New Possibilities of Raw Cotton Pre-treatment before reactive dyeing

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Abstract Cotton fiber is one of the most used materials among other natural fibers in the textile and clothing industry. On the other hand, environmental pollutants are formed during the processing of cotton industry especially in conventional wet processes such as bleaching, scouring for raw cotton. In order to make alteration to those processes enzymes can be also used in some of them such as: bleaching and scouring. Due to the fact that conventional textile finishing processes with intensive energy, water and chemical consumption are not environmentally friendly; it is necessary to develop more “green” and economic production methods. Plasma technology and enzymes are promising techniques to support eco-friendly production in textile industry. These eco-friendly methods can also be combined to produce high quality materials and to reduce production cost. The aim of this study is to investigate the effect of plasma treatment combined with enzymatic bioscouring system over raw cotton fabric.

Several techniques of characterization were used to study the effects caused by the interaction between plasma discharge/enzymes and cotton fabric, such as: static and dynamic contact angle, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectrometer (FTIR) and reflectance spectrophotometer. All analyses performed in this study showed that DBD plasma discharge combined with enzymes, when applied on cotton fiber, produces significant modifications on the surface of this substrate, improving hydrophilicity and whiteness without altering its intrinsic properties. Thus, proving the effectiveness of the synergy of two important technologies to textile industry.

Keywords—Plasma, enzyme, reactive dye, raw cotton, uniformity

I. INTRODUCTION

In the couple last decades, it has become important to save inputs in a process to create a product. Textile industry is one of the locomotive sectors for many countries, which is using certain amounts of water, energy, chemical and raw materials. In this case it is important to use eco-friendly and energy saving methods for production [1], [2].

In finishing processes of textile materials, there are several modification methods to make some changes on fibers. It is possible to make these modifications in three ways; chemical, biochemical and physicochemical methods [3], [4]. Conventional wet finishing processes are in the group of chemical modifications. In chemical modifications, hydrogen bridges or covalent bonds can be formed between certain groups of fibers. With chemical process it is possible to improve or modify the wettability, adhesion and staining properties of the material’s surface [5-7]. However, during the chemical alteration processes, the need for chemical amount and the requirement of the energy is much higher than in the other modifications [8].

Physicochemical methods include applications with ionized gases such as plasma, corona discharge, heat treatment, UV and ozone.

Plasma is defined as a partially ionized gas composed of electrons (0-10 eV), ions (10-30 eV), photons, atoms, molecules and is named as the fourth state of matter [9-11]. Free electrons, photons and ion clouds begin to be formed, and some atoms continue to remain neutral and the mixture of atoms, ions and electrons form the plasma [12-14]. Figure 1 illustrates the main plasma constituents.
Plasma technology is an effective modification method, to improve the surface properties of materials by taking advantage of the electrons, ions and radical components formed as a result of electrical discharges [13], [15], [16]. Plasma treatment of textile materials has become one of the high growing technology topics and appealing method due to its advantages [11]. Plasma creates effective modifications on the material surface by minimizing (or no use) the load of waste, usage of water and chemical to compare with conventional wet finishing methods [17], [18].

In this method, surface modification and formation of some functional groups can be achieved. Unlike other methods, it modifies the surface of the substrate only a few micrometers thick without any change in the bulk properties of the material [19], [20].

Dielectric barrier discharge (DBD) plasma applied in atmospheric conditions is a widely used process in order to modify the surface properties of different textile polymers [21]. DBD plasma has low energy consumption, low cost, quiet operating conditions and ease of use can be pointed as advantages. The system of DBD plasma has two electrodes (at least one of them coated with insulating dielectric material), which are placed parallel to each other [22]. In many studies DBD plasma technology when applied to textile processing has revealed to be an efficient technique to modify the surface properties of different types of fibers, such as cotton [23], [3], [24], polyamide 6,6 [25], PA/PES [26], wool/cashmere [27], PA [18], [28], PET/CO [29], wool [30], linen [31], silk [32], aramid [33], PET [34].

Biochemical modification is one of the improved methods for eliminating the disadvantages of chemical modifications. Studies have been carried out on fiber modifications using a number of microorganisms for instance fungi, bacteria and enzymes [8].

