Playing with fabric roughness to improve water (and oil?) repellency

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Interreg France-Wallonie-Vlaanderen
GoToS3
DURATEX
Avec le soutien du Fonds européen de Développement Régional
Met de steun van het Europees Fonds voor Regionale Ontwikkeling
Wallonie
met de steun van west-vlaanderen de gedreven provincie

1

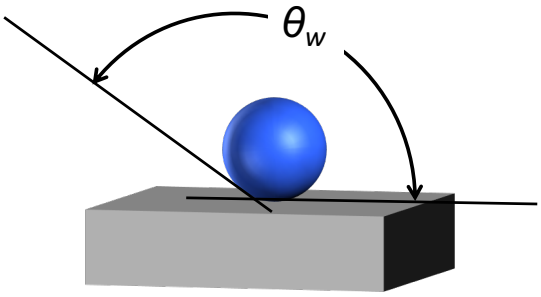
Why were long chain perfluoroalkyls used for water repellence?

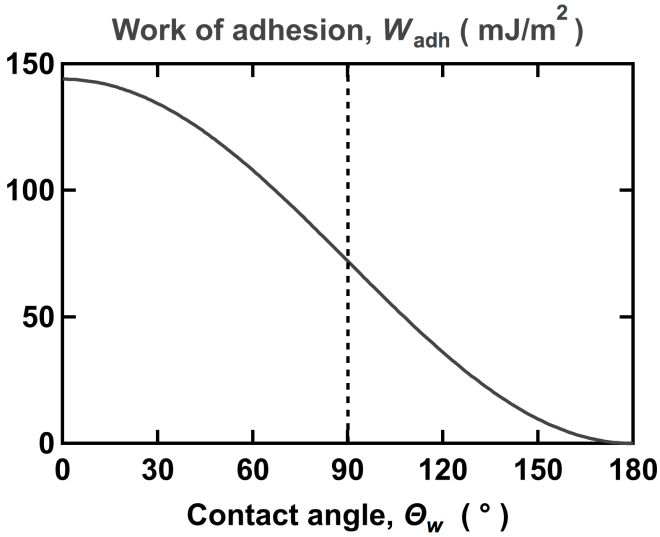
2

The contact angle of a water droplet provides its work of adhesion on a flat surface, W_{adh}

$$W_{adh} = \gamma_w (1 + \cos\theta_w)$$

~72 mJ/m²

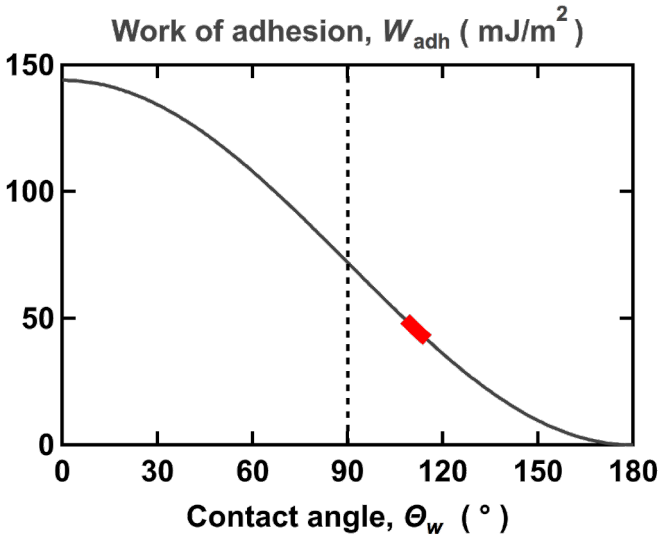




3

Long perfluoroalkyl chains result in a low work of adhesion and provide very good water repellence

Long perfluoroalkyl chains



4

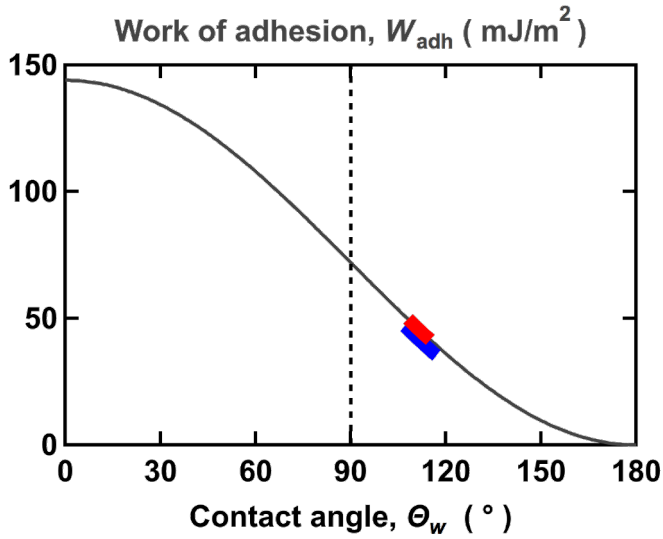
Are there possible replacements for long chain fluoroalkyls?

