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Resistant amphiphobic textile coating by plasma induced polymerization of a pyrrole derivative grafted to silica nanoparticles and short fluorinated alkyl chains

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Abstract

Hydrophobic and oleophobic resistant coatings are realized on nylon and cotton textiles by plasma induced polymerization of modified pyrrole monomers. This process creates a chemical bond between the polymer and the textile fibers for an improved mechanical adherence. A chemical *post*-grafting with short fluorinated chains gives the non-wetting properties. Two other improvements are tested and compared in terms of adherence and wetting properties. The first one consists of inducing a crosslinking to improve the adhesion of the coating, and the second one of grafting silica nanoparticles to enhance the amphiphobicity.

Keywords: oleophobic, hydrophobic, textile, plasma induced polymerization, nanoparticles, pyrrole.

PEDOT	poly(3,4-ethylenedioxythiophene)
Рру-ОН	poly(2-(1H-pyrrol-3-yl)ethanol)
ру-С ₃ -ру	1,3-di(1H-pyrrol-1-yl)propane
ру-С6-ру	1,6-di(1H-pyrrol-1-yl)hexane
ру-С ₁₀ -ру	1,10-di(1H-pyrrol-1-yl)decane
Pyrrole-OH	2-(1H-pyrrol-3-yl)ethanol

Abbreviations:

1. Introduction

Hydrophobic and oleophobic textiles have been extensively studied in the past decade, but the large majority of oleophobic coatings on fabrics cited in the literature are using long chain fluorinated compounds, that are today heavily restricted [1,2]. These coatings are realized using various processes and materials: dip-coating of fluorinated silsesquioxane polyhedric oligomers [3-5] or fluorinated copolymers [6-9], Chemical Vapor Deposition (CVD) of fluorinated silane [10] or silicone nanofilaments [11, 12] covered by a fluorinated coating with Plasma Enhanced Chemical Vapor Deposition (PECVD) [13]. PECVD was also used to homogeneously polymerize perfluorodecylacrylate [14-16] and obtain oleophobic fabrics.

Many techniques also employ nanoparticles to add a nanometric roughness on the meshes of the textile and therefore enhance the overall oleophobicity [17-20]. The additional roughness added on the fabric fibers could also be a way to reduce the use of long chain fluorinated compounds without reducing the non-wetting properties.

Oleophobic properties were also reached on textile using conducting polymer such as polyaniline by wet processing [21], or polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT) by CVD [22, 23]. Conducting polymers coatings on textiles have indeed been developed at the first place for smart textiles or EMI shielding applications [23-27]. A better resistance of the conductive polymer coating and its adherence to the textile fibers have therefore been developed through different techniques: adding layers between the conducting polymers (polyaniline or polypyrrole) and the textile [22], processing solvent treatments [28, 29], or laser treatments for nanocellulose coating [30]. A very promising technique enhancing the coating adherence seems to be the plasma treatment. Indeed, the surface etching caused by the plasma creates physical interactions between the substrate and the coating [31]. The plasma also chemically modifies the surface to induce a chemical bond [32, 35].

The plasma induced graft polymerization [36] applied to textiles aims to perform a polymerization on a fabric wetted in a monomers solution, by a simple plasma treatment [37, 38]. This process has been tested once with conducting polymers on wool fabrics [39]. The plasma treatment seems to introduce enough radicals and functional groups on the textile fibers to promote alone the oxidation polymerization. The polymers seem to be chemically bonded to the plasma treated fibers, inducing the coating adherence. The etching of the fibers also provides roughness that could possibly increase wetting properties.

In this study, we aimed to realize amphiphobic textile coatings using non-toxic short fluorinated chains and with enhanced resistance properties. Therefore we accomplished plasma induced graft polymerization of modified pyrrole, chosen for its synthesis ease. We report hydrophobic and oleophobic highly resistant coatings on cotton fabric and also nylon, known to be difficult to graft [32, 40]. The wetting properties are achieved by the addition of short fluorinated chains by a chemical *post*-grafting as well as the nanostructures created by the plasma etching on the fibers. To further improve the adherence and wetting properties, several methods were tested. Another monomer with two pyrrole units was copolymerized to induce crosslinking. Silica nanoparticles grafted with 4-(3-pyrrolyl)butyric acid were copolymerized in order to further increase the roughness on the textile fibers. The adherence and wetting properties of each method are compared.

2. Experimental Section

2.1 Materials

Sefar Nitex®nylon 6,6 fabrics (Sefar AG, Switzerland) of mesh sizes 100 µm and commercial cotton fabrics of approximative mesh sizes 100-150 µm were used in the experiments. The dimensions of textile samples were 2 x 4 cm. Pyrrole, 2-naphtalene sulfonic acid, fumed silica nanoparticles with a diameter of 14 nm, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), N-hydroxy-succinimide (NHS), (3-aminopropyl)triethoxysilane, 4-(dimethylamino)pyridine (DMAP), 4-(3-pyrrolyl)butyric acid and solvents were purchased from Sigma Aldrich and used as received. 2-(1H-pyrrol-3-yl)ethanol (Pyrrole-OH), 1,3-di(1H-pyrrol-1-yl)propane, 1,6-di(1H-pyrrol-1-yl)hexane and 1,10-di(1H-pyrrol-1-yl)decane were prepared as described below.

