XIONEER®

Joint Project

Amorphous printing and annealing of Victrex AM200™ filament (PAEK) with Xioneer® VXL soluble support and Digimat-AM

HEXAGON

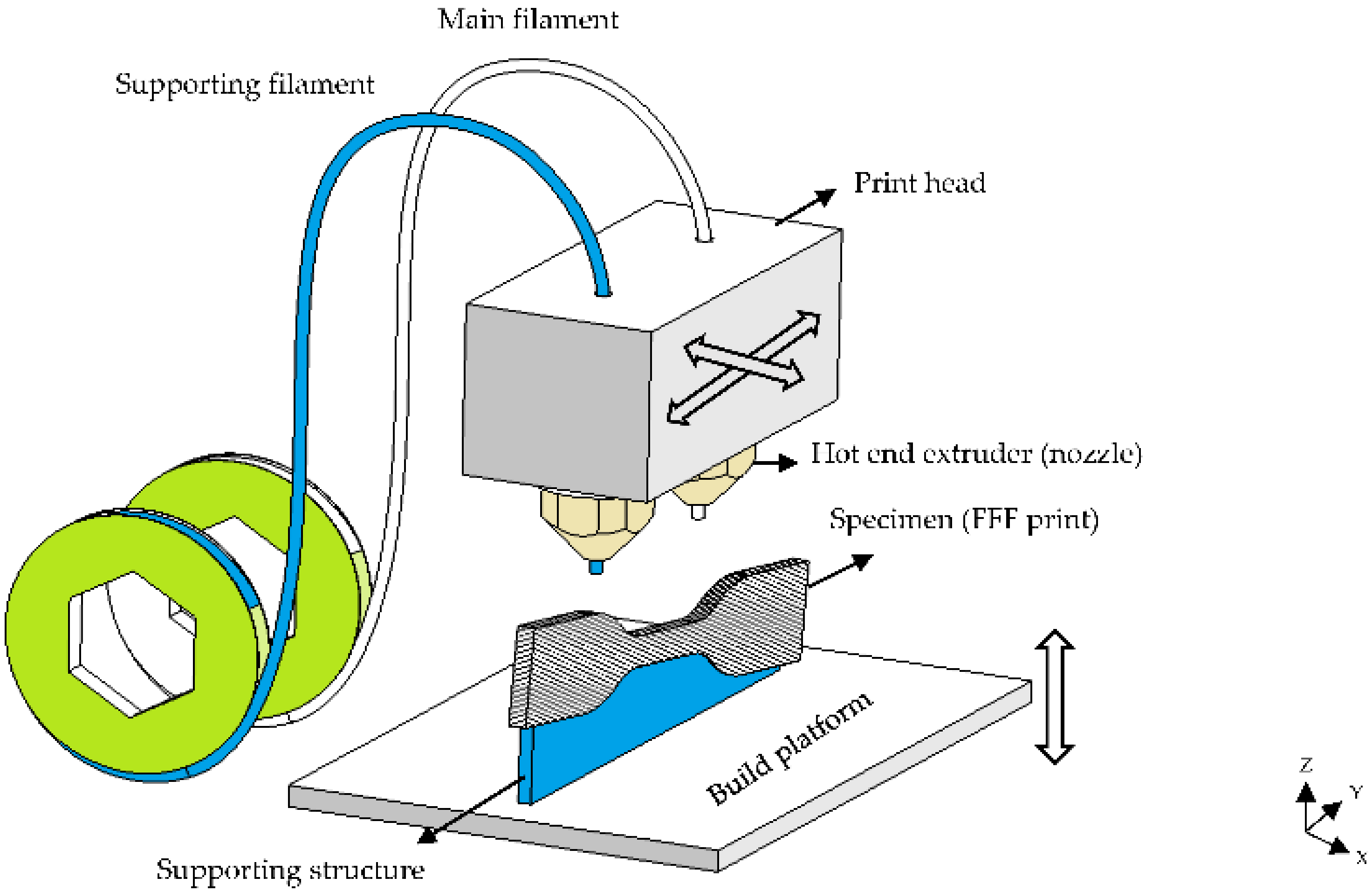
XIONEER®

victrex

Christoph Strasser, Xioneer

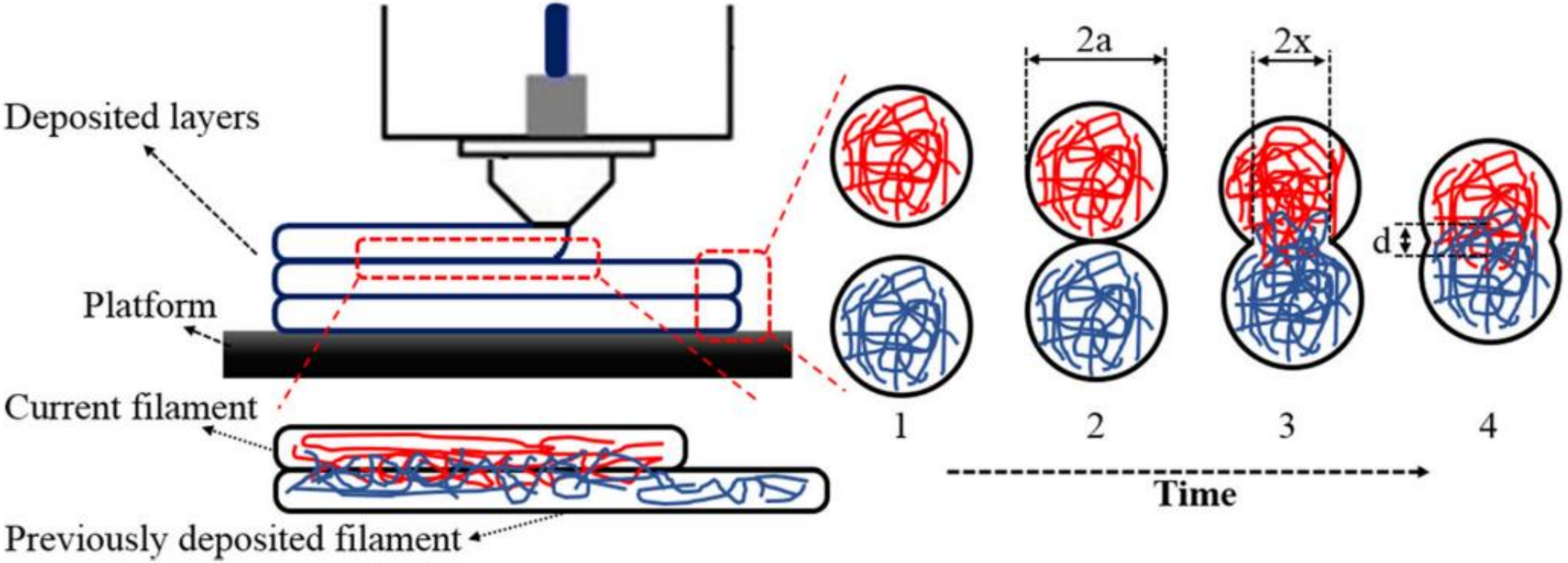
13.09.2023, K-Tag Bayreuth

Introduction: FFF 3D printing



Source: **Accessed 02.06.2023**
Bakhtiari, H.; Aamir, M.; Tolouei-Rad, M. Effect of 3D Printing Parameters on the Fatigue Properties of Parts Manufactured by Fused Filament Fabrication: A Review. *Appl. Sci.* **2023**, *13*, 904.
https://doi.org/10.3390/app13020904

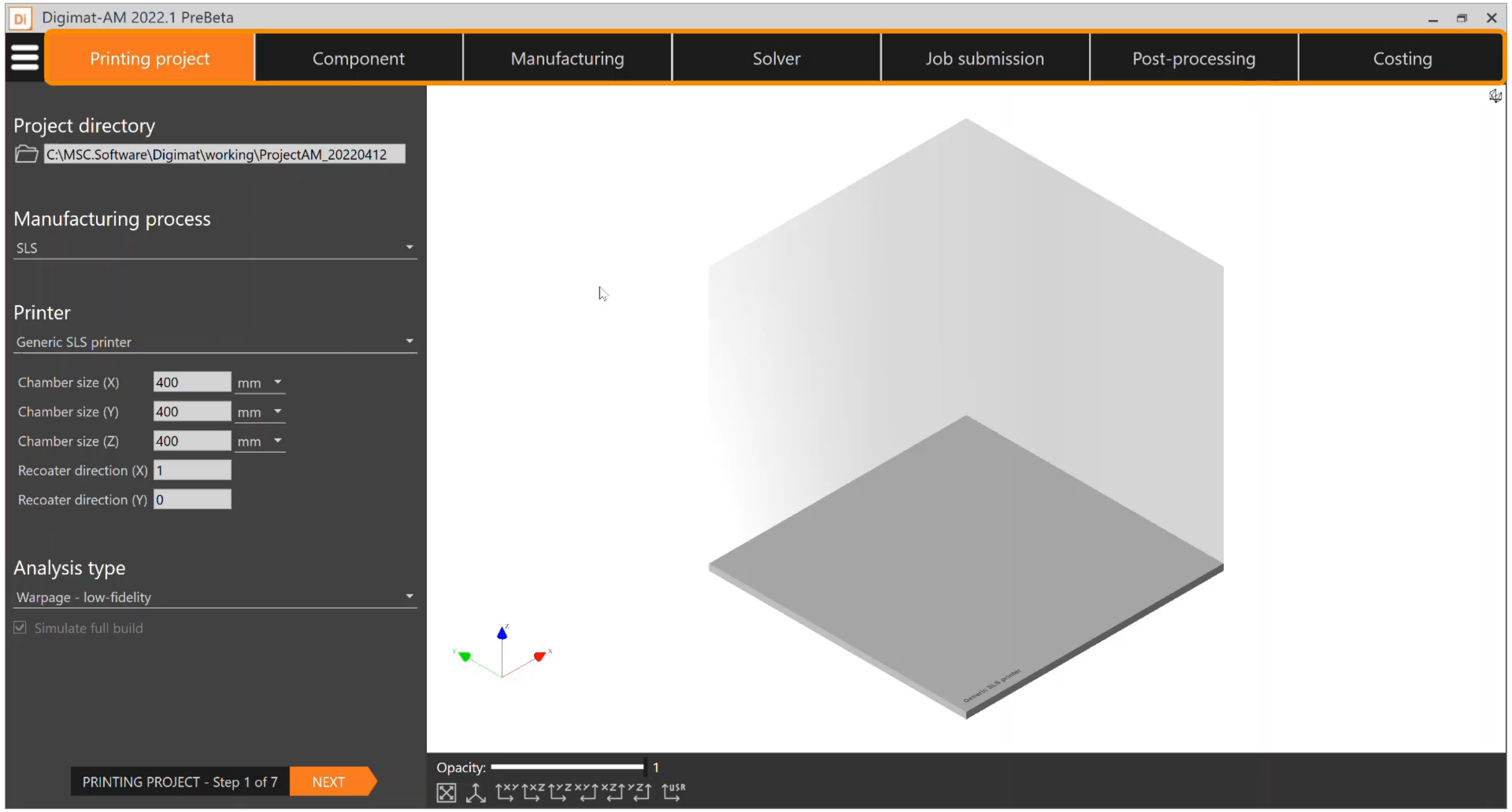
Introduction: Layer Bonding mechanism



(1) surface rearrangement, (2) surface approach, (3) wetting, (4) diffusion and randomization.

