

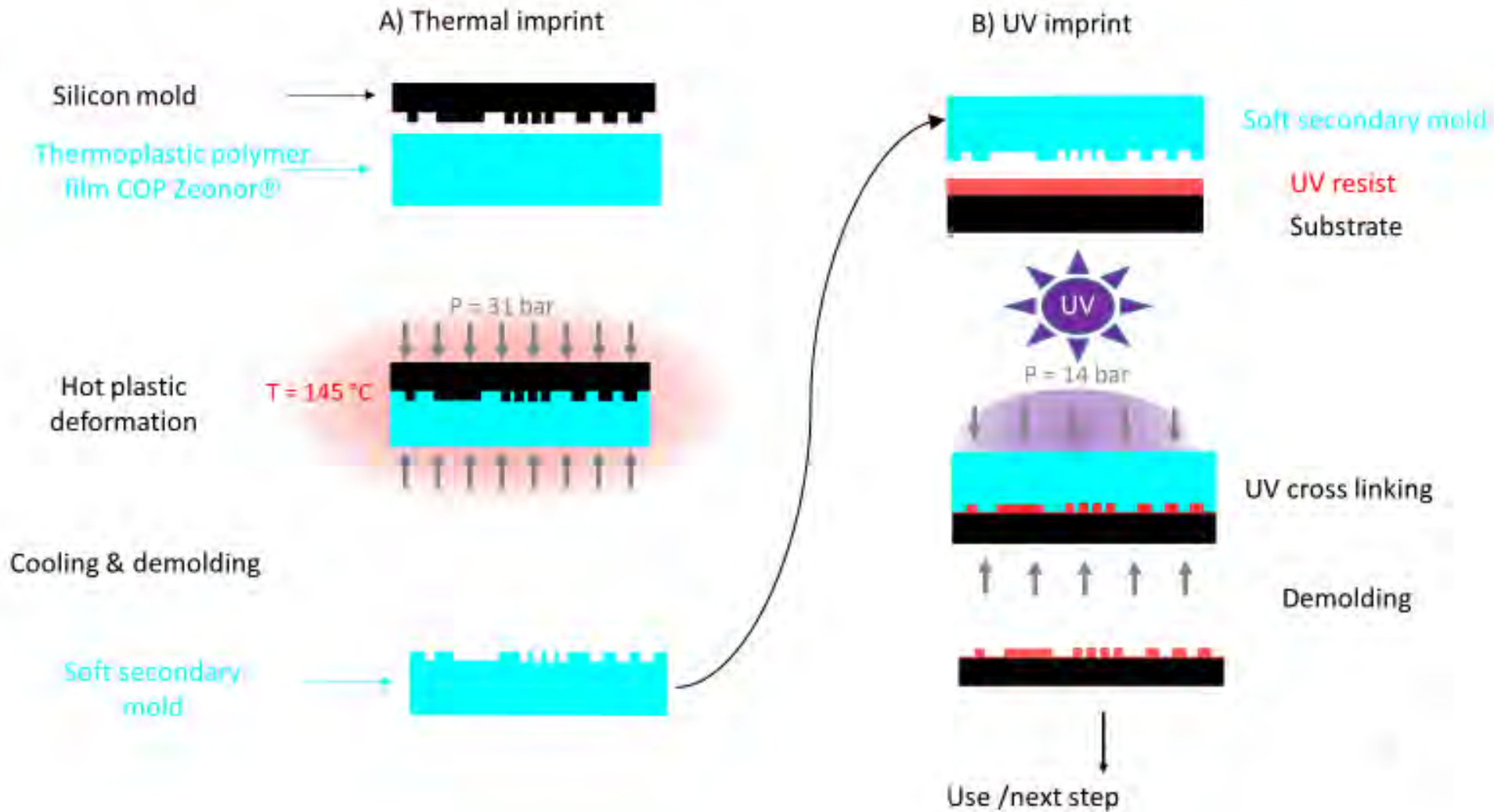
study of nano-printing in a biomaterial and its use as a secondary polymer mold

