Plasma Treatment of NIL polymers to enhance anti-adhesion properties

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Objective

to enhance the anti-adhesion behavior via plasma functionalization of the polymer surface in order to avoid the problems of adhesion between the stamp and the substrate during the de-moulding in the NIL process.

A process for low pressure plasma treatment has been developed, including the nature of reactive gases and the configuration of the plasma reactor.

SF_6 + Ar
CF_4 + Ar

- **CVD-RF (ASM) at 13,56MHz:**

a) tubular reactor, low pressure and capacitive-coupled plasma.
b) Power: 25-150 W
c) Time: 1-5 min
d) Flow of reactive gases: 25-225 sccm

- **MW plasma (Iplas) at 2,45GHz:**

a) Remote cold plasma
b) Distance to plasma: 8 to 20cm
c) Power: 1500-3000 W
d) Time: 3-20 min
e) Flow of reactive gases: 50-225 sccm

Characterization

- **Contact Angle**: verification of stability and lifetime of treatments

- **AFM**: roughness and thickness modification

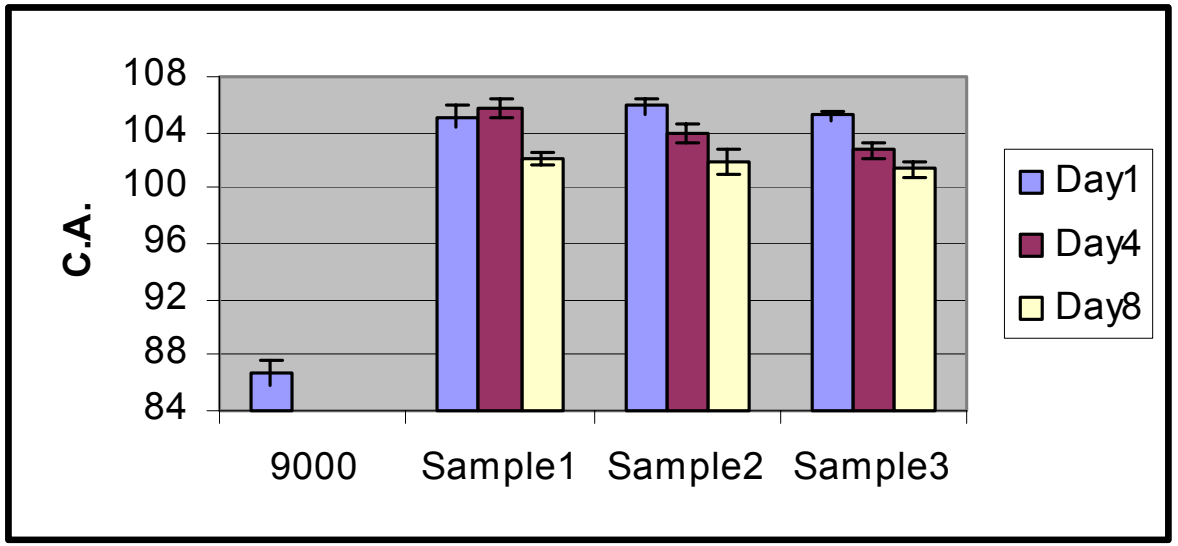
- **XPS**: chemical composition and in-depth profile

MATERIALS

- **mr-I 9030** (allyl from mrt) ⇒ 300nm thickness
- **PDAP** (allyl from mrt) ⇒ 280 nm thickness

- **mr-I 8030** (acrylate from mrt) ⇒ 300 nm thickness
- **mr-I 7030** (acrylate from mrt) ⇒ 300 nm thickness
- **PMMA** (acrylate from mrt) ⇒ 500 nm thickness

