Oxygen Plasma Treatment to Reduce the Dyeing Temperature of Wool Fabrics

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ABSTRACT: The possibility of reducing the dyeing temperature of wool fabrics by means of an oxygen low-temperature plasma etching pretreatment at different discharge powers was investigated. We dyed fabrics at 98, 85, and 80°C, replicating the dyeing recipe and process of a dyeing mill on a laboratory-scale machine. The plasma treatment modified the surface morphology and greatly increased the wettability and initial dyeing rate and shortened the half-dyeing time, improving the diffusion of the dyes into the fibers at lower dyeing temperatures. In particular, the pretreatment allowed us to dye the wool fabrics at 85°C without affecting their dyeing performances in terms of final bath exhaustion and colorfastnesses. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1173–1183, 2010

Key words: cold plasma; fibers; morphology; dyeing

INTRODUCTION

The textile dyeing and finishing industry is affected by environmental issues related to water consumption and wastewater loads, energy and chemical usage, production of solid wastes, emissions to the atmosphere, site contamination, and noise. For this reason, its environmental performance must be improved in an affordable, sustainable, and efficient way; its resource consumption must be reduced; and its compliance with regulatory requirements must be increased.[1] This goal can be reached by means of the development and practical application of innovative technologies.

From an energetic point of view, it is estimated that the dyeing process alone accounts for about 25% of the total energy consumed in the entire textile production process,[2,3] and the major use of energy involves the heating of water for the dye bath to facilitate a quick dyeing process and better dye penetration into textile materials.[4] With the aim of enhancing the energy efficiency and reducing the energy consumption, the use of low-temperature technologies, with a review of dyeing programs and the reduction of temperatures, time, and bath ratio, has to be considered.

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In particular, wool dyeing has been the subject of many investigations on improving its environmental impact. Studies have been done on non-water-based dyeing processes with supercritical fluids,[5,6] microencapsulation with liposomes as carriers for dyes,[7,8] the use of enzymes as auxiliary agents,[9] and the application of enzymatic[10–12] or low-temperature plasma[10,13–15] pretreatments.

Conventional methods used in wool dyeing involve prolonged periods at or near boiling; this is necessary to obtain good leveling and dye penetration into the fiber,[16] but this translates into high energy costs. Therefore, it is important to promote technological development aimed specifically at lowering the dyeing temperature; moreover, it has been recognized for many years that fiber damage caused by dyeing is reduced markedly when wool is dyed at temperatures below boiling, and studies on the relationship between the morphological structure and the dyeing properties of wool have led to several approaches for dyeing wool at lower temperatures (usually 85–90°C).[16,17]

The wettability and dyeing performances of wool are governed by its surface morphology and chemical structure. The fiber structure plays a key role in the mechanism of wool dyeing by an exhaustion method, that is, a three-stage process that includes (1) the diffusion of the dye through an aqueous dye bath to the fiber surface, (2) the transfer of the dye across the fiber surface, and (3) the diffusion of the dye from the surface throughout the whole fiber.[16] To obtain satisfactory shade development and fastness properties, complete penetration of dye into the fiber interior is essential, and the rate at which this

occurs is controlled by the rate of the dye diffusion across the fiber surface and then throughout the whole interior.[16] However, a small capacity for dye exists at the fiber surface because of the thin hydrophobic epicuticle, the highly crosslinked A-layer of the exocuticle, and the lipids present at the intercellular junctions that act as resistant barriers to dye penetration, which produce the so-called surface barrier effect.[16,18] Different dyeing behaviors may be shown when fiber surface has been chemically or physically altered. For these reasons and for its peculiarities, plasma treatment can be used to chemically or physically alter the fiber surface by means of reactions confined to the outermost layer of the fiber (plasma species reach a penetration depth of few 10 s of nanometers[19]) without altering its bulk properties and can improve the diffusion of dyes into the fiber and, thus, make wool dyeing at temperatures below boiling viable.

The specific goal of this study was to investigate oxygen low-temperature plasma etching as a pretreatment of wool fabrics to reduce the dyeing temperature and maintain the performance in terms of bath exhaustion and colorfastnesses. Treatments were carried out in laboratory-scale low pressure equipment. Different discharge powers were applied, and the effects of the treatment on the surface morphology were examined. Wool fabrics were dyed on a laboratory-scale dyeing machine at different temperatures (98, 85, and 80°C) with an industrial recipe that involved three 1 : 2 metal–complex dyes (blue, yellow, and violet) and according to a batch procedure that replicated the industrial-plant process conditions of a dyeing mill.

EXPERIMENTAL

Materials and dyeing recipe

Experiments were carried out on 130 g/m^2 standard ready-to-dye wool fabric (ISO 105-F01) in which surface contaminants (grease, suint, dirt, and vegetable matter) had been removed. The mean fiber diameter, determined by a projection microscope (Reynolds & Branson, Leeds, UK) according to specification IWTO-8-04, was 18.9 μm. The oxygen (purity level $\geq$ 99.5%) used in the plasma treatments was purchased from SIAD (Bergamo, Italy).

