# Fluor-Free Superhydrophobic and Eco-Friendly Superoleophobic Textiles

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CENTEXBEL

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Interreg France-Wallonie-Vlaanderen
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Avec le soutien du Fonds européen de Développement Régional
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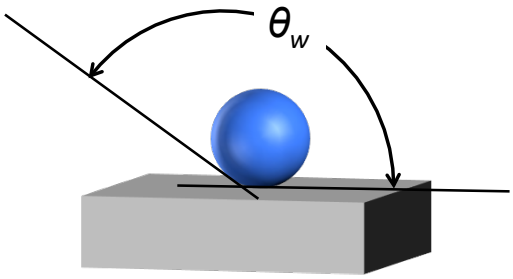
Wallonie
met de steun van west-vlaanderen de gedreven provincie

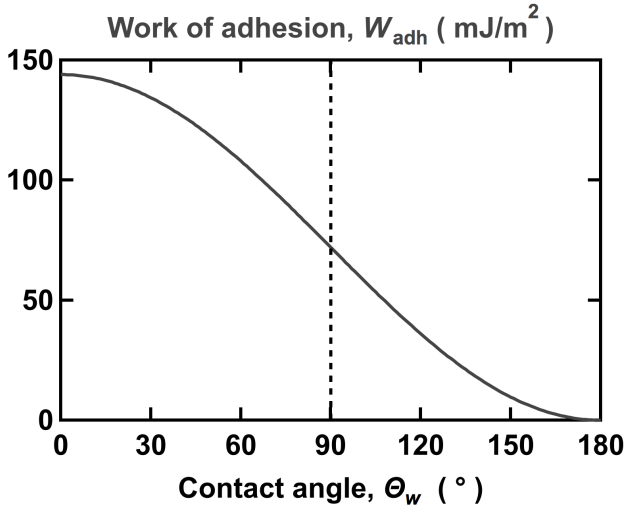
## Why were long chain perfluoroalkyls used for water repellence?

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

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

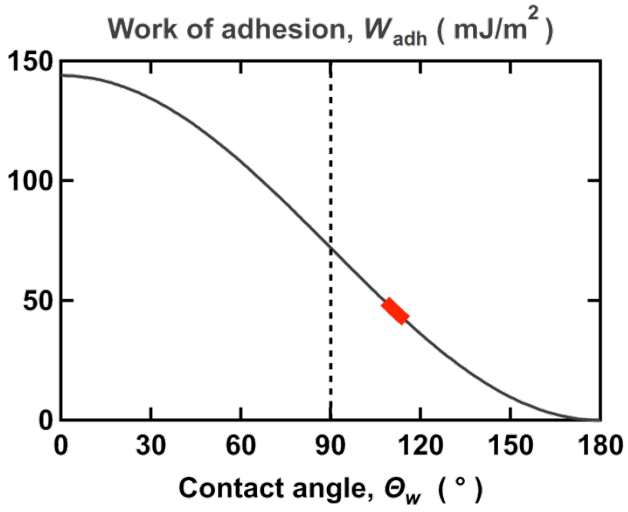
~72 mJ/m²




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

Long perfluoroalkyl chains

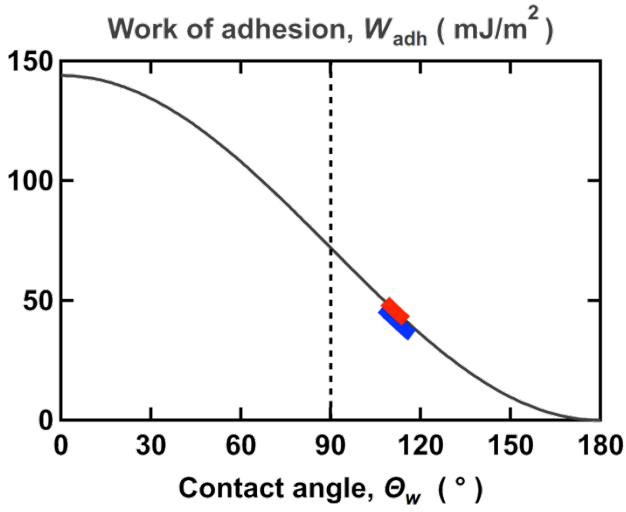


Are there possible replacements for long chain fluoroalkyls?

## Other candidates are possible

Silicones

Long perfluoroalkyl chains

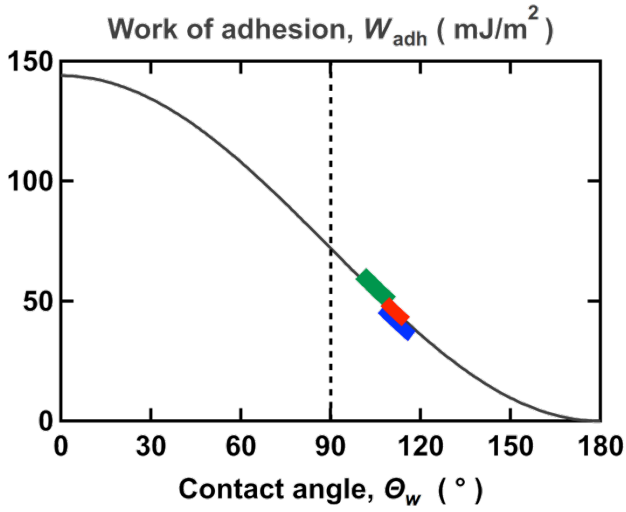


## Other candidates are possible

Alkyl chains (waxes)

