One-Step Aqueous Spraying Process for the Fabrication of Omniphobic Fabrics Free of Long Perfluoroalkyl Chains

Ronggang Cai,*‡ David De Smet,‡ Myriam Vanneste,‡ Bernard Nysten,‡ Karine Glinel,†‡ and Alain M. Jonas*‡†

‡Bio & Soft Matter, Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Croix du Sud 1/box L7.04.02, 1348 Louvain-la-Neuve, Belgium
†Centexbel, Technologiepark 70, 9052 Zwijnaarde, Belgium

ABSTRACT: We report on a simple and versatile method for the preparation in one-step of omniphobic textiles, using only aqueous suspensions of silica particles and polyurethane devoid of long perfluoroalkyl chains (C8) that are now legally-banned because of severe environmental concerns. The omniphobic coatings can be applied on different substrates including fabrics, can resist acidic and basic conditions and a moderate number of washing cycles, and repel liquids such as n-octane, dodecane, hexadecane, ethylene glycol, glycerol, olive oil, and water. Analysis of the wetting properties of coated fabrics indicates that the liquid repellence results from the trapping of air in the re-entrant roughness created by aggregates of silica particles, together with the low surface tension of the polyurethane which bears legally accepted short perfluoroalkyl chains (C4). Our study is a significant step forward toward achieving more environmentally-friendly and robust omniphobic textiles.

INTRODUCTION

Water repellence and oil repellence are important properties for outdoor and professional fabrics. This repellence is customarily provided by coatings comprising long perfluoroalkyl chains of structure R-(CF2)n-R’ (long meaning n > 6 in the present context). However, serious environmental and health concerns have emerged regarding the use of materials containing long perfluoroalkyl chains, because these degrade into long-chain perfluoroalkyl acids which are very persistent in the environment and bioaccumulate in wildlife and human bodies.1,2 Therefore, the use of fluorinated materials containing long perfluoroalkyl chains, even when grafted as side chains, is under strict regulatory control in the EU and USA.3,4 Even better, an agreement among more than 180 countries was reached on May 3, 2019, to definitively ban the production and use of long perfluoroalkyl chains, resulting in a global phasing-out of these chemical products of very high concern.5

Although a series of alternative products exist for water repellence, such as silicone- or wax-based formulations, effective oil-repellent formulations devoid of long perfluoroalkyl chains remain much more elusive. Oil- and solvent repellence is required, for example, for protective personal equipment, medical items, or fabrics used in the proximity of fuels and lubricants. Not surprisingly, most scientific publications reporting on strongly oleophobic coatings are still based on long perfluoroalkyl chains and nonsustainable processing methodologies.6−14 They also frequently involve the use of organic solvents compatible with perfluorinated compounds, which are often severely toxic and/or environmentally harmful (e.g., dichloropentafluoro propane15). As an alternative, materials containing shorter perfluoroalkyl side chains (n ≤ 6) have been developed by manufacturers. Unfortunately, they are, when n ≤ 4, significantly less effective in terms of oleophobicity compared to longer perfluoroalkyl chain-containing materials (shorter chains being worse in this respect). Even though such short fluorocarbon chains also rise concerns and might as well become controlled in a longer-term future,7 their more widespread use could nevertheless be considered as a significant step forward in the transition toward environmentally-friendly and sustainable oleophobic coatings.

Here, we show that the oil repellence of fabric coatings based on polyurethane comprising only short perfluoroalkyl chains (n = 4) can be significantly boosted by increasing the coating roughness with silica particles, using a simple one-step aqueous-based spraying process leading to coatings with reasonably good chemical and washing resistance. The resulting coatings are thus not only compatible with the current ban of longer perfluoroalkyl chains but they are also made from a very benign solvent in a trivially simple and green process.

