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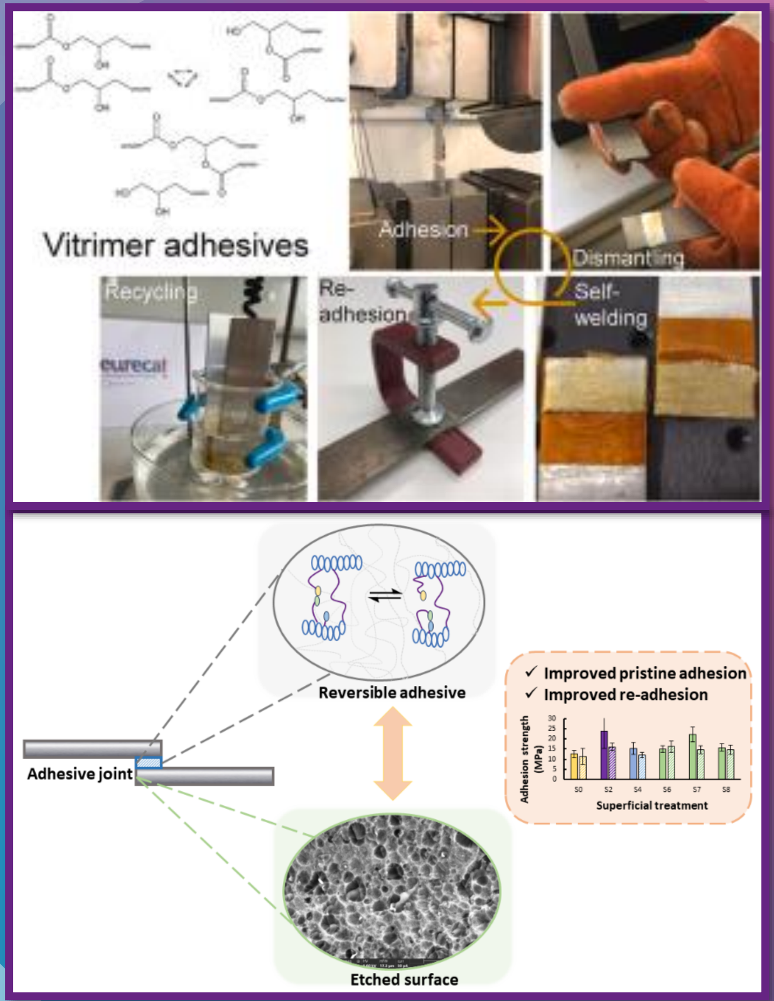
Development of epoxy-vitrimers as versatile reversible estructural adhesives

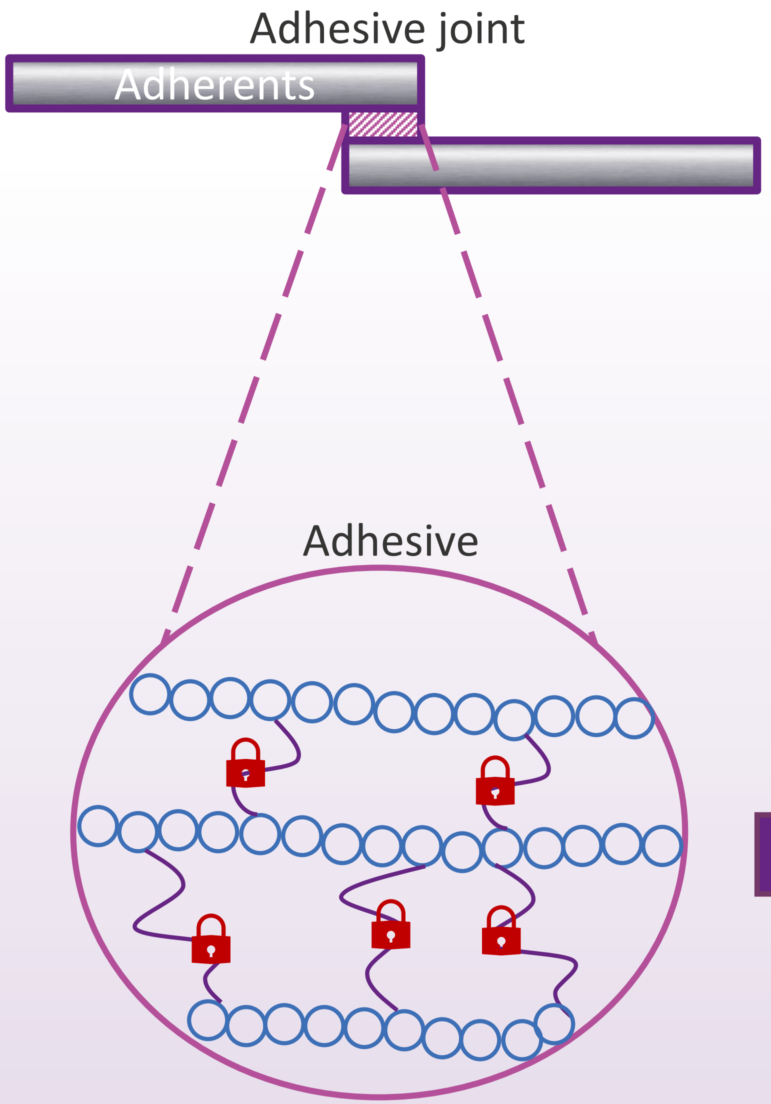
Marc Surós, David Santiago, Pere Verdugo, Marina Pedrola, Silvia De la Flor

"innovating with businesses"

SUSMATx



Benefits and drawbacks of thermosetting adhesives



Pros
- ❑ High strength/weight ratio
- ❑ Uniform distribution of stress
- ❑ Join dissimilar materials
- ❑ Resist fatigue and cyclic loads

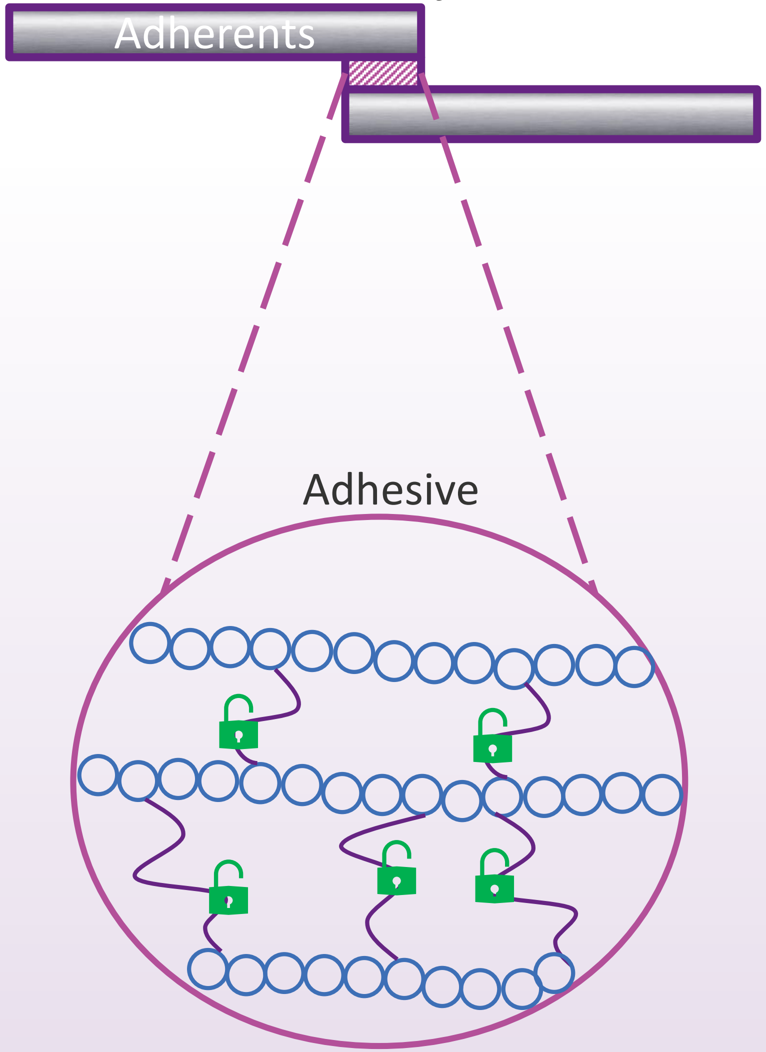
Cons
- ❑ Dismantling the joint damages the adherents
- ❑ Difficult removal of adhesive remains
- ❑ Limited open time (curing)

All disadvantages are due to **permanent cross-links**

Compos. Part B Eng. **2018**, *151*, 71–77

Vitrimers as reversible adhesives

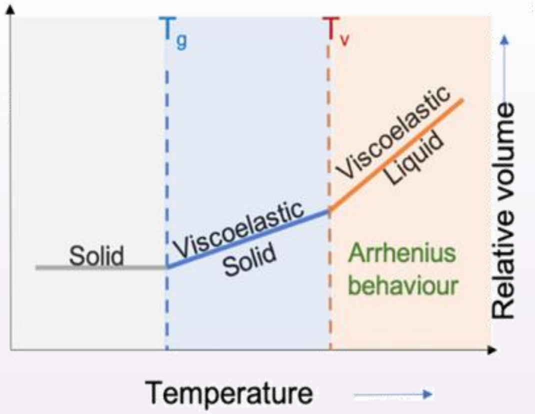
Adhesive joint



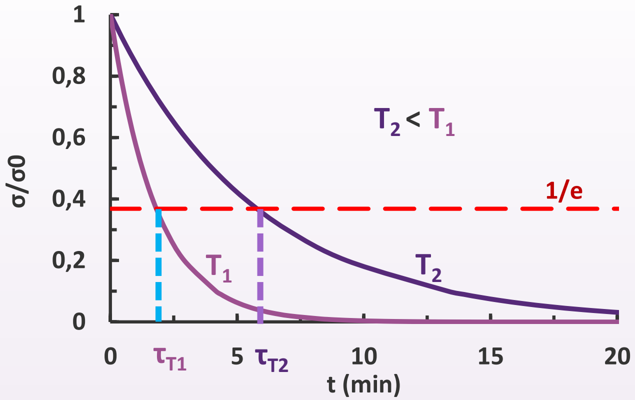
Reversible covalent bonds

Vitrimers are a type of thermosetting polymers that can undergo topological rearrangements through reversible reactions.

