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Effect of Plasma on Dyeability of Fabrics

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1. Introduction

The unique physical and chemical characteristics of the plasma environment make it attractive for textile processing. Plasma is an ionized gas, i.e. it contains electrons, ions and neutral atoms and/or molecules. However, not all of the ionized gases used in textile processing will exhibit the properties associated with plasmas, mainly because of their low charge state densities compared to the neutral gas density or are produced by transient phenomena.

Plasma activation is being used in several fabric and nonwoven applications in the textile industry. (Pane *et al.*, 2003)

There are many industrial applications of thin film deposition by plasma sputtering or plasma polymerization in the technical textile and nonwoven industry. Roughly, the coatings deposited in those industries can be categorized under either (permanently) hydrophilic coatings or hydrophobic/oleophilic coatings. In most cases, the deposited coatings give rise to unique products that are difficult or even impossible to produce using other technologies.

The textile market is trying to make deep, dark colours and this is not easy to achieve. (Svensson, 2004)

One way to do this is to reduce the specular component of reflection of the fabric surface after dyeing. A plasma etching leads to a controlled nano or micro-roughness, increasing diffuse reflectance and minimizing the specular component. In consequence, the dyed fabric will have an intense darker colour after plasma etching.

In various research programs, it has been shown that pick-up of dyestuff can be strongly improved after plasma pre-treatment of natural and synthetic fibre fabrics.

Polypropylene fibers have such excellent properties as low specific weight (0.91 g/cm^3 only), high strength (42-53 CN/ Tex) and good resistance to acids and alkalis, and they also possess good thermal resistance and antibacterial properties. The poor wettability (only 0.05 % at 20 ^oC) and dyeability have, however, limited the application of these fibers in garments and other industries (Huang et al, 2006). It is of importance to improve the wet ability and dyeability of PP fabrics for many applications. Although chemical modification of the fibers has been somewhat successful in improving hydrophilic and antistatic properties, there are environmental concerns related to the disposal of chemical after

treatment. Plasma treatment, as a clean, dry and environmental friendly physical technique, opens up a new possibility in this field. So in this chapter we focused on investigation about the improving the dye and printability of PP fabrics in section 2 to 4.
In the other point of view, natural dyes are generally understood to be colorants (dyes and pigments) that are obtained from animal or vegetable matter without chemical processing. They are mainly mordant dyes, although some natural vat, solvent, pigment, direct and acid types are known. In recent years, concern for the environment has created an increasing interest in natural dyes. Conventional wisdom leads to the belief that natural dyes are friendlier to the environment than their synthetic counterparts, although the issue is not necessarily quite so straightforward. The natural dyeability of wool fabrics is investigated in section 5-6. In textile processing, the interactions of the plasma generated species with and on the surfaces in contact with the plasma are of great importance and these are discussed in this chapter, respectively.

2. Effect of using cold plasma on dyeing properties of polypropylene fabrics

The dye-ability of hydrophobic fabrics, such as the PP fabrics is very poor. (Chun Liu et al, 2006) It is known that introducing hydrophilic sites on the hydrophobic fabrics can improve the dyeability of these fibers. Plasma modifications resulting in unsaturated bonds and/ or free radicals on the surface of the fabrics have a significant influence on the overall surface changes and consequently on dyeability (Shahidi et al, 2007). PP fabrics have been treated with Low Temperature Plasma (LTP) of oxygen and nitrogen for different period of times, different condition of power and pressure. The best condition was treatment for 7 min at the power of 120 watt and pressure of 5×10^{-2} torr. As it can be seen in Figures 1 to 4, the reflection factors of dyed LTP treated samples were less than dyed untreated sample. The results show that the O_2 and N_2 plasma treatments are effective in increasing the dye exhaustion of PP with anionic, cationic, disperse and direct dyes. Furthermore, the colors achieved much more brilliant shades with the LTP treatment. The results show that, the average of K/S between wavelength of 350-500 was first increased with prolonged LTP exposure time, reached a maximum generally at about 7 min, and then decreased since by increasing time of exposure some Al particles are deposited on the surface of the samples. (Shahidi et al, 2007). As it can be seen in Figures, and as is evident from the FTIR measurement, O_2 plasma treated PP incorporates oxygen in the form of C-O and O-H (negative sites) in the fiber surface and increases electronegativity. So the dye exhaustion for cationic (basic) dye with positive sites increases considerably. It can be seen that, average K/S value of O_2 -7 min sample, which was dyed with this dye, is 3 times more than average K/S value of untreated one. Furthermore, by creating N-H groups (positive sites) on the surface of PP fabrics with N_2 LTP treatment, the dye exhaustion for direct and anionic dyes (with negative sites) increases. Note that there were no significant color changes either with repeated washing cycles or with a long period of storage, which indicates that the stability of dye attachment to the fabrics. It can be seen in Figure 4 that the reflection factor of dyed O_2 LTP treated sample with disperse dye is less than Dyed N_2 LTP treated one. It shows that the disperse dye exhaustion of O_2 LTP treated sample is more than N_2 LTP treated one. But it is not noticeable because Disperse dyes don't have any positive or negative sites.

