

EFFECT OF LOW TEMPERATURE PLASMA ON DIFFERENT WOOL DYEING SYSTEMS

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Abstract:

In this paper, the effects of low temperature plasma (LTP) treatment on the dyeing properties of wool were studied. Wool fibres were treated with oxygen plasma and three types of dyeing systems that are 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 LTP-treated wool fibre was greatly increased, but the final dyeing exhaustion equilibrium did not show any significant change. For chrome dyeing, the dyeing rate of LTP-treated wool fibre was increased, but the final dyeing exhaustion equilibrium was increased only to a small extent. In addition, the rate of the afterchroming process was similar to the chrome dyeing process. In the case of reactive dyeing, the dyeing rate of LTP-treated wool fibre was greatly increased and also the final dyeing exhaustion equilibrium was increased significantly.

As a result, it may be concluded that the LTP treatment could improve the dyeing behaviour of wool fibre under different dyeing systems.

Key words:

barriers, fibres, surfaces, plasma treatment and textiles.

Introduction

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

Experimental Data

Wool fibre

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

LTP treatment

A glow discharge generator (Showa Co. Ltd., Japan) was used for the treatment of the wool fibres. The glow discharge apparatus was a radio-frequency etching system operating at 13.56 MHz and using an aluminium chamber with an internal diameter of 200 mm. The chamber external diameter was 380 mm with a height of 180 mm. The distance between the electrodes was fixed at 50 mm. Fibres 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 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 80W and 10 Pa respectively, and the duration of treatment was 5 minutes. Finally, the LTP-treated wool fibres (PO) were conditioned before conducting further experiments.

Dye samples

Commercial dye samples were used directly without purification in the dyeing experiment. The dye samples included (a) acid dye (C.I. Acid Red 183), (b) chrome dye (C.I. Mordant Black 11) and (c) reactive dye (C.I. Reactive Blue 50).

Acid dyeing

The dyeing process of acid dye was carried out in an oscillating sampling machine manufactured by Tung Shing Dyeing Machines Factory Ltd. Thirteen identical dyebaths were prepared and thirteen wool fibre samples (1g each) were used. The dye liquor for 1% depth of dyeing was composed of 19 ml of 1% sulphuric acid and 5% Glauber's salt (o.w.f.) at a liquor ratio of 1:150. The dyeing system was maintained at pH 4.2 using 0.05M 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 fibre samples. The dyes were then added to each dyebath, which were maintained at 70°C for a 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 of exhaustion was calculated according to Equation (1).

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

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

Chrome dyeing was carried out with 4% o.w.f. of dye at pH 4.5 using a Ahiba Nuance Top Speed dyeing machine at a liquor ratio of 100:1 (1 gram of wool fibre). The dye was added at 50°C for 5 minutes and the liquor was then raised to a boil over a period of 50 minutes and kept at this temperature for a further 60 minutes. The dyeing rate was measured after 5 minutes of dyeing (defined as zero minute of measurement) and the concentration measurements were done at 0, 1, 3, 5, 8, 10, 15, 30, 45, 60, 75, 90 and 110 minutes of dyeing time 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 under the same conditions as chrome dyeing over a period of 60 minutes at 98°C. The chromium concentration was measured after 5 minutes of the afterchroming process (defined as the

zero minute of measurement) and the concentration measurements were done at 0, 3, 5, 10, 20, 30, 45, 60, 90 and 110 minutes of afterchroming time 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

Reactive dyeing was carried out with 2% o.w.f. of dye at pH 6 using a Ahiba Nuance Top Speed dyeing machine at a liquor ratio of 100:1 (1 gram of wool fibre). The dye, auxiliaries (Albegal FFA = 0.5g/l and Albegal B = 1% on-weight of fibre) 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 100°C over a period of 45 minutes. The mixture was kept at 100°C for a 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 the zero minute of measurement) and the concentration measurements were done at 0, 5, 8, 10, 20, 40, 60, 90 and 120 minutes of dyeing time 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 the unfixed dye concentration was determined, and thus the fixation was calculated.

Substantivity

The substantivity, K, which represents a measure of the extent to which dye prefers the fibre to the dyebath in the particular dyebath condition, was calculated by Equation (2) [9].

$$K = \frac{\%E \times L}{100 - \%E} \quad (2)$$

where: K = substantivity,
 %E = percentage of exhaustion at equilibrium,
 L = liquor ratio.

