Chemical Composition and Physical Properties of *Gonometa rufobrunnae* Silk

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SYNOPSIS

Chemical composition and physical properties of silk fibers from *Gonometa rufobrunnae*, a silkworm belonging to the family Lasiocampidae (order Lepidoptera, class Insecta) have been studied. *G. rufobrunnae* silk fibroin contains a large amount of glycine and alanine, as well as hydroxyl, acidic, and basic amino acids. The gly/ala ratio is 1.5, similar to that of *Bombyx mori* silk fibroin. The ratio between polar and nonpolar amino acids is higher than that of either domestic (family Bombycidae) or wild (family Saturniidae) silk fibroins. The sericin is characterized by a large amount of hydroxyl amino acids, mainly serine. The infrared spectrum of *G. rufobrunnae* silk fibroin showed characteristic absorptions at 1630, 1530, and 700 cm^{-1} attributed to the β structure and at 1650 and 1540 cm^{-1} due to the random-coil conformation. The birefringence and isotropic refractive index values were 0.027 and 1.559, respectively. The differential scanning calorimetry (DSC) curve showed two minor endothermic peaks at 222 and 288°C, together with a major endothermic peak at 344°C, attributed to the decomposition of the fibroin with β conformation. The fibers exhibited a maximum contraction peak (4.3%) at about 230°C. The dynamic storage modulus (E') exhibited an abrupt drop at 190°C, while the loss modulus (E'') curve increased above 185°C with a sharp slope. The surface of degummed *G. rufobrunnae* silk fibers was very smooth. The shape of the cross section was triangular, round, or roundish shaped. Some fibers were very flat, showing a ribbonlike shape.

INTRODUCTION

Silks are a wide group of fibrous proteins secreted by several species of insects and spiders for building structures external to the body such as cocoons and webs. Comprehensive reviews dealing with many aspects of the chemistry, reactivity, and structure of silk fibers have been published.[1-4] However, only a few silks have been extensively investigated by scientists and technologists, mainly because of their great commercial importance as textile fiber source. This especially applies to the so-called cultivated or domestic silks produced by many varieties of the silkworm *Bombyx mori* (family Bombycidae), and "wild or tussah" silks produced by several *Antheraea* species (family Saturniidae).

Since the beginning of this century the fibroin of *B. mori* has been considered an attractive model to investigate the relationship between chemical composition and physical properties of structural proteins.[1] In recent years silk fibroin has attracted a new considerable academic and practical interest. The reactivity of silk fibers has been extensively studied, and many attempts have been made to improve their properties and some minor textile performances by reaction with vinyl monomers, epoxides, and other modifying agents.[5-8] Furthermore, the increasing requirements for new materials with selected functional performances suitable for specific applications in the field of biotechnology and biomedical science have stimulated many researchers to study the properties of natural polymeric materials such as silk fibroins.[9,10] It is noteworthy to mention the production of oxygen-permeable membranes and biocompatible materials for medical applications,[11-13] as well as the use of silk fibers as substrate for enzyme immobilization.[14,15]

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Journal of Applied Polymer Science, Vol. 48, 99-106 (1993)
 CCC 0021-8995/93/010099-08

The *Gonometa rufobrunnae* silk has been recently exploited as a new source of fibers for textile purposes. The *G. rufobrunnae* silkworm belongs to the family Lasiocampidae (order Lepidoptera, class Insecta). It lives in Botswana and neighboring countries and feeds on mophane leaves. The biology of this insect, as well as some physico-chemical and technological characteristics of cocoons and degummed silk fibers have been recently reported.[16,17] In the early 1960s, Lucas et al.[18] and Warwicker[19] isolated and analyzed a great number of silk fibroins in order to find some correlations between chemical composition, crystal structure, taxonomy, and biological function. The group of silkworms belonging to the family Lasiocampidae did not include the *Gonometa* species. On the basis of X-ray diffraction patterns,[19] all the Lasiocampidae fibroins were classified as β silks with a crystal structure representative of the 3a and 3b X-ray groups, except the fibroin of *Lasiocampa quercus* (group 4). The amino acid composition was reported for only four of them.[18] Though considerable variations in amino acid composition were found, the content of amino acid residues with short side chains (glycine, alanine, and serine) was always high.

