Structural Integrity and Reliability of Advanced Materials obtained through additive Manufacturing

SIRAMMi

H2020-WIDESPREAD-2018

European Commission

1st Winter School on

Trends on Additive Manufacturing for Engineering Applications

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Review on AM of polymeric materials

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OUTLINE

1. INTRODUCTION & OBJECTIVES
2. BASIC CONCEPTS ON THE MECHANICS OF POLYMERS
3. AM TECHNOLOGIES FOR POLYMERS
4. AM PROCESS PARAMETERS IN POLYMERS
5. SELECTIVE LASER SINTERING (SLS): EXP/SIMULATIONS
6. PHOTOPOLYMERIZATION (SLA, DLP): EXP/SIMULATIONS
7. CONCLUSIONS

1. Introduction & Objectives

- Polymers are among the most diffused synthetic materials in modern applications.
- Their good mechanical properties, lightweight and low cost have enhanced their diffusion among the most diverse application fields.
- Their underlying microstructure provides a mechanical behavior mimicking that of biological materials (tissues, organs, etc.)
- They can be easily printed by using different technologies to obtain complex objects even at very small dimensional scale

- Understand the microstructure of a polymer
- Presents some basic concepts of the mechanics of polymers
- Illustrate the main AM technologies used for polymers
- Presents some in-depth aspects related to SLS (*selective laser sintering*) technology
- Presents some in-depth aspects related to SLA (*stereolithography*) technology

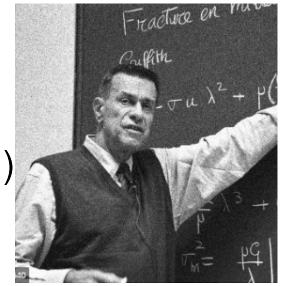
2. Basic concepts on the mechanics of polymers

Some concepts on the physics & mechanics of polymers

- Polymer microstructure
- Chains and cross-links
- Deformation of polymers
- Deformation Energy (entropic)

Paul Flory
Nobel prize in Chem. (1974)
For physical chemistry of macromolecules

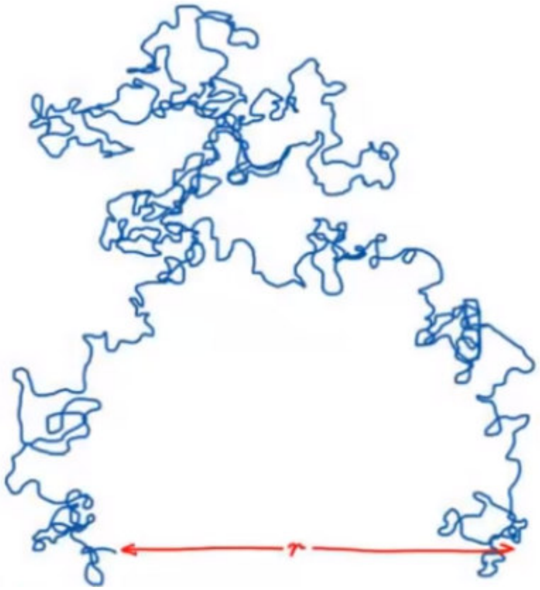
P.G. De Gennes
Nobel prize in Physics (1991)
For complex forms of matter, liquid crystals and polymers

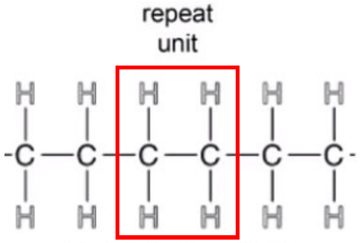


- P. Flory, *Principles of Polymer Chemistry*. Cornell University Press, 1954
- P. G.de Gennes; L. Leger, *Dynamics of Entangled Polymer Chains*. *Annu. Rev. Phys. Chem*. **1982**, 33 (1), 49–61
- M. Doi, *Introduction to polymer physics*, Oxford university press, 1996
- L. R. Treloar, *The Physics of Rubber Elasticity*. Oxford Univ. Press, 2005
- Treloar, L. R. (1974). The mechanics of rubber elasticity. In *Journal of Polymer Science: Polymer Symposia* (Vol. 48, No. 1, pp. 107-123). New York: Wiley Subscription Services, Inc., A Wiley Company.

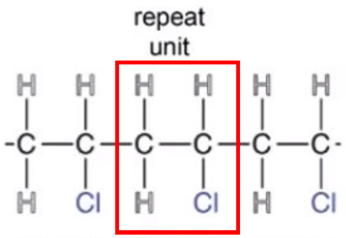
Poly **mer**
Many **Units**

Definition:

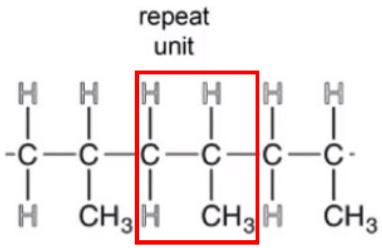




Polyethylene(PE)



Poly(vinyl chloride) (PVC)



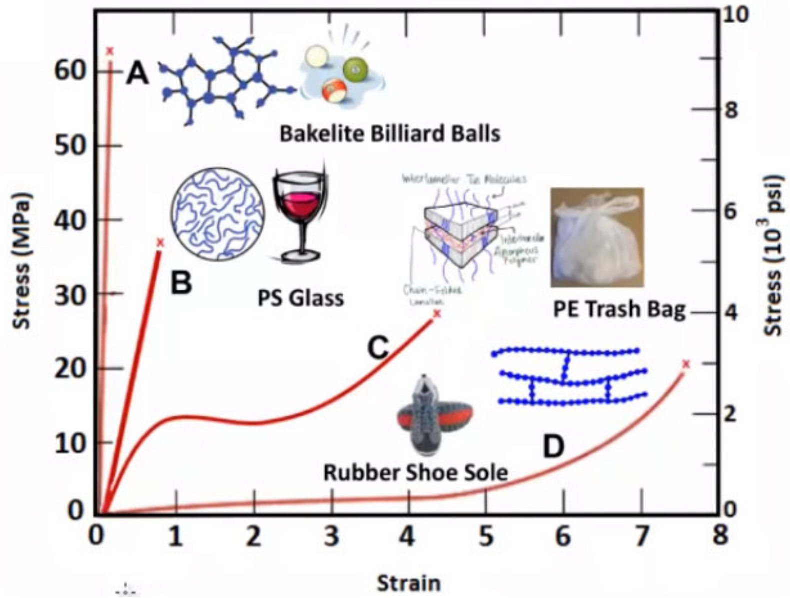
Polypropylene (PP)


PE Milk Container


PVC Pipe

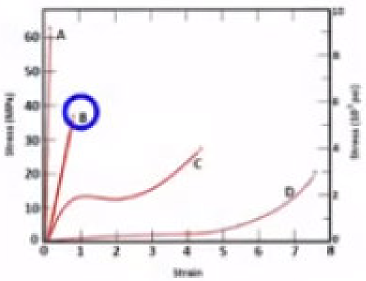

PP Rope

Polymer	E (MPa)	TS (MPa)	%EL
Natural Rubber	2.5	20	600-1000%
HDPE	830	28	300-600%
Polystyrene	3100	40	1.2-2.5%
Bakelite	6900	55	0.1%



Thermoplastic Polymers

Amorphous Polymer



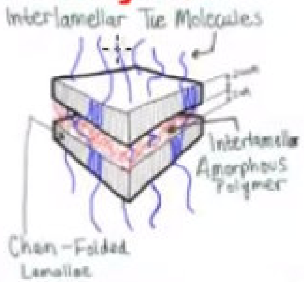
PS Glass

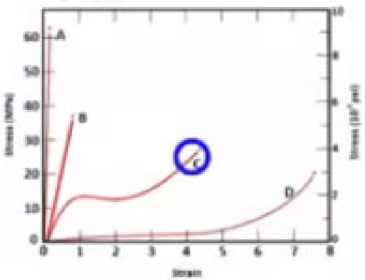
Tg = 100C

T25 < Tg

Glassy

Semicrystalline Polymer





PE Trash Bag

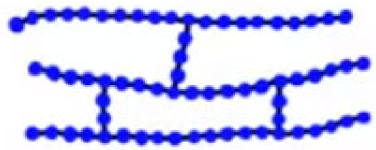
Tg = -90C; Tm = 130C

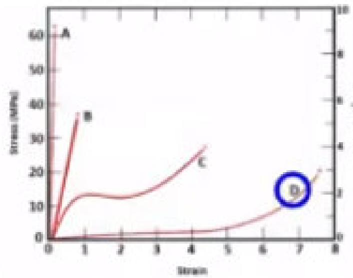
Tg < T25 < Tm

Flexible

Heat Set Polymers

Lightly X-linked Elastomer





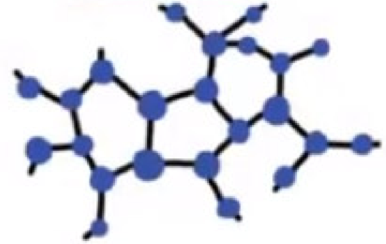
Rubber Shoe Sole

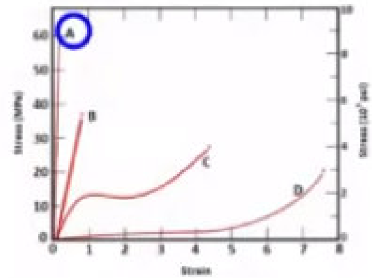
Tg = -103C

Tg < T25

Elastic

Heavily X-linked Thermoset





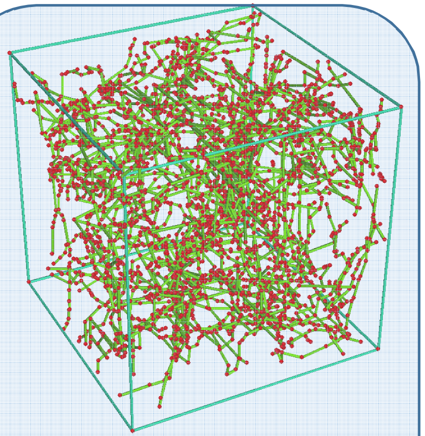
Bakelite Billiard Balls

Tg = 163C

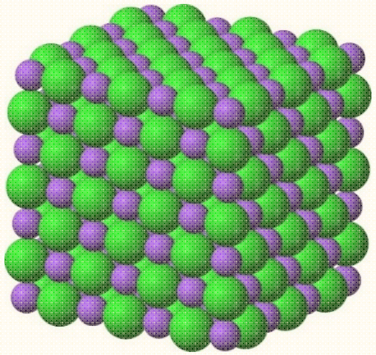
T25 < Tg

Rigid

Tg = Glass Transition Temperature, below which a polymer is rigid and brittle



Polymer network:
entropic elasticity



Crystalline material:
enthalpic elasticity

Polymer's structure:

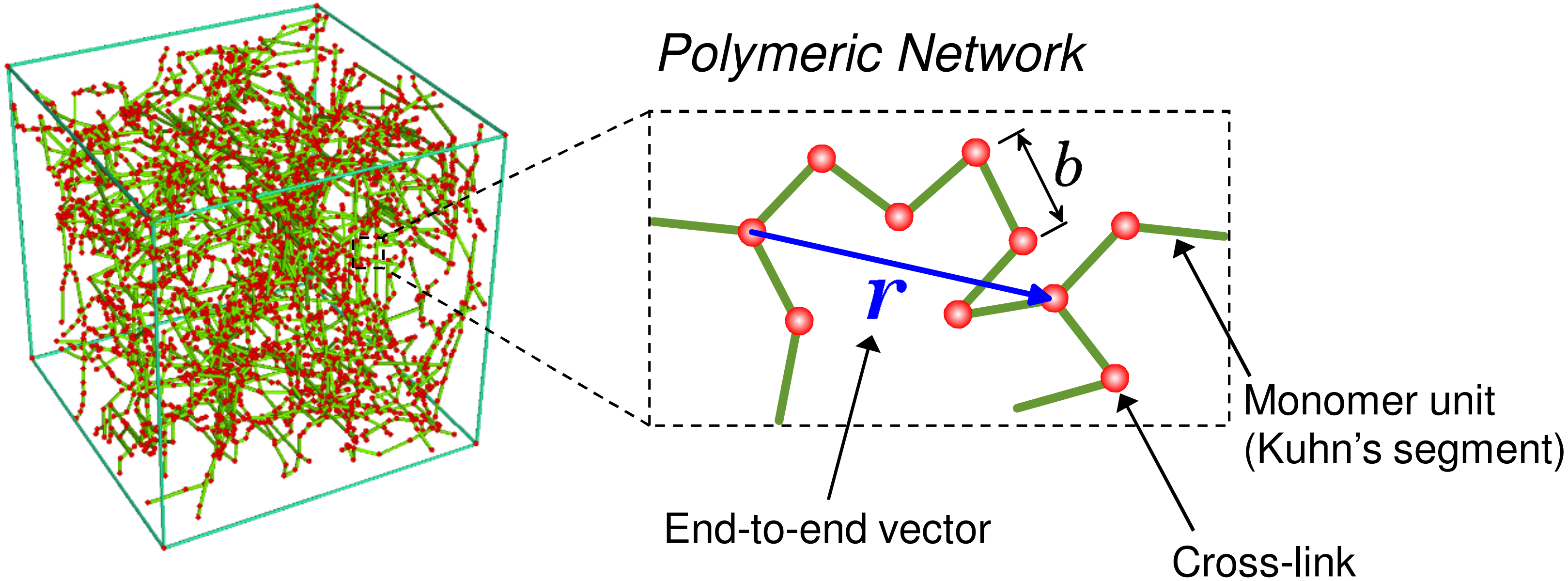
Network of long molecular chains linked together.

The mechanical behaviour is ruled by entropic energy ΔS

Polymers have a high fracture toughness due to the **high deformability** because of the **alignment capability of chains** in the tensile direction.

Mechanical response greatly depends on the **strain rate** because of the time-dependent phenomena occurring in the polymeric network.

Polymeric Network



$$\begin{cases} \boldsymbol{r} & = \text{current end-to-end vector} \\ \boldsymbol{r}_0 & = \text{reference end-to-end vector} \\ \boldsymbol{F} & = \text{deformation gradient tensor} \end{cases}$$

$$\Psi(\boldsymbol{F}) = -T \cdot \Delta S = \frac{1}{2} k_B T [\mathrm{tr}(\boldsymbol{F}^T \boldsymbol{F})^T - 3]$$

Fundamental relations in the mechanics of polymers:

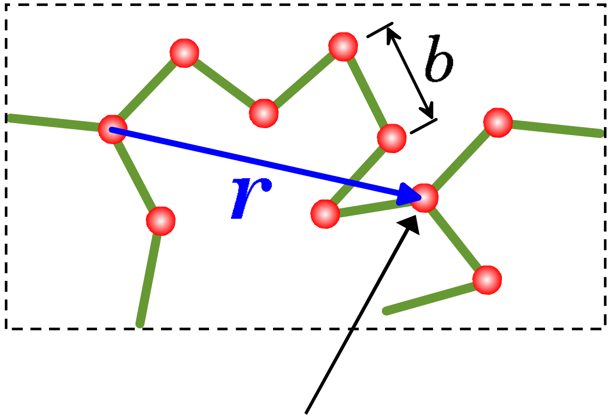
$G = n\, K_B T$ Shear modulus

$\nu = \sim 0.5$ Polymers are nearly incompressible

n = No. of chains per unit volume

K_B = Boltzmann constant

T = absolute temperature



Types of chain bonds:

- **Weak** physical bond
  (ionic, dipole bonds, H bonds, van der Waals)

  → thermoplastic polymers

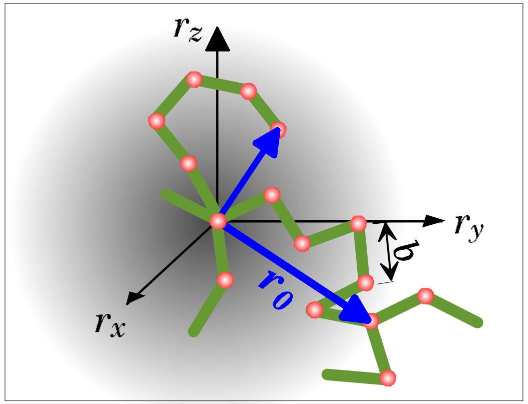
- **Strong** (covalent bond)

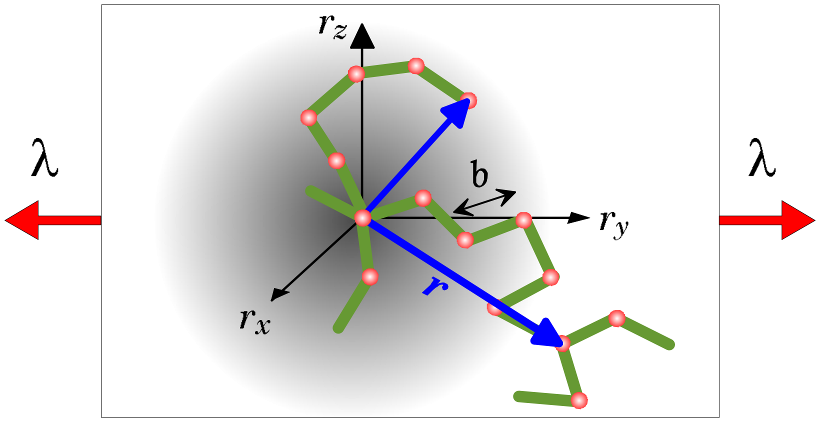
  → thermoset elastomer (coarse bonds)

  → thermoset polymers (dense bonds)

- Bergstrom, J.S. (2015). *Mechanics of solid polymers: theory and computational modeling*. William Andrew.
- Fakirov, S. (2017). *Fundamentals of polymer science for engineers*. Wiley-VCH.
- Rajagopal, K.R., Wineman, A. S. (2001). *Mechanical Response of Polymers: an introduction*. Cambridge University Press