5

Other candidates are possible

Silicones

Long perfluoroalkyl chains



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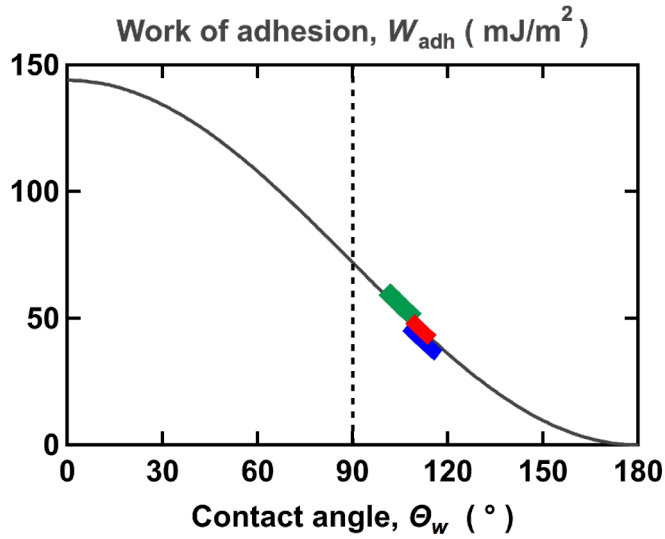
Other candidates are possible

Alkyl chains (waxes)

Silicones

Long perfluoroalkyl chains



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Chemistry is not the only parameter one can play with

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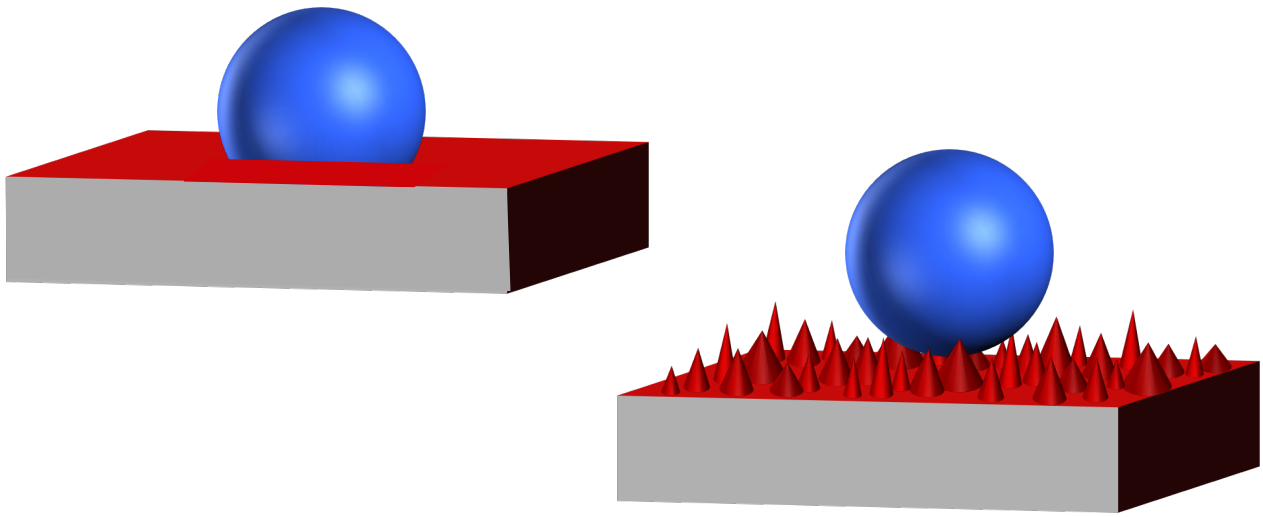
Surface roughness is another parameter controlling the contact angle



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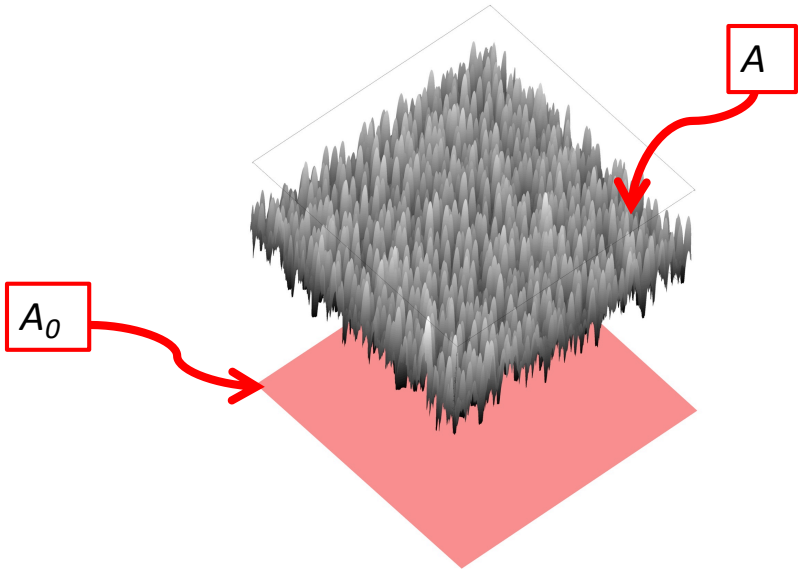
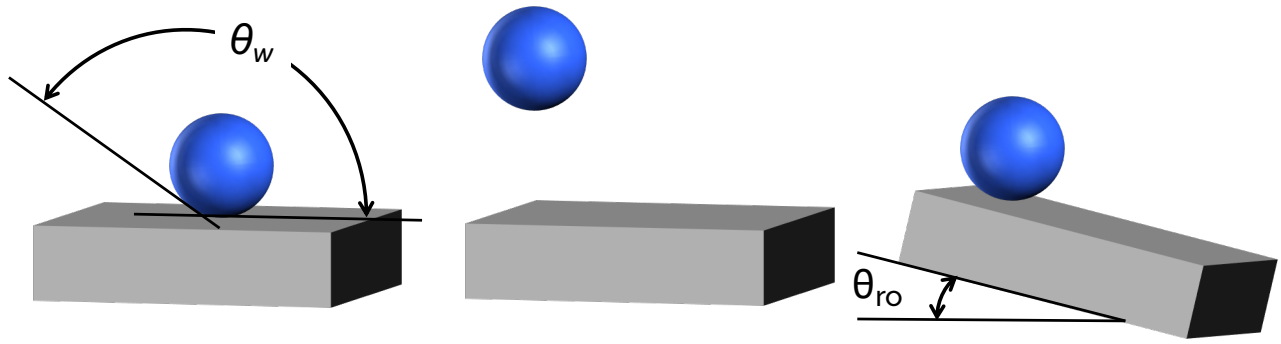
The roughness is defined as the increase of surface area



