Fibers and Polymers 2004, Vol.5, No.1, 52-58

Surface Characterization of Low Temperature Plasma Treated Wool Fiber –The Effect of the Nature of Gas–

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(Received September 24, 2003; Revised December 23, 2003; Accepted December 30, 2003)

Abstract: Previous investigation results revealed that after the Low Temperature Plasma (LTP) treatment, the hydrophilicity of wool fiber was improved significantly. Such improvement enhances the wool dyeing and finishing processes which might be due to the changes of the wool surface to a more reactive one. In this paper, wool fibers were treated with LTP with different gases, namely, oxygen, nitrogen and gas mixture (25 % hydrogen/75 % nitrogen). Investigations showed that chemical composition of wool fiber surface varied differently with the different plasma gas used. The surface chemical composition of the different LTP-treated wool fibers was evaluated with different characterization methods, namely FTIR-ATR, XPS and saturated adsorption value. The experimental results were thoroughly discussed.

Keywords: Low temperature plasma, Wool surface, FTIR-ATR, XPS, Saturated adsorption value

Introduction

With the reference to previous researches [1,2], the low temperature plasma treatment has been confirmed to enhance the hydrophilicity and to improve the dyeability of the wool. Exposure to a suitable plasma can produce a more reactive surfaces and affect surface properties without altering the desirable properties of the bulk material [3,4]. As a result, the aim of this paper was to investigate the surface chemical and physical composition of the low temperature plasma treated wool under the influence of plasma gas with different nature. The understanding of the surface composition can provide more information about the induced surface properties of low temperature plasma treated wool.

Experimental

Material

Greasy raw wool fibers (64 s, 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 rinse twice with deionised water. The fibers were finally dried in an oven at 50 °C for 30 minutes and were then air dried. The vegetable matters and impurities were removed by hand. Finally, the wool fibers were conditioned according to ASTM Designation: D1776.

Unbleached 100 % pure 2/1 twill fabrics, made from 64 s wool fibers of 180 g/m^2 with 41 ends/cm (31 tex) and 25 picks/cm (36 tex) was scoured with dichloromethane for 4 hours using Soxhlet extraction. The aftertreatment of the solvent scoured fabric was the same as that of fiber prior to further treatment.

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Low Temperature Plasma (LTP) Treatment

A glow discharge generator (Showa Co. Ltd., Japan) was used for the treatment of wool fibers. The glow discharge apparatus was a radio-frequency etching system operating at 13.56 MHz and using an aluminum chamber with an internal diameter of 200 mm. The chamber diameter was 380 mm with a height of 180 mm. Fibers are dried in an oven at 40 °C for 24 hours to minimize the water content and then made parallel by means of a comb sorter before being placed in the reactor chamber. Three non-polymerising gases with a flow rate of 20 cc/minute were used, namely (i) oxygen (PO, oxygen plasma treatment), (ii) nitrogen (PN, nitrogen plasma treatment) and (iii) 25 % hydrogen/75 % nitrogen gas mixture (PM, gas mixture plasma). The discharge power and system pressure were set at 80 W and 10 Pa respectively. The duration of LTP treatment was 1, 3, 5, 8, 10, 15, 20, 30, 45, and 60 minutes respectively. After LTP treatment, the fabric and fiber were conditioned before use.

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

The Infrared (IR) spectra of wool fabric were determined by means of Perkin Elmer 16 PC FTIR spectrometer in ATR reflection mode using a zinc selenide crystal. To ensure a reproducible contact between the crystal faces and the fabric, a pressure of 68.9 kPa was applied to the crystal holder by means of a calibrated torque screw driver. 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 studied are given in Table 1 [5,6].

X-ray Photoelectron Spectroscopy (XPS) Analysis

The XPS spectra of 5-minutes LTP-treated wool fabrics with different plasma gases were obtained using a Perkin

Table 1. Characteristic IR absorbance frequencies

Species	Structure	Wavenumber (cm^{-1})
NH bending	-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
Carbon-carbon (stretching) single bond	-C-C-	1000

Elmer PHI 5600 combined spectrometer. An AlK_α x-ray source operated at 15 kV and 400 W was used under the working pressure of 5×10^{-10} torr. The peak positions were corrected for charging relative to hydrocarbon peak at 285.0 eV, and the relative intensities of C_{1s} (285 eV), O_{1s} (533 eV), N_{1s} (400 eV), and S_{2p} (163 eV).

