



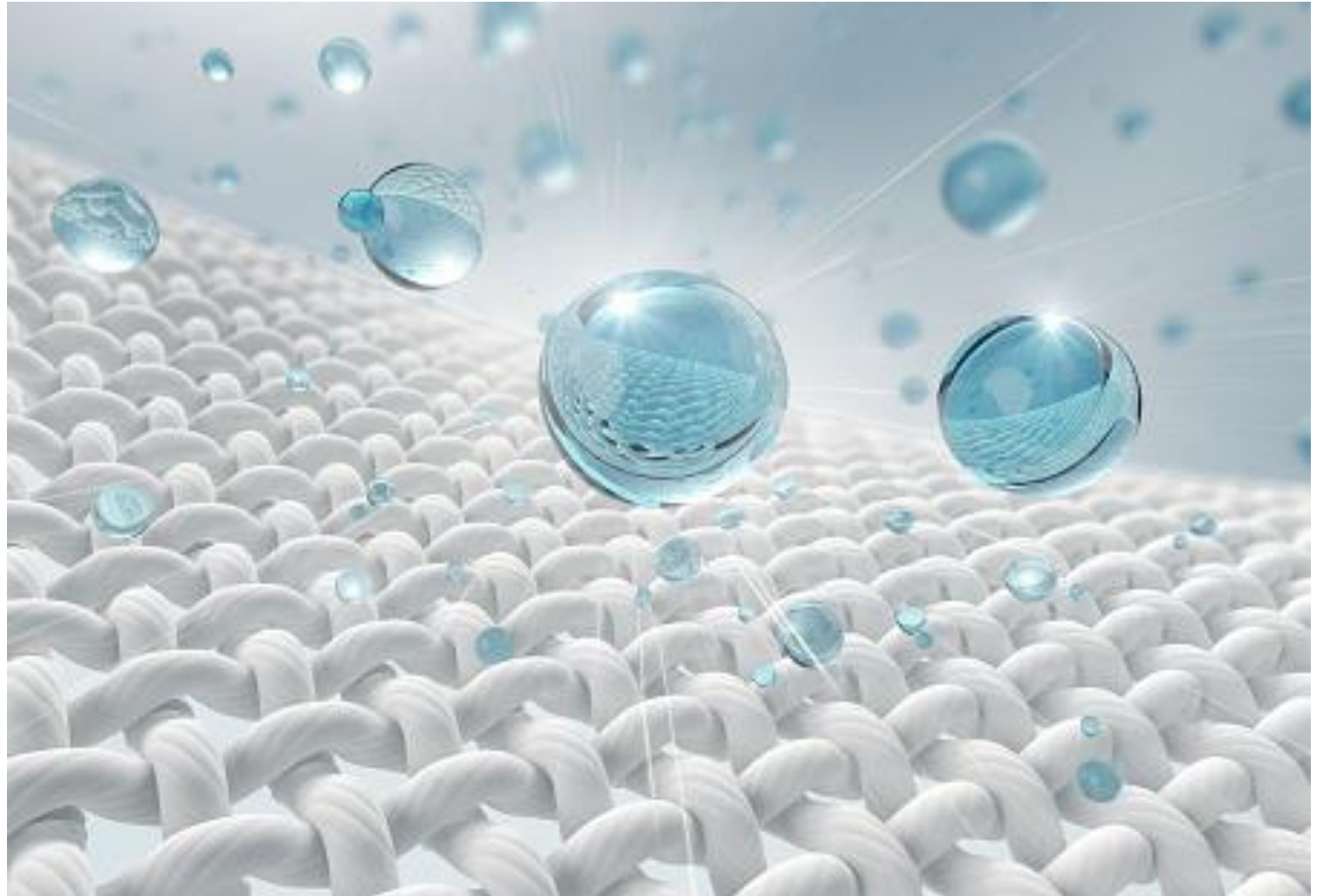
Hydrophilic and hydrophobic materials

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When Water Meets a Fiber

-Why does water soak into one textile and repell from another?

-How can we design the interaction between water and a fiber?



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Part 1: The water droplet:

Imagine putting the same drop of water on different surfaces....



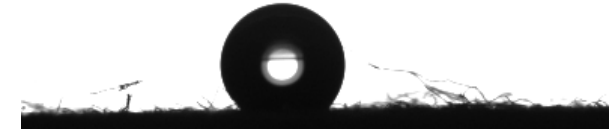
water interacts with the surface

HYDROPHILIC

HYDROPHOBIC



spreads



forms a droplet

depends on the surface below it

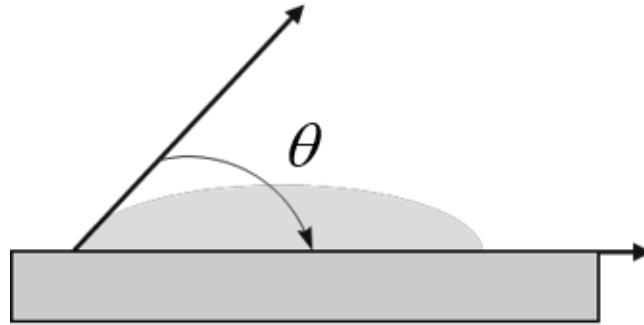


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Part 1: The water contact angle (WCA)

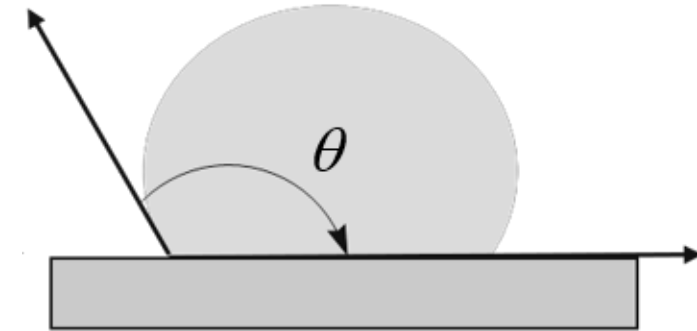
= Interaction between a liquid and a solid (surface)



$$\theta < 90^\circ$$

HYDROPHILIC

- Strong affinity for water = strong water–surface interactions
- Water spreads or penetrates
- Capillary uptake can be rapid



$$\theta > 90^\circ$$

HYDROPHOBIC

- Lower affinity for water = water–surface interactions are less favourable
- Water forms a droplet
- Repellency depends on chemistry + structure
- **For textiles: porosity and roughness complicate the picture**

A contact angle is not the same as textile performance.



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Part 2: What controls wettability?

The wettability is governed by three core pillars:

1. CHEMICAL COMPOSITION

- Polar groups
- Hydrogen bonding
- Surface energy
- Chemical functionality

2. STRUCTURE

- Roughness
- Porosity
- Fiber geometry
- Air pockets

3. PROCESSING

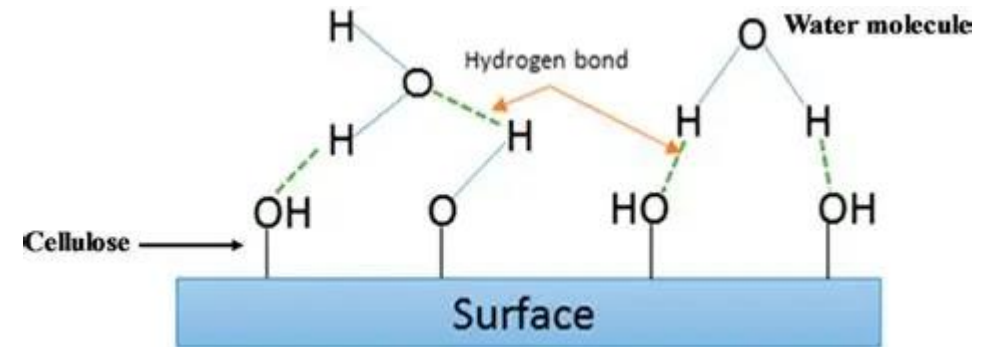
- Coating process
- Number of layers
- Nanoparticles, plasma
- Chemical modification

**Wettability is not controlled by one single parameter.
All three pillars work together.**

Part 2: Molecular origin - Why does water like some surfaces and not others? Why is cellulose naturally water-loving?