$$\mathcal{R} = \frac{A}{A_0}$$

10

Surfaces of sufficiently high roughness may become superhydrophobic



Water contact angle
$\theta_w > 150^\circ$

Droplet bouncing

Droplet roll-off
$\theta_{ro} < \sim 5^\circ$

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What is the role of fabric roughness in water repellence?

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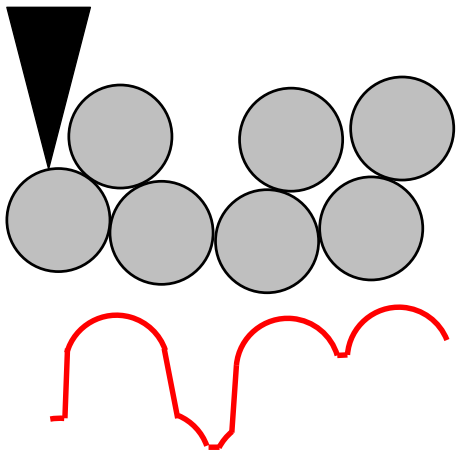
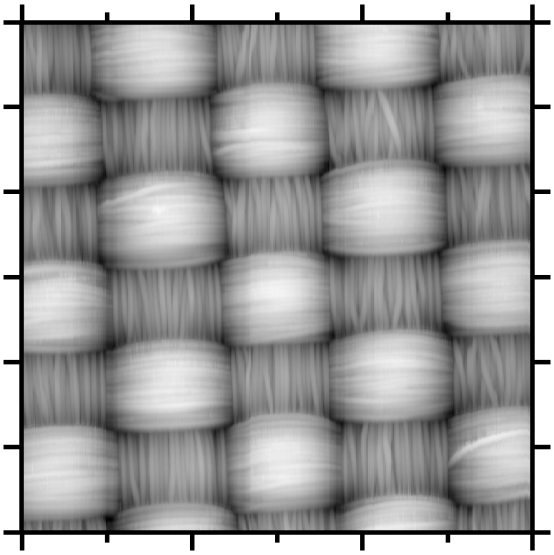
An experimental roughness can be measured by profilometry and AFM





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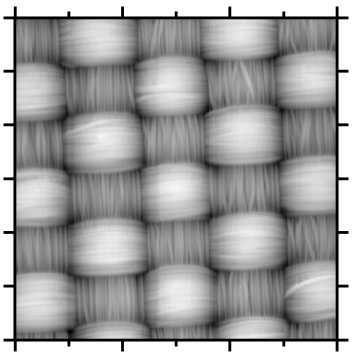
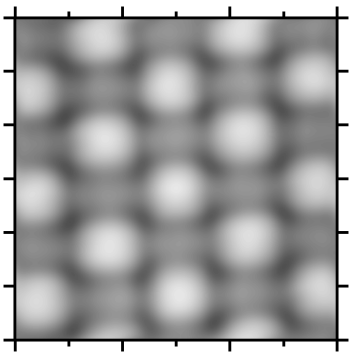
The profilometry roughness arises from the weave pattern and the fiber packing in the yarns



Fabric pattern

$\mathcal{R}_{\text{prof}}$

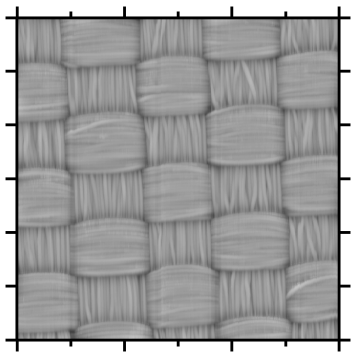
=



Weave pattern

$\mathcal{R}_{\text{W}}$

+



Fiber packing in yarns

$\mathcal{R}_{\text{Y}}$

$$\mathcal{R}_{\text{prof}} = \mathcal{R}_{\text{W}} + \mathcal{R}_{\text{Y}} - 1$$

