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Effect of dielectric barrier discharge parameters on properties of mulberry silk fibre

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A dielectric barrier discharge reactor operated at atmospheric pressure has been used to modify the properties of plain woven silk fabrics. Operating parameters, such as treatment time, and the intensity of current across the electrodes has been changed in the presence of air as a plasma gas. Properties such as wickability, absorbency, tensile strength, tear strength, dyeability measurements; Fourier transform infrared spectroscopy FTIR analysis; and surface topology investigations have been carried out in this study. The findings reveal that the plasma treatment results in surface etching and generation of new functional groups mainly oxygen and oxygen-containing groups. Newly formed functional groups contribute to the improvement in water absorbency and the rate of vertical wicking on silk stripe. Selected acid and basic dye uptakes on treated samples are found to increase almost linearly, but the values decrease with the increase in treatment duration at a higher discharge current. A slight increase in tensile and tear strength is observed in air plasma treated silk fabrics. Air plasma treatment of silk fabric in high energy barrier discharge results in an increase in yellowness. SEM micrographs clearly confirm the formation of ripple like surface morphology in the form of micro-roughness created by etching effect of active species of air plasma.

Keywords: Colour yield, Dielectric barrier discharge, Silk fabric, Tensile strength, Whiteness

1 Introduction

As a unique material with an exquisite performance and superior properties, silk fibre is a popular material for apparel manufacturing in the world[1]. The main components of raw silk fibres include a core of fibroin (a highly crystalline fibrous protein) involved in a sheet of a gummy protein known as sericin. The sericin constitutes about 30% (in weight), of raw silk and, it must be removed from the raw silk fibre before apparel manufacturing to explore its unique properties. In industrial processing, the removal of sericin (degumming) is performed in a water bath at high temperature with the help of soap[2]. From last few years, extensive research is being carried out on the plasma treatment of natural silk fibres to modify their dyeing properties & printing properties, tensile properties, shrink resistance, flame-retardant, anti-bacterial properties, biocompatibility, and hydrophilicity[3]. Plasma treatment is a surface modification technique, mainly used to achieve surface change on the fibrous material by creating the functional groups on the fibre surface and by changing the topography of the fibres[4, 5]. Exposure to suitable plasma is able to alter the uppermost atomic layers of the material surface, while leaving the desirable bulk properties unaffected[6-8]. In addition, the plasma process itself is rapid and environmentally amenable, involving no chemicals to achieve surface modification without having significant effect in the bulk of the fabric fibres[9-12].

The plasma effect can be tuned to a significant degree by varying the conditions of treatment (discharge current density, plasma processing gas pressure and gas flow rate, kind of plasma forming medium, and the position of material to be treated relative to the electrodes)[13]. Nitrogen, oxygen and argon are often used in cold plasma devices. In the case of oxygen, two reactions exist simultaneously, namely (i) etching of polymer surface due to formation volatile products, resulted from the reaction between oxygen atoms and surface carbon atoms, and (ii) formation of oxygen-containing functional groups on polymer surface due to reactions of active species in plasma and surface atoms[14]. All newly generated radicals can take part in subsequent reactions such as introducing functional groups, forming cross-linking construction, etc. These succeeding reactions are especially important in surface modification of fibrous materials[15]. There is a growing interest in the investigation of the industrial application of barrier discharge technology due to its several advantages over

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another type of discharges. Dielectric barrier discharge (DBD) plasma reactor is simple in construction in many cases require no vacuum system and can be effectively used for the processing of large samples[16].

In the present work, an attempt has been made to enhance the physical and chemical properties of silk fibres by treating them in a DBD plasma reactor by using air as plasma gas. Treatment parameters such as exposure duration and current across the electrodes has been changed in order to modify the chemical and physical properties of mulberry silk fibre, and then effects on whiteness, yellowness, water wicking height and colour yield of acid and basic dyes are studied.