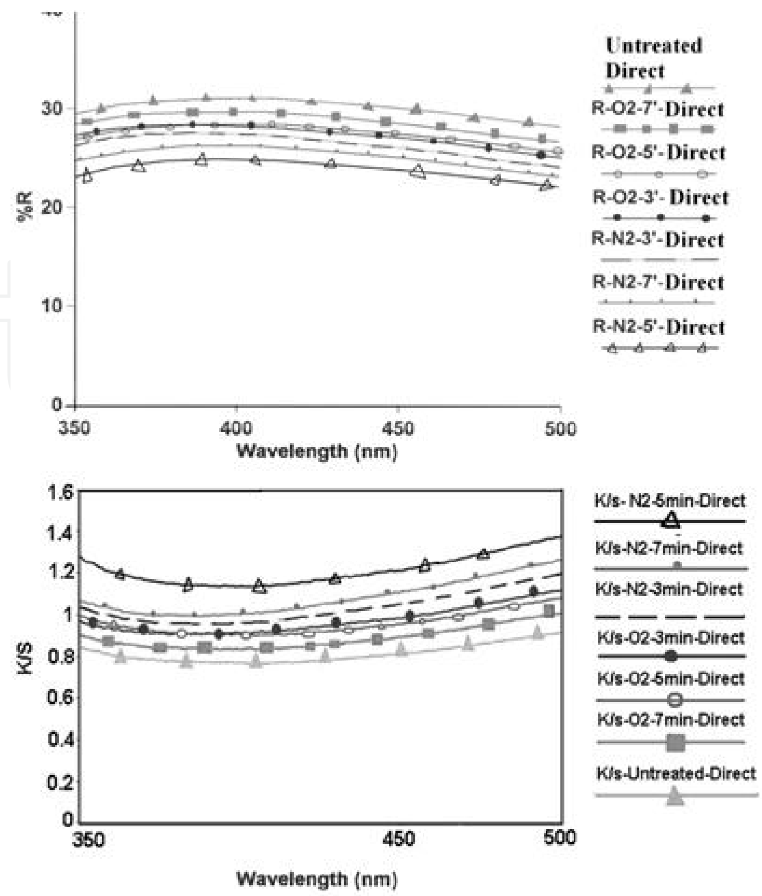


Fig. 1. R% and K/S Value of dyed samples with Direct Dyes

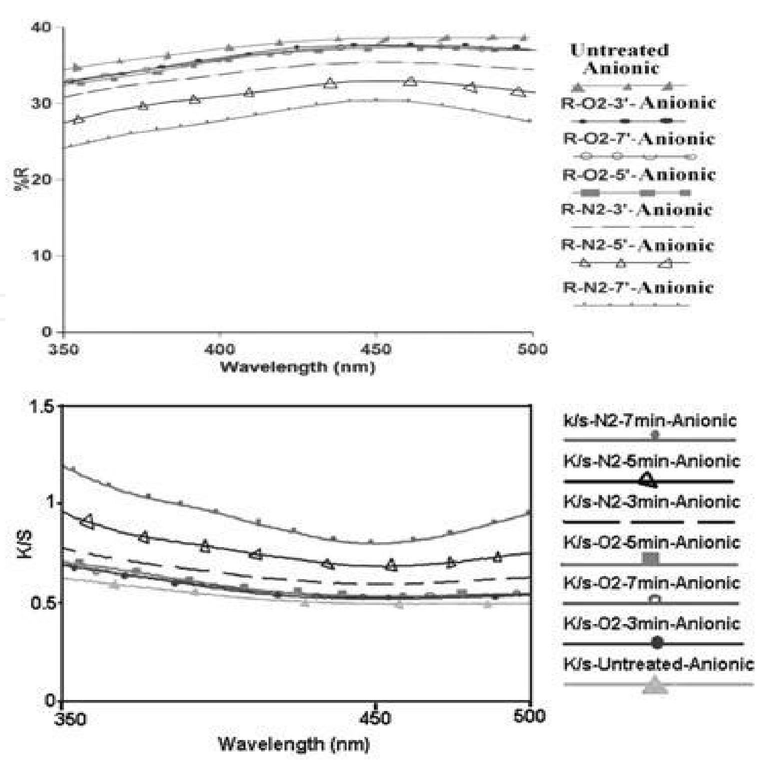


Fig. 2. R% and K/S Value of dyed samples with Anionic Dyes

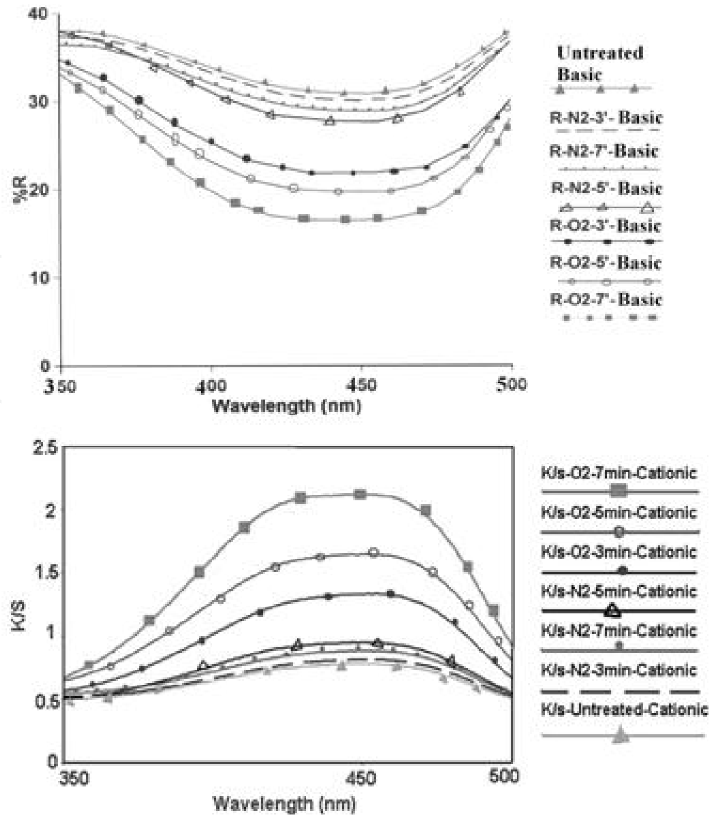


Fig. 3. R% and K/S Value of dyed samples with Cationic Dyes

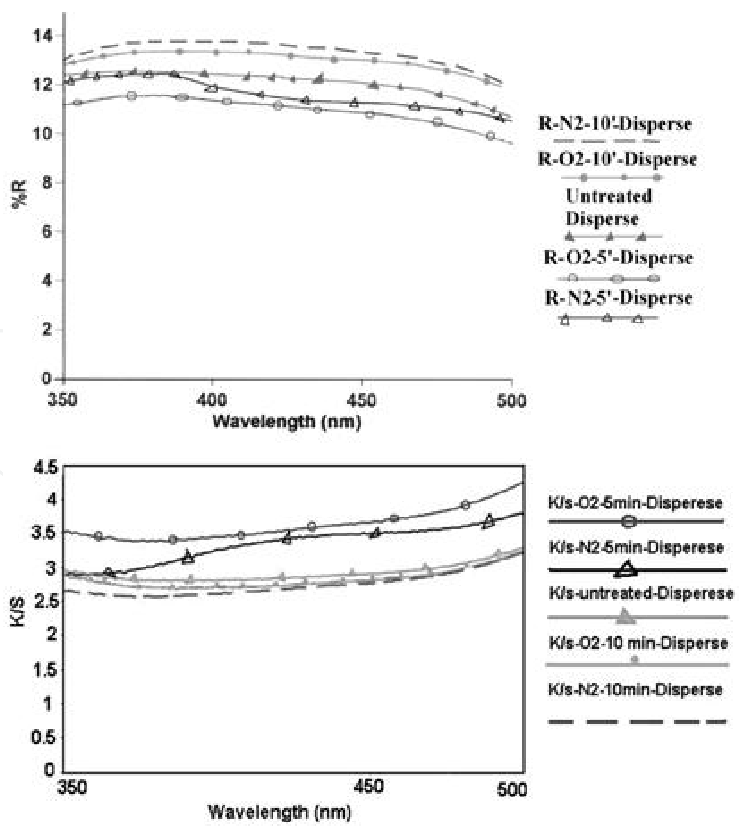


Fig. 4. R% and K/S Value of dyed samples with Disperse Dyes

SEM micrographs of PP fabric treated, respectively, with the two non-polymerizing plasma gases (O_2, N_2) are shown in Figure 5, only 3 and 7 min treated samples being presented here. It can be seen that, after prolonged LTP treatment, ripple like patterns oriented in a fiber axis are developed (see Figure 5 (d, e)). O_2 plasma gives more distinct effect than N_2 plasma.

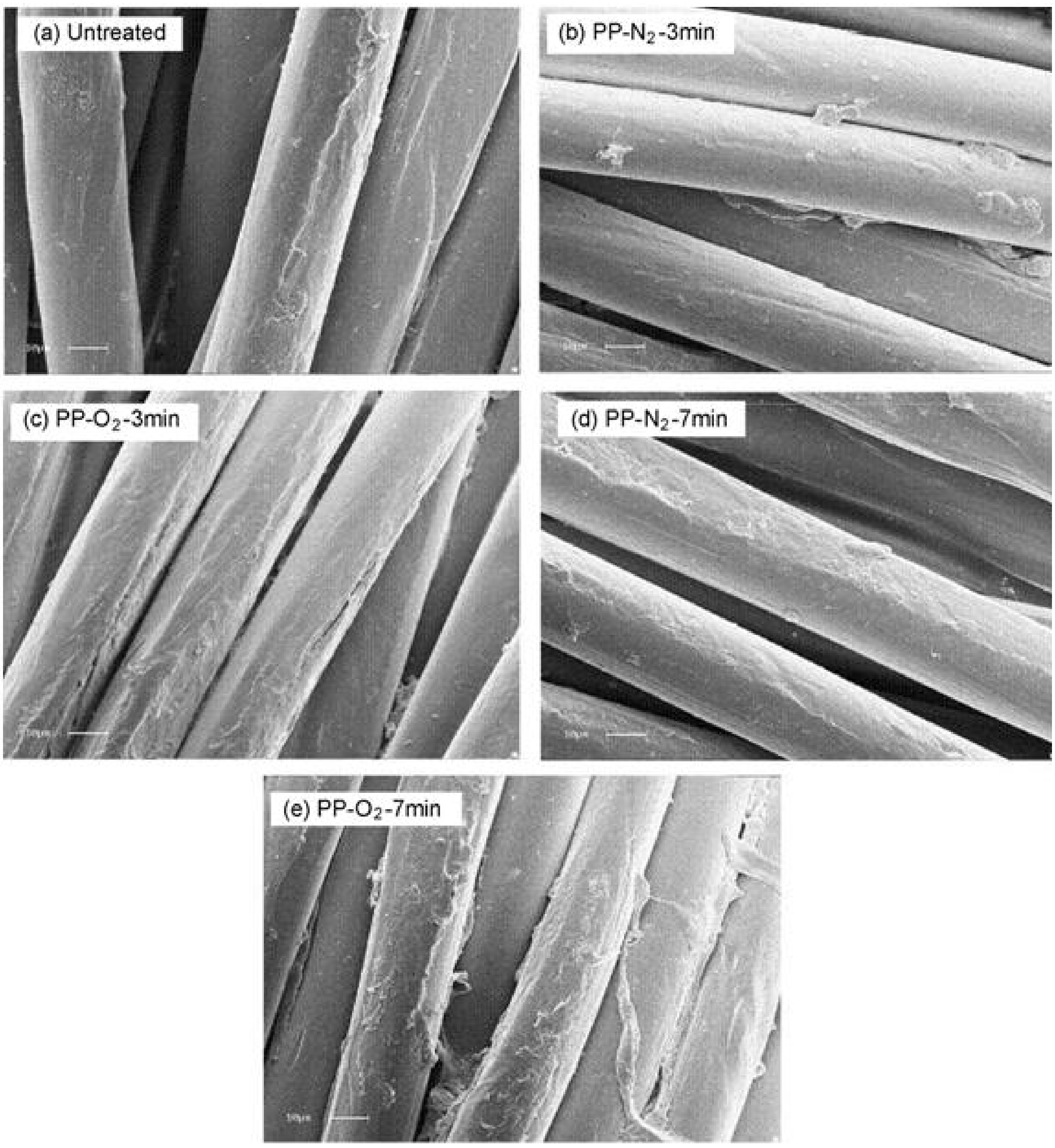


Fig. 5. SEM Images of Treated and untreated samples

X-ray diffraction (XRD) is a crystal structure analysis method using the atomic arrays within the crystals as a three dimensional grating to diffract a monochromatic beam of X-rays. The angles at which the beam is diffracted are used to calculate the interplaner atomic spacing (d-spacing) giving information about how the atoms are arranged within the crystalline compounds. X-ray diffraction is also used to measure the nature of polymer and extent of crystallinity present in the polymer sample. The results of XRD analysis are reported in Figure 6. Study of the data of this analysis shows no noticeable changes in the value of d or FWHM (size of crystals) of the PP fibers, but the LTP treatment slightly increased the total crystallinity. This indicates that the treatment has not changed the arrangement or decreased the strength of the fabrics.

