Studies on Composite Fibers Produced from Fibroin of Wild Silkmoths and Cellulose

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(Received February 20, 2002; Accepted July 2, 2002)

Silk fibroin and cellulose were dissolved in cuprammonium solution using degummed silk of various wild silkmoths and spun into thread. Produced composite fibers exhibited lustrous color, typical of each component silk fibroin, and showed the mechanical properties necessary to withstand the practical use of it as clothing and as a functional polymeric material as well. There is a possibility to make the composite fibers more durable against stretching by improving the spinning procedure. The cocoons of S. c. ricini, C. trifrenestrata and of Rhodinia fugax are unable to be spun to obtain a long thread. This kind of disadvantage can be overcome by producing the composite fiber.

Key words: Silk fibroin, wild silkmoth, cellulose, spinning, composite fiber, mechanical property

INTRODUCTION

In the preceding paper we reported that silk fibroin could be the partner of a composite fiber with cellulose (Kanekatsu et al., 2000). The silk fibroin used was of Bombyx mori and the produced fibers had enough strength equal to those of commercial chemical fibers of a cellulose origin. At present, we have been able to produce fibroin-cellulose composite fibers using degummed silk of various wild silkmoths according to the manufacturing process applied in the preceding study. This paper is to report this new application.

MATERIALS AND METHODS

Production of fibroin-cellulose composite fibers

The fibroins used for the experiments were those of Antheraea yamamai, Antheraea pernyi, Samia cynthia ricini, Cricula trifrenestrata, and Rhodinia fugax. Cocoons of A. yamamai, A. pernyi and R. fugax were collected by us. Cocoons of S. c. ricini were donated by Dr. O. Shimizu of Gunma Sericultural Experiment Station. Degummed floss of C. trifrenestrata was a kind gift by Ms. M. Hayashi of Nagahama Industrial Co. Ltd.

Cocoon shells of these wild silkmoths were boiled in a 100-fold 0.5% Marseilles soap solution containing 0.08% sodium carbonate for 1 h twice, each time with a newly prepared degumming solution, and rinsed thoroughly with tap water afterward. The degumming losses of A. yamamai and A. pernyi silks were 28.7% and 14.4%, respectively. The degumming loss of S. c. ricini silk was not put on record. On a side note, the inner layer of the cocoon shell of the R. fugax cocoon was degummed three times since it was rather difficult to degum. The degumming loss was 9.8% in both the outer and inner layers. The fibroins from the outer and inner shell layers were tested separately.

In order to prepare spinning solutions, copper (II) hydroxide was added to an equal amount of degummed silk and commercial cotton wool first, and aqueous ammonia was added in a ratio of 24 ml to 1 g of cotton wool (and 1 g fibroin) afterwards, then they were stored overnight at 4 °C according to the procedure prescribed in the preceding paper (Kanekatsu et al., 2000). The minimum amount of copper (II) hydroxide needed to dissolve the polymeric materials was 0.58 g for 1 g of fibroin regardless of its origin and 0.84 g for 1 g of cotton wool. The aqueous ammonia used was prepared by diluting a commercial reagent to one-third of its original concentration (29%). The polymer concentration of the spinning solution obtained was about 7.7%.

The spinning solution was squeezed out through a mouthpiece of Teflon tubing with an inner diameter of 1 mm into distilled water using a peristaltic pump (Furue Science, Model RP-MV5) to solidify the solute polymers. The solidified polymeric compound was then pulled off in a bath containing 5% sulfuric acid at the spinning rate of 170 cm/min using a revolving cylinder to regenerate a composite fiber.

Properties of composite fibers

The amount of nitrogen in the composite fibers obtained was measured with a Yanaco CHN-corder (Model MT-3) to estimate the fibroin content in the composite fibers. Load-extension curves were measured at the stretch-
ing rate of 0.088 cm/sec with 10-cm specimens using the tensile tester devised by one of the authors (E. I.); the tensile strength, elongation and Young's modulus were derived from the obtained curves. Measurements were carried out under the atmospheric condition of 22°C and 65% RH. Using a Rigaku Denki geigerflex model 2028 (Cu-Kα line, 40 kV-20mA), X-ray diffraction patterns were photographed to check the degree of orientation, and the intensity of X-ray diffraction was recorded (2θ = 5-50°) to measure the degree of crystallinity according to the routine simplified procedure. In doing so, the area under an intensity distribution curve was divided into two parts, one for a crystalline region and the other for an amorphous region. The shape of the intensity curve for the amorphous region was obtained using a completely amorphous specimen and the degree of crystallinity was obtained as the ratio of areas. Composite fibers were tied up into 1 mm diameter bundles as specimens.