2 Materials and Methods

2.1 Materials

Commercially available plain woven, degummed, 100 % mulberry silk fabric (warp count of 20 denier and, weft count of 40 denier) with average weight of 45 gm^{-2}, supplied by Piyush Syndicate (Mumbai, India), was used for the study. Before the plasma treatment, to minimise the chances of contamination, silk fabric was washed with 0.5 % non-ionic detergent solution (Enkamole LFS, Yogeshwar Chemical Ltd. India) at 50 ^oC water for 30 min, then rinsed with plain water for another 15 min, and finally dried at ambient temperature.

2.2 Plasma Treatment

Plasma treatment of silk fabrics was carried out in a DBD plasma reactor, designed by Facilitation Centre for Industrial Plasma Technologies, India. The reactor is equipped with an Al_2O_3 ceramic electrode with active area 40 cm × 50 cm and a high power supply unit (500 W). The gap between the electrodes could be adjusted in the range of 0.5–2.5 mm. However, the gap between electrodes was kept 2 mm and the air was used as plasma gas for the treatment of silk fabric. The silk fabric was treated with 2.5, 3.0 and 3.5 kV electrode current for 2.5 min, 5.0 min and 7.5 min respectively, and then the samples were conditioned in 65 % RH (relative humidity) at 27 ± 2 ^oC before use.

2.3 Dyeing

Untreated and treated samples were dyed with acid dyes (Acid Blue 37 and Acid Red 48) and basic dyes (Basic Blue 7 and Basic Red 12), supplied by Coloutex Industries Ltd, India, by classical exhaustion method in a laboratory rota dyer machine manufactured by Tex Lab Industries, India. The dye solutions were prepared by dissolving 1 g of dye powder in 100 mL hot distilled water, and then the samples were dyed in 1.5 % (o.w.f) shade with material-to-liquor ratio of 1:30. The dye-baths for acid and basic dyes were set with required quantity of water, and acetic acid to maintain the pH of bath 3.5 – 4.0. The untreated and treated samples were kept in their respective bath and temperature was raised to 40 ^oC at 3 ^oC min^{-1} rate. The addition of required quantity of dyes was made and the temperature was raised to 80 ^oC at the rate of 3 ^oC min^{-1}. The samples were allowed to remain in those conditions for 60 min, and after complete exhaustion of dye-bath the samples were mild washed in a bath containing 2 gL^{-1} non-ionic detergent at 50 ^oC for 30 min, followed by washing with cold distilled water and then drying at ambient temperature.

2.4 Testing and Analysis

2.4.1 Absorbency

To study the effect of air plasma treatment on the water absorbency of silk fabric, the wettability of untreated and treated silk fabrics were evaluated according to the AATCC standard test methods 79:2007.

2.4.2 Wicking Height

The test for the wicking behaviour of treated and untreated samples was carried out according to the German standard test method DIN 53924. The wicking heights of untreated and treated samples were measured in warp and weft directions and average values were reported

2.4.3 Whiteness and Yellowness

Measurement of whiteness and yellowness indices of untreated and air plasma treated silk fabrics was carried out with the help of Macbeth colorage 3000 spectrophotometer with 10^o observer under the D_{65} light source. Each sample was scanned for four times and average of whiteness index was expressed according to the CIE, ASTMD1925 equation and yellowness according to the TAPPI 452/ISO2470 equation.

2.4.4 Tensile Strength

Analysis of tensile strength of untreated and treated silk samples was done according to the ASTM D5035 (1995) standard test method with the help of Instron tester, after conditioning the fabric samples at 65 ± 2 % RH and 27 ± 2 ^oC temperature for 24 h.

2.4.5 Tear Strength

Comparison of the tear strength of untreated and treated samples was carried out with "Elma-tear tear strength tester (James and Heal Co. UK) according to the IS 6489-1971standard test method.

2.4.6 Colour Yield (K/S)

Dyeing behaviour of acid and basic dyes on treated samples was studied by comparing the colour yield of acid dyes and basic dyes on untreated and treated samples. Macbeth colorage 3000 spectrophotometer with colour lab software was used to measure the *K*/*S* values of acid and basic dyed silk samples. The colour yield expressed in terms of *K*/*S* value according to Kubelka Munk equation.

