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Dyeing Behavior of Low Temperature Plasma Treated Wool

C. W. Kan*

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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Abstract: In this paper, the effects of low temperature plasma (LTP) treatment on the dyeing properties of the wool fiber were studied. The wool fibers were treated with oxygen plasma and three types of dye that commonly used for wool dyeing, namely: (i) acid dye, (ii) chrome dye and (iii) reactive dye, were used in the dyeing process. For acid dyeing, the dyeing rate of the LTP-treated wool fiber was greatly increased but the final dyeing exhaustion equilibrium did not show any significant change. For chrome dyeing, the dyeing rate of the LTP-treated wool fiber was also increased but the final dyeing exhaustion equilibrium was only increased to a small extent. In addition, the rate of afterchroming process was similar to the chrome dyeing process. For the reactive dyeing, the dyeing rate of the LTP-treated wool fiber was greatly increased and also the final dyeing exhaustion equilibrium was increased significantly. As a result, it could conclude that the LTP treatment could improve the dyeing behavior of wool fiber in different dyeing systems.

Keywords: Wool, Low temperature plasma, Acid dyeing, Chrome dyeing, Reactive dyeing

Introduction

Wool, unlike other natural fibers, has a complicated surface structure and it is one of the important fibers in the textile industry. However, it has some technical problems such as wettability (which affecting the dyeability). The wool fiber surface is hydrophobic in nature which is due to the presence of a high number of disulphide cystine crosslinkages (-S-S-) in the A-layer of the exocuticle and the fatty acids on the fiber surface [1-4]. This surface morphology is thought to determine the diffusion in wool fiber [5]. Many chemical methods, such as chlorination and polymer deposition, have been developed for modifying the wool fiber surfaces. These methods are effective in improving the hydrophilic behavior of the wool fiber, but the unreacted chemicals left after chemical processing are seen to create a potential effluent problem leading to the environmental awareness. Nowadays, the low temperature plasma (LTP) treatment is one of the commonly used physical methods to replace chemical methods for treating wool fibers. Previous studies [6-8] demonstrated that LTP treatment could help to improve the dyeability and wettability properties of wool fibers. The aim of this paper was to study the dyeing properties of LTP-treated wool fiber with different types of dye.

Experimental

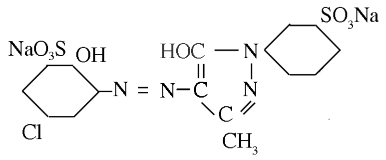
Materials

Raw wool fibers (21 μm diameter) were scoured with dichloromethane (A.R. grade) for 24 hours using Soxhlet extraction. The solvent-scoured wool fibers were washed twice with 98 % ethanol and rinsed twice with deionised water. The fibers were finally dried in an oven at 50 °C for 30 minutes and then air-dried. The vegetable materials and impurities were removed by hand-wash. Finally the wool fibers were conditioned in accordance with ASTM D1776 before use.

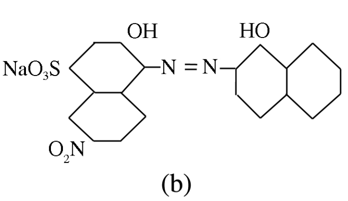
Commercial dye samples were used in the dyeing experiment. The dye samples included (a) acid dye (Neolan Red GRE 200 % (C.I. Acid Red 183)), (b) chrome dye (Eriochrome Black T 250 % (C.I. Mordant Black 11)) and (c) reactive dye (Lanasol Blue 3R (C.I. Reactive Blue 50)). The chemical structures of the acid and chrome dyes were shown in Figures 1(a) and 1(b), respectively.

Low Temperature Plasma (LTP) Treatment

A glow discharge generator (Showa Co. Ltd., Japan) was used for the treatment of wool fibers and fabrics. The glow discharge apparatus was a radio-frequency etching system operating at 13.56 MHz. Fibers were first dried in an oven at 40 °C for 24 hours to minimise the water content and then made parallel by means of a comb sorter before being placed



(a)



(b)

Figure 1. (a) Chemical structure of Neolan Red GRE 200 % (C.I. Acid Red 183), (b) chemical structure of Eriochrome Black T 250 % (C.I. Mordant Black 11).

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*Corresponding author: tccwk@inet.polyu.edu.hk in the reaction chamber. Oxygen gas was used for the LTP treatment and the flow rate of gas was adjusted to 20 cc/min during the LTP treatment. The discharge power and pressure were 100 W and 10 Pa respectively, and the duration of treatment was 5 minutes. Finally, the LTP-treated wool fibers (PO) were conditioned before conducting further experiments.