Source: **Accessed 02.06.2023**
Hamidreza Vanaei, Kaddour Raissi, Michael Deligant, Mohammadali Shirinbayan, Joseph Fitoussi, et al.. Toward the understanding of temperature effect on bonding strength, dimensions and geometry of 3D-printed parts. Journal of Materials Science, 2020, 55 (29), pp.14677-14689. ff10.1007/s10853- 020-05057-9ff. ffhal-02974929f

Introduction: Process simulation with Digimat-AM



CAPABILITIES
- SLS process simulation
- FDM process simulation

BENEFITS
- Print right the first time
- Optimise process parameters
- Estimate printing costs

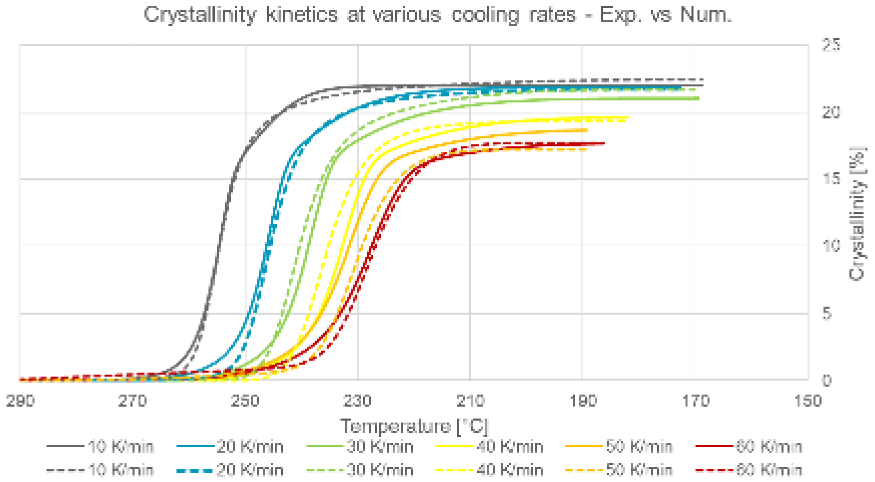
FEATURES
- Crystallinity prediction
- Warpage compensation
- Healing indicator for layer adhesion

Introduction: Simulating semi-crystalline thermoplastics

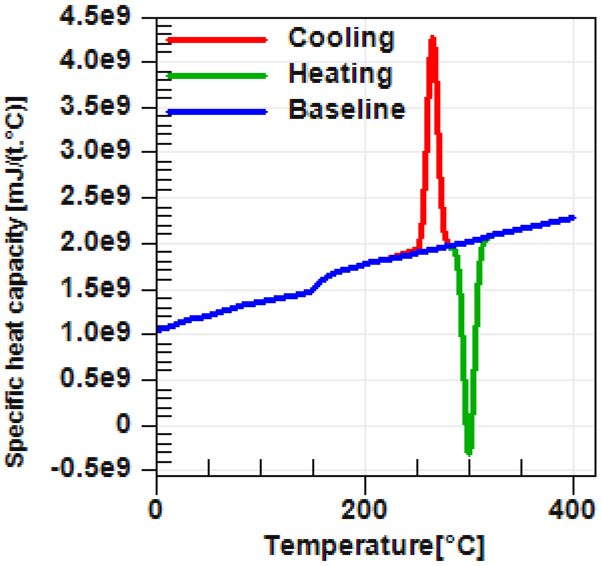
- Rather new in the industry
- Complex analysis, much more so than for amorphous materials
- Extensive analysis of material properties necessary to make material card for mathematical model

Nakamura crystallinity model

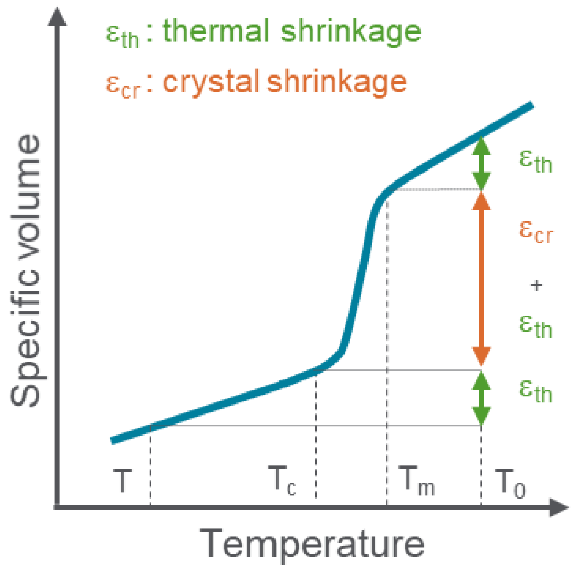
$$\frac{dX(t)}{dt} = nK'(T)\left(1 - X(t)\right)\left[ln\left(\frac{1}{1 - X(t)}\right)\right]^{\frac{n-1}{n}}$$



Latent heat



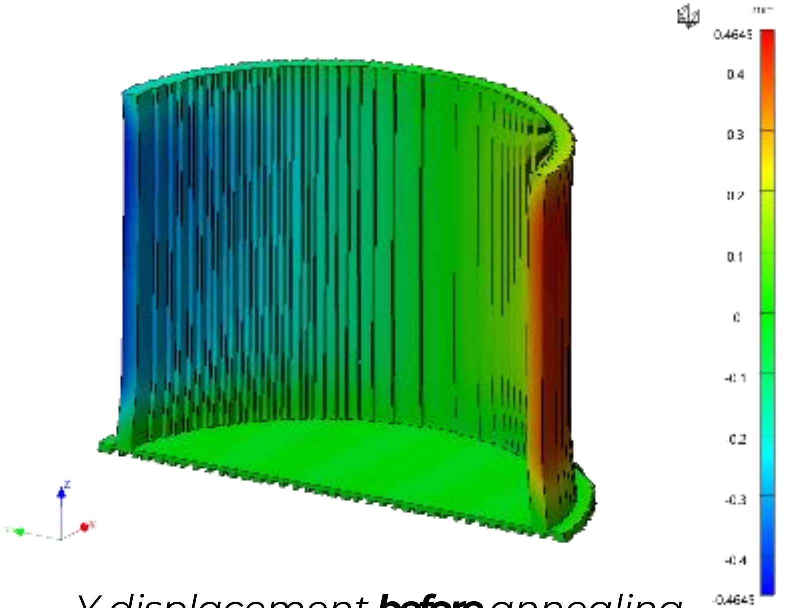
Crystallization shrinkage



Why do we need simulation?

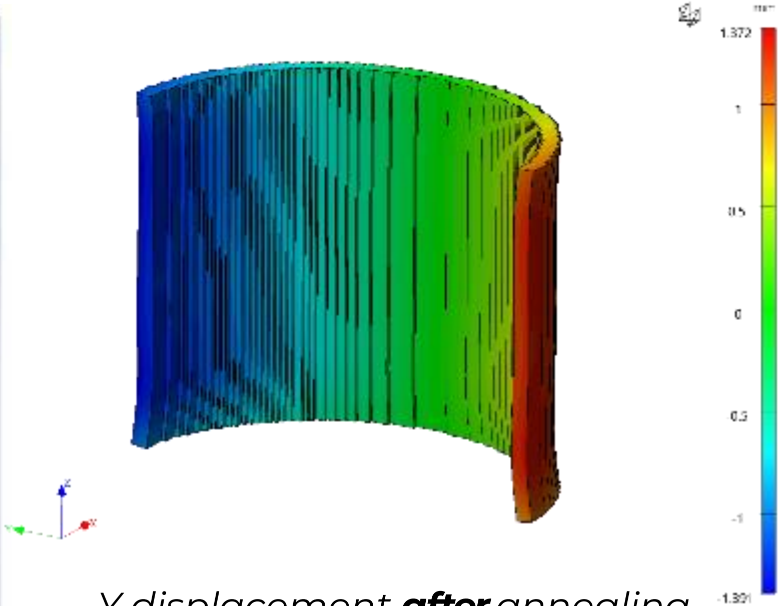
- Reduce trial and error
  - Check whether printing conditions are OK
  - Vary print settings before actual print
- Even with ideal printing conditions, some geometries are not printable without deformation
- Simulation allows for calculating deformation and creation of predeformed model

Before annealing



*Y displacement **before** annealing (scale factor x3)*

After annealing



*Y displacement **after** annealing (scale factor x3)*

Introduction: Specialized PAEK material for FFF

- Like in other AM processes, not every material from other processes is best suited for FFF
- Victrex AM™ 200 an LMPAEK™ polymer based filament is designed for FFF