The characterization of naturally occurring fibrous polymers is one of the most important subjects of our research work.[5–8,16,20] This study was undertaken in order to investigate the chemical and physical properties of *G. rufobrunnae* silk fibers. The chemical and structural features of *G. rufobrunnae* silk will be discussed referring to either the characteristics of domestic and wild silks, or to the few available data on other Lasiocampidae silks. We recently demonstrated[16] that *G. rufobrunnae* silk can successfully compete with both domestic and wild silks as far as fineness, mechanical properties, and dyeing behavior are concerned. We believe that the results reported in this study could allow a better technological exploitation of this new silk fiber in the textile field. Furthermore, this study could contribute to extend our knowledge of the relationship between structure and functional properties of silk fibroins in view of their use not only as textile material but also as substrate for bio-related applications.

EXPERIMENTAL

Materials

Gonometa rufobrunnae cocoons and silk tops were kindly supplied by Shashe Silk Ltd. (Botswana).

Sericin was removed from cocoon fibers by degumming at 95°C for 60 min in a bath containing vegetable soap and soda ash. The aqueous protein solution was dialized against water to remove small molecular weight contaminants, salts, and degumming agents and freeze-dried and thus sericin sample was prepared. The powder sericin was kept in a desiccator before acid hydrolysis.

Measurements

Silk fibers and sericin from *G. rufobrunnae* cocoons were hydrolyzed by heating at 105°C for 24 h under vacuum in HCl 6*N*. The hydrolyzed samples were filtered through a glass disk to remove small amount of solid residue and dried. An aliquot of the hydrolyzate was used for the derivatization with phenylisothiocyanate (PITC). The phenylthiocarbamate amino acids were analyzed by reverse-phase high-performance liquid chromatography.

Infrared spectra were recorded with a Perkin Elmer FTIR-1750 spectrophotometer. The KBr disk method was adopted for sample preparation.

Refractive indices were measured with the Becke's line method using a polarized microscope under the monochromatic light (Na light) at 20°C and 65% RH. The conditions for measurement have been described in detail elsewhere.[8]

The differential scanning calorimetry (DSC) measurements were carried out under nitrogen at a heating rate of 10°C/min using a Mettler TA-3000 thermoanalytical system.

A Rigaku Denki model CN-8361 apparatus for thermomechanical analysis (TMA) was used to detect the thermal expansion and contraction properties in the course of heating process. The heating rate was 10°C/min and dry nitrogen was swept to provide the inert atmosphere.

The dynamic mechanical properties were measured using a Toyoseiki Rheolograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from 25 to 250°C and the samples were heated at a heating rate of 2°C/min.

The surface characteristics were examined with a Cambridge Stereoscan 100 scanning electron microscope after gold coating.

RESULTS AND DISCUSSION

Amino Acid Composition

Table I lists the amino acid composition of fibroin and sericin of *G. rufobrunnae* fibers. The fibrous material remaining after removal of both silk sericin

Table I Amino Acid Composition of Fibroin and Sericin from *G. rufobrunnae* Cocoon Fibers

Amino Acids (mol %)	Fibroin	Sericin
Asp	7.06	18.08
Glu	1.84	8.95
Ser	12.88	21.51
Gly	35.95	20.59
His	0.13	1.06
Arg	6.07	3.67
Thr	1.08	1.29
Ala	23.75	11.52
Pro	2.07	1.55
Tyr	5.11	2.90
Val	1.12	1.80
Met	0.12	0.16
Cys	0.06	Traces
Ile	0.74	1.41
Leu	1.04	2.13
Phe	0.53	2.28
Lys	0.49	1.13

and other minor cocoon components (mineral contaminants and cocoon waxes) accounts for 80–83% by weight.[17] The amino acid composition of fibroin is characterized by the presence of glycine and alanine in very large amount (about 60 mol %). The hydroxyl amino acids (serine, threonine, and tyrosine) comprise ca. 19 mol %. The content of acidic and basic amino acid residues accounts for about 15 mol %, while the others with polar and bulky side chains are present only in traces. The *G. rufobrunnae* fibroin shows a high proportion of a few types of amino acids. This is a general feature of the fibrous component of many silks.[18] The sum of the three simplest natural amino acids—glycine, alanine, and serine—has been shown to range from 70 to 90%, rarely falling below 60%. The typical primary structure of many silk fibroins has been demonstrated to be the chemical basis of their characteristic crystal structure.[1,2,19] Furthermore, both chemical and physical features have been closely related to the specific biological function performed by these fibrous proteins.[1,18]

Lucas et al.[18] reported the amino acid composition of four fibroins secreted by silkworms belonging to the family Lasiocampidae. It seems that the *G. rufobrunnae* fibroin resembles those produced by *Braura truncata* and *Pachypasa otus* species, especially as concerns the amount of glycine, alanine, serine, aspartic acid, and arginine.

