Effect of preparation method of powdered silk on the mechanical properties of moulded silk

Daijirou Akiyama and Kiyoshi Hirabayashi*
Department of Molecular Biotechnology, Faculty of Technology, Tokyo University of Agriculture and Technology, Nakamachi, Koganei-shi, Tokyo 184, Japan
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The physical properties of moulded silk were influenced by the properties of fibroin powder. Very little breakage was observed in the moulded silk made from silk fibroin treated with calcium chloride. When treated with sulfuric acid, however, the amorphous region of fibroin was damaged and highly crystalline powder was produced. Longer treatment with sulfuric acid damaged the crystalline part, decreasing the strength of the moulded silk. Treatment with sulfuric acid for 2 h was most suitable for silk moulding. The strength of moulded silk was high when the fibroin powder contained 8% water. Treatment for 30 min at 120°C under a pressure of 750 kg cm^{-2} were the optimum conditions.

(Keywords: silk; fibroin; moulding)

INTRODUCTION

Silk powder is used for silk moulding. Gelation occurs when silk is dissolved in a concentrated solution of neutral salt, dialysed, and citric acid added to the solution to the pH of the isoelectric point. Subsequent freeze-drying of the gel gives silk powder. Silk powder can also be obtained through hydrolytic degradation by treatment with hydrochloric acid or sulfuric acid following by grinding. Different powdering methods result in different molecular weights and structures of the powders obtained, and cause differences in the strength and properties of the mouldings.

The best mouldings were obtained by applying heat and pressure. Rapid evaporation of water is expected at the time of compression[1]. The water content of silk also has a remarkable effect on the physical properties of the mouldings, because it is the best binder for casein plastics[2]. Moreover, to maintain the whiteness and brilliance of silk, the moulding conditions, such as temperature and time, are important[1].

In the present study, silk was reduced to powder by two different methods and their effects on the moulding product were examined. A sheet moulding was prepared by controlling the water content of powdered silk, and the tensile and breaking strengths and thermal properties of the sheet were investigated. In addition, sheet prepared under different moulding conditions was compared in terms of the tensile and breaking strengths and yellowness. Thus conditions for silk moulding were optimized.

* To whom correspondence should be addressed

EXPERIMENTAL

Samples

Cocoons were treated with 0.5% sodium carbonate solution to remove sericin. Fibroin powder was obtained by the following methods.

(1) Fibroin was dissolved in a 50% solution of calcium chloride, and dialysed with running water for 4 days. Citric acid was then added to the solution, for the adjustment of pH and quick gelation. After freeze-drying, the gel was ground into powder.

(2) Fibroin was treated with a 7% aqueous solution of sulfuric acid. The supernatant was immediately removed and the precipitates were washed, dried and ground into powder. Powdered samples were prepared 1, 2, 3 and 5 h after hydrolytic treatment.

These powdered samples were subjected to thermal analysis, i.r. spectroscopy and electron microscopy. After moulding into sheets, their tensile and breaking strengths were determined.

Measurements

A desiccator containing a saturated solution of sodium nitrate was sealed and placed in an air-conditioned room at 20°C. The humidity inside the desiccator was 66%[3]. Silk powder samples in Petri dishes were placed in the desiccator for 48 h. For other samples the humidity was adjusted by the use of different saturated salt solutions. The water contents of these samples were calculated from thermogravimetric (t.g.) data.

Aliquots (3 g) of the silk powder samples with different water contents were weighed and placed between two

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plates (55 × 55 mm) and compressed under 750 kgf cm^{-2} at 150°C for 10 min. The sheets produced were cut into strips (5 × 20 mm) and tested for their breaking and tensile strengths using a multitension tester (model Tensilon UTM-3, Toyo Sokki, K.K.), under the following conditions: maximum loading on a load cell 20 kg; descending rate of lower chuck 5 mm min^{-1}; gauge length 5 mm; chart speed 50 mm min^{-1}. Based on the thickness measurement of each strip, the strengths per unit cross-sectional area were obtained.

A fragment of each of the three sheets with different water contents was ground and differential thermal analysis (d.t.a.) was carried out on a thermal analyser (Shimadzu DT-30) under the following conditions: heating rate 10°C min^{-1}; range 100 V; temperature range 20–500°C.

From the results of the above experiments, the water content of moulded silk was determined.

Fibroin powder adjusted to the optimal water content (8%) was weighed, placed between the two plates and compressed at 750 kgf cm^{-2} at 150°C for 10, 30, 60 and 90 min; other samples were compressed at 750 kgf cm^{-2} for 90 min at 90, 120 or 150°C. The sheets thus moulded were cut into strips (5 × 20 mm) and their breaking and tensile strengths were determined. Their yellowness was determined on a colour difference meter (TC-1500MC, Tokyo Denshoku, K.K.). They were also subjected to t.g.–d.t.a. and d.s.c. measurements and their densities were calculated.

