A biomimetic surface treatment to obtain durable omniphobic textiles

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ABSTRACT: A bio-inspired surface treatment to make fabrics omniphobic is reported, exploiting the ability of dopamine – a widespread naturally occurring biological neurotransmitter – to give substrate adhesion and surface immobilization. Standard polyester and polyacrylonitrile fabrics, which are intrinsically rather hydrophilic, are first dip-coated in an aqueous solution of dopamine and then treated with a fluorocarbon-based solution. After the treatment, fabrics show a strong omniphobic behavior, while remaining quite permeable to water vapor. The efficiency of the proposed biomimetic treatment is investigated by Optical Contact Angle, Environmental Scanning Electron Microscopy (ESEM), and X-ray Photoelectron Spectroscopy (XPS). Moreover, the mechanical durability of the surface treatment is tested through Martindale abrasion resistance measurements. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42404.

INTRODUCTION

Omniphobic textiles have many potential applications, including protective clothes, rainwear, sportswear, and separation filters. There are many approaches to make fabrics omniphobic, mainly based on the use of fluorosilanes and fluoroacrylates, but no methods is so versatile for all type of substrates.[1–10] Here we present a bio-inspired method based on the use of dopamine to achieve omniphobicity. Dopamine is a biological neurotransmitter widely diffused in living organisms. Dopamine is able to undergo oxidative polymerization in alkaline conditions resulting in the formation of a polydopamine (PDA) network that can interact in different ways with the substrate. Surface modifications and coatings with PDA were reported on inorganic[11] as well as organic substrates.[12] For polymer substrates, even intrinsically release materials like polytetrafluoroethylene have been successfully coated with PDA.[13] Recently, cotton[14] and polyester[15] fabrics were functionalized with PDA and silver nanoparticles to obtain antibacterial surfaces, but no example exist so far concerning the use of PDA coating to obtain durable hydrophobic and oleophobic fabrics. In particular, the affinity of PDA coating towards thiol groups and silver nanoparticles was exploited to successfully functionalize fabrics with low surface tension fluorocarbon molecules.

EXPERIMENTAL

Materials

Polyester and polyacrylonitrile fabrics were industrial samples supplied by Parà Tempotest, Italy. These fabrics were indicated in the following as Polyester (PET) (Areal density: 295 g/m^2; Warp: 26.5 ends/cm; Weft: 17.5 picks/cm) and Polyacrylonitrile (PAN) (290 g/m^2; Warp: 30.6 ends/cm; Weft: 14.5 picks/cm). Dopamine Hydrochloride (DA), Silver Nitrate ($AgNO_3$), 1H,1H,2H,2H-perfluorodecanethiol (PF10SH), Ethanol (EtOH), and Trizma® Base (pH 8.4) were purchased from Sigma Aldrich, and used as received.

Biomimetic Coating of Fabrics

PDA solution was prepared by dissolving DA (4 mg/mL) in 10 mM Trizma® Base (pH 8.4). PAN and PET fabrics were cut in circular shape and put in Petri dishes of approximately the same diameter (Ø 90 mm). For each Petri dish 7.5 mL of PDA solution were added, in order to have a slight layer of PDA solution to enhance the oxygen diffusion and the consequent DA oxidative polymerization onto PAN and PET fabrics surfaces. After 24 h, the pH-induced oxidation of DA results in a clear darkening of the fabrics Figure 1 and confirmed by the colorimetric analysis, as shown in Table I.

The PDA coated PAN and PET fabrics, called respectively PAN-DA and PET-DA in the following, were rinsed several times in abundant distilled water and dried in oven at 50°C for 30 min.

PDA coatings can be further functionalized via Michael addition reactions,[16] according to the mechanisms represented in Figure 2.

Here we exploited the affinity of PDA towards –SH groups[13] to promote the surface linking of a hydrophobic fluorocarbon

Figure 1. PAN (on the left) and PET (on the right) fabrics coated with PDA (in the inset, the pristine PAN and PET fabrics). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 2. (a) and (b) Schiff base and Michael addition reaction of primary amine; (c) Michael addition of a thiolated-molecule.

molecule, namely PF10SH. PAN-DA and PET-DA were dipped in a diluted PF10SH solution (1% v/v) in EtOH, left to react for 24 h in nitrogen atmosphere to prevent the oxidation of the PF10SH with the air, then washed in EtOH several times and dried on a hotplate at 50°C for 1 h. PAN-DA and PET-DA fabrics functionalized with PF10SH were indicated respectively as PAN-DA-PF10SH and PET-DA-PF10SH.
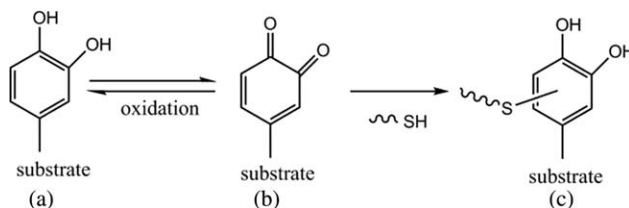
In order to make easier the adhesion of PF10SH onto fabrics coated with PDA, some PAN-DA and PET-DA specimens were dipped in a diluted AgNO$_3$ aqueous solution (1 mg/mL) for 24 h before functionalization with PF10SH, since thiols form robust complex of silver thiolate with AgNO$_3$.[17] In the following, PAN-DA and PET-DA functionalized with both AgNO$_3$ and PF10SH were indicated respectively as PAN-DA-AgNO$_3$-PF10SH and PET-DA-AgNO$_3$-PF10SH.