Chain and polymer deformation





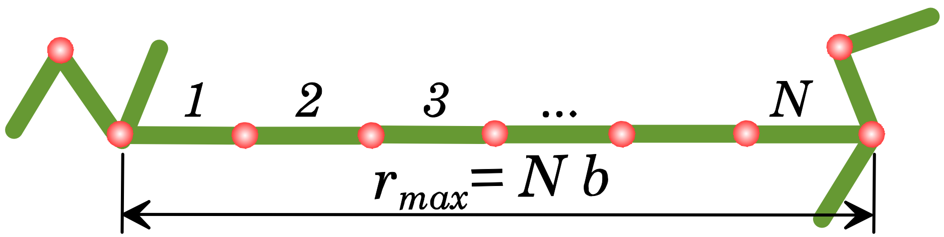
Mean end-to-end distance

$$r_0 = b\sqrt{N}$$

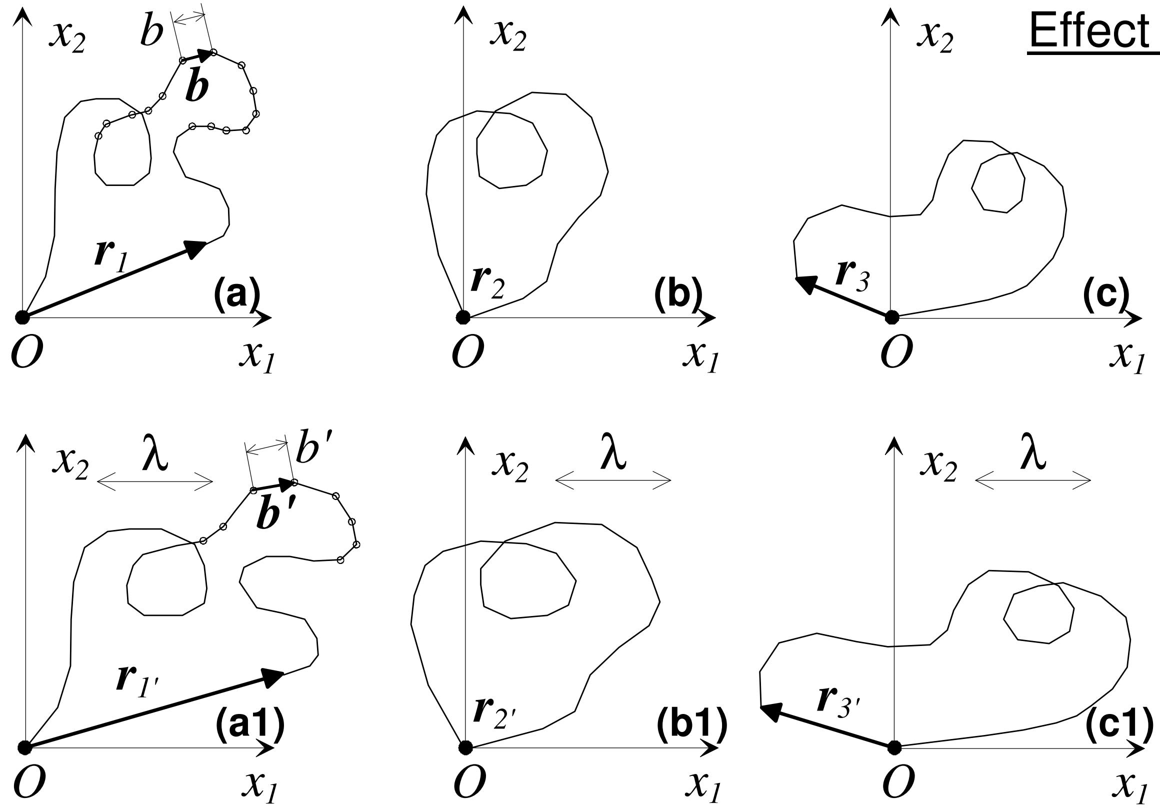
$$r = \lambda\, r_0 = \lambda\, b\sqrt{N}$$

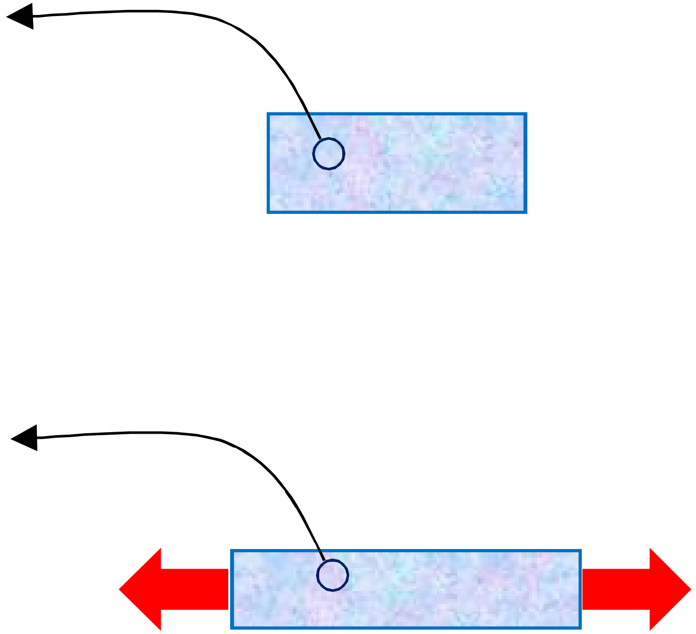
$$r_{max} = bN \rightarrow \lambda_{max} = \sqrt{N}$$

Max allowable stretch



Effect of stretch on chain conformation



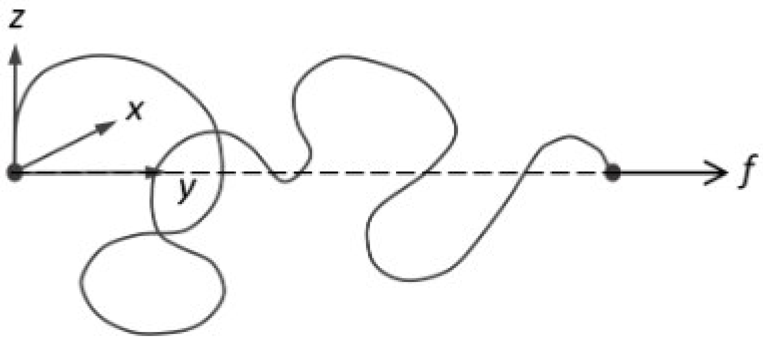


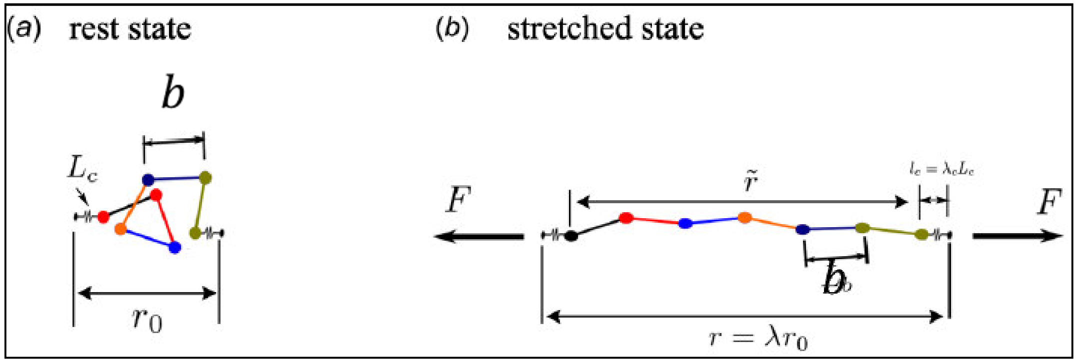
Work variation, related to the entropy of a single stretched chain:

$$\Psi(\mathbf{F}) = \tfrac{1}{2}\, k_B T \left[\mathrm{tr}(\mathbf{F}^T \mathbf{F}) - 3\right]$$

$$\Psi(\boldsymbol{\lambda}) = -T \cdot \Delta S = \tfrac{1}{2}\, k_B T \left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right]$$

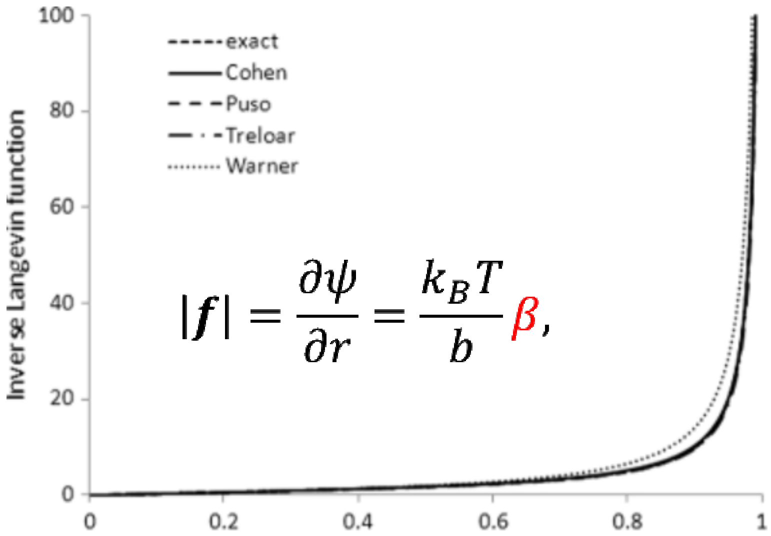
Chain stretch





$$\lambda_{max} = \sqrt{N}$$

Langevin statistics:



$$|f| = \frac{\partial \psi}{\partial r} = \frac{k_B T}{b} \beta,$$

$$\lambda / \lambda_{max}$$

$$\psi(r) = k_B T \left(\frac{r}{bN} \beta + \ln \frac{\beta}{\sinh \beta} \right),$$

$$\beta = \mathcal{L}^{-1} \left(\frac{r}{bN} \right)$$

$$\mathcal{L}(x) = \coth(x) - x^{-1}$$

3. AM TECHNOLOGIES FOR POLYMERS

AM processes for polymers

CATEGORY	1 powder bed fusion	2 vat photopolymerisation	3 material extrusion	4 material jetting	5 binder jetting	6 sheet lamination
DENOMINATIONS	SLS - Selective Laser Sintering SHS - Selective Heat Sintering MJF - Multi Jet Fusion	SLA - Stereolithography DLP - Digital Light Processing DLS - Digital Light Synthesis	FDM - Fused Deposition Modeling FFF - Fused Filament Fabrication	PolyJet MJM - Multi-Jet Modeling	3DP - 3D Printing	LOM - Laminated Object Manufacture SFP - Solid Foil Polymerisation
STATE	powder	liquid	solid	liquid	powder	solid
MATERIALS	polyamides, PEEK, polypropylene (PP), polycarbonate (PC), polystyrene (PS), thermoplastic elastomers (TPE)	epoxy or acrylic photopolymers	polylactic acid (PLA), ABS, PC	acrylic photopolymers	polycaprolactone (PCL), polyvinyl alcohol (PVA), PLA	PMMA, PVC
PRINCIPLE	selective fusion and solidification	light reactive photopolymer curing	extrusion of melted material and solidification	jetting of melted material and solidification / UV curing	consolidation through binder	lamination through thermal or chemical bonding

For a comprehensive review on AM of polymers see:

J Mater Sci (2021) 56:961–998

Review

Check for updates

Laser-based additively manufactured polymers: a review on processes and mechanical models

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182 up-to-date references!

Classification of AM categories according to ASTM

1) powder bed fusion
   AM process in which thermal energy selectively fuses regions of a powder bed
2) vat photopolymerization
   AM process in which liquid photopolymer in a vat is selectively cured by light-activated polymerization
3) material extrusion
   AM process in which material is selectively dispensed through a nozzle or orific
4) material jetting
   AM process in which droplets of build material are selectively deposited and solidified
5) binder jetting
   AM process in which a liquid bonding agent is selectively deposited to join powder materials
6) sheet lamination
   AM process in which sheets of material are bonded and selectively cutted to form a part

ISO/ASTM 52900:2015(E)

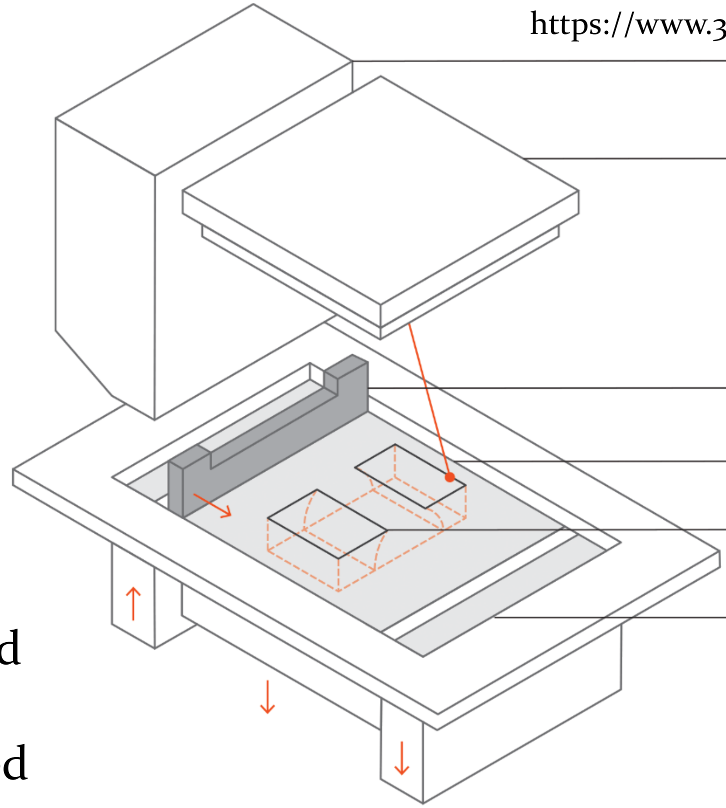
Standard Terminology for Additive Manufacturing – General Principles – Terminology[1,2]

6 categories for polymeric materials

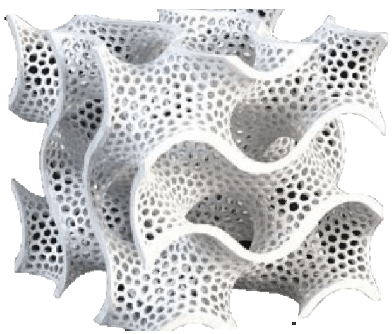
1) Powder bed fusion

raw material form: powder
principle: selective fusion and solidification
resolution: 50-100 μm
printed materials:
polyamides, polystyrene, PEEK, thermoplastic elastomers

https://www.3dhubs.com

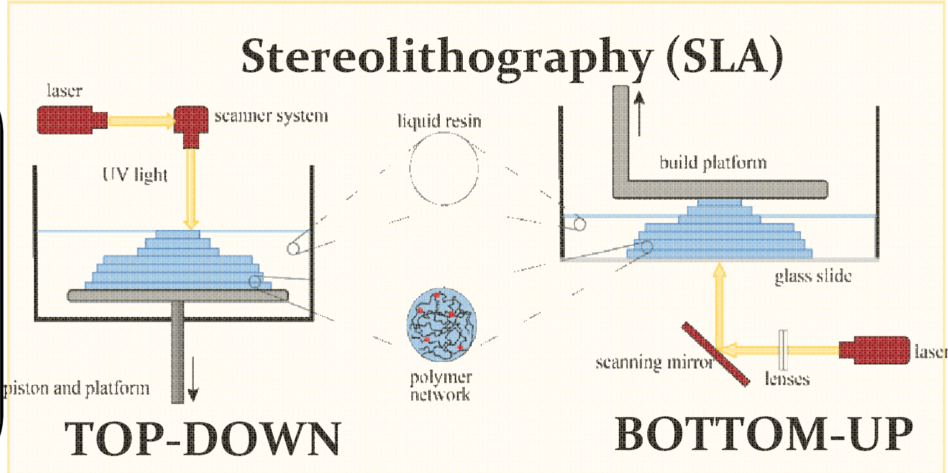


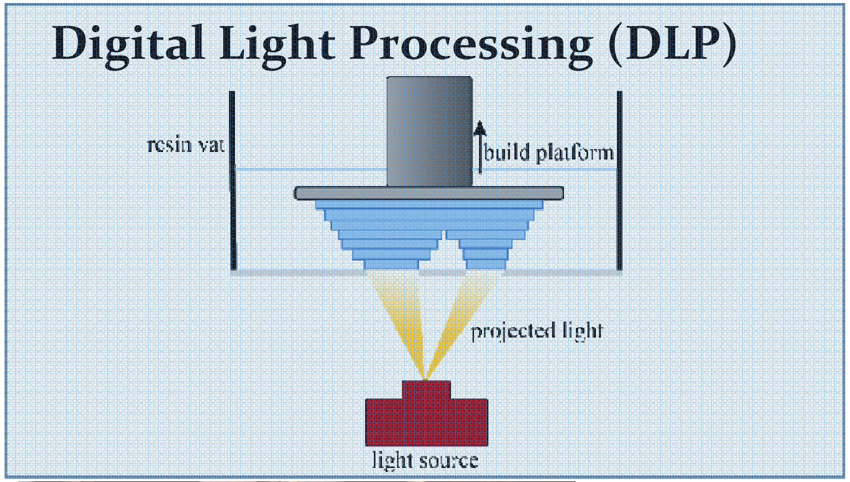
- comprises Selective Laser Sintering (SLS) and MultiJet Fusion
- particles are heated and then selectively fused by a moving laser scan
- advantages: good mechanical properties, low anisotropy
- disadvantages: porosity, rough surfaces

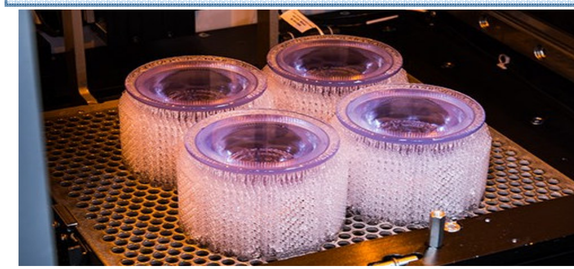


2) Vat photopolymerization

raw material form: liquid
principle: polymerization through light
resolution: 10-30 μm
printed materials:
Epoxy or acrylic photopolymers



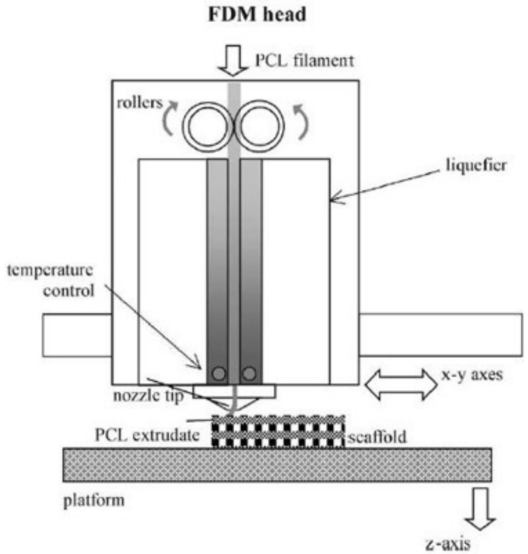


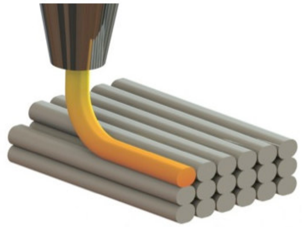


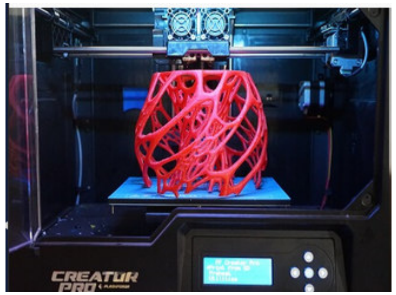
- a liquid resin initially placed in a vat is selectively irradiated and solidified (cured)
- based on two main technologies: Stereolitography (a moving laser solidifies a layer) and Digital Light Processing (a layer is solidified in one shot)
- advantages: fast, extremely high resolution, allows multi-material AM
- disadvantages: post-treatment needed, expert users requiring, liquid resin manipulation

3) Material extrusion

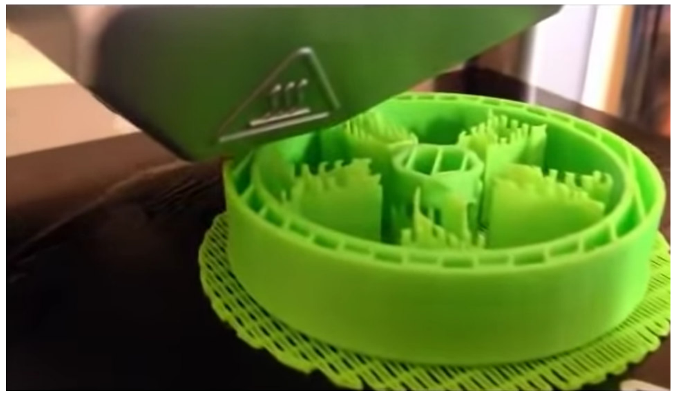
raw material form: solid
principle: extrusion of melted material and solidification
resolution: 200 μm
printed materials: polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC)







