Int J Plast Technol (June 2013) 17(1):1–9
DOI 10.1007/s12588-013-9043-y

RESEARCH ARTICLE

Low temperature oxygen plasma assisted surface modification of raw silk fibre and their characterizations

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Received: 14 September 2012 / Accepted: 8 March 2013 / Published online: 19 March 2013

Abstract Raw silk fibre was treated with low temperature oxygen plasma with an aim to improve its dyeability. The XRD study reveals that a fraction of the macromolecules on the surface and in the inner part of silk fibres are oxidized during plasma treatment. The overall crystallinity of the fibre surface is reduced and the short range order is increased. Plasma treated fibre showed gradual increase of peak intensity in the Raman spectrum, and the peak shifts to lower wave numbers. Change in the micro-structural properties was observed in the scanning electron microscope images but the mechanical property of silk fibre was found to be insignificant. Smooth and homogeneous coating of a natural dye extracted from the Indian mulberry (*Morinda citrifolia*) was observed in the case of plasma-etched silk fibre.

Keywords Silk fibre · Plasma · Dyeability · Morphology

Introduction

For many decades, biologists and material scientists have been fascinated by the favorable mechanical properties of spider silk. Its resilience, elasticity, tensile strength and fracture energy are equivalent or superior to those of common metallic and non-metallic structural materials. Several studies have been reported on the bulk structural characteristics of silk fibre, such as amino acid composition, molecular weight, crystallinity, and molecular conformations [1]. However, few studies have been conducted on the surface structures of silk fibre or the differences between its surface and the bulk structures [2]. Many important properties of natural as well as synthetic polymers such as luster, ease of handling, adhesion, friction, hydrophilicity, wettability, and dyeability, are known to be largely influenced by their surface characteristics. The properties are related to initial alignments of the protein chains and have

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practical importance. In the case of synthetic polymers these properties can be suitably modified during synthesis. However in the case of natural polymers, the surface properties can only be altered by changing their surface chemical structure or morphology [3].

It is known that any change of properties of silk fibre via processing involves cost and in this context new treatment methods that would lower the cost and simultaneously increase productivity must be accepted in the industry. For this reason plasma treatment of textile materials has emerged as a major possibility for replacing many current wet chemical processes. Low-temperature plasma treatment has been very well studied at laboratory scale involving textiles for several years [4, 5], though it is not yet used and accepted in the industry. The excited particles in plasma such as electrons, protons, ions, etc., have energies higher than that of covalent and other bonds, and can initiate various chemical reactions [6, 7]. Furthermore, the energetic particles emanating from plasma can result in an etching effect on the surface of any substrate upon physical bombardments [7–10]. The type of reaction largely depends on the type of gas used in the plasma. For instance, inert gases such as argon and helium typically cause surface activation to take place. Compounds that contain oxygen are commonly used as etching gases [11]. Low-pressure plasma treatments allow for very controlled conditions where intricate processes can be conducted and optimized. Hence employing low-temperature plasma devices for surface treatment one could develop better silk material.

Low temperature plasma treatment is widely applied in surface modifications in various industries, especially in polymer and textiles. The processes typically involve plasma polymerization, ablation, grafting, surface cleaning and etching [12–14]. To date, the applications of low-pressure plasma in textile industry mainly include the surface modifications of polyester [15], acrylic [16], wool [17], flax [18], cotton [19], silk [20], and polyacrylonitrile [21], for improving wettability, dyeability, printability, water or oil repellency, hydrophobicity and soil resistance, antibacterial activity, reduction in felting, shrink resistance or improving the adhesion of substrate materials [22]. In plasma process oxygen, nitrogen, argon, helium, carbon dioxide, fluorine, carbon tetrafluoride, sulfur hexafluoride, air or water vapor, are usually employed as working gas [23]. Thus the low temperature plasma system for textile treatment is a versatile one that mostly desired to affect the surface properties. However, there is a lack of characterization and understanding of the processing conditions that influence the surface modification of silk fibre. This forms the basis of our research work and the theme of the paper. We have tried to focus on the morphology of raw silk samples treated in low temperature RF-plasma for improving the dyeability efficiency of the fibre.