2.2 Monomers synthesis

2-(1H-pyrrol-3-yl)ethanol (pyrrole-OH) was synthesized in four steps from pyrrole (**Scheme 1**). [41-44] A tosyl group is used to protect the amine function of the pyrrole. The protection reaction is realized with potassium *tert*-butoxide in DMF. The second step consists in a Friedel-Crafts acylation using AlCl₃. The third step is a derivation from the Willgerodt reaction using thallium nitrate as catalyst supported on Montmorillonite K10. The Montmorillonite is protecting the catalyst which is acid and substitute the perchloric or sulfuric acid often used [45, 46] The last step is the reduction of the ester to form the alcohol using dimethylsulfide-boran and the basic hydrolysis of the tosyl group.



Scheme 1. Chemical route to pyrrole-OH.

Tosyl-pyrrole

Yield 66%, white solid.

1H NMR (200 MHz, CDCl3): 7.74 (2H, d, tosyle), 7.28 (2H, d, tosyle), 7.15 (2H, t, pyrrole), 6.28 (2H, t, pyrrole), 2.39 (3H, s, tosyle).

Tosyl-3-acétyl-pyrrole

Yield 40%, colorless oil.

1H NMR (200 MHz, CDCl3): dH(200 MHz, CDCl3): 7.79 (2H, d, tosyle), 7.71 (2H, t, pyrrole), 7.33 (2H, d, tosyle), 7.13 (1H, m, pyrrole), 6.68 (1H, m, pyrrole), 2.43 (3H, s), 2.40 (3H, s).

Methyl 2-(1-tosyl-3-pyrrolyl)acétate

Yield 63%, brown oil.

1H NMR (200 MHz, CDCl3): 7.74 (2H, d, tosyle), 7.29 (2H, d, tosyle), 7.11-7.06 (2H, m, pyrrole), 6.24 (1H, m, pyrrole), 6.68 (1H, m, pyrrole), 3.71 (3H, s, CO-Me), 3.45 (2H, s, CH2-CO), 2.40 (3H, s, tosyle).

2-(1H-pyrrol-3-yl)ethanol

Yield 40%, colorless liquid.

1H NMR (200 MHz, CDCl3): 8.16 (1H, s, -NH), 6.77 (1H, q, pyrrole), 6.67 (1H, m, pyrrole), 6.13 (1H, m, pyrrole), 3.79 (2H, t, CH2-OH), 2.76 (2H, t, CH2-CH2-OH), 1,60 (1H, s, -OH).

1,3-di(1H-pyrrol-1-yl)propane, 1,6-di(1H-pyrrol-1-yl)hexane and 1,10-di(1H-pyrrol-1-yl)decane monomers (abbreviated as $py-C_n-py$) were synthesized in 2 steps from pyrrole

(Scheme 2). Potassium pyrrolate was first synthesized adding drop by drop pyrrole (1 eq) to potassium metal (1.5 eq) in THF and under argon atmosphere. After a day the salt was washed with THF. [47] Dibromo-propane, -hexane or -decane (1 eq) in THF, were then added to potassium pyrrolate (2 eq) in DMSO and stirred a day. Water was then added and the product was extracted with ethyl acetate and purified by column chromatography with eluent (chloroform/cyclohexane) (1/1). [48]



Scheme 2. Synthesis step to pyrrole-alkyl-pyrrole.

1,3-di(1H-pyrrol-1-yl)propane (Py-C₃-py):

Yield 12%.

1H NMR (200 MHz, CDCl3): 6.64 (1H, t, pyrrole), 6.18 (1H, t, pyrrole), 3.84 (1H, t, -N-CH2-

), 2.24 (0,5H, t, -N-CH2-CH2-).

13C NMR (50 MHz, CDCl3): 120.53, 108.35, 46.15, 32.77, 26.89.

1,6-di(1H-pyrrol-1-yl)hexane (Py-C₆-py):

Yield 35%.

1H NMR (200 MHz, CDCl3): 6.64 (1H, m, pyrrole), 6.15 (1H, m, pyrrole), 3.86 (2H, t, -N-CH2-), 1.76 (1H, t, -N-CH2-CH2-), 1,30 (1H, t, -N-CH2-CH2-CH2-). 13C NMR (50 MHz, CDCl3): 120.40, 107.84, 49.39, 31.34, 26.29.

$\textbf{1,10-di(1H-pyrrol-1-yl)decane} (Py-C_{10}-py):$

Yield 34%.
1H NMR (200 MHz, CDCl3): 6.66 (1H, t, pyrrole), 6.15 (1H, t, pyrrole), 3.87 (1H, t, -N-CH2-), 1.76 (1H, t, -N-CH2-CH2-), 1,28 (3H, m).
13C NMR (50 MHz, CDCl3): 120.58, 107.88, 49.75, 31.69, 29.50, 29.28, 26.86.

2.3 Nanoparticles grafting

Nanoparticles of diameter 64 nm were synthetized as followed, according to a literature method [49]. Absolute ethanol (100 mL) was mixed with 10 mL of ammonia (35%) and stirred

during 15 min at 55°C. Tetraethoxysilane (5 mL) was added dropwise and the mixture was stirred during 24h at 55°C. The particles were centrifuged at 10 000g for 10 min, then washed thrice with ethanol and dried in an oven at 90°C to provide 1.45g of silica nanoparticles.

