

# Multifunctional Hydrophobic, Oleophobic and Flame-retardant Polyester Fabric

## *Večfunkcionalna vodo- in oljeodbojna ter ognjevarna poliestrska tkanina*

Original Scientific Article/Izvirni znanstveni članek

Received/Prispelo 11-2018 • Accepted/Sprejeto 1-2019

---

### Abstract

Technical textile materials with multifunctional protective properties represent one of the largest and fast growing segments of the textile industry. Multifunctional water- and oil-repellent and flame-retardant coating on polyester (PES) fabric was prepared in this research using fluoroalkyl-functional siloxane (FAS) as the water- and oil-repellent finishing agent and organophosphonate (OP) as the flame-retardant agent. A finishing solution containing FAS and OP of appropriate concentrations was applied to the untreated and oxygen plasma-treated PES fabric samples using the pad-dry-cure method. For comparison, single-component FAS and OP finishing solutions were applied to the fabric samples under the same conditions. The coated PES samples were washed under standard conditions. The morphological, chemical and functional properties of the coated PES samples were determined with scanning electron microscopy, Fourier transform infrared spectroscopy, wet pick up, liquid contact and sliding angles measurements as well as oil repellence and vertical burning tests. The results reveal that oxygen plasma treatment prior to finishing significantly increased the wettability of the PES fibres, which directly resulted in increased concentration of the absorbed finishing agents. This treatment enabled the creation of PES fabric with simultaneous superhydrophobic, oleophobic and flame-retardant properties. Although the superhydrophobic and oil-repellent characteristics of the coating were preserved after washing, the flame retardancy was hindered because of the removal of OP in the washing bath.

Keywords: polyester fibre, finishing, multifunctional properties, water and oil repellence, flame retardancy, washing fastness

### Izvleček

*Tehnični tekstilni materiali z večfunkcionalnimi zaščitnimi lastnostmi so eden največjih in najhitreje rastočih segmentov tekstilne industrije. V raziskavi so pripravljene večfunkcionalne vodo- in oljeodbojne ter ognjevarne apreture na poliestrski (PES) tkanini z uporabo fluoroalkil-funkcionalnega siloksana (FAS) kot vodo- in oljeodbojnega apreturnega sredstva in organofosfonata (OP) kot ognjevarnega apreturnega sredstva. Apreturna kopel, ki je vključevala FAS in OP ustrezne koncentracije, je bila nanesena na neobdelano in s plazmo kisika predhodno obdelano tkanino PES s postopkom, ki je vključeval impregniranje, sušenje in kondenziranje. Za primerjavo sta bili na tkanino PES pri enakih pogojih naneseni tudi enokomponentni apreturni kopeli s FAS oziroma z OP. Apretirani vzorci tkanine PES so bili oprani pri standardnih pogojih. Morfološke, kemijske in funkcionalne lastnosti apretiranih vzorcev so bile določene z vrstično elektronsko mikroskopijo, infrardečo spektroskopijo s Fourierjevo transformacijo, nanosom kopeli, stičnimi koti in koti zdrsa tekočin, oljeodbojnostjo in ognjevarnostjo. Iz rezultatov je razvidno, da je obdelava s plazmo kisika pred apretiranjem močno povečala omočljivost vlaken PES, kar je neposredno vplivalo na povečanje koncentracije adsorbiranih apreturnih sredstev. Takšna kombinacija obdelave je*

omogočila pripravo tkanine PES s hkratnimi superhidrofobnimi, oleofobnimi in ognjevarnimi lastnostmi. Medtem ko sta se superhidrofobnost in oleofobnost ohranili tudi po pranju, se je ognjevarnost poslabšala zaradi postopne odstranitve sredstva OP med pranjem.

*Ključne besede:* poliestrsko vlakno, apretura, večfunkcionalne lastnosti, vodo- in oljeodbojnost, ognjevarnost, pralna obstojnost

## 1 Introduction

Technical textile materials with multifunctional protective properties represent one of the largest and fast growing segments of the textile industry, and these materials have wide uses in different economic sectors. In technical applications, polyester fibres are the most frequently used synthetic material because of their low cost, durability, ease of care, good dimensional stability, low moisture absorbency and compatibility with cotton in blends [1]. These extraordinary properties enable polyester to be increasingly applied in the production of textile materials for protective clothing and in the sport and leisure, transportation, construction and agricultural industries. However, in addition to the desired characteristics, polyester fibres suffer from certain important disadvantages related to their functionality, such as electrostatic charging and flammability, which decrease the value and usefulness of the end products. The susceptibility of polyester fibres to electrostatic problems is directly influenced by their hydrophobicity, leading to generation and accumulation of electrostatic charges [2–4]. The latter attract particulate soils from the air, resulting in fibre soiling. In contrast, due to the hydrophobic properties of polyester, wetting and swelling of fibres with detergent solution during laundering is hindered, which importantly decreases the effectiveness of removal of the adhered soil [5–7]. To overcome these problems, tailoring of a self-cleaning coating characterised by superhydrophobic, oleophobic and low-adhesive properties is crucial. According to the theory, self-cleaning biomimetic solid surfaces exhibit low-adhesion superhydrophobicity, which is simultaneously characterised by a static water contact angle greater than  $150^\circ$  and a water sliding angle less than  $10^\circ$  as a result of a low contact angle hysteresis [8]. These surfaces include micro- and nanoscale roughness topographies coated with water-repellent polymer films [9–12]. However, in addition to particulate soils, oily stains are important contaminants of textile fibres, and thus creation of a coating with oleophobicity is of great importance.

A coating that is simultaneously oleophobic and self-cleaning could effectively repel different types of soils and prevent their adhesion as well as ensure removal of adherent soils via their collection by water droplets when rolling off the surface.