Cellulose –OH groups + H₂O → hydrogen bonding → high water affinity

- Cellulose contains many hydroxyl (–OH) groups.
- These groups can form hydrogen bonds with water.
- Cotton therefore readily wets and can wick/absorb water.
- But the textile response also depends on fibre architecture and finishing.



Q: Can we take a naturally hydrophilic material and engineer its surface to become more hydrophobic?

Part 3: Why are textiles special? A textile is not a flat surface.

FIBERS – YARNS – FABRIC →
Between everything there are pores and air spaces. **Textile = 3D architecture**

Water can:

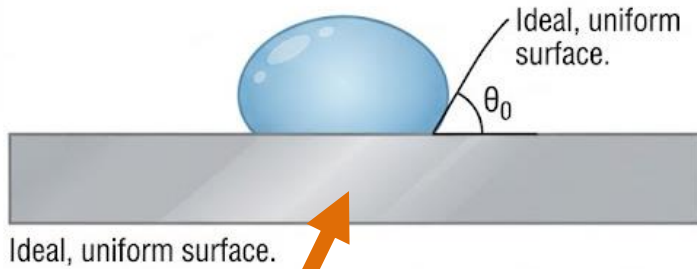
- sit on the fiber surface.
- penetrate between fibers.
- move through yarn capillaries.
- be absorbed into the fiber itself.

This makes textile wetting much more complicated than simply placing a droplet on a perfectly flat material!



Part 3: Roughness changes the game

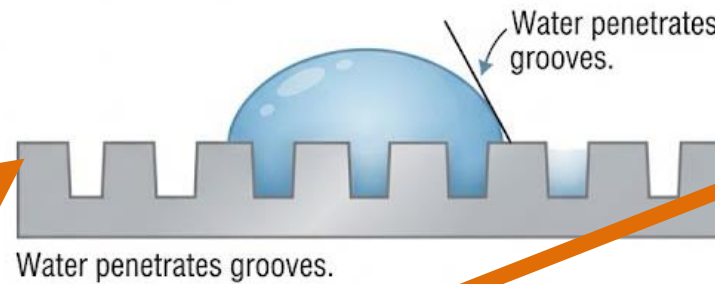
Smooth surface



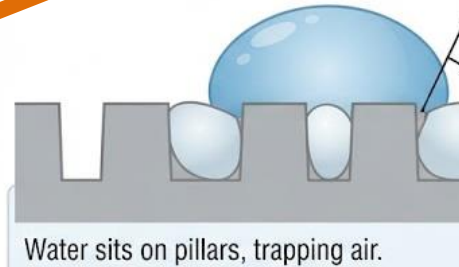
These changes strongly affect how a water droplet behaves!

Rough surface

WENZEL **Sits on peaks and valleys**



CASSIE-BAXTER

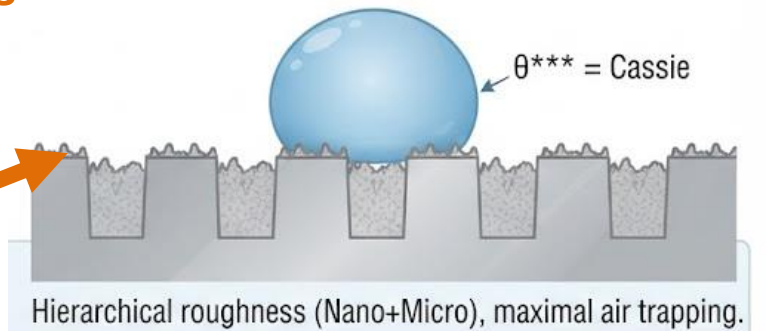


WHEN WE DESIGN A HYDROPHOBIC SURFACE, WE DON'T ONLY CHANGE THE CHEMISTRY, WE CAN ALSO CHANGE THE SURFACE STRUCTURE.

Air trapped underneath

Nano/micro-rough surface

SUPERHYDROPHOBIC (hierarchical)



Part 4: Why PFAS entered the story? Excellent performance created a difficult legacy

(Per- and polyfluoroalkyl substances)

WHY THEY WERE ATTRACTIVE

- **Very effective water / oil repellency**
(extremely low polarizability makes the surface both hydrophobic and oleophobic)
- **Unique chemical structure: C-F bond:**
fluorine atoms along the whole carbon chain created a molecule with extreme characteristics
- **Extremely durable and stable finishes**
Widely useful in textiles and other applications

WHY ARE WE MOVING AWAY

- Environmental persistence (due to extreme stability) – forever chemicals
- Toxicity, bioaccumulation
- Regulatory pressure and phase-out efforts
- Need for safer, more sustainable alternatives

A major challenge:
How can we achieve the required textile performance without relying on persistent fluorinated chemistry?



Part 5: A deeper look into green chemistry challenges

Moving away from PFAS is not as simple as replacing one chemical with another.



Feedstock Variability

Natural waste extracts (like plant polyphenols or starch sources) exhibit **batch-to-batch inconsistencies** driven by seasonal changes, soil composition, and geography, complicating standard industrial recipes.



Industrial Processing Windows

Transitioning from laboratory-scale green synthesis to continuous roll-to-roll textile finishing requires adjusting curing temperatures, drying speeds, and binder compatibility without losing eco-friendly metrics.