Scanning Electron Microscopic (SEM) Picture

The surface morphology of the gold-plate wool specimen was studied using Lecia Steroscan 440 scanning electron microscope.

X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were obtained with a Perkin Elmer PHI 5600 combined spectrometer. Al K_α X-ray sources operated at 15 kV and 400 W were used under the working pressure of 5×10^{-10} torr. The peak position were corrected for charging relative to hydrocarbon peak at 285.0 eV and the relative intensities of C_{1s} (285.0 eV), O_{1s} (533.0 eV), N_{1s} (400.0 eV) and S_{2p} (163.0 eV) peaks were determined.

Fourier Transform Infrared with Attenuated Total Internal Reflectance Mode Analysis (FTIR-ATR)

The infra-red spectra of wool fabric were determined by means of Perkin Elmer 16PC FTIR spectrometer in ATR reflection mode using a zinc selenide crystal. The spectra were analysed at an average of 100 scans using a resolution of 4 cm^{-1} and the area of the relevant signal in second-order derivative spectrum was measured. Characteristic IR absorbance frequencies assigned to be studied were given in Table 1.

Table 1. Characteristic IR absorbance frequencies

Species	Structure	Wavenumber (cm^{-1})
NH bending group	-N-H	1600
Cystine dioxide	$-SO_2-S-$	1121
Cystine monoxide	-SO-S-	1071
Cysteic acid	$-SO_3^-$	1040
S-sulphonate (Bunte Salt)	$-S-SO_3^-$	1022

Acid Dyeing

The dyeing process of acid dye was carried out in an oscillating sampling machine manufactured by Tung Shing Dyeing Machines Factory Ltd. The dye liquor for 1 % o.w.f. was composed of 19 m*l* of 1 % sulphuric acid and 5 % Glauber's salt (o.w.f.) at a liquor ratio of 1:150 (1 gram of wool fiber). The dyeing system was maintained at pH 4~5 using 0.05 M sodium acetate with appropriate acetic acid. The dyebath was kept at a temperature of 70 °C for 10 minutes after the addition of auxiliaries and wool fiber samples. The dyes were then added to each dyebath, which were maintained at 70 °C for further 5 minutes before raising the temperature to the boil at a heating rate of 1 °C/minute. The dye concentrations in the dyebath were measured at the start and after 5, 10, 15, 30, 45, 60, 75, 90, 120, 150, 180 and 240 minutes. The dye concentration in each exhaust dyebath was measured at λ_{max} (488 nm) in a 10 mm quartz absorption cell (Pye Unicam Ltd.) using a Philips PU 8620 UV/VIS/IR spectrophotometer. All measurements of dye solution were conducted at room temperature and the percentage exhaustion was calculated according to equation (1).

$$\%E = \left(\frac{A_o - A_t}{A_o}\right) \times 100\% \qquad (1)$$

where $\%E$: percentage exhaustion at time t

A_o: absorbance of dye solution at 0 minute

A_t: absorbance of dye solution at time t

Chrome Dyeing

The chrome dyeings were carried out with 4 % o.w.f. of dye at pH 4.5 using an Ahiba Nuance Top Speed dyeing machine at a liquor ratio of 100:1 (1 gram of wool fiber). The dye was added at 50 °C for 5 minutes and the liquor was then raised to the boil over a period of 50 minutes and kept at this temperature for further 60 minutes. The dyeing rate was measured after 5 minutes of dyeing (defined as zero minute of measurement) and the duration of concentration measurement was 0, 1, 3, 5, 8, 10, 15, 30, 45, 60, 75, 90 and 110 minutes, respectively. The concentration of dyeing liquor in each dyebath was measured at λ_{max} (521 nm) in a 10 mm quartz absorption cell (Pye Unicam Ltd.) using a Philips PU 8620 UV/VIS/IR spectrophotometer and the percentage of exhaustion of chrome dyeing was calculated according to equation (1).

Afterchroming

The afterchroming process of 1 % o.w.f. was performed in a fresh bath using potassium dichromate at pH 3.5 with the same condition as chrome dyeing over a period of 60 minutes at 98 °C. The measurement of chromium concentration was started after 5 minutes of the afterchroming process (defined as zero minute of measurement) and the duration of measurements were 0, 3, 5, 10, 20, 30, 45, 60, 90 and 110 minutes, respectively.