2.4.7 FTIR Analysis

In order to determine the surface functional group changes caused by air plasma treatment, infrared spectroscopy assessment was carried out by using FTIR instrument (Shimadzu 8400, Japan) in ATR sampling method at 1 cm^{-1} resolution. An average of 15 scans was recorded in the %T (transmittance) mode in the range of 4000-600 cm^{-1}.

2.4.8 SEM Study

The change in surface morphology of treated samples was investigated using scanning electron microscope (JEOL-5400, Japan). The samples were sputtered with gold particles to avoid opacity. The surface morphology of untreated and treated samples was observed at a magnification ranging from ×1000 to ×5000 times.

3 Results and Discussion

3.1 Absorbency

Water absorbency of untreated and treated samples was measured immediately after treatment and results are shown in Table 1. The air plasma treatment results in significant improvement in liquid absorbency due the chemical as well as physical modification of silk. The absorbency time of treated silk is decreased from 118 s to 14 s. High energetic discharge over the surface of silk fibre results in the modification of surface topology as well as surface free energy. The fundamental mechanism of dielectric emission operated at the ambient temperature is to oxidise the surface of the material. Oxidation of the surface by oxygen present in the atmospheric air leads to the generation of oxygen and oxygen-containing groups (O=N-C, C=O, O-C-O, and OCOO) in the polymeric materials[17]. The newly formed oxygen-containing groups may cause increase in the surface free energy which leads to the decreased absorbency time of air plasma treated silk[18]. However, treatment of silk in high energy discharge field causes dramatic change in the surface morphology. The SEM micrographs evidence that the roughness of the surface improves and micro cracks are created, which may allow a path for the rapid penetration of liquid into the core of the silk fibre[19].

Table 1 — Water absorbency behaviour of untreated and treated silk fabric

Electrode current, kV	Treatment duration, min	Absorbency duration, s
Untreated silk	0.00	118
2.5	2.5	14
	5.0	15
	7.5	16
3.0	2.5	19
	5.0	14
	7.5	15
3.5	2.5	17
	5.0	18
	7.5	17

3.2 Wicking Height Study

In order to study the hydrophilicity characteristics of treated silk fabric, the wicking height is compared with untreated silk. The results obtained are found to be very similar to the absorbency behaviour of treated silk samples. The rate of capillary rise is found rapid for all treated silk strips, and height of capillary rise is found high as compared to the untreated silk strip. Figure 1 shows the difference, in wicking height of untreated and treated samples. As shown in Fig. 1 (a-c),

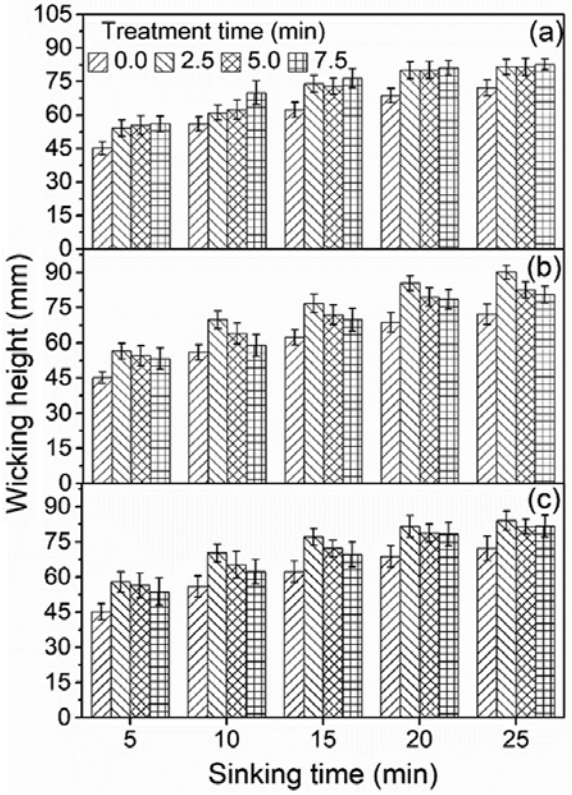

Fig. 1 — Wicking height of untreated and treated silk fabric at different treatment duration with 2.5 kV (a), 3.0 kV (b), and 3.5 kV (c) electrode current

