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Study on *Bombyx mori* silk treated by oxygen plasma*

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Abstract: Study of the morphology, aggregation structure and properties of *Bombyx mori* silk treated by low temperature oxygen plasma showed that slight flutes appeared on the surface of *Bombyx mori* silk fiber and that its surface structure changed after plasma treatment. The conformation also changed and crystalline degree decreased. The stannic filling rate of treated fiber was improved. Because of etching, the weight of the fiber decreased but the breaking strength changed little after short-time treatment.

Key words: Oxygen plasma, *Bombyx mori* silk, Morphology, Structure, Properties
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INTRODUCTION

B. mori silk produced by cultivated silkworm is a textile fiber highly appreciated for its outstanding properties (handle, luster, comfort). In recent years there has been an increasing interest in exploiting low-temperature plasma treatment (LTP) of textile fibers.

Low-temperature plasma treatment is an environmental friendly technique for modifying the fibers surface to improve surface wettability (Molina *et al*., 2003), shrink resistance (Jin and Dai, 2002), interfacial adhesion (Moon and Jang, 1998), hydrophilicity (Riccardi *et al*., 2003) and dyeing properties (Kin and Kang, 2002). Based on earlier studies (Chen *et al*., 2001), the structure and properties of degummed *B. mori* silk treated by oxygen plasma were further studied in this work.

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EXPERIMENTS AND METHODS

Materials

Degummed *B. mori* silk yarns (40/44×8D) were used for the experiments.

Treatments

(1) Plasma treatment

Plasma treatments were performed with oxygen using a model HD-1B plasma reactor with reactor power of 50 W and pressure of 50 Pa.

(2) Stannic treatment

Samples (*B. mori* silk yarns untreated and treated with oxygen plasma) were treated according to the following process. The samples were first immersed in stannic chloride solution, then washed with cold water, and then treated with disodium hydrogen phosphate dodecahydrate solution and washed with cold water. After the above steps repeated once again, the samples were treated with sodium silicate solution and washed with cold wa-

ter. After a final treatment with sodium carbonate, the samples were washed, dehydrated, dried and balanced. All the treatments were performed for some time at some temperature (Lin *et al*., 2002).

Methods

(1) Determination of the weight loss

Weight of degummed *B*. *mori* silk yarns before and after oxygen plasma treatment were measured on model TG328A analysis instrument as G_1 (before treatment) and G_2 (after treatment). So the weight loss could be calculated as follows: $(G_1-G_2)/G_1\times100\%$.

(2) Analysis by SEM

The morphology of modified silk fiber was observed on Model S-520 scanning electron microscope. The samples were mounted and gold sputtered to give the samples electronic conductivity under vacuum prior to observation.

(3) Determination of crystallinity

Density of samples was determined on a model MD-01 density meter. Two kinds of solutions were used. One (low density) was xylene and the other (high density) was tetrachloromethane. Then the crystallinity can be calculated from the density of the silk fiber (Chen *et al*., 2000).

(4) Analysis by X-ray diffraction

X-ray diffraction spectra were obtained with a model 2027 X-ray detector diffraction system at voltage of 40 kV, current of 30 mA and scan rate of 2°/min.

(5) Infrared spectrum analysis

Both FT/IR and ATR/IR spectra were recorded on a model Magna infrared spectrometer, by using KBr disk method and ATR cell with a crystal, respectively. The measurements were performed at a temperature of 20 °C and a relative humidity of 65%. The samples were directly put on the stage and then investigated by using attenuated total reflectance method to study the surface structure of the fibers.

(6) Determination of breaking load and elongation

Breaking loads of *B*. *mori* silk fiber yarns (untreated and treated with oxygen plasma) were determined at an effective gage length of 250 mm and extension rate of 250 mm/min on a tensile strength testing machine (model YG020 electron single strand meter).

RESULTS AND DISCUSSION

Weight character

Degummed *B*. *mori* silk yarns were first dried and then put into reaction chamber of plasma treatment device. The samples were treated for different time intervals (such as 1 min, 5 min, 10 min, etc.). Data obtained are shown in Fig.1.

