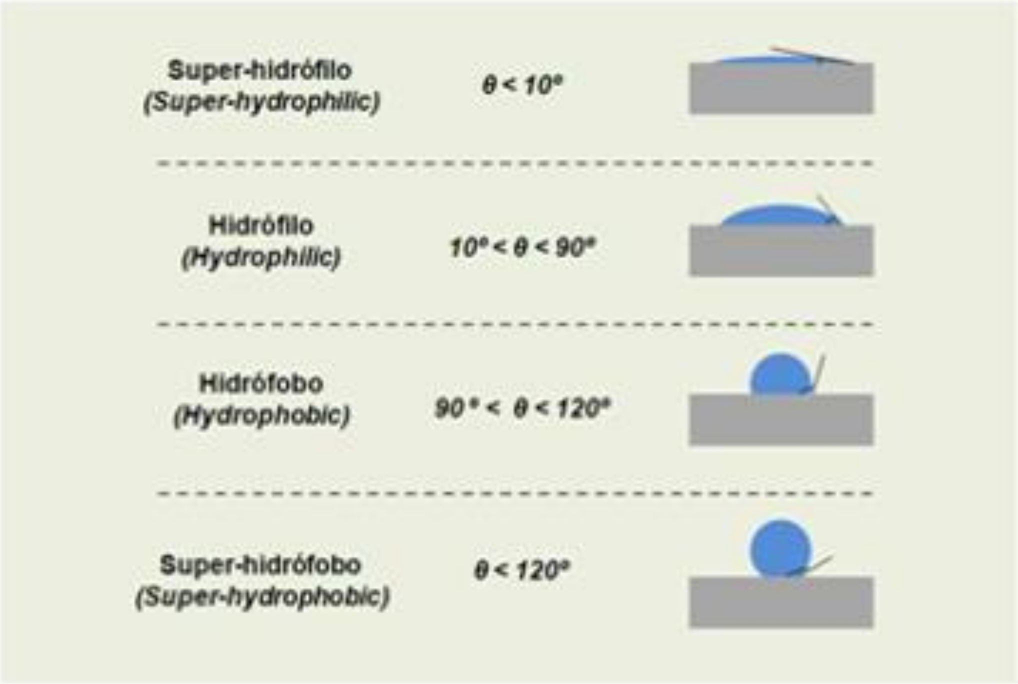
The fear of periodic polymer surfaces to water

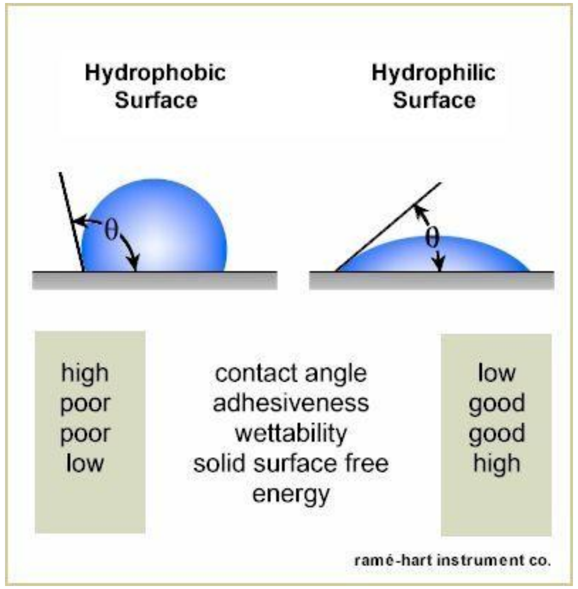
Patricia Martínez García

SOFTMATPOL group
Collaboration with IQFR

Hydrophobic and hydrophilic materials



https://www.co-nantec.com/post/recubrimiento-hidrof%C3%B3bico-y-sus-usos



Cleaning and anti-reflective (AR) hydrophobic coating of glass surface: a review from materials science perspective (springer.com)

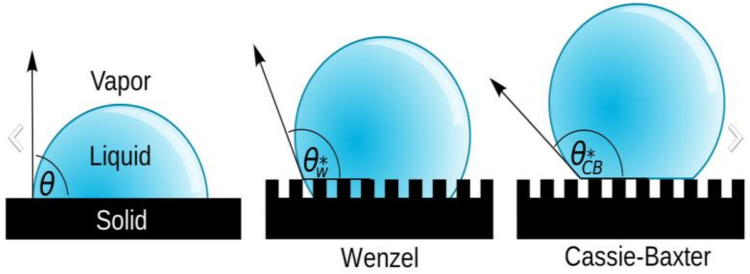
Wenzel

(homogeneous surfaces)

$$r = \frac{real\ surface}{projected\ area}$$

$$\cos\theta_{Eq} = r\cos\theta_i$$

https://ddd.uab.cat/pub/trerecpro/2013/hdl_2072_234675/PFC_AgustinFernandezCanete.pdf



https://nanoslic.com/nanoslic-hydrophobic-coating/angle2/

Cassie

(heterogeneous surfaces)

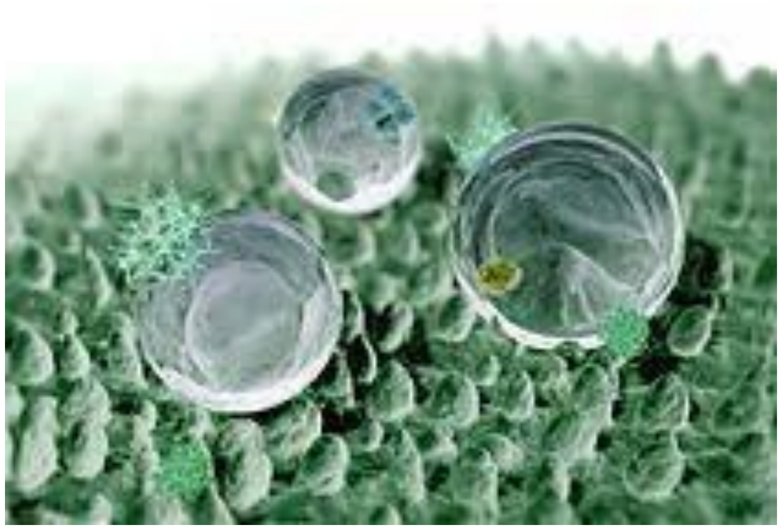
Cassie-Baxter equation:

$$\cos\theta_c = \gamma_1\cos\theta_1 + \gamma_2\cos\theta_2$$

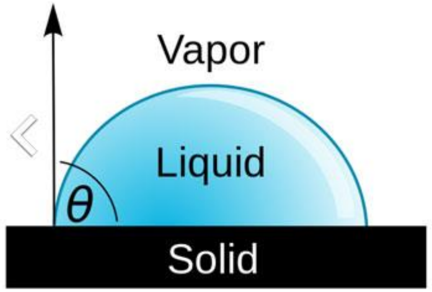
https://es.frwiki.wiki/wiki/Loi_de_Cassie

MOTIVATION

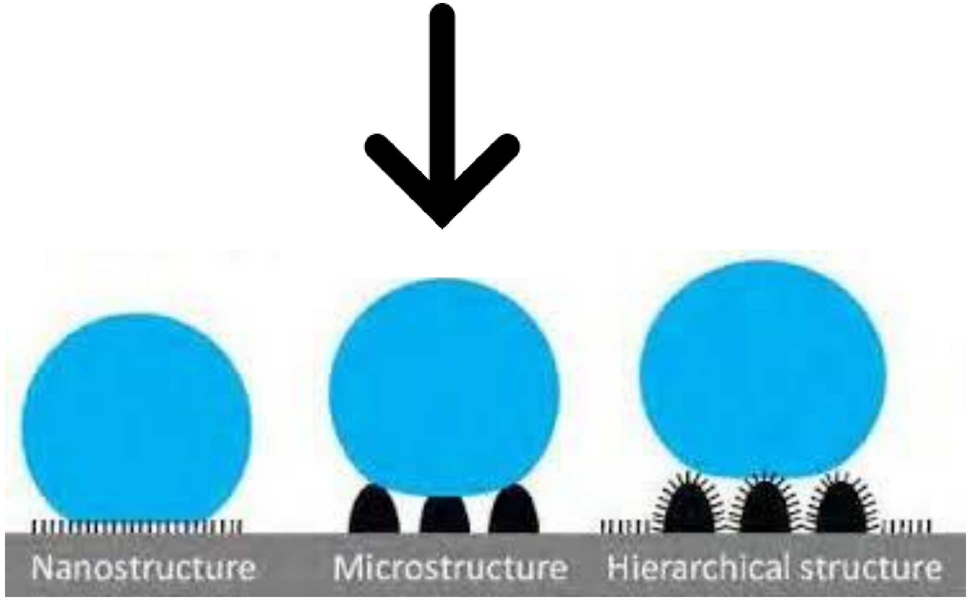
http://chemizest.blogspot.com/2016/12/lotus-effect.html



https://id1.toaksgogreen.org/janine-benyus-biomimicry-is-innovation-inspired-by-nature-3797