Lower Printing Temperatures

Easier Flow

Less Warpage

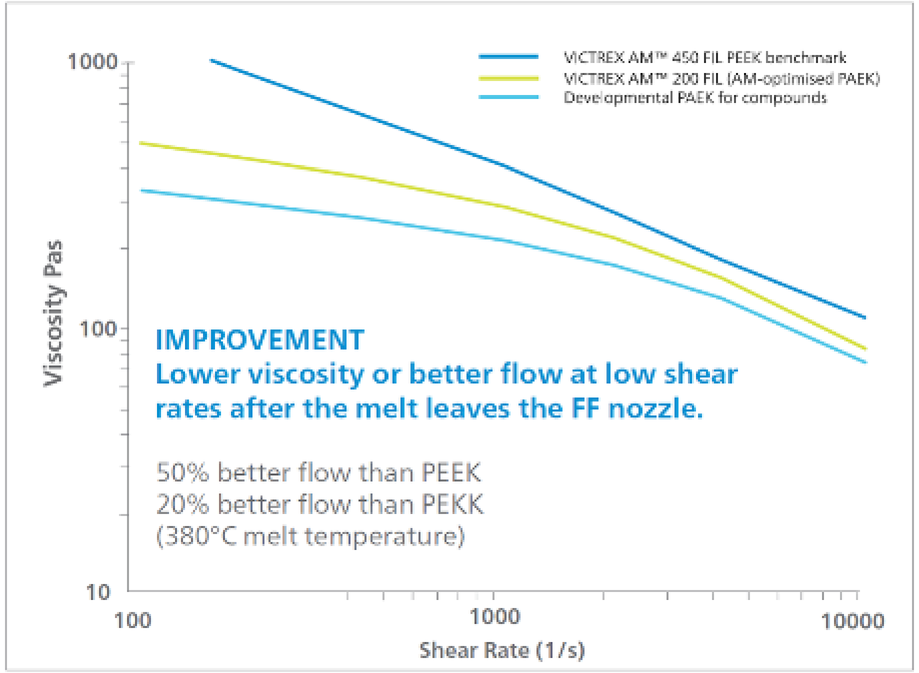
Stronger Parts

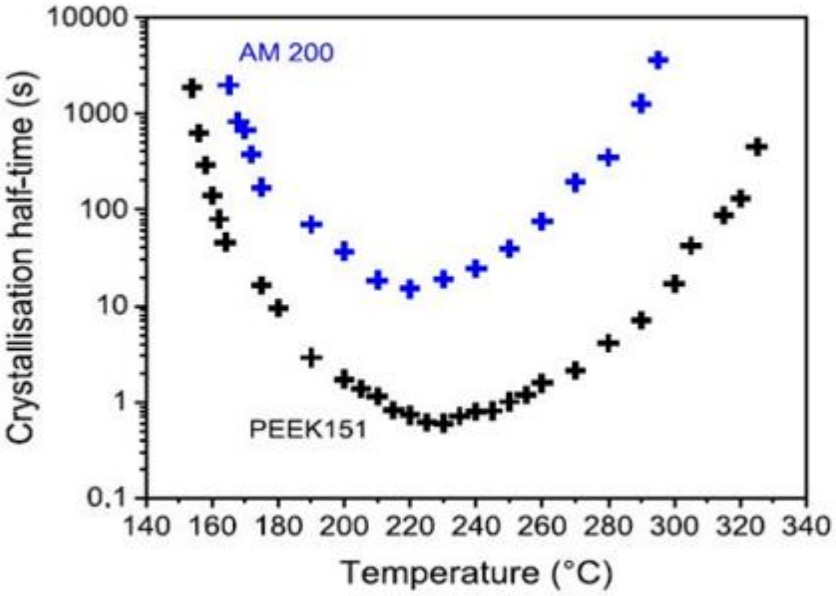
Design Flexibility

Victrex AM™ 200 an LMPAEK™ polymer based filament is designed for FFF

- **Lower viscosity** at **low shear rates**, conditions that mimic well nozzle extrusion and deposition
- **Slow crystallisation rate** that allows good inter-layer bonding and the ability to easily **print amorphous**

= Better **interlayer bonding** = **Higher Z strength**





Y. Nan, R. Davies, A. Chaplin, P. McCutchion and O/ Ghita, Slow and fast crystallizing poly aryl ether ketones (PAEKs) in 3D printing: Crystallisation kinetics, morphology, and mechanical properties, Additive Manufacturing, Volume 39, 2021, ISSN 2214-8604, https://doi.org/10.1016/j.addma.2021.101843.

Why do we need special model materials?

- Standard PEEK materials crystallize very fast
  - Difficult to use
  - Additional to normal shrinkage (melt to solid) we have to deal with crystallization shrinkage
  - Energy input must be sufficient to remelt crystals in previous layers and allow for reptation
- Expensive equipment necessary to process PEEK directly crystalline:
  - High temperature extruder (not so difficult)
  - Chamber temperature and platform > 200 °C (difficult)

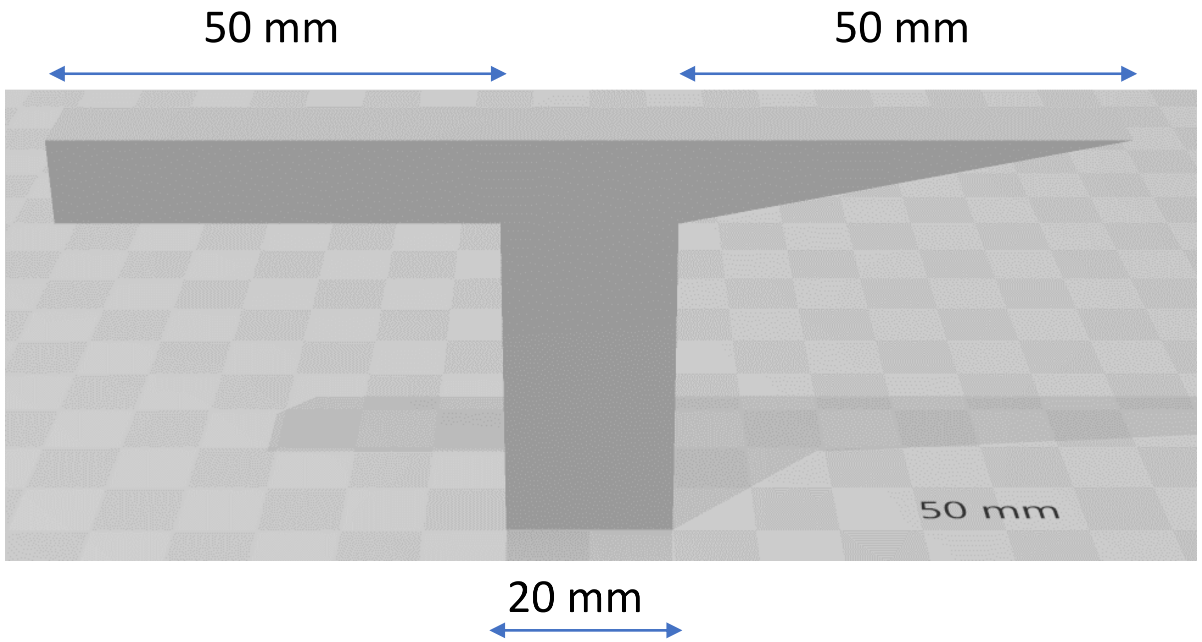
Introduction: No high temperature soluble support for PAEK

- Soluble support for temperatures above 120 °C is the holy grail of FFF/FDM printing
  - Not counting organic soluble support materials
- So far, PEI, PEEK, PPSU materials can only have breakaway support
- PVA, BVOH and compounds thereof don‘t have sufficient temperature stability
- VXL materials usable only up to 120 °C chamber temperature
  - Up to 120 °C AM200 can be printed amorphous

Manifold: AM200™ with VXL 111

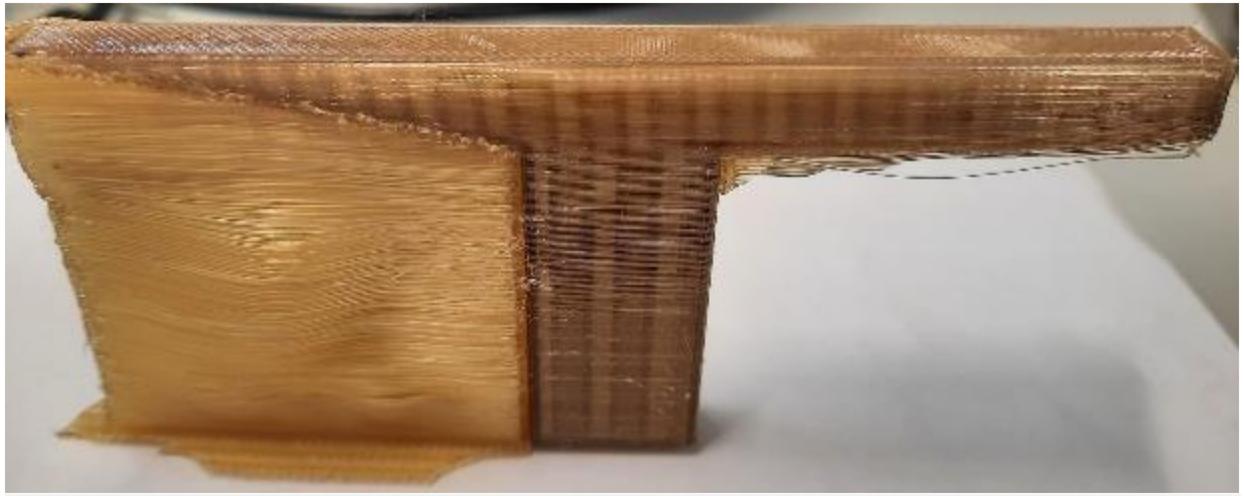
Testing of different soluble support materials

- AM200 was printed with VXL111, VXL130 and three competing materials in a hammer geometry and with the same support geometry
- Chamber temperature set at 80 °C
- Printing temperature of AM200 set at 400 °C
- Build plate temperature set at 110 °C
- Examination of adhesion, cohesion and warpage



Testing of different soluble support materials: Material A

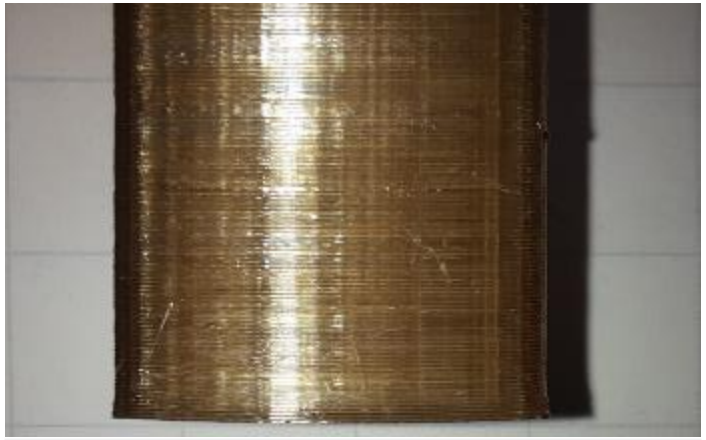
- Strong adhesion between AM200 and Material A
- Hammer shows warpage
  - Not strong enough at 80 °C, gets streched
- Support shows significant warpage and buldging



