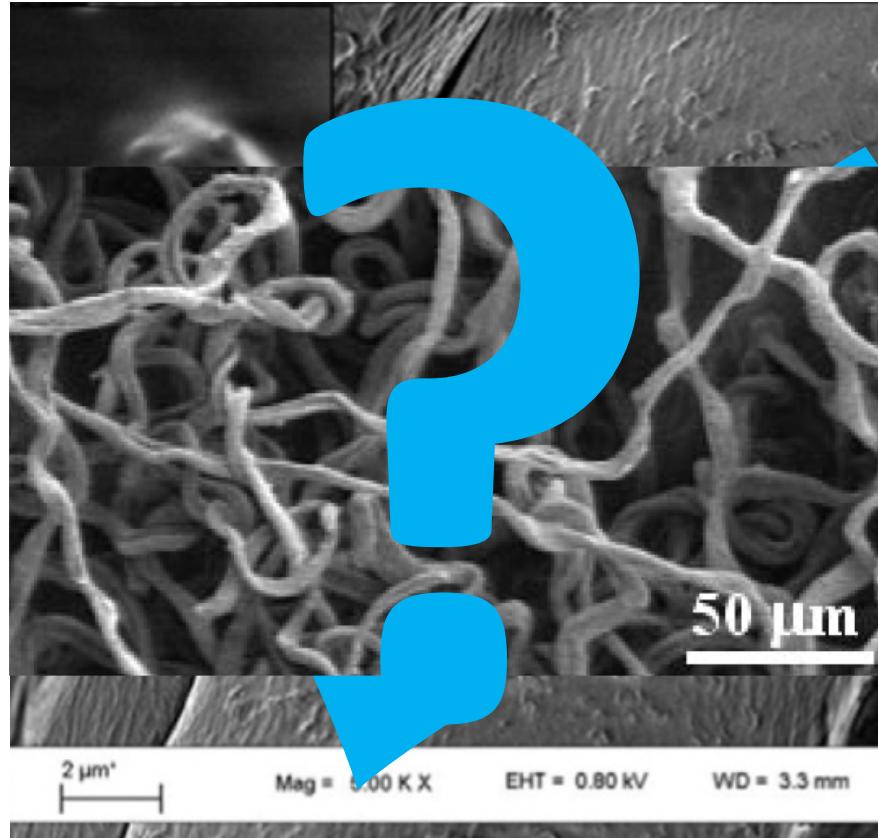


Greener Solutions to Fluorinated Durable Water Repellency

Marianna Augustine, Emily Cook, Erin Creel, Sumana
Raj, John Wright

December 5, 2017

Outline



Background

Eliminations

Improvables

Nanosols

Spinning

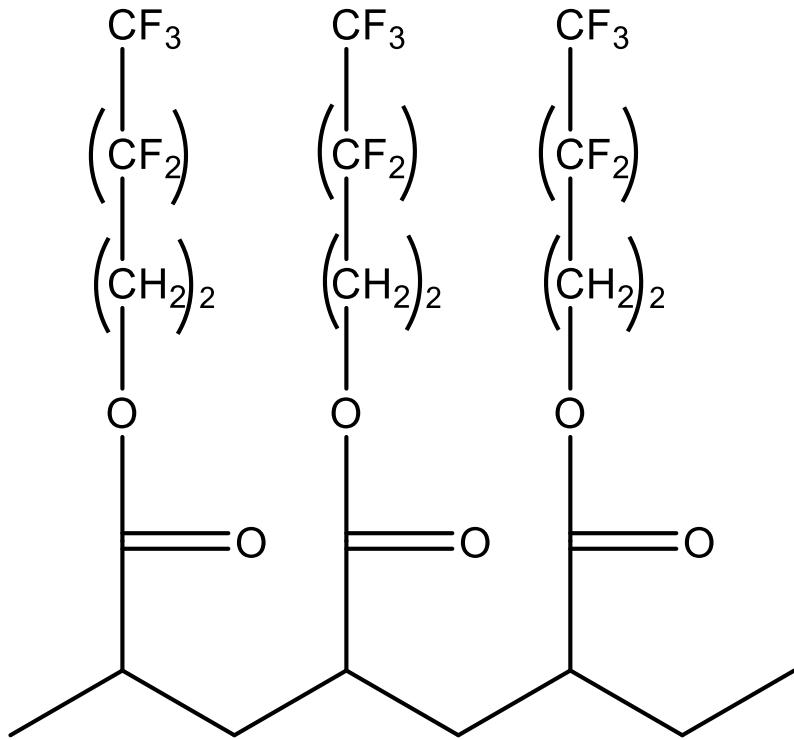
Conclusion

High demand for oleophobic and hydrophobic textiles

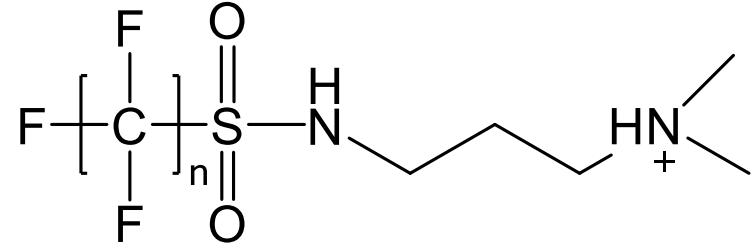


Durable water repellency (DWR) is best achieved using perfluorinated chemicals

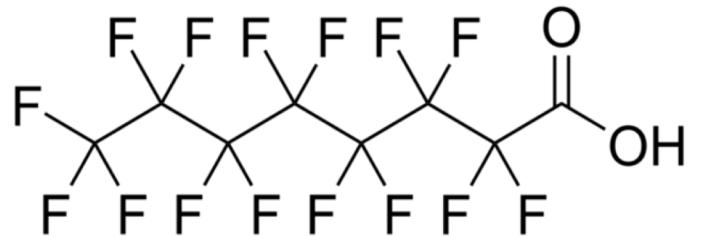
Effective DWR textiles currently require hazardous PFASs



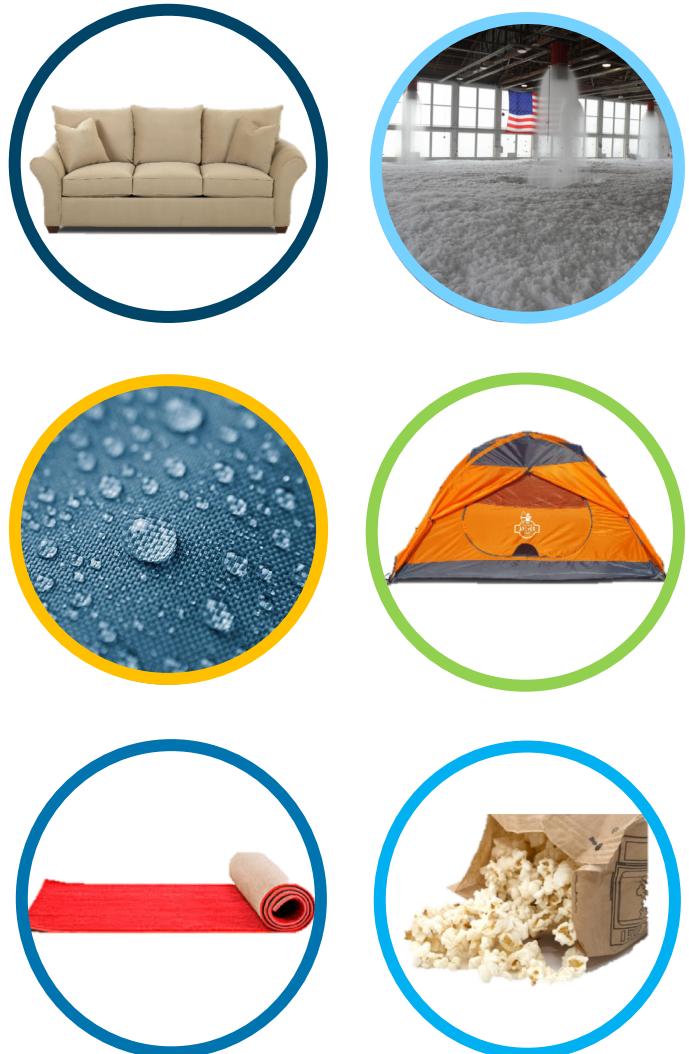
Fluoroacrylate Polymers



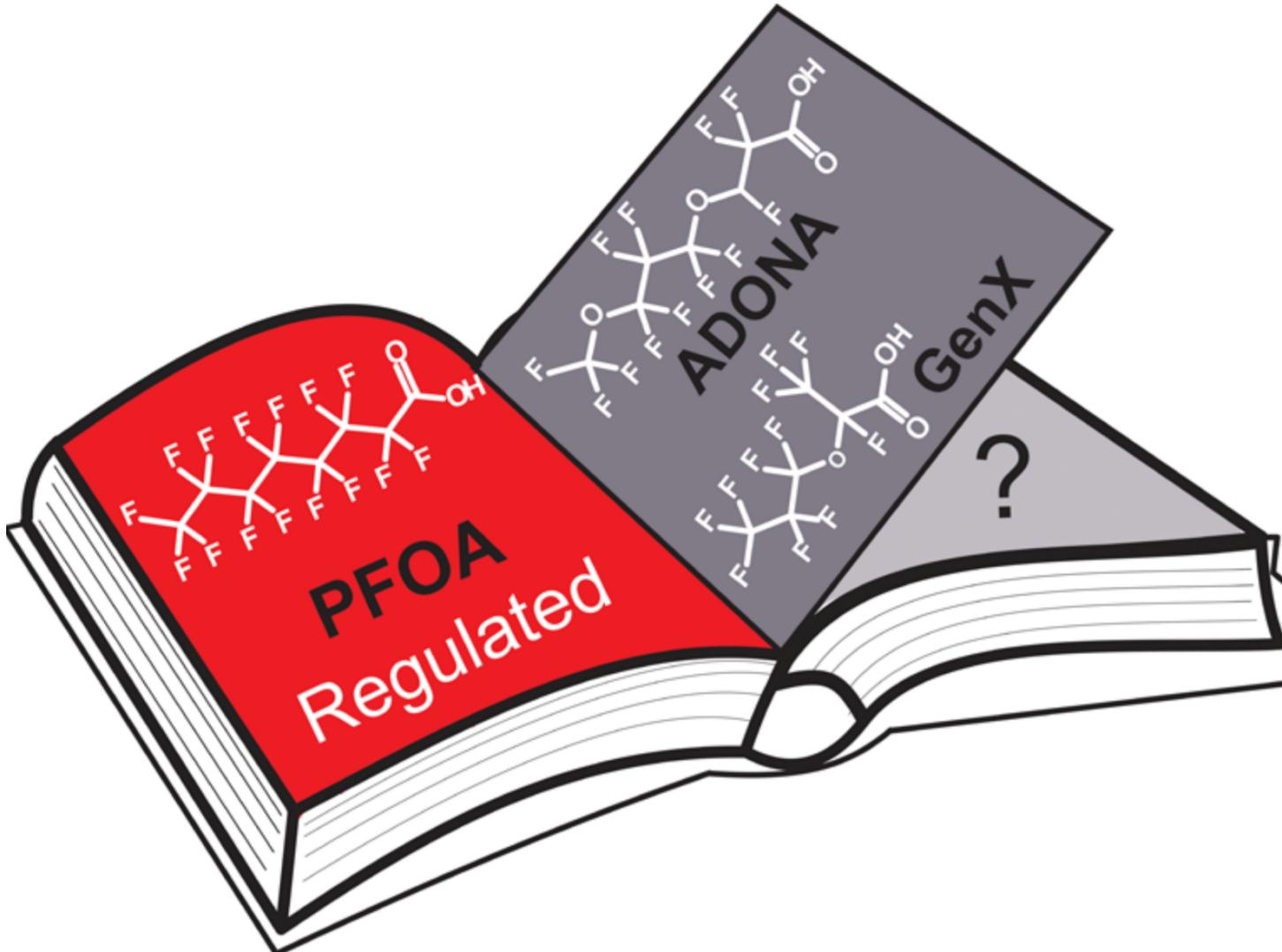
Polyfluorinated Alkyl Chain



Perfluorinated Alkyl Chain



Fluorinated definitions and current restrictions



Prohibited under Stockholm Convention:

S (an 8-carbon perfluorinated sulfonate)
S-F (an 8-carbon perfluorinated sulfonyl
ride)

Prohibited by the U.S. Environmental Protection Agency:

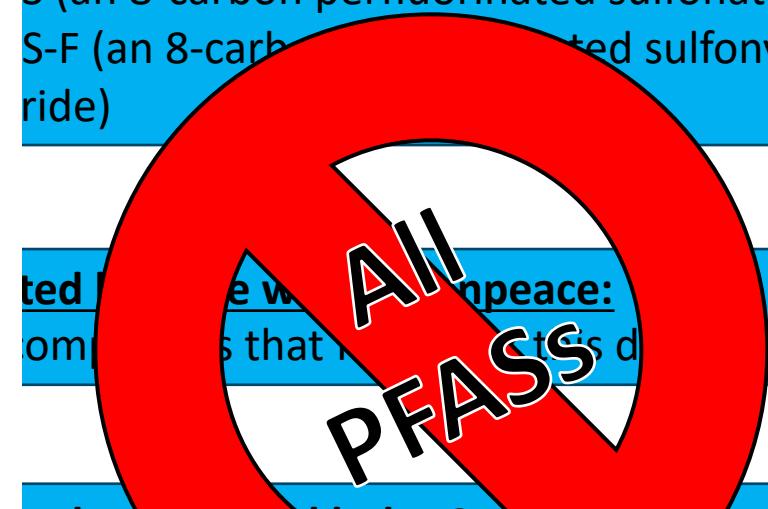
PFASs that are persistent, bioaccumulative, and toxic to human health or the environment

Prohibited under Stockholm Convention:

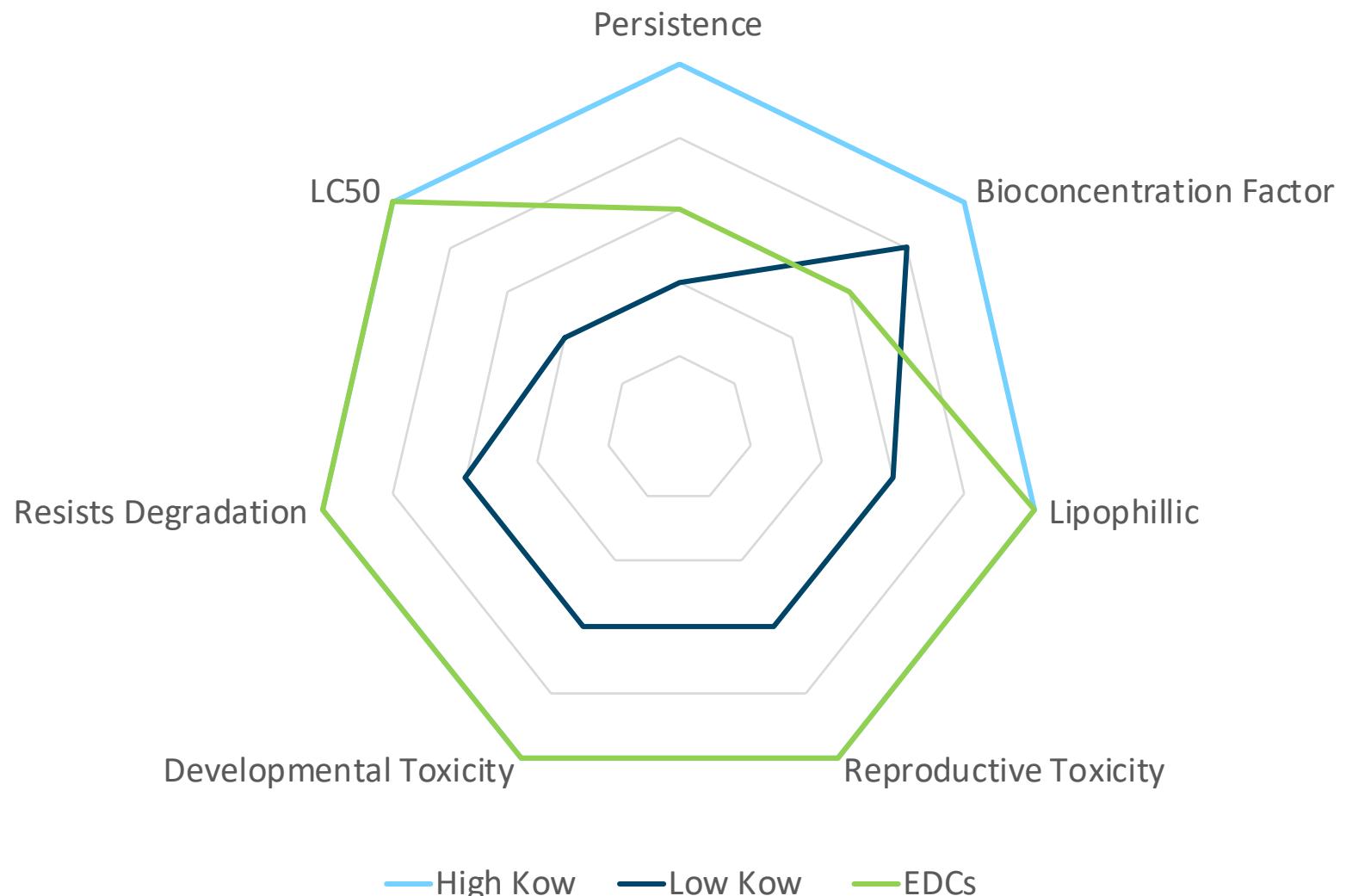
S (an 8-carbon perfluorinated sulfonate)
S-F (an 8-carbon perfluorinated sulfonyl
ride)

Regulated by EPA:

S – 70 ppt drinking water health advisory
A – 70 ppt drinking water health advisory