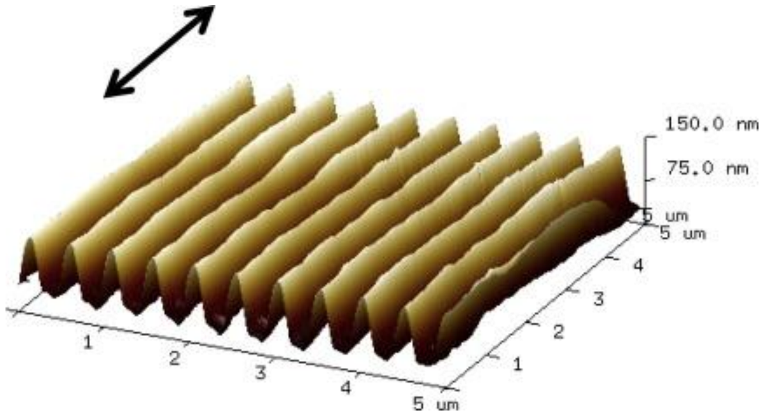
https://nanoslic.com/nanoslic-hydrophobic-coating/angle2/

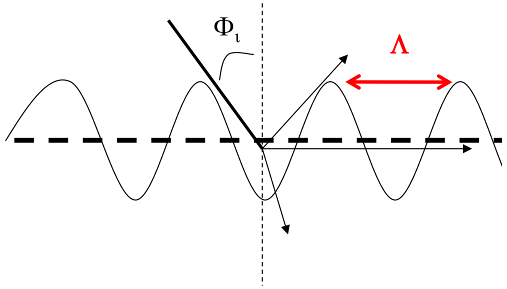


https://ddd.uab.cat/pub/trerecpro/2013/hdl_2072_234675/PFC_AgustinFernandezCanete.pdf

Laser-Induced Periodic Surface Structures (LIPSS)

Interference mechanism between the incident and scattered beams.





$$\Lambda = \frac{\lambda}{n - \sin(\theta)}$$

Laser characteristics:

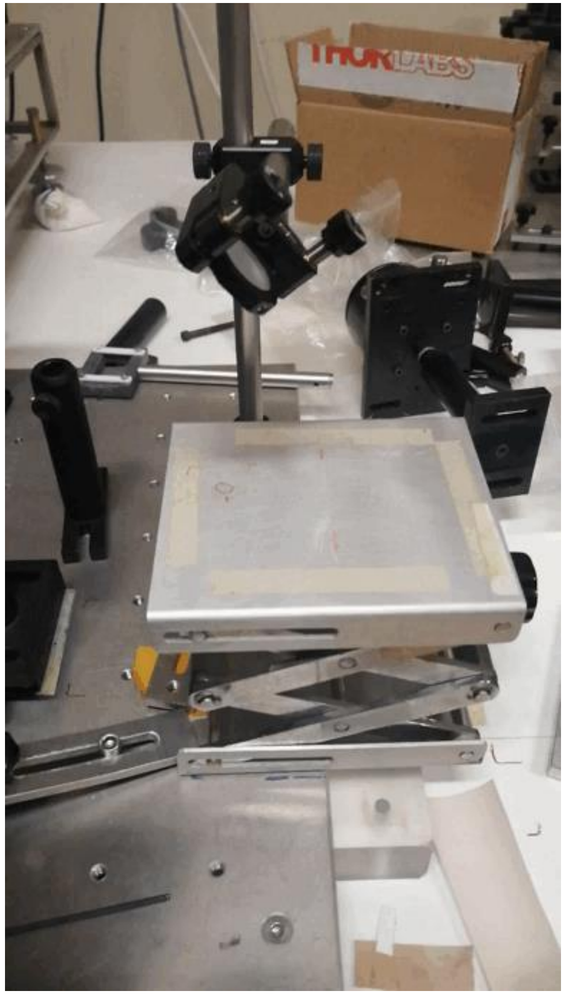
Laser LOTIS

Fourth harmonic wavelenght: 266 nm

Pulse duration: 8 ns

Frequency: 10 Hz

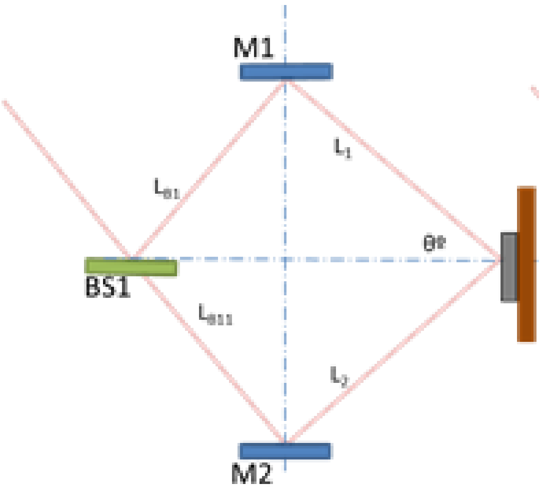
Iris + diverging lens



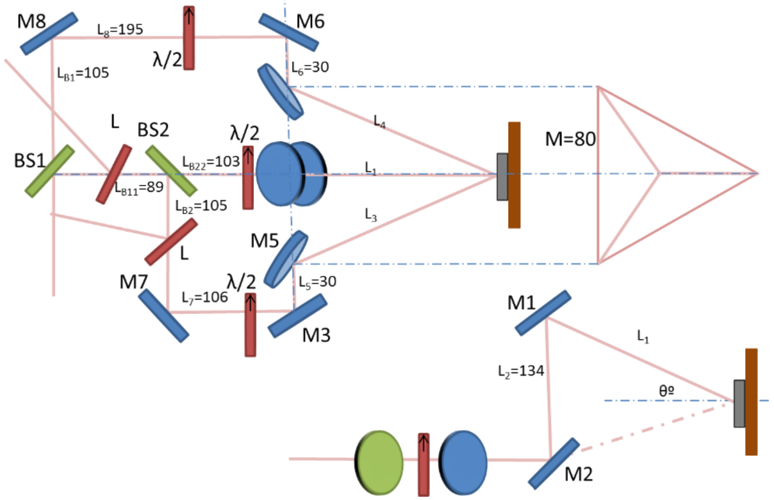
Laser Interference Lithography (LIL)

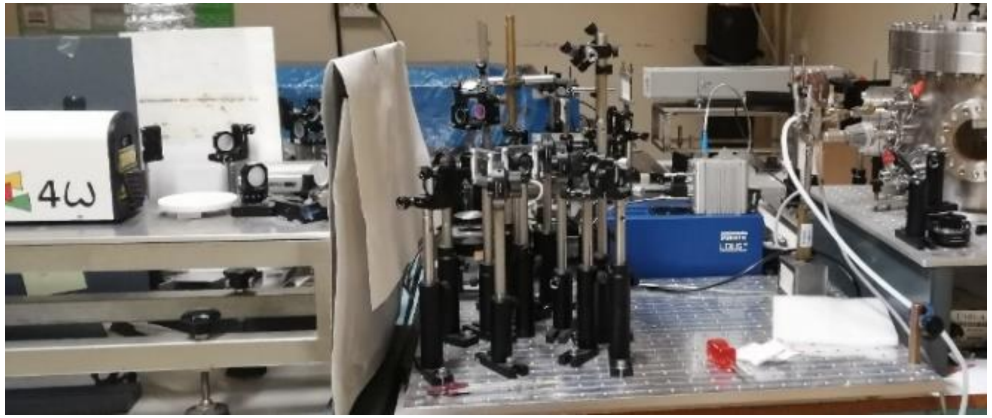
Interference mechanism between the laser beams.