Our coatings are actually very close to superomniphobic, combining (super)hydrophobicity and (super)oleophobicity. Omniphobic surfaces provide access to attractive properties such as stain-proofing and self-cleaning,9,10 chemical shielding,17 or easy droplet manipulation.7,8 Superhydrophobicity is well known to result from the roughening of the surface of a material of low surface tension,6,18,19 which can be achieved by a variety...
of straightforward methodologies as reviewed elsewhere.\textsuperscript{20−22} An example from our own work is provided by environmentally-friendly superhydrophobic fabrics made by a three-step dip-coating process in water-based silicone and particle suspensions.\textsuperscript{23} In contrast, more stringent and critical requirements have to be met to reach superoleophobicity: re-entrant surface structures (overhangs) and extremely low surface tensions are usually needed.\textsuperscript{10,15,17,24−29} Creating re-entrant surface structures was performed before by a variety of methodologies such as lithography, etching, replica molding, layer-by-layer deposition, phase separation, or polymerization.\textsuperscript{8−11,12,14−17,24−28} Here, we demonstrate that the combination of silica particles and a polymer bearing only short-chain perfluoralkyl chains can lead to efficient omniphobic coatings for textile applications, using a simple, one-step aqueous methodology. We study quantitatively the correlation between roughness and repellence of the coatings and indicate the main design parameters which control omniphobicity. Our study thus aims at demonstrating that it is possible to design efficient coatings while moving away from environmentally harmful processes and systems and at providing rational ways to design more sustainable oleophobic textile coatings.

## RESULTS AND DISCUSSION

The water-based suspension comprised of silica particles (Tixosil 365 from Solvay), polyurethane containing short perfluoralkyl chains (n = 4, PM-900 from 3M), and an oxime-protected isocyanate chain extender (PHOBOL XAN from Huntsman). All materials are commercially available, and no organic solvent was employed in the formulation. The absence of C6 and C8 perfluoralkyl substances and fluorotelomer alcohols was verified with chromatography coupled to mass spectrometry (see Table S1 in the Supporting Information). The omniphobic surfaces were obtained by spray-coating the omniphobic formulation on the substrate (Figure 1).

![Figure 1](image1.png)

Figure 1. Sketch of the one-step preparation of omniphobic coatings on a substrate by spraying the water-based formulation developed in this work.

followed by thermal annealing to dry the coating and promote the reaction between the hydroxyl groups of the polyurethane and the isocyanate groups of the temperature-deprotected extender.

The polyester (PES) fabric shown in Figure 2 is a typical omniphobic fabric obtained by spray-coating a one-pot water-based formulation containing 1.2 wt % polyurethane, 0.12 wt % chain extender, and 1.25 wt % silica particles. The measured water and olive oil contact angles on this specific sample are 148° and 144°, respectively, indicating super repellence to both water and olive oil (Figure 2a). Movies S1 and S2 in the Supporting Information show the easy roll-off of water and olive oil when dropped onto the tilted treated omniphobic fabric. Figure 2b,c shows top-view scanning electron microscopy (SEM) images of the modified fabric, indicating a good uniformity of the coating and confirming the presence of nanoscale porous structures on the fiber surface arising from aggregates of the silica particles. In order to obtain a three-dimensional view of the coating, also micromotomed cross-sections of the treated fabric were analyzed (Figure 2d–f). The large-scale optical microscopy image of Figure 2d provides a view of the fabric structure, whereas the SEM image of Figure 2f reveals the distribution of silica particles in the coating and confirms the existence of large porosity and the presence of re-entrant structures and overhangs. The thickness of the coating was found to vary from ca. 1 to 10 μm depending on location. Figure 2e is a time-of-flight secondary ion mass spectrometry (ToF-SIMS) image of the cross-section of the treated fabric, showing the distribution of the fluorinated polyurethane in the coating. From this image, it can be seen that the polymer penetrates ca. 30 μm into the fabric, thereby providing mechanical anchoring. The omniphobicity of the coated fabrics results from their high roughness r\textsubscript{T}, defined as the ratio between their developed and projected surfaces. If the components of the formulation adsorb randomly without significant smoothing of the underlying fabric texture, the total roughness of the fabric r\textsubscript{T} is\textsuperscript{25,30}

\[
r_T = r_P \cdot r_f
\]

(1)

with r\textsubscript{P} and r\textsubscript{f} being the roughness due to the fabric texture and the surface of the fibers, respectively. The fabric textural roughness was estimated by stylus profilometry (Figure 2g,h), which provided a view on topography at a lateral resolution of ca. 1 μm because a stylus of 0.7 μm radius was used. The roughness of the surface of the fibers was characterized by atomic force microscopy (AFM, Figure 2i) by scanning the tip over surfaces much smaller than the diameter of the textile fibers (ca. 10 μm). For the sample of Figure 2, the roughness of the fiber surface, r\textsubscript{f}}

