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Environmentally Friendly Surface Treatment of Wool Fiber with Plasma and Chitosan for Improved Coloration with Cochineal and Safflower Natural Dyes

Aminoddin Haji[1]*, Saba Ashraf[2], Majid Nasiriboroumand[2,3], and Caroline Lievens[4]

[1]*Department of Textile Engineering, Yazd University, Yazd 89195-741, Iran*
[2]*Department of Carpet, Shahid Bahonar University of Kerman, Kerman 7616914111, Iran*
[3]*Department of Developmental Bioengineering, MIRA Institute for Biomedical Technology and Technical Medicine, University of Twente, Enschede 7500 AE, Netherlands*
[4]*Faculty of Geo-Information Science and Earth Observation, Geoscience Laboratory, University of Twente, Enschede 7514 AE, Netherlands*

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Abstract: In this study, the effect of surface modification of wool fiber with oxygen plasma and chitosan (PC) on the color strength of the samples dyed with cochineal and safflower natural dyes has been studied. According to colorimetric measurements, plasma and chitosan treatments resulted in notable improvements in dyeability of wool fibers. The plasma and chitosan-treated wool sample could be dyed in less time and at lower temperature compared with untreated one. The dyebath pH had a prominent effect on color strength, which showed that the electrostatic force has an important role in dye adsorption. The optimum pH for maximum dye absorption was 3.6. The fastness properties, tensile strength, and elongation at break of dyed wool were improved after PC treatment. Scanning electron microscopy (SEM) images and ATR-FTIR analysis proved the coating of wool scales with a uniform thin layer of chitosan, which caused the improved dyeability of wool fibers with safflower and cochineal.

Keywords: Wool, Plasma, Chitosan, Cochineal, Safflower

Introduction

The application of natural dyes in the coloration of textiles goods was declined drastically following the introduction of synthetic dyes to the market in the mid 19th century. The interest in natural dyes has been revived in recent years because of the increasing ecological and environmental awareness of people besides the legal bans regarding the use of some synthetic dyes with specific chemical structures [1-5]. Also, textiles dyed with some natural dyes exhibit antibacterial and antifungal and UV protection properties [6,7]. Although it is supposed that natural dyes are friendlier to the environment, they exhibit drawbacks such as low exhaustion and fixation on textile fibers and poor fastness properties [8].

The wool fibers structure is complex and highly cross-linked. The surface of wool fiber is covered by scales with a hydrophobic character which is responsible for hydrophobicity and significantly influences the dyeing behavior of wool [9-11]. The low affinity of most natural dyes toward wool fibers is an important problem in the development of natural dyeing processes [8,12,13].

Metallic mordants are the most commonly used chemicals for enhancement of the exhaustion, fixation, color strength, and fastness properties of natural colorants on textile fibers like cotton, silk, and wool [14-20]. However, they produce residual toxic metal ions in the wastewater, which negatively influence the environment and may cause significant health and allergic problems [8,21].

Several methods have been studied to enhance the natural dyeing of wool or other natural fibers without the use of metallic mordants. These methods include the use of ultrasound energy [22-24], microwave heating [25-27], gamma ray [28], UV radiation [29], enzyme treatment [30], and plasma treatment [31-35]. Furthermore, nanoclay treatment [30,36], chitosan finishing [37,38], employment of a hybrid of chitosan and polypropylene imine dendrimer [39], and bio-mordanting [40-43] are other wet processes studied for the improvement of dyeability of wool fibers with various natural dyes.

Chitosan is a biologically compatible natural polysaccharide with amino groups which can gain positive charge in acidic to the neutral solution and readily bind to negatively charged surfaces and molecules like textile fibers and dyes. Chitosan treatment of wool fibers can improve their uptake of anionic synthetic and natural dyes in acidic media [33,38,44,45]. It has been approved by the FDA for use in wound dressings [46,47].

Plasma technology as an environmentally friendly surface treatment process can enhance the adhesion, wettability, dyeability, and reactivity of wool fibers [48,49]. It can be used for the enhancement of adsorption of chitosan onto the wool fabric and produce the functional sites needed for bonding the chitosan to the surface of the wool fibers [33,50].