2 beams

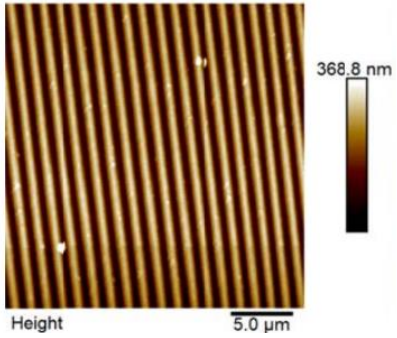


3 beams

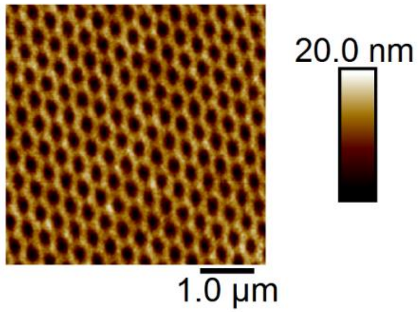




$$\Lambda = \frac{\lambda}{2\sin(\theta)}$$



$$\Lambda = \frac{\lambda}{\sqrt{3}\sin(\theta)}$$



Laser characteristics:

Laser Quantel Brilliant B

Fourth harmonic wavelenght: 266nm

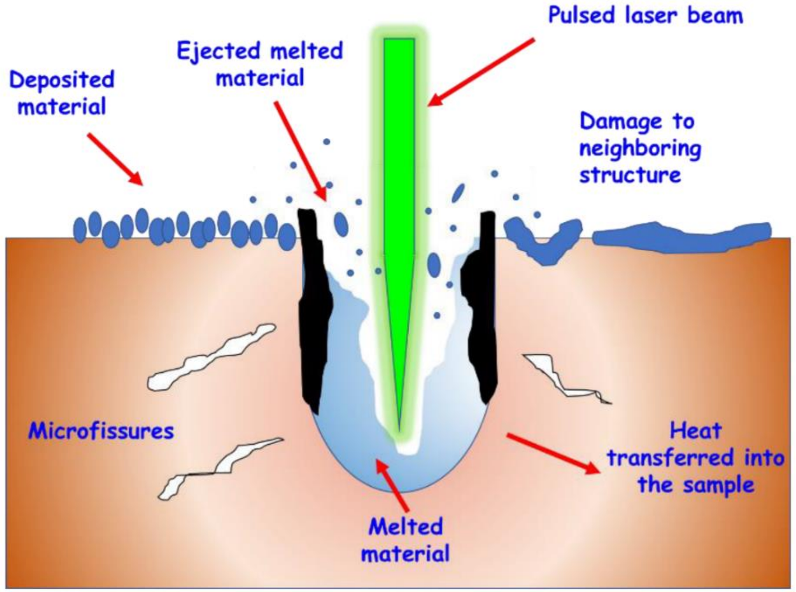
Pulse duration: 4 ns

Frequency: 10 Hz

1 pulse

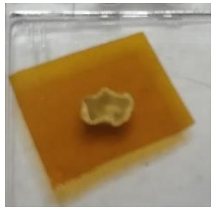
Laser Ablation

Removing macroscopic amounts of material by laser pulse.



Nanomaterials | Free Full-Text | Advances in Laser Ablation Synthesized Silicon-Based Nanomaterials for the Prevention of Bacterial Infection | HTML (mdpi.com)

Ablated samples (532 nm)



1 single shot

3 single shots

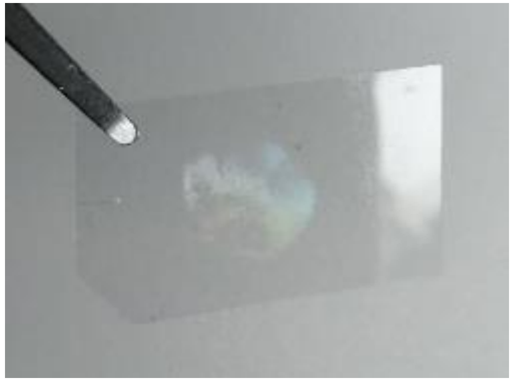
Laser characteristics:
Laser Quantel Brilliant B
Fundamental hatmonic wavelenght: 1064 nm
Second harmonic wavelenght: 532 nm
Fourth harmonic wavelenght: 266nm
Pulse duration: 4 ns
Frequency: 10 Hz

3D Printer

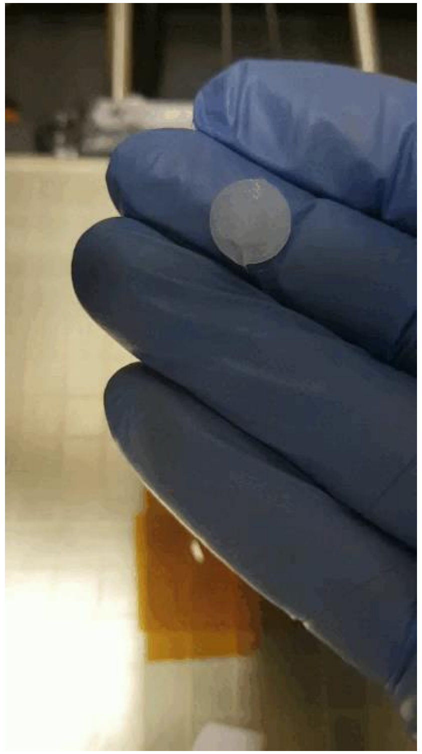
LulzBot Mini 2 3D Printer

https://shop.lulzbot.com/lulzbot-mini-v2-0-boxed-for-retail-na-kt-pr0047na

PET Mold



PCL Replica

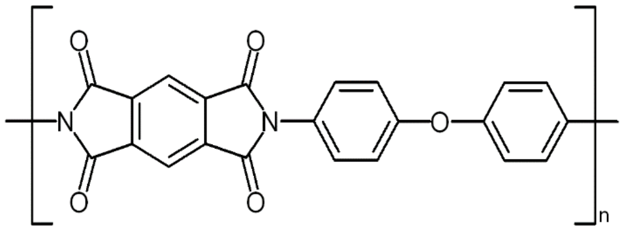


Polymers

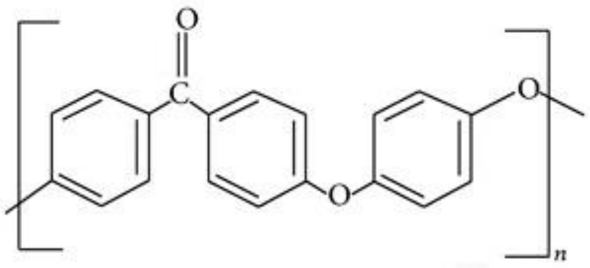
Free-standing films

Laser

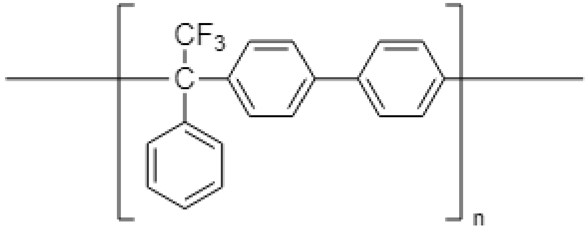
KAPTON



PEEK



3F-BIF



KAPTON properties:

- Mechanical and thermal resistance.
- Effective insulator.
- Resistance to radiation and chemicals.

PEEK properties:

- Thermoplastic.
- Mechanical, thermal and chemical resistance.

PET properties:

- Mechanical, thermal and chemical resistance.

PCL properties:

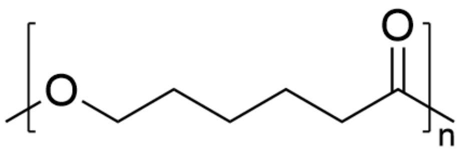
- Low viscosity and easy processing.
- Miscible.
- It melts easily and is non-toxic.

3F-BIF properties:

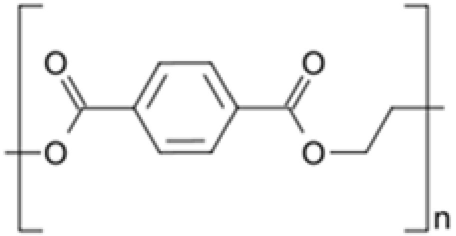
- Contact angle greater than 90°.

3DP

PCL



PET

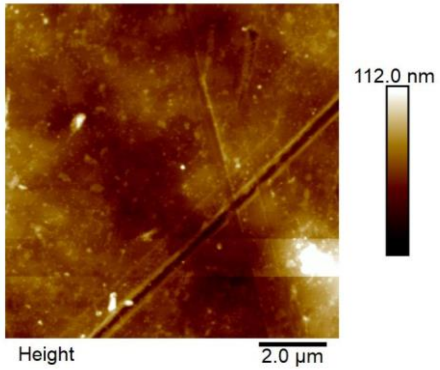


Material	Glass transition temperature (Tg)	Melting point
KAPTON	360°C - 410°C	-
3F-BIF	330°C	-
PEEK	145°C	340°C
PET	73°C - 80°C	265°C
PCL	-60°C	60°C

