The Effect of Plasma Treatment on Some Properties of Cotton

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ABSTRACT

Treatment of cotton fibres has been studied in air and oxygen plasma and the treatment time, nature and flow rate of the gas, and plasma power have been varied. In order to establish the chemical effect of plasma treatment on cotton fibres the following tests have been performed: Cuprammonium fluidity test, weight loss measurement, determination of carboxyl groups, carbonyl group identification, FTIR analysis and measurement of the ASTM yellowness of the untreated and plasma treated cotton fabrics. In addition, vertical wicking studies and the effect of ageing of the plasma treated samples on the rate and the amount of dye uptake have been investigated. The plasma treatments lead to surface erosion of the cotton fibres which generates a weight loss, accompanied by an increase in the fibre carboxyl group and carbonyl group contents. The increase in fibre carboxyl group content leads to a more wettable fibre and the rate of fabric vertical wicking is increased. The direct dye (chloramine Fast Red K) uptake of treated samples increases almost linearly with the increase in fibre carboxyl group content caused by plasma treatment, but progressively decreases with increase in the ageing time after oxygen plasma treatment. Ageing after plasma treatment also increases the fabric yellowness.

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Key Words:
cold plasma;
plasma treatment;
cotton;
dye uptake;
free radicals.

INTRODUCTION

Low-temperature low-pressure plasma treatment has been shown to be a useful and suitable technique to modify a polymer surface, especially natural polymers like cellulose [1-6], in a dry and pollution-free system [7]. A plasma is on the average an electrically neutral gas consisting of free particles, in which the potential energy of a typical particle due to its nearest neighbour is much smaller than its kinetic energy [8]. A simple way to produce a plasma discharge without the risk of damaging or

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deforming the solid material is by using strong electric or magnetic fields [5, 9-11]. This will create highly energetic electrons which can generate new chemically-active species of atoms, ions, and free radicals [5, 12]. The highly energetic particles produced in the plasma chamber are only able to affect the surface of the polymer being treated [5,13]. This report concerns the chemical effect of plasma treatment on the cellulosic fibres of cotton printcloth.

EXPERIMENTAL

Materials

A plain weave, desized, scoured and bleached cotton fabric with the following specifications was used in all the experiments:

- 25 ends 21 picks per cm;
- 122.2 g/cm^2 weight per unit area (conditioned 65% r.h., 21°C).

The dye used in this work was chloramine Fast Red K (Clariant-C.I.Direct Red 81) with a molecular weight of 675, which is a class A (disazo) direct dye with poor exhaustion and maximum affinity at 60°C [14]. Other chemicals: Methylene Blue (BDH-C.I. Basic Blue 9), hydrochloric acid, sodium bicarbonate, sodium chloride, anhydrous sodium hydroxide, methyl red indicator, carbon dioxide-saturated distilled water, 2,4-dinitrophenyl hydrazine, and copper sulphate and sodium potassium tartrate crystals (Fehling's solution).

Procedure and Equipment

The fabric samples were treated with oxygen low-temperature plasma under different treatment times, at a pressure of 9 Pa using a Chemprep 100 barrel (standard R100 Chemex unit, Chemex Consultants, Durham) plasma reactor, which consisted of a cylindrically shaped reaction chamber with the following specifications; diameter: 10 cm, length: modified to 30 cm, capacity: 2.25 L, power source: 13.56 MHz radio frequency (r.f.), 140 Watts.

Test Methods

Fabric Weight Loss

Bone dry untreated cotton fabric samples were weighed on an electronic balance, subjected to air or oxygen plasma treatment, reweighed, and then washed at 60°C for 60 min in distilled water at a liquor ratio of 40:1. They were then bone dried and reweighed. The weight loss was calculated as a percentage of the bone dry cotton fabric weight.

Cuprammonium Fluidity Test

In order to establish the amount of fibre damage caused by the plasma treatment, the changes in the cotton fibre cuprammonium fluidity were studied before and after different plasma treatment conditions. The fluidity measurements have been performed using cuprammonium hydroxide under standard conditions (BS 2610: 1955). The viscometer was used for diluted solutions of cellulose in the standard cuprammonium solvent, and as specified in BS 2610: 1955 the density of the solution was taken as constant and equal to that of the solvent, namely 0.94. The density was then included in the constants of the following equation [15].

$$F = \frac{C/d}{T - K/T} = \frac{C'}{T - K/T}$$

Where, F, fluidity of the liquid; C, fluidity constant (Cí = C/0.94); K, kinetic energy constant (which is a correction constant and has to be applied for fluidities greater than 12 (T 200 s), d, density of the liquid, and T , the value of the time of flow. In order to express the amount of damage on the cotton samples, it was considered useful to calculate the results as the degree of polymerization (DP) of the cotton samples by using the following equation [16-17]:

$$DP = 2032 \log_{10}\left(\frac{74.35 + F}{F} - 573\right)$$

It can also be expressed as the damage factor (S) by using the following equation, originally proposed by Eisenhut, to determine the degree of damage in cotton after chemical treatment[18]:

$$S = \log_{10}\left(\frac{2000}{pt_x} - \frac{2000}{pt} + 1\right) / \log_{10} 2$$

where, pt = DP before treatment; pt_x = DP after treatment; and 2000 = reference value.

