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Surface Modifications of Natural Kanchipuram Silk (Pattu) Fibers Using Glow Discharge Air Plasma

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Abstract: Experimental investigations have been carried out to modify the surface properties of natural Kanchipuram silk (pattu) fibers using a low temperature DC glow discharge air Plasma. Silk is an externally spun fibrous protein secretion formed into fibers. Plasma treatment is an eco-friendly, dry, and clean process over wet chemical method and does not suffer from any environmental and health concerns. Experiments have been performed considering three parameters such as discharge current, treatment time, and working pressure. The structural, thermal, morphological, optical, and mechanical studies of raw and plasma treated silk fibers have been obtained out using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectroscopy, X-ray diffraction (XRD), thermo gravimetric analyzer (TGA), scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS), diffuse absorbance spectroscopy, and tensile test. A comparative study has been done for the untreated and different treated fibers. Various characterization analyses reveal that surface roughness of the plasma treated silk fiber is increased and also crystallite size of treated samples is enhanced, plasma treated silk fibers maintain the whiteness effect and it is observed that UV transmittance region (A & B) is more for the treated fiber which signifies enhanced UV protection.

Keywords: Plasma treatment, Protein polymer fibers, Etching, Roughness, UV Protection

Introduction

The textile and clothing industries are facing big challenges today, largely because of the globalization process. So the technical textiles are deemed to be essential for their sustainable growth [1]. In recent years, plasma plays an important role in many industrial applications, such as thermal coating, etching in microelectronics, metal cutting, welding, vehicle exhaust cleanup, etc. Plasma surface modification is an emerging and popular technology in many fields, including textile department [2]. As a part of more environmental awareness, textile industries are now slowly adopting the implementation of water-less (dry) or low water based processing technologies, such as digital printing, spray and foam finishing, and plasma processing. Hence, plasma processing being a completely dry method, is a promising technology in fiber modification. Plasma is a partially ionized gas composed of many types of species, such as positive and negative ions, electrons, neutrals, excited molecules, photons, and UV light. It has the potential to be commercialized in textile processing for the development of value-added home, apparel, and technical textiles at a lower cost, while addressing the problems associated with environmental pollution. It changes only the physical and chemical part of uppermost atomic layers of a material surface, while the bulk properties are unaffected because of the low range penetrations [3]. The surface modification of textiles using plasma can be carried out using non polymerizing gases, such as oxygen (O_2), nitrogen (N_2), air, argon (Ar), helium (He), or fluorine (F) for surface activation, cleaning, oxidation, changes in surface energy, increases in surface roughness/area, etching, coating/deposition, and the creation of nano-structures [4]. The plasma treatment for many kinds of fabrics such as cotton [5], wool [6], nylon [7], etc have been reported. *Bombyx Mori* (*B. Mori*) silk is an animal natural protein polymer fiber from the silkworm [8-11] and consists of 18 kinds of amino acids, 90 % of which are composed of glycine, alanine, serine, and tyrosine. Mulberry and non mulberry silks are available in India. Mulberry silk (*B. Mori*) is considered to be superior in quality as compared to others. About 92 % of the country's total production is comprised of mulberry silk. With the increasing popularity of natural products, demands of silk are not only for the clothing, but likewise for personal care product and biomaterial, silk plays an important role in economics of many countries. Silk clothes are exposed to numerous things like stain, poor winkle recovery abilities, and poor anti-microbial abilities [12]. The interest in plasma treatment on silk fibers is due to the value addition by choosing a proper plasma treatment process for changing various properties such as etching/re-deposition, liquid repellency [13], viz., water, oil, inks, alcohols, hydrophilicity, wettability, dyeability [14], printability, etc. Moreover, it is a dry clean process and does not suffer from any environmental and health hazards. It has major advantages over conventional wet chemical process in terms of reduction of waste and pollution problems, water, energy, and time [15].