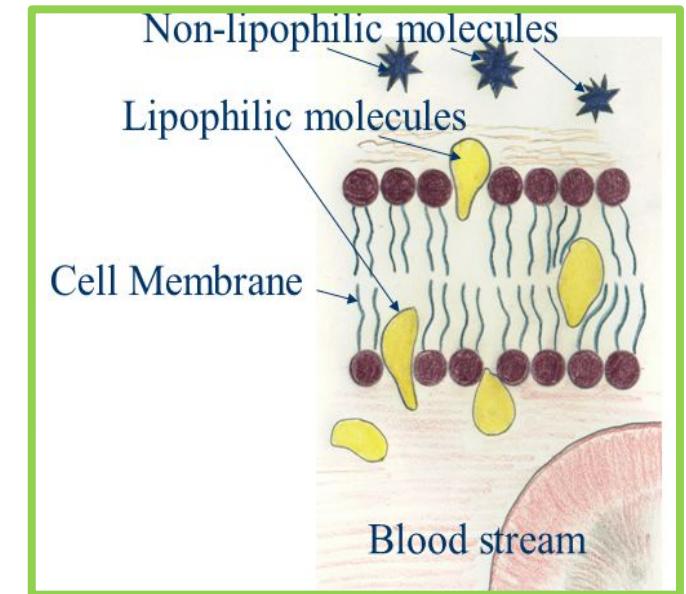


Fluorinated compounds are persistent



Lipophilic chemical classes:

PCBs, POPs, PAHs, flame retardants



PBT criteria: EPA, REACH

Hazard: High BCF

Background

Eliminations

Improvables

Nanosols

Spinning

Conclusion

PFASs hazards

| Human Toxicity | | | | Environmental Toxicity | | | |
|--|---|---|-----------------------------|--|--|---|----------------------|
| Mutagenicity | Organ | Respiratory | Reproductive | Persistence | Aquatic | Fate | |
| PFOA 8-carbon perfluorinated alkyl chain | Kidney, breast, and testicular cancer | High cholesterol; liver, kidney, heart, blood toxicant | Some airway inflammation | <i>Reproductive and developmental toxicity</i> | Bio-accumulation; persistent organic pollutant | <i>Fish and invertebrate toxicity</i> | Not biodegradable |



**Italics: based on animal studies*

Criteria for greener alternatives

Hydrophobicity

Oleophobicity

Durability & Washability

Appearance & Feel



Criteria for greener alternatives

Hydrophobicity

PFAS performance:

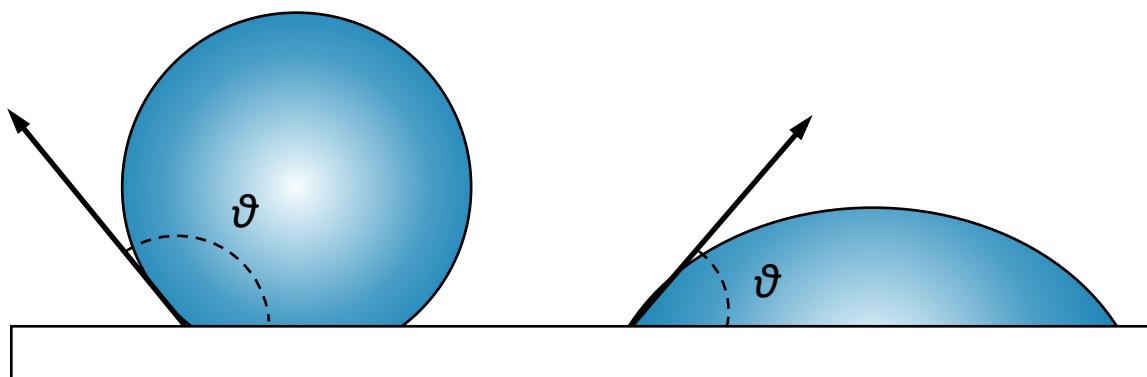
Static: 118°

Metrics:

Static contact angle (CA)

High CA (phobic)

Low CA (philic)



Criteria for greener alternatives

Hydrophobicity

Gore goals:

Advancing > 115°

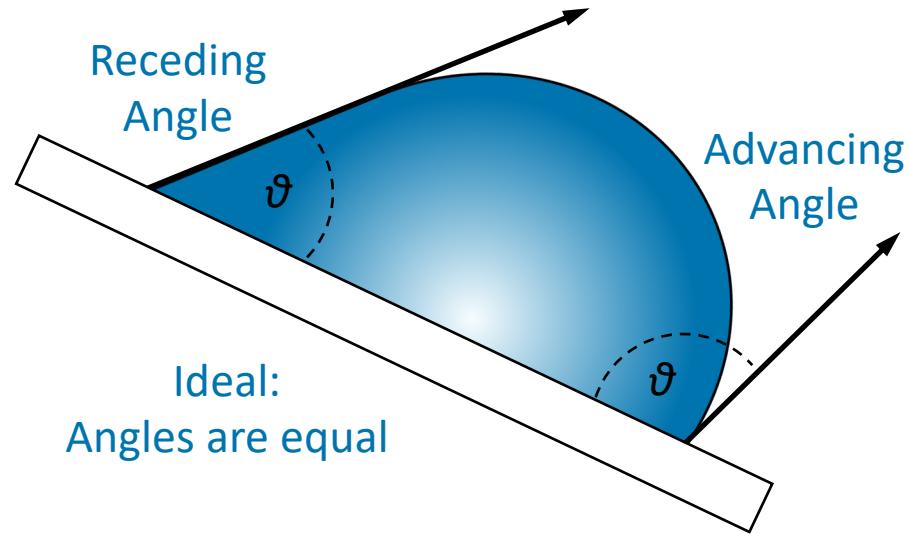
Receding > 95°

PFAS performance:

Static: 118°

Metrics:

Dynamic contact angles



Contact angle hysteresis

Advancing angle – Receding angle

Ideal: 0

Criteria for greener alternatives

Hydrophobicity

Gore goals:

Advancing > 115°

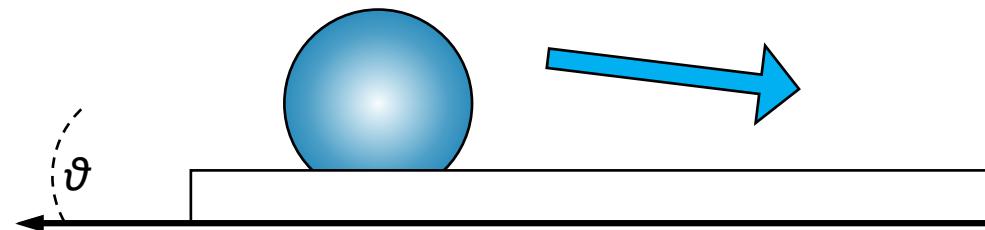
Receding > 95°

PFAS performance:

Static: 118°

Metrics:

Roll-off angle



Criteria for greener alternatives

Hydrophobicity

Oleophobicity

Gore goals:

Advancing > 115°

Receding > 95°

PFAS performance:

Static: 118°

Gore goals:

No penetration of high surface tension oils for 30 s

Proxy: oil contact angle

PFAS performance:

n-heptane: 40°

n-hexadecane: 70°

Criteria for greener alternatives

Hydrophobicity

Gore goals:

Advancing > 115°
Receding > 95°

PFAS performance:

Static: 118°

Oleophobicity

Gore goals:

No penetration of high surface tension oils for 30 s
Proxy: oil contact angle

PFAS performance:

n-heptane: 40°
n-hexadecane: 70°

Durability & Washability

Gore goals:

Resist 20 laundry wash cycles with detergent

PFAS performance:

Meets requirements

Criteria for greener alternatives

Hydrophobicity

Gore goals:

Advancing > 115°
Receding > 95°

PFAS performance:

Static: 118°

Oleophobicity

Gore goals:

No penetration of high surface tension oils for 30 s
Proxy: oil contact angle

PFAS performance:

n-heptane: 40°
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Durability & Washability

Gore goals:

Resist 20 laundry wash cycles with detergent

PFAS performance:

Meets requirements

Appearance & Feel

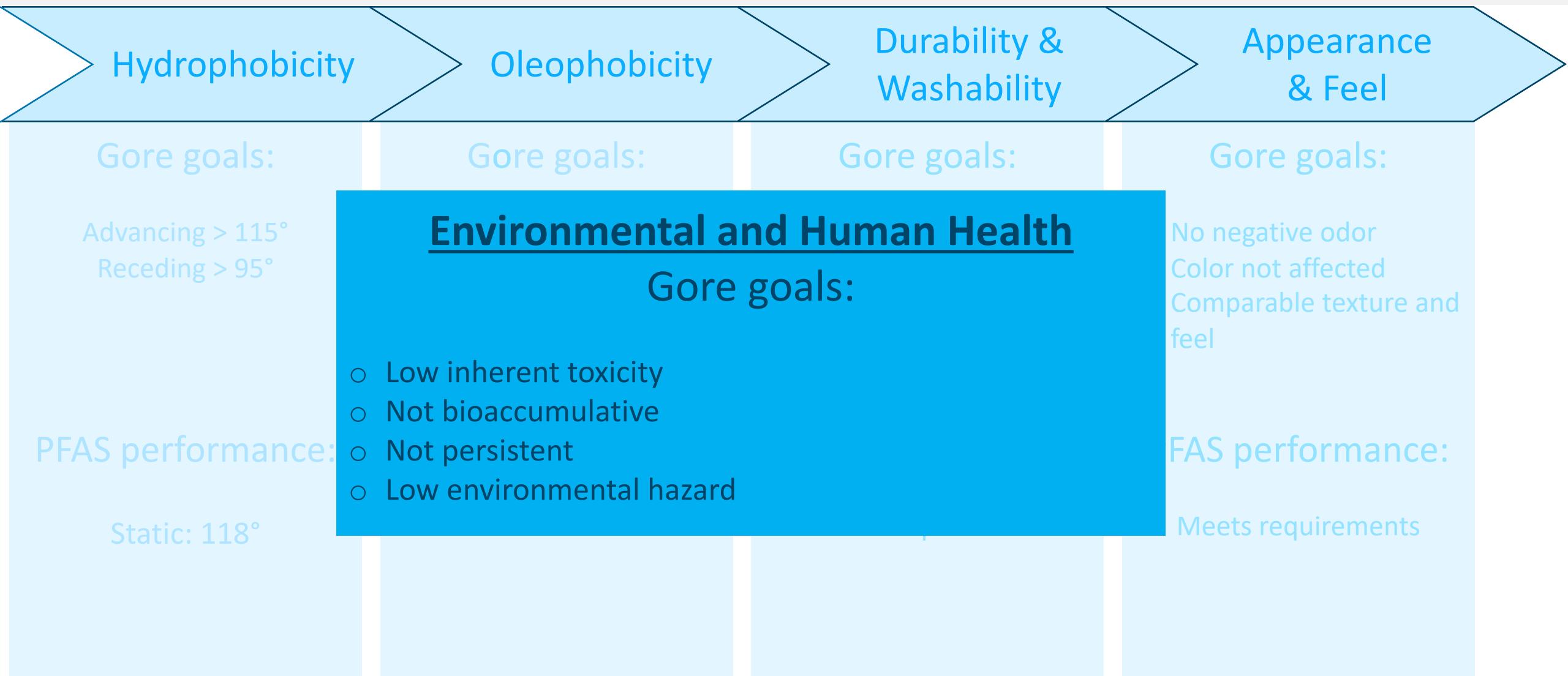
Gore goals:

- No negative odor
- Color not affected
- Comparable texture and feel

PFAS performance:

Meets requirements

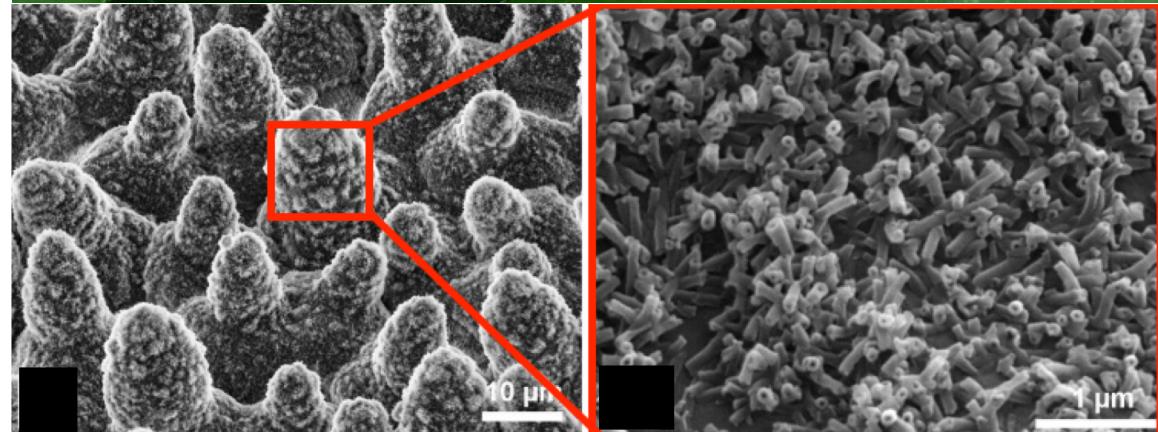
Criteria for greener alternatives



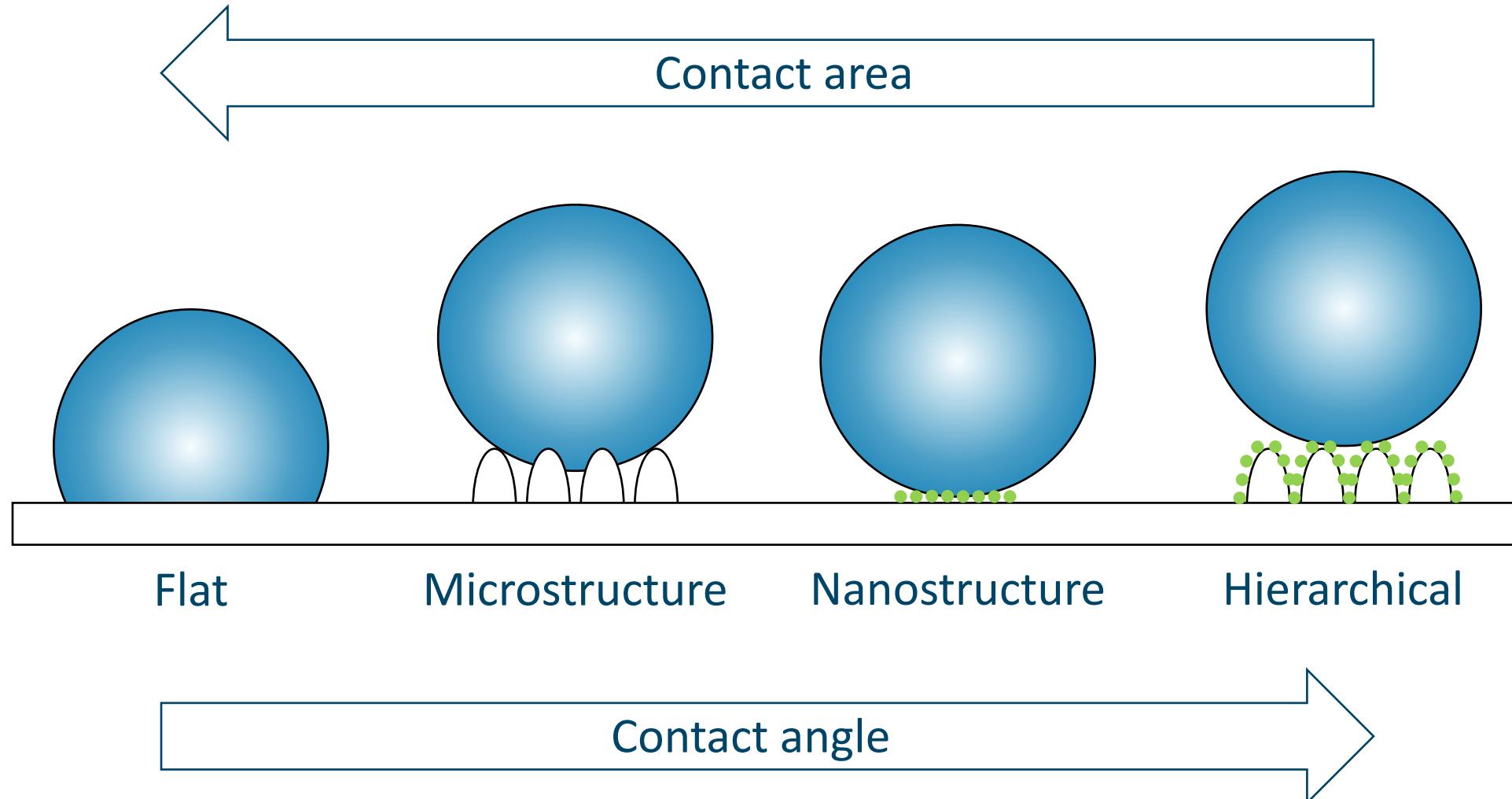
Looking to nature for inspiration

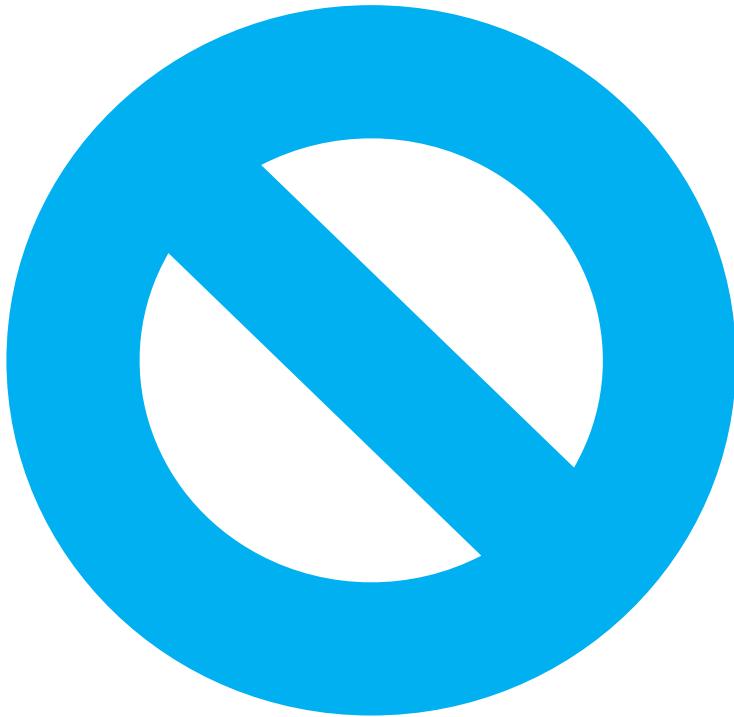


Darmanin et al. Materials Today (2015).