Optical Contact Angle

The contact angle (CA) measurements were performed using an optical video contact angle system (OCA-15-plus, Dataphysics). Water (Chromasolv® water for HPLC, Sigma Aldrich) having a surface tension of 78.2 mN/m, and Nujol oil (Mineral oil CAS 8042-47-5, Sigma Aldrich) having a surface tension of 31.2 mN/m were used as test liquids to assess the hydrophobicity and oleophobicity of the treated fabrics. The static contact angle was measured using the sessile drop method with dedicated software (Software for Contact Angle (SCA) 2.0) determining the CA based on the Young-Laplace fitting. A 1 μL droplet of liquid was dispensed on the samples using the electronic syringe unit of the instrument equipped with a 500-μL Hamilton syringe. The dynamic CA was measured using the needle in sessile drop method, dispensing and removing 3 μL of liquid at a rate of 1

μL/s, for four cycles, with a delay time of 1 s, determining the CA based on the elliptic fitting.

Environmental Scanning Electron Microscopy

We evaluated the surface morphology of the functionalized fabrics by Environmental Scanning Electron Microscopy (ESEM) (Zeiss EVO 50® Extended Pressure SEM system) operating at 20 kV and 250 pA.

X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) was used for investigating the coatings composition and oxidation state. An M-probe apparatus (Surface Science Instruments) was employed, the source was a monochromatic Al K α radiation. For each sample, survey analysis were performed in the whole X-ray spectra range (0–1000 eV Binding Energy) and high resolution analysis were performed in the C- and Ag- typical bonds regions. The 1s-level of hydrocarbon contaminant carbon (284.6 eV) was taken as the internal reference for peak shift corrections. Fittings were performed by using Gaussian's peaks, Shirley's baseline and no constraints.
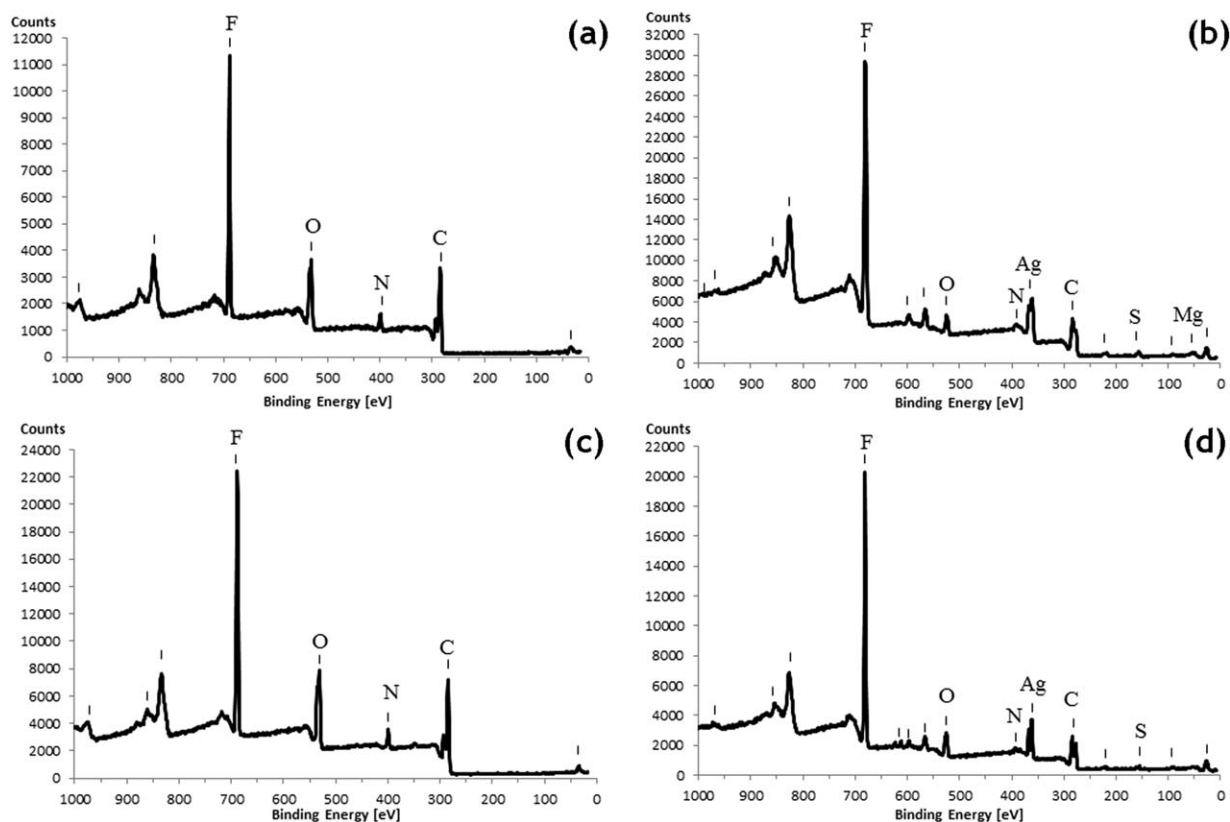
Permeability Tests

