SURFACE ENGINEERING OF STAINLESS STEEL FOR DAIRY FOULING MANAGEMENT

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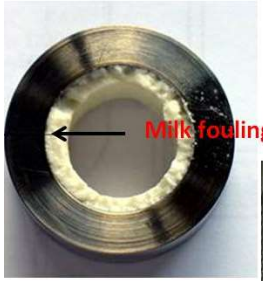
N.I.C.E. INTERNATIONAL RENDEZ-VOUS
Nature Inspires Creativity Engineers

Why milk fouling ?

Patented in 1865

https://www.palais-decouverte.fr/



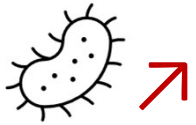
Raw milk

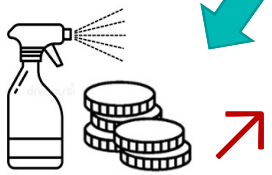
Pasteurization

- ✓ Kills pathogenic bacteria
- ✓ Extends shelf life

Milk processing

Milk fouling





Cleaning: 4h/day

Waste management

80 % of production costs owed by dairy fouling

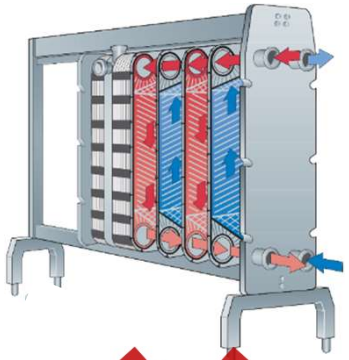
P. Van Asselt, *et al. Proceedings of Heat Exchanger Fouling and Cleaning: Challenges and Opportunities*, 2005

Mitigation of milk fouling ?

Milk composition

[prot], [Ca], pH

Standardization of milk ✗



Process parameters

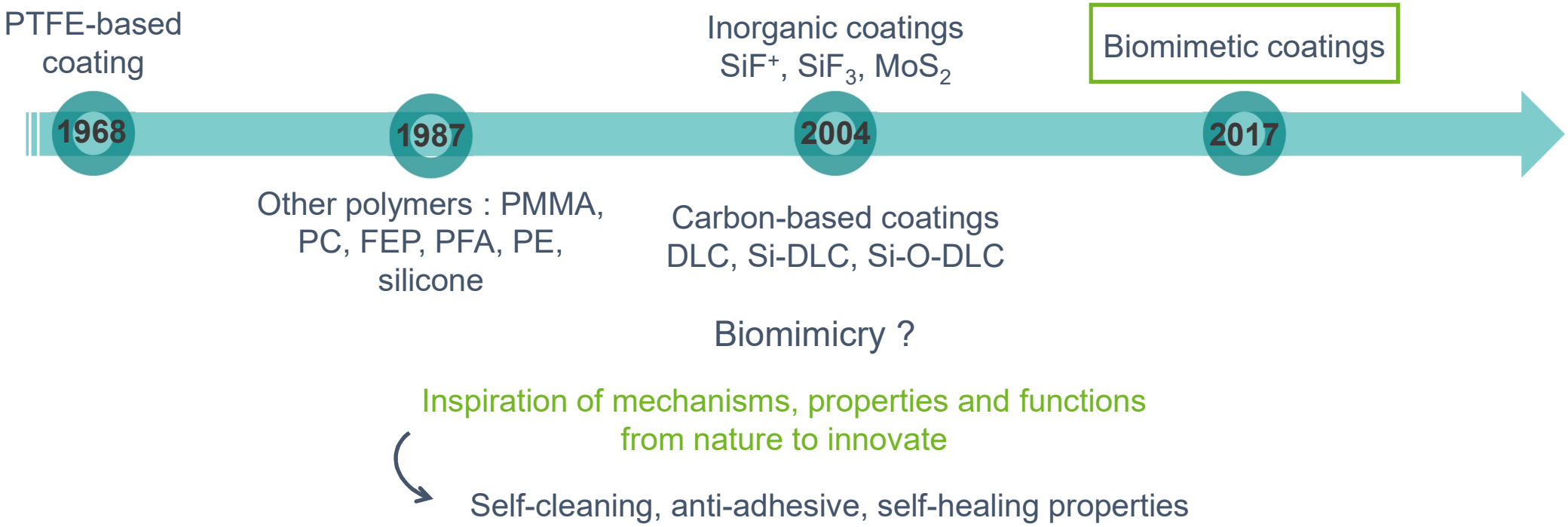
Q, Re, T°C

Mainly optimized in food industries

Surface properties of stainless steel

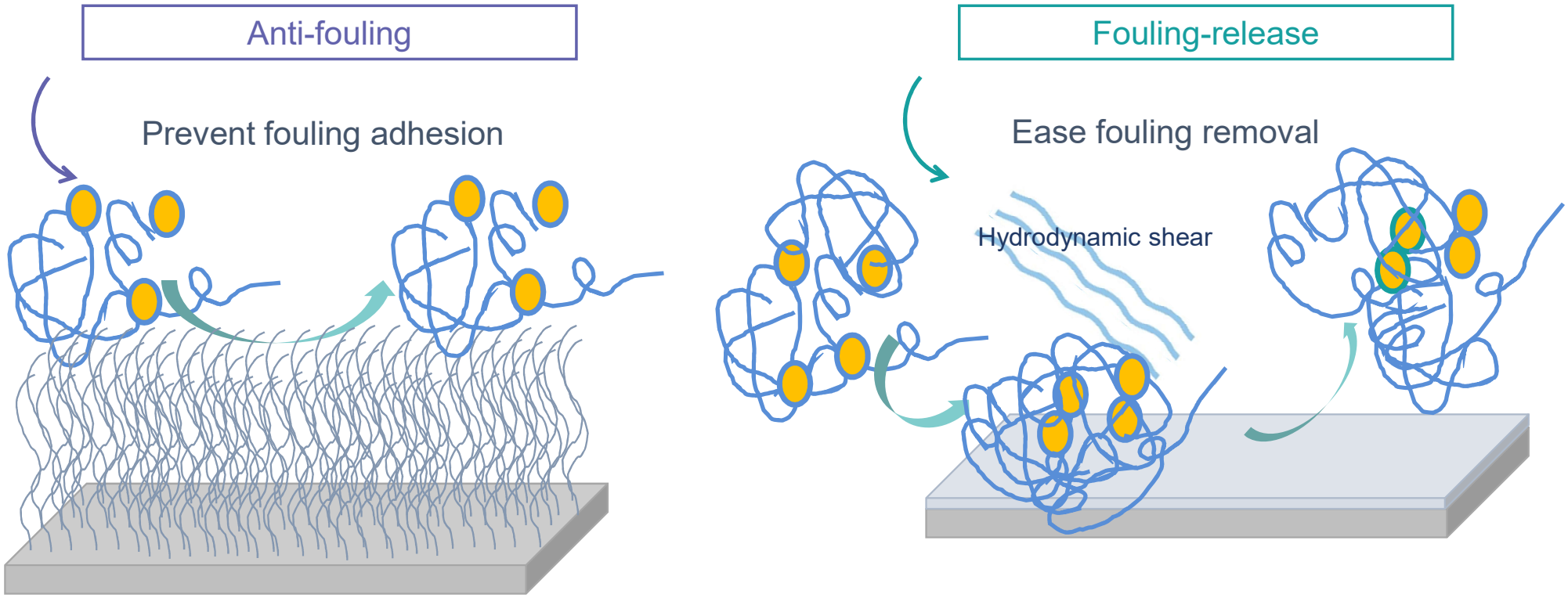
Physical and chemical parameters

Surface engineering for milk fouling mitigation ?

