Environmentally-friendly superhydrophobic and superoleophobic fabrics prepared from water-based suspensions

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DURATEX

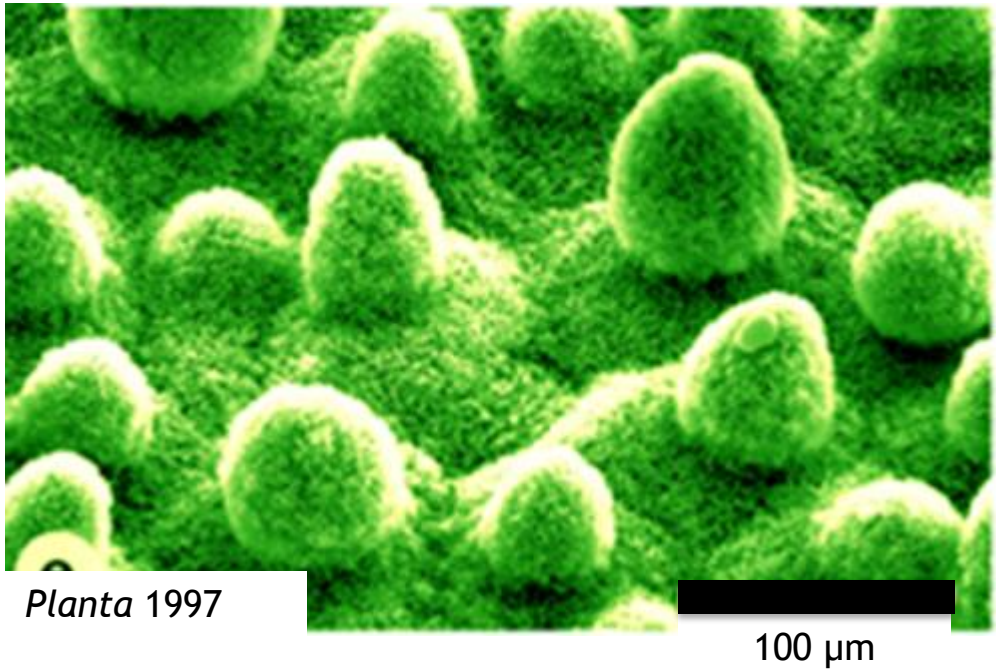
Avec le soutien du Fonds européen de Développement Régional
Met de steun van het Europees Fonds voor Regionale Ontwikkeling

Wallonie

met de steun van
west-vlaanderen
de gedreven provincie

Motivation – Super-water-repellency

Lotus leaf



Planta 1997

Motivation – Super-water-repellency

Lotus leaf

Anti-staining clothing

UltraTech International

Outline

- Theoretical background
  - Wenzel Model and Cassie-Baxter Model
  - Parameters to control wetting behaviors

- Results
  - Fabrics treated by
    a water-based suspension of C4 fluorinated polymer + silica particles
  - Fabrics treated by
    water-based silicone rubber and silica particle suspensions

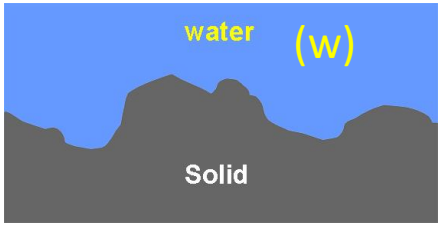
- Conclusions

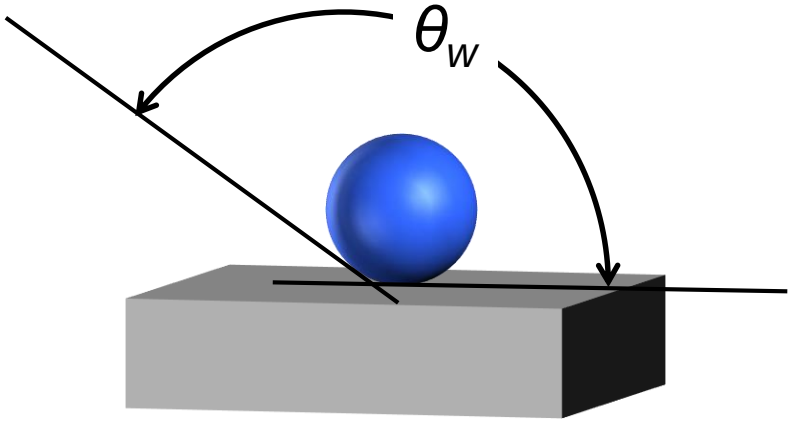
Theoretical background

Wenzel's model

$$\cos\theta_w = R \cos\theta_0$$

θ_0 : contact angle on an ideal flat surface depending on surface chemistry





Theoretical background

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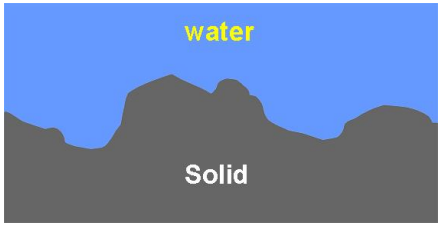
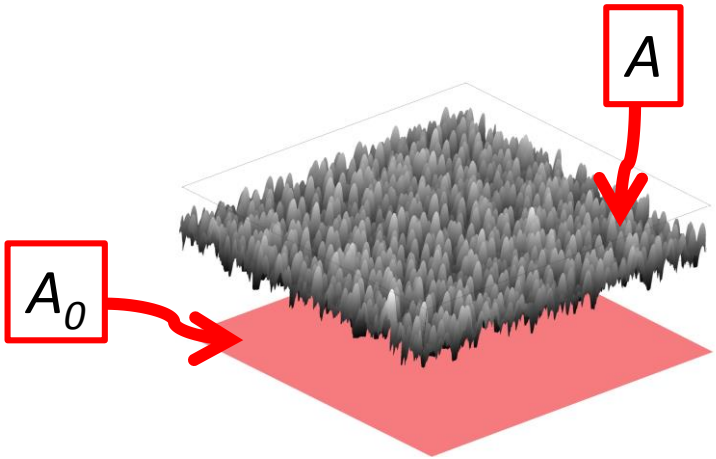


$$\cos\theta_w = R\cos\theta_0$$

θ_0 : contact angle on an ideal flat surface depending on surface chemistry

R : surface roughness



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

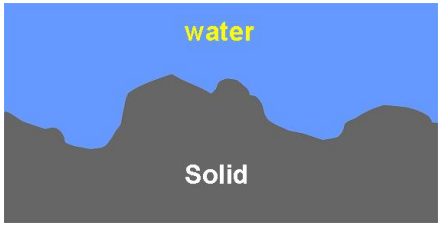
Theoretical background

Wenzel's model

$$\cos\theta_w = R \cos\theta_0$$

θ_0 : contact angle on an ideal flat surface depending on surface chemistry

R : surface roughness

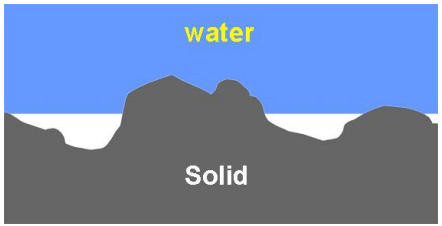


Cassie-Baxter model

$$\cos\theta_w = f_s (R \cos\theta_0 + 1) - 1$$

f_s : surface fraction of solid

$1-f_s$: surface fraction of air-filled cavities



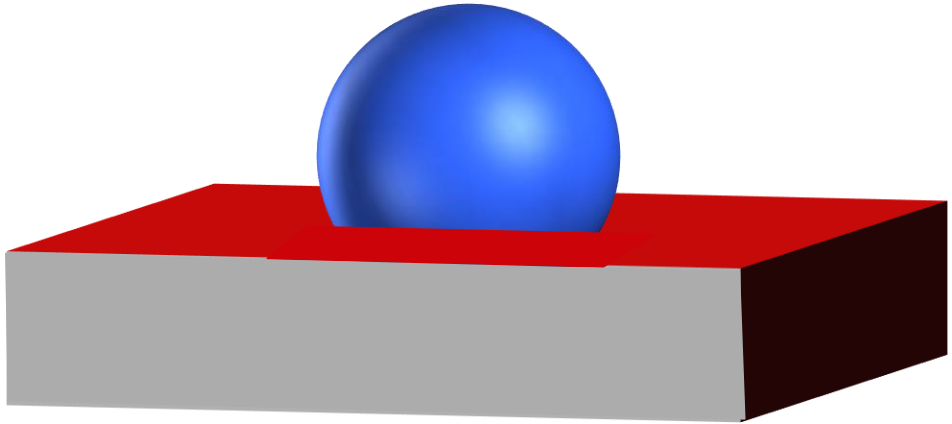
Theoretical background

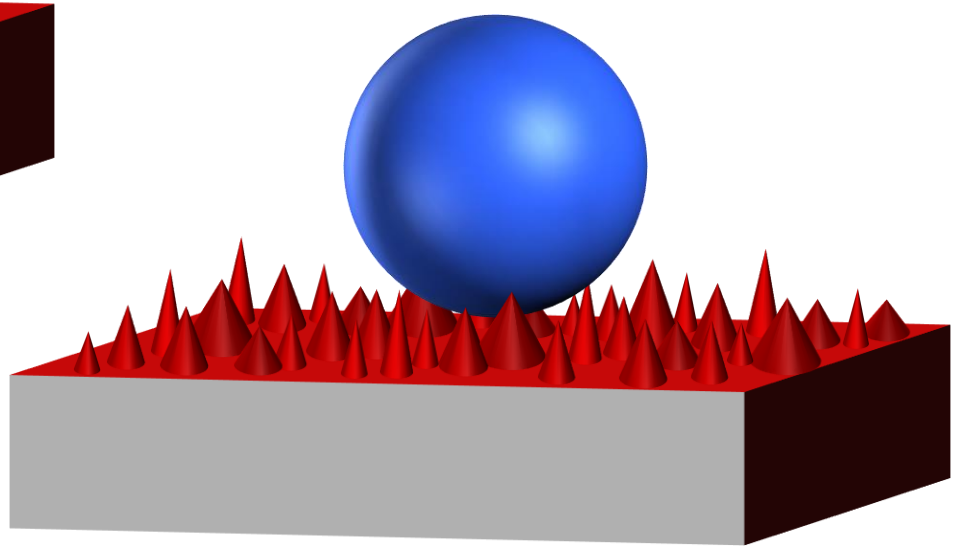
Two general parameters to control wetting behaviors:

- **Surface roughness/structure:** R **and** f_s
- **Surface chemistry:** θ_0

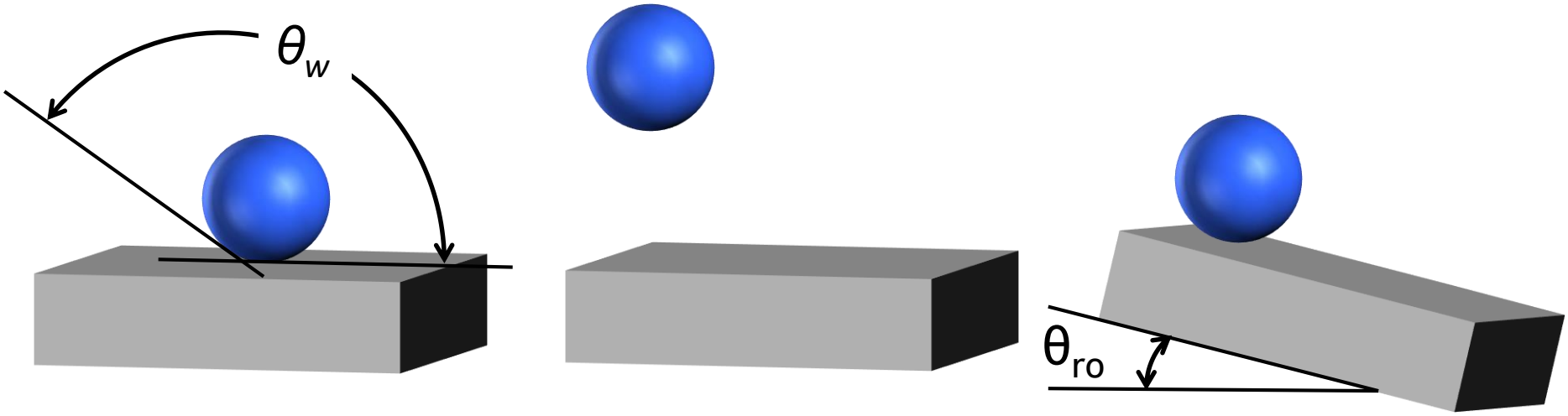
No.1:
Surface roughness/structure

Surface roughness is one parameter controlling the contact angle





Surfaces of sufficiently high roughness may become superhydrophobic



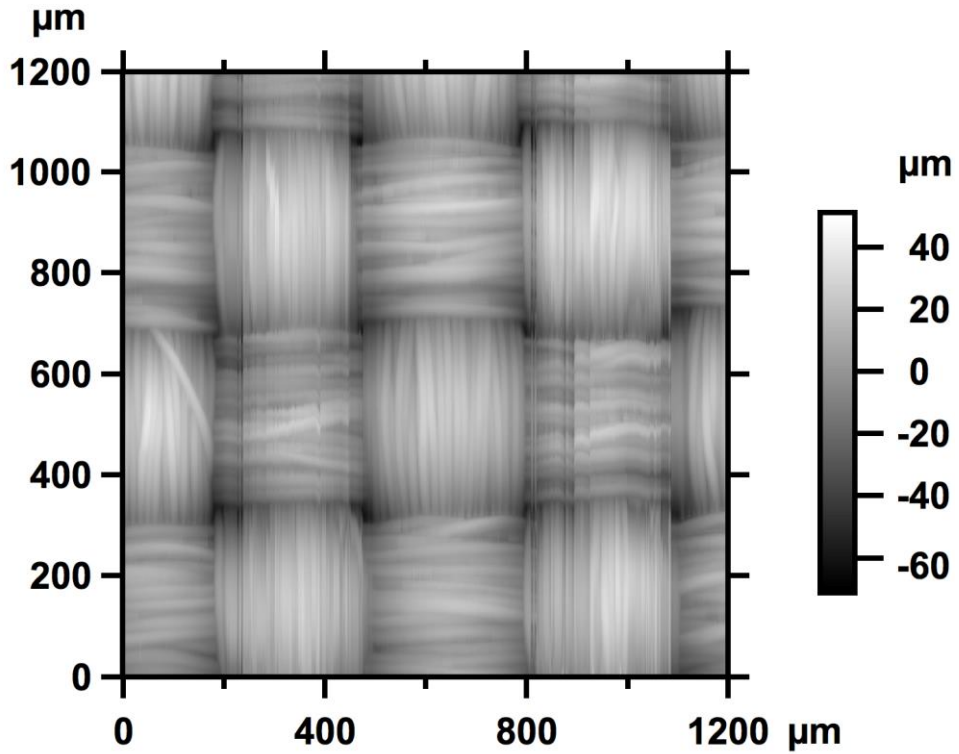
Water contact angle
$\theta_w > 150^\circ$

Droplet bouncing

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

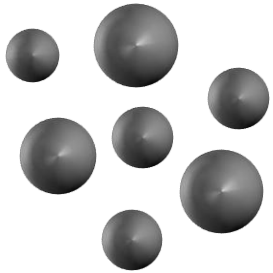
What does contribute
to the fabric roughness ?

Woven fabric has an intrinsic roughness (R_F) which can be measured by profilometry



R_F = 1.30

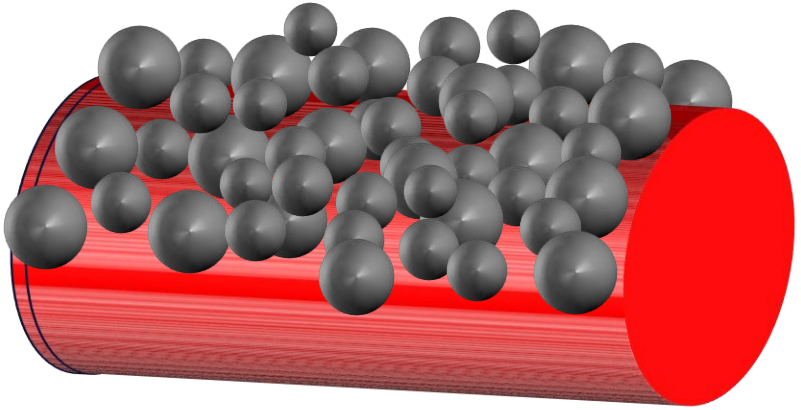
Boosting fiber roughness (R_f) with silica particles