Permeability tests were carried out according to a standard procedure (see ASTM E96, water vapor transmission rate (WVTR)). All fabric samples were cut in circular shape (Ø 50 mm). For each type of fabric sample three weighting cups provided with gasket flange were used. Each test cup (Ø 40 mm) was filled with 50 g of deionized water and the fabric samples were inserted between the gasket flange. The permeability tests were conducted in a ventilated oven at 40°C. The complete apparatus, containing the fabric sample, was weighted before and during the test, at periodic intervals, to monitor the water vapor transmission rate (WVTR) through the fabric sample.

Abrasion Resistance Tests

The Martindale abrasion tester, according to the procedure UNI EN ISO 12497-2, was used to evaluate the mechanical durability of the treatment. Hydrophobized PAN-DA-AgNO$_3$-PF10SH and PET-DA-AgNO$_3$-PF10SH fabric specimens were mounted flat and rubbed at a nominal pressure of 12 kPa using a piece of worsted wool cloth as the abrading counterpart. CAs against water were periodically measured to assess the persistency of the hydrophobic surface treatment. The tests were performed at 2000, 5000, and 10,000 cycles.

Colorimetric Analysis

To give a semi quantitative evaluation of darkening we performed colorimetric analysis by a spectrophotometer (Konica Minolta): it illuminates the samples and records the light they

Table I. Colorimetric Analysis of PAN and PET Before (Pristine) and After the Coating (DP-AgNO$_3$-PF10SH)

	PAN		PET	
	Pristine	DP-AgNO$_3$-PF10SH (%)	Pristine	DP-AgNO$_3$-PF10SH (%)
L	89.13	46.56 ± 1.98	87.99	55.06 ± 1.31
A	−0.28	5.68 ± 0.09	−2.02	4.62 ± 0.13
B	1.02	14.68 ± 0.45	4.91	15.05 ± 0.73

Figure 3. XPS spectra related to (a) PAN-DA-PF10SH, (b) PAN-DA-AgNO₃-PF10SH, (c) PET-DA-PF10SH, and (d) PET-DA-AgNO₃-PF10SH.

reflect. The resulting spectra can be described by three parameters: a (which represents the scale of colors from red to green), b (the scale from yellow to blue), and L which is the lightness and represents when $a = b = 0$ the achromatic scale of greys from black to white.

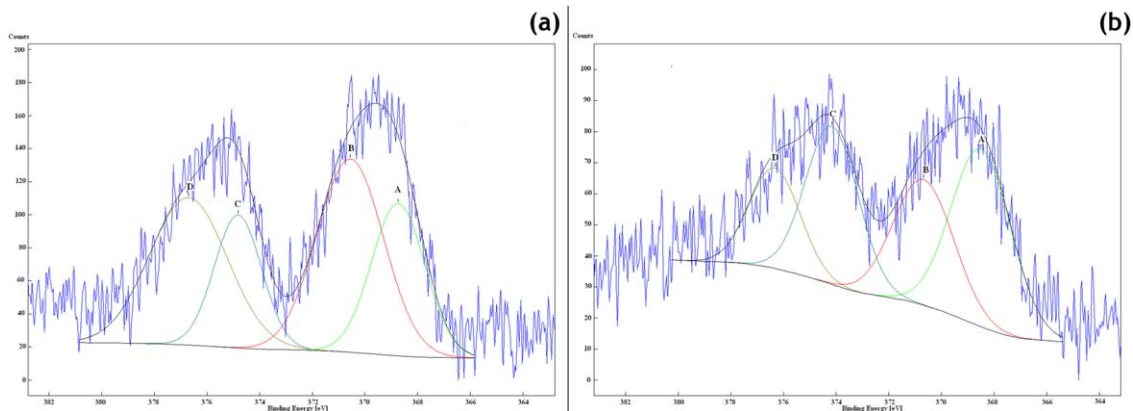## RESULTS AND DISCUSSION

Surface Chemistry Characterization

XPS was used for the chemical characterization of the treated PAN and PET fabrics. XPS spectra related to PAN-DA-PF10SH and PAN-DA-AgNO3-PF10SH are shown in Figure 3(a,b), while XPS spectra related to PET-DA-PF10SH and PET-DA-AgNO3-PF10SH are shown in Figure 3(c,d). Atomic abundance of the various samples are shown in Table II.

