Safe and sustainable by design replacement of PFAS in water and oil-repellent glass-like hybrid coatings

BIO-SUSHY

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Horizon's Europe GA number: 101091464

Introduction

PFAS, What?

PFAS (per and polyfluorinated alkyl substances) provide excellent water and oil repellency properties.

Why is it a problem?

PFAS are known as ‘forever chemicals’ due to their resistance, widespread, and linked to environmental and health problems like cancer and decreased fertility.

How?

Exposure could happen through eating, drinking, or using consumer products containing PFAS.

You may have assumed PFAS without knowing it

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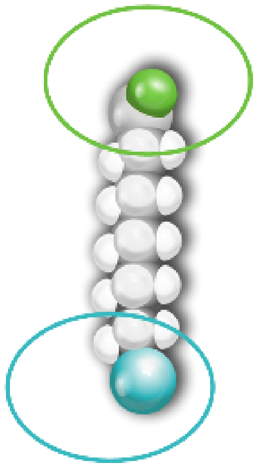
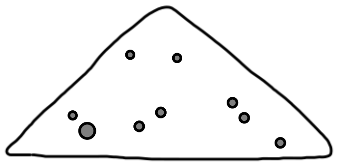
Objective

Develop 3 PFAS-free bio-based coatings

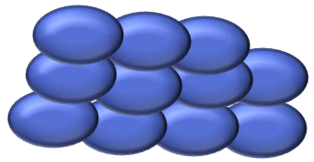


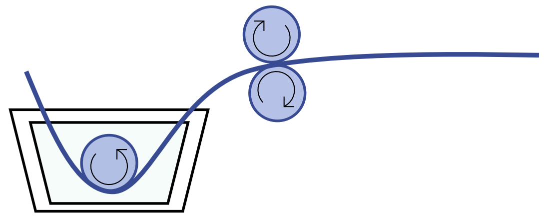
Hydro/oleophobic additives

Thermoplastic Bio-based powder

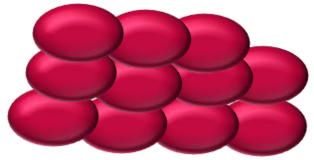


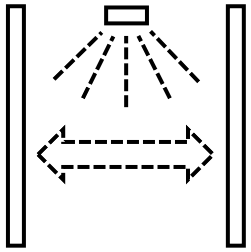
Water-based Hybrid sol-gel organic





Solvent-based Hybrid sol-gel inorganic





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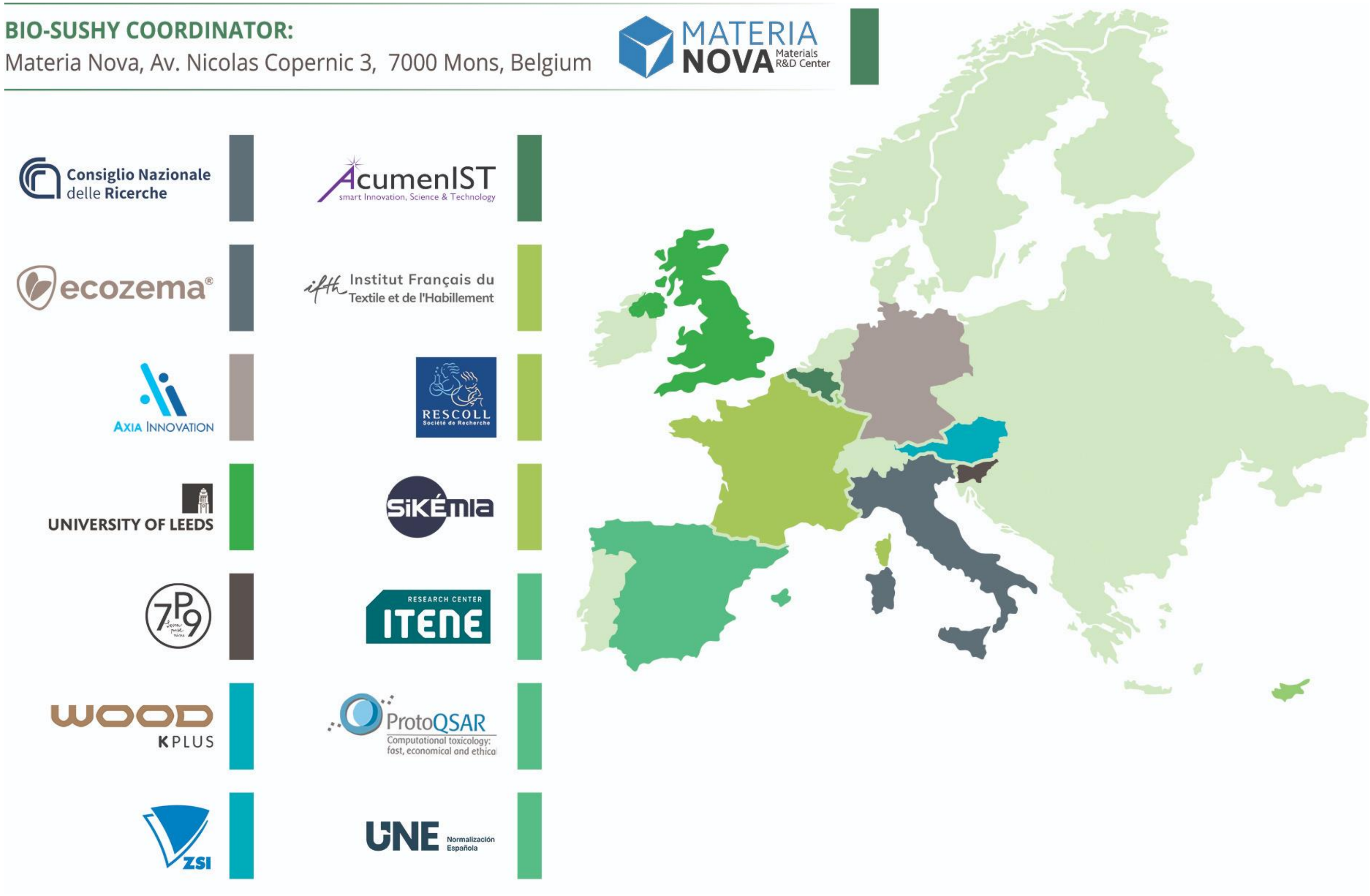
Team

The BIO-SUSHY project
is a collaboration between 14 partners from 7 EU countries and 1 EU-associated country: 6 RTDs, 5 SMEs, 1 large company, 1 university, and 1 national association.