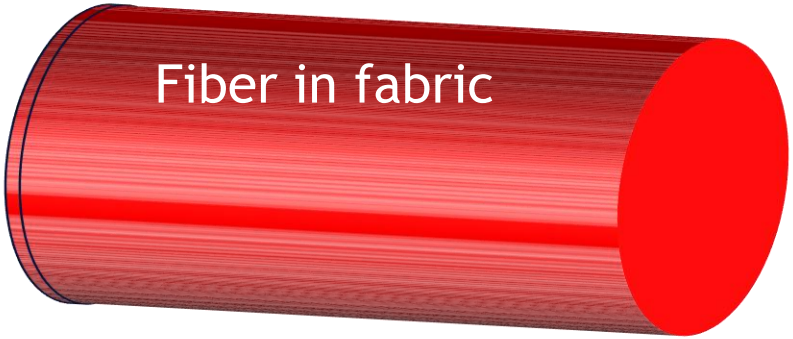


Silica particles

+ coating formulation

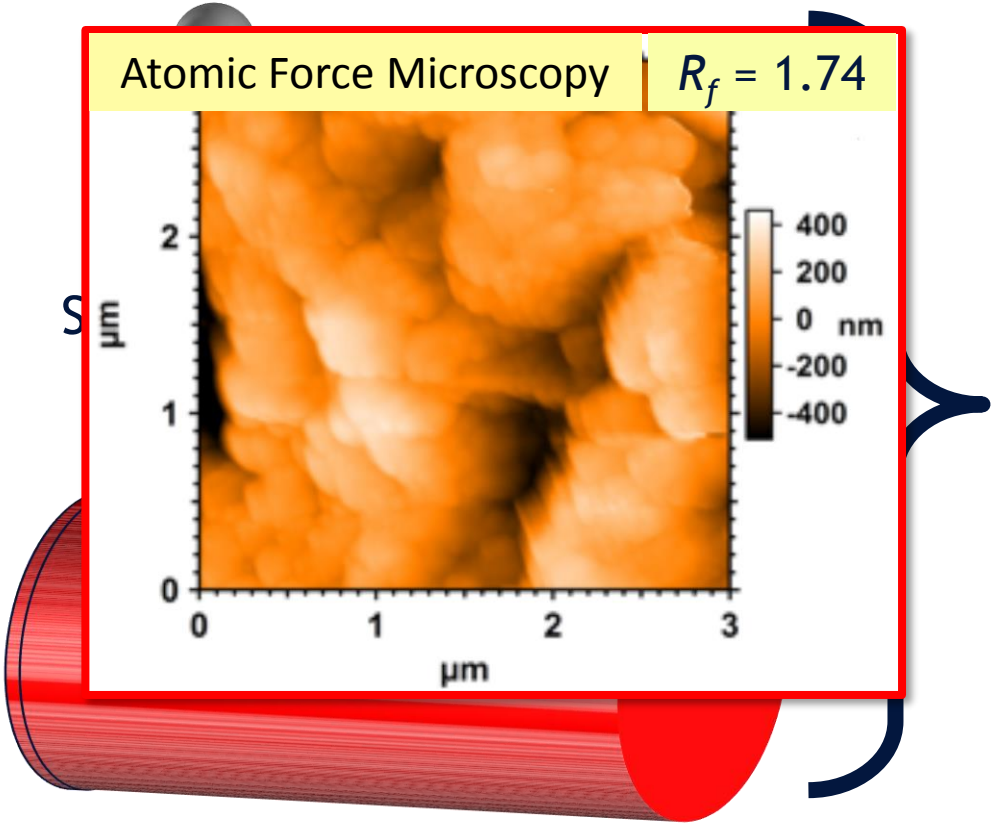
Fiber roughness



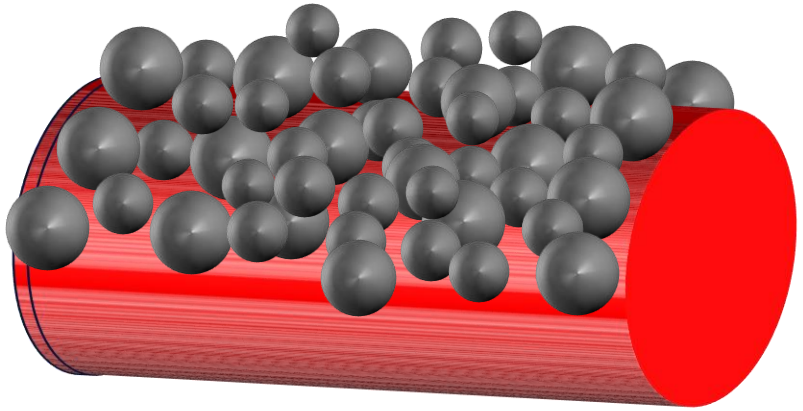


$R_f > 1$

Boosting fiber roughness with silica particles

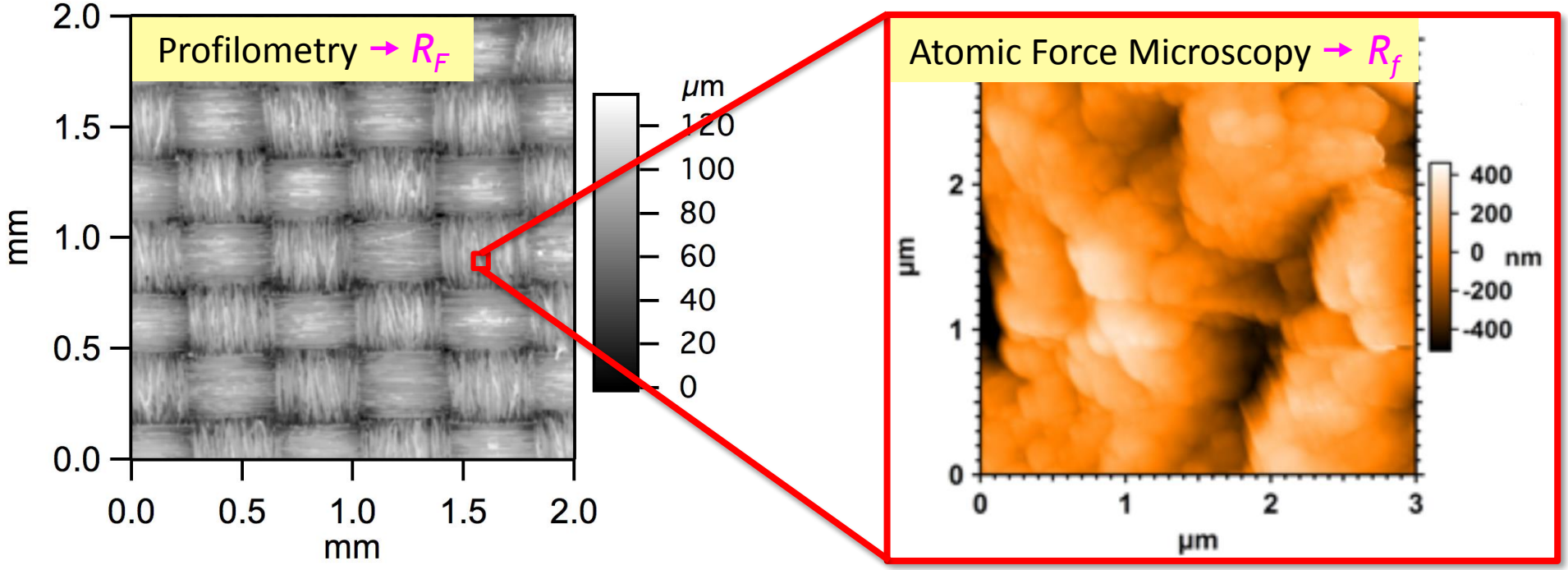


Fiber roughness



$R_f > 1$

Total fabric roughness (*R*)

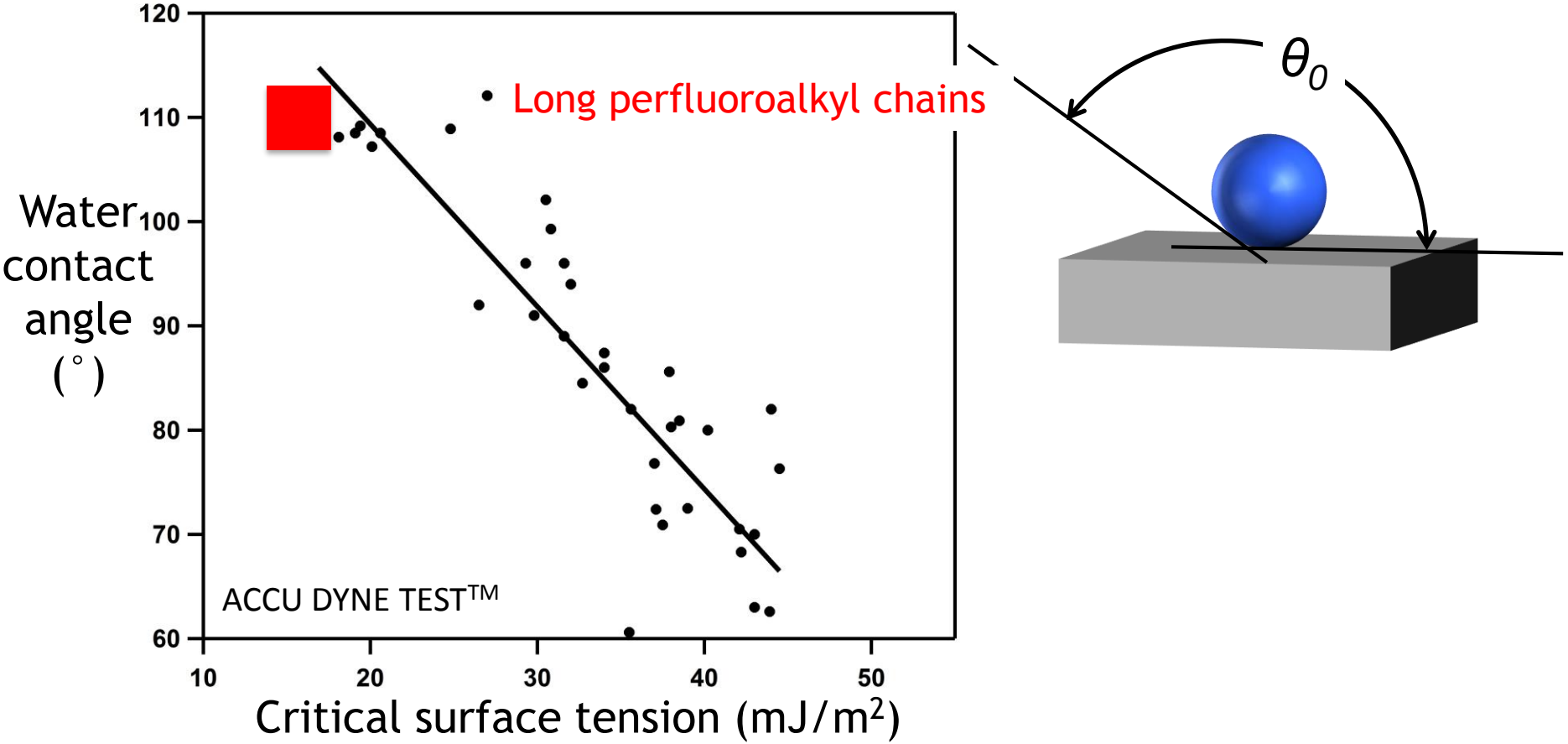


$$R = R_F \times R_f = 1.30 \times 1.74 = 2.26$$

No. 2:
Surface Chemistry

Why were long perfluoroalkyl chains used for water repellency?

Long perfluoroalkyl chains provide low surface tension



‘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

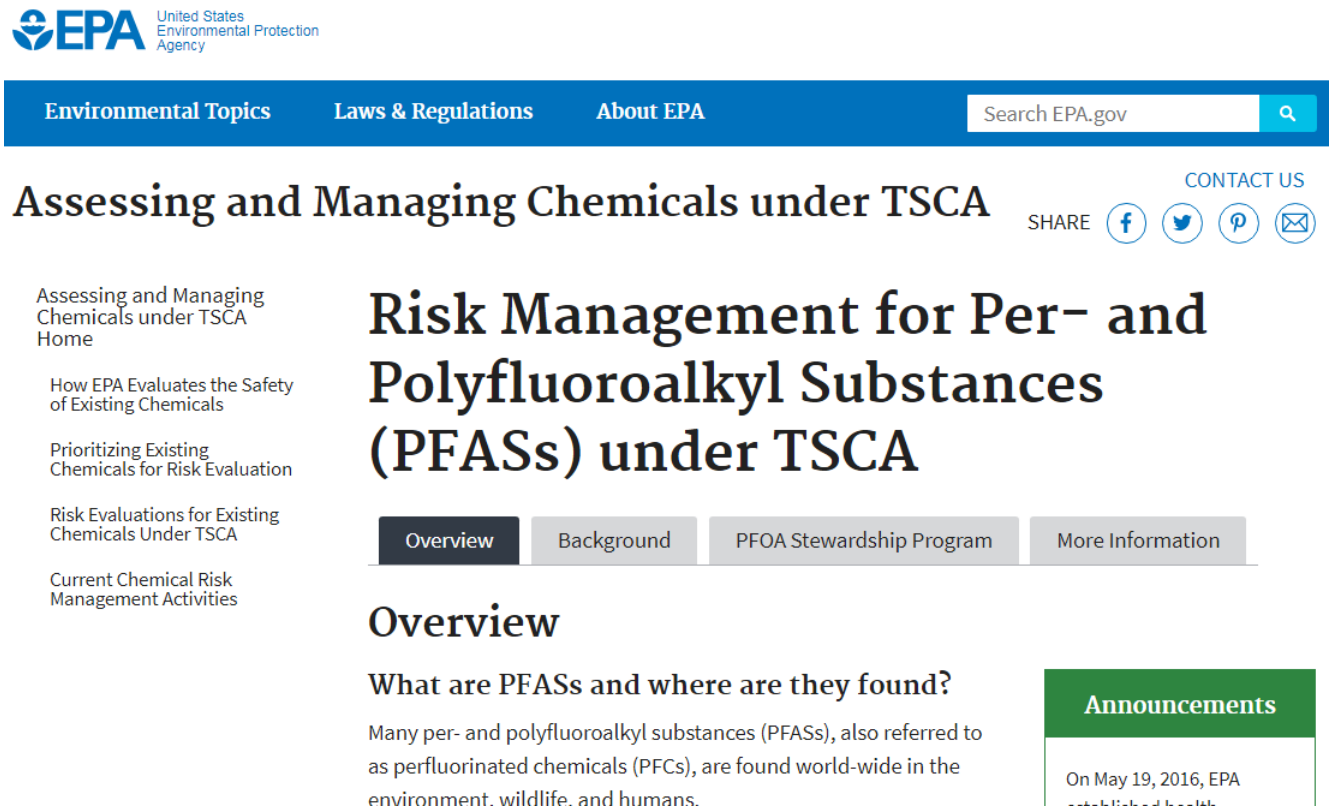
(Text with EEA relevance)

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,

‘Long’ (C8) perfluoroalkyl chains are being banned



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Assessing and Managing Chemicals under TSCA

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- How EPA Evaluates the Safety of Existing Chemicals
- Prioritizing Existing Chemicals for Risk Evaluation
- Risk Evaluations for Existing Chemicals Under TSCA
- Current Chemical Risk Management Activities

Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA

Overview | Background | PFOA Stewardship Program | More Information

Overview

What are PFASs and where are they found?

