Ecological Materials and Methods in the Textile Industry: Atmospheric-Plasma Treatments of Naturally Colored Cotton

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ABSTRACT: Naturally colored cotton, in accordance with currently increasing interest in ecological textile products and methods, has increased in popularity. Commerce is another of the primary reasons along with interest in environmentally friendly and niche-concept approaches. However, the color palette is limited; no bleaching or dyeing process is used. Instead, only a pretreatment to make the fibers hydrophilic is necessary. This can be induced with several different methods. In this respect, atmospheric-plasma treatments have emerged as an alternative. In this study, knitted and naturally colored cotton fabrics were treated with argon and air atmospheric plasma. The hydrophilicity, wickability, surface friction coefficient, air permeability, water vapor permeability, thermal conductivity, thermal resistance, and fastness were investigated. The surfaces of untreated and plasma-treated fabrics were analyzed with Fourier transform infrared/attenuated total reflectance and scanning electron microscopy to detect and compare the chemical and morphological modifications. The results revealed that atmospheric-plasma treatments are capable of modifying the surface of naturally colored cotton fabrics without any important loss in the color strength or fastness and thermal properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1410–1416, 2011

Key words: FTIR; plasma polymerization; thermal properties

INTRODUCTION

Natural fibers, especially cotton, are very important for achieving environmentally friendly textile production.[1] Demonstrations of tolerable production performance have spawned a niche market among the environmentally conscious who desire reduced usage of man-made chemicals such as dyestuffs.[2,3] In this respect, naturally colored cotton has recently emerged as an attractive material. Naturally colored cotton is not a new phenomenon; actually, it has been around the world for 5000 years. Especially in the last 15 years, naturally colored cotton has gained the interest of commerce instead of being a mere curiosity. In the preceding years, the yields of naturally colored cotton were low, and the fibers were too short to be machine-spun. In 1988, commercially available naturally colored cotton with sufficient quality for spinning appeared on the market, but the amount was extremely limited.[4–6]

Naturally colored cotton has the same structure as ordinary cotton. The only difference between the two species is the pigmentation, which is lodged at the center of the lumen of naturally colored cotton fibers.[7] The color shade is most likely the product of a variety of pigments that are bound to cellulose by sugar-related links along with lignins, tannins, and other noncellulosic material.[8]

As previously mentioned, naturally colored cotton is mainly composed of cellulose along with some noncellulosic components, just like ordinary cotton. These noncellulosic components (wax, pectin, and protein) are mainly found in the cuticle layer and in the primary wall, which are the outermost layers of naturally colored cotton fibers. These hydrophobic impurities (especially cotton wax) affect the hydrophilicity of the fibers. To remove these impurities from the natural cotton surface, several chemical or biochemical methods can be implemented. However, these methods should not adversely affect the color or bulk properties of the fibers. The energy requirements, water consumption, and environmental impact are important in terms of the concept of environmentally friendly processes. In this respect, atmospheric-plasma treatment is an important alternative for rendering fibers hydrophilic. Plasma treatment can be implemented as an effective technique for modifying the surface properties of naturally colored cotton fabrics without modifying the interior of the fibers.[9,10]

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Plasmas can be classified according to their temperature and pressure intensities. Cold plasmas (near the ambient temperature) are some of the most implemented types in industrial applications. Plasmas can be classified according to pressure as low and atmospheric plasmas. Both plasma types can be used to induce surface modifications to achieve cleaning, surface activation, surface etching, crosslinking, chain scission, oxidation, grafting, and deposition effects on materials. The two types yield similar effects, but atmospheric plasma has many advantages over vacuum plasma. Atmospheric plasma can be generated under atmospheric conditions and requires no vacuum systems for continuous and open perimeter fabric flow.[11,12]

In this study, fabrics made from organically cultivated, naturally colored cotton fibers from the Aegean region of Turkey were used. These fibers were registered under the trademark Emirel in April 2009. Instead of conventional chemical treatments, the naturally colored cotton fabrics were treated with ecological methods (i.e., air and argon atmospheric-plasma processes) to improve their hydrophilicity and functional properties.