Iriyama *et al.* observed treated silk with O_2, N_2, and H_2 plasma increased deep dyeing [14]. Chen *et al.* reported that oxygen plasma treatment decrease the crystallinity of silk [16]. Long *et al.* found that low-pressure argon plasma was successfully applied to establish the novel degumming process

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[17]. Moreover Sarmadi observed that surface roughness increased after low-temperature argon-plasma-treated silk fiber [18].

Kanchipuram silk is traditionally used extensively in southern part of India since the ancient times and its demand is still increasing till date. So far, no reports are seen elsewhere regarding the plasma treatment on this type of silk. The main objective of this present work is to investigate the structural, morphological, optical, thermal, and mechanical properties of raw and plasma treated silk fibers by using low temperature glow discharge air plasma and to optimize the conditions for plasma parameter which are suitable for textile applications. The raw and plasma treated silk fiber have been analyzed using various characterization instruments such as XRD, ATR-FTIR, TGA, SEM-EDS, DRS, and universal testing machine AG-X pulse 50 kN. Various analyses of the plasma treated silk fibers in this current investigation reveal that certain properties such as enhanced surface roughness, UV protection percentage, tensile strength, etc. are in favor of the endusers.

Experimental

Materials

An original silk fiber reeled from the cocoon, as called raw silk fiber, is a composite material. It includes two-filament fibroin core and fiber cementing gum, as called sericin, for gluing and holding the filaments together and keeping the structure of cocoon [18]. Figure 1 shows that *B. mori* raw silk (Kanchipuram silk) fibers are used in this research work. It is white in color, which is offered by Tamil Nadu Co-operative Silk Yarn Producer Federation Ltd-Kanchipuram.

Plasma Treatment

The experiment has been carried out in thermal evaporation unit with DC power supply. It consists of a cylindrical chamber with 40 cm in height and 30 cm in diameter. The schematic diagram of the experimental setup is shown in Figure 2. The anode is a stainless steel rod and the chamber acts as a cathode to produce plasma. In this case, important plasma parameters such as working pressure and discharge current are kept at fixed value and treatment time (5, 10, 20 min) is made varying. The fibers are kept uniformly in the glass slide and the edges are taped with cellophane tape, placed in a substrate holder inside the chamber. The chamber is evacuated by using rotary pump and diffusion pump under continuous pumping condition. The base pressure of the system has been maintained at 4×10^{-5} mbar. Allowing air inside the chamber, glow discharge plasma is produced at working pressure 3×10^{-2} mbar by applying DC power supply of 80 V and current of 1.93 A. After the plasma treatment, the vacuum is released in the chamber and samples are removed from the substrate holder and kept it in desicator to avoid the surface contaminations.

Figure 1. *B. mori* silk fibers.

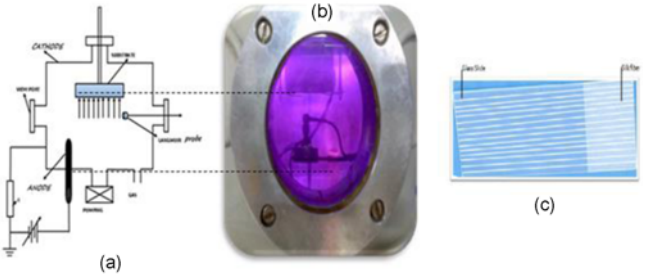

Figure 2. Experimental setup; (a) schematic diagram of setup, (b) during plasma treatment, and (c) silk fiber kept in glass slide.

X-ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns of silk fibers is obtained from an X-ray diffractometer which is equipped with CuK_{α} radiation generated at voltage of 40 kV and current of 30 mA. The X-ray diffraction curves of raw and plasma treated silk fibers are measured in order to study the crystalline structure. The crystallite size of the raw and plasma treated silk fibers is determined by using the Debye-Scherrer formula,

$$D=K\lambda/\beta\cos\theta$$

K: shape factor (0.89-1.39), K=0.89, β: FWHM of the observed peak (rad), λ: wavelength of the X-ray diffraction (λ=1.5406 Å), θ: angle of incidence (rad).