Durability vs. Biodegradability

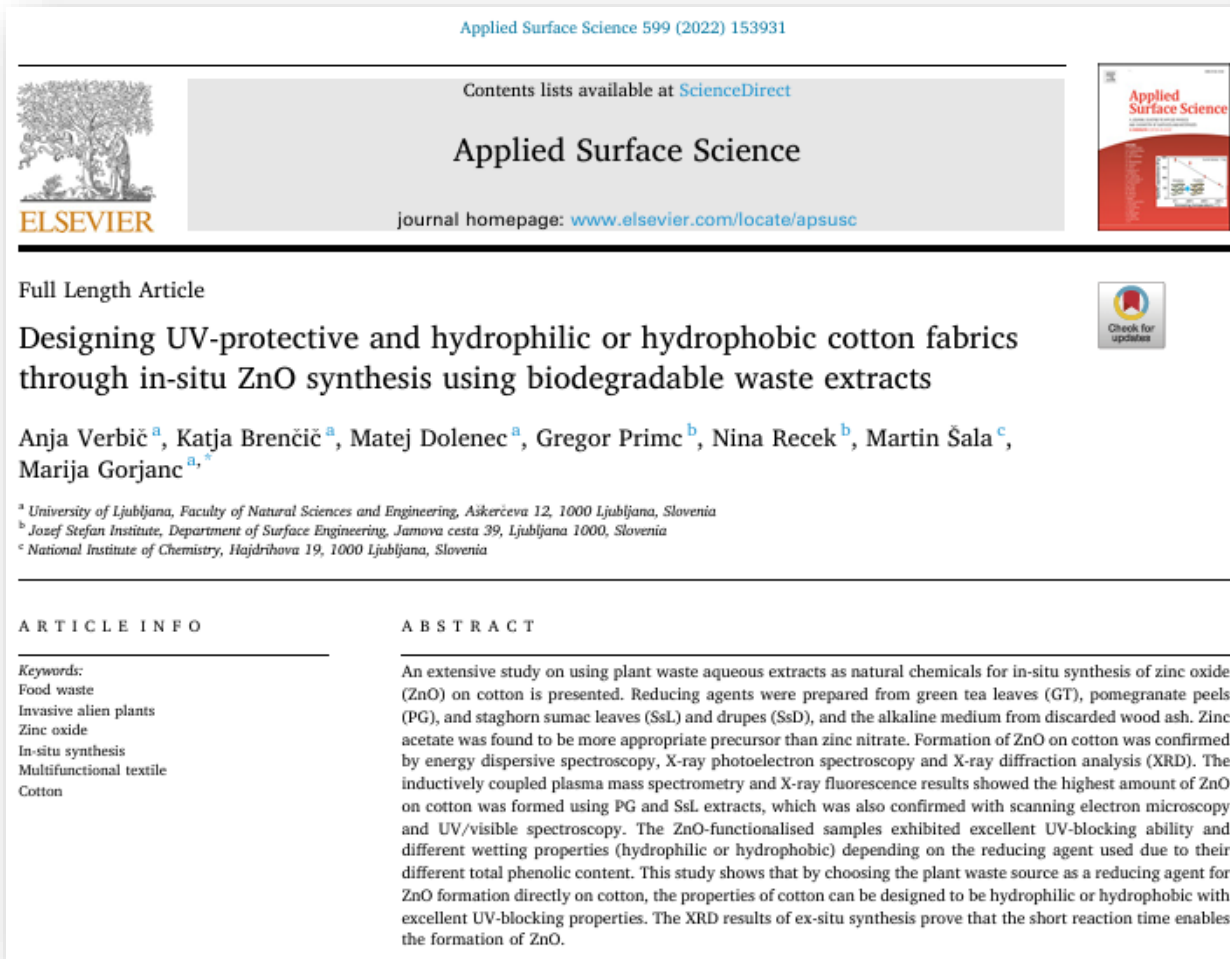
The ultimate **paradox** of green functional textiles: coatings must resist severe laundering, UV exposure, and mechanical abrasion while remaining completely benign and biodegradable at their end-of-life. We want the material to be **very stable when we use it, but much less persistent after its useful life.**



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Case study 1: Design cotton surface properties



Q: If cotton is naturally hydrophilic, can we make its surface hydrophobic?

- In situ synthesis of ZnO: Cotton fabric + Zn precursor + plant-waste extract (to provide OH groups – polyphenols, and appropriate pH)
- Green tea, pomegranate peel, and staghorn sumac extracts investigated.

ZnO synthesized directly on cotton using biodegradable waste extracts



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Case study 1: Design cotton surface properties

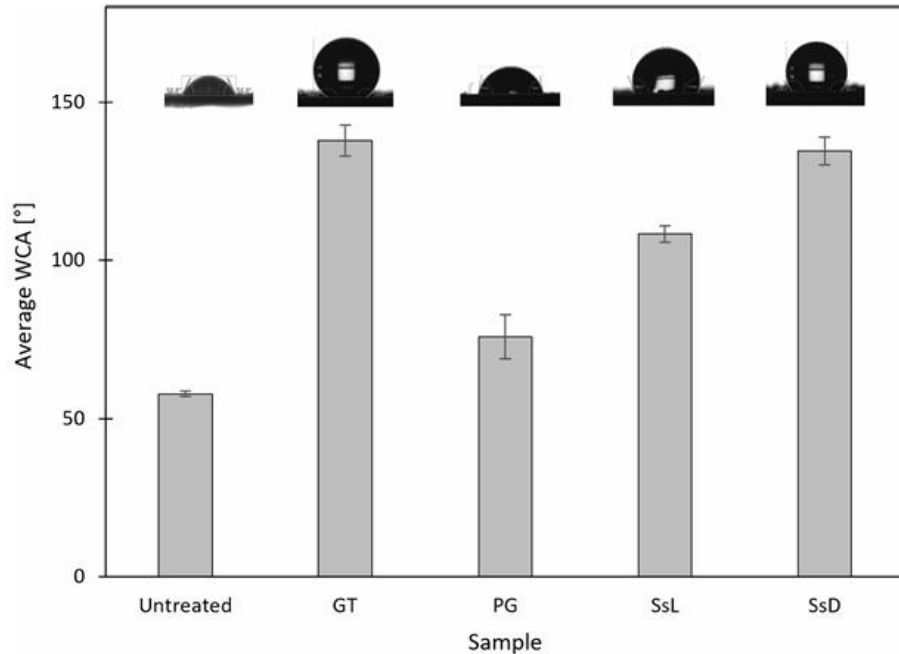


Fig. 5. Water contact angle measurements of untreated and functionalised cotton samples with in-situ synthesised ZnO using green tea (GT), pomegranate peels (PG), staghorn sumac leaves (SsL) and staghorn sumac drupes (SsD) extracts as reducing agents.

Table 2

Ultraviolet protection factor (UPF), the transmission of UVA and UVB radiation (T(UVA) and T(UVB)), UVA and UVB blocking, protect the samples.

Sample	UPF	T (UVA) %	T (UVB) %	UVA blocking	UVB blocking	Protection category
Untreated	3.9	28.9	24.8	71.1	75.2	Insufficient
GT	108.9	1.6	0.9	98.4	99.1	Excellent
PG	277.6	0.6	0.4	99.4	99.6	Excellent
SsL	1010.9	0.2	0.1	99.8	99.9	Excellent
SsD	60.9	4.2	1.6	95.8	98.4	Excellent

Key lesson

**The same fiber can be engineered toward different properties.
Different plant extract = different wetting behaviour = different UV protection**

**ZnO + polyphenol-rich extracts
= chemistry + structure**

Case study 2: What about polyester?

Cellulose	Polyester
Natural polysaccharide	Synthetic polymer
Repeating glucose units	Repeating ester-containing units
Strong hydrogen bonding with water	Much fewer accessible polar groups
Highly hydrophilic	Less hydrophilic



**HARD TO
FUNCTIONALIZE**

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REGULAR ARTICLE



Plasma-Assisted Green Synthesis of ZnO Directly on Polyethylene Terephthalate Fabric

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Abstract

This article presents green in situ synthesis of ZnO directly on polyethylene terephthalate (PET) fabrics using pomegranate peel extract. The surface of PET was activated by environmentally friendly oxygen plasma, and the process was compared to alkali treatment where the extract of wood ash was used instead of classical chemicals. Sorption analysis showed that the hydrophilic character of the plasma-treated sample was much better than that of the alkali-treated and untreated samples. Both treatments slightly decreased the breaking strength and elongation of the fabric. Scanning electron microscopy, colour measurements, dispersive X-ray spectroscopy, and antioxidant activity investigations showed that the ZnO particles were successfully synthesised on alkali- and plasma-treated PET. The liquid chromatography-mass spectrometry results showed that ellagic acid and punicalagin were the most abundant compounds in the pomegranate peel extract that enabled the synthesis of ZnO. The UV protection, amount of ZnO, and uniformity were the highest for the ZnO prepared on the PET samples by the plasma-assisted green synthesis. Additional optical assessment of fabric porosity and thickness measurements confirmed that these fabrics have excellent UV protection due to the presence of ZnO.

