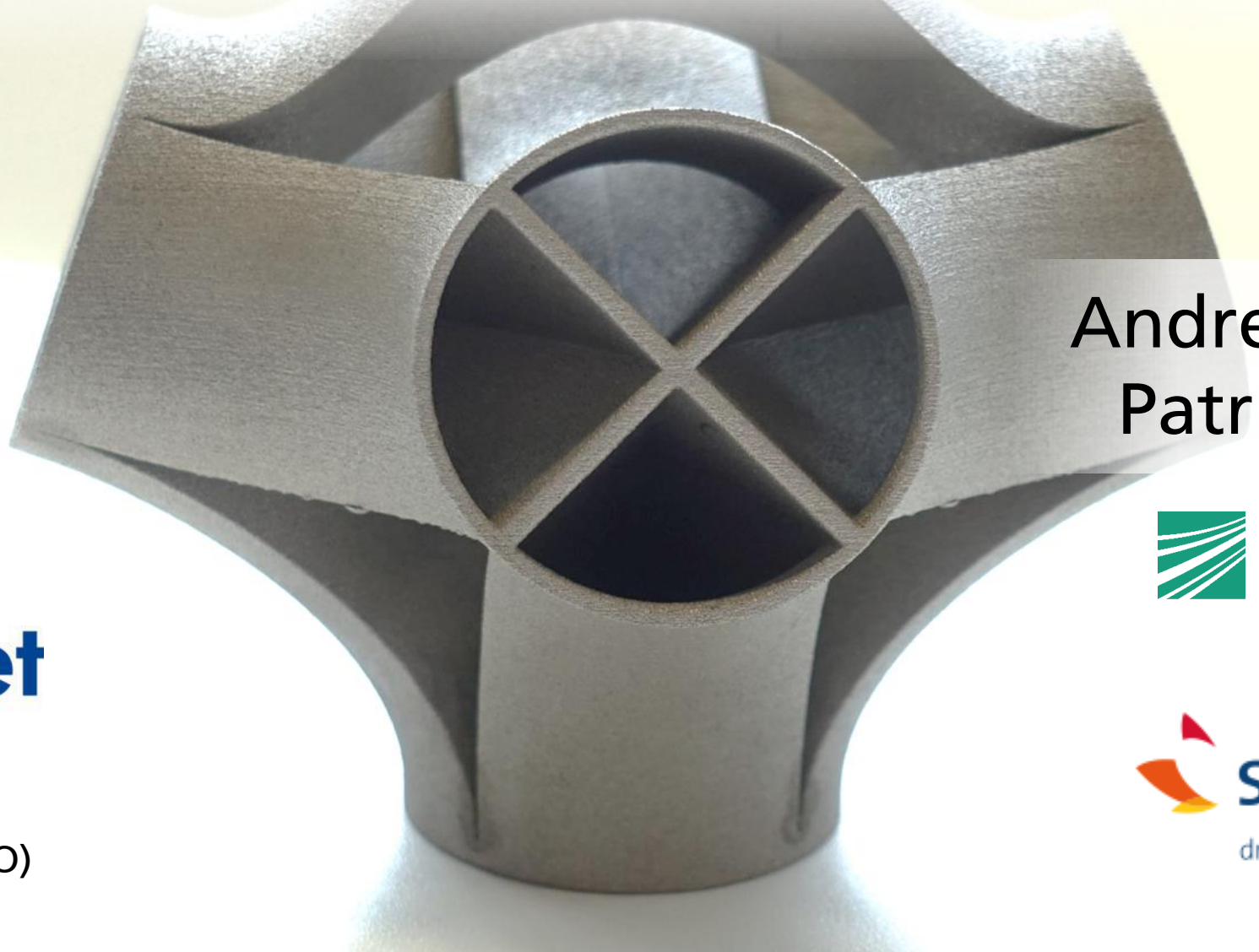
OBERFLÄCHEN UND BESCHICHTUNG ADDITIV GEFERTIGTER POLYMERTEILE



Andreas Holländer
Patrick Cosemans

Fraunhofer
IAP

cornet

IGF-15/09 (EFDS)
166 EBR (AIF)
IWT.150827 (VLAIO)

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Outline

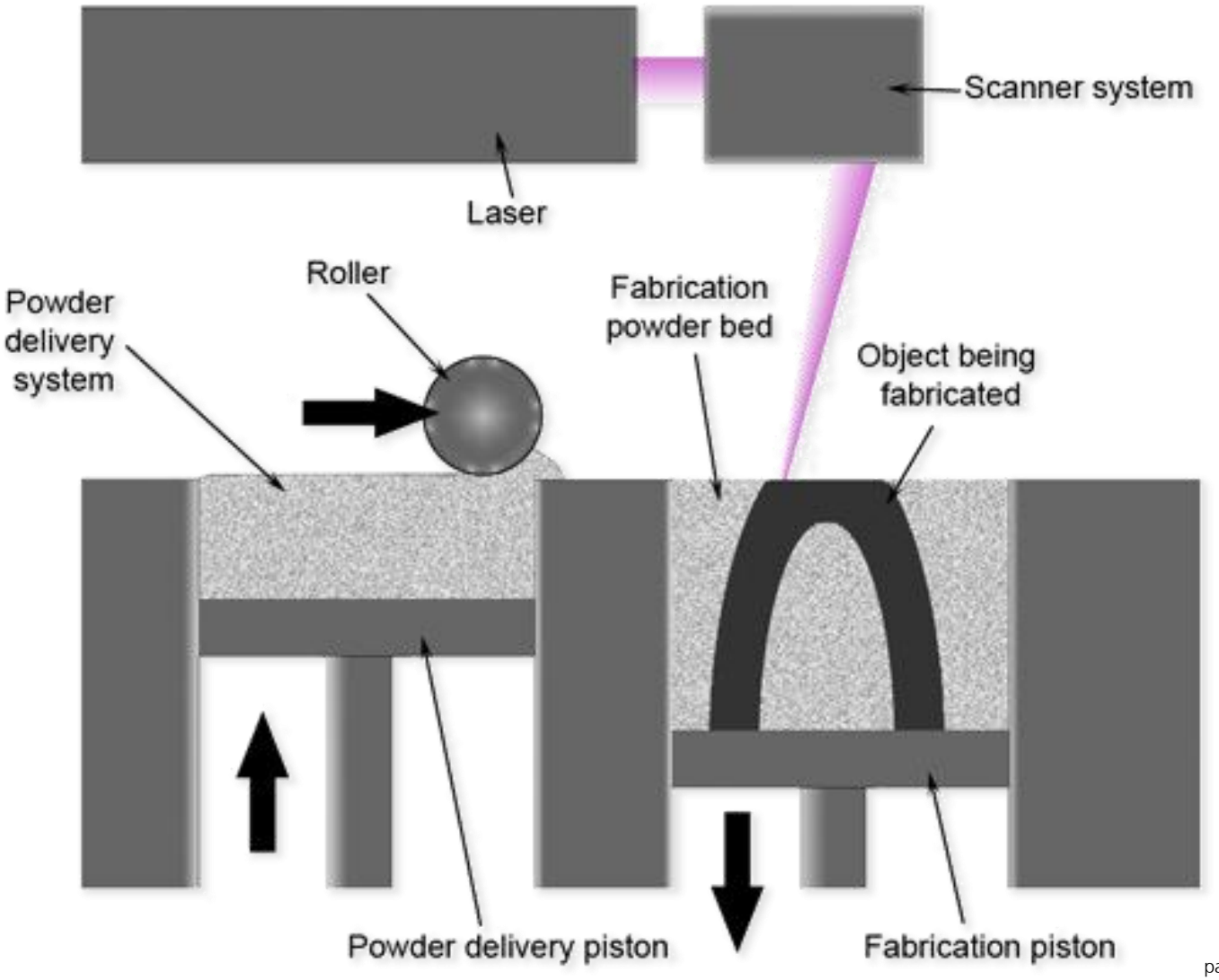
- Additive Manufacturing (AM)
- Surface analysis
- Surface activation
- Smoothing by lacquering
- Metallization
- Conclusions
- Acknowledgement

Additive Manufacturing

Selective laser sintering (SLS)

materials

- PA12
- PA11, TPU



https://en.wikipedia.org/wiki/Selective_laser_sintering

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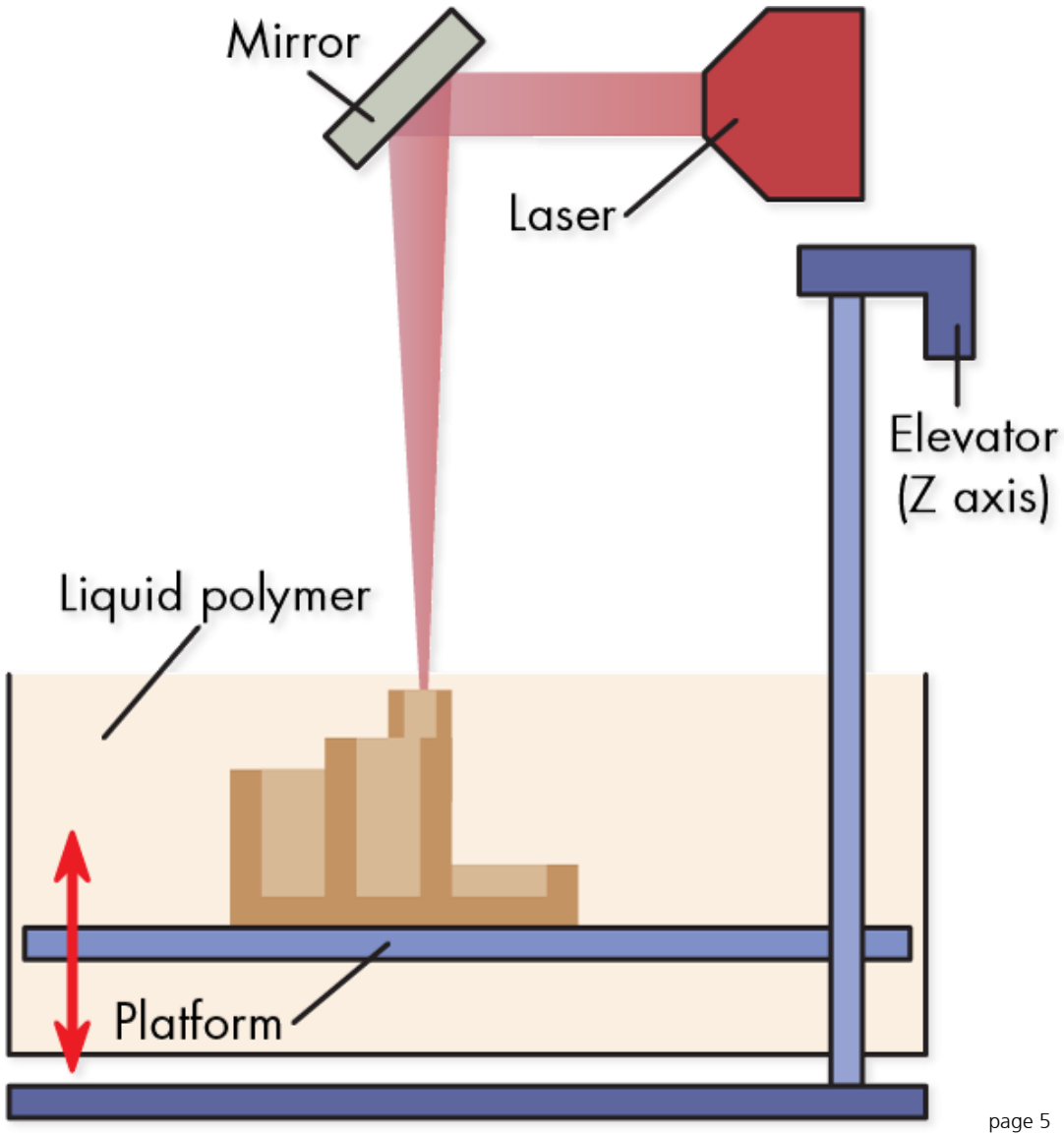
Stereo lithography (SLA)

materials

- light curable resins
  epoxy, acrylic …



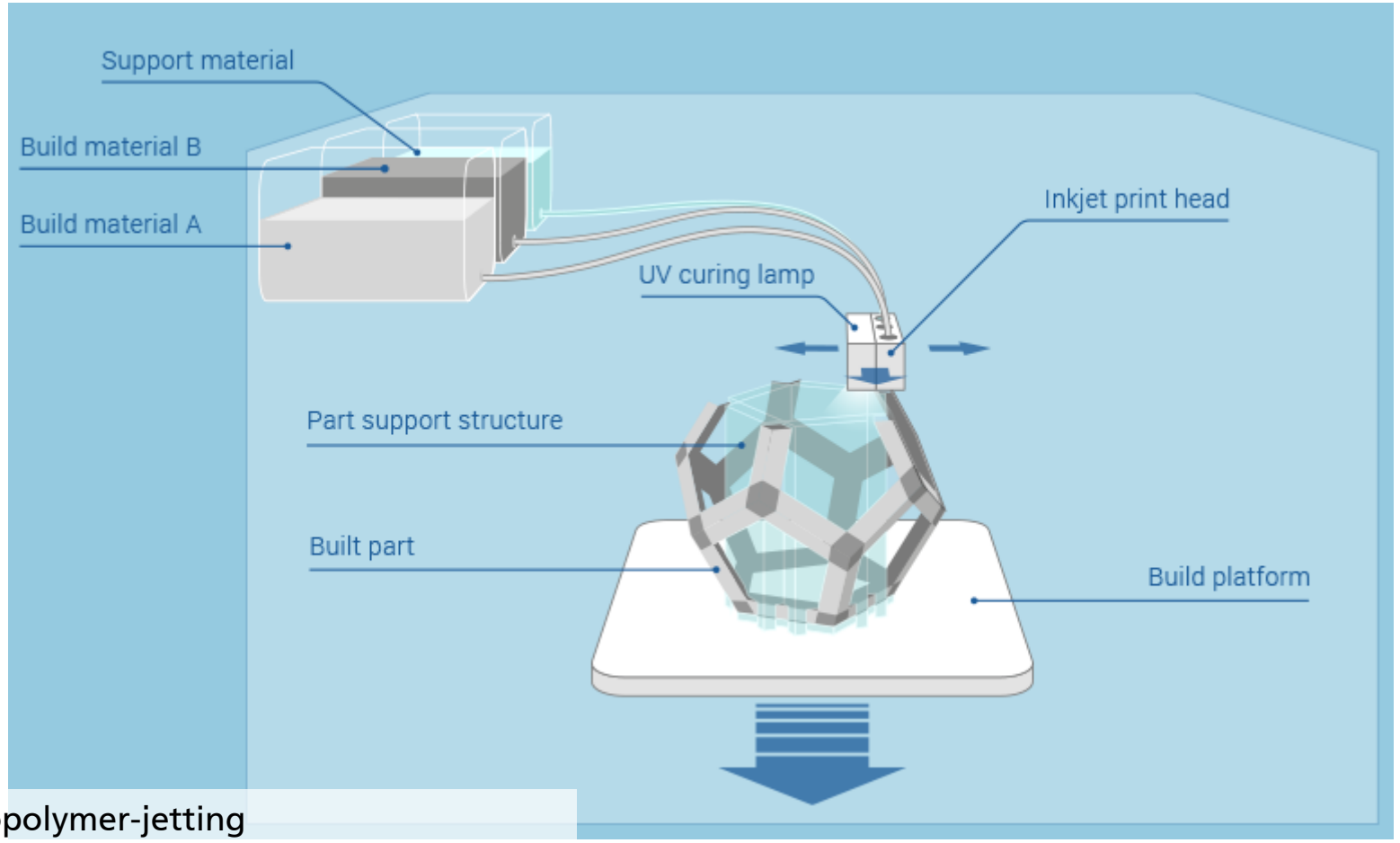
https://en.wikipedia.org/wiki/Stereolithography