The method of calculation of crystallinity index (C.I) of silk fibers by height is given below.

$$\text{C. I }\% = h_c/h_t\times100$$

h_c: height of main crystalline peak
h_t: total height of main crystalline peak

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR)

One of the most important infrared spectroscopy methods used in studies of polymer is attenuated total reflection Fourier transform infrared (ATR-FTIR). Spectra of the treated fibers have been recorded by a Nicolet ATR-FTIR Spectrometer (IS10).

Thermo Gravimetric Analysis

The thermo gravimetric analysis (TGA, TG/DTA 7200 EXSTAR instrument) has been carried out under argon gas atmosphere for measuring the thermal stability and moisture content in raw and plasma treated silk fibers.

Surface Morphology

Initially the samples are gold sputtered using gold sputtering unit (Hitachi-E1010). High resolution scanning electron microscope (HR-SEM, Hitachi S-4800-type) was used to investigate the surface morphology of samples. The accelerating voltage was 3 kV.

UV-Absorbance and Transmittance

In order to determine the impact of plasma treatment on silk fibers, the absorbance and transmittance in the near ultraviolet (UV) and visible (VIS) wavelength range is measured as a function of the plasma treatment duration using an Evolution 300 UV-VIS spectrophotometer in the wavelength range of 200 to 800 nm. The absorbance and transmittance spectra have been recorded for raw and plasma treated silk fibers.

Tensile Strength

The Tensile strength measurement of the silk material is carried out by a universal testing machine AG-X pulse 50 kN. The silk fiber is cut into 20 cm in height for enabling it for the tensile strength testing.

Results and Discussion

In accordance with the fact that crystalline region and amorphous region have different contribution to X-ray diffraction, changes of crystallite size and crystallinity index (height method) of silk fiber before and after plasma treatment could be observed by X-ray diffraction method. As any treatment that can change the morphology, hence it may sometimes lead to crystallization or decrystallization. That is why it has been considered worthwhile to investigate the changes due to plasma treatment on silk fiber [20]. Figure 3 shows the X-ray diffraction pattern of raw and plasma treated silk fibers. Two set of peaks are identified, one is quite narrow at 9.69° and another is a broad peak at 20.64° corresponding to the semi crystalline nature of silk fibers [21,22]. The crystalline structure represents only the portion of silk fibroin. It is seen that the X-ray diffraction patterns of raw and plasma treated silk fibers are similar; no significant change is observed [23]. Table 1 shows that the crystallinity index starts to slightly decrease after the plasma treatment in the crystalline region. This can be due to partial oxidation or decomposition by plasma etching during the air plasma treatement. So conclusion could be drawn that decrease of crystallinity may be due to the broken polypeptide chains and recombination of macromolecules [24].

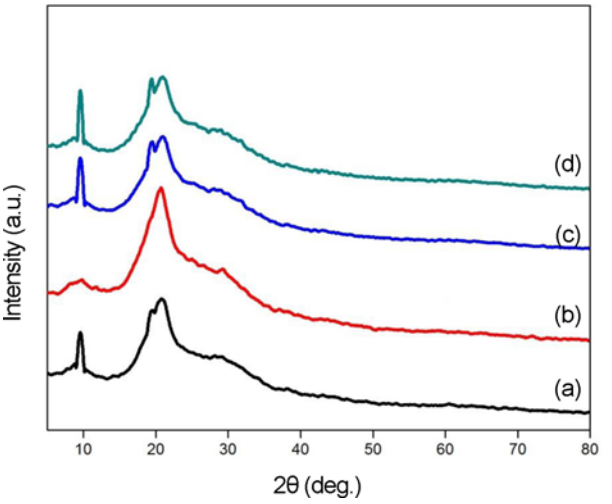

Figure 3. XRD patterns of (a) raw and plasma treated silk fibers; (b) 5 min, (c) 10 min, and (d) 20 min.