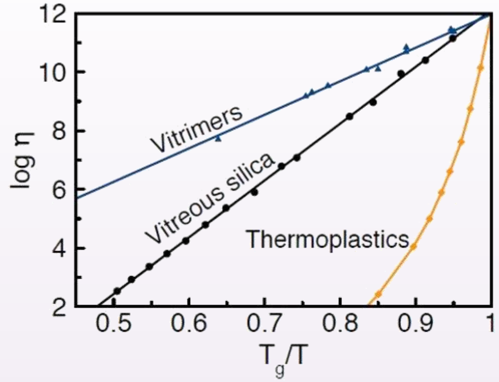
Rheology



Stress relaxation



Vitreous behaviour

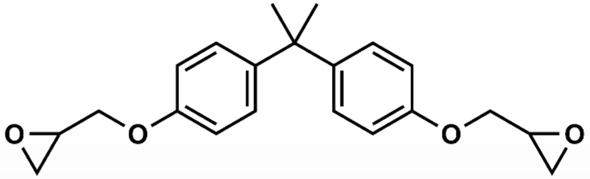


- ✓ Self-healable
- ✓ Self-welding
- ✓ Thermal activation
- ✓ Chemical reactivity

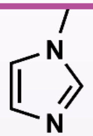
Re-adhesion
Long operating times
Storage of preassembled joints
Ease of removal of adhesive remains

Chem. Eng. J., **2020**, 385, 123820.
Prog. Polym. Sci., **2018**, 80, 39-93

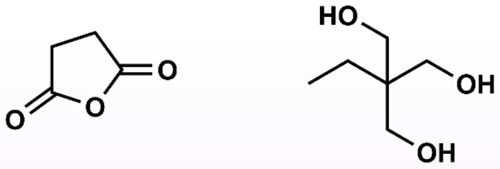
Polymer formulations



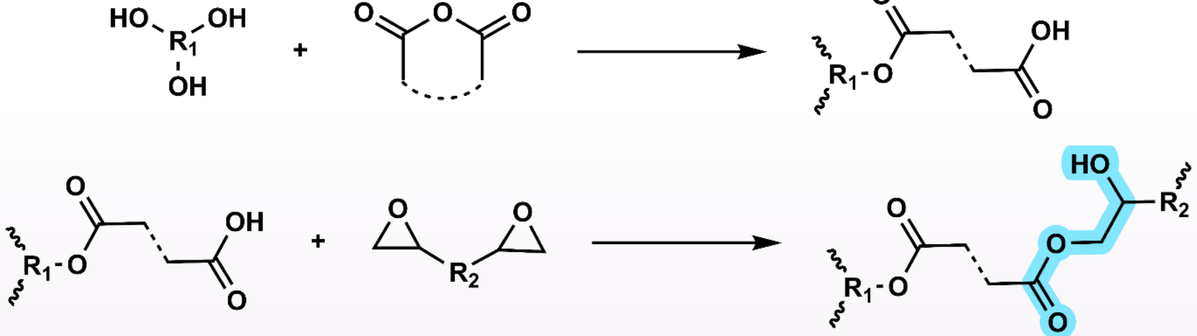
Epoxy monomer



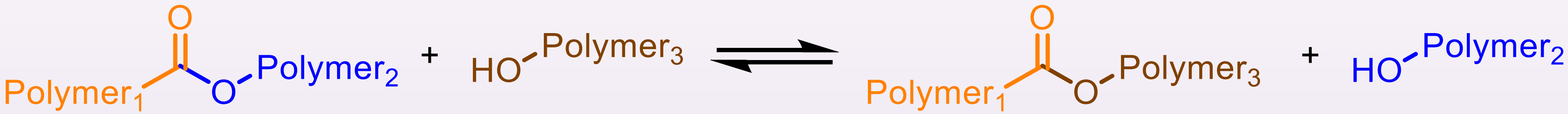
Catalyst



Anhydride and triol curing agents



β-hydroxy ester

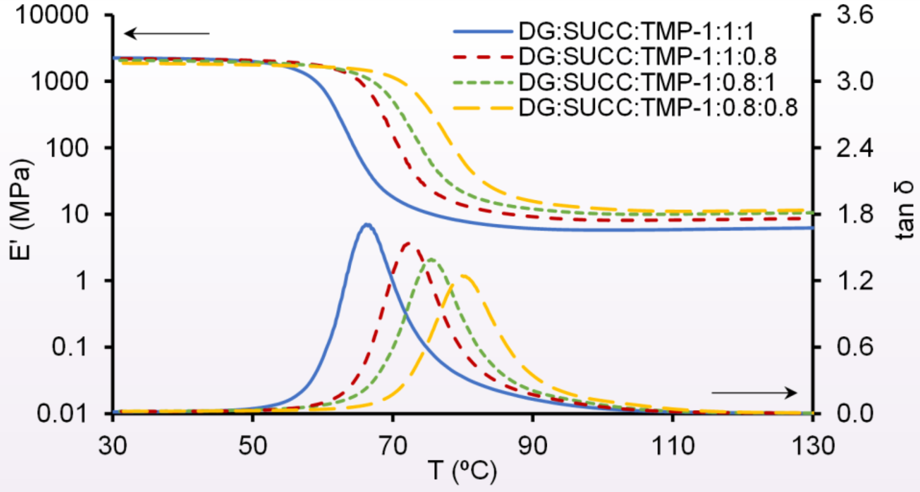


Formulation	DG (wt.%)	SUCC (wt.%)	TMP (wt.%)	1MI (wt.%)
DG:SUCC:TMP-1:1:1	53.3	31.4	14.0	1.3
DG:SUCC:TMP-1:1:0.8	54.9	32.3	11.5	1.3
DG:SUCC:TMP-1:0.8:1	58.6	27.6	12.3	1.4
DG:SUCC:TMP-1:0.8:0.8	60.1	28.3	10.1	1.4

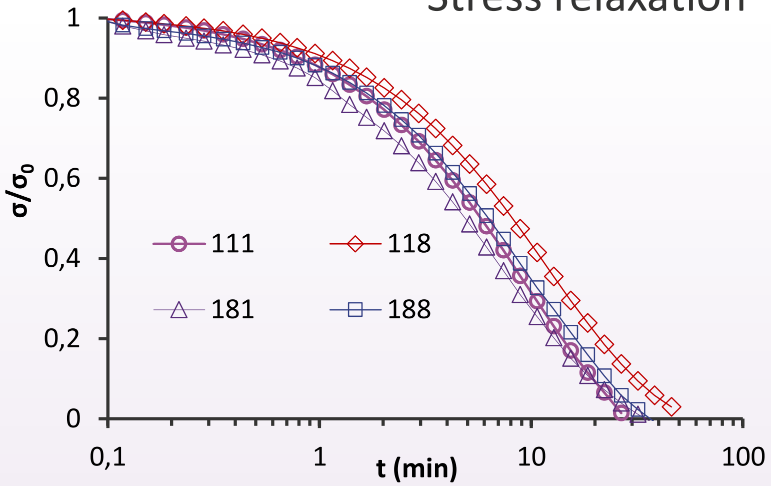
Thermomechanical and vitrimeric characterization

T_g (ºC)	T_v (ºC)	$\tau_{180ºC}$ (min)	$T_{2\%}$ (ºC)
66 - 80	84 - 123	7,5 - 9.5	277 – 326

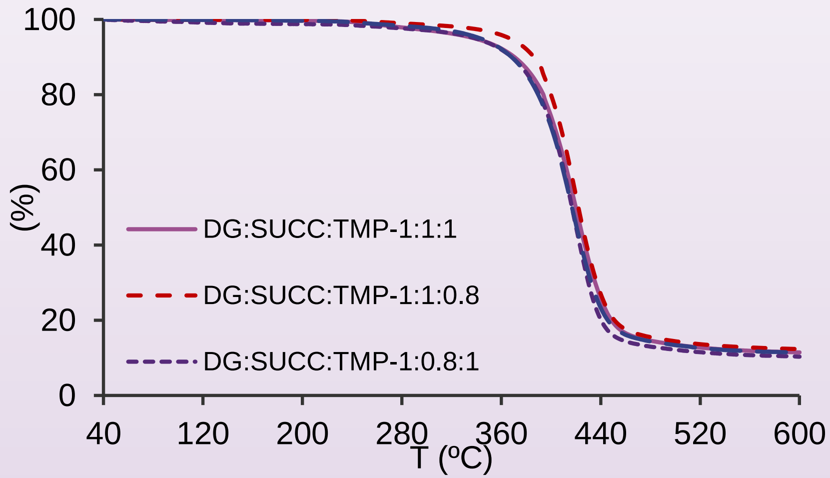
DMA



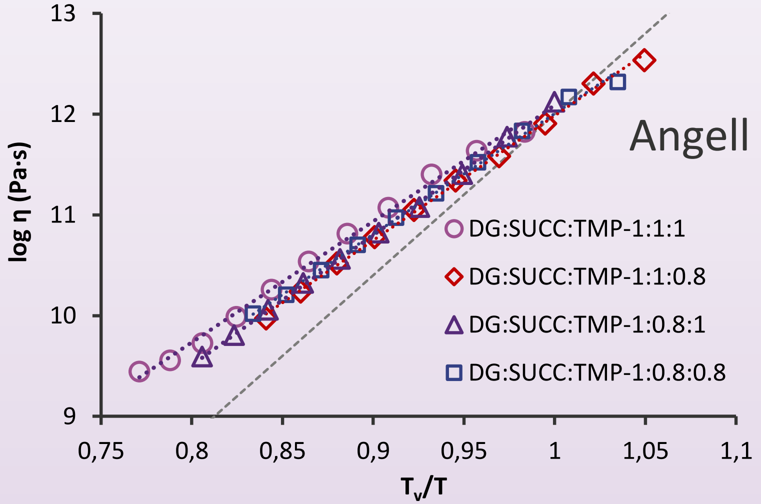
Stress relaxation



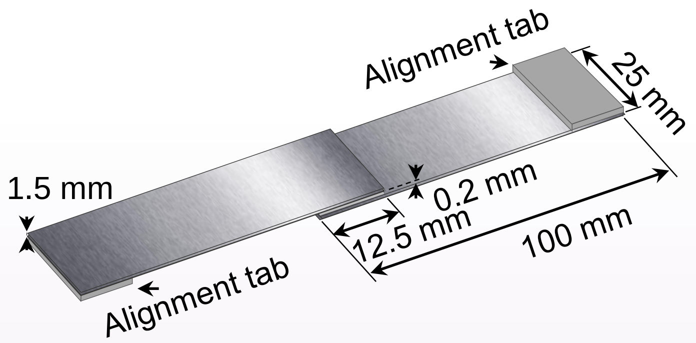
TGA



Angell fragility plot

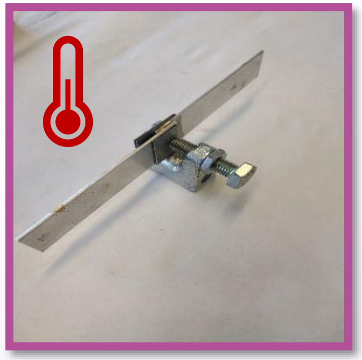


Adhesion and re-adhesion methodologies



Single lap joint

Failure surface



Re-adhesion setup

Coated plates

Debonded joint

Pristine adhesion
Re-adhesion after failure
Re-adhesion after thermal debonding
Self-welding