Chromium Determination

Total chromium concentration was determined by means of atomic absorption spectroscopy (Solar System, Unicam Limited) as described in DIN 384406. The hexavalent chromium (Cr(VI)) was assessed by photometric estimation using diphenylcarbazide according to DIN 38405-D24. The trivalent chromium (Cr(III)) was calculated by subtracting the Cr(VI) content from the total chromium content.

Reactive Dyeing

The reactive dyeings were carried out with 2 % o.w.f. at pH 6 using a Ahiba Nuance Top Speed dyeing machine at a liquor ratio of 100:1 (1 gram of wool fiber). The dye, auxilaries (Albegal FFA = 0.5 g/*l* and Albegal B = 1 % o.w.f) and 2 % o.w.f. of 80 % acetic acid were added at 50 °C for 15 minutes and then the temperature of the mixture was raised to the 100 °C over a period of 45 minutes. The mixture was kept at 100 °C for further 60 minutes. The dyeing rate was measured after 5 minutes of dyeing (i.e. 5 minutes after the addition of dye and this time was defined as zero minute of measurement) and the duration of concentration measurement was 0, 5, 8, 10, 20, 40, 60, 90 and 120 minutes respectively. The concentration of dyeing liquor in each dyebath was measured at λ_{max} (600 nm) in a 10 mm quartz absorption cell (Pye Unicam Ltd) using a Philips PU 8620 UV/VIS/IR spectrophotometer and the percentage of exhaustion of reactive dyeing was calculated according to equation (1).

After dyeing, the dyed samples were washed off with 50 % (w/v) urea solution repeatedly, the pH remained at 7.0 and the liquor ratio was 100:1. All the solutions were collected and then determine the unfixed dye concentration and thus the percentage of fixation were calculated.

Substantivity

In addition, the substantivity, K, which represents a measure of the extent to which dye prefers the fiber to the dyebath in the particular dyebath condition was calculated by equation (2) [9].

$$K = \frac{\%E \times L}{100 - \%E} \tag{2}$$

where K: substantivity
$\%E$: percentage exhaustion at equilibrium
L: liquor ratio

Results and Discussion

Surface Morphology

Figure 2 showed the SEM picture of untreated wool fiber in which the escarpments are prominent and well defined. There was no evidence of separation between the neighbouring cuticular cells. Cleft lines were ill-defined. A smooth fiber surface could be pronounced to the untreated fiber surface. After LTP treatment, it was illustrated, as shown in Figure 3, which continuous grooves were located parallel in the direction of the fiber axis and scales edge were lightly eroded and rounded.

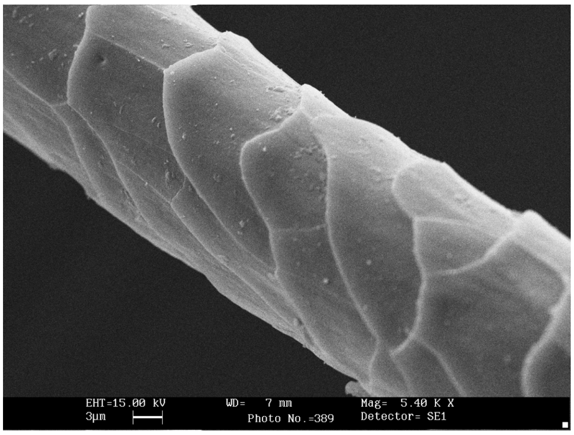

Figure 2. SEM picture of untreated wool fiber.

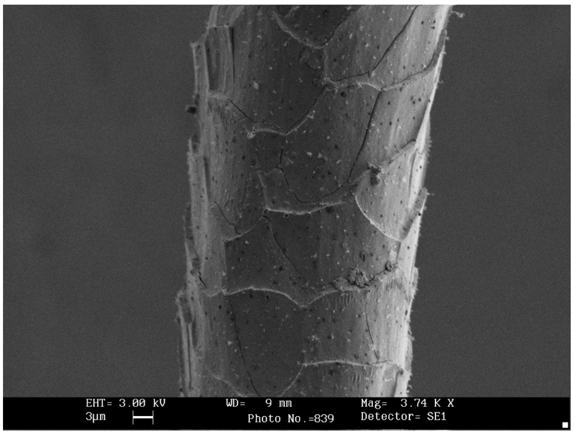

Figure 3. SEM picture of LTP-treated wool fiber.

