Preparation of superhydrophobic cotton fabrics based on fluorocarbon compounds by plasma methods

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Abstract: Functionalized cotton fabrics have been obtained by magnetron sputtering deposition of polytetrafluorethylene-like (PTFE), and sulphur hexafluoride (SF_6) plasma treatment. The influence of each of the investigated plasma processes on the cotton fabrics surface properties, chemical composition and wettability on both sides of textiles are reported. The obtained cotton fabrics submitted to SF_6 plasma treatment and PTFE coating present very repellent and stable surfaces.

Keywords: plasma deposition and treatment, non-staining textiles, cotton fabrics.

1. Introduction

Recently, superhydrophobic surfaces with water contact angle higher than 145° have attracted great attention for their practical applications such as improved corrosion resistance, transparent and antireflective coatings, water-repellence, self-cleaning, anti-sticking and anti-fouling surfaces [1]. In the textile market, the needs for smart fabrics (water repellent, improved staining résistance, etc.) have continuously increased. While cotton fabrics are comfortable, biodegradable and low-cost, it renders some drawbacks as easiness of wetting and staining [2]. In this context, an efficient strategy to obtain smart textiles with very repellent and self-cleaning properties is represented by plasma functionalization or coating of surfaces with very thin fluorinated layers. The present work illustrates the strategy for obtaining highly hydrophobic, or even super hydrophobic coatings by using fluorine containing discharges. Namely, magnetron sputtering of polytetrafluoroethylene, and sulphur hexafluoride plasma treatment were employed for deposition on, or treatment of, cotton textiles surfaces.

2. Experimental

2.1 Materials

The substrates used in this comparative analysis were 100% cotton fabrics with woven structure and specific mass of 400 g/m^2. The gas used to insure the ignition of plasma was Ar. Two types of fluorine-based chemicals were utilized for fabrics hydrophobization, namely SF_6 in the case of plasma treatment, respectively polytetrafluorethylene (PTFE) for plasma deposition.

2.2. Surface fluorination by plasma deposition and treatment

SF_6 plasma treatment on the cotton supports was conducted in a spherical stainless-steel vacuum chamber evacuated by a turbomolecular/rotary pumping system down to a base pressure of $1x10^{-2}$ Pa. The chamber is equipped with a homemade shower-like capacitively-coupled plasma source and a magnetron head (Kurt J. Lesker), both mounted with their axes at 45° inclination to the vertical of substrate surface, and at 9 cm distance in respect to the substrate holder, which serves also as grounded electrode. The substrate holder is rotating during the plasma exposure in order to insure better uniformity over large area. For the plasma treatment, SF_6 at a gas flow rate of 25 sccm is injected in the discharge, establishing a working pressure of 3.0 x 10^{-1} Pa. The SF_6 plasma treatment experiments of the cotton fabrics were conducted to observe the effects of the applied RF power in the range of 10÷50 W and process time in the range 1÷5 min, considered as key parameters for the surface hydrophobization of the analysed materials. Herein, we will focus on the results obtained upon 5 minutes plasma treatment time, and 40 W the injected RF power.

The RF sputtering process was conducted in Ar using a flow rate of 80-100 sccm with RF power of 80 W, and at a working pressure in the range of 0.8 - 1.2 Pa. The deposition time was set 5, 10, and 15 min. In this study we detail the obtained results for 10 minutes deposition time, and 80 W applied RF power.

The schematic picture of experimental set-up is presented in detail elsewhere [3].

2.3. Chemical and wettability investigation methods

The chemical composition and bonding investigations were conducted by means of X-ray photoelectron spectroscopy (XPS) performed on a K-Alpha Thermo Scientific apparatus equipped with a hemispherical analyser. For the excitation of photoelectrons, X-ray radiation of an aluminium anode (AlKα, 1486.6 eV) generated at a tube voltage of 12 kV and current emission of 3 mA was used. Peak position was calibrated according to the standard C1s peak (284.8 eV). Survey spectra were recorded to determine the elemental composition of the cotton fabrics sample, while high resolution spectra for C1s, F1s, and O1s were recorded in order to evaluate the chemical bonding on the surface as resulted upon plasma treatment/deposition.