Experimental

Commercial mulberry raw silk yarns of 20/22 D were procured from Govt. of India, Silk Weavers Association Service center, Bhubaneswar**.** Surface modification of the silk fibre was carried out using the Nano Low Pressure Plasma System (Diener Electronics, Germany) which is basically a capacitively-coupled RF-induced oxygen

plasma (13.56 MHz). The plasma operating conditions were set at a pressure of 0.38 mbar with RF power of 288 W. The DC bias power supply was applied with voltage of 200 V and current of 0.0576 A. The plasma exposure time was maintained for 15 and 45 min. X-ray diffraction analysis was carried out with X'pert PRO (Pan Analytica) X-ray diffraction unit using Ni filtered Cu Kα (λ=1.54 Å) radiation. The voltage and current of the x-ray source were 40 kV and 20 mA, respectively. Fourier transform infrared spectra were recorded on a FTIR system (spectrum GX model supplied by Perkin Elmer instrument, USA). Differential scanning calorimetry (DSC) measurements were performed on a Pyris Diamond DSC (Perkin Elmer, USA) at a heating rate of 10 °C/min and the temperature range studied was from 30 to 400 °C. Thermo gravimetric analysis (TGA) was run under N_2 on a METLER TGA/SDTA 851^e (Switzerland) instrument. The heating rate and the temperature range were maintained at 10 °C/min and 30 to 400 °C respectively. Raman spectra were recorded on an Invia Renishaw (UK) equipped with CCD detector employing a 514 nm laser source. All spectra were obtained by using a 50× objective lens to focus the laser beam onto a spot with 1 μm diameter. The surface morphology of treated and untreated Fibres were observed in a scanning electron microscope (JEOL JSM-5800, observation conditions V—20 kV, I—0.6 nA) after coating with gold. Tensile properties were measured in standard conditions with Universal Testing Machine (Instron 3382, UK). The rate of strain was 10 μm/s on sample of 50 mm length. It should be mentioned that each reported value is the average of seven fibre samples. Dynamic mechanical analysis (DMA) was measured using a Universal V4.5A TA instrument. The frequency of oscillation was adjusted to 1 Hz. The temperature range studied was from 30 to 275 °C with a heating rate of 2 °C/min. The loaded sample is of 15 mm length and was subjected to a strain level of 0.03 % and tension of 102 %. The storage modulus (E′), loss modulus (E″) and the loss tangent (tan δ) were recorded as a function of temperature.

Results and discussion

Oxygen plasma etching effect on raw silk Fibre was characterised by X-ray diffraction analysis. As shown in Fig. 1, after oxygen plasma treatment, the relative intensity of the characteristic diffraction peak for raw silk fibres at 2θ angle of 20^o decreases. This suggests that the crystalline structure in sericin and/or even fibroin core was affected due to plasma treatment. It appears the physical bombardments of ions and even chemical reactions induced by plasma treatment had affected all the way into the sericin layers. It has also affected the attached impurities such as sizing agents, and even the fibroin core. The average crystallite size of the sample has been determined by line broadening method using Scherer's equation. It is seen that the average crystallite size of the fibre is decreased from 10 to 7.5 nm due to plasma exposure (Table 1).

FTIR spectra of silk fibre after oxygen plasma treatment are shown in Fig. 2a. We observed common absorption bands of amide I (C=O stretching) at 1680 cm^{-1}, amide II (N–H deformation) at 1557 cm^{-1}, and amide III (C–N stretching) at 1235 cm^{-1}. Although no change was observed in FTIR spectra, slight change in the peak position was observed from Raman measurement (Fig. 2b). Plasma treated fibre

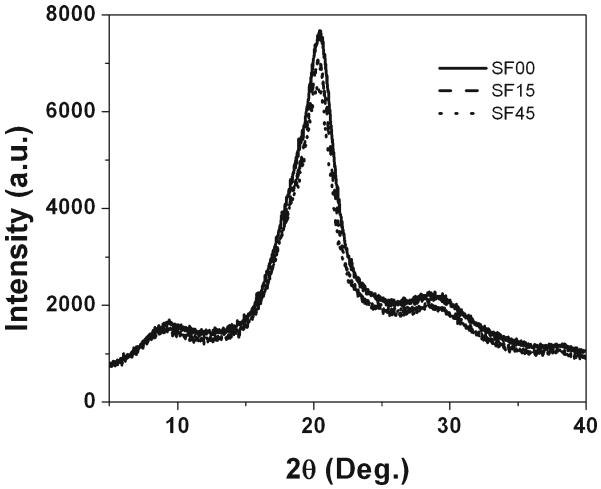

Fig. 1 X-ray diffraction curve of silk fibre before and after plasma treatment

shows gradual increase of peak intensity in the Raman spectrum, and the peak shifts to lower wave number. This indicates that the surface amorphization of the silk fibre has taken place which reduces the overall crystallinity.