The surface grafting of fluorocarbon molecules is proved by the high atomic percentage of fluorine and sulfur, detected in all the samples. The presence of dopamine can be revealed by the nitrogen content; the atomic ratio C/N determined for PET and PAN fabrics treated with the dopamine and the fluoropolymer is 10.5 and 10.7 respectively, while for the PAN and PET fabrics treated with dopamine, AgNO₃, and the fluoropolymer, is 10 and 8.6. The C/N ratio is thus very similar in all the treated fabrics examined, confirming the obtainment of a homogeneous layer of PDA and the reproducibility of the treatment used for PDA formation on the fabrics. Both the PAN and PET samples treated with AgNO₃ show the presence of Ag atoms, specifically the atomic ratio C/Ag is 0.5 for PAN-DP-AgNO₃-PF10SH sample and 0.7 for PET-DP-AgNO₃-PF10SH sample, which suggest

a very similar formation of Ag nanoparticles on PET and PAN fabrics. The presence of silver nanoparticles in the AgNO₃ treated samples can be confirmed by the XPS high resolutions spectra of Ag 3d, reported in Figure 4(a) for PAN-DP-AgNO₃-PF10SH and Figure 4(b) for PET-DP-AgNO₃-PF10SH. The Ag 3d doublet is very broad and a two components curve-fitting is necessary in order to correctly fit the peak. Specifically the lower energy components (peaks A and C) are referred to Ag(0) species, while the higher energy components (peaks B and D) correspond to the formation of an Ag species bound to a more electron attractive species, probably fluorine. The interaction

Table II. Atomic Abundance of PAN-DP and PET-DP Treated with PF10SH and with PF10SH and AgNO₃

	PAN		PET	
	DP-PF10SH (%)	DP-AgNO₃-PF10SH (%)	DP-PF10SH (%)	DP-AgNO₃-PF10SH (%)
O	18	3	18	6
C	49	21	49	25
N	5	2	5	3
F	28	26	28	29
Ag	–	41	–	36
Cl	–	–	–	1
S	–	1	–	–
Mg	–	6	–	–

