EPFL

Advanced Ceramic Technologies

Shaping

M. Stuer

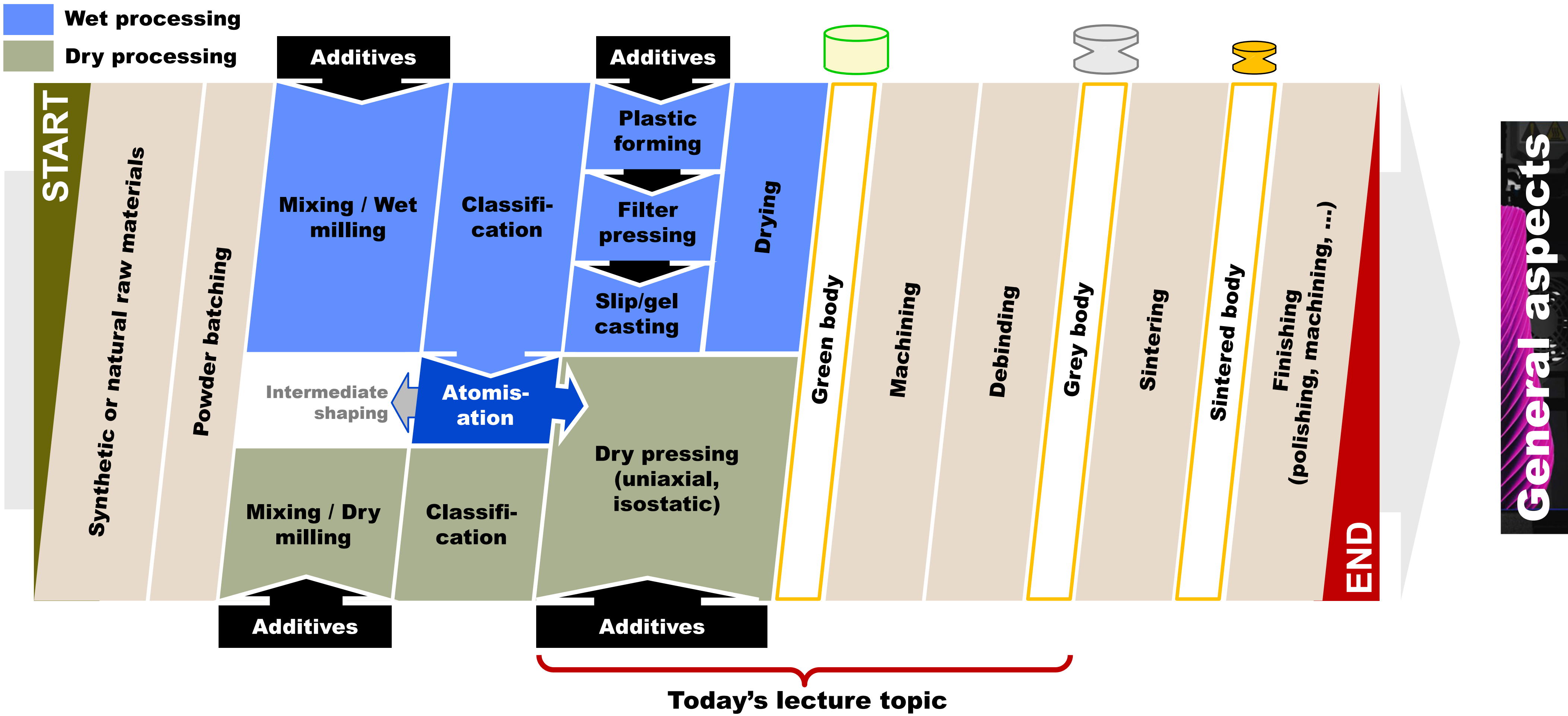
Outline

- Shaping in the global ceramic process map
- Dry pressing
- Wet shaping
  - From slurries: Slip-casting, filtre pressing and tape casting
  - From pastes: extrusion, jiggering and injection
- Additive manufacturing
  - 3D shaping techniques
- Drying and debinding
- Case study: Shaping of micro-medical devices

Learning objectives:

- Refresh typical shaping techniques
- Be able to chose the appropriate shaping technique
- Awareness of critical process steps
- Prepare for knowledge-based decision taking

Global ceramic powder processing chain



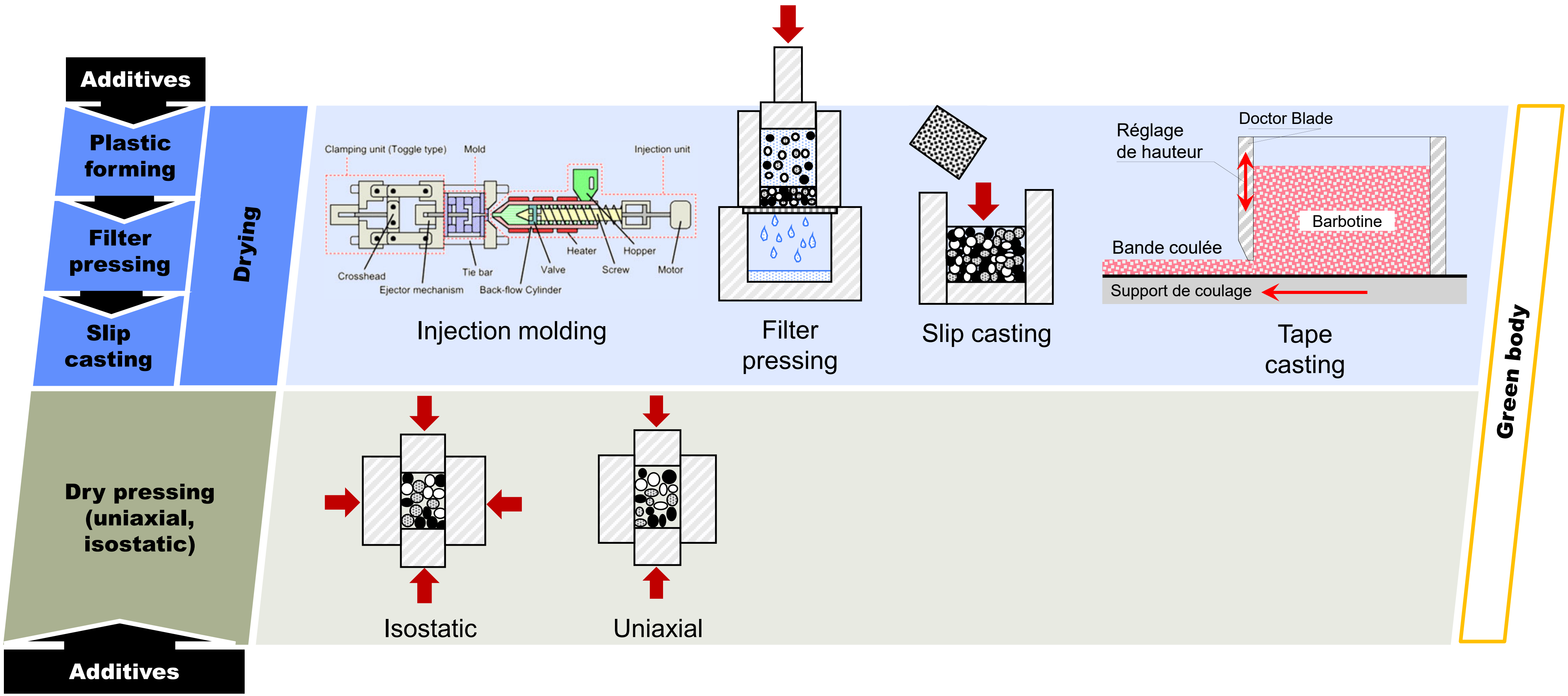
General shaping aspects

- **Shaping:**

  Transformation *of a ceramic* ***powder*** *into a* ***green body*** *which shall be ideally* ***near-net-shape*** *due to the high machining costs of sintered ceramics!*

- **Numerous shaping methods** exist or are under development. There is **no "single best method"**.
- The shaping method shall be **selected based on part**:
  - **Size**
  - **Shape complexity**
  - **Dimensional tolerances**
  - **Production volume**
  - **Production rate**

Typical established wet and dry shaping techniques



General aspects

If machining required, **preferential to machine in the green/pre-sintered state**! (e.g. machining costs)

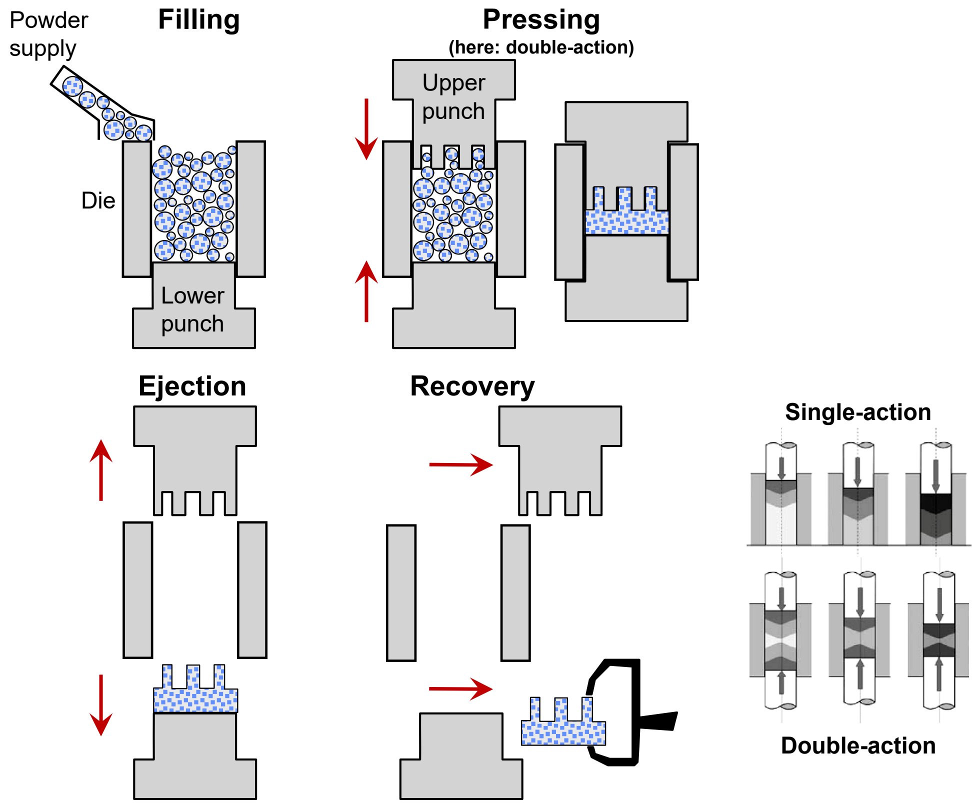
- DRY SHAPING -

Dry powder pressing

M. Stuer

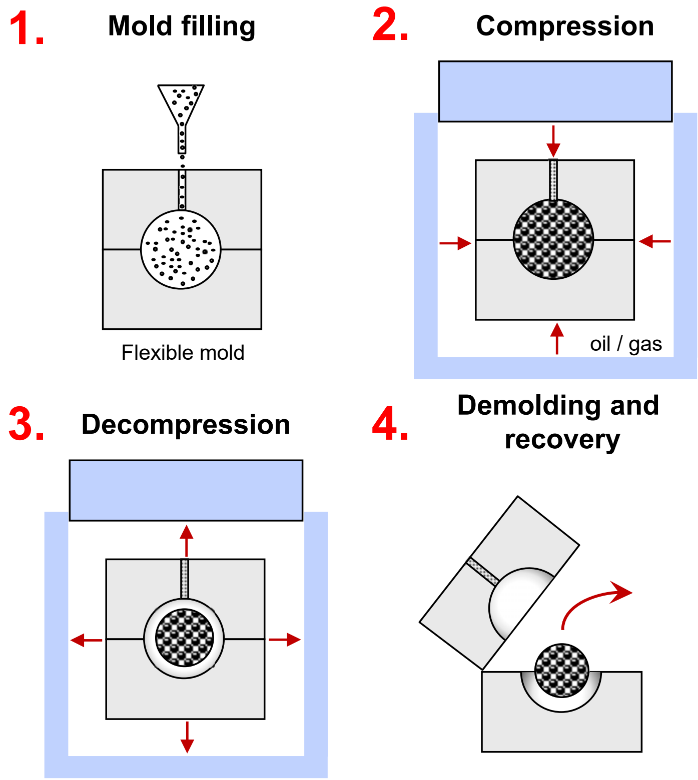
Dry pressing: Schematic process representations

#1_uniaxial pressing



Watch here: https://www.azom.com/materials-video-details.aspx?VidID=386

#2_cold isostatic pressing (CIP)



Watch here: https://youtu.be/77fu_aiEJkM

Dry pressing: Key process facts

#1_ uniaxial pressing

Typical use cases:
Rather parts with simple shapes (2D+) and typically millimeter scale thickness

Advantages:
- High **production rate** (up to 1000 pcs/hr)
- Can be widely **automatized**
- **Dimensional tolerances**
  (± related to mold except for the thickness)

Limitations:
- **Tooling costs**
- **Part complexity** is limited
- **Part size** is limited
- Pressure/ejection cycle induced **part flaws**
- **Part thickness tolerances** depend on mold filling variability

#2_ cold isostatic pressing (CIP)

Typical use cases:
Parts with simple or complex shapes and dimensions unsuitable for uniaxial pressing

Advantages:
- **Homogeneity** of green body
- **Density** of green body
- Compatibility with **large and complex part shapes**

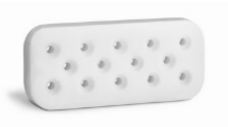
Limitations:
- Can only be **semi-automated**
  → low production rates (and volumes)
- **Dimensional tolerances** (deformable molds)
  → resurfacing typically required

Dry pressing: Process use case examples

#1_uniaxial pressing

pistons, valves,…

Printer heads



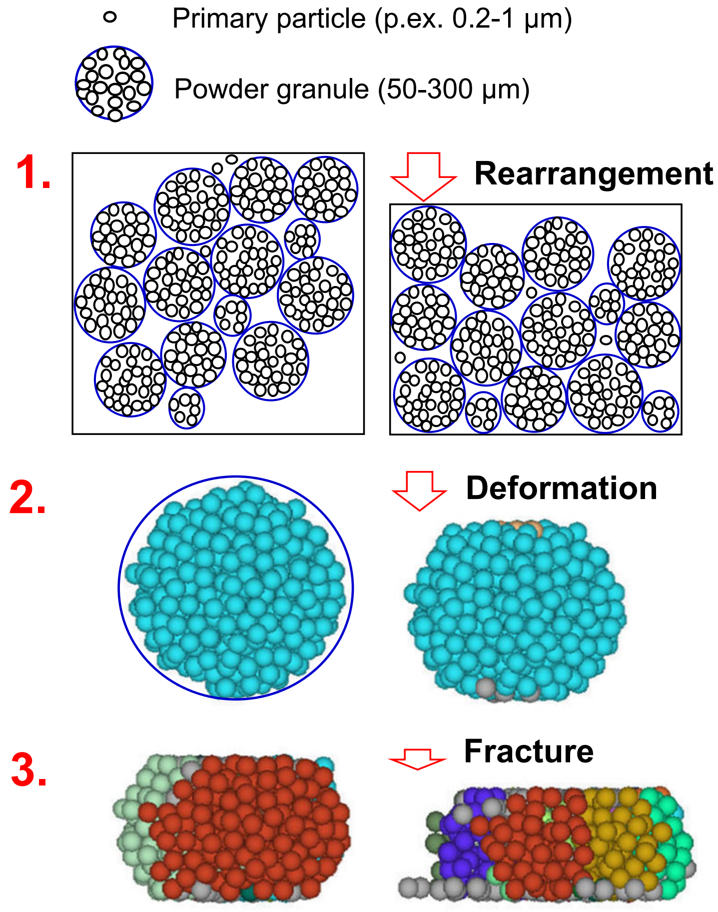
Insulators

#2_cold isostatic pressing

Medical implants

Dry pressing: Objectives and process stages

- **Dry pressing** (ideally) requires **granulated powder feedstocks** (e.g. flow to fill molds)
- Dry pressing aims at achieving green bodies that are:
  - **dense**
    - **Promote sintering** and **minimize shrinkage**
  - **homogeneous** and **defect free**
    - Prevents **distortions** during sintering
    - Prevents **microstructural flaws** and inhomogeneities
- Dry pressing is **influenced by** properties of:
  - **Primary particles** (morphology, shape, size distribution)
  - **Granules** (flowability, additives, density, size distribution, …)
- Dry pressing follows **3 stages:**
  1. Granule **rearrangement**
  2. Granule **deformation**
  3. Granule **fracture** and **densification**



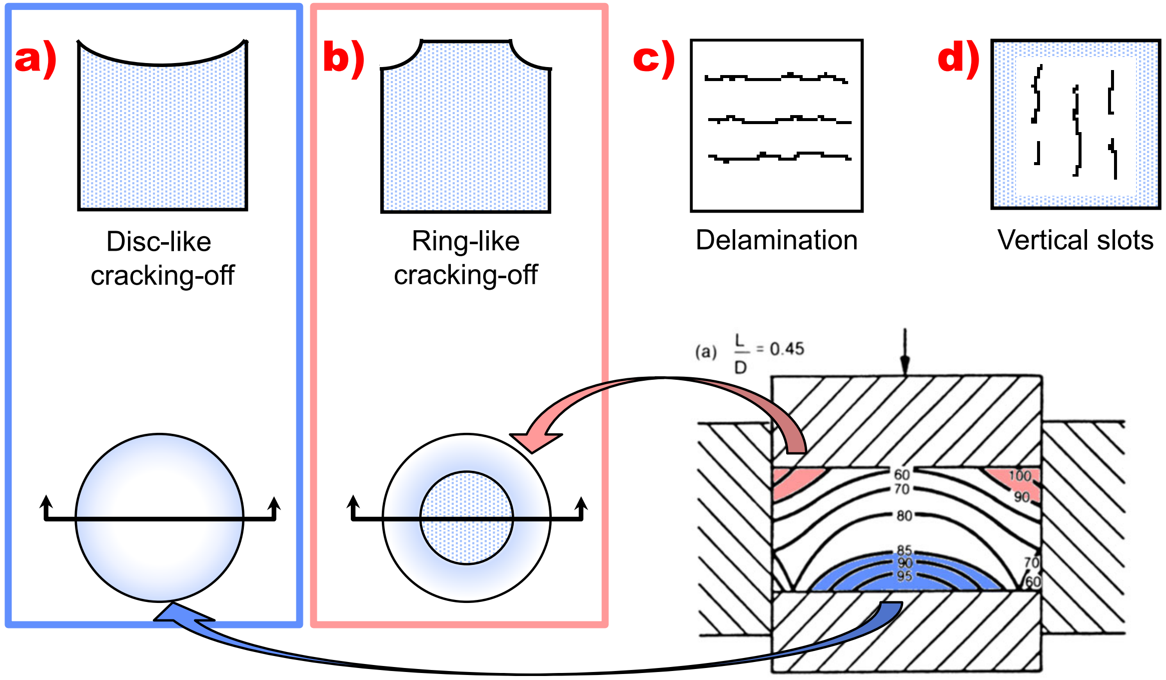
same color = same granule fragment
grey = primary particle detached from granule fragments