Thermal analysis is a useful tool for monitoring important processing and end-use properties of textile fibres. In our tests, the degradation temperature was found to increase with oxygen plasma exposure time (Table 1). The DSC thermogram of silk fibres was characterized by a broad endothermic transition around 325 °C, attributed to the thermal decomposition of silk fibroin with oriented β-sheet crystalline structure. With plasma treatment the change in enthalpy increased with increase in plasma exposure time (Table 1). This change in enthalpy can be attributed to the loss of structure which was confirmed from XRD and Raman measurements.

Surface morphology of raw silk fibres after oxygen plasma treatment was investigated by a scanning electronic microscope (SEM), as shown in Fig. 3. We observed that in comparison to the control raw silk fibre, a notable oxygen plasma etching effect is present with pits or grooves on the fabric surface (Fig. 3d). It seems that the sericin layers were broken by the plasma due to physical bombardment of ions. Many

Table 1 Change in basic properties of Silk fibre after oxygen plasma treatment

Sample Name	Crystallite size (nm)	Raman shift (cm−1)	Degradation temp. (°C)[a]		ΔH (J/g)[b]	Peak temp. (°C)[b]
			Before dye	After dye		
SF00	10.0	Broad peak	333	335.7	661.15	325.64
SF15	8.5	Broad peak	337	342.0	668.92	322.30
SF45	7.5	1892	337	341.0	921.23	324.00

[a] Obtained from TGA

[b] Obtained from DSC measurement.

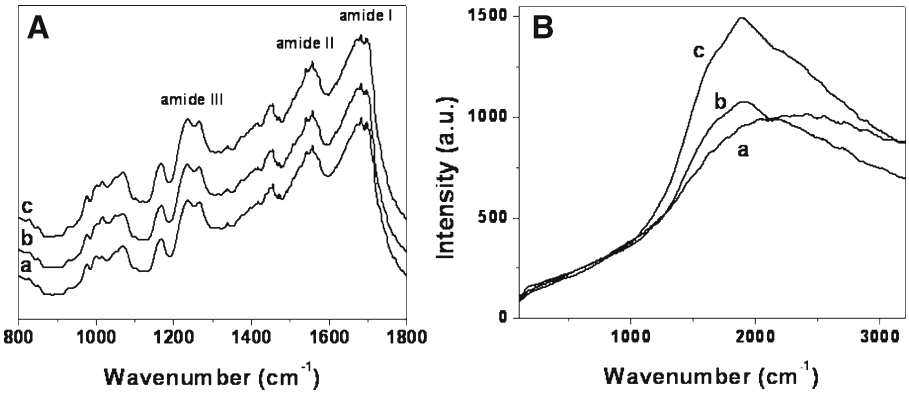

Fig. 2 FTIR (**a**) and Raman (**b**) spectra of untreated (**a**) and plasma treated silk fibre; 15 mint. (**b**) 45 mint. (**c**).

dents, grooves, and holes were produced on the surfaces of the yarns. Figure 4 shows the cross sectional SEM photographs of silk fibre, both control as well as the one treated with oxygen plasma. Fibrillar unit appears quite clearly on the section of fibres after oxygen plasma treatment as shown in Fig. 4d. Meanwhile, the micropits that formed on the flank of filaments after oxygen plasma treatment could be observed from the SEM photographs. These observations led us to believe that oxygen plasma treatment not only had effect on the surface of silk fibre but also on its inner part. We infer that the polypeptide chain was broken and macromolecules recombined during the plasma treatment process. The inner structure of silk fibres