Water contact angle technique (sessile drop method) was used to investigate the wettability properties of the untreated and plasma deposited/treated cotton fabric samples. The measurements were carried out at room temperature by a contact angle goniometer Optima VCA (AST products) equipped with a CCD camera. Double-distilled water droplets of 2 μL volume each were released manually on the initial and plasma modified cotton fabrics surface for contact angle measurements.

3. Results and discussion

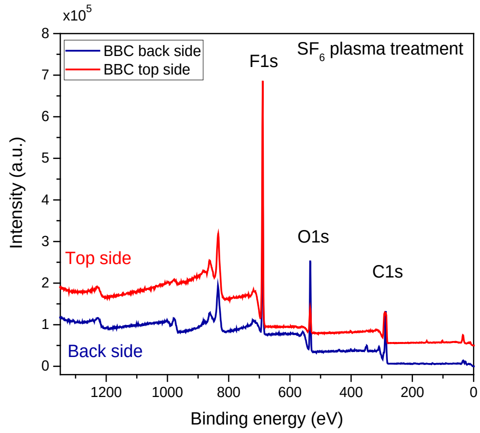
3.1. Chemical composition of the cotton fabrics surface processed by fluorine containing plasma (XPS)

X-ray Photoelectron Spectroscopy (XPS) survey spectra revealed on the cotton fabrics surface the presence of carbon, oxygen and fluorine as the main elements both for the SF_6 plasma treatment, and PTFE-like material deposition (Figure 1). In order to elucidate whether the fluorine-based species penetrate inside the cotton fabrics, the XPS measurements were performed on both sides of the fabrics. Therefore, from now on we will nominate as "top side" the surface of cotton fabrics oriented to plasma during deposition/treatment, and respectively "back side" the surface of cotton fabrics oriented toward the substrate holder.

The atomic composition of investigated materials, as determined from the XPS survey spectra processing, is reported in Table 1. The ratio between fluorine and the carbon atomic concentrations (F/C ratio) are also included.

For the SF_6 plasma treatment of the cotton fabrics surface, we found upon XPS measurements that F/C ratio is 0.66 for the top side of the fabric, while for the back side it reaches even higher values of 0.71. This behaviour is explained by the difference in the plasma process taking place under the investigated cases: for the SF_6 plasma treatment, the fluorine species generated upon decomposition in the plasma penetrates the woven material and are covalently attached to the carbon from the cotton fibres. Furthermore, a possible plasma etching process given by the high amount of reactive fluorine present in the discharge conducts to an enlargement of the space between the textile fibres and therefore to the easiness of the fluorine penetration inside the textile itself. On the other hand, one must notice that the ratio of O/C is around 0.5 for both sides of textile, slightly lower than in the case of raw cotton [4].

In the case of magnetron sputtered PTFE-like material, the F/C ratio is 1.03 for the top side and as low as 0.05 on the back side. During PTFE magnetron sputtering process, the number of fluorine reactive atoms is much smaller and they are accompanied by carbon atoms and small fragments ejected from the PTFE target which are contributing to the deposition. Moreover, the deposition process itself conducts to the lowering of the space between the fibers due to the growing coating and therefore the penetration of the species is much limited, conducting eventually to a smaller amount of fluorine on the back side of the textile. This explanation is enforced by the O/C ratio of the PTFE deposited cotton- on the top side, which is coated, the O/C The high-resolution C1s spectra recorded for the SF_6 plasma treatment of the BBC fabrics surface, both for the top side and back side are displayed in Figure 2. The deconvolution of C1s spectrum of SF_6 plasma treated BBC reveals six components, corresponding to C-C or C-H bond surface (dark blue line), as well as the C1s spectrum for the SF_6 plasma treatment of cotton fabrics surface (red line) at 285 eV, C-O-C bond at 287 eV, C-F bond at 289 eV, O-C=O bond at 290 eV, CF_2 bond at 292 eV and CF_3 bond at 294 eV, suggesting complex chemical structure of the surface fabrics resulted upon plasma treatment both on the top side and back side of the treated fabrics.



