Effect of Plasma Treatment on Physico-chemical Properties of Cotton

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***Abstract*—Plasma, an ionized gas composed of ions, electrons, photons, UV-radiation and neutral active species can be used for nano-scale surface modification of textile substrates without using water. Among the various types of plasma, only atmospheric pressure cold plasma (non-thermal plasma) is suitable for surface modification of heat sensitive polymeric textile substrates in a continuous manner. In the present study, atmospheric pressure cold plasma was generated in the presence of helium (He) and helium-oxygen (He/O_2) mixture, and cotton fabric was plasma treated for 30 s to 4 min. The plasma treated fabric was found to be more hydrophilic in nature as exhibited by its wicking property due to generation of more hydrophilic groups resulting in better water transport, even though the treatment was found to increase the surface crystalline index (CI) of cotton. In the He plasma treated sample, formation of radicals was more. The improvement in colour value in terms of K/S, a and c in case of He/O_2 plasma treated samples for 2 and 4 min was also noted. The observations made in the study have been explained from the analysis of EDX, ATR-FTIR, ESR and SEM studies on both the untreated and plasma treated cotton textiles.**

Key words: Plasma, Cotton, Textile, Radical formation, Colouration

I. INTRODUCTION

Wet chemical processing of textile is very important as it imparts highest value to the textile substrate. However, the process is water and energy intensive. As such, to process a Kg of cotton textile roughly 100 litres of water is used, which is finally discharged as an effluent contaminated with unused colouring material and chemicals. It is well-known that the discharge of effluent in the water streams has a serious impact on flora and fauna, besides affecting the fertility of agricultural land. Shortage of water soon will have a serious adverse impact in textile chemical processing. Therefore, textile industries are now slowly gearing up towards implementing waterless or low water based processing technologies, such as digital printing, spray and foam finishing and plasma processing. The main attraction of plasma in industrial application is to avoid the chemical effluents. Other advantages are saving large quantities of water, chemicals and energy [1-3]. Plasma, an ionized gas can be used for nano-scale surface engineering of textiles by attaching a small molecule like oxygen, nitrogen, fluorine, or by plasma reaction of big molecules containing hydroxyl, carbonyl, carboxyl and acrylate group. Generation of radicals on the fibre surface followed by plasma reaction of a precursor has been reported to help in developing advanced textiles with water and oil repellency, hydrophilic, antimicrobial, flame retardant and UV-protective properties [4-6]. Plasma processing of textiles can also be used in improving dyeing, printing and surface adhesion strength [7-8]. Mainly, the low-pressure plasma has been explored for such applications. However, the process technology has not been commercialized for textile processing because of its several inherent limitations. On the other hand, the atmospheric pressure plasma is an emerging technology that can overcome the limitations of low-pressure plasma technology and therefore, it is gaining attention in the research community. Plasma has been reported to impart hydrophobic to super-hydrophobic functionality in the hydrophilic textile [9-10]. It has also been used for imparting hydrophilic functionalization in the otherwise hydrophobic nylon, polyester and polypropylene textile [11]. Plasma pre-treatment on protein fibre such as wool for improvement in colouration and felting has also been reported [12]. However, little information is available on the plasma treatment of the cellulosic textile, like cotton except some research improvement in colouration, crease recovery, desizing and scouring [13-15].

In the present study, atmospheric pressure plasma was generated in the presence of helium (He) and helium-oxygen (He/O_2) to treat and study its effect on physical and chemical properties, and colouration of cotton (cellulose) textiles. Postulations supported by the various scientific analyses have been made for the changes brought out in cotton textiles by plasma treatment and presented.

II. MATERIALS AND METHODS

A. Materials

A desized and bleached 100% cotton woven fabric with an areal density of 123 g/m^2 having 110 ends per inch (EPI) in the vertical direction (warp) and 90 picks per inch (PPI) in the horizontal direction (weft) was used in the study. Before plasma treatment, the fabric was rinsed in acetone and dried in an air oven at 90°C for 10 min to remove contamination and trapped moisture from the textile structure. Different gases used in this study were bought from Alchemie gases Pvt. Ltd.

B. Plasma treatment

Plasma treatment was carried out in an indigenously developed atmospheric pressure plasma reactor in the presence of helium (He) and He/O_2 gases. Plasma was generated between two rectangular aluminium electrodes of size 7×6 cm^2 at discharge voltage and frequency of 3.8-4.2 kV and 21.8 kHz, respectively. Both the plasma electrodes were covered with Teflon dielectric sheets having 1 mm thickness. During He plasma treatment, the helium gas flow rate was kept at 450 ml/min, and for He/O_2 plasma treatment, He flow rate was kept at 400 ml/min and oxygen at 50 ml/min, i.e., a total gas flow rate of 450 ml/min using two mass flow controllers (Made by Alicat Scientific, USA). Textile samples were plasma treated for 30 s to 4 min both in the presence of He and He/O_2 gases.

C. Water wicking time

Water wicking time was measured by dipping a rectangular strip of the fabric sample in water. The fabric was dipped 1 cm in water and kept straight vertically by putting a weight at the bottom. The time for water to travel each centimetre in the vertical direction was recorded. Lesser the water wicking time, more the sample is hydrophilic and comfortable for apparel use.

D. Optical emission spectroscopy (OES) of plasma

Light emitted by the excited atoms and molecules over the wavelength of 300 to 900 nm was analyzed using an Optical Emission Spectrometer (OES), Mikropack model of PlasCalc 2000. Off-line analysis of the OES data was carried out using the Specline 2.1 software.

E. ATR-FTIR Spectroscopy of plasma treated samples

The ATR-FTIR analysis of the untreated and plasma treated samples was carried our in FTIR-Prestige 21 Shimadzu spectrometer with HATR multiple reflection accessory using ZnSe prism over the wavelength of 700 to 4500 cm^{-1}.

