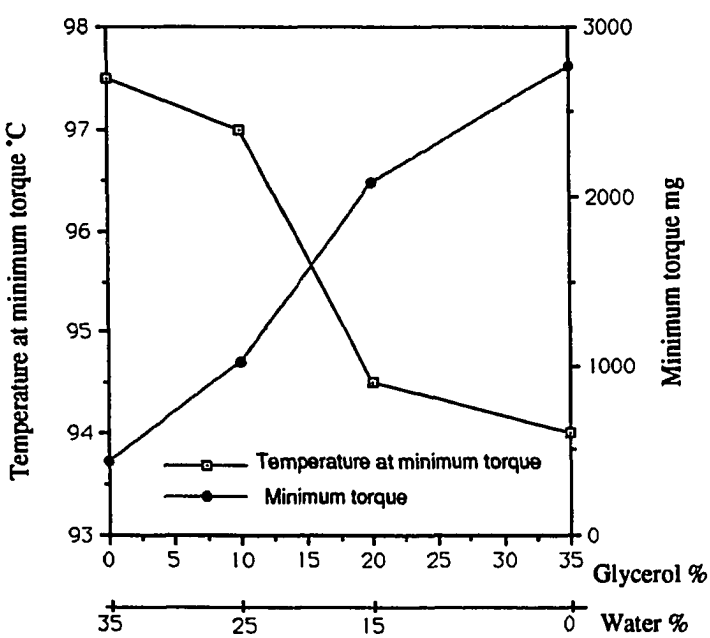


Figure 9. The relataionships among glycerol-water content, temperature at minimum torque and minimum torque in mixing evaluations.

Table 13. The formulations of soy protein mixtures for extrusion with various plasticizers

Materials (%)	Formulations									
	I	II	III	IV	V	VI	VII	VIII	IX	X
Protein	60	45	45	45	45	45	45	45	45	45
Water	40	40	40	40	40	40	40	40	40	40
Glycerol	0	15	7.5	0	15	15	15	15	15	15
Sorbitol	0	0	7.5	15	0	0	0	0	0	0
$ZnCl_2$	0	0	0	0	2	4	2	0	0	0
$CaCl_2$	0	0	0	0	0	0	2	2	4	0
Na_2HPO_4	0	0	0	0	0	0	0	0	0	4
Total %	100	100	100	100	102	104	104	102	104	104

tendencies occurred repeatedly during these studies. Presumably, as humidity increased hydrogen bonds between protein molecules were replaced by hydrogen bonds between protein and water which decreased tenacity and modulus. This hypotheses is supported by the data of the increased moisture regain (Table 14). Soy protein fibers extruded from only protein and water mixtures were very brittle and easily broken by bending stresses. Among the plasticizers, glycerol gave the greatest tenacity and elongation. Fibers plasticized with sorbitol had very poor tenacity when tested at higher humidities.

Scanning electron micrographs of fibers made with glycerol and sorbitol as a plasticizer are shown in Figure 27 of the appendix. Sorbitol fibers exhibited the properties typical of weak fibers while glycerol fibers exhibited those of stronger fibers.

In order to improve fiber flexibility, inorganic salts such as zinc chloride, calcium chloride and sodium phosphate dibasic were added to the protein-glycerol-water mixtures before extrusion. These salts increased fiber flexibility (Tables 16 and 17). Among these

Table 14. The properties of fibers using glycerol and sorbitol as plasticizers and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
0% Glycerol	122 ± 7^{a}	1.49 ± 0.15^{ab}	0.5 ± 0.1^{c}	291 ± 28^{a}	1.59 ± 0.02^{a}
15% Glycerol	113 ± 4^{b}	1.57 ± 0.32^{a}	1.6 ± 0.2^{a}	97 ± 8^{b}	1.61 ± 0.13^{a}
15% Sorbitol	98 ± 3^{c}	0.38 ± 0.07^{c}	0.7 ± 0.1^{c}	59 ± 17^{c}	1.20 ± 0.01^{b}
7.5% Glycerol & 7.5% Sorbitol	119 ± 3^{a}	1.23 ± 0.29^{b}	1.3 ± 0.4^{b}	106 ± 3^{b}	1.24 ± 0.01^{b}
LSD	5.4	0.28	0.3	20.4	0.18
65% humidity					
0% Glycerol	133 ± 6^{a}	0.31 ± 0.14^{b}	0.6 ± 0.2^{b}	31 ± 10^{ab}	9.99 ± 0.21^{d}
15% Glycerol	128 ± 2^{b}	0.56 ± 0.06^{a}	73.4 ± 16.6^{a}	25 ± 3^{bc}	14.32 ± 0.14^{a}
15% Sorbitol	113 ± 2^{c}	0.33 ± 0.07^{b}	1.2 ± 0.2^{b}	35 ± 3^{a}	11.88 ± 0.08^{c}
7.5% Glycerol &7.5% Sorbitol	124 ± 2^{b}	0.54 ± 0.03^{a}	8.5 ± 3.0^{b}	22 ± 3^{c}	13.07 ± 0.06^{b}
LSD	4.2	0.10	10.2	6.8	0.38
In water					
0% Glycerol	163 ± 12^{a}	0.090 ± 0.030^{a}	1.9 ± 0.9^{a}	3.7 ± 2.0^{a}	63.19 ± 0.60^{b}
15% Glycerol	155 ± 3^{b}	0.076 ± 0.023^{a}	3.9 ± 2.6^{a}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
15% Sorbitol	132 ± 4^{d}	---	---	---	86.82 ± 0.58^{a}
7.5% Glycerol & 7.5% Sorbitol	143 ± 3^{c}	---	---	---	87.59 ± 0.75^{a}
LSD	7.7	0.057	3.0	4.9	2.28

--- Values too low to determine.

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

Table 15. The flexibility of fibers using glycerol and sorbitol as plasticizers in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
0% Glycerol													X
15% Glycerol										X			
15% Sorbitol													X
7.5% Glycerol and 7.5% Sorbitol										X			
65% humidity													
0% Glycerol			X										
15% Glycerol		X											
15% Sorbitol						X							
7.5% Glycerol and 7.5% Sorbitol		X											

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 16. The properties of fibers using salts as coplasticizers with glycerol and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density	Tenacity	Extension at	Modulus	Wt % moisture
11% humidity	tex	g/tex	break %	g/tex	regain
Glycerol	113 ± 4^{bc}	1.57 ± 0.32^{a}	1.6 ± 0.2^{bc}	97 ± 8^{a}	1.61 ± 0.13^{a}
2% $ZnCl_2$	113 ± 3^{bc}	1.08 ± 0.15^{b}	1.8 ± 0.3^{ab}	68 ± 9^{b}	1.27 ± 0.01^{bc}
4% $ZnCl_2$	86 ± 2^{d}	1.12 ± 0.26^{b}	2.1 ± 0.7^{a}	65 ± 4^{bc}	1.37 ± 0.08^{b}
2% $CaCl_2$	110 ± 4^{c}	0.55 ± 0.10^{d}	1.1 ± 0.3^{c}	53 ± 9^{d}	1.26 ± 0.03^{bc}
4% $CaCl_2$	118 ± 4^{a}	0.81 ± 0.23^{c}	1.3 ± 0.5^{c}	67 ± 12^{bc}	1.36 ± 0.01^{b}
2% $ZnCl_2$ & 2% $CaCl_2$	115 ± 4^{ab}	0.74 ± 0.19^{cd}	1.2 ± 0.3^{c}	69 ± 7^{b}	1.20 ± 0.02^{c}
4% Na_2HPO_4	113 ± 3^{bc}	0.75 ± 0.12^{cd}	1.8 ± 0.5^{ab}	57 ± 11^{cd}	1.53 ± 0.01^{a}
LSD	4.1	0.24	0.5	10.5	0.14
65% humidity					
Glycerol	128 ± 2^{d}	0.56 ± 0.06^{a}	73.4 ± 16.6^{a}	25 ± 3^{a}	14.32 ± 0.14^{cd}
2% $ZnCl_2$	127 ± 2^{d}	0.25 ± 0.01^{c}	18.8 ± 5.2^{c}	9 ± 2^{de}	13.96 ± 0.06^{d}
4% $ZnCl_2$	93 ± 3^{e}	0.28 ± 0.05^{bc}	19.1 ± 1.6^{c}	12 ± 4^{cd}	14.90 ± 0.56^{bc}
2% $CaCl_2$	150 ± 4^{b}	0.21 ± 0.04^{d}	23.3 ± 6.5^{c}	8 ± 2^{e}	15.09 ± 0.13^{ab}
4% $CaCl_2$	162 ± 4^{a}	0.25 ± 0.01^{cd}	60.1 ± 19.7^{b}	10 ± 2^{de}	15.45 ± 0.08^{ab}
2% $ZnCl_2$ & 2% $CaCl_2$	133 ± 4^{c}	0.31 ± 0.03^{b}	17.7 ± 5.6^{c}	16 ± 6^{b}	14.03 ± 0.01^{d}
4% Na_2HPO_4	128 ± 2^{d}	0.26 ± 0.02^{cd}	17.7 ± 4.9^{c}	13 ± 2^{bc}	15.51 ± 0.25^{a}
LSD	3.5	0.04	12.4	3.7	0.60
In water					
Glycerol	155 ± 3^{c}	0.076 ± 0.023	3.9 ± 2.6	7.3 ± 4.6	88.82 ± 1.13^{f}
2% $ZnCl_2$	145 ± 2^{d}	---	---	---	122.77 ± 0.64^{d}
4% $ZnCl_2$	114 ± 2^{f}	---	---	---	146.69 ± 0.74^{ab}
2% $CaCl_2$	168 ± 5^{b}	---	---	---	127.88 ± 1.97^{c}
4% $CaCl_2$	173 ± 2^{a}	---	---	---	150.48 ± 4.33^{a}
2% $ZnCl_2$ & 2% $CaCl_2$	147 ± 3^{d}	---	---	---	142.42 ± 2.54^{b}
4% Na_2HPO_4	139 ± 3^{e}	---	---	---	106.15 ± 1.00^{e}
LSD	3.5				5.08

--- Values too low to determine, and $^{a-f}$ values within each column with the same letter are not significantly different ($p>0.05$).

Table 17. The flexibility of fibers using salts as coplasticizers with glycerol in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Glycerol										X			
2% $ZnCl_2$								X					
4% $ZnCl_2$							X						
2% $CaCl_2$								X					
4% $CaCl_2$								X					
2% $ZnCl_2$ & 2% $CaCl_2$								X					
4% Na_2HPO_4								X					
65% humidity													
Glycerol		X											
2% $ZnCl_2$	X												
4% $ZnCl_2$	X												
2% $CaCl_2$	X												
4% $CaCl_2$	X												
2% $ZnCl_2$ & 2% $CaCl_2$	X												
4% Na_2HPO_4	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

salts, fibers treated with zinc chloride had better dry tenacity than treatments with other salts. Zinc might associate with carboxyl and amino groups of soy proteins and form a metal complex. According to cumulative formation constants for metal complexes with glycine, zinc has higher constants (5.52 for $\log K_1$ and 9.96 for $\log K_2$) than calcium (1.38 for $\log K_1$ and 0 for $\log K_2$) (Dean, 1979). The higher constants indicate a stronger association of the coordination complex. However, the fibers became more hygroscopic by addition of these salts. Salt addition significantly decreased the wet tenacity and significantly increased the moisture regain of fibers. The tenacity of these fibers significantly decreased with increasing relative humidity of testing conditions. Treatments with these ions probably increased the osmotic values of the fibers and increased the ionizations of the acidic and basic groups of the protein. The increased ionization increased the solubilities and swellings of the fibers and decreased their wet tenacities.

Other plasticizers examined in extrusion included ethylene glycol, lecithin, monoacetin, diacetin, triacetin, monostearin, monoolein, maltodextrin, chitosan, dioctyl phthalate (DOP), polyvinyl chloride (PVC), polyvinyl ethylene, polyethylene glycol and polyvinyl alcohol (PVA). Ethylene glycol was similar to glycerol as a plasticizer in extrusion. Lecithin, monoacetin, diacetin, triacetin, monostearin, monoolein, maltodextrin, chitosan, dioctyl phthalate (DOP), polyvinyl chloride (PVC), polyvinyl ethylene and polyethylene glycol as plasticizers were not completely compatible with soy proteins and produced short discontinuous fibers that were very weak and brittle. PVA was compatible with soy protein as a plasticizer in the presence of lecithin and water; however, such mixtures needed to be extruded at 115 °C, which gave puffy and brittle fibers.

Plasticizers in wet spinning

Glycerol and oleic acid were tested as plasticizers in wet spinning by using 1016-μ and 386-μ spinnerettes respectively. The formulations of spinning dopes and conditions are listed in Table 18.

The tenacities of wet-spun fibers using glycerol and oleic acid as plasticizers were lower than the tenacities of fibers without a plasticizer (Table 19). The flexibility of fibers using glycerol and oleic acid was only modestly improved (Table 20). Possibly, the glycerol in the protein dopes was extracted into the coagulating solution during acid coagulation. Other plasticizers such as zinc chloride and calcium chloride were tested by mixing with soy protein, sodium hydroxide and water, however; the protein dopes with 0.5% zinc chloride or 0.5% calcium chloride became very viscous gels with viscosity > 320 poise that made wet spinning impossible. The viscosity of protein dopes with zinc chloride or calcium chloride increased as amount of zinc chloride or calcium chloride increased.

Zinc chloride (10%), calcium chloride (10%), combinations of zinc chloride (5%) and calcium chloride (5%) or sodium chloride (10%) were added to the 4% HCl coagulation solution to test the plasticization effects of these ions when added after fiber formation. There were significant differences among three salts in the fiber properties and moisture regain ($p<0.01$). Table 21 shows that fibers treated with combinations of 5% of zinc chloride and 5% of calcium chloride had better tenacity than fibers in zinc chloride or calcium chloride alone. Fibers coagulated in 10% zinc chloride had better flexibility than the other three ion treatments in 11% RH (Table 22). The addition of zinc and calcium chlorides to the coagulation solution increased moisture regain of the fibers, and some of the increased flexibility of these fibers may be caused by plasticization by this moisture.

Table 18. The formulations, pHs, viscosities and coagulation solutions used in wet spinning when testing glycerol and oleic acid as plasticizers

Formulation	I	II	III	IV	V
Soy protein (g)	750	750	750	750	750
Water (Kg)	2.7	2.55	2.4	2.6	2.6
10% NaOH (g)	375	375	375	470	470
Glycerol (g)	0	150	300	0	0
Oleic acid (g)	0	0	0	75	75
Fresh pH	10.45	10.42	10.39	10.58	10.57
Fresh viscosity (poise)	25.50	30.00	30.00	59.00	60.00
1 day aging pH	10.36	10.39	10.37	10.53	10.53
1 day aging viscosity (poise)	57.50	64.00	62.00	150.00	150.00
Coagulation solution	*	*	*	*	**

* means 10% sodium chloride in 4% HCl solution.
** means 10% sodium chloride in 4% H_3PO_4 solution.

IV. Derivatization of Amino and Carboxyl Groups of Soy Proteins

Finishing treatment of fibers by anhydrides

Soy protein fibers that were treated with acetic anhydride or benzoic anhydride after spinning had significantly improved wet tenacity and flexibility (Tables 23-26). Presumably this resulted from derivitization of amine groups. Acylation of soy proteins has been reported to change the conformation of glycinins and increased surface hydrophobicity (Barman et al., 1977). The chemical reaction is illustrated in Figure 10. The higher the concentration of acetic anhydride used, the better the tenacity, elongation and flexibility of fibers ($p< 0.01$). Seemingly, at high concentrations of acetic anhydride in the finishing treatment, there was

Table 19. The properties of wet-spun fibers using glycerol and oleic acid as plasticizers and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
I	415 ± 32^{b}	1.24 ± 0.53^{a}	0.85 ± 0.46^{a}	160 ± 25^{a}	1.09 ± 0.02^{b}
II	586 ± 51^{a}	0.38 ± 0.22^{b}	0.59 ± 0.19^{ab}	55 ± 30^{b}	1.49 ± 0.02^{a}
III	596 ± 58^{a}	0.22 ± 0.13^{b}	0.39 ± 0.12^{b}	36 ± 15^{b}	1.53 ± 0.02^{a}
LSD	59.6	0.42	0.36	29.7	0.054
IV	68 ± 5^{a}	0.26 ± 0.02^{b}	0.22 ± 0.06^{b}	75 ± 18^{b}	1.65 ± 0.04^{a}
V	70 ± 5^{a}	0.72 ± 0.22^{a}	0.39 ± 0.09^{a}	122 ± 25^{a}	1.56 ± 0.03^{a}
LSD	6.8	0.20	0.09	27.7	0.16
65% humidity					
I	430 ± 14^{b}	0.80 ± 0.28^{a}	0.97 ± 0.32^{a}	111 ± 22^{a}	6.58 ± 0.15^{c}
II	672 ± 26^{a}	0.19 ± 0.09^{b}	0.83 ± 0.34^{a}	24 ± 9^{b}	9.23 ± 0.33^{b}
III	677 ± 45^{a}	0.14 ± 0.09^{b}	0.39 ± 0.17^{b}	9 ± 5^{b}	12.42 ± 0.30^{a}
LSD	38.4	0.22	0.35	17.9	0.87
IV	102 ± 5^{a}	0.22 ± 0.11^{a}	0.70 ± 0.26^{b}	37 ± 9^{a}	14.31 ± 0.11^{a}
V	95 ± 4^{b}	0.17 ± 0.05^{a}	1.65 ± 0.82^{a}	19 ± 4^{b}	12.42 ± 0.03^{b}
LSD	5.4	0.12	0.78	8.9	0.35
In water					
I	1037 ± 40^{c}	---	---	---	79.80 ± 0.48^{c}
II	1259 ± 72^{b}	---	---	---	101.73 ± 2.25^{b}
III	1537 ± 41^{a}	---	---	---	107.21 ± 1.51^{a}
LSD	65.4				5.06
IV	124 ± 7^{a}	---	---	---	126.24 ± 2.94^{a}
V	122 ± 7^{a}	---	---	---	119.28 ± 1.61^{a}
LSD	8.9				10.21

--- Values too low to determine.

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

I-V See Table 18.

Table 20. The flexibility of wet-spun fibers using glycerol and oleic acid as plasticizers in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
I												X	
II											X		
III											X		
IV											X		
V											X		
65% humidity													
I					X								
II	X												
III	X												
IV		X											
V		X											

I-V See Table 18.
X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 21. The properties of wet-spun soy protein fibers coagulated in zinc chloride, sodium chloride or calcium chloride acid baths and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
10% NaCl	95 ± 3^{a}	0.68 ± 0.10^{b}	0.5 ± 0.1^{b}	150 ± 12^{a}	1.06 ± 0.06^{d}
10% $ZnCl_2$	78 ± 3^{a}	0.26 ± 0.13^{c}	0.7 ± 0.2^{a}	55 ± 10^{b}	1.47 ± 0.07^{c}
10% $CaCl_2$	76 ± 3^{a}	1.06 ± 0.44^{a}	0.6 ± 0.1^{ab}	143 ± 37^{a}	2.58 ± 0.07^{a}
5% $ZnCl_2$ 5% $CaCl_2$	72 ± 3^{c}	1.06 ± 0.24^{a}	0.6 ± 0.1^{ab}	131 ± 14^{a}	2.00 ± 0.02^{b}
LSD	3.9	0.32	0.2	25.5	0.16
65% humidity					
10% NaCl	105 ± 3^{a}	0.35 ± 0.18^{ab}	0.4 ± 0.1^{b}	68 ± 17^{b}	8.23 ± 0.15^{d}
10% $ZnCl_2$	87 ± 3^{c}	0.25 ± 0.12^{bc}	1.5 ± 0.2^{b}	27 ± 9^{c}	12.61 ± 0.36^{c}
10% $CaCl_2$	98 ± 6^{b}	0.056 ± 0.033^{c}	5.9 ± 3.9^{a}	4 ± 2^{d}	30.08 ± 1.03^{a}
5% $ZnCl_2$ 5% $CaCl_2$	82 ± 4^{d}	0.55 ± 0.25^{a}	0.7 ± 0.3^{b}	84 ± 16^{a}	22.44 ± 0.08^{b}
LSD	4.9	0.20	2.4	15.2	1.53
In water					
10% NaCl	120 ± 3^{a}	---	---	---	83.15 ± 1.43^{d}
10% $ZnCl_2$	108 ± 3^{b}	---	---	---	101.12 ± 1.43^{c}
10% $CaCl_2$	122 ± 4^{a}	---	---	---	213.14 ± 1.76^{a}
5% $ZnCl_2$ 5% $CaCl_2$	101 ± 3^{c}	---	---	---	185.12 ± 1.41^{b}
LSD	3.7				3.85

--- Values too low to determine.

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

Table 22. The flexibility of wet-spun fibers coagulated in zinc chloride, sodium chloride or calcium chloride acid baths in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
10% NaCl													X
10% $ZnCl_2$									X				
10% $CaCl_2$													X
5% $ZnCl_2$ 5% $CaCl_2$												X	
65% humidity													
10% NaCl		X											
10% $ZnCl_2$	X												
10% $CaCl_2$	X												
5% $ZnCl_2$ 5% $CaCl_2$	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 23. The properties of fibers at 11% relative humidity finished by acetic anhydride-acetic acid and benzoic anhydride-acetic acid treatments compared with those in which monoacetin and diacetin replaced glycerol

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
15% Glycerol	113 ± 4^{a}	1.57 ± 0.32^{b}	1.6 ± 0.2^{b}	97 ± 8^{ab}	1.61 ± 0.13^{a}
Acetic anhydride: acetic acid (v/v)					
9: 1	115 ± 2^{a}	2.31 ± 0.13^{a}	4.7 ± 1.2^{a}	105 ± 5^{a}	0.77 ± 0.01^{b}
7: 3	110 ± 2^{b}	1.02 ± 0.12^{c}	0.9 ± 0.3^{c}	102 ± 12^{ab}	0.85 ± 0.04^{b}
5: 5	109 ± 2^{b}	0.80 ± 0.08^{c}	0.8 ± 0.2^{c}	93 ± 9^{b}	0.94 ± 0.02^{b}
LSD	3.1	0.22	0.5	10.9	0.19
Acetic anhydride: acetic acid (v/v)					
9: 1	115 ± 2^{a}	2.31 ± 0.13^{a}	4.7 ± 1.2^{a}	105 ± 5^{a}	0.77 ± 0.01^{b}
Benzoic anhydride: acetic acid (w/w)					
9: 1	111 ± 6^{a}	1.83 ± 0.13^{b}	3.1 ± 1.2^{b}	88 ± 15^{b}	0.85 ± 0.01^{a}
LSD	5.8	0.17	1.3	14.1	0.061
15% Glycerol[d]	115 ± 2^{a}	2.31 ± 0.13^{a}	4.7 ± 1.2^{a}	105 ± 5^{a}	0.77 ± 0.01^{b}
15% Monoacetin	93 ± 3^{c}	0.72 ± 0.09^{b}	1.1 ± 0.4^{b}	65 ± 12^{b}	0.93 ± 0.04^{a}
15% Diacetin	112 ± 2^{b}	0.32 ± 0.13^{c}	0.8 ± 0.2^{b}	40 ± 19^{c}	0.87 ± 0.02^{a}
LSD	2.5	0.15	0.6	16.6	0.08

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

[d] Finished with acetic anhydride: acetic acid (9: 1, v/v).

Table 24. The properties of fibers at 65% relative humidity finished by acetic anhydride-acetic acid and benzoic anhydride-acetic acid treatments compared with those in which monoacetin and diacetin replaced glycerol

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
15% Glycerol	128 ± 2^{c}	0.56 ± 0.06^{c}	73.4 ± 16.6^{a}	25 ± 3^{c}	14.32 ± 0.14^{a}
Acetic anhydride: acetic acid (v/v)					
9: 1	140 ± 3^{a}	1.07 ± 0.12^{a}	1.8 ± 0.8^{b}	113 ± 13^{a}	5.52 ± 0.02^{c}
7: 3	135 ± 4^{b}	0.75 ± 0.27^{b}	0.8 ± 0.2^{b}	100 ± 14^{b}	6.37 ± 0.05^{b}
5: 5	135 ± 4^{b}	0.56 ± 0.08^{c}	0.7 ± 0.2^{b}	95 ± 6^{b}	6.50 ± 0.07^{b}
LSD	4.1	0.18	10.0	12.5	0.23
Acetic anhydride: acetic acid (v/v)					
9: 1	140 ± 3^{a}	1.07 ± 0.12^{a}	1.8 ± 0.8^{b}	113 ± 13^{a}	5.52 ± 0.02^{b}
Benzoic anhydride: acetic acid (w/w)					
9: 1	134 ± 2^{b}	0.64 ± 0.03^{b}	75.5 ± 11.2^{a}	16 ± 3^{b}	6.22 ± 0.04^{a}
LSD	3.7	0.11	10.2	12.7	0.13
15% Glycerol[d]	140 ± 3^{a}	1.07 ± 0.12^{a}	1.8 ± 0.8^{b}	113 ± 13^{a}	5.52 ± 0.02^{c}
15% Monoacetin	101 ± 2^{c}	0.35 ± 0.26^{b}	38.9 ± 26.2^{a}	31 ± 8^{b}	12.41 ± 0.43^{a}
15% Diacetin	118 ± 2^{b}	0.13 ± 0.02^{c}	5.5 ± 2.6^{b}	19 ± 3^{c}	10.29 ± 0.89^{b}
LSD	3.1	0.20	18.7	11.3	1.82

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

[d] Finished by acetic anhydride: acetic acid (9: 1, v/v).

Table 25. The properties of fibers after soaking in water that were finished by acetic anhydride-acetic acid and benzoic anhydride-acetic acid treatments compared with those in which monoacetin and diacetin replaced glycerol

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
15% Glycerol	155 ± 3[a]	0.076 ± 0.023[d]	3.9 ± 2.6[d]	7.3 ± 4.6[a]	88.82 ± 1.13[a]
Acetic anhydride: acetic acid (v/v)					
9: 1	145 ± 2[b]	0.58 ± 0.05[a]	89.0 ± 4.9[a]	5.9 ± 1.0[a]	16.61 ± 0.04[d]
7: 3	140 ± 2[c]	0.45 ± 0.07[b]	77.3 ± 9.9[b]	0.8 ± 0.3[b]	18.67 ± 0.10[c]
5: 5	139 ± 2[c]	0.34 ± 0.04[c]	32.8 ± 11.8[c]	0.8 ± 0.3[b]	21.05 ± 0.88[b]
LSD	2.8	0.07	9.9	2.8	2.07
Acetic anhydride: acetic acid (v/v)					
9: 1	145 ± 2[a]	0.58 ± 0.05[a]	89.0 ± 4.9[a]	5.9 ± 1.0[a]	16.61 ± 0.04[b]
Benzoic anhydride: acetic acid (w/w)					
9: 1	142 ± 5[a]	0.30 ± 0.03[b]	66.5 ± 9.2[b]	2.3 ± 0.5[b]	19.78 ± 0.49[a]
LSD	4.6	0.05	9.5	1.1	1.94
15% Glycerol[d]	145 ± 2[a]	0.580 ± 0.050[a]	89.0 ± 4.9[a]	5.9 ± 1.0[a]	16.61 ± 0.04[c]
15% Monoacetin	124 ± 2[c]	0.049 ± 0.024[b]	5.6 ± 3.0[b]	4.6 ± 1.3[a]	79.04 ± 1.77[a]
15% Diacetin	133 ± 2[b]	0.015 ± 0.004[b]	1.8 ± 0.5[b]	2.9 ± 0.9[b]	64.65 ± 1.54[b]
LSD	2.5	0.040	4.1	1.4	4.37

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

[d] Finished by acetic anhydride: acetic acid (9: 1, v/v).