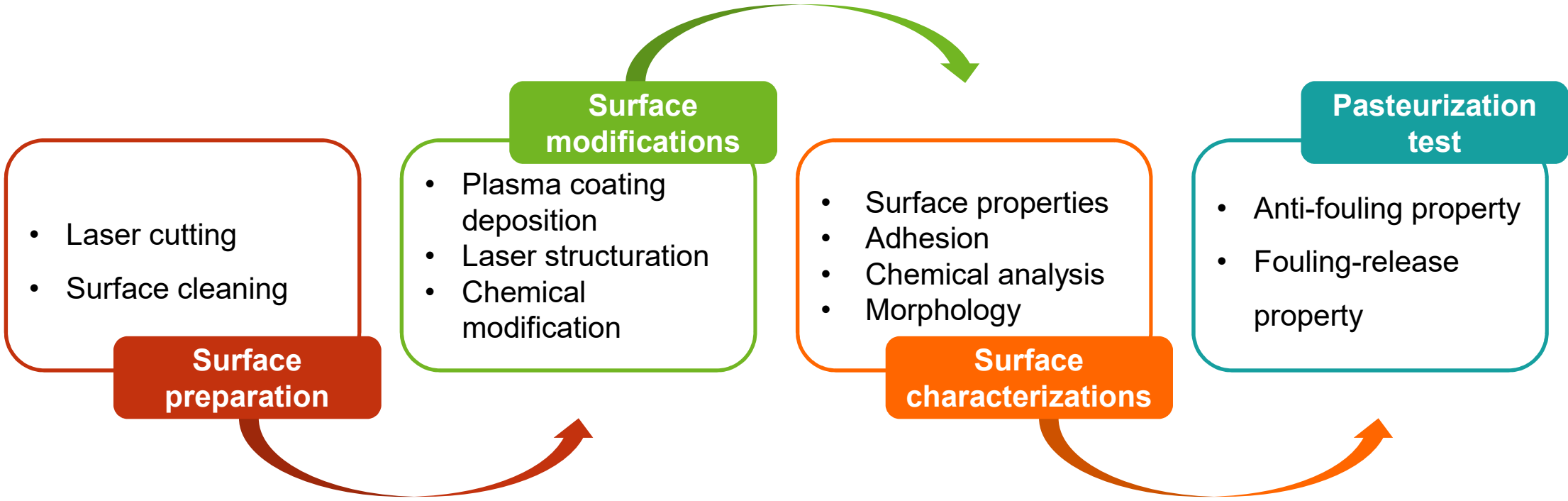


- https://en.bioxegy.com
- **M. Saget, C.F. Almeida, V. Fierro, A. Celzard, G. Delaplace, V. Thomy, Y. Coffinier, M. Jimenez**, A critical review on surface modifications mitigating dairy fouling, **Comprehensive Reviews in Food Science and Food Safety 5, 4324 - 4366 (2021)**
- **S. Zouaghi, S. Bellayer, V. Thomy, T. Dargent, Y. Coffinier, C. André, G. Delaplace, M. Jimenez**, Biomimetic surface modifications of stainless steel targeting dairy fouling mitigation and bacterial adhesion, **Food and Bioproducts Processing 113, 32-38 (2019)**

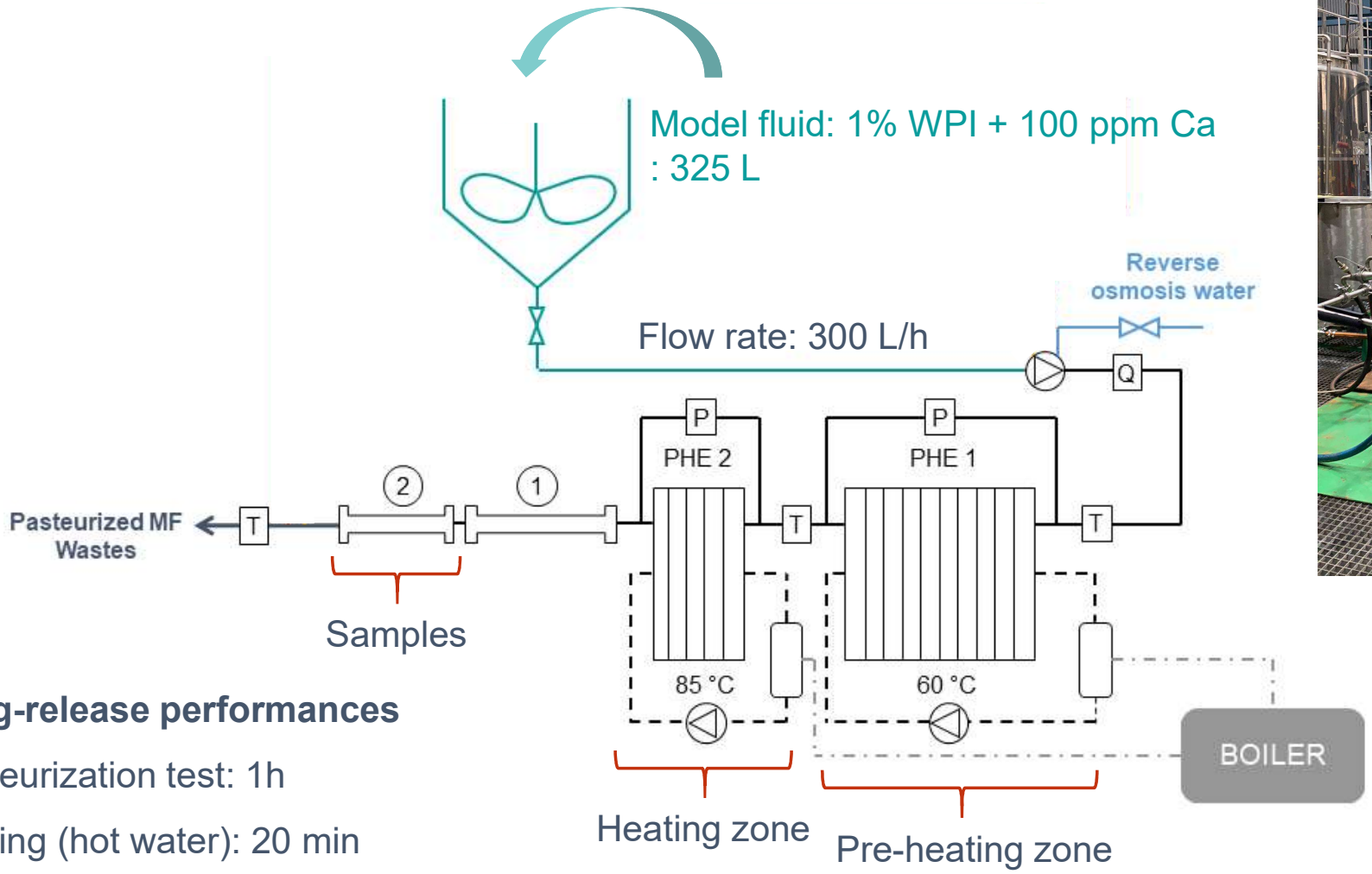
Two ways for fouling mitigation



General strategy for surface engineering



Pasteurization test

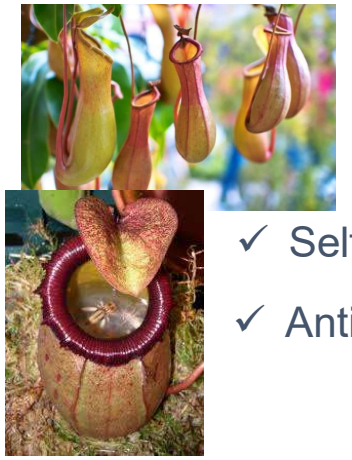


Fouling-release performances

- Pasteurization test: 1h
- Rinsing (hot water): 20 min

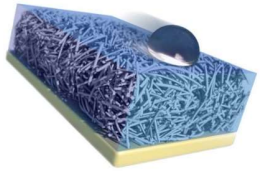
Biomimetic approaches

Nepenthes, Carniverous plant



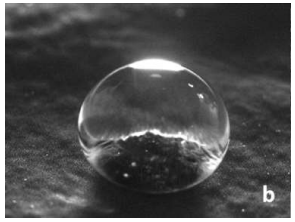
- ✓ Self-healing
- ✓ Anti-adhesive

Slippery Liquid-Infused Surface (SLIS) by laser ablation and lubricant infusion



S. Zouaghi et al. ACS Applied Materials & Interfaces 9 26565-26573 (2017)
M. Saget et al., Applied surface science, submitted (2023)
A.S. Vaillard et al., Surfaces and interfaces, submitted (2023)

Lotus leaves

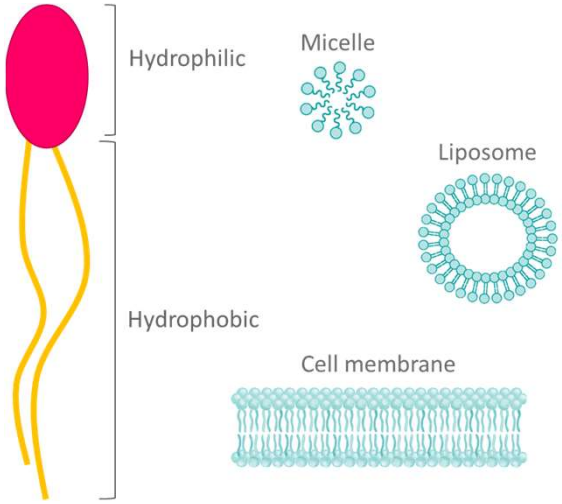


- ✓ Anti-adhesive
- ✓ Self-cleaning

3D printing of microtextured stainless steel + nanotextured bilayers by atmospheric pressure plasma