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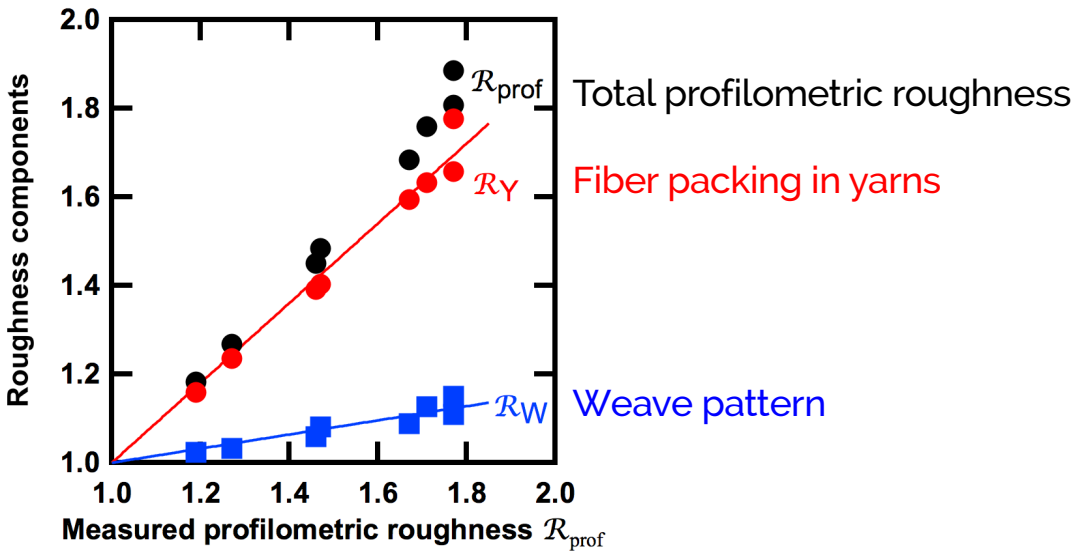
The fiber-in-yarn roughness dominates the roughness of woven fabrics



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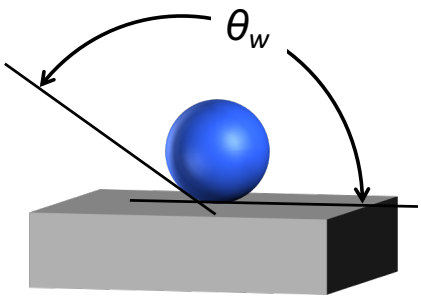
Static contact angle of coated woven fabrics



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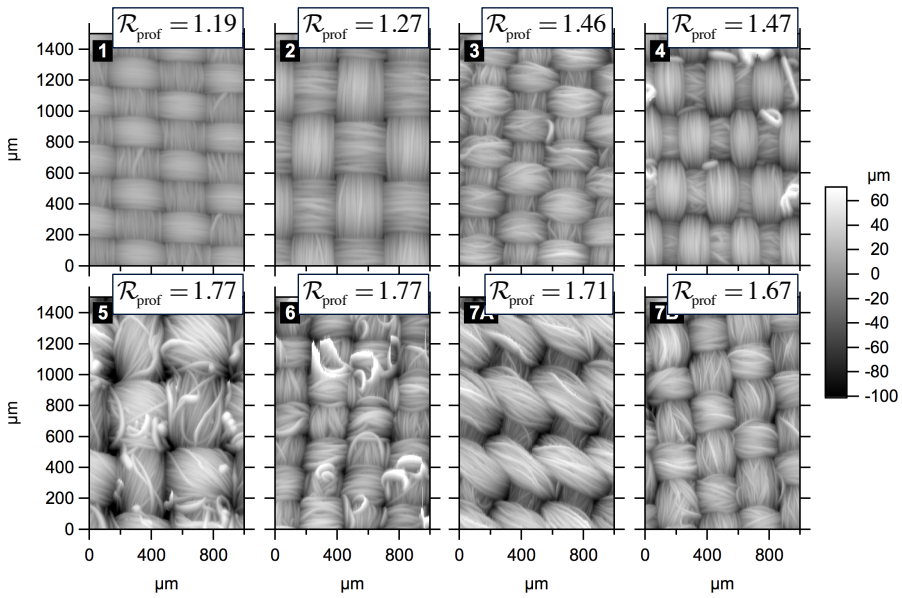
10 fabrics selected

roughness

1.77

1.19



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Three aqueous formulations of similar θ_w are used to dip-coat our fabrics

	Θ_w (H_2O, flat surface) (°)
Wax-modified melamin resin	110
Silicone rubber	111
Perfluorobutyl (C4) -modified PUR	110

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Short perfluoroalkyls raise concerns

Brendel *et al. Environ Sci Eur (2018) 30:9*
https://doi.org/10.1186/s12302-018-0134-4
Environmental Sciences Europe

RESEARCH

Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH

Stephan Brendel*, Éva Fetter, Claudia Staude, Lena Vierke and Annegret Biegel-Engler

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Silicones might also rise concerns in the public

kft-blog.com

ECHA: Siloxanes D4, D5, and D6 Classified as SVHC

Posted on 5. July 2018 by kftchemieservice

The Member State Committee (MSC) of the ECHA has approved the classifica
D4, D5, and D6 as substances of very high concern (SVHC). The German Envi
Ministry submitted the required reports (Annex XV Report on D4 and Annex
Annex XV – Identification of D4 and D5 as SVHC in March of this year. The E
the Report on D6.