Table 26. The flexibility of fibers finished by acetic anhydride-acetic acid and benzoic anhydride-acetic acid and fibers in which monoacetin and diacetin replace glycerol in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
15% Glycerol										X			
Acetic anhydride: acetic acid (v/v)													
9: 1		X											
7: 3		X											
5: 5			X										
15% Monoacetin											X		
15% Diacetin													X
Benzoic anhydride: acetic acid (w/w)													
9: 1		X											
65% humidity													
15% Glycerol		X											
Acetic anhydride: acetic acid (v/v)													
9: 1	X												
7: 3	X												
5: 5	X												
15% Monoacetin	X												
15% Diacetin					X								
Benzoic anhydride: acetic acid (w/w)													
9: 1	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

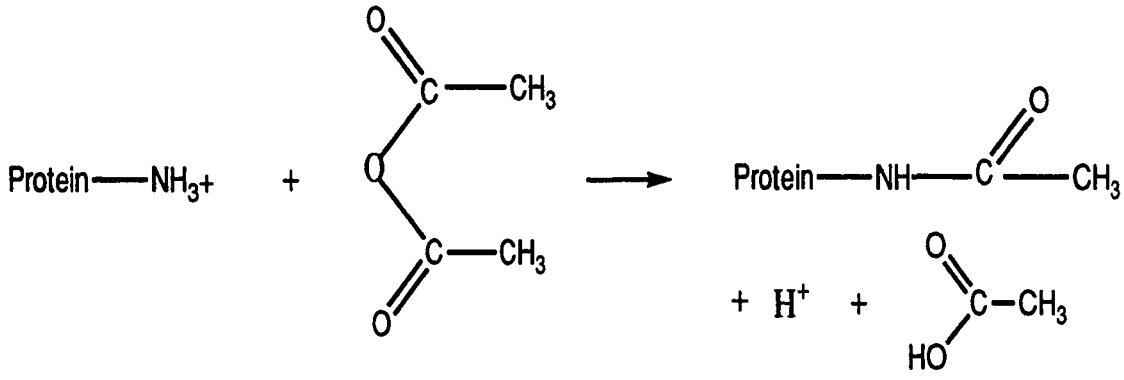


Figure 10. Acylation of ε-amino groups of proteins by acetic anhydride.

good penetration into fibers and the charged amino groups were readily acylated. There were significant differences between acetic anhydride and benzoic anhydride finishing treatments ($p<0.01$). Benzoic anhydride treatment improved the fibers less than acetic anhydride treatment, possibly because the benzoic anhydride is larger and penetrates the fiber interior less readily than acetic anhydride. Since glycerol was present, it was possible the effect of anhydrides on the fibers was to acylate the glycerol. To test this possibility, monoacetin and diacetin were incorporated in the extrusion mixtures in place of glycerol. Fibers using monoacetin and diacetin were softer and weaker than fibers containing glycerol as a plasticizer and glycerol-containing fibers finished by acetic anhydride. Monoacetin performed better than diacetin. Table 26 shows fibers made with monoacetin and diacetin replacing glycerol had poorer flexibilities than finished fibers and fibers plasticized with glycerol. This showed that the effect of acetic anhydride during the finishing treatment was not caused by acylation of glycerol.

Scanning electron micrographs of fibers finished with acetic anhydride are shown in Figure 28 of the appendix. They showed a smooth surface and tight structure typical of fibers with good tenacity.

The moisture regain of fibers was significantly decreased after fibers were finished by anhydrides. This indicated acylation blocked the polar groups of soy proteins and made them less polar, which was one way to improve their wet tenacity.

Finishing treatment of fibers by acetaldehyde

Formaldehyde was often used as a finishing treatment for fibers during the 1930's and the 40's. Now formaldehyde is considered a carcinogen. Acetaldehyde was tested as a possible replacement for formaldehyde. Acetaldehyde is expected to block amine groups by forming a Schiff base. The chemical reaction is illustrated in Figure 10.

Fibers finished by a treatment with acetaldehyde had significantly improved tenacities ($p<0.01$). The tenacity increased with increasing concentrations of acetaldehyde (Table 27). There were no differences in flexibilities among fibers finished by various concentrations of acetaldehyde (Table 28). The moisture regains of acetaldehyde-finished fibers were significantly decreased. This was in agreement with the effect of acetic anhydride and indicated that acetaldehyde blocked polar groups such as amines and caused the fibers to become less polar.

Fibers produced with soy protein modified by acetic anhydride and acetaldehyde prior to extrusion compared with the same fibers after a finishing treatment with acetic anhydride after extrusion

Tables 23 to 25 show that finishing soy protein fibers using 1: 1 and 7: 3 ratios of acetic anhydride-acetic acid improved fiber tenacity less than finishing the treatment using a 9: 1 ratio of acetic anhydride-acetic acid. The fibers finished with 9: 1 of acetic anhydride-acetic acid had significantly improved properties. To study this treatment further, soy proteins were modified by a mild acetic anhydride treatment before extrusion. This treatment was expected to change the molecular conformation and hydrophobicity. However, soy proteins modified by

Table 27. The properties of soy protein fibers finished with various concentrations of acetaldehyde for 30 min and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
Soy fiber	113 ± 4^{a}	1.57 ± 0.32^{b}	1.6 ± 0.2^{a}	97 ± 8^{c}	1.61 ± 0.13^{a}
10% acetaldehyde	104 ± 3^{c}	1.44 ± 0.33^{b}	0.7 ± 0.1^{c}	232 ± 29^{b}	1.00 ± 0.06^{b}
15% acetaldehyde	107 ± 3^{bc}	1.74 ± 0.46^{ab}	0.8 ± 0.1^{bc}	240 ± 23^{ab}	0.97 ± 0.01^{b}
20% acetaldehyde	108 ± 3^{b}	1.81 ± 0.32^{ab}	0.8 ± 0.1^{bc}	249 ± 30^{ab}	0.87 ± 0.04^{bc}
25% acetaldehyde	110 ± 3^{b}	2.19 ± 0.79^{a}	0.9 ± 0.2^{b}	267 ± 38^{a}	0.76 ± 0.03^{c}
LSD	3.6	0.57	0.2	32.4	0.17
65% humidity					
Soy fiber	128 ± 2^{a}	0.56 ± 0.06^{c}	73.4 ± 16.6^{a}	25 ± 3^{d}	14.32 ± 0.14^{a}
10% acetaldehyde	122 ± 5^{b}	0.46 ± 0.10^{c}	0.7 ± 0.1^{b}	80 ± 20^{c}	9.99 ± 0.45^{b}
15% acetaldehyde	124 ± 3^{ab}	0.69 ± 0.32^{bc}	0.7 ± 0.1^{b}	96 ± 8^{bc}	9.30 ± 0.02^{c}
20% acetaldehyde	122 ± 3^{b}	0.85 ± 0.28^{ab}	0.8 ± 0.1^{b}	115 ± 25^{b}	9.08 ± 0.01^{c}
25% acetaldehyde	123 ± 3^{b}	1.02 ± 0.27^{a}	0.8 ± 0.1^{b}	153 ± 17^{a}	8.34 ± 0.17^{d}
LSD	3.7	0.28	8.8	19.8	0.58
In water					
Soy fiber	155 ± 3^{a}	0.076 ± 0.023	3.9 ± 2.6^{c}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
10% acetaldehyde	156 ± 4^{a}	0.12 ± 0.03^{cd}	16.7 ± 5.8^{b}	2.0 ± 0.5^{c}	44.67 ± 0.07^{b}
15% acetaldehyde	158 ± 5^{a}	0.14 ± 0.03^{bc}	29.3 ± 5.6^{a}	2.7 ± 0.4^{bc}	42.82 ± 0.06^{c}
20% acetaldehyde	159 ± 4^{a}	0.17 ± 0.03^{ab}	29.5 ± 2.7^{a}	3.6 ± 0.6^{bc}	41.72 ± 0.13^{c}
25% acetaldehyde	158 ± 5^{a}	0.20 ± 0.04^{a}	31.1 ± 6.8^{a}	4.7 ± 1.7^{b}	40.27 ± 0.04^{d}
LSD	4.7	0.046	5.9	2.5	1.31

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 28. The flexibility of fibers finished with various concentrations of acetaldehyde for 30 min in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
10% acetaldehyde								X					
15% acetaldehyde								X					
20% acetaldehyde								X					
25% acetaldehyde								X					
65% humidity													
Soy fiber		X											
10% acetaldehyde								X					
15% acetaldehyde								X					
20% acetaldehyde								X					
25% acetaldehyde								X					

X Fibers could be looped around the smallest diameter glass rod without breaking.

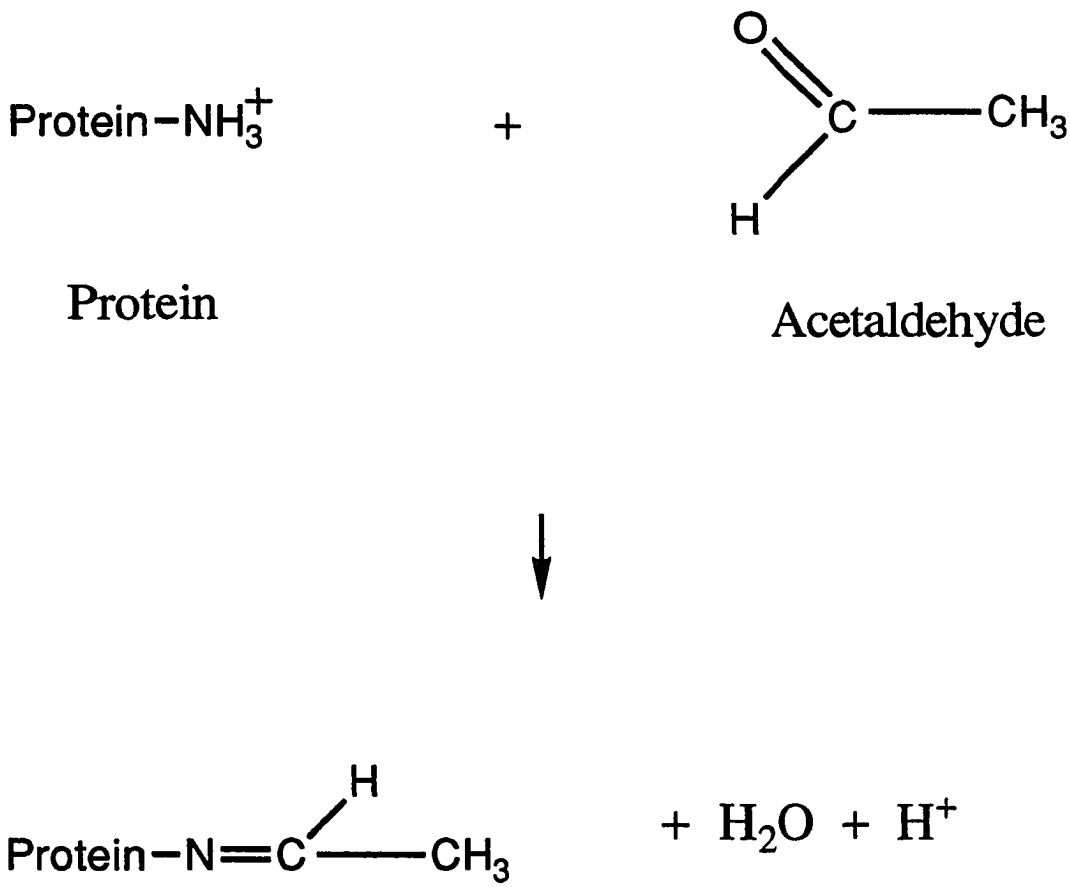


Figure 10. Chemical reaction of acetaldehyde and protein.

5, 7.5 and 12.5% of acetic anhydride-acetic acid in xylene solution before extrusion did not give fibers that were consistently better than fibers from unmodified soy protein. The results are given in Tables 29-32. Among the fibers, tenacity was positively correlated with modulus (r= 0.80) and negatively correlated with linear density (r= -0.75) and moisture regain (r= -0.61). Table 33 shows that there were significant differences among the testing humidity, fiber finishing treatment and protein modification in the measurements of tenacity, elongation,

Table 29. The properties of fibers at 11% relative humidity made from soy protein treated with xylene, acetic anhydride and acetaldehyde before extrusion compared with the same treatments finished with acetic anhydride after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	113 ± 4^{b}	1.57 ± 0.32^{a}	1.6 ± 0.2^{c}	97 ± 8^{a}	1.61 ± 0.13^{a}
Protein modified before extrusion					
Xylene	119 ± 2^{a}	0.85 ± 0.20^{d}	2.6 ± 1.4^{ab}	52 ± 5^{e}	1.21 ± 0.08^{b}
5% acetic anhydride	120 ± 2^{a}	1.40 ± 0.07^{ab}	3.1 ± 0.5^{a}	76 ± 8^{c}	1.31 ± 0.01^{b}
7.5% acetic anhydride	119 ± 2^{a}	1.07 ± 0.06^{c}	2.2 ± 0.3^{bc}	57 ± 5^{de}	1.29 ± 0.05^{b}
12.5% acetic anhydride	118 ± 2^{a}	0.98 ± 0.06^{cd}	1.8 ± 0.2^{c}	64 ± 6^{d}	1.25 ± 0.03^{b}
10% acetaldehyde	118 ± 3^{a}	1.34 ± 0.23^{b}	2.0 ± 0.4^{bc}	85 ± 6^{b}	0.96 ± 0.04^{c}
LSD	3.0	0.22	0.8	7.3	0.17
Acetic anhydride finished after extrusion					
Soy fiber	115 ± 2^{c}	2.31 ± 0.13^{a}	4.7 ± 1.2^{a}	105 ± 5^{c}	0.77 ± 0.01^{bc}
Xylene	118 ± 3^{d}	2.01 ± 0.16^{ab}	3.6 ± 1.5^{b}	96 ± 9^{c}	0.81 ± 0.01^{ab}
5% acetic anhydride	116 ± 2^{bc}	1.99 ± 0.57^{ab}	1.3 ± 0.3^{c}	151 ± 13^{a}	0.82 ± 0.03^{a}
7.5% acetic anhydride	113 ± 2^{c}	1.96 ± 0.88^{ab}	1.5 ± 0.6^{c}	132 ± 22^{b}	0.76 ± 0.01^{c}
12.5% acetic anhydride	109 ± 2^{d}	1.67 ± 0.77^{b}	1.4 ± 0.6^{c}	121 ± 6^{b}	0.69 ± 0.01^{d}
10% acetaldehyde	122 ± 3^{a}	2.23 ± 0.15^{ab}	3.1 ± 0.6^{b}	104 ± 7^{c}	0.66 ± 0.03^{d}
LSD	2.8	0.64	1.0	15.7	0.05

[a-e] Values within each column with same the superscript are not significantly different ($p>0.05$).

Table 30. The properties of fibers at 65% relative humidity made from soy protein treated with xylene, acetic anhydride and acetaldehyde before extrusion compared with the same treatments finished with acetic anhydride after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	128 ± 2^{b}	0.56 ± 0.06^{a}	73.4 ± 16.6^{a}	25 ± 3^{a}	14.32 ± 0.14^{a}
Protein modified before extrusion					
Xylene	139 ± 5^{a}	0.17 ± 0.01^{e}	8.1 ± 2.2^{d}	7 ± 1^{d}	13.89 ± 0.14^{bc}
5% acetic anhydride	131 ± 3^{b}	0.41 ± 0.03^{b}	48.3 ± 13.7^{b}	15 ± 2^{b}	14.14 ± 0.14^{ab}
7.5% acetic anhydride	129 ± 2^{b}	0.33 ± 0.03^{c}	44.9 ± 11.5^{b}	13 ± 2^{bc}	14.03 ± 0.13^{ab}
12.5% acetic anhydride	128 ± 2^{b}	0.27 ± 0.05^{d}	26.4 ± 10.7^{c}	12 ± 3^{bc}	13.95 ± 0.14^{bc}
10% acetaldehyde	130 ± 3^{b}	0.26 ± 0.03^{d}	10.4 ± 3.9^{d}	11 ± 2^{c}	13.66 ± 0.15^{c}
LSD	3.2	0.05	13.0	2.7	0.35
Acetic anhydride finished after extrusion					
Soy fiber	140 ± 3^{ab}	1.07 ± 0.12^{a}	1.8 ± 0.8^{a}	113 ± 13^{a}	5.52 ± 0.02^{a}
Xylene	140 ± 3^{ab}	0.52 ± 0.11^{c}	0.7 ± 0.4^{b}	91 ± 6^{bc}	4.87 ± 0.01^{d}
5% acetic anhydride	140 ± 2^{ab}	0.70 ± 0.11^{b}	0.9 ± 0.3^{b}	103 ± 7^{ab}	5.19 ± 0.01^{b}
7.5% acetic anhydride	139 ± 2^{ab}	0.61 ± 0.05^{bc}	0.9 ± 0.3^{b}	95 ± 9^{bc}	5.04 ± 0.02^{c}
12.5% acetic anhydride	138 ± 3^{b}	0.57 ± 0.04^{bc}	0.9 ± 0.3^{b}	90 ± 10^{c}	4.91 ± 0.02^{d}
10% acetaldehyde	141 ± 2^{a}	0.99 ± 0.24^{a}	1.1 ± 0.2^{b}	114 ± 17^{a}	4.30 ± 0.05^{e}
LSD	3.1	0.15	0.5	13.2	0.06

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 31. The properties after soaking in water of fibers made from soy protein treated with xylene, acetic anhydride and acetaldehyde before extrusion compared with the same treatments finished with acetic anhydride after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	155 ± 3^{a}	0.076 ± 0.023^{a}	3.9 ± 2.6^{a}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
Protein modified before extrusion					
Xylene	150 ± 2^{bc}	0.031 ± 0.024^{b}	2.2 ± 1.7^{ab}	2.8 ± 1.4^{bc}	83.21 ± 0.99^{c}
5% acetic anhydride	149 ± 4^{c}	0.046 ± 0.022^{ab}	1.6 ± 0.9^{b}	5.3 ± 1.1^{ab}	88.69 ± 1.27^{ab}
7.5% acetic anhydride	145 ± 3^{d}	0.031 ± 0.021^{b}	1.3 ± 0.8^{b}	3.1 ± 1.6^{bc}	86.99 ± 0.92^{ab}
12.5% acetic anhydride	140 ± 2^{e}	0.022 ± 0.013^{b}	1.1 ± 0.7^{b}	1.9 ± 0.5^{c}	86.04 ± 1.37^{b}
10% acetaldehyde	153 ± 3^{ab}	0.034 ± 0.023^{b}	2.1 ± 1.1^{b}	1.4 ± 0.5^{c}	79.16 ± 0.85^{d}
LSD	3.6	0.036	1.7	2.5	2.70
Acetic anhydride finished after extrusion					
Soy fiber	145 ± 2^{a}	0.58 ± 0.05^{a}	89.0 ± 4.9^{ab}	5.9 ± 1.0^{a}	16.61 ± 0.04^{a}
Xylene	143 ± 2^{b}	0.45 ± 0.12^{b}	72.5 ± 24.5^{c}	3.7 ± 1.0^{c}	16.02 ± 0.34^{a}
5% acetic anhydride	142 ± 2^{bc}	0.53 ± 0.04^{ab}	90.9 ± 2.6^{a}	3.8 ± 0.9^{c}	16.83 ± 0.58^{a}
7.5% acetic anhydride	141 ± 2^{cd}	0.51 ± 0.08^{ab}	84.7 ± 14.1^{abc}	4.4 ± 0.8^{bc}	14.71 ± 0.42^{b}
12.5% acetic anhydride	140 ± 2^{d}	0.47 ± 0.04^{b}	80.4 ± 8.1^{abc}	5.1 ± 0.9^{ab}	14.63 ± 0.54^{b}
10% acetaldehyde	140 ± 2^{d}	0.44 ± 0.12^{b}	73.7 ± 16.2^{bc}	4.1 ± 0.7^{bc}	13.03 ± 0.76^{c}
LSD	1.8	0.10	16.4	1.1	1.29

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 32. The flexibility of fibers made from soy protein treated with xylene, acetic anhydride and acetaldehyde before extrusion compared with the same treatments finished with acetic anhydride after extrusion in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
Xylene										X			
5% acetic anhydride										X			
7.5% acetic anhydride										X			
12.5% acetic anhydride										X			
10% acetaldehyde										X			
Acetic anhydride finished after extrusion													
Soy fiber		X											
Xylene			X										
5% acetic anhydride		X											
7.5% acetic anhydride		X											
12.5% acetic anhydride			X										
10% acetaldehyde		X											
65% humidity													
Soy fiber		X											
Xylene	X												
5% acetic anhydride	X												
7.5% acetic anhydride	X												
12.5% acetic anhydride	X												
10% acetaldehyde	X												
Acetic anhydride finished after extrusion													
Soy fiber	X												
Xylene	X												
5% acetic anhydride	X												
7.5% acetic anhydride	X												
12.5% acetic anhydride		X											
10% acetaldehyde	X												

Fibers could be looped around the smallest diameter glass rod without breaking.

Table 33. The significant differences among testing conditions, fiber finishing and protein modification on physical properties of soy fibers

	Linear Density	Tenacity	Extension	Modulus	Moisture Regain
Testing humidity	**	**	**	**	**
Fiber finishing	NS	**	**	**	**
Protein modification	**	**	**	**	**

** Significant at $p < 0.01$ level of probability.
NS Not significant at $p > 0.05$.

modulus and moisture regain ($p<0.01$). There were no significant differences among fiber finishing treatments in linear density ($p>0.85$).

Finishing treatment by acetic anhydride significantly increased tenacity and flexibility and decreased moisture regain (Tables 29-32). Xylene was used as one of the control treatments because the lower concentrations of solutions of acetic anhydride-acetic acid was diluted with xylene. Xylene treatment reduced the tenacity of the soy fibers. The tenacities of acetic anhydride-modified fibers were greater than those of xylene-treated fibers ($p<0.01$). Probably, xylene which is a non-polar solvent, changed in the conformation of soy protein. However, the tenacity of unmodified control soy fiber was greater than those of fibers made from protein modified with acetic anhydride or acetaldehyde before extrusion. The tenacity of fibers made from acetic anhydride modified protein decreased with increasing concentrations of acetic anhydride-acetic acid. Modification of soy proteins with more than 15% of acetic anhydride in xylene or 20% of acetaldehyde gave proteins that did not produce fibers on extrusion.

Scanning electron micrographs of fibers made from acetic anhydride treated protein are shown in Figure 27 of the appendix. Fibers made from acetic anhydride treated protein

exhibited a rougher surface and less tightly packed structures in cross sections than unmodified control soy fibers. In general, weak fibers exhibited a rough surface and voids inside the fibers instead of a smooth surface and the tightly packed structures typical of strong fibers.

Controls, xylene-, acetic anhydride- and acetaldehyde-modified fibers had significantly improved properties after finishing with a second 9: 1(v/v) acetic anhydride-acetic acid treatment after extrusion ($p<0.01$).

In all three testing humidities, the tenacities of fibers made from control and acetic anhydride- and acetaldehyde-modified proteins significantly increased after the finishing treatments. Probably, this was because the finishing treatment with acetic anhydride chemically modified the charged amino groups of soy protein, increased fiber surface hydrophobicity and made fibers less polar and water soluble.

In the wet condition, elongation as well as tenacity was significantly improved by the acetic anhydride finishing treatment. Presumably under wet conditions, water plasticized the fibers which were held together by increasing non-polar interactions.

Titrations of the fibers given various treatments showed that soy protein treated with acetic anhydride or acetaldehyde before or after extrusion contained fewer titratible groups than control fibers (Figures 12-14) ($p<0.01$). This result showed that acetic anhydride finished fibers had about 46% of their titratible groups derivatized. The soy proteins modified before extrusion by 5, 7.5 and 12.5% acetic-anhydride and 10% acetaldehyde had about 22, 28, 35 and 23%, respectively, of their titratible groups derivatized. Figures 15 and 16 show that the moisture regains of acetic anhydride-finished fibers significantly decreased, and the moisture regain of fibers made from acetic anhydride-modified protein decreased as the concentration of acetic anhydride in the treatment increased ($p<0.01$). These all indicated that acetic anhydride and acetaldehyde modified polar groups to make them less polar.

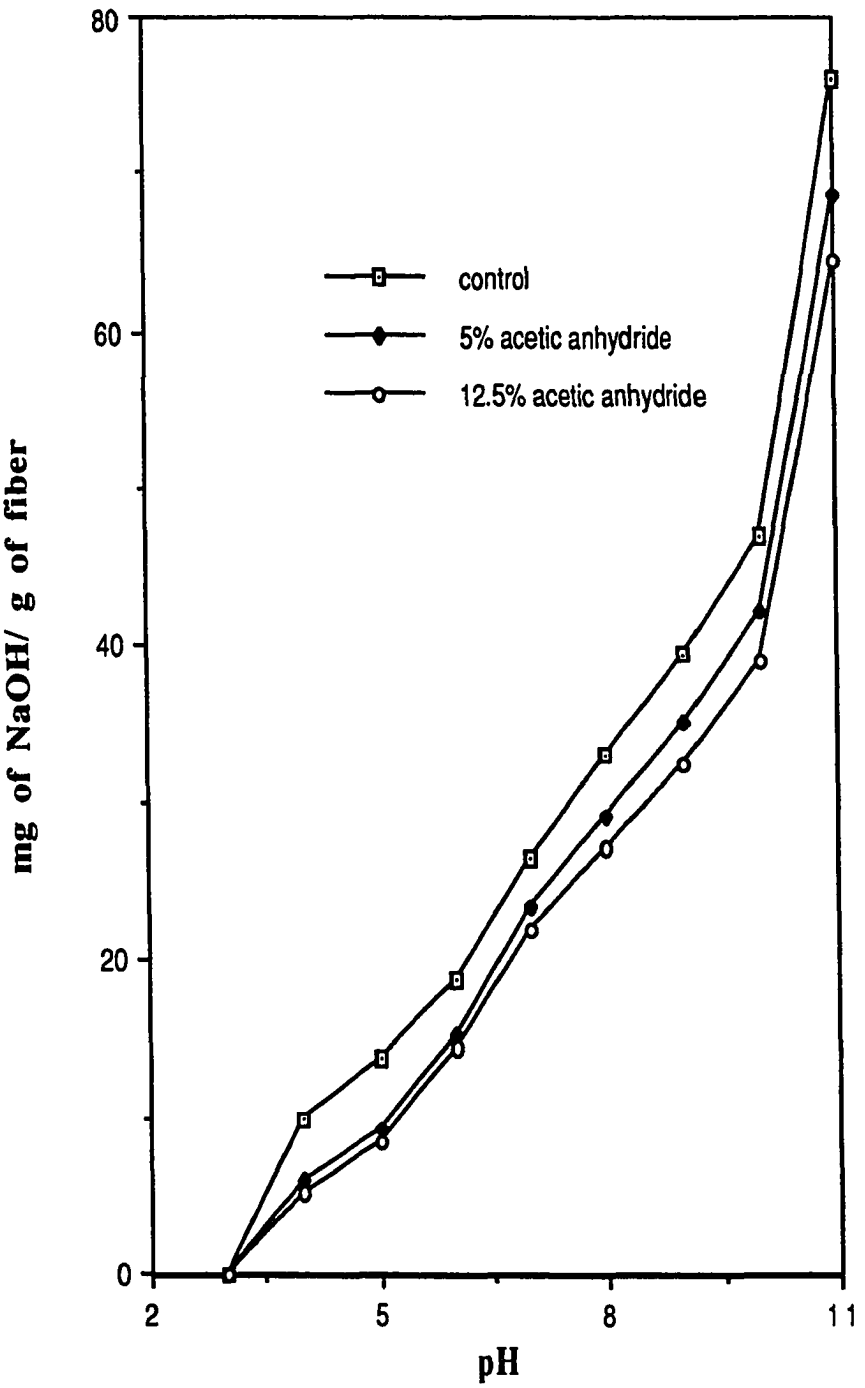


Figure 12. Titration curves of control fibers and fibers made form proteins modified with 5% or 12.5% acetic anhydride.