Silica nanoparticles (both commercial fumed silica nanoparticles with a diameter of 14 nm and synthetized nanoparticles of diameter 64 nm) were functionalized using (3-aminopropyl)triethoxysilane following the literature [50,51]. 2 g of fumed silica nanoparticles previously dried in an oven were added with 100 mL of anhydrous toluene under argon atmosphere in a round-bottom flask. Then, 7 mL of (3-aminopropyl)triethoxysilane was added and the reaction was carried out at reflux for 4h. The nanoparticles were washed by centrifugation (8000g, 5 min) with toluene, ethanol and deionized water, and dried overnight in an oven at 90°C.

Functionalized nanoparticles were then grafted to the monomer 4-(3-pyrrolyl)butyric acid. A mixture of EDC (1.5 eq/monomer) and NHS (1/15 of EDC) was added to a solution of monomer in ethanol (2.5 mL/mg of monomer) and was stirred during 1 h at room temperature. A solution of nanoparticles in water (25 mg/mL) (0.9 eq/monomer) was then added and the reaction was prolonged 5 days at room temperature. The product was purified by dialysis (MWCO: 3500) and washed by centrifugation.

Nanoparticles were measured on SEM pictures of the coated fabrics, their sizes are 22 ± 4 nm (for the commercial ones) and 64 ± 9 nm (for the synthetized ones).

2.4 Plasma parameters

The textile samples were irradiated using oxygen plasma produced from a P300 plasma device (Alliance Concept, France). The schematic diagram and the complete details of the device is described in [52]. The vacuum chamber was first evacuated using a 20 m³/h rotary pump and the base pressure was achieved at 6.0 x 10^{-2} mbar. Oxygen gas was then injected inside the vacuum chamber at a constant flow rate of 20 sccm, the operating pressure stabilized at 2.41 x 10^{-1} mbar before plasma was ignited. The excitation frequency was fixed at 13.56 MHz with a pulsing duty cycle of 50%. For the nylon samples, two sets of plasma parameters were used: 100 W power at an irradiation time of 120 s and 50 W power for 60 s. The DC selfbias voltage for the said parameters were 452 V and 305 V, respectively. For the cotton samples, the power used was 100 W at an irradiation time of 10 min to achieve a DC self-bias voltage of 394 V that gave a microscopically similar etching as the etched nylon samples.

2.5 Polymerization

Immediately after the plasma treatment the nylon samples were immerged in a solution of NSA and a solution of monomers (10 mM) in deionized water for Pyrrole-OH and ethanol for the others was added. The concentrations ratio in the polymerization bath (20 mL) were (1/0.45) (monomer/salt). The samples were stirred during 24 h at room temperature (48 h for copolymerization with nanoparticles). They were then profusely washed with distilled water and ethanol and dried overnight at ambient temperature.

2.6 Fluorinated post-grafting

The corresponding fluoro acid (1 eq.) was mixed to 1.9 eq. of EDC and a catalytic amount of DMAP in 20 mL of dichloromethane. After stirring for 30 min, the pyrrole-OH grafted nylon sample (copolymerized with py- C_n -py or with 4-(3-pyrrolyl)butyric acid grafted nanoparticles) was added to the mixture and stirred for 5 days at room temperature (**Scheme 3**).



Scheme 3. Post-functionalization of the nylon samples grafted with pyrrole-OH.

2.7 Surface characterization

Fourier Transform infrared spectroscopy

The IR spectroscopy of nanoparticles was realized on a Spectrum 100 FT-IR spectrometer (Perkin Elmer, USA) with a diamond attenuated total reflectance (ATR) top plate accessory. The samples were scanned 3 times at 1 cm⁻¹ spectral resolution over the range of 450 cm⁻¹ to 4000 cm⁻¹. The spectra reported in this paper were obtained by subtracting the background spectra from the measured spectra.

Contact angle measurements

The contact angle measurements were performed using a DSA30 goniometer (Krüss). The static contact angles were determined with the sessile-drop method using 2 μ L droplets of probe liquids of various surface tensions: water (72.8 mN/m), diiodomethane (50.8 mN/m), hexadecane (27.6 mN/m).

Scanning electron microscopy

The morphology was evaluated by the scanning electron microscopy (SEM) with a Phenom ProX microscope and a 276 JEOL 6700F microscope after a platinum coating.

Adherence tests

The test was performed in accordance with PSTC 101 standards. An adhesive tape (Elcometer 9358) was pasted on the fabric and removed horizontally using a 200 g weight.



3. Results and Discussion

Scheme 4. Summary of the 3 different methods realized in this study.

3.1 Characterization of nylon and cotton fabrics treated with plasma induced polymerization and co-polymerizations

First of all, nanoparticles were characterized by FT-IR spectroscopy at each step of their modification (**Figure 1**). Silica bands are present around 1060 and 800 cm⁻¹. After the functionalization, amino bands appear at 3650 cm⁻¹ (vNH), and 1560 cm⁻¹ (δ NH). Alkanes vCH2 bands are visible at 2956 and 2885 cm⁻¹. After the grafting with 4-(3-pyrrolyl)butyric acid, the spectra show alkanes vCH2 bands at 2928 and 2850 cm⁻¹ but also amide ones : vNH at 3320 cm⁻¹, δ NH at 1670 and 1625 cm⁻¹, aromatic amine at vCN à 1310 cm⁻¹ and aromatic carbons vCC at 1534 and 1571 cm⁻¹.