JNIL 11-12/05/23 LYON

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- > Secondary polymer mold
 - Principle
 - Avantages
 - The environmental problem : cyclo olefin polymer versus polylactic acid
- > Our results with polylactic acid
- > Conclusions and perspectives

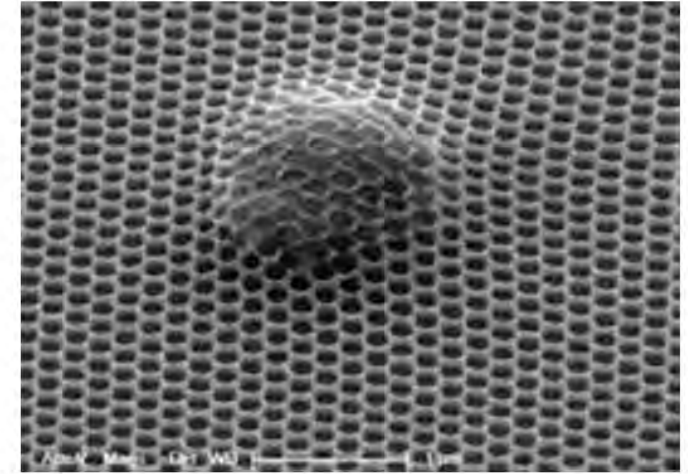
Secondary polymer mold principle



Advantages and a drawback of the secondary polymer mold process

✓ Advantages

- ✓ In UV imprint, the original mold does not need to be transparent (silicon OK)
 - ✓ The original mold is preserved (no hard/hard contact)
 - ✓ Fewer non-uniform print issues
 - ✓ Easier demolding
 - ✓ No polarity reversal (what was protruding remains protruding)
- But : with zeonor[®], use of petro-based and non-degradable disposable polymer materials



Pattern printed on a contaminating particle on the substrate

Zeonor® petrosourced non biodegradable



Polymer with an alicyclic structure in its main chain produced by the polymerization of cyclo olefin

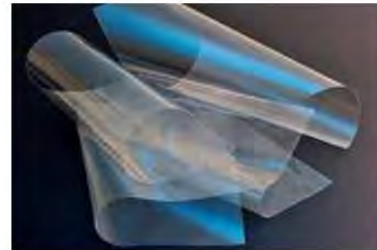
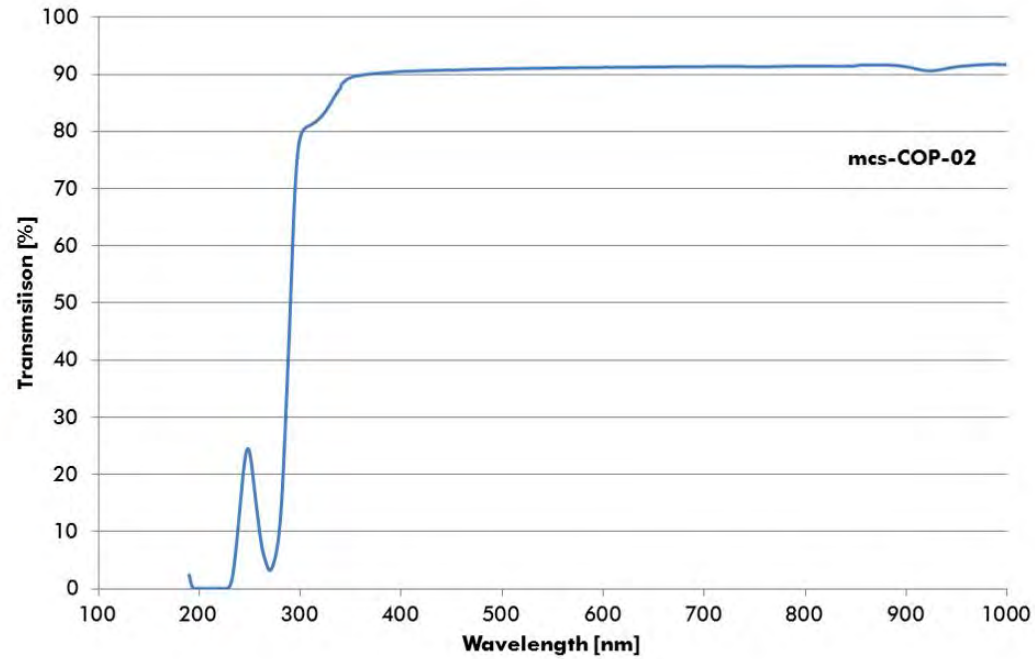
(C1CC(R1)CC(R2)C1)n
ZEONEX®
ZEONOR®

