

Solution Spinning and Characterization of Poly(vinyl alcohol)/Soybean Protein Blend Fibers

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ABSTRACT: Soybean protein/poly(vinyl alcohol) (PVA) blend fibers were processed using wet spinning, after modifying the protein solution by thermal denaturation without alkali. Dynamic mechanical properties as well as scanning electron microscopy studies suggest compatibility between PVA and soybean protein. The effect of crosslinking agent, crosslinking time, and heat-treatment temperature on the mechanical properties of blend fibers was studied. The soy-

bean protein fibers or the blend fibers containing less than 40% PVA were unoriented amorphous, whereas the blend fibers containing more than 40% PVA exhibited the crystalline structure of PVA. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 716–721, 2003

Key words: crosslinking; proteins; poly(vinyl alcohol) (PVA); blend fibers; denaturation

INTRODUCTION

Regenerated protein fibers received considerable attention during the 1930s and 1940s.^{1–6} With the introduction of petroleum-based fibers, not much attention has been paid to this class of fibers during the past 50 years. However, because of environmental considerations, there is renewed interest in these fibers.^{7,8} Garments based on soybean fibers have recently been developed in China.⁸

The soybean protein obtained from soybean seeds through a process of dehulling, defatting, extraction, centrifugation, and precipitation retains its native state,⁹ and is mainly composed of 7S and 11S fractions.¹⁰ The soybean protein in the native state (globular) is not suitable for fiber spinning; before being spun, it has to undergo denaturation. After denaturation, only the primary structure of the protein is retained, and other higher-order structures are broken down, resulting in unfolded linear protein chains. A number of studies on thermal denaturation of soybean protein have been reported in the literature.^{11–13} It has been pointed out that the denaturation temperatures for 7S and 11S fractions are in the 72–80°C and 85–95°C range, respectively.^{14–16} High pH,^{17,18} urea,^{19,20} β -mercaptoethanol,²⁰ organic solvent,⁹ and deter-

gent²¹ have also been used to denature soybean protein solutions. Under extreme pH conditions, severe hydrolysis of protein occurs, especially at high temperatures.²² The reducing agent sodium sulfite is used to break disulfide bonds in the soybean protein.^{23,24} The soybean protein fiber had poor tensile strength, especially in the wet state.^{25–27}

Attempts are now being made to combine the soybean protein with a synthetic polymer either in the bicomponent⁷ fiber geometry or as a blend. PVA is water soluble and can be processed into fiber using similar methods as for soybean protein, and has high strength and modulus.^{28,29} Moreover, both soybean protein³⁰ and PVA exhibit hydrogen bonding. In this investigation, we report the results of processing and characterization study on soybean protein/PVA blend fibers, where soybean protein was thermally denatured without alkali.

EXPERIMENTAL

Soybean protein powder, food-grade Supro 620, was obtained from Protein Technologies International (St. Louis, MO). PVA powder in the molecular weight range of 125,000 to 186,000 g/mol (99+% hydrolyzed) was obtained from Aldrich Chemical Co. (Milwaukee, WI).

A 17 wt % soybean protein solution was prepared by adding 35 g of the soybean protein powder into the aqueous solvent composed of 57.6 g urea, 1.0 g of sodium sulfite, and 115 mL of distilled water. This mixture became viscous and appeared to be homogeneous after mechanical stirring at room temperature for 4 h and subsequently at 85°C for 20 min. Solution homogeneity and increased viscosity appeared to be a result of thermal denaturation.

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TABLE I
Fiber Spinning Conditions

Fiber designation	PVA/protein weight ratio	Fiber spinning temperature (°C)	Fiber draw ratio ^a
PVA	100/0	70	5.8
PS9010	90/10	70	5.5
PS7030	70/30	70	3.0
PS4060	40/60	70	2.0
PS2080	20/80	70	1.8
Soybean protein	0/100	70	1.5

^a Maximum achievable draw ratio at which fiber can be taken up.

