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Improvements of Surface Functionality of Cotton Fibers by Atmospheric Plasma Treatment

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Abstract: This study aims to investigate the viability of atmospheric plasma treatment over raw cotton fabric surfaces as an alternative method for superseding the wet textile pre-treatment processes. For this purpose, the fabric samples were treated with air plasma and argon atmospheric plasma. Thereafter, the hydrophilicity and the wickability of plasma treated samples increased, and also the contact angles decreased significantly. Chemical changes were analyzed by FTIR-ATR and XPS. Morphological changes were observed by SEM. The results were inspected for assessing to what extent the replacement might be achieved by inducing this surface modification method.

Keywords: Atmospheric plasma, Air plasma, Argon plasma, Surface modification, Cotton

Introduction

Cotton is mainly composed of cellulose with some non-cellulosic components. These non-cellulosic components are waxes, pectin and some proteins, and they are mainly found in the cuticle layer and the primary wall which are the outermost layers of the cotton fiber. These hydrophobic impurities, especially cotton wax, affect the uptake of dyeing and finishing solutions. To remove these impurities from the cotton surface, certain chemical methods are used in the textile industry. These conventional methods are energy-consuming processes with negative environmental impact [1]. In this concern, many alternative environmentally friendly methods were developed. Plasma treatment is one of those methods and can be used as an effective technique for modifying the surface properties of cotton fabric without altering the interior part of the fiber [2-4].

Plasma is generated when a gas is exposed to an electro-magnetic field at low pressure and near ambient temperature. The chemistry of the plasma takes place in non-equilibrium conditions [5]. Plasmas can be classified as low pressure and atmospheric plasmas. Both plasmas can be used for surface modification of materials. Vacuum systems are time-, space-, and energy-consuming processes, and some material properties, such as thickness and size, are highly dependent on the dimension of the device and, in addition, the process is not a continuous one. On the other hand, atmospheric plasma can be generated under atmospheric conditions and does not require vacuum systems with continuous and open perimeter fabric flow [6]. The efficiency of plasma treatments depend on treatment conditions of time, pressure, power and gas. The species that participate in plasma reactions, such as excited atoms, free radicals and metastable particles, electrons and ions, can interact either physically or chemically with substrates [7].

Numerous researches have been carried out to improve wettability, water repellency and soil releasing property of textile fibers and fabrics by using plasma technology [8-11]. Additionally, modifications of conventional dyeing, printing and finishing properties have been achieved by plasma treatment methods. However, low-pressure plasma was used in most of the studies. In this study, the effects of air and argon atmospheric plasma treatments on the functionality of cotton fabrics were investigated.

The wet processes in textile finishing unfortunately require great amounts of water. This requisite leads enormous energy consumption along with the pollution of subterranean water with wastewater as well as thermal pollution. Therefore the main purposes of this study are to investigate the potential of viability of the atmospheric plasma methods for reducing energy consumption and water pollution as being an alternative method i.e. replacement of wet textile pre-treatment processes.

Experimental

Materials

In this study, 100 % raw cotton fabric, plain weave, 153 g/m^2, 45 ends cm^{-1}, 26 picks cm^{-1} samples were used.

Atmospheric Plasma Treatments

For plasma treatment, a dielectric barrier discharge (DBD) atmospheric plasma device was used [12]. The samples were placed between the electrodes and the distance between the electrodes was 0.2 cm. In all treatments, air and argon were used as the processing gas with the power of 50, 100, 130 watts with different time intervals, namely 20, 40 and 60 seconds.

Characterization Techniques

The hydrophilicity (absorbency) of fabrics was measured according to AATCC 79-1995 standard. In this standard, a drop of water was allowed to fall from a fixed height onto

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*Corresponding author: esen.ozdogan@ege.edu.tr the taut surface of a test specimen. The time required for the specular reflection of the water drop to disappear was measured and recorded as wetting time.