Photopolymer jetting (PJ, MJ)

also known as material jetting (MJ), polyjet modeling, multijet modeling, polyjetting, multijetting, jetted photopolymer

materials

- UV curable resins



https://www.additively.com/en/learn-about/photopolymer-jetting

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Surface Analysis

Homogeneity of PA12 sheets (SLS)

- sheet 10 cm x 10 cm
- advancing water contact angles, [°]
- cleaned with water, i-PrOH

original				cleaned		
130.0	110.7	117.3		114.0	113.0	101.6
130.0	114.0	113.0		111.9	115.0	116.8
122.0	103.3	108.1		108.0	114.5	108.6
109.0	105.0	120.4		105.1	115.0	121.0
av	**115.2**			av	**112.0**	
av. dev.	**7.3**			av. dev.	**4.2**	

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PA12 sheets (SLS), XPS

elemental concentrations

PA12
[C] = 85.7 at%
[O] = 7.1 at%
[N] = 7.1 at%

position	[C] at%	[N] at%	[O] at%
top 1	83.4	6.9	9.7
top 2	84.0	6.0	10.1
top 3	84.1	4.6	11.4
average:	**83.8**	**5.8**	**10.4**
av. dev.:	**0.3**	**0.8**	**0.7**
back 1	83.3	4.7	12.0
back 2	83.3	6.1	10.6
back 3	84.3	5.0	10.7
average:	**83.6**	**5.3**	**11.1**
av. dev.:	**0.4**	**0.6**	**0.6**

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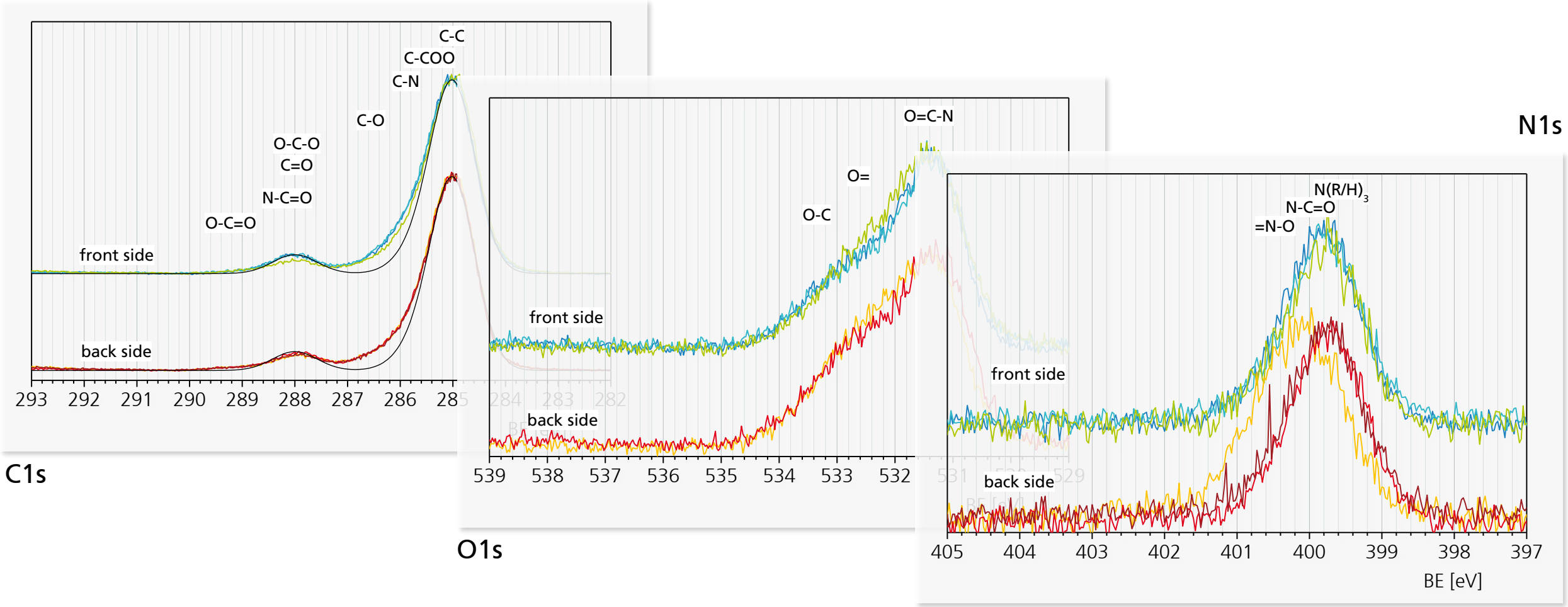
PA12 sheets, XPS high resolution data



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Epoxy resin sheets (SLA), XPS

elemental concentrations
(Accura Clearvue)

position	[C] at%	[O] at%	[F] at%	[Ca] at%	[Cl] at%	[Sb] at%
top 1	68.0	26.0	3.4	1.0	0.7	0.9
top 2	68.0	25.9	3.4	1.1	0.8	0.8
top 3	69.7	25.4	2.9	1.2	0.4	0.5
top 4	70.5	26.0	1.6	0.3	0.8	0.8
top 5	70.6	26.7	1.4	0.2	0.4	0.6
top 6	71.2	26.2	1.2	0.5	0.4	0.5
average:	**69.7**	**26.0**	**2.3**	**0.7**	**0.6**	**0.7**
av. dev.:	1.1	0.3	0.9	0.4	0.2	0.1
back 1	72.6	24.4	1.5	0.9	0.6	
back 2	73.0	23.6	1.7	1.0	0.7	
back 3	71.0	25.6	1.8	1.6	0.0	
back 4	68.7	27.3	2.6	1.1	0.4	
average:	**71.3**	**25.2**	**1.9**	**1.1**	**0.4**	
av. dev.:	1.5	1.2	0.3	0.2	0.2	

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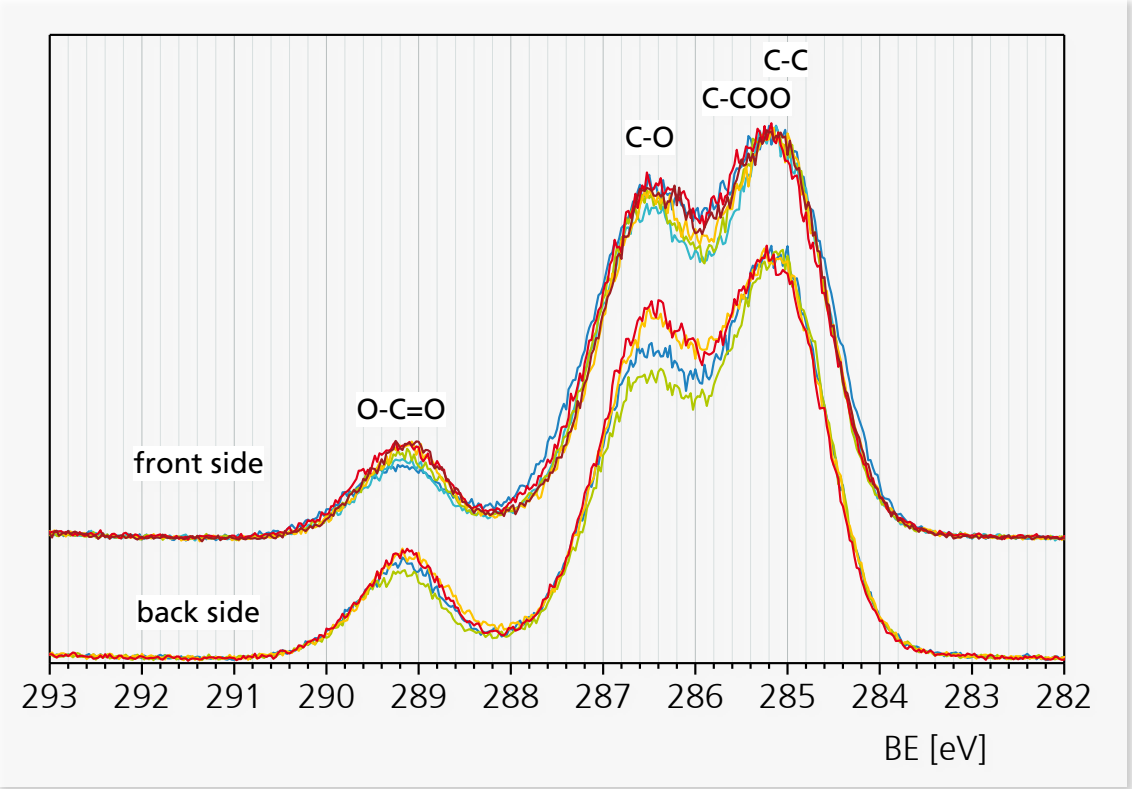
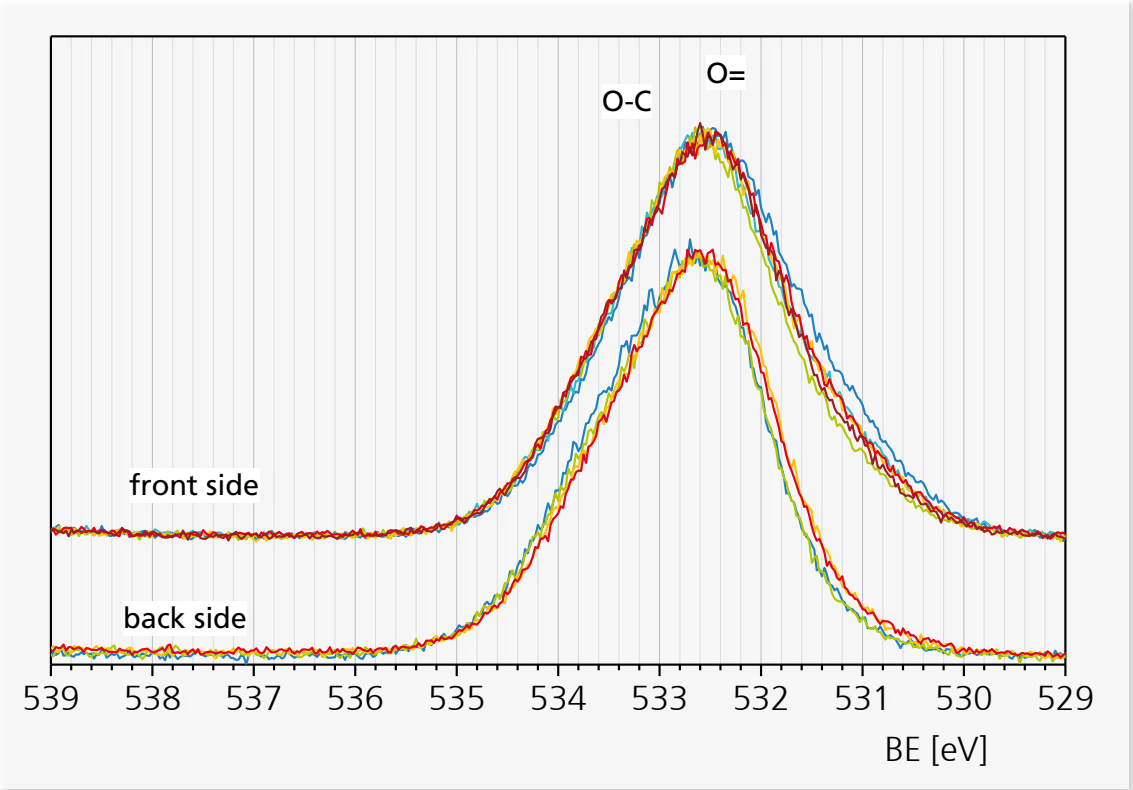
Epoxy resin sheets (SLA), XPS high resolution data



C1s



O1s

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Acrylic resin sheets (MJ), XPS

elemental concentrations
(Accura VeroBlack)

position	[C] at%	[N] at%	[O] at%	[Ca] at%
top 1	74.3	2.6	22.5	0.6
top 2	73.9	3.0	22.5	0.6
top 3	74.4	3.3	21.7	0.7
top 4	74.1	3.3	21.0	0.7
top 5	73.1	3.5	22.5	0.9
top 6	73.6	3.2	22.5	0.7
average:	**73.9**	**3.1**	**22.1**	**0.7**
av. dev.:	**0.4**	**0.2**	**0.5**	**0.1**
back 1	74.3	3.7	21.4	0.6
back 2	73.9	3.3	22.0	0.8
back 3	73.4	3.5	22.4	0.8
back 4	73.7	1.5	24.3	0.6
average:	**73.8**	**3.0**	**22.5**	**0.7**
av. dev.:	**0.3**	**0.8**	**0.9**	**0.1**

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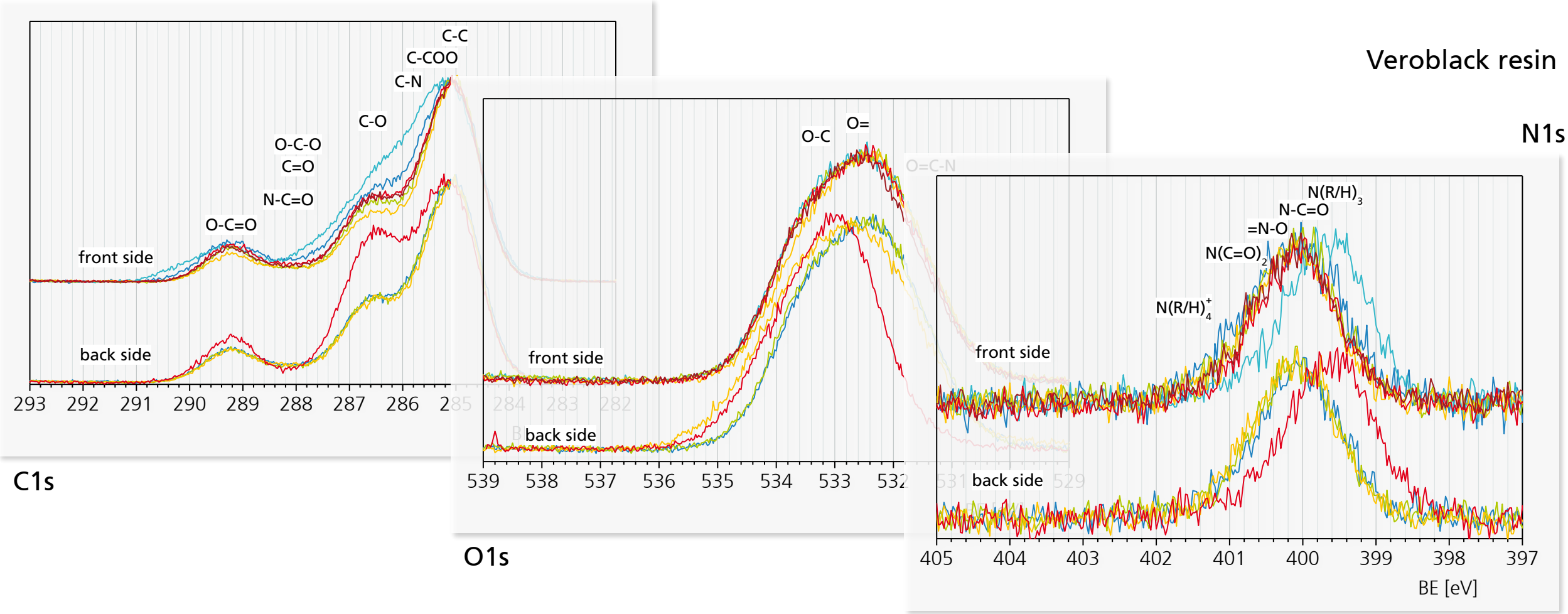
Acrylic resin sheets (MJ), XPS high resolution data