The soybean protein/PVA blend solutions for fiber spinning were prepared from 17 wt % protein and 15 wt % PVA solutions. Soybean protein and PVA solutions giving desired PVA/soybean protein weight ratios were mixed by vigorous mechanical stirring at 85°C for several minutes followed by centrifuging to eliminate bubbles. Above 17 wt % protein concentrations, thermally denatured protein solution appeared to gel and was not suitable for fiber spinning.

A spinning machine (Bradford University Research Ltd.) was used in fiber spinning. The setup included a piston-driven spinning unit, coagulation bath I, and coagulation bath II. Fiber spinning was conducted at 70°C, and the spinneret was submerged in the coagulation bath I. Crosslinking, washing, drawing, and heat treatment were done off-line. The coagulation baths contained saturated solutions of equal weight percentage of sodium sulfate and ammonium sulfate in water with 1M sulfuric acid. The temperature of the coagulation bath I was maintained at 50°C and bath II at 70°C. The coagulation bath temperatures were selected based on the PVA spinning conditions.²⁸ Fibers were drawn in the second coagulation bath. The fiber draw ratio was calculated based on the ratio of the take-up speed (which was after the second coagula-

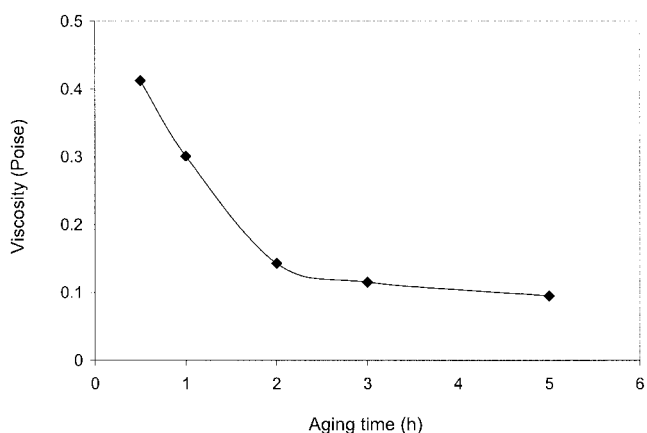


Figure 1 Solution viscosity versus aging time measured at 70°C for alkali-denatured soybean protein solution.

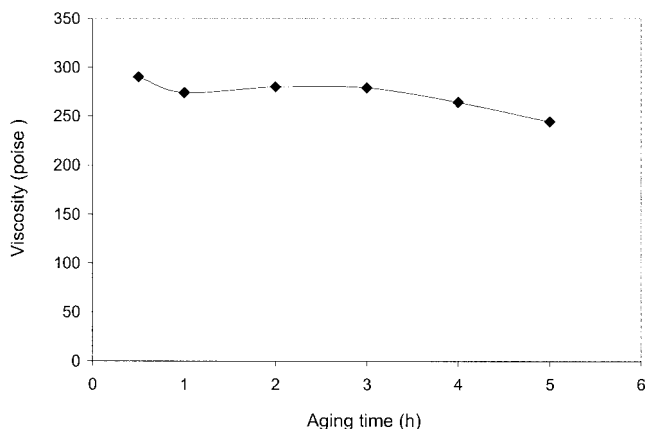


Figure 2 Solution viscosity versus aging time measured at 70°C for thermally denatured soybean protein solution.

tion) and the roller speed between the first and the second coagulation baths. Fiber spinning and drawing parameters are listed in Table I. The coagulated fiber was then kept in the crosslinking bath, which was composed of either 7 wt % glutaric dialdehyde or 7 wt % formaldehyde in water for the desired amount of time at room temperature. Crosslinked fibers were heat-treated in an oven in the 110 to 190°C temperature range at about 20 MPa stress.

