Fluor-free superhydrophobic and ecofriendly superomniphobic coatings

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CENTEXBEL

In collaboration with

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How to prevent rain from soaking us?

Perfluororoalkyl derivatives have been extensively used for several decades

Textile protection

Fire-fighting foams

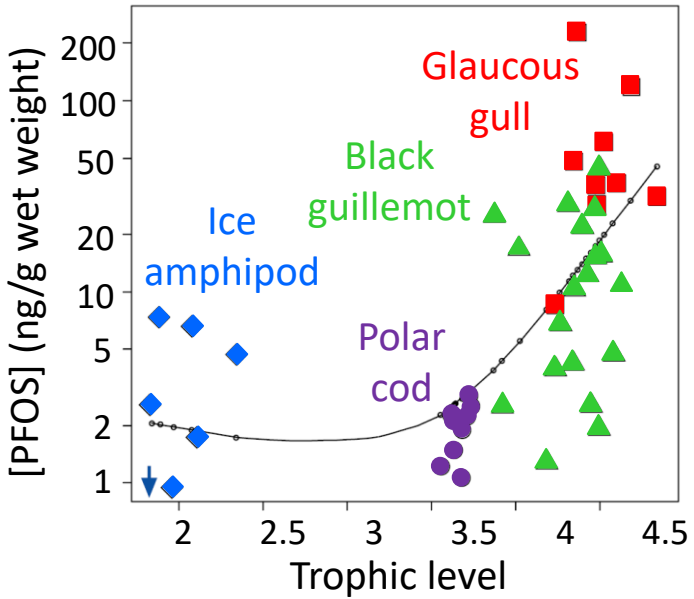
Environmental concerns related to perfluororoalkyl derivatives

Environmental concerns related to perfluororoalkyl derivatives

- ✓ High thermal, chemical and biological inertness
- ✓ Strong diffusion capacity
- ✓ Very poorly metabolized by living organisms

Extremely persistent
in the environment!

Bioaccumulation
of perfluorooctane sulfonate (PFOS)
in selected species
from the Barents Sea food web



Adapted from M. Haukås et al. Environ. Pollut. 148 (2007) 360e371

‘Long’ (C8) perfluoroalkyl chains are being banned

COMMISSION REGULATION (EU) 2017/1000

of 13 June 2017

amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards perfluorooctanoic acid (PFOA), its salts and PFOA-related substances

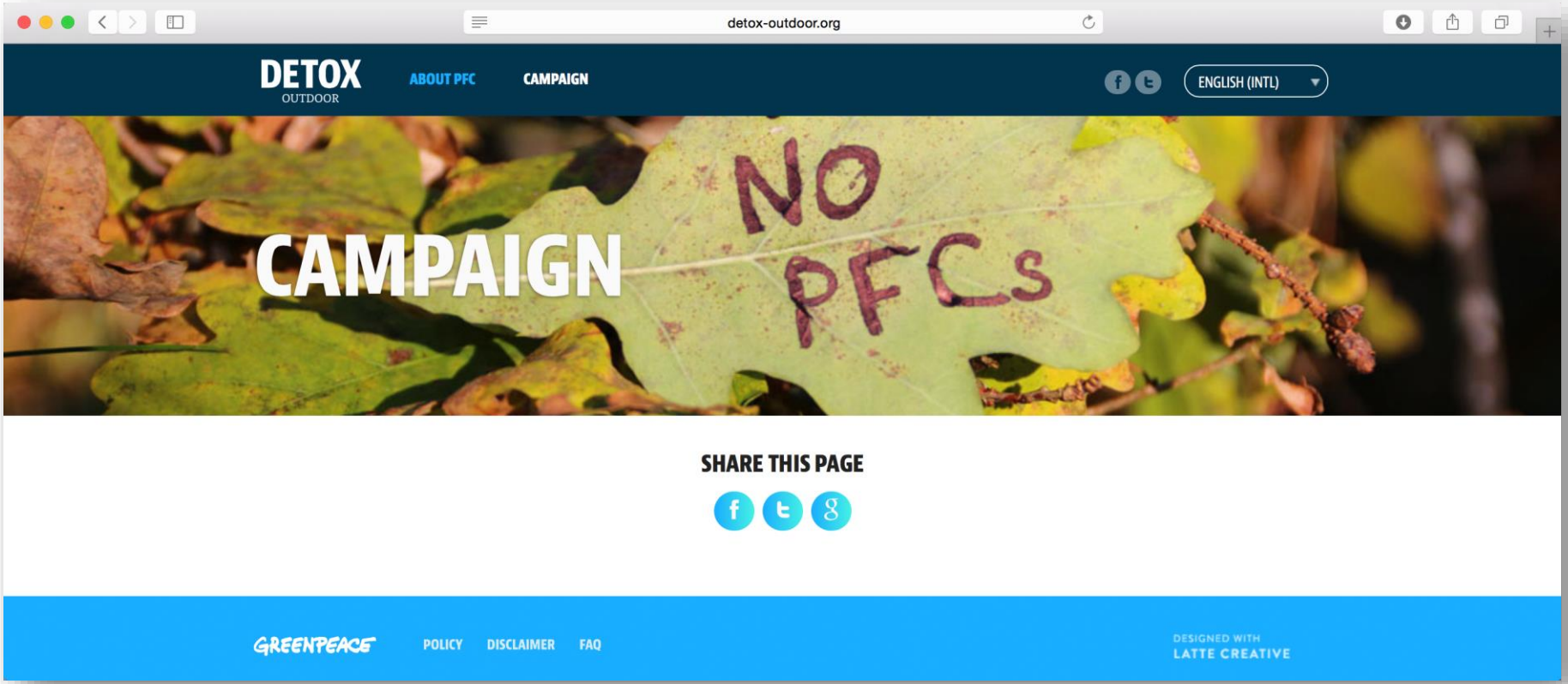
(Text with EEA relevance)

THE EUROPEAN COMMISSION,

Having regard to the Treaty on the Functioning of the European Union,

Having regard to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC ([1]), and in particular Article 68(1) thereof,

The general public is concerned



Lawsuits emerge against C8 perfluoroalkyl chains

Chemistry news from the week

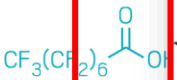
Chemical & Engineering News, Feb. 20, 2017

POLLUTION

DuPont, Chemours settle PFOA suits

Deal will provide $670 million
they were sickened by exposur

DuPont and Chemours have agreed to pay $670 million to settle 3,550 lawsuits in Ohio and West Virginia by residents who say they were sickened by drinking water contaminated by per-fluorooctanoic acid (PFOA) released from a former DuPont plant in Parkersburg, W.Va.



Perfluorooctanoic a

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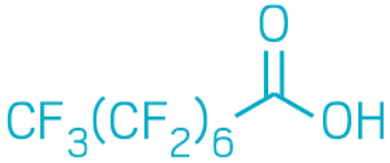


Perfluorooctanoic acid

Scientists are concerned

FLUORINATED FAMILY

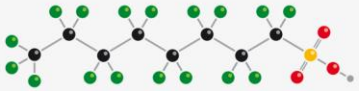
Chemicals with fluorinated carbon chains (PFASs) are found in clothes, carpets, foams and other products. They don't degrade in the environment; researchers have listed more than 4,500 structures.

HARMFUL LEGACY

A first generation of PFASs contained chains of eight or more carbons. Some of these are being phased out because of health concerns and their persistence in the environment.

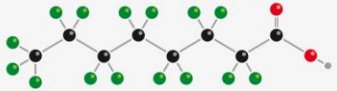
● Carbon ● Fluorine ● Sulfur ● Oxygen ● Hydrogen ● Nitrogen

PFOS (8-carbon chain)



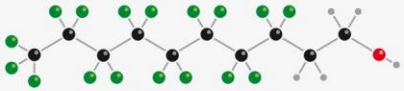
Production now heavily restricted.

PFOA (8-carbon chain)



Expected to be similarly restricted this year.

8:2 FTOH (10-carbon chain)



Hundreds of precursor compounds can degrade into PFOS or PFOA in the environment.

FLUORINE DETECTIVES

EARCHERS ARE BATTLING TO IDENTIFY AND ASSESS A WORRYING CLASS OF PERSISTENT CHEMICALS.

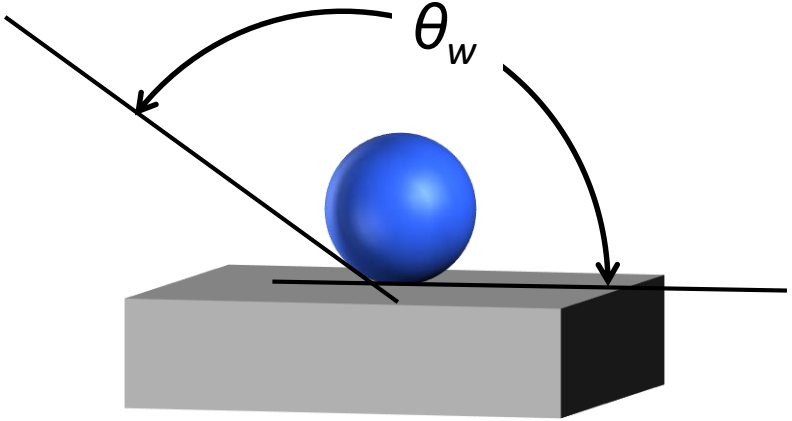
LIM | NATURE | VOL 566 | 7 FEBRUARY 2019

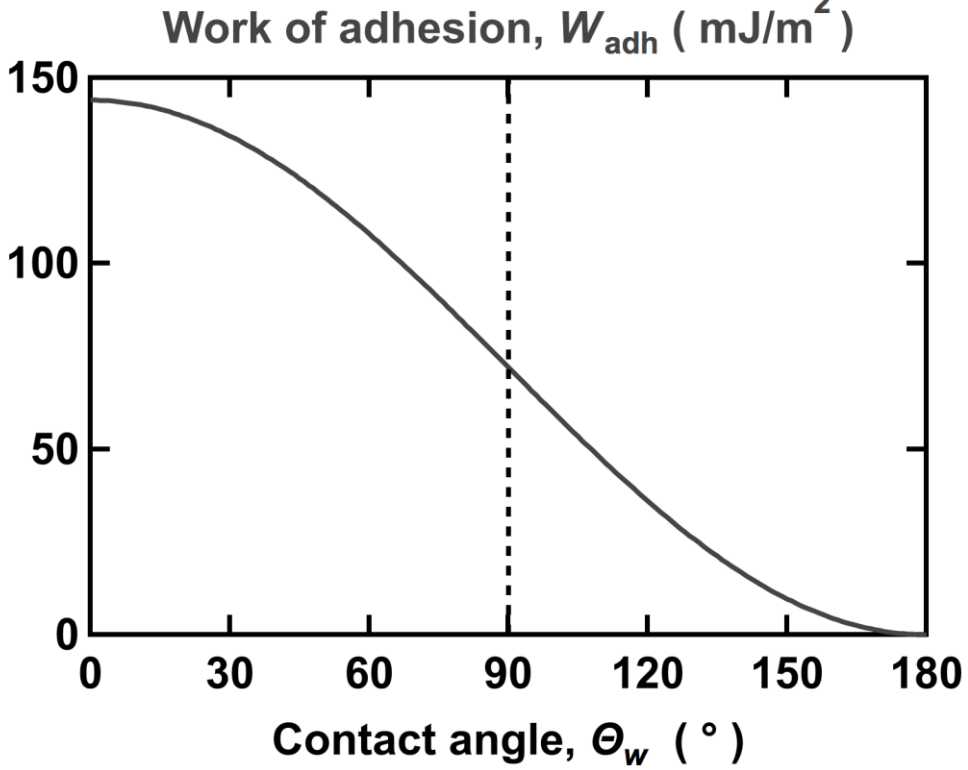
Why were long perfluoroalkyl chains used for water repellence?