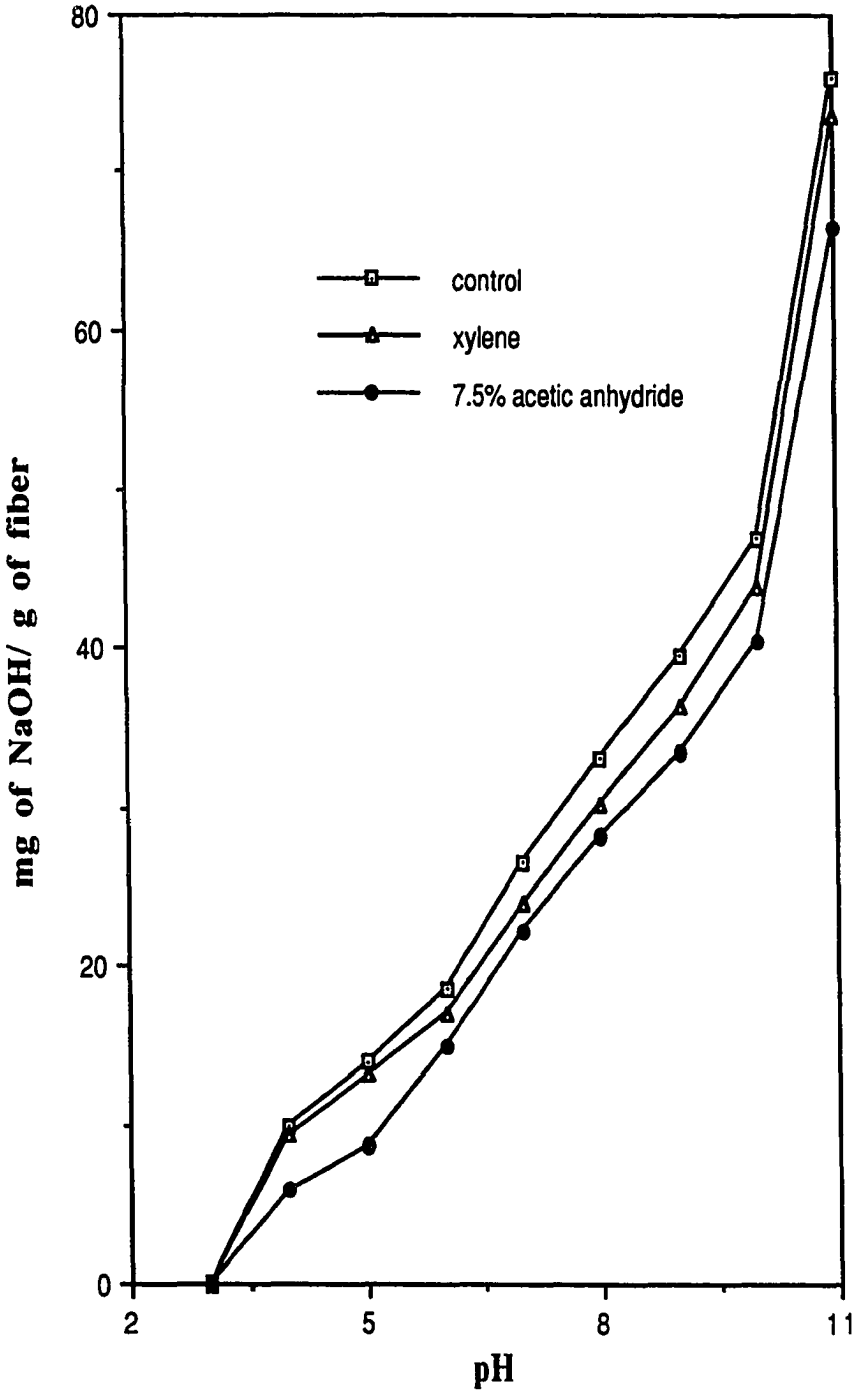


Figure 13. Titration curves of control fibers and fibers made form protein that was xylene-treated or modified with 7.5% acetic anhydride.

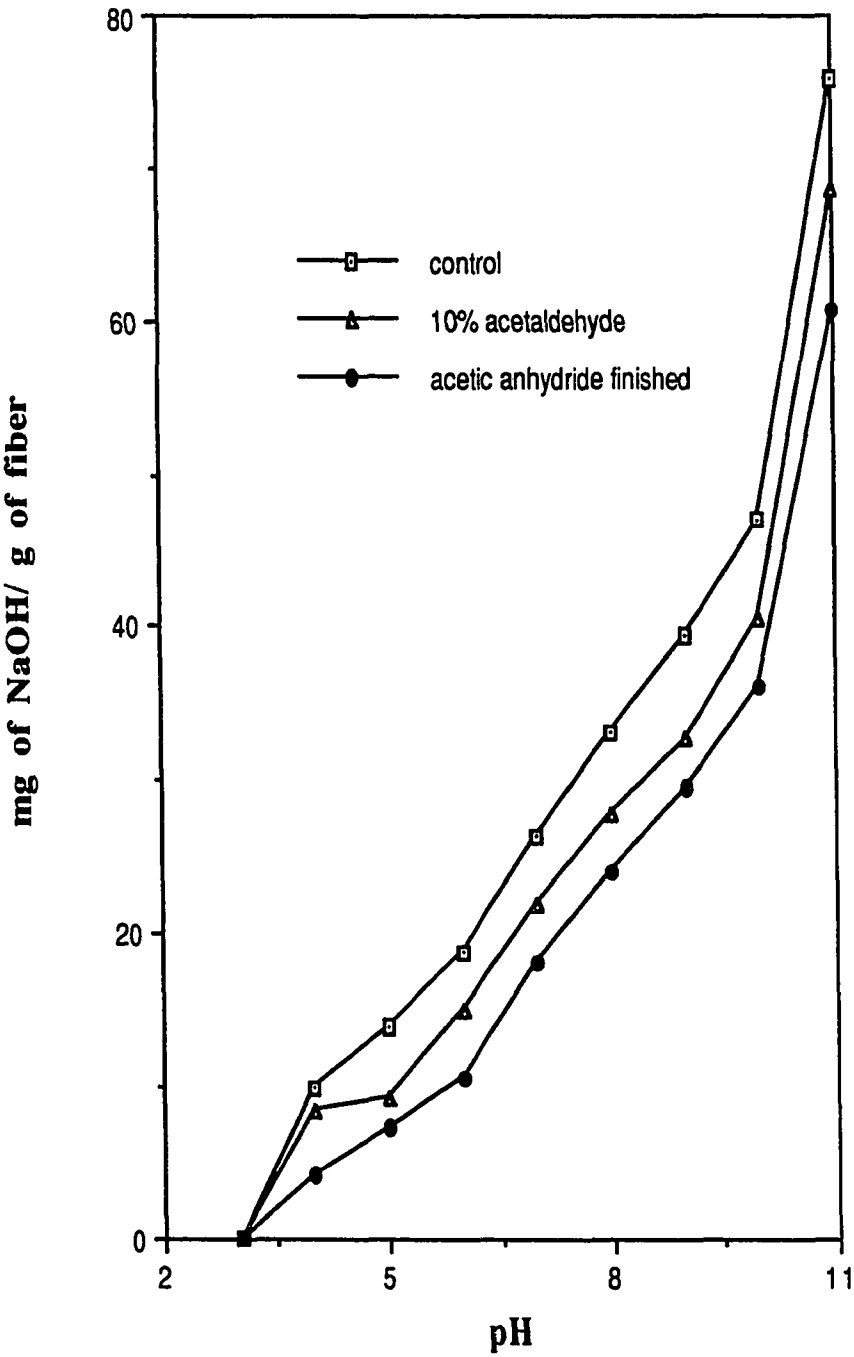


Figure 14. Titration curves of control fibers, fibers made form protein modified with 10% acetaldehyde and control fibers finished with acetic anhydride.

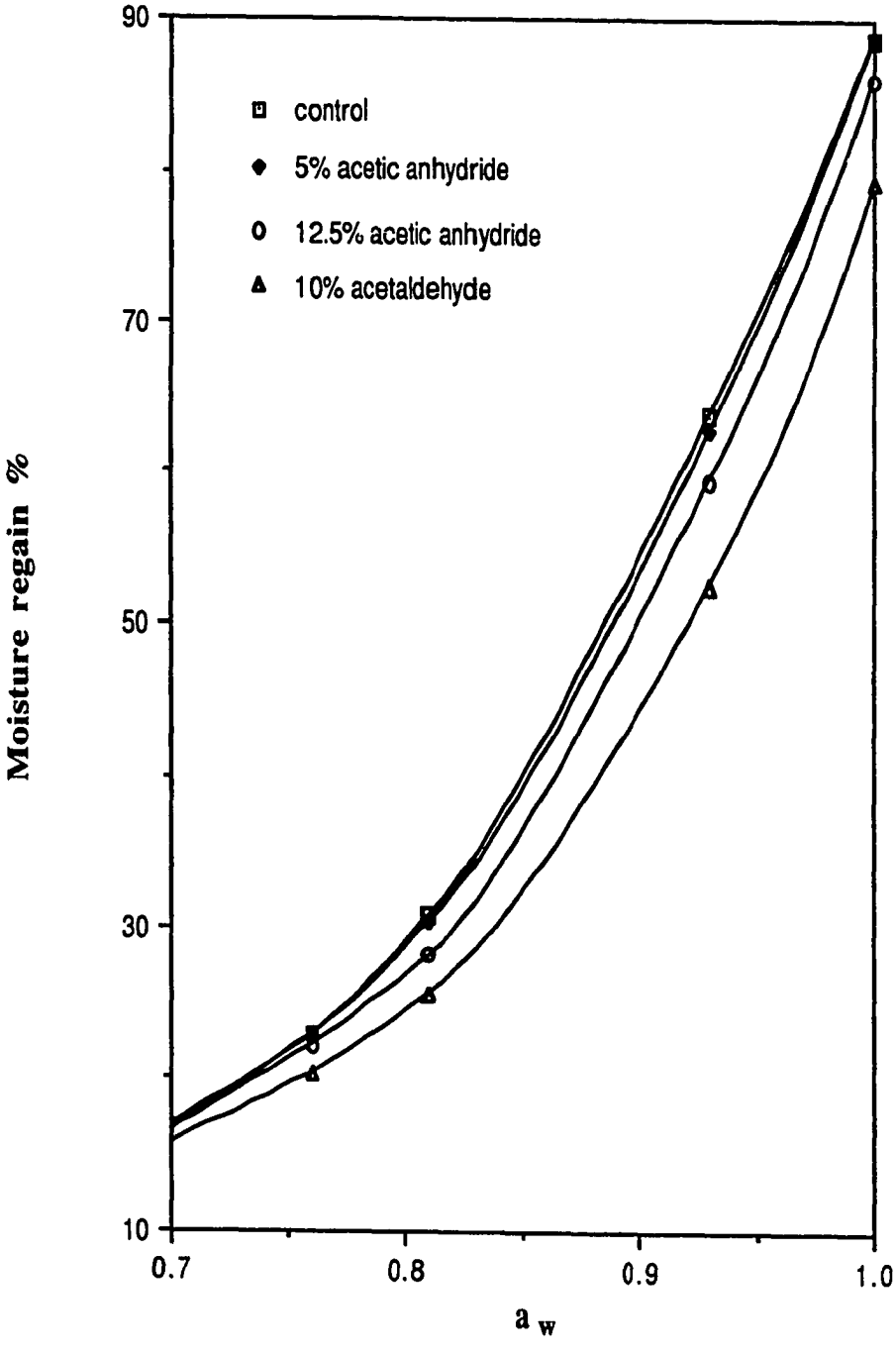


Figure 15. Moisture regain curves of control fibers, fibers made form proteins modified with 5% and 12.5% acetic anhydride or 10% acetaldehyde.

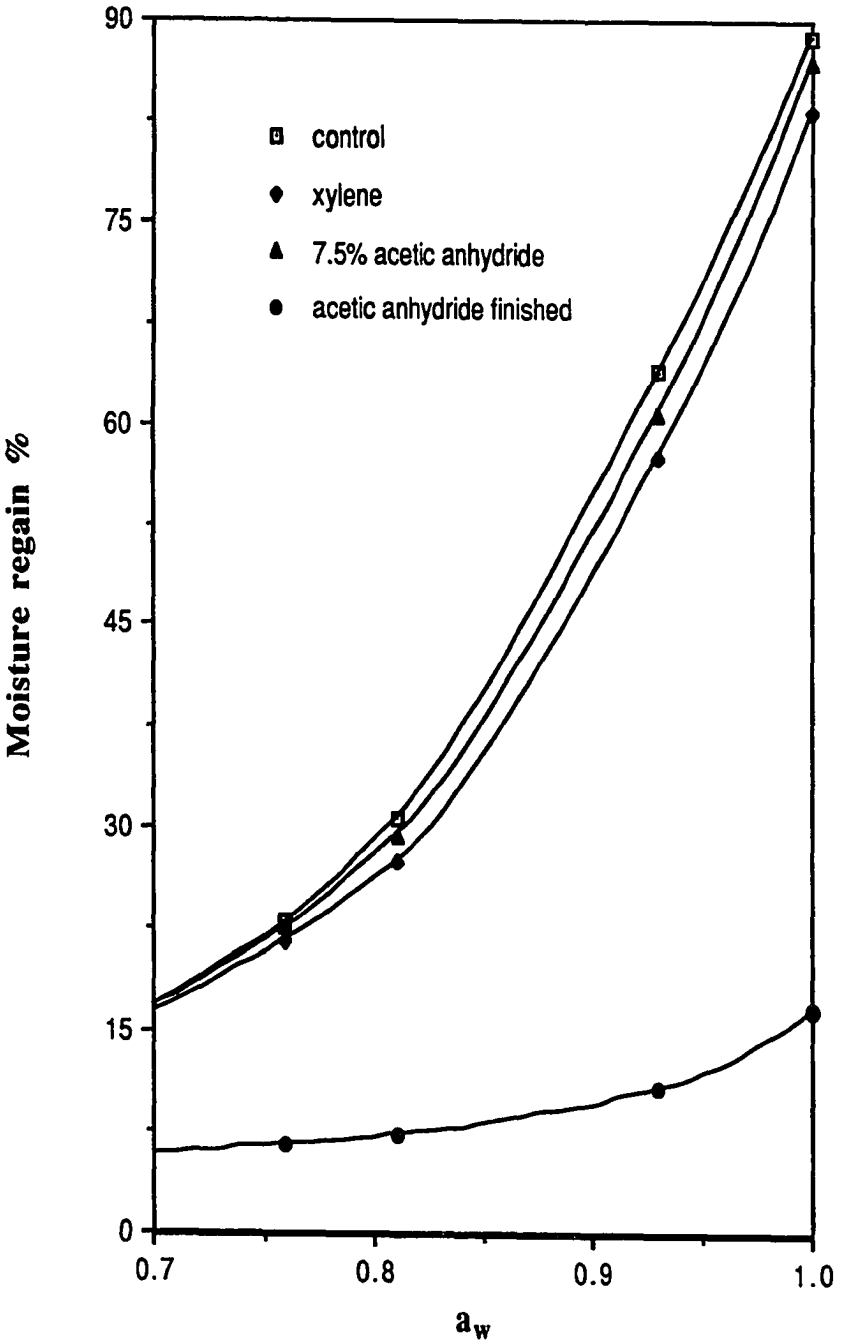


Figure 16. Moisture regain curves of control fibers and fibers made form proteins that was xylene-treated or modified with 7.5% acetic anhydride and control fibers finished with acetic anhydride.

Alcohol esterified fibers vs. fibers finished by acetic anhydride

Soy protein contains considerable proportions of polar amino acids such as glutamic acid and aspartic acid. These polar groups probably do not favor formation of fibers with good tenacity and diminish the wet tenacity of fibers by attracting water. Therefore, soy proteins were esterified with ethylene glycol, butanol or propanol to block and modify these carboxyl groups before extrusion to form fibers. The water of esterification was removed by using benzene azeotropic distillation. These esterified fibers also were subjected to a finishing treatment with acetic anhydride-acetic acid (9: 1, v/v). The results are given in Tables 34-36. There were significant differences of fiber properties ($p<0.01$) among alcohols tested, acetic anhydride finishing treatment and testing humidity.

Soy proteins esterified with butanol exhibited the best tenacity among the alcohols tested. All the esterified fibers had significantly lower tenacities than those of unmodified soy fibers (Tables 34-36). The flexibility of the esterified fibers and esterified fibers finished by acetic anhydride increased as the moisture increased (Table 37). Acetic anhydride finishing treatments of all esterified fibers showed significant improvements in fiber properties ($p<0.01$). According to the titration results, esterified fibers had about 11% of their carboxyl groups derivatized (Figure 17). There were no significant differences in titration curves among the fibers made from protein esterified by ethylene glycol, propanol and butanol ($p>0.31$). Fibers made from butanol-esterified protein and finished with acetic anhydride had about 47% of their titratible groups derivatized ($p<0.01$). The results also showed that the moisture regain significantly decreased because esterification and acetic anhydride blocked carboxyl and amino groups. Possibly, the conformation changes and denaturation of soy proteins occurred during the benzene azeotropic distillation to remove the water. The acid catalyst used in esterification may have caused some hydrolysis of peptides bonds. These effects could cause the production of weaker fibers.

Table 34. The properties of fibers at 11% relative humidity made form soy proteins esterified with ethylene glycol, butanol or propanol before extrusion compared with the same treatments finished with acetic anhydride after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	113 ± 4^{bc}	1.57 ± 0.32^{a}	1.6 ± 0.2^{b}	97 ± 8^{b}	1.61 ± 0.13^{a}
Ethylene glycol	112 ± 4^{c}	0.56 ± 0.12^{b}	2.9 ± 1.2^{a}	34 ± 9^{c}	1.12 ± 0.06^{b}
Butanol	119 ± 3^{a}	0.75 ± 0.12^{b}	0.7 ± 0.2^{c}	119 ± 20^{a}	1.06 ± 0.07^{b}
Propanol	117 ± 3^{ab}	0.57 ± 0.08^{b}	0.7 ± 0.2^{c}	44 ± 4^{c}	1.15 ± 0.07^{b}
LSD	3.9	0.22	0.8	14.1	0.24
Acetic anhydride finished					
Soy fiber	115 ± 2^{bc}	2.31 ± 0.13^{a}	4.7 ± 1.2^{a}	105 ± 5^{b}	0.77 ± 0.01^{a}
Ethylene glycol	113 ± 2^{c}	1.77 ± 0.38^{b}	2.0 ± 0.6^{b}	102 ± 8^{b}	0.75 ± 0.01^{ab}
Butanol	117 ± 4^{b}	2.05 ± 0.61^{ab}	1.5 ± 0.4^{b}	145 ± 5^{a}	0.72 ± 0.01^{bc}
Propanol	120 ± 2^{a}	1.65 ± 0.35^{b}	1.7 ± 0.4^{b}	105 ± 5^{b}	0.69 ± 0.01^{c}
LSD	2.7	0.49	0.7	7.0	0.04

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 35. The properties of fibers at 65% relative humidity made form soy proteins esterified with ethylene glycol, butanol or propanol before extrusion compared with the same treatments finished with acetic anhydride after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	128 ± 2^{b}	0.56 ± 0.06^{a}	73.4 ± 16.6^{a}	25 ± 3^{a}	14.32 ± 0.14^{a}
Ethylene glycol	133 ± 5^{a}	0.14 ± 0.01^{c}	10.4 ± 3.2^{b}	6 ± 1^{b}	13.76 ± 0.15^{b}
Butanol	130 ± 4^{ab}	0.49 ± 0.09^{b}	11.1 ± 3.4^{b}	22 ± 3^{a}	12.84 ± 0.04^{c}
Propanol	129 ± 3^{ab}	0.15 ± 0.03^{c}	6.6 ± 1.5^{b}	23 ± 6^{a}	12.92 ± 0.03^{c}
LSD	4.4	0.06	10.4	4.3	0.29
Acetic anhydride finished					
Soy fiber	140 ± 3^{a}	1.07 ± 0.12^{a}	1.8 ± 0.8^{a}	113 ± 13^{a}	5.52 ± 0.02^{a}
Ethylene glycol	134 ± 1^{b}	0.43 ± 0.05^{c}	1.7 ± 0.4^{a}	18 ± 4^{d}	4.83 ± 0.05^{b}
Butanol	134 ± 4^{b}	0.67 ± 0.18^{b}	1.7 ± 0.1^{a}	80 ± 12^{b}	4.22 ± 0.23^{c}
Propanol	132 ± 2^{b}	0.48 ± 0.17^{c}	1.3 ± 0.7^{b}	44 ± 8^{c}	4.27 ± 0.04^{c}
LSD	3.7	0.17	0.3	12.1	0.34

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 36. The properties after soaking in water of fibers made form soy proteins esterified with ethylene glycol, butanol or propanol before extrusion compared with the same treatments finished with acetic anhydride after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	155 ± 3^{a}	0.076 ± 0.023^{a}	3.6 ± 2.6^{a}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
Ethylene glycol	147 ± 3^{b}	0.016 ± 0.001^{b}	1.3 ± 1.0^{b}	1.4 ± 0.8^{b}	81.55 ± 1.13^{b}
Butanol	147 ± 3^{b}	0.016 ± 0.001^{b}	3.9 ± 1.5^{a}	1.4 ± 0.5^{b}	79.06 ± 0.74^{c}
Propanol	148 ± 4^{b}	0.010 ± 0.000^{b}	1.4 ± 0.4^{b}	1.1 ± 0.5^{b}	81.05 ± 0.48^{bc}
LSD	4.1	0.033	2.1	3.0	2.47
Acetic anhydride finished					
Soy fiber	145 ± 2^{a}	0.58 ± 0.05^{a}	89.0 ± 4.9^{a}	5.9 ± 1.0^{a}	16.61 ± 0.40^{a}
Ethylene glycol	140 ± 2^{b}	0.30 ± 0.05^{b}	98.7 ± 17.5^{a}	1.9 ± 0.8^{b}	11.53 ± 0.16^{b}
Butanol	145 ± 4^{a}	0.28 ± 0.02^{b}	24.0 ± 3.0^{b}	2.4 ± 0.2^{b}	10.49 ± 0.18^{c}
Propanol	144 ± 4^{a}	0.26 ± 0.07^{b}	22.7 ± 5.4^{b}	1.6 ± 0.2^{b}	10.73 ± 0.02^{c}
LSD	3.4	0.06	11.6	1.9	0.65

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

Table 37. The flexibility of fibers made form soy proteins esterified with ethylene glycol, butanol or propanol before extrusion compared with the same treatments finished by acetic anhydride after extrusion in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
Ethylene glycol											X		
Butanol												X	
Propanol													X
Acetic anhydride finished													
Soy fiber		X											
Ethylene glycol			X										
Butanol							X						
Propanol										X			
65% humidity													
Soy fiber	X												
Ethylene glycol	X												
Butanol	X												
Propanol			X										
Acetic anhydride finished													
Soy fiber	X												
Ethylene glycol	X												
Butanol							X						
Propanol										X			

X Fibers could be looped around the smallest diameter glass rod without breaking.

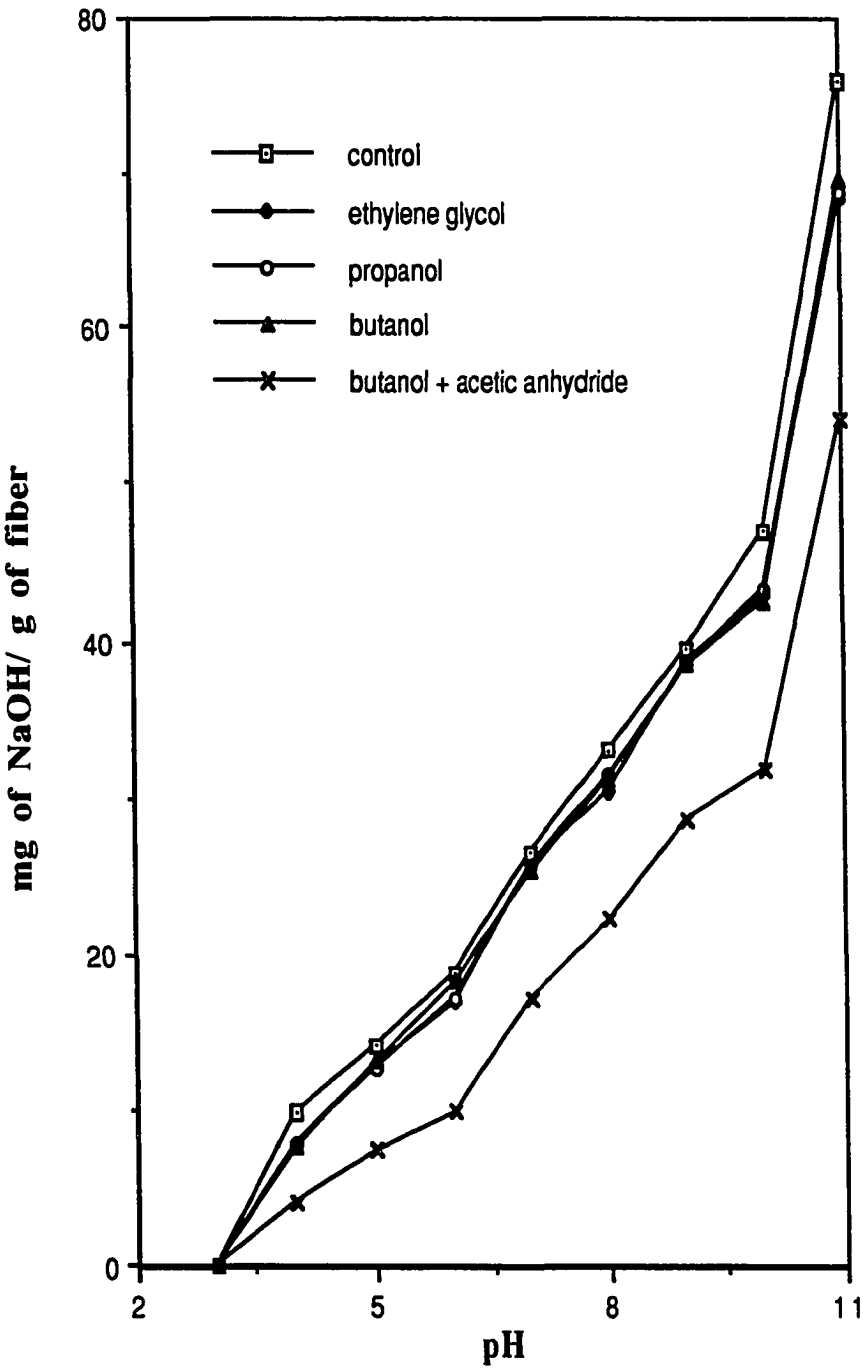


Figure 17. Titration curves of control fibers, fibers made from proteins esterified with ethylene glycol, propanol or butanol and butanol-esterified fibers finished with acetic anhydride.

Other protein modification prior to extrusion or wet spinning

Other modifying chemicals applied to soy protein before extrusion included propionaldehyde, glutaraldehyde and hydrogen peroxide. Propionaldehyde and glutaraldehyde would be expected to react with amine groups similar to those reacted with acetaldehyde except that glutaraldehyde might be capable of cross-linking protein molecules. Hydrogen peroxide was used to oxidize sulfhydryl bonds to disulfides and cross-link soy protein molecules. Modification of soy protein by these chemicals prior to extrusion did not improve the properties of the resulting fibers. Soy protein modified in these ways produced wet-spinning dopes that were extremely viscous and were difficult to pass through a spinnerette.

V. Cross-linking of Soy Protein fibers

Soy fibers were improved in their wet tenacities by acylation. However, the tenacities of soy fibers were still much lower than those of wool and silk. Cross-linking before spinning tended to increase viscosity and make spinning difficult. Therefore, the possibility of increasing tenacity by cross-linking the protein molecules after extrusion or spinning was studied.

Finishing treatment by dianhydrides

Dianhydrides were made by reacting two moles of acetic anhydride and one mole of various dibasic acids as shown in Figure 18. It was hoped that the two acyl groups of the dianhydrides would react with two ε-amino groups that would sometimes be on separate molecules and cross-link the protein molecules.

The results of fibers finished with dianhydrides are given in Tables 38-42. There were significant differences among treatments for the dianhydride reagents ($p<0.01$). There were no significant differences among dianhydride treatments in the linear density of fibers ($p>0.124$).