S. Zouaghi et al. Applied surface science 455 392-402 (2018)
M. Saget et al., ACS surface and interfaces , submitted (2023)
K. Dourgaparsad et al., Additive manufacturing, to be submitted (2023)

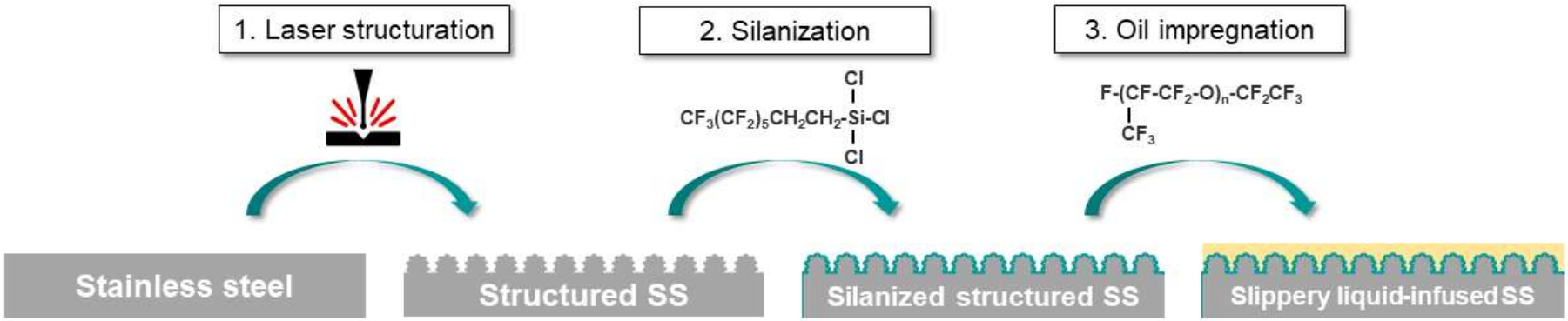
Amphiphiles



Synthetic amphiphiles

S. Zouaghi et al., Biofouling 34(7) 769-783 (2018)
S. Zouaghi et al. ACS Sustainable Chemistry & Engineering, 7(10), 9133-9142 (2019)
M. Jimenez et al., manuscript in preparation

Biomimetic approaches: SLIPS



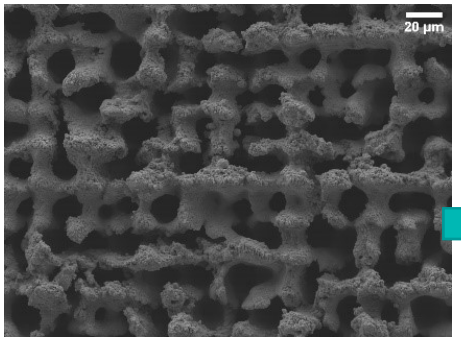
- Anti-fouling and Fouling-release properties
- Fluorinated oil not compatible with food industry

