

# Effect of Atmospheric Pressure Helium Plasma on Felting and Low Temperature Dyeing of Wool

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**ABSTRACT:** Wool fabrics were treated with atmospheric pressure helium glow discharge plasma in an attempt to improve felting and dyeing behavior with cold brand reactive dyes using cold pad-batch method at neutral pH. On glow plasma treatment, the hydrophilicity of wool surface and its resistance toward felting was greatly improved without any significant damage to the cuticle layer. The color strength of the plasma treated dyed wool on the surface (in terms of *K/S*) was found to be nearly double of the color strength of dyed untreated wool fabric. However, the corresponding total dye uptake of the treated wool increased by a much lower value of 40%–50%. The reason behind this altered dyeing behavior was investigated by studying the dye kinetics using infinite

bath and surface characteristics using SEM and SIMS. It was found that the glow plasma treatment greatly transformed the chemical surface of the wool fibers. It resulted in uniform removal of hydrophobic cuticular layer, which resulted in better diffusion of the dye molecules into the fiber, and formation of hydrophilic  $-\text{NH}_2$  groups near the surface, which helped in anchoring the dye molecules close to the surface giving higher color strength than expected. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4289–4297, 2012

**Key words:** atmospheric pressure glow discharge (APGD); plasma; pad-batch dyeing; cold brand reactive dye; dye kinetics

## INTRODUCTION

Plasma treatment is a physical method used for surface modification. It affects the surface both physically and chemically without altering the material bulk properties. The main advantages of plasma technology are the extremely short treatment time and low application temperature, along with the fact that it is regarded as an environmentally friendly process. Plasma can be formed either at low pressure or at atmospheric pressure. Low pressure plasma is a batch process and consumes more time and energy. On the other hand, atmospheric plasma can provide similar effect in shorter treatment times and can be used for continuous treatment. Among the various kinds of atmospheric pressure plasmas, glow plasma gives more uniform effect and results in lesser damage to the substrate<sup>1</sup>.

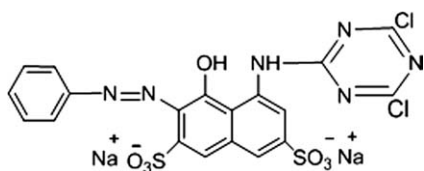
Wool is one of the important natural fibers in the textile industry. However, it has some technical problems such as wettability which also affects its dyeability. Wool fibre surface is hydrophobic in nature which is because of the presence of high num-

ber of disulphide cystine cross linkages in the exocuticle and fatty acids (18-methyl-eicosanoic acid) on the fibre surface<sup>2</sup>. Atmospheric pressure plasma has been used to alter the surface properties of wool and its effect on wettability, felting property, and dyeing properties<sup>1,3–5</sup>.

Effect of plasma treatment on dyeability of wool has been studied using different classes of dyes such as acid dyes,<sup>5–8</sup> chrome dyes,<sup>5,7</sup> reactive dyes,<sup>5,7,9,10</sup> and natural dyes<sup>11</sup>. A significant increase in dye exhaustion and decrease in half dyeing time of plasma treated wool have been reported<sup>5–11</sup>. Reactive dyes offer a distinct advantage over other classes of dyes as these dyes exhibit very high wash fastness properties. There are some studies on the effect of plasma treatment on dyeing of wool with reactive dyes using exhaust method of dyeing at conventional high temperatures of around 95°C–100°C.<sup>5,6,9</sup> A couple of studies have investigated the possibility of lowering the dyeing temperature from conventional 100°C to 85°C–80°C.<sup>10,12,13</sup> Dyeing at these temperatures for prolonged periods translates into high energy cost as well as fibre damage. Therefore, an alternative approach can be cold pad-batch dyeing of wool using cold brand reactive dyes.

Pad-batch method has proved to be a very successful method of dyeing cotton with reactive dyes, offering advantage in terms of increased color yield, minimum use of water and energy, and increased

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**Figure 1** Structure of C.I. Reactive Red 2 dye.

productivity<sup>14</sup>. Pad-batch dyeing would also lead to better preservation of wool fibers and, unlike exhaust dyeing, there is minimal felting of wool. The machinery and the infrastructure required is also minimal, hence this method is highly suitable for small scale processors, cottage industry, and artisans. However, the basic problem in this approach is the nonuniform and slow wetting of wool during padding. The surface of wool fibre being hydrophobic in nature hinders the uptake of dye during short padding periods. Consequently, large amounts of urea (200–300 g/L) along with sodium bisulphite are required to bring about fibre swelling, leading to increased dye uptake<sup>14</sup>. This adds to the pollution in the wastewater. Moreover, urea causes tendering and yellowing of fabric, and sodium bisulphite adversely affects the stability of the dye liquor. Any treatment or dyeing method that significantly reduces the chemical loading would be beneficial both for the environment and the substrate.