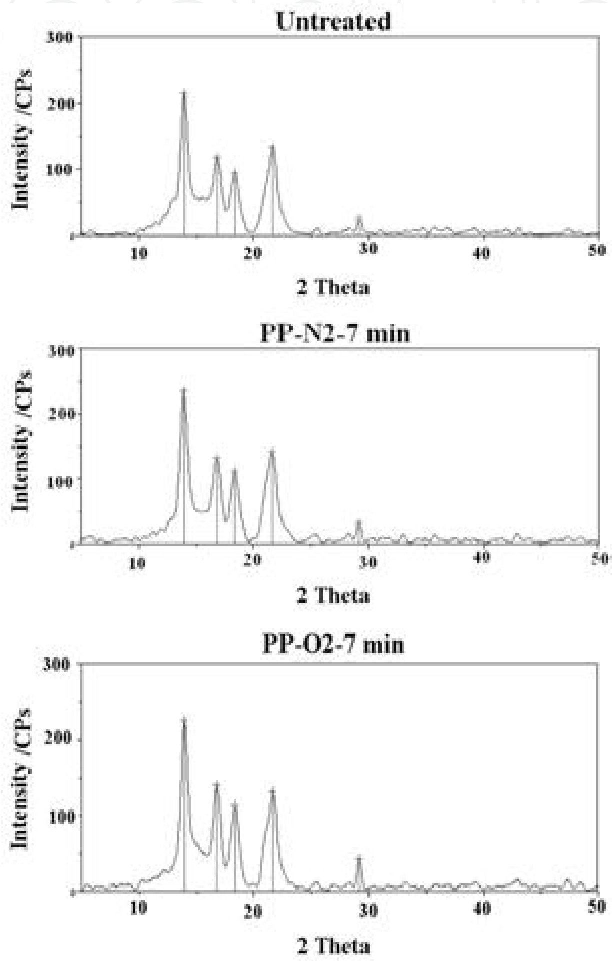


Fig. 6. XRD Results of Treated and Untreated Samples

In this research work, the dye-ability of Polypropylene Fabrics was improved by using low temperature plasma treatment. The dye-ability of PP fabrics treated with LTP of N_2 is increased with anionic dyes, and by creating OH and C=O groups on the surface of the fabrics with O_2 LTP treatment, the dye exhaustion for cationic dye increases noticeably. So we can dye PP-O_2 LTP treated sample with cationic dyes easily (Shahidi et al, 2007). And we can have new usage of PP fabrics as textile garments. The present examples show that plasma technology performed under reduced pressure, leads to a variety to processes to modify fiber or textile materials to fulfill additional highly desirable requirements. It is to be expected that, this technology, which has been known for a long time and is being used in different branches of industry, in the near future will conquer textile as well (Errifai et al, 2004; Shahidi et al, 2007).

3. Effect of electron irradiation on printability of polypropylene (PP) fabrics, (novel method for decoration of PP fabrics)

Textile printing is the area of textile processing used for applying color in a localized design or pattern to textile material, normally fabric. Depending on the fiber composition and the construction of the fabric to be printed, as well as the proper selection of dyes or pigments, the printed patterns can exhibit good to excellent colorfastness. From a practical point of view, textile printing is the process which incorporates artistic design, engineering, and chemical technology to produce unique patterns which can then be accurately repeated on large volumes of the fabric. Textile printing is probably best described as an industrial art, having a long history and an assured future. Printing is actually local dyeing. The dye is a part of a printing paste, which is applied on the textile material by different printing techniques. After printing, it is usual to steam the textile material, to achieve colorfastness (wash, light, and rubbing fastness).

Textile print was created thanks to man's desire to decorate fabrics designated for clothing, and later for home decoration (Petrinic, Andersen, Ostar-Turk, & Le Marechal, 2007). It has logically gone through many development steps. The steps were aimed at improving the mechanization and automation of each printing technology phase. Each printing technique was created and improved step by step (Burton, 2005).

In traditional textile printing, colored images on the fabrics are produced by using textile print paste which consists of highly concentrated thickened solutions of textile dyes or pigments. Unfortunately, the use of these print pastes can lead to intensely colored waste products.

Environmental issues are of major concern to most textile printers (Moser, 2003). For many years, improving the quality of prints was the main goal in product development. Lately, economic, environmental, and toxicological considerations have become more important. Using more environmentally friendly print paste preparations and auxiliary products, for example reducing or to eliminating formaldehyde on the fabric, is currently one of the major concerns in the textile printing industry (El-Molla & Schneider, 2006).

In many cases relating to the processing of fibers, powders, and films, the modification of polymer surface functional groups composition is often required.

The development of methods for the controllable modification of polymers in order to adjust their physicochemical, mechanical, optical, and other properties without any chemical processing is one of the most important areas of polymer science and technology.

Accelerated electrons generated by an electron beam (EB) may be considered one of the most important sources of ionizing radiation in the recent years. The effects of ionizing radiation, in general, and accelerated electrons in particular range from the basic phenomena of interaction of radiation with matter, radiation physics and chemistry to industrial applications. Among the different chemical systems, polymeric materials show marked changes when subjected to the action of ionizing radiation. These changes are mainly cross-linking or degradation, which result in the formation of products with modified physical and chemical properties.

Radiation curing by EB has become a well accepted technology, which has found a large number of industrial applications mainly in the coating and printing fields, in the manufacture of adhesives, and in microelectronics (El-Naggar, Zohdy, Said, El-Din, & Noval, 2005).

The modification of polymers is an important area of EB technologies providing an effective way to surface modification of various chemically inert materials, such as polyethylene imparting them with the reactivity required for the formation of polymer blends and grafted layers. Particularly, the high density EB treatment of polypropylene (PP) was found to promote the formation of oxygen-containing groups (mainly C=O) on the polymer surface and enhancement of PP compatibility with hydrophilic inorganic materials (El-Naggar et al., 2005; Ibrahim, Salmawi, & Ibrahim, 2005; Iller, Kukie ka, Stupi ska, & Miko ajczyk, 2002; Kondo et al., 2006; Leonhardt, Muratore, & Walton, 2004; Mahapatra, Bodas, Mandale, Gangal, & Bhoraskar, 2006; Timusa, Cincub, Bradleyc, Craciuna, & Mateescua, 2000; Vasiljeva, Mjakin, Makarov, Krasovsky, & Varlamov, 2006; Zagórski, 2004; Zsigmond, Halasz, & Czvikovszky, 2003).

I.S. Bhardwaj and his coworkers researched on the modification of PP fiber with EB. In this work, PP filaments were irradiated by different doses of EB in the presence of monomers like acrylic acid, 2-4 vinyl pyridine. The solubility, crystallinity, and tenacity of the treated fibers has been determined. There appears to be a marked improvement in the tenacity of the fiber and dye take-up (Bhardwaj & Heusinger, 1978). Also, EB treatment studies have been carried out by H.M. Abdel-Hamid to investigate the potential for improvements in the dielectric properties of the PP film (Abdel-Hamid, 2005). F. Poncin-Epaillard reported that, surface grafting of polymeric materials, such as films and fibers, may improve their surface properties and this improvement on PP active sites should initiate a surface postgrafting that can be formed by an EB irradiation. EB modified PP was also functionalized through an aging reaction, emphasized by a high radical concentration. Active surface films are susceptible to react with monomers in a postgrafting reaction (Poncin-Epaillard, Chevet, & Brosse, 1994).

In this work, the PP fabric is irradiated with electrons to form oxygen containing groups on its surface. By creating these functional groups, the uncovered part of PP fabric can be dyed by cationic dyes easily without any hazardous materials (Shahidi et al, 2007). Thus, just by dyeing the fabrics can be printed.

The aim of this research is the development of an environmental-friendly process with no thickeners in order to enable good quality printing and to minimize water pollution.

Due to low surface energy, polypropylene has very weak hydrophilic properties and doesn't have any affinity to cationic dyes. In this study, some parts of polypropylene fabrics (PP) have been covered by mask, and then they were irradiated by electrons with different energies (Figure 7). After electron irradiation, the samples have dyed with cationic dyestuff. The electron irradiated parts can be dyed and by this work we can print or decorate the polypropylene fabrics and films easily. The treated surfaces were characterized by Scanning Electron Microscopy (SEM), reflective spectroscopy and FTIR. Also, light and wash fastnesses of printed samples were measured. As we know, pigment printing method requires additional materials such as gauze, screen, screen frame, screen lake, etc. and these affect product costs. Moreover, this process requires longer times compared to Electron Beam (EB) designing. On this account EB designing is more advantageous. One of the advantages of the EB designing is the good repeatability of the designs. Besides, desired physical effects can be fully ensured. In pigment printing method printing time is lengthening and reproducibility decreases due to the difficulties such as paste preparation, squeegee motion, clogging of the screen and the necessity to print the same area for each sample. Moreover, EB designing process does not include any after-treatments such as drying and fixating which increase the production time and costs. The results from this work show that the EB-based designing process represents a serious competitor of the conventional technologies. And just by dyeing the electron irradiated samples, the printed look appeared on the surface of PP fabrics, it is because of this matter that, PP doesn't have any affinity to cationic dyestuffs, but after EB treatment, cationic dye can be absorbed by irradiated parts of fabrics easily.

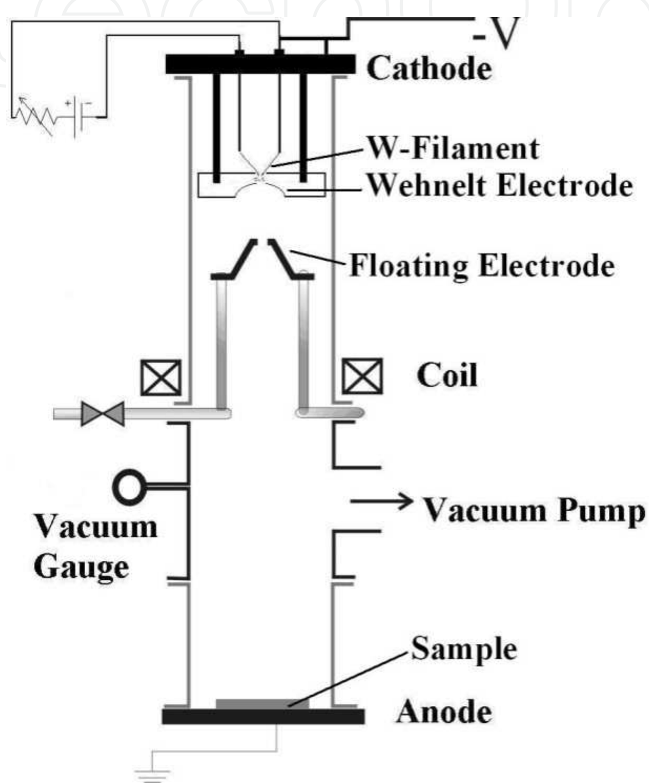


Fig. 7. The Schematic view of experimental setup.