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BIO-SUSHY Methodology – Based on 3 pillars

SAFE AND SUSTAINABLE BY DESIGN

MODELLING

R&I COATING DEVELOPMENT

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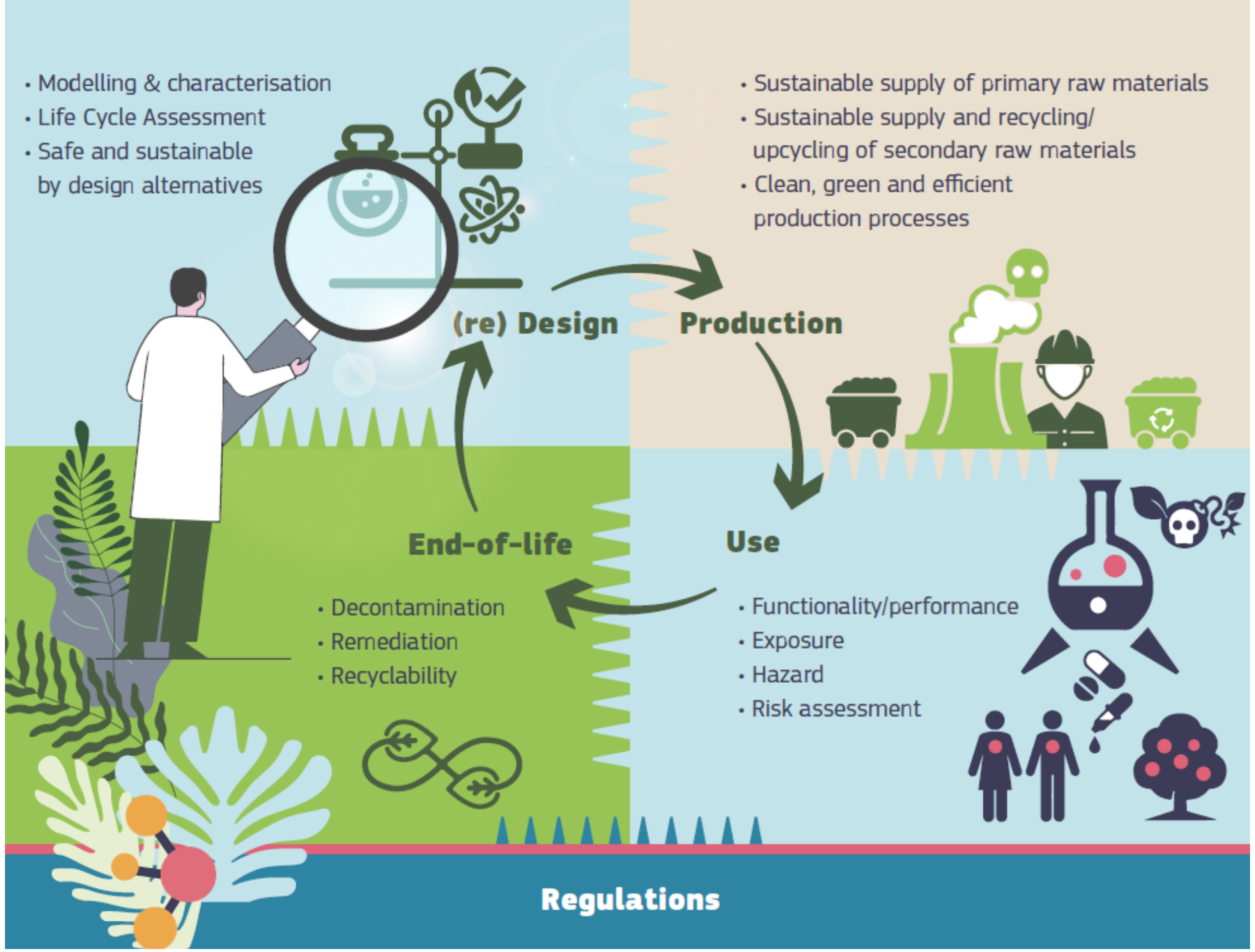
Safe and Sustainable by Design



- SSbD Framework applied to PFAS-free coatings
  - safe by material design,
  - safe by process design,
  - toxicological studies,
  - LCA, LCC, SLCA
- Social acceptance
- Standardisation roadmap

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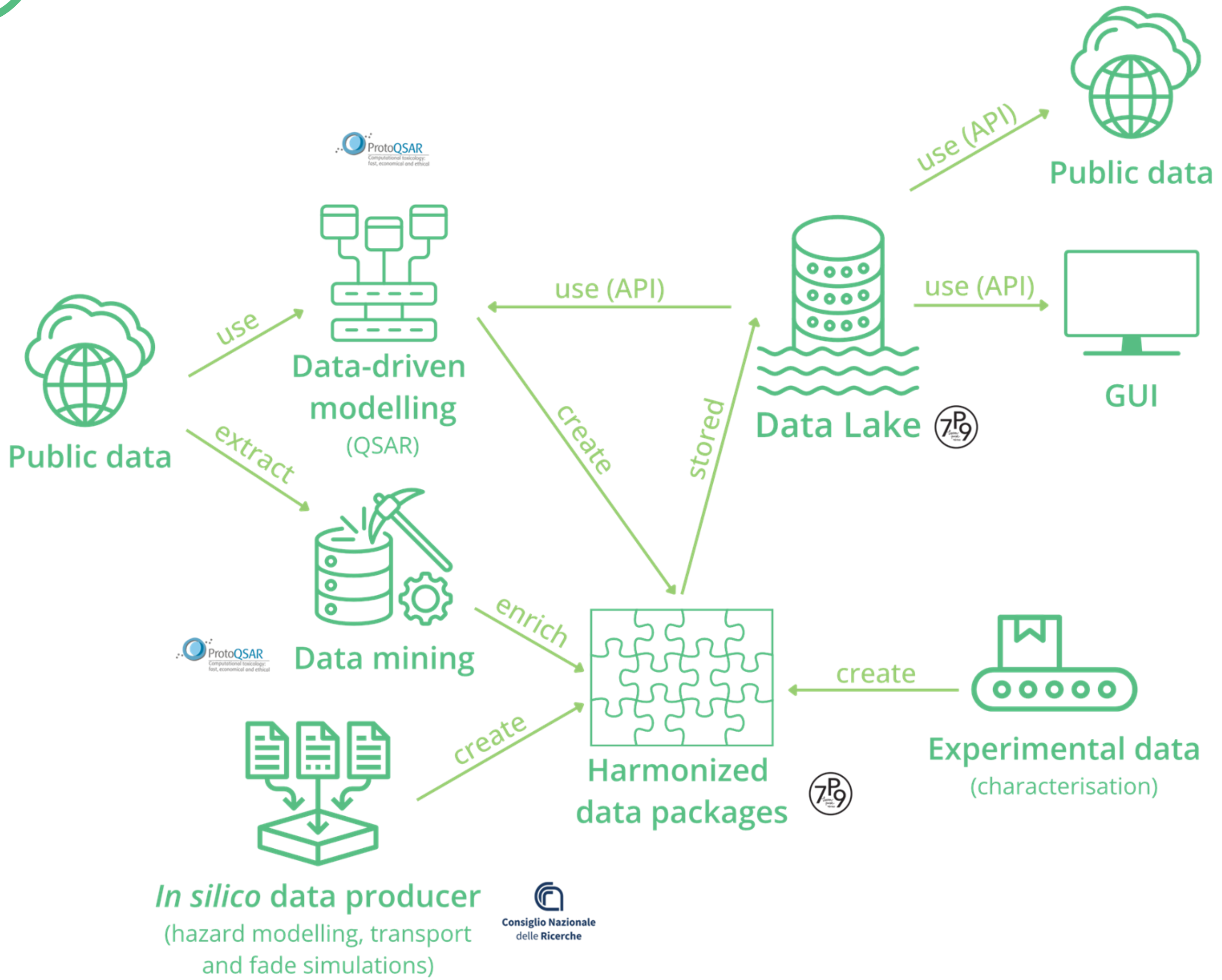
Data-Driven Approaches



