Additive Manufacturing of Ceramics using Preceramic Polymers

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Why Preceramic Polymers ?

- PPs usually contain Si atoms in the backbone (carbosilanes, silazanes, siloxanes → *SiC*, *SiNC*, *SiOC*)
- Ceramization occurs through the elimination of organic moieties. Thermal (*pyrolysis*) or non-thermal (*ion irradiation*) processing
- *Nano-structured* Amorphous Covalent Ceramics (β-SiC and C nano-crystals)
- Possibility of adding *inert* or *active fillers* (mullite, cordierite, wollastonite, SiAlON…)
- Possibility of *Plastic Forming* (injection molding, extrusion, resin transfer molding, melt spinning, coating from solution…)
- Interesting/unique properties (high microstructural stability, high creep resistance, high viscosity, high modulus, high hardness, high wear resistance, high oxidation resistance, high refractoriness, high chemical durability, electronic conduction (SiCN- or C clusters), luminescence (C, Si, SiC nano-clusters)

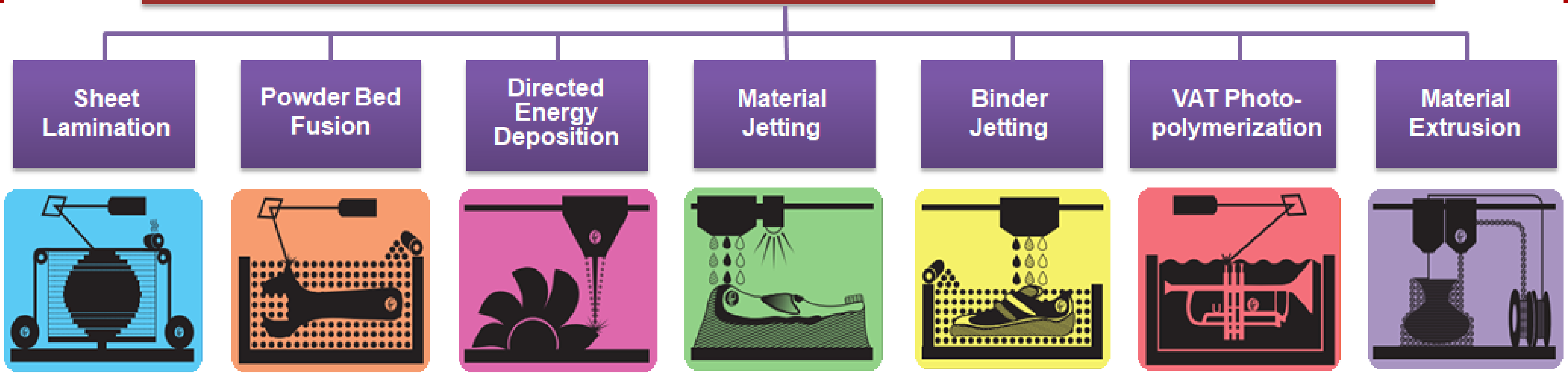
Top ranking paper published in JACerS

The ***Journal of the American Ceramic Society*** has the #1 cited paper published in the past 10 years in the Materials Science, Ceramics category

Polymer-Derived Ceramics:
40 Years of Research and Innovation in Advanced Ceramics
Paolo Colombo, Gabriela Mera, Ralf Riedel, Gian Domenico Soraru̇

P. Colombo et al., J. Am. Ceram. Soc., ***93*** *(2010) 1805*

Additive Manufacturing technologies (ISO/ASTM 52900:2021)



AM Technology	Feedstock (liquid, paste, powder, filament)	Part dimension$ (size that can be produced economically)	Surface (quality of parts, not of single struts)	Printing resolution
Binder jetting	Powder	M-XL	Medium	100 µm
Inkjet printing	Liquid	XS-M	High	10 µm
Laminated object manufacturing	Paste	M-L	Low	100 µm
Direct ink writing	Paste	S-XL	Low	60 µm
Fused deposition modeling	Filament	M-XL	Low	100 µm
Vat photopolymerization	Liquid	XS-M	High	25 µm
Two-photon polymerization	Liquid	XS-S	High	< 1 µm

$: XS = 100 µm; S = 1 mm; M = 10 mm; L = 0.1 m; XL = 1 m

- Both Direct and Indirect AM technologies can be used with PPs

P. Colombo, J. Schmidt, G. Franchin, A. Zocca, J. Günster, Bull. Am. Ceram. Soc., ***96*** *(2017) 16*

R.P. Chaudhary, C. Parameswaran, M. Idrees, A.S. Rasaki, C. Liu, Z. Chen, P. Colombo, Prog. Mater. Sci., ***128*** *(2022) 100969*

- **Cross-linking** of the preceramic polymer is necessary before pyrolysis, to retain the shape of the printed component
- High ceramic yield is preferred

Powder vs Liquid-based feedstocks for AM of ceramics

Issues with powder-based feedstocks

1. Very viscous slurries (special DLP equipment required → expensive)
2. Light scattering, penetration depth and index matching (vat photopolymerization)
3. Stabilization of particles in non aqueous-medium is difficult
4. Particle size controls nozzle dimension (DIW) → limit in feature size and surface quality
5. Clogging of nozzle (DIW)

Issues with all liquid-based feedstocks

1. Not all of the potential all liquid feedstocks (preceramic polymers, sol-gel, geopolymers) can be used with every class of AM technology (BJ, FDM, SLS/SLM)
2. The compositional range of the resulting ceramics is rather limited for all but sol-gel-based formulations

Nevertheless, all liquid feedstocks have advantages that can be exploited

Vat photopolymerization of Pure Preceramic Polymers (DLP)

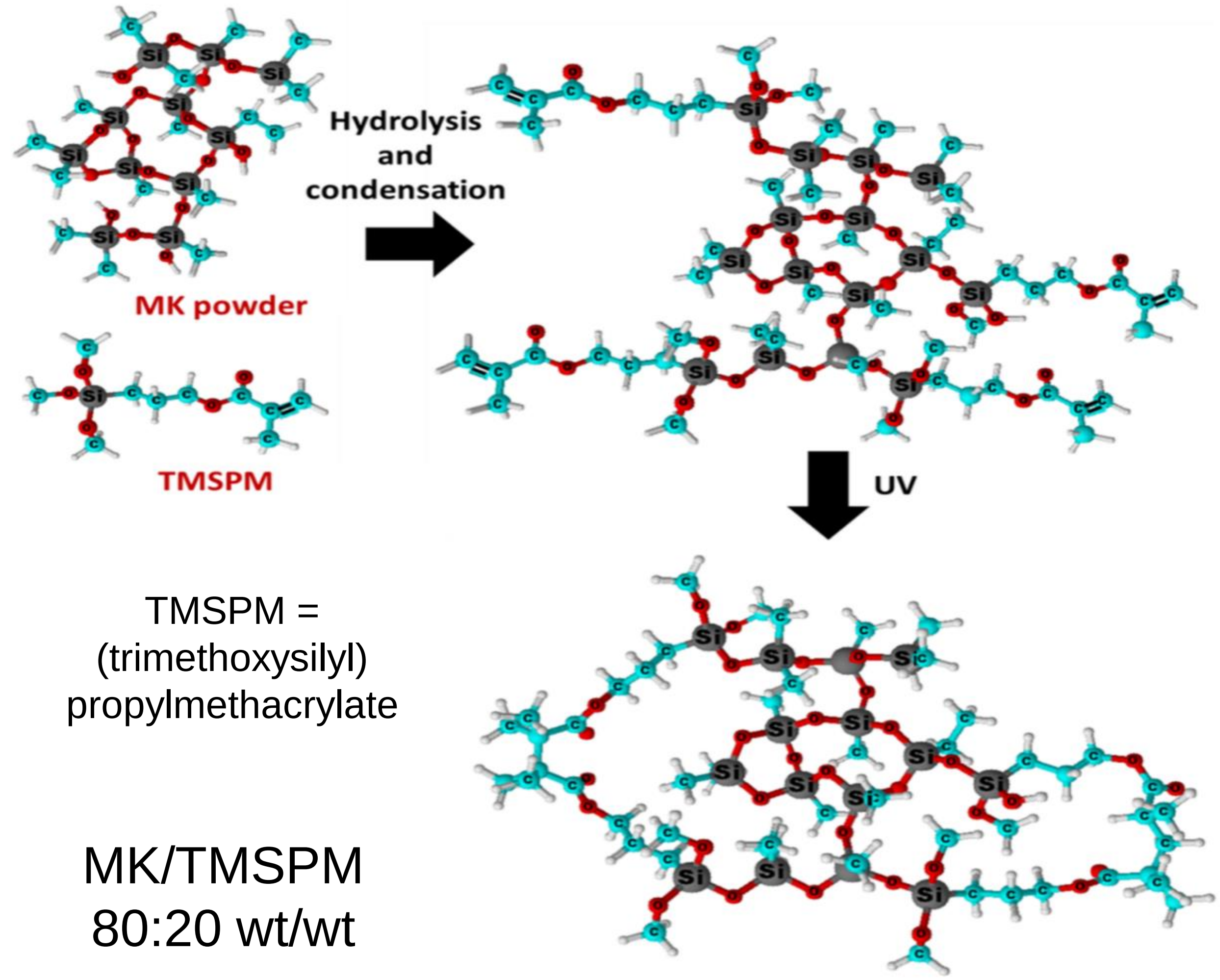
Five different approaches can be followed in order to process preceramic polymers via SLA/DLP, maintaining a suitably high ceramic yield:

1. Using commercially available, high ceramic yield preceramic polymers that contain reactive groups (e.g. acrylic, vinyl, or epoxy groups): low ceramic yield or slow reactions (→ see 3))
2. Synthesizing preceramic polymers with high ceramic yield and suitable photocurable groups
3. Building up of a preceramic polymeric structure starting from the photo-induced reaction of two distinct (monomeric or oligomeric) precursors → thiol-ene click chemistry (S and O contaminations)
4. Chemical modification of a commercially available, high ceramic yield preceramic polymer by grafting of photocurable moieties
5. Blending of a photocurable polymer with a non photocurable, high ceramic yield preceramic polymer. In this case, no crosslinking reaction between the two different polymers occurs upon light illumination, and the preceramic polymer does not need to have specific functional groups

Indirect AM: first a layer of material is deposited, then the cross section (slice) of the part is inscribed in the layer and then the excess material surrounding the part is removed to release the final object

Approach 4: grafting

Modification of a commercially available silicone resin (MK, Wacker) to add photocurable moieties → addition of a organically modified Si alkoxide containing crosslinkable acrylic groups (polycondensation reaction with silicone resin to chemically attach photo-crosslinkable moieties to main Si backbone)



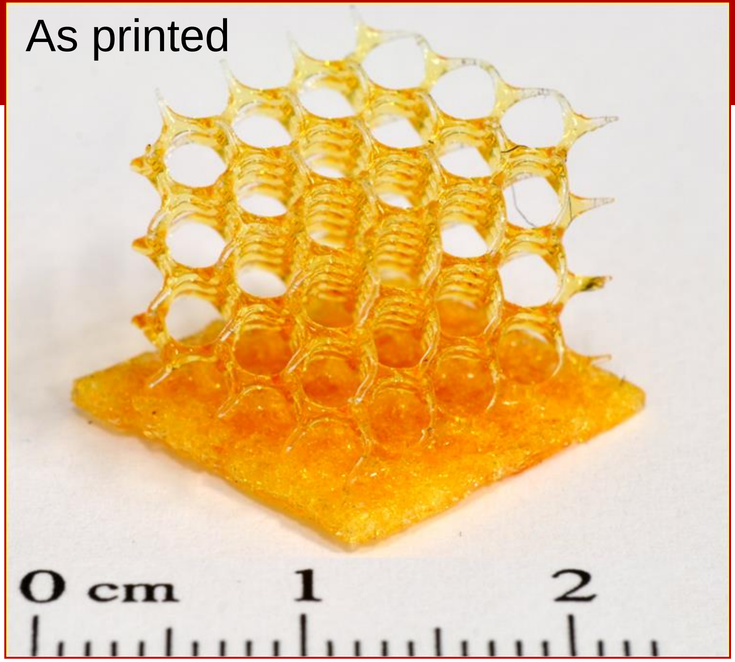
Reasonably high ceramic yield (~52-65 wt%)

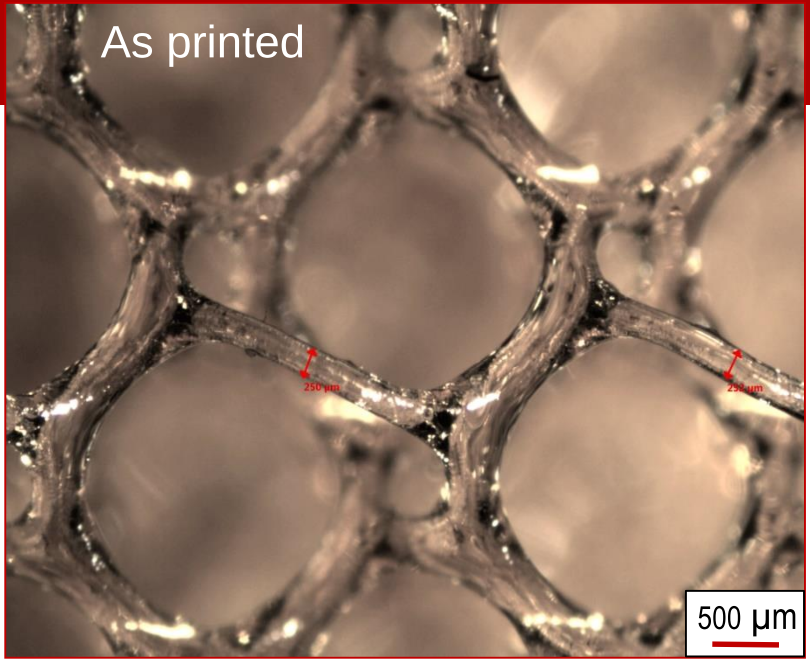
TMSPM = (trimethoxysilyl) propylmethacrylate

MK/TMSPM 80:20 wt/wt

In collaboration with Lithoz (AT)

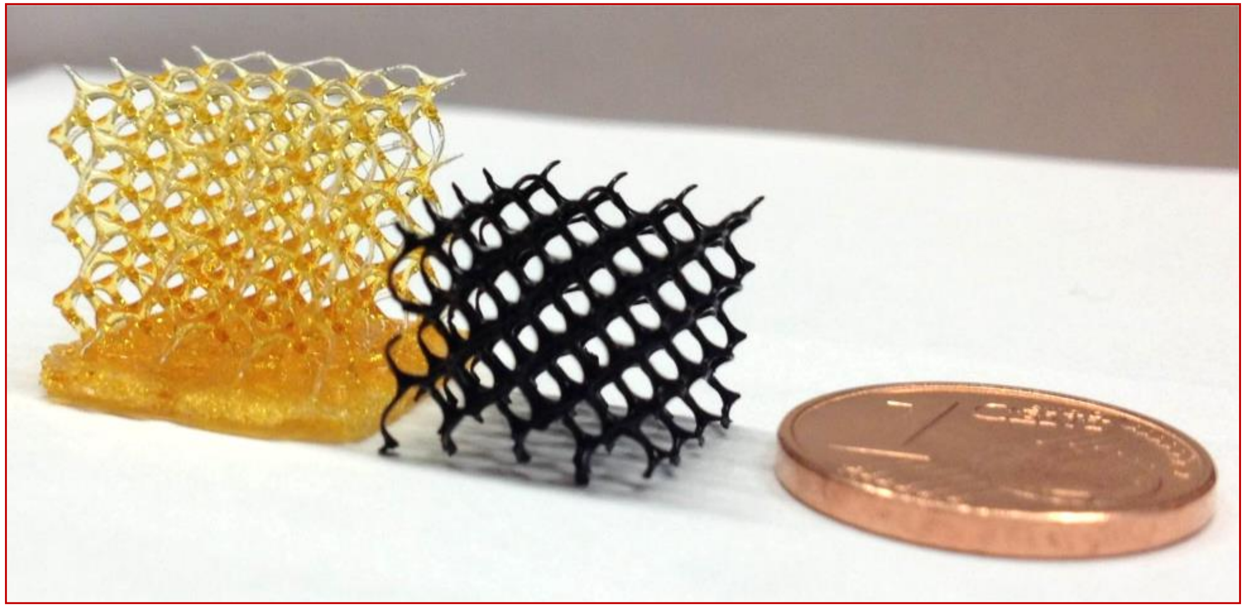
DLP





No cracks or bubbles

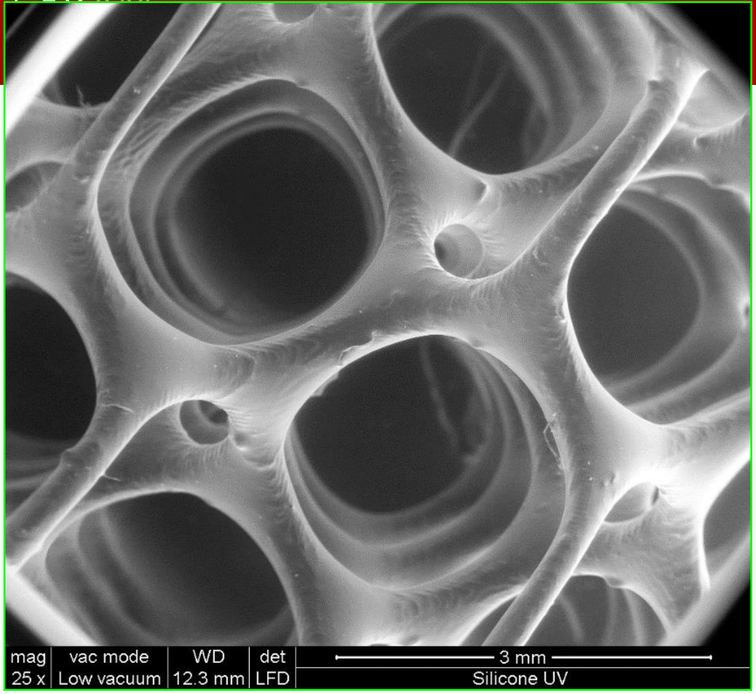
- Linear shrinkage ~25%. Total porosity ~96 vol%
- No melting (during pyrolysis) → adequate cross-linking

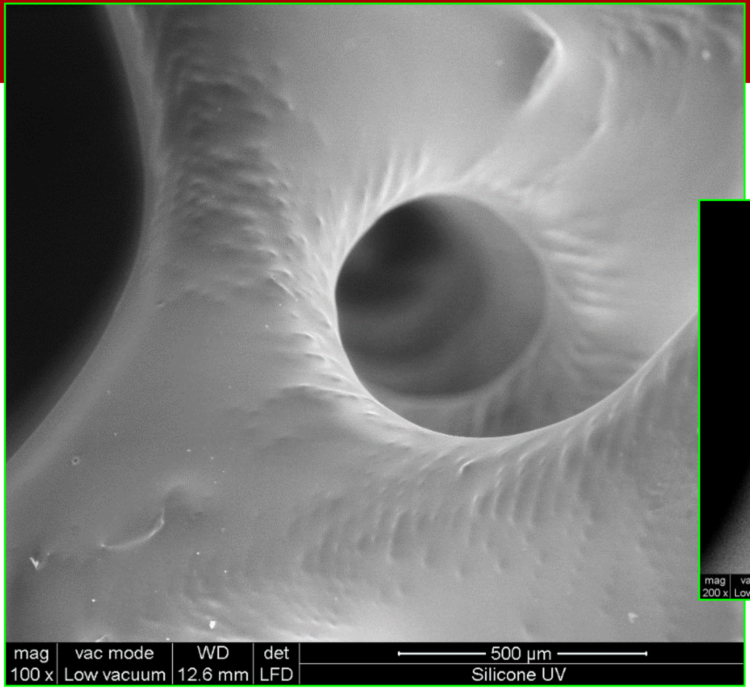


E. Zanchetta, M. Cattaldo, G. Franchin, M. Schwentenwein, G. Brusatin and P. Colombo, Adv. Mater., ***28*** *(2016) 370*

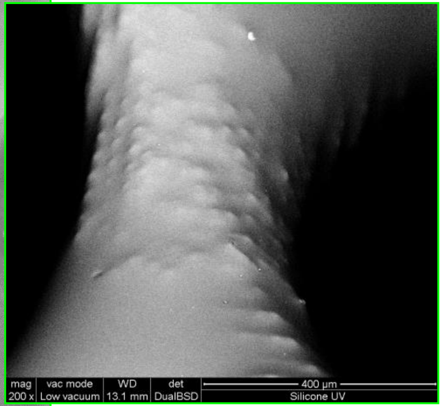
DLP

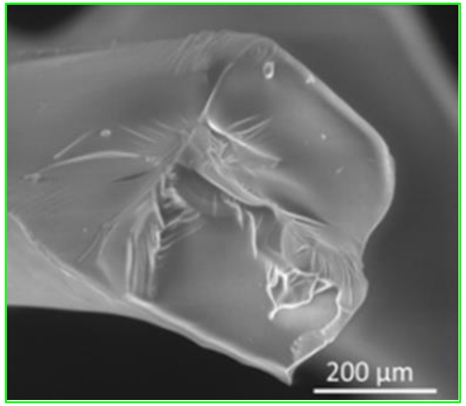
SiOC



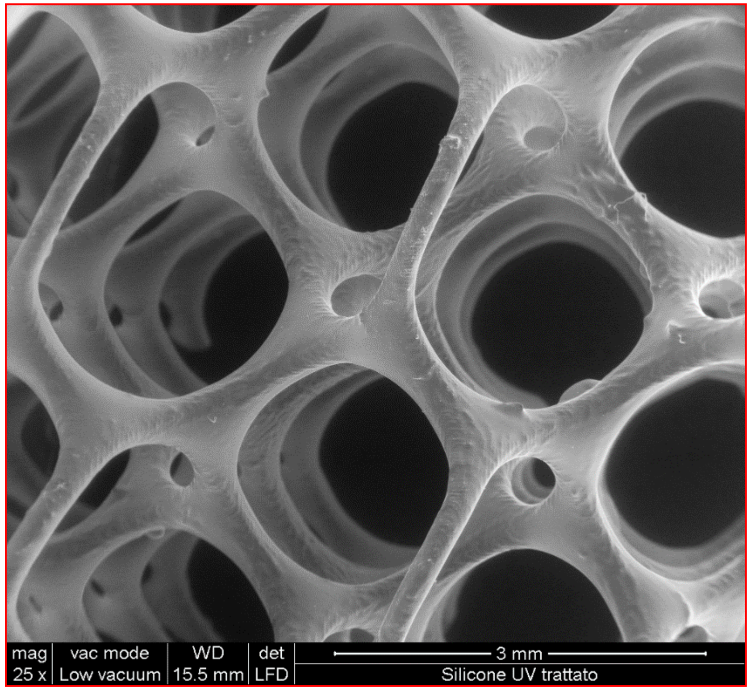


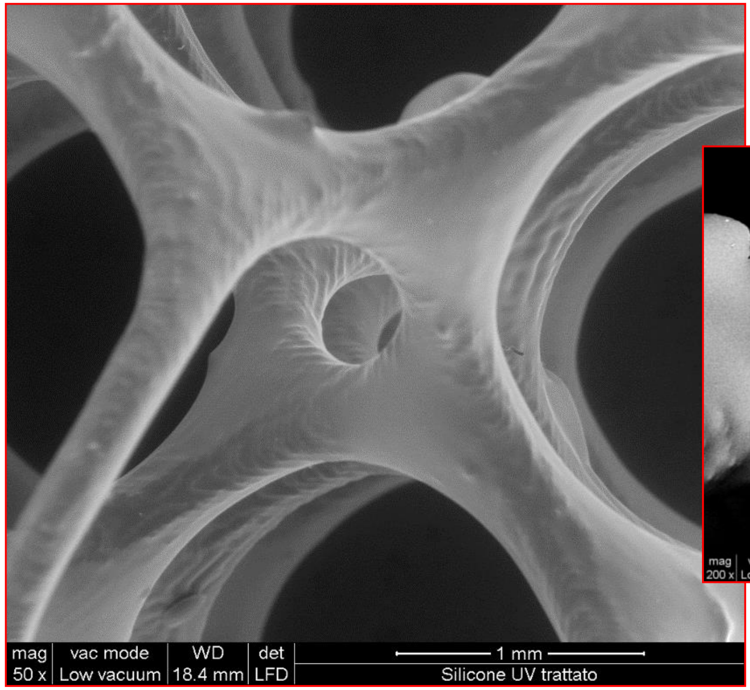
As printed

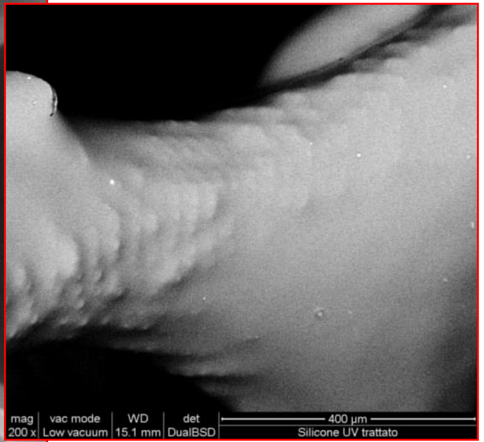


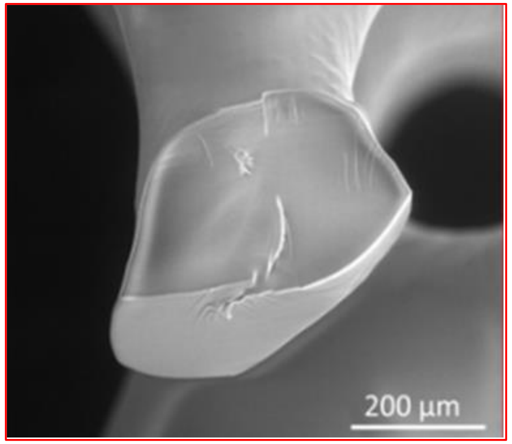


- Dense struts
- Smooth surfaces
- No defects nor cracks after pyrolysis









Ceramized

Approach 5: blending

a) Photo-curable preceramic polymer

- Commercially available (polysiloxane-acrylate (PSA) with high amount of acrylic groups)
- Low ceramic yield of 7.4 wt%

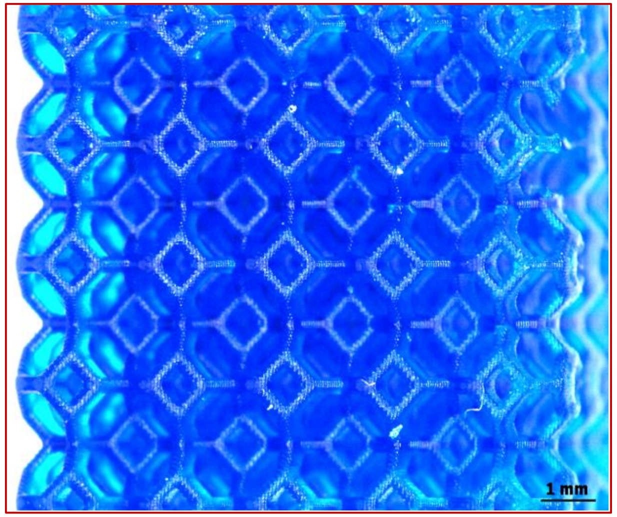
b) Non photo-curable preceramic polymer

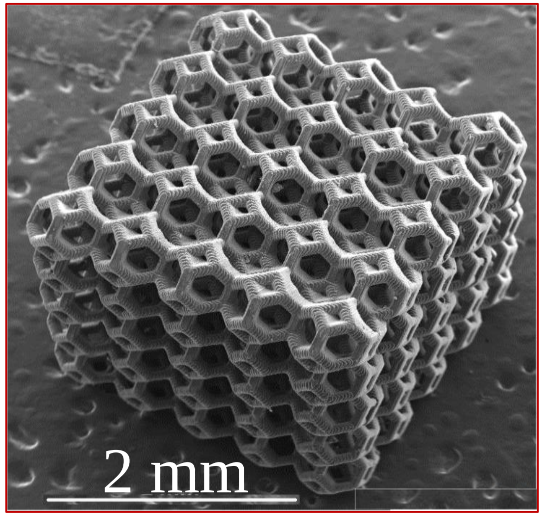
- Two different preceramic polymers (Pol1, Pol2), compatible with PSA (no phase separation when mixing)
- Phenyl- (Pol1) and Phenyl-Methyl- (Pol2) side groups
- High ceramic yields: 67 wt% (Pol1) and 77 wt% (Pol2)