F. Electron Spin Resonance (ESR) analysis

Electron spin resonance (ESR) of both the untreated and the plasma treated samples were carried out in a JEOL ESR, Model JES - FA200 ESR Spectrometer with X and Q band to study the radical formation. During the measurement the various machine parameters were kept as follows: Standard Frequency (X band) - 8.75-9.65 GHz, Sensitivity - 7x109 spins/0.1mT, Frequency- 9131 MHz, Field centre- 275 mT, Power- 0.988 mW, Sweep time- 4.0 min, and Phase CH1=0.00 and CH2=0.00.

G. Scanning electron microscopy (SEM) and EDX analysis

The surfaces of both the untreated and the plasma treated samples were analyzed using a Scanning Electron Microscope, Model Philips XL 30. The samples were gold coated before the analysis. The energy dispersive X-ray (EDX) analysis of these samples was also carried out in a Field Emission Gun Scanning Electron Microscope (FEG-SEM).

H. Colouration of textile and measurement of colour parameters

The untreated and both the helium (He) plasma treated and the helium-oxygen (He/O_2) plasma treated samples were dyed using a cold reactive dye, namely Procion Brill Red M-5B. The shade percentage was 1 on the weight of the fabric. In the dyeing bath, 40 gpl of salt and 12 gpl of soda were added and the dyeing was carried out for an hour. Thereafter, the colour parameters such as K/S, L, a*, b*, c and h values were measured using a Perkin-Elmer double beam spectrophotometer of model Lambda 35 equipped with an integrating sphere. The depth of colour (shade) of the dyed fabrics was determined by colour strength (K/S) from the reflectance data using Kubelka– Munk equation as follows:

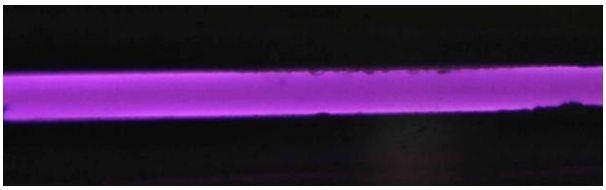
$$K/S = (1-R)^2 / (2R)$$

where, K is the absorption coefficient, S the scattering coefficient and R the reflectance of the treated fabric at a wavelength of the maximum absorption. K/S was determined at 540 nm (λ_{max}) of the respective dye. Other colour parameters such as L (lightness-darkness), a* (red-green), b* (blue-yellow), c (strength/saturation of a particular shade) and h (a particular shade) were measured using the Win lab software delta-E 1976.

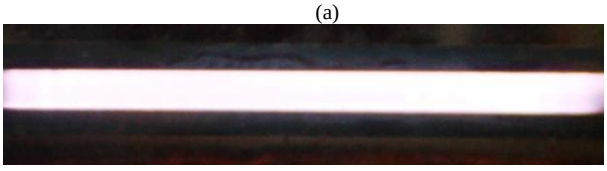
III. RESULTS AND DISCUSSION

A. Generation of plasma and its optical properties

Atmospheric pressure plasmas were produced in the presence of helium (He) and helium-oxygen (He/O_2) gaseous mixture. The colour of a particular plasma depends on the atomic and He molecular species present in the plasma zone as well as photons emitted by the excited species. As every gas has a distinct excitation level indicating a particular emission characteristic in the excited state, it produces a particular colour. For example, in the present study, when He gas was ionized, it gave a light bluish purple colour as shown in Figure 1(a). Visually, it looks like a glow plasma, free from any micro-discharge. However, when oxygen was introduced with He, it's color changed to milky white as shown in Figure 1(b); helium-oxygen (He/O_2) plasma was also found to be free from any micro-discharge.



(a)



(b)

Fig. 1: Colour of different plasmas such as: (a) Helium (He) and (b) He+oxygen (He/O_2)

Fig. 2 shows the OES spectrum of the He plasma. On ionization, He emits photons at different wavelengths such as at 706 nm, 655 nm, 667 nm, 587 nm, 727.5 nm, 388 nm, 356 nm, and 336 nm. Among the various atomic lines of helium (He) at different wavelengths, the He peak at 706 nm and 655 nm are the most prominent. The other peaks present in He spectrum, particularly in the wavelength of 300 to 500 nm are mainly due to the atomic lines of nitrogen. The presence of trace amount of nitrogen in He gas might have produced such peaks at lower wavelengths.

Fig. 3 plots the intensity of He 706 nm line with plasma discharge time during online analysis of plasma. It can be seen the intensity of He 706 nm line remains constant with the plasma discharge time. Since the emission intensity of a particular species is directly proportional to its concentration, this observation implies that ionization of helium happens uniformly at a steady state. Therefore, the glow plasma was

