Easy-to-apply chemical pre-treatment for long lasting bonding with typical adhesives on industrial polyolefins

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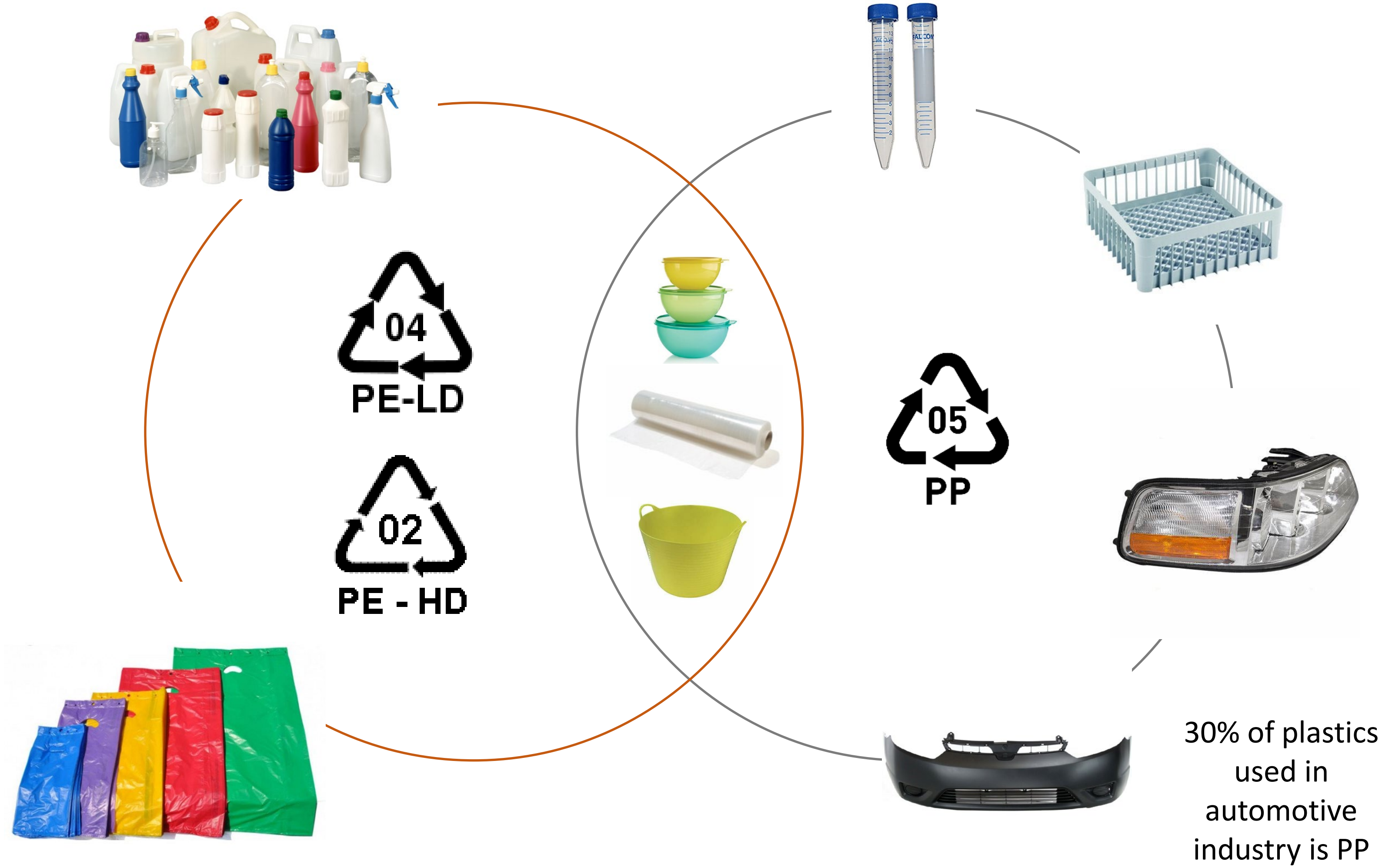
Coffee Lectures: Polymers for the Future 25.01.2023



In 2017, the total production capacity of polyethylene (PE) and polypropylene (PP) worldwide amounted to 172 million metric tons.

M. Garside, May 2020

How are components assembled in a production line?

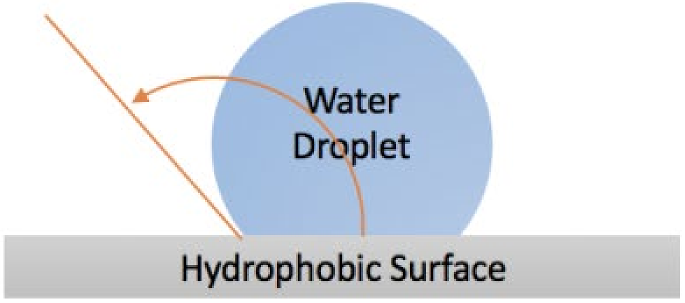
Interlocking

Gluing

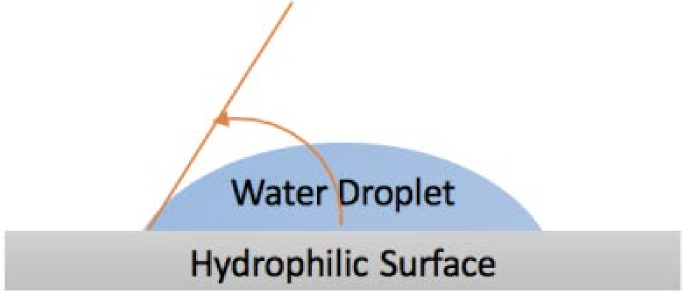
REUSE

TRA SH

Why are PE and PP challenging to glue?



Low Surface Energy = Poor Adhesion

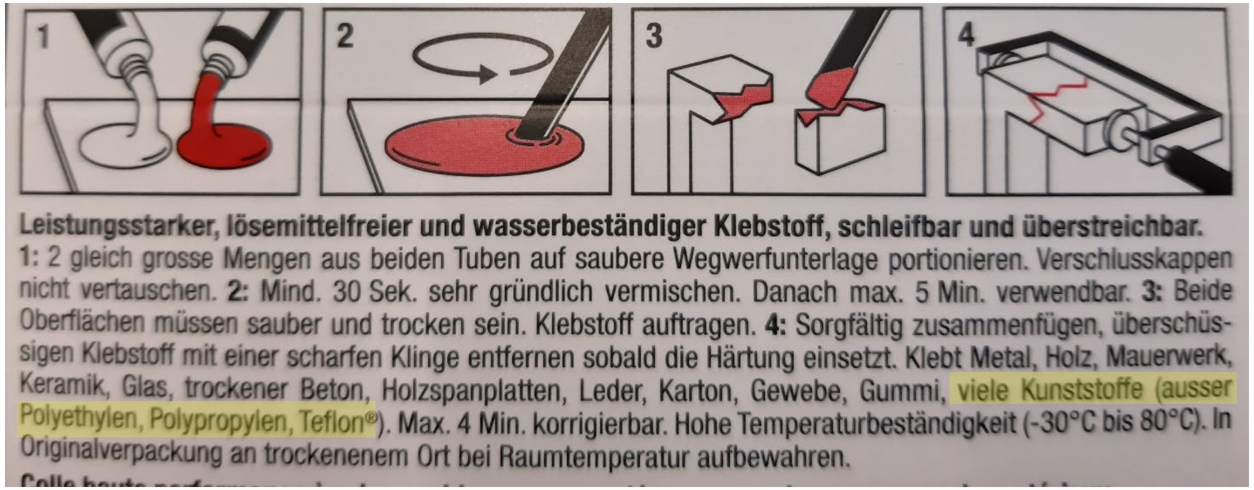


High Surface Energy = Good Adhesion

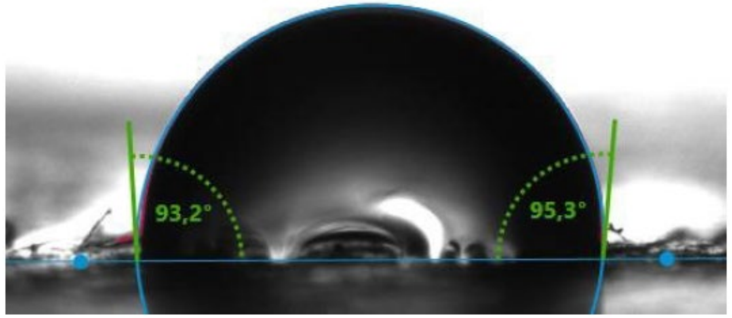
Material	Surface energy (mN/m)
Teflon	20
PP	29
PE	31
PET	38
PS	41
PU	42
PA6	44

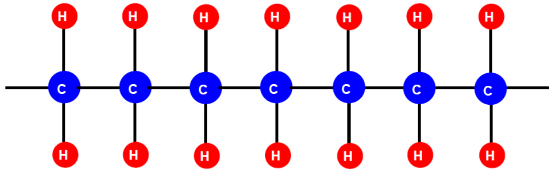
Material	Surface energy (mN/m)
Glass	83
Aluminum oxide	169
Silica	287

Why are PE and PP challenging to glue?