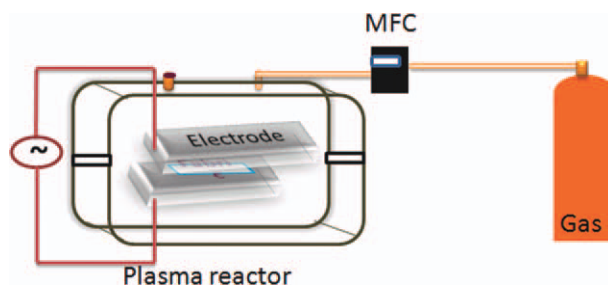
It was, therefore, of interest to study the effect of atmospheric pressure glow plasma treatment on dyeing of wool with dichlorotriazine based reactive dyes by cold pad-batch method. Effect of pH, sodium bisulfate, and urea concentration on color yield of untreated and plasma treated wool was studied. Effect of plasma treatment on diffusion coefficient and kinetics of dyeing at low temperature was also investigated. Plasma treated wool was tested for its wettability and felting. Change in wettability of plasma treated wool on ageing and laundering was observed. Scanning electron microscopy and secondary ion mass spectroscopy were carried out to elucidate the effect of plasma treatment on surface characteristics of wool.

## EXPERIMENTAL

### Materials

Wool woven fabric 100% (52 × 40) was scoured with a solution of 5 g/L nonionic detergent (Lissapol N) at 50°C for 45 min followed by cold rinsing and air drying.

The reactive dye used was a dichlorotriazine based dye, C.I. Reactive Red 2 (Reactofix Red M5B, Jaysynth Dyechem Ltd., India). The structure of the dye is given in Figure 1. Other chemicals used were urea, sodium bisulphite, Turkey Red Oil (TRO),

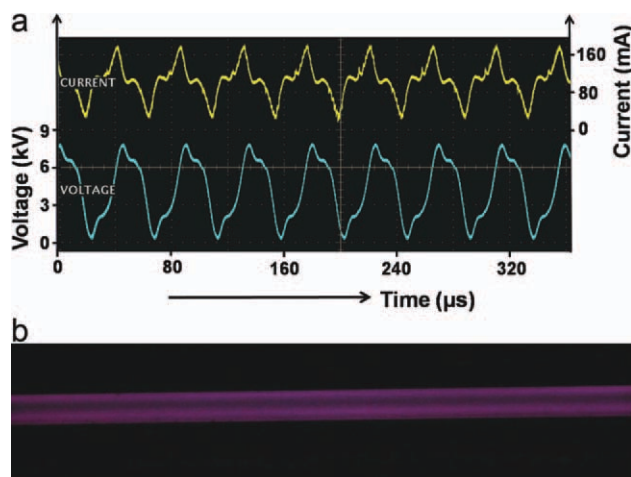


**Figure 2** Schematic of reactor for plasma treatment. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sodium chloride, pyridine, acetic acid, 90% formic acid, sodium hydroxide, all of which were reagent grade. All dyes and chemicals were used as obtained except for developing calibration curve, for which the dye was purified as follows: dye was dissolved in DMSO at 50°C, filtered, precipitated in *n*-butanol, washed with ethanol and with diethyl ether. The purified dye was dried at 40°C in vacuum oven.

### Plasma treatment

Wool fabric samples (8 cm × 5 cm) were treated in stable atmospheric pressure glow plasma (APGP) open air reactor developed in-house for the purpose is shown in (Fig. 2). The glow cold plasma was generated in the presence of He gas (discharge voltage, 3 kV; frequency, 20 kHz; gas flow rate, 1 L/min.). The plasma treatment time was 6 min. The quality of the generated atmospheric pressure plasma was determined by studying the current-voltage (*I-V*) waveform using digital oscilloscope, model Tektronix DPO 3012 attached with P6015A high voltage and TCP 0030 current probes. *I-V* profile and color of He plasma is shown in Figure 3(a,b). It can be



**Figure 3** (a) *I-V* waveform and (b) color of He plasma. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

seen that the plasma glow of a high quality has been generated as the current waveform is completely free from spikes.

### Cold pad-batch dyeing

The dyeing pad liquor consisted of 5 g/L or 10 g/L reactive dye, 10 g/L TRO, 0–300 g/L urea, and 0–10 g/L sodium bisulphite. The pH of the bath was kept at either five or seven for two different sets. Wool fabric was padded at the room temperature (30°C–35°C) with the padding liquor by three dip, three nip method on Lab padder-HVF (Mathis, Switzerland) at a pressure of 2 kg. The liquor pickup was calculated on dry weight of fabric. Thereafter, moist samples were wrapped in aluminium foil and batched for 24 h at 35°C. Fabrics were then rinsed in cold water and dried. Each sample was padded in a separate bath. *K/S* values were measured using UV-VIS spectrometer Lambda 35 (Perkin Elmer, USA). Unfixed and hydrolyzed dye was removed by treating rinsed samples in a solution containing 10% pyridine, 20% of formic acid and 70% water (by volume) for 5 min at boil. The treatment was repeated till the clear solution was obtained. Fabric samples were then rinsed thoroughly and dried. The *K/S* values of these samples were measured again. *K/S* value is based on the Kubelka-Munk theory that equation defines the relationship between (*R*) reflectance, (*K*) absorption, and (*S*) scattering characteristics of sample.