LIPSS Results

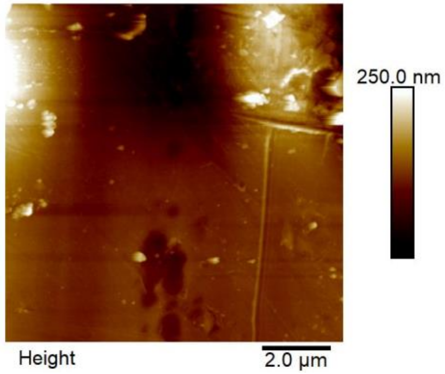
Non-irradiated samples

PEEK



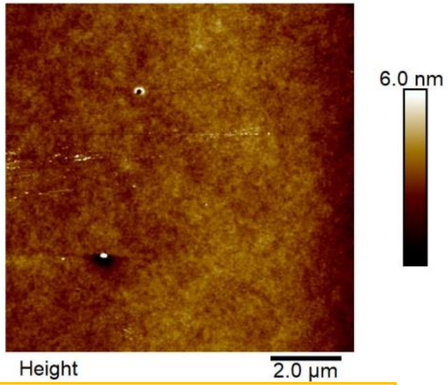
Roughness = (9,5 ± 0,5) nm

KAPTON



Roughness = (15 ± 11) nm

3F-BIF



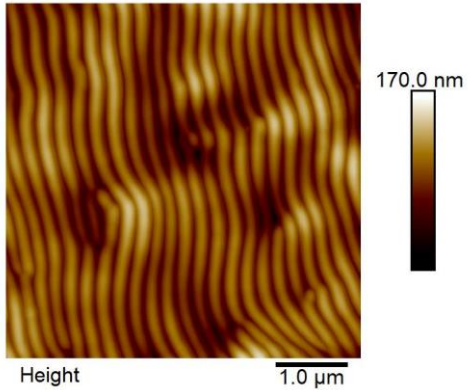
Roughness = (0,44 ± 0,07) nm

Irradiated samples

PEEK

F = 8 mJ/cm²

6000 pulses

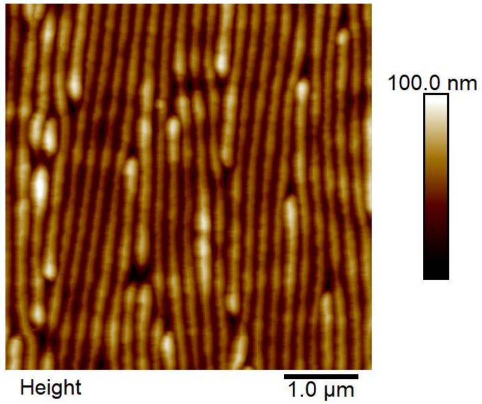


Period = (0,23 ± 0,01) µm
Depth = (51 ± 18) nm

KAPTON

F = 14 mJ/cm²

9000 pulses

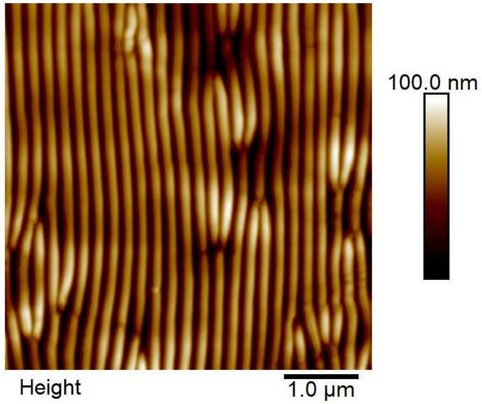


Period = (0,21 ± 0,01) µm
Depth = (31 ± 7) nm

3F-BIF

F = 13 mJ/cm²

1800 pulses

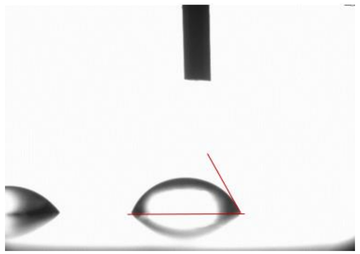


Period = (0,20 ± 0,01) µm
Depth = (29 ± 10) nm

Contact angle

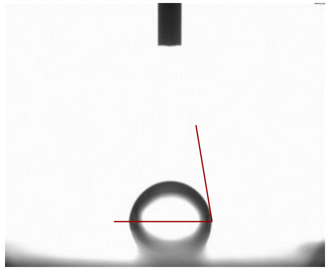
KAPTON

Unirradiated



CA = (66±5) °

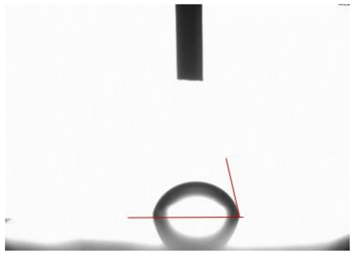
Irradiated



CA = (86±3) °

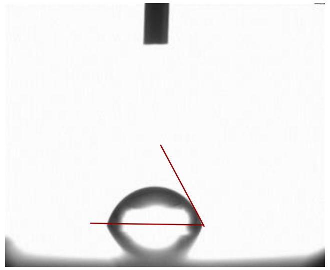
PEEK

Unirradiated



CA = (78±4) °

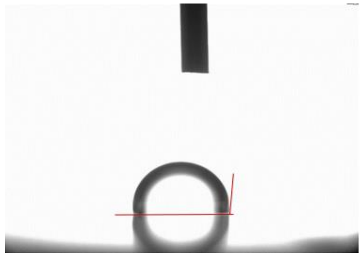
Irradiated



CA = (74±1) °

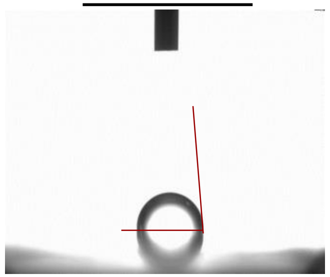
3F-BIF

Unirradiated

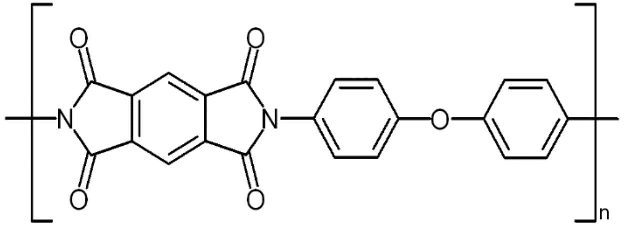


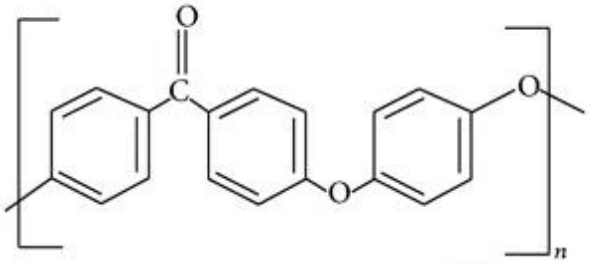
CA = (95±6) °

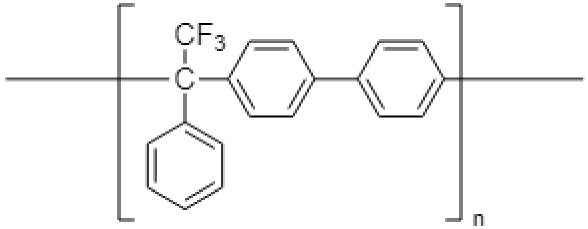
Irradiated



CA = (89±2) °



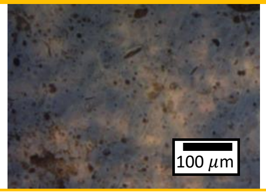




Laser Ablation Results at 266 nm

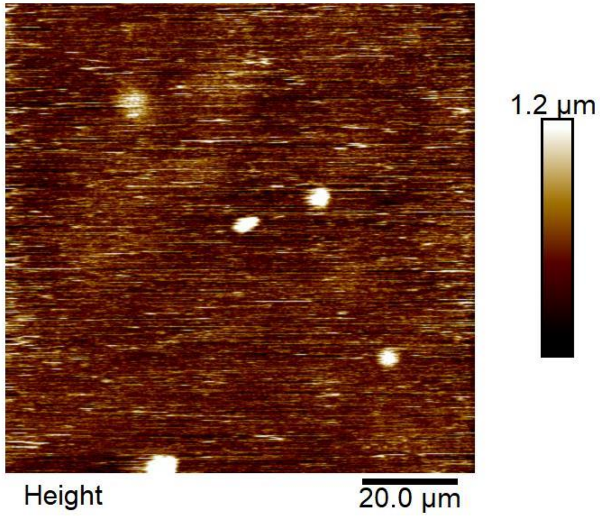
- $F_{damage\_threshold}$ = (21 ± 4) mJ/cm2
- Irradiation carried out with a fluence 8 × $F_{damage\_threshold}$: F = 164 mJ/cm2