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

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

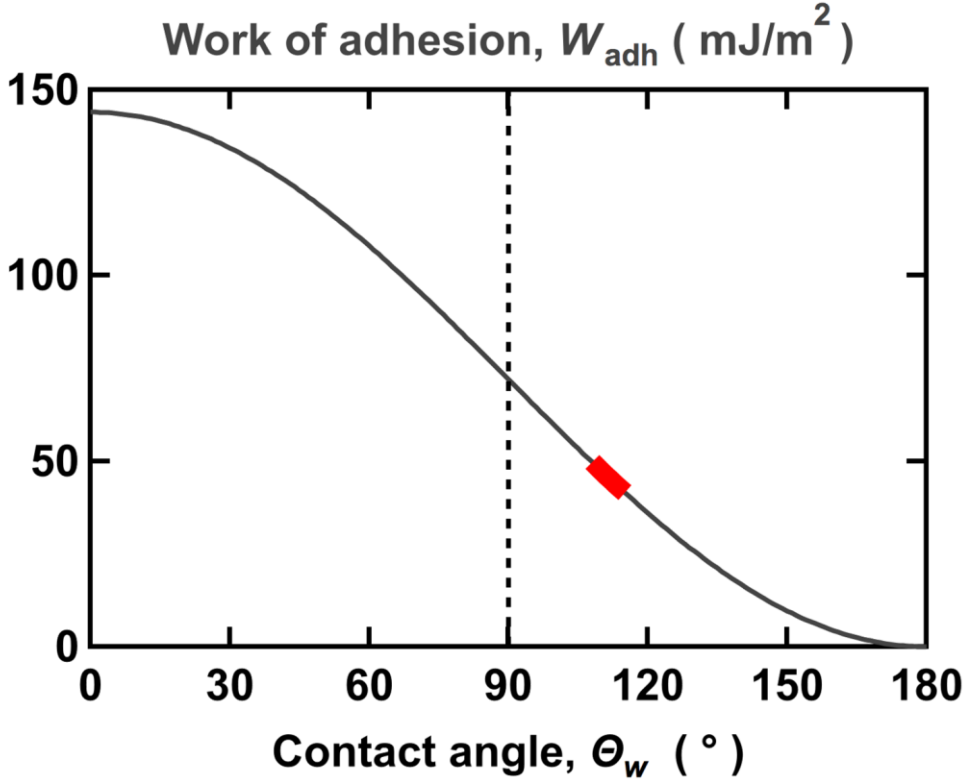
~72 mJ/m^2





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

Long perfluoroalkyl chains

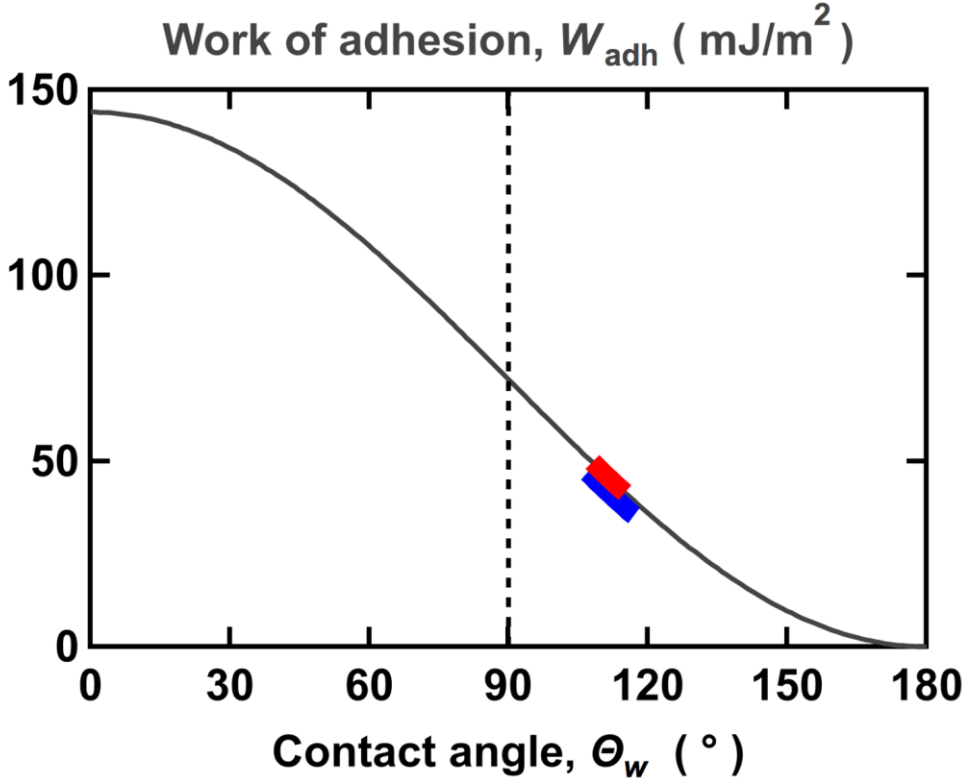


Are there possible replacements for long perfluoroalkyl chains?

Other candidates are possible

Silicones

Long perfluoroalkyl chains

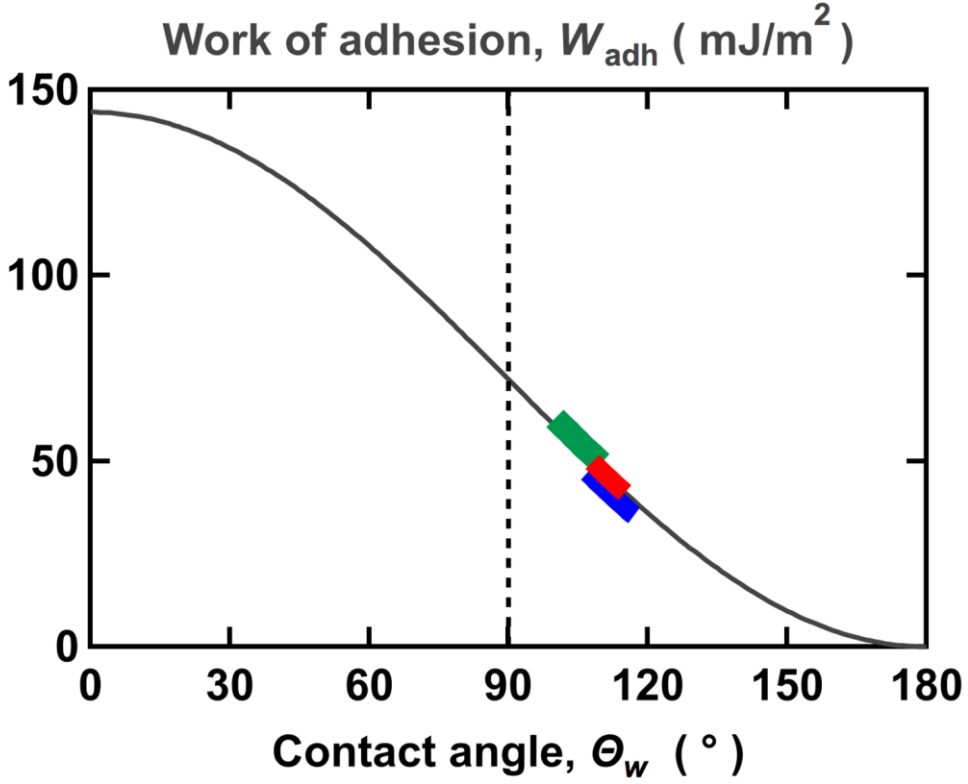


Other candidates are possible

Alkyl chains (waxes)

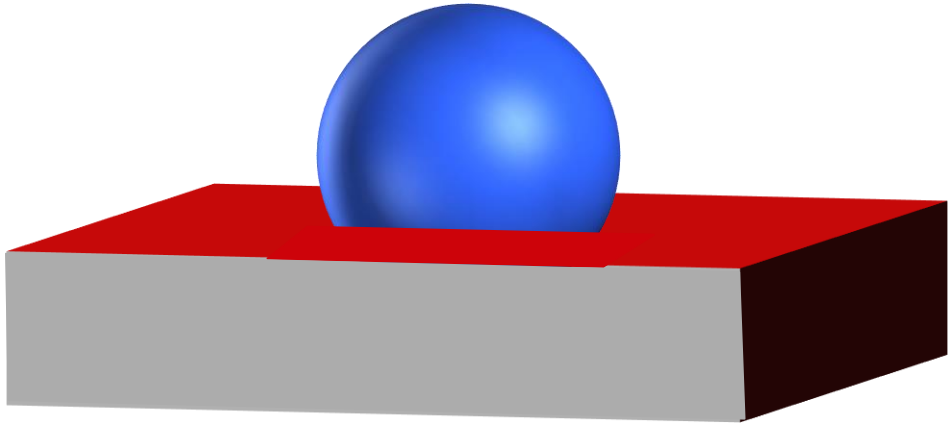
Silicones

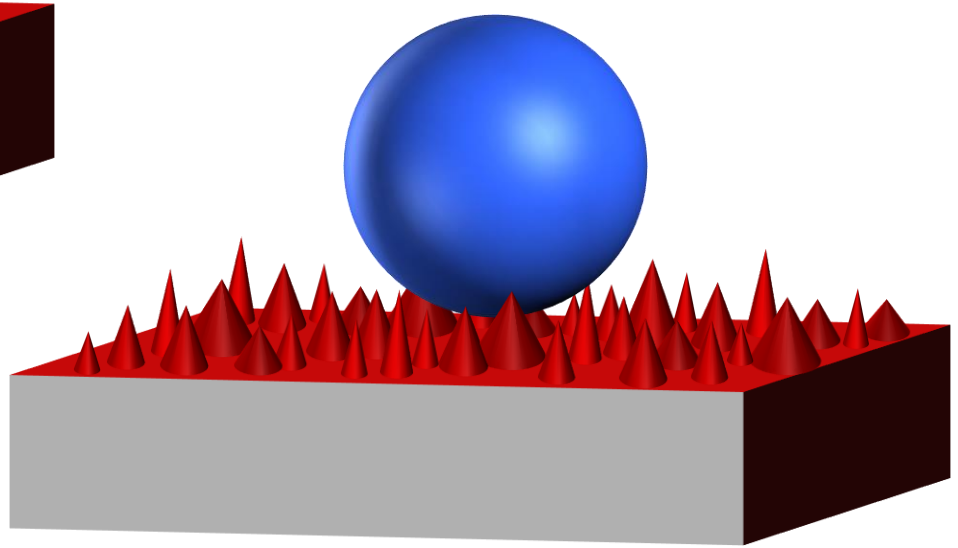
Long perfluoroalkyl chains



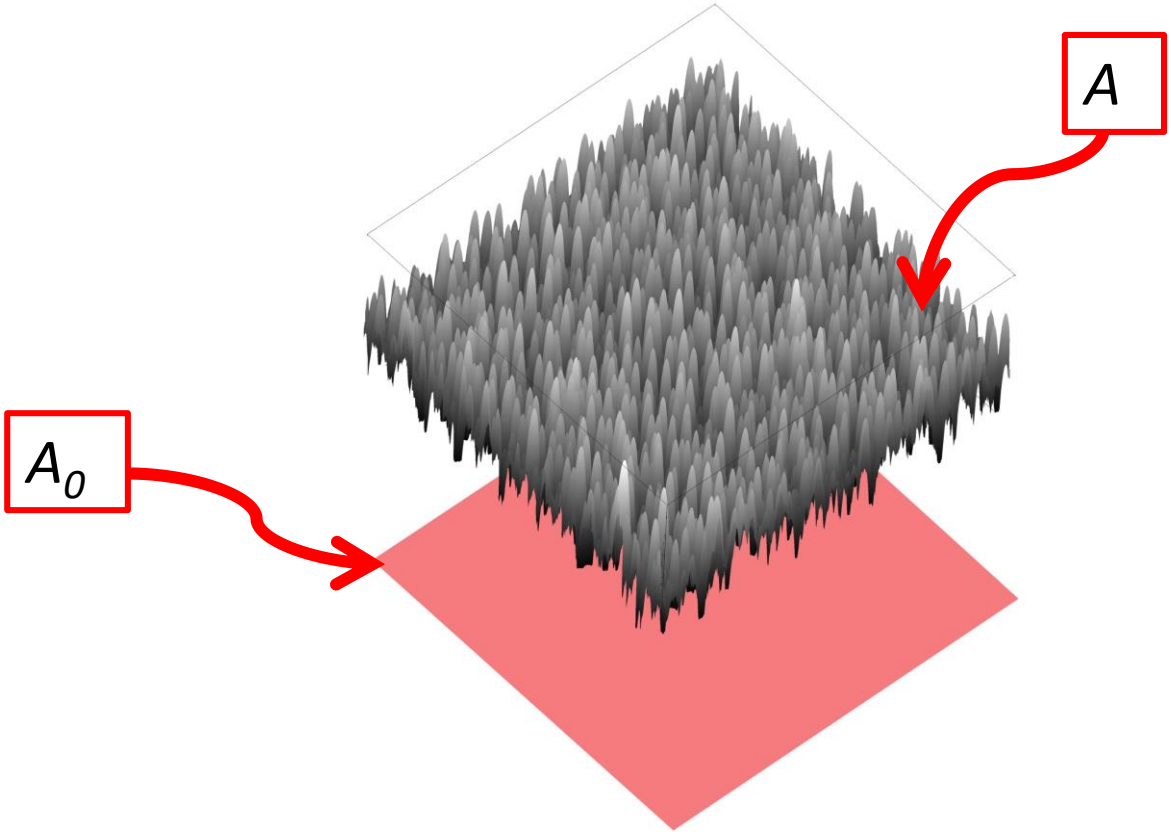
Chemistry is not the only parameter one can play with