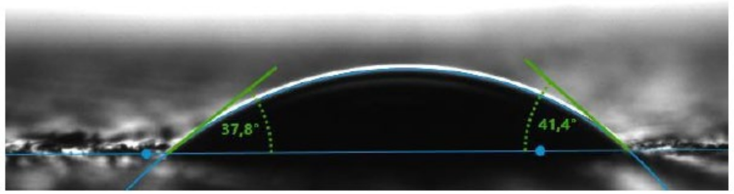


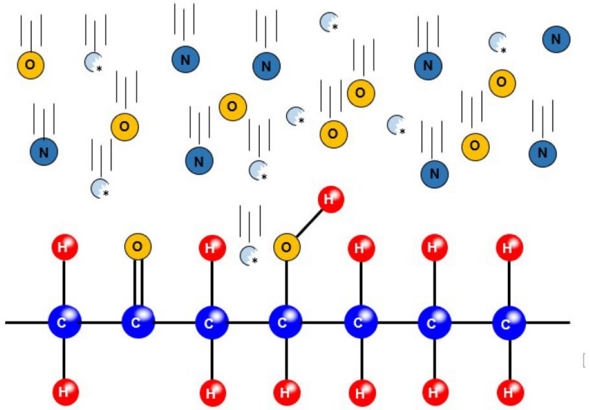
How to increase the surface energy?





Plasma treatment

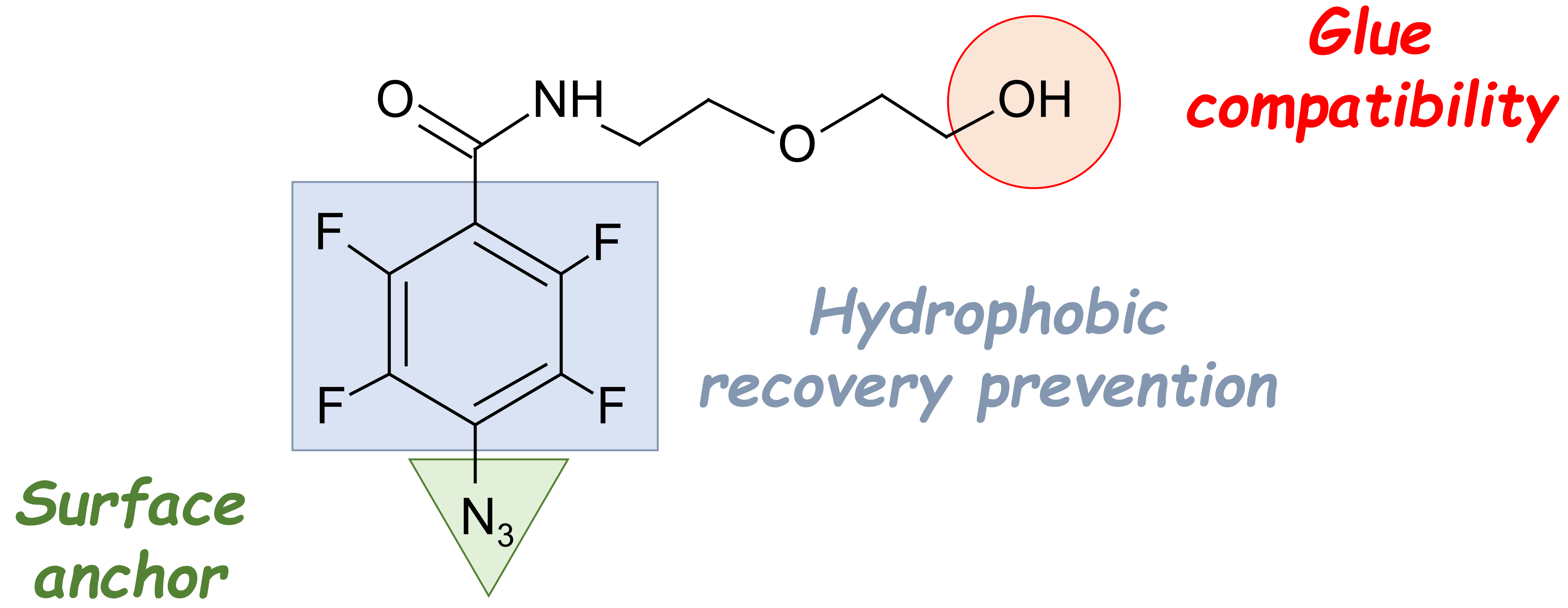




Drawbacks of plasma treatment

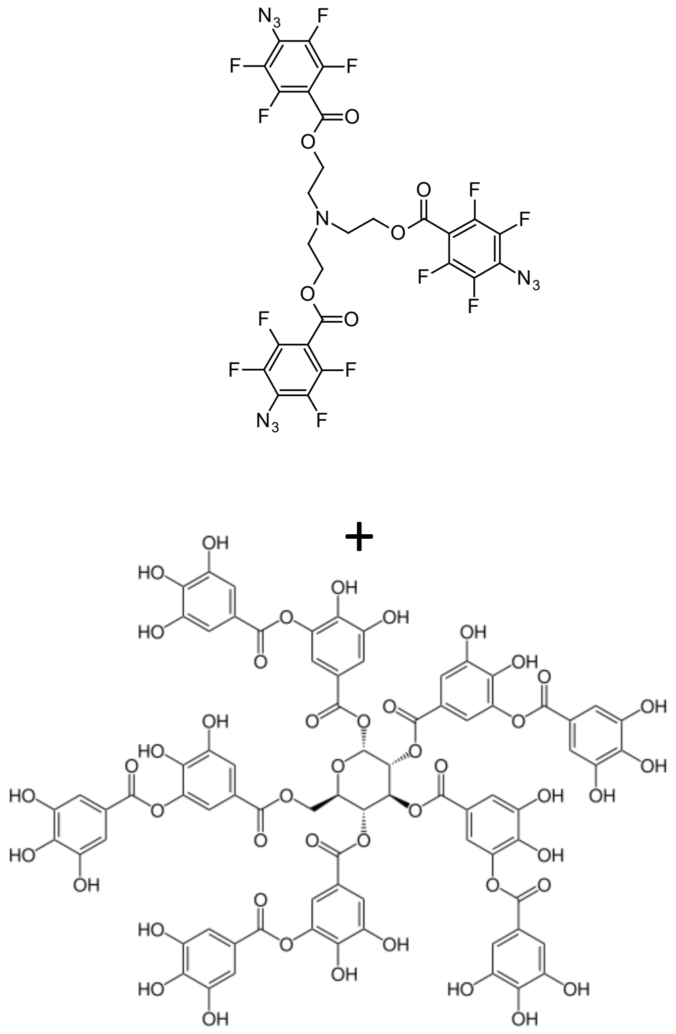
- Formation of multiple reactive groups (unspecific bonding with adhesives)
- Hydrophobic recovery (transient activation)
- Degration of the polymer chains (harsh treatment)
- Special infrastructure (vacuum)

Our approach: example



Formulations into play

Commercial



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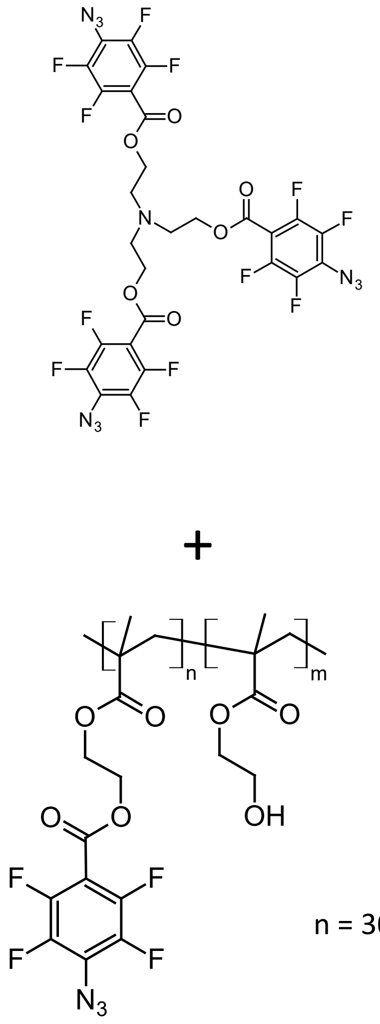