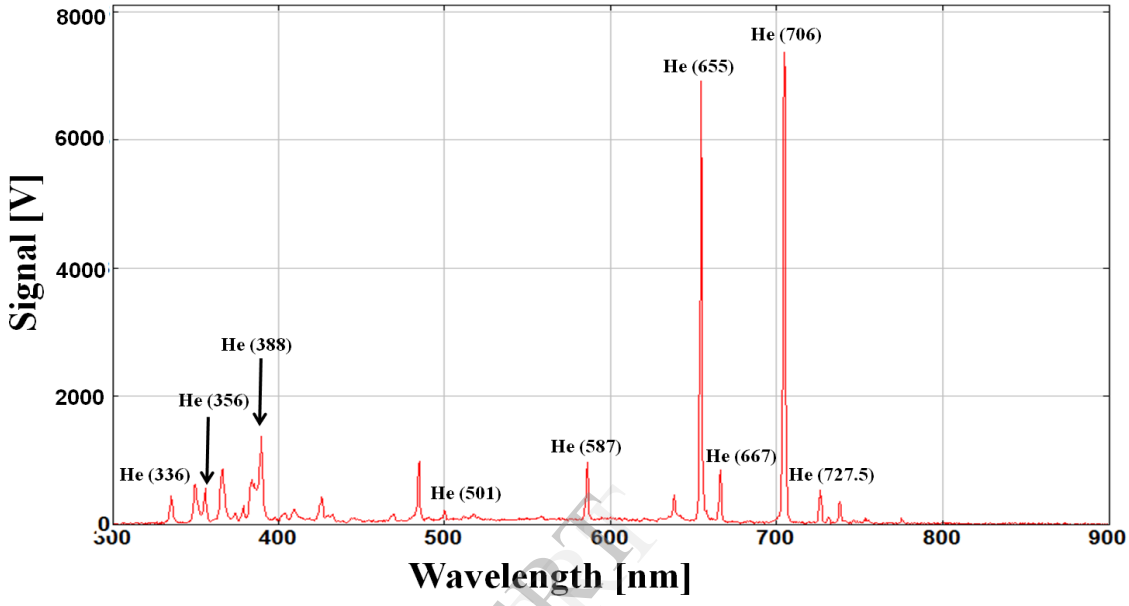


Fig. 2: Optical emission spectrum (OES) of helium (He) plasma

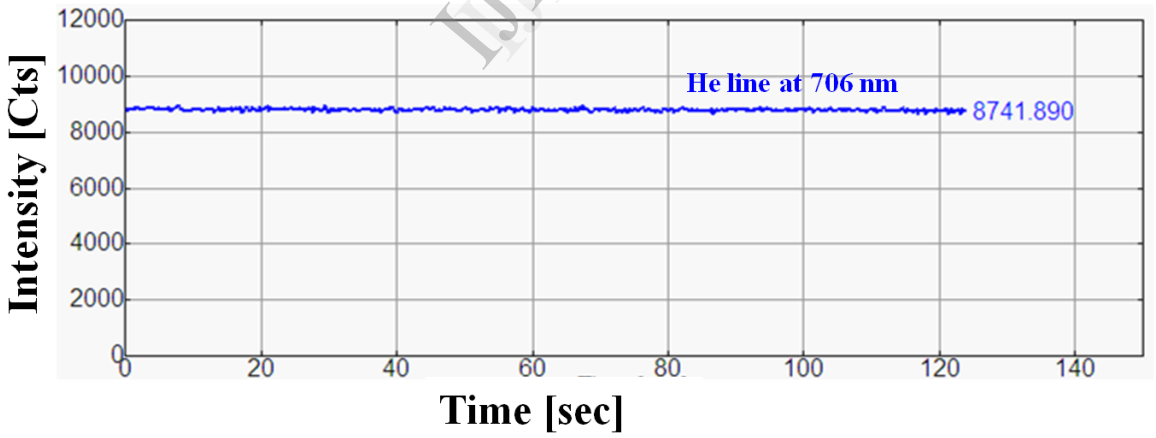


Fig. 3: Intensity of He atomic line at 706 nm with plasma discharge

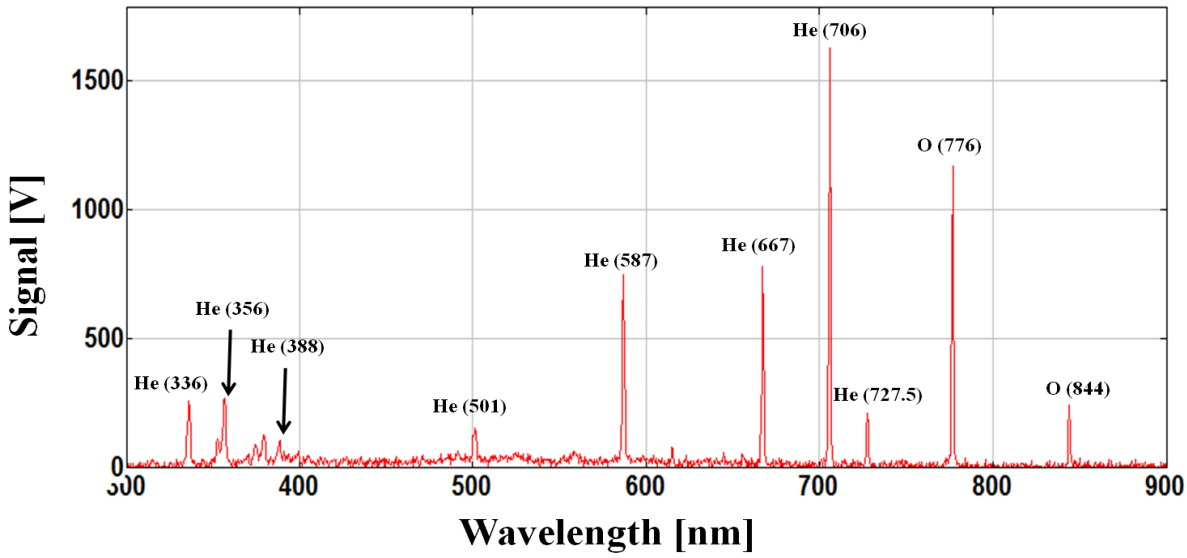


Fig. 4: Optical emission spectrum of helium-oxygen (He/O_2) plasma

established in a pure gas. The presence of any filaments or micro-discharges in plasma would have resulted in fluctuation of the intensity of He lines. In He/O_2 plasma, helium also showed a similar atomic emission like in the He plasma and oxygen showed atomic lines at 776 and 844 nm as shown in Figure 4. These are characteristic atomic lines of oxygen plasma. A similar result has also been reported in the literature [16]. It was interesting to observe that the strong atomic line of He at 655 nm in He plasma disappeared in He/O_2 plasma. Table 1 shows the ratio of intensity of the atomic lines of helium in He and He/O_2 plasmas. The ratio of He 706/587 nm lines was 7.6 in helium plasma, which decreased to 2.2 in He/O_2 plasma. Similarly, the ratio of He 706/667 nm lines decreased from 8.7 to 2.1. However, the ratio of He 667/587 nm lines slightly increased in case of He/O_2 plasma. This implies that helium ionizes in different patterns in pure helium as well as in a helium-oxygen mixture.