Source: https://doi.org/10.1208/s12249-017-0719-z

Dry pressing

Dry pressing: Defect occurrence during uniaxial pressing

Inappropriate pressing conditions (pressure, lubrication, tool adjustment) **and granule properties** may generate various types of part defects:



Uniaxial pressing
(here: single action = only 1 punch mobile)

Potential root causes by defect type:

- a) b): Excessive pressure, friction, bad tool adjustment
- c): Excessive pressure
- d): Granules' solid loading too small → compaction rate too high

Dry pressing: Density gradients

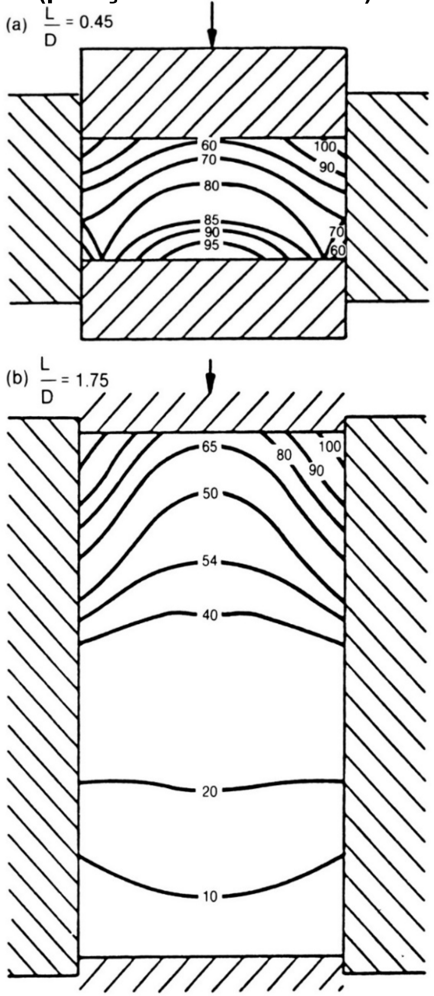
Density and internal energy gradients occur due **friction** between
- particles themselves (particle-particle interaction)
- particles and the mold (particle-mould interaction)

leading to **pressure drops**

Resulting gradients cause
- Part **deformations** or **failures** during part ejection or sintering
- Microstructural **inhomogeneities** due to non-uniform sintering

Corrective measures:
- Use of double-action mold → transmission de pression
- Addition of lubricants → oleic acid, stearic acid, …
- Isostatic pressing → reduces gradient substantially but slow and expensive

Pressage uniaxial simple (poinçon du haut mobile)



- WET SHAPING -

Shaping of suspensions

M. Stuer

Slip casting

Use:

- Large parts and/or parts with complex shapes
  (ex. sinks, cups, …)

Advantages:

- Green body density close to theoretical maximum
  (= stable suspensions, dense particles arrangement)
- Compatible with large and complex shapes

Limitations:

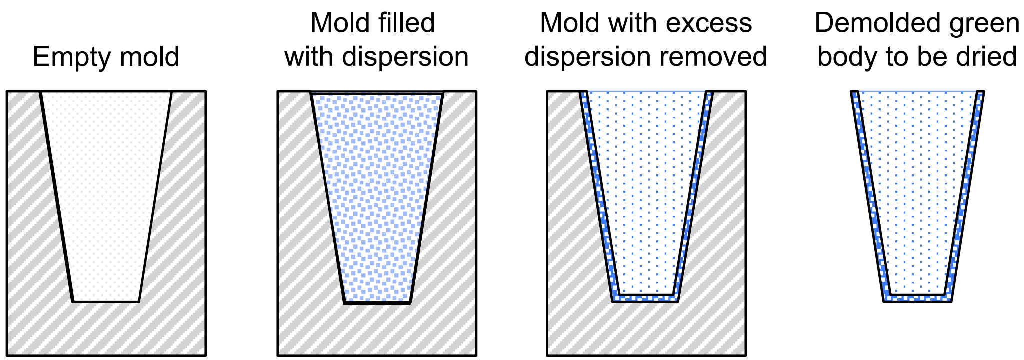
- **Wall thickness** limited to **~1 cm maximum**
- **Slow** process:
  - Slip casting time: Open: 80 minutes
    Pressure: 2 minutes
  - But **drying step**: **6 days**
- **Partially automatable**

Note: It takes 1 week of preparation to mix, homogenize and mill the dispersion!

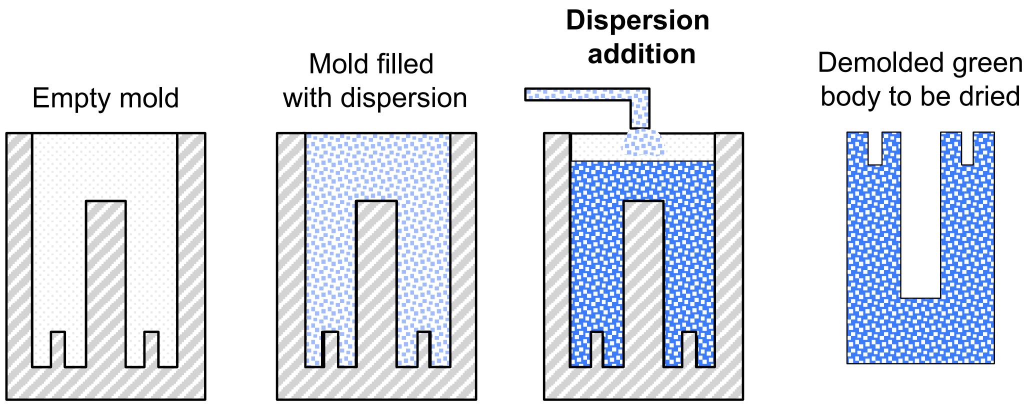
Watch Laufen factory visit:
https://www.designboom.com/design/laufen-factory-visit-ceramic-casting/

Illustration of the slip casting process

“open” or **“recessed”** slip casting



“between plasters” or **“plain”** slip casting



- **Principle:**
  - **Porous mold** absorbs water by capillary action
  - Ceramic particles carried by the water form a **dense layer on the mold**.
  - Layer follow Darcy’s law (next slide)
- **Variants:**
  - Open
  - Between plasters

Slip casting can be **accelerated by** adding **pressure** (e.g. pressure casting)

A specific variant of slip casting is filter pressing, replacing the plaster with a filter (next slide)

Watch: https://youtu.be/FZzOTX9Ihqs

Filter pressing

Advantages:

- Maximal green body density
- Possibility to seed texture at high flow rates (e.g. anisometric particles)

Limitations:

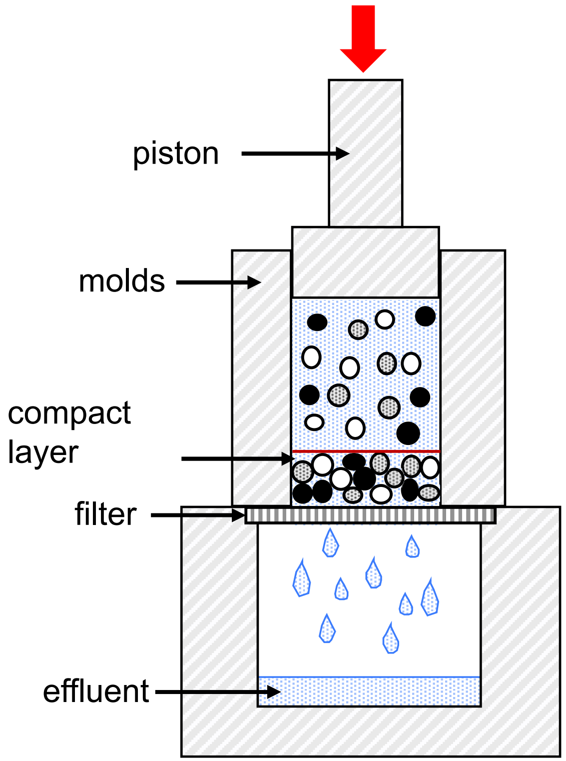
- **Part thickness** limited at **~1 cm maximum**
- **Simple part shapes** (2D+ like for uniaxial pressing)

Filtration kinetics:

- Follow a parabolic law derived from **Darcy's law** (also applicable to slip casting: pressure = capillary pressure and pressure casting: pressure = applied pressure)
- Compact layer thickness d can be expressed by:

$$d = \left[\frac{2K_pPt}{\eta}\left(\frac{\upsilon_1}{\upsilon_0} - 1\right)\right]^{\frac{1}{2}} \Rightarrow \mathbf{d} \propto \sqrt{\boldsymbol{t}}$$

- K_p : permeability of compact layer
- P : applied pressure
- t : time (since process start)
- η : viscosity of liquid (effluent)
- υ_1 : volume fraction of particles in compact layer
- υ_0 : volume fraction of particles in suspension/disperion



Tape casting

Use:

- Production of thick (10-1250 µm) ceramic tapes (typically large and flat)

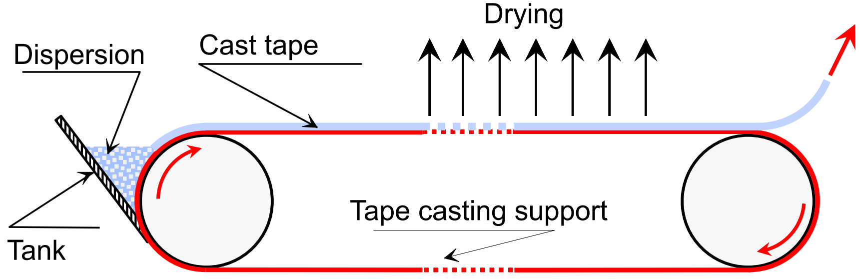
Advantages:

- High production **volume and speed** (automatable)
- Tape thickness control
- Possibility to generate **texture** with anisometric particles (e.g. shear stresses under doctor blade)
- Possibility to **cosinter tapes** of different materials (ex. electrodes and dielectric ceramics ➔ capacitors)

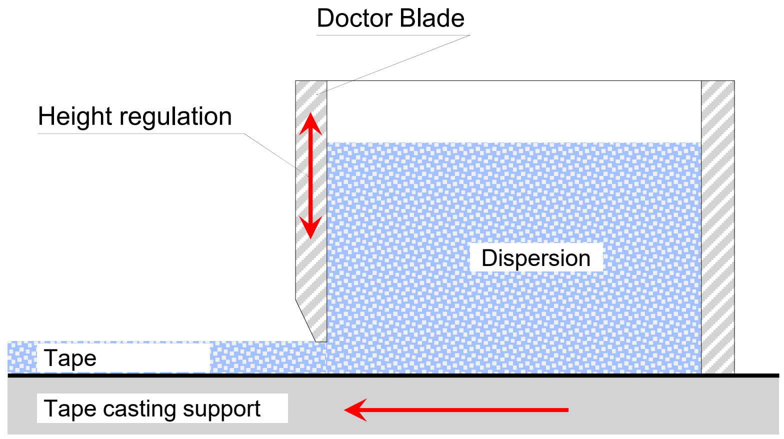
Limitations:

- Maximum film thickness is limited
- Typically uses (expensive) organic binders and solvents
- Careful debinding needed

Tape casting by **dragging**



Tape casting **by calendering or doctor blade**



Watch: https://youtu.be/JF9G8FaOb-s

- WET SHAPING -

Shaping of pastes

M. Stuer

Common plastic forming techniques

Extrusion

Use:

Shapes with 2D structures extruded from **aqueous or organic** pastes

Advantages:

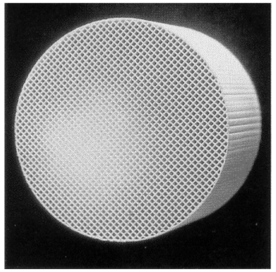
- **Continuous production**
- Production volume and speed
- Automatable

Limitations:

- Stretched 2D shapes only
- Equipment and tooling **costs**

Examples:

- Bricks
- Catalyst supports



Catalyst support for car

Jiggering

Use:

Relativement simple shapes from **aqueous** pastes

Advantages:

- Production volume **flexibility** (single parts to large volumes)

Limitations:

- Ideally shapes with circular symmetry
- Dimensional precision and tolerances

Examples:

- Tableware
- Artisanal potteries

Tableware

Injection

Use:

Rather small precision parts with complex shapes from **organic** pastes

Advantages:

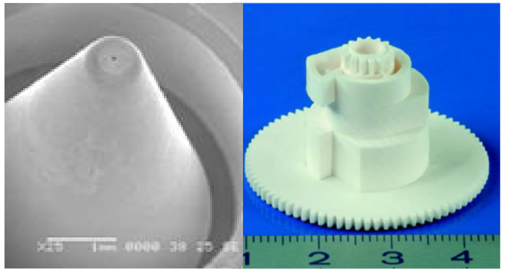
- Production volume and speed
- Automatable
- Precision and tolerances

Limitations:

- Equipment and tooling **costs**
- Careful debinding

Examples:

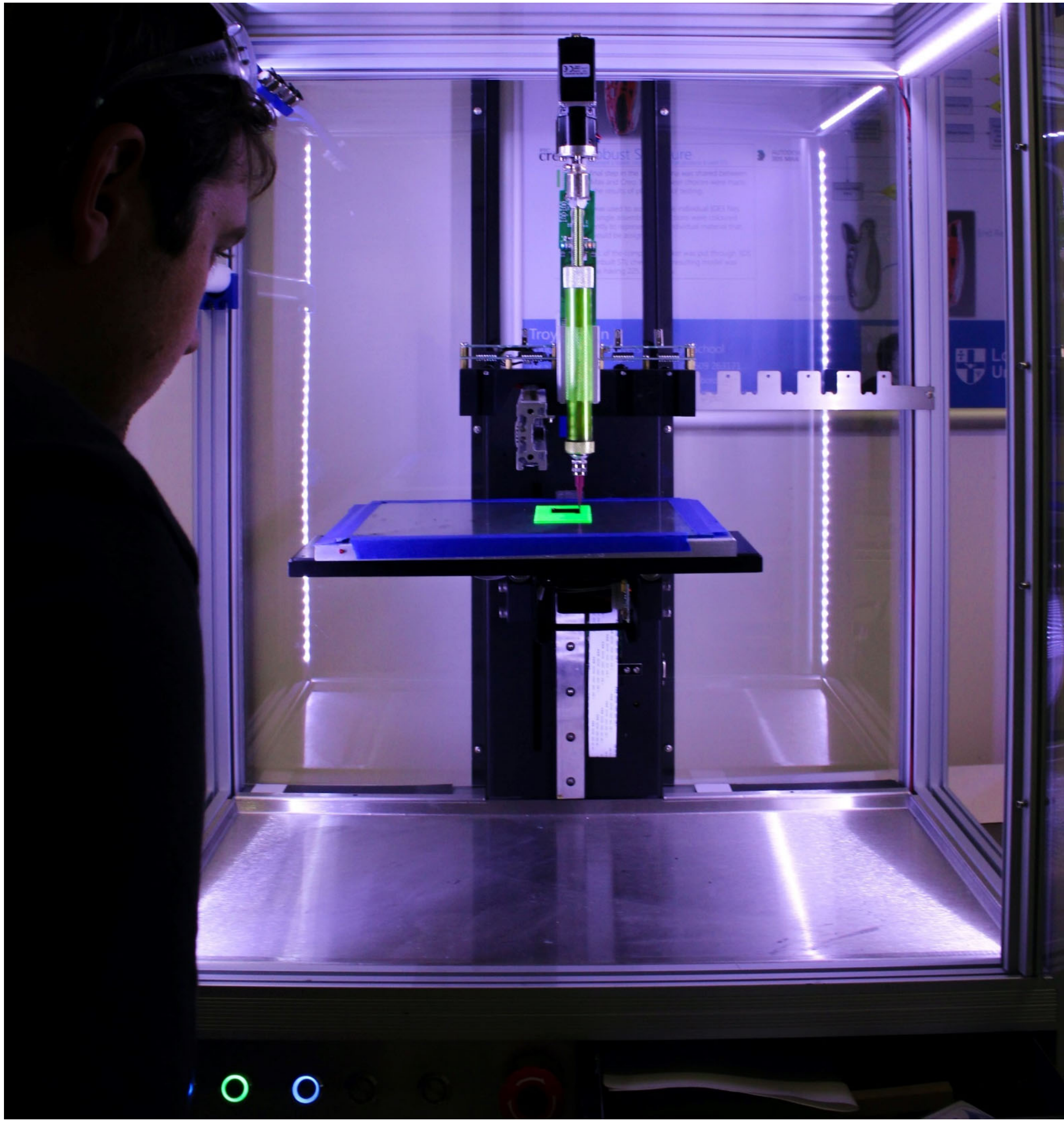
- Nozzles
- Gears



Nozzle and gear
Source: SPT-Group

Additive manufacturing

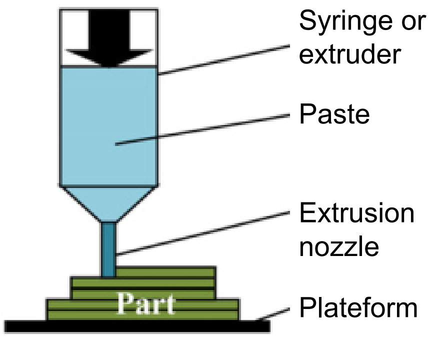
M. Stuer



Selection of additive manufacturing techniques

Direct ink writing (DIW)

Paste extruded continuously through a cylindrical nozzle



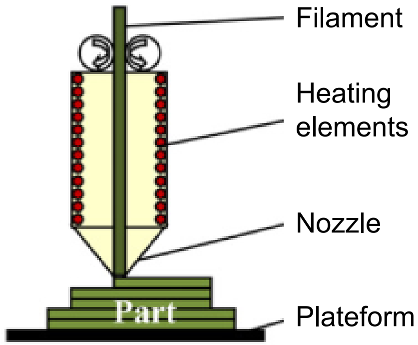
Characteristics:

- Resolution and speed depend on the nozzle and rheological properties of the paste
- Delicate drying required
- Fast debinding due to low organic additives content

Watch: https://youtu.be/N1LF14QhNyY

Fused deposition modelling (FDM)