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

### Kinetic study

Effect of plasma treatment on diffusion coefficient and half dyeing time were determined by dyeing untreated and plasma treated wool with the reactive dye in an infinite bath at 40°C. Dye bath consisted of 1 g/L dye and 20 g/L sodium chloride. MLR was maintained at 1:900. Dyeing was carried out using HTHP dyeing machine for different time periods ranging from 10 min to 30 h. Dyed samples were rinsed in cold water and unfixed dye was removed as described earlier. *K/S* values were measured before and after stripping unfixed dye. Concentration of dye in fibre (dye uptake) was determined by dissolving dyed fabric in 4% sodium hydroxide solution and measuring the optical density in UV-VIS spectrometer.

### Surface characterization

The effect of plasma treatment on surface morphology of wool was observed on environmental scan-

ning electron microscope Quanta FEI 200 (FEI, Netherland) without coating at high vacuum and low kV mode. Surface composition of wool fabric was analyzed by using mini SIMS (Milibrook, UK). Mass spectrum and depth profiling of selected masses were taken using negative ion spectra.

### Fabric performance

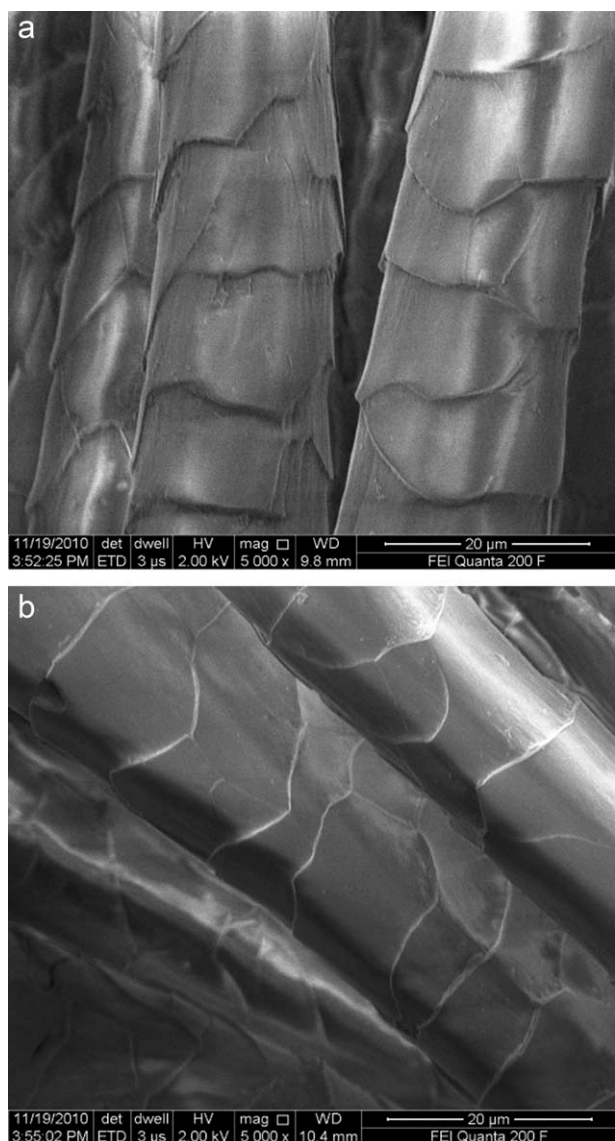
Wettability of wool fabric was characterized with respect to drop disappearance time. Drop of 40  $\mu$ L deionized water was put on the surface of the wool fabric from a height of 1 cm and the time taken for spreading of the drop was measured. Test was repeated at five different places for each sample and average of the readings was taken. Effect of ageing up to 9 weeks and washing up to 30 wash cycles on wettability was observed. Washing was done in launderometer as per the AATCC 61 2A method. Felting shrinkage of the untreated and glow plasma treated sample on repeated machine washing was determined up to 30 wash cycles using AATCC 61 2A method.

## RESULTS AND DISCUSSION

### Surface characterization of plasma treated wool

From the scanning electron microscope images, it can be seen that the surface morphology of both untreated and treated wool are quite similar Figure 4 (a,b). The long plasma treatment of 6 min has not resulted in destruction of the scales. The only morphological change appears to be a little smoothing of the surface of the scales. From physical appearance, it may be concluded that the changes in physical morphology are not significant compared with the untreated wool sample. This could be because of the uniform nature of glow plasma, which might have resulted in very uniform and thin etching of the fibre surface to change the frictional characteristics and the chemical nature of the surface.