Table 38. The properties of fibers finished with various concentrations of dianhydride reagents in xylene and tested after equilibration to 11% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Xylene	117 ± 1	0.60 ± 0.13	0.73 ± 0.13	85 ± 11	1.17 ± 0.03
Acetic anhydride 0.32M	119 ± 4^{a}	0.47 ± 0.13^{b}	0.77 ± 0.17^{b}	84 ± 10^{a}	1.21 ± 0.07^{b}
Adipic 0.16M	117 ± 3^{a}	0.75 ± 0.15^{ab}	1.00 ± 0.25^{a}	79 ± 9^{a}	0.84 ± 0.03^{c}
Azelaic 0.16M	113 ± 4^{b}	0.73 ± 0.37^{ab}	0.89 ± 0.22^{ab}	89 ± 7^{a}	1.41 ± 0.07^{a}
Succinic 0.16M	116 ± 2^{ab}	0.79 ± 0.22^{a}	1.02 ± 0.16^{a}	82 ± 10^{a}	1.09 ± 0.01^{b}
LSD	4.0	0.29	0.24	11.0	0.15
Acetic anhydride 0.64M	120 ± 5^{a}	0.59 ± 0.20^{b}	0.83 ± 0.16^{b}	87 ± 11^{b}	1.13 ± 0.03^{a}
Adipic 0.32M	118 ± 4^{ab}	0.98 ± 0.21^{a}	1.42 ± 0.42^{a}	85 ± 9^{b}	0.74 ± 0.04^{c}
Azelaic 0.32M	114 ± 3^{b}	0.87 ± 0.21^{a}	0.75 ± 0.25^{b}	123 ± 31^{a}	1.06 ± 0.06^{a}
Succinic 0.32M	115 ± 2^{b}	1.05 ± 0.15^{a}	1.73 ± 0.46^{a}	78 ± 5^{b}	0.87 ± 0.01^{b}
LSD	4.8	0.23	0.41	20.8	0.10
Acetic anhydride 1.28M	120 ± 3^{a}	1.17 ± 0.32^{ab}	0.95 ± 0.25^{b}	135 ± 12^{a}	1.08 ± 0.08^{a}
Adipic 0.64M	117 ± 3^{ab}	1.12 ± 0.11^{ab}	1.84 ± 0.23^{a}	85 ± 2^{b}	0.57 ± 0.06^{b}
Azelaic 0.64M	118 ± 3^{ab}	0.93 ± 0.17^{b}	0.78 ± 0.19^{b}	123 ± 21^{a}	0.98 ± 0.02^{a}
Succinic 0.64M	116 ± 3^{b}	1.20 ± 0.16^{a}	2.06 ± 0.38^{a}	89 ± 8^{b}	0.68 ± 0.01^{b}
LSD	3.6	0.25	0.33	15.4	0.15
Acetic anhydride 2.56M	121 ± 5^{a}	1.56 ± 0.29^{ab}	1.22 ± 0.22^{d}	144 ± 21^{a}	0.91 ± 0.09^{a}
Adipic 1.28M	117 ± 5^{ab}	1.57 ± 0.06^{a}	4.20 ± 1.38^{b}	76 ± 8^{b}	0.53 ± 0.04^{b}
Azelaic 1.28M	116 ± 2^{b}	1.39 ± 0.03^{b}	2.85 ± 0.53^{c}	68 ± 9^{b}	0.82 ± 0.04^{a}
Succinic 1.28M	117 ± 3a^{b}	1.61 ± 0.07^{a}	5.93 ± 1.00^{a}	72 ± 4^{b}	0.63 ± 0.04^{b}
LSD	4.8	0.18	1.11	14.7	0.15
Acetic anhydride 3.84M	122 ± 5^{a}	1.91 ± 0.26^{a}	2.37 ± 0.73^{c}	134 ± 13^{a}	0.70 ± 0.01^{a}
Adipic 1.92M	117 ± 4^{b}	1.78 ± 0.16^{a}	4.09 ± 1.50^{b}	95 ± 6^{b}	0.51 ± 0.01^{b}
Azelaic 1.92M	116 ± 3^{b}	1.46 ± 0.04^{b}	1.92 ± 0.49^{c}	77 ± 8^{c}	0.70 ± 0.03^{a}
Succinic 1.92M	116 ± 3^{b}	1.77 ± 0.10^{a}	5.52 ± 0.29^{a}	87 ± 7^{bc}	0.55 ± 0.01^{b}
LSD	4.5	0.20	1.07	11.1	0.05

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

Table 39. The properties of fibers finished with various concentrations of dianhydride reagents in xylene and tested after equilibration to 65% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Xylene	132 ± 4	0.48 ± 0.06	80.5 ± 10.8	7 ± 1	12.12 ± 0.06
Acetic anhydride 0.32M	136 ± 4^{a}	0.37 ± 0.04^{b}	32.0 ± 13.5^{d}	28 ± 5^{a}	11.19 ± 0.04^{a}
Adipic 0.16M	132 ± 4^{b}	0.50 ± 0.05^{a}	141.4 ± 5.1^{a}	6 ± 2^{c}	9.12 ± 0.01^{c}
Azelaic 0.16M	130 ± 2^{b}	0.48 ± 0.04^{a}	98.5 ± 10.4^{b}	12 ± 1^{b}	10.85 ± 0.31^{ab}
Succinic 0.16M	129 ± 2^{b}	0.51 ± 0.04^{a}	83.3 ± 16.1^{c}	8 ± 2^{c}	10.44 ± 0.05^{b}
LSD	3.4	0.05	14.5	3.3	0.44
Acetic anhydride 0.64M	134 ± 5^{a}	0.42 ± 0.08^{b}	48.1 ± 18.6^{b}	25 ± 3^{a}	10.81 ± 0.18^{a}
Adipic 0.32M	132 ± 3^{a}	0.56 ± 0.08^{a}	108.9 ± 21.3^{a}	16 ± 2^{b}	8.77 ± 0.13^{c}
Azelaic 0.32M	130 ± 3^{a}	0.51 ± 0.06^{ab}	90.2 ± 15.0^{a}	15 ± 4^{b}	9.46 ± 0.31^{b}
Succinic 0.32M	131 ± 2^{a}	0.58 ± 0.08^{a}	64.6 ± 9.1^{b}	15 ± 2^{b}	9.06 ± 0.25^{bc}
LSD	4.1	0.09	20.0	3.3	0.64
Acetic anhydride 1.28M	135 ± 3^{a}	0.67 ± 0.03^{a}	61.2 ± 19.2^{c}	28 ± 9^{a}	10.07 ± 0.13^{a}
Adipic 0.64M	133 ± 7^{a}	0.60 ± 0.04^{ab}	109.1 ± 9.9^{a}	11 ± 1^{c}	7.56 ± 0.19^{c}
Azelaic 0.64M	131 ± 2^{a}	0.53 ± 0.03^{b}	80.3 ± 13.1^{b}	19 ± 3^{b}	8.21 ± 0.23^{b}
Succinic 0.64M	131 ± 3^{a}	0.63 ± 0.12^{a}	58.1 ± 7.7^{c}	13 ± 2^{c}	7.78 ± 0.04^{bc}
LSD	5.0	0.08	15.9	5.7	0.46
Acetic anhydride 2.56M	135 ± 4^{a}	0.80 ± 0.07^{a}	50.1 ± 12.8^{ab}	33 ± 5^{a}	8.16 ± 0.17^{a}
Adipic 1.28M	132 ± 4^{a}	0.80 ± 0.03^{a}	58.2 ± 6.6^{a}	30 ± 2^{a}	5.72 ± 0.01^{c}
Azelaic 1.28M	131 ± 2^{a}	0.57 ± 0.02^{b}	40.7 ± 11.5^{b}	21 ± 4^{b}	6.26 ± 0.07^{b}
Succinic 1.28M	132 ± 3^{a}	0.85 ± 0.07^{a}	25.9 ± 5.3^{c}	24 ± 4^{b}	6.13 ± 0.11^{b}
LSD	4.1	0.06	11.6	4.6	0.30
Acetic anhydride 3.84M	136 ± 3^{a}	1.02 ± 0.17^{a}	5.6 ± 1.1^{b}	56 ± 8^{a}	5.87 ± 0.08^{a}
Adipic 1.92M	132 ± 6^{ab}	0.91 ± 0.03^{a}	24.9 ± 10.2^{a}	40 ± 6^{b}	5.37 ± 0.03^{c}
Azelaic 1.92M	131 ± 4^{b}	0.76 ± 0.09^{b}	22.1 ± 5.1^{a}	27 ± 5^{c}	6.01 ± 0.04^{a}
Succinic 1.92M	131 ± 2^{b}	0.94 ± 0.11^{a}	9.1 ± 2.2^{b}	26 ± 3^{c}	5.64 ± 0.13^{b}
LSD	4.5	0.13	7.1	7.0	0.22

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

Table 40. The properties of fibers finished with various concentrations of dianhydride reagents in xylene and tested after soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Xylene	154 ± 6	0.027 ± 0.004	1.9 ± 0.73	1.5 ± 0.4	65.65 ± 0.62
Acetic anhydride 0.32M	156 ± 4^{a}	0.021 ± 0.010^{c}	5.6 ± 1.8^{d}	2.6 ± 1.0^{a}	107.43 ± 0.62^{a}
Adipic 0.16M	153 ± 4^{a}	0.085 ± 0.013^{a}	85.4 ± 16.6^{a}	1.1 ± 0.5^{bc}	45.39 ± 0.06^{c}
Azelaic 0.16M	152 ± 5^{a}	0.034 ± 0.010^{b}	26.3 ± 4.3^{c}	0.6 ± 0.1^{c}	52.14 ± 1.48^{b}
Succinic 0.16M	150 ± 4^{a}	0.081 ± 0.010^{a}	61.3 ± 6.8^{b}	1.6 ± 0.2^{b}	47.01 ± 0.53^{c}
LSD	5.2	0.011	11.1	0.7	2.35
Acetic anhydride 0.64M	154 ± 4^{a}	0.026 ± 0.011^{d}	14.6 ± 3.6^{c}	1.7 ± 0.5^{b}	97.21 ± 1.36^{a}
Adipic 0.32M	154 ± 4^{a}	0.100 ± 0.020^{b}	90.0 ± 21.5^{a}	0.9 ± 0.3^{c}	39.24 ± 0.73^{c}
Azelaic 0.32M	156 ± 4^{a}	0.068 ± 0.018^{c}	33.2 ± 15.1^{b}	1.6 ± 0.3^{b}	44.65 ± 0.72^{b}
Succinic 0.32M	156 ± 3^{a}	0.170 ± 0.010^{a}	102.5 ± 5.1^{a}	2.6 ± 0.5^{a}	41.51 ± 1.88^{b}
LSD	4.4	0.02	16.2	0.5	3.53
Acetic anhydride 1.28M	157 ± 6^{a}	0.038 ± 0.013^{c}	18.3 ± 6.5^{c}	2.7 ± 1.1^{b}	83.96 ± 1.83^{a}
Adipic 0.64M	154 ± 4^{a}	0.15 ± 0.02^{b}	79.0 ± 13.2^{b}	1.4 ± 0.7^{b}	28.76 ± 0.05^{d}
Azelaic 0.64M	156 ± 4^{a}	0.14 ± 0.02^{b}	82.5 ± 14.9^{b}	2.7 ± 1.0^{b}	36.81 ± 0.95^{b}
Succinic 0.64M	156 ± 3^{a}	0.25 ± 0.02^{a}	112.0 ± 3.6^{a}	9.3 ± 1.7^{a}	32.64 ± 0.72^{c}
LSD	5.4	0.02	12.8	1.4	3.03
Acetic anhydride 2.56M	154 ± 4^{a}	0.16 ± 0.03^{b}	41.2 ± 10.8^{c}	3.0 ± 0.9^{b}	71.71 ± 2.04^{a}
Adipic 1.28M	154 ± 3^{a}	0.24 ± 0.03^{a}	90.0 ± 10.2^{ab}	1.0 ± 0.2^{b}	23.87 ± 0.11^{c}
Azelaic 1.28M	156 ± 6^{a}	0.23 ± 0.05^{a}	85.6 ± 12.0^{b}	3.5 ± 0.5^{b}	26.99 ± 0.04^{b}
Succinic 1.28M	156 ± 3^{a}	0.26 ± 0.04^{a}	101.0 ± 14.4^{a}	12.9 ± 4.1^{a}	24.75 ± 0.59^{bc}
LSD	5.0	0.05	14.4	2.6	2.97
Acetic anhydride 3.84M	155 ± 3^{a}	0.36 ± 0.05^{a}	38.3 ± 9.1^{d}	3.9 ± 0.6^{b}	21.02 ± 1.22^{b}
Adipic 1.92M	152 ± 6^{a}	0.27 ± 0.02^{bc}	74.7 ± 8.4^{b}	2.1 ± 0.6^{c}	21.55 ± 0.40^{ab}
Azelaic 1.92M	156 ± 5^{a}	0.23 ± 0.03^{c}	54.4 ± 11.3^{c}	3.7 ± 1.0^{bc}	23.36 ± 0.20^{a}
Succinic 1.92M	156 ± 3^{a}	0.28 ± 0.03^{b}	110.5 ± 14.9^{a}	13.1 ± 2.3^{a}	22.49 ± 0.49^{ab}
LSD	5.5	0.04	13.5	1.6	1.93

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

Table 41. The flexibility of fibers finished with various concentrations of dianhydride reagents in xylene in terms of the smallest rod diameter around which fibers could be looped without breaking at 11% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
Xylene													X
Acetic anhydride 0.32M								X					
Adipic 0.16M					X								
Azelaic 0.16M								X					
Succinic 0.16M					X								
Acetic anhydride 0.64M								X					
Adipic 0.32M				X									
Azelaic 0.32M						X							
Succinic 0.32M			X										
Acetic anhydride 1.28M						X							
Adipic 0.64M			X										
Azelaic 0.64M					X								
Succinic 0.64M		X											
Acetic anhydride 2.56M						X							
Adipic 1.28M		X											
Azelaic 1.28M		X											
Succinic 1.28M	X												
Acetic anhydride 3.84M					X								
Adipic 1.92M	X												
Azelaic 1.92M	X												
Succinic 1.92M	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 42. The flexibility of fibers finished with various concentrations of dianhydride reagents in xylene in terms of the smallest rod diameter around which fibers could be looped without breaking at 65% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
Xylene	X												
Acetic anhydride 0.32M	X												
Adipic 0.16M	X												
Azelaic 0.16M	X												
Succinic 0.16M	X												
Acetic anhydride 0.64M	X												
Adipic 0.32M	X												
Azelaic 0.32M	X												
Succinic 0.32M	X												
Acetic anhydride 1.28M	X												
Adipic 0.64M	X												
Azelaic 0.64M	X												
Succinic 0.64M	X												
Acetic anhydride 2.56M	X												
Adipic 1.28M	X												
Azelaic 1.28M	X												
Succinic 1.28M	X												
Acetic anhydride 3.84M	X												
Adipic 1.92M	X												
Azelaic 1.92M	X												
Succinic 1.92M	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

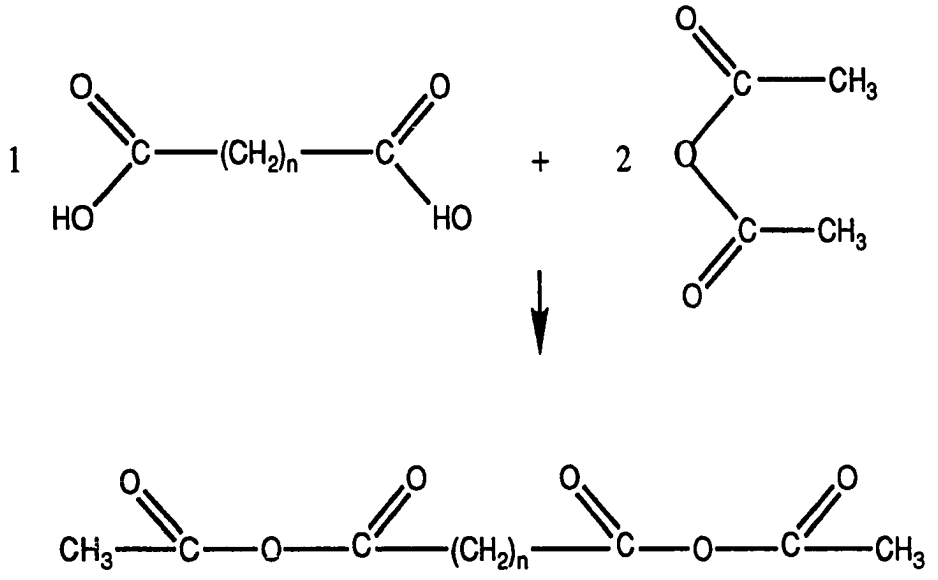


Figure 18. The formation of dianhydrides from one mole dibasic acid and two moles acetic anhydride.

Soy fibers finished by dianhydrides had increased tenacity and flexibility and these properties increased with increasing dianhydrides concentration. Xylene-treated fibers were used as the control because the reactions with dianhydrides were carried out in xylene. Elongation and flexibility increased and tenacity decreased as testing humidity increased. Succinic acid, a four carbon dibasic acid, had a better effect on fiber properties than did adipic acid and azelaic acid, which are 6 and 9 carbon dibasic acids (Tables 38-42). Fibers finished by dianhydrides had better tenacity, elongation and flexibility than the fibers treated with acetic anhydride alone at lower anhydride concentrations, but not at higher concentrations. This may be because the concentration of dianhydride that yields maximum cross-linking is fairly low, and the effect of excess dianhydride is simply to acylate amine groups. Overall, fibers finished by dianhydrides presented better elongation and flexibility than fibers finished with acetic anhydride.

Finishing treatment by glutaraldehyde and glyoxal

Aldehydes can be used to modify amino groups of protein to form stable Schiff bases, so difunctional aldehydes should make good cross-linking agents for protein molecules. The chemical reaction of proteins and difunctional aldehydes, such as glutaraldehyde, is illustrated in Figure 19.

Concentration

Glyoxal and glutaraldehyde were used to cross-link soy fibers. These two reagents significantly increased fiber tenacity and flexibility and decreased moisture regain with increasing concentrations of the reagents ($p<0.01$) (Tables 43-46). Glutaraldehyde improved fiber properties more than glyoxal. This may be because the glyoxal exists as a polymer. Fibers finished by cross-linking agents could not be elongated much at humidities of 11 and 65%, but under wet conditions they could be elongated considerably. The tenacity and

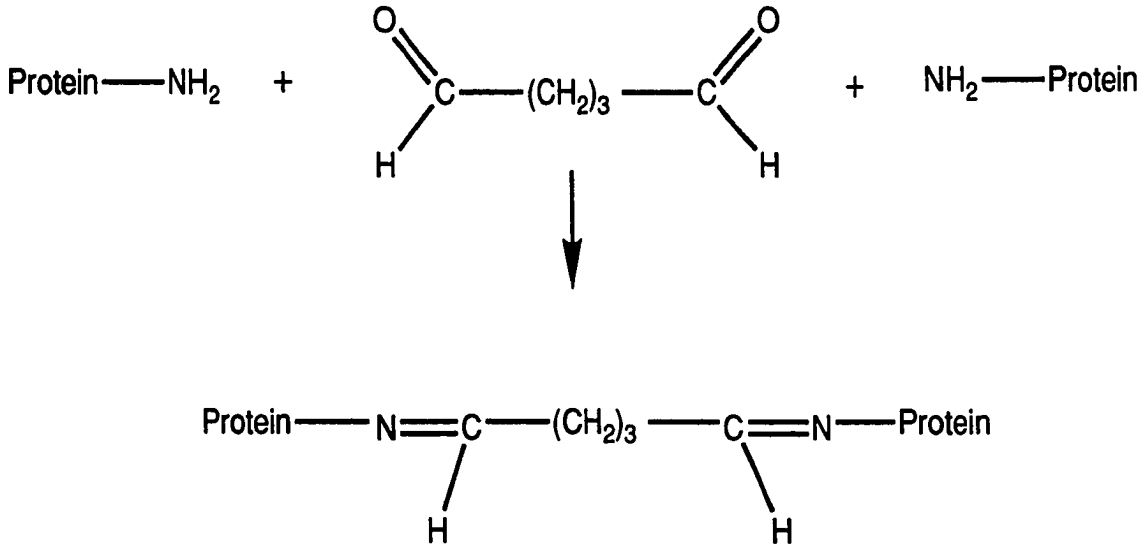


Figure 19. Chemical reaction of glutaraldehyde cross-linked proteins.

Table 43. The properties of protein fibers finished with various concentrations of glyoxal for 30 min and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex.	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
Soy fiber	113 ± 4^{a}	1.57 ± 0.32^{ab}	1.6 ± 0.2^{a}	97 ± 8^{c}	1.61 ± 0.13^{a}
10% Glyoxal	107 ± 2^{c}	1.34 ± 0.14^{b}	0.5 ± 0.1^{c}	199 ± 17^{b}	1.46 ± 0.18^{a}
15% Glyoxal	109 ± 2^{bc}	1.47 ± 0.24^{ab}	1.1 ± 0.4^{b}	205 ± 10^{b}	1.31 ± 0.13^{ab}
20 % Glyoxal	112 ± 2^{ab}	1.52 ± 0.16^{ab}	0.6 ± 0.1^{c}	204 ± 18^{b}	1.08 ± 0.11^{bc}
25% Glyoxal	114 ± 2^{a}	1.71 ± 0.24^{a}	0.5 ± 0.1^{c}	231 ± 33^{a}	0.90 ± 0.04^{c}
LSD	3.7	0.27	0.3	22.9	0.32
65% humidity					
Soy fiber	128 ± 2^{a}	0.56 ± 0.06^{d}	73.4 ± 16.6^{a}	25 ± 3^{d}	14.32 ± 0.14^{a}
10% Glyoxal	120 ± 3^{c}	1.88 ± 0.38^{c}	3.5 ± 0.5^{b}	94 ± 11^{b}	8.80 ± 0.14^{b}
15% Glyoxal	121 ± 3^{c}	2.21 ± 0.13^{b}	4.6 ± 1.1^{b}	81 ± 14^{c}	7.09 ± 0.13^{c}
20% Glyoxal	122 ± 3^{bc}	2.39 ± 0.20^{b}	2.5 ± 0.1^{b}	112 ± 9^{a}	6.92 ± 0.11^{c}
25% Glyoxal	124 ± 4^{b}	2.85 ± 0.37^{a}	3.8 ± 0.7^{b}	120 ± 7^{a}	6.72 ± 0.29^{c}
LSD	3.4	0.31	8.9	11.6	0.45
In water					
Soy fiber	155 ± 3^{b}	0.076 ± 0.023^{c}	3.9 ± 2.6^{b}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
10% Glyoxal	159 ± 3^{a}	0.21 ± 0.06^{b}	76.0 ± 21.1^{a}	1.1 ± 0.3^{b}	32.27 ± 1.10^{b}
15% Glyoxal	156 ± 4^{ab}	0.25 ± 0.06^{ab}	72.3 ± 12.5^{a}	1.5 ± 0.8^{b}	28.00 ± 1.00^{c}
20% Glyoxal	160 ± 3^{a}	0.28 ± 0.04^{a}	81.6 ± 3.6^{a}	1.4 ± 0.3^{b}	25.87 ± 1.53^{c}
25% Glyoxal	157 ± 3^{ab}	0.31 ± 0.06^{a}	82.1 ± 11.7^{a}	1.7 ± 0.4^{b}	25.12 ± 1.08^{c}
LSD	4.0	0.06	14.7	2.1	3.00

[a-d] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 44. The flexibility of fibers finished with various concentrations of glyoxal for 30 min in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
10% Glyoxal									X				
15% Glyoxal									X				
20% Glyoxal									X				
25% Glyoxal									X				
65% humidity													
Soy fiber		X											
10% Glyoxal			X										
15% Glyoxal		X											
20% Glyoxal		X											
25% Glyoxal		X											

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 45. The properties of protein fibers finished with various concentrations of glutaraldehyde for 30 min and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex.	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
Soy fiber	113 ± 4^{a}	1.57 ± 0.32^{b}	1.6 ± 0.2^{a}	97 ± 8^{d}	1.61 ± 0.13^{a}
10% Glutaraldehyde	101 ± 2^{b}	1.44 ± 0.21^{b}	0.8 ± 0.1^{b}	191 ± 17^{c}	1.11 ± 0.03^{b}
15% Glutaraldehyde	101 ± 3^{b}	1.55 ± 0.26^{b}	0.8 ± 0.2^{b}	207 ± 10^{c}	1.22 ± 0.08^{b}
20% Glutaraldehyde	102 ± 2^{b}	1.85 ± 0.48^{ab}	0.8 ± 0.1^{b}	239 ± 36^{b}	1.27 ± 0.03^{b}
25% Glutaraldehyde	102 ± 2^{b}	2.10 ± 0.57^{a}	0.8 ± 0.2^{b}	273 ± 36^{a}	1.53 ± 0.01^{a}
LSD	3.4	0.47	0.2	29.4	0.18
65% humidity					
Soy fiber	128 ± 2^{a}	0.56 ± 0.06^{d}	73.4 ± 16.6^{a}	25 ± 3^{c}	14.32 ± 0.14^{a}
10% Glutaraldehyde	107 ± 4^{b}	2.09 ± 0.13^{c}	1.3 ± 0.4^{b}	176 ± 14^{b}	6.91 ± 0.04^{c}
15% Glutaraldehyde	107 ± 3^{b}	2.29 ± 0.42^{bc}	1.2 ± 0.2^{b}	195 ± 19^{a}	7.08 ± 0.19^{c}
20% Glutaraldehyde	107 ± 2^{b}	2.44 ± 0.37^{b}	1.1 ± 0.1^{b}	166 ± 15^{b}	7.61 ± 0.04^{b}
25% Glutaraldehyde	109 ± 2^{b}	3.28 ± 0.21^{a}	2.4 ± 0.4^{b}	178 ± 12^{b}	7.86 ± 0.13^{b}
LSD	6.1	0.33	8.8	16.3	0.32
In water					
Soy fiber	155 ± 3^{a}	0.076 ± 0.023^{d}	3.9 ± 2.6^{d}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
10% Glutaraldehyde	154 ± 4^{a}	0.41 ± 0.03^{c}	51.5 ± 8.1^{c}	1.8 ± 0.3^{b}	22.20 ± 0.85^{e}
15% Glutaraldehyde	157 ± 3^{a}	0.46 ± 0.13^{c}	62.4 ± 13.8^{b}	2.9 ± 0.5^{b}	27.20 ± 0.65^{d}
20% Glutaraldehyde	157 ± 5^{a}	0.57 ± 0.11^{b}	74.5 ± 10.5^{a}	4.2 ± 1.9^{b}	32.60 ± 0.63^{c}
25% Glutaraldehyde	158 ± 4^{a}	0.70 ± 0.08^{a}	77.4 ± 4.1^{a}	4.1 ± 1.3^{b}	37.30 ± 0.19^{b}
LSD	4.7	0.10	10.5	2.8	1.94

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 46. The flexibility of fibers finished with various concentrations of glutaraldehyde for 30 min in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
10% Glutaraldehyde								X					
15% Glutaraldehyde								X					
20% Glutaraldehyde								X					
25% Glutaraldehyde								X					
65% humidity													
Soy fiber		X											
10% Glutaraldehyde			X										
15% Glutaraldehyde			X										
20% Glutaraldehyde			X										
25% Glutaraldehyde			X										

X Fibers could be looped around the smallest diameter glass rod without breaking.

flexibility of fibers increased as the concentrations of glyoxal and glutaraldehyde increased. The wet tenacity was significantly improved by both reagents. Both finished fibers exhibited higher tenacity at 65% relative humidity than at 11%. The titration results showed that fibers finished by glyoxal or glutaraldehyde had about 7% and 12%, respectively, of their titratible groups derivatized (Figure 20). Figure 28 in the appendix shows scanning electron micrographs of fibers finished with a glutaraldehyde treatment. These fibers had a smooth and tightly packed structure. The amount of glyoxal and glutaraldehyde necessary to give maximum effect on tenacity was much greater than the amount that could react with the amino groups in the fiber. To understand why this was so, the reaction was explored further.

pH

Finishing treatments at various pH's were tested to establish the best condition for finishing fibers with glutaraldehyde (Table 47, Figure 21 and Tables 80-82 in the appendix). There were significant differences in fiber properties among the pH's used to finish the fibers ($p<0.01$). As the pH of glutaraldehyde-finished fibers declined, their tenacities decreased. At 65% relative humidity, fiber flexibility increased at lower pH's. The fibers may have swelled and imbibed more water when the pH was farther away from the pI of soy protein, which would increase their flexibility and decrease their tenacity.