- the 3DP machine contains a plastic wire spool feeding a print head (nozzle) which extrudes thin filament of melted plastic
- mainly known with two acronyms (equivalent techniques): Fusion Deposition Modelling (FDM) and Fused Filament Fabbrication (FFF)
- advantages: lower cost, accessibility (even house-machine)
- disadvantages: slow, poor resolution, high anisotropic components

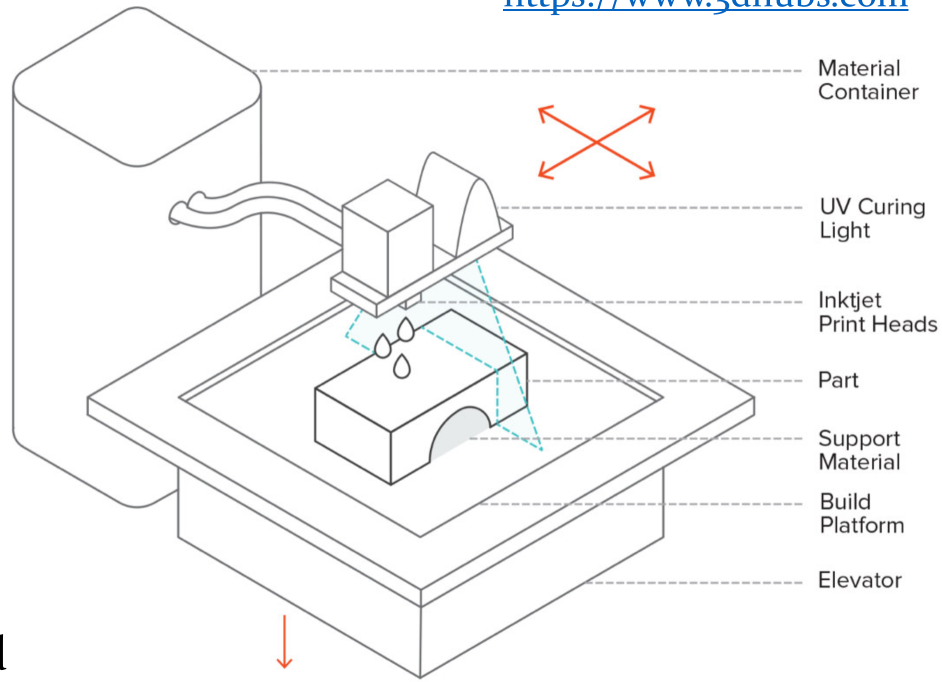


https://www.youtube.com/watch?v=ik39_sv-wgQ

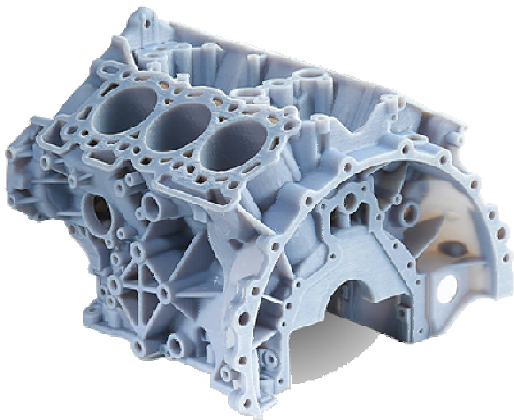
4) Material jetting

https://www.3dhubs.com

raw material form: liquid
principle: thermal solidification or UV curing
resolution: 25 μm
printed materials:
acrylic photopolymers



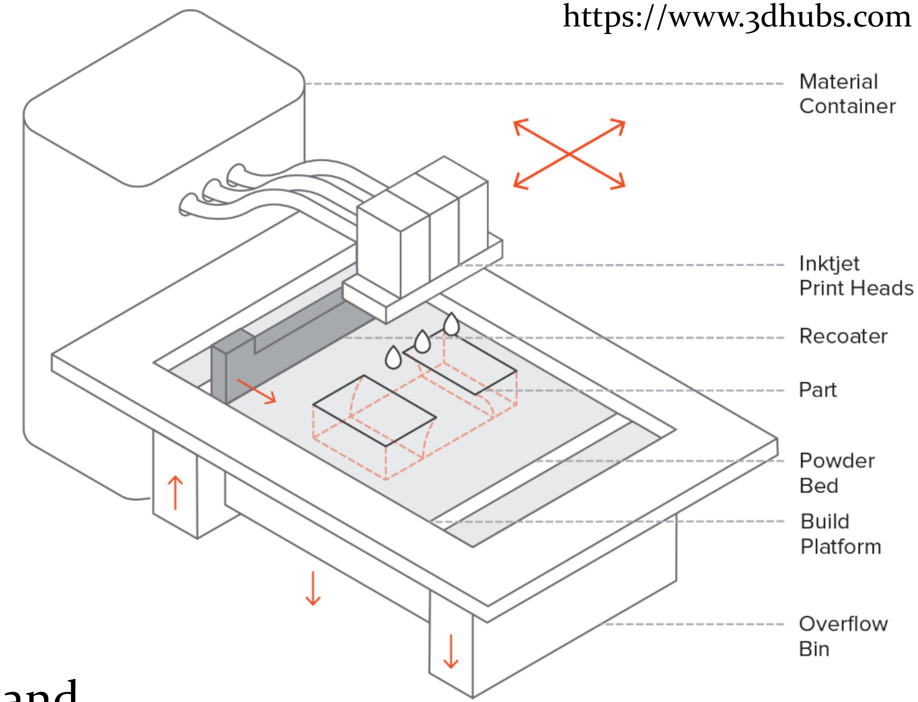
- comprises thermal inkjet and inkjet-based lithography (PolyJet and MultiJet Modelling)
- heated droplets of photopolymer are deposited and cured by a UV light source
- advantages: fast, allows multi-material AM, high accuracy, homogeneous materials
- disadvantages: limited strength, photosensitive parts, high cost



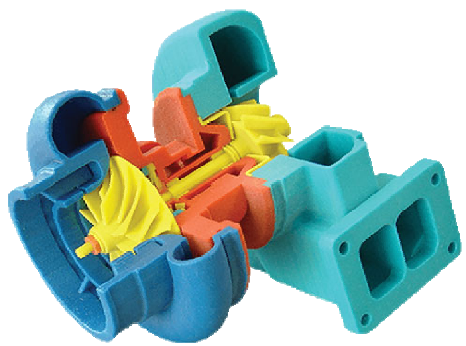
5) Binder jetting

https://www.3dhubs.com

raw material form: powder
principle: consolidation through binder
resolution: 100 μm
printed materials:
polylactic acid, polycaprolactone, polyvinyl alcohol, PMMA

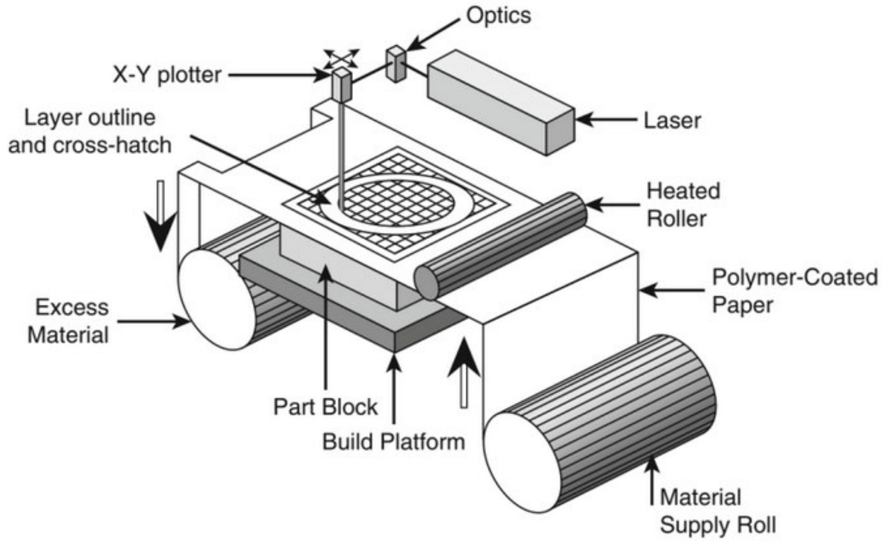


- also known as 3D printing
- powder layers are spread over the platform and a liquid ink then bonds or fuses the particles
- advantages: fast, allows multi-material AM, room temperature binding, no support
- disadvantages: limited strength, rough surfaces, limited material selection



6) Sheet lamination

raw material form: solid
principle: deposition of sheet material with adhesives and successive laser cutting
resolution: 200-300 μm
printed materials: actually not enough diffused in polymers (more metals)



- material bonded with adhesive layer-by-layers and cutted with the required shape
- two basic technologies: laminated object manufacturing (LOM) and ultrasonic additive manufacturing (UAM)
- advantages: low temperature, no phase change, no support needed
- disadvantages: not so widespread, limited materials, poor resolution, high anisotropic components, waste of material

4. AM PROCESS PARAMETERS IN POLYMERS

To print a certain component with one of the previously shown AM techniques, we have to correctly set the process parameters.

Aim of design in AM:

1. **Choice of the AM process to print the desired component;**
2. **Decision of the optimuum combination of the process parameters (of those involved in the chosen AM process) which provide a component with the desired characteristics**

depending by the final application of the component itsfelf

- Load bearing capacity (mechanical properties);
- Surface quality;
- Hardness and wear performance;
- Designed porosity (example in bio-printing, scaffolds etc.);

Here we focus on the mechanical properties

How mechanical properties of the final AM material are influenced by the raw material used and by the printing parameters?

Issue: how mechanical properties of the printed component are related to AM process parameters?

The majority of the existing studies

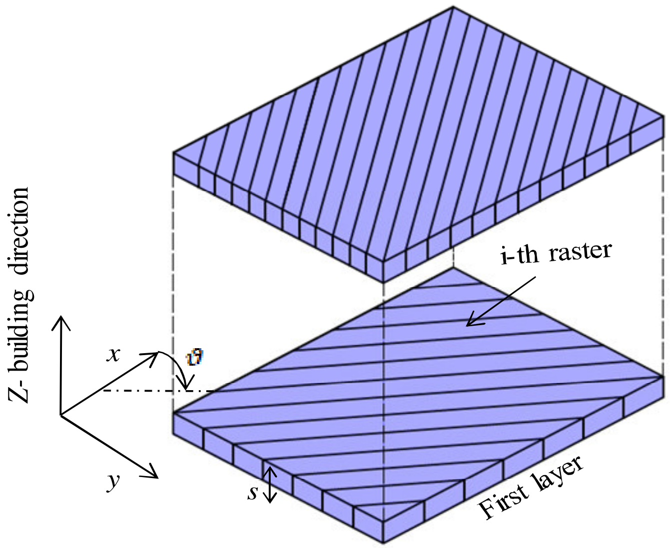
- **Experimental approaches or statistical simulation-based**
  - Help to visualize AM parameters – mechanical properties trend
  - Fail to accurately predict mechanical properties
  - Not able to explain the reason of such differences

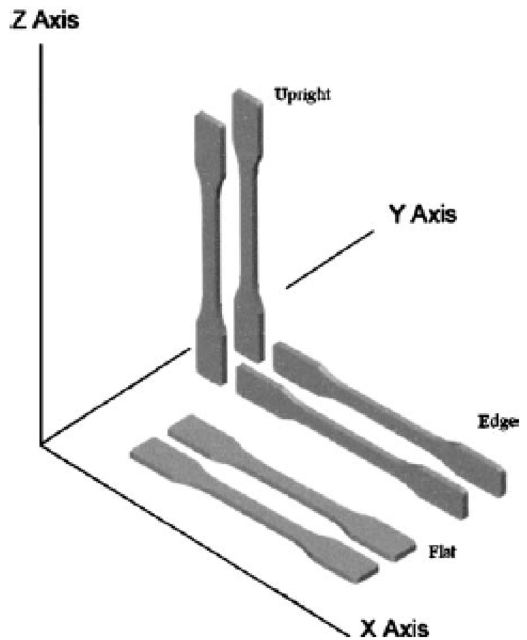
Recently proposed studies

- **Engineering approaches based on a mathematical formulation**
  - Should provide quantitative prediction of the mechanics behaviour
  - Able to explain the understanding of a certain mechanical behavior in relation to a specific process parameter to improve performance of AM component in a more targeted way
  - "Tool" in the office for rapid prediction (experimental tests reduction)

AM process parameters

- Common to different AM processes
  - Layer thickness
  - Raster orientation
  - Building orientation
- Specific for an AM process, examples:
  - Nozzle temperature (FDM)
  - Laser energy irradiated (SLA and SLS)
  - Powder particle size (SLS)

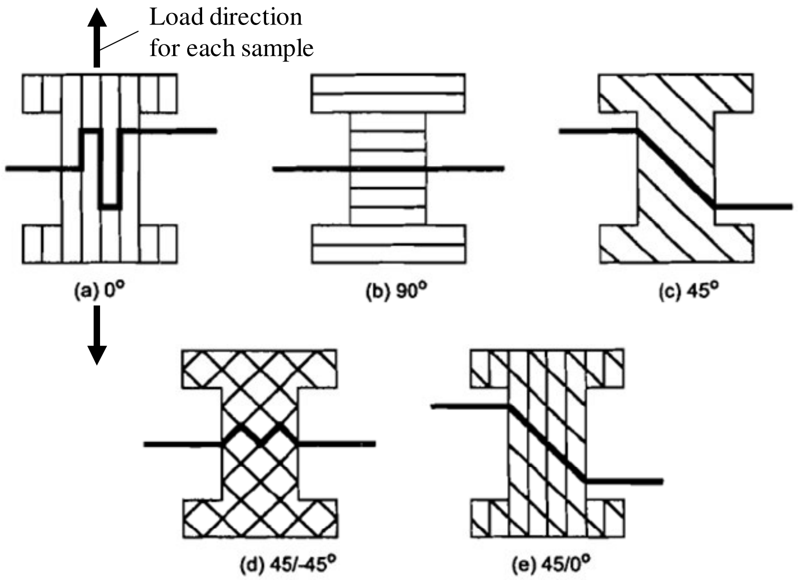




Fusion Deposition Modeling (FDM)

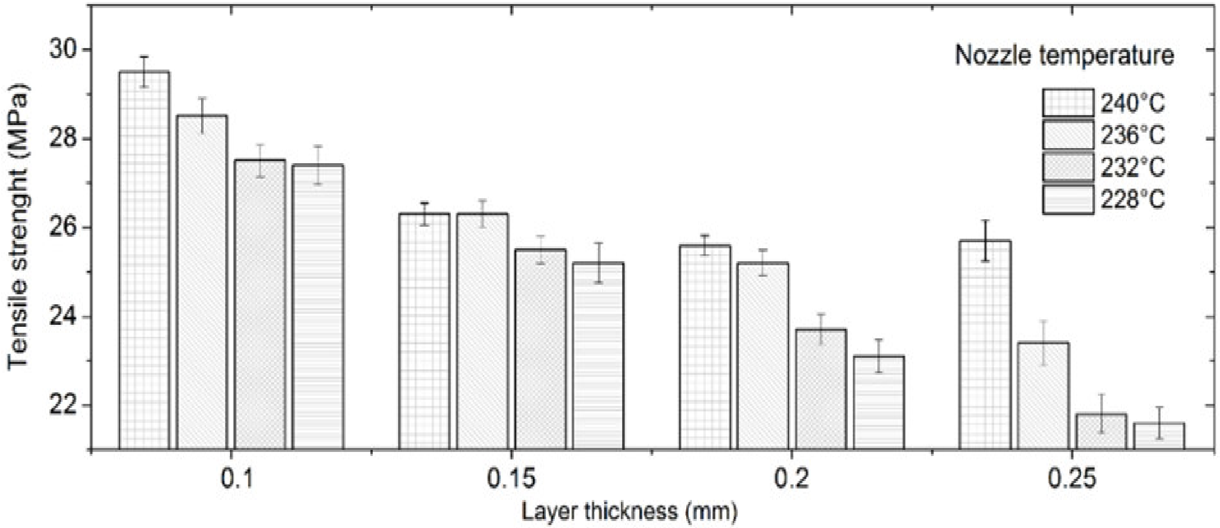
- Raster orientation

Schematic representation of rupture geometry on ABS samples printed with FDM process by varying only raster orientation



Es-Said, O. S. *Materials and Manufacturing Processes* **2000**, *15*(1), 107-122

- Layer thickness
- Nozzle temperature



Maloch, J. In: *Materials Science Forum* **2018** (Vol. 919, pp. 230-235).

Binder jetting (3D printing)

- powder properties
  - particle diameter ($d > 5\ \mu$m)
  - particle shape (spherical is better)
- binder
  - type (acqueous vs non-acqueous ink)
  - saturation
  - properties (viscosity, surface tension)
- post-processing treatments
  - infiltrations with resins
  - sintering or cold pressing

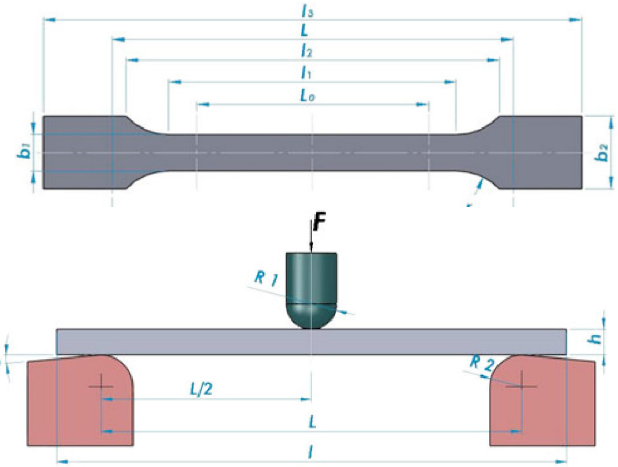
⇨ spreading, pore size, surface roughness, resolution

↑ large particles ensure easier spreading

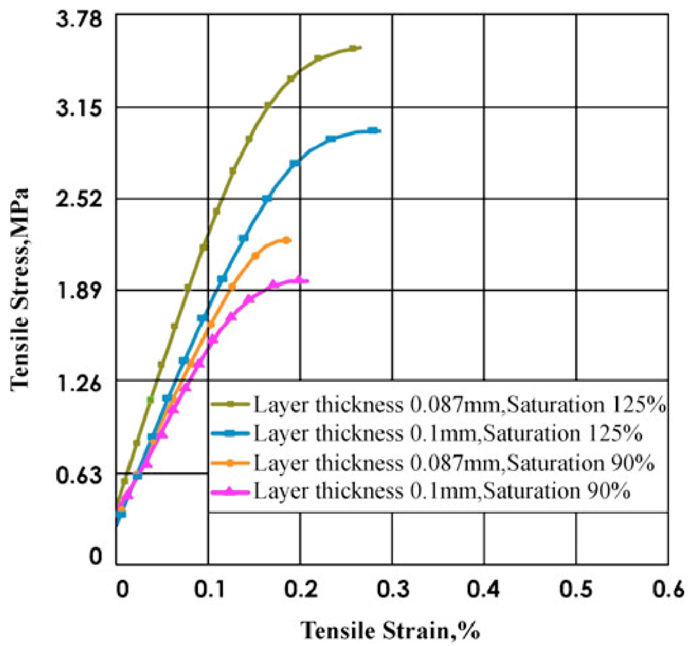
↓ small particles ensure increased resolution and reduced roughness