EXPERIMENTAL

Materials

In this study, Ne 30 yarn spun from dark brown, naturally colored cotton fibers used for knitting interlock fabric constructs (unit weight = 275 g/m^2) was used.

Atmospheric-plasma treatments

In this study, a dielectric-barrier discharge atmospheric-plasma device was used.[13] The samples were inserted between electrodes placed 0.2 cm apart from each other. Air and argon were used as process gases for each treatment at powers of 50, 100, and 130 W with time intervals of 20, 40, and 60 s.

Characterization methods

The color intensities of the naturally colored cotton fabric samples were measured with a HunterLab ColorQuest II (Hunter Associates Laboratory, Inc. Reston, VA) spectrophotometer over the wavelength range of 390–700 nm. In a typical test, reflectance (R) values were measured, and the relative values of the color strength (K/S; K and S are the absorption and scattering coefficients, respectively) were then evaluated according to the Kubelka–Munk equation:

$$K/S = [(1-R)^2/2R]$$

The washing, light, and rubbing fastness properties were evaluated in accordance with the standard test methods of the American Association for Textile Chemists and Colorists.[14,15]

A vertical wicking test was applied to the samples in distilled water. Samples were cut to 3 × 25 cm^2 and immersed in distilled water 1 cm deep. The wicking height was measured after 30 min. The wicking length in a vertically positioned sample displayed an indication for hydrophilicity: the longer, the better.

A Frictorq instrument (Minho University, Portugal) was used for measuring the kinetic friction coefficients of the surfaces of the fabric samples, as described by Lima et al.[16]

Pilling tests were carried out with a Martindale wear and pilling tester (James Heal, England) according to ISO Standard 12945-2 with the usual five-grade scale.

The thermal conductivity and thermal resistance were measured with an Alambeta device (Sensora-Check Republic) from Hes.[17]

The relative water vapor permeability was measured on a Permetest instrument (Sensora, Check Republic) in accordance with ISO Standard 11092.[18]

The air permeability values of the treated samples were measured according to EN ISO Standard 9237 with an FX 3300 (Textest, Switzerland) air permeability tester.

Scanning electron microscopy (SEM) was implemented to inspect possible modifications on the fabric surface. SEM photographs were taken with a Phillips XL-30S FEG scanning electron microscope (EES EQUIPMENT EXCHANGE & SERVICE GmbH Überlingen, Germany). Gold was sputtered over the fabric samples, which were mounted in the vacuum medium before observation.

The IR spectra of the cotton fabrics were measured with a PerkinElmer 100 (Perkin Elmer Inc. Shelton, CT) Fourier transform infrared (FTIR) spectrometer in the attenuated total reflectance (ATR) reflection mode with 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 screwdriver. Ten scans were taken on average with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

K/S values

No significant changes were observed in the measured K/S values of the samples after the atmospheric-plasma treatments. The reason was most likely the nature of the plasma treatment, which did not penetrate beyond the location of the color pigments in the structure of the fibers because the pigmentation of naturally colored cotton is lodged around the center or lumen of the fibers.[7] Another explanation might be that the range of plasma effects was not more than 1000 Å[2–4] through the surface, so

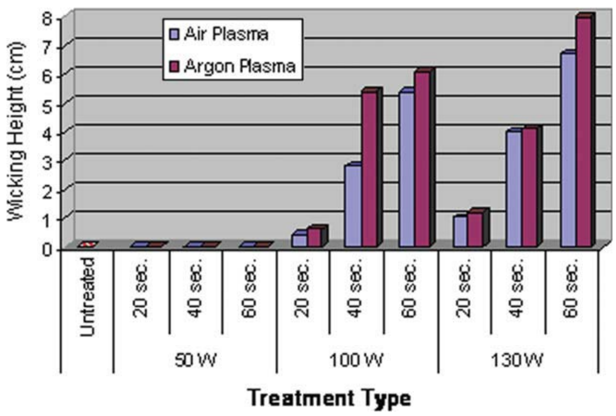

Figure 1 Wicking results for the samples treated with atmospheric plasma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the partial decomposition of the hydrophobic layer did not affect the K/S values of the samples.[10,19]

