NOVEL CERAMICS AND COMPOSITES PROCESSING TECHNOLOGIES FOR ENERGY-INTENSIVE APPLICATIONS

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CEM-WAVE

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Additive manufacturing of ceramics from preceramic polymers

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Why (all) liquid feedstocks? Liquid *vs* Powder feedstocks

Typically, AM of ceramics is carried out using **powder-based** feedstocks

Powder-based feedstocks

- ☹ Stabilization of fine ceramic powders dispersed in non-aqueous liquids is difficult
- ☹ High viscosity even with a limited amount of powder (~40%vol) → special equipment
- ☹ Light scattering and index matching limit the resolution and penetration depth (DLP, SLA)
- ☹ Particle size controls nozzle dimension (DIW) → limit in resolution, feature size and surface quality
- ☹ Clogging of nozzle (DIW)
- ☹ Green bodies with adequate strength

Liquid feedstocks

- ☺ Liquid systems exploit the more advanced stage of development of AM technologies for polymers
- ☺ Densification occurs at lower temperatures and generally results in denser bodies
- ☺ Stronger and more reliable green parts
- ☺ Unique material properties retained (i.e., glass transparency)
- ☹ Not suitable for all AM technologies (BJ, FDM, SLS/SLM, DED)
- ☹ Compositional range is (so far) limited → sol-gel-based formulations

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), sensing, EMW absorption, ...
- High ceramic yield preferred. **Cross-linking** before pyrolysis useful/necessary

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 Sorarù

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

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

*R.P. Chaudhary, Z. Chen, P. Colombo et al., Prog. Mater. Sci., **128** (2022) 100969*

Approach 5: blending

a) **Photo-curable** preceramic polymer (*or a **fully organic photo-polymer***)

- Commercially available (polysiloxane-acrylate (PSA) with high amount of acrylic groups)
- Low ceramic yield of 7.4 wt% (*or ~0 wt%*)

b) **Non photo-curable** preceramic polymer

- Different preceramic polymers (Pol1, Pol2), compatible with PSA or organic PPs (no phase separation when mixing) → different hydrophobicity
- Phenyl- (Pol1) and Phenyl-Methyl- (Pol2) side groups
- High ceramic yields: 67 wt% (Pol1) and 77 wt% (Pol2) → different C content

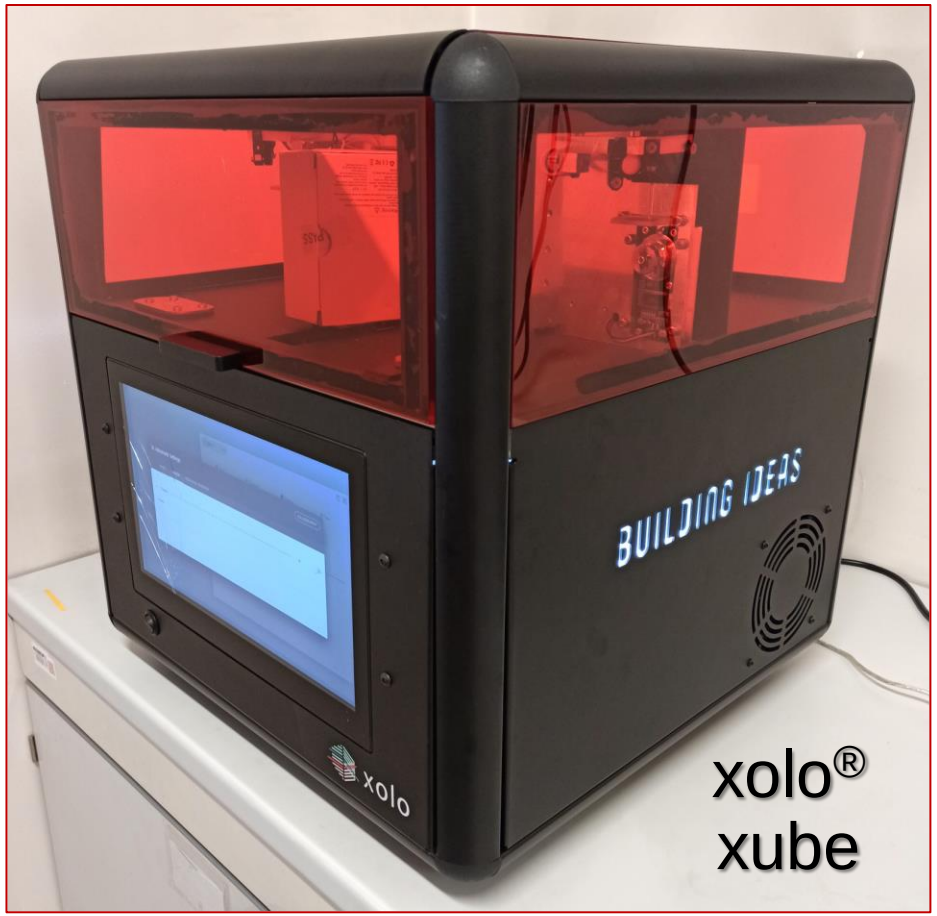
Weight ratio PSA/Pol1,Pol2	1	9/1	7/3	5/5	3/7
PSA content (wt%)	100	87.10	63.64	42.86	24.32
Pol1 or Pol2 content (wt%)	-	9.68	27.27	42.86	56.76
Toluene content (wt%)	-	3.23	9.09	14.28	18.92

*J. Schmidt and P. Colombo, J. Eur. Ceram. Soc., **38** (2018) 57*

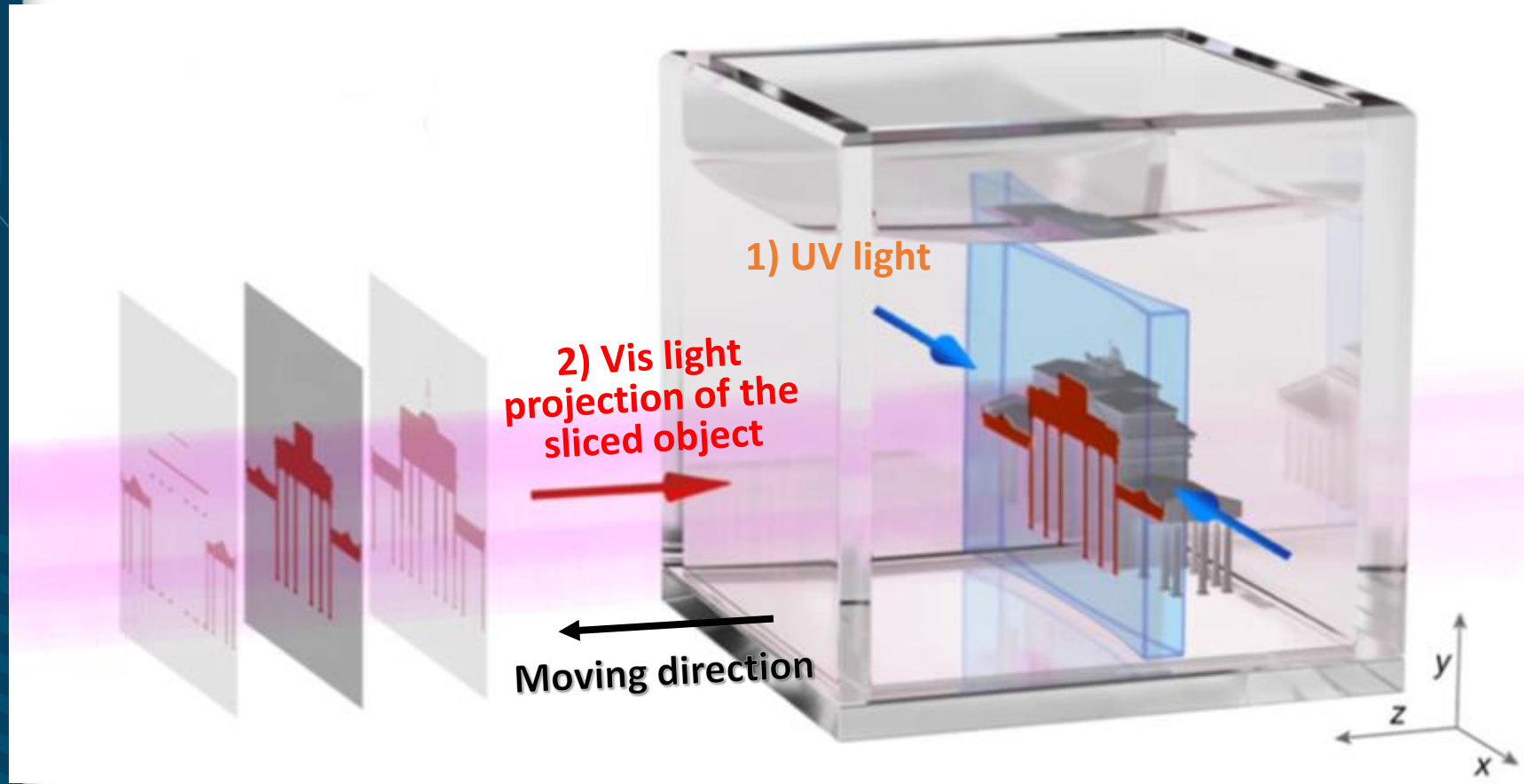
Linear Volumetric AM: xolography

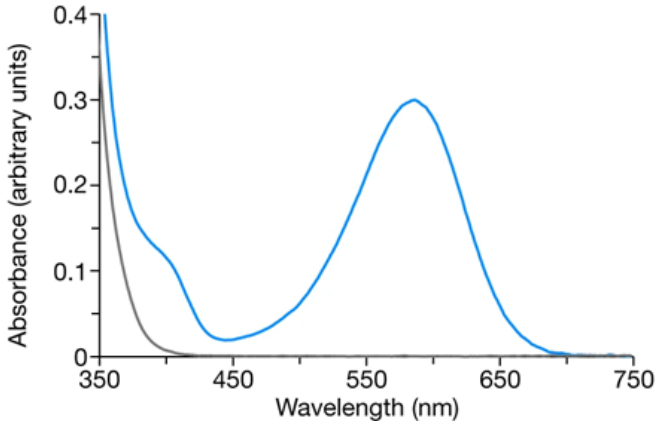
Xolography is a novel (2020) **linear volumetric 3D printing** process in which complex objects are manufactured using two intersecting light beams of different wavelengths to solidify localized regions, which are stabilized by the surrounding viscous fluid matrix (see https://www.xolo3d.com/ and https://www.nature.com/articles/s41586-020-3029-7 - 2020)

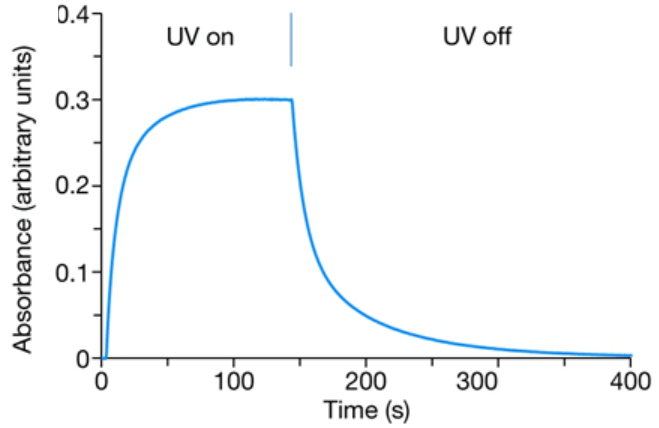
- Local polymerization inside a confined monomer volume → **volumetric 3D printing**
- Dual color technique using photo-switchable initiators (DCPI)
- Linear excitation by intersecting light beams of different wavelengths (UV and visible)
- No oxygen inhibition or layer rebuild → **fast**
- Printing rates up to ~1 cm^3/s, with resolution of 10-50 µm, are possible
- Printing speed: 20 to 100 times faster than DLP and 10 times faster than CAL
- No stair-stepping effect; No printing supports



The dual-color photoinitiator added to the resin is activated by a first wavelength (**UV**) (1), while absorption of the second wavelength (**visible**) (2) generates the excited moiety that, in combination with the co-initiator, initiates the radical polymerization process







Basics of xolography

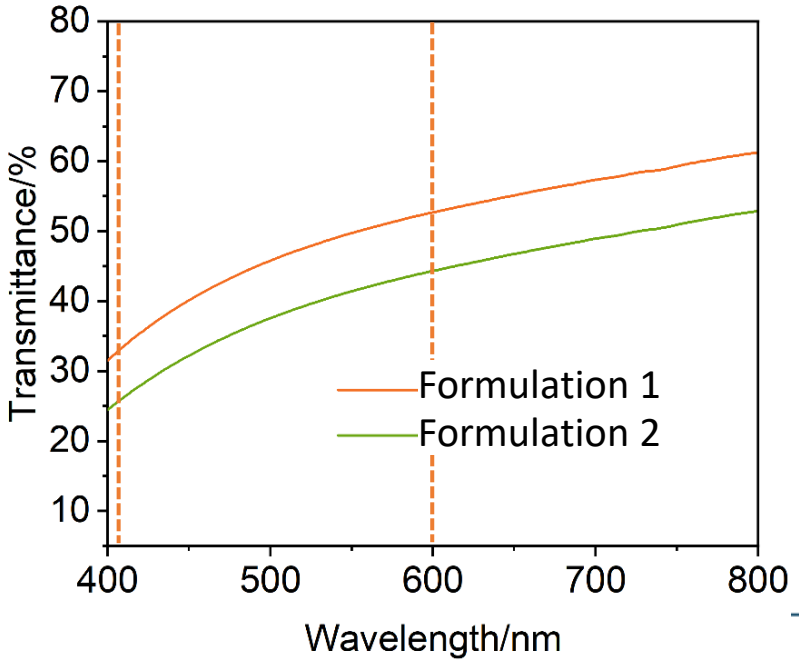
Complex requirements for the photocurable fluid:

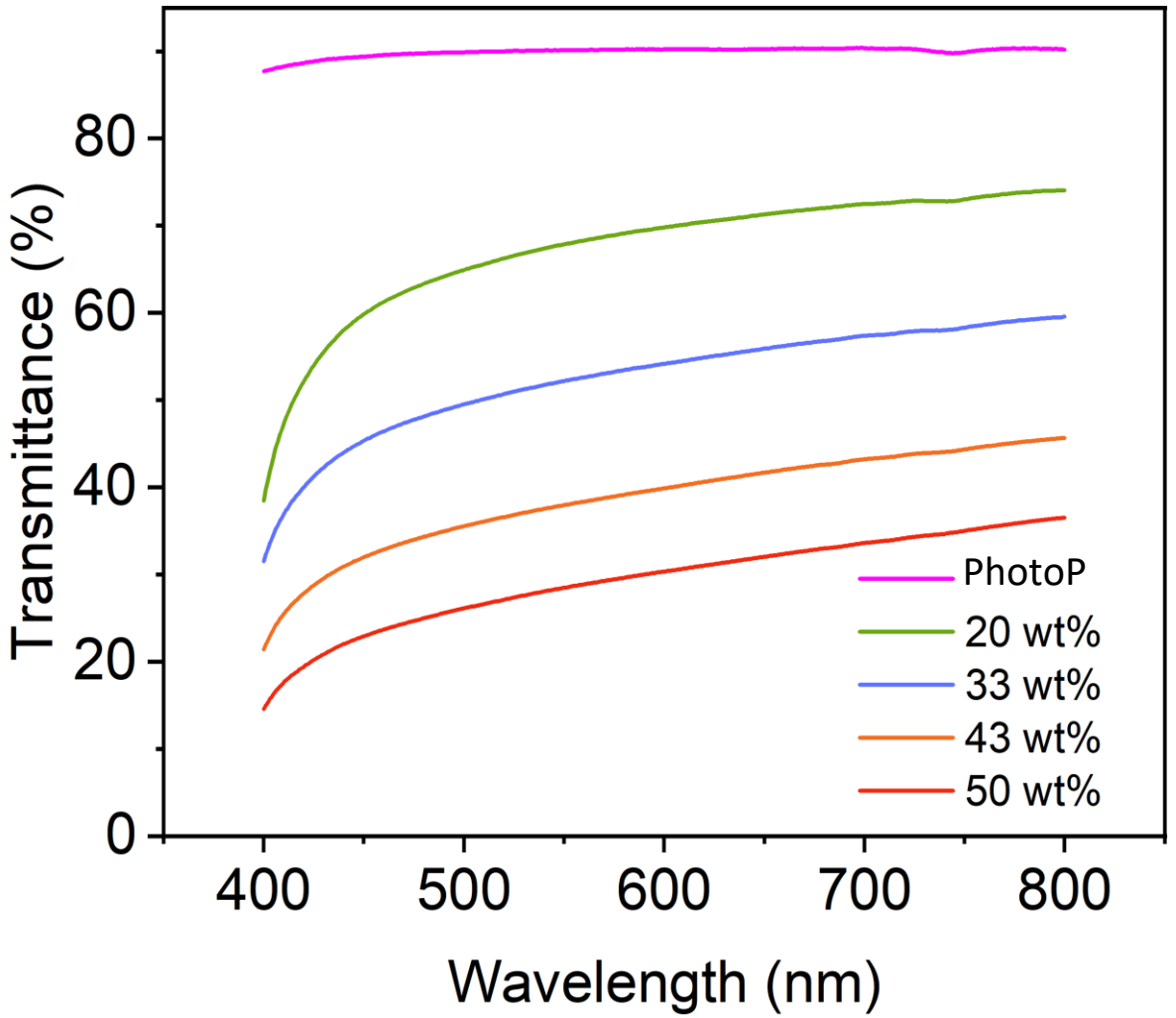
- Compatibility with proprietary **dual color photoswitchable initiator** system
- **Higher viscosity** compared to conventional vat photopolymerization
  → the printed part is supported by the unreacted material surrounding it
  → no additional supports for overhanging features needed
- Photopolymers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

Is it suitable for **preceramic polymers**? → **Physical blend** of a highly reactive photopolymers and a non-photocurable preceramic polymer with high yield

Transmittance

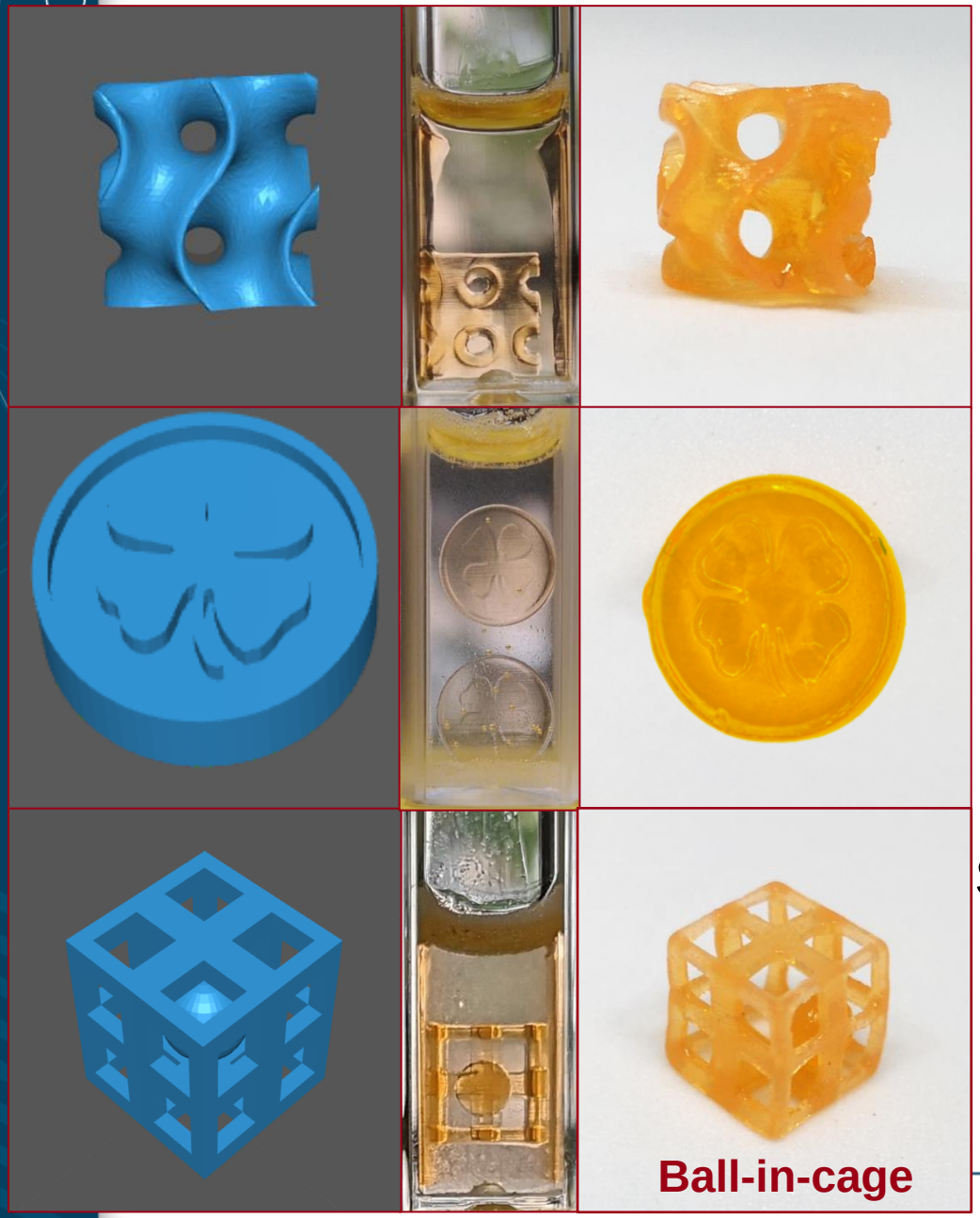
- Mixtures become less transparent with increasing amount of preceramic polymer
- A high viscosity is needed for supporting the structures being printed
- A too high viscosity hinders diffusion of radicals → slow polymerization
- It is difficult to extract the printed parts from highly viscous mixtures





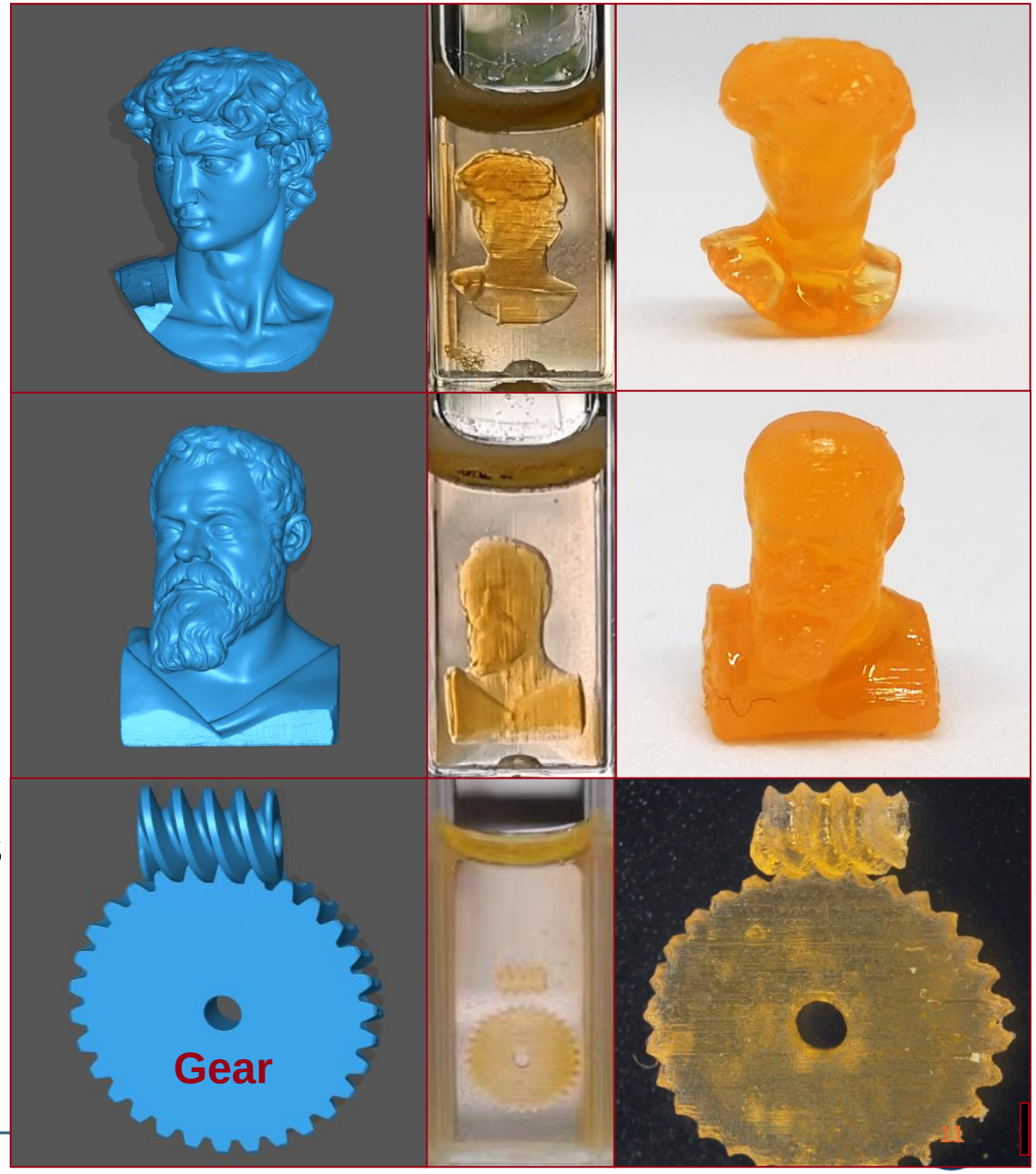
K. Huang, G. Franchin, P. Colombo, Small, (2024) 2402356