Results and Discussion

Acid dyeing

The exhaustion curves of the untreated and LTP-treated samples are shown in Figure 1, while Table 1 summarises the results of time of half dyeing ($t_{1/2}$) and percentage of exhaustion at equilibrium (%E at Em), obtained from Figure 1. The exhaustion percentage curve shows the variation of dyebath concentrations over time, and from it the characteristics of a dyeing system, i.e., $t_{1/2}$, %E at Em and the initial rate of dyeing (strike) can be determined.

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

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

The values in brackets represent the increase or decrease in percentage when compared with the untreated sample.

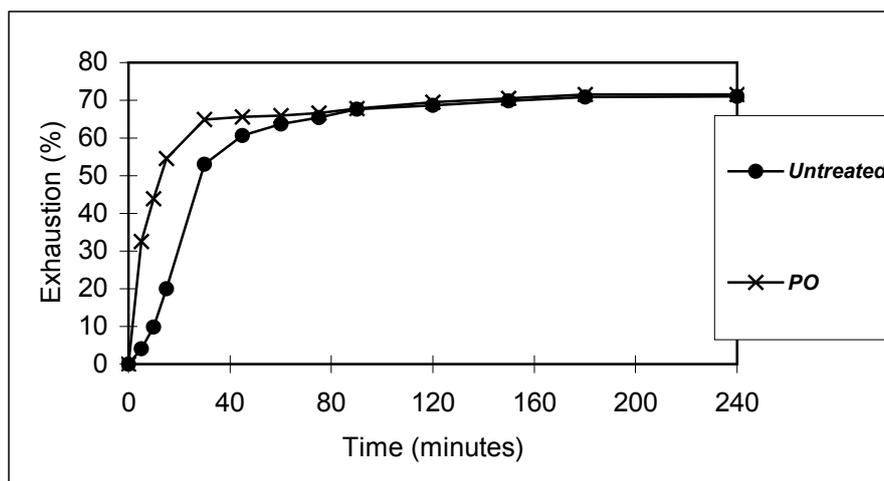


Figure 1. Percentage of dyebath exhaustion of different wool samples with acid dye.

From Figure 1 it may be seen that the slopes of the curves representing LTP-treated fibre at the initial stage of dyeing are steeper than that of the untreated fibre sample, which implies that the initial dyeing rate of the LTP-treated fibre was faster than the untreated fibre. This phenomenon is probably due to the fact that the diffusion rate of dye molecules became relatively faster for LTP-treated fibres as a result of surface modification. In addition, the time to reach the dyeing equilibrium also became significantly shorter for the LTP-treated fibre, i.e., the exhaustion percentage curve started to flatten in a shorter time than in the case of untreated fibres. A previous study showed that the nature of the plasma played an important role in altering the surface composition of the fibre [6]. Oxygen plasma increases the cysteic acid content on the wool fibre surface [6]. The cysteic acid groups facilitate the hydrophilic and wetting character of the wool fibre and hence increase the dyeability of the wool fibre.

Furthermore, the experimental results shown in Table 1 also indicate that the LTP treatment can alter the dyeing rate. 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 LTP-treated fibre was found to be greatly reduced when compared with untreated fibre, but the change of %E at E_m was not significant. This interesting observation may be due to the number of available dyesites present in the wool fibres, which would affect the percentage of exhaustion at equilibrium. The dyesites of the fibre are generally associated with the internal structure of the fibre, thus any change of the internal fibre structure may alter the amount of dyesites. However, the plasma species could only penetrate to a depth of 0.1 μm [7] of the fibre 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 fibre. As a result, most of the available dyesites will remain unchanged after LTP treatment, having little effect on the final dyebath exhaustion.

Chrome dyeing

In previous research [8], microscopic studies elucidated the fact that LTP treatment could influence the dyeing behaviour of wool fibre. Light microscopic studies demonstrated that the LTP-treated wool fibre could easily be penetrated by dyes which were evenly distributed over the cross-section of the fibre [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 fibre surface. These two surface morphology changes obviously facilitate a transcellular dye diffusion in addition to the intercellular dye diffusion. Transmission electron microscopy investigations [8] also showed that LTP treatment only modified the A-layer of the cuticle to certain 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 fibre for dyes is thus increased. The increase in 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].