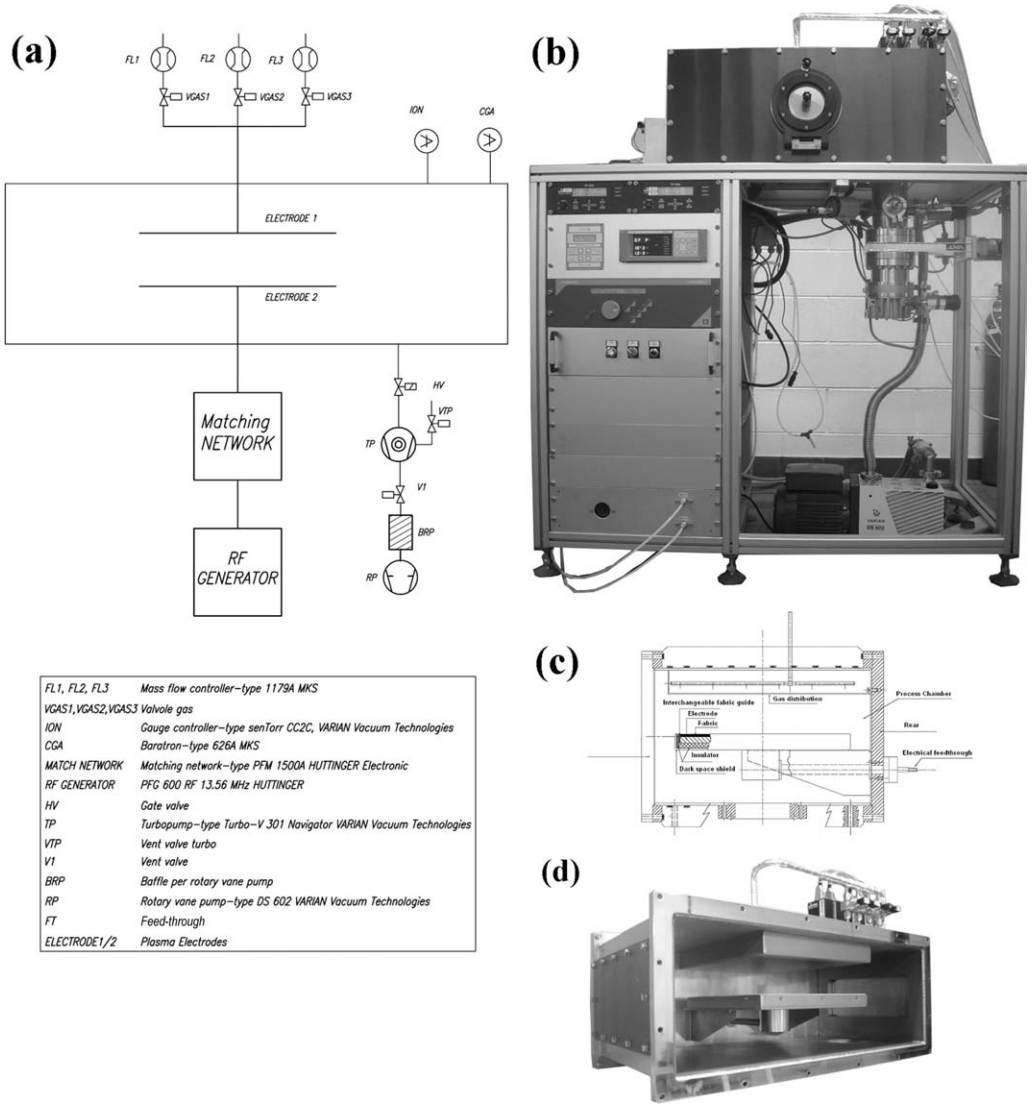
Dyeing involved an industrial recipe provided by the dyeing mill Tintoria Tonella (Ponzone di Trivero, Italy) and recommended by the dyestuff manufacturer. The recipe was based on a combination of three commercially available metal–complex (1 : 2 premetalized) dyes and auxiliary agents: CI Acid Blue 284 (2.6% owf), CI Acid Yellow 151 (0.53% owf), and CI Acid Violet 85 (0.48% owf) from Manifattura Chimica Italiana Trading (Muggiò, Italy); dispersing agent Adipal IW (1.5 g/L) and equalizing agent Adipal MK/A (0.5 g/L) from Forniture Tessili Riunite (Albano Sant'Alessandro, Italy); 60 vol % acetic acid (0.5 cc/L) from Honeywell Riedel-de Haën (Seelze, Germany); and ammonium sulfate (1.5 g/L) from Carlo Erba Reagenti (Rodano, Italy).

Plasma equipment and treatments

Laboratory-scale, low pressure plasma equipment, designed and manufactured by Kenosistec (Binasco, Italy), was used for the plasma treatment. Schematic drawings and photographic details of the equipment are reported in Figure 1. The system consisted of a stainless steel reactor (inside dimensions about 250 mm high $\times$ 650 mm wide $\times$ 400 mm deep) with front and rear aluminum flanges equipped with a 13.56-MHz radio frequency (RF) generator (PFG 600 RF, Hüttinger Electronic, Freiburg, Germany) tuned by means of an impedance matching network (PFM 1500 A, Hüttinger Electronic). The reactor was evacuated with a turbomolecular pump (Turbo-V 301 Navigator, Varian Vacuum Technologies, Leini, Italy) and a dual-stage rotary vane pump (DS 602, Varian Vacuum Technologies). Inside the vacuum chamber, a plane parallel electrode arrangement was attached.

The upper electrode was grounded. The fabric was located on the lower, RF-driven electrode over an interchangeable guide having a square shape (side length = 300 mm). The gas was fed through a gas distribution grid (9 $\times$ 9 matrix with holes 1 mm in and a 35-mm interhole distance) built in the upper electrode, centered with respect to the guide, whose function was to obtain a uniform gas flow over the substrate. The gap between the electrodes was adjustable. A RF electrical feed-through was used to transfer electrical power through the vacuum system wall. The reactor was fitted with one inlet for the processing gas, whose flow was measured and controlled by means of a mass flow controller (type 1179A, MKS Instruments, Andover), and the pressure was monitored by a capacitance manometer (Baratron Type 626A, MKS Instruments) and a gauge controller (senTorr CC2C, Varian Vacuum Technologies).

The 300-mm-side square fabric samples were first dried in an oven at 105°C for 2 h to minimize the water content before they were treated. The distance between the electrodes was set at 80 mm. The surface of the wool samples was etched by means of the plasma excitation of oxygen, with the flow rate maintained at 20 sccm and the working pressure in a range of about 10^{-1} mbar for 5 min. Four different discharge powers were investigated: 30, 50, 60, and 80 W. After treatment, each wool sample was conditioned under standard laboratory conditions (20 $\pm$ 2°C and 65 $\pm$ 2% relative humidity) before further experiments were conducted.



FL1, FL2, FL3	Mass flow controller–type 1179A MKS
VGAS1,VGAS2,VGAS3	Volvole gas
ION	Gauge controller–type senTorr CC2C, VARIAN Vacuum Technologies
CGA	Baratron–type 626A MKS
MATCH NETWORK	Matching network–type PFM 1500A HUTTINGER Electronic
RF GENERATOR	PFG 600 RF 13.56 MHz HUTTINGER
HV	Gate valve
TP	Turbopump–type Turbo–V 301 Navigator VARIAN Vacuum Technologies
VTP	Vent valve turbo
V1	Vent valve
BRP	Baffle per rotary vane pump
RP	Rotary vane pump–type DS 602 VARIAN Vacuum Technologies
FT	Feed-through
ELECTRODE1/2	Plasma Electrodes

Figure 1 (a) Schematic drawing of the plasma equipment, (b) picture of the plasma equipment, (c) schematic drawing of the reaction chamber, and (d) photographic detail of the interior of the reaction chamber.

