

Superhydrophobic polyester-based fabrics modified by barrier discharge plasma and organosilanes

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Abstract

In this paper, a diffuse coplanar surface barrier discharge plasma at atmospheric pressure has been used to surface modification of polyester/cotton (PESc) fabric, that was subsequently modified by sol-gel process using suitable organofunctional silanes to enhance its hydrophobicity. Modified PESc fabric surfaces were conditioned during the gelling process to obtain the permanent hydrophobicity. The contact angle of water before washing of plasma and sol gel pre-treated PESc fabric was found to be of 154°, and 151° after standardized washings. It was also demonstrated that the process is applicable at the industrial scale.

Key words: *cotton, fabric, plasma treatment, polyester, sol gel, silanes, hydrophobicity*

Introduction

Polyester/cotton (PESc) fabrics are the most produced fabrics in the textile industry. Their surfaces are rich in polar groups, which make them hydrophilic, but in some special cases, there is a need for hydrophobic surfaces. There are many methods with which to modify the surface of polymeric fabrics, one of which is low-temperature discharge plasma technology. This modification method has become more and more popular because it does not require a large amount of conventional chemicals, benefitting not only the economy but also the environment. Sol-Gel chemistry is relatively low cost process running at low temperature in environmentally friendly solvents which allows a formation of infinity number of different structures (1). It is based on the polycondensation of molecular precursors such as metal alkoxides, consisting of silicon, titanium, zirconium or other metallic elements in their structure (2). Hydrolysis and condensation of these alkoxides lead to the formation of metal oxopolymers. The mild characteristics offered by the sol-gel process allows the introduction of organic molecules inside an inorganic network what also increases a variability of a potential application (3-5). The nanostructures based on sol gel chemistry can be prepared in the form of particles, bulk material, fibers, and, mainly as thin films which can be deposited on the surface of various substrates including plastics and fabrics (6 – 10). From these reason it is clear that those technologies attracted an attention of researchers, textile producers and converters to design textile materials with enhanced functionality.

In this contribution we refer the results on the development of new hydrophobic plasma treatment of polyester/cotton fabrics by barrier discharge plasma and subsequently sol – gel procedure using a combination of alkylsilane and fluorosilane. The fixation of silica deposits on the fabric was insured by diffuse coplanar surface barrier discharge (DCSBD) plasma. The washing fastness test demonstrated a high stability of treated surface. The applied route was successfully tested at semi-industrial scale.

Experimental

The PES/cotton fabrics – mixed PES and cotton in the ratio 1:1 (an average thickness of the fiber diameter of 10 μm , the surface density of 195 g/m^2) (Hedva, Czech Republic) was used. As organosilanes we used (tetraethoxy)silane (TEOS), 3-(glycidoxypropyltrimethoxy)silane (GLYMO), (triethoxyoctyl)silane (OCTEO) and (1H,1H,2H,2H-(perfluorooctyltriethoxy) silane) (FAS). n-propanol was used as the solvent and HCl as the catalyst (Aldrich Chemicals Co., USA).

In this work, a diffuse coplanar surface barrier discharge (DCSBD) plasma generated in an air atmosphere was used to modify the PES surface of the fabrics. The DCSBD plasma equipment was operated at 300 W under atmospheric pressure. The samples were prepared by cutting the fabrics into strips without dimensions 5 \times 5 cm. After that, each sample was fixed on a moveable table, using two-sided adhesive tape, onto the glass holder of the plasma source.

The silica sol was prepared via the hydrolysis of a mixture of selected silanes [TEOS (1.4 g), OCTEO (1.8 g), GLYMO (2.7 g), FAS (0.1g)] and n-propanol. The ratio OCTEO/FAS was optimized before to get high hydrophobicity at the appropriate price of the final mixture. A mixture of 0.9 ml HCl (0.01 M) and 4.5 ml n-propanol was continually added dropwise from a burette tube for 20 hours while continually mixing with a magnetic stirrer to form a silica hydrosol.