In this study, oxygen plasma was utilized as a pretreatment for etching and surface functionalization of wool fibers with the aim of improvement of chitosan attachment to wool

*Corresponding author: ahaji@yazd.ac.ir

fibers. The raw, plasma-treated, and chitosan-coated woolen samples were dyed with safflower and cochineal natural dyes. The effect of the pre-treatments and the dyeing conditions on color strength and fastness properties of the dyed samples was evaluated and compared.

Experimental

Materials

Wool fabric with plain weave structure (260 g/m^2, warp density=20 ends/cm, weft density=17 ends/cm, Nm=48/2) was supplied from Iran Merinos Textile Company, Iran. To remove any natural or synthetic impurities, the samples were scoured with 1 % non-ionic detergent in distilled water (Triton X-100, Sigma-Aldrich, USA) at 50 °C for 30 min, then thoroughly washed with distilled water and dried at ambient temperature. The scoured raw wool is denoted as W in this paper. All chemicals were purchased from Sigma-Aldrich, USA. Safflower natural dye (*Carthamus tinctorius* L.) was obtained from a local store in Yazd, Iran and cochineal (*Dactylopius coccus*) was purchased from Canaturex, Spain.

Methods

Preparation of Stock Solution of Natual Dyes

Plant material was washed and dried. Then 10 g of each natural dye was powdered and boiled in 1 *l* of distilled water for 2 h and filtered. Some water was evaporated during the boiling, so distilled water was added again to reach the volume of the solution to the initial amount. The concentration of the resultant stock solution is 1% w/v.

Plasma Treatment

Junior advanced plasma equipment working at low-pressure and radio frequency power generator (13.56 MHz) manufactured by Europlasma Co., Belgium was employed for the pre-treatment of samples before dyeing and chitosan grafting. Oxygen (purity: 99.99 %) was used as the plasma processing gas. The base pressure of the sample chamber, power, and oxygen flow rate was 20 Pa, 150 W, and 100 m*l*/min, respectively. The plasma treatment was done for 5 min. The oxygen plasma-treated wool sample is denoted as P in this paper.

Chitosan Treatment

Plasma activated samples were readily impregnated in 20 m*l* of a solution containing 0.5 % w/v of chitosan and 1 % w/v of glacial acetic acid in distilled water for 1 h, then padded with 100 % wet pick up and dried at 80 °C for 1 h. To remove the non-reacted chitosan, the samples were finally scoured with 1 % non-ionic detergent in distilled water at 50 °C for 15 min and air dried at ambient temperature. The chitosan-treated wool is denoted as PC in this paper.

Dyeing Procedure

Dyeing of the samples was performed using 40 % owf of safflower or 5 % owf of cochineal (L:G=50:1) and the solution pH was adjusted according to the experimental design using acetate buffer solutions. The temperature was around 40 °C at the beginning of the dyeing, and the dyebath temperature was raised to the final temperature (40, 60, and 80 °C) with the rate of 2 °C/min and then continued for 1 h. Finally, the samples were rinsed with tap water and dried at ambient temperature.

Color Strength Measurement

To measure color strength of each dyed sample, a reflectance spectrophotometer was used (Color-eye 7000A, X-rite, USA) with the setting of the D65 as illuminant and 10 ° standard as a standard observer. Minimum reflectance in the range of 360-720 nm was selected (R) to calculate the color strength (K/S) using the Kubelka-Munk equation:

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

Color Fastness Evaluation

The process for evaluation of color fastness to washing and light was performed according to ISO 105-C01: 1989(E), and ISO 105-B02:1994(E), respectively.