X-ray Photoelectron Spectroscopy (XPS) Measurement

The results of XPS analysis as summarised in Table 2 provides the elemental composition of the wool surface. It was found that the carbon content was significantly reduced after the LTP treatment. This reduction was probably due to the following reasons: (i) the eroding effect of the LTP treatment on the wool fiber resulting in the removal of fiber surface material and (ii) the oxidation of the wool fiber surface may reduce the carbon element content by bringing about oxygen introduction. Also, the living radicals formed by the LTP treatment may be another source for the oxidation if the sample was taken out in the air soon after the LTP treatment. From the SEM pictures, it clearly showed that the oxygen plasma imparted obvious eroding effect by introducing groove along the fiber axis. The grooving effect induced by oxygen plasma may reduce the carbon content as obtained by the XPS analysis.

The nitrogen content of the wool fiber was increased to different extent after the LTP treatment. This enhancement of nitrogen content on the wool fiber may be probably increased the -NH content of the wool fiber. Under acidic condition such as dyeing process, the -NH groups in wool fiber will be protonised carrying positive charge on the wool fiber and

Table 2. XPS analysis (wt.%) of wool after LTP treatment

Sample	C_{1s}	N_{1s}	O_{1s}	S_{2p}
Untreated	74.72	8.78	13.55	2.58
PO	65.61	8.88	20.16	2.26

made the wool fiber more acceptable for anionic dyes such as acid dyes.

The oxygen content of the LTP-treated wool fiber was found to be increased significantly, so it may say that an oxidising effect was introduced after LTP treatment with the oxygen. The increased amount of oxygen content may enhance the hydrophilicity of the wool fiber which increased the wettability and dyeability of the wool.

The sulphur content after LTP treatment was slightly decreased. It could be explained by the fact that since the cuticle composed of large amount of disulphide bond (-S-S-), the LTP eroding effect removed the cuticular material from the wool fiber and consequently reduced the sulphur content. The removal of cuticular material will improve the due diffusion behavior of the wool fiber.

FTIR-ATR Measurement

The FTIR-ATR technique could analyse to a depth of 500 nm which is good enough to detect the surface chemical component of the wool fiber. Therefore, the FTIR-ATR technique could offer both qualitative and quantitative methods for measuring the composition of the wool surface. The intensity of the selected band frequencies as shown in Table 1 were compared with the peptide frequency (Amide III, 1232 cm^{-1}) as band ratio which was related to the concentration of the surface component. The amount of different functional groups, expressed as absorbance ratio on the wool fiber surface were summarised in Table 3.

After the LTP treatment, the amount of Bunte salt was increased. Beside Bunte salt formation, cysteic acid also formed as a result of the cleavage of disulphide linkage. The presence of the cysteic acid on the polypeptide chain together with the Bunte salt provide a polar surface for the wool fabric which in turn can help to improve the wettability of the wool fabric. On the other hand, the cleavage of the disulphide bonds help to remove the surface barrier of the wool fiber. The amount of cysteic acid increased to a very large extent after the LTP treatment. Apart from Bunte salt and cysteic acid, the other cystine residues studied were the cystine monoxide and cystine dioxide. Both residues were believed to be the intermediate cystine oxidation product. The cystine monoxide and the cystine dioxide are interesting because they represent a more reactive form than the parent disulphide. The formation of cystine monoxide and cystine dioxide in wool will generate a more reactive substrate which provides a suitable site for the introducing agents such as dyes carrying nucleophilic reactive groups. After the LTP treatment, the amount of cyctine monoxide induced to the wool fiber was largely increased. When the amount of cystine dioxide was compared with the cystine monoxide content, it was found that the cystine dioxide suffered a lesser amount than the cystine monoxide content because there may have a spontaneous conversion of cystine dioxide to cyeteic acid resulting in smaller amount of cystine dioxide, It was also observed that the amount of cysteic acid of LTP-treated wool was slightly greater than the cystine dioxide content.

Table 3. The absorbance ratio on wool fiber surface

Functional groups	Absorbance ratio	
	Untreated	PO
Cystine dioxide (-SO_2-S-)	1.00	1.75
Cystine monoxide (-SO-S-)	0.83	2.50
Cysteic acid (-SO_3^-)	1.02	2.50
S-sulphonate (Bunte Salt) (-S-SO_3^-)	1.10	2.75
NH bending group (-N-H)	0.02	0.73

Although the wool fiber itself contained amino groups (-NH_2), further introduction of amino groups may enhanced the absorption of anionic dye during dyeing process. The NH content increased after LTP treatment reflecting that the plasma used can impart amino groups to the wool fiber. The increment of amino content may improve the dyeability of wool because of the newly introduced dyeing sites on the wool fiber.