Weight ratio PSA/Pol1,Pol2	1	9/1	7/3	5/5	3/7
PSA content (wt%)	100	87.10	63.64	42.86	24.32
Pol1 or Pol2 content (wt%)	-	9.68	27.27	42.86	56.76
Toluene content (wt%)	-	3.23	9.09	14.28	18.92

DLP of preceramic polymers

SiOC

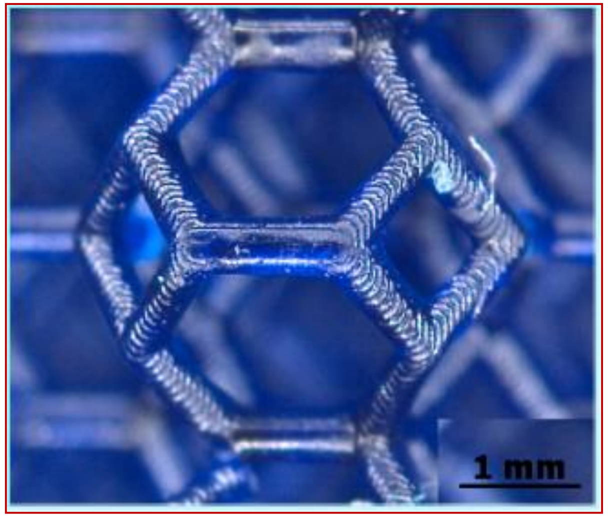


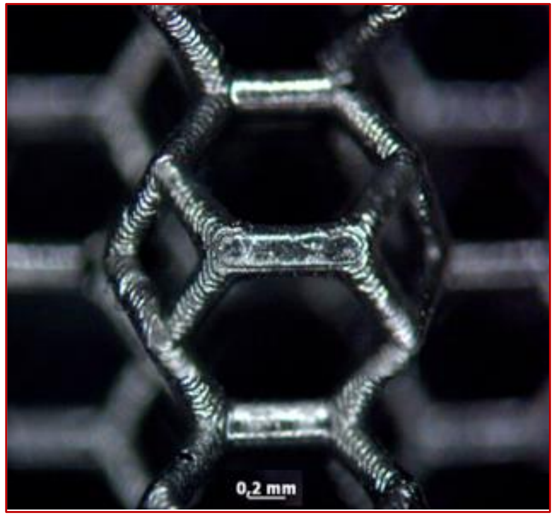


PSA
Shrinkage = ~68%
Ceramic yield = 7.3%

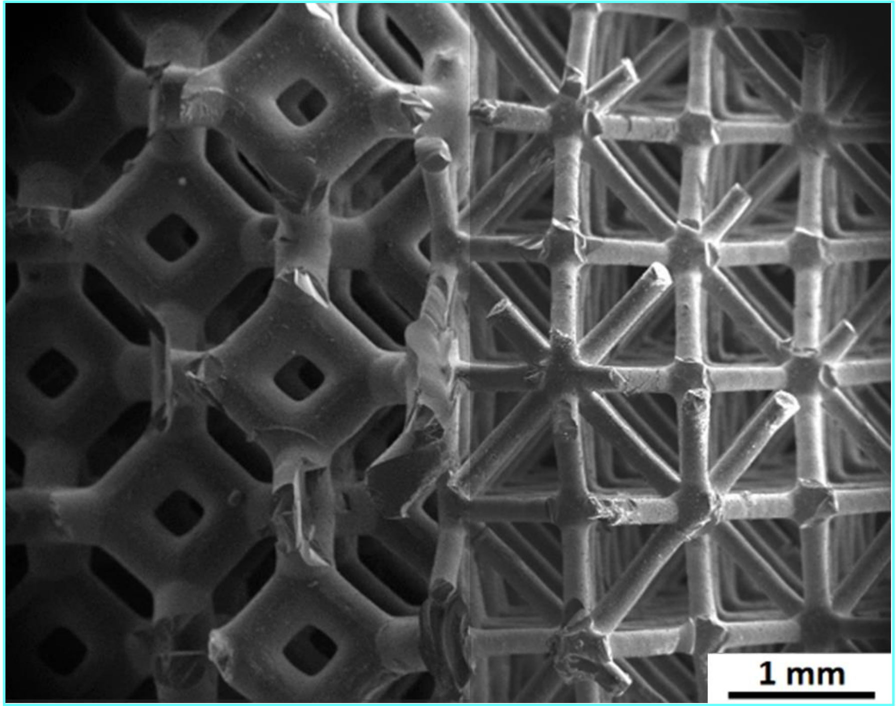
Before pyrolysis

After pyrolysis





Mixed Kelvin and octet cell design

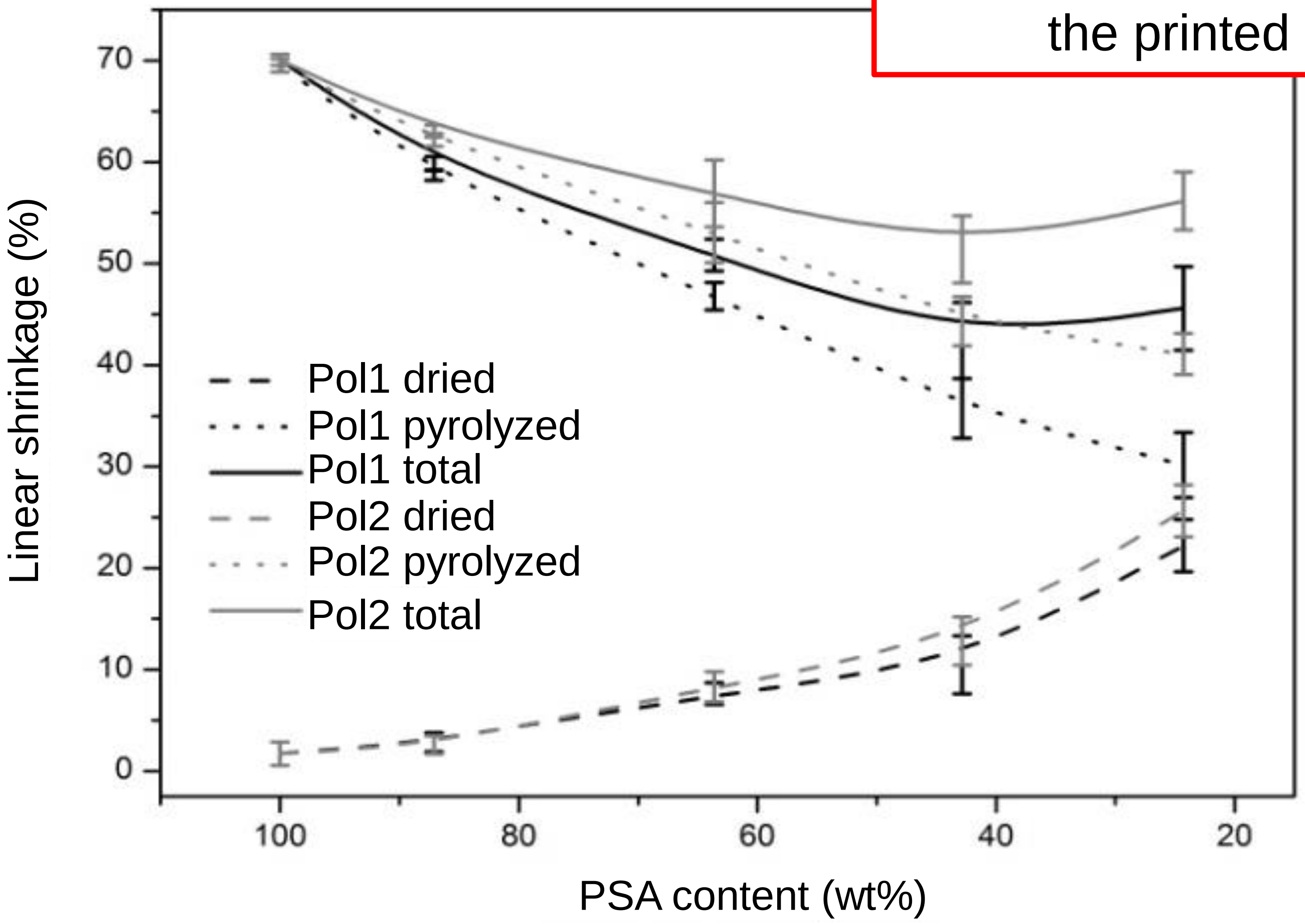


PSA+Pol2 5/5
Shrinkage = ~44%
Ceramic yield = 40.1%

J. Schmidt and P. Colombo, J. Eur. Ceram. Soc., ***38*** *(2018) 57*
N.R. Brodnik, J. Schmidt, P. Colombo, K.T. Faber, Add. Manuf., ***31*** *(2020) 100957*

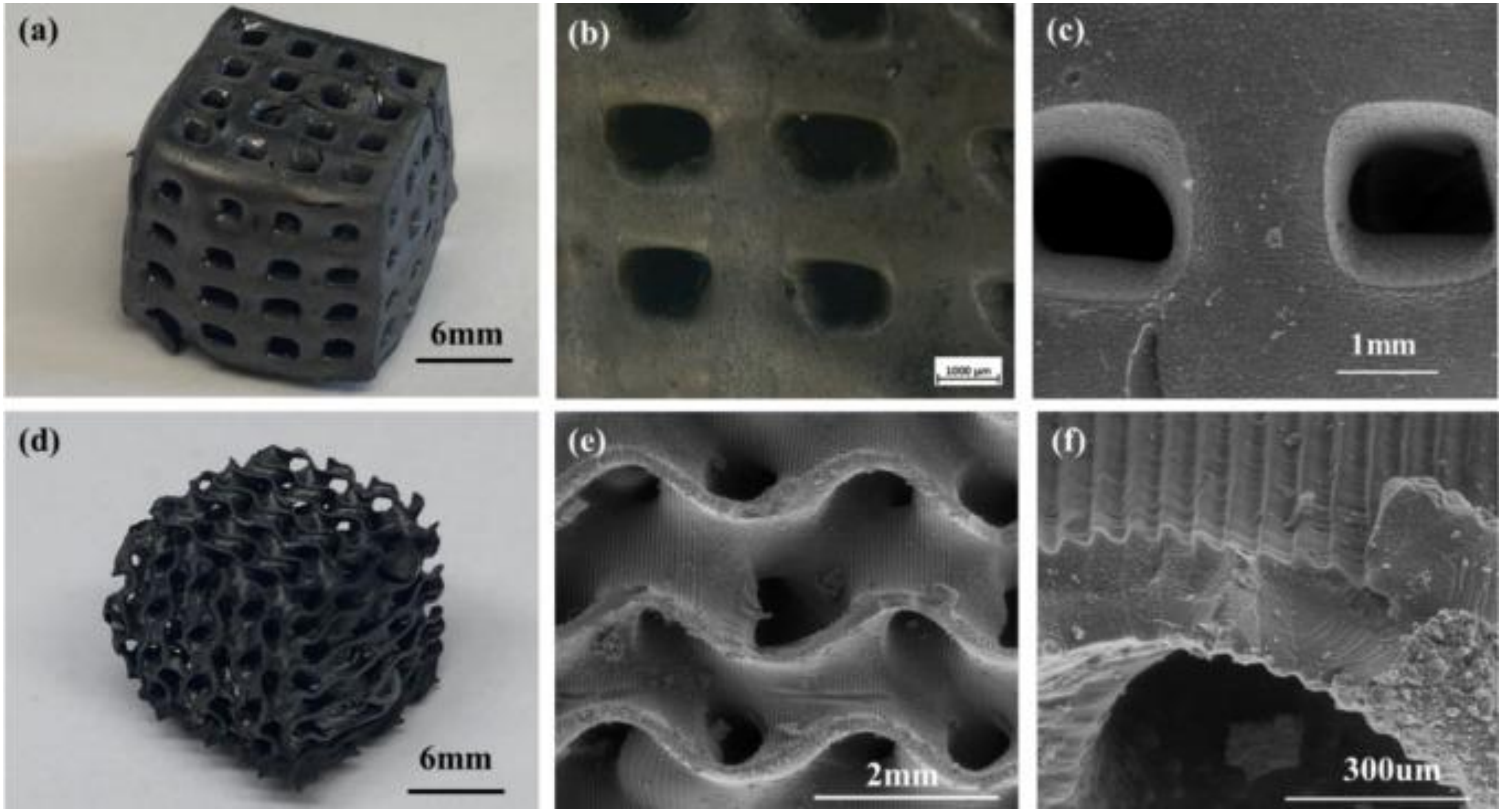
Shrinkage

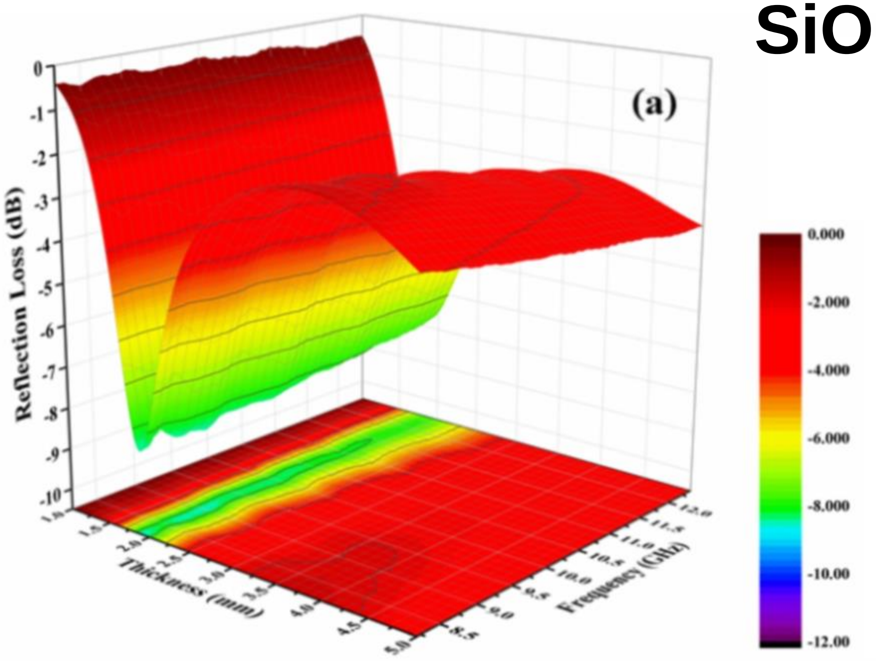
→ Control of the final dimensions of the printed ceramic part



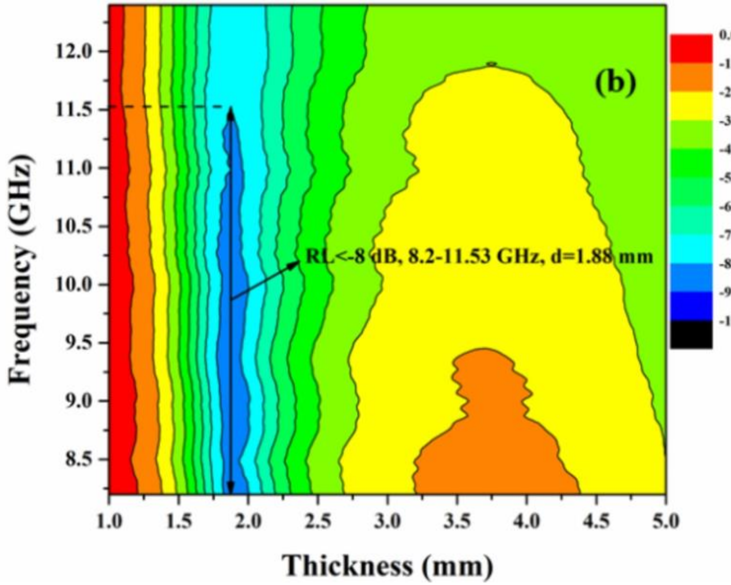
Average drying shrinkage, pyrolysis shrinkage and total shrinkage of blends

DLP
SiOC





Reflection Loss of 3D-SiOC ceramics in X band



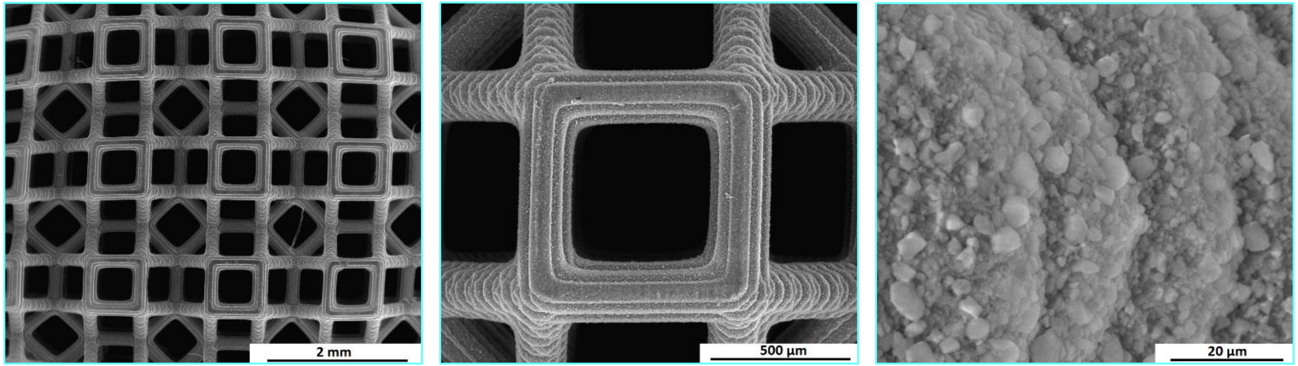
EMW absorption of SiOC ceramics with integration of structure and function

Y. Feng, X. Guo, H. Elsayed, G. Franchin, H. Gong, P. Colombo, J. Eur. Ceram. Soc., ***41*** *(2021) 6393*

DLP of mullite

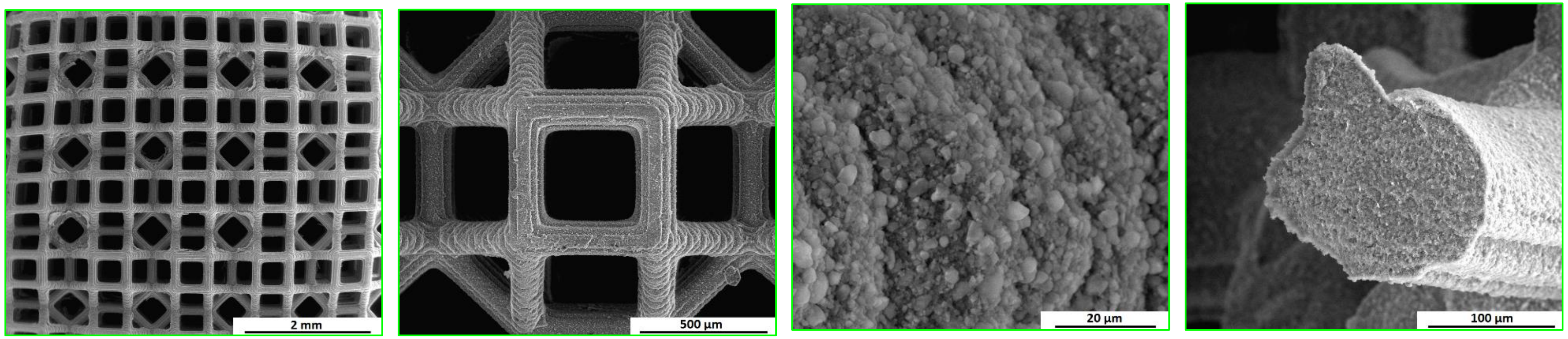
- Silicone resin + γ-alumina nano-powders → pure mullite (1350°C in air)

Before pyrolysis

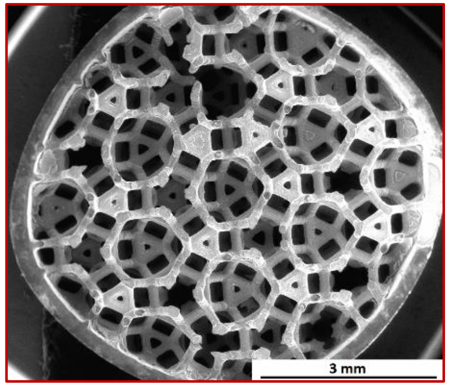


- No microcracks
- Dense struts
- Pore-free
- Density 3.1 g/cm^3

After pyrolysis



Some unreacted Al_2O_3 particles at the struts' surface

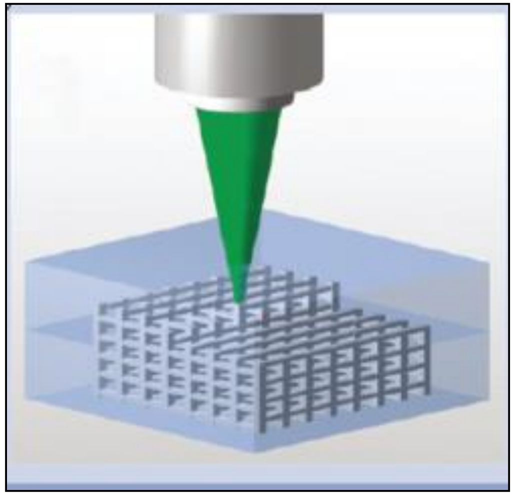


J. Schmidt, P. Colombo, et al., J. Eur. Ceram. Soc., ***39*** *(2019) 1336*

Indirect AM of Pure Preceramic Polymers (TPP)

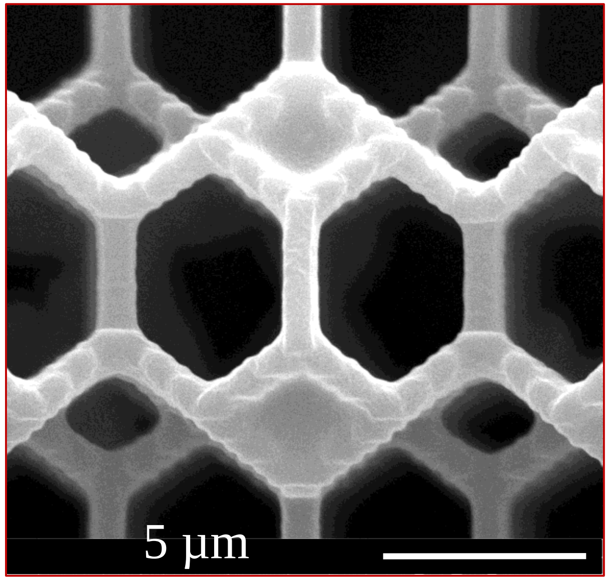
- Lateral resolution: <1 µm
- Slice thickness: 800 nm
- Printing envelope: 3 mm (height); 10x10 cm (plane)

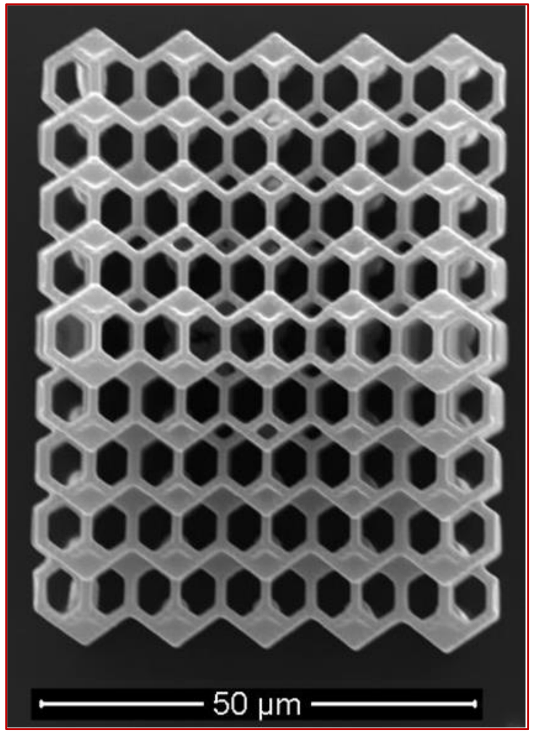
2 Photon Polymerization: printing voxel-by-voxel



Fabrication time ~10 min

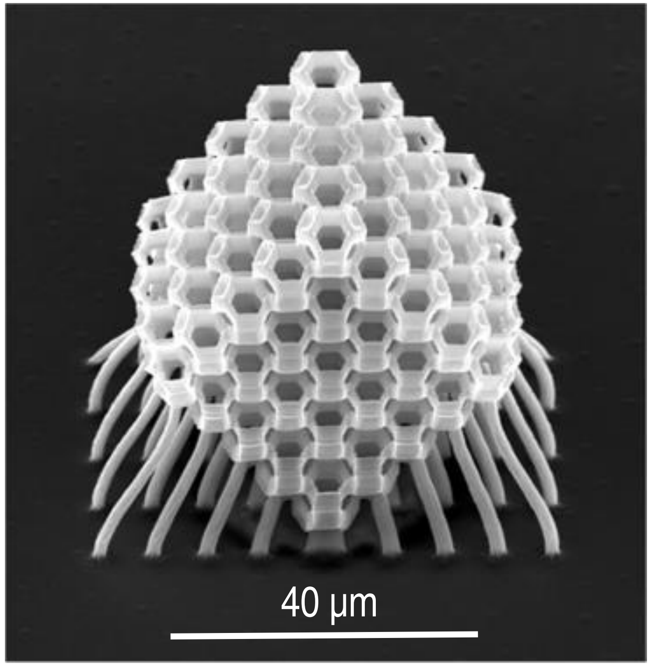
Before pyrolysis



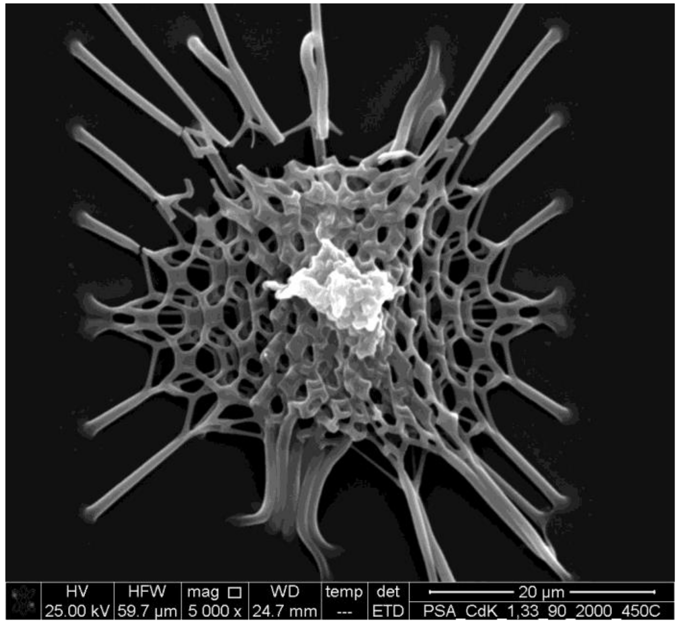


In collaboration with G. Brusatin (University of Padova)