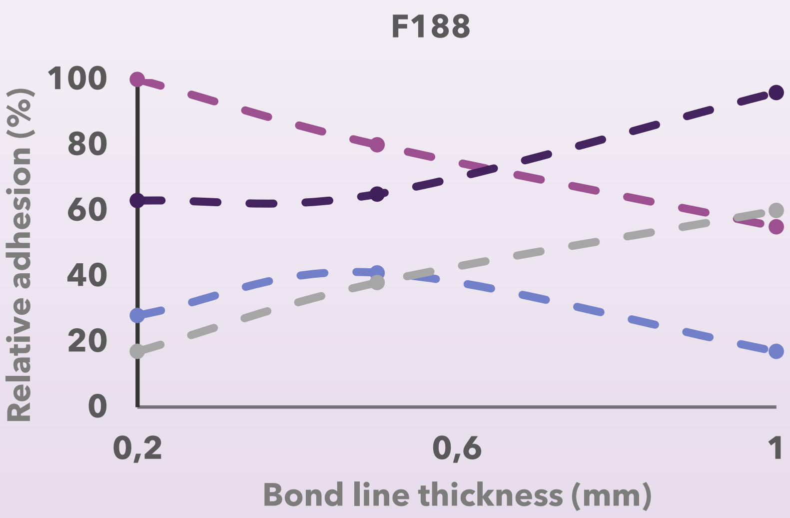
Adhesion and re-adhesion results

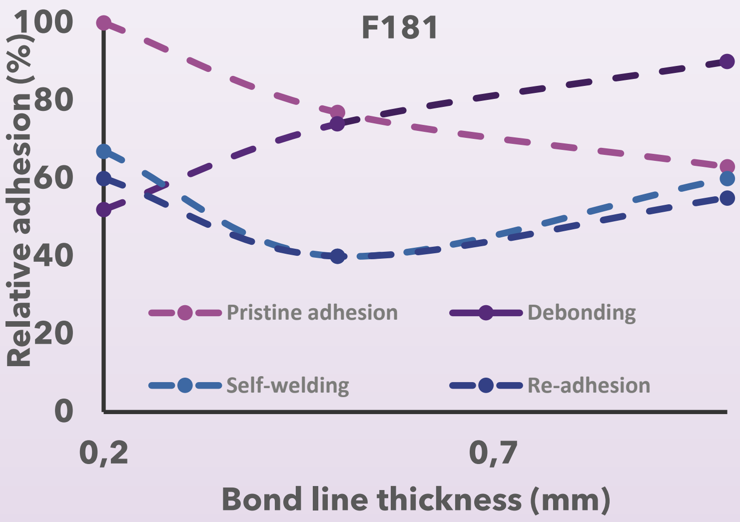
Formulation	Bond line thickness (mm)	Lap shear stress (MPa)	Re-adhesion after failure (MPa)		Re-adhesion after thermal debonding (MPa)		Adhesion after self-welding (MPa)	
DG:SUCC:TMP-1:1:1	0.2	25.6 ± 2.3	11.0 ± 2.5	(43 %)	12.7 ± 2.6	(50 %)	8.4 ± 1.7	(33 %)
DG:SUCC:TMP-1:1:0.8	0.2	23.4 ± 2.1	9.5 ± 2.0	(41 %)	12.3 ± 2.5	(52 %)	6.9 ± 1.0	(29 %)
DG:SUCC:TMP-1:0.8:1	0.2	20.2 ± 1.8	12.2 ± 1.7	(60 %)	10.5 ± 4.1	(52 %)	13.4 ± 5.9	(67 %)
DG:SUCC:TMP-1:0.8:0.8	0.2	25.8 ± 2.9	7.2 ± 2.1	(28%)	16.4 ± 3.1	(63%)	5.7 ± 2.1	(22%)

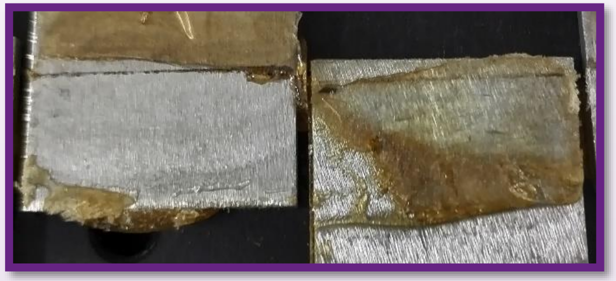
Adhesion and re-adhesion results

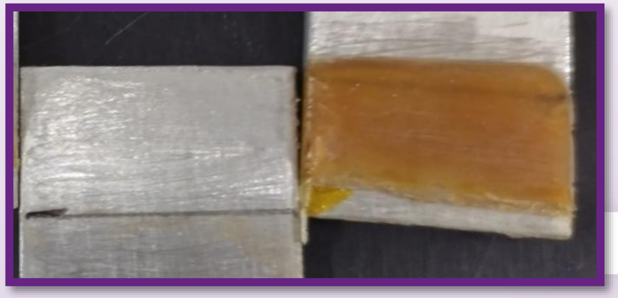
Effect of bond-line thicness

Formulation	Bond line thickness (mm)	Lap shear stress (MPa)	Re-adhesion after failure (MPa)		Re-adhesion after thermal debonding (MPa)		Adhesion after self-welding (MPa)	
DG:SUCC:TMP-1:0.8:1	0.2	20.2 ± 1.8	12.2 ± 1.7	(60 %)	10.5±4.1	(52 %)	13.4±5.9	(67 %)
	0.5	15.4 ± 1.8	6.2 ± 2.8	(40 %)	11.4±3.5	(74 %)	6.1±1.0	(40 %)
	1	12.6 ± 1.9	6.9 ± 0.8	(55 %)	11.3±3.9	(90 %)	5.5±2.4	(44 %)
DG:SUCC:TMP-1:0.8:0.8	0.2	25.8 ± 2.9	7.2 ± 2.1	(28%)	16.4±3.1	(63%)	5.7±2.1	(22%)
	0.5	20.8 ± 1.8	8.5 ± 3.4	(40%)	13.5±0.9	(65%)	7.8±4.2	(38%)
	1	14.3 ± 1.3	5.0	(35%)	13.7±0.6	(96%)	8.6±2.4	(60%)





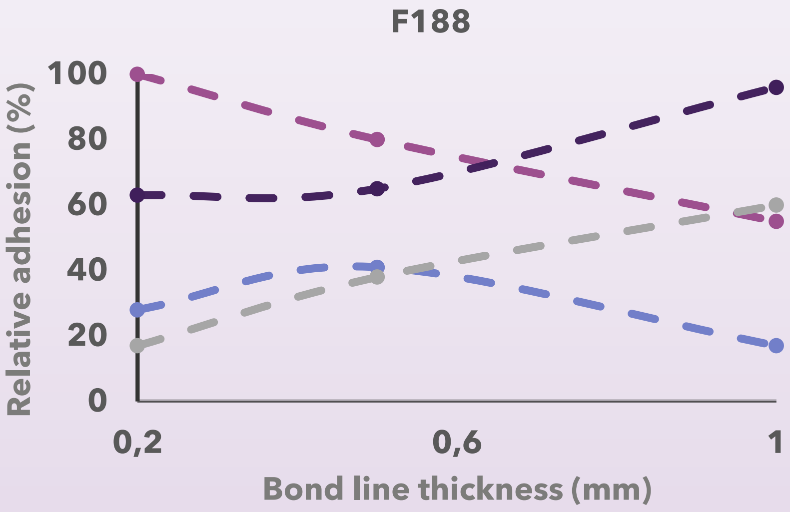


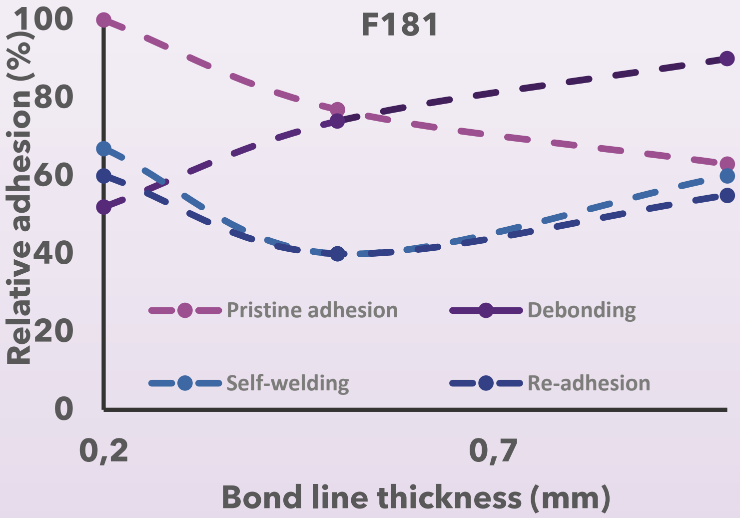


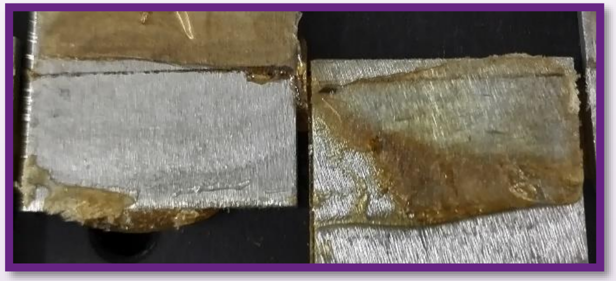
Adhesion and re-adhesion results

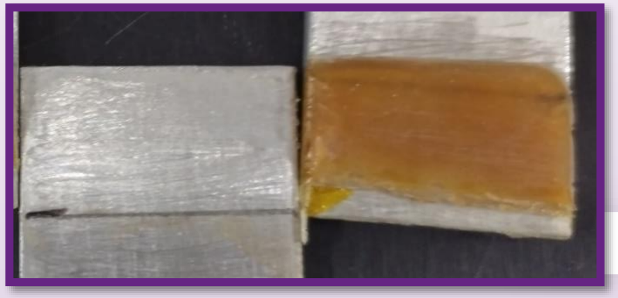
Effect of bond-line thicness

Thicker bond-line thicknesses **improve re-adhesion** performance (covalent forces), but **adversely affect adhesive forces.**
Superficial modification can increase adhesive forces without affecting cohesive interactions, potentially reducing this compromise.