when the treatment voltage is 2.5 kV the capillary height is much higher in the sample treated for 7.5 min as compared to the untreated samples; no significant difference is observed for the samples treated for 5.0 min and 2.5 min. However, the wicking behaviour of silk treated with 3.0 kV and 3.5 kV electrode current is found different from the samples treated with 2.5 kV electrode current. The capillary height of silk stripe treated with 3.0 kV and 3.5 kV electrode current for 2.5 min is found higher as compared to the stripes treated for 5.0 min and 7.5 min. The increase in wicking height due to short treatment durations in high energetic discharge conditions (3.0 and 3.5 kV) might be attributed to the rapid change in first few layers in the order of few seconds[20]. However, extended exposure duration at the higher energetic discharge lead to degradation of the surface of the fibre by erosion. Treatment at lower energetic discharge leads to the less rate of erosion of fibre surface, and hence in this case, the capillary height is a function of exposure duration; that is, a longer duration of treatment results in significant increase in capillary height. These observations suggest that with increasing voltage across the electrodes, the silk fibres may become more hydrophilic. This could be explained by the facts that the increase in discharge power results in an increase in number of reactive plasma species. Since wettability is a prerequisite for wicking, a liquid that does not wet fibres cannot wick into a fabric. Moreover, due to plasma etching effect, the effective pores present in the silk fibres may reduce the capillary pressure, thus increasing the wicking ability[21, 22]. The presence of more plasma species leads to the increased wettability and/or an increased wicking ability due to a more intense bombardment on the fibre surface[23]. These aspects are further explored by performing SEM micrograph and infrared spectrum measurements, to observe the chemical and physical properties of the air plasma-treated silk.

3.3 Whiteness and Yellowness

The dependency of whiteness and yellowness of silk samples on the electrode current and treatment time with air plasma is illustrated in Fig. 2. It is clear that DBD emission causes a slight yellowing as compared to the untreated silk fabric. When the exposure time of high energy discharge treatment is prolonged, the degree of yellowness increases and whiteness decreases accordingly. This might be due to the pyrolysis and oxidation of the surface components[24]. The untreated silk fabric sample has the lowest yellowness while the fabric sample exposed to longer duration and high electric discharge (3.5 kV for 7.5 min) shows the highest yellowness index values. However, the overall changes in yellowness and whiteness are not so obvious when the current of high energy barrier discharge treatment increases from 2.5 kV to 3.5 kV electrode voltage and time from 2.5 min to 7.5 min. It is observed that the oxygen (present in air) damages the fibre surface after a certain period. The longer the exposure time, the greater will be the fibre damage. Hence, the degree of yellowness and whiteness are dependent on the treatment conditions, such as treatment time, plasma gas and voltage across the electrodes[24,25]. It could be assumed that the ratio of specific light absorption and scattering coefficient is lowered because of rough surface, and hence the whiteness of the treated fabric decreases to a certain extent.

3.4 Tensile Strength

Tensile strength is one of the important properties in the quality of treated fabric. Hence, the tensile strength of treated samples has been compared with that of the untreated fabric. The variation in tensile strength of untreated and treated samples as a function of treatment time and the voltage across the electrodes are given in Table 2. It is evidenced that on several occasions the tensile strength of treated sample is slightly higher than that of the untreated silk samples.