Biotechnological studies have led to use enzymes in textile industry. Enzymes are high molecular proteins with catalytic activity. They are working on specific substances that they have interest in. Processes with enzymes have advantages due to their safer and environmentally friendly working conditions. Moreover, enzymes did not produce effluents at the end of the processes.

Some of conventional wet processes such as bleaching, scouring for raw cotton, involve the use of chemicals that may cause pollution problems. In order to make alterations to those processes enzymes can be used in some of them like bioscouring. Bioscouring provides enzymatic removal of the natural hydrophobic substances present in the fibre/fabric, which is an ecofriendly method of textile production [35], [36]. Silva et al., studied on enzymatic pool in bioscouring with cellulase, lipase and pectinase of cotton fabric. They reported in this work, bioscouring with three enzyme combinations has led to best results in terms of degree of whiteness, pectin removal and hydrophilicity [40]. There are many studies on the use of several types of enzymes for cleaner production, such as laccase [37], [38], lipase and pectinase [39] applied on cotton fibers.

Because it is an environmentally friendly and gentle process, plasma discharge treatment is being studied in several applications together with enzymes.

Zhang and Wang applied DBD plasma on wool fabrics and enzymatic treatment with protease and transglutaminase to modify wool fabrics cleaner and eco-friendly [36]. Radetic et al. applied a RF plasma discharge on flax followed by a treatment with cellulase enzyme. After the treatment, the fabrics were dyed at low temperature with direct and acid dyes. The results of the combined plasma/enzyme treatment showed a decrease of the dye bath exhaustion attributed to plasma-facilitate enzymatic degradation of the amorphous areas of the hemp fibres [41]. Wong et al. obtained similar results after treating flax fibres in low-temperature plasma using oxygen and argon gases [42]. Pectinase enzyme treatment subsequent to atmospheric air or argon plasma surface modification was applied in flax fabric by Karaca et al. Results clearly proved that the efficiency of pectinase in improving flax water absorbency can be significantly enhanced by plasma pre-treatment [43].
Cotton fiber includes cellulosic and non-cellulosic substances. These non-cellulosic components such as waxes, pectin, lignin, protein and others give hydrophobic characteristic of cotton nature. They need to be removed from the fiber before dyeing and finishing processes. Table I. shows the chemical composition of the raw cotton fibre.

TABLE I
THE CHEMICAL COMPOSITION OF RAW COTTON

| Percentages in the fiber composition | Substance  |
|-----------------------------------|------------|
| % 88-96                           | Cellulose  |
| % 1-1.9                           | Protein    |
| % 0.4-1.2                         | Waxes      |
| % 0.4-1.2                         | Pectin     |
| % 0.7-1.6                         | Others     |

Conventional methods consume huge amounts of chemicals, water and energy. Moreover, they cause environmental problems due to their heavy effluents. In this case it is important to use environmentally friendly methods in every step of textile finishing processes as much as we can. Thus, the aim of this study is to investigate the effect of DBD plasma treatment combined with enzymes bioscouring system before reactive dyeing of cotton fabric.

II. MATERIAL AND METHODS

A. Materials
A commercial 100% raw cotton fabric with a taffeta structure, a mass per unit area of 162 g m\(^{-2}\) and a texture of 19 threads/cm in warp and 14 threads/cm in weft direction was used in this study.
Bioprep 3000L containing pectinase and lipase were kindly supplied by Aquitex. Procion® (Dystar) reactive dyes were used for dyeing processes.
Conventional bleaching was made with sodium hydroxide and hydrogen peroxide and they were of analytical grade.

B. Plasma treatment
Plasma treatment was carried out with a semi-industrial prototype (Softal/University of Minho). The working conditions were: velocity 4 m/min, power 1 kW and 5 passages per each side. Working plan of the experiment is presented in Fig. 2.

C. Scouring of cotton fabrics
After plasma treatment bioscouring process was performed with pectinase or lipase+pectinase combination. Scouring with pectinase process conditions were pH 6-7, temperature 50°C, time interval between 30-60 min, bath ratio of 1:20 with appropriate amount of enzyme.
Scouring with lipase was carried out with pH 5, temperature 50°C, time 60 min, bath ratio of 1:30 and appropriate amount of lipase enzyme was used. The enzymes inactivation process was performed with hot distilled water washing.
Conventional bleaching was performed using sodium hydroxide and hydrogen peroxide with a standard recipe.
at boiling temperature.