Deposition of a thermoplastic wire filled with ceramic powder



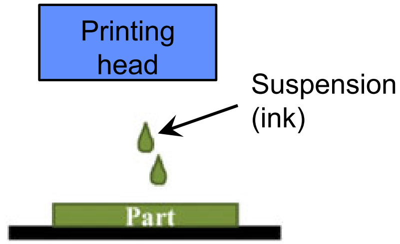
Characteristics:

- Resolution depends on nozzle and rheological properties of thermoplastic composite filament
- Delicate debinding required
- Fast building speed compared to other 3D techniques

Watch: https://youtu.be/GxLjDNrQBgs

Direct inkjet printing (DIP)

Inkjet printing of a particle loaded ink (i.e. suspension)



Characteristics:

- Colloidal suspensions only
- Layer thicknesses and therefore manufacturing speeds are very low
- Mainly used in microelectronics and micromechanics

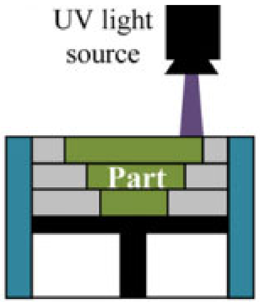
Watch: https://youtu.be/0ba7KkUV-GA

source: https://doi.org/10.1111/jace.14705

Selection of additive manufacturing techniques

Stereolithography (SLA/DLP)

Photo-polymerization of a photosensitive powder slurry



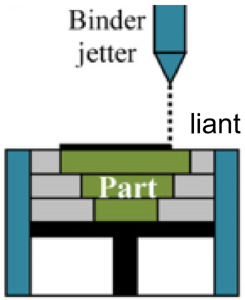
Characteristics:

- Homogeneous layers require highly stable dispersions
- Dispersions with compatible viscosity and high solid loadings preferred
- Difficult with powders that absorb light

Watch: https://youtu.be/NM55ct5KwiI

Powder-based 3D Printing (3DP)

Deposition/printing of an organic binder on a powder bed



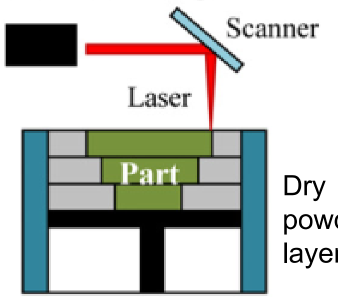
Characteristics:

- Compatible with powders or granules that do not easily form aerosols
- Avoids typically need of support structures
- Resolution depends on particle size and binder diffusion

Watch: https://youtu.be/4Bftt_4DQKE

Selective laser sintering (SLS)

Densification of a powder bed by laser sintering or laser fusion



Characteristics:

- Difficult due to thermal shock sensitivity of ceramics
- Controlled laser-material coupling required
- Easier with glass / glass-ceramics with low glass transition temperature

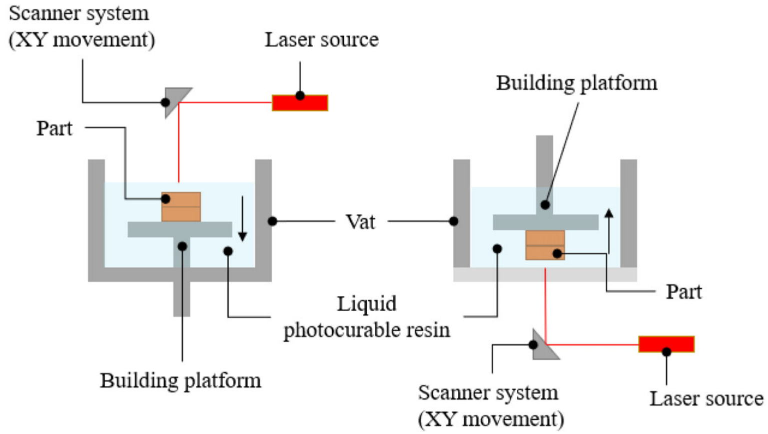
source: https://doi.org/10.1111/jace.14705

Stereolithography based techniques

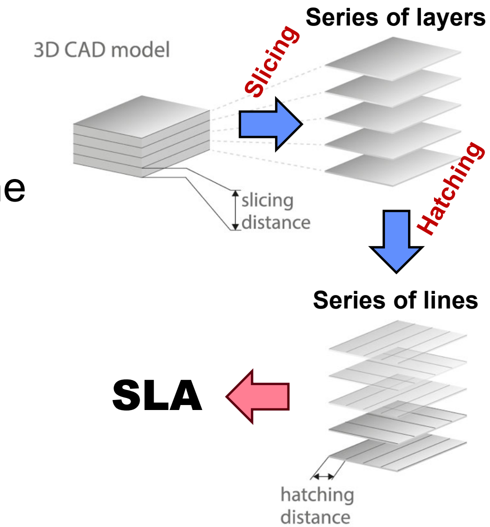
Techniques can be distinguished based on:

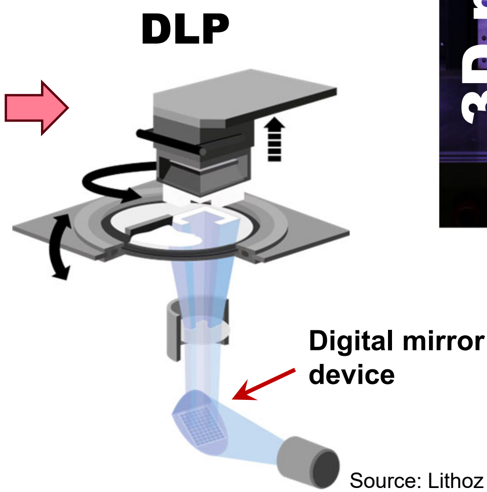
- **Built-direction**
  - **Top-down:** The part is descending and immersed in the photocurable slurry
    - ***Pros:*** *No peeling forces*
    - ***Cons:*** *Slurry volume*
  - **Bottom-up:** The part is ascending and pulled-out of the slurry
    - ***Pros:*** *Uses less slurry, multi-material*
    - ***Cons:*** *Peeling forces/deformation*

- **Light exposure strategy**
  - **Vector scanning:** Vector-by-vector scanning of the resin surface by a single-point laser with a galvanoscanner.
    ➔ slicing + hatching
  - **Projection:** Use of a digital mirror device to project the layer onto the resin
    ➔ slicing



Source: 10.3390/app12073591



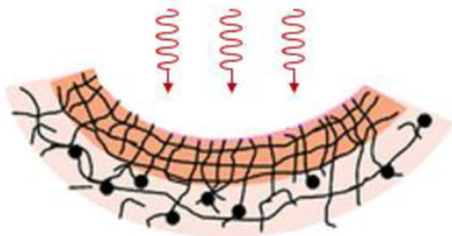


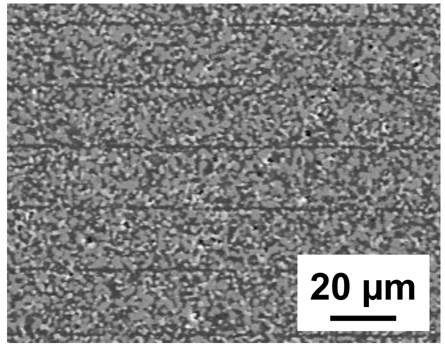
Source: Lithoz

Slurry formulation for stereolithographic printing is delicate

- Formulations depend on the ceramic material powder properties as well as the AM system requirements
- They typically contain:
  - Monomers
    - Low viscosity
    - High polymerization shrinkage (c.f. internal stresses ➔ deformation/delamination risk)
  - Oligomers
    - High viscosity
    - Low polymerization shrinkage
    - Strengthening of green body
  - Dispersants
    - Powder dispersion stabilization
  - Photoinitiators(/Sensitizers)
    - Initiate local photopolymerization
  - Photoinhibitors/dyes
    - Confine photopolymerization reaction
    - Increase printing resolution
  - Non-reactive diluents
    - Reduce slurry viscosity
    - Facilitate debinding
- Weakly **flocculated suspensions** are preferred to **prevent powder setting** between layers (see right image).

Polymerization shrinkage induced distortion





source: 10.3390/app12073591

SLA/DLP related metrics

- The cure depth (C_d) is given by:

$$C_d = D_p \ln\left(\frac{E}{E_c}\right)$$

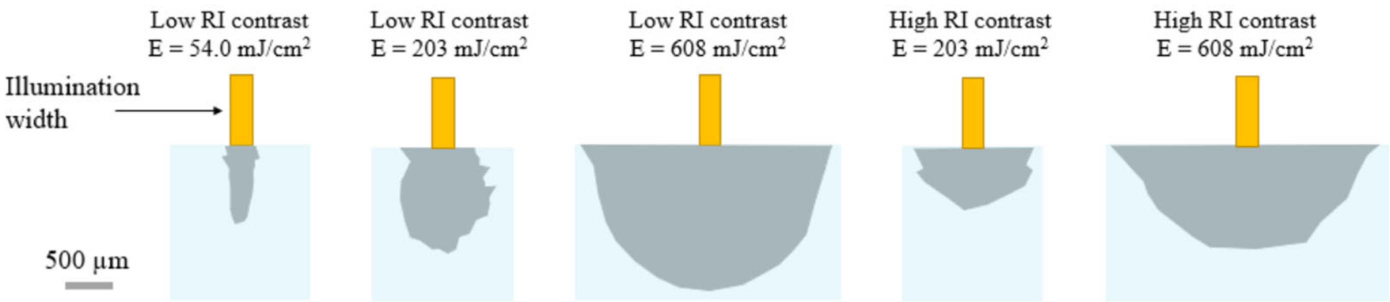
  - E: applied energy dose
  - E_c: critical energy dose for gelation
  - D_p: attenuation length

- For a given particle size and distribution

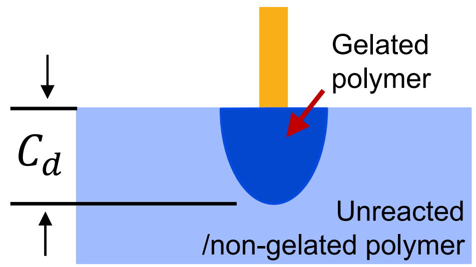
$$C_d \propto \frac{1}{(\Delta n)^2}$$

  - Δn: refractive index (RI) contrast between powder and resin

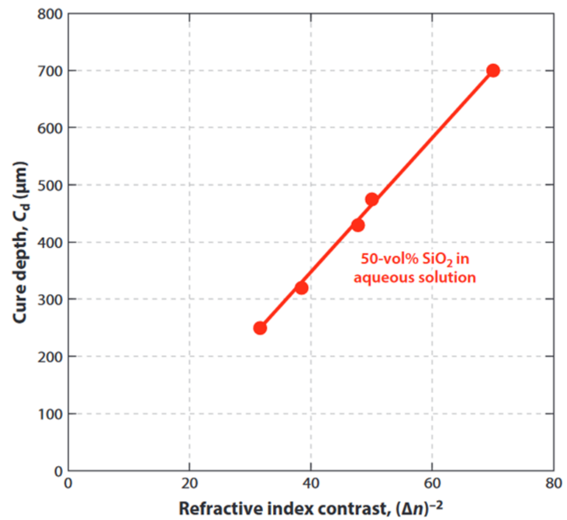
- Refractive index contrast and applied energy dose affect gelation volume



Cure depth illustration



Cure depth vs RI contrast

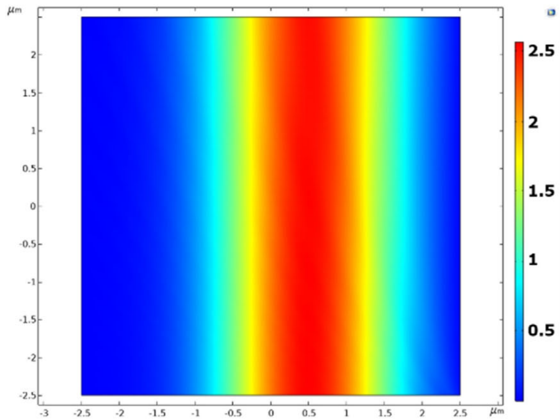


source: 10.1146/annurev-matsci-070115-031841

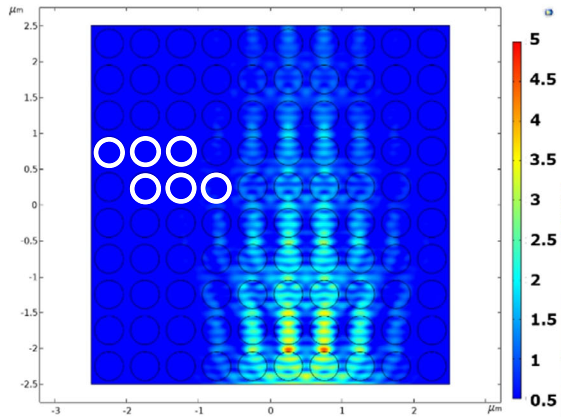
Light scattering due to particle size/distribution

- In concentrated powder suspensions, Rayleigh-Gans or Mie scattering approaches are not applicable
- Light scattering depends on particle arrangement, size and distribution

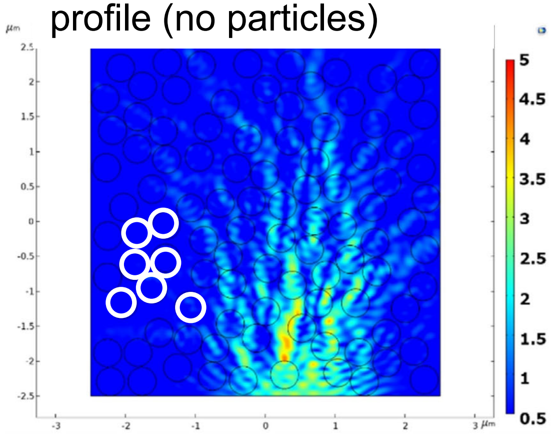
➔ **Fine tuning** of the energy dose, photoinitator and photoinhibitor concentration needed **for each powder**



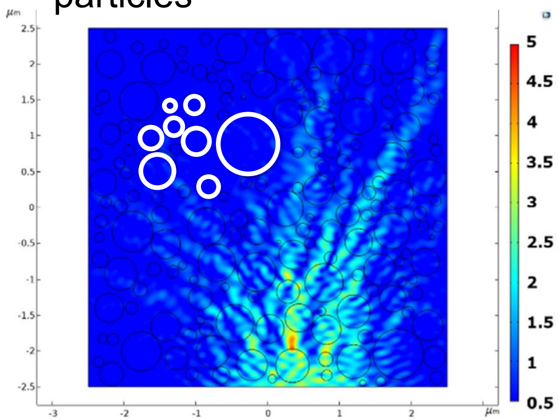
Gaussian beam intensity profile (no particles)



Array of monodisperse particles



Disordered monodisperse particles



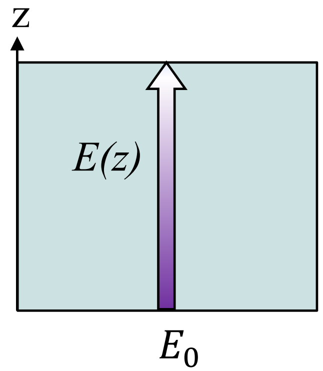
Disordered particles with gaussian size distribution

Subsurface energy dose at z-depth

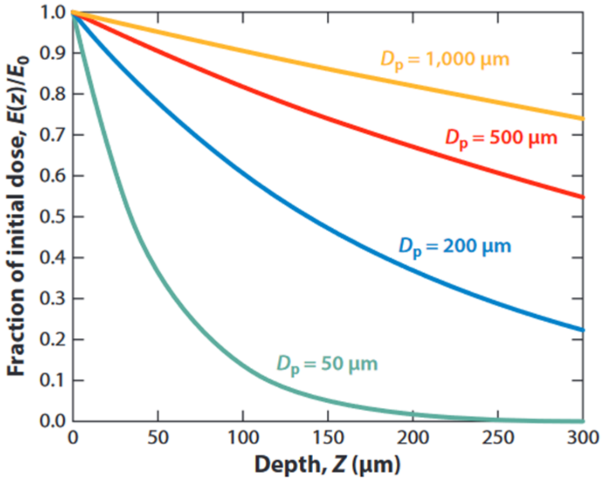
- The energy dose $E(z)$ at position z from the surface can be approximated following a Lambert-Beer law:

$$E(z) = E_0 \exp\left(\frac{-z}{D_p}\right)$$

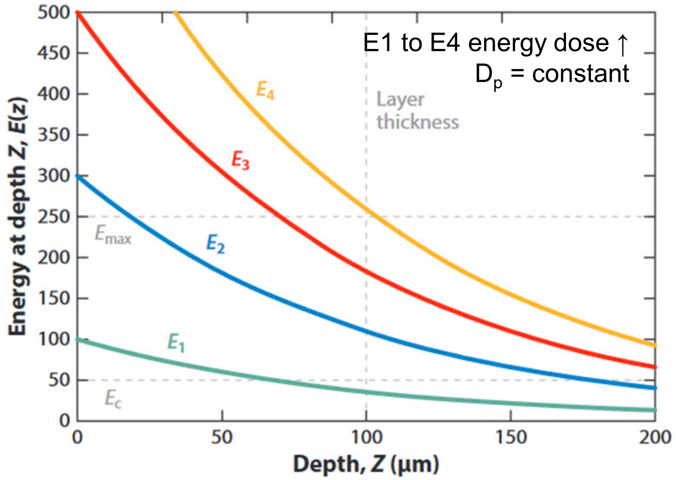
- To ensure optimal layer curing the energy dose and or layer thickness have to be adjusted depending on D_p



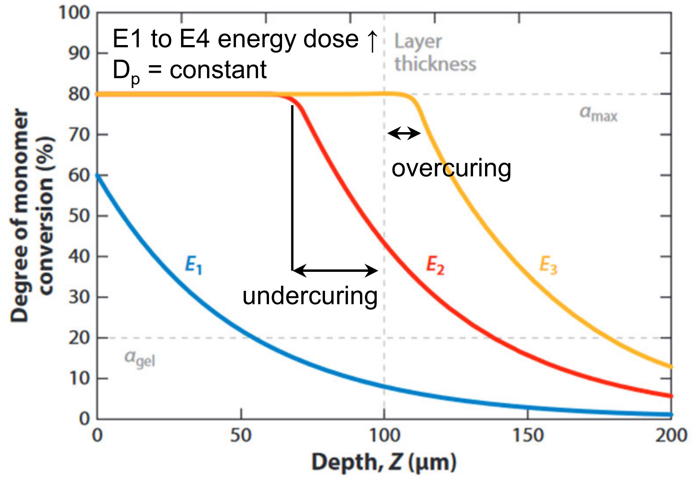
Normalized energy versus depth



Energy profile



Mono-/Oligomer conversion profile



E_{max}: Energy dose to reach max conversion rate α_{max}
Ec: Energy dose for gelation

source: 10.1146/annurev-matsci-070115-031841

Pre-sintering parts conditioning:

Drying

M. Stuer

Green body drying

- **Drying** is a delicate and **slow** process after wet part shaping, since associated **shrinkage** may lead to part **cracking**!
- **Level of shrinkage** depends on:
  - **Shaping method**
  - **Solid loading** of the suspensions (=volume of powder in a suspension)
  - **Examples:**
    - **Slip casting:**
      ➔ linear shrinkage **between 1.5 and 7%**
    - **Tape casting or sol-gel:**
      ➔ linear shrinkage **between 50 and 90%**
- Note that invisible defects in a wet tablet may lead to part failure during drying.