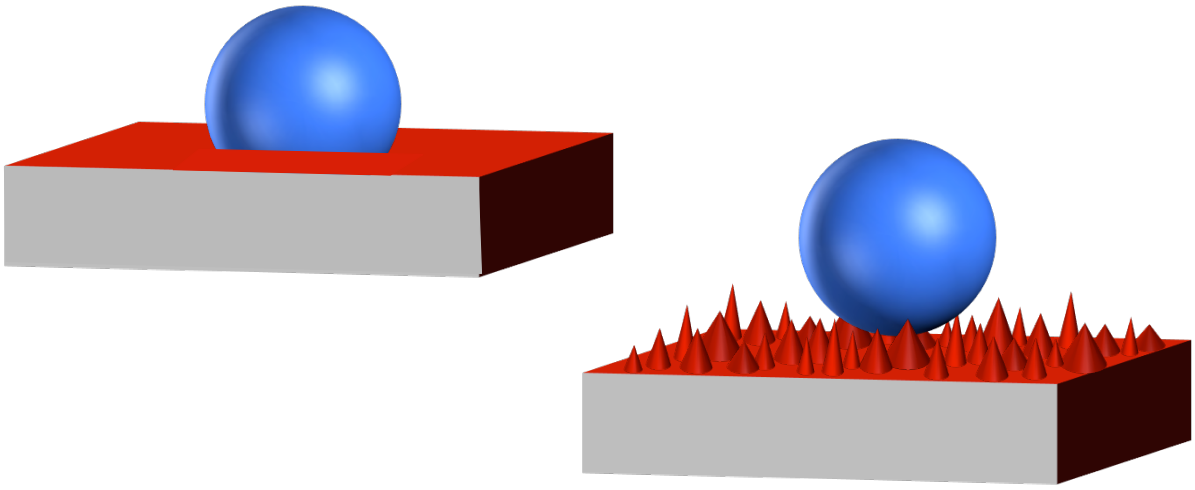
Silicones

Long perfluoroalkyl chains

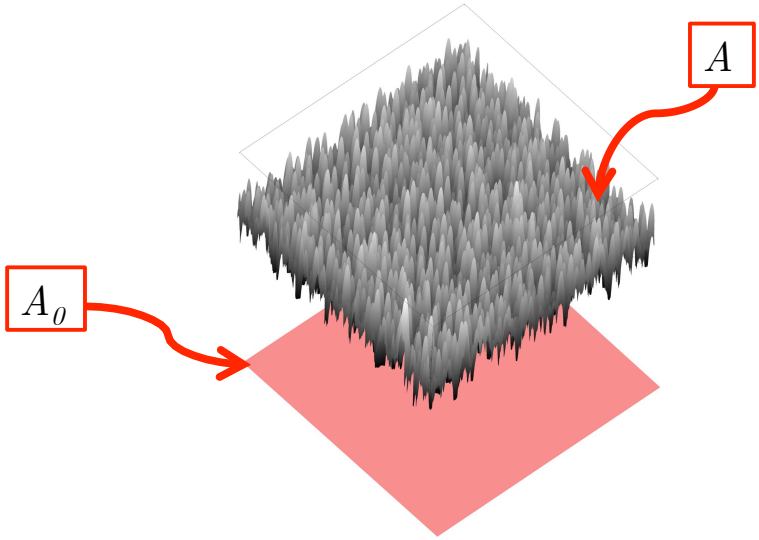



Chemistry is not the only parameter one can play with

## Surface roughness is another parameter controlling the contact angle

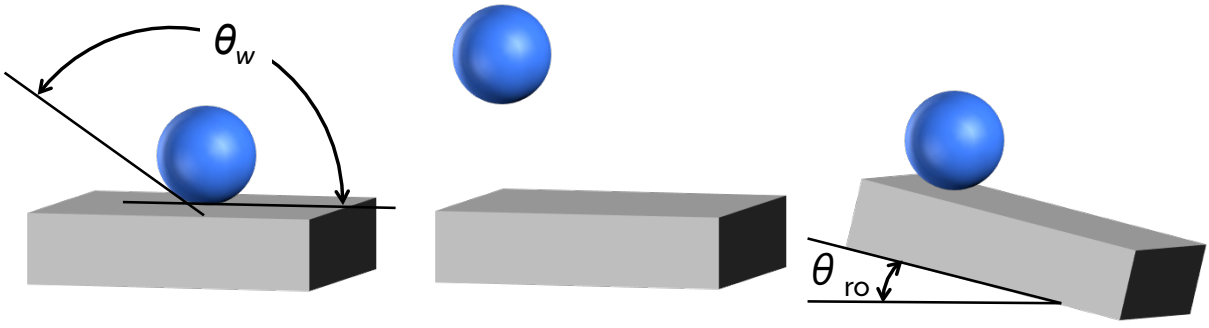


## The roughness is defined as the increase of surface area




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

