

# Fibers from Soybean Protein and Poly(vinyl alcohol)

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**ABSTRACT:** Bicomponent fibers were wet-spun from soybean protein and poly(vinyl alcohol). The protein core of the spun bicomponent fiber was brittle and showed a high frequency of core breakage upon drawing. Our effort was then to study the soybean protein solution, with the aim of trying to understand the cause for fiber brittleness and to determine the optimum solution conditions for fiber spinning. The effects of alkali, urea, and sodium sulfite on the viscosity of the soybean protein solution were examined. The hydrolytic stability of the soybean protein solution was examined at various pH values at two temperatures (room temperature and 60°C). Both the viscosity and gel electrophoresis were used for this purpose. The degradation of the soybean protein and the existing microgels in the protein spinning solution were thought to be the causes for the poor fiber drawability. Extent of protein denaturation will also effect the fiber drawability. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 11–19, 1999

**Key words:** Biocomponent fiber, soybean, poly(vinyl alcohol), protein, solution spinning.

## INTRODUCTION

Fibers based on casein, soybean, peanut, zein, gelatin, glue, collagen, and other proteins have received considerable attention in the United States, Europe, and Japan as an inexpensive substitute for wool and silk fibers.<sup>1–11</sup> In 1935, the Italian firm Sina Viscosa began large-scale production of casein fibers known as Lanital.<sup>2</sup> Shortly afterward, Courtaulds in England adopted the Ferretti process to produce milk and soybean protein fibers.<sup>2</sup> Production of these fibers was also started by Enka in the Netherlands.<sup>2</sup> The Ford Motor Co. built a pilot plant to

develop soybean protein fibers and was planning a large-scale commercial facility for producing automobile seat fabrics just prior to the United States entry into World War II.<sup>1</sup> The large-scale introduction of petroleum-based fibers during the 1940s and 1950s changed the commercial outlook of the man-made protein fibers. Nevertheless, research efforts in Japan were continued and a new silklike fiber based on a protein/PAN copolymer, called Chinon, was introduced in 1969.<sup>12,13</sup> The protein in the copolymer was in the 10–60 wt % range, the rest being grafted polyacrylonitrile together with minor amounts of a vinyl or vinylidene chloride for flame retardation.

The process for obtaining plant protein raw material for fibers involves the extraction of the seed oil, followed by solubilization, precipitation, and removal of the protein curd.<sup>2</sup> This separation of the seed meal into number of fractions can

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enhance the total value of the agricultural material. The important positive aspects of textile fabrics made from protein fibers are comfort, high moisture regain of 11–12%, a soft warm comfortable hand, and a competitively priced renewable source for starting materials. The primary deficiencies of regenerated protein fibers are their poor wet strength, about 0.4 g/den, and a high degree of shrinkage in boiling water.<sup>14</sup> These properties can be improved in bicomponent fiber geometry. Mixed-component spinning solutions (polyblends) with other water-soluble polymers is also a potential method for improving properties and one such system with poly(vinyl alcohol) was developed in Japan during 1960s.<sup>15</sup> The system does not appear to have been commercialized.

Poly(vinyl alcohol) fibers have been commercialized since the 1950s and are used in textiles as a silk substitute.<sup>15</sup> High tensile strength and modulus of PVA,<sup>16</sup> have also led to many industrial applications of this fiber such as in tire cords, belts, and ropes. Poly(vinyl alcohol) and plant protein fibers are unique in that both types of fibers are usually spun, coagulated, oriented, and crosslinked under essentially similar conditions.

The protein backbone is held by covalent peptide bonds, and the folded (native) conformation of the globular protein is held by hydrophobic interactions, disulfide bonds, hydrogen bonds and electrostatic interactions. In the preparation of fibers from protein, the key step is to modify the protein solution into spinnable dope. It is important to understand the structural changes in the soybean protein both during the dissolution process and during the fiber formation process. There are two essential processes, denaturation and degradation, that occur in the protein solution.<sup>17,18</sup> The process of degradation breaks the peptide bonds, while the process of denaturation results only in a conformational change that unfolds the protein molecule. Acids, alkalis, enzymes, and heat can degrade the protein. The denaturation of the protein molecule is affected by the temperature, pH, urea, salts, organic solvents, and solutes. The degradation and denaturation processes often accompany each other. The controlled denaturation process, which increases the viscosity and drawability of the solution, is considered a prerequisite for the fiber formation. On the other hand, protein degradation is detrimental to the production of high-strength fibers.