Examples of printed structures

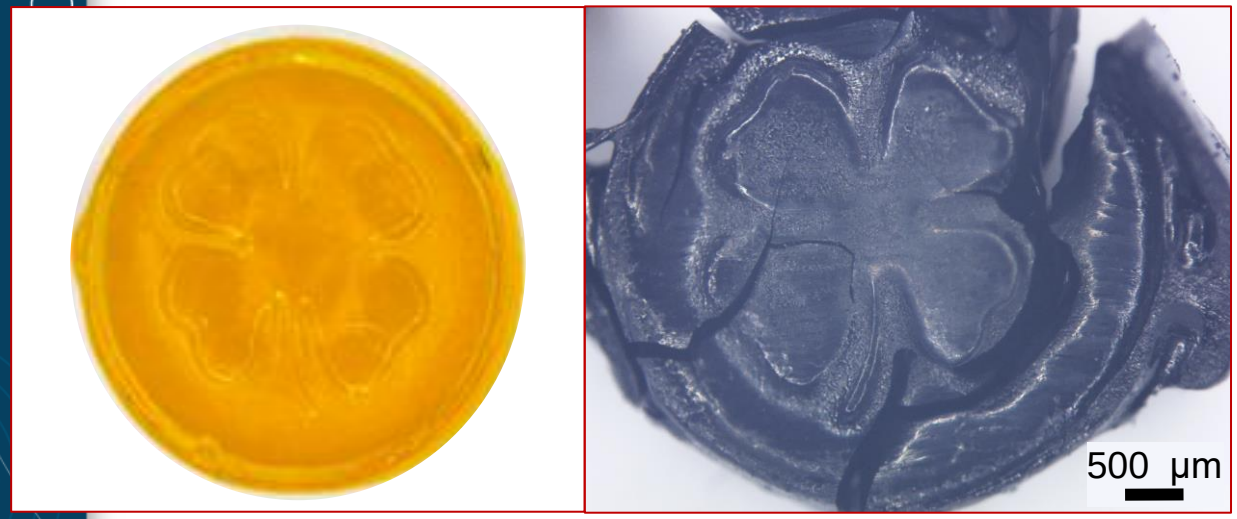


Cuvette size
= 1x1x3 cm^3

Simultaneous printing of **separate, interlocked objects**



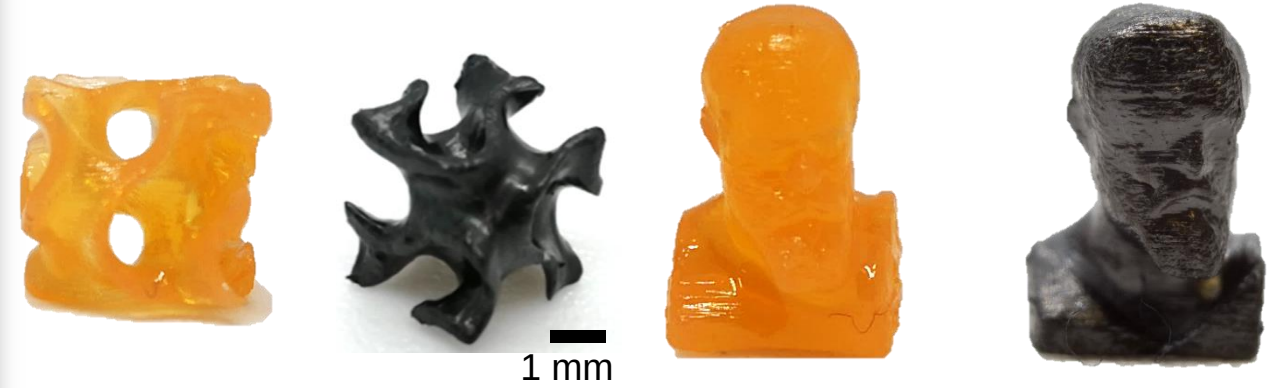
Pyrolyzed structures

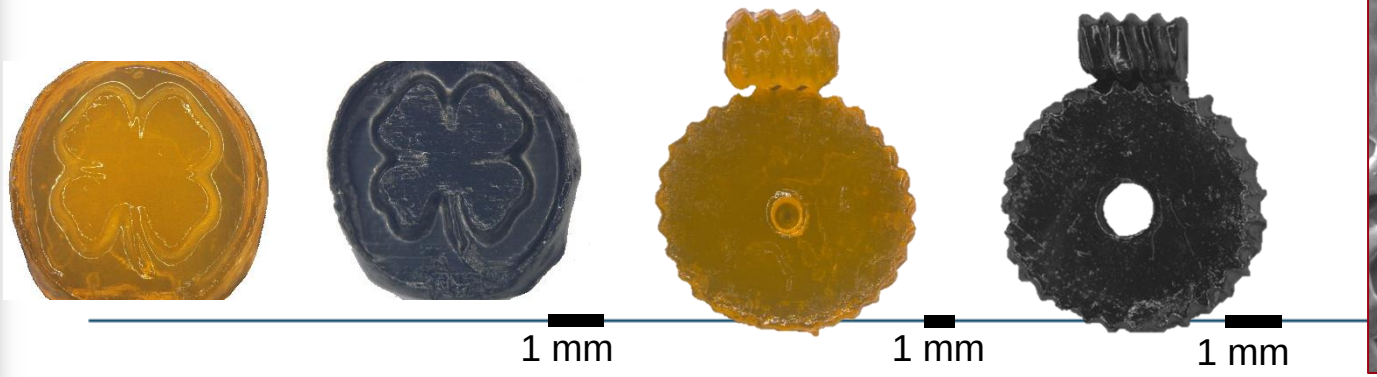


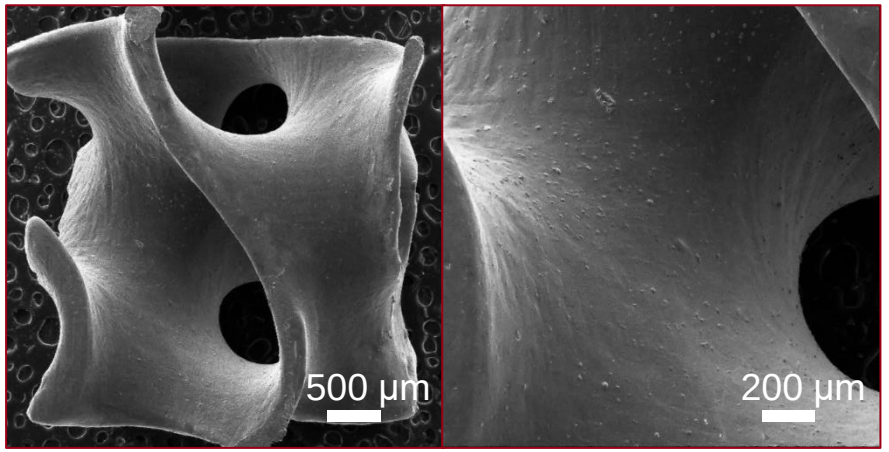
Without porogens → cracked parts

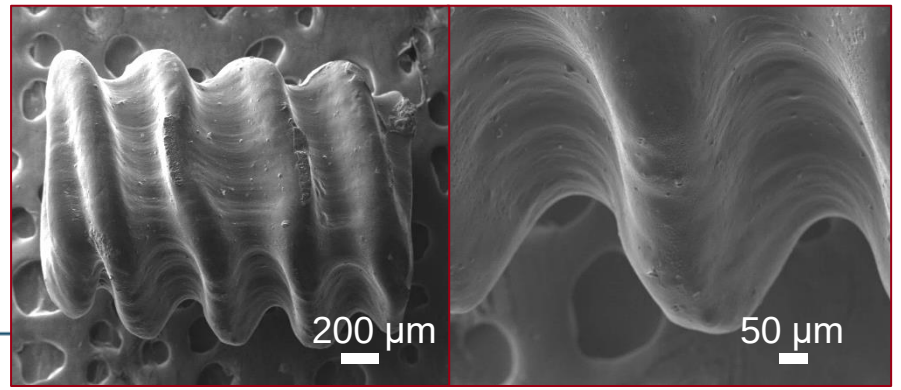
With improved formulation:

- Crack-free components
- Resolution is maintained



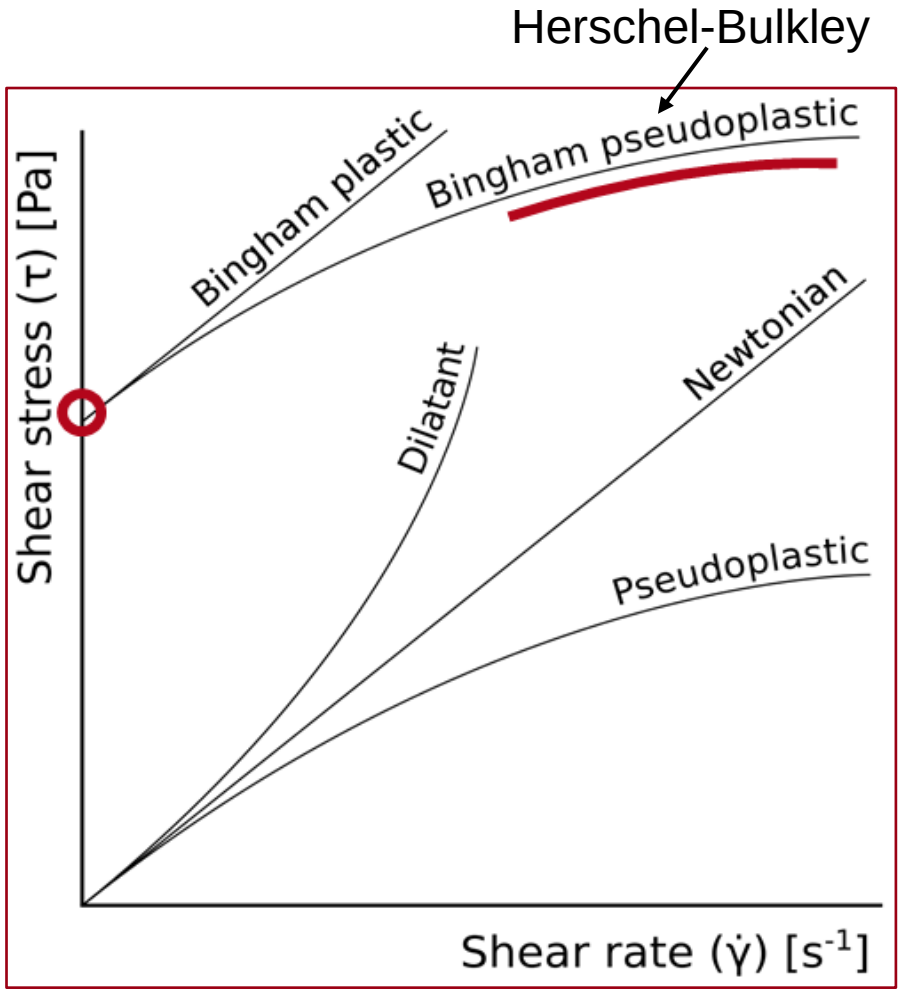






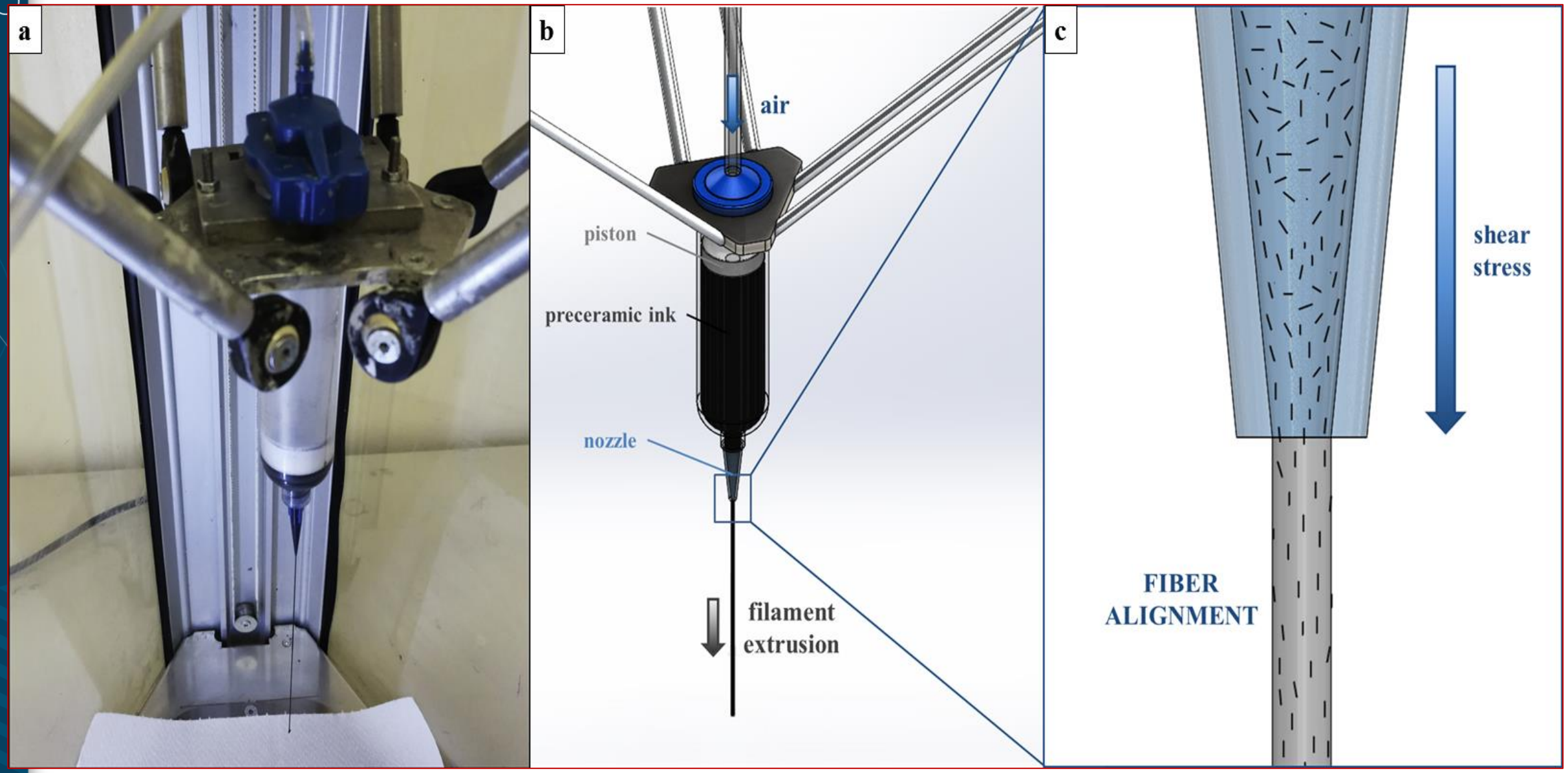
DIW (Robocasting)

- 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 CMCs

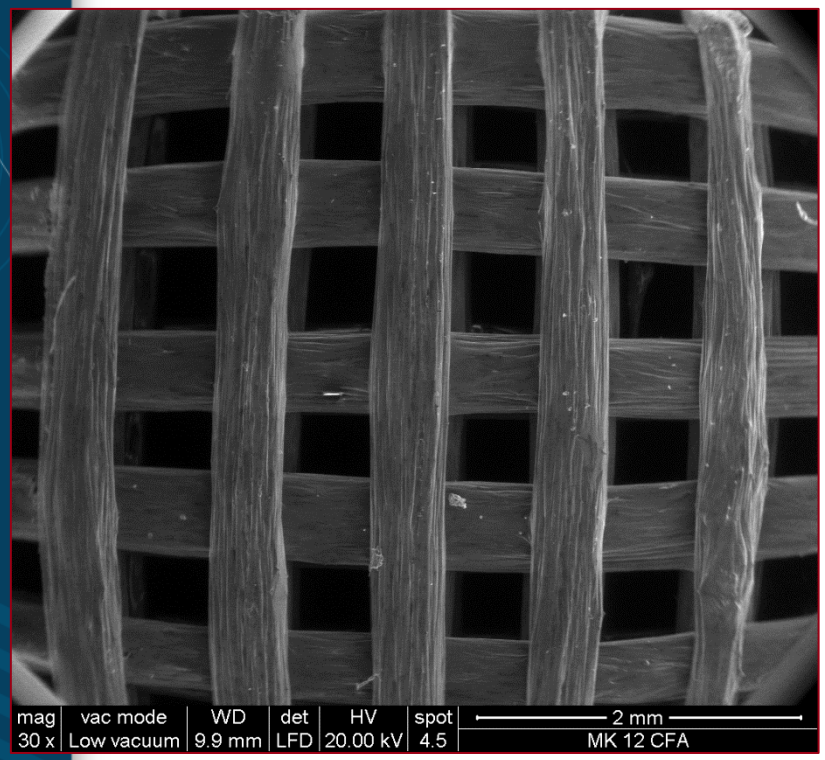


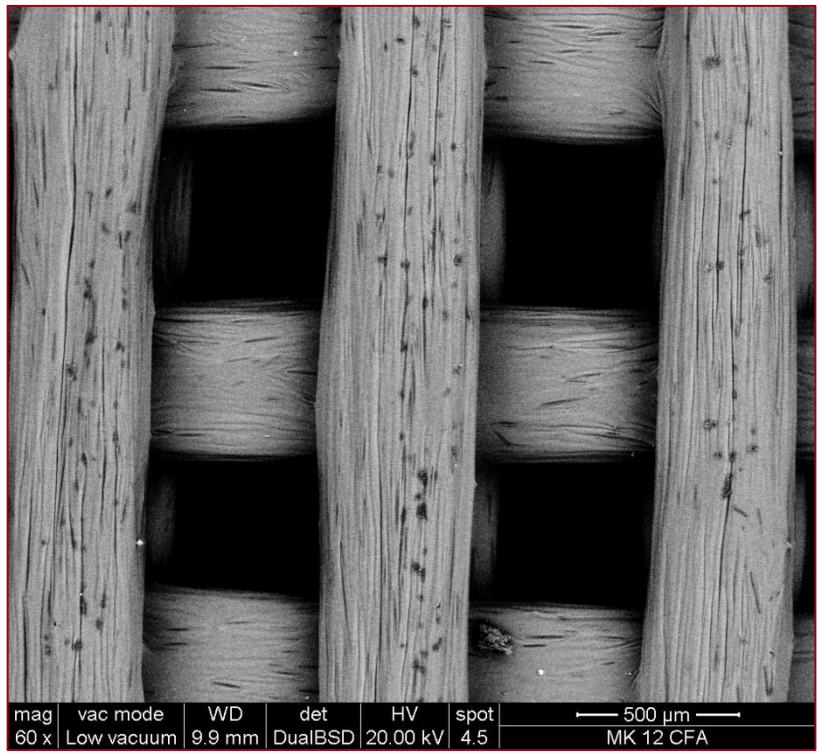
G. Franchin, L. Wahl, P. Colombo, J. Am.Ceram. Soc., ***100*** (2017) 4397