Microscale and nanoscale surface morphology

The microscale and nanoscale surface morphology of the fibers before and after plasma exposure were investigated with scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively.

Samples about 10 × 10 mm^2 were spread on double-sided conducting adhesive tape pasted onto a metallic stub, sputter-coated with gold by means of a K550 instrument (Emitech, Ashford, UK) at 20 mA for 4 min to ensure electrical conductivity, and observed by means of a LEO 435 VP scanning electron microscope (LEO Electron Microscopy, Cambridge, UK) operating at an accelerating voltage of about 15 kV with a working distance of 19 mm and magnification up to 5000×.

AFM imaging was performed by means of a Nano-R_2 atomic force microscope (Pacific Nanotechnology, Santa Clara). Because we were dealing with soft surface specimens, the vibrating (or close contact) mode was chosen for measuring the force on the cantilever as the probe encountered changes in the sample topography; in this technique, the tip-not-tap the surface and the changes in probe vibrations were monitored to establish the interactive force of the probe with the surface.[20] Fabric samples about 10 × 10 mm^2 were mounted on the sample puck; AFM data were acquired by means of SPM Cockpit software and processed and analyzed by means of NanoRule+ software, which were both provided with the Nano-R_2 system.

Wettability

The wettability of the fabric before and after treatment was evaluated with the drop test according to

BS 4554:1970. A drop of 0.1 mL of deionized water was allowed to fall on the sample surface. A stop watch was started when the drop reached the fabric surface and stopped when the drop had completely penetrated into the fabric; the elapsed time was recorded.

The wettability was used as an indirect indicator of the longevity and durability of the treatment and the stability of the modified surface. For this purpose, plasma-treated samples were allowed to age under standard laboratory conditions, and their wettability was evaluated day to day for 60 days after the treatment. In accordance with specification IWTO-52-00, after each test, wool fabric samples were dried in a mechanically ventilated oven at 50°C for 4 h to ensure that the subsequent conditioning in the standard atmosphere, performed before the next test, commenced from the dry state.

Dyeing process

Dyeings were conducted with a Teintolab laboratory-scale dyeing machine, furnished by Comeureg (Haubourdin, France). This was a diagnostic equipment that allowed online measurements of the dye-bath monitoring parameters, such as pH, temperature, and dye-bath exhaustion.

Fabric samples of about 11 g were dyed at 98, 85, and 80°C with a liquor-to-wool ratio of 65 : 1 and at neutral pH with the industrial recipe mentioned previously and according to a batch procedure that followed a recommended time/temperature profile to simulate industrial-plant process conditions. The process started loading fabric and auxiliaries in 40°C water. After 3 min of wetting of the fabric, the dyes were added, and the dye bath was maintained at the same temperature for a further 2 min. Then, the temperature was raised at a gradient of 1°C/min until it reached the chosen dyeing temperature and maintained for as many minutes as necessary to ensure that the total time of raising and maintenance of the bath temperature was 100 min. Subsequently, the temperature was reduced to 60°C at a gradient of 5°C/min. Finally, the fabric was rinsed in cold water, unloaded, and dried in air at room temperature.

The dyeing of the untreated fabric at 98°C was the reference industrial-like dyeing. This dyeing was tuned by the Tintoria Tonella dyeing mill to obtain good levelness and colorfastnesses. The dyeings of the treated fabrics were conducted within 3 days after the plasma treatment.

Color measurement and fastnesses

We performed the color measurement according to ISO 7724-2:1984, measuring the spectral photometric characteristics (spectral reflectances) with a spectrophotometer (Spectraflash SF600XV) from Datacolor (Dietlikon, Switzerland) under the Commission Internationale de l'Eclairage (CIE) standard illuminant D_{65} and a 10° observer. Color differences (ΔE_{00}), lightness differences ($\Delta L'$), chroma differences ($\Delta C'$), and hue differences ($\Delta H'$) between the dyed specimens and the reference specimen, untreated and dyed at 98°C, were calculated according to ISO 7724-3:1984, ISO 105-J03:1995, and the CIE 2000 color-difference formula.[21,22]

Colorfastness to organic solvents was evaluated according to ISO 105-X05:1994 by means of a Linitest machine from Original Hanau (Hanau, Germany) with extrapure tetrachloroethene from Honeywell Riedel-de Haën.

Colorfastness to artificial light (a D_{65} light source representative of natural daylight) was assessed according to ISO 105-B02:1994 with a xenon arc fading lamp (Xenotest Alpha) from Atlas Material Testing Technology (Linsengericht, Germany).

Colorfastness to rubbing was determined according to ISO 105-X12:2001 with a crockmeter from SDL (Stockport, UK).

RESULTS AND DISCUSSION

Surface morphology as determined by SEM and AFM

SEM analysis pointed out that there was a progressive effect of the discharge power on the surface morphological changes caused by the plasma treatment, as shown in Figure 2. Etching of the polymer surface, a light incision of the scales and chipping of the scale edges, and a fragmentation of cuticle particles already present on the untreated fiber were observed, which were more and more evident with increasing power. This behavior was in accordance with the fact that the higher the discharge power was that was applied, the more kinetic energy the plasma species carried and the stronger the intensity of the plasma action was.[23]

The etching of the fiber surface resulted in a rougher and larger surface area.[24] This was confirmed by AFM analysis, which revealed more surface details. The AFM three-dimensional image profiles illustrated in Figure 3 showed that the untreated fiber presented a relatively smooth topography, whereas the oxygen-plasma-treated fiber showed a somewhat rougher surface, with the formation of aggregates of various sizes. Surface roughness area measurements, performed on 10-μm^2 areas, confirmed the differences in roughness between the untreated fiber (values of average roughness ranging from 80 to 377 nm) and treated fibers and a tendency toward increasing surface

