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Plasma and Sol-Gel Technology for Creating Nanostructured Surfaces of Fibrous Polymers

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For a modification of natural and synthetic fibrous polymers low-pressure ICRF plasma and liquid repellent sol-gel fluoroalkyl-functional siloxane precursor were used. Plasma induced surface chemical and morphological changes on fluorinated poly(ethylene terephthalate) and cellulose were analysed using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Wettability properties of sol-gel functionalized polymers were determined by the goniometric water contact angles and water sliding angle measurements. After plasma treatment the oxygen content on the surface of both polymers increased (increase of O/C ratio) and a nanostructured surface roughness appeared. Plasma ablation caused partially defluorinated nanostructured surface of fluorinated poly(ethylene terephthalate) polymer and increased its hydrophilicity. Plasma activation and etching of cellulose polymer contributed to the creation of highly adhesive and wash resistant sol-gel coating with superhydrophobic, oleophobic and self-cleaning properties.

Keywords: plasma, sol-gel, modification, ablation, surface activation, nanostructure, XPS, AFM, poly(ethylene terephthalate), cellulose.

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1. INTRODUCTION

Non-equilibrium plasma represents an extremely powerful medium for a modification of the surface properties of solid materials. A medium of particular interest is weakly ionized highly dissociated oxidative plasma that can be sustained in high frequency discharges in oxygen, air, carbon dioxide, water vapour, and mixtures of these gases with a noble gas. Such plasma has been successfully utilized in an extremely wide range of applications from nanoscience to fusion reactors [1-6]. The advantages of using plasma are ecological and economical. Moreover, the fibrous polymers subjected to the treatment are modified without an alteration of the bulk properties [7]. Plasma treated fibrous polymers have a higher specific surface area, which leads to new or improved properties of the treated surface, i.e. increased surface activity, hydrophilic or hydrophobic properties, and increased absorption capacity towards different materials, i.e. nanoparticles and nanocomposites [8-12]. The nanocomposites have broken through in the production of advanced fibrous materials (i.e. textiles) as sol-gel coatings [13]. These substances comprise a class of composite organic-inorganic materials that, under the appropriate application conditions, form a dense three-dimensional polymer film approximately 10-nm thick, with a high level of chemical functionality. Sol-gel technology has opened new possibilities for the creation of fibres with novel functional and protective properties, such as hydrophobicity, oleophobicity, decreased flammability and antimicrobial activity [14-18]. For our research low-pressure plasma was used for a modification of synthetic fibrous polymer fluorinated poly(ethylene terephthalate) in order to achieve hydrophilicity of the polymer. The same plasma parameters were used for a modification of cellulose to achieve better adhesion of liquid repellent sol-gel fluoroalkyl-functional siloxane precursor and to achieve superhydrophobic and self-cleaning properties of cellulosic fibrous polymer.

2. EXPERIMENTAL

2.1 Materials

For a research natural and synthetic fibrous polymers, such as cellulose (CO) and fluorinated poly(ethylene terephthalate) (PET-F) were used.

2.2 Plasma treatment

Polymers were modified using low-pressure inductively coupled radiofrequency plasma. The discharge chamber was a cylindrical Pyrex tube with a diameter of 27 cm and a length of 30 cm. Polymeric substrates were put onto a glass holder mounted in the centre of the discharge chamber. After closing the chamber the desired pressure of 0.2 mbar was achieved by a two-stage rotary pump with a nominal pumping speed of 65 m^3/h. Water vapour was used as a working gas and the source of water vapour was the polymer itself. By switching on the RF generator, the gas in the discharge chamber was partially ionized and dissociated, starting the plasma modification of the polymers. The plasma treatment time was 30 s.

2.3 Application of sol-gel

Sol-gel method was used for creating water and oil repellent properties of substrates. As a precursor fluoroalkyl-functional siloxane (FAS) was used. The sol was prepared with 10 % concentration of FAS in a water medium at pH 5 by stirring with a high-speed stir-

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rer for about 1 hour at the room temperature. The sols were applied onto untreated and plasma treated cellulosic substrates by the pad-dry-cure method, including full immersion at room temperature, wet pick-up of 85 %, drying at 100 °C and curing at 150 °C for 5 min. The substrates were then left for 14 days under standard atmospheric conditions to complete the polymerization process.

2.4 Analysis and measurements

Information on the chemical composition and chemical bonds of surface atoms of untreated and plasma modified substrates was obtained with XPS analysis. In the photoelectron spectrum, which represents the distribution of emitted photoelectrons as a function of their binding energy, peaks can be observed which are typical of elements from the sample surface up to about 6 nm in depth.