The vertical wicking test was applied to DIN 53924 standard to the samples with distilled water. Samples were cut as 3×25 cm pieces and poured into water of 1 cm depth. After 60 minutes, the wicking height was measured. The outcomes of the test demonstrated wicking length of a vertically positioned sample as a function of treatment time and applied power.

Contact angles were measured by using a goniometric system, which was composed of a microliter syringe for dosing the liquids, and an optical system combined with VHS video recorder, along with a computer for data analysis. To measure the contact angle, 0.1 m*l* of deionized water droplet mounted with a micrometer pipette was placed on the surface of the cotton fabric, and the computer software supplied with the equipment was used for obtaining a photograph of the image. The droplets position after 3 seconds was manually captured with the aid of the software, and the computer program calculated the two angles of contact at the water/air/solid interface and gave the arithmetical mean.

To measure the kinetic friction coefficient of the fabric surface, the Frictorq instrument was used as described by Lima *et al*. [13].

The Infra-red (IR) spectra of cotton fabrics were measured on a Perkin Elmer 100 FTIR spectrometer in ATR reflection mode by using a diamond/zinc selenide crystal. To ensure reproducible contact between the crystal faces and the fabric, a pressure of 80 kPa was applied to the crystal holder with the aid of a calibrated torque screw driver. An average of 15 scans was taken with a resolution of 4 cm^{-1}.

X-ray photoelectron spectroscopy was employed to monitor the modifications produced over the outermost (5-10 nm) cotton fiber surface. In our studies, the measurement depth was 7 nm. The cotton fabric samples were analyzed using SPCS XPS system with a Mg K_α X-ray source operated at 10 kV and 200 W. The pressure inside analysis chamber was 10^{-8} to 10^{-9} torr. Survey scans were taken with a passing energy of 48 eV. The peak positions were corrected for charging relative to the C-C bond which was assigned a binding energy of 284.5 eV.

For surface observation, the changes in the fabric surface were evaluated using scanning electron microscopy (SEM). SEM observations were performed with a Phillips XL-30S FEG scanning electron microscope.

Results and Discussion

Absorbency

Plasma treatments improved the hydrophilicity of cotton fabrics [14]. Etching by atmospheric plasma treatment destroyed the hydrophobic layer partially and as a result of this, the hydrophilicity increased. As can be seen from Table 1, the improvement of hydrophilicity depended on the duration, power and the type of the plasma treatment. As Table 1 reveals, the argon plasma was more effective than the air plasma. This could be attributed to the significant etching affect of the noble gas [15].

Table 1. Hydrophilicity outcomes (sec.)

Treatment	Air plasma	Argon plasma
Untreated	Hydrophobic	
50 W, 20 sec.	Hydrophobic	5
50 W, 40 sec.	Hydrophobic	1.2
50 W, 60 sec.	Hydrophobic	1
100 W, 20 sec.	8.6	1
100 W, 40 sec.	4.7	1
100 W, 60 sec.	3.5	1
130 W, 20 sec.	7.7	1
130 W, 40 sec.	1.4	1
130 W, 60 sec.	1	1

Table 2. Contact angles (°)

Treatment	Air plasma	Argon plasma
Untreated	107.83	
50 W, 20 sec.	105.33	41.74
50 W, 40 sec.	103.41	0
50 W, 60 sec.	98.32	0
100 W, 20 sec.	71.72	0
100 W, 40 sec.	46.12	0
100 W, 60 sec.	32.82	0
130 W, 20 sec.	59.3	0
130 W, 40 sec.	0	0
130 W, 60 sec.	0	0

Partial decomposition of the hydrophobic layer by atmospheric plasma caused the formation of new hydrophilic groups on the surface which increased the value of surface energy and therefore the contact angles decreased [14]. When the air plasma was used, contact angles decreased gradually along with intensifying the plasma treatment in terms of exposure time and applied power. On the other hand, at 50 W for 40 sec. argon plasma exposure was enough to decrease the contact angle to 0 º. Figure 1 depicts these issues overtly. Figure 1 depicts these issues overtly. Further treatments were not necessary. As seen in Table 2, the argon plasma was more effective than the air plasma, consistent with the hydrophilicity outcomes.