Figure 1. FT-IR spectra of pure nanoparticles (yellow), functionalized ones (orange) and nanoparticles grafted with 4-(3-pyrrolyl)butyric acid.

Plasma treated samples are observed by SEM (**Figure 2**). The plasma parameters for nylon samples were chosen in order to obtain an etched surface (452 V DC self-bias voltage) and almost a smooth one (305 V DC self-bias voltage) [50]. These samples are used later to determine the role of the etching in the adherence of poly(2-(1H-pyrrol-3-yl)ethanol) (ppy-OH) on nylon fibers. The asperities on the etched nylon formed submicrometric to almost micrometric hollows. Etched cotton samples presented micrometric peaks. The oxygen plasma treatment also modified the chemical composition of the exposed surface of the fabrics, as reported in the literature [33, 34, 55].



Figure 2. SEM images of plasma treated nylon and cotton fabrics with DC self-bias voltages indicated. All scale bars are 1µm long.

After the plasma induced polymerization and the fluorinated *post*-grafting, every cotton sample showed a brownish color except the one with nanoparticles sized 22 nm (**Figure 3**). On the contrary, all the other coated nylon samples did not show a real change in color. The blackened edges of some samples may be due to a graphitization of the fabric by the plasma treatment, because of a higher potential developing at the sample edges. However, every following characterizations were performed in the middle of the samples. Even though the coatings did not seem macroscopically homogeneous, microscopic observations revealed similar pictures at different spots of the samples.



Figure 3. Photo of the fabrics. (top: cotton, bottom: nylon, left to right: pure fabric, C_4F_9 , Py-C₃-Py + C₄F₉, NP 22 + C₄F₉, NP 64 + C₄F₉, both NP + C₄F₉).



Figure 4. SEM images of coated nylon fabrics with the 3 methods of plasma induced polymerization (A, B and C).

Figures 4 and 5 present SEM pictures of nylon and cotton fabrics treated by each 3 methods with plasma induced polymerization. Even though it is difficult to distinguish the polymer sediments on the etched nylon surfaces, some whiter roughness which may be some polymers coatings are visible in between the etching on the substrates. It is maybe clearer with

the fabric etched with a DC self-bias voltage of 305 V which presents less engraving but the same sediments (**Fig. 4 A2 and A3**). The *post*-grafting of ppy-OH with fluorinated alkyls did not change the surface morphology compared to the nylon meshes coated with ppy-OH only, and thus for every method (**Fig. 4 A1/ A2, B1/B2, C1/C2**). Neither the carbon chains length of the crosslinker (**B2 and B3**), nor the fluorinated tail of the *post*-grafting (**C2 and C3**) modified the visual aspect of the coating. The nanoparticles deposit was clearly characterized on the SEM pictures (**C**).

The polymer coating is also not visible by SEM on cotton fabrics except maybe when a crosslinker is used (**Fig. 5 B**). The nanoparticles deposit takes place in the etching as seen on the **Figure 5 C1 and C2**.



Figure 5. SEM images of coated nylon fabrics with the 3 methods of plasma induced polymerization (A, B and C). Nanoparticles are observed on insets.

The wettability data can however show that pyrrole-OH really polymerized on nylon fabrics. The contact angles for water indeed reduce from $91^{\circ} \pm 2^{\circ}$ for pure nylon to around 30° for ppy-OH (**Fig. 6**). If $\theta^{Y} < 90^{\circ}$ for Ppy-OH as it is surely the case, the roughness enhances the hydrophilicity in the Wenzel state. Here the contact angle is reduced when the plasma power increases because of more etching and roughness.

Furthermore, samples with copolymers $py-C_n-py$ and pyrrole-OH are more hydrophobic than only ppy-OH, the bifunctional pyrroles are indeed more hydrophobic than pyrrole-OH, but less hydrophobic than pure nylon because of ppy-OH. Nylon samples with nanoparticles were more hydrophilic.



Figure 6. Hydrophobicity data for nylon samples coated with ppy-OH, copolymers and nanoparticles.

EDX analyses enabled to further characterize the polymer coatings on cotton samples (**Fig. 7**). EDX spectra show the presence of nitrogen which is only present on the cotton samples inside the coating. EDX analyses also confirmed the efficiency of the fluorinated *post*-grafting for every method (**Fig. 7 and 8**). The amount of fluorine did noy change with the length of the fluorinated chains because it depends also on the grafting rate. The peak of silicon can also be noticed on the spectra corresponding to the silica nanoparticles.



Figure 7. EDX spectrum of cotton fabrics mapping for each method.



Figure 8. EDX spectrum of nylon fabrics mapping for each method.