Hierarchical structures for improved phobicity





Background

Eliminations

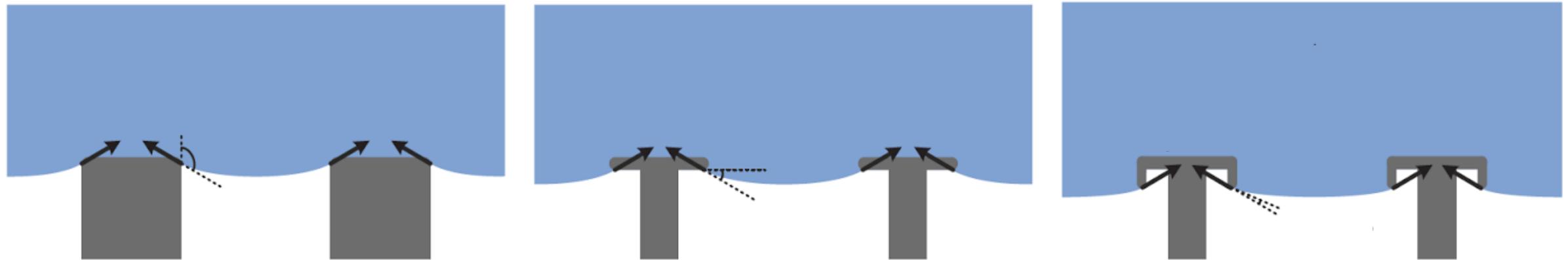
Improvables

Nanosols

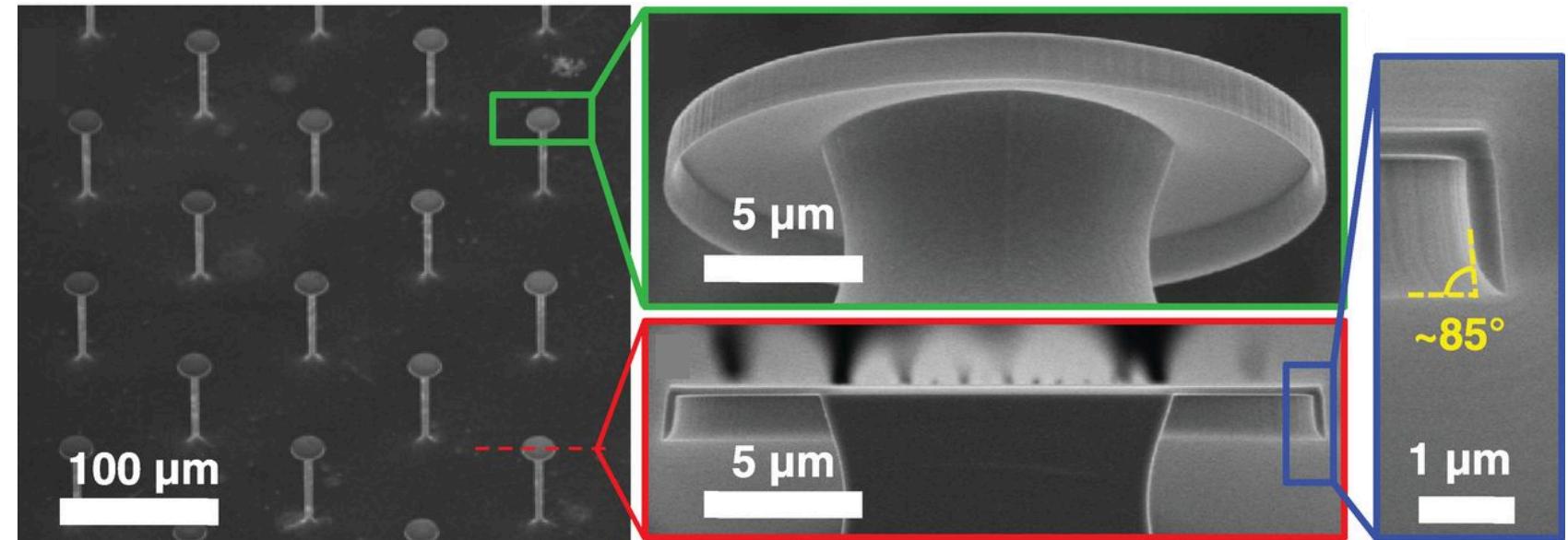
Spinning

Conclusion

Lithography and 3D printing are impractical

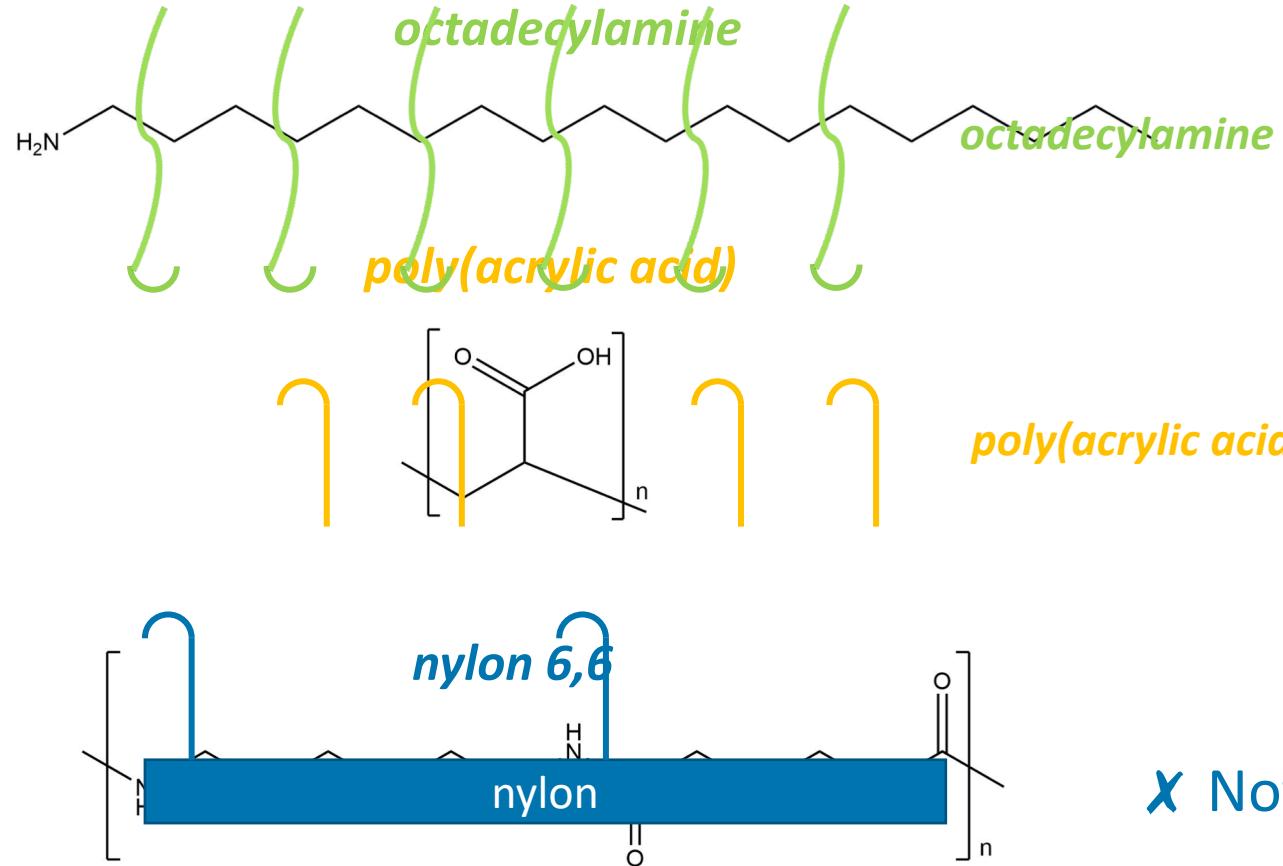


- ✓ Omniphobic
- ✓ No fluorinated compounds
- ✗ Expensive
- ✗ Easily damaged

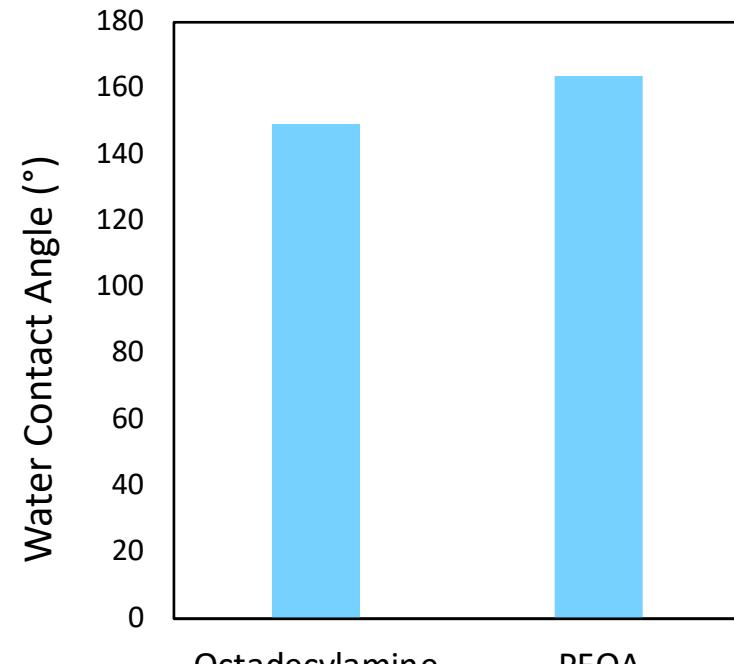
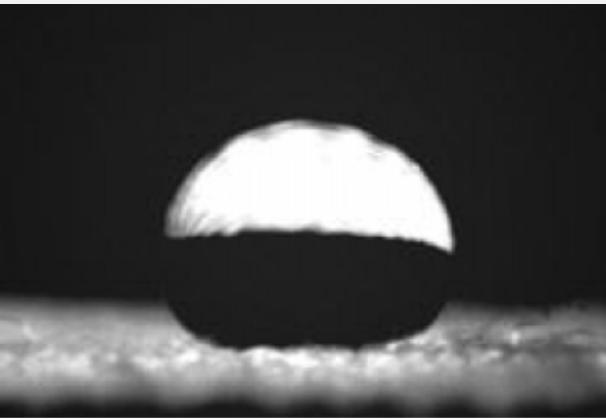


Liu et al. Science (2014).

Graft hydrophobic functional groups on nylon



✗ Not oleophobic



Michielsen et al. Langmuir (2007).

Background

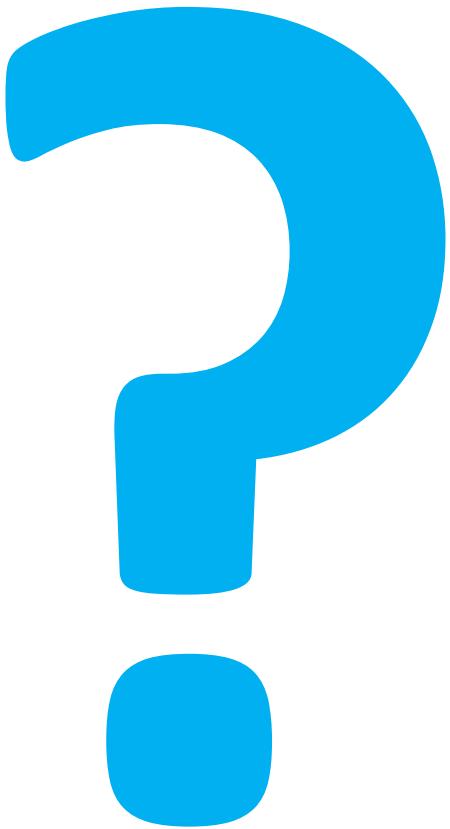
Eliminations

Improvables

Nanosols

Spinning

Conclusion



Background

Eliminations

Improvables

Nanosols

Spinning

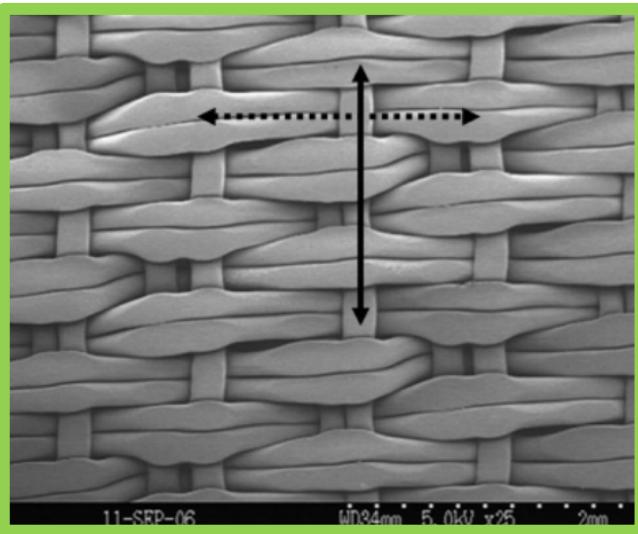
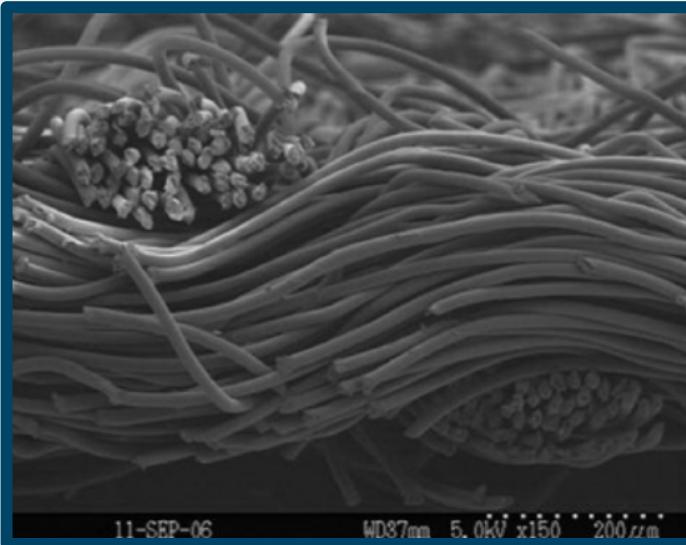
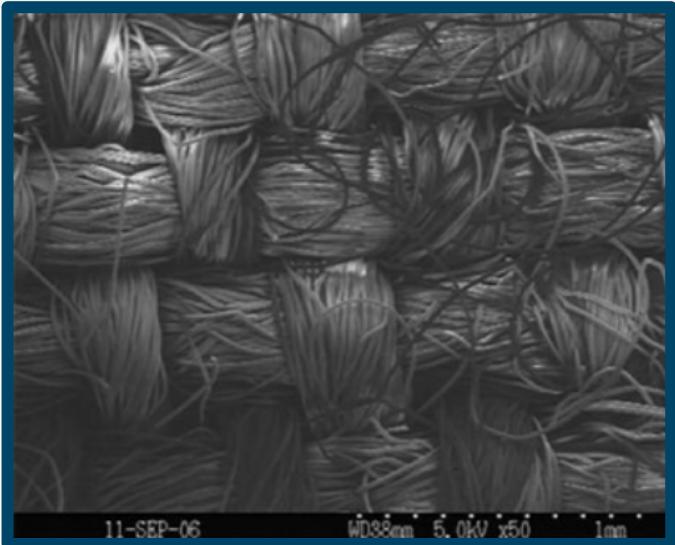
Conclusion

Choice of fabric substrate

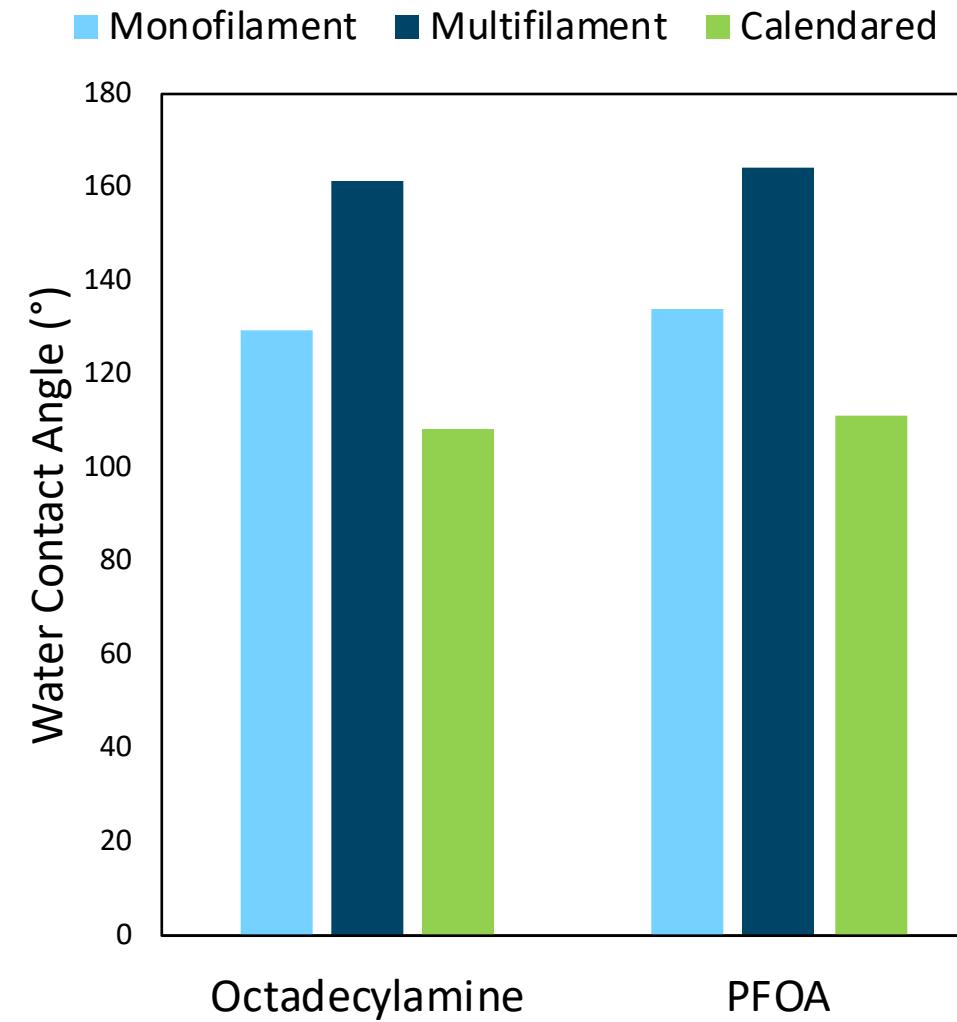
| Textile | Hydrophobic |
|-----------------------------------|-------------|
| Cellulosic fibers (cotton, rayon) | X |
| Protein fibers (wool, silk) | X |
| Spandex | X |
| Nylon | moderately |
| Vinyl fibers (vinyon, saran) | |
| Polyolefin | |
| Polyester | |

X Not oleophobic

Multifilament yarns improve hydrophobicity through texturing



✗ Not oleophobic



Michielsen et al. Langmuir (2007).

