Supporting Information

Environmentally Friendly Super-Water-Repellent Fabrics Prepared from Water-Based Suspensions

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SI 1 - Materials

PDMS emulsion HC 303, which is an emulsion of PDMS chains with 3-((2-aminoethyl)amino)propyl)methoxysilyl ether end groups, stabilized by non-ionic surfactants, was obtained from Wacker Chemie. The emulsion is very stable when stored in the conditions described in the safety data sheet provided by Wacker Chemie. The silica particles (Tixosil® 365) were kindly provided by Solvay (Belgium). The average size of individual particles was measured to be *ca.* 50 nm by transmission electron microscopy (TEM) (results not shown). However, when dispersed in water then sonicated, the particles tend to form aggregates as also observed by TEM. The Phobol XAN cross-linker used to further cross-link PDMS was provided by Huntsman Corporation (Belgium). CONTRAQUA WE wax emulsion was supplied by Thor. The woven polyester (PES) fabric (105 g/m^2) was obtained from Concordia Textiles (Belgium) and was washed and desized prior to functionalization.

SI 2 - Processing conditions to modify fabric samples by water-based PDMS and silica particle suspensions

Preparation of water-based suspensions. PDMS emulsions of concentration *X* (*X* = 1, 1.5 or 2 wt%) were prepared by diluting the original Wacker HC 303 PDMS emulsion (~ 17 wt% active content) using Milli-Q water. These diluted PDMS emulsions were stirred for 5 min at room temperature. Silica particle suspensions of concentration *Y* (*Y* = 0.5 wt%, 0.75, 1 or 1.25 wt%) were prepared by mixing a proper amount of Tixosil® 365 silica particles and Milli-Q water followed by 30 min sonication in an ultrasonic bath.

Preparation of superwater-repellent fabrics from water-based suspensions. A first adhesive anchoring layer was deposited by immersing the PES fabric into the water-based PDMS emulsion for 3 min followed by 1 min annealing at 120 °C on a hot plate. Afterwards, the silica particles were deposited by immersing the PDMS-modified PES fabric into the aqueous silica particle suspension for 3 min followed by 3 min annealing at 150 °C on a hot plate. Finally, the sample was immersed into the water-based PDMS emulsion again for 3 min followed by 3 min annealing at 150 °C on a hot plate. Annealing after each deposition step was performed to remove the excess of water from the coating and react the methoxysilyl groups for cross-linking or grafting on the silica particles. The existence of a cross-linked network was confirmed by the fact that tetrahydrofuran, although swelling the layer, did not dissolve it.

Further cross-linking of the superwater-repellent coating deposited on fabric. To further cross-link the samples, the Phobol XAN cross-linker was added into the water-based PDMS emulsion (~ 1:8 solid weight ratio with respect to PDMS) followed by 5 min stirring. The PDMS/cross-linker emulsion was only used for the top PDMS layer which provides the low

surface tension. The bottom PDMS anchoring layer was prepared by dip-coating in the PDMS emulsion without the presence of the cross-linker. The cross-linking of PDMS occurred by reaction of the cross-linker (oxime-blocked bis-isocyanate) with the amine end groups of the PDMS during the annealing step (150 °C, 3 min) performed just after the dip-coating of the fabric in the PDMS/cross-linker emulsion. The supplementary cross-linking was confirmed by the fact that swelling by tetrahydrofuran decreased after Phobol XAN addition. This supplementary cross-linking did not improve the resistance of the coatings to machine washing, as shown in Figure S3.

SI 3 - Processing conditions to modify fabric samples from water-based PDMS, silica particle and paraffin wax suspensions

Preparation of water-based suspensions. PDMS emulsion (1.5 wt%) and silica particle suspension (1 wt%) were prepared using the methodology described in SI 2. Paraffin wax emulsion (4 wt%) was prepared by diluting the original commercial CONTRAQUA WE emulsion with Milli-Q water. Because the active solid content of the original emulsion is not specified by the supplier, the concentration was calculated as the ratio between the weight of the original emulsion (*i.e.* water + solid content, 2 g) and the weight of the final diluted emulsion (50 g).

Preparation of superwater-repellent fabrics from water-based suspensions. A first adhesive anchoring layer was deposited by immersing the PES fabric into the water-based PDMS emulsion for 3 min followed by 1 min annealing at 120 °C on a hot plate. Afterwards, the silica particles were deposited by immersing the PDMS-modified PES fabric into the aqueous silica particle suspension for 3 min followed by 3 min annealing at 150 °C on a hot plate. Finally, the sample was immersed into the water-based paraffin wax emulsion again for 3 min followed by 3 min annealing at 150 °C on a hot plate.

