

Studies on Regenerated Protein Fibers. III. Production of Regenerated Silk Fibroin Fiber by the Self-Dialyzing Wet Spinning Method

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SYNOPSIS

The spinnable dope containing 20 wt % of silk fibroin dissolved in the MU solvent (e.g., LiBr · H₂O = 40 wt %, and EtOH : H₂O = 100 : 0 in volume) was spun into a coagulant and subsequently drawn, to give the following results.

1. Methanol, ethanol, and isopropanol were a predominant coagulant for the dope, and the coagulant containing 10% LiBr · H₂O is best.
2. Spinnability depended upon the ratio of nozzle hole length to diameter (L/D) and was improved by increasing L/D from 4 to 10. Coagulativity was not sufficient at the SF concentration of 16%, but improved by raising it up to 20%. Drawability of the spun filaments in water was improved at a temperature above 60°C.
3. The drawn fiber showed excellent mechanical properties, especially tensile toughness when as-spun fiber was drawn in water at 61°C. An X-ray diffraction diagram of the drawn fibers indicated their crystalline axes were partially oriented along the fiber axis. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In 1930 Yazawa et al. dissolved silk fibroin (SF) in a concentrated magnesium nitrate solution to produce a raw dope, which was then dialyzed and concentrated before spun into a saturated ammonium sulfate solution. They reported that the regenerated fiber had a breaking strength of 2.5 g/den at an elongation of 20–25%.¹

Yazawa's report was followed by many similar proposals in which SF was dissolved in various inorganic salt aqueous solutions, and the salts were removed by dialysis to prepare spinnable dopes. Those dopes were also coagulated in a saturated solution of inorganic salt such as ammonium sulfate

or sodium sulfate, to produce some regenerated materials of various shapes. However, they did not succeed in producing any regenerated SF fiber. The reason for such a failure in the past resides in the fact that any suitable system of solvent/nonsolvent was not established by them.² The later proposals that relied on the dialysis of the dope not only involved very intricate operations but gellation of SF or a like phenomena of the dope. Consequently, the regenerated fibers were not free from undesirable variation in their mechanical and/or other properties. To overcome such drawbacks inherent in prior methods, a novel system of solvent/nonsolvent was established by us.

We found that the *Matsumoto/Uejima* (MU) solvent as previously reported³ is an excellent solvent for a spinning dope, and that methanol and others are appropriate nonsolvents that can coagulate the spinning dope even if undialyzed.

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The results of spinning experiments carried out on our basic concept mentioned above are reported as follows.

EXPERIMENTAL

Raw Material

Silkworm cocoons produced in the farm at the Kyoto Institute of Technology were used. After removing sericin by the conventional method, the cocoons were dried to provide SF. Some cocoons were divided into their strata, each composed of a continuous filament, before removing sericin by the conventional method so as to prepare a discrete SF sample for each stratum. Further, initial filaments that the cocoons had spun at first for sticking their succeeding length of filament to were also collected separately from the succeeding normal filaments, and their sericin was removed by this method.

Preparation of SF solution

Given amounts of the dried SF were mixed well with the MU solvents of varied compositions, and heated to 70°C while being stirred. The SF thus dissolved in the solvents provided the SF solutions.

Preparation of Coagulant

Ion-exchanged water was used, together with ethanol, methanol, or isopropanol (Wako Junyaku Co., Ltd.), which were of the highest reagent grade. Lithium bromide was the industry grade (Wako Junyaku Co., Ltd.). These reagents were used alone or blended at varied ratios to provide the coagulant.

Formation of Sample Films

An appropriate amount of the concentrated SF solution was poured on a glass plate, and a knife was used to spread the dope over the plate with the caution not to involve any bubbles. After keeping the plate horizontal to make a smooth surface of the poured dope, the glass plate was immersed in a coagulant bath at 20°C to form a film. The fully coagulated film was desalted and kept in a methanol aqueous solution to prevent hardening and decaying.

Measurement

Viscosity of the Diluted Solutions

Viscosity of the solution of specific amounts of SF dissolved in MU solvents (each comprising 40% by weight of LiBr · H₂O in ethanol)³ was measured using an Ubberohe viscometer at 30°C. The data were used to calculate the values η_{sp}/C , and the relationship between η_{sp}/C and C was plotted to give straight lines. Those lines were then extrapolated to $C = 0$ so as to determine intrinsic viscosity. $[\eta]$.