Fastness values

The color fastness versus washing and dry and wet rubbing was compared for untreated and plasma-treated fabric samples. The outcomes of testing of color fastness versus washing revealed staining and color change values in the range of 4–5. The outcomes of testing of fastness versus dry and wet rubbing revealed similar values of staining (ranging from 4 to 5 for dry rubbing and from 3 to 4 for wet rubbing) for all fabric samples. The outcomes of light-fastness testing of the treated and untreated fabric samples did not differ significantly and were rated within the range of 5.5–6. Both air-plasma and argon-plasma treatments yielded similar values, including the values of all the fastness tests.

Wicking

Wetting and wicking properties are very important during the processing and overall application of fibrous materials. Wicking occurs when a fabric is completely or partially immersed into a liquid or is in contact with a limited amount of a liquid, such as a drop placed on fabric (Fig. 1).[20]

The plasma-treated fibers showed surface roughness in SEM photomicrographs (Fig. 4) that resulted from chemical reactions and microetching on the fiber surface. The cracks that formed on the surface were the cause of the decrease in the capillary pressure, which improved the wickability. However, surface roughness was not the primary reason for the improved wettability but may have increased it. The atmospheric-plasma treatment could increase the downward wicking rate under all treatment conditions. The downward wicking method is more suitable for distinguishing the effects of plasma treatments under various conditions.[20,21]

As mentioned previously, plasma treatment causes mainly chemical modifications and increases wetting and adhesion properties. The results revealed that the atmospheric-plasma treatments improved the hydrophilicity and wickability properties of the samples. The etching effect of the treatment should have made a great contribution to these improvements. Partial decomposition of the hydrophobic layer by atmospheric plasma caused new hydrophilic groups to form on the surface, which increased the value of the surface energy and made the fiber more wettable.[22]

Wicking results provide information about surface modification with respect to hydrophilicity measurements. They also show the homogeneity of the treatment.[23] If the treatment is homogeneous, the wicking tendency is similar in every part of the fabric. At higher powers and with longer exposure times, homogeneous wickability was observed. Besides this, differences between the two plasmas could be seen clearly from the wicking measurements. In general, samples treated with argon gas (130 W at 60 s) had higher hydrophilicity and wicking values than samples treated with argon plasma (Fig. 1). This was probably caused by the dominant etching effect of argon gas. As is known, noble gases have a higher etching tendency.[24]

Thermophysiological comfort properties

Comfort, which is defined as "the absence of displeasure or discomfort" or "a neutral state compared to the more active state of pleasure," has become one of the most important features along with the recent developments of textile technology.[25] A garment is expected to help to protect the thermal balance of the body and to maintain the body temperature and humidity.[26]

Plasma treatment has the ability to modify the surface structure of fibers. Thus, the occurrence of various enhancements related to the comfort properties of fabrics can also be assumed. In this study, we aimed to explore the effects of plasma treatment on the comfort properties of naturally colored cotton fabric, which is a relatively novel topic. Thus, the thermal conductivity, thermal resistance, relative water-vapor permeability, and air permeability of the fabric samples were investigated.