S. Zouaghi, *et al. ACS Appl. Mater. Interfaces*, 9, 26565−26573, 2017

Biomimetic approaches: a more food compatible SLIPS

Development of new SLIS

Laser structured surface



PFTS

Chemical modification

Silanized structured SS

Food-compatible SLIS

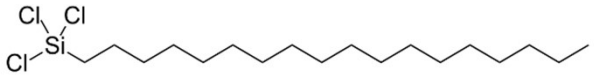
Coconut oil

Impregnation

Slippery liquid-infused SS

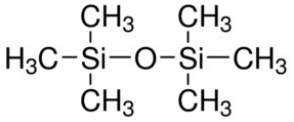
No chemical modification

Silanization: OTS



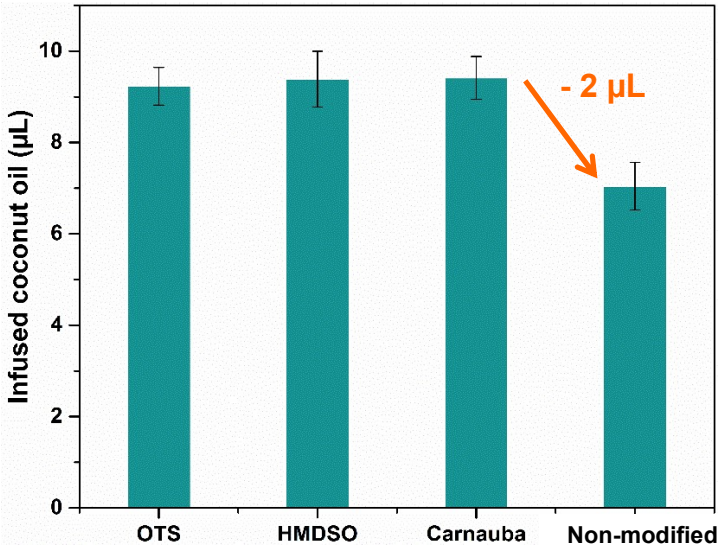
Carnauba wax

HMDSO coating

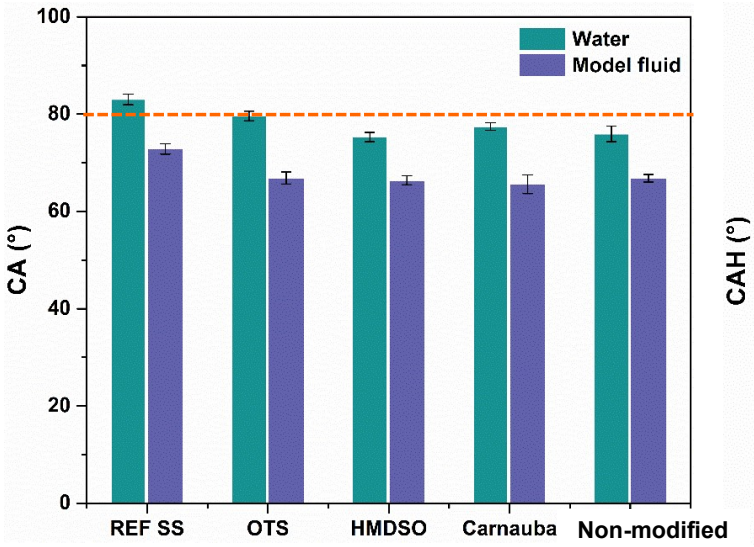


Coconut oil-based SLIS characterizations

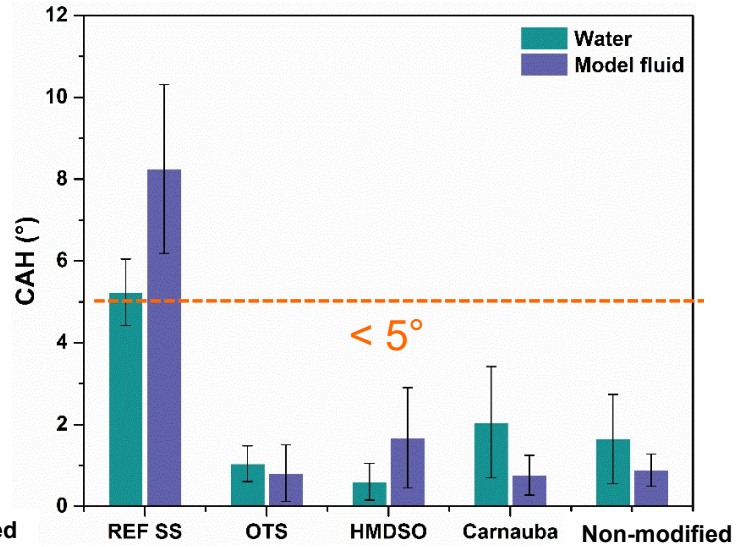
- Effect of chemical modification ? ✓



- Volume influence on wettability ? ✗



- Volume influence on slippery interface ? ✗

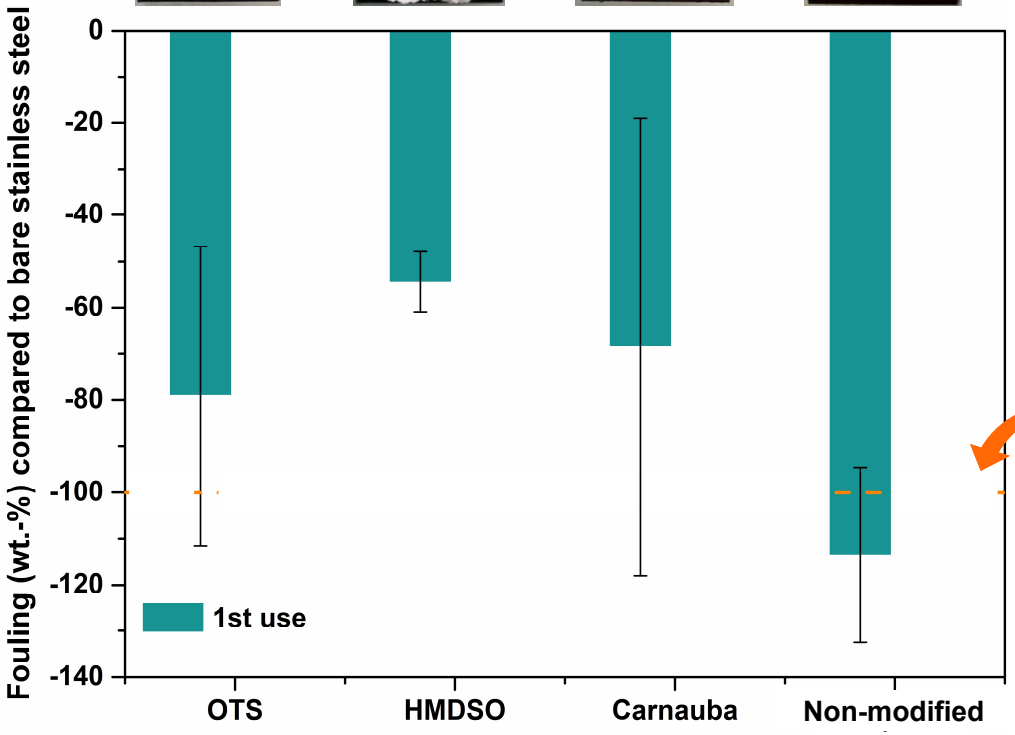


Influence on wettability and slippery behaviour ?

Fouling-release performances ?

Fouling-release performances of coconut oil-based SLIS

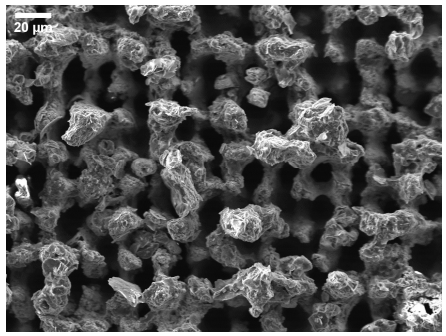
After the 1st use



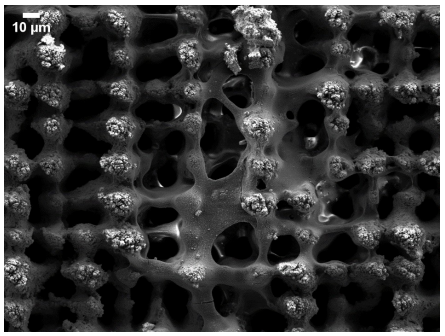
Loss of oil

Less efficient with chemical modification

Carnauba wax



HMDSO



Not homogeneous → promote fouling adhesion

→ Oil loss and fouling formation after one cycle

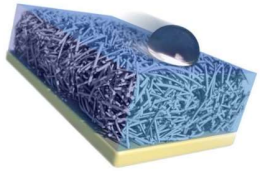
Biomimetic approaches

Nepenthes, Carniverous plant

✓ Self-healing

✓ Anti-adhesive

Slippery Liquid-Infused Surface (SLIS) by laser ablation and lubricant infusion



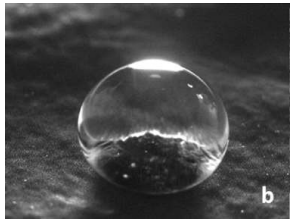
S. Zouaghi et al. ACS Applied Materials & Interfaces 9 26565-26573 (2017)
M. Saget et al., Applied surface science, submitted (2023)
A.S. Vaillard et al., Surfaces and interfaces, submitted (2023)

→ **Proof on concept validated**

→ **Alternative oil and greener impregnation method explored**

→ **Further investigation to make the system last longer and/or regenerate it**

Lotus leaves



✓ Anti-adhesive

✓ Self-cleaning

3D printing of microtextured stainless steel + nanotextured bilayers by atmospheric pressure plasma

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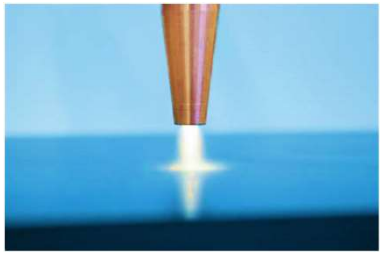
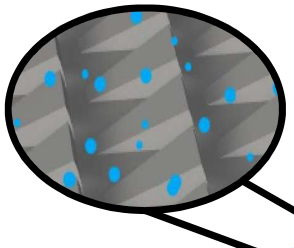
Biomimetic surfaces

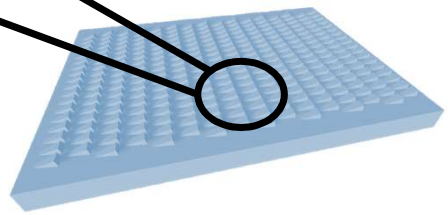
3D printing

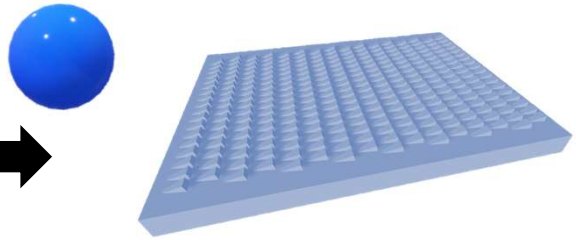
Vacuum-assisted casting



Atmospheric pressure plasma polymerization

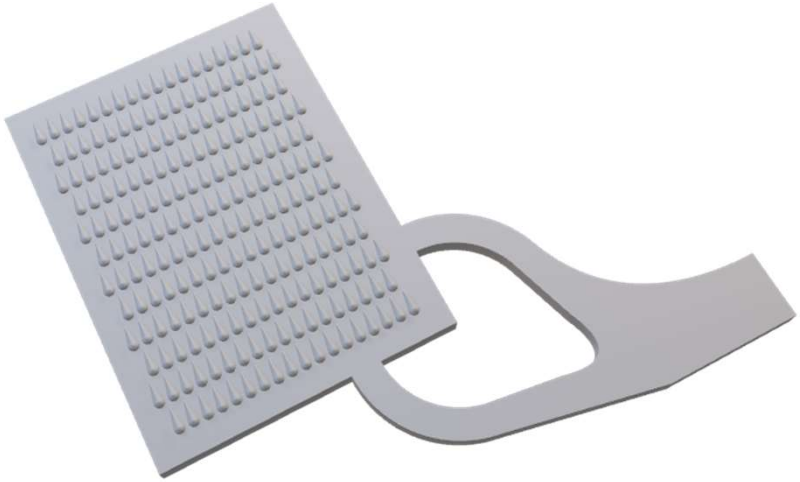






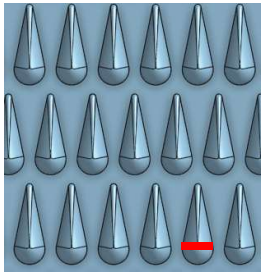
Water repellency !

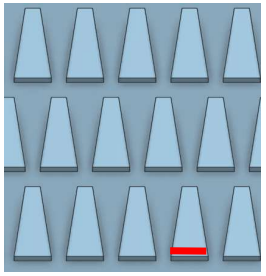
Design a bio-inspired micro-scaled surface

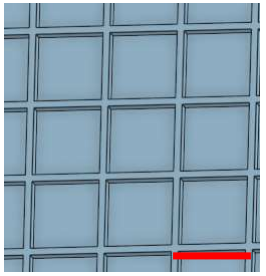


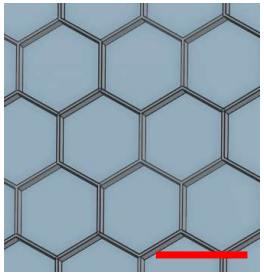
Coupons :

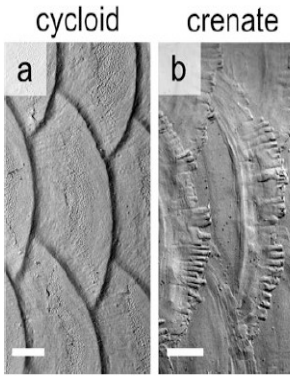
- 20x15x1,5 mm^3
- 2 feeding systems
- Different types of bio-inspired surface architectures