Several groups have studied the soybean protein solution. Wolf<sup>19</sup> studied the effects of alkali, urea, mercaptoethanol, and sodium sulfite on the

denaturation of soybean protein molecules. Ishino and Okamoto<sup>20</sup> reported the effects of pH on the denaturation of soybean protein. Kelley and Pressey<sup>21</sup> examined the effects of pH, sodium sulfite, urea, and mercaptoethanol on the solubility and ultracentrifuge patterns of acid-precipitated protein. Motonoga et al.<sup>22</sup> postulated a reaction mechanism in which sodium sulfite breaks the disulfide bonds in proteins. Dosako et al.<sup>23</sup> examined the effect of aging time on the rheological and chemical properties of a casein protein solution. Traill<sup>24</sup> reported a crosslinking mechanism of soybean protein by formaldehyde. From the analysis of sodium dodecyl sulfate–polyacrylamide gel electrophoresis (SDS–PAGE), Wolf et al.<sup>25</sup> identified the composition of soybean protein. Two major storage proteins,  $\beta$ -conglycinin and glycinin, plus numerous minor proteins with biological activities, for example, trypsin inhibitors, lipoxygenases, and pectins, were identified. Other studies on the characterization of soybean protein using SDS–PAGE were also reported.<sup>26,27</sup> We followed the stability of the soybean protein solution using SDS–PAGE and viscosity.

## EXPERIMENTAL

Soybean protein powder, soy 9000Z, was obtained from Protein Technologies International, Inc., St. Louis, MO, Poly(vinyl alcohol) powder of molecular weights 125,000 and 186,000 g/mol was obtained from Air Products and Chemicals, Inc. Protigel, 30% (w/v) acrylamide, and a 0.8% (w/v) bisacrylamide stock solution (37.5 : 1) were obtained from National Diagnostics Compact Co.

### Protein and PVA Solutions

The protein powder was mixed in water at the desired concentration and vigorously stirred. The initial spinning trials were carried out at a protein concentration of 15 wt %, while the subsequent protein stability and solution viscosity studies were carried out with a 10 wt % solution. Viscosity at a pH of 11.5 at room temperature was about 400 poise for the 15 wt % solution and 40–45 poise for the 10 wt % solution. The pH was controlled by the addition of a NaOH stock solution. Boyer<sup>1</sup> recommended the use of xanthate in spinning soybean protein fibers. The xanthate reacts with amino groups, forming carbamindithio groups (—NHCSSH), which prevents the gelation of the protein solution and enhances its elasticity.

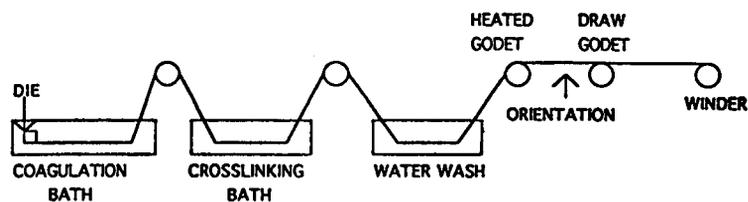


Figure 1 Schematic of the wet fiber spinning line.