![Figure 2](image2.png)

Figure 2. Topographical and morphological characterization of a spray-coated PES fabric, prepared by spraying a water-based formulation containing 1.25% silica particles, 1.2% polyurethane, and 0.12% chain extender. (a) Droplets of water and oil resting on the coated fabric. (b,c) Top-view SEM images of the coated fabric. (d–f) Cross-sectional views of the coated fabric obtained by optical microscopy (d), ToF-SIMS (e), and SEM (f). In the ToF-SIMS image, the green color represents F \textsuperscript{−} anions from the fluorinated polymer, and the red color represents C\textsubscript{8}H\textsubscript{17}O\textsubscript{2}− anions from the PES fibers. (g,h) Stylus profilometry images of the bare and coated fabric, respectively. (i) AFM topography image of the surface of the fibers after coating.
was significantly modified by the coating process, increasing from 1.04 ± 0.02 before to 1.81 ± 0.06 after spraying. In contrast, the fabric textural roughness \( r_T \) only increased from 1.30 to 1.34 upon spraying. Therefore, for the sample of Figure 2, the total roughness \( r_T \) increased from 1.35 to 2.42 (according to eq 1), indicating that the dominant contribution to the total roughness arises from the silica particles, not from the fabric texture.

Both AFM and stylus profilometry only provide access to the apparent roughness because the tip or stylus does not probe the sample surface below overhangs nor in very narrow channels. This actually explains why the roughness of the fabric measured by profilometry does not change much upon coating. Overhangs are also responsible for imaging artifacts in AFM images, such as seen on the left of the central cleft in Figure 2i. One might thus wonder whether these measured values of roughness are significant for our analysis of wetting properties. This is actually the case when the liquid is not impregnating the fabric, which is the case considered in this article. The contact angles of water and olive oil on flat substrates coated with the polyurethane/chain extender only are 110 and 95°, respectively; because they are larger than 90°, the impregnation parameter is negative, corresponding to a capillary descent of the fluid in narrow channels. Therefore, the coated fabric resists impregnation and traps air in its texture, resulting in the droplets exploring surfaces that are not too different from what is probed by the profilometer stylus or AFM tip. Nevertheless, one should keep in mind that the “liquid-felt” roughness might differ from the measured roughness by some factor of order unity.

The correlation between the water and olive oil contact angles, and the amount of solid material deposited on the fabric surface was also studied using the same formulation as for the sample of Figure 2, while changing the spraying conditions. The result is shown in Figure S5 (Supporting Information) and suggests that a critical value of the amount of the deposited solid material (ca. 0.3 mg/cm²) should be reached to achieve strong omniphobicity. Figure 2i also indicates that the aggregate size of silica particles should be in the range of 200−500 nm for efficient repellence. To understand further the influence of the structure and roughness of the coating on the water and oil repellence, a series of coated fabric samples were prepared with different combinations of concentrations of polyurethane, silica particles, and chain extender. Reference samples were a pure polyurethane/chain extender 10:1 w/w film of 1.2 μm thickness deposited on a flat silicon wafer, a fabric sample coated with this silica-free formulation, and the bare fabric. The roughness of the fiber surface, \( r_f \), was measured by AFM for all samples, and the textural roughness of the coated fabrics, \( r_D \), was determined by stylus profilometry. The average textural roughness of the coated fabrics was 1.32 with a standard deviation of 0.04 for the ten different samples, not significantly different from the value of the bare fabric (1.30), in agreement with the conclusion drawn from the examination of the specific sample displayed in Figure 2. Therefore, the total roughness of the samples was simply computed as the product of the roughness of the bare fabric and \( r_T \) (eq 1).