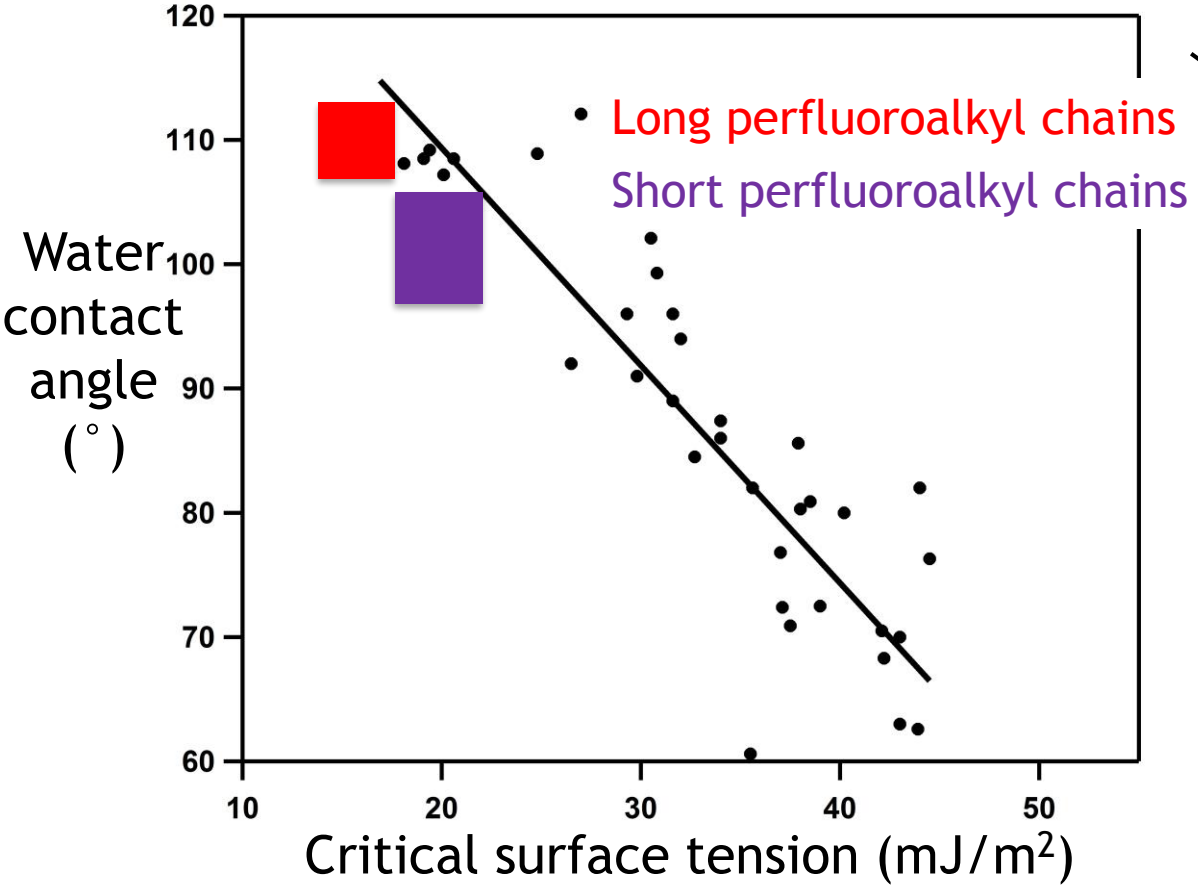
Many per- and polyfluoroalkyl substances (PFASs), also referred to as perfluorinated chemicals (PFCs), are found world-wide in the environment, wildlife, and humans.

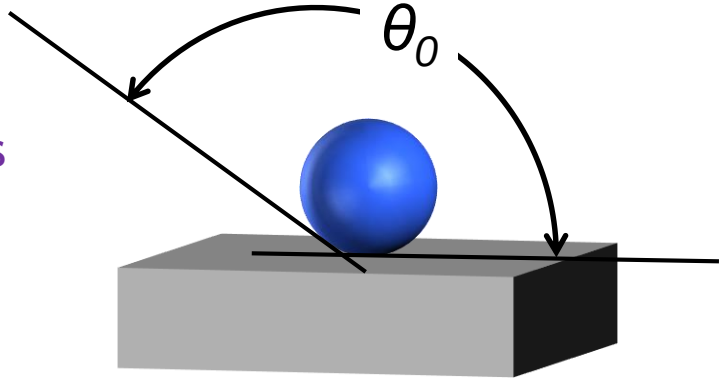
Announcements

On May 19, 2016, EPA

Are there possible alternative compounds to replace long perfluoroalkyl chains?

Other candidates are possible





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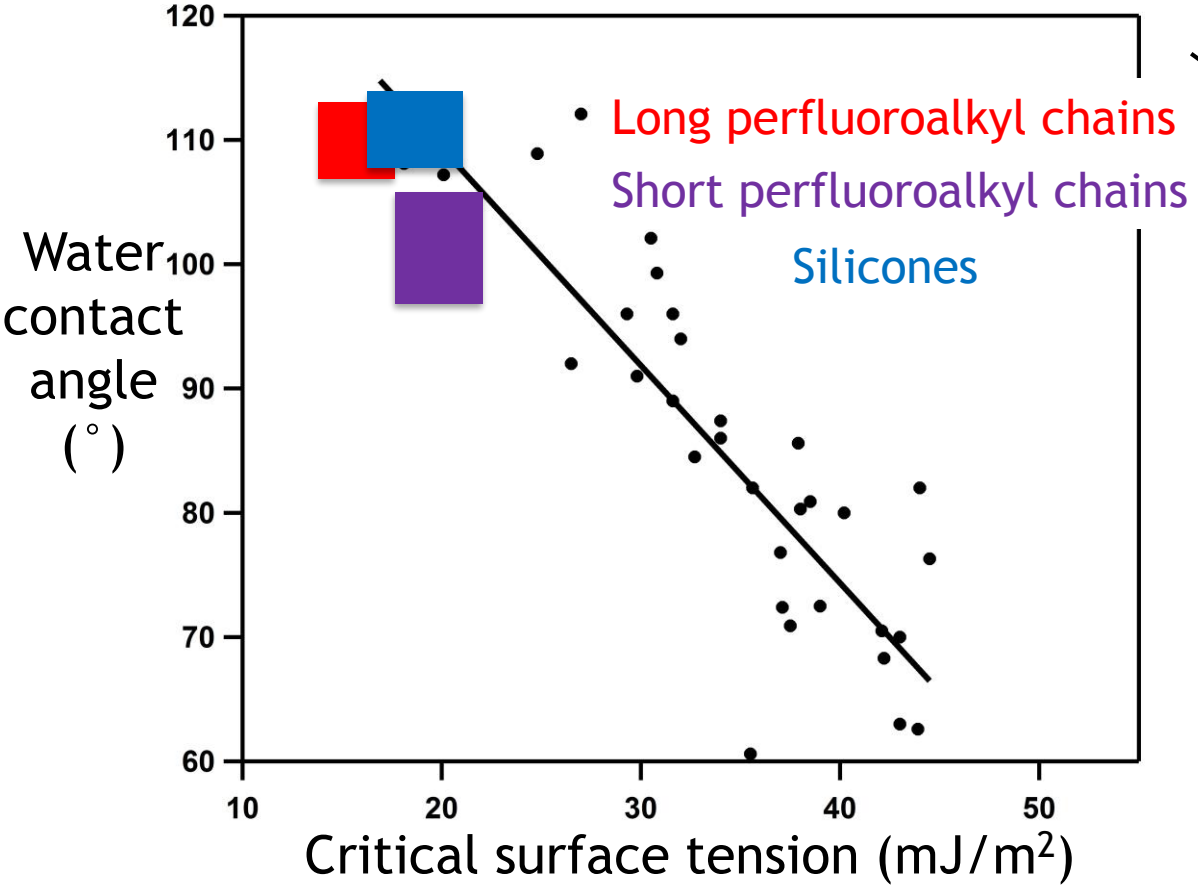

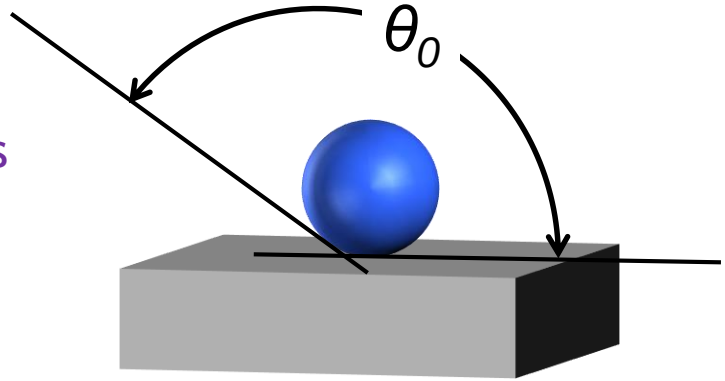

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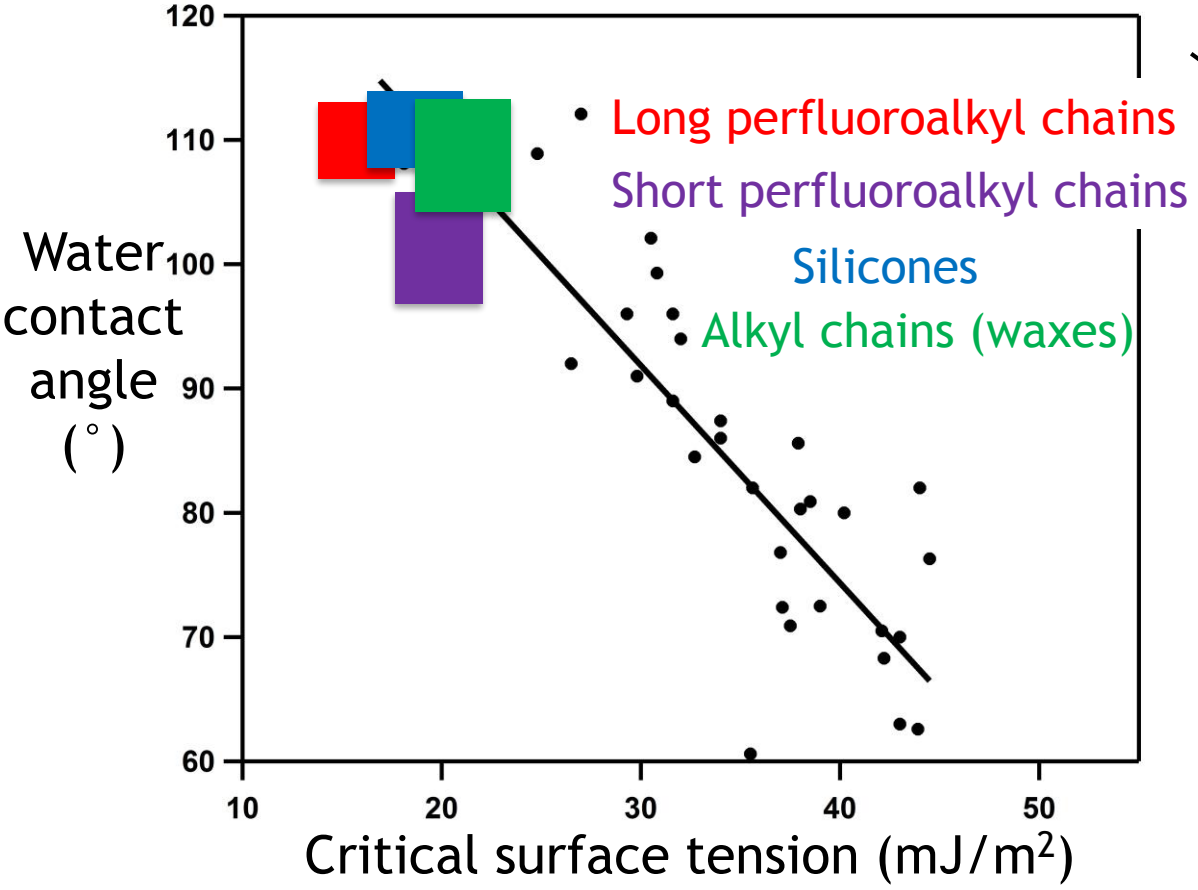

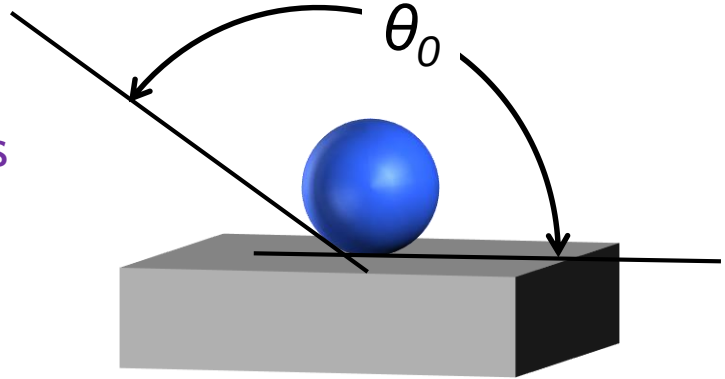

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One step deposition
of an aqueous suspension containing:

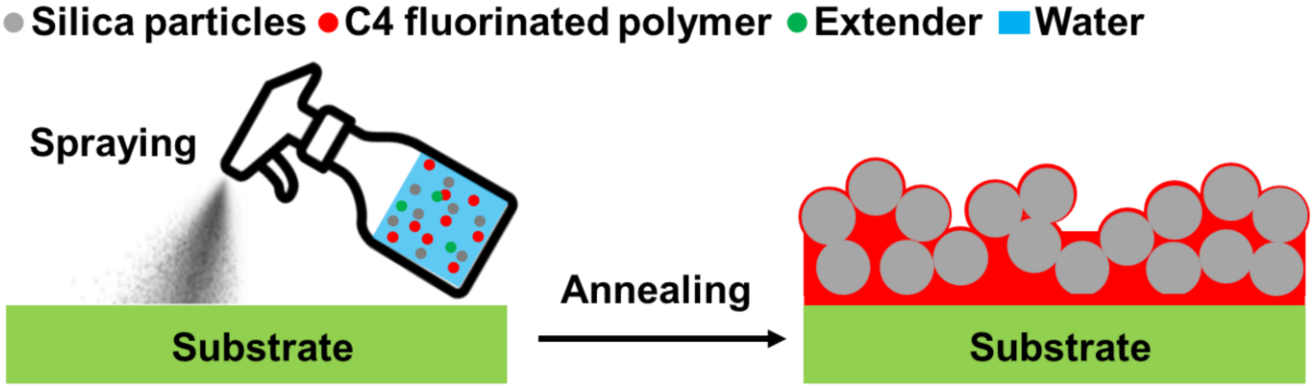
Polyurethane bearing short (C4) perfluoroalkyl chains (*PM900®, 3M*)

+

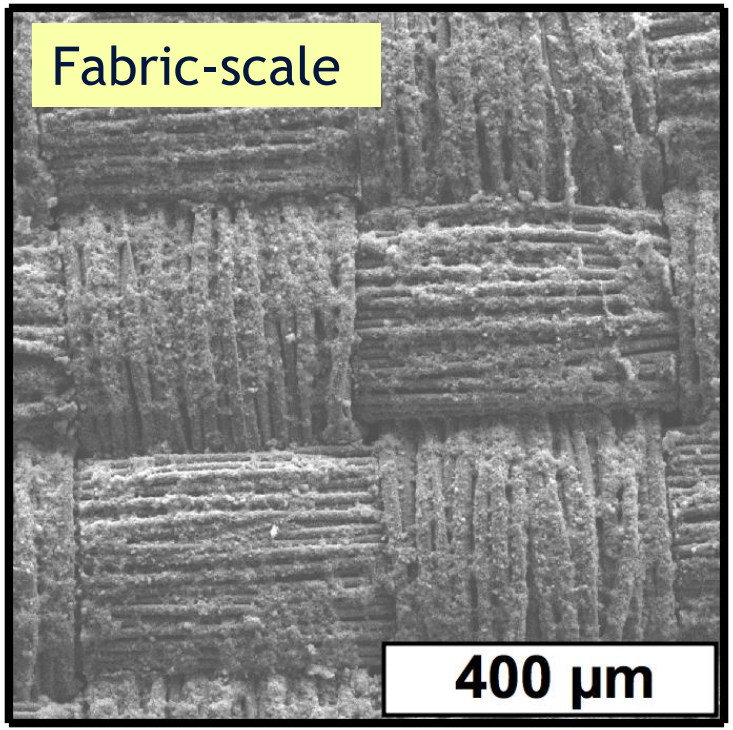
Silica particles (*Tixosil®, Solvay)*

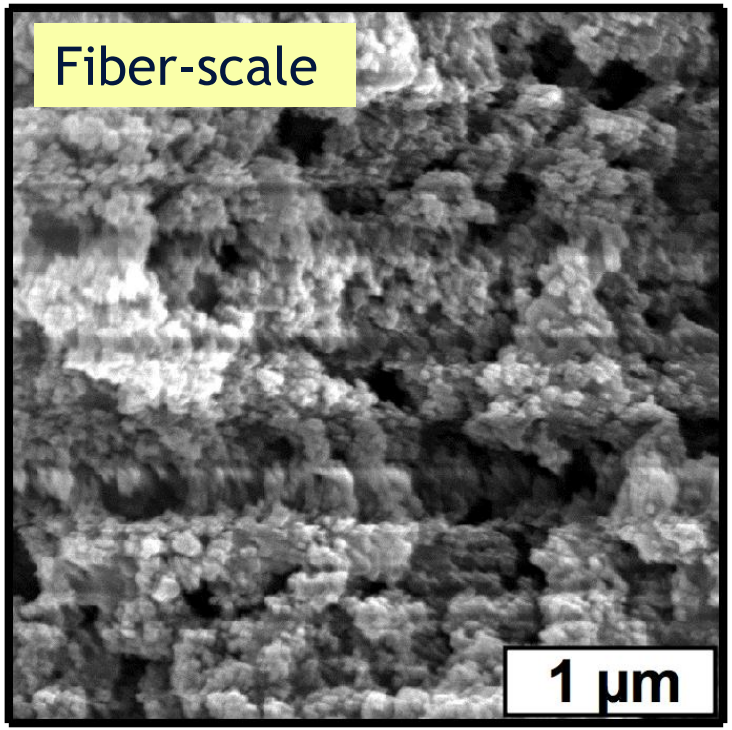
Manuscript submitted

Spraying the one-pot aqueous formulation

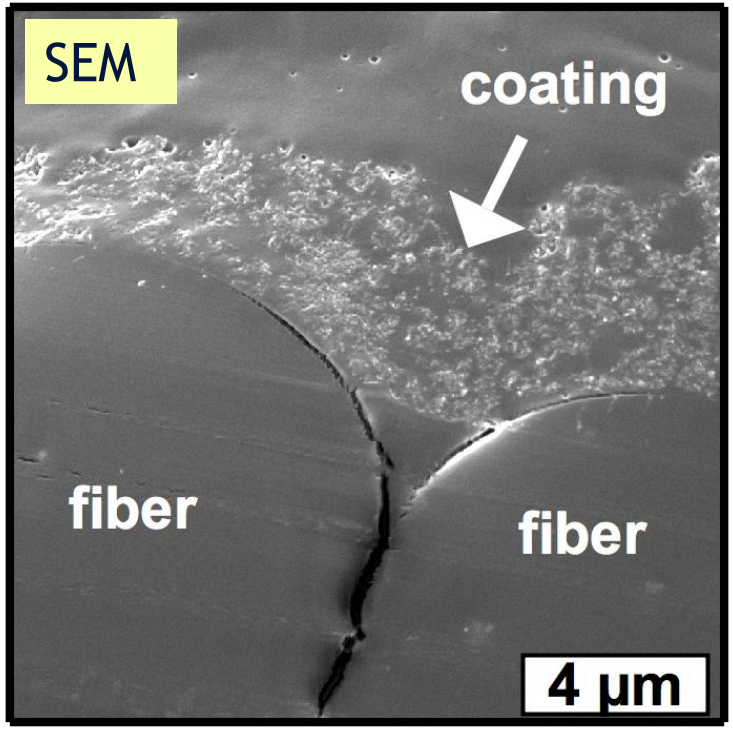


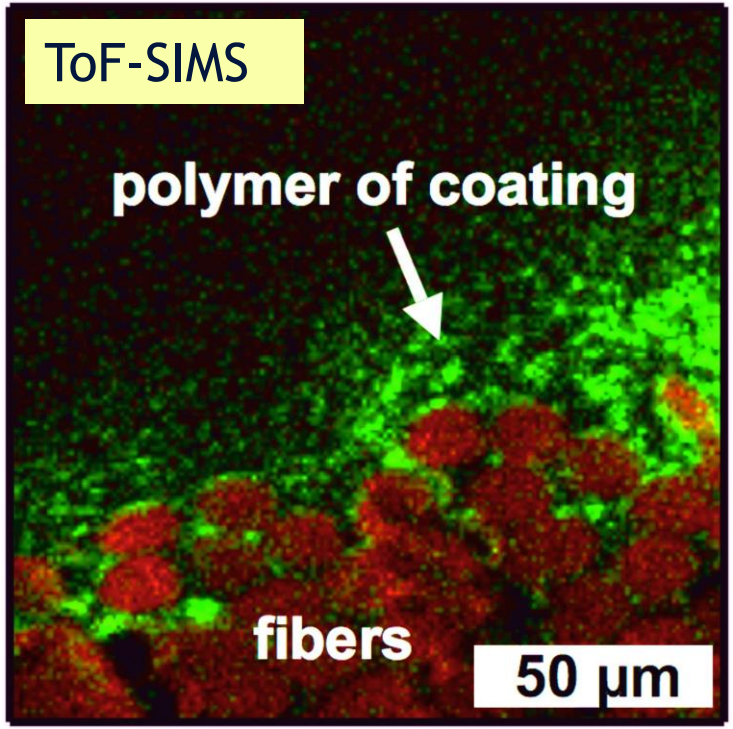
Surface morphology of a typical sample (SEM)



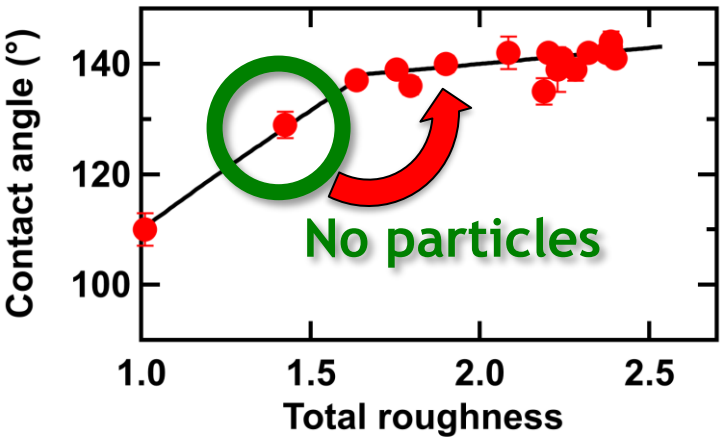


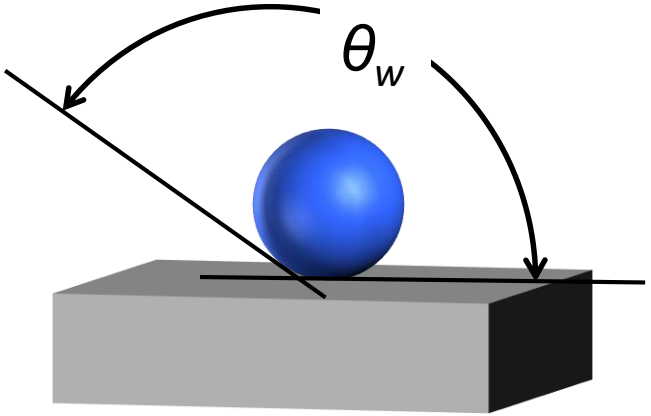
A typical transverse cut





Increasing the roughness of the fibers results in increased water repellency





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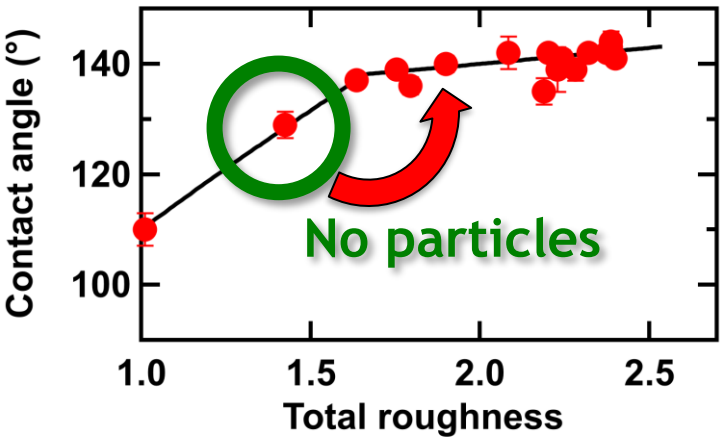

