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Extrusion-based 3D printing of novel silicone elastomers with advanced properties.

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Rubber in Engineering

I·M3

Introduction

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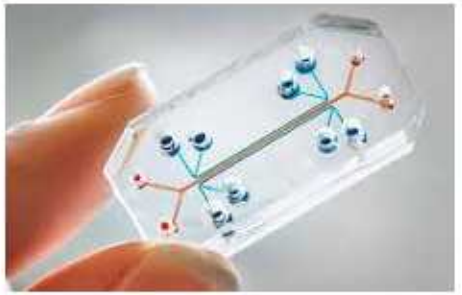
Silicone elastomers are often used as matrix for:

- Medical implants
- Microfluidic microfabrication
- Advanced *in vitro* cell culture models



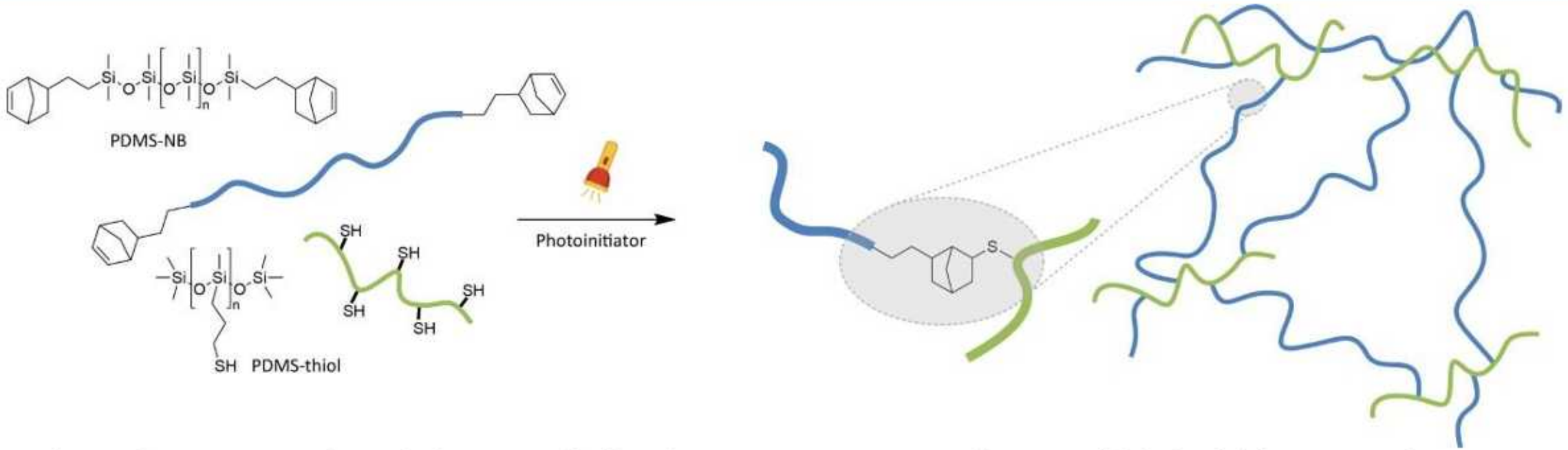
- Most common used silicone for these applications: SYLGARD 184
- Takes 35 minutes at 100°C or 2 days at RT to cure

UV curable silicone elastomers useful in the fabrication of complex microfluidic and organ-on-chip devices
Advantage: fast processing point of view,
Disadvantage: requirement of an inert atmosphere.

Our research focused on:

- **Development UV curable PDMS matrices that are tolerant to oxygen with fast curing kinetics**
- Optimisation of formulations to achieve self-supporting **extrusion-based 3D printable inks**, with a single UV cure method, print organ-on-chip devices

Novel thiol-ene silicone system



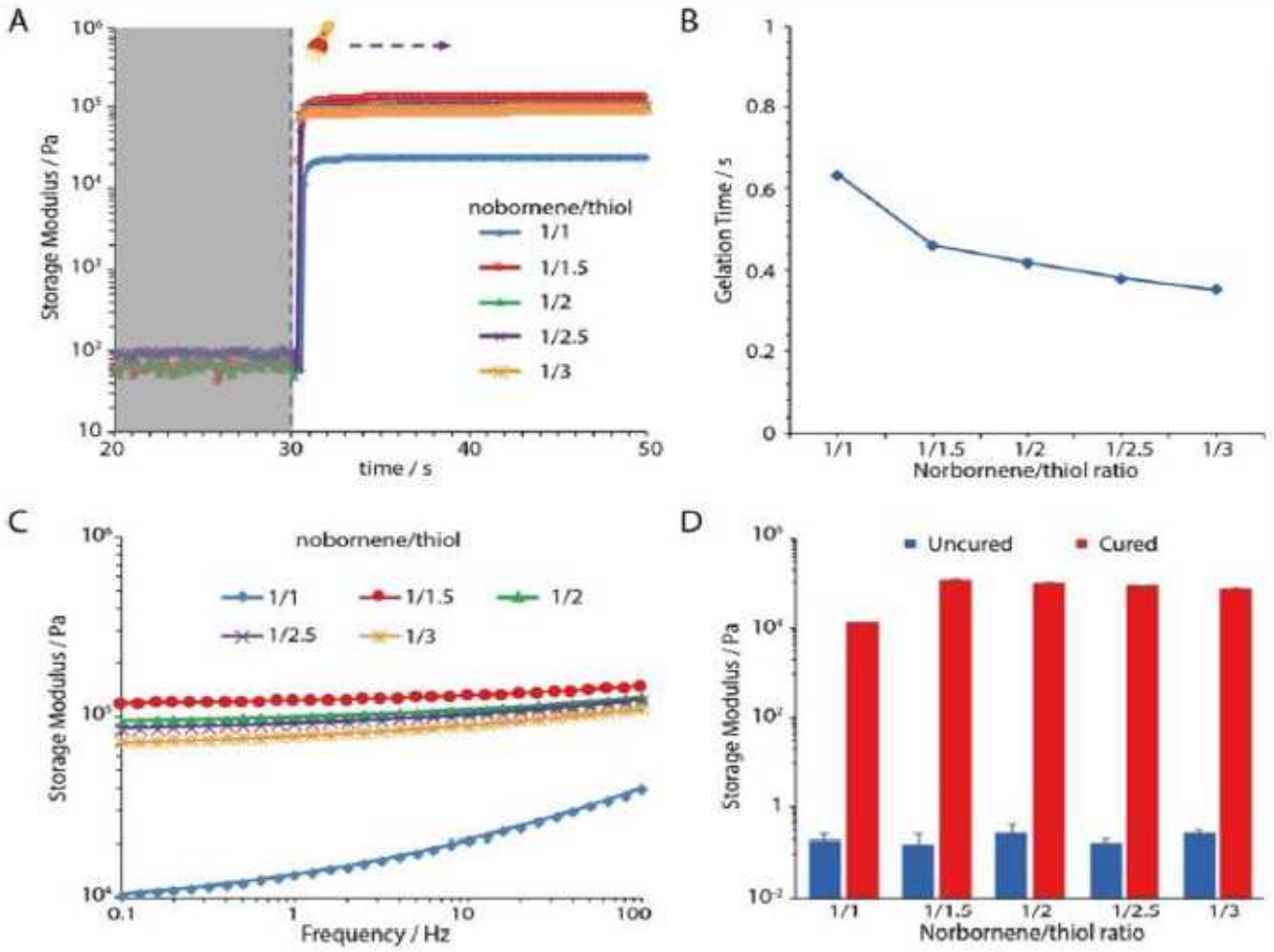
Schematic representation of photocrosslinking between PDMS-NB and PDMS-thiol *via* thiol-ene reaction.

