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Rational design of perfluorocarbon-free oleophobic textiles

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Supplementary Information

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Supplementary Tables

Supplementary Table 1. Porosity of common fabric weaves¹.

Weave type	Percent Open Area (%OA)	$D^* = \frac{1}{1 - \sqrt{\%OA}}$
Sateen-regular	42%	2.8
Sateen-irregular	47%	3.2
Plain or Tabby weave	50%	3.4
Warp and weft faced twill	50%	3.4
Balanced twill	50%	3.4
Warp rib weave-regular	51%	3.5
Herring bone twill	53%	3.7
Warp rib weave-irregular	55%	3.9
Matt rib weaves-irregular	57%	4
Ordinary honeycomb	56%	4
Satin-sateen checks	58%	4.2
Huck-a-back weave	59%	4.3
Weft rib weave-regular	59%	4.4
Weft rib weave-irregular	60%	4.5
Pointed twill	63%	4.8
Matt weave-regular	66%	5.3
Warp-faced twill	70%	6
Weft-faced twill	73%	6.8
Satin-irregular	73%	6.9
Satin-regular	77%	8.1

Supplementary Table 2. Densities² and surface tensions (measured) of the ethanol-water mixtures.

Water wt%	Ethanol wt%	Ethanol mole fraction	γ_{LV} (mN m⁻¹)	Density at 20°C (g cm⁻³)	Density at 25°C (g cm⁻³)
100	0	0	71.93	0.998	0.997
99.24	0.76	0.003	66.42	0.997	0.996
94.32	5.68	0.023	53.35	0.988	0.987
88.36	11.64	0.049	45.74	0.980	0.978
79.62	20.38	0.091	38.22	0.968	0.966
73.60	26.40	0.123	34.75	0.960	0.957
72.00	28.00	0.132	33.97	0.957	0.954
70.26	29.74	0.142	33.71	0.954	0.951
68.56	31.44	0.152	32.29	0.951	0.948
66.43	33.57	0.165	31.00	0.948	0.944
64.20	35.80	0.179	31.34	0.943	0.940
61.45	38.55	0.197	30.21	0.938	0.934
58.10	41.90	0.22	30.22	0.931	0.927
53.19	46.81	0.256	28.98	0.921	0.917
48.07	51.93	0.297	28.51	0.910	0.905
43.04	56.96	0.341	27.83	0.898	0.894
38.05	61.95	0.389	27.41	0.887	0.882
33.05	66.95	0.442	26.55	0.875	0.871
28.03	71.97	0.501	25.81	0.863	0.859
23.94	76.06	0.554	25.61	0.853	0.849
18.87	81.13	0.627	24.86	0.841	0.836
15.66	84.34	0.678	24.30	0.833	0.828
13.09	86.91	0.722	24.13	0.826	0.822
10.67	89.33	0.766	23.94	0.820	0.815
9.36	90.64	0.791	23.62	0.816	0.812
8.05	91.95	0.817	23.38	0.813	0.808
6.65	93.35	0.846	23.17	0.809	0.805
5.52	94.48	0.87	22.84	0.806	0.801
4.164	95.84	0.9	22.62	0.802	0.798
2.44	97.56	0.94	22.50	0.797	0.792
1.20	98.80	0.97	22.37	0.793	0.789
0	1	1	22.28	0.789	0.785

Supplementary Note 1

Porosity determination of woven fabrics and wire meshes: In Extended Data Fig. 7a, a unit cell of fibers with diameter $2R$ (shaded rectangle) and open area (white square) with side length $2D$ is depicted. The hatched square indicates the pick of the weave, i.e. where the fibers overlap. The air fraction is the ratio of air surface area to total surface area. Typically, woven metal meshes are characterized by the percent open area (%OA) of the mesh. This can be readily converted to D^* by,

$$D^* = \frac{R+D}{R}, \frac{1}{D^*} = \frac{R}{R+D}, 1 - \frac{1}{D^*} = \frac{D}{R+D}$$

$$\%OA = \frac{2D \times 2D}{(2R+2D)^2} = \frac{4D^2}{4(R+D)^2} = \frac{D^2}{(R+D)^2} = \left(1 - \frac{1}{D^*}\right)^2$$

$$D^* = \frac{1}{1 - \sqrt{\%OA}}$$

In order to measure D^*_{fiber} for fabrics, twenty different weaves were selected from Gokarneshan's text¹. Using ImageJ, the weave design was separated into air and fiber areas via image thresholding, and the open area percentage was calculated. For example, for a plain weave with %OA = 50% (Supplementary Table 1), the porosity parameter would be,

$$D^* = \frac{1}{1 - \sqrt{0.5}} = \frac{\sqrt{2}}{\sqrt{2} - 1} = 2 + \sqrt{2} \approx 3.4$$