Table 1. XRD crystallinity index and crystallite size

Silk fibers	2θ (°)	FWHM (deg.)	Crystallinity index height	Crystallite size (nm)
Raw	20.64	2.075	59.95	3.02
5 min	20.69	1.945	59.80	3.33
10 min	20.89	1.935	57.14	3.88
20 min	20.89	1.935	57.14	3.88

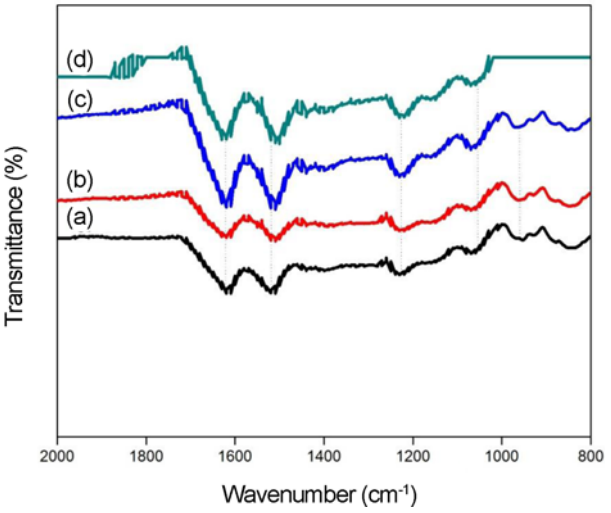

Figure 4. ATR-FTIR transmittance of (a) raw and plasma treated silk fibers: (b) 5 min, (c) 10 min, and (d) 20 min.

Figure 4 shows the ATR- FTIR spectra with assigned peaks for the Raw and Air plasma-treated silk fibers for several treated times viz., 5 minutes, 10 minutes and 20 minutes. Amino acids (AAs) are the basic building blocks of peptides and proteins. ATR-FTIR spectra of different AAs are obtained in the region 1800-800 cm^{-1} [25]. As seen from

Table 2, the ATR-FTIR spectra shows characteristic bands of amide I (C=O Stretching) at 1,620 cm^{-1} which are due to the beta conformation of the crystal-line region, and the band appearing at 1,521 cm^{-1} is amide II (N-H deformation) which is due to the random coil conformation of fibroin molecules. The peaks that appeared at 1,226 cm^{-1} are attributed due to the presence of an amino acid group amide III (C-N Stretching). The band at 1066 cm^{-1} is due to the presence of Gly-Ala peptide chain of silk fiber [26]. The peak positioned at 960 cm^{-1} signifies the Ala-Ala linkages in the crystalline portion of the silk [21]. The ATR-FTIR transmittance goes up after plasma treatment. This may be the evidence of occurrence of etching. It is found that the air plasma treatment changes surface chemical composition of the fiber.

Table 2. ATR-FTIR transmittance peaks and structural bond

Wavenumber (cm^{-1})	Structural bond	Amide groups
1620	C=O Stretching	Amide I
1521	C-N Deformation	AmideII
1226	C-N Stretching	Amide III
1066	C-N Stretching	Gly-Ala Peptide chain
960	C-N Stretching	Ala-Ala linkages