Keywords Green synthesis · ZnO · Plasma-assisted · Textile · PET · UV protection

terephthalate (PET) fabric and the in situ synthesis of ZnO particles. The alkaline medium and reducing agent for ZnO synthesis were prepared as aqueous extracts from wood ash and pomegranate peel, respectively. Due to the hydrophobic nature of the PET fabric, oxygen plasma treatment was included in the process. The influence of plasma treatment in different synthesis steps on the formation of ZnO and consequently on the morphological, colour and ultraviolet (UV) protective properties of the samples was discussed. The study showed that incorporating oxygen plasma treatment before immersing the samples in each solution for the ZnO in situ synthesis (natural alkaline medium of wood ash, zinc salt and natural reducing agent from pomegranate peel) produced PET fabric with the most uniform ZnO layer without visible cracks and the highest UV-blocking ability with a UV protection factor (UPF) of 300+. The colour measurements showed that increasing the number of plasma treatments leads to higher colour strength of the samples. Herein, a novel protocol for the production of protective PET fabrics is presented, which is also an example of a completely environmentally benign textile functionalization process.

Keywords: polyester; ZnO; zinc oxide; in situ synthesis; green synthesis; oxygen plasma



Article
**Eco-Friendly
Oxygen Plasma**
Anja Verbič^{1,*}, Ka



Citation: Verbič, A.; Brenčič, K.; Primc, G.; Mozetič, M.; Gorjanc, M. Eco-Friendly In Situ ZnO Synthesis



Case study 2: What about polyester?

Plasma can change the surface without changing the whole polymer

PET → oxygen plasma → ZnO *in situ* → multifunctional textile

PET

- Synthetic polyester
- Limited water affinity compared with cellulose – harder to functionalize!
- Good mechanical / processing properties

O₂ PLASMA

- Activates the surface, introduces active sites
- Improves hydrophilicity / sorption
- Creates a better platform for subsequent functionalization

Key lesson

Polyester needs surface activation

Part 6: Now the problem becomes industrial

Hydrophobicity is useful—but performance is not enough

~~WE HAVE NON-PFAS
HYDROPHOBICITY.
PROBLEM SOLVED.~~

**A USEFUL TEXTILE
FINISH NEEDS:**

**FUNCTIONALITY
(WATER REPELLENCY)**

WASH DURABILITY

ABRASION

SAFETY

STABILITY

END OF LIFE

- A textile finish is only useful if it survives real handling.
- For a sustainable alternative, we must consider entire system: chemistry, durability, processing, and end-of-life.

Case study 3: BREAKING FREE FROM PFAS

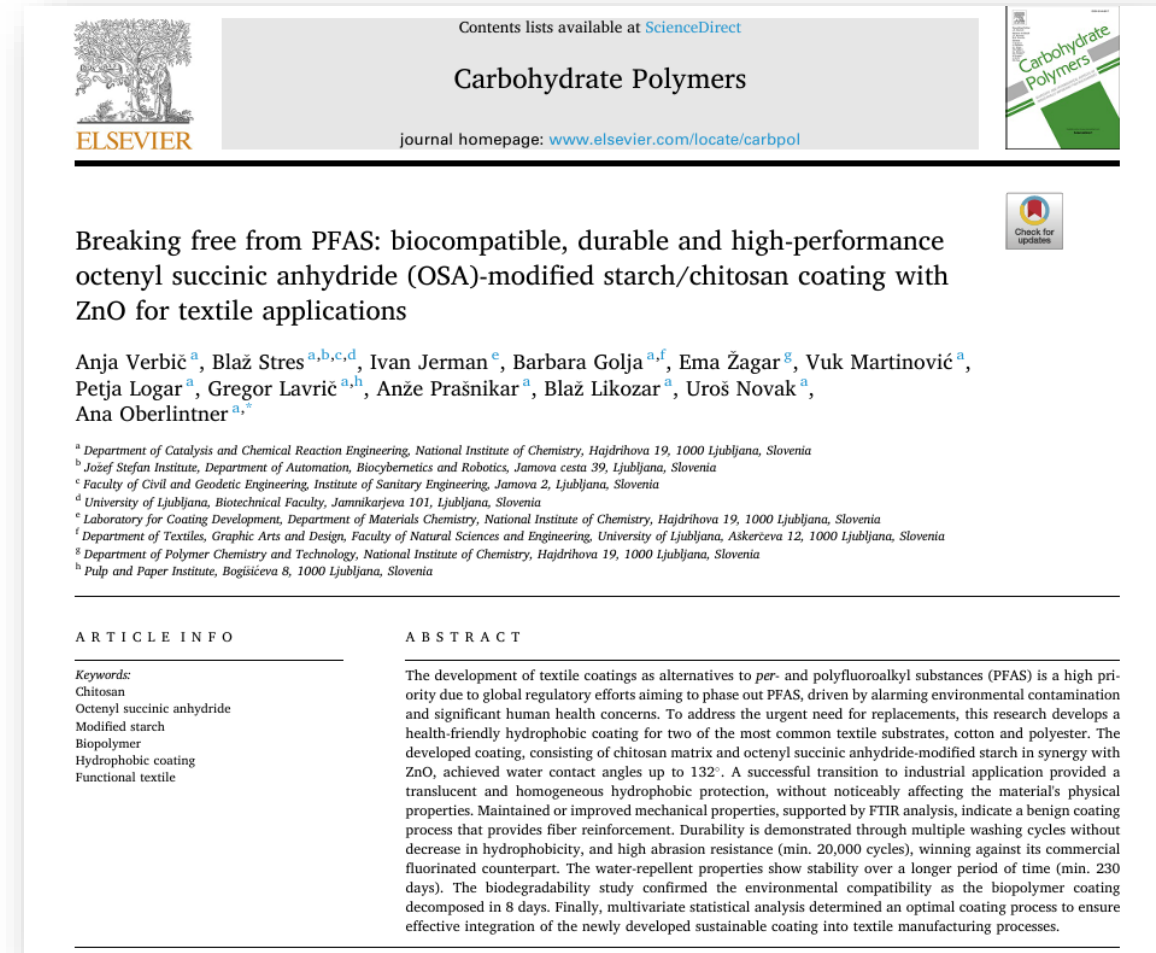
Verbič et al. 2025

([10.1016/j.carbpol.2025.123792](https://doi.org/10.1016/j.carbpol.2025.123792))



„Can polysaccharides provide hydrophobicity?“

- Starch & chitosan = hydrophilic
- By modifying their chemistry, combining different components, and introduce hydrophobic groups, can we engineer a surface with hydrophobic behaviour?