Saturated Adsorption Value, n_m^s

In the saturated adsorption value measurement [7], the experimental tolerance was limited to 5 % throughout the experiment.

Preparation of Calibration Curve

A stock solution containing 0.1 g of Methylene Blue was dissolved in a 1-litre volumetric flask using water as solvent. A series of standard solutions containing 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 7.0, 10.0, 15.0, 20.0, 30.0, and 40.0 m*l* respectively were pipetted from the stock solution and made up to 50 m*l* in the respective volumetric flasks using deionised water. A calibration curve was prepared by using the series of standard solutions. The measurements of absorbance at each dye concentration were made at 665 nm in 10 mm quartz absorption cell (Pye Unicam Ltd.) using Philips PU 8620 UV/VIS/IR Spectrophotometer. The calibration curve was a plot of absorbance against dye concentration.

Adsorption Measurement

Six 1 gram wool fibers were cut to a snippet form of about 3-5 mm long and then placed in six contaminant-free plastic bottles. In each bottle, 30 m*l* of the six standard Methylene Blue solutions, i.e. 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0 m*l*, were added to the bottle respectively. The bottles were then well-screwed and shaken in the Lab-line Junior Orbit Shaker (Lab-line Instruments, Inc.) for 8 hours at 25 °C. After shaking the bottles, the remaining unabsorbed Methylene Blue solution was measured by spectrophotometric method. The adsorption values, n^s, for each concentration were calculated by equation (1):

$$n^s = \frac{v(c_o - c)}{m} \quad (1)$$

where C_o = initial concentration of Methylene Blue (g/*l*)

C = concentration of Methylene Blue at equilibrium (g/*l*)

v = volume of solution added (30 m*l*)

m = mass of fibre (1 gram)

From equation (1), a plot of c/n^s versus c gave a straight line; the value of $1/n_m^s$ was given as the slope of the line and hence the n_m^s values could be determined.

Results and Discussion

FTIR-ATR Measurement

Since the amino acid analysis methods can cause the breakdown of intermediate cystine products during the acid hydrolysis stage [6], therefore, FTIR-ATR spectroscopy with second-order derivative spectroscopic analysis can offer the benefits of non-destructive testing. Comparison of FTIR-ATR spectrum of zero- and second-order reveals that the intensities obtained in the zero-order derivative spectra were inverted in the second-order derivative spectra [8,9]. FTIR signal assignments to the functional groups are shown in Table 1. The intensity of each signal depends on the concentration of the number of the concentration of the functional group. FTIR-ATR technique can analyse to a depth of 500 nm that is good enough to detect the surface chemical components of the wool fiber. Therefore, FTIR-ATR technique offers both qualitative and quantitative methods for measuring composition of the wool surface. The absorbance of the selected band frequencies, i.e. 1600 cm^{-1}, 1121 cm^{-1}, 1071 cm^{-1}, 1040 cm^{-1}, 1022 cm^{-1}, 1000 cm^{-1} were divided by absorbance of the peptide frequency (Amide III, 1232 cm^{-1} which was used as an internal reference) and the absorbance ratio was related to the concentration of the surface component.

In the past, determination of Bunte Salt was based on a colorimetric technique which did not allow direct determination. However, the Bunte salt concentration can now be determined non-destructively by means of the FTIR-ATR technique. Figure 1 illustrates that the amount of Bunte salt increased with increasing treatment time.

Of the three differently LTP-treated wool fabrics, the highest absorbance ratio obtained was the case of oxygen plasma-treated fabric followed by nitrogen plasma and gas

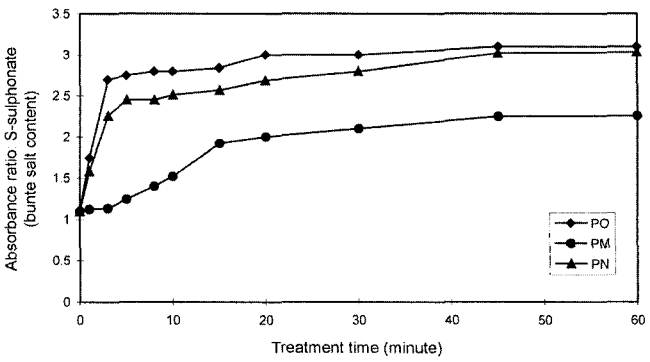

Figure 1. FTIR-ATR absorbance ratio for S-sulphonate (Bunte salt, 1022 cm^{-1}) content as a function of treatment time.