## Surfaces of sufficiently high roughness may become superhydrophobic

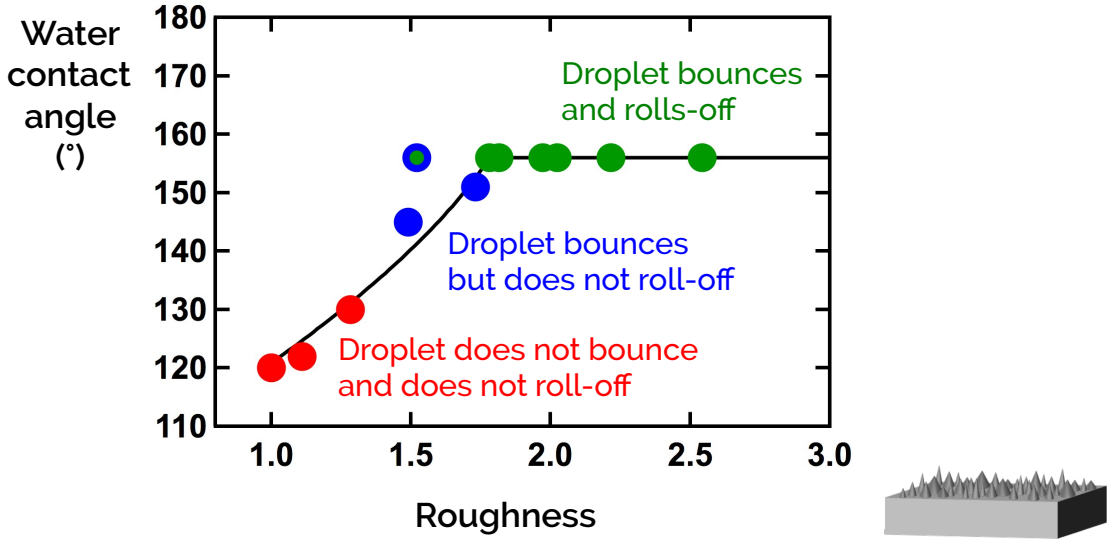



Water contact angle
$\theta_w > 150^\circ$

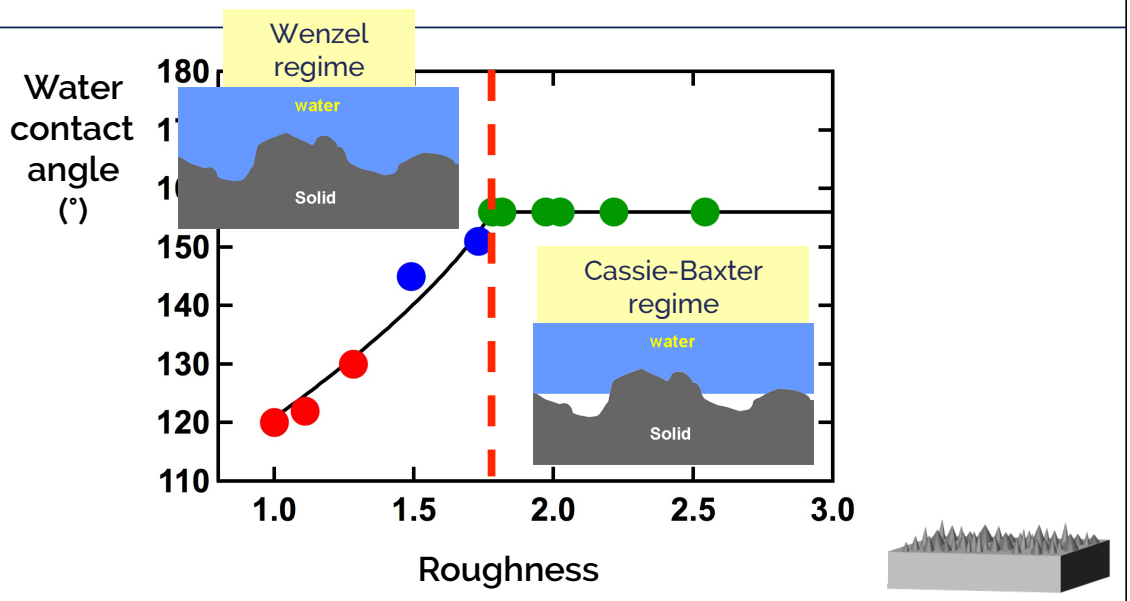
Droplet bouncing

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

## The contact angle increases with roughness

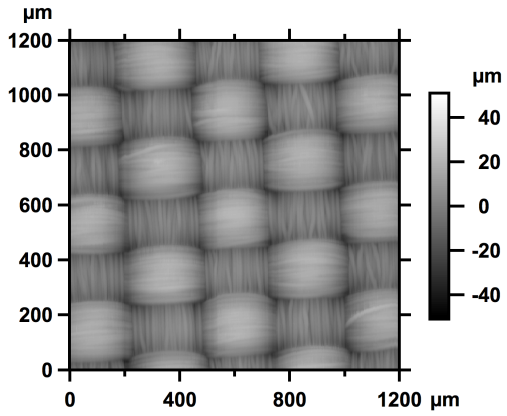


## There exists a critical roughness for superhydrophobicity

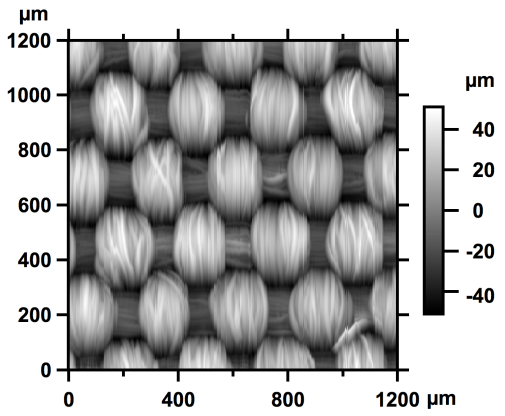



What is the role of fabric roughness in water repellence?