Table S2 lists the different roughness values of the samples, together with their water and olive oil contact and roll-off angles. The roughness of the fiber surface first increases with increasing concentration of silica particles in the formulation and then displays a small decrease above 1 wt % (Figure S1a). In contrast, no systematic trend can be found when varying the concentration of the polyurethane in the formulation (Figure S1a). Likewise, the highest contact angles are obtained for a concentration of silica particles between 1 and 1.25%, with little if any effect of the concentration in polyurethane (Figure S1c,d). The contact and roll-off angles of the samples are plotted versus total roughness \( r_T \) in Figure 3. Below a threshold roughness \( r_T^a \) of 1.6 and 1.8 for water and olive oil, respectively, contact angle \( \theta_c \) rapidly increases with \( r_T \) with no roll-off observed; above \( r_T^a \), the contact angle increases much more slowly with total roughness, whereas the roll-off angle \( \theta_s \) rapidly decreases.

Two factors control the contact angle \( \theta_c \) of the liquids on the prepared coatings: the increased contact surface resulting from roughness and the trapping of air in the cavities of the roughness as discussed above. More precisely:

\[
\cos(\theta_f) = \phi_s (\cos(\theta_c) + 1) - 1
\]

with \( \theta_f \) being the contact angle measured for a flat and smooth polyurethane/chain extender film, \( \theta_c \) is the effective roughness of the areas on which the liquid is in contact with the solid (close to the triple line), and \( (1 - \phi_s) \) is the surface fraction of air-filled cavities. This equation simultaneously combines the classical Wenzel\(^{19}\) and Cassie\(^{18}\) relationships, with the Wenzel equation \( \cos(\theta_c) = r \cos(\theta) \) being recovered in the absence of air-trapping cavities \( (\phi_s = 1) \), and the classical Cassie equation \( \cos(\theta) = \phi_s (\cos(\theta_c) + 1) - 1 \) being obtained in the absence of roughness below the liquid/solid contact areas.

To model the obtained results, we assumed that, at low roughness, the liquid/solid interface is a composite of trapped air and solid regions of relatively large size having a roughness identical to the total sample roughness, \( r_T = r_T^a \). Above the threshold roughness \( r_T^a \), droplets leave this composite regime to enter a pure Cassie “fakir” state, in which a substantial amount of air is trapped in the porosity of the coating and the liquid/solid contact areas are restricted to very small regions of limited roughness, \( r_s \approx 1 \). Based on these premises, and assuming that the fraction of air trapped in the fabric texture increases linearly with total roughness, with two different slopes below and above \( r_T^a \), eq 2 could be satisfactorily fitted to the contact angle data.
Figure 4. Resistance of the coated fabrics to liquids and washing. The data were obtained on the fabric sample displayed in Figure 2. (a) Cosine of the contact angle of liquids of different solubility parameters, measured on the smooth polyurethane film deposited on a silicon wafer (θ\text{c}(\text{top panel}) and on the coated fabric (θ\text{c}(\text{bottom panel}). The test liquids (5 μL droplet) include n-octane (1), n-dodecane (2), n-hexadecane (3), cyclohexane (4), toluene (5), isopropanol (6), dimethyl sulfoxide (7), ethylene glycol (8), glycerol (9), water (10), and olive oil (11). Red crosses indicate that the test liquid swells the polyurethane film, resulting in the progressive shift of the values measured on the smooth film (the red arrows show the variation between the contact angles measured 10 s and 2 min after droplet deposition). (b) Cosine of the contact angles measured over the rough coated fabrics (cos θ\text{c}) vs the one obtained over the smooth polyurethane film (cos θ\text{c}) for the same series of test liquids as in panel (a). Red arrows again indicate the change between values of the contact angle obtained 10 s or 2 min after deposition of a swelling liquid. The solid line is a fit of eq 2 to the data, with r on fixed to 1. (c) Evolution of the water contact and roll-off angles with number of washing cycles (10 μL water droplet). (d) i.d. for oil; red crosses mean no roll-off (5 μL oil droplet).