A novel thiol-ene silicone system based on:

- a PDMS bearing terminal norbornene groups (PDMS-NB)
- a highly functionalised thiol PDMS (PDMS-thiol)
- to achieve particularly **fast cross-linking** with **very limited oxygen inhibition** even in ambient atmosphere, without requirement for deoxygenation.

Nguyen et al. (2021). Manuscript Accepted , ACS Publications

Impact of norbonene to thiol ratio



(A) *In-situ* photorheology.

(B) Gelation times as a function of norbornene:thiol ratios.

(C) Frequency sweeps of cross-linked PDMS. Frequency dependency of moduli as function of thiol:alkene stoichiometry.

(D) Comparison of G' of the resins before UV and cross-linked silicones.

- ❖ Fast curing speed (less than 1s)
- ❖ Excellent tolerance to the inhibition by oxygen.

Impact of norbornene:thiol molar ratio on the kinetics and the mechanical properties of cross-linked PDMS network *via* thiol-ene chemistry.

Nguyen et al. (2021). Manuscript Accepted , ACS Publications

Rheological analyses

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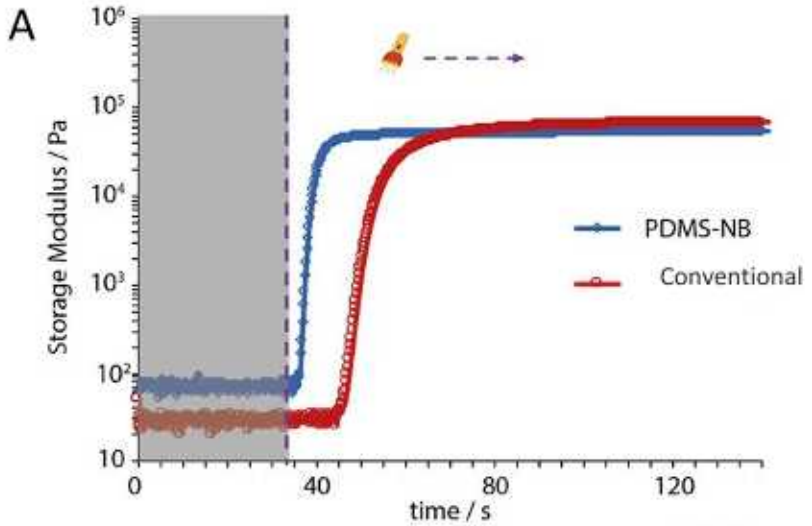
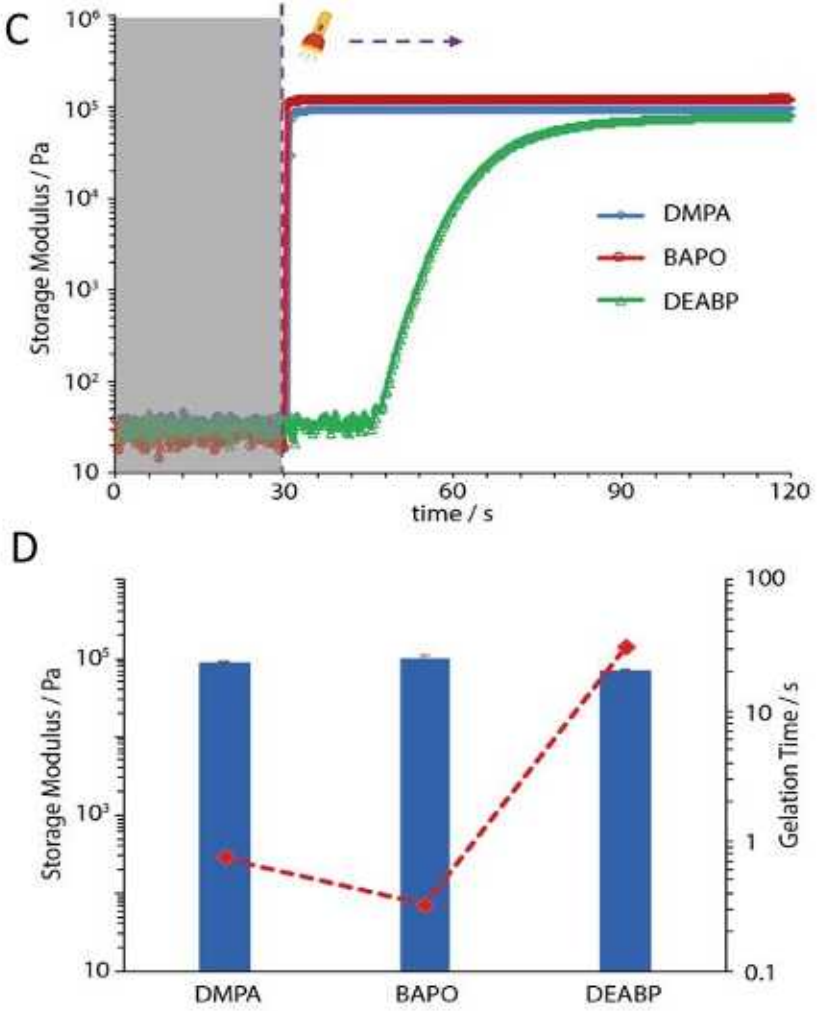
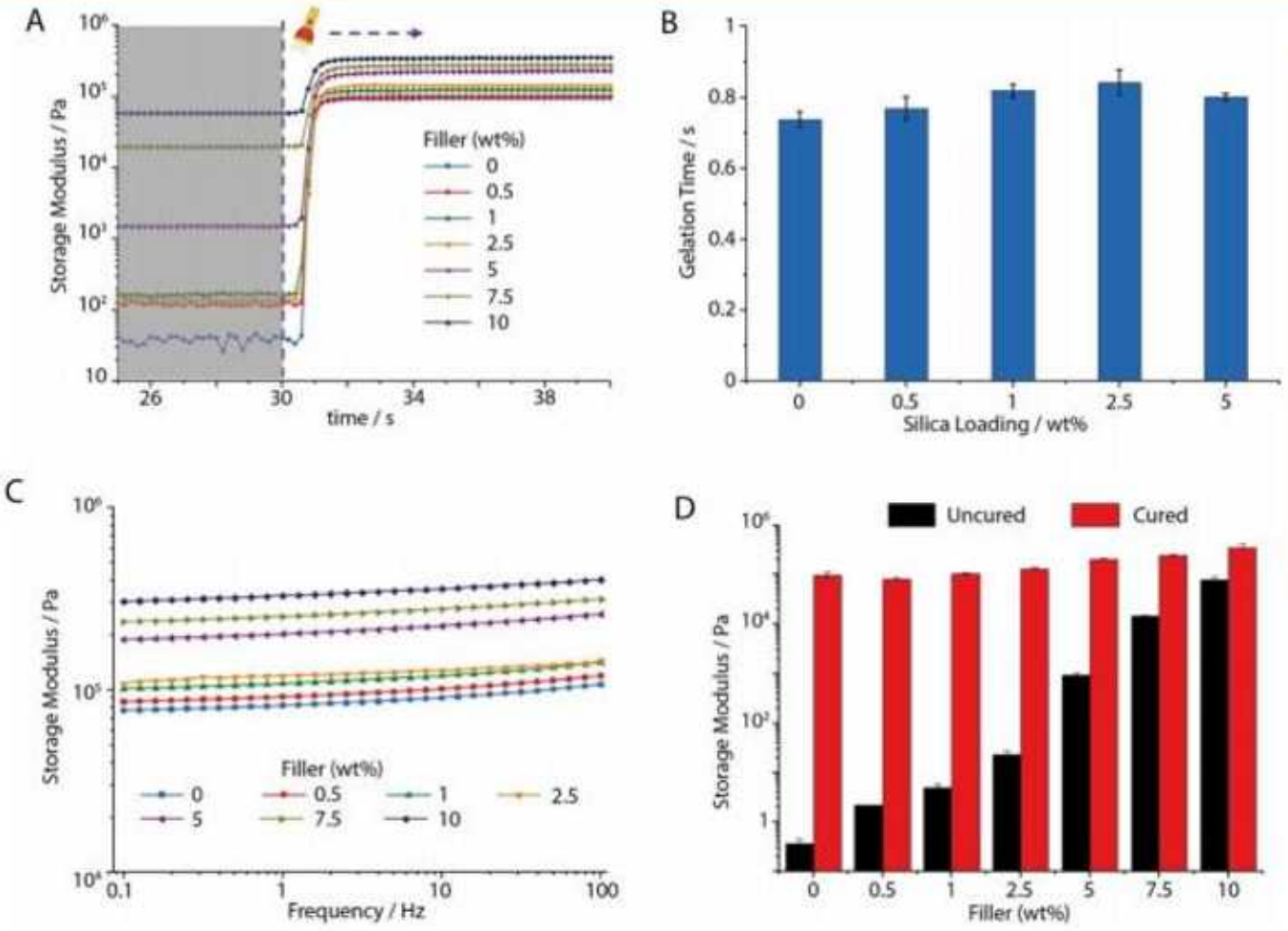