Table II summarizes the composition of *G. rufobrunnae* silk fibroin in comparison with both the domestic (*B. mori*) and wild (*Antheraea pernyi*) fibroins. Though the total amount of glycidyl and alanyl residues is different, *G. rufobrunnae* and *B. mori* show the same value of the gly/ala ratio. As is well known, all the fibroins belonging to the family Saturniidae contain more alanine than glycine and exhibit a gly/ala ratio < 1.[4,18] An interesting feature of the *G. rufobrunnae* fibroin is the comparatively high concentration of aspartic acid and arginine, which contributes to increase the total amount of polar amino acids. It follows that this fibroin shows the highest value of the ratio between polar and nonpolar amino acids among the fibroins listed in Table II. This feature has been reported to affect the dyeing behavior, enhancing the dyebath exhaustion to a value higher than *A. pernyi* and *B. mori* silk fibroins, either using acid or reactive dyes.[16]

The sericin contains acidic and hydroxyl amino acids in very large amount, higher than 50 mol % (Table I). The concentration of serine is 21.5 mol %, a value very close to that exhibited by the same protein fraction extracted from Saturniidae silks.[4]

Table II Comparative Amino Acid Composition

Amino Acids (mol %)	*G. rufobrunnae* (Lasiocampidae)	*B. mori*[16] (Bombycidae)	*A. pernyi*[6] (Saturniidae)
Gly + Ala	59.70	74.37	72.08
Gly/Ala	1.51	1.55	0.71
Polar AA			
Acidic	8.90	2.82	6.01
Basic	6.69	0.99	3.75
Hydroxy	19.07	17.28	16.13
Total	34.66	21.09	25.89
Other AA	5.64	4.54	2.03
P/NP[a]	0.53	0.27	0.35

[a] Ratio between polar (P) and nonpolar (NP) amino acids.

Note the very low concentration of threonine. This amino acid usually accounts for about 8–9 mol % in *B. mori* and about 14–15 mol % in several species of *Antheraea* silk sericins.[4]

Infrared Spectroscopy

The IR spectrum of *G. rufobrunnae* silk fibroin measured in the range from 2000 to 400 cm^{-1} (Fig. 1) exhibited clearly resolved absorption bands characteristic of silk fibroin[21,22] at 1650 and 1630 cm^{-1} (amide I), 1540 and 1530 cm^{-1} (amide II), 1235 cm^{-1} (amide III), and 700 and 625 cm^{-1} (amide V), in addition to other minor bands at 1170, 1070, 1050, 1030, and 965 cm^{-1}.

According to the results already reported on either domestic[23,25–27] or wild silks,[24,27] the absorption bands at 1630, 1530, and 700 cm^{-1} should be attributed to the β structure of crystalline regions, while those at 1650 and 1540 cm^{-1} to the random-coil conformation of fibroin molecules. The absorption at 625 cm^{-1} seems to be related to that exhibited by *A. pernyi* silk fibroin and attributed to the α form conformation,[24] which should arise from sequential alanine polymer.

The region between 1200 and 800 cm^{-1} has been reported to characterize the spectrum of individual proteins,[21] mainly as concerns their primary structure. Therefore, the sharp absorption band at 965 cm^{-1} should be related to the presence of alanine–alanine linkages in the fibroin chains.[21,27] No evidence of either glycine–glycine linkage or glycine–alanine periodic arrangement was found, whereas the presence of glycine–alanine random linkage in the amino acid sequence of *G. rufobrunnae* fibroin could not be excluded.[21]