Surface roughness is another parameter controlling the contact angle



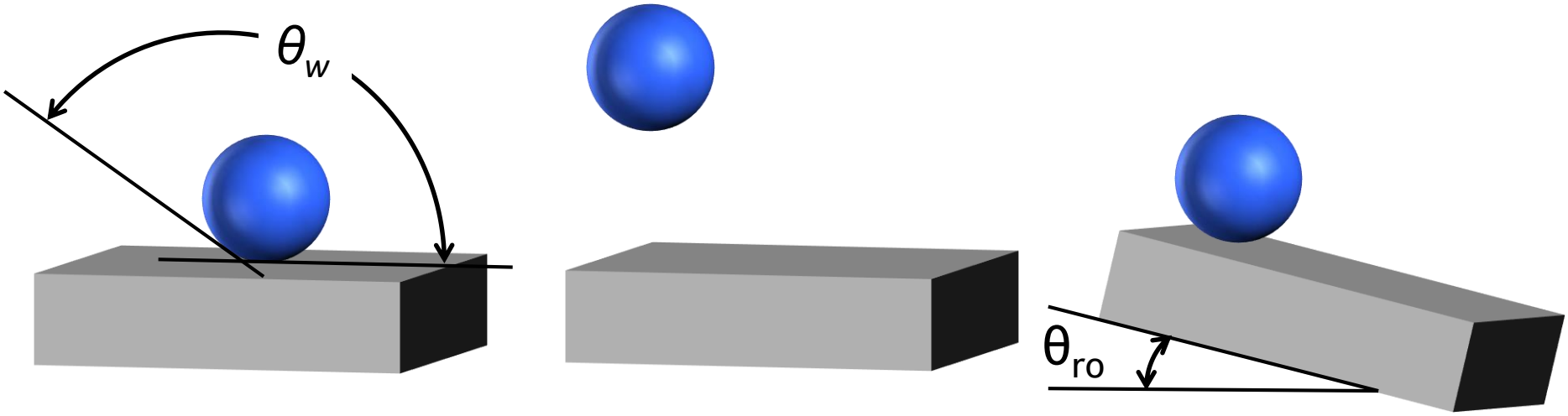


The roughness is defined as the increase of surface area



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

Surfaces of sufficiently high roughness may become superhydrophobic

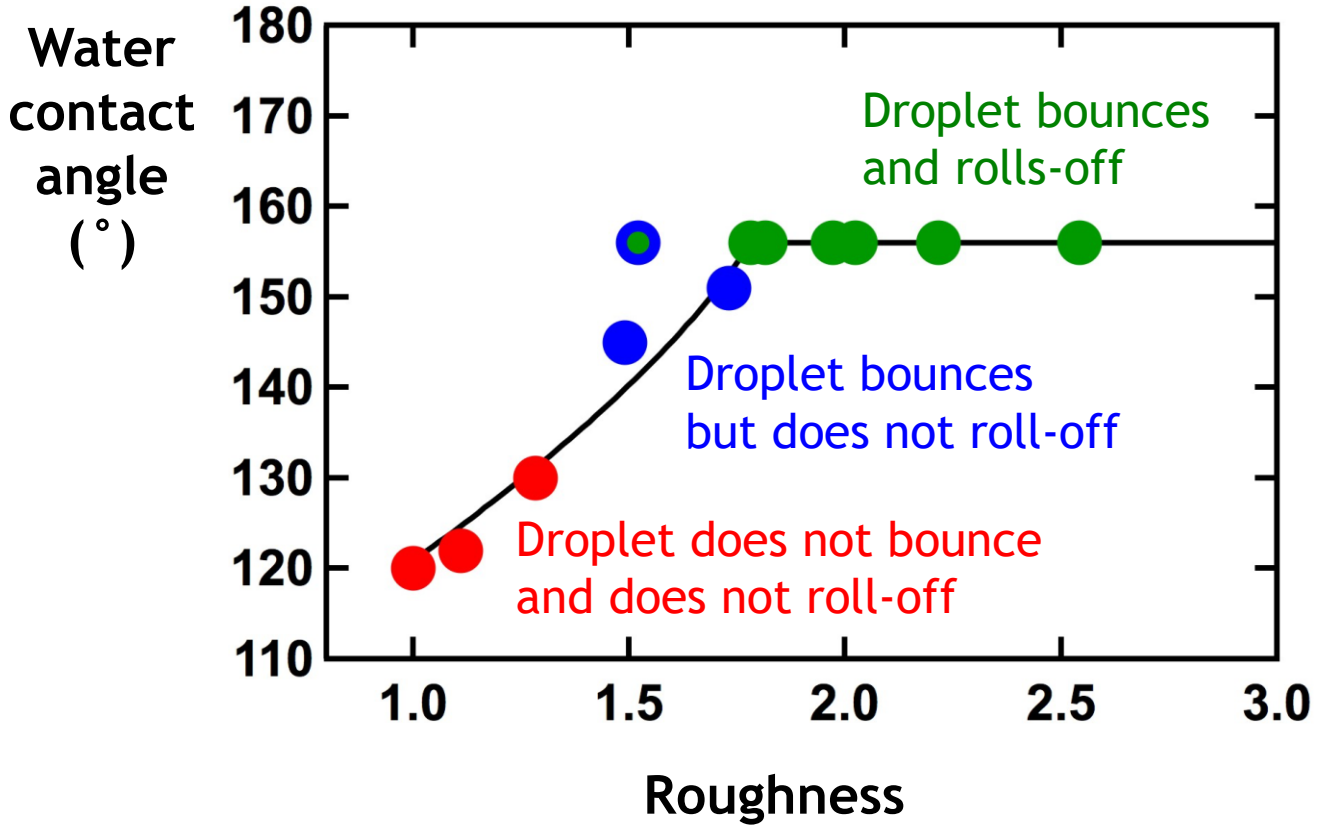


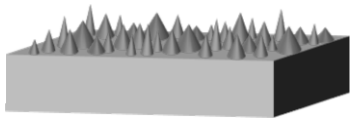
Water contact angle
$\theta_w > 150^\circ$

Droplet bouncing

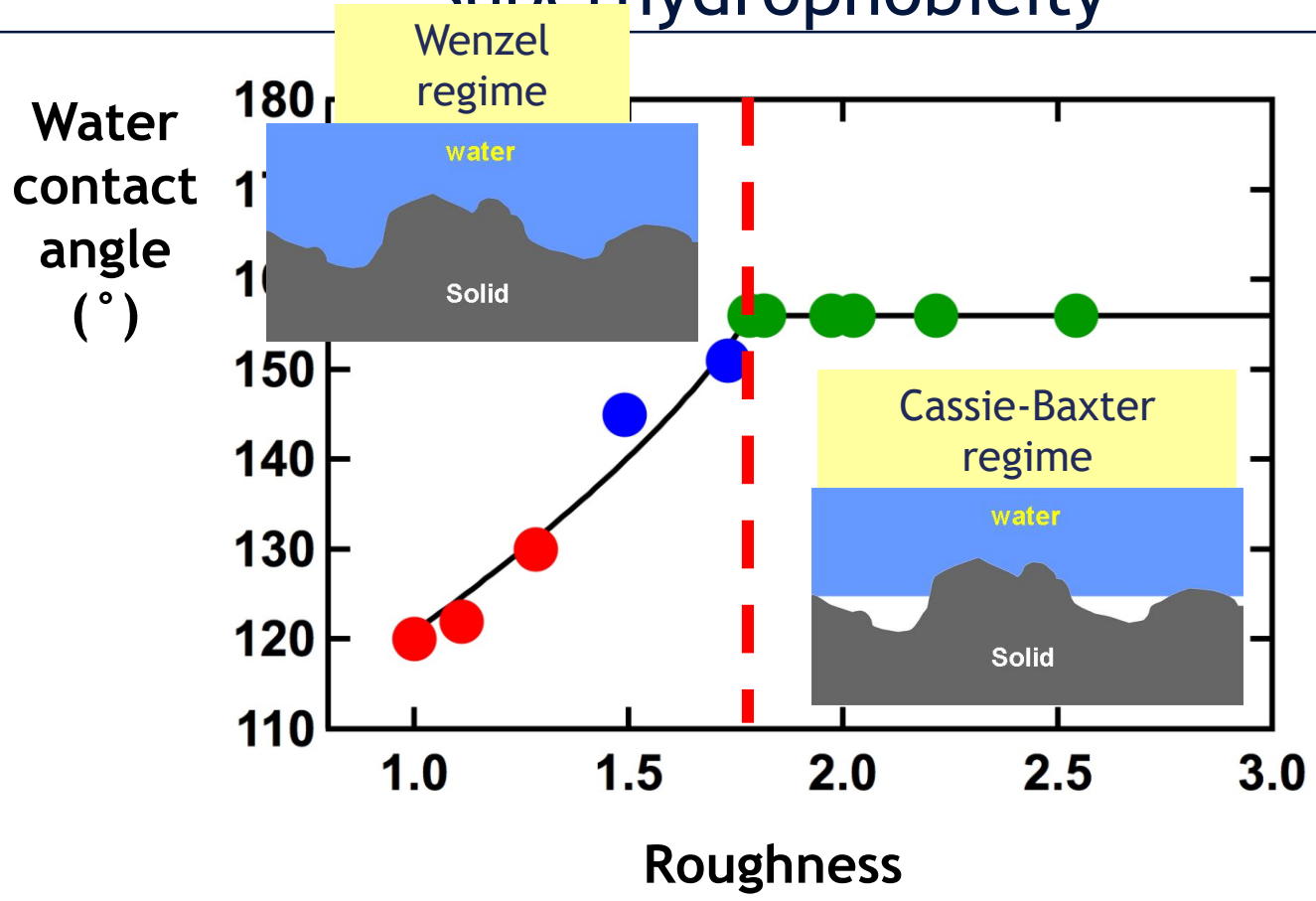
Droplet roll-off
$\theta_{ro} < \sim 5^\circ$

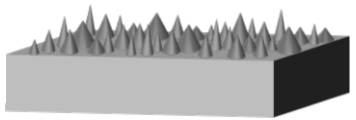
The contact angle increases with roughness