Levelness Measurement

Reflectance values of ten randomly selected spots on the dyed sample was measured using a reflectance spectrophotometer in the visible spectrum range. The relative unlevelness index (RUI) was obtained as shown in equation (3), where S_λ is the standard deviation (obtained from equation (2)), and R_m is the means of reflectance values of n measurements for each wavelength and V_λ is photopic relative luminous efficiency function. R_i is the reflectance value of the measurement number i for each wavelength. RUI<0.2 was considered as excellent levelness, and 0.2<RUI<0.49 was considered as good levelness. RUI between 0.5 and 1 means poor levelness and RUI values greater than 1 indicate bad levelness [51,52].

$$S_\lambda = \sqrt{\frac{\sum_{i=1}^{n}(R_i - R_m)^2}{n-1}} \tag{2}$$

$$RUI = \sum_{\lambda=390}^{\lambda=700}(S_\lambda/R_m)V_\lambda \tag{3}$$

Dye Uptake Measurement

The concentration of each dye in the dyebath, before and after dyeing, was measured using a DR 5000 UV-vis spectrophotometer (HACH, USA). Percentage dye exhaustion (uptake) for each dye was calculated using equation (4).

$$\%E = \frac{(C_0 - C_1)}{C_0} \times 100 = \frac{(A_0 - A_1)}{A_0} \times 100 \tag{4}$$

In this equation, C_0 and C_1 are the concentrations of the dye before and after dyeing (g/dm^3), respectively; A_0 and A_1 are the absorbances of the dyebath before and after dyeing at the λ_{max} of each dye (501 nm for cochineal, and 405 nm for safflower), respectively.

Dye Fixation Measurement

To evaluate the dye fixation, dyed samples were washed at 50 ºC for 30 min. The dye fixation (F%) was calculated using equation (5), where $(K/S)_a$ and $(K/S)_b$ are the color strength values of the dyed samples after and before washing.

$$F\% = (K/S)_a/((K/S)_b \times 100 \quad (5)$$

Evaluation of Wettability

To determine the effect of plasma and chitosan treatments on the wettability of wool samples, vertical wicking test was performed according to the method described in [50,53].

Scanning Electron Microscopy

To study any changes in the morphology of wool fibers after plasma and chitosan treatments, scanning electron images were taken using an LEO 1450 VP scanning electron microscope (Zeiss, Germany) after coating the samples with gold.

ATR-FTIR Analysis

Fourier Transform Infrared (FTIR) tests were carried out using an IRAffinity-1 instrument (Shimadzu, Japan) with a resolution of 4 cm^{-1}. An average of 45 scans was recorded. The measurements were done in the attenuated total reflection (ATR) mode for fabric samples.

Tensile Strength Measurement

The woolen yarn was randomly selected and separated from each fabric sample. To evaluate any changes in physical properties of the wool yarns due to the modifications, tenacity, and elongation at the break for ten individual yarns of the wool fabrics was measured according to ASTM D 2256. The gauge length was set at 25 cm, and the crosshead speed was fixed on 30 cm/min. The woolen yarn was randomly selected and separated from fabric.

Results and Discussion

Effect of Surface Modification on Color Strength

Color strength (K/S) values of dyed fibers with safflower and cochineal are presented in Figures 1 and 2. At pH=3.6, wool fibers which were modified through plasma and chitosan treatments showed higher color strength values compared with the raw and plasma-treated fibers. With increase of pH to 4.6 and 5.6, the same correlation between the modification type and color strength was seen, and it could be concluded that the modification of wool fiber with plasma and chitosan resulted in more absorption of safflower and cochineal at pH rang of 3.6 to 5.6. Chitosan contains amino side groups in its chemical structure, which protonate in acidic solution and then can make ionic bonds with anionic dyes such as carminic acid and carthamin which are present in cochineal and safflower respectively. Carminic acid is the main colorant of the cochineal (Figure 3) which has an anionic charge in dyebath due to the presence of one carboxylic acid and eight hydroxyl groups in its chemical

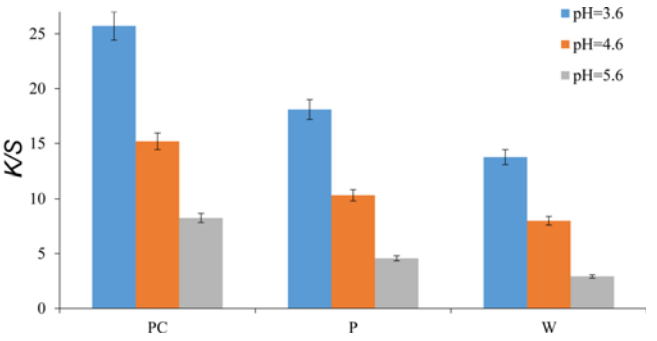

Figure 1. Effect of pH on the color strength of samples dyed with cochineal (90 ºC, 60 min).