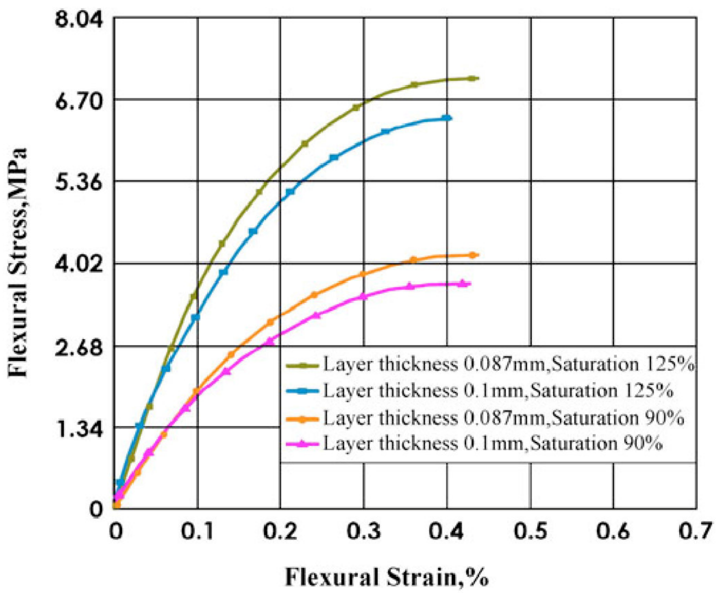
Binder jetting (3D printing)

- effect of increased layer thickness:
  - better surface uniformity
  - reduced tensile strength
  - decreased flexural strength
- effect of increased binder saturation:
  - increased tensile and flexural strength



Vaezi, M. *Int. J. Adv. Manuf. Technol.* **2011**, *53*, 275-284

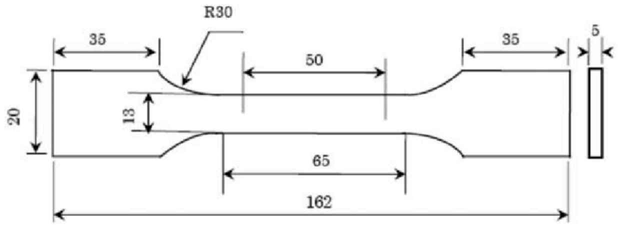


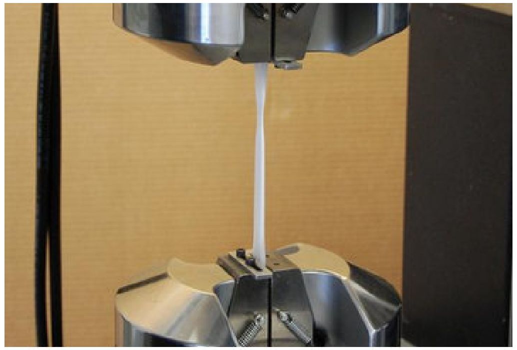


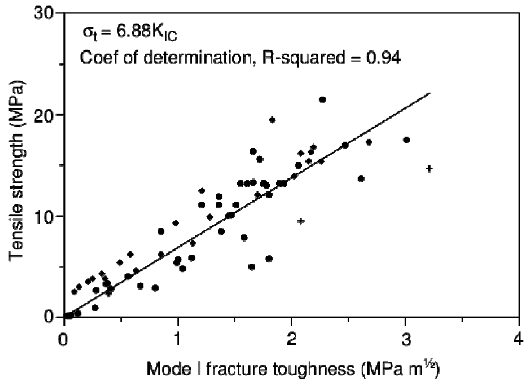
SIRAMM H2020-WIDESPREAD-2018 European Commission

ENGINEERING APPROACHES TO THE DESIGN OF LASER-BASED AM POLYMERIC MATERIALS

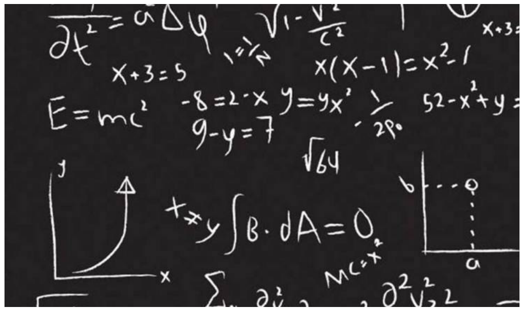
1) Experiments

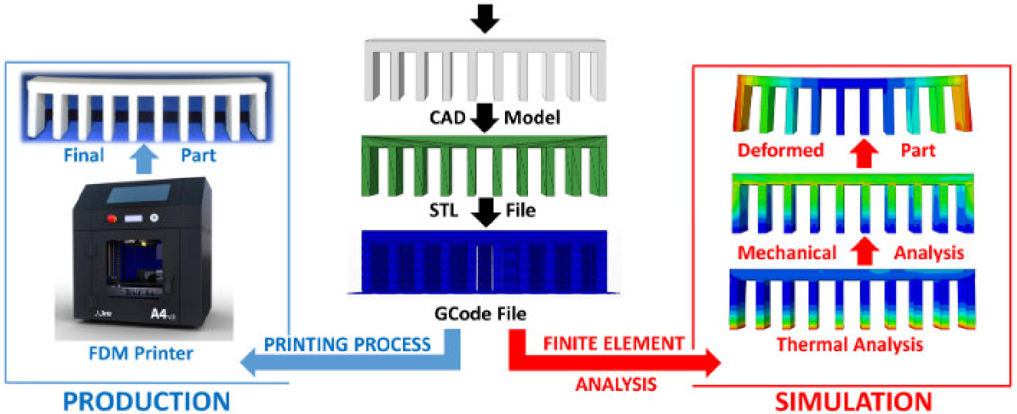






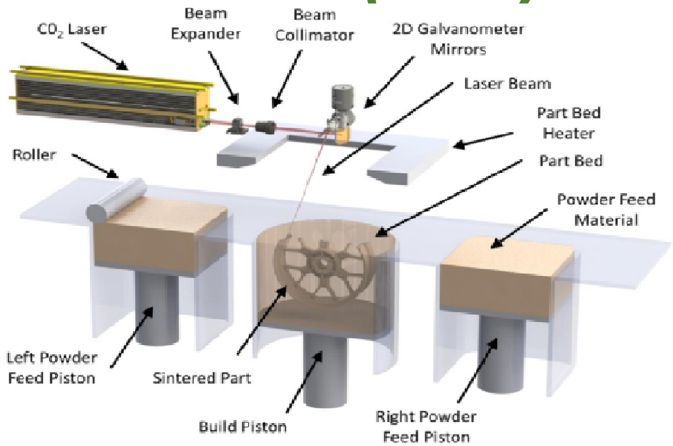
2) Simulations

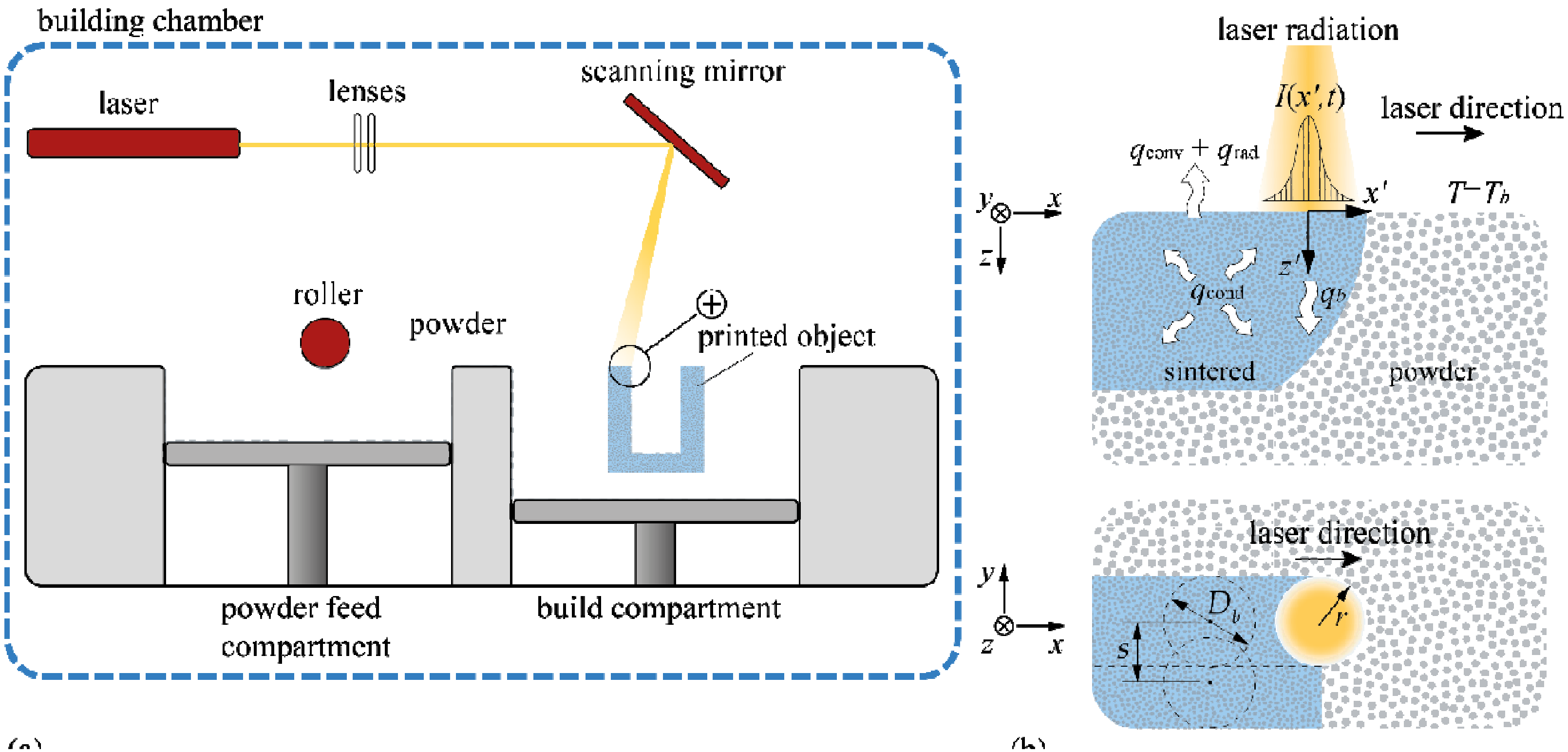


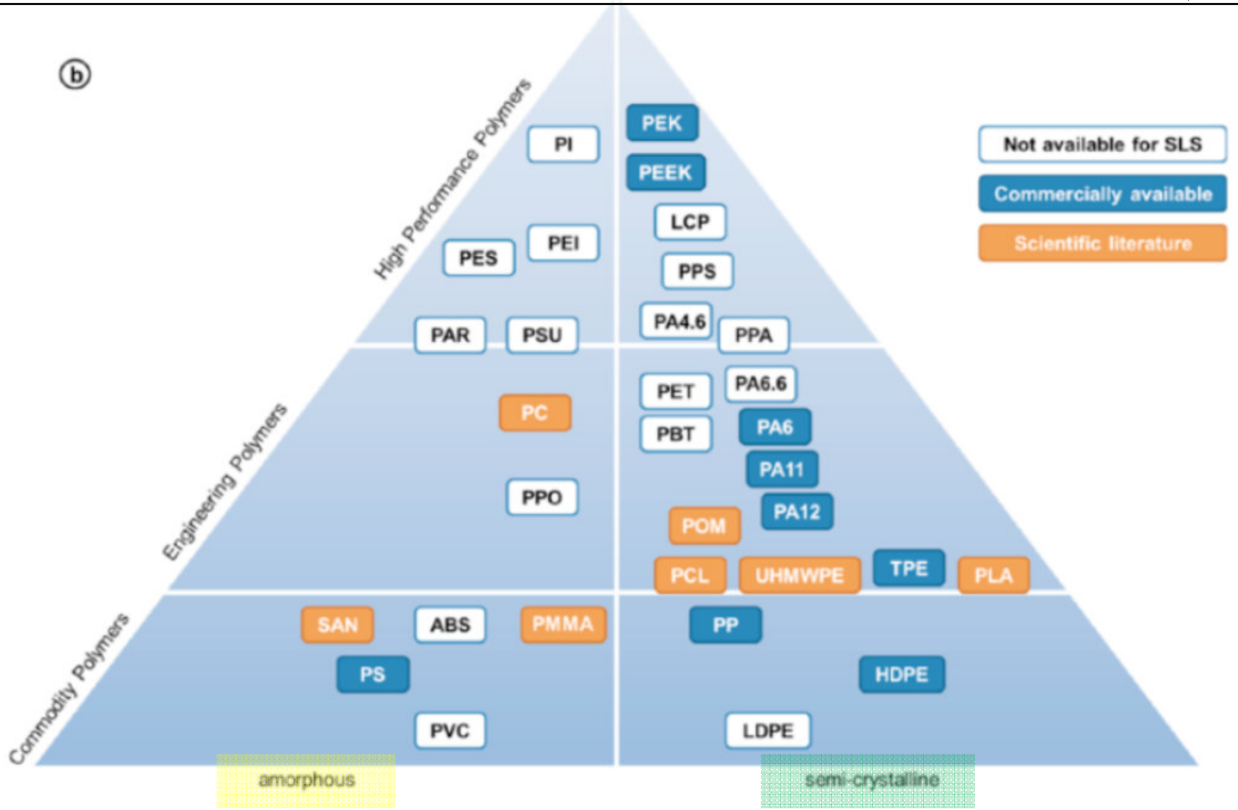


A brief illustration on these approaches is reported in the following slides for as concerning selective laser sintering (SLS) and photopolymerization (SLA) processes

5. Selective Laser Sintering (SLS): Exp/Simulations







Amorphous

PS: Polystyrene; SAN: Styrene acrylonitrile; PMMA: Poly-methyl methacrylate; PC: Polycarbonate.

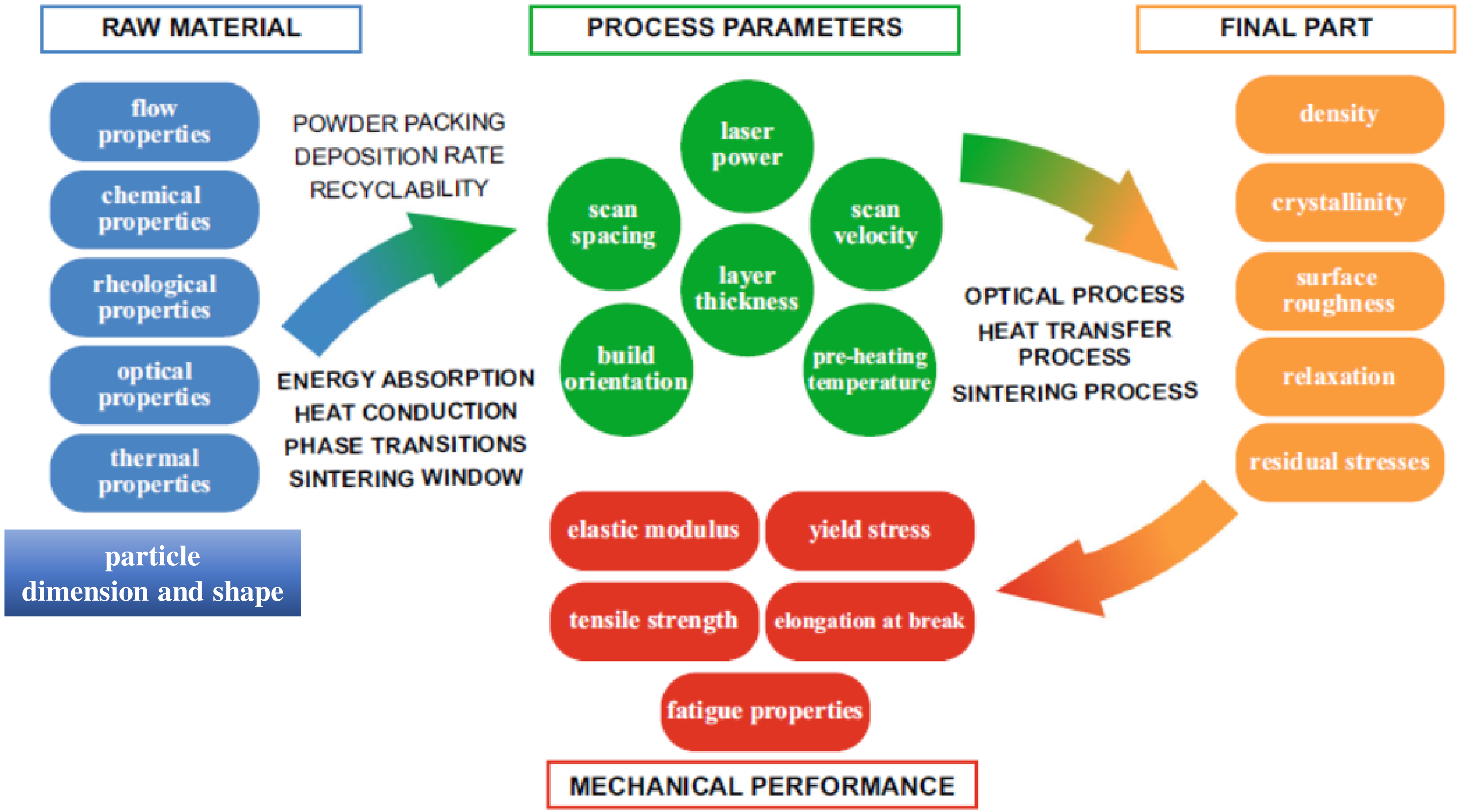
Not available for LS: PVC: Polyvinyl chloride; ABS: Acrylonitrile Butadiene Styrene; PPO: Polyphenylene oxide; PSU: Polysulfone; PES: Polyethersulfone; PEI: Polyetherimide; PI: Polyimide.

Semicrystalline

HDPE: High Density Polyethylene; PP: Polypropylene; PA*n*: Polyamide-*n*; PLA: Polylactic acid; UHMWPE: Ultra-high-molecular-weight polyethylene; PCL: Polycaprolactone; POM: Polyoxymethylene; PEEK: Polyether ether ketone; PEK: Polyetherketone.

Not available for LS: LDPE: Low Density Polyethylene; PBT: Polybutylene terephthalate; PET: Polyethylene terephthalate; PPA: Polyphthalamide; PPS: Polyphenylene sulfide; LCP: Liquid-crystal polymers.

