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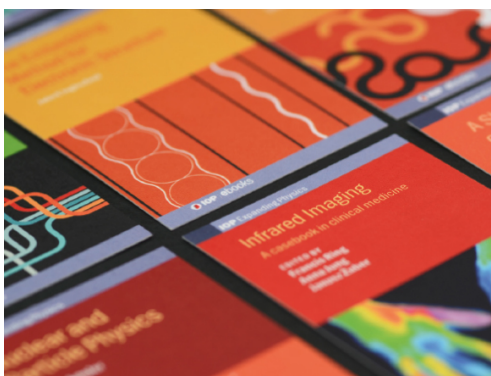
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## Environmental impact of plasma application to textiles

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**Abstract.** Plasma technology is currently implemented in a wide range of industrial processes due to high efficiency, low environmental impact and simplicity. Low-temperature plasma treatment can be an alternative to traditional wet processes in textile preparation and finishing, causing modification of the fibre surface, which is mainly responsible for the material end-use properties i.e. wettability, dyeability, printability, shrinking, pilling etc. Appropriate choice of gas and control of plasma operation conditions provide a variety of effects on textiles (improvement of dyeability, printability and colour fastness, improvement of adhesion properties of coated fabrics, increase in hydrophobicity and water resistance, etc.). However, in spite of extraordinary efficiency, multifunctionality and simplicity, low-temperature plasma treatments still cannot replace all wet finishing processes, though they can be viable pre-treatments that offer plenty of environmental and economical benefits.

### 1. Introduction

Maintenance of a cleaner environment recently became one of the most important global concerns. Growing industrialization significantly contributed to an increase of pollution, but insufficient efforts have been made to continue further industrial progress by adopting cleaner production technologies. The introduction of rigorous ecological legislation particularly in developed countries in the last decade forced the companies to face the environmental problems and to consider not only the issue of industrial wastes but also a possible replacement of conventional processes with treatments that can provide equal or even higher efficiency and lower environmental impact. However, solving the environmental problems in textile industry is not an easy task because of the fact that it comprises of too many different sectors, which use a variety of toxic, hazardous and poor biodegradable compounds and auxiliaries. High water and energy consumption, high oxygen demand of several input materials being used as well as a generation of huge amounts of effluents with high chemical oxygen demand (COD), excessive colour, pH and toxicity are only some of the items illustrating the complexity of textile processing environmental impact. In general, desizing (the process of removing the size chemicals from textiles), dyeing, washing and finishing are the main sources of effluent pollution.

Positive experience and interest for plasma processing in microelectronics production, automotive industry, biomedical applications and modification of polymers [1-2] is being slowly transferred to the textile industry though still more at a scientific level. Nonequilibrium plasma treatment of textiles offers plenty of functional, environmental and economical benefits. It can be carried out at low-pressures and atmospheric pressure (corona and dielectric barrier discharge treatments). While there

are numerous studies on development of atmospheric pressure non-equilibrium (glow) plasmas [3-4], low-pressure treatment offers much better stability, control and reproducibility [5].

The multifunctionality of plasma processing is reflected in the possibility of using one system for modification of different kinds of fibres (natural protein and cellulose, synthetic) and textile forms with highly flexible product functional design [6]. Thus, appropriate choice of gas ( $O_2$ ,  $N_2$ ,  $H_2$ , air, Ar, He,  $NH_3$ , hydrocarbons, fluorocarbons) and control of plasma operating conditions (treatment time, power, pressure, gas flow rate) provide intrinsic effects on textiles:

- improved hydrophilicity
- improved hydrophobicity/oleophilicity
- enhanced chemical reactivity of naturally inert materials
- improved adhesion of coatings and matrices
- improved material chemical and mechanical resistance.

The fibre surface modification is a crucial point in numerous processes and applications since the fibre surface is mostly responsible for the majority of end-use properties of textile products (wettability, dyeability, printability, felting shrinkage in case of wool, pilling, electrostatic properties, water resistance) [7]. Therefore, plasma treatment seems to be very convenient because it is confined to the fibre surface, leaving the bulk properties unchanged [8-9]. However, the main advantage of plasma processing is that it is a dry treatment. Additionally, it is a very energy efficient and clean process. In general, the environmental benefits of plasma treatment can be summarized as:

- reduced amount of chemicals needed in conventional processing
- better exhaustion of chemicals from the bath
- reduced BOD/COD of effluents
- shortening of the wet processing time
- decrease in needed wet processing temperature
- energy savings.