In order to study the chemical modification of the electron irradiated part of fabrics, Fourier transform infrared spectroscopy is used. FTIR was used to examine the functional groups of the corresponding samples investigated in Figure 8. As shown only slight increase in absorbance at 1720 cm^{-1} (C=O) band and 3400 cm^{-1} (O-H) band and 1080-1300 cm^{-1} (C-O) after electron irradiation can be noticed. The improvement of dye-ability properties of these uncovered parts confirmed that, electron bombardment activated successfully the surface of uncovered PP fabrics. The main effect of electron beam treatment of a polymer is the transfer of energy towards the respective polymer surface .In function of the molecular structure of the polymer, one of the following events could proceed : cross-linking , chain scission or radical stabilization. In the case of polymer treatments by Electron Beam, electrons are accelerated towards the exposed surface and lead to an increased reactivity of the respective surface. This fact is possible due to the breaking of the different bonds and further formation of free radicals. After the polymer samples are brought out from the reactor, the reaction of the oxygen from the atmosphere with the free radicals takes place, and thus surface functionalization is obtained. This functionalization is more important for the materials that have no oxygen-containing groups in their initial composition. The improvement of dye-ability properties of these uncovered parts confirmed that, electron bombardment activated successfully the surface of uncovered PP fabrics.

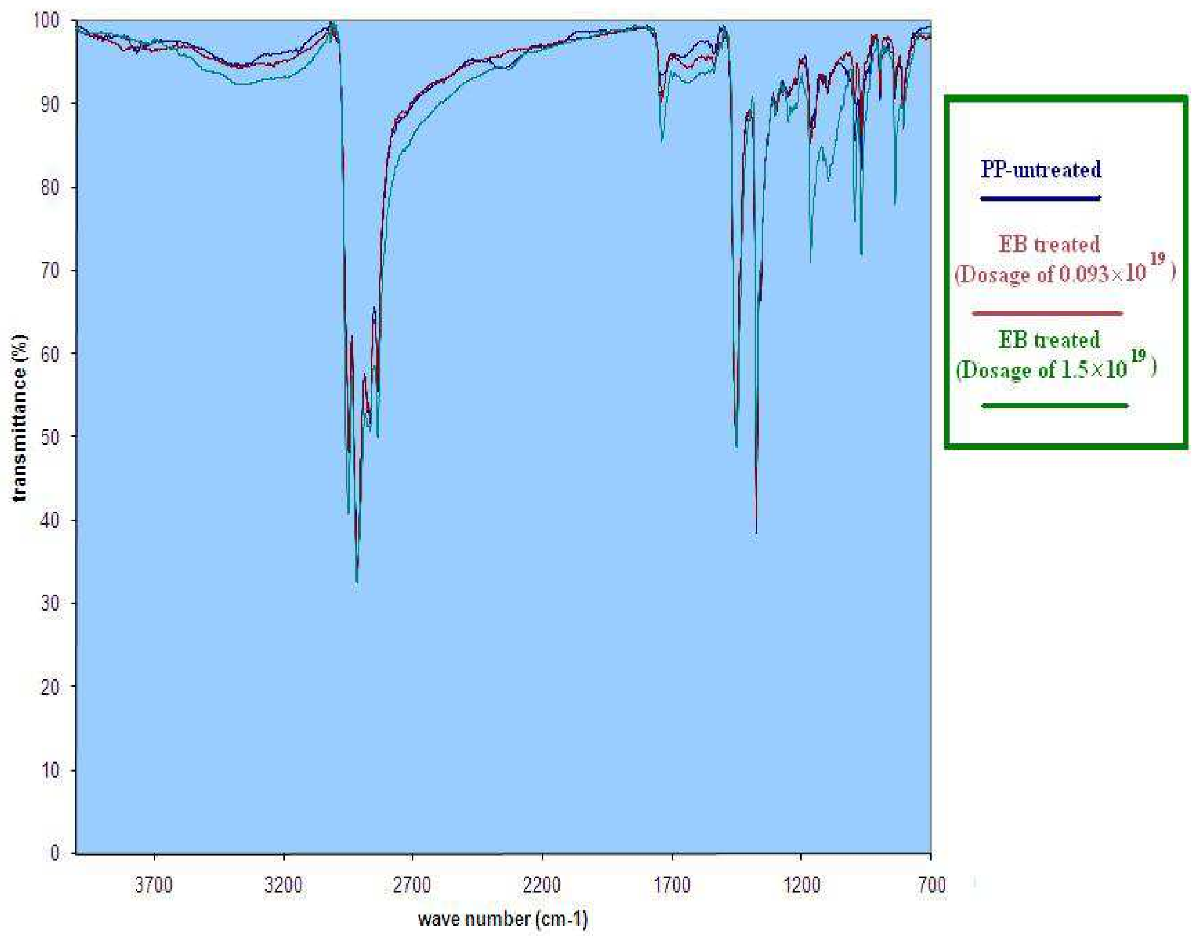


Fig. 8. The FTIR results of untreated and treated samples.

In this study, Electron Beam Irradiation has been used as a novel method for decoration of PP Fabrics. The highest relative color strength (K/S) is obtained and the fastness properties range between good and excellent for samples printed using electron irradiation, this is true irrespective of the type of printed fabric. In this research work, the physical and chemical properties of PP fabrics were improved by using electron beam irradiation with different energy of bombardment. By this treatment, the wet ability and Dye ability of PP were increased significantly through creating (-O-H), (C=O) and (C-O) groups on the surface of samples where hydrophobic properties changes to hydrophilic.

And we could dye the uncovered electron irradiated parts of PP fabrics with cationic dyestuff and decorate the PP fabrics without any thickener and auxiliaries as it can be seen in Figure 9(d). It is expected that, EB irradiation which has been known for a long time and is being used in different branches of industry, in the near future will conquer polymer as well (Payamara et al, 2010).