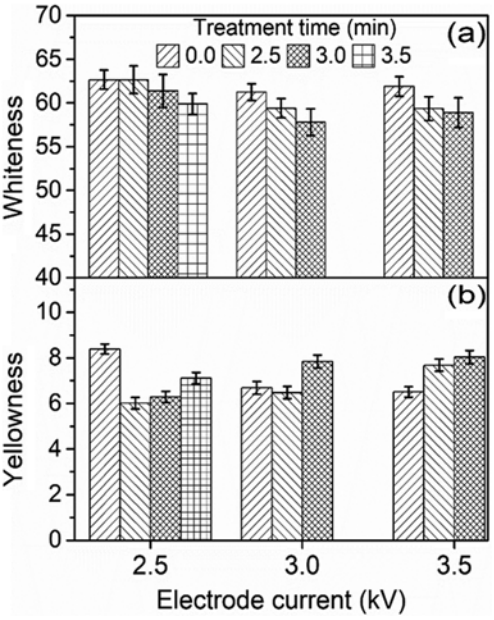

Fig. 2 — Effect of discharge current and treatment duration on whiteness (a), and yellowing property (b), of air plasma treated silk fabric

Table 2 — Tensile and tear strengths of untreated and treated silk fabric

Electrode current kV	Treatment duration min	Tensile strength N		Tear strength N	
		Warp	Weft	Warp	Weft
Untreated silk	0.0	304.00	416.78	10.06	10.65
2.5	2.5	310.39	427.22	10.19	19.60
	5.0	311.91	428.45	10.19	19.92
	7.5	313.12	430.11	10.10	13.63
3.0	2.5	310.99	428.86	10.19	21.61
	5.0	312.51	432.62	10.10	19.67
	7.5	311.31	419.62	10.18	20.73
3.5	2.5	312.21	431.78	10.10	22.74
	5.0	316.16	433.86	10.11	18.72
	7.5	310.53	429.27	10.18	15.78

The average value of the increase in tensile strength in the warp as well as weft directions is 2–3 %. However, treatment with higher electrode current results in serious degradation of fibre surface, and hence the tensile strength of plasma treated samples at 3.0–3.5 kV electrode current for a longer duration (7.5 min) is found slightly lower than that treated for short durations (2.5 and 5.0 min). The increment might be due to the formation of polar groups (enhancement of carbon content) and also functional units C-O, C-O-C, C-C, C-H, C=N and OCOO on the treated fibres. However, exposure time of 7.5 min at a voltage from 3.0 kV to 3.5 kV, the tensile strength decreases up to 2.2 %. This reduction in tensile strength might be due to a decrease in carbon content and C-O, C-O-C, C-C, C-H and C=N units in the fibre when treated for a longer time[26]. By the action of air plasma on the silk fibre surface, these groups are responsible for an increase in inter-fibre cohesion and, in consequence, the better mechanical properties[27, 28]. In addition, with the change in functional group, the change in surface topography is also responsible for the slight increase in the tensile strength[27]. From the SEM micrographs, it is evidenced that the high energy discharge over the silk results in the surface erosion and, hence roughness of the surface is increased. The increase in the surface roughness leads to the adhesion of fibres and yarn. However, the effect of plasma surface erosion is limited to nanoscale depth and, therefore it does not affect the tensile strength negatively[28]. Treatment for longer duration leads to the serious erosion of fibre surface, and hence the tensile strength is changed negatively.

3.5 Tear Strength

The tear strength of untreated and air plasma treated silk fabrics under different discharge current is shown in Table 2. The findings reveal the slight improvement in tear strength of silk fabric. The tear strength of treated samples is increased 0.25-0.45 % both in warp and weft directions, as compared to untreated samples. The highest strength is observed when the duration of treatment is 2.5–5.0 min for 2.5–3.5 kV respectively. As discussed in the previous section, the increase in tear strength might be due the increased inter-yarn and inter-fibre friction, because the surface modification by the plasma treatment restricts the sliding action of yarn during tearing, and thereby increasing the fabrics tearing strength[29]. A slight reduction in tear strength is observed when silk samples are treated for 7.5 min at 2.5 kV - 3.5 kV. Treatment at a higher voltage for longer duration may cause serious damage to the surface of silk fabric, therefore causing reduction in tear strength[30].

