# LOW TEMPERATURE PLASMA TREATMENTS OF TEXTILES

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**Key words:** plasma, discharge, afterglow, oxygen, functionalization, textile, wool, polyamide

**Abstract:** Textile finishing is the stage at which their final properties are imparted to fabrics, conferring them with one or many functional properties such as shrink-resistance, water-resistance, softness, antibacterial, etc. At this stage of the textile chain is where a high number of chemicals are used, and often highly polluted wastewaters may be produced, so considering the increasingly strict environmental legislation, low temperature glow discharge plasmas (LTP) have emerged as an environmentally friendly technique for the finishing of textiles. Plasma processes need only small amounts of selected chemicals (if any) and do not produce waste waters or chemical effluents, so the use of plasma processes in textile finishing can reduce its environmental impact. Another advantage of plasma processes is modifying the textile fibre surfaces to a depth of nanometres without altering the bulk properties of the fibres, such as mechanical properties, of relevance in textiles. In the present review work, an overview is given on some outstanding plasma treatments of natural and synthetic fibres. For instance, the effects of plasmas (radiofrequency plasma, microwave post-discharge) on wool fibres and fabrics are shown with respect to their wettability, shrink-resistance, softness and adhesion of polymers. In parallel, the effects of plasma on polyamide 6 fibres and fabrics are shown related to their wettability, ageing properties, post-deposition of biopolymers and dyeability.

# Obdelava tekstilnih materialov z nizkotemperaturno plazmo

**Kjučne besede:** plazma, razelektritev, porazelektritev, kisik, funkcionalizacija, tekstil, volna, poliamid

**Izvleček:** Zadnja stopnja pri obdelavi tekstilnih materialov določa njihove funkcionalne lastnosti, kamor sodijo na primer odpornost proti krčenju, prepustnost za vodne kapljice in paro, mehkost in morebitna bakteriostatičnost. V zadnji stopnji pri obdelavi tekstilij se običajno uporablja obilo kemikalij. Poleg tega so odpadne vode, ki so posledica spiranja kemikalij pogosto močno onesnažene, zaradi česar se iščejo alternativni postopki obdelave. Zaradi vedno ostrejših okoljskih predpisov se vedno bolj širi uporaba okolju prijaznih tehnik, ki temeljijo na uporabi nizkotemperaturne plinske plazme. Pri plazemskih procesih uporabimo zelo majhne količine kemikalij, pogosto pa njihova uporaba sploh ni potrebna, da bi dosegli določene funkcionalne lastnosti tekstilij. Pri plazemskih tehnologijah tekstilij ni potrebno spirati z vodo, zaradi česar se bistveno zmanjša onesnaževanje okolja. Druga pomembna prednost plazemskih tehnologij je možnost modifikacije zgolj površinske plasti debeline nekaj nanometrov, medtem ko ostanejo siceršnje lastnosti materiala nespremenjene. V pričujočem preglednem članku podajamo pregled najpomembnejših dosežkov na področju plazemske modifikacije naravnih in sintetičnih vlaken. Najboljše lastnosti tekstilij dobimo z uporabo plazme, ki jo generiramo z radiofrekvenčno ali mikrovalovno razelektritvijo, pogosto pa namesto plazme uporabimo porazelektritveni del. V prispevku podrobneje predstavimo vpliv plazemske obdelave na volnena vlakna in tekstil. Prikazujemo spremembo omočljivosti, odpornosti proti krčenju, spremembo mehkobe volnenega blaga in sposobnost površinske vezave polimerov. Prav tako prikazujemo vplive plazemske obdelave na sintenična vlakna in tekstilije izdelane iz poliamida PA-6, kjer poseben poudarek posvečamo pojavu staranja vlaken in tekstila,j pa tudi naknadni depoziciji biopolimerov in barvanju.