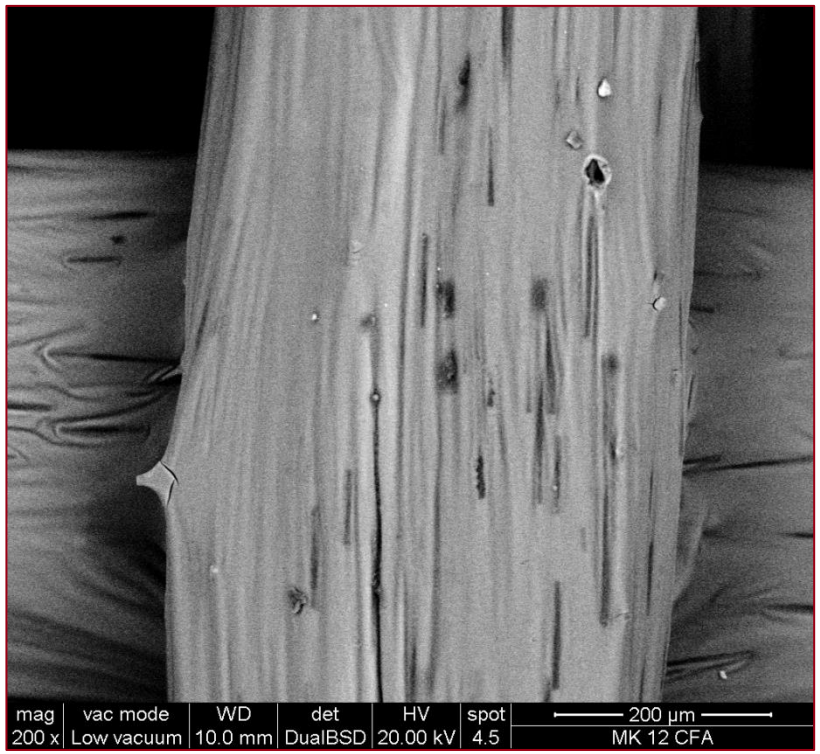
DIW of CMCs

- C_{sf} fibers (dimension: 150 µm)
- Fiber amount: 5 to 20 vol%
- Rheology controlled by amount of preceramic polymer and 2-5 wt% colloidal silica
- 800 µm nozzle tip

Before pyrolysis







- Fibers well aligned along printing direction
- No cracks

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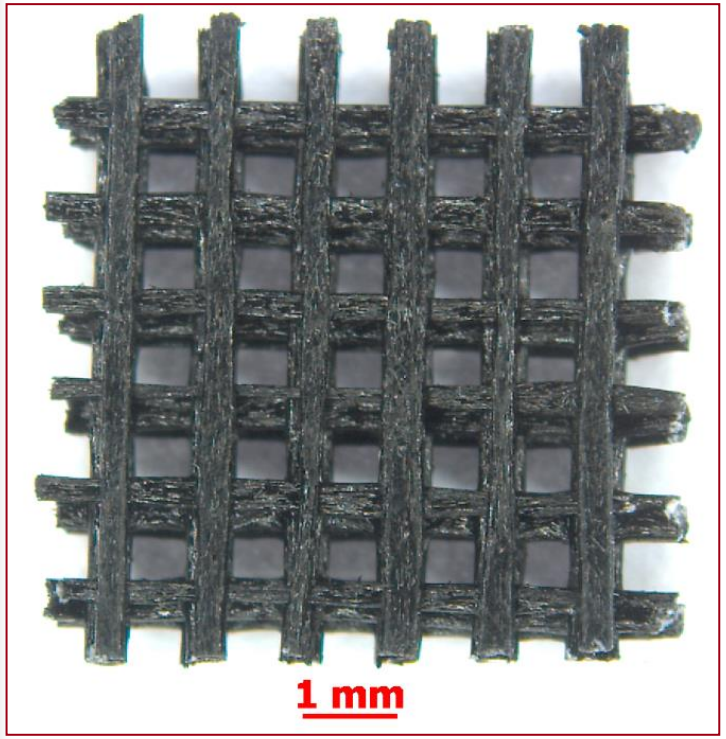
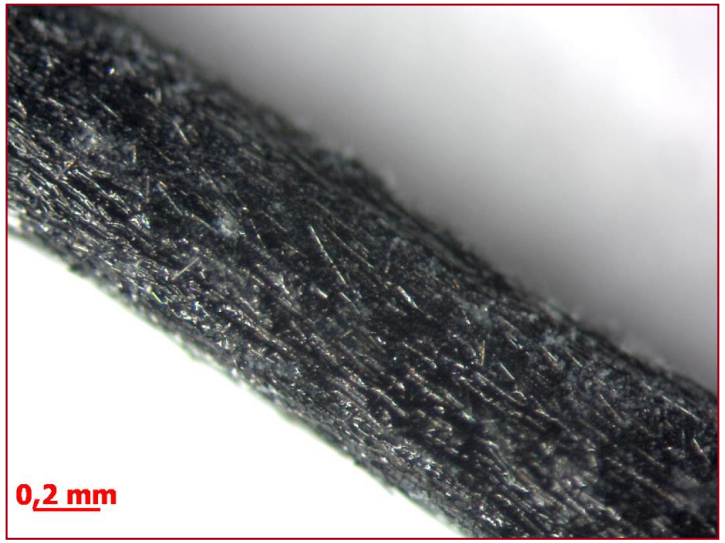
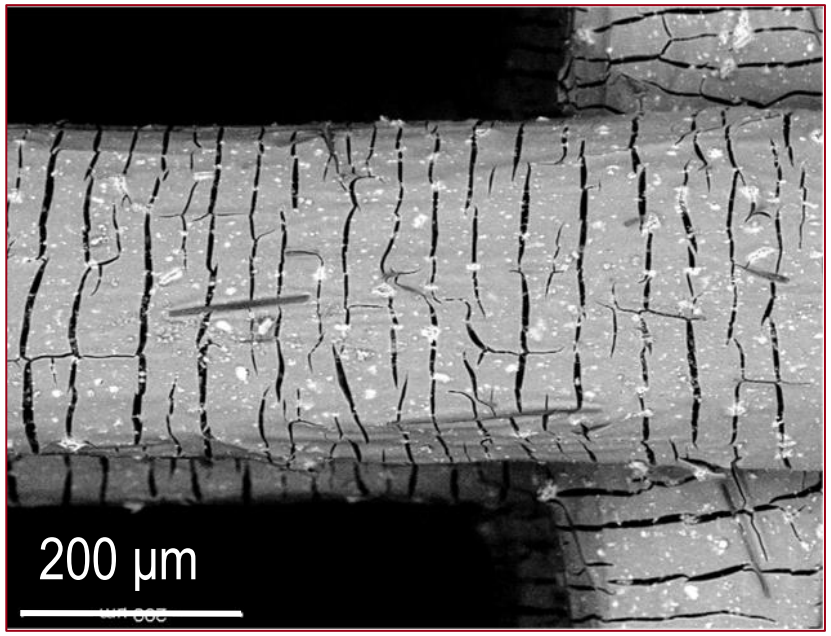
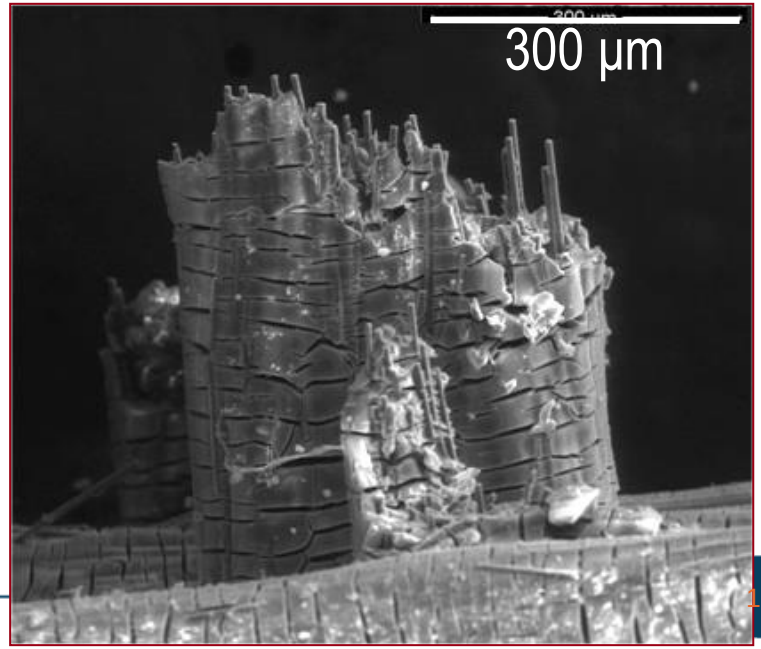
DIW of CMCs



After pyrolysis







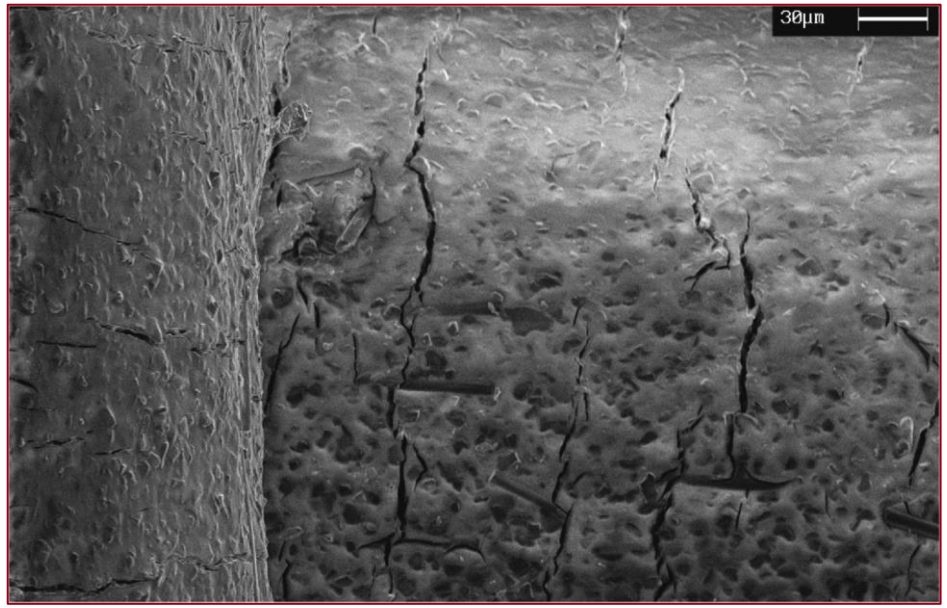
- Issues with cracking after pyrolysis (constrained shrinkage)
- Pull out visible

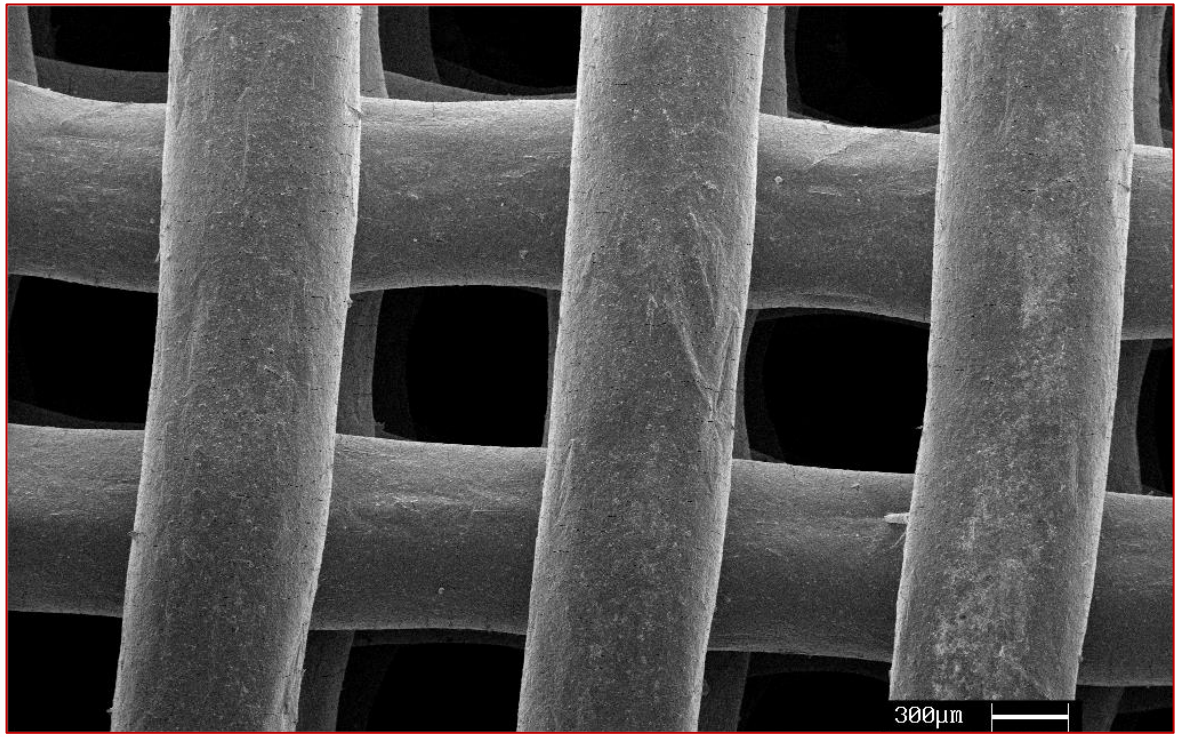
G. Franchin, L. Wahl, P. Colombo, J. Am.Ceram. Soc., ***100*** *(2017) 4397*

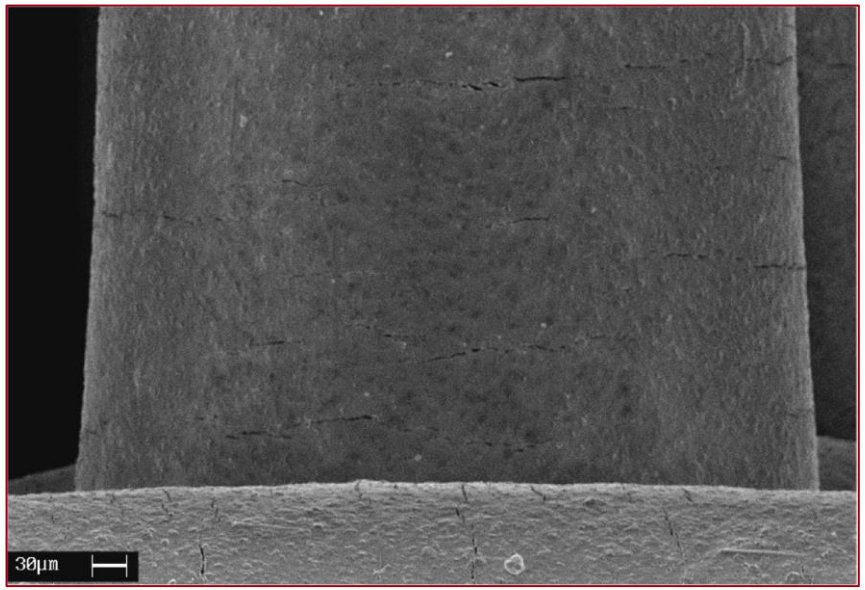
DIW of CMCs

- C_{sf} fibers (dimension: 150 µm)
- Fiber amount: 10 to 17 vol%
- Addition of fillers (20 to 50 wt% SiC powder)
- 410 and 580 µm nozzle tip