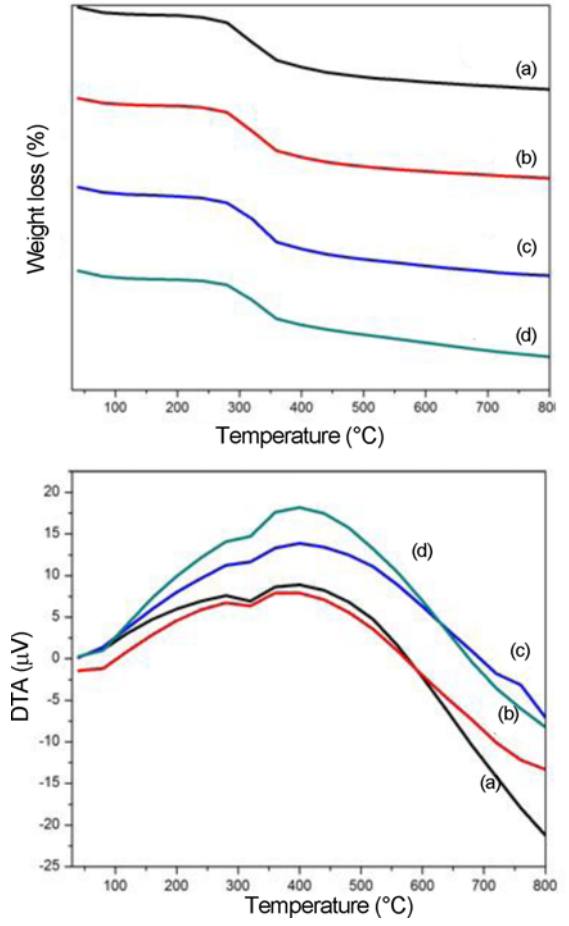

Figure 5. TGA and DTA of (a) raw and plasma treated silk fibers: (b) 5 min, (c) 10 min, and (d) 20 min.

Table 3. Weight loss (%) and char residue of raw and plasma treated silk fibers

Temperature range (°C)	Weight loss (%)			
	Raw	5 min	10 min	20 min
40-280	13.72	12.89	14.16	09.09
280-360	34.26	34.95	35.66	34.56
360-800	26.47	25.19	30.59	34.48
Char residue at 800 (°C)	25.55	26.97	19.59	21.87

To identify the thermal degradation process of raw and plasma treated silk fibers, Thermogravimetric analysis (TGA) of the fiber sample is carried out and it is shown in Figure 5. Observation reveals that the raw silk fiber has three mass loss processes: 1) 40-280 °C, which is assigned due to the loss of absorbed moisture of silk fibers and a small amount of protein degradation, with mass loss of 13.72 % 2) 280-360 °C, which is attributed due to silk fiber decomposed into small molecules such as CO_2, H_2O and other flammable substances, the major decomposition stage with mass loss of 34.26 % 3) 360-800 °C, which is mainly caused by char decomposition of silk fibers, with mass loss of 26.47 % [28]. It is found that for 20 minutes plasma treatment of the silk fibers, the thermal stability is improved. Table 3 shows the weight loss (%) and the char residue of raw and plasma treated silk fibers. For raw silk fibers the maximum degradation rate was recorded at 320.3 °C. Thermal degradation behavior of raw and plasma treated silk fibers are further supported by differential thermal analysis (DTA) in Figure 5. There is an endothermic peak at 321 °C, which reflects the thermal degradation of silk fibers. The range of 320-324 °C corresponds to the thermal degradation of raw and plasma treated silk fibers. It is also seen from DTA graph that the raw silk fibers have the lower value of maximum degradation rate than plasma treated one. It reveals that plasma treatment of silk fiber can improve the thermal stability and plasma treatment time 20 minutes is considered to be the best fitted one.

The SEM micrographs of single silk fibers of raw and plasma treated are shown in Figure 6. Figure 6(a) shows that the raw silk fiber is smooth with fewer defects and free from roughness. After plasma treatment the surface roughness increases with increasing treatment time due to ion sputtering on the fibers [29]. In 10 minutes plasma treatment, there is a cleavage of sericin layer due to physical bombardments of ions and dry degumming processes [17]. The plasma treatment is more effective to achieve the surface etching phenomena.