Therefore, it should be possible to reach superhydrophobicity even with moderately hydrophilic compounds.25

The resistance to machine washing of the omnipinic fabric displayed in Figure 2 was also examined. The contact and dynamic roll-off angles for both water and olive oil are shown versus the number of washing cycles in Figure 4c,d. After five cycles of machine washing followed by drying at room temperature, the coated fabric remained (super)hydrophobic with only a slight decrease of its water repellent properties (Figure 4c). Additionally, the coated fabric remained (super)-oleophobic up to three washing cycles, with a slight decrease of its olive oil contact angle from ca. 142° to ca. 139° and a larger increase of the dynamic roll-off angle from 20° to 23° to 58°−70°. However, the coated fabric lost its (super)oleophobicity for a larger number of washing cycles, with no roll-off of olive oil droplets. SEM images of the coated fabric after washing (Figure S2) indicate that the progressive abrasion of the coating is responsible for this decrease of performance. However, because the strategy we developed in this work is a one-pot spray coating method, the coating might be easily reapplied on the fabrics to restore the omnipinic properties after a series of washing cycles.
For comparison, the durability of an omniphobic fabric sample, prepared from an extender-free formulation (no PHOBOL) containing the same concentration of polyurethane (1.2 wt %) and silica particles (1.25 wt %), was also assessed. The as-prepared sample was measured to have water contact and roll-off angles similar to the extender-containing sample. However, after one washing cycle, the coated fabric lost its omniphobic, with the water contact angle decreasing to 129° only and no roll-off observed for both water and olive oil, confirming the role of the chain extender in the washing resistance of the film. The resistance of the same extender-containing omniphobic coating to acidic (HCl, pH 2) and alkaline (NaOH, pH 12) conditions was also evaluated for different immersion times (Figure S3). After 3 h immersion in these aqueous solutions, the coated fabrics remained omniphobic with only a slight decrease of the contact angles and a slight increase of the roll-off angles for both water and olive oil.

The developed omniphobic formulations were also applied on other substrates such as silicon and glass. Figure S4 of the Supporting Information shows pictures of droplets of various liquids (including water, glycerol, ethylene glycol, olive oil, hexadecane, and dodecane) resting on the coated fabric, glass, and silicon samples. This indicates that the developed omniphobic formulations are versatile and can be easily applied on various textured or flat substrates. Hence, the re-entrant roughness generated by the coating itself is generally sufficient to result in omniphobicity and does not necessarily need the supplementary roughness provided by the fabric texture.

### CONCLUSIONS

In conclusion, a simple one-step method to prepare omniphobic coatings is developed. The super repellence is achieved by combining the roughness and porosity provided by silica particles with the low surface tension of polyurethane with short perfluoroalkyl chains (C4). The method, which uses a simple spray-coating technique and commercially available water-based suspensions, is cost-effective, provides omniphobic coatings which can resist a moderate number of washing cycles and may easily be reapplied if necessary. Crucially, it relies on compounds which are not banned by environmental regulations. As such, it is thus a significant step toward more environmentally friendly robust superoleophobic textiles, even though the complete elimination of perfluorinated compounds is still to be achieved. Analysis of the wetting properties of the coatings reveals that droplets of liquids ranging from n-octane to water settle in a Cassie “fakir” state with a proportion of trapped air of ca. 70–80% due to the presence of re-entrant roughness. Only liquids which swell the polyurethane were found to be able to impregnate the coatings. Additionally, the good versatility of the method affords to produce omniphobic surfaces on different substrates, no matter textured or flat. Therefore, it can be easily integrated into industrial processes and has a strong potential for the mass production of environment-friendly and cost-effective omniphobic surfaces.

### EXPERIMENTAL SECTION

**Materials.** The silica particles (Tixosil 365) were kindly provided by Solvay (Belgium). The average size of individual particles was measured to be ca. 30–50 nm by transmission electron microscopy (Figure S6 of the Supporting Information).

However, when dispersed in water followed by sonication, the particles tend to form aggregates. The short perfluoroalkyl chain (C4) polyurethane emulsion in water (PM-900) was kindly provided by 3M (USA). The PHOBOL XAN chain extender/cross-linker (oxime-blocked bis-isocyanate) was provided by Huntsman Corporation (Belgium). The woven PES fabric (105 g/m²) was purchased from Concordia Textiles (Belgium) and was washed and desized prior to functionalization. Milli-Q water (resistivity 18.2 MΩ-cm) was obtained from a Merck Millipore system (Milli-Q reference). Olive oil (Extra Virgin, produced in Italy) was purchased from a local supermarket (Delhaize); n-octane (>99%, extra pure), n-dodecane (99%, pure), n-hexadecane (99%, pure), ethylene glycol (99%, extra pure), glycerol (>99%, extra pure), cyclohexane (99%, pure), toluene (>99%, extra pure), isopropanol (>99.5%, extra pure), and dimethyl sulfoxide (>99%, extra pure) were from Acros Organics.