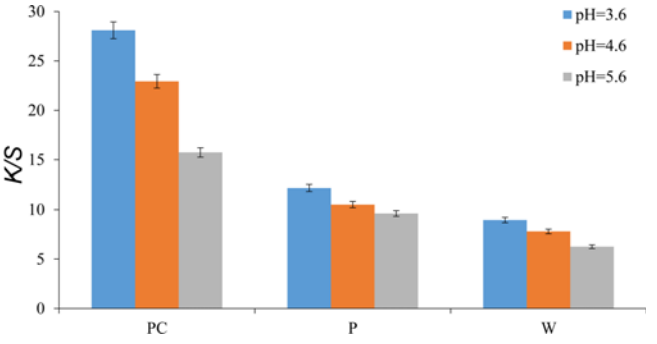

Figure 2. Effect of pH on the color strength of samples dyed with safflower (90 ºC, 60 min).

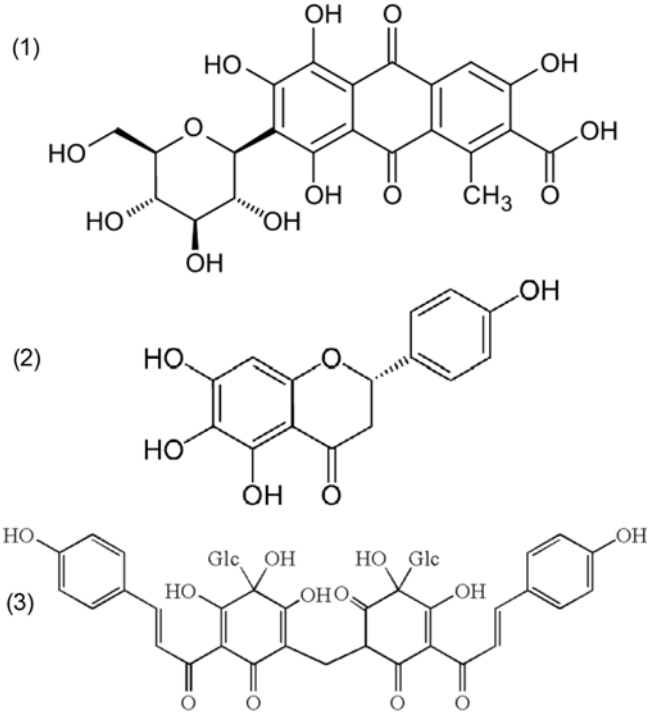

Figure 3. Chemical structure of carminic acid (1), carthamidin (2), and carthamin (3).

structure. The anionic charge of carminic acid in water caused to have substantivity to positively charged amino groups of chitosan which are present on the modified wool fibers using plasma and chitosan treatments. An increase of pH from 3.6 to 5.6 resulted in a decrease in absorption of cochineal and safflower to plasma and chitosan modified fiber (PC). Due to the numerous ionizable amino side groups of chitosan, the pH of dye solution is an effective factor on surface charge. Due to the decrease of positively charged amino groups in chitosan at higher pH values, less position for the absorption of anionic dye is available, and color depth is decreased. This mechanism had the same effect on the absorption of anionic colorant molecules in safflower. Safflower petals contain two pigments viz. red (carthamin) and yellow (carthamidin) which are negatively charged in water and therefore at higher pH values absorb less due to a decrease in positively charged side groups of chitosan which are present on PC modified wool.