Hammer: AM200^{TM} with Material A

Side-View of support

Interface, hammer bent upwards



Hammer base

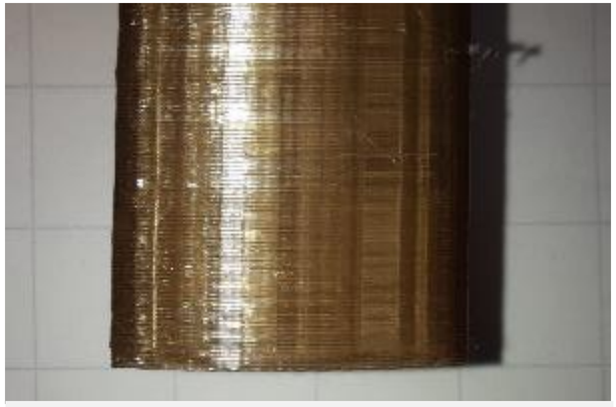
Testing of different soluble support materials: Material B

- Good adhesion between Material B and AM200
- Poor layer adhesion in the support structure even at high printing temperatures (up to 295 °C)
  - Cohesive failure in support structure
- Hammer shows warpage
- Support shows warpage

Hammer: AM200^{TM} with Material B

Side-View of support

Interface, hammer bent upwards



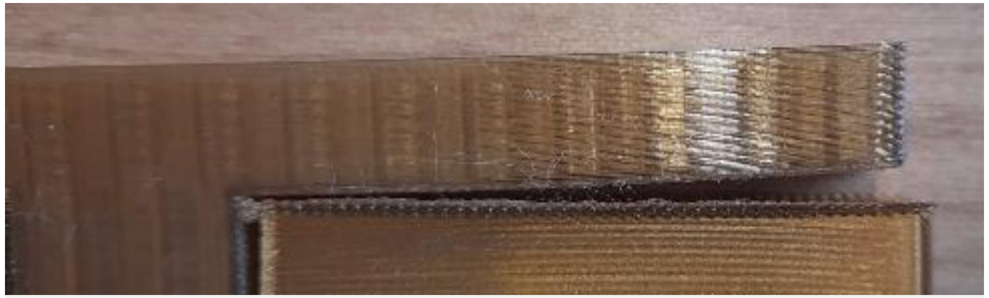
Hammer base

Testing of different soluble support materials: Material C

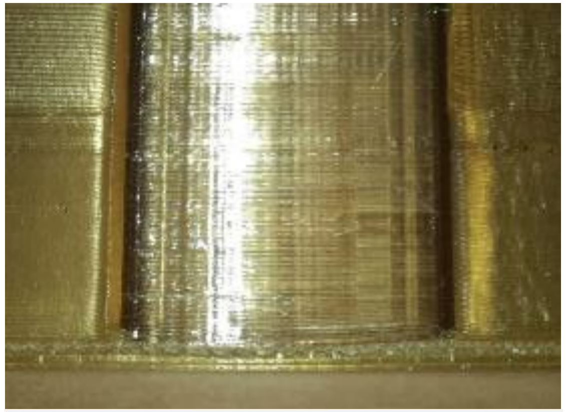
- Poor adhesion between AM200 and Material C
  - Adhesive failure in interface
- Support shows significant warpage
- Hammer shows significant warpage

Hammer: AM200^{TM} with Material C

Side-View of support



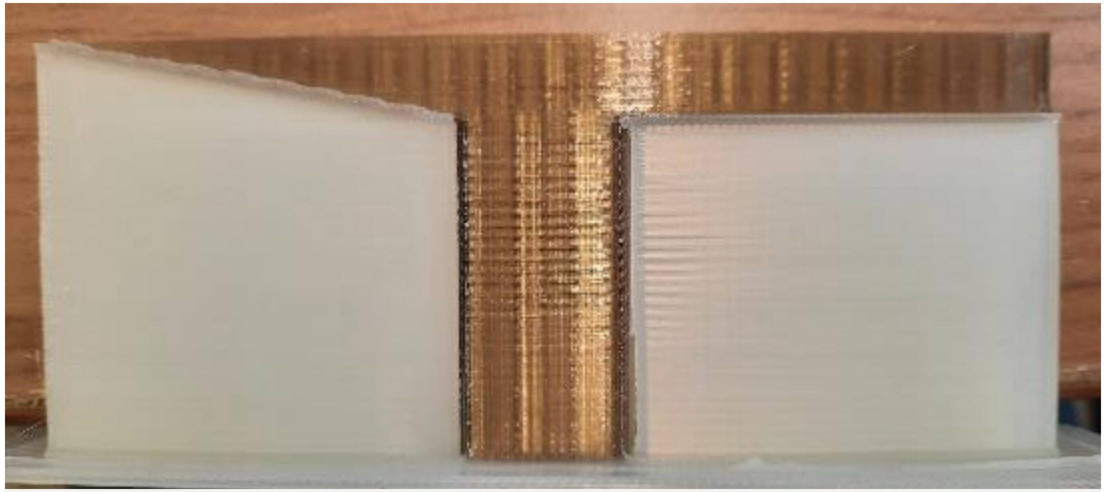
Interface, hammer bent upwards



Hammer base

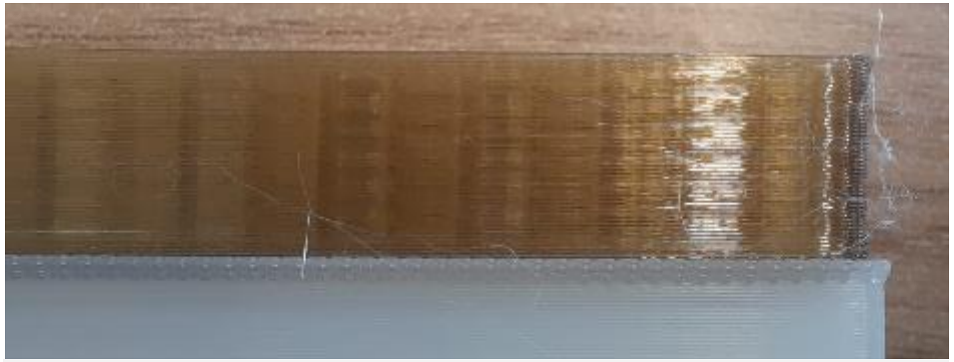
Testing of different soluble support materials: VXL 111

- Good adhesion between VXL111 and AM200
- VXL111 can act like break-away
- Hammer shows only slight warpage
- Support shows only slight warpage

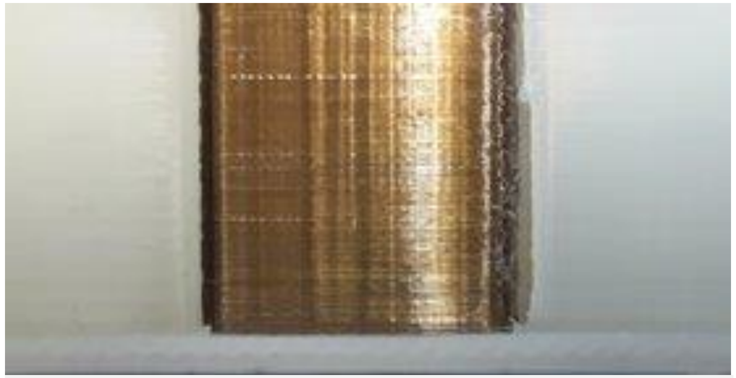


Hammer: AM200™ with VXL 111

Side-View of support



Interface, hammer flat



Hammer base

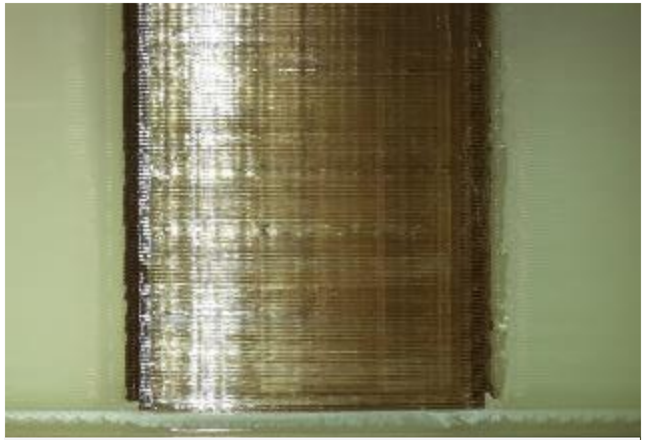
Testing of different soluble support materials: VXL 130

- Good adhesion between VXL130 and AM200
- VXL130 can act like break-away
- Hammer shows only slight warpage
- Support shows only slight warpage

Hammer: AM200™ with VXL 130

Side-View of support

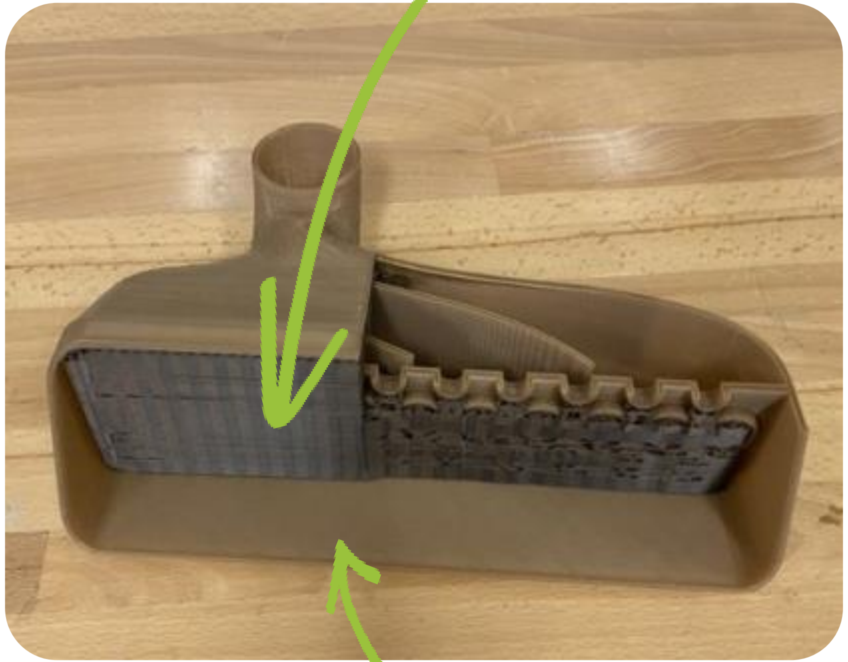
Interface, hammer flat

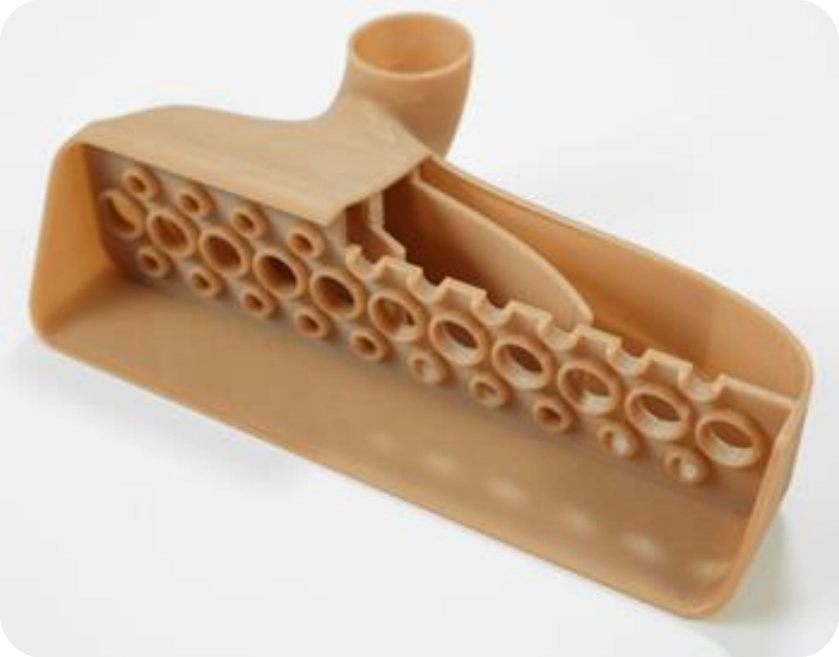


Hammer base

Printing Amorphous + Soluble Supports: Why Does It Matter?