mrI-9000: RF plasma

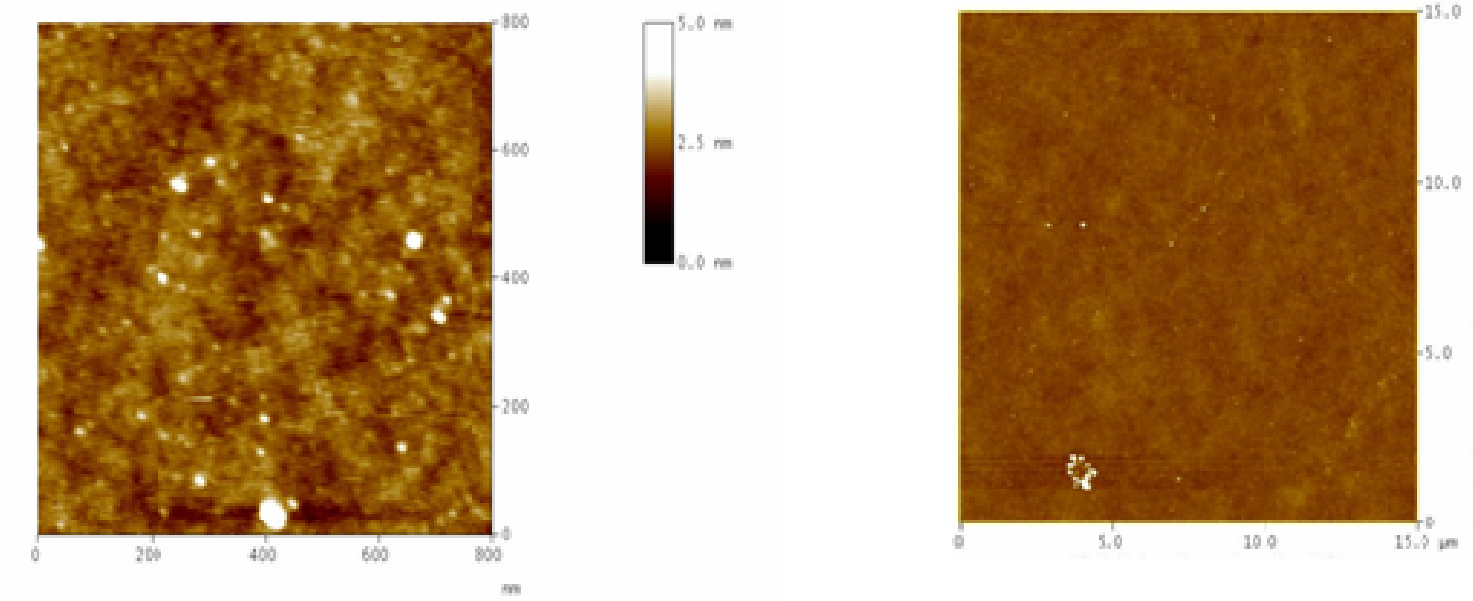


Sample1 Time=2min Power=100W SF_6=37,5 Ar =150
Sample2 Time=2min Power=25W SF_6=50 Ar =200
Sample3 Time=2min Power=100W SF_6=200 Ar =0

AFM (mr-I 9000)

Before treatment:
CA=86°

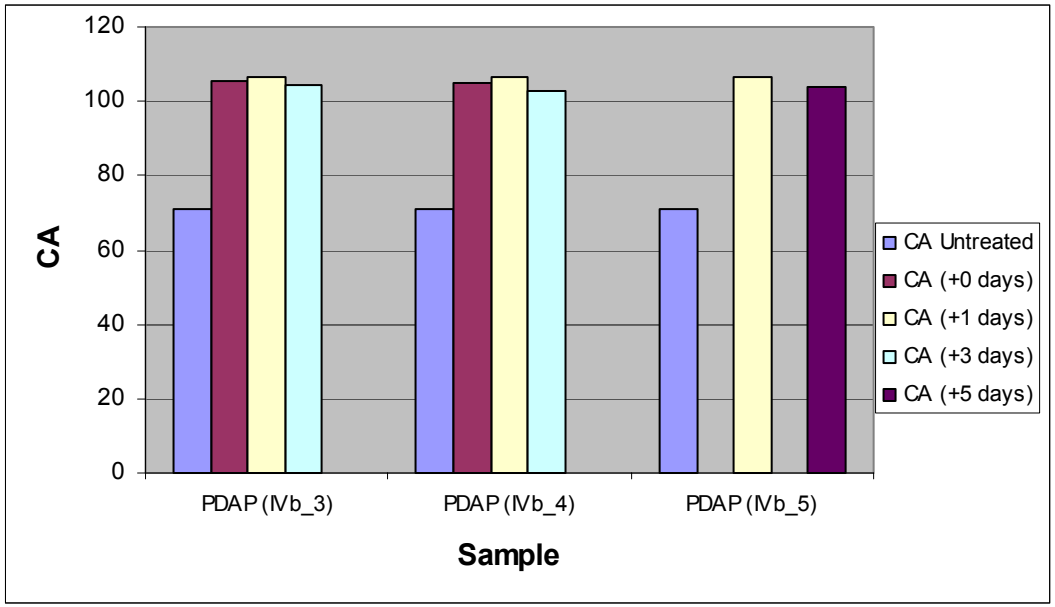
After treatment
CA=105,9 ± 1,2° °



RF PLASMA *Time =2min Power =25W* SF_6*= 50sccm Ar =200sccm*

- **Before treatment:** thickness = 287,86nm; roughness = 0,62nm
- **After treatment:** thickness = 248,84nm; roughness = 0,353nm