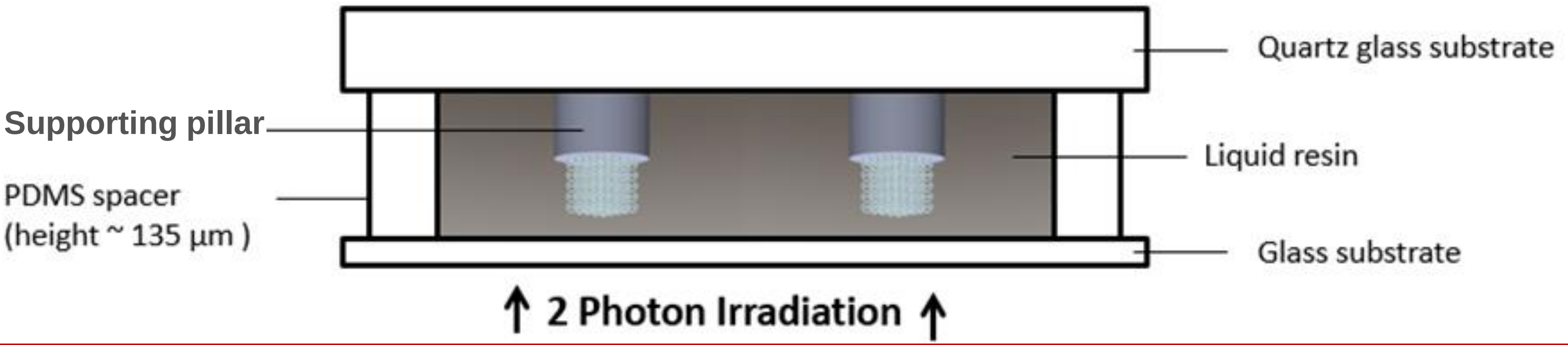
Pyrolyzed structures



Pre-pyrolysis
@450°C

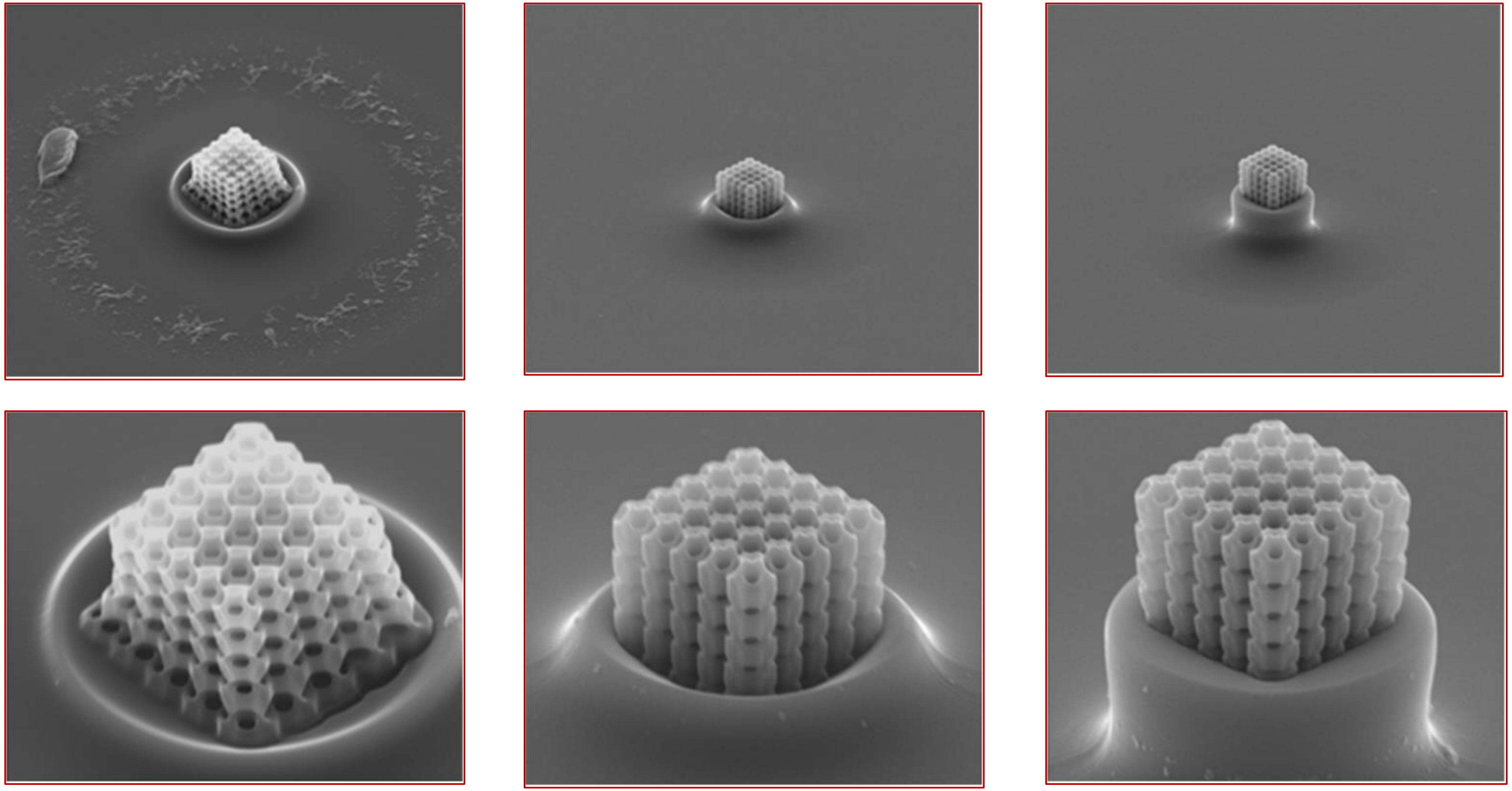


Printing upside down for quartz substrate for pyrolysis @1000°C
→ Printing of support possible without shadowing effect during fabrication



Pyrolyzed structures

1000°C, N_2 → Increasing support height →



Inhomogeneous shrinkage (anchoring on glass substrate)

Homogeneous shrinkage

*L. Brigo, J.E.M. Schmidt, A. Gandin, N. Michieli, P. Colombo, G. Brusatin, Adv. Sci., **5** (2018) 1800937*

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Hybridization of vat-photopolymerization-based technologies for the fabrication of multiscale ceramic components

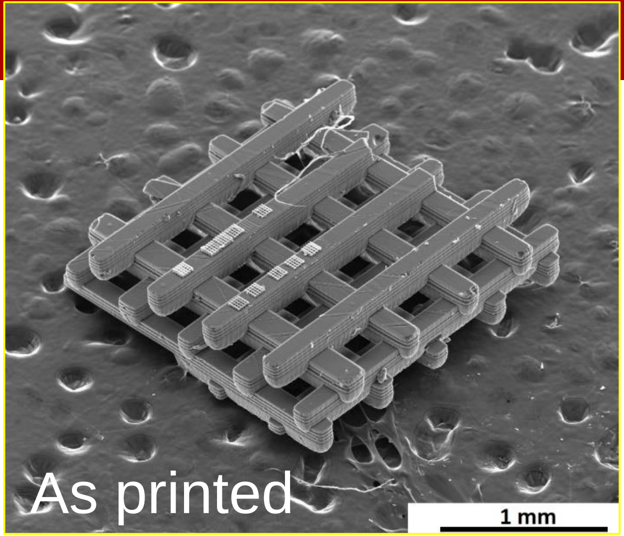
Hybrid additive manufacturing processes combine (in series or in parallel) additive manufacturing with one or more secondary process or energy source which are synergistically coupled to enhance part quality, functionality and performance of part and/or process.

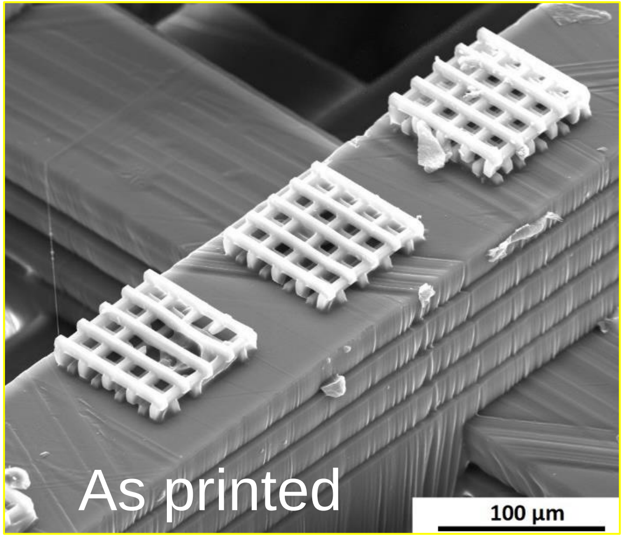
DLP	TPP
+ Macro components (mm/cm)	+ Resolution limit (nm)
+ Free standing component	– Micro components (µm)
+ Easy handling	– Connected to glass substrate
– Resolution limit (~100 µm)	– Not detachable

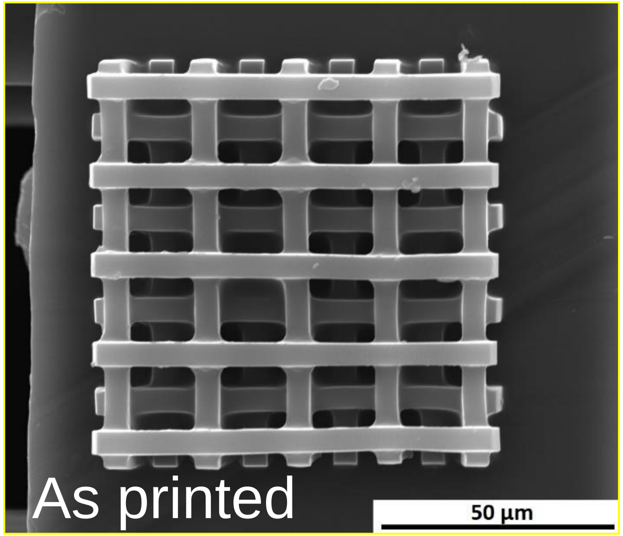
Hybridization of the two technologies extends both printing ranges, combining macro-dimensional printing with nm-sized elements

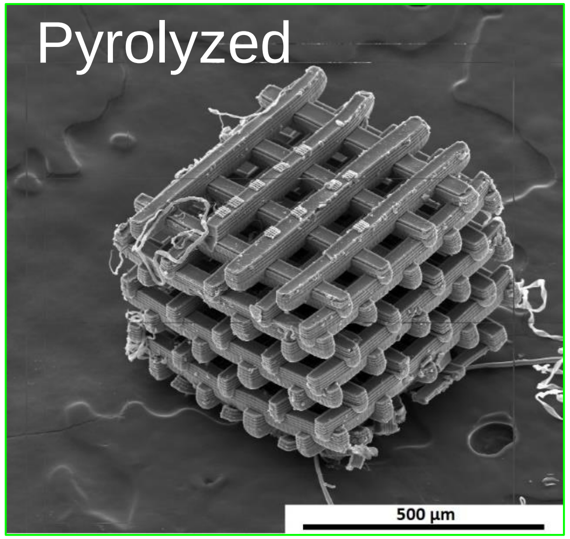
*J. Schmidt, L. Brigo, A. Gandin, M. Schwentenwein, P. Colombo, G. Brusatin, Add. Manuf., **30** (2019) 100913*

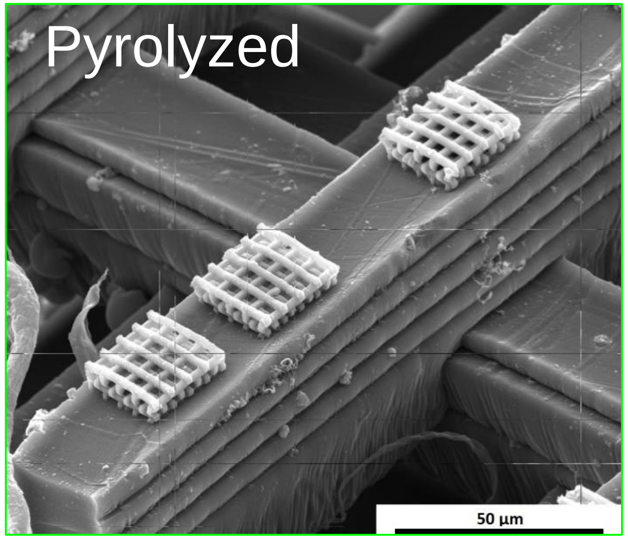
Combination of DLP and TPP

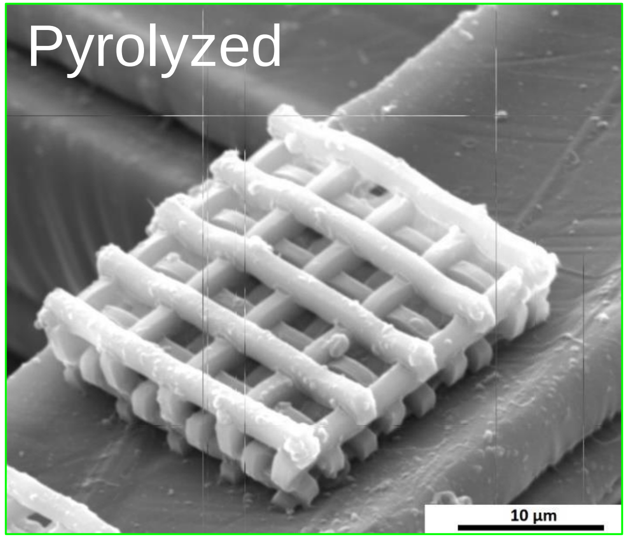












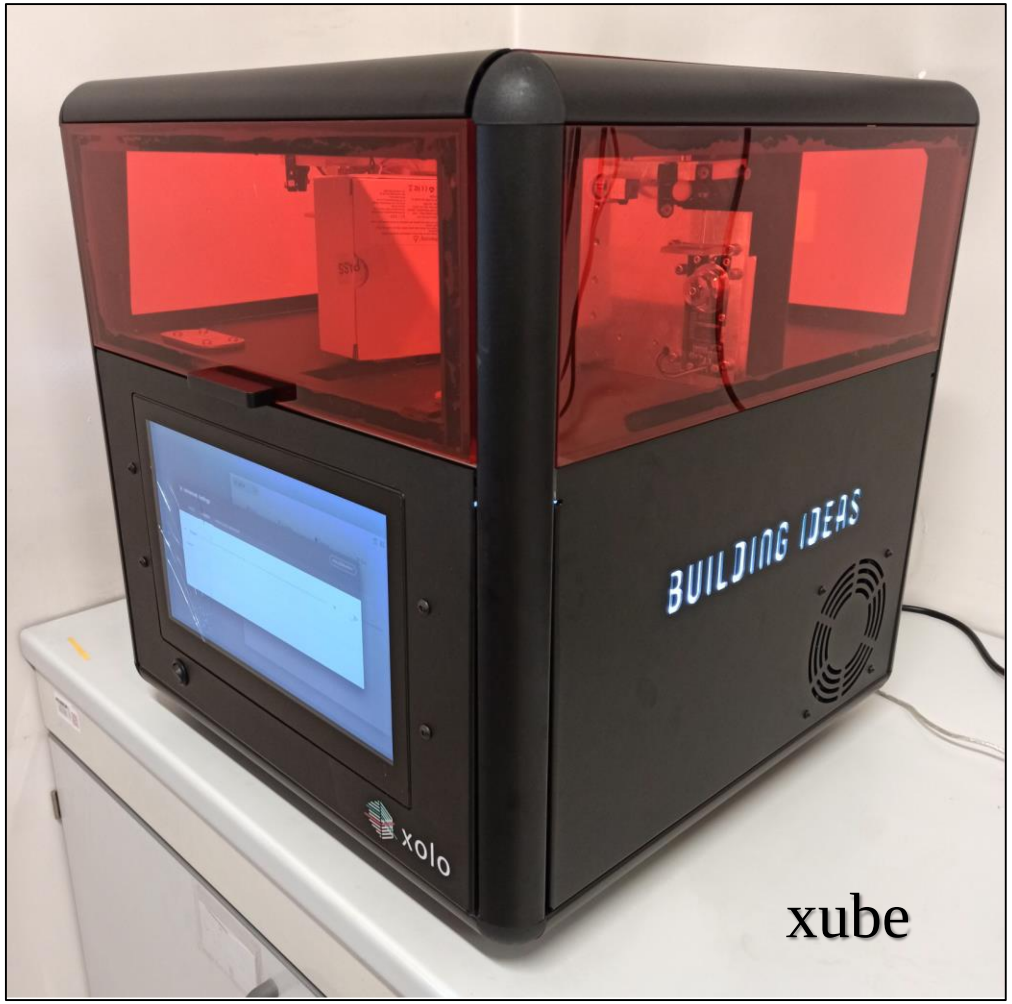
- No detachment
- Good surface integration
- No shrinkage mismatch

In collaboration with Lithoz (Vienna, Austria) and G. Brusatin (Univ. Padova)

Volumetric AM: Xolography

- Xolography is a novel **volumetric 3D printing** process in which complex objects are manufactured using two intersecting light beams of different wavelengths to solidify localized regions, which are stabilized by the surrounding viscous fluid matrix (see https://www.xolo3d.com/ and https://www.nature.com/articles/s41586-020-3029-7).

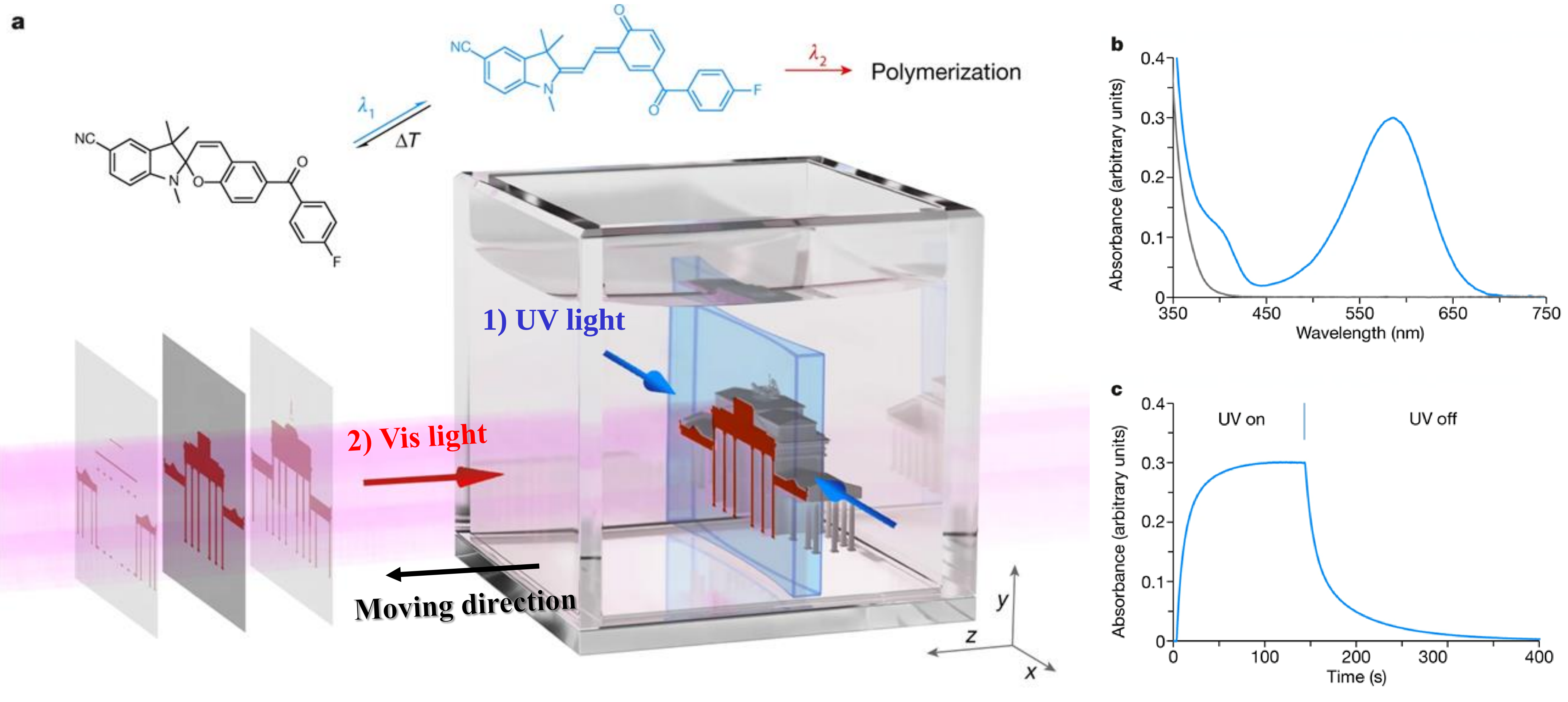
- Dual color technique
- Photo-switchable initiators (DCPI)
- Linear excitation by intersecting light beams of different wavelengths (UV and visible)
- Local polymerization inside a confined monomer volume → **volumetric 3D printing**
- No oxygen inhibition or layer rebuild → **fast**
- Printing rates up to ~1 cm^3/s, with resolution 10-50 µm, are possible



xube

Principle of Xolography

Two-color photoinitiator added to the resin, activated by a first wavelength (1), while absorption of the second wavelength (2) initiates photopolymerization (via formation of radicals)



Principle of Xolography

Complex requirements for the photocurable fluid:

- Compatibility with proprietary **dual color photoswitchable initiator** system
- **Higher viscosity** compared to conventional vat photopolymerization
  → the printed part is supported by the unreacted material surrounding it
  → no additional supports for overhanging features needed
- Photopolymers with **high reactivity** and high T_g
  → fast prints
  → **strong, rigid parts** that can be extracted from the viscous resin without damage
  i.e.: pentaerythritol tetraacrylate (PETA), diurethane dimethacrylate (**UDMA**)
- **Highly transparent material**
  (high transmittance at UV and visible wavelengths)
  → not suited for ceramic particle-based suspensions

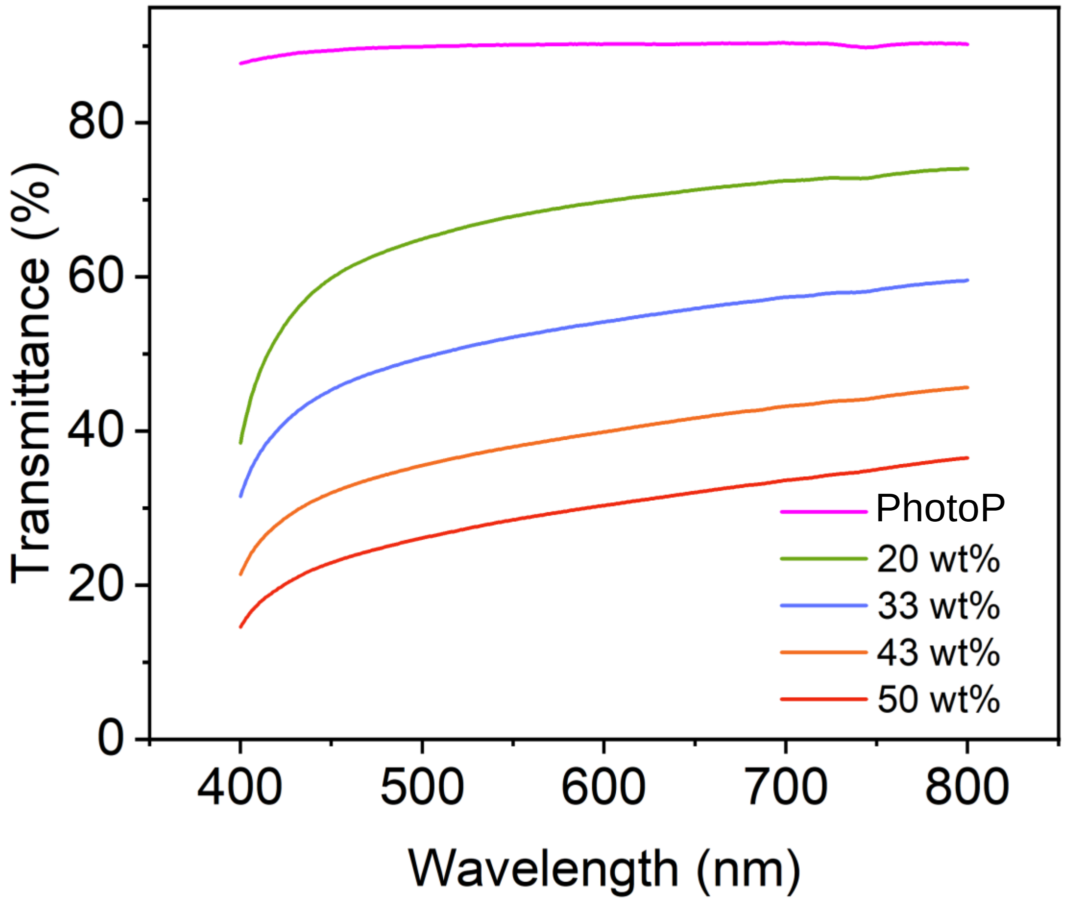
→ is it suitable for **preceramic polymers**?