C1=CC(R1)C(R2)C1 (NB) $\xrightarrow{\text{ROMP}}$ (C1CC(R1)CC(R2)C1)n (ROP) $\xrightarrow{\text{H}_2}$ (C1CC(R1)CC(R2)C1)n (COP)

* R1 and R2 are non-polar groups

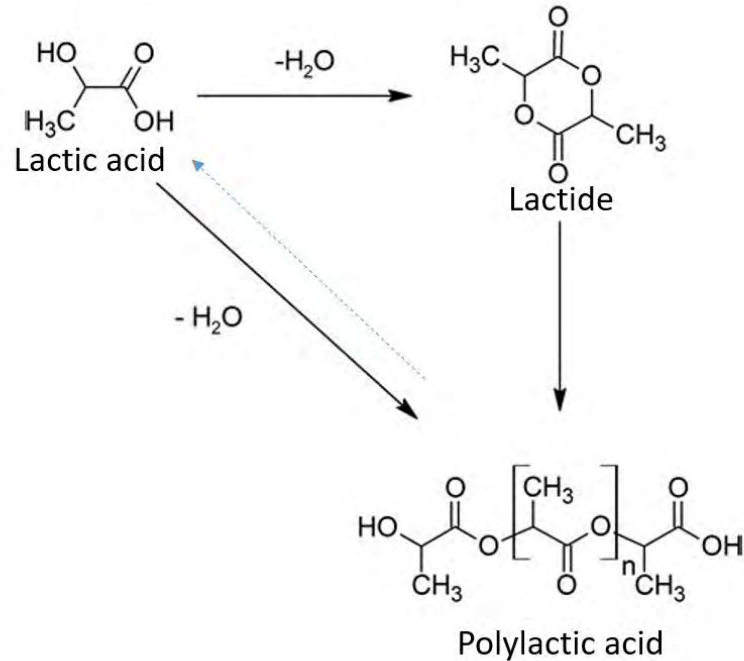
Manufacturing films with the sheet extrusion process

ZeonorFilm™



Polylactic acids : biosourced, biocompatible, biodegradable polymer

Lactic acid : endogenous molecule

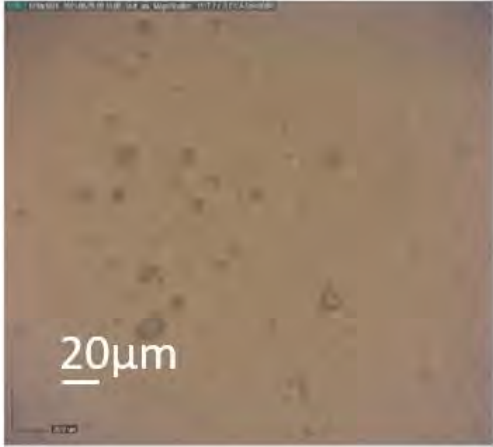


Peer, A., Dhakal, R., Biswas, R., & Kim, J. (2015). Nanoscale patterning of poly (L-lactic acid) films with nanoimprinting methods. Nanoengineering: Fabrication, Properties, Optics, and Devices XII, Proc. of SPIE 2015 Vol 9556, doi.org/10.1117/12.2188888

Farahani, A., Zarei-Hanzaki, A., Abedi, H. R., Tayebi, L., & Mostafavi, E. (2021). Polylactic acid piezo-biopolymers: Chemistry, structural evolution, fabrication methods, and tissue engineering applications. Journal of Functional Biomaterials, 12(4). https://doi.org/10.3390/jfb12040071