Background

Eliminations

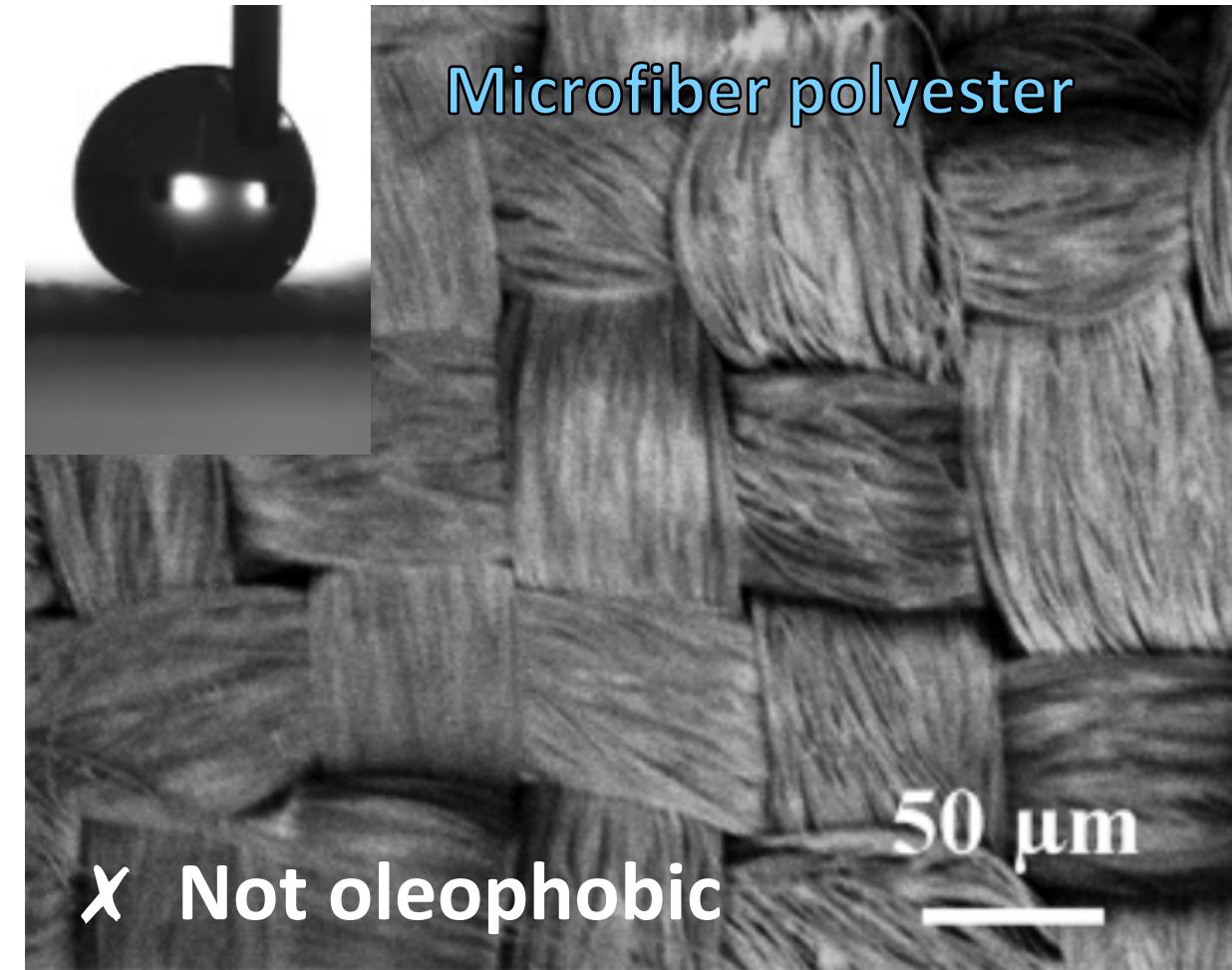
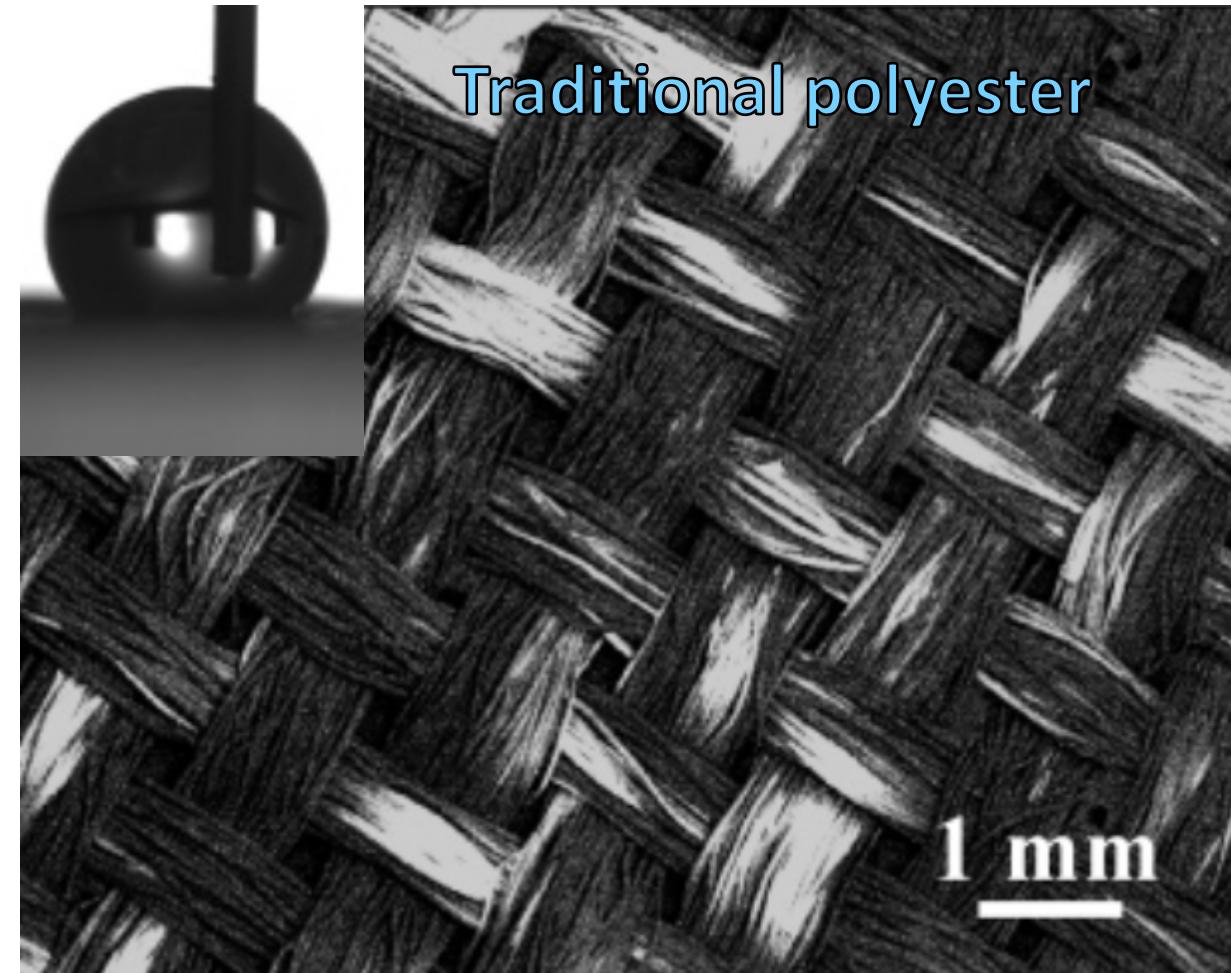
Improvables

Nanosols

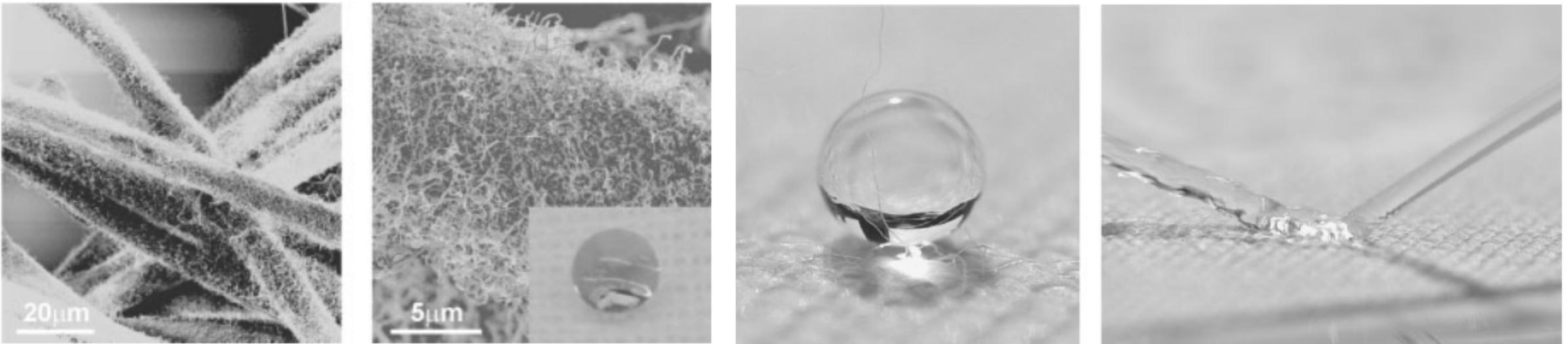
Spinning

Conclusion

Microfiber improves hydrophobicity



Silicone nanofilaments



- ✓ Hydrophobicity
- ✓ Handle
- ✓ Color



Water contact
angle after
washing

- ✗ Washability
- ✗ Oleophobicity

Background

Eliminations

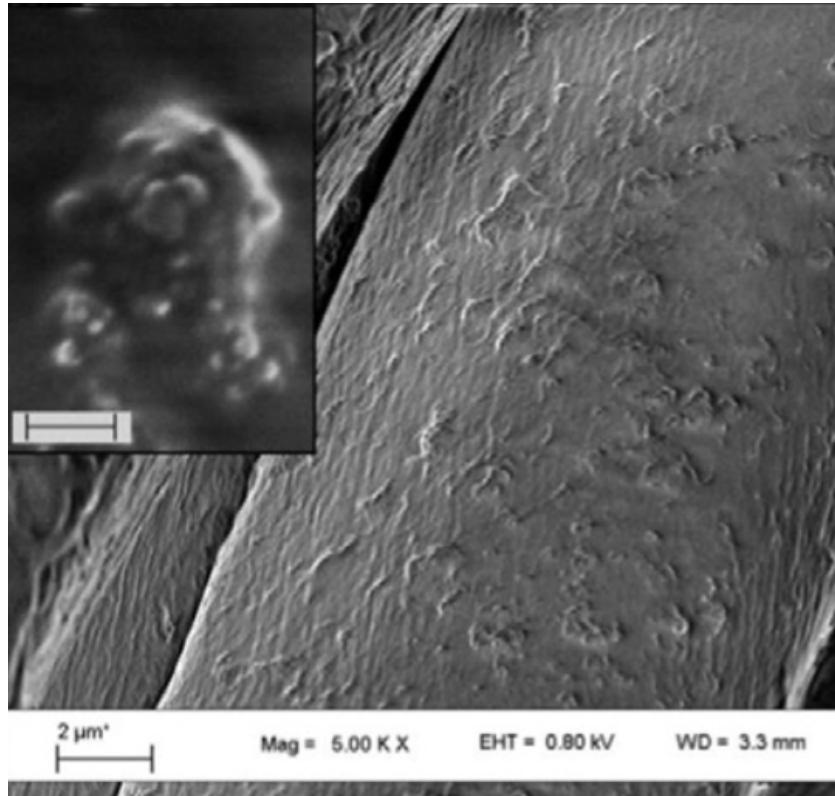
Improvables

Nanosols

Spinning

Conclusion

Zimmermann et al. Adv. Funct. Mater. (2008).



Background

Eliminations

Improvables

Nanosols

Spinning

Conclusion

Silica nanosols provide nanotexture

SiO_2 nanoparticles or precursor

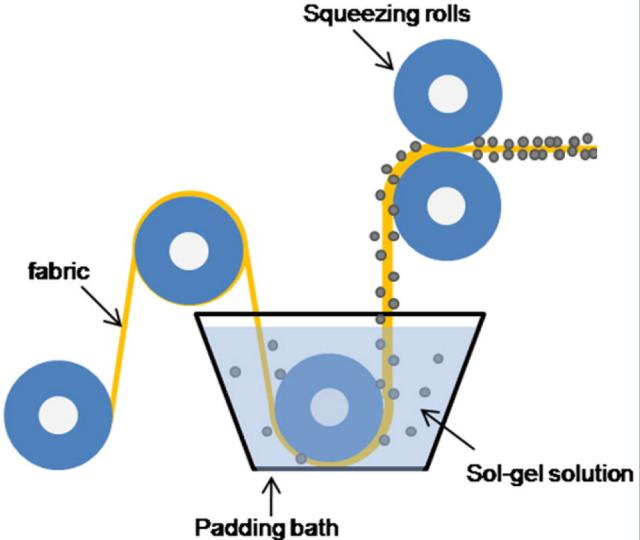


organosilanes

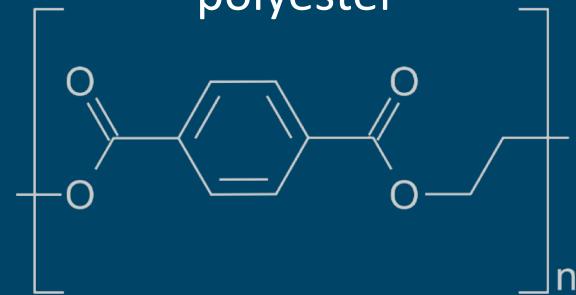


water

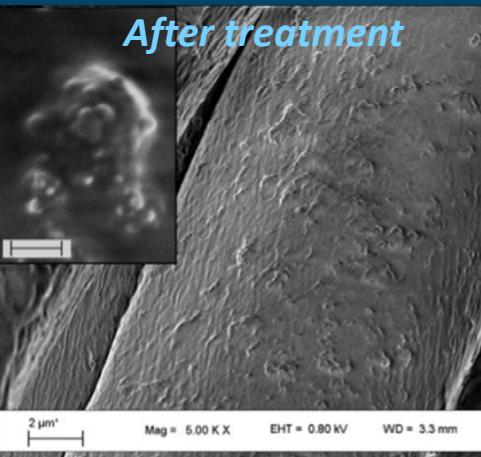
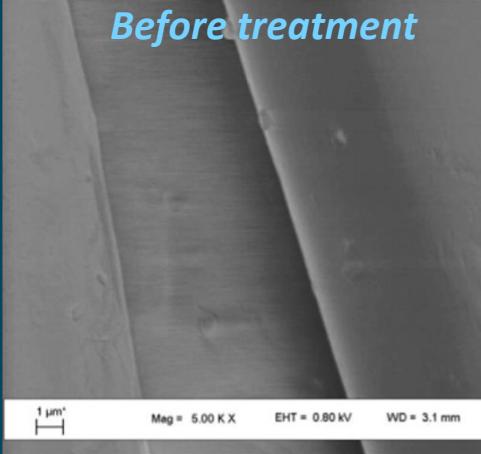
Dip and nip application



Polyester



Texturized fabric



Zhao et al. Materials and Design (2016).

Background

Eliminations

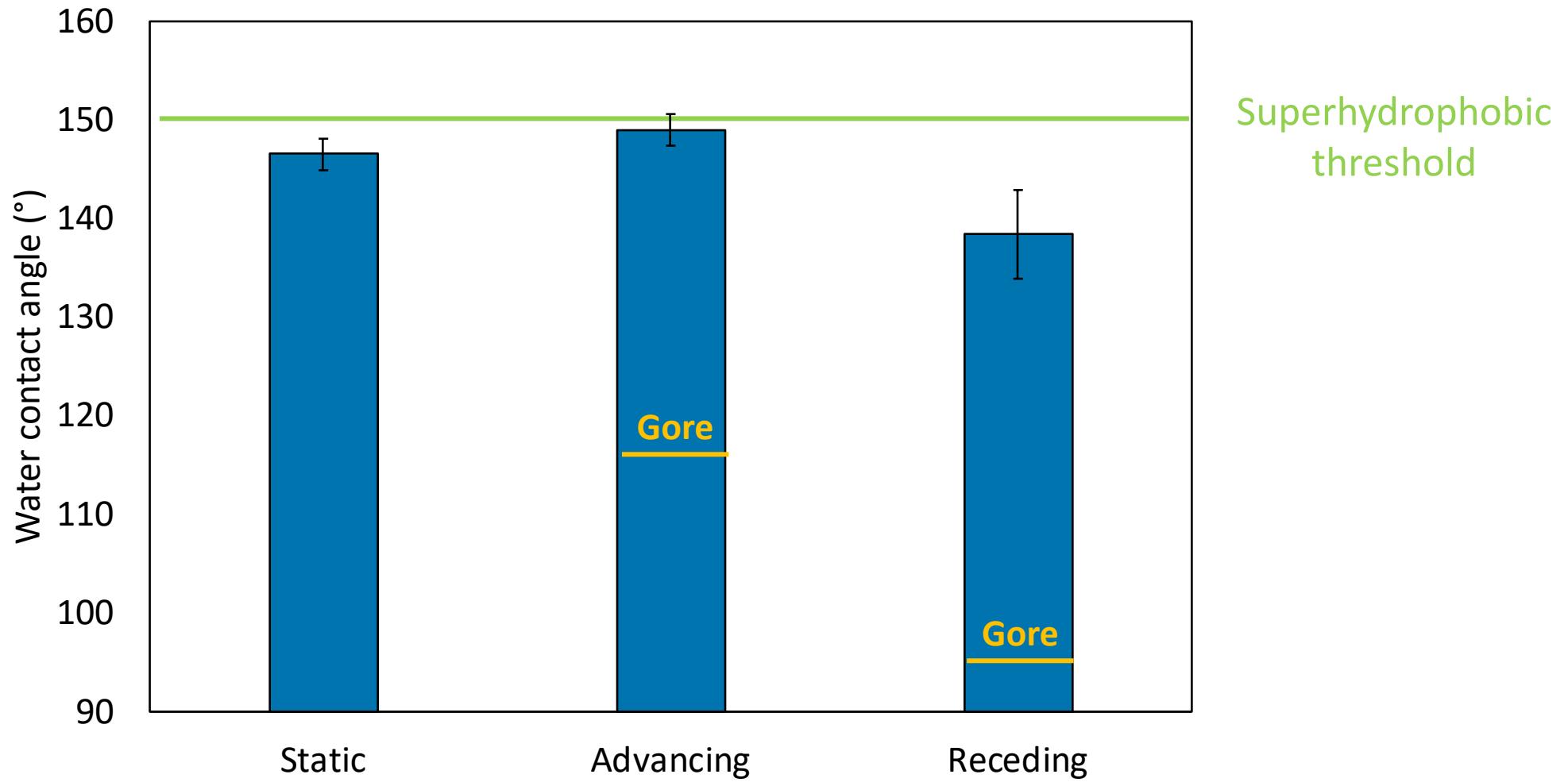
Improvables

Nanosols

Spinning

Conclusion

Silica nanosols are highly hydrophobic on polyester



Zhao et al. Materials and Design (2016).