X-Ray Diffraction Analysis

X-Ray equipment made by Rigaku Denki Co. Ltd. was used under the following conditions: Ni-filtered Cu-K α line was used as the X-ray source, voltage of 40 kV, current of 20 mA, exposure for 3 h, and camera length of 32.31 mm.

Infrared Absorption Spectrum

An infrared spectrometer IRA-1 made by Nihon Bunko Co. Ltd. was used under the following conditions: wavelength range of 4000 to ~650 cm⁻¹, resolving power of 4 cm⁻¹, scan speed of 4 cm, and temperature of 20°C.

Density

Density gradient columns with mixtures of *n*-heptane and carbon tetrachloride were used at 30°C.

Rating of Coagulativity

Visual Inspection. The dope was coagulated in a series of coagulants in the manner described above. The coagulated films were classified by inspection of their overall coagulativity as shown in Table I.

A droplet of 10% SF solution (dope) on a preparation glass was sandwiched with a cover glass, as shown in Figure 1. The dope was then gently pressed to spread it around, and to make a thickness of 0.5 mm using the pulp spacer. The dope was dipped in the coagulant at 20°C for a specific time, then the length of a coagulated portion was measured under a microscope without removal from the coagulant.

Mechanical Properties

A uniaxial tensile tester made by Iwamoto Seisakusho Co. Ltd. was used under the following conditions: gauge length of specimens of 20 mm and close head speed of 25 mm/min. The moisture content of samples was regulated under standard conditions.

Table IA Results of Film Forming Test

Coagulation Agent	Composition of Solvent: EtOH/H ₂ O ^a (vol %)			
	100/0	80/20	65/35	45/55
MeOH	○/C	○/C	○A,C	△/A,B,C
EtOH	▲/C	▲/C	▲/A,C	×
<i>i</i> -PrOH	●/C	▲/A,B	▲/A,C	×
H ₂ O	×	×	×	×
MeOH/H ₂ O (vol %)				
97/3	○/C	△/C	○/A,C	×
95/5	○/B	○/C	△/A	×
90/10	△/C	△/C	△/C	×
85/15	△/C	△/C	△/C	×
MeOH/LiBr·H ₂ O (wt %)				
95/5	○/C	○/C	△/C	△/C
89/11	⊙/C	○/C	○/C	△/C
85/15	○/C	○/C	△/C	△/C

^a LiBr·H₂O/EtOH,H₂O = 50/50 (wt %) constant. Bath temperature, 20°C. Key: ⊙, better; ○, good; △, bad; ×, did not coagulate; A, contains small bubbles; B, a little swelling; C, effusion. Open marks signify translucent film. Solid marks signify white film.

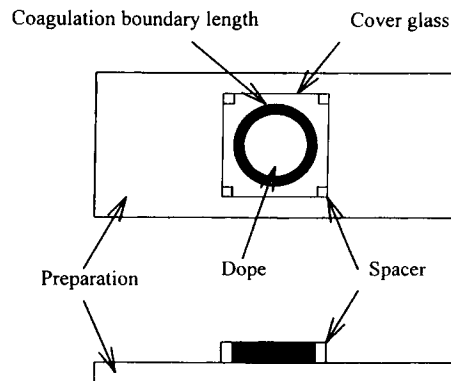
Spinning Conditions

A test apparatus as shown in Figure 2 was used for wet spinning for the dope samples. The dope extruded through a nozzle was coagulated in a coag-

Table IB Results of Film Forming Test

Coagulation Agent	Composition of Solvent: EtOH/H ₂ O ^a (vol %)			
	100/0	80/20	65/35	45/55
MeOH	○/A	○/B	○A,B	△/A,B
EtOH	●/A	●/A	●/A,B	▲/A,B
<i>i</i> -PrOH	●/A	●/A,B	▲/A,B	▲/A,B
H ₂ O	×	×	×	×
MeOH/H ₂ O (vol %)				
97/3	○/A	○/A	○/A	○/A
95/5	○/A	○/A	○/A,C	△/A,B,C
90/10	○/A	○/C	△/A,C	△/A,C
85/15	△/C	△/C	△/C	△/C
MeOH/LiBr·H ₂ O (wt %)				
95/5	○/C	○/B,C	○/B	○/B
89/11	⊙/C	○/C	⊙/C	⊙/C
85/15	○/C	○/C	○/C	○/C

^a EtOH/H₂O = 90/10 (vol %) constant. Bath temperature, 20°C. Key: ⊙, better; ○, good; △, bad; ×, did not coagulate; A, contains small bubbles; B, a little swelling; C, effusion. Open marks signify translucent film. Solid marks signify white film.