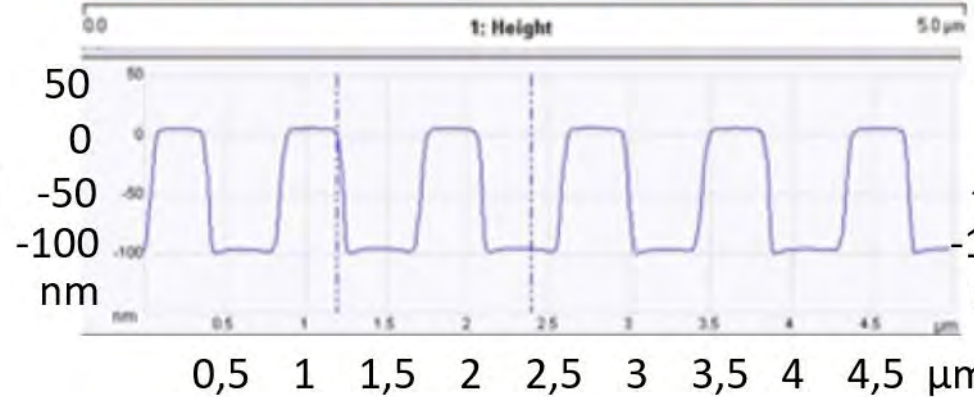
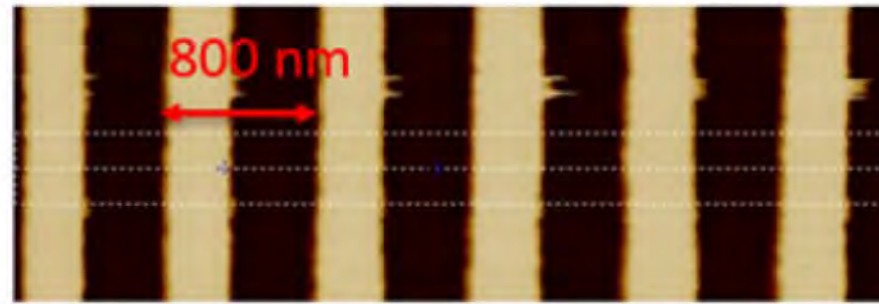
First tests on a commercial 50 μm thick PLLA film

- Numerous microscale round shape defects on the commercial film before imprint
- Numerous ~ 100 nm defects on the secondary mold after imprint

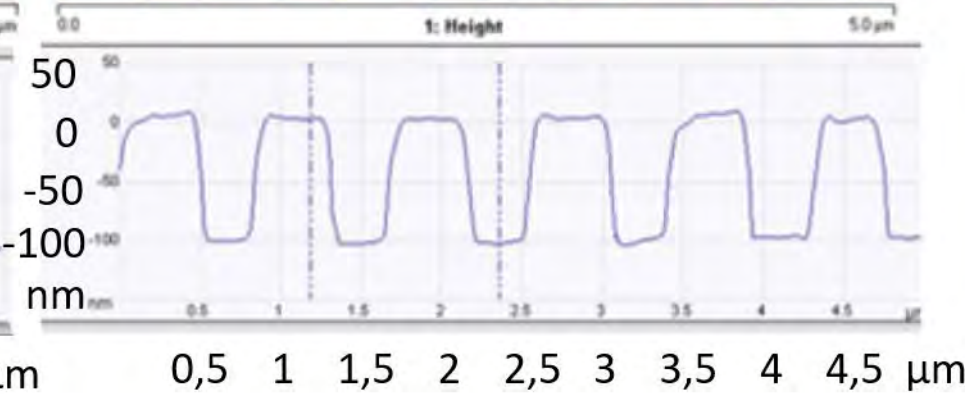
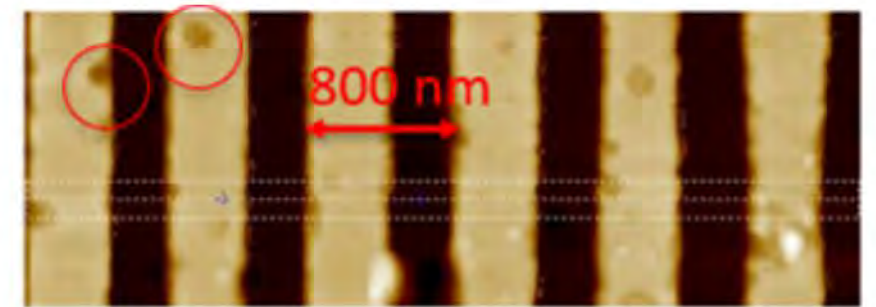