Reaction time

Glutaraldehyde needs to penetrate fibers to react with their amino groups. There were significant differences in fiber properties treated with cross-linking agents when various reaction times were tested ($p<0.01$) (Figure 22 and Tables 83-85 in the appendix). The fibers lost their tenacity and flexibility with a long reaction time (Figure 22 and Table 48); however, a reaction time < 10 min was not enough for glutaraldehyde to penetrate and react with amino

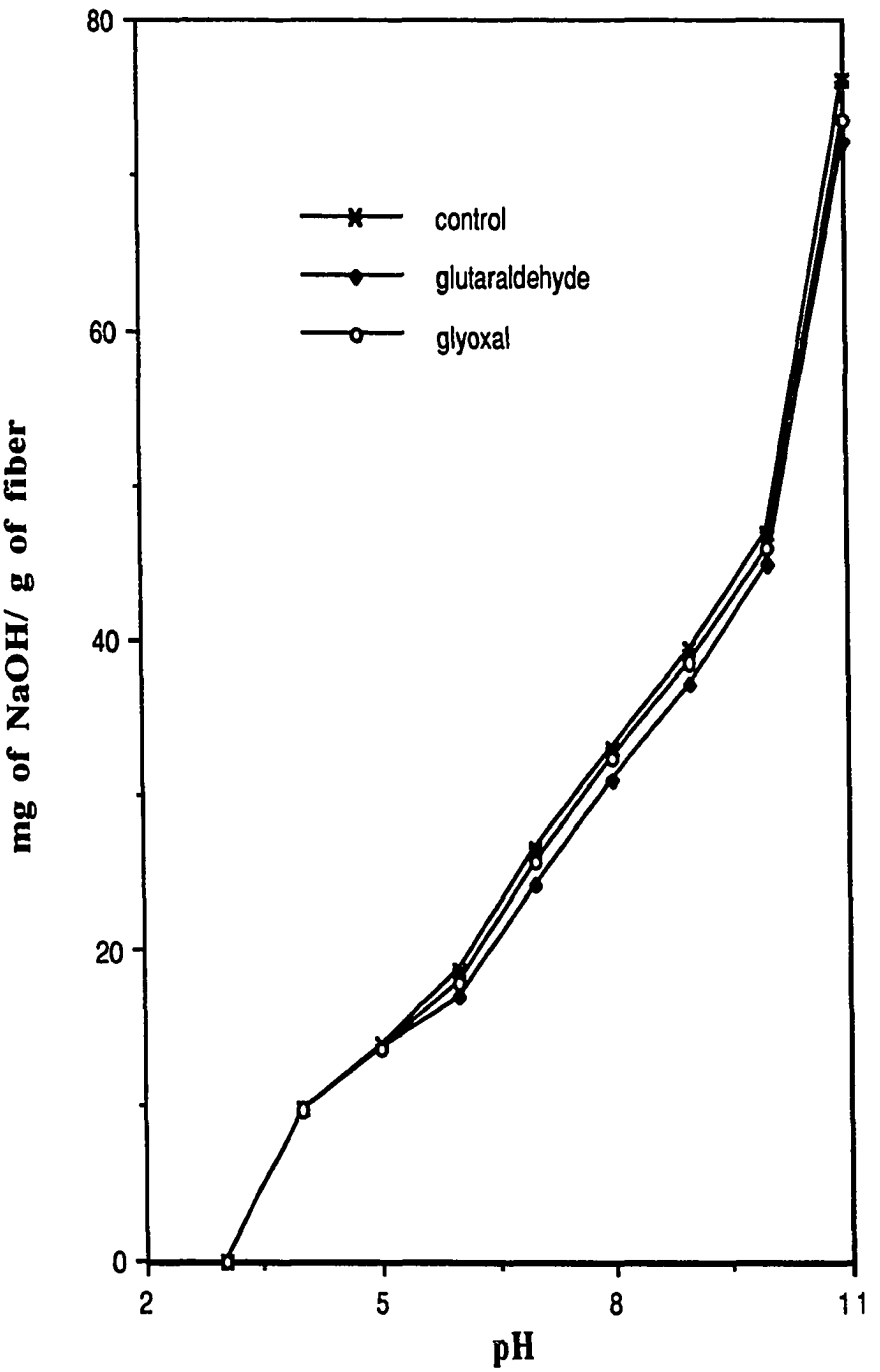


Figure 20. Titration curves of control fibers and control fibers finished with glyoxal or glutaraldehyde.

Table 47. The flexibility of fibers finished with glutaraldehyde at various pH's in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
pH 3.5								X					
pH 3.0								X					
pH 2.5								X					
pH 2.0								X					
pH 1.5								X					
65% humidity													
pH 3.5			X										
pH 3.0		X											
pH 2.5	X												
pH 2.0	X												
pH 1.5	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

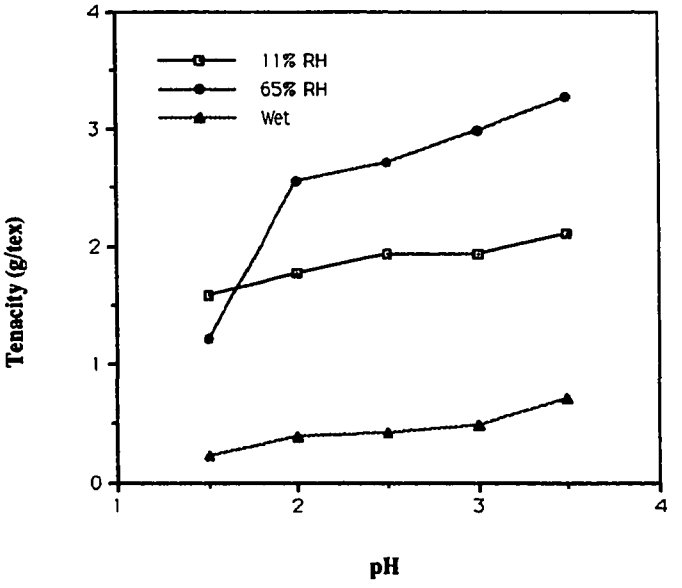


Figure 21. The tenacity of fibers finished with glutaraldehyde at various pH's.

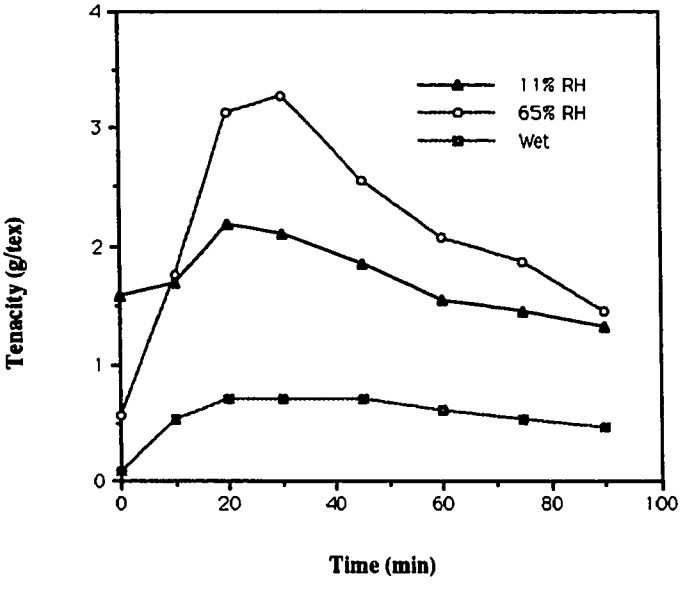


Figure 22. The tenacity of fiber finished with glutaraldehyde at various reaction times.

Table 48. The flexibility of fibers finished with glutaraldehyde at various treatment times in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
10 min							X						
20 min								X					
30 min								X					
45 min									X				
60 min										X			
75 min												X	
90 min													X
65% humidity													
10 min	X												
20 min			X										
30 min			X										
45 min			X										
60 min				X									
75 min					X								
90 min							X						

X Fibers could be looped around the smallest diameter glass rod without breaking.

groups of soy protein fibers. Soy protein fibers finished with glutaraldehyde for 20 to 30 min had the best tenacity. It may be that long reaction times with excess reagent leads to less cross-linking and more glutaraldehyde attached to protein at only one end of the glutaraldehyde molecule.

Temperature and stretching

There were significant differences in fiber properties among various reaction temperatures and stretching treatments ($p<0.01$) (Figure 23 and Tables 86-88 in the appendix). Increasing the reaction temperature decreased fiber tenacity and flexibility (Figure 23 and Table 49). This may be similar to the effect seen with increased reaction time. Stretching significantly increased tenacity and flexibility presumably by changing fiber orientation to a more linear arrangement (Figure 24 and Table 49). However, stretching fibers too much can decrease their tenacities. Stretching fibers to about 150% of their original lengths gave the best tenacity and flexibility (Tables 50 and 51). Strain hardening of materials that are plastic under tensile stress is well known. It occurs because as protein molecules flow past each attractive groups on adjoining molecules have a greater possibility of interacting. There also might be a tendency to make protein molecular chains more linear so that they can interact with adjoining molecules at more points.

Glycerol

One explanation for the large stoichemetric excess of dialdehyde that was needed for maximum tenacity of soy fibers might be that dialdehyde is reacting with glycerol that was added to the soy protein as a plasticizer before extrusion. To see if this was important, several experiments were tried. The soy protein fibers were soaked in water or various concentrations of glyoxal or glutaraldehyde, and the amount of the water or aqueous solutions imbibed by the fibers was measured. The results in Table 52 show that the greater the concentration of

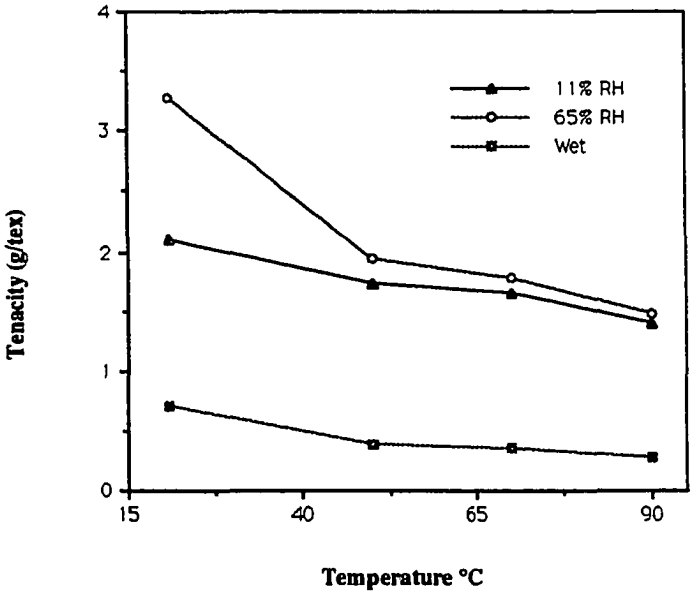


Figure 23. The tenacity of fibers finishedwith glutaraldehyde at various temperatures without stretching.

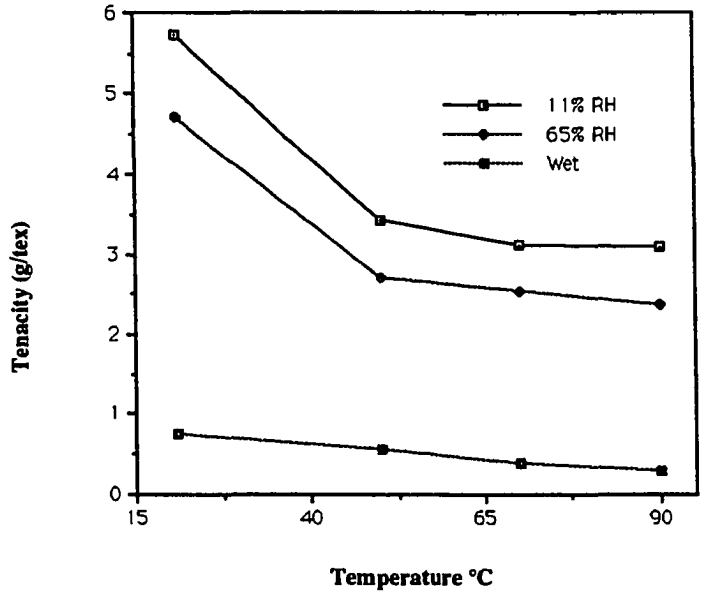


Figure 24. The tenacity of fibers finished with glutaraldehyde at various temperatures and stretched to 150% of their original length.

Table 49. The flexibility of fibers finished with glutaraldehyde at various temperatures and stretched to 150% of their original length in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Room temperature								X					
50° C								X					
70° C									X				
90° C										X			
Stretching to 150%													
Room temperature				X									
0° C				X									
70° C						X							
90° C						X							
65% humidity													
Room temperature			X										
50° C			X										
70° C					X								
90° C					X								
Stretching to 150%													
Room temperature	X												
50° C	X												
70° C			X										
90° C				X									

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 50. The properties of protein fibers finished with 25% glutaraldehyde and stretched to 110, 130, 150 and 170% of their original lengths, respectively, and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
170%	71 ± 3^{e}	4.13 ± 1.04^{b}	1.3 ± 0.3^{bc}	321 ± 18^{a}	1.53 ± 0.01^{a}
150%	79 ± 3^{d}	5.74 ± 0.66^{a}	2.1 ± 0.2^{a}	306 ± 13^{a}	1.40 ± 0.02^{c}
130%	84 ± 3^{c}	4.19 ± 0.65^{b}	1.4 ± 0.3^{b}	312 ± 13^{a}	1.51 ± 0.02^{ab}
110%	95 ± 2^{b}	3.08 ± 0.78^{c}	1.0 ± 0.3^{cd}	302 ± 8^{a}	1.48 ± 0.01^{b}
100%	102 ± 2^{a}	2.10 ± 0.57^{d}	0.8 ± 0.2^{d}	273 ± 36^{b}	1.53 ± 0.01^{a}
LSD	2.8	0.90	0.3	24.2	0.04
65% humidity					
170%	76 ± 3^{e}	4.39 ± 0.56^{b}	4.5 ± 1.9^{a}	206 ± 28^{a}	7.25 ± 0.26^{b}
150%	83 ± 2^{d}	4.73 ± 0.10^{a}	4.1 ± 1.2^{a}	218 ± 17^{a}	6.87 ± 0.22^{b}
130%	88 ± 2^{c}	4.34 ± 0.12^{b}	3.9 ± 0.3^{a}	185 ± 10^{b}	7.19 ± 0.16^{b}
110%	100 ± 3^{b}	4.16 ± 0.11^{b}	2.4 ± 0.4^{b}	213 ± 10^{a}	7.10 ± 0.24^{b}
100%	109 ± 2^{a}	3.28 ± 0.21^{c}	2.4 ± 0.4^{b}	178 ± 12b	7.87 ± 0.13^{a}
LSD	2.8	0.33	1.3	20.1	0.47
In water					
170%	101 ± 4^{e}	0.69 ± 0.12^{a}	57.6 ± 9.7^{c}	2.6 ± 0.6^{b}	37.17 ± 0.44^{a}
150%	106 ± 3^{d}	0.75 ± 0.05^{a}	62.2 ± 3.7^{bc}	4.9 ± 0.7^{a}	36.13 ± 0.41^{a}
130%	117 ± 2^{c}	0.70 ± 0.06^{a}	65.7 ± 3.7^{b}	2.7 ± 1.1^{b}	36.21 ± 0.30^{a}
110%	136 ± 2^{b}	0.70 ± 0.13^{a}	62.7 ± 9.7^{bc}	4.3 ± 1.2^{a}	34.79 ± 0.91^{b}
100%	158 ± 4^{a}	0.70 ± 0.08^{a}	77.4 ± 4.1^{a}	4.1 ± 1.3^{a}	37.10 ± 0.19^{a}
LSD	3.6	0.11	8.1	1.2	1.32

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 51. The flexibility of fibers finished with 25% glutaraldehyde and stretched to 110, 130, 150 and 170% of their original lengths, respectively, in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
170%						X							
150%				X									
130%						X							
110%								X					
100%								X					
65% humidity													
170%			X										
150%	X												
130%	X												
110%			X										
100%			X										

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 52. Absorption of glyoxal and glutaraldehyde of soy protein fibers

Glyoxal (%)	Wt gain % of wet fibers	Wt % at 11%	Washed Wt % at 11%
0	88.36 ± 0.47	-21.87 ± 1.24[a]	-21.87 ± 1.24
10	62.82 ± 0.04	14.76 ± 0.34	-19.04 ± 1.13
15	66.27 ± 1.01	16.07 ± 0.13	-18.82 ± 1.16
20	71.45 ± 0.21	17.07 ± 0.11	-18.25 ± 1.06
25	76.02 ± 0.04	17.80 ± 0.29	-17.96 ± 0.64
Glutaraldehyde (%)			
10	42.14 ± 0.24	9.22 ± 0.04	-17.30 ± 0.07
15	39.28 ± 0.33	10.37 ± 0.23	-16.08 ± 0.11
20	36.79 ± 0.45	11.11 ± 0.09	-15.06 ± 0.11
25	33.85 ± 0.21	12.32 ± 0.33	-13.88 ± 0.17

[a] The mixture extruded was 25% glycerol, so approximately 87.5% of this weight was lost by soaking in water, assuming all the weight loss was glycerol.

glyoxal or glutaraldehyde, the less the weight of solution that was taken up. Presumably this is because the osmotic value of the fibers attracted water into the fibers, and the greater the osmotic value of the soaking solution, the less the amount of the aqueous solution that would be taken up. The fiber took up less glutaraldehyde solution than glyoxal solution presumably because the glyoxal tends to be polymerized and has a lower osmotic value.

Table 52 also shows that when the fiber was dried to 11% relative humidity after soaking in water, it lost about 22% of its weight. Presumably most of this loss of weight is glycerol which should make up 25% of the fiber weight. This suggests that 87.5% of the glycerol could be removed by soaking in water. The fibers that had been treated with glyoxal and glutaraldehyde gained from 9 to 18% weight. If these fibers were then washed, most of this weight gain was lost in the wash water, but the fibers that had been reacted with the

dialdehydes did not lose as much weight as those washed only with water. The net weight gain was greater with a greater concentration of dialdehyde used in the reaction. Glutaraldehyde-finished fibers retained more weight than those finished with corresponding percentages of glyoxal. This gain in weight could be attributed to the dialdehyde that reacted with the fibers, but it also was possible that dialdehydes reacted with glycerol and kept it from being leached from the fibers.

To gain further insight, the fibers were washed with water before they were reacted with the dialdehydes. These results are shown in Table 53. The washed fibers took up less weight during the reaction with dialdehydes than the unwashed fibers. This is to be expected from the reduced osmotic value of the washed fibers. As expected, the fibers had gained less weight when they were dried to 11% relative humidity since they absorbed less of the reagents. When these fibers were washed a second time to remove the excess dialdehydes, they all lost more weight than fibers that were reacted with dialdehydes before being washed. This suggests that some glycerol may react with the dialdehydes and be fixed in fibers by the reaction.

Tables 54-57 show the effects of washing fibers on the tenacity and flexibility of the fibers after they had been reacted with dialdehydes. Tenacity and flexibility were decreased by washing under all conditions tested. This may be partly caused by the removal of glycerol, which makes the fibers more brittle. It also may be that the cross-linking brought about by dialdehydes is reversible and that washing out the excess reagents decreased the extent of cross-linking.

Wet-spun fiber finished by glutaraldehyde

Wet-spun fibers coagulated in an acid bath without any salts were too weak to handle. The addition of inorganic salts were used to improve the tenacity so they could be handled and tested. The coagulating solutions used to coagulate wet-spun fibers were as follows:

Table 53. Absorption of glyoxal and glutaraldehyde of washed soy protein fibers

Glyoxal (%)	Wt gain % of wet fibers	Wt % at 11%	Washed Wt % at 11%
10	58.79 ± 0.52	-10.86 ± 0.88	-20.91 ± 0.08
15	62.47 ± 0.18	-9.92 ± 0.31	-20.21 ± 0.46
20	66.06 ± 0.61	-8.84 ± 0.28	-19.65 ± 0.19
25	69.11 ± 0.15	-7.72 ± 0.42	-18.61 ± 0.21
Glutaraldehyde (%)			
10	27.93 ± 0.68	-13.22 ± 0.28	-18.24 ± 0.33
15	25.97 ± 0.30	-12.34 ± 0.11	-17.43 ± 0.25
20	23.08 ± 0.93	-11.42 ± 0.15	-16.62 ± 0.20
25	20.73 ± 0.30	-10.56 ± 0.19	-15.08 ± 0.06

(1) 10% NaCl in 4% HCl, (2) 2% $ZnCl_2$ and 8% NaCl in 4% HCl, (3) 5% $ZnCl_2$ and 5% NaCl in 4% HCl, (4) 8% $ZnCl_2$ and 2% NaCl in 4% HCl, (5) 10% $ZnCl_2$ in 4% HCl, (6) 10% $MgCl_2$ in 4% HCl, (7) 10% $CaCl_2$ in 4% HCl, (8) 5% $ZnCl_2$ and 5% $CaCl_2$ in 4% HCl, (9) 5% $CaCl_2$ and 5% NaCl in 4% HCl and (10) 3.33% $ZnCl_2$, 3.33% $CaCl_2$ and 3.33% NaCl in 4% HCl.

Tables 58-60 show that a combination of sodium chloride, calcium chloride and zinc chloride in the coagulating bath conferred the greatest tenacity on the fibers compared with other inorganic salts. The wet tenacities of wet-spun fibers coagulated in acid-salt baths were too small to be detected. There were significant differences in fiber properties among the treatments with inorganic salts ($p<0.01$). The flexibility increased with increasing the test humidity (Tables 61 and 62). Zinc chloride-treated fibers had the best flexibility among these salts. Wet-spun fibers finished with 25% glutaraldehyde had significantly increased wet

Table 54. The effect of washing on the properties of soy protein fibers and fibers finished with 25% glyoxal or 25% glutaraldehyde at pH 3.5 at room temperature for 30 min and tested after equilibration to 11% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	113 ± 4^{a}	1.57 ± 0.32^{b}	1.6 ± 0.2^{a}	97 ± 8^{c}	1.16 ± 0.13^{a}
Glyoxal	114 ± 2^{a}	1.71 ± 0.24^{ab}	0.5 ± 0.1^{c}	231 ± 33^{b}	0.90 ± 0.04^{b}
Glutaraldehyde	102 ± 2^{b}	2.10 ± 0.57^{a}	0.8 ± 0.2^{b}	273 ± 36^{a}	1.53 ± 0.01^{a}
LSD	4.4	0.50	0.2	35.3	0.24
Washed by water					
Soy fiber	92 ± 2^{b}	0.76 ± 0.11^{b}	0.6 ± 0.1^{b}	135 ± 33^{c}	1.77 ± 0.11^{a}
Glyoxal	97 ± 3^{a}	0.97 ± 0.31^{b}	0.6 ± 0.1^{b}	186 ± 27^{b}	1.61 ± 0.04^{a}
Glutaraldehyde	96 ± 2^{a}	1.89 ± 0.35^{a}	0.9 ± 0.2^{a}	241 ± 31^{a}	1.44 ± 0.08^{b}
LSD	2.6	0.34	0.2	37.3	0.16

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 55. The effect of washing on the properties of soy protein fibers and fibers finished with 25% glyoxal or 25% glutaraldehyde at pH 3.5 at room temperature for 30 min and tested after equilibration to 65% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	128 ± 2^{a}	0.56 ± 0.06^{c}	73.4 ± 16.6^{a}	25 ± 3^{c}	14.32 ± 0.14^{a}
Glyoxal	124 ± 4^{b}	2.85 ± 0.37^{b}	3.8 ± 0.7^{b}	120 ± 7^{b}	6.72 ± 0.29^{c}
Glutaraldehyde	109 ± 2^{c}	3.28 ± 0.21^{a}	2.4 ± 0.4^{b}	178 ± 12^{a}	7.78 ± 0.13^{b}
LSD	3.4	0.30	11.8	10.1	0.64
Washed by water					
Soy fiber	106 ± 4^{b}	0.19 ± 0.02^{c}	1.6 ± 0.3^{a}	34 ± 5^{c}	11.26 ± 0.35^{a}
Glyoxal	103 ± 2^{b}	1.22 ± 0.06^{b}	0.9 ± 0.2^{b}	138 ± 8^{b}	10.80 ± 0.17^{ab}
Glutaraldehyde	110 ± 5^{a}	1.99 ± 0.61^{a}	1.0 ± 0.2^{b}	183 ± 23^{a}	10.51 ± 0.01^{b}
LSD	4.6	0.44	0.3	17.9	0.72

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

Table 56. The effect of washing on the properties of soy protein fibers and fibers finished with 25% glyoxal or 25% glutaraldehyde at pH 3.5 at room temperature for 30 min and tested after soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	155 ± 3^{a}	0.076 ± 0.023^{c}	3.9 ± 2.6^{b}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
Glyoxal	157 ± 3^{a}	0.31 ± 0.06^{b}	82.1 ± 11.7^{a}	1.7 ± 0.4^{b}	25.12 ± 1.08^{c}
Glutaraldehyde	158 ± 4^{a}	0.70 ± 0.08^{a}	77.4 ± 4.1^{a}	4.1 ± 1.3^{ab}	37.30 ± 0.19^{b}
LSD	4.1	0.08	9.0	3.4	2.90
Washed by water					
Soy fiber	140 ± 2^{b}	0.024 ± 0.010^{c}	2.6 ± 0.6^{c}	1.7 ± 0.4^{b}	62.08 ± 2.36^{a}
Glyoxal	139 ± 4^{b}	0.15 ± 0.04^{b}	31.9 ± 11.7^{b}	1.6 ± 0.5^{b}	39.44 ± 2.12^{b}
Glutaraldehyde	147 ± 3^{a}	0.63 ± 0.10^{a}	51.3 ± 14.6^{a}	3.8 ± 1.0^{a}	25.36 ± 0.30^{c}
LSD	4.1	0.08	13.3	0.8	5.86

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 57. The flexibility of soy protein fibers and fibers finished with 25% glyoxal or 25% glutaraldehyde and then washed in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
Glyoxal									X				
Glutaraldehyde								X					
Washed by water													
Soy fiber													X
Glyoxal													X
Glutaraldehyde												X	
65% humidity													
Soy fiber	X												
Glyoxal			X										
Glutaraldehyde		X											
Washed by water													
Soy fiber													X
Glyoxal											X		
Glutaraldehyde											X		

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 58. The properties of wet-spun soy protein fibers coagulated in various salt-acid baths and tested after equilibration to 11% relative humidity

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
10% NaCl (1)	95 ± 3^{a}	0.68 ± 0.10^{cd}	0.5 ± 0.1^{bc}	150 ± 12^{cd}	1.06 ± 0.06^{h}
2% $ZnCl_2$ 8% NaCl (2)	76 ± 3^{bc}	0.89 ± 0.16^{bc}	0.5 ± 0.1^{bc}	189 ± 38^{b}	1.07 ± 0.04^{gh}
5% $ZnCl_2$ 5% NaCl (3)	73 ± 2^{cd}	0.51 ± 0.27^{de}	0.4 ± 0.1^{c}	115 ± 20^{ef}	1.23 ± 0.03^{fg}
8% $ZnCl_2$ 2% NaCl (4)	68 ± 2^{e}	0.88 ± 0.32^{bc}	0.5 ± 0.1^{bc}	173 ± 31^{bc}	1.31 ± 0.14^{ef}
10% $ZnCl_2$ (5)	78 ± 3^{b}	0.26 ± 0.13^{e}	0.8 ± 0.2^{a}	55 ± 10^{g}	1.47 ± 0.07^{de}
10% $MgCl_2$ (6)	75 ± 3^{bcd}	0.51 ± 0.29^{de}	0.5 ± 0.2^{bc}	149 ± 21^{cd}	2.18 ± 0.08^{b}
10% $CaCl_2$ (7)	76 ± 3^{bc}	1.06 ± 0.44^{b}	0.6 ± 0.1^{b}	143 ± 37^{cde}	2.58 ± 0.07^{a}
5% $ZnCl_2$ 5% $CaCl_2$ (8)	72 ± 3^{d}	1.06 ± 0.24^{b}	0.7 ± 0.1^{ab}	131 ± 14^{def}	2.00 ± 0.02^{c}
5% $CaCl_2$ 5% NaCl (9)	76 ± 3^{bc}	0.81 ± 0.22^{bcd}	0.8 ± 0.3^{a}	110 ± 21^{f}	1.95 ± 0.04^{c}
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	77 ± 4^{bc}	1.84 ± 0.34^{a}	0.5 ± 0.1^{bc}	354 ± 35^{a}	1.61 ± 0.10^{d}
LSD	3.6	0.31	0.2	30.1	0.16

[a-h] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 59. The properties of wet-spun soy protein fibers coagulated in various salt-acid baths and tested after equilibration to 65% relative humidity

