Plasma treatment effects on the processes involved in fabrics dyeing

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Atmospheric-pressure plasma is used for surface modification of synthetic woven fabrics, aiming to increase the efficiency of the dyeing. Plasma allows controlling the material-fluid interface, by shifting the equilibrium between the main processes involved, i.e. diffusion through the woven material and adsorption/absorption onto polymeric fibers surface, conducting to better dye adhesion.

1. Introduction

Adhesion is crucial concern for most textile applications, since dyeing, painting or functional coatings deposition is necessary to define textile functionality in applications [1-3]. Adhesion governs, in complex manner, the optical aspect, the functioning and the stability of the material, it dictates aqueous and solvent wash fastness of textile finishing, the durability of coatings, and the quality of composites and laminates.

Accordingly, studies on the adhesion mechanisms and the development of specific surface treatments constitute a major research field in textile-related science and industry, where various processing technologies have been tested and developed to meet the complex adhesion requirements imposed to textile materials.

In this respect, plasma technology applied to the treatment of textiles, both for adhesion promotion and deposition, has developed markedly during the past two decades, due to its potential environmental and energy conservation benefits [4-13]. Since adhesion is surface-dependent property, mediated at molecular scale, plasma can effectively achieve modification of this near-surface region without affecting the bulk properties of materials.

In this context, atmospheric-pressure plasma represents particularly suitable technology for treating textiles, with specific advantages as short treatment time, room temperature operation, versatile geometry, flexibility with respect to the type of the material, its dimensions and shape.

Taking this into account, we are studying here the surface modification of synthetic woven textiles, using atmospheric-pressure plasma, for improved dyeing of fabrics, pointing to the plasma effect in shifting the equilibrium between processes involved in the flow of a fluid across the fabric sample.

2. Experimental

The plasma is produced using dielectric barrier discharge (DBD), in asymmetrical electrode configuration, run in helium, ensuring uniform treatment of a circular area 3 cm in diameter (Figure 1). The surface processing is carried out for variable exposure time 10 - 60 s, on one side or both sides of the fabric.

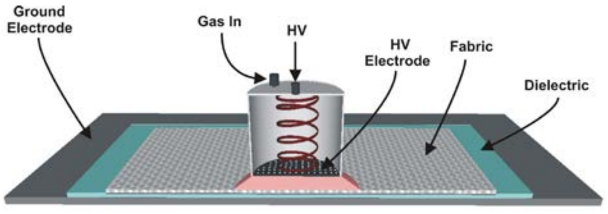

Figure 1. DBD set-up for surface processing

The treated fabrics are two types (S1 and S2) of commercial polyester woven (PES 167, 33.3 Tex / 96 filaments), presented as raw materials, with different weaving parameters (Table 1), intending to establish the relation between the process components and their characteristics, i.e. fiber (physical and chemical properties), fabric (weaving characteristics, “direction-specific” properties, “application-specific” properties), plasma.

Table 1. Weaving parameters of fabrics S1 and S2

Sample	warp	weft	density (g/m^2)
S1	3200	6	240
S2	5400	8	485

The DBD parameters are established by electrical measurement and optical emission spectroscopy, whereas the treated materials are analyzed by wettability/wickability, optical microscopy, SEM, XPS, also evaluation of color changes on dyed fabrics ΔE^* in CIELAB color space.

Since dyeing of structures permeable to fluids is governed by the adhesion onto the fibers and the diffusion of the dye in the material, the plasma treatment influence on the mechanisms at the interface between the material and a test liquid is established by a diffusion method. The measurement is carried out with the woven placed between two cells, where *cell 1* is filled with dye solution and *cell 2* with the same amount of distilled water. The absorbance measurement is performed at given time intervals, until equilibrium is reached in both cells, at fixed wavelength (535 nm) with UV-VIS spectrophotometer. The data calibration shows that the absorbance is proportional to the dye concentration, for all experimental conditions tested here.

3. Results and discussion

The discharge diagnosis points out that the stability, reproducibility and efficiency of the discharge are better in presence of the woven material between the electrodes. Thus, monitoring the current amplitude, in absence and in presence of the fabric between electrodes, shows that the woven substrate reduces the variations of the current peak by a factor of about 2. Also, the calculation of the energy applied to the discharge, using the DBD voltage and current waveforms, shows values higher with about 40% in presence of the fabric between the electrodes.