Figure 5(a,b) shows the secondary negative ion spectra of the untreated and plasma treated wool. The intensity counts of the OH and NH groups have increased whereas intensity count of CH group has decreased after the plasma treatment. Figure 6(a,b) show the change in intensity of the selected ions with increasing depth of the samples. In the untreated sample, the intensity of CH ion is very high compared to OH and NH<sub>2</sub> ions. This is likely because of the presence of fatty acid layer on the cuticle surface. The relative ratios of the CH to OH and NH<sub>2</sub> do not seem to change significantly with depth of up to 10 etched layers. However, in the plasma treated samples, the intensity of CH ions has reduced significantly compared to the untreated



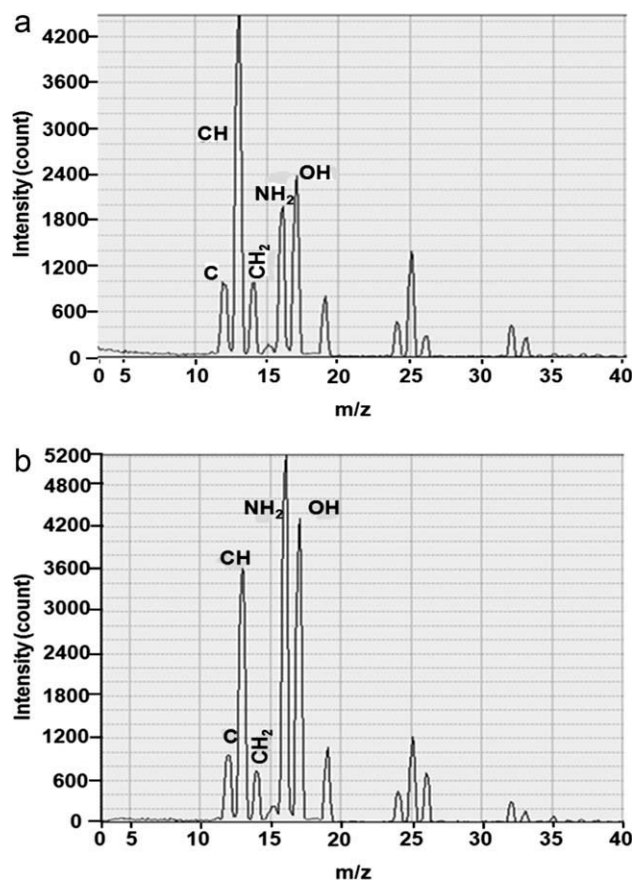
**Figure 4** Scanning electron microscopic images of (a) untreated wool (b) plasma treated wool.

wool. At the same time, intensities of OH and  $\text{NH}_2$  ions are much higher in the first few layers. With increasing depth, the intensity of OH and  $\text{NH}_2$  ions drop to the values similar to the untreated sample. The CH concentration, however, remains low throughout with a gradual increase in its concentration with increasing depth. The depth profile shows that the effect of plasma treatment is mainly on the surface, where the fatty acid molecules seems to have been etched out and polar groups from peptide chains generated.

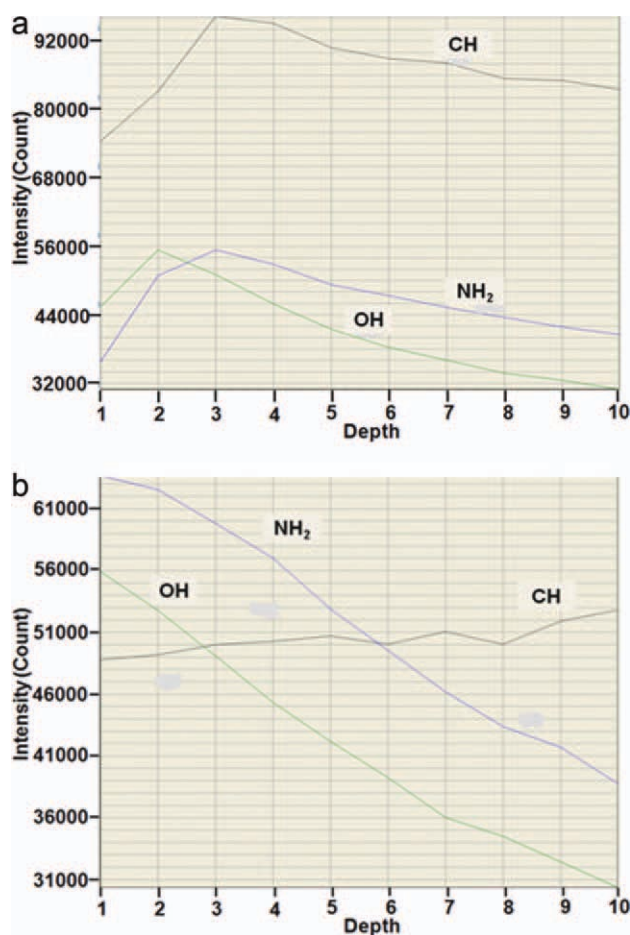
The wettability of wool after plasma treatment was enhanced significantly as the water absorption time decreased from more than 1 h in the case of untreated wool to less than 1 s in the case of helium glow plasma treated wool. There was no detectable effect of ageing (up to 9 weeks) as well as 30 wash