Today's soluble support requires
low printing temperatures





VICTREX AM™ 200 prints amorphous
at these temperatures

Example of a part printed by Stratasys® on a Fortus 450mc™ printer with VICTREX AM™ 200 filament printed amorphously and Stratasys SR100 soluble support. Photos used with permission, courtesy of Stratasys, all rights reserved.

How to solve this dilemma?

- It has been established that semicrystalline materials can be printed amorphous and annealed at a second stage
- AM200 can be printed amorphous in the range between 80 – 120 °C
  - Ideal temperature for VXL soluble support materials
- Slow crystallization of AM200 allows for controlled annealing after printing
- Shrinkage and deformation during printing and annealing complicate this process
- **Solution:** Combine process with simulation to generate predeformed part before printing


Amorphous AM200™ part with VXL 111


Annealed AM200™ part with VXL 111

Things to consider: Airtight parts

- A cylinder was printed and annealed
- Apparently, the cylinder was printed airtight
- Air inside cylinder expanded during heat up and inflated the part

Amorphous part

Annealed part

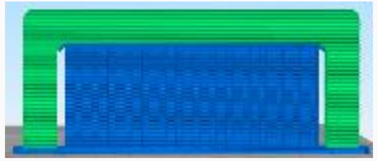
A New Approach To Amorphous 3D Printing and Annealing

Innovative Approach

CAD Model

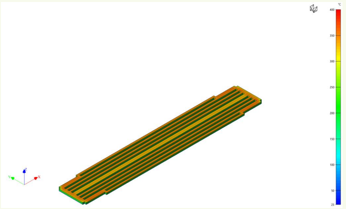
Design your model

GCODE



Generate print-file

Simulation



Simulate print file for **distortion and shrinkage**

New CAD Model

Generate new CAD model with pre-deformed and scaled geometry – to **account for shrinkage and distortion**

3D Print

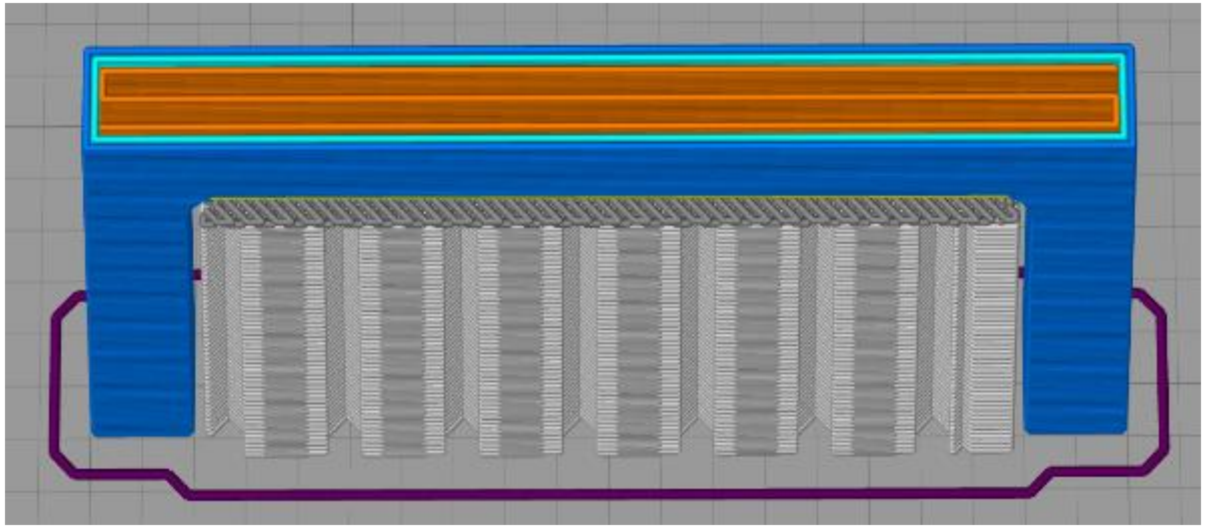
Print pre-deformed model

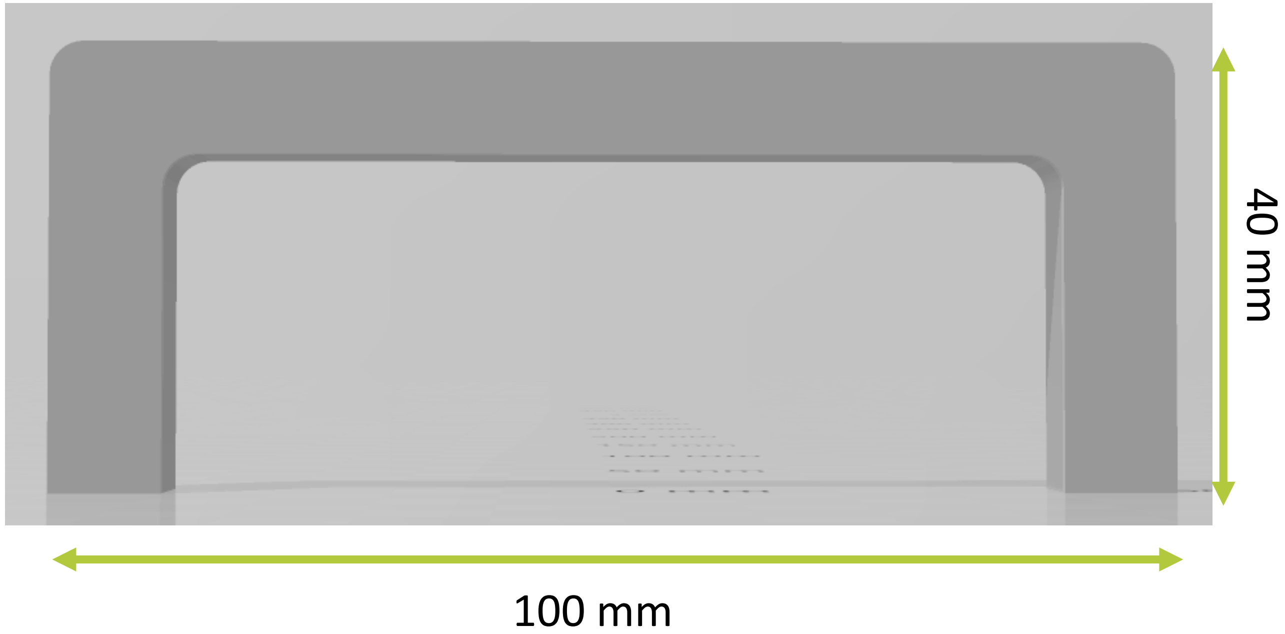
Anneal

Anneal amorphous part to get a final crystalline part

Test specimen for simulation: Bridge

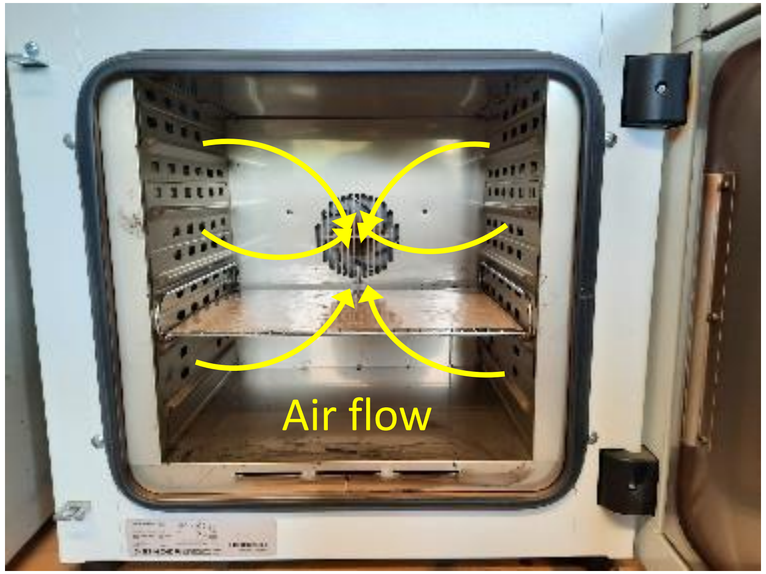
- Simple bridge geometry to promote residual stress
  - Infill at 30 % parallel to long sides to maximise residual stress
  - Thickness of shape = 10x10 mm