Inherent flammability with intensive burning melt/dripping and release of toxic smoke represents a serious hazardous drawback of polyester, which poses great risk and danger to human lives and material goods [13]. Because highly effective flame retardants including brominated diphenyl esters, brominated phosphates and tri-aryl-phosphates have been restricted and prohibited by the European Union's Registration, Evaluation and Authorisation of Chemicals (REACH) because of their toxicological problems and environmental unsustainability, different environmentally friendly phosphorous-containing compounds have been synthesised to produce flame-retardant polyester [14–16]. The flame-retardant mechanism of phosphorous-containing compounds is directly influenced by their chemical structure. In general, depending on the oxidation state of the phosphorous atom, flame-retardant substances are active in both the condensed phase and the gas phase [14, 17, 18]. In the condensed phase, phosphorous compounds promote char formation by influencing the fibre decomposition pathway, and in the gas phase, phosphorous compounds decompose to radical scavengers, which terminate oxidative radical chain reactions in the combustion cycle.

In this study, we first prepared multifunctional water- and oil-repellent and flame-retardant polyester fabric with the use of two chemical finishes, i.e., fluoroalkyl-functional siloxane as a water- and oil-repellent agent and organophosphonate as a flame-retardant agent. To enhance the hydrophilicity of polyester fibres and consequently increase their absorptivity to the finishing solution, fibre functionalisation with oxygen-rich groups was performed using an oxygen plasma pretreatment. It has been established that oxygen plasma treatment can cause an increase in the surface activity and also an increase in surface roughness [19–23], therefore an important goal of our research was to

investigate whether the coating exhibits self-cleaning properties. To determine the coating durability, the functional properties of polyester fabric were investigated before and after washing.

## 2 Experimental

### 2.1 Textile material and finishing agents

Plain-weave 100 % polyester (PES) woven fabric with a weight of 67 g/m<sup>2</sup> was used in the study. The fabric was washed with a solution of non-ionic surfactant at a concentration of 2.5 g/l. After washing, the fabric was rinsed in distilled water, squeezed and dried at room temperature. Two commercially available finishing agents were chosen, i.e., fluoroalkyl-functional water-born siloxane (FAS) as a water- and oil-repellent agent under the trade name Dynasylan F 8815 (Degussa, Germany) and organophosphonate (OP) as a flame-retardant agent under the trade name Apyrol CEP (Bezema, Switzerland). Both finishing agents can be mixed with water to any desired concentration.

### 2.2 Plasma treatment, finishing and washing

PES fabric samples with a size of 20 x 20 cm were treated with oxygen plasma (O<sub>2</sub> gas) for 30 seconds under 60 Pa pressure in a low-pressure inductively coupled radiofrequency plasma system.

Untreated and plasma-treated PES samples were finished with a mixture of 100 g/l FAS and 200 g/l OP using the pad-dry-cure process. Acetic acid was used in pH adjustment of the finishing bath to pH 4–5. The process included full immersion of samples for one minute at room temperature, squeezing between padded rollers at a constant pressure and roller velocity, followed by drying at 100 °C and curing at 150 °C for 5 minutes. For comparison, single-component FAS and OP finishing agents were also applied to the untreated and plasma treated PES samples under the same conditions. The PES samples codes and the procedures for the fabric surface modifications are listed in Table 1.

The finished PES samples were washed in a Gyrowash 815 (James Heal, UK) testing instrument according to the EN ISO 105C06 standard. Washing was performed in 150 ml of 4 g/l ECE phosphate reference detergent B solution at 40 °C for 45 min in the presence of ten steel balls that supply an accelerated washing treatment that corresponds to 5 domestic washes. After washing, the samples were rinsed in

distilled water at 40 °C, rinsed in cold tap water, and dried at room temperature.

Table 1: PES fabric sample codes and procedures for fabric surface modifications

Sample code	Procedure of the fabric surface modification
PES-Un	No treatment
PES-P	Plasma treatment
PES/FAS	Finishing with 100 g/l FAS
PES-P/FAS	Plasma treatment followed by finishing with 100 g/l FAS
PES/OP	Finishing with 200 g/l OP
PES-P/OP	Plasma treatment followed by finishing with 200 g/l OP
PES/FAS+OP	Finishing with the mixture of 100 g/l FAS and 200 g/l OP
PES-P/FAS+OP	Plasma treatment followed by finishing with the mixture of 100 g/l FAS and 200 g/l OP

### 2.3 Analytical methods

#### Wettability of PES fabric samples

The wettability of PES fabric samples was determined based on the amount of the finishing solution applied to the samples in the “wet on dry” process. To this end, the pressure and the velocity of the padded rollers were set to 300 kPa and 1.5 m/min, respectively, and held constant during the squeezing process. The amount of the applied finishing solution was referred to as the wet pickup (WPU), which was calculated by the following equation [2]:

$$WPU = \frac{\text{mass of solution applied}}{\text{mass of dry fabric sample}} \times 100 (\%) \quad (1)$$

Five measurements were performed for each sample, and the corresponding WPU value was reported in terms of the mean value and the standard error.

#### Scanning electron microscopy (SEM)

SEM images of the untreated and treated PES fibres were obtained using a JSM 6060 LV scanning electron microscope (JEOL, Japan) operated with a primary electron beam accelerated at 10 kV. All samples were coated with a thin layer of gold prior to observation to supply conductivity and enhance the quality of the images.

### Fourier transform infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) spectra were obtained on a Spectrum GX I spectrophotometer (Perkin Elmer, Great Britain) equipped with an attenuated total reflection (ATR) cell and a diamond crystal ( $n = 2.0$ ). The spectra were recorded over a range of  $4000\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  using 32 scans at a resolution of  $4\text{ cm}^{-1}$ .