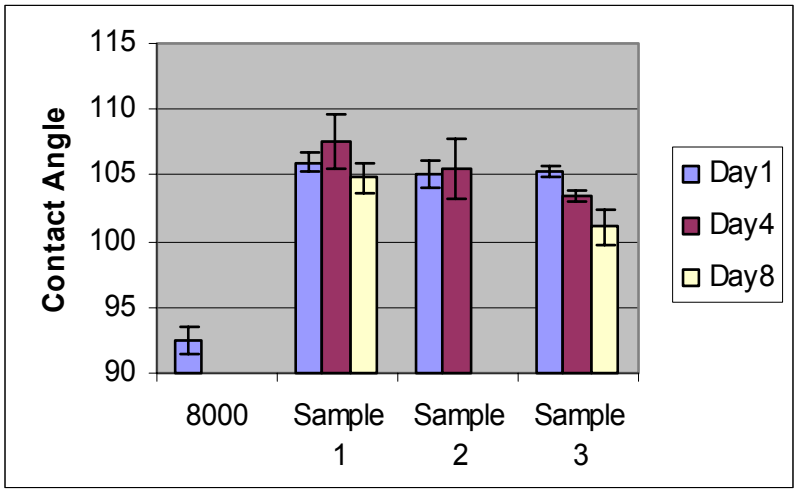
PDAP: MW plasma

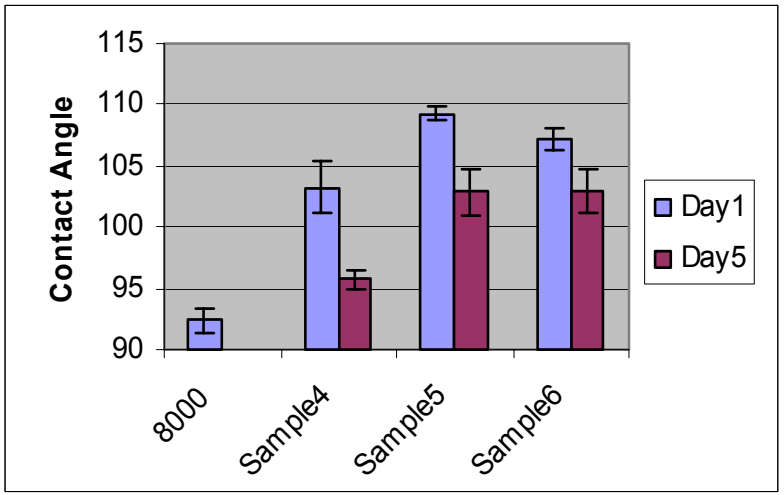


- PDAP (IVb_3) **MW** 2500W 15min 200SF6 50Ar
- PDAP (IVb_4) **MW** 2500W 5min 200SF6 50Ar
- PDAP (IVb_5) **MW** 2000W 5min 200SF6 50Ar

No modification in the thickness, slight increase of the roughness

mrI-8000: RF plasma

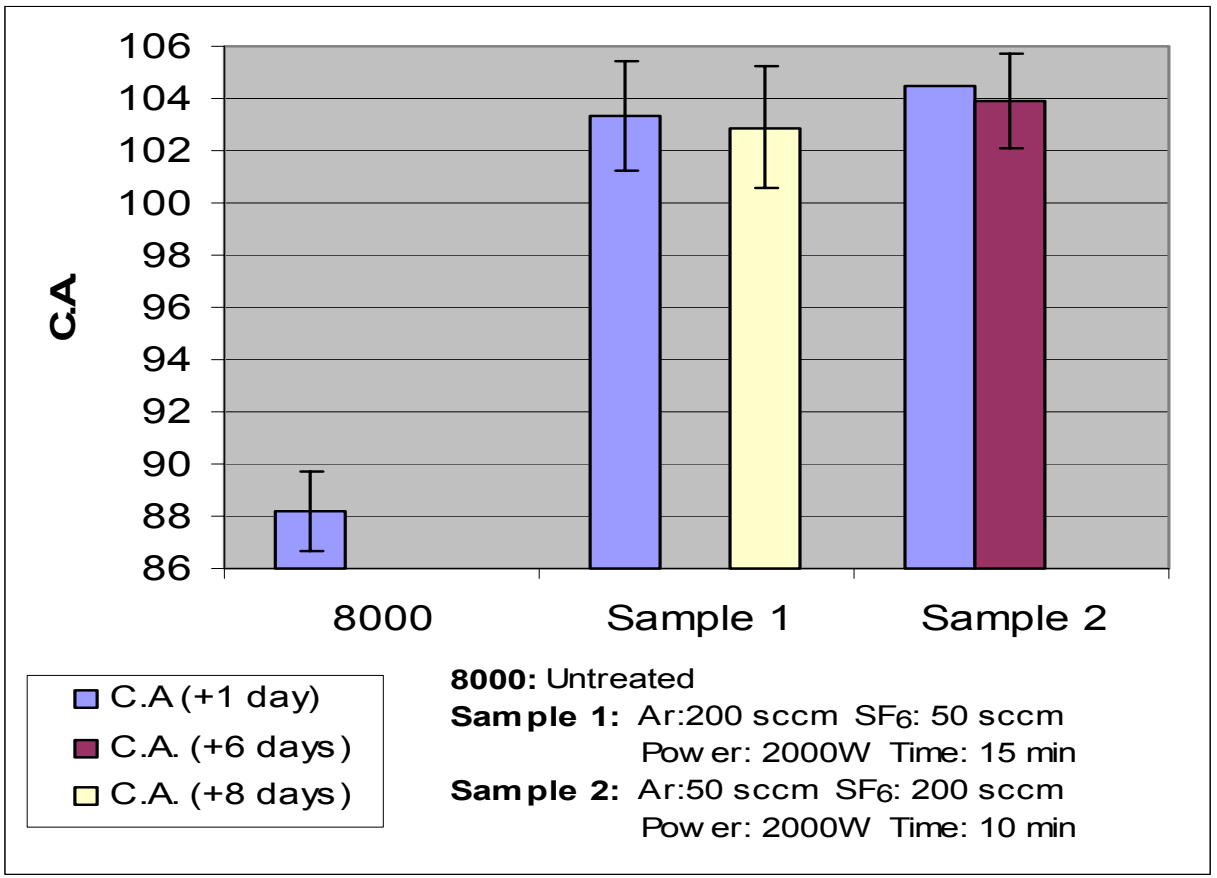




Sample1 Time=2min Power=100W SF_6=37,5 Ar =150
Sample2 Time=2min Power=25W SF_6=50 Ar =200
Sample3 Time=2min Power=100W SF_6=200 Ar =0

