Surface morphology of low-temperature argon-plasma-treated *Bombyx mori* silk fibroin fiber

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The effects of argon-plasma treatment on the morphological and topographical surface structures of a *Bombyx mori* silk fibroin (SF) fiber were studied by using atomic force microscopy (AFM) and lateral modulation friction force microscopy (LM-FFM). Surface changes were analyzed in image and in quantity for different plasma treatment times. The AFM and LM-FFM analyses showed that the roughness of the fiber surface increased after plasma treatment because of plasma bombardment and etching. A longer treatment time, resulting in a rougher surface, progressively changed the fiber surface, thereby leading to the formation of a new surface. These results revealed that low-temperature argon-plasma treatment is an effective method to improve the performance of SF fibers.

**Keywords:** silk fiber, argon-plasma treatment, surface modifications, atomic force microscopy (AFM), lateral modulation friction force microscopy (LM-FFM).

**INTRODUCTION**

Silk fibroin (SF), the protein-based biopolymer spun by the *Bombyx mori* (*B. mori*) silkworm, has been used as clothing materials for thousands of years because of their unique gloss, handling, and mechanical properties. Many studies have been reported on the bulk structural characteristics of SF, such as bulk chemical ingredients, amino acid composition, molecular weight, crystallinity, orientation, and molecular conformations (Marsh, *et al*., 1955; Robson, *et al*., 1998; Sasaki, *et al*., 1973). However, few studies have been conducted on the surface structures of SF or the differences between the SF surface and the bulk structures (Shao, *et al*., 2002).

Many important properties of fibers/polymeric materials, such as luster, handling, adhesion, friction, hydrophilicity, wettability, and dyeability, are known to be largely influenced by their physical and chemical surface characteristics. In the case of synthetic polymers, these properties can be suitably modified and tailored during
synthesis. However, in the case of natural polymers, the surface properties can be altered only by changing their surface chemical structure or morphology (Behnisch, et al., 1997).

Plasma technology has been widely used as an effective method for the surface modification of textile fibers such as wool, linen, flax, sisal, keratin, bamboo, and other polymeric materials (Dai, et al., 2001; Wong, et al., 2000, 2001; Martin, et al., 2002; Molina, et al., 2003; Poletti, et al., 2003). Some studies with regard to the plasma treatment of SF have also been carried out (Iriyama, et al., 2003; Zhang, et al., 1997; Selli, et al., 2001). However, extensive investigations have been very few, and until recently, little attention has been paid to the characterization of the low-temperature argon-plasma treatment of SF.

Low-temperature plasma (LTP) treatment is commonly employed as an effective tool for the surface morphology modification of textile fibers in order to enhance certain properties (Wang et al., 2005). Exposure to suitable plasma is able to alter the uppermost atomic layers of the material surface while leaving the desirable bulk properties unaffected (Jahagirdr, et al., 2004). The LTP reaction primarily depends on machine power supply, gas type, gas pressure, and treatment time.

Atomic force microscopy (AFM) and lateral modulation friction force microscopy (LM-FFM) were developed as instruments mainly used for surface science research. AFM is frequently applied to polymer surfaces, primarily to reveal the surface morphology, nanostructure, chain packing, and chemical conformation. It also provides information on nanometer-scale features, which cannot be obtained by other microscopic techniques (Gould, et al., 1999). FFM is widely used to study various surfaces in order to investigate friction, lubrication, and wear of materials (Scherer, et al., 1999).

In this study, low-temperature argon plasma was employed to treat the natural biopolymer B. mori SF fibers. AFM and LM-FFM were utilized to study the morphology of the plasma-modified SF fibers in detail.

**EXPERIMENTAL**

**Materials**

The dominant B. mori SF was used in the experiment. In order to remove sericin from the raw silk, the degumming process was carried out by the standard Marseille soap/soda ash method (Kato, et al., 1968). This process removed almost all the sericin. The degummed SF fiber was soft and smooth with a fine sheen.

**Plasma treatment**

Fig. 1 shows the schematic diagram of the plasma treatment apparatus. The plasma treatment reactor consists of parallel round electrodes with a 13.56 MHz radio frequency (RF) generator. The diameter of the powered electrode on which the sample is placed is 18 cm, and the distance between the two electrodes is 5 cm. The samples were placed between the slide glasses, as shown in Fig. 2. In this experiment, the chamber was evacuated below 0.02 Torr, and a carrier argon gas flow was introduced in order to
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- maintain the chamber pressure of 0.1 Torr at a steady state. The plasma output power was 60 W. The durations of plasma treatment of the SF samples were 5, 10, and 15 min.