Background

Eliminations

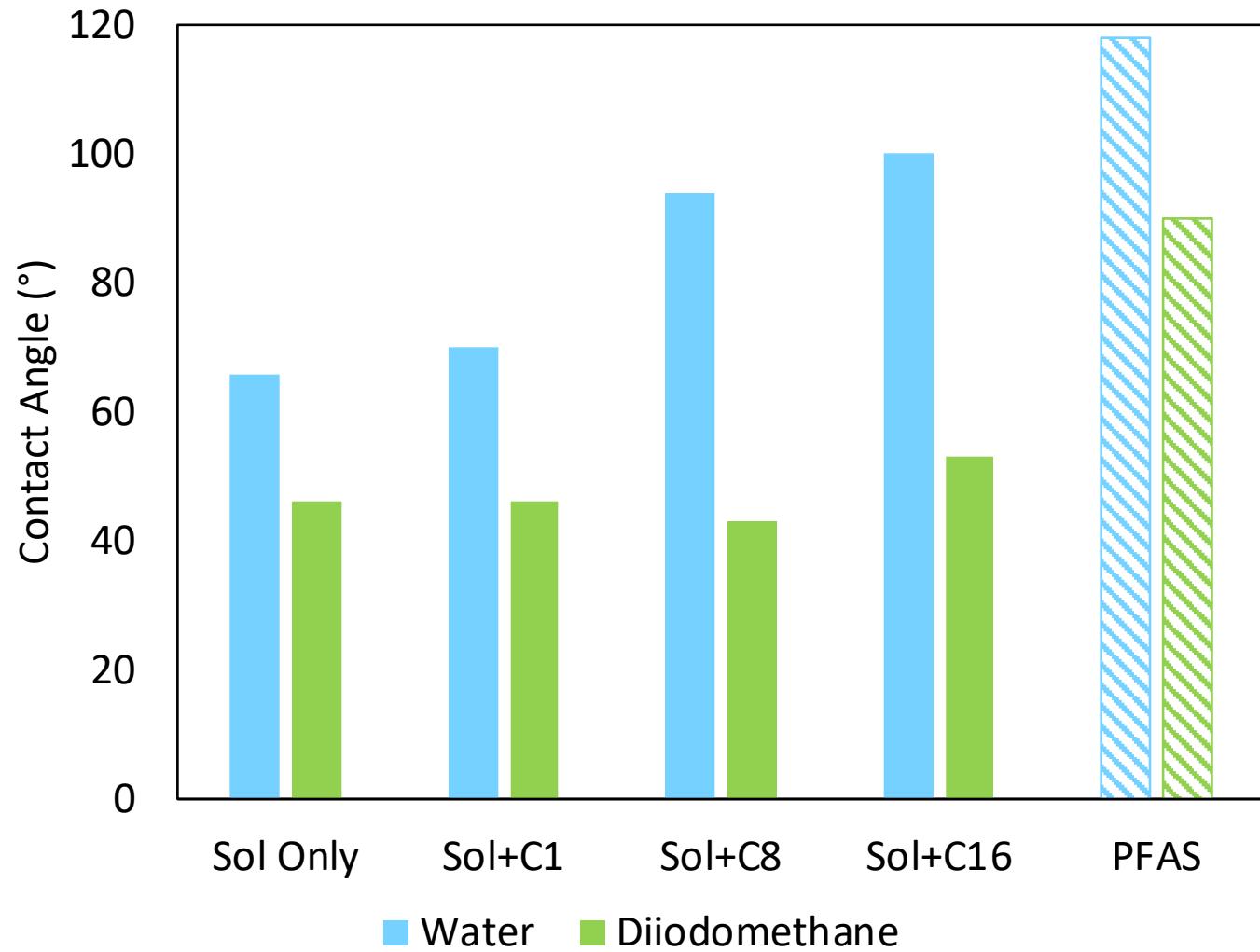
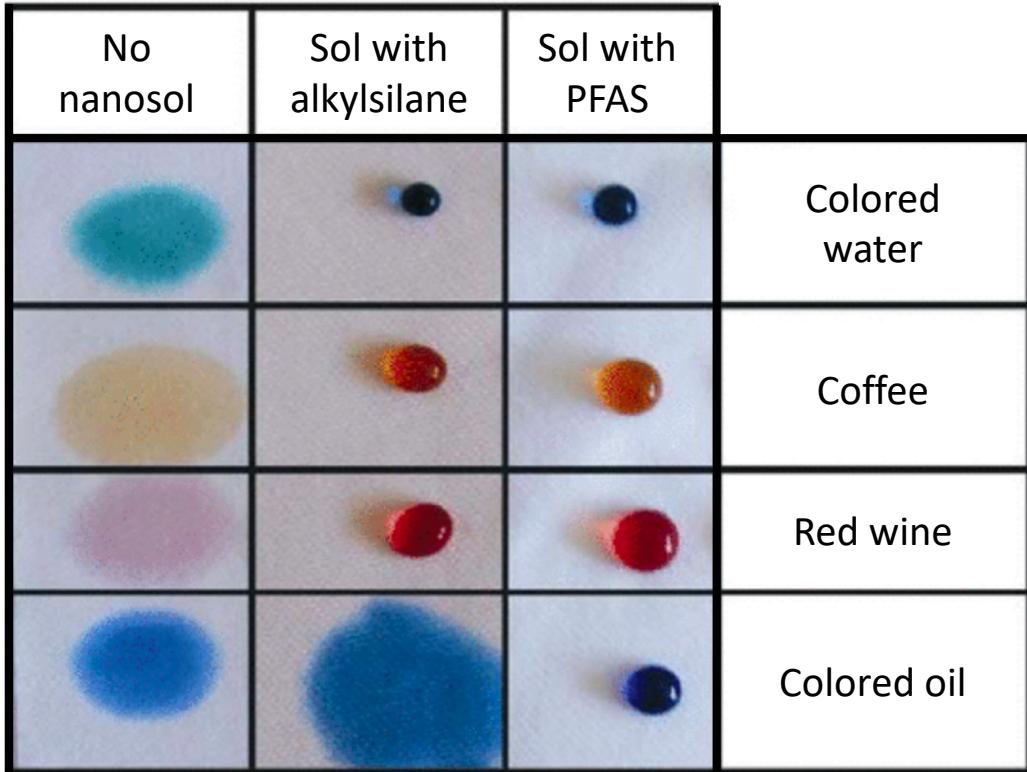
Improvables

Nanosols

Spinning

Conclusion

Organosilanes have poor oleophobicity



Mahltig et al. Nanosols and Textiles (2008).

Background

Eliminations

Improvables

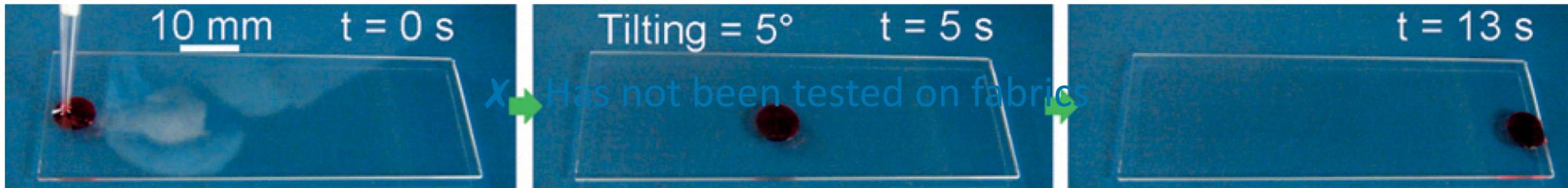
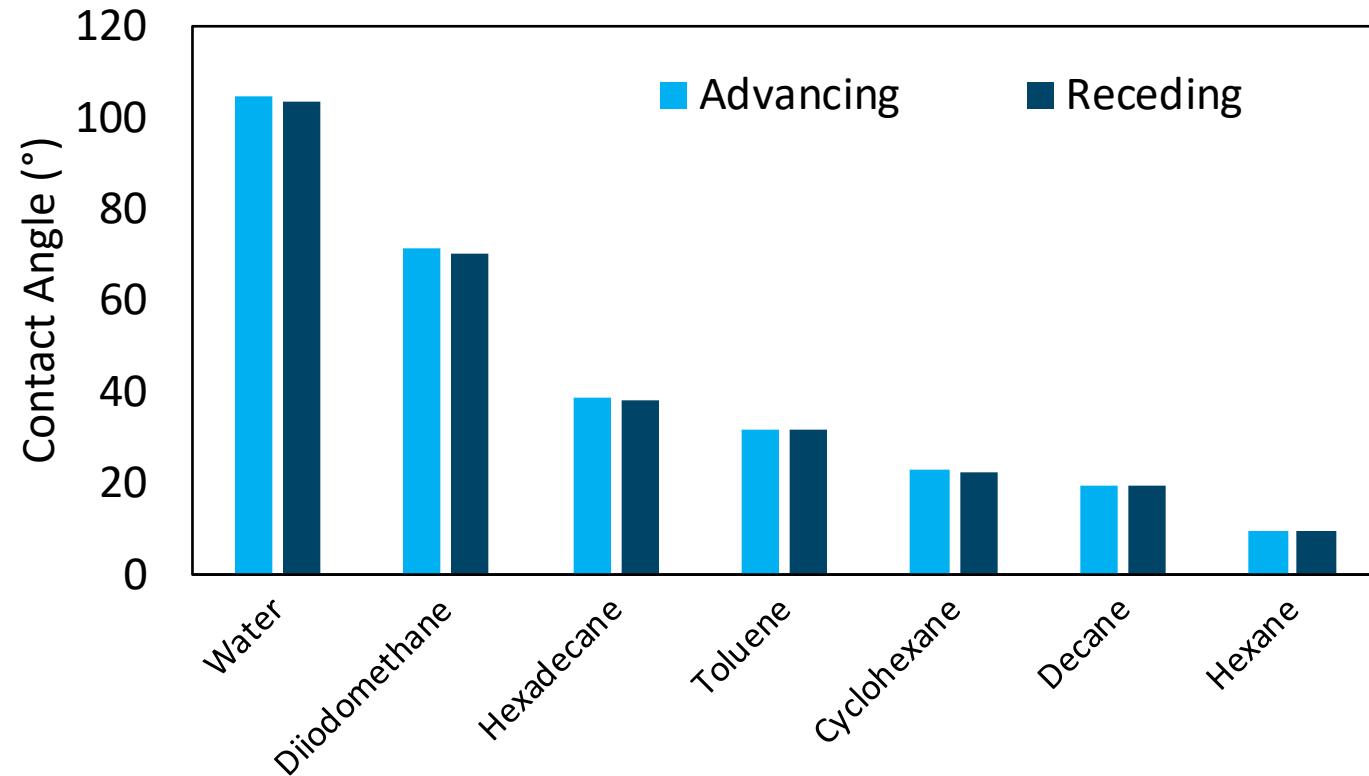
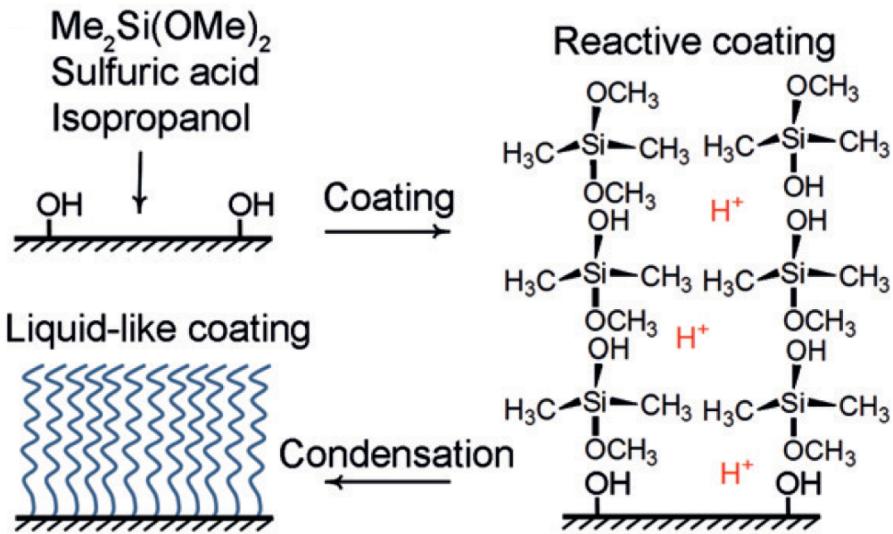
Nanosols

Mahltig et al. J. Sol-Gel Sci. and Tech 27, 1 (2003).

Spinning

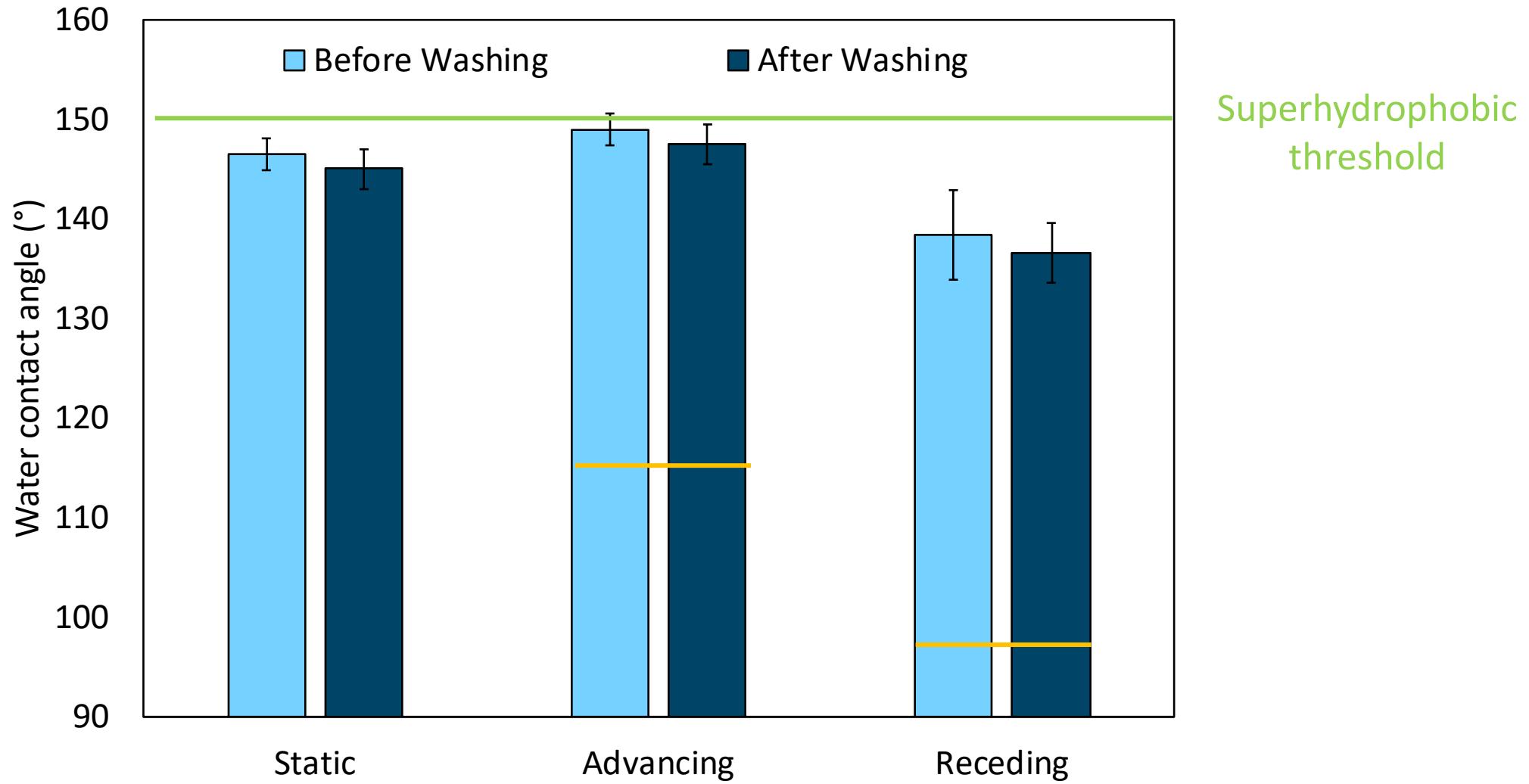
Conclusion

Improved oleophobicity with dimethyldimethoxysilane



Wang et al. Angewandte Chemie (2016).

Silica-based nanosols are washable and durable



Zhao et al. Materials and Design (2016).