The EDS graphs shown in Figure 7 explain that quantitative analysis of elemental composition of carbon and oxygen present in the silk fibers. The weight % of carbon content is found to increase and weight % of oxygen content decreases after plasma treatment. The quantitative values of the same are shown in Table 4. This is attributed due to the plasma

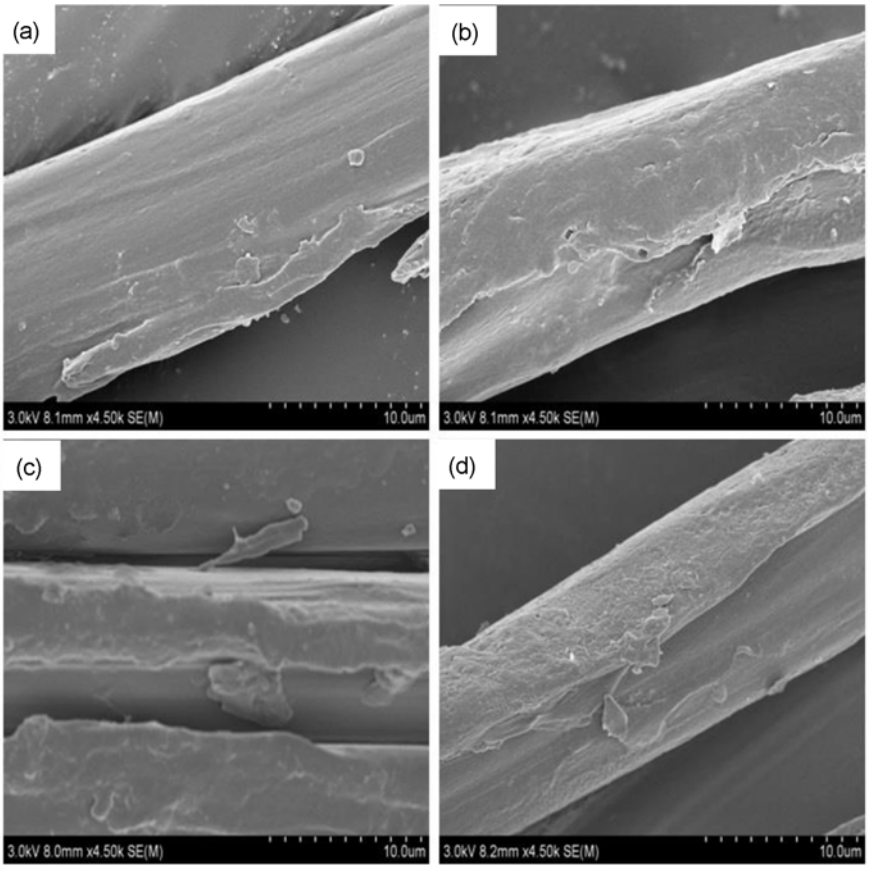

Figure 6. SEM micrographs of (a) raw and plasma treated silk fibers: (b) 5 min, (c) 10 min, and (d) 20 min.