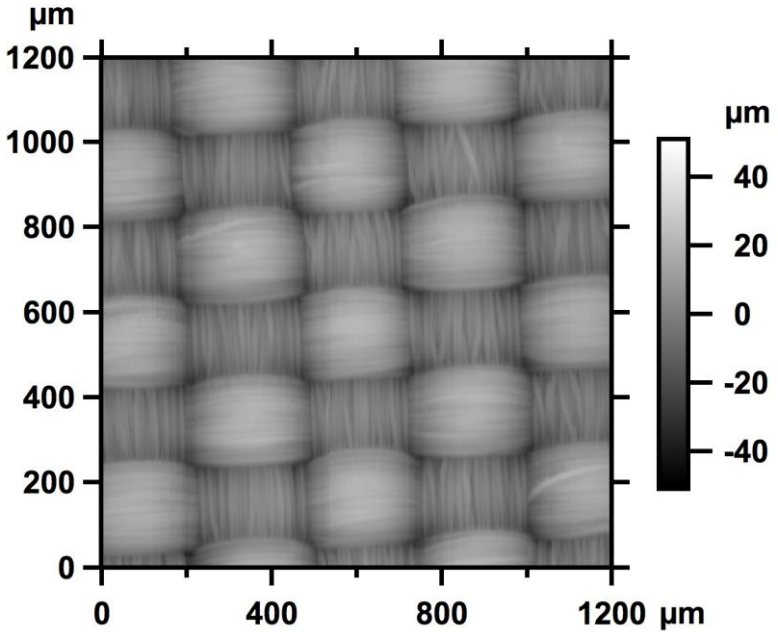
There exists a critical roughness for superhydrophobicity



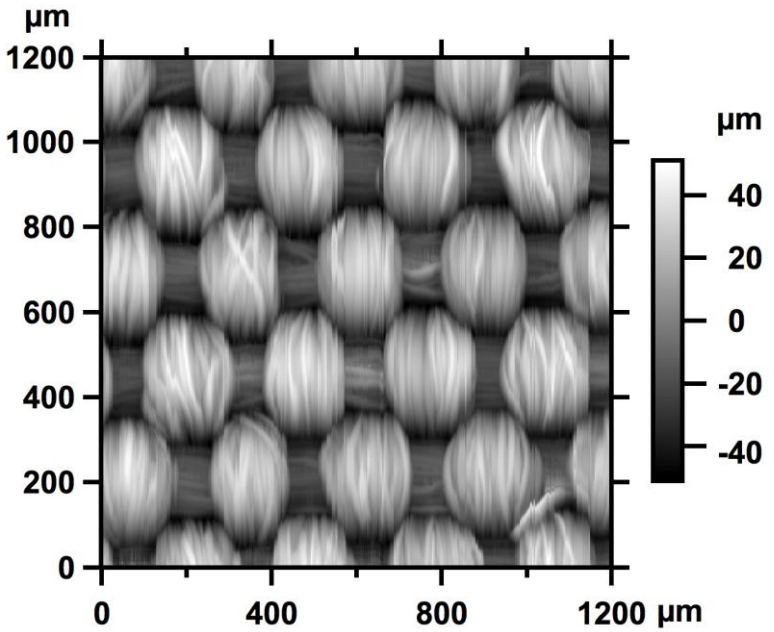


What is the role
of fabric roughness
in water repellence?

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

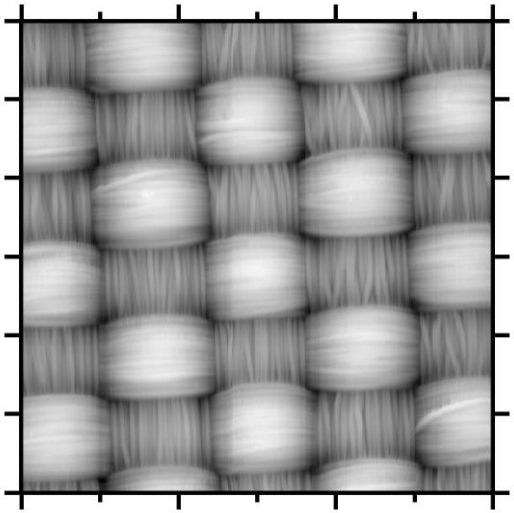


$\mathcal{R} = 1.15$



$\mathcal{R} = 1.57$

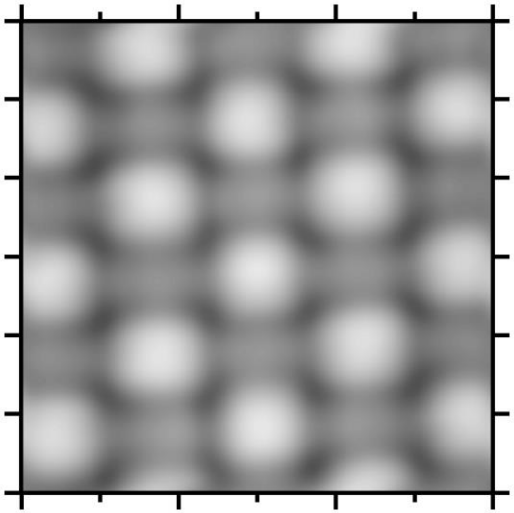
A fabric roughness arises from the weave pattern and the fiber packing in the yarns



Fabric pattern

$\mathcal{R}$

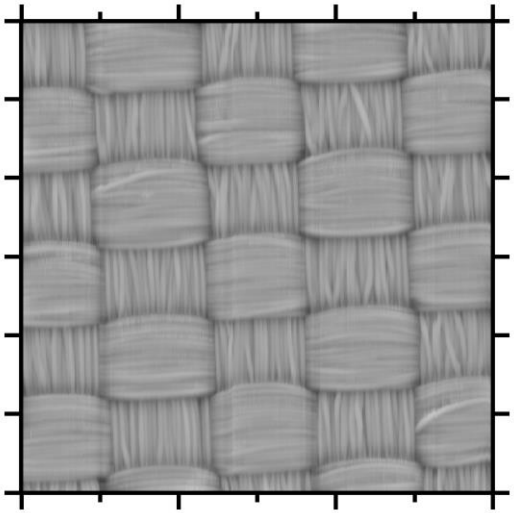
=



Weave pattern

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

+

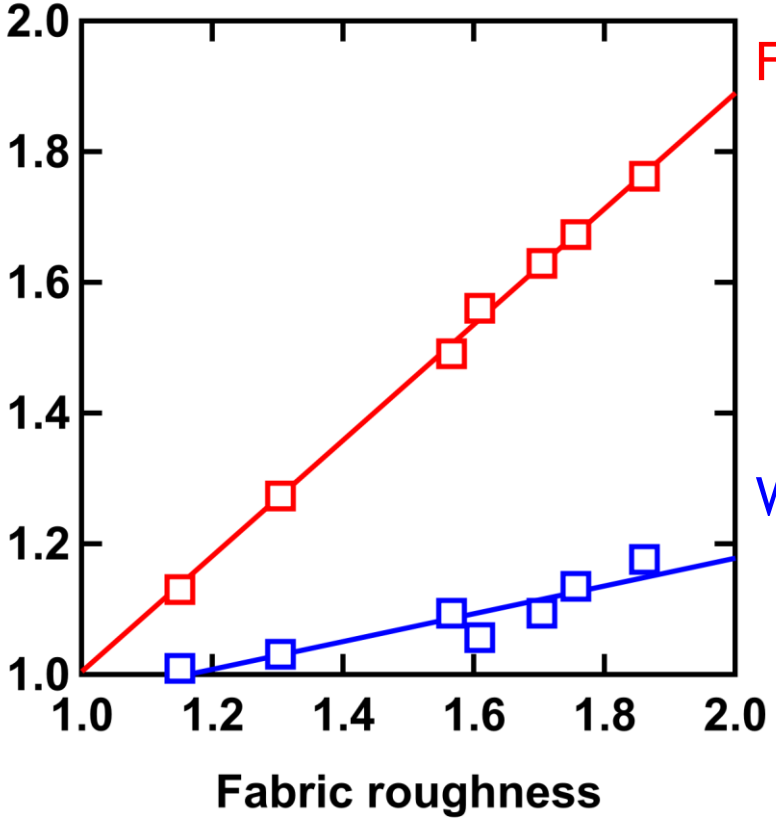


Fiber packing in yarns

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

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

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



Fiber packing in yarns

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

Weave pattern

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

Is the intrinsic fabric roughness high enough to provide superhydrophobicity?

10 fabrics selected

1.85

Roughness

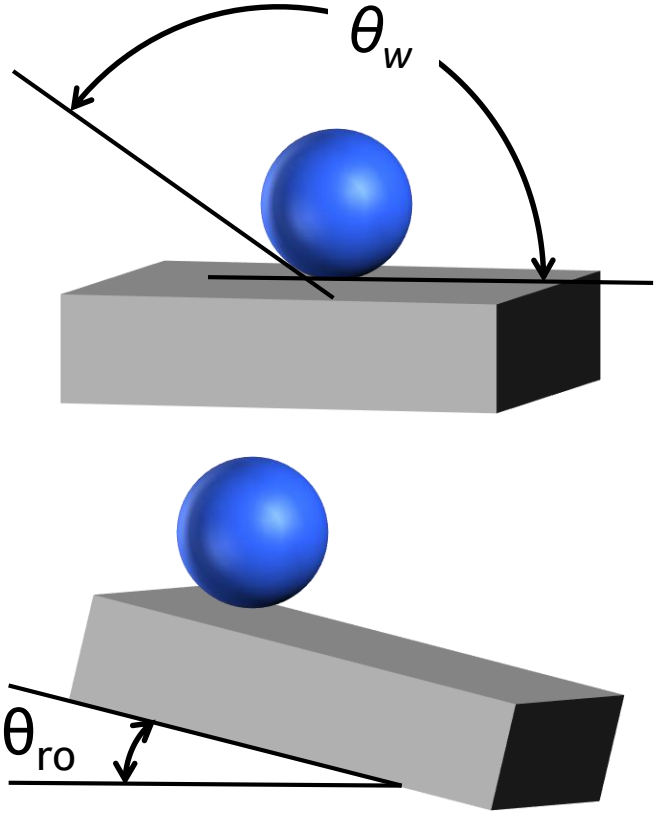
1.15

Dip-coated by 3 **aqueous formulations**

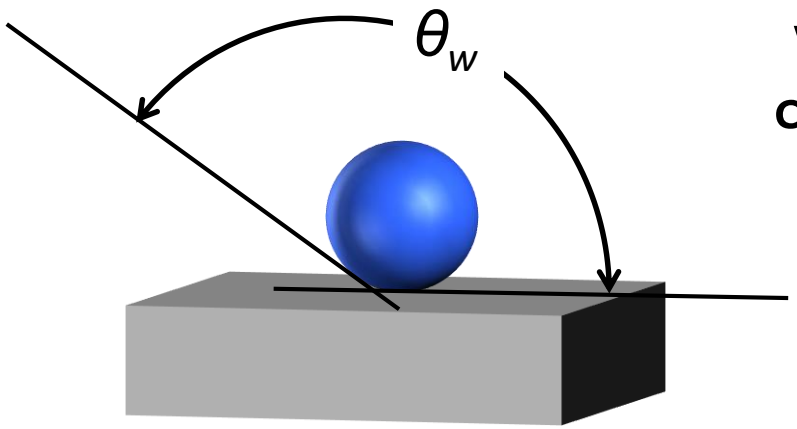
Short perfluoroalkyl chains (C4)
(3M™ PM900, 3M)