Thermal conductivity and thermal resistance

The thermal resistance and conductivity values of the samples are given in Table I. As the thermal resistance increased, the thermal conductivity decreased gradually in accordance with the power and exposure time of the treatment. In other words, plasma-treated fabrics delivered better insulation

TABLE I
Thermal Resistance and Conductivity of the Samples

	Thermal resistance (m^2 K/W)		Thermal conductivity (W m^{-1} K^{-1})	
Treatment	Air plasma	Argon plasma	Air plasma	Argon plasma
Untreated	0.01284		0.04474	
50 W for 20 s	0.01352	0.01366	0.04386	0.04406
50 W for 40 s	0.01376	0.01396	0.04350	0.04352
50 W for 60 s	0.01383	0.01450	0.04312	0.04320
100 W for 20 s	0.01374	0.01404	0.04308	0.04308
100 W for 40 s	0.01416	0.01448	0.04220	0.04236
100 W for 60 s	0.01428	0.01460	0.04136	0.04144
130 W for 20 s	0.01416	0.01444	0.04266	0.04274
130 W for 40 s	0.01424	0.01456	0.04202	0.04210
130 W for 60 s	0.01472	0.01540	0.04048	0.04060

properties than untreated fabric samples. The thermal properties of a fabric greatly depend on the air trapped within it.[19] As stated previously, the atmospheric-plasma treatment had an etching effect on the fiber surface and increased the fabric surface roughness and the amount of voluminous space; this may have increased the amount of air trapped between the yarns and fibers.[27] The air trapped inside the fabric could act as a good insulation medium, help to prevent the heat loss of the fabric, and thus contribute to the increased thermal resistance and the decreased thermal conductivity. The argon-type plasma yielded more effective enhancements than the air plasma.

Relative water-vapor permeability

For fibrous materials, the surface characteristics and pore structure have an enormous influence on the liquid-transfer properties. The atmospheric-plasma treatments, which formed grooves and cracks on the fiber surface, increased the water vapor permeability of the cotton fabrics. This may have induced a certain decrease in the capillary pressure, which enabled a higher degree of water vapor permeability.[21,22] Increased vapor transfer provided better comfort. The relative water vapor permeability results are displayed in Figure 2.

Air permeability

Air permeability results indicated that the atmospheric-plasma-treated fabrics had poorer air permeability (Fig. 3). Etched fibers acted as a boundary and hindered the airflow through the fabric; this eventually caused a reduction in the air permeability of the fabrics. Air was kept inside the plasma-treated fabric and could not escape easily.[28]

SEM analysis

SEM photographs were taken to observe the topographical changes over the surface. The SEM photographs of the untreated, argon-plasma-treated, and air-plasma-treated samples are displayed in Figure 4.

The SEM photographs show that the untreated cotton fiber had a smoother surface. The microcracks and grooves can be conspicuously seen in the photographs of the plasma-treated samples. As the photographs indicate, the argon-plasma-treated cotton fiber had more grooves than the air-plasma-treated

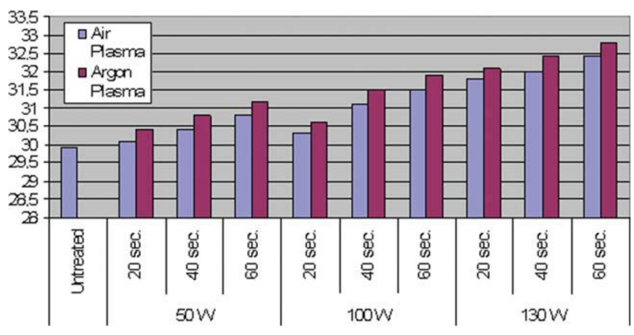

Figure 2 Relative water vapor permeability (%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

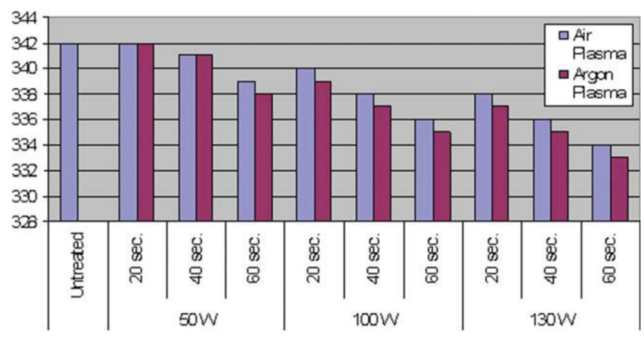

Figure 3 Air permeability (l/m^2 s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