1) Experiments



1) Experiments

Definition of energy density

surface energy density $E_s = \frac{P}{sv}$ (P – laser power, s – scan spacing, v – scan velocity)

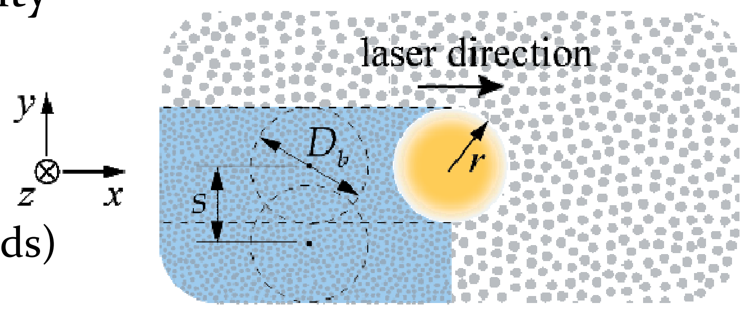
or

$E_s = \frac{P}{sv} OL$, overlay $OL = D_b/s$ (D_b – laser diameter)

volumetric energy density $E_v = \frac{P}{svd}$ (d – layer thickness)

Pilipović, A. *Adv. Mech. Eng.* **2014**, *6*(1), 648562

- positive correlation of energy density with density and mechanical properties



optimal energy density ⇨ increased part density
low energy density ⇨ incomplete sintering (voids)
high energy density ⇨ thermal degradation

1) Experiments

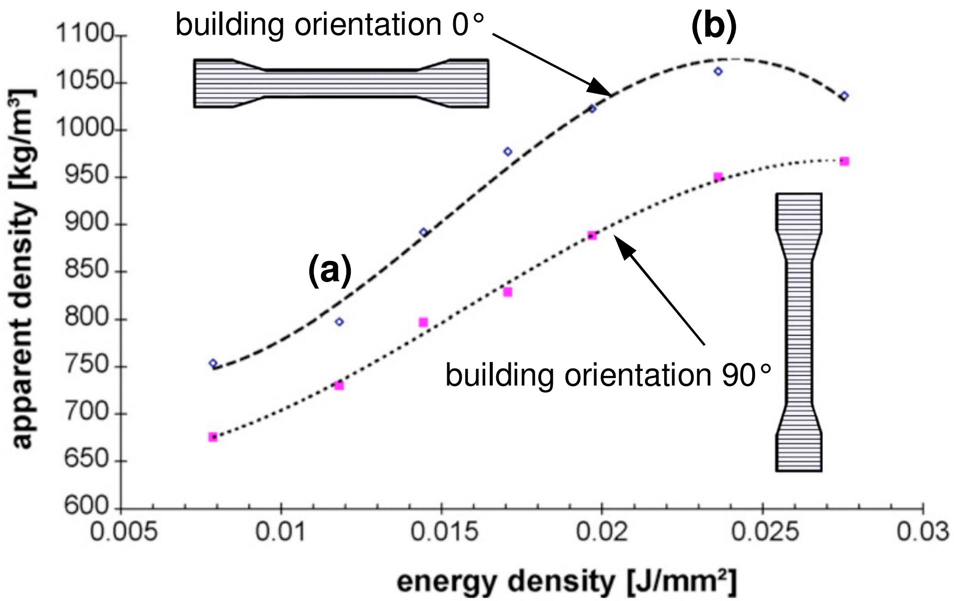
Effect of energy density on part density

void fraction, gas density

apparent density

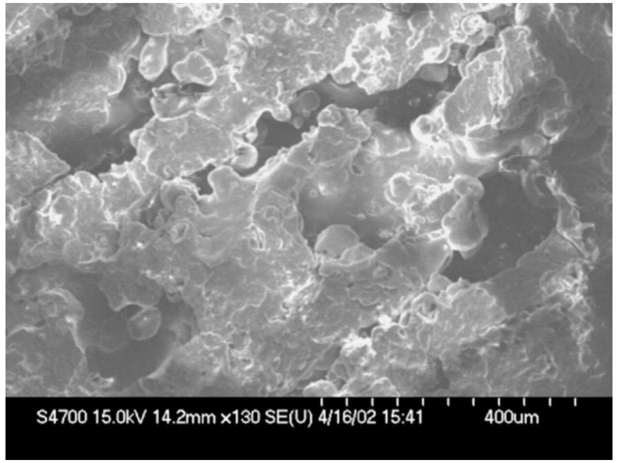
$$\rho = (1-\phi)\rho_S + \phi\rho_G$$

solid density

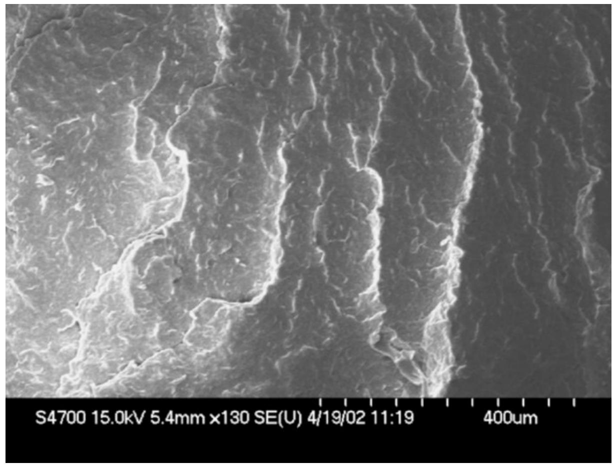


material: polyamide 12 (DuraForm PA)
scan spacing s = 0.15 mm
scan velocity v = 5080 mm/s

(a) $E_s = 0.012$ J mm^{-2}



(b) $E_s = 0.024$ J mm^{-2}



Caulfield, B. *J. Mater. Process. Technol.* **2007**, *182*(1-3), 477-488

1) Experiments

Effect of energy density on mechanical behaviour

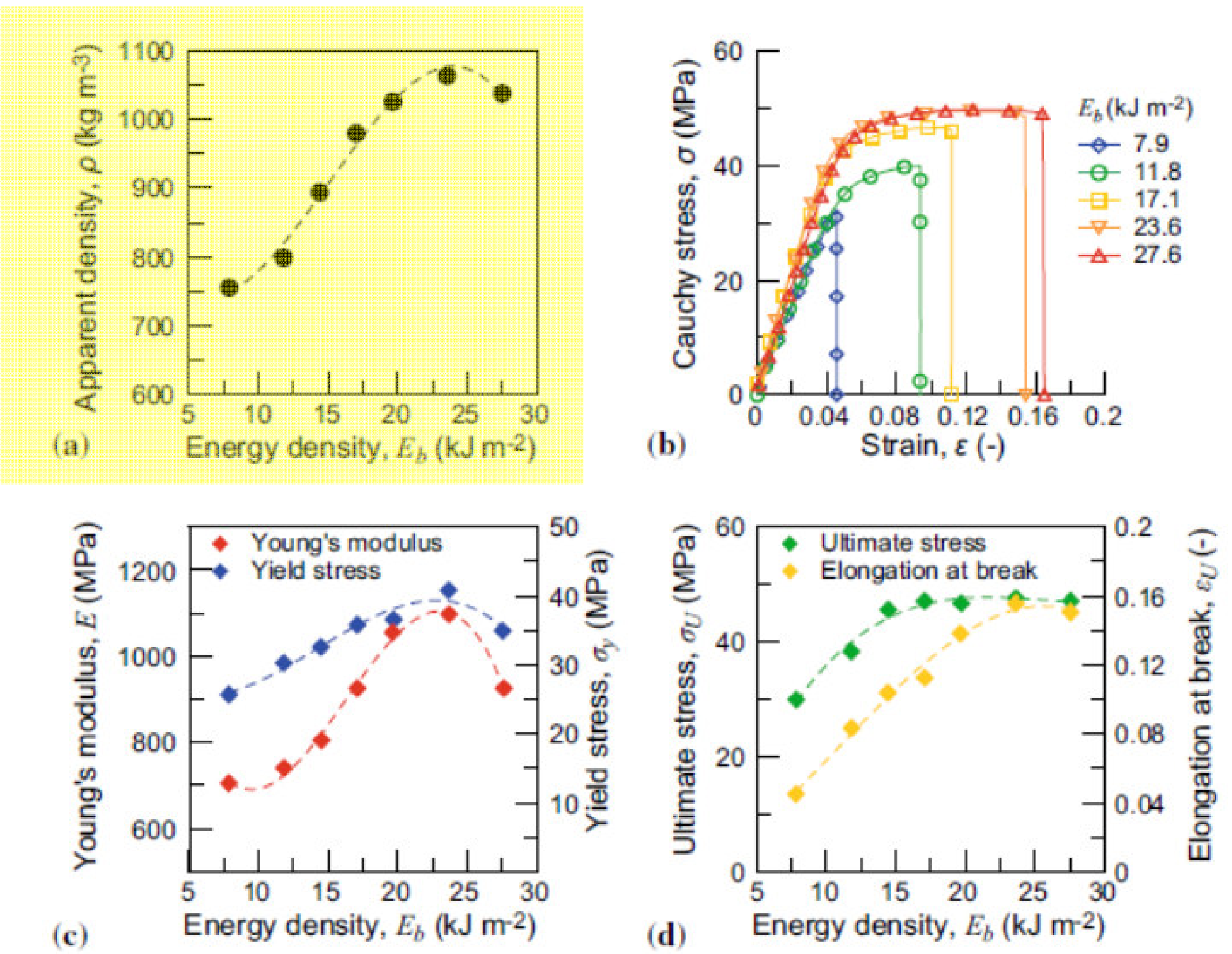
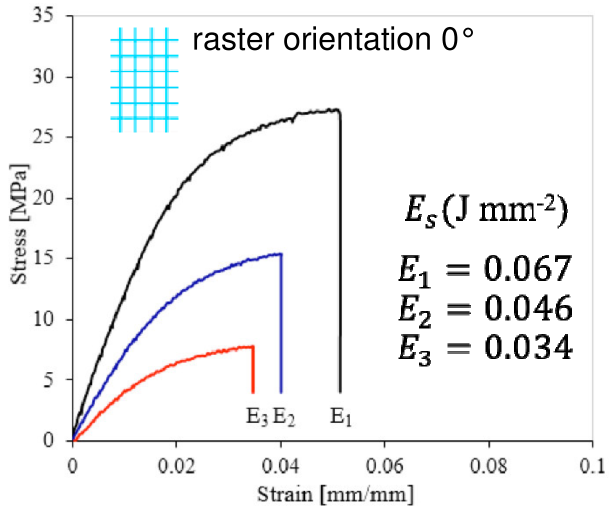
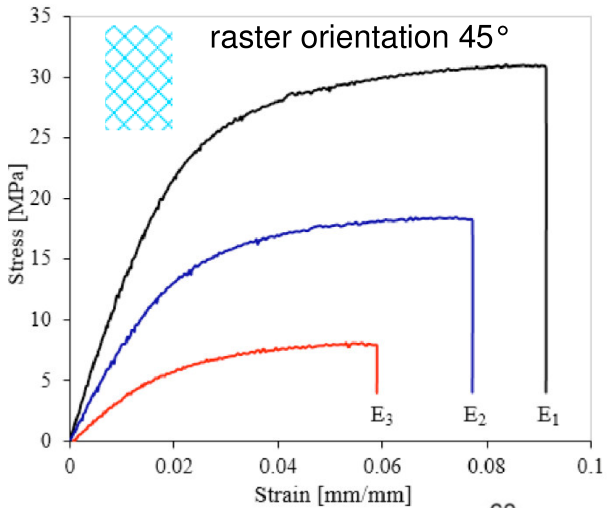


Figure 3 Dependence of the mechanical properties of printed samples on the surface energy density E_b. **a** Apparent part density. **b** Stress–strain curves. **c** Young's modulus and yield stress. **d** Ultimate stress and elongation at break (from uniaxial tension experiments, parallel to build orientation). Material is PA12 (P = var., $v_b = 5.1\,\mathrm{ms}^{-1}$, $s = 150\,\mu\mathrm{m}$). Adapted from [48].

1) Experiments

Effect of energy density on mechanical behaviour

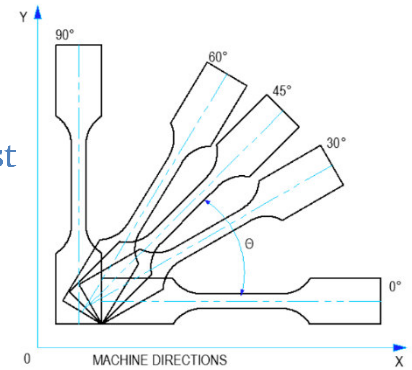




Stoia, D.I. *Polymers*. **2019**, *11*(11), 1850

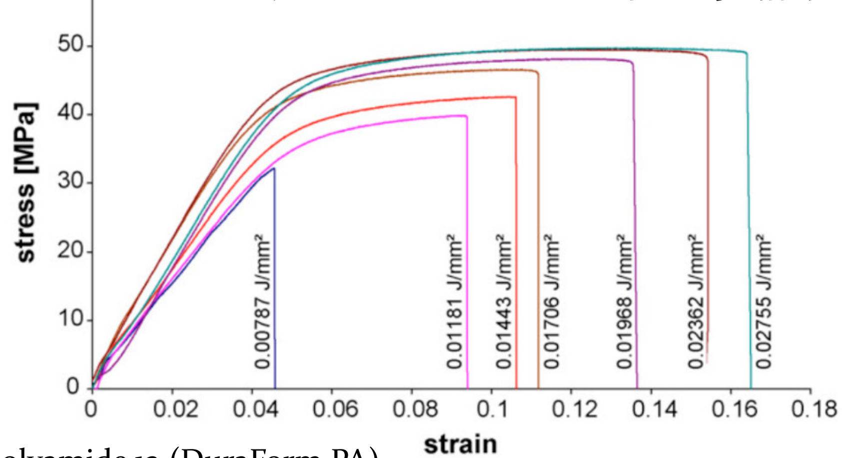
- in general, we observe a positive correlation between energy density and the mechanical behaviour, in terms of increased stiffness and ductility

uniaxial tensile test



material: polyamide 12 (PA2200)
scan spacing s = 0.25 mm
scan velocity v = 1500-2500 mm/s

Caulfield, B. *J. Mater. Process. Technol.* **2007**, *182*(1-3), 477-488



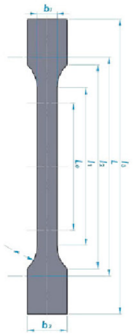
material: polyamide 12 (DuraForm PA)
scan spacing s = 0.15 mm
scan velocity v = 5080 mm/s

1) Experiments

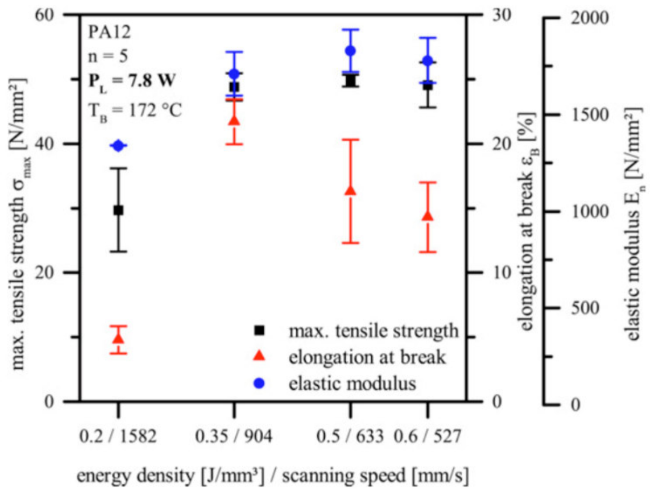
Effect of energy density on ultimate properties

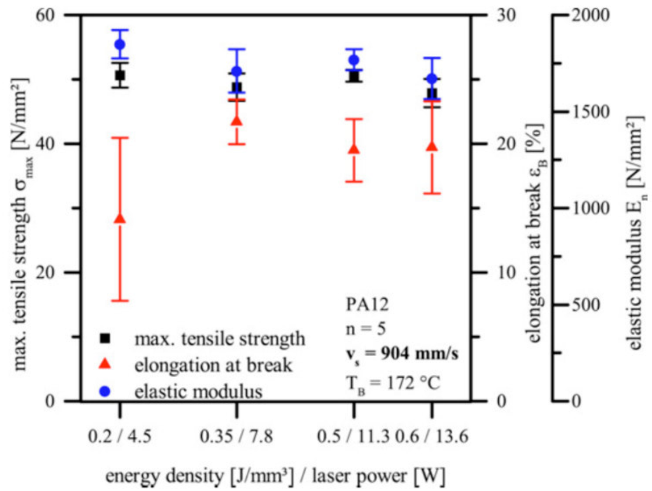
Drummer, D. *Phys. Procedia*. **2014**, *56*, 176-183

uniaxial tensile test

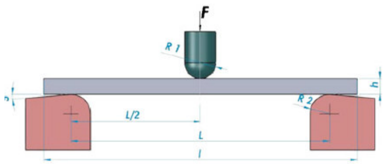


material: polyamide 12 (PA2200)
scan spacing *s* = 0.25 mm
scan velocity *v* = 527-1582 mm/s



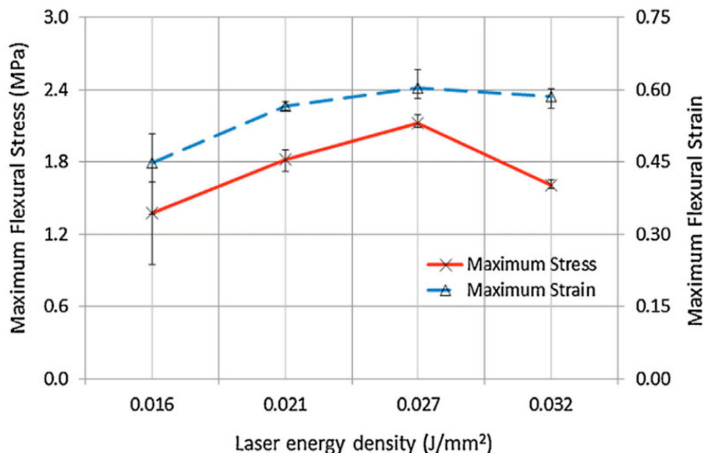


three-point bending test



material: UHMWPE
scan spacing *s* = 0.15 mm
scan velocity *v* = 2500 mm/s

Khalil, Y. *Addit. Manuf.* **2016**, 10, 67-75



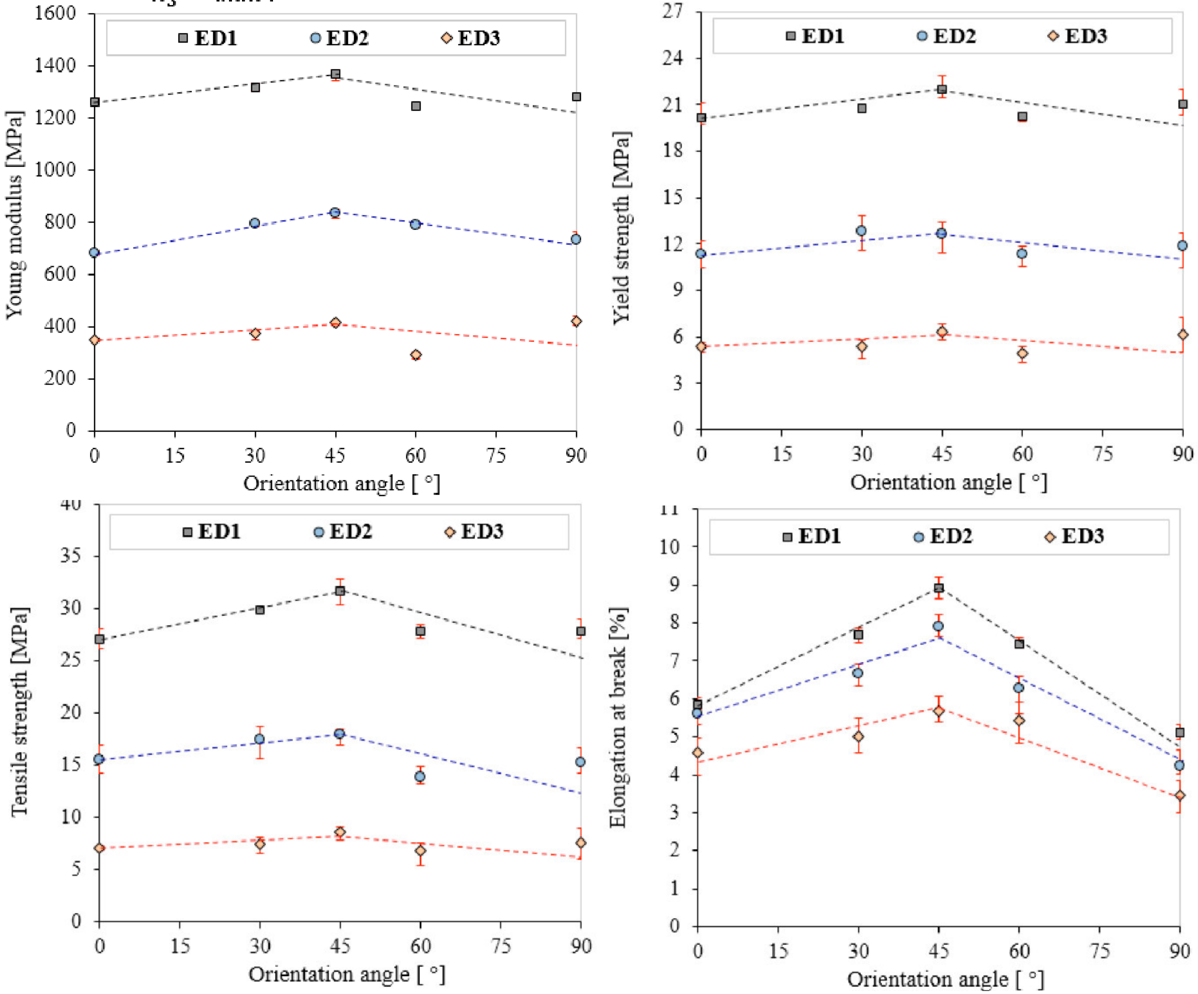
- ultimate properties, such as maximum tensile strength, elongation at break and flexural strength are deeply affected by energy density because of the different part density