Surface treatment methods

A) Degreasing surface preparation methods:

S0 Mechanical abrasion and acetone wiping
S1 Degreasing solution
S2 Mechanical abrasion and degreasing solution

B) **Plasma exposure surface preparation methods:**

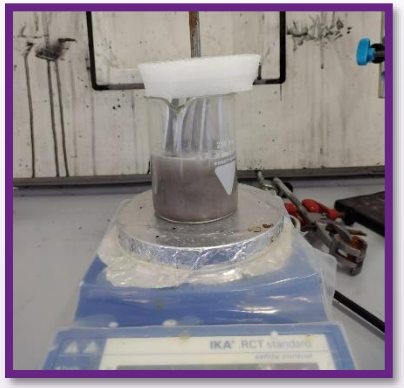
S3 Plasma exposure (5 min)
S4 Plasma exposure (5 min) and abrasion
S5 Plasma exposure (10 min) and abrasion

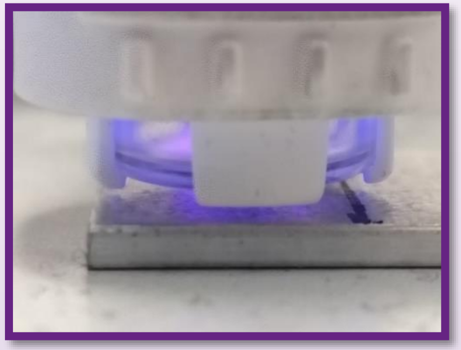
C) Chemical etching surface preparation methods:

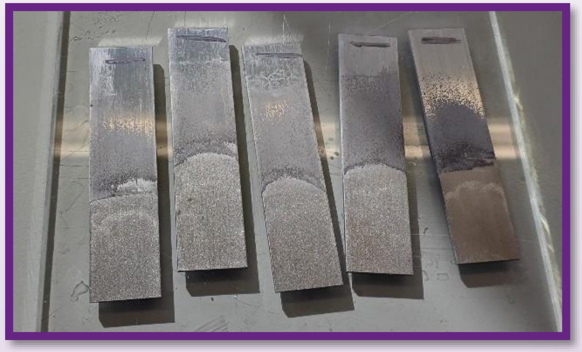
S6 Nitrate etching solution
S7 NaOH 0.1 M etching solution (ultrasounds)
S8 P2 etching solution

1% Na_2SiO_3
1% Na_2CO_3
1.5% Na_3PO_4
0.5% SDBS
(4% $NaNO_3$)