Determination of Carboxyl Groups

Methylene Blue Test

In this test, the untreated and oxygen plasma treated cotton samples (1 g each) were put in separate conical flasks containing 50 mL of 1% methylene blue (BDH-C.I. Basic Blue 9) dye solution and shaken for 5 min at room temperature. They were then rinsed thoroughly in tap water, air dried and their reflectance was measured using a Colourgen CS 1100 spectrophotometer. In this instrument the samples were irradiated with a standard illuminate D65 (tungsten halogen lamp) 10° observer. Then the degree of fabric staining (K/S value), which normally is dependent on the presence of carboxyl groups was then calculated using the following (Kubelka-Munk) equation [19]:

$$K/S = \frac{(1-R)^2}{2R}$$

where, K, the absorption coefficient, S, the scattering coefficient, and, R, the observed reflection for monochromatic light.

Sodium Bicarbonate-sodium Chloride Solution Test

In this method for determination of carboxyl group content of cotton fibres [20], cotton samples were extracted with dilute hydrochloric acid, washed, reacted with sodium bicarbonate-sodium chloride solution, and filtered. Then the filtrate was titrated with hydrochloric acid (0.01 M) in the presence of methyl red (as an indicator). The data collected from the above test were calculated with the following formula to determine the carboxyl group concentration in terms of milliequivalents (meq.) per 100 g of the bone dried treated and untreated samples.

Where:

A: volume of 0.01M HCl (mL) consumed in titration of 25 mL of the filtrate solution.

$$\text{Carboxyl group concentration}(\text{meq.}/100\text{g}) = \left[B-(A+\frac{A\times C}{50})\right]\times M\times\frac{200}{W}$$

B: volume of 0.01M HCl (mL) consumed in titration of 25 mL of the sodium carbonate - sodium chloride original solution.

C: weight (g) of water in the test specimen.

M: molarity of HCl used in titration (0.01M).

W: weight (g) of bone dried specimen.

It has to be mentioned that the constant amount of 50 is the volume of the sodium carbonate-sodium chloride solution used in the test and the constant amount of 200 is derived as 2 multiplied by 100, where 2 is the factor to account for the used volume ratio between the sodium carbonate - sodium chloride solution and the filtrate used in the test, and 100 is to express the results on 100 g of specimen.

Carbonyl Group Identification

2,4-Dinitrophenyl Hydrazine Test

This method will immediately identify carbonyl groups (both aldehyde and ketone groups) on cotton fibres. 2,4-Dinitrophenyl hydrazine in presence of carbonyl compounds (including many quinones) gives sparingly soluble dinitrophenyl hydrazones [21]. In this test, 0.1 g of the cotton sample was added to 3 mL of the 2,4-dinitrophenyl hydrazine solution in a glass test tube and shaken for 10 min.

Colorimetric Test for Aldehyde Groups

In order to make sure that aldehyde groups have been generated in oxygen plasma-treated cotton fibres, it was necessary to perform the following test. Aldehyde groups reduce Fehling's solution to give a precipitate of red cuprous oxide. Therefore, the areas on the fibre carrying -CHO groups will be coloured pink or red and may often be seen under the microscope [22]. A small piece of cotton fabric sample was boiled for about 10 min in a tube containing 10 mL of Fehling's solution. Then the cotton sample was removed from the tube, and rinsed well in water. The remaining solution was filtered and the filter paper was checked for any red precipitate remaining. The fibres were then examined under an optical microscope. Both untreated and plasma treated cotton samples were tested.

The Vertical Wicking Test

This test has been performed on untreated bone dried (90°C) and then oxygen plasma-treated bone dried cotton samples were cooled in a desiccator over silica gel for half an hour and cut into strips (25 cm in the warp direction and 5 cm in the weft direction). Each sample was vertically suspended and the test was started when 2 cm of the lower end of the fabric sample was placed in the water container. The height of water front in each strip was recorded as a function of time separately. The test was carried out at room temperature and the duration

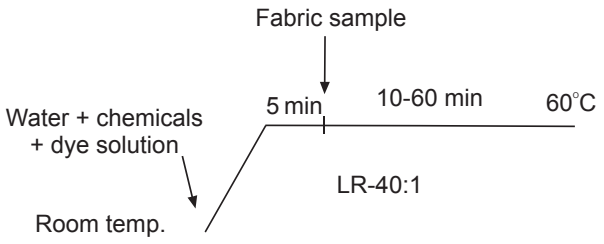

Figure 1. Schematic chart of dyeing processes.

of each test was 30 min.