After pyrolysis





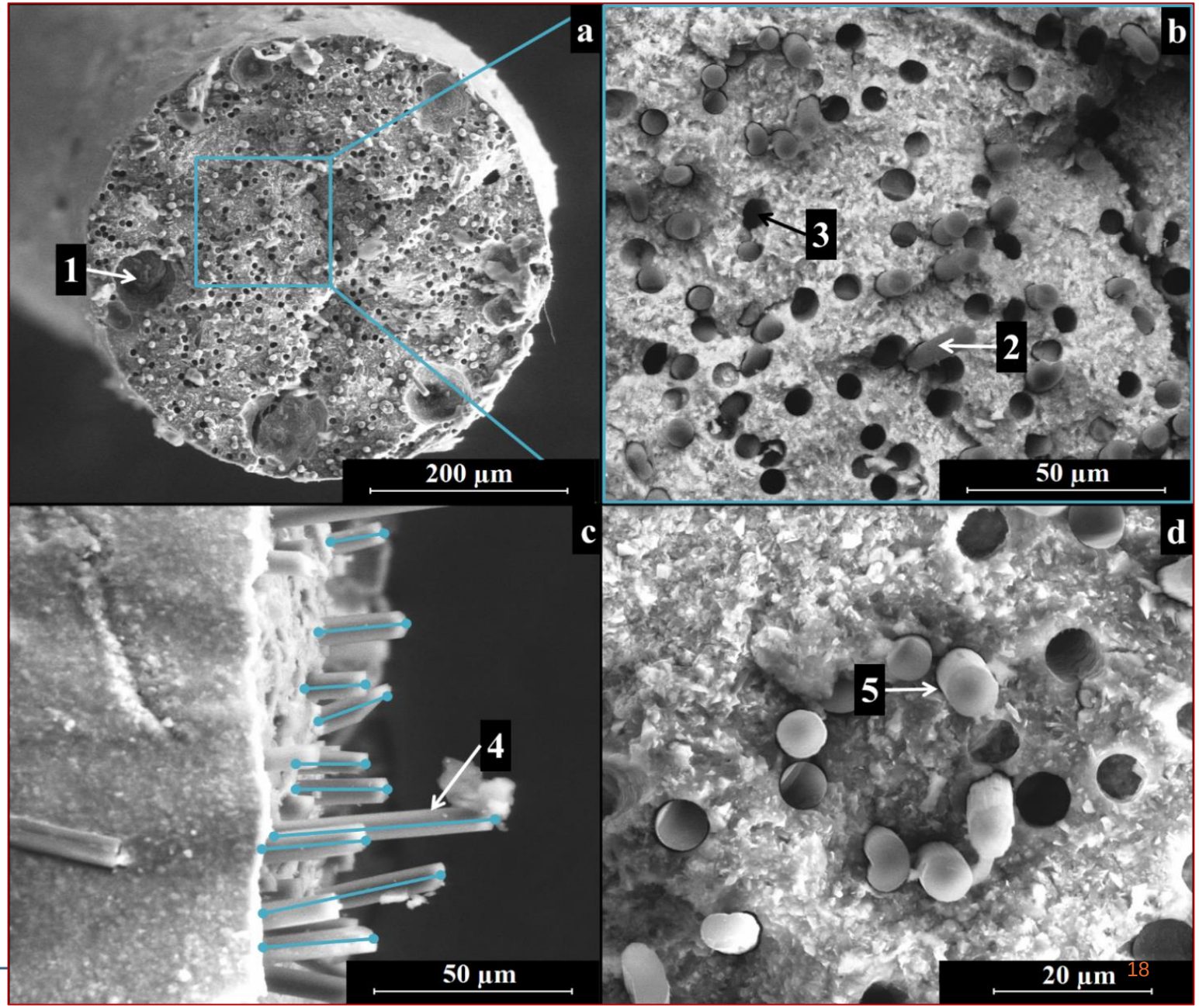


- Very few cracks with filler addition

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

After pyrolysis

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



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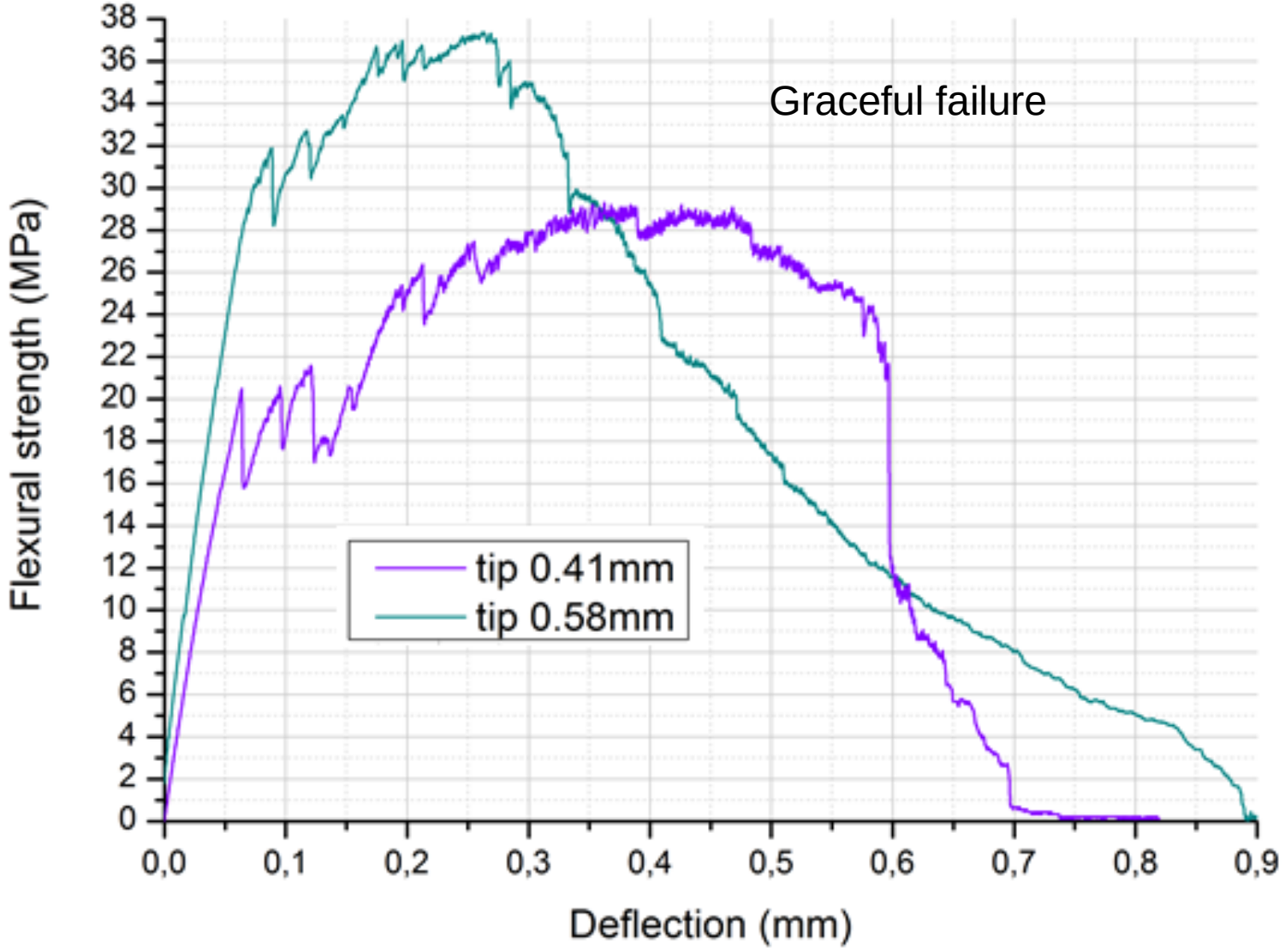
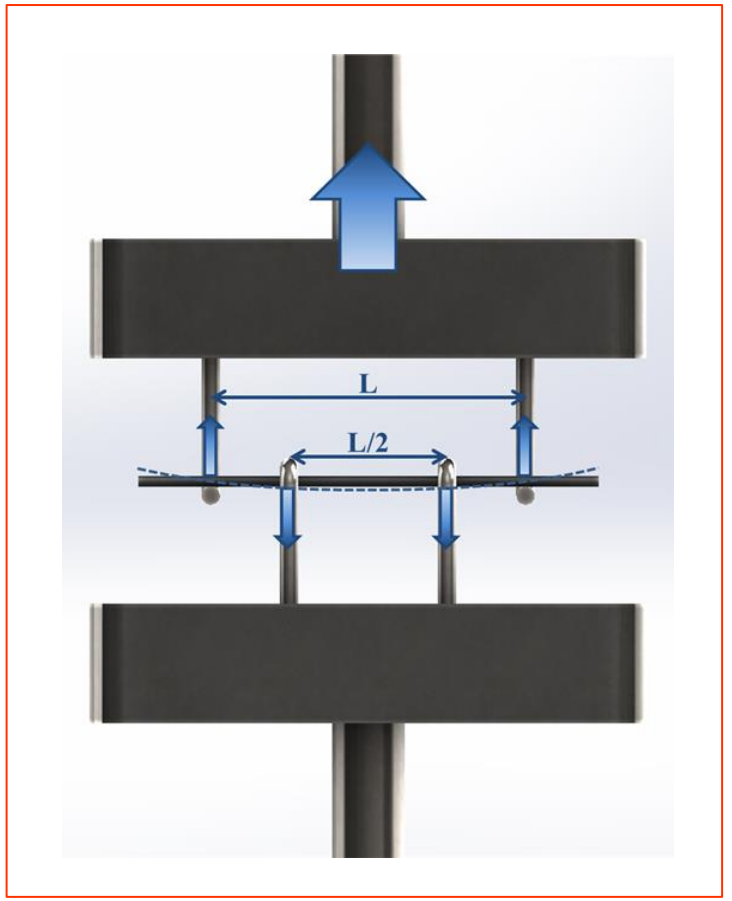
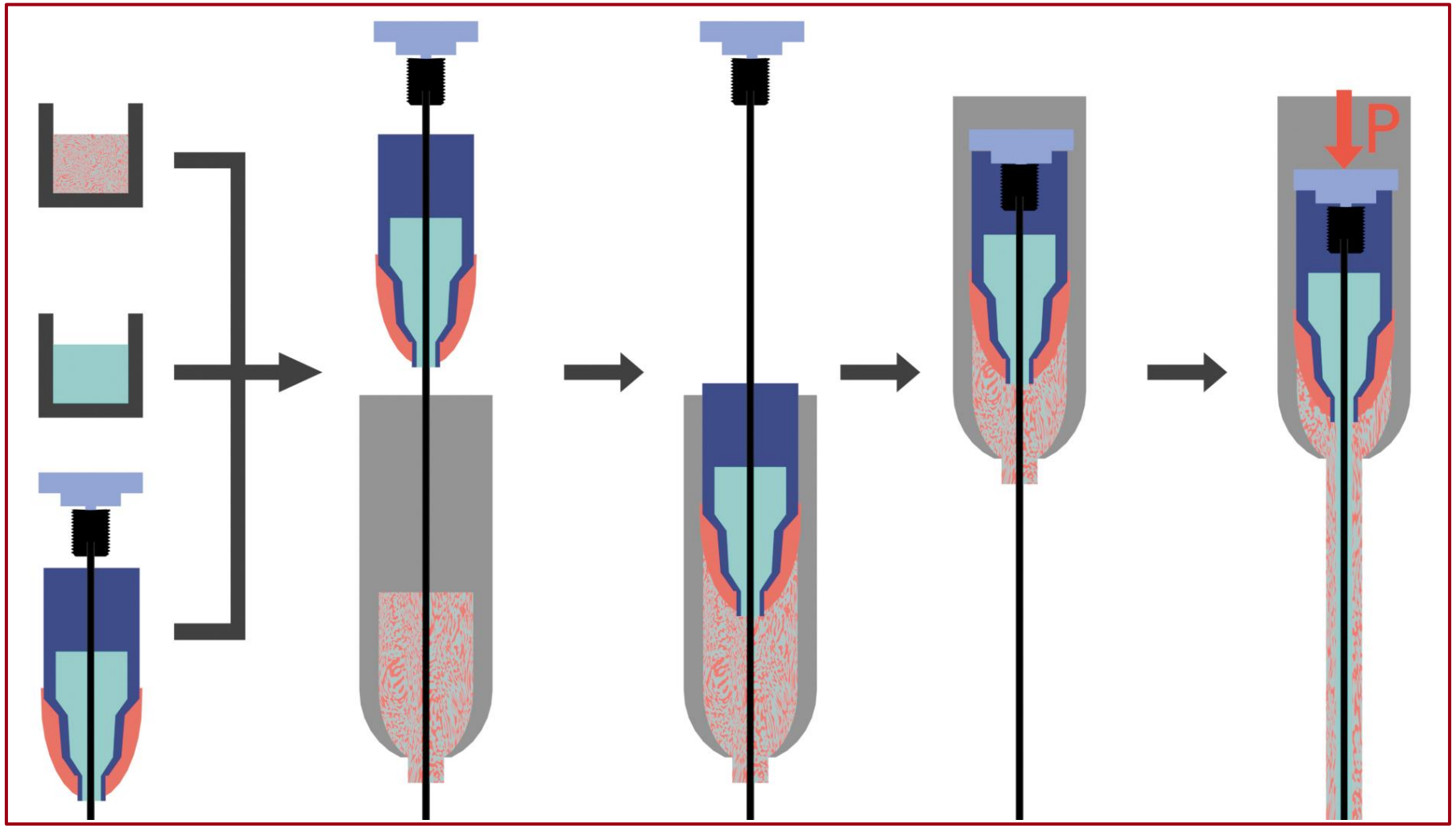
- Single filaments



