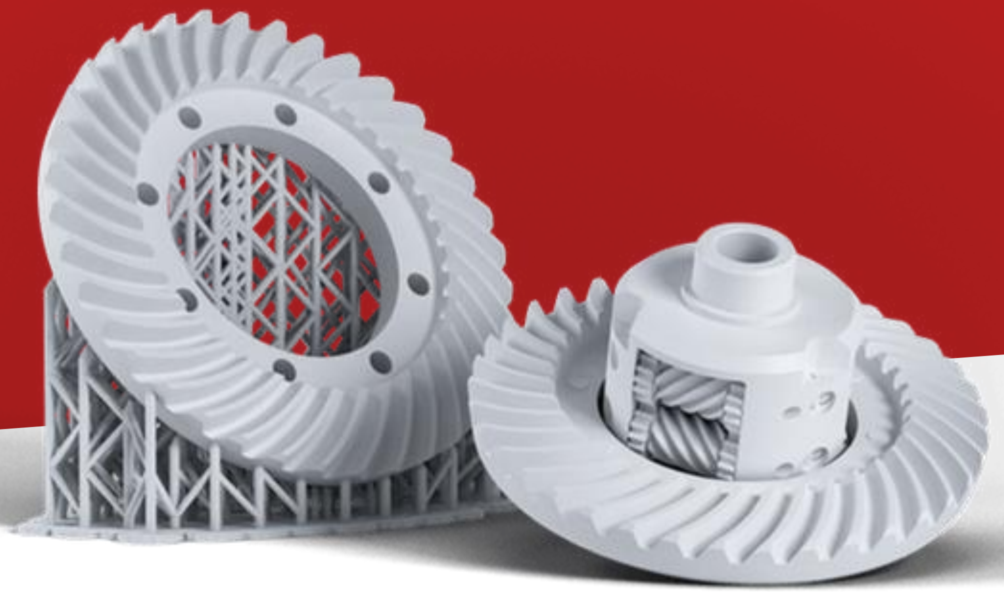
ME-413

AM for Polymer Materials

Yilang HU
Zixu Lu
Shize Guan



EPFL

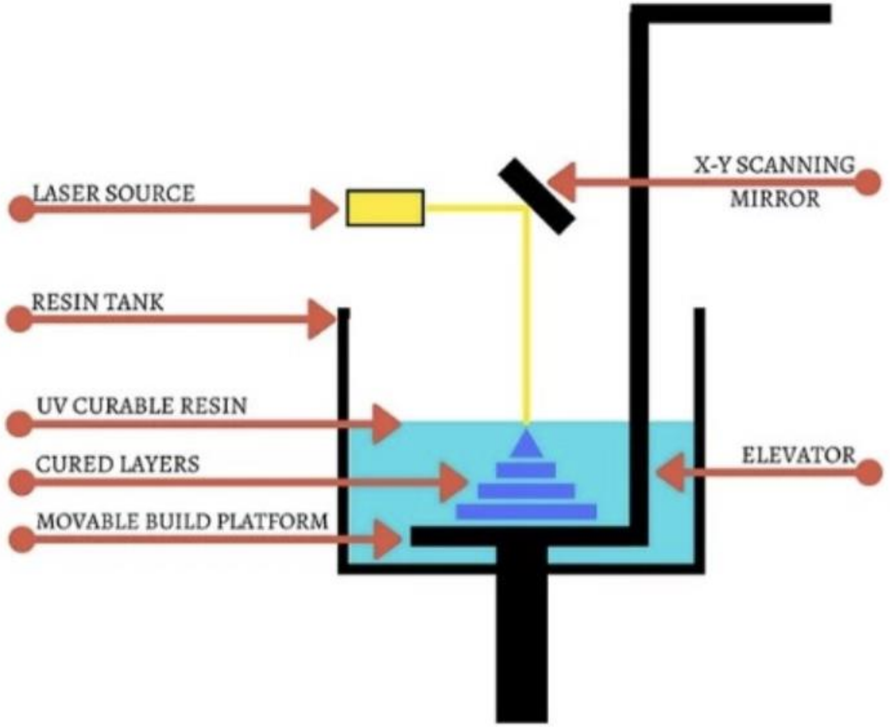
Introduction

- Additive Manufacturing
  - A variety of technologies are developed to make complex structures
    - Powder bed fusion
    - Vat photopolymerization
    - Material jetting/extrusion…
- Polymer
  - A great range of different polymers are synthesized, with
    - Biocompatibility
    - Great mechanical property
    - Temperature resistivity…

Motivation: Combine functional polymer with advanced fabricating technology to make useful devices in multiple domains of industry!

Stereolithography Apparatus

Stereolithography Apparatus



1. Focus a laser with specific wavelength and intensity on the surface of the material to cure one layer according to the cross-sectional pattern design

2. Lifting platform moves vertically by one layer height to position for the next layer

3. Repeat the process layer by layer to form a three-dimensional object

Material requirements

Material requirements

Functional groups

Functional group	Mechanical strength	Toughness	Curing velocity
Acrylate	High	Low	Fast
Urethane Acrylates	Medium-high	High	Fast
Epoxy Acrylates	High	Medium	Medium
Polyester Acrylates	Medium to High	Medium	Fast
Thiol-ene Systems	Medium-high	High	Very fast

Material requirements

Active diluents

- Reduce viscosity
- Adjust properties
- Participate in curing reaction

Photoinitiator/Photosensitizer

- Initiator/catalyst

Material requirements

Curing velocity:

$$\frac{d\alpha}{dt} = K(T, I_a) \cdot \alpha^m \cdot (1-\alpha)^n$$

t: reaction time
α: degree of curing
m & n: fitting parameters
K: rate constant

Beer-Lambert's law:

$$I(a) = I_0 \cdot \exp(-\epsilon \cdot c \cdot z)$$

I0: incident light intensity
ϵ: molar absorption coefficient
c: solution concentration
z: light penetration distance

$$I(D_p) = I_0 \cdot \exp(-1) = \frac{I_0}{e}$$

$$D_p = \frac{1}{\epsilon \cdot c}$$

$$E_c = E(d) = I_0 \cdot \exp(-\epsilon \cdot c \cdot d) \cdot t$$

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

Material requirements

Viscosity

- Add reactive diluents
- Increase temperature

  High temperatures will accelerate the curing rate of the material

Polymer in SLA

Polymer in SLA

Photosensitive resins

- Flexible photosensitive resins
- Tough photosensitive resins
- Rigid photosensitive resins

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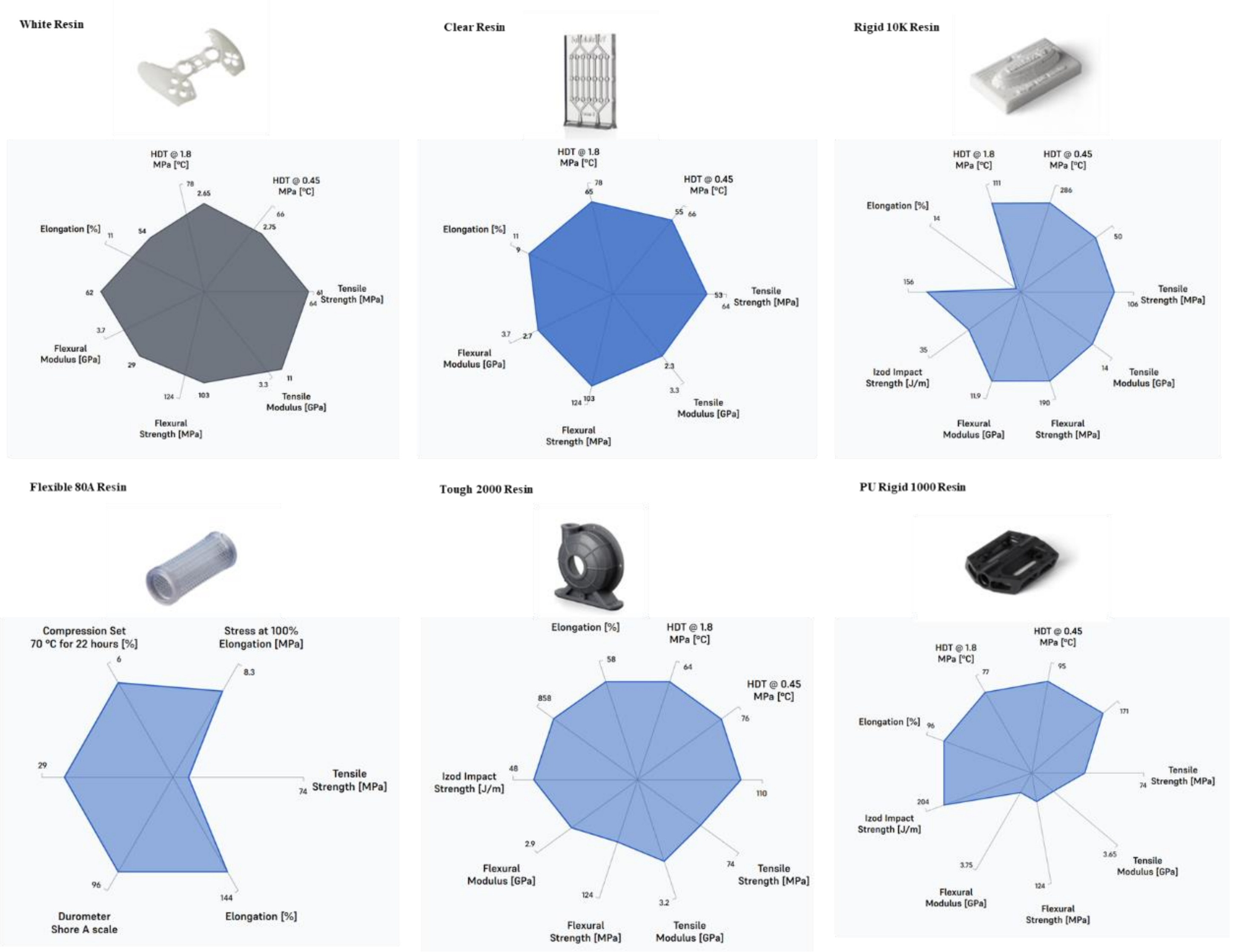
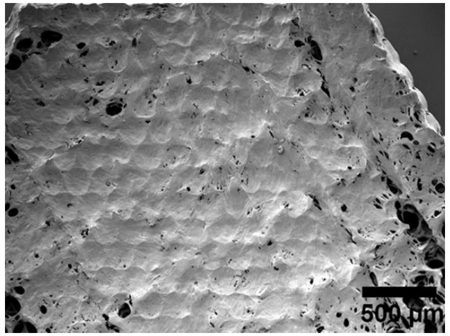
Achieve the desired performance by balancing elongation and tensile strength