Figure 4. XPS Ag 3d high resolution spectra: (a) PAN-AgNO3-PF10SH sample, binding energy: A=368.74 eV, B= 370.56 eV, C=374.82 eV, D=376.70 eV; (b) PET-AgNO3-PF10SH, binding energy: A= 368.50 eV, B=370.68 eV, C=374.16 eV, D=376.33 eV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
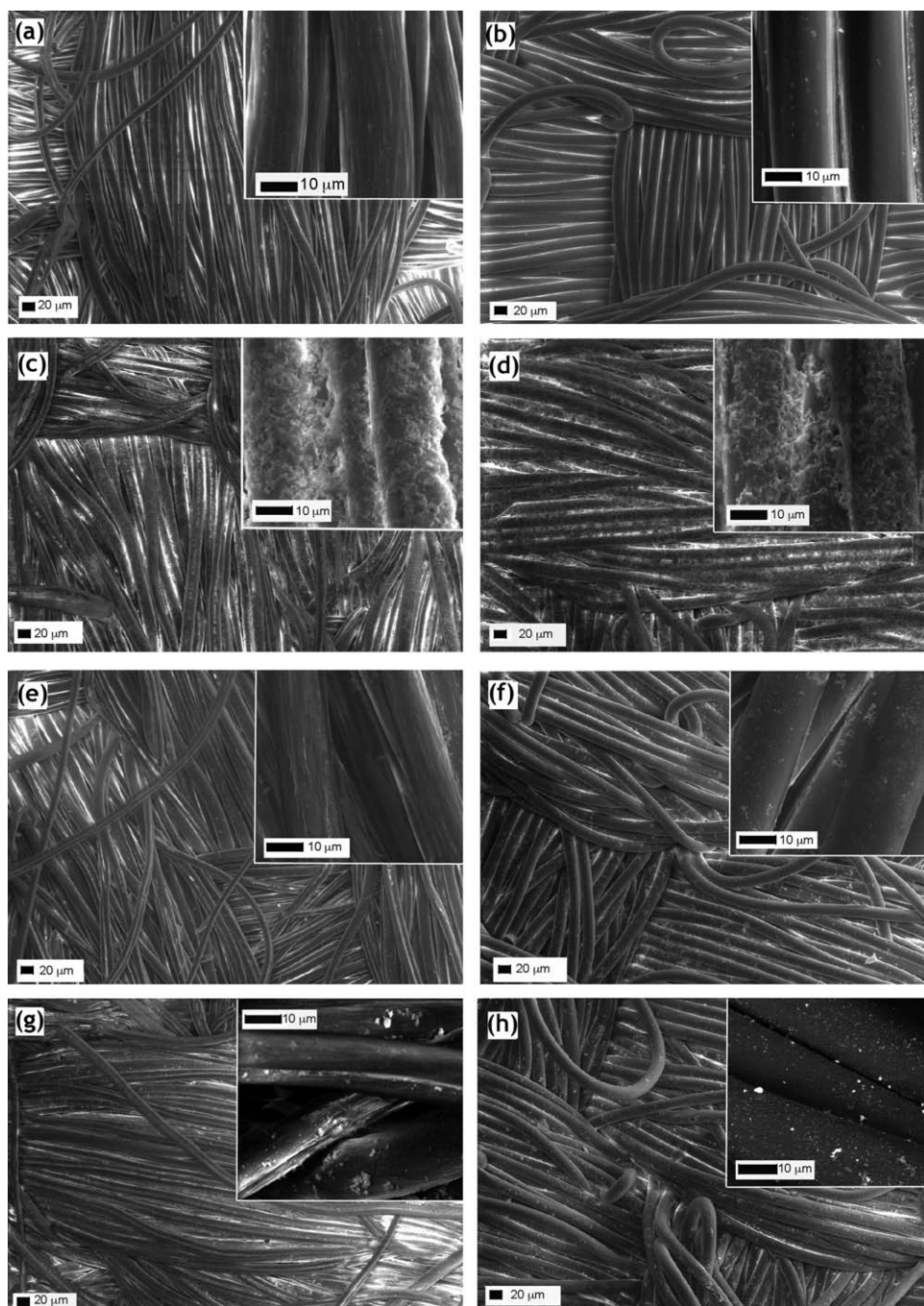
Figure 5. ESEM images of PAN (a), PET (b), PAN-DA (c), PET-DA (d), PAN-DA-PF10SH (e), PET-DA-PF10SH (f), PAN-DA-AgNO$_3$-PF10SH (g), and PET-DA-AgNO$_3$-PF10SH (h) (magnifications in the insets).
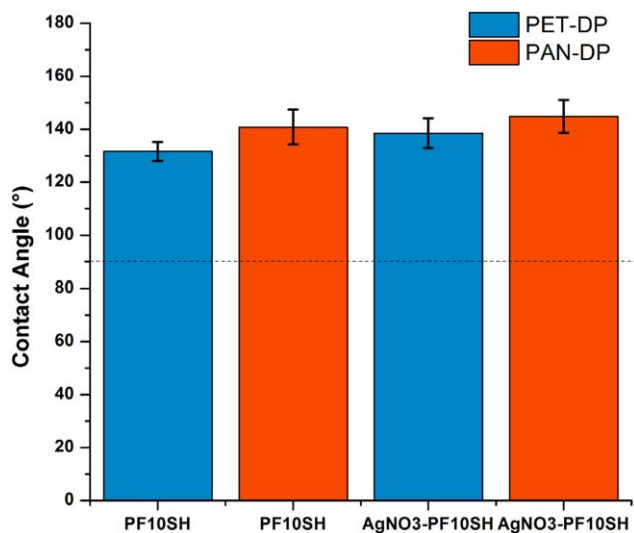
Figure 6. Static CA vs water of PAN-DP (in red) and PET-DP (in blue) coated with PF10AH and AgNO₃-PF10SH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between F and Ag confirms the role played by the AgNO₃ treatment to favor the adhesion of the fluoropolymer on the fabrics.

Morphological Characterization

Fabrics were morphologically characterized by ESEM. PDA uniformly coats the fabrics [Figure 5(c,d)] increases their surface roughness, which seems to be smoother after the treatment with PF10SH [Figure 5(e,f)]. Formations of silver nanoparticles,

due to treatment in AgNO₃ solution, are evident in the inset of the ESEM images [Figure 5(g,h)].

Physical Characterization

The omniphobicity of fabrics treated with the biomimetic approach here presented was assessed through optical contact angle (OCA) measurements against water and hydrocarbon oil. First, static and dynamic CA measurements vs water were carried out before and after the treatment. The CA value on pristine fabrics was unmeasurably small since both water and oil droplets were immediately absorbed by the fabrics, since bulk PAN and PET polymers are oleophilic and have a CA vs water less than 90°, and the microscopic roughness induced by the fabric texture drastically reduce their wettability as a consequence of the Wenzel's law.[18] In fact, changes in surface wettability may be due to roughness effects and/or to modification of surface chemistry. Two different theories are invoked to explain the effect of surface roughness on wettability. The former is described by the Wenzel equation[18]:

$$\cos\theta_W = r\cos\theta_Y$$

where θ_W is the actual CA on a real rough surface or Wenzel's angle, r is the ratio of the actual area of the solid surface to its nominal area, and θ_Y is the equilibrium Young CA observed on ideally smooth surface. Because r is always greater than one, this model predicts an enhanced hydrophilicity ($\theta_W < \theta_Y$) for hydrophilic surfaces ($\theta_Y < 90°$), and an enhanced hydrophobicity ($\theta_W > \theta_Y$) for hydrophobic surfaces ($\theta_Y > 90°$). This model takes into account a complete wetting of droplet with the underneath substrate. The latter theory was derived by Cassie and Baxter[19,20] and assumes that the liquid does not completely
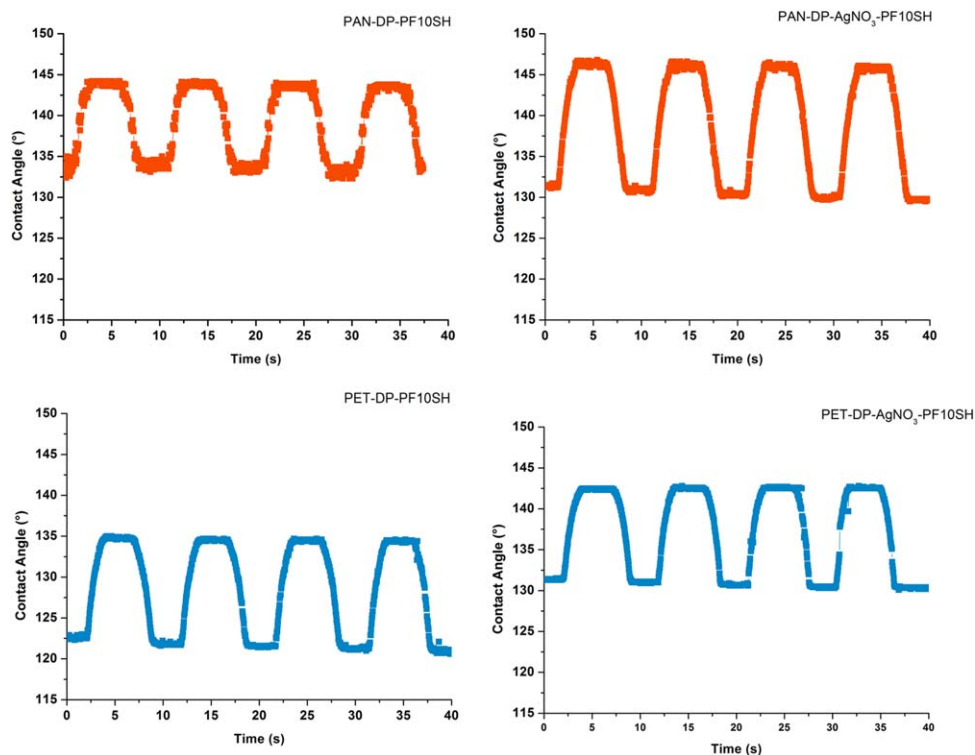
Figure 7. Dynamic CA vs water on PAN-DP-PF10SH, PAN-DP-AgNO₃-PF10SH, PET-DP-PF10SH, and PET-DP-AgNO₃-PF10SH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
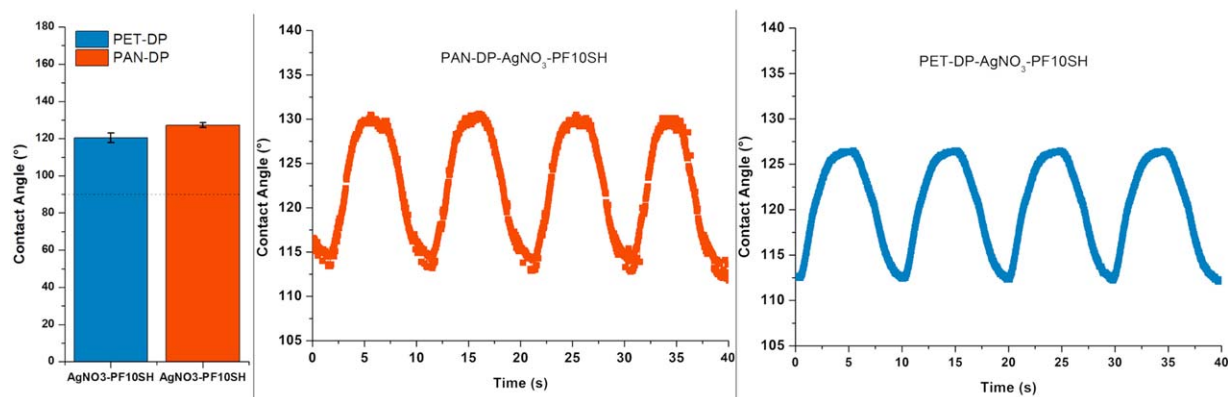
Figure 8. Static and dynamic CA vs Nujol oil on PAN-DP-AgNO$_3$-PF10SH and PET-DP-AgNO$_3$-PF10SH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
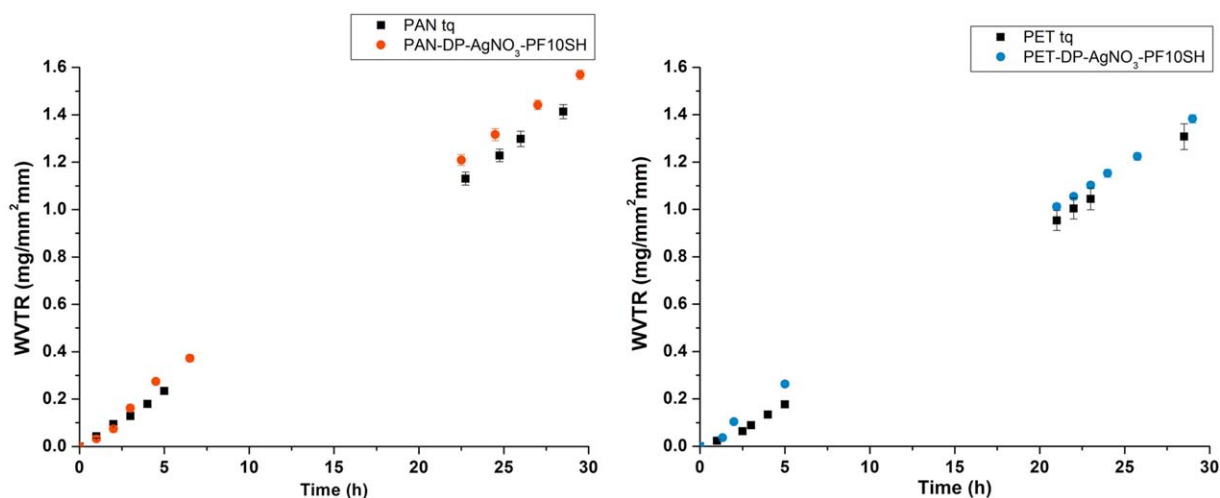

