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Plasma Treatment of Thermoactive Membrane Textiles for Superhydrophobicity

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Expedition clothes have to fulfill high requirements, especially in terms of resistance, thermal comfort and moisture transport. Thermoactive membrane textile materials are commonly used to satisfy all these needs. To improve visual properties of these textiles, a modification to achieve self-clean superhydrophobic surface (known as "Lotus Effect") can be used. As an implementation of this idea, glow discharge RF capacitively coupled plasma processing of industry materials with inert as well as polymerizing gases was performed. The self-clean properties were checked empirically with dust and solid particles with good results. To compare different treatment conditions, water contact angle (CA) was measured. In most cases significant increase of the CA in relation to raw materials was observed, with the best values achieving 155°. Surface analyses by scanning electron microscopy (SEM) and SEM-EDX spectroscopy were performed. A thin deposited layer with characteristic globular structure was found at the fiber surface treated by organosilicon plasma.
Keywords: thermoactive membrane textiles, hydrophobicity, lotus effect, water-repellence, plasma treatment.

INTRODUCTION

In this paper the method to achieve self-cleaning surface of thermoactive membrane textiles will be presented. The best example of this kind of surface is known from nature as "Lotus Effect". Lotus leaves are highly hydrophobic (called superhydrophobic) with water contact angle (CA) 150° – 164° [1, 2]. Water droplets are roughly like spheres so they easily roll down the lotus leaves and take with them dust and dirt particles. The reason of its superhydrophobicity is caused by special surface topography with multiple-length-scale roughness and low surface free energy (chemical composition of hydrophobic "waxes") [1]. It was revealed that nano as well as micro structures or a combination with hierarchical structures are the essence of superhydrophobicity and low adhesion [2, 3]. Due to the roughness gas is entrapped under the drop which minimizes the contact between water and the surface.

There are several ways to increase hydrophobicity of natural and synthetic textile fibers. First, there are water-repellent agents, mostly based on fluorine compounds which are known to have a low free surface energy. The agents are generally used in industry because they are cost-effective, but most of them are easily removable in washing cycles. Another approach is a nanoparticle attachment to the fibers which increases surface roughness [4 – 7]. As an example of commercial application BASF Mincor® can be mentioned, where silicate and fluorocarbon nanoparticles are firmly embedded in a binder and form a highly textured layer.

This paper focuses on plasma techniques which are being increasingly used for textile treatment [8 – 10]. Especially cold (non-equilibrium) plasma glow discharges are attractive for textile applications because of low plasma temperature which allows treating even soft materials without damages, good cost-efficiency and a lack of wastes. Important plasma processes to obtain self-clean effects are etching, chemical activation and vapor deposition. Due to the fiber etching, microroughness can be formed [11]. The plasma deposition of low free surface energy compounds can build in turn a thin hydrophobic film with designed roughness. Especially coatings from plasma polymerized siloxane are known to have a high hydrophobicity [12 – 15].

In this work the plasma treatment for superhydrophobicity will be performed on thermoactive membrane textile materials for high mountain expedition clothes. This kind of textiles stands out with abrasion resistance, water-repellency, moisture permeability. The treatment aims to obtain self-clean effect by the maximum increase in the water-repellency but without changing other textile characteristics. The results of this study will be used to prepare an industrial implementation of self-clean expedition clothes.

EXPERIMENTAL

Experiments were performed on commercially available synthetic textiles which are based on polyester. The list of chosen materials is presented in Table 1. Almost all materials (except material No. 3) are pre-treated by the manufacturer for water-repellence and hydrophobicity.

To analyze microstructure of fibers before and after treatment, a scanning electron microscope (SEM) FEI model Quanta 200F was used. The measurements were

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performed in water vapor atmosphere at 100 Pa with multiple magnifications in range from 50 to 25000 times. A quantitative analysis of elemental composition was performed with SEM microscope adapter EDX type from Oxford Instruments with X-Max 50 detector. 400 times magnification was used, which gives about 0.16 mm^2 of observed sample surface area. For every sample, four analyses have been made, where results standard deviation did not exceed 5 %. Two scanning electron beam energy (EBE) was used, 3.5 keV for a fiber surface analysis and 20 keV for a fiber volume analysis.