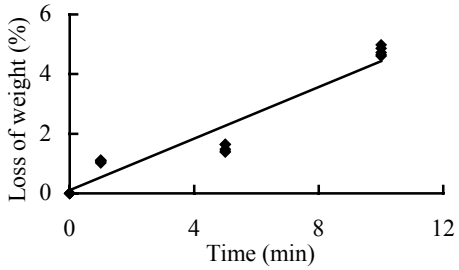
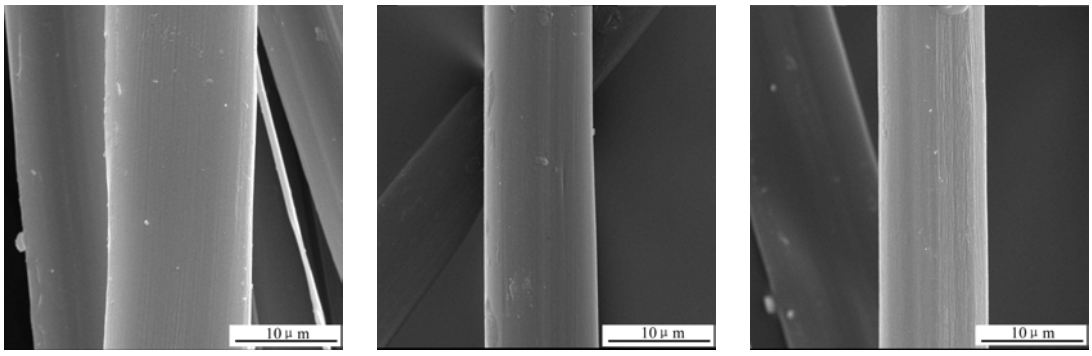


Fig.1 Variation of weight of *B*. *mori* silk fibers with oxygen plasma treatment time

The weight of *B*. *mori* silk fibers decreased sharply with increasing oxygen plasma treatment time (Fig.1). This can be explained as follows: As the bombardment on the fiber surface by oxygen plasma became severe, more and more parts peeled off the fiber with increasing treatment time. To some extent, oxygen plasma treatment of the material is a destructive process. So in practice, the treatment time should be strictly controlled to avoid destruction of the material and the optimum process parameter should be used to improve some properties of the materials.

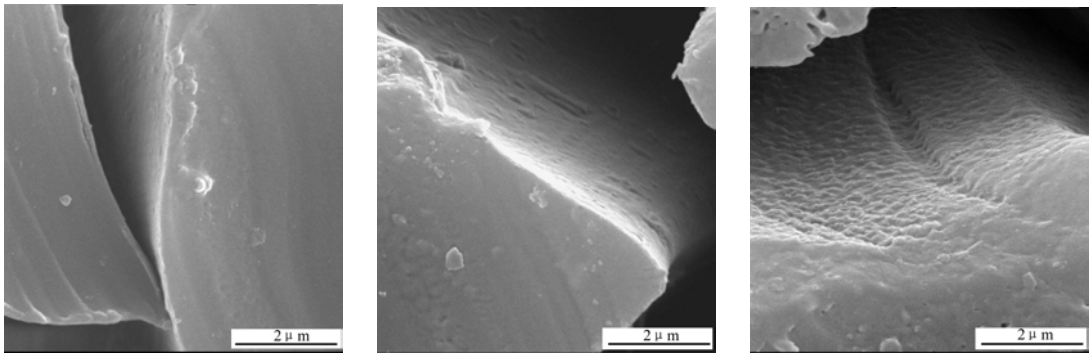
Morphologies of silk fiber

Changes of the surface morphology of degummed *B*. *mori* silk fiber after oxygen plasma treatment were investigated using SEM (Fig.2 and Fig.3). Control sample showed a clean and smooth surface (Fig.2a), while slight longitudinal flutes appeared on the surface of treated *B*. *mori* silk fiber (Fig.2b and Fig.2c). This phenomenon was the result of etching by plasma.