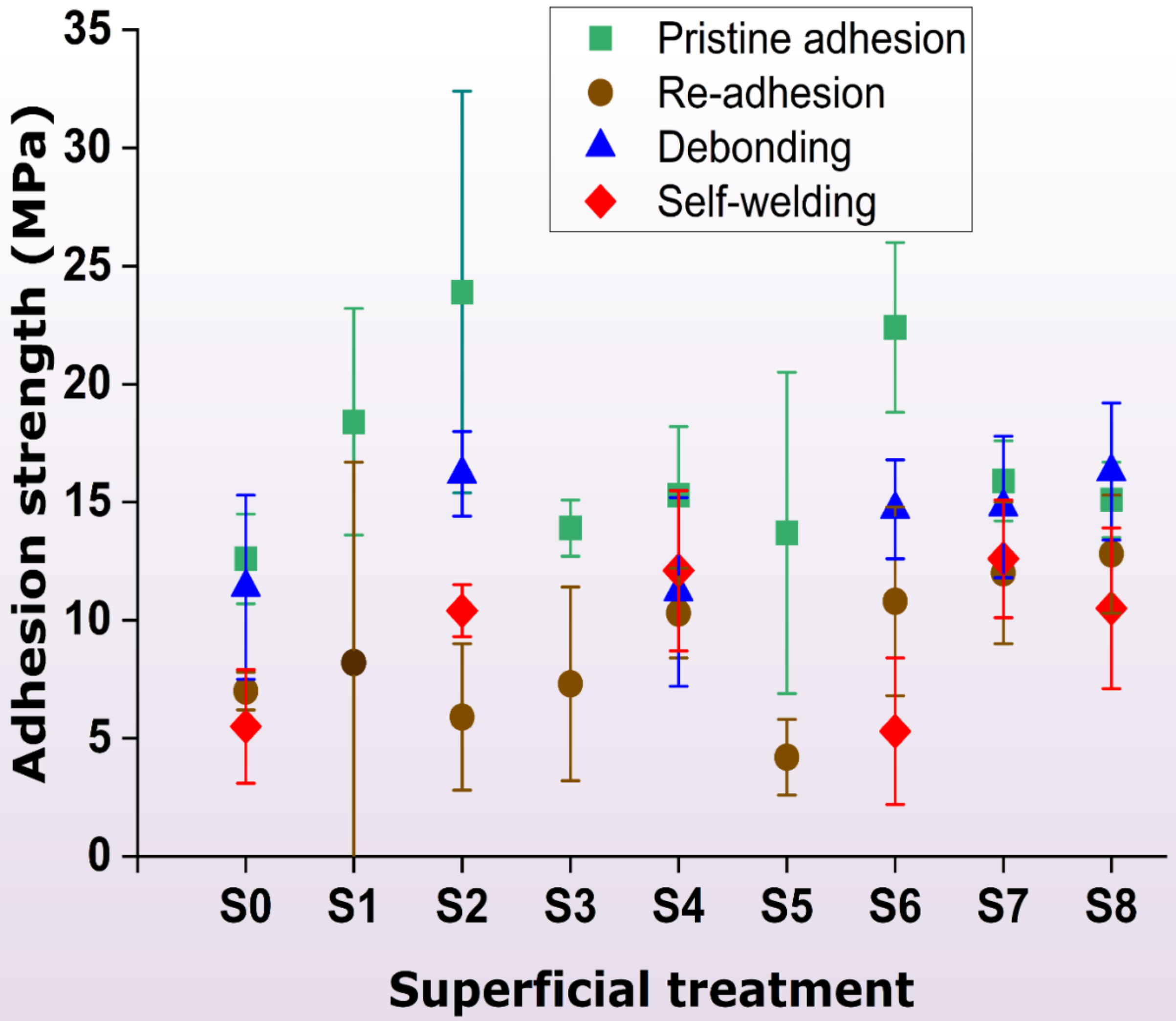
135g/L $Fe_2(SO_4)_3$
30% H_2SO_4







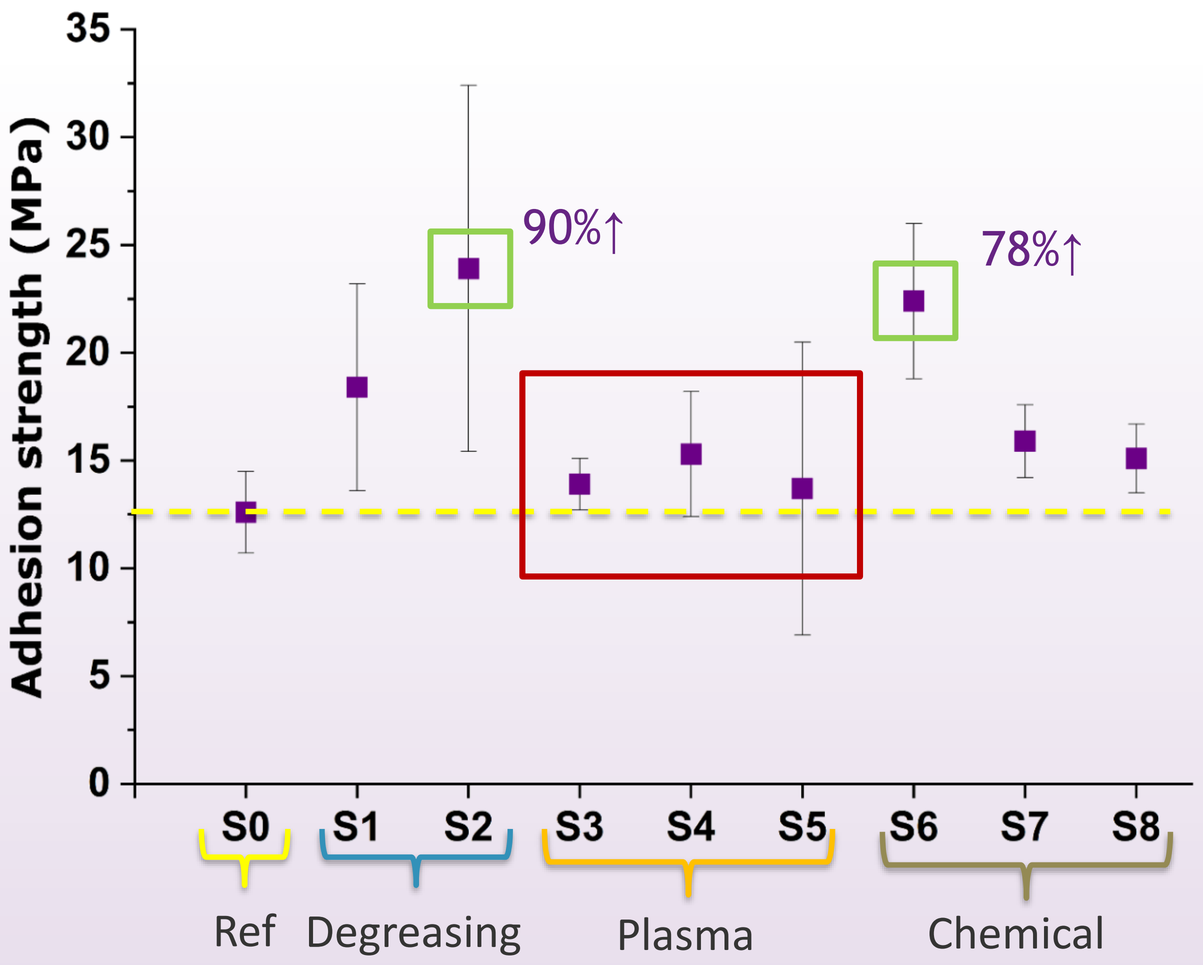
Surface treatment adhesion results

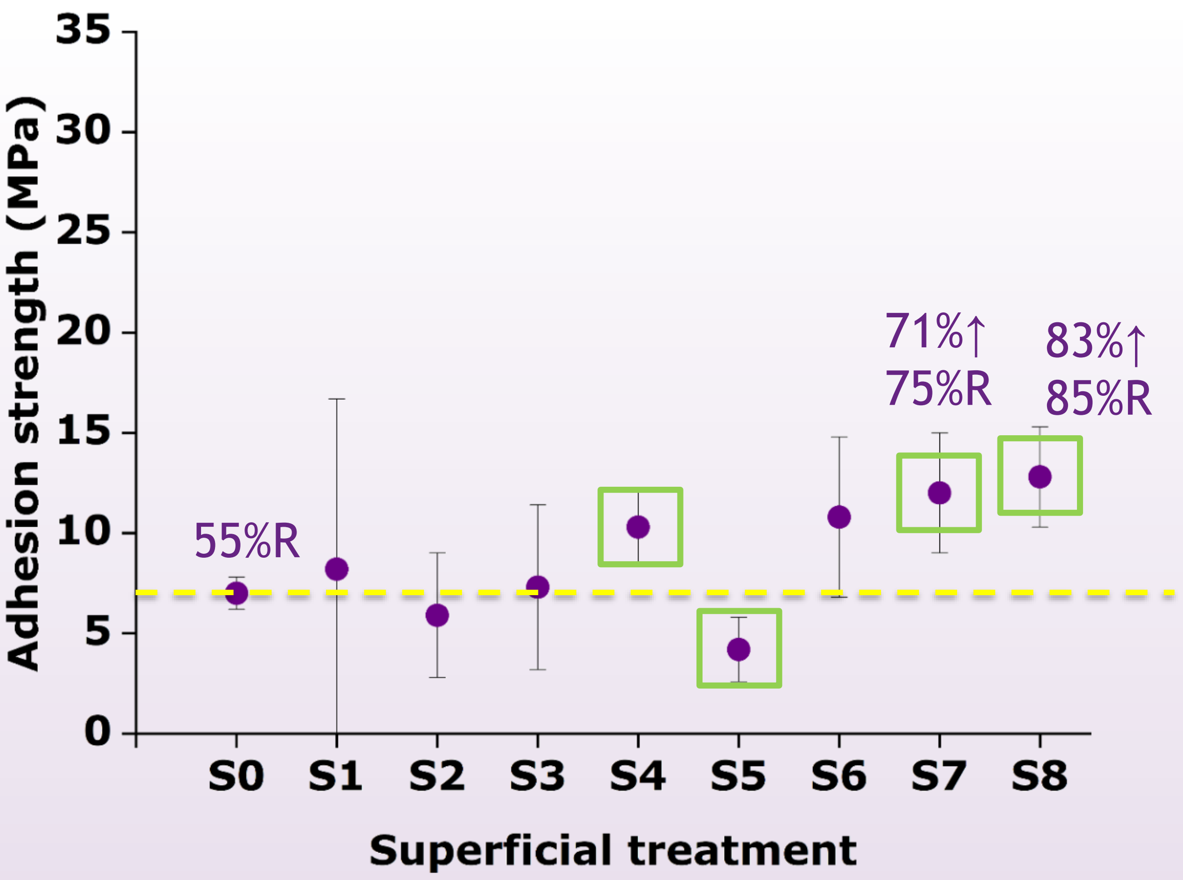


- ❑ High dispersion of results. Need of statistical analyses.
- ❑ Superficial treatments affect pristine adhesion as well as re-adhesion methodologies.
- ❑ Re-adhesion methodologies are influenced differently by superficial treatment.

Effect of surface treatments

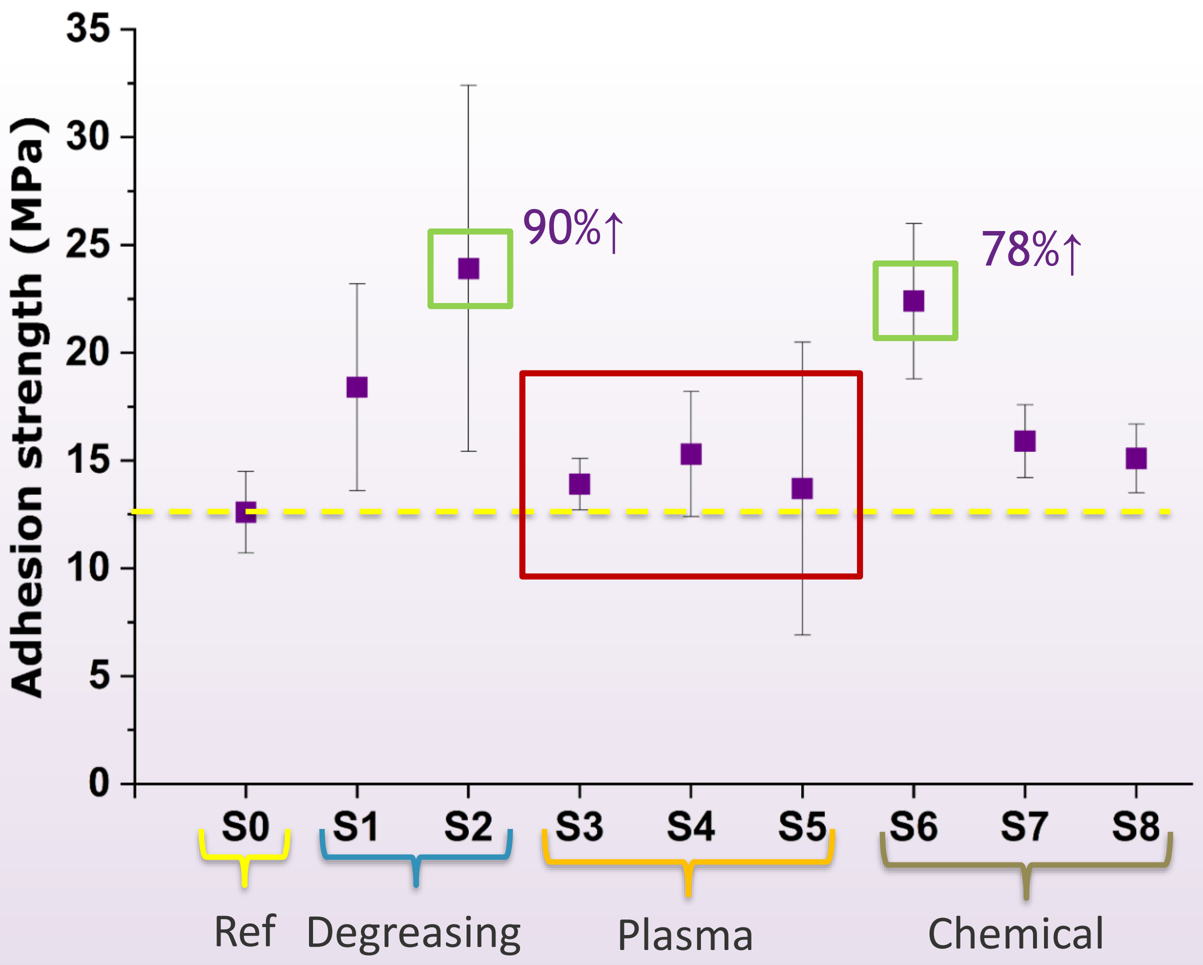
Pristine adhesion and re-adhesion after failure