The formula to make a xanthate solution followed that of Boyer.<sup>1</sup> One milliliter of ethyl alcohol was reacted to completeness with 10 mL of a 1.3 g/cm<sup>3</sup> specific gravity sodium hydroxide solution, forming sodium ethylate. To this mixture, 1 mL of carbon disulfide was added and allowed to react to completeness to form sodium ethyl xanthate, a compound of yellow–orange color. It was permitted to age for 15 days. Water, 90 mL and PVA, 10 g, were heated in a closed bottle in a water bath at 95°C for 1.5 h. A clear PVA solution resulted from this treatment, which was ready for spinning. Solution viscosity was measured using a Brookfield LVTDV-I digital display viscometer. Initial viscosity trials were carried out at four spindle speeds to examine the effect of the shear rate. Protein solutions showed pseudoplastic (shear thinning) behavior. All viscosity data presented in this article were carried out at a spindle rotation speed of 12 rpm.

### Fiber Spinning

The fiber spinning line (schematic shown in Fig. 1) includes the spinning apparatus, coagulation, crosslinking, and washing baths and a drawing unit. The coagulation bath contained saturated sodium sulfate with 1M sulfuric acid. The temperature of the coagulation bath was maintained at 50°C. After winding, the coagulated fiber was sent into the crosslinking bath which contained 8% formaldehyde in water. The fiber was kept in the crosslinking bath for 3 h at room temperature. Crosslinked fiber was subsequently drawn. Crosslinking studies were carried out in the batch process.

The schematic of the bicomponent extrusion apparatus is shown in Figure 2. All the units were connected by a 0.25-in. outer diameter stainless-steel tube. Two 200-mL pressure filter containers were installed for soybean protein and PVA solutions. Two zenith BPB-5566 metering pumps with 0.067 mL per revolution throughput were used. By changing the gears of the metering pumps and

the concentration of the spinning solution, the relative amounts of the protein and PVA in the fiber could be controlled. A back pressure of 50–70 psi was provided by a nitrogen gas tank. The solution container, pumps, and tubes were heated with band, strip, and tape heaters, respectively. All heaters were connected to temperature controllers. A core-sheath die, shown in Figure 3, was used.

### Gel Electrophoresis

SDS–PAGE was performed using a Hooper Scientific Instruments Model SE 600 on a 1.5-mm poly-

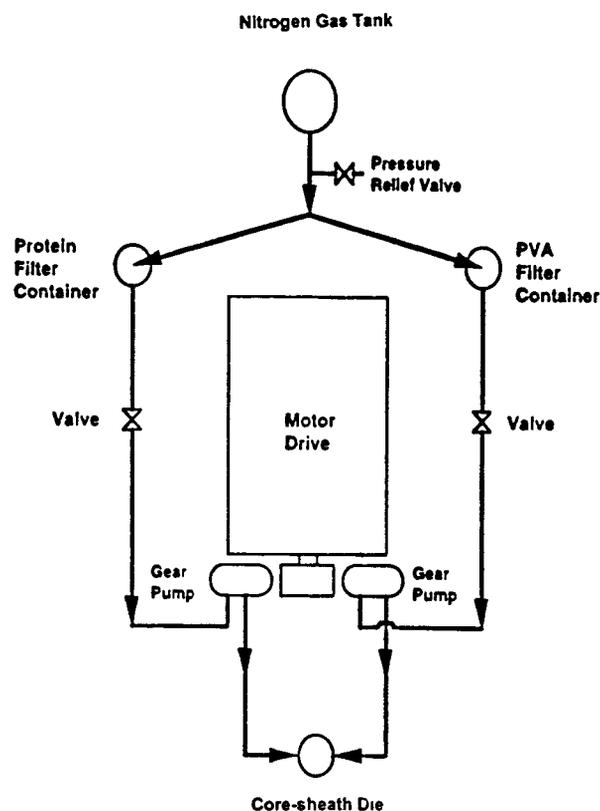
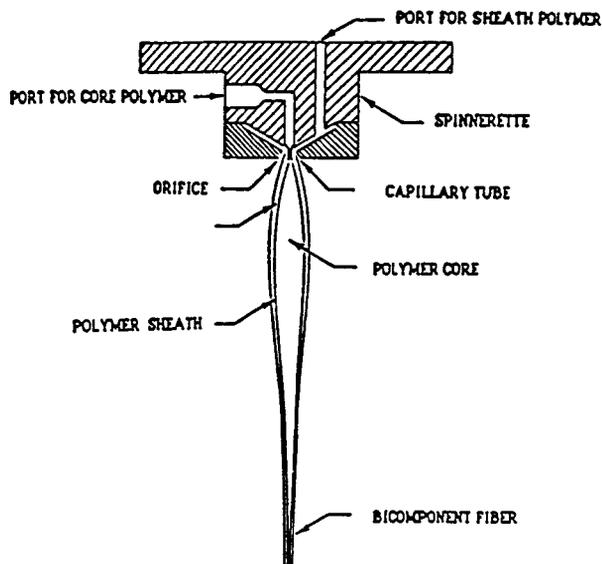