Figure 1. Contact angle images of (a) untreated fabric, (b) fabrics treated with air plasma under 130 W for 60 sec, and (c) treated with argon plasma under 130 W for 60 sec.

Table 3. Wicking height (cm)

Treatment	Air plasma	Argon plasma
Untreated	0	
50 W, 20 sec.	0.1	0.8
50 W, 40 sec.	0.2	4.6
50 W, 60 sec.	0.3	5.5
100 W, 20 sec.	2.2	7.1
100 W, 40 sec.	4.3	7.8
100 W, 60 sec.	4.8	9.0
130 W, 20 sec.	3.9	7.2
130 W, 40 sec.	7.8	8.4
130 W, 60 sec.	8.0	9.2

As could be seen from the outcomes of the Table 3, plasma treatments improved the wickability of raw cotton fabrics [14]. The wicking height increased remarkably as hydrophilicity and the contact angle values, but the difference between two plasmas could be seen more clearly from wicking results. In Tables 2 and 3, it could be seen that the 130 W treatments for 60 sec. had the same hydrophilicity and contact angle values, but the wicking heights were higher with argon gas. This was probably caused by the etching effect of argon gas. As stated before, noble gasses have higher etching tendency. As could be seen from SEM pictures, modification of the surface by argon plasma was more effective than the air plasma. The cracks formed on the surface were the cause of the decrease of capillary pressure which improved the wickability [16].

Wicking results gave comparatively more extensive information about the surface modification phenomenon than hydrophilicity and contact angle measurement. It also revealed homogeneity of the treatment [17]. If the treatment induced a homogenous structure, then the wicking tendency would be similar in every part of the fabric. We observed homogenous wickability on the higher power and longer exposure times of induced samples.

FTIR/ATR Analysis

FT-IR ATR is a simple method which is utilized to characterize the waxes and other impurities of cellulose located in the outermost layer of cotton fibers [18]. Characteristic bands related to the chemical structure of cellulose were the hydrogen bonded OH stretching at 3550-3100 cm^{-1}, the CH stretching at 2900 cm^{-1}, and the CH wagging at 1315 cm^{-1} [18-20]. FTIR-ATR spectra of all untreated and treated fabrics showed these bands but there were some distinct peaks at 2943 cm^{-1}, 1737 cm^{-1}, C-H stretching region at 2800-3000 cm^{-1} was related with the amount of waxes left on the fabric. Waxes were mixtures of hydrocarbons, alcohols, esters and free acids which have long alkyl chains [18]. A new peak formed at 2943 cm^{-1}, as seen on Figure 2(b), which was symmetric CH_2 stretching (long alkyl chain), which might be attributed to a partial decomposition of waxes caused by the atmospheric plasma treatment.

Peaks around 1735 cm^{-1} were indicators of pectic polysaccharides and represented the ester groups of pectin [21]. The wax components were believed to be located in the primary cell wall with the highest concentration at the surface, and to be closely connected with the pectic substances [22]. A broad band at 1737 cm^{-1}, apparent on Figure 2(a), for the argon plasma might correspond to pectic substances under the waxy layer which became more detectable after argon