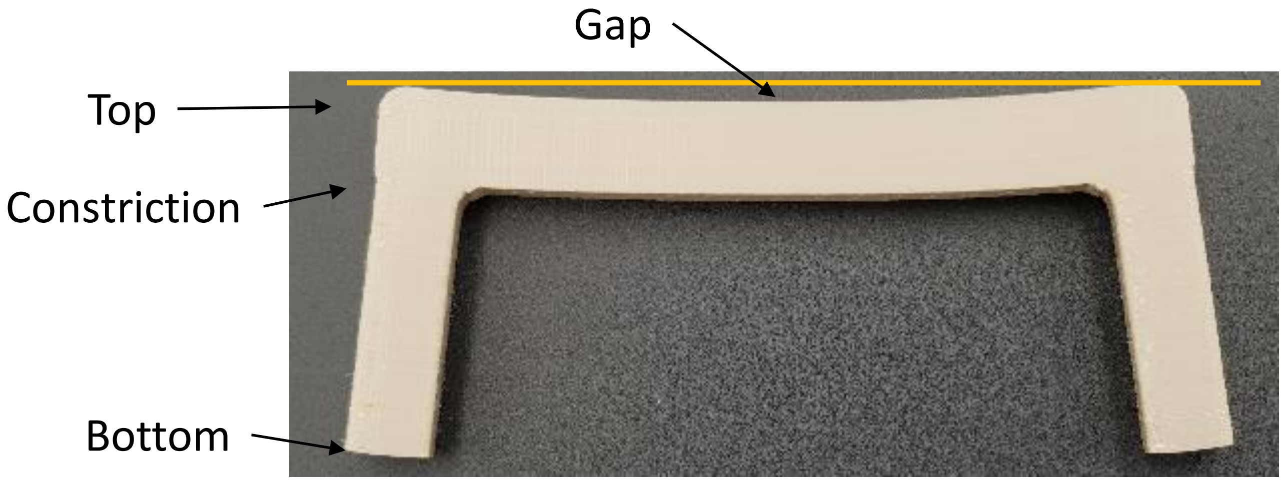
Printing and annealing: Experimental setup

- Annealing procedure:
- Carried out in a laboratory circulating oven (no active cooling)
- Temp. profile: RT ↗ (3 K/min) 175 °C → (180 min) 175 °C ↘ (2 h) 50 °C



Printing and annealing: Bridge

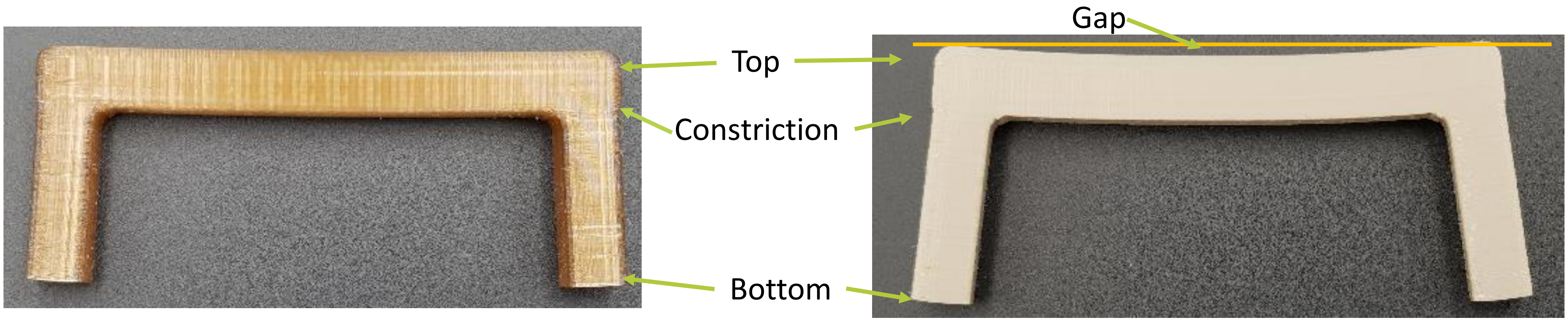
- Deformation and constriction visible after printing
- More pronounced after annealing