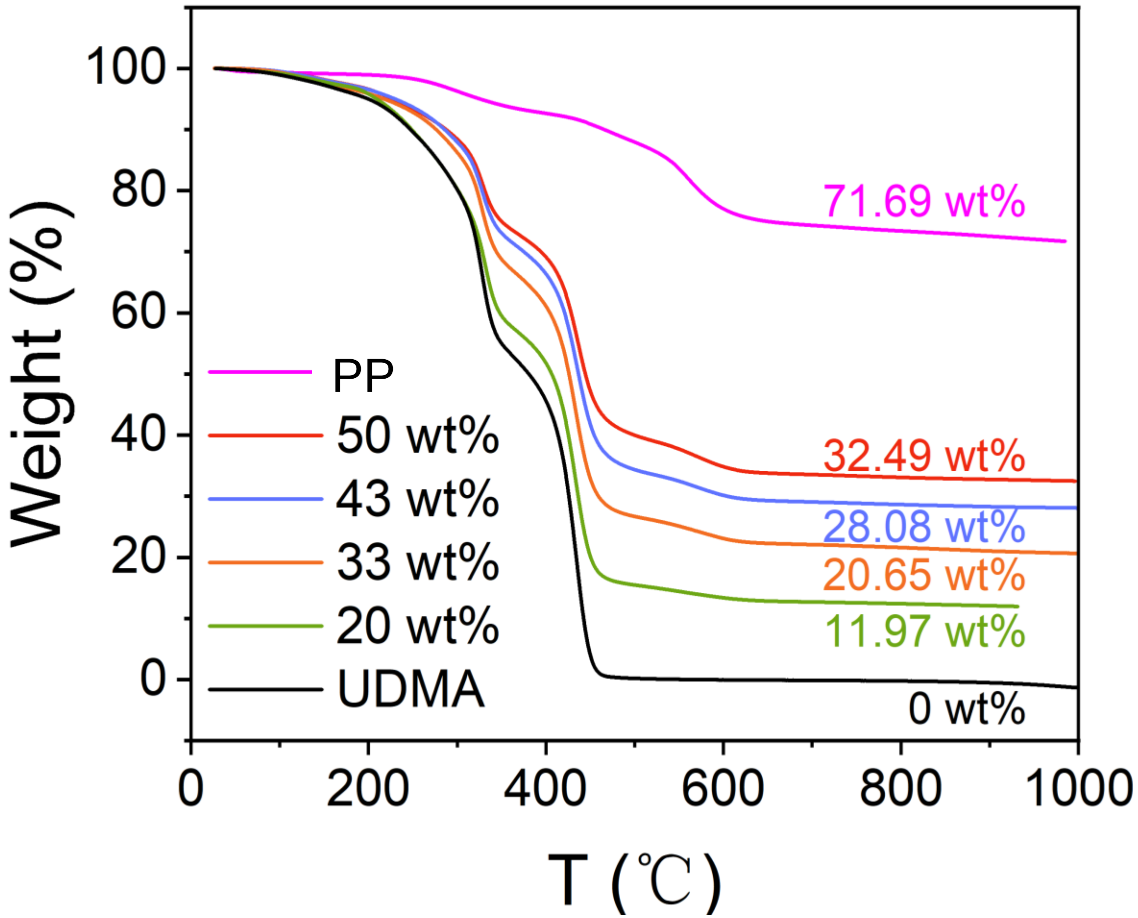
- **physical blend** of a highly reactive photopolymer (UDMA) and a non-photocurable preceramic polymer with high yield (H44)

Volumetric AM: Xolography

- A high viscosity is needed for supporting the structures being printed
- A too high viscosity hinders radicals diffusion
- It is difficult to extract the printed parts from highly viscous mixtures

- UDMA crosslinks into a rigid structure whose decomposition occurs at higher temperatures compared to other acrylates





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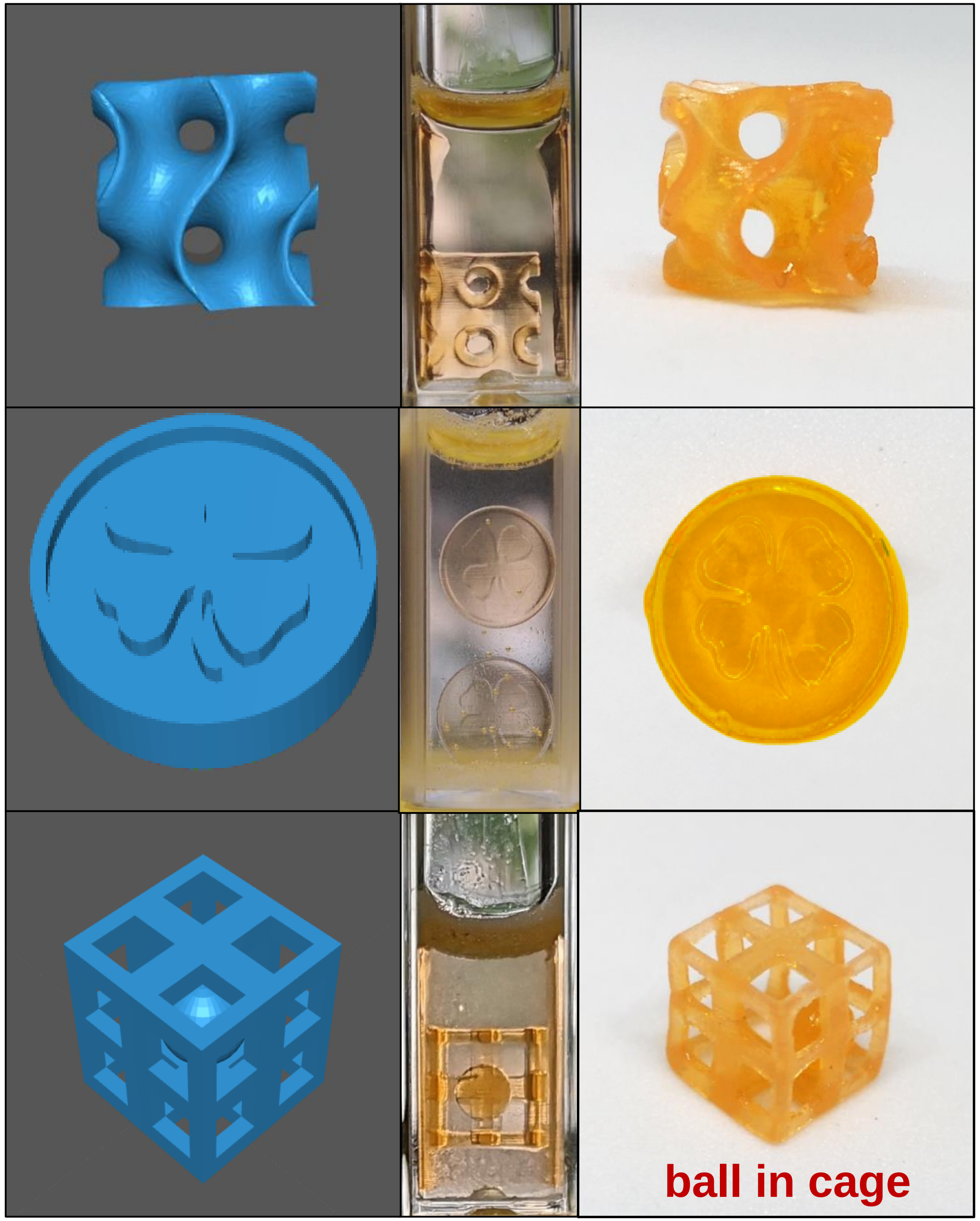
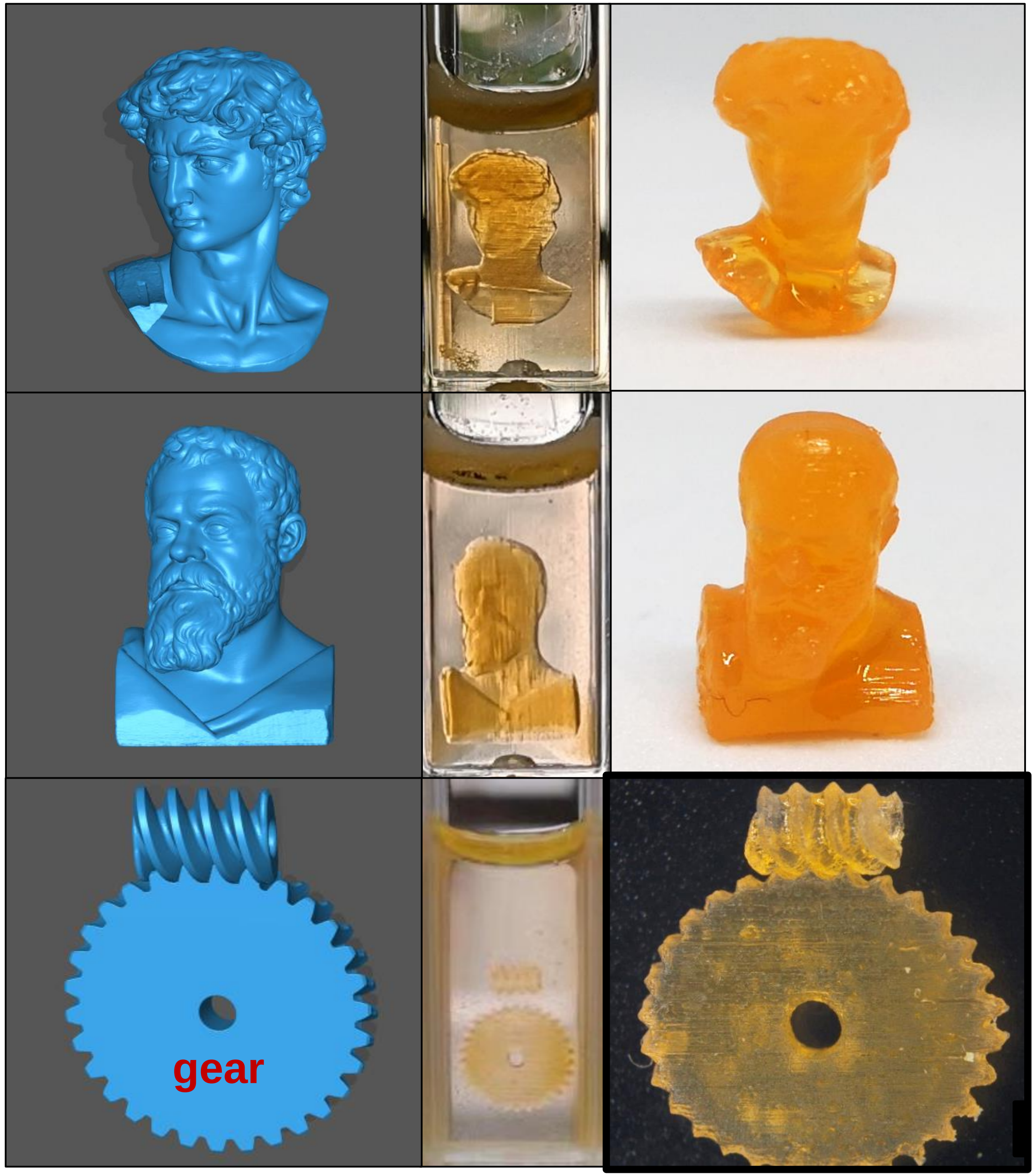
Volumetric AM: Xolography



Cuvette side
= 1 cm

Simultaneous printing of **separate, interlocked objects**

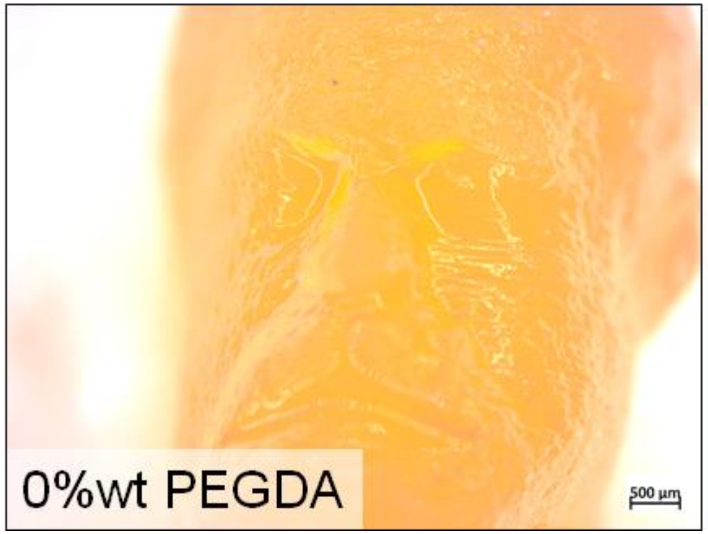


Volumetric AM: Xolography

- Ceramization by pyrolysis is possible (but very careful control of printing formulation and pyrolysis conditions is required)
- Pyrolysis at 1000°C: samples can be cracked
- Blending helps (but loss of resolution)
- Experiments currently undergoing

Before pyrolysis

After pyrolysis



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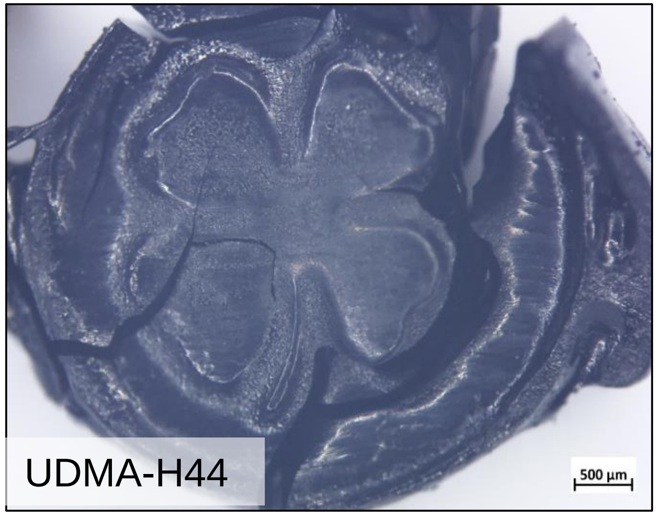
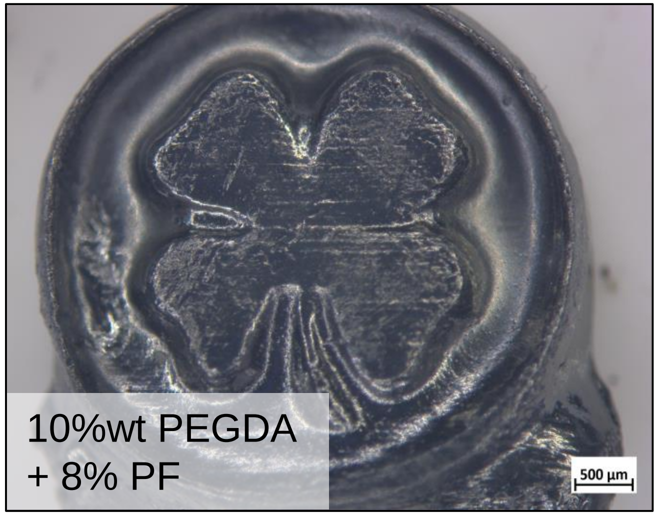
Volumetric AM: Xolography

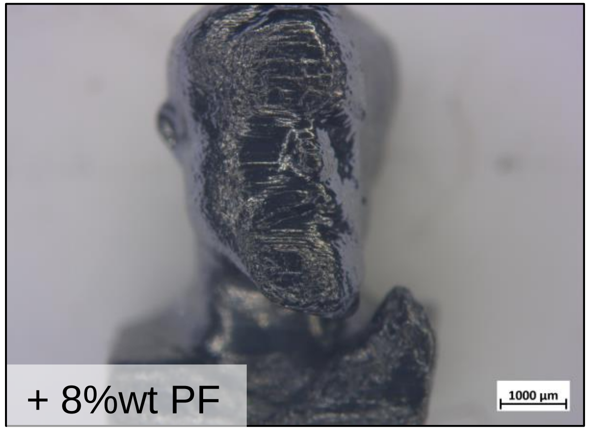
Cracks upon pyrolysis → hindered release of decomposition gases → partial substitution of UDMA with PEGDA + addition of a low T release component (PF):

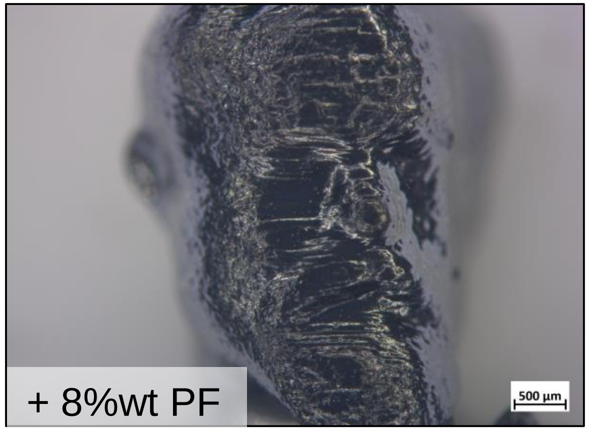
+ Creation of a transient, open porous structure at low T → path for gas release





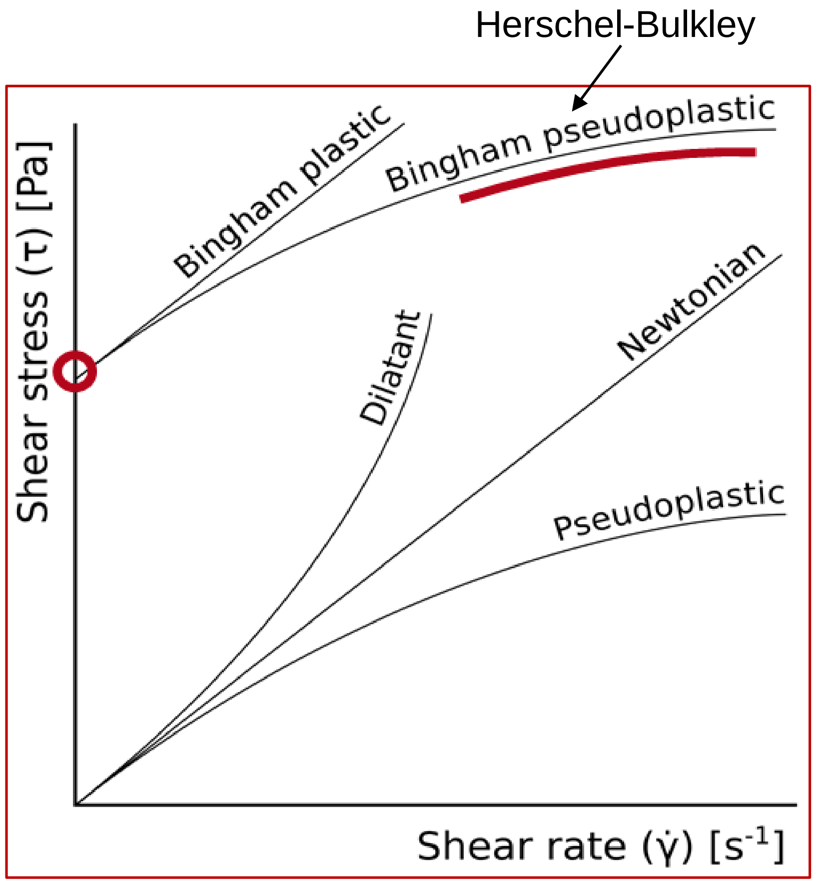
+ crack-free components
+ resolution is maintained





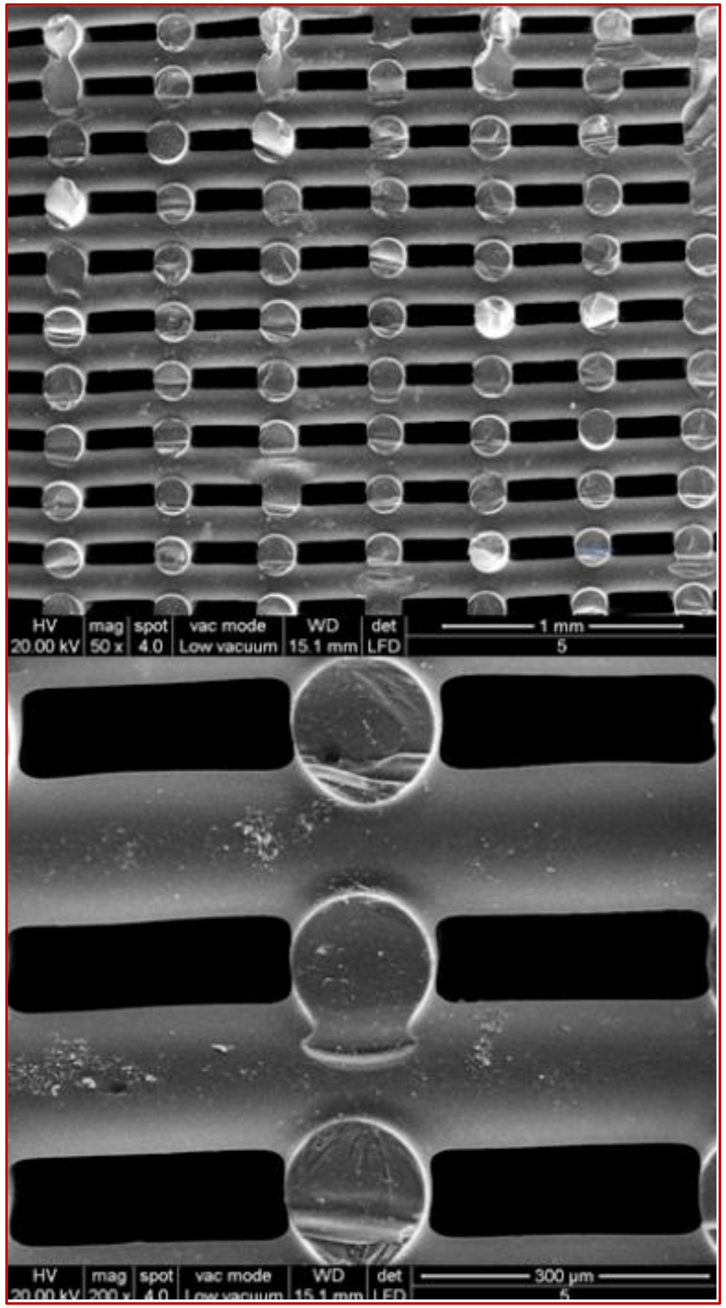
DIW (Robocasting)

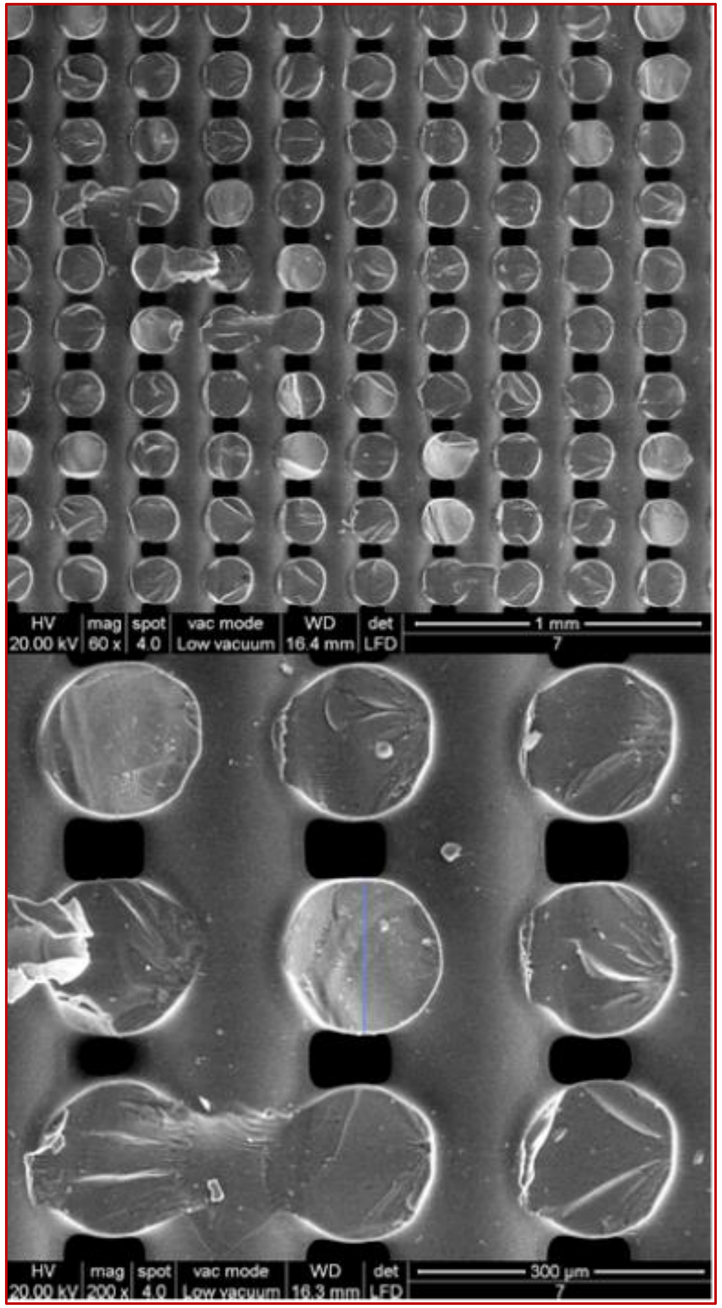
- The ink should behave as a ”shear-thinning with yield stress” fluid (i.e. a fluid that shows an initial yield stress and whose viscosity decreases with increasing the shear rate - Herschel-Bulkley fluid with n<1).
- The realization of thin walls and spanning features is challenging and requires an optimization of the ink rheology → addition of fillers to control rheology
- Use of pure preceramic polymers or of preceramic polymers + fillers (→ bioceramics)

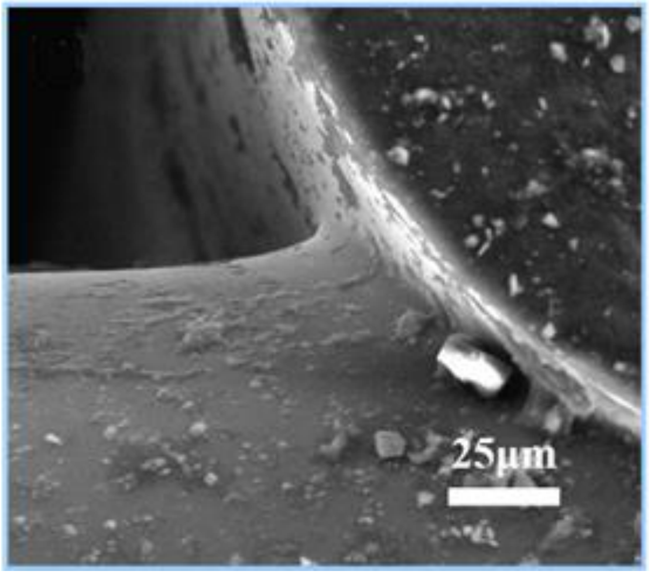


Direct AM: the material is directly deposited only in the position giving the desired shape of the final object