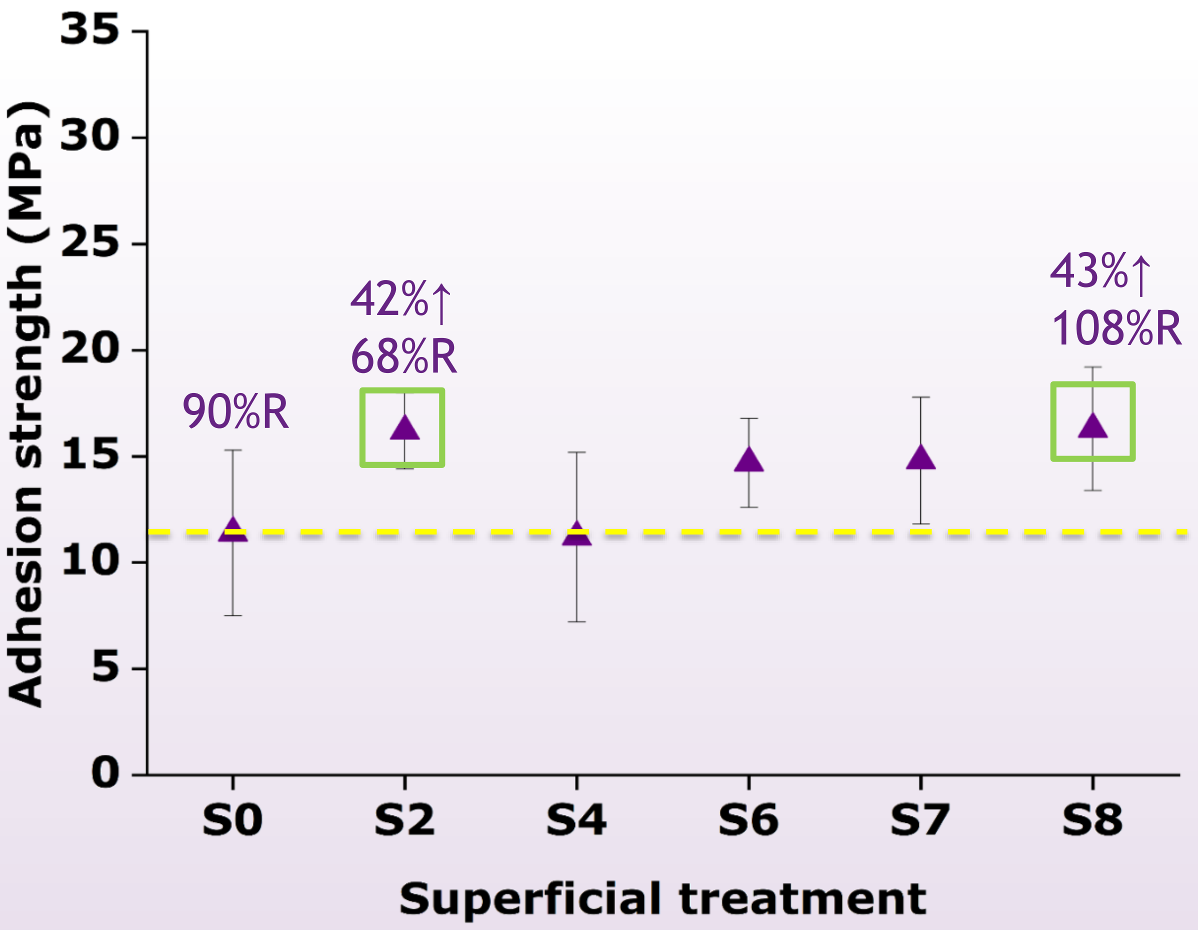




Effect of surface treatments

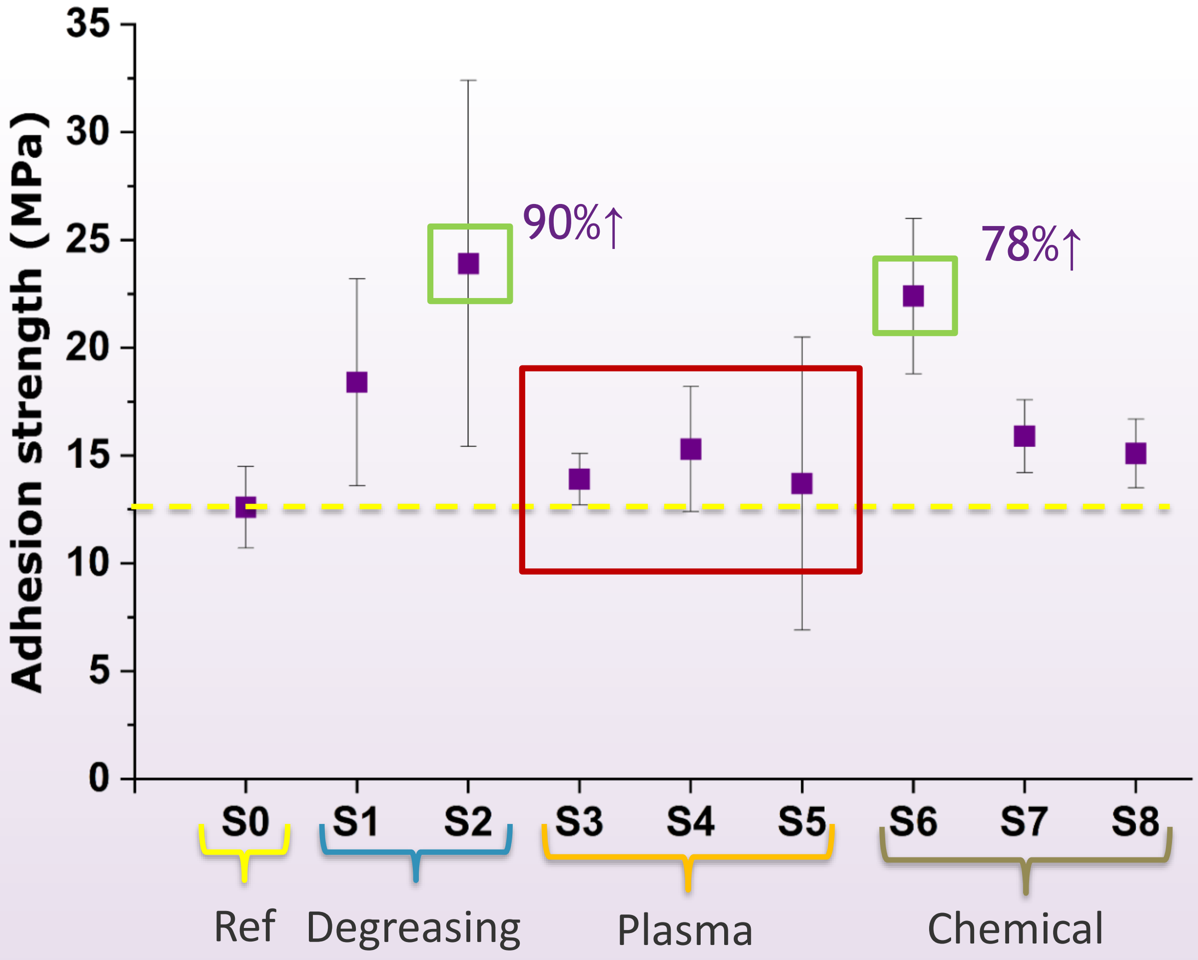
Re-adhesion after thermal debonding

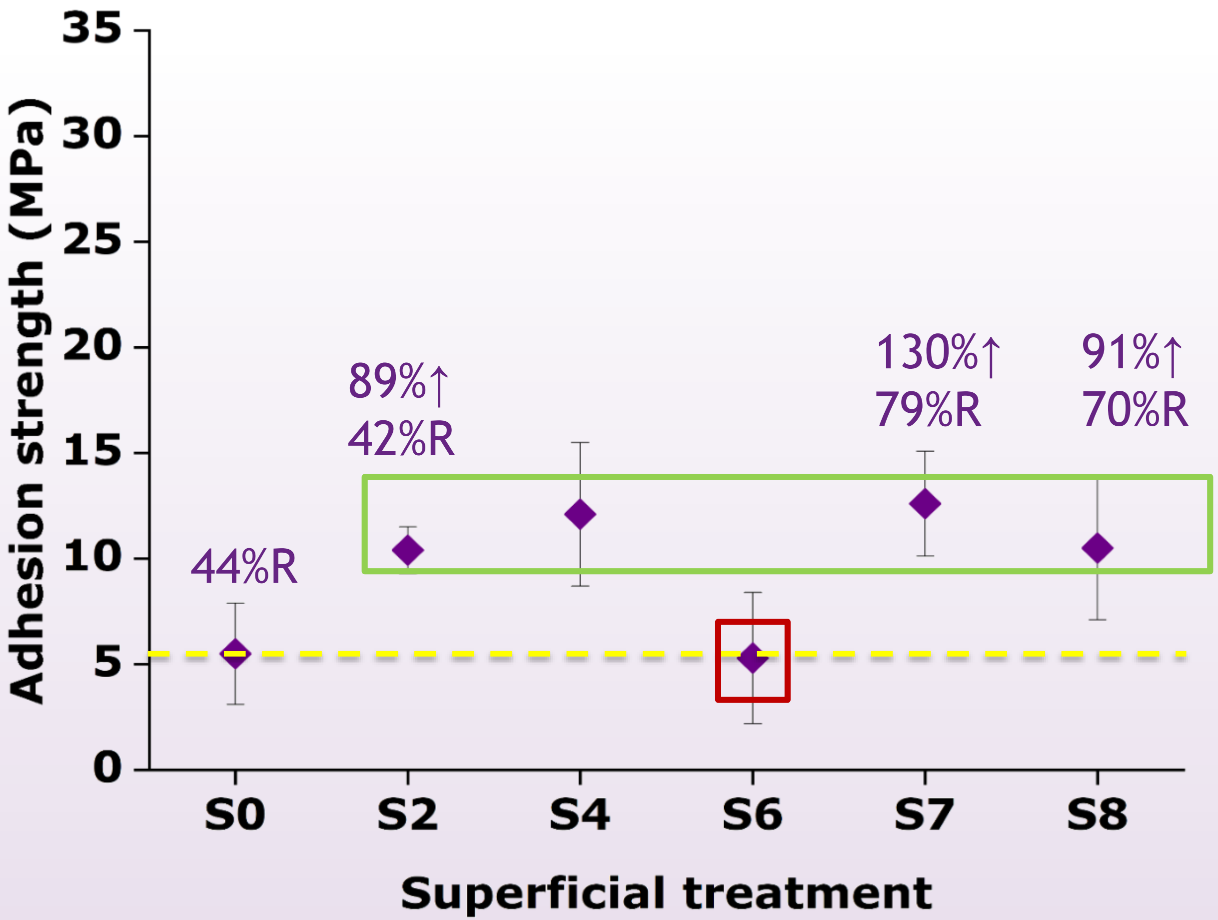




Effect of surface treatments

Adhesion after self-welding

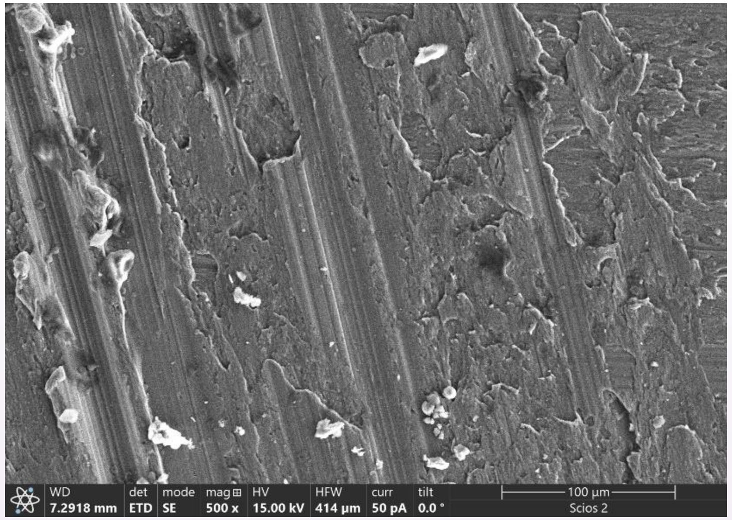


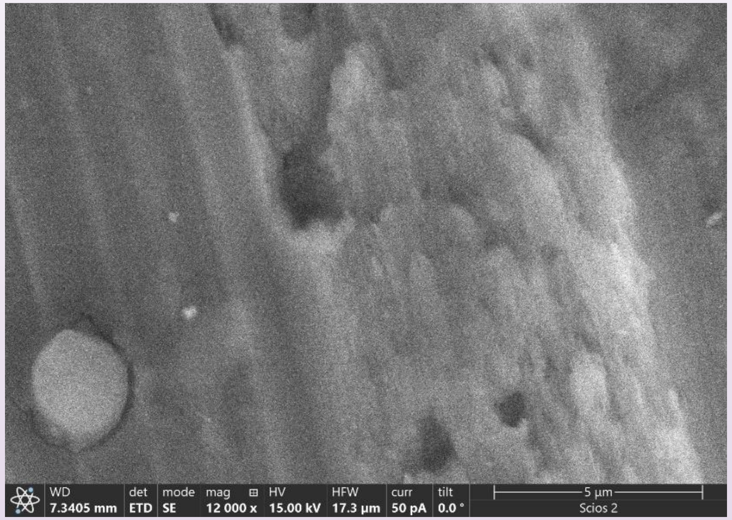


Effect of surface treatments

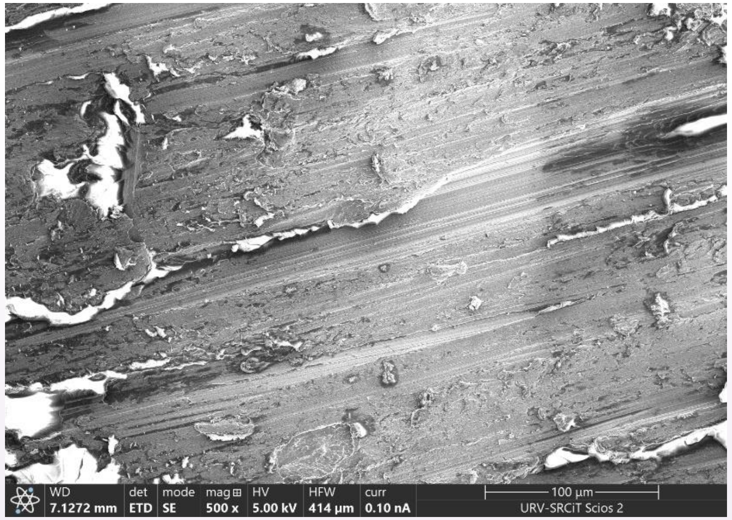
Superficial characterization