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
10% NaCl (1)	105 ± 3^{a}	0.35 ± 0.18^{c}	0.4 ± 0.1^{c}	68 ± 17^{d}	8.23 ± 0.15^{g}
2% $ZnCl_2$ 8% NaCl (2)	84 ± 3^{de}	0.37 ± 0.11^{bc}	0.4 ± 0.1^{c}	98 ± 9^{ab}	8.40 ± 0.23^{g}
5% $ZnCl_2$ 5% NaCl(3)	80 ± 3^{f}	0.28 ± 0.07^{c}	7.7 ± 6.1^{a}	30 ± 14^{e}	11.76 ± 0.05^{f}
8% $ZnCl_2$ 2% NaCl (4)	74 ± 3^{g}	1.05 ± 0.17^{a}	6.1 ± 5.1^{ab}	76 ± 16^{cd}	13.12 ± 0.30^{e}
10% $ZnCl_2$ (5)	87 ± 3^{cd}	0.25 ± 0.12^{c}	1.9 ± 0.2^{c}	27 ± 9^{e}	12.61 ± 0.36^{ef}
10% $MgCl_2$ (6)	81 ± 3^{ef}	0.022 ± 0.010^{d}	2.5 ± 1.3^{bc}	4 ± 2^{f}	22.91 ± 0.52^{b}
10% $CaCl_2$ (7)	98 ± 6^{b}	0.056 ± 0.033^{d}	5.9 ± 3.9^{ab}	4 ± 2^{f}	30.08 ± 1.03^{a}
5% $ZnCl_2$ 5% $CaCl_2$ (8)	82 ± 4^{ef}	0.55 ± 0.25^{b}	0.7 ± 0.3^{c}	84 ± 16^{bc}	22.44 ± 0.08^{b}
5% $CaCl_2$ 5% NaCl (9)	82 ± 4^{ef}	0.38 ± 0.29^{bc}	0.2 ± 0.4^{c}	100 ± 10^{a}	21.15 ± 0.20^{c}
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	90 ± 2^{c}	1.13 ± 0.13^{a}	2.2 ± 0.6^{c}	91 ± 18^{ab}	18.81 ± 0.73^{d}
LSD	4.1	0.19	3.7	14.7	1.04

[a-g] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 60. The properties of wet-spun soy protein fibers coagulated in various salt-acid baths and tested after soaking in water

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
10% NaCl (1)	120 ± 3^{a}	---	---	---	83.15 ± 1.43^{h}
2% $ZnCl_2$ 8% NaCl (2)	102 ± 3^{c}	---	--	---	86.16 ± 2.77^{gh}
5% $ZnCl_2$ 5% NaCl.(3)	97 ± 3^{e}	---	---	---	89.13 ± 1.40^{fg}
8% $ZnCl_2$ 2% NaCl.(4)	97 ± 3^{e}	---	---	---	92.97 ± 0.73^{f}
10% $ZnCl_2$ (5)	108 ± 3^{b}	---	---	---	101.12 ± 1.43^{e}
10% $MgCl_2$ (6)	101 ± 2^{cd}	---	---	---	207.37 ± 1.05^{a}
10% $CaCl_2$ (7)	122 ± 4^{a}	---	---	---	213.14 ± 1.76^{a}
5% $ZnCl_2$ 5% $CaCl_2$ (8)	101 ± 3^{cd}	---	---	---	185.12 ± 1.41^{c}
5% $CaCl_2$ 5% NaCl (9)	98 ± 3^{de}	---	---	---	177.24 ± 6.51^{d}
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	104 ± 2^{c}	---	---	---	198.19 ± 2.89^{b}
LSD	3.4				5.88

--- Values too low to determine.

a-h Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 61. The flexibility of wet-spun fibers coagulated in various salt-acid baths in terms of the smallest rod diameter around which fibers could be looped without breaking at 11% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
10% NaCl (1)													X
2% $ZnCl_2$ 8% NaCl (2)													X
5% $ZnCl_2$ 5% NaCl (3)												X	
8% $ZnCl_2$ 2% NaCl (4)												X	
10% $ZnCl_2$ (5)									X				
10% $MgCl_2$ (6)													X
10% $CaCl_2$ (7)													X
5% $ZnCl_2$ 5% $CaCl_2$ (8)												X	
5% $CaCl_2$ 5% NaCl (9)												X	
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl (10)													X

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 62. The flexibility of wet-spun fibers coagulated in various salt-acid baths in terms of the smallest rod diameter around which fibers could be looped without breaking at 65% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
65% humidity													
10% NaCl (1)		X											
2% $ZnCl_2$ 8% NaCl (2)		X											
5% $ZnCl_2$ 5% NaCl (3)	X												
8% $ZnCl_2$ 2% NaCl (4)	X												
10% $ZnCl_2$ (5)	X												
10% $MgCl_2$ (6)	X												
10% $CaCl_2$ (7)	X												
5% $ZnCl_2$ 5% $CaCl_2$ (8	X												
5% $CaCl_2$ 5% NaCl (9)		X											
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl (10)		X											

X Fibers could be looped around the smallest diameter glass rod without breaking.

tenacity and flexibility (Tables 63-67). The moisture regain of wet-spun fibers finished with glutaraldehyde was significantly decreased ($p<0.01$).

The coagulating solutions contained 3.33% $ZnCl_2$, 3.33% $CaCl_2$ and 3.33% NaCl with 6% glutaraldehyde in 4% HCl and 3.33% $ZnCl_2$, 3.33% $CaCl_2$ and 3.33% NaCl with 12% glutaraldehyde in 4% HCl were tested to improve their wet tenacity. Adding glutaraldehyde to the acid-salt bath so that cross-linking occurred with protein coagulation significantly also increased tenacity ($p<0.01$) (Tables 68-71).

Stretching fibers to 170% of their original length after they were coagulated in a bath containing acid, sodium chloride, calcium chloride and zinc chloride and finished with 25% glutaraldehyde yielded the best wet-spun fibers .

Other cross-linking agents

Attempts to use other cross-linking agents were not successful. Phosphorus oxychloride added to moistened fibers destroyed they as a result of the high temperature and low pH that resulted from the hydrolysis of the phosphorus oxychloride. Soy protein fibers that were rendered anhydrous by benzene azeotropic distillation before finishing with epichlorohydrin or adipoyl chloride in pyridine could not be penetrated by the reagents. Malonaldehyde bis (dimethyl acetal) was acid hydrolyzed and heated to produce malonaldehyde (a three carbon dialdehyde) for finishing soy fibers. This trial did not improve fiber tenacity as well as glutaraldehyde, possibly because methanol, produced from acid hydrolysis of the acetal, associated with protein molecules and interrupted the cross-linking reaction. Attempts to finish fibers by toluene 2,4-diisocyanate were not successful because the reagent was not water soluble and could not penetrate the fiber in benzene solution. Seemingly to be successful, a fiber modifying agent must be active in aqueous solutions or in acetic acid. Otherwise it will not penetrate the dried protein matrix, or if it is an aggressive agent, it will destroy the fibers.

Table 63. The properties of wet-spun soy protein fibers coagulated in various salt-acid baths and finished with 25% glutaraldehyde at room temperature for 30 min and tested after equilibration to 11% relative humidity

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Finished by glutaraldehyde					
10% NaCl (1)	98 ± 6^{a}	0.65 ± 0.21^{e}	0.5 ± 0.1^{c}	144 ± 24^{ef}	0.96 ± 0.02^{e}
2% $ZnCl_2$ 8% NaCl (2)	77 ± 3^{bc}	0.74 ± 0.08^{e}	0.8 ± 0.3^{a}	129 ± 26^{f}	1.04 ± 0.01^{d}
5% $ZnCl_2$ 5% NaCl (3)	70 ± 3^{ef}	0.96 ± 0.17^{cde}	0.5 ± 0.1^{c}	201 ± 31^{d}	1.19 ± 0.06^{b}
8% $ZnCl_2$ 2% NaCl (4)	72 ± 2^{def}	1.34 ± 0.36^{b}	0.5 ± 0.1^{d}	331 ± 39^{b}	1.14 ± 0.03^{bc}
10% $ZnCl_2$ (5)	78 ± 4^{bc}	0.93 ± 0.12^{cde}	0.6 ± 0.2^{bc}	214 ± 24^{cd}	1.16 ± 0.03^{b}
10% $MgCl_2$ (6)	68 ± 3^{f}	0.87 ± 0.37^{de}	0.5 ± 0.1^{c}	188 ± 71^{de}	1.29 ± 0.01^{a}
10% $CaCl_2$ (7)	81 ± 2^{b}	1.44 ± 0.29^{b}	0.5 ± 0.1^{c}	258 ± 54^{c}	1.35 ± 0.01^{a}
5% $ZnCl_2$ 5% $CaCl_2$ (8)	74 ± 4^{cde}	1.23 ± 0.41^{bc}	0.8 ± 0.2^{a}	196 ± 22^{d}	1.08 ± 0.03^{cd}
5% $CaCl_2$ 5% NaCl (9)	76 ± 5^{cd}	1.21 ± 0.39^{bcd}	0.8 ± 0.3^{a}	228 ± 22^{cd}	1.18 ± 0.03^{b}
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	78 ± 4^{bc}	2.53 ± 0.50^{a}	0.7 ± 0.1^{ab}	407 ± 56^{a}	1.13 ± 0.07^{bc}
LSD	4.2	0.36	0.2	46.8	0.08

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

Table 64. The properties of wet-spun soy protein fibers coagulated in various salt-acid baths and finished with 25% glutaraldehyde at room temperature for 30 min and tested after equilibration to 65% relative humidity

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Finished by glutaraldehyde					
10% NaCl (1)	111 ± 3^{a}	0.62 ± 0.28^{f}	4.2 ± 1.6^{b}	48 ± 3^{bcd}	6.41 ± 0.24^{c}
2% $ZnCl_2$ 8% NaCl (2)	90 ± 4^{bc}	0.91 ± 0.27^{bcd}	4.1 ± 1.8^{b}	51 ± 10^{bc}	6.59 ± 0.03^{c}
5% $ZnCl_2$ 5% NaCl (3)	77 ± 3^{e}	0.91 ± 0.16^{bcde}	2.0 ± 1.4^{de}	42 ± 7^{cde}	7.68 ± 0.43^{ab}
8% $ZnCl_2$ 2% NaCl. (4)	79 ± 2^{e}	1.18 ± 0.33^{ab}	3.2 ± 0.6^{bcd}	52 ± 6^{bc}	7.23 ± 0.23^{b}
10% $ZnCl_2$ (5)	94 ± 3^{b}	0.75 ± 0.34^{cdef}	8.1 ± 2.5^{a}	37 ± 19^{de}	7.42 ± 0.11^{ab}
10% $MgCl_2$ (6)	78 ± 3^{e}	0.61 ± 0.12^{f}	1.2 ± 0.6^{e}	29 ± 12^{ef}	7.46 ± 0.47^{ab}
10% $CaCl_2$ (7)	86 ± 3^{d}	0.97 ± 0.24^{bc}	4.6 ± 2.7^{b}	60 ± 8^{ab}	7.84 ± 0.07^{a}
5% $ZnCl_2$ 5% $CaCl_2$ (8)	89 ± 4^{cd}	0.66 ± 0.20^{def}	3.9 ± 0.4^{bc}	22 ± 4^{f}	7.23 ± 0.03^{b}
5% $CaCl_2$ 5% NaCl (9)	89 ± 3^{cd}	0.63 ± 0.24^{ef}	2.1 ± 1.0^{cde}	35 ± 21^{def}	7.54 ± 0.02^{ab}
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	90 ± 4^{bc}	1.34 ± 0.11^{a}	4.7 ± 0.9^{b}	71 ± 5^{a}	7.43 ± 0.35^{ab}
LSD	4.0	0.28	1.8	13.0	0.57

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

Table 65. The properties of wet-spun soy protein fibers coagulated in various salt-acid baths and finished with 25% glutaraldehyde at room temperature for 30 min and tested after soaking in water

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Finished by glutaraldehyde					
10% NaCl (1)	126 ± 3^{a}	0.16 ± 0.05^{cd}	21.1 ± 10.5^{cd}	1.8 ± 0.6^{abc}	29.13 ± 1.37^{f}
2% $ZnCl_2$ 8% NaCl (2)	103 ± 3^{c}	0.24 ± 0.08^{bc}	31.7 ± 16.5^{c}	1.9 ± 0.8^{abc}	29.63 ± 2.12^{f}
5% $ZnCl_2$ 5% NaCl (3)	87 ± 3^{f}	0.24 ± 0.04^{bc}	46.5 ± 10.3^{b}	1.3 ± 1.4^{c}	41.84 ± 1.53^{ab}
8% $ZnCl_2$ 2% NaCl (4)	98 ± 2^{d}	0.31 ± 0.04^{ab}	20.7 ± 12.4^{cd}	2.0 ± 1.3^{abc}	36.62 ± 0.84^{cd}
10% $ZnCl_2$ (5)	109 ± 3^{b}	0.15 ± 0.05^{de}	14.2 ± 4.0^{d}	2.6 ± 0.6^{ab}	35.92 ± 1.29^{cd}
10% $MgCl_2$ (6)	92 ± 2^{e}	0.072 ± 0.031^{ef}	18.5 ± 10.4^{cd}	2.2 ± 0.7^{abc}	38.79 ± 0.52^{bc}
10% $CaCl_2$ (7)	114 ± 4^{b}	0.054 ± 0.031^{f}	18.4 ± 11.0^{cd}	2.7 ± 2.4^{a}	45.23 ± 1.29^{a}
5% $ZnCl_2$ 5% $CaCl_2$ (8)	103 ± 4^{c}	0.16 ± 0.06^{cd}	22.3 ± 10.8^{cd}	1.3 ± 0.5^{bc}	31.63 ± 2.14^{ef}
5% $CaCl_2$ 5% NaCl (9)	102 ± 4^{c}	0.24 ± 0.11^{bc}	57.9 ± 20.3^{b}	1.1 ± 0.2^{c}	31.84 ± 1.53^{ef}
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	102 ± 4^{c}	0.38 ± 0.14^{a}	83.1 ± 13.7^{a}	1.6 ± 0.6^{abc}	33.25 ± 2.45^{de}
LSD	3.5	0.08	14.6	1.2	3.60

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

Table 66. The flexibility of wet-spun fibers coagulated in various salt-acid baths and finished with glutaraldehyde in terms of the smallest rod diameter around which fibers could be looped without breaking at 11% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Finished by glutaraldehyde													
10% NaCl (1)												X	
2% $ZnCl_2$ 8% NaCl (2)											X		
5% $ZnCl_2$ 5% NaCl (3)											X		
8% $ZnCl_2$ 2% NaCl (4)											X		
10% $ZnCl_2$ (5)										X			
10% $MgCl_2$ (6)											X		
10% $CaCl_2$ (7)											X		
5% $ZnCl_2$ 5% $CaCl_2$ (8)											X		
5% $CaCl_2$ 5% NaCl (9)											X		
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl (10)											X		

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 67. The flexibility of wet-spun fibers coagulated in various salt-acid baths and finished with glutaraldehyde in terms of the smallest rod diameter around which fibers could be looped without breaking at 65% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
65% humidity													
Finished by glutaraldehyde													
10% NaCl (1)			X										
2% $ZnCl_2$ 8% NaCl (2)		X											
5% $ZnCl_2$ 5% NaCl (3)	X												
8% $ZnCl_2$ 2% NaCl (4)	X												
10% $ZnCl_2$ (5)	X												
10% $MgCl_2$ (6)	X												
10% $CaCl_2$ (7)	X												
5% $ZnCl_2$ 5% $CaCl_2$ (8)	X												
5% $CaCl_2$ 5% NaCl (9)		X											
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl (10)	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 68. The properties of wet-spun soy protein fibers coagulated in combinations of sodium chloride, zinc chloride and calcium chloride-acid baths with 6% or 12% glutaraldehyde and wet-spun fibers finished with 25% glutaraldehyde and stretched to 170% of their original lengths and tested after equilibration to 11% relative humidity

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	77 ± 4^a	1.84 ± 0.34^b	0.5 ± 0.1^a	354 ± 35^b	1.61 ± 0.10^a
(10)+ 6% Glutaraldehyde	78 ± 2^a	2.97 ± 0.41^a	0.7 ± 0.1^a	429 ± 32^a	1.80 ± 0.04^a
(10)+ 12% Glutaraldehyde	78 ± 2^a	3.06 ± 0.52^a	0.6 ± 0.2^a	408 ± 13^a	1.74 ± 0.06^a
LSD	3.4	0.53	0.2	35.0	0.23
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	77 ± 4^a	1.84 ± 0.34^b	0.5 ± 0.1^b	354 ± 35^b	1.61 ± 0.10^a
Finished by 25% glutaraldehyde after spinning					
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl	78 ± 4^a	2.53 ± 0.50^b	0.7 ± 0.1^b	407 ± 56^a	1.13 ± 0.07^b
and stretched to 170%	47 ± 2^b	6.43 ± 1.62^a	2.1 ± 0.5^a	352 ± 32^b	1.15 ± 0.02^b
LSD	4.0	1.23	0.4	52.1	0.23

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

Table 69. The properties of wet-spun soy protein fibers coagulated in combinations of sodium chloride, zinc chloride and calcium chloride-acid baths with 6% or 12% glutaraldehyde and wet-spun fibers finished with 25% glutaraldehyde and stretched to 170% of their original lengths and tested after equilibration to 65% relative humidity

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
65% humidity					
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	90 ± 2^a	1.13 ± 0.13^c	2.2 ± 0.6^a	91 ± 18^c	18.81 ± 0.73^a
(10)+ 6% Glutaraldehyde	89 ± 3^a	2.06 ± 0.28^b	1.5 ± 0.3^b	224 ± 12^a	14.61 ± 0.21^b
(10)+ 12% Glutaraldehyde	90 ± 3^a	2.90 ± 0.42^a	1.7 ± 0.3^b	197 ± 12^b	12.09 ± 0.36^c
LSD	3.6	0.37	0.5	17.6	1.54
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	90 ± 2^a	1.13 ± 0.13^b	2.2 ± 0.6^c	91 ± 18^b	18.81 ± 0.73^a
Finished by 25% glutaraldehyde after spinning					
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl	90 ± 4^a	1.34 ± 0.11^b	4.7 ± 0.9^a	71 ± 5^b	7.43 ± 0.35^b
and stretched to 170%	51 ± 2^b	6.26 ± 0.82^a	3.1 ± 0.6^b	299 ± 62^a	7.53 ± 0.35^b
LSD	3.5	0.59	0.9	46.1	1.62

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

Table 70. The properties of wet-spun soy protein fibers coagulated in combinations of sodium chloride, zinc chloride and calcium chloride-acid baths with 6% or 12% glutaraldehyde and wet-spun fibers finished with 25% glutaraldehyde and stretched to 170% of their original lengths and tested after soaking in water

Fiber (coagulation bath)	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
In water					
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	104 ± 2^a	---	---	---	198.19 ± 2.89^a
(10)+ 6% Glutaraldehyde	102 ± 2^a	0.11 ± 0.01^b	2.7 ± 0.5^a	0.9 ± 0.2^b	97.47 ± 1.29^b
(10)+ 12% Glutaraldehyde	103 ± 2^a	0.15 ± 0.02^a	2.8 ± 0.7^a	1.4 ± 0.3^a	86.08 ± 0.78^c
LSD	2.5	0.03	0.8	0.4	5.99
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	104 ± 2^a	---	---	---	198.19 ± 2.89^a
Finished by 25% glutaraldehyde after spinning					
3.3% $CaCl_2$ 3.3% $ZnCl_2$ and 3.3% NaCl (10)	102 ± 4^a	0.38 ± 0.14	83.1 ± 13.7^a	1.6 ± 0.6^b	33.25 ± 2.45^b
and stretched to 170%	63 ± 3^b	0.72 ± 0.15	59.7 ± 14.2^b	8.1 ± 1.4^a	29.17 ± 1.45^b
LSD	3.9	0.19	17.9	1.4	7.46

--- Values too low to determine.

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

Table 71. The flexibility of wet-spun soy protein fibers coagulated in combinations of sodium chloride, zinc chloride and calcium chloride-acid baths with 6% or 12% glutaraldehyde and finished with 25% glutaraldehyde and stretched to 170% of their original length in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl (10)													X
(10)+ 6% Glutaraldehyde									X				
(10)+ 12% Glutaraldehyde									X				
Finished by 25% glutaraldehyde after spinning													
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl											X		
and stretched to 170%									X				
65% humidity													
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl (10)		X											
(10)+ 6% Glutaraldehyde		X											
(10)+ 12% Glutaraldehyde		X											
Finished by 25% glutaraldehyde after spinning													
3.3% $CaCl_2$ 3.3% $CaCl_2$ and 3.3% NaCl	X												
and stretched to 170%	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

VI. Combinations of Finishing Treatments

Fibers finished by a combination of glutaraldehyde and acetic anhydride

Finishing treatments with both glutaraldehyde and acetic anhydride showed significant improvements in fiber properties of extruded soy protein fibers ($p<0.01$), and physical stretching of the fibers increased their strength. So, a combination of these chemical and physical treatments was applied to improve the fiber properties. Tables 72 and 73 show that these combined treatments significantly improved their properties of extruded soy fibers. Experience showed that to finish fibers with this combination of treatments, the fibers should be first reacted with glutaraldehyde and then treated with acetic anhydride, because if the amine groups of soy fibers were reacted first with acetic anhydride they were not available for later reaction with glutaraldehyde to cross-link the fibers. Figure 25 shows that more ε-amino groups of soy fibers were reacted with acetic anhydride than glutaraldehyde in titration ($p<0.01$). The titration results showed that there were about 12, 47 and 53% of their titratible groups derivatized by glutaraldehyde, acetic anhydride, and a combination of glutaraldehyde and acetic anhydride, respectively.

Scanning electron micrographs of extruded and wet-spun fibers finished with glutaraldehyde and stretched to 150% and 170%, respectively, of their original length are shown in Figure 29 in the appendix. Both extruded and wet-spun fibers finished with glutaraldehyde and stretched to 150% and 170%, respectively, of their original length exhibited similar structures. Stretched fibers showed more uniform structures than non-stretched fibers (Figures 28 and 29 of the appendix). Stretching the fibers might change the fiber orientation to crystalline and the fiber structure become more linear and finer. This rearrangement of fiber structures significantly increased tenacity and flexibility.

Table 72. The properties of soy protein fibers finished with a combination of glutaraldehyde and acetic anhydride treatments, stretched to 130 and 150% of their original lengths, respectively, and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
100%	80 ± 4^{a}	3.50 ± 0.40^{c}	8.8 ± 2.1^{a}	185 ± 19^{c}	1.42 ± 0.12^{a}
130%	73 ± 2^{b}	8.53 ± 0.37^{b}	5.2 ± 1.2^{b}	321 ± 30^{b}	1.49 ± 0.05^{a}
150%	63 ± 3^{c}	9.11 ± 0.25^{a}	5.7 ± 1.2^{b}	353 ± 19^{a}	1.50 ± 0.06^{a}
LSD	3.3	0.42	1.9	28.5	0.26
65% humidity					
100%	105 ± 2^{a}	2.79 ± 0.03^{b}	31.0 ± 6.4^{a}	181 ± 9^{b}	7.99 ± 0.31^{a}
130%	79 ± 2^{b}	4.87 ± 0.61^{a}	5.0 ± 1.2^{b}	205 ± 17^{ab}	8.19 ± 0.28^{a}
150%	68 ± 1^{c}	5.23 ± 0.59^{a}	9.2 ± 4.1^{b}	223 ± 31^{a}	8.22 ± 0.13^{a}
LSD	2.0	0.60	5.5	26.3	0.80
In water					
100%	115 ± 4^{a}	1.16 ± 0.11^{b}	58.5 ± 6.7^{a}	14.9 ± 2.6^{b}	16.55 ± 0.64^{a}
130%	91 ± 2^{b}	2.09 ± 0.17^{a}	63.9 ± 5.5^{a}	34.6 ± 7.7^{a}	16.78 ± 0.80^{a}
150%	78 ± 2^{c}	2.36 ± 0.41^{a}	39.3 ± 8.2^{b}	38.5 ± 7.4^{a}	17.00 ± 0.76^{a}
LSD	3.4	0.32	8.5	7.8	2.34

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 73. The flexibility of fibers finished with a combination of glutaraldehyde and acetic anhydride treatments, stretched to 130 and 150% of their original lengths, respectively, in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
100%		X											
130%		X											
150%		X											
65% humidity													
100%	X												
130%	X												
150%	X												

X Fibers could be looped around the smallest diameter glass rod without breaking.

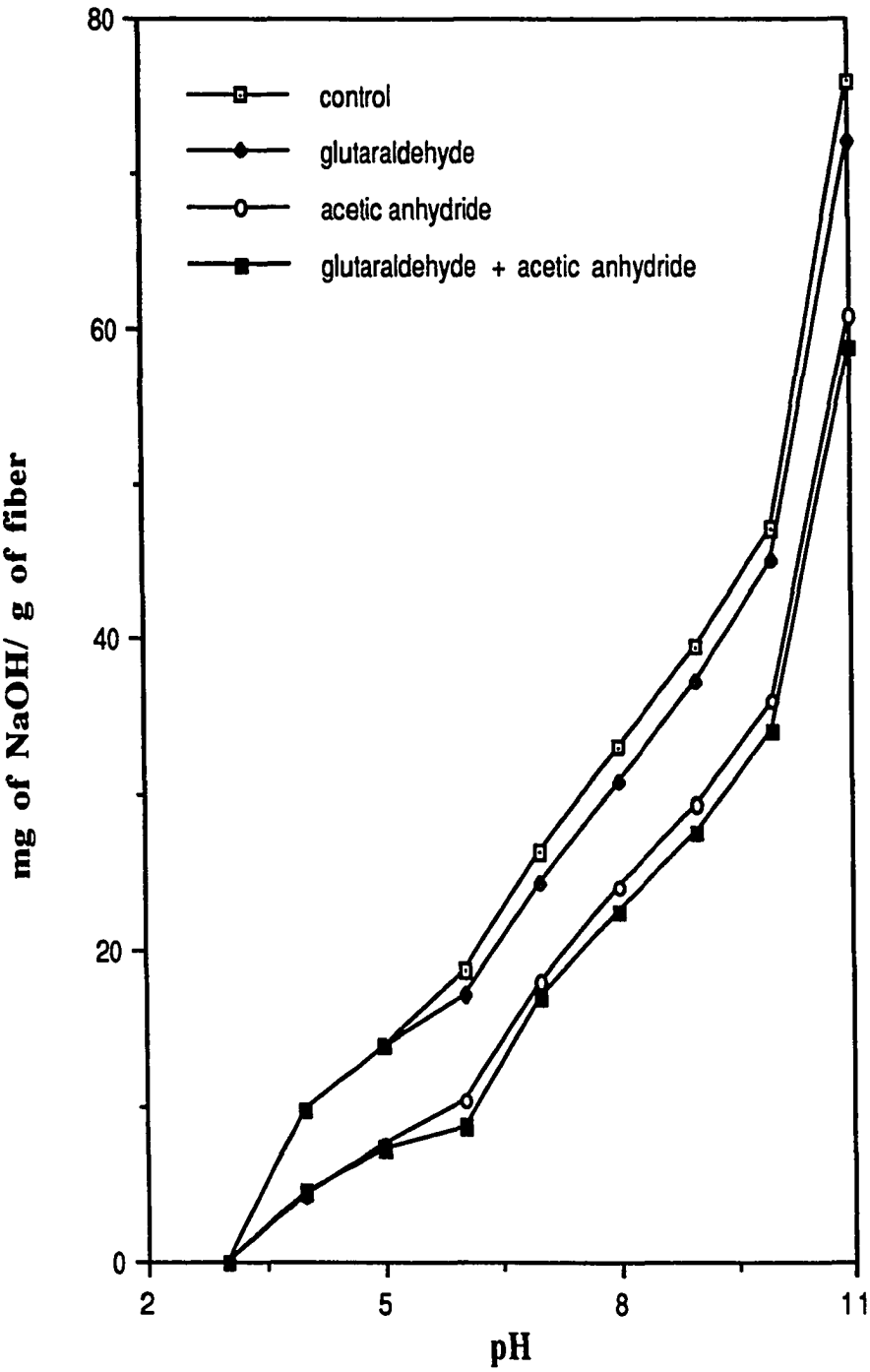


Figure 25. Titration curves of control fibers and control fibers finished with glutaraldehyde, acetic anhydride or a combination of glutaraldehyde and acetic anhydride.