SI 4 - Processing conditions to modify sponge samples from water-based PDMS and silica particle suspensions

Preparation of water-based suspensions. A PDMS (Wacker HC 303) emulsion (1.5 wt%) and a silica particle (Tixosil® 365) suspension (0.75 wt%) were prepared using Milli-Q water, according to the protocols described in SI 2.

Preparation of superwater-repellent sponges. The first adhesive anchoring layer was deposited by immersing a commercial scrubbing sponge (Scotch Brite, 3M) into the PDMS emulsion for 3 min followed by 5 min annealing at 160 °C on a hot plate. Afterwards, the sample was immersed into the silica suspension for 3 min followed by 5 min annealing at 160 °C on a hot plate. Finally, the sample was immersed into the PDMS emulsion again for 3 min followed by 5 min annealing at 160 °C on a hot plate. During each annealing step, the sponge was deposited on the hot plate with the scrubbing side up and was compressed by ~ 75% in the vertical direction. The final sample was dried at room temperature for several days.

SI 5 - Characterization of the prepared samples

The water-repellent performance of the prepared fabrics was first characterized by contact angle measurements performed with an OCA 20 goniometer from Dataphysics. For each sample, a water droplet of 10 µL was used 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. Roll-off angle tests were also performed. For this, a 10 µL water droplet almost in contact with the surface was released onto the tilted sample. The roll-off angle was determined as the tilt angle for which the droplet started to roll-off on the sample surface. The morphology of the samples (~ 15 nm-thick Au layer was deposited on the sample surface) was characterized by scanning electron microscopy (SEM, JEOL 7600F, 15 kV accelerating voltage). The topography of the samples was characterized by optical profilometry (AltiSurf 500 from Altimet) and by atomic force microscopy (AFM, ICON Dimension from Bruker) in tapping mode. A silicon cantilever from Nanosensors (force constant ~ 40 N/m, apex radius of curvature < 7 nm) was used. The average values of the rms and Wenzel roughnesses shown in Table 1 of the manuscript were calculated based on four AFM topography images (3 x 3 μm^2 scanning size) recorded for each sample. The washing tests were performed using a Zanussi washing machine (model ZWG 1140M). The washing program includes washing, rinsing and spinning at 30 °C using a minimum water quantity programed by the machine. 5 g detergent (Le Chat Sensitive) was added during the washing step. The UV resistance tests were performed using the following conditions: the UV source was UVA 340 nm; alternately UV exposure and condensation were applied (0.80W/m^2 intensity and 340 nm wavelength) at a temperature of 55°C for 4 hours during the UV exposure, and at a temperature of 45°C for 2 hours during condensation. The total exposure time was 20 days. The mechanical resistance of the samples was tested by performing

peeling tests. For this, a *ca.* 1 x 2 cm^2 adhesive tape was applied on the sample surface then gently peeled off. The contact angle of the sample was systematically measured after a given number of application/peeling cycles.

SI 6 - Extraction of the textural roughness

The textural roughness of the bare fabric was obtained by optical profilometry. 2 x 2 mm^2 surfaces were imaged at 1 µm resolution and flattened numerically to remove the tilt. Because the computation of the developed surface is very sensitive to noise, smoothing of the images was required. Therefore, the images were smoothed in Fourier space, using Gaussian low pass filters of standard deviation *d* from 0 to 140 µm; the rms roughness and Wenzel roughness of the smoothed images were then computed and plotted versus the standard deviation of the used smoothing filter (Figure S1). The rms roughness first decreases rapidly and linearly with *d*, then enters a second regime of linear decrease; the first decrease is due to the removal of noise, the second to the smoothing of the texture by the Gaussian filter. We defined the optimal smoothing parameter as the one corresponding to the intersection between the two extrapolated linear regimes as shown in Fig. S1. The optimal standard deviation of the Gaussian low pass filter was 15.9 µm, leading to a Wenzel roughness of 1.44 for the fabric.