Taking into account broad field of plasma applications and the limitation of space to review them all, this paper discusses only our results on plasma treatment of different textile materials from environmental standpoint.

## **2. Environmental impact of plasma on textile dyeing and printing**

Low-pressure RF plasma treatment (in further text plasma treatment) ( $O_2$ ,  $N_2$ ,  $H_2$ , air, Ar, He,  $NH_3$ ) leads to an increase in textile wettability even in case of highly hydrophobic synthetic materials [6]. Our results indicated that Ar,  $O_2$  and air plasma drastically improved the wettability of wool knitted fabric [10-11]. The wetting time of untreated wool was more than 3 hours. However, only 2.5 minutes of plasma treatment shortened wetting time to 2-2.5 s depending on applied gas. No significant influence of pressure on wettability was observed as shown in figure 1 [10]. Additionally, plasma treatment brought about enhanced swelling of wool fibres (figure 2) [10]. Swelling was the most pronounced in case of oxygen plasma, whereas air plasma performed swelling degree of the same order as conventionally chlorinated sample [12-13].

Improved wettability and swelling of wool are attributed to plasma modification of layer of covalently bound fatty acids known as F-layer, which is mostly responsible for natural hydrophobicity of wool fibre surface [14-15]. The bombardment of material with different plasma particles (ions, radicals, metastables, neutrals) induces the etching and oxidation of fibre surface. Prolongation of treatment time may cause not only modification but also partial removal of surface layers due to severe plasma etching. Consequently, fibre becomes more accessible to water and dye molecules.

It is suggested that plasma etching is likely responsible for an increase in water retention of hemp woven fabric [16-17]. Water retention of hemp fabric treated for 5 minutes in air plasma (100 W, 0.27 mbar) was higher for approximately 9% compared to untreated sample.

Increase in wettability and swelling after plasma treatments significantly affect the dyeing and printing properties of wool [18-22]. The dye-exhaustion curves of untreated, chlorinated and

differently plasma treated (100 W, 0.5 mbar, 10 min) wool knitted fabrics for acid dyes C.I. Acid Green 25 and C.I. Acid Blue 40 are shown in figures 3 and 4, respectively [13, 21]. Obviously, plasma treatment caused a slight increase in final dye exhaustion, but this is very much influenced by the type of the dye studied. No significant difference in dyeing behaviour between plasma treated samples modified under different operating conditions (pressure and treatment time) occurred. However, plasma treatment of wool led to a remarkable increase in dyeing rate. The equilibrium exhaustion was established much faster compared to untreated or conventionally chlorinated sample. Furthermore, dye fastness is significantly improved after plasma treatment [21].

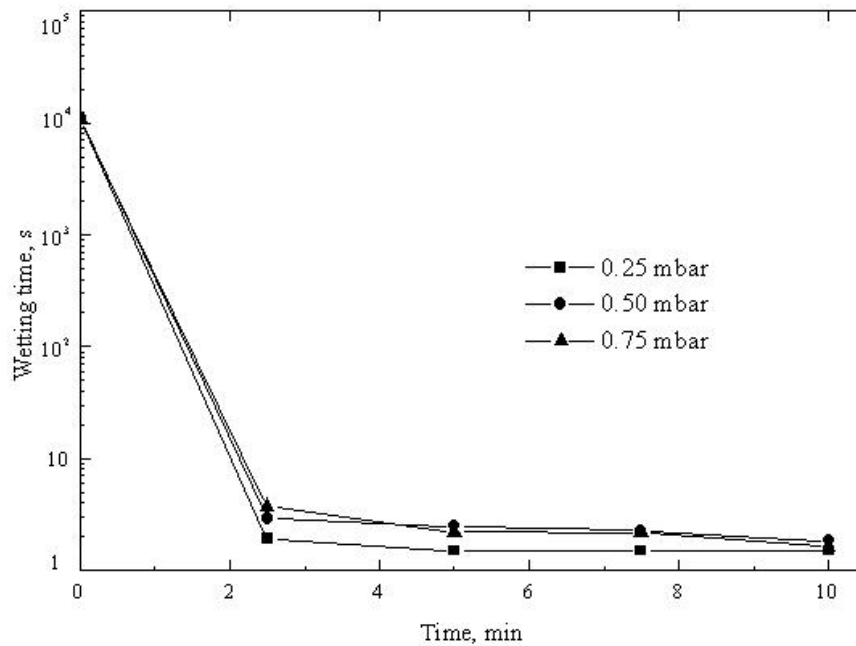


Figure 1. Wetting time vs. treatment time of air plasma treated wool knitted fabric (P=100 W) [10].