Yellowing Tendency of the Oxygen Plasma-treated Cotton

In order to measure the change in yellowing tendency of cotton fabrics caused by the oxygen plasma treatment, the untreated, oxygen plasma treated, and the oxygen plasma treated fabrics which had been kept for a period of ageing, both for washed and unwashed cotton samples, were air dried and the reflectance was measured on the Colourgen CS 1100 spectrophotometer. The results are expressed in ASTM yellowness units and ASTM whiteness units.

FTIR Analysis

A Perkin Elmer Fourier transform infrared spectrometer (FTIR) (1725X) and standard settings with a KRS-5 (Thallium bromide-iodide) crystal were used in this study to detect any changes in the chemical structure of cotton at the fabric surface on untreated and oxygen plasma treated cotton samples.

The Effect of Ageing Period After Plasma Treatment

In order to establish the presence and to study the stability of free radicals created on cotton fibres during the oxygen plasma treatment, it was considered important to investigate the effect of an ageing period on samples after being subjected to oxygen plasma treatment just before starting the dyeing process (Figure 1). In this way it was possible to observe the dye uptake and the rate of dyeing differences between samples with different ageing periods (1, 2, 4, and 7 days). The samples were kept in a desiccator over silica gel during the ageing period.

The dyeing or washing off processes were carried out using a Rotadyer (Mark I) laboratory dyeing machine (John Jeffrey Ltd, Rochdale). Then the samples were removed from the tubes, washed and oven dried and the residual dye bath solutions were examined using a Unicam SP 1800 spectrophotometer at room temperature to calculate the amount of dye uptake in the cotton samples.

Table 1. The effect of plasma treatment on the absorption of Methylene blue on cotton fibres.

Plasma power (Watts)	Gas flow rate (mL/min)	Treatment time (min)	K/S Value
Untreated	Untreated	Untreated	5.44
120	30 (oxygen)	60	3.72

It is important to note that, because of the weight loss of the plasma treated samples due to the etching effect, which occurs in the plasma chamber, the weight loss leads to the total surface area of the plasma treated fibres being effectively changed. Thus, all the dye uptake data on plasma treated samples have been normalized to correct for the change in weight of the original sample after plasma treatment.

RESULTS AND DISCUSSION

Determination of Carboxyl Groups

Methylene Blue Test

The calculated K/S data for the test samples are shown in Table 1, which, surpisingly, indicate that the carboxyl group content of the oxygen plasma treated cotton samples are less than the untreated cotton fabrics, because the surface oxidation of cellulose is known to generate carboxyl groups [23]. In order to confirm this results of the above test, it was necessary to perform a titration to determine accurately the carboxyl group contents of the untreated and plasma treated cotton samples.

The results of the titration method are given in Table 2, and they show that the carboxyl group content of the plasma treated cotton samples is greater than that of the untreated cotton sample, and therefore it suggests that the results of the Methylene blue test are not valid. This effect has been observed previously [24] on bleached cotton fabrics. The explanation is considered to arise from the changes in the scattering coefficient (S) of the dyed oxygen plasma-treated cotton samples. It seems that the scattering coefficient (S) can only be altered as results of: (a) The surface erosion / damage after oxygen plasma treatment; (b) the presence of

Table 2. The effect of change in plasma power, gas nature and flow rate, and the rest time after being treated on the carboxyl group contents and the damage caused by the plasma treatment on cotton samples (dyed in distilled water, LR ≈ 40:1, at 60°C, and for 60 min).

Plasma treatment			Fibre properties			Dyeing
Plasma power (Watts)	Gas flow rate (mL/min)	Ageing period (days)	Carboxyl group contents (meq. / 100 g)	Fluidity test (damage factor) (S)	Weight loss (%)	Dye exhaustion (normalized) (%)
Untreated	Untreated	Untreated	1.85	-	-	13.6
20	30 (oxygen)	-	2.17	0.06	10.1	14.8
	20 (oxygen)	-	2.49	0.10	15.6	18.5
	30 (air)	-	2.41	0.09	15.1	18.3
70	30 (oxygen)	-	2.89	0.14	20.4	20.7
	30 (oxygen)	7	3.93	0.14	20.4	14.8
	40 (oxygen)	-	3.69	0.22	26.5	18.8
120	30 (oxygen)	-	4.17	0.29	35.2	18.1

finer, and thus a greater number of fibres in the same weight of oxygen plasma-treated and of untreated samples.