Figure 2 Schematic of the bicomponent fiber spinning apparatus (top view).



**Figure 3** Schematic of the sheath–core die.

acrylamide gel. Two gel systems were made: (A) 14.6 mL Protogel (37.5 : 1)/13.1 mL R buffer solution /7.35 mL distilled water and (B) 5 mL Proatgel (37.5 : 1)/1.25 mL S buffer solution/7.10 mL distilled water. The modified procedure was same as that used by Petrucci and Anon.<sup>30</sup> Protein (2 mg/mL) was dissolved in the sample buffer. Lower molecular weight protein standards of phosphorylase, bovine serum albumin, ovalbumin, carbonic anhydrase, soybean trypsin inhibitor, and  $\alpha$ -lactalbumin were run with the sample solution. The gel was stained with Coomassie Brilliant Blue R-250 (Sigma). After destaining for 24 h, the gel was dried on Gel Bond PAG film at room temperature. The SDS–PAGE bands were identified on the basis of purified  $\beta$ -conglycinin, glycinin, kunitz trypsin inhibitor, and agglutinin (Sigma) and based on those reported in the literature.<sup>25</sup>

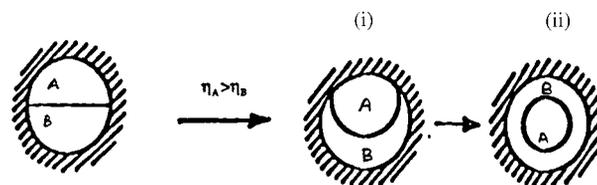
## RESULTS AND DISCUSSION

Our initial spinning trial utilized a 15 wt % soybean protein solution (pH 11.5) modified by xanthate. The protein solution was put in a centrifuge to remove any trapped air. The viscosity of this solution was about 400 poise and was considered appropriate for fiber spinning. The protein solution was placed in the container at room temperature and heated to 45°C prior to the entry into the die. The 10 wt % PVA solution after centrifuging had a viscosity of about 40 poise,

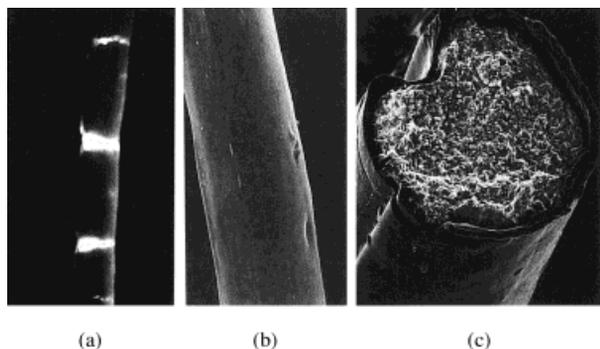
which was also considered suitable for spinning strong and drawable fibers. Lower than 10 wt % PVA results in frequent fiber breakage, while concentrations greater than 12 wt % resulted in frequent seizures of the metering pump. The PVA solution was placed into the container at 60°C to prevent microcrystal formation and was cooled down to 45°C just before entering the die.