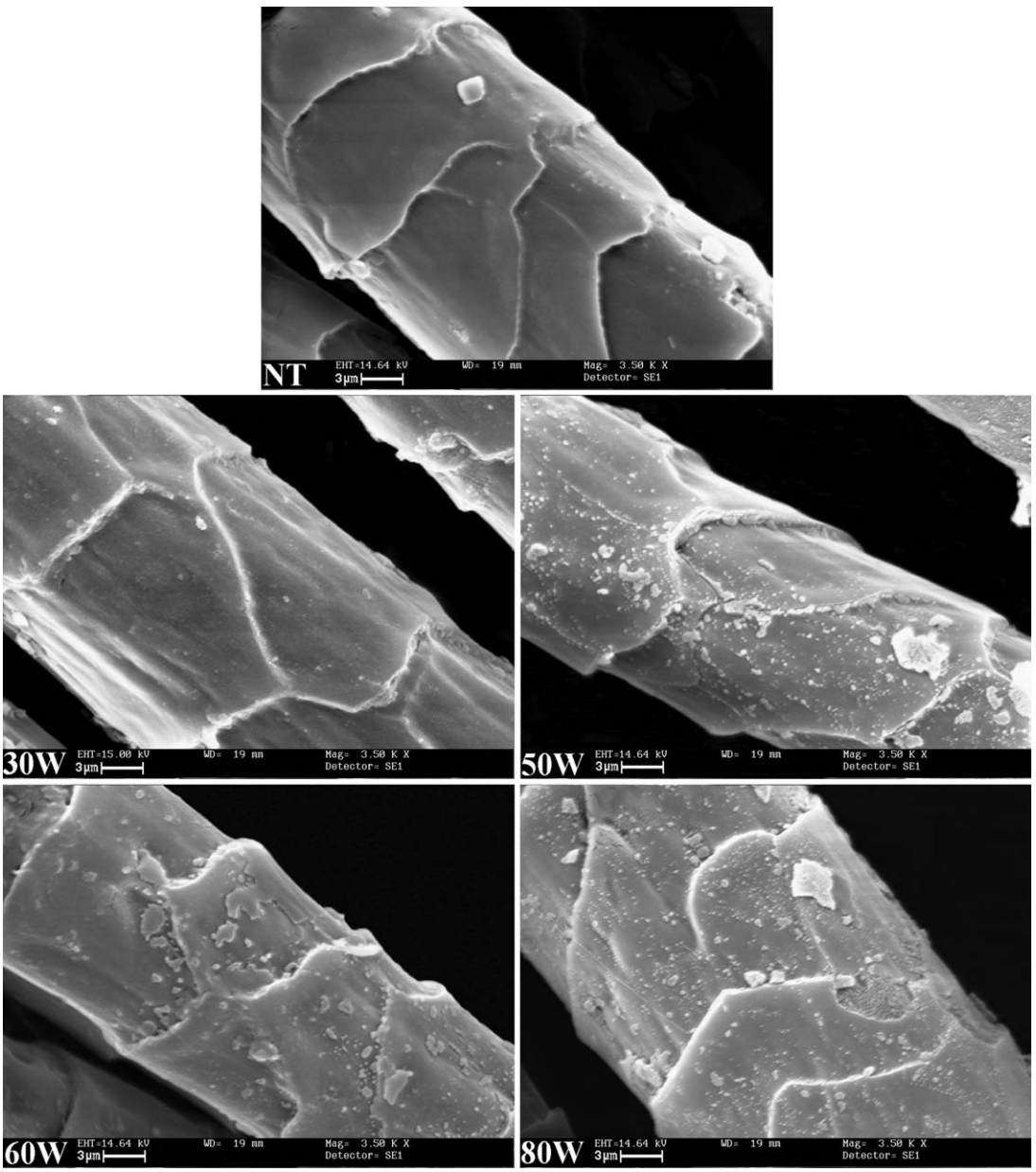


Figure 2 SEM images of the untreated wool fiber (NT) and plasma-treated fibers at different discharge powers (30 W, 50 W, 60 W, and 80 W).

roughness with increasing discharge power (values of average roughness ranging from 120 to 407 nm for 30 W, from 79 to 490 nm for 50 W, from 70 to 533 nm for 60 W, and from 46 to 558 nm for 80 W).

Wettability

Wettability is governed by the fiber surface, and increasing it means improving the performance in dyeing. The wettability of the wool fabric was increased drastically by the oxygen plasma treatment. Water-drop penetration time decreased from more than 1 h for the untreated fabric to less than 1 s for all of the plasma-treated fabrics; the treated fabrics absorbed water drops practically instantly (Fig. 4). The plasma treatment modified the wool fiber surface by turning it from highly hydrophobic to highly hydrophilic. There was a decrease in wool surface tension that could be ascribed to different factors, both physical and chemical: (1) the partial removal of scales and lipids, and an increase in the surface roughness, due to the etching effect; (2) a reduction in the number of disulfide bonds, and an increase in the cysteic acid due to oxidation of the amino acid cystine of the cuticle cells as a consequence of the oxygen-bearing plasma.[23–25]

Because a plasma-treated surface can undergo aging, which leads to hydrophobic recovery (the grafted hydrophilic oxygen-containing functional groups are polar and unstable and tend to rearrange