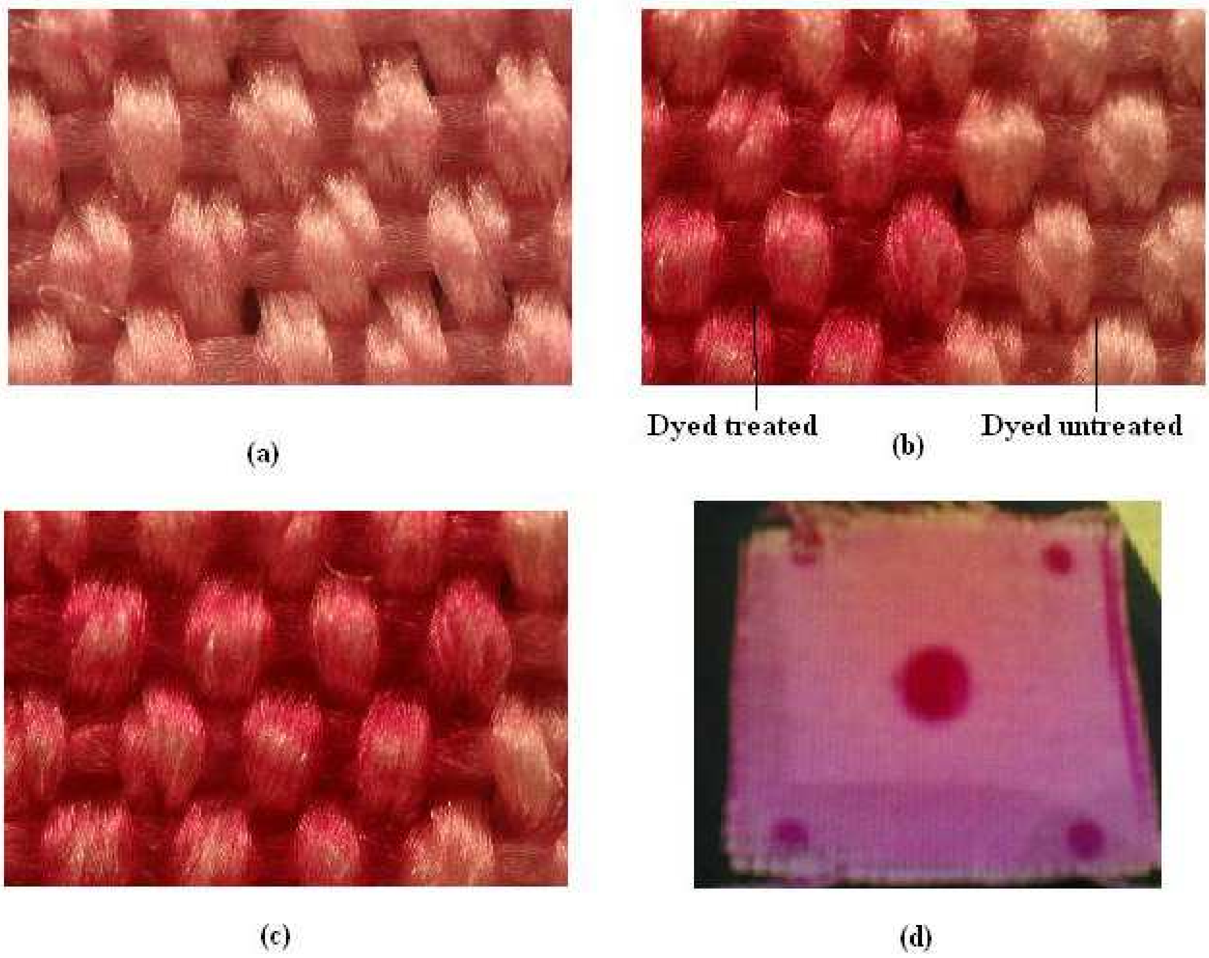


Fig. 9. The photo of printed samples

4. Ion beam modification of polypropylene fabrics

The main goal of this work was examination of structural and compositional changes in the polypropylene (PP) fabrics caused by ion irradiation. In this work, the PP fabric has been irradiated with CO_2 ions. The implantation conditions (i.e, exposure time, beam current, and discharge power) were changed to control the extent of surface modification. And the effects of irradiation were studied using different instruments. Also dye ability of the untreated sample and treated under different conditions were investigated by using a 3% wt aqueous solution of a basic dyestuff. The obtained data show that, ion beam processing of PP fabrics allows an adjustable modification of their surface properties. The functional groups on the surface of samples were examined using FTIR spectrometer. Moreover, dyeing properties for treated fabrics have been tested. Significant increase in color strength has been achieved. Morphology of samples was examined by Scanning Electron Microscopy (SEM). The PP fabric was mounted on a sample holder and placed inside a vacuum system Fig 10. Carbon dioxide ion beams at energies of 1 and 2 keV were implanted, using an Ion Beam Sputtering system with Kauffman Ion Source, at the Plasma Physics Research Center (Tehran, Iran). Vacuum chamber was evacuated to the base pressure of 9×10^{-3} torr using rotary pump, and then to pressure of 10^{-5} torr using turbo pump. After filling the chamber with 10^{-2} torr of working gas (CO_2), the filament, discharge, accelerator and focusing system were generated , respectively. The ions were produced via a multi-step process: that is, ions are initially formed by stripping electrons from source atoms in plasma. The beam of ions is then accelerated using a potential gradient column. A series of electrostatic lens elements shapes the resulting ion beam and scans it over an area in a work chamber containing the samples to be treated. One side of samples was treated for duration of 3 minutes. The dosage of 1×10^{11} ions/cm^2 was used, and the implantation was done with different beam current below 1mA to avoid excessive heating and thermal degradation.

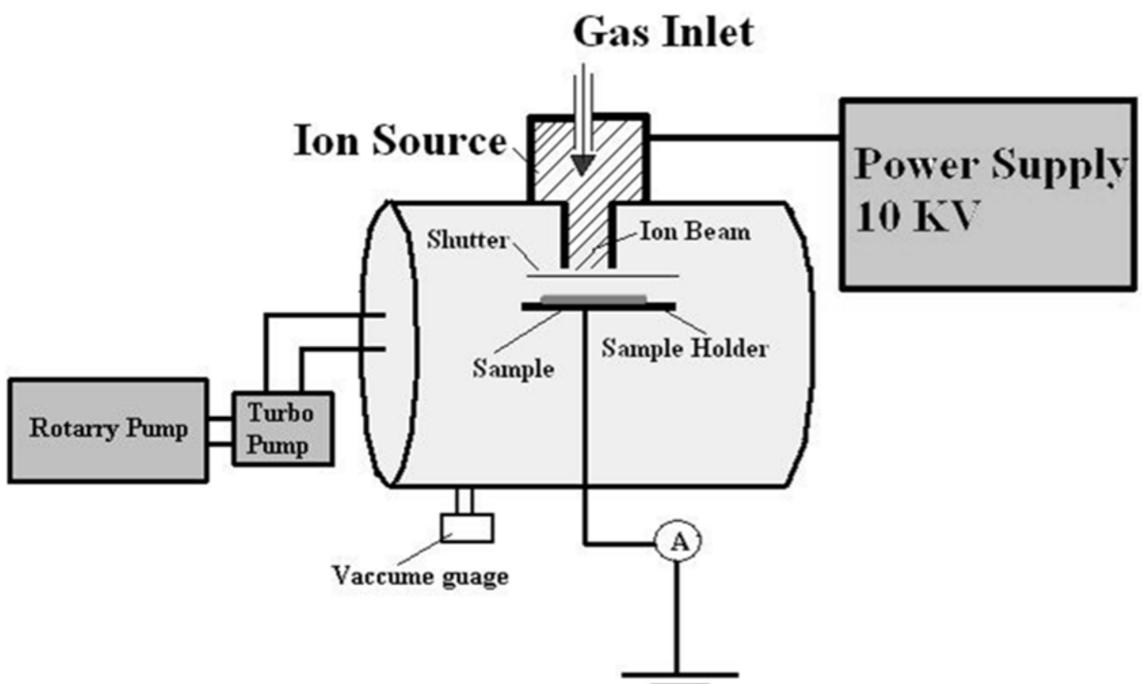


Fig. 10. Schematic view of Ion Implantation set up.

In this research work, the dye-ability of polypropylene fabrics is improved by using ion implantation treatment. The cationic dye-ability of treated PP fabrics by creating OH and C=O groups on the surface of the fabrics increases noticeably. So we can dyes PP-Ion implanted samples with cationic dyes easily. And we can have new usage of PP fabrics as textile garments. The present examples show that ion implantation technology performed under reduced pressure, leads to variety to processes to modify fiber or textile materials to fulfill additional highly desirable requirements. However it should be mentioned that, the dye ability of PP fabrics using electron beam can be improved significantly in same dosage of energetic particles. Ion implantation is promising for the compatibilization of PP fiber and matrix with various compound in blends and production of multilayered composites for versatile applications such as laminates and supported compound. (Payamara et al, 2008)

5. Study of surface modification of wool fabrics using low temperature plasma

Owing to the selective modification of wool surface, LTP leads to the formation of new surface groups. Plasma treatment of wool is confined to the fabric surface, leaving the bulk properties unchanged. In this work, plasma was produced by DC glow discharge in a cylindrical glass tube evacuated up to 10^{-3} torr by mechanical pumps. The surface characterization was performed using XRD, FTIR and SEM imaging, so allowing the selection of treatment parameters for reproducible, efficient and stable surface modification. The absorption time were utilized to analyze the result of the treated samples. The changes in these properties are belived to be related closely to the inter-fiber/ inter-yarn frictional force induced by LTP treatment. For sample preparation, size residue and contamination on the fabrics were removed by conventional scouring processes, which the fabrics were washed with 0.5 gl^{-1} sodium carbonate and 0.5 gl^{-1} anionic detergent solution (dilution ratio to water =1:10) at 80^0C for 80 min and then washing was conducted twice with distilled water at 80^0C for 20 min and once at ambient temperature for 10 min. The DC magnetron sputtering reactor has been used to treat the wool fabrics, and non-polymerizing reactive gases, such as O_2, N_2 and Ar were used to modify the wool surface. In the reaction chamber, a sheet of wool fabric was placed on the anode or cathode. Details of samples are shown in Table 1. Before the process started air and old gases had to be pumped out by the vacuum pump, thus almost a vacuum level was created in the reaction chamber. Afterwards, plasma gas was introduced into the reaction chamber. Discharge voltage was 500V, discharge current was 200 mA and the inter-electrode distance was 35 mm. The pressure remained at 0.02 Torr for the entire glow-discharge period.

Sample	Description
No1	Sample was placed on the cathode. Ar gas was used for 7 min
No2	Sample was placed on the cathode. O_2 gas was used for 7 min
No3	Sample was placed on the Anode. O_2 gas was used for 7 min
No4	Sample was placed on the Anode. N_2 gas was used for 7 min

Table 1. Description of samples.

The SEM analysis of surface morphology reveals slight changes which occur on the surface of wool fibers as a result of plasma modification. The rising parameters of LTP treatment (time and power) lead to a slight increase in these changes causing a rounding of scales, microcracks, recesses and tiny grooves, all caused by the etching of the material . SEM micrographs of wool fibers after plasma modification are shown in figure 11. As it can be seen in Figure 11, the scale of samples which were put on the cathode was destroyed more than other samples. It showed that by putting samples on the cathode the rate of etching is increased and it can help to anti felting of wool fibers. For N_2 and O_2 plasma treatment, that, samples that were put on the anode, minimal damage occurs to the scale structure as a result of the glow discharge treatment. The most important effect of LTP treatment of wool is the change in the character of the wool fiber surface from hydrophobic to hydrophilic and anti felt.

For dyeing process, aqueous solutions, containing 3.0 wt. % of the acid dye were employed for dyeing wool fabrics. The bath ratio was 1:100 (1 g of fiber in 100 ml of dye solution). The following dyeing condition was adopted: Initial temperature 40 ^{0C}, followed by a temperature increase of 3 $^{o}Cmin^{-1}$ up to 80 ^{o}C, holding for 30 min at 80 ^{o}C. 5 g/lit of acetic acid for pH adjustment, were added for anionic dyeing processes. After dyeing, the fabrics were rinsed with cold-hot-cold water and then dried at room temperature. As it can be seen in Figures 12, the reflection factor of dyed LTP treated samples was less than dyed untreated sample. The results show that the O_2 and Ar-Cathode plasma treatment are more effective in increasing the dye exhaustion of wool with anionic dye. Furthermore, the colors achieved much more brilliant shades with the LTP treatment.