## 1 Introduction

Wool is a natural fibre mainly constituted by keratins. Morphologically, the fibres are formed by cortical and cuticular cells and cell membrane complex. Cuticular cells are located in the outermost part of the fibre, surrounding the cortical cells. The cuticle consists of a layer of flat scales of approximately 1 μm thickness overlapping one another like tiles on a roof (Fig. 1a), and forming a ratchet-like structure, which provokes a directional frictional effect /1/ which has traditionally been considered the main responsible for felting shrinkage of wool fabrics. Felting shrinkage is a process which comprises compacting and entanglement of fibres submitted to mechanical action, friction and pressure in presence of heat and humidity, and accounts for the undesirable and irreversible reduction of the area of the fabrics. From the chemical point of view, the outermost part of cuticle cells is of hydrophobic nature due to the presence of the "Fatty Layer", a thin layer of 18-methyl eicosanoic acid (18-MEA) covalently bound via a thioester linkage to the protein layer of cuticle /2/. It has recently been shown that the presence of this fatty layer on the surface influences the shrinkage behaviour of wool fabrics during aqueous washing /3/.

Polyamide 6 is a chemical fibre, also known as nylon 6 (H-[NH-$C_5H_{10}$-CO]$_n$-OH), is an aliphatic polyamide obtained through polycondensation reaction of ε-caprolactam. It is characterized by recurring amide groups (-CONH-) in the polymeric chain and amino and carboxylic end groups /4/.

Low temperature glow discharge plasmas (LTP) are considered as an emerging technique in the achievement of wool with shrink-resistant properties by environmentally friendly methods /5/, as well as on the surface modification of textile fibres in general, as they modify the fibre surface to a depth of nanometers, without altering the bulk properties of the fibre. Plasma processes need only small amounts of selected chemicals and do not produce wastewater or chemical effluents, so plasma is efficient, economical, and can reduce the environmental impact caused by the use of chemicals in the textile industry, traditionally extensive in the consumption of water and chemicals. Plasma is a partially ionized gas generated by an electrical discharge, and consists of neutral particles (molecules, ex-

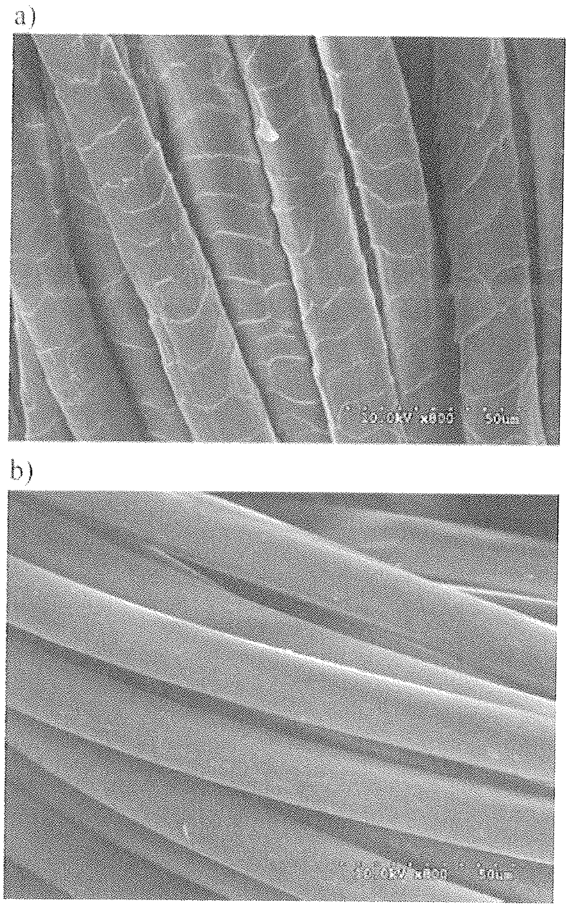


*Fig. 1: Morphology of (a) wool and (b) polyamide 6 fibres.*

cited atoms, free radicals and metastable particles), charged particles (ions and electrons) and UV and V radiation. Plasma chemistry takes place while the gas remains at relatively low temperatures, close to room temperature /6/. Due to these oxidative processes the wetting properties of the surface of fibres are improved, and therefore the adhesion properties /7,8/. In the plasma discharge, high density of species such as ions, electrons and UV radiation in addition to the active atoms already mentioned, can act on the fibre surface. Such ions disappear by recombination with electrons at the end of the discharge, as well as UV and other excited species, so in the post-discharge only stable atoms are present /9/.