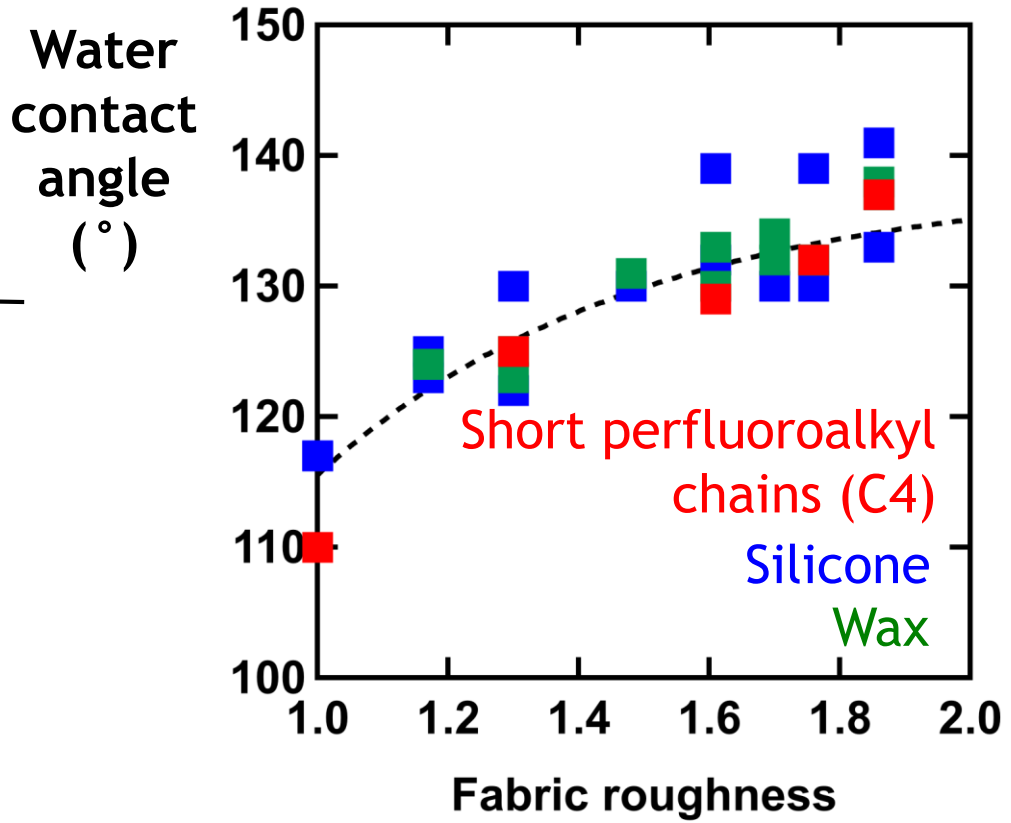
Silicone
(Wacker®HC303)

Wax
(Acti-Chem, Contraqua WE)

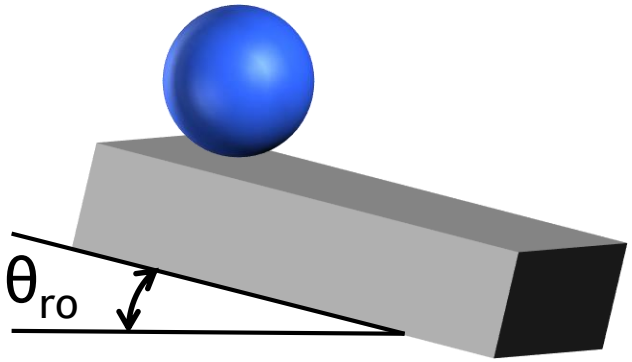


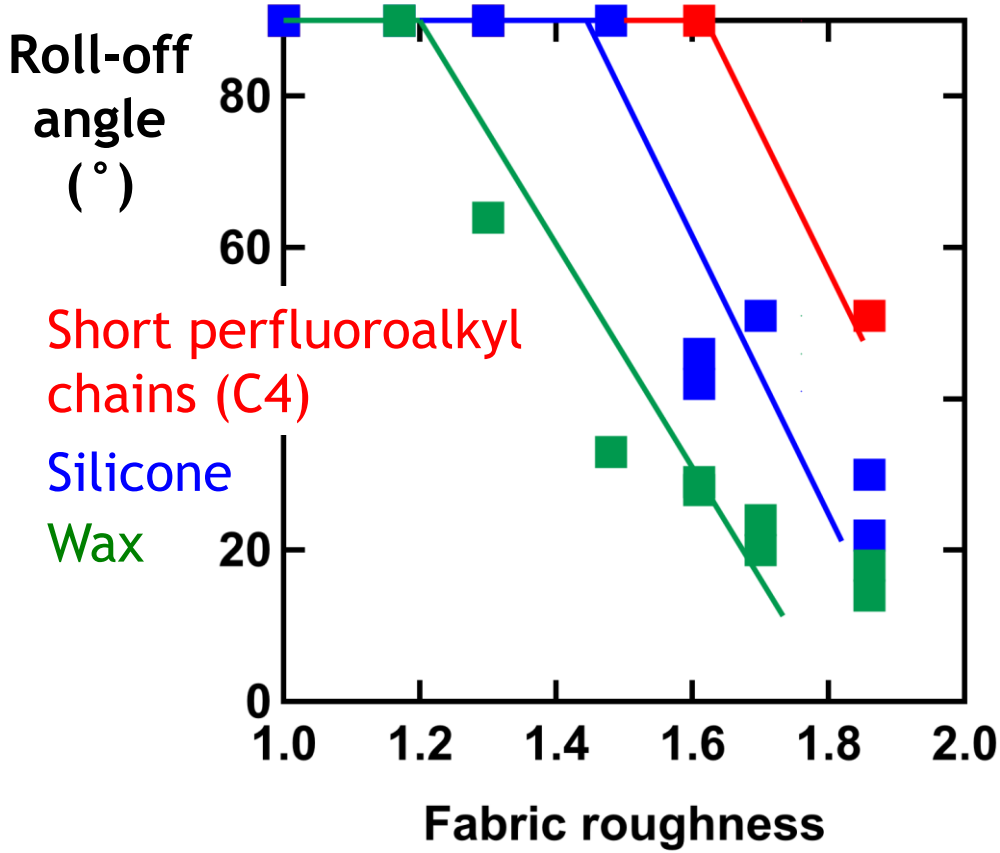
The contact angle increases with fabric roughness but does not discriminate between different coatings





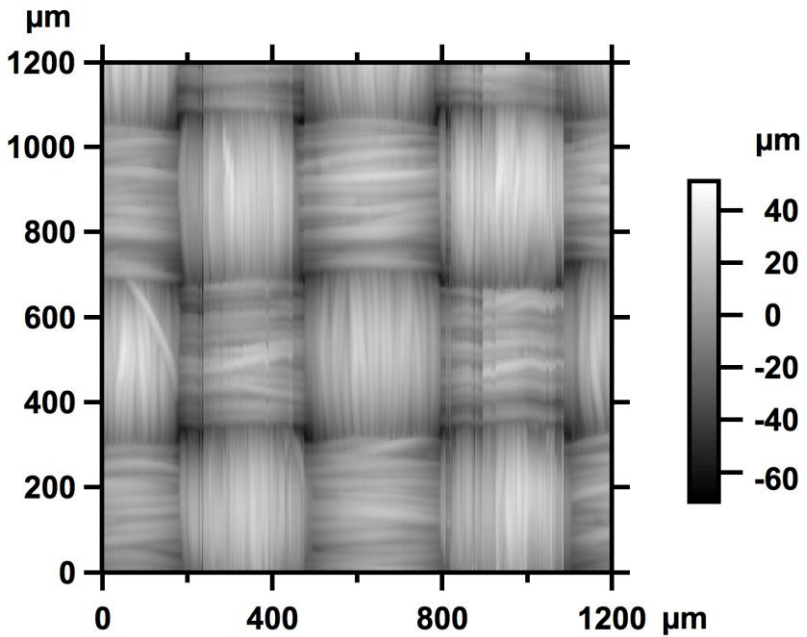
The roll-off angle decreases with fabric roughness and discriminates between different coatings

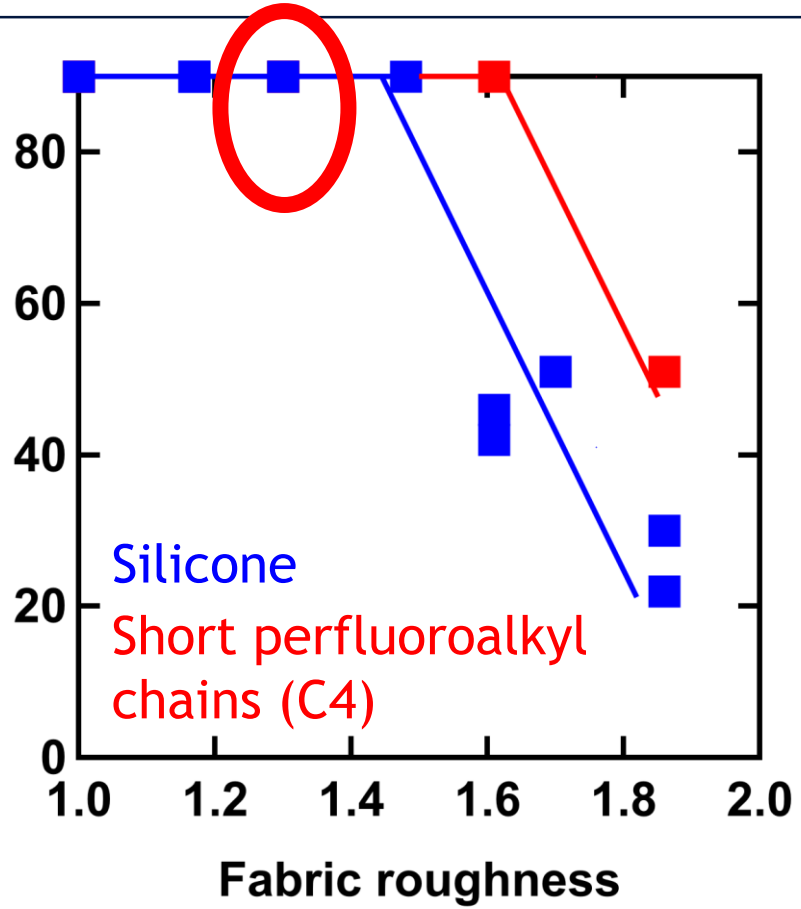




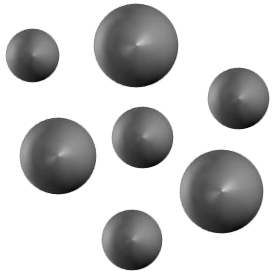
Can we improve the hydrophobicity of a fabric of low roughness?

We selected a fabric of low roughness (1.3)





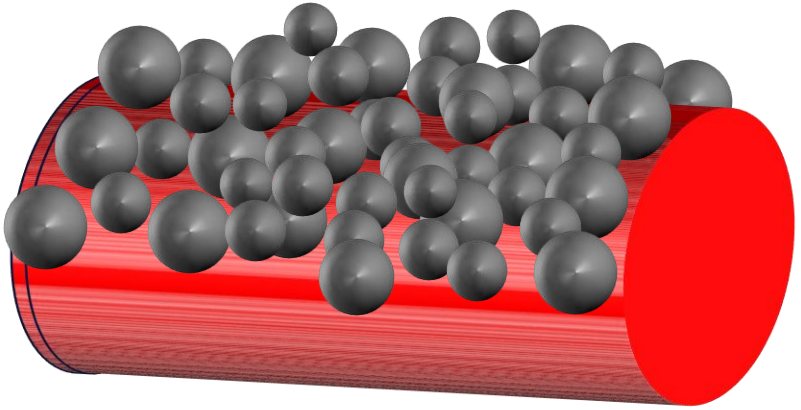
Boosting fiber roughness with silica particles