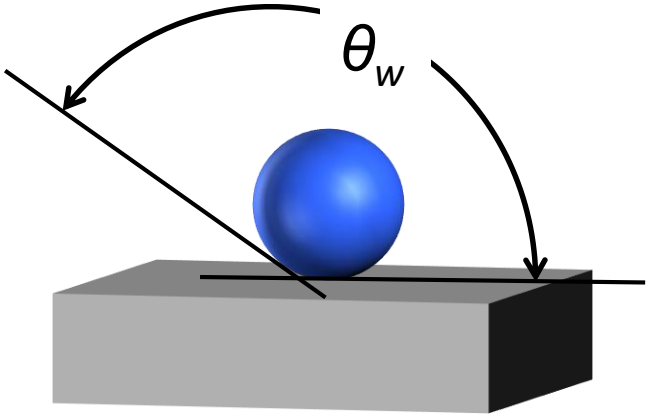

Fitting using Cassie-Baxter equation:

$\cos\theta_w = f_s\,(R\cos\theta_0 + 1) - 1$

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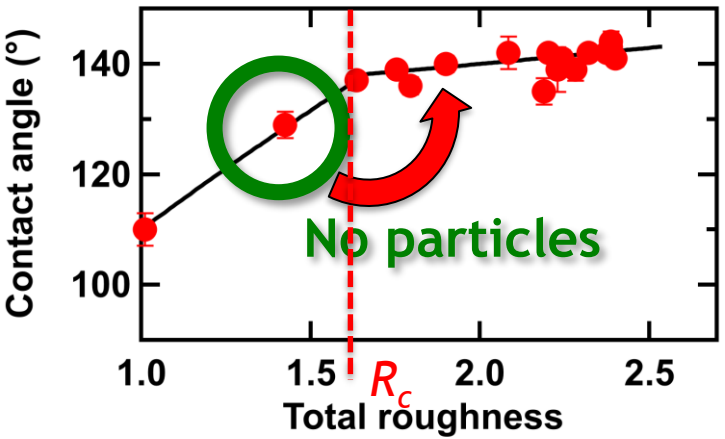
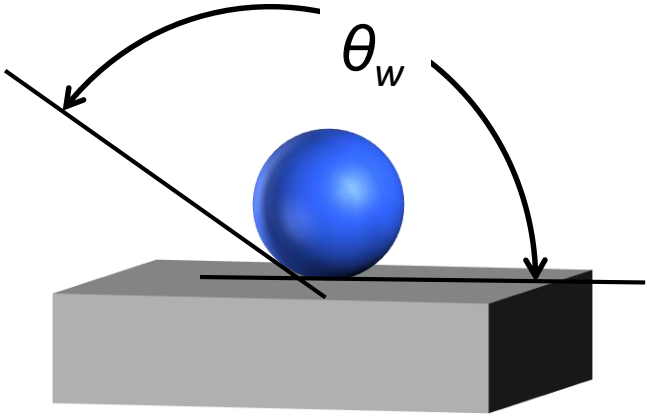




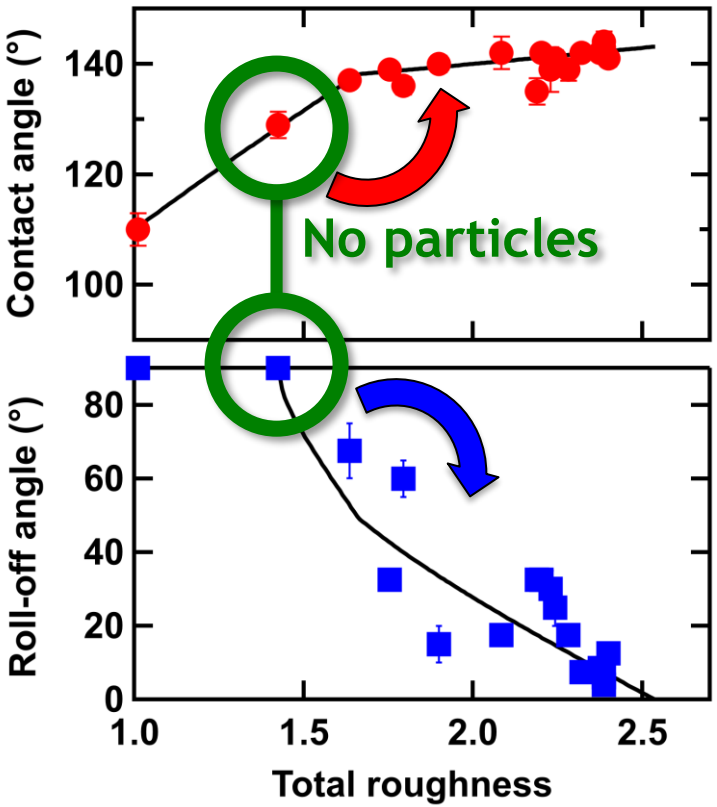
Fitting using Cassie-Baxter equation:

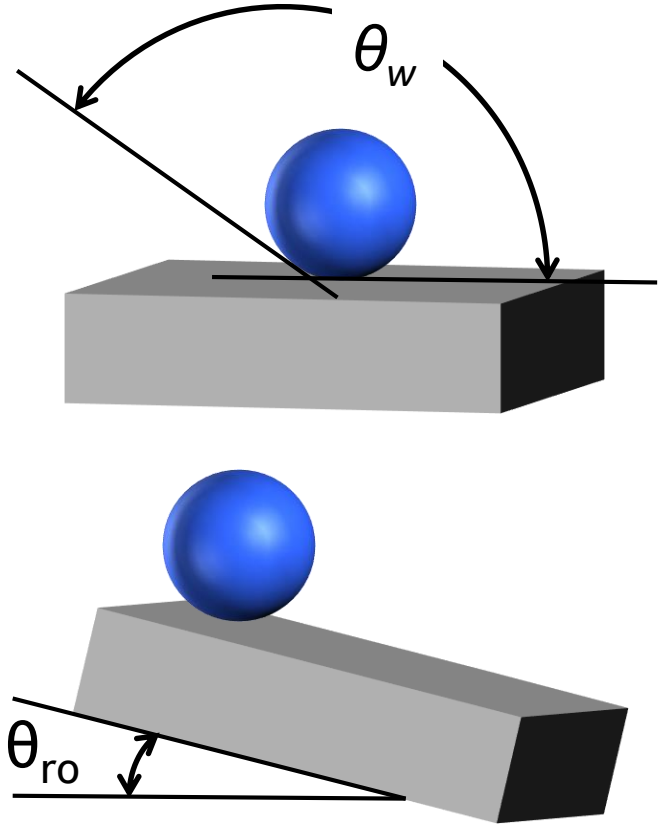
$\cos\theta_w = f_s\,(R\cos\theta_0 + 1) - 1$

$1-f_s$ = 0.71 (fraction of trapped air)

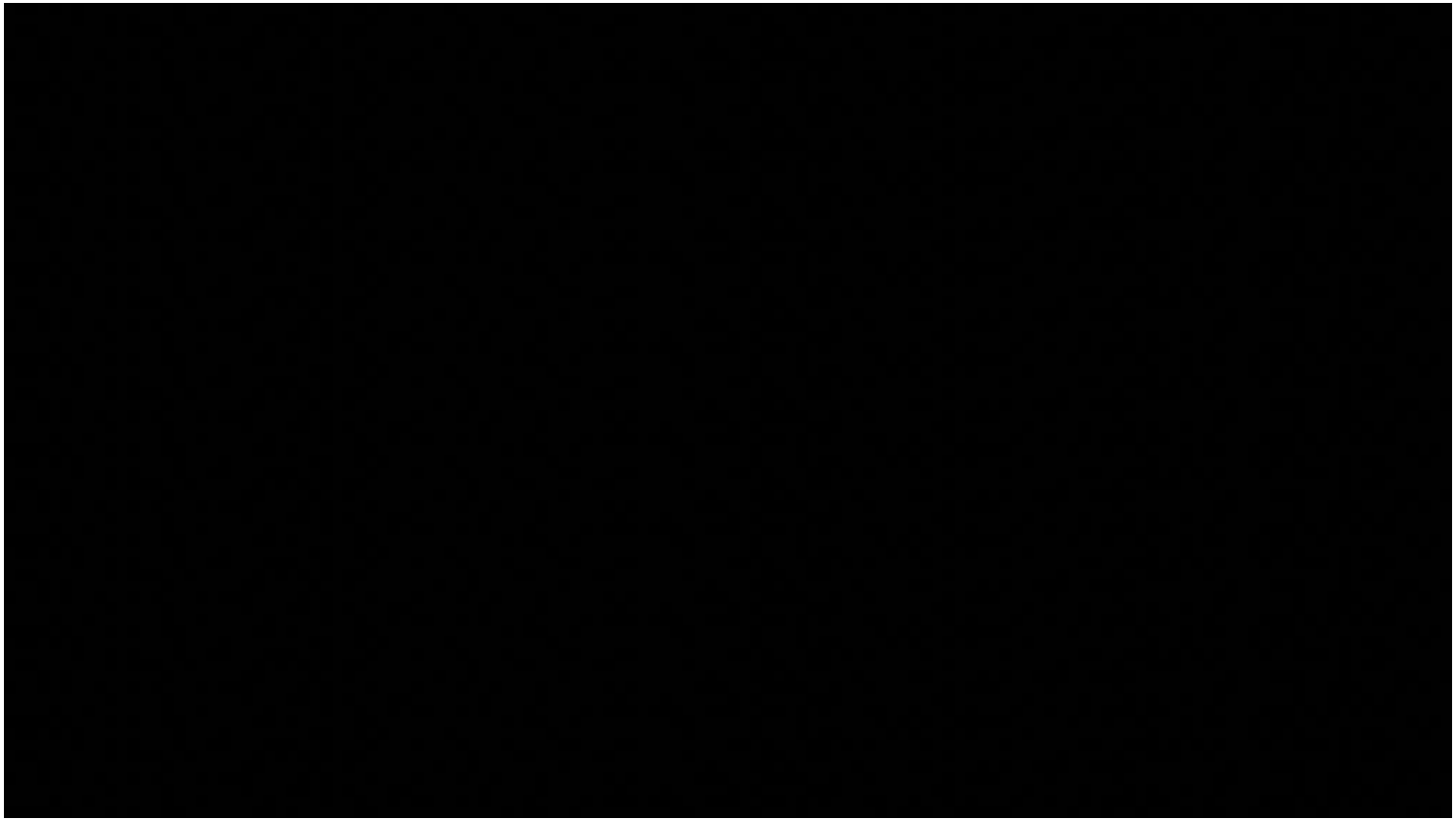
R_c = 1.6 (critical roughness)