Effect of Dyeing Temperature on Color Strength

Figure 4 shows the effect of dyeing temperature on the color strength of raw and modified wool samples after dyeing with safflower. The increase of temperature between 30 ºC and 90 ºC has resulted in more dye absorption on all kinds of wool samples. The same trend was seen for dyeing with cochineal, as shown in Figure 5. This increase is due to the higher molecular energy of dye molecules and wool fiber at the elevated temperatures that result in higher exhaustion yields. Furthermore, the use of higher temperatures leads to more fiber swelling and breakdown of dye molecule aggregates, which consequently enhance the dye diffusion into the wool fibers [4,16,54].

Effect of Dyeing Time on Color Strength

As shown in Figures 6 and 7, the color strength of samples dyed with both natural dyes increased as the time increased from 20 min to 60 min. Then, it declined with increasing the dyeing time to 90 min. It seems that the dyeing process has reached equilibrium after 60 min. Heating for a long time disturbs the equilibrium, and dyed yarn may face stripping, which results in lower *K/S* values [2]. This decrease in the color strength may also be attributed to the partial degradation of the natural dye molecules due to prolonged exposure to high temperature [4].

SEM Investigations

Scanning electron microscopy was used to evaluate the morphological changes of wool fibers after modification with oxygen plasma and chitosan. As can be seen in Figure 8, raw wool fibers possess overlapping scales, which are hydrophobic and cause the poor wettability of wool fibers. After plasma treatment, the scales have been destroyed in

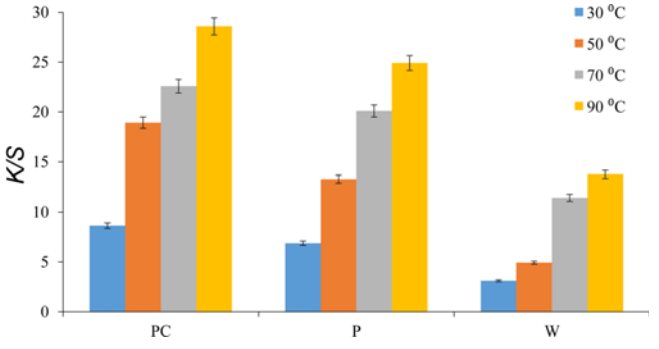

Figure 4. Effect of dyeing temperature on the color strength of samples dyed with safflower (pH=3.6, 60 min).

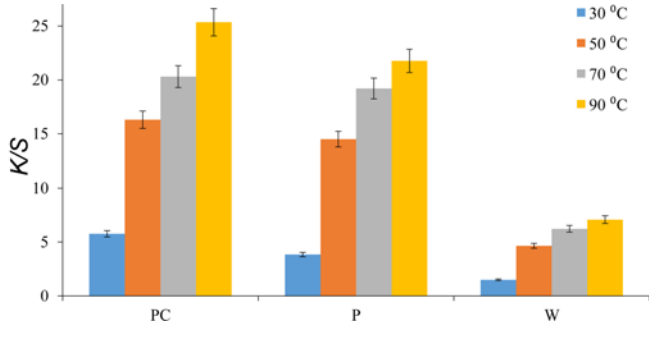

Figure 5. Effect of dyeing temperature on the color strength of samples dyed with cochineal (pH=3.6, 60 min).

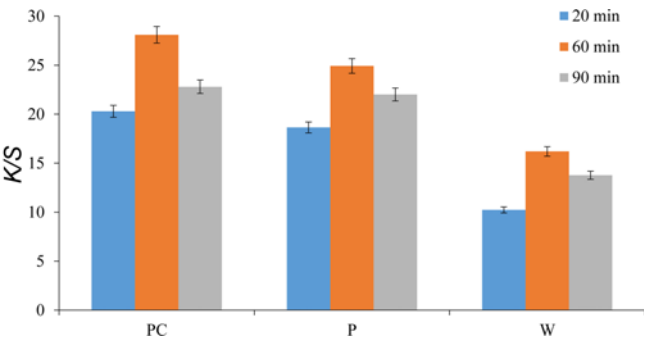

Figure 6. Effect of dyeing time on the color strength of samples dyed with safflower (90 ºC, pH=3.6).