- Development of the BIO-SUSHY set of computation tools for SSbD of coatings
- Development of integrated approaches supported by the BIO-SUSHY HUB for effective data management and sharing (FAIR)

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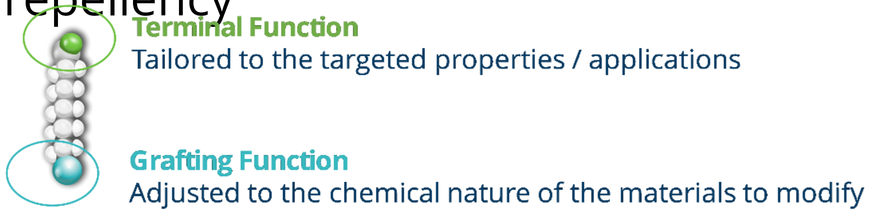
R&I Coating Development

- Development of 3 novel SSbD coatings materials with water and oil repellency



- Validation of coating materials with 3 case studies
  - Textile
  - Food packaging
  - Glass packaging

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Hybrid sol gel coating for glass packaging

Glass packaging for visqueous liquids: solutions to allow high liquid sliding without leaving any residue from the surface

- Waste reduction (up to 25%)
- Aesthetics : keep clean surface (crucial for cosmetic applications)
- Facilitate reuse of the container (easy cleaning)

BIO-SUSHY COATING for GLASS PACKAGING

- Hybrid PFAS free hybrid sol gel coatings for water and oil repellencies
- Solvent based with high inorganic content and bio-based content up to 25%
- Neutral coating to avoid migration from both side of the coating with a very limited release that would not alter the emulsion (skin contact, flavour…)
- Requirements of packaging and particularly cosmetic industry
- Compatible with industrial process (spray, curing)
- Transparency/translucency

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MATERIA NOVA SiKÉMIA

Requirements of glass packaging for comestic applications

Inner application of cosmetic glass containers with targeted chemical and mechanical properties :

- Hydrophobicity/oleophobicity : 10 < surface tension < 20 mN.m-1
- Durability
- Compatible with skin contact

Specifications		Standards
Adhesion	Cross-cut test	ISO 2409
Scratch resistance	Sclerometer hardness test Pencil hardness tester	ISO4586
Abrasion resistance	Washability and scrubbing resistance tester	ISO11998
Water repellency (WCA) Water sliding angle	>100° < 20° (drop 50 μL)	ISO19403-2

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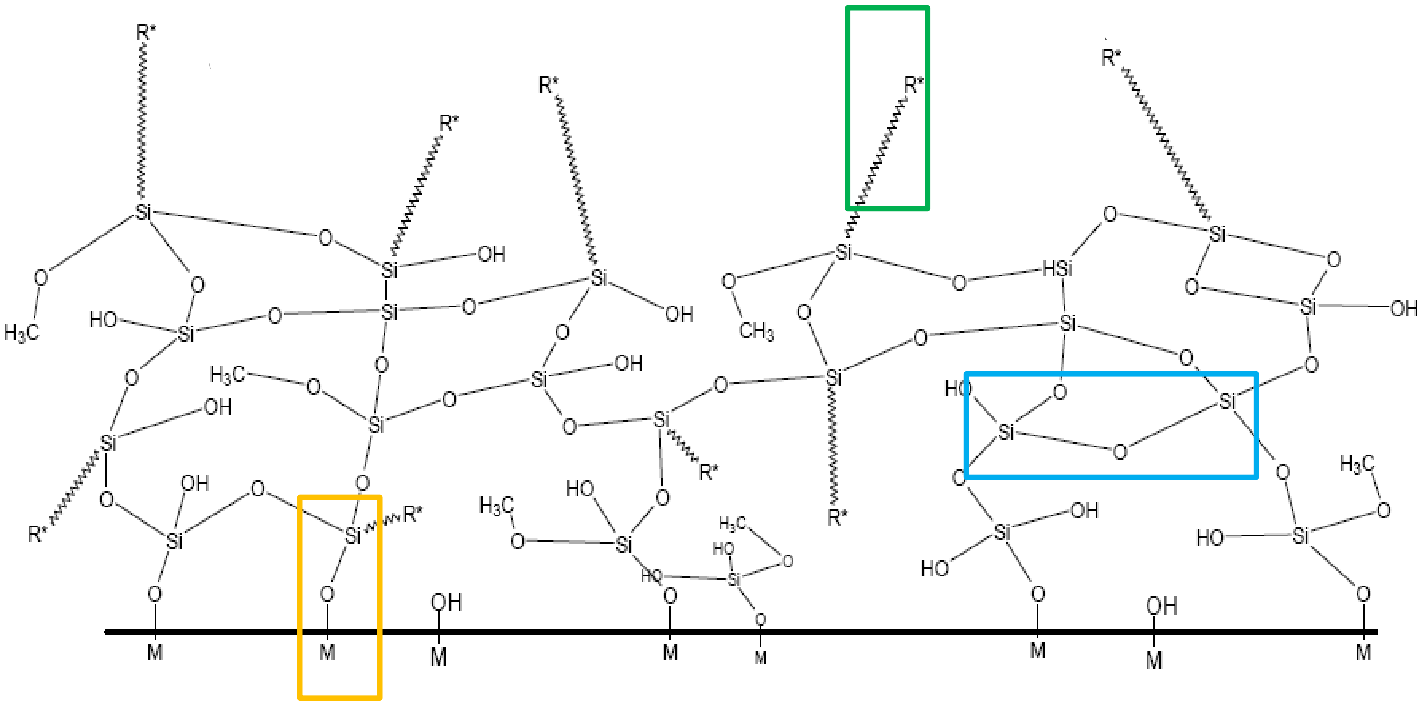
Hybrid sol gel coating for glass packaging



- ✓ Organic/inorganic modulable ratio to cover a large panel of properties/applications
- ✓ Low thickness of the coating inducing small modification of the surface aspect and topography
- ✓ Good mechanical, thermal and chemical resistance
- ✓ Flexibility (compatible with shaping) by increasing organic content
- ✓ Versality of the application process making possible application on site or in industrial chains of 3D complex shapes.
- ✓ Possible to apply on various substrates (glass, metals, polymeric substrates, paper,…)

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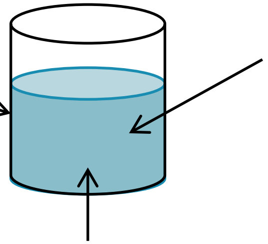
Hybrid sol gel coating for glass packaging

Metal alkoxides precursors



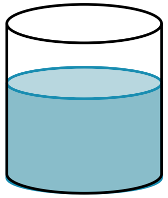
Catalyst/solvents

Additives
- Hydrophobic chains
- (Nano)fillers

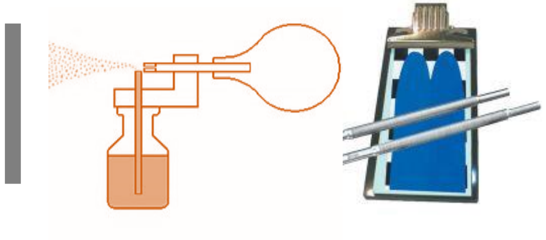
- Nature of the additives
- Influence of the additives amount
- Curing: UV or thermal
- Ratio of precursors