Table 3 — Colour yield K/S of untreated and air plasma treated silk fabrics dyed in 1.5 % o.w.f shade with acid and basic dyes

Electrode current kV	Treatment duration min	*K*/*S* values			
		Basic Blue 7	Basic Red 12	Acid Blue 37	Acid Red 48
Untreated silk	0.0	75.24	32.64	20.70	25.46
2.5	2.5	77.84	33.91	21.33	28.41
	5.0	79.74	35.30	23.31	27.21
	7.5	82.83	36.89	25.11	27.01
3.0	2.5	80.54	39.34	20.90	30.62
	5.0	78.01	36.64	22.20	26.70
	7.5	75.99	33.20	20.35	28.07
3.5	2.5	75.99	33.29	21.69	28.85
	5.0	75.84	33.58	22.09	26.12
	7.5	75.72	38.95	20.20	25.55

3.6 Colour Yield

Effect of discharge current and exposure duration during plasma treatment on the colour yield of silk fabric dyed with acid dyes and basic dyes in 1.5% (o.w.f) shade is illustrated in Table 3. It is observed that the colour yield of silk fabric improves after air plasma treatment. Plasma treatment at an ambient temperature in a higher electrical discharge leads to the formation of microcracks and voids over the surface of protein fibre[31, 32]. Since the micro fibroins of silk are made from highly ordered crystalline region of the native protein and peptide bridge[33], the extended stiff protein chains act as a barrier for the reactant products such as dye molecules and finishing chemicals during diffusion inside the fibre structure. Therefore, the reaction only takes place in the amorphous region as well as functional groups present over the surface of the crystalline region. The newly formed cracks and grooves on the surface of protein fibre expose the axial polymeric chain to react with the acid and basic dye

molecules. The formed voids on the fibre structure allow a path for the rapid diffusion of dye molecules inside the fibre structure[12, 34].

As shown in Table 3, the colour yield behaviour of acid and basic dyes on treated silk shows the identical behaviour. However, it is observed that the high electric discharge for 2.5 min exposure duration results in significant increase in colour yield for all acid as well as basic dyes. Longer exposure duration at high electrode current results in the serious degradation of the silk and some polar groups might be lost. Hence, the colour yield of acid and basic dyes remains less, as compared to the samples treated at 2.5 kV electrical discharge. In addition, the root cause for the enhanced colour yield increase by plasma treatment may be governed by the improved absorbency, increased surface area of fibre and creation of reactive sites for Acid and Basic dyes[35]. The higher hydrophilicity of the fibre produces a faster adsorption and diffusion of the dyestuff from the dye bath to the fibre. The increased number of hydrophilic groups allows a higher number of molecules to bind to the fibre surface[3, 24].

3.7 FTIR Analysis

FTIR measurement is a simple method to characterise the functional groups in the outermost layer of silk fibres. Hence, FTIR analyses were performed on untreated and treated samples, and their corresponding spectra are shown in Fig. 3. The FTIR spectra show characteristics bands at 1622 cm^{-1} (amide I), which are due to the β confirmation of the crystalline region, while the band appearing at 1515 cm^{-1} (amide II) is due to the random coil conformation of fibroin molecules[3]. The peaks that appeared at 1224 and 1440 cm^{-1} are attributed to the presence of an amino acid group of CH-stretching of CH_3 deformation of the silk. The peak positioned at 975 cm^{-1} signifies the Ala-Ala linkages in the crystalline position of the silk; whereas the band at 1058 cm^{-1} appears due to the presence of the Gly-Ala peptide chain of silk fibre[36]. Moreover, the appearance of the absorption bands at 3288 cm^{-1} is caused by the free-OH stretching and NH- stretching vibrations[3, 37]. CH_4 groups of alanine exhibit an absorption peak at 1440 cm^{-1}. From the spectra, it is apparent that after air plasma treatment in high electrical discharge (2.5–3.5 kV) for different durations (2.5–7.5 min), a significant change in peak positions and intensity is observed in the wavenumber region of 1622 cm^{-1} - 1620 cm^{-1} corresponding to amide I β-sheet band, which reflects