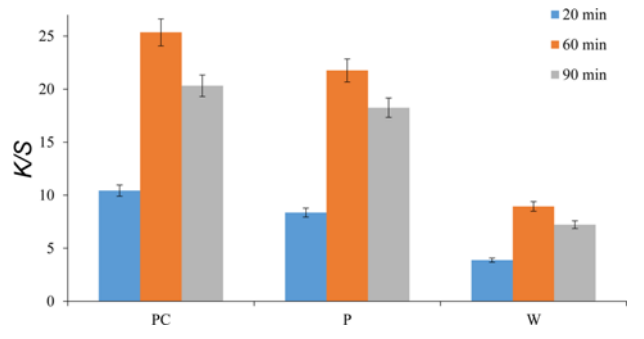

Figure 7. Effect of dyeing time on the color strength of samples dyed with cochineal (90 ºC, pH=3.6).

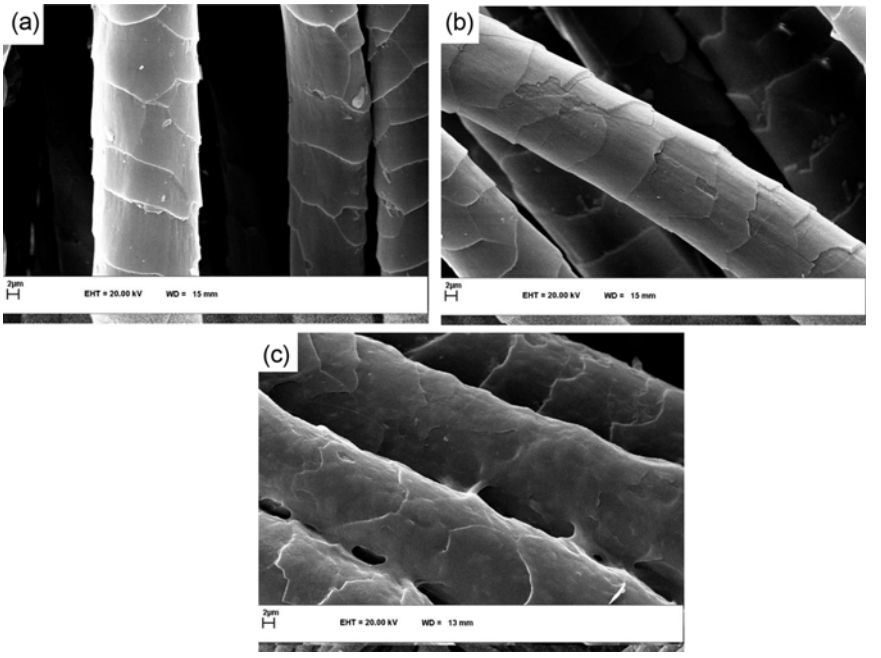

Figure 8. SEM images of raw (a), plasma-treated (b), and chitosan-treated (c) samples.

random places which in conjunction with the chemical changes made by reactive radicals present in oxygen plasma [11,55]; make the wool fibers ready for wetting, diffusion of dyes and chemicals, and attachment of different macro-molecules. The SEM image of the PC sample shows the coating of wool scales with a uniform thin layer of chitosan, which caused the improved dyeability of wool fibers with cochineal and safflower natural dyes.

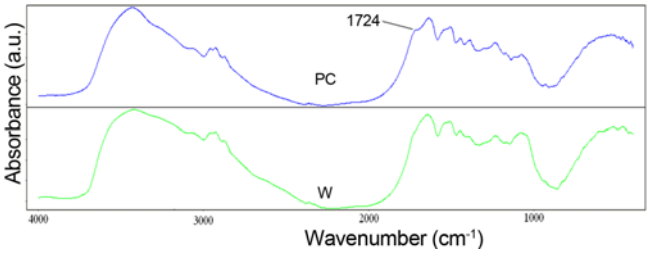

Figure 9. ATR-FTIR spectra of raw (W) and plasma-chitosan-treated samples (PC).