Polymer in SLA

New polymer material

- Biocompatible materials



- Conductive photosensitive resin
- High-temperature resistant photosensitive resin

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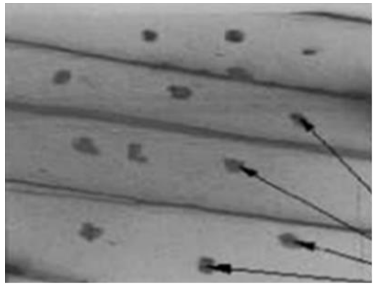
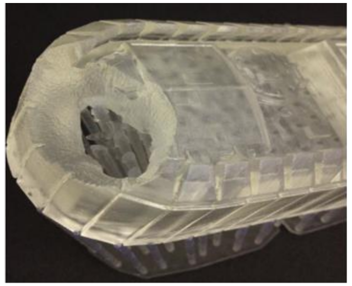
Analysis of defects & performance

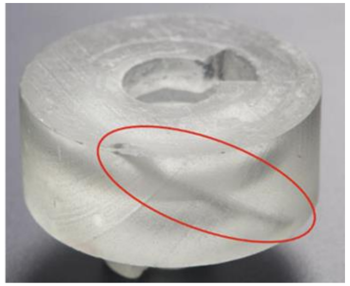
Analysis of defects & performance

performance

- **Low accuracy**
  - Curing depth
    High temperature and light intensity, low Ec and high Dp
  - Light bleed
- **Material shrinkage**
  - Content of the photoinitiator
  - Light intensity
  - Layer thickness
    Solution: use cationic polymerization
- **Cavity, porosity, cuts …**


Voids


Undeveloped features


Cuts

Analysis of defects & performance

Post-processing

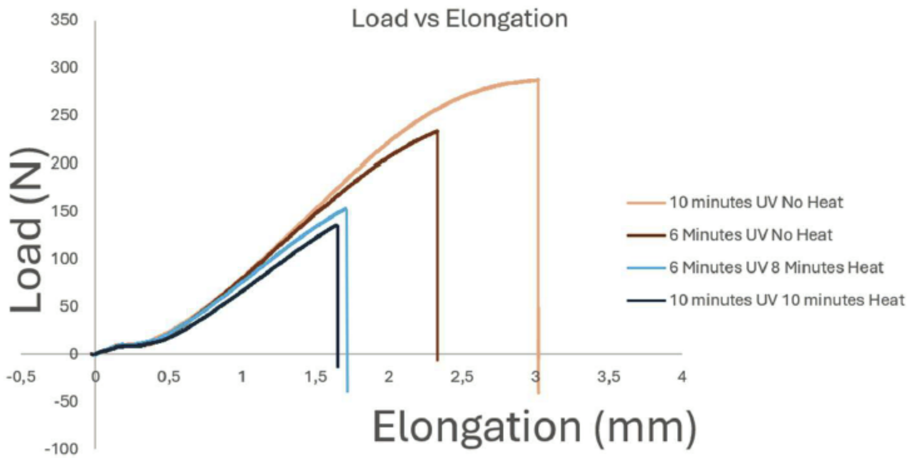
- Cleaning
- Post-curing
  - UV light post-curing
  - Thermal post-curing

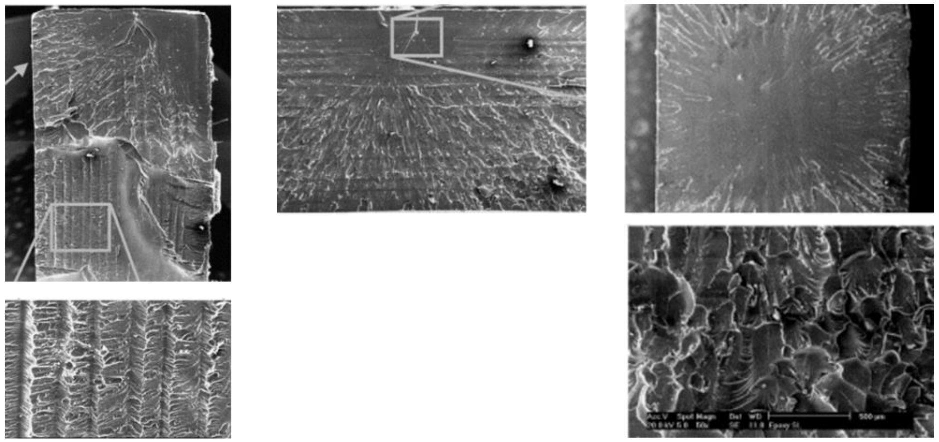
Promote further cross-linking of molecular chains

Analysis of defects & performance

performance

- Prepolymers
- Ratio of material
- Layer thickness
- Curing process
  - Temperature
  - Time
  - Light intensity
  - Curing method
- Print direction





Untreated Ultraviolet Heating

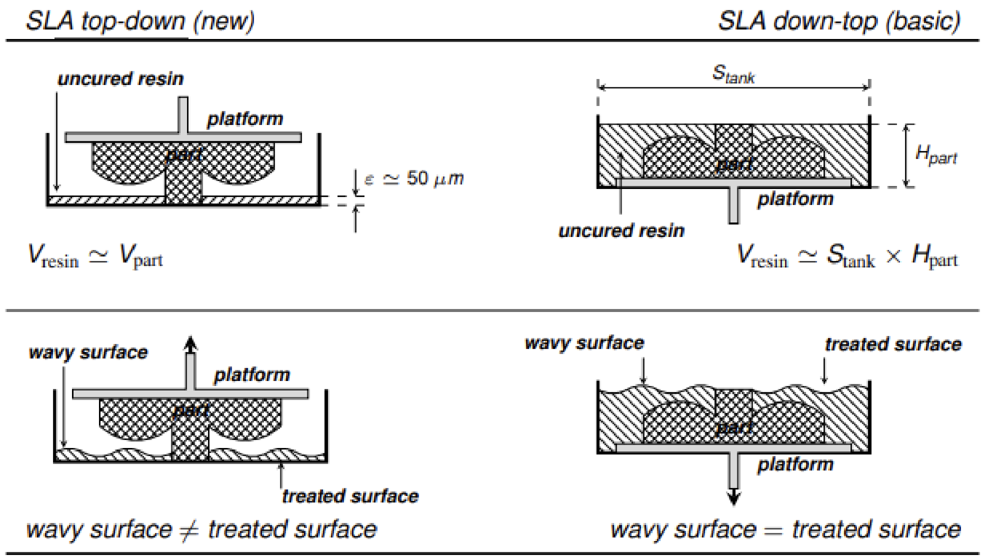
Analysis of defects & performance

The failure mechanism of the material is usually chain slippage, but after curing, the parts become isotropic, the layered structure of the material disappears, and chain slippage is no longer the main cause of fracture