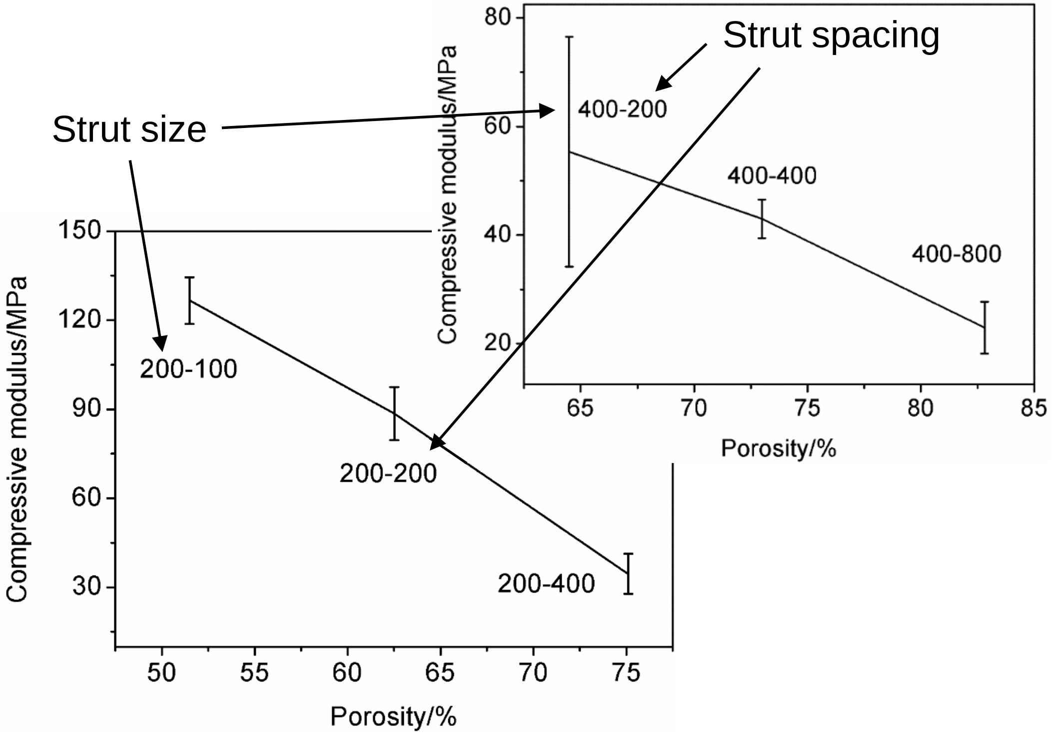
DIW of Pure Preceramic Polymers



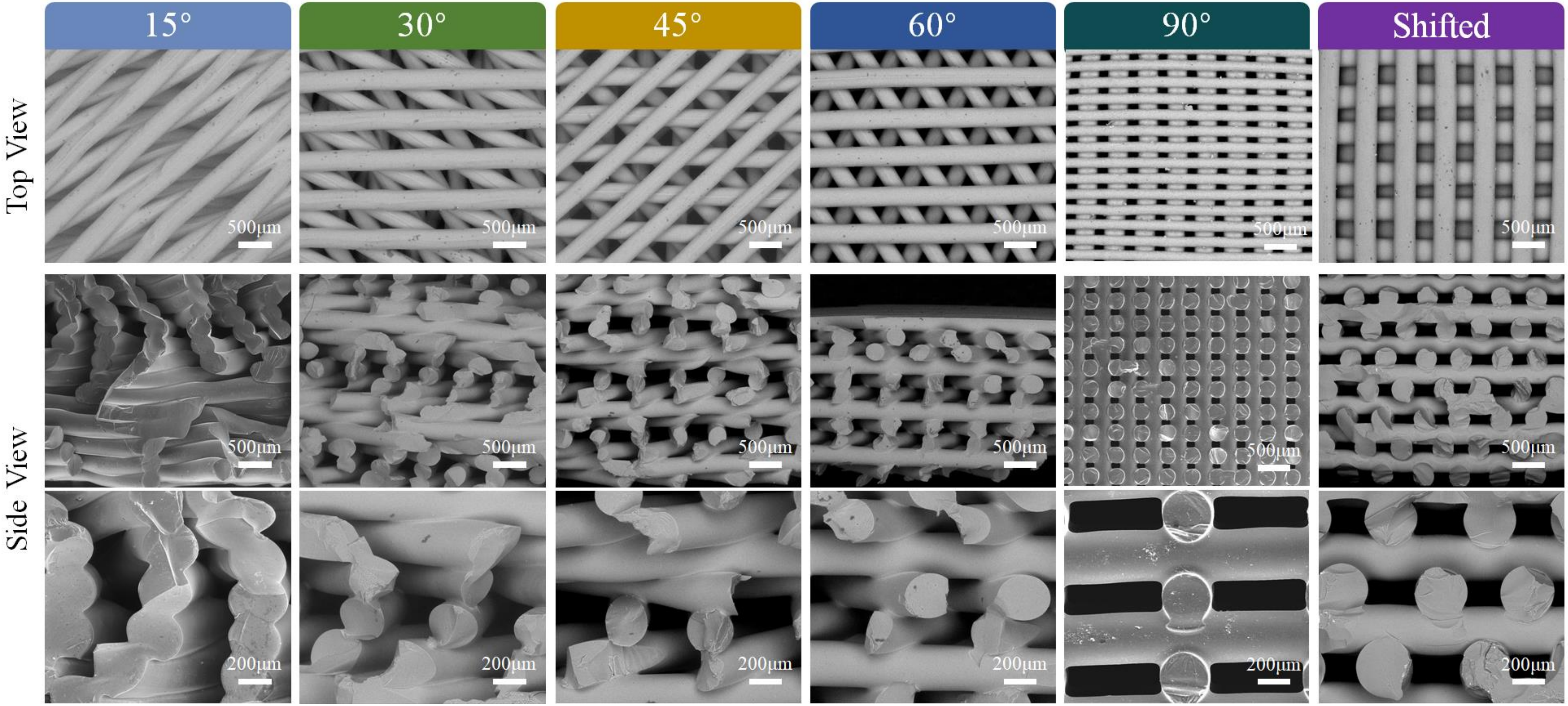




Effect of porosity and strut size and spacing on strentgh



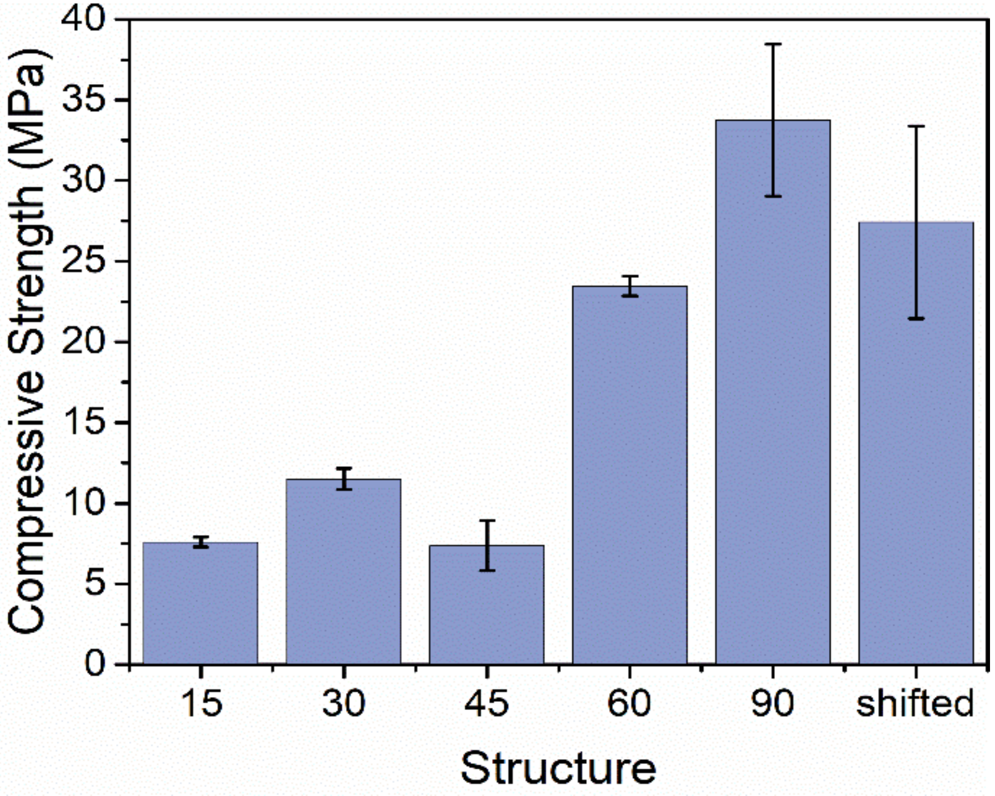
DIW of Pure Preceramic Polymers

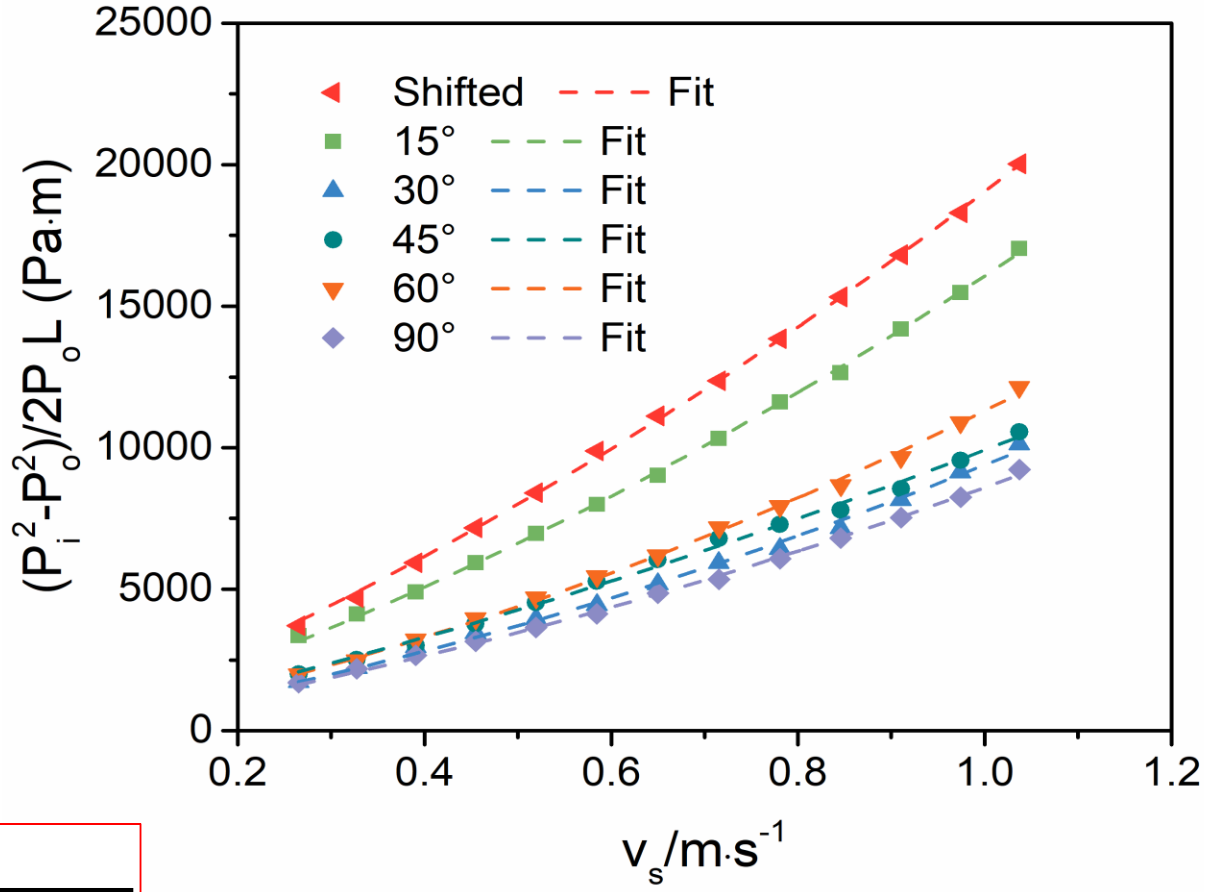


- Complex structures possible → effect of the architecture on mechanical strength and permeability

K. Huang, H. Elsayed, G. Franchin, P. Colombo, *J. Eur. Ceram. Soc.*, **41** (2021) 7552

DIW of Pure Preceramic Polymers



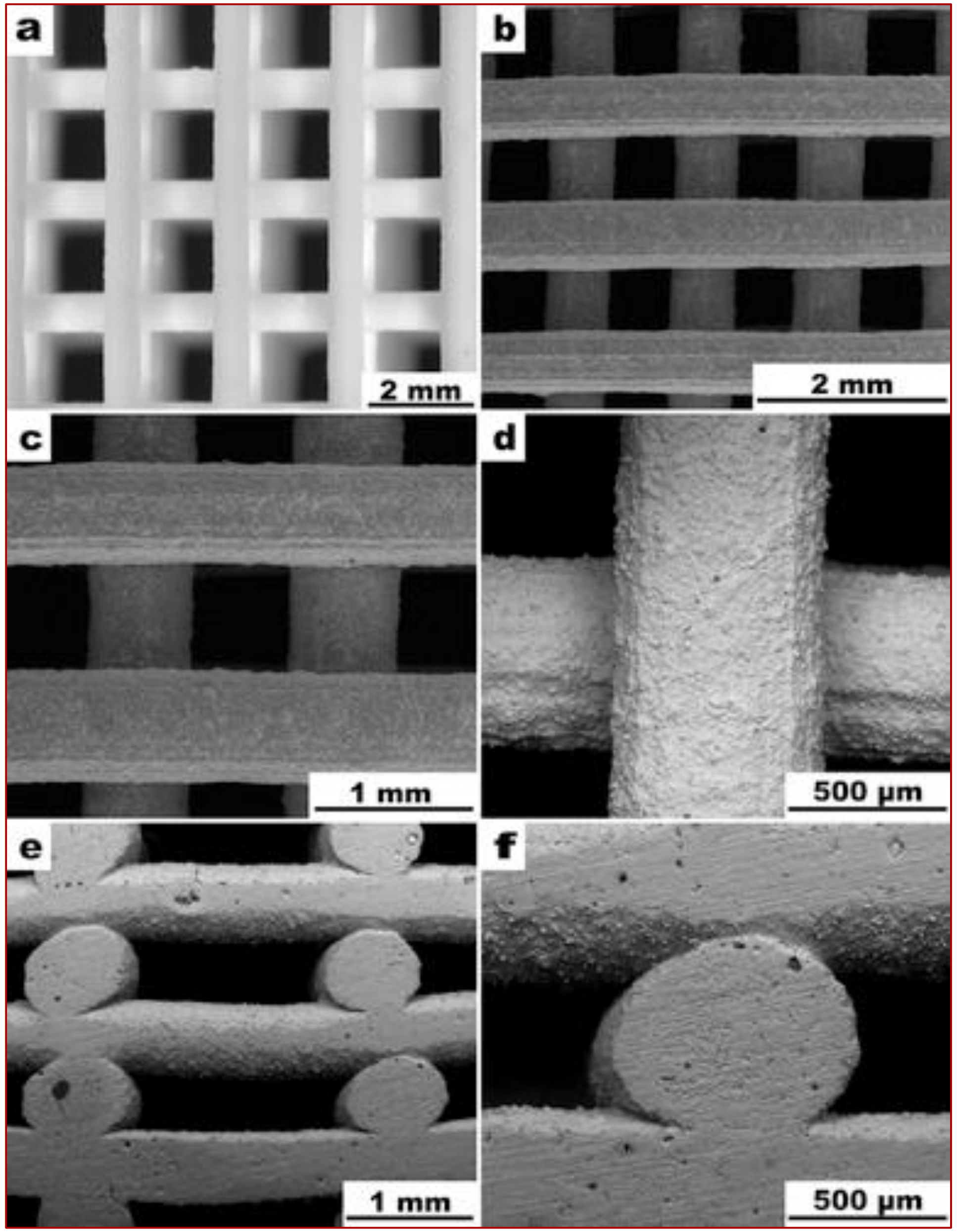


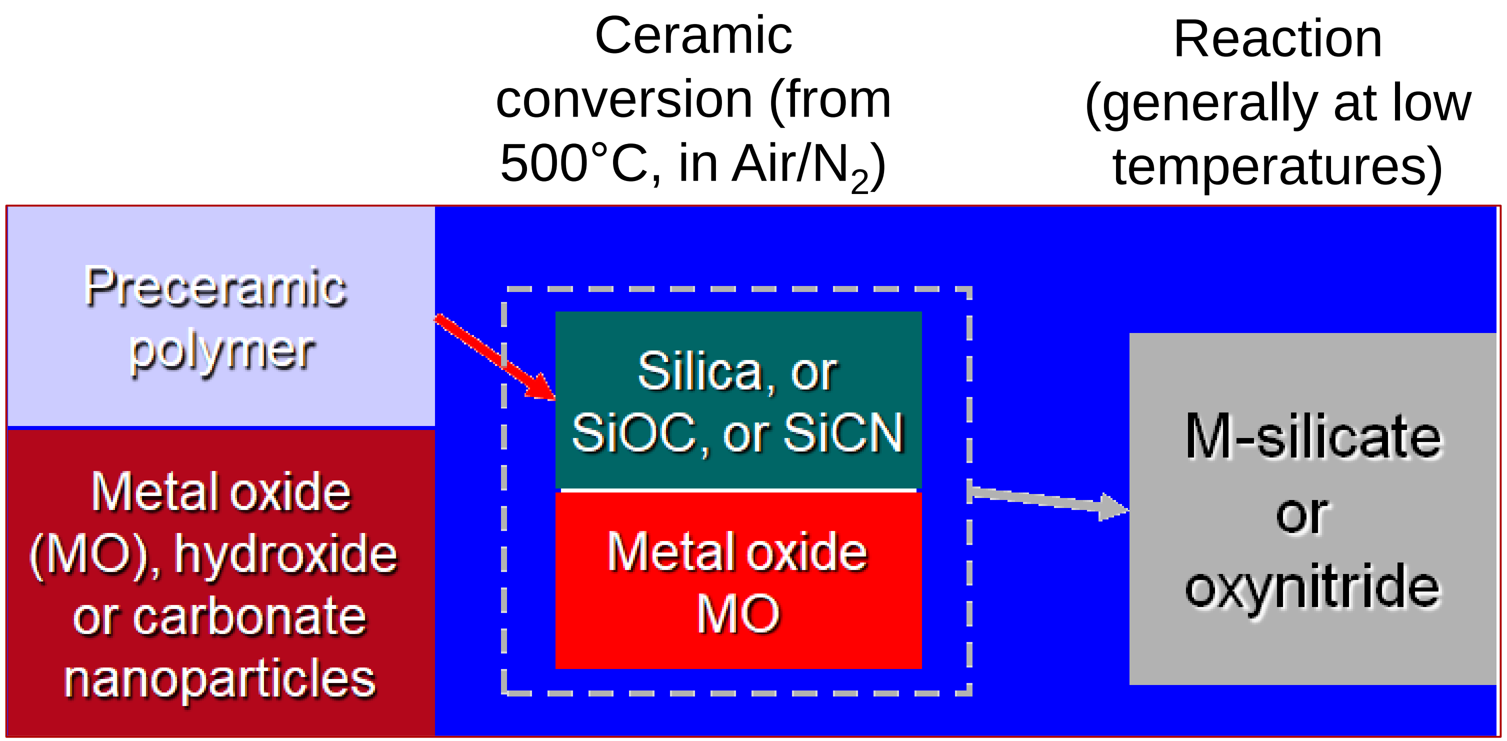
Summary of permeability coefficients according to Forchheimer's equation.

Permeability coefficients	15°	30°	45°	60°	90°	Shifted
$k_1(m^2) \times 10^{-9}$	1.75	3.34	2.56	2.93	3.46	1.41
$k_2(m) \times 10^{-4}$	2.15	3.08	4.34	2.38	3.64	1.98

- Architecture affects mechanical strength and permeability → results applicable to other ceramic systems

Bioceramics (siloxane + fillers)



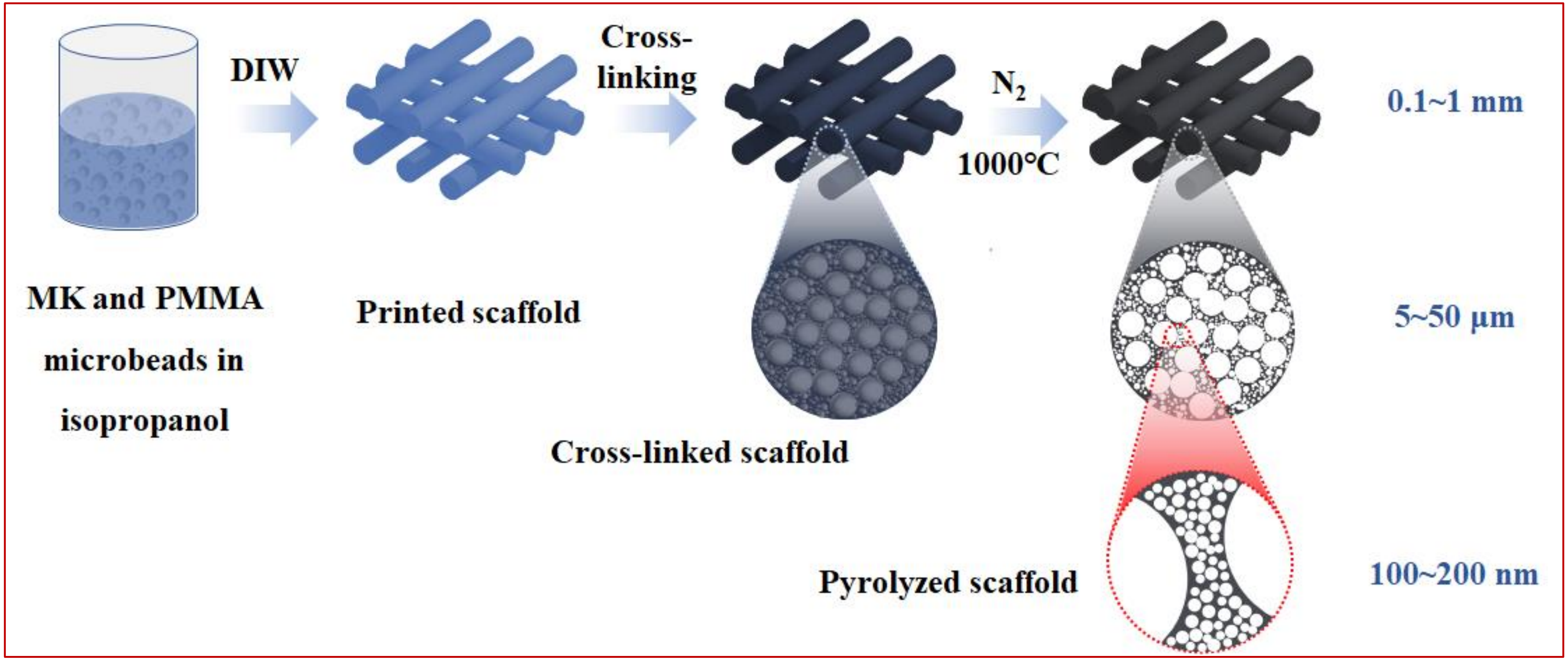


Several bioceramic (silicate) phases can be obtained

In collaboration with E. Bernardo (University of Padova)

A. Zocca, P. Colombo et al., J. Am. Ceram. Soc., ***99*** *(2016) 1960*

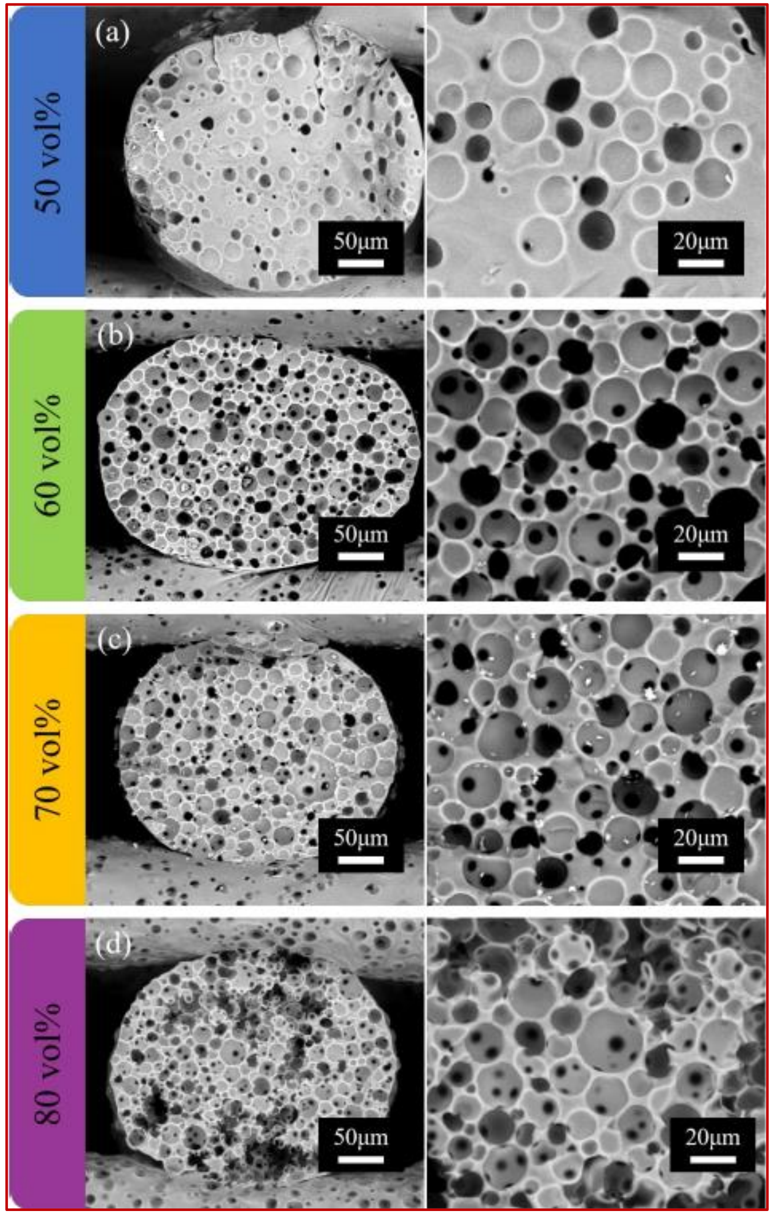
DIW of scaffolds with porous struts



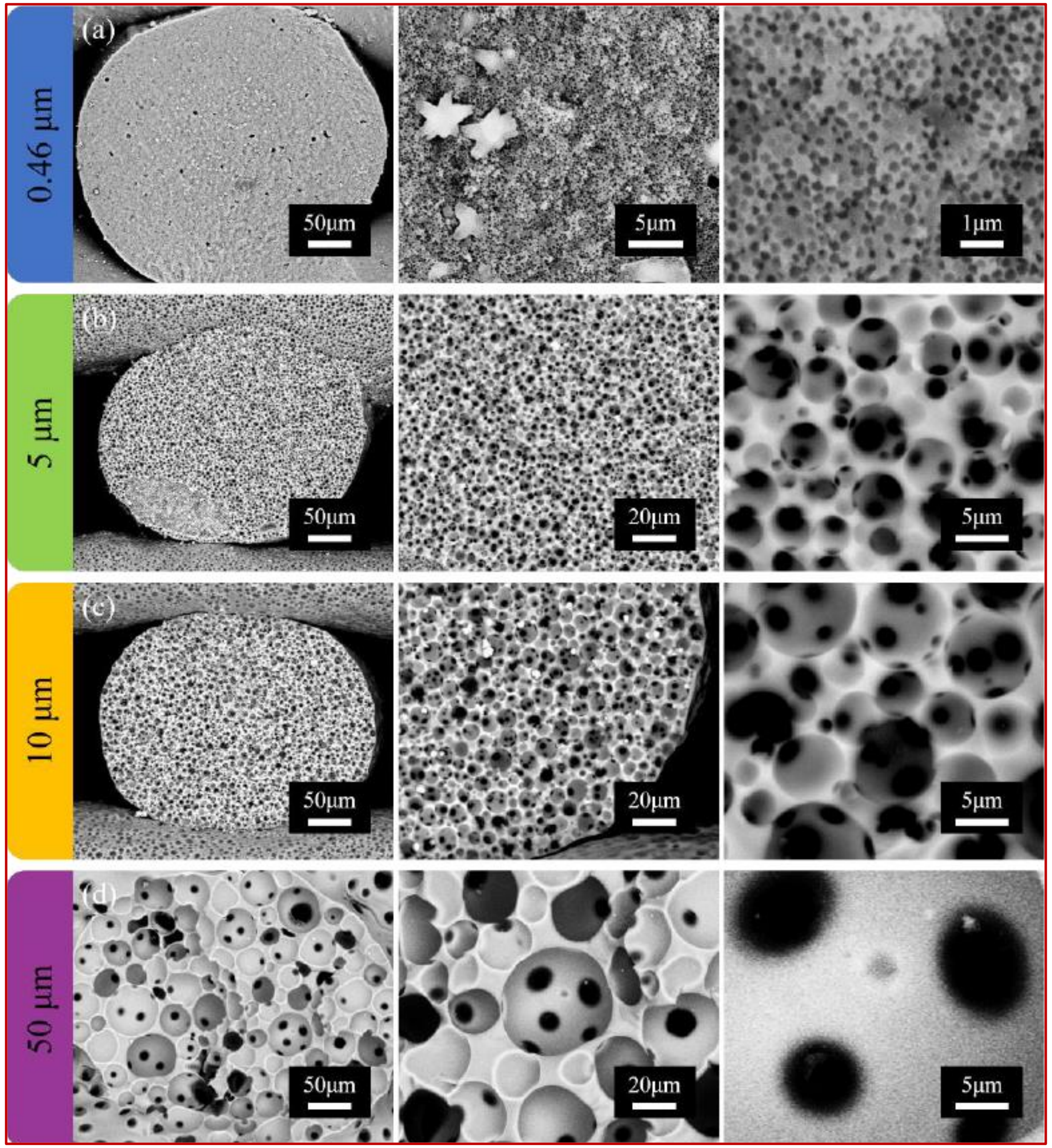
- Methyl-phenyl-siloxane (MK, Wacker Chemie)
- Sacrificial PMMA microbeads (0.5-50 μm)
- Up to ~80 vol% porosity in the struts