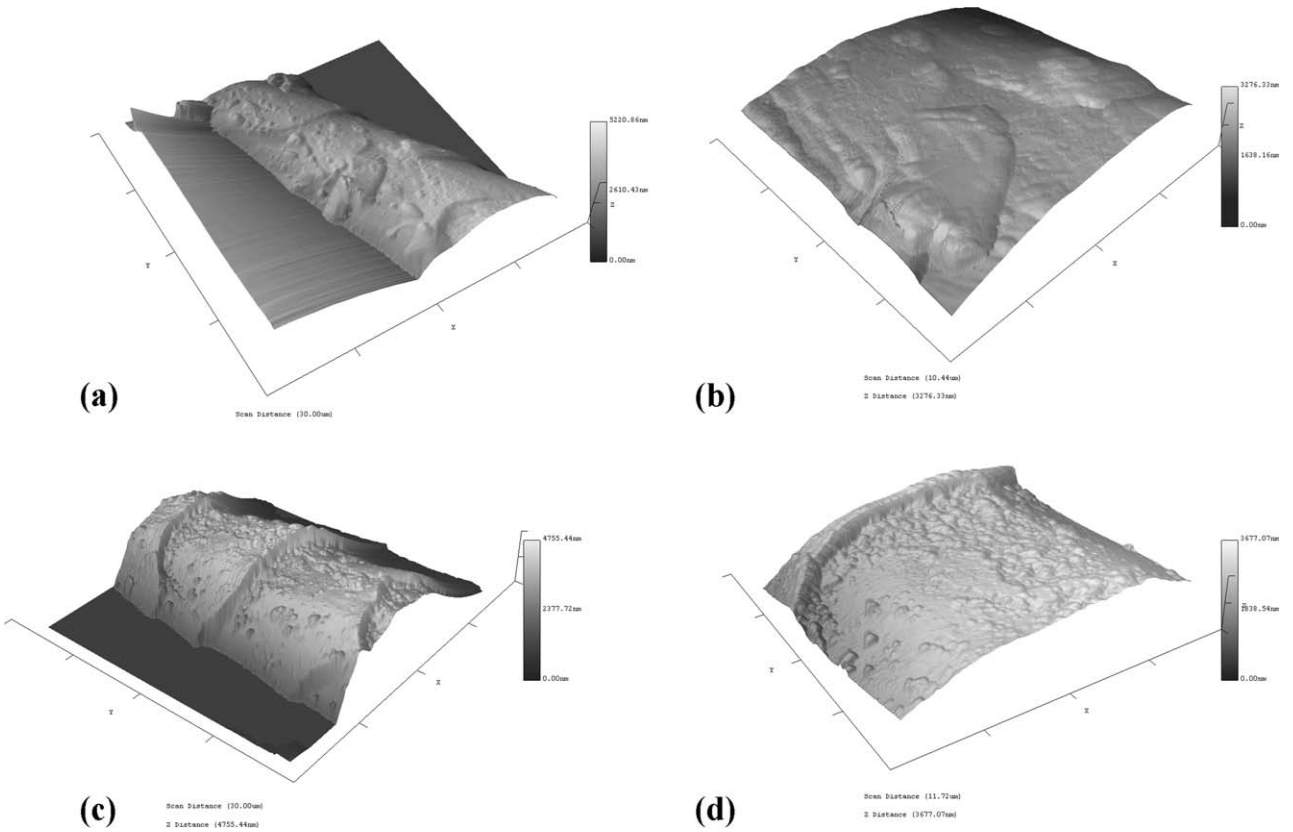


Figure 3 AFM images of (a,b) untreated wool fiber and (c,d) 50-W-treated fiber: (a,c) 30 × 30 and (b,d) 10 × 10 μm^2 scan areas.

and reorientate toward the bulk material to a more stable situation) and a worsening of the hydrophilicity-dependent properties,[26–28] we verified whether the wettability was deteriorating with time. As shown in Figure 5, the water-drop penetration was instantaneous within the first 10 days after the treatment. Then, a slight decay of wettability was reported, and after 3 weeks, the drop penetration time stabilized between 3.5 and 7 s. Therefore, there was a partial recovery of hydrophobicity that could be reasonably ascribed to a small chemical rearrangement of the polar groups generated by the plasma treatment, but the surface remained highly hydrophilic. The permanence of the greatly increased wettability was mainly due to the definitive physical removal of the wool surface barrier rather than the mild surface oxidation promoted by the treatment.

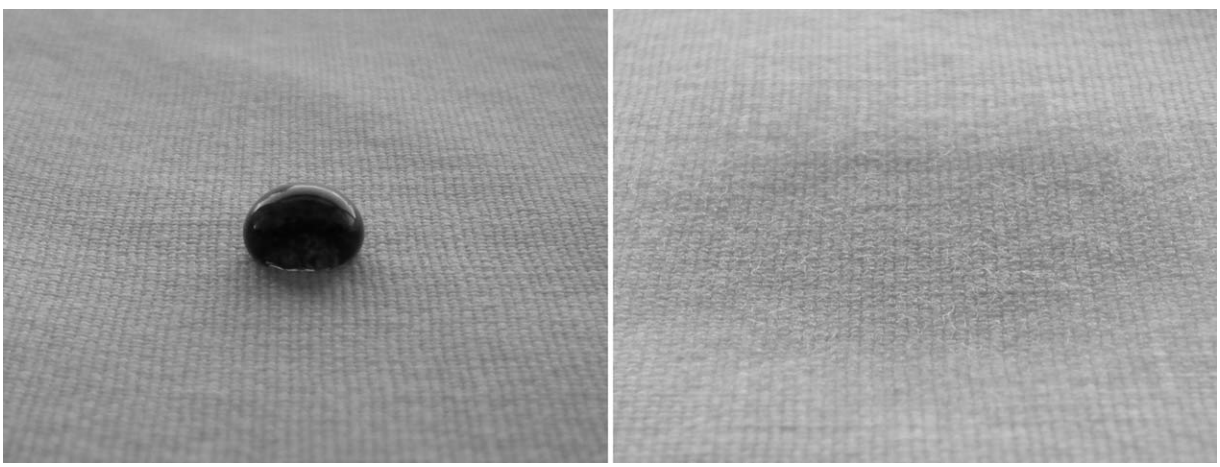


Figure 4 Dyed water drop 10 s after it reached the surface of the untreated fabric (left) and the 30-W-treated fabric (right).