Deposition process

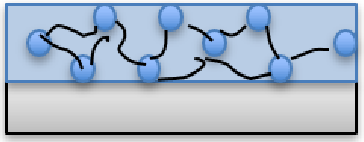
Hydrophobic formulation



Spray or bar coating



Curing



Final thickness : 0.5 -3 µm

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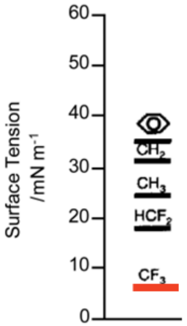
PFAS replacement strategy

(1) Substitution of PFAS by methyl group

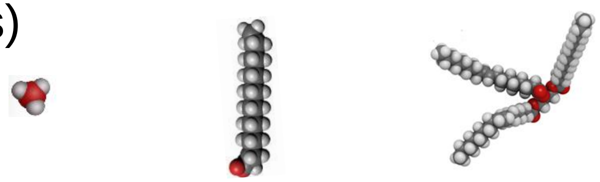


Basis of the following order of increasing surface energy

$$CF_3 < CF_2 < CH_3 < CH_2$$

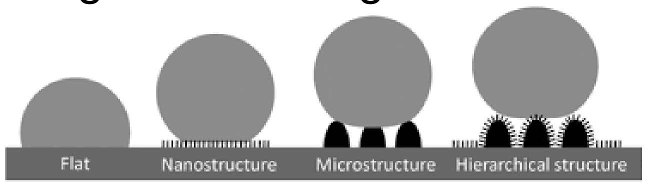
Replacement of PFAS by $–CH_3$ group at the top surface of the coating

(2) Increasing density of $–CH_3$ group at the surface (fillers)

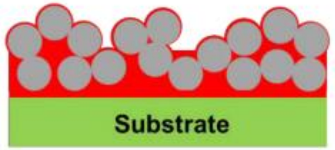


Maximize the $–CH_3$ group at the top surface of the coating

(3) Controlling surface roughness



Surface structuration by incorporation of (nano)fillers



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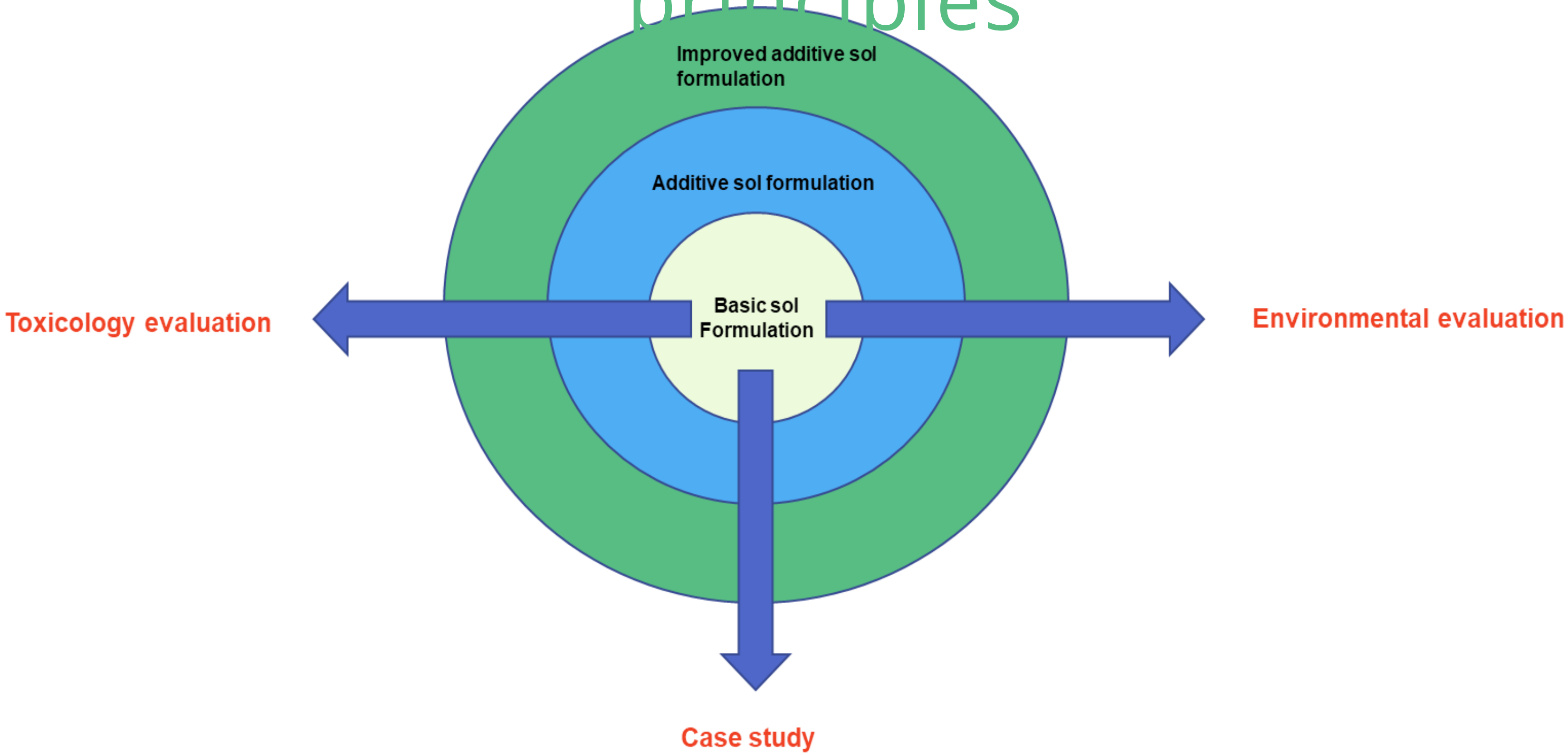
Iterative development process guided by SSbD principles



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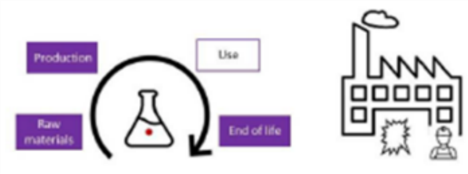
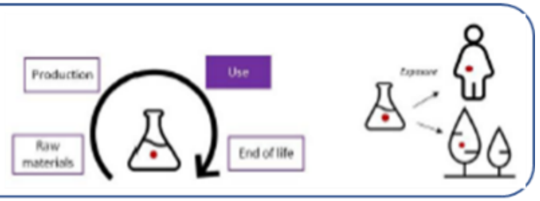
SSbD assessment workflow

Step 1. Hazardous properties of the chemical/material in question

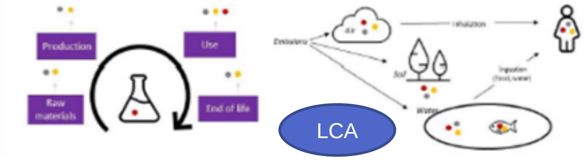
Step 2. Human health and safety aspects of production and processing



Step 3. Hazards and risks of the final application of the chemical or material in question



Step 4. Environmental impacts throughout the life cycle of the chemical or material in question



[Commission Recommendation – EU Assessment Framework for "safe and sustainable by design" chemicals and materials – Link]