Figure 1 Measurement of the coagulation length.

ulation bath, stretched between the first and second roll, and then wound on a take-up roll. Important spinning conditions were as follows: the nozzle had six spin holes having a diameter (D) of 0.3 ~ 0.5 mm and a length (L) of 0.6 ~ 4 mm. The throughput of the dope was 1 cm³/min, with the coagulation bath of methanol and the stretching bath of water or methanol. The spinnable dopes were prepared by dissolving 16 or 20% by weight of SF in MU solvents prepared by dissolving 40% by weight of LiBr·H₂O in a mixture of EtOH and water, with the ratio of EtOH to H₂O being 100 : 0.

RESULT AND DISCUSSION

Inter- and Intracocoon DP of SF

It is an established but questionable theory that SF molecules are of varied molecular weight falling within a range of 10⁴ to 10⁶, and the thickness of the SF filament varies among the portions of each cocoon.⁴ Note that SF is inevitably decomposed in the course of preparation to determine the viscosity of diluted SF solutions in the solvents used conventionally. However, the MU solvent keeps the SF molecule in the solutions without degradation. We employed the MU solvent to determine intrinsic viscosity [η] of SF and to examine the variation of inter-

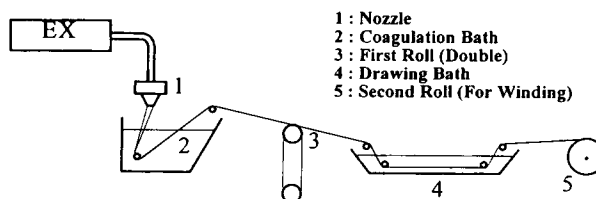

Figure 2 Spinning apparatus.

Table II Intra- and Intercocoon DP Variation of SF

	Inner	Intermediate	Outer	Average	Standard Deviation
[η] (dL/g)	0.62	0.58	0.65	0.62	0.03
	0.84	0.68	0.72	0.75	0.07
	0.63	0.66	0.69	0.66	0.02
	0.74	0.68	0.83	0.75	0.06
	0.71	0.76	0.71	0.73	0.02
Average	0.71	0.67	0.72	—	—
Standard deviation	0.08	0.06	0.06	—	—

and intracocoons. Table II summarizes results of our measurement. There is no or almost no difference in the viscosity—average degree of polymerization (DP) between or in each of the cocoons that were produced at the same time and the same area.

Production of Regenerated Silk Fibroin Fiber

Coagulativity of the Concentrated Silk Fibroin Solution

Coagulating Ability. Coagulation of SF aqueous solution has been studied for many years, and, generally, saturated aqueous solutions of inorganic salts have been used in the so-called salting-out method.⁵ However, the solubility in water of SF is not high, so that an aqueous solution of SF separates SF in a gel state easily; SF molecules in aqueous solution cannot be presumed to be stable. Thus, it is unlikely that the SF molecules would be salted out in their well-extended state. The MU solvents² are alcoholic-

aqueous solutions of inorganic salt. Both the alcohol and lithium bromide in each MU solvent behave as a good solvent in that SF molecules can fully extend.^{2,6} On the contrary, water acts as a poor solvent in which SF molecules shrink when the solution of SF dissolved in MU solvent is dialyzed by the traditional method,⁵ and the inorganic salt (i.e., lithium bromide) and alcohol are removed, thereby undesirably rendering spherical the SF molecules that had been in their extended state. Dialysis of such a solution will thus produce an unsatisfactory dope for the spinning process. From this viewpoint, we have sought a novel coagulation system from which SF molecules can coagulate in the extended state. We had observed in our previous research that less than 30 wt % of $\text{LiBr} \cdot \text{H}_2\text{O}$ can never dissolve the SF, at any ratio of alcohol/water in MU solvents. We expected that such an MU solvent with low content of $\text{LiBr} \cdot \text{H}_2\text{O}$ could act as a favorable poor solvent, which ensures the extended state of SF mol-