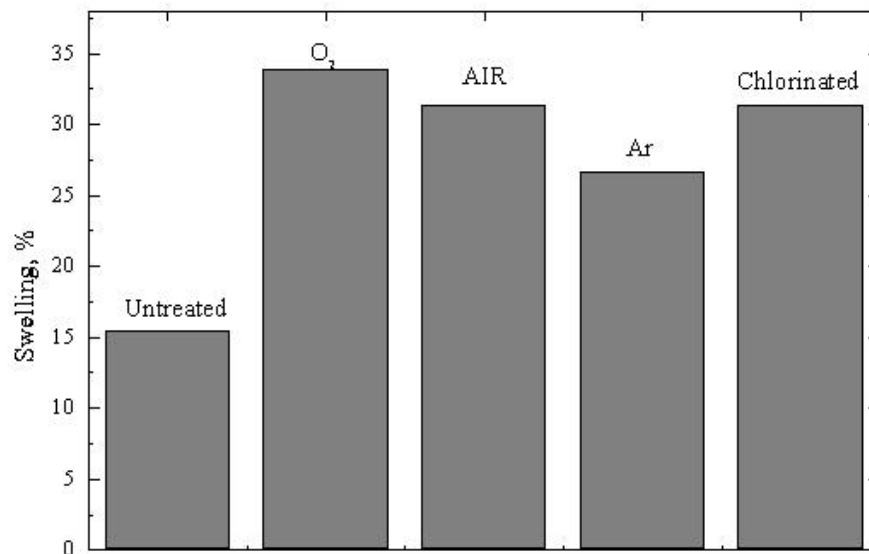
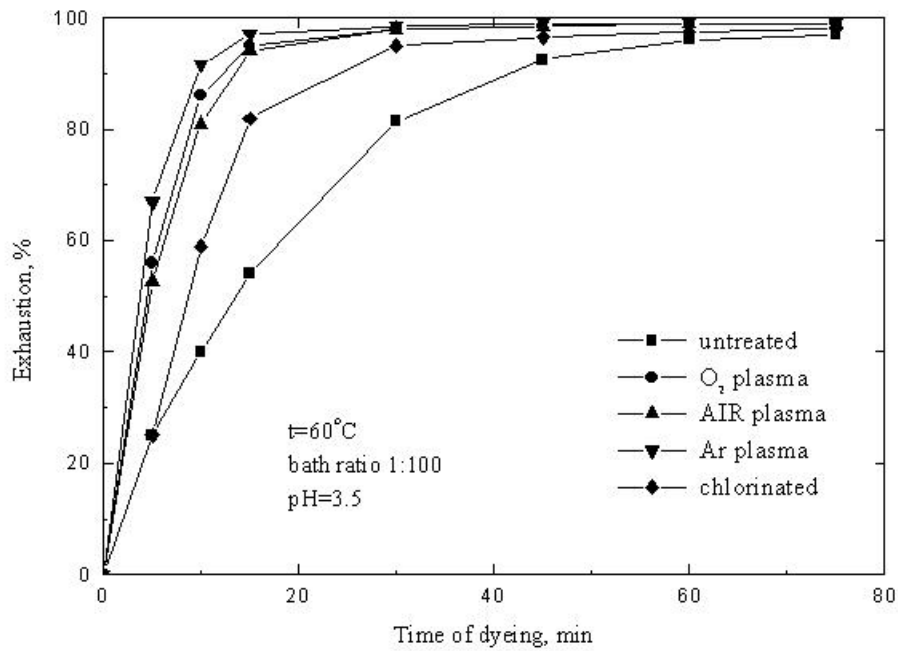
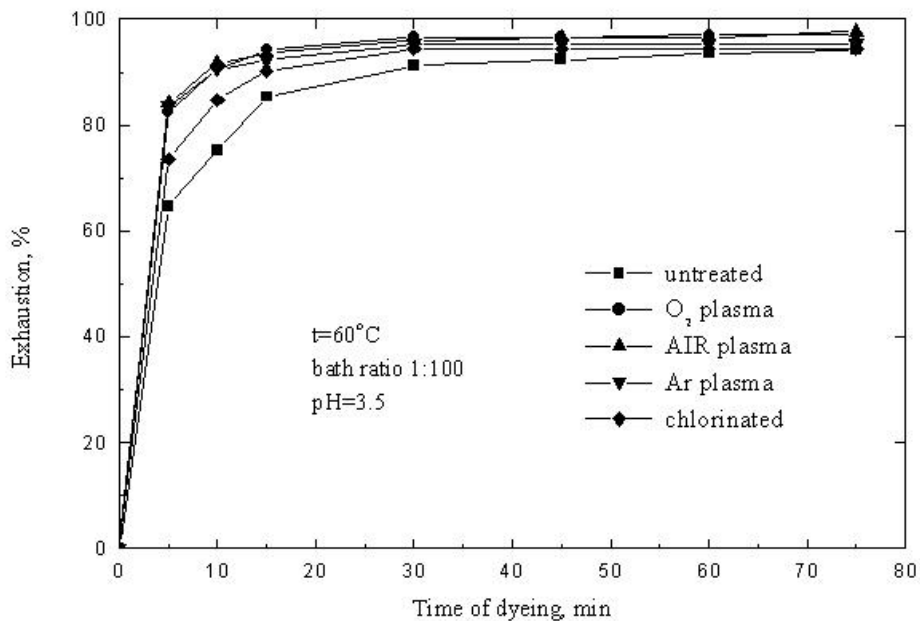