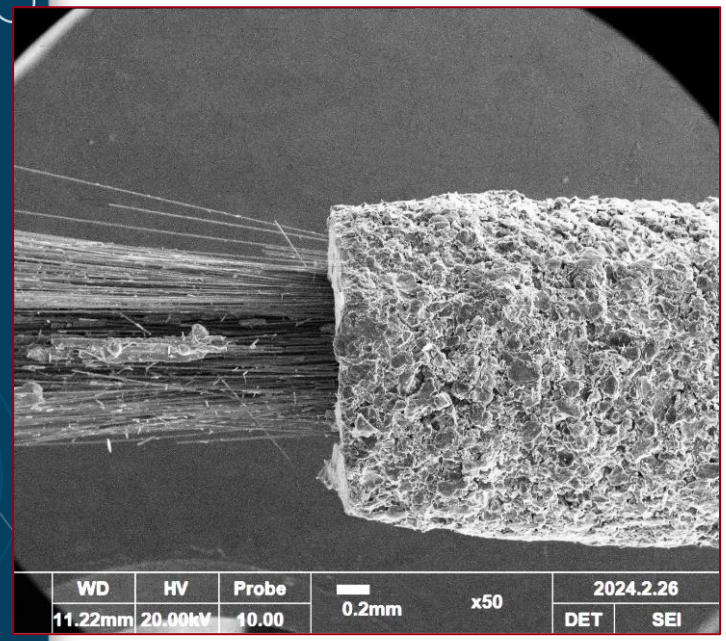


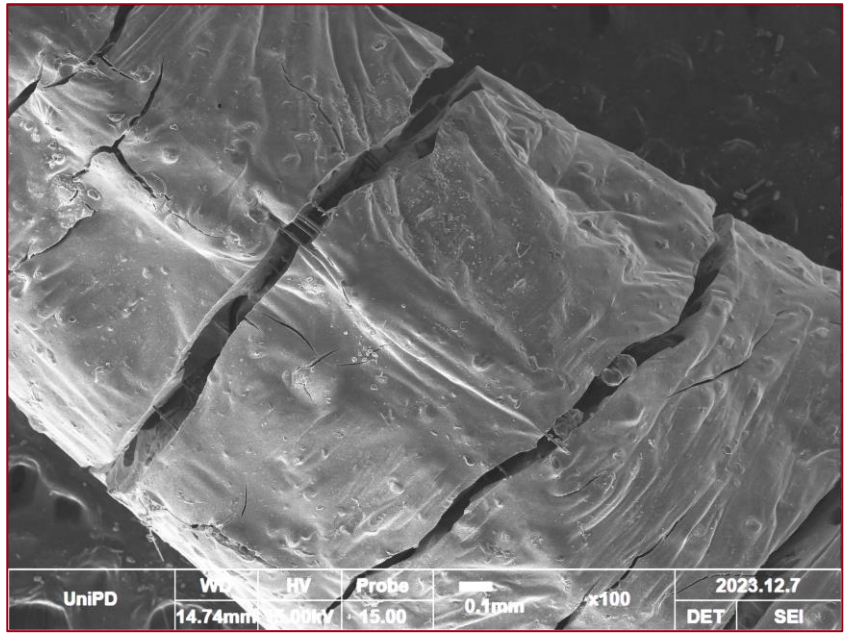
DIW of CMCs: continuous fibers

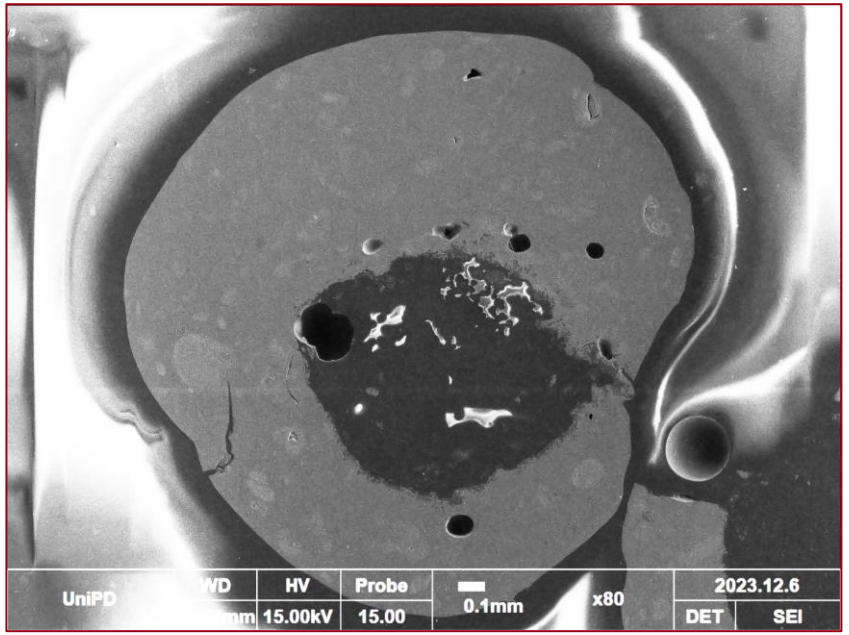


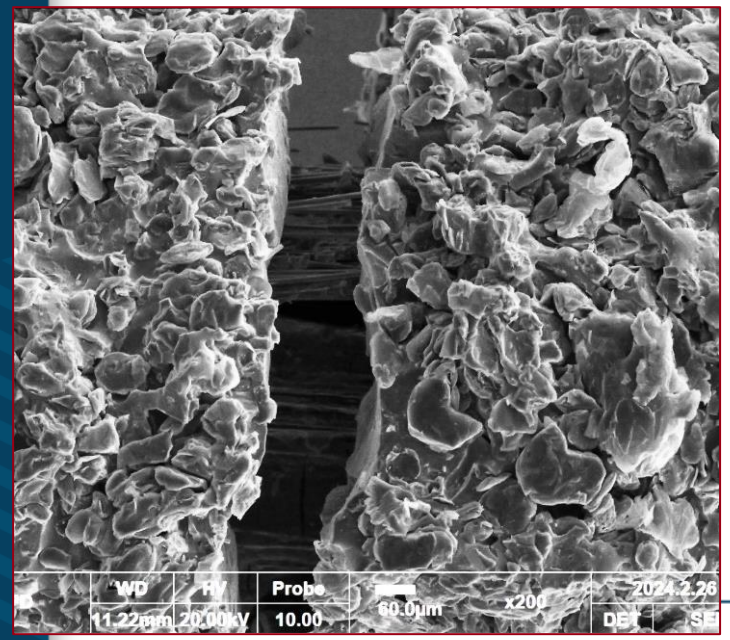
- Continuous C fibers
- Pre-preg inside syringe before extrusion
- Matrix based on a PCP and fillers
- 840 µm nozzle tip

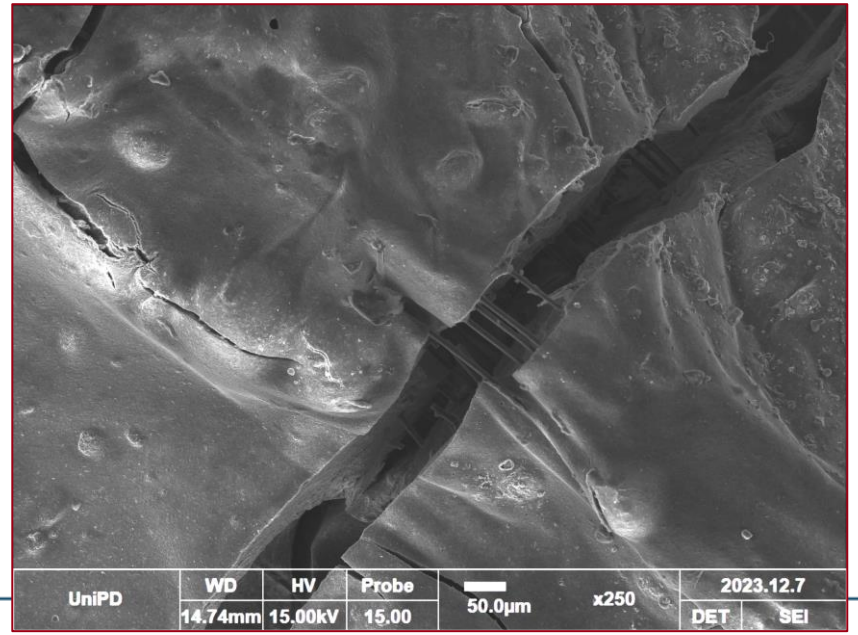
DIW of CMCs: continuous fibers

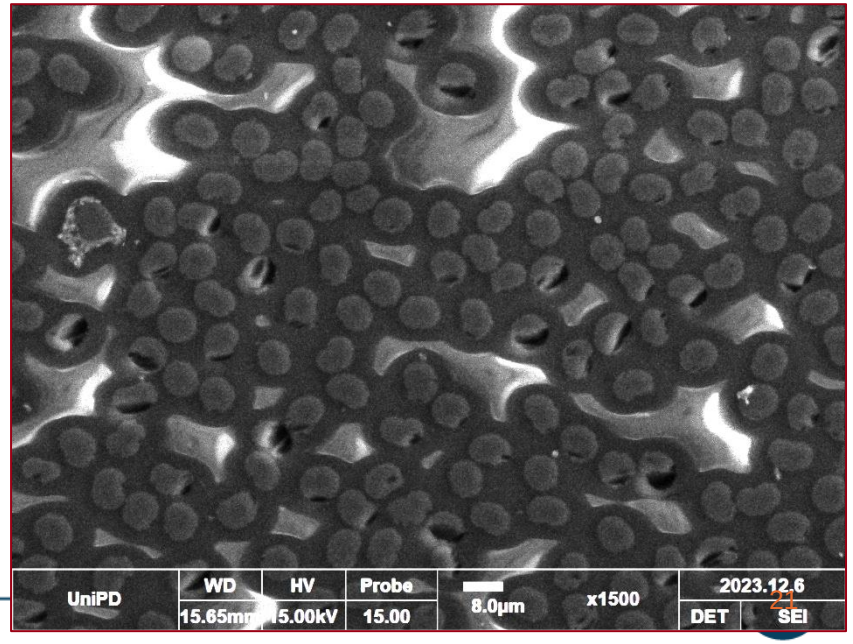






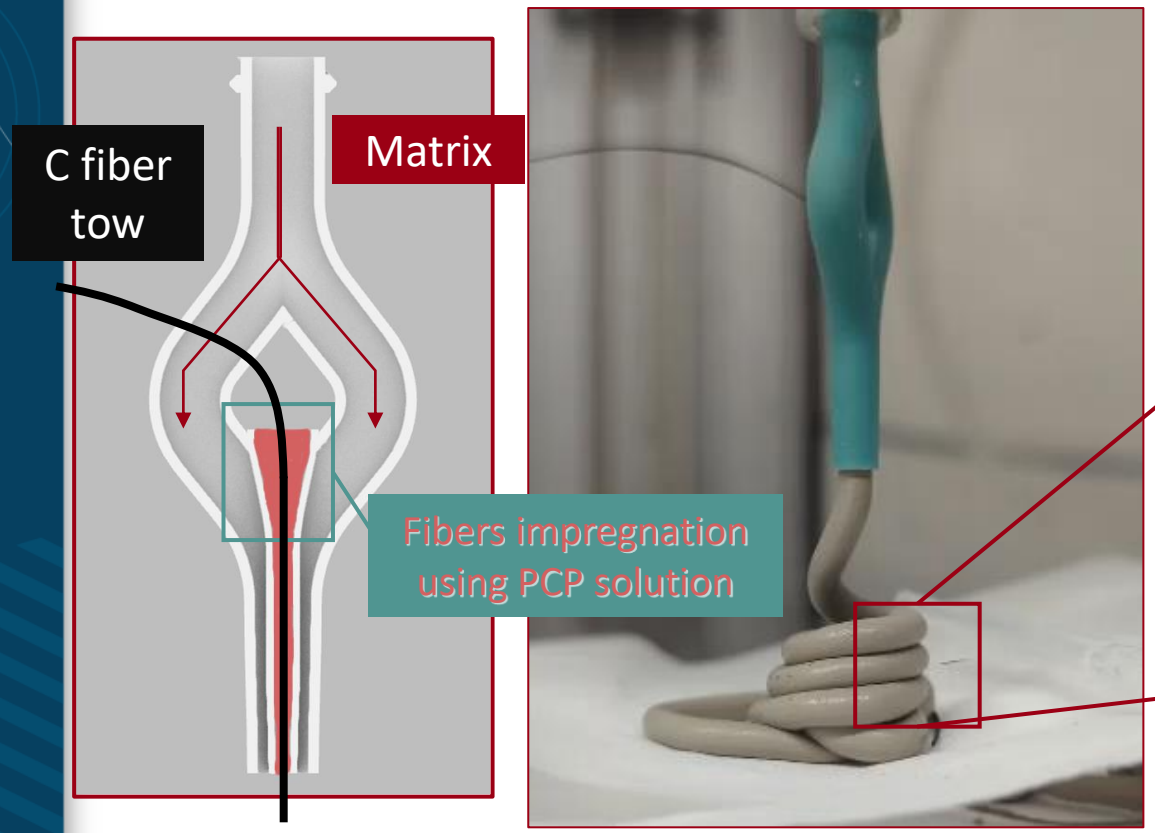




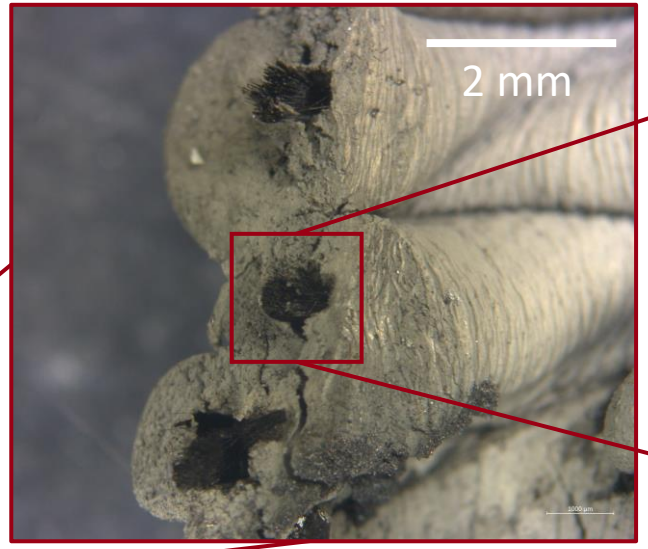


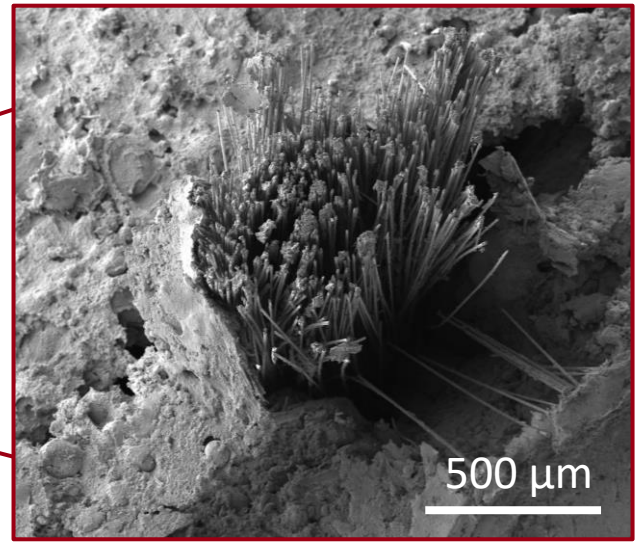
DIW of CMCs: continuous fibers

- **Reinforcement:** continuous C fibers (1K tow)
- **Matrix:** SiC based-ink with controlled rheology using colloidal silica (1 wt%), preceramic polymer and dispersing agent
- **Setup:** DIW 3-axis printer with **custom co-axial nozzle** (d_{out}= 3.5 mm) → C fibers dragged down by matrix extrusion during printing