D. Dyeing of cotton fabrics

The dyeing method was carried out with 5 g of cotton fabric in a laboratorial Ahiba Spectradye-Datacolor machine equipped with infra-red heating with a liquor ratio of 1:20 with dye concentration of 1% (o.w.f) Procion®.

For dyeing process, the program was started at 25°C and raised at a rate of 2°C min⁻¹ up to 80°C, and kept at this temperature for 60 minutes. The chemicals and auxiliary agents were used according to the producers’ recommendations. After dyeing washing steps were applied.

E. Scanning electron microscopy (SEM) analysis

Morphological analysis of cotton fabrics was carried out in an ultra-high resolution field emission gun SEM instrument (NOVA 200 Nano SEM, FEI Co. Oregon, USA). Previously, the samples were coated with a thin layer of gold palladium.

F. Contact angle measurement

To determine hydrophilicity of the samples before and after the treatments processes, contact angle measurement was carried out in Dataphysics instrument (Filderstadt, Germany) using OCA20 software with a video system, for the capturing of images in static and dynamic modes.

G. Fourier-transform infrared spectroscopy (FTIR) measurements

A Shimadzu Iraffinity-1S spectrometer (Japan) was used to determine changes in the main characteristic groups of raw cotton surface. The spectra were collected over the range 400-4000 cm⁻¹ at room temperature.

H. Whiteness and color strength

The whiteness degree, colorimetric coordinates and color strength of the bleached and dyed fabrics were measured using Datacolor Spectraflash SF600 Plus CT spectrophotometer at standard illuminant D65 and observer 10° combination.

III. RESULTS AND DISCUSSIONS

The effects of the plasma and enzymes bioscouring treatments in the wettability, whiteness degree and dyeing properties of raw cotton fabrics were evaluated with different characterization techniques.

A. Surface evaluation

Plasma and enzyme treated fiber surface become cleaner with a smooth effect. The reason of the smoothness can be attributed to the etching effect of plasma treatment. Fig. 3 shows the cotton surface morphology by SEM images under different treatment conditions.
SEM images of cotton fabrics indicate that with plasma and enzyme treatments there are considerable surface changes over fibers. Conventional bleaching of raw cotton uses harsh chemicals and high temperature that cause the damages of the cotton surface (Fig. 3b). Fig. 3c shows the images of cotton fiber treated with plasma. The surface of the cotton fabric is smoother with the combined treatment of plasma application and enzyme (Fig. 3d). With the use of plasma and enzymes for treatment of raw cotton, conditions are much milder and do not create any damages of the surface on cotton fabrics.

B. Hydrophilicity

Hydrophobic nature of raw cotton fabric is not able to absorb water easily due to non-cellulosic substances. Due to these compounds, raw cotton fabric has a highly hydrophobic character. Plasma and enzymatic treatment create changes on the fiber surface improving the hydrophilicity as can be observed in the Table 2.

**TABLE 2**

| Fabric                              | Result (°) |
|-------------------------------------|------------|
| Raw cotton                          | 161,3      |
| Raw cotton + Plasma                 | 107,4      |
| Raw cotton + Pectinase + Lipase     | 137,5      |
| Raw cotton + Plasma + Pectinase + Lipase | 103,6 |

The results obtained by dynamic contact angle measurement show higher hydrophilicity with plasma and enzyme combination treated fabrics.