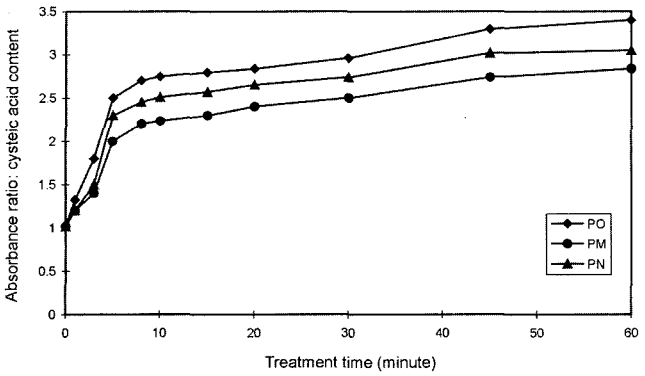

Figure 2. FTIR-ATR absorbance ratio of cysteic acid content as a function of treatment time.

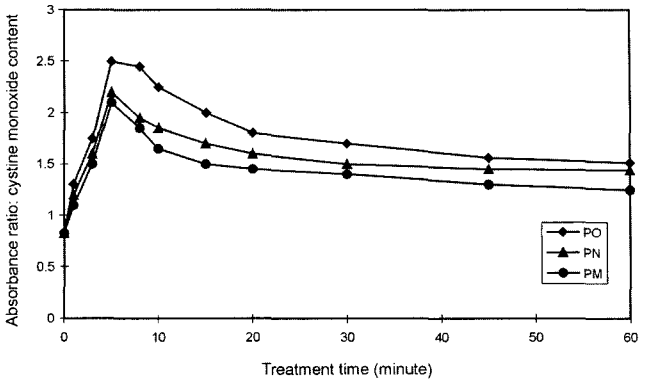

Figure 3. FTIR-ATR absorbance ratio of cystine monoxide content as a function of treatment time.

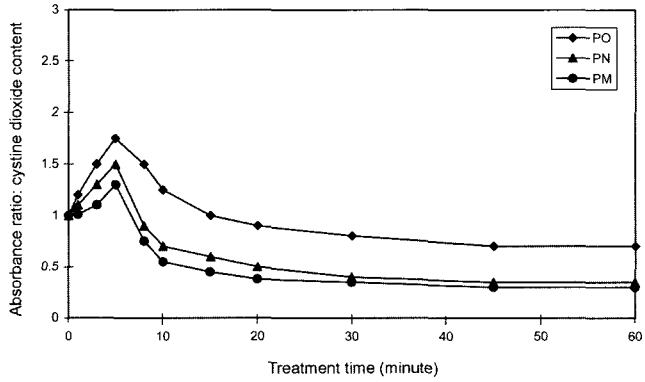

Figure 4. FTIR-ATR absorbance ratio of cystine dioxide as a function of treatment time.

mixture plasma. For the oxygen and nitrogen plasma treatments, the initial rate (1-5 minutes) of the formation of Bunte salt was much faster than that of the gas mixture plasma treatment. However in the case of gas mixture plasma treatment, the formation rate of Bunte salt increased gradually throughout the duration of treatment. On the whole, this formation of Bunte salt probably relates to improved shrink-resistance properties of wool [10].

Beside Bunte salt formation, cysteic acid was also formed as a result of the cleavage of disulphide linkage [6]. The presence of the cysteic acid on the polypeptide chain, together with the Bunte salt provides a polar surface for the wool fabric, which in turn helps to improve the wettability of the wool fabric [11]. Further, the cleavage of the disulphide bonds helps to remove the surface barrier of the wool fiber. The absorbance ratio of cysteic acid as a function of time is shown in Figure 2.