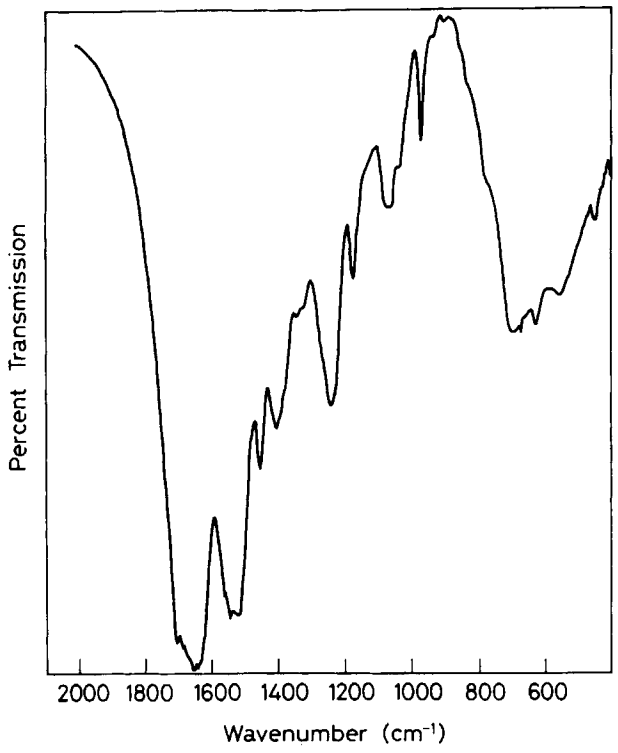

Figure 1 Infrared spectrum of *G. rufobrunnae* silk fibroin.

On the basis of these findings and taking into account the amino acid composition reported in Table I, we suggest that *G. rufobrunnae* silk fibroin should be regarded as a typical β silk as the other Lasiocampidae silks already characterized.[18,19]

Refractive Indices

In order to further elucidate the physical structure of *G. rufobrunnae* silk fibers, we measured the refractive indices and calculated the birefringence (Δn) and the isotropic refractive index (n_{ISO}), two optical parameters related to the average molecular orientation and to the degree of order and crystallinity of the polymer chains, respectively.

The Δn and n_{ISO} values obtained on *G. rufobrunnae* silk fibers were 0.027 and 1.559, respectively. While the isotropic refractive index is very close to the values reported for both domestic and wild silks,[20] the birefringence is about one-half that of *B. mori* (0.053) and is even lower than that of *A. pernyi* silk fibers (0.034).[20]

As far as the refractive indices results are concerned, the silk of *G. rufobrunnae* is more similar to *A. pernyi* than to *B. mori* silk fibers. The low birefringence value of *A. pernyi* silk fibers has been partly related to the physical structure of noncrystalline fibroin molecules, i.e., to the low content of "laterally ordered" regions, a transition phase between the crystalline and amorphous domains of the fiber.[20] From the chemical point of view, this feature has been attributed to the large amount of amino acids with bulky and polar side chains, which are preferentially distributed along the amorphous polypeptide sequences, thus hindering the formation of wide portions of "laterally ordered" regions.[19] The data listed in Table II show that also the fibroin of *G. rufobrunnae* is reached in amino acids with bulky side chains.

The similarities between *Antheraea* and *Gonometa* silk fibroins could be extended to other physical characteristics, such as the tensile properties, which reflect the fine structure of the fibers. The stress–strain curve of both *Antheraea* and *Gonometa* silk fibers showed a plateau region above the yield point,[16] attributed to the extension of the fibroin

chains in the amorphous regions.[28] *B. mori* silk fibers, on the contrary, did not show any evidence of this behavior. Further studies are in progress to deeply investigate the physical structure of either crystalline and amorphous domains of *G. rufobrunnae* silk fibers.

Thermal Properties

The DSC curve (Fig. 2) showed two minor and broad endothermic peaks at 222 and 288°C, together with a major endothermic peak at 344°C. It is reasonable to attribute the latter thermal transition to the decomposition of silk fibers with oriented β conformation.[29] This assumption is supported by the results obtained on other β silks. *B. mori*[7] and *A. pernyi*[28] silk fibroins decompose at about 315 and 365°C, respectively. The higher decomposition temperature of wild silk fibroin has been attributed to the thermal stability of the $-(ala)_n-$ sequences forming the crystalline regions.[30] The thermal behavior of *G. rufobrunnae* fibroin cannot be completely explained because we still lack basic knowledge of the fiber fine structure. However, the presence of alanine–alanine linkages estimated by IR results (Fig. 1) should be taken into account to explain the relatively high decomposition temperature, because the intramolecular hydrogen bonds of α helix have a higher thermal stability.[31]