3.2 Wettability properties of the treated fabrics

Table 1 presents the wettability results of the textiles treated with the first method (A) that consisted of the plasma induced polymerization of Ppy-OH on the fabrics followed by a fluorinated *post*-grafting. The contact angles of the fabrics increase after the *post*-grafting due to the added fluorinated alkyl chain. The *post*-grafted nylon fabrics are all hydrophobic with water contact angles up to 134° . The C₆F₁₃-grafted chains are slightly less hydrophobic than the others while remaining as oleophobic or more than the C₄F₉-ones, that may be explained by a lower yield of *post*-grafting for the C₆F₁₃ chains. This is also in agreement with literature data realized by XPS using similar conditions [56]. The samples containing PPy-C₈F₁₇ are the most oleophobic ones with best contact angles of 116° and 109° for diiodomethane and hexadecane respectively. The samples treated with a 452 V DC self-bias voltage plasma are slightly more oleophobic than with 305 V, especially for C₆F₁₃ and C₈F₁₇ chains. The etching of the fibers at 452 V induces indeed a supplementary roughness that enhances the oleophobicity. This plasma parameter was hence selected for the rest of the study. For the cotton fabric which is very hydrophilic, the water droplets were absorbed by the samples except for the C₆F₁₃-grafted one

which was hydrophilic with a contact angle of 60° . Nevertheless, both fluorinated grafted samples exhibited oleophobic properties with diiodomethane with contact angles between 115 and 120°.

Table 1. Wettability data for the nylon and cotton fabrics treated with the first method (A: plasma induced polymerization of Ppy-OH and fluorinated post-grafting). Contact angles are given for water, diiodomethane and hexadecane. (Results for nylon are the mean values on two different samples.) (x indicates cotton samples with parameters set not realized.)

			Nylon			Cotton	
Polymer	Plasma	A [deg]	A [deg]	A [deg]	A [deg]	A [deg]	$\theta_{\rm hexa}$
i orymer	1 lasilla	ow [deg]		Unexa [ucg]	o _w [deg]		[deg]
Pure fabric	Х	91.0 ±1.6	0	0	0	0	0
Рру-ОН	452 V	29.8 ±5.5	0	0	0	0	0
	305 V	37.9 ±5.3	0	0	х	х	х
Ppy-C ₄ F ₉	452 V	125.3 ±13.1	101.5 ± 18.5	73.1 ±33.0	0	111.8 ±8.3	0
	305 V	121.3 ±6.8	102.7 ± 9.5	73.2 ± 6.0	х	Х	Х
Ppy-C ₆ F ₁₃	452 V	109.9 ±27.9	114.1 ±2.8	105.7 ± 8.0	59.8 ±12.4	118.5 ±8.3	0
	305 V	111.8 ± 18.8	103.3 ± 14.4	83.5 ±17.9	х	Х	Х
Ppy-C ₈ F ₁₇	452 V	134.2 ± 10.8	116.4 ± 5.6	109.2 ± 0.4	Х	Х	Х
	305 V	128.1 ±7.4	$110.8\pm\!3.0$	103.4 ± 0.5	х	Х	Х

The second method (B) consisted of the plasma induced co-polymerization of Ppy-OH and Py-C_n-Py on the fabrics, followed by a fluorinated *post*-grafting. The C₄F₉ *post*-grafted coating was the most hydrophobic on nylon fabrics with contact angles reaching 125° for each crosslinking length (**Table 2**). The shorter fluorinated chains certainly gave the best hydrophobic results because once again of a higher yield of *post*-grafting. On the contrary the C₆F₁₃ grafted samples were the most oleophobic, contact angles reaching 120° with diiodomethane and 111° with hexadecane, whereas the C₄F₉ ones reached barely 90° with diiodomethane and fell to 35° with hexadecane. No major differences in the wetting properties were observed between the different crosslinking length tested. As Py-C₃-Py gave the best contact angles, the method was tested on cotton samples. The treated cotton fabrics remained hydrophobic but showed good oleophobic properties with diiodomethane contact angles up to 118° with both short-fluorinated chains.

Table 2. Wettability data for the nylon and cotton fabrics treated with the second method (B: plasma induced co-polymerization of ppy-OH and py-Cn-py and fluorinated post-grafting). Contact angles are given for water, diiodomethane and hexadecane. (x indicates cotton samples with parameters set not realized.)

Nylon						Cotton			
Fluorinated grafting	Cross-linker	$\theta_{\rm w}$ [deg]	$ heta_{ ext{diiodo}} \left[ext{deg} ight]$	$\theta_{\rm hexa}$ [deg]	$\theta_{\rm w}$ [deg]	$ heta_{ m diiodo}$ [deg]	θ _{hexa} [deg]		
Pure fabric		91.0 ±1.6	0	0	0	0	0		
C ₄ F ₉	Py-C ₃ -Py	124.9 ±1.9	92.4 ± 11.4	34.6 ±8.3	0	118.6 ± 10.7	0		
C_4F_9	Py-C ₆ -Py	124.8 ±2.5	73.5 ± 6.1	12.5 ± 8.3	х	Х	х		
C_4F_9	Py-C ₁₀ -Py	122.3 ± 7.4	95.7 ± 10.5	0	Х	Х	х		
C ₆ F ₁₃	Py-C ₃ -Py	86.9 ± 8.4	120.8 ± 12.2	101.6 ±5.6	66.7 ±5.7	118.9 ±8.6	0		
$C_{6}F_{13}$	Py-C ₆ -Py	64.8 ±11.1	106.1 ± 8.1	111.0 ± 4.0	х	Х	х		
$C_{6}F_{13}$	Py-C ₁₀ -Py	60.8 ± 10.4	107.0 ± 5.5	111.6 ±4.6	Х	Х	Х		

Table 3 presents the wettability results of the textiles treated with the third method (C) that consisted of the plasma induced co-polymerization of pyrrole-OH and NP grafted to (pyrrolyl)butyric acid monomers followed by a fluorinated *post*-grafting. Two sizes of nanoparticles were tested: 22 and 64 nm, as well as a mixture of both. Best hydrophobic and oleophobic properties were obtained with the bigger nanoparticles, with contact angles up to 137° with water, 126° with diiodomethane and 127° with hexadecane for the longer fluorinated chain. The nanoparticles add again a roughness on the fibers that enhances the hydrophobicity and oleophobicity compared to the second method (B). Fabrics coated with the mixture of nanoparticles showed even higher hydrophobic properties for cotton (143°) but not for nylon and also higher or equivalent oleophobic properties (up to 133° for diiodomethane and 132° with hexadecane). A multiscale structuration is indeed known to enhance the wetting properties [29, 54].