Figure 2 clearly shows that the amount of cysteic acid content increased considerably after the LTP treatment. The three LTP treatments demonstrate similar graph patterns, i.e., after a rapid initial increase the cysteic acid content continue to increase gradually throughout the treatment time. However, oxygen plasma gave the largest absorbance ratio and the sequence was found to be the same as that of Bunte salt formation, i.e., PO > PN > PM.

Apart from the Bunte salt and cysteic acid, the other interesting cystine residues to be studied were cystine monoxide and cystine dioxide. Both cystine residues were believed to be intermediate cystine oxidation products (disulphide → monoxide → dioxide → sulphonic acid) [12]. Cystine monoxide and cystine dioxide are interesting because they represent a more reactive form than the parent disulphide [6]. The formation of cystine monoxide and cystine dioxide in wool thus generates a more reactive substrate, which provides a suitable site for introducing agents such as dyes and softeners carrying nucleophilic reactive groups [13]. Figures 3 and 4 illustrate the variations in the absorbance ratios of cystine monoxide and cystine dioxide to Amide III as a function of treatment time respectively.

Both graphs in Figures 3 and 4 exhibit a similar pattern, i.e., the absorbance ratio after showing an initial increase, decreased gradually over prolonged treatment. In both cases, the absorbance ratio increased rapidly during the first five minutes but thereafter, it started to decrease and reached a nearly constant signal. Figure 4 also shows that in all cases the amount of cystine dioxide was less in treated wool fabrics than the untreated wool fabric after 20 minutes treatment time. The effect was more pronounced in case of PN and PM as compared to PO. This decreased amount of cystine dioxide content may be due to the spontaneous conversion of cystine dioxide to cysteic acid. It may be seen from Figure 2 that the rate of formation of cysteic acid within treatment time of 5 to 8 minutes of the nitrogen plasma and gas mixture plasma is faster than that of the oxygen plasma. This suggests that the nitrogen plasma and gas mixture plasma-treated wool fabrics, after 8 minutes treatment time, had a lower cystine dioxide content than the untreated wool fabrics. Figure 5 demonstrates the conversion relationship between different cystine oxidation products as a function of treatment time with the reference of oxygen plasma treatments.

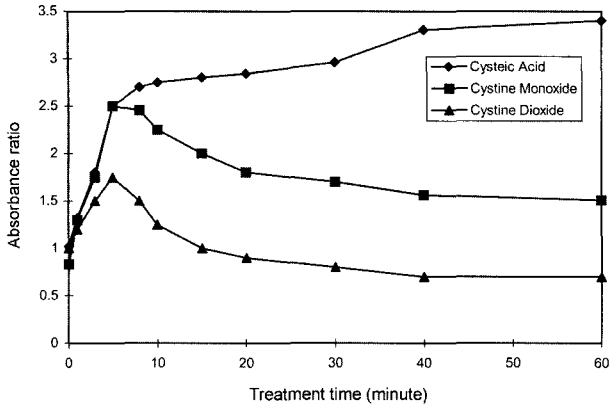

Figure 5. FTIR-ATR absorbance ratio of cysteic acid, cystine monoxide, and cystine dioxide content as a function of treatment time (Oxygen plasma treatment).

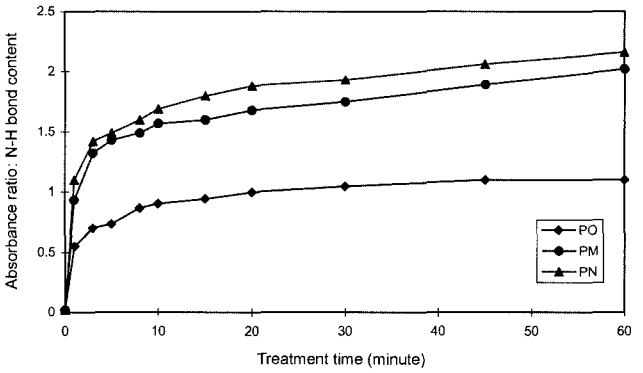

Figure 6. FTIR-ATR absorbance ratio of NH bending group as a function of treatment time.