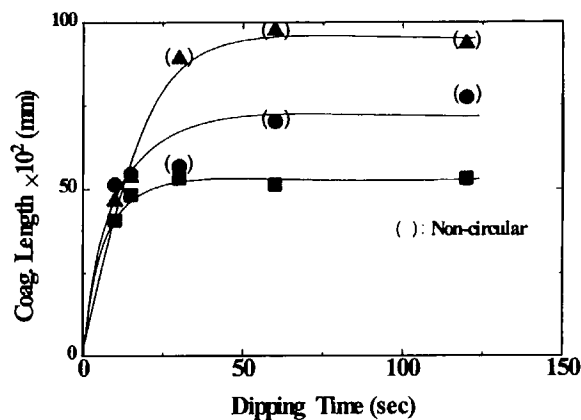


Figure 3 The initial coagulation rate for the SF solution of MU solvents ($\text{LiBr} \cdot \text{H}_2\text{O}/\text{ROH} = 50/50$) R; CH_3 \blacksquare , C_2H_5 \bullet , $i\text{-C}_3\text{H}_7\text{OH}$ \blacktriangle , at 27°C.

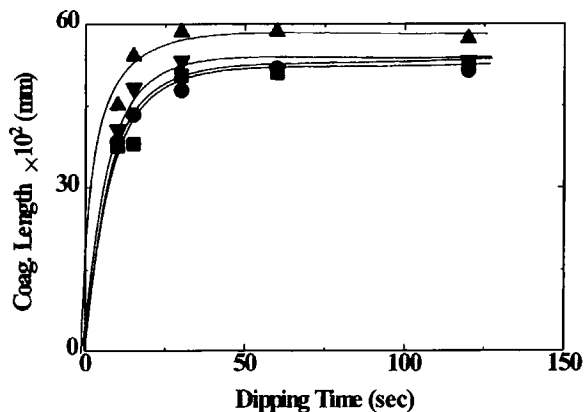


Figure 4 Effect of the ratio of $\text{C}_2\text{H}_5\text{OH}$ to H_2O (∇ 100/0, \blacktriangle 95/5, \bullet 90/10, \blacksquare 87/13) in the MU solvent ($\text{LiBr} \cdot \text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 50/50$) on the initial coagulation rate in CH_3OH at 27°C.

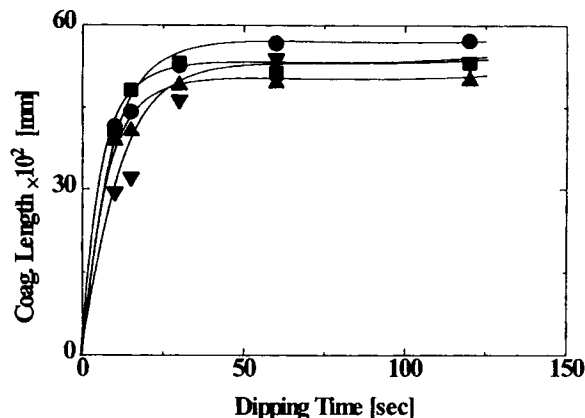


Figure 5 The initial coagulation rate of SF solution dissolved in MU solvents ($\text{LiBr} \cdot \text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 50/50$) for the concentration of $\text{LiBr} \cdot \text{H}_2\text{O}$; ■ 0, ● 5, ▲ 10, ▼ 13 wt % in CH_3OH ($\text{LiBr} \cdot \text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$) at 27°C .

ecules being coagulated. Following this scheme, we prepared a series of specified MU solvents in which $\text{LiBr} \cdot \text{H}_2\text{O}$ content was varied, with the blend ratio of alcohol/water kept constant to evaluate their coagulating ability.