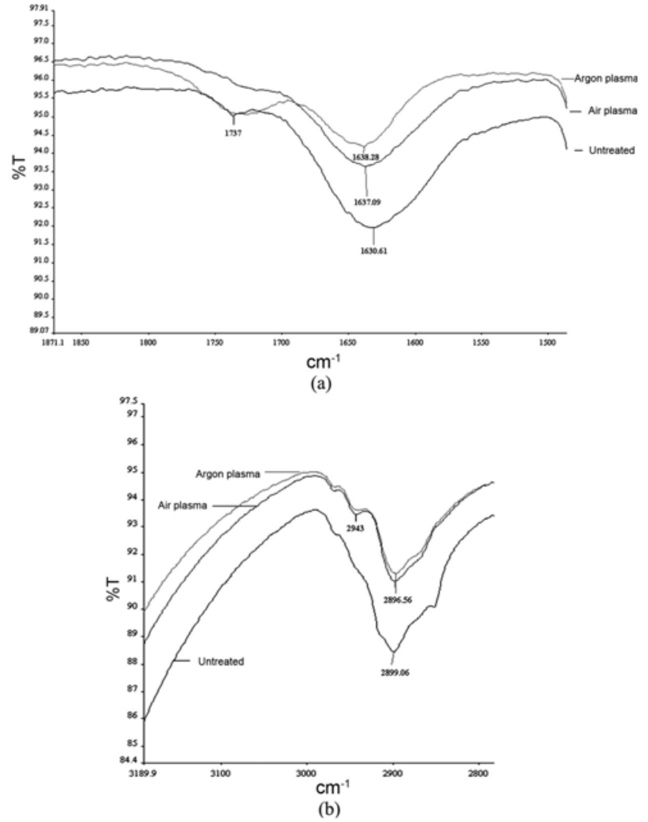

Figure 2. FTIR-ATR spectra of untreated, air plasma treated and argon plasma treated cotton fabrics at (a) 1871-1500 cm^{-1} and (b) 3189-2800 cm^{-1}.

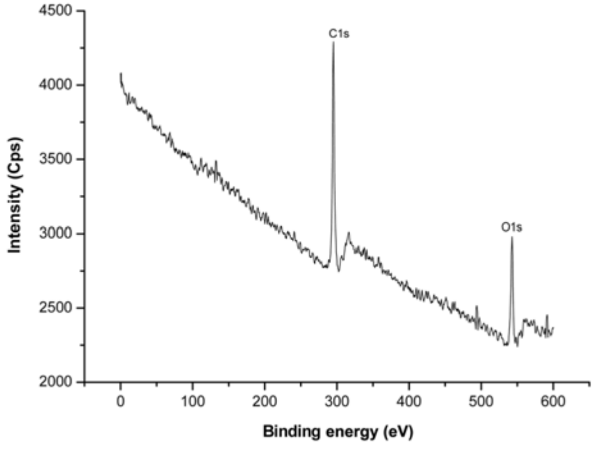

Figure 3. XPS survey scan of untreated cotton fabric.

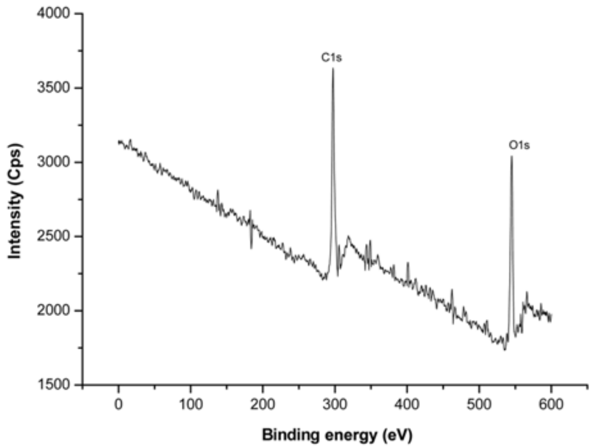

Figure 4. XPS survey scan of air plasma treated cotton fabric.

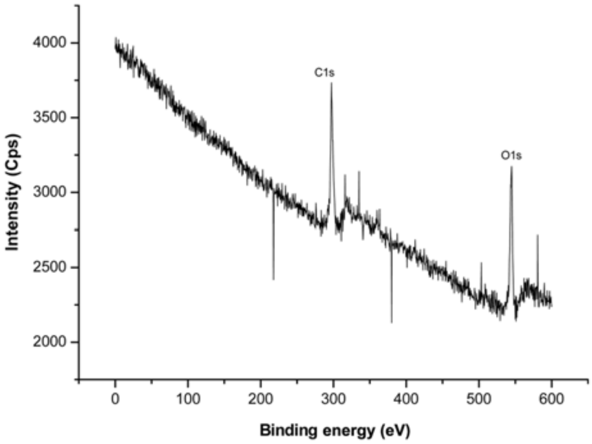

Figure 5. XPS survey scan of argon plasma treated cotton fabric.