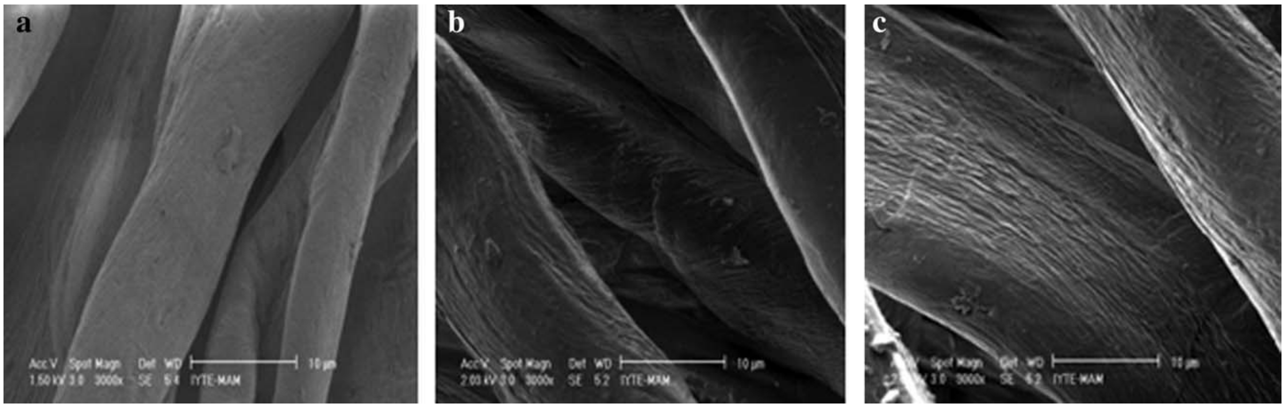

Figure 4 SEM photographs of (a) untreated, (b) air-plasma-treated, and (c) argon-plasma-treated cotton fabric samples.

fiber as a direct result of argon's higher etching tendency.[23,29] The photographic appearance of the surfaces is consistent with the surface friction coefficient values (Fig. 5).

Surface friction properties

As can be easily noticed in Figure 5, the values tended to increase with the prolongation of the treatment and with increased power in compliance with the etching effect of the atmospheric plasma. The surface friction coefficient increased from 0.2894 to 0.3373 for the air-plasma-treated samples and to 0.3383 for the argon-plasma-treated samples.

Although the quantity of this increase was not substantially high, the obtained outcomes were quite consistent and could be justified by the nature of the plasma interaction because it affected the surface by not more than 1000 Å.[28,30]

FTIR–ATR results

The FTIR–ATR method is used for the characterization of the waxes and other impurities of cellulose located in the outermost layer of cotton fibers.[30] Characteristic bands of the chemical structure of cellulose are hydrogen-bonded OH stretching at 3550–3100 cm^{-1} and CH stretching around 2900 cm^{-1}.[31–33]

A peak around 1625 cm^{-1} was due to absorbed water.[31] During the plasma treatment, the water molecules in the structure of the cotton evaporated, and this tended to increase the transmittance of the cotton fibers.[34] This could obviously be seen in the FTIR–ATR spectrum (Fig. 6).