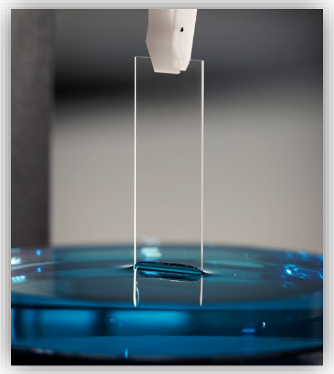
n = 30; m = 70

1t_2.5TA

1t_2P30

*Finding an **easy to use** chemical pre-treatment: **2-steps process***

1



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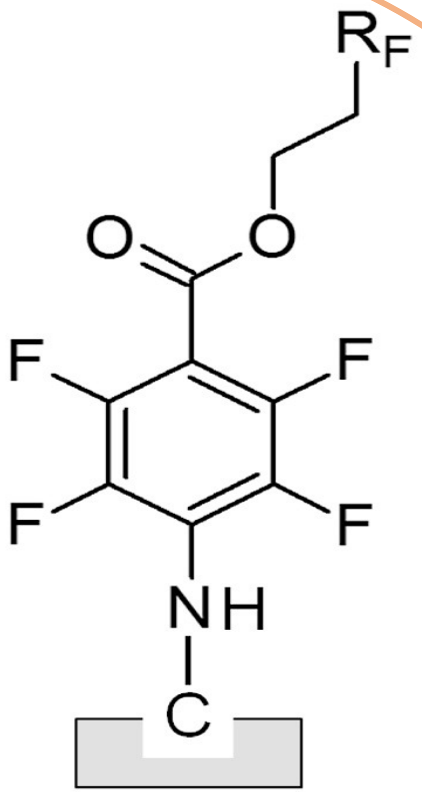
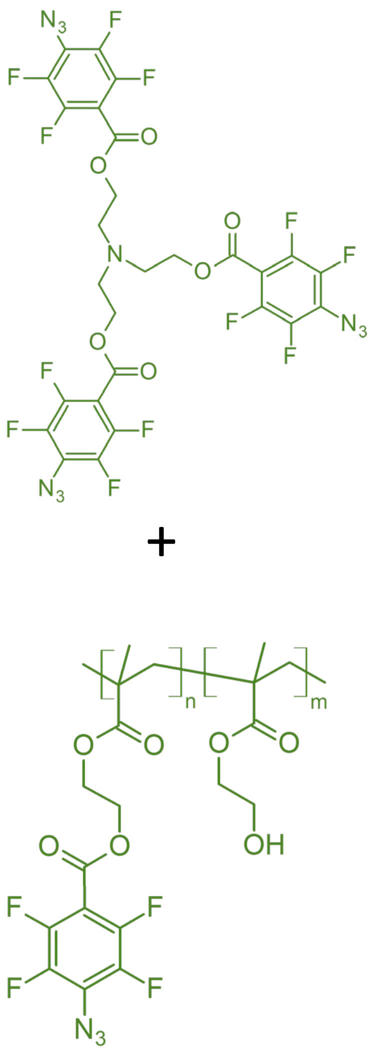
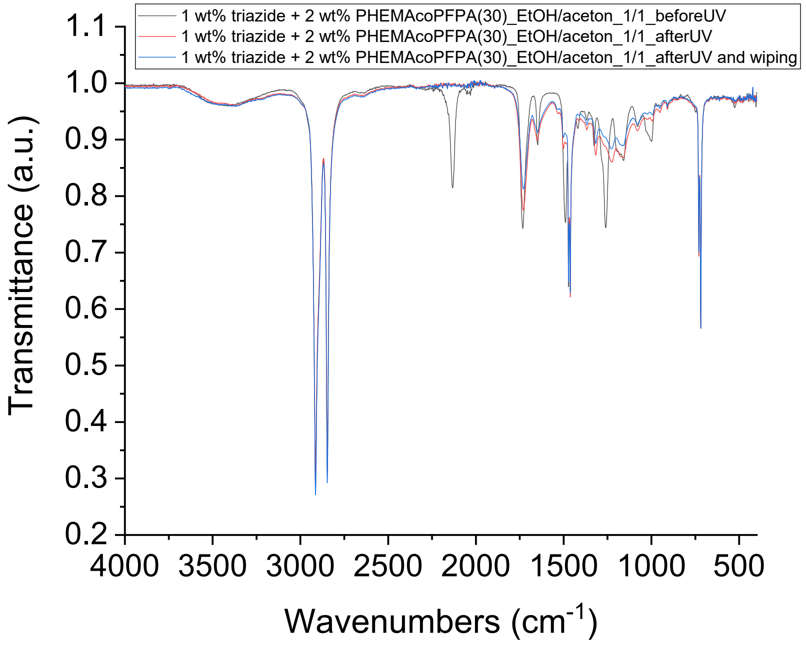
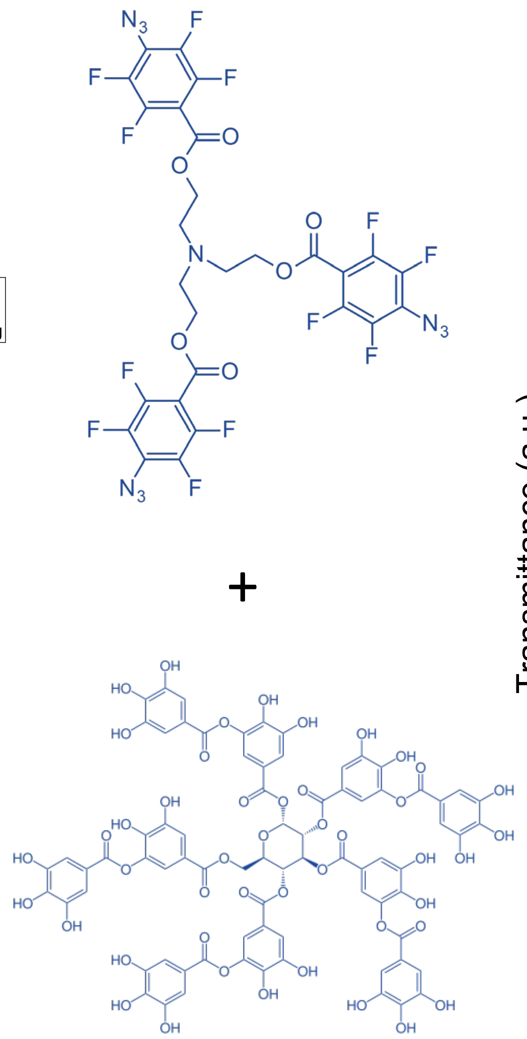