Different kinds of plasmas have been extensively studied /10-23/ and characterized /24-28/ for the synthesis of ordered nanostructures /20-33/, for the engineering of materials /34-37/ and for surface functionalisation /38-51/ for example.

In the present paper an overview is given on the effects of plasma and post-discharge plasma treatments on natural (wool) and chemical fibres (polyamide 6), and its possible combination with different chemical post-treatments for obtaining textiles with different functionalities.

## 2 Experimental

### 2.1 Materials

Botany knitted merino wool fabric with a cover factor of 1.22 $tex^{1/2}mm^{-1}$ was used throughout the work. Keratin hair fibers were used as a model for the wool fiber on the determination of contact angle due to their chemical and morphological similarities /52/. Before treatment, fabrics and fibers were washed with a solution of 2 $g.L^{-1}$ of the non-ionic surfactant Cadetram 9M (Comp. Suministros Cades S. A.), at 25°C for 15 min and then thoroughly rinsed with deionized water and dried at ambient temperature.

PA6 microfiber fabrics were used throughout this work and washed with 2 $g.L^{-1}$ of surfactant solution (Nekanil LN) at 95°C for 45 min and then thoroughly rinsed with deionized water and dried at ambient temperature.

PA6 rods (Goodfellow Ltd, UK) of 2 mm diameter were used for the determination of contact angle. Prior to any treatment, they were cleaned by Soxhlet extraction with benzene (Probus, Spain) and acetone (Merck, Germany).

### 2.2 Methods

A radio-frequency (RF) reactor (Fig. 2) operating at 13.56 MHz was employed /53/ using air, nitrogen or water vapour as plasma gases. The distance between the electrodes was 8.5 cm, and the sample was hung equidistant between the electrodes. During treatments, the pressure and the incident power were kept constant at 100 Pa and 100 W, respectively. This power was uniformly distributed on a 400 $cm^2$ cathode surface.

A flowing post-discharge (PD) reactor (Fig. 3) was used /54/, composed of a pyrex cylinder of 15 cm of internal diameter (i.d.) and 20 cm height separated 70 cm from

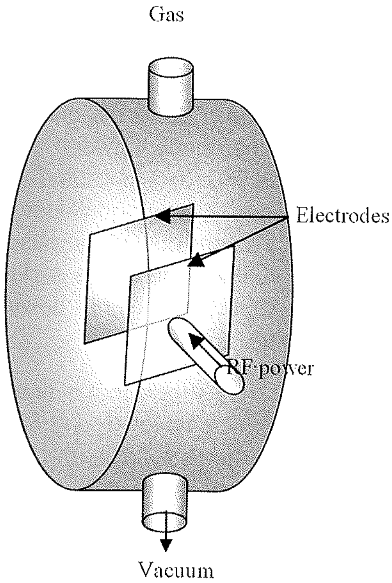


*Fig. 2. Schematic description of the stainless steel reaction chamber*

the plasma source by a 5 mm i.d. quartz tube. The discharges were generated by a 2.45 GHz microwave source using 60 W of incident power. The discharge tube is sealed to a bent quartz tube of 15 mm i.d. which is connected to the post-discharge reactor. The gas flow rate was set constant at 1 $L.min^{-1}$ and the pressure in the reactor was 533 Pa (4 Torr). The samples were hung vertically in the center of the reactor.