The experts in the MSC rated D4 as persistent, bioaccumulative (it accumulat
chain), and toxic (PBT), but they assigned only persistent and bioaccumulative
to D5 and D6. Nevertheless, D5 and D6 can also be classified as PBT when bot
show D4 impurities in a concentration equal to or greater than 0.1% by weigh

Silicone compounds D4 (cyclotetrasiloxane), D5 (cyclopentasiloxane), and D6
(cyclohexasiloxane) are often found in personal care products and flow into the
along with waste water. They are also important source materials for certain si
often found as residues in finished products.

ECHA
EUROPEAN CHEMICALS AGENCY

Substance Name:
Octamethylcyclotetrasiloxane (D4)
EC Number: 209-136-7
CAS Number: 556-67-2

MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF OCTAMETHYLCYCLOTETRASILOXANE (D4) AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS PBT[1] AND vPvB[2] PROPERTIES

(ARTICLE 57D&E)

Adopted on 13 June 2018

[1] PBT means persistent, bioaccumulative and toxic
[2] vPvB means very persistent and very bioaccumulative

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A mathematical model of wetting was developped

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How roughness controls the water repellency of woven fabrics

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[b]Centexbel, Zwijnaarde, Belgium

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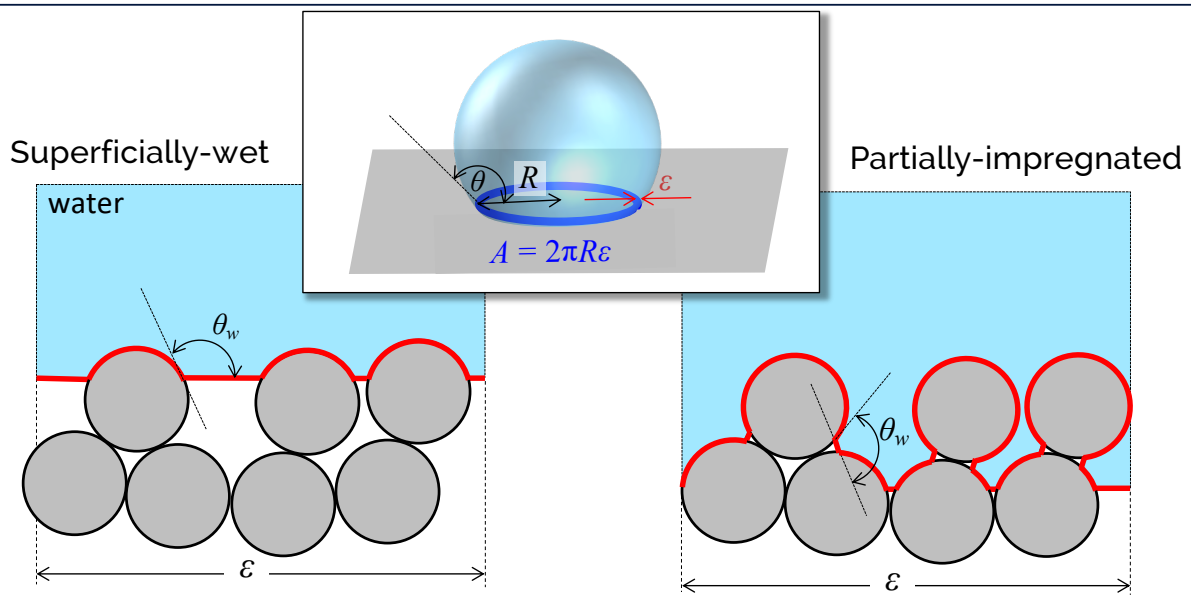
Two main wetting regimes exist



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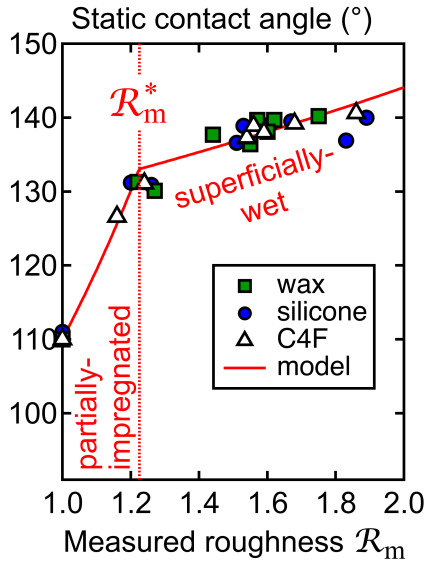
Contact angles can be predicted from roughness, and give similar results for our three coatings