Case study 3: BREAKING FREE FROM PFAS

COTTON + POLYESTER SUBSTRATE
+
CHITOSAN BIOPOLYMER NETWORK
+
**OCTENYL SUCCINIC ANHYDRID (OSA)-
MODIFIED STARCH**
(hydrophobic modification)
+
ZnO nanoparticles
(surface structure & synergy)

Key idea

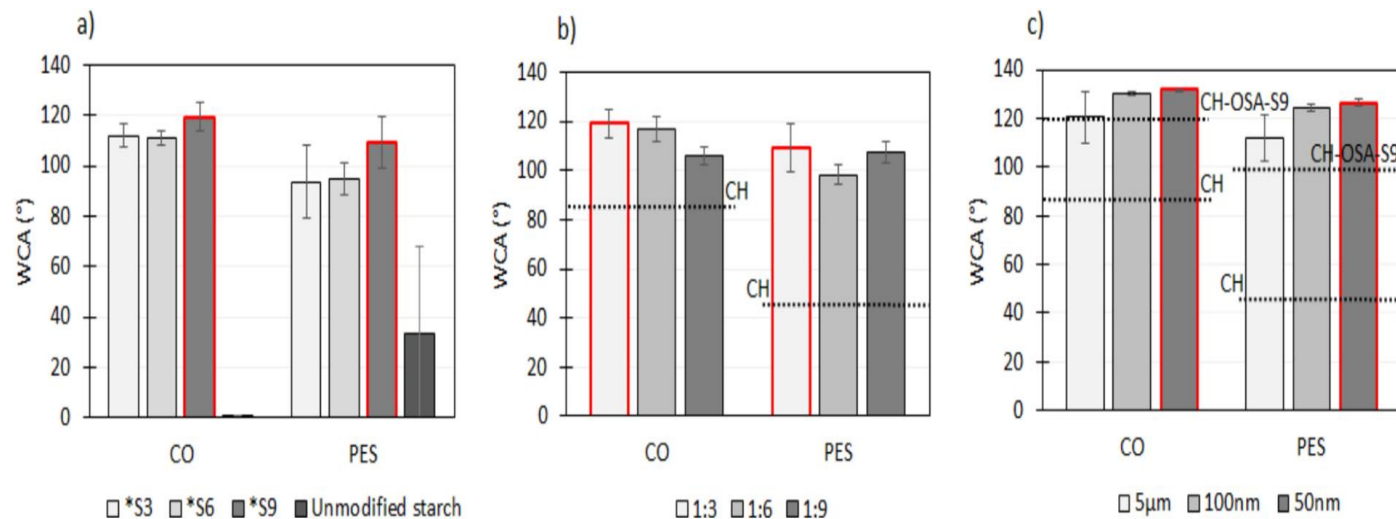
**Hydrophobicity is a property
of the final surface—not a
label attached to the word
'polysaccharide'.**

THE RESULT → HYDROPHOBIC TEXTILE



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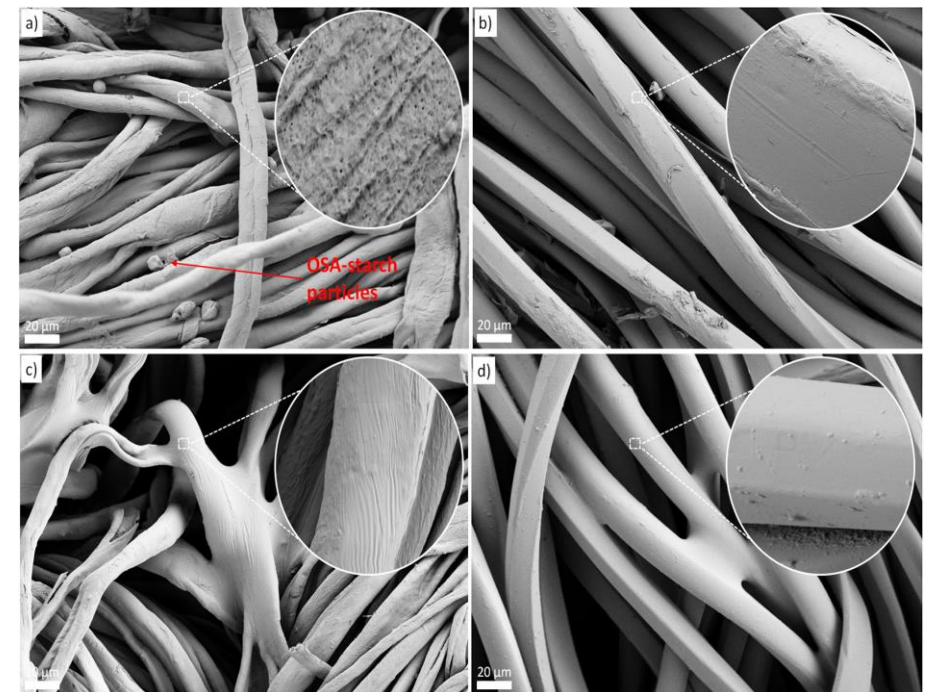


- **Cotton: 132°, polyester: 126°**
- **OSA (hydrophobic) modification of starch gives a good foundation.**
- **The increase of WCA associated with surface roughness (AFM) achieved with the addition of ZnO and particle size effects.**

Formulation matters

- Increasing the degree of starch modification with OSA increased hydrophobicity in the laboratory screening: **9%**
- The chitosan:modified-starch ratio also mattered: **1:3**
- Addition of ZnO - ZnO size changes the surface (<5 µm, <100 nm, and <**50 nm**)

Fig. The SEM micrographs of the bio-based scaled-up (UP3) a) CO and b) PES sample and PFAS coated c) CO and d) PES sample at 1000× and 10,000× magnification

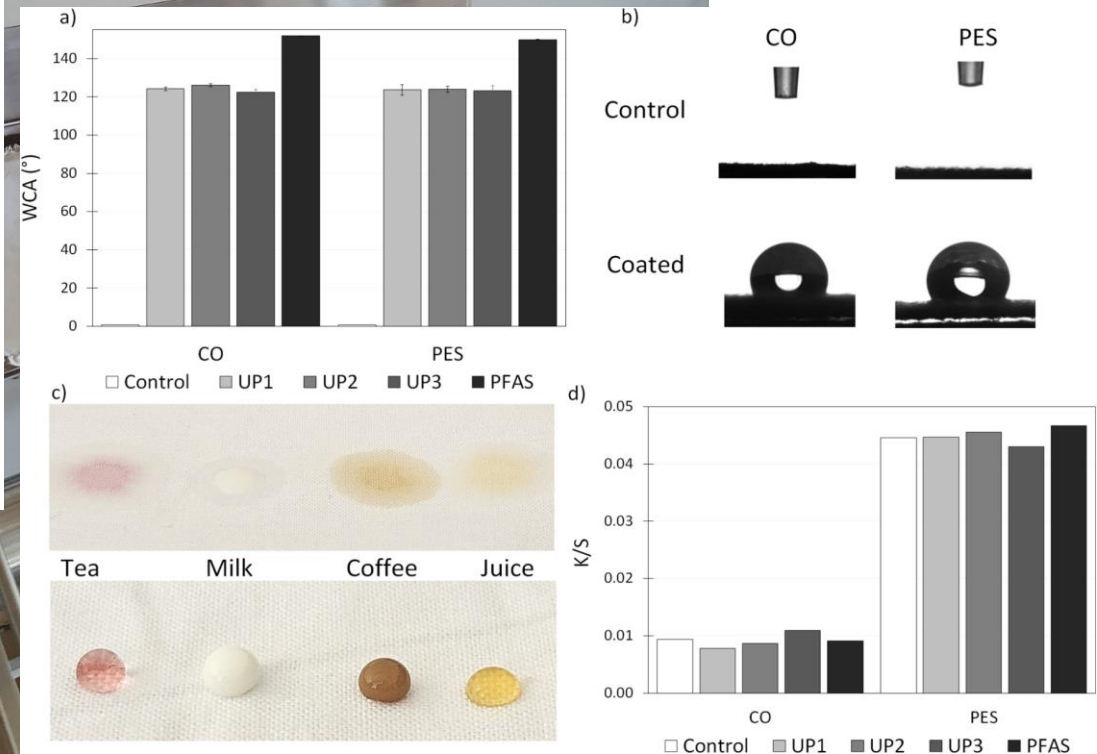


Scale-up: can it leave the laboratory?