RESULTS AND DISCUSSION

Feature of fibroin-cellulose composite fibers

The nitrogen content of the obtained composite fibers and estimated fibroin content in the composite fibers are shown in Table 1. In doing so, the nitrogen content of pure fibroins is assumed to be 18% according to their amino acid compositions (Fukuda, 1987; Yamada and Tsubouchi, 2001). The estimated fibroin content of the composite fibers ranged from 19 to 34% depending on the species. Although the intended fibroin content of 50% was not attained, there seems to be a possibility to raise the fibroin content by increasing the ratio of it in a spinning solution.

Fig. 1 shows photographs of the composite fibers of various wild silks. The *A. yamamai* fibroin integrated fiber is a pale yellowish green color, the *A. pernyi* fibroin integrated fiber is lustrous brown, the *S. c. ricini* fibroin integrated fiber is gentle white, and the *C. trifenestrata* fibroin integrated fiber is pale yellow. As for the *Rhodinia fugax* fibroin integrated fiber, it is a pale green color when the fibroin from the outer layer of a cocoon shell was used, and it is dark green when the fibroin from the inner layer of a cocoon shell was used. All these results show that the color and luster of degummed silk are well reflected in the composite fibers. Recently, it has been reported that *C. trifenestrata* silk yellow pigment is contained not only in the sericin layer but also in the fibroin core even in larger amount (Yamada et al., 2001). This report suggests that pigment can be contained in degummed non mulberry silk fibroin, which supports our result shown above.

Physical properties of fibroin-cellulose composite fibers

X-ray diffraction photographs of a few composite fibers are shown in Fig. 2. These fibers show much of the same diffraction pattern indicating a molecular orientation along the fiber axis; however, the degree of orientation is rather low. The other composite fibers show a similar behavior. It seems that there is still room to raise the molecular orientation to improve the fibrous structure, considering their high degree of crystallinity as will be described later.

Fig. 3 shows load-extension curves of two kinds of composite fibers together with their corresponding component fibers. As is usual with the degummed silk of *Saturniid* silkmoths, load-extension curves of degummed silks of *A. pernyi* and of *S. c. ricini* show a reduced increase in the

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**Table 1. Fibroin content in fibroin-cellulose composite fibers**

<table>
<thead>
<tr>
<th>Blended fibroin (Species)</th>
<th>Nitrogen content (%)</th>
<th>Fibroin fixed in composite fiber (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Antheraea yamamai</em></td>
<td>4.06</td>
<td>31</td>
</tr>
<tr>
<td><em>Antheraea pernyi</em></td>
<td>3.41</td>
<td>28</td>
</tr>
<tr>
<td><em>Samia cynthia ricini</em></td>
<td>2.12</td>
<td>19</td>
</tr>
<tr>
<td><em>Cricula trifinestrata</em></td>
<td>3.94</td>
<td>31</td>
</tr>
<tr>
<td><em>Rhodinia fugax</em> (outer layer)</td>
<td>4.64</td>
<td>34</td>
</tr>
<tr>
<td><em>Rhodinia fugax</em> (inner layer)</td>
<td>4.69</td>
<td>34</td>
</tr>
</tbody>
</table>

1 Amount of nitrogen (w/w) found in the composite fiber samples using CHN-corder.
2 Amount of fibroin fixed in the composite fibers (w/w) calculated from the nitrogen contents shown on the 1st column.

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**Fig. 1.** Photographs of fibroin-cellulose composite fibers of wild silks. a, *A. yamamai*; b, *A. pernyi*; c, *S. c. ricini*; d, *C. trifinestrata*; e, *Rhodinia fugax* (outer layer); f, *Rhodinia fugax* (inner layer).
load (an elbow-shaped bend) for a while after reaching the limit of elasticity; whereas, the load increases lethargically throughout without a remarkable drop in cellulose fiber. The load-extension curves of the composite fibers have an elbow-shaped bend similar to those of degummed Saturniid silks, although composite fibers snap before recovering from the steep increase in load. The load of the composite fibers is situated between those of cotton and the corresponding degummed silks at the same rate of extension. These results indicate that the mechanical properties of each component fiber are reflected in the composite fiber although its breaking extension (elongation) has a close resemblance to cellulose fiber. This was the case in all the other composite fibers tested. Table 2 summarizes the mechanical properties of the composite fibers. The data in the table are averages of at least 10 measurements.