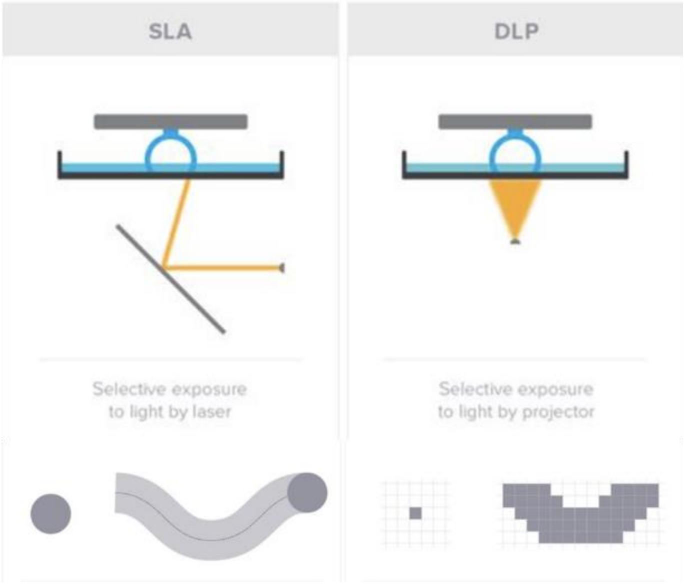
Technique improvement

Technique improvement

Top-down



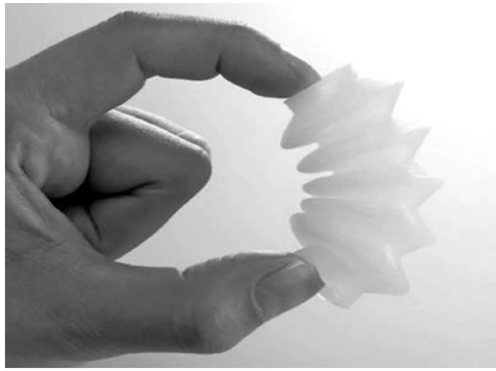
DLP



Applications

Applications

Elastic photosensitive resin

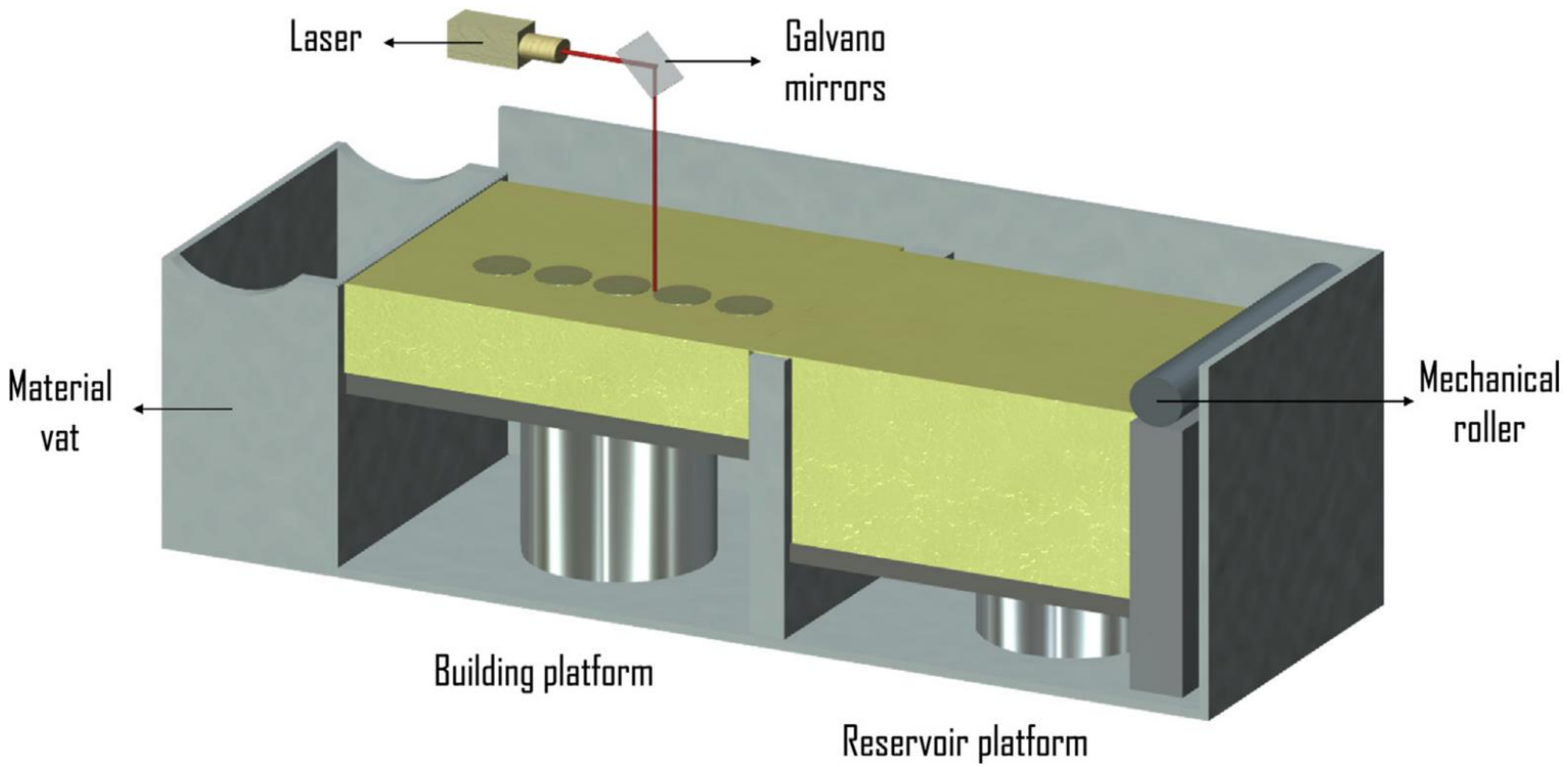


Tough photosensitive resin

Biocompatible photosensitive resin

Selective Laser Sintering

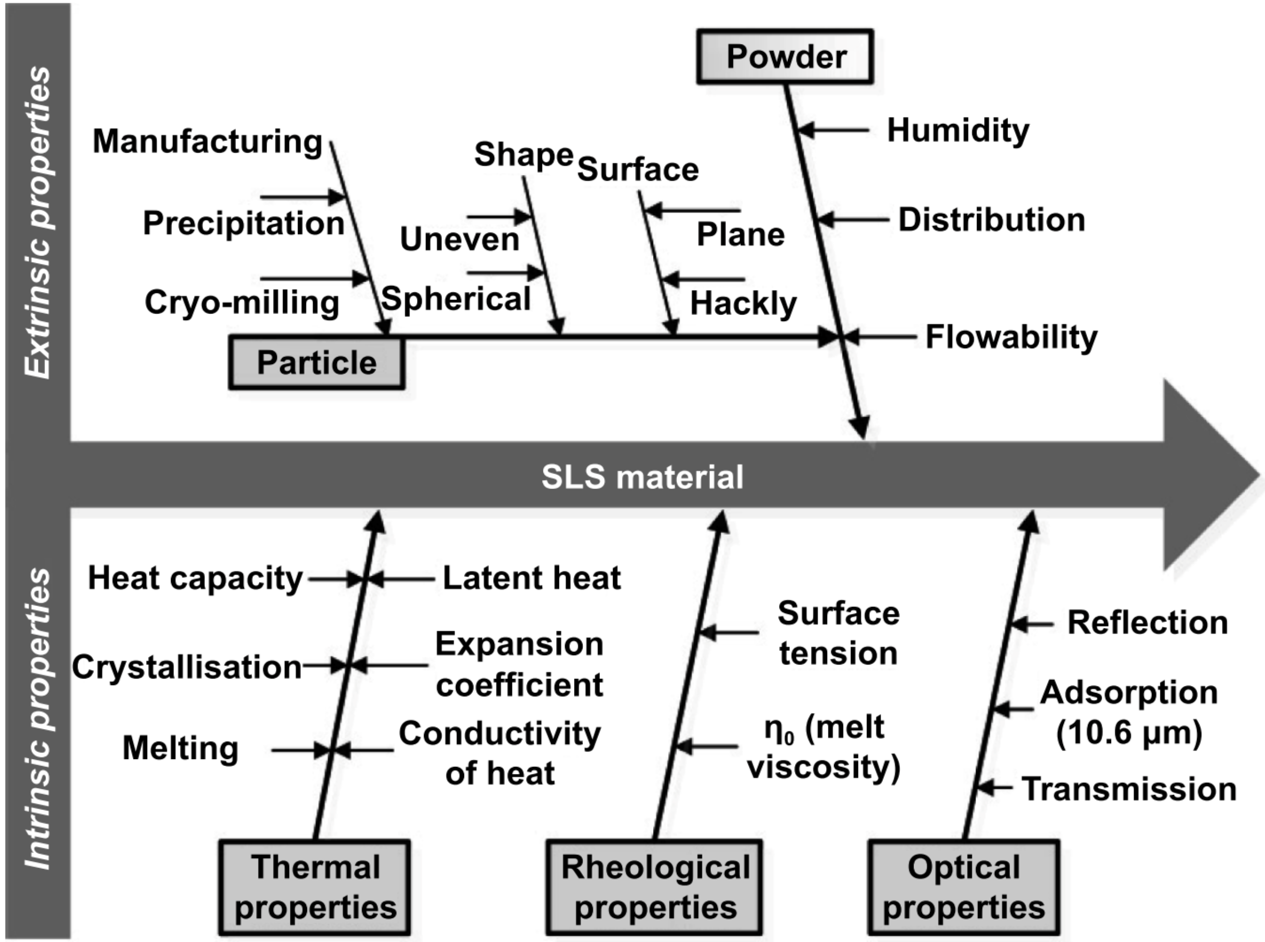
Selective Laser Sintering



1. Laser scans the layer point to point, melting the exposed area to transfer the pattern onto the layer.
2. The platform moves down and another layer of powder is fed.
3. Iterate 1 and 2 until the whole 3D structure is printed.