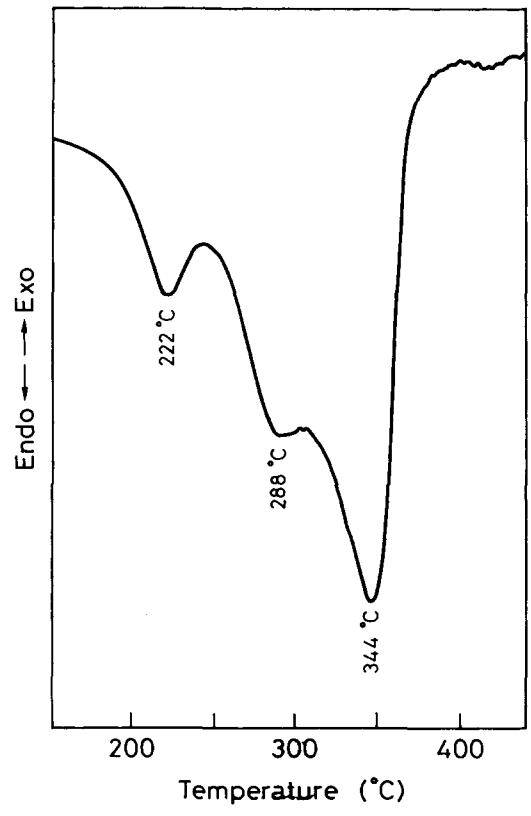

Figure 2 Differential scanning calorimetry curve of *G. rufobrunnae* silk fibroin.

The endothermic transitions from 200 to 300°C seem to be closely related to those exhibited by *A. pernyi* silk,[6] attributed to conformational changes of the amorphous regions induced in the course of the heating process. *B. mori* fibroin, on the contrary, has proved to be very stable in the same temperature range.[7]

The thermal expansion and contraction properties measured by thermomechanical analysis are shown in Figure 3. The *G. rufobrunnae* silk fibers showed a prominent two-step contraction in the range from room temperature to 250°C. The first step appeared below 100°C and was mainly due to the evaporation of water. At about 190°C the slope of the TMA curve showed a second abrupt change and attained the maximum shrinkage value (4.3%) at 230°C, which suggests a rubber elastic contraction of oriented noncrystalline molecules. Then the fiber begun to extend quite rapidly, due to the breaking of interchain bonds and to the partial thermal decomposition. The thermal movement of the fibroin chains in the less ordered regions of the fiber was mainly responsible for the high extent of contraction. As the temperature increased the fibroin molecules were induced to reorganize and strengthen their mutual interactions by breaking and reforming of interchain linkages and probably by chain folding. The occurrence of conformational transitions could not be excluded, as shown by the behavior of the DSC curve at above 200°C (Fig. 2).

Dynamic Mechanical Behavior

In order to further investigate the thermal behavior of *G. rufobrunnae* silk fibers, we studied the temperature dependence of the dynamic mechanical properties (Fig. 4).

Both the dynamic storage (E') and loss (E'') modulus curves showed a positive inflection starting from room temperature and reached a plateau at about 100°C. The fiber shrinkage registered in this temperature range was probably due to the molecular motion of the fibroin chains in the amorphous regions following the evaporation of absorbed water. Then, as the temperature increased, the storage modulus slightly decreased until 190°C, when the E' value showed a very sharp drop. The loss modulus curve likewise started to change at about 185°C, increasing with a very sharp slope.

The results of the dynamic mechanical behavior of *G. rufobrunnae* silk fibers are consistent with those