Background

Eliminations

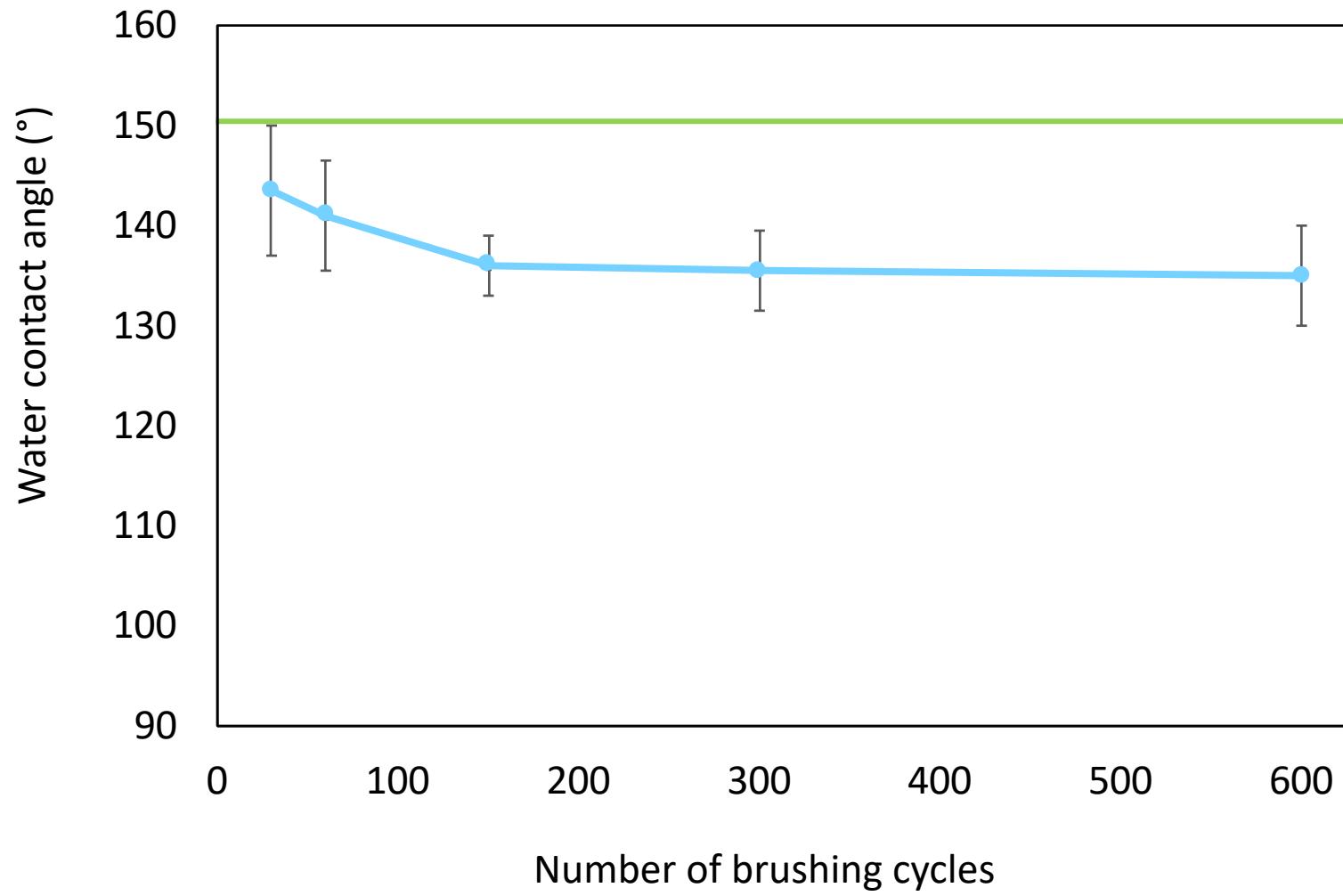
Improvables

Nanosols

Spinning

Conclusion

Silica-based nanosols are washable and durable



Zhao et al. Materials and Design (2016).

Background

Eliminations

Improvables

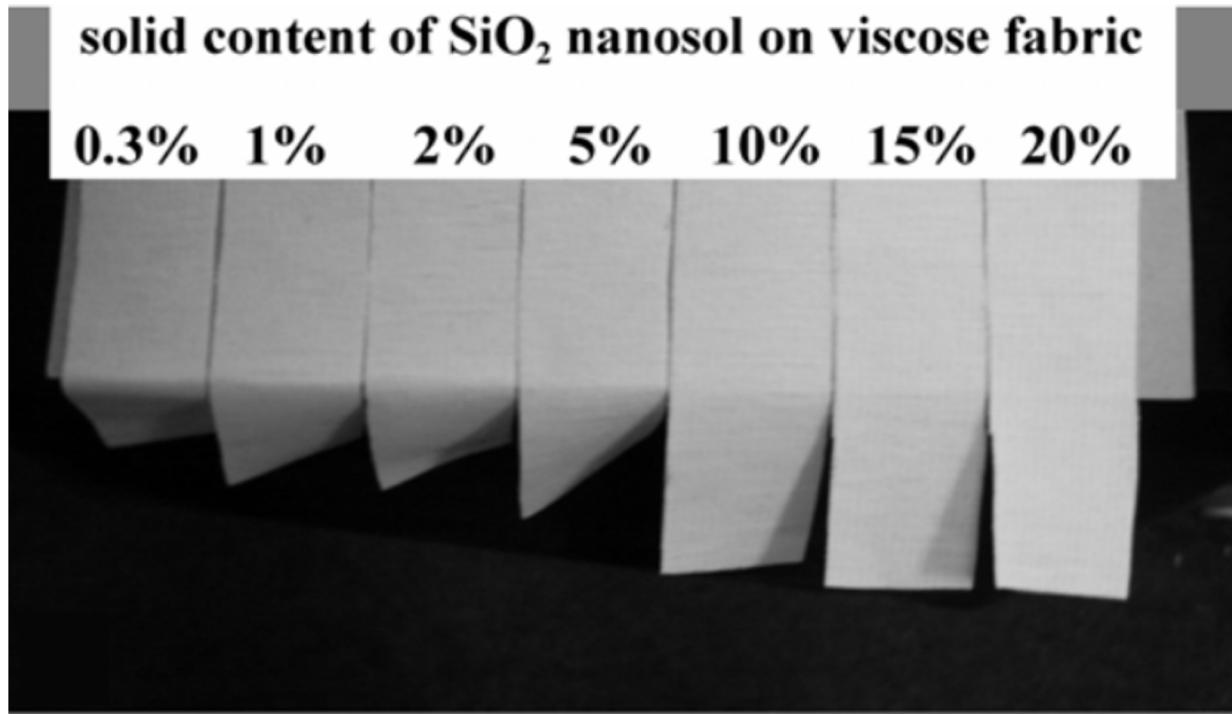
Nanosols

Spinning

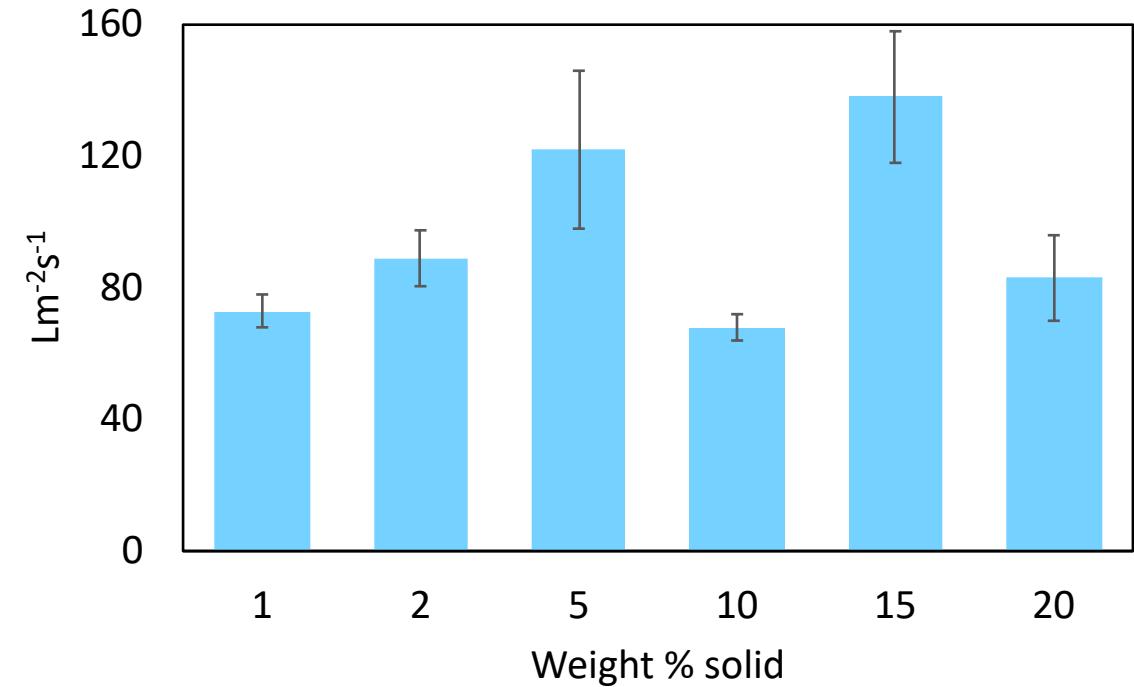
Conclusion

Thin coatings do not affect aesthetics

Stiffness

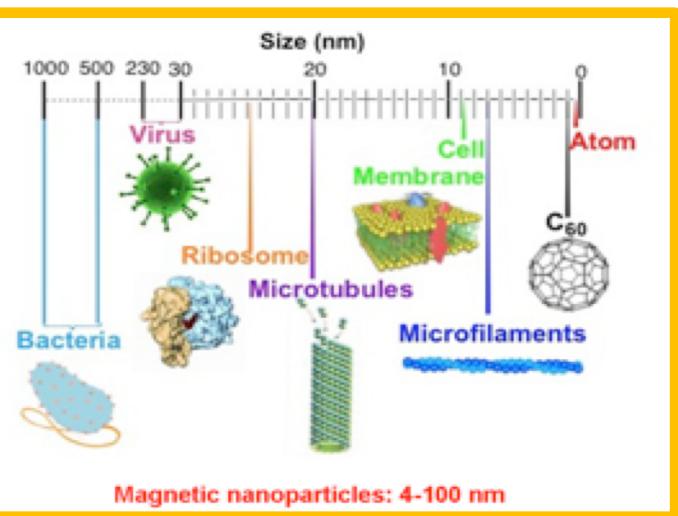


Breathability



Nanoparticle background and applications

High surface to volume ratio

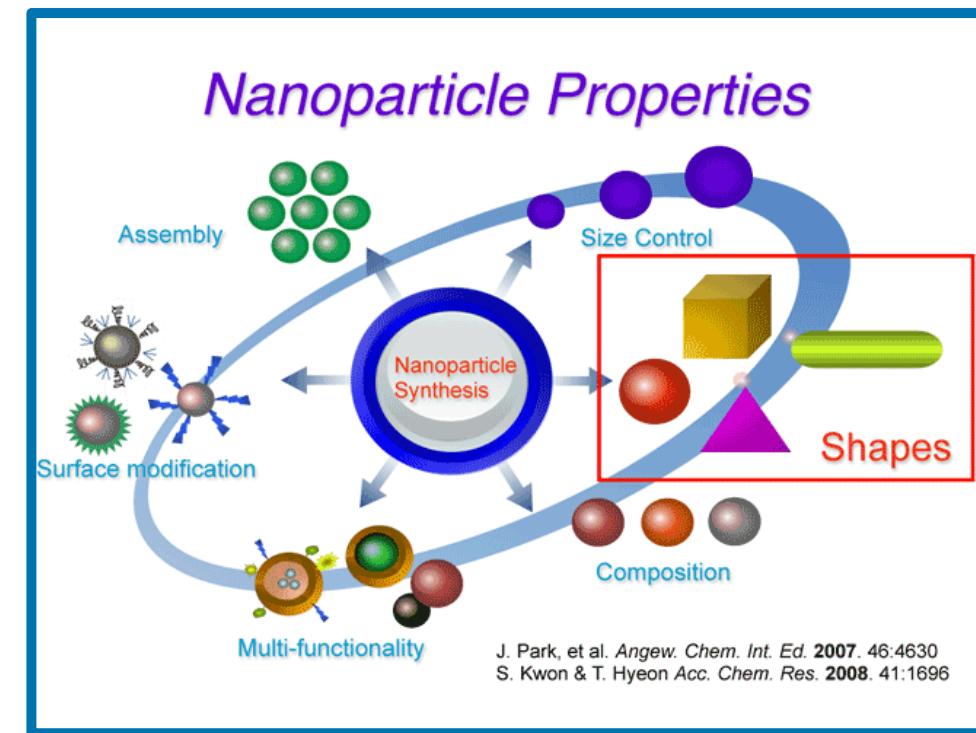


Nanoscale: 1-100 nm

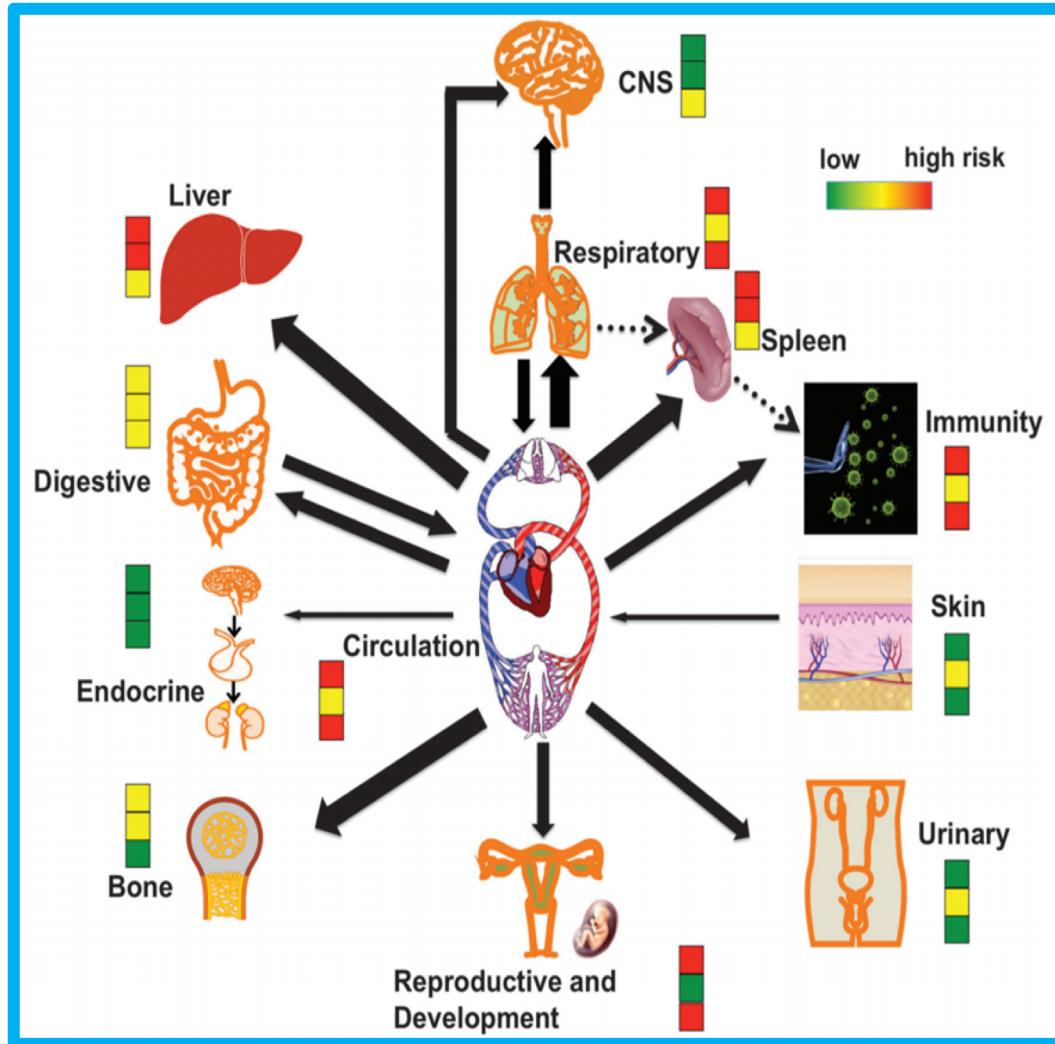


Diverse sources

Diverse Functionality



Nanomaterials target specific body systems



Silica

Size dependent toxicity
Penetrate cell barriers
Respiratory toxicity
Cellular toxicity
Aquatic toxicity
Environmental toxicity

Nanosols

Respiratory irritant
Kidney toxicity

Nanosol hazard profile

| Compound | Human Toxicity | | | | Environmental Toxicity | | |
|---|----------------|--------------------|-------------|--------------|------------------------|--------------|---------|
| | Mutagenicity | Organ | Respiratory | Reproductive | Persistence | Aquatic | Fate |
| Silica nanoparticles Amorphous Silica | | | Yellow | | | Red | Not PBT |
| (3-aminopropyl) triethoxysilane (APTES) | | Skin, eye irritant | | | Not bioaccumulative | Aquatic risk | Not PBT |
| Hexadecyltrimethoxysilane (HDTMS) | | Skin, eye irritant | Yellow | | Not bioaccumulative | Aquatic risk | Not PBT |



Background

Eliminations

Improvables

Nanosols

Spinning

Conclusion

Persistence of nanosol coating

| Partition | EPA PBT Criteria | Silanes | PFOA |
|---------------------------|------------------|---------|------|
| Water (days) | >60 | 38 | 180 |
| Soil (days) | >60 | 75 | 360 |
| Air (days) | >2 | 0.3 | 31 |
| Sediment (days) | >60 | 340 | 1600 |
| Bioconcentration factor | 1000-5000 | 4.6 | 56 |
| Fish chronic value (mg/L) | <10 | 2.4 | 1.3 |