Solution viscosity was measured using the Brookfield LVTDV-I digital display viscometer (Middleboro, MA). Thermal-transition temperatures were measured using TA Instruments DSC Q100 differential scanning calorimeter (TA Instruments, New Castle, DE) in the modulated mode at a heating rate of 4°C/min, under nitrogen gas flow. Thermogravimetric analysis (TGA) was carried out using TA Instruments TGA 2950 at a heating rate of 10°C/min in air. Dynamic mechanical thermal analysis was carried out at a heating rate of 10°C/min by RSA III (Rheometrics Scientific, Piscataway, NJ), 25.4-mm gauge length,

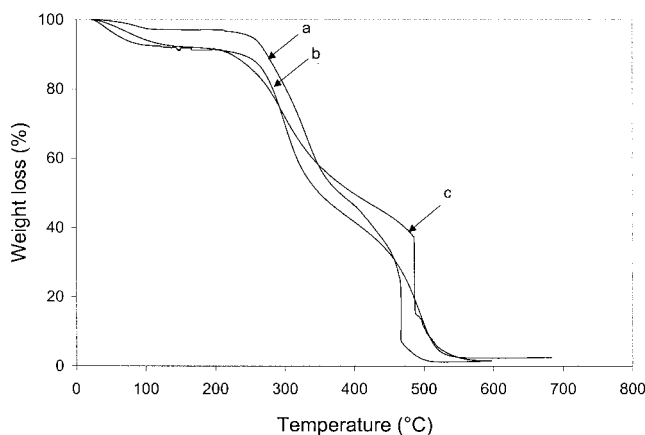


Figure 3 Thermogravimetric analysis of PVA/soybean protein fibers in air at a heating rate of 10°C/min: (a) PVA fiber; (b) PS7030 blend fiber; (c) soybean protein fiber.

TABLE II
Effect of Crosslinking Agent on the Mechanical Properties of PVA/Soybean Protein Blend Fibers^a

Fiber	Crosslinking agent	Elongation at break (%)	Modulus (GPa)	Breaking strength (MPa)
PS9010	Formaldehyde	30 ± 7	2.2 ± 0.4	134 ± 15
	Glutaric dialdehyde	12 ± 1	3.2 ± 0.2	145 ± 10
PS2080	Formaldehyde	84 ± 8	2.3 ± 0.2	36 ± 4
	Glutaric dialdehyde	52 ± 6	3.1 ± 0.3	48 ± 6

^a All fibers were crosslinked for 8 h and no heat treatment was given to these fibers.

around 30 MPa pretension, and 1 Hz frequency. Tensile properties were determined using an Instron 5576 Universal Tensile Tester at a gauge length of 25.4 mm and a crosshead speed of 3 mm/min. The wide-angle X-ray diffraction (WAXD) patterns of the fibers were obtained using a Rigaku RU-H3R (Rigaku, Tokyo, Japan) equipped with an image plate. The fiber morphology was investigated by LEO 1530 scanning electron microscope (SEM). Fiber samples were cooled in dry ice/acetone mixture and were cut with a blade and were subsequently sputter-coated with gold using Scancoat Six Sputter Coater (Edwards High Vacuum Internationals, West Sussex, UK).

RESULTS AND DISCUSSION

The disulfide, hydrogen, and ionic bonds and even steric and hydrophobic interactions in the native state of the protein, which are responsible for forming higher-order structures, have to be broken down to make a spinnable solution. Sodium sulfite and urea have been known to be effective for breaking disulfide bonds

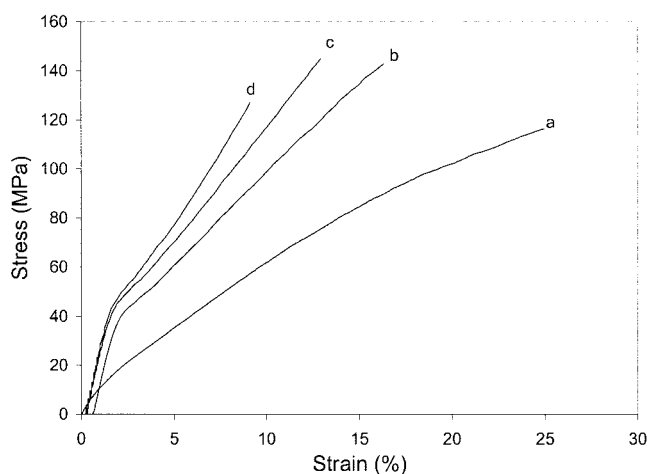


Figure 4 Effect of crosslinking time on the mechanical properties of PVA/soybean protein blend fiber (PS9010) at a draw ratio of 4.2: (a) 2 h, (b) 4 h, (c) 8 h, (d) 24 h.