## Woven fabrics have an intrinsic roughness which can be measured by profilometry

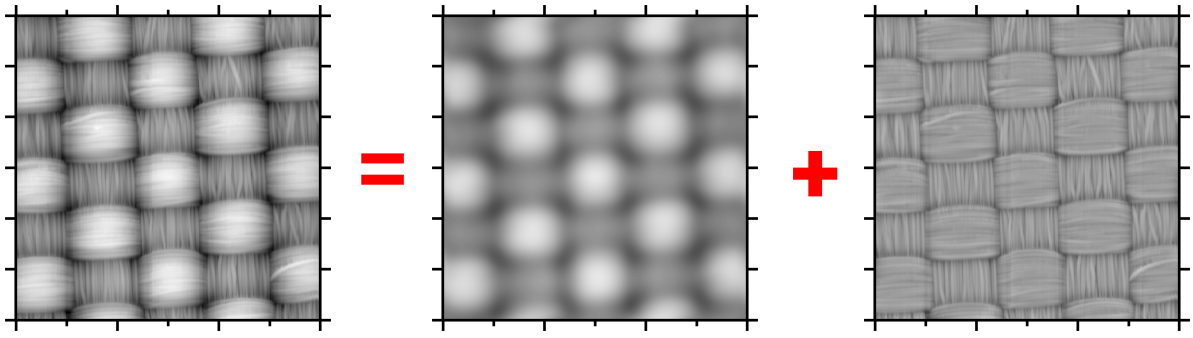



$\mathcal{R} = 1.15$




$\mathcal{R} = 1.57$

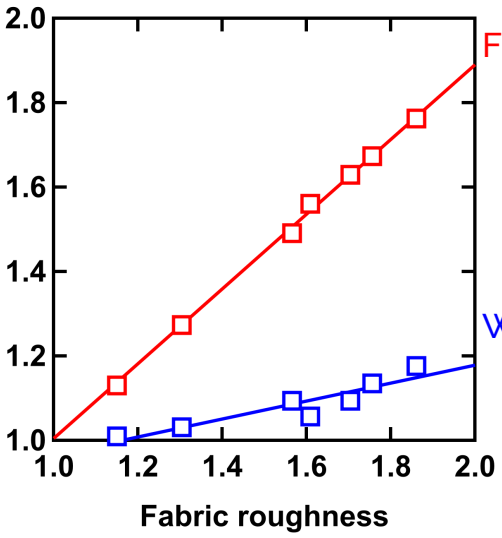
## A fabric roughness arises from the weave pattern and the fiber packing in the yarns



Fabric pattern $\mathcal{R}$ = Weave pattern $\mathcal{R}_W$ + Fiber packing in yarns $\mathcal{R}_Y$

$$\mathcal{R} = \mathcal{R}_W + \mathcal{R}_Y - 1$$

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




Fiber packing in yarns

$\mathcal{R}_Y$

Weave pattern

$\mathcal{R}_W$

## Is the intrinsic fabric roughness high enough to provide superhydrophobicity?

10 fabrics selected

roughness

1.85

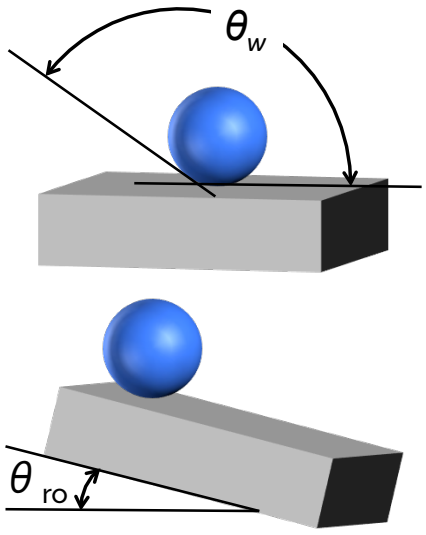
1.15

Dip-coated by 5 aqueous formulations

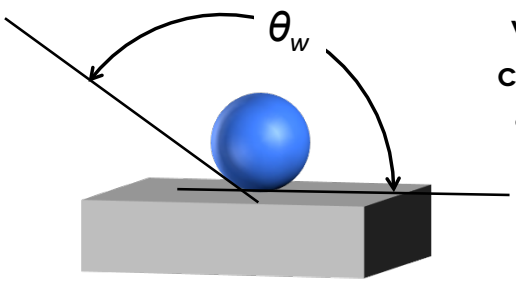
Short perfluoroalkyl chains (C4)