Optical micrograph of the PLLA commercial Goodfellow film, thickness 0.05 mm

AFM of silicon mold



AFM of replica in PLLA film



Calendering of commercial PLA pellets



PLA pellets LX530
Corbion

Introduction
of PLA pellets

PLA 165 °C
Heating and
mixing

Extrusion of
molten PLA

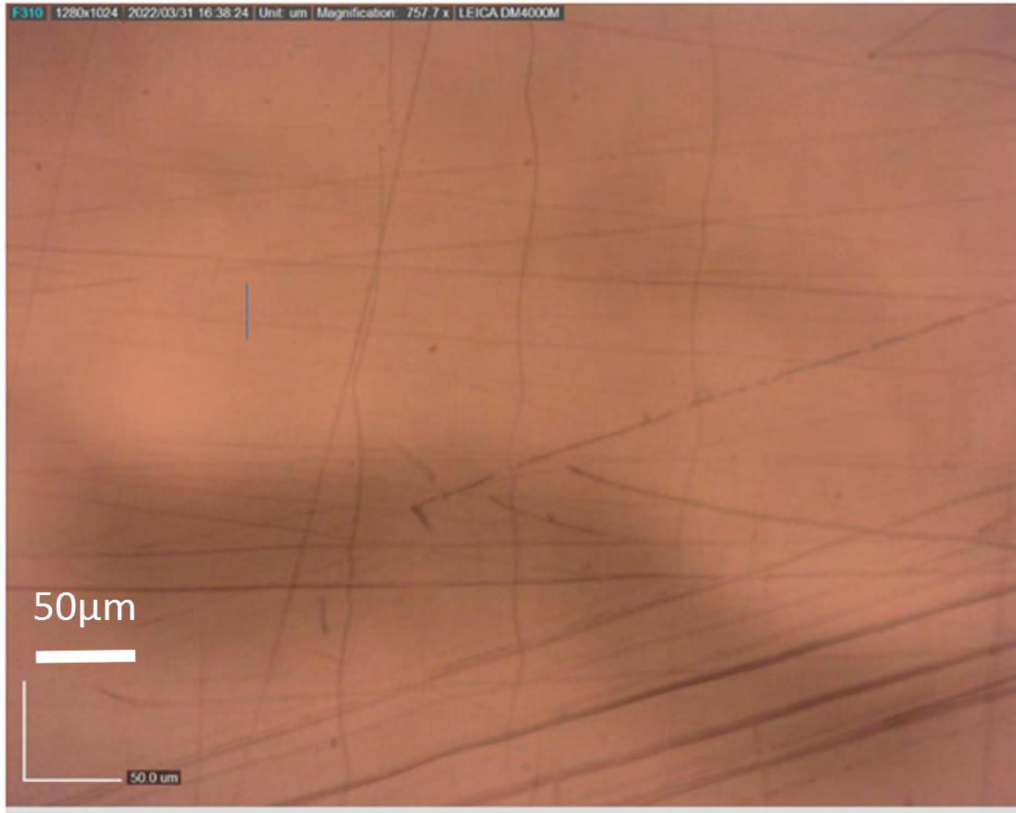


cooling

Winding
of the
PLA film

Laboratoire de Chimie Agro-industriel; Toulouse

Observation of the PLA calandered ~200 μ m thick film



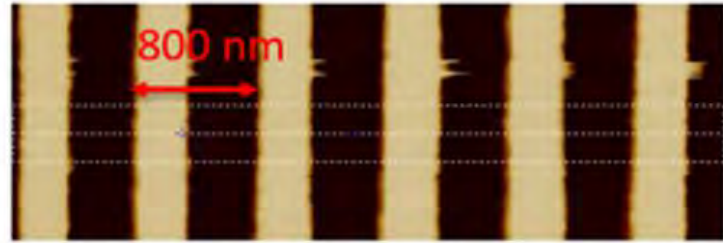
Optical micrograph of the calandered PLA film