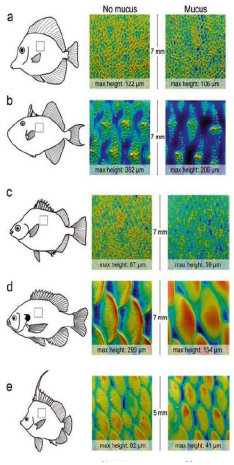






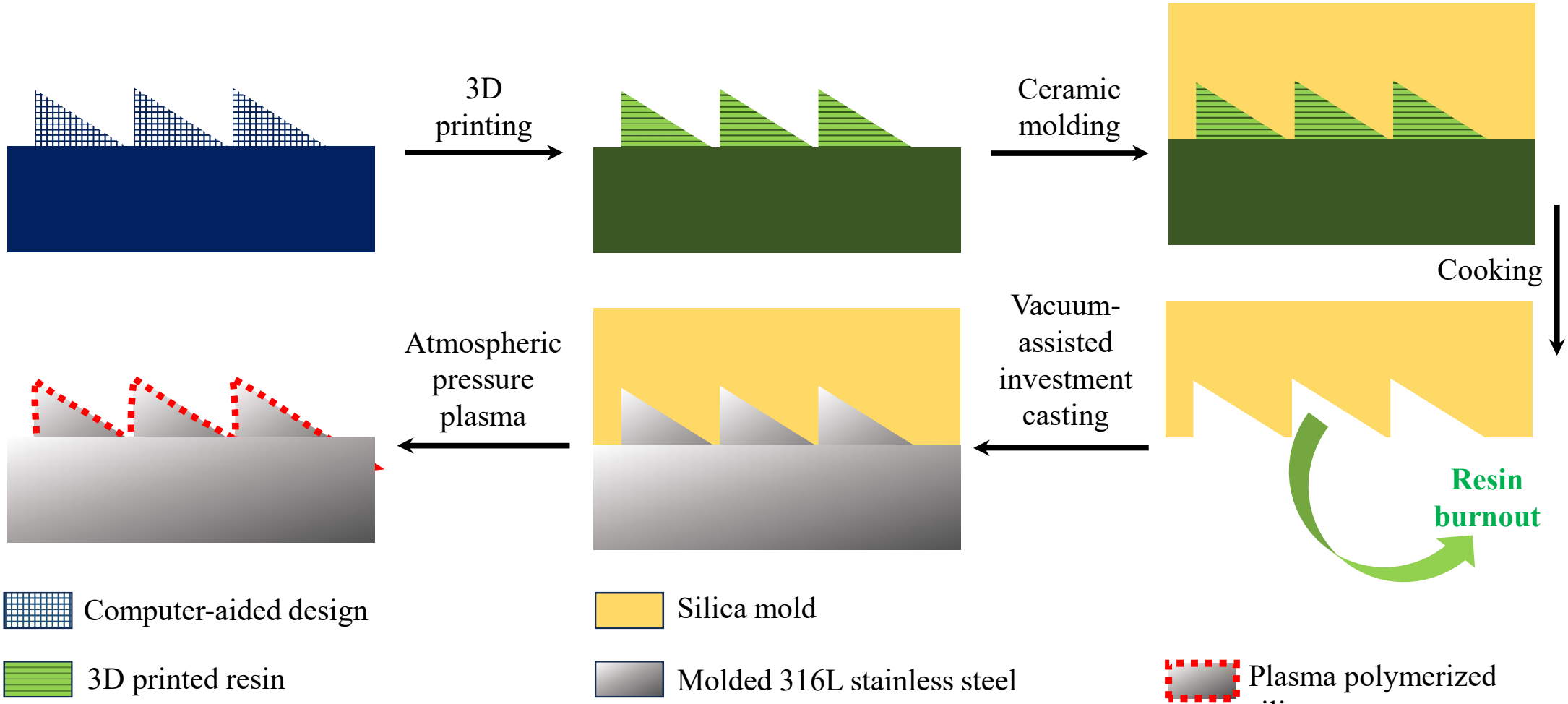






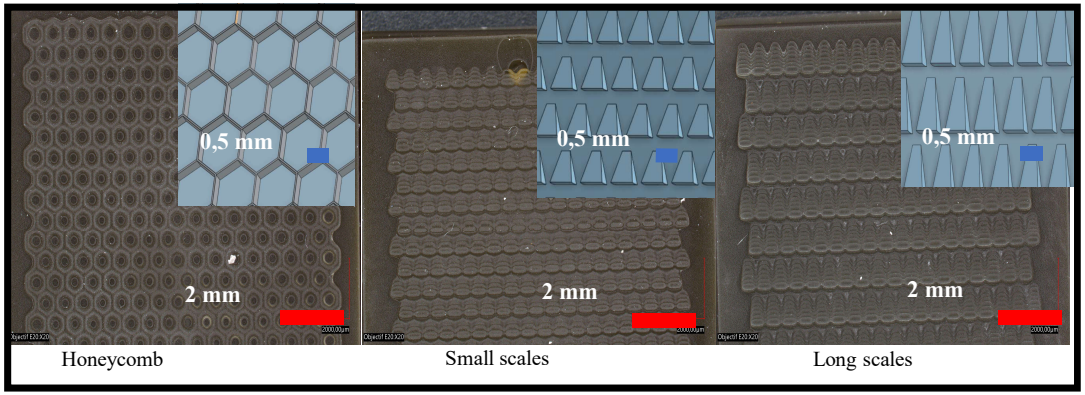
Scale bar = 500 µm

Manufacturing process

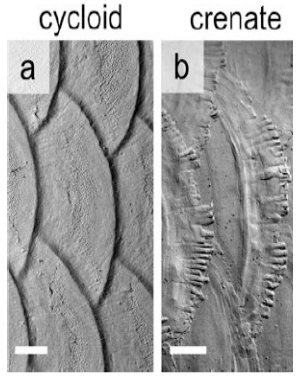


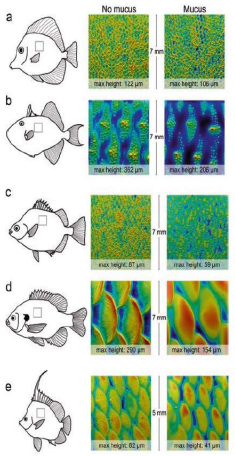
Microtextured bio-inspired surfaces

Bio-inspiration

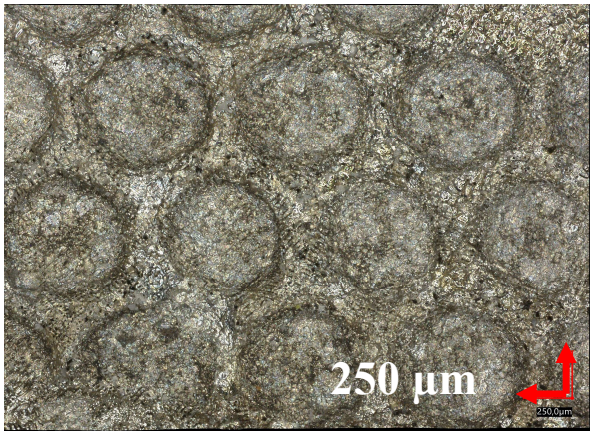


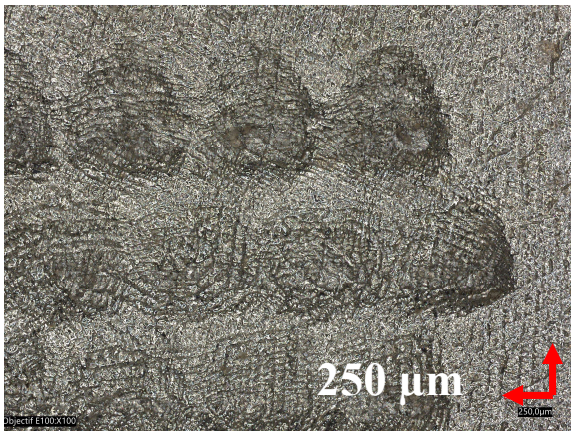
Bio-inspiration

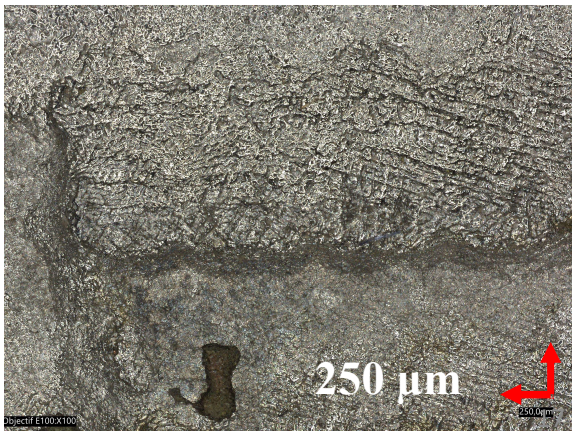




Moulding in stainless steel







Nanotexturation process: Atmospheric pressure plasma

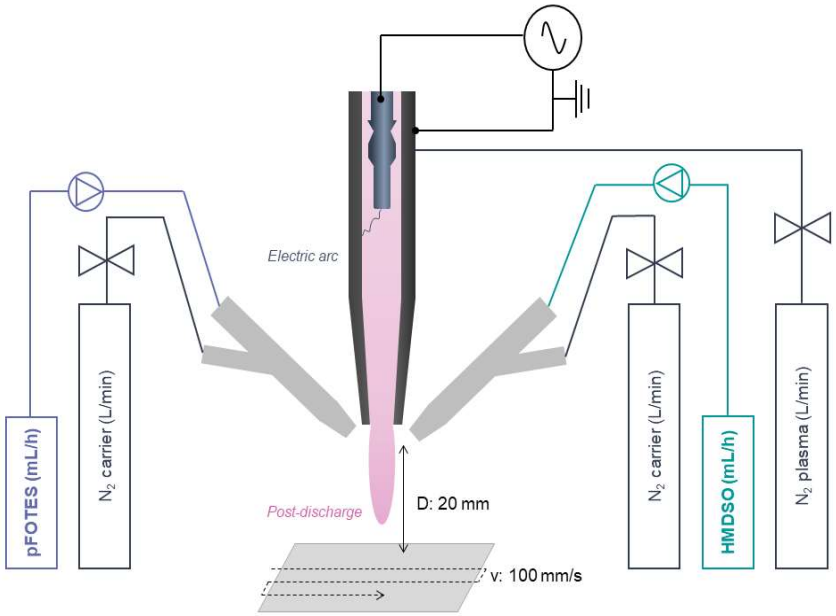
Advantages

- ✓ Versatile
- ✓ Solvent and catalyst-free
- ✓ Rapid process
- ✓ Integrable in production line

Superhydrophilic coating

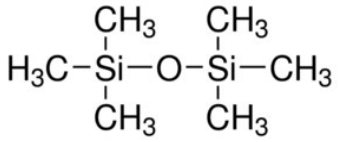
Highly hydrophobic coating