Supplementary Note 2

A comment on the robustness parameter of hierarchical, non-wetted surfaces: In the literature it has been assumed that the addition of a second layer of texture does not impact the robustness of a hierarchical, non-wetted interface, i.e. $A^*_{\text{hierarchical}} = A^*_{\text{fiber}}$ ³. This was assumed because the liquid will wet along the path of lowest capillary resistance, and the pores of the larger-scale texture

will typically be much bigger than the pores of the smaller-scale texture. However, the meniscus of the liquid on fibers decorated with this second layer of texture should sit at $\theta_{\text{particle}}^*$ and not θ_Y (Extended Data Fig. 6a,b). The effect of this difference on the robustness of the Cassie state is illustrated in Extended Data Fig. 6c for hexadecane and silicone chemistry. For all $\theta_{\text{particle}}^* > \theta_Y$, greater capillary resistance is predicted.

Supplementary Note 3

Derivation of Equation 6 from the main manuscript: For a fabric finish exhibiting a given $\theta_{\text{particle}}^*$, $D_{\text{fiber_max}}^*$ indicates the maximum porosity of a fabric that can support the Cassie-Baxter state when treated with this finish. Assuming $A_{\text{hierarchical}}^* = 1$, the surface would wet for any $D_{\text{fiber}}^* > D_{\text{fiber_max}}^*$. This was depicted by the red region in Figures 3b and 3c in the main manuscript. $D_{\text{fiber_max}}^*$ is found by rearranging Equation 5 and then solving the quadratic,

$$A_{\text{hierarchical}}^* = \frac{\ell_{\text{cap}}}{R_{\text{fiber}} (D_{\text{fiber}}^* - 1)} \frac{(1 - \cos \theta_{\text{particle}}^*)}{(D_{\text{fiber}}^* - 1 + 2 \sin \theta_{\text{particle}}^*)}$$

$$\frac{\ell_{\text{cap}} (1 - \cos \theta_{\text{particle}}^*)}{(A_{\text{hierarchical}}^*) R_{\text{fiber}}} = (D_{\text{fiber}}^* - 1)(D_{\text{fiber}}^* - 1 + 2 \sin \theta_{\text{particle}}^*)$$

$$\frac{\ell_{\text{cap}} (1 - \cos \theta_{\text{particle}}^*)}{(A_{\text{hierarchical}}^*) R_{\text{fiber}}} = (D_{\text{fiber}}^* - 1)^2 + (D_{\text{fiber}}^* - 1) 2 \sin \theta_{\text{particle}}^*$$

$$\frac{\ell_{\text{cap}} (1 - \cos \theta_{\text{particle}}^*)}{(A_{\text{hierarchical}}^*) R_{\text{fiber}}} = ((D_{\text{fiber}}^* - 1) + \sin \theta_{\text{particle}}^*)^2 - \sin^2 \theta_{\text{particle}}^*$$

$$\sin^2 \theta_{\text{particle}}^* + \frac{\ell_{\text{cap}} (1 - \cos \theta_{\text{particle}}^*)}{(A_{\text{hierarchical}}^*) R_{\text{fiber}}} = ((D_{\text{fiber}}^* - 1) + \sin \theta_{\text{particle}}^*)^2$$

$$\sqrt{\sin^2 \theta_{\text{particle}}^* + \frac{\ell_{\text{cap}} (1 - \cos \theta_{\text{particle}}^*)}{(A_{\text{hierarchical}}^*) R_{\text{fiber}}}} = D_{\text{fiber}}^* - 1 + \sin \theta_{\text{particle}}^*$$

$$D_{\text{fiber_max}}^* = 1 - \sin \theta_{\text{particle}}^* + \sqrt{\sin^2 \theta_{\text{particle}}^* + \frac{\ell_{\text{cap}} (1 - \cos \theta_{\text{particle}}^*)}{(A_{\text{hierarchical}}^*) R_{\text{fiber}}}}$$