Formulations as coatings

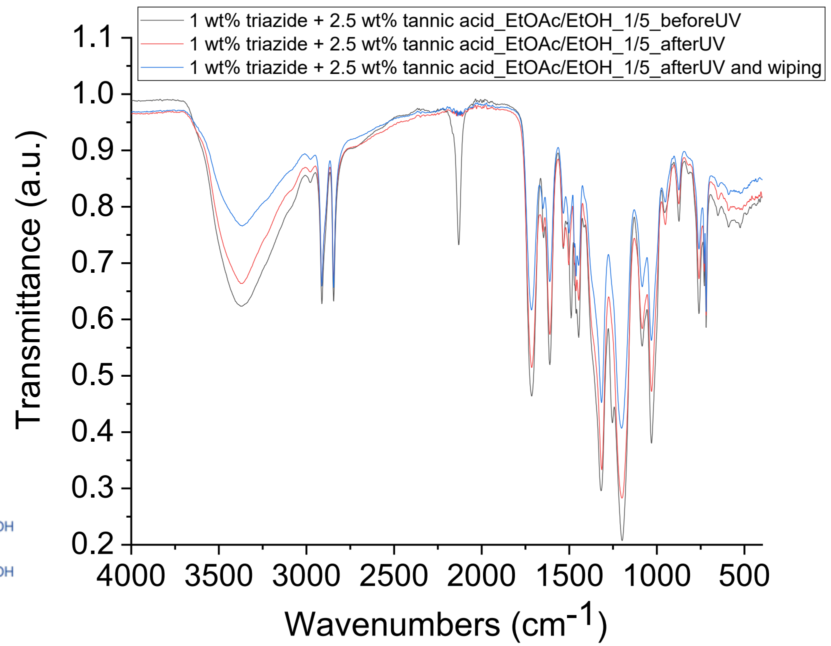


1t_2P30/1t_2P40





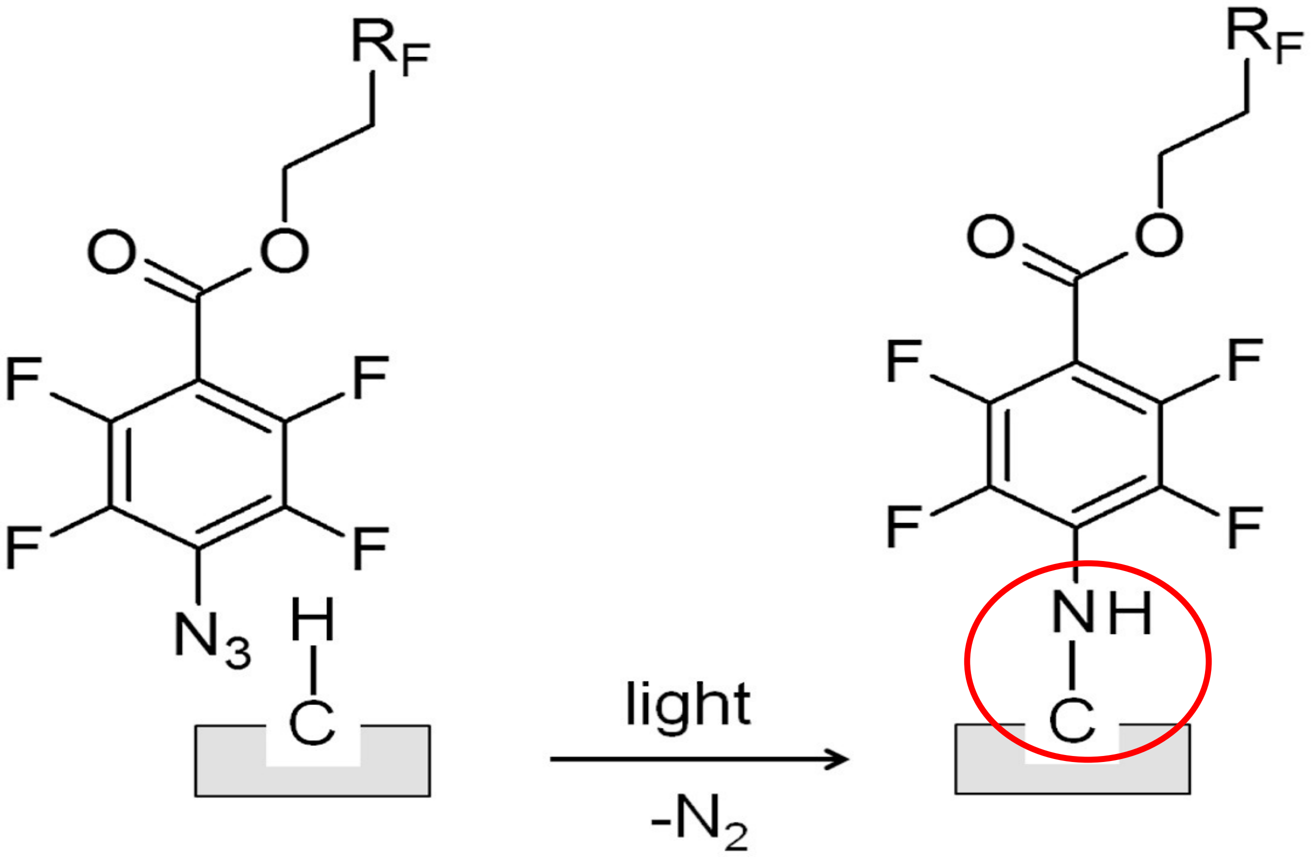
1t_2.5TA



- UV-Activation induces the azide reaction
- Wiping with a good solvent does not result in material loss

- UV-Activation induces the azide reaction
- Wiping with a good solvent results in material loss

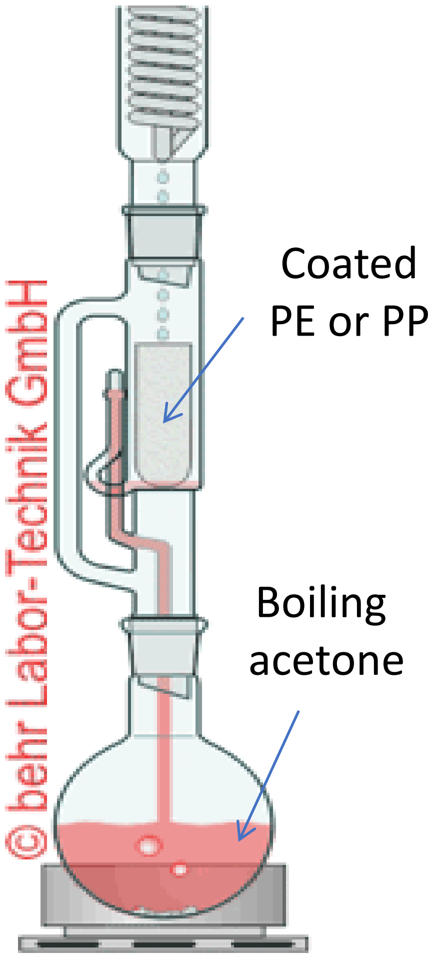
*Formulations as **coatings***

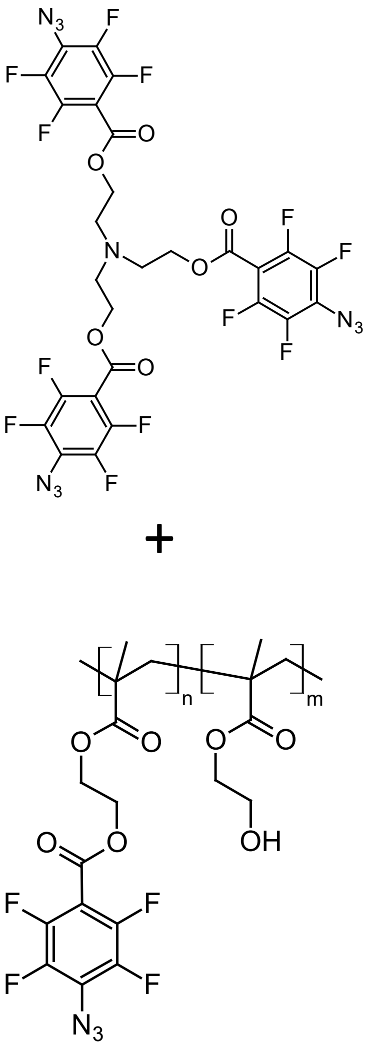


Is the reaction really occurring?

Are we creating a covalent bond between the primer and the surface?

Formulations as coatings





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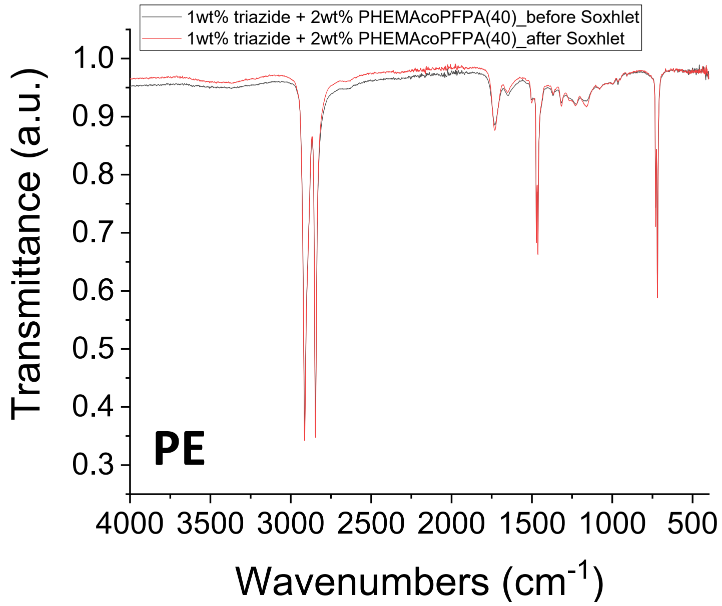
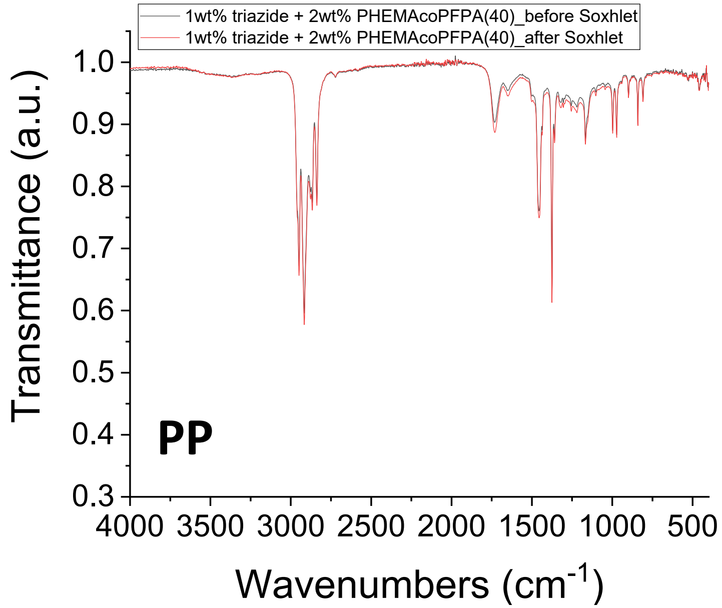




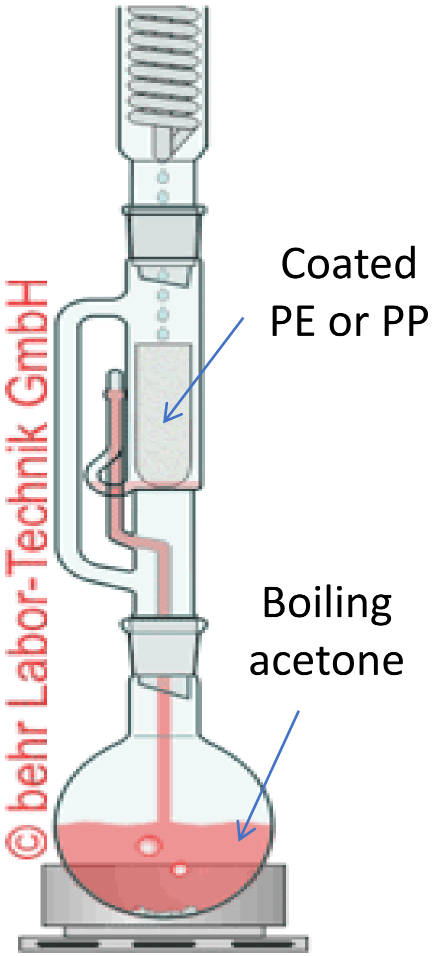
XPS

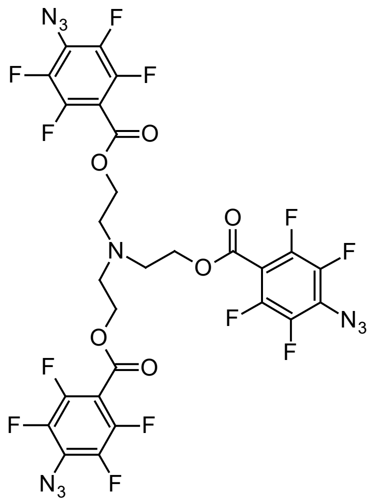
PE	Before Soxhlet	After Soxhlet
C1s	62.9	64.7
N1s	5.2 ± 0.4	4.8 ± 0.2 **(100%)**
O1s	22.5	20.2
F1s	9.4 ± 0.5	10.2 ± 0.3 **(100%)**

PP	Before Soxhlet	After Soxhlet
C1s	65.7	65.5
N1s	5.4 ± 0.3	4.7 ± 0.4 **(100%)**
O1s	19.5	22.2
F1s	9.4 ± 0.2	9.6 ± 0.5 **(100%)**

Both molecules are covalently bound.
The adhesion after Soxhlet is as good as before Soxhlet.