The morphological surface properties of fibrous polymers and their changes after plasma modification were studied using AFM where the primary objective is the measurement of the topographic surface properties in nanometre scale, from which the roughness of the sample can be obtained.

Wettability properties of polymers were determined by the static water drop contact angle measurements using DSA 100 contact angle goniometer, the function of which is based on the principle of the goniometer-sessile drop technique. Ten water drops (volume of 5 μL) were placed on different points on the substrate samples and were used for the determination of the average contact angle values. All values reported here correspond to contact angles obtained under stationary conditions, i.e. 60 s after the water drops were applied to the substrate.

Since sliding behaviour of water droplets on solid surfaces are among the fundamental results of wettability, the sliding angles were measured on a tilting base where the slope of the sample was slowly increased from the horizontal state. At a critical slope angle, the sliding angle was reached, where the water droplet rolled of the substrate.

The oil repellency of sol-gel coated substrates was determined by hydrocarbon resistance test (ISO 14419:2000) which is applicable to the evaluation of a substrate's resistance to absorption of a selected series of liquid hydrocarbons of different surface tensions. The repellency rating was expressed by the surface tension of the test liquid which did not wet and penetrate the substrate in 30 seconds.

Wash durability of sol-gel coating was determined after repetitive washing in an AATCC Atlas Launder-O-Meter Standard Instrument, which is widely used for evaluating laundry results on a laboratory scale. The duration of the washing cycles was 30 min, at a temperature of 40 °C. The washing cycles were carried out in a solution of standard detergent at a concentration of 5 g/l. After washing, the samples were rinsed in cold distilled water and then held under cold tap water for 10 min, squeezed and dried at a room temperature. The quality of sol-gel coatings was assessed after the first and fifth washing cycle by measuring static water drop contact angles.

3. RESULTS AND DISCUSSION

The plasma effects on fibrous polymers are dependent on the chemical and morphological properties of polymers [19] and since fluorinated poly(ethylene terephthalate) has properties opposite of those of natural cellulose with respect to chemical composition, morphology and wetting behaviour the results are presented for each polymer separately.

In Table 1 the results of AFM and XPS analysis with measurements of static water drop contact angles on PET-F before and after plasma modification are presented. The results show that water vapour plasma induced the nanostructuring of PET-F polymer surface due to plasma ablation. The surface roughness increased from 2.70 nm to 7.23 nm. After plasma modification the activation of the polymer was noticeable also; the surface of PET-F contained a higher O/C ratio, which means that it contained more of the oxygen and less of the carbon atoms. The atomic concentration of fluorine was decreased after plasma modification, and as a result of that lower static water drop contact angle was measured. The results show that plasma activated and functionalized the surface of PET-F polymer with oxygen rich functional groups and induced the surface nanostructuring and cleaning of the polymer.

Table 1 – Results of AFM and XPS analysis with measurements of static water drop contact angles on PET-F before and after plasma modification

Sample	AFM Surface roughness (nm)	XPS		θ(°)
		O/C ratio	F (at.%)	
Untreated	2.70	0.16	34.2	140
Plasma	7.23	0.39	13.5	129

The increased hydrophilic properties of PET-F after plasma modification were especially noticeable after ten repetitive washings (Fig. 1). The static water drop contact angle of untreated PET-F was 140° and after washing 137°, while for plasma modified PET-F, the static water drop contact angle was 129° and after washing 80°.

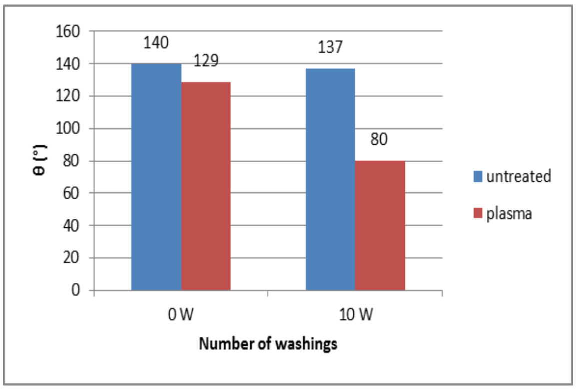

Fig. 1 – Static water drop contact angles on untreated and plasma modified PET-F before and after repetitive washing

In Fig. 2 and Fig. 3 a practical demonstration of increased hydrophilic properties of PET-F after plasma modification are shown. The droplets of different liquids, such as water (w), paraffin oil (o) and n-hexadecane (C16) were put on the PET-F substrate. The untreated PET-F is hydrophobic and oleophobic. After plasma modification the substrate immediately becomes oleophilic but stays hydrophobic. After ten repetitive washings the plasma modified substrate becomes both oleophilic and hydrophilic, while the substrate that was not modified by plasma retains its hydrophobic and oleophobic properties even after ten washings.