The bicomponent fiber consisted of a core–sheath and side-by-side configurations. In the side-by-side configuration, splitting occurred at the interface and was attributed to a large difference in the degree of swelling between the two components in the coagulation bath, with the protein estimated to swell five times more than the PVA. To overcome this difficulty, the fiber geometry was changed to a core–sheath structure. The lower degree of swelling in the PVA skin would provide the compressive stress on the protein core. A number of investigators have studied the factors that influence the evolution of the interface shape of two fluid components.<sup>28,29</sup> The most important factors influencing the interface shape are (i) the viscosity ratio of the two solutions and (ii) the length-to-diameter ratio of the die. The effect of the  $L/D$  ratio on the interface is shown in Figure 4. This shows that by controlling the solution viscosity and the  $L/D$  ratio in the die even a single component die can be used to produce core–sheath bicomponent fibers. In our spinning trials, protein solution viscosity was 10 times the viscosity of the PVA solution, and we also used a bicomponent die. These factors resulted in a core–sheath (soybean protein–PVA) fiber configuration.

After being extruded from the die, the two-component fluid goes through coagulation and crosslinking processes. An acidified sodium sulfate solution was used for the coagulation. The partial crosslinking step after coagulation was carried out in formaldehyde.<sup>24</sup> The optical and scanning electron micrographs of the fibers are shown in Figure 5. In the as-spun fiber, both the



**Figure 4** Schematic showing the evolution of change of interface shape in the side-by-side coextrusion through a circular die: (i) small  $L/D$  ratio; (ii)  $L/D$  ratio greater than a critical value.<sup>28</sup>



**Figure 5** (a) Optical and (b,c) scanning electron micrographs of core-sheath (protein-PVA) fiber.

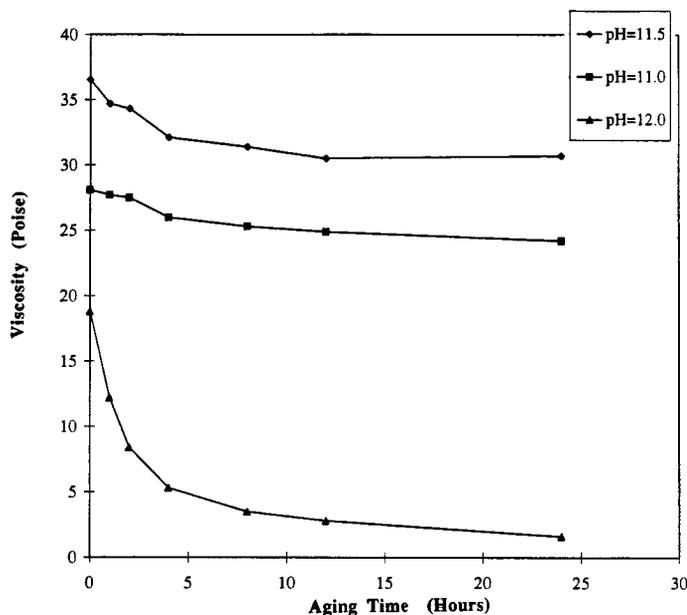
protein core and the PVA sheath were continuous. After drawing, the PVA sheath was essentially intact, but the protein core is fragmented [Fig. 5(a)]. The fiber cross section shown in Figure 5(c), clearly demonstrates the development of sheath-core morphology in our spinning setup.

#### Effect of pH

With the addition of alkali, at pH 11.0, the soybean protein could be dissolved in water after stirring for about 30 min. The dissolution is presumed to be due to sufficient unfolding of the protein molecules. From a pH of 11.0 to 11.5, the extent of protein unfolding increases, resulting in

the viscosity increase as shown in Figure 6. Above a pH of 11.5, the viscosity decreased, and this decrease was considered a result of protein degradation. At pH 11.0 and 11.5, the protein solution was fairly stable, as only a small decrease in viscosity occurs in 24 h. At pH 12.0, the viscosity decreases rapidly, resulting from the hydrolytic cleavage of the protein backbone.