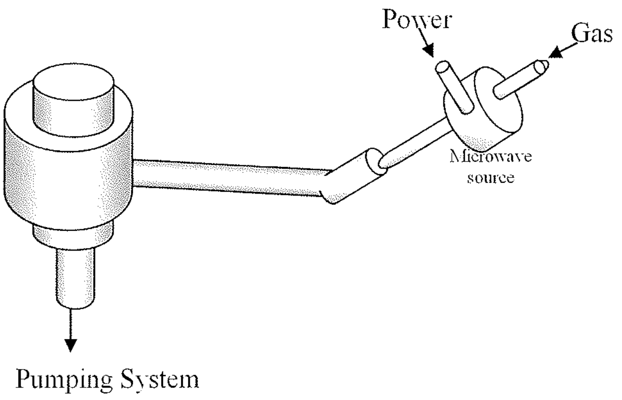


*Fig. 3. Scheme of the pyrex post-discharge reaction chamber*

Optical emission spectroscopy and catalytic probes was used to characterize post-discharges as described in /55/. Contact angles, X-ray photoelectron spectroscopy, scanning electron microscopy and shrink-resistance methods were carried out as described in /53, 56/.

## 3 Results and discussion

In the course of different works, we have compared the effects of plasma and post-discharges (PD) on the properties of wool and polyamide 6 fibres and fabrics.

### 3.1. Effects of plasma on wool

One of the main features characterizing wettability of untreated (UT) wool fibres is their different receding adhesion tension as a function of scale direction (Fig. 4a), attributed to chemical differences between the frontal and the dorsal of the scales (Fig. 5). After both RF plasma and PD (Figs. 4 b and c) with oxygen-containing gases, this feature is no longer present due to increased chemical homogeneity of the cuticle scales. The surface of the fibres becomes hydrophilic, with higher advancing adhesion tension (F/L) values.

Previous studies /57/ had shown that a direct $N_2$ plasma treatment produced a decrease of around 58° in the contact angle of keratin fibres after 2 min, and thus an important increase in the wettability, while 15 min of $N_2$ PD resulted in a decrease of 42° /55/. Consequently, both post-discharge plasmas and direct plasmas are efficient for producing hydrophilic wool surfaces, although slightly longer treatment times are required for achieving similar hydrophilicity with PD than with direct discharges.

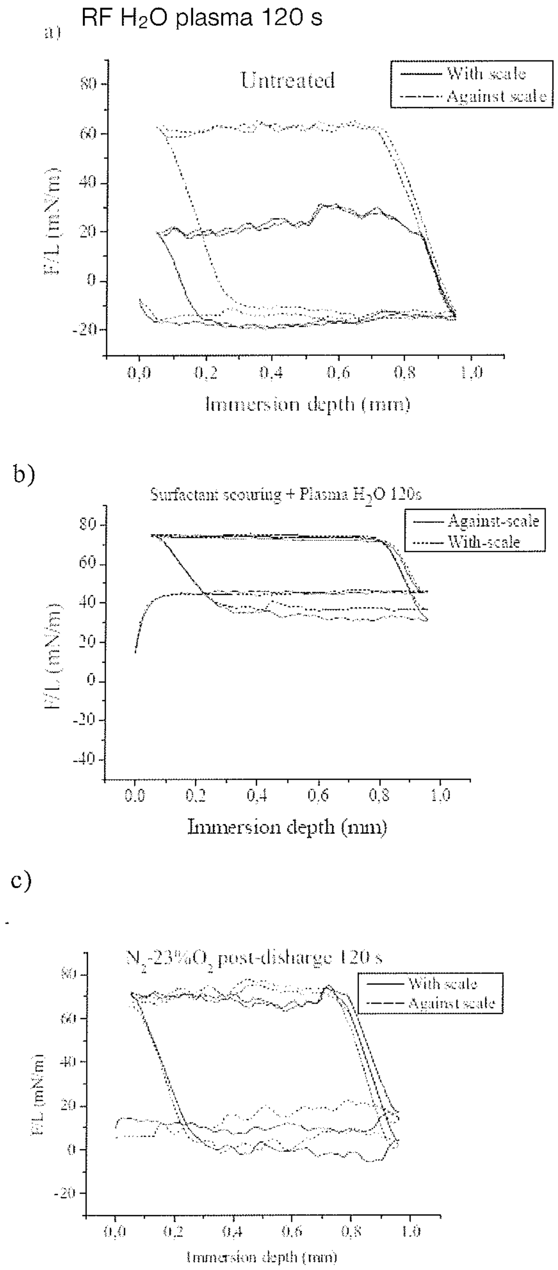


*Fig. 4: Adhesion tension wetting hysteresis cycles of UT (a), $H_2O$ RF plasma treated (b) and $N_2$-23% $O_2$ PD treated (c) keratin fibres in water.*