1) Experiments

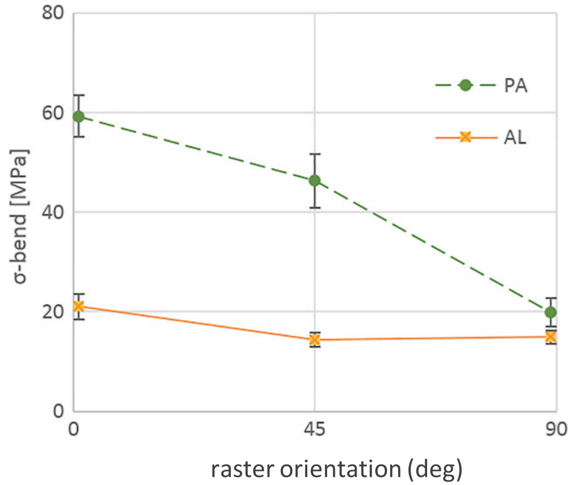
Effect of raster orientation on mechanical properties

E_s(J mm^{-2}) $E_1 = 0.067$ $E_2 = 0.046$ $E_3 = 0.034$

uniaxial tensile test



three-point bending test



Marsavina, L. *Mater. Des. Process. Commun.* **2020**, *2*(1), 1-5

material: polyamide 12 (PA2200)
scan spacing s = 0.25 mm
scan velocity v = 2000 mm/s

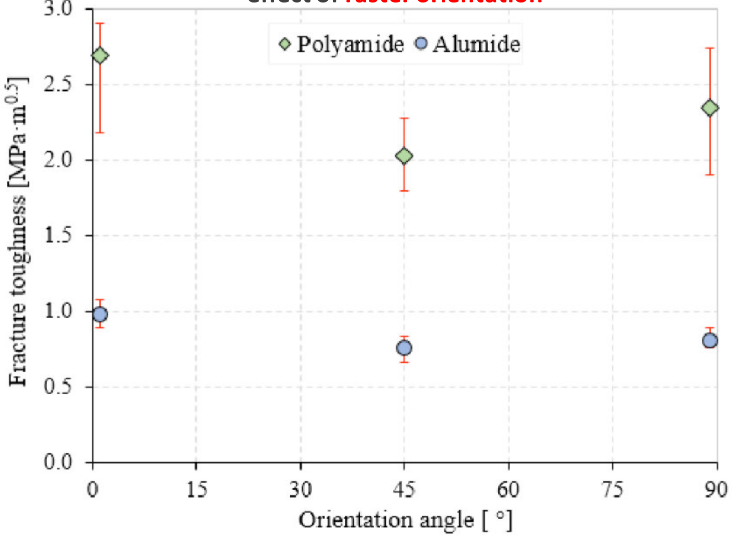
Stoia, D.I. *Polymers*. **2019**, *11*(11), 1850

material: polyamide 12 (PA2200)
scan spacing s = 0.25 mm
scan velocity v = 1500-2500 mm/s

1) Experiments

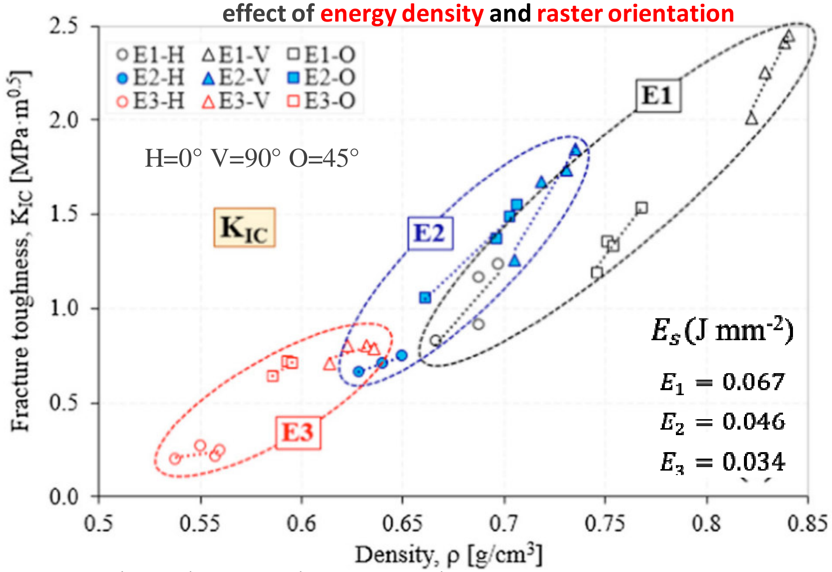
Effect of process parameters on fracture properties

effect of raster orientation



Stoia, D.I. *Polymers*. **2020**, *12*(3), 640

effect of energy density and raster orientation

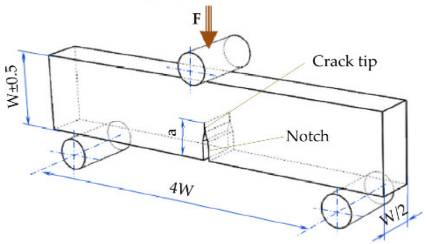


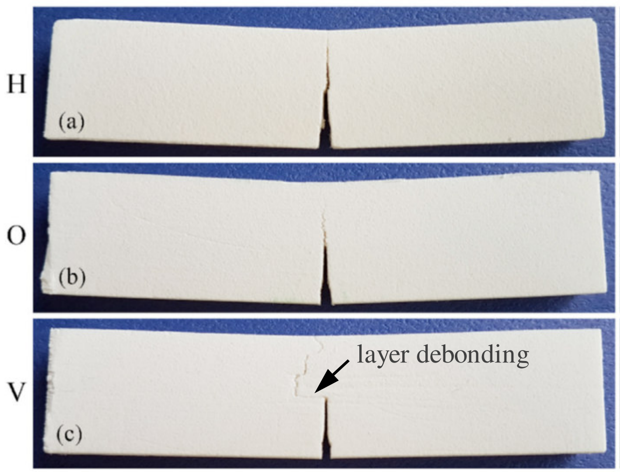
Linul, E. *Theor. Appl. Fract. Mech.* **2020**, *106*, 102497

material: polyamide 12 (PA2200)
scan spacing s = 0.25 mm
scan velocity v = 1500-2500 mm/s

fracture toughness (three-point bending)

$$K_{IC} = \frac{F_{crt}}{BW^{0.5}} f\left(\frac{a}{W}\right)$$



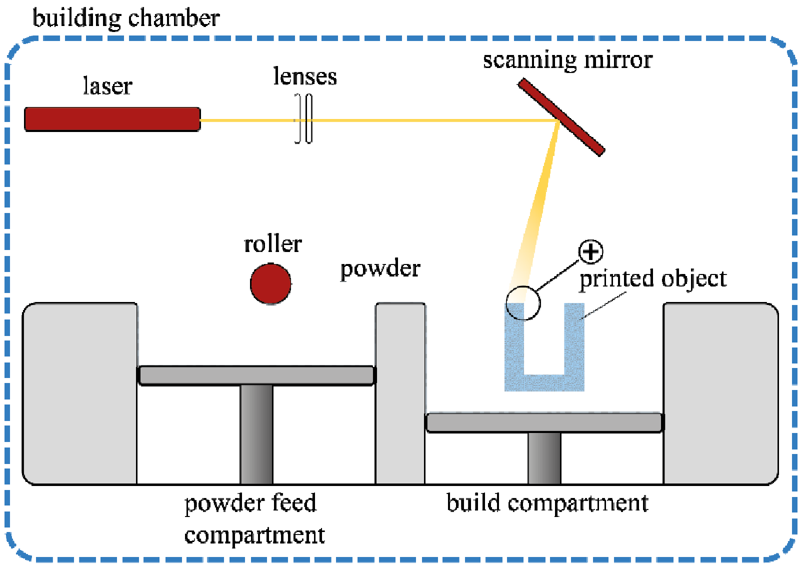


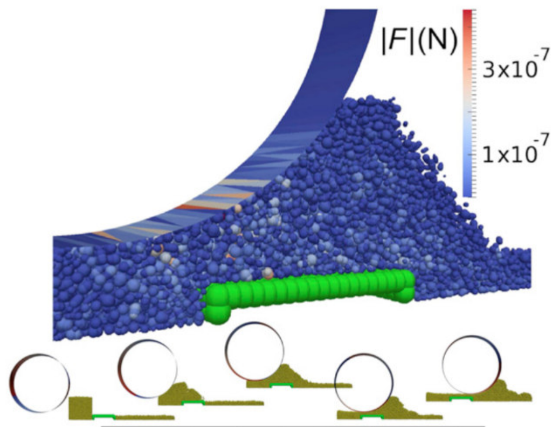
- raster orientation affects the crack path, with layer debonding followed by crack growth in the 90° orientation

2) Simulations

Processes in Selective Laser Sintering:

1. powder spreading ⇨ models of powder recoating
2. energy absorption and heat transfer ⇨ optical and heat transfer models
3. sintering and cooling ⇨ sintering models

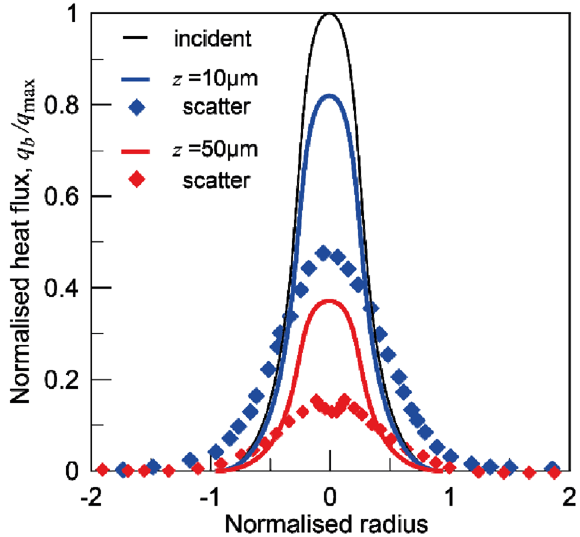




Parteli, E.J.R., et al. *Powder Technol.* **2016**, *288*, 96–102

- mechanical behaviour of printed parts ⇨ mechanical models

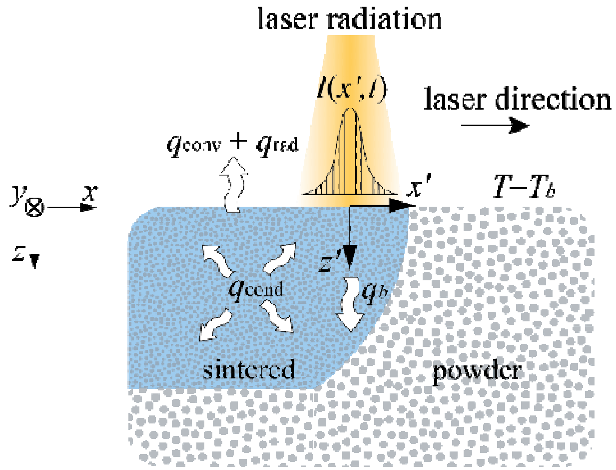
Xin, L. *Add. Manufact.* **2017**, *18*, 121–135



2) Simulations

Optical model

- the optical model describes the laser energy deposition in the powder bed, based on the interaction between the electromagnetic radiation and the optical properties of the material
- it should describe the heat flux emitted by a moving light source and the energy absorption in depth (according to Lambert-Beer law)
- advanced models account for the effect of powder transparency and light scattering through ray-tracing algorithms



surface heat flux

$$I(x,y,t) = I_0 \exp\{-c[(x-vt)^2 + (y-vt)^2]\}$$

maximum light intensity — scan velocity

heat flux density

$$q_b(x,y,z,t) = (1-R_R)\, e_R\, I_0 \exp\{-c[(x-vt)^2 + (y-vt)^2] - e_R z\}$$

attenuation coefficient — reflectivity

2) Simulations

Heat transfer model

- heat transfer in the powder bed, including phenomena of conduction, convection and radiation, is described by the equation of heat conduction

volumetric heat generation

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \, \nabla T) + q_g$$

specific heat — thermal conductivity

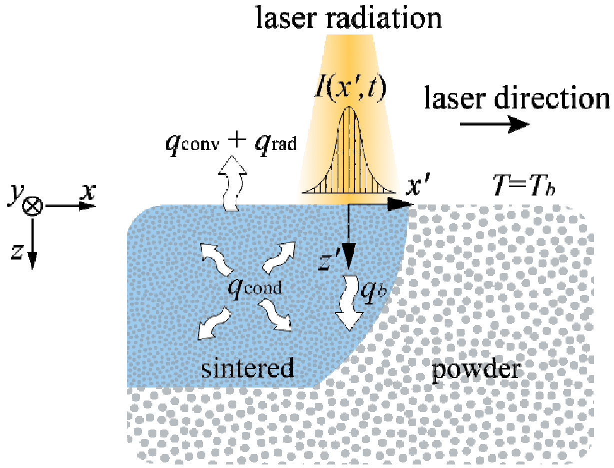
- boundary conditions account for energy losses through radiation and convection on the powder bed surface
- the volumetric term includes the heat flux generated by the laser beam and phase transitions that are associated with latent heat

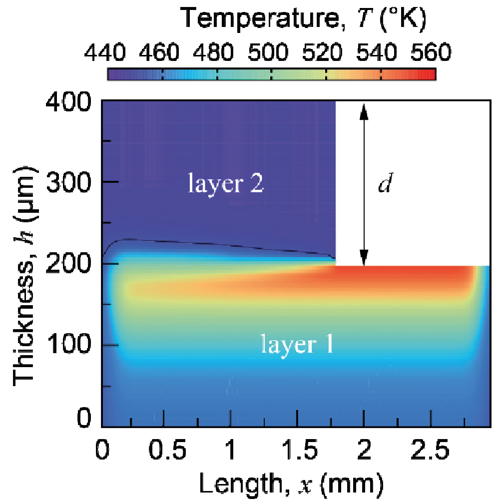
crystallisation

$$q_g = q_b + s_f + s_c$$

laser heat flux — melting

⇨ phase transitions depend on the polymeric material!



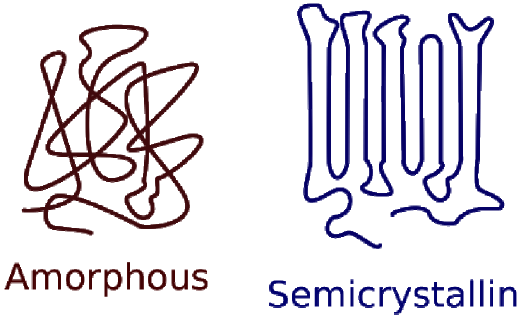


Mokrane, A. *CR Mecanique* **2018**, *346*(11), 1087-1103

2) Simulations

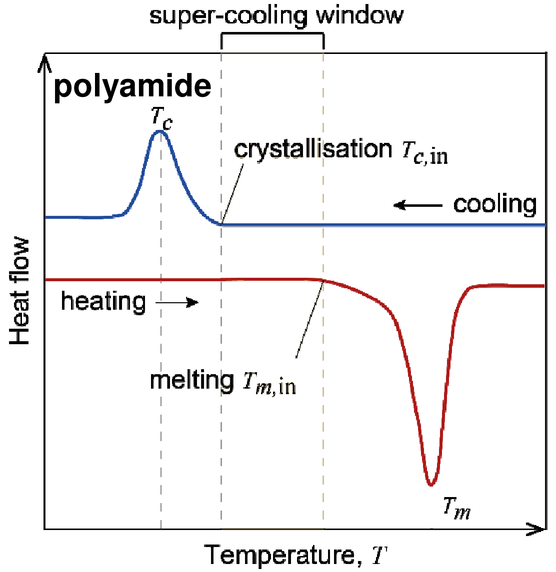
Heat transfer model: phase transitions

- a fundamental distinction in the morphology of polymers is between amorphous and semi-crystalline materials
- the amorphous phase undergoes glass transition, upon which the material becomes soft and viscous; the crystalline phase undergoes melting and crystallisation, which take place at different temperatures



(e.g. polycarbonate, polystyrene) (e.g. polyamide, polyethylene, PEEK)

⇨ optimal processing depends on the polymer's morphology!



- glass transition, as a second-order transformation, is not related to any latent heat ⇨ heat conduction (amorphous)

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + q_b$$

- optimal processing of semi-crystalline materials occurs within the so-called super-cooling window ⇨ heat conduction (semi-crystalline)

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + q_b + s_f + s_c$$

⇩

models of crystallisation kinetics

2) Simulations

Sintering model

- sintering describes the transformation through which the polymeric powder is converted into a porous solid, under the action of surface tension and viscous flow
- densification of the material occurs in non-isothermal conditions in two different stages:
  (1) powder coalescence
  (2) densification of the molten mass
- sintering is usually described by empirical relationships:

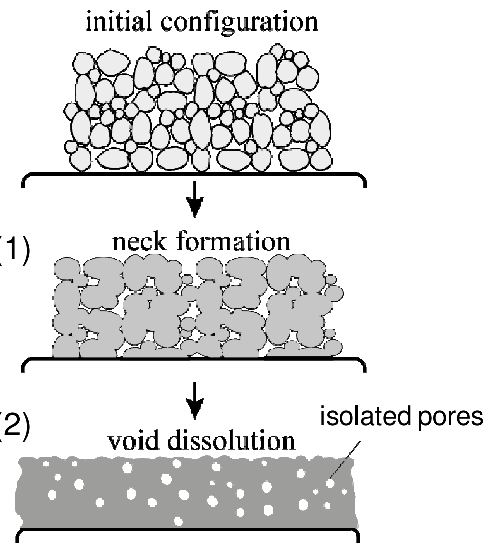
activation energy

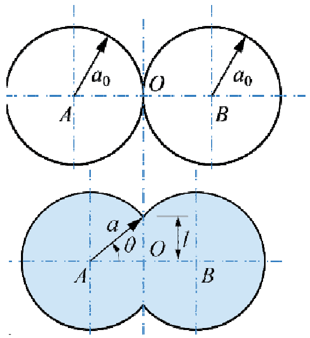
theoretical density

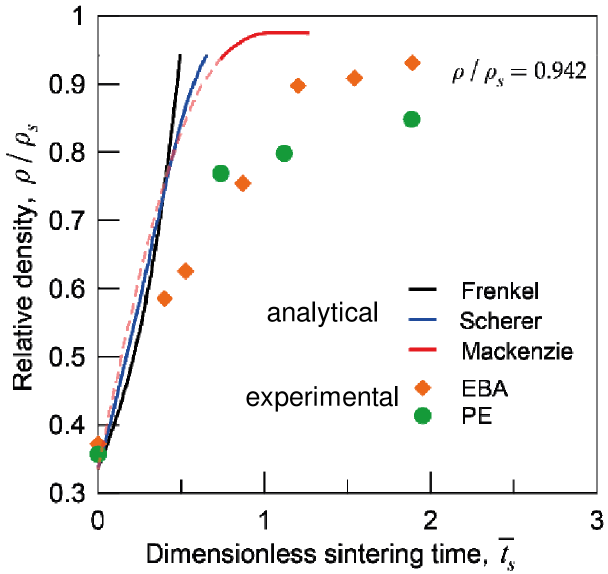
$$\frac{\partial \rho}{\partial t} = A \exp\left(-\frac{\Delta E}{RT}\right)(\rho_\infty - \rho)$$

universal gas constant

- recently, particle-based methods implemented analytical sintering models in large-scale simulations of SLS (Frenkel, Scherer, etc.)