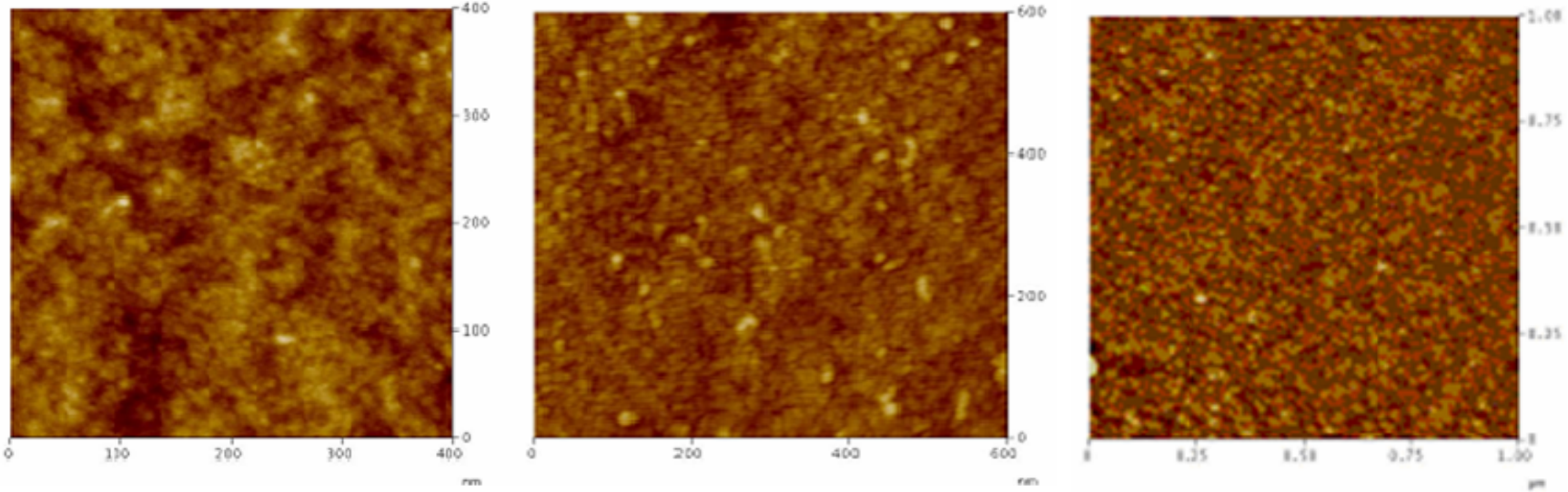
Sample4 Time=1min Power=125W SF_6=37,5 Ar= 100
Sample5 Time=1min Power=125W SF_6=175 Ar=25
Sample6 Time=1min Power=125W SF_6=225 Ar= 25

mrI-8000: MW plasma



AFM (mr-I 8000)

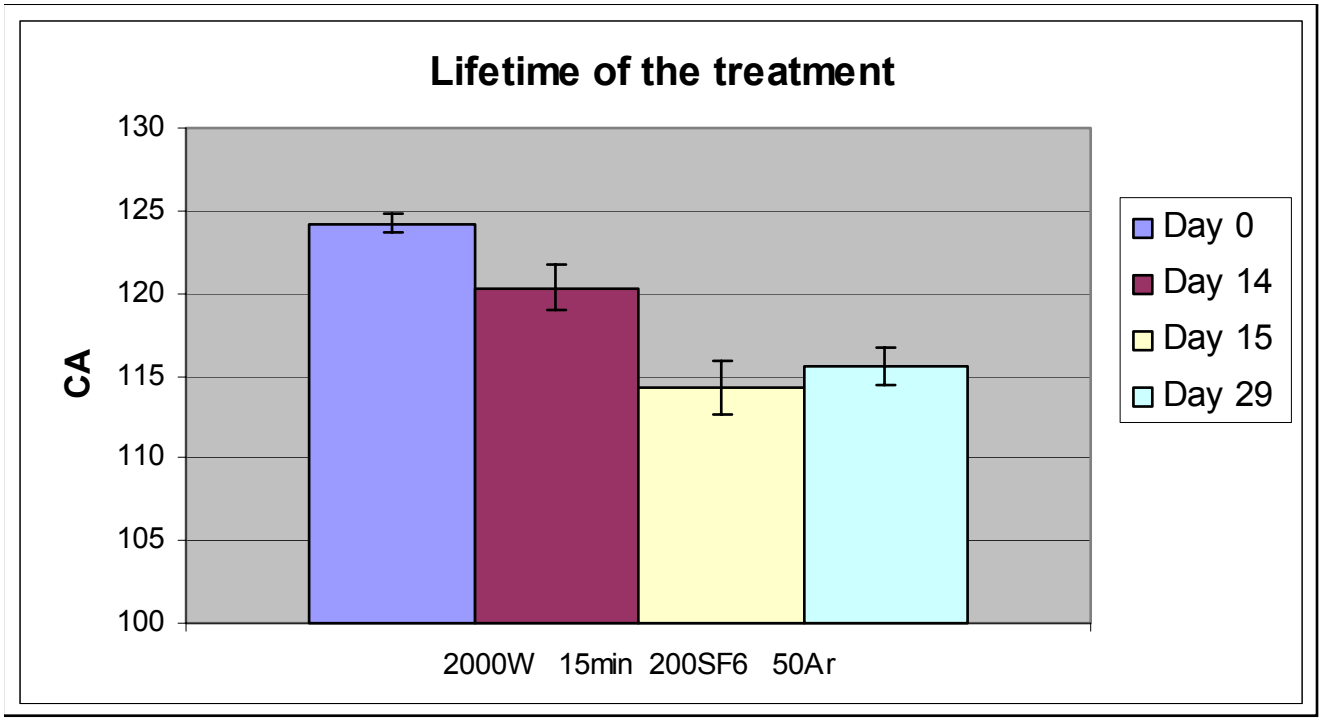
Before treatment: CA=92°	After RF treatment CA=101,8 ± 1,6°	After MW treatment CA=104,5 ± 2,1°