K. Huang, H. Elsayed, G. Franchin, P. Colombo, Add. Manuf., ***36*** *(2020) 101549*

Different amounts of PMMA particles and different PMMA size

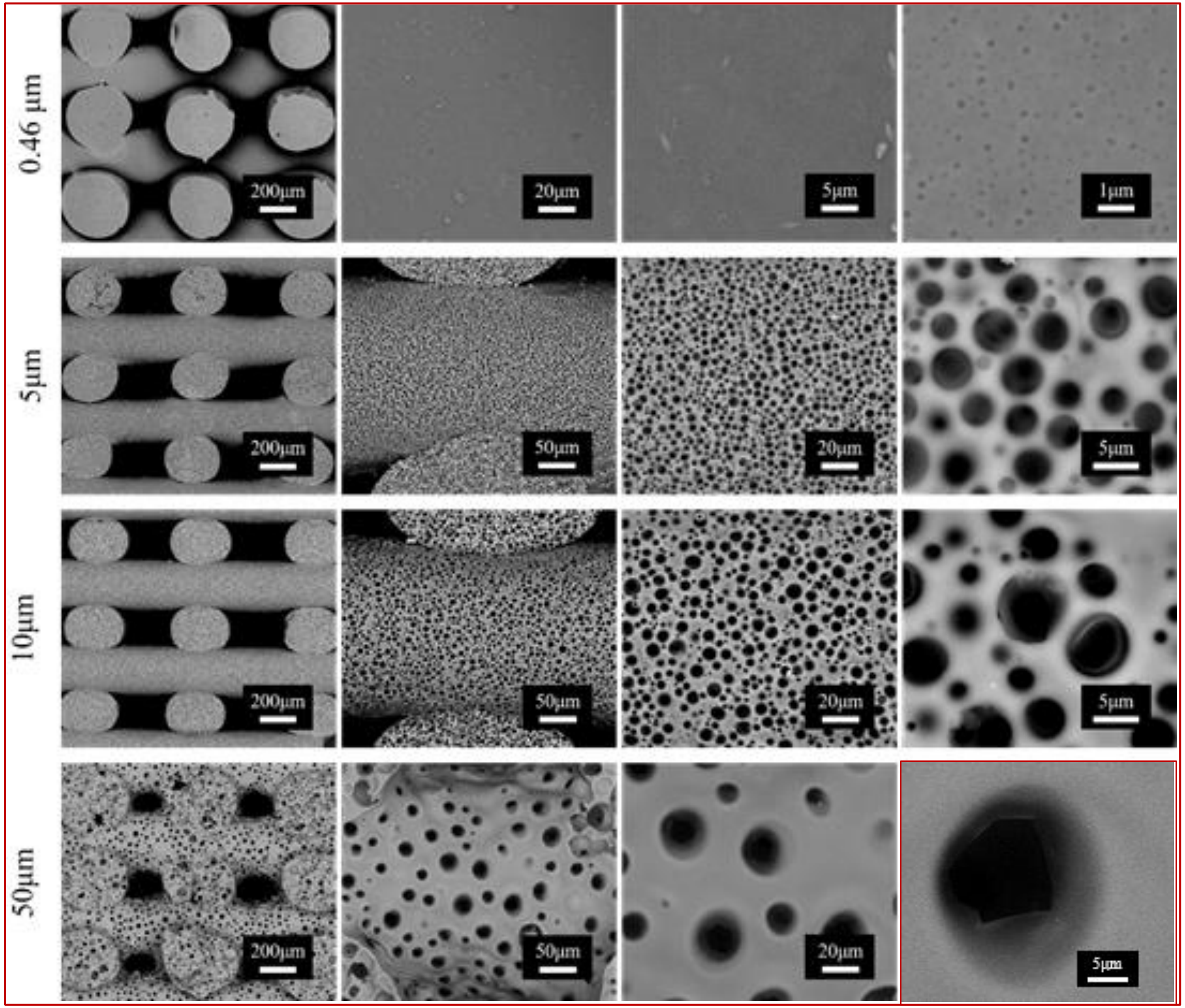


Different vol% PMMA filler (25 µm)



Different filler size (80 vol% PMMA filler)

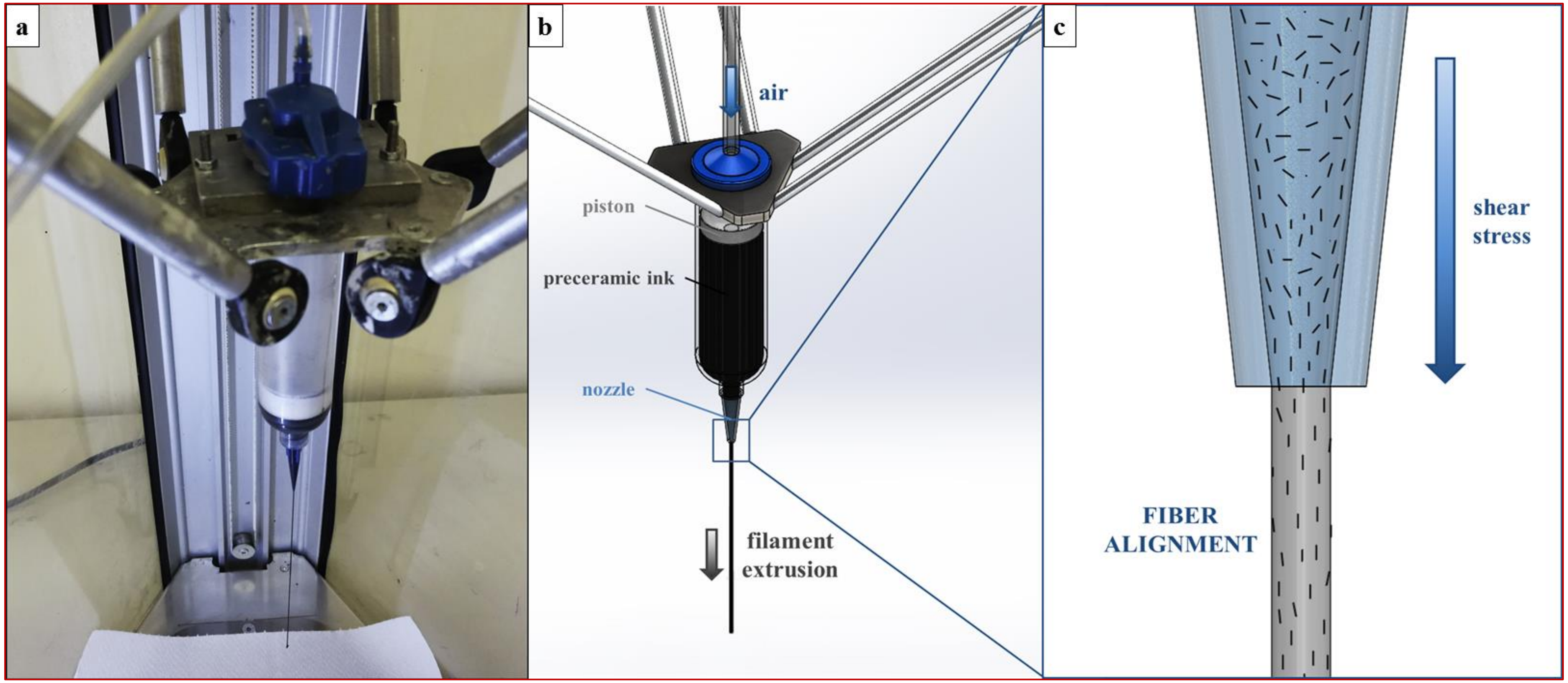
Surface of struts



Surface of filaments from scaffolds fabricated using inks containing 80 vol% of particles of different size: 5, 10, 50 µm
(left image: cross-section of the scaffolds)

→ **porous filament surface**

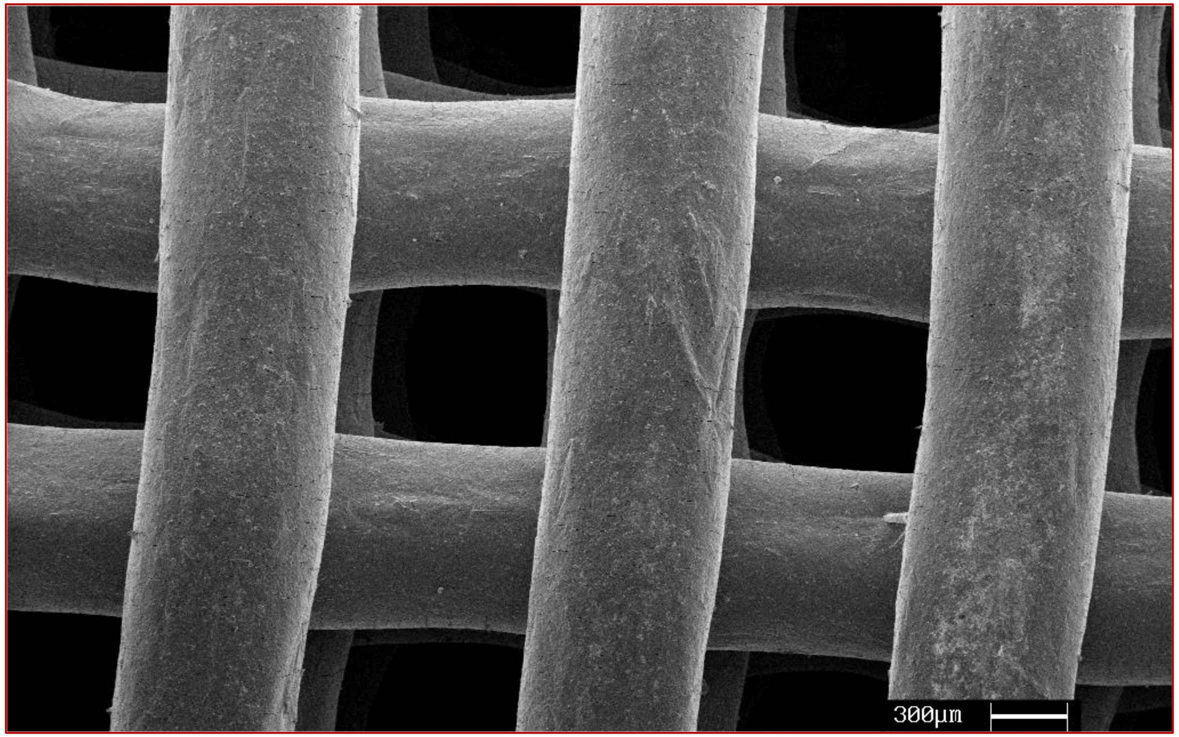
DIW of CMCs



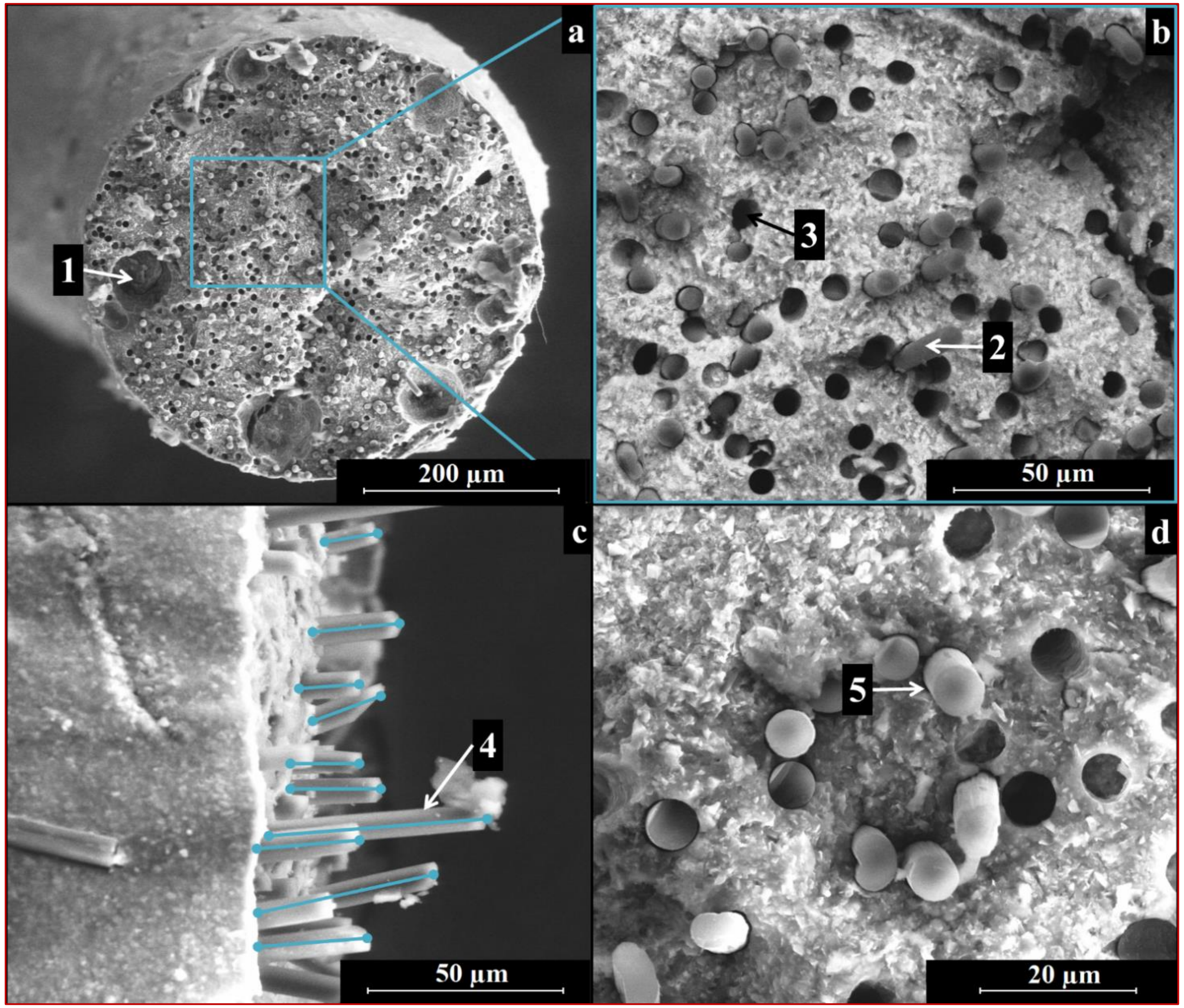
- C fibers (dimension: 150 μm)
- Fiber amount: 20 vol%
- Rheology controlled by amount of preceramic polymer and fillers
- 410 and 580 μm nozzle tip

G. Franchin, L. Wahl, P. Colombo, J. Am.Ceram. Soc., ***100*** *(2017) 4397*

DIW of CMCs



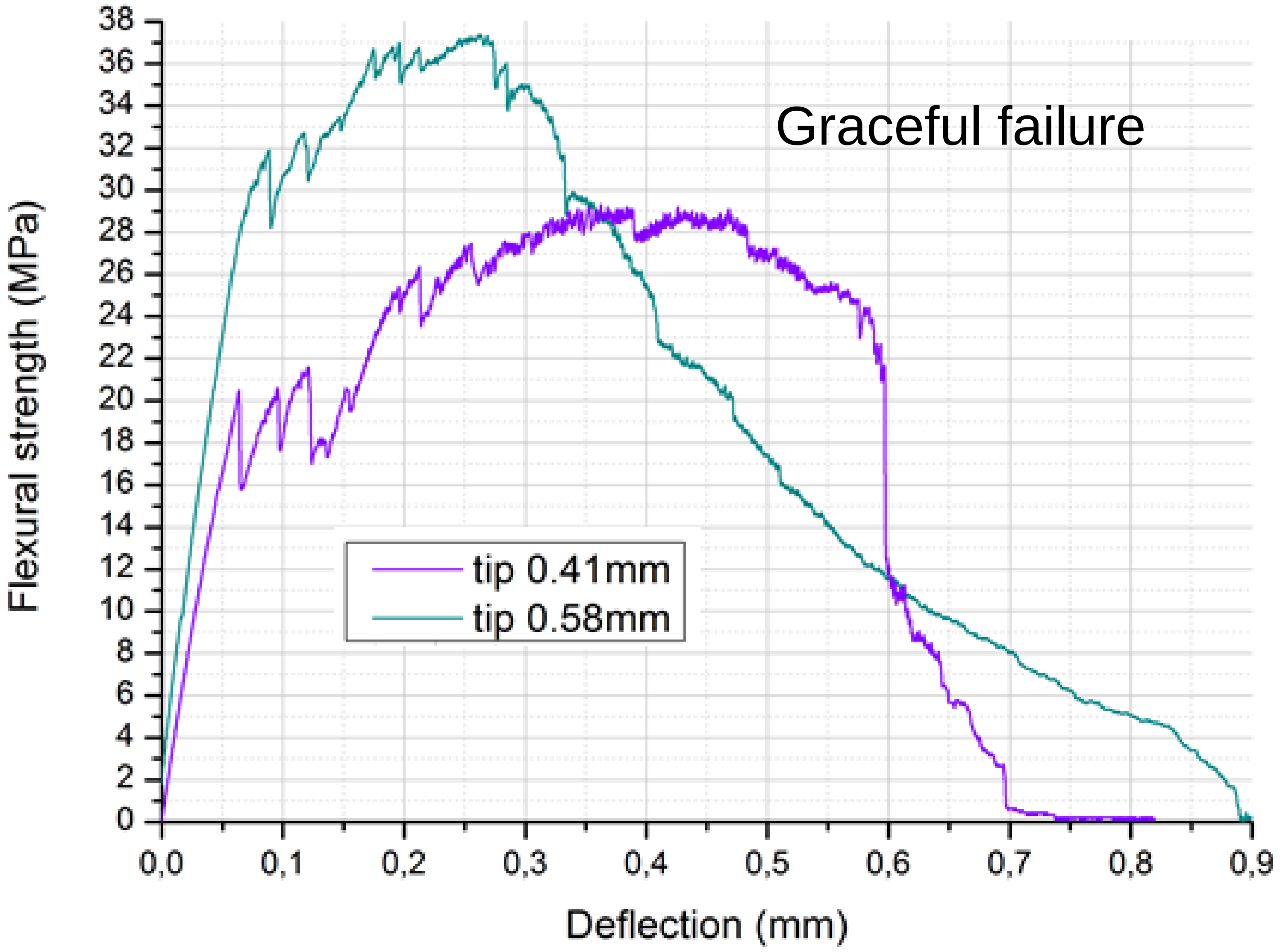
After pyrolysis



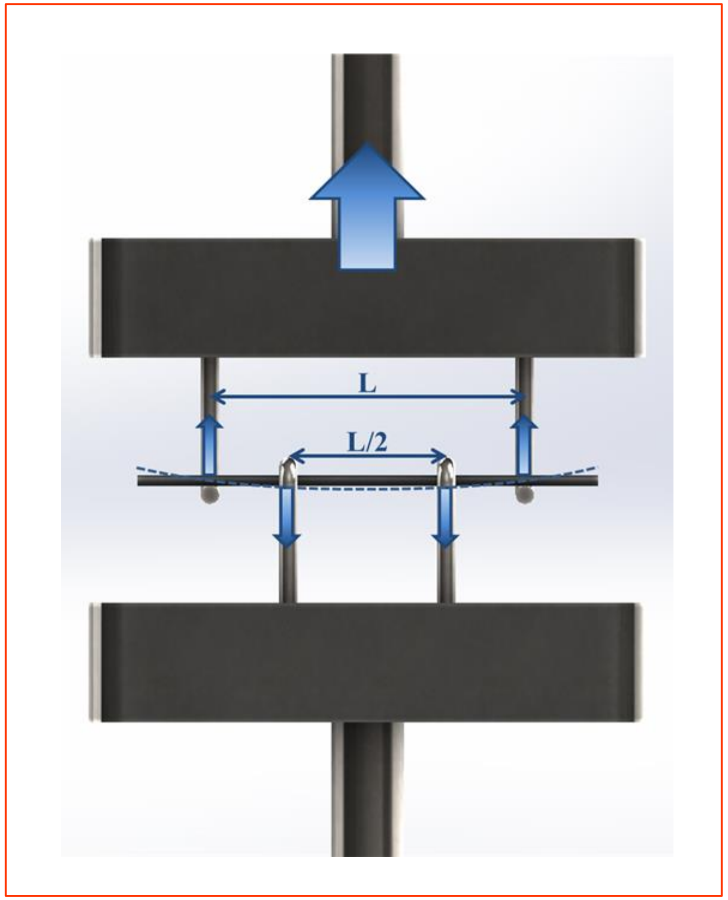
- Fiber pull out
- Some residual porosity (mixing of ink)

G. Franchin, H.S. Maden, L. Wahl, A. Baliello, M. Pasetto, P. Colombo, Mater., ***11*** *(2018) 515*

DIW of CMCs

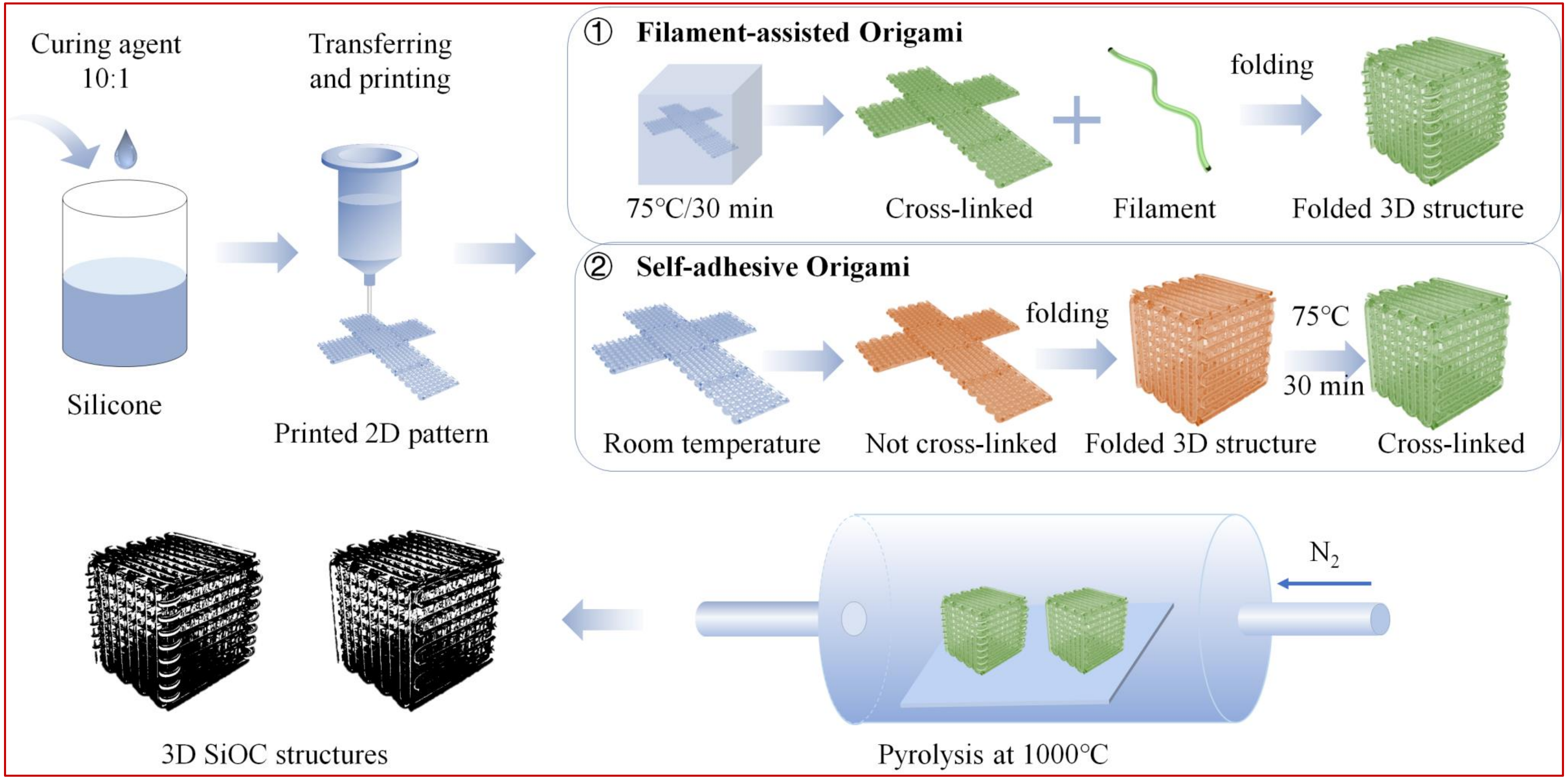


Graceful failure
tip 0.41mm
tip 0.58mm
Flexural strength (MPa)
Deflection (mm)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9



L
L/2

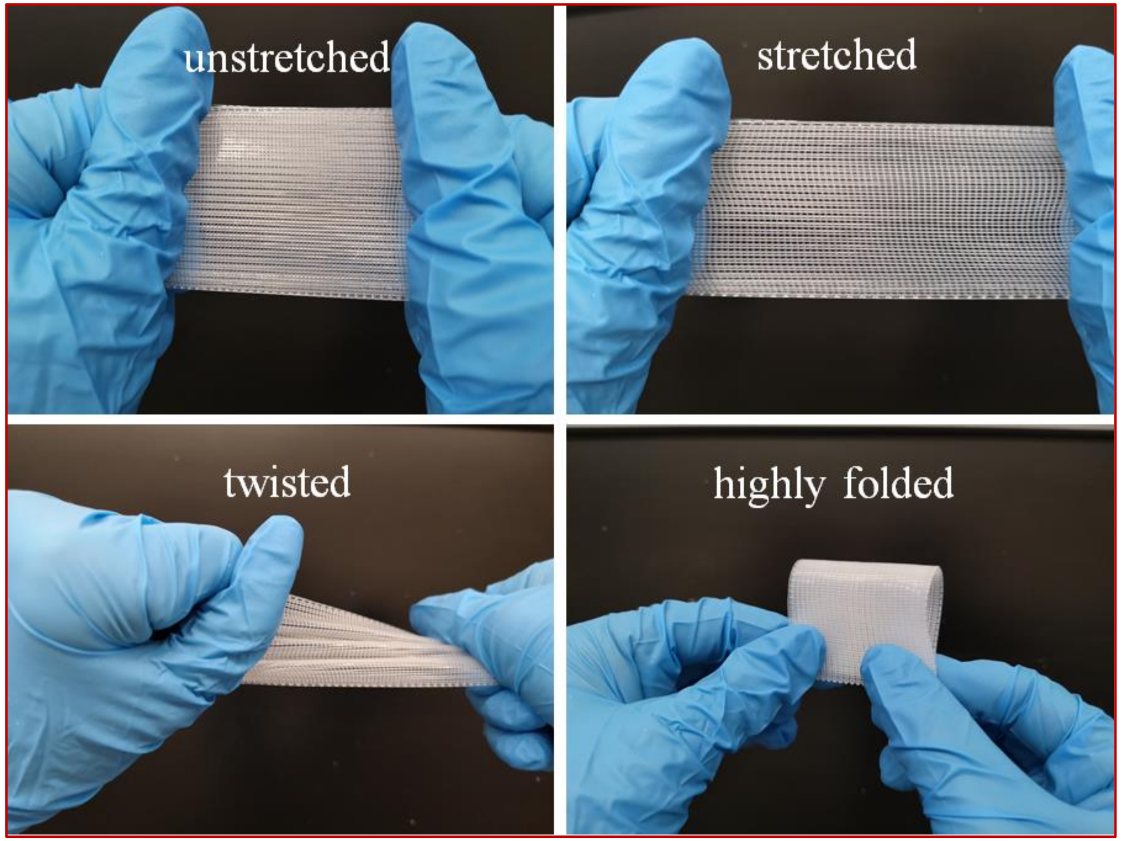
DIW of elastomeric silicone
(printing of 3D SiOC Complex Geometries from 2D Patterns and Origami)