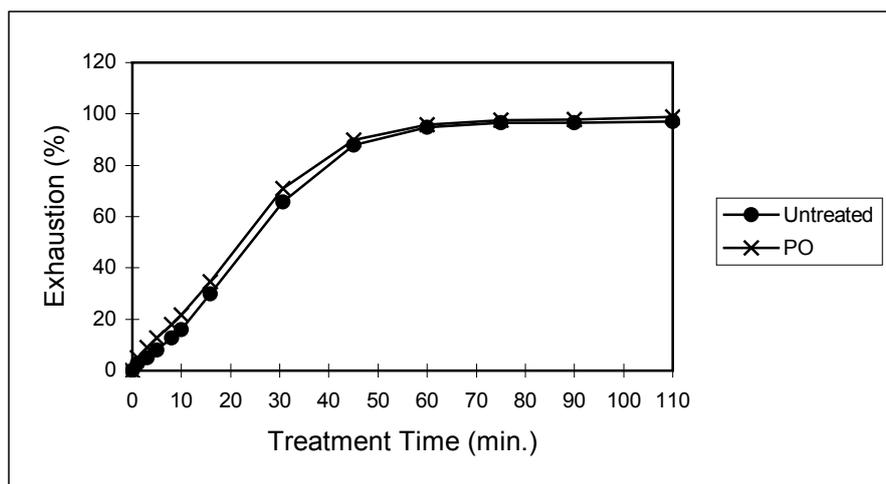


Figure 2. Percentage of dyebath exhaustion for different wool samples with chrome dye.

Figure 2 shows the results of bath exhaustion during the dyeing process. The results demonstrate that the LTP treatments can influence the dyeing behaviour of wool to different extents. Table 2 shows the time of half dyeing and final bath exhaustion derived from Figure 2.

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

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

The values in brackets represent the increase or decrease in percentage when compared with the untreated sample.

In Figure 2 it may be seen that the dyeing rate increased for the LTP-treated fibre and in Table 2, the values of time of half-dyeing provided a good support for determination of the dyeing rate. The time of half-dyeing for the LTP-treated fibre was changed significantly when compared with the untreated fibre. The reduction in the time of half-dyeing indicates that the LTP treatment could lead to a considerable shortening of dyeing time, thereby reducing energy consumption and hence improving the dyeing operation. In addition, the final bath exhaustion percentages shown in Table 2 did not demonstrate significant changes. As the final dyebath exhaustion percentage depended greatly on the available dyesites of the wool fibre, and since the penetration of LTP species was to a depth of about 0.1µm [7], the depth of penetration and etching is not sufficient to alter the internal structure of fibre or to induce any new dyesites in the fibre. Therefore, only a small increase in the exhaustion percentage of the final dyebath took place.

Hexavalent chromium determination

C.I. Mordant Black 11 was chosen because this dye required a removal of yellowish staining by an ammonia aftertreatment, during which chromium could be extracted from the wool fibre, 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 fibres are shown in Figure 3. Clearly, the hexavalent chromium concentration decreased during the afterchroming process. The chromium uptake by the fibres occurred more rapidly for the LTP-treated fibre than the untreated fibre and the effect was very similar to the results obtained for 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 3), showed that a large amount of the chromium had already been exhausted by the LTP-treated fibre, whereas the untreated wool fibre still showed a relatively lower affinity for chromium at the beginning of the afterchroming process. For the first 10 minutes of the afterchroming process, the LTP-treated fibre

showed a similar rate of chromium exhaustion to the untreated fibre. But after 10 minutes of the afterchroming process, it was clearly demonstrated that the LTP-treated fibre had a faster rate of chromium exhaustion than the untreated fibre, and that 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 a state of equilibrium.

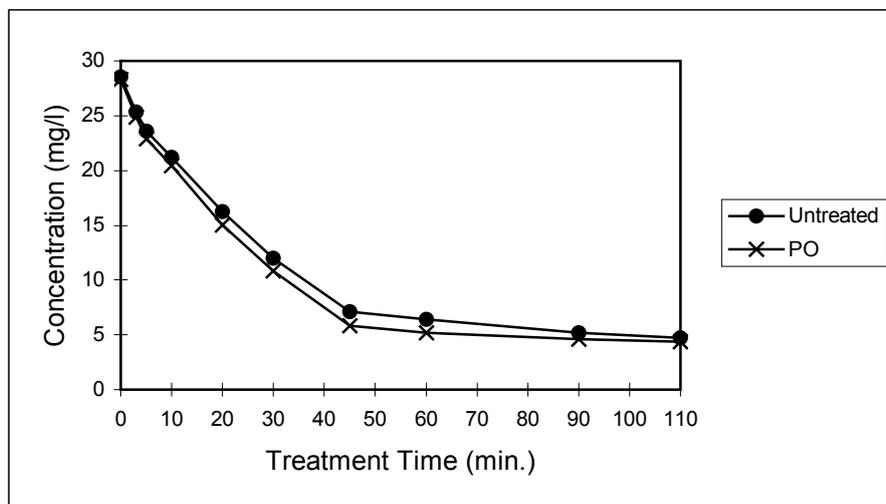


Figure 3. Concentration of hexavalent chromium in afterchrome treatment bath.