Film Formation in Coagulant. Methanol (MeOH), ethanol (EtOH), or iso-propanol (*i*-PrOH) was used and the alcohol component of the coagulant. The coagulant ability was inspected in terms of the ability to form a film; results are summarized in Table I. Among the alcohols, MeOH could produce a better film than the other alcohols, for the SF solution with MU solvent comprising $\text{EtOH} : \text{H}_2\text{O} > 65 : 35$. Neither bubbles nor swelled portions were observed in this case. An increased ratio of the water in MU solvent did cause bubbles in the regenerated film, nevertheless alcohol was used to formulate the coagulant. MeOH would be regarded as one of the best candidate alcohols in the coagulant. As far as the content of water in the coagulant is concerned, the ratio of MeOH to $\text{H}_2\text{O} > 95 : 5$ gave a better film. The $\text{LiBr} \cdot \text{H}_2\text{O}$ content in coagulant was also altered, and $\text{MeOH} : \text{LiBr} \cdot \text{H}_2\text{O}$ at $89 : 11$ made coagulation satisfactory. These results suggest the best candidates for the solution and the coagulant for SF regeneration are as follow: the solvent is MU solvent those water content is 20% or less and the coagulant is composed of another MU solvent containing 11% or less of $\text{LiBr} \cdot \text{H}_2\text{O}$ dissolved in MeOH as the alcohol blended with 5% or less of water.

Rate of Initial Coagulation. The initial coagulation rates in the coagulant are shown in Figures 3–6. Fig-

ure 3 shows the initial coagulation rate for the different alcohols. *i*-PrOH gives the largest coagulation length, MeOH gives the smallest length, and EtOH gives an intermediate one. However, the alcohols, except MeOH, failed to produce a film whose round contour was distinct and clear. This fact means that a certain quantity of the SF dope drained out at the initial stage of coagulation with the alcoholic coagulants composed of *i*-PrOH or EtOH. This result also shows that MeOH is the best alcohol to formulate the coagulant.

Figure 4 shows the effect of ratios of EtOH to water in the MU solvent for dissolving SF, on the coagulation in MeOH-based coagulant. Coagulation length is greatest at a ratio of alcohol to water at $95 : 5$. The increase of water content in coagulant made the coagulativity poorer as previously summarized. It is concluded that the richer water content in coagulant allowed a greater amount of dope to drain out into the coagulant.

Figures 5 and 6 show the effects of the blend ratio of MeOH to $\text{LiBr} \cdot \text{H}_2\text{O}$. The initial coagulation rate, defined as the value at 10 s dipping, was decelerated as the $\text{LiBr} \cdot \text{H}_2\text{O}$ concentration exceeded 10% in the bath, in a case wherein SF dissolved in an MU solvent whose $\text{LiBr} \cdot \text{H}_2\text{O}$ content was 50% and the ratio of EtOH to water was $100:0$. With an increase of $\text{LiBr} \cdot \text{H}_2\text{O}$ concentration of more than 13%, the boundary region of coagulation became so indefinite that coagulation length could not precisely be measured. In the wet spinning process, fiber formation (i.e., dope coagulation) is regarded as a “phase separation process”⁷ of a certain kind. One of the factors determining the rate of this process is the ratio of diffusion rate of a solvent to that of a nonsolvent. In

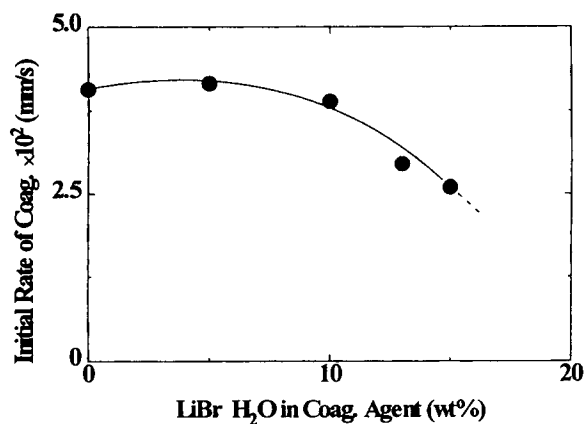


Figure 6 Relation between the initial rate of coagulation and concentration of $\text{LiBr} \cdot \text{H}_2\text{O}$ in CH_3OH ($\text{LiBr} \cdot \text{H}_2\text{O} = 50\%$).