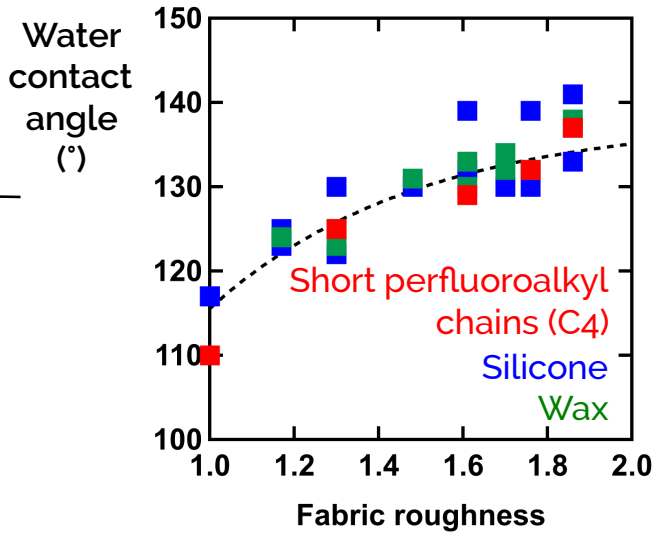
Silicone

Wax

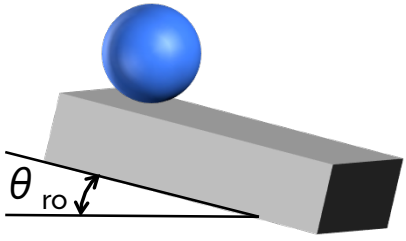


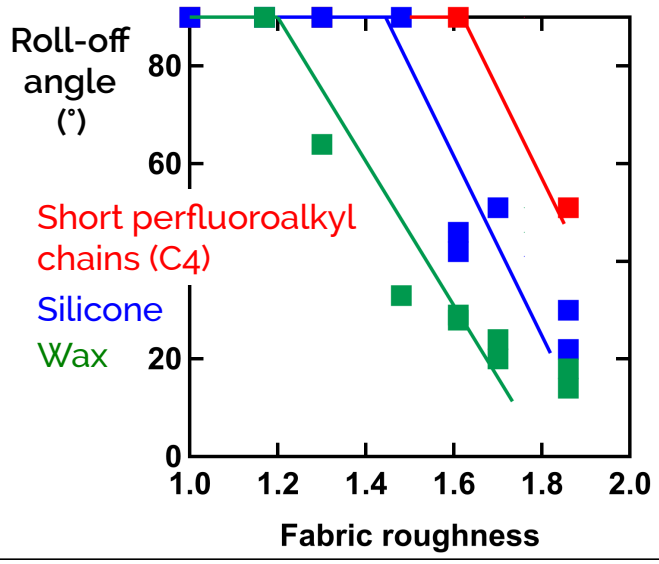
## The contact angle increases with fabric roughness but does not discriminate between different coatings



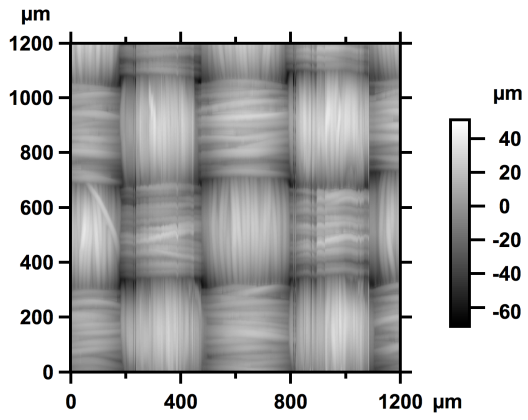

## The roll-off angle decreases with fabric roughness and discriminates between different coatings

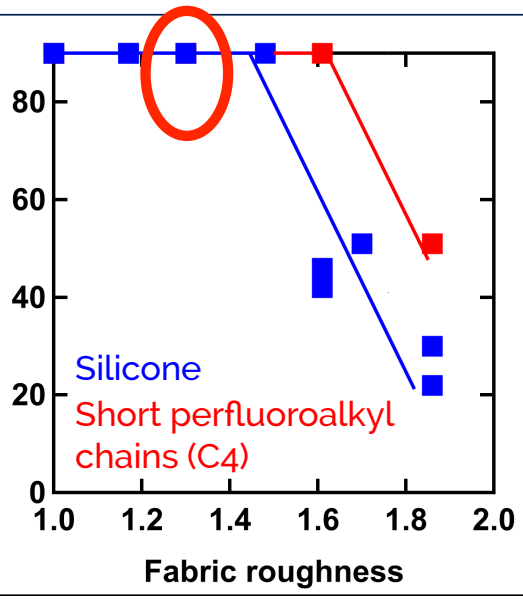


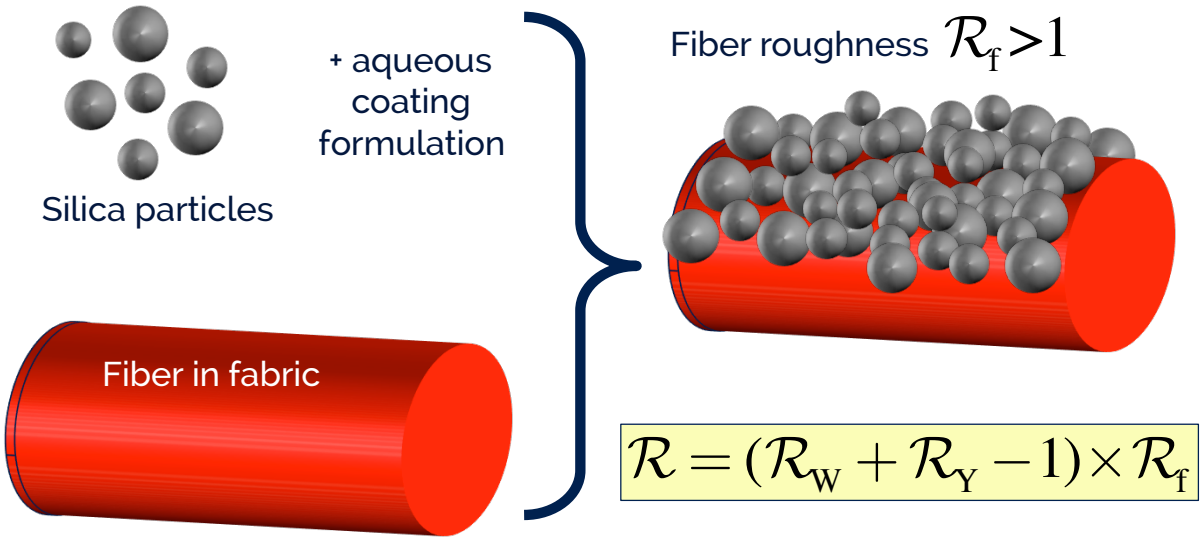
Can we improve the hydrophobicity of a fabric of low roughness?