**Preparation of Formulations, Coatings, and Cross-Sections of Coated Fabrics. Formulations.** Tixosil 365 silica particles were first mixed with water followed by a 10 min ultrasound bath to form silica particle suspensions of concentration X (X = 0.5, 0.75, 1, 1.25, or 1.5 wt % in the final formulations). Then, the PM-900 polyurethane and the PHOBOL XAN cross-linker (10:1 weight ratio) emulsions were added to the silica particle suspension, followed by 5 min stirring. The concentration of polyurethane in water, Y, was 0.6, 1.2, or 1.8 wt % in the final formulations thereby homogeneous formulations containing silica particles, polyurethane, and chain extender were obtained.

**Coatings.** The as-prepared formulations were placed into a small sprayer purchased from a local supermarket. The coatings were prepared by spraying the formulation from the sprayer which was ca. 5 cm away from the horizontally placed substrate until the formulation fully covered the whole substrate, followed by thermal annealing at 150 °C for 5 min to cross-link the polyurethane.

**Cross-Sections of Coated Fabric.** The coated fabric was embedded into a protective epoxy resin (Epoxi cold-setting embedding resin, purchased from Electron Microscopy Sciences). The cross-sections were obtained by cutting the protected fabric by a microtome (Leica Reichert UMFC6) at room temperature. The thickness of the cross-sections was 5 μm.

**Characterization of the Coated Samples.** Contact angle measurements were performed with an OCA 20 goniometer from DataPhysics. For each sample, a liquid droplet of a certain volume was used (usually 5 or 10 μL when indicated), and the contact angle measurements were performed at four randomly selected positions. An average value was computed from these four tests, together with the standard deviation. It is worth noting that, due to the fact that the fabric is inherently nonsmooth, there is some uncertainty in the definition of the limiting lines representing the ideal interface between the fabric and the testing liquid. This results in the measured contact angle values to be underestimated; in particular, when entering the Cassie regime, the contact angle is measured to be ca. 140°, lower than the conventionally expected value of 150° (see Figure 3).

Roll-off angle measurements were performed by releasing a liquid droplet (10 μL for water and 5 μL for olive oil) almost in contact with the surface onto the tilted sample. The roll-off angle was determined as the tilt angle for which the droplet started to roll off the sample surface. SEM was performed with a JEOl 7600F operated at 15 kV accelerating voltage. A thin layer of gold (15 nm) was deposited on the sample surface by sputtering prior to SEM characterization. Stylus profilometry was done with a DektakXT from Bruker, using a stylus of 0.7 μm curvature.
radius scanned at a rate of 300 μm/s over the fabric surface, with a sampling resolution of 1 μm in the y-direction, and 2 μm in the x-direction. AFM was performed in the tapping mode on Icon Dimension from Bruker. A silicon probe from nanosensors (force constant ≈ 40 N/m, apex radius of curvature < 7 nm) was used. AFM and profilometry images were deglitched, flattened by subtracting a second-order bidimensional polynomial, and the Wenzel roughness was computed as the average of the function \(1 + (\partial h/\partial x)^2 + (\partial h/\partial y)^2\)^{1/2}, in which \(h(x,y)\) is the height at location \((x,y)\).

The ToF-SIMS image was obtained by using a ToF-SIMS 5 instrument (IONTOF GmbH, Münster, Germany). A Bi^3+ liquid metal-ion source was used to produce the analytical primary beam (energy 60 keV). An ac target current of 0.003 pA was used with the analytical burst mode (1 pulse selected with the sine blanker). Only negative secondary ion species were analyzed. A raster of 512 × 512 data points over an area of 150 μm × 150 μm was used. The total primary ion beam dose for each analyzed area was always kept below 10^{11} ions/cm², ensuring static conditions. Lateral resolution of 0.3 μm and mass resolution \(m/\Delta m >2000\) at 49 m/z were maintained for acquisition of both images and corresponding spectra for negative ions. Charge compensation was done by the electron flood gun (\(E_f = 20 \) eV).