Pilling

The pilling of textile fabrics refers to an appearance caused by bunches or balls of tangled fibers held to the surface. This unpleasant appearance can seriously compromise the acceptability of fabrics for apparel.[35] There are many factors that affect the pilling tendency of a fabric. These can be classified as fiber, yarn, and fabric properties, finishing processes, and end-use parameters. In some cases, the reduction of the pilling tendency through the control of the fiber, yarn, and fabric parameters becomes difficult because the controlling factors may negatively affect desirable properties of a fabric. In this respect, various types of mechanical and chemical finishes can be useful in effectively reducing the number of fabric pills. However, side effects of these finishes should be taken into consideration. Atmospheric-plasma treatment, a physicochemical method, can be used for this purpose.[36]

In Table II, the pilling results for untreated, air-plasma-treated, and argon-plasma-treated cotton fabric samples are displayed. The pilling behavior of the fabric samples decreased as the power and exposure time of the plasma process increased. We assume that the etching action of the atmospheric-plasma treatment weakens the structure of the anchor fibers, and they become more fragile.[36] This suggests that atmospheric plasma enhances pill detachment while reducing the rate of pill formation.

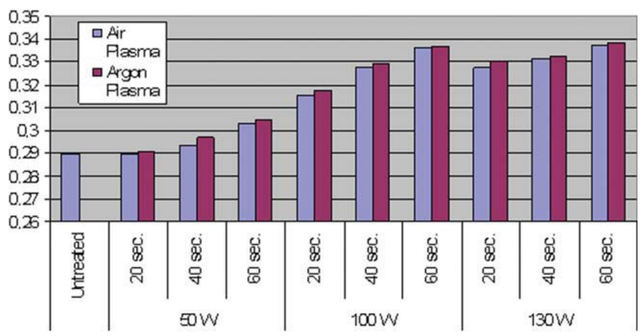

Figure 5 Kinetic friction coefficients. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