### Contact angle measurements

The static contact angles  $\theta$  of water and n-hexadecane on the PES samples were measured using a DSA 100 contact angle goniometer (Krüss, Germany). Liquid droplets of  $5\ \mu\text{l}$  were placed on different points of each fabric sample, and the values of  $\theta$  were determined after 30 seconds of droplet deposition using the Young-Laplace fitting method. Ten measurements were collected for each fabric sample, and the corresponding  $\theta$  value was reported as the mean value and the standard error.

### Sliding angle measurements

The water-sliding (or roll-off) angles  $\alpha$  were measured in the warp direction of the fabric samples and determined as the critical angle at which the droplet of  $50\ \mu\text{l}$  began to slide or roll off the gradually inclined fabric surface. Five measurements were collected for each fabric sample, and the corresponding  $\alpha$  value was reported as the mean value of the standard error.

### Oil-repellent properties

The oil repellence of the PES samples was determined under static conditions using AATCC test method 118-1978 with eight hydrocarbon liquids in a series of decreasing surface tension. Paraffin oil was denoted with the rating number 1 and n-heptane was given the rating number 8. Drops of the standard test liquids were placed on the fabric surface and observed for wetting. The repellence rating was the highest numbered test liquid that did not wet the fabric in 30 seconds.

### Vertical test of flammability

The combustion behaviour was determined via the vertical test of flammability according to DIN 53906. A fabric sample of size  $15 \times 7.5\text{ cm}$ , arranged vertically, was exposed to a propane flame for 6 s at the bottom of the sample. After removal of the flame source, the after-flame time and after-glow time

were determined. Seven measurements were collected for each sample in the warp direction, and the measured quantities were reported as the mean values and the standard deviations.

## 3 Results and discussion

### 3.1 Characterisation of PES fabric samples

The results of WPU are presented in Figure 1. It can be observed that the value of WPU is directly influenced by the sample pretreatment as well as the characteristics of the finishing solutions. Plasma treatment of fabric samples prior to the finishing process significantly increased the WPU of all finishing solutions regardless of their properties, which was attributed to the increased wettability of the plasma-treated PES fibres. This result confirms that the oxygen plasma treatment caused the formation of new polar functional groups on the surface of PES fibres, which significantly increases their hydrophilicity and thus their wettability. The enhanced fibre wettability directly resulted in an increased concentration of the absorbed finishing agents. Furthermore, in the case of the untreated fabric samples, the surface tension of the finishing solution importantly influenced the WPU. Accordingly, the WPU of the FAS solution with low surface tension was 2 times lower than the WPU of the high-surface-tension PO solution. Because this phenomenon was insignificant in the case of the plasma-treated samples, this difference represents an important advantage of oxygen plasma treatment of hydrophobic textile fibres.

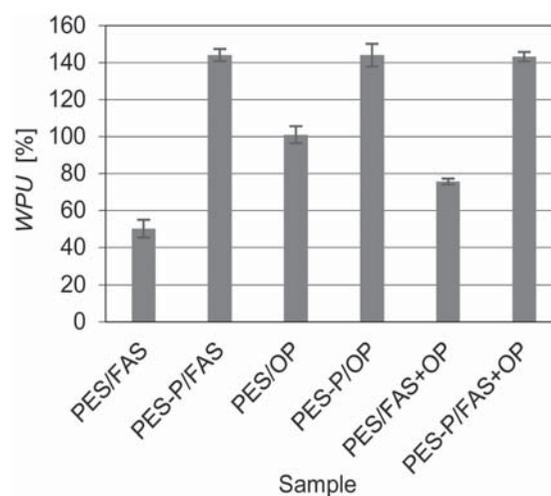
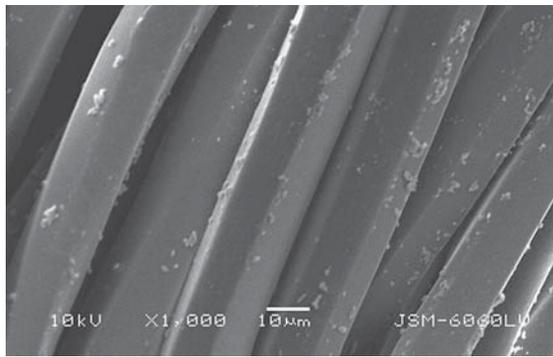
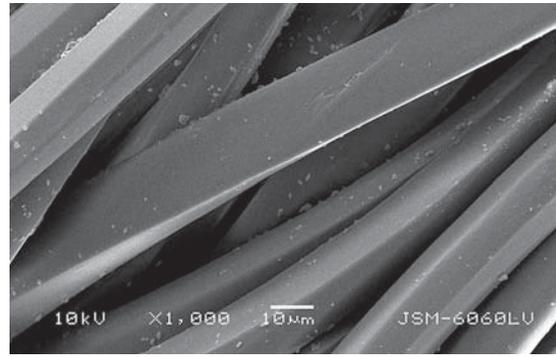


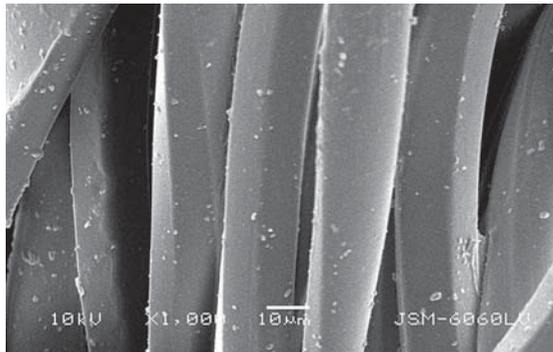
Figure 1: Wet pickup (WPU) of untreated and plasma-treated fabric samples



