

The Surface Characterization of Mulberry Silk Grafted with Acrylamide by Plasma Copolymerization

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Received 9 April 1996; accepted 30 September 1996

ABSTRACT: The effects of plasma-induced graft copolymerization and simultaneous plasma-treated graft copolymerization with acrylamide (AAm) on the structure of mulberry silk are investigated. Through scanning electron microscopy, transmission infrared (IR), and attenuated total reflectance-IR and x-ray photoelectron spectroscopy (XPS) studies, changes of the surface morphology, structure, and composition are observed. The results show that plasma-induced graft copolymerization has more influence on the original structure of silk than does simultaneous plasma-treated graft copolymerization. The former brings the AAm branch polymer into the main chain of silk by the initiation of some kind of oxygen and nitrogen groups formed by the plasma, but the latter directly forms the AAm branch or cross-linking polymers with oxygen and nitrogen groups on the silk surface. This is the reason for the high elastic recovery angle of silk fabric modified by the two plasma graft copolymerizations. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1713–1717, 1997

Key words: silk fabric; plasma graft copolymerization; surface structure analysis

INTRODUCTION

Surface modification of macromolecules by inactive gas plasma treatment has been intensively studied and practically used.^{1–4} However, there has been growing interest in utilizing plasma copolymerization in the surface modification of macromolecules.^{5–7} This is because plasma is quite effective in initiating graft copolymerization. Meanwhile, the results of surface modification by plasma graft copolymerization can be maintained better than plasma treatment.

The ordinary way of plasma graft copolymerization is plasma-induced graft copolymerization in which a macromolecule substrate is treated by plasma before it undergoes subsequent graft copolymerization in a monomer solution. A mechanism of peroxide induction is proposed for this reaction.⁸ Recently, some authors developed a

novel plasma graft copolymerization of simultaneous plasma-treated graft copolymerization,^{9,10} in which a macromolecule substrate preadsorbed with a layer of reactive monomer is treated by plasma; therefore, the monomer with required functional groups is specifically introduced to the surface of the macromolecules. However, the mechanism of this method has not been fully discussed.

In this study, two methods of plasma graft copolymerization are applied to the modification of mulberry silk fabric. The silk fabrics grafted with acrylamide by the two methods show increases of average recovery angle by 20 and 30% at a low graft degree of about 1 wt %, respectively. Their mechanical properties do not change significantly. This article deals with the effect of plasma graft copolymerization on the surface structure of silk and intends to give an explanation for the increases of the recovery angle. Attenuated total reflectance–infrared (ATR-IR), XPS, and scanning

electron microscopy (SEM) measurements have been applied in this study.

EXPERIMENTAL

Materials

The white plain mulberry silk fabric is obtained from Shanghai No. 1 Silk Weaving Mill and is used after the silk glue is removed by refining. The acrylamide monomer (AAM) is of chemical pure grade and is redistilled to remove the inhibitor.

Plasma Graft Copolymerization

The plasma reactor system was described previously.¹¹ The frequency is 30 MHz. Two internal plates with a diameter of 20 cm are placed 2 cm apart from each other in the glass column jar. The work gas is air because a greater graft degree can be obtained by using it. The work pressure remains about 5 torr. Plasma graft copolymerization is performed by the following two methods.

Plasma Graft Copolymerization (A)

Silk fabric is inserted between the two electrodes and treated for the required duration. Then, it is immersed immediately into the aqueous acrylamide solution for graft copolymerization. The monomer concentration, the temperature, and the reaction time are determined for the maximum of graft degree.

Plasma Graft Copolymerization (B)

Silk fabric is immersed in the aqueous acrylamide solution with a certain concentration for 0.5 h. Then, it is dried at 50°C and placed into the plasma reactor for graft copolymerization. When the plasma graft copolymerizations (A) and (B) are over, the fabric is treated by soaping for 5 min and washing with water at 60°C for 10 h until homopolymer and unreacted acrylamide are removed.

SEM

SEM (with a Model Camscan-series-4 scanning electron microscope) is used in this study.