RESULTS AND DISCUSSION

Comparison of preparation methods

Thermal analysis data for each powder are shown in *Figure 1*, i.r. data in *Figure 2* and electron micrographs in *Figure 3*. As seen from the thermal analysis data (*Figure 1*), the temperature at which sheets began to decompose was highest for those treated with sulfuric acid for 2 h, whereas moulded sheet from the calcium chloride solution method began to decompose at lower temperatures. The i.r. spectrum of the powder prepared by the calcium chloride method (*Figure 2b*) showed two peaks at 1630 and 1655 cm^{-1} from amide I, a peak at 1520 cm^{-1} from amide II, and peaks at 1240 and 700 cm^{-1} from amides III and V, respectively[4]. In spite of evidence showing a transformation to the β type, much random coil conformation remained[5]. In contrast, powdered samples prepared by treatment with sulfuric

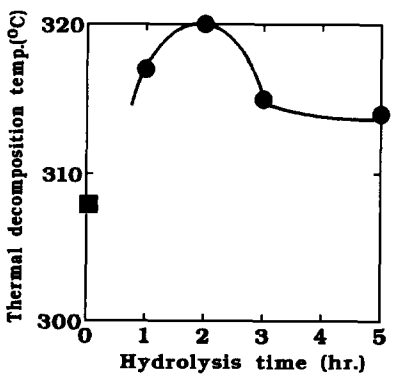

Figure 1 Thermal decomposition temperature of fibroin powders prepared by: ■, calcium chloride solution method; ●, sulfuric acid treatment

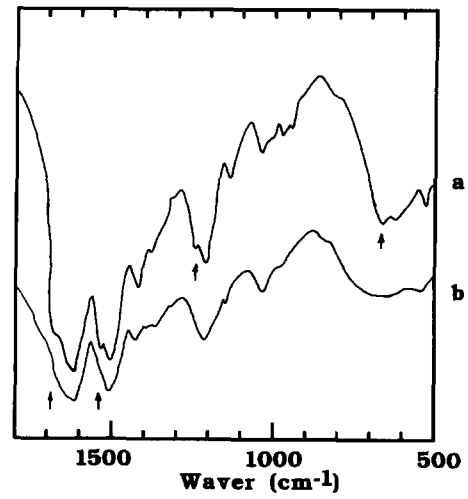

Figure 2 I.r. spectra of fibroin powders prepared by: (a) sulfuric acid treatment; (b) calcium chloride solution method

acid (*Figure 2a*) showed peaks near 1700, 1630, 1520 and 700 cm^{-1}, indicating that the β type was dominant. The electron micrographs (*Figure 3*) revealed that the powder particles were round after hydrolysis for 1 h but became smaller as hydrolysis continued for more than 2 h. *Figure 4* shows the breaking strength of the sheets. The powder obtained by sulfuric acid treatment for 2 h was found to have the highest strength. From these findings, it can be concluded that the most suitable condition for silk moulding is treatment with sulfuric acid for 2 h

Optimum water content

As shown in *Figure 5*, the water contents of fibroin powders stored at 66, 84 and 98% humidity were 8, 11 and 20%, respectively.

The sheets moulded from fibroin powder with 20% water had many cracks and air-bubbles and could not be used for the breaking and tensile strength tests. These cracks and air-bubbles may be due to the rapid evaporation of excessive amounts of water. Silk powder containing 3% water or less could not be moulded, and remained in a powdered state even after compressing. Fibroin powder with water contents of 8 or 11% could be moulded into sheets, and the breaking and tensile strengths were determined. *Figure 6* shows that sheets made of fibroin powder containing 8% water gave satisfactory results with respect to breaking and tensile strengths.

Thermal properties of moulded silk

Figure 7 shows the d.t.a. curves of three different sheets. The peaks of the d.t.a. curves in the lower temperature region were almost the same (about 105°C) for all three sheets. However, in the high temperature region the peaks ranged from 282 to 304°C with increasing water content. The peaks at the lower and higher temperature regions reflect the evaporation of water and the thermal decomposition of the sheets, respectively. This suggests that increased crosslinking may be the reason for the high thermal decomposition temperature. For sheets with water contents of 8, 11 and 20%, the decomposition temperatures from t.g. were 306, 315 and 324°C, respectively. T.g. results also showed that an increase in water content increased the thermal decomposition temperature.