Figure 9. Water vapor transmission rate vs time of pristine and hydrophobized PAN and PET fabric samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wet the roughened substrate. The proposed expression for describing this situation is given by the following equation[20]:

$$\cos\theta_{CB} = r_f f \cos\theta_Y + f - 1$$

where θ_{CB} is the Cassie-Baxter CA, f is the fraction of the solid surface in contact with the liquid, and r_f is the surface ratio of the wet area to its nominal area. When $f = 1$ and $r_f \equiv r$, the Cassie-Baxter equation becomes the Wenzel equation. Since f and r_f are always less than one, the Cassie-Baxter model predicts that roughening a surface always increases the CA. The Cassie-Baxter model is appropriate for describing surfaces that are largely heterogeneous, as is the case of polymeric materials. If a surface is rough enough so that air may be entrapped between the liquid and the solid, the interface becomes composite and the CA increases, as in case of treated fabrics. Here the grafting of PF10SH, that is the chemical modification of the surface with fluorine groups, is responsible in increasing the CA, but this effect is further strengthened by the fabric microtexture, which leads towards a Cassie-Baxter wetting state. This effect is actually greater on PAN compared to PET, since PAN fibers have a thinner diameter [Figure 5(a,b)], determining a
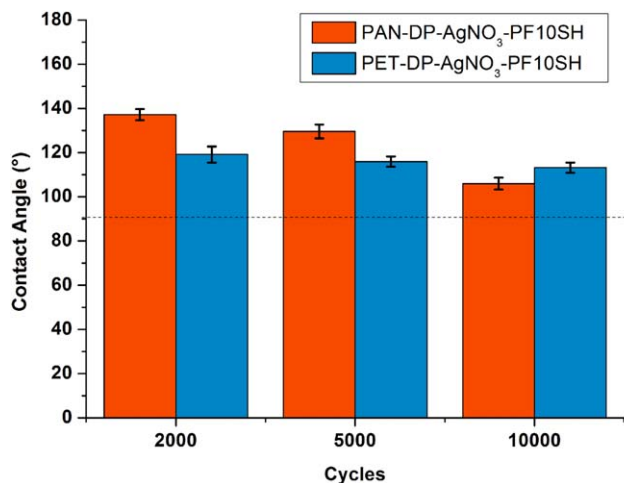
Figure 10. Static CA vs water on PAN-DP-AgNO$_3$-PF10SH and PET-DP-AgNO$_3$-PF10SH after 2000, 5000, and 10,000 rubs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
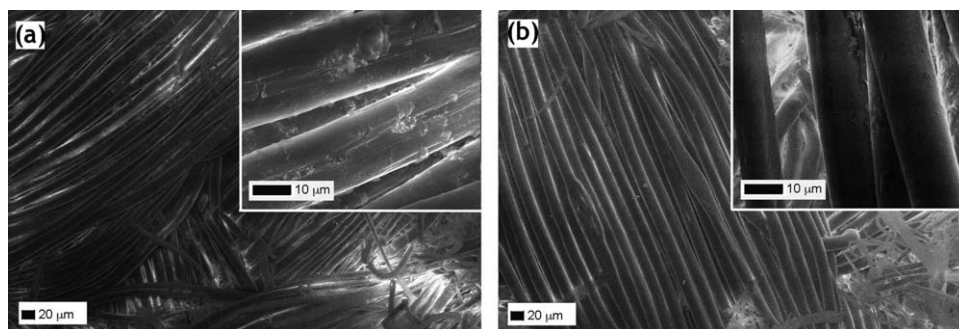
Figure 11. ESEM images of PAN-DP-AgNO$_3$-PF10SH (a) and PET-DP-AgNO$_3$-PF10SH (b) after 10,000 rubs (magnifications in the insets).