Non-irradiated sample

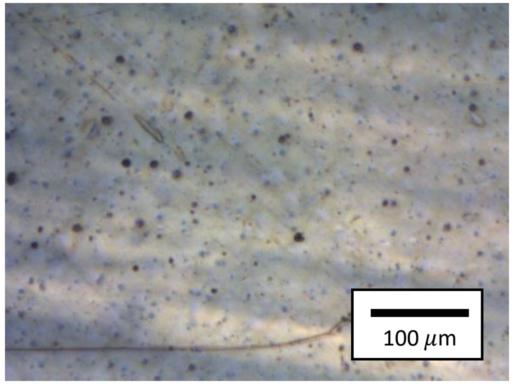


Roughness = (15 ± 11) nm

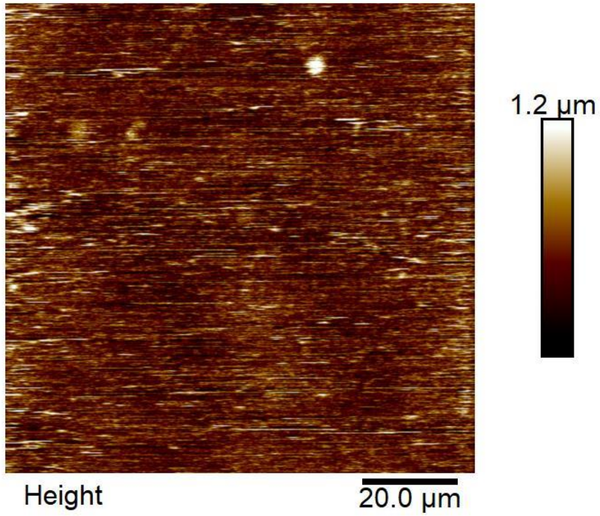
1 single shot



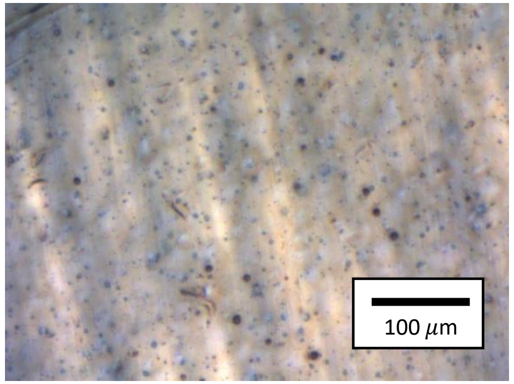
Roughness = 136 nm



3 single shots

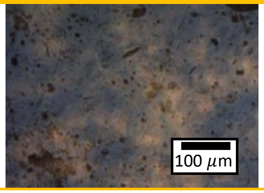


Roughness = 134 nm



Laser Ablation Results at 532 nm

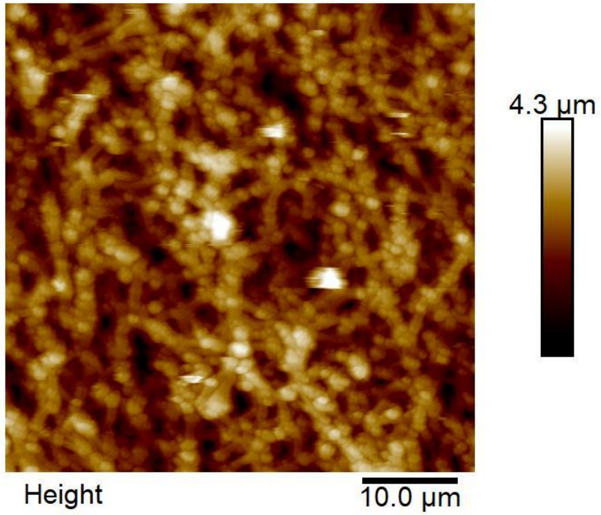
Non-irradiated sample



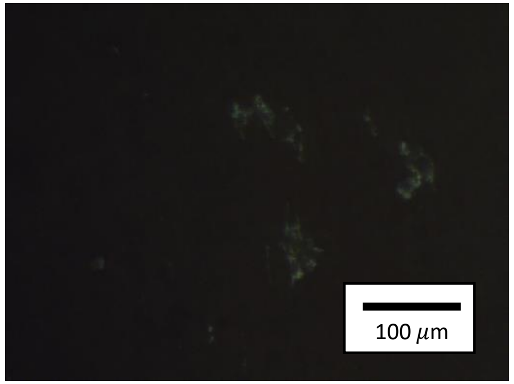
Roughness = (15 ± 11) nm

- $F_{damage\_threshold}$ = (402 ± 57) mJ/cm2
- Irradiation carried out with a fluence 8,6 × $F_{damage\_threshold}$: F = 3441 mJ/cm2

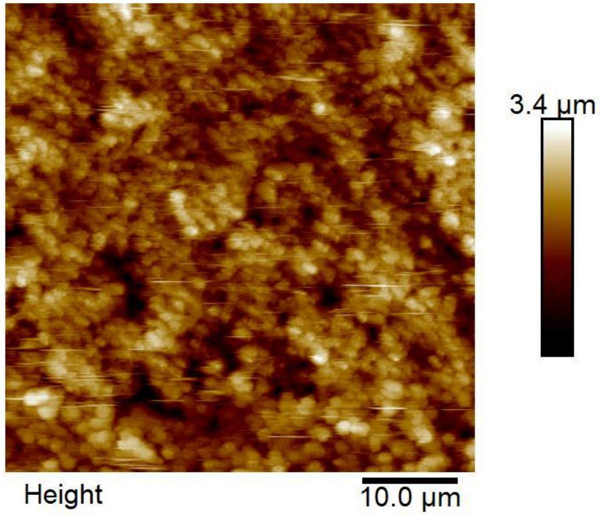
1 single shot



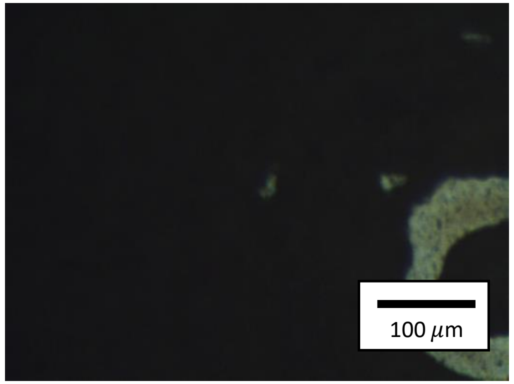
Roughness= 484 nm



3 single shots

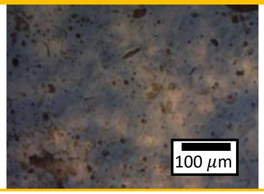


Roughness = 379 nm



Laser Ablation Results at 1064 nm

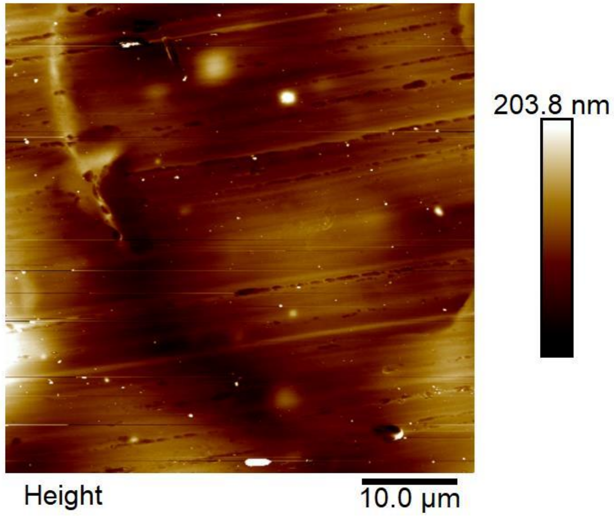
Non-irradiated sample



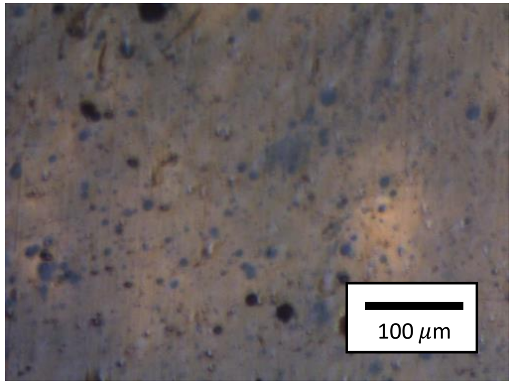
Roughness = (15 ± 11) nm

- $F_{damage\_threshold}$ = (525 ± 175) mJ/cm2
- Irradiation carried out with a fluence $8{,}8 \times F_{damage\_threshold}$: F = 4611 mJ/cm2

1 single shot

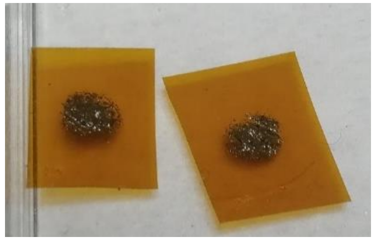


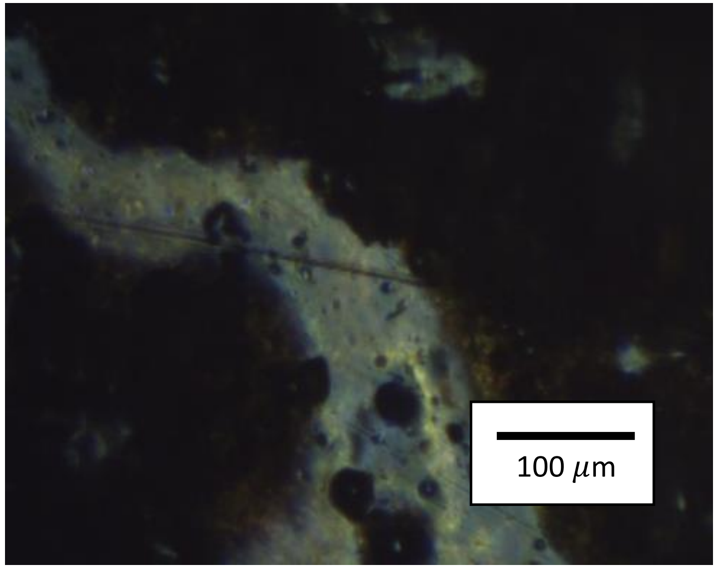
Roughness = 22 nm



3 single shots

- AFM image could not be obtained because surface was too rough.