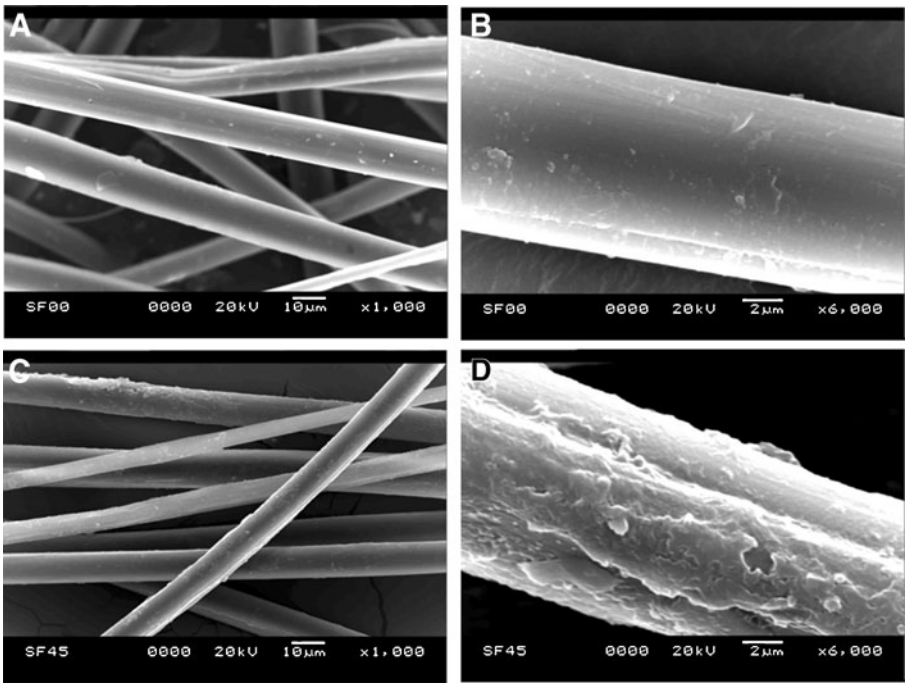

Fig. 3 SEM photographs of silk fibres; control (**a**, **b**) and 45 mint plasma treated (**c**, **d**) Fibre with different magnification

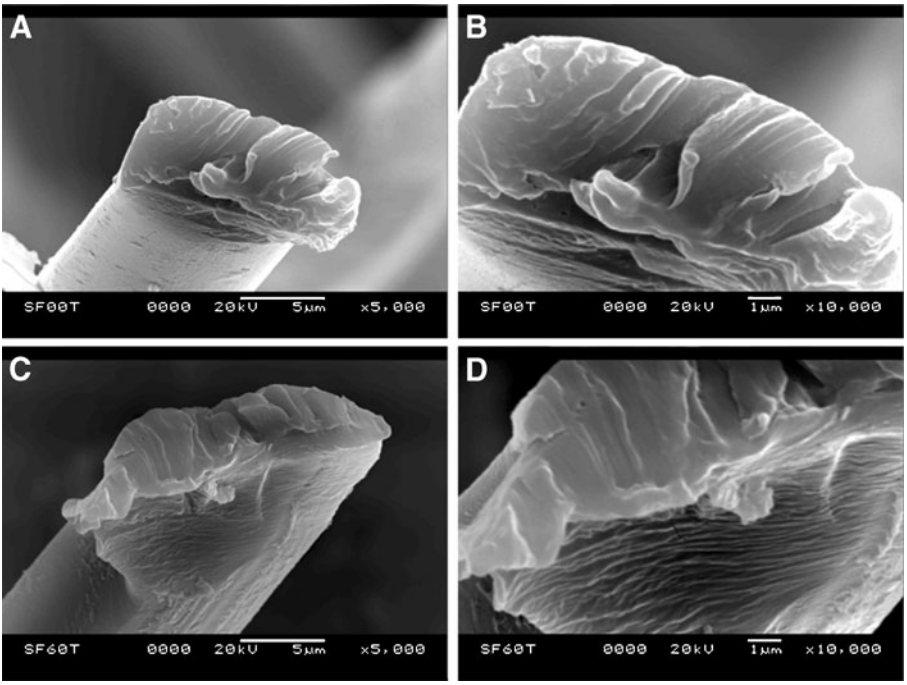

Fig. 4 Cross-sectional SEM photographs of silk fibres; control (**a**, **b**) and 45 mint plasma treated (**c**, **d**) at two different magnifications

became relatively loose. Part of the crystal region was oxidized and decomposed because of etching that reduced the crystallinity, which was noticed in the XRD study.

Silk fibre can be considered as a composite of protein elastomers. The mechanical properties are expected to change because of the plasma etching of silk fibre. So the tensile property of the treated silk fibre was investigated. Table 2 shows the tensile strength for plasma treated and untreated fibre samples. Oxygen plasma treatment slightly changed the tensile strength. The decrease of the strength for plasma treated fibre is reflected even at molecular scale due to the degradation of the fibroin proteins. Further, the dynamic mechanical property was also studied. Table 3 shows the temperature dependence of the dynamic loss modulus, storage modulus and tan(δ) of the plasma treated and untreated samples. Similar behavior was observed for both the silk fibre samples. With increase in temperature both the storage modulus and the loss modulus decrease. Silk fibres with the same degree of crystallinity displayed close similarity with respect to dynamic mechanical behavior. As it is observed from our experiments, the plasma surface modification had not largely affected the

Table 2 Mechanical properties of Silk fibre after oxygen plasma treatment

Sample	Tensile strength (MPa)	Elongation at break (%)
SF00	0.34 ± 0.03	26.62 ± 2.03
SF15	0.29 ± 0.04	35.18 ± 3.91
SF45	0.29 ± 0.03	31.67 ± 3.00