higher density of air pockets compared to PET, as on PAN-DP and PET-DP fabrics treated with AgNO$_3$ compared to those not, for the presence of silver nanoparticles [Figure 5(g,h)] that enhance the Cassie-Baxter effect (see Figure 6).

The same behavior was observed for dynamic CAs measurements as shown in Figure 7. The CA hysteresis is quite low (~15°) and the receding CA is always greater than 130°, thus the treated fabrics remain highly hydrophobic even if certain external pressure, in this case given by increasing the droplet volume during the dynamic measurements, is applied.

To assess the omniphobicity of treated fabrics, a hydrocarbon oil (Nujol) was used as low surface tension test liquid. As shown in Figure 8, also in this case CA routinely exceed 120°, and both static and dynamic measurements reveal an omniphobic behavior of the treated fabrics.

Permeability Tests
WVTR tests showed PAN and PET fabric samples were efficiently hydrophobized without changing their water permeability behavior (see Figure 9), which is an important feature in textile technology.

Martindale Tests
As shown in Figure 10, the abrasion tests at 2000, 5000, and 10,000 cycles caused only a minor reduction of the hydrophobicity of the fabric samples. The drop in the CA values with the

Table III. Atomic Abundance Determined by XPS Survey Analyses on PAN-DP-AgNO3-PF10SH and PET-DP-AgNO3-PF10SH Fabrics, Before and After 10,000 Cycles Martindale Test

	PAN-DP-AgNO$_3$-PF10SH (%)		PET-DP-AgNO$_3$-PF10SH (%)	
	Pristine	After 10000 cycles	Pristine	After 10000 cycles
F	37	7	41	8
O	7	6	5	16
Ag	2	0.4	3	0.54
C	49	72	46	71
S	2	–	2	–
Cl	1	–	0.7	–
N	2	5	3	4

number of cycles is slightly more marked for PAN compared to PET, likely due to the texture of the pristine PAN and PET fabric samples, since PAN fibers are thinner thus the loss of the air pockets due to the cycles of rubs may result more accentuated. In any case both textiles showed an excellent retention of their hydrophobic behavior after the abrasion tests, beside both textiles appear frayed (Figure 11) and the surface density of silver nanoparticles seem to be lowered.

XPS survey analyses (Table III) performed on PET and PAN fabrics, before and after 1000 cycles, confirmed a partial deterioration of the fluoropolymer layer after the abrasion test. The atomic ratio F/C, measured on sample PAN-DA-AgNO$_3$-PF10SH, diminishes from 0.74 to 0.09, while on PET-DA-AgNO3-PF10SH from 0.89 to 0.12. The decrease in F/C ratio is thus very similar between the two samples, attesting a similar deterioration of the fluoropolymer in the two fabrics. Also Ag content decreases after the abrasion test, however the F/Ag ratio increases after the Martindale test, from 15.9 to 17.1 for PAN sample and from 13.8 to 15.1 for PET sample, indicating a higher resistance of the inorganic component compared to the polymeric one. The nitrogen content otherwise only slightly decreases, C/N ratio in PAN fabric is 21.8 before the abrasion test and 15 after the test, similarly in PET fabric C/N ratio decreases from 17.8 to 15. Thus we can suppose that the PDA layer resists against the mechanical stresses induced by the Martindale test. The good hydrophobic behavior detected on the fabrics after the Martindale tests can be indeed explained by the high resistance of the PDA layer; moreover we can suppose that the fluoropolymer deterioration, occurred after 10,000 cycles, is not enough for determining a consistent decrease of the hydrophobic behavior of the DP-AgNO$_3$-PF10SH coated fabrics.

CONCLUSIONS

In this article, polyester and polyacrylonitrile fabrics were successfully made omniphobic through a simple biomimetic surface treatment based on coating in dopamine solution followed by perfluorocarbon treatment. Since dopamine is able to cover ideally any material, this method might be easily extended to make omniphobic textile fabrics of any chemical composition.

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