TABLE 1: Ratio of intensity of helium atomic lines in He and He/O_2 plasma

Different plasma	He 706/587	He 706/667	He 667/587
He Plasma (He)	7.6	8.7	0.87
He-Oxygen plasma (He/O_2)	2.2	2.1	1.0

B. Water wicking

Figure 5 presents the vertical water wicking property in the untreated and the 4 min plasma treated cotton woven fabrics. Cotton being pure cellulose in nature, it has good liquid absorbency and transport properties. It can be seen that water took nearly the same time to travel up to 2 cm vertically in the both untreated and plasma treated samples. However, water took more time (110 s) to travel up to 3 cm height in the untreated sample against 102 s and 99 s in the 4 min He and He/O_2 plasma treated samples, respectively.

It can also be seen the He/O_2 plasma treated samples took a bit lower time compared to the He plasma treated samples to travel the same height. A similar trend was observed through the wicking experiment. However, the He/O_2 plasma treated sample took slightly more time to travel up to 7 cm. The result showed the plasma treatment has helped in better liquid transport. This might be due to the etching of the cotton surface by plasma treatment as discussed for SEM analysis in section 3.6. Bombardment of high energy plasma species such as electron, ion and neutral active species on the cotton fibres and fabric might have increased the gaps between the fibres or opened some capillaries that promote vertical wicking of water. Besides, the formation of more oxygen containing polar groups such as carbonyl, carboxyl and hydroxyl on the surface of cotton fibre by oxidation of cellulosic polymer has also helped in better transport of water by capillary action.

C. EDX analysis

Fig. 6 depicts the energy dispersive X-ray images of both the untreated and plasma treated cotton samples. Cotton fibre after chemical treatment meant to remove fat, waxy and other contaminants become pure cellulose. As expected only atomic peaks of carbon (C) and oxygen (O) could be found in both the samples. The EDX can not identify hydrogen (H) atom. It can be seen (Fig. 6) that intensity of the peak height of oxygen is more in the plasma treated samples compared to the untreated sample. Table 2 shows the atomic percentage in the different samples. It can be seen that untreated cotton sample has 44.5% oxygen and

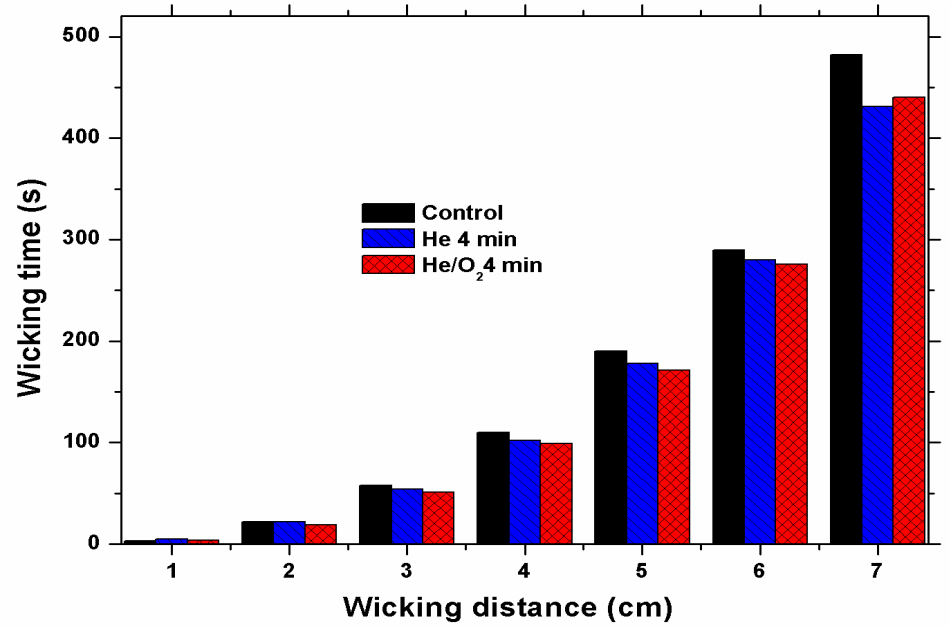


Fig. 5: Water wicking time in untreated and 4 min He and He/O_2 plasma treated cotton fabric

55.5% carbon, which is similar to the theoretical value of carbon and oxygen reported in the literature for the cellulosic substrates [9].

However, the oxygen percentages were found to increase to 48% and 48.2% in the He and He/O_2 plasma treated samples, respectively, corresponding to 3.5% and 3.7% increase in surface oxygen. In both He and He/O_2 plasma treated samples, ~3.5% more oxygen compared to control sample might have helped the formation of more oxygen containing molecules such as carbonyl, carboxyl and hydroxyl as discussed below. The formation of such polar groups could be ascribed to the better water wicking property observed in the case of plasma treated samples.

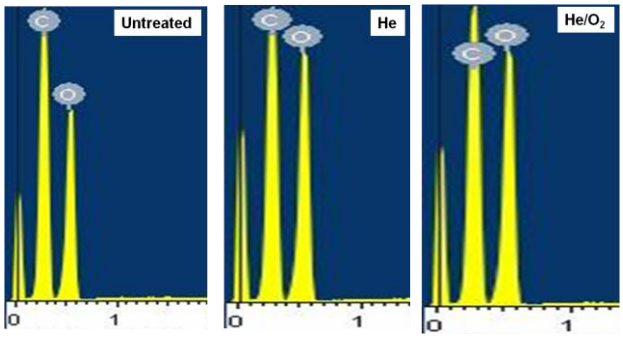


Fig. 6: EDX images of untreated and plasma treated cotton textiles

TABLE 2: Atomic percentage in the untreated, He plasma and He/O_2 plasma treated samples

Sample description	Atomic percentage	
	Carbon (C) %	Oxygen (O) %
Untreated (control)	55.5	44.5
He plasma treated	52	48
He/O_2 plasma treated	51.8	48.2