(a) (b) (c)

Fig.2 The longitudinal SEM photographs of degummed *B. mori* silk fiber with oxygen plasma: (a) control (0 min); (b) 1 min; (c) 5 min



(a) (b) (c)

Fig.3 Cross sectional SEM photographs of degummed *B. mori* silk fiber with oxygen plasma: (a) control (0 min); (b) 5 min; (c) 15 min

In order to clearly observe the changes in the inner structure of untreated and oxygen plasma treated *B. mori* silk fibers, another set of samples treated for longer time spans (compared with the samples in Fig.2) were used. Fig.3 shows the cross sectional SEM photographs of degummed *B. mori* silk fiber, untreated and treated with oxygen plasma. Fibrillar unit appeared quite clearly on the section of fibers after oxygen plasma treatment, and was especially evident in Fig.3c. Meanwhile, the micropits that formed on the flank of filaments after oxygen plasma treatment could be observed from the SEM photographs. All these showed that oxygen plasma treatment had effect not only on the surface of silk fiber but also on its inner part.

Aggregation structure of silk fiber

Crystallinity of *B. mori* silk with oxygen plasma treatment is shown in Table 1. Crystallinity of the silk fibers decreased after plasma treatment. It probably can be explained that the polypeptide chain was broken and macromolecule recombined during plasma treatment. The inner structure of *B. mori* silk fibers became looser. Part of the crystal region was oxidized or decomposed because of etching, so the crystallinity decreased.

In accord with the fact that crystalline region and amorphous region have different contribution to X-ray diffraction, changes of crystallinity of *B. mori* silk, before and after treatment could be observed by X-ray diffraction method (Fig.4).

It was seen that the X-ray diffraction patterns of untreated and oxygen plasma treated *B. mori* silk were similar and that there was a broad peak at 2θ=20.58° and 20.5° respectively, which were app-

Table 1 Crystallinity of *B. mori* silk yarn

Treatment time (min)	0	10	30
Crystallinity (%)	27.14	23.56	21.02

roximately the same. The diffraction intensity decreased after plasma treatment as compared with control sample. So conclusion could be drawn that crystallinity of plasma treated *B. mori* fiber decreased. It confirmed the result obtained by density meter method. Part of the macromolecules on the surface and in the inner part of silk fibers being in the ion field oxidized during oxygen plasma treatment. So the crystalline part became looser and crystallinity decreased.

FTIR spectra of *B. mori* silk fiber after oxygen plasma treatment are shown in Fig.5. Characteristic value changes in the infrared absorbance spectra were seen, i.e. the amide II band changed from 1520 cm^{-1} to 1516.2 cm^{-1}; the spectra of the random coil at amide II became less obvious with increased treatment time. This reflects the increasing β-sheet structure and the conformation changed from random coil to β-sheet. This was the result of oxidation during treatment and deoxidization after the treatment. The macro-molecular group partly decomposed and reorganized, so the β-sheet structure of *B. mori* silk fiber increased. At the same time, an absorption peak appeared at band 1385.0 cm^{-1} after plasma treatment, which showed that the bending vibration of C-H group greatly changed.

ATR (attenuated total reflectance) method is a convenient, quick, non-destructive testing method and is often used to analyze surface structure of textile materials. Here ATR/IR was used to study the surface structure of treated *B. mori* silk (Fig.6).

The amide I β-sheet band gradually changed from 1631.9 cm^{-1} to 1630.3 cm^{-1}, then to 1628.0 cm^{-1}, and the spectra peak gradually strengthened, which reflected the increasing β-sheet structure after oxygen plasma treatment. At the same time, the peak at the amide II random coil band 1543 cm^{-1} disappeared after treatment. There was no peak at the amide II β-sheet band of 1521.6 cm^{-1} in curve A and curve B, but it appeared in curve C. Conformation of *B. mori* silk changed from that of random coil to β-sheet after oxygen plasma treatment, and the amide II β-sheet was mainly formed

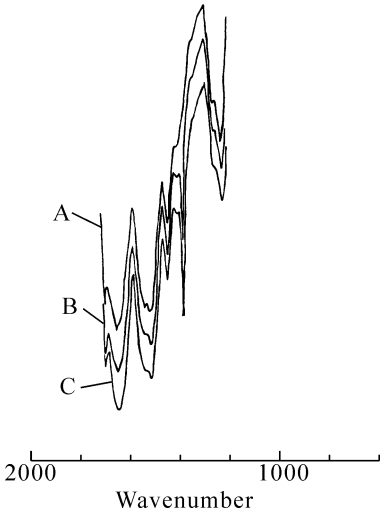


Fig.5 FTIR spectra of *B. mori* silk with oxygen plasma: (A) control; (B) 15 min; (C) 30 min