RF PLASMA *Time= 1min Power= 125W* CF_4 *= 175sccm Ar= 25sccm*
MW PLASMA *Time= 10min Power= 2000W* SF_6 *= 200sccm Ar= 50scc*

- **Before treatment:** *thickness* = 385-400nm ; *roughness* = 2-3nm
- **After RF treatment :** *thickness* =373,69nm; *roughness* = 0,3-0,4 nm
- **After MW treatment :** *thickness* =379,14nm; *roughness* = 1-3 nm

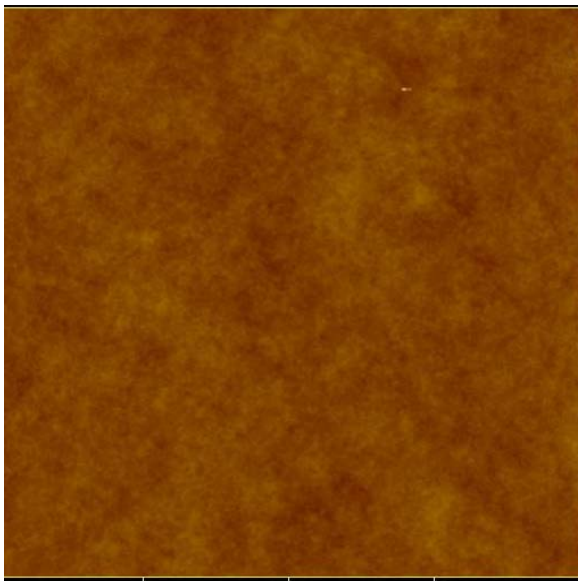
mrI-7000: MW plasma

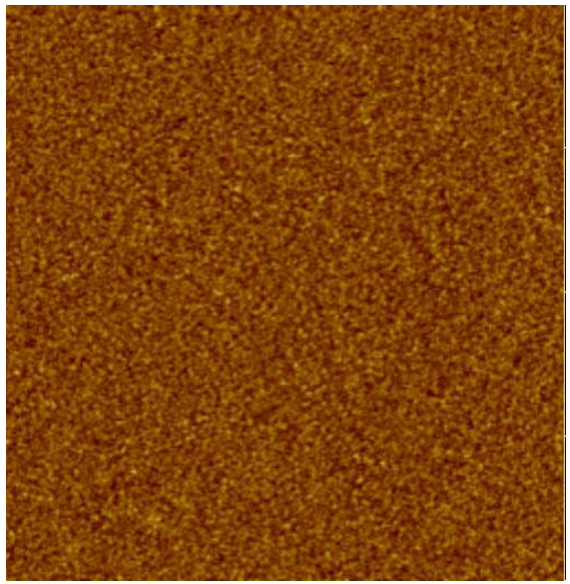


mrI-7000: 2000W 15min 200:50, SF6:Ar

AFM (mr-I 7000)

Before treatment: CA=80,7°	After treatment CA=126,9°

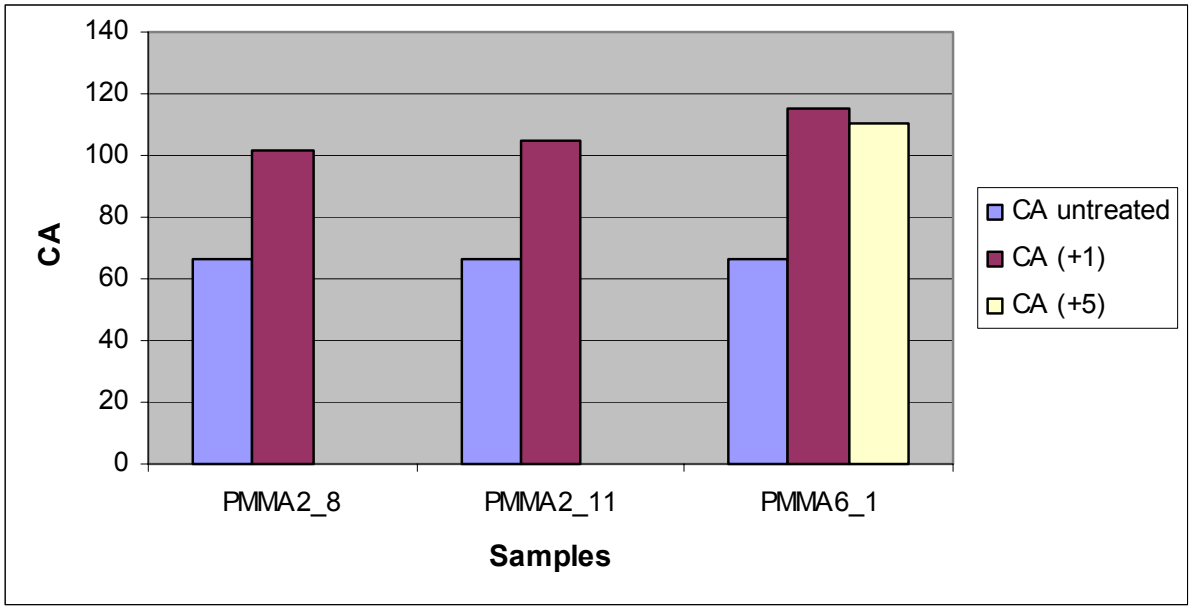




MW PLASMA *Time =10min Power =2000W* SF_6 *= 200sccm Ar =50sccm*

- **Before treatment:** *thickness* = 326,89nm ; *roughness* = 0,265nm
- **After treatment:** *thickness* = 303,68nm; *roughness* = 6,399nm