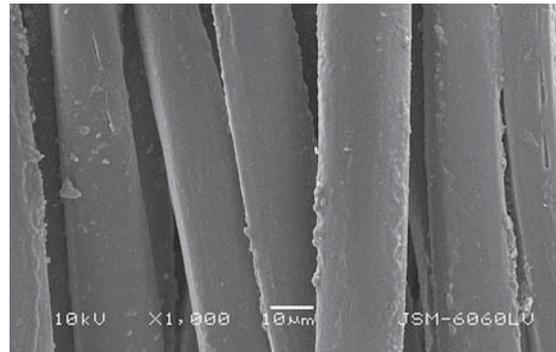
a) PES-Un



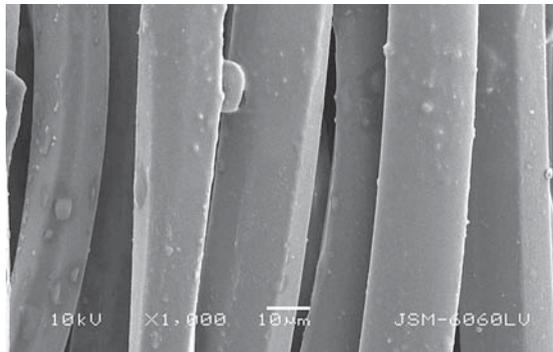
b) PES-P



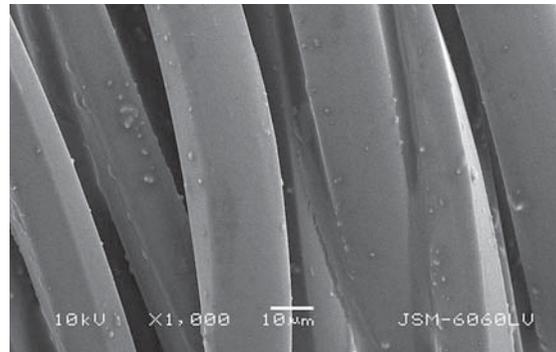
c) PES/FAS



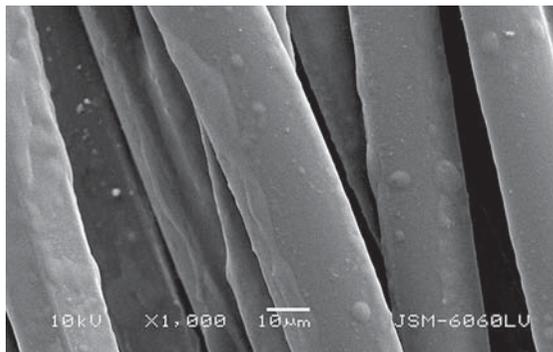
d) PES-P/FAS



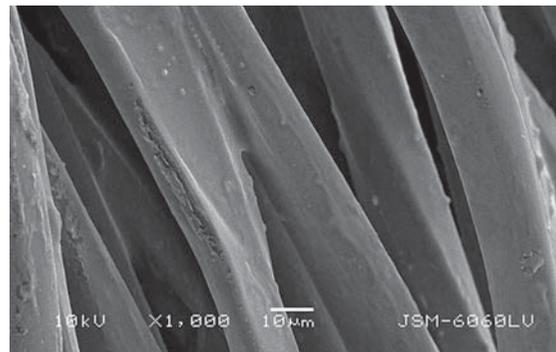
e) PES/OP



f) PES-P/OP



g) PES/FAS+OP



h) PES-P/FAS+OP

Figure 2: SEM images of untreated and plasma-treated PES fibres and PES fibres finished with different finishing solutions

SEM images of the PES fibres before and after different procedures for the fabric surface modifications are presented in Figure 2. It can be observed from the images that the oxygen plasma treatment did not significantly change the surface morphology of the fibres, suggesting that the bulk properties of the fibres remained undamaged. It is also evident that the applied finishing agents coated the fibres, which caused light thickening and gluing of the fibres in certain places on the surface. The latter was the most pronounced when the mixture of FAS and OP was applied to the plasma-treated fabric sample. Figure 3 shows the ATR FT-IR spectra of representative plasma-treated and finished PES fabric samples as well as the untreated sample for comparison. In all spectra, the following bands that are characteristic for PES fibres can be observed: the absorption band of low intensity at  $3340\text{ cm}^{-1}$  due to intermolecular O–H bonds; the absorption bands in the  $3000\text{--}2850\text{ cm}^{-1}$  spectral region attributed to stretching of  $\nu\text{CH}_2$ ,  $\nu\text{CH}_3$  and C–H; the absorption band at  $1710\text{ cm}^{-1}$  due to strong C=O stretching vibrations of the carbonyl group of the ester bond; the band at  $1577\text{ cm}^{-1}$  due to asymmetric stretching of the C–O bond of the carboxylate anions; the absorption bands at  $1372$ ,  $1338$ ,  $1240$  and  $1095\text{ cm}^{-1}$  caused by the  $\delta(\text{C–O})$  and  $\nu_{\text{as}}(\text{C–O–C})$  vibrations of the polyester fibres; and the absorption bands at  $848$ ,  $793$  and  $721\text{ cm}^{-1}$  due to the C–H and C–C vibrations of the benzene ring [24, 25]. The oxygen plasma treatment did not change the spectrum of the PES fibres, which suggests that the concentration of new functional groups incorporated onto the fibre surface was too