The use of PAGE in the presence of SDS permits the rapid analysis of soybean protein, which is a complex mixture consisting of two major storage proteins,  $\beta$ -conglycinin and glycinin, plus numerous minor proteins with biological activities, for example, trypsin inhibitors, lipoxygenases, and lectins. The storage proteins have multimetric structures and are high in molecular weight.  $\beta$ -Conglycinin has a trimeric structure, and three different subunits,  $\alpha'$ ,  $\alpha$ , and  $\beta$  have been identified.<sup>30</sup> Glycinin is made up of six subunits, each consisting of a basic polypeptide (B polypeptide) and an acid peptide (A polypeptide) which are connected by a single disulfide bond forming the AB subunits. Figure 7 shows the SDS-PAGE patterns of soybean protein solution at pH 11.0 at room temperature. The bands in the left column are molecular weight markers, composed of a group of single-component proteins with known molecular weights as identified in the figure. The attribution of each band in the soybean is indicated according to the literature.<sup>25</sup>



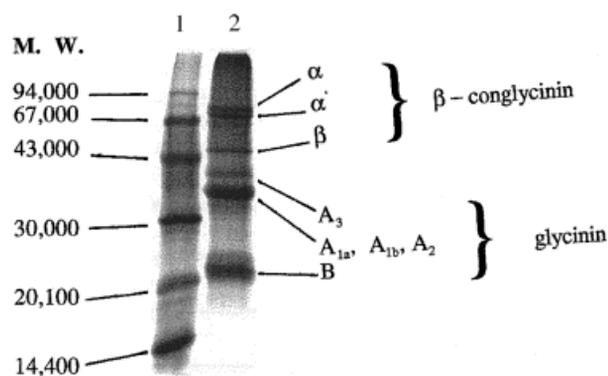
**Figure 6** Hydrolytic stability of 10% protein solution (with 10 mM sodium sulfite) at various pH values at room temperature.

Figure 8 shows the SDS-PAGE in the aging process at room temperature at pH 11.0 and 12.0, respectively. At pH 11, no change is observed in the 24 h, indicating that the alkali treatment only results in the denaturation of soybean protein. At pH 12.0, characteristic bands became weaker with time, and after 24 h, no bands were present. This is due to covalent breakage of peptide backbone into small fragments. The SDS-PAGE results are consistent with the viscosity data. Based on this study, it was concluded that pH 11.5 was ideal for fiber spinning.

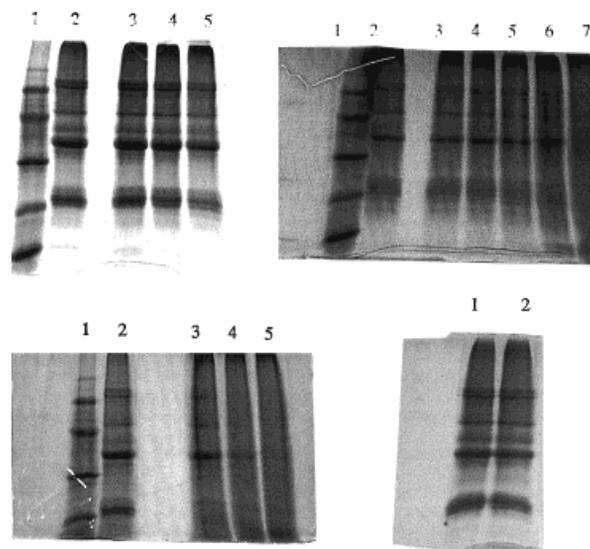
### Heating Effect

Heating the soybean protein solution may result in two irreversible processes<sup>17</sup>: First, the interchange of disulfide bonds and sulfhydryl groups in soybean protein may result in the irreversible crosslinking. Second, heating may result in hydrolysis of the protein polypeptide chains. Figure 9 shows the viscosity change (measured at room temperature) in 10 wt % protein solutions at pH 11.0 during the aging process at room temperature and at 60°C. The viscosity of the solution aged at 60°C decreased rapidly. This was a result of degradation and was confirmed from the SDS-PAGE pattern shown in Figure 8 (bottom left). Heating causes the breakage of peptide bonds which decreases the molecular weight and, hence, a decrease in solution viscosity.