Figure 5 shows the graphical pattern in which the amount of cystine monoxide and cystine dioxide increased rapidly to a maximum value in the first five minutes of LTP treatment. Thereafter, the amount of these oxides started to decrease and reached a nearly constant absorbance ratio. The amount of these oxides started to decrease after five minutes of treatment time, at which time the cysteic acid content started to increase. Since cystine oxides are not stable and may easily be converted to cysteic acid [6], it is hard to quantify accurately the formation of each product in relation to cysteic acid at different LTP treatment time. Cysteic acid was the main oxidation product within the wool fiber. However, the presence of cystine monoxide and cystine dioxide suggests that cysteic acid is probably formed from these intermediates as proposed in a previous model [12].

Similar graph patterns were found in Figures 1 to 4 suggesting that all types of gas plasma treatments used in this study could generate the same functional groups on the wool fabric surface but with different concentrations. Of the three gases used, the oxygen plasma treatment had the highest absorbance ratio followed by nitrogen plasma treatment and gas mixture plasma treatment. This may have been due to the fact that the functional groups studied were the oxidation products of cystine. Generally speaking, the nature of the plasma depends much on the nature of the gas used [14,15]. If oxygen gas, which is oxidative in nature, is used as the plasma gas, the wool surface will be oxidised to such an extent that the oxidation products signal can be easily detected. On the other hand, the oxidising power of nitrogen is lower than that of oxygen. As a result, the signal intensities of the nitrogen plasma-treated fabric are not as strong as oxygen. In the case of gas mixture plasma treatment, the signal is quite similar to that of nitrogen plasma treatment because the former was 100 % nitrogen gas while the latter still contained 75 % nitrogen gas. As the gas mixture plasma was mixed with 25 % hydrogen gas which is reductive in nature, it might finally reduce the oxidation effect of the nitrogen gas resulting in the weakest signal intensity of the selected functional groups.

A previous study [16] showed that amino groups ($-NH_2$) were introduced to polyester after nitrogen or gas mixture plasma treatment. Although the wool fabric itself contained amino groups ($-NH_2$), further introduction of amino groups may have enhanced the absorption of anionic dye during the dyeing process [17,18]. Figure 6 shows the variation of concentration of NH as a function of treatment time.

Figure 6 shows the NH content of the LTP-treated wool fabrics as a function of treatment time. Obviously, the NH content in all cases studied is increased. For oxygen plasma, the NH content increased only moderately while the increase was very pronounced in case of nitrogen and gas mixture plasma treatment. Although the NH contents of nitrogen and gas mixture plasma treated wool fabric sample were comparable, those treated with the nitrogen plasma showed more NH content than those treated with gas mixture plasma. This increase of NH content may provide an explanation for the previous dyeing results [17,18], i.e., the nitrogen plasma and gas mixture plasma-treated fibers had a higher percentage of exhaustion at equilibrium (%E at Em) value than the untreated fiber. This may be due to the increase of plasma-induced NH groups on the fiber. The induced NH groups on the wool fiber surface introduced new dyesites on the fiber, enhancing the dye absorption ability of the wool fiber.

Hydrogen in gas mixture plasma may be changed to reactive hydrogen such as H^+ and H_2^+ under conditions of electrical initiation. The reactive hydrogen has high level of reactivity [16]. When these reactive species bombard the fiber surface, a free radical may be formed by eliminating an atom from a saturated compound as shown in Scheme 1(a). However, it was postulated that the free radical on the polymer chain combines together as shown in Scheme 1(b).

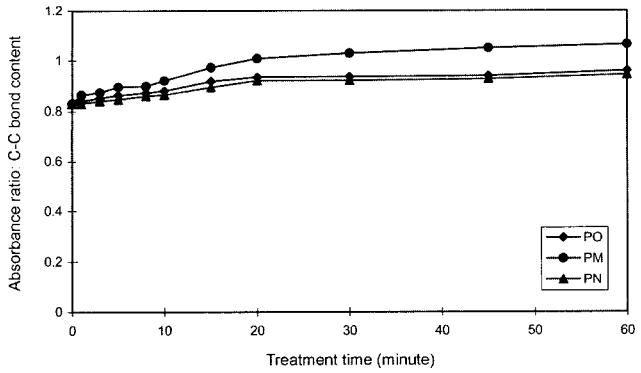

Figure 7. FTIR-ATR absorbance ratio of carbon-carbon (stretching) single bond as a function of treatment time.