cycles on the wettability of plasma treated wool. This indicates that the effect of plasma treatment under the specified conditions was permanent. The change in fibre wettability is likely to be because of the removal of the covalently bound fatty acid layer from the surface of the wool fibers resulting in the exposure of the underlying hydrophilic protein material<sup>6</sup> and generation of additional polar groups. This is evident from the results of secondary ion mass spectroscopy discussed above.

The felting shrinkage was found to be 13% for the untreated woven samples after 30 machine wash cycles. The plasma treated samples did not show any felting shrinkage under the similar conditions. In the literature, mostly reduced shrinkage values have been reported for the plasma treated wool samples, where the scales were significantly damaged<sup>15,16,1</sup>. In contrast, in our samples, there is no shrinkage even though the scales are more or less intact. It appears that the treatment with glow plasma has smoothened the surface of the fibers and the edges of the scales by uniformly etching out a few layers, possibly resulting in lower frictional properties, to bring about the observed effect.



**Figure 5** Negative ion mass spectra of (a) untreated wool (b) plasma-treated wool.



**Figure 6** Depth profile of selected negative ions from mass spectra of (a) untreated wool (b) plasma-treated wool. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Cold pad-batch dyeing

Application of reactive dyes by cold pad-batch method requires addition of urea and sodium bisulphite in the pad liquor to improve both dye fixation and subsequent levelness of the resultant dyeing<sup>14</sup>.

Urea is reported to increase the fibre swelling and disaggregation of dye leading to improved dye penetration, whereas sodium bisulphite reacts with the disulphide residues in wool to generate highly nucleophilic cysteine thiol groups. Presence of these additives would however increase the chemical loading of the waste water. Any treatment which could otherwise reduce the surface barrier of wool fibers and make it more reactive would result in reducing the use of the above chemicals in cold pad-batch dyeing of wool. Plasma treatment not only reduced the surface barrier by modifying the surface but also generated more reactive groups as is evident from the SIMS results (Figs. 5 and 6). It was therefore decided to study the effect of plasma treatment on the color yield of reactive dye on wool in cold pad-batch dyeing under the varying conditions of urea and sodium bisulphite concentrations as well as pH of the padding liquor. Dichlorotriazine based reactive dye was used for the study as it can react with the fibre under cold conditions.

Atmospheric pressure helium glow plasma treatment resulted in significant improvement in the color yield of reactive dye on wool (Table I). Both the dye pick-up and fixation on wool increased by almost twice based on *K/S* values after the plasma treatment. The expression of wool was found to increase substantially from 60%–70% in untreated wool to 105%–115% after plasma treatment. This increase in expression led to a very high concentration of dye application on the surface of plasma treated wool fibers as can be seen from the *K/S* values of the dyed wool samples before the removal of the unfixed dye (Table I). As discussed earlier, the increased absorption of dye liquor appears to be because of the removal of surface barrier and increased wettability of wool after the plasma treatment. This becomes especially beneficial in the case of cold pad-batch dyeing wherein the contact time between the fibre and the dye liquor is very short as

**TABLE I**  
Effect of Plasma Treatment on Color Yield of C. I. Reactive Red 2 Dye on Wool at Varying Concentrations of Urea and Sodium Metabisulphite

Sample	<i>K/S</i> of dyed wool at different concentrations of urea (g/L)								Fixation % at varying concentration of urea (g/L)			
	Before stripping				After stripping							
	0	100	200	300	0	100	200	300	0	100	200	300
Acid + sb UT	2.33	2.43	3.15	3.55	1.77	1.73	2.27	2.55	75	70	72	71
Acid + sb T	4.66	4.95	4.34	5.37	3.68	3.98	3.66	4.15	78	80	84	77
Acid UT	2.55	2.82	2.91	2.67	2.11	2.51	2.55	2.49	82	88	87	93
Acid T	4.83	5.03	5.42	5.54	4.02	4.32	4.50	4.57	80	86	82	82
Neu + sb UT	2.11	2.38	2.64	2.43	1.49	1.87	2.29	1.94	70	78	86	79
Neu + sb T	5.62	5.07	5.60	5.62	3.70	3.74	4.63	4.27	65	73	82	75
Neu UT	2.95	2.61	3.06	2.77	2.49	2.07	2.49	2.31	84	79	81	83
Neu T	4.94	5.88	5.77	5.58	4.26	4.35	4.19	4.31	86	73	72	77

Acid, acidic pH 5; Neu, neutral pH; sb, 10 g/L sodium metabisulphite; T, plasma treated; UT, untreated. Dye concn: 5 g/L.