- Faster curing speed (mostly less than 1s)
- Excellent tolerance to the inhibition by oxygen.
- Capable to achieve a complete cure without any oily residues on the surface of the elastomer
- Compatible with different photoinitiating systems.



Impact of nanosilica fillers



Impact of nanosilica fillers on the curing kinetics and silicone network's properties.

(A) *In-situ* photorheology.

(B) Gelation times of unfilled and different filled silica/silicone composites.

(C) Frequency sweeps (oscillation amplitude of 1% strain) of cross-linked nanocomposite.

(D) Comparison of G' of the resins before UV irradiation and the cross-linked nanocomposite.

Thiol-norbornene silicone composites filled with fumed nanosilica were investigated for application in 3D printing.

Nguyen et al. (2021). Manuscript Accepted , ACS Publications

Extrusion 3D printing

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Multi print-heads

RegenHU 3D Discovery printer

Material is extruded by air pressure or mechanical force
Continuous printing in layer-by-layer manner

Advantages

- Print directly on substrates (cover slips, 6 well plates).
- Multiple materials: heterogenous properties, incorporation of different stiffnesses
- UV curing (integrated UV lamp of the 3D DiscoveryTM (360 mW, PH5)
- One step manufacturing process
- Sterile conditions (within bio hood)

Quantification of shape fidelity, filament bridging

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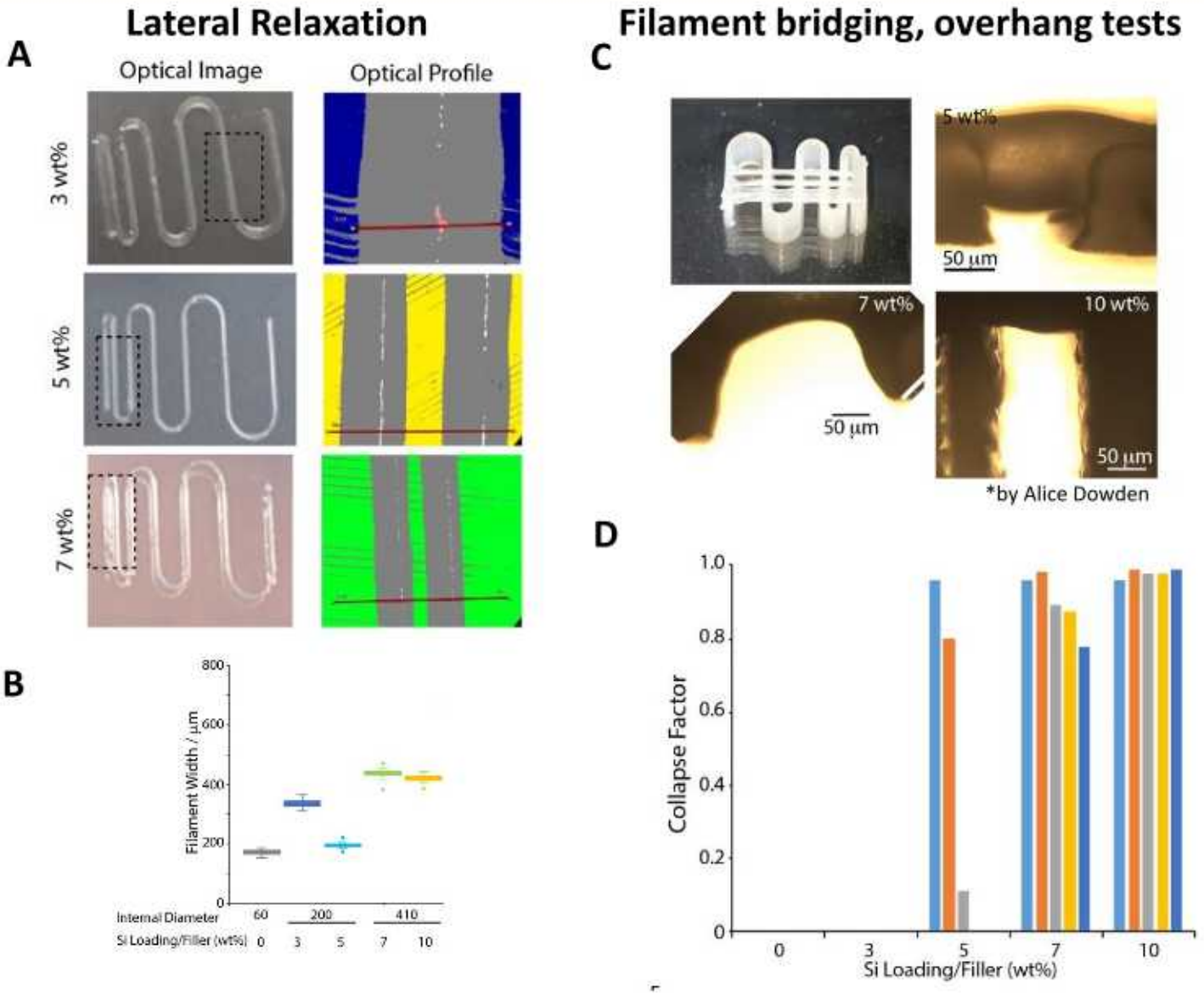
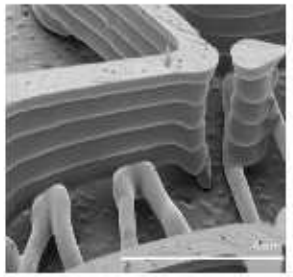
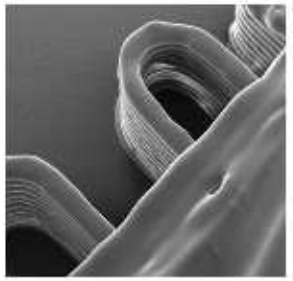