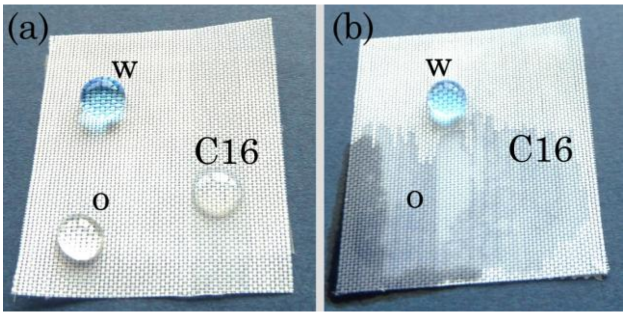

Fig. 2 – Picture of different liquid droplets on (a) untreated and (b) plasma modified PET-F substrate

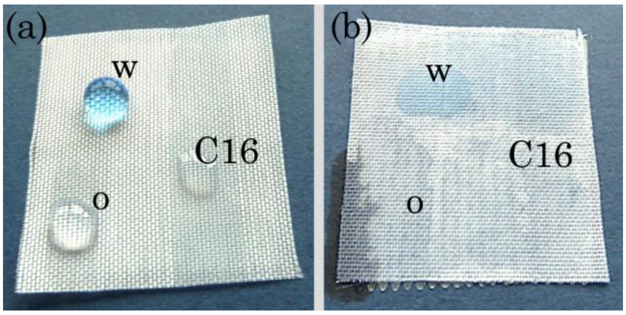

Fig. 3 – Picture of different liquid droplets on (a) untreated and (b) plasma modified PET-F substrate after 10 washings

Plasma modification for achieving surface activation and nanostructuring was applied to a hydrophilic polymer (CO). The purpose was to combine plasma and sol-gel technologies in order to achieve a surface with the »lotus effect«. In Table 2 the results of AFM and XPS analysis before and after plasma modification of CO are presented. The measurements of static water drop contact angles and water sliding angles on sol-gel coated CO polymers before and after plasma modification are presented also.

Table 2 – Surface roughness and O/C ratio of CO before and after plasma modification, static and sliding water contact angles and oleophobicity measurements of sol-gel coated CO polymers before and after plasma modification

Sample	AFM Surface roughness (nm)	O/C ratio	Static water drop contact angle (°)	Sliding water angle (°)	Oleophobicity (mN/m)
Untreated	4.01	0.44	148	13	23.5
Plasma	13.08	0.63	152	7	23.5

The results summarised in Table 2 show that increased surface roughness of CO (from 4.01 nm to 13.08 nm) resulted in increased static water drop contact angle from 148° for sol-gel coated CO to 152° for plasma modified sol-gel coated CO. The static water drop contact angle higher than 150° denotes the superhydrophobic properties of a substrate. As mentioned previously, the measurements of sliding angle are among the fundamental results of wettability. From our results it can be observed when static contact angle is increased (from 148° to 152°), the sliding angle is decreased (from 13° to 7°). The sliding angle on plasma modified and sol-gel coated CO is below 10°, which denotes the surface of a substrate with »lotus effect« properties. The CO samples also exhibit oleophobic properties regardless of the treatment. Increased O/C ratio on the surface of plasma modified polymer resulted in increased bonding of sol-gel coating on the CO surface, which resulted in better wash durability of the coating. In Fig. 4 the results of measurements of static water drop contact angles before and after repetitive washing are presented. The static water drop contact angle starts to decrease after one washing for untreated and sol-gel coated sample (from 148° to 146°) and reaches 141° after five washings. Plasma modified and sol-gel coated sample exhibits better wash durability. After one wash the static water drop contact angle on the sample does not change and after five washings the contact angle reaches 146°.