Acid Dyeing

The exhaustion curves of the LTP-treated sample and the untreated sample are shown in Figure 4, while Table 4 summarises the results of time of half dyeing ($t_{1/2}$) and percentage of exhaustion at equilibrium (%E at E_m) obtained from Figure 4. The percentage exhaustion curve shows the variation of dyebath concentrations against time and the characteristics of a dyeing system, i.e., $t_{1/2}$, %E at E_m and the

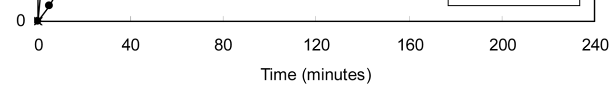

Figure 4. Comparison of percentage dyebath exhaustion between untreated and LTP-treated wool samples with acid dye.

Table 4. Time of half dyeing ($t_{1/2}$) and percentage exhaustion at equilibrium (%E at E_m) of different wool samples with acid dye

Sample	Time of half dyeing ($t_{1/2}$) (minutes)	%E at E_m (%)
Untreated	23.43	70.98
PO	6.43 (↓72.56 %)	71.56 (↑0.83 %)

The figures inside the bracket indicate the increase or decrease in value when treated sample compared with control.

initial rate of dyeing (strike) can be determined.

In Figure 4, it was clearly indicated that the slopes of the curves representing LTP-treated fiber sample at the start of dyeing are steeper than that of the untreated fiber sample which implies that the initial dyeing rate of the LTP-treated fiber sample was faster than the untreated fiber sample. This phenomenon may be due to the fact that the diffusion rate of dye molecules became relatively faster for the LTP-treated fiber sample as a result of surface modification. In addition, the time to reach the dyeing equilibrium also became significantly shorter for the LTP-treated fiber sample, i.e., the percentage exhaustion curve started to flatten in a faster time than the untreated fiber sample. The changes in surface composition probably affect the dyeing behavior of a dyeing system. Based on the result of surface analysis, the introduction of amino (-NH_2) and cysteic acid groups to the wool fiber surface could facilitate the hydrophilic character of the wool fiber and so increase the wool fiber dyeability. In addition, the eroding effect of LTP species on the wool fiber also eliminated the surface barrier. The SEM picture in Figure 3 showed that some grooves were appeared on the LTP-treated wool fiber surface. Such grooves could enhance the diffusion ability of the dye molecule into the wool fiber at a faster rate.

Furthermore, experimental results shown in Table 4 also indicate that the LTP treatment can kinetically alter the dyeing system. The time of half dyeing ($t_{1/2}$) defined as the time required to reach half equilibrium was used as an effective value to quantify the rate of dyeing in a dyeing system. The $t_{1/2}$ value of the LTP-treated fiber sample was found to be greatly reduced when compared with that of the untreated fiber sample, but the change of %E at E_m was not significant. This interesting observation may be due to the number of available dyeing sites present in the wool fibers which would affect the percentage of exhaustion at equilibrium. The dyeing sites of the fiber are generally associated with the internal structure of the fiber, thus any change of the internal fiber structure may alter the amount of dyeing sites. However, the plasma species could only penetrate to a depth of 0.1 μm [7] at the fiber surface within the duration of the treatment time. This penetration of plasma species was not deep enough to alter the whole or partial internal structure of the wool fiber. As a result, most of the available dyeing sites will remain unchanged after LTP treatment leading to a little effect on the final dyebath exhaustion.

Chrome Dyeing

In previous research work [8], microscopic studies elucidating the LTP treatment could influence the dyeing behavior of wool fiber. Light microscopic studies demonstrated that the LTP-treated wool fiber could easily be penetrated by dyes which were evenly distributed over the cross-section of the fiber [8]. This phenomenon could be due to both the plasma-induced cystine oxidation in the A-layer of the exocuticle and the reduced number of cross-linkages at the fiber surface. These two surface morphology changes obviously facilitate a transcellular dye diffusion in addition to the intercellular dye diffusion. Transmission electron microscopy investigation [8] also showed that LTP treatment only modified the A-layer of the cuticle to various extents due to sputtering resulting in a partial swelling of the A-layer. In addition, the etching of the A-layer leads to the formation of grooves in this layer. Due to a partial degradation of the A-layer, which acted as a barrier to the diffusion of dyes and other chemicals, the affinity of the fiber for dyes would thus be increased. The increase of dye absorption was most probably caused by the modification of the endocuticle and the neighbouring cell membrane complex which resulted in a modification of the intercellular path of diffusion [8].