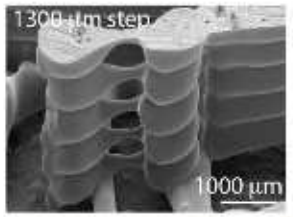
- Retain very fast cure speed (only ~200ms slower than pristine resin).
- Comparable mechanical properties of cross-linked silicone networks.
- Good resolution of 3D printing with the ability to print the overhanging part.

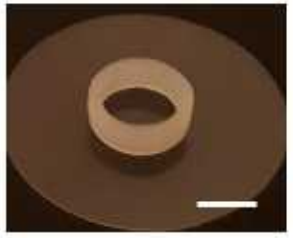
Extrusion 3D printing

*by Alice Dowden









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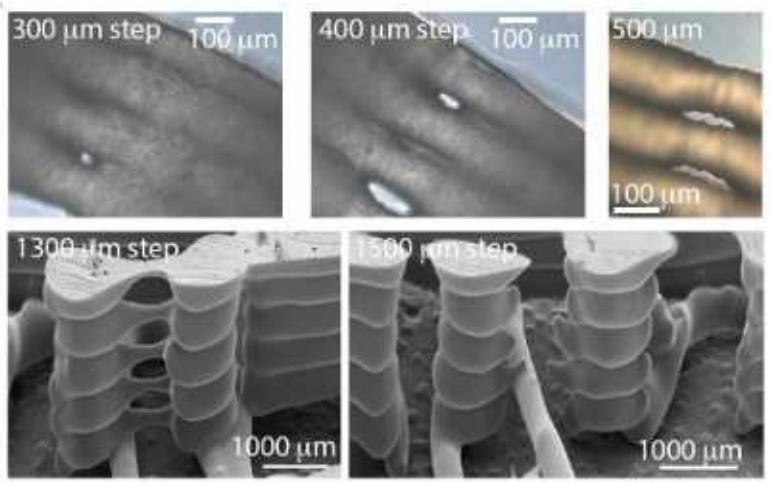

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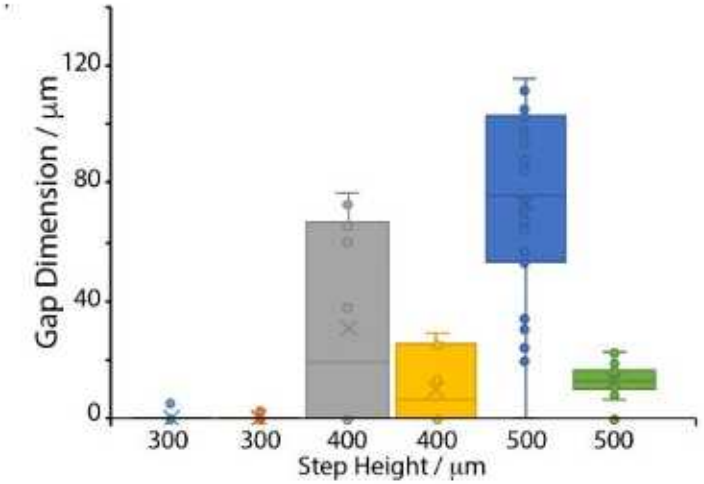

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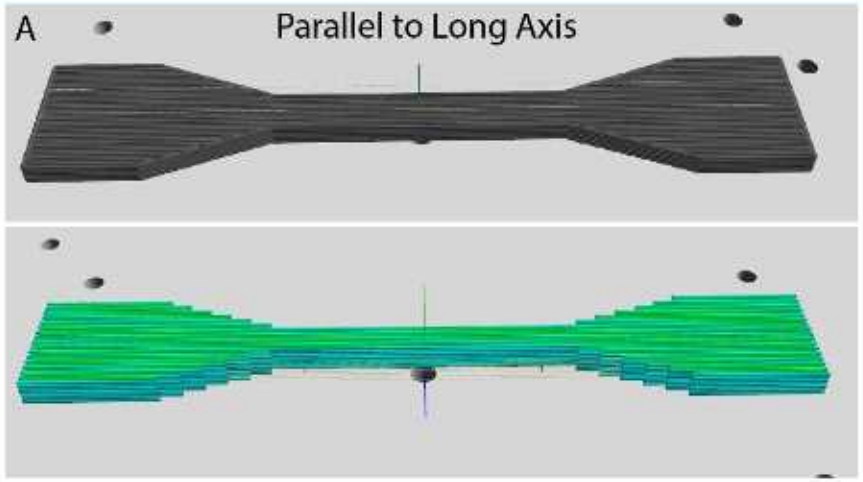
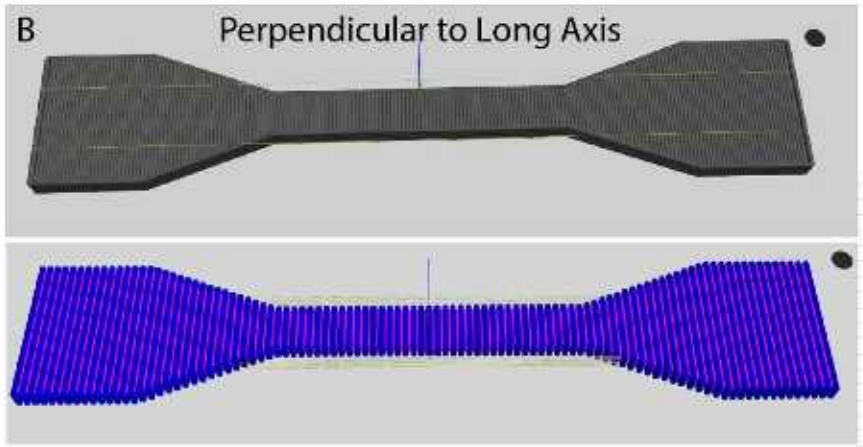
Scale bar: 3mm