The weight loss during oxygen plasma treatment means that for the same weight of sample the untreated sample will contain fewer fibres. The carboxyl group content for oxygen plasma treated cotton fabrics appears to be lower than that determined by titration. Thus the Methylene blue test is not reliable for the detection of the change of carboxyl group contents of samples in which a fibre weight loss has occurred.

Sodium Bicarbonate - sodium Chloride Solution Test

As expected, by increasing the plasma power, changing the plasma gas atmosphere (from air to oxygen), and increasing the plasma gas flow rate, the cotton fibre carboxyl group contents increased significantly. It is shown in Figure 2 that oxygen plasma treatment results in an almost linear increase in the fibre carboxyl group content and the extent of fibre damage as measured by the fibre damage factor [25].

Figure 3 shows that by increasing the carboxyl group contents of the plasma treated cotton fibres, the normalized direct dye exhaustion increases markedly up to around 3 meq. / 100 g and then it decreases gradually. Also, according to data reported in Table 2, after an ageing period of seven days the oxygen plasma treated cotton sample exhibits a higher carboxyl group content and a lower direct dye uptake than a similar plasma treated sample with no ageing period. This demonstrates that further oxidation of the plasma treated fibres must continue in air and over the ageing period the oxidation will continue, which in turn will increase the fibre carboxyl group content and decrease the direct dye uptake of the fibres because of the higher electronegative surface potential. One explanation for these chemical changes is to postulate that plasma treatment leads to free radical formation in the cotton fibres. These free radicals will react with oxygen, or the oxygen in the atmosphere (air) to create more carboxyl groups on the fibres and hence tend to decrease the direct dye uptake through electrostatic repulsion of the direct dye anions. This theory is in agreement with Bradley's work on plasma treated polyester film 26. He has pointed out that by storing the plasma treated samples in hot air, these tend to regain oxygen and this would lead to a net increase in surface oxidizing groups. But in the absence of oxygen, the surface free radicals have time to recombine forming a cross-link, thus decreasing the oxidizing power of the surface [26].

Carbonyl Group Identification

2,4-Dinitrophenyl Hydrazine Test

The colour of the plasma treated cotton sample, after the test, turned reddish-yellow and a crystalline precipitate was formed which is an indication of the presence of carbonyl groups on plasma treated cotton samples.

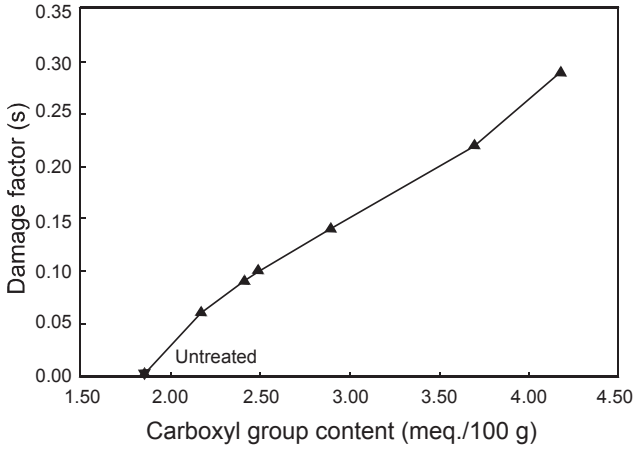

Figure 2. The relation between the carboxyl group contents of the plasma treated cotton fibres and the damage caused by the plasma treatment (70 Watts power, 30 mL/min oxygen gas flow rate, 60 min).

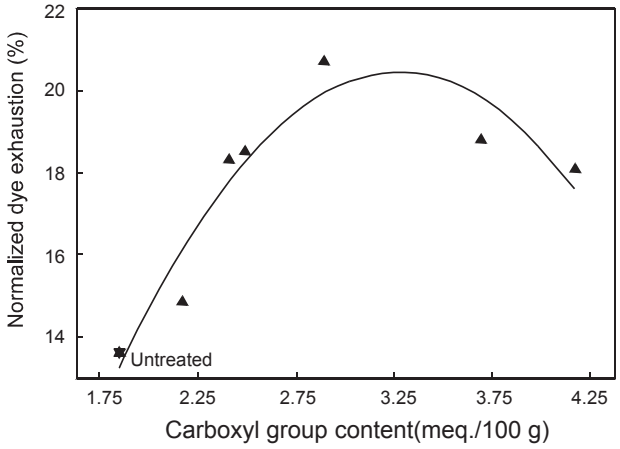

Figure 3. The effect of change in cotton carboxyl group contents on direct dye exhaustion of the plasma treated (70 Watts power, 30 mL/min oxygen gas flow rate, 60 min) cotton fibres (dyed in distilled water, LR ≈ 40:1, at 60°C, and for 60 min).

But with the untreated cotton sample, the colour changed to faint yellow and there was no sign of crystalline precipitate in the remaining solution.