Veroblack resin



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Activation

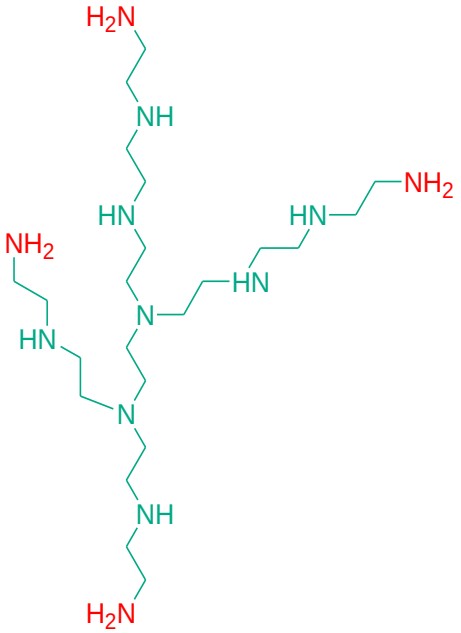
Pore penetration ability of activation processes

Analysis of penetration

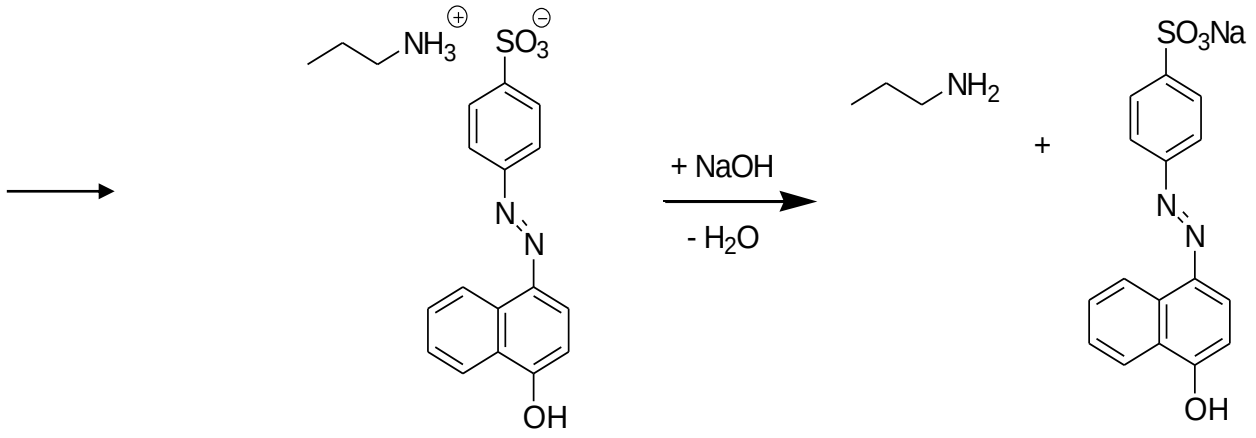
A. Holländer PSE 2004
Surface and Coatings Technology, 200/1-4, p. 561–564 (2005)

dye staining

- oxidized polymer surface binds poly(ethylene imine)



+ Tropaeolin



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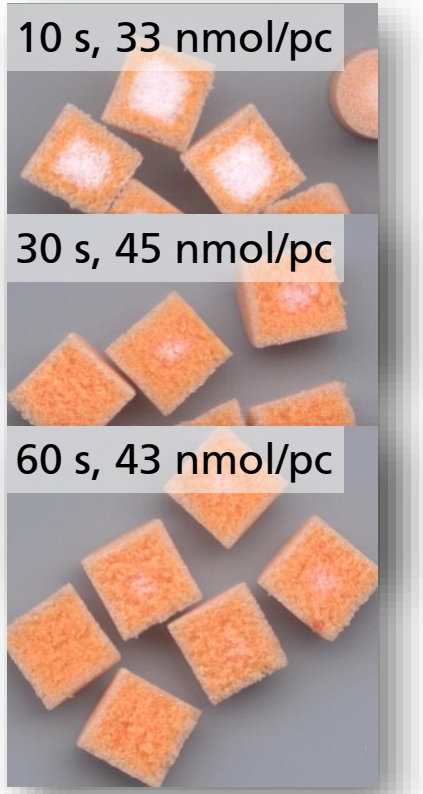
Tropaeolin stain – pore sizes

10 sccm O_2, 13 Pa, 20 W RF, PEI

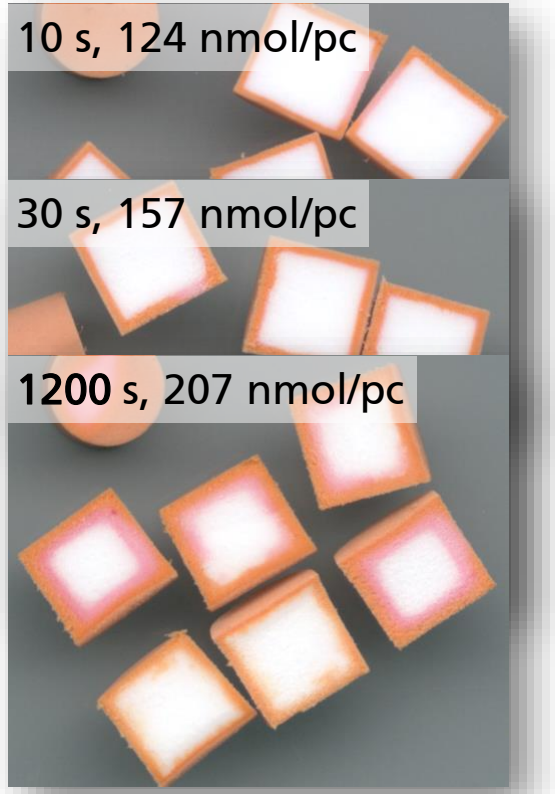
plasma treatment time, [NH_x]

nominal pore size
80 µm

40 µm



7 µm



5 mm

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Plasma activation

Homogeneity of PA sheets (SLS)

- advancing water contact angles [°]

cleaned			plasma treated			plasma treated + 1 week		
114.0	113.0	101.6	12.0	8.0	20.6	47.3	44.2	30.5
111.9	115.0	116.8	0.0	10.0	25.6	48.0	35.2	30.9
108.0	114.5	108.6	11.0	14.9	11.0	46.5	37.4	33.9
105.1	115.0	121.0	0.0	20.0	0.0	38.2	42.6	39.7
av	**112.0**		av	**11.2**		av	**39.5**	
av. dev.	**4.2**		av. dev.	**6.8**		av. dev.	**5.2**	

water, i-PrOH

30 s, 50 W RF, 20 sccm O_2

stored in lab atmosphere

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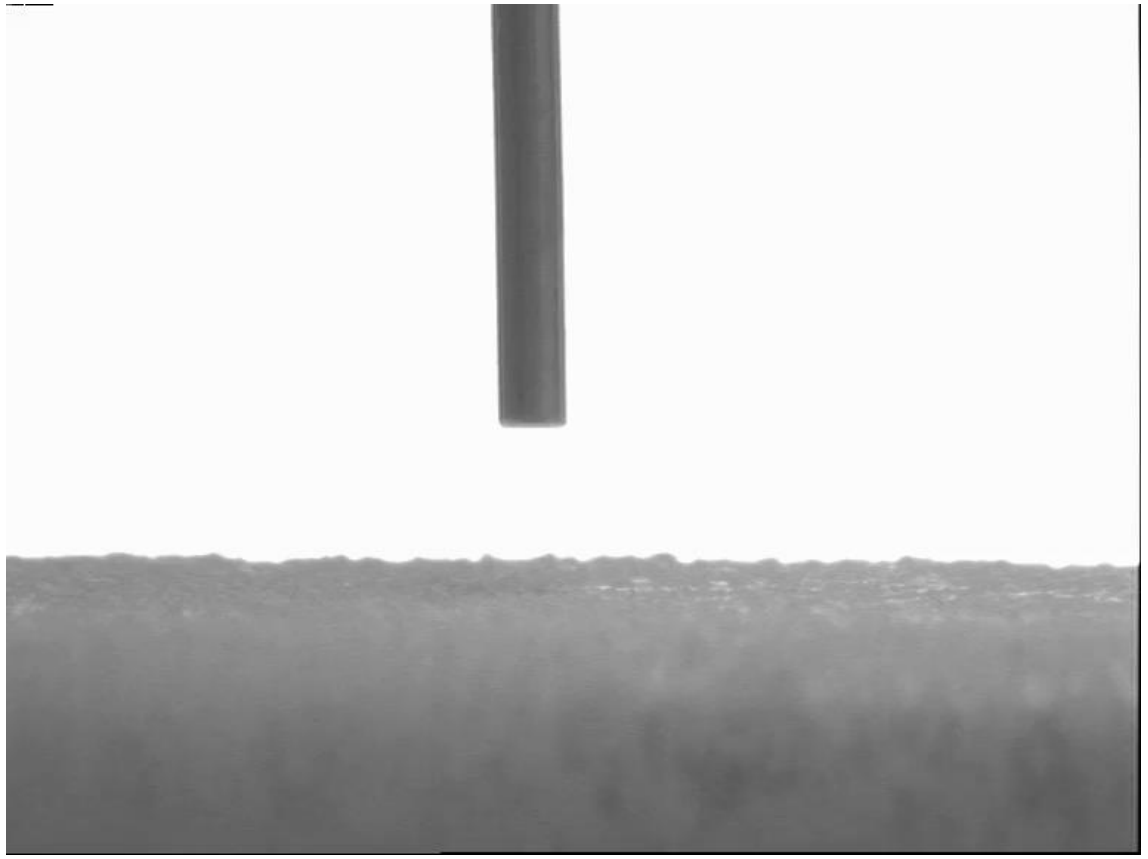
Plasma treated PA sheets, water

- directly after plasma treatment

- 10 days after plasma treatment



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Plasma treatment of PA sheets

- RF plasma with 20 sccm O_2

plasma		XPS					XPS after 10 d					CAG	
P	t	C	N	O	P	Si	C	N	O	P	Si	1 h	10 d
W	s	at%	at%	at%	at%	at%	at%	at%	at%	at%	at%	[°]	[°]
		83.3	5.6	9.7	0.6	0.8	81.4	6.0	11.3	0.6	0.8	102.0	
20	2	69.2	6.3	22.6	1.5	0.5	74.3	6.9	17.2	0.6	1.0	12.0	31.7
20	30	65.9	5.9	25.0	2.0	1.2	70.0	5.9	21.8	1.1	1.2	17.0	34.8
50	2	73.2	5.8	19.6	1.0	0.4	74.3	6.3	18.5	0.4	0.5	16.7	34.4
50	30	68.4	6.4	22.4	1.3	1.6	69.1	6.4	21.8	0.9	1.8	0.0	23.9

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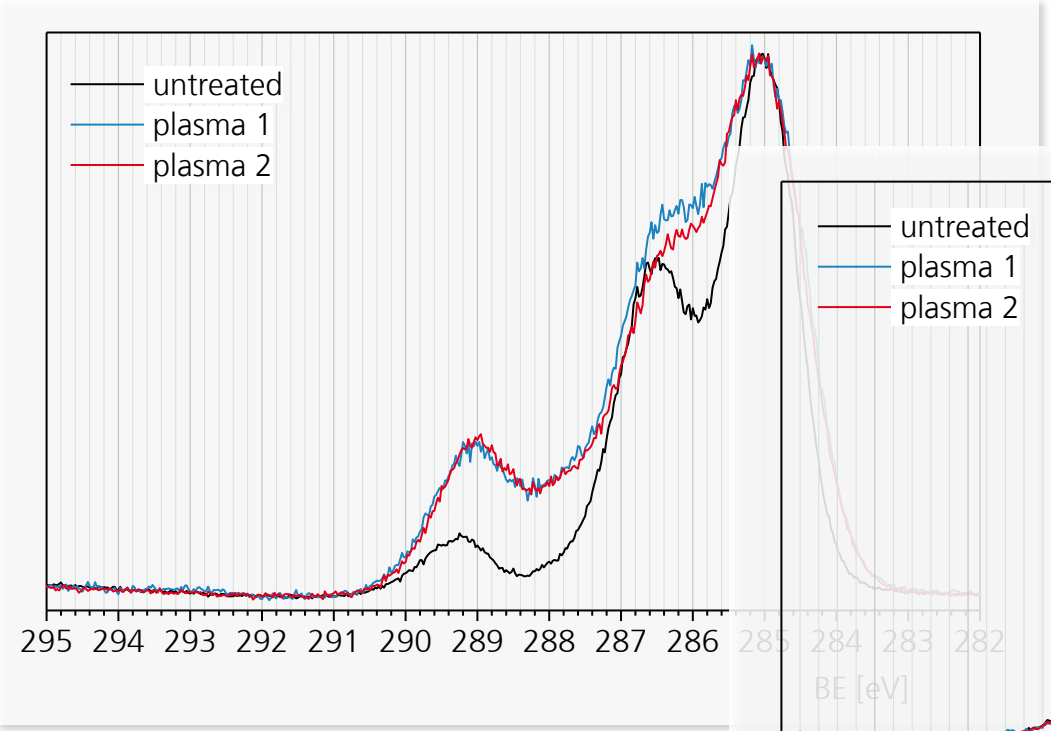
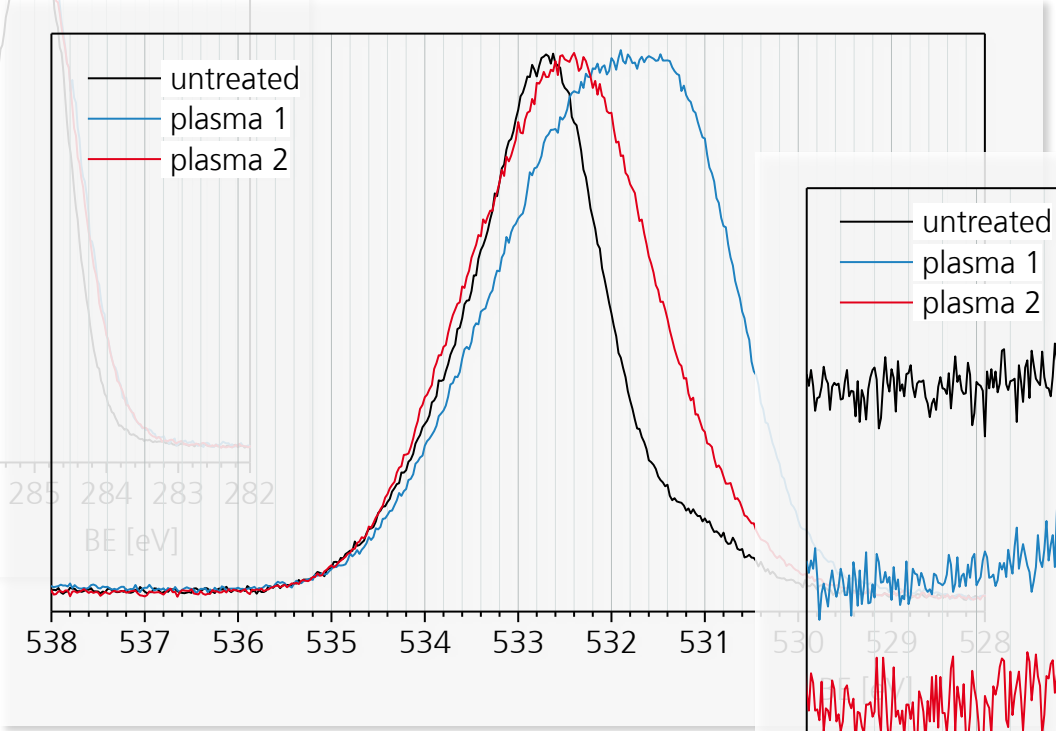
Epoxy resin (SLA), XPS