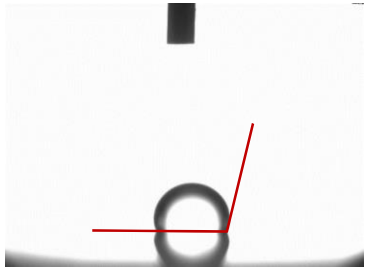


Contact angles in water at 266 nm

CAi = (66±5) °

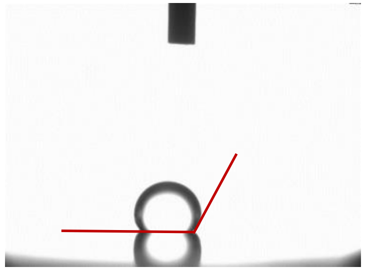
Day 1

1 single shot



CA = (106±3) °

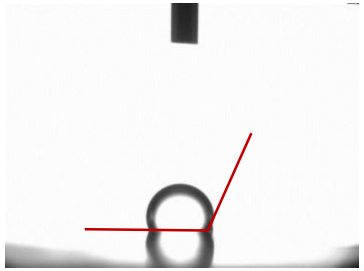
3 single shots



CA = (120±1) °

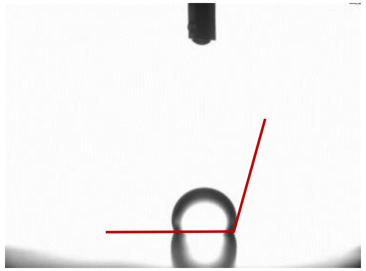
Day 6

1 single shot



CA = (123±10) °

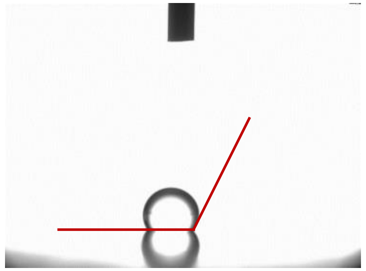
3 single shots



CA = (111±7) °

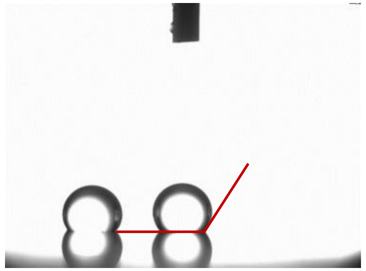
Day 12

1 single shot



CA = (127±5) °

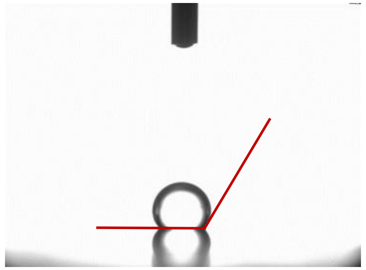
3 single shots



CA = (131±6) °

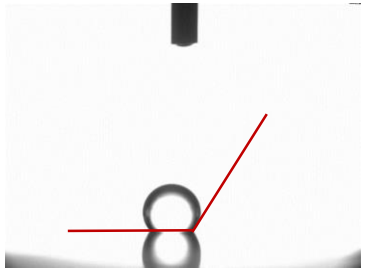
Day 19

1 single shot



CA = (133±1) °

3 single shots



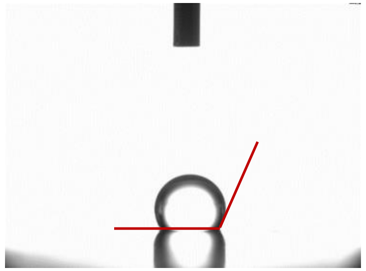
CA = (132±2) °

Contact angles in water at 532 nm

CAi = (66±5) °

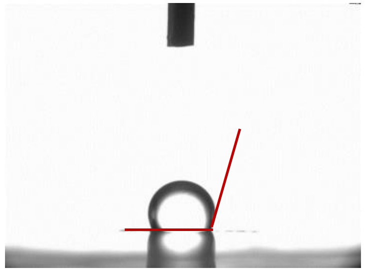
Day 1

1 single shot



CA = (124±4) °

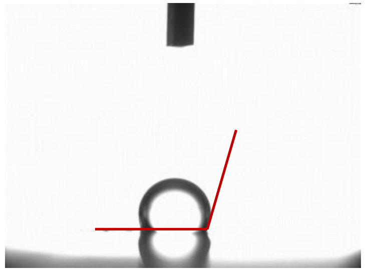
3 single shots



CA = (115±14) °

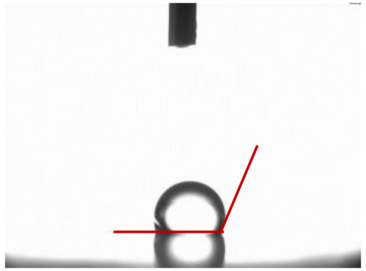
Day 6

1 single shot



CA = (118±4) °

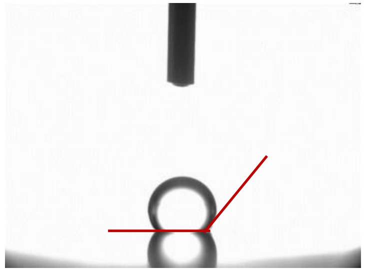
3 single shots



CA = (119±11) °

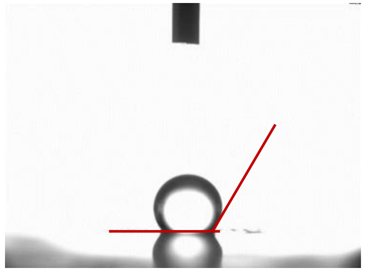
Day 12

1 single shot



CA = (131±3) °

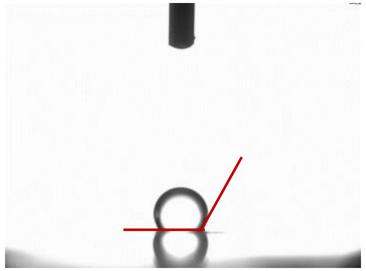
3 single shots



CA = (129±9) °

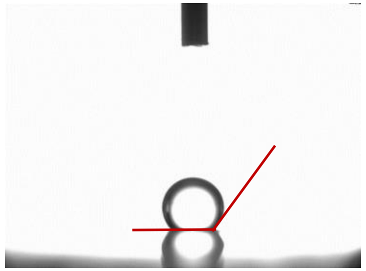
Day 19

1 single shot



CA = (130±5) °

3 single shots



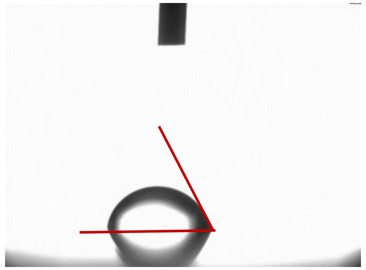
CA = (129±6) °