Fibers made from esterified soy proteins and finished by acetic anhydride, glutaraldehyde or a combination of glutaraldehyde and acetic anhydride

Tables 74-78 show the results of finishing fibers made from esterified soy proteins with glutaraldehyde, acetic anhydride or a combination of both treatments. There were significant differences in fiber properties among alcohols, finishing treatments and testing humidities ($p<0.01$). All treatments showed significant improvements in fiber properties as well as unmodified fibers ($p<0.01$).

Reacting the polar groups of fibers made from esterified soy proteins with glutaraldehyde and acetic anhydride significantly increased the tenacity. There were significant differences in titration curves among unmodified fibers, butanol-esterified fibers and butanol-esterified fibers after finishing treatments ($p<0.01$). The titration results (Figure 26) showed that the butanol-esterified fibers became less polar and had about 10, 47 and 51% of their titratible groups derivatized after being finished by glutaraldehyde, acetic anhydride or a combination of glutaraldehyde and acetic anhydride.

Comparison the best fibers from extrusion and wet spinning with other commercial fibers

The best wet-spun fibers were produced with a 19.61% soy protein dope, coagulated in a 4% HCl solution containing 3.3% sodium chloride, 3.3% zinc chloride and 3.3% calcium chloride, finished with 25% glutaraldehyde and then stretched to 170% of their original lengths. 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% of their original lengths. Table 79 shows the comparison of commercial fibers, such as cotton, flax, silk, wool and polyester, with wet-spun and extruded soy protein fibers. The tenacities of wet-spun and extruded fibers are lower than these commercial fibers.

Table 74. The properties of fibers at 11% relative humidity made form soy protein esterified with various alcohols before extrusion compared with the same treatments finished with acetic anhydride, glutaraldehyde or both treatments after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	113 ± 4^{bc}	1.57 ± 0.32^{a}	1.6 ± 0.2^{b}	97 ± 8^{b}	1.61 ± 0.13^{a}
Ethylene glycol	112 ± 4^{c}	0.56 ± 0.12^{b}	2.9 ± 1.2^{a}	34 ± 9^{c}	1.12 ± 0.06^{b}
Butanol	119 ± 3^{a}	0.75 ± 0.12^{b}	0.7 ± 0.2^{c}	119 ± 20^{a}	1.06 ± 0.07^{b}
Propanol	117 ± 3^{ab}	0.57 ± 0.08^{b}	0.7 ± 0.2^{c}	44 ± 4^{c}	1.15 ± 0.07^{b}
LSD	3.9	0.22	0.8	14.1	0.24
Glutaraldehyde finished					
Soy fiber	102 ± 2^{c}	2.10 ± 0.57^{a}	0.8 ± 0.2^{a}	273 ± 36^{ab}	1.53 ± 0.01^{a}
Ethylene glycol	113 ± 3^{b}	1.50 ± 0.44^{b}	0.7 ± 0.1^{a}	245 ± 68^{c}	1.17 ± 0.06^{b}
Butanol	117 ± 4^{a}	1.92 ± 0.39^{ab}	0.7 ± 0.1^{a}	321 ± 44^{a}	1.11 ± 0.02^{bc}
Propanol	117 ± 3^{a}	1.43 ± 0.09^{b}	0.5 ± 0.1^{b}	316 ± 35^{a}	1.05 ± 0.04^{c}
LSD	3.3	0.50	0.2	57.5	0.11
Acetic anhydride finished					
Soy fiber	115 ± 2^{bc}	2.31 ± 0.13^{a}	4.7 ± 1.2^{a}	105 ± 5^{b}	0.77 ± 0.01^{a}
Ethylene glycol	113 ± 2^{c}	1.77 ± 0.38^{b}	2.0 ± 0.6^{b}	102 ± 8^{b}	0.75 ± 0.01^{ab}
Butanol	117 ± 4^{b}	2.05 ± 0.61^{ab}	1.5 ± 0.4^{b}	145 ± 5^{a}	0.72 ± 0.01^{bc}
Propanol	120 ± 2^{a}	1.65 ± 0.35^{b}	1.7 ± 0.4^{b}	105 ± 5^{b}	0.69 ± 0.01^{c}
LSD	2.7	0.49	0.7	7.0	0.04
Combination of glutaraldehyde and acetic anhydride finishing treatments					
Soy fiber	80 ± 4^{c}	3.50 ± 0.40^{a}	8.8 ± 2.1^{a}	185 ± 15^{a}	1.42 ± 0.12^{a}
Ethylene glycol	106 ± 4^{b}	2.27 ± 0.31^{b}	1.3 ± 0.4^{b}	154 ± 9^{bc}	0.86 ± 0.03^{b}
Butanol	119 ± 4^{a}	2.48 ± 0.39^{b}	1.5 ± 0.2^{b}	172 ± 20^{ab}	0.78 ± 0.03^{b}
Propanol	118 ± 3^{a}	2.05 ± 0.40^{b}	1.7 ± 0.5^{b}	143 ± 7^{c}	0.74 ± 0.06^{b}
LSD	4.3	2.09	1.3	18.0	0.19

a-e Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 75. The properties of fibers at 65% relative humidity made form soy protein esterified with various alcohols before extrusion compared with the same treatments finished with acetic anhydride, glutaraldehyde or both treatments after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	128 ± 2^{b}	0.56 ± 0.06^{a}	73.4 ± 16.6^{a}	25 ± 3^{a}	14.32 ± 0.14^{a}
Ethylene glycol	133 ± 5^{a}	0.14 ± 0.01^{c}	10.4 ± 3.2^{b}	6 ± 1^{b}	13.76 ± 0.15^{b}
Butanol	130 ± 4^{ab}	0.49 ± 0.09^{b}	11.1 ± 3.4^{b}	22 ± 3^{a}	12.84 ± 0.04^{c}
Propanol	129 ± 3^{ab}	0.15 ± 0.03^{c}	6.6 ± 1.5^{b}	23 ± 6^{a}	12.92 ± 0.03^{c}
LSD	4.4	0.06	10.4	4.3	0.29
Glutaraldehyde finished					
Soy fiber	109 ± 2^{c}	3.28 ± 0.21^{a}	2.4 ± 0.4^{a}	178 ± 12^{b}	7.87 ± 0.13^{a}
Ethylene glycol	123 ± 4^{b}	0.62 ± 0.12^{c}	0.7 ± 0.2^{b}	115 ± 15^{c}	7.28 ± 0.06^{b}
Butanol	131 ± 3^{a}	1.35 ± 0.16^{b}	0.9 ± 0.2^{b}	207 ± 18^{a}	6.79 ± 0.11^{c}
Propanol	131 ± 4^{a}	0.64 ± 0.12^{c}	0.7 ± 0.1^{b}	181 ± 17^{b}	7.12 ± 0.13^{b}
LSD	4.2	0.19	0.3	18.5	0.31
Acetic anhydride finished					
Soy fiber	140 ± 3^{a}	1.07 ± 0.12^{a}	1.8 ± 0.8^{a}	113 ± 13^{a}	5.52 ± 0.02^{a}
Ethylene glycol	134 ± 1^{b}	0.43 ± 0.05^{c}	1.7 ± 0.4^{a}	18 ± 4^{d}	4.83 ± 0.05^{b}
Butanol	134 ± 4^{b}	0.67 ± 0.18^{b}	1.7 ± 0.1^{a}	80 ± 12^{b}	4.22 ± 0.23^{c}
Propanol	132 ± 2^{b}	0.48 ± 0.17^{c}	1.3 ± 0.7^{b}	44 ± 8^{c}	4.27 ± 0.04^{c}
LSD	3.7	0.17	0.3	12.1	0.34
Combination of glutaraldehyde and acetic anhydride finishing treatments					
Soy fiber	105 ± 2^{d}	2.80 ± 0.03^{a}	31.0 ± 6.4^{a}	181 ± 9^{a}	7.99 ± 0.31^{a}
Ethylene glycol	118 ± 4^{c}	1.41 ± 0.24^{c}	2.4 ± 0.4^{b}	115 ± 4^{b}	6.79 ± 0.13^{b}
Butanol	126 ± 4^{b}	1.74 ± 0.28^{b}	2.3 ± 0.3^{b}	117 ± 9^{b}	6.35 ± 0.06^{b}
Propanol	129 ± 3^{a}	1.45 ± 0.12^{c}	2.0 ± 0.3^{b}	103 ± 8^{c}	6.47 ± 0.11^{b}
LSD	4.2	0.23	3.9	9.6	0.50

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 76. The properties after soaking in water of fibers made form soy protein esterified with various alcohols before extrusion compared with the same treatments finished with acetic anhydride, glutaraldehyde or both treatments after extrusion

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	155 ± 3^{a}	0.076 ± 0.023^{a}	3.6 ± 2.6^{a}	7.3 ± 4.6^{a}	88.82 ± 1.13^{a}
Ethylene glycol	147 ± 3^{b}	0.016 ± 0.001^{b}	1.3 ± 1.0^{b}	1.4 ± 0.8^{b}	81.55 ± 1.13^{b}
Butanol	147 ± 3^{b}	0.016 ± 0.001^{b}	3.9 ± 1.5^{a}	1.4 ± 0.5^{b}	79.06 ± 0.74^{c}
Propanol	148 ± 4^{b}	0.010 ± 0.000^{b}	1.4 ± 0.4^{b}	1.1 ± 0.5^{b}	81.05 ± 0.48^{bc}
LSD	4.1	0.033	2.1	3.0	2.47
Glutaraldehyde finished					
Soy fiber	158 ± 4^{a}	0.70 ± 0.08^{a}	77.4 ± 4.1^{a}	4 ± 1^{d}	37.30 ± 0.19^{a}
Ethylene glycol	138 ± 4^{c}	0.29 ± 0.03^{b}	15.6 ± 3.3^{b}	8 ± 1^{b}	23.22 ± 0.72^{b}
Butanol	149 ± 5^{b}	0.37 ± 0.03^{b}	16.1 ± 2.9^{b}	10 ± 1^{a}	23.34 ± 0.32^{b}
Propanol	145 ± 3^{b}	0.30 ± 0.14^{b}	13.4 ± 1.7^{b}	6 ± 1^{c}	21.25 ± 0.46^{c}
LSD	4.9	0.10	3.7	1.3	1.33
Acetic anhydride finished					
Soy fiber	145 ± 2^{a}	0.58 ± 0.05^{a}	89.0 ± 4.9^{a}	5.9 ± 1.0^{a}	16.61 ± 0.40^{a}
Ethylene glycol	140 ± 2^{b}	0.30 ± 0.05^{b}	98.7 ± 17.5^{a}	1.9 ± 0.8^{b}	11.53 ± 0.16^{b}
Butanol	145 ± 4^{a}	0.28 ± 0.02^{b}	24.0 ± 3.0^{b}	2.4 ± 0.2^{b}	10.49 ± 0.18^{c}
Propanol	144 ± 4^{a}	0.26 ± 0.07^{b}	22.7 ± 5.4^{b}	1.6 ± 0.2^{b}	10.73 ± 0.02^{c}
LSD	3.4	0.06	11.6	1.9	0.65
Combination of glutaraldehyde and acetic anhydride finishing treatment					
Soy fiber	115 ± 4^{c}	1.16 ± 0.11^{a}	58.5 ± 6.7^{a}	15 ± 3^{b}	16.55 ± 0.64^{a}
Ethylene glycol	128 ± 4^{b}	0.53 ± 0.15^{c}	44.3 ± 14.7^{b}	5 ± 1^{c}	11.69 ± 0.18^{b}
Butanol	136 ± 3^{a}	0.70 ± 0.04^{b}	17.9 ± 1.8^{c}	20 ± 4^{a}	10.58 ± 0.17^{c}
Propanol	140 ± 3^{a}	0.42 ± 0.07^{c}	25.2 ± 7.2^{c}	5 ± 2^{c}	10.64 ± 0.17^{c}
LSD	4.6	0.12	10.7	2.9	0.98

a-e Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 77. The flexibility of fibers made form soy protein esterified with various alcohols before extrusion compared with the same treatments finished with acetic anhydride, glutaraldehyde or both treatments after extrusion in terms of the smallest rod diameter around which fibers could be looped without breaking at 11% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber										X			
Ethylene glycol											X		
Butanol												X	
Propanol													X
Glutaraldehyde finished													
Soy fiber								X					
Ethylene glycol												X	
Butanol													X
Propanol													X
Acetic anhydride finished													
Soy fiber		X											
Ethylene glycol			X										
Butanol							X						
Propanol										X			
Combination of glutaraldehyde and acetic anhydride finishing treatments													
Soy fiber		X											
Ethylene glycol			X										
Butanol							X						
Propanol										X			

X Fibers could be looped around the smallest diameter glass rod without breaking.

Table 78. The flexibility of fibers made form soy protein esterified with various alcohols before extrusion compared with the same treatments finished with acetic anhydride, glutaraldehyde or both treatments after extrusion in terms of the smallest rod diameter around which fibers could be looped without breaking at 65% relative humidity

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
65% humidity													
Soy fiber	X												
Ethylene glycol	X												
Butanol	X												
Propanol			X										
Glutaraldehyde finished													
Soy fiber			X										
Ethylene glycol								X					
Butanol										X			
Propanol												X	
Acetic anhydride finished													
Soy fiber	X												
Ethylene glycol	X												
Butanol							X						
Propanol										X			
Combination of glutaraldehyde and acetic anhydride finishing treatments													
Soy fiber	X												
Ethylene glycol	X												
Butanol							X						
Propanol										X			

X Fibers could be looped around the smallest diameter glass rod without breaking.

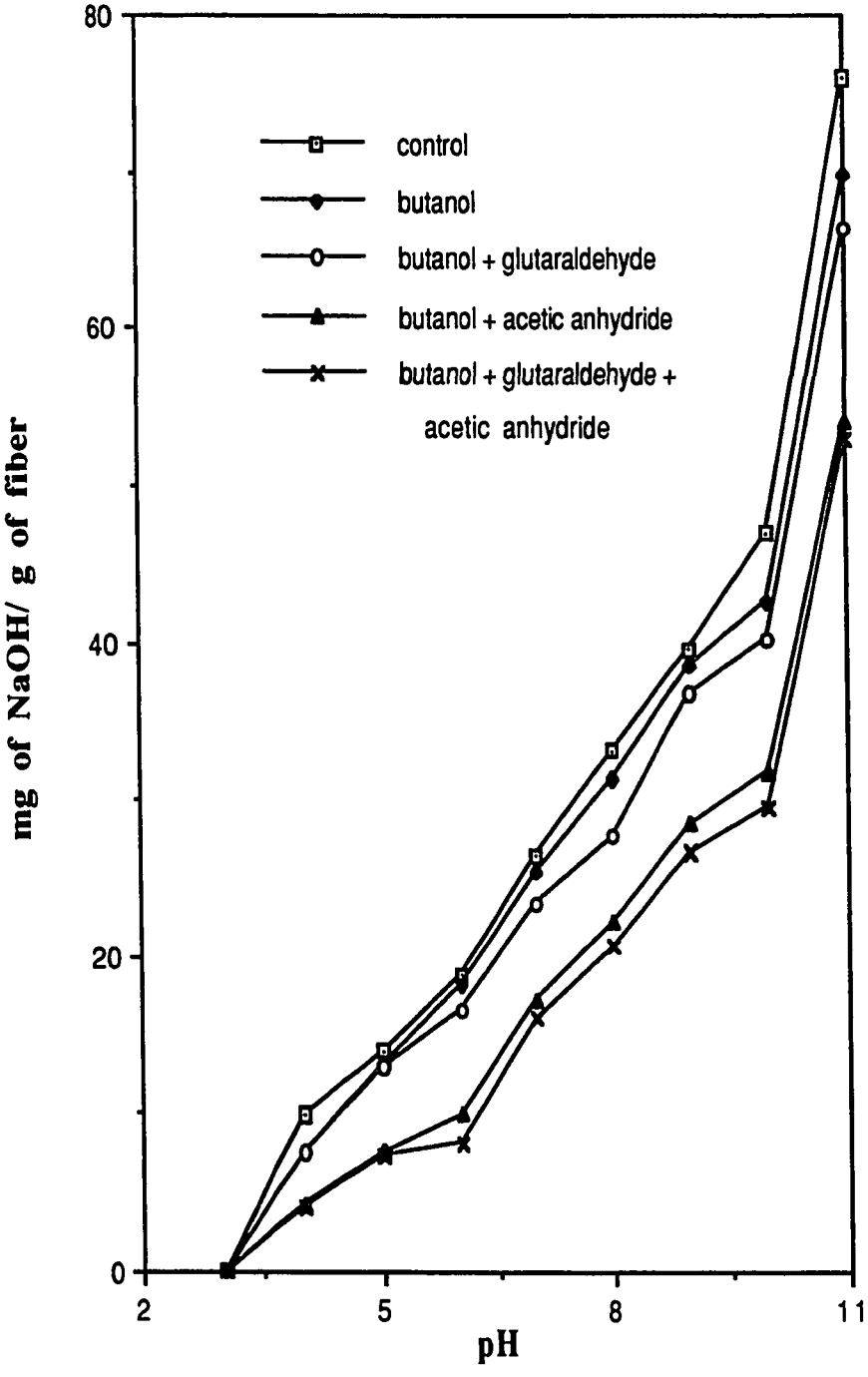


Figure 26. Titration curves of control fibers, fibers made from proteins esterified with butanol and butanol-esterified fibers finished with glutaraldehyde, acetic anhydride or a combination of glutaraldehyde and acetic anhydride.

Table 79. A comparison of dry and wet tenacities of the best wet-spun and extruded fibers produced from soy protein with those of commercial fibers

Fiber	Tenacity g/tex		
	Dry[d]	Dry[e]	Wet
Wet-spun fiber[a]	6.4	6.3	0.7
Extruded fibers[b]	9.1	5.2	2.4
Natural Fibers			
Cotton[c]		31.5 - 36.0	40.5 - 45.0
Flax[c]		31.5 - 45.0	58.5
Silk[c]		40.5	25.2 - 36.0
Wool[c]		14.0	9.0
Manufactured Fibers			
Acetate[c]		10.8 - 12.6	9.0 - 11.7
Polyester[c]		21.6 - 49.5	21.6 - 49.5

[a] Finished with 25% glutaraldehyde and then stretched to 170% of their original lengths.
[b] Finished with a combination of glutaraldehyde and acetic anhydride and then stretched to 150% of their original lengths.
[c] Adapted from Joseph, 1988.
[d] 11% relative humidity.
[e] 65% relative humidity.

VII. Factors Affecting Fiber Properties and Fiber Theory Development

Soy protein fibers were successfully produced by extrusion and wet spinning. The fibers produced from these two methods exhibited some differences in properties. Various factors affected fiber properties.

Water

Water played an important role in fiber formation and affected fiber properties. Soy protein contains more than 50% of polar amino acids whose hydrophilic groups favored interaction of protein and water. Amounts of water between 30% to 40% plasticized the soy protein used in fiber extrusion and provided good extensibility and flexibility. Although moisture higher than 40% increased fiber flexibility, tenacity decreased possibly because the hydrogen bonding between water and protein competed with hydrogen bonding between protein molecules. In the wet-spinning process, water was used as a medium in which alkaline treatments could denature and possibly unfold the protein structure. The amounts of water in the protein dopes controlled their viscosity. When the proportion of water in protein dopes became too great, the coagulum in the precipitating bath was too weak to hold together, and the protein formed a precipitate rather than a fiber.

Relative humidity

The properties of both extruded and wet-spun fibers were affected by the relative humidity. In general, the tenacity decreased and the elongation and flexibility increased as humidity increased. However, the properties of cross-linked fibers were exceptions to this generalization. Cross-linked fibers exhibited the greatest tenacity at 65% RH. This was possibly because moisture improved the fiber flexibility, which shifted the maximum tenacity to 65% RH. Generally extruded and wet-spun fibers exhibited the lowest tenacity and

elongation values in wet conditions probably because the hydrogen bonding between water and protein competed with hydrogen bonding between protein molecules.

Hartman (1978) stated that the basic structural requirement for a biopolymer was a high degree of polarity. However, the results of soy protein fibers showed that soy protein contained too many polar groups to have good wet tenacity. Zein, silk and spider web proteins are less polar than soy protein, and fibers made from these proteins are very strong. Soy protein contains > 50% polar amino acids. The high content of polar groups in soy protein results in the lower tenacity of its fibers in high humidity conditions. Soy protein might be modified by molecular genetics to improve its properties. However, if the protein becomes too non-polar, it might be too difficult to plasticize with water. On the other hand, if the protein contains more non-polar groups, it might have stronger wet tenacity.

Glycerol or plasticizers

Water was a plasticizer for soy proteins and the fibers made from it; however, water easily evaporated leaving the fiber brittle. Glycerol has three hydroxyl groups that made it quite hydrophilic and its high boiling point prevents its evaporation from fibers. The disadvantage of glycerol as a textile fiber plasticizer is that it is easily removed by washing with water. Using glycerol as a plasticizer improved fiber tenacity, elongation and flexibility. Attempts to use other substances as plasticizers, such as lecithin, triacetin, monostearin and monoolein were not successful. When these materials were extruded with soy protein, they formed discontinuities in the fibers. Attempts to use other polymers as plasticizers, such as maltodextrin containing about 40 glucose units, chitosan, dioctyl phthalate, polyvinylchloride, polyvinylethylene and polyethylene glycerol also were not successful. Probably, these polymers were not compatible with soy protein. Polyvinyl alcohol seemed to be compatible with soy protein when extruded along with lecithin and water at 115°C. This mixture produced continuous fibers, but they puffed on exiting the extruder because of the high temperature that

was required, and they were very brittle. We did not succeed in discovering a suitable plasticizer to replace water.

Protein modification prior to extrusion or wet spinning

Modification of soy protein prior to extrusion with acetaldehyde, acylation or esterification to make the protein less polar but did not improve the properties of resulting fibers. Soy proteins modified in these ways produced protein dopes that were extremely viscous and were difficult to pass through a spinnerette. Refluxing soy protein in xylene reduced the strength of fibers made subsequently. This may have resulted from a change in conformation. The acid used in esterification probably break peptide bonds, which decreased the molecular size of soy proteins and the strength of fibers made from them. As a result, finishing treatment of extruded and wet-spun soy fibers was more effective in improving the properties of soy protein fibers.

Finishing treatments after extrusion or wet spinning

After proteins were extruded or wet spun to form fibers, application of finishing treatments significantly improved tenacity, elongation and flexibility, especially if the fibers were made less polar by acylation or cross-linked by glutaraldehyde or a combination of two treatments. Fibers finished by a combination of glutaraldehyde and acetic anhydride treatments must be treated with glutaraldehyde first and acetic anhydride second.

pH

The main difference between extruded fibers and wet-spun fibers was that wet-spun fibers were weaker than extruded fibers. This may be because wet-spun fibers were coagulated at a pH lower than the pI of soy protein. Probably the alkali treatment used to make

spinning dopes also hydrolyzed the protein, which would decrease fiber tenacity. Extruded fibers had pH's near the pI of soy protein, and this made these fibers tougher.

Using extrusion technology to produce soy protein fibers is appealing because it would avoid the potential problems of disposing of large quantities of the aqueous salt and acid solutions produced in wet spinning. Production of soy protein fiber by extrusion limits the fineness that could be achieved. Possibly, finer fibers might be achieved by filtering alkaline dopes of the protein before coagulation and also by stretching the fibers when fresh fibers exit the die of extruder.

Although soy fibers have been successfully produced by both extrusion and wet-spinning techniques and their properties have been improved by chemical and physical treatments, the fibers lack the wet tenacity and dry flexibility needed for commercial exploitation as textile fibers. From the observations of this research, decreasing the amount of polar amino acids of soy proteins must be an important factor in improving the properties of soy fibers.

SUMMARY AND CONCLUSIONS

The rise in petroleum prices in recent years makes possible the penetration of agriculturally-produced commodities into markets presently dominated by petroleum. The textile industry is one of the large markets and an attractive target for utilization of soy proteins. The production of soy protein-based textile fibers could make a significant impact on soy protein utilization.

Two methods of producing fibers by extrusion and wet spinning from soy protein isolate have been developed. For extrusion, the soy protein was equilibrated with 40% of water and 15% of glycerol for 24 hours at room temperature before extrusion at 96°C at 20 rpm with a Brabender twin screw machine fitted with a die with eight of 368-μ openings. In wet spinning, a soy protein dope was prepared by mixing 19.61% soy protein, 79.32% water and 1.07% sodium hydroxide to achieve pH of 10.75. After one day aging at room temperature, the soy protein dope had a viscosity around 95 poise and was ready to spin using an apparatus consisting of an air compressor, a filter, a high viscosity pump and a spinnerette having five 368-μ openings attached to a coagulating bath.

Extruded soy fibers made by soy protein isolate alone with water tended to be quite brittle. Glycerol as well as several inorganic ions was helpful in reducing brittleness, and among the ions, the most effective was zinc. Modification of soy proteins prior to extrusion by acylation, esterification or other treatments to block the high amount of polar groups did not increase fiber tenacity. The tenacity of soy fibers was significantly improved by finishing fibers with acetaldehyde, acetic anhydride, glyoxal, glutaraldehyde or a combination of glutaraldehyde and acetic anhydride. The tenacity of finished-fibers increased as the concentration of acetaldehyde, acetic anhydride, glyoxal or glutaraldehyde increased. The most suitable pH and reaction time of glutaraldehyde finishing treatments were 3.5 and 20 to 30 min,

respectively. Extruded soy fibers finished with a combination of glutaraldehyde and acetic anhydride and then stretched to 150% of their original length resulted in tenacity of 9.11 g/tex at 11% relative humidity, which is close to that the tenacity of wool. In general, fiber properties were improved by blocking the polar groups of the protein by acylation and cross-linking with a dialdehyde.

Wet-spun soy fibers were successfully produced in 4% HCl baths containing various inorganic salts. Among these salts tested in the coagulating bath, a combination of sodium chloride, zinc chloride and calcium chloride improved fiber tenacity the most. Wet-spun fibers finished with glutaraldehyde were significantly improved in wet tenacity. The wet-spun fibers finished by glutaraldehyde and stretched to 170% of it original length had tenacity of 6.43 g/tex at 11% relative humidity.

Although soy fibers have been successfully produced by both extrusion and wet-spinning techniques and improved by chemical and physical treatments, considering the problems of waste disposal and economical factors, extrusion has a greater potential than wet spinning.

These experiment have yielded considerable insight into the factors controlling the production of good fibers but did not result in methods for producing fibers of acceptable strength and stability. The results suggest that soy protein might be modified by molecular genetics to improve their fiber-producing properties by decreasing the number of polar groups and increasing the number of points for cross-linking.

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APPENDIX

Table 80. The properties of soy protein fibers finished with 25% glutaraldehyde at various pH's for 30 min and tested after equilibration to 11% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	113 ± 4	1.57 ± 0.32	1.6 ± 0.2	97 ± 8	1.61 ± 0.13
pH 3.5	102 ± 2^{a}	2.10 ± 0.57^{a}	0.8 ± 0.2^{a}	273 ± 36^{ab}	1.53 ± 0.01^{a}
pH 3.0	103 ± 3^{a}	1.93 ± 0.32^{ab}	0.7 ± 0.1^{ab}	263 ± 26^{ab}	0.55 ± 0.01^{b}
pH 2.5	101 ± 3^{ab}	1.93 ± 0.44^{ab}	0.7 ± 0.1^{ab}	283 ± 27^{ab}	0.47 ± 0.01^{c}
pH 2.0	101 ± 3^{ab}	1.76 ± 0.50^{ab}	0.6 ± 0.2^{bc}	258 ± 26^{b}	0.44 ± 0.01^{c}
pH 1.5	99 ± 3^{b}	1.58 ± 0.17^{b}	0.5 ± 0.1^{c}	294 ± 17^{a}	0.39 ± 0.01^{d}
LSD	3.1	0.51	0.2	32.2	0.03

[a-d] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 81. The properties of soy protein fibers finished with 25% glutaraldehyde at various pH's for 30 min and tested after equilibration to 65% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	128 ± 2	0.56 ± 0.06	73.4 ± 16.6	25 ± 3	14.32 ± 0.14
pH 3.5	109 ± 2[a]	3.28 ± 0.21[a]	2.4 ± 0.4[b]	178 ±12[a]	7.87 ± 0.13[a]
pH 3.0	109 ± 3[a]	2.98 ± 0.14[b]	1.8 ± 0.1[b]	185 ± 8[a]	6.02 ± 0.03[b]
pH 2.5	107 ± 3[ab]	2.72 ± 0.16[c]	1.8 ± 0.4[b]	179 ±14[a]	5.88 ± 0.04[b]
pH 2.0	107 ± 2[ab]	2.56 ± 0.32[c]	1.8 ± 0.3[b]	176 ±13[a]	5.56 ± 0.11[c]
pH 1.5	105 ± 2[b]	1.21 ± 0.11[d]	9.8 ± 2.1[a]	72 ± 8[b]	4.53 ± 0.11[c]
LSD	3.0	0.24	1.2	13.4	0.24

[a-d] Values within each column with the same superscript are not significantly different (p>0.05).