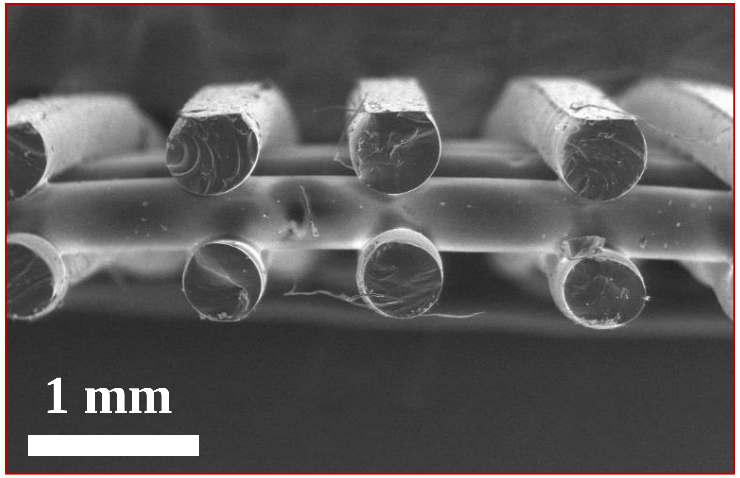


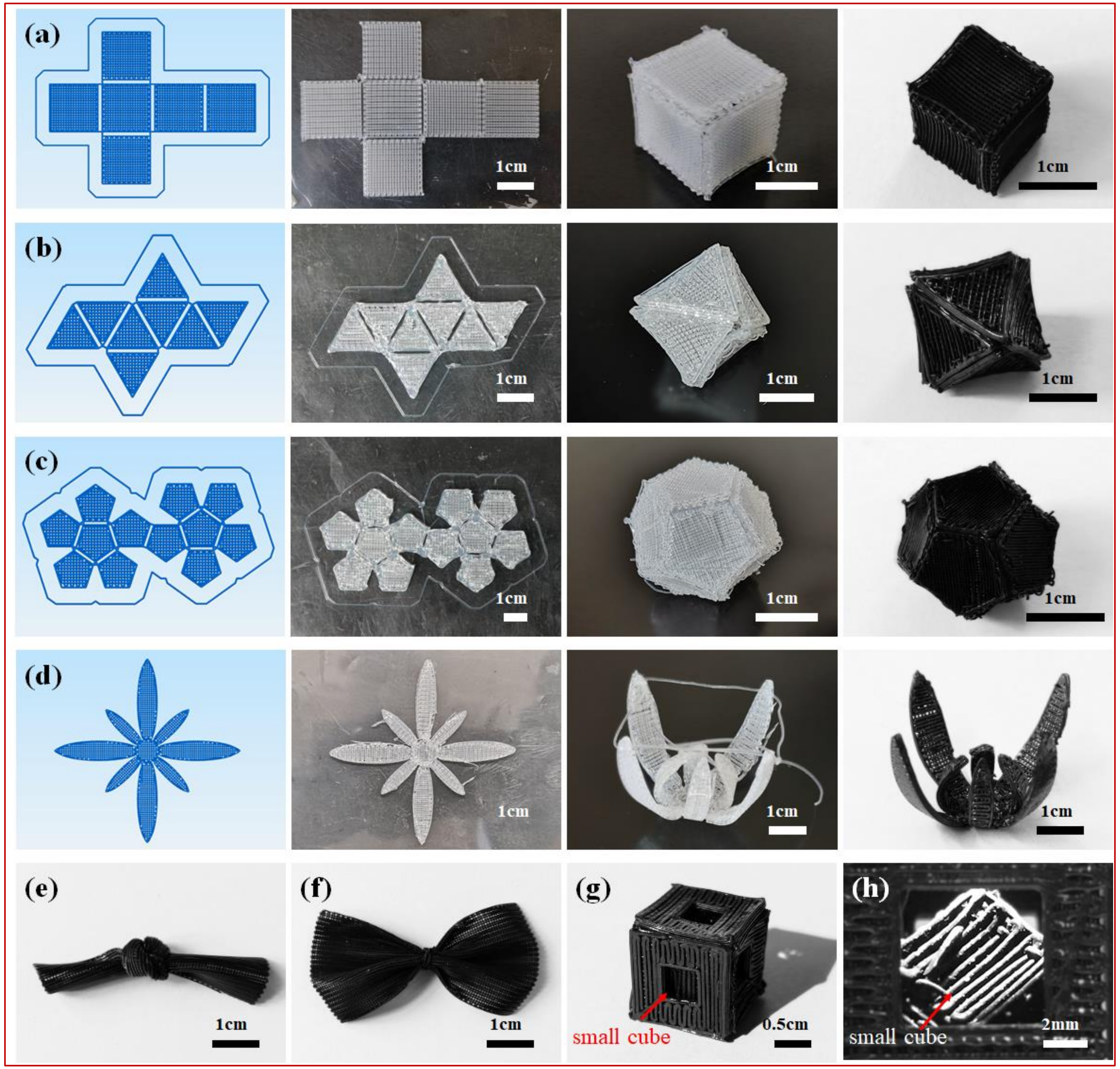
2-parts silicone adhesive (commercially available)

K. Huang, H. Elsayed, G. Franchin, P. Colombo, Add. Manuf., ***33*** *(2020) 101144*

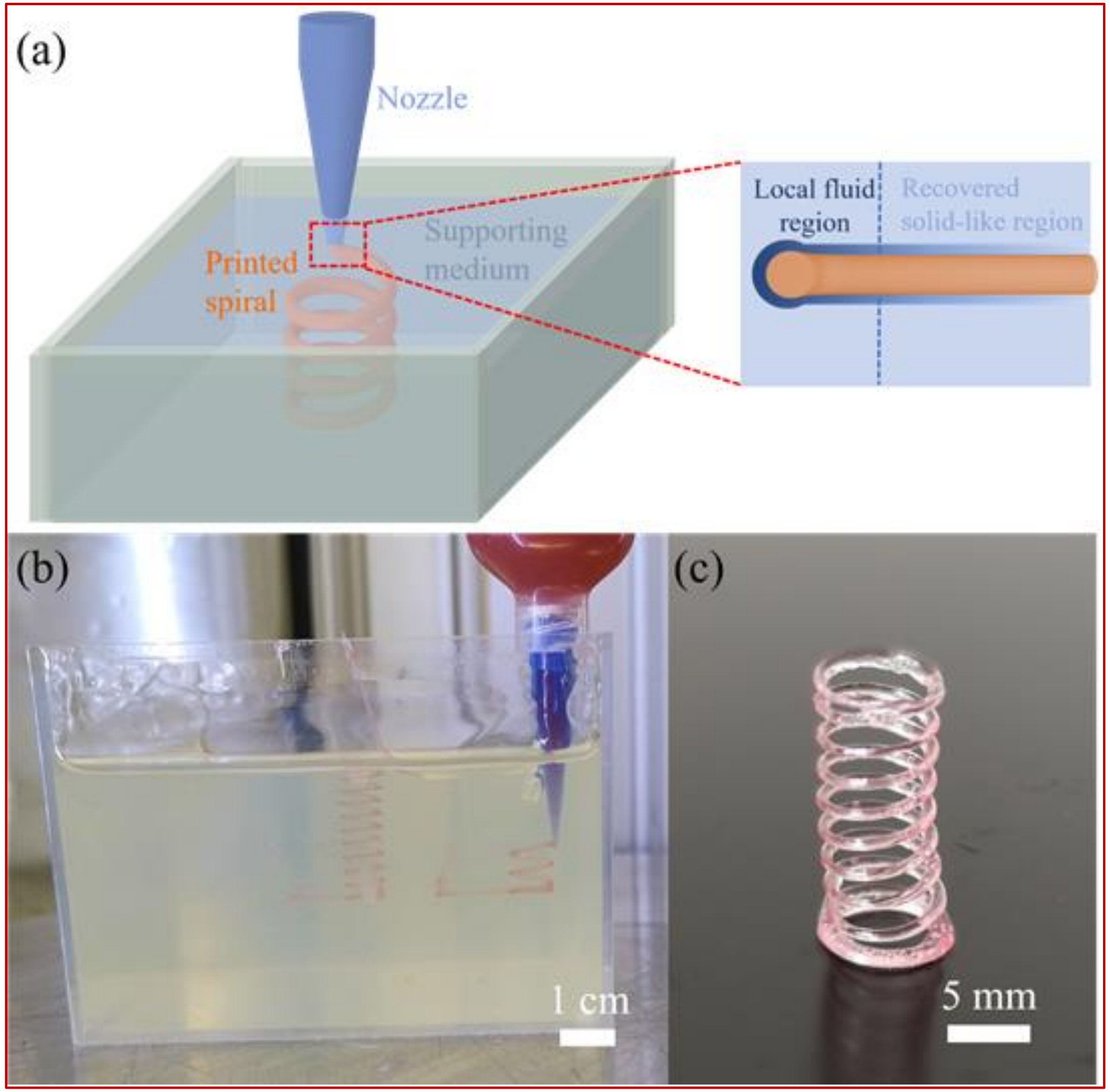
Origami


unstretched
stretched
twisted
highly folded

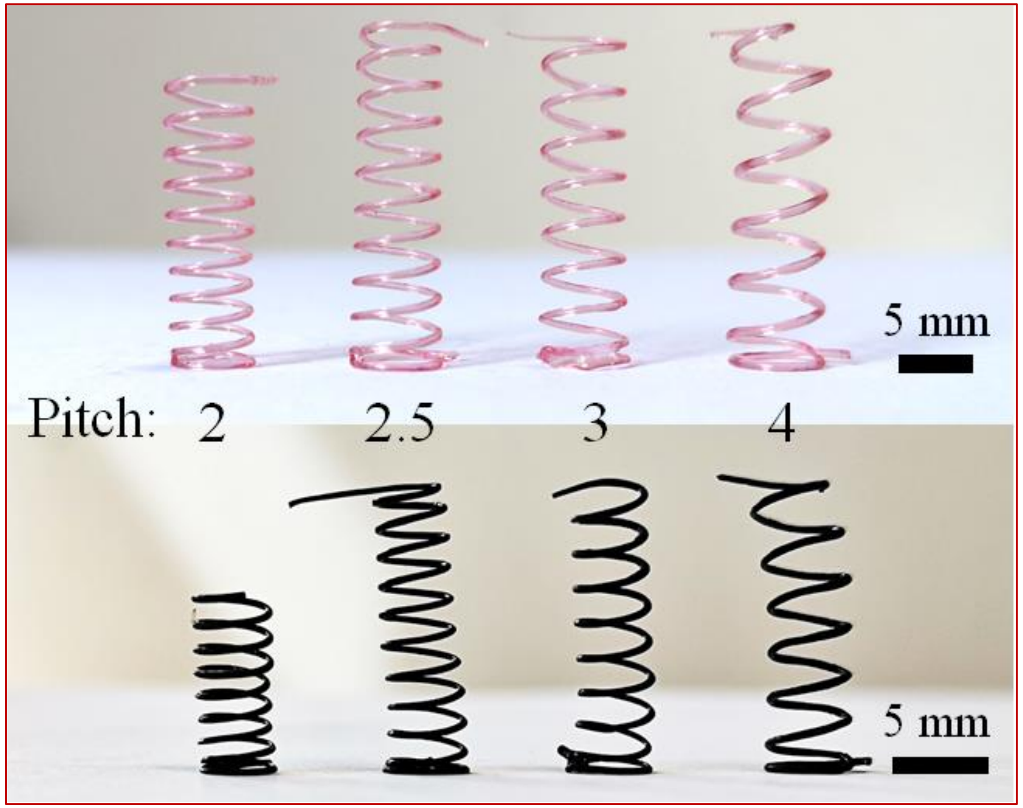

1 mm


(a)
1cm
1cm
1cm
(b)
1cm
1cm
1cm
(c)
1cm
1cm
1cm
(d)
1cm
1cm
1cm
(e)
1cm
(f)
1cm
(g)
small cube
0.5cm
(h)
small cube
2mm

Embedded Direct Ink Writing (E-DIW) of silicones



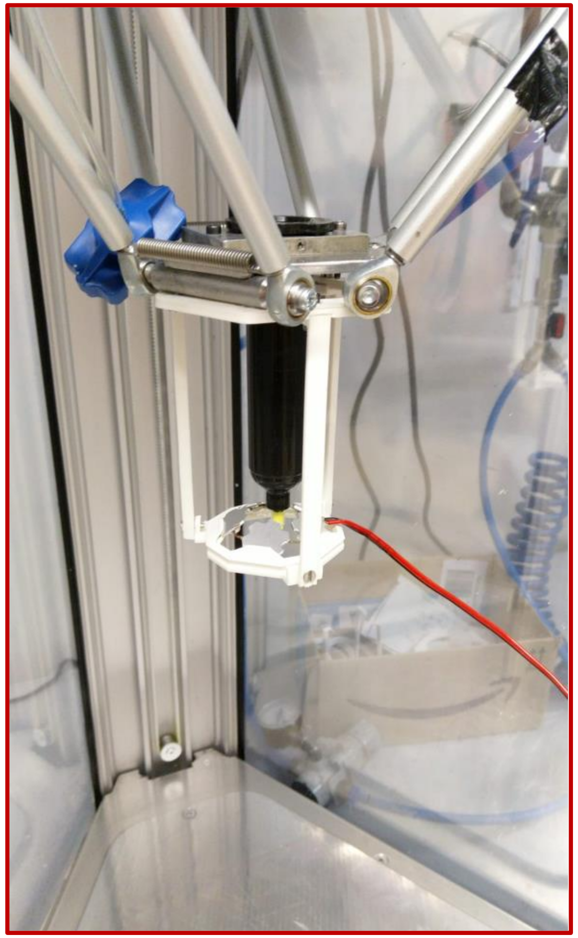
- Limited control of the ink rheology is required
- Freeforming is possible
- Metal or ceramic particle-based inks also possible

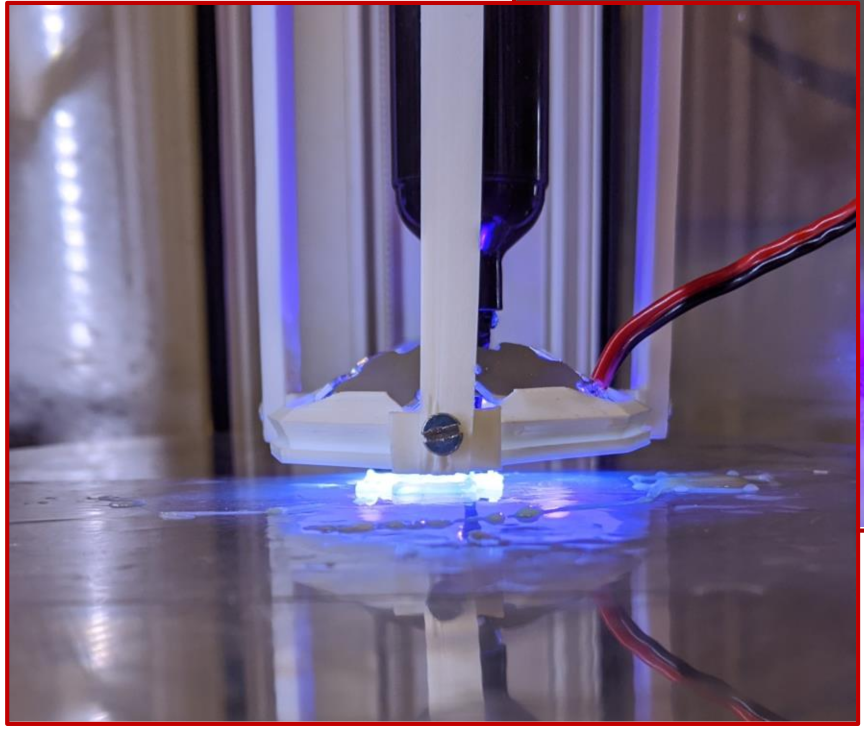


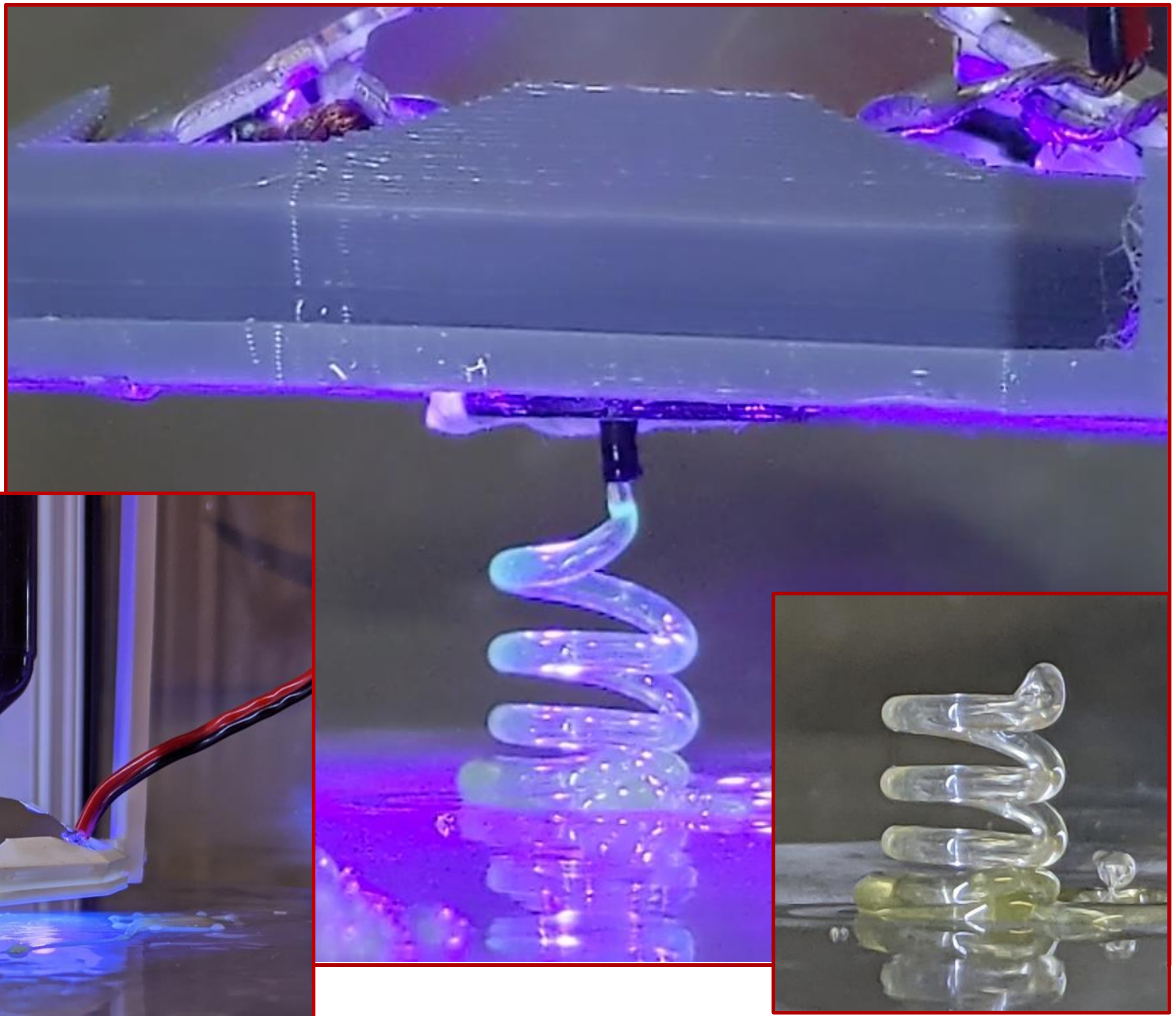
K. Huang, H. Elsayed, G. Franchin, P. Colombo, *Appl. Mater. Today*, **23** (2021) 101005

DIW + UV curing

- UV-assisted DIW → Free Forming
- No need to control rheology of inks
- → liquid preceramic polymers → very thin nozzles possible

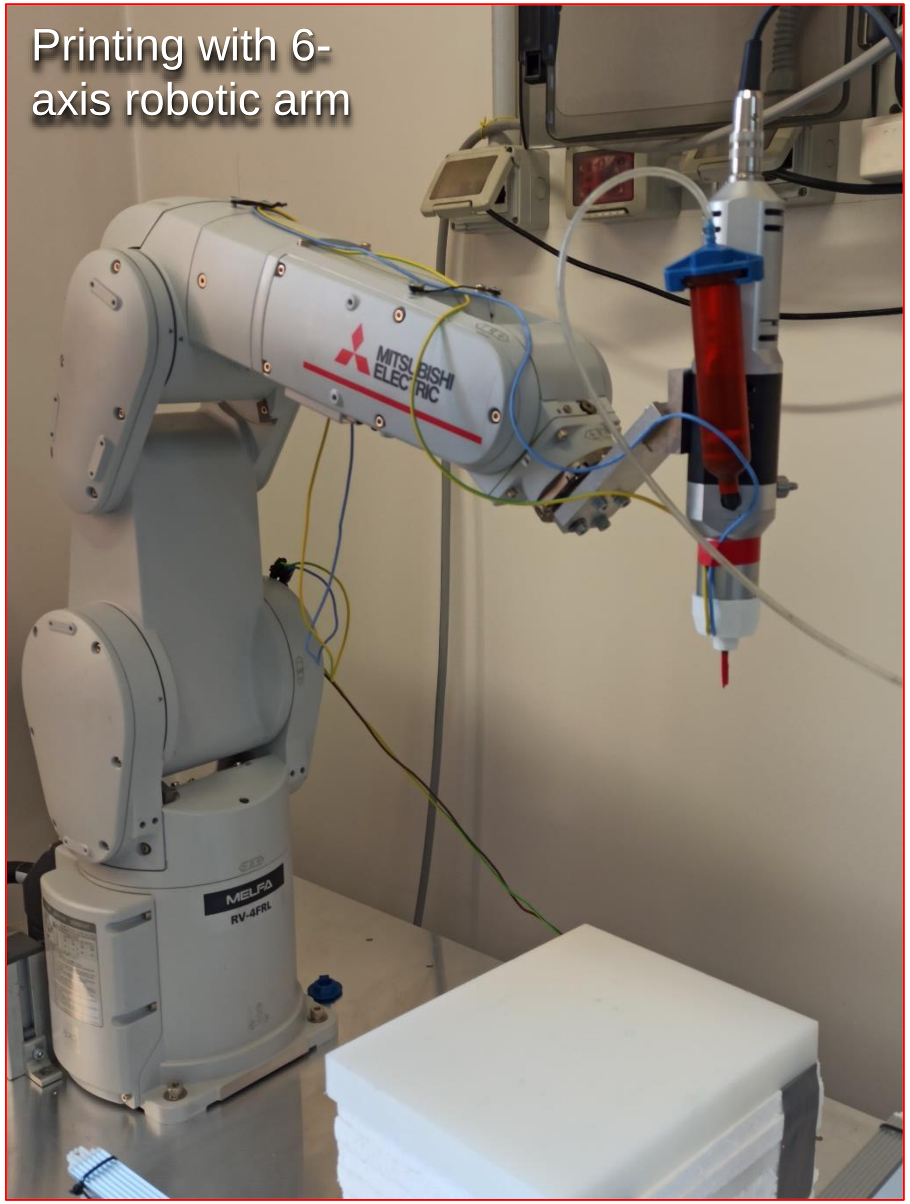


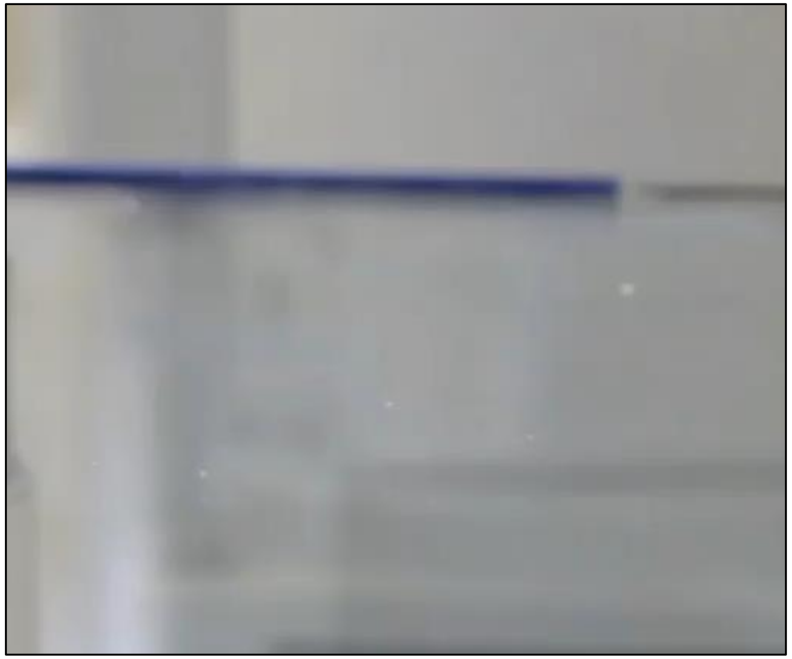


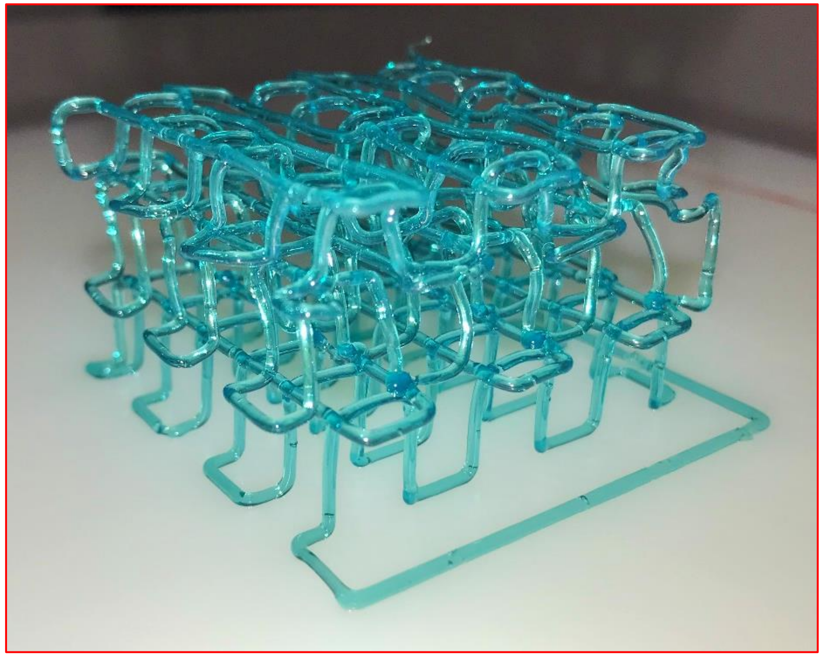


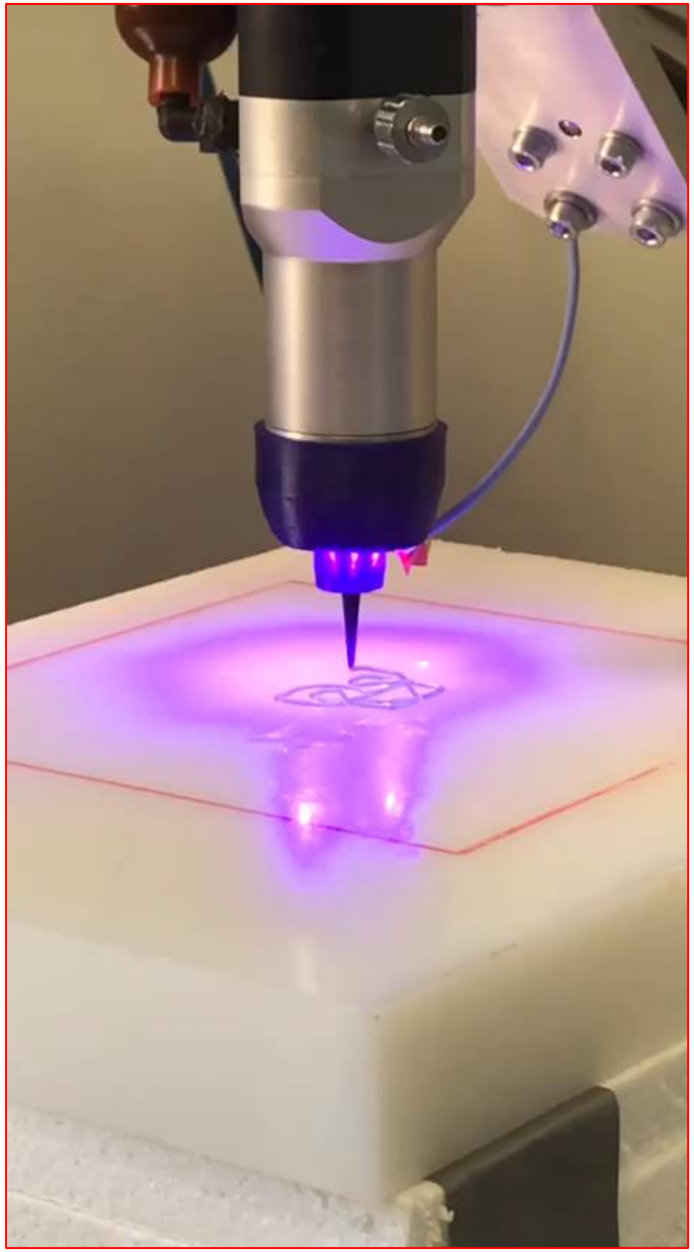
A. De Marzi, K. Huang, G. Franchin, P. Colombo, manuscript in preparation