Contact angles in water at 1064 nm

CAi = (66±5) °

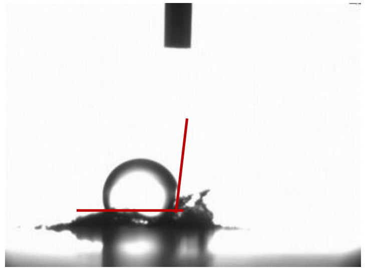
Day 1

1 single shot



CA = (77±7) °

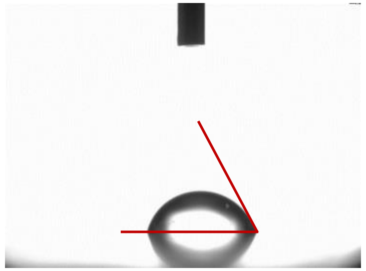
3 single shots



CA = (109±5) °

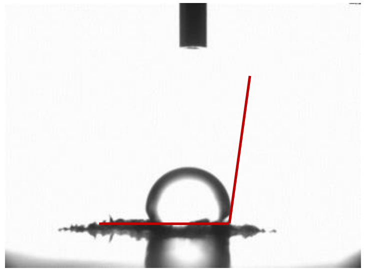
Day 6

1 single shot



CA = (74±3) °

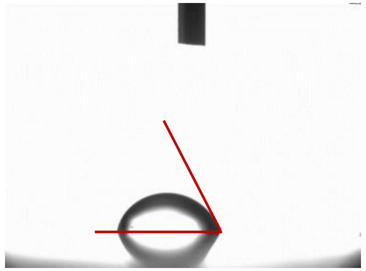
3 single shots



CA = (108±2) °

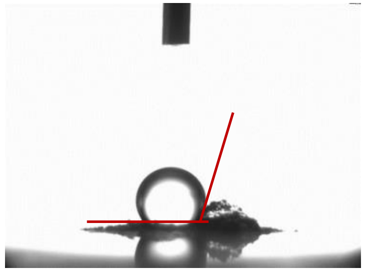
Day 12

1 single shot



CA = (73±7) °

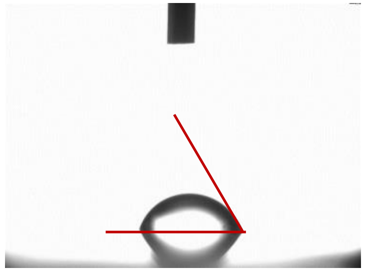
3 single shots



CA = (120±8) °

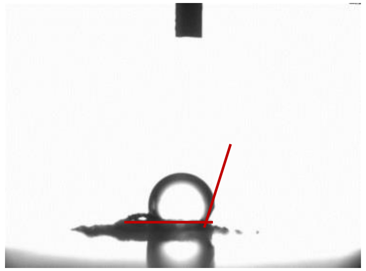
Day 19

1 single shot



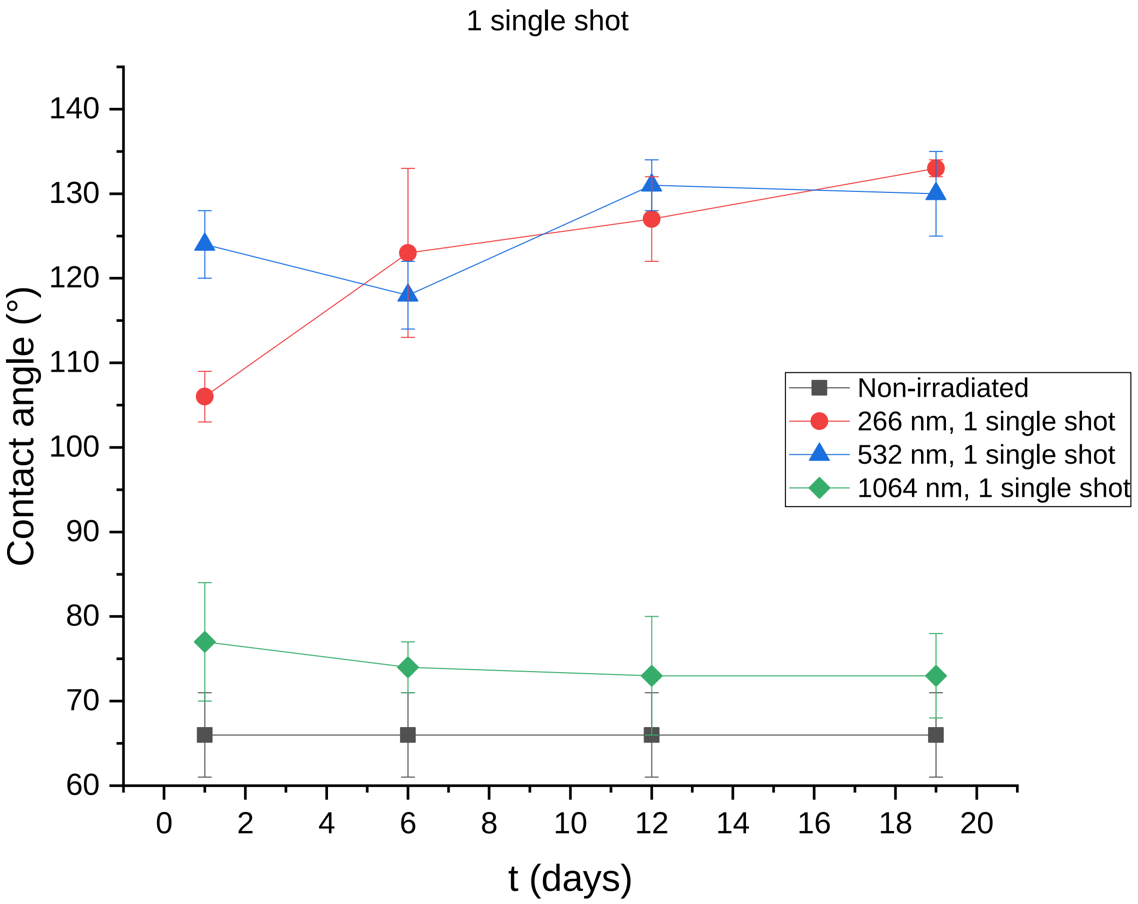
CA = (73±5) °

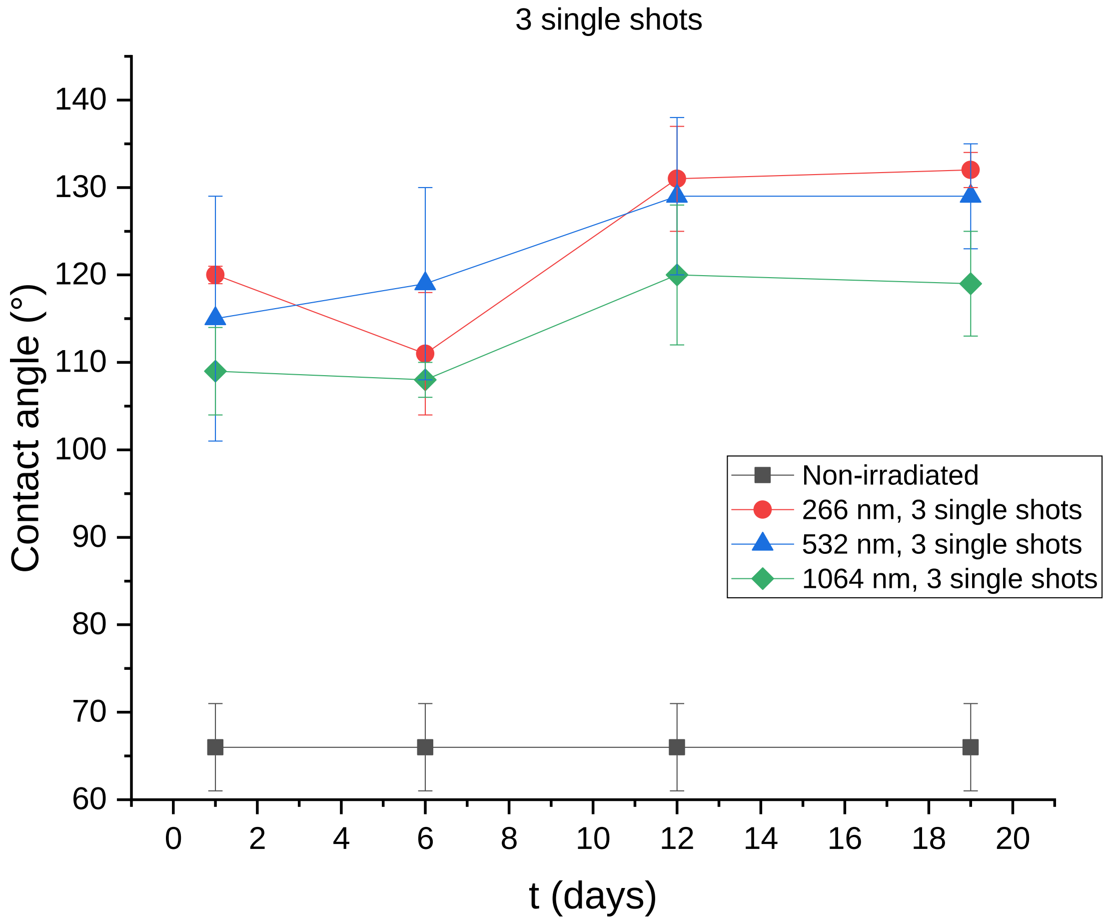
3 single shots



CA = (119±6) °

Graph of contact angle with time for different wavelengths

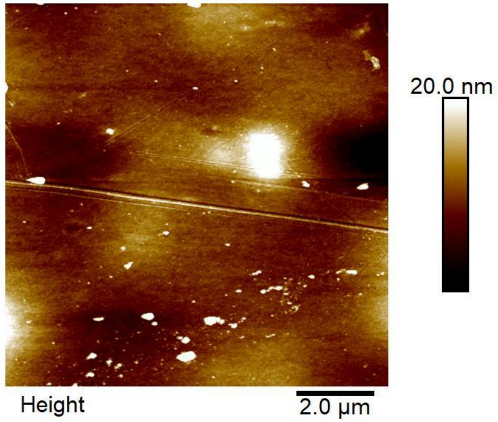




3D Printing Results

PET Molds

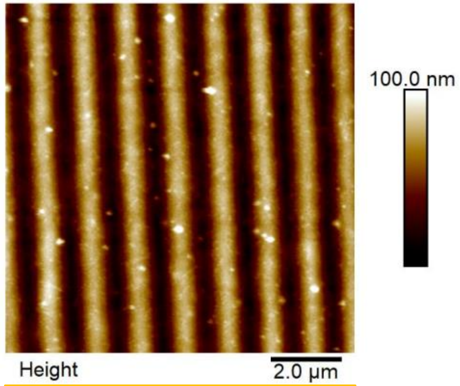
Mold Transparency



Roughness = 2 nm

Mold LIL

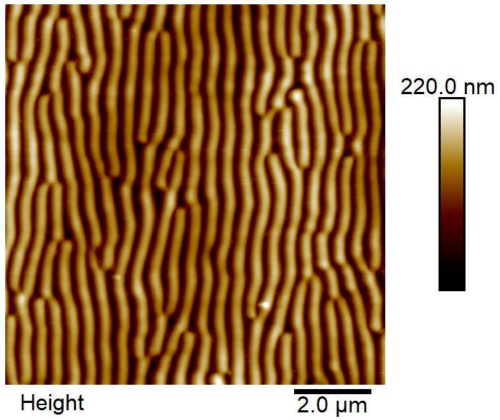
F = 35,8mJ/cm2, 1 pulse, 2 beams



Period = (1,26 ± 0,03) µm
Depth = (63 ± 6) nm

Mold LIPSS

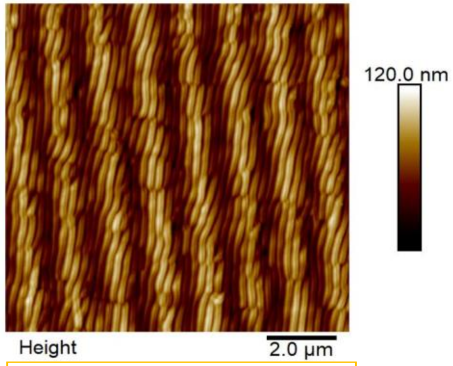
F = 8,4 mJ/cm2, 2400 pulses, 45 °



Period = (0,45 ± 0,01) µm
Depth = (108 ± 14) nm

Mold LIL + LIPSS

LIL: F = 37,8 mJ/cm2, 1 pulse, 2 beams
LIPSS: F = 8 mJ/cm2, 600 pulses

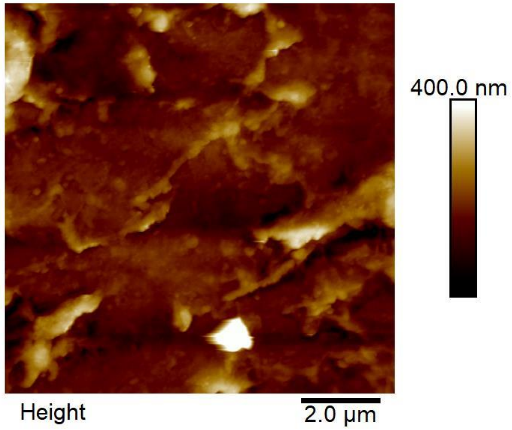


Period = (1,29 ± 0,01) µm
Depth = (61 ± 12) nm

Period = (0,26 ± 0,01) µm