Increasing the roughness of the fibers results in increased water repellency

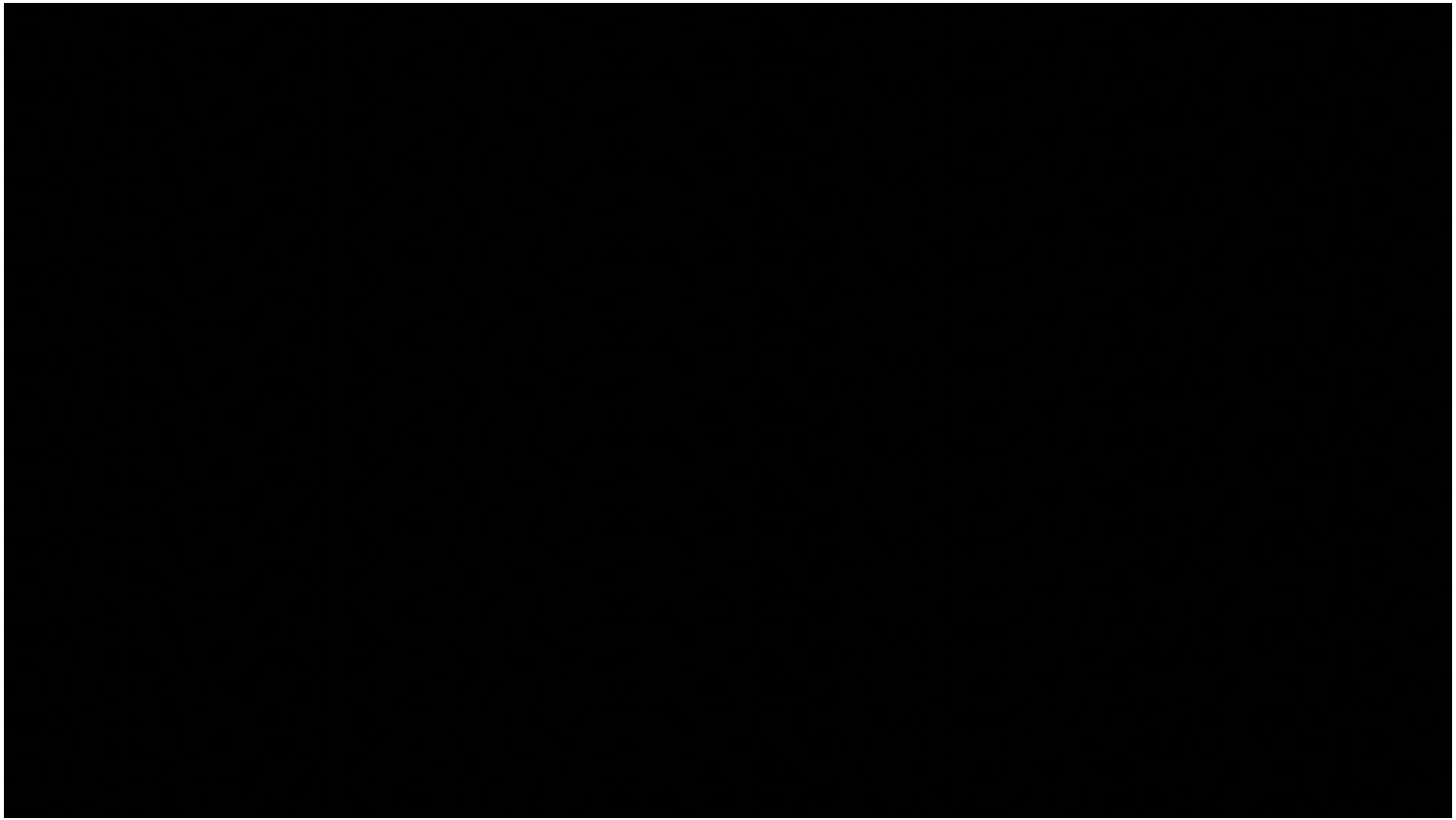




Water roll-off on a superhydrophobic C4-based fabric

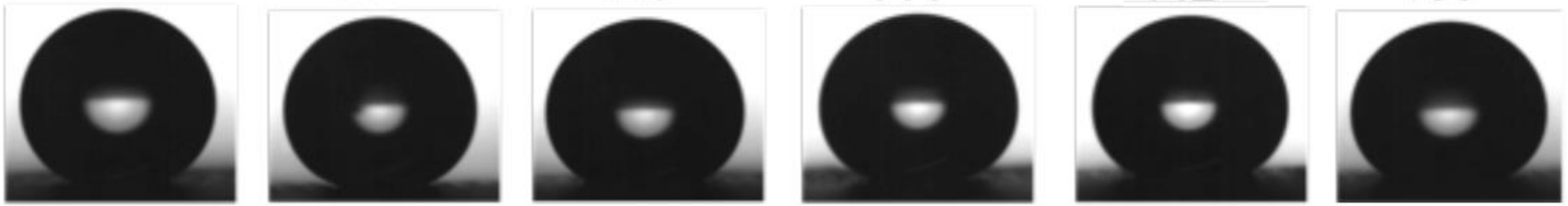


The short C4 perfluoroalkyl chains also lead to superoleophobicity

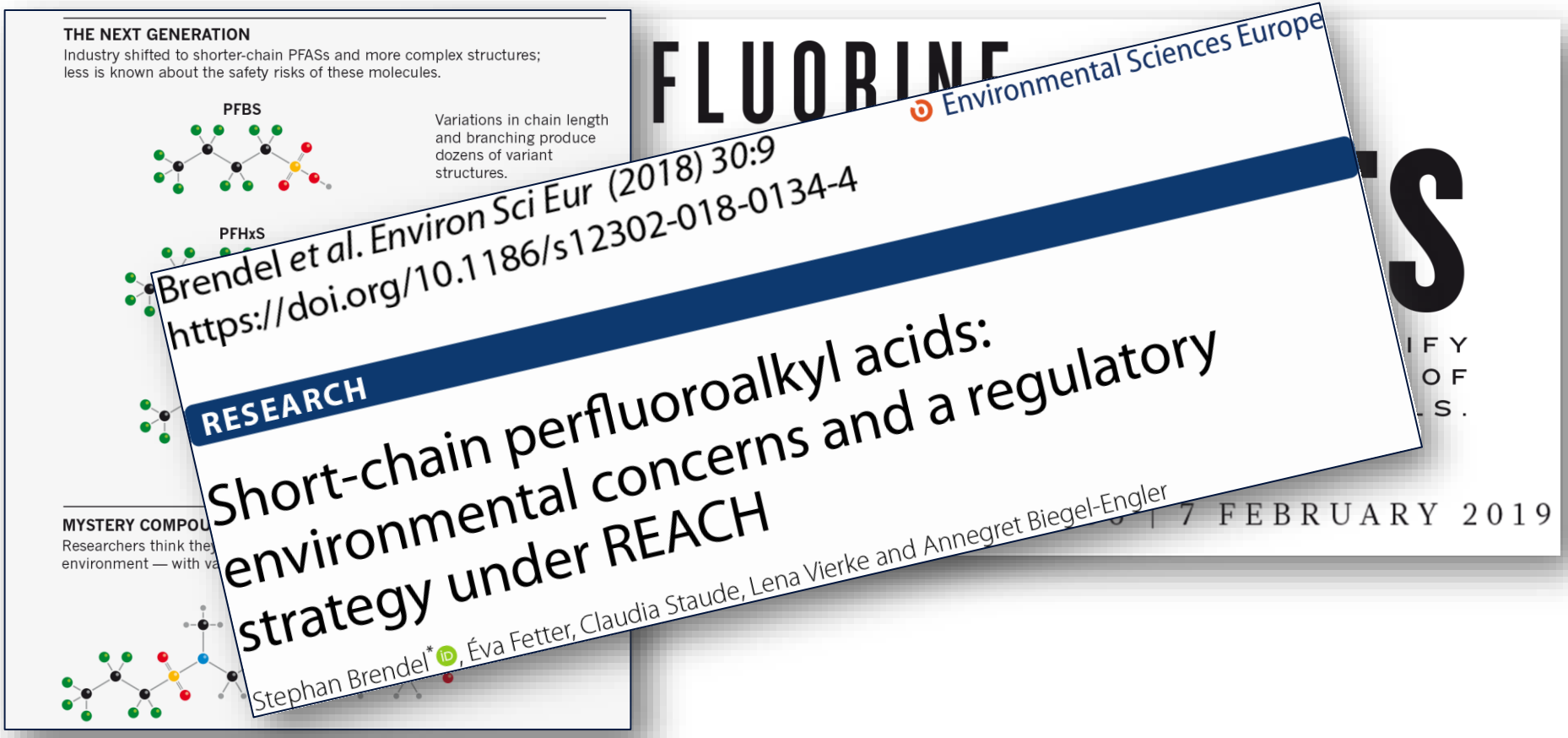


The short C4 perfluoroalkyl chains also provide resistance to some organic solvents

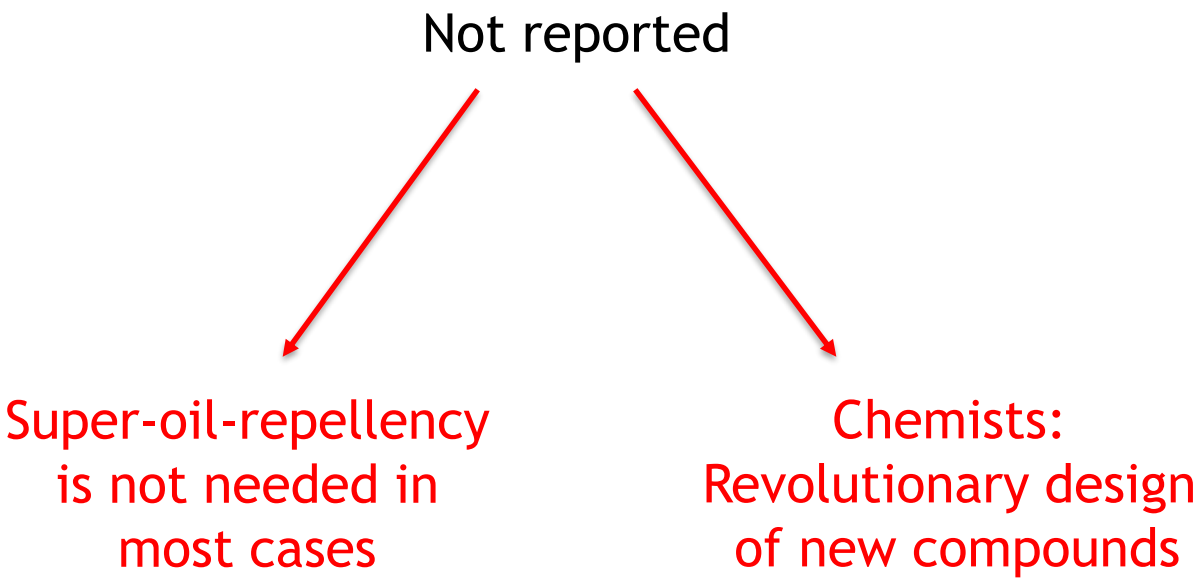
water	glycerol	ethylene glycol	olive oil	*n*-hexa-decane	*n*-dodecane
148°	151°	143°	144°	142°	139°