## We selected a fabric of low roughness (1.3)



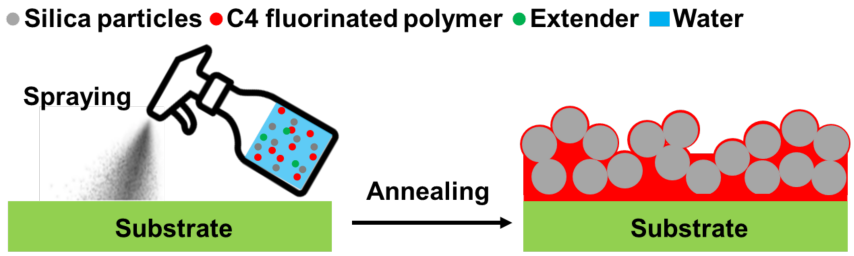
## Boosting fiber roughness with silica particles

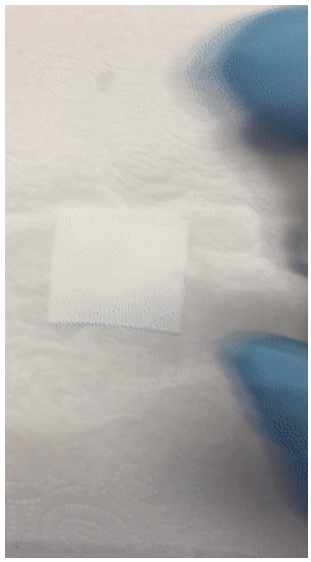



Results with a polyurethane having short perfluoroalkyl chains

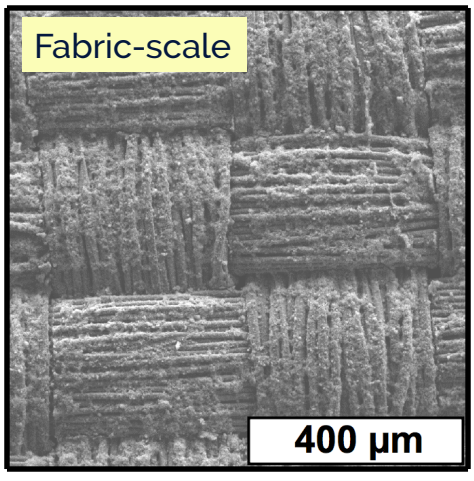
*(aqueous emulsion, PM900, 3M)*

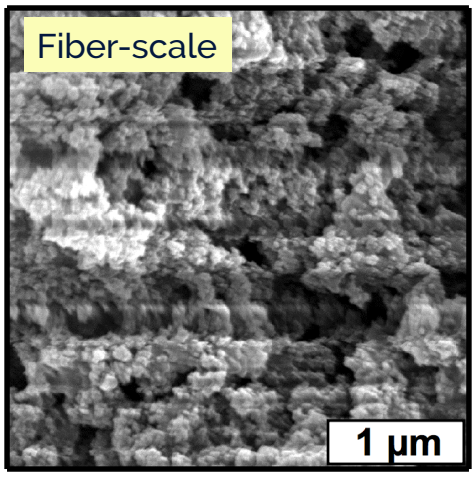
## Spraying the one-pot aqueous formulation



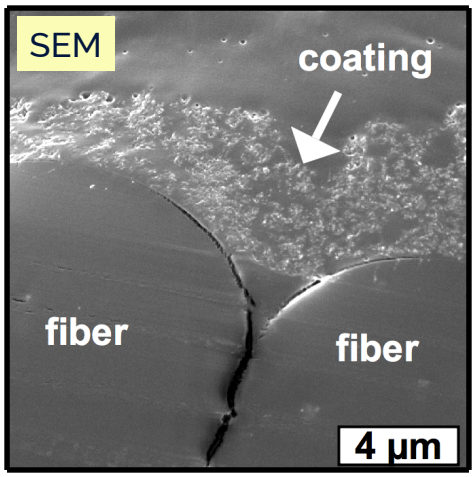



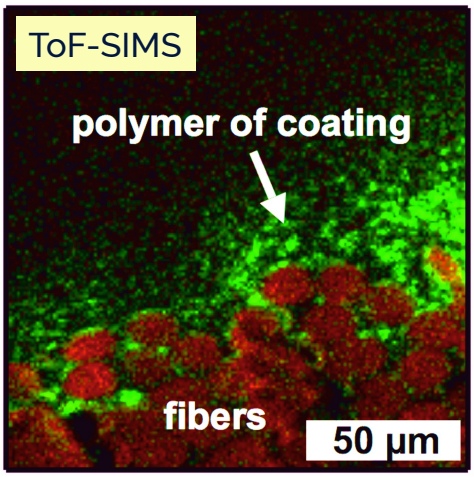
## A typical resulting microstructure seen by SEM