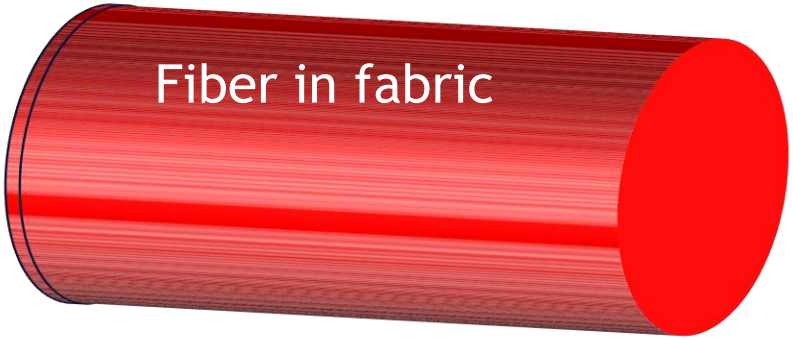


Silica particles

+ aqueous coating formulation

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



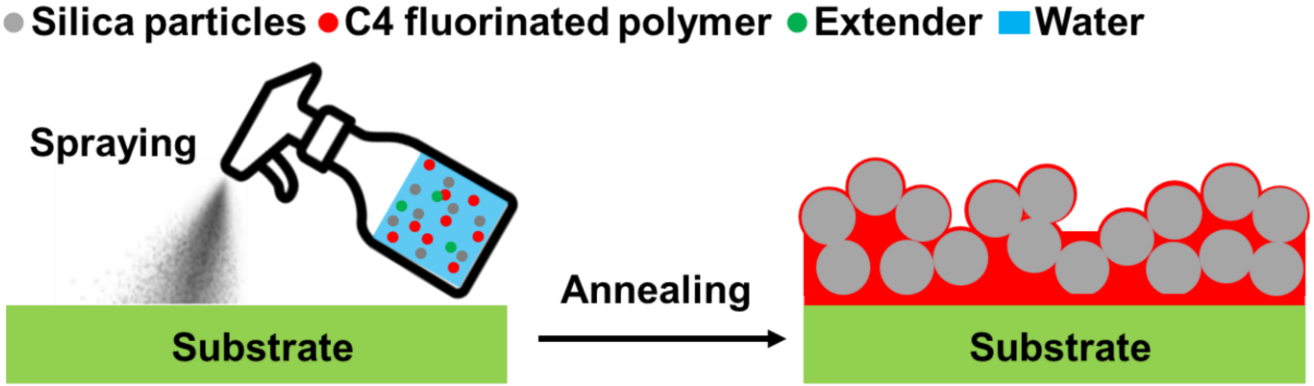


$$\mathcal{R} = (\mathcal{R}_W + \mathcal{R}_Y - 1) \times \mathcal{R}_f$$

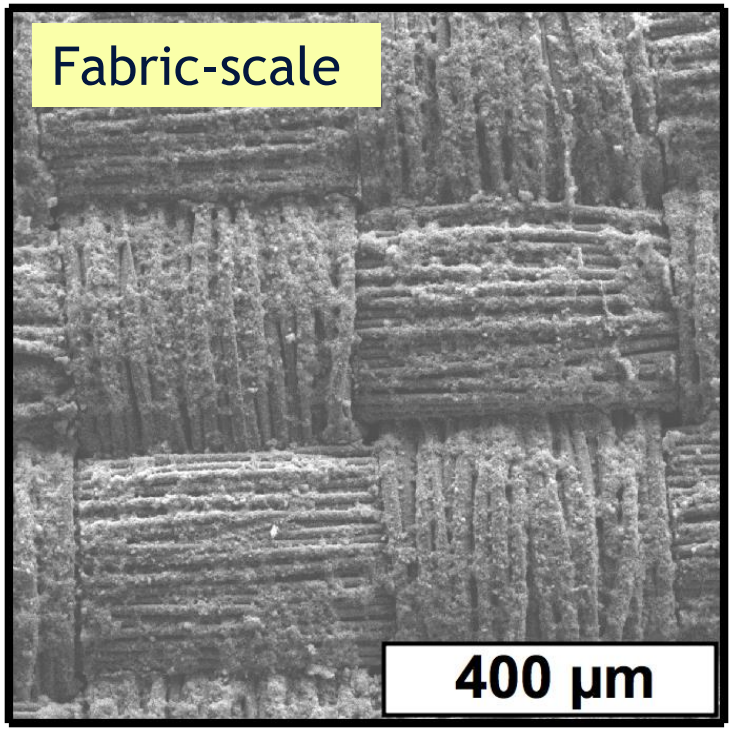
Results with a polyurethane having short perfluoroalkyl chains

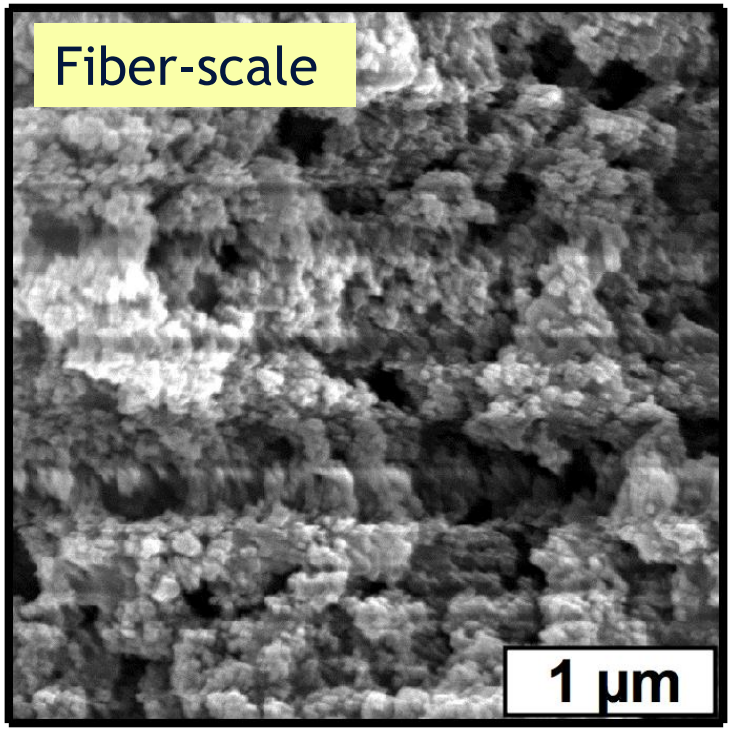
(*aqueous emulsion, PM900, 3M*)

Spraying the one-pot aqueous formulation

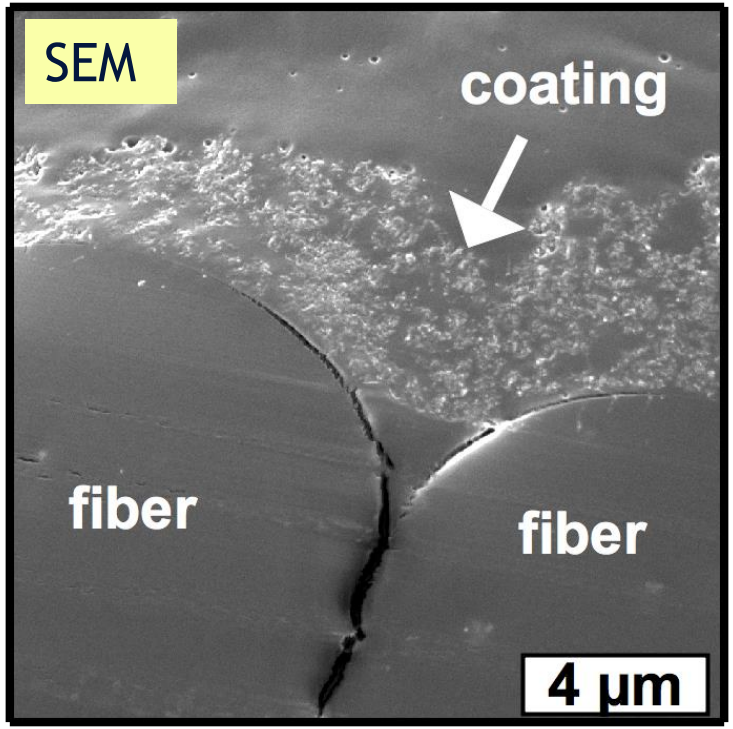


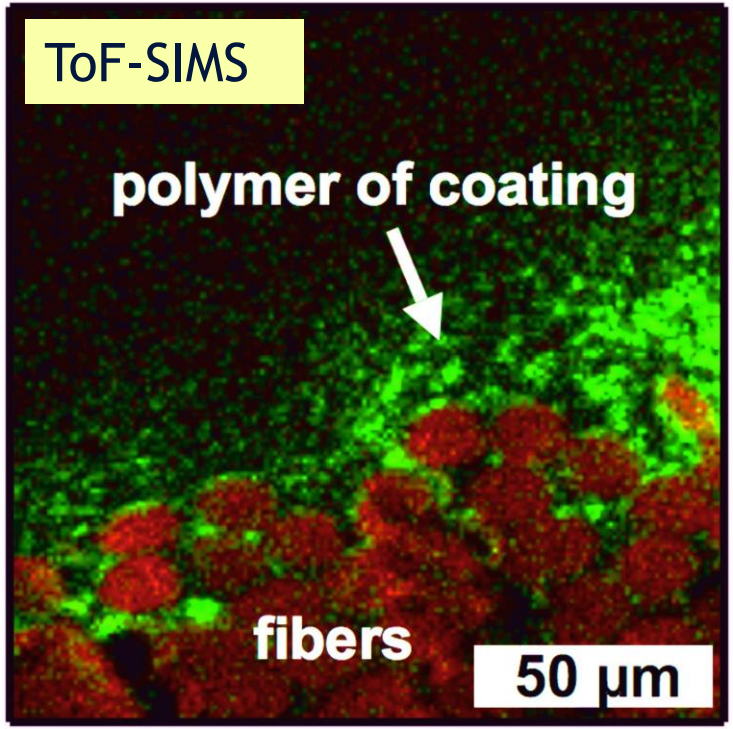
A typical resulting microstructure seen by SEM



