Effect of Plasma Treatment on the Structure and Allied Textile Properties of Mulberry Silk

G. S. NADIGER* and N. V. BHAT, *Department of Chemical Technology, University of Bombay, Matunga, Bombay-400 019, India*

Synopsis

Studies on the effect of nitrogen plasma on morphology and textile properties of mulberry silk fibers and fabrics have been conducted. The changes in the morphological structure have been monitored by transmission electron microscopy, X-ray diffraction, and internal reflection infrared spectroscopy. The changes in some of textile properties such as wettability, drying rate, and crease recovery owing to plasma treatment have also been investigated. It has been found that the surface of mulberry silk gets etched away, even affecting the crystalline region. This behavior is opposite to our findings on tassar silk. Therefore, an explanation of this differential behavior of mulberry with tasar on the basis of amino acid linkages vis-à-vis bonding, wettability, drying rate, and water retention capacity has been attempted. These results have been used to arrive at an understanding of internal structure of mulberry.

INTRODUCTION

There are three types of plasma energy employed for modification of surface of polymers in general and textiles in particular. They are low radio frequency, high radio frequency, and direct current discharge.[1]

The possible modifications due to plasma treatment envisaged are surface etching, crosslinking, and chain scission, decrystallization and oxidation.[2] These modifications to some extent are exploited suitably to meet the end use requirements. Further, plasma can be employed for polymerization to obtain defect-free thin films of organic polymers.[3]

There are a number of parameter involved in the plasma generation as well as treatment, and they are discussed in detail by Thompson and Mayhan.[4] It has also been shown that the nature of plasma treatment is quite different from reactions induced by ionization radiations such as γ or β.[5] Plasma treatment has also been shown to be one of the ideal methods for surface modification of natural polymers.[6–8]

In the case of synthetic textile materials, it has been shown that plasma treatment improves their dyability, antisoil property, and water repellency,[9–11] which has been tried even on an industrial scale.[12] Jung et al.[13] have studied the effect of argon plasma treatment on cotton fabric surface. It has been shown that water absorption of cotton is enhanced by the treatment. Likewise, it has been observed that plasma treatment lead to free radical formation. In our laboratory the investigation of morphological aspects of synthetic and natural polymers was undertaken.[14,15] Modification of the surface by rf plasma treatment using different gases was done for

* Present address: Karnataka State Sericulture Development Institute, Thalaghattapura, Bangalore-560062, India.

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PET, nylon, and cotton fabrics. In the earlier stages of this work, more emphasis was put on the inner layer structural studies. Due to the high potential in improving surface properties of textiles, investigation of polymeric materials with respect to their structural and textile properties was undertaken. Specifically, our studies on tasar silk fibers and fabrics indicated that the nitrogen cold plasma technique could be successfully used for modifying silk to get certain desirable properties, viz., increase in drying rate, water retention capacity, surface etching to get better feel, and increase in wettability.[16] Therefore, we attempted to study the effect of the nitrogen cold plasma on the structure and properties of mulberry silk and the results of which are discussed in this paper. Likewise, the differential behavior of the mulberry and tasar silks are also discussed with a view to identify the structural differences between them.

MATERIAL AND METHODS

Mulberry silk yarn and fabric were obtained from Central Sericultural Research and Training Institute, Mysore and M/s. Binny Mills, Ltd., Bangalore, respectively. Mulberry fabric was white in color. Nitrogen gas used in the plasma chamber was of commercial grade and was supplied by M/s. Indian Oxygen, Ltd. The water containing 0.05% nonionic surfactant was prepared using auxipan NP 1000.

Plasma Treatment

A plasma reactor designed in our laboratory[16] was used for the plasma treatment of fabrics and fibers of mulberry as well as tasar. A rectangular piece of size 2.5×1.5 cm^2 was inserted in the plasma reactor and was treated for the required duration. In order to estimate the real amount of surface etching of the fabrics, the kinetics of weight loss due to vacuum and then the kinetics of weight loss due to plasma treatment were studied respectively for the reactor residence time ranging from 3 to 90 min for tasar.

Methods of Characterization

Transmission Electron Microscopy

A transmission electron microscope (Russian Model EM-7) was used in these studies. A two-stage replica technique was adopted for sample preparation.[17] Shadowing was done at an angle of 20° using C.Pd to enhance the contrast.

Infrared Spectroscopy

Transmission as well as internal reflection IR spectroscopic studies of the plasma modified silk fabric was done using a Perkin-Elmer Model 377 (RS attachment using KRS 5 crystal).

X-Ray Diffraction

A X-ray diffractometer together with Philips X-Rays Generator Model PW 1009 was used to determine the X-ray crystallinity.