Formulations as coatings





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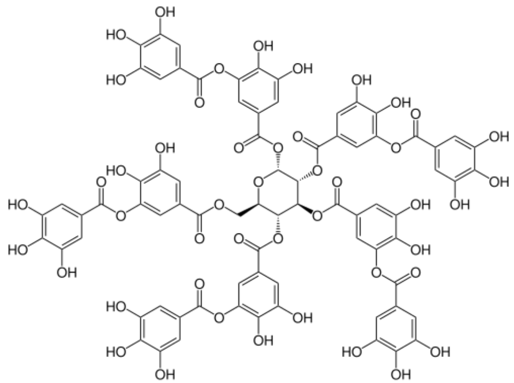

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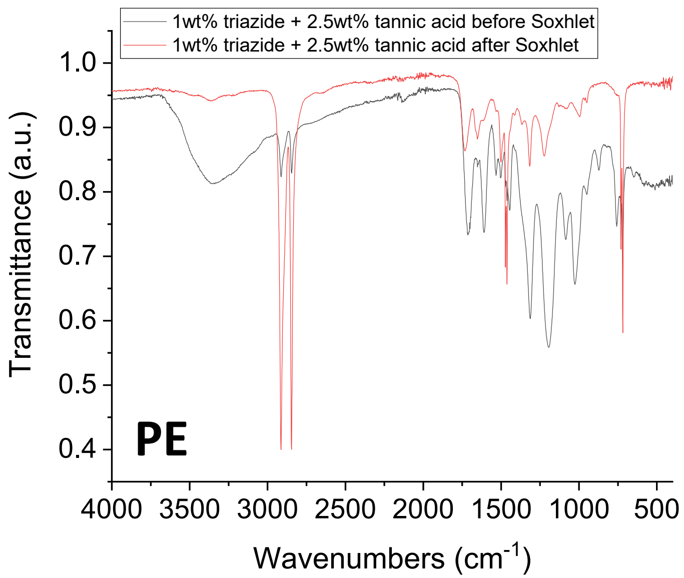
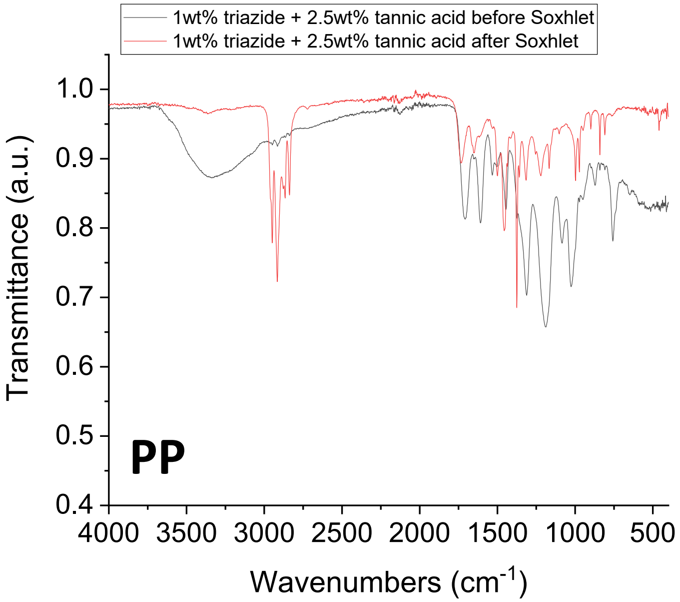




XPS

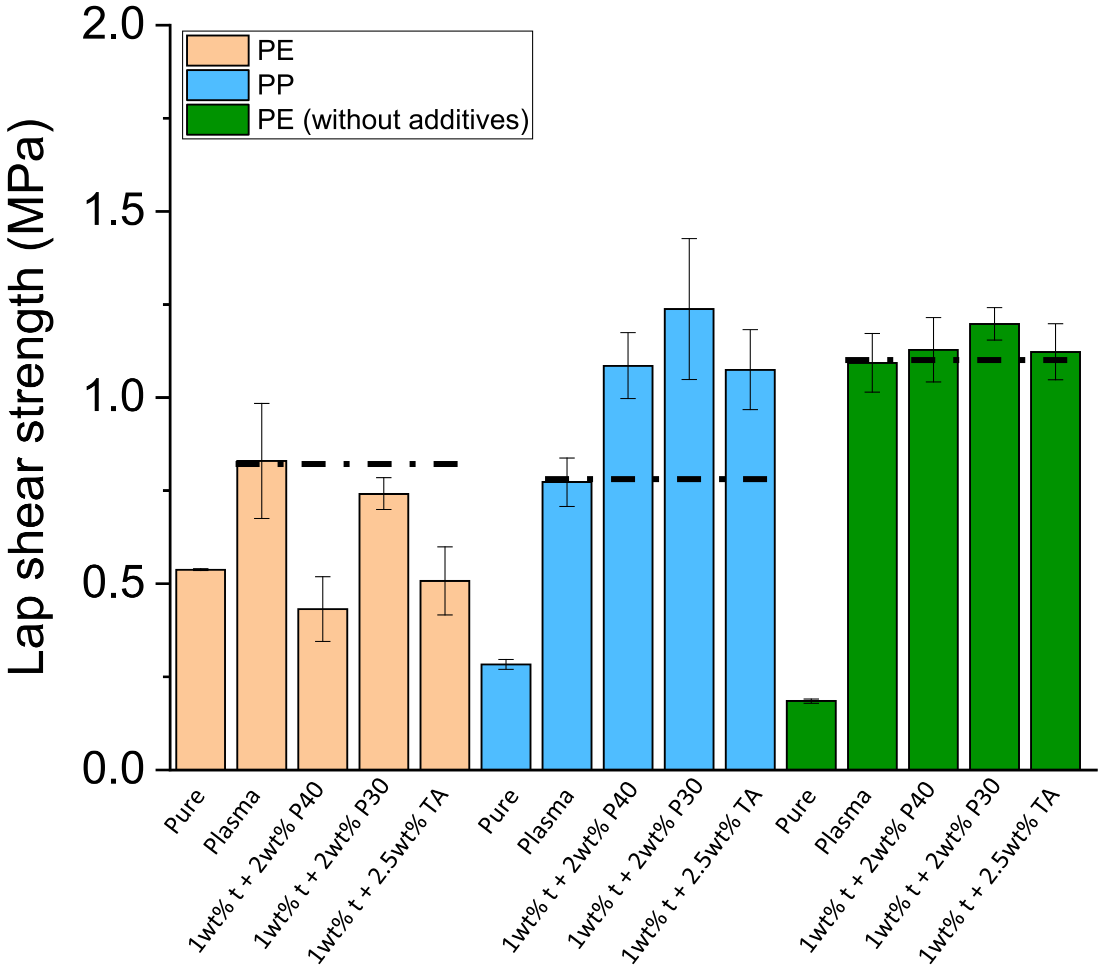
PE	BeforeSoxhlet	After Soxhlet
C1s	73.5	72.2
N1s	2.5	4.1 **(x1.6)**
O1s	20.5	16.9
F1s	3.5	6.7 **(x1.9)**

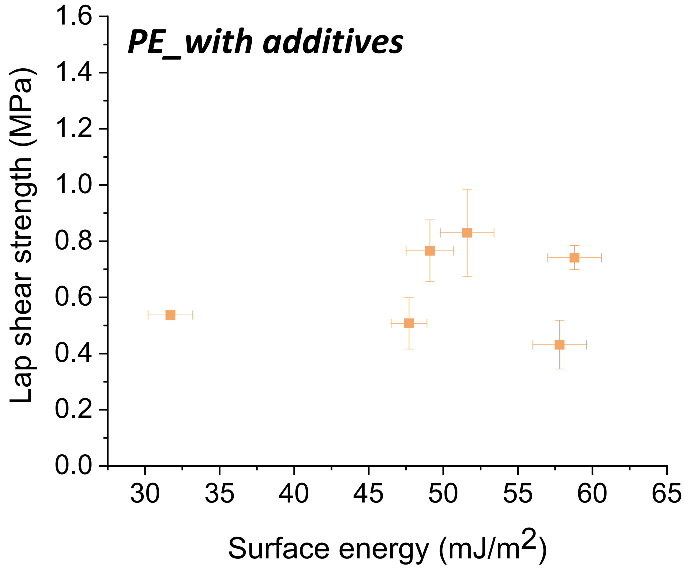
PP	Before Soxhlet	After Soxhlet
C1s	80.7	75.4
N1s	2.2	4.4 **(x2)**
O1s	13.9	13.3
F1s	3.2	6.9 **(x2)**