Table III Mechanical Properties of Fibers

Sample No.	Strength Bath	Strength Ratio	Fineness (den)	Density (g/mL)	Tensile Strength (d/g)	Elongation (%)	Young's Modulus (g/d)
1	Air	1.0 ×	391/6f	1.345	0.70	1.7	46
2	Air	2.2 ×	202/6f	1.347	0.96	2.4	49
3	Water (18.5°C)	2.8 ×	151/6f	1.347	1.17	2.5	59
4	Water (61.0°C)	3.2 ×	134/6f	1.347	1.09	11.0	56
Reference data (Silk)		—	—	1.33 ~ 1.45	3.0 ~ 4.0	15 ~ 25	50 ~ 100
Reference data (Wool)		—	—	1.32	1.0 ~ 1.7	25 ~ 35	11 ~ 25

the present case, this factor depends on the difference in $\text{LiBr} \cdot \text{H}_2\text{O}$ concentration between the two MU solvents. Dilution of $\text{LiBr} \cdot \text{H}_2\text{O}$ in the dope becomes more difficult with a decrease in the difference of concentration, and the coagulation is rendered less expeditious. The indefinite contour of the film coagulated in the bath containing 13% or more of $\text{LiBr} \cdot \text{H}_2\text{O}$ content is probably a result of such a phenomenon.

Spinnability

The spinnability of the solution of SF dissolved in MU solvent is excellent. Therefore, we presumed that a proper coagulant could make the regenerated SF into the shape of fiber. From the result of a coagulation test, an optimum coagulant is an MeOH solution of $\text{LiBr} \cdot \text{H}_2\text{O}$ and the concentration is below 11%. When the concentration of $\text{LiBr} \cdot \text{H}_2\text{O}$ is small, coagulation was early, and the fiber that was obtained is easy to take up. From these result, if methanol was employed as a coagulant, then SF dissolved in MU solvent could be regenerated to form a good fiber, without dialyzing the SF solution in advance as previously mentioned. We also applied methanol as a coagulant for the spinning of the dopes, which were prepared by dissolving SF at varied concentrations in the MU solvent, which was composed of 40% $\text{LiBr} \cdot \text{H}_2\text{O}$ dissolved in $\text{EtOH}/\text{H}_2\text{O}$ ($\text{EtOH}/\text{H}_2\text{O} = 100/0$).

Coagulativity of Extruded Dope Streams. A dope containing 16 wt % SF did not show good coagulativity. Presumably, retardation in phase separation of SF was caused in this case by a retarded mutual exchange of the solvent components between the dope and the coagulant. To resolve this problem, we increased the SF content in dope up to the SF content of 20% by weight, and found that the coagulativity and spinnability of the extruded dope were improved.

Dope Sticking Problem to Nozzle Surface. Although the coagulativity was improved by raising the SF con-

tent, the dope's adhesion to the nozzle surface was so good that some extruded filaments could not be spun. We visually inspected the running state of those dope streams near the nozzle holes, and found a phenomenon that resembled the so-called "Barus" effect.⁸

Our countermeasures were as follows: an increased ratio of L/D of nozzle holes, a reduced as-spun rate for the dope, and a reduced dope viscosity.⁹ The reduction of as-spun rate did not improve the problems. Increasing the L/D ratio from 0.6/0.3 (=2) to 2.0/0.5 (=4) seemed to be better. Therefore, we further raised the L/D ratio up to 4.0/0.4 (=10). As a result, the sticking problem was remarkably improved.

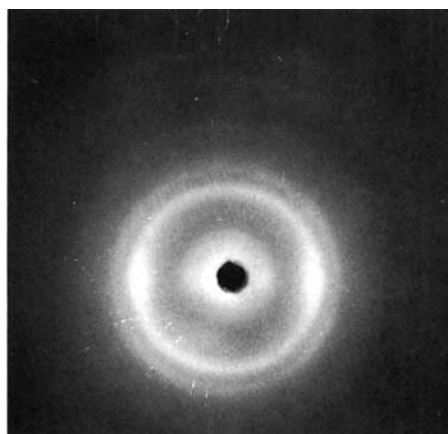
Drawability

Coagulated filament was drawn to make the filament mechanically stronger by giving orientation to the SF molecules. The coagulated SF filament has ductile properties, but becomes somewhat brittle after drying from this state. The brittleness after drying may be caused by poor orientation of SF molecules along the fiber axis. We therefore drew the as-coagulated (as-spun) yarn under varied conditions to produce filaments that have sufficient strength. The drawing ratios given in Table III were maximum ratios for the respective conditions. The hotter the water in the drawing bath, the more extensively the as-coagulated (as-spun) yarns could be drawn.