Material requirements

Material requirements



- Polymer property
  - High absorption of laser power
  - Low viscosity
  - Large process window between melting point and crystallization temperature
- Powder property
  - Spherical shape (ideally)
  - Proper size distribution (50 µm ~80 µm normally)

Polymer in SLS

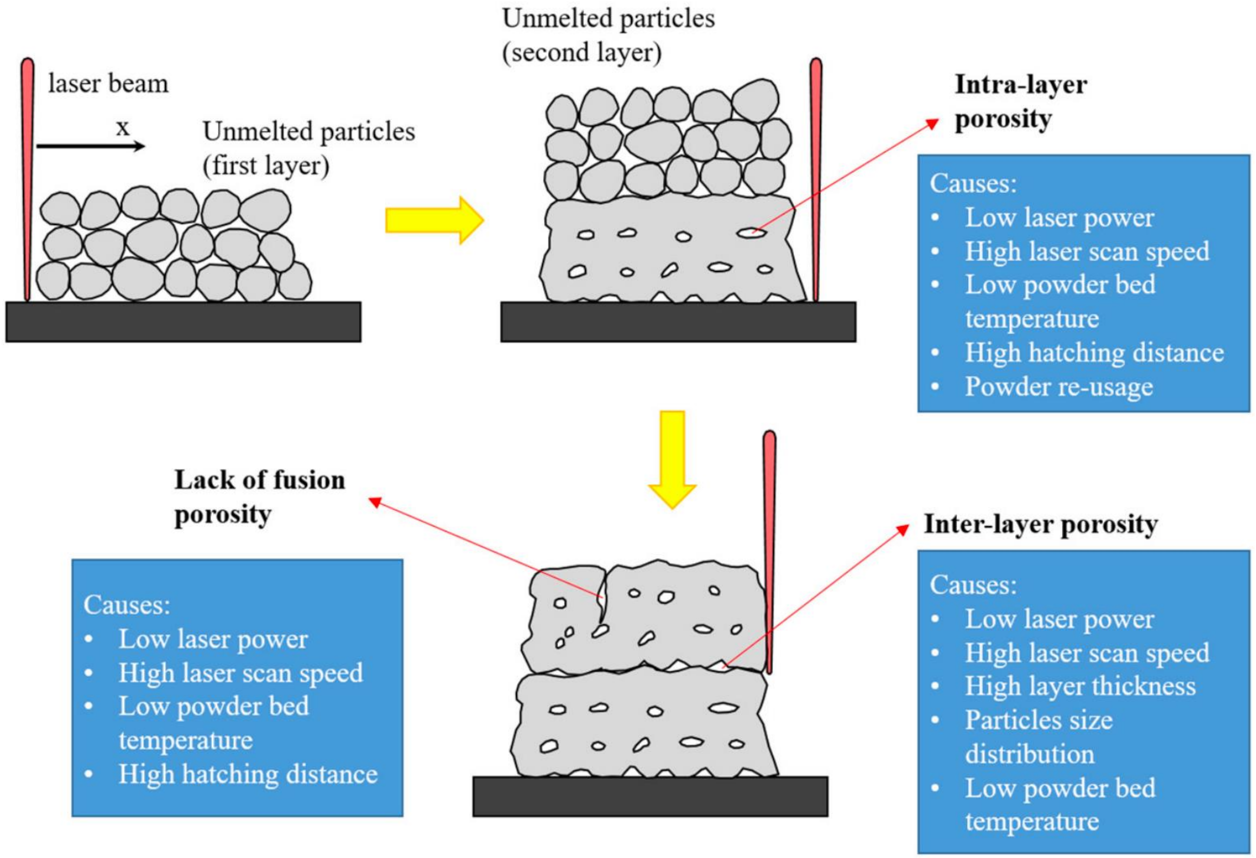
Polymer in SLS

Polymer	Melting point (°C)	Crystallization temperature (°C)	Tensile strength (MPa)	Coefficient of thermal expansion ($\times 10^{-6}$/°C)
Polyamide 12	180	159	48-53	120-140
Polyamide 11	189	155	45-50	85-120
Polycarbonate	295-315	N/A(amorphous)	55-75	60-70
Polystyrene	240	220-240	30-50	60-80
Polyether-etherketone	343	240	80-120	25-50

- PA11/12: large process window, high mechanical strength and biocompatibility
- PC: great mechanical strength and high-temperature resistivity
- PS: low-cost and low thermal expansion (thus good accuracy)
- PEEK: excellent mechanical strength and high-temperature resistivity, low thermal expansion and biocompatibility