TABLE III
Effect of Heat-Treatment Temperature on the Mechanical Properties of PVA/Soybean Protein Blend Fibers^a

Sample	Heat-treatment temperature (°C)	Elongation to break (%)	Modulus (GPa)	Breaking strength (MPa)
PS9010	None	16 ± 1	2.9 ± 0.3	140 ± 16
	110	15 ± 1	3.2 ± 0.4	195 ± 5
	150	12 ± 0.7	4.3 ± 0.1	245 ± 5
PS2080	190	11 ± 0.6	5.3 ± 0.3	260 ± 11
	None	73 ± 7	2.5 ± 0.2	38 ± 5
	110	64 ± 10	2.3 ± 0.2	50 ± 7
	150	65 ± 4	2.6 ± 0.3	52 ± 6
	190	57 ± 3	3.0 ± 0.3	57 ± 5

^a All fibers were crosslinked in glutaric dialdehyde for 4 h.

and, to some extent, to prevent the gel formation of the solution. In addition, protein denaturation using either high pH condition or heat is needed to obtain a suitable dope for spinning. Although the high pH can be used to denature the soybean protein solution at room temperature, this solution was not stable at higher temperatures, as seen from the viscosity data presented in Figure 1. The alkali denaturation process is similar to the thermal denaturation process except for adjusting pH value to 13 and without subsequent heating. Viscosity of the alkali-denatured soybean protein solution, aged at 70°C, decreased rapidly, a result of peptide chain breakage. After 6 h of aging, even the color of the basic solution began to become darker and the protein began to precipitate from solution. The reason to check the stability of the spinning solution at 70°C is that aqueous solutions of PVA exhibit good spinnability above this temperature. Based on the viscosity data in Figure 1, it was con-

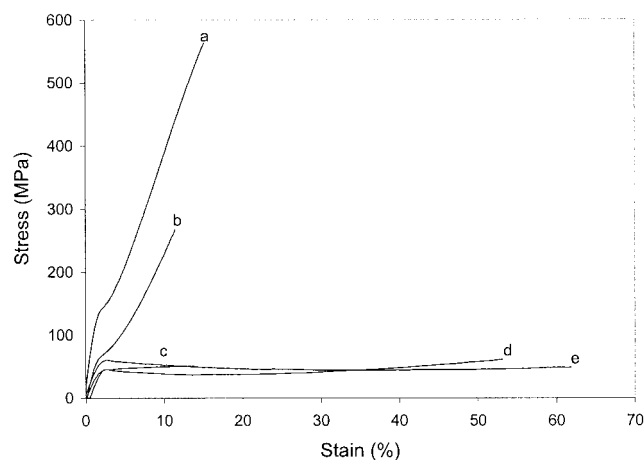


Figure 5 Tensile stress-strain curves for PVA/soybean blend fibers at various compositions: (a) PVA; (b) PS9010; (c) PS4060; (d) PS2080; (e) pure soybean protein fiber. All these fibers were drawn to maximum drawing ratio as shown in Table I and crosslinked with glutaric dialdehyde for 4 h and heat-treated.

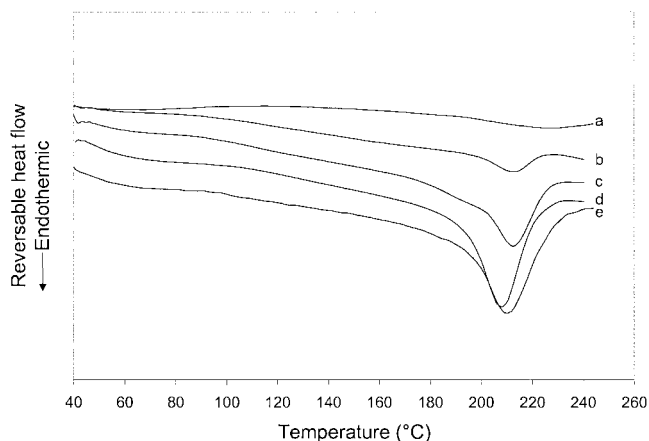


Figure 6 MDSC curves of PVA/soybean protein blend fibers: (a) soybean protein fiber; (b) PS2080; (c) PS7030; (d) PS9010; (e) PVA. All the fibers used in this study were drawn to maximum draw ratio followed by crosslinking and heat treatment.