1000 °C, 2.5 h
N_2 atmosphere



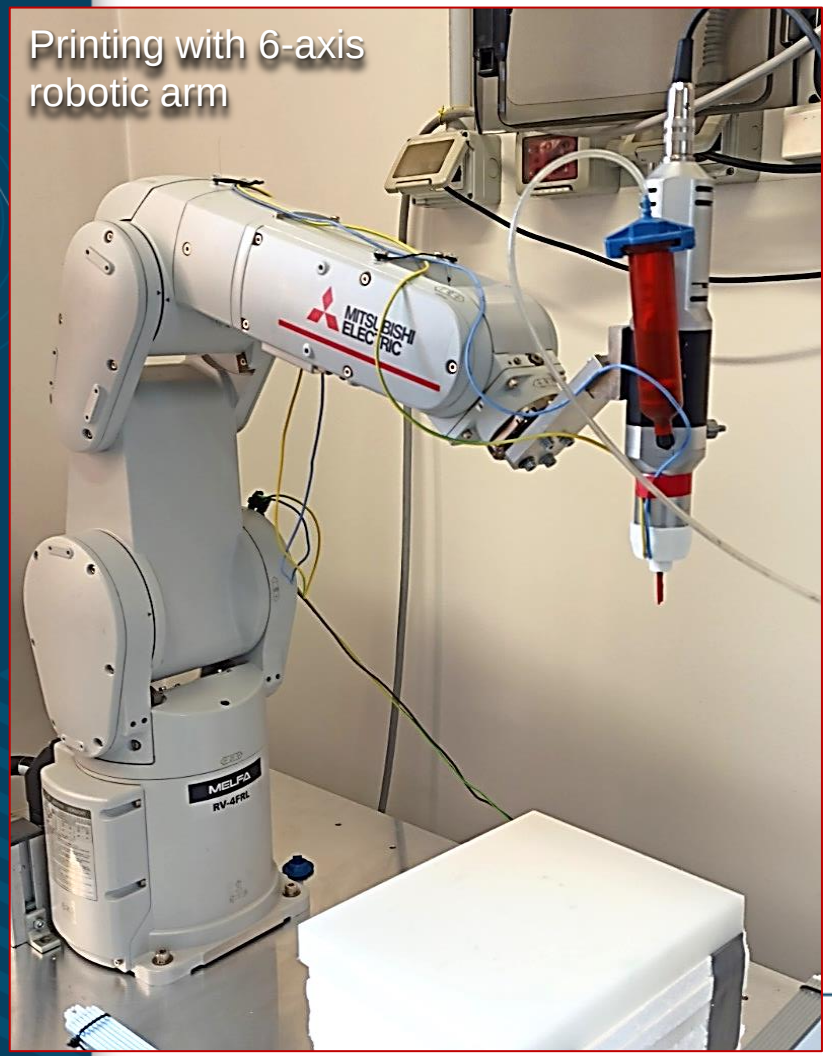


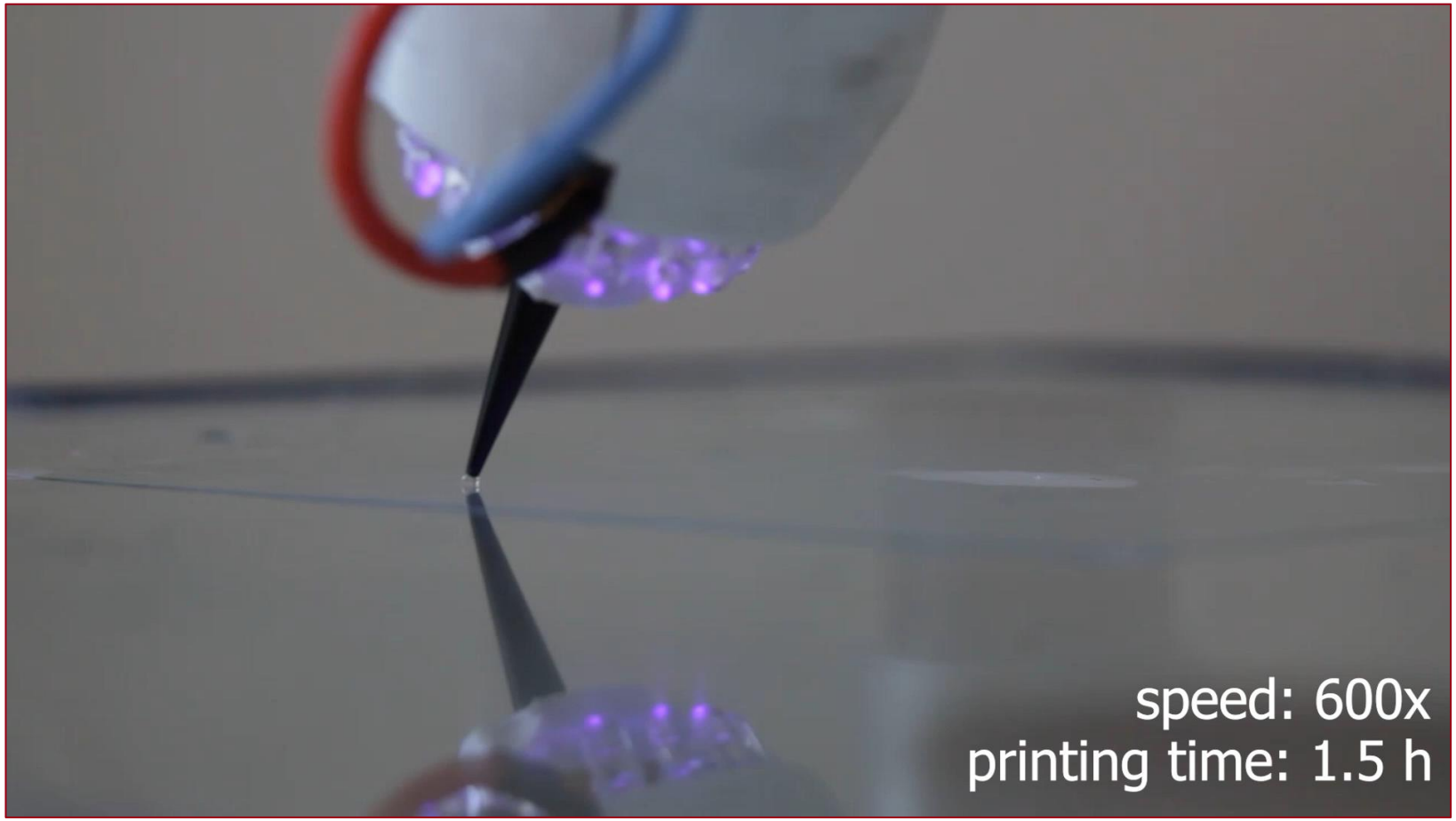
Current work

- Optimization of fiber bundle impregnation and adhesion to the matrix

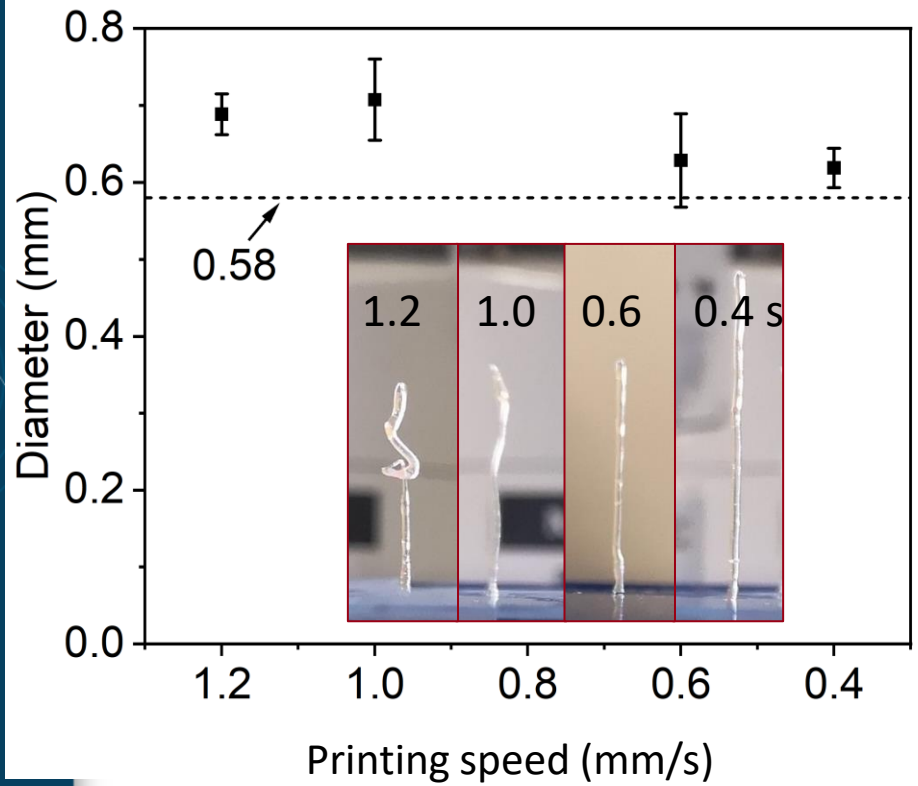
Hybridization: UV-assisted DIW (Robotic Additive Manufacturing - RAM)

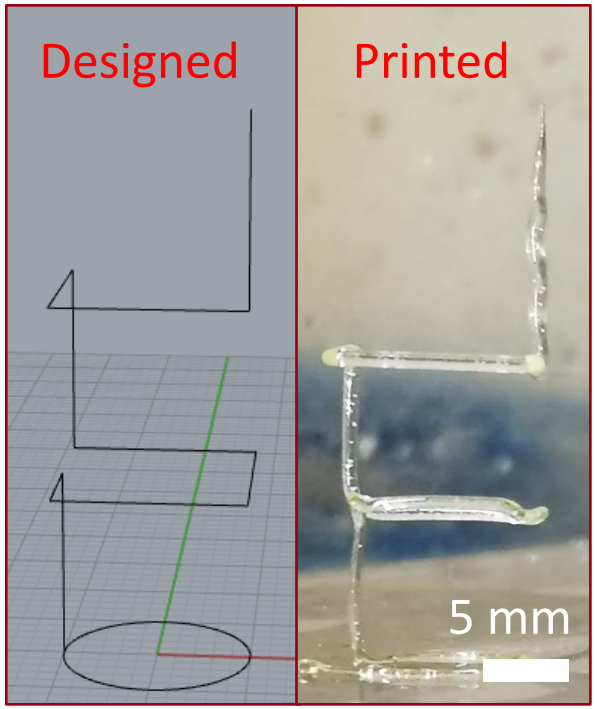
- UV-assisted DIW → **Free Forming** and **large printing envelope (RAM)**
- No need to control rheology of inks → liquid preceramic polymers → very thin nozzles possible

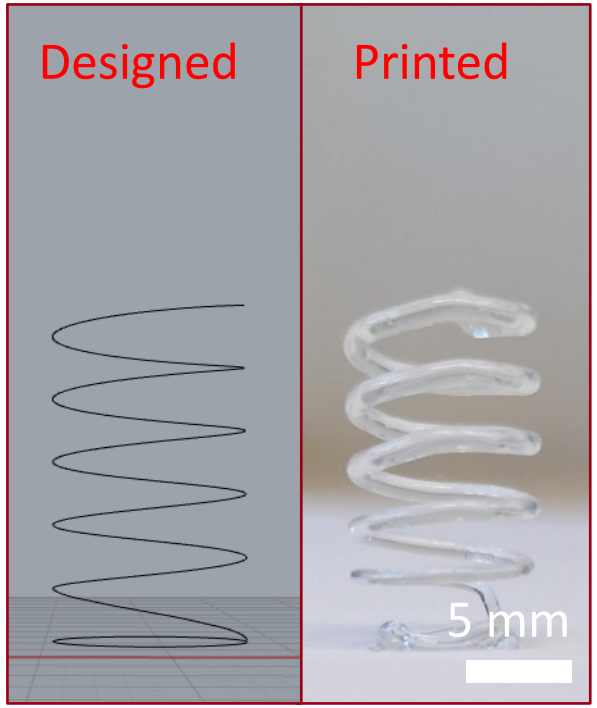




Hybridization: UV-assisted DIW (Robotic Additive Manufacturing - RAM)







- **Self-supporting** 3D printing is possible
- Printing speed controls shape retention (collapsing and change in filament size)