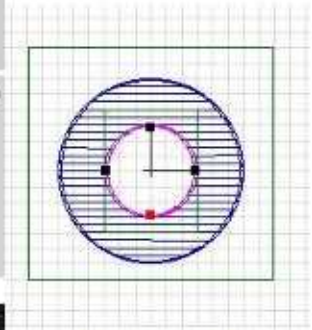
Extrusion 3D printing

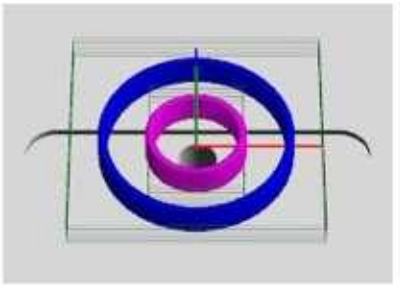


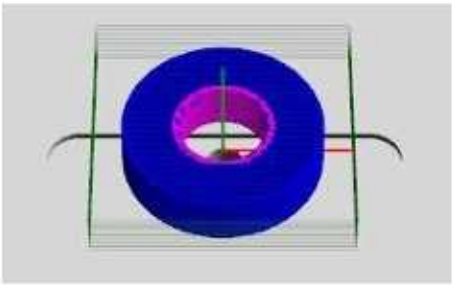


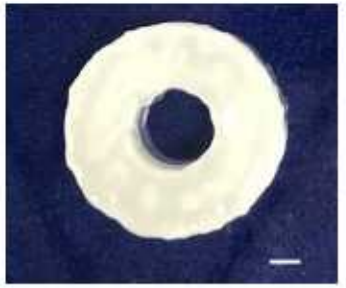
*by Alice Dowden

- Filament orientation
- Dual printing
- Ability to multi-print different materials for complex designs.
- Effectively tailored mechanical properties of silicone network.
- Good interfacial adhesion between printing materials.









Scale bar: 2mm

Actuation of 3D printed devices

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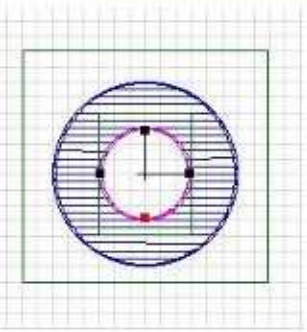
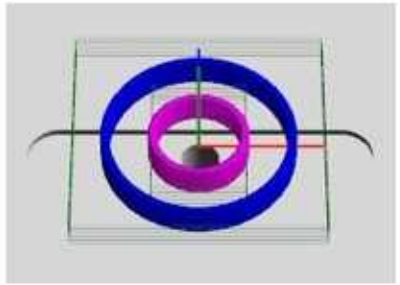
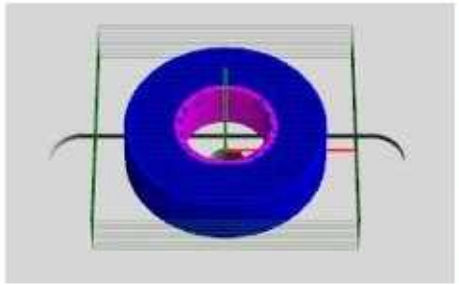
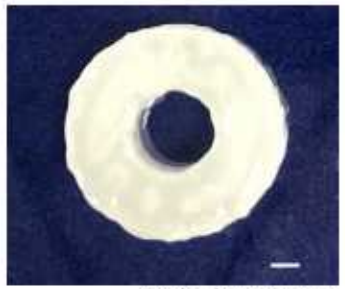
3D printing silicones with **different stiffness** ⟶ **Actuation** of devices via **pneumatic systems**



Stiff PDMS
Soft PDMS
UV light







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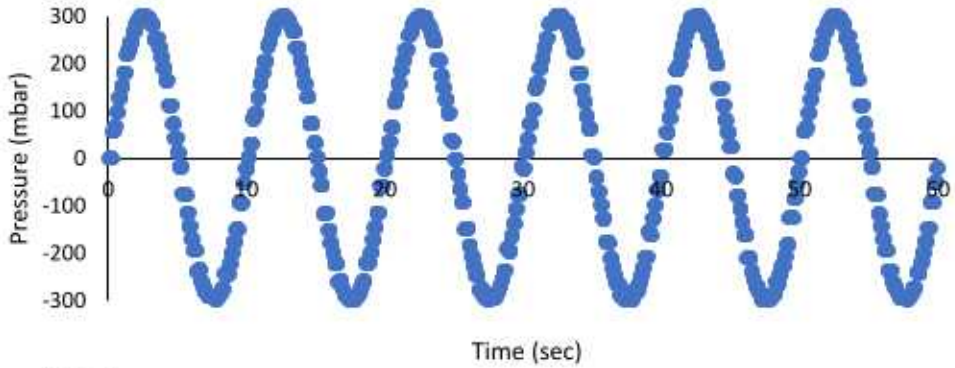