Background

Eliminations

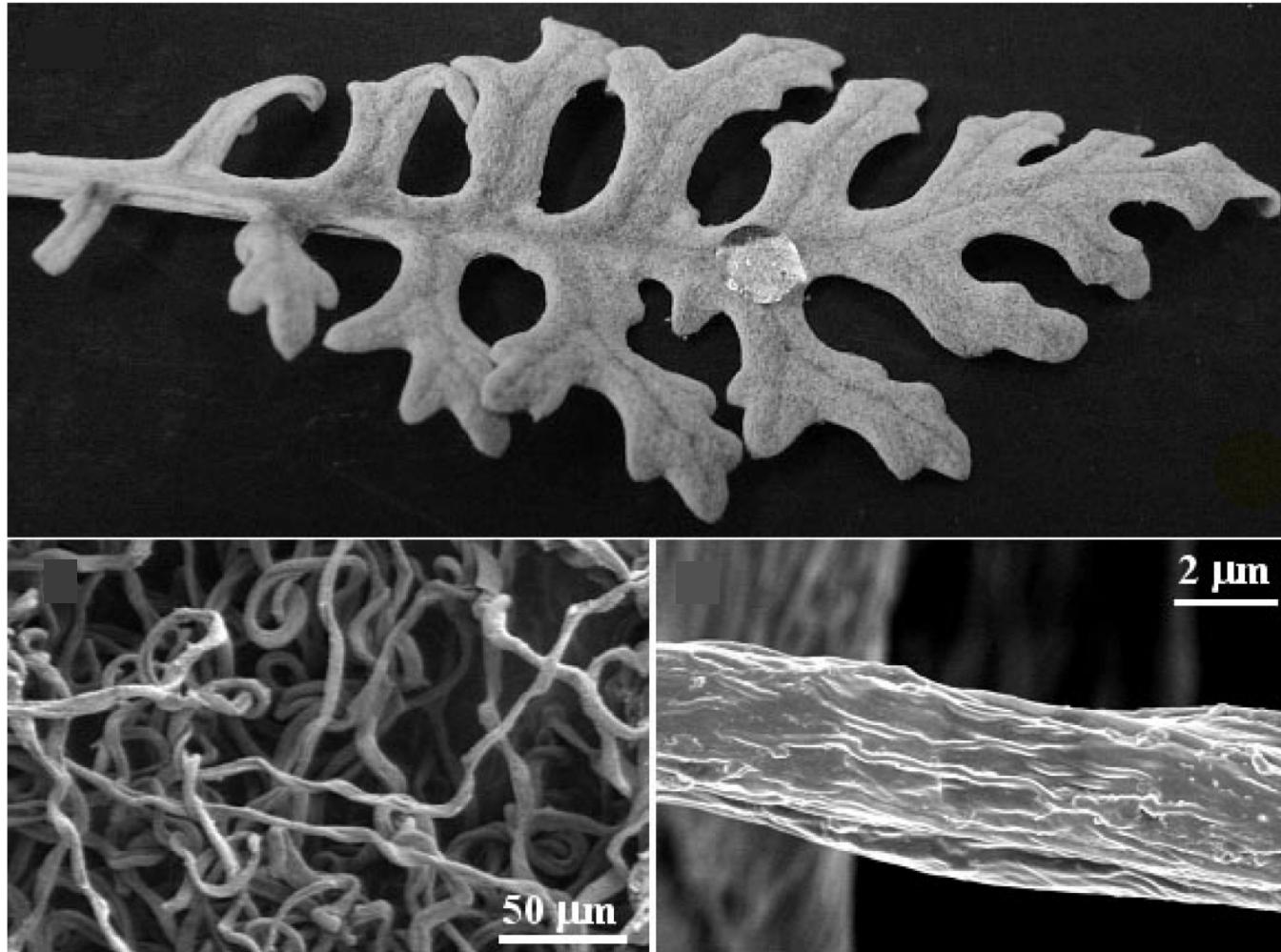
Improvables

Nanosols

Spinning

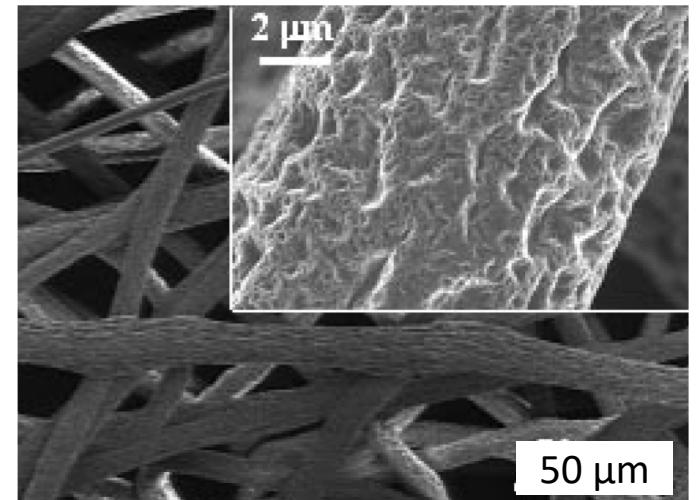
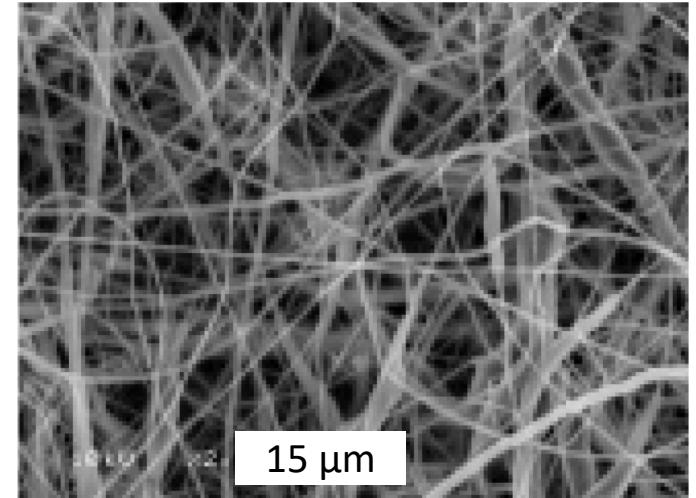
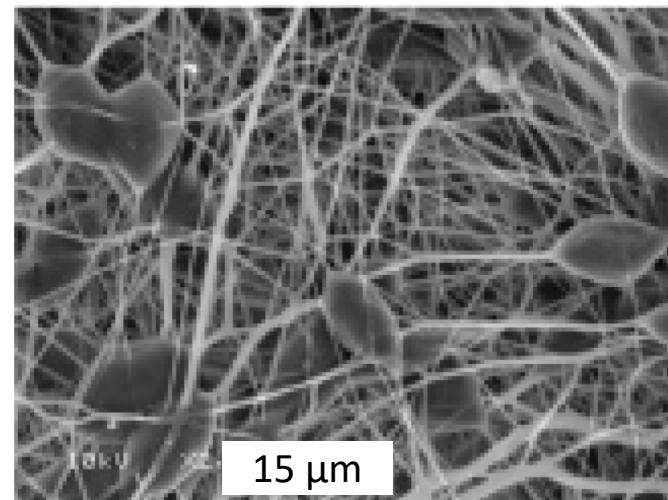
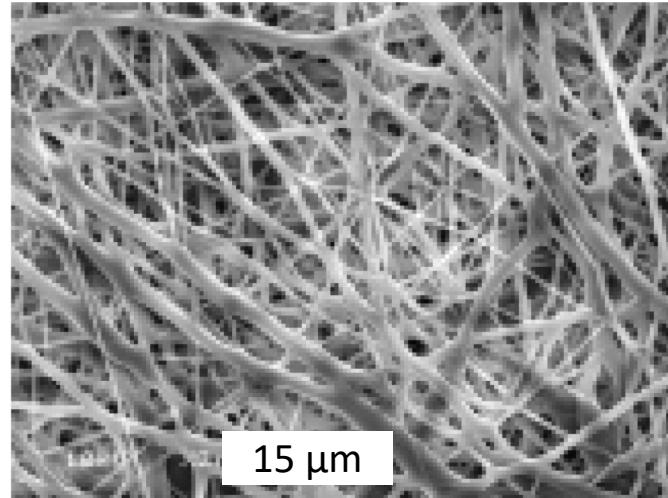
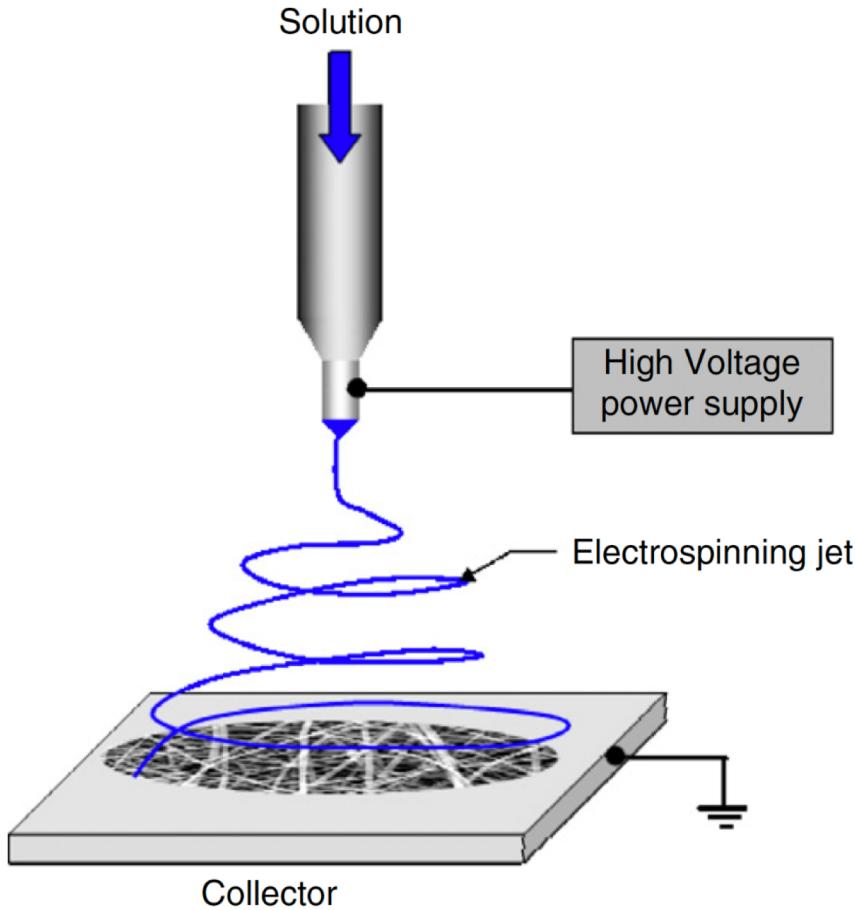
Conclusion

Inspiration for spinning: the silver ragwort leaf



147° water contact angle

Electrospinning textured fiber mats



Teo et al. Nanotechnology (2006).

Miyauchi et al. Nanotechnology (2006).

Ma et al. Macromolecules (2005).

Background

Eliminations

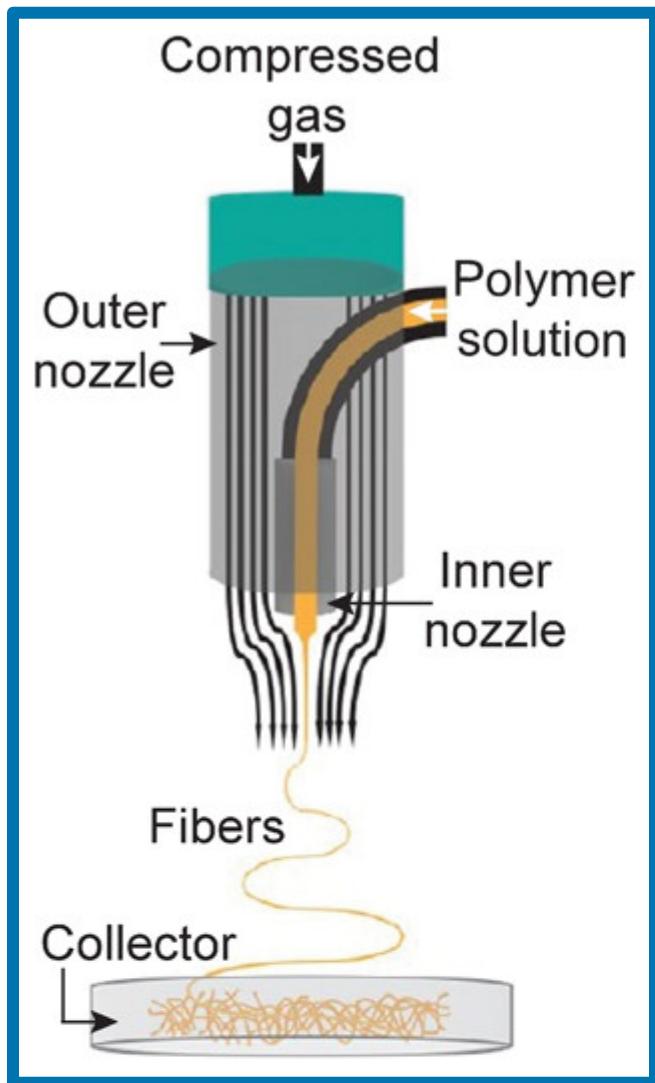
Improvables

Nanosols

Spinning

Conclusion

Solution blow spinning for manufacturing



- ✓ Safer solvents
- ✓ Faster
- ✓ Easier to scale up

Daristotle et al. ACS Appl. Mater. Interfaces (2016).

Background

Eliminations

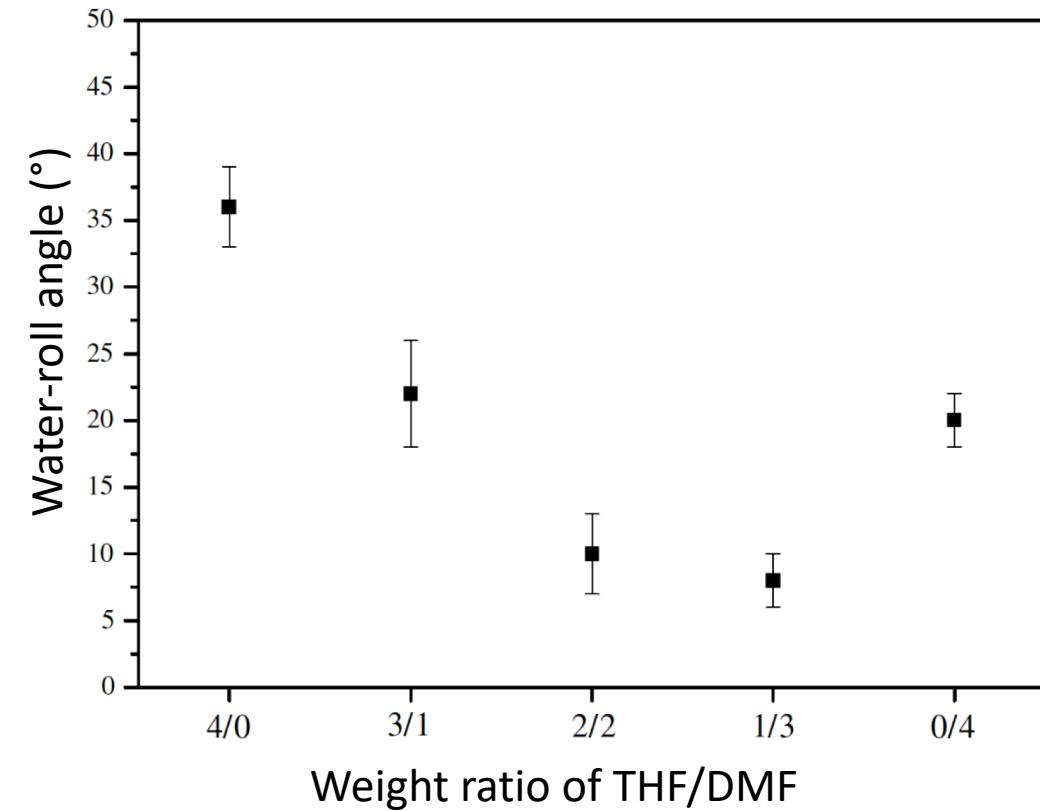
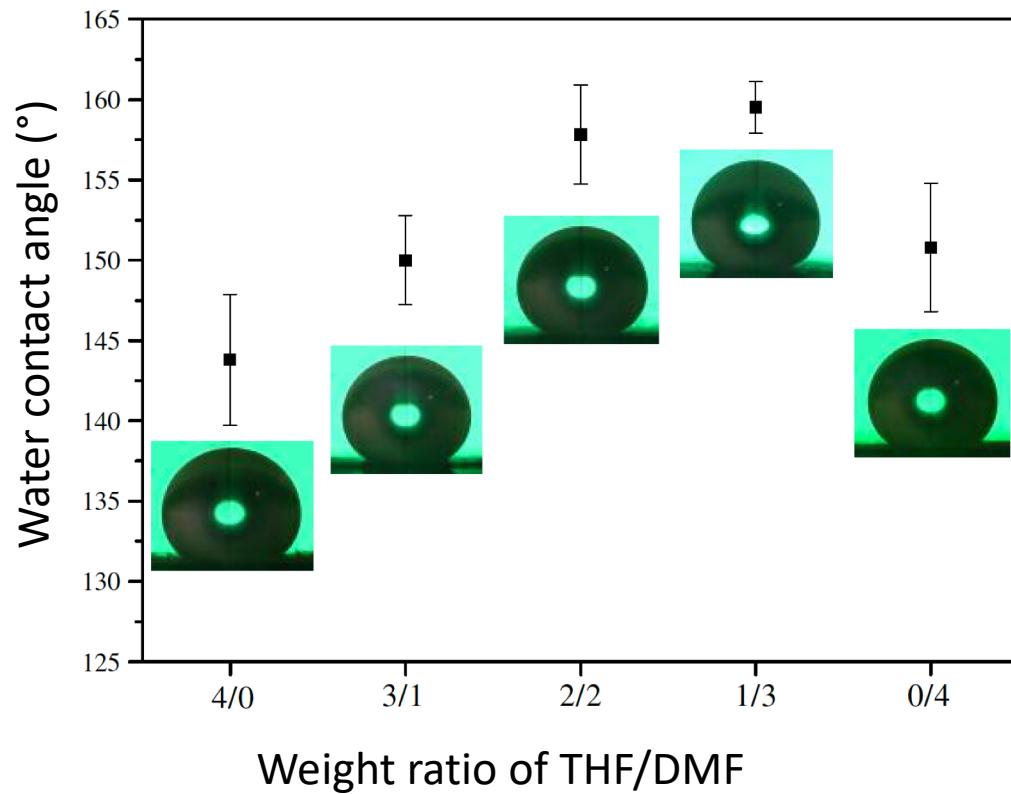
Improvables