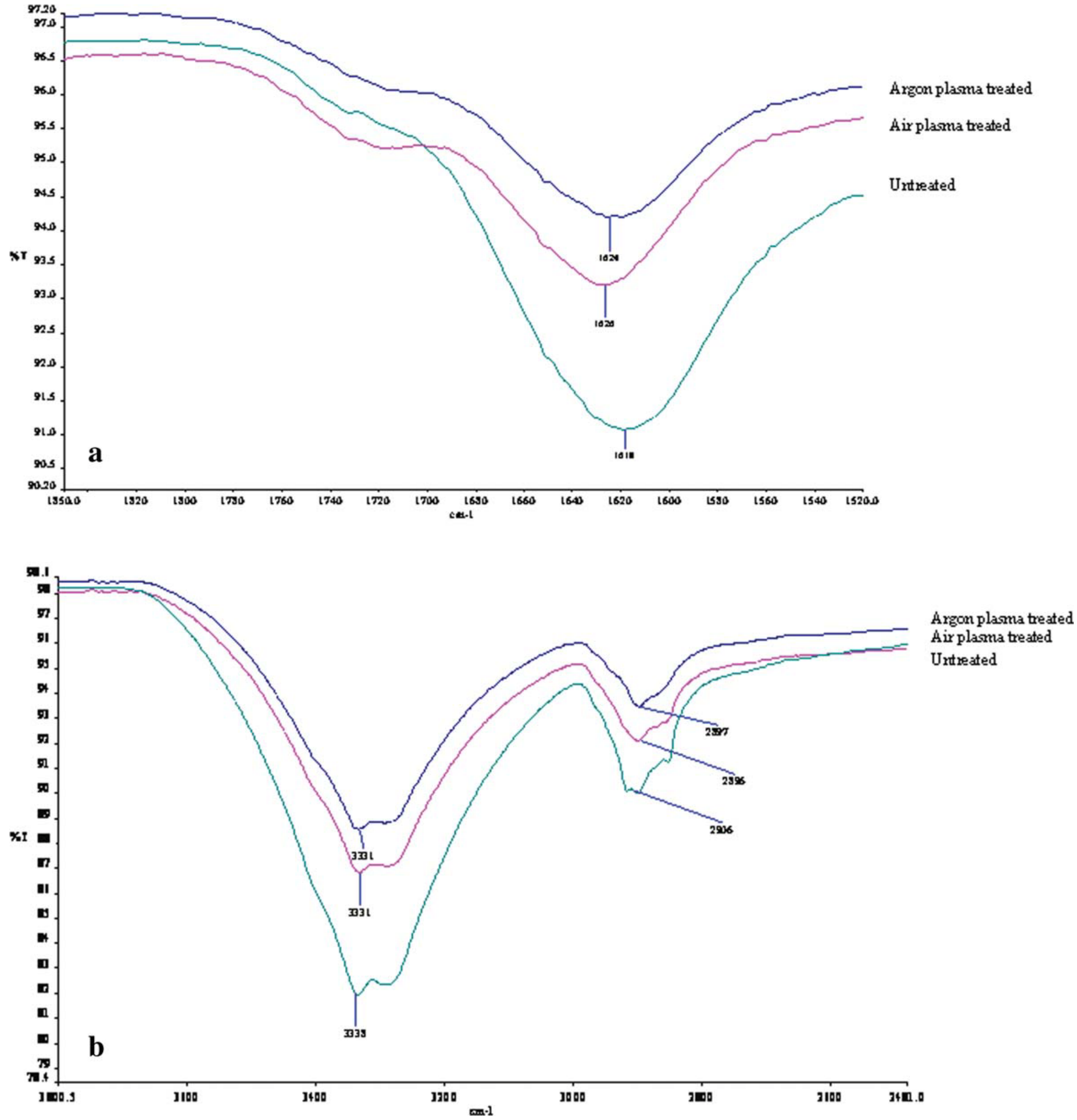

Figure 6 FTIR–ATR spectra of untreated, air-plasma-treated, and argon-plasma-treated fabrics at (a) 1850–1520 and (b) 3800–2481 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Pilling Results for the Untreated, Air-Plasma-Treated, and Argon-Plasma-Treated Cotton Fabrics

Treatment	Air plasma	Argon plasma
Untreated	2.2	
50 W for 20 s	2.3	2.5
50 W for 40 s	2.4	2.6
50 W for 60 s	2.5	2.7
100 W for 20 s	2.4	2.6
100 W for 40 s	2.6	2.7
100 W for 60 s	2.7	2.9
130 W for 20 s	2.6	2.8
130 W for 40 s	2.7	2.9
130 W for 60 s	2.9	3.1

CONCLUSIONS

Naturally colored cotton is a novel and environmentally friendly alternative for the textile industry because it enables customers to have clothing, furnishing, and household textile items without polluting the environment through the elimination of chemical agents. These issues are becoming a prime concern for the buying decisions of consumers worldwide, especially in advanced industrial countries.

The main aim of this research was to investigate the effects of atmospheric-plasma treatments on the surfaces of fabrics based on naturally colored cotton because plasma treatments have the potential to substitute for or maybe even replace wet textile finishing processes without requiring any chemical agents or water. This may lead the textile industry to an environmental friendly phase along with the incorporation of naturally colored cotton fiber usage. The outcomes indicate that the hydrophilicity, pilling resistance, and comfort properties of naturally colored cotton fabrics increase considerably without the need for any chemical agent or water consumption. FTIR–ATR spectra revealed that the best results were obtained with argon-plasma-treated samples, and this was also consistent with the hydrophilicity values. As can be seen from the friction coefficient values and SEM photographs, the atmospheric-plasma treatment made the surface rougher because of an etching effect. In other words, atmospheric-plasma treatments could influence not only the chemical properties but also the physical properties of naturally colored cotton fibers. The modification degrees of plasma treatments are influenced significantly by the duration, power, and plasma type. In general, the argon-plasma treatment showed more effective results than the air-plasma treatment. This should be a direct result of the higher etching tendency of argon gas.

Naturally colored cotton species, especially organically cultivated ones, have unique environmentally friendly potential. Naturally colored cotton species do not necessitate the implementation of any bleaching or dyeing process. The only required textile finishing treatment for naturally colored cotton fibers is the hydrophilicity improvement process. In this respect, the plasma treatment, an ecological textile method, is a promising alternative.

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