Plasma Functionalization of Textiles: Specifics and Possibilities

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Abstract: Plasma technology offers many interesting possibilities for the production of high value added textiles. Nevertheless, textiles can have a considerable structural and chemical complexity and their properties must be taken into account for the implementation of plasma processes. The influences of some of these properties are highlighted through several examples of recent interesting applications.

Keywords: textiles, activation, metallization, plasma polymerization

1. Introduction

A shift toward highly functional and added-value textiles is now recognized as being essential to the sustainable growth of the textile and clothing industry in developed countries. The demand for tailored surface modifications for water repellence, long-term hydrophilicity, anti-bacterial properties, etc, is therefore increasing. At the same time, the environmental restrictions concerning the waste water produced by conventional textile finishing techniques are getting more and more severe. In this context, plasma processing is seen as an attractive alternative method to add new functionalities to textiles since it is a versatile and eco-friendly (dry) technology. Because plasma processing results in a nano-scaled surface modification, it also has the advantage of preserving the bulk properties as well as the touch of the textiles. Plasma processing can be applied to both individual yarns and fabrics, which adds a lot of flexibility and broadens the field of application. With examples taken from the research done at Empa, this contribution aims at giving an overview of some of the properties specific to textiles and their impact on the related plasma processes and applications. Some of the interesting possibilities offered by the application of plasma technology to textiles will also be outlined.

2. Surface cleaning and metallization

The structure and the surface chemical composition of textiles usually vary a lot from one fabric to the other and plasma processes often benefit from being adapted specifically to every textile type. In spite of these variations, the different textiles have in common the fact that their surface is very often covered by a substantial layer of oils and sizes. These may be introduced during various steps in the production chain (i.e. fiber spinning, weaving, etc). Cleaning is therefore a very important step preceding the deposition of a thin film with PECVD or sputtering, for instance. Usually, this can be adequately done by etching with O-containing plasmas. An example is shown in Figure 1 for polyester yarns [1]. The yarns are cleaned in-situ with He/O₂ RF plasma prior to their metallization with Ag by magnetron sputtering. The quantity of residual oil at the surface of the untreated yarns is about 1.2 w%. As shown in Figure 1, this can be effectively reduced by about two orders of magnitude with the plasma cleaning step.

![Fig. 1 Quantity of residual oil on polyester yarns as a function of the He/O₂ plasma cleaning duration. Unwashed yarns are compared to yarns that were washed in a detergent solution before the plasma cleaning](image)

Not surprisingly, the quality of the silver coating (conductivity, adhesion and wash-fastness) scales with the cleanliness of the yarns. Figure 1 also shows that a wet-chemical industrial cleaning of the yarns can be used to decrease the duration of the plasma cleaning step. Nevertheless, by all practical means the industrial washing does not remove all the oil and a plasma pre-cleaning step leads to a marked improvement of the Ag coating. Beyond the removal of oil and sizes at the surface of the yarns, the He/O₂ plasma treatment also improves the adhesion of the Ag coating by functionalizing the polyester surface. The possibility of cleaning and functionalizing the surface of the yarns in-situ before metallization is a clear advantage of plasma processes in comparison to other technologies (including wet-chemical electroless coating). With a suitable design of the plasma cleaning and sputtering system, an integrated air-to-air process has been developed which allows the Ag-coating of polyester yarns at a speed of a
few hundred meters per minute. The coated yarns have a relatively good conductivity (resistance ~ 10-20 Ω/cm) and are wash-fast. Textile electrodes embroidered using these yarns remain very well conductive after up to 100 washing cycles at 60°C. The metallization of yarns and fabrics currently receives a lot of interest for various textile-based applications, ranging from antistatic garments to textile-integrated electronics.

3. Enhancement of wicking properties

Wicking and liquid transport in textiles mainly depend on the capillary action in the interstices between the individual fibers [2, 3]. This is an important property for so-called moisture management garments, where the fabric is designed to achieve a rapid transport of sweat. It is possible to enhance the wicking properties of a textile with plasma treatments under vacuum. The latter are then used to increase of the hydrophilicity at the surface inside of the textile capillary structure. For that purpose, the diffusion of the active plasma species in the textile structure (in the interstices between the filaments) is obviously very important. This effect is strongly influenced by the plasma parameters: the use of a lower gas pressure increases the mean free path of the active species generated in the plasma and generally allows a more efficient treatment of the inner fiber surfaces [4]. On the other hand, the density of active plasma species increases with the pressure. This generally leads to faster surface cleaning and activation, which is economically advantageous from an industrial point of view. The interplay between these two effects can lead to a necessary compromise, where an “optimal” pressure is determined at which both the penetration and the speed of the plasma treatment are reasonable for a given application. This is illustrated in Figures 2 and 3 for the Ar/O₂ (gas ratio 4/1) RF plasma hydrophilization of a well-defined and clean polyester multifilament weave.