IR Spectroscopy

Transmission and ATR-IR spectroscopy studies of the acrylamide-grafted silk are done with a Perkin-Elmer Model 983-G.

XPS

XPS spectra are taken with a Model NP-1 spectrometer.

RESULTS AND DISCUSSION

SEM Investigations

Scanning electron micrographs of control, air plasma treated, and (A) and (B) plasma-grafted silk are shown in Figure 1. After air plasma treatment, the silk surface becomes cleaner and smoother and the microfibrils parallel to the fiber can be clearly seen. This is caused by the plasma etching effect, in which small molecules attached to the fiber surface are leached out. However, after plasma graft copolymerization with AAM, the silk surface appears rough again. Some microfibrils separate from the fibroins and tangle with each other. It is obvious that the roughness of the silk surface is due to the AAM graft copolymerizing with the silk. The microfibrils separating from the fibroins is because of soaping and washing after copolymerization.

IR Spectroscopic Studies

In order to investigate the effect of plasma graft copolymerization on the silk structure, transmission and ATR-IR spectrum studies are conducted. As shown in Figure 2, the transmission IR spectra of control, air plasma-treated, and plasma-grafted silk do not show any differences from each other. However, differences exist in their ATR-IR spectra (Fig. 3). This verifies that the plasma graft copolymerization is really limited to the surface region of silk and that its bulk structure does not change. This is the reason that the silk mechanical properties do not change significantly.

The molecular structures of polyacrylamide (PAAM) and silk are shown in Figure 4. PAAM bands at 1,650, 1,620, and 1,125 cm^{-1} correspond to the C=O stretching, the NH_2 scissoring bending, and out-of-plane bending absorbances, respectively.

As shown in Figure 3, the three characteristic absorbances of PAAM are all observed in AAM