Figure 4 shows the wetting behavior of the treated and untreated cotton fabrics. Especially, after the application with plasma and enzyme combinations wetting properties of raw cotton were significantly improved, as we can observe in Figure 4. The hydrophilicity of the cotton fabrics was measured in terms of water contact angle. When a water drop was placed onto the fabric surface (with plasma and enzymatic treatment combination), it is instantly absorbed. Thus, fabrics treated with plasma and then followed by enzymatic incubations have significantly improved the wetting time, absorption rates and spreading speed results.
C. Fourier-transform infrared spectroscopy (FTIR) measurements

Surface chemistry of cotton fabrics was analyzed with FTIR. The spectra obtained gave similar results among the samples treated and untreated because the bulk compositions of the fabrics are similar (Fig. 5). However, the results confer that the pectin and wax impurities were removed from the cotton surface in both the raw pectinase-lipase and plasma pectinase lipase scoured fabrics. The characteristic peak around 1730 cm⁻¹ which represents the impurities such as waxes and pectin, were present in the raw cotton but almost disappeared in the bioscourd samples. The purpose of the scouring process was to remove hydrophobic substances (wax components, long chain alcohols, fatty acids) in the fiber to produce high wettability. It proved that the enzymes had successfully removed all the pectin and wax impurities from cotton thus increasing hydrophilicity as previously observed.

D. Color strength and whiteness degree

Conventional wet treatments of cotton fabrics aim to remove the hydrophobic substances such as natural non-cellulosic particles and starch, from the fiber. These impurities cause serious dyeing problems. For this reason, it is important that these impurities should be removed before the dyeing process. Application with plasma, wetting properties of raw cotton were significantly improved especially treatments when combined with enzymes. Before the dyeing processes the color measurements of the samples were measured (Table 3). The results showed higher whiteness degree and lower yellow (coordinate b) for the samples treated with enzyme and plasma when compared with raw cotton fabric. The combined application of enzymes + plasma and just enzyme treatment did not show any significant difference.

| Samples             | L*  | a*  | b*  | C*  | h    | Whiteness Deg. (Berger) |
|---------------------|-----|-----|-----|-----|------|-------------------------|
| R                   | 84,42 | 1,99 | 13,14 | 13,29 | 81,38 | 10,9                     |
| R+Pec+Lip           | 84,69 | 1,82 | 11,48 | 11,62 | 80,98 | 17,4                     |
| R+Pl+Pec+Lip        | 84,63 | 1,97 | 11,43 | 11,60 | 80,20 | 17,3                     |

R: Raw cotton, R+Pec+Lip: Raw cotton + Pectinase + Lipase, R+Pl+Pec+Lip: Raw cotton + Plasma + Pectinase + Lipase
Table 4 shows the color coordinates and color strength of the dyed cotton samples treated with plasma + enzyme and untreated raw cotton fabrics (Table 4).

| Color   | L*  | a*  | b*  | C*  | h   | K/S |
|---------|-----|-----|-----|-----|-----|-----|
| Blue    | 46.11 | -7.56 | -16.54 | 18.18 | 245.44 | 64.70 |
|         | 45.47 | -7.44 | -16.74 | 18.32 | 246.03 | 71.56 |
| Red     | 49.30 | 46.98 | -7.39 | 47.56 | 351.06 | 62.08 |
|         | 49.66 | 47.97 | -7.56 | 48.57 | 351.05 | 64.37 |
| Yellow  | 69.11 | 17.37 | 46.51 | 49.64 | 69.52 | 54.41 |
|         | 67.66 | 17.36 | 45.07 | 48.30 | 68.93 | 54.28 |

The results of the combined plasma/enzyme treatments showed similar dye bath exhaustion and the equilibrium uptake of a reactive dye remained.

IV. CONCLUSION

The aim of this study was to investigate a green and alternative process instead of wet conventional treatments of cotton fabrics. As implied before, conventional wet treatments cause environmental problems. In order to improve treatment methods of the cotton fabrics, this study applied atmospheric plasma and enzymatic treatments combinations on the raw cotton fabrics. Application of the pectinase and lipase removed non-cellulosic impurities in order to create scouring effect on the cotton fiber.

Results clearly proved that the efficiency of pectinase in improving cotton water absorbency can be significantly enhanced by plasma pre-treatment.

No significant difference was observed in the dyeing properties of the samples with and without treatment. Operating under controlled conditions, plasma/ enzymatic treatments of textiles are particularly intriguing for research on different types of fibers. However, enzymatic treatment and plasma parameters must be strictly controlled in order to avoid unacceptable weight loss and reduction of strength. Despite that, the synergetic combination of plasma and enzyme technologies reveals without any doubt a great potential for textile applications.

The overall results showed that eco-friendly pre-treatment methods are acceptable when compared with conventional ones.

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