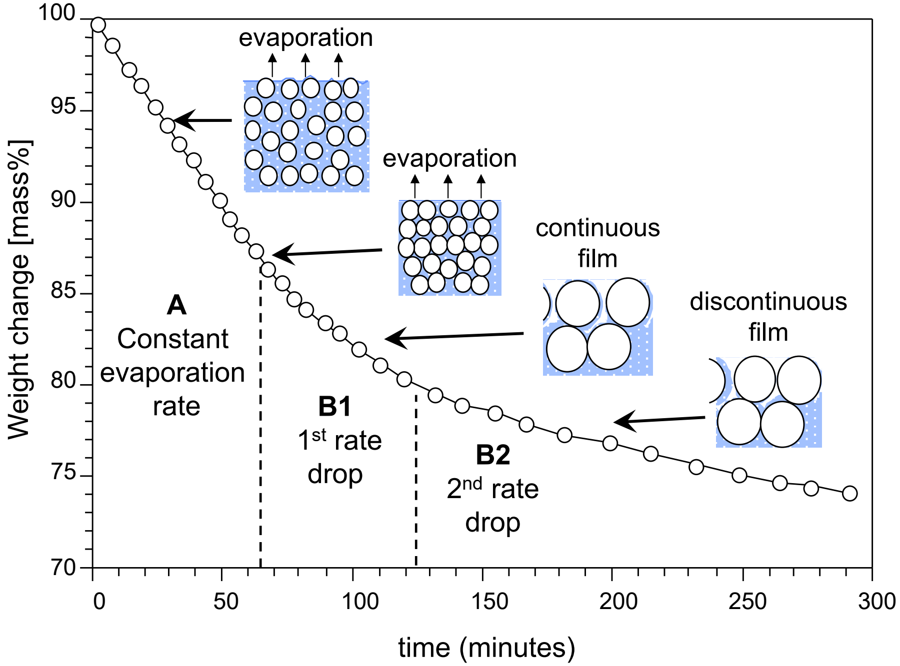
Example slip casting

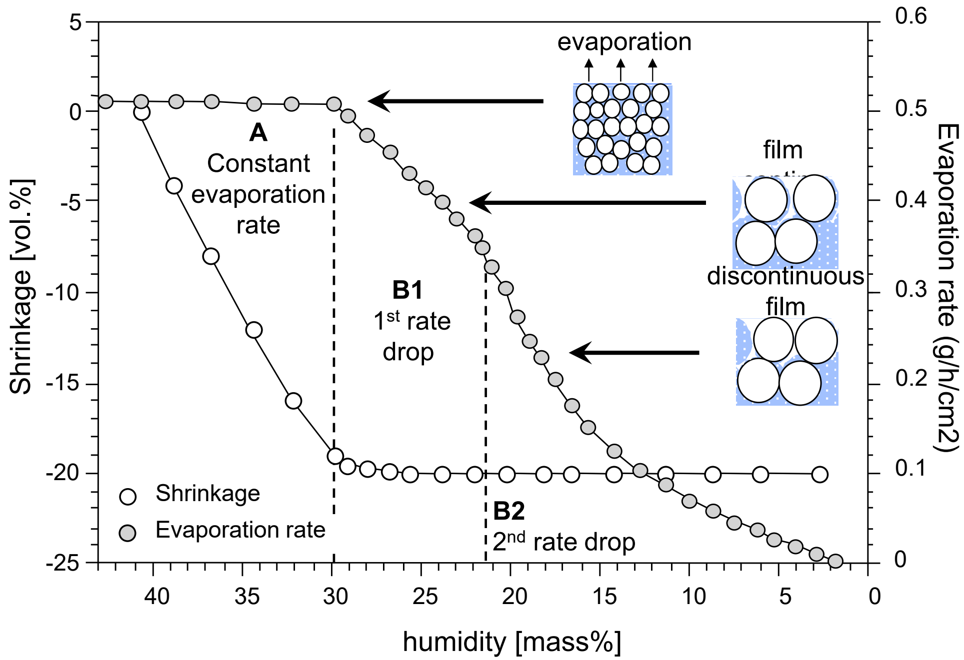
- **Shaping:**
  - without pressure ➔ **80 mins**
  - with pressure ➔ **2 mins!!**
- **Drying:**
  - Maximum wall thickness 1 cm
    ➔ **6 days!!!!!**

Drying stages and graphical representations

A: Constant evaporation rate phase

- Pores saturated with liquid and **evaporation** takes place directly at the **surface**
- **Surface tension** of liquid **compresses** part
  ➔ particles rearrange and move closer
  ➔ **drying shrinkage** nearly complete at end of this stage

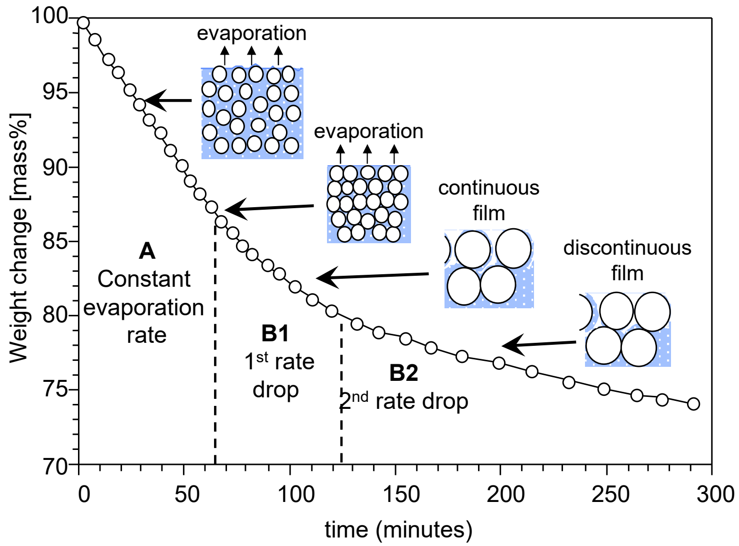


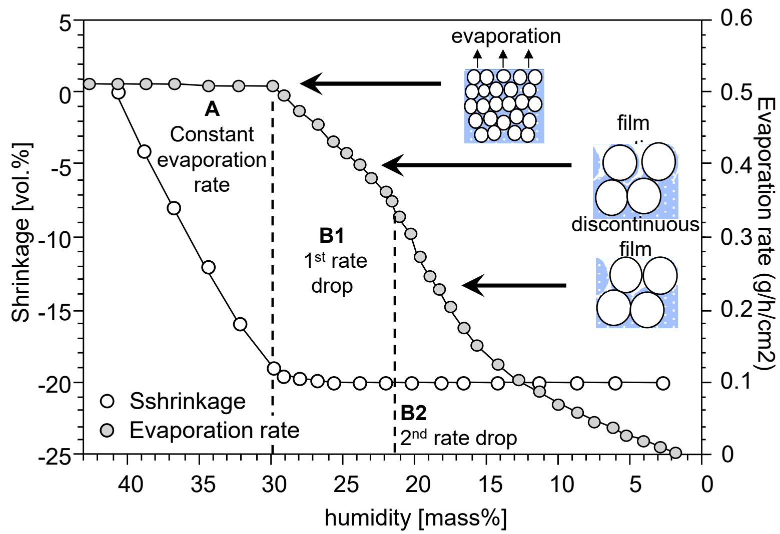


Drying stages and graphical representations

B: Decreasing evaporation rate phase

- **Transition** from stage A to B when **liquid-gas interface moves into the pore network**. The dry area is no longer under compression ➔ **cracking may occur !**
- Distinction made between decreasing evap. rate phase with:
  - **Continuous film**
    ➔ liquid is transported by **capillarity** to the surface of the part where it evaporates
  - **Discontinuous film**
    ➔ liquid evaporates within the part and vapor diffuses through pore network ➔ reduced drying rate





Mechanisms leading to part failure during drying

- **Cracking** occurs due to **capillary pressures** in the pore network within the green body
- Local capillary pressures P_c vary following:

$$P_c = \frac{-2\gamma_{lv} \cos\theta}{r}$$

- γ_{lv}: surface tension (liq/vap)
- θ : wetting angle (l/v)
- r : (cylindric) pore radius

If r **changes** locally, the **pressure changes** locally as well

It follows that:

- **Inhomogeneous particle packing** leads to a inhomogeneous porosity
  - ➔ Resulting **pressure gradients** lead to differential shrinkage and thus **internal stresses**
  - ➔ Associated **inhomogeneous permeability** (e.g. fluid dynamics) further amplify the internal stresses (see next slide)

Mécanisme provoquant la fissuration pendant le séchage

- **Internal stresses** also depend on the **liquid transport dynamics** in the pore network, and thus on the **evaporation rate.**

- Empirically, the drying stresses σ follow a type law:

$$\sigma \propto \frac{L\eta_l V_e \gamma_{lv}}{3K_p}$$

- L: characteristic part dimension
- η_l: viscosity of liquid
- V_e: evaporation rate
- K_p :permeability of pore network
- γ_{lv}:surface tension(liq/vap)

It is necessary to ensure **even drying** and reduce de **surface tension** and/or dry **slowly**

EPFL

Pre-sintering parts conditioning:

Debinding

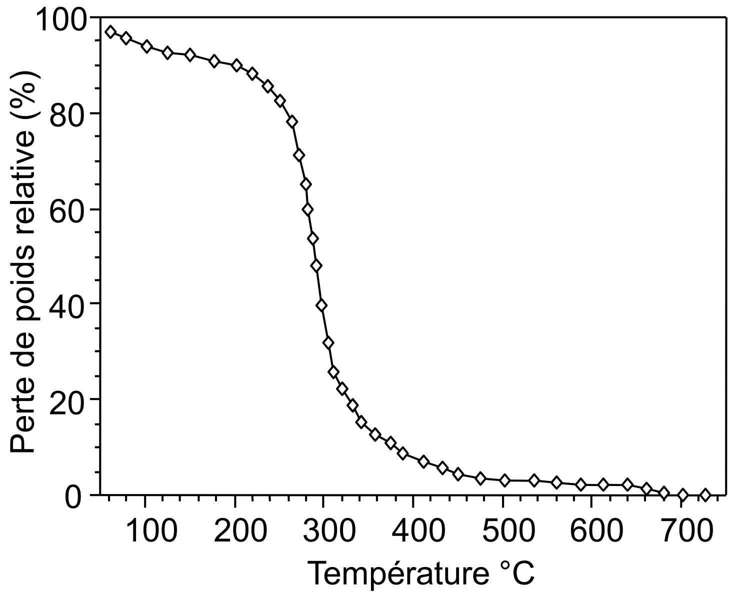
M. Stuer

General aspects related to debinding

Organic additives have to be **removed before sintering** to prevent part cracking and/or carbonaceous residues during sintering

- Most widespread method is thermal **decomposition and pyrolysis in air** with dwells at different temperature ranging from 300-600°C.
  (slow heating rates (0.25-1°/min), temperature profiles established from thermogravimetric analysis (TGA))
- **Mecanisms:**
  - Evaporation
  - Oxydation
  - Decomposition
- **Cross-linking of organics** (e.g. oxygen deficiency, heating rate too fast, …) must be avoided as it can result in **carbon residues** (e.g. graphite-like) that are difficult to remove.
- Upon **incomplete organics removal**, rapid gas formation during sintering may lead to part **swelling and even cracking**.

Typical debinding TGA curve



Estimation of thermal debinding temperatures

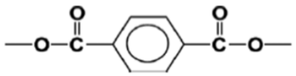
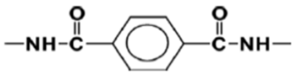
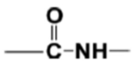
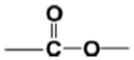
Average decomposition temperature (T_d) of polymers based on their **chemical structure**

- **Assumptions:**
  - Numerical value $(Y_{d,i})$ assigned to each chemical group in binder molecule
  - For repeating units (e.g. polymers) account only once for repeating chemical structure

- **Decomposition temp. estimation:**

$$T_d = \left(\sum_i N_i Y_{d,i}\right) / \sum_i M_i$$

  - $Y_{d,i}$: Contribution of i^th group to the decomposition temperature of the binder
  - N_i: Amount of i^th group in the binder
  - M_i: Molecular weight of i^th group in the binder

Group	Source (e.g.)	Y_d (K · kg/mol)
$-CH_2-$	Ethylene	9.5
$-CH(CH_3)-$	Propylene	18.5
$-CH(C_6H_5)-$	Styrene	60
$-CH(COOCH_3)-$	methyl acrylate	56.5
$-CH(OCOCH_3)$	vinyl acetate	42.5
$-C(CH_3)(COOCH_3)$	methyl methacrylate	37.5
-CHF-	vinyl fluoride	18
-CHCl-	vinyl chloride	23.5
-CH(CN)-	Acrylonitrile	28
-CH(OH)-	vinyl alcohol	14
$-CF_2-$	tetrafluoroethylene	38.5
-CH=CH-	Neoprene	18
	Phenyl	64
	aromatic polyester	119
	aromatic polyamide	135
-O-	Oxide	8
-S-	Sulfide	33
-NH-	Amine	16
>C=O	Ketone	20
	Amide	22.5
	Ester	33.5

Source: https://doi.org/10.1080/10426914.2011.560233

CASE STUDY:

Shaping process development

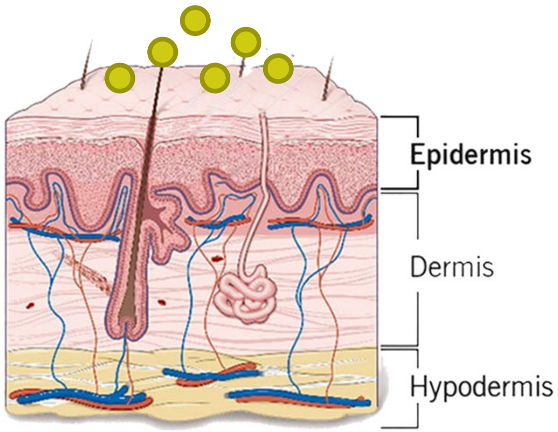
M. Stuer

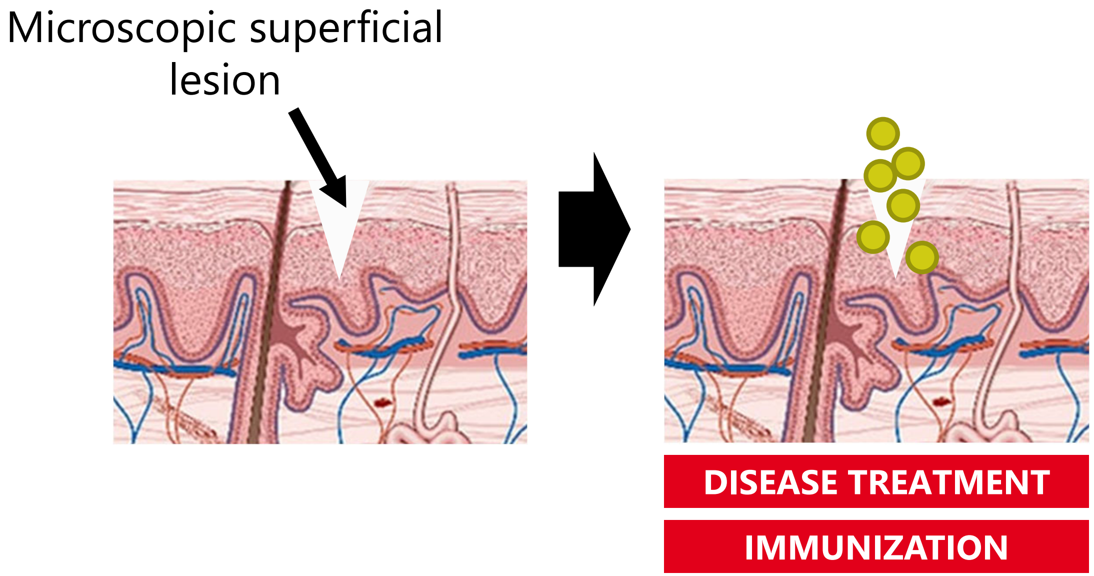
25/03/2025

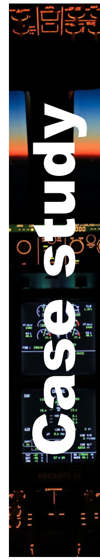
Background and motivation

Background and motivation: Skin barrier

- **Stratum corneum barrier** layer prevents permeation of large drugs







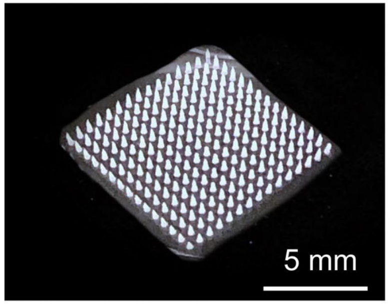
- **Microscopic lesions required** for local skin delivery of drugs and vaccines

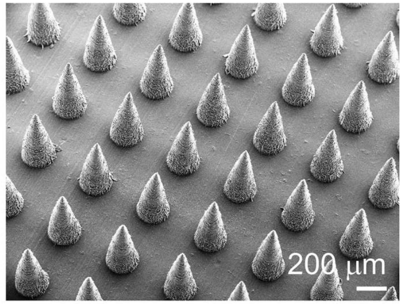
Background and motivation: Microlesion creation

- **Microneedle patches** exist but limited to treatment of
  - **Small** areas
  - Areas with **good accessibility**

➔ Ceramic **STAR particles** developed to overcome those issues

- For large scale application **reliable** and **economical** fabrication approach needed





Credit: NC State University

nature medicine

LETTERS

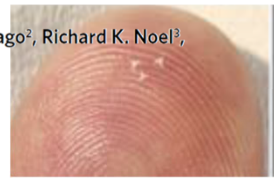
https://doi.org/10.1038/s41591-020-0787-6