When the plasma is generated by an oxidative gas, such as air, oxygen or water vapour, the wool fibre surface is oxidized progressively by forming C-OH, C=O, HOC=O groups, and promoting an ablation effect of the fatty layer. Also, the cystine residues of wool are oxidized to cysteic acid residues increasing the anionic groups on the wool fibre surface /52, 54, 58/.

It has been shown that the effects produced by plasma and PD treatments on the surface are mainly due to the neutral atoms of the discharges /54/, as detected by optical emission spectroscopy. The use of catalytic probes for O detection during PD treatment of wool /59/ revealed that the etching process of the fatty layer, which takes place

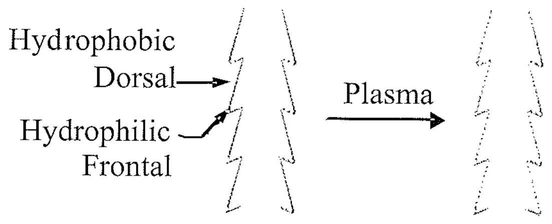


*Fig. 5: Schematic representation of the chemical homogeneisation of the dorsal and frontal of the wool cuticle scales by the action of plasma*

at the early stages of treatment, represents a great source of consumption of atoms.

Several publications have shown the shrink-resistance effect promoted by plasma on wool fabrics. Comparison (Fig. 6) of the shrink-resistance effect of direct and post-discharge $N_2$ plasma on wool fabrics /55/ revealed the equivalent effectiveness of both treatments, although to achieve equivalent shrinkage reduction percentages, longer treatment times have to be applied with post-discharge plasma. The slightly longer times required to achieve similar shrinkage reduction percentages (as well as similar contact angles) on $N_2$ PD treated wool can be explained by the fact that only N atoms are present, while in direct plasmas, the added effect of ions and UV radiation has to be considered.

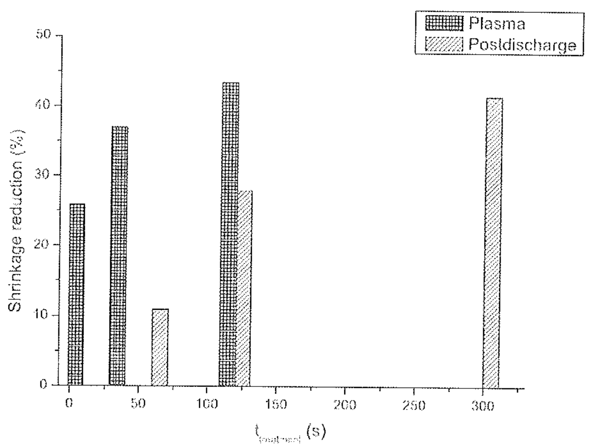


*Fig. 6. Comparison of the shrinkage reduction attained by direct plasma treatment or by post-discharge plasma.*

Post-application of finishing products on the surface of wool after plasma treatment has been the object of different studies, and its interest lays in the wide number of textile finishes which would benefit from increased adhesion product-fibre, or the possibility of employing lower quantities of chemicals. One of the critical points in plasma treatment of wool is the improvement of handle of the fabrics, which is harsher after the plasma treatment. Given the ageing in wettability observed /60/, it is advisable to carry out such post-treatments as soon as possible after plasma.

Through the application of acid chlorides on UT and RF plasma treated wool it was shown that the presence of the fatty-layer on the surface of UT wool exerts a strong influence on the post-deposition of products /3/. After the oxidation and partial elimination of the fatty-layer through a plasma treatment, post-application of acid chlorides of different chain length revealed a clear relationship between wettability and shrink-resistance (Fig. 7). The higher the wettability, the better the shrink-resistance. In addition, handle evaluation showed, as expected, that the longer the chain length, the better the softness perceived.