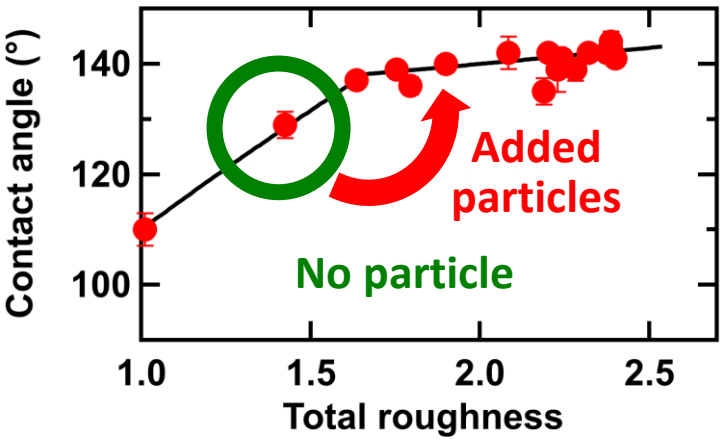


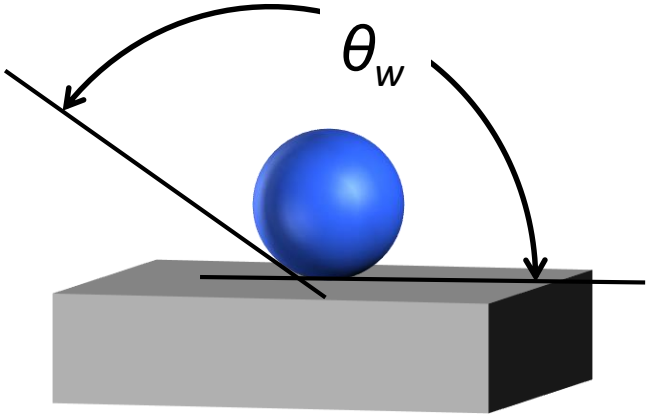
A typical transverse cut



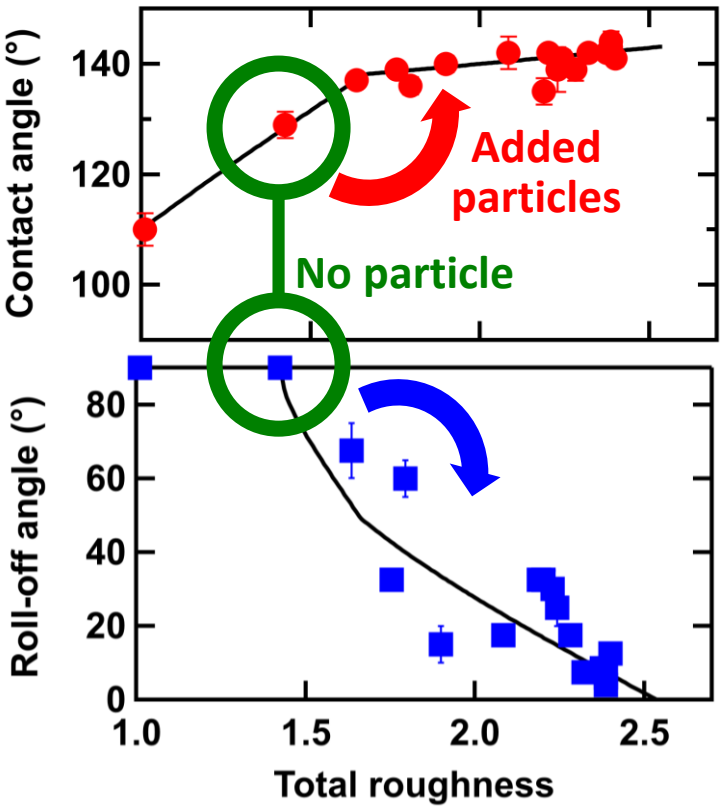


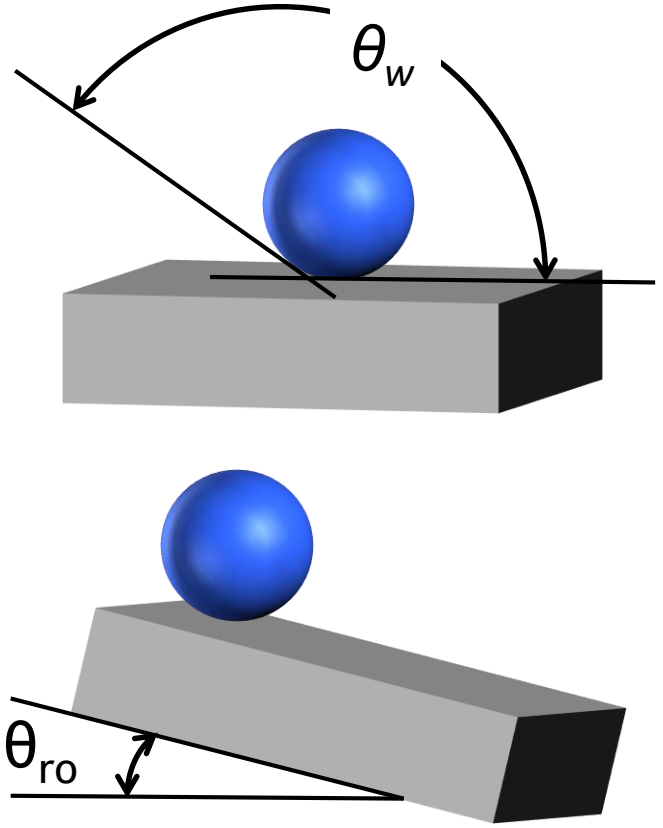
Increasing the roughness of the fibers results in increased water repellence