Figure 5 shows the results of dyebath exhaustion during the chrome dyeing process. The results demonstrate that the LTP treatments can influence the dyeing behavior of wool fiber to different extents. Table 5 shows the time of half dyeing and final bath exhaustion derived from Figure 5.

In Figure 5, it may be seen that the dyeing rate increased for the LTP-treated fiber sample and in Table 5, the values of time of half-dyeing did provide a good support for the determination of rate of dyeing. The time of half-dyeing for the LTP-treated fiber sample was reduced when compared with the untreated fiber sample. The reduction in the time of half-dyeing indicated that the LTP treatment could lead to a considerable shortening of dyeing time, thereby reducing the energy consumption and hence improving the dyeing operation.

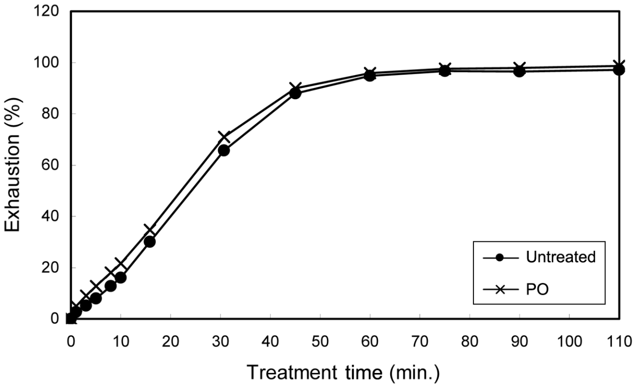

Figure 5. Comparison of percentage dyebath exhaustion between untreated and LTP-treated wool samples with chrome dye.

Table 5. Time of half dyeing ($t_{1/2}$) and percentage exhaustion at equilibrium (%E at E_m) of different wool samples with chrome dye

Sample	Time of half dyeing ($t_{1/2}$) (minutes)	%E at E_m (%)
Untreated	22.53	97.16
PO	21.06 (↓6.52 %)	98.73 (↑1.62 %)

The values in the bracket showed either increase or decrease in percentage when compared with the untreated sample.

In addition, the final bath exhaustions shown in Table 5 did not show significant changes. As the final dyebath exhaustion depended much on the available dyeing sites of the wool fiber and since the penetration of LTP species to a depth of about 0.1 μm [7], the depth of penetration and etching is not sufficient enough to alter the internal structure of fiber or to induce any new dyeing sites in the fiber. Therefore, only a small increase of the final dyebath exhaustion resulted.

Hexavalent Chromium Determination

C.I. Mordant Black 11 was chosen because this dye required to remove the yellowish staining by an ammonia aftertreatment during which chromium could be extracted from the wool fiber resulting in a further effluent load.

The changes in hexavalent chromium levels in the treatment bath during the afterchroming process for both the untreated and LTP-treated fiber samples are shown in Figure 6. It was obvious that the hexavalent chromium concentration decreased during the afterchroming process. The chromium uptake by the fibers occurred more rapidly for the LTP-treated fiber sample than the untreated fiber sample and the effect was very similar to the results obtained in the rate of dyeing. The first effluent sample collected 5 minutes after the application of potassium dichromate at 50 °C (denoted as zero-treatment time in Figure 4) showed that a large amount of the chromium had already been exhausted by the LTP-treated fiber sample, whereas the untreated wool fiber still showed a relatively lower affinity for chromium at the beginning of the afterchroming process. For the first 10 minutes of afterchroming process, the LTP-treated fiber sample showed a similar rate of chromium exhaustion to the untreated fiber sample. After 10 minutes of the afterchroming process, it was clearly demonstrated that the LTP-treated fiber sample had a faster rate of chromium exhaustion than the untreated fiber sample. This phenomenon was maintained until the end of the afterchroming process. Although the concentration of hexavalent chromium was decreased during the afterchroming process, the decrease finally reached to an equilibrium.