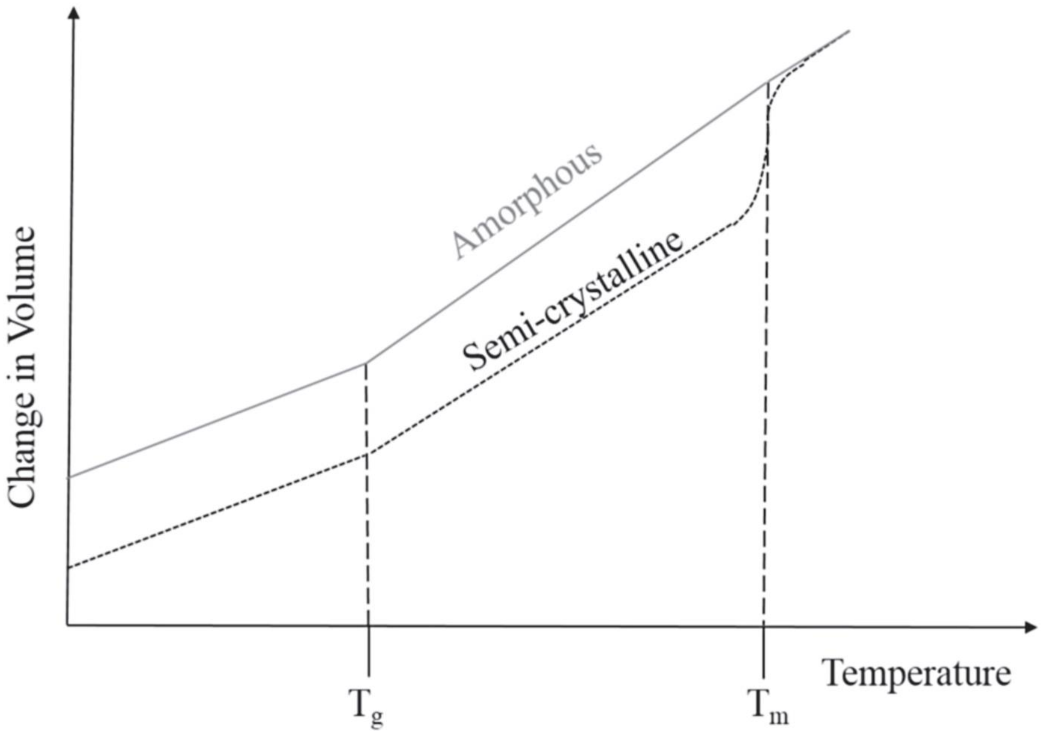
Analysis of defects

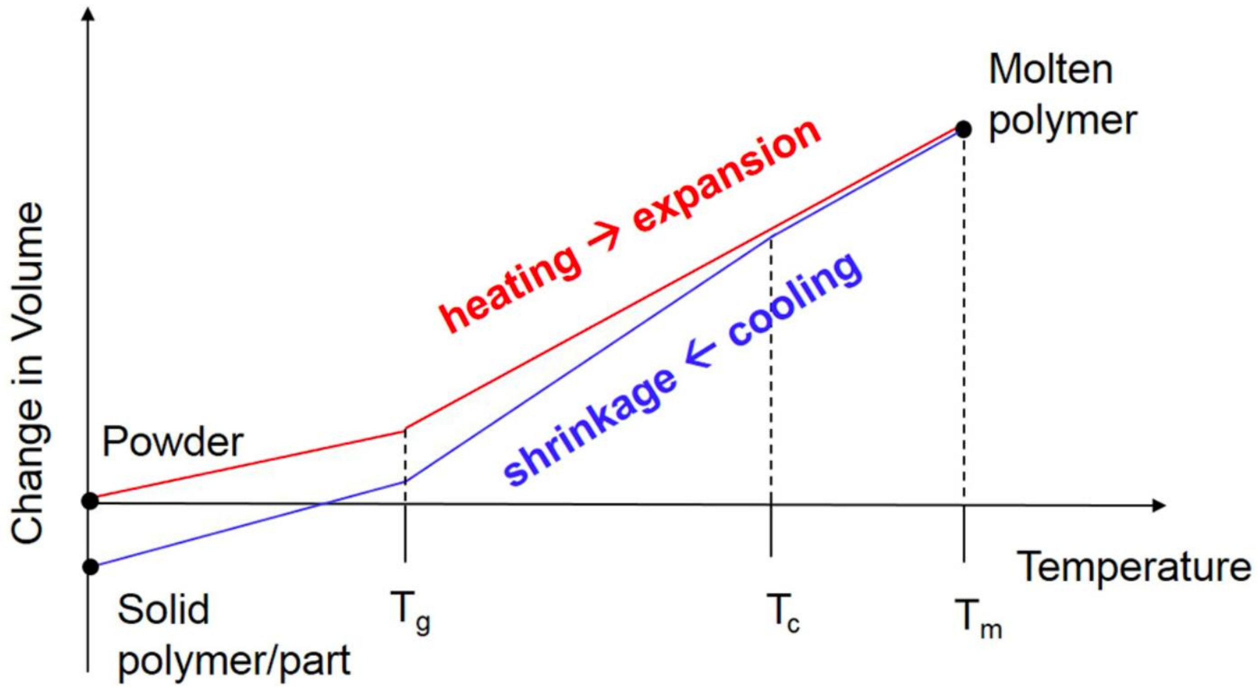
Analysis of defects



- Intra-layer porosity
  Mainly caused by insufficient melting and low flowability
- Inter-layer porosity
  Affected by both melting and layer thickness

Analysis of defects



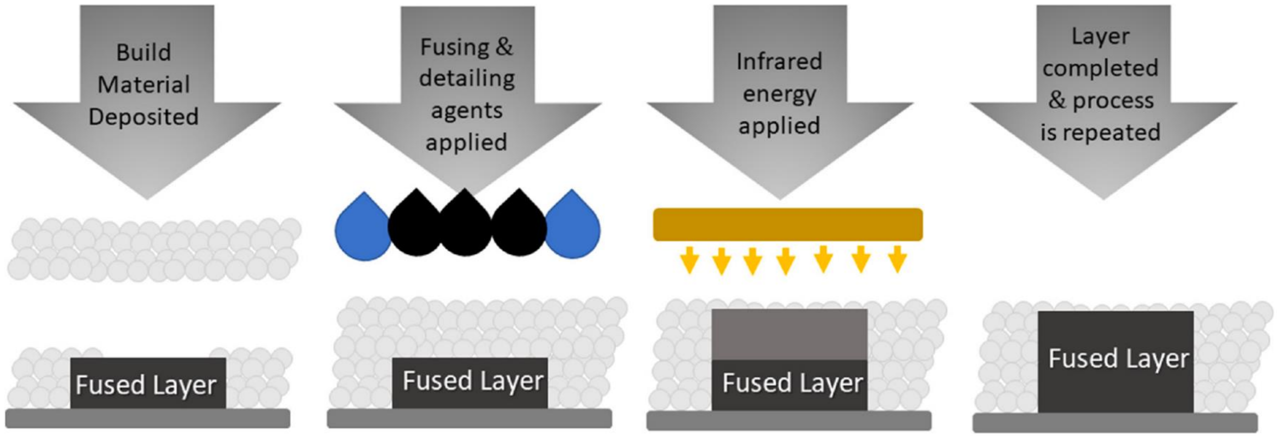


- Shrinkage
  - Temperature change induced
  - Crystallization induced
  - Process parameter determined

Technique improvement

Technique improvement

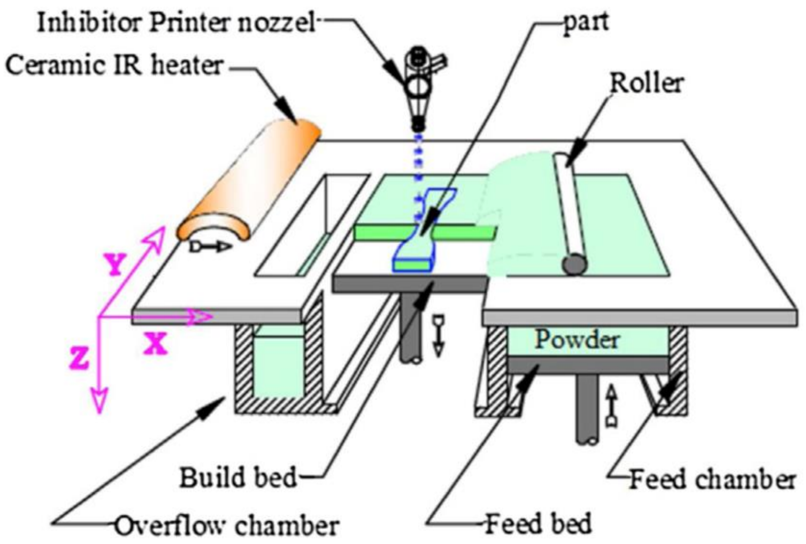
MJF (Multi-jet fusion)



Fusion agent: jet onto laser-exposed region to promote laser absorption

Detailing agent: jet onto border to prevent adjacent powder from melting to have high accuracy

SIS (Selective inhibition sintering)

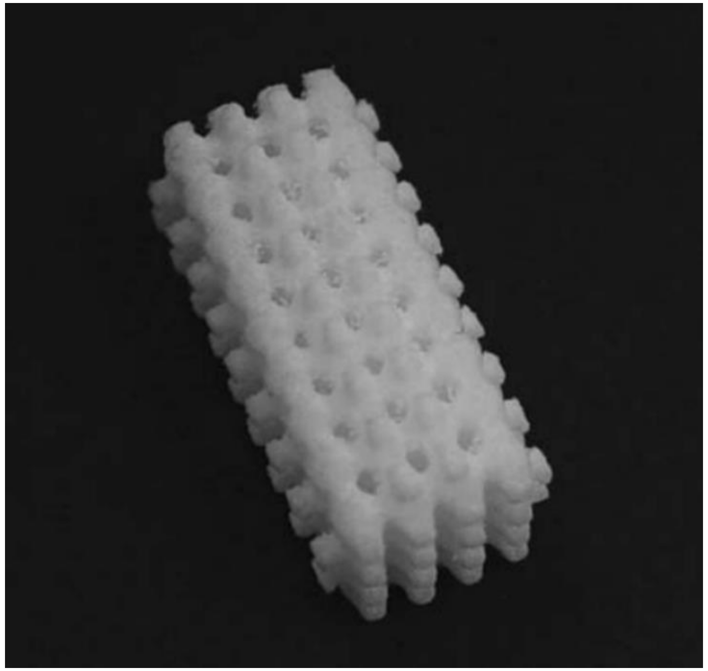


Inhibitor: jet onto the border to elevate the melting point of the margin thus separating the part from its surrounding resin