This is Equation 6 from the main manuscript. Because A^* is defined for a specific liquid, Equation 6 can be used to calculate the necessary A^* values for one liquid, considering the capillary resistance of another. For example, in the main manuscript we stated that a fabric capable of repelling heptane ($A_{\text{heptane}}^* > 1$) would require $A_{\text{hexadecane}}^* > 3.1$. This was found as follows.

We consider a non-wetting ($A_{\text{heptane}}^* = 1$) heptane droplet on fibers ($R_{\text{fiber}} = 10 \mu\text{m}$) decorated by particles utilizing an alkyl-based chemistry and exhibiting an apparent contact angle $\theta_{\text{particle_heptane}}^* = 35^\circ$. The capillary length of heptane is $\ell_{\text{cap}} = 1.7 \text{ mm}$. The maximum fiber porosity is found using Equation 6 and gives $D_{\text{fiber_max}}^* \approx 6$, *i.e.* more open fabric constructions will cause wetting to occur.

Using Equation 2 from the main manuscript, the porosity of particles, D_{particle}^* , may be found assuming $\theta_Y^{\text{heptane}} = 25^\circ$ on a wax-based chemistry. This gives

$$D_{\text{particle}}^* = \frac{\pi(1 + \cos \theta_Y)^2}{2\sqrt{3}(1 + \cos \theta_{\text{particle}}^*)} \approx 1.81.$$

Knowing $\theta_Y^{\text{hexadecane}} = 46^\circ$ on a wax-based surface chemistry and using $D_{\text{particle}}^* = 1.81$, the apparent contact angle of hexadecane on the particles is found using Equation 2, $\theta_{\text{particle_hexadecane}}^* \approx 64^\circ$. The robustness parameter of hexadecane ($\ell_{\text{cap}} = 1.9 \text{ mm}$) may then be found using Equation 5 as,

$$A_{\text{hierarchical}}^* = \frac{\ell_{\text{cap}}}{R_{\text{fiber}} (D_{\text{fiber}}^* - 1)} \frac{(1 - \cos \theta_{\text{particle}}^*)}{(D_{\text{fiber}}^* - 1 + 2 \sin \theta_{\text{particle}}^*)} \approx 3.1.$$

Supplementary Note 4

Derivation of Equation 7: To derive the contact angle of the plain weave jacket fabric, a unit cell of yarns and open areas was considered with total area $(2R + 2D)^2$ (Extended Data Fig. 7b, c). If each yarn is treated as a single fiber, the total contact line lengths per area for liquid/air (ϕ_{air}) and liquid/solid (ϕ_s) may be found:

$$\phi_{\text{air}} = \frac{2(R - R \sin \theta)(4D + 2R) + 4D^2}{4(R + D)^2} = 1 - \sin \theta_Y \left[\frac{2RD + R^2}{(R + D)^2} \right] = 1 - \sin \theta_Y \left(\frac{2D^* - 1}{D^{*2}} \right)$$

$$\phi_s = \frac{(\pi - \theta)(4R^2 + 8RD)}{4(R + D)^2} = (\pi - \theta) \left(\frac{2D^* - 1}{D^{*2}} \right)$$

The Cassie-Baxter equation then becomes,

$$\cos \theta_{\text{fabric}}^* = \phi_s \cos \theta_Y + \phi_{\text{air}} \cos \pi = -1 + \frac{2D_{\text{fiber}}^* - 1}{(D_{\text{fiber}}^*)^2} [(\pi - \theta_Y) \cos \theta_Y + \sin \theta_Y]$$

which is Equation 7 from the main manuscript. Note that if instead of assuming all yarns adopt θ_Y , but rather half remain non-wetted, Equation 1 is recovered. If half of those yarns are wetted, the contact angle may be found by an average of Equations 1 and 7, which is shown as a dashed line in Figure 6.

Supplementary References

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