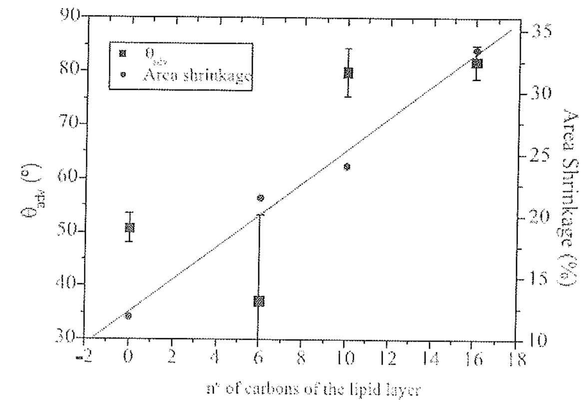


*Fig. 7: Relationship between advancing contact angle ($\Theta_{adv}$) and area shrinkage as a function of the number of carbons theoretically present on the surface, playing the role of fatty-layer.*

The application of conventional cationic softeners on RF plasma treated wool fabrics reverts in high shrinkage values /60/. The application of certain cationic or polar polysiloxane softeners on $H_2O$ RF plasma-treated wool improves the handle of the fabrics and the deposition of the softener while conserving an acceptable shrink-resistance /56/. A possible mechanism of interaction between the different polysiloxane groups and the surface of untreated (UT) and LTP-treated wool was proposed, as shown in Fig.8.

## 3.2. Effects of plasma on polyamide 6

Contrarily to wool, untreated polyamide 6 (PA6) is a chemical fibre of hydrophilic nature (see Table 1). As can be seen, when air and nitrogen were used as RF plasma gases, an important increase in the hydrophilicity of polyamide surface was achieved, with very similar advancing contact angle values /61/. The treatment with water vapor plasma was the most effective to generate highly hydrophilic PA6 surfaces, reducing the advancing contact angle to 34.7°.

The ageing process of RF plasma treated PA6 was studied by means of contact angle /61/ as a function of storage time after treatment.

Figure 9 shows an increase in hydrophobicity of the plasma treated PA6 as a function of the time elapsed after plasma treatment, indicating that the concentration of hydrophilic groups on the surface decreases, which could

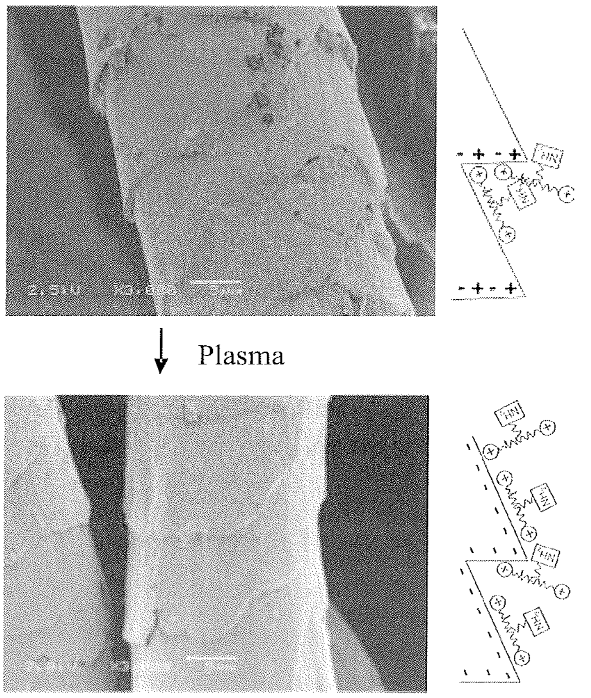


*Fig. 8: SEM images and proposed mechanism of interaction between wool (UT - up, and $H_2O$ plasma treated - down) and a cationic polysiloxane.*