Washing tests were performed using a Zanussi washing machine (model ZWG 1140M). The washing program includes washing at 30 °C, rinsing, and spinning using minimum water quantity programmed by the machine. Five grams of the detergent (Le Chat Sensitive) was added during the washing step.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02583.

Influence of the silica particle and PM-900 concentration on fiber roughness and water and olive oil contact angle; SEM images of coated fabrics after machine washing; chemical resistance of coated fabrics; pictures of different liquid droplets on coated PES fabric, glass, and silicon substrates; correlation between water and olive oil contact angles, and amount of the solid material deposited on the fabric surface; detailed information about the fiber roughness, total roughness, water and olive oil contact angles, and water and olive oil roll-off angles measured on PES fabrics (PDF)

Water roll-off on an omniphobic fabric (AVI)

Olive oil roll-off on an omniphobic fabric (AVI)

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: ronggang.cai@uclouvain.be (R.C.).
*E-mail: alain.jonas@uclouvain.be (A.M.J.).

ORCID

Ronggang Cai: 0000-0001-9095-7823
Karine Glinel: 0000-0002-2000-0169
Alain M. Jonas: 0000-0002-4083-0688

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank Solvay, 3M, and Huntsman for kindly providing Tixosil 365, PM-900, and PHOBOL XAN, respectively. Claude Poleunis, Cécile D’Haese, and Pascale Lipnik are acknowledged for their assistance to obtain ToF-SIMS images, profilometry data, and microtommed cross-sections, respectively. This work was financed by the Interreg V program France-Wallonia-Flanders (http://www.interreg-fwwl.eu/nl), a cross-border collaboration program with financial support of the European Fund for Regional Development and co-financed by the province West Flanders and the Walloon Region through the project Duratex. K.G. is Research Associate of the F. R. S.-FNRS.

**REFERENCES**

1. Williams, J. *Waterproof and Water Repellent Textiles and Clothing*. Elsevier, 2018.
2. Brendel, S.; Fetter, É.; Staude, C.; Viekte, L.; Biegel-Engler, A. Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH. *Environ. Sci. Eur.* 2018, 30, 9.
3. Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA. https://www.epa.gov/assessing-and-managing-chemicals-under-tscarisk-management-and-polyfluoroalkyl-substances-pfas (accessed on Aug 30, 2018).
4. Commission Regulation (EU) 2017/1000. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32017R1000&from=EN (accessed on Aug 30, 2018).
5. Coge, H. Govers endorse global PFOA ban, with some exemptions. *Chem. Eng. News* 2019, 97, 5.
6. Wong, W. S. Y.; Liu, G.; Nasiri, N.; Hao, C.; Wang, Z.; Tricoli, A. Omnidirectional Self-Assembly of Transparent Superoleophobic Nanotextures. *ACS Nano* 2017, 11, 587–596.
7. Jang, H.; Lee, H. S.; Lee, K.-S.; Kim, D. R. Facile Fabrication of Superomniphobic Polymer Hierarchical Structures for Directional Droplet Movement. *ACS Appl. Mater. Interfaces* 2017, 9, 9213–9220.
8. Movafaghi, S.; Wang, W.; Metzger, A.; Williams, D. D.; Williams, J. D.; Kota, A. K. Tunable superomniphobic surfaces for sorting droplets by surface tension. *Lab Chip* 2016, 16, 3204–3209.
9. Leng, B.; Shao, Z.; de With, G.; Ming, W. Superoleophobic Cotton Textiles. *Langmuir* 2009, 25, 2456–2460.
10. Wang, W.; Salazar, J.; Vahabi, H.; Joshi-Imre, A.; Völt, W. E.; Kota, A. K. Metamorphic Superomniphobic Surfaces. *Adv. Mater.* 2017, 29, 1700295.
11. Vahabi, H.; Wang, W.; Movafaghi, S.; Kota, A. K. Free-Standing, Flexible, Superomniphobic Films. *ACS Appl. Mater. Interfaces* 2016, 8, 21962–21967.
12. Golovin, K.; Lee, D. H.; Mabry, J. M.; Tuteja, A. Transparent, Flexible, Superomniphobic Surfaces with Ultra-Low Contact Angle Hysteresis. *Angew. Chem., Int. Ed.* 2013, 52, 13007–13011.
13. Grigoryev, A.; Tokarev, I.; Kornev, K. G.; Luzinov, I.; Minko, S. Superomniphobic Magnetic Microtextures with Remote Wetting Control. *J. Am. Chem. Soc.* 2012, 134, 12916–12919.
14. Deng, X.; Mammen, L.; Butt, H.-J.; Vollmer, D. Candle Soot as a Template for a Transparent Robust Superamphiphobic Coating. *Science* 2012, 335, 67–70.
15. Pan, S.; Guo, R.; Bjørnmal, M.; Richardson, J. J.; Li, L.; Peng, C.; Bertleff-Zischang, N.; Xu, W.; Jiang, J.; Caruso, F. Coatings super-repellent to ultralow surface tension liquids. *Nat. Matter.* 2018, 17, 1040–1047.
16. Brown, P. S.; Bhushan, B. Mechanically durable, superomniphobic coatings prepared by layer-by-layer technique for self-cleaning and anti-smudge. *J. Colloid Interface Sci.* 2015, 456, 210–218.
17. Pan, S.; Kota, A. K.; Mabry, J. M.; Tuteja, A. Superomniphobic Surfaces for Effective Chemical Shielding. *J. Am. Chem. Soc.* 2013, 135, 578–581.