Trivalent chromium determination

The trivalent chromium concentration absorbed by LTP-treated fibres is shown in Figure 4, in which the LTP-treated fibre indicates an increase in the amount of absorbed trivalent chromium content throughout the afterchroming process when compared with untreated fibres. These results are closely related to the amount of hexavalent chromium exhausted by the wool fibres. It may also be observed that Figure 4 is almost an inverted graph of Figure 3. Similarly, the fixation of final trivalent chromium is slightly increased for the LTP-treated fibre 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] has shown that the LTP treatment of wool fibres not only facilitates the uptake of chromium by the fibre, but also reduces its discharge in the effluent. The present research showed similar results to the previous findings [8].

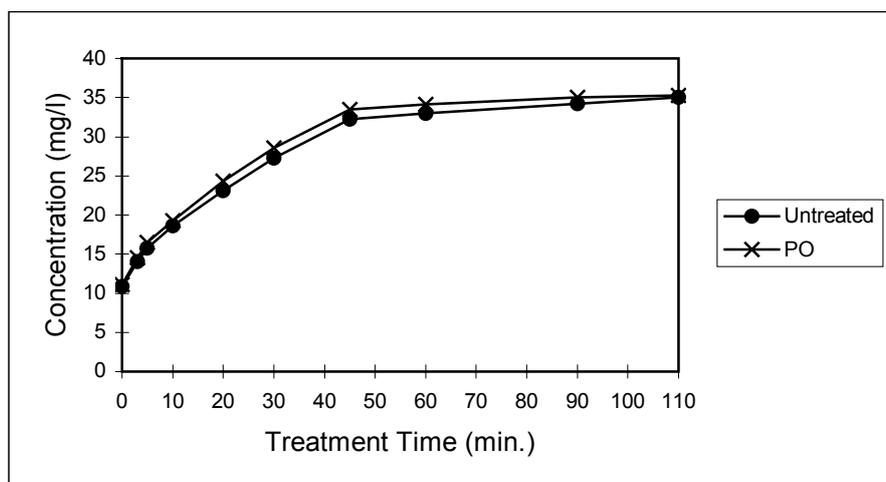


Figure 4. Uptake of trivalent chromium by differently LTP-treated fibre in the afterchrome process as a function of treatment time.

Reactive dyeing

Figures 5 and 6 show the exhaustion and fixation curves of reactive dyed wool fibres. Based on Figure 5, the time of half dyeing and the final dyeing exhaustion equilibrium are determined, and summarized in Table 3.

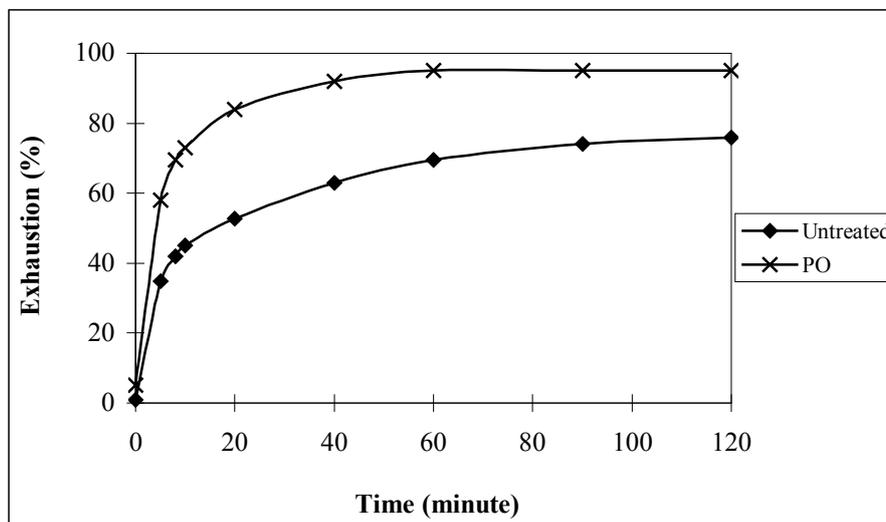


Figure 5. Exhaustion curve of different wool samples with reactive dye.