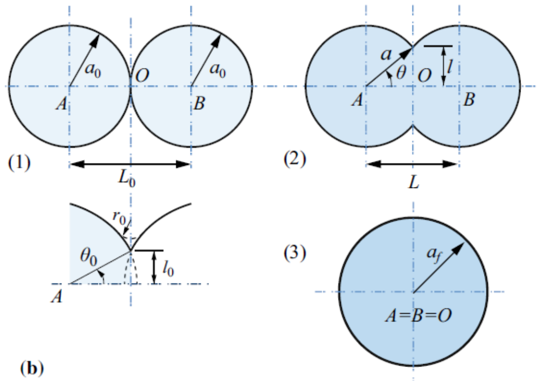






2) Simulations

Frenkel JJ *J Phys (USSR)* **1945** 9:385–391

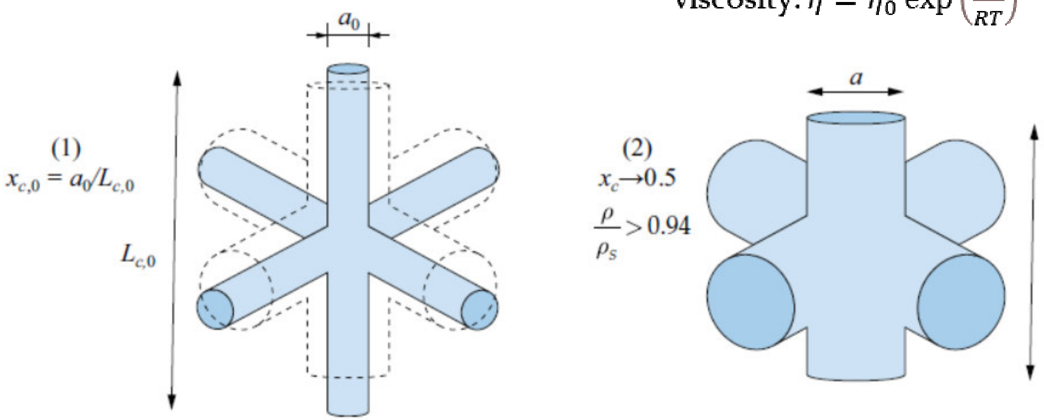


Sintering models: Frenkel's vs Scherer's

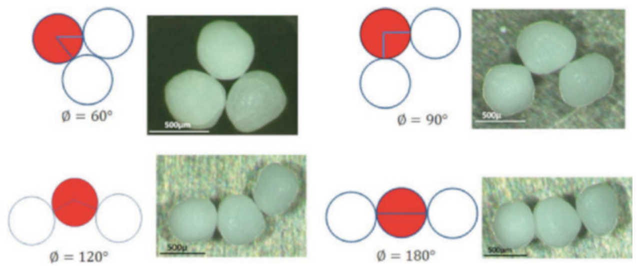
surface tension

$$\left(\frac{l}{a}\right)^2 = \frac{\gamma}{\eta a_0} t$$

viscosity: $\eta = \eta_0 \exp\left(\frac{\Delta E}{RT}\right)$

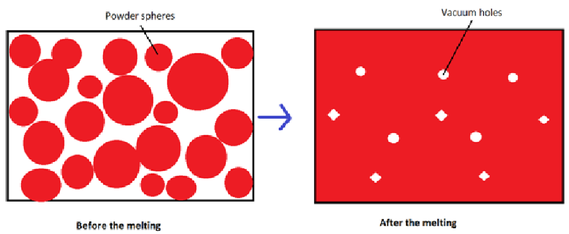


$$\frac{\partial x_c}{\partial t} = \frac{\gamma}{2\eta L_c}$$



Scherer GW *I. Theory. J Am Ceram Soc* **1977** 60(5–6):236–239

Sintering models: bubble dissolution (e.g. see Mackenzie's model)



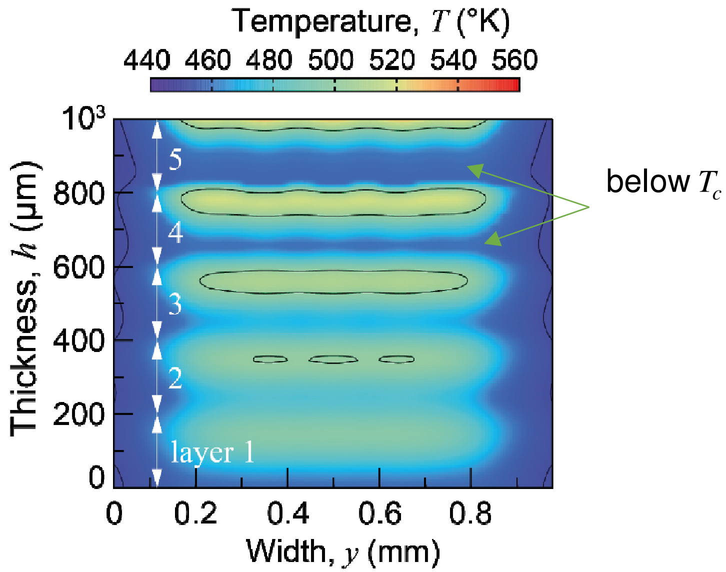
Mackenzie JK, Shuttleworth R (**1949**) *Proc Phys Soc B* 62(12):833–852.

2) Simulations

Models of the mechanical behaviour

- the fundamental stage in which the material develops its mechanical properties is the cooling phase. However, due to the multi-layered construction, temperature evolves non-uniformly during printing, resulting in residual stresses and inhomogeneous crystallisation

⇨ the mechanical problem is coupled with the thermal and sintering problems because the material properties evolve during printing



Mokrane, A. *CR Mecanique* **2018**, *346*(11), 1087-1103

material: polyamide 12 (PA2200)
melting temperature T_m = 461°K
crystallisation temperature T_c = 454°K

- the main aspects to be addressed are:
  - role of part porosity
  - role of the crystalline phase
  - time- and temperature-dependence

- most existing approaches consider the mechanical problem separated from the printing process!

2) Simulations

Models of the mechanical behaviour: role of crystallisation

- the mechanical behaviour of semi-crystalline polymers subjected to tensile loading is governed by rupture and reorientation in the crystalline regions, followed by deformation in the amorphous region
- the resulting time- and temperature-dependent response can be modelled by generalised viscoelastic models and time-crystallisation-temperature superposition

relaxation modulus

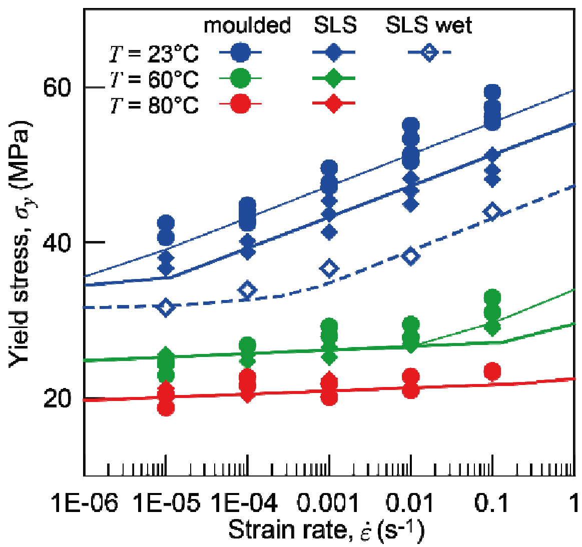
$$\mu(t,\alpha,T) = \mu_\infty + \sum_i \mu_i(\alpha_{\text{ref}},T)\exp\left(-\frac{t}{A_C(\alpha,T)\tau_i}\right)$$

degree of crystallinity (α) — shift function ($A_C(\alpha,T)$) — relaxation time (τ_i)

- the yield stress of semi-crystalline materials can be expressed with a modified form of Ree-Eyring's activated flow theory

$$\sigma_y(\dot{\varepsilon},T) = \frac{k_B T}{V_1^*}\sinh^{-1}\left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,1}}\exp\left(\frac{\Delta E_1}{RT}\right)\right] + \frac{k_B T}{V_2^*}\sinh^{-1}\left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,2}}\exp\left(\frac{\Delta E_2}{RT}\right)\right]$$

First term: deformation of crystalline phase; second term: deformation of amorphous phase



Paolucci, J. *J. Appl. Polym. Sci.* **2020**, *137*(14), 48525

2) Simulations

Models of the mechanical behaviour: role of porosity

- depending on the microstructure, failure of porous materials under tensile conditions occurs with either brittle or ductile mechanisms
- ductile failure can be modelled with a mechanism of void growth, according to Gurson-Tvergaard-Needleman (GTN) damage model

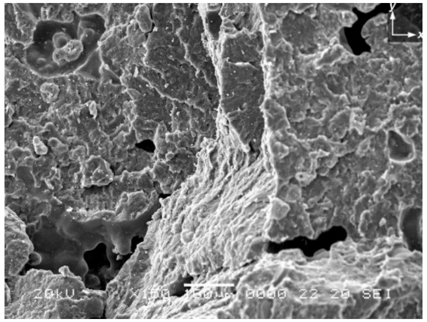
GTN yield function

$$\psi(\boldsymbol{\sigma}, \sigma_y, \phi) = \left(\frac{\sigma_{VM}}{\sigma_y}\right)^2 + 2q_1\phi^* \cosh\left(\frac{3}{2}q_2\frac{\sigma_h}{\sigma_y}\right) - \left(q_3\phi^{*2} + 1\right) = 0$$

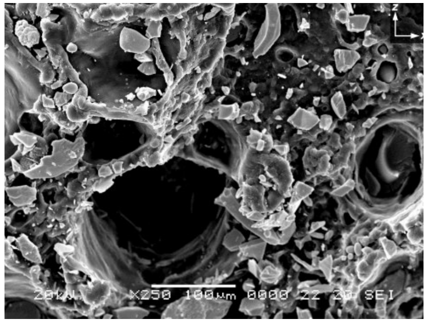
modified void fraction (ϕ^*); yield stress (σ_y)

q_1, q_2, q_3 = temperature-dependent parameters

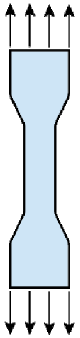
brittle fracture

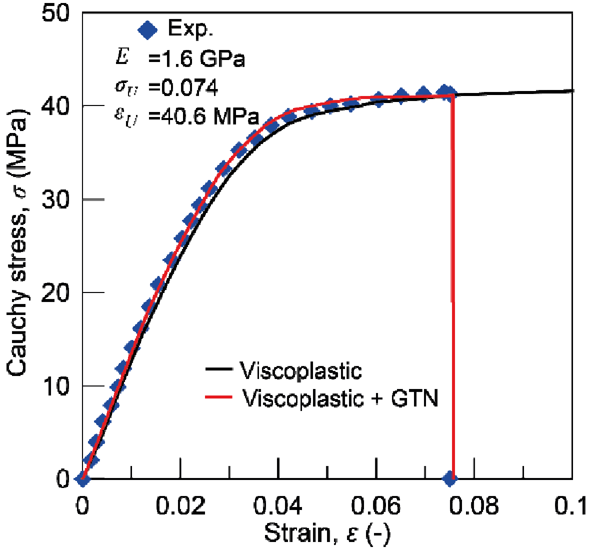


ductile fracture



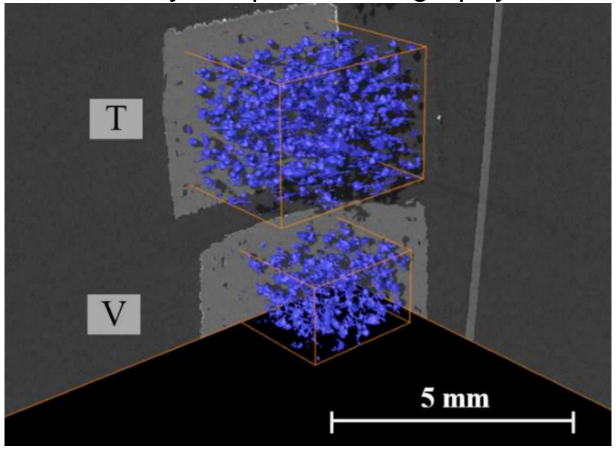
Leigh, K. **2012.** *23rd Annu. Int. Solid Free. Fabr. Symp.* 574-605





Schob, D. *Eng. Fract. Mech.* **2020**, *229*, 106841

X-ray computed tomography



pore distribution in virgin (V) and under tension (T)

Schob, D. *Arch. Mech.* **2019**, *71*(4-5), 507-526

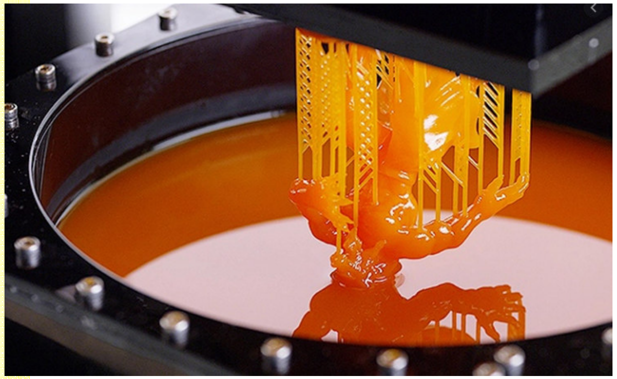
material: polyamide 12 (PA2200)

6. PHOTOPOLYMERIZATION (SLA, DLP): EXP/SIMULATIONS

Photopolymerization is a technique that uses light (visible or ultraviolet, UV) to initiate and propagate a polymerization reaction to form a linear or crosslinked polymer structure.

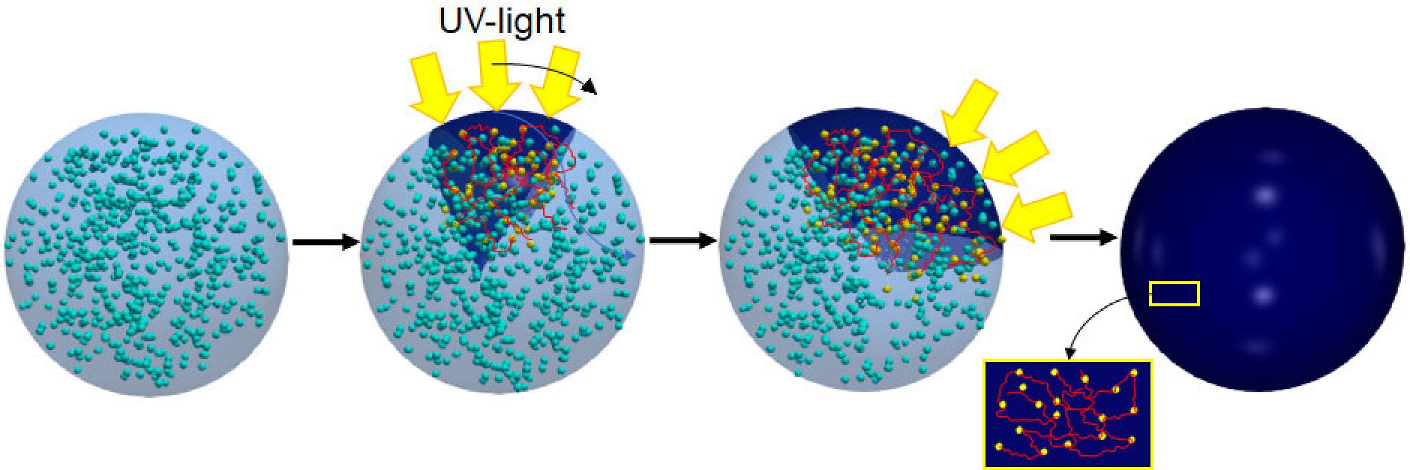
Printable polymers:

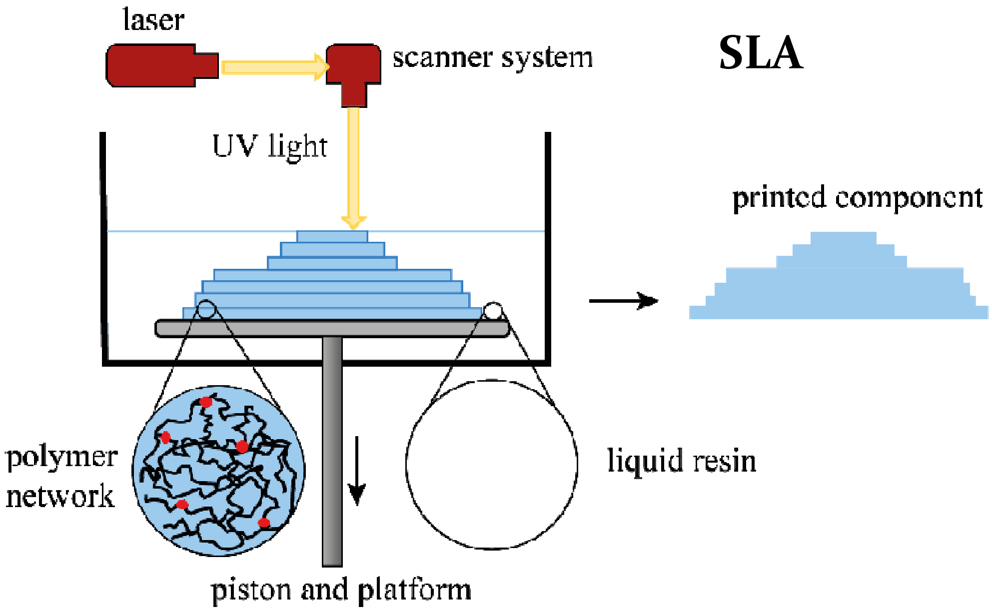
- all the types of photopolymer resins, such as polyester acrylate (PEA), epoxy acrylates (EA), urethane acrylates (UA).
  Many commercial resins for SL are available



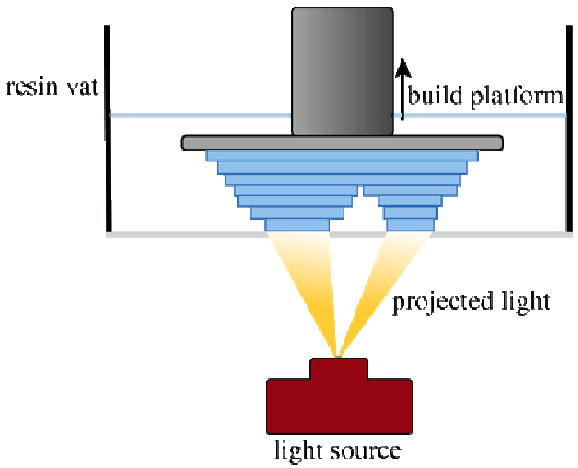
For instance, some commercial SL-resins are based on:

- PEGDA: Poly(ethylene glycol) dyacrylate monomer
- PTMC: Poly(trimethylene carbonate) monomer
- HDDA: hexamethylene dyacrylated monomer