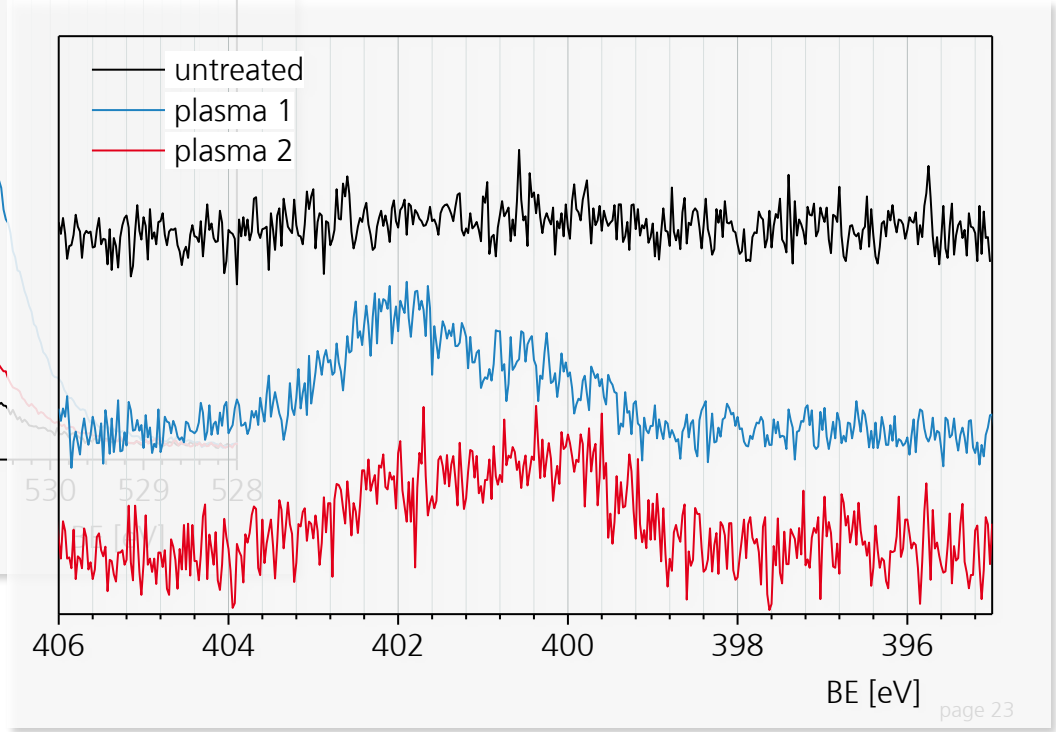


C1s



O1s

N1s



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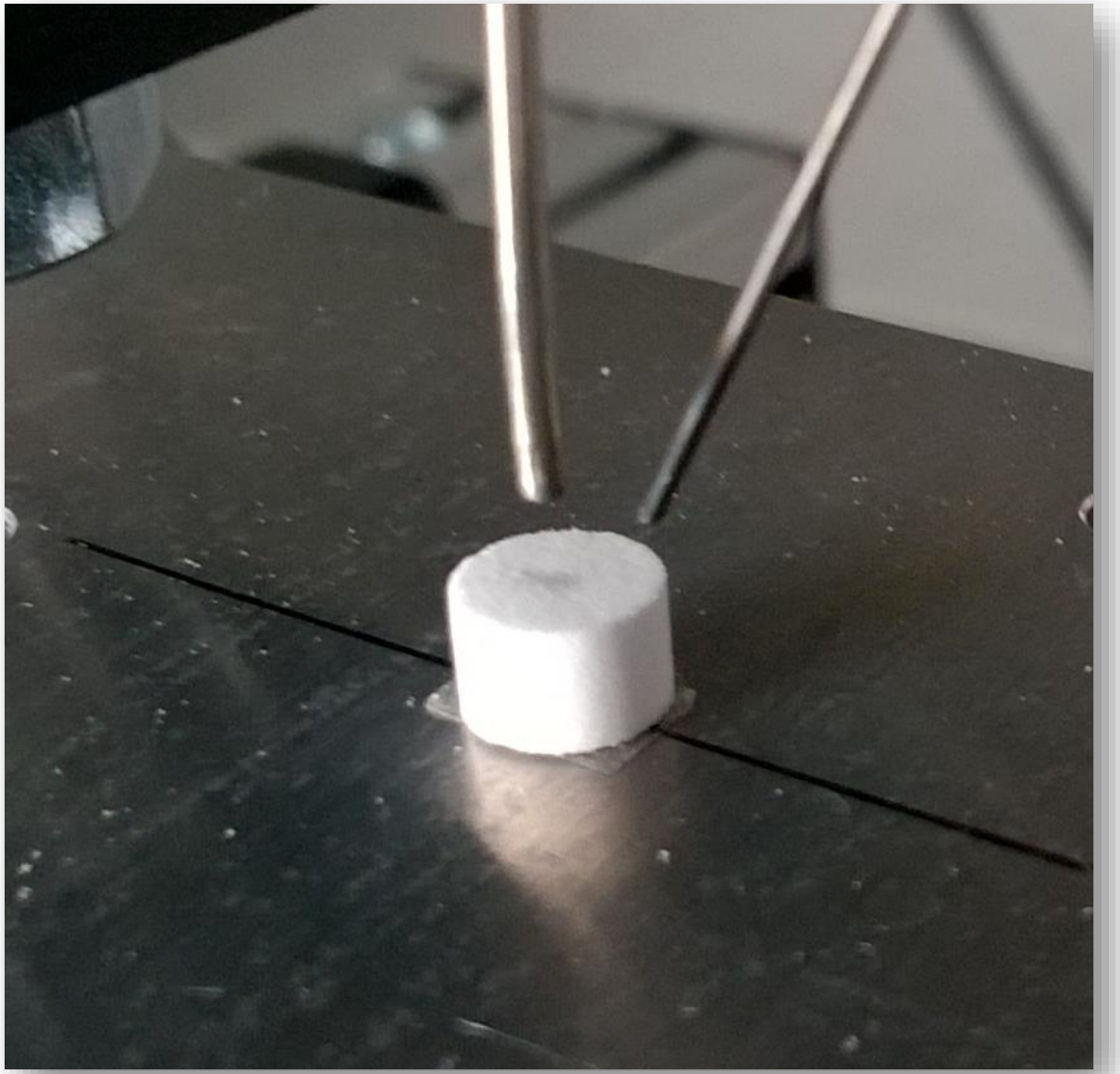
Activation by µ-flames

Micro-flame treatment

- gas supply via capillary
- spark ignition
- movable



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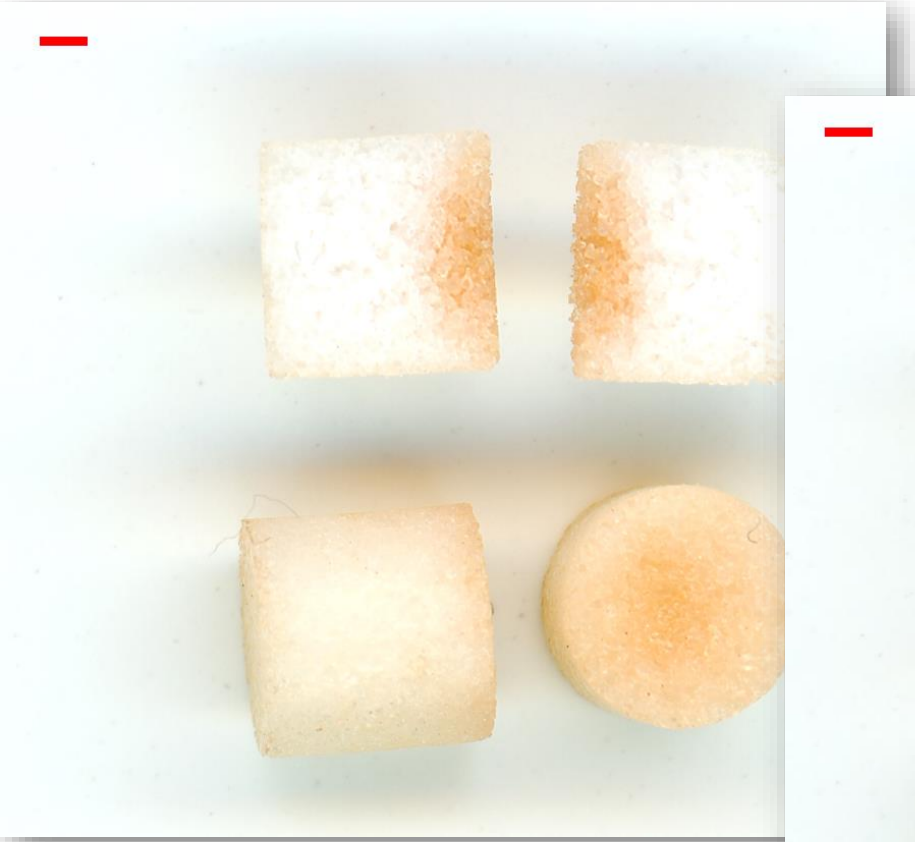
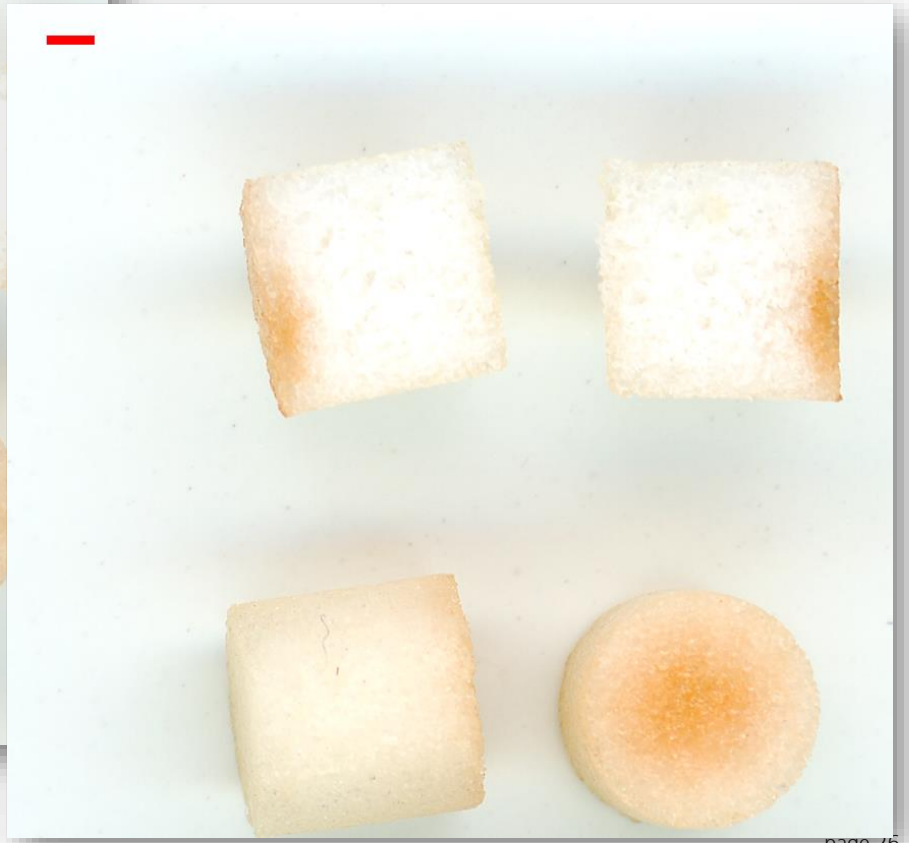
Pulsed flame treatment, tropaeolin stain

- sintered PE cylinders
  - left 80 µm
  - right 40 µm
- treated on circular side

pictures:
- top: cut cylinder
- bottom left: side view
- bottom right: treated side





acetylene/ oxygen
10 pulses

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Flame treatment PA sheets

- Butane/ oxygen micro-flame pulses

flame		XPS				
pulses		C	N	O	P	Si
		at%	at%	at%	at%	at%
		83.3	5.6	9.7	0.6	0.8
1		76.5	6.5	16.0	0.6	0.3
2		72.8	6.6	19.6	0.6	0.5
5		70.3	6.7	22.0	0.5	0.6

PEI coupling,
tropaeolin stain

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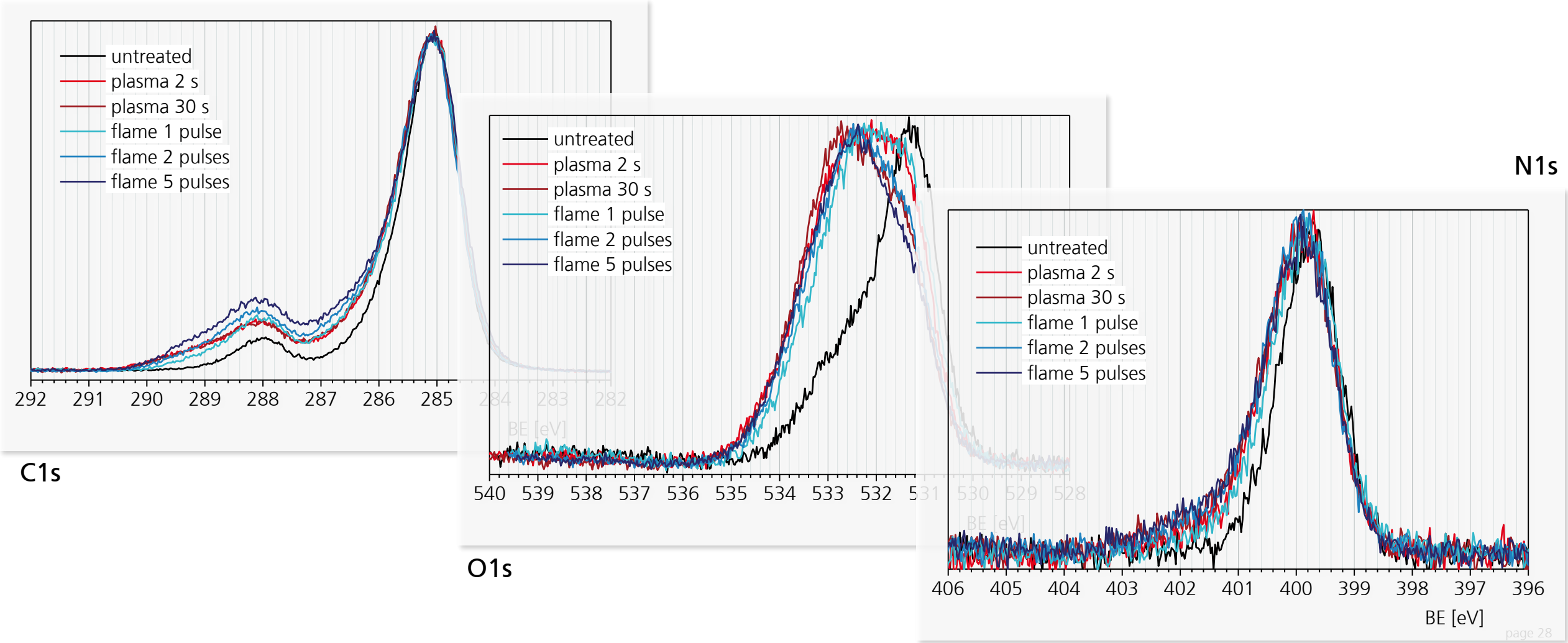
PA sheets, XPS high resolution data