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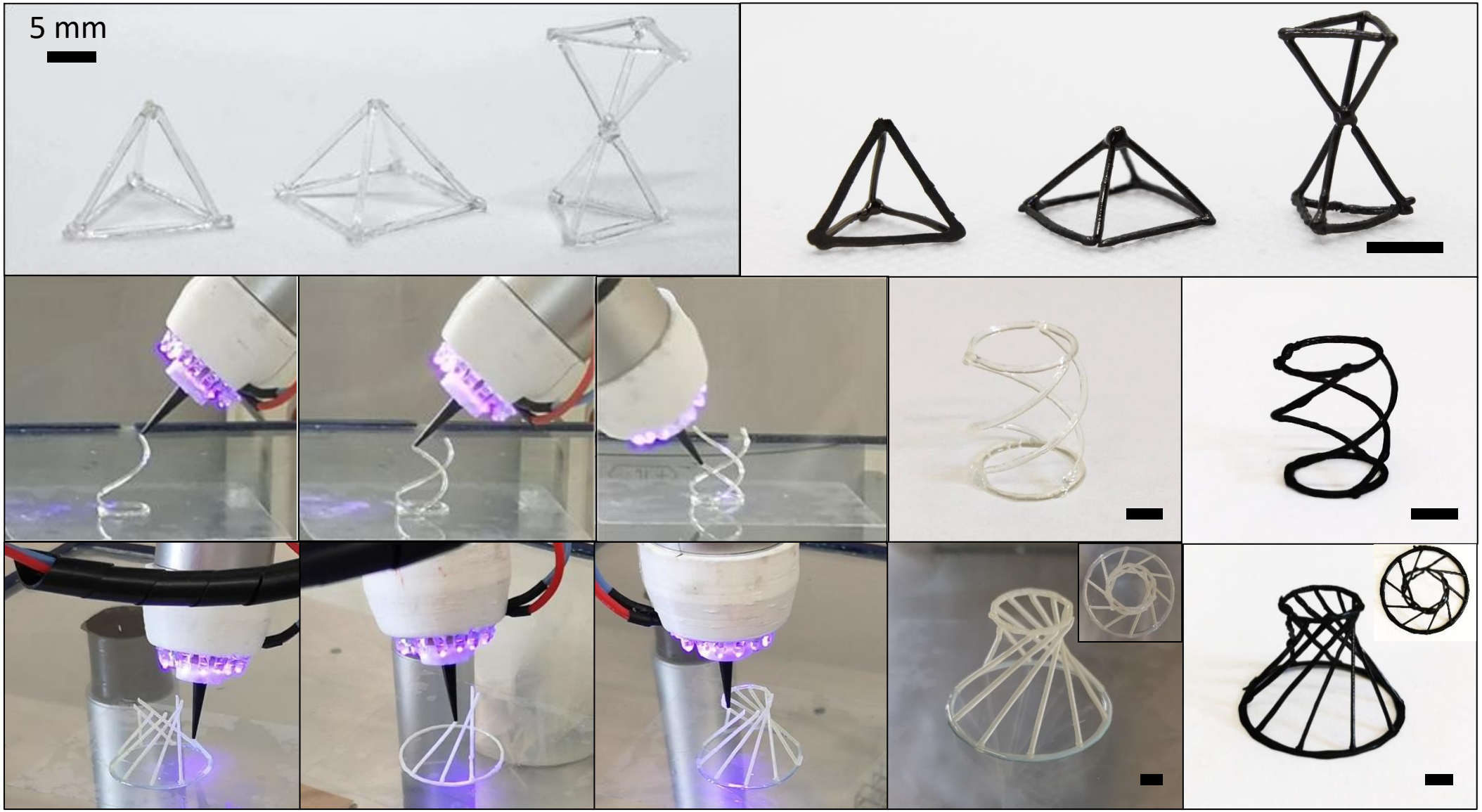
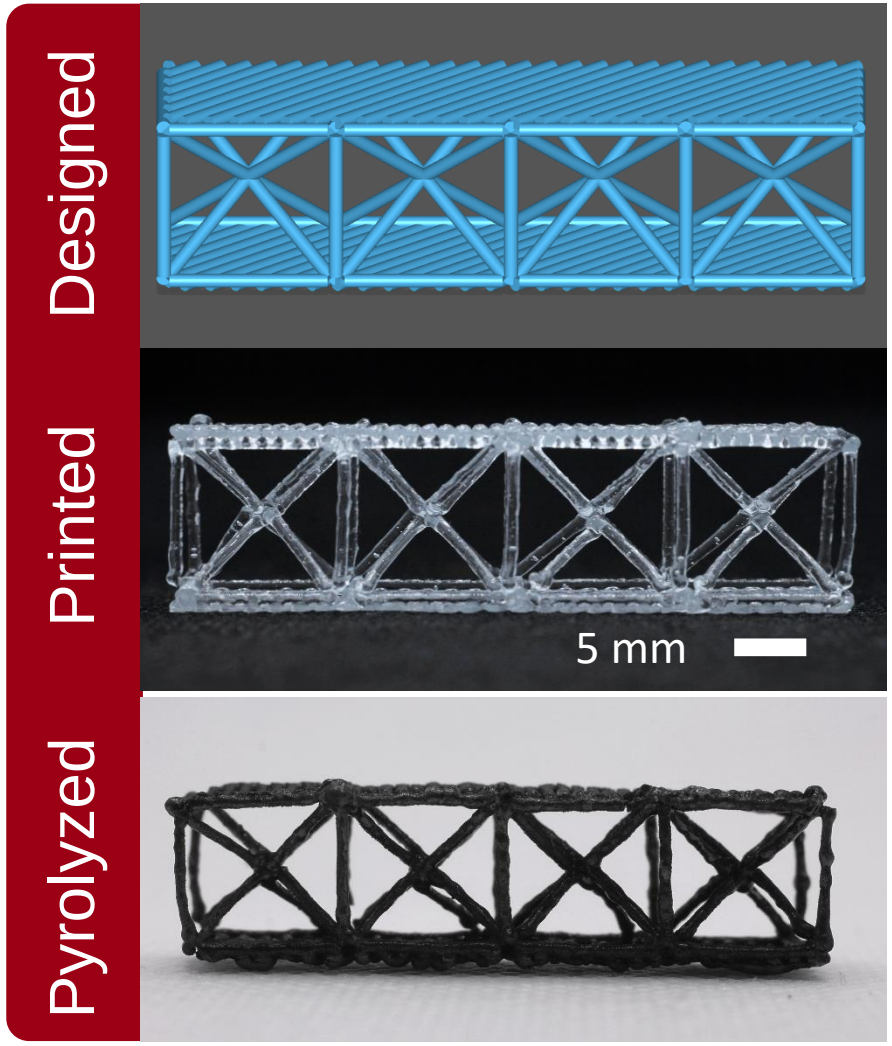
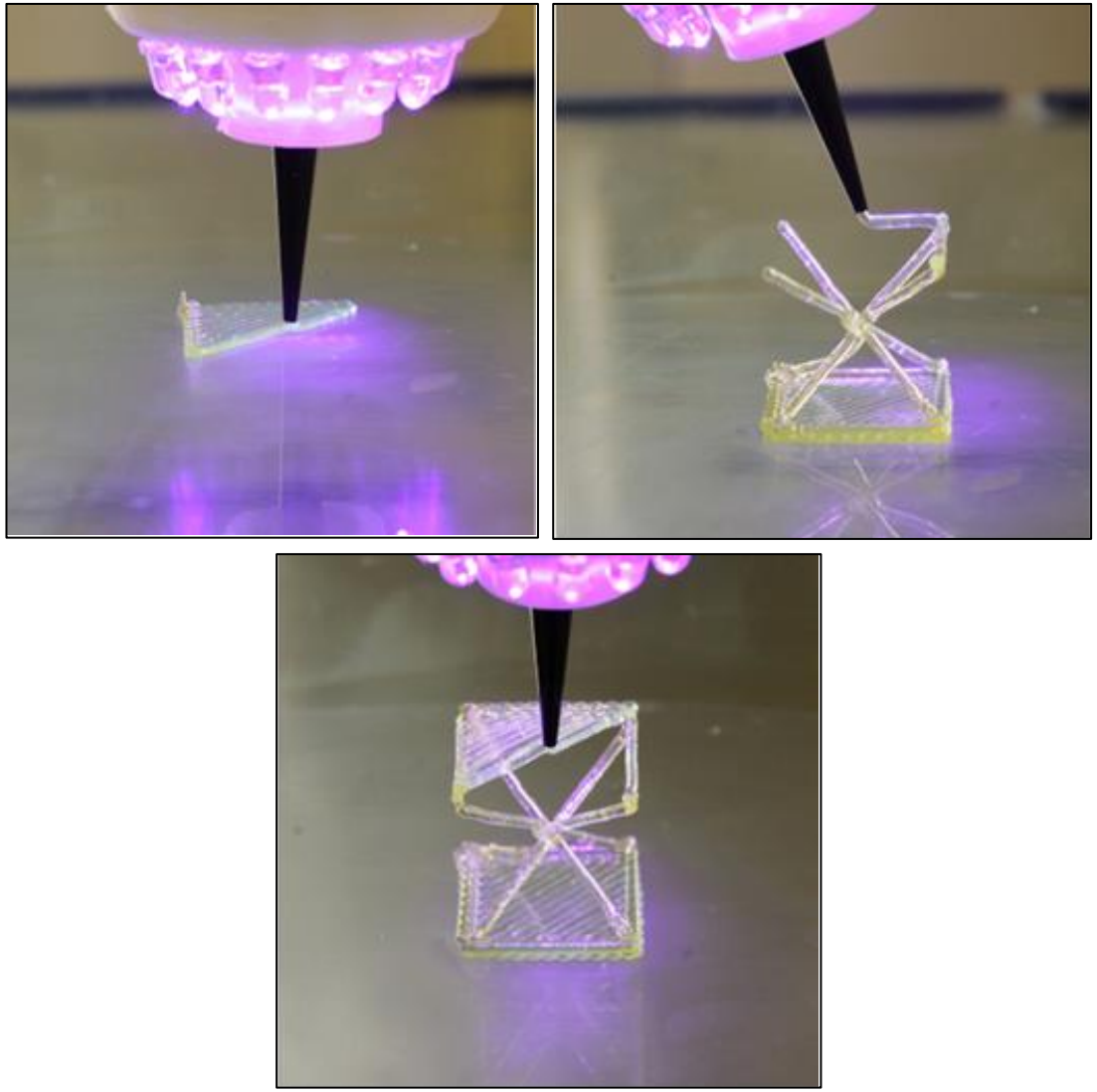
Hybridization: UV-assisted DIW (Robotic Additive Manufacturing - RAM)



- Free-from 3D printing is possible

Hybridization: UV-assisted DIW (Robotic Additive Manufacturing - RAM)

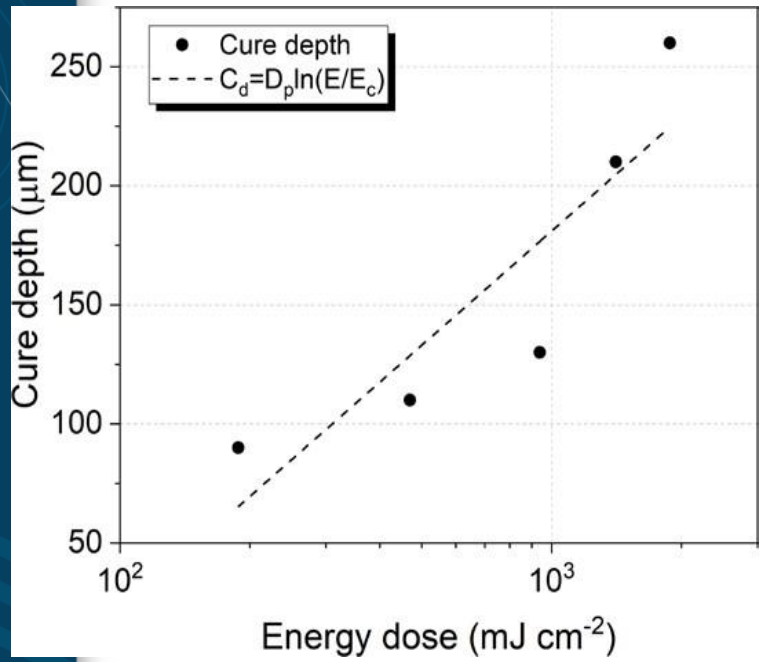


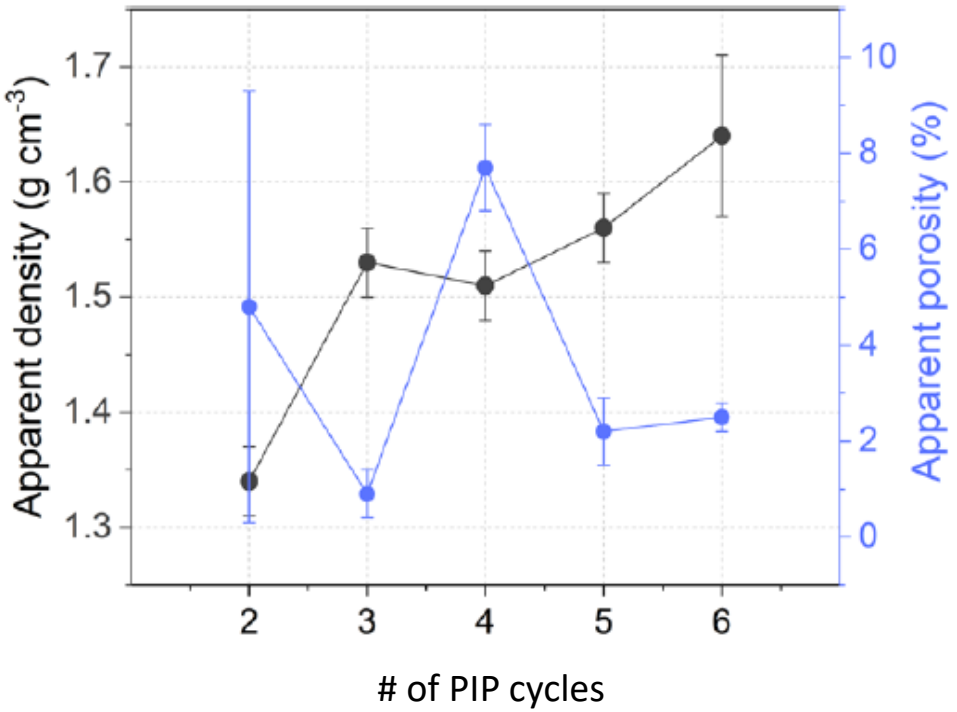


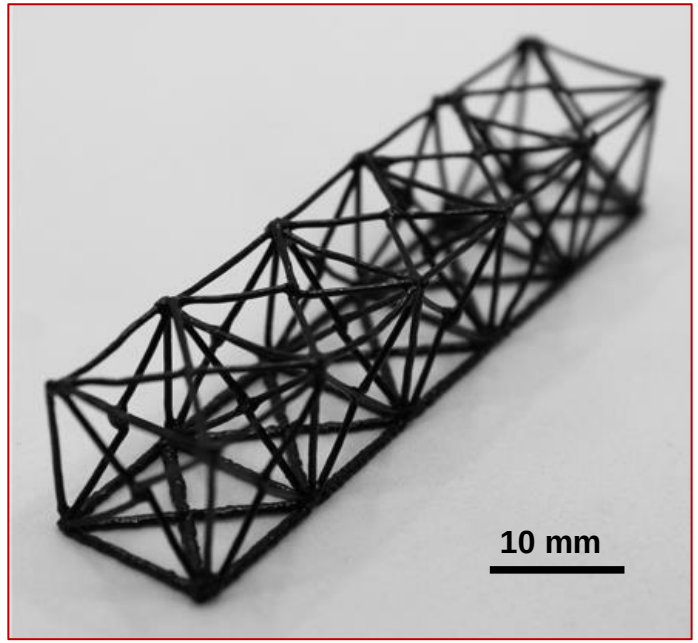
- Sandwich panels with octahedral truss core are possible

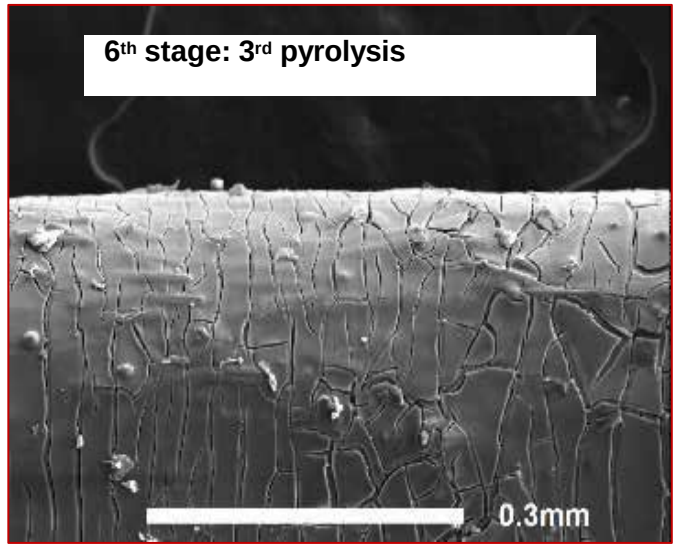
Hybridization: UV-assisted DIW (RAM) of CMCs

- C_{sf} fibers (dimension: 150 μm)
- Fiber amount: 20 vol%
- Addition of fillers (1 wt% silica fume)
- 580 μm nozzle tip









Prof.sa Giorgia Franchin, UNIPD

Conclusions

- Liquid feedstocks based on **preceramic polymers** (*plus fillers*) enable producing ceramic components (*in a wide range of compositions*) using a wide range of Additive Manufacturing technologies based on **photo-polymerization** (DLP, 2PP, Xolo, DIW+UV)
- Highly porous, complex 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
- It is possible to additively manufacture **CMCs** with short and continuous fibers
- Combination of DIW and UV curing (**hybridization**) → **free forming**

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Questions?

Answer

What do you want from me?
I didn't even work on this project!

Why in the world are you asking me this question?

NOVEL CERAMICS AND COMPOSITES PROCESSING TECHNOLOGIES FOR ENERGY-INTENSIVE APPLICATIONS

27 SEPTEMBER, 2024

THANK YOU

CEM-WAVE

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