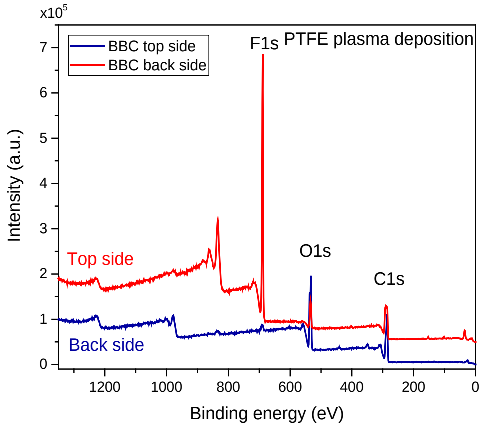


Fig. 1. Survey spectra for SF_6 plasma treatment (up) and magnetron sputtered PTFE-like material (down) of BBC fabrics: top side (red line); back side (dark blue line)

Table 1. Atomic composition of the investigated materials and F/C ratio for the SF_6 plasma treated and magnetron sputtered PTFE-like films of cotton fabrics surface.

Sample/ process	F (%)	C (%)	O (%)	F/C	O/C
	BBC SF_6 plasma treated				
Top side	29.92	45.56	24.52	0.66	0.54
Back side	31.96	44.9	23.14	0.71	0.52
	BBC PTFE coated				
Top side	46.73	45.18	8.09	1.03	0.18
Back side	2.83	60.19	36.98	0.05	0.61

ratio is very low, while on the back side the value corresponds to that of the initial fabric.

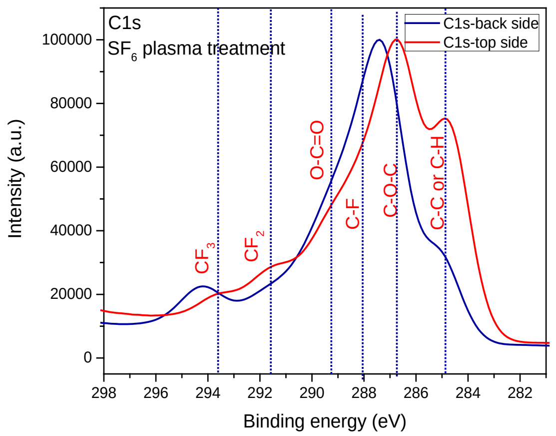


Fig. 2. High-resolution spectra of C1s region for SF_6 plasma treated BBC fabrics surface: top side (red line); back side (dark blue line) bond at 292 eV, suggesting the lower degree of fluorination on the uncoated side of the BBC fabrics surface.

The high-resolution C1s spectra recorded for magnetron sputtered PTFE-like material of the BBC fabrics surface, both for the uncoated (back side) and coated (top side) sides are displayed in Figure 3. The processing of C1s spectrum for BBC surface PTFE-like material uncoated side (dark blue line) indicates 5 components which correspond to: C-C or C-H bond at 285 eV, C-O-C bond at 287 eV, C-F bond at 288 eV and CF_2.

The deconvolution of C1s spectrum for the PTFE-like material coated BBC surface (red line) reveals 6 components assigned as follows: C-C or C-H bond at 285 eV, C-O-C bond at 287 eV, C-F bond at 289 eV, O-C=O bond at 290 eV, CF_2 bond at 292 eV and CF_3 bond at 294 eV.