Figure 2. Swelling of wool fibres [10].



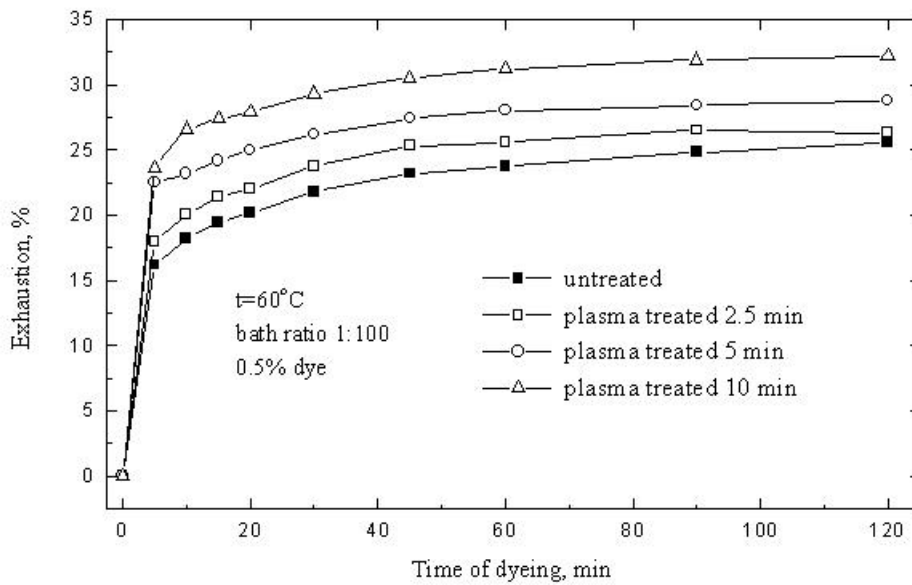
**Figure 3.** Dye-exhaustion curves of untreated and plasma treated wool knitted fabrics (C.I. Acid Green 25, P=100 W, p=0.5 mbar,  $\tau=10$  min) [13, 21].