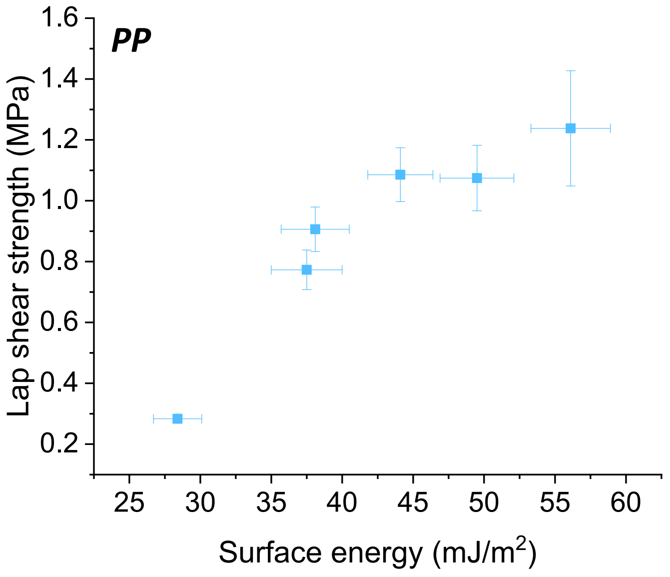
Tannic acid is only physisorbed and Soxhlet leaves on the surface only the covalently bound layer (the triazide).

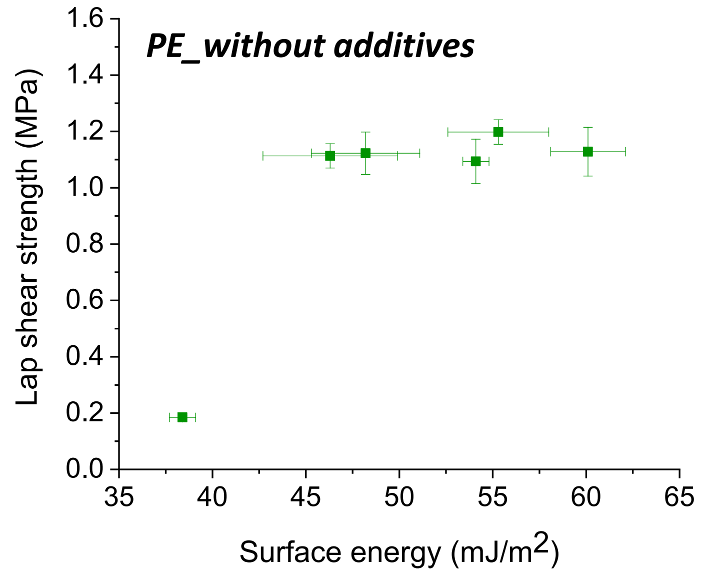
Formulations as adhesion primers

Epoxy adhesive







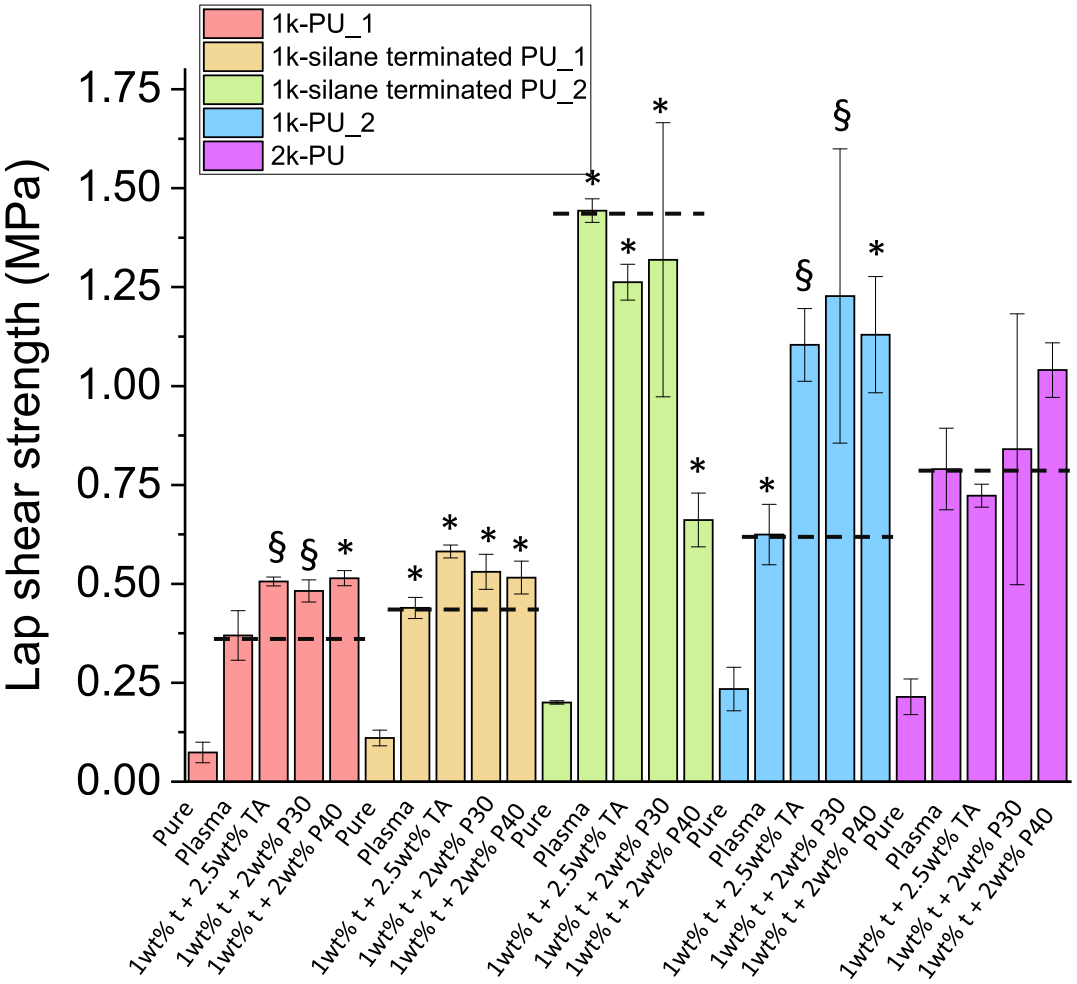


*Formulations as **adhesion primers***

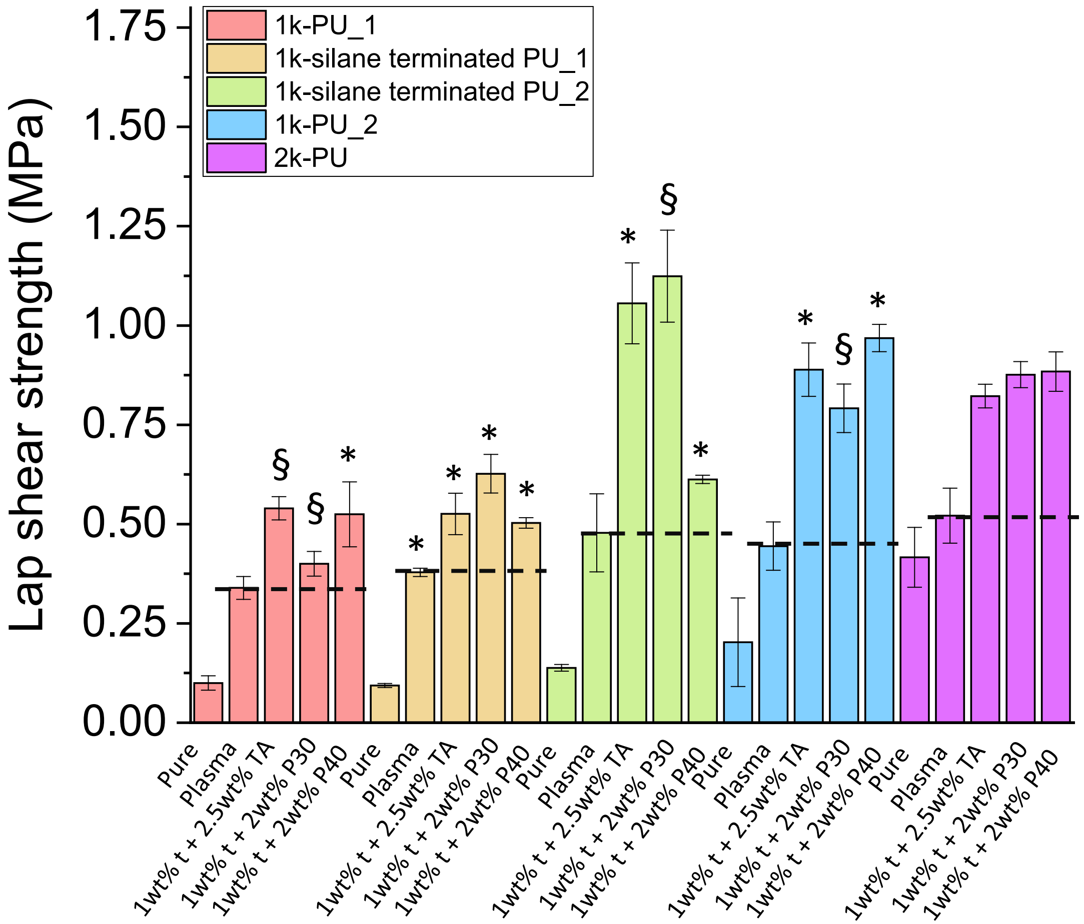
§ = cohesive/adhesive failure * = cohesive failure