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Smoothing by lacquering

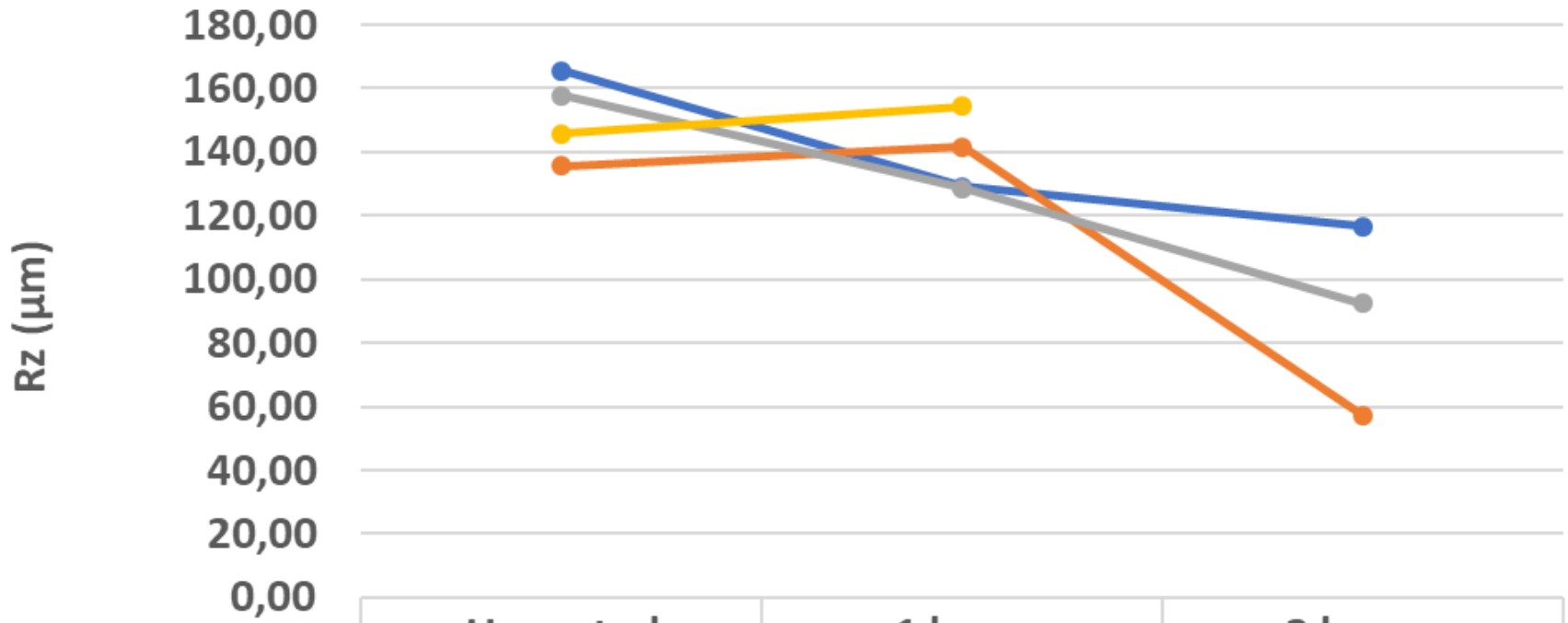
Selection of coatings

Different types of coatings tested:

- UV curable high solid coating
- Polyester gel coating
- Polyurethane clearcoat
- Polysilazane coating

- Best results with high solid coating and polyester gel coating

Comparison roughness change – PA12 (SLS)



	Uncoated	1 layer	2 layers
Polyurethane	165,60	129,2	116,6
UV-cured high solids	135,65	141,53	57,18
Polyester gel coating	157,60	128,67	92,33
Polysilazane coating	145,85	154,20	

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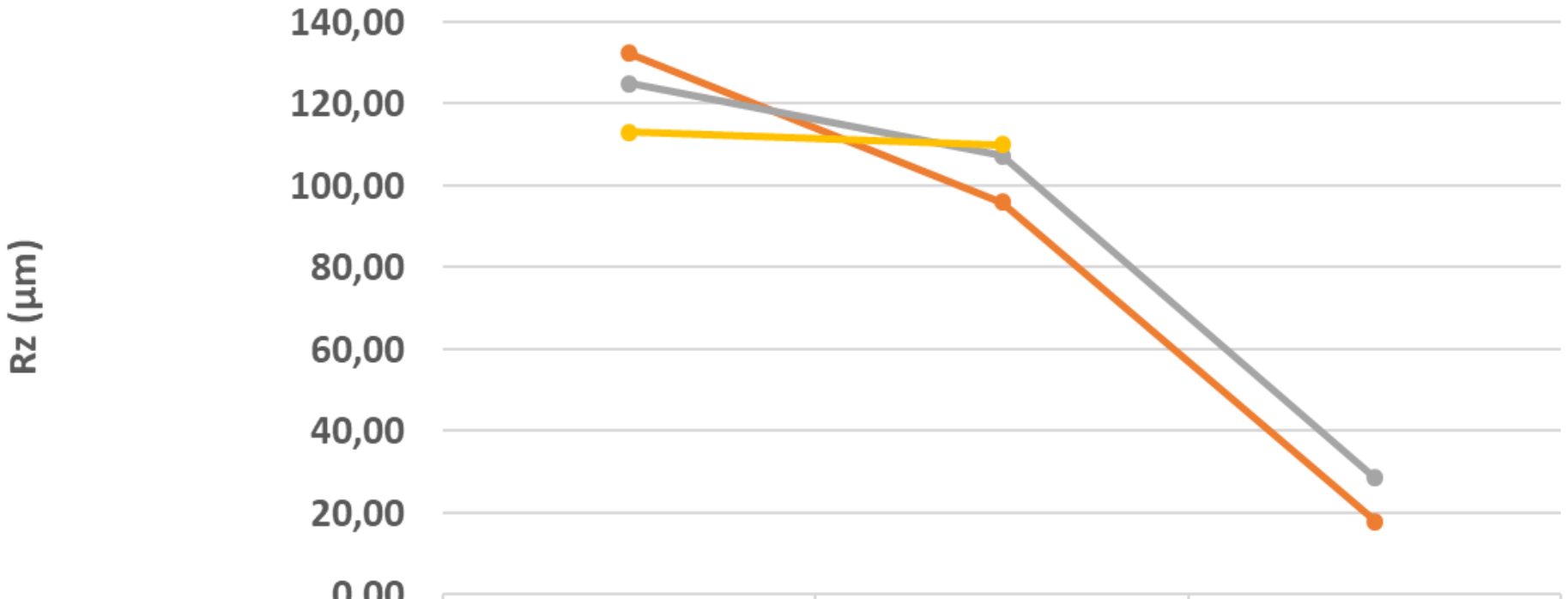
Comparison roughness change – acrylic resin (MJ)



	Uncoated	1 layer	2 layers
UV-cured high solids	132,35	95,88	18,00
Polyester gel coating	124,90	107,26	28,62
Polysilazane coating	113,00	109,97	

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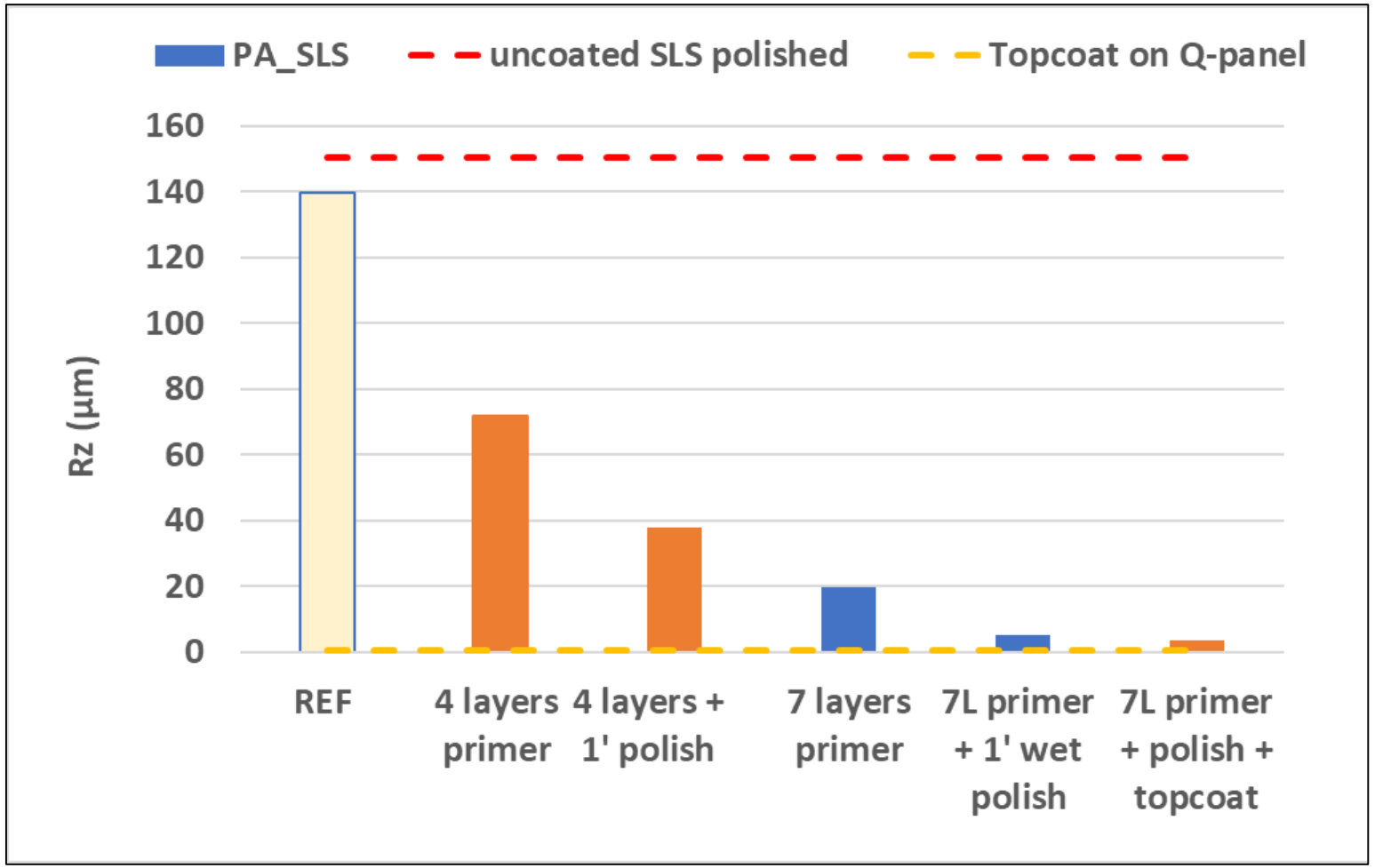
Use of high build filler/primer - SLS

- 1 layer ~ 35 µm
- Several layers required to reduce initial roughness
- reduction by lacquering to 20 µm (Rz), 4 µm (Ra)
- lacquering+polishing Rz ~ 5 µm or Ra < 1 µm



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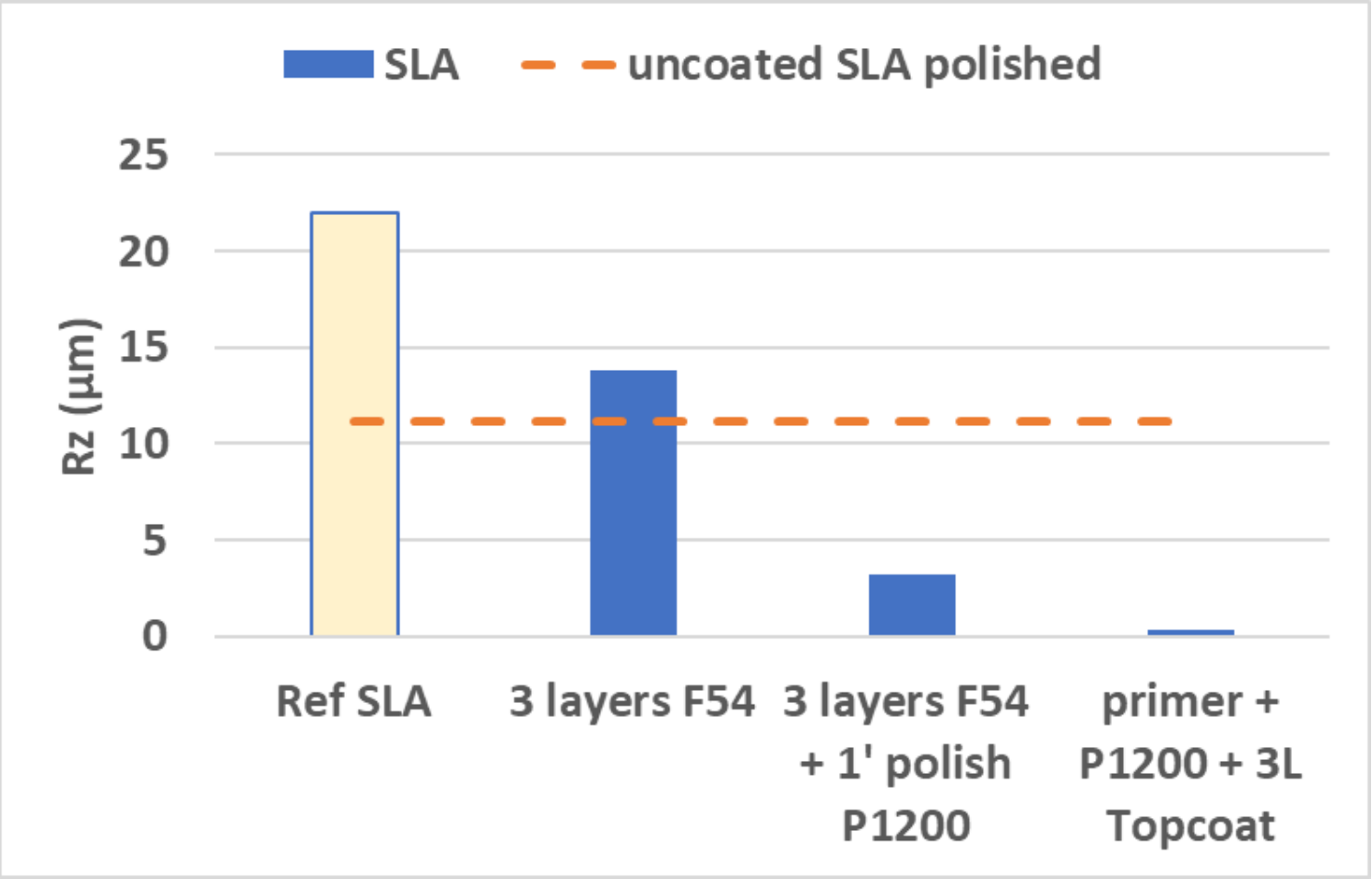
Use of high build filler/primer - SLA