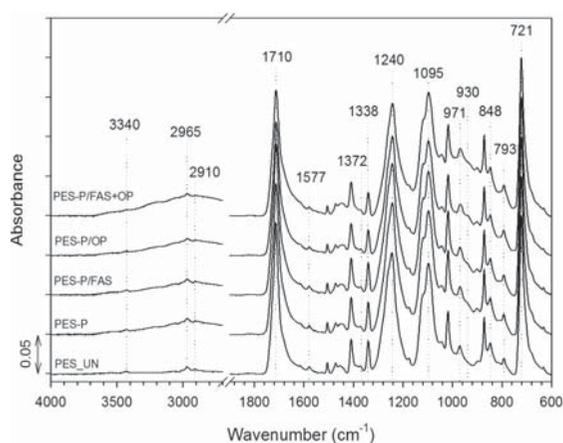


Figure 3: ATR spectra of representative PES fabric samples: PES-Un, PES-P, PES-P/FAS, PES-P/OP and PES-P/FAS+OP

low to be detected by FT-IR spectroscopy. Furthermore, in the case of the PES-P/FAS sample, the bands belonging to the FAS finishing agent at  $1238\text{ cm}^{-1}$  due to  $\nu_a(\text{CF}_2)$  mixed with rocking ( $\text{CF}_2$ ), at  $1144\text{ cm}^{-1}$  due to  $\nu_s(\text{CF}_2)$  modes, and at  $1208\text{ cm}^{-1}$  due to  $\nu_a(\text{CF}_2)$  and  $\nu_a(\text{CF}_3)$  vibrations [24, 26, 27] were blurred by the polyester fingerprint. The same applies to the band at  $1227\text{ cm}^{-1}$  in the spectrum of the PES-P/OP sample, which corresponds to the P=O bonds of phosphonate [24, 28] and is characteristic of the OP finishing agent. However, a detailed insight into the spectrum of the PES-P/OP sample reveals an appearance of a broad band of low intensity at  $930\text{ cm}^{-1}$  due to P–O stretching vibrations of phosphonate [24].

### 3.2 Functional properties of PES fabric samples

The results of the water and n-hexadecane static contact angle measurements on the unwashed and washed samples containing FAS are presented in Figures 4 and 5. For the PES fabric samples that were not finished with FAS, i.e., PES-Un, PES-P, PES/OP and PES-P/OP, the liquid static contact angles were less than  $90^\circ$  and therefore could not be measured. The results in Figure 4 reveal that the presence of the FAS coating supplied excellent water repellence to the PES fibres, with contact angles in the range of  $148^\circ$  to  $153^\circ$ , which could be characterised as notably high superhydrophobic properties. A comparison of the PES/FAS and PES-P/FAS samples shows that pretreatment of PES fibres with oxygen

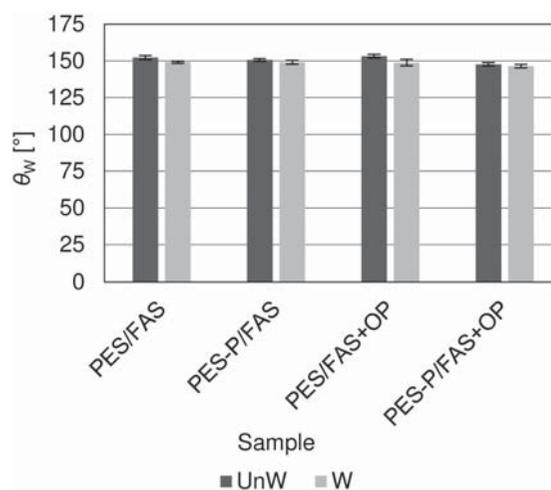


Figure 4: Static contact angles of water ( $\theta_w$ ) determined on unwashed (UnW) and washed (W) PES fabric samples finished with FAS

plasma did not improve their water repellence, despite the fact that the WPU and the concentration of the applied FAS were increased on the plasma-treated sample. This result suggests that the FAS coating can create a superhydrophobic fabric surface at notably low concentration. The higher WPU of the FAS and OP mixture for the PES-P/FAS+OP sample compared with the PES/FAS+OP sample resulted in a slight reduction in water repellence. The reason for this result was attributed to a higher uptake of the hydrophilic OP finishing agent in the mixture, which hindered the superhydrophobic performance of FAS but still resulted in notably high hydrophobicity with a water contact angle equal to  $148^\circ$ . The FAS coating exhibited excellent washing fastness with an insignificant decrease of the water contact angles in the case of all washed samples.

However, the concentration of FAS uptake by the untreated PES/FAS and PES/FAS+OP samples was too low to supply sufficient oleophobicity of the PES fibres. On these samples, n-hexadecane did not form stable drops of constant shapes on the fabric surface but slowly spread and penetrated into its porous structure, which resulted in a decrease of the contact angles and therefore prevented the static contact angle measurements. In contrast, the increase of the WPU of the oxygen plasma-treated PES fibres (PES-P/FAS and PES-P/FAS+OP samples) influenced the creation of the uniform oleophobic FAS coating with n-hexadecane contact angles in the range of  $120$  to  $124^\circ$ , which exceeded

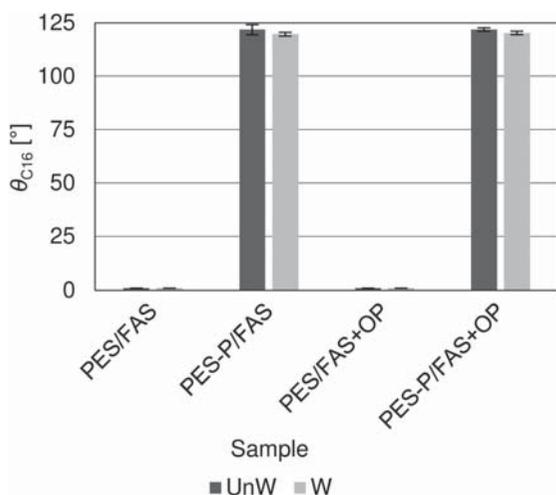


Figure 5: Static contact angles of n-hexadecane ( $\theta_{C16}$ ) determined on unwashed (UnW) and washed (W) PES fabric samples finished with FAS

$119^\circ$  even after sample washing. Accordingly, oxygen plasma treatment prior to the finishing process is crucial to supply simultaneous water repellence and oil repellence properties to PES fibres.