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SSbD assessment workflow

Step 1. Hazardous properties of the chemical/material in question

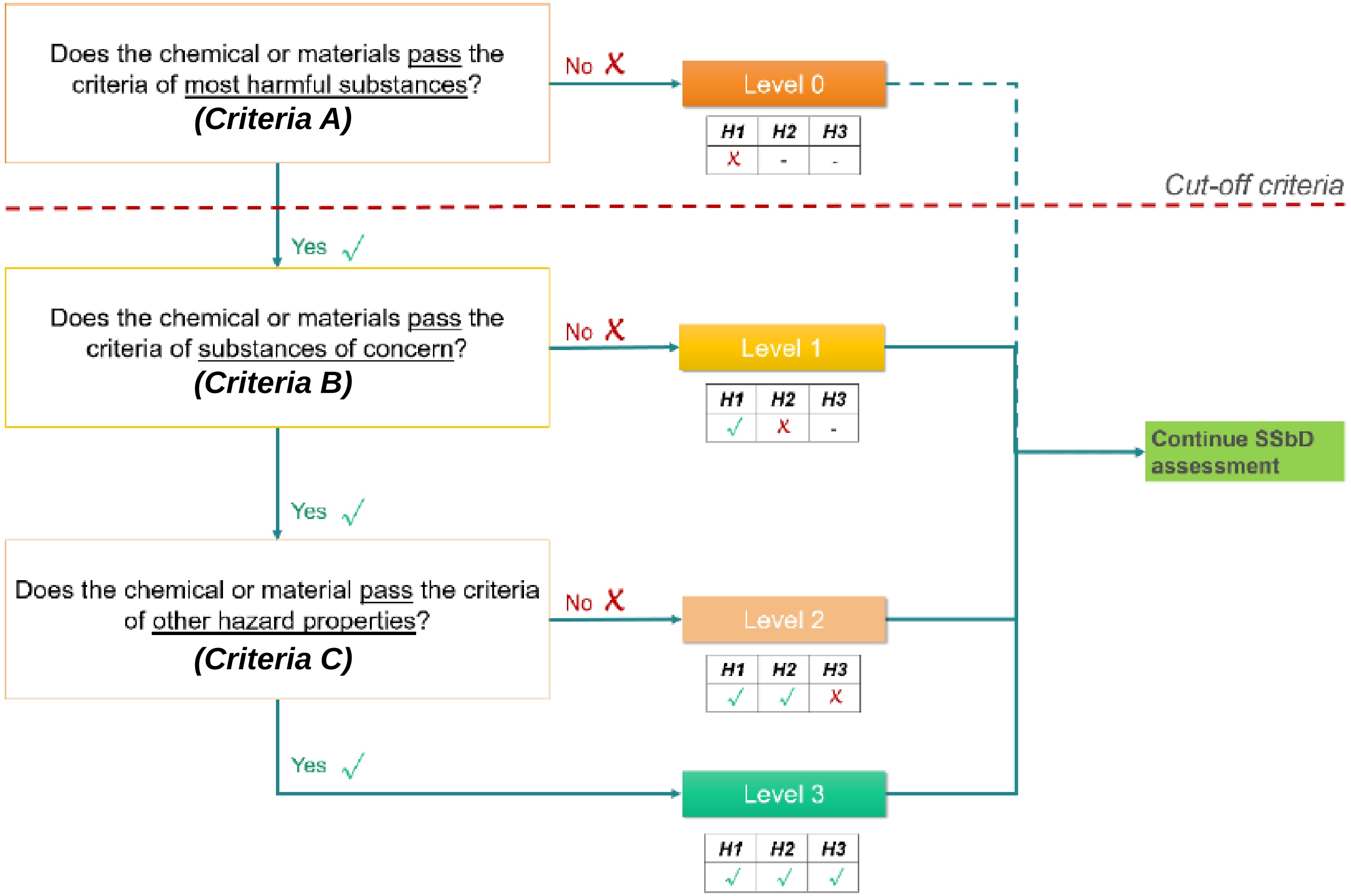
For Step 1, four levels are currently defined (*from 'Level 0' to 'Level 3'*) that will allow the assessor to rank a specific chemical based on these levels and further to integrate the results of the hazard-based evaluation to the overall SSbD assessment.

Level 0 - chemicals or materials considered most harmful substances (Group A) → Prioritized for substitution

Level 1 - chemicals or materials that induce chronic effects, part of the substances of concern (Group B) → Substituted as far as possible

Level 2 - chemicals or materials with other hazardous properties (not included in Group A and B) → Flagged for review and eventually reduce toxic effects

Level 3 - chemicals or materials that pass all safety criteria in Step 1.



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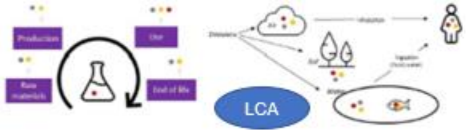
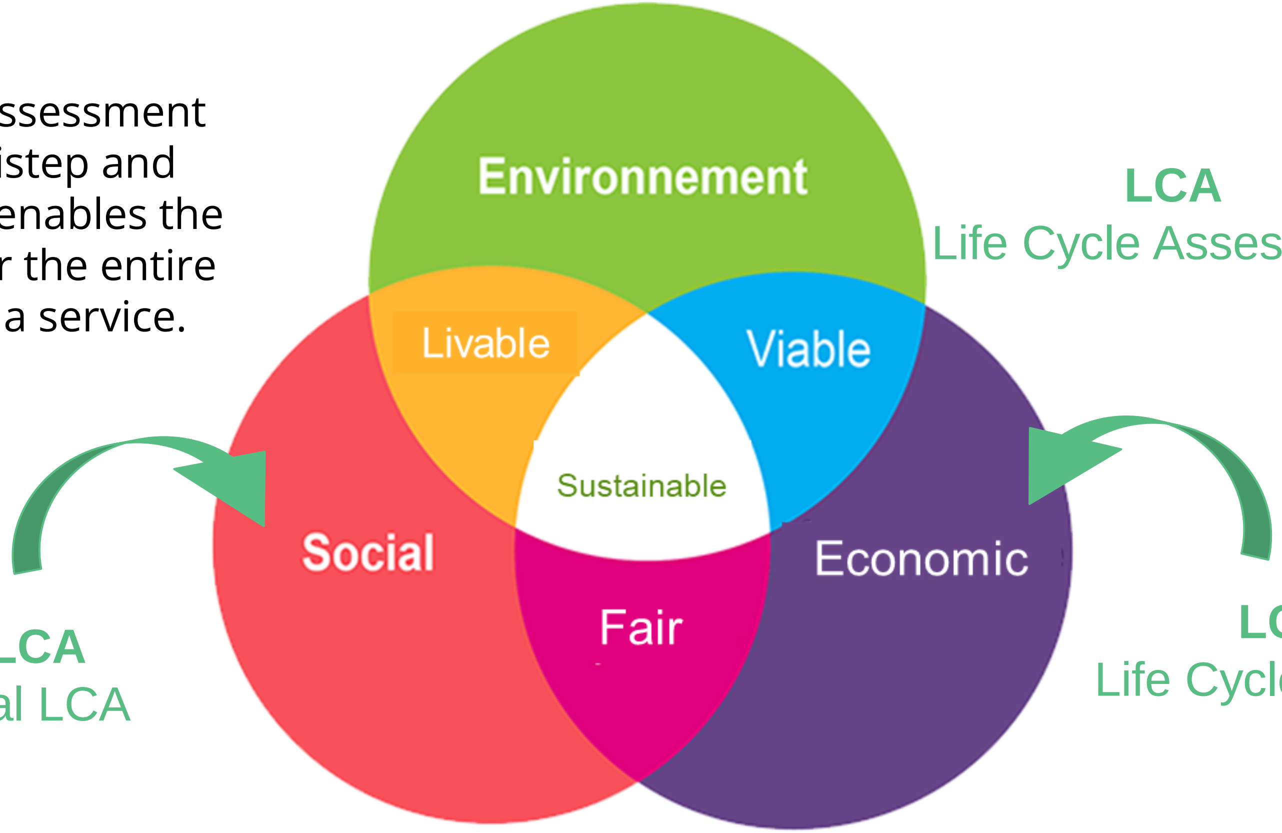
SSbD assessment workflow

Step 4. Environmental impacts throughout the life cycle of the chemical or material in question



Life Cycle Sustainability Assessment (LCSA) is a holistic, multistep and multicriteria method that enables the evaluation of impacts over the entire life cycle of a product or a service.