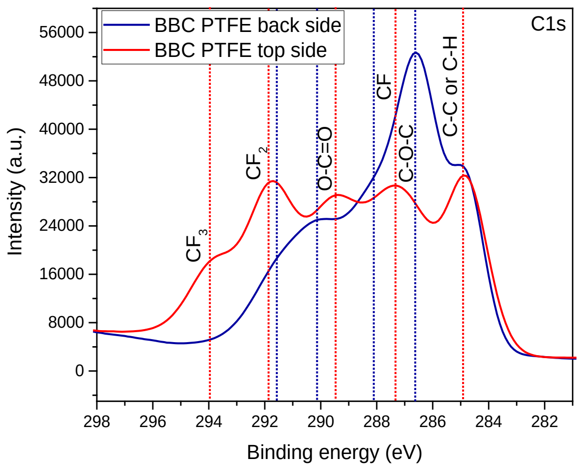


Fig. 3. High-resolution spectra of C1s region for magnetron sputtered PTFE-like material onto BBC fabrics surface: top side (red line); back side (dark blue line)

3.2. Wettability and ageing investigations

Wettability investigations of the BBC fabrics treated by SF_6 low pressure plasma showed that water contact values exceeding 140° corresponding to superhydrophobic behaviour of the textile can be obtained in optimized treatment conditions. A slight recovery of the properties, leading to a decrease of WCA down to 115 ° is noticed 3 months after the treatment. In the case of BBC fabrics deposited by PTFE, the water contact values are as high as 125° for the investigated conditions, and it remains stable in time.

In order to evaluate the fabrics resistance to staining, as well as the stability of the plasma treated and deposited fabrics, we prepared various water-based solutions having various consistencies, colours and pH. Figure 4 presents images of various staining liquid drops (tomato juice, methylene blue dye, acidulated orange juice, and coffee) released on more than 300 days stored cotton fabrics. Because the fluorine containing plasma modification of textile conducts to non-wetting surfaces, the tomato and orange juice, methylene blue and coffee drops form spheres on these surfaces. Contrary, on the untreated/uncoated cotton fabric the liquids drops are fully absorbed, leading to staining. Important to note that the aging effect of plasma treated fabrics is low: the wettability properties are not significantly changed in time indicating good durability of the effect of treatment. Concluding, cotton fabrics submitted to SF_6 plasma and PTFE coating present very repellent and stable surfaces.

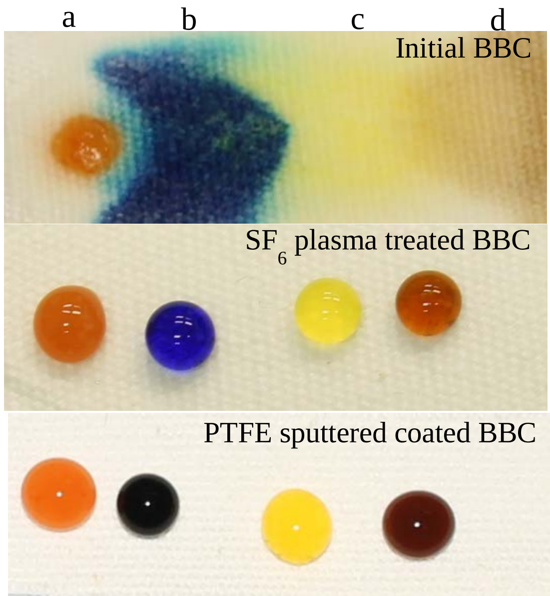


Fig. 4. Images of various staining liquids drops on the initial, SF_6 plasma treated, PTFE-like coated BBC fabrics surface: a) tomato juice; b) methylene blue; c) orange juice, d) coffee

4. Conclusions

Plasma deposition and treatment of cotton fabrics allowed the obtaining of fluorine containing surfaces with significant amount of fluorine, at least on the treated face (top side). The water contact angle indicates a stable hydrophobic behaviour for the PTFE coated textile, and a superhydrophobic surface with a slight tendency of recovery for the SF6 treated textiles. Nevertheless, both approaches allowed to obtain stain resistance to water-based compounds even a year after the plasma modification of the surfaces was applied.

Acknowledgements

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5. References

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