PMMA



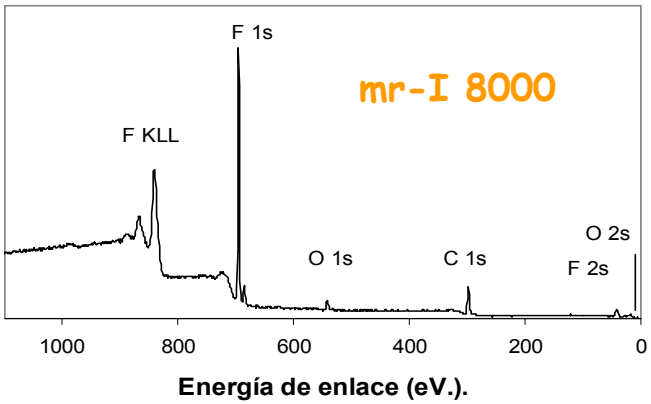
PMMA2_8 **RF** 125W 1min 175SF6 25Ar
PMMA2_11 **RF** 25W 2min 50SF6 200Ar
PMMA6_1 **MW** 2000W 5min 200SF6 50Ar

Basically no modification in the thickness and roughness after MW plasma, higher after RF treatment

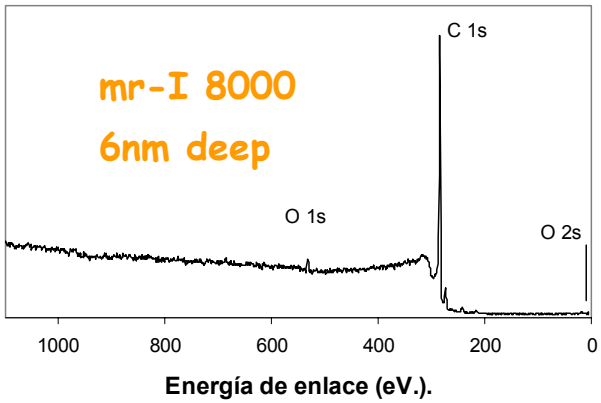
XPS results (In-depth profile)