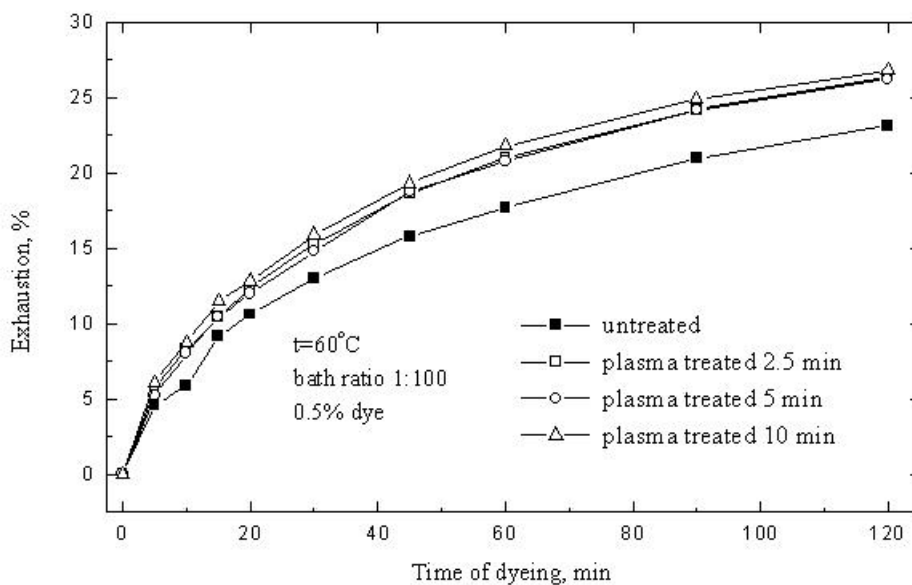
**Figure 4.** Dye-exhaustion curves of untreated and plasma treated wool knitted fabrics (C.I. Acid Blue 40, P=100W, p=0.5 mbar,  $\tau=10$  min) [13, 21].

Dye-exhaustion curves for dyeing of air plasma treated (100 W, 0.27 mbar, 10 min) and untreated hemp fabrics with dyes C.I. Acid Blue 113 and C.I. Direct Red 81 are shown in figure 5 and 6, respectively. Apparently, plasma treatment induced considerable increase in dyeing rate and final dye exhaustion. The longer the plasma treatment time, the higher the final exhaustion in case of acid dye [17, 21-22]. However, prolongation of plasma treatment time in case of direct dye demonstrated no

significant influence on the dye exhaustion and obviously dye-exhaustion curves overlapped. Enhanced dye exhaustion and higher dyeing rates of treated samples are attributed to plasma etching and oxidation [17]. It is likely that plasma etching increased fiber porosity and induced minor topographical changes that make hemp fiber more susceptible to dye and water molecules. Easier diffusion of dye into the fiber caused by plasma treatment is not sufficient for an increase in dye exhaustion as it is also considerably influenced by the structure, molecular weight and state of dye in dyeing bath. Therefore, direct dye as a dye with high substantivity and rate of diffusion is easily bound to active sites of the fiber and consequently it is poorly affected by prolongation of plasma treatment time. On the contrary, acid dye exhibits low substantivity and dyeing is mainly controlled by diffusion, which is remarkably promoted by plasma treatment.



**Figure 5.** Dye-exhaustion curves of untreated and plasma treated hemp fabrics (C.I. Acid Blue 118,  $p=0.27$  mbar,  $P=100$  W) [22].

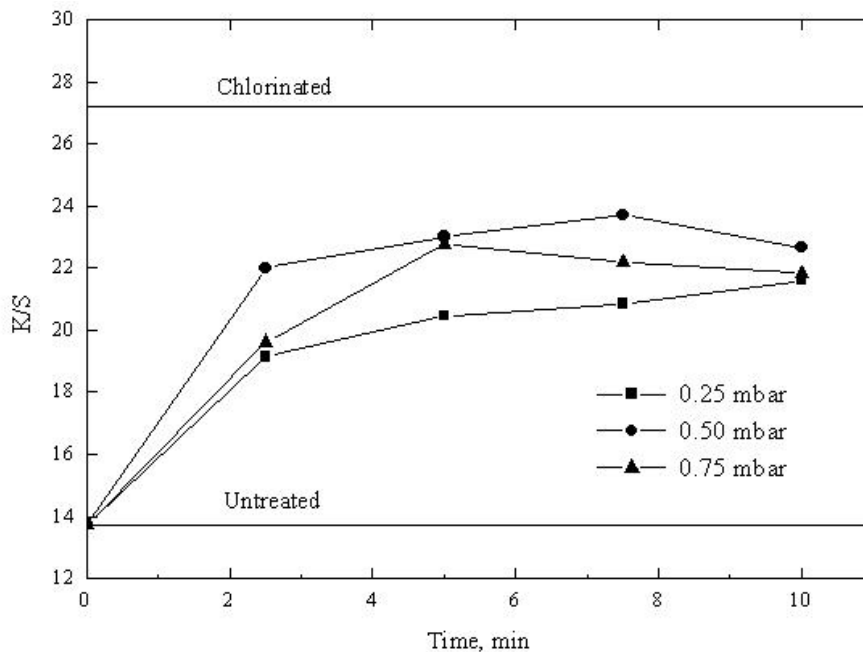


**Figure 6.** Dye-exhaustion curves of untreated and plasma treated hemp fabrics (C.I. Direct Red 81,  $p=0.27$  mbar,  $P=100$  W) [22].