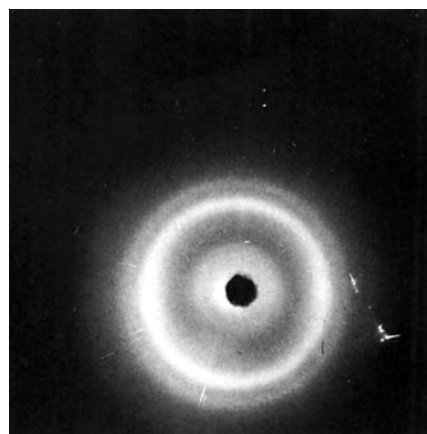
Micro Structures and Physical Properties of the Regenerated Silk Fibroin Fiber

X-Ray Diffraction

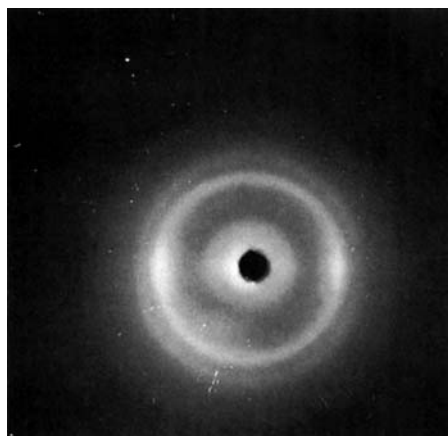
Figure 7 (a-d) shows wide angle X-ray diffraction diagrams of the fibers produced in the described manner.¹⁰ Deby-Sherrer rings, which appear in the photograph of sample 1 at $2\theta = 20.7^\circ$ and 24.8° , are inherent in undrawn fibers. The more intensive Deby-Sherrer ring at $2\theta = 20.7^\circ$ indicates the so-called " β structure."¹⁰



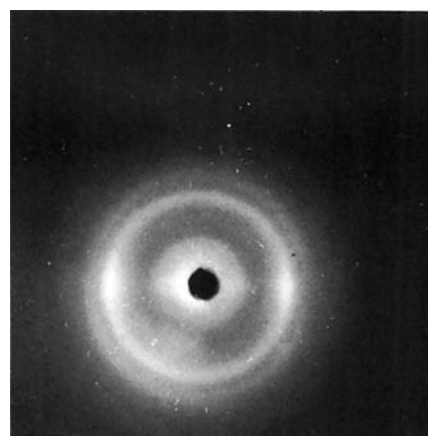
(a)



(b)



(c)



(d)

Figure 7 The X-ray diffraction photography of the regenerated fiber of (a) SF (1), (b) SF (2), (c) SF (3), and (d) SF (4).

Samples 2-4 also show similar Debye-Sherrer rings, but some intensive diffraction at 20.7° appears on the equatorial. This means that crystallization oriented to the fiber axis proceeds by drawing of as-spun fiber.

Density

Table III shows the measured density. The drawing of fibers slightly increased their density, though no

significant difference was found between the drawing conditions.

Infrared Spectrum

Figure 8 shows the IR spectrum of Samples 1 and 4. As seen in Figure 8, broad absorption bands were detected at $1630\text{--}1660$, 1530 , and 1540 cm^{-1} , which were obviously caused by the amide-I group and

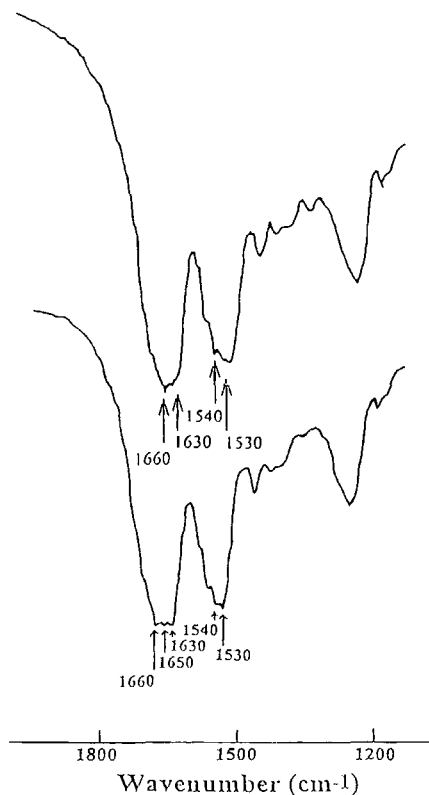


Figure 8 Infrared spectrum of fiber: SF (1) and SF (4).

amide-II group, respectively. The spectrum of sample 1 shows bands at 1660 and 1540 cm^{-1} , which are inherent in the random-coiled polymer molecules, and the spectrum of sample 4 shows bands at 1630 and 1530 cm^{-1} , which are inherent in the β structure.¹¹ These data indicate that SF molecules in sample 4 aligned along the fiber axis by drawing in water at 61°C.