D. ATR-FTIR analysis

The changes in the surface molecules up to a few micrometers were studied in an attenuated total reflection-FTIR to investigate the effect of plasma treatment on cellulose chemistry. It can be seen from ATR-FTIR spectra (Fig. 7) that in all the plasma treated samples such as (b) 4 min He, (c) 2 min He/O_2, and (d) 4 min He/O_2 plasma, there are new peaks formed at 1710 cm^{-1} in contrast to no such peak in the untreated (control) sample. Denes et al., reported identification of a carbonyl peak that resulted from the oxidation of free radicals formed by the cleavage of C1-C2 bonds of the pyranosidic ring of cellulose by argon plasma treatment [17-19]. Similar observation was noted in our present study when the cotton samples were plasma treated in the presence of both helium (He) or He/O_2 plasmas. The intensity of this peak was found to be more in the case of 2 min He/O_2 plasma treated sample due to increase in cross-linking within the cellulosic chains. Besides, there was an increase in the intensity at 2850 cm^{-1}, attributed to methylene stretch. Also, there is a decrease in intensity of the –OH peak in the range of 3300-3400 cm^{-1}, which may be related to a decrease in trapped moisture in the fabric or dissociation of –OH group upon plasma treatment. However, there is an increase in intensity of the carboxylic acid –OH group at 3750 cm^{-1} in plasma treated samples due to the formation of carboxylic acid groups. From the ATR-FTIR analysis of individual spectrum intensities at different wavelengths for various plasma treated cotton fabric, the order of increasing intensity is as follows: 4 min He/O_2 plasma treated > 4 min He plasma > 2 min He/O_2 plasma > 2 min He plasma.

The absorbance at 1420 cm^{-1} (–CH_2 bending) and 893 cm^{-1} (–C–O stretching) are sensitive to the amount of the crystalline portion versus amorphous portion in the cellulosic substrate (Fig. 8). Broadening of these bands reflects more disordered structure of cellulose. The absorbance ratio at A1420 cm^{-1} and A893 cm^{-1} has been

defined as an empirical crystalline index (CI). In 1958, O'Connor proposed the term, Lateral Order Index (LOI, A1420/A893) to calculate the crystalline index (CI) for cellulose material [20]. Table 3 shows the crystalline index of the untreated and the plasma treated samples. It can be seen that the untreated sample has CI of 1.09, which increased to 1.23 and 3.27 in 2 and 4 min He plasma treated

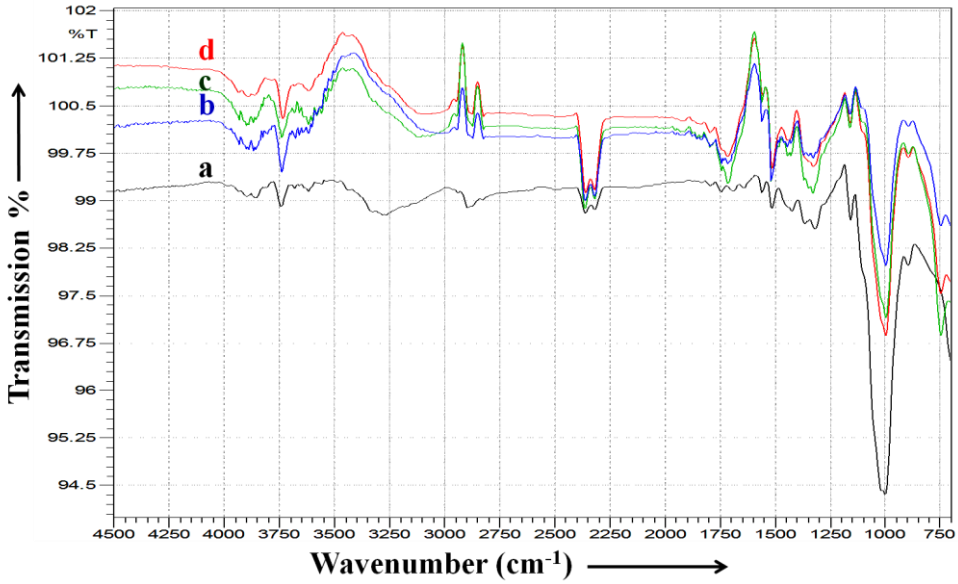


Fig. 7: ATR-FTIR spectra of different cotton fabrics: (a) untreated (b) 4 min He plasma treated (c) 2 min He/O_2 plasma treated and (d) 4 min He/O_2 plasma treated

samples, respectively. This corresponds to 12.8% and 200% increase in surface crystallinity. Similar improvement in CI was also observed in the He/O_2 plasma treated samples. The result indicates that the plasma treatment has increased surface crystallinity of cotton fibres. With increasing crystallinity, while the intensity of peak at 893 cm^{-1} decreases; the peak at 1420 cm^{-1} increases. Table 4 shows the normalized peak ratio of the different molecules of cellulose. It can be seen that the ratio of carbonyl peak at 1710 cm^{-1} increased in both 2 and 4 min He plasma treated samples. In the 2 min He/O_2 plasma treated sample, there was increase in the carbonyl peak. However, in the 4 min He/O_2 plasma treated sample, the peak ratio was similar to that of the untreated sample. It can be seen that the normalized peak ratio for –OH increased from 3.63 in the untreated sample to 4.57 in the 2 min He plasma treated sample; this corresponds to 25.9% increase in surface –OH groups. A similar result was also observed for the 4 min He plasma treated sample. In the He/O_2 plasma treated samples, the ratio was more compared to He plasma treated sample. There was 51 and 45.7% increase in surface –OH groups in 2 min and 4 min He/O_2 plasma treated samples, respectively. Similar improvement was also observed for –C–H asymmetric stretching at 2922 cm^{-1}. The increase in –C=O and –OH oxygen containing hydrophilic groups in the He and the He/O2 plasma treated samples have helped the cotton samples to be more hydrophilic. In the plasma treated sample water wicking time was found to be less, possibly due to formation of more hydrophilic groups on the surface.