**TABLE II**  
**K/S Values of Plasma Treated and Untreated Wool Dyed with 5 and 10 g/L Reactive Dye Solutions Using Cold Pad-Batch Method**

Dye (g/L)	Expression (%)		K/S of unstripped wool		K/S of stripped wool		Fixation (%)	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	treated
5	65	110	2.95	4.94	2.49	4.26	84	86
10	74	111	4.33	10.80	3.27	6.17	75	57

compared with that in exhaust dyeing. Even after the removal of unfixed dye, the *K/S* values increased by almost 100% (from a range of 1.5–2.5 for untreated wool to 3.7–4.6 in case of plasma treated wool). The percentage fixation was in the range of 80%  $\pm$  5% for both untreated and treated wool. This translated to a net increase in the amount of dye fixed in the treated fiber as the dye uptake was significantly higher in this case. It appears that the generation of new amino groups during plasma treatment may have contributed toward the increased fixation of the dye on the treated fibre. Thus plasma treatment has resulted in an overall improvement in the color yield of the reactive dye.

Increase in urea concentration from 0 to 300 g/L resulted in slight increase in the color yield in both untreated as well as treated wool, though the effect was not very significant. Sodium metabisulphite and acidic pH did not appear to have any effect on the color yield. The results may, however, be specific to the dye used in the study and may vary with other dyes, especially those with higher molecular weight. In fact, the *K/S* value of plasma-treated wool at neutral pH without the addition of urea and sodium metabisulphite was almost double (4.26) as compared with that of the untreated wool dyed under similar conditions (1.77) or in acidic pH in the presence of 300 g/L urea and 10 g/L sodium metabisulphite (2.55) (Table I). This shows that cold pad-batch dyeing of plasma treated wool can give very high color yields thus greatly reducing the need for such additives for higher dye uptake. The advantage of using plasma treatment in lieu of additives may be even more significant for high molecular weight dyes.

Cold pad-batch dyeing of untreated and plasma treated wool was further carried out using increased concentration of reactive dye (10 g/L) in the dye bath at neutral pH and without any additives. The pickup of dye on the treated wool increased by approximately double on increasing the dye concentration from 5 to 10 g/L (Table II), whereas, in the case of untreated wool, the increase was lower. The percentage of fixed dye was on an average 60%  $\pm$  5% in the case of treated wool as against  $\sim$  75% in the case of untreated wool. However, the resultant *K/S* of the stripped samples was still significantly higher in the treated samples, whereas untreated

wool showed only a small increase. The lower fixation percentage in treated wool was probably due to the saturation of the dye sites in the treated fibers. It thus appears that the plasma treatment results in a significant modification of the wool surface thus leading to very high levels of dye pick up as is also evident from the % expression (Table II). But all the extra dye taken up by the fibers may not be able to react since the new polar groups are generated only on the surface and these may not be sufficient to bind all the dye molecules.

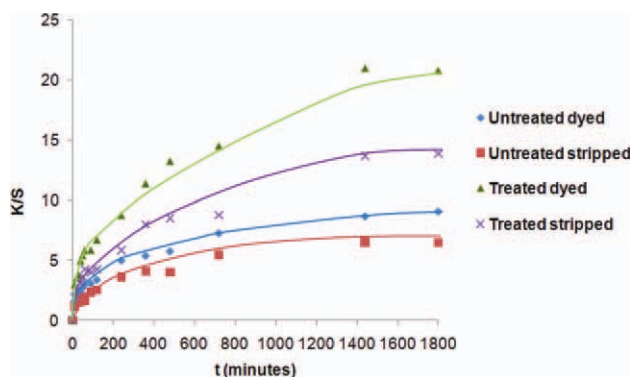
### Dyeing kinetics

To elucidate the change in the kinetics of dyeing after plasma treatment, the dye kinetics of reactive dye on wool was studied in infinite bath at 40°C using exhaust method of dyeing. The dye uptake after different dyeing periods was determined by measuring the *K/S* values of the dyed fabric as well as by measuring the optical density of the dissolved dyed fabric.

As observed in the cold-pad-batch experiments, the *K/S* values in the exhaust dyeing were also found to be almost double in the case of the treated samples as compared to that of the untreated samples (Fig. 7). The increase in the exhausted and fixed dye on treated wool could be seen right from the initial dyeing period and the extent of the increase was maintained till the equilibrium.