Best results were obtained with C_8F_{17} , but compounds with number of perfluorinated carbon higher than 8 are known to be bio-accumulative [2]. With shorter fluorinated chains, fabrics are more hydrophobic with C_4F_9 and more oleophobic with C_6F_{13} . This result is a consequence of the lower grafting yield of the C_6F_{13} chains. In order to enhance the wetting properties with short fluorinated compounds, fabrics coated with bigger nanoparticles or with the mixture of nanoparticles of both sizes were first *post*-grafted with C_6F_{13} and then with C₄F₉. The hydrophobicity of the resulting samples was indeed enhanced compared to a simple *post*-grafting, and the oleophobicity was higher than for samples post-grafted with C_4F_9 only but lower than with C_6F_{13} only. This last method with a double *post*-grafting gives a compromise between hydrophobicity and oleophobicity using only short fluorinated compounds but does not compete with the results obtained with longer fluorinated chains.

Table 3. Wettability data for the nylon and cotton fabrics treated with the third method (C: plasma induced co-polymerization of pyrrole-OH and NP grafted to (pyrrolyl)butyric acid monomers and fluorinated post-grafting). Contact angles are given for water, diiodomethane and hexadecane.

			Nylon			Cotton	
Fluorinated grafting	NP size	$\theta_{\rm w}$ [deg]	$\theta_{ m diiodo}$ [deg]	θ_{hexa} [deg]	$\theta_{\rm w}$ [deg]	$\theta_{\rm diiodo}$ [deg]	$\theta_{\rm hexa} [{ m deg}]$
Pure fab	oric	91.0 ±1.6	0	0	0	0	0
C ₄ F ₉	22 nm	82.4 ± 2.2	87.9 ± 5.6	6.9 ±15.5	127.4 ±9.3	122.6 ±5.7	0
C_4F_9	64 nm	130.2 ± 3.9	114.3 ± 0.8	52.5 ± 17.8	130.6 ± 6.7	118.7 ± 7.0	0
C_4F_9	both	109.4 ± 4.0	106.0 ± 4.8	28.9 ± 2.4	127.1 ± 5.5	127.1 ± 8.2	0
C ₆ F ₁₃	22 nm	8.8 ±19.7	105.4 ±11.3	111.2 ±4.6	0	127.1 ±11.2	122.6 ±3.6
C ₆ F ₁₃	64 nm	113.5 ± 6.7	119.5 ± 5.3	123.6 ± 6.6	120.6 ± 8.4	132.9 ± 3.9	119.1 ± 8.4
$C_{6}F_{13}$	both	115.6 ± 4.0	133.1 ± 6.2	118.3 ± 4.0	133.6 ± 7.7	132.7 ± 3.6	132.3 ± 3.6
C ₈ F ₁₇	22 nm	103.8 ± 7.5	111.2 ±6.9	76.6 ±29.9	121.9 ±8.2	121.9 ±8.2	0
C_8F_{17}	64 nm	137.1 ± 7.8	125.4 ± 7.2	104.0 ± 7.2	138.7 ± 5.0	126.5 ± 7.8	127.0 ± 6.0
C ₈ F ₁₇	both	131.8 + 4.6	130.5 + 7.0	111.7 + 7.5	143.2 + 7.6	131.9 + 7.3	$111.0 \pm$
	bour	101.0 - 1.0	100.0 - 7.0	111.7 _ 7.5	113.2 _ 7.0	101.9 _ 7.8	10.2
$C_4F_9 + C_6F_{13}$	64 nm	137.3 ± 3.4	115.6 ± 2.5	86.9 ± 15.6	139.2 ± 6.4	115.1 ± 6.1	0
$C_4F_9 + C_6F_{13}$	both	113.6 ± 3.6	119.9 ± 8.3	80.1 ± 3.3	135.8 ± 5.2	120.0 ± 2.6	0

3.3 Adherence tests

The advantage of the plasma induced polymerization is the better adherence of the polymer to the substrate [29-32]. In order to characterize this adherence, water and diiodomethane contact angles were measured after performing the adherence tests on the fabrics (**Fig. 9**).

For almost every sample treated with the first method (A), the contact angles decreased, even more with diiodomethane, demonstrating a loss of the polymer coating. This loss did not depend on the DC self-bias voltage of the plasma treatment (305 V or 452 V). The etching was more important with 452 V so the roughness of the surface didn't cause a supplementary physic adhesion of the polymer.