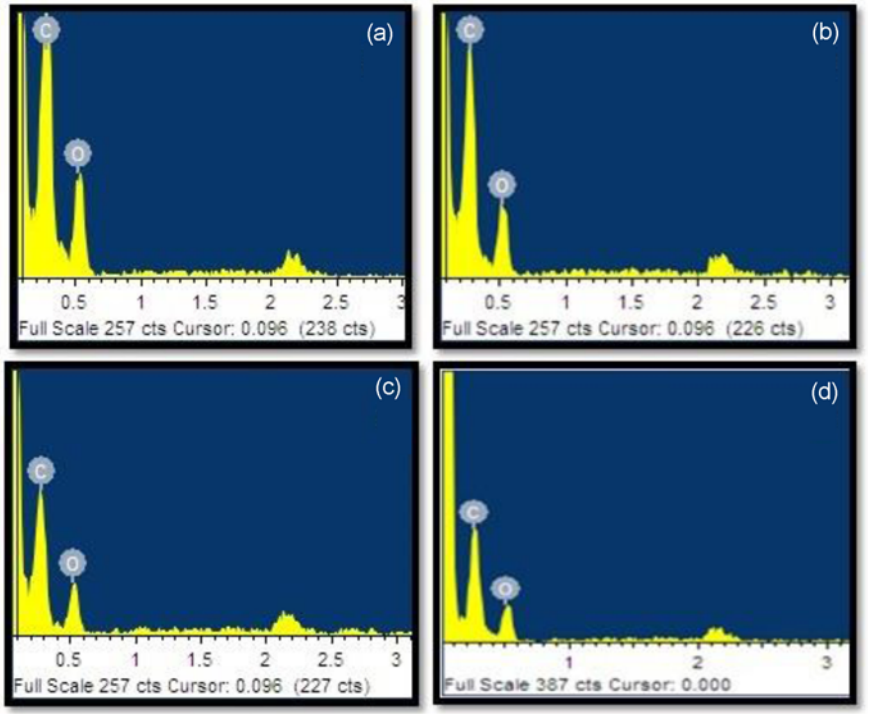

Figure 7. EDS of (a) raw and plasma treated silk fibers: (b) 5 min, (c) 10 min, and (d) 20 min.

Table 4. Weight (%) of elemental compositions of raw and plasma treated silk fibers

Elements	Weight (%)			
	Raw	5 min	10 min	20 min
C	56.52	57.91	57.49	57.50
O	43.48	42.09	42.51	42.50

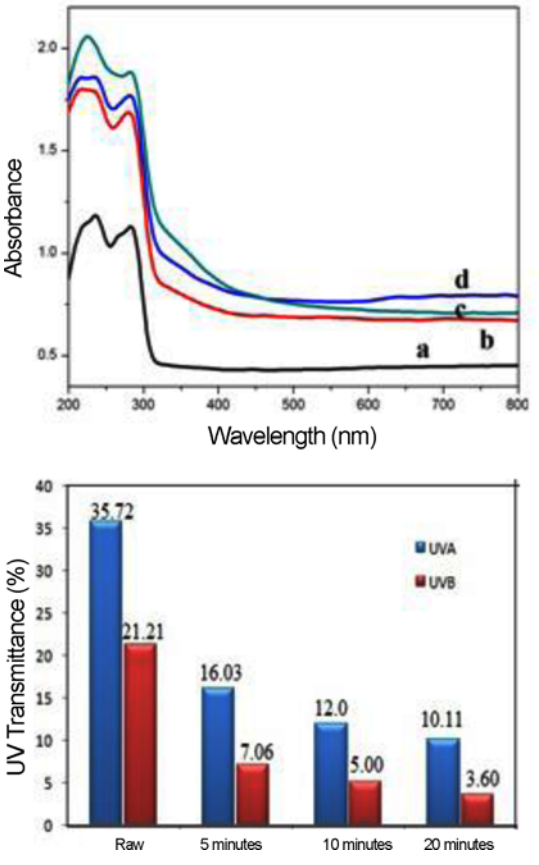

Figure 8. UV absorbance and transmittance of UVA and UVB region of (a) raw and plasma treated silk fibers: (b) 5 min, (c) 10 min, and (d) 20 min.

etching processes taking place in the reactor chamber.

Figure 8 shows a DRS Absorbance spectrum of raw and plasma treated silk fibers. Absorbance is a measure of the amount of light absorbed and it is observed in the UV region (200-380 nm). The UV absorbance peaks at 235 nm and 282 nm are due to amino acids tryptophan, tyrosine and cysteine. When silk fibers are treated with air plasma, the energetic charged particles inside the plasma are able to interact with the surface. The significant change that happens is that the absorbance increases with increasing exposure of plasma treatment time.

The UV Transmittance of UVA and UVB region was calculated by Australian/New Zealand AS/NZS 4399. Figure 8 shows a significant difference between raw and plasma treated silk fibers; raw fabrics yield a high UV transmittance.