The test results indicate that plasma treatment could produce carbonyl (i.e., aldehyde or ketone or both) groups on cotton fibres in addition to carboxyl groups.

Colorimetric Test for Aldehyde Groups

The filter paper for the remaining solution test of the plasma treated sample showed the presence of some red substance. However, for the untreated cotton sample the filter paper was clear. Also the light microscopic examination of the plasma treated fibres after the test showed much more local deposits of copper oxide granules than the untreated fibres, which suggests the presence of more aldehyde groups on plasma treated cotton fibres compared with untreated cotton samples.

However, we were not succeeded to find the mechanism of aldehyde groups generation on cellulose by plasma treatment in the literature.

The Vertical Wicking Test

The vertical upward wicking test was carried out on oxygen plasma treated (70 and 120 Watts of plasma treatment power) and untreated cotton samples using the above test procedure. The results are recorded in Figures 4 and 5. The higher rate of vertical wicking by oxygen plasma treated cotton samples can be explained by several possibilities which are:

(i) The higher level of polar carboxyl groups and carbonyl groups generated by fibre damage during oxygen plasma treatment, yield a more polar and more wettable fibre surface.

(ii) The physical effect of the oxygen plasma treatment which through surface erosion removes the layer of cotton wax on the fibre surfaces may thereby render the fibres more wettable by water.

(iii) Oxygen plasma treatment results in a fabric weight loss as a result of surface erosion of the fibres. Thus the shape and size distribution of the inter-fibre and inter-yarn capillary spaces will be modified. This may also lead to the unblocking of some capillaries, and hence promote more rapid wicking.

Figure 4 indicates that the greater hydrophilic nature of the cotton as a result of the increasing number of carboxyl groups created by the oxygen plasma treatment gives rise to a higher fabric wettability and hence to a greater vertical wicking rate. This increased fabric wettability after oxygen plasma treatment may also aid in increasing the rate of direct dye uptake.

It is also shown in Figure 4 that the rate of vertical wicking would be greater with greater the applied plasma power. Thus the creation of more polar hydrophilic groups under a high power plasma treatment and / or greater surface damage to the fibres caused by the severe plasma treatment may lead to a higher rate of vertical wicking.

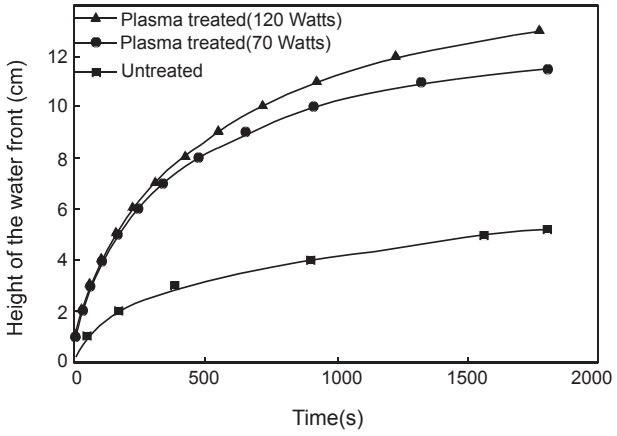

Figure 4. The effect of oxygen plasma treatment on the vertical wicking of cotton fabrics.

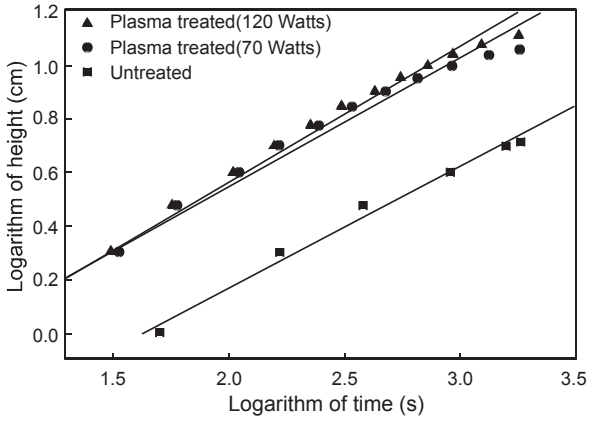

Figure 5. The relation between the logarithms of height and time in the vertical wicking test of oxygen plasma treated and untreated cotton fabrics.

Figure 5 reveals that there is a good relationship between the logarithm of the vertical wicking height and the logarithm of the wicking time for both plasma treated and untreated cotton fabrics. This relation has been claimed by De Boer [27] to be valid for desized and scoured cotton fabrics and also for mercerized and reactant-finished cotton fabrics.

Yellowing Tendency of the Oxygen Plasma-treated Cotton

From the yellowing results shown in Table 3, the oxygen plasma treated samples are seen to be unstable and change colour with increasing time of storage (ageing) which, according to Lewin's theory [28], is due to the creation of more aldehyde groups on the cellulosic chain molecules of cotton fibres. This may be caused by the unstable nature of the free radicals created during the plasma treatment which, as Wakida has claimed [29], can decay according to the storage time and temperature of the oxygen plasma treated samples.