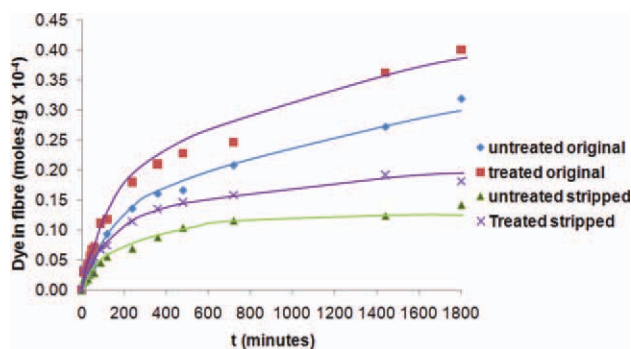
When the total concentration of the dye in the treated sample was determined by optical density, it was found to be higher only by 40%–50% as compared to the untreated sample (Fig. 8). This difference in the *K/S* values and total dye uptake revealed an interesting behavior of the treated samples. It shows that a large amount of dye is being absorbed and reacted on the surface of the fibre after the plasma treatment, though only a part of it is diffusing inside the fibre.

Further, the concentration of dye in fibre (before stripping) was plotted against the square root of the dyeing time for plasma treated and untreated wool fabric for initial dyeing period of 60 min (Fig. 9), as well as, for longer dyeing periods of up to equilibrium (Fig. 10). Curves were linear as is also mentioned for wool in the literature<sup>17</sup>. For initial periods of dyeing, the slope of the treated sample was  $0.9 \times$

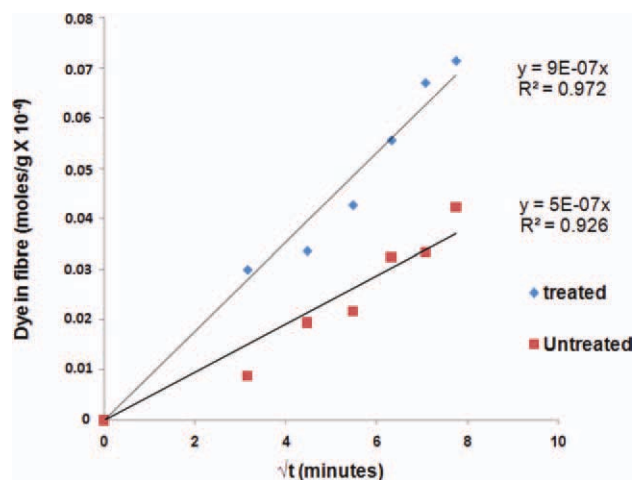


**Figure 7** K/S values of plasma-treated and untreated wool dyed in infinite bath of C.I. Reactive Red 2 for different dyeing periods. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$10^{-6} \text{ mol/g s}^{0.5}$  as for untreated one was  $0.5 \times 10^{-6} \text{ mol/g s}^{0.5}$ . The ratio of the slope for the treated wool to that of the untreated wool was 1.8. For longer dyeing times, the slope of the line for the treated fabric was  $1.0 \times 10^{-6} \text{ mol/g s}^{0.5}$  as for the untreated fabric was  $0.8 \times 10^{-6} \text{ mol/g s}^{0.5}$ , and ratio of treated to the untreated was 1.2. As the slope of line is proportional to the square root of the diffusion coefficient, it shows that the initial difference in dye uptake is due to significantly faster diffusion through the modified cuticular layer of the plasma treated wool. For longer dyeing times, there was only a small difference in the average diffusion coefficient between the treated and untreated wool. This indicates, as also expected, that the diffusion coefficient of dye inside the fibre has not changed significantly. However, the higher concentration of dye inside the treated fibers may also have been a result of higher concentration gradient of dye present between the surface and the inside of the fibre. The above results confirm to the fact that the plasma treatment mainly changed the surface properties of wool.



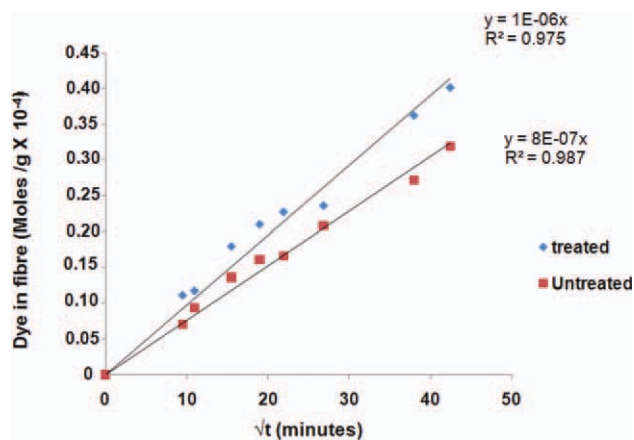
**Figure 8** Amount of dye taken up by plasma-treated and untreated wool dyed in infinite bath of C. I. Reactive Red 2 for different dyeing periods. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