Depth = (34 ± 10) nm

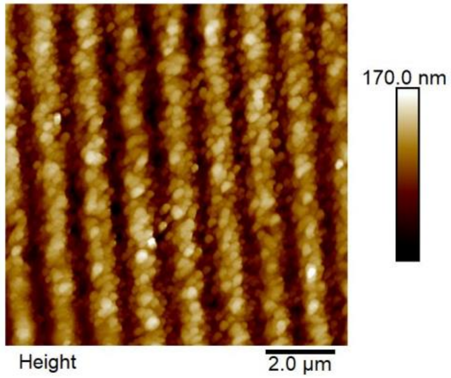
PCL Replicas

Replica Transparency



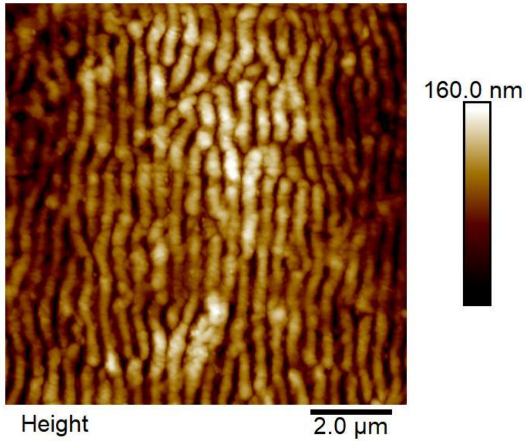
Roughness = 36 nm

Replica LIL



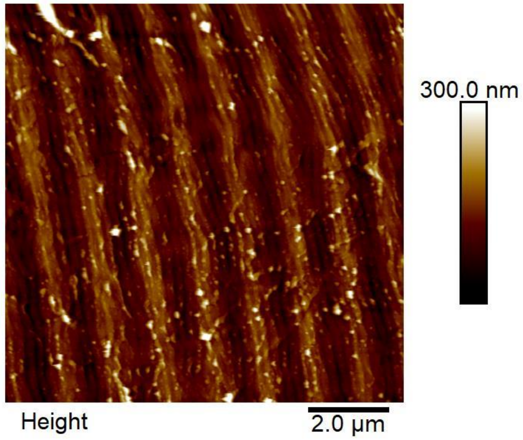
Period = (1,22 ± 0,01) µm
Depth = (81 ± 16) nm

Replica LIPSS



Period = (0,44 ± 0,01) µm
Depth = (56 ± 18) nm

Replica LIL + LIPSS



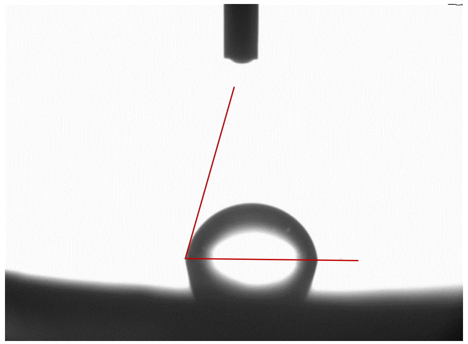
Period = (1,24 ± 0,01) µm
Depth = (86 ± 18) nm

Period = (0,24 ± 0,01) µm
Depth = (31 ± 16) nm

Contact angle

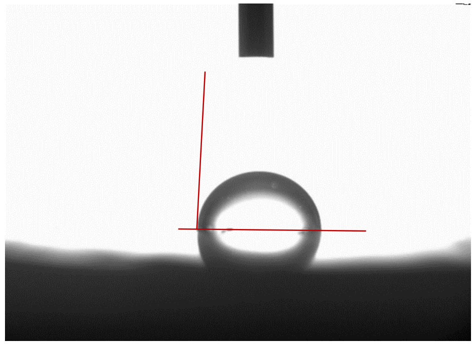
PCL Replicas

Replica Transparency



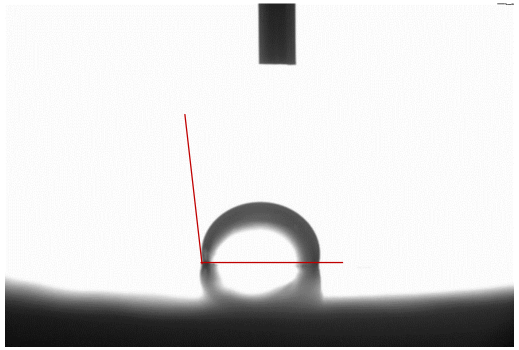
CA = (80±1) °

Replica LIL



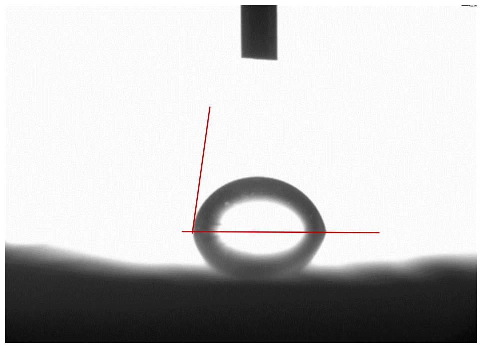
CA = (87±1) °

Replica LIPSS



CA = (104±5) °

Replica LIL + LIPSS



CA = (81±3) °

Conclusions

- After the formation of LIPSS on the selected polymers the surfaces remained hydrophilic.
- The contact angle after LIPSS formation in KAPTON increased.
- Laser ablation at different wavelengths allowed to obtain hydrophobic surfaces on KAPTON, probably influenced by the chemical changes that the surface undergoes.
- An increase in the contact angle of the ablated polymer was observed with time in the samples that were hydrophobic.
- Obtaining replicas by means of a 3D printer seems to be an optimal method to obtain hydrophobic surfaces on materials that do not absorb at the wavelength of lasers.

Questions