MW PLASMA

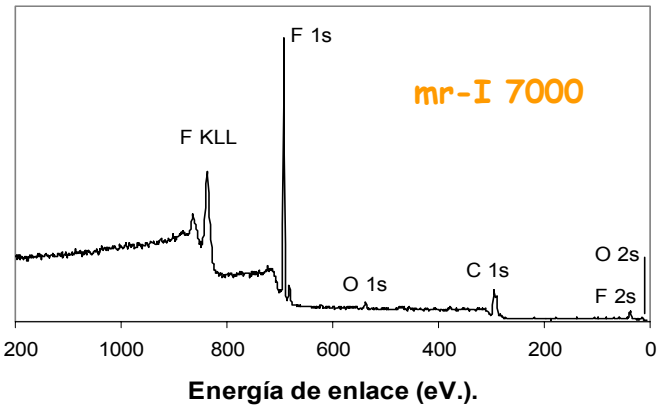
Surface

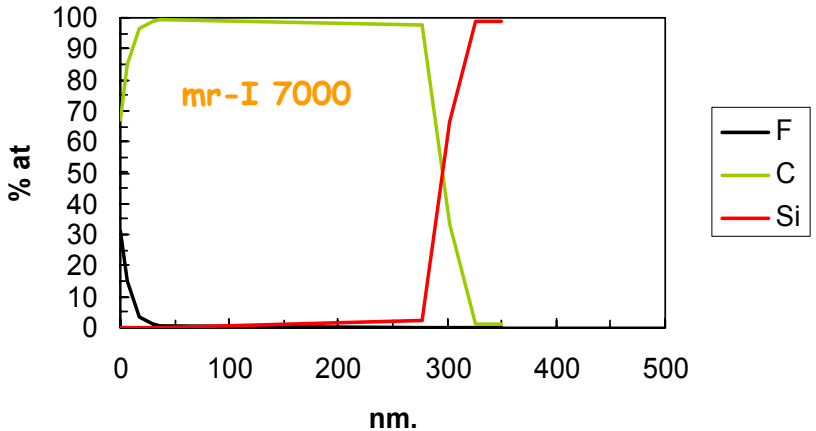


Bulk



Element	Surface	Bulk
O	3,344	3,361
C	33,36	96,639
F	63,296	∅



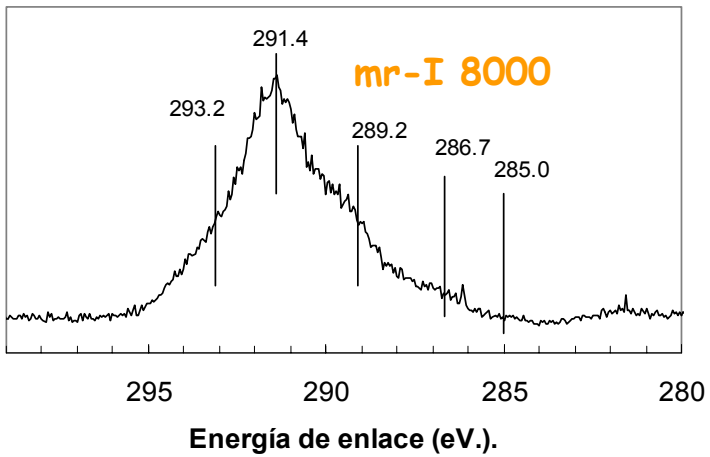


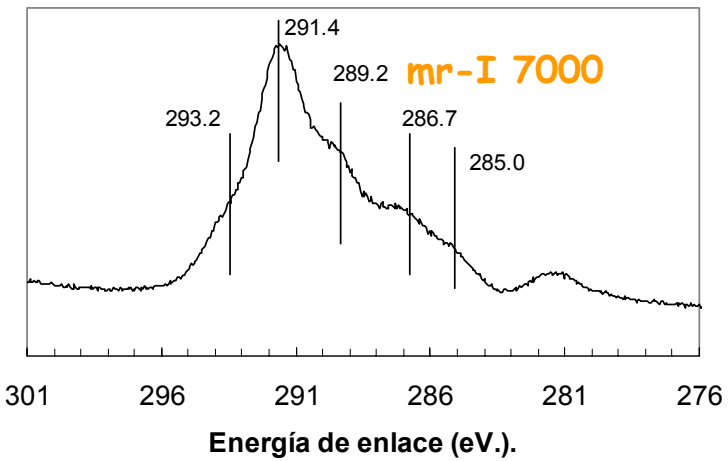
- In-depth spectra show no fluorine groups after few nanometers (~6nm)

XPS results (Functional groups)

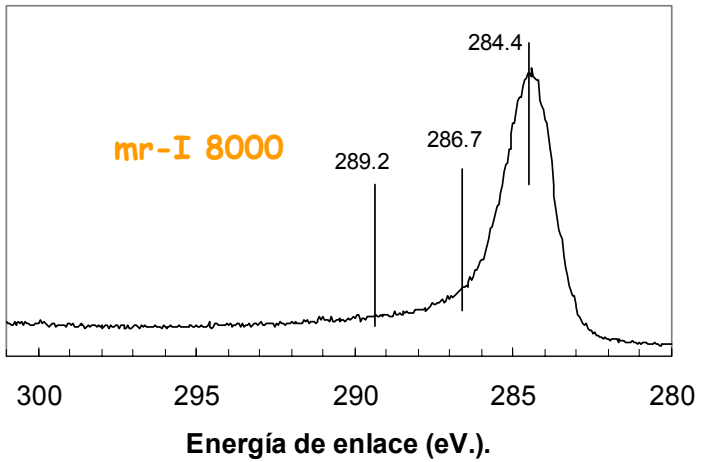
C peak

Surface





Bulk



- CF_2 (291,4eV) and CF_3 (293,2eV) are the main groups responsible for the anti-adhesion.
- The spectrum of mr-I 7000 has more intensity in this region. (Higher CA)

Imprinting trials (I)

Stamp	Plasma	Power (W)	Time (min)	SF_6	Ar	Contact Angle
Silane (2 PDMS)	Untreated	---	---	---	---	aprox.81º
Si (1 PDMS)	MW	3000	10	200	50	128,11º
Si (2 PDMS)	MW	3000	10	200	50	129,66º
Si (1 PDMS)	RF	25	2	50	200	116,59º
Si	MW	3000	10	200	50	Aprox. 127º

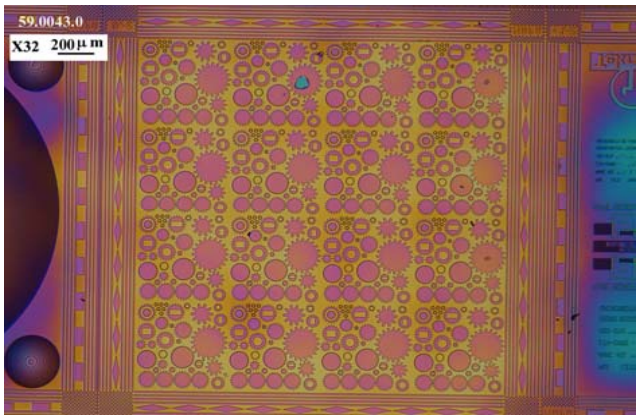
All the tests were made under the same imprint conditions that were optimized previously by Tekniker:

- Temperature of 140°C
- Force of 50000N (≈63 bar)
- Embossing time of 5 minutes (total time of each imprint aprox. 20min).

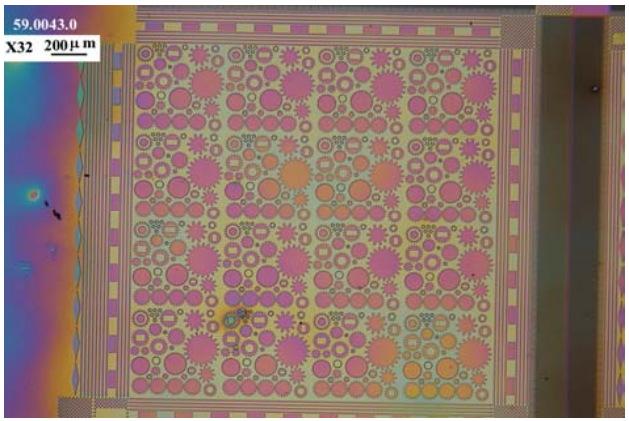
Imprinting trials (II)

- Characteristics well defined and good filling of the patterns.