To determine whether the superhydrophobic PES fabric samples are self-cleaning, the sliding angles of water were determined and are presented in Figure 6. As shown in Figure 6, the lowest water sliding angles of  $15^\circ$  and  $13^\circ$  were obtained for the PES/FAS and PES-P/FAS samples, respectively, indicating the nearly full self-cleaning properties of these samples. However, to decrease the water sliding angle, the low surface free energy micro- to nanostructured roughness of the fibres surface should be created in the chemical modification process, which could allow air to become trapped in the fibre topography, thus creating a composite surface that minimises the solid/water interface and maximises the water/air surface area. However, according to the SEM images, the oxygen plasma treatment and the finishing process did not significantly affect the topography of the PES fibres, which remained nearly unchanged. The results also show that the presence of OP in the coating increased the water sliding angles of the PES/FAS+OP and PES-P/FAS+OP samples to a great extent due to the sticking of the water droplet to the fibre surfaces. This phenomenon indicates that the hydrophilic character of OP strongly increased the adhesion between water and the coating. It is clear that OP does not contribute to creation of the self-cleaning properties of the

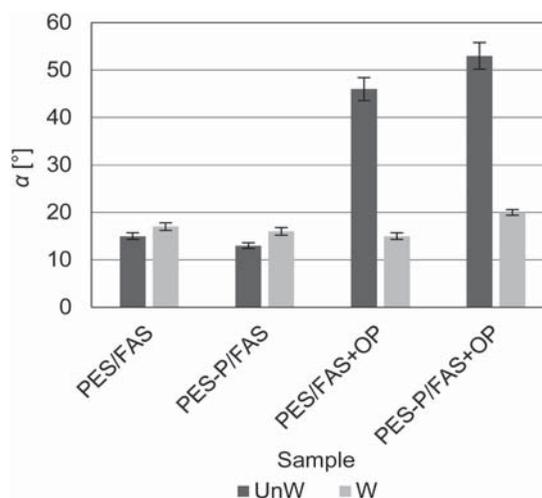


Figure 6: Sliding angles of water ( $\alpha$ ) determined on unwashed (UnW) and washed (W) PES fabric samples finished with FAS

coating. Although the water sliding angles for the PES/FAS and PES-P/FAS samples only slightly increased after washing, the water sliding angles dramatically decreased for the PES/FAS+OP and PES-P/FAS+OP samples. This result suggests that the coating structure was changed during washing and that the OP finishing agent released from the fibre surface.

The results of the oil repellence rating summarised in Table 2 gave additional information to the results presented in Figure 5. Although n-hexadecane penetrated into the PES fabric porous structure of the PES/FAS and PES/FAS+OP samples, the mixture of paraffin oil and n-hexadecane with a 1.6 mN/m higher surface tension than n-hexadecane did not wet these samples in 30 minutes. Because the same applies for paraffin oil, this result indicates that the PES/FAS and PES/FAS+OP samples were still repellent for different oils. The results in Table 2 also show the high oleophobicity of the PES-P/FAS and PES-P/FAS+OP samples, which repelled even n-decane with much a lower surface tension than n-hexadecane. The sample repellence only slightly deteriorated after washing.

The results of the burning behaviour of the PES fabric samples determined by the vertical test of flammability are summarised in Table 3. The results show that the samples differ from each other in the after-flame time and that none of the samples exhibited after-glow behaviour. The PES-Un and PES-P samples ignited easily and burned for between 20 and 30 seconds after the withdrawal of the igniting flame, and the time of burning significantly

increased if the single-component FAS coating was present on the samples. This result suggests that the FAS polymer film stabilised the PES melt in the pyrolysis zone, causing prolongation of the burning time. In contrast, the presence of OP in the coating supplied excellent flame-retardant behaviour to the PES/OP and PES-P/OP samples, which did not burn after flame withdrawal and showed superior self-extinguishing behaviour. The application of FAS in combination with OP significantly impaired the flame retarding efficiency of OP, which was reflected by the increased after-flame time of the PES/FAS+OP sample, suggesting that the concentration of the adsorbed OP was too low to provide sufficient flame retardancy. Nevertheless, as stated before, plasma treatment influenced the increase of the FAS and OP adsorption, resulting in an excellent flame-retardant behaviour to the PES-P/FAS+OP sample which was comparable to that of the samples PES/OP and PES-P/OP. However, the results of burning behaviour of washed samples reveal that OP was neither covalently bonded to the PES fibre surface nor to the FAS polymer network but was only physically incorporated into the coating, which resulted in the movement of OP from the PES fibres during the washing process. Consequently, all washed PES fabric samples burned easily. These results also confirm our assumption based on the water sliding angle measurements that the reason for the sliding angle decrease on the PES/FAS+OP and PES-P/FAS+OP samples after washing was the absence of the OP finishing agent.

Table 2: Oil repellence rating of unwashed (UnW) and washed (W) PES fabric samples finished with FAS determined under static conditions using AATCC test method 118-1978.