Table 82. The properties of soy protein fibers finished with 25% glutaraldehyde at various pH's for 30 min and tested after soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Soy fiber	155 ± 3	0.076 ± 0.023	3.6 ± 2.6	7.3 ± 4.6	88.82 ± 1.13
pH 3.5	158 ± 4^{ab}	0.70 ± 0.08^{a}	77.4 ± 4.1^{b}	4.1 ± 1.3^{a}	37.30 ± 0.19^{a}
pH 3.0	159 ± 5^{a}	0.48 ± 0.04^{b}	72.6 ± 4.7^{bc}	3.3 ± 0.5^{ab}	27.57 ± 0.45^{b}
pH 2.5	156 ± 3^{abc}	0.41 ± 0.04^{c}	70.5 ± 7.9^{c}	2.7 ± 0.7^{bc}	23.47 ± 0.28^{c}
pH 2.0	154 ± 4^{bc}	0.38 ± 0.02^{c}	71.6 ± 4.1^{bc}	2.5 ± 0.5^{bc}	21.47 ± 0.52^{d}
pH 1.5	152 ± 3^{c}	0.22 ± 0.03^{d}	88.4 ± 6.2^{a}	2.1 ± 0.7^{c}	19.80 ± 0.26^{e}
LSD	4.5	0.06	6.6	0.9	0.92

[a-e] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 83. The properties of soy protein fibers finished with 25% glutaraldehyde at various treatment times and tested after equilibration to 11% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
10 min	104 ± 2^{ab}	1.68 ± 0.31^{bcd}	0.8 ± 0.1^{a}	257 ± 23^{ab}	1.66 ± 0.11^{a}
20 min	101 ± 3^{c}	2.18 ± 0.71^{a}	0.7 ± 0.2^{a}	277 ± 28^{a}	1.54 ± 0.04^{a}
30 min	102 ± 2^{bc}	2.10 ± 0.57^{ab}	0.8 ± 0.2^{a}	273 ± 36^{ab}	1.53 ± 0.01^{a}
45 min	102 ± 3^{bc}	1.84 ± 0.32^{abc}	0.7 ± 0.2^{a}	267 ± 27^{ab}	1.57 ± 0.01^{a}
60 min	104 ± 2^{ab}	1.55 ± 0.28^{cd}	0.8 ± 0.1^{a}	256 ± 39^{ab}	1.57 ± 0.07^{a}
75 min	103 ± 3^{ab}	1.44 ± 0.14^{cd}	0.7 ± 0.1^{a}	250 ± 37^{ab}	1.53 ± 0.08^{a}
90 min	106 ± 2^{a}	1.32 ± 0.27^{d}	0.7 ± 0.1^{a}	237 ± 26^{b}	1.53 ± 0.02^{a}
LSD	2.8	0.49	0.2	36.8	0.14

[a-d] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 84. The properties of soy protein fibers finished with 25% glutaraldehyde at various treatment times and tested after equilibration to 65% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
10 min	107 ± 3^{d}	1.75 ± 0.25^{cd}	0.9 ± 0.1^{c}	143 ± 15^{b}	8.17 ± 0.04^{a}
20 min	107 ± 2^{d}	3.14 ± 0.23^{a}	2.3 ± 0.1^{a}	174 ± 12^{a}	7.90 ± 0.08^{b}
30 min	109 ± 2^{bcd}	3.28 ± 0.21^{a}	2.4 ± 0.4^{a}	178 ± 12^{a}	7.87 ± 0.13^{bc}
45 min	108 ± 3^{cd}	2.56 ± 0.36^{b}	1.5 ± 0.8^{b}	162 ± 22^{ab}	7.71 ± 0.03^{cd}
60 min	111 ± 4^{abc}	2.08 ± 0.43^{c}	1.1 ± 0.4^{bc}	150 ± 19^{b}	7.67 ± 0.11^{de}
75 min	111 ± 2^{abc}	1.86 ± 0.23^{c}	1.2 ± 0.2^{bc}	151 ± 26^{b}	7.52 ± 0.03^{ef}
90 min	$113 \pm 2a$	1.45 ± 0.16^{d}	1.0 ± 0.1^{c}	119 ± 10^{c}	7.36 ± 0.01^{f}
LSD	3.3	0.33	0.5	20.5	0.18

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

Table 85. The properties of soy protein fibers finished with 25% glutaraldehyde at various treatment times and tested after soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
10 min	154 ± 2^{b}	0.53 ± 0.08^{b}	60.9 ± 11.0^{cd}	4.2 ± 1.6^{ab}	48.36 ± 1.60^{a}
20 min	156 ± 2^{ab}	0.70 ± 0.11^{a}	73.8 ± 7.8^{ab}	5.6 ± 2.3^{a}	37.41 ± 1.03^{b}
30 min	158 ± 4^{a}	0.70 ± 0.08^{a}	77.4 ± 4.1^{a}	4.1 ± 1.3^{ab}	37.30 ± 0.19^{b}
45 min	152 ± 2^{b}	0.70 ± 0.19^{a}	69.7 ± 11.4^{abc}	3.9 ± 1.5^{ab}	36.17 ± 0.95^{b}
60 min	142 ± 2^{c}	0.60 ± 0.07^{ab}	67.9 ± 6.6^{abc}	4.7 ± 1.7^{ab}	34.95 ± 1.85^{b}
75 min	142 ± 2^{c}	0.53 ± 0.11^{b}	64.8 ± 13.6^{bc}	3.2 ± 0.5^{b}	31.66 ± 1.00^{c}
90 min	140 ± 5^{c}	0.47 ± 0.04^{b}	51.2 ± 6.7^{d}	3.6 ± 1.6^{b}	28.27 ± 1.68^{d}
LSD	4.1	0.13	11.1	1.9	3.13

[a-d] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 86. The properties of soy protein fibers finished by 25% glutaraldehyde at pH 3.5 at various temperatures for 30 min, stretched to 150% of their original length and tested after equilibration to 11% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Room temperature	102 ± 2^{b}	2.10 ± 0.57^{a}	0.8 ± 0.2^{b}	273 ± 36^{a}	1.53 ± 0.01^{a}
50° C	116 ± 3^{a}	1.74 ± 0.26^{ab}	1.7 ± 0.8^{a}	215 ± 13^{bc}	1.51 ± 0.02^{a}
70° C	118 ± 2^{a}	1.66 ± 0.23^{ab}	1.0 ± 0.1^{b}	207 ± 16^{c}	1.40 ± 0.03^{b}
90° C	118 ± 3^{a}	1.39 ± 0.39^{b}	0.9 ± 0.3^{b}	236 ± 22^{b}	1.34 ± 0.03^{b}
LSD	2.9	0.48	0.4	28.6	0.07
Stretched to 150%					
Room temperature	79 ± 3^{b}	5.74 ± 0.66^{a}	2.1 ± 0.2^{a}	306 ± 13^{a}	1.40 ± 0.02^{b}
50° C	88 ± 2^{a}	3.41 ± 1.08^{b}	1.5 ± 0.1^{bc}	271 ± 12^{bc}	1.53 ± 0.01^{a}
70° C	88 ± 2^{a}	3.11 ± 0.78^{b}	1.5 ± 0.4^{b}	252 ± 22^{c}	1.41 ± 0.02^{b}
90° C	88 ± 3^{a}	3.09 ± 0.36^{b}	1.2 ± 0.3^{c}	272 ± 18^{b}	1.30 ± 0.03^{c}
LSD	2.8	0.92	0.4	19.1	0.06

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 87. The properties of soy protein fibers finished by 25% glutaraldehyde at pH 3.5 at various temperatures for 30 min, stretched to 150% of their original length and tested after equilibration to 65% relative humidity

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Room temperature	109 ± 2^{b}	3.28 ± 0.21^{a}	2.4 ± 0.4^{c}	178 ± 12^{a}	7.87 ± 0.13^{a}
50° C	122 ± 3^{a}	1.95 ± 0.04^{b}	62.4 ± 15.6^{a}	84 ± 12^{b}	7.74 ± 0.04^{a}
70° C	123 ± 2^{a}	1.79 ± 0.13^{c}	50.7 ± 10.7^{b}	74 ± 12^{b}	6.68 ± 0.06^{b}
90° C	123 ± 3^{a}	1.48 ± 0.10^{d}	58.0 ± 12.0^{ab}	83 ± 11^{b}	6.55 ± 0.19^{b}
LSD	2.9	0.16	9.8	14.0	0.22
Stretching to 150%					
Room temperature	83 ± 2^{b}	4.73 ± 0.10^{a}	4.1 ± 1.2^{b}	218 ± 17^{a}	6.87 ± 0.22^{b}
50° C	96 ± 3^{a}	2.71 ± 0.08^{b}	52.4 ± 18.0^{a}	114 ± 8^{b}	7.23 ± 0.11^{a}
70° C	98 ± 4^{a}	2.54 ± 0.20^{bc}	53.6 ± 16.1^{a}	104 ± 15^{b}	6.75 ± 0.04^{bc}
90° C	98 ± 4^{a}	2.36 ± 0.20^{c}	39.9 ± 8.7^{a}	96 ± 19^{b}	6.48 ± 0.01^{c}
LSD	3.8	0.21	15.5	18.6	0.34

[a-d] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 88. The properties of soy protein fibers finished by 25% glutaraldehyde at pH 3.5 at various temperatures for 30 min, stretched to 150% of their original length and tested after soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
Room temperature	158 ± 4^{a}	0.70 ± 0.08^{a}	77.4 ± 4.1^{a}	4.1 ± 1.3^{a}	37.30 ± 0.19^{a}
50° C	143 ± 3^{b}	0.39 ± 0.08^{b}	70.8 ± 10.7^{a}	1.2 ± 0.7^{b}	32.01 ± 0.64^{b}
70° C	142 ± 3^{b}	0.36 ± 0.04^{bc}	73.6 ± 3.3^{a}	0.8 ± 0.3^{b}	27.81 ± 0.47^{c}
90° C	143 ± 3^{b}	0.27 ± 0.09^{c}	59.0 ± 13.0^{b}	0.9 ± 0.2^{b}	25.79 ± 0.88^{d}
LSD	3.8	0.09	10.6	0.9	1.67
Stretching to 150%					
Room temperature	106 ± 3^{b}	0.75 ± 0.05^{a}	62.2 ± 3.7^{b}	4.7 ± 0.7^{a}	36.13 ± 0.41^{a}
50° C	115 ± 2^{a}	0.55 ± 0.10^{b}	73.5 ± 7.5^{a}	1.2 ± 0.2^{b}	33.63 ± 0.69^{b}
70° C	117 ± 3^{a}	0.38 ± 0.07^{c}	62.7 ± 7.8^{b}	1.4 ± 0.4^{b}	29.17 ± 0.35^{c}
90° C	118 ± 3^{a}	0.29 ± 0.05^{d}	50.8 ± 9.9^{c}	1.0 ± 0.2^{b}	27.00 ± 0.20^{d}
LSD	3.0	0.08	9.1	0.6	1.21

[a-d] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 89. The properties of soy protein fibers washed with water first and finished by 25% glyoxal and glutaraldehyde at pH 3.5 at room temperature for 30 min, respectively, and tested after equilibration to 11% and 65% relative humidity and soaking in water

Fiber	Linear density tex	Tenacity g/tex	Extension at break %	Modulus g/tex	Wt % moisture regain
11% humidity					
Soy fiber	92 ± 2^{c}	0.76 ± 0.11^{c}	0.6 ± 0.1^{a}	135 ± 33^{b}	1.77 ± 0.11^{a}
Glyoxal	111 ± 5^{a}	1.27 ± 0.23^{b}	0.6 ± 0.2^{a}	263 ± 12^{a}	1.13 ± 0.02^{b}
Glutaraldehyde	100 ± 4^{b}	1.87 ± 0.34^{a}	0.7 ± 0.1^{a}	238 ± 16^{a}	0.87 ± 0.04^{c}
LSD	4.1	0.31	0.2	27.0	0.09
65% humidity					
Soy fiber	106 ± 4^{b}	0.19 ± 0.02^{c}	1.6 ± 0.3^{a}	34 ± 5^{c}	11.26 ± 0.35^{a}
Glyoxal	123 ± 2^{a}	1.55 ± 0.15^{b}	1.6 ± 0.2^{a}	165 ± 21^{b}	9.70 ± 0.07^{b}
Glutaraldehyde	108 ± 3^{b}	2.06 ± 0.34^{a}	1.1 ± 0.3^{b}	209 ± 15^{a}	6.77 ± 0.29^{c}
LSD	3.6	0.27	0.3	18.5	0.85
In water					
Soy fiber	140 ± 2^{c}	0.024 ± 0.010^{c}	2.6 ± 0.6^{c}	1.7 ± 0.4^{b}	62.08 ± 2.36^{a}
Glyoxal	155 ± 4^{a}	0.22 ± 0.03^{b}	79.6 ± 7.3^{a}	1.7 ± 0.7^{b}	43.28 ± 1.97^{b}
Glutaraldehyde	146 ± 4^{b}	0.59 ± 0.11^{a}	32.4 ± 9.2^{b}	5.9 ± 1.4^{a}	24.25 ± 1.21^{c}
LSD	4.2	0.08	8.4	1.1	6.06

[a-c] Values within each column with the same superscript are not significantly different ($p>0.05$).

Table 90. The flexibility of fibers wash with water first and finished with 25% glyoxal and glutaraldehyde at pH 3.5 at room temperature for 30 min, respectively, in terms of the smallest rod diameter around which fibers could be looped without breaking

Fiber	Diameter of glass rod (mm)												
	1.5	2	2.5	3	3.5	4	5	11	16	21	25	34	45
11% humidity													
Soy fiber													X
Glyoxal													X
Glutaraldehyde												X	
65% humidity													
Soy fiber													X
Glyoxal								X					
Glutaraldehyde								X					

X Fibers could be looped around the smallest diameter glass rod without breaking.

Figure 27. Scanning electron microscopic pictures of soy protein fibers and acetic anhydride modified soy protein fibers using glycerol and sorbitol as a plasticizer. (scale bar represented 100 μm)

A. Surface of soy protein fiber using glycerol as a plasticizer.

B. Cross-section of soy protein fiber using glycerol as a plasticizer.

C. Surface of soy protein fiber using sorbitol as a plasticizer.

D. Cross-section of soy protein fiber using sorbitol as a plasticizer.

E. Surface of a fiber made from modified soy protein treated with 5% acetic anhydride and using glycerol as a plasticizer.

F. Cross-section of a fiber made from modified soy protein treated with 5% acetic anhydride and using glycerol as a plasticizer.

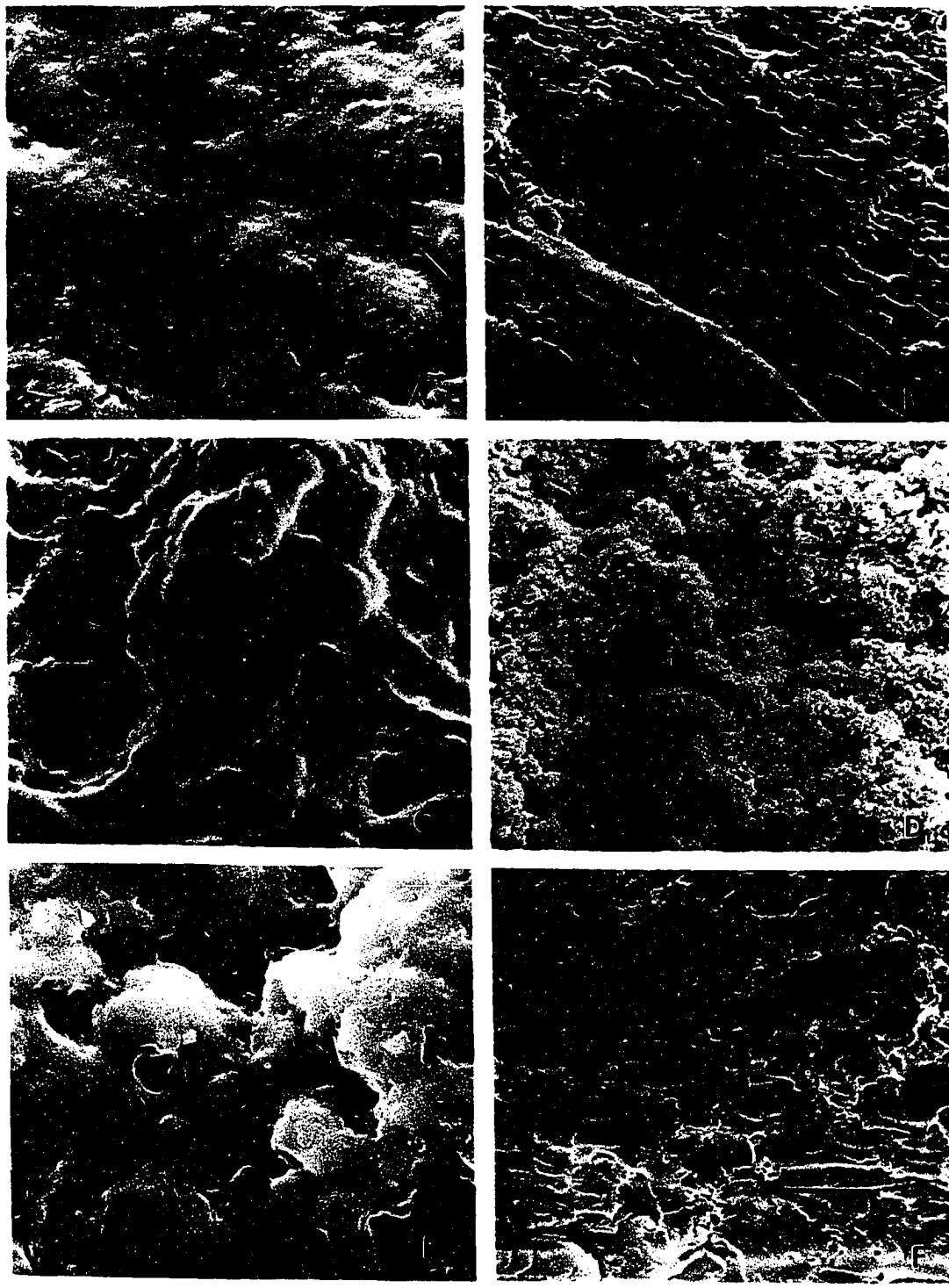

D
F

Figure 28. Scanning electron microscopic pictures of soy protein fibers finished by glutaraldehyde, acetic anhydride, or combination of glutaraldehyde and acetic anhydride. (scale bar represented 100 μm)

A. Surface of soy protein fiber finished by glutaraldehyde.

B. Cross-section of soy protein fiber finished by glutaraldehyde.

C. Surface of soy protein fiber finished by acetic anhydride.

D. Cross-section of soy protein fiber finished by acetic anhydride

E. Surface of soy protein fiber finished by combination of glutaraldehyde and acetic anhydride.

F. Cross-section of soy protein fiber finished by combination of glutaraldehyde and acetic anhydride.

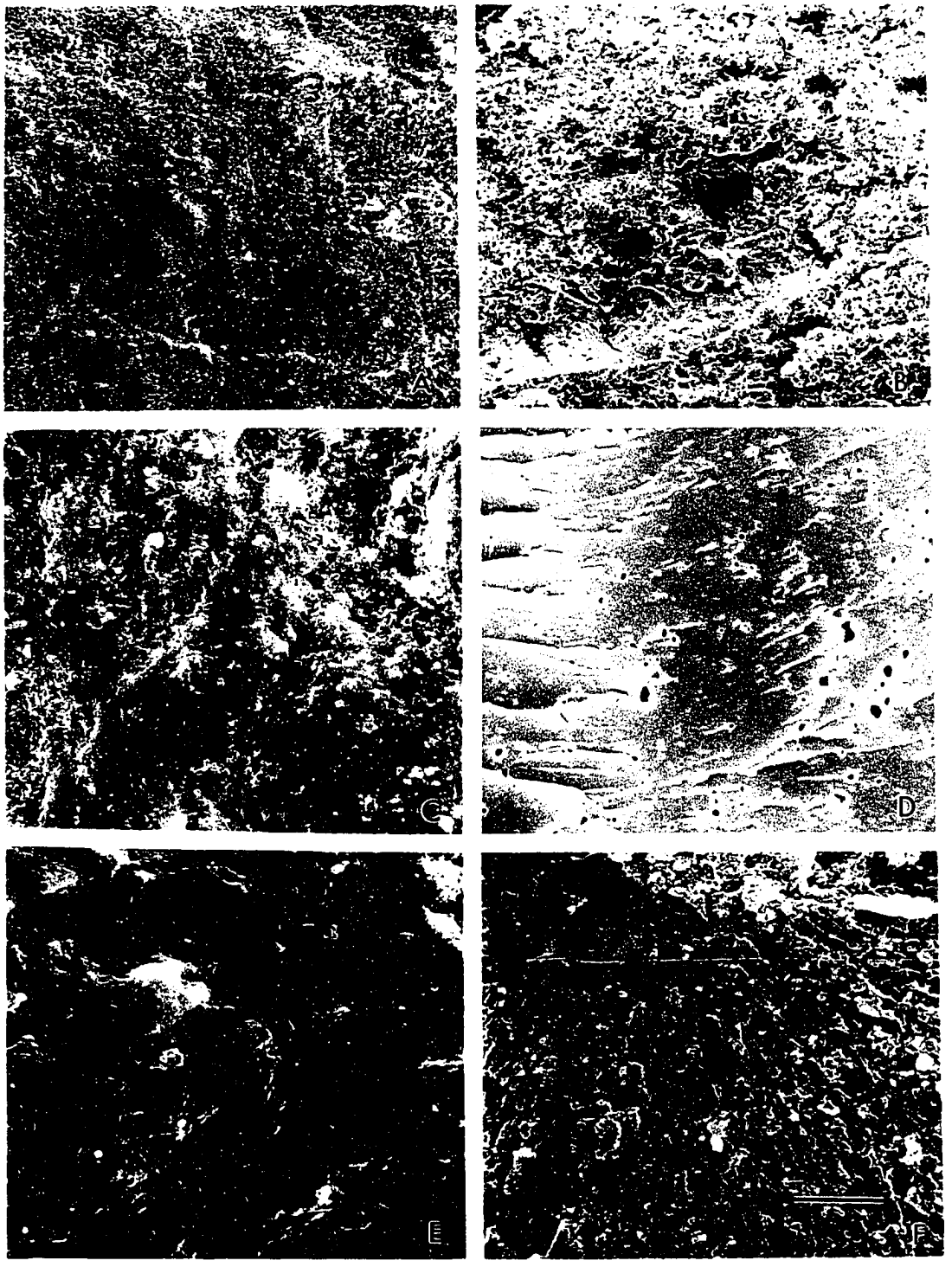

A
B
C
D
E
F

Figure 29. Scanning electron microscopic pictures of extruded and wet-spun soy protein fibers finished by glutaraldehyde or combination of glutaraldehyde and acetic anhydride and stretched to 150% or 170% of their original lengths (scale bar represented 100 μm)

A. Surface of soy protein fiber finished by glutaraldehyde and stretched to 150% of its original length.

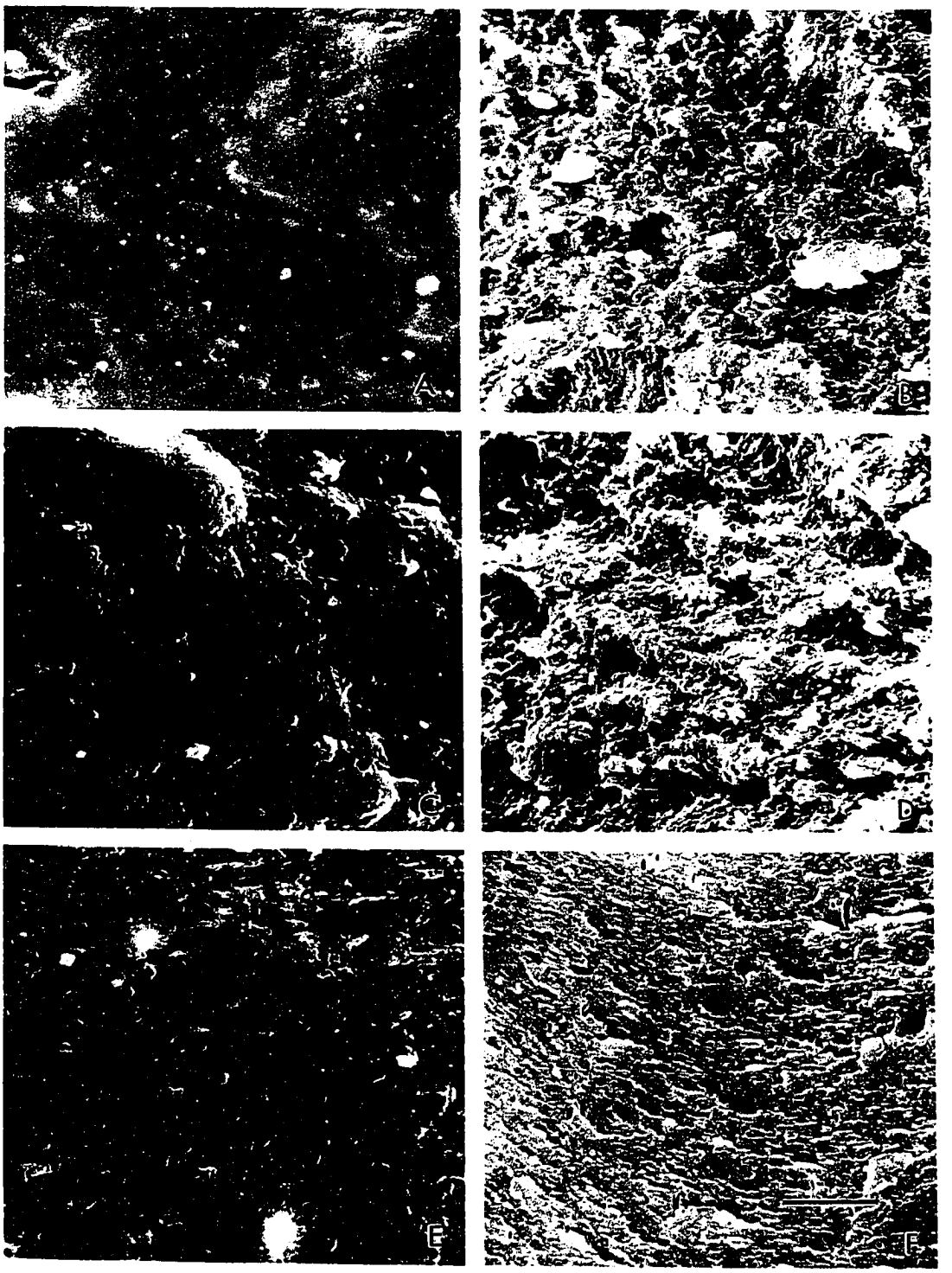
B. Cross-section of soy protein fiber finished by glutaraldehyde and stretched to 150% of its original length.

C. Surface of soy protein fiber finished by combination of glutaraldehyde and acetic anhydride and stretched to 150% of its original length.

D. Cross-section of soy protein fiber finished by combination of glutaraldehyde and acetic anhydride and stretched to 150% of its original length.

E. Surface of wet-spun soy protein fiber finished by glutaraldehyde and stretched to 170% of its original length.

F. Cross-section of wet-spun soy protein fiber finished by glutaraldehyde and stretched to 170% of its original length.


A
B
C
D
E
F