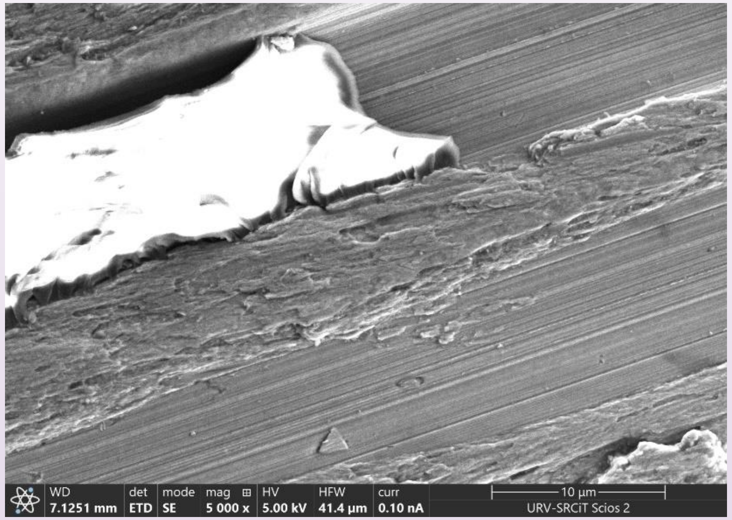
Before bonding S0

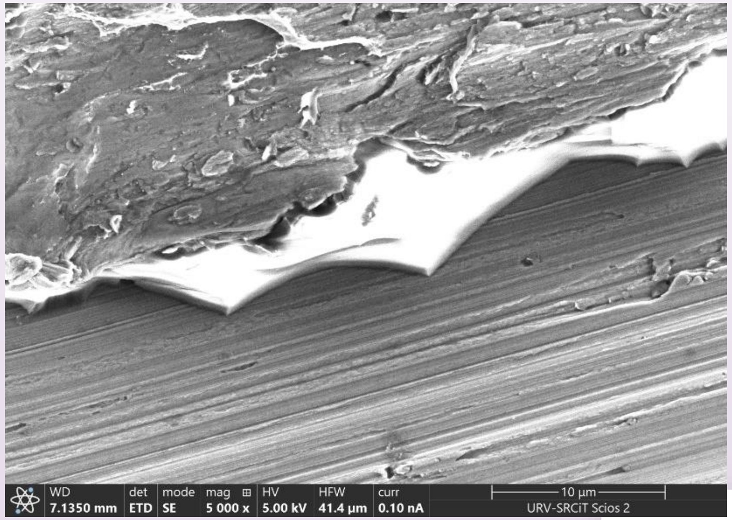




After adhesive failure (S0)



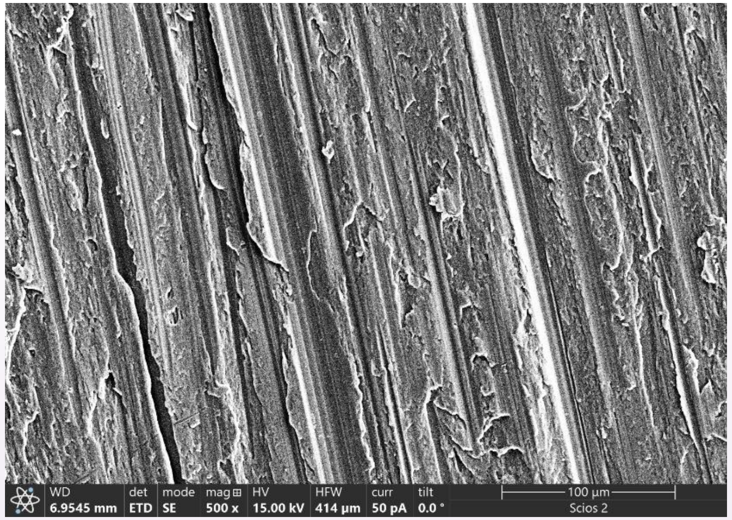


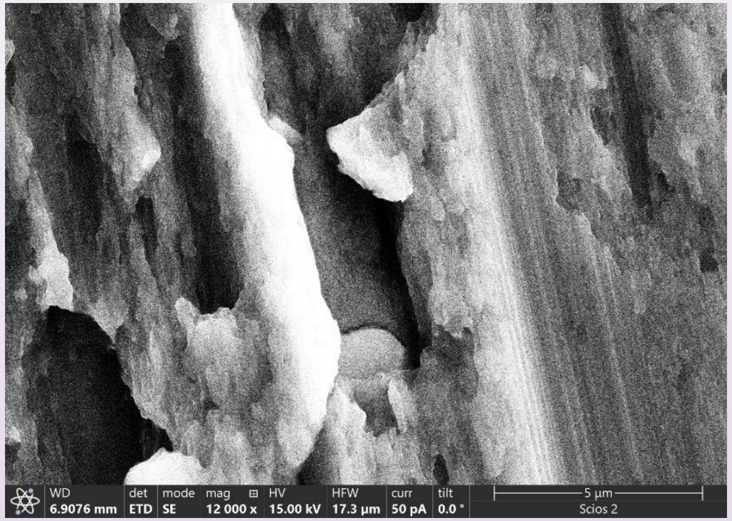


Effect of surface treatments

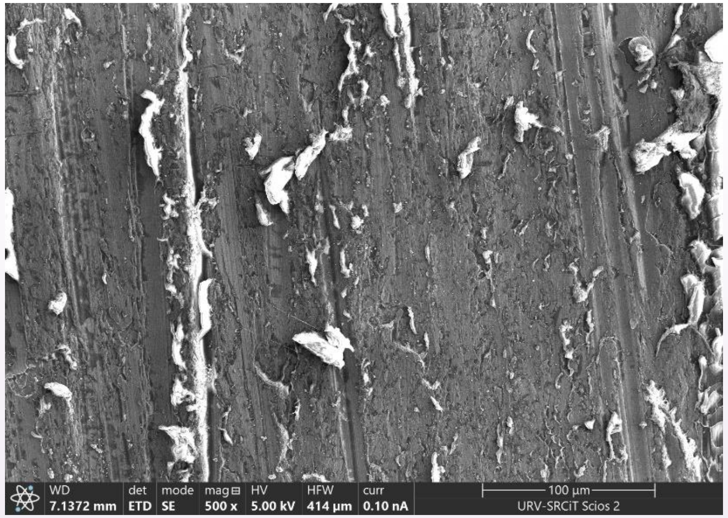
Superficial characterization

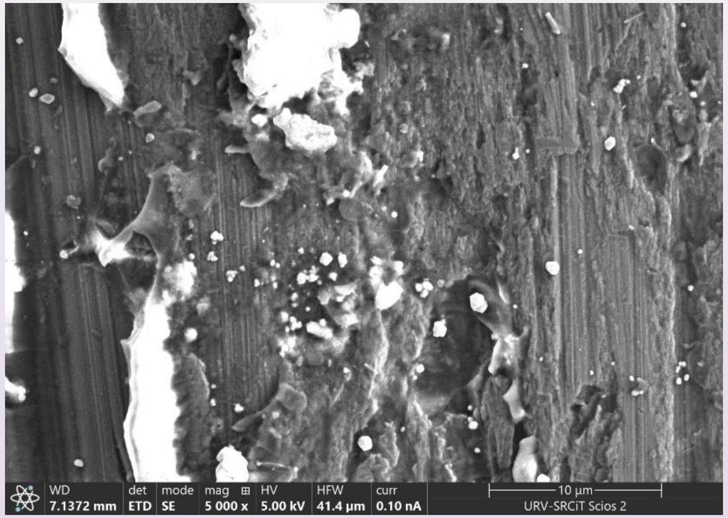
Before bonding S2





After adhesive failure (S2)