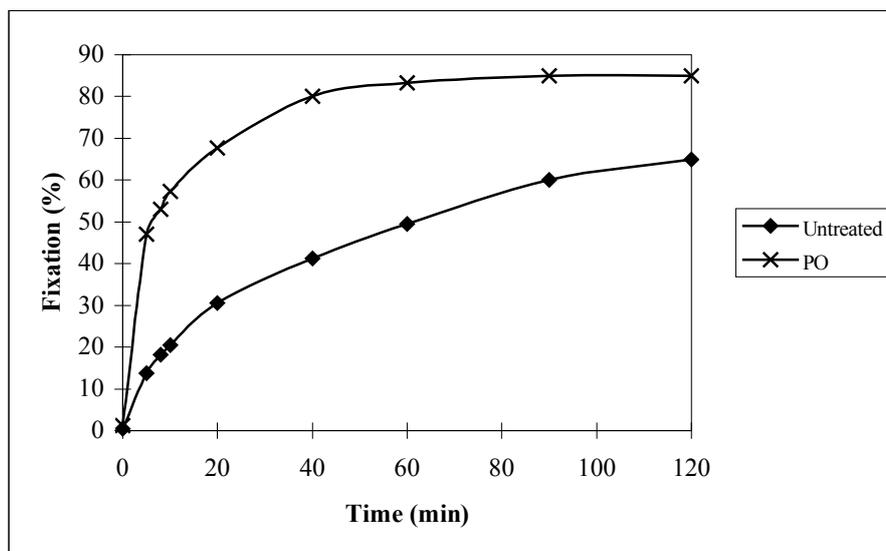


Figure 6. Fixation curve of different wool samples with reactive dye.

Table 3. Time of half dyeing ($t_{1/2}$) and exhaustion percentage at equilibrium (%E at Em) of different wool samples with reactive dye.

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

The values in brackets represent the increase or decrease in percentage when compared with the untreated sample.

Similar to acid and chrome dyeing, the dyeing rate of reactive dyeing of LTP-treated fibre is faster than that of the untreated fibre. This result could be due to the fact that the diffusion rate of dye molecules becomes relatively faster for LTP-treated fibres as a result of surface modification. Also the time to reach the dyeing exhaustion equilibrium becomes shorter for LTP-treated fibres.

However, the change of exhaustion percentage at equilibrium showed a significant increase. This phenomenon is absent in acid and chrome dyeing, but the percentage exhaustion at equilibrium is a dependence on the number of available dyesites presence in the wool fibres. Although the plasma species in LTP treatment could only penetrate to a depth of 0.1 μ m [7] at the fibre surface throughout 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 fibre, 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 are introduced in the fibre surface [10]. The oxygen functional groups so induced in the fibre surface could enhance the dye-fibre reaction between the reactive dye and wool fibre [2]. As a result, the available dyesites are increased and thus the final dyebath exhaustion and dye fixation on fibre are increased accordingly.

Substantivity

The substantivity, K, can be used as a simple tool to measure the extent which dye prefers the fibres to the dyebath in particular dyebath conditions. It can also represent the general nature of the relationship between substantivity, liquor ratio, and the percentage of exhaustion at equilibrium. The K value reflects how efficiently dye has been transferred from the bath to the fibre. The greater the value of K, the better the dye is retained in the fibre. Table 4 shows the K values of different dyeing systems and it is obvious that after the LTP treatment, the K values are increased significantly; especially in the cases of chrome and reactive dyeing. Therefore, it could be concluded that the LTP treatment on wool fibre is an effective method to promote dye exhaustion on the fibre.

Table 4. K values of different dyeing systems.

Dyeing system	Sample	%E at Em (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

Conclusions

The influence of LTP treatment on the dyeing properties of wool fibres using different dyeing systems was studied. The dyeing rate of three dyeing systems were increased significantly, but in the cases of acid and chrome dyeing, the exhaustion percentage at equilibrium did not show any significant change. Such a slight change in the exhaustion percentage at equilibrium could be explained by the fact that the depth of penetration and etching caused by LTP was not sufficient to alter the internal structure of the fibre or to induce any new dyesites in the fibre. However, in the case of reactive dyeing, where LTP treatment has been done previously to the reactive dyeing, it has introduced oxygen functional groups in the fibre surface. These oxygen functional groups induced in the fibre surface enhance the dye-fibre reaction between reactive dye and wool fibre. As a result, the available dyesites were increased and thus the final dyebath exhaustion and dye fixation on fibre rates were increased accordingly. For the chrome dyeing system, it was noted that both the dyeing and afterchroming processes were improved after LTP treatment.

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