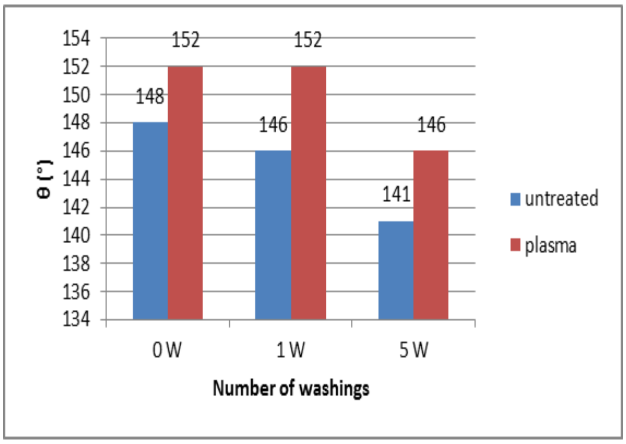

Fig. 4 – Static water drop contact angles on untreated sol-gel coated and plasma modified sol-gel coated CO before and after repetitive washing.

4. CONCLUSIONS

Low-pressure ICRF plasma was used for a modification of hydrophobic synthetic fibrous polymer and hydrophilic natural fibrous polymer. Plasma modification of oleophobic and hydrophobic fluorinated poly(ethylene terephthalate) fibrous polymer caused ablation of perfluorinated film on the surface of the polymer resulting in partially defluorinated nanostructured surface, increased oleophilic properties and after washing the increased hydrophilic properties of the polymer. The effects of plasma ablation, nanostructuring and functionalization with oxygen rich atoms were exploited for the purpose of increasing the static water drop contact angle and decreasing the sliding angle of sol-gel functionalized cellulose polymer. By using plasma modification and sol-gel fluoroalkyl-functional siloxane precursor the surface of the cellulosic polymer exhibited oleophobic, superhydrophobic and self-cleaning (lotus effect) properties with a good wash durability.

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REFERENCES

1. M. Mozetic, U. Cvelbar, M.K Sunkara, S. Vaddiraju, *Adv. Mater.* **17**, 2138 (2005).
2. R. Zaplotnik, A. Vesel, M. Mozetic, *Sensors* **12**, 3857 (2012).
3. M. Mozetic, *Vacuum.* **86**, 867 (2012).
4. A. Drenik, A. Vesel, M. Mozetič, *J. Nucl. Mater.* **386-388**, 893 (2009).
5. A. Vesel, M. Mozetic, *Vacuum.* **86**, 773 (2012).
6. J.A. Ferreira, F.L. Tabares, D. Tafalla, *J. Vac. Sci. Technol. A.* **25**, 746 (2007).
7. M. Gorjanc, P. Recelj, M. Gorenšek, *Tekstilec.* **50**, 10-12 (2007).
8. M. Gorjanc, V. Bukosek, M. Gorensek, A. Vesel, *Text. Res. J.* **80**, 557 (2010).
9. M. Gorensek, M. Gorjanc, V. Bukosek, J. Kovac, P. Jovancic, D. Mihailovic, *Text. Res. J.* **80**, 253 (2010).
10. M. Gorenšek, M. Gorjanc, V. Bukošek, J. Kovač, Z. Petrović, N. Puač, *Text. Res. J.* **80**, 1633 (2010).
11. M. Gorjanc, V. Bukošek, M. Gorenšek, M. Mozetič, *Text. Res. J.* **80**, 2204 (2010).
12. M. Gorjanc, M. Mozetič, M. Gorenšek, *Tekstilec.* **52**, 10-12 (2009).
13. B. Simoncic, B. Tomsic, L. Cerne, B. Orel, I. Jerman, J. Kovac, M. Zerjav, A. Simoncic, *J. Sol-Gel Sci. Techn.* **61**, 2 (2012).
14. B. Tomsic, P.K. Lavric, B. Simoncic, B. Orel, D. Jocic, *J. Sol-Gel Sci. Techn.* **61**, 3 (2012).
15. B. Tomsic, B. Simoncic, B. Orel, M. Zerjav, H. Schroers, A. Simoncic, Z. Samardzija, *Carbohyd. Polym.* **75**, 618 (2009).
16. B. Tomsic, B. Simoncic, B. Orel, L. Cerne, P.F. Tavcer, M. Zorko, I. Jerman, A. Vilcnik, J. Kovac, *J. Sol-Gel Sci. Techn.* **47**, 44 (2008).
17. M. Fir, J. Vince, A.S. Vuk, A. Vilcnik, V. Jovanovski, G. Mali, B. Orel, B. Simoncic, *Acta Chim. Slov.* **54**, 210 (2007).
18. B. Tomsic, D. Klemencic, B. Simoncic, B. Orel, *Polym. Degrad. Stabil.* **96**, 1286 (2011).
19. M. Gorjanc, M. Gorenšek, *Book of proceedings: AUTEX 2012* (2012).