Results and discussion

SEM measurements

For the barrier plasma-treatment optimization, the PESc fabric fibers were analyzed via SEM measurement. The degree of fiber damage was judged. The SEM measurement confirms that the fiber surface of the unmodified PESc fabric sample (Fig. 1a) is smooth and free of defects. In contrast, the modified sample (Fig. 1b) exhibits partial physical damage on the surface after 20 seconds of plasma treatment. This partial physical damage is desirable for the purpose of increasing the surface area to improve the adhesion of the sol to the cotton fiber surface. In the case of a longer pre-treatment time (60 seconds) by barrier discharge plasma, the delamination of the super layer of the cotton fibers is visible in the SEM picture (Fig. 1c).

Atomic force microscopy (AFM)

Table 1 summarizes the results of the AFM measurements for pristine PESc fabrics and PESc modified by DCSBD plasma and sol-gel. The R_a value is the average height of the irregularities in a perpendicular direction towards the sample surface. The significant increase of the mean roughness R_a of the PESc fabrics after treatment by DCSBD plasma and sol-gel modification was observed. The mean roughness of the plasma and sol gel-modified PESc fabrics, as determined by AFM measurement, increased from 0.4 to 10.8 nm.

Table 1 AFM measurement results for pristine PESc fabrics and PESc fabrics modified by DCSBD plasma and sol-gel pre-treatment

Material	Surface area, μm^2	R_q^* , nm	R_a^{**} , nm	R_{max}^{***} , nm
PESc fabrics pristine	1.00	0.5	0.4	3.9
PESc fabrics, barrier plasma + sol-gel treatment	1.05	5.2	10.8	74.7

R_q^* (Rms): standard deviation of the Z values within a given area

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R_a^{**} (mean roughness): mean value of the surface relative to the center plane

R_{max}^{***} (max height): difference in height between the highest and lowest points on the surface relative to the mean plane

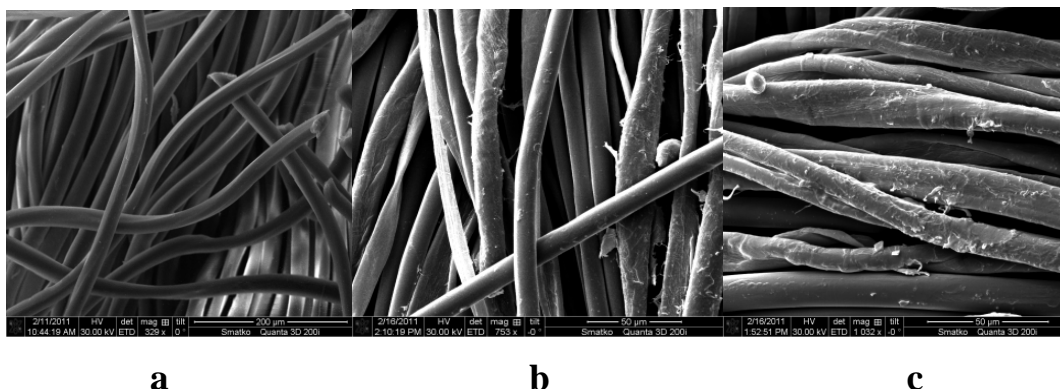


Figure 1 SEM images of PESc fibers: a - unmodified (magnification - 329x), b - after plasma treatment, 20 seconds (magnification - 753x), c - after plasma treatment, 60 seconds (magnification - 1032x)

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were used for the quantification of the characteristic presence of typical elements in the PESc untreated and plasma and sol-gel-modified PESc fabrics, unwashed and washed 4 times. The unmodified PESc fabric contains 75.6 at.% C (by C1s peak) and 24.4 at.% O (by O1s peak). The XPS measurements of the surface composition of the PESc fabrics modified by atmospheric barrier plasma/sol-gel are shown in Table 2.

Table 2 XPS analysis of PESc fabric samples

Element	Unmodified	Modified*	Washed**
	at.%		
C1s	75.6	62.8	62.1
O1s	24.4	25.0	27.1
Si2p	-	11.6	10.6
F1s	-	0.4	-
N1s	-	0.2	0.2

* Modified: PESc fabric modified by plasma and sol gel process

** Washed: 4 times washed PESc fabric modified by plasma and sol gel process

The amount of C in the PESc fabric sample decreased after modification by plasma/sol-gel from 75.6 at.% to 62.8 at.%, and the amount of O increased from 24.4 at.% to 25.0 at.%; this sample also contains 11.6 at.% Si, and negligibly amount of F (0.4 at.%) and N (0.2 at.%). The chemical composition of the plasma and sol-gel modified PESc fabric after washing 4 times led contains a higher amount of O (27.1 at.%), a slightly lower (10.6 at.%) amount of Si in compare with unwashed samples, which confirms stability of the modification process. The absence of F after washing was probably caused by very thin silane layer on PESc fabric.