In our initial spinning trials, to prevent the seizures of the metering pump, the PVA solution was heated up to 60°C, and the soybean solution, up to 45°C, at pH 11.5. These two solutions were spun through a core-sheath die into a 50°C coag-



**Figure 7** SDS-PAGE patterns of protein solution at room temperature at pH 11. Column 1 is molecular weight marker and column 2 is soybean protein used in our preliminary study.

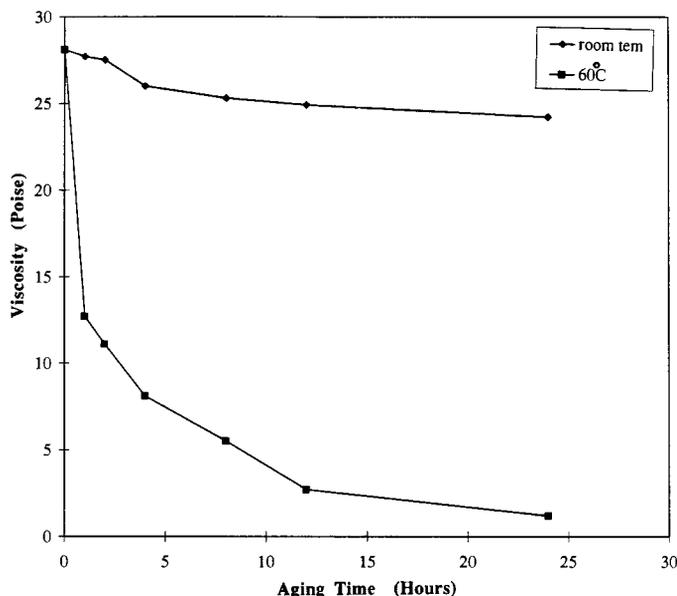


**Figure 8** SDS-PAGE patterns of protein solutions. (Top left) At room temperature and pH 11. Column 1 is molecular weight marker. Columns 2, 3, 4, and 5 correspond to the sample solutions at aging times of 0, 1, 8, and 24 h, respectively. (Top right) At room temperature and pH 12. Column 1 is molecular weight marker. Columns 2, 3, 4, 5, 6, and 7 correspond to the sample solutions at aging times of 0, 1, 2, 4, 8, and 24 h, respectively. (Bottom left) At 60°C and pH 11. Column 1 is molecular weight marker. Columns 2, 3, 4, and 5 correspond to the sample solutions at aging times of 0, 1, 8, and 24 h, respectively. (Bottom right) 10% protein solution at pH 11 at room temperature: (a) contains no sodium sulfite; (b) contains 10 mM sodium sulfite.

ulation bath to form the bicomponent fiber. The protein core of the fiber under such conditions was brittle. From the above discussion about the effect of heating, it was inferred that the brittleness was in part related to the breakage of the peptide bonds caused by relatively high temperatures used for fiber spinning and coagulation processes.

### Effect of Sodium Sulfite

Disulfide bonds, hydrogen bonds, hydrophobic interactions, and other secondary forces together result in a globular conformation of soybean protein molecules. Disulfide bonds are both intra- and intermolecular in nature. The interchange of disulfide bonds and sulfhydryl groups can influence the denaturation of soybean protein molecules. Sodium sulfite was used as the disulfide bond breaker. The reaction mechanism of sodium



**Figure 9** Hydrolytic stability of 10 wt % protein solution at pH 11 during the aging process at 60°C (viscosity measured at room temperature). For comparison, the aging data at room temperature is also given.

sulfite breaking of disulfide bonds is shown below<sup>22</sup>:

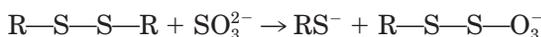


Table I shows the effect of a 10 mM sodium sulfite on the viscosity of 10 wt % soybean protein solution. The solution with sodium sulfite has lower viscosity than that without sodium sulfite. However, the difference was not large. SDS-PAGE patterns in Figure 8 (bottom right) show that the addition of 10 mM sodium sulfite did not change the composition of the soybean protein.