Polyurethan-based adhesives

PE



PP



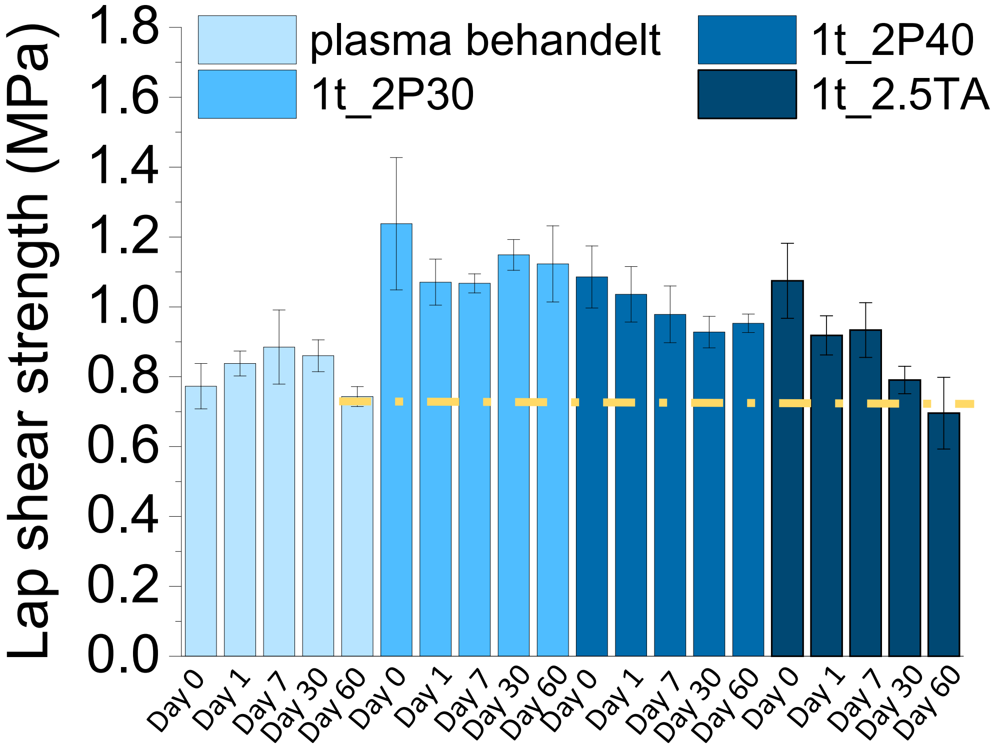
Almost all formulations perform better than plasma on PE and PP.

Formulations as ***adhesion primers***

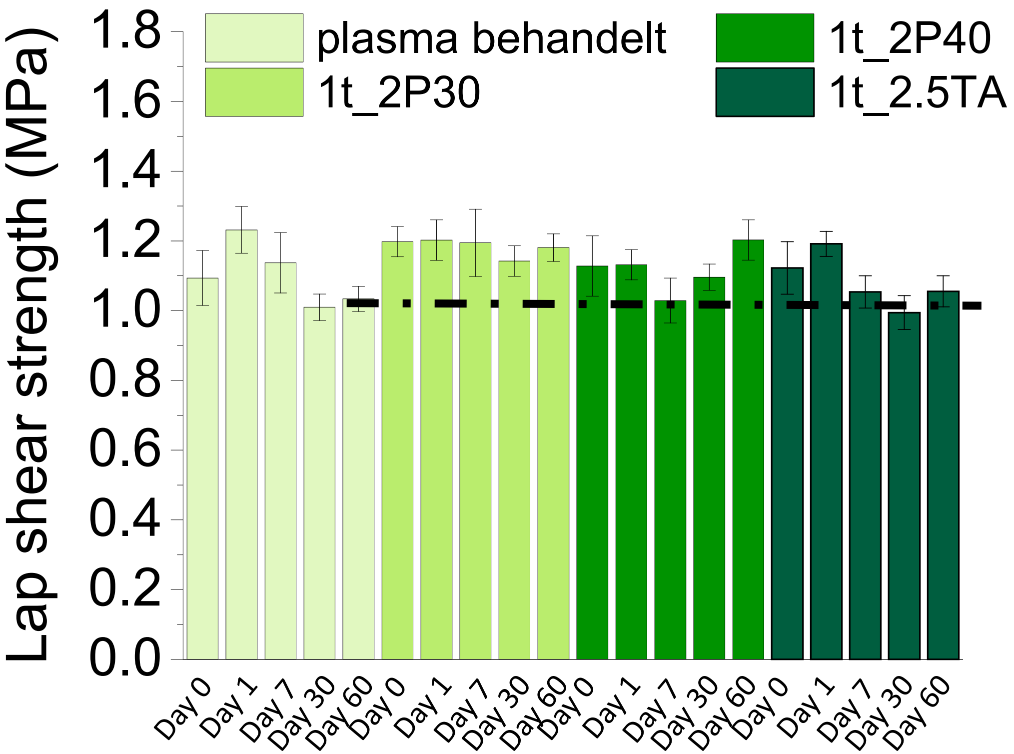
Storage stability

Adhesion-Performance (Epoxy Adhesive)

PP



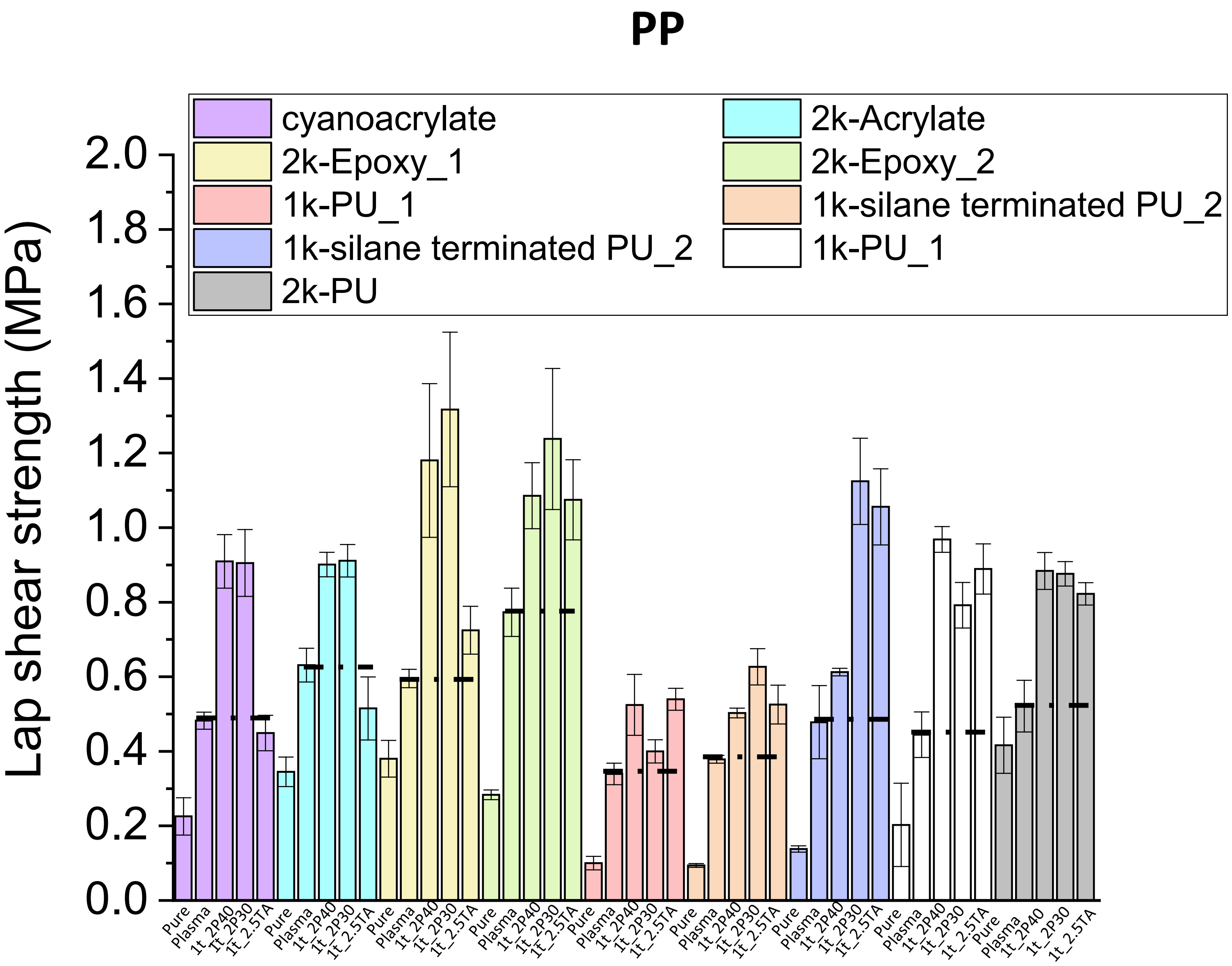
PE_ohne Zusätzte



The formulations show a high storage stability with PU-based adhesives too.