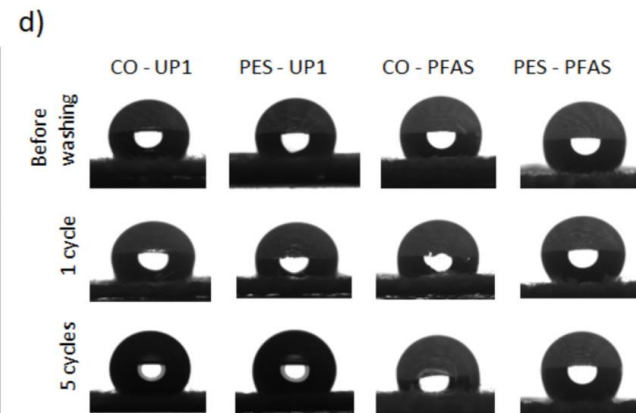
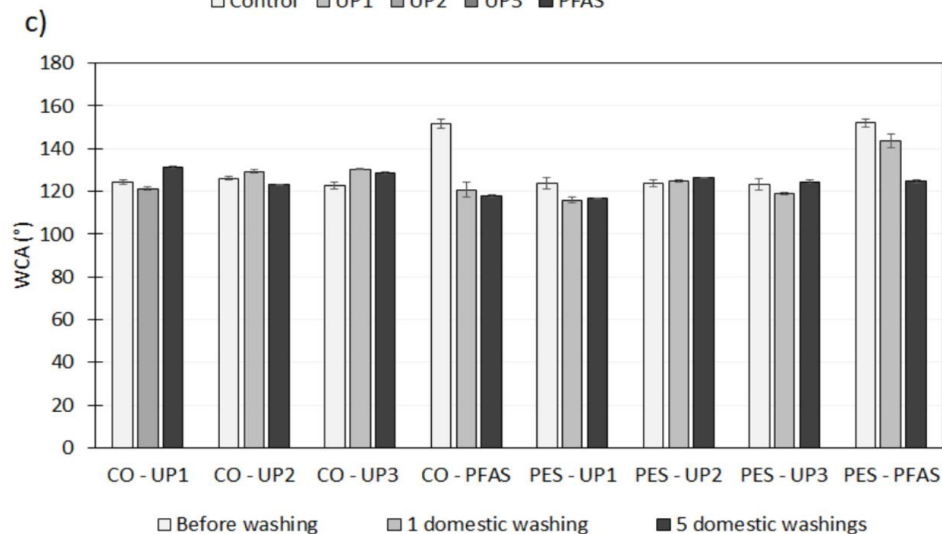
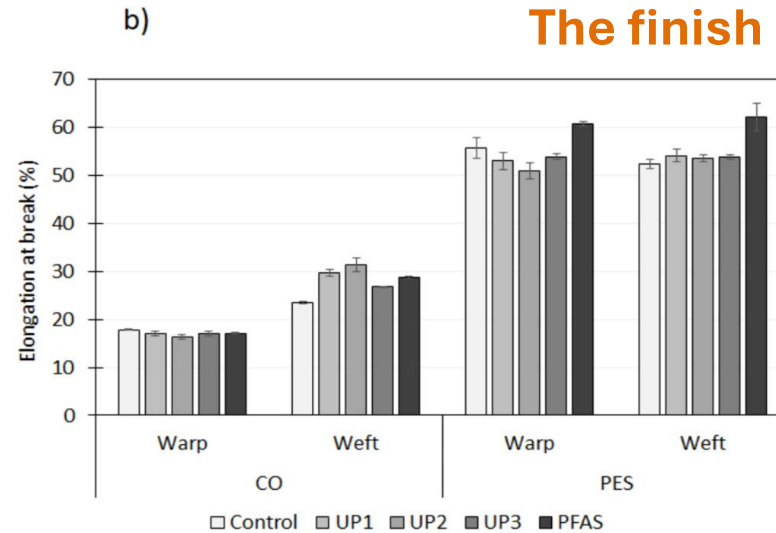
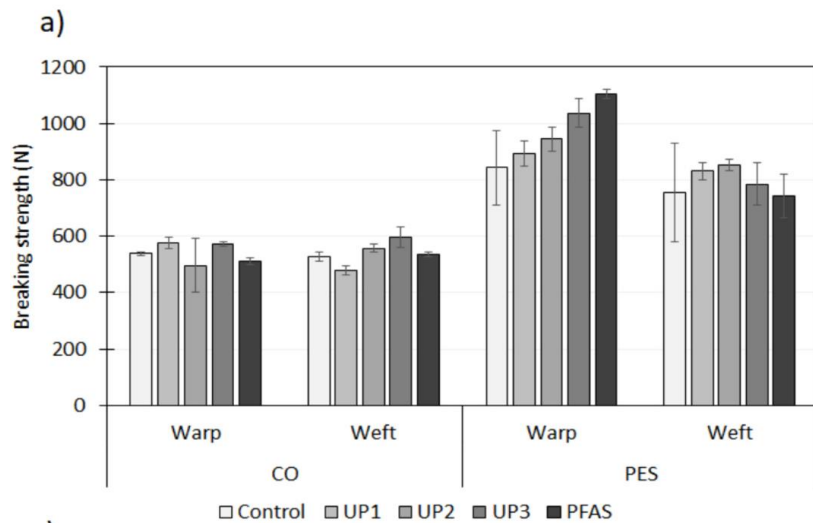
Industrial relevance changes the questions

- The coating was transferred from laboratory scale toward pilot / industrially relevant processing.
- Hand feel and stiffness were not noticeably affected.
- The coating resisted several common liquids.
- The dynamic wetting behaviour was also investigated.
- This is much closer to a real textile use than a static contact-angle measurement.

Research question → process window → manufacturing



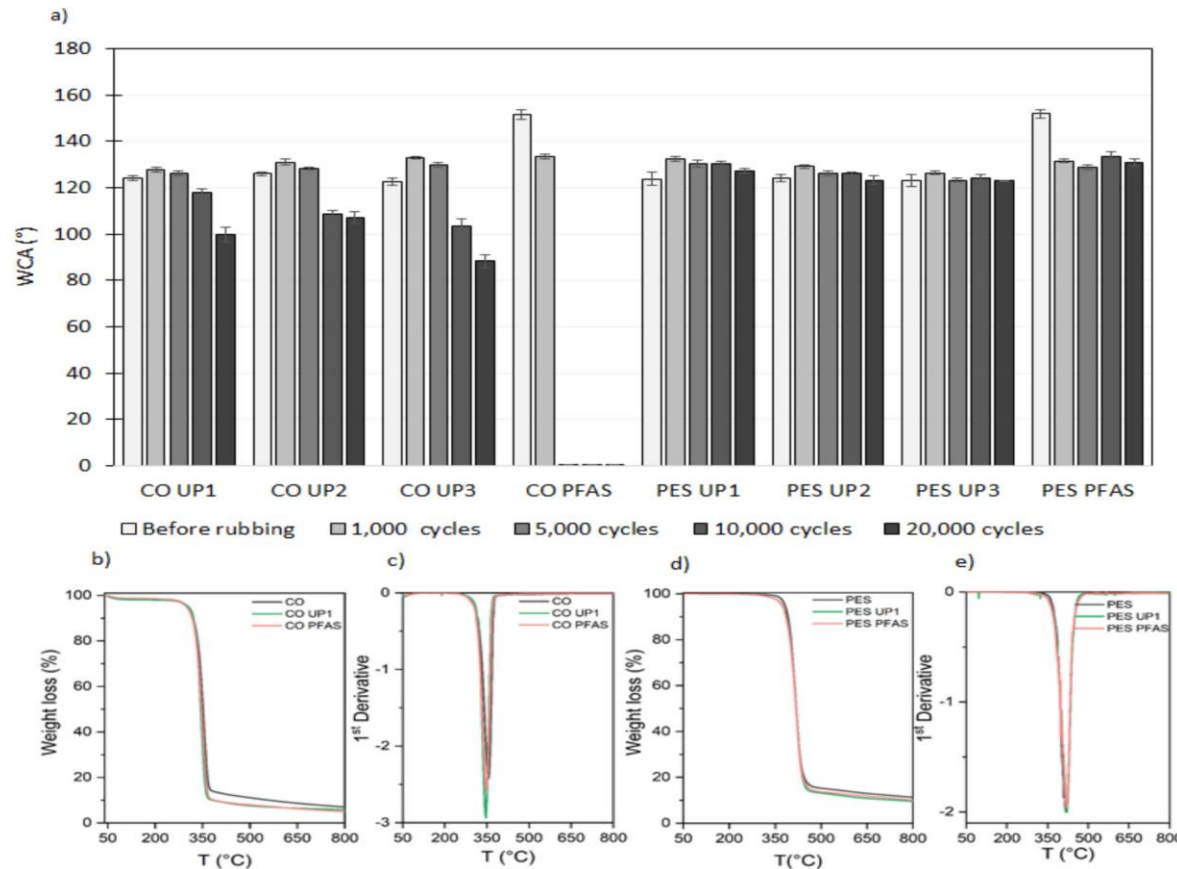
Durability test #1: Mechanical strength & performance after washing