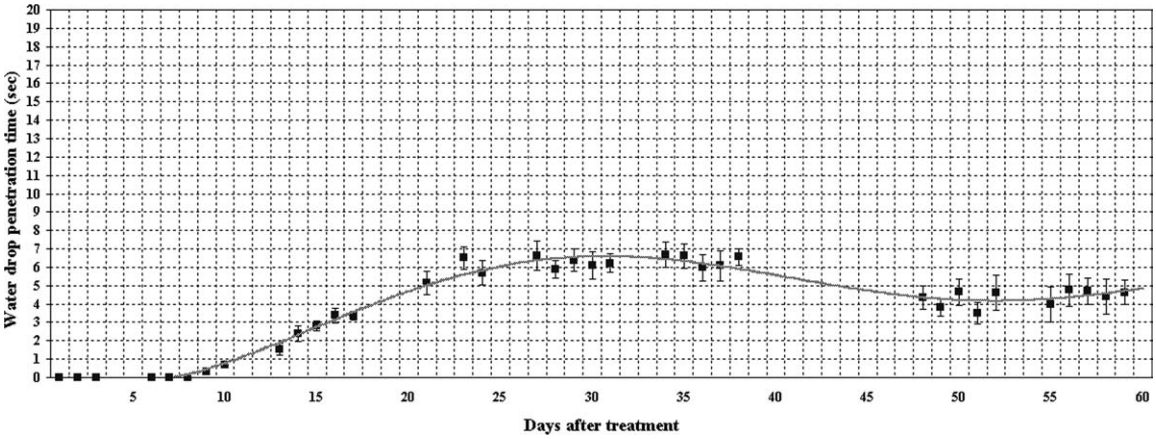


Figure 5 Water-drop penetration time as a function of aging time for plasma-treated fabric at 50 W.

Dyeing behavior

For each dyeing, the exhaustion curve, final bath exhaustion, and half-dyeing time were investigated. In this study, the half-dyeing time was calculated as the time required for the dye bath to reach half the value of its final exhaustion. In light of the wettability results, as expected, the plasma pretreatment had a great influence on the dyeing performance, particularly with regard to the dyeing kinetics.

Figure 6 shows the exhaustion curves, final bath exhaustions, and half-dyeing times of the dyeings performed at 98°C. The plasma pretreatment modified the dyeing behavior and improved the transfer of dyes across the fiber surface and the diffusion of dyes from the surface throughout the whole fiber; this made the wool more accessible to the dyes. In fact, the curves relative to the dyeings of the plasma-treated fabrics rose and started to flatten, reaching a plateau, before the curve relative to the reference dyeing of the untreated fabric, and the half-dyeing times of the plasma-treated fabrics were lower than that of the reference. Plasma-treated wool was more easily penetrated by the dyes as consequence of the degradation of the natural diffusion barrier in the fiber surface.[24] With regard to the values of bath exhaustion at the end of the dyeing, those of the dyeings of treated fabrics were slightly higher than that of the reference dyeing.

This study continued with the investigation of the dyeings at 85°C. Figure 7 compares the exhaustion curves, final bath exhaustions, and half-dyeing times of the dyeings at 85°C with those of the reference dyeing. As expected, the dyeing at 85°C of the untreated fabric was characterized by a value of final bath exhaustion (84%) significantly lower than that of the reference dyeing at boiling (91.8%). However, the dyeings at 85°C of the plasma-pretreated fabrics reached final bath exhaustion very close to that of the reference; the difference ranged from 2.7% for the 30-W-treated fabric to 2.3% for the 80-W-treated fabric. The final bath exhaustions for the treated fabrics at different discharge powers were very similar; nevertheless, the results showed a slight increase with increasing applied power. We

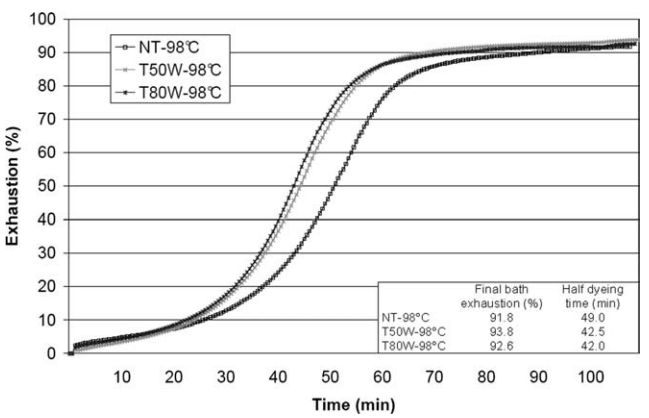


Figure 6 Exhaustion curves, final bath exhaustions, and half-dyeing times for the dyeings at 98°C of untreated (NT), 50-W-treated (T50W) and 80-W-treated (T80W) fabrics.

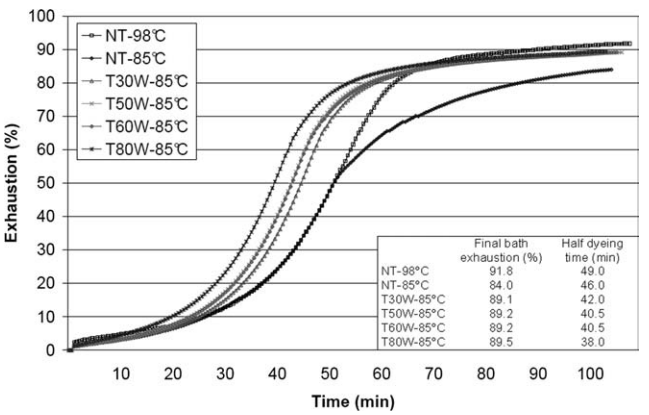


Figure 7 Exhaustion curves, final bath exhaustions, and half-dyeing times for reference dyeing and dyeings at 85°C of untreated (NT), 30-W-treated (T30W), 50-W-treated (T50W), 60-W-treated (T60W), and 80-W-treated (T80W) fabrics.

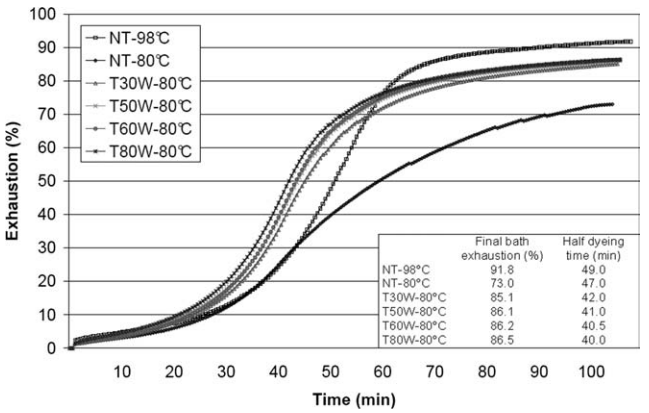


Figure 8 Exhaustion curves, final bath exhaustions, and half-dyeing times for reference dyeing and dyeings at 80°C of untreated (NT), 30-W-treated (T30W), 50-W-treated (T50W), 60-W-treated (T60W), and 80-W-treated (T80W) fabrics.

confirmed that the plasma treatment greatly affected the rate of absorption of the dyes and shortened the half-dyeing time, and the higher the power was, the more evident this behavior was. This last could be explained by a slightly higher etching rate with increasing power.