Are the tested formulations universal?

9 different adhesives were tested



*On **PP** the primers*

- *1wt% triazide + 2wt% PHEMAcoPFPA(30)*
- *1wt% triazide + 2wt% PHEMAcoPFPA(40)*

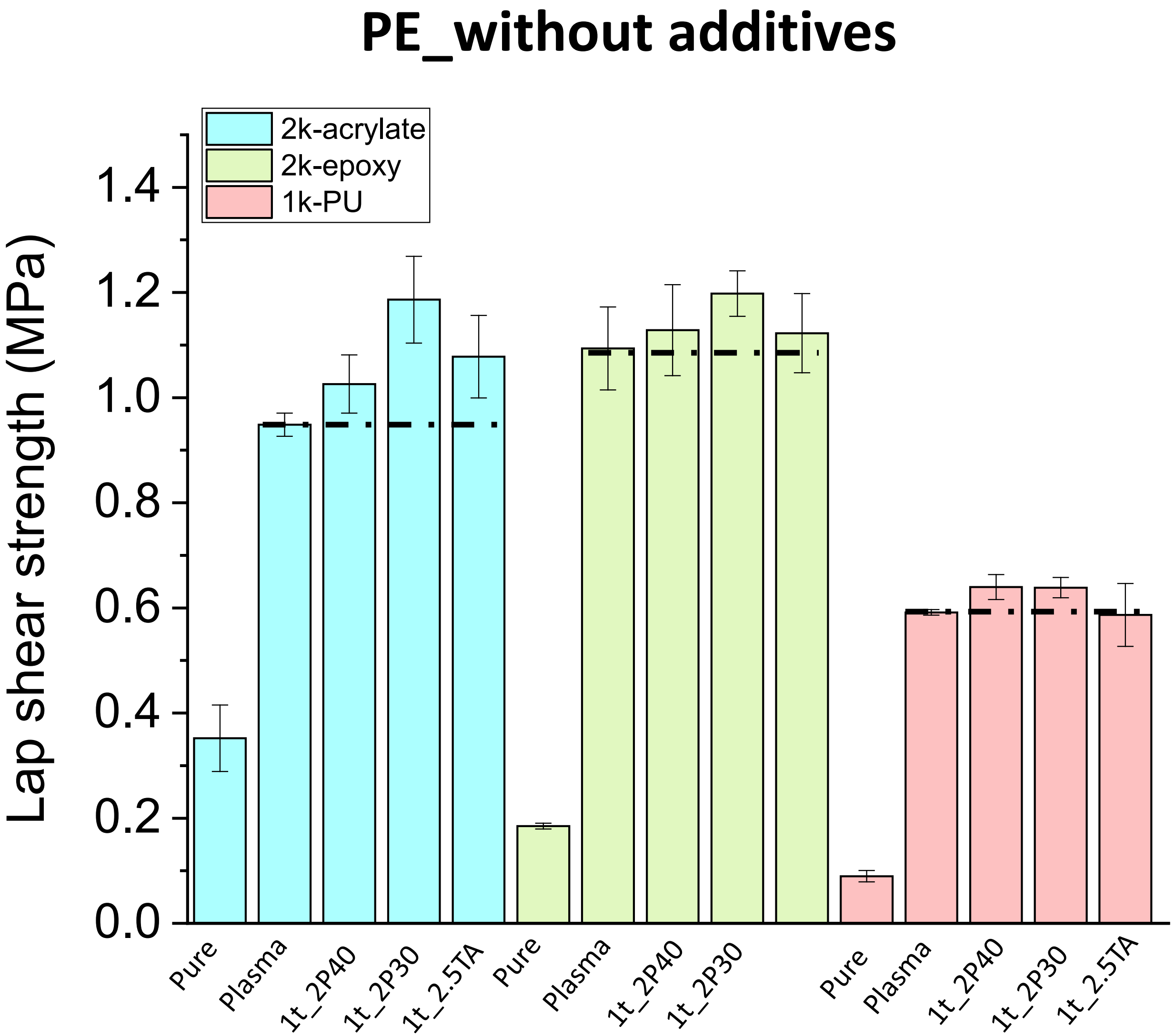
*perform **better than plasma** with **ALL** the adhesives tested*

- *1wt% triazide + 2.5wt% TA*

*perform **as good as** or **better than plasma** with **ALL** the adhesives tested*

Are the tested formulations universal?

3 different adhesives were tested



*On **PE (without additives)** the primers*

- *1wt% triazide + 2wt% PHEMAcoPFPA(30)*
- *1wt% triazide + 2wt% PHEMAcoPFPA(40)*
- *1wt% triazide + 2.5wt% TA*

*perform **as good as** or **better than plasma** with **ALL** the adhesives tested.*

Conclusions

Only hydrophobic enough primers bind onto hydrophobic substrates:
2 components formulations (hydrophobic + OH-bearing) are needed to allow covalent bonding and adhesion

Both the components of the formulation should contain azide groups to allow chemisorption of the OH-bearing molecules

Using as second component a molecule without azide results in physisorption of this component: instability upon exposure to water or solvents + shorter life time

The presence of additives in the substrate induces a worse performance of the primer

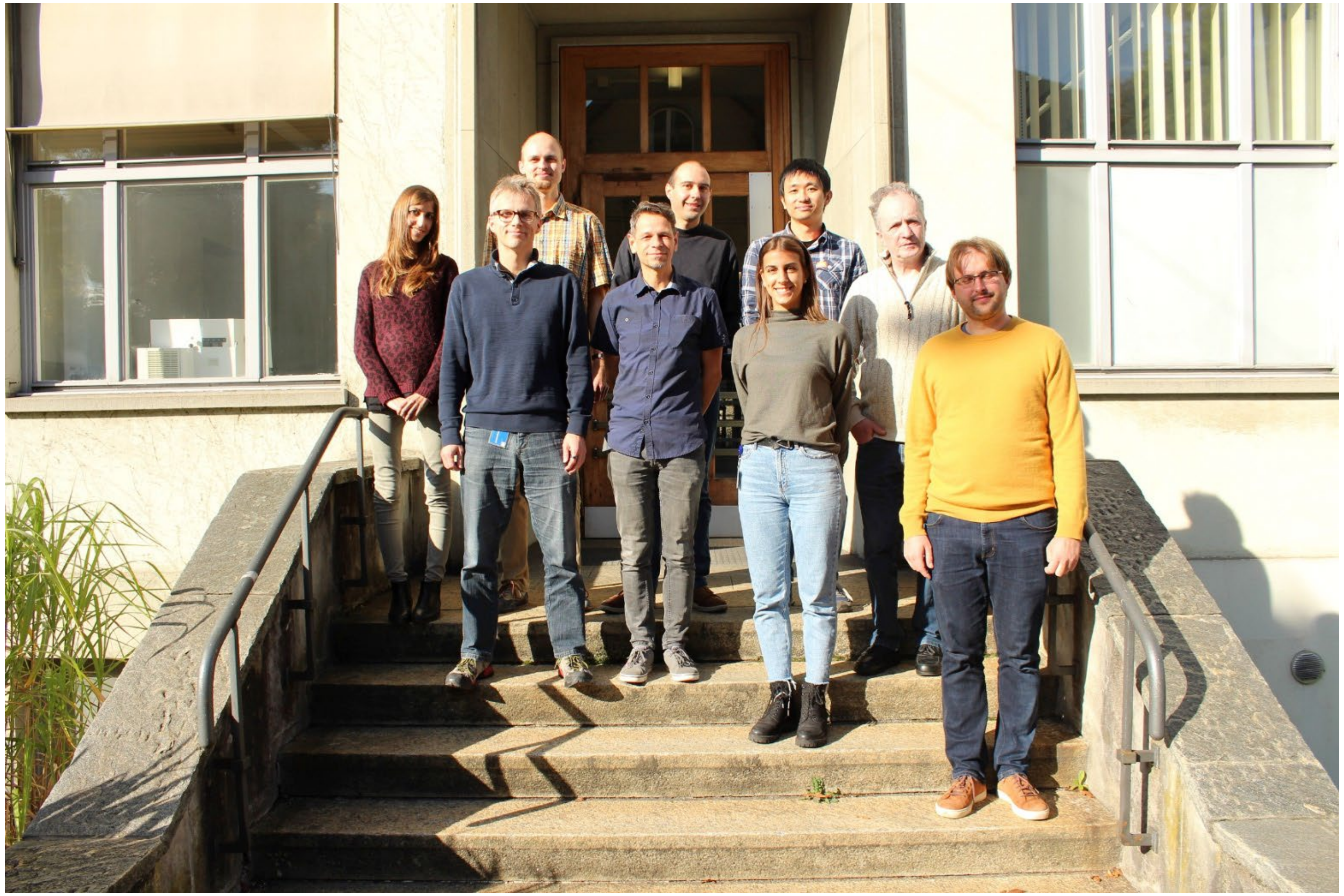
The formulations tested perform always better than plasma on PP and
as good as or better than plasma on PE-without additives

Acknowledgements

Zürcher Hochschule
für Angewandte Wissenschaften

School of
Engineering

Labor für Polymere Beschichtungen



Thank you
for your attention