LCA
Life Cycle Assessment

S-LCA
Social LCA

LCC
Life Cycle Costing

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1st iteration: substitution of PFAS by PDMS and oleic acid

Sol formulation	Precursors	Additive	MEK test	WCA (°)	HCA (°)	Surface energy (Nm/m)	Adhesion	Sclerometer
BS3	TEOS/MTES	-	ok	82 ± 1	36 ± 1	31 ± 1	Cat 0	30N ok
BS14	TEOS/MTES	PDMS	ok	85 ± 1	27 ± 1	30 ± 1	Cat 0	30N ok
BS16	TEOS/MTES	Oleic acid	ok	89 ± 1	42 ± 1	26 ± 1	Cat 0	30N ok
BS17	TEOS/MTES	PDMS/Oleic acid	ok	100 ± 1	48 ± 1	21 ± 1	Cat 0	30N ok

HCA teflon foil: 46.5°

Current composition		SSbd assessment harmonized	Replacement
Precursors	TEOS	Low risk	-
	MTES	**Negligible risk**	-
Catalyst	Acetic acid	Medium risk	**Citric acid**
Solvents	Methoxypropanol	Low risk	-
Additives	PDMS	Low risk	**PDMS from Sikemia**
	Oleic acid	Low risk	-

LCA: Impact of PDMS on the formulation on Ozone depletion impact category

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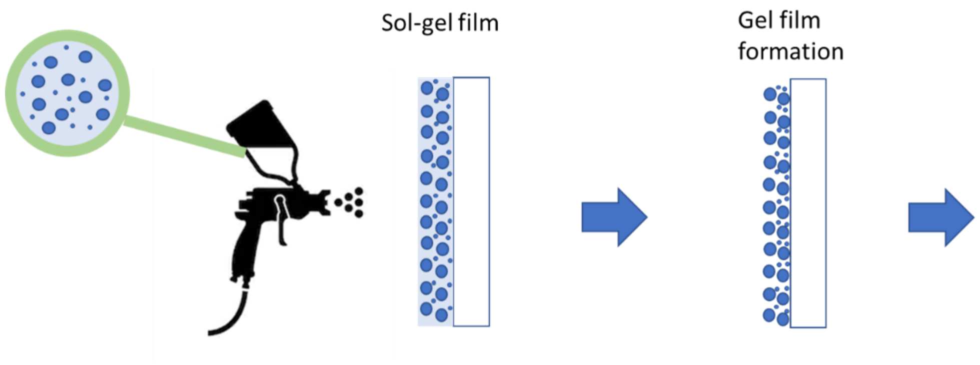
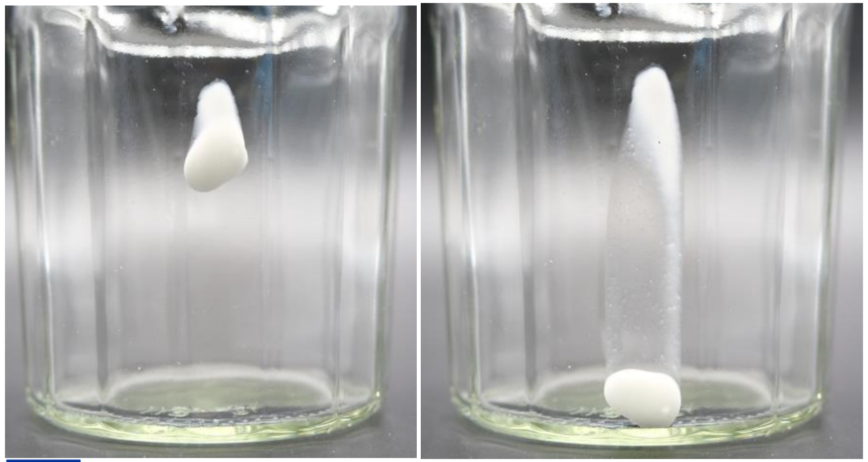
CASE STUDY Coating application and performances

Spray-coating technique deposition : industrial processing

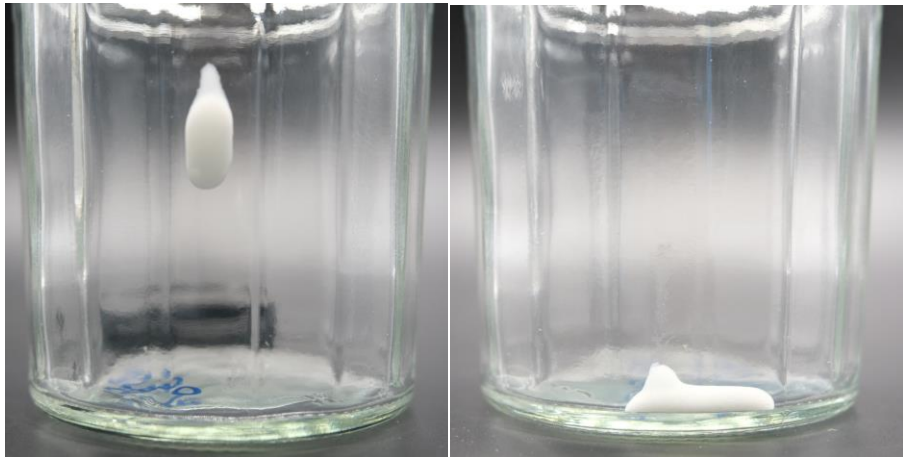


Without coating



Water-based cream

With SG coating without PFAs



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CASE STUDY Coating application and performances

Improvement of the coating chemically (WCA, sliding) vs mechanically (durability, adhesion)

Sol-Gel	Additives				Water sliding angle (50µl) (°)	WCA (°)	HCA (°)
	PDMS 3	Cx	PDMS 5	PDMS 6			
BS85	0.001-1%	0.001-1%	-	-	18	93 ± 1	31 ± 1
BS88	-	0.001-1%	0.001-1%	0.001-1%	16	102 ± 2	35 ± 1
BS90	-	0.001-1%	0.001-1%	0.001-1%	13	103 ± 2	37 ± 1

- **Hydrophobic** (WCA 103 ± 2°)
- **Oleophobic** (HCA 37 ± 1°)
- **Low surface energy** (22 ± 1 Nm/m)
- Water **sliding angle** (13 ± 1° for 50µl water)
- Good **mechanical properties** (Adhesion cat 0 and sclerometer 30N)
- **Durability** : Immersion test **in water (after 14d)** :
  WCA 103 ± 2°
  Water sliding angle 21 ± 3° for 50µl water

  in glycerol (after 14d)
  WCA 102 ± 1°
  Water sliding angle 9 ± 2° for 50µl water