Applications

Applications

Scaffold for bone tissue engineering



Biocompatible and degradable polymer

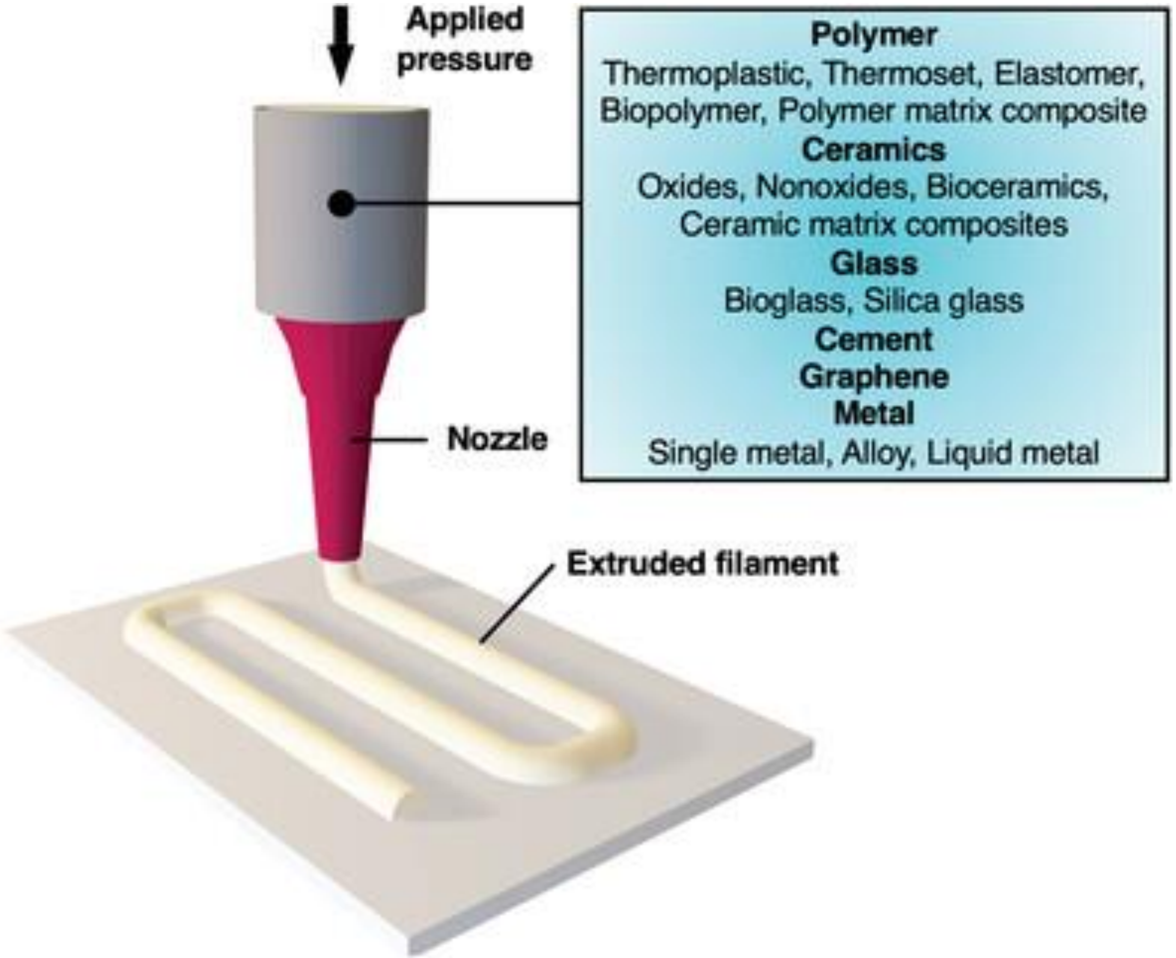
Hydrogenation porous catalysts

Chemically stable and heat resistive polymer

Direct Ink Writing

Direct Ink Writing

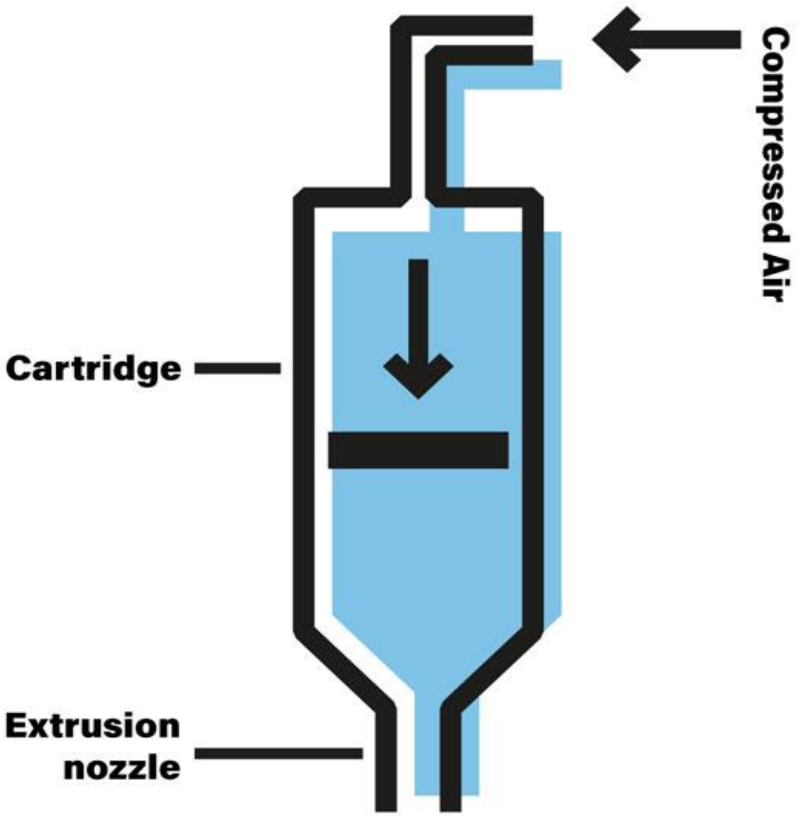
Introduction



- create complex three-dimensional structures
- extruding material through a nozzle in a controlled way
- can be applied to many materials

Introduction

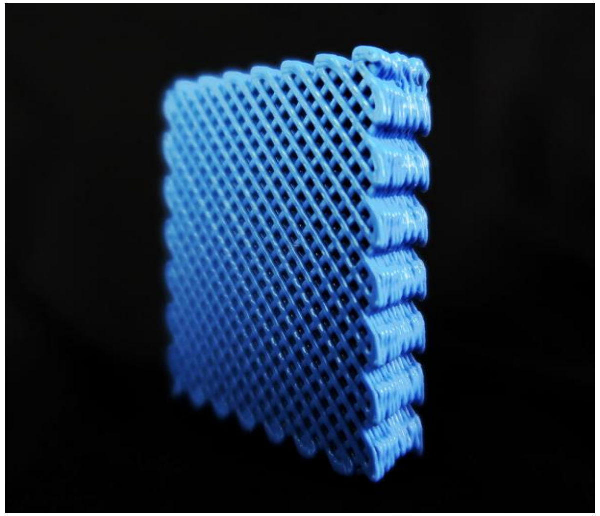
How does it apply pressure



- Pneumatic Pressure
  - compressed air
- Mechanical Pressure
  - mechanical piston
- Screw Extrusion
  - rotating screw

Introduction

Some products from DIW



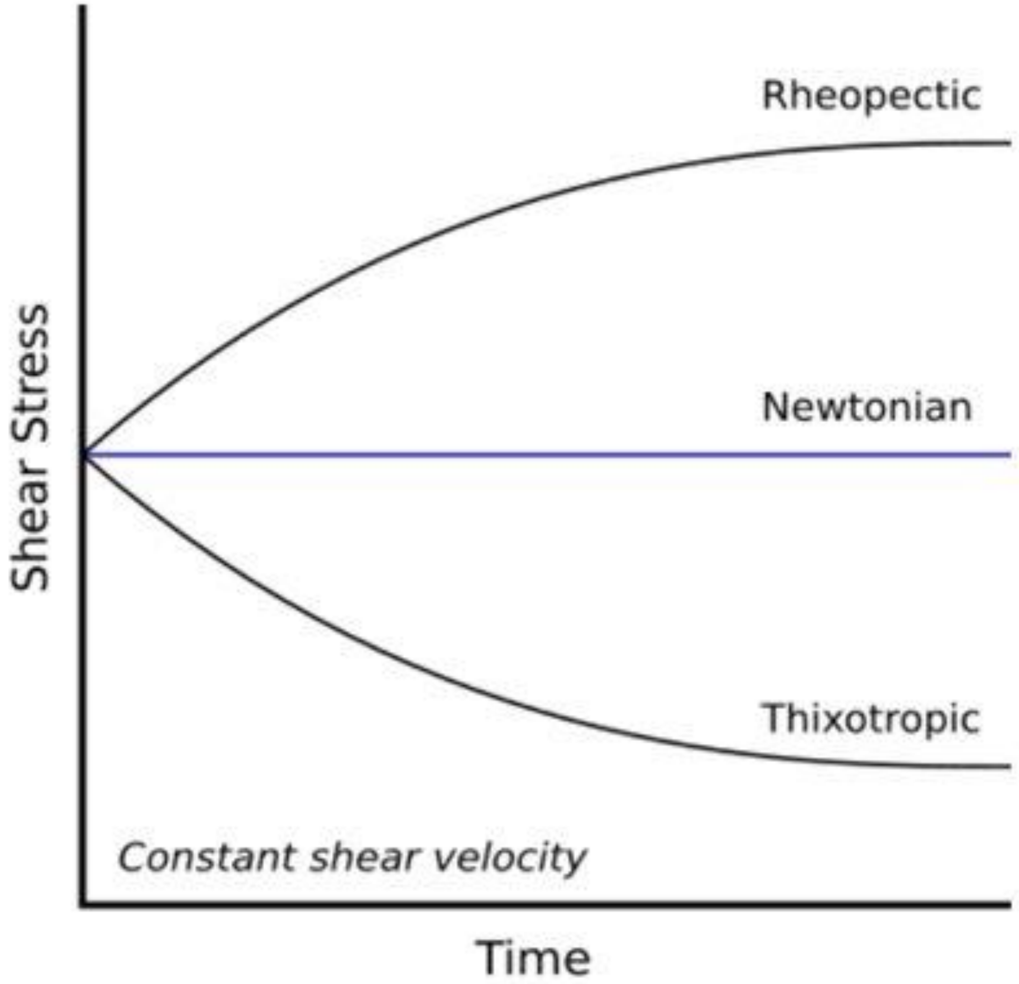
- Particularly valuable for printing functional materials
- Polymer materials have excellent versatility, mechanical tunability, and biocompatibility