Higher dye exhaustion in case of plasma treated textiles pointed out that these materials may require less amounts of dyestuff for a desired shade. Since dye exhaustion is strongly affected by the initial dye concentration, a decrease in the amount of dye used can possibly contribute to a diminished effluent load [23]. Higher dyeing rates indicate the possibility of shortening the dyeing time and the reduction in energy consumption since less time is needed to obtain the desirable state of dyeing [24].

Recently, it was established that plasma treated recycle-wool based non-woven material can be used as an efficient sorbent for removal of acid dyes and heavy metal ions from water [25-26].

It is well known that adequate preparation of wool prior to printing provides high quality prints [27]. Corona and low-pressure plasma treatments cause the significant improvement of wool printability [10, 19, 28]. The Kubelka-Munk values (K/S) were used as a measure of the colour yield at the surface of the print [10, 19, 28-29]. The influence of treatment time and pressure on K/S values of argon plasma treated wool is shown in figure 7 [10, 28]. Only 2.5 min of plasma treatment led to a remarkable increase in colour yield. The prolongation of treatment time resulted in improved printability. Similar results were obtained in case of air and oxygen plasma treated wool [10, 28]. Improved printability can be attributed to enhanced wettability and swelling since the fibre became more accessible to water and dye molecules which could penetrate much easier to the fibre interior [10]. The effect of pressure on colour yield increased in following order: 0.50 mbar > 0.75 mbar > 0.25 mbar that is explained by the pressure dependent efficiency of the production of active plasma particles [10].



**Figure 7.** K/S values vs. treatment time of Ar plasma treated and subsequently printed (Bemacid Red CM-2G) wool knitted fabric ( $\tau=2.5$  min,  $P=100$  W) [10, 28].

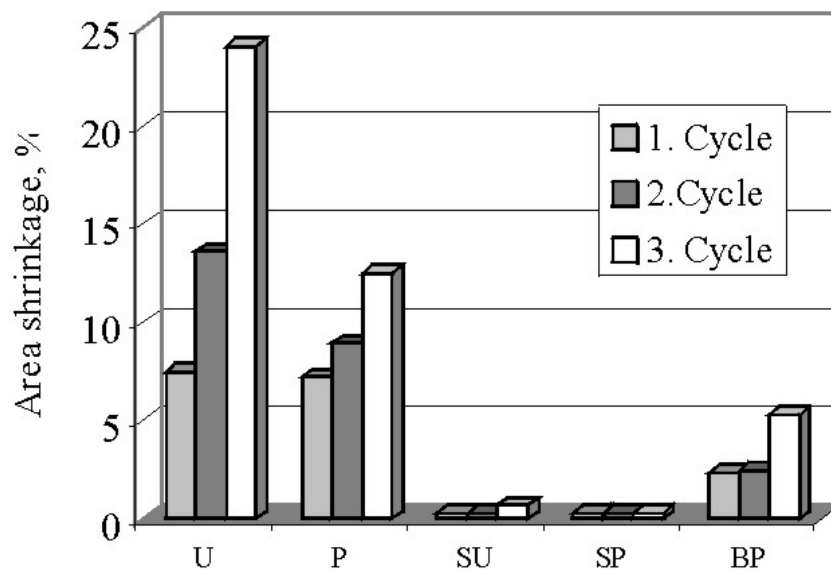
The results also revealed that colour yield of plasma treated samples did not reach the efficiency of a conventionally chlorinated sample, but even short plasma treatments ensured sufficient preparation of wool knitted fabric prior to printing. This is very important from environmental point of view since conventional preparation of wool for dyeing and printing as well as for imparting of felting shrinkage resistance to wool products is carried out by Chlorine-Hercosett process [30-31]. Despite its high efficiency, high water consumption and generation of adsorbable organo halides (AOX) make this treatment environmentally unfriendly. The adoption of advanced chemicals may improve process

efficiency, but these compounds or their by-products can deteriorate already complex wastewater composition. Therefore, the implementation of preferentially dry and clean technologies is required.