#### Effect of Urea

Soybean protein solutions in water usually at concentrations above 20% (at pH ~ 12 and at room

temperature) forms a gel-like structure. Figure 10 shows that with an increasing amount of urea (a strong hydrogen-bond breaker) 10 wt % protein solution viscosity decreased dramatically. SDS-PAGE patterns (not shown here) confirm that this viscosity change on the addition of urea is not a result of degradation.

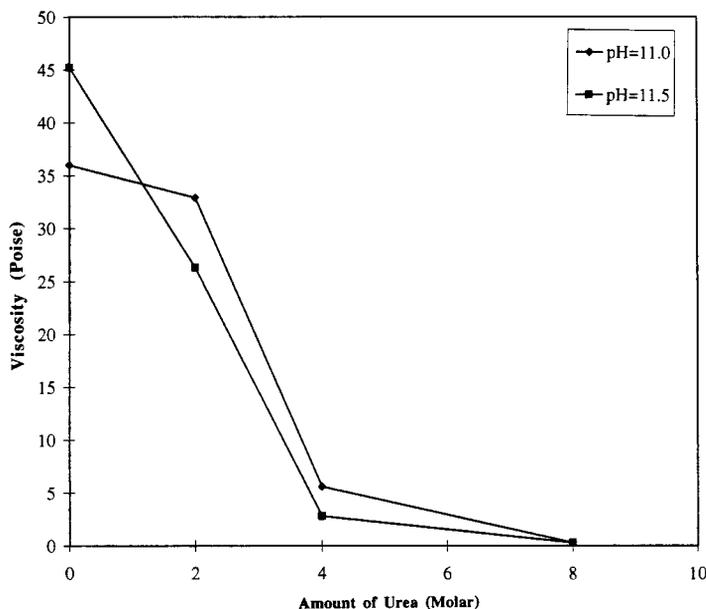
The core breakage during spinning could be due to the degradation and/or the protein microgel formation. Microgels were observed in the spinning process and the larger ones were hindered by a 325-mesh filter in the spinning line. The smaller microgels would pass through the filter and be present in the extruded fiber, resulting in the fiber heterogeneity. The microgels left on the mesh filter could be dissolved in 8M urea. Spinning may also be carried out by pretreating soybean protein with urea. The extent of protein denaturation, obviously, will also effect the fiber drawability.

**Table I** Effect of Sodium Sulfite on the Viscosity of 10% Protein Solution

pH	Viscosity with 10 mM Sodium Sulfite (Poise)	Viscosity Without Sodium Sulfite (Poise)
11	28	36
11.5	36	45
12	19	23

#### CONCLUSIONS

A bicomponent fiber having a protein core and PVA sheath were spun using 15 wt % protein solution treated with xanthate and 10 wt % PVA solutions. Protein/PVA fibers were coagulated in saturated Na<sub>2</sub>SO<sub>4</sub> solution containing



**Figure 10** Effect of urea on the viscosity of 10% protein solution at room temperature.

1M H<sub>2</sub>SO<sub>4</sub>. The fibers were then crosslinked in a 8 wt % formaldehyde solution. The protein core of the fiber was brittle and could not be drawn. The poor drawability of the fiber was attributed to the protein degradation and to the microgel formation in the protein spinning solution.

Rapid cleavage of peptide bonds in protein was observed above pH 11.5 or at 60°C. For obtaining maximum denaturation and avoiding degradation, it is recommended that the spinning solution be prepared at pH 11.5 and should preferably be maintained at room temperature. The addition of 10 mM sodium sulfite at room temperature did not change the solution viscosity significantly. But the addition of 8M urea caused at least a 20-fold decrease in viscosity. The use of urea pretreated protein is suggested to reduce the microgel formation. Plans to overcome the brittle behavior of the protein phase fall into the following three categories: (i) increased denaturation of the protein molecules by complete breaking of the hydrogen and disulfide bonds while limiting the extent of chain cleavage of the backbone; (ii) plasticization of the protein molecules; and (iii) the addition of small amounts of other compatible polymer that will undergo similar coagulation and crosslinking reactions as the protein.

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