DIW + UV curing (Robotic additive manufacturing - RAM)



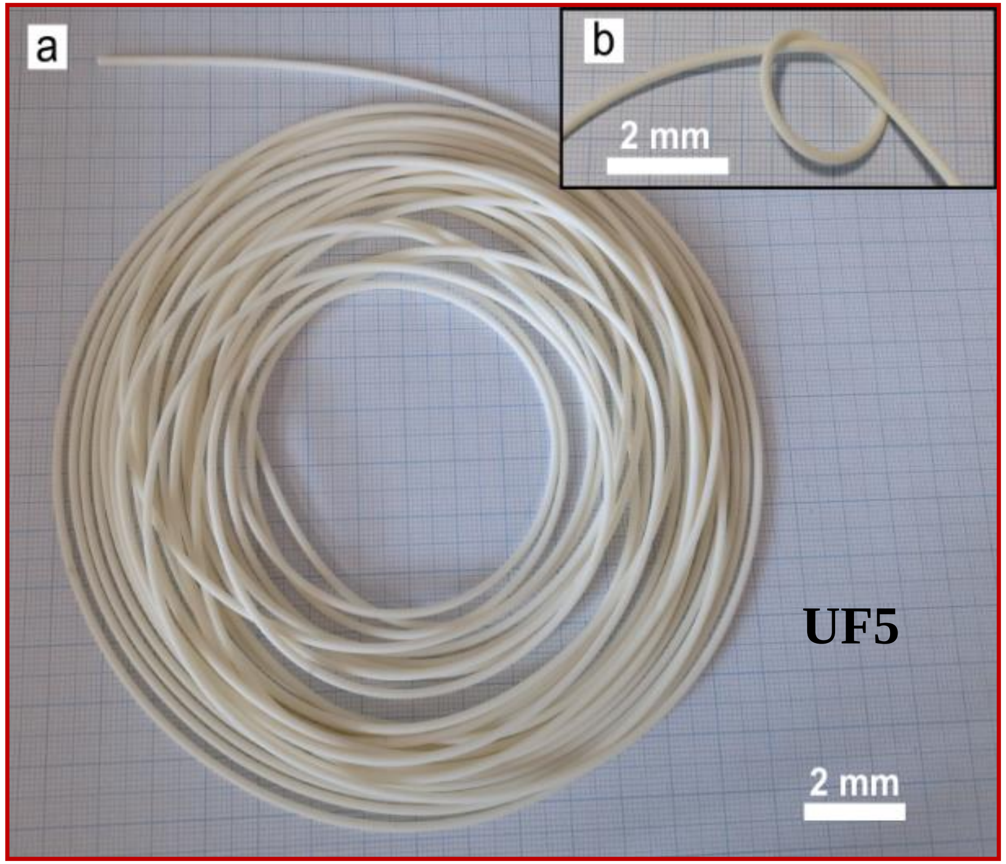


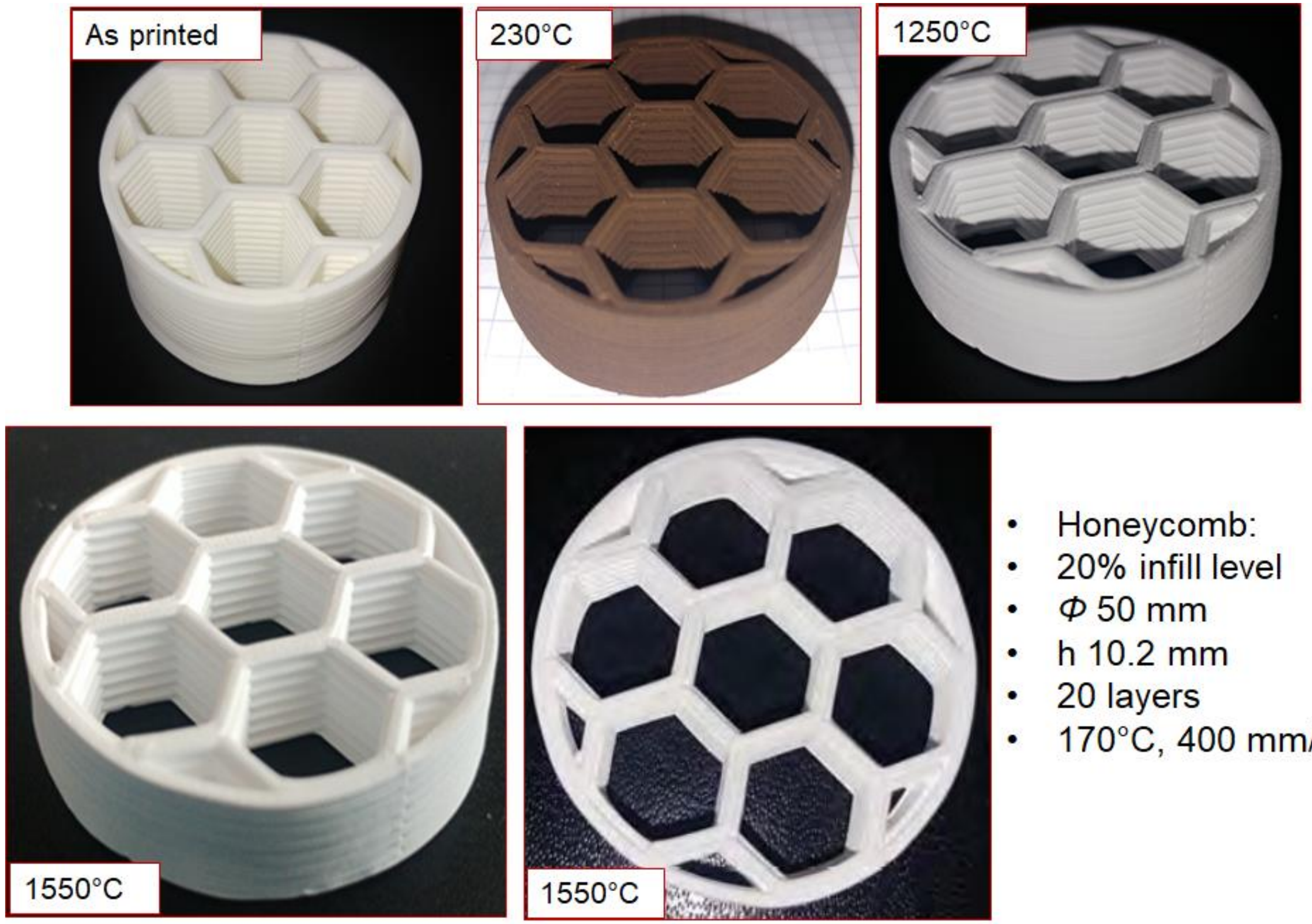




FDM of Preceramic Polymers

- Fabrication of filaments based on silicone resins, Ethylene Vinyl Acetate and γ-alumina powders → Mullite
- Filament printable at 170°C





- Honeycomb:
- 20% infill level
- Φ 50 mm
- h 10.2 mm
- 20 layers
- 170°C, 400 mm/min

In collaboration with F. Clemens (EMPA)

L. Gorjan, R. Tonello, T. Sebastian, P. Colombo, F. Clemens, J. Eur. Ceram. Soc., ***39*** *(2019) 2463*
F. Sarraf, E. Abbatinali, L. Gorjan, T. Sebastian, P. Colombo, et al., J. Eur. Ceram. Soc., ***41*** *(2021) 6677*

BJ of Preceramic Polymers

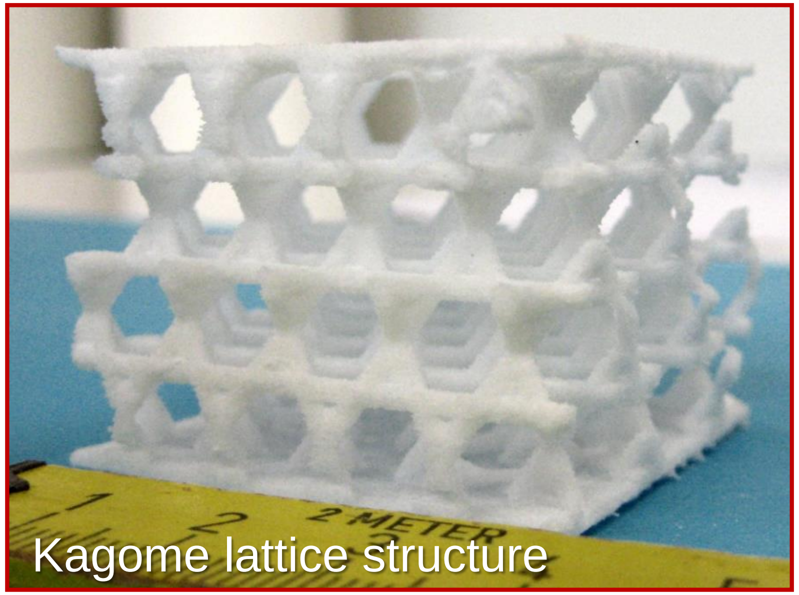
Powder bed: preceramic polymer powder (MK silicone resin)

1. Catalyst (1 wt% Zr AcAc) mixed with dissolved preceramic polymer and then powder was granulated and sieved (45–90 µm; Hausner ratio 1.25*) → printing liquid: *isopropanol*
2. Catalyst (1 wt% liquid tin octoate) mixed with proprietary Voxeljet binder (*1-hexanol and hexylacetate*) (50–90 µm; Hausner ratio 1.23*)

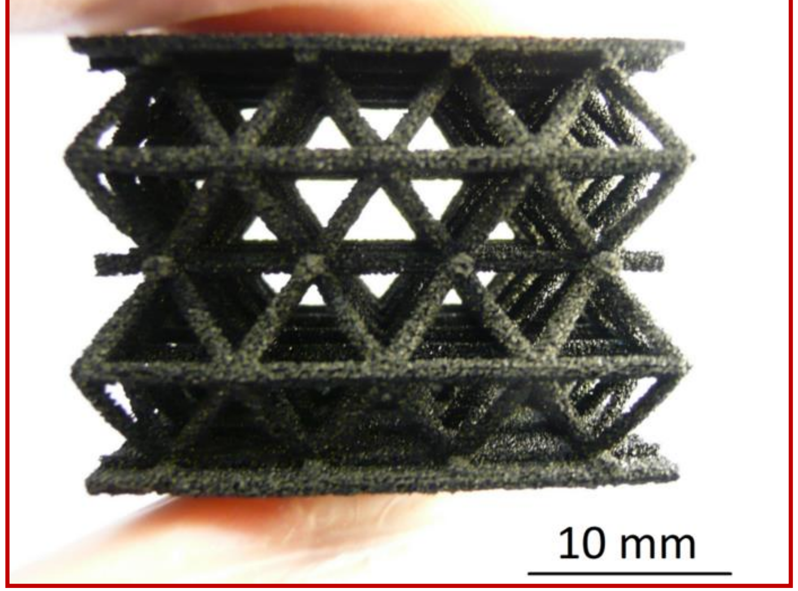
- Green parts printed with hexanol: density ~80%, starting from a powder bed with ~45% density → very good densification!
- Green parts printed with isopropanol: density ~49% → lower solvent concentration and higher vapor pressure of isopropanol → high porosity

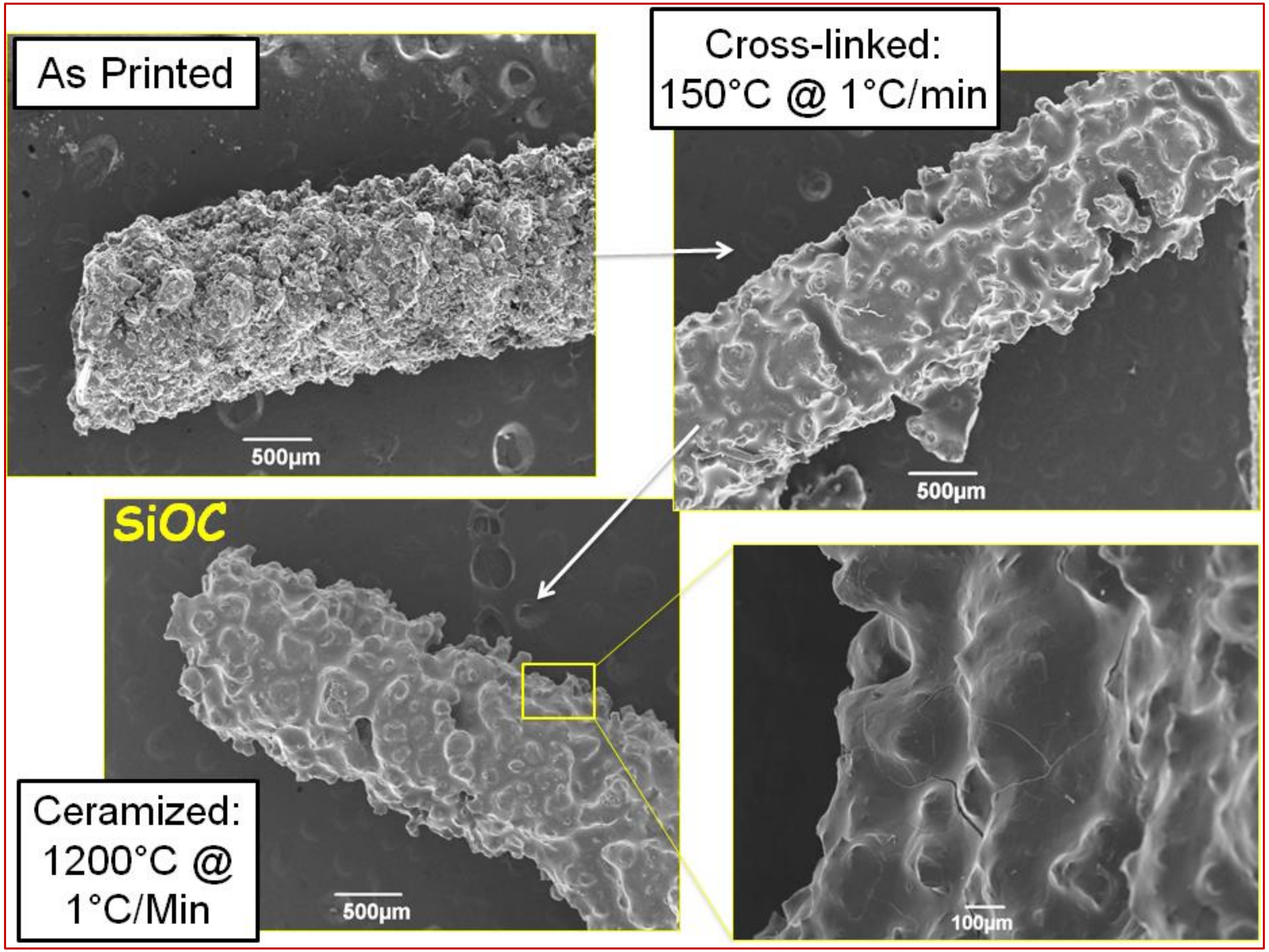
A. Zocca, C.M. Gomes, J. Guenster, A. Staude, E. Bernardo and P. Colombo, J. Mater. Res., ***28*** *(2013) 2243*

Binder Jetting



Ceramized octahedral structure

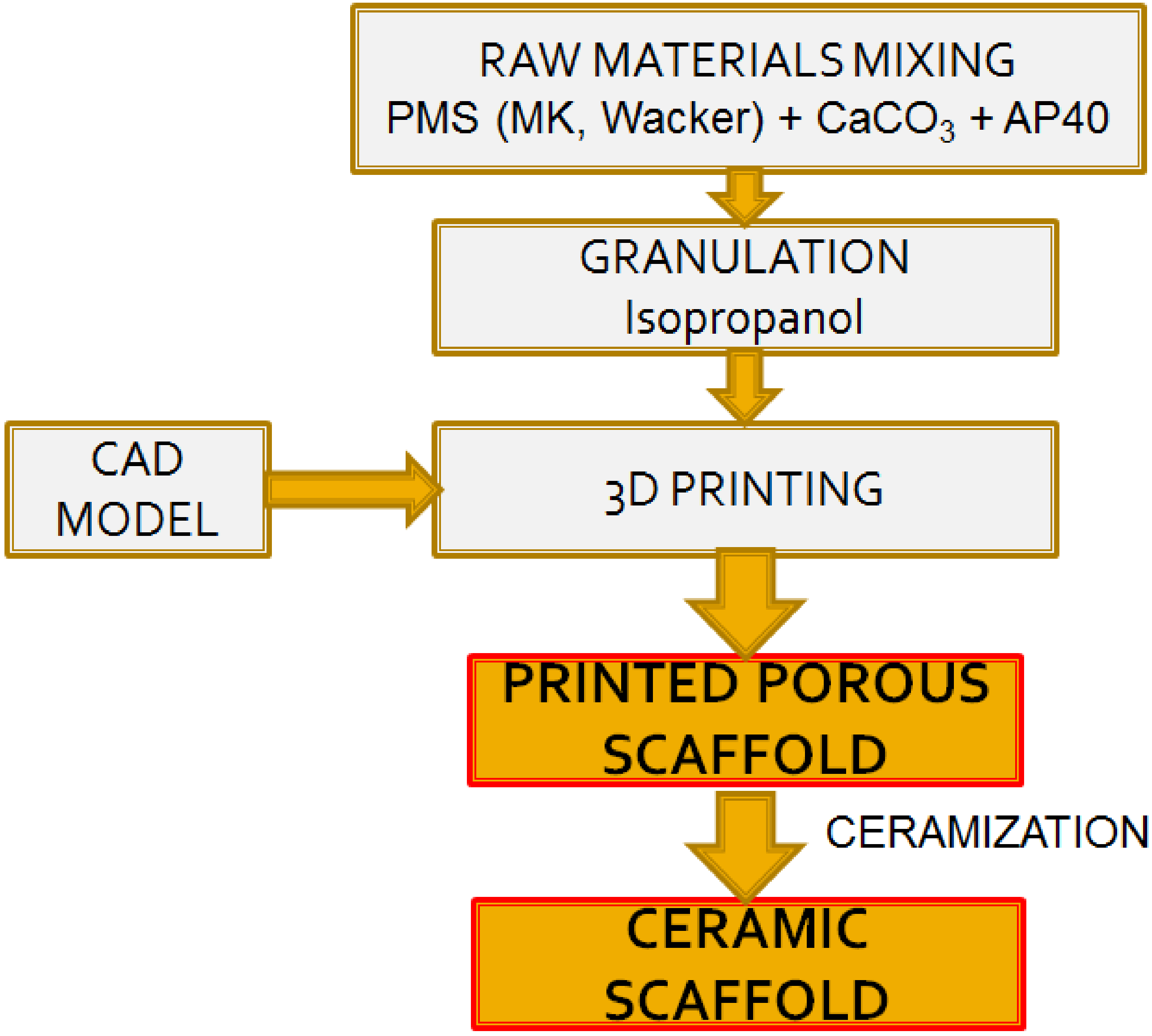




In collaboration with J. Guenster, A. Zocca (BAM)

BJ of Preceramic Polymers + fillers

$CaCO_3$ ca. 10 µm
AP40 <45 µm
MK <45 µm

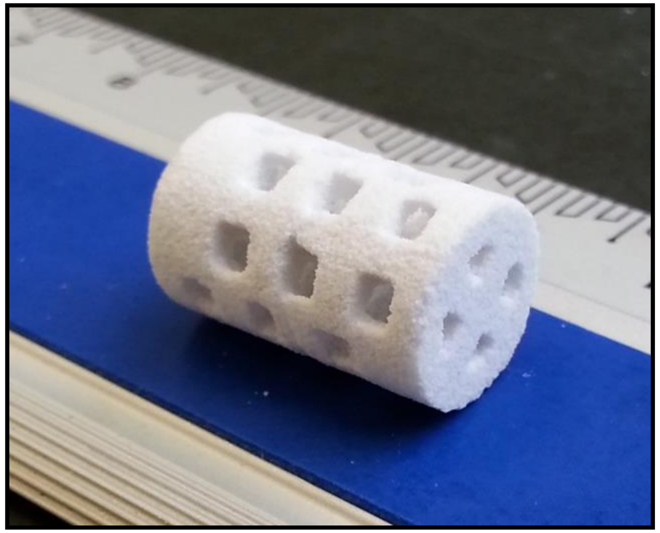


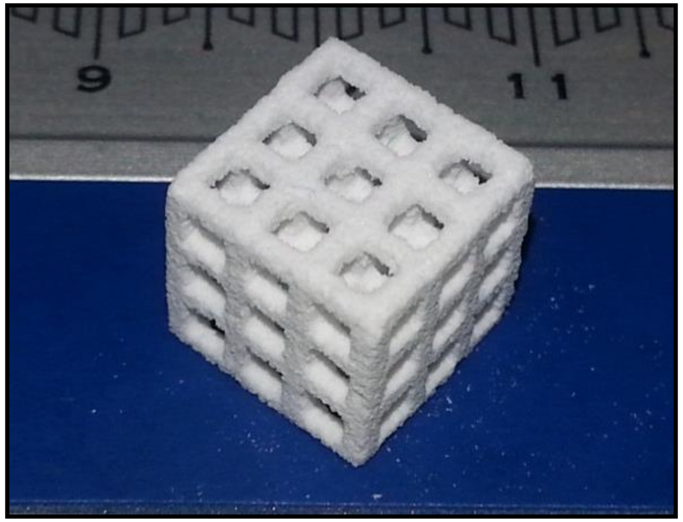
CERAMIZATION 900 °C / 1h (2°C/min)

A. Zocca, P. Colombo, J. Guenster, et al., Biofabric., ***7*** *(2015) 025008*

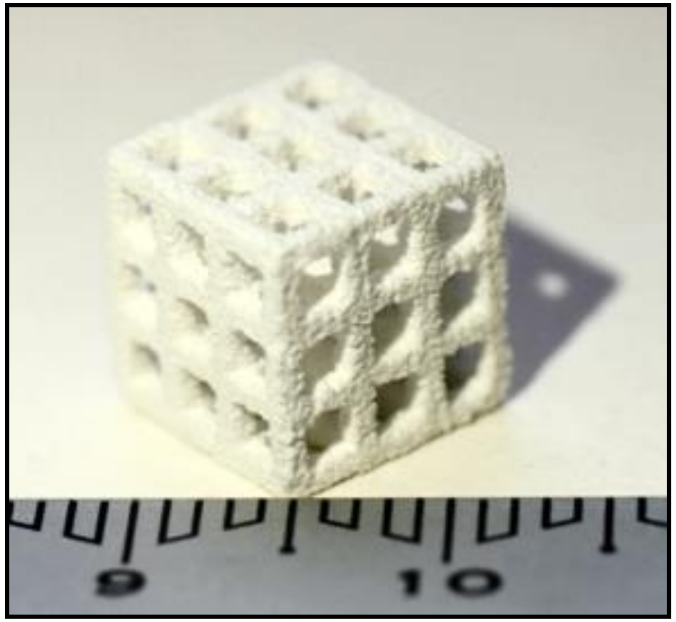
BJ of Preceramic Polymers + fillers

20 wt% Wollastonite, 80 wt% AP40 bioglass (→ Fluoroapatite+Wollastonite)





As printed



Ceramized

Conclusions

- Preceramic polymers (*plus fillers*) offer the potential to produce relatively easily ceramic components in a wide range of compositions using a large variety of Additive Manufacturing technologies based on photo-polymerization (DLP, 2PP, Xolo, DIW+UV), extrusion (DIW, E-DIW, DIW+UV, RAM), or other (FDM, BJ)
- Highly porous structures with controlled (non stochastic) architecture can be produced
- Several processing parameters (type of precursor, type of filler, heating time and atmosphere) as well as printing parameters need to be optimized for reaching the desired results
- Combination of DLP macrofabrication and TPP microfabrication (**hybridization**) → µm-sized surface structuring of cm-sized objects
- Combination of DIW and UV curing (**hybridization**) → free forming
- **Volumetric printing** is possible

Acknowledgements

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J. Schmidt
K. Huang
A. De Marzi
F. Da Rin Betta
Y. Feng

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- EIT-KIC ”IDEAL”
- H2020-MSCA-RISE ”AMITIE”
- MIUR PRIN
- Companies

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Questions? Issues? PROBLEMS?

UEFA Euro 2020/1