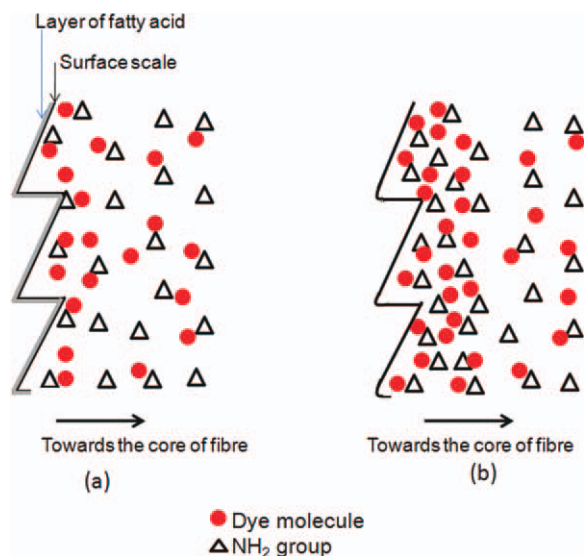
**Figure 9** Plot of dye in fiber vs. square root of dyeing time (minutes) for initial dyeing period of 1 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Fastness properties

In the earlier discussion, it is proposed that the higher amount of dye taken up by the treated wool fiber stays preferably near the surface. This is expected as the new dye sites are likely to be created only near the surface, hence the fixation of dye molecules on these sites causes an increase in the higher dye uptake on the surface. The fixation of the dye near the fiber surface may affect the fastness properties of the dyed material and render the plasma treatment undesirable. Therefore, the dyed wool samples were subjected to one washing cycle as per AATCC 61- 2A method, which is equivalent to five cycles of machine washing. As desired for reactive dyes, the wash fastness rating came out to be five for both treated as well as untreated wool. Also, the light fastness ratings of 4 were obtained for both



**Figure 10** Plot of dye in fiber vs. square root of dyeing time (minutes) for dyeing time of 30 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11** Schematic representation of dyeing mechanism in (b) plasma-treated wool in comparison with (a) untreated wool. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

plasma treated and untreated samples (ISO 105-B02). Rating of fastness to crocking was 5 for both the samples (AATCC 8-2007). These results indicate that the increased amount of dye present in the fibers has fixed well at the existing and newly generated polar groups due to the plasma treatment. The increased dye uptake has not resulted at the cost of the fastness properties of the dyed fiber.

#### Proposed mechanism of dyeing of plasma treated wool

The results of morphological and dyeing studies indicate a possible mechanism of dyeing in plasma treated wool, which is shown schematically in Figure 11(a,b). Due to the reduced surface barrier in treated wool, higher amount of dye is able to diffuse quickly through the cuticular layer compared to the untreated wool. This is seen as an increase in the dye uptake by the treated fibre by about 40%–50% (determined by dissolving the fibres). Since the bulk properties of wool do not change with plasma treatment, not all of this adsorbed dye is able to diffuse inside the fibre toward the core. The plasma treatment is also able to increase the concentration of polar groups near the surface, in particular  $\text{NH}_2$  groups, which helps in fixing the absorbed reactive dye in the top few layers of the treated wool. This is manifested as a much higher color yield by almost 100% in terms of  $K/S$  values of the plasma treated wool. Interestingly, in spite of being a surface phenomenon, the dye fastness properties are not compromised, which suggests that plasma treatment can be effectively used to bring about significant change in the overall dyeing behavior of the wool fibres with reactive dyes.

#### CONCLUSIONS

Cold pad batch dyeing of wool using reactive dyes is an important process for small scale industries as it is carried out at near room temperature. However, the process suffers from low color yield due to poor pick-up of dye liquor during the padding process and from generating high chemical load in effluents due to the use of additives, which are required to improve dye fixation and levelness.

In this study, atmospheric pressure glow plasma using helium gas was used as a pretreatment of the wool fabrics to modify the dyeing behavior of wool in cold pad batch dyeing. The expression of wool during the padding process was found to increase substantially from 60%–70% in untreated wool to 105%–115% in plasma treated wool.

The treatment improved both dye uptake and fixation of dichlorotriazine based reactive dye resulting in substantially higher color yield compared with the control sample. The high color yield was obtained even when the plasma treated wool was dyed at neutral pH and in the absence of various additives such as urea and sodium metabisulphite.

The morphological and dyeing kinetic studies revealed an interesting dyeing behavior of the treated wool. Due to the reduced barrier of the cuticular layer, the treated fabric was able to diffuse in more amount of dye by about 40%–50% compared to the untreated fabric, however, most of this dye got fixed near the surface due to the availability of higher concentration of  $\text{NH}_2$  groups generated by the plasma treatment. This fixation of dye near the surface manifested in substantially higher color yield at about 100% in terms of  $K/S$ , whereas the net increase in dye pick up was much lower. It was also interesting to note that even though the dye appears to have fixed near the surface, the fastness properties of the dyed plasma treated fabric remained unaffected. Further, the felting shrinkage of plasma treated wool fabric was found to be nil even after 30 machine-wash-cycles as against 13% shrinkage in untreated fabric. To conclude, it may be inferred that the atmospheric plasma treatment can be gainfully used to improve the surface properties of wool and color yield of reactive dyes in wool using more ecofriendly cold pad-batch method of dyeing.

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