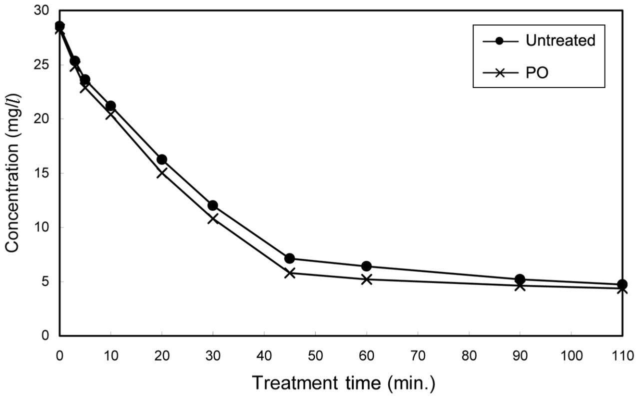

Figure 6. Concentration of hexavalent chromium in afterchroming treatment bath.

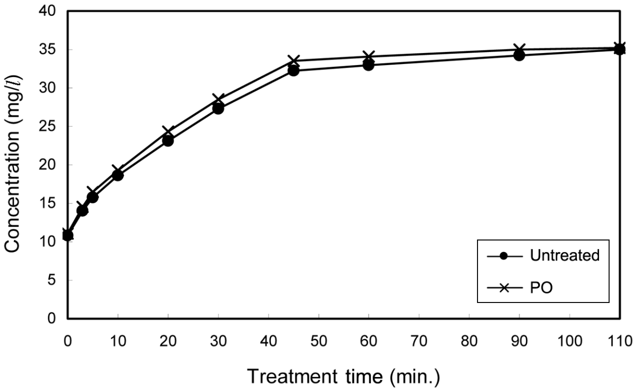

Figure 7. Uptake of trivalent chromium by differently LTP-treated fiber sample in the afterchroming process as a function of treatment time.

Trivalent Chromium Determination

The trivalent chromium concentration absorbed by LTP-treated fiber sample is shown in Figure 7 in which the LTP-treated fiber sample indicates an increase in the amount of absorbed trivalent chromium content throughout the afterchroming process when compared with the untreated fiber sample. Such results are closely related to the amount of hexavalent chromium exhausted by the wool fibers. It may also be observed that Figure 7 is almost an inverted graph of Figure 6. Similarly, the fixation of final trivalent chromium is slightly increased for the LTP-treated fiber sample and this phenomenon is similar to the results of final dyebath exhaustion.

The improved trivalent chromium fixation and hexavalent chromium exhaustion will reduce the amount of effluent load discharged to the environment. Previous research [8] showed that the LTP treatment of wool fibers would not only facilitate the uptake of chromium by the fiber but also reduce its discharge in the effluent. The present research gave a good agreement to previous finding [8].

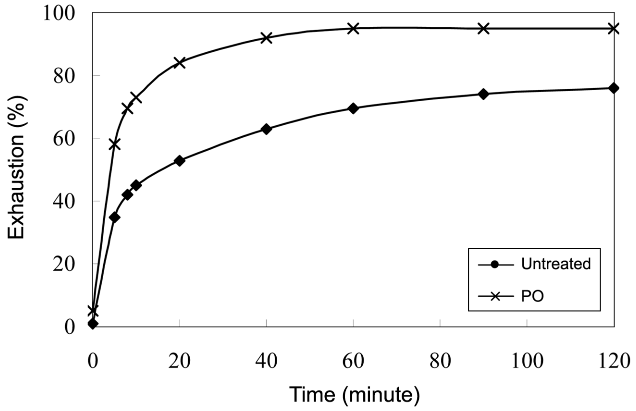

Figure 8. Exhaustion curve of different wool samples with reactive dye.

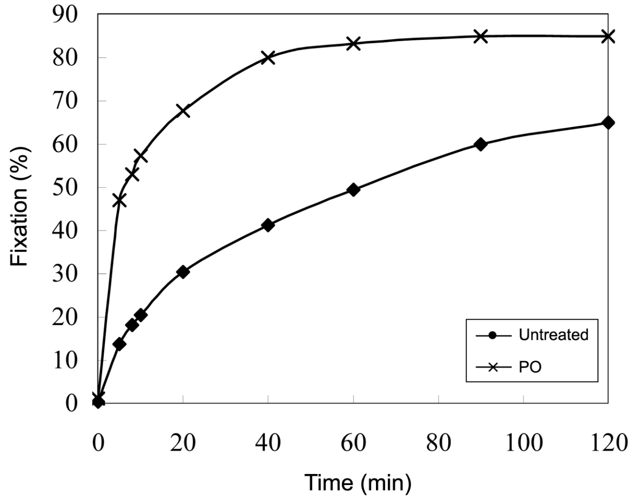

Figure 9. Fixation curve of different wool samples with reactive dye.