Surface properties durability

Most synthetic fibers, such as polyester, are hydrophilic. The water contact angle of the untreated PESc was 72°, and by atmospheric plasma-modified PESc fabrics (air, 300 W, 2.5 sec) decreased to 66°.

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 Zde může být upoutávka na vaši firmu, stane-li se PATRONEM ČÍSLA, a její jméno bude na každé stránce!

For increasing the water repellence, it is necessary that the coating surface energy be lower than the surface energy of the polymeric substrate. In general, a simple inorganic nanosol will not meet the demands of the textile industry for water-repellence. This is especially true if a basically inorganic nanosol is modified with an epoxyalkylsilane (GLYMO) to improve the adhesion of a coating to the fabric. The introduction of polar groups into the sol-gel network will increase the surface energy of the resulting coatings. By modification with hydrophobic functionalities, silanes can be used to prepare lower surface energy coatings. In this case, a mixture of alkoxy silane with alkyl groups, (tetraethoxy)silane (TEOS), 3-(glycidoxypropyltrimethoxy) silane (GLYMO), (triethoxyoctyl) silane (OCTEO), and (perfluorooctyltriethoxy) silane (FAS) was used. These compounds, in the course of the hydrolysis of the precursor (tetraethoxysilane, TEOS) as well as during the gelation process, were chemically bonded to the inorganic nanosol, and the water contact angle reached a value typical for superhydrophobic surfaces, higher than 150° . The water contact angle of the plasma/sol gel pre-treated unwashed PESc fabrics was 153° , and after 4 times washing, the value of the contact angle was practically the same (Figure 2 a, b).

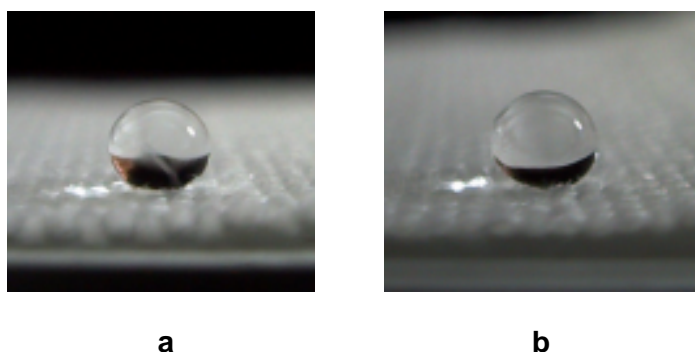


Figure 2 Water contact angle (WCA) on the unwashed PESc fabric plasma/sol-gel treated surface (a) WCA = 153° , and 4 time washed sample (b) WCA = 151°

Conclusion

A combination of octadecylsilane and fluoro silane catalyzed by HCl was selected and tested. It was found that pretreatment of PESc surface by barrier plasma before coating significantly improves wash fastness maintaining the hydrophobicity of the fabric. On the base of SEM results, the optimal time for the PESc barrier plasma-treatment was 20 seconds. The plasma-treated PESc fabrics containing individual sol-gel particles are rougher and the surface is much more heterogeneous compared to the untreated PESc fabrics. A significant increase in the mean roughness R_a , as measured by AFM, of the PESc fabrics after treatment by DCSBD plasma and sol-gel modification was observed. The R_a of the plasma/sol-gel treated PESc fabrics increased from 0.4 to 10.8 nm. The chemical composition of the plasma and sol/gel modified PESc fabric after 4 times washing contains a slightly lower content of Si (10.6 at.%) in compare with unwashed samples, where Si content was 11.6 at.%. The water contact angle of the PESc fabrics treated by a combination of plasma pre-treatment and sol-gel process is typical by a superhydrophobic surface. The water contact angle of the plasma/sol gel pre-treated unwashed PESc fabric was 153° , and after four standardized washings, the water contact angle decreased only slightly to 151° , which confirm the stability of the modified PESc fabric.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-14-0518.

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