Ma *et al.*, *Applied Surface Science*, 535, 147032, 2021

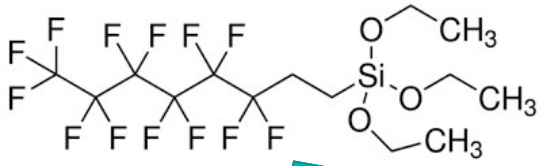


Monomers for hydrophobic coatings

Hexamethyldisiloxane
HMDSO

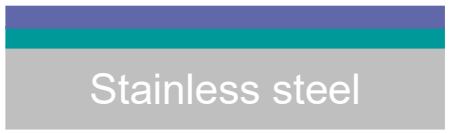


1H,1H,2H,2H-perfluorooctyltriethoxysilane
pFOTES

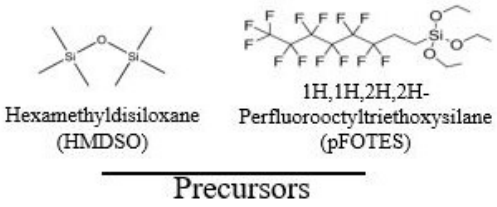


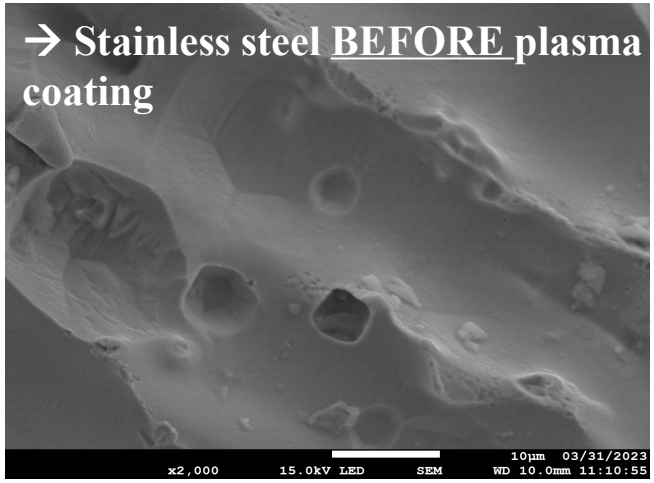
First time in the literature

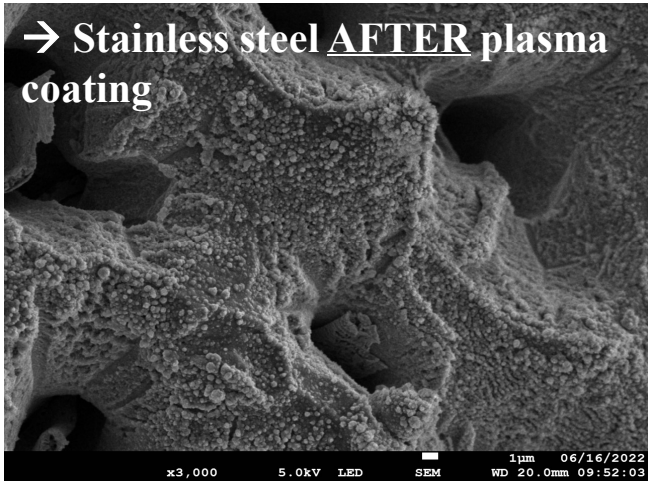
Alternative injection

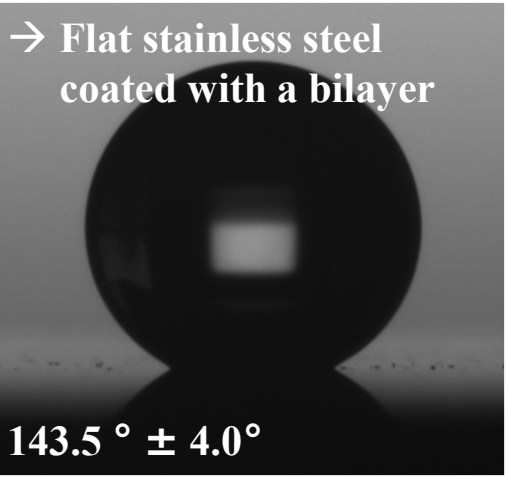


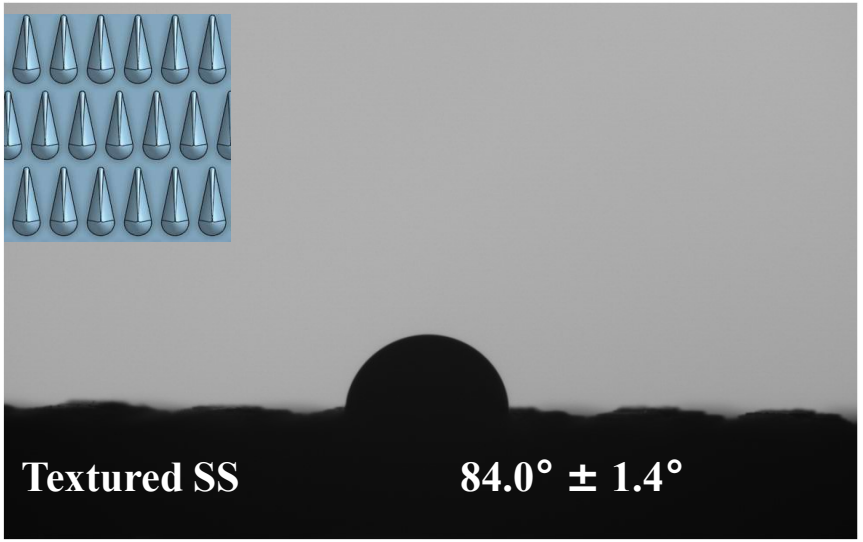
Nanotexturing process : wettability

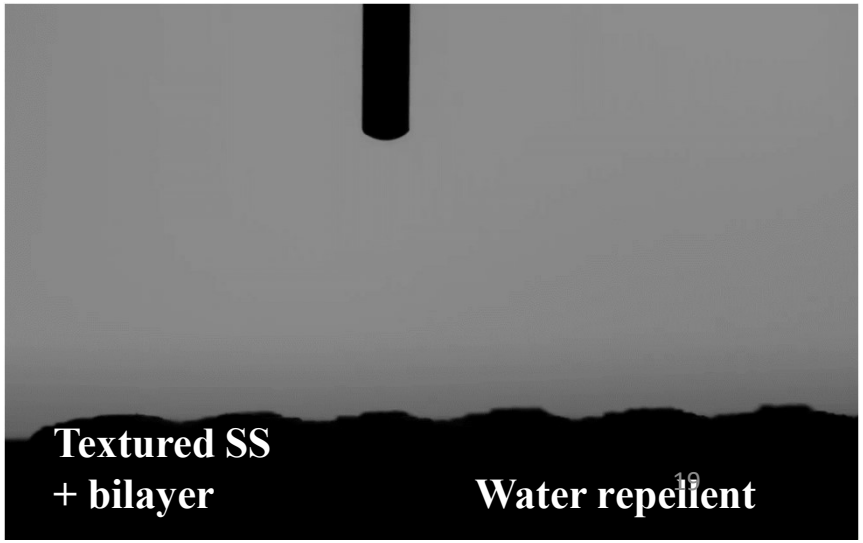












Summary

Antifouling surfaces: a multi-parameters challenge

Many issues: high fluxes, high temperatures, poor adhesion to stainless steel, …

Bio-inspired solutions proposed:

- **Micro/nanotextured surfaces**

→ Proof of concept of stainless steel microtexturation by 3D Printing

→ Nanotexturation by atmospheric plasma bilayer

- **Slippery surfaces (SLIPS)** using laser texturation + a lubricant

- **Amphiphilic coatings**: outstanding results but adhesion is key issue

→ self-stratifying amphiphilic coatings

→ Self-healing self-stratifying amphiphilic coatings

Potential applications in bio-fouling, marine fouling, anti-icing , …

THANKS FOR YOUR ATTENTION !

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Unité Matériaux Et Transformations

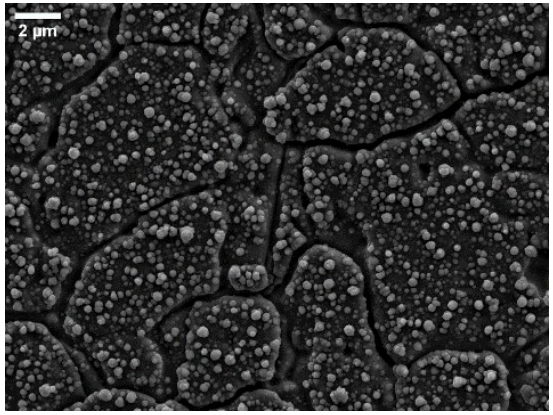
Plasma coating deposition

Plasma parameters

Plasma gas (N_2)	60 L/min
Power	1515 W
Distance	20 mm
Scanning speed	100 mm/s
Carrier gas (N_2)	1.1 L/min
Cycle	1 for monolayer

HMDSO: 20 mL/h

Stainless steel

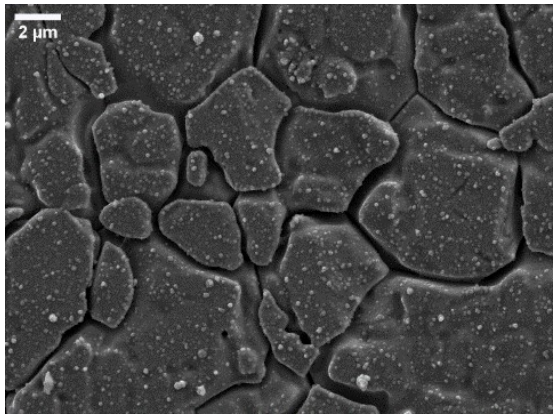


WCA: 108 ± 3°

Nano-structures

pFOTES: 20 mL/h

Stainless steel



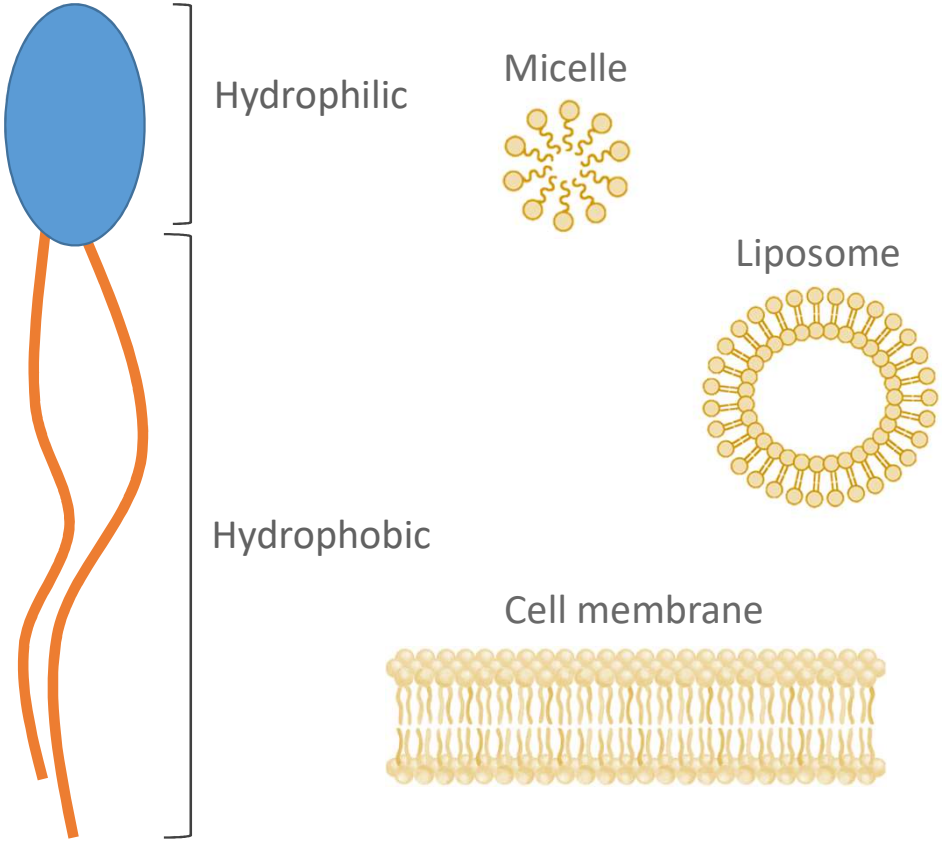
WCA: 138 ± 3°

Highly hydrophobic

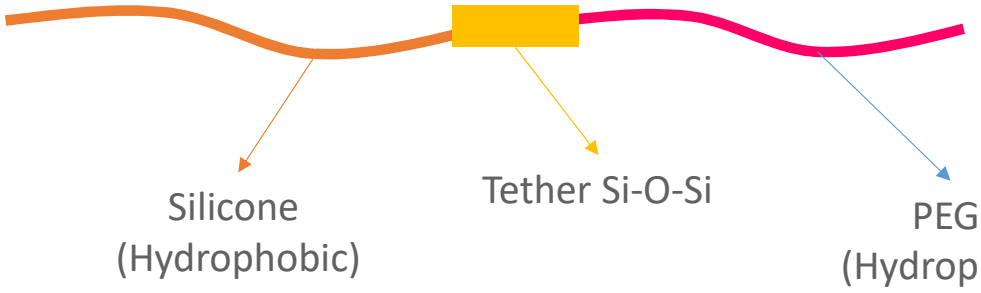
Combination → Superhydrophobic coating ?