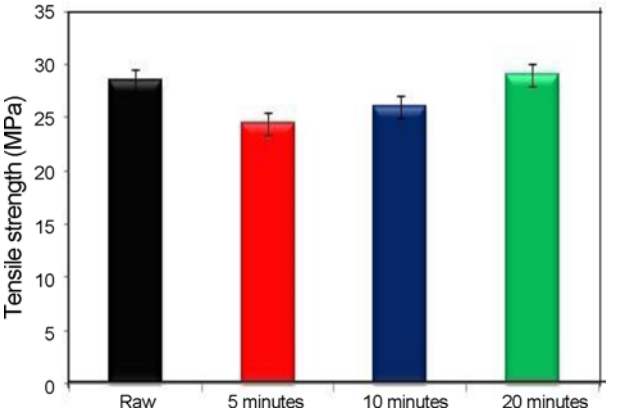

Figure 9. Tensile strength of (a) raw and plasma treated silk fibers: (b) 5 min, (c) 10 min, and (d) 20 min.

The UV transmittance of the raw silk is in the range of about 21.21 % in the UV-B band and about 35.72 % in the UV-A band indicating that the resistance of the raw fabrics to ultraviolet rays is very poor, while the UV transmittance of the plasma treated silk fibers appeares to be lower than 4 % in the UV-B region. It is clearly seen that after plasma treatment, most of the UVA and UVB radiation starts to decrease and it is observed being reflected, refracted, or scattered so that less UV radiation can penetrate through the fabrics [28]. The UV protection property of fabrics is evaluated as “good” when the UV transmittance is less than 5 % [30].

The Tensile strength of the raw and plasma treated silk fibers are shown in Figure 9. The Figure shows that the raw silk fibers have more strength initially when compared to the lesser plasma treatement time (5 minutes) of the silk fibers. The reason for decrease in tensile strength is due to protein dehydration. But, it is also observed that when treatment time is increased (10 minutes & 20 minutes), tensile strength starts increasing again, revealing the fact that there may be some optimum condition for enhancing the tensile strength. This is a significant result in terms of the enhancement of tensile strength of the silk fiber as we can expect to increase the lifespan of the fiber. In this context, we will further our work & report elsewhere accordingly.

Conclusion

Experimental and analytical observations of plasma treated natural raw silk fiber have been carried out in DC glow discharge air Plasma to understand the impact of treatment time (viz., 5 minutes, 10 minutes & 20 minutes) on the surface properties. Morphological and structural changes of treated fibers have been investigated by various characterizing techniques such as XRD, ATR-FTIR, TGA, SEM, DRS (Absorbance, Transmittance) and Universal Testing Machine. Plasma treated fibers are compared with the raw fibres. The XRD studies revealed that surface crystallinity index is

decreased due to plasma etching. The ATR-FTIR reveals that the characteristic value in the spectra i.e., transmittance increases after plasma treatment and it is seen to be maximum for 20 minutes treatment time. However, it does not affect the chemical composition of the fiber. SEM micrographs show that the micro roughness increases and dry degumming process takes place after plasma treatment. It is observed that exposure to more treatment time enhances the surface dents, holes & grooves. This is leading to decrease in crystallinity index; also confirmed by XRD results. This is considered to be an effective result as due to the roughness property, specific surface area increases and leads to more adhesiveness of the silk fiber. EDS shows that carbon content increases and oxygen content decreases after plasma treatment. The absorbance of plasma treated silk fibers increases with increasing exposure time. It is also observed that plasma treated silk fibers (20 minutes plasma exposure time shows maximum UV protection) are acquiring resistance to UV radiation. More importantly, it is also confirmed that the mechanical property of the silk fiber changes with the plasma treatment time. Overall, it is seen that plasma treated samples with more exposure time shows better surface modification in terms of adhesiveness, thermal resistance, UV protection and tensile strength. Hence, it is suggested that low temperature glow discharge air plasma with the optimum exposure time may be an effective, low cost, less time consuming, water saving and environment friendly technique to enhance the silk fiber properties.

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