16665 DOI: 10.1021/acsomega.9b02583 ACS Omega 2019, 4, 16660–16666
(18) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. Trans. Faraday Soc. 1944, 40, 546–551.
(19) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. Ind. Eng. Chem. 1936, 28, 998–999.
(20) Yong, J.; Chen, F.; Yang, Q.; Huo, J.; Hou, X. Superoleophobic surfaces. Chem. Soc. Rev. 2017, 46, 4168–4217.
(21) Chen, L.; Guo, Z.; Liu, W. Outmatching superhydrophobicity: bio-inspired re-entrant curvature for mighty superamphiphobicity in air. J. Mater. Chem. A 2017, 5, 14480–14507.
(22) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. Progress in superhydrophobic surface development. Soft Matter 2008, 4, 224–240.
(23) Cai, R.; Glinel, K.; De Smet, D.; Vanneste, M.; Mannu, N.; Kärtheuser, B.; Nysten, B.; Jonas, A. M. Environmentally Friendly Super-Water-Repellent Fabrics Prepared from Water-Based Suspensions. ACS Appl. Mater. Interfaces 2018, 10, 15346–15351.
(24) Choi, J.; Jo, W.; Lee, S. Y.; Jung, Y. S.; Kim, S.-H.; Kim, H.-T. Flexible and Robust Superomniphobic Surfaces Created by Localized Photofluidization of Azopolymer Pillars. ACS Nano 2017, 11, 7821–7828.
(25) Liu, T. L.; Kim, C.-J. C. Turning a surface superrepellent even to completely wetting liquids. Science 2014, 346, 1096–1100.
(26) Kota, A. K.; Kwon, G.; Tuteja, A. The design and applications of superomniphobic surfaces. NPG Asia Mater. 2014, 6, No. e109.
(27) Hensel, R.; Helbig, R.; Aland, S.; Voigt, A.; Neinhuis, C.; Werner, C. Tunable nano-replication to explore the omniphobic characteristics of springtail skin. NPG Asia Mater. 2013, 5, No. e37.
(28) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. Robust omniphobic surfaces. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 18200–18205.
(29) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. Designing Superoleophobic Surfaces. Science 2007, 318, 1618–1622.
(30) Groten, J.; Rühe, J. Surfaces with Combined Microscale and Nanoscale Structures: A Route to Mechanically Stable Superhydrophobic Surfaces? Langmuir 2013, 29, 3765–3772.
(31) de Gennes, P.-G.; Brochard-Wyart, F.; Quéré, D. Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves; Springer: New York, 2004.
(32) Pan, S.; Guo, R.; Xu, W. Investigating and biomimicking the surface wetting behaviors of ginkgo leaf. Soft Matter 2014, 10, 8800–8803.