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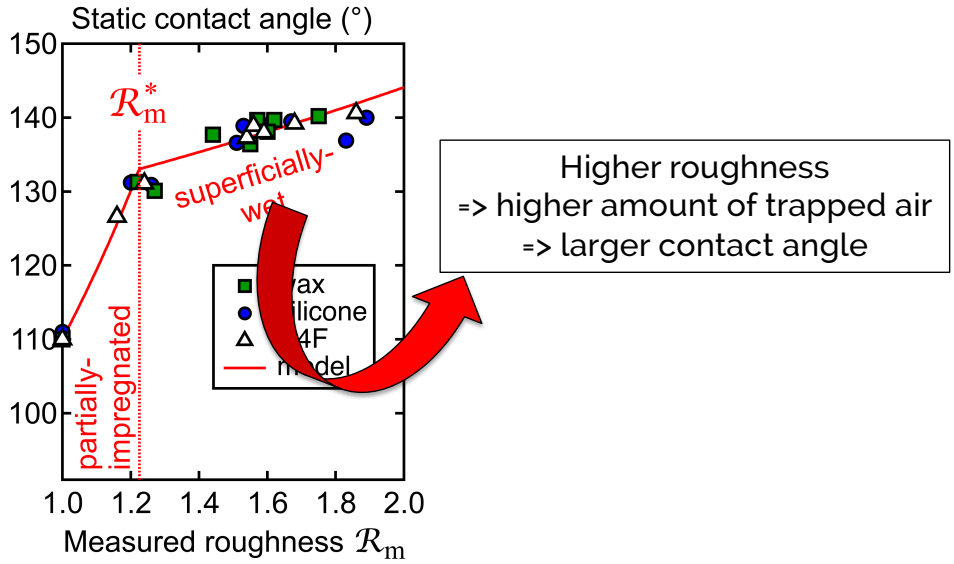

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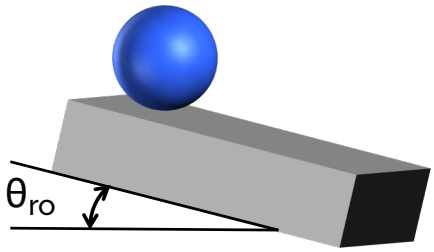
Roll-off/sliding angle of coated woven fabrics



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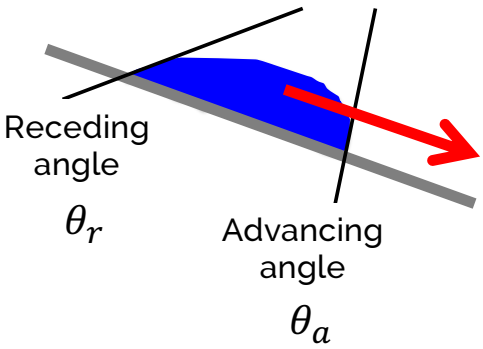
The roll-off/sliding angle is linked to the pinning of the droplet on the surface



$$mg\sin\theta_{ro} = 2R\gamma(\cos\theta_r - \cos\theta_a)$$

Gravitational pull

Resistance to sliding

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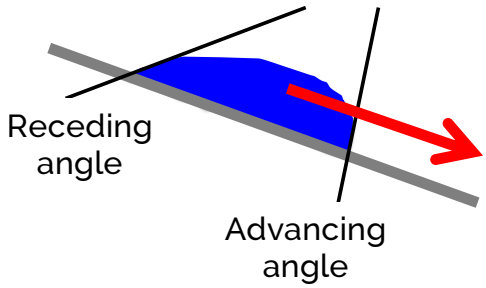
The roll-off/sliding angle is linked to the pinning of the droplet on the surface



$$mg\sin\theta_{ro} = 2R\gamma(\cos\theta_r - \cos\theta_a)$$
$$= 2R\mu$$

Pinning parameter (N/m)

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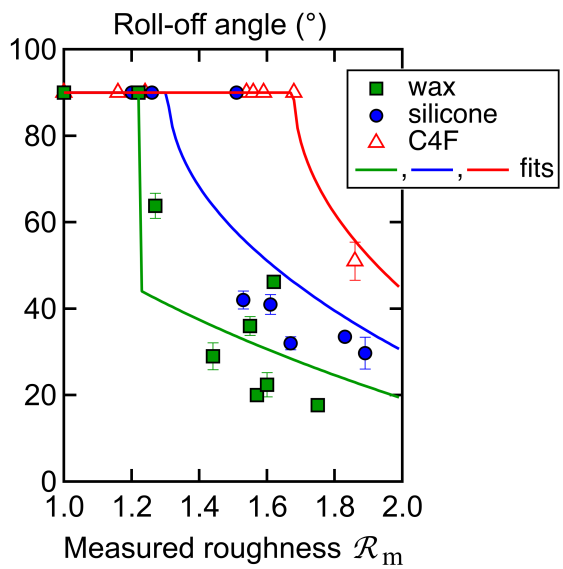
The roll-off angles discriminate the different coatings