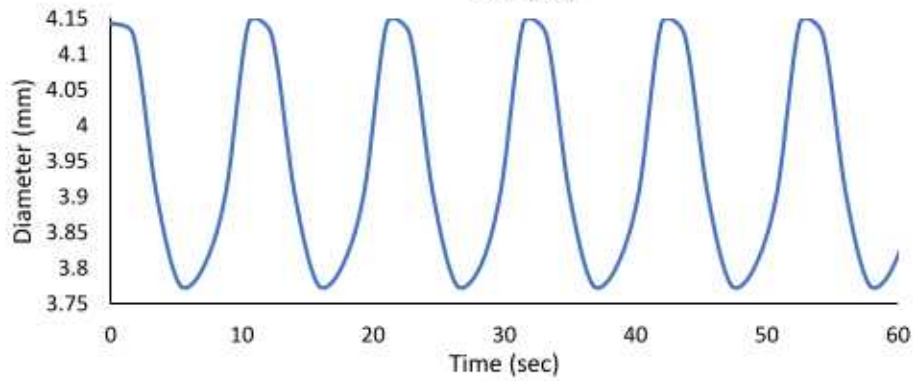

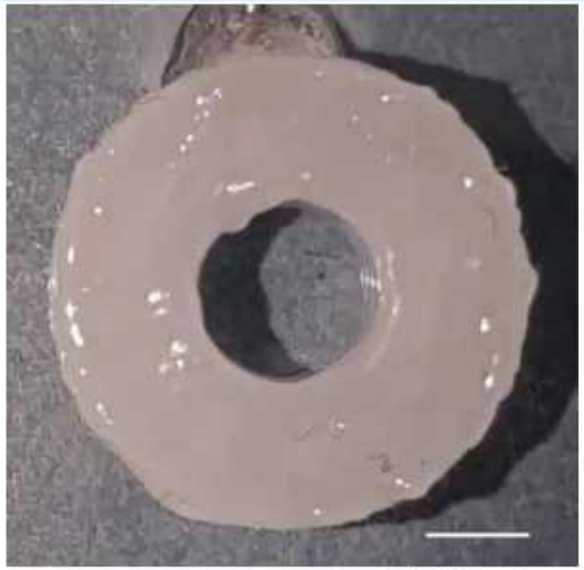

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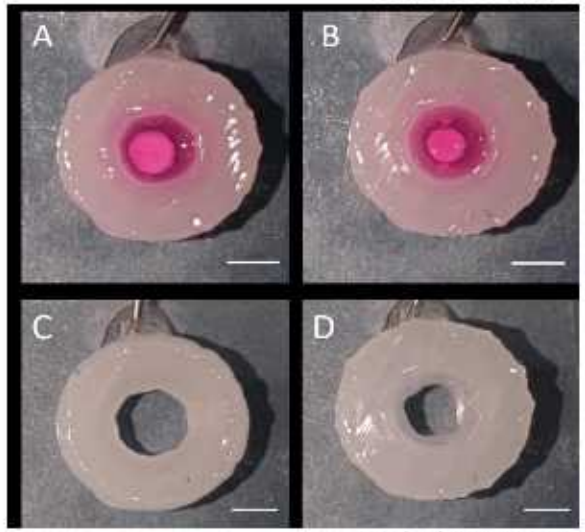
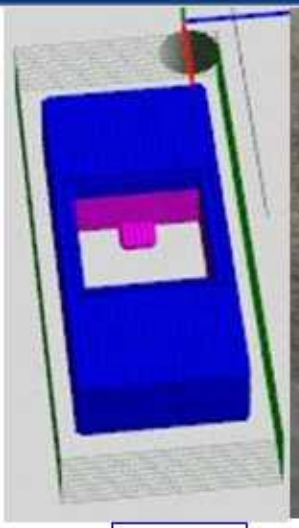
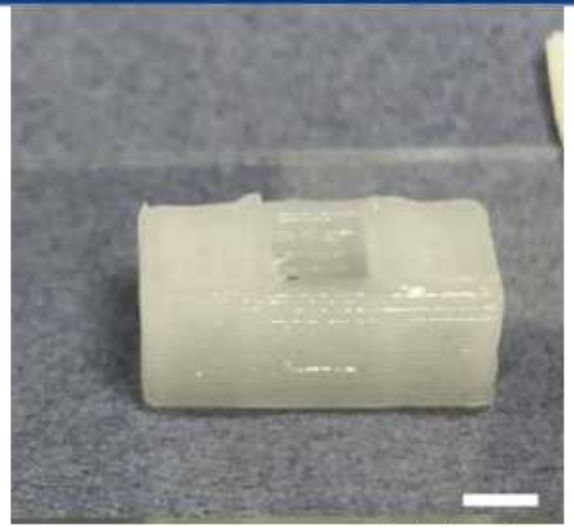