The thread size ranges from 9 to 16 denier, whereas the tenacity ranges from 1.1 to 1.4 g/d. The elongation ranges from 4.4 to 9.1% and the Young's modulus, from 6.5 to 10.2 GPa. In all the composite fibers, the tenacity shows a value comparable to that of a commercial acetate, although it is lower than those of the component fibers as may be seen in Table 3. The elongation is far lower than any of the corresponding component silk fibers, and it is close to that of cotton (6.4%) except for S. c. ricini fibroin-cellulose and Rhodinia fugax fibroin-cellulose composite fibers, which shows a value somewhat larger than those of the other blended fibers (7.1-9.1%).

One of the S. c. ricini fibroin-cellulose composite fibers showed an elongation of 20%, accidentally, and gave a larger standard deviation in Table 2, suggesting that there was a possibility to make the composite fibers more durable against stretching by improving the spinning procedure. The produced composite fibers may have a defect, such as the non-uniformity in thread size and scratches on the surface of the fiber where the stress is concentrated making the fibers easy to snap. As for Young's modulus of the composite fibers, it ranges from 6.5 to 10.2 Gpa, which is roughly half the magnitude for cotton (16.0 GPa). However, it is sufficiently higher than 2.24 GPa of B. mori fibroin-cellulose composite fiber (Kanekatsu et al., 2000). These results show that the obtained composite fibers are able to withstand practical use for clothing and functional materials as far as the mechanical point of view is concerned.

The degree of crystallinity showed values of around 40% except for that of C. trifenestrata fibroin integrated

Table 2. Mechanical properties of fibroin-cellulose composite fibers

<table>
<thead>
<tr>
<th>Blended fibroin</th>
<th>Size (d)</th>
<th>Tenacity (g/d)</th>
<th>Elongation ± s.d. (%)</th>
<th>Young's modulus (Gpa)</th>
<th>Degree of crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. yamamai</td>
<td>10.6</td>
<td>1.17</td>
<td>4.9±0.2</td>
<td>8.7</td>
<td>38</td>
</tr>
<tr>
<td>A. perny</td>
<td>9.0</td>
<td>1.38</td>
<td>4.4±0.15</td>
<td>10.2</td>
<td>40</td>
</tr>
<tr>
<td>S. c. ricini</td>
<td>16.1</td>
<td>1.33</td>
<td>8.8±0.5</td>
<td>8.4</td>
<td>37</td>
</tr>
<tr>
<td>C. trifenestrata</td>
<td>10.9</td>
<td>1.07</td>
<td>5.7±0.7</td>
<td>6.5</td>
<td>48</td>
</tr>
<tr>
<td>Rhodinia fugax (outer)</td>
<td>11.4</td>
<td>1.17</td>
<td>7.1±0.8</td>
<td>8.0</td>
<td>43</td>
</tr>
<tr>
<td>Rhodinia fugax (inner)</td>
<td>12.5</td>
<td>1.35</td>
<td>9.1±0.9</td>
<td>8.5</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 2. X-ray diffraction photographs of a few fibroin-cellulose composite fibers. a, A. pernyi; b, S. c. ricini; c, C. trifenestrata.

Fig. 3. Load-extension curves of a couple of fibroin-cellulose composite fibers accompanied by the corresponding component fibers. a, cotton; b, degummed silk of A. pernyi; c, degummed silk of S. c. ricini; d, A. pernyi-cellulose composite fiber; e, S. c. ricini-cellulose composite fiber.
composite fiber (48%). These values are close to those of Antheraea silks which show high molecular orientation (Iizuka, 1994). Moreover, the degree of orientation is low in the composite fibers as aforesaid; it is lower compared with that for B. mori fibroin integrated composite fibers (Kanekatsu et al., 2000). A convincing explanation for these conflicts is yet to be heard for the present studies. One of the explanations may be the following: microcrystals generated in the spinning procedures are not well arranged in one direction because of the low spinning rate.

We know that the cocoons of A. pernyi are easily spun into filaments and that they are widely utilized, however those of A. yamamai have a little difficulties in the spinning procedure. Moreover, most of the wild silk is used only as staple fibers because of the difficulties in spinning out of cocoon filaments. Applying the method of composite fiber shown in this report could provide some ways for these wild cocoons to be utilized as filament fibers. Especially, as the Samia larvae are easily maintained and their cocoons are constantly produced, we believe that the Samia cocoon fibroin would be one of the best partners to produce composite fibers. In fact, the composite fiber with Samia fibroin showed a favorable mechanical characteristics in this report.

ACKNOWLEDGMENTS

We wish to thank Dr. O. Shimizu and Ms. M. Hayashi for the donation of the cocoons used in this study. Thanks are also due to Dr. Y. Gotoh of our Faculty for the use of a Rigaku X-ray diffractometer.

REFERENCES