Investigation of Textile Properties

(A) Moisture content was determined by the standard method.[18]

(B) Wettability was determined by the changes observed in the wicking action. The amount of water absorbed (g/gm fabric sample) was measured as a criterion for wettability.[13]

(C) Drying rates of fabrics before and after nitrogen plasma treatment were measured by completely immersing the sample in distilled water for 24 h. The water absorbed after 24 h immersion was taken as the total water holding capacity of the silk. The loss of weight of water (g/gm fabric) for successive time intervals was measured and was defined as the drying rate.[13]

(D) Crease recovery angles of the fabric before and after the treatment were measured using a shirley crease recover tester.[19]

RESULTS AND DISCUSSIONS

Morphological Studies

Electron Microscopic Investigations

Figure 1 shows the surface structure of the control mulberry as observed under TEM. Likewise, Figure 2 shows the surface structure of the plasma treated mulberry. As can be seen from Figure 1, the microfibrils are parallel and aligned to the fiber axis. The fibrillar width is about 1000 Å.[20] It has been stipulated by our earlier studies that the plasma treatment could be utilized to reveal the inner layer structure of textiles. Such a kind of study could be done by chemical etching, or by cross sectioning. However, chemical

Fig. 1. Electron Photomicrograph of control mulberry silk (C-Pd replica shadow angle 20°); fiber axis indicated by an arrow.

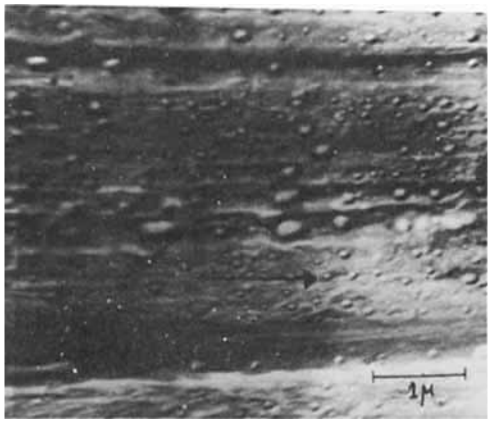

Fig. 2. Electron photomicrograph of plasma treated (for 5 min) mulberry silk (C-Pd replica shadow angle 20°); Fiber axis indicated by an arrow.

etching is found to be unsuitable for textile fibers, as it may cause degradation of polymer as a whole and gives rise to artifacts during the evaporation of the solvent from the surface. Likewise, cross sectioning has been found to be tedious and time consuming. Moreover, the embedding and shadowing process employed for sample preparation are likely to affect the real structure. Therefore, plasma etching has been employed for investigating the inner layer structure. It was found that the fibriller structure fades and vanishes as the time for etching increases, which may be due to any of the following reasons:

(i) No fibrillar structure exists in the inner layer of the fiber. This possibly cannot be true as the microfibrillar nature of the morphological unit of the silk fibroin has been investigated earlier.

(ii) The fibrillar structure does exist, but due to the small width of the fibrils and also compact packing, the visual observation is rather difficult.

(iii) Selective leaching out of the fibrillar surface is leading to smoothening effect. It has been proved in our studies on PET and nylon fibers that the plasma etching is a process in which the amorphous portion of the fiber is selectively leached away.[14]

X-Ray Diffraction Studies

Like any other textile fiber, silk also exists in a semicrystalline state. The crystalline structure represents only that portion of silk fibroin which is cent percent in a ordered state. X-ray diffraction studies lead to understand the crystalline structure on one hand and the degree of crystalline portion on the other. As any treatment that can change the morphology may sometimes lead to crystallization or decrystallization, it was thought worthwhile to investigate the changes due to plasma treatment on mulberry silk[21]. The X-ray diffraction studies of different varieties of silk was carried out and the unit cell parameters were determined.[22-24] The crystalline content of a polymer can be determined by the general formula for resolution factor proposed by Manjunath et al.[25] On similar lines, the plasma treated mulberry silk samples were studied by X-ray diffraction technique. No significant change was observed due to plasma treatment, indicating thereby that the treatment does not give bulk effect which is in conformity with our earlier findings on other textile fibers[26] including tasar silk.[16]

IR Spectroscopic Studies

In order to confirm the results obtained by X-ray diffraction studies, we have also conducted infrared spectral studies. The transmission IR spectra of plasma-etched mulberry silk was found to be the same as that of the control sample, which confirms our conclusion that plasma treatment does not change the bulk crystallinity.