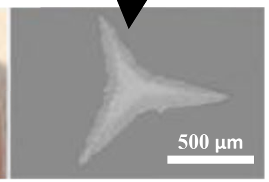
Check for updates

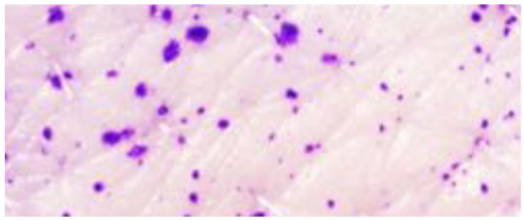
STAR particles for enhanced topical drug and vaccine delivery

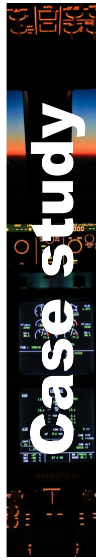
Andrew R. Tadros[1], Andrey Romanyuk[1], Ian C. Miller[2], Andrea Santiago[2], Richard K. Noel[3], Laura O'Farrell[3], Gabriel A. Kwong[2] and Mark R. Prausnitz[1,2]

Laser machined! $$$







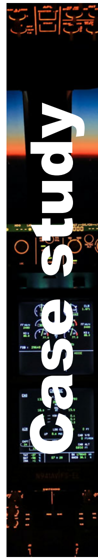


Background and motivation: Some key figures

QUANTITY — **16'600 STARS** — in 1 gram of shaped material → **Short process times**

COSTS — **100+ TIMES** — Cost reduction vs laser cutting required → **Simple batch process**

SCALING — **1000+ Kg** — Rapid scale increase from g to kg → **Easy scalability**



- Background and motivation
- **Functional analysis and fabrication strategy**
- Mold fabrication
- Slurry formulation and casting
- Demolding, debinding and sintering

Functional analysis and fabrication strategy

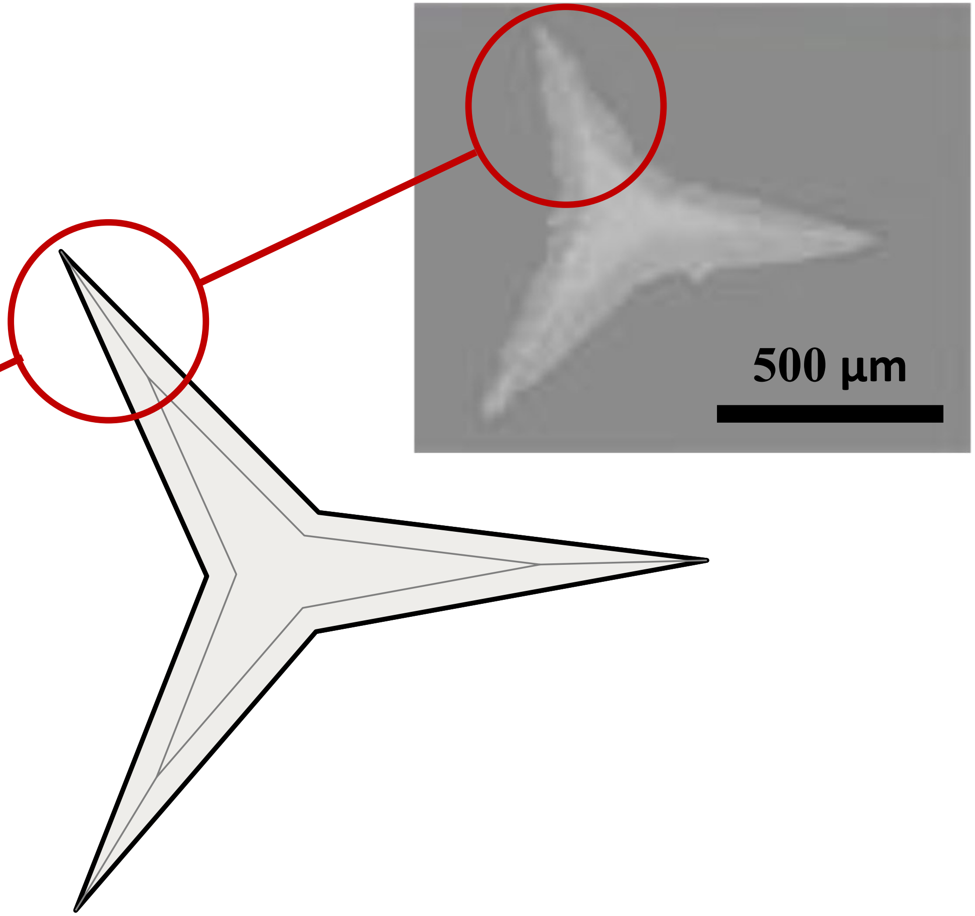
M. Stuer

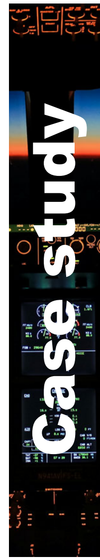
25/03/2025

Functional analysis

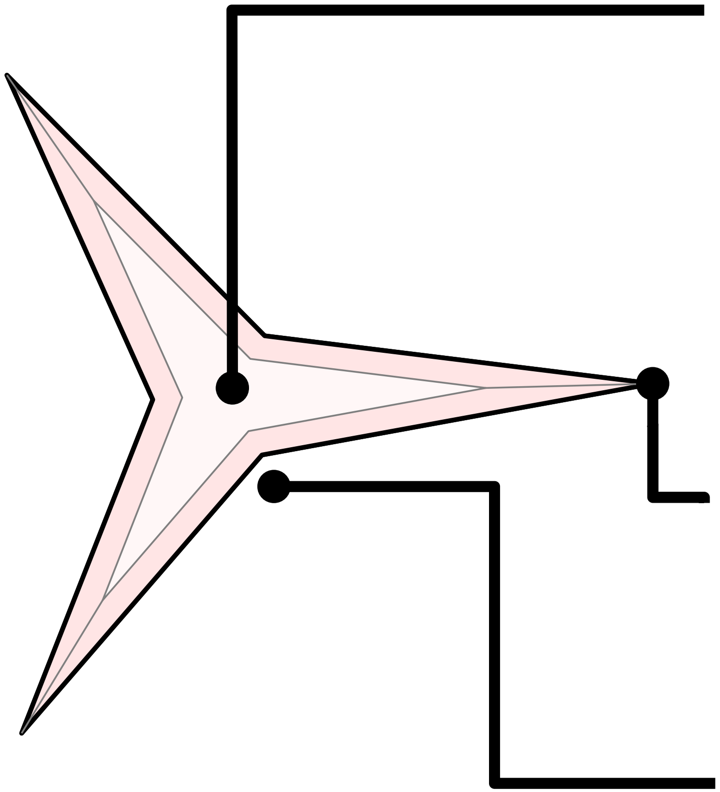
- **Critical part features**
  - Material
  - Arm length
  - Tip radius
  - Part thickness
  - **Tapering of the tip**
    - **Effect from CO_2 laser cutting**
      - ➔ **Mean surface curvature**

➔ **3D shaping problem !**

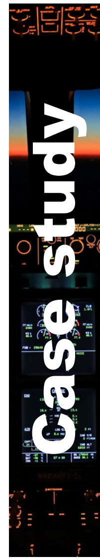




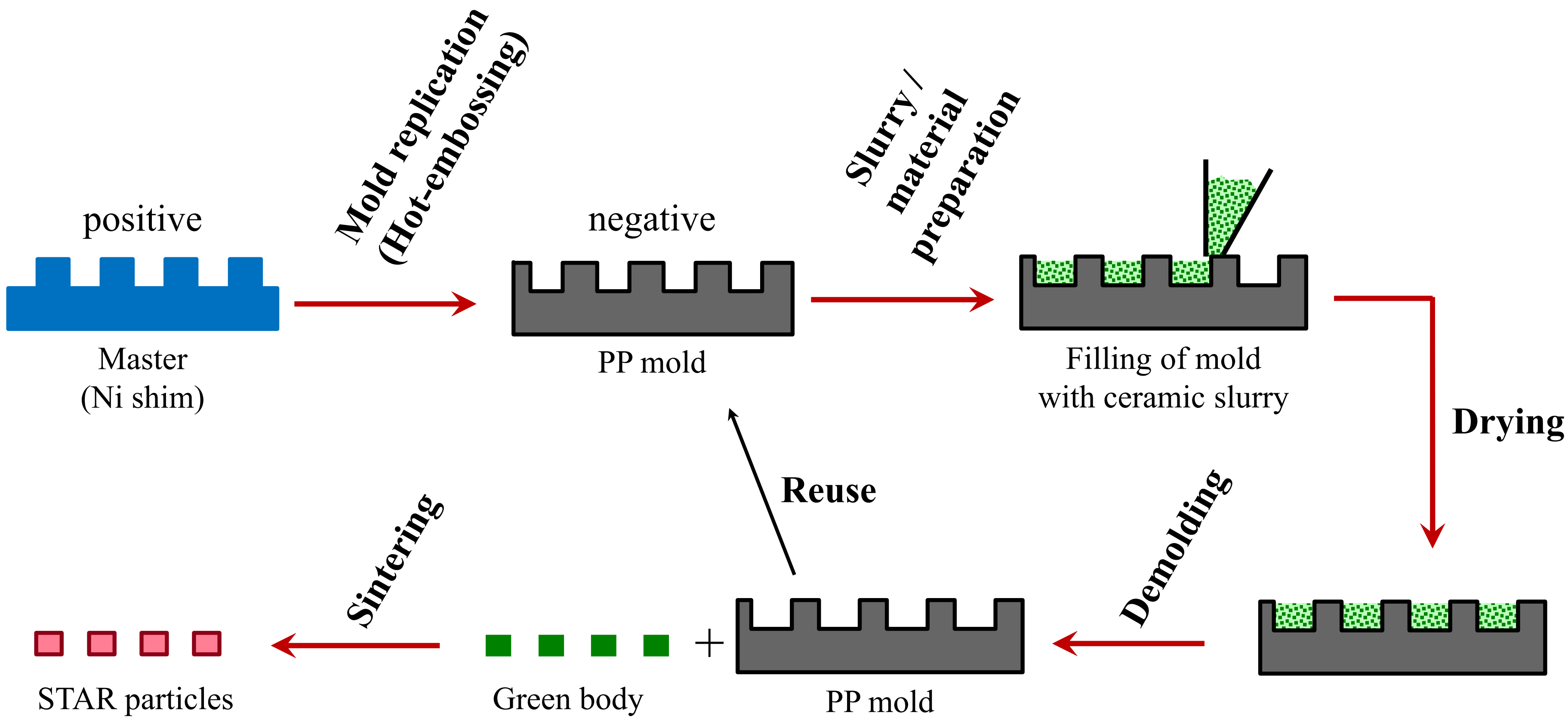
Functional analysis and fabrication strategy

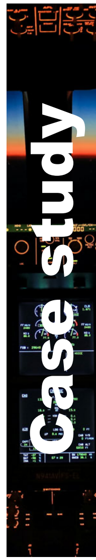


- **Material**
  - Alumina-based
  - Biocompatible / non-allergenic
  - No failure risk during use (e.g. no debris in skin)
  - ➔ **Aim for zirconia toughened alumina**
- **Tip diameter**
  - The sharper (XY and XZ) the better
  - ➔ **Aim for diameter <10 µm**
- **No stress concentration zones**
  - ➔ **No sharp corners**

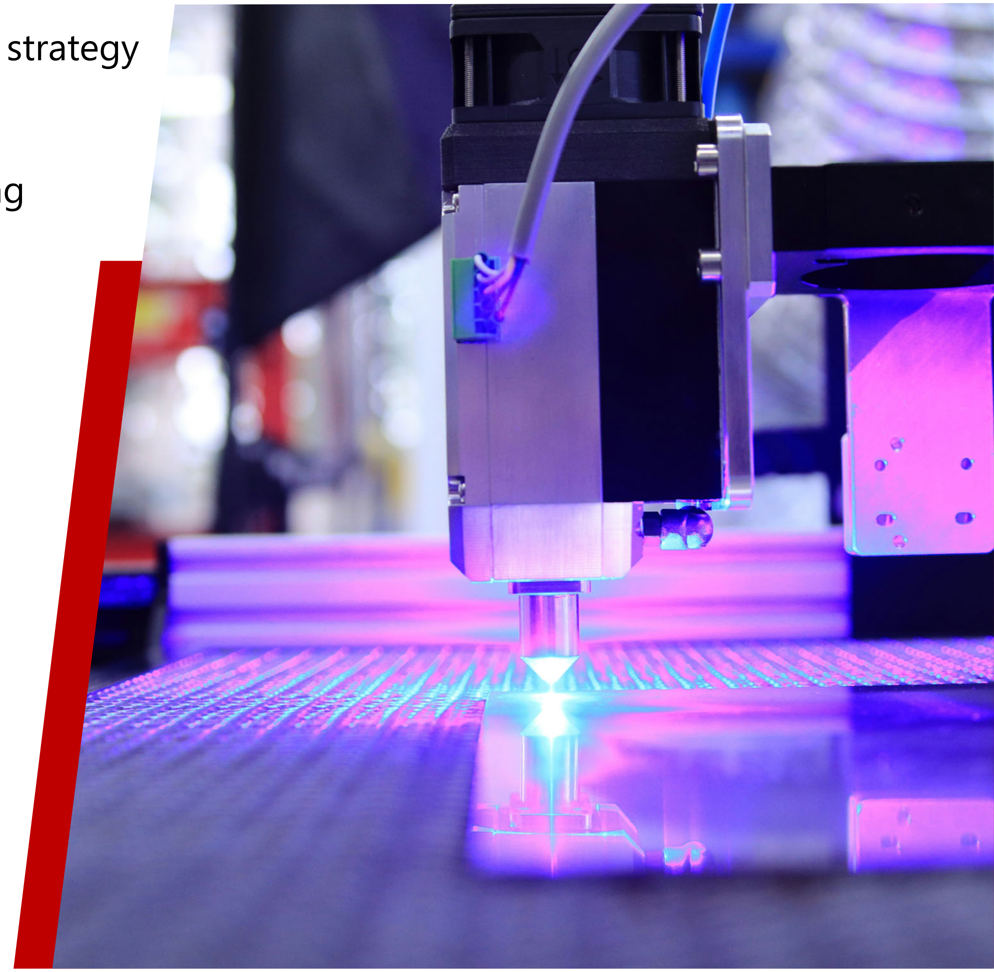


Selected fabrication strategy (simplified)





- Background and motivation
- Functional analysis and fabrication strategy
- **Mold fabrication**
- Slurry formulation and casting
- Demolding, debinding and sintering



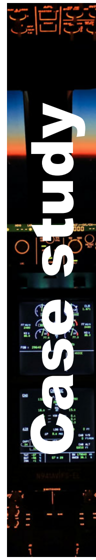
Mold manufacturing

M. Stuer

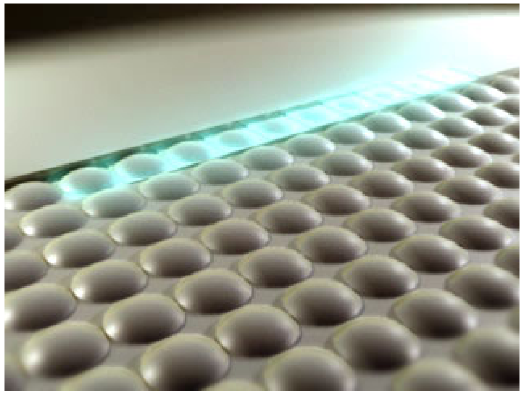
25/03/2025

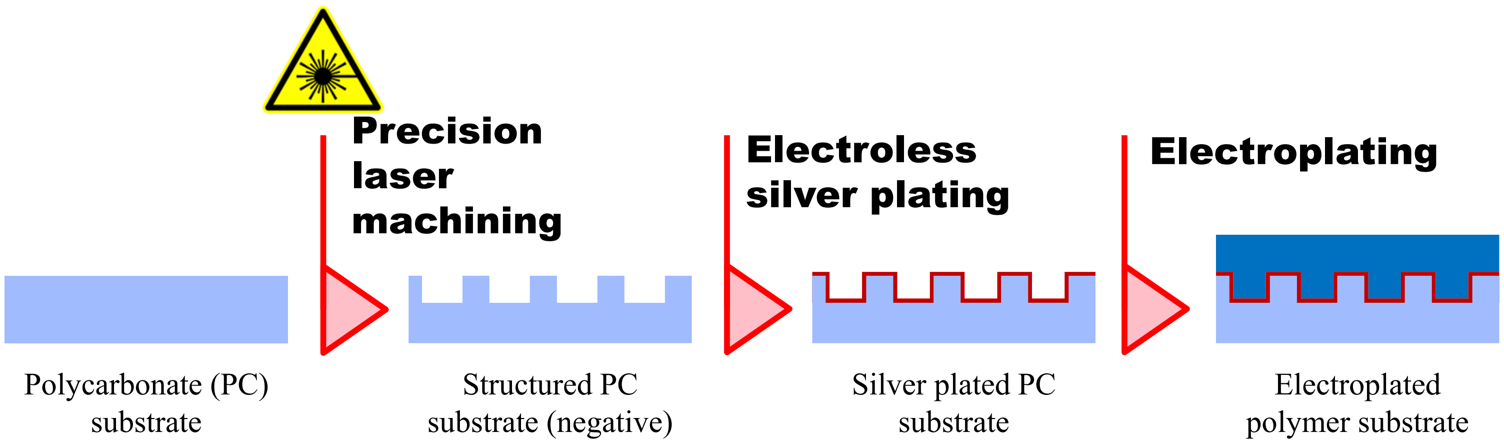
2-step mold fabrication process (mass replication compatible):

1. **Nickel shim:** Laser machining + electroplating (**cost intensive**)
2. **PP mold:** Hot embossing with Nickel shim (**low cost**)