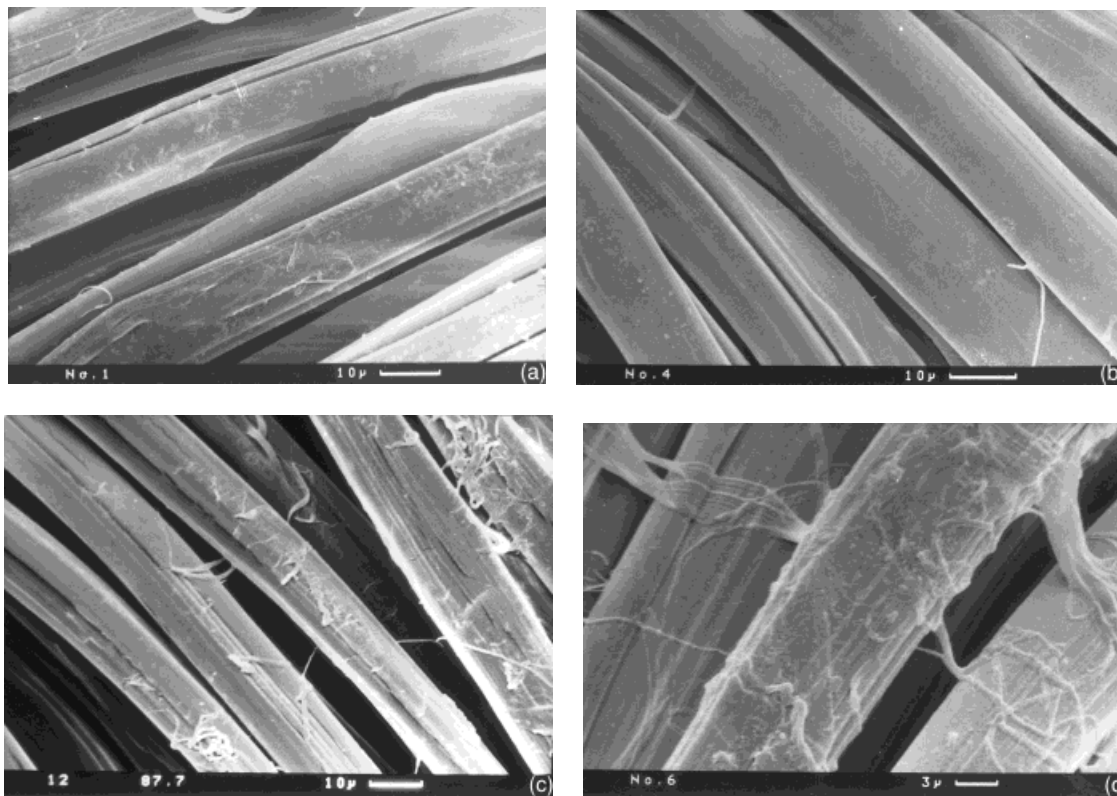


Figure 1 Scanning electron micrograph of (a) control silk, (b) air plasma-treated silk, (c) plasma-grafted silk by method (A), and (d) plasma-grafted silk by method (B).

plasma-grafted silk by methods (A) and (B). Moreover, the band intensities at 695 and 615 cm^{-1} assigned, respectively, to the bending vibration absorptions of $\text{O}=\text{C}-\text{N}$ and $\text{N}-\text{H}$ in the silk structure decrease greatly in the plasma-grafted sample by method (A). This indicates that



Figure 2 Transmission IR spectra for (a) control silk, (b) air plasma-treated silk, (c) AAm plasma-grafted silk by method (A).

the plasma graft copolymerization by method (A) brings the acrylamide branch into the chain of the silk molecule by covalent bonds and that the grafting sites are where the bending vibrations of $\text{O}=\text{C}-\text{N}$ and $\text{N}-\text{H}$ are affected. Because the binding energy of $\text{C}=\text{O}$ is greater than that of other bonds in silk¹² and its IR absorption intensity does not decrease after grafting, it is less likely to be broken by plasma. Additionally, because the side groups of the R group are farther from $\text{O}=\text{C}-\text{N}$ and $\text{N}-\text{H}$ than other groups, they seem to be less fragmented by plasma, too. The probable graft positions in method (A) are expressed in terms of the dotted line in the silk molecule, as shown in Figure 4(b).

The spectrum of plasma-grafted silk by method (B) displays the same absorption intensity at 615 and 619 cm^{-1} as that of control silk. This may be due to any of the following reasons:

- 1) Because of a layer of AAm on the silk surface, silk is less fragmented by plasma.
- 2) The initiating site may be at the side groups of the R group, which have little effect on

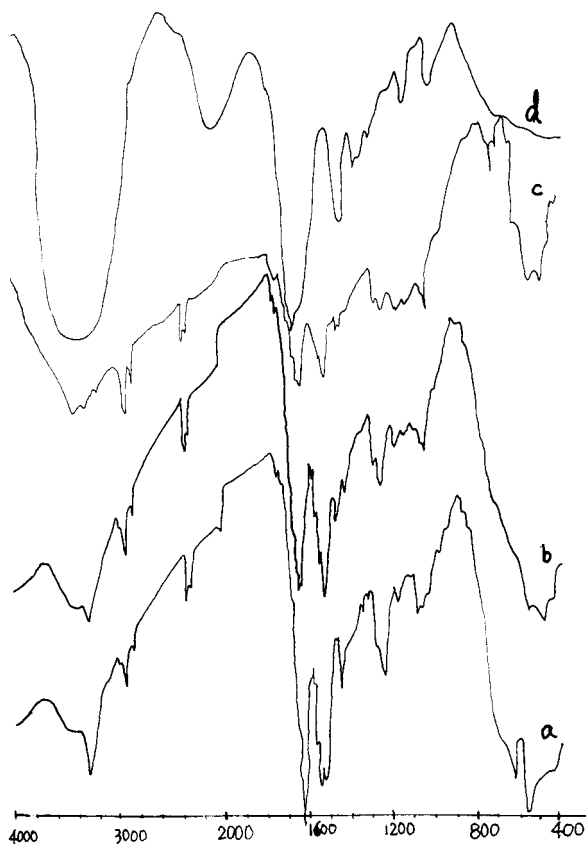


Figure 3 ATR-IR spectra for (a) control silk, (b) AAm plasma-grafted silk by method (A), (c) AAm plasma-grafted silk by method (B), and (d) transmission IR of PAAm solution.

the O=C—N and N—H bending vibrations.