Scheme 1(a)

$$-C-C-H + H^+ \rightarrow -C-C\bullet + H_2^+$$

Scheme 1(b)

$$2\ -C-C\bullet \rightarrow -C-C-C-C-$$

The above Scheme demonstrates that as a consequence of treatment a crosslinking reaction may occur thus Figure 7 shows the carbon-carbon single bond content on the fiber surface after LTP treatments.

Figure 7 illustrates that the carbon-carbon (stretching) single bond content is increased after LTP treatment. However, in the case of gas mixture plasma, the carbon-carbon single bond content increased considerably more as compared to oxygen and nitrogen plasma. It may be proposed that the gas mixture plasma treatment enhances the carbon-carbon single bond formation on the wool fiber surface as depicted in Scheme 1(b). These cross-linkages on the fiber surface may impart hydrophobicity and hinder diffusion through the surface. On the other hand the gas mixture plasma can improve the wettability and hence the dyeability by introducing the amino groups to the fiber surface, causing the wool fiber to become more hydrophilic. The dyeing absorption behaviour of the gas mixture plasma-treated wool fiber may be the compromise of these two opposing factors.

XPS Surface Analysis

After 5 minutes of LTP treatment with different plasma gases, the microanalytical data of the surface elemental composition of different samples were collected and are summarised in Table 2.

Table 2. Elemental analysis (wt.%) and atomic ratio of wool treated with different plasma gas

	Elemental concentration (wt.%)				Atomic ratio	
Sample	C_{1s}	N_{1s}	O_{1s}	S_{2p}	C/N	O/C
Untreated	74.72	8.78	13.55	2.58	8.51	0.18
PO	65.61	8.88	20.16	2.26	7.39	0.31
PN	68.31	10.19	18.86	2.23	6.70	0.27
PM	68.67	9.34	18.82	2.14	7.35	0.27

It may be seen that the carbon content is significantly reduced after plasma treatment. This reduction is probably due to the etching effect of LTP treatment on the wool fiber resulting in the removal of fiber surface material. After the etching process, the inner surface of the wool fiber was exposed and also the chemical effect due to the plasma species introduced new functional group. Both factors contributed together causing a change of the surface composition. Scanning electron microscopic pictures in previous researches [19,20] has clearly shown that the oxygen plasma imparted the most significant surface etching effect by introducing grooves along the fiber axis. This grooving effect induced by oxygen plasma was most pronounced followed by nitrogen and then the gas mixture. This sequence agrees with the order of reduction in carbon content as obtained by the XPS analysis.

The nitrogen content of the wool fiber has increased to different extents after different LTP treatments. The nitrogen plasma induced the highest amount of nitrogen component into the wool fiber, followed by the gas mixture and then the oxygen plasma. This enhancement of nitrogen content on the wool fiber reflects increase in NH content of the wool fiber.

The oxygen content of the LTP-treated wool fiber was found to increase. It may therefore be deduced that oxidation has occurred during the LTP treatment and that the oxygen plasma showed the strongest effect followed by nitrogen gas and then the gas mixture. However, nitrogen plasma and gas mixture plasma produced quite a similar oxidation effect on the wool fiber. Since the gas mixture was composed of nitrogen and hydrogen, its oxidising effect will obviously be minimal which may explain the sequence of results shown in Table 2. The increased amount of oxygen may enhance the hydrophilicity of the wool fiber which increases the wettability of the wool. As a result, the dye uptake and polymer adhesion during finishing were also enhanced.