ATR-FTIR Analysis

It was shown in our previous studies [33,55] that the intensity of bands at 1645 cm^{-1} and 1534 cm^{-1} was increased after treatment of wool fibers with oxygen plasma. This finding confirmed the presence of newly introduced oxygen-containing groups on the surface of wool fibers as a result of plasma treatment. Here in Figure 9, the ATR-FTIR spectra of raw wool and the PC sample are compared. The peak at 1650 cm^{-1} is related to the amino groups in the protein molecular chain of wool. After modification of wool with oxygen plasma and chitosan, a shoulder in carbonyl region

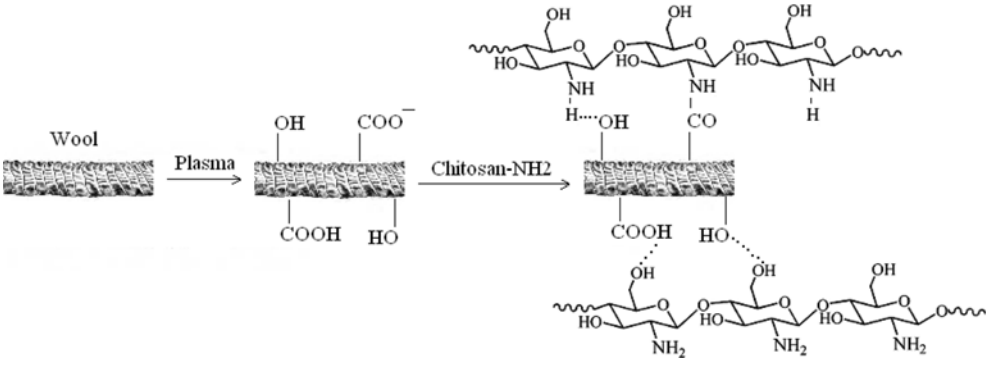

Figure 10. Proposed mechanism for attachment of chitosan to plasma-treated wool fibers.

of absorbance spectrum has appeared at 1724 cm^{-1} which could show the formation of new amide groups due to formation amide bonds between amine groups of chitosan and carboxyl groups of plasma-treated wool. The tentative reaction is presented in Figure 10. This figure shows the probable mechanism of attachment of chitosan to plasma-treated wool fibers through hydrogen and amide bonds. It should be noted that wool fiber (without plasma treatment) contains several hydroxyl, amine, and carboxyl groups that some hydrogen and amide bonds may occur between these groups and appropriate side groups of chitosan as well (these bonds are not shown in Figure 10).

Wettability

Figure 11 shows the wicking properties of the raw, plasma-treated, and chitosan-treated samples. The rate and height of water wicking in the plasma-treated sample was pronouncedly higher compared with the raw wool sample. This is due to the introduction of new functional groups and increasing surface roughness of wool fibers, which was confirmed by FTIR and SEM images as well. The wicking ability of the fabric was a little lowered after chitosan treatment, which may be due to the partial filling of the spaces between the wool fibers, as can be seen in Figure 8. This improvement in wettability can improve the dyeability of the fibers as well.

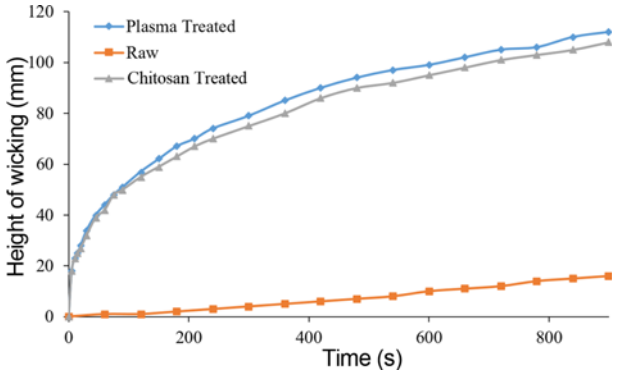

Figure 11. Water wicking of raw, plasma-treated, and chitosan-treated samples.