Further, the effect of the plasma treatment on the changes in surface crystallinity to ascertain the surface effect was investigated by the attenuated total reflection (ATR) spectra. The spectra obtained for the control and the samples etched for different duration are reproduced in Figure 3. In the case of mulberry silk the bands assigned for the β-structure are 1630, 1530, 1265, and 700 cm^{-1} corresponding to amide I, amide II, amide III, and amide V, respectively. Similarly for α-random coil conformation, the bands assigned are 1660, 1540, 1235, and 650 cm^{-1}, corresponding to amide I, amide II, amide III, and amide V, respectively.

In the control fibers of mulberry silk, we found both α and β forms indicated by the presence of most of the IR bands in the infrared spectra. Further, Magoshi et al.[27] have shown that the bands in the range 800–1200 cm^{-1} are characteristics of a specific polypeptide with respect to amino

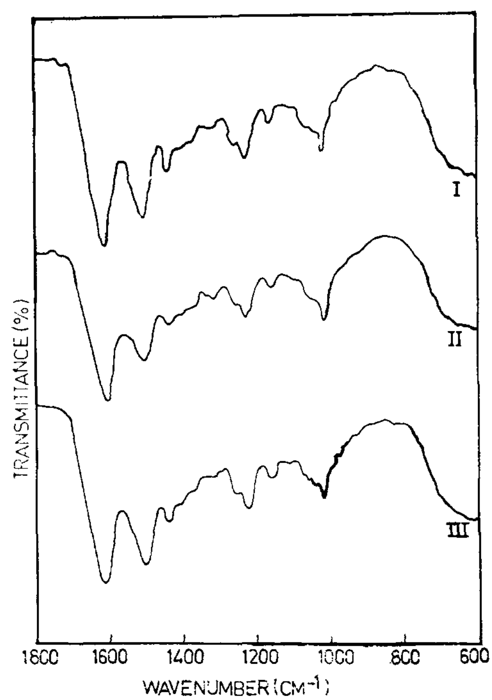

Fig. 3. ATR spectra of mulberry fabric: (I) control; (II) plasma treated for 30 min; (III) plasma treated for 60 min.

acid linkages. The bands at 1015 and 970 cm^{-1} have been assigned to the glycine—glycine linkage and alanine—alanine linkage, respectively. Similarly, the bands at 998 and 975 cm^{-1} have been assigned to the alanine–glycine or glycine—alanine linkages. From our earlier studies, we have found that the 1015 and 970 cm^{-1} bands are present in tasar silk and the 970 cm^{-1} band intensity increases significantly due to partial acid hydrolysis. Similarly, the 1015 cm^{-1} almost vanishes in the spectra of partial hydrolysates of tasar. These indicated that the crystalline region of tasar has mostly alanine—alanine[28] linkage. Likewise, the IR spectra of mulberry silk showed the presence of the bands at 975 and 998 cm^{-1}, which intensified on partial acid hydrolysis, indicating thereby that the crystalline region of mulberry has predominantly gly—ala linkages.

However, in order to find out the surface crystallinity for control and plasma-treated mulberry silk, we have used the bands at 1265 cm^{-1} (crystalline) and 1235 cm^{-1} (amorphous) as they are present in both tasar and mulberry silks. Table I gives the data on IR crystallinity index for control and plasma-treated mulberry and tasar silk. It may be seen from the Table I that the surface crystallinity index decreased from 0.62 to 0.56. But, similar studies on tasar silk showed an increasing trend, indicating thereby that there is an apparent increase in IR crystallinity. The differential behavior may be possibly due to differences in the sequences of amino acids in the crystalline regions of these two varieties. Mulberry has mostly gly—ala and gly—ser sequences in the crystalline region whereas tasar has only ala—ala linkages. The ala—ala linkages in the crystalline region may be comparatively less accessible to plasma etching. It has been established by earlier work[14,26] on synthetic polymer that plasma treatment is more predominant for the amorphous region. Therefore, the increase in the IR crystallinity index of tasar could be easily understood as being caused by etching away of the amorphous portion. However, when one turns one's attention to decrease in the IR crystallinity index of mulberry, it is necessary to look out for all types of interactions which could possibly occur due to plasma on the polymer surface.

Plasma contains electrons, ions, excited species, accelerated electrons, and neutral molecules as well as short-wave radiation (UV). Further, several types of linkages such as gly—gly, gly—ala, and gly—ser are possible in the crystalline region of mulberry. A rough estimation of dissociation energies of such bondings reveal that it may be easier to break such bonds rather than ala—ala (values estimated from those reported for C—H, C—

TABLE I
IR Crystallinity Index of Mulberry and Tasar Fabrics Using ATR Techniques

Sample no.	Details of samples	Crystallinity = OD 1265/OD 1235	
		Mulberry	Tasar
1	Control	0.62	0.27
2	30 min plasma treated	0.57	0.31
3	60 min plasma treated	0.56	0.41
4	90 min plasma treated	—	0.47

C, C=O, etc.). Therefore, during plasma treatment the bondings in the crystalline region are also broken along with those in the amorphous region. This is mainly possible due to radiative transfer of energy. Hence the IR crystallinity index shows slight decrease for mulberry. However, the ala—ala bonds, are more predominant in tasar and less likely to be attacked by plasma. Therefore, the IR crystallinity increases. This proves that the selective etching of the amorphous region is a more probable process in the case of tasar whereas decrystallization is possibly found on the surface of mulberry.