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CASE STUDY Coating application and performances

Sol-Gel	Additives				Water sliding angle (50µl) (°)	WCA (°)	HCA (°)
	PDMS 3	Cx	PDMS 5	PDMS 6			
BS90	-	0.001-1%	0.001-1%	0.001-1%	13	103 ± 2	37 ± 1

Sol gel pigmented to check application uniformity within the flask

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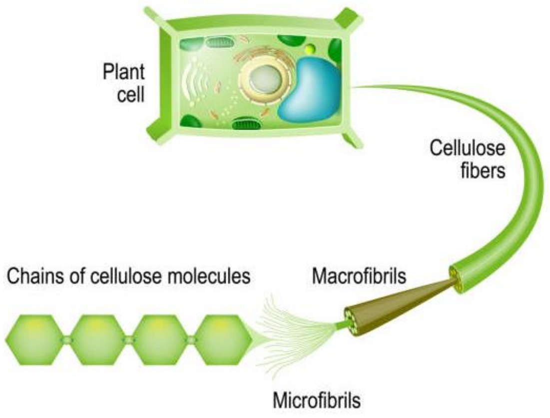
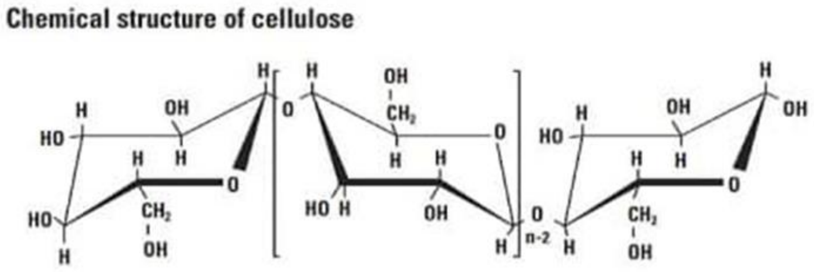
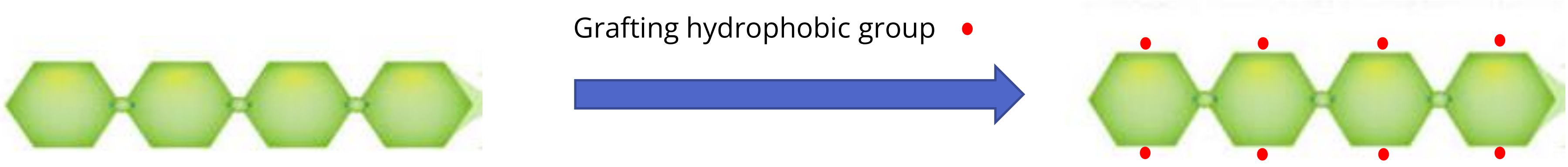
2nd iteration: Replacement of PDMS by functionalized cellulose





LCA: functionalized cellulose lowered impact Ozone depletion impact (vs PDMS)



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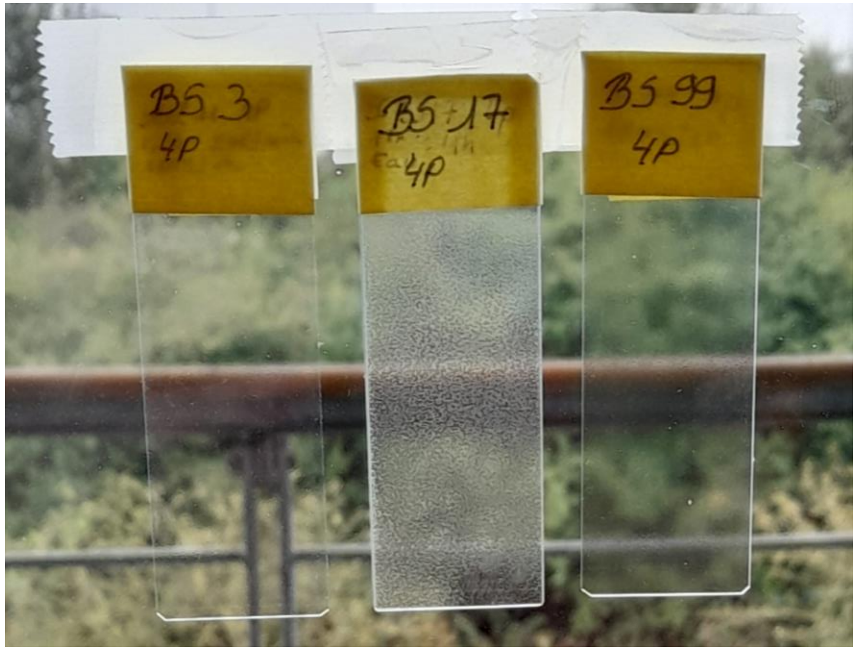
2nd iteration: Replacement of PDMS by functionalized cellulose

Sol-Gel	Additives	MEK test	WCA (°)	HCA (°)	Sliding angle (50 µl)
BS102	Unmodified cellulose	OK	84+/-2	<20	41,4+/-1,1
BS98	Modified cellulose + Cx	OK	94+/-1	34+/-1	13,7+/-0,4
BS99	Modified cellulose	OK	96 ± 1	35 ± 1	12