- One and five domestic washing cycles were simulated.
- Hydrophobicity remained comparable after washing for 5 domestic cycles.
- Mechanical strength remained comparable to the benchmark samples.

Durability test #2: Abrasion

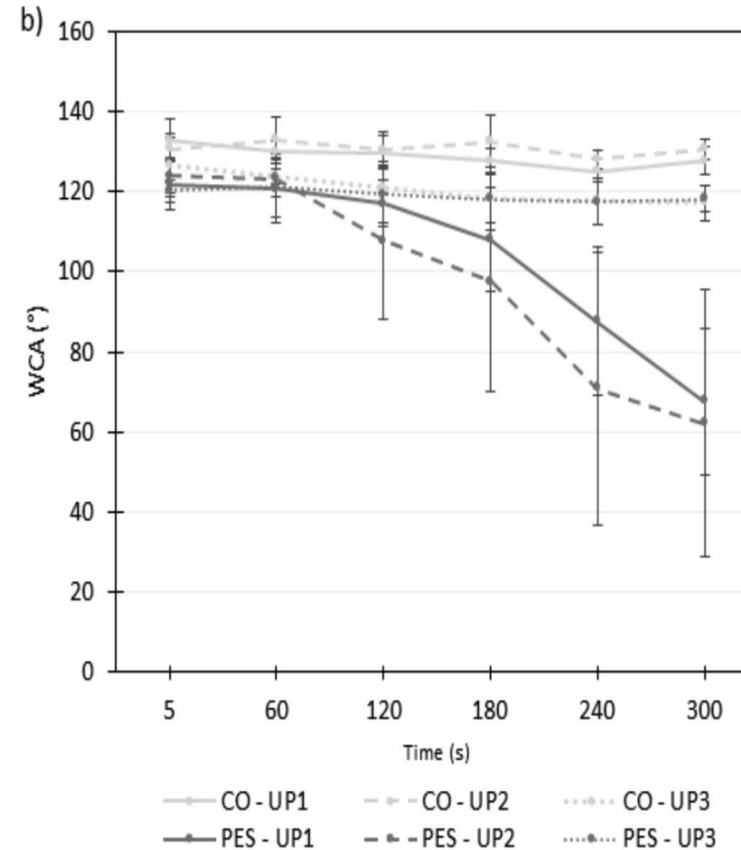
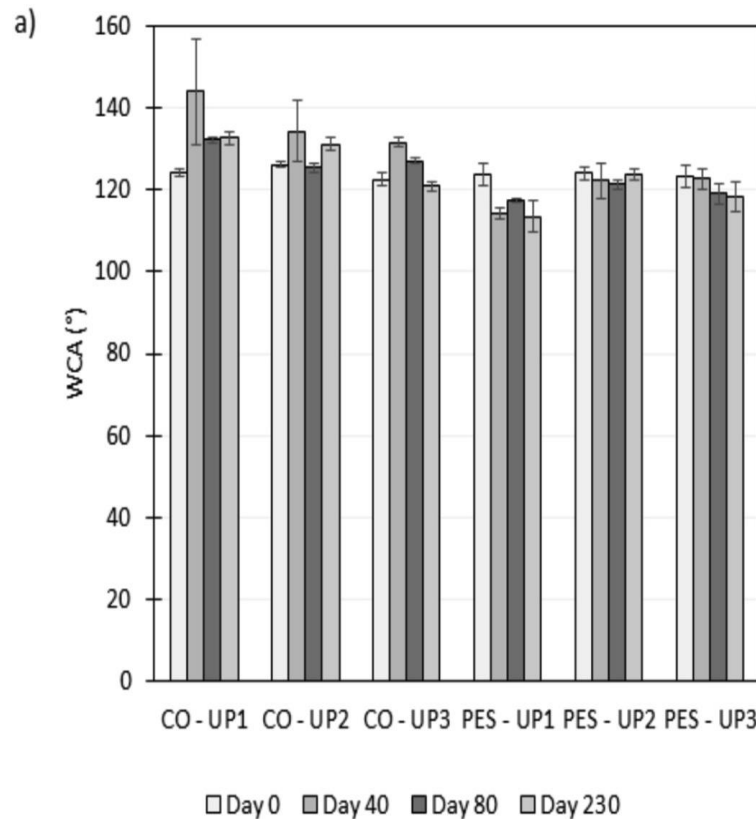
Is this surface still hydrophobic after the mechanical stresses that a textile experiences?



- Martindale abrasion was tested at 1,000; 5,000; 10,000; and 20,000 cycles.
- The bio-based coating remained hydrophobic through the reported abrasion test.
- It outperformed the commercial fluorinated counterpart in abrasion resistance.