Sample	Rating number <sup>a)</sup>		Test liquid <sup>b)</sup>		Surface tension <sup>c)</sup> [mN/m]	
	UnW	W	UnW	W	UnW	W
PES/FAS	2	1	PO:C16 (65:35)	PO	28.7	31.2
PES-P/FAS	6	5	C10	C12	23.5	25.1
PES/FAS+OP	2	2	PO:C16 (65:35)	PO:C16 (65:35)	28.7	28.7
PES-P/FAS+OP	6	5	C10	C12	23.5	25.1

a) Rating is the highest numbered test liquid which did not wet the fabric in 30 seconds.

b) Name of the highest numbered test liquid: PO – paraffin oil, C16 – n-hexadecane, C12 – n-dodecane, C10 – n-decane.

c) Surface tension of the highest numbered test liquid at 25 °C.

Table 3: After-flame time  $t_F$  and after-glow time  $t_G$  of unwashed (UnW) and washed (W) PES fabric samples determined via the vertical test of flammability according to DIN 53906

Sample	$t_F$ [s]		$t_G$ [s]	
	UnW	W	UnW	W
PES-Un	27 ± 3	25 ± 5	0	0
PES-P	24 ± 3	26 ± 3	0	0
PES/FAS	44 ± 5	32 ± 6	0	0
PES-P/FAS	43 ± 7	41 ± 5	0	0
PES/OP	0	25 ± 4	0	0
PES-P/OP	0	18 ± 4	0	0
PES/FAS+OP	14 ± 3	43 ± 5	0	0
PES-P/FAS+OP	0	45 ± 6	0	0

## 4 Conclusion

In this research, we successfully tailored the multifunctional superhydrophobic, oleophobic, and flame-retardant coating on PES fabric using a two-step chemical modification procedure consisting of oxygen plasma treatment followed by pad-dry-cure application of an FAS and OP mixture. A comparison of the functional properties of PES fabric treated by the FAS and OP mixture with those treated by single-component FAS or OP finishing solutions reveals the following:

- Application of the FAS finishing agent supplied washing-resistant superhydrophobic properties to the PES fibres, which was insignificantly affected by the presence of OP in the mixture;
- Oxygen plasma treatment of the surface of PES fibres dramatically increased the wet pick up of the fibres and therefore preserved the conditions for the creation of the uniform oleophobic coating with n-hexadecane contact angles in the range of 120 to 124°, which exceeded 119° even after sample washing;
- The presence of OP in the coating notably increased the water sliding angles because of the enhanced adhesion between water and the PES fibres surface, resulting in complete deterioration of the self-cleaning properties;
- Application of the OP finishing agent created excellent flame-retardant behaviour of the PES fibres, which did not burn after flame withdrawal and showed superior self-extinguishing behaviour;

- The flame retardancy of the PES fibres was not wash-resistant because OP was only physically incorporated into the coating and was removed during the washing process.

### Acknowledgements

*This work was carried out in the framework of the courses Advanced Finishing Processes and Chemical Functionalisation of Textiles in the Master Study Programme, Textile and Clothing Planning. The research was supported by the Slovenian Research Agency (Program P2-0213, Infrastructural Centre RIC UL-NTF). The authors would like to thank the employees at the Department of Surface Engineering and Optoelectronics at Jožef Stefan Institute who enabled us to work on plasma.*

## References

1. EAST, A. J. Polyester fibres. In Synthetic fibres: nylon, polyester, acrylic, polyolefin. Edited by J. E. McIntyre. Cambridge : Woodhead Publishing, 2005, pp. 95–166.
2. SCHINDLER, W. D. and HAUSER, P. J. Chemical finishing of textiles. Cambridge : Woodhead Publishing, 2004, pp. 121–128.
3. PERUMALRAJ, Rathinam. Characterization of electrostatic discharge properties of woven fabrics. *Journal of Textile Science & Engineering*, 2016, 6(1), 6, doi:10.4172/2165-8064.1000235.
4. SUH, M., SEYAM, A. M., OXENHAM W., THEYSON T. Static generation and dissipation