From the above discussions, it appears that various processes such as etching, bond formation, and radiative transfer of energy are possible, and, as a result, it may not be appropriate to assign the absolute values to the degree of crystallinity. These values can only be used to find the relative changes with respect to the control sample. However, such an analysis could give a clue to understand the mechanism involved in the plasma treatment. The exact interpretation is further complicated by the fact that oxidation due to impurities present in the commercial nitrogen gas (0.1%) cannot be ruled out. Wax and other finishing material on the surface of the fabric would be either etched or oxidized to some extent.

TEXTILE PROPERTIES

Weight Loss Studies

It has been found from our studies on tasar fibers and fabrics[16] that the apparent loss in weight due to plasma treatment is partly due to removal of moisture and partly due to surface etching. The loss in weight increases due to increase in treatment time. Since the surface of mulberry shows a decrease in surface crystallinity apart from removal of extraneous material/ amorphous material on the surface, the crystalline region also gets affected.

Wettability

Table II summarises the water uptake of mulberry silk fabric treated with plasma for different durations. It can be seen that the wettability of mulberry silk fabric increased due to plasma treatment which is similar to

TABLE II
Data on Wettability of Control and Plasma Treated Samples of Mulberry Fabrics

Sample no.	Reactor residence time (min)	Water uptake (g of water/g air dry wt of fabric) 15 s wettability: Water containing 0.05% nonionic surfactant
	Control	0.43
1	10	—
2	20	0.68
3	30	0.94
4	40	0.84
5	50	0.83

what has been observed for tasar silk. In fact, the increase in wettability for the treated sample was found to be twice than that of control.

Drying Rate

The effect of plasma treatment on the rate of drying was determined by immersing the fabrics in distilled water for 24 h and allowing these to dry under ambient conditions. An immersion of 24 h has been found to give complete saturation water-holding capacity of the fabric. It may be seen from Figure 4 that the drying rate increased due to plasma treatment. However, water retention capacity showed a slight decreasing trend when compared to that of tasar.

Crease Recovery Measurements

The mean crease recovery angle of the warp and weft for control mulberry was observed to be 104° for the control which dropped to 96° on treating the mulberry fabric with plasma. These results are in conformity with tasar.[16] However, this is in contradiction to the results obtained by Thorsen[29] on cotton using corona discharge.

CONCLUDING REMARKS

Based on these studies, it has been found that in the case of mulberry silk surface decrystallization takes place due to plasma treatment. Likewise, water retention capacity increased. However, the tasar silk[16] showed an apparent increase in surface crystallinity due to plasma treatment and the water retention capacity increased. Further, actual water holding capacity

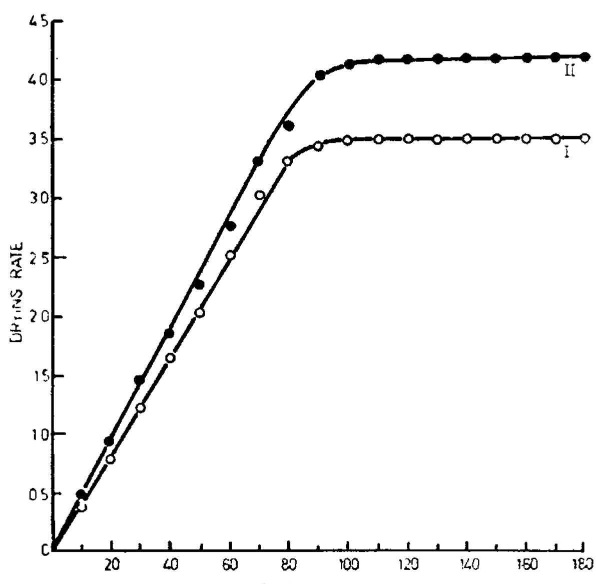

Fig. 4. Drying rate vs. time for: (I) mulberry control and (II) mulberry plasma treated for 30 min.

for tasar (8) is found to be on the higher side when compared to mulberry[16] (3). This may be due to the fact that the void content in tasar is quite high.[30]

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