Material requirements

Material requirements

- Rheopectic Behavior
  - increasing viscosity under shear
  - stabilize printed structures
  - preventing deformation and collapse
- Thixotropy
  - shear-thinning
  - reducing viscosity under shear
  - allow easy extrusion and then recovering viscosity

Material requirements



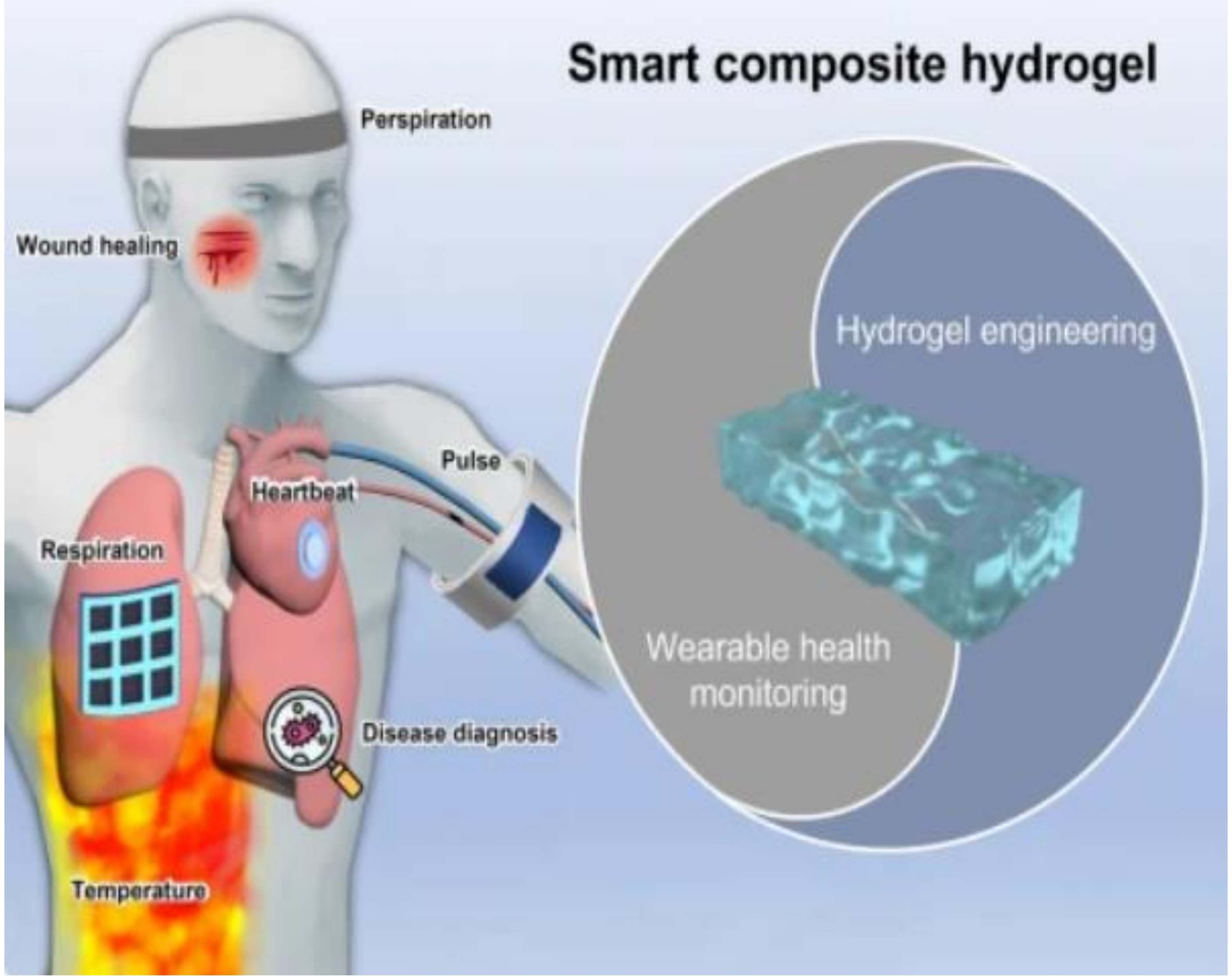
Rheopectic behavior and thixotropy are balanced.

Material requirements

- Self-healing
  - enhance long-term integrity
  - autonomously repair minor damage
  - soft robotics or tissue engineering

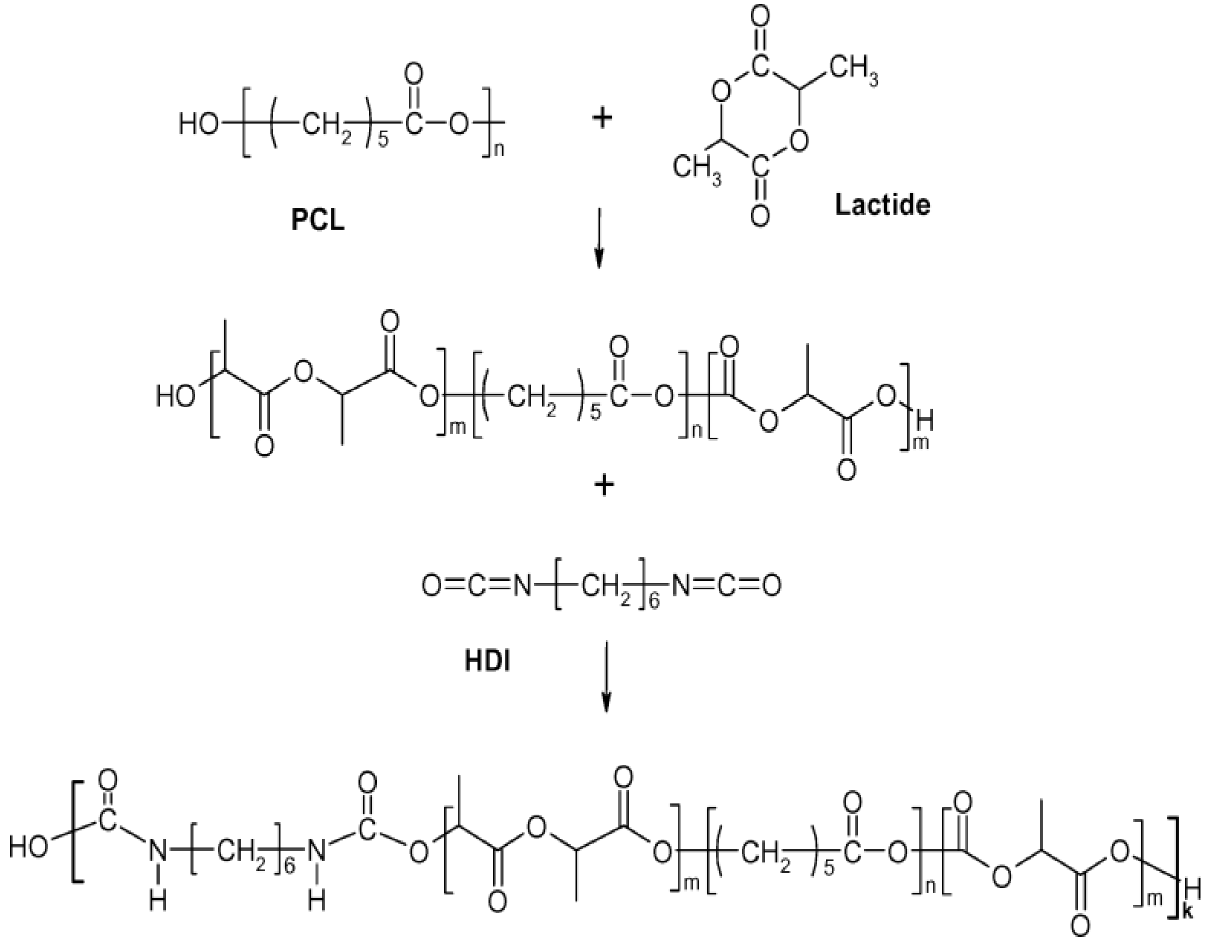
Polymer in DIW

Polymer in DIW



- Natural Polymers and Hydrogels
  - Hydrogels
    - biocompatibility and support for cell growth
  - Cellulose and its derivatives
    - biodegradability and high-resolution print fidelity

Polymer in DIW



- Synthetic Polymers
  - PCLA
    - copolymer formed from PLA and PCL

Synthesis and structure of PCLA multiblock copolymers.