Also, the data in Table 3 show that after washing the samples in warm tap water for one minute, the ASTM yellowness of the fabric decreases, and the fabrics then appear whiter, but are still yellower than the original (untreated) cotton fabric (which was obtained in the bleached state). This can be explained on the basis that oxygen plasma treatments mostly affect the surfaces of cotton fibres. As scanning electron micro-

Table 3. The effect of change in plasma power, ageing and washing off process on the yellowing tendency of the oxygen plasma treated and untreated cotton samples.

Sample treatments					Test results	
Plasma power (Watts)	Gas flow rate (mL/min)	Treatment time (min)	Ageing time (week)	Washing * off	ASTM (yellowness)	ASTM (whiteness)
Untreated	Untreated	Untreated	-	-	4.43	67.63
			-	-	4.56	65.63
			1	-	7.97	53.96
70	30 (oxygen)	60	4	-	11.95	41.02
			4	After ageing	7.30	55.73
			4	Before ageing	5.12	64.16
120	30 (oxygen)	60	-	-	5.42	63.89

(*) The samples were washed in warm tap water for one minute.

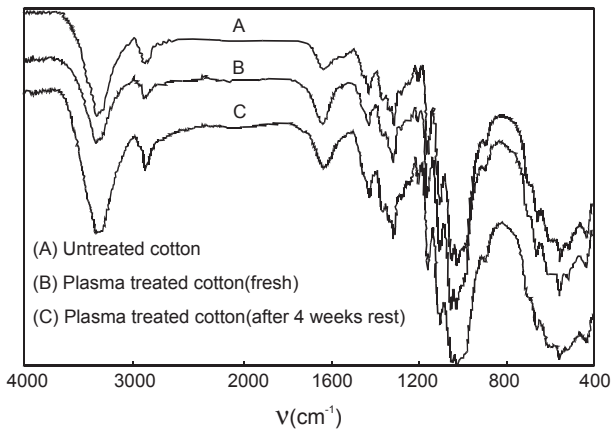

Figure 6. FTIR Spectra recorded from the untreated, oxygen plasma treated (70 Watts power, 30 mL/min gas flow rate, 60 min), and aged oxygen plasma treated cotton samples.

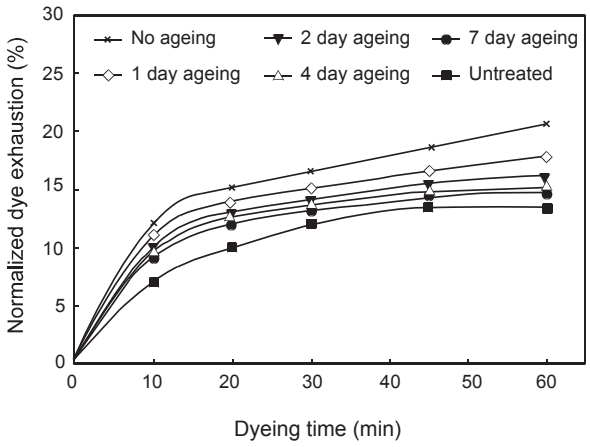

Figure 7. Normalized graph of the effect of ageing period on 2% (owf) chloramine Fast Red K (60°C) dye exhaustion of oxygen plasma treated cotton (oxygen and air, 70 Watts power, 30 mL/min gas flow rate, 60 min).

graphs have shown[25], these treatments create loose fragments on the oxygen plasma-treated cotton fibre surface. During the washing treatment, these fibre fragments may be removed and the aldehyde groups created on their surface by oxygen plasma treatment, which are largely responsible for the yellowing on plasma treated cotton, will be partly washed off thereby whitening the resultant plasma-treated samples. On the other hand by washing the samples after the oxygen plasma treatment and before the ageing period, the free radicals and loose fragments are more likely to be removed so that the fabric then appears to be more stable in respect of its whiteness after an ageing period compared with an unwashed oxygen plasma treated sample.

FTIR Analysis

The FTIR analyses were performed on the untreated, and oxygen plasma treated cotton (70 Watts power, 30 cm^3/min oxygen gas flow rate, 60 min) which had then been stored for 4 weeks, and their corresponding spectra (Figure 6) were recorded. The spectra obtained are very similar, but the spectra for the oxygen plasma treated cotton sample show some alteration from the untreated cotton sample in the area of 1728 cm^{-1} (5.8 μm) that represents the C=O groups in the carbonyl structure [30]. This is in agreement with the results of Ward's work [5, 13], which have been carried out on cotton using argon plasma and ammonia plasma treatments. Also, by comparing the spectrum of fresh oxygen plasma treated cotton with a similar sample after an ageing period of 4 weeks, the height of the 1728 cm (5.8 m) peak appears to be greater after the ageing period. This indicates the instability of the oxygen plasma-treated samples, and the relation of the change in this peak to the creation of more aldehyde groups (as indicated by the increased yellowing observed in the previous section) through the action of free radicals and oxygen on the plasma treated samples.