Table 4. Chemical composition of the untreated the air plasma treated and the argon plasma treated cotton fabrics

Treatment	C	O	O/C
Untreated	81.9	17.1	0.208
130 W, 60 sec, air plasma	75.6	24.4	0.322
130 W, 60 sec, argon plasma	73.3	26.7	0.364

plasma etching.

A peak around 1640 cm^{-1} was due to the absorbed water [18]. During the treatment the water molecules in the structure of the cotton were evaporated and this tended to increase the transmittance of cotton fiber [23]. This could be observed over the spectrum clearly.

XPS Analysis

Due to the chemical effects of the plasma species, new functional groups occurred which caused various changes over the surface composition. It could be seen from Figure 3, 4, 5 and from Table 4 that the carbon content was significantly reduced from 81.9 to 75.6 with the air plasma treatment, and from 81.9 to 73.3 with the argon plasma treatment. This reduction evolved most probably due to the etching effect of the atmospheric plasma treatment.

The intensity of the oxygen peaks of the argon and the air plasma treated surfaces were significantly much stronger than the peaks of the untreated surfaces. The oxygen content increased from 17.1 to 24.4 with the air plasma treatment and to 26.7 with the argon plasma treatment. The O/C ratio of samples increased from 0.208 to 0.322 with the air plasma treatment and to 0.364 with the argon plasma treatment. These changes could be attributed to radical formations by bond breakage between C_1 and ring oxygen; C_1 and glycoside bond oxygen, dehydrogeneration and dehydroxylation between C_2 and C_3 after the ring opening of anhydroglucose of cellulose chains [24-27].

The increased amount of oxygen caused an improvement of the hydrophility and wickability and also a decrease in the contact angles of the cotton fibers, suggesting that the argon plasma was being more effective than the air plasma.

SEM Analysis

In order to observe topographical changes, SEM observa-

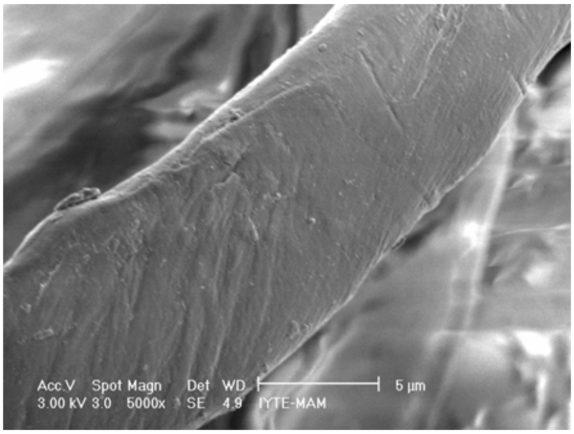

Figure 6. SEM photograph of untreated cotton sample.

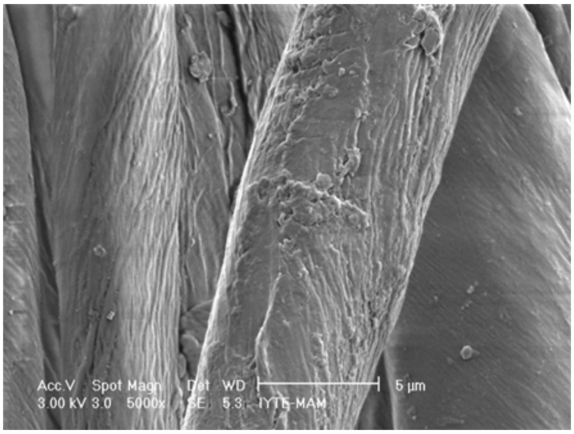

Figure 7. SEM photograph of air plasma treated cotton sample under 130 W for 60 sec.