In consideration of the interesting results from the dyeings at 85°C, we decided to reduce the wool dyeing temperature further, trying with 80°C. Figure 8 shows the exhaustion curves, final bath exhaustions, and half-dyeing times of the dyeings at 80°C and the reference dyeing. The 80°C dyeing of the untreated fabric showed very bad performances: the bath exhaustion at the end of the dyeing stopped at 73%, which was far lower than that of the reference dyeing. The dyeings of the treated fabrics reached similar final bath exhaustions, ranging from 85.1% (30 W) to 86.5% (80 W). There was a further confirmation of the great influence of the plasma pretreatment on the dyeing performances, but the values of final bath exhaustion were not acceptable in comparison to the value relative to the reference dyeing.

In conclusion, Figure 9 compares the exhaustion curves of the reference dyeing and the dyeings of treated fabric at 50 W. As shown, the plasma pretreatment modified the dyeing kinetics and improved the dyeing rate (the dye exhaustion was generally more rapid) at each temperature as a consequence of surface changes. The surface barrier was eliminated by plasma treatment, which opened penetration paths for dyes. The final bath exhaustion was obviously affected by the chosen dyeing temperature and increased with increasing temperature. The results highlight that the dyeing at 85°C (13°C less than the reference dyeing) was satisfactory after the fabrics were pretreated by means of oxygen plasma.

Color differences and fastnesses

à The ΔE_{00}, $\Delta L'$, $\Delta C'$, and $\Delta H'$ values between the dyed specimens and the reference specimen (untreated and dyed at 98°C) are presented in Table I.

ΔE_{00} showed changes in color for all of the plasma-treated fabrics dyed at different temperatures. Significant changes ($\Delta E_{00} > 3$) were pointed out for all of the treated fabrics dyed at 98°C and the 80-W-treated fabric dyed at 85°C. The component that most affected these differences was the lightness; at each dyeing temperature, the treated fabrics (with the exception of the 30-W-treated fabric dyed at 80°C) were darker ($\Delta L' < 0$) than the reference, and the lightness decreased with increasing discharge power and dyeing temperature. On the contrary, untreated fabrics dyed at temperatures below boiling were paler ($\Delta L' > 0$). No significant $\Delta C'$s were observed for the chroma; this indicated that the intensity and purity of color basically remained unchanged. All of the samples, treated and untreated, showed slight $\Delta H'$s with respect to the reference. The hue angles of all of the plasma-treated fabrics dyed at different temperatures were wider ($\Delta H' > 0$) than that of the reference (266°), more and more with increasing applied power, whereas those of the untreated fabrics dyed below boiling were narrower ($\Delta H' < 0$). Practically, the color of the treated fabrics showed a reddish hue shift, whereas the untreated fabrics showed an increased greenish hue when they were dyed at lower temperatures. This could be explained by different absorptions of the three dyes because of a change in the affinity between the single components of the tern and the fiber, which was dependent on both the treatment and the dyeing temperature.

Table II summarizes the colorfastness properties of the dyed wool fabrics.

With regard to the colorfastness to organic solvents, all of the dyed fabrics showed an excellent resistance. In particular, all the plasma-treated fabrics

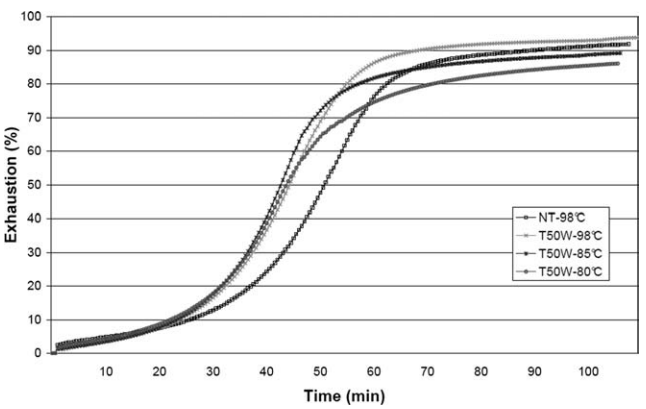


Figure 9 Exhaustion curves for reference dyeing of untreated fabric (NT) and the dyeings at 98, 85 and 80°C of treated fabric at 50 W (T50W).

TABLE I
ΔE_{00}, $\Delta L'$, $\Delta C'$, and $\Delta H'$ Values Between the Dyed Specimens and the Reference Specimen Untreated and Dyed at 98°C

		Reference: Untreated and dyed at 98°C			
		$\Delta L'$	$\Delta C'$	$\Delta H'$	ΔE_{00}
Dyed at 98°C	Treated at 50 W	−2.93	−1.46	0.45	3.31
	Treated at 80 W	−3.06	−0.70	0.70	3.22
Dyed at 85°C	Untreated	1.58	0.00	−0.67	1.71
	Treated at 30 W	−1.61	−0.10	0.57	1.71
	Treated at 50 W	−2.08	0.03	0.81	2.24
	Treated at 60 W	−2.21	−0.18	0.90	2.40
	Treated at 80 W	−3.22	−0.58	1.01	3.42
Dyed at 80°C	Untreated	2.01	−0.79	−0.95	2.36
	Treated at 30 W	0.19	0.29	0.55	0.65
	Treated at 50 W	−1.72	0.33	0.91	1.97
	Treated at 60 W	−2.04	0.03	0.85	2.21
	Treated at 80 W	−2.35	0.57	1.05	2.64

dyed at different temperatures showed the same performance as the reference with respect to staining on wool and staining on cotton (grade 5, the best rating), whereas the performance was an insignificant half a grade less with respect to color degradation. The high colorfastness to artificial light of the reference (grade 7) was reached also by all of the plasma-pretreated fabrics dyed at different temperatures (ratings of 7 or 6–7). This means that the treated wool fabrics were capable of resisting artificial light when they were dyed at temperatures below boiling, whereas the results show a little worsening for the untreated fabric when it was dyed at 80°C (grade 6). In conclusion, with regard to the colorfastness to rubbing, the untreated fabrics dyed at different temperatures showed very good performances under both dry and wet conditions; also, the rubbing fastness of the treated fabrics was good and comparable to that of the reference. In particular, dyeing at 85°C gave the best results. Only the 30-W-treated fabric dyed at 80°C showed a lack of fastness to rubbing, particularly when it was wet (grade 2–3).