TEKNIKER

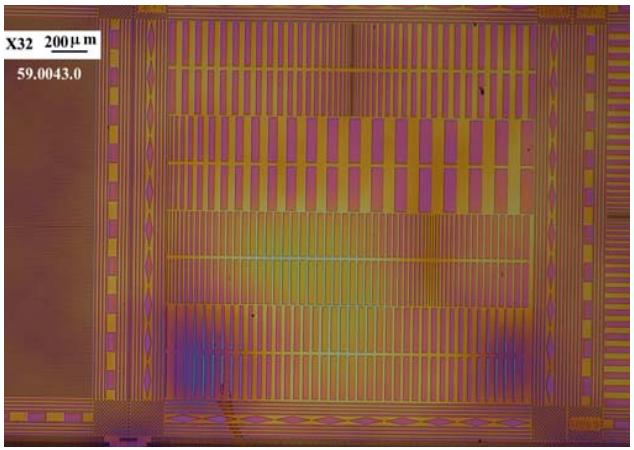


INASMET



- The colour pattern of the residual layer shows no differences.

TEKNIKER



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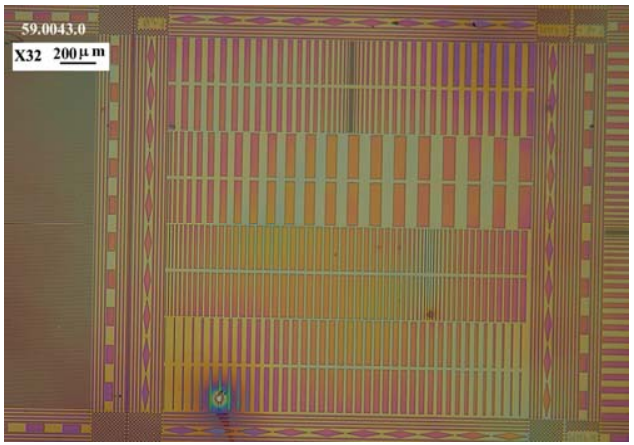
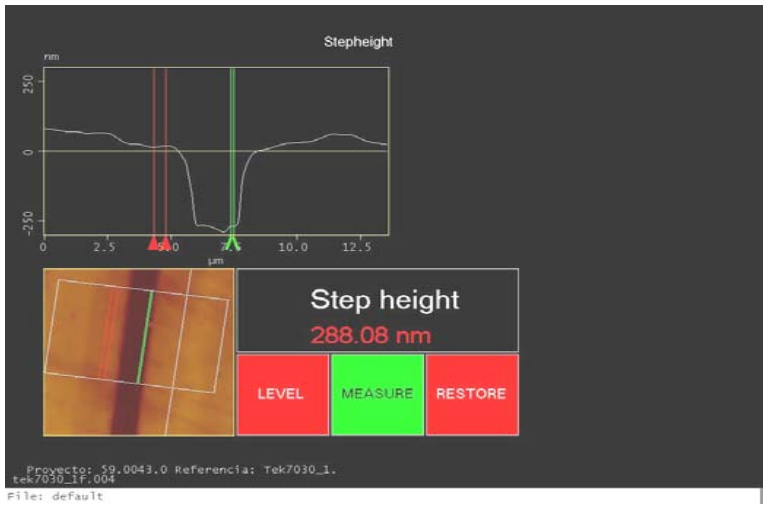
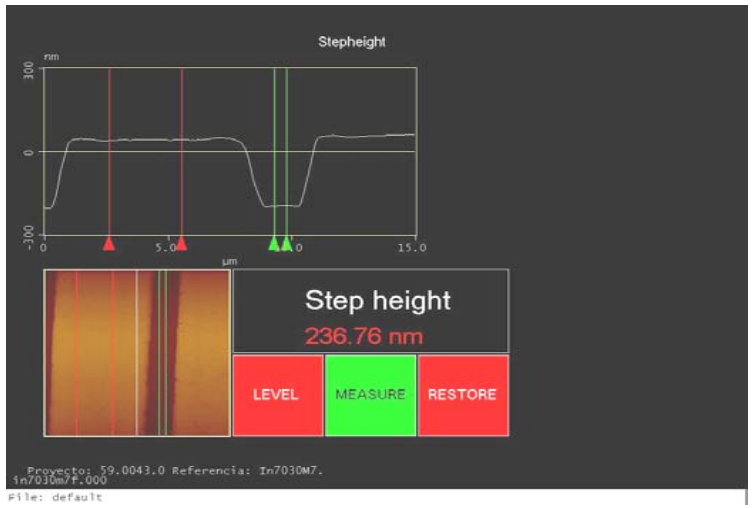


Imprinting trials (III)

TEKNIKER



INASMET



- Treated samples do not adhere at all during demoulding, although some resist sticks on the walls of the stamp after several imprints.
- The process was correct: filling correct, details well defined, …
- The treated polymer has the same etch rate as the untreted one.
- More regular pattern obtained with the Inasmet sample.

Conclusions

A short process for low pressure plasma treatment has been developed, which improves the pattern transfer and eliminates the manual de-moulding needed after NIL processing

-This has been proved on several polymers

-A complete characterization of the surface of the different polymers has been performed

Thank you for your attention

The partial support of the EC-funded project NaPa
(Contract no.NMP4-CT-2003-500120) is gratefully acknowledged