cluded that the alkali-denatured solution was not suitable for fiber spinning of soybean protein/PVA blends. Figure 2 shows the change in viscosity measured at 70°C versus the aging time at 70°C for the thermally denatured protein solution. Based on this viscosity data, it was concluded that the solution is thermally stable at 70°C for about three 3 h. Therefore, the thermally denatured protein solution was used for the spinning of soybean protein/PVA blend fibers. Even at low aging times, the viscosity of the basic solution was three orders of magnitude lower than that of thermally denatured solution resulting from the hydrolysis induced by alkali during the solution preparation process.

Pure PVA and pure soybean protein fibers showed the onset of degradation temperature in air at 213 and

190°C, respectively, as shown in Figure 3. The onset of degradation for the blend fibers was between these two temperatures. In nitrogen atmosphere, degradation temperatures for these fibers shifted to higher temperature by about 10°C. Based on the TGA results, the heat-treatment temperature for various blends fibers was chosen to be at or below 190°C. Initial weight loss (up to 100°C) was believed to be the result of absorbed moisture.

Glutaric dialdehyde and formaldehyde have been used to crosslink proteins and PVA.^{6–8,26,31} To study the effectiveness of these crosslinking agents for the blend fibers, both agents were used for PS9010 and PS2080 fibers. The results in Table II showed that for both blend fibers, glutaric dialdehyde appeared to be more effective as judged by the fiber modulus. Figure 4 shows the effect of crosslinking time on the mechanical properties of PS9010 fiber when glutaric dialdehyde was used as the crosslinking agent. As seen in the figure, modulus and breaking strength exhibited maximum values after 4 to 8 h of crosslinking. Therefore glutaric dialdehyde and crosslinking time of 4 h were selected for subsequent fiber studies. The tensile strength and modulus of the blend fibers, PVA-rich PS9010 and protein-rich PS2080, could be improved by heat treatment, as seen in Table III. Figure 5 shows tensile stress–strain curves for the pure and blend fibers, crosslinked and heat-treated at 190°C. Limited improvement in tensile strength of the soybean fiber was observed with the addition of PVA, at low PVA content. Only PS9010 fiber exhibited markedly higher tensile strength than that of the pure soybean fiber. The hydroxyl, acidic, and sulfur groups in the soybean protein are responsible for the crosslinking reaction with glutaric dialdehyde. Only about one third of the repeat units in soybean protein are crosslinkable. In

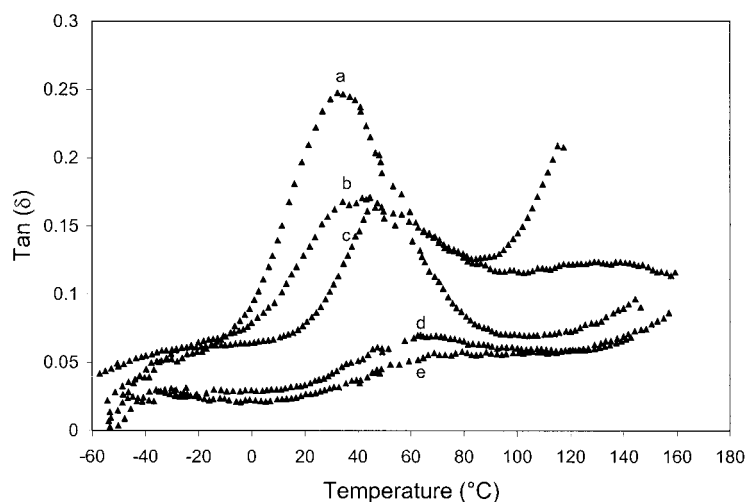


Figure 7 Loss $\tan \delta$ as a function of temperature for the PVA/protein blend fibers: (a) PVA; (b) PS9010; (c) PS7030; (d) PS2080; (e) soybean protein fiber. All the fibers used in this study were drawn to maximum draw ratio followed by crosslinking and heat treatment.