Table 1. Advancing ($\Theta_{adv}$) contact angle and contact angle hysteresis ($\Delta\Theta$) of PA6 UT and treated for 2 min in plasma or PD of different gases

| **Treatment** | $\theta_{adv}$ ± 2.2° (°) | $\Delta\theta$ (°) |
|---|---|---|
| *Untreated* | *71.4* | *55.8* |
| Air RF plasma | 53.4 | 46.2 |
| $N_2$ RF plasma | 49.7 | 41.3 |
| *$N_2$ post-discharge* | *43.3* | *30.1* |
| $H_2O$ plasma | 34.7 | 26.1 |
| *$O_2$ post-discharge* | *45.8* | *28.4* |

be due to migrarion or reorientation of these groups towards the bulk phase of PA6 during their storage in air environment. This point was confirmed by immersion of the aged samples in water /61/, which revealed a partial recovery of the wetting properties, or even complete recovery in PA6 treated in oxidizing plasma gases.

Relevant topographical modifications (in general undesirable for textile finishing purposes), are only achieved in relatively aggressive conditions, such as oxygen treatments for long times in both RF plasmas or post-discharges (Fig. 10).

Post-application of finishing products on PA6 can be aimed to different effects, such as improving dye exhaustion or increasing colour intensity (K/S) of dyeings. Chitosan is a polycationic biopolymer which has been applied to fabrics to confer antibacterial properties. In this case, its application was studied to enhance efficiency of dyeings.

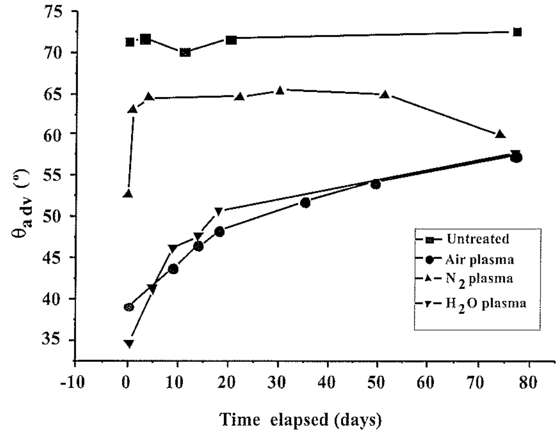


*Fig. 9: Evolution of advancing water contact angle as a function of time elapsed after the treatment.*

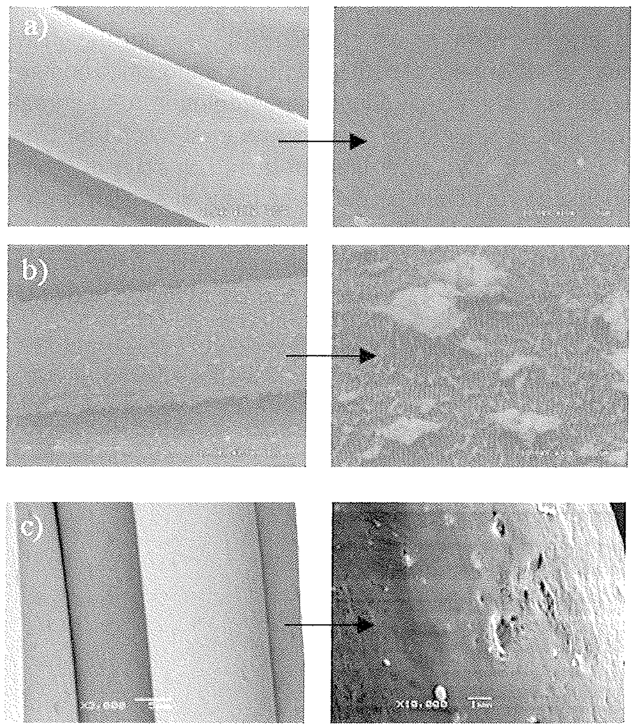


*Fig. 10: Scanning Electron Micrographs of PA6 (a) Untreated, (b) 5 min $O_2$ RF plasma and (c) 15 min $O_2$ post-discharge treated.*

Contact angle results (Fig. 11) showed improved adhesion of chitosan on the surface of $H_2O$ RF plasma-treated PA6.