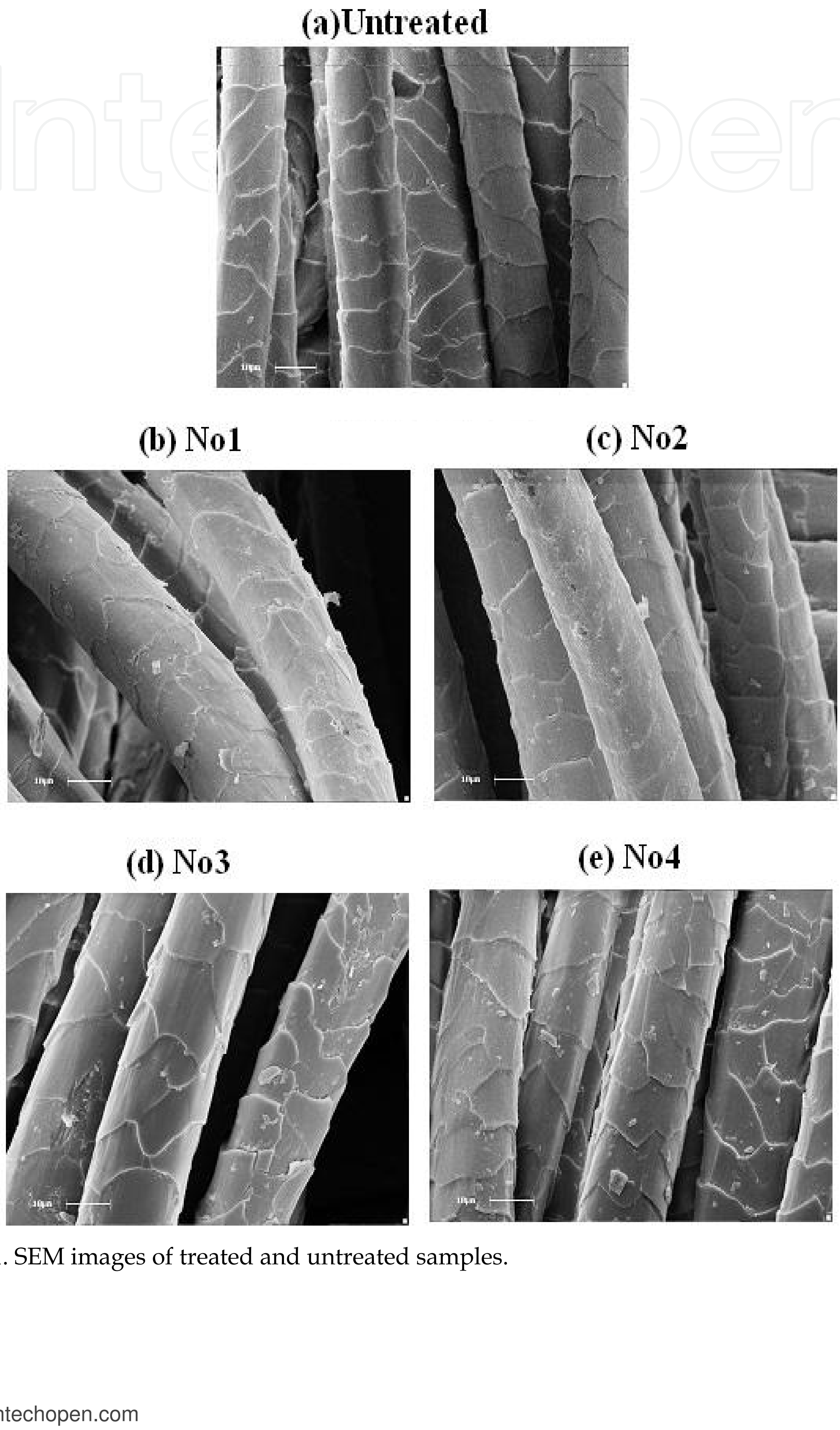


Fig. 11. SEM images of treated and untreated samples.

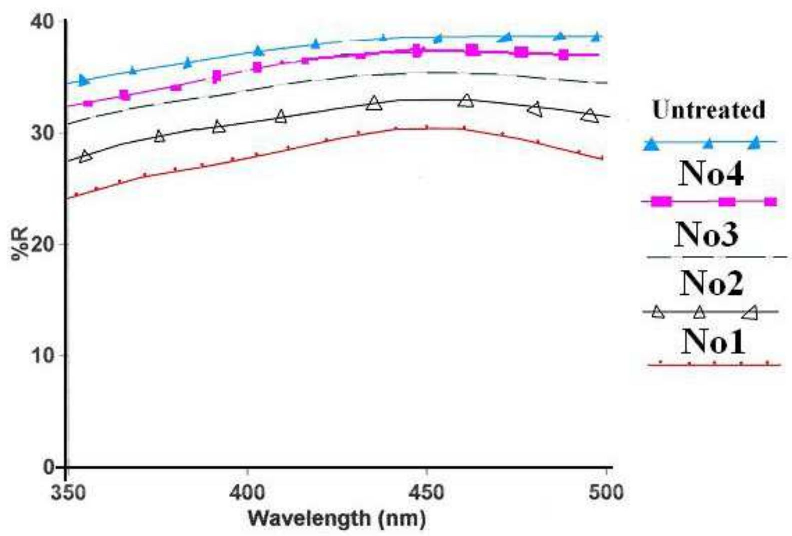


Fig. 12. Reflection spectroscopy of untreated and treated samples.

The quality of water repellency of the samples were evaluated by water drop test in which drops of controlled size were placed at a constant rate upon the fabric surface and the duration of the time required for them to penetrate to the fabrics have been measured. The results are shown in Table 2 in which the absorption times have been recorded for different treated and original samples. As seen after LTP treatment the water absorption time is much decreased. However this time is very low for O_2 –cathode LTP treatment.

Sample	Absorption time
Untreated	20 min
No1	5 sec
No2	1 sec
No3	2 sec
No4	3 sec

Table 2. Absorption time of treated and untreated samples

In this research work, the surface of wool samples were changed both physically and chemically by using LTP treatment. The situation of wool samples in LTP reactor is very important factor. By putting samples on the cathode and using oxygen as a working gas, the wet ability and dye ability of wool samples were increased (Shahidi et al, 2010)

6. Influence of plasma sputtering treatment on natural dyeing and antibacterial activity of wool fabrics

In this paper, the effect of plasma sputtering treatment on the natural dyeing properties of wool and the possibility of substituting it for mordant treatment have been studied. Madder and weld as natural dyes and copper sulfate ($CuSO_4$) as a metal mordant have been used. Also, copper as the electrode material, in a DC magnetron plasma sputtering device was used. The color strength of samples was analyzed using a reflective spectrophotometer and washing and light fastnesses were investigated according to I.S.O. standard recommendations. The results show that, the color strength and fastness of dyed wool samples have been improved after plasma treatment. The antibacterial counting test was also used for determining the antibacterial efficiency of plasma treated and mordanted samples and the durability of antibacterial properties of them was compared. The scoured wool fabric was divided in 2 parts, one was mordanted by copper sulfate, and the other deposited by a plasma sputtering device. The chamber was evacuated to the pressure of 2×10^{-5} torr, using a rotary and also a diffusion pump, and then argon gas was introduced