SLA

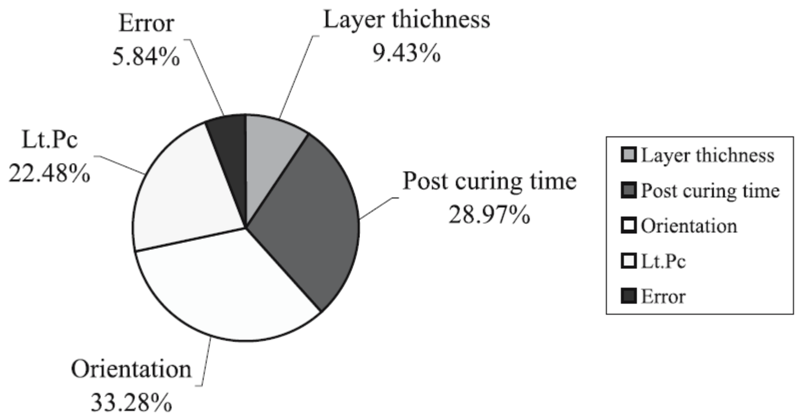


Digital Light Processing (DLP)

1) Experiments

Parameter	Range	Level 1	Level 2	Level 3
Lt	0.1–0.15 mm	0.1	0.125	0.15
Pc	60–120 min	60	90	120
O	HX, VX, HY, VY	HX	VX	HY

- Layer thickness
- Post-curing time
- Building orientation



Influence of the selected input AM parameters on the mechanical properties

Experiment number	Level		
	Layer thickness (*Lt*)	Post-curing time (*Pc*)	Orientation (*O*)
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	1
5	2	2	2
6	2	3	3
7	3	1	2
8	3	2	3
9	3	3	1
10	1	1	3
11	1	2	1
12	1	3	2
13	2	1	2
14	2	2	3
15	2	3	1
16	3	1	3
17	3	2	1
18	3	3	2

ANOVA statistical analysis

Chockalingam, K. *The International Journal of Advanced Manufacturing Technology* **2006**, *29*(1-2), 79-88

1) Experiments

Figure 1 Tensile test specimen YS and UTS

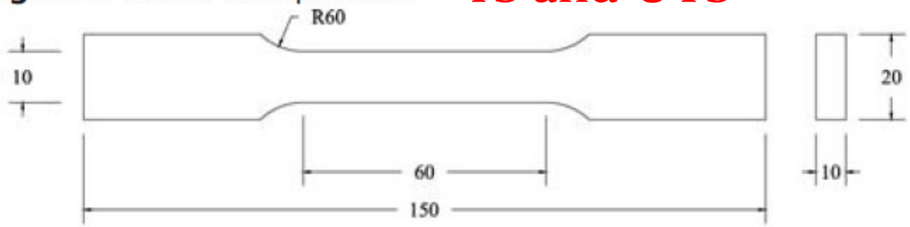
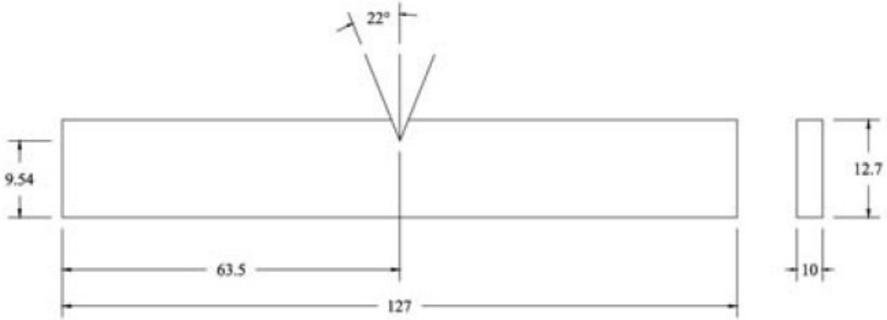


Figure 2 Impact test specimen E and IS



Chockalingam, K. *The International Journal of Advanced Manufacturing Technology* **2006**, 29(1-2), 79-88

Effect of layer thickness on:

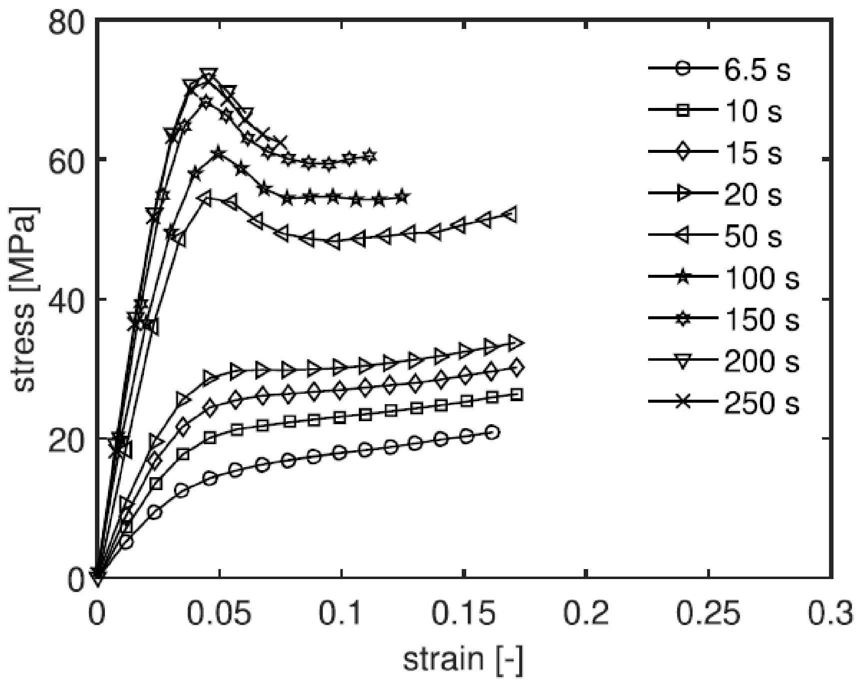
- Yield strength (YS)
- Ultimate tensile strength (UTS)
- Impact toughness (E)
- IS=E/W (W=width of the specimen= 10 mm)

▪ Layer thickness

Test Number	Lt (µm)	Average values of ten specimens Average YS (N/mm^2)	Average UTS (N/mm^2)	Average E in (J)	Average IS in (J/m)
1	100	68.24	70.05	0.2926	29.25
2	125	60.76	68.50	0.2539	25.39
3	150	49.92	56.00	0.2125	21.25

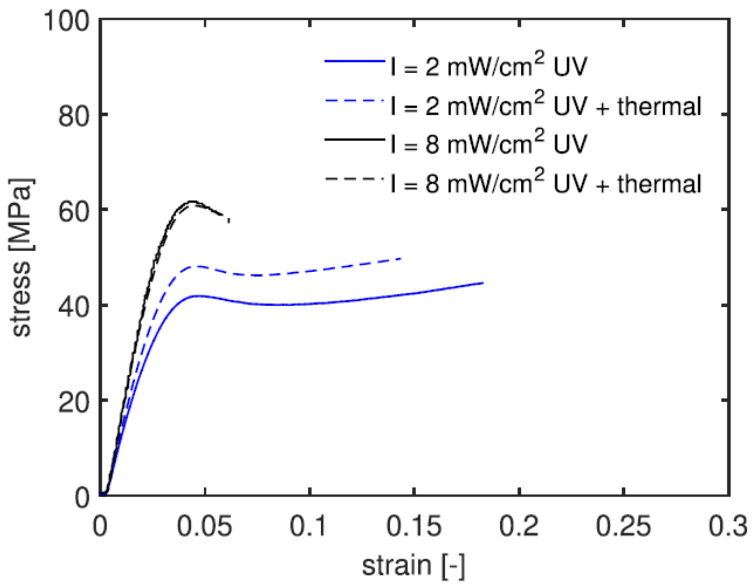
Optimum value
(best mechanical properties)

1) Experiments



Stress-strain curves for different <u>curing time</u> at a fixed ligth intensity of 8 mW/cm²

- UV-light intensity
- Curing time
- Post-curing time



Effect of post-curing time

On the material printed with the highest light intensity, no effect of post-curing time

Why....? Theoretical models are needed to explain this aspect

Anastasio, R. *Macromolecules* **2019**, 52(23), 9220-9231

1) Experiments

- Building orientation

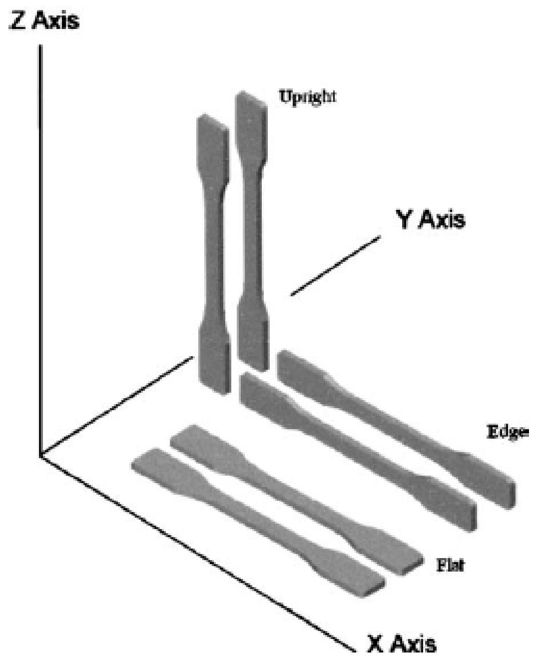


TABLE I Isotropy/anisotropy test results for SL 7560

Mechanical properties	Build orientation			Max. % variation
	Flat	Edge	Upright	
Max. tensile strength (Mpa)	54.9	56.4	53.7	4.8
Young's modulus (GPa)	2.6	2.7	2.7	3.7
Flexural strength (MPa)	92.5	96.3	95.3	3.9
Flexural modulus (GPa)	2.1	2.2	2.1	4.5
Impact strength (kJ/m^2)	2.5	2.4	2.4	4.0

So, a photopolymerized-component is ISOTROPIC or ANISTROPIC?

The problem is still under investigation…

2) Simulations

Polymer **chain length and crosslink density** evolve according to the **degree of cure** evolution

→ The mechanics of a polymer depends on the amount of the degree of cure

$$\varrho(\boldsymbol{x},t) = 1 - \frac{C_M(\boldsymbol{x},t)}{C_M(\boldsymbol{x},t=0)}$$

KINETIC MODELS OF PHOTOPOLYMERIZATION (recently developed)

They aim at calculating in different ways the degree of cure, in order to relate it with the mechanics of a printed component

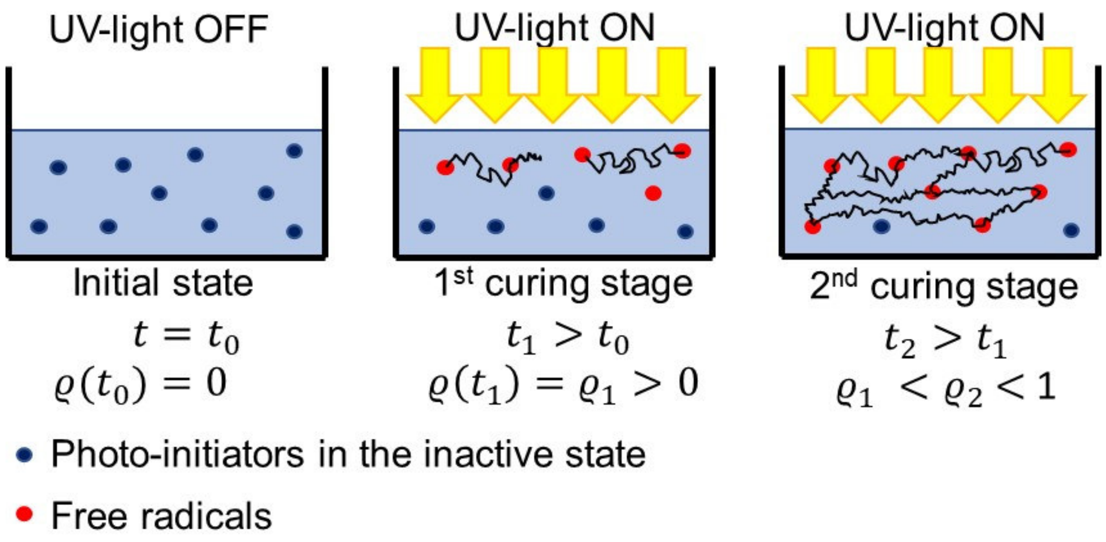
- **Phenomenological**

  The degree of cure evolution is modelled by means of only one differential equation (for as concerning the kinetic model of photopolymerization)

- **Mechanistic**

  The degree of cure is obtained by solving a system of differential equations taking into account the concentration evolution of the species involved in the problem

2) Simulations



The mechanical behavior of a component printed with Photopolymerization depends by the degree of cure (ϱ) achieved during the printing process itself, which is affected by the process parameters adopted

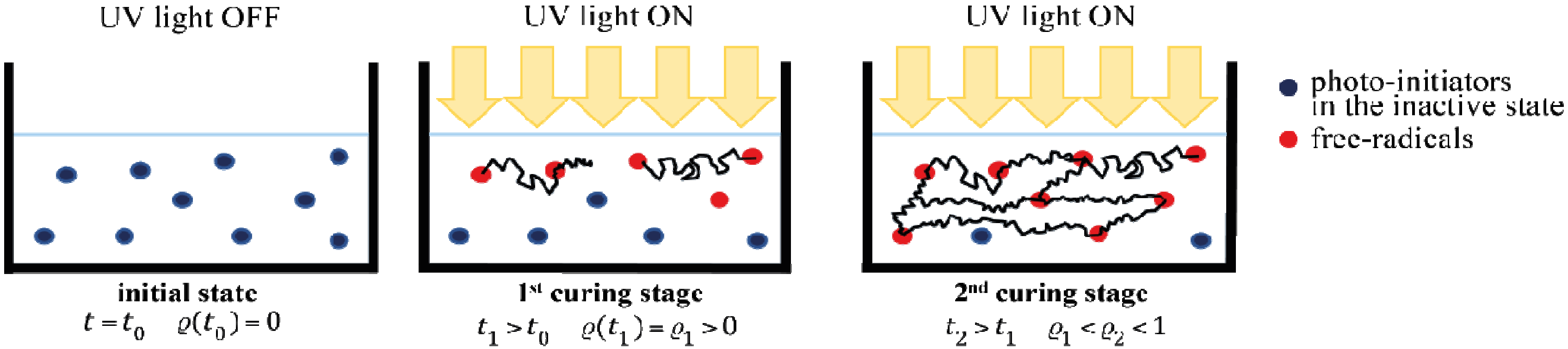
What physically represents the **degree of cure**? It is an **internal variable** (typically expresses as a percentage) used for quantifying:

- Quantity of monomer conversion
- Quantity of $C = C$ bonds (liquid state) converted in $C - C$ bonds (polymeric state) as typically happens in acrylates photopolymerization

Brighenti, R. *J. Mater. Sci.* **2021**

2) Simulations

Simulation of the photopolymerization process (SLA)



(1) Photo-initiators decomposition: $Ph_I \xrightarrow{\beta} 2R^{\bullet}$

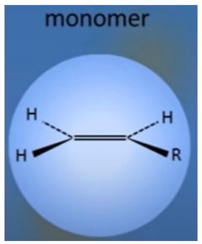
(2) Initiation of a polymer chain: $R^{\bullet} + M \xrightarrow{kp} P^{\bullet}$

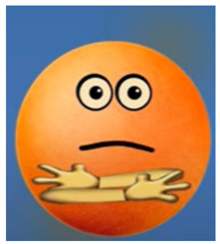
(3) Propagation of a polymer chain: $P^{\bullet} + M \xrightarrow{kp} P^{\bullet}$

(4) Termination: $P^{\bullet} + P^{\bullet} \xrightarrow{kt} P_{\text{dead}}$, $P^{\bullet} + R^{\bullet} \xrightarrow{kt} P_{\text{dead}}$

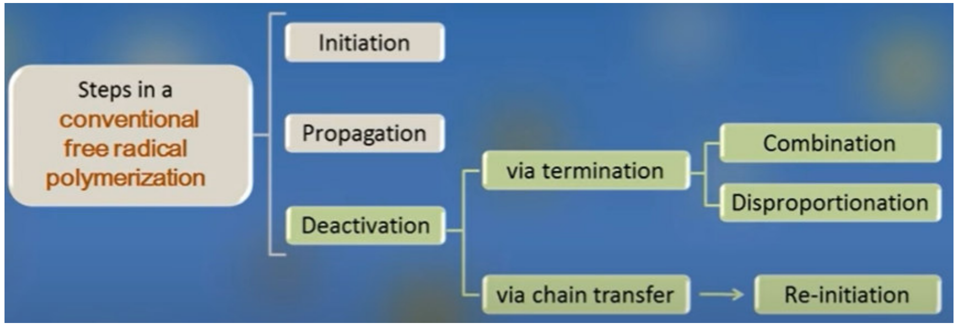
Wee need to describe a multiphysics problem involving:

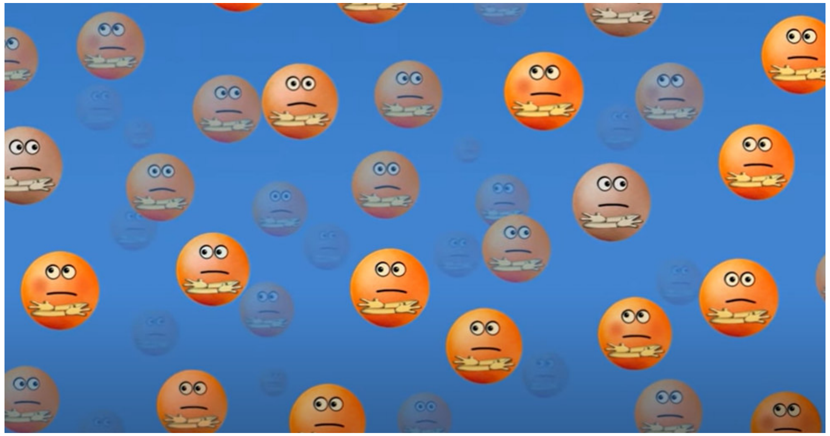
1) Light propagation (Beer-Lambert law)
2) Kinetics of chemical species evolution
3) Chain density (shear modulus)

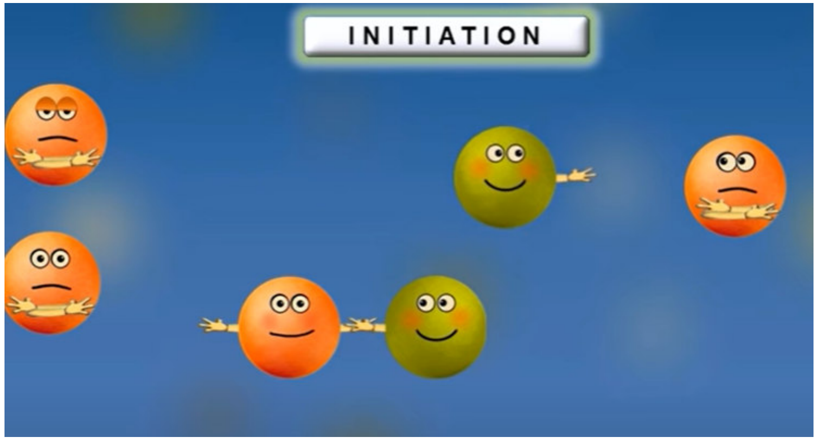




2) Simulations







- Photo-initiators rate $\dot{C}_I$
  (consumed to provide activation of free radicals)

$$\dot{C}_I(x,t) = -