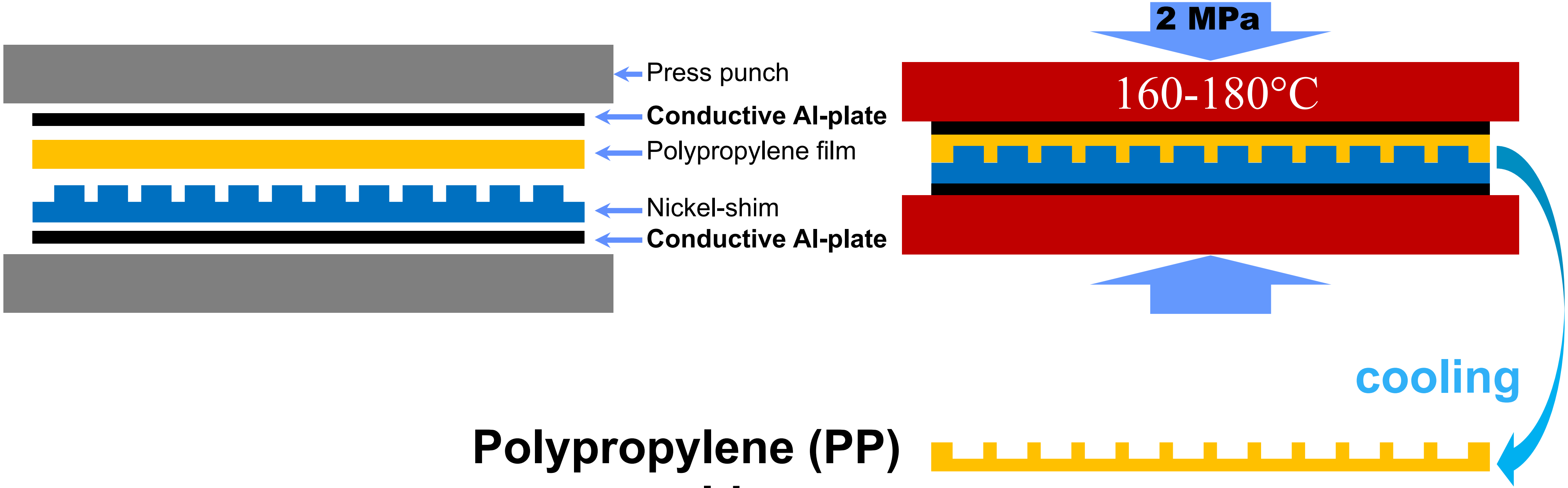
1. Nickel shim fabrication



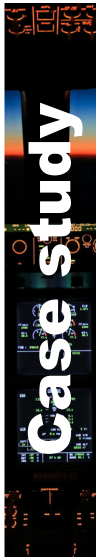


2. Hot embossing process

Temperature and pressure on:
- Polymer film material
- Imprint area/motif



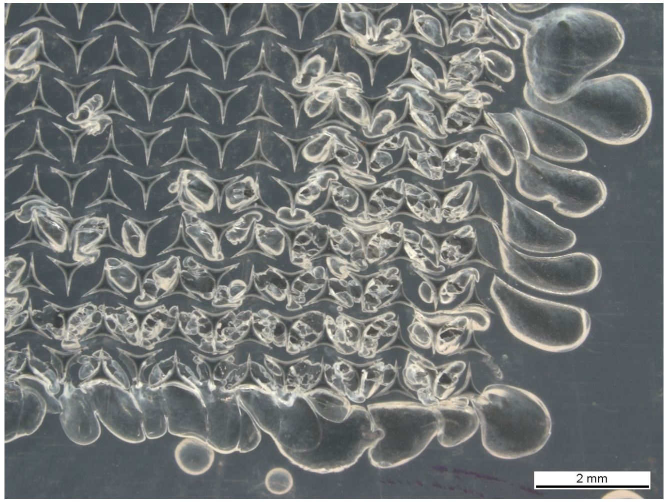
Polypropylene (PP) mold

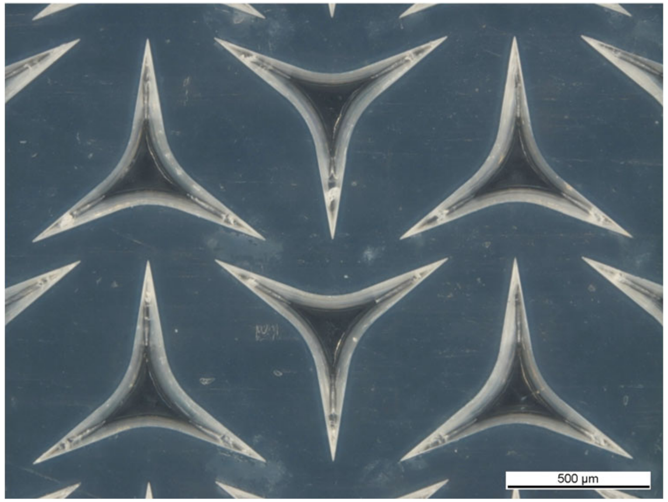


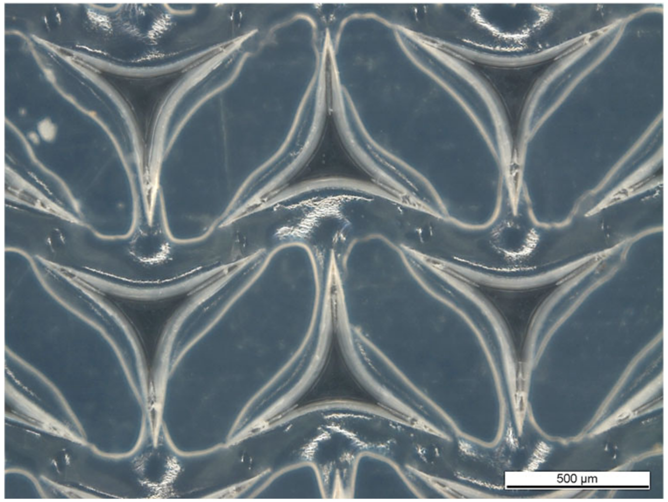
Effect of temperature and pressure

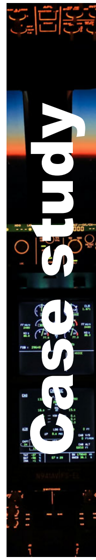
Mold artefacts

Bubbles and flaws | **Rounded edges**









Unstable temperature / Temperature too high

Pressure too low

- Background and motivation
- Functional analysis and fabrication strategy
- Mold fabrication
- **Slurry formulation and casting**
- Demolding, debinding and sintering

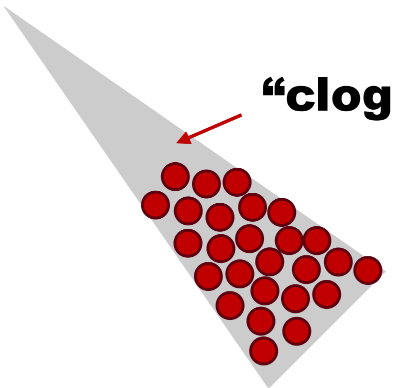
Slurry formulation and casting

M. Stuer

25/03/2025

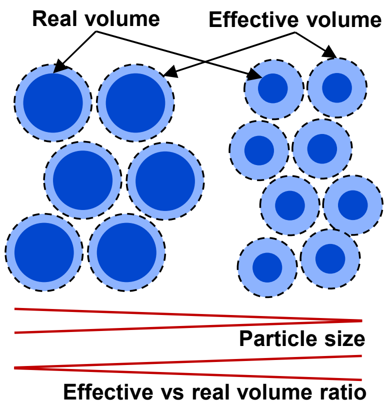
Target

1 Reliable tip filling



- **Clogging prevention**
  - ➔ Particle size (D_{v50}) ~6-8x lower than target tip radius
  - ➔ **D_{v50} < 0.38 µm** (for 3 µm)

2 Low shrinkage and high GB strength



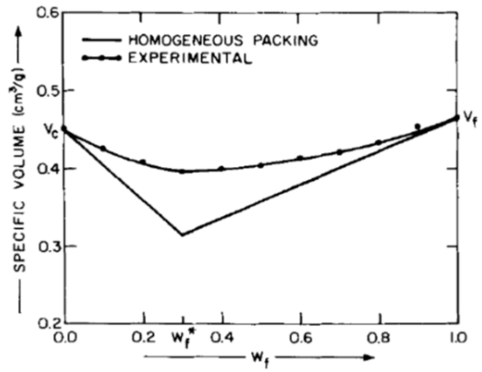


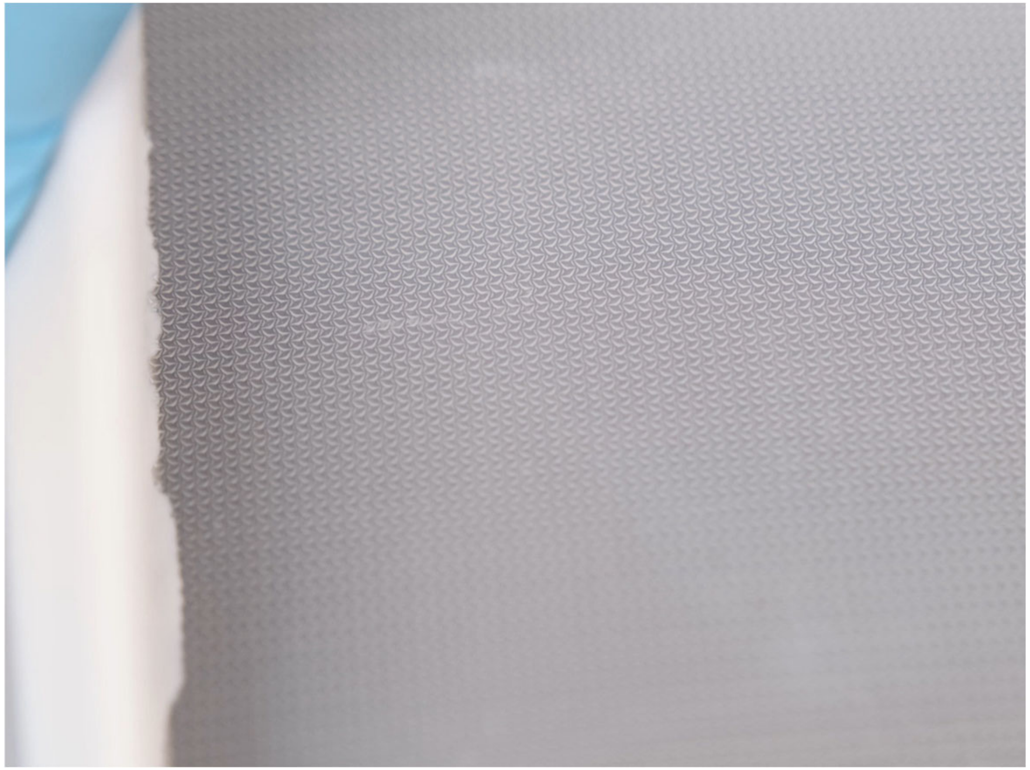
Fig. 1. Theoretical and experimental packing results for binary mixtures compacted at 207 MPa.

Smith, J. P. and G. L. Messing (1984).
doi: 10.1111/j.1151-2916.1984.tb18838.x

- **High solid loading**
  - ➔ Bimodal particle size distribution to preserve flowability

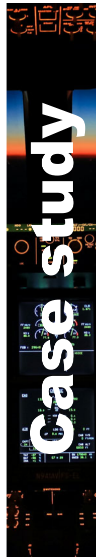
Case study

Casting requirements



Reliable casting requires:

- Full mold **filling**
  a. **Contact angle**
- **Defect-free** drying
  b. **Solid loading & drying stress**
- Good green body **strength**
  c. **Interparticle forces and/or binders**



Materials & dispersant concentration

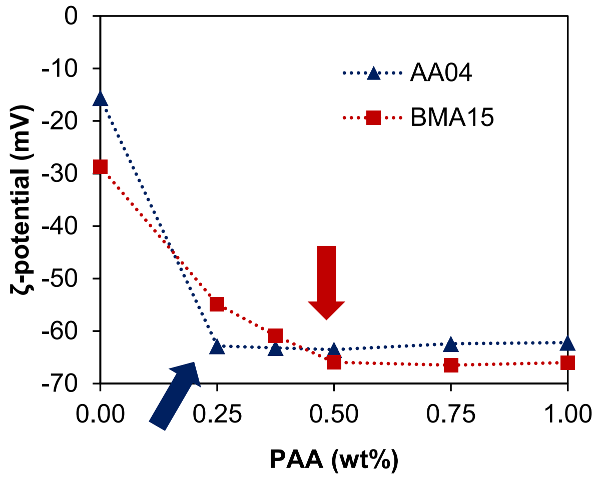
Raw materials

- Inorganic binder
- Microstructure refiner (Zener pinning)
- Material toughener

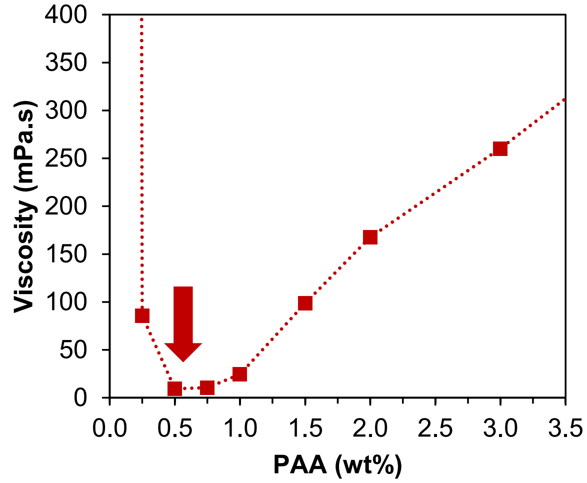
	AA04	BMA15	ZrO_2 sol
D_{v50} [nm]	450	120	10
Span	**1.77**	**1.33**	**-**
S_{BET} [m^2/g]	**4.4**	**14.6**	**180**

- Dispersant: PAA M_w=2000

Titration with PAA (R1.5) @ pH 10

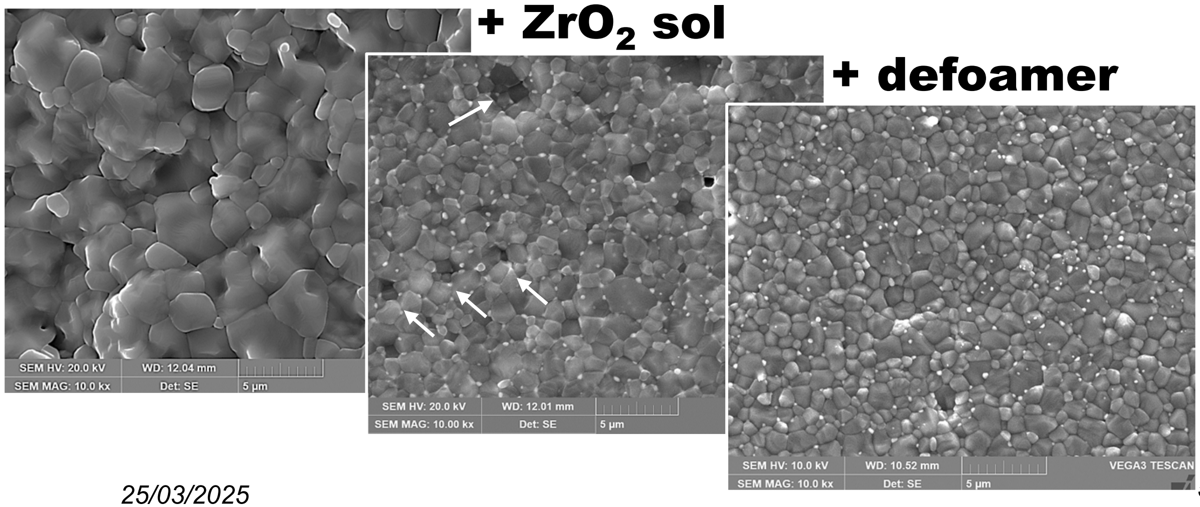


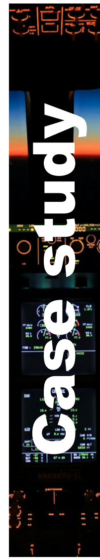
Viscosity @ 100 s^{-1} for 30 vol.% BMA15



Slurry preparation

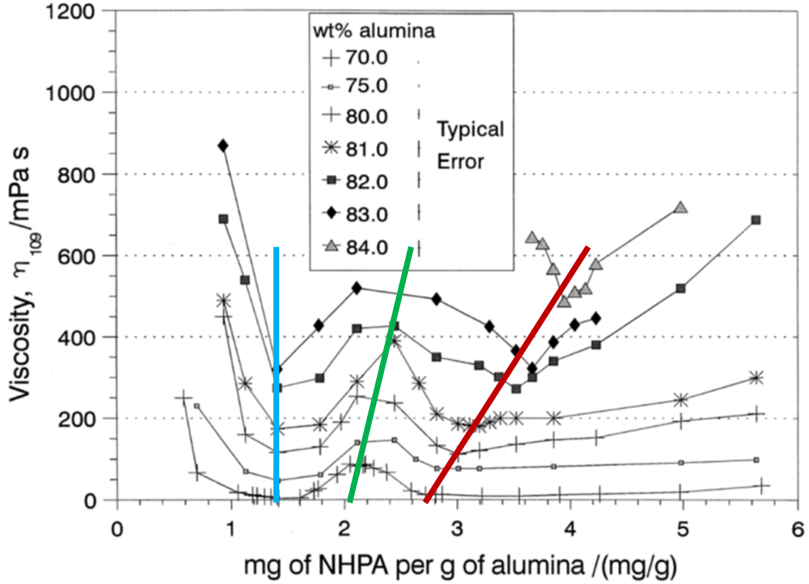
- Ball milling
- Homogenization (>30 hrs) on rolling bench (see next slide)
- Defoamer addition
- Degazing