Scale bars: 3mm

ELVEFLOW
PLUG & PLAY MICROFLUIDICS

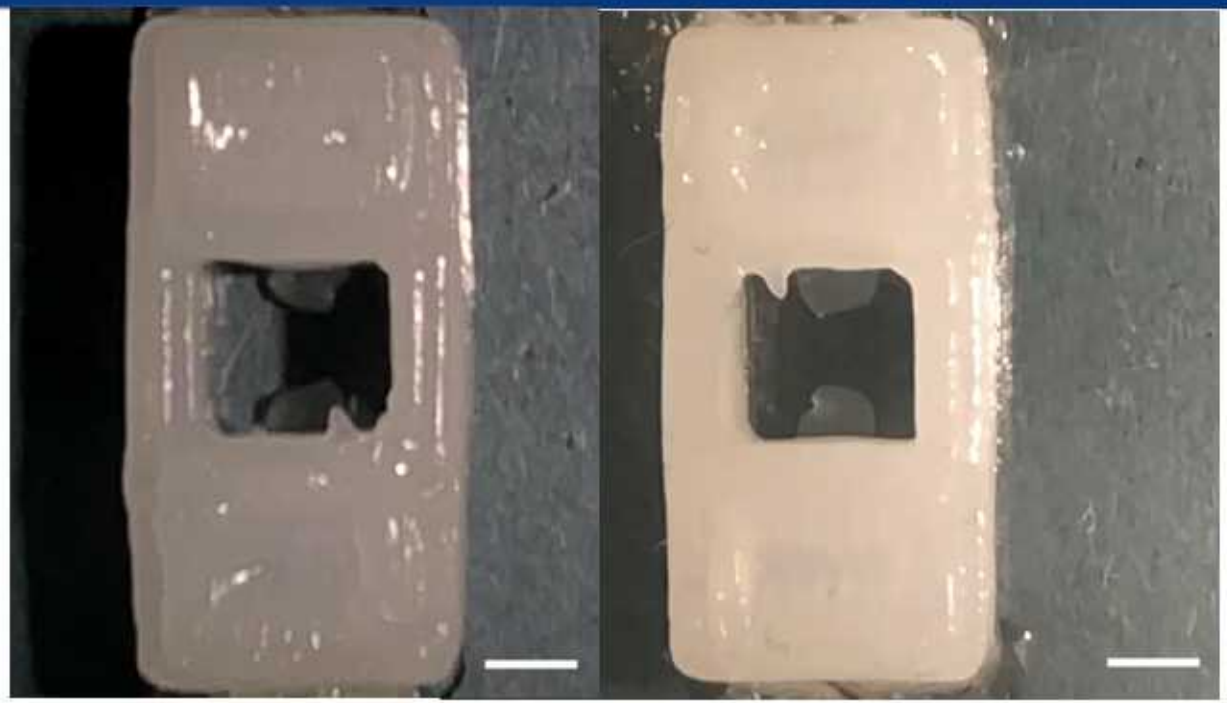
Actuation of 3D printed devices





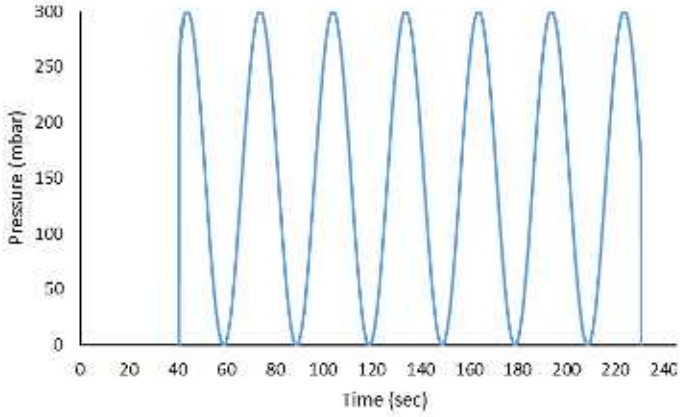
Scale bars: 3mm

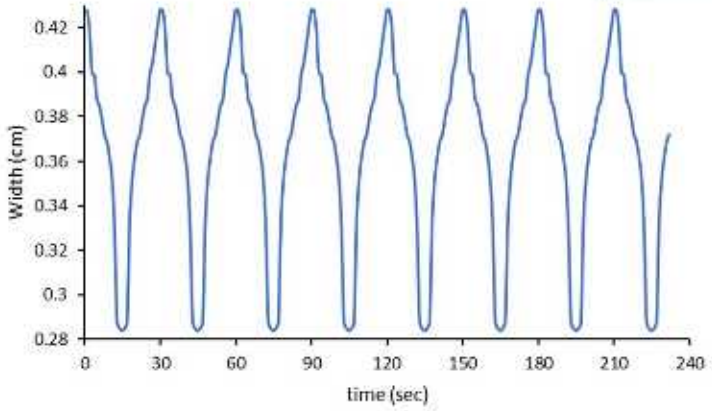
Stiff PDMS
Soft PDMS
UV light



Scale bar: 2mm

Scale bar: 2mm





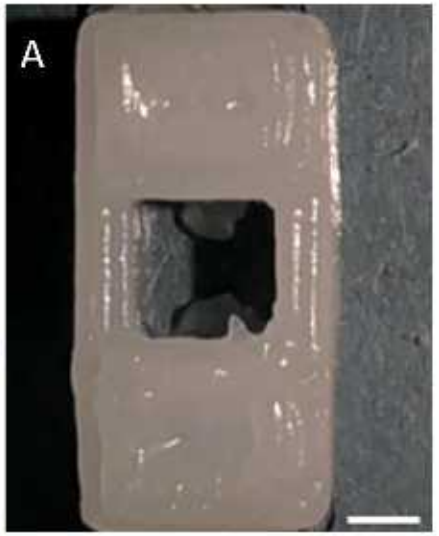
Pressure: 0-300mbar

Pressure: 0-1000mbar

ELVE FLOW
PLUG & PLAY MICROFLUIDICS

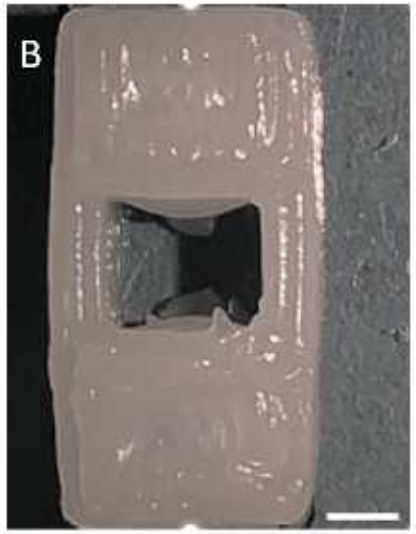
Bioapplications

Scale bar: 5mm

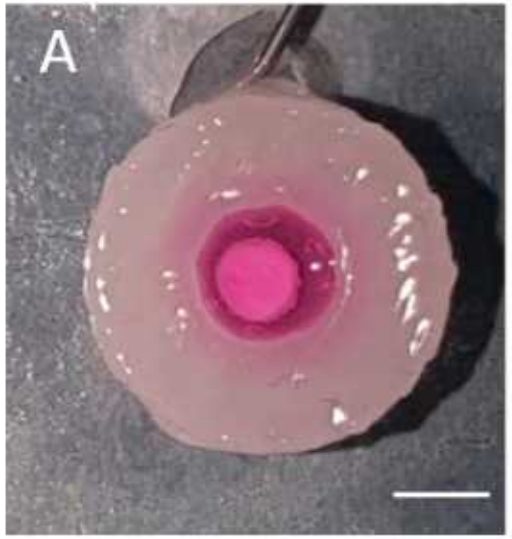


At rest

Scale bars: 3mm

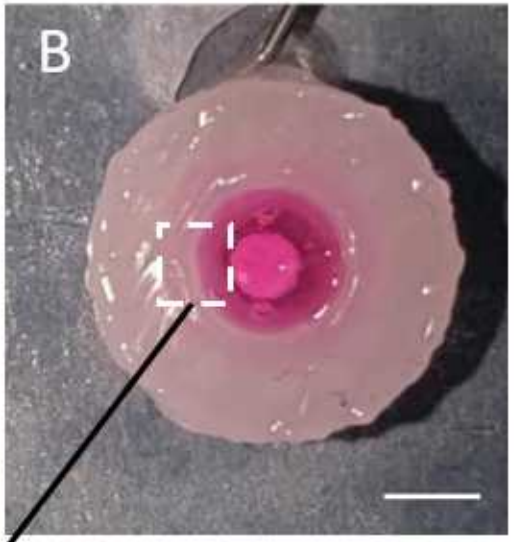


300mbar Pressure



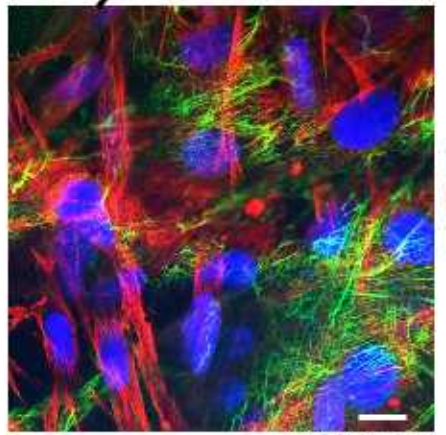
At rest

Scale bars: 3mm



300mbar Pressure

This actuation will allow future mechanical cell-stimulation introducing mechanical stresses to an *in vitro* tissue in 3D.