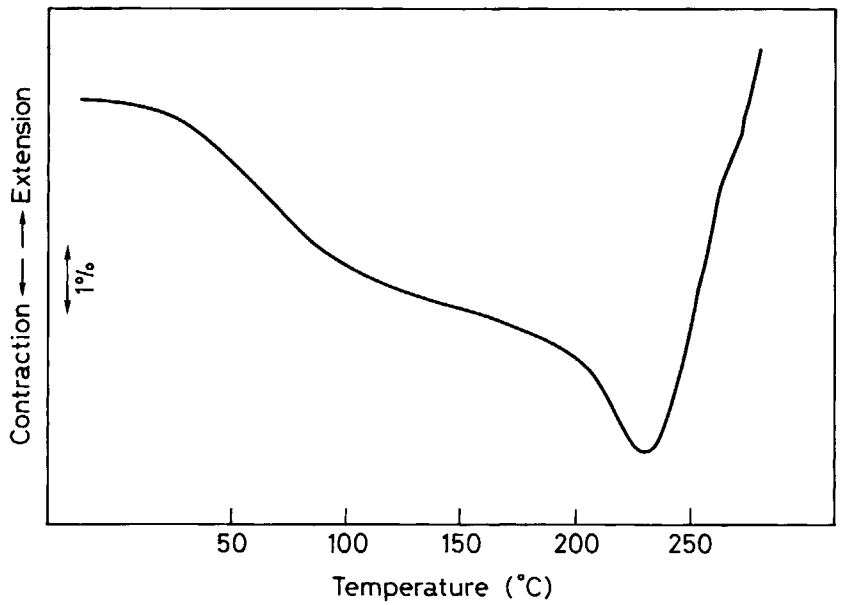

Figure 3 Thermomechanical analysis curve of *G. rufobrunnae* silk fibers.

of domestic and wild silk fibroins.[20,23,25,28] This suggests that the same basic model of fine structure should apply to all these fibers in order to explain their thermal behavior. When subjected to thermal treatment, the mobility of the fibroin chains in the amorphous regions increases quite slowly, and the chains are held together as a firmly crosslinked network by hydrogen bonds.

It has been reported that the glass transition temperature of *B. mori* fibroin is 175°C[32] while that of different wild silk fibroins ranges from 170 to 200°C.[24,33] These data draw our attention on the high thermal stability of silk fibers and the results obtained on the fibroin of *G. rufobrunnae* seem to confirm this feature. Above the glass transition temperature, at about 200°C upward, the fibers become softer and softer and behave as a rubberlike material. The thermal movement of the fibroin molecules is very strong, and the chains are supposed to be in a state of dynamic equilibrium, with hydrogen bonds continuously breaking and reforming. Conformational transitions have been reported to occur in the

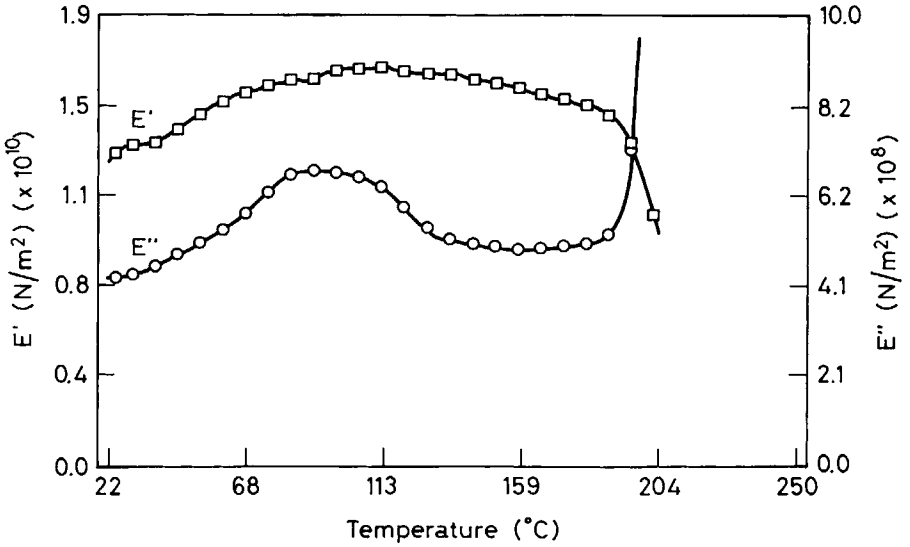

Figure 4 Dynamic mechanical storage (E') and loss (E'') modulus of *G. rufobrunnae* silk fibers.