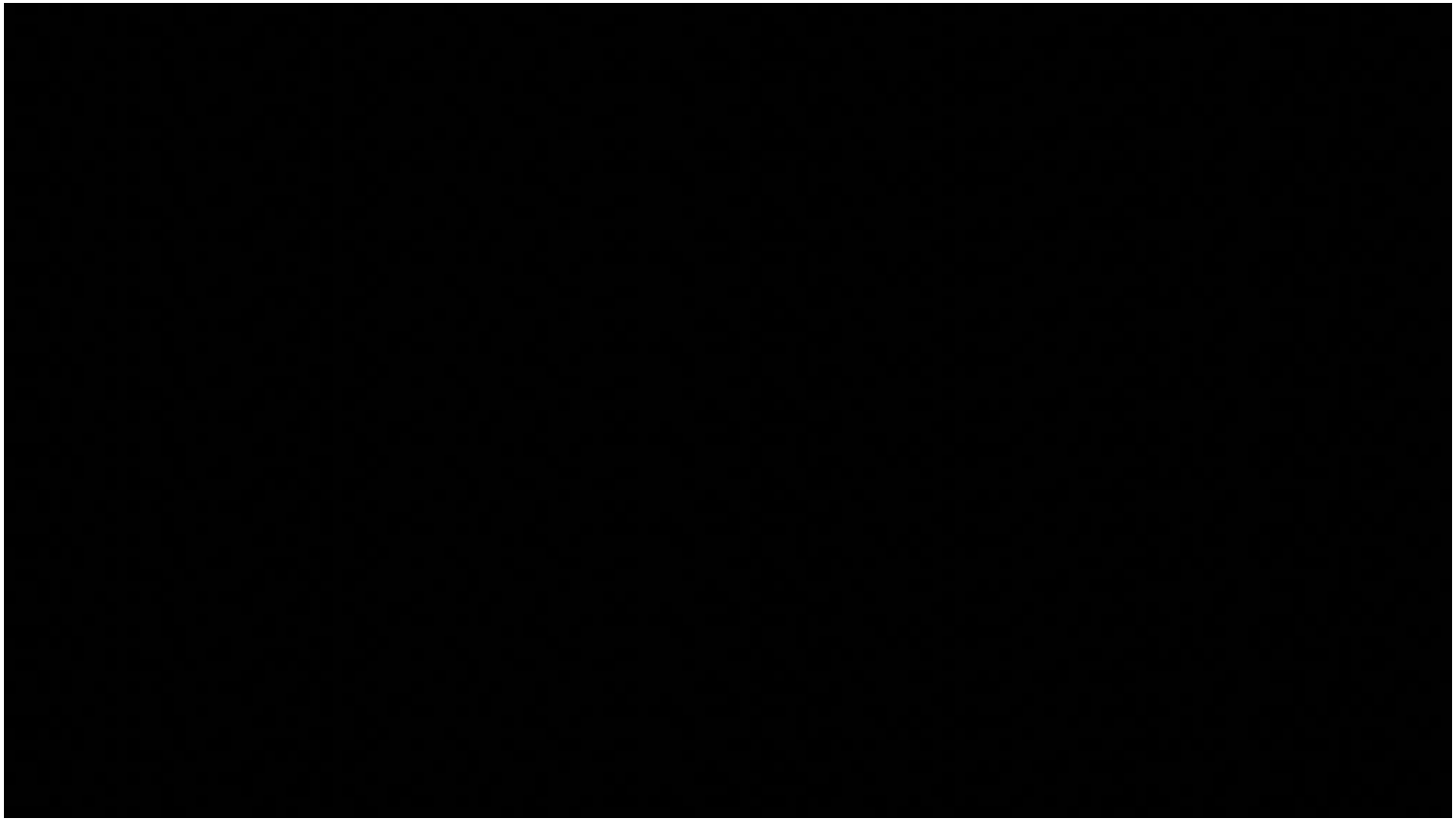


Increasing the roughness of the fibers results in increased water repellence

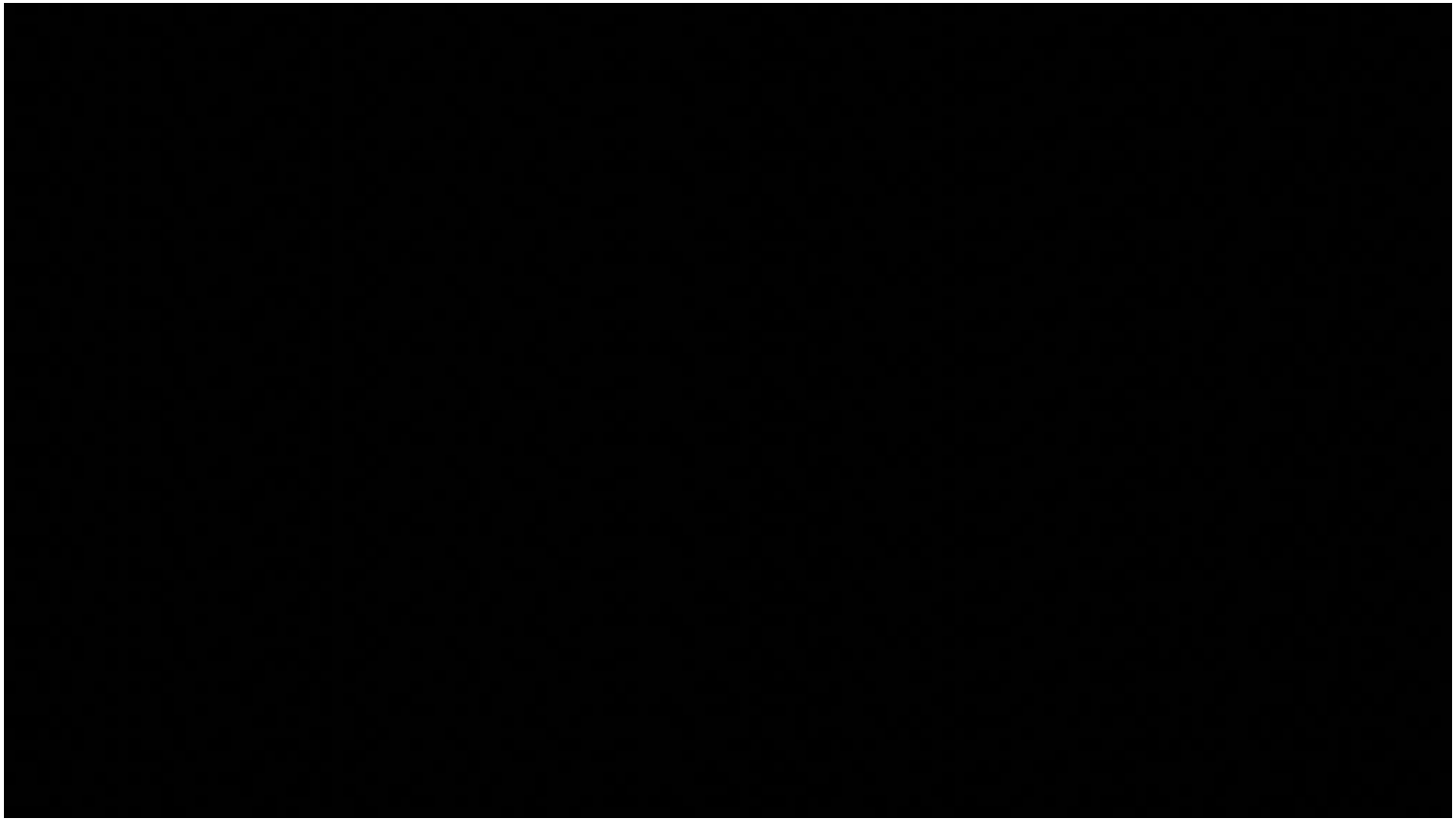




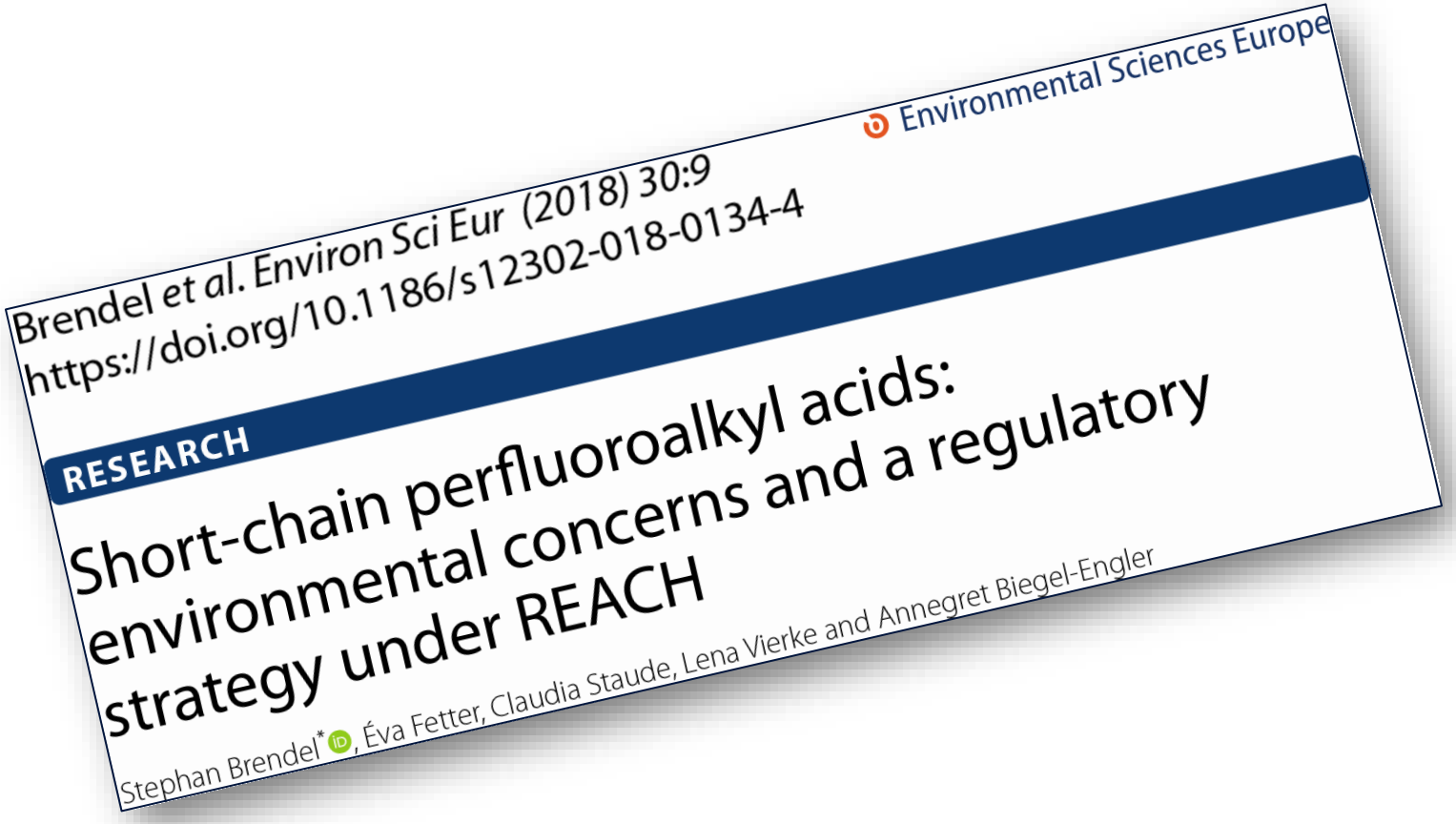
A superhydrophobic C4-based sample in action



The short C4 perfluoroalkyl chains also lead to superoleophobicity



However, shorter perfluoroalkyls also 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

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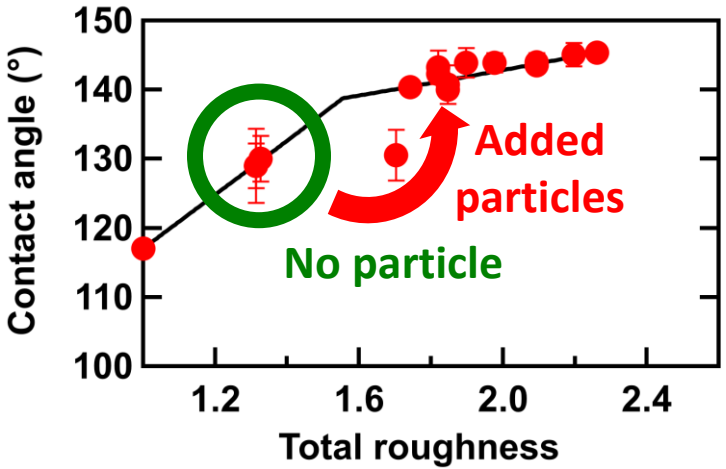
Results obtained with
a crosslinked silicone rubber

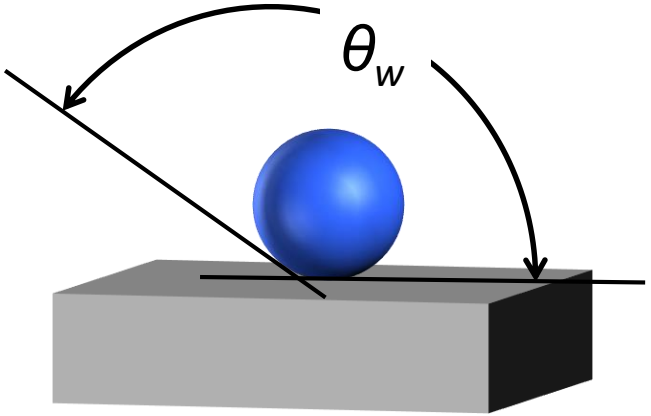
(*aqueous emulsion*, *HC303*, *Wacker*)

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

ACS Appl. Mater. Interfaces 2018, 10, 15346−15351

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





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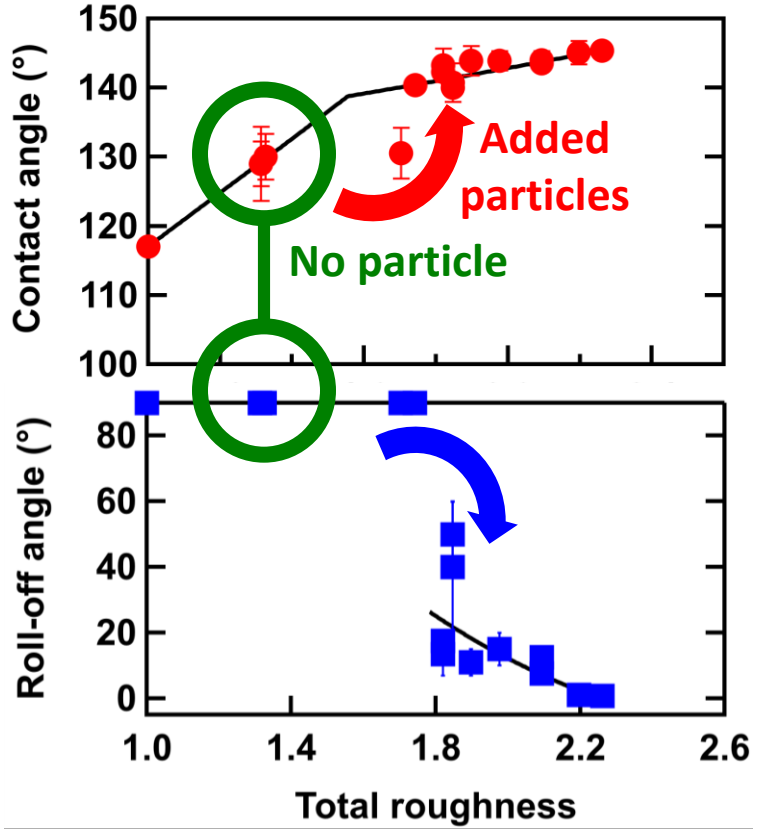
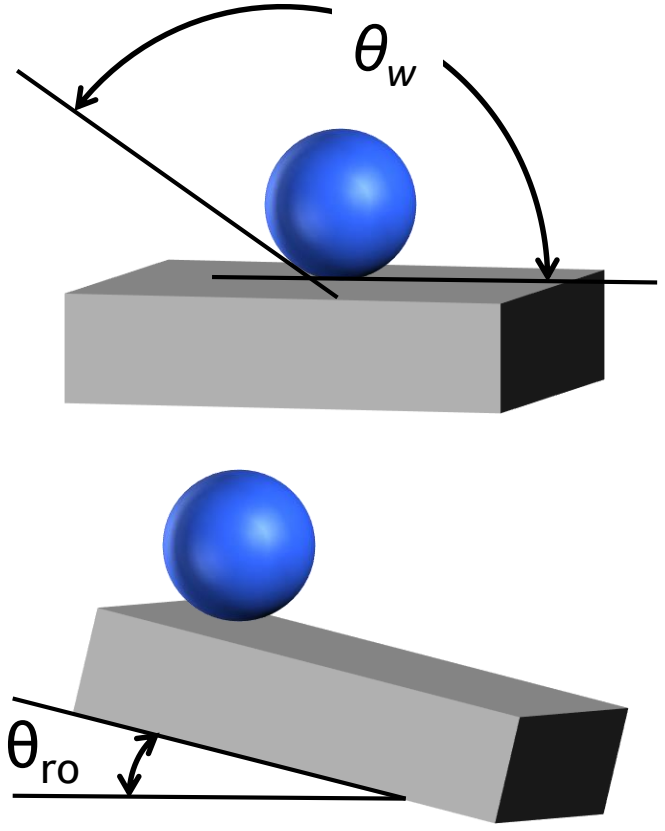
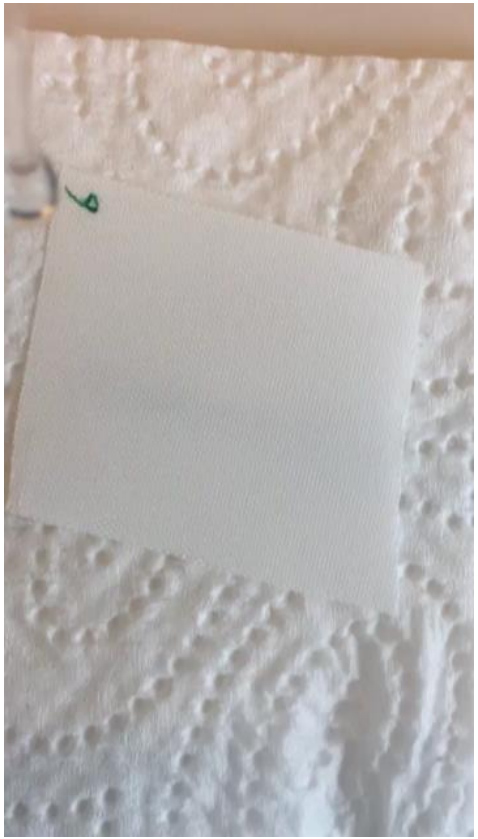




Water repellence of a silicone-based superhydrophobic fabric prepared from aqueous suspensions



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 weight

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)

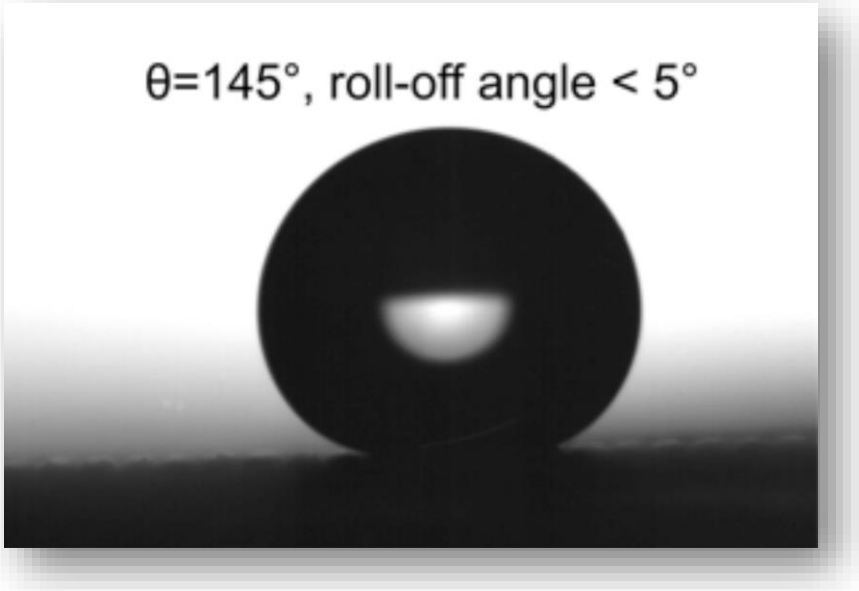
Adopted on 13 June 2018

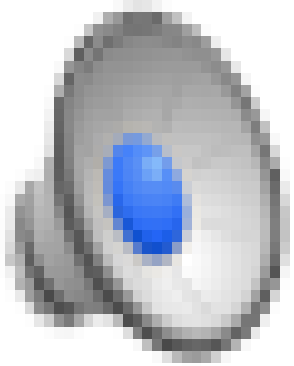
[1] PBT means persistent, bioaccumulative and toxic
[2] vPvB means very persistent and very bioaccumulative

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 with particles: 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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EUROPESE UNIE

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