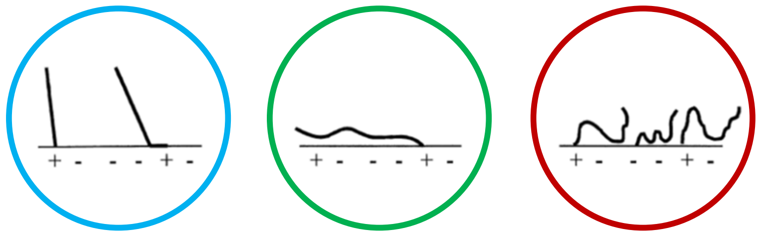




Concentration/time effect on PAA configuration

Concentration dependent configuration

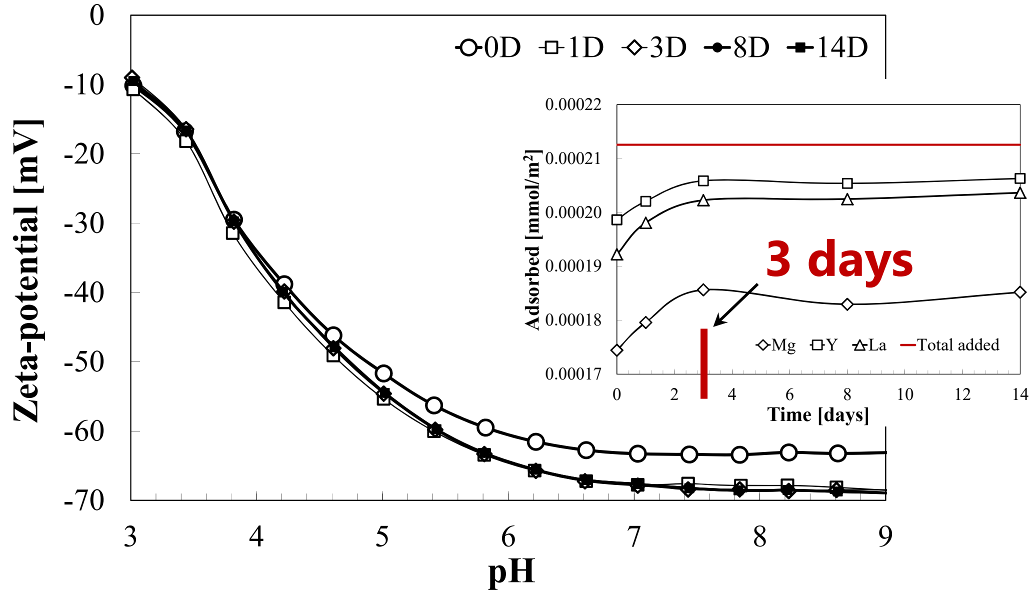




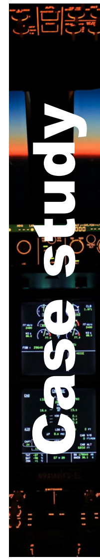
1st min | max | 2nd min

Davies, J. and J. G. P. Binner (2000). doi: 10.1016/S0955-2219(00)00012-1

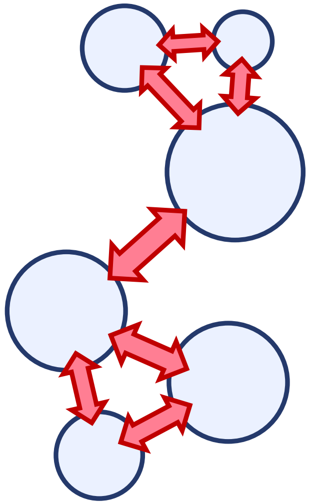
Time dependent configuration



Speciation reactions may take **up to 3 days to reach steady state**



Interparticle potential and solid loading effect on yield stress

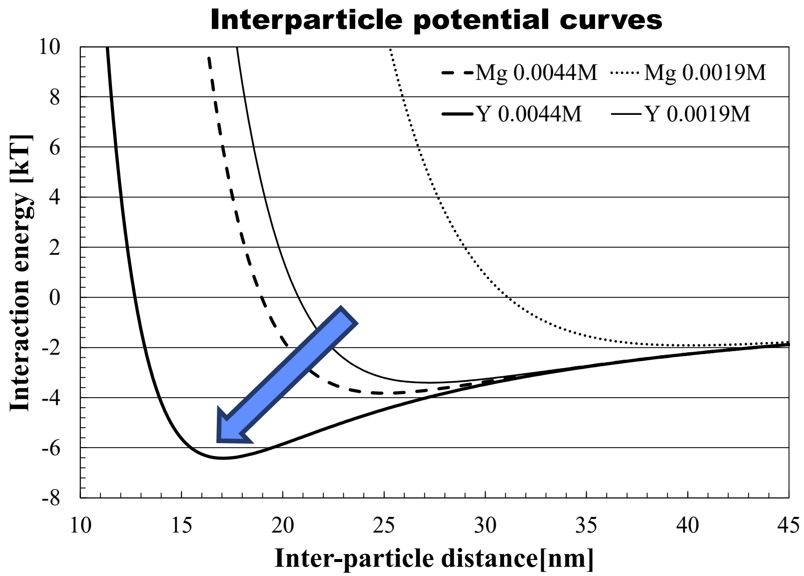


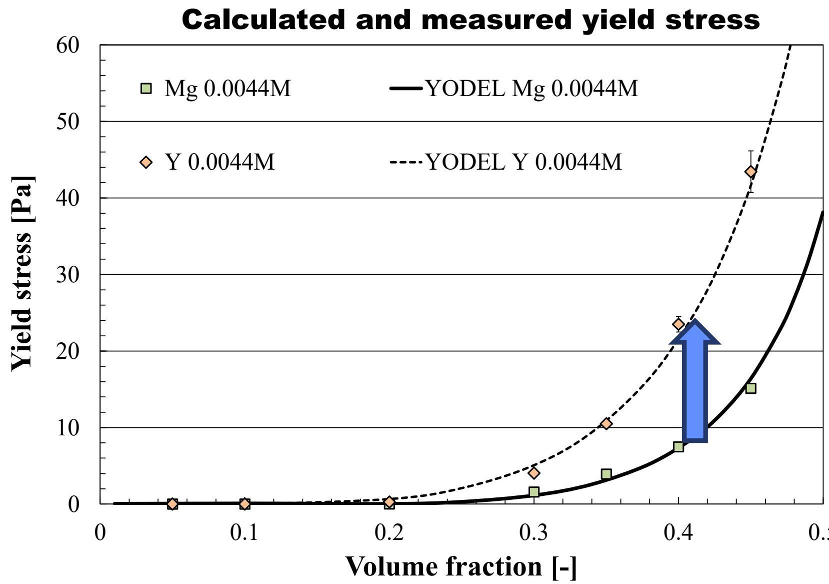
Yield stress related to **attractive interaction** between particles

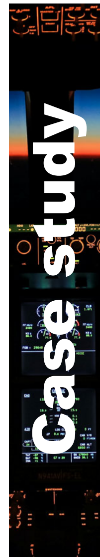
- YODEL model:

$$\tau = \boldsymbol{m_1} \frac{\Phi(\Phi - \Phi_0)^2}{\Phi_{max}(\Phi_{max} - \Phi)}$$

- Φ: vol. solid loading
- Φ_{max}: vol. solid loading at maximum packing
- Φ_0: vol. solid loading at percolation threshold
- m_1: function of the interparticle potential and particle morphology







Solid loading effect on viscosity

Viscosity increases with solid loading

- For dilute suspensions ($\Phi < 0.01$) following the Einstein equation:

$$\frac{\mu_{eff}}{\mu_{bf}} = \frac{1}{(1-\Phi)^{[\eta]}}$$

Very limited particle interactions

- For medium concentrated suspensions ($0.01 < \Phi < 0.1$) a Taylor series development is necessary. For spherical particles:

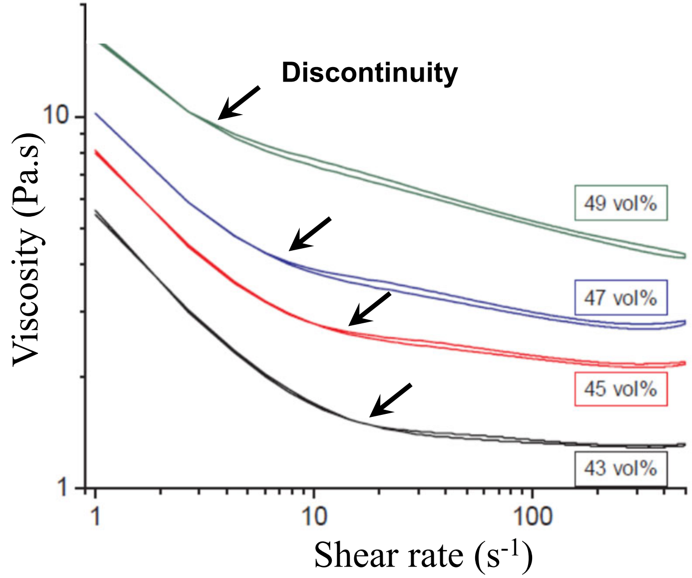
$$\frac{\mu_{eff}}{\mu_{bf}} = 1 + 2.5\Phi + 6.2\Phi^2 + O(\Phi^3)$$

Single particle and pair-particle interactions

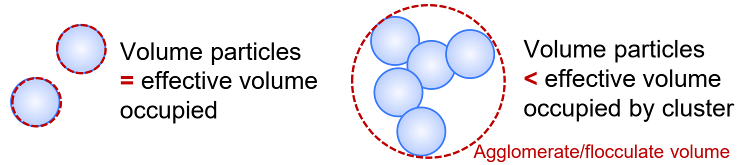
- For concentration suspensions ($\Phi > 0.1$) following the Krieger-Dougherty equation:

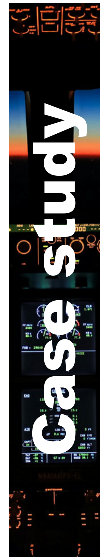
$$\frac{\mu_{eff}}{\mu_{bf}} = \left(1 - \frac{\Phi_{cs}}{\Phi_m}\right)^{[\eta]\Phi_m}$$

Multi-particle interactions



– μ_{eff}: effective viscosity [Pa.s]
– μ_{bf}: viscosity of basefluid [Pa.s]
– $[\eta]$: intrinsic viscosity [Pa.s]
  = 2.5 for hard sphere suspensions
– Φ: particle volume fraction
– Φ_m: maximum particle volume fraction
– Φ_{cs}: volume fraction of cluster spheres
  = Φ in absence of agglomerates/flocculates



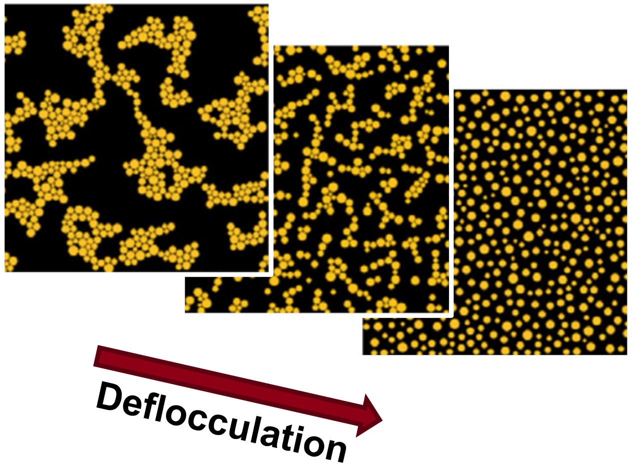


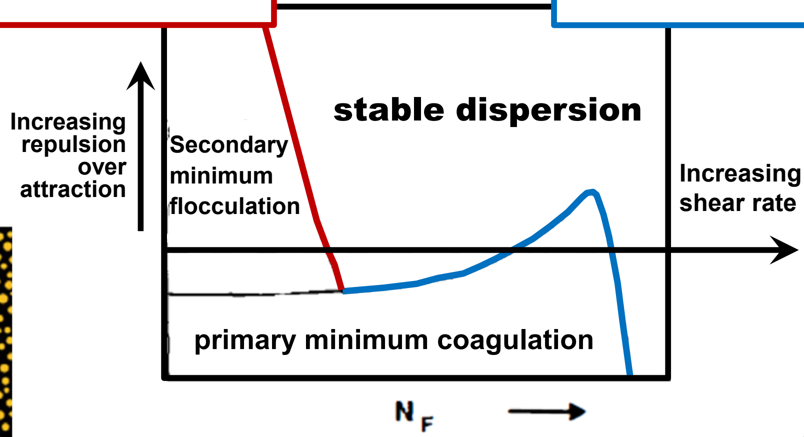
Shear stress effect on deflocculation and coagulation

Discontinuities in the viscosity-shear rate curves may be related to:

Deflocculation induced morphology changes

Morphology changes due to **shear induced coagulation**





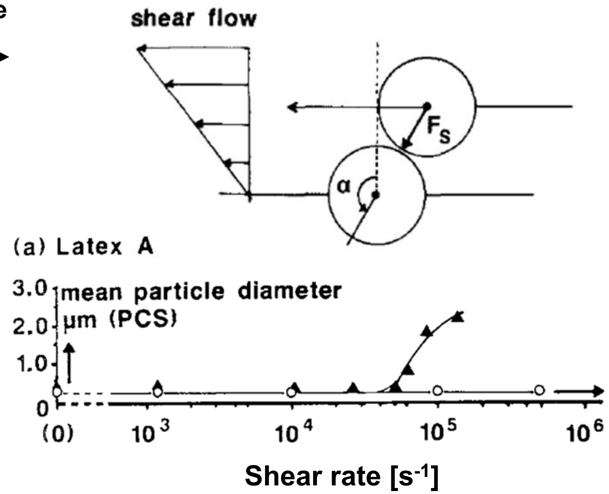
Importance of hydrodynamic vs attractive forces:

$$N_F = 6\pi\eta a^3\dot{\gamma}/A \text{ [-]}$$

- η: viscosity
- $\dot{\gamma}$: shear rate
- a: particle radius
- A: Hamaker constant

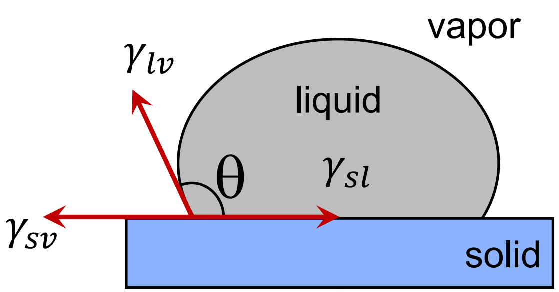
For equal spheres:

$$F_S^{(max)} \propto 6\pi\eta a^2\dot{\gamma}$$



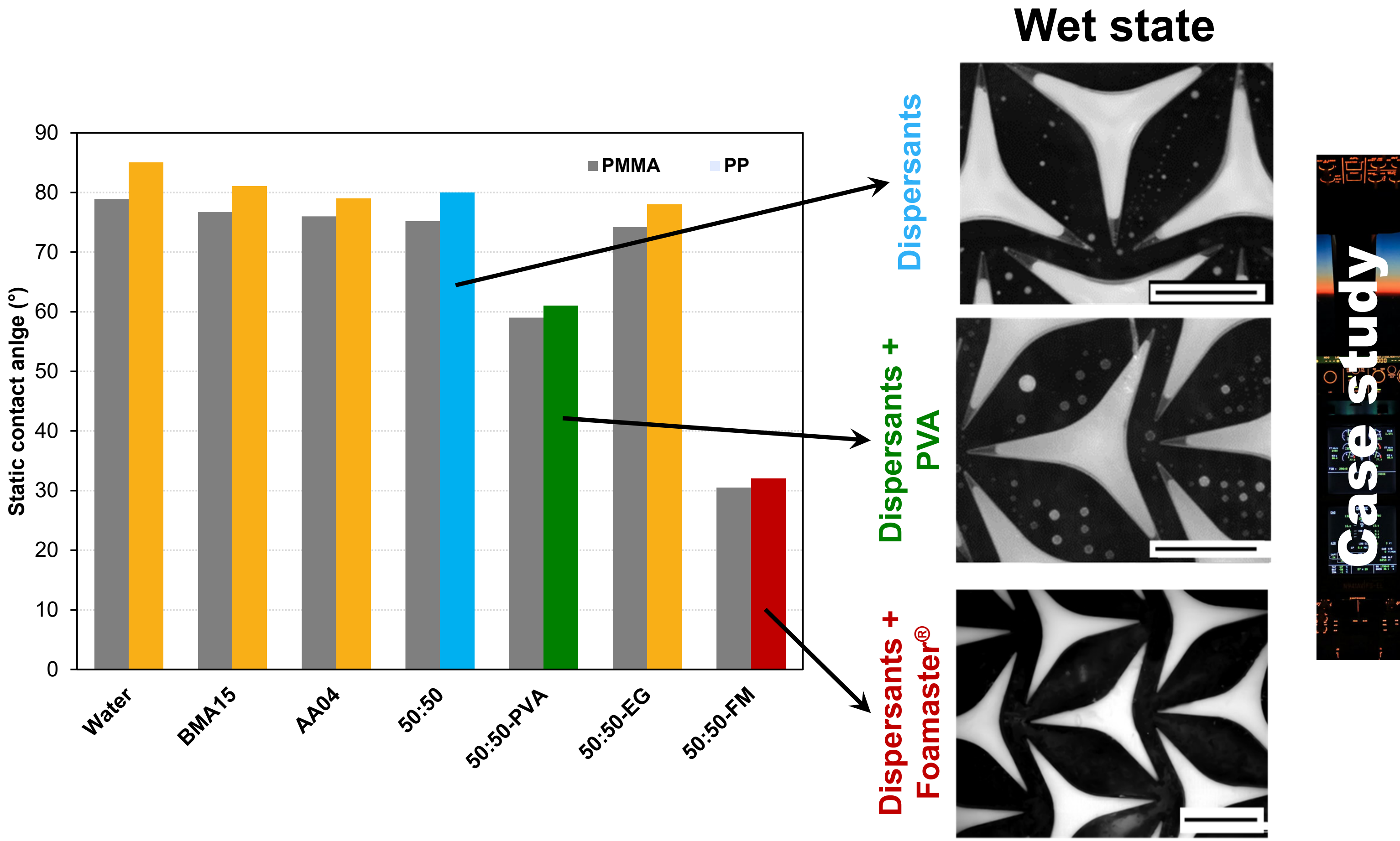
Husband, J. C. and J. M. Adams (1992). doi: 10.1007/Bf01095060

a. Effect of contact angle on mold filling

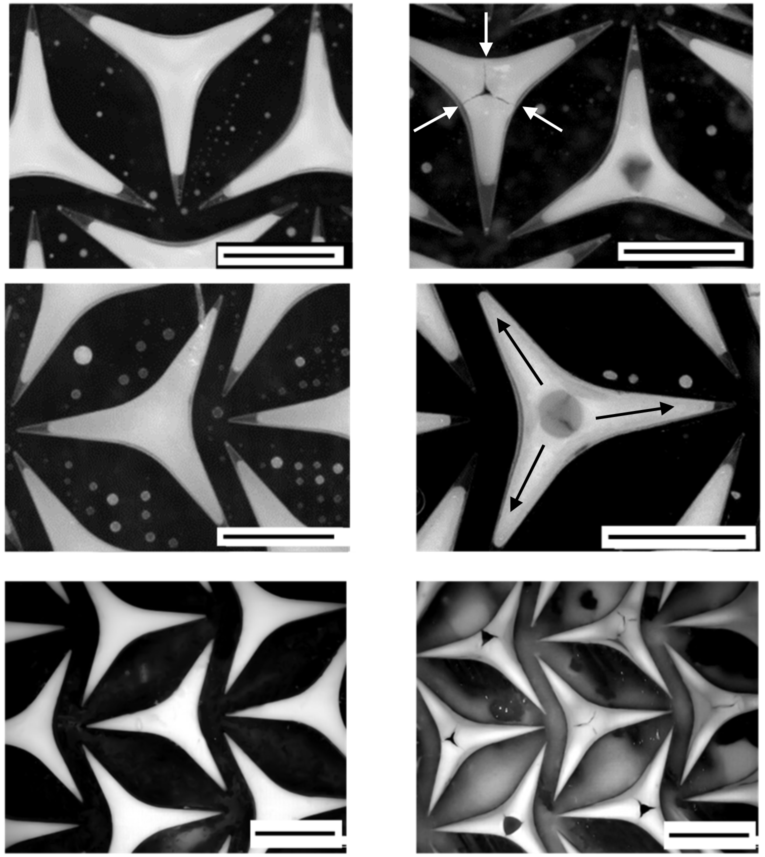


$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Young equation



b. Defect formation during drying



Green body defects may occur due to:

1. **Particle migration** towards star tips due to capillary pressure "pulling" slurry during drying (e.g. drying flow + capillary pressure gradient)

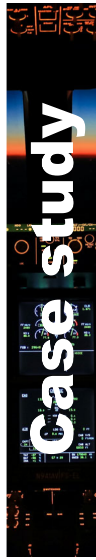
$$P_c = \frac{-2\gamma_{lv}\cos\theta}{r}$$

- γ_{lv}: surface tension (liq/vap)
- θ : contact angle (l/v)
- r : characteristic pore radius

2. **Crack formation** due to drying stresses

$$\sigma \propto \frac{L\eta_l V_e \gamma_{lv}}{3K_p}$$

- L: characteristic part dimension
- η_l: viscosity of liquid
- V_e: evaporation rate of liquid
- K_p: permeability of pore network
- γ_{lv}: surface tension (liq/vap)



b.1. Mitigation of particle migration

Considered approaches

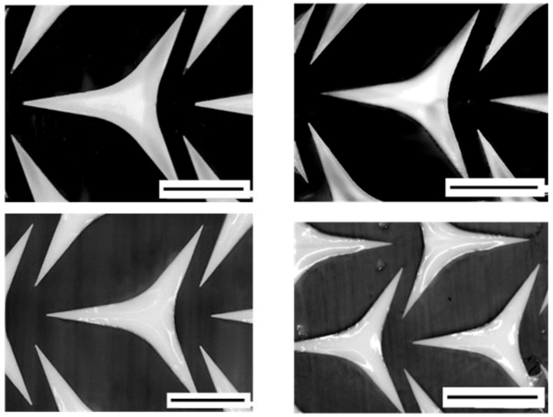
1

Gel-casting / Curing

Wet state | Dry state

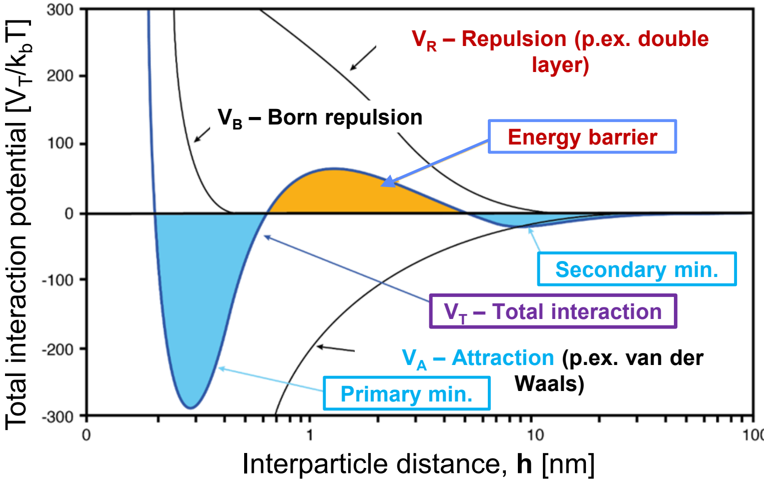
Dispersants + Agar

Dispersants + UV curable resin



2

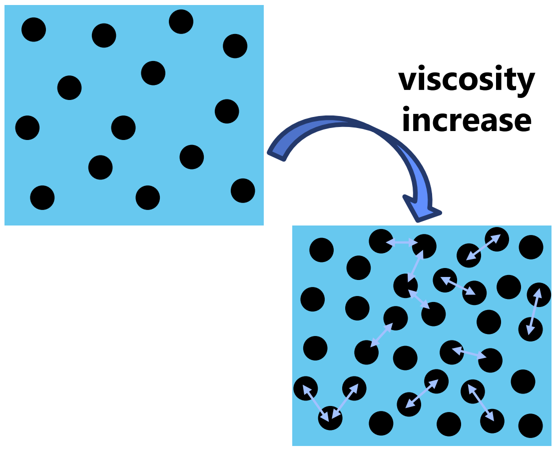
Flocculate dispersion (yield stress)

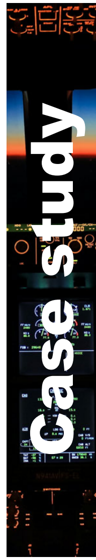


source: Wikipedia

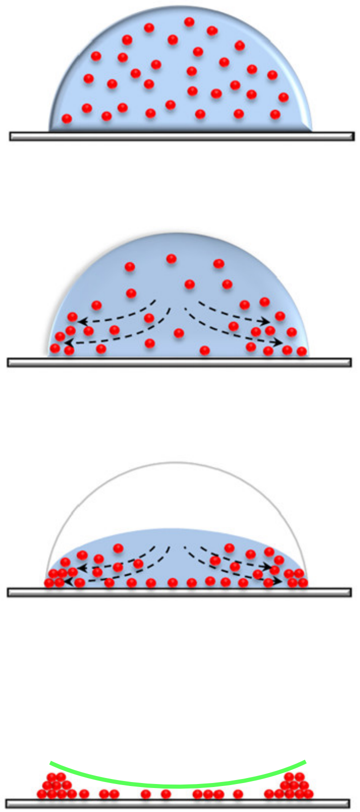
3

Increase particle loading

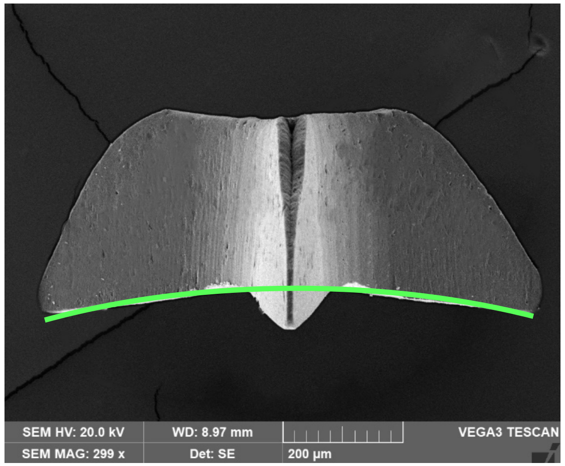


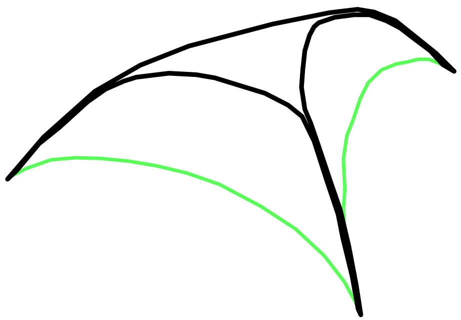


b.1. Mitigation of particle migration: Design benefits



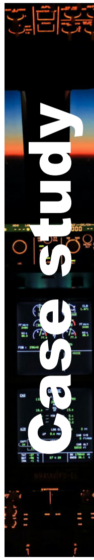
Source: Al-Milaji, K. N. and H. Zhao (2019).
doi: 10.1021/acs.langmuir.8b03406





Curved star particles with appropriate contact angle and solid loading

➔ Improved rolling and punctuation performance



Shape and process patents

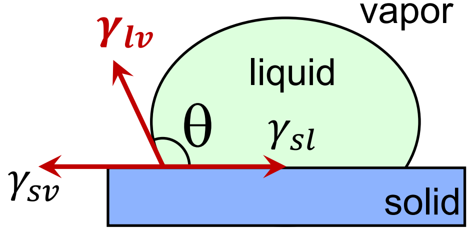
b.2. Mitigation of drying cracks

Decrease drying stress

- Addition non-volatile co-solvent preserving appropriate contact angle

$$\sigma \propto \frac{L\eta_l V_e \gamma_{lv}}{3K_p}$$

- L: characteristic part dimension
- η_l: viscosity of liquid
- V_e: evaporation rate of liquid
- K_p: permeability of pore network
- γ_{lv}: surface tension (liq/vap)



$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Young equation

Case study

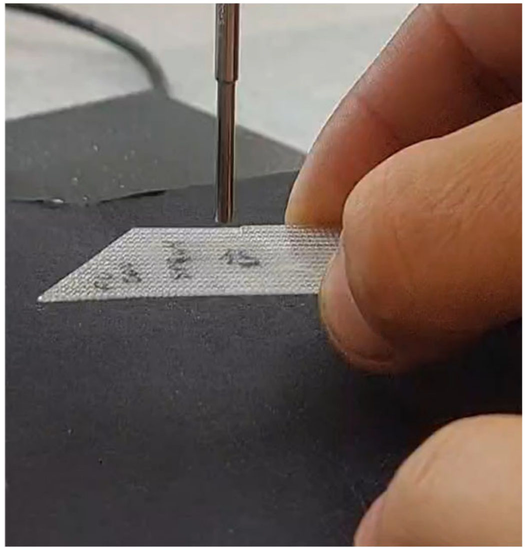
- Background and motivation
- Functional analysis and fabrication strategy
- Mold fabrication
- Slurry formulation and casting
- **Demolding, debinding and sintering**

Demolding, debinding and sintering

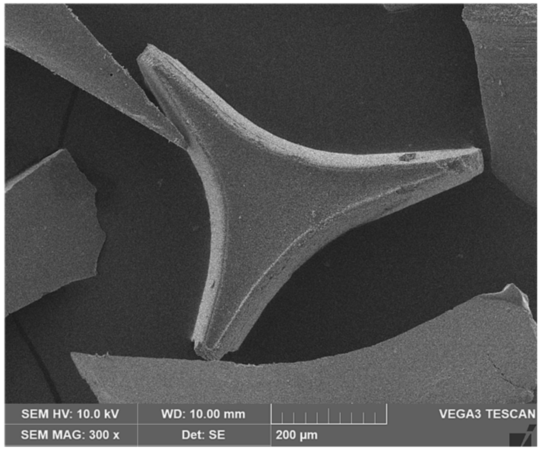
M. Stuer

25/03/2025

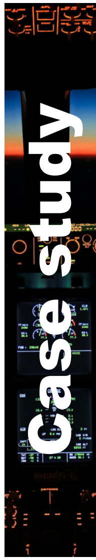
Ultrasound demolding



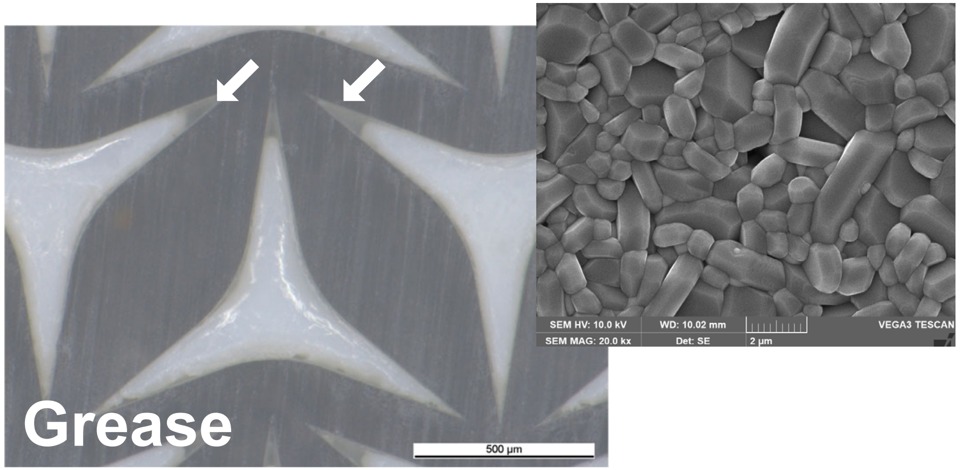
- **Part removal by mold ashing**
  - Part **cracking** due to mold deformation (i.e. thermoplastic)
  - **Carbon footprint** of process
- **Demolding by ultrasound**
  - Part cracking due to adhesion forces



Demolding strategy needed → **Mold surface modification** / **Slurry modification**



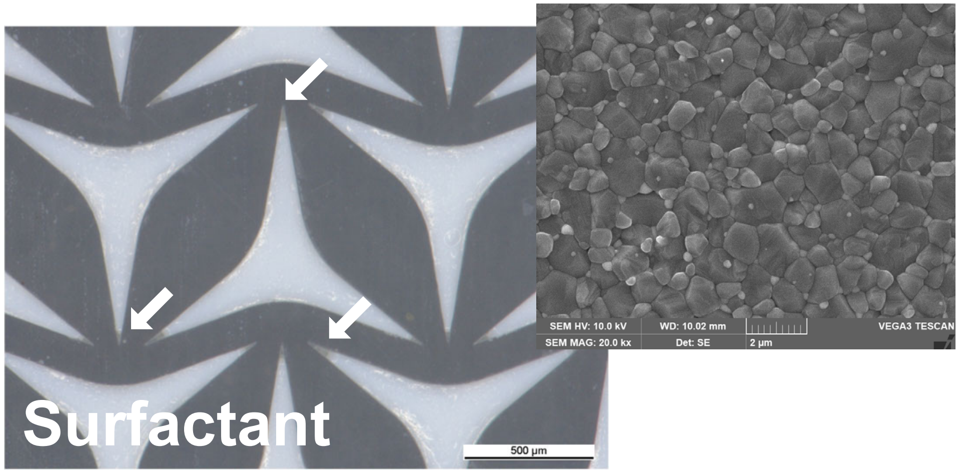
Mold modification



Application of grease film

- Filling issues
- Removal of zirconia sol at surface

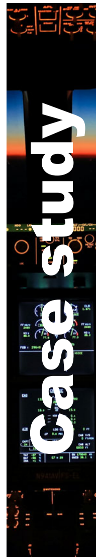
➔ But significantly decreases part loss



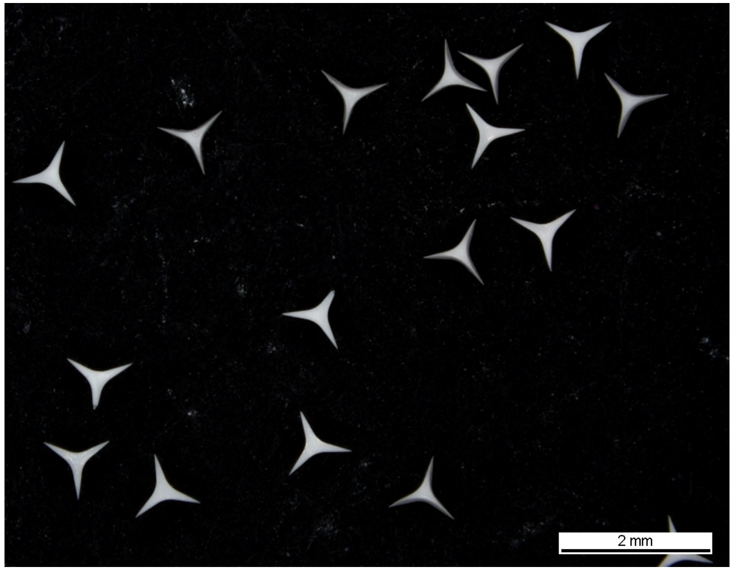
Application of surfactant film

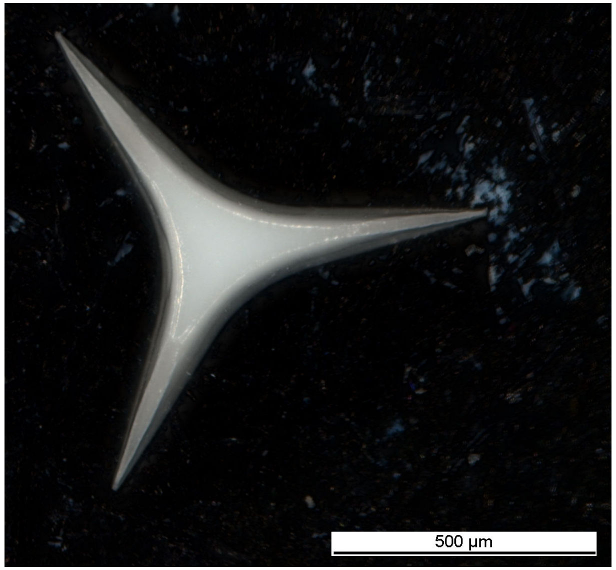
- Filling issues with excess surfactant

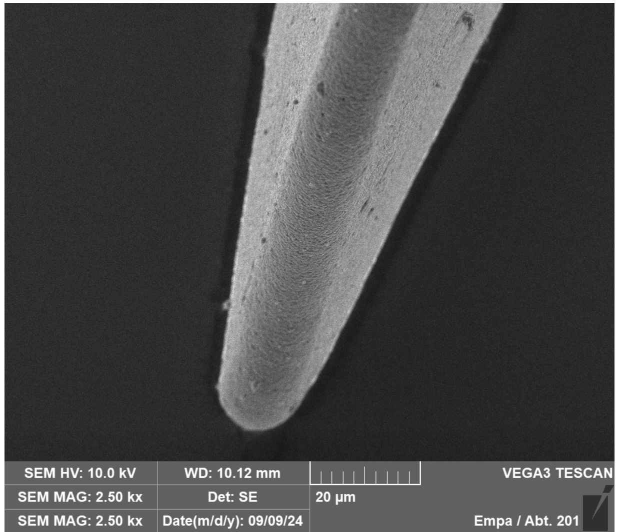
➔ **Combination of mold treatment with surfactant and surfactant addition to slurry**

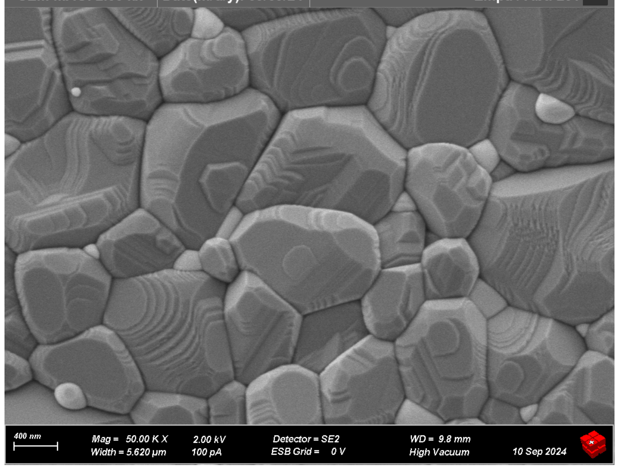


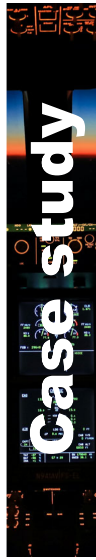
After slurry modification with surfactant











Some process metrics

- Process yield >90%
- Tip diameter <10 µm

The end

- **Summary**
  - Review of typical dry and wet shaping techniques
  - Additive manufacturing techniques with focus on stereolithography-based ones
  - Critical aspects related to drying and debinding
  - Use case: Development of a scalable process for large scale shaping of ceramic microdevices
- **Questions?**