Mechanical Properties

Table III shows the mechanical properties of samples 1–4. Tensile strength as well as Young's modulus of each fiber generally increased with increasing stretch ratio, however, the strength of sample 4 is inferior to sample 3. The same relationship was found also in their Young's modulus. However, the elongation at breakage of sample 4 was greater than the others and the shape of its stress–strain curve greatly differed from the others, as seen in Figure 9. This difference indicates that sample 4 has a higher tensile toughness, afforded by the following mechanism. The stretching temperature and ratio for sample 4 were higher than those for sample 3. A noncrystalline film of silk fibroin was treated by

Magoshi¹² in hot water, and it was found that its crystalline structure had changed at a temperature above 60°C. It was also reported¹³ that a similar phenomenon had occurred when stretching the film. Our sample 4 was stretched at 61°C, significantly higher than the temperature used for sample 3, and also at a somewhat higher stretch ratio than for sample 3. Such a stretching temperature for sample 4 is presumably near the critical temperature, which allows the deformation of crystals. Therefore, the drawing at this temperature in our research would have rendered the twined SF molecules more ready to be loosened and to convert themselves into β structure, i.e., the predominant crystalline structure of SF, whereby polymer chains were oriented along the fiber axis.

The fresh spun filaments can be stretched advantageously under proper conditions, especially at higher temperature, such that the chain molecules are oriented along the fiber axis and crystallize so as to produce a regenerated silk fibroin fiber of improved mechanical properties.

CONCLUSION

1. Methanol, ethanol, and isopropanol were evaluated as the predominant ingredient of coagulant for the concentrated solution of SF dissolved in MU solvents. A methanol solution of $\text{LiBr} \cdot \text{H}_2\text{O}$ makes an excellent film as a coagulant, and the coagulant containing 10% by weight of $\text{LiBr} \cdot \text{H}_2\text{O}$ is best for the SF solutions in the MU solvent with the ratio of EtOH to H_2O 65 : 3 or more.

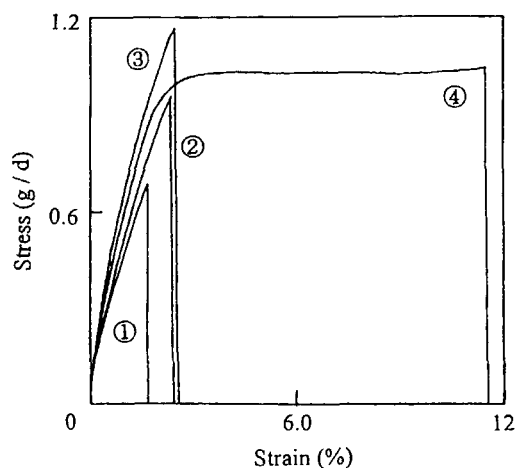


Figure 9 Stress–strain curve of fiber.

2. Coagulation length of the dope in a coagulant was measured in terms of coagulativity for the concentrated SF solutions in MU solvent. It was found that the leveled off coagulation length was smallest when using methanol, and the contour of the coagulated region was more distinct than with other alcohols.
3. The spinnable dope containing 20 wt % of silk fibroin dissolved in the MU solvent (e.g., LiBr · H₂O = 40%, and EtOH : H₂O = 100 : 0 in volume) was spun into methanol as a coagulant and subsequently drawn to give the following results. Spinnability depended on the ratio of nozzle hole length to diameter (L/D) and was improved by increasing L/D from 4 to 10. Coagulativity was not sufficient at a SF concentration of 16%, but improved by raising it up to 20%. Drawability of the spun filaments in water was improved at a temperature above 60°C. The drawn fiber showed excellent mechanical properties, especially tensile toughness, when an as-spun fiber was drawn in water at 61°C. An X-ray diffraction diagram of the drawn fibers indicated their crystalline axis was partially oriented along the fiber axis.

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