Current and future perspectives

Before we conclude, it is important to mention the current limits and future perspectives of this study. The most important limiting factors of the plasma equip-

TABLE II
Colorfastness

		Colorfastness					
		Organic solvent				Rubbing	
		Color degradation[a]	Staining on wool[b]	Staining on cotton[b]	Artificial light[c]	Dry[b]	Wet[b]
Dyed at 98°C	Untreated	5	5	5	7	4–5	4
	Treated at 50 W	4–5	4–5	5	7	3–4	3–4
	Treated at 80 W	–	–	–	–	–	–
Dyed at 85°C	Untreated	4–5	5	5	6–7	4–5	4–5
	Treated at 30 W	4–5	5	5	7	4–5	4
	Treated at 50 W	4–5	5	5	7	4–5	4
	Treated at 60 W	4–5	5	5	7	4	4
	Treated at 80 W	4–5	5	5	7	4–5	4–5
Dyed at 80°C	Untreated	4–5	5	5	6	4–5	4
	Treated at 30 W	4–5	5	5	7	3–4	2–3
	Treated at 50 W	4–5	5	5	7	4	3–4
	Treated at 60 W	4–5	5	5	6–7	4	4
	Treated at 80 W	5	5	5	6–7	4	4

[a] Rated according to the gray scale for assessing change in color, which ranges from 1 (poor) to 5 (excellent), as described in ISO 105-A02:1993.
[b] Rated according to the gray scale for assessing staining, which ranges from 1 (poor) to 5 (excellent), as described in ISO 105-A03:1993.
[c] Rated according to the blue scale for assessing color fastness to light, which ranges from 1 (very low) to 8 (very high), as described in ISO 105-B01:1994.

ment used were, obviously, the sample size and the absence of a roll-to-roll system, but this was a laboratory-scale investigation aimed at finding the best possible benefits and applications of the proposed process. The next step will take into account the disadvantages of this study before the solution is upscaled to a preindustrial level up to an industrial application.

Oxygen gas was chosen on the basis of previous studies,[10,13–15,19,29] but it must be considered that, for an industrial process, working in pure oxygen would require special safety installations, which could be unrealistic for the textile industry. For this reason, future investigations will extend the study to air and/or argon/oxygen mixtures. Moreover, it will be necessary to study the impact of other plasma parameters. In particular, the treatment time must be reduced drastically to become acceptable for an industrial roll-to-roll process.

The plasma we used ran under low pressure, and we recognize that vacuum plasmas are not compatible with continuous, online processing and can only be used in batch mode. However, there are studies regarding the economics of vacuum plasma treatments for fabrics and nonwovens that show their economic feasibility for the textile industry.[30] Industrial-scale equipment for textile applications are commercially available. For example, Europlasma NV (Oudenaarde, Belgium) offers a gas plasma system tailored for textile surface treatment capable of treating textile rolls 1800 mm in width with diameter of up to 1000 mm and a speed of up to 20 m/min. It is also true that an atmospheric pressure plasma could better meet the basic manufacturability criteria for textile processing, and several atmospheric pressure plasma types or configurations have been recently developed.[31] The research in the textile field continues to consider both cold plasma processing technologies, and at the moment, no killer application exists to prove that one technology or solution prevails over another.

CONCLUSIONS

In this research, we explored the possibility of reducing the dyeing temperature of wool fabrics by means of oxygen low-temperature plasma pretreatment. The substrates were etched at different discharge powers (30, 50, 60, and 80 W), and the surface morphology was analyzed by means of SEM and AFM. There was a progressive effect of the discharge power on the surface morphological changes caused by the plasma treatment that resulted in an ablation of the polymer surface and an increase in the surface roughness. The wettability of the wool fabric increased drastically, and the wool fiber surface turned permanently from hydrophobic to hydrophilic.

We dyed treated and untreated wool fabrics at different temperatures (98, 85, and 80°C), replicating the dyeing recipe (involving three 1 : 2 metal–complex dyes to obtain a dark shaded blue) and process of a dyeing mill on a laboratory-scale machine, and exhaustion curves of the dye bath were determined.

For each dyeing temperature, improvements in the dyeing kinetics and final bath exhaustions were obtained for plasma-treated fabrics with respect to the untreated ones, and there were no significant differences in terms of final bath exhaustion and half-dyeing time between the treated fabrics at different discharge powers. The plasma treatment greatly increased the initial dyeing rate and shortened the half-dyeing time, improving the diffusion of the dyes into the fibers at lower dyeing temperatures. The final bath exhaustions of the dyeings at 85°C of the plasma-treated fabrics were comparable with that of the reference (the untreated fabric dyed at 98°C), unlike the dyeings at 80°C of the plasma-treated fabrics. As expected, even the final bath exhaustions for the 85 and 80°C dyeings of untreated fabrics were not acceptable.

Furthermore, the resistances of the color of fabrics to organic solvents, to the action of an artificial light source representative of natural daylight, and to rubbing were not changed by the plasma pretreatment.

The treated fabrics were darker than the reference, and the lightness decreased with increasing discharge power and dyeing temperature. On the contrary, the untreated fabrics dyed at temperatures below boiling were paler. Moreover, the color of the treated fabrics showed a reddish hue shift, whereas the untreated fabrics showed an increased greenish hue when they were dyed at lower temperatures. All these differences in color were consequences of a different absorption of the three dyes due to a change in the affinity between the single components of the tern and the fiber, which was dependent on both the treatment and dyeing temperature. However, this behavior could be corrected, if necessary, by modification of the dye percentages in the recipe. Also, these differences are expected to be less relevant with pale-shade dyeing.

In conclusion, this laboratory-scale investigation highlighted that plasma pretreatment allows one to reduce the dyeing temperature (from 98 to 85°C) of wool fabrics without affecting their dyeing performances. On the basis of the aforementioned current limits, future investigations will evaluate the requirements for upscaling the process.

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