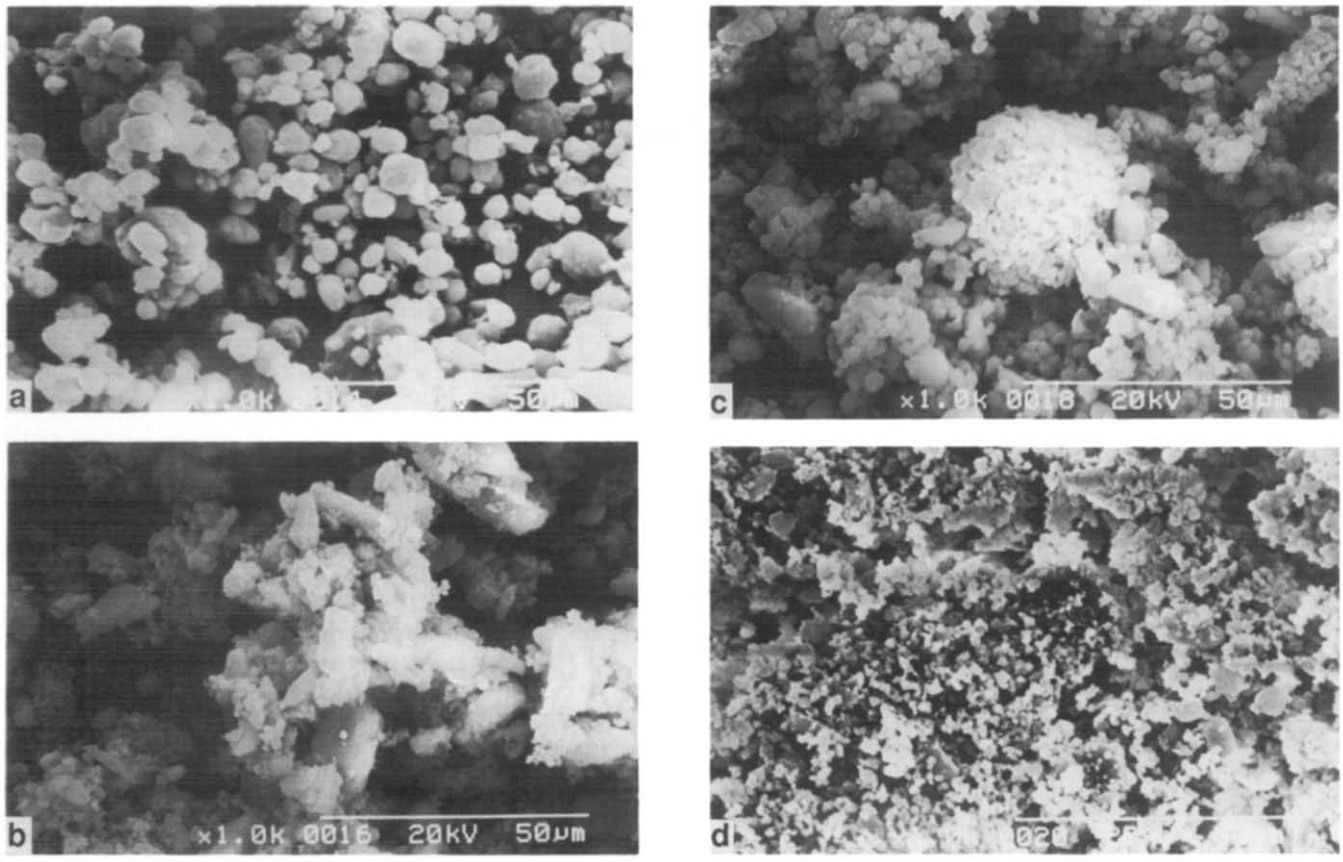

Figure 3 Electron micrographs of fibroin powder. Hydrolysis time: (a) 1 h; (b) 2 h; (c) 3 h; (d) 5 h

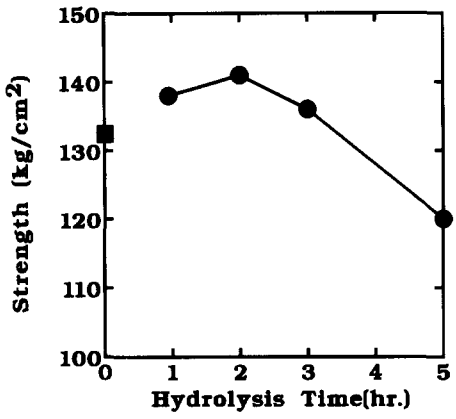

Figure 4 Mechanical properties of moulded fibroin powder prepared by: ■, calcium chloride solution method; ●, sulfuric acid treatment

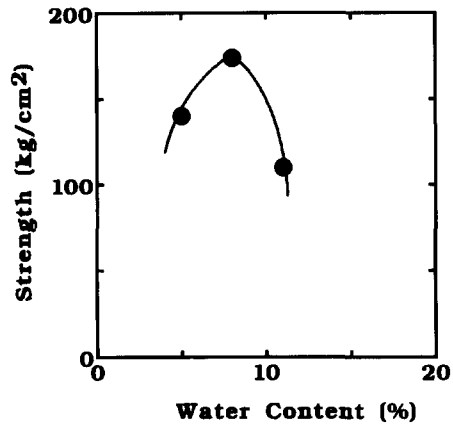

Figure 6 Mechanical properties of moulded fibroin powders in relation to water content (150°C, 700 kg cm^{-2})