During these treatments, the samples were attached on the RF-driven electrode of a symmetrical capacitive plasma reactor (described in details elsewhere [5]). The wicking properties of the treated fabrics were evaluated by measuring the sink time of a 10 µL water droplet deposited on their surface. The sink time, which is defined as the time necessary for the complete absorption of a droplet by the fabric, is about 600 s for the untreated samples. Figure 2 shows that the plasma treatment time required to reduce the sink time to a given value decreases considerably upon increasing the pressure from 0.05 mbar to 0.9 mbar (for a constant plasma power of 400 W). However, this pressure increase is also accompanied by a decrease of the mean free path of the active species (by about an order of magnitude, from 1 mm to less than 0.1 mm [4]). Correspondingly, the penetration of the plasma treatment in the textile structure should also get lower. As judged from Figure 3, this apparently results in a reduction of the stability of the improved wicking property imparted by the plasma modification. The increase of the sink time values with the storage time is attributed to the hydrophobic recovery of the plasma-modified surface of the polyester fibers. In the case of the samples treated at higher pressure (0.3-0.9 mbar), the hydrophilization of the filaments that are not directly exposed at the surface of the weave is probably much weaker. This leads to a quick reduction of the capillary action after hydrophobic recovery, since only the topmost fibers retain a sufficient degree of hydrophilicity. Comparing Figures 2 and 3, one could identify the pressure range between 0.1 mbar and 0.3 mbar as being a good compromise between processing speed and treatment stability. Obviously, the definition of the optimal conditions will depend on the precise application. Likewise, the penetration of the active plasma species in a textile will also strongly depend on its structure (thickness, compactness). These considerations are also relevant for other fields of application, including the func-

![Fig. 2 Water droplet (10µL) sink time value as a function of the Ar/O₂ plasma treatment time and pressure for a polyester multifilament weave.](image)

![Fig. 3 Evolution of the water droplet sink time values with storage time in air (65% RH, 21°C) after the Ar/O₂ plasma treatment of a polyester weave at different pressures. In all cases, a treatment duration of 300s and a power of 400 W were used.](image)
tionalization of non-woven textiles used in filtration devices.

4. Surface functionalization with plasma polymerization: new perspectives

Plasma polymerization offers an attractive possibility to deposit functional thin films on textiles [6]. By using appropriate combinations of gas mixtures and plasma parameters, a rather broad range of surface properties can be imparted to textiles. In comparison to plasma activation (where no film is deposited), the surface properties resulting from plasma polymerization are relatively independent of the chemical nature of the textile substrate. Moreover, a high degree of crosslinking can give the plasma polymer film an extra stability and limit adverse phenomena like hydrophobic recovery. The thickness of the plasma polymer thin films can be well-controlled and kept within a range (~ 100 nm) where the bulk properties of the textiles are not significantly altered.

For industrial applications, the use of relatively simple gas mixtures consisting of a short-chain hydrocarbon monomer (CH₄, C₂H₄ or C₃H₆, for instance) and a N- or O-containing reactive gas (N₂, NH₃, CO₂) can have practical and economical advantages. These processes are rather robust and they do not require a liquid monomer introduction system, for instance. The deposition of thin films from NH₃/C₂H₄ discharges is an interesting example. For high NH₃/C₂H₄ gas ratio, the films contain a lot of N and show very hydrophilic properties [7]. Generally, the films deposited from NH₃/C₂H₄ mixtures were also shown to contain a good fraction of amino groups [8, 9]. This is interesting, since amino groups have chemical properties that can be useful for various applications. They are known to promote cell adhesion [9], and their chemical activity can be used for the covalent attachment of functional molecules (see [10] and references therein). Within the NH₃/C₂H₄ gas ratio and the energy input (power/monomer flow) parameter ranges, a window has been identified where the resulting films have a lower density. As shown in Figure 4, the density of the films generally rises with NH₃/C₂H₄, probably due to an increasing etching effect. Nevertheless, a dip is observed for NH₃/C₂H₄ values around 1. These films might be regarded as nanoporous [8], and results have shown that their whole volume is available for the attachment of functional molecules. These properties render possible a range of applications, where the coatings can be used as templates for the attachment of various functional molecules. Initial experiments on the anchoring of fluorocarbons have shown rather promising results. Coated textiles can be made oil repellent, and the properties of the coatings are rather wash fast and abrasion resistant.

The penetration of the film-forming plasma species in the textile structure is also often desired for applications based on plasma polymers. The above-mentioned trends as a function of the process pressure should therefore also be considered in the implementation of these processes. The deposition of plasma polymer films at a pressure of about 0.1 mbar usually leads to good results for textiles.

References