- MEK test: OK
- Cross cut: Class 0
- Sclerometer: 30N OK

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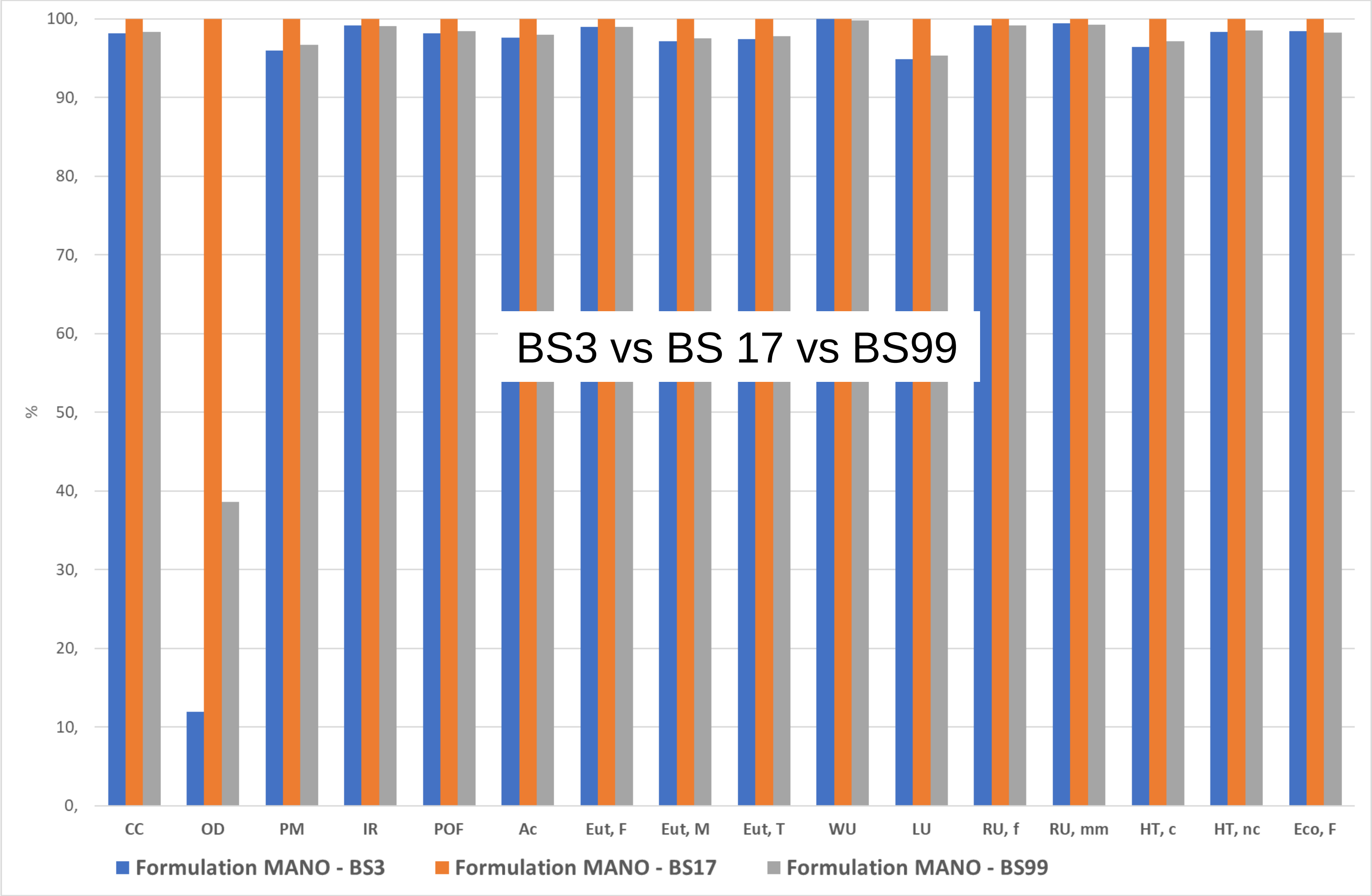
SSbD – Steps 1-4

- Step 1 and 2: data missing for modified cellulose -> next steps
- Step 3: to be done
- Step 4: LCA shows that with BS99 (replacement of PDMS by modified cellulose): improved ozone depletion impact compared to PDMS containing formulation



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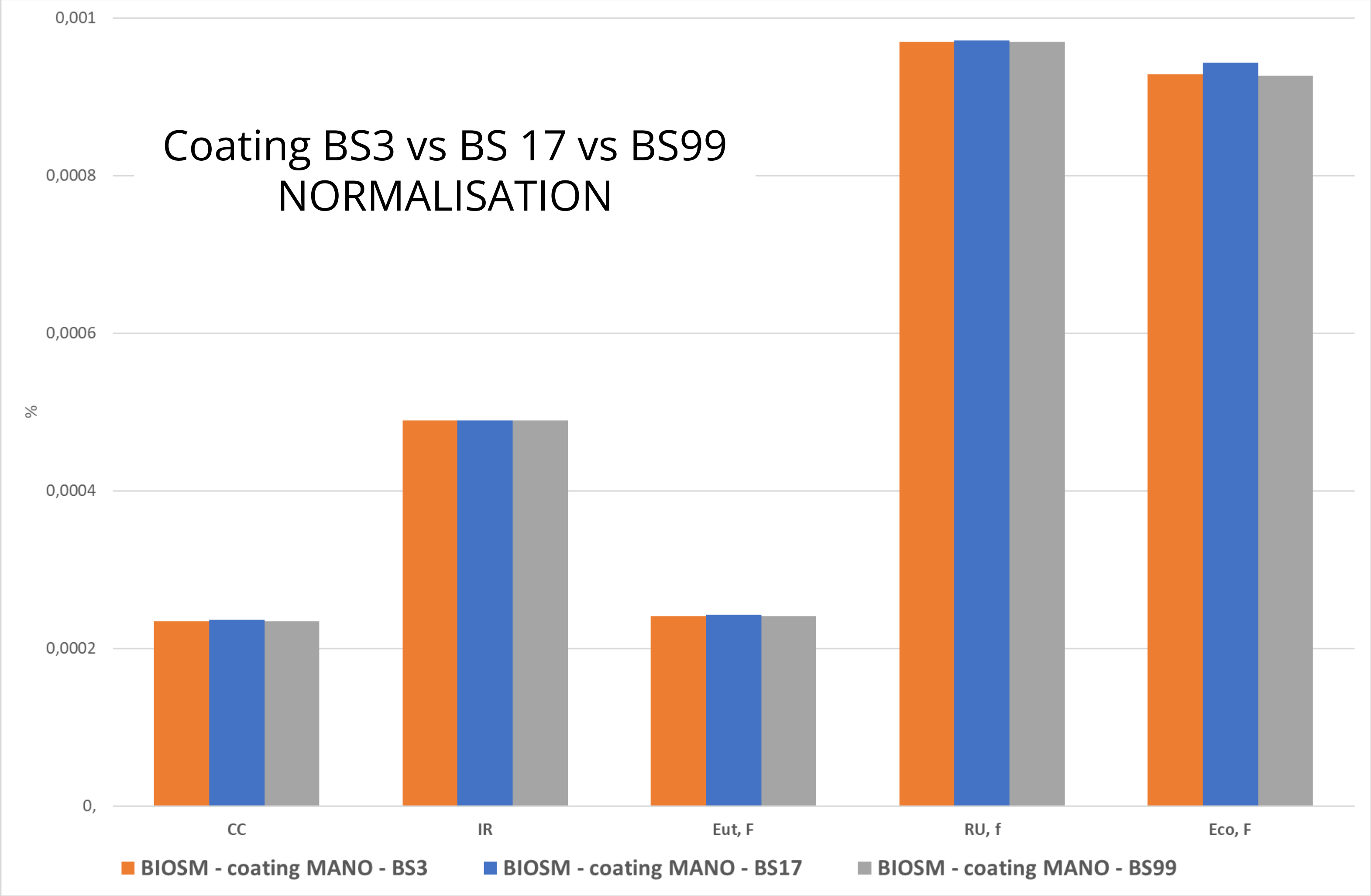
SSbD – Steps 1-4

- Step 1 and 2: data missing for modified cellulose -> next steps
- Step 3: to be done
- Step 4: LCA shows that with BS99 (replacement of PDMS by modified cellulose): improved ozone depletion impact compared to PDMS containing formulation
- After impact normalisation: almost the same impacts for all the coatings



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Conclusions and next steps

- SSbD: used as eco-design tool in an iterative approach to obtain satisfying performances with a safe and sustainable product and process
- Product :
  - Promising results for PFAS replacement in hydrophobic sol gel coatings
  - Oleophobic properties still need to be further improved
  - % biobased content
  - Replacement of solvent -> water
- Process: to be modelled
- End-of-life scenarios: recycling or reuse, both will be evaluated

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BIO-SUSHY project

- Starting Date : January 1st 2023
- Duration : 48 months
- Coordination : Materia Nova

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- Call and topic : HORIZON-CL4-2022-RESILIENCE-01-23 - Safe-and sustainable-by-design organic and hybrid coatings (RIA)
- GA number: 101091464

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Learn more about the BIO-SUSHY project

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THANK YOU!

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