The content of sulphur after LTP treatment decreased slightly. This may be because LTP treatment may have etched away the cuticle which contains a large number of disulphide bonds (-S-S-). Of the three plasma gases used, the

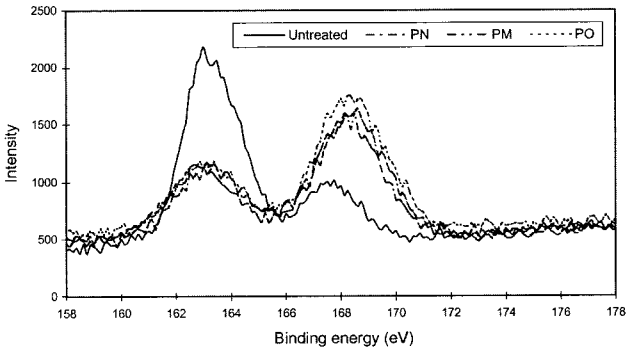

Figure 8. Sulphur peak (S_{2p}) spectra of wool before and after treatment with LTP.

gas mixture showed the largest reduction in sulphur content followed by nitrogen plasma and then oxygen plasma. In addition, Figure 8 shows XPS spectrum where two broad S_{2p} peaks at binding energy values of 163 eV and 168 eV can be seen. In the untreated wool fiber, the 163 eV peak intensity was stronger than the intensity at 168 eV peak. After LTP treatment, the 168 eV peak intensity is stronger than that of 163 eV peak. This shift of S_{2p} peak to higher binding energy is an indicator of the increase in the oxidation state of the sulphur atoms at the fibre surface [21], which suggests conversion of cystine residues to cysteic acid residues [22,23] according to the following equation (2),

$$W\text{-}S(II)\text{-}S\text{-}W \rightarrow W\text{-}S(VI)O_3H, \quad (2)$$

where W = wool

Since the 168 eV peak is rather broad, it is possible that intermediate oxidation products of cystine may also have been present.

The XPS surface analysis could be used for monitoring the superficial chemical changes (depth about 10 nm) after the LTP treatment [23]. The LTP treatment had shown a decrease in the relative atomic concentration of carbon and an increase in the relative atomic concentration of oxygen, suggesting the oxidation of the fatty layer present on the outermost part of the epicuticle [23].

The C/N atomic ratio had decreased from 8.51 for LTP treated wool to 7.39 (oxygen-plasma treated wool0, 6.60 (nitrogen-plasma treated wool) and 7.35 (gas mixture plasma-treated wool) for different-gas treated wool, while O/C atomic ratio increased significantly compared to the untreated wool. These changes suggested that a partial oxidation of the hydrocarbon chains of the F-layer without the epicuticle removal [24].

Saturated Adsorption Value

The results of saturated adsorption value, n_m^s, for each sample were measured from the slope of equation (1). The plots are shown in Figures 9-12 and the respective n_m^s values are shown in Table 3. The n_m^s values indicated the amount of monolayer of Methylene Blue molecules adsorbed on the sample. The distribution of the monolayer was dependent on the total surface area of the fiber. If the areas occupied by one Methylene Blue molecule are known, the specific surface area of the wool fiber can be calculated by:

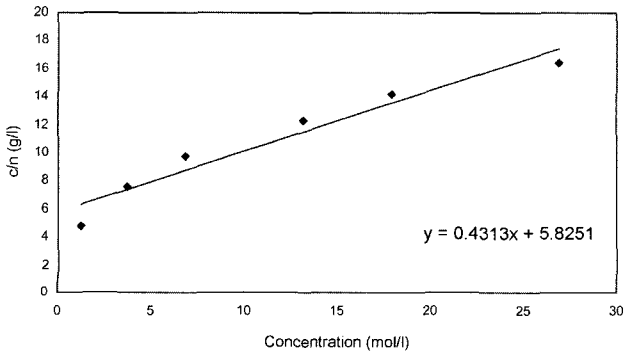

Figure 9. Saturated adsorption value of untreated wool fiber.

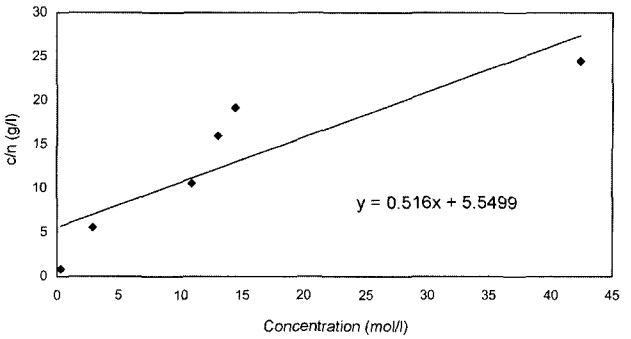

Figure 10. Saturated adsorption value of oxygen plasma treated wool fiber.