- No microscale round shape defects
- But grooves from the cooling roll can be seen on the film
- Much larger stripes millimeter size can be seen if the rolls speed is not adapted

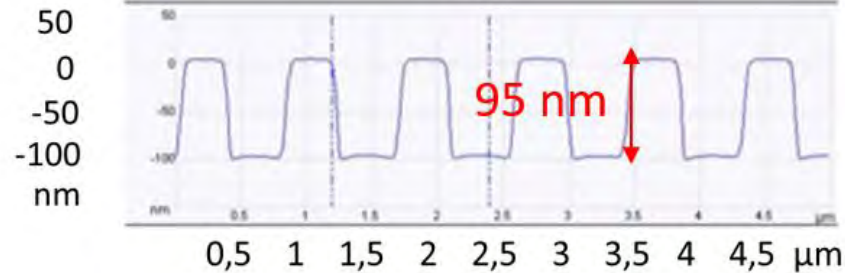
A) Thermal imprint of PLA film

AFM

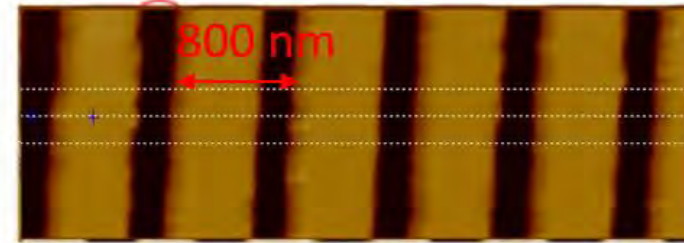
Silicon mold



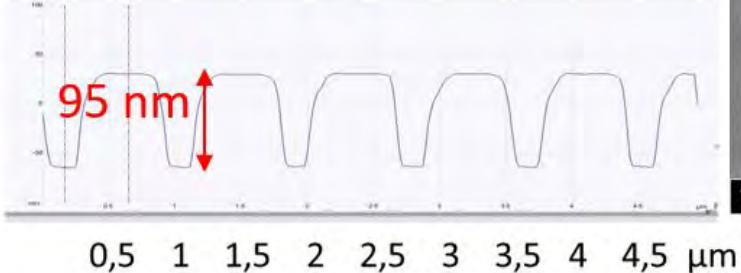
00 t: Height 50 μm



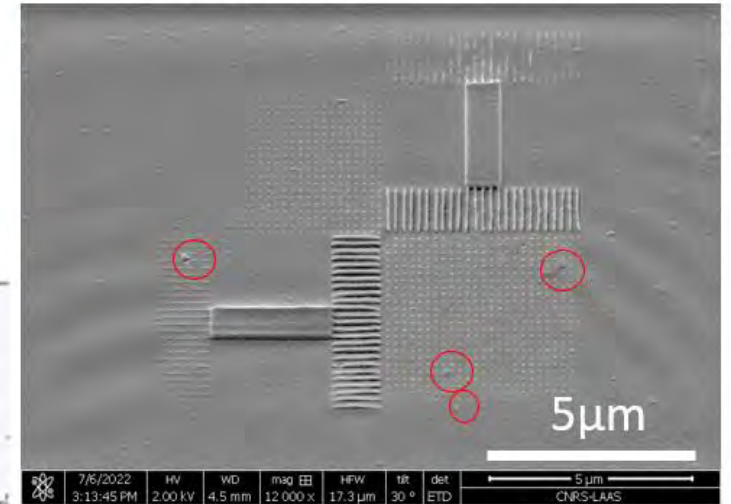
Imprinted PLA film



00 t: Height 50 μm

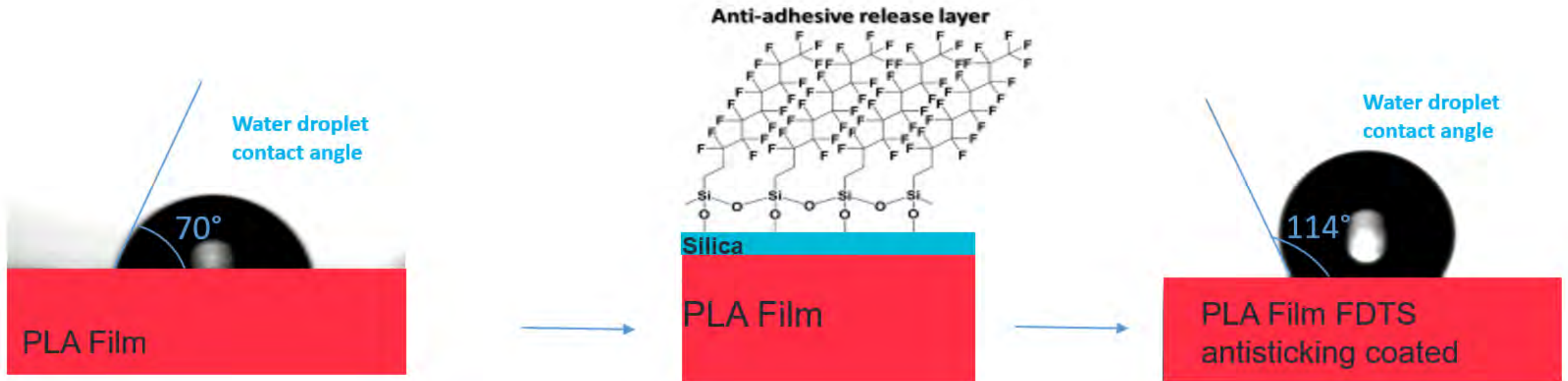