However, shorter perfluoroalkyl chains also raise concerns



Super-oil-repellency without fluorinated compounds



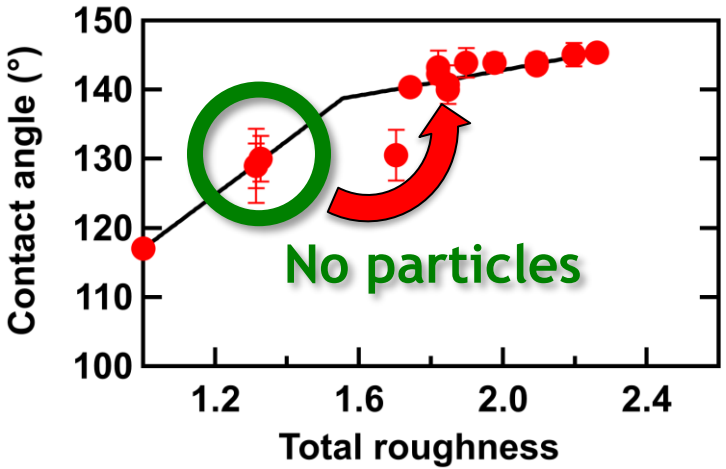
Step-by-step deposition of aqueous suspensions incorporating:

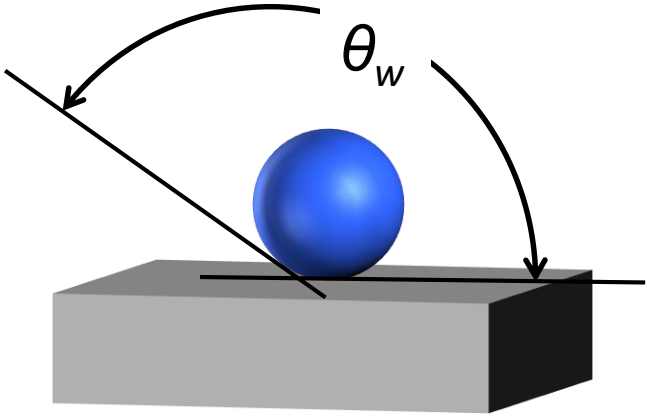
a crosslinked silicone rubber
(*HC303®, Wacker*)
+
Silica particles (*Tixosil®, Solvay)*

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

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

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





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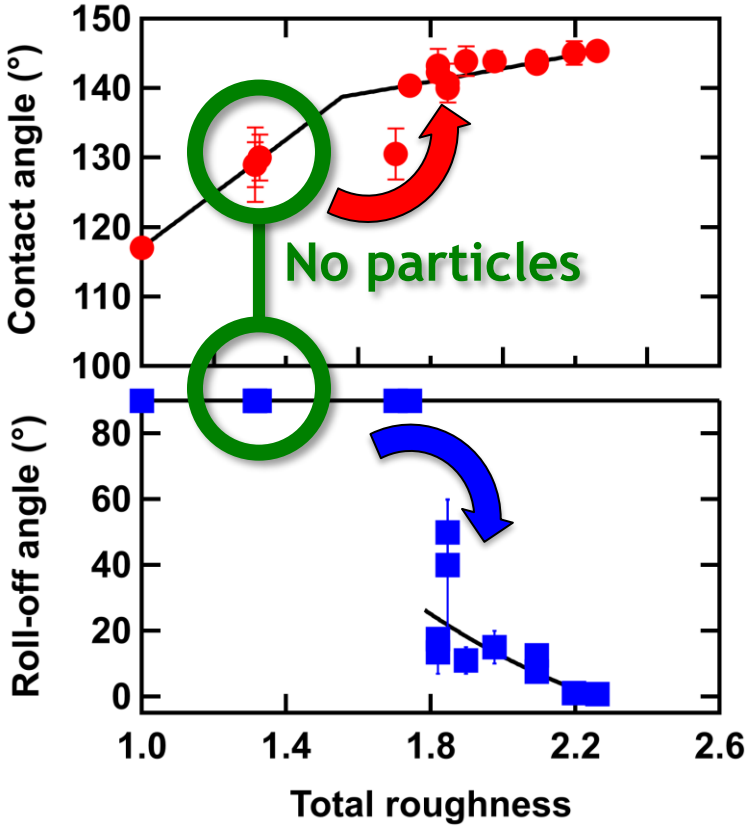
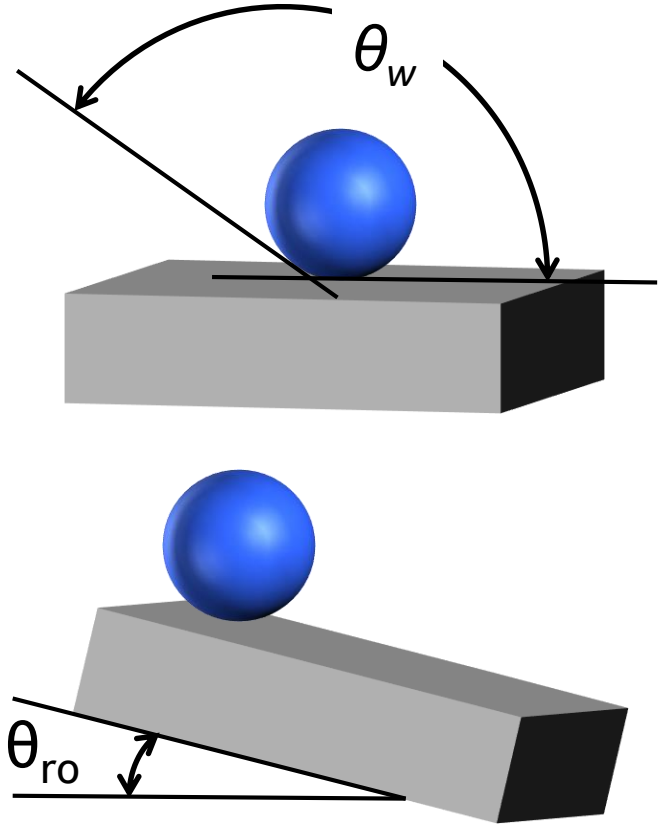
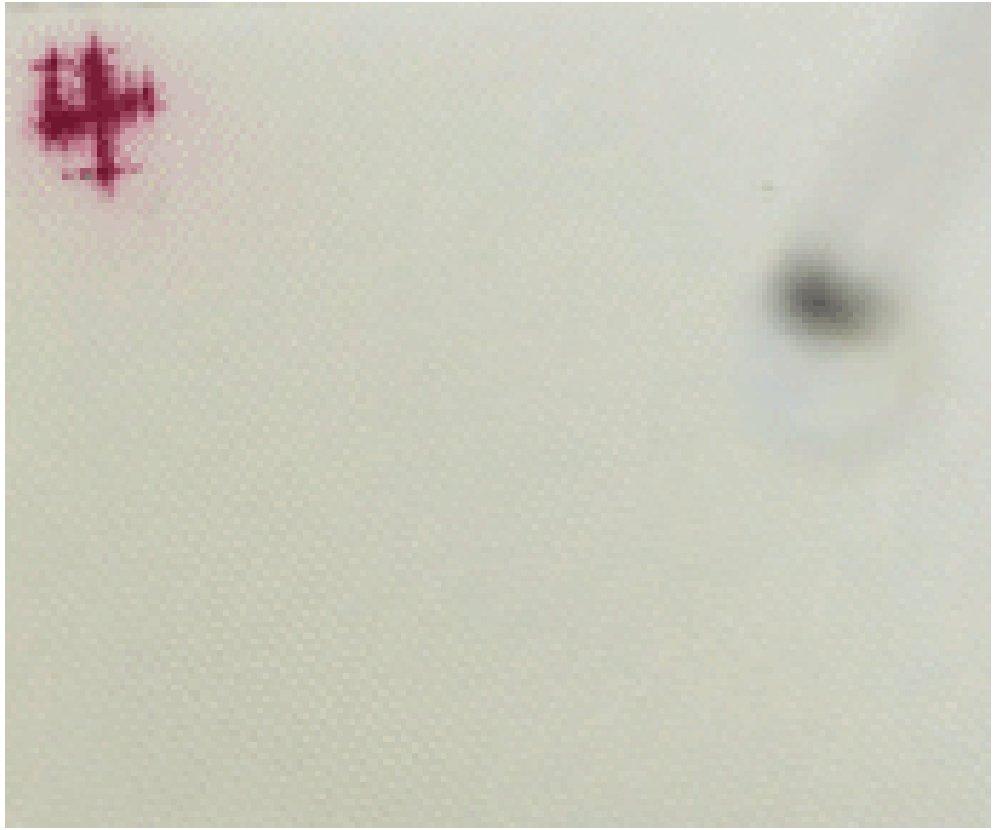




Water roll-off on a silicone-based superhydrophobic fabric



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

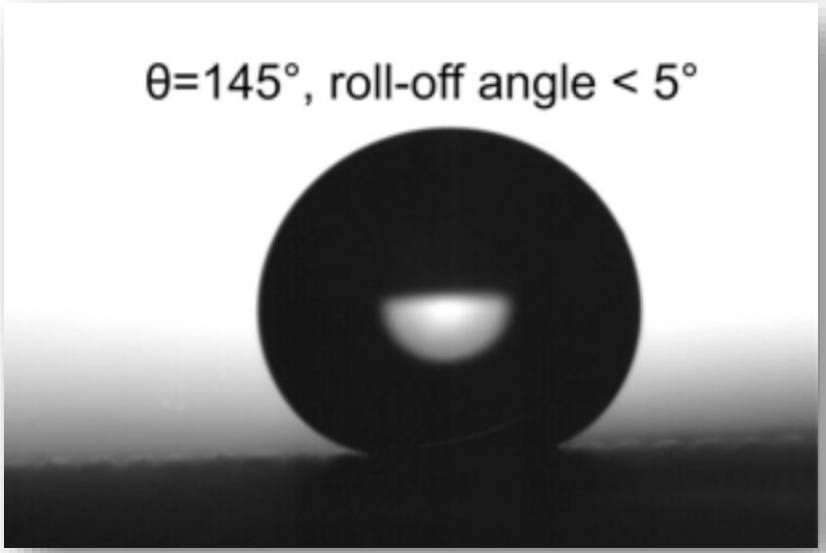
(ARTICLE 57D&E)

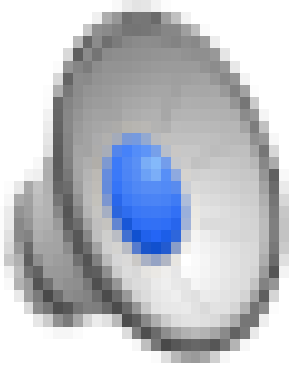
Adopted on 13 June 2018

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

Preliminary studies indicate wax-based alternatives to be promising

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





Main conclusions

1. Total roughness is a predictor of water repellent performance;
   other parameters may have to be considered

2. Total roughness $R = R_F \times R_f$

3. Fiber surface roughness can be boosted by silica particles;
   other methods certainly exist

4. Superhydrophobic fabrics can be obtained by using non-fluorinated compounds such as waxes and silicones , in combination with silica particles

5. Short perfluoroalkyl chains (C4) can be used to replace long ones to achieve super-water/oil-repellency, in combination with silica particles

Acknowledgments

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EUROPESE UNIE

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