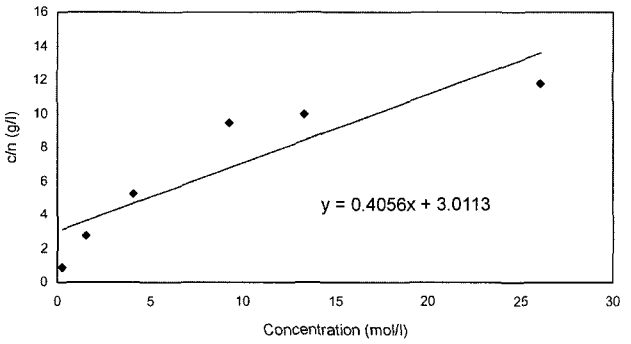

Figure 11. Saturated adsorption value of nitrogen plasma treated wool fiber.

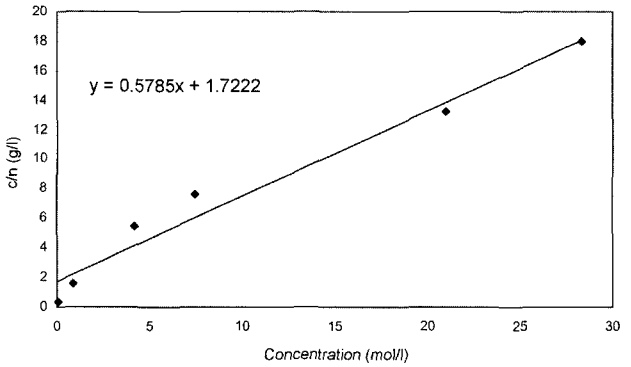

Figure 12. Saturated adsorption value of gas mixture plasma treated wool fiber.

Table 3. The n_m^s values of the samples

Sample	Untreated	PO	PN	PM
n_m^s	31.14	51.60	40.56	52.67
($molg^{-1}$)		(↑ 65.70 %)	(↑ 30.25 %)	(↑ 69.14 %)

Parentheses indicate rate of increase in saturated adsorption value of LTP-treated wool sample compared to untreated sample.

$$S = n_m^s \times \sigma \times 6.023 \times 10^{23} \quad (3)$$

where S = specific surface area (m^2g^{-1})

σ = surface area occupied by one Methylene Blue molecule ($nm^2/10^{-18}m^2$)

n_m^s = saturated adsorption value ($molg^{-1}$)

6.023×10^{23} = Avogadro's Number (mol^{-1})

In equation (3), S was proportional to n_m^s in which value might reflect the specific surface area of the wool fiber. Since Methylene Blue has very low affinity to the wool fiber due to its basic nature, its molecules will be adsorbed on the surface only. The value of n_m^s was employed to indicate a relative saturated adsorption value for each sample. It was found that the surface-modified wool samples gave a larger n_m^s value than that of the untreated wool fiber. As a result, the surface areas were dramatically increased after the low temperature plasma treatment. This enlargement of the surface area would help to promote adsorbates, such as dyestuffs, to approach and adhere on the fiber surface. From the values obtained from saturated adsorption value measurements, PM showed the largest increase in specific surface area followed by PO and PN.

Conclusions

After the LTP surface modification treatments, significant changes within the surface properties of the wool fiber were observed. In the FTIR-ATR study, the surface composition of the LTP-treated wool fiber was found to be varied differently with different plasma gas. Functional groups were studied and it was found that the concentration of these functional groups influences the properties of the wool fiber which assists for providing explanations of the previous reported results [17,18]. In the XPS study, it showed the LTP treatment changes the composition of elements at the surface of the wool, e.g. nitrogen and oxygen contents were increased while carbon and sulphur contents were decreased in the surface layer. In addition, a shift of sulphur peak from 163 eV to 168 eV demonstrated the change of sulphur state from S(II) to S(VI) after different LTP treatments. The saturated adsorption values reflected the change in the surface area of the fiber that was dramatically increased after LTP surface modification. The results of this investigation helped to characterise the surface composition and determine the effect of LTP treatment on the surface properties of wool fiber. These properties might seriously affect both dyeing processes and finishing processes such as shrinkproofing treatments.

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