The presence of chitosan on the surface of the fibres increased colour intensity of the dyeings (Fig. 12), with respect to those only treated with plasma. This is most probably due to the good interaction of the sulfonic groups of the acid dyestuff studied with the amine groups of the chitosan biopolymer deposited on the surface of polyamide 6 fibres.

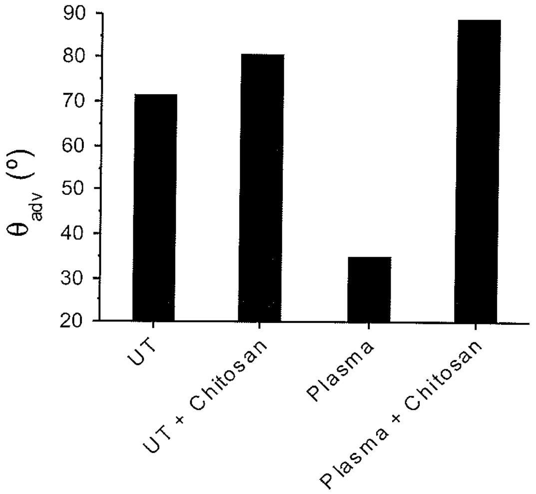


*Fig. 11: Advancing contact angle of UT and $H_2O$ RF plasma treated PA6 post-treated with chitosan.*

(a)

(b)

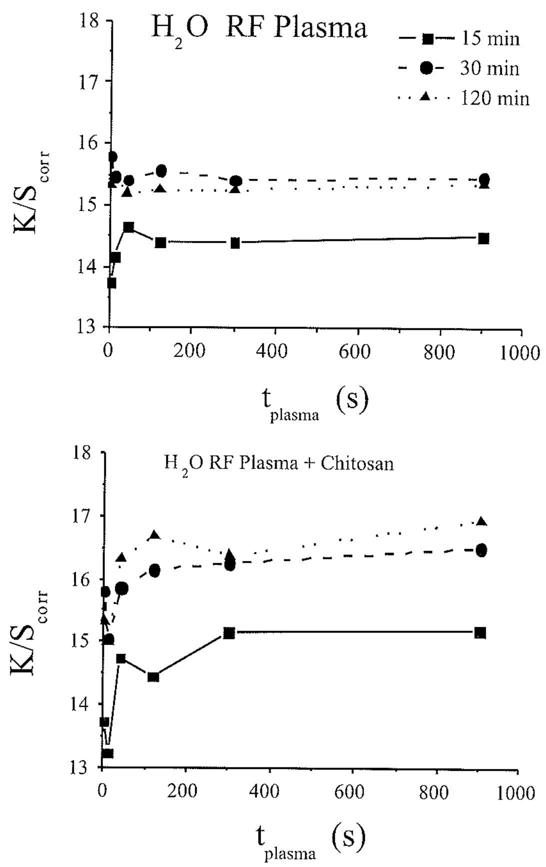


*Fig. 12: $K/S_{corr}$ of PA6 fabric treated different times in $H_2O$ plasma (a) and post-treated with chitosan (1.25 g/l) (b) in dyeings with acid dyestuff.*

## 4 Conclusions

Consumers increasingly demand for fabrics with improved properties, and are also more environmentally conscious. In this context plasma treatment of fibers and fabrics provides an alternative technology which allows complying with both requirements.

As reviewed in the paper, plasma and post-discharge treatments improve wool and PA6 wettability, reduce shrink-resistance of wool, and the etching of the fatty-layer on the surface of wool allows control over the wetting properties in the post-application of different finishing products (such as softeners). The ageing of wetting properties is a parameter to control in the post-application of finishing products. The application of a biopolymer on PA6 fabrics has been enhanced by plasma treatments, and it promotes higher colour intensity in dyeing with acid dyes.

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