- of polyester continuous filament yarn, *The Journal of The Textile Institute*, 2010, 101(3), 261–269, doi: 10.1080/00405000802377250.
5. DATYNER, Arved. *Surfactants in textile processing*. New York, Basel: Marcel Dekker, 1983, pp. 1–65.
  6. ISLAM, Md. Mazedul, KHAN, Adnan Maroof. Functional properties improvement and value addition to apparel by soil release finishes – A general overview. *Research Journal of Engineering Sciences*, 2013, 2(6), 35–39.
  7. KALAK, Tomasz, CIERPISZEWSKI, Ryszard. Correlation analysis between particulate soil removal and surface properties of laundry detergent solutions. *Textile Research Journal*, 2015, 85(18), 1884–1906, doi: 10.1177/0040517515578329.
  8. ZHANG, Xi, SHI, Feng, NIU, Jia, JIANG, Yugui, WANG, Zhiqiang. Superhydrophobic surfaces: from structural control to functional application. *Journal of Materials Chemistry*, 2008, 18, 621–633, doi: 10.1039/b711226b.
  9. BAE, Geun Yeol, JEONG, Young Gyu, MIN, Byung Gil. Superhydrophobic PET Fabrics achieved by silica nanoparticles and water-repellent agent. *Fibers and Polymers*, 2010, 11(7), 976–981, doi: 10.1007/s12221-010-0976-x.
  10. ZHOU, Cailong, CHEN, Zhaodan, YANG, Hao, HOU, Kun, ZENG, Xinjuan, ZHENG, Yanfen, CHENG, Jiang. Nature-inspired strategy toward superhydrophobic fabrics for versatile oil/water separation. *ACS Applied Materials and Interfaces*, 2017, 9(10), 9184–9194, doi: 10.1021/acsami.7b00412.
  11. OH, Ji-Hyun, PARK, Chung Hee. Robust fluorine-free superhydrophobic PET fabric using alkaline hydrolysis and thermal hydrophobic aging process. *Macromolecular Materials and Engineering*, 2018, 303(7), doi: 10.1002/mame.201700673.
  12. ROSU, Cornelia, LIN, Haisheng, JIANG, Lu, BREEDVELD, Victor, HESS, Dennis W. Sustainable and long-time ‘rejuvenation’ of biomimetic water-repellent silica coating on polyester fabrics induced by rough mechanical abrasion. *Journal of Colloid and Interface Science*, 2018, 516, 202–214, doi: 10.1016/j.jcis.2018.01.055.
  13. ALONGI, Jenny, HORROCKS, Richard A., CAROSIO, Federico, MALUCELLI, Giulio. Update on flame retardant textiles: State of the art, environmental issues and innovative solutions. *Shawbury : Smithers Rapra Technology*, 2013, pp. 207–239.
  14. WEIL, Edward D., LEVCHIK, Sergei V. *Flame retardants for plastics and textiles : practical applications*. Munich : Carel Hanser, 2016, pp. 141–160, doi: 10.3139/9783446430655.
  15. ALONGI, Jenny, CIOBANU Mihaela, TATA, Jennifer, CAROSIO, Federico, MALUCELLI, Giulio. Thermal stability and flame retardancy of polyester, cotton, and relative blend textile fabrics subjected to sol–gel treatments. *Journal of Applied Polymer Science*, 2011, 119, 1961–1969, doi: 10.1002/app.32954.
  16. JIANG, Zhenlin, WANG, Chaosheng, FANG, Shuying, JI, Peng, WANG, Huaping, JI, Chengchang. Durable flame-retardant and antidroplet finishing of polyester fabrics with flexible polysiloxane and phytic acid through layer-by-layer assembly and sol-gel process. *Journal of Applied Polymer Science*, 2018, 135(27), 46414, doi: 10.1002/app.46414.
  17. *Fire retardant materials*. Edited by A. R. Horrocks, D. Price. Cambridge : Woodhead Publishing, 2001, pp. 31–181.
  18. VELENCOSO, Maria M., BATTIG, Alexander, MARKWART, Jens C., SCHARTEL, Bernhard, WURM, Frederik R. Molecular firefighting – how modern phosphorus chemistry can help solve the flame retardancy task. *Angewandte Chemie-International Edition*, 2018, 57(33), 10450–10467, doi: <https://doi.org/10.1002/anie.201711735>.
  19. VESEL, Alenka, JUNKAR, Ita, CVELBAR, Uroš, KOVAČ, Janez, MOZETIC, Miran. Surface modification of polyester by oxygen- and nitrogen-plasma treatment. *Surface and Interface Analysis*, 2008, 40(11), 1444–1453, doi: 10.1002/sia.2923.
  20. ZHANG, Chunming, ZHAO, Meihua, WANG, Libing, QU, Lijun, MEN, Yajing. Surface modification of polyester fabrics by atmospheric-pressure air/He plasma for color strength and adhesion enhancement. *Applied Surface Science*, 2017, 400, 304–311, doi: 10.1016/j.apsusc.2016.12.096.
  21. NOVÁK, I., POPELKA, A., LUYT, A. S., CHEHIMI, M. M., ŠPÍRKOVÁ, M., JANIGOVÁ I., KLEINOVÁ A., STOPKA, P., ŠLOUF, M. VANKO, V., CHODÁK, I., VALENTIN, M.

- Adhesive properties of polyester treated by cold plasma in oxygen and nitrogen atmospheres. *Surface and Coatings Technology*, 2013, 235, 407–416, doi: 10.1016/j.surfcoat.2013.07.057.
22. ÖMEROĞULLARI, Zeynep, KUT, Dilek. Application of low-frequency oxygen plasma treatment to polyester fabric to reduce the amount of flame retardant agent. *Textile Research Journal*, 2012, 82(6), 613–621, doi: 10.1177/0040517511420758.
  23. GOUVEIA, Isabel C., ANTUNES, Laura C., GOMES, Ana P. Low-pressure plasma treatment for hydrophilization of poly(ethylene terephthalate) fabrics. *The Journal of The Textile Institute*, 2011, 102(3), 203–213, doi: 10.1080/00405001003616777.
  24. SOCRATES, George. *Infrared and Raman characteristic group frequencies: Tables and charts*. 3rd ed., Chichester, et al. : John Wiley & Sons, 2001.
  25. PARVINZADEH, Mazeyar, MORADIAN, Siamak, RASHIDI, Abosaeed, YAZDANSHENAS, Mohamad-Esmail. Surface characterization of polyethylene terephthalate/silica nanocomposites. *Applied Surface Science*, 2010, 256(9), 2792–2802, doi: 10.1016/j.apsusc.2009.11.030.
  26. LENK, T. J., HALLMARK, V. M., HOFFMANN, C. L., RABOLT, J. F., CASTNER, D. G., ERDELEN, C. & RINGSDORF, H. Structural investigation of molecular-organization in self-assembled monolayers of a semifluorinated amidethiol. *Langmuir*, 1994, 10, 4610–4617, doi: 10.1021/la00024a037.
  27. RABOLT, John F., RUSSELL, T. P., TWIEG, R. J. Structural studies of semifluorinated n-alkanes. 1. Synthesis and characterization of  $F(CF_2)_n(CH_2)_mH$  in the solid state. *Macromolecules*, 1984, 17(12), 2786–2794, doi: 10.1021/ma00184a045.
  28. HEINZE Thomas, SARBOVA Velina, NAGEL Matilde Calado Viera. Simple synthesis of mixed cellulose acylate phosphonates applying n-propyl phosphonic acid anhydride. *Cellulose*, 2012, 19, 523–531, doi: 10.1007/s10570-011-9646-4.