The comparative cost analysis of conventional chlorination and plasma processing of wool [31-32] demonstrated that energy costs for chlorination are 7 kWh/kg wool whereas for low-pressure plasma treatment only 0.3-0.6 kWh/kg wool. The application of low-pressure plasma for the modification of 120 t/year of wool can save 27000 m<sup>3</sup> of water, 44 t of sodium hypochlorite, 16 t of sodium bisulphite, 11 t of sulphuric acid and 685 MWh of electrical energy [32-33].

### 3. Environmental impact of plasma on anti-felting treatment of wool

One of the most difficult problems wool industry must deal with is felting shrinkage. Felting of wool occurs primarily because of the specific scale-like, hydrophobic surface of fibre. In addition to increase in fibre surface hydrophilicity, plasma treatment induces the morphological and frictional changes, reducing the felting shrinkage of wool [34-42]. The area shrinkage of untreated wool fabric and wool fabric treated in dielectric barrier-discharge (dbd) after three 5A washing cycles carried out in accordance with Woolmark TM31 is shown in figure 8 [12]. Plasma treatment significantly reduced the tendency of wool to shrink. The changes of fibre frictional coefficients, oxidation of the fibre surface and modification of fibre surface F-layer are claimed to be the main reasons for the improvement of shrinkproofing of plasma treated wool [19, 43]. Although the surface became very rough and the fibre/fibre friction increased, felting shrinkage was significantly reduced because of the decrease in differential frictional effect (DFE) [43]. However, area shrinkage of plasma treated wool fabric exceeded the maximum approved value and subsequent treatment with suitable polymer is necessary [3, 37, 44]. The application of polymers resulted in considerable decrease in area shrinkage particularly in case of Synthappret BAP (figure 8), indicating that further decrease in DFE occurred [45], imparting the machine washable wool (i.e. super wash wool).



**Figure 8.** Area Shrinkage of untreated (U), plasma (dbd) treated (P), untreated+Synthappret BAP treated (SU), plasma (dbd)+Synthappret BAP treated (SP) and plasma (dbd)+Basolan MW treated wool fabric [12].

Evidently, machine washable wool can be produced by combined plasma/polymer treatments. Elimination of water in plasma treatment, which is impossible in conventional chlorination as well as the fact that it is AOX-free process are the main advantages of this treatment. Special contribution to

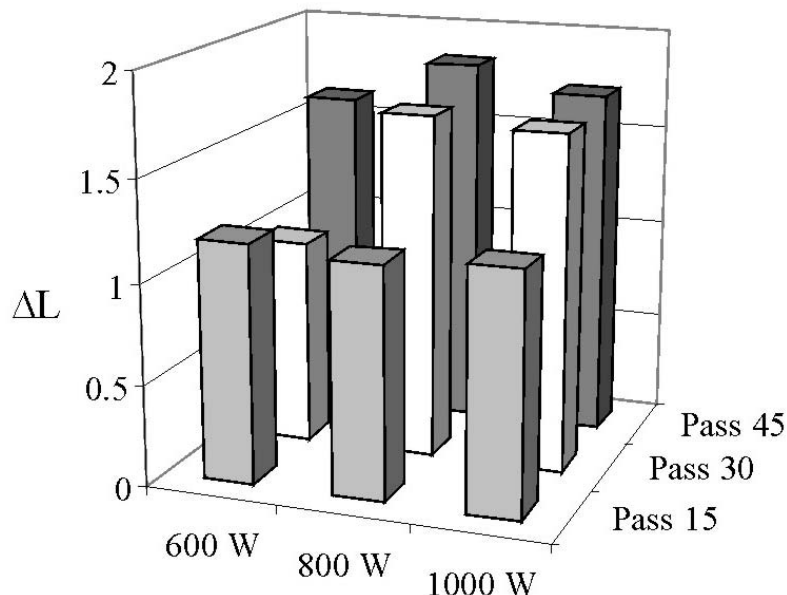


lowering environmental impact can be obtained by replacing commercially available synthetic polymers with biopolymers such as collagen or chitosan [46-47].