- 1 layer ~ 35 µm
- Several layers required to reduce initial roughness
- Line structure still visible under certain angles



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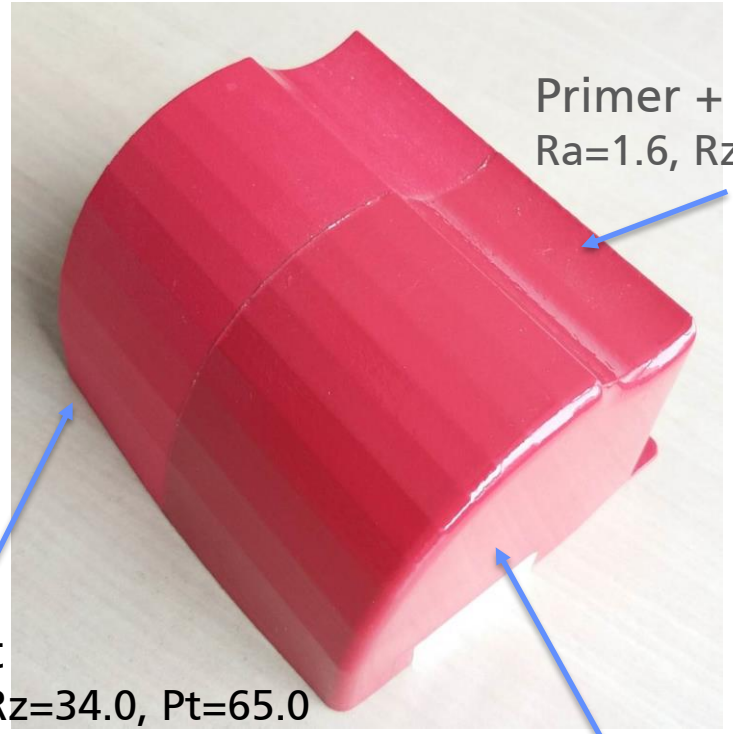
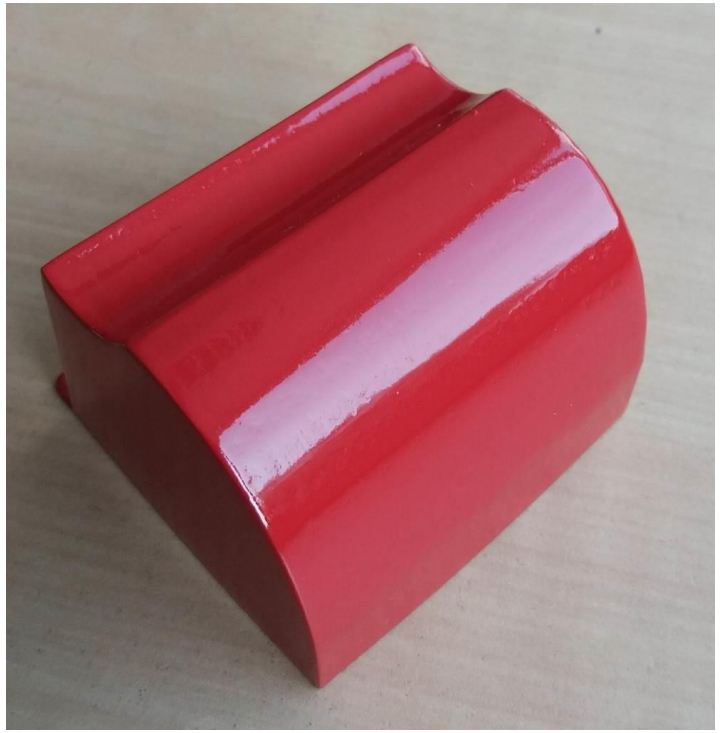
3D SLS test part: finishing using spray coating



Primer + topcoat
Ra=1.6, Rz=7.6, Pt=29.5

Topcoat
Ra=6.3, Rz=34.0, Pt=65.0

Primer + polish (5 min) + topcoat
Ra=0.04, Rz=0.2, Pt=3.6



2 spray + topcoat
Ra=0.05, Rz=0.6, Pt=2.3

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3D SLS part: finishing using dip coating

- Printing technique: Promaker P1000
- Material PA12
- 2K acrylic primer (40% thinner)
- Manual dipping – 1 layer
- Topcoat

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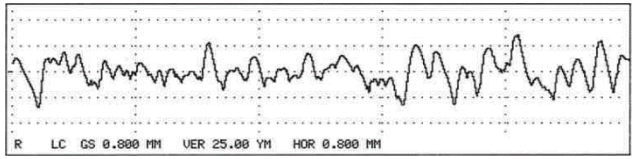
3D SLS part: finishing using dip coating and Physical Vapour Deposition (PVD)

- Vibrofinish / sandblasted samples
- 2K acrylic primer + 20% thinner
- Manual dipping - 1 layer
- No manual polishing

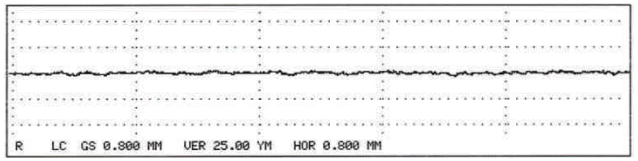
- PVD Cr Coating (5 min.)

	Ra	Rz
sandblasted	17,5	138,0
sandblasted + primer	0,8	4,6
vibrofinish	10,3	94,6
vibrofinish +primer	0,9	5,4

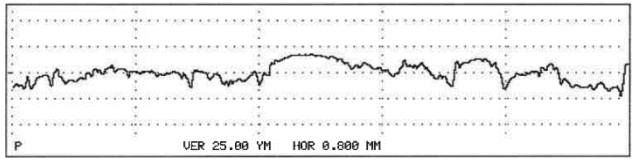
Sandblasted



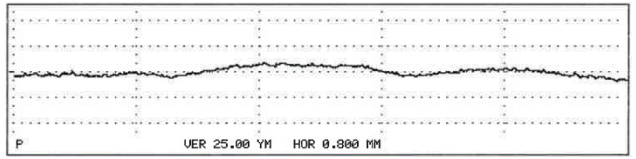
Sandblasted + primer

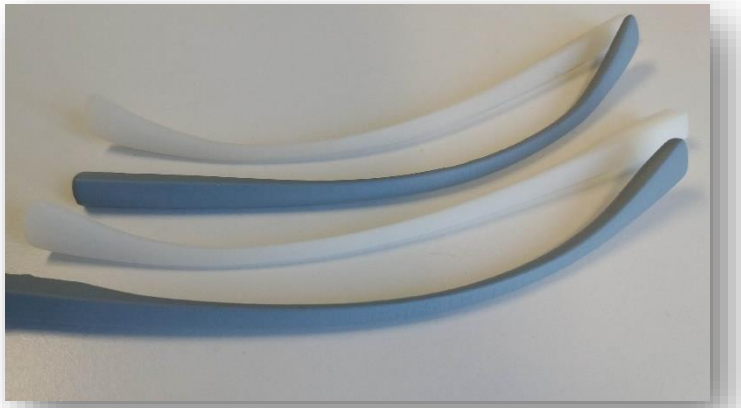


Vibrofinish



Vibrofinish + primer





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Metallization

Metallization

why?

- additional functionalization
- test smoothing ability of galvanic plating

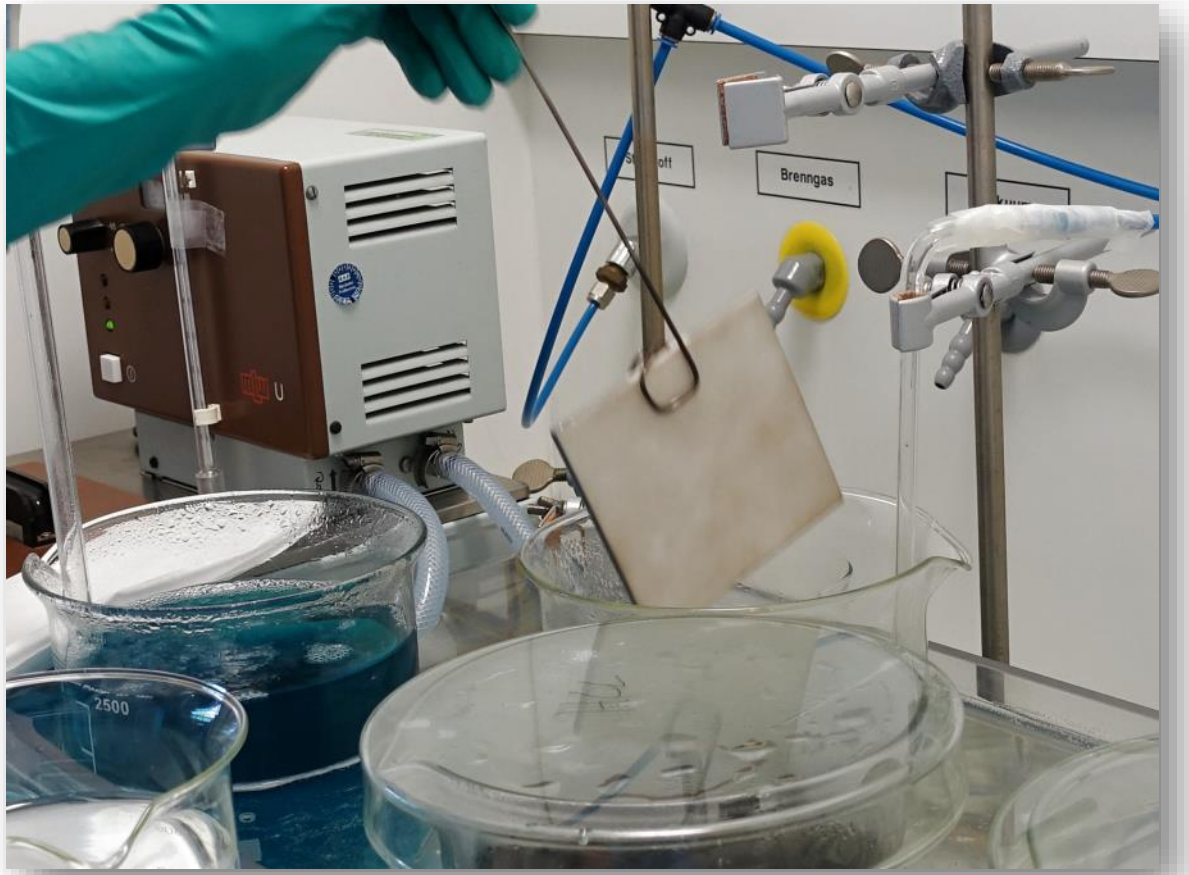
procedure

- with as-prepared parts and lacquered parts
- surface treatment with low-pressure plasma
- Pd activation
- electroless plating of nickel
- galvanic plating of copper (atotech)

test

- cross-cut test of Ni plated parts
  - ➢ no failure on pristine side and on lacquer
- peel test after Cu plating

Metallization of sheets



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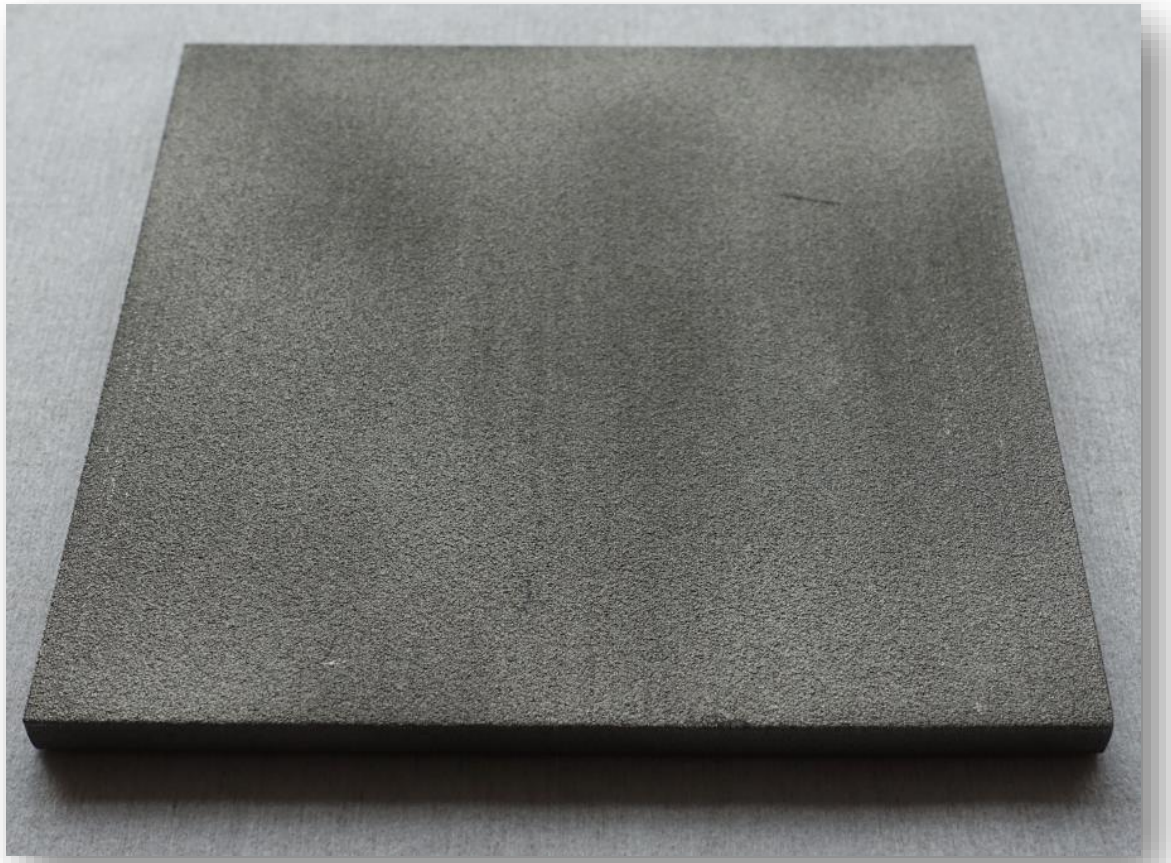
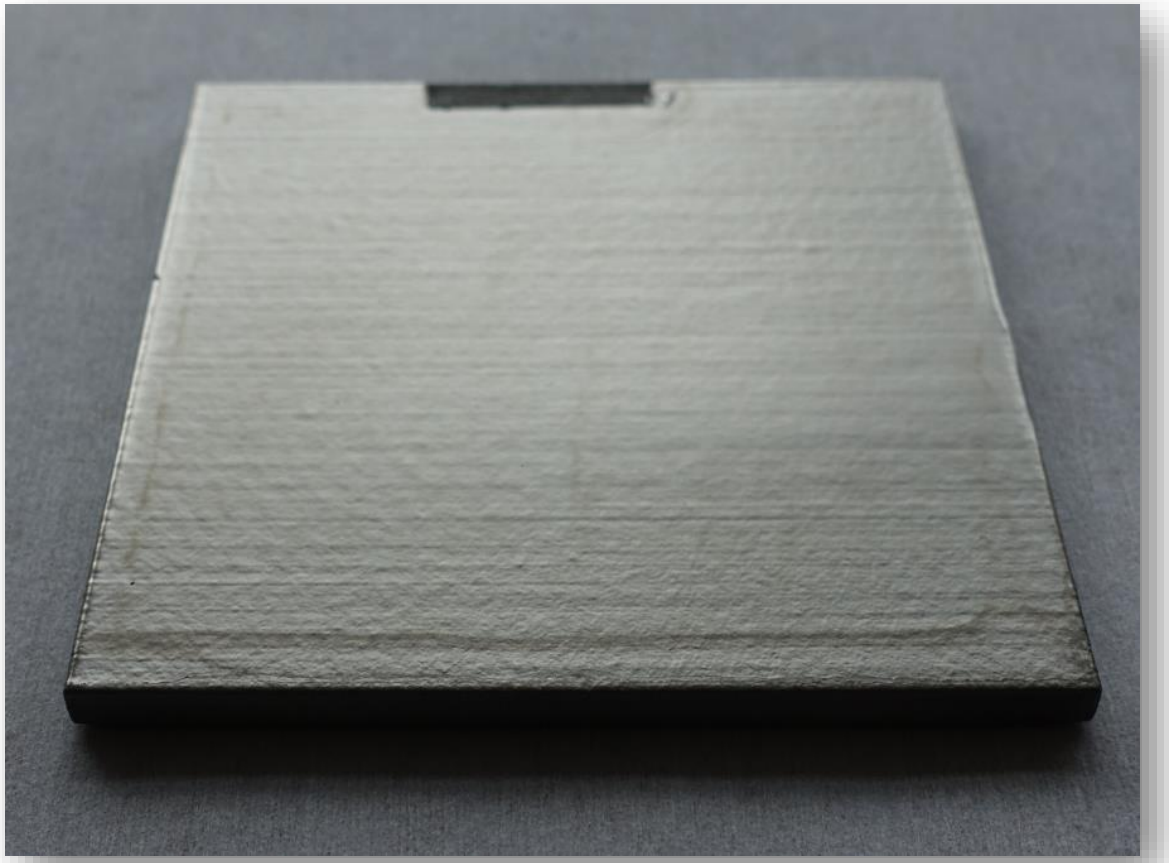
Ni plated SLS-PA, back side & lacquered side