The crosslinking in the second method (B) improved a lot the adherence of the coating, as seen with the diiodomethane contact angles. The crosslinking length did not show any difference of adherence. With the third method (C) almost no differences in the contact angles measured on the fabrics were observed after the adhesion test. The nanoparticles are here playing the role of the crosslinker thanks to their grafting to the copolymer. Similar results are obtained with cotton fabrics (**Supplementary data**).





Figure 9. Contact angles differences of the treated nylon fabrics between before and after performing the adherence test. **A**: first method (plasma induced polymerization of ppy-OH and fluorinated post-grafting); **B**: second method (plasma induced co-polymerization of ppy-OH and py-Cn-py and fluorinated post-grafting); **C**: third method (plasma induced co-polymerization of ppy-OH and NP grafted to (pyrrolyl)butyric acid monomers and fluorinated post-grafting).

4. Conclusion

In this study, we reported hydrophobic and oleophobic resistant coatings on nylon and cotton textiles by plasma induced polymerization of a pyrrole derivative monomer. The polymerization was induced by radicals and surface modifications formed by plasma treatment. A chemical *post*-grafting added fluorinated chains to the coating to give the non-wetting properties. Different methods were tested and described. The factors enhancing the amphiphobic properties are the plasma etching of the fibers and the addition of nanoparticles of controlled sizes. The adherence was mainly improved by a crosslinking of the polymers or a chemical grafting between the nanoparticles. Oleophobic and hydrophobic properties were obtained using compounds with short fluorinated chains that are not bio-accumulative.

In the future, others conducting monomers could be tested, especially sulfured ones to enhance the oleophobicity. The polymer coating could also be doped to obtain conductive properties and form an anti-wetting smart textile.

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6. Declaration of interests

Caroline Fradin reports financial support was provided by Agence Innovation Defense. Thierry Darmanin reports a relationship with University of Cote d'Azur that includes: employment and non-financial support. All the authors have patent TEXTILES OLEOPHOBES BIO-INSPIRES pending to REF. / BECKER: DB2796FR00; REF. / SATT: 1322. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. Author's contribution

Caroline Fradin: Methodology, Investigation, Data curation, Writing - original draft. Hernando Salapare III: Investigation. Sonia Amigoni: Supervision, Conceptualization. Frédéric Guittard: Funding acquisition, Conceptualization. Thierry Darmanin: Supervision, Writing - review & editing.

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Figures captions

Scheme 1. Chemical route to pyrrole-OH.

Scheme 2. Synthesis step to pyrrole-alkyl-pyrrole.

Scheme 3. Post-functionalization of the nylon samples grafted with pyrrole-OH.

Scheme 4. Summary of the 3 different methods realized in this study.

Figure 1. FT-IR spectra of pure nanoparticles (yellow), functionalized ones (orange) and ones grafted with 4-(3-pyrrolyl)butyric acid.

Figure 2. SEM images of plasma treated nylon and cotton fabrics with DC self-bias voltages indicated. All scale bars are 1µm long.

Figure 3. Photo of the fabrics. (top: cotton, bottom: nylon, left to right: pure fabric, C_4F_9 , Py- C_3 -Py + C_4F_9 , NP 22 + C_4F_9 , NP 64 + C_4F_9 , both NP + C_4F_9).

Figure 4. SEM images of coated nylon fabrics with the 3 methods of plasma induced polymerization (A, B and C).

Figure 5. SEM images of coated nylon fabrics with the 3 methods of plasma induced polymerization (A, B and C). Nanoparticles are observed on insets.

Figure 6. Hydrophobicity data for nylon samples coated with ppy-OH, copolymers and nanoparticles.

Figure 7. EDX spectrum of cotton fabrics mapping for each method.

Figure 8. EDX spectrum of nylon fabrics mapping for each method.

Figure 9. Contact angles differences of the treated nylon fabrics between before and after performing the adherence test. **A**: first method (plasma induced polymerization of ppy-OH and fluorinated post-grafting); **B**: second method (plasma induced co-polymerization of ppy-OH and py-Cn-py and fluorinated post-grafting); **C**: third method (plasma induced co-polymerization of ppy-OH and NP grafted to (pyrrolyl)butyric acid monomers and fluorinated post-grafting).

Table 1. Wettability data for the nylon and cotton fabrics treated with the first method (A: plasma induced polymerization of Ppy-OH and fluorinated post-grafting). Contact angles are given for water, diiodomethane and hexadecane.

		Nylon				Cotton	
Polymer	Plasma	$\theta_{\rm w}$ [deg]	$\theta_{ m diiodo}$ [deg]	$\theta_{\rm hexa}$ [deg]	$\theta_{\rm w}$ [deg]	$\theta_{\rm diiodo}$ [deg]	$\theta_{\rm hexa}$ [deg]
Pure fabric	Х	91.0 ±1.6	0	0	0	0	0
Рру-ОН	452 V	29.8 ±5.5	0	0	0	0	0
	305 V	37.9 ±5.3	0	0			
Ppy-C ₄ F ₉	452 V	116.1 ±3.1	88.4 ± 4.4	49.8 ±6.0	0	111.8 ± 8.3	0
	305 V	116.5 ± 3.0	95.9 ± 6.7	65.9 ± 4.8			
Pnv-C ₆ F ₁₂	452 V	90 2 +26 2	112.1	1114+36	59.8	118 5 +8 3	0
1 py Col 13	152 1	<i>y</i> 0.2 <u>-</u> 20.2	±10.9	111.1 ±3.0	±12.4	110.5 ±0.5	Ū
	305 V	98.4 ± 8.5	$93.2\pm\!\!6.3$	70.8 ± 16.0			
Ppy-C ₈ F ₁₇	452 V	126.6 ±4.1	112.4 ± 5.9	108.9 ± 2.3			
	305 V	122.9 ±2.0	108.6 ±4.3	$103.0\pm\!\!5.9$			

Table 2. Wettability data for the nylon and cotton fabrics treated with the second method (B: plasma induced co-polymerization of ppy-OH and py-Cn-py and fluorinated post-grafting). Contact angles are given for water, diiodomethane and hexadecane.