Table 1. Materials used in experiments

No.	Name	Symbol
1	Fluff tight fiber	GWMSS
2	Fluff tight fiber	PIUMI
3	Polartech PowerDry	9037
4	Polartech 200	7617M
5	SoftShell	555/IMP/6000/M/150
6	SoftShell	FX 76410+KS55
7	SoftShell	EJ-3626
8	Polartech Power Stretch	7310/M/Res

Materials hydrophobicity was determined by the CA measurement using optical goniometer from KSV Instruments, model Theta. At least 10 droplets (20 µl) of distilled water were deposited on each sample. To estimate adhesion forces, magnitude of sliding angle (SA) was determined in a simple experiment. It was checked whether droplets stayed at samples set at angle 10°.

Plasma processing was performed in a laboratory capacitively coupled plasma reactor with two parallel electrodes in a radio frequency (RF, 13.56 MHz) glow discharge. Electrodes surface was 64 cm^2, a gap between electrodes was 2.5 cm.

To check roughness formation due to the plasma etching, treatment in inert gas (argon) was performed. Discharge power was selected at 80 W, a gas flow rate was 2 sccm which gives 6.5 Pa chamber pressure. Two different exposition times have been chosen: 15 s and 10 min.

For experiments with plasma chemical vapor deposition, hexamethyldisiloxane (HMDSO) was selected. To find the optimal treatment conditions, series of experiments with no pre-treated by the manufacturer material No. 3 were performed. The best CA was achieved for 80 W discharge power and 2.5 Pa chamber pressure. These conditions were used for the plasma treatment of other materials.

RESULTS AND DISCUSSION

Almost all materials used in the experiments are originally hydrophobic, with the CA in range 120° – 142° (besides material No. 3, which absorbs water). The measured CA of particular materials was plotted in Fig. 1. In this case quite high hydrophobicity does not mean low adhesion, important to achieve self-clean effect. Only for material No. 6, the SA was lower than 10°, so there is still much to improve.

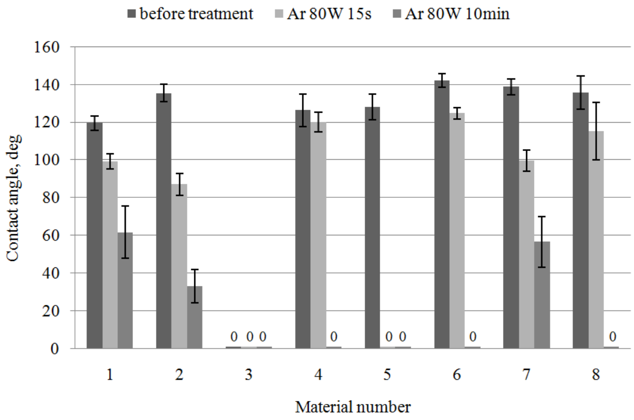
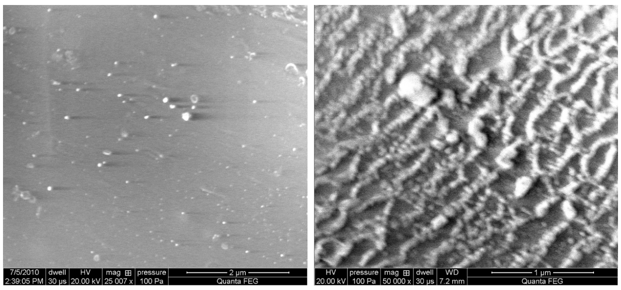


Fig. 1. Contact angle after argon treatment

From EDX analysis two main types of materials can be distinguished. First are fluff tight fibers (No. 1, 2) with volume composition (20 keV EBE) around 75 % of carbon, 14 % of oxygen and 12 % of nitrogen. In these materials addition of 34 % titanium has been detected at surface by a 3.5 keV EBE test. The second type of fibers are materials No. 3 – 8, with volume composition around 70 % of carbon and 29 % of oxygen. At the surface of materials No. 4 – 8 fluorine component in the range of 3 % –8 % has been found.

After 10 min of argon plasma etching, a micro texture at fibers has been created. As an example, close SEM images of fiber No. 3, before and after plasma exposition. are presented in Fig. 2. Longer etching times were not used because it can cause weight loss which has a consequence in decreasing tensile strength [9, 11].