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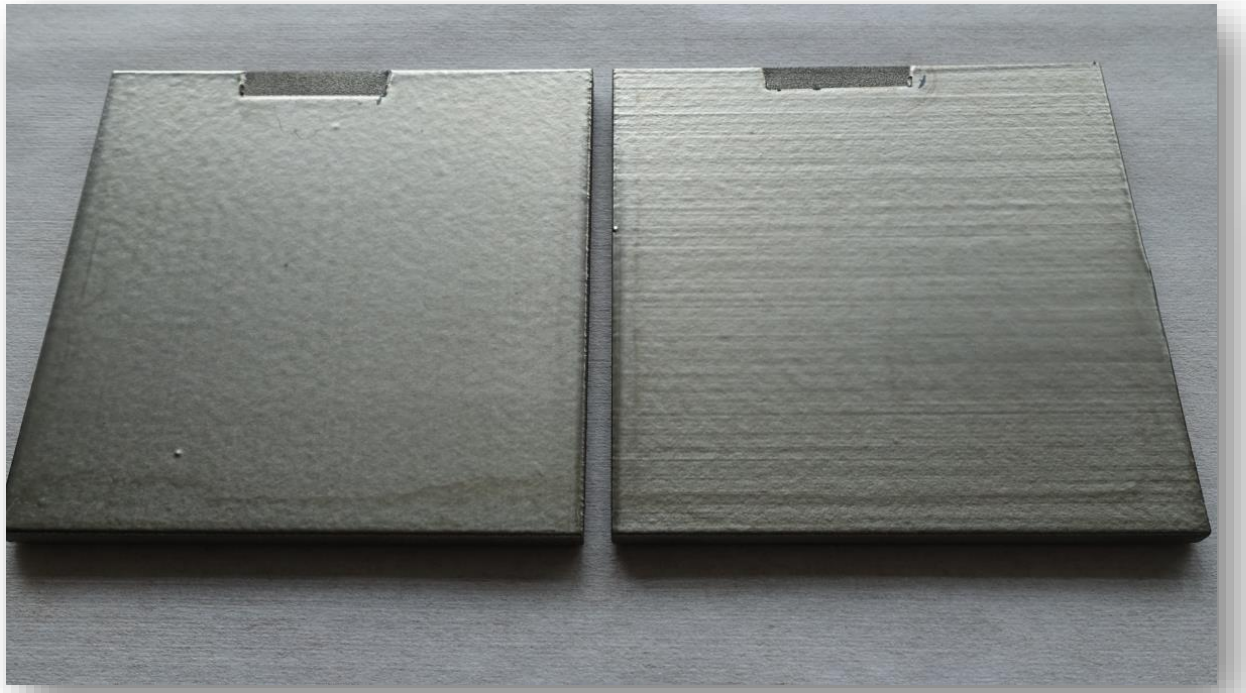
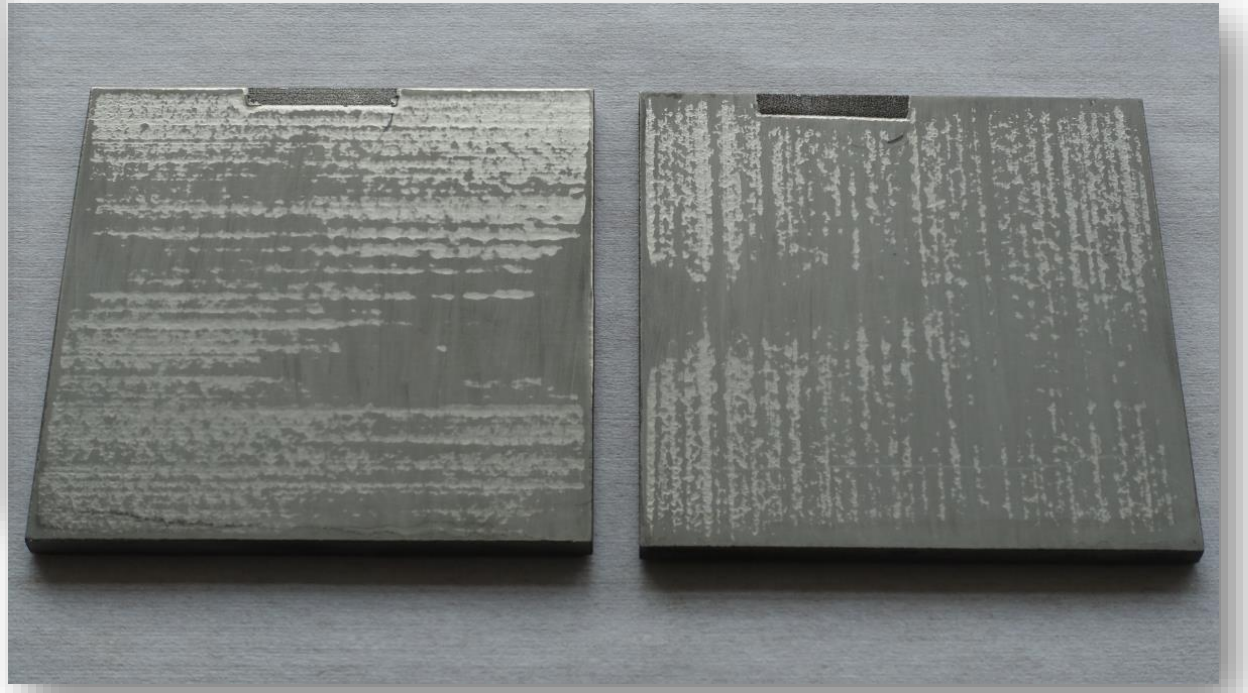
Ni plated SLS-PA, lacquered and polished





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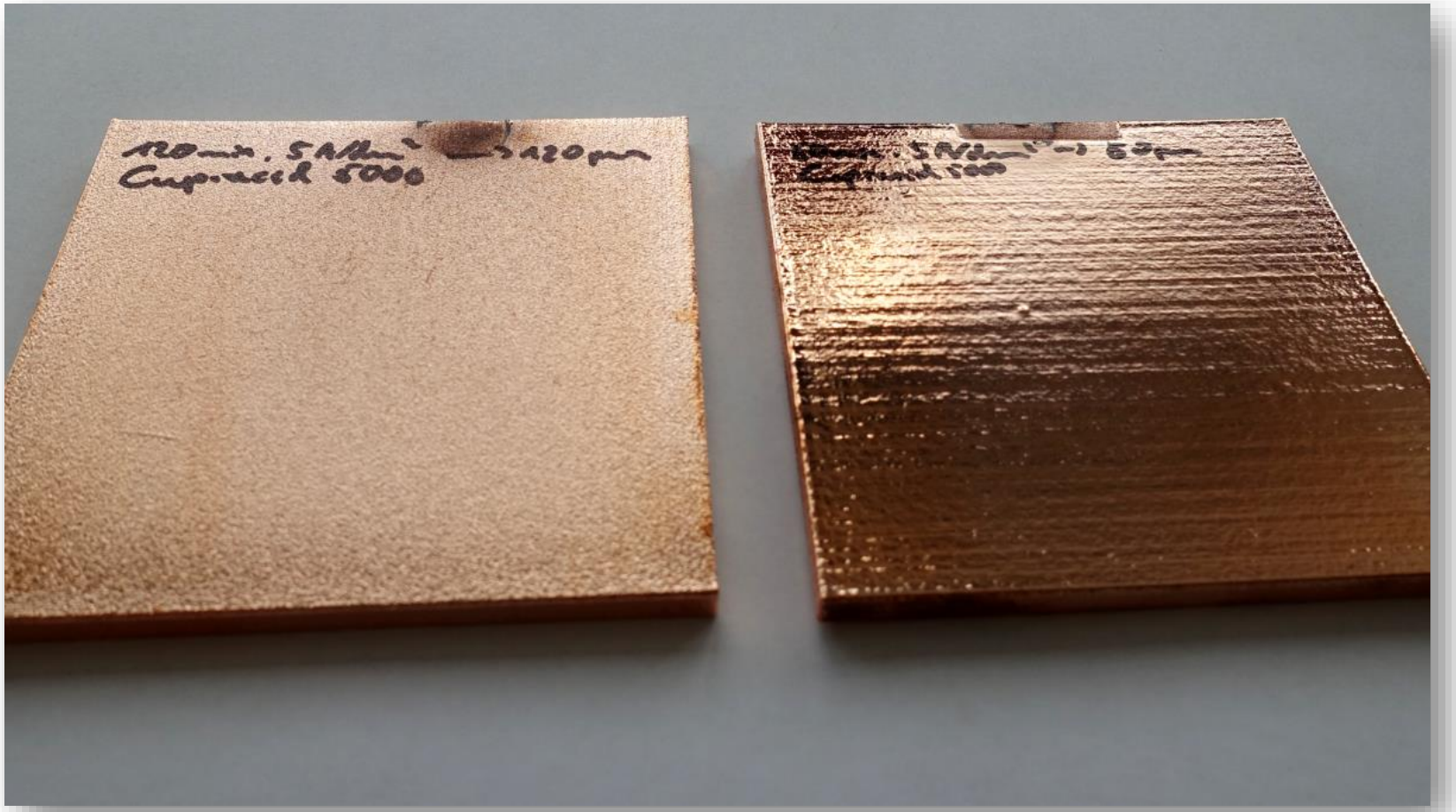
SLS-PA, lacquered, Ni plated, Cu plated

- left not lacquered
- 120 µm Cu



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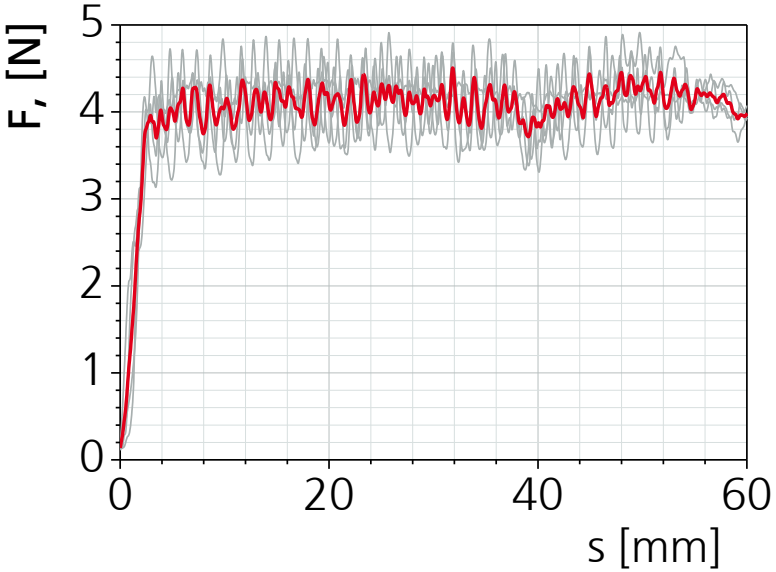
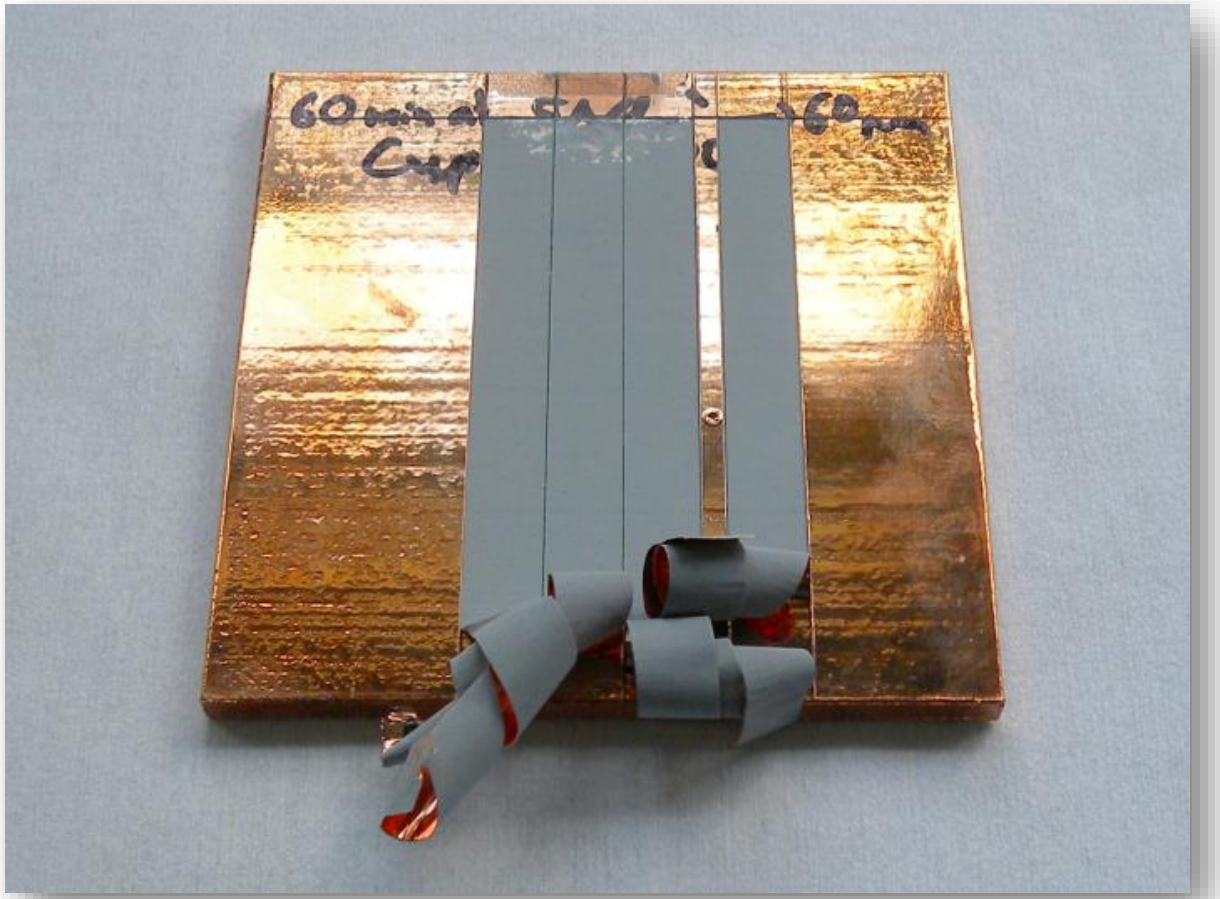
Peel test of Cu plated SLS-PA