			Nylon			Cotton	
Fluorinated grafting	Cross-linker	$\theta_{\rm w}$ [deg]	$ heta_{ ext{diiodo}} \left[ext{deg} ight]$	$\theta_{\rm hexa}$ [deg]	$\theta_{\rm w}$ [deg]	$ heta_{ m diiodo}$ [deg]	$ heta_{hexa}$ [deg]
Pure	fabric	91.0 ±1.6	0	0	0	0	0
C ₄ F ₉	Py-C ₃ -Py	124.9 ±1.9	92.4 ± 11.4	34.6 ±8.3	0	118.6 ± 10.7	0
C ₄ F ₉	Py-C ₆ -Py	124.8 ± 2.5	73.5 ± 6.1	12.5 ± 8.3			
C ₄ F ₉	Py-C ₁₀ -Py	122.3 ± 7.4	95.7 ±10.5	0			
C ₆ F ₁₃	Py-C ₃ -Py	86.9 ± 8.4	120.8 ± 12.2	101.6 ± 5.6	66.7 ±5.7	118.9 ±8.6	0
$C_{6}F_{13}$	Py-C ₆ -Py	64.8 ± 11.1	106.1 ± 8.1	111.0 ± 4.0			
$C_{6}F_{13}$	Py-C ₁₀ -Py	60.8 ± 10.4	107.0 ± 5.5	111.6 ±4.6			
C ₈ F ₁₇	Py-C ₃ -Py	95.1 ± 8.0	10.3 ± 23.0	0			
C ₈ F ₁₇	Py-C ₆ -Py	93.1 ± 4.6	4.4 ± 9.7	4.4 ± 9.7			
C ₈ F ₁₇	Py-C ₁₀ -Py	95.3 ± 5.6	28.8 ± 29.6	6.3 ± 14.0			

Table 3. Wettability data for the nylon and cotton fabrics treated with the third method (C: plasma induced co-polymerization of pyrrole-OH and NP grafted to (pyrrolyl)butyric acid monomers and fluorinated post-grafting). Contact angles are given for water, diiodomethane and hexadecane.

			Nylon			Cotton	
Fluorinated grafting	NP size	$\theta_{\rm w}$ [deg]	$ heta_{ m diiodo}$ [deg]	$\theta_{\rm hexa}$ [deg]	$\theta_{\rm w}$ [deg]	$ heta_{ m diiodo}$ [deg]	$\theta_{\rm hexa}$ [deg]
Pure fab	oric	91.0 ±1.6	0	0	0	0	0
C ₄ F ₉	22 nm	82.4 ± 2.2	87.9 ± 5.6	6.9 ± 15.5	127.4 ±9.3	122.6 ± 5.7	0
C_4F_9	64 nm	130.2 ± 3.9	114.3 ± 0.8	52.5 ± 17.8	130.6 ± 6.7	118.7 ± 7.0	0
C_4F_9	both	109.4 ± 4.0	106.0 ± 4.8	28.9 ± 2.4	127.1 ± 5.5	127.1 ± 8.2	0
C ₆ F ₁₃	22 nm	8.8 ±19.7	105.4 ±11.3	111.2 ±4.6	0	127.1 ±11.2	122.6 ±3.6
C ₆ F ₁₃	64 nm	113.5 ± 6.7	119.5 ± 5.3	123.6 ± 6.6	120.6 ± 8.4	132.9 ± 3.9	119.1 ± 8.4
C ₆ F ₁₃	both	115.6 ± 4.0	133.1 ± 6.2	118.3 ± 4.0	133.6 ± 7.7	132.7 ± 3.6	132.3 ± 3.6
C ₈ F ₁₇	22 nm	103.8 ± 7.5	111.2 ±6.9	76.6 ±29.9	121.9 ±8.2	121.9 ±8.2	0
C ₈ F ₁₇	64 nm	137.1 ± 7.8	125.4 ± 7.2	104.0 ± 7.2	138.7 ± 5.0	126.5 ± 7.8	127.0 ± 6.0
C ₈ F ₁₇	both	131.8 ± 4.6	130.5 ± 7.0	111.7 ± 7.5	143.2 ± 7.6	131.9 ± 7.3	111.0 ± 10.2
$C_4F_9 + C_6F_{13}$	64 nm	$13\overline{7.3 \pm 3.4}$	$11\overline{5.6 \pm 2.5}$	86.9 ± 15.6	139.2 ± 6.4	$11\overline{5.1 \pm 6.1}$	0
$C_4F_9 + C_6F_{13}$	both	113.6 ± 3.6	119.9 ± 8.3	80.1 ± 3.3	135.8 ± 5.2	120.0 ± 2.6	0

Graphical Abstract