E. Electron Spin Resonance (ESR) analysis

Electron spin resonance (ESR) was used to understand the free radical formation in various cotton textiles. In the untreated (control) sample, no ESR peak was found and the plot is almost a straight line parallel to X-axis ((Fig. 9). This is due to the fact that the saturated cellulosic polymer does not have any free radical. However, in both He and He/O_2 plasma treated samples there were ESR peak at a magnetic field strength of 326 mT with gyration (g) value of 2.00; similar result has also been reported in the literature for the cellulosic substrates [21-23]. The helium plasma treated cotton sample showed 5 lines in the spectrum due to triplets, while helium-oxygen (He/O_2) plasma treated sample showed only 3 lines due to duplets. The result indicates that in both He and He/O_2 plasma treated samples, there were significant formation of free radicals. As the intensity of the

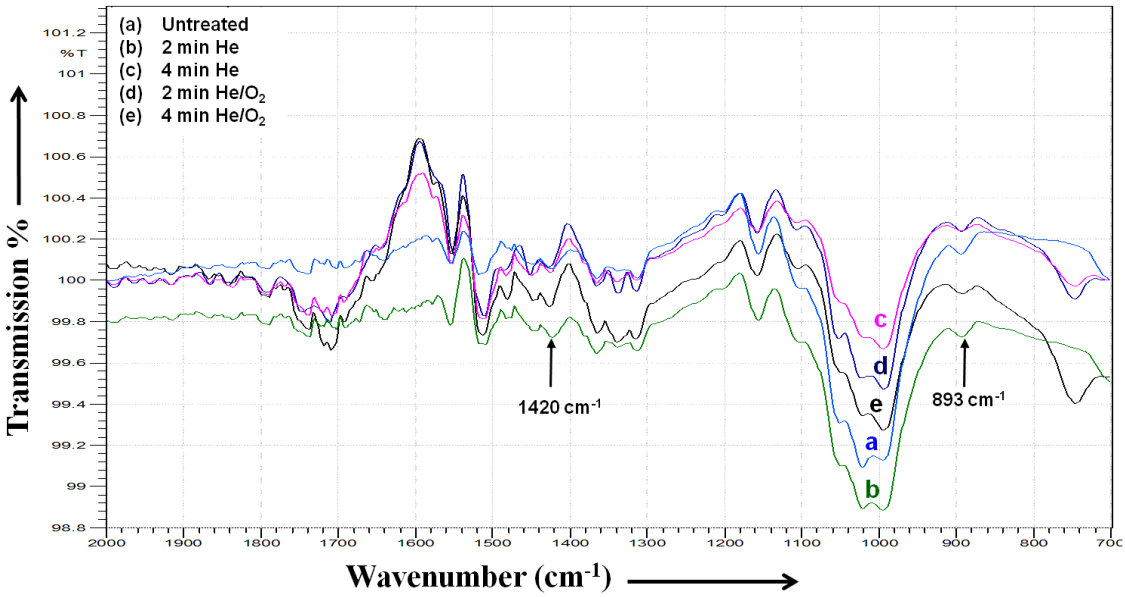


Fig. 8: High resolution ATR-FTIR spectra of the different cotton samples over the wavenumber of 700-2000 cm^{-1} : (a) untreated (b) 2 min He plasma treated (c) 4 min He plasma treated (d) 2 min He/O_2 plasma treated and (e) 4 min He/O_2 plasma treated

TABLE 3: Crystallinity Index (CI) for different cotton samples

Different samples	**Ratio of corrected intensities (A 1420 / A 893 cm^{-1})**	**Crystalline Index (CI)**
Untreated (Control)	0.0682/0.0626	1.09
2 min He plasma treated	0.0688/0.0559	1.23
4 min He plasma treated	0.0900/0.0275	3.27
2 min He/O_2 plasma treated	0.0883/0.0534	1.65
4 min He/O_2 plasma treated	0.1203/0.0396	3.04

TABLE 4: Normalized peak ratios of different molecules in untreated and plasma treated samples

Samples	**–C=O at 1710 cm^{-1}**	**–OH in 3300-3400 cm^{-1}**	**–C–H asymmetric stretching at 2922 cm^{-1}**
Untreated (control)	1.00	3.63	1.83
2 min He plasma	1.35	4.57	2.61
4 min He plasma	1.35	4.35	1.91
2 min He/O_2 plasma	1.38	5.48	2.63
4 min He/O_2 plasma	1.00	5.29	3.00

*Peak ratio was calculated by normalizing the peak height withglycosidic ether peak (C–O–C) at 1082 cm^{-}

peak is directly related to the amount of free radical formation, it is concluded that the helium plasma treated sample produced about 36% more free radicals compared to He/O_2 plasma treated lines. Bombardment of high energy electrons, ions, UV radiation and photons during plasma treatment might have broken various bonds of cellulose resulting formation of more free radicals in the He plasma treated sample. In contrast, the He/O_2 plasma mostly does the surface etching by removing the surface molecules resulting in less formation of radicals. The five-line spectra for the He plasma treated cellulose could be due to the summation of two different 3-line spectra. It may be noted

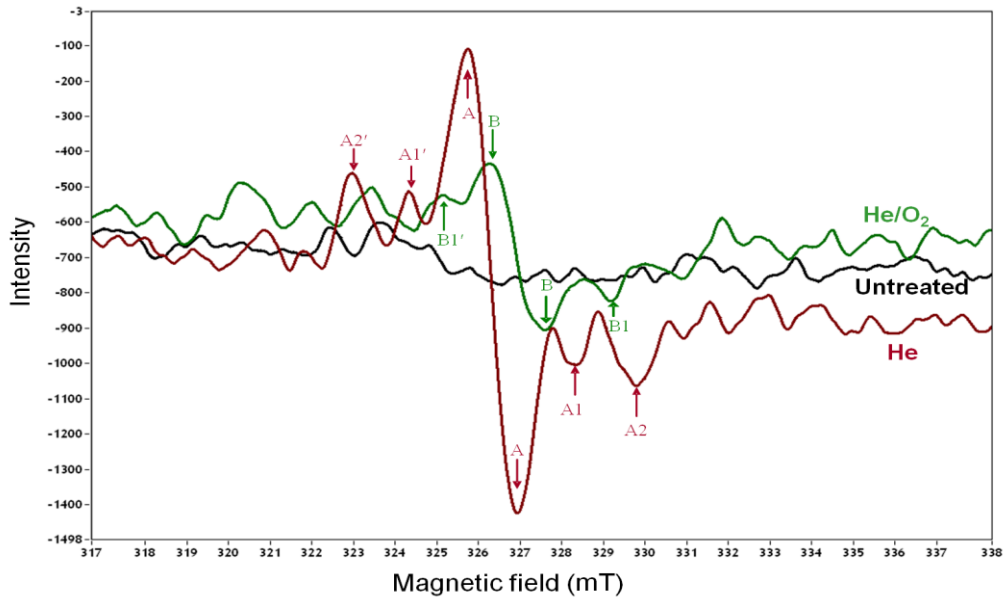


Fig. 9: Electron spin resonance curve of the untreated and plasma treated cotton textiles