This behavior can be related to the particular nature of the sample, which has heterogeneous structure at macroscopic level, from both mechanical and electrical point of view. The woven allows the flow of the gas through, presenting also complex dielectric structure, with insulating and conducting regions, due to polymeric fibers and gas "cells" inside the woven, respectively. Thus, on one side, the fabric changes the speed of gas flow in a significant region of the discharge, and, on the other side, it represents a second dielectric layer in the discharge, besides the compact dielectric film placed on the ground electrode, with patterned dielectric characteristics.

It results, accordingly, that the presence of a permeable substrate between the electrodes is advantageous, compared to the case when there is only dielectric compact film on the grounded electrode, for setting the discharge parameters and controlling the treatment.

The assessment of the plasma-treated fabric properties also points to particular treatment outcomes in the present case.

Thus, the enhanced adhesion properties of the plasma-treated samples are suggested by SEM images and color analysis on plasma-treated and dyed samples.

SEM shows that for untreated fibers, the dye forms, to some extent, a film on the fiber surface, whereas the treated fibers are smooth and uniform after dyeing, indicating better absorption of the dye in the fiber. Also, the performance of the finished product is proven by increased color variation observed on plasma-treated samples, compared to untreated ones, thus associated to more intense color (Table 2).

Table 2. Color variation on untreated and plasma-treated fabrics (ΔE^*, CIELAB coordinates)

Sample	ΔE^* (untreated)	ΔE^* (treated)
S1	1.7	3.0
S2	1.2	2.6

Nonetheless, the physical and chemical modification of the fabrics by plasma exposure is difficult here to render to evidence, because polyester is highly polar polymer, with oxygen-rich chemical structure, therefore the degree of oxidation induced by plasma is inherently limited, due to the maximum level of functionalization attainable [14, 15]. Then, due to the woven nature of the material, the fabrics are hydrophilic, in that these absorb fast aqueous solutions, so, the modification in the wettability/wickability is within error bars.

Thus, there is measurable effect of the plasma on the adhesion properties, which, yet, cannot be explicitly assigned to the modification of the surface chemistry, as tested by XPS. In addition, the roughness modification may also be reduced, due to the mild plasma conditions here, involved with inert gas environment, also to the short treatment time.

The dyeing process is mainly governed by the mechanisms involved in the flow of the dye solution through the pores of the woven heterogeneous samples. In this respect, the kinetics of the flow can be discussed considering three mechanisms, the adsorption, absorption and diffusion, respectively, which are simultaneously occurring at the contact between a permeable substrate and a fluid, where, of course, adsorption is the first necessary condition for absorption.

The diffusion and adsorption/absorption mechanisms operate at different levels in the substance, i.e. macroscopic and nano-level, respectively, being controlled, therefore, by different parameters.

Thus, adsorption relates to surface properties, absorption relates to surface and bulk properties, whereas diffusion relates to the permeability of the woven and the fluid features (concentration, viscosity, temperature).

Under constant conditions for the fluid phase, there are two variables in the process, associated to the solid phase, i.e. the weaving parameters of the fabric and the surface properties of fibers, which influence both diffusion and adsorption.

The separation of these variables could be solved by testing, as in the present case, two samples, S1 and S2, having the same chemical structure and different weaving parameters. Here, the adsorption factor of individual fibers is the same. Yet, the higher weaving density of sample S2 implies increased adsorption, due to higher number of fibers in material's section, and lower permeability, at the same time. These are opposite effects which could compensate as well.

The diffusion experiments show that the fluid flow conducts to similar monotonous variation of the concentration in both diffusion cells, c_1 and c_2, respectively, with fast evolution during the first few hours, followed by a slow tendency to level out (Figure 2).

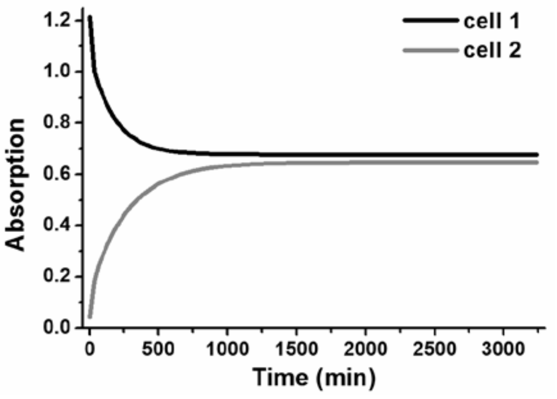

Figure 2. Absorption measurement in diffusion cells

Yet, the dye concentration does not reach the same equilibrium value for cell 1 and cell 2. Thus, the time interval required to reach equilibrium τ_{eq} and the difference between the equilibrium concentrations Δc_{eq} yield information on the shift of the flow process, since τ_{eq} represents the time interval for the active sites on the material to saturate with dye molecules and Δc_{eq} relates to the amount of dye adsorbed on the fibers.