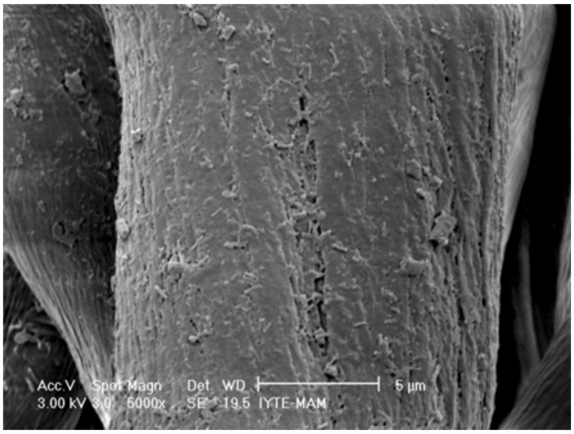

Figure 8. SEM photograph of argon plasma treated cotton sample under 130 W for 60 sec.

Table 5. Friction coefficients of cotton fabrics (μkin)

Treatment	Air plasma	Argon plasma
Untreated	0.2114	
50 W, 20 sec.	0.214	0.2149
50 W, 40 sec.	0.2202	0.2209
50 W, 60 sec.	0.2236	0.2249
100 W, 20 sec.	0.2209	0.2227
100 W, 40 sec.	0.2279	0.2286
100 W, 60 sec.	0.2296	0.2328
130 W, 20 sec.	0.2252	0.2259
130 W, 40 sec.	0.2374	0.2405
130 W 60 sec.	0.2381	0.2415

tions were made. Atmospheric pressure plasma treatment causes micro cracks and tiny grooves, which happened to be formed due to the etching of the materials. Figures 6, 7 and 8 displayed the depth of surface appearances of the untreated and the treated cotton samples.

The surface appearance of an untreated cotton fiber was examined by the SEM. It could be observed that the untreated cotton fiber had a smoother surface. The micro cracks and groves that formed by the etching effect of plasma treatment were clearly visible over the picture. The argon plasma was apparently more effective than air plasma. The argon plasma treated cotton fiber contained more amount of groves than the air plasma treated one because of the higher etching tendency of argon gas [15]. These images did not present a consistent scheme with the surface friction coefficient properties. Surface friction coefficient values of cotton fabrics were given in the Table 5. As it might be easily noticed, after the plasma treatment, the values tended to increase with the prolonged treatment duration and with the increased power, because of the etching effect of the atmospheric plasma [28,29]. Although the quantity of this increase was not substantially large, the obtained outcomes were quite consistent and could be justified with the nature of the plasma interaction because it affected the surface not more than 1000 Å [2-4].

Conclusion

Atmospheric plasma treatment could modify the surface of cotton fabrics to some extent. The primary aim of this study was to investigate the effects of atmospheric plasma on the raw cotton fabrics. The hydrophilicity and the wickability of plasma treated samples increased, and also the contact angles decreased significantly. This modified structure was achieved by the enhancement of the surface modification as depicted in FTIR-ATR, XPS pictures. As the friction and SEM outcomes suggested, the atmospheric plasma treatment made the surface structure into a rougher state because of the etching effect. In other words, the atmospheric plasma treatment had the potential of influencing not only the chemical properties but also the physical properties of the raw cotton fibers. The argon plasma treatment was a more effective mean than the air plasma treatment.

Plasma treatment can be used as an effective technique for cotton pre-treatment with the advantages of extremely short treatment time and low application temperature without the necessity of any chemical substance, water consumption and without imposing any alteration in the interior part of the fiber.

The atmospheric plasma method may evolve as a partially substitutional method for superseding the wet pre-treatment processes. It does not necessarily constitute a total replacement. However, it may overlap a segment within the spectrum at least for dark color shades. With combination of other viable methods, the magnitude of this segment has prospect for expansion. Severe environmental impact of conventional wet textile pre-treatment processes might be alleviated to some extent, perhaps not for great extent with the present technology.

This research attempted to make a small contribution towards achieving less energy demanding, clean and dry textile finishing processes. But the reader should be cautioned that this research was carried on merely at the laboratory scale. For the mass production, a different set up and approach would be necessary in future.

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