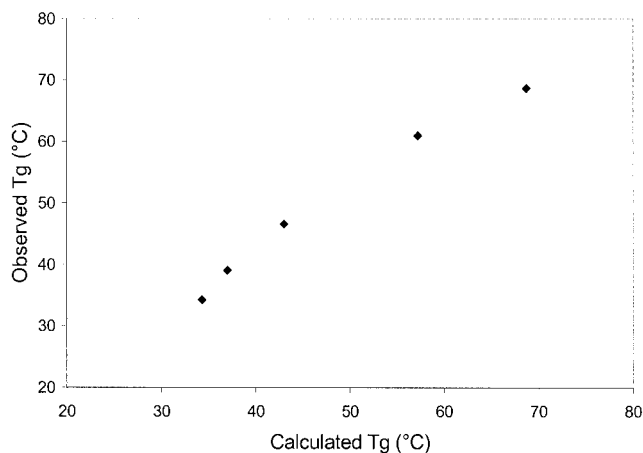


Figure 8 Plot of calculated T_g based on Fox equation versus observed T_g of blend fibers.

addition, crosslinking conditions, such as pH range, that were not used in our experiment provide further room for process.

The melting behavior of the crosslinked and heat-treated fibers was investigated using modulated DSC during the first heating cycle. Modulated DSC can separate reversible and irreversible heat components. Heat flow resulting from soybean and PVA degradation is irreversible, whereas heat flow attributed to melting is reversible. Modulated DSC can separate these two components using the cyclic heating mode. Using this process, the melting behavior of PVA may be clearly observed, as seen in Figure 6, which shows the reversible heat flow in various fibers. The heat of fusion for the 100% PVA fiber was 26 J/g. Based on the heat of fusion of 156 J/g for the 100% crystalline

PVA,³² the degree of crystallinity in PVA was calculated to be 18%. Judging by the DSC scans, fibers containing soybean protein had lower degrees of crystallinity.

DMA experiments were carried out to understand how the composition affects the dynamic mechanical behavior of blend fibers. Figure 7 shows $\tan \delta$ of the pure and blend fibers as a function of temperature. As shown in the figure, the peak temperature of $\tan \delta$ shifted to higher temperatures with increasing soybean protein content. Moreover, a single $\tan \delta$ peak appeared in the glass-transition (T_g) region of each blend. The calculated T_g based on the Fox equation³³ versus the observed T_g values are plotted in Figure 8. Based on the dynamic mechanical plots given in Figure 8, T_g for the pure PVA was taken to be 35°C and that for the pure soybean protein fiber was taken to be 69°C. The observed T_g values for the blend fibers correspond quite well with the Fox equation prediction, suggesting compatibility between PVA and soybean protein.

WAXD patterns of the heat-treated fibers are given Figure 9. PVA and PVA-rich blend fibers exhibited both orientation and crystallinity [Fig. 9(a)–(c)]. On the other hand, soybean protein and PS2080 fibers exhibited almost no molecular orientation and no significant crystallinity. Low crystallinity in PS2080 was also observed from DSC studies.