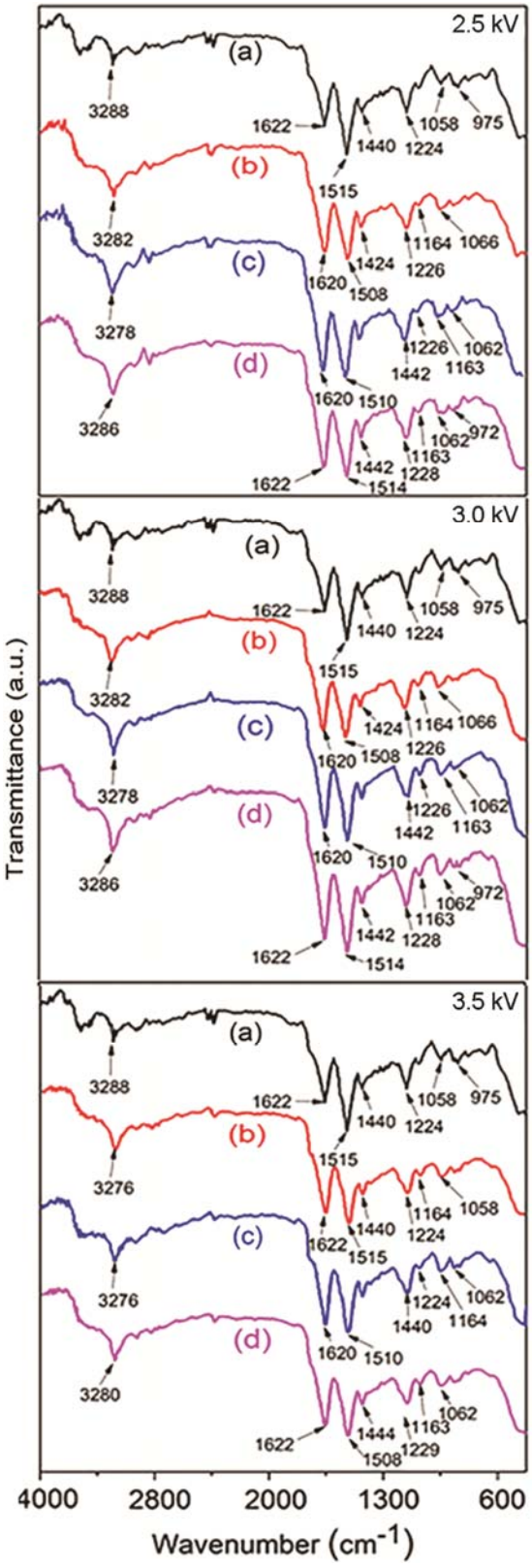

Fig. 3 — FTIR spectra of plasma and treated silk fabric with 2.5 kV (I), 3.0 kV (II), and 3.5 kV (III) electrode current (a) untreated silk, (b) treated for 2.5 min, (c) 5.0 min, (d) 7.5 min

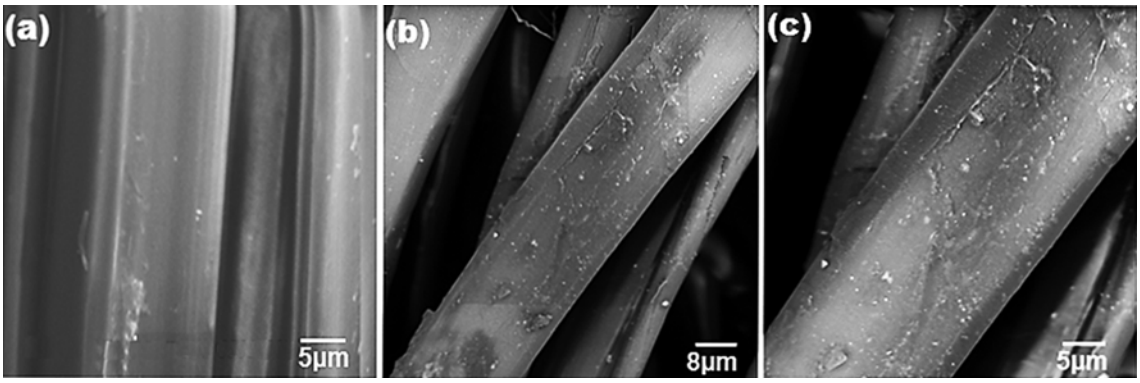

Fig. 4 — Micrographs of untreated silk (a), air plasma treated with 2.5 kV for 7.5 min at ×3000 magnification (b), and ×5000 magnification (c)