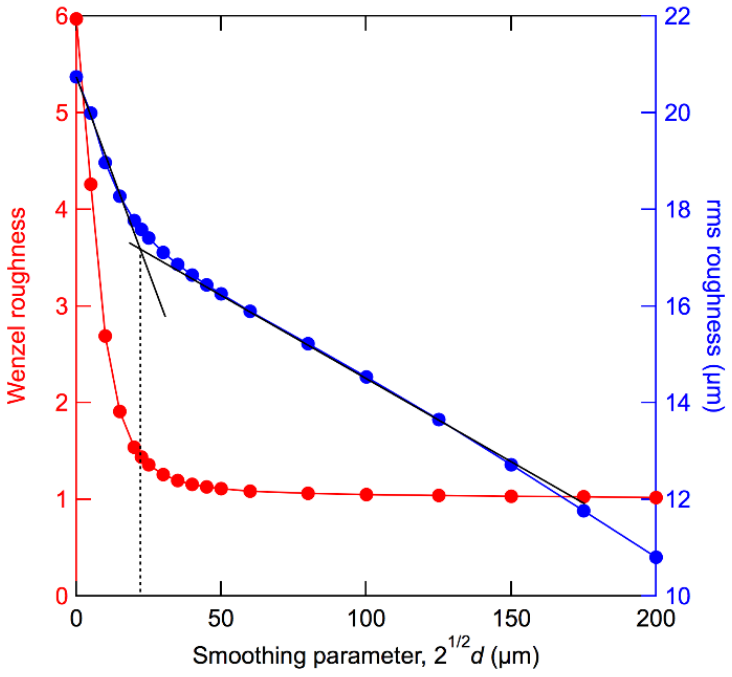

Figure S1. Variation of the rms roughness (blue, right axis) and of the Wenzel roughness (red, left axis) versus the degree of smoothing of the profilometry image of the fabric. The optimal smoothing parameter is found at the intersection between the two linear regimes of variation of the rms roughness, as indicated in the Figure. *d* is the standard deviation of the Gaussian low pass filter used for smoothing.

SI 7 - Water repellence after the tape peeling test

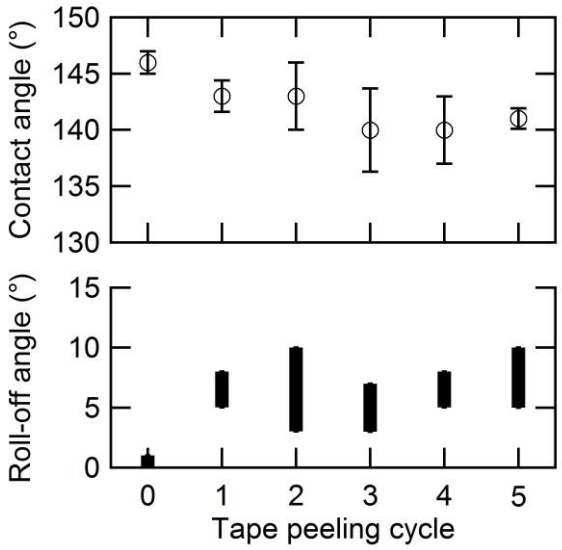

Figure S2. Variation of the water contact angle (top) and roll-off angle (bottom) as a function of the number of adhesive tape peeling cycles performed on a superhydrophobic fabric coated with PDMS(1.5 wt%)/silica particles(1 wt%)/PDMS(1.5 wt%).

SI 8 - Water repellence of a sample with supplementary cross-linking

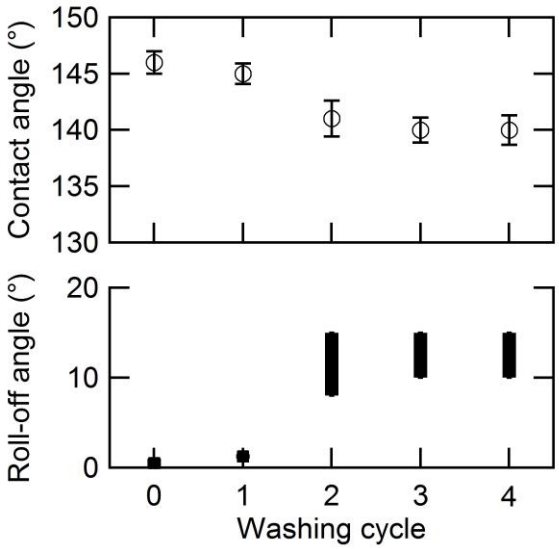

Figure S3. Variation of the water contact angle (top) and roll-off angle (bottom) versus the number of machine washing cycles, measured for PDMS(1.5 wt%)/silica particle(1 wt%)/PDMS(1.5 wt%) coating, for which the external PDMS layer was further cross-linked with the addition of Phobol XAN.