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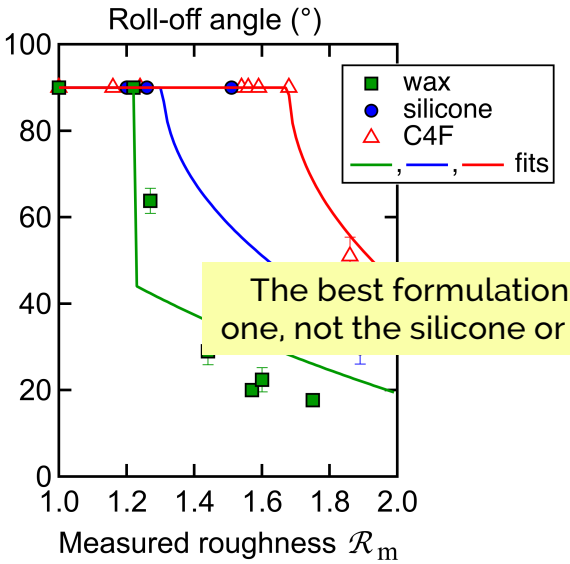
The roll-off angles correlate to roughness and to the pinning parameter



The best formulation is the wax-based one, not the silicone or the fluorinated one

Formulation	μ (N/m) meas.
wax	0.024
	0.029
C4F	0.086

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Future work: bouncing droplets

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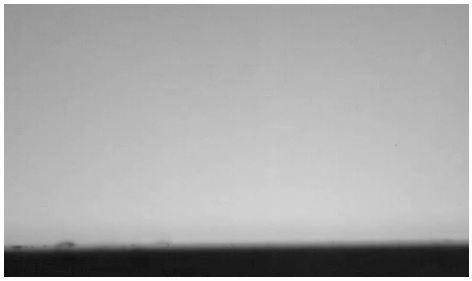
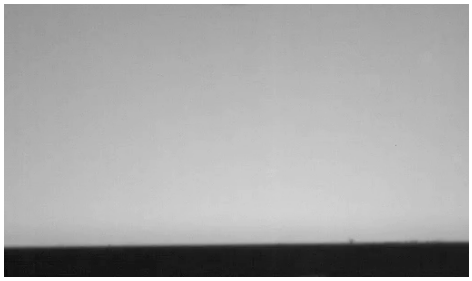


Wax-based



C4F-based

silicone-based

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Can we improve the hydrophobicity of a fabric of low roughness?

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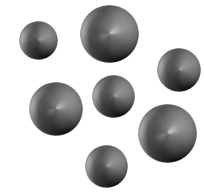
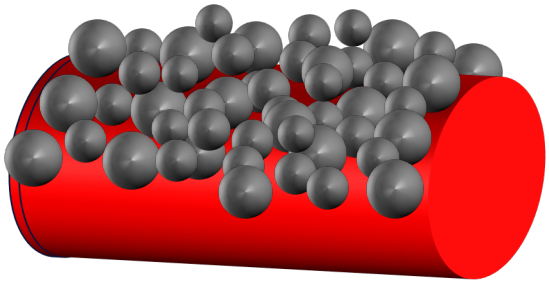
Boosting fiber roughness with silica particles



Silica particles

+ aqueous coating formulation

Fiber roughness $\mathcal{R}_f > 1$



$$\mathcal{R} = (\mathcal{R}_W + \mathcal{R}_Y - 1) \times \mathcal{R}_f$$

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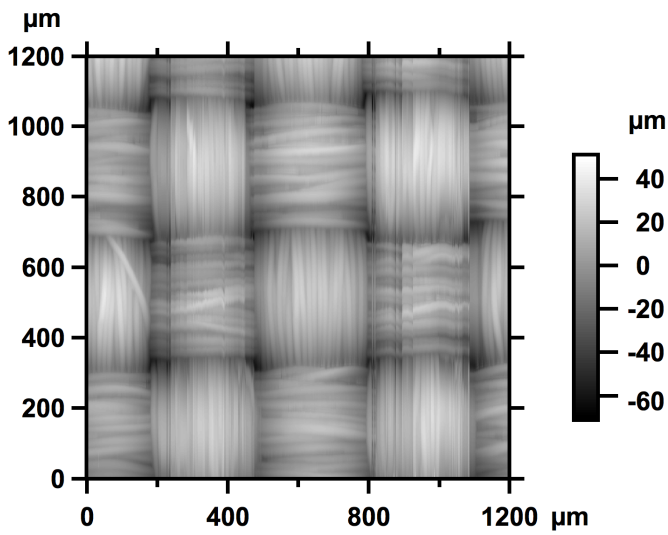
We selected a fabric of low roughness (1.3)



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Results obtained with
a crosslinked silicone rubber

(*aqueous emulsion, HC303, Wacker*)

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Silicone-based superhydrophobic coatings (dip-coating from aqueous suspensions)

ACS Applied Materials & Interfaces (2018, 10, 15346–15351)