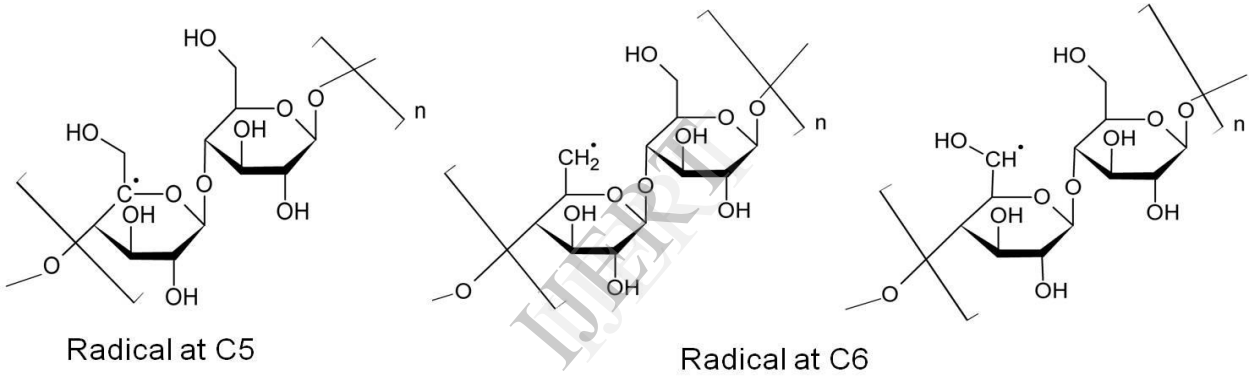
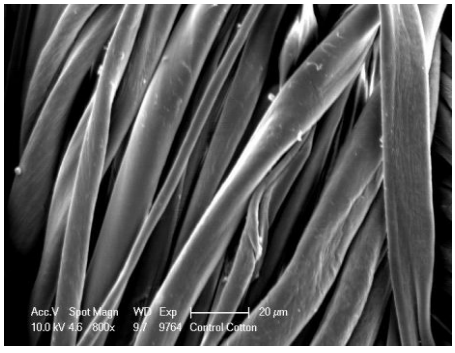


Figure 10: Formation of radicals in β-glucopyranose repeating unit of cellulose

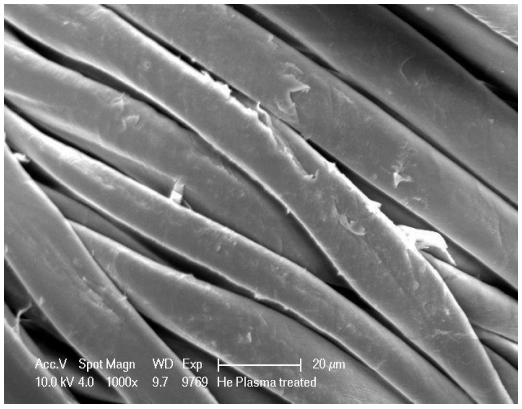
that the principal central line of the spectra of these radicals occurred at the same value and the less intense lines for each radical have occurred at different line widths (side peak 1 and side peak 2). One radical would like to form at C5 and the second one at C6 due to cleavage of H or OH from the C6 as indicated in the Fig. 10. One radical would like to form at C5 and the second one at C6 due to cleavage of H or OH from the C6 as indicated in the Fig. 10. The triplet ESR spectrum of the He/O_2 plasma treated cellulose is due to interactions between the two hydrogen atoms at the C6 position of the glucose unit with the unpaired electron formed by the removal of the hydrogen atom at the C5 position of the glucose unit by the plasma treatment.

F. Scanning electron microscope (SEM)

Figure 11 shows the scanning electron micrographs of the different samples. It can be seen [Fig. 11(a)] that untreated sample has smooth surface and individual cotton fibres are easily visible. The surface of the cotton fibre became rougher after treatment in the presence of He plasma [Fig. 11(b)]. The surface became further rougher when the sample was subjected to He/O_2 plasma treatment [Fig. 11(c)]. Bombardment of high energy ions, electrons, UV light and photon might have etched the fibre surface by removing few surface molecules resulting in an increase in surface roughness during theplasma treatment. It may be noted the effect of surface etching was more profound in case of He/O_2 plasma treated sample compared to He plasma treated sample.



(a)



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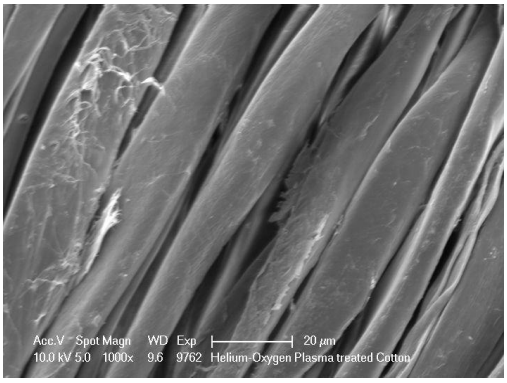

(c)

Figure 11: SEM micrographs of the different cotton samples: (a) untreated (b) He plasma treated and (c) He/O_2 plasma treated

G. Analysis of colour parameters

Table 5 shows the result on analysis of various colour parameters of the sample in terms of L, a, b, c, h and K/S values. The L denotes the brightness (+) and darkness (-) of the sample. The positive value of 'a' indicates the redness of a sample, but negative value indicates green in color. Similarly, positive and negative of 'b' indicates the colour of the sample is either blue or yellow. The 'c' value indicates the saturation (strength) of the particular colour. Higher the value of 'c', the stronger is that particular colour. And 'h' value indicates the hue in a particular colour. From the reflectance value From the reflectance value of light, the K/S was calculated using the spectrophotometer software.