SEM of the calandered and nanoimprinted PLA film



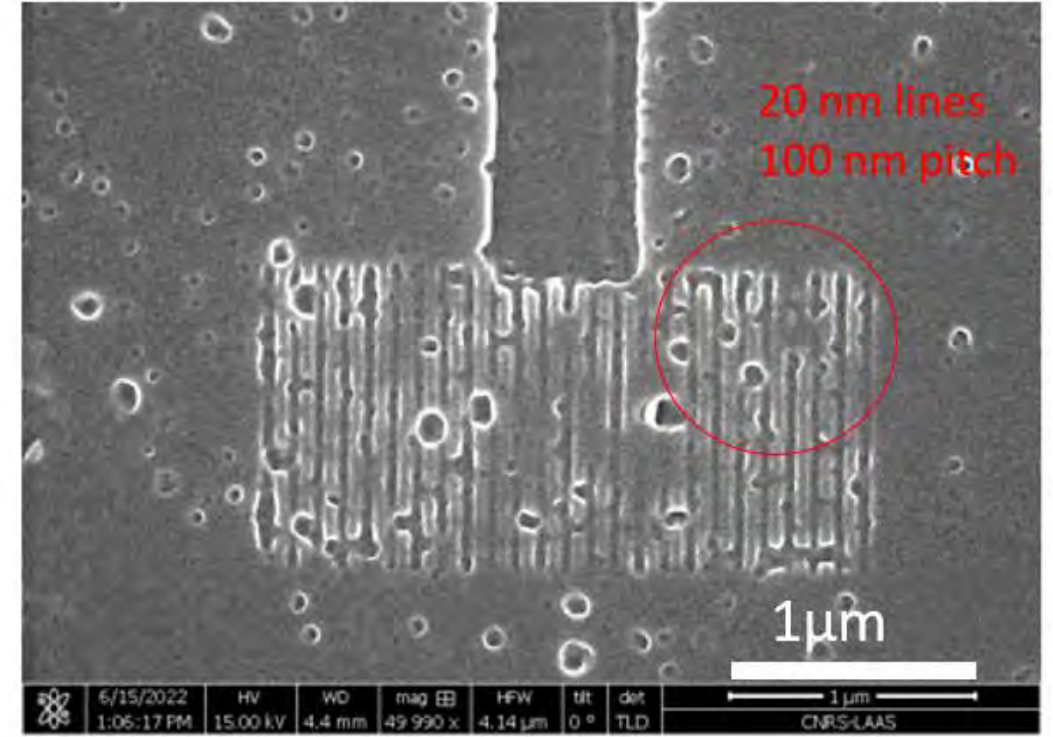
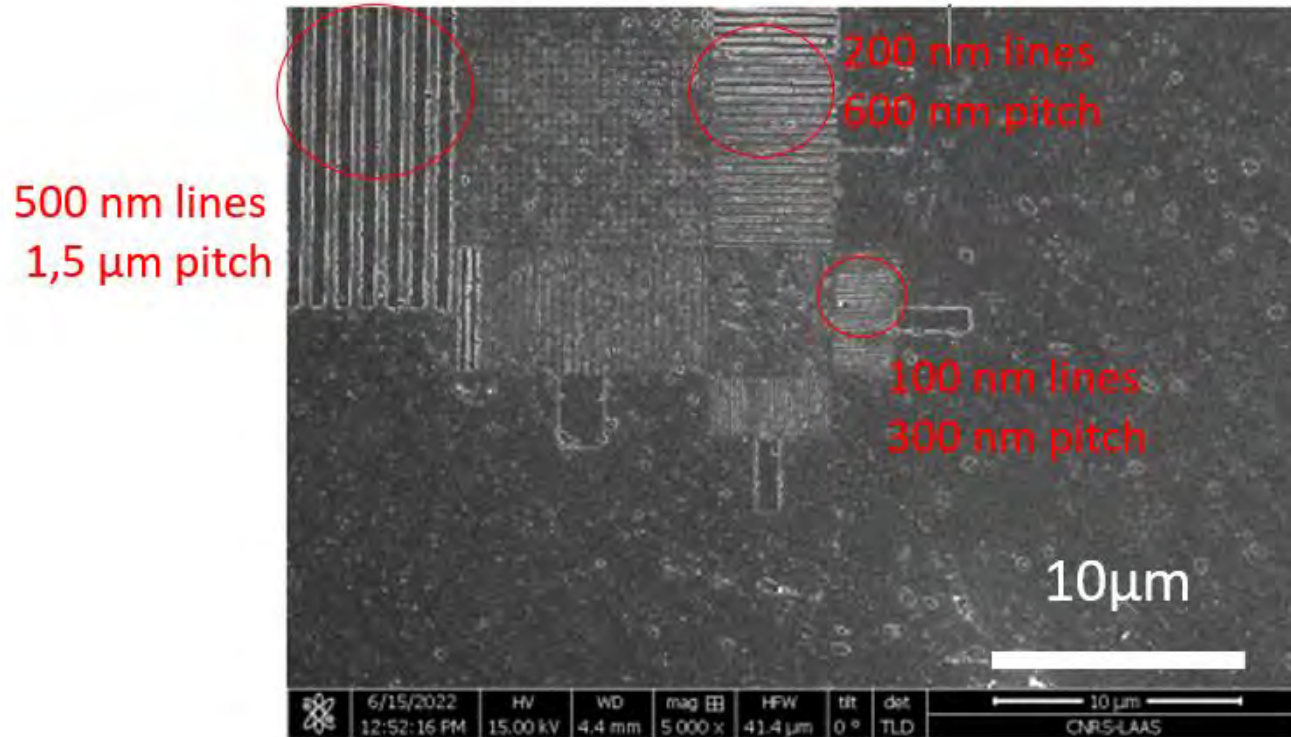
- > Accurate pitch and depth
- > Inverted structures
- > Some Defects

Antisking surface treatment on the PLA secondary mold



- > 1) Thin silica layer deposit
- > 2) FDTs anti sticking layer deposit on the silica

B) imprint of UV resist with PLA secondary mold



SEM of UV imprinted resist thanks to PLA secondary mold

Conclusions and perspectives

	Zeonor®COP	Goodfellow PLLA film	Calandered PLA film
Nanoscale printing hability	yes	yes	yes
antisticking needed for UV printing?	no	yes	yes
Milliscale defects	no	no	Yes, but improvable
μscale defects	no	yes	no
Nanoscale defects	no	yes	Yes, improvable ?
biosourced	no	yes	yes
biocompatible	yes	yes	yes
biodegradable	no	yes	yes

- The films can certainly be used in some needs for biology
- Further studies including calendering improvement or needed to see if ok for micronanotechnology