Table 6. Time of half dyeing ($t_{1/2}$) and percentage exhaustion at equilibrium (%E at E_m) of different wool samples with reactive dye

Sample	Time of half dyeing ($t_{1/2}$) (minutes)	%E at E_m (%)
Untreated	6.6	76
PO	4 (↓39.40 %)	94 (↑23.68 %)

The values in the bracket showed either increase or decrease in percentage when compared with the untreated sample.

Table 7. K values of different dyeing system

Dyeing system	Sample	%E at E_m (E)	Liquor ratio (L)	Substantivity (K)
Acid	Untreated	70.98	150	366.88
	PO	71.56	150	377.43
Chrome	Untreated	97.16	100	3421.13
	PO	98.73	100	7774.02
Reactive	Untreated	76	100	316.67
	PO	94	100	1566.67

Reactive Dyeing

Figures 8 and 9 show the exhaustion and fixation curves of the reactive dyed wool fiber respectively. Based on Figure 8, the time of half dyeing and the final dyeing exhaustion equilibrium are obtained and summarized in Table 6.

Similar to acid and chrome dyeings, the dyeing rate of reactive dyeing of LTP-treated fiber sample is faster than that of the untreated fiber sample. This result could be due to the fact that the diffusion rate of dye molecules became relatively faster for the LTP-treated fiber as a result of surface modification by the formation of grooves on the fiber surface Also the time to reach the dyeing equilibrium becomes shorter for the LTP-treated fiber sample.

However, the change of percentage exhaustion at equilibrium was increased significantly. This observation is not similar to acid and chrome dyeing but the percentage exhaustion at equilibrium is a dependence on the number of available dyeing sites present in the wool fibers. Although the plasma species in LTP treatment could only penetrate to a depth of 0.1 μm [7] at the fiber surface within the duration of the treatment time and this penetration of plasma species is not deep enough to alter the whole or partial internal structure of the wool fiber, the oxygen plasma used in this paper could be classified as chemical etching in which the oxygen functional groups including C-O, C=O, O-C=O, C-O-O, -OH and -OOH groups would be introduced in the fiber surface [10]. The oxygen functional groups so induced in the fiber surface could enhance the dye-fiber reaction between reactive dye and wool fiber [2]. In addition, upon the oxygen plasma treatment, the -NH bending groups to the wool fiber increased accordingly which implying the newly introduction of amino group of the wool fiber. As a result, the available dyeing sites are increased and thus the final yields of dyebath exhaustion and dye fixation on fiber are increased significantly. Furthermore, the reactive dye used in this paper contains α-bromoacrylamido reactive group which has an excellent stability to hydrolysis under weakly acid condition (pH 6) [11]. Since the reactive dye used is stable under the dyeing condition, the dye loss due to the hydrolysis was reduced. As a result, more dyes could react with the wool fiber. In couple with the increased available dyeing sites and more dyes for reaction during the dyeing process, the final exhaustion and fixation yields increase significantly.

Substantivity

The substantivity, K, can be used as a simple tool to demonstrate the measure of the extent which dye prefers the fibers to the dyebath in the particular dyebath conditions. It can also represent the general nature of the relationship between substantivity, liquor ratio and percentage of exhaustion at equilibrium. The K value reflects how efficiently dye has been transferred from the bath to the fiber. The greater the K value, the better dye retains in the fiber. Table 7 shows the K values of different dyeing system. From Table 7, it is obvious that after the LTP treatment, the K values are increased significantly especially in case of chrome and reactive dyeing. Therefore, it could conclude that the LTP treatment on the wool fiber is an effective method to enhance dye exhaustion on the fiber.

Conclusion

The influence of the LTP treatment on the dyeing properties of the wool fibers with different dyeing system was studied. The dyeing rate of three dyeing systems were increased significantly but in the case of acid and chrome dyeing system, the percentage exhaustion at equilibrium did not show any significantly change. Such slightly change of percentage exhaustion at equilibrium would be deal to the fact that the depth of penetration and etching caused by LTP was not sufficient enough to alter the internal structure of fiber or to induce any new dyesites in the fiber. However, in the case of reactive dyeing, the LTP treatment introduced oxygen functional groups in the fiber surface. These oxygen functional groups so induced in the fiber surface could enhance the dye-fiber reaction between reactive dye and wool fiber. As a result, the available dyesites were increased and thus the final dyebath exhaustion and dye fixation on fiber were increased accordingly. For the chrome dyeing system, the rate of afterchroming process was similar to the dyeing process.

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