Table 3 Dynamic mechanical properties of Silk fibre after oxygen plasma treatment

Sample	Storage modulus (N/tex)			Loss modulus (N/tex)			tan δ		
	50 °C	75 °C	100 °C	50 °C	75 °C	100 °C	50 °C	75 °C	100 °C
SF00	5.737	4.287	1.475	0.287	0.226	0.093	0.050	0.052	0.063
SF15	5.279	4.471	2.543	0.173	0.176	0.129	0.032	0.039	0.051
SF45	5.808	4.503	2.493	0.289	0.245	0.149	0.049	0.054	0.059

mechanical property of the silk fibre and hence this process could be useful in textile manufacturing.

The plasma treated silk fibre was further coated with natural dye using Indian mulberry (*Morinda citrifolia*). Simple visual observations show better dyeability for plasma treated silk fibre than the control one. To confirm its dyeability, SEM images were taken and Fig. 5 shows the micrographs of raw and plasma treated silk fibre before and after dye coating. Better dyeability was observed for the plasma treated (45 min) samples in comparison with the untreated sample. In the untreated silk fibre dye is adsorbed as a lumpy mass on the surface (Fig. 5b). The oxygen plasma treatment readily breaks the outer layers (the sericin layers) of raw silk fibres, which

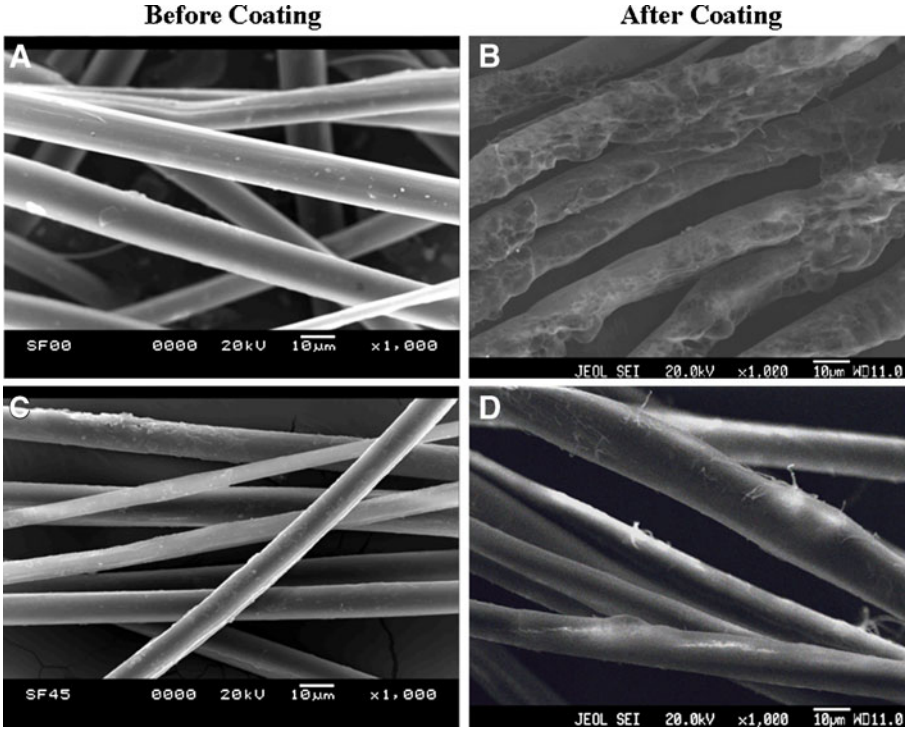

Fig. 5 SEM photographs of silk fibres before and after dye coating; control (**a**, **b**) and 45 mint plasma treated (**c**, **d**).

enhances diffusion of chemical species, into sericin layers and the fabric yarns, resulting in the improvement of raw silk fabric processing with respect to dye adsorption (Fig. 5d).

Conclusion

Raw silk fibre has been treated with low temperature oxygen plasma to study its dyeability. A notable etching effect including physical bombardments and/or plasma chemical reactions by excited plasma species on sericin layers was observed from SEM micrographs and XRD data. The mechanical properties of plasma treated samples did not show much difference despite some variations in roughness which was picked by the SEM. Plasma treated samples shows better dyeability as compared to untreated samples and comparable surface tethering of fabrics were obtained as found in the conventional method.

Acknowledgement The authors acknowledge the valuable suggestion rendered by Dr. B. S. Acharya, Dr. A. Nayak and Dr. N. B. Das of Institute of Minerals and Materials Technology, Bhubaneswar.

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