The Effect of Ageing Period After Plasma Treatment

The experimental data obtained from the above mentioned tests are illustrated in Figures 7 and 8.

From Figures 7 and 8, it seems clear that as the ageing period increases, the rate of dyeing and the dye uptake of the plasma-treated cotton samples decrease markedly up to the fourth day of ageing, but then the effect tends to slow down and nearly levels off. This suggests that the stability of the free radicals generated on cotton samples by oxygen plasma treatment depends considerably on the ageing time before the dyeing process, which agrees with Wakida's work on cotton samples [29].

It is possible that the free radicals might decay and convert to other chemical groups (e.g., carbonyl groups), which also do not have an attraction for direct dyes. In addition the cellulosic chains of the cotton sample may lose some -OH groups and this will lead to a decrease in dyeing rate and the final amount of dye exhaustion at the equilibrium.

It is to be noted that the cotton fabric samples were kept in a desiccator at room temperature during the age-

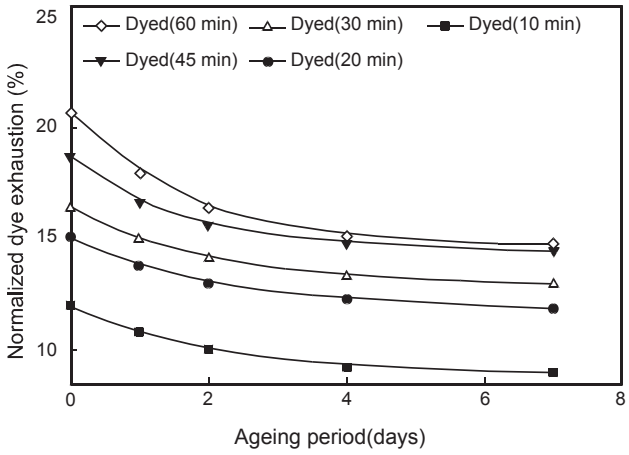

Figure 8. Normalized graph of the effect of ageing period on 2% (owf) chloramine Fast Red K (60°C) dyeing rate of oxygen plasma treated cotton (oxygen and air, 70 Watts power, 30 mL/min gas flow rate, 60 min).

ing period in order to avoid moisture from the atmosphere interacting with the free radicals. It is known that under higher temperatures or in a high moisture content atmosphere free radicals could decay quite easily [29] and conceivably the dye uptake could then be even lower than for the untreated cotton samples.

CONCLUSION

The effects of air and oxygen plasma treatment upon the physico-chemical properties of cotton fabric have been studied with respect to the treatment time, plasma power and gas flow rate. As expected oxygen plasma treatment generates greater changes in fibre and fabric properties under the experimental conditions used. The plasma treatments lead to surface erosion of the cotton fibres, which generates a weight loss, accompanied by an increase in the fibre carboxyl group and carbonyl group contents. The increase in carboxyl group contents has been determined titrimetrically and it has shown that measurement of K/S after dyeing with Methylene blue does not correlate because of changes in the fibre scattering power.

The increase in fibre carboxyl group content leads to a more wettable fibre and the rate of fabric vertical wicking is increased. The increase in fibre carboxyl group content after air and oxygen plasma treatment increases further after an ageing period of four weeks. It has been concluded that this may occur as a result of the action of free radicals within the fibres originally generated during plasma treatment. The uptake of a direct dye (Chloramine Fast Red K) progressively decreases with increase in the ageing time after oxygen plasma treatment. Ageing after plasma treatment also increases the fabric yellowness, but this can be decreased by a washing treatment before and after the ageing period. This suggests that low molecular weight degradation products are washed out of the fibre surface, and indeed a weight loss is observed on washing.

The results of the cuprammonium fluidity test have shown that the fibre damage factor increases almost linearly with the increase in fibre carboxyl group content. However, the uptake of a direct dye (Chloramine Fast Red K) first increases with increase in fibre carboxyl group content, but then decreases in the region above a carboxyl group content of 3.25 meq./100g.