The evolution of the concentration obeys a variation law of type e^{Kt}, where K [s^{-1}] is the process rate.

In this respect, Figure 3 shows the graph representation of the function $\ln[(c_1 - c_2)/(c_{1,0} - c_{2,0})]$ versus time (where $c_{1,0}$ and $c_{2,0}$ are the initial values), for sample S1, which can be fitted, for the interval before saturation, with two slopes, K_1 and K_2. These could represent the rates associated to the two components of the flow, adsorption/absorption and diffusion, respectively.

For sample S2, the graph can be fitted with only one slope, K, which is obviously related to the more dense woven structure, implying significantly lower permeability, compared to sample S1, which hinders the two-slope trend of evolution.

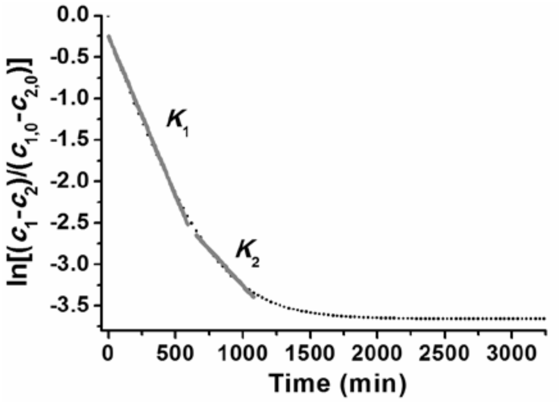

Figure 3. Linear fit of the time evolution of the concentration during the flow across fabric

The values of these slopes, associated to the process rates, are calculated for the flow across fabric before and after plasma treatment, as shown in Table 3.

Table 3. Process rates related to the flow across the woven samples (in 10^{-5} s^{-1} units)

Sample		K_1	K_2	K
S1	untreated	6.40	2.92	
	treated	6.35	3.41	
S2	untreated			1.29
	treated			1.37

It results that plasma exposure is affecting the fabrics permeability to fluid flow, shifting the parameters associated to the adsorption /diffusion mechanisms. The evolution observed for sample S1 shows measurable modification of only one of the two rates. This behavior could be consistent with the XPS results, showing in qualitative manner, no measurable chemical modification of the material, and implying that the adsorption, at level of the individual fibers, is not modified.

It results that plasma treatment accelerates the diffusion through the woven during the fluid flow, which could be related to an effect on the capillarity phenomena established as a balance between adhesive and cohesive forces at the interface. Tests on fabrics S1 and S2, having different density of fibers/surface unit, demonstrates this plasma effect on the treated material. The mechanical cleaning, by removal of the molecules and small fragments, including gas and vapors, adsorbed in the entire woven matrix, favors the diffusion and improves the dyeing process of fabrics.

4. Conclusion

Atmospheric-pressure plasma is used for surface modification of synthetic woven fabrics, aiming to enhance the adhesion properties and increase the efficiency of the dyeing.

The discharge diagnosis shows that the woven material represents spatially heterogeneous substrate which improves imparting the discharge energy and enhances the stability. The presence of the permeable substrate between the electrodes is, thus, advantageous, for setting the discharge parameters and controlling the treatment.

An experimental model for kinetics analysis of the flow across the fabric sample, which is paramount for dyeing of fabrics, renders to evidence two major processes, adsorption/absorption and diffusion, controlled by different parameters of the solid/fluid interface. The plasma is shifting the equilibrium between these processes, accelerating the diffusion of the fluid across the woven.

Atmospheric pressure plasma can be used to control the interface processes, related, in particular, to the adhesion properties of the fabrics. These results could be extended to other applications, for example, to control the adsorption/ diffusion relative contributions in biomedical use of permeable materials, as meshes or membranes.

5. Acknowledgement

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6. References

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