- 90° peel test with 1 cm strips

➢ 4 N/ cm

➢ cohesive failure in lacquer





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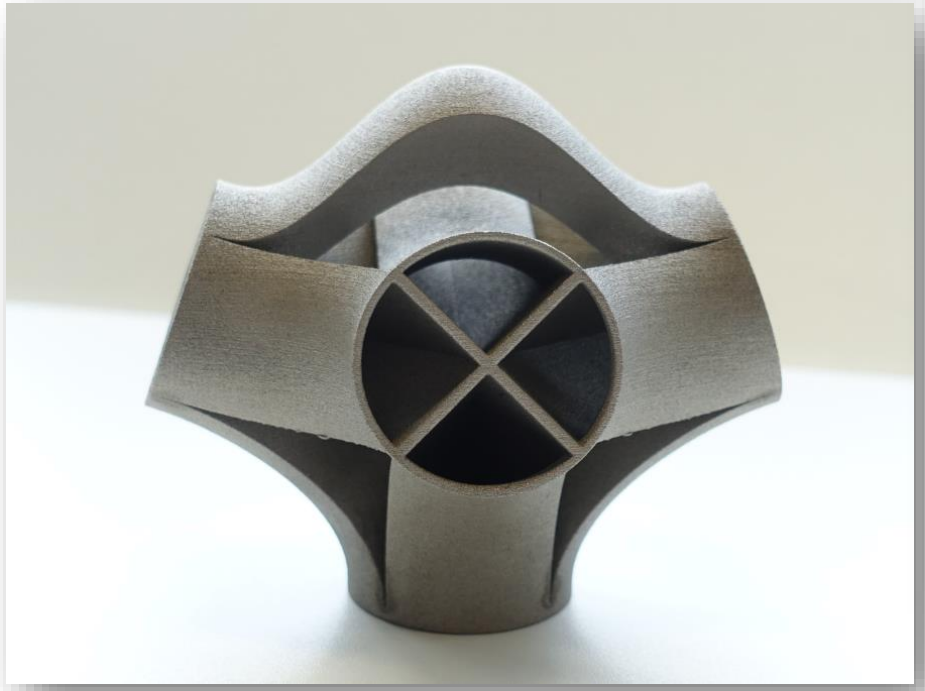
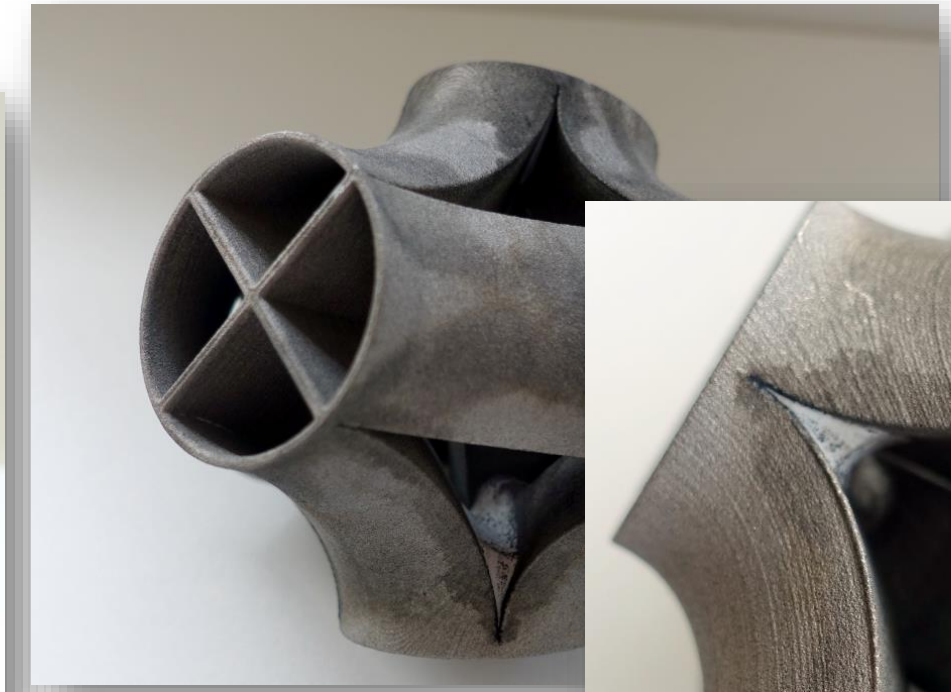
SLS-PA, Ni plated

new PA type





old PA type

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SLS-PA, lacquered, Ni plated

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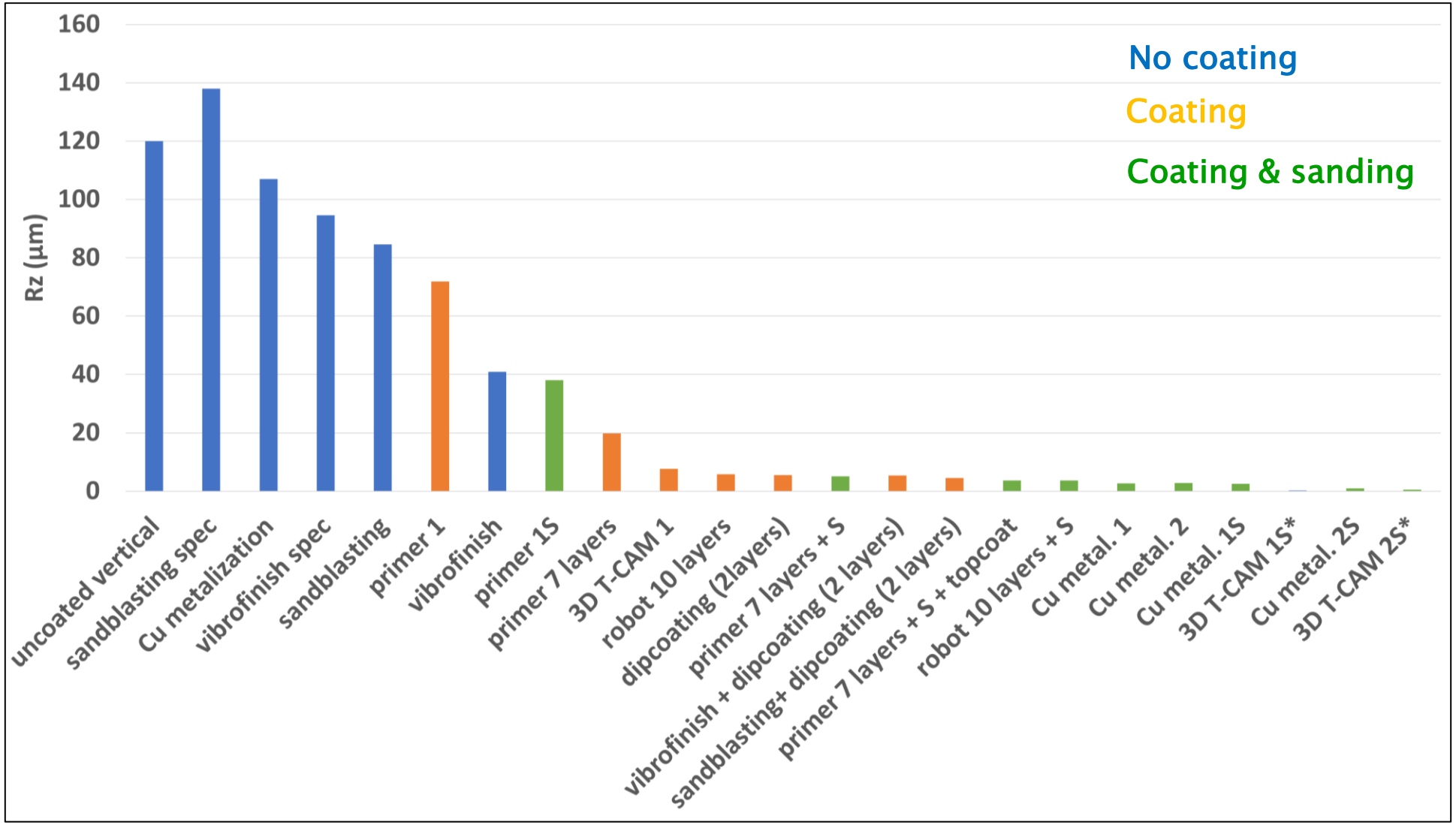
Conclusions

Comparison of the effect of different techniques applied on roughness Rz



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Conclusions

- surfaces of 3D printed parts (as investigated in the project)
  - heterogeneous
  - contaminated
- surfaces seem to be well suited for coatings
- plasma can penetrate deeply into printed structures

- lacquering easily closes pores
- lacquering results in smoother surface
- level of smoothing limited
  - ➢ combination of different techniques (lacquering, polishing)

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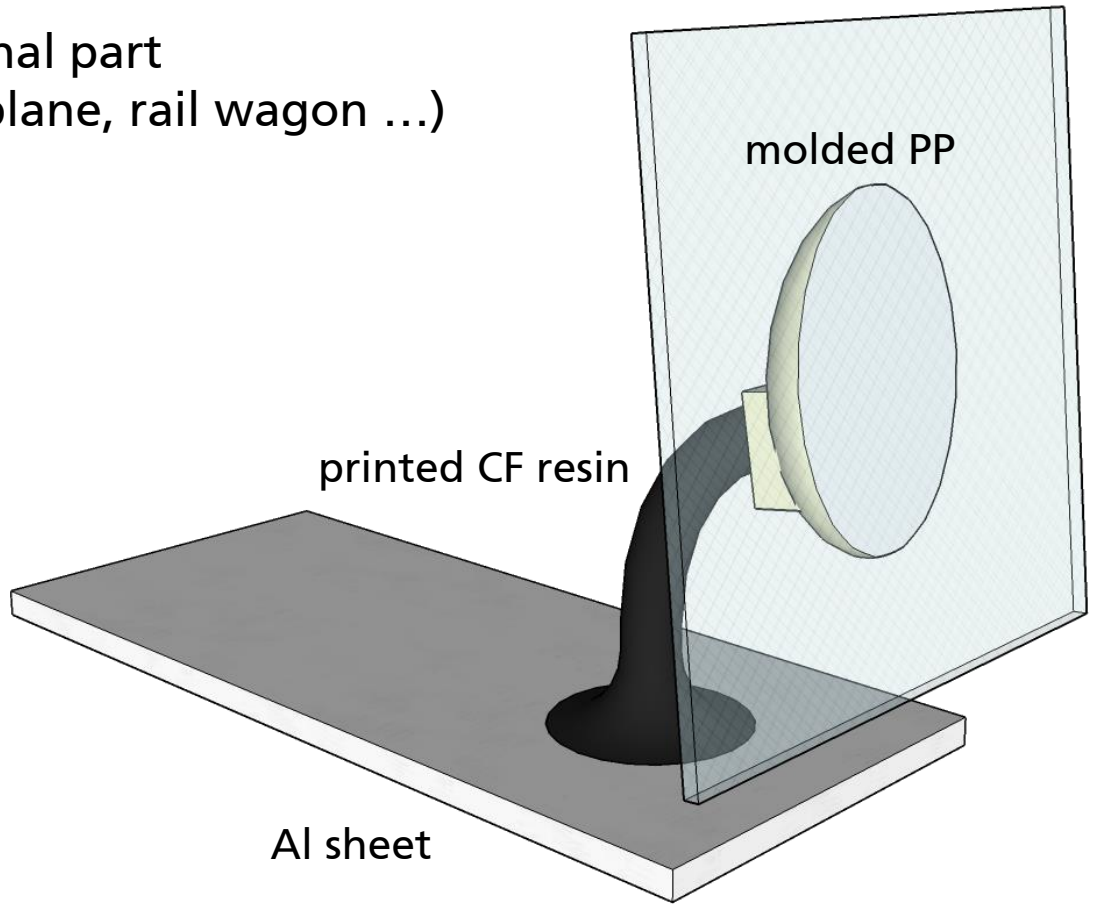
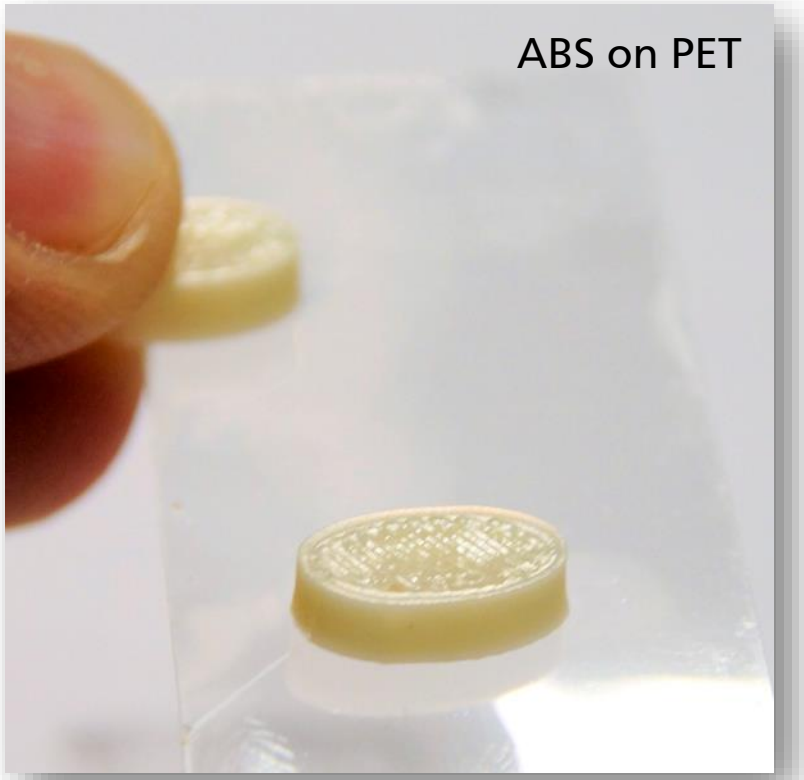
Vision

fictional part
(car, plane, rail wagon …)





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