Table 1. Physical properties of raw, plasma-treated and chitosan-coated woolen yarns

Sample	Tensile strength (cN/Tex)		Extension at maximum load (%)	
	Mean	CV%	Mean	CV%
PC	393.5	18.98	51.03	24.12
P	427.4	10.57	53.6	14.79
W	369.9	9.38	42.94	17.31

Physical Properties

Table 1 shows the tensile properties of different types of modified woolen samples. Plasma treatment increased the tensile strength of the woolen yarn. This is due to the increase of adhesion and friction between the wool fibers inside the plasma-treated yarns [56]. The tensile strength of the PC sample is a small amount lower than the plasma-treated sample. This is because of heat treatment during the drying process, which had been used after impregnation with the chitosan solution. Despite a reduction in tensile strength after-the coating process, the strength of this sample is still higher than the raw woolen yarns. The same trend was seen for the extension at maximum load values. These results have been explained according to the interlocking mechanism [56].

Fastness and Levelness Properties

Table 2 shows the fastness properties and RUI values of W, P, and PC samples dyed at pH=3.6 for 60 min at 90 ºC. The plasma-treated sample showed better wash, light, and rub fastness properties compared with the untreated wool. The wash and light fastness properties were further improved by chitosan treatment. The highest wash and light fastness were obtained when the wool fabric was treated with oxygen plasma and coated with chitosan. As stated earlier, the plasma and chitosan-treated samples absorbed more dye molecules compared with the untreated wool sample. The higher concentration of dye molecules inside the fibers caused the increase in light fastness properties of modified wool fibers. The improvement of wash fastness is due to the chemical bonds between the modified wool fibers and dye molecules.

The RUI values in Table 2 show that the levelness of

Table 2. Fastness properties and RUI values of wool samples dyed with cochineal and safflower (pH=3.6, 60 min, 90 ºC)

Sample	Dye	Wash fastness	Light fastness	Dry rub fastness	Wet rub fastness	RUI
W	Cochineal	3-4	6	4	3-4	0.25
	Safflower	3-4	5-6	4	3-4	0.23
P	Cochineal	4	6-7	4-5	4	0.09
	Safflower	4	6	4-54	4	0.12
PC	Cochineal	4-5	7-8	4	3-4	0.15
	Safflower	4-5	7	4	3-4	0.16

Table 3. Dye uptake and dye fixation values of wool samples dyed with cochineal and safflower (pH=3.6, 60 min, 90 ºC)

Sample	Dye	Dye uptake (*E*%)	Dye fixation (*F*%)
W	Cochineal	31.74	63.1
	Safflower	47.48	59.2
P	Cochineal	77.22	87.5
	Safflower	73.04	83.2
PC	Cochineal	89.96	95.1
	Safflower	82.36	93.6

dyeing of wool samples was improved from good to excellent when the samples were treated with oxygen plasma and chitosan. These modifications improved the levelness of the dyeing because the surface of wool fibers was evenly decontaminated and functionalized by oxygen plasma, which resulted in better and more uniform absorption of dye molecules.

Dye Uptake and Dye Fixation Studies

The dye uptake and dye fixation of different samples were calculated according to equation (4) and equation (5), respectively. As can be seen in Table 3, plasma treatment improved the dye uptake and dye fixation of both dyes on wool fibers. This increase was higher for the samples treated with chitosan after the plasma treatment. In both cases, the chemical interactions between the newly introduced functional groups (carboxyl groups in case of plasma treatment and amine groups in case of chitosan treatment) and dye molecules caused a significant improvement in dye uptake and dye fixation.

Conclusion

Surface modification of wool with plasma and chitosan was studied. Both treatments resulted in a notable increase in dyeability of wool fiber with cochineal and safflower and a decrease in the minimum of temperature and time for the dyeing process. Dye uptake, dye fixation, levelness, fastness, wicking, and tensile properties of wool samples were improved due to the plasma modification and chitosan treatment. SEM images and FTIR spectra confirmed the successful attachment of chitosan to wool fibers after plasma treatment. This simple and environmentally friendly method could be a suitable alternative for the traditional process of wool mordanting in natural dyeing and elimination of toxic mordant salts from this process.

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