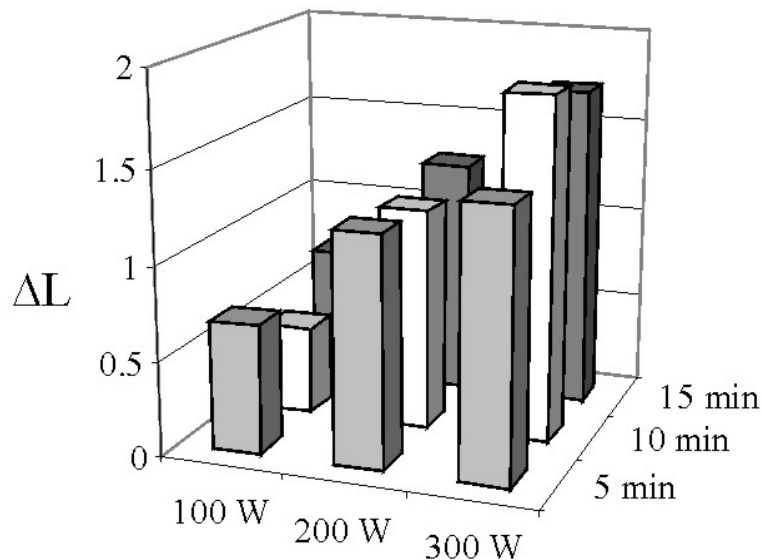
#### 4. Environmental impact of plasma on denim finishing

The popularity of “worn look” of denim products lasts more than two decades. Originally, abrasive action of pumice stones on the garment surface was used to achieve this effect. Though efficient, traditional stonewashing often caused the damage of garments and machines. Additionally, the problem of a huge amount of pumice dust in the laundry environment and reduction of machine capacity due to high proportion of stones (up to 1 kg of stones per kg of jeans) occurred. The development of enzymatic stonewashing (bio-stoning) partially or completely replaced stonewashing. Bio-stoning with enzymes cellulase provides soft handle and desired look [48-49]. However, bio-stoning requires high quantity of water and chemicals that are released into effluents, making the process less eco-friendly.

Recently, low-pressure plasma and corona treatments for obtaining “worn look” effect on denim fabrics are proposed [50-51]. In our study, CIE Lab colorimetric system was used for determination of colour difference between untreated and plasma treated denim fabrics. The lightness difference between untreated and corona and low-pressure argon plasma treated denim fabrics are demonstrated in figures 9 and 10, respectively. Apparently, the higher the power and number of passes in case of corona treatment, the higher the lightness. Similarly, in case of argon plasma treatment, the prolongation of treatment time and increase in power brought about increase in fabric lightness. In both cases, under severe treatment conditions samples became more yellow (higher values of  $b^*$ ), but yellowness disappeared after washing. Mechanical properties of the material were not changed after plasma treatments. These results can encourage further research on possibility of plasma implementation in denim finishing because of water- and chemical-free processing, low energy costs and short treatment time compared to conventional bio-stoning (approximately 90 min). However, plasma treatment induces harsher handle of denim fabric, indicating the need for some after treatment.



**Figure 9.** Lightness difference between corona treated (4 m/min) and untreated denim fabrics.



**Figure 10.** Lightness difference between low-pressure argon plasma (0.27 mbar) treated and untreated denim fabrics.

## 5. Conclusions

Plasma treatment became a negligible part of many industrial processes. Despite the obvious intrinsic effects and environmentally friendly approach, it is still claimed as “potential” or “promising” treatment in textile industry. It might be due to too traditional and rigid textile industry, which finds an excuse in expansive vacuum pumps required for plasma processing at low pressures. However, treatments at atmospheric pressures are available as well. The substantial shortcoming of plasma treatment of textiles is that it cannot replace all wet processes, but it can be a viable pretreatment, which provide plenty of environmental and economical benefits. Therefore, textile industry should consider the concept of higher initial investments in equipment that will be paid off quickly with respect to environment-related savings and the profit of the sale of high added value products.

We may add at the end that comparative study of different plasmas in textile treatment should be carried out in order to outline the best strategy for plasma technologies in the industry. The need to achieve non-equilibrium plasma operation and at the same time preference for using and atmospheric pressure have led to the design of a number of atmospheric pressure devices. However, stability of operation under those conditions and the need to use helium as the buffer gas may reduce the advantages of operation at atmospheric pressure and make the low pressure reactors more practical.

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