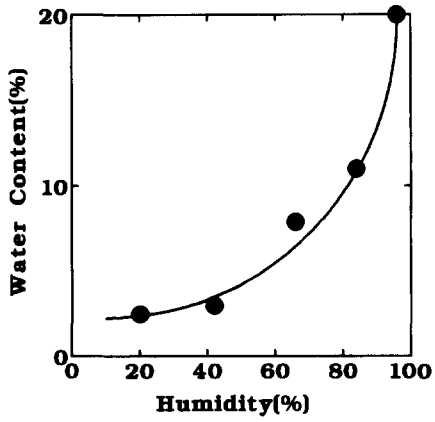

Figure 5 Water content of fibroin powders as a function of storage humidity

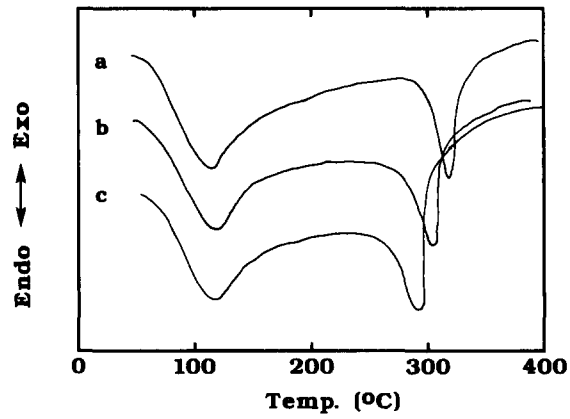

Figure 7 D.t.a. curves of moulded fibroin powder. Water content: (a) 20%; (b) 11%; (c) 8%

Table 1 Mechanical properties in relation to the processing time (150°C, 750 kg cm^{-2})

Time (min)	Strength (kg cm^{-2})	Yellowness index[a]
10	146	66.1
30	91	87.5
60	78	93.6
90	Not measured	102.4

[a] At 20°C

Table 2 Mechanical properties in relation to the processing temperature (90 min, 750 kg cm^{-2})

Temp. (°C)	Strength (kg cm^{-2})	Elongation (%)	Yellowness index[a]
150	Not measured	3.2	102.4
120	103	3.8	61.1
90	42	6.2	52.1

[a] At 20°C

Table 3 Density in relation to the processing temperature (10 min, 750 kg cm^{-2})

Temp. (°C)	Density
150	1.36
120	1.35
90	1.33

Effects of moulding time and temperature on physical properties of sheets

Table 1 shows the effect of moulding time on the breaking and tensile strengths and yellowness of sheets, and *Table 2* shows the effect of moulding temperature. The yellowness index (YI) was estimated from the following equation based on three chromaticity co-ordinate values (X, Y and Z):

$$YI = 100 \times (1.28 \times 1.06 \times Z)/Y$$

Table 1 shows that the strength decreased and YI values increased with increase in the moulding time, i.e. the longer the moulding time, the more brittle the sheets became. *Table 2* shows that the moulded silk produced at 120°C was stronger than those obtained at 90 and 150°C. This suggests that moulding of the powder requires a certain degree of heating, but excessive heating accelerates deterioration. As far as the present experiments are concerned (pressure, 750 kg cm^{-2}), the optimum processing conditions were at 120°C for 30 min. At this temperature, water molecules contained in the fibroin powder may take part in hydrogen bonding and thereby have important effects on sheet formation.

Table 3 shows the density of sheets obtained at different moulding temperatures. This indicates that the higher the breaking strength, the lower the density. In other words, the higher the density, the more brittle the sheets became. This suggests that the decrease in the amorphous region caused a decrease in strength.

CONCLUSION

The different procedures for producing fibroin powder caused changes in the powder structures and affected the physical properties of the mouldings.

Prolonged hydrolysis ruptures the crystalline regions of fibroin, and decreases the strength of moulded silk. But this silk powder contains a large amount of β structures. It can be concluded that the fibroin powder prepared by treatment with sulfuric acid for 2 h is the most suitable for moulding.

Silk sheets with the highest strength were obtained under the following conditions: water content of fibroin 8%, moulding temperature 120°C and moulding time 30 min.

A processing temperature of 150°C is most appropriate for evaporation of water, for accelerating the formation of hydrogen bonds and for increasing the strength of the sheets. A moulding time of 10 min is the lower limit for successful moulding without deterioration of the sheets. This finding was also supported by the density of the sheets.

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