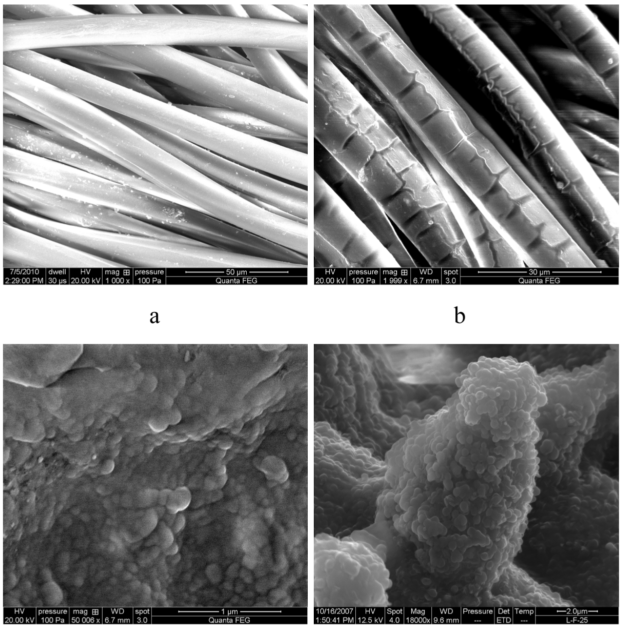


a b

Fig. 2. SEM micrographs of material No. 3 fiber: a – before and b – after argon plasma treatment

The CA values for the investigated textiles, after 15 s and 10 min treatments by Ar plasma, are presented in Fig. 1. For all cases clear decreasing of the CA with argon exposition time can be observed. In some cases materials even start to absorb water. EDX analysis has proved that a fluor component was removed from the surface of textiles No. 4 – 8. It points that hydrophobicity of raw materials was caused by compounds imposed by the manufacturer, which was removed during the argon etching. The surface roughness created by plasma does not improve hydrophobicity, thus another solution is needed.

The next approach was textile plasma treatment with polymerizing vapor of HMDSO. The optimization of the process was performed with material No. 3. The pressure in chamber was set to 1.6 Pa. In higher pressures, the discharge passes to another mode, and polymerization does not occur in a desired way. The time of 1 minute with 80 W discharge power was enough to get continuous layer of plasma polymer at the fiber surface. In higher power and longer exposition time, the CA values and the surface topography does not change distinctly. SEM images of fibers after 1 min treatment are shown in Fig. 3, b and c. As it can be seen, a thin polymer layer covers the entire fiber. For a comparison, the image before the treatment is shown in Fig. 3, a. Characteristic globular structures (Fig. 3, c) similar to lotus leaves nanostructures (Fig. 3, d) have been obtained.



a b

c d

Fig. 3. SEM micrographs of material No. 3 fibers: a – before; b, c – after 1 min HMDSO deposition; d – view of lotus leaf from Wang et al. [1]

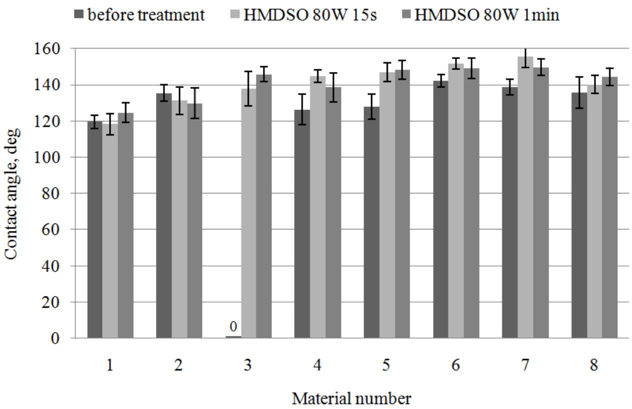


Fig. 4. Contact angle for the textiles treated by HMDSO plasma

The values of CA after HMDSO deposition for all materials in two deposition times (15s and 1min) are shown in Fig. 4. The CA increase was observed in all cases except material No. 2. One of the highest values of 145° was achieved for material No. 3, which absorbed water before processing and was not pre-treated for hydrophobicity by the manufacturer. It is important that all of the materials have now the SA values lower than 10°, which points at low surface adhesion. The high CA and low SA values indicate that a self-clean property has been obtained. To check it empirically, dust and solid particles were used with positive result in case of all materials. An example of this test is shown in Fig. 5.

Fig. 5. Self-clean effect. Water droplets with contaminations on material No. 3 after HMDSO deposition

CONCLUSIONS

The experiments were performed for industrial textile materials. The EDX measurements associated with argon plasma treatment provided information about their composition. There were two groups of materials with different hydrophobic surface compositions, based on titanium or fluorine.

Argon plasma etching removed original surface compounds and create new high texture of fibers surface. This change proved to be insufficient to produce the lotus effect.

It has been found, however, that plasma deposition of HMDSO increased the CA to superhydrophobic level and decreased the SA of the investigated textiles. A thin polymer layer has been deposited on each fiber with lotus leaves similar globular nanostructures. Self-clean properties of the materials have been obtained. Further improvement of this effect, however, requires additional study.

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