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REFERENCES

1. Ward T.L., Jung H.Z., Hinojosa O., and Benerito R.R., Characterization and use of RF plasma-activated natural polymers, *J. Appl. Polym. Sci.,* **23**, 1987-2003 (1979).
2. Pavlath A.E. and Slater, R.F., Low-temperature plasma chemistry, I. Shrink proofing of wool, *Appl. Polym. Symp.,* **18**, 1317- 1324 (1971).
3. Riccobono P.X. and Rolden L., Plasma treatment of textiles: A novel approach to the environmental problems of desizing, *Textile Chem. Color.,* **5**, 239- 248 (1973).
4. Stone R.B., *Jr*., and Barrett J.R., *Jr., U.S.D.A.*, Study reveals interesting effects of gas plasma radiations on cotton yarn, *Textile Bull.,* **88**, 65-68 (1962).
5. Jung H.Z., Ward T.L., and Benerito R.R., The effect of argon cold plasma on water absorption of cotton, *Textile Res. J.,* **47**, 217- 222 (1977).
6. Ward T.L., Jung H.Z., Hinojosa O., and Benerito R.R., Effect of RF cold plasmas on polysaccharides, *J. Surface Sci.,* **76**, 257-273 (1978).

7. Shishoo L.R., *Plasma Treatment-Industrial Applications and its Impact on the C&L Industry,* The 6th. Int. Conf. on Tex. Coat. & Lam., Dusseldorf 35-47 (1996).
8. Lieberman M.A. and Lichtenberg, A.J., Ch. 1: Introduction, *Principle of Plasma Discharges and Materials Processing,* John Wiley, New York ,1-53 (1994).
9. Rakowski W., Okoniewski M., Bartos K., and Zawadzki J., Plasma treatment of textiles - potential applications and future prospects, *Melliand Textilber.* **63**, 301- 313(1982).
10. Marsh D.E., Plasma torch cutting of textiles, *Melliand Textilber.* **68**, 558-560 (1987).
11. Venugopalan, M., Ch. 1: The plasma state, *Reactions Under Plasma Conditions,* Venugopalan, M., Ed., Vol.I, John Wiley, New York,1-72 (1971).
12. Benerito R.R., Ward T.L., Soignet D.M., and Hinojosa O., Modifications of cotton cellulose surfaces by use of radiofrequency cold plasma and characterisation of surface changes by ESCA, *Textile Res. J.,* **51**, 224-232 (1981).
13. Ward T.L. and Benerito R.R., Modification of cotton by radio frequency plasma of ammonia, *Textile Res. J.,* **52**, 256-263 (1982).
14. Colour Index, Vols. 2 and 4, 3rd ed., The Society of Dyers and Colourists and The American Association of Textile Chemist and Colorists, *p. 2104* (1971).
15. Garner W., *Textile Laboratory Manual,* Vol. 6: Additional Methods, 3rd ed., Heywood Books, London, p.163, (1967)
16. Hickman W.S., Ch. 2: Preparation, *Cellulosics Dyeing,* Society of Dyers and Colourists, Bradford, p.145, (1995)
17. Interox Chemicals Ltd., *A Bleachers'Handbook,* p.57, (1981)
18. Eisenhut O., Zur Frage der Bestimmung des Schadigungswertes Von Fasern, Garnen Oder Geweben aus Zellulose und Von Zellstoffen, *Melliand Textilber.* **22**, 424-429 (1941).
19. Kubelka P. and Munk F., Ein beitrag zur optik der farbenstriche, Z. *Tech. Physik,* **12**, 593-598 (1931).
20. TAPPI Standard Test Method, Carboxyl Content of Pulp, T 237 os-77,1-7 (1977).
21. Vogel A.I., *A Text Book of Practical Organic Chemistry,* 4th ed, Longman, London, p.1070, (1978)
22. Garner W., Ch. 2: Vegetable fibres, *in: Textile Laboratory Manual,* National Trade, London, 42-43 (1949).
23. Shenouda S.G., Chapter 7: The structure of cotton cellulose, *in : Applied Fibre Science,* Happy F., Ed., Academic, London, 92-145 (1979).
24. Panti I.A., *PhD Thesis,* The wettability of cotton fabrics, The University of Leeds, Department of Textile Industries, 54-93 (1984).
25. Malek R.M.A. and Holme I., (unpublished work).
26. Bradley A. and Heagney T.R., Analysis for surface peroxides, *Anal. Chem.,* **42**, 894-901 (1970).
27. De Boer J.J., The wettability of scoured and dried cottn fabrics, *Text. Res. J.,* **50**, 624-632 (1980).
28. Lewin M., Epstein J.A., Ben-Bassat A., and Albeck M., The yellowing of cotton cellulose (Part II), *Text. Res. J.* **35**, 935-943 (1965).
29. Wakida T., Takeda K., Tanaka I., and Takagashi T., Free radicals in cellulose fibers treated with low temperature plasma, *Textile Res. J.,* **59**, 49-53 (1989).
30. Tipson R.S., *Infrared Spectroscopy of Carbohydrates,* Institute for Materials Research, National Bureau of Standards Monograph 110, U.S. Department of Commerce, D.C. 20234, p.197, (June 1968).