It can be seen from Table 5 that in He plasma treated samples for 30 s and 60 s, K/S decrease significantly (24%-30%) resulting in decrease of 'a' value. However, for the He plasma treated samples for 2 and 4 min, there was no significant change in K/S value and other colour parameters. The He/O_2 plasma treated samples also showed almost similar result except in the case of samples with 2 and 4 min treatment time, where significant improvement was observed. The percentage K/S value increased to 110 in the plasma treated samples compared to 100 in the untreated sample (control). Due to improvement in K/S value, the red value, i.e. 'a' was found to increase from 46.39 to 47.14 in the 2 min He/O_2 plasma treated sample. Similar saturation value (c) of red colour was observed, where it increased from 46.51 in the untreated sample to 47.27 and 47.12 in the 2 min and 4 min He/O_2 plasma treated samples, respectively. As expected in all the plasma treated samples there was no significant change in the hue value (h). It may be noted that for cellulosic textiles, the reactive dye uptake and the resulting K/S value depend on the several parameters during dyeing such as (i) number of hydroxyl groups, (ii) number of carboxylic acid –OH group, (iii) presence of carbonyl groups, (iv) surface and bulk crystallinity, (v) surface charge i.e the zeta potential, (vi) amount of free radicals, and (vii) surface roughness. Some of these factors are in favour of dyeing of cotton with reactive anaionic dye, while others have an adverse effect. Mainly except surface roughness, majority of the parameters play adverse roles in dyeing.

TABLE 5: Colour parameters in untreated and different plasma treated cotton samples

Different sample	**L**	**a**	**b**	**c**	**h**	**K/S**	**In %**
Plasma treatment time	*He Plasma Treated*						
0 s (Control)	62.61	47.63	-3.10	47.74	356.27	2.391	100
30 s	65.22	41.71	-3.93	41.89	354.61	1.679	70
1 min	64.55	42.99	-3.85	43.16	354.88	1.820	76
2 min	62.70	47.32	-3.05	47.42	356.31	2.359	99
4 min	62.64	47.28	-3.07	47.38	356.27	2.359	99
Plasma treatment time	*He/O_2 Plasma Treated*						
0 s (Control)	60.84	46.39	-3.26	46.51	355.98	2.493	100
30 s	62.79	42.99	-3.73	43.16	355.04	1.961	79
1 min	61.52	45.30	-3.72	45.45	355.30	2.300	92
2 min	59.78	47.14	-3.52	47.27	355.73	2.742	110
4 min	59.72	46.97	-3.79	47.12	355.39	2.733	110

In the plasma treated samples, there was formation of more hydroxyl groups as reported in the preceding ATR-FTIR analysis section. The formation of more hydroxyl groups will produce more negative charge in the dye bath that actually repel the anaionic reactive dye molecules. In addition, formation of free radicals can degrade the dye molecules due to reducing effect. This is also true for the formation of more carbonyl groups (act as a reducing group) at a lower plasma treatment time. In addition, more surface crystallinity and total number of free radicals (especially for He plasma) reduce the dye uptake. Therefore, the 30 s and 1 min plasma treated samples showed lower K/S value. For 2 and 4 min He/O_2 plasma treated samples, the dye uptake was more due to formation of fewer carbonyl groups and less radicals. It was observed that after plasma treatment surface of the cotton fabric became rougher (more in He/O_2 plasma). If the surface of a material is rougher, scattering of light during the measurement of K/S will also be more, resulting in higher K/S value.

IV. CONCLUSION

Atmospheric pressure plasma was generated in the presence of helium (He) and helium-oxygen (He/O_2) mixture. It was observed that helium on ionization produces bluish purple colour and He/O_2 produces milkish white colour. The intensity of the produced plasma species was found to remain constant with plasma discharge time (OES analysis). The admixture of oxygen with helium gas changes the ionization pattern of helium. Cellulosic cotton woven textile was plasma treated in those plasmas for 30 to 240 s and various physical and chemical properties were studied in details. It was observed that for both He and He/O_2 plasma treatments, cotton became more hydrophilic in nature due to formation of more number of –OH and –C=O groups as evidenced by EDX, and ATR-FTIR studies. It was ovserved that the formation of free radicals was more in the He plasma treatred sample than the He/O_2 plasma treated sample. It is inferred the bombardment of high-energy electrons, ions, UV radiation and photons during plasma treatment might have broken various bonds of cellulose at C5 and C6 position (β-glucopyranose repeating unit of cellulose) resulting formation of more free radicals in the plasma treated samples. The plasma treatment also eatched the fabric surface, making it rougher particularly for He/O_2 plasma treatment with fewer formation of surface radicals as supported by the presence of a triplet ESR spectrum. Because of increase in surface roughness and the presence of more oxygen containing hydrophilic groups, water wicking time decreased significantly in both 4 min He and He/O_2 plasma treated samples compared to the untreated fabric even though the surface crystalline index (CI) was found to increase in plasma treated samples. Similarly, both for 2 and 4 min He/O_2 plasma treated samples, there was a improvement in the K/S value due to the fewer number of carbonyl group formation, less radical formation and increase in surface roughness. The same is not true for lower treatment time and for He plasma because of formation of the more carbonyl group and radicals that act as a reducing group. Plasma processing of textile is carried out at dry state without usage of water and it does not later the major physical and chemical properties of textile substrates. Therefore, atmospheric pressure plasma can be used for surface physico-chemical modification of cellulosic substrates while avoiding the usage of water for similar modification.

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