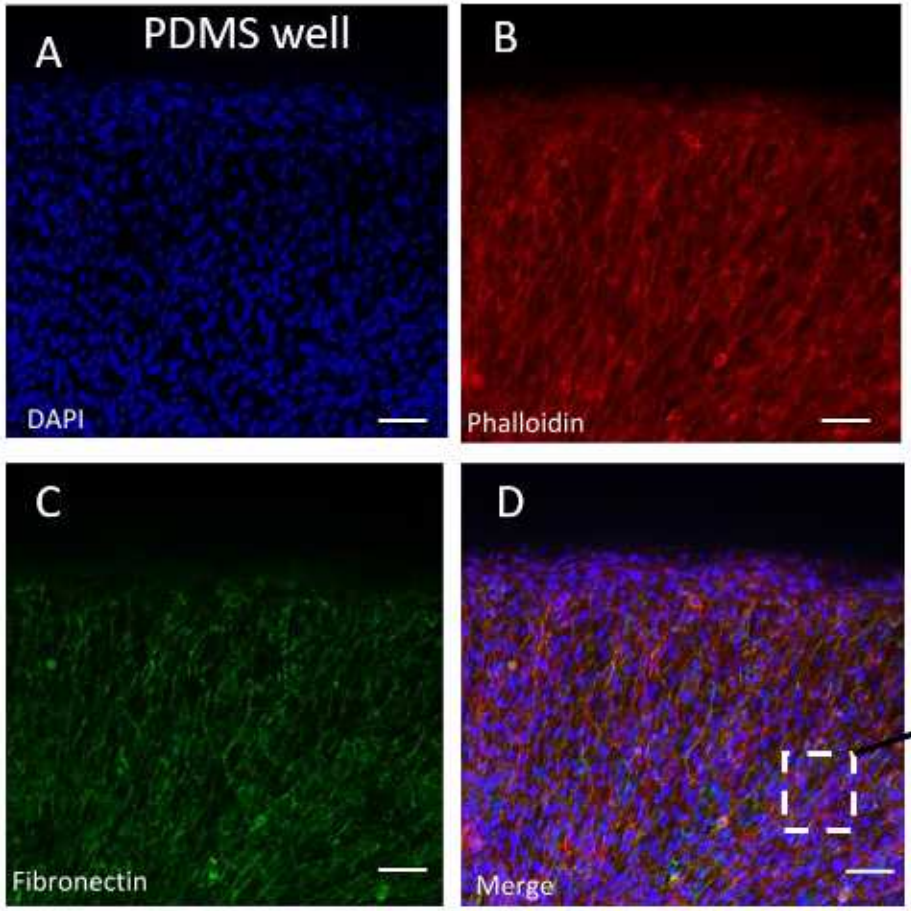
DAPI
Phalloidin
Fibronectin

Scale bar: 10 µm

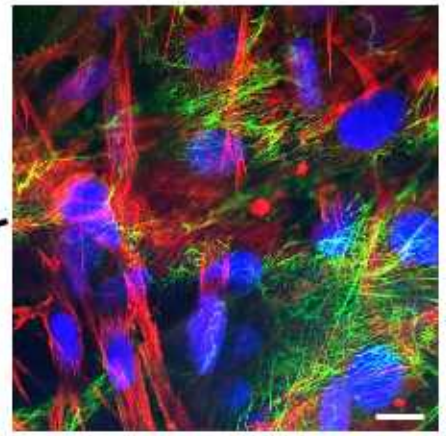
Magnification:63x

- Mature fibronectin deposition
- Clear fibers.

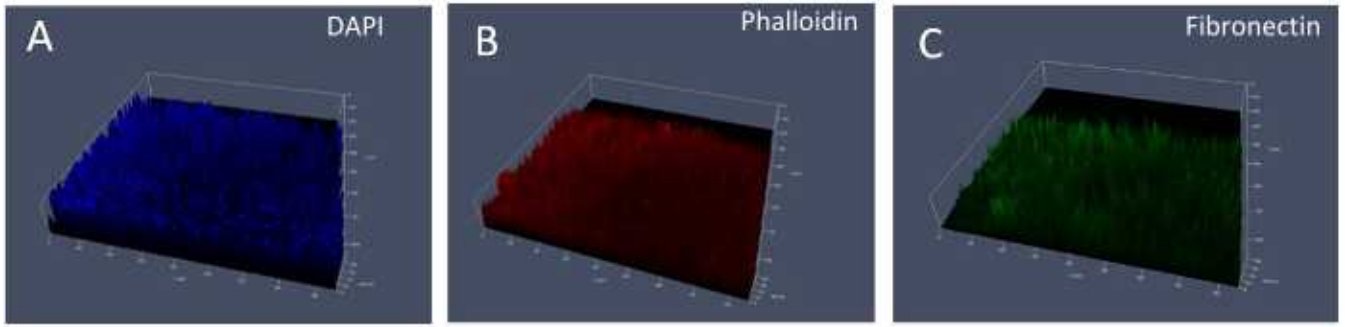
Bioapplications



Scale bars: 100 µm

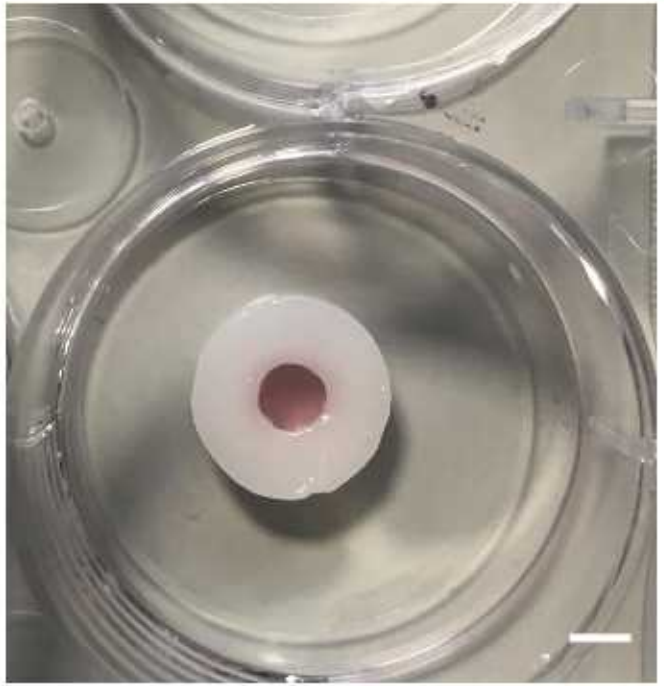


Scale bar: 10 µm



Cytocompatible

DAPI
Phalloidin
Fibronectin



Scale bar: 3mm

HCA2 in fibrin gels

Conclusion

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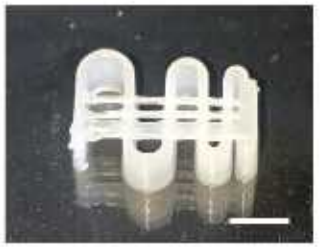
- Thiol-ene silicone systems with excellent control of kinetics and mechanical properties in ambient atmosphere.
- Excellent tolerance to oxygen, ultrafast curing process.
- Successful printing of thiol-ene silicones **in air**, no need of inert atmoshere
- Excellent candidate for **extrusion 3D printing**: viscosity, rapid crosslinking, shape fidelity, adhesion to glass slides or petridishes, excellent cured mechanical properties.
- Possibility to print complex 3D structures, **organ-on-chip devices**
- Possibility to **actuate these 3D structures,** future **mechanical cell-stimulation**



Scale bar: 5mm

Scale bar: 3mm

Thanks

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SEMS

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Barts and The London

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thank you

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