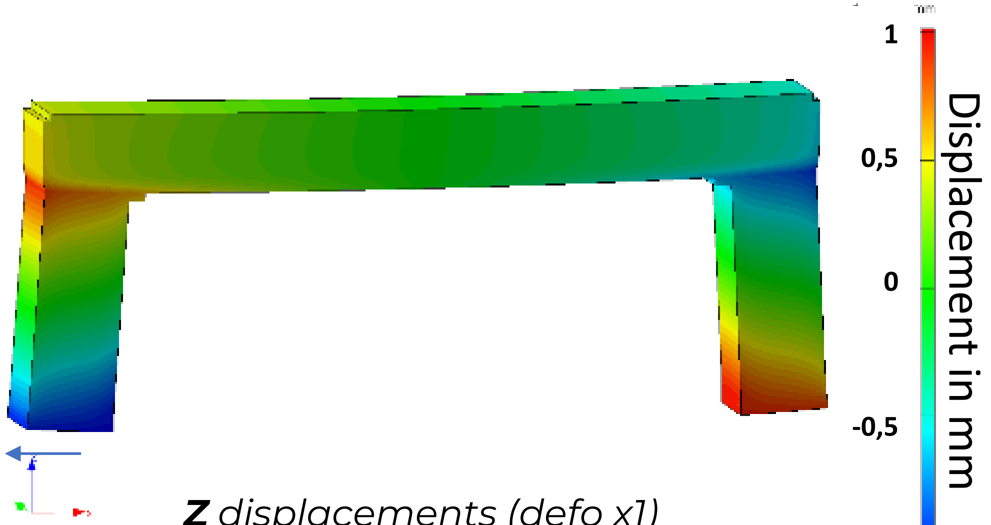


Printing and annealing: Why trial and error is not the solution

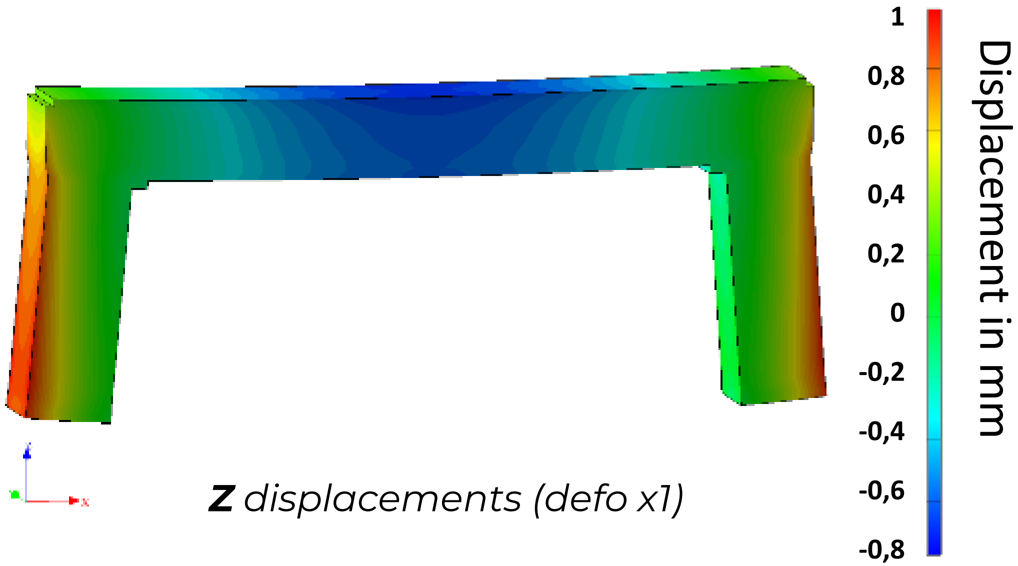
Before Annealing: Slight deformation

After Annealing: Significant deformation





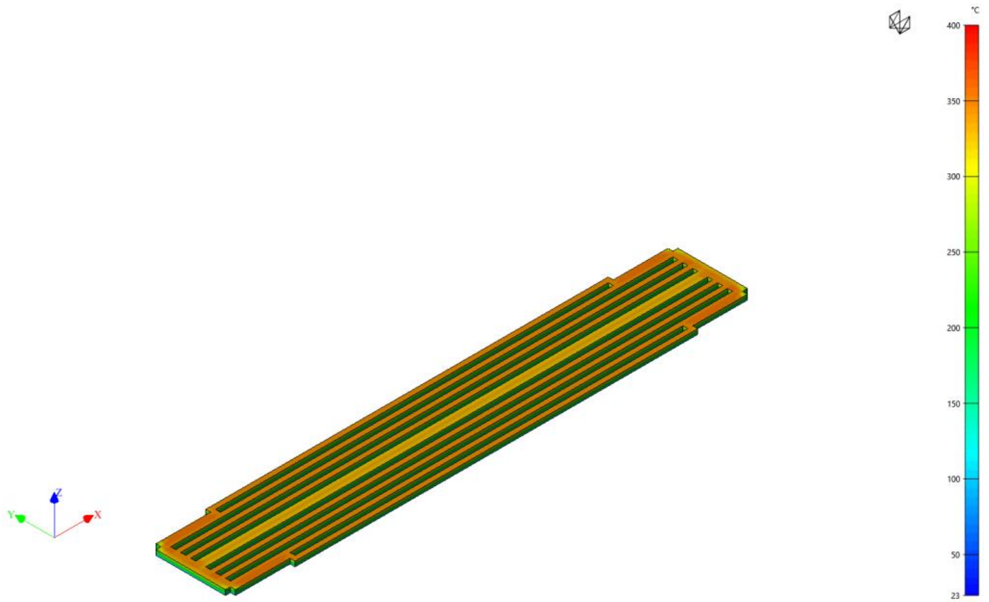
***Z** displacements (defo x1)*



***Z** displacements (defo x1)*

Printing and annealing: Predeform Shape

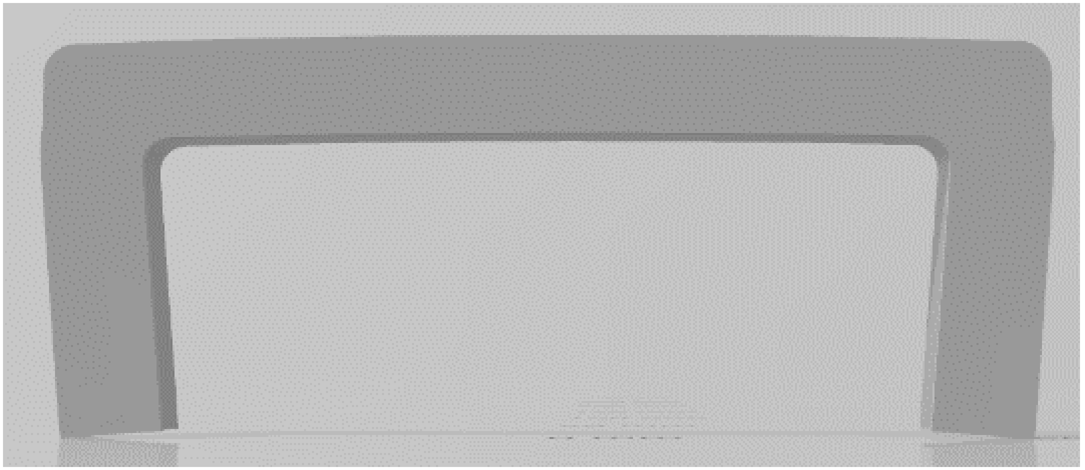
Thermomechanical simulation of bridge

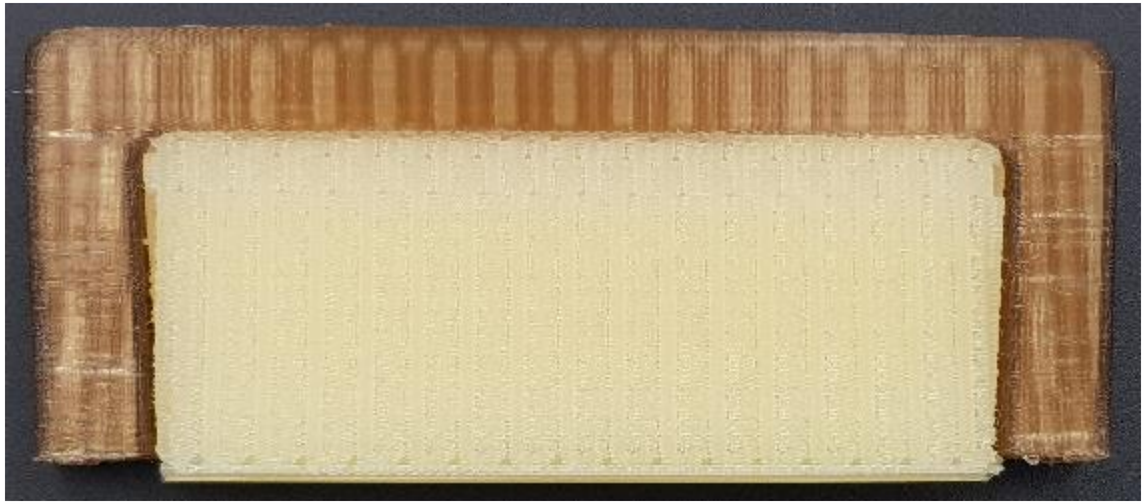


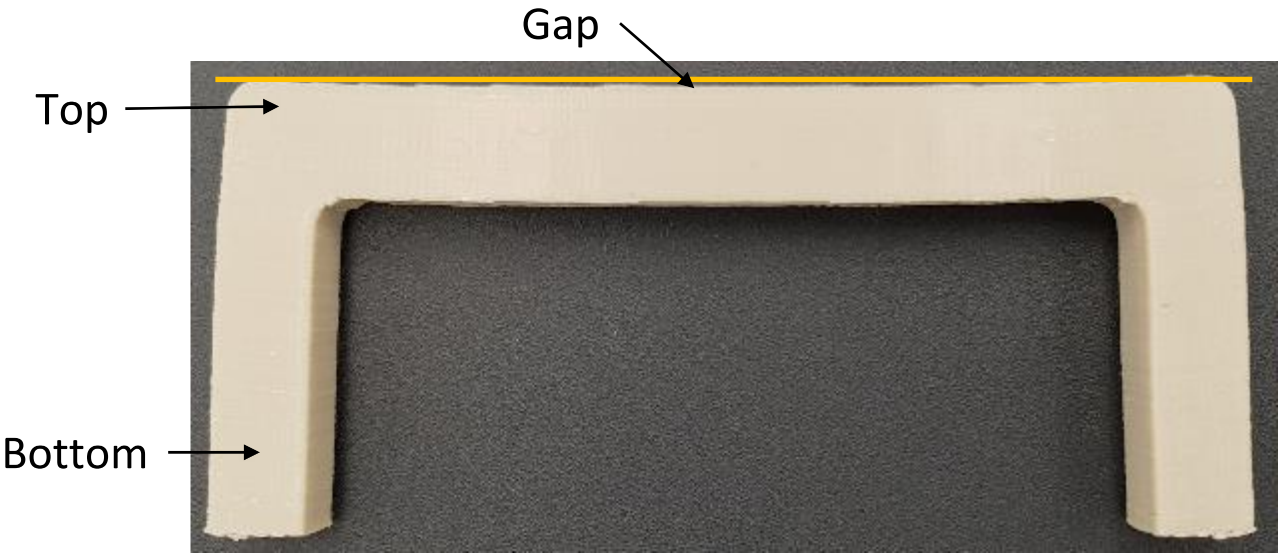
Predeformed geometry from simulation

Printing and annealing: Predeform Shape

- Simulate bridge to make predeformed geometry
- Slice predeformed geometry and print
  - Constriction gone
  - Only slight deformation after printing
  - Almost no deformation after annealing







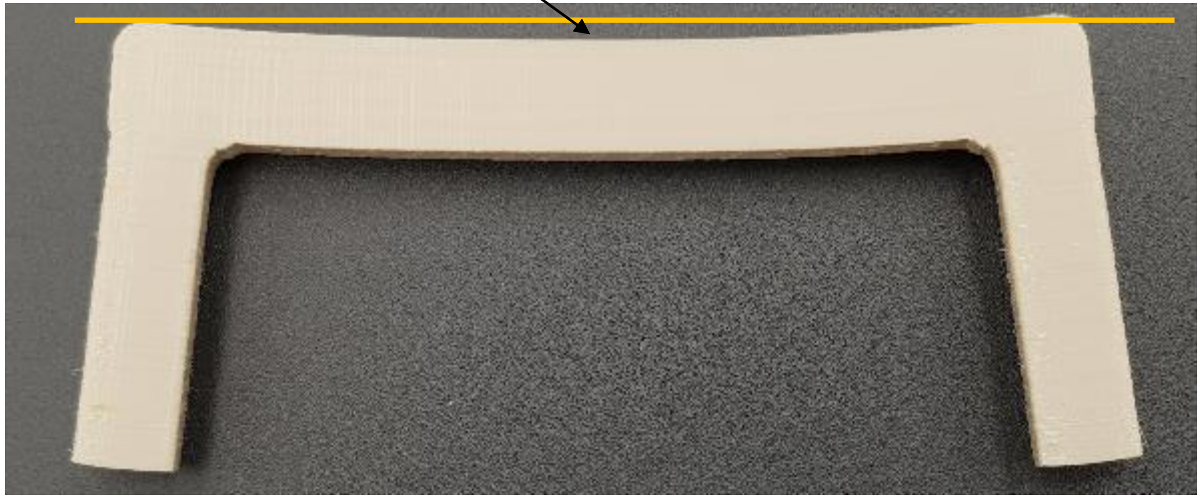
Comparing Deflection and Crystallinity

- Deflection at top better, but still needs some improvement
- Gap reduced from 1,6 mm to 0,3 mm

Regular bridge	Before Annealing	After Annealing
Width Bottom	100,7 mm	100,2 mm
Width Top	99,7 mm	94,6 mm
Gap Width	0,5 mm	1,6 mm

Predeformed bridge	Before Annealing	After Annealing
Width Bottom	100,8 mm	99,6 mm
Width Top	102,8 mm	97,4 mm
Gap Width	/	0,3 mm