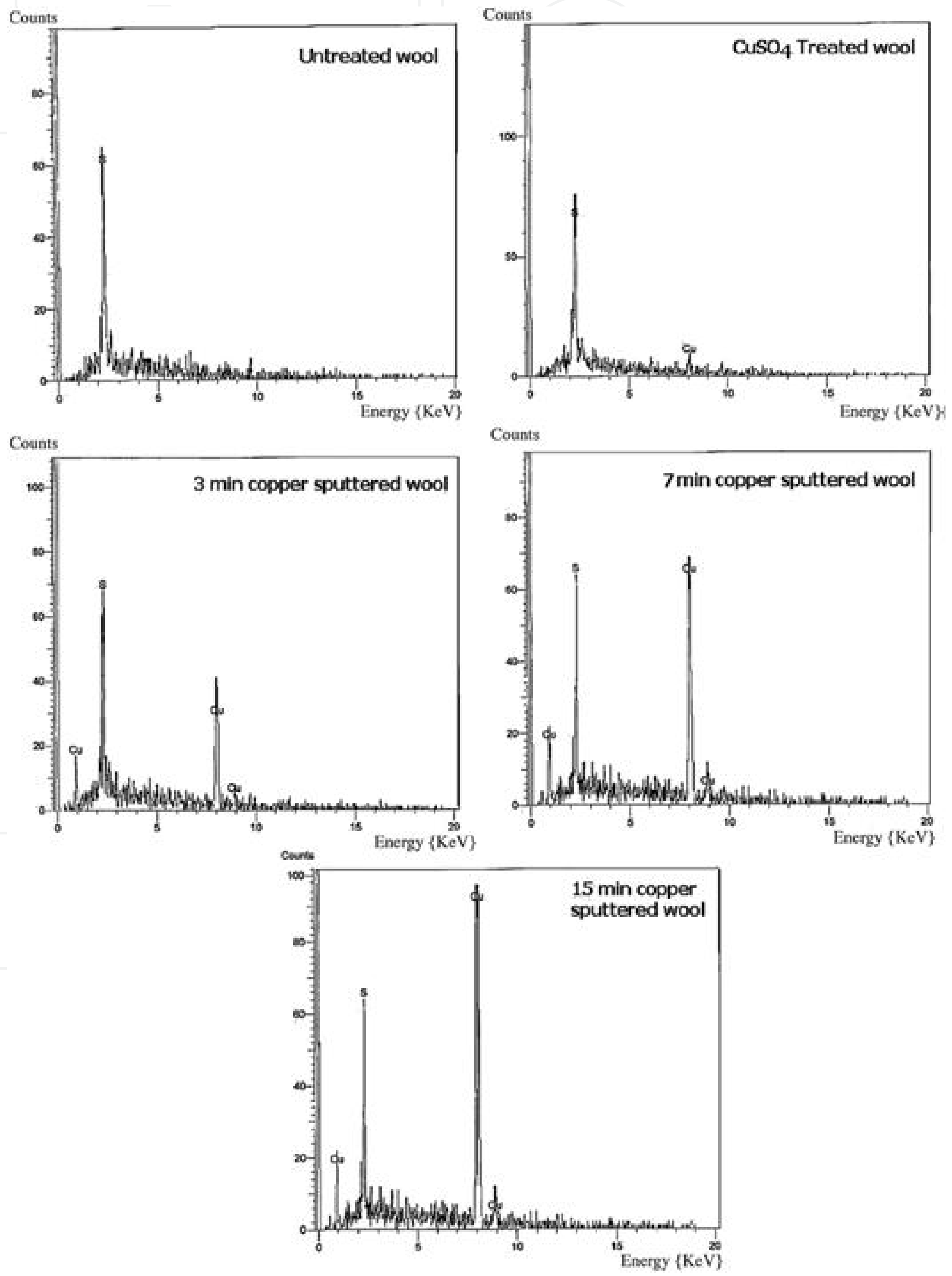


Fig. 13. The EDX results of sputtered wool

into it at a pressure of 2×10^{-2} torr. Voltage was kept at 2000 V and the discharge current was 220 mA. The duration of Cu deposition was 3, 7 and 15 min for different samples. All samples were analyzed using EDX for comparing the amount of copper on the samples. As it is shown in Figure 13, the amount of copper on plasma sputtered samples is more than $CuSO_4$ treated one which demonstrates that in a very short time of plasma sputtering, large amount of copper has covered the surface of the samples. Thus by increasing the time of sputtering, it is possible to increase the amount of copper sputtered on the samples.
After dyeing the samples, the color intensity of them has been measured and compared using a reflective spectroscopy in the range of 400-700 nm. The results are shown in Figure 14 and 15. As it can be seen in Figure 14, the reflection factor for the mordanted sample by

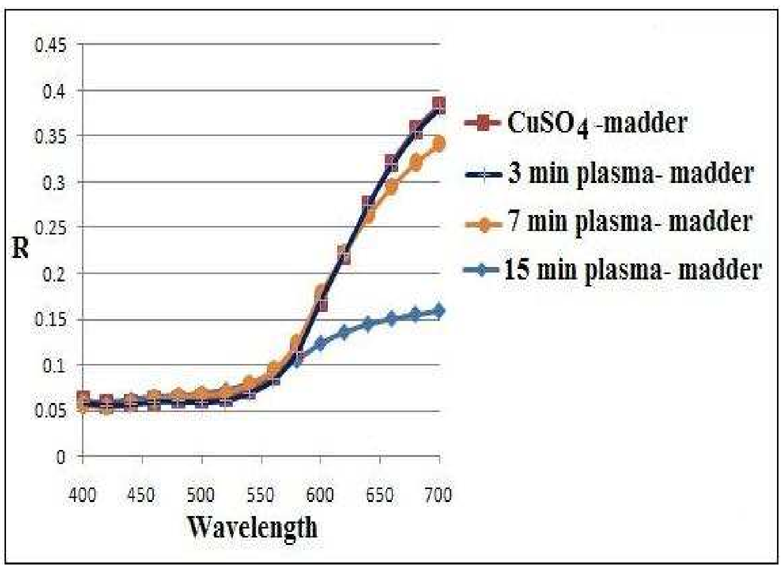


Fig. 14. The Reflection factors of dyed samples with madder

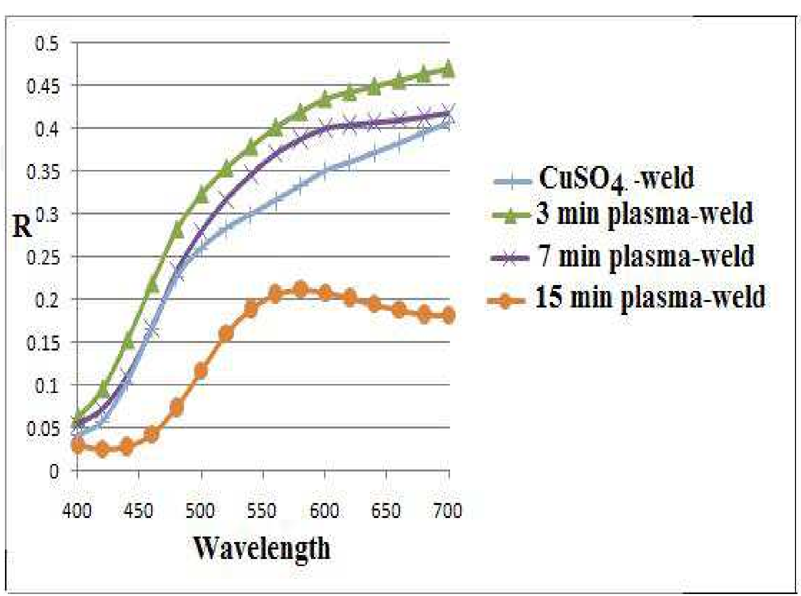


Fig. 15. The reflection factor of dyed samples with weld

$CuSO_4$ when dyed by madder is very close to the Cu-deposited samples with 3 minutes plasma treatment. However in Figure 15 which shows the case of dyeing with weld, the reflection factor of 7 min Cu-sputtered sample is close to the reflection factor of $CuSO_4$ mordanted sample. The K/S values of the samples corresponding to the cases of Figures 14 and 15 are shown in Figures 16, 17 respectively. The Figures show that by choosing a proper condition for sputtering, it is possible to improve the natural dying properties of wool

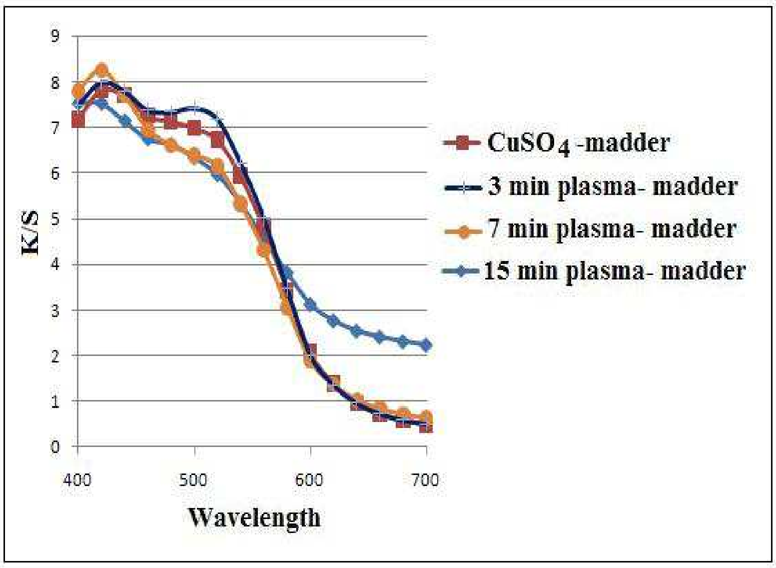


Fig. 16. The K/S values for dyed samples with madder

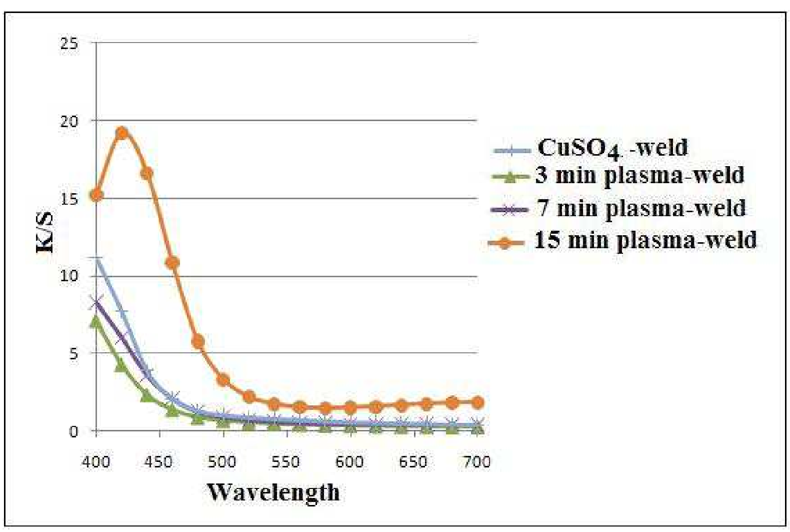


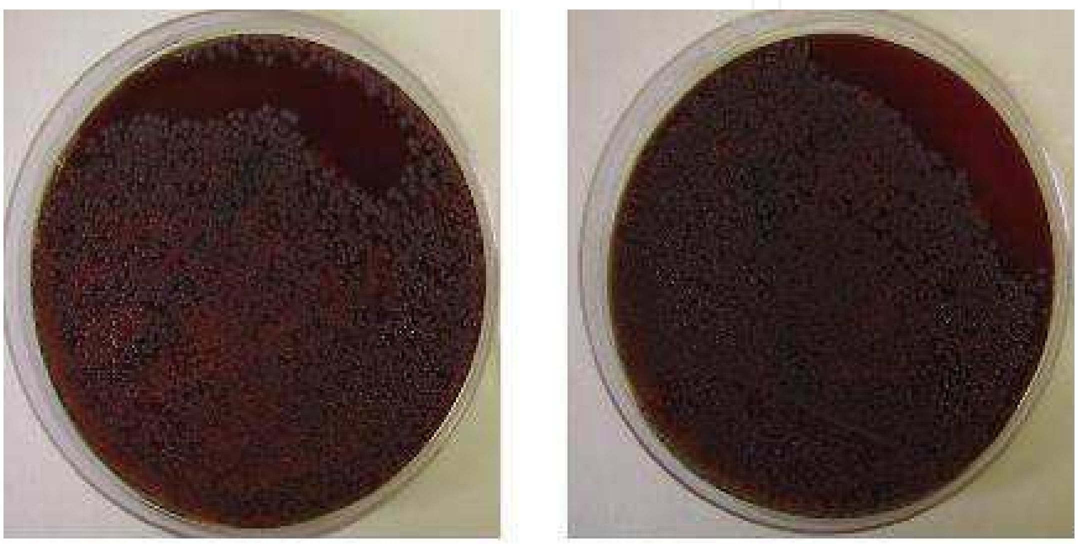
Fig. 17. The K/S values for the dyed samples with weld