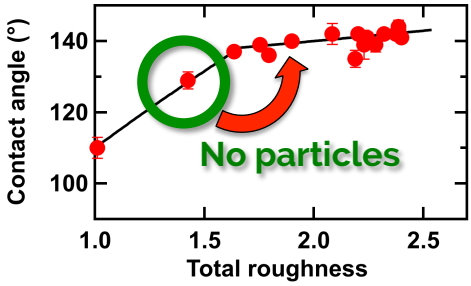



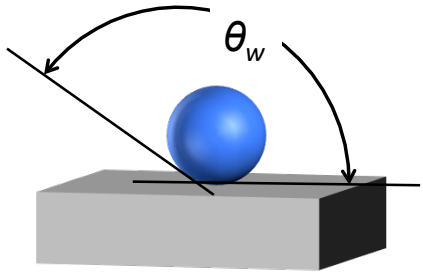
## A typical transverse cut




## Increasing the roughness of the fibers results in increased water repellence



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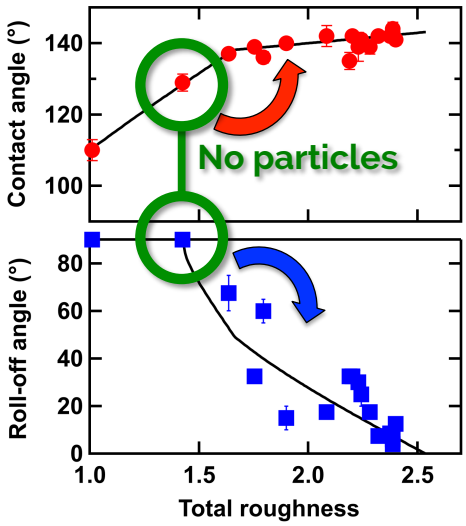
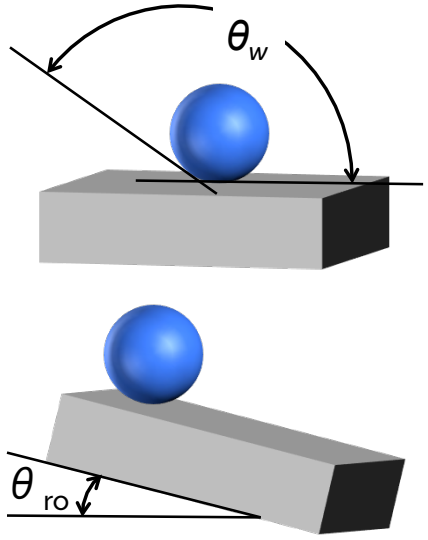
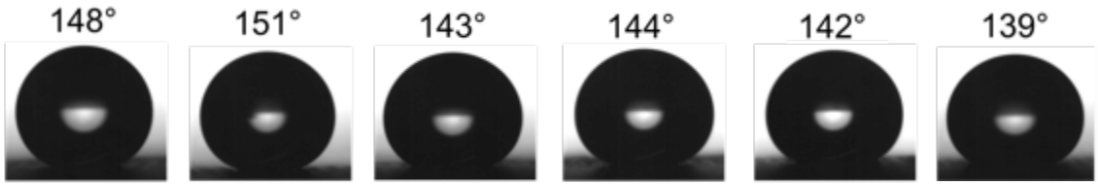