**AFM and LM-FFM analysis**

An SPI3800N system (Seiko Instruments Inc.) with a SPA-400 multi-function type scanning probe microscopy was used for the measurements. The measurements were performed using AFM and LM-FFM contact modes. The dimensions of the scanned areas were 2 µm × 2 µm (AFM) and 1 µm × 1 µm (LM-FFM). The scanning line frequencies were 0.5 Hz (scanned area: 2 µm × 2 µm) and 1 Hz (scanned area: 1 µm × 1 µm). All the scanned images were obtained using a 20 µm scanner.

For contact-mode images, we used an SN-AF01 cantilever and a tip (Si3N4, Fig. 1. Schematic diagram of RF plasma apparatus. Fig. 2. Schematic diagram of sample arrangement
triangular base, 100 µm long) with a radius of 20 µm. Its natural resonance frequency was 40 kHz and spring constant was 0.09 N/m.

RESULTS AND DISCUSSION

The AFM images of the SF surfaces are illustrated in Fig. 3. It is observed that the surface topography of the SF fibers changes qualitatively after the argon-plasma treatment. The surface of untreated SF was smooth. After the argon plasma treatment of SF for 5 min, many concavo-convex states were observed. Simultaneously, pits approximately 200 nm in width and 150 nm in depth appeared on the SF surface. Plasma treatment for more than 10 min made the SF surface notably uneven, and the depth and number of pits increased; moreover, many irregular condensation clusters appeared on the SF surface. In particular, when the plasma treatment time was 15 min, large hollows appeared on the surface. It is well known that high-energy electrons, radicals, and excited molecules and atoms are emitted during plasma discharge. Concurrently, ultraviolet rays, visible rays, etc, are emitted from the excited molecules and atoms. Further, the plasma electric discharge would cause physical and chemical changes on the surface of polymers because of the presence of various activity groups (Schonhorn, et al.,

![3D AFM topographic images of SF fiber for different times of exposure to low-temperature argon plasma: (a) untreated, (b) 5 min, (c) 10 min, and (d) 15 min.](image-url)
Table 1 Surface roughness of SF fiber as a function of different argon-plasma treatment time determined from AFM analysis.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Average roughness (nm)</th>
<th>Maximum vertical excursion (nm)</th>
<th>RMS roughness (nm)</th>
<th>Surface volume (nm³)</th>
<th>Ratio of surface volume (×100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>10.41 ± 1.09</td>
<td>80.59 ± 2.90</td>
<td>15.13 ± 2.32</td>
<td>(4.081 ± 0.027) E+06</td>
<td>1.0210 ± 0.0071</td>
</tr>
<tr>
<td>5 min</td>
<td>20.45 ± 2.49</td>
<td>151.3 ± 3.10</td>
<td>25.73 ± 1.69</td>
<td>(4.240 ± 0.112) E+06</td>
<td>1.0606 ± 0.0278</td>
</tr>
<tr>
<td>10 min</td>
<td>20.43 ± 2.24</td>
<td>170.7 ± 8.10</td>
<td>25.93 ± 1.88</td>
<td>(5.053 ± 0.069) E+06</td>
<td>1.1896 ± 0.1224</td>
</tr>
<tr>
<td>15 min</td>
<td>27.17 ± 1.77</td>
<td>279.9 ± 17.6</td>
<td>39.82 ± 5.99</td>
<td>(4.574 ± 0.132) E+06</td>
<td>1.1441 ± 0.0331</td>
</tr>
</tbody>
</table>

SF fibers are natural polyamide fibers (chain polymers condensed from α-amino acids) spun by silkworms (Minagawa, et al., 1981). In the beginning of plasma treatment, the activity groups (electrons, excited molecules and atoms, radicals, ions, etc.) attacked protein macromolecule chains, and the weak structures of the fiber surfaces were etched. Meanwhile, macromolecule radicals were generated on the surface. With an increase in the plasma treatment time, the macromolecule radicals became unstable, the molecular backbones were segmented, and irregular condensation clusters [Fig. 3(c)] were formed due to the accumulation of molecules via multiplex combination. When the plasma treatment time increased (treatment time = 15 min), it was observed that the irregular condensation clusters were destroyed, and the weak structures on the surface were exfoliated.