the increase in β-sheet structure of treated silk. A dramatical change is observed at amide II random coil band. The peak corresponding to amide II at 1515 cm^{-1} shifts towards 1510 cm^{-1}. It confirms that the random coil β-sheet is destructed after plasma treatment. This indicates that in the present investigation, the air plasma treatment significantly affects the chemical composition of fibres. However, for the untreated silk fibre, the intensity of the bands at 3200 cm^{-1} is higher than those of all the plasma-treated silk fibres. This may be attributed to the breakage of some of the H-bonded amide groups due to energetic ion bombardment to the substrate[35].

3.8 SEM Study

Plasma treatment can induce a substantial change in the morphology of fibre surface especially enhancing its surface roughness and consequently improving surface energy, wettability, dyeability and other mechanical properties. Therefore, SEM micrographs were observed to comprehend the alteration of surface morphology of untreated and treated fibres. It is found that 2.5 kV exposure for 7.5 min of air plasma treatment time shows improvement in overall properties of silk. Thus, the SEM image of air plasma-treated silk fabric with 2.5 kV for 7.5 min treatment time has been selected for study and their corresponding micrographs are shown in Fig. 4. It is observed from Fig. 4(a) that the untreated silk fibre surface shows smooth, uniform and free from roughness. The surface topography of silk fibre is uniformly modified in the form of the ripple-like structure of sub nano size as shown in Figs 4 (b) and (c). Treatment of silk with highly reactive plasma species, promotes ablation (etching) of surface and leads to increased roughness and change in other surface properties such as hydrophilicity and mechanical properties. Therefore, the water absorbency, water wick-ability, tensile strength, tear strength, and dyeability of individual fibres are improved after air plasma treatment. The change in silk fibre surface appearance might be due to the localised erosion of the surface layer, causing a surface damage[38, 39]. The presence of nanopores on the fibre surface indicates this predominant effect of the interaction of air plasma (chemical etching) with the fibre surface. The differential etching of crystalline and amorphous regions might be the origin of the roughness. Beside the etching process, the bombardment of the highly energetic electrons on the fibre surfaces during plasmatic discharge leads to the formation of new functional groups by interacting with nitrogen and oxygen-related molecules. This process leads to the almost complete breakdown of the relatively small number of molecules on the fibre surface into a very low molecular components[24].

4 Conclusion

As expected air plasma treatment by using DBD plasma reactor results in considerable improvement in silk fibre properties due to surface erosion under the experimental conditions used. Treatment at 2.5–3.0 kV for 2.5 min results in significant improvement in absorbency and wicking behaviour. Treatment at higher electrode current for longer duration causes adverse effect on the surface whiteness, tensile strength, tear strength and colour yield of fabrics dyed with Acid and Basic dyes. However, overall performance is found considerably higher than the untreated silk fabric, even after treatment at higher current for a longer duration. The dyeing behaviours of acid and basic dyes on the treated samples show significant improvement in colour yield. The result evidenced that air plasma treatment in a high energy barrier discharge reactor has the potential to enhance the dyeing performance of acid and basic dyes. Air

plasma treatment at high electrical discharge results in 2 % increase in tensile strength and 3 % increase in tear strength due to increased surface roughness. Treatment conditions such discharge current and duration of treatment have a considerable impact on silk fibre properties. Silk fibre properties treated with 2.5 kV and 3.0 kV discharge are not affected significantly even after treatment for 7.5 min. Hence, under experimental conditions used in this study, these electrode currents are considered as the suitable discharge current for effective modification of silk fibre properties.

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