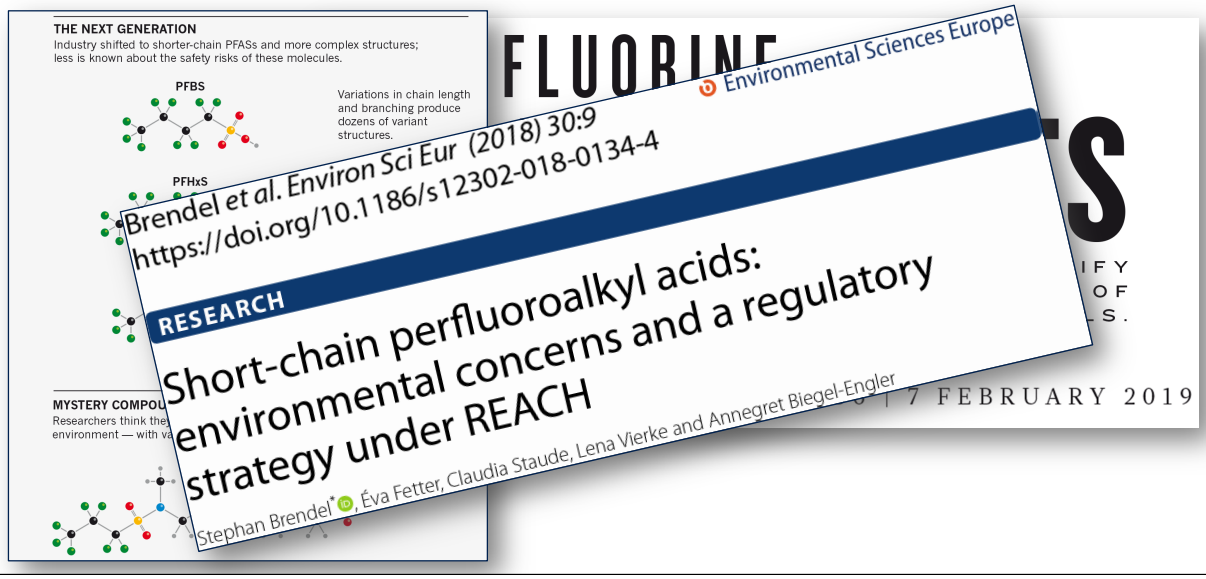

## A superhydrophobic C4-based sample in action

## The short C4 perfluoroalkyl chains also lead to superoleophobicity

## The short C4 perfluoroalkyl chains also provide resistance to some organic solvents



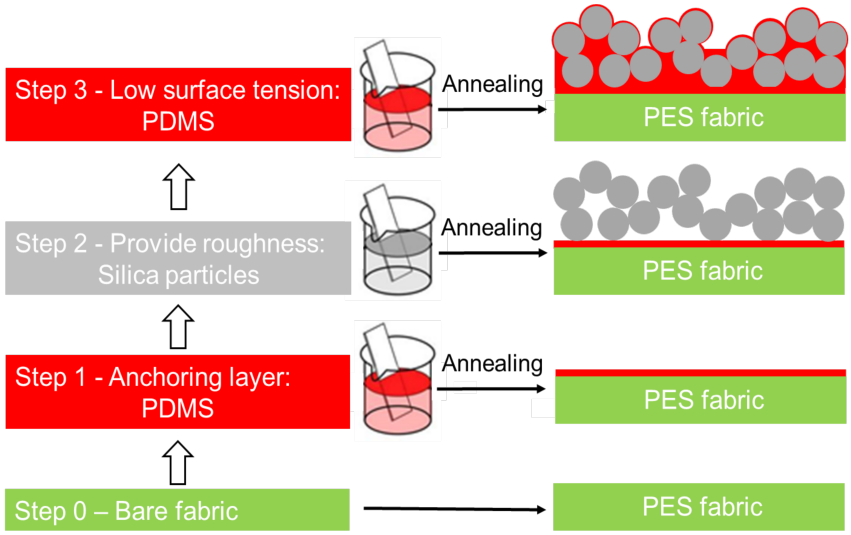
## However, shorter perfluoroalkyls also raise concerns




Results obtained with
a crosslinked silicone rubber

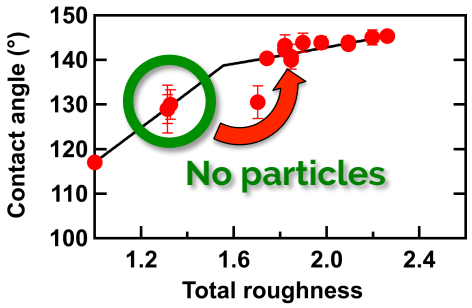
(*aqueous emulsion, HC303, Wacker*)

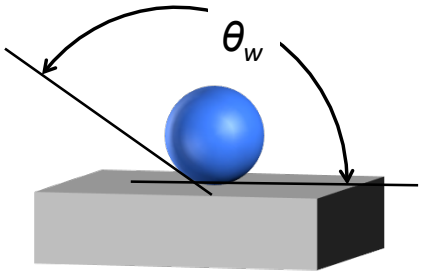
## Silicone-based superhydrophobic coatings (dip-coating from aqueous suspensions)



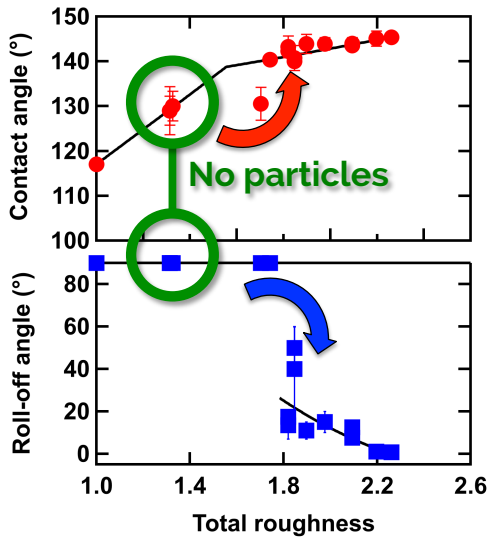

ACS Applied Materials & Interfaces (2018, 10, 15346−15351)

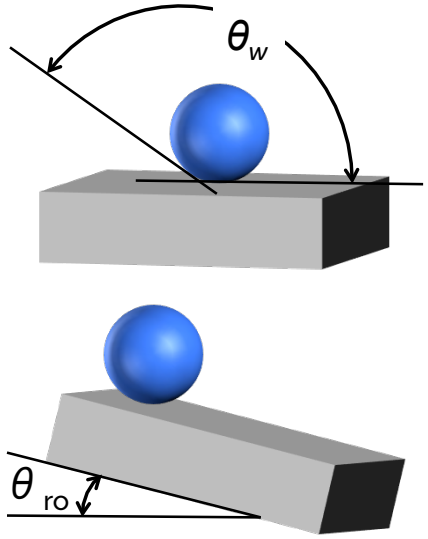
## Again, increasing the roughness of the fibers results in increased water repellence



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




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

# 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)**

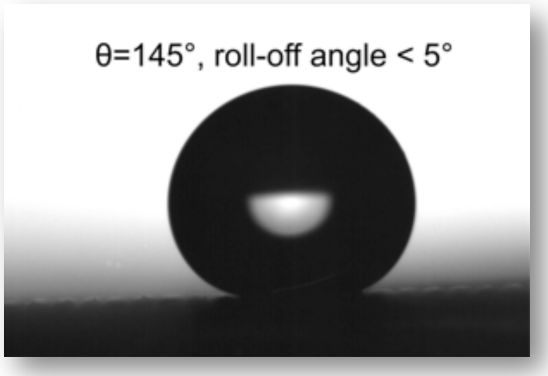
**Adopted on 13 June 2018**

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

# Wax-based coatings are used in nature

## Preliminary studies indicate wax-based alternatives to be promising

Silicone replaced by water-based paraffin wax (Contraqua WE)
(total roughness: 1.3 x 1.72 = 2.23)




## Main conclusions

1. Total roughness is a predictor 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

# Acknowledgments

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Special thanks to:

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Certech: Nicolas Mannu & Benoît Kartheuser

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