Table 1 shows the values of the surface roughness of SF for different plasma treatment times obtained by AFM analysis. The data were obtained from the measurements of the 2 µm × 2 µm AFM images. The average roughness \( R_a \) is defined as the average of the absolute values of the difference between the standard level and the selected level. It is defined as JIS BO601 and expressed by the following formula.

\[
R_a = \left\{ \frac{1}{S_0} \right\} \int_{x_0}^{x} \int_{y_0}^{y} \left| F(x,y) - Z_0 \right| dX dY
\]  

where \( F(x,y) \) is the field which all measurement data shows; \( S_0 \) is the area when the selected level is assumed to be ideally flat; \( Z_0 \) is the average of the values of \( Z \) within the selected level. The root mean square roughness \( R_{rms} \) is the square root of the average of the square of the deviation from the standard level to the selected level.

It is clear that at the initial stages of plasma treatment, \( R_a \) and \( R_{rms} \) increase rapidly. The increase is gradual thereafter (from 5 to 10 min) and rapid from 10 to 15 min. It is considered that with an increase in the plasma treatment time, the generation of concavo-convex states, pits, clusters, and hollows on the surface is useful to increase the surface roughness; however, the minute concavo-convex states or tiny particles are destroyed after the formation of clusters by the accumulation of molecules via multiplex combination. Moreover, the weak particle structures on the surface begin to be exfoliated. The progressive formation of concavo-convex states, particle structures,
pits, clusters, and surface damage of the plasma-treated SF fibers imply that the surface area increases significantly. The effect of the increase in the surface area is estimated from the 2 µm × 2 µm AFM images using the "surface volume" measurement. Table 1 shows that the surface volume gradually increases at the initial stage of plasma treatment, rapidly increases from 5 to 10 min, and decreases for a longer time from 10 to 15 min. The decrease in the surface volume implies that the exfoliation and destruction on the surface increase for the longer exposure time. Further, the ratio of the surface volume follows the same trend.

To elucidate the surface properties of argon-plasma-treated SF in detail, LM-FFM observation was carried out. The images are shown in Fig. 4. The distribution image of the frictional force of the untreated SFs resembled a series of slightly flat and regular striations on the surface. The plain and regular states indicate a uniform microstructure, the fibril morphology of the original SF fiber [Fig. 4(a)]. After plasma treatment for 5 min, many concavo-convex states and bulges were observed on the SF surfaces [Fig. 4(b)], and many craters formed on

![Image of 3D LM-FFM topographic images of SF fiber for different times of exposure to low-temperature argon plasma: (a) untreated, (b) 5 min, (c) 10 min, and (d) 15 min.](image-url)

Fig. 4. 3D LM-FFM topographic images of SF fiber for different times of exposure to low-temperature argon plasma: (a) untreated, (b) 5 min, (c) 10 min, and (d) 15 min.
Table 2 Surface roughness values of SF fiber surface as a function of different argon-plasma treatment time determined from LM-FFM analysis.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Average roughness (nm)</th>
<th>Maximum vertical excursion (v)</th>
<th>RMS roughness (nm)</th>
<th>N-points average roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>21.55 ± 2.14</td>
<td>1.049 ± 0.459</td>
<td>27.52 ± 3.82</td>
<td>329.8 ± 83.6</td>
</tr>
<tr>
<td>5 min</td>
<td>95.10 ± 18.95</td>
<td>1.672 ± 0.435</td>
<td>124.7 ± 31.1</td>
<td>412.5 ± 73.9</td>
</tr>
<tr>
<td>10 min</td>
<td>136.3 ± 43.3</td>
<td>2.008 ± 0.165</td>
<td>150.4 ± 72.3</td>
<td>676.6 ± 85.0</td>
</tr>
<tr>
<td>15 min</td>
<td>198.1 ± 11.4</td>
<td>2.496 ± 0.377</td>
<td>259.2 ± 17.2</td>
<td>530.6 ± 64.1</td>
</tr>
</tbody>
</table>

the SF surface after 10 min [Fig. 4(c)]. When the plasma treatment time increased to 15 min, few hollows appeared on the fiber surface, and fibril structures of 50–80 nm were exposed on the surface because of etching and exfoliation [Fig. 4(d)].

The surface roughness was also calculated from the LM-FFM images of untreated and plasma-treated SF. The estimated mean values are summarized in Table 2. It is observed that the roughness of the region in which the frictional force is high is large. The trends of the average roughness and RMS roughness are the same as those of these values in the AFM analysis.

These findings indicate that the remarkable effects of argon plasma treatment on the SF fiber surface observed by AFM and LM-FFM are due to plasma bombardment on the surface and the splitting of the macromolecule chains, which rearrange themselves and form a new surface morphology. Simultaneously, while the silk surface is polarized, concavo-convex roughness surface is attached, and the surface area increases. This result will cause an increase of the adhesive property, wettability, etc., on the silk fiber surface.

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