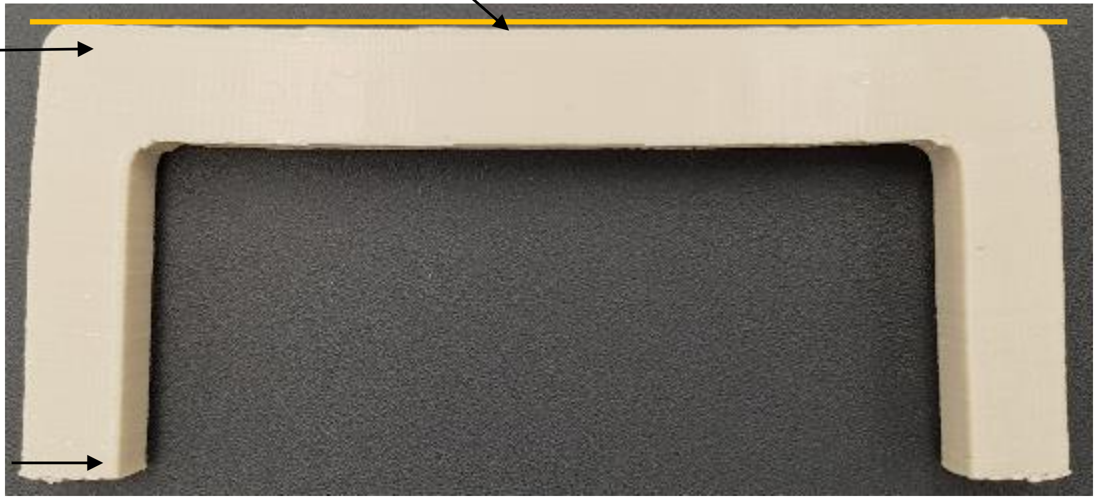
Gap



Top

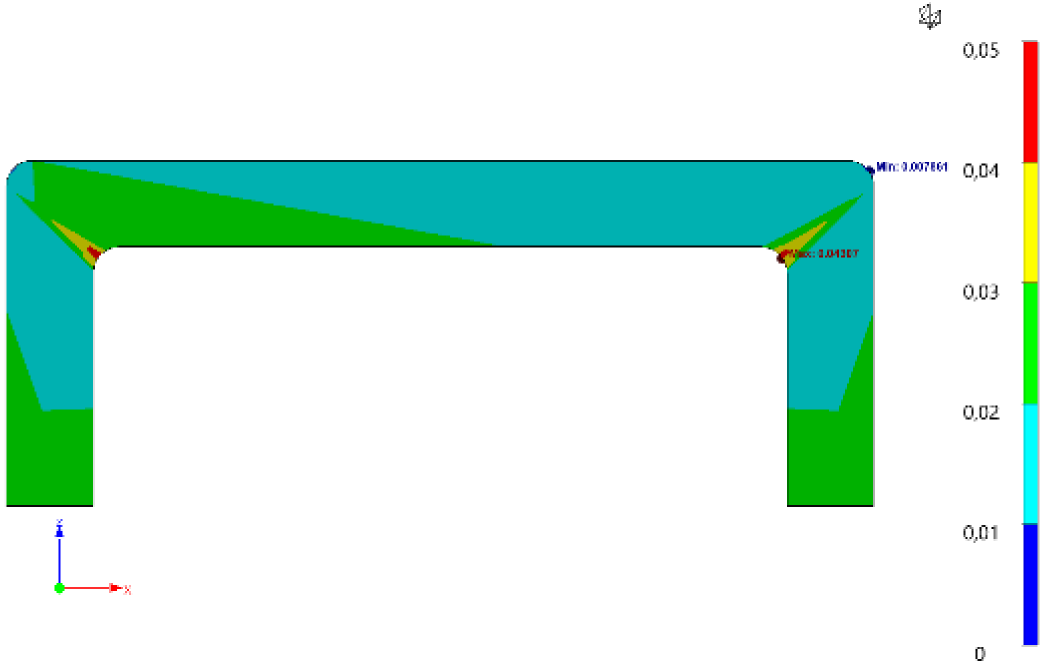
Bottom

Gap

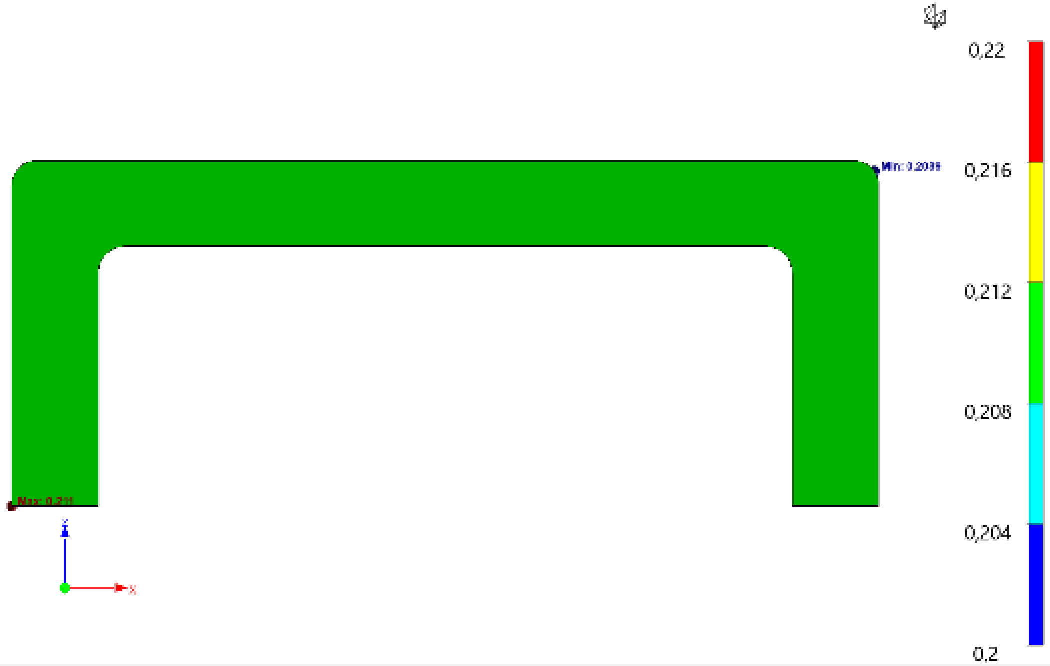


Comparing Deflection and Crystallinity

- Simulated crystallinity within **2 %** correct compared to DSC measurements (as printed)
- Simulated crystallinity within **1 %** correct compared to DSC measurements (as annealed)



Simulated crystallinity after printing: ~ 2-4 %
Measured via DSC: 4,5 % ± 0,5 %

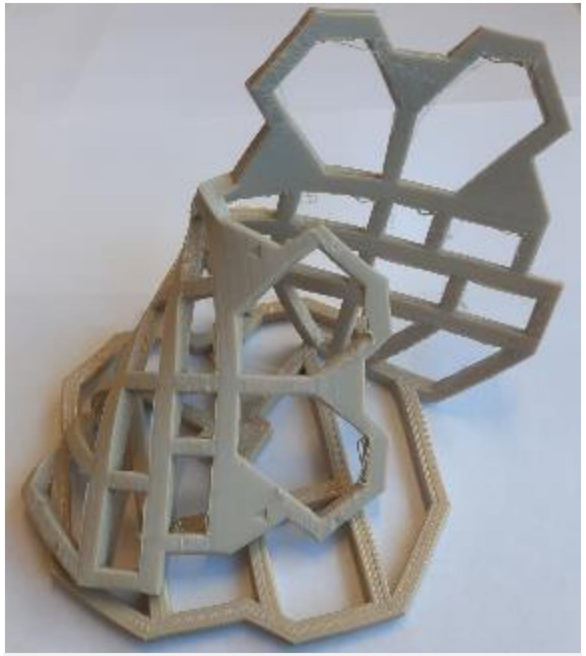


Simulated crystallinity after annealing: ~ 21 %
Measured via DSC: 21,5 % ± 1 %

Things to consider: Gravity

- A fine structured calibration part was annealed
- Due to gravity, the structure collapsed on itself during annealing
- Possible solution:
  - Encase in support during annealing
  - Use different annealing cycle with holding time

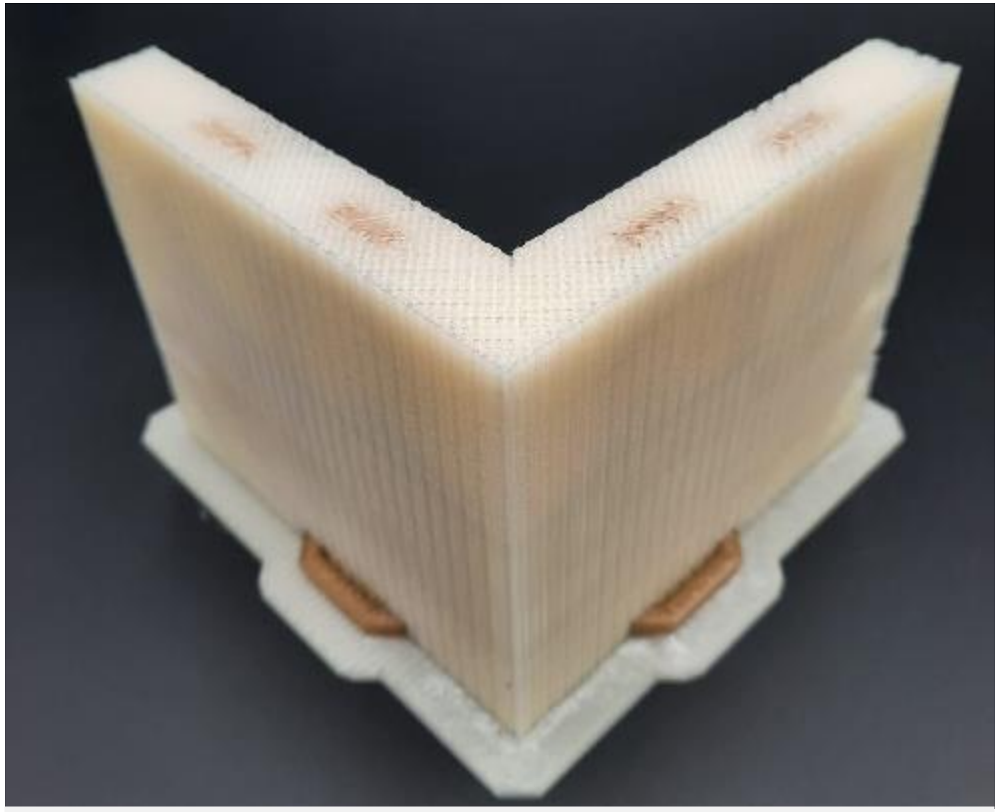
Amorphous part



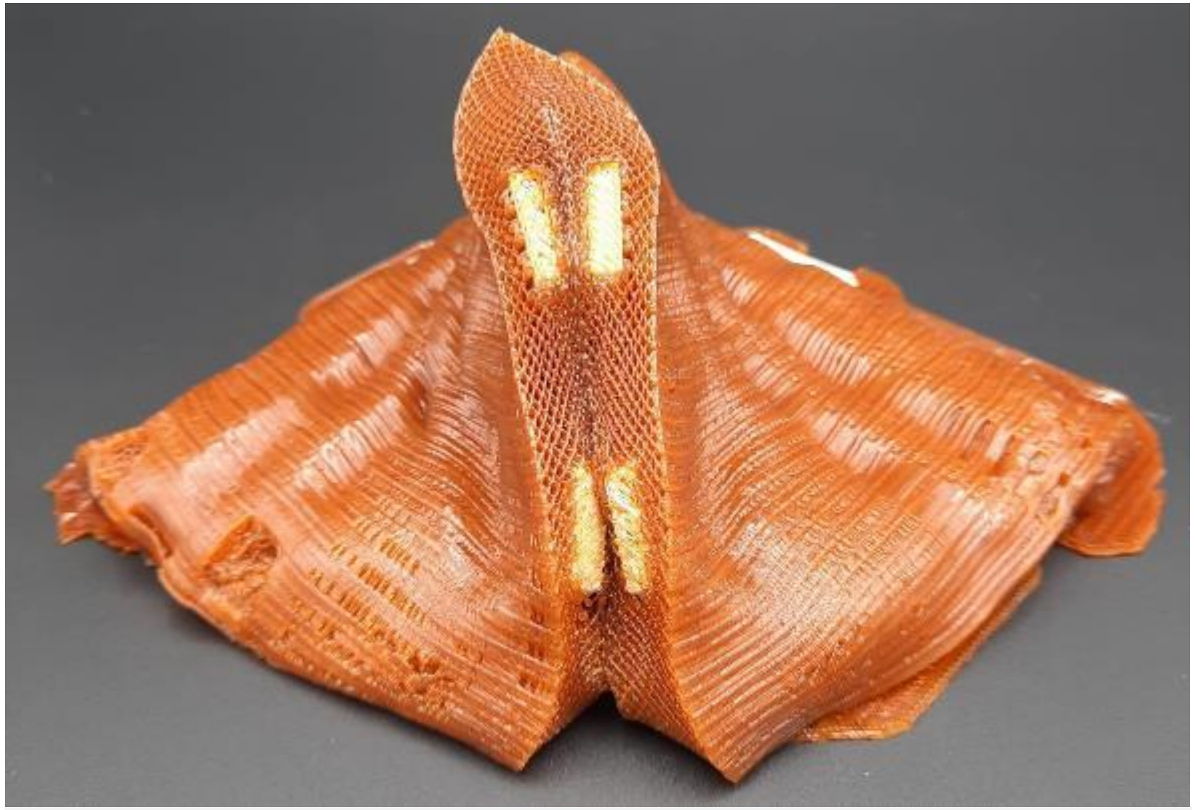
Annealed part

Things to consider: Gravity

- VXL 111 does not have high enough HDT to support part during annealing



Amorphous part



Annealed part

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Stay tuned for more…

Questions?

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