Biomimetic amphiphile

Amphiphiles in Nature

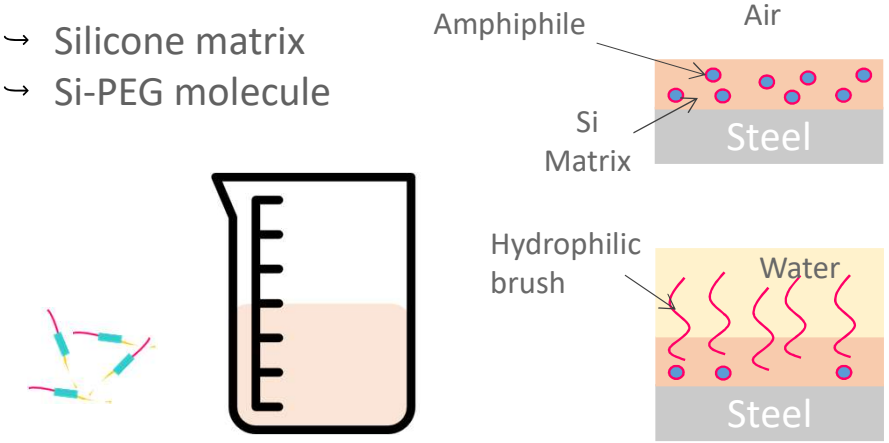


Synthetic Amphiphile



Coating formulation

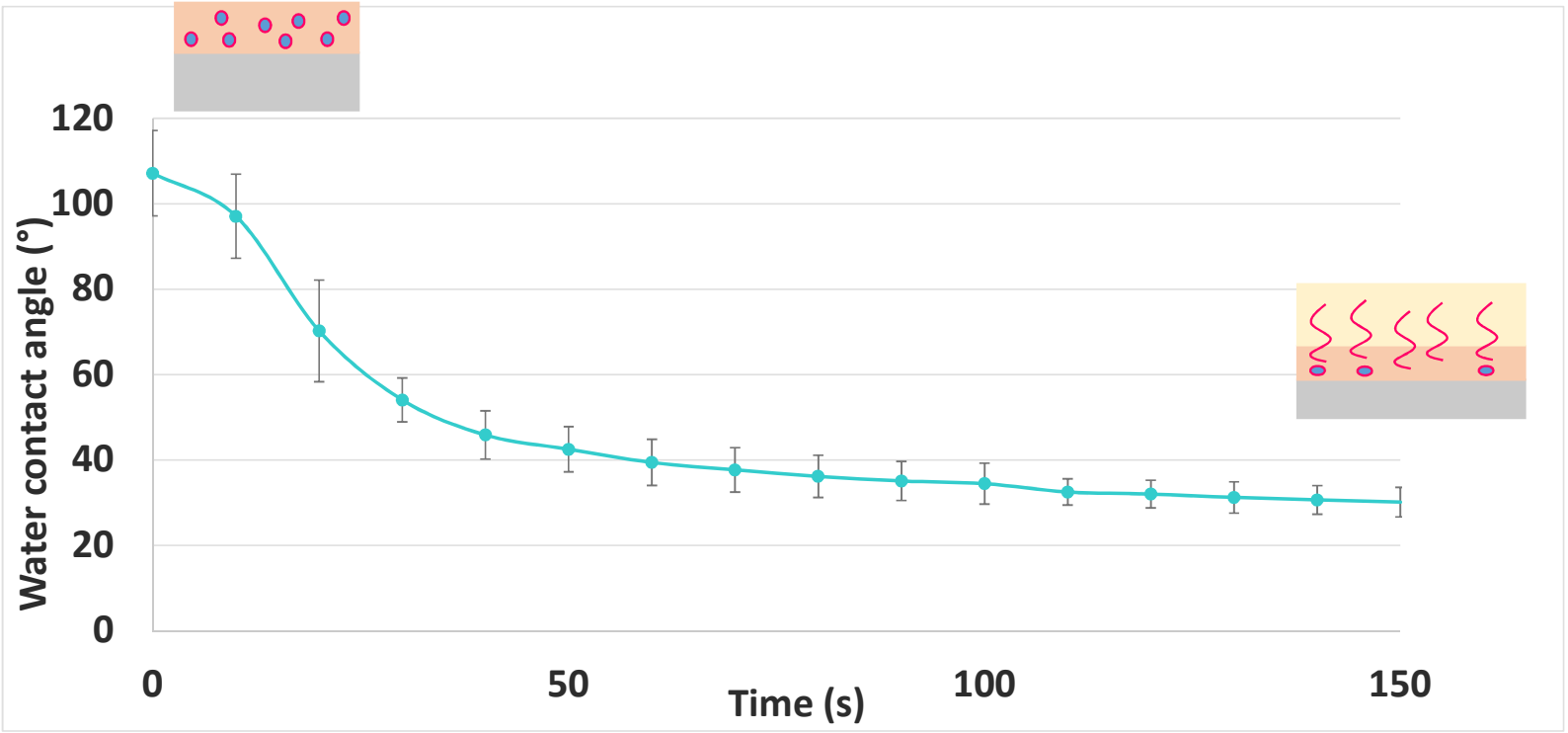
- Silicone matrix
- Si-PEG molecule



Zouaghi et al. Biofouling.

Properties of the coating

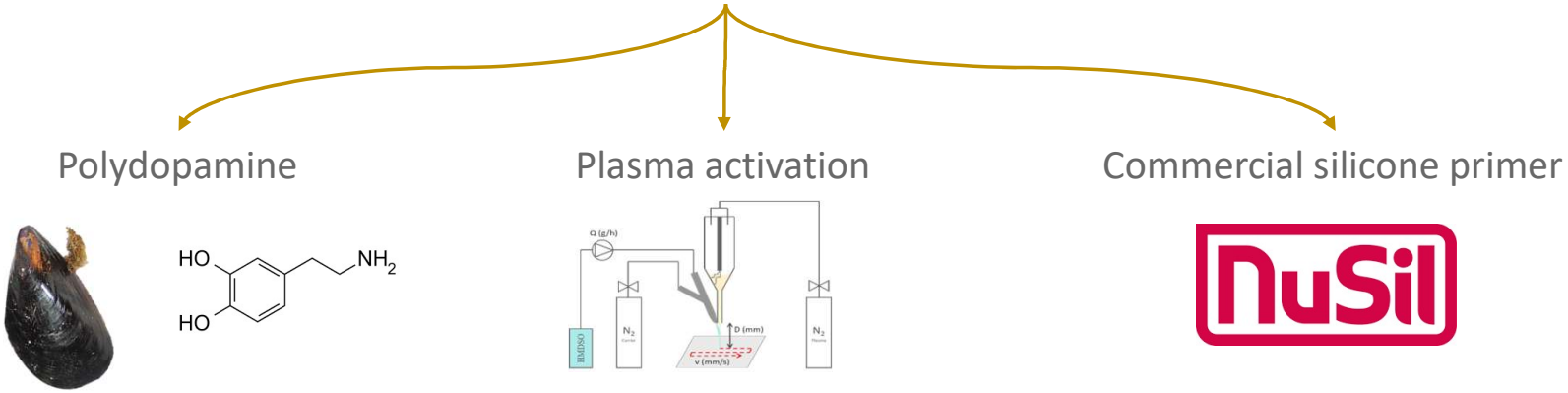
Surface restructuration leading to high hydrophilicity

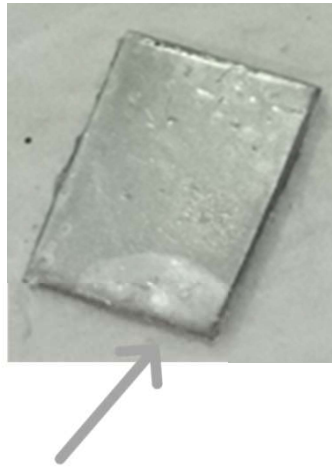


Coating adhesion to the substrate

Poor adhesion of the coating to the substrate

↪ Use of different **pre-treatments** to enhance coating-substrate compatibility

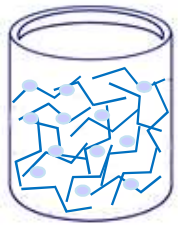


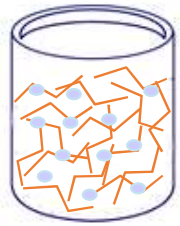


Designation	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
0-(Si-PEG)	✓	✗			
	✓	✓	✗		
	✓	✓	✓	✗	
	✓	✓	✓	✓	✓

Self-stratifying concept

Polymer 1





Polymer 2

→ Blend of incompatible polymers

Air

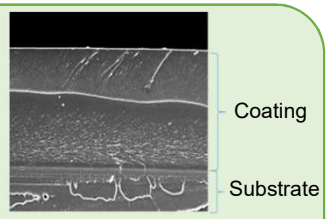
Stratifying resin

Base resin

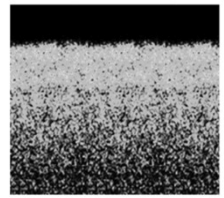
Substrate

Polymer 1
Polymer 2

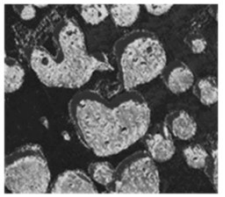
⇢ Degree of stratification[3]



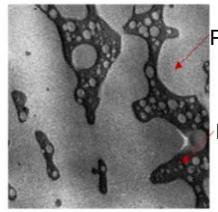
Type I
Perfect stratification



Type II
Homogeneous concentration gradient



Type III
Isolated spherical particles



Type IV
Large island shaped regions

3. A. Toussaint, "Self-stratifying coatings for plastic substrates," Prog. Org. Coatings, vol. 28, pp. 183–195, 1996.