Cross-sectional shapes of the fibers were investigated by SEM. PVA and PS9010 showed typical, kidney bean-like cross-sectional shapes, whereas soybean protein and PS2080 had relatively round shapes, as shown in Figure 10. It is generally known that the cross-sectional shape of solution-spun fibers relates to

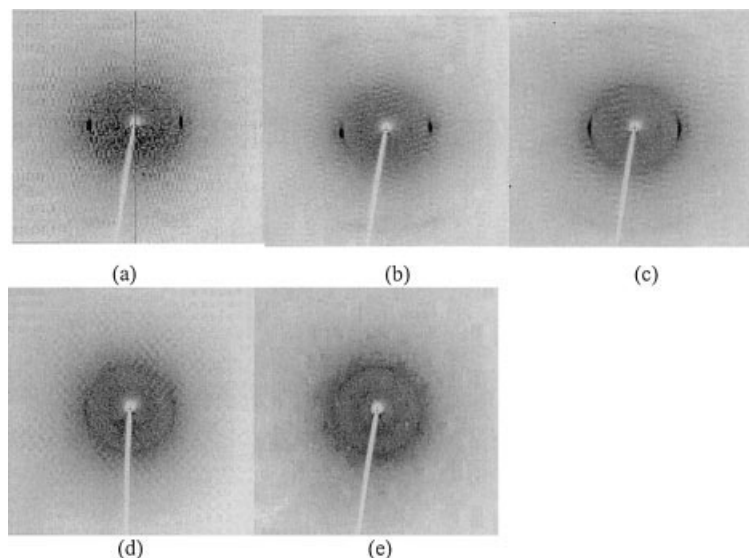


Figure 9 Wide-angle X-ray diffraction patterns of various blend fibers: (a) PVA; (b) PS9010; (c) PS7030; (d) PS2080; (e) soybean protein. All the fibers were drawn to maximum ratio, crosslinked (glutaric dialdehyde), and heat-treated (5 min at 190°C).

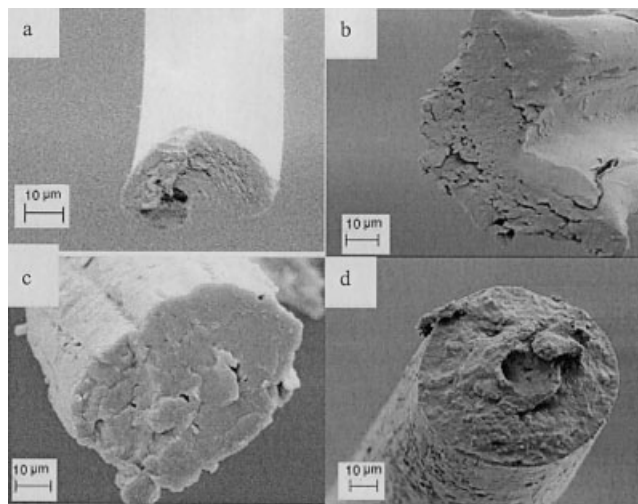


Figure 10 Scanning electron micrographs of various fibers: (a) PVA, (b) PS9010, (c) PS 4060, (d) soybean protein.

the coagulation rate,³⁴ that is, a higher rate results in a noncircular cross section. Therefore, the round shape of soybean protein fiber implies that its coagulation rate is slower than that of PVA. Scanning electron micrographs of the blend fibers do not exhibit any phase separation, which is consistent with the observation of single T_g as discussed earlier. These observations suggest that PVA and soybean protein are compatible, at least in the concentration range and other conditions used for fiber spinning in this work. Other factors such as denaturation conditions may influence compatibility. These issues were not addressed in this work.

CONCLUSIONS

The PVA/soybean protein blend fibers were processed by wet spinning after modifying the protein solution through thermal denaturation without alkali. It was determined that the denaturation of the soybean protein using extreme basic conditions was not suitable for the preparation of the blend fibers with PVA because of the instability of the basic protein solution at high temperature, where spinnability of the aqueous PVA solution was obtained. Scanning electron microscopy and dynamic mechanical properties data suggested compatibility between soybean protein and PVA, under the fiber-spinning conditions used in this work. The mechanical properties of soybean protein fiber could be enhanced by introducing PVA to form a blend fiber. Crosslinking and heat treatment are important steps for improving the final properties, although much optimization remains to be

done in both areas as well as in studying the phase behavior of PVA/soybean blend system. Based on the PVA/soybean compatibility demonstrated in this study, we expect that further studies on PVA/soybean blend should prove to be quite valuable.

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