- 3) Plasma graft copolymerizations in methods (A) and (B) have different mechanisms.

XPS Investigations

The XPS measurement is taken to confirm the results of IR spectra. The core-level spectrum of C1s is divided into two peaks according to Gaussian distribution. The main peak at about 285.0 eV is attributed to all of the carbon atoms bound to hydrogen in silk. The peak at about

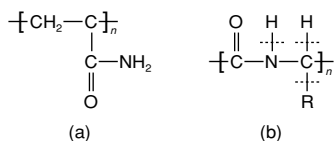


Figure 4 (a) PAAm and (b) silk structure (80% of R is H, CH₃CH(CH₃)₂)_n, 20% of R is CH₂OH, etc.)

Table I XPS Intensity Ratios of [C—O]/[C—H], [O]/[C], and [N]/[C]

Sample	[C—O]/[C—H]	[O]/[C]	[N]/[C]
Control silk	0.46	0.47	0.18
Air plasma-treated silk	0.70	0.57	0.28
Plasma-grafted silk by method (A)	0.43	0.39	0.14
Plasma-grafted silk by method (B)	0.56	0.65	0.32

287.4 eV is assigned to the carbon bound to oxygen as in the C=O and C—O groups.

Table I gives the intensity ratios of [C—O]/[C—H], [O]/[C], and [N]/[C] of control, air plasma-treated, and plasma-grafted silk by methods (A) and (B). From Table I, the [C—O]/[C—H], [O]/[C], and [N]/[C] values in air plasma-treated silk increase. However, after plasma graft copolymerization by method (A), these data decrease below that of air plasma-treated and untreated silk. This result is in accord with that of Suzuki et al.⁸ According to their reports, the oxygen atoms increase in the form of peroxides after plasma treatment and the subsequent graft copolymerization is induced by the peroxide decomposition. In addition, because the atom ratios of [C—O]/[C—H], [N]/[C], and [O]/[C] are 1 : 2, 1 : 3, and 1 : 3, respectively, in AAm, these ratios of AAm-grafted silk by method (A) decrease below that of untreated silk. So, the XPS data further confirm the occurrence of plasma graft copolymerization in method (A), and the plasma graft copolymerization in method (A) is caused not only by the decomposition of some kind of oxygen groups but also by the decomposition of nitrogen groups.

In plasma-grafted silk by method (B), the ratios of [C—O]/[C—H], [O]/[C], and [N]/[C] are all larger than that of control silk, just like that of air plasma-treated silk. This confirms one deduction in IR studies that plasma graft copolymerizations (A) and (B) have different mechanisms. Because the covalences of AAm are easily fragmented by active particles in plasma,¹² active sites seem more likely to be produced on its molecules than on silk molecules. The AAm with active sites may react with silk molecules, oxygen and nitrogen in plasma, or other AAm molecules to form some kind of branch polymers or crosslinking polymers with oxygen and

nitrogen groups on the silk surface. Therefore, the silk elastic recovery angle rises.

CONCLUSIONS

The above SEM, IR, and XPS investigations and analyses give an understanding of the effect of plasma graft copolymerization with AAm on the structure of silk. In method (A), the oxygen and nitrogen groups caused by air plasma initiate the subsequent graft copolymerization and bring the AAm branch into the positions where O=C—N and N—H bending vibration modes in the main chain of silk are affected. In method (B), AAm molecules are more likely to be fragmented and cause active sites than silk. The AAm molecules with active sites can form branch or crosslinking polymers with oxygen and nitrogen groups on the silk surface. The details of this mechanism need further investigation. Because AAm branch or crosslinking polymers are brought into the surface molecules of silk, its recovery angle increases markedly.

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