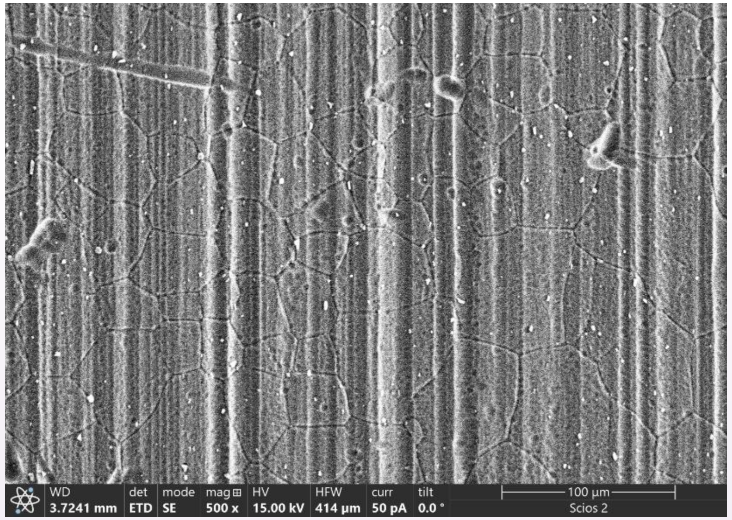


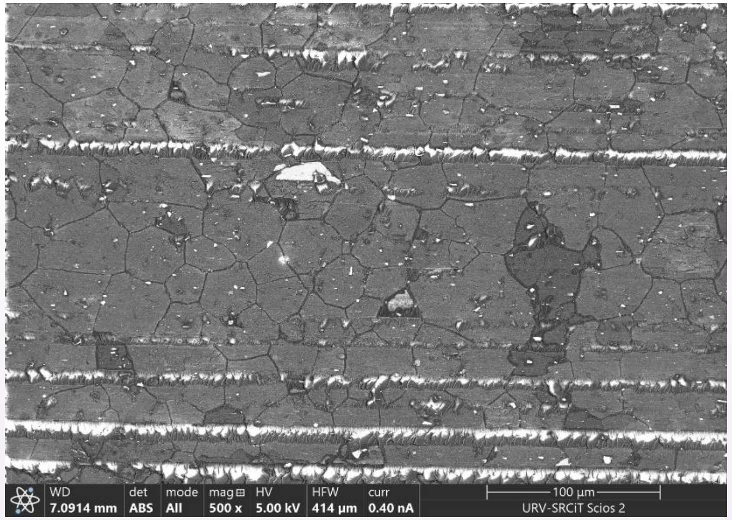
Effect of surface treatments

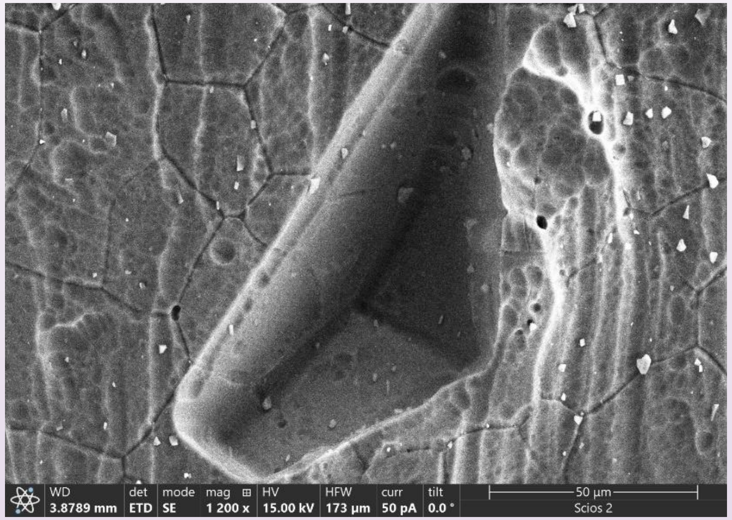
Superficial characterization

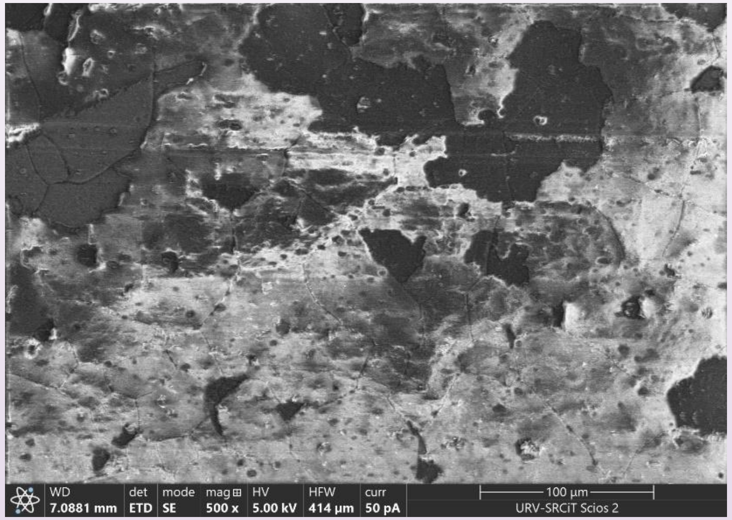
Before bonding S7

After bonding(S7)









Effect of superficial treatment

Results comparison

Formulation	Bond line thickness (mm)	Superficial treatment	Lap shear stress (MPa)	Re-adhesion after failure (MPa)		Re-adhesion after thermal debonding (MPa)		Adhesion after self-welding (MPa)	
DG:SUCC:TMP-1:0.8:1	0.2	S0	20.2 ± 1.8	12.2 ± 1.7	(60%)	10.5 ± 4.1	(52%)	13,4 ± 2.1	(67%)
	0.5		15.4 ± 1.8	6.2 ± 2.8	(40%)	11.4 ± 3.5	(74%)	6.1 ± 1.0	(40%)
	1		12.6 ± 1.9	6.9 ± 0.8	(55%)	11.3 ± 3.9	(90%)	5.5 ± 2.4	(44%)
	1	S2	23.9 ± 8.5	5.9 ± 3.1	(25%)	16.2 ± 1.8	(68%)	10.4 ± 1.1	(44%)
		S6	22.4 ± 3.6	10.8 ± 4.0	(48%)	14.7 ± 2.1	(66%)	5.3 ± 3.1	(24%)
		S7	15.9 ± 1.7	12.0 ± 3.0	(75%)	14.8 ± 3.0	(93%)	12.6 ± 2.5	(79%)
		S8	15.1 ± 1.6	12.8 ± 2.5	(85%)	16.3 ± 2.9	(108%)	10.5 ± 3.4	(70%)

Conclusions

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- Different vitrimer formulations were obtained using **commercial reagents**. They can be tweaked to obtain different glass transition temperatures and stress-relaxation behaviors.
- When tested as adhesives, they showed **high adhesion strength** and could be re-adhered, self-welded or debonded on demand thanks to their vitrimeric characteristics.
- Study of bond-line thickness showed that thicker BLs imply a decrease of pristine adhesion strength but an improvement of **re-adhesion performance**.
- **Surface treatment technology** not only improved pristine adhesion strength but also improved re-adhesion performance.

"innovating with businesses"

Thank you

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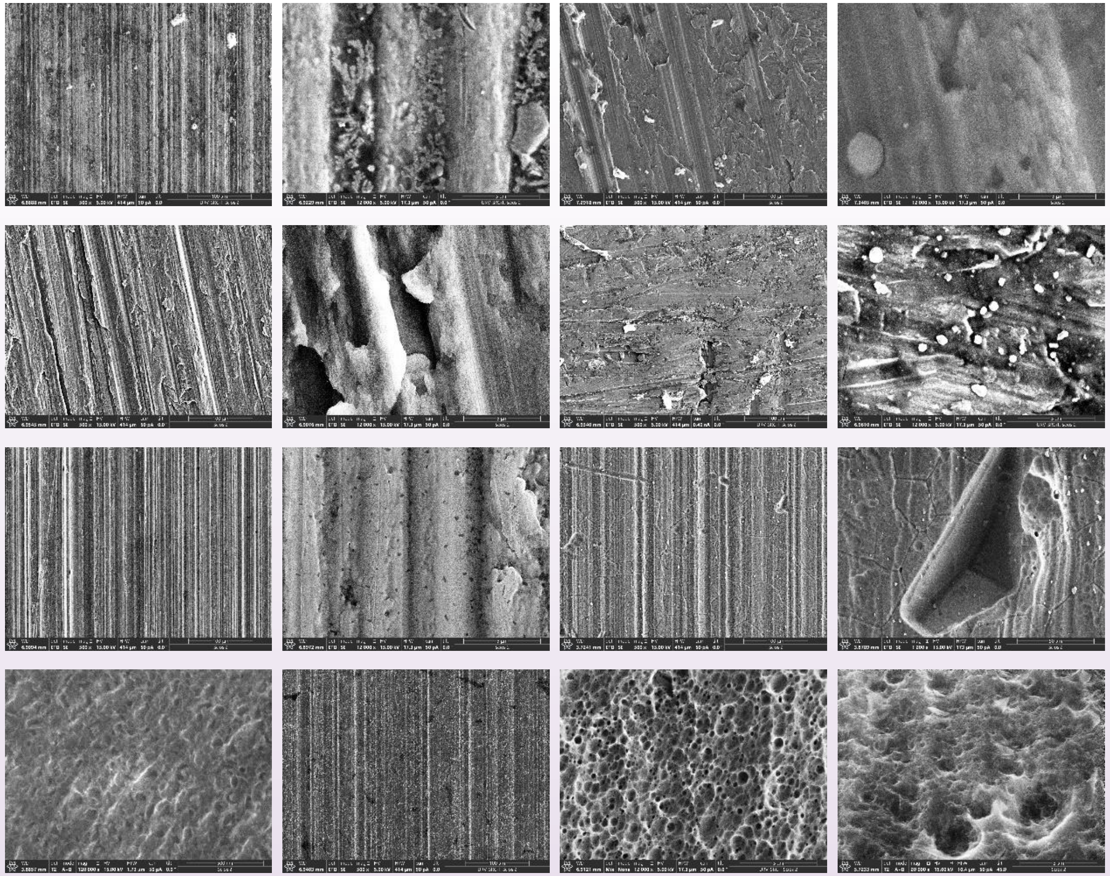
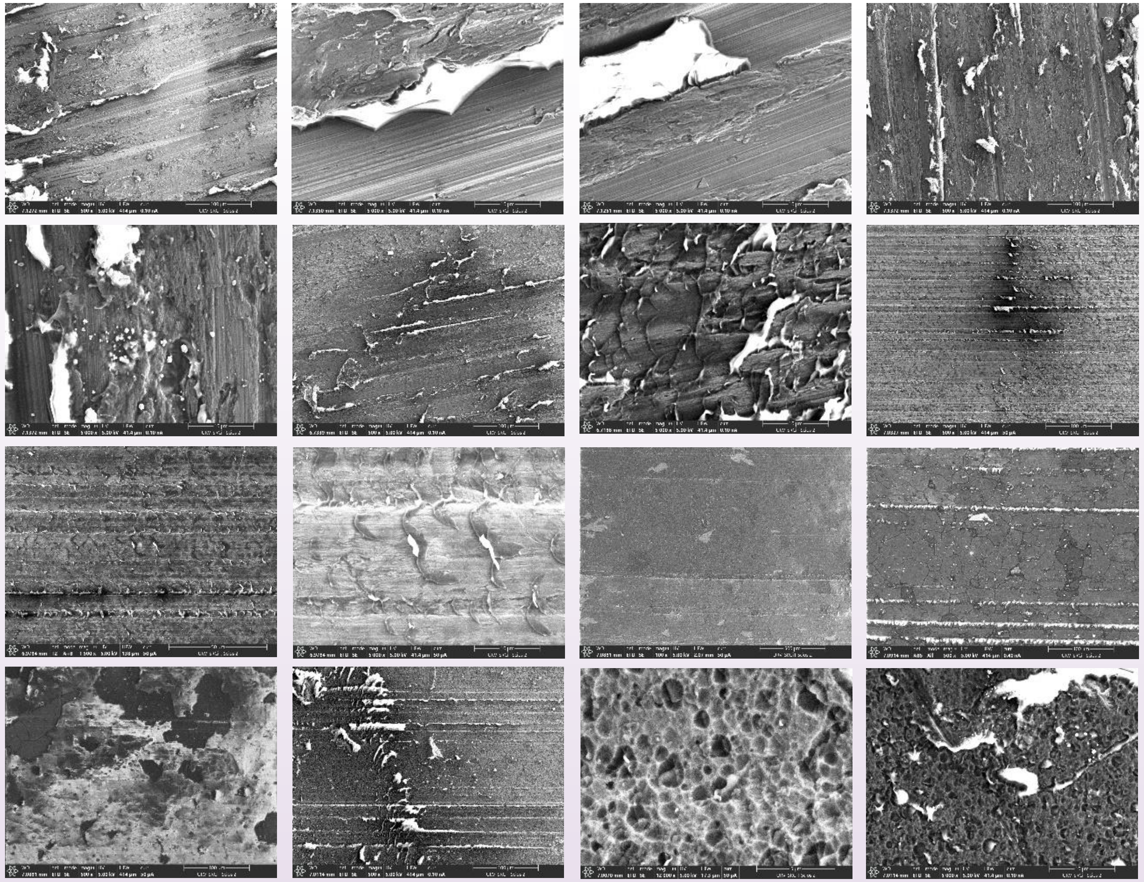
Effect of surface treatments

Superficial characterization

Before bonding



After adhesive failure



Effect of superficial treatment

Surface characterization

Treatment	As received	S0	S2	S4	S6	S7	S8
Apparent water contact angle (º)	38.4	88.9	13.4	45.3	22.9	23.9	8.3