As we mentioned before, the durability of dyed wool fabrics has been also evaluated in terms of fastness towards washing and light, using the gray and blue scale according to ISO standard recommendations. The results are shown in Table 3. Assessment of fastness involves a visual determination of either change in shade or staining of an adjacent material and the graduation of the gray tones in the scales is defined as the smallest difference in depth, which is of commercial significance. As shown in Table 3, the fastness properties of the Cu sputtered dyed fabrics are improved and fastness in range between good to excellent has been achieved. As mentioned before, the wash and light fastness of natural dyes are not satisfactory, so many research are carried out for improving these fastnesses. Here it has shown that by using plasma sputtering technique we can dye wool samples by natural dyes easily with very good wash and light fastness. This technique may found many applications in carpet industry as well.

Samples	Wash Fastness	Light Fastness
$CuSO_4$ treated madder dyed wool	4	5-6
3min-coated-madder dyed wool	4	5-6
7min-coated-madder dyed wool	4-5	7-8
15 min-coated-madder dyed wool	4-5	7-8
$CuSO_4$ treated weld dyed wool	3-4	5
3min-coated-weld dyed wool	5	7-8
7min-coated-weld dyed wool	5	7-8
15min- coated-weld dyed wool	5	7-8

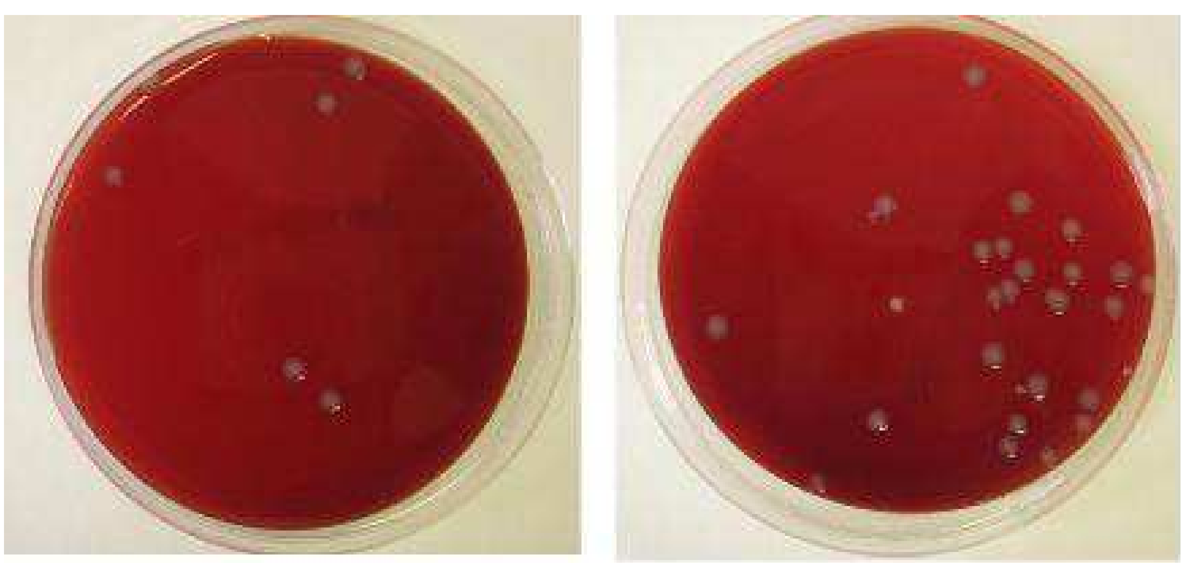
Table 3. The results of wash and light fastness

In another point of view, in recent years, the demand for antibacterial fabrics in domestic and abroad markets has grown significantly because of more awareness of the potential threat of spreading diseases. Bio-protective fabrics such as medical clothes, protective garments, and hygienic textiles are the main application of the antibacterial fibers (Schmidt-Przewozna et al. 2008). Natural textiles such as those made from cellulose and protein fibers are often considered to be more vulnerable to microbe attack than man-made fibers because of their hydrophilic porous structure and moisture transport characteristics. Thus, the use of antibacterial agents to prevent or retard the growth of bacteria is becoming a standard finishing for textile goods. However, conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments) generally use wet-chemical process steps and produce a lot of wastewater. Plasma treatment, on the other hand, is a dry and eco-friendly technology, which offers an attractive alternative to add new functionalities such as water repellence, long-term hydrophilicity, mechanical, electrical and antibacterial properties as well as biocompatibility due to the nano-scaled modification on textiles and fiber. Moreover, the bulk properties as well as the touch of the textiles remain unaffected (Hegemann et al, 2007 ; Yuranova et al, 2003 ; Chen et al, 2008 ; Yu et al, 2003, Park et al, 2008 ; Ghoranneviss et al, 2007). In this paper in addition to investigation about the effect of plasma sputtering and mordant treatment on wool natural dyeing, the antibacterial efficiency of both plasma treated and mordanted samples have been also studied. The tests done to evaluate antibacterial textiles were divided into two types, agar based zone of inhibition tests and bacteria counting tests. The agar culture medium is transparent, when the bacterium is inhibited from growth, a transparent area in the form of a halo around the fabric will be observed. No halo for untreated wool fabrics has been observed. This control test shows that the original fabric does not have any antibacterial property, while the $CusO_4$ treated and Cu-coated samples show very good antibacterial activity. The reason is that the interaction between copper ions and bacteria can change the metabolic activity of bacteria and eventually cause its death. The diameter of the halo is shown in Table 4. As it is shown, coating the samples by Copper has produced an antibacterial effect in it. Figure 18 illustrates the results of counting test for untreated wool sample. As it is seen, too many bacteria are spread over the plate. The results of treated samples are shown in Figure 19. As shown, coating the samples by copper for 7 minutes has significantly decreased the amount of survival bacteria colonies. Similar results were achieved for the rest of the coated samples. We should mention here that the amount of bacteria spread over the agar plate is also decreased for the $CuSO_4$ treated samples. However these process which are done in a wet medium under a long duration, at least 60 minutes [Chen et al, 2008 ; Hong and Sun, 2008 ; Kumar et al, 2005 ; Chen & chiang, 2008], are not comparable with easily obtained treatment through plasma sputtering technique.



E.Coli S.Aureus

Fig. 18. The photo of bacteria spread over the plate in case of untreated wool



S.Aureus E.Coli

Fig. 19. The antibacterial activity of copper coated sample for 7 min.

Samples before dyeing	Counting test (Reduction percentage of bacteria), S.Aureus	Counting test (Reduction percentage of bacteria), E.coli	Inhibition zone, S.Aureus	Inhibition zone, E.coli
$CuSO_4$ treated wool	99.4	99.4	4 mm	4 mm
3 min copper sputtered wool	99.5	99.5	4 mm	4 mm
7 min copper sputtered wool	99.5	99.5	4 mm	4 mm
15 min copper sputtered wool	99.6	99.5	4 mm	4 mm

Table 4. The antibacterial activity of the treated samples before dyeing

So by Cu-sputtering , not only the wool fabrics could be dyed easily in a short time without need to any wet medium , but also they could gain very good antibacterial properties. The results show that, the sputtering has improved the natural dying properties of wool fabrics. It has also improved the wool resistance to washing and light. The dyed treated samples have also gained very good antibacterial properties (Shahidi et al, 2011).

7. Conclusion

As has been demonstrated, plasma treatments of textiles look very promising. They can be used both in substitution of conventional processes and for the production of innovative textile materials with properties that cannot be achieved via wet processing. They are applicable, in principle, to all substrates, even to those that cannot be modified by conventional methods. In general, no significant alteration of bulk properties is produced.

They are fast and extremely gentle, as well as environmentally friendly, being dry processes characterised by low consumption of chemicals and energy. When they cannot replace an existing wet process (dyeing and some finishing), if used as pre-treatments, they can reduce markedly the amount of chemicals required by the process and the concentration of pollutants in the effluents.

The great advances of the last decades in the field of the science of materials are now ready to enter into the field of textiles and it is already possible to envisage that, in the next ten years, the clothing–textile industry will undergo a dramatic revolution. Smart textiles, completely new fibres (nanofibres, etc.), and new textile applications in unexpected fields can be expected. Also, our way to consider clothing is going to change completely. Environmental aspects are going to play a more and more important role. Under these perspectives, plasma processes are certainly going to supersede many traditional finishing processes.

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