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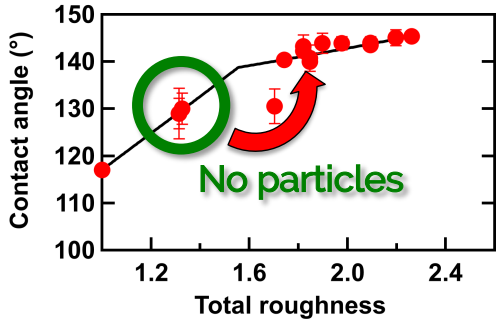
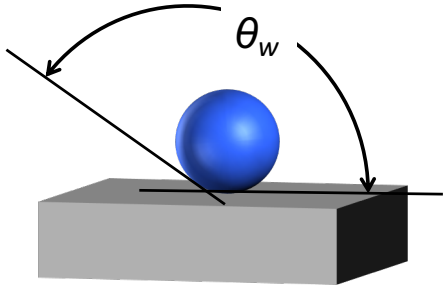
Increasing the roughness of the fibers results in increased water repellence





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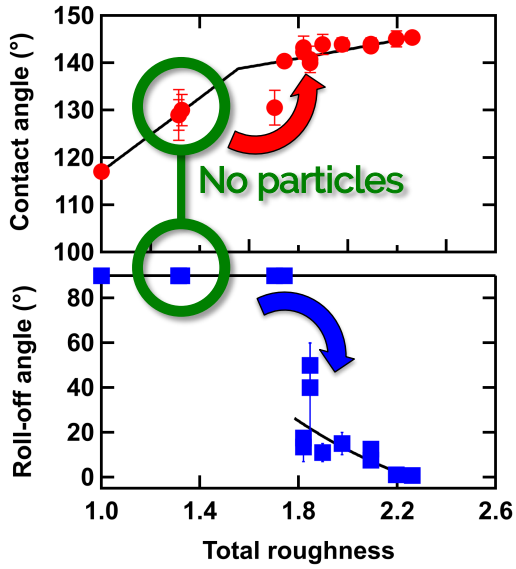
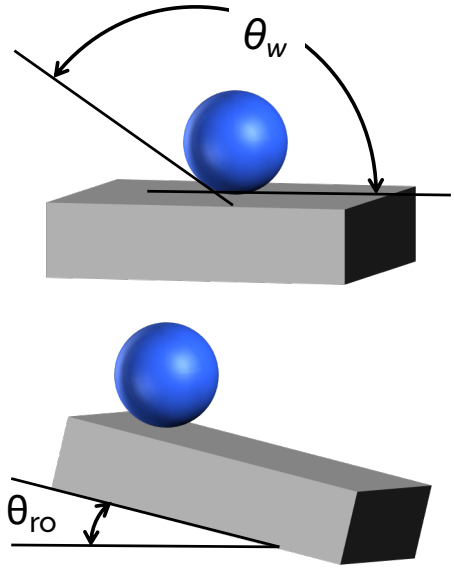
Again, increasing the roughness of the fibers results in increased water repellence





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Water repellence of a silicone-based superhydrophobic fabric prepared from aqueous suspensions

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Future work: oleophobicity

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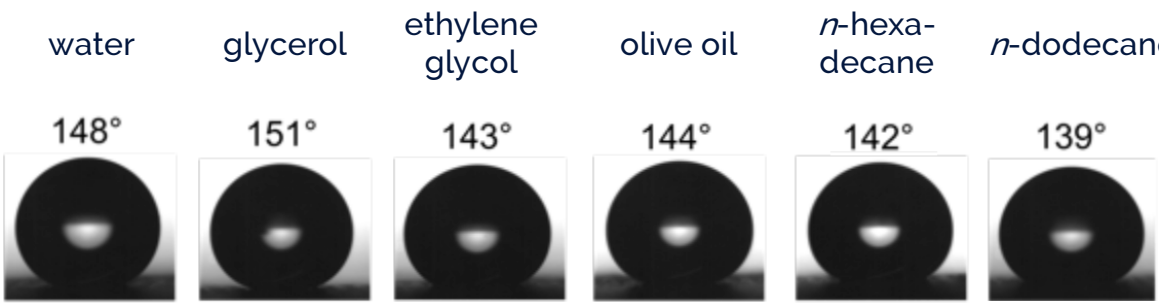
The short C4 perfluoroalkyl chains also provide resistance to some organic solvents, with roughened fibers



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The short C4 perfluoroalkyl chains also lead to superoleophobicity with roughened fibers

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Main conclusions

1. Total roughness and pinning are predictors of water repellence performance (*other parameters may have to be considered*)
2. Total roughness $\mathcal{R} = (\mathcal{R}_W + \mathcal{R}_Y - 1) \times \mathcal{R}_f$

   - $\mathcal{R}_W$ → Weave pattern (limited)
   - $\mathcal{R}_Y$ → Fibers-in-yarn (important)
   - $\mathcal{R}_f$ → Fiber surface (very important)
3. Fiber surface roughness can be boosted by silica nanoparticles; *other methods certainly exist*
4. Different formulations can be discriminated by the roll-off angle measured on a set of fabrics of different roughness
5. Our studies suggest: waxes > silicones > C4 perfluoroalkyls

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Acknowledgments

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UNION EUROPÉENNE EUROPESE UNIE
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Wallonie
met de steun van west-vlaanderen de gedreven provincie

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