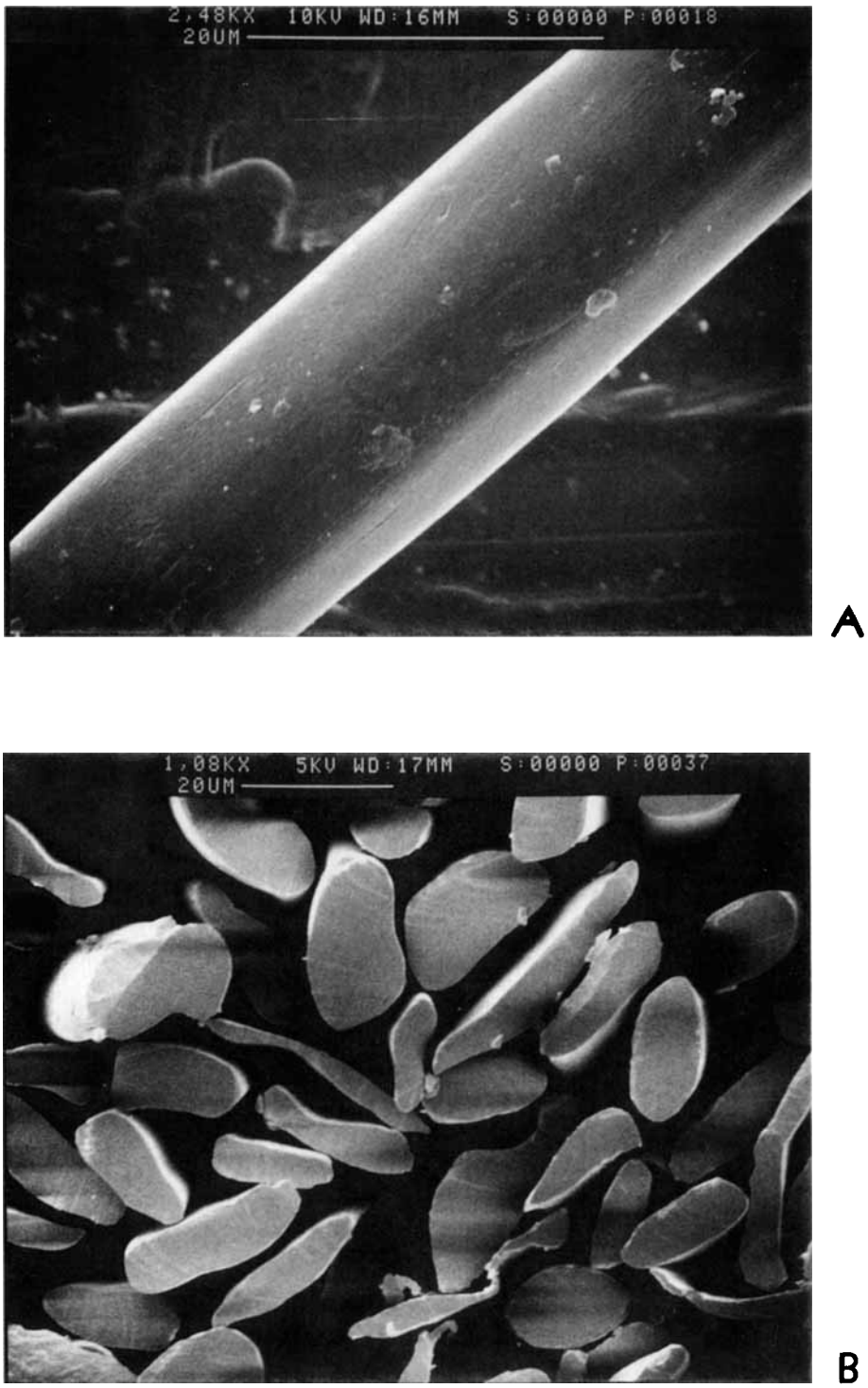

Figure 5 Scanning electron micrographs of *G. rufobrunnae* silk fibers after degumming. (A) Longitudinal view, (B) cross-sectional view.

amorphous and laterally ordered regions.[24,32] Furthermore, relaxation phenomena in the crystalline regions, i.e., slip motion in the β-form crystals, have been demonstrated to characterize the thermal behavior of silk fibers at above 190–200°C.[31,34]

Surface Characteristics

The surface characteristics of *G. rufobrunnae* fibers were investigated by scanning electron microscopy. Figure 5(A) shows a longitudinal view of a de-

gummed fiber. The surface appears very smooth. Only very thin longitudinal streakings are visible. This characteristic is mainly responsible of the lustrous appearance of the combed staple and yarn obtained in industrial tests from the cocoons of *G. rufobrunnae* and is highly appreciated for textile applications.

The fiber cross sections are variously shaped [Fig. 5(B)]. Most of them are triangular, round, or roundish shaped. Some of the fibers are very flat and appear like a ribbon. It has been reported that the mean diameter of the fibers is 17.8 μm, corresponding to a fineness of 2.6 dtex.[16] This value is about twice that of *B. mori,* but only half of that measured on *A. pernyi* silk fibers.[16] It is noteworthy that the fiber fineness is an important technological characteristic. From this point of view the *G. rufobrunnae* silk promises to become a very interesting source of textile fibers for the production of precious and valuable articles.

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Received February 13, 1992
Accepted June 1, 1992