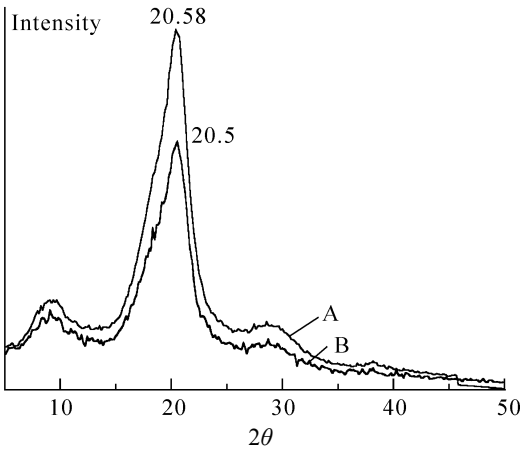


Fig.4 X-ray diffraction curve of *B. mori* silk fiber with oxygen plasma: (A) control; (B) 10 min

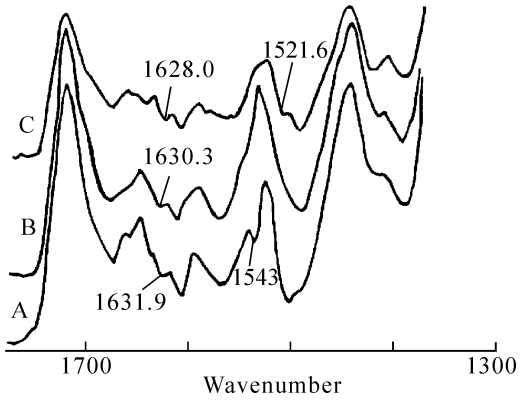


Fig.6 ATR spectra of *B. mori* silk after treatment with oxygen plasma: (A) control; (B) 15 min treatment and put in air for 30 min, then measured; (C) 15 min treatment and put in air 18 hours, then measured

during the reversion after low temperature oxygen plasma treatment. This is related to the oxidation and deoxidation.

Characterization of treated *B. mori* silk

Stannic acid treatment can effectively characterize the microvoids of *B. mori* silk (Kawahara and Shioya, 1999). The quantity of stannic gel filling into silk fiber is shown in Fig.7.

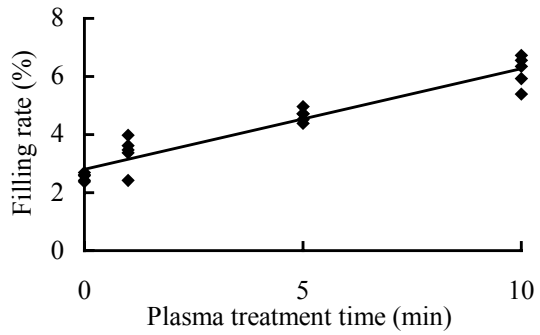


Fig.7 Filling rate of silk fiber

The quantity of stannic acid filling into the treated *B. mori* silk fiber was higher than into untreated fiber and the filling rate increased with the increasing plasma treatment time. In other words, stannic acid filled into the treated fiber easily. This reflected that microvoids were formed on the surface and inner part of the *B. mori* silk after oxygen plasma treatment, which was consistent with the results obtained from morphology and aggregation structure analysis.

Mechanical properties of silk yarn

Because of the etching of plasma on *B. mori* silk yarn, the mechanical properties would probably be different. So the breaking strength of treated silk yarn was investigated.

Breaking strength of *B. mori* silk yarn with short-time oxygen plasma treatment changed only slightly (Table 2), which showed that short-time plasma treatment have little influence on the strength of silk fiber yarn.

Table 2 Breaking strength of *B. mori* silk yarn treated with oxygen plasma

Plasma treatment (min)	0	1	5	10
Breaking strength (cN/dtex)	3.64	3.66	3.62	3.61

CONCLUSION

The weight of *B. mori* silk yarn decreased after low temperature oxygen plasma treatment and decreased more with increasing treatment time. It was a result of etching by oxygen plasma. Slight flutes appeared on the surface of treated fiber and fibrillar units became more evident on the section of treated fiber. The β-sheet conformation increased and crystallinity decreased after plasma treatment. The strength of silk yarn changed little after short-time plasma treatment.

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