Nanosols

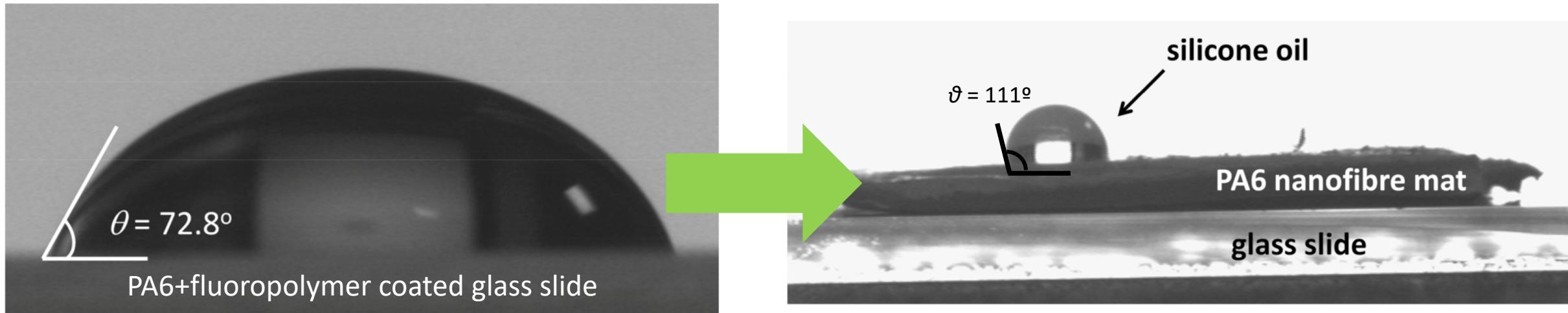
Spinning

Conclusion

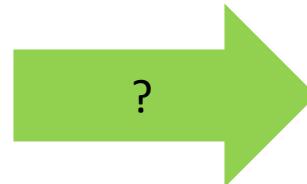
Highly tunable polystyrene nanofiber mats



Oleophobicity from structuring

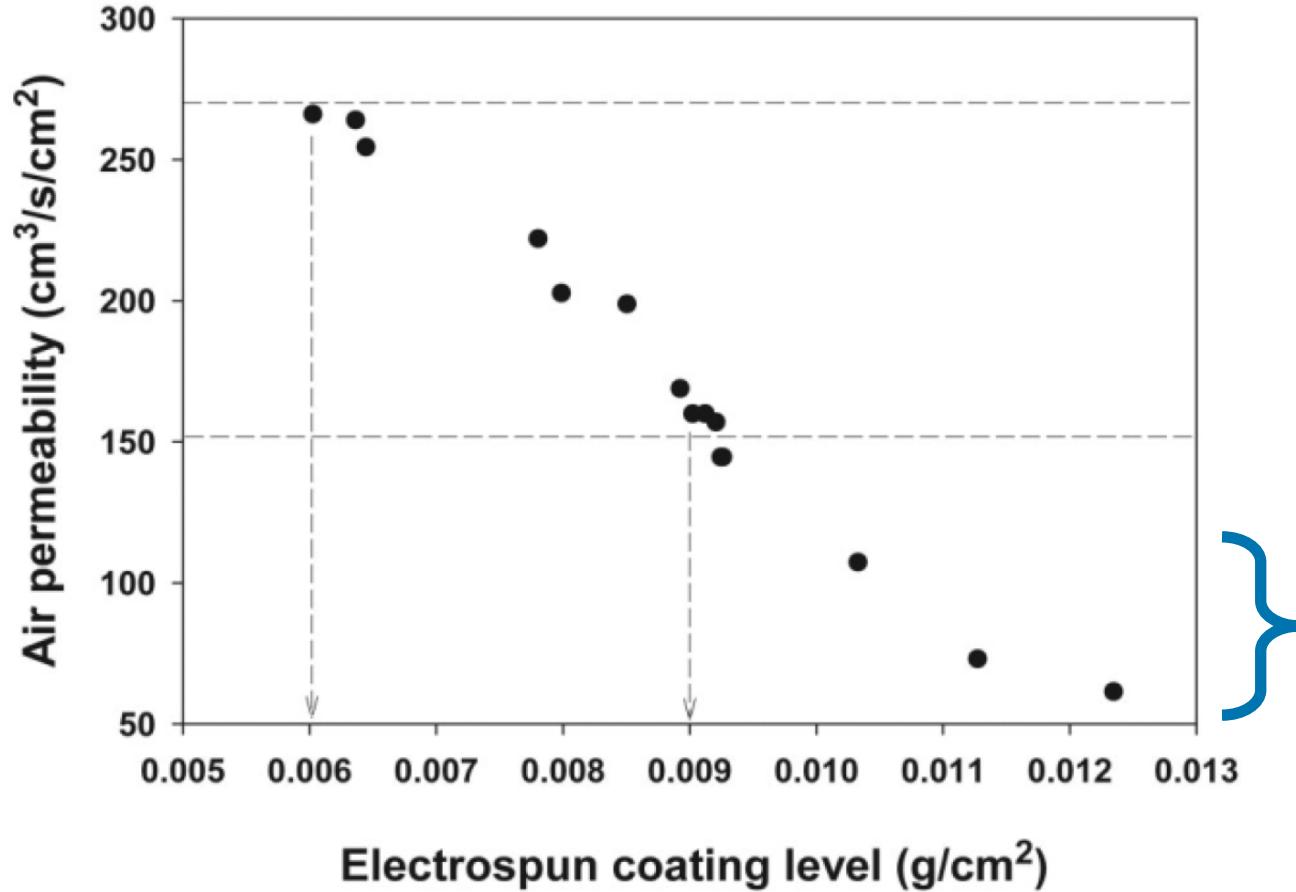


53° contact angle on
siloxane-coated slide



>90° contact angle on
siloxane nanofiber mat

Breathable thin fabric coatings



- ✓ Washable
- ✓ Flexible
- ✓ Transparent

Lee et al. J. Appl. Polym. Sci. (2006).

Background

Eliminations

Improvables

Nanosols

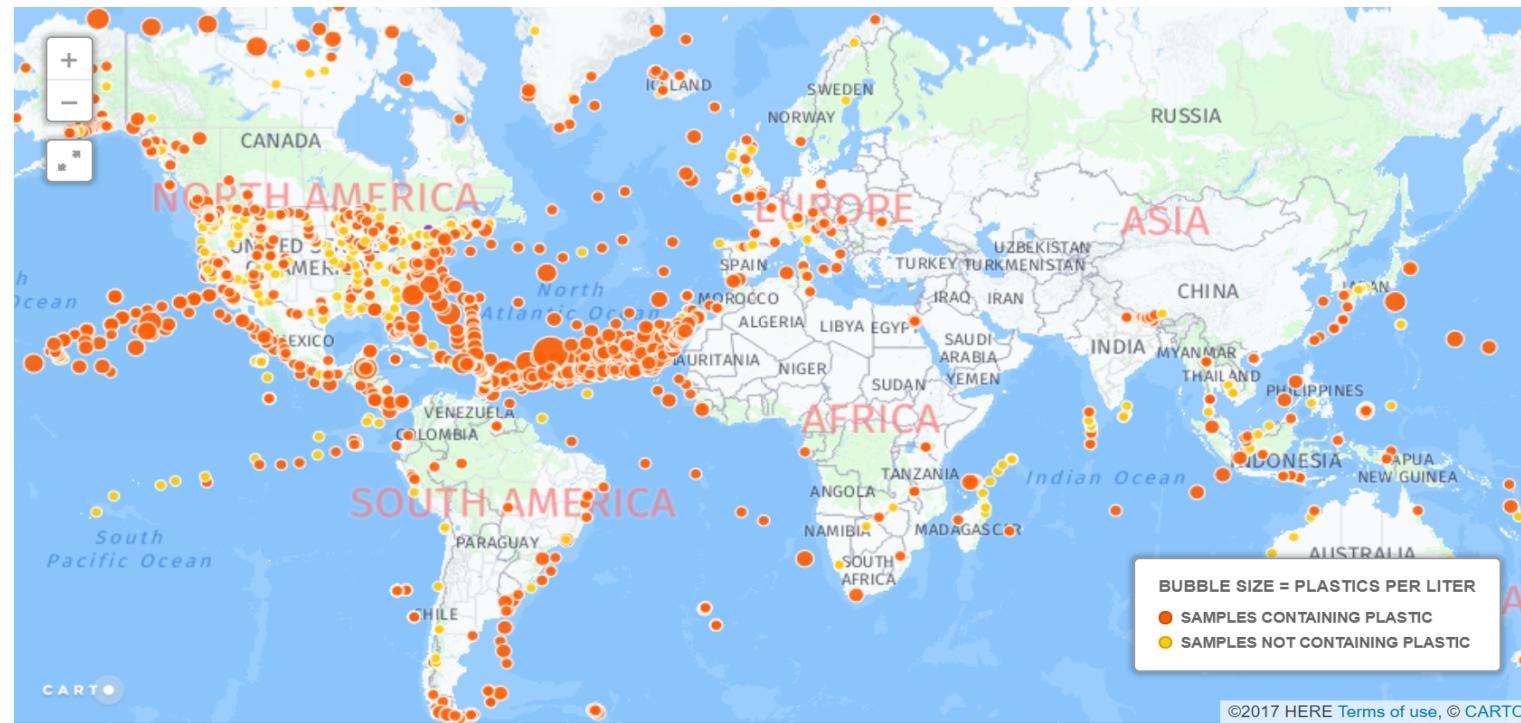
Spinning

Conclusion

Microfibers: emerging ecosystem pollutant



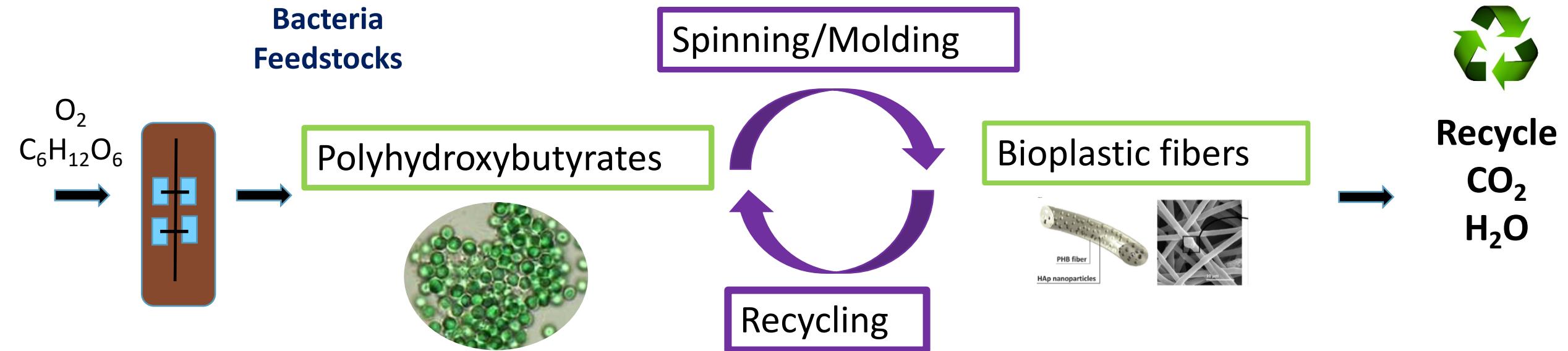
**Size <5mm
Non-Biodegradable
Accumulate
Long life cycle**



- >80% of plastic in water is <5 mm
- Marine invertebrates accumulate <1 mm
- Microplastic particles are 200 µm – 5 mm
- Plastics break down to 40 – 100 µm

Cole, 2016. Scientific Reports Rochman, C. 2016. ET&C.

Short life cycle of bioplastics meets ASTM biodegradation standards



1

Possibilities:

- Poly(lactide) PLA, P(3HB)
- Microbial Polyesters & Blends

Harding, K et al., 2007. J. of Biotechnology; Anjum, et al. 2016. Int J. Biol. Macromol.

Background

Eliminations

Improvables

Nanosols

Spinning

Conclusion

Spinning solvent hazards

| Compound | Human Toxicity | | | | Environmental Toxicity | | |
|---------------------------|---------------------------|---|-------------|--------------|------------------------|---------|---------|
| | Mutagenicity | Organ | Respiratory | Reproductive | Persistence | Aquatic | Fate |
| Tetrahydrofuran (THF) | Carcinogen: liver, kidney | Skin, eye irritant | Respiratory | | Short half life (days) | | not PBT |
| Dimethylformamide (DMF) | | Eye, skin irritant; chronic toxicity (liver, digestive) | Respiratory | | Short half life (days) | | not PBT |
| Dimethyl sulfoxide (DMSO) | | | | | | | not PBT |
| Acetone | | Skin, eye irritant | | | | | not PBT |



Hazard scale Low Medium High



Background

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Background

Eliminations

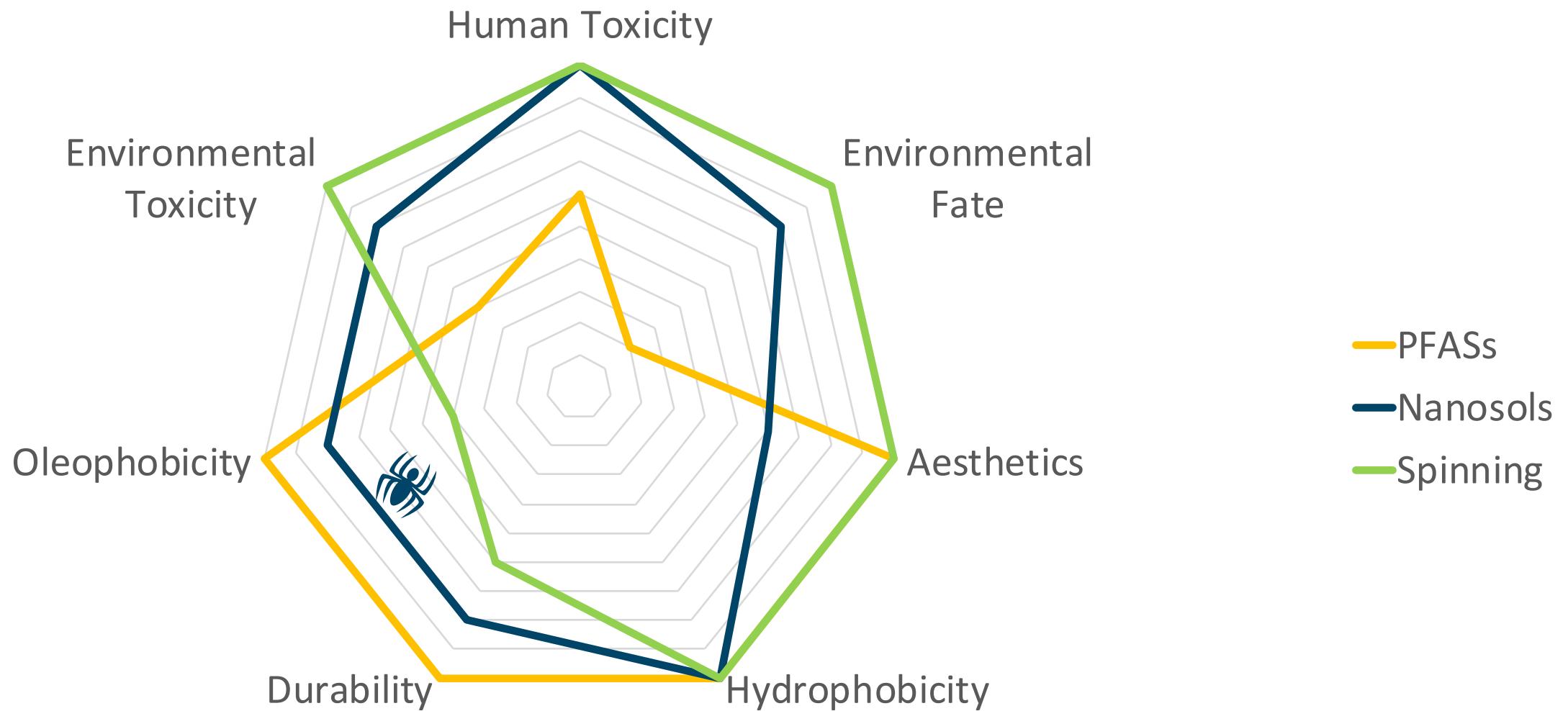
Improvables

Nanosols

Spinning

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Strategy summary



Background

Eliminations

Improvables

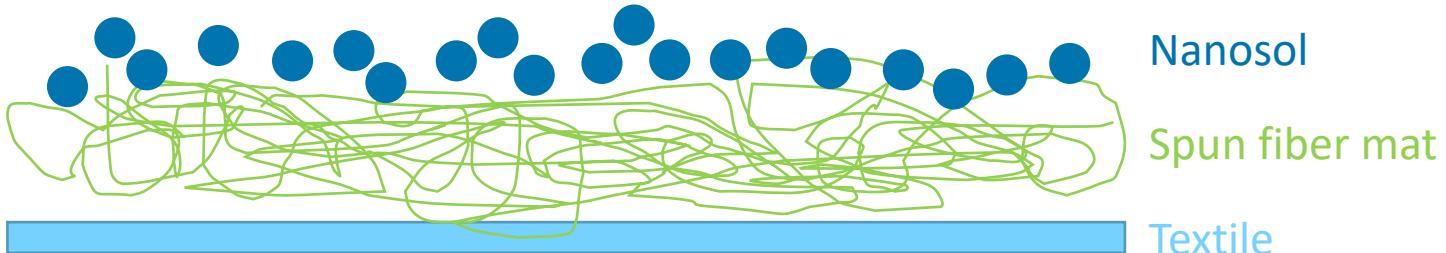
Nanosols

Spinning

Conclusion

Research needs for future development

1. Improve oleophobicity
 - Nanosols: test dimethyldimethoxysilane on fabrics
 - Spinning: incorporate a nanosol
2. Optimize spinning using the least hazardous solvents and additives
3. Fully test durability and aesthetic of alternatives
 - 20 home wash-dry cycles
 - Abrasion testing



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