Durability test #3: Time

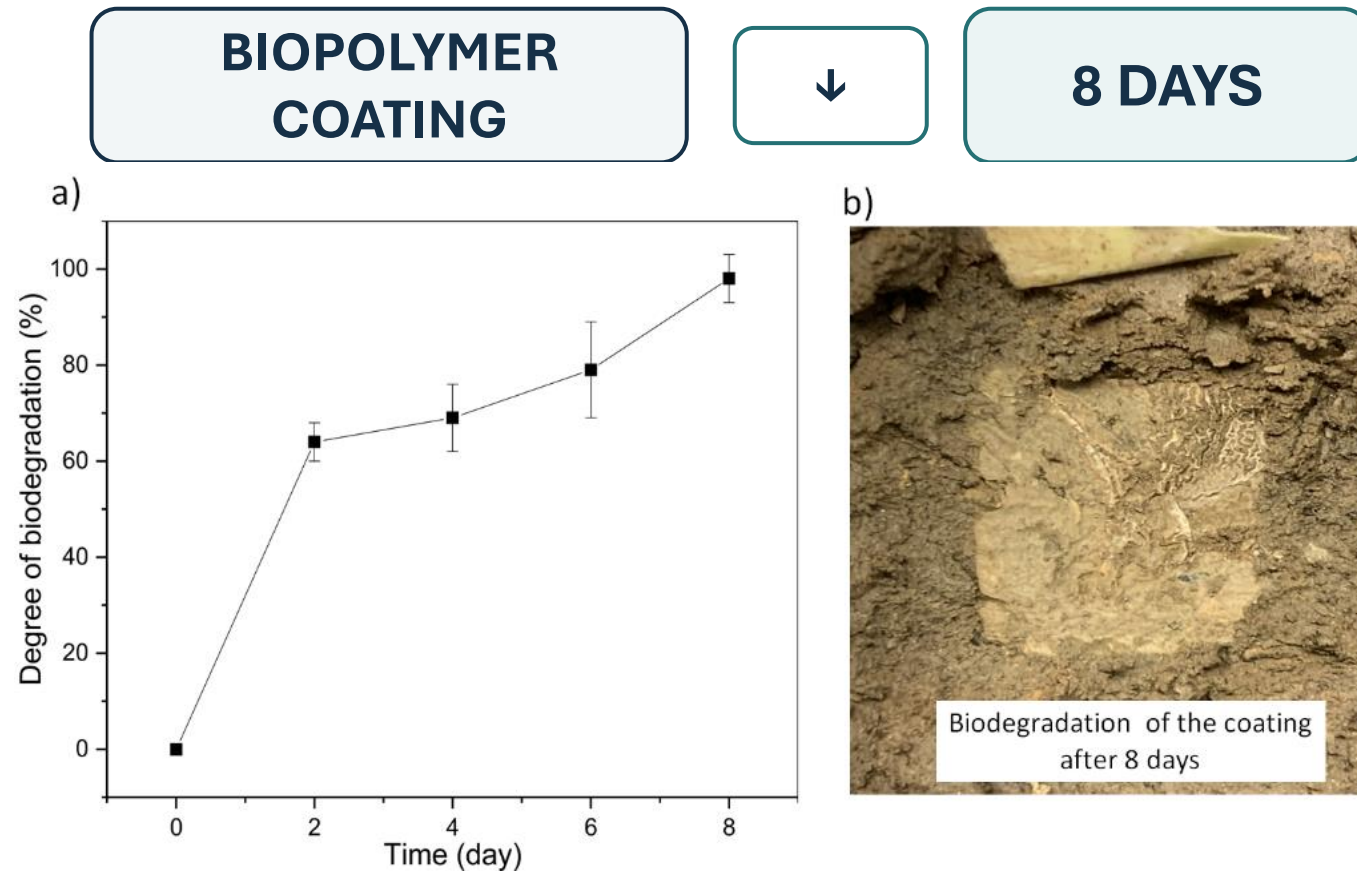
Hydrophobicity after 230 days



- WCA was monitored immediately after production and later during storage.
- The hydrophobic performance remained stable for **at least 230 days on CO and PES (3 layers)**.
- Long-term stability matters because frequent reapplication can undermine the sustainability advantage.
- If we have to reapply a finish every few weeks, then even a bio-based formulation may not be the ideal solution.**

End of life: Biodegradation in soil

- The biopolymer component of the coating fully degraded under the study conditions in 8 days.
- Inorganic residue remained.



The most important result regarding sustainability : **A coating can be durable in use and still be designed for degradation afterwards.**

The bigger lesson: Sustainability is a system property

CHEMISTRY

FUNCTION

DURABILITY

PROCESS

END OF LIFE

- A renewable feedstock is not automatically a sustainable material.
- A durable textile is not automatically sustainable if its chemistry creates persistent pollution.
- **The goal is a balanced design:** performance + safety + durability + realistic processing + responsible end of life.

Where this goes next

- Multivariate statistics can identify interactions that are difficult to see one variable at a time.
- The next step is prediction:
formulation → structure → surface → performance.
- GOAL: Less experiments – more results

PREDICTION OF HYDROPHOBIC PROPERTIES IN BIOPOLYMER-BASED COATINGS VIA FORMULATION DATA MODELLING (2025): Anja Verbič, Vuk Martinović, Rubén Saborido, ..., Blaž Stres*



NATIONAL INSTITUTE
OF CHEMISTRY



PREDICTION OF HYDROPHOBIC PROPERTIES IN BIOPOLYMER-BASED COATINGS VIA FORMULATION DATA MODELLING

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PROBLEM

The urgent need to replace toxic and environmentally persistent per- and polyfluoroalkyl substances (PFAS) in hydrophobic coatings, has sparked a growing interest in developing sustainable alternatives using natural biopolymers. The development and optimization of these formulations to achieve specific functional performance remain challenging.

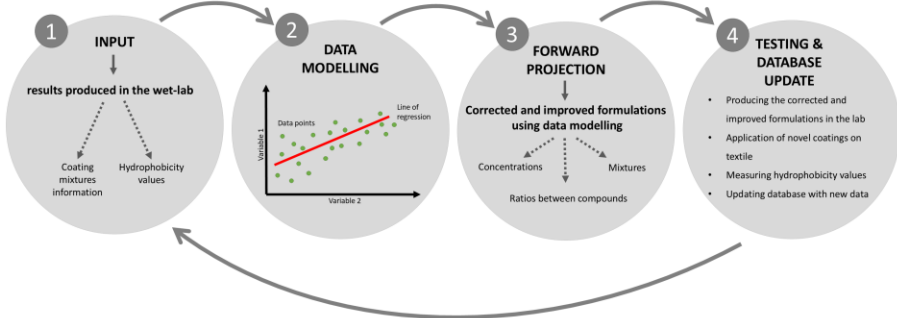
CHALLENGES

The traditional experimental approaches are time-consuming, laborious and resource-intensive, limiting the pace of innovation. To address this, our study integrates data modelling to analyze the relationship between coating formulation and hydrophobicity determined as Water Contact Angle (WCA).

OUR APPROACH

By applying simple linear regression to experimental data from diverse biopolymer mixtures, water contact angles (WCA) can be predicted based on the coating composition. This enables rapid screening and optimization of the formulations, significantly reducing the need for extensive laboratory testing and chemical use, accelerating the coatings development and supporting green industrial practices.

EXPERIMENTAL



RESULTS & CONCLUSIONS

- ✓ Improved formulations were identified by optimizing: coating composition, concentrations, ratios and including or excluding specific compounds.
- ✓ Predictions were validated experimentally by preparing the optimized formulations and measuring hydrophobicity.
- ✓ The measured functional properties are in close agreement with the projected ones.
- ✓ Some tested formulations exceeded the projected functional properties.

- The model's potential to identify superior coatings was confirmed.
- Reliable predictions were achieved from a relatively small dataset (<50 data points), demonstrating the model's efficiency.
- Expanding the dataset or merging multiple experimental databases and incorporating additional variables could further improve the formulation predictions, their complexity and novelty in the extent not tested or explored before.

PRO PLANET

Acknowledgement: This work was financially supported by the Horizon Europe project PROPLANET (Grant agreement number 10109842) and Slovenian Research Agency (Research core funding No. P2-0152).

Co-funded by the European Union

Take-home messages

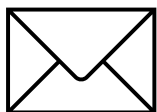
1. WETTABILITY IS A SURFACE PROPERTY

2. POLYSACCHARIDES CAN BE PART OF HYDROPHOBIC SURFACES

3. PFAS-FREE DOES NOT MEAN PERFORMANCE-FREE

The challenge is to design the whole surface—its chemistry, structure, and functionality—to achieve durable performance and sustainability.

Thank you! 😊



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