Polymer in DIW

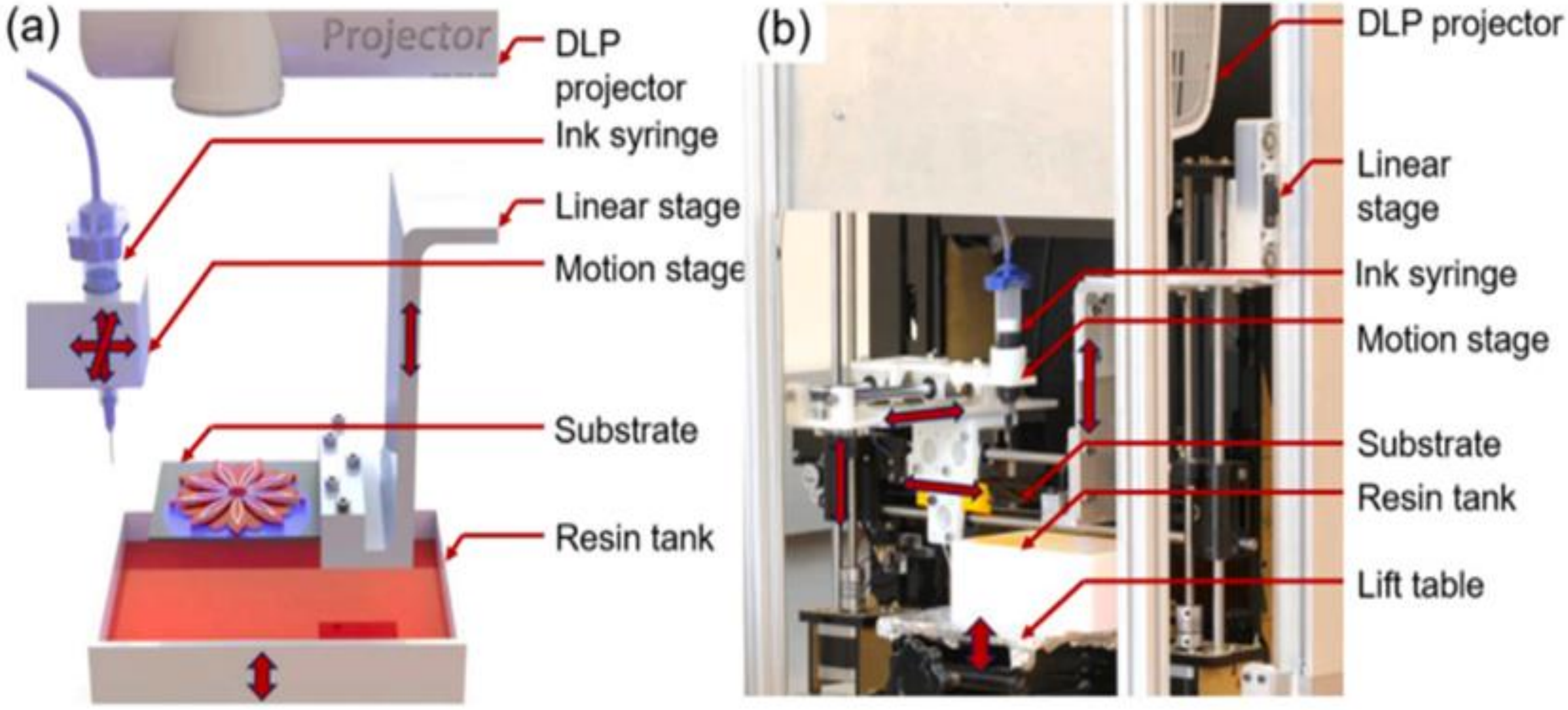
- Synthetic Polymers
  - Polyethylene Glycol (PEG)
    - Hydrophilic, biocompatible and soluble
    - drug delivery and soft tissue engineering

Polymer in DIW

- Polymer Composites
  - Fiber-reinforced polymer composites
    - anisotropic mechanical properties
    - providing higher stiffness along specific directions

Technique improvement

Technique improvement



- Hybrid Printing Systems
  - combining DIW with Digital Light Processing (DLP)

Technique improvement

- Resolution Enhancement and Real-Time Process Control
  - micron-scale features using nozzles as small as 0.5 µm
  - dynamically adjusting settings to improve precision and avoid defects

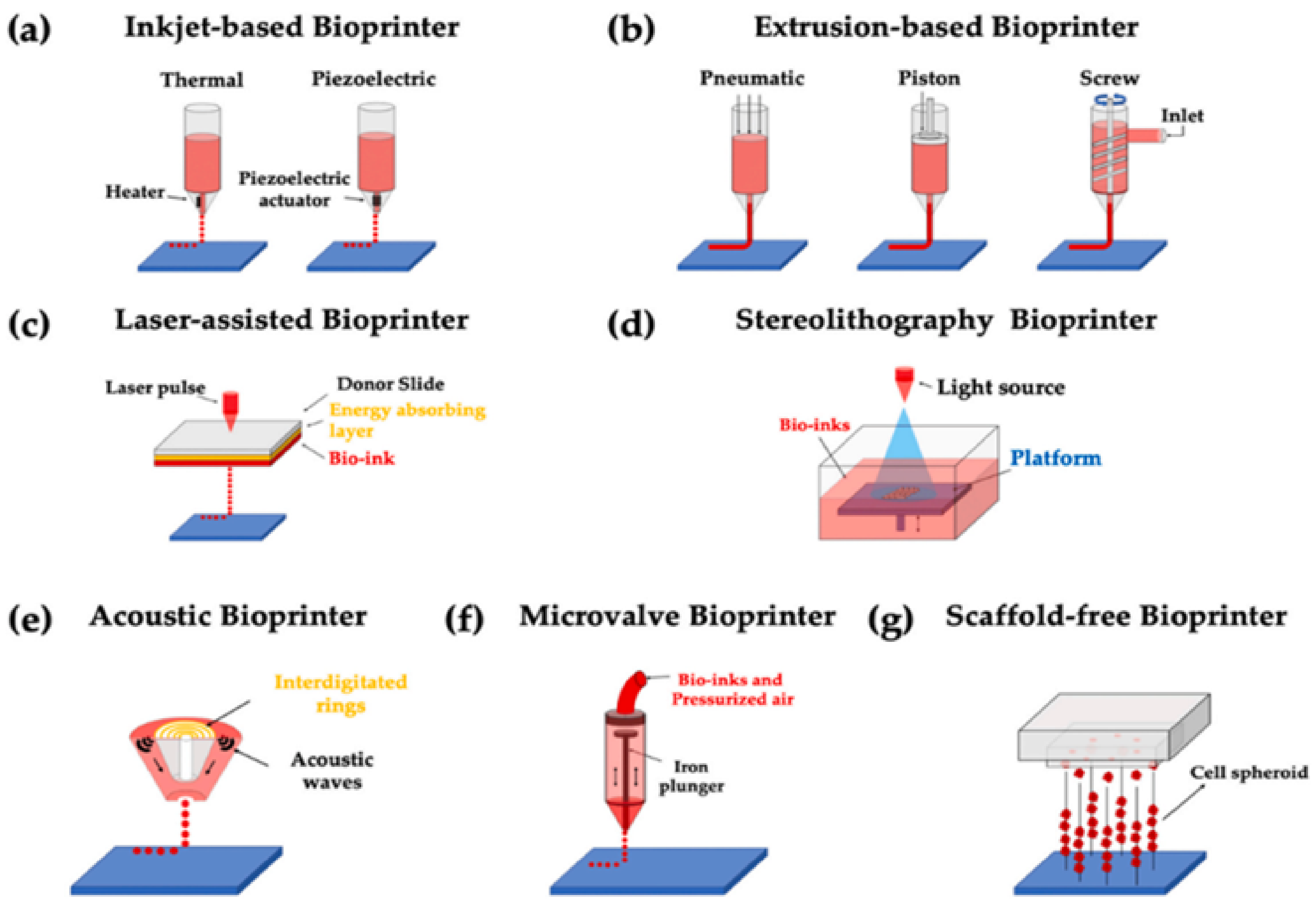
Technique improvement

- Multi-Scale and Multi-Material Printing
  - combining nozzles of different sizes
    - create structures that combine macro- and micro-level details
  - use multiple print heads simultaneously
    - facilitates the production of gradient or heterogeneous materials

Applications

Applications

- Biomedical Applications



Applications

- Environmental Applications
  - fabricate membranes and filters for water purification and wastewater treatment
  - create catalytic filters with embedded catalytic nanoparticles
- Flexible Electronics and Wearable Devices
  - printing conductive polymer inks with additives like carbon nanotubes or metallic nanoparticles
  - maintain functionality under bending and stretching

EPFL

Conclusion

- **Existing problems**
  - For polymer materials, they may be not as good as inorganic substance when high temperature and wear resistance are crucial
  - For AM process, reproducibility and precision still need improvement for mass production
- **Future perspective**
  - With the development of material science, polymers with better performance will be synthesized and applied in AM process, which broadens the potential of AM fabrication
  - New manufacturing technology like Multi-material printing is promising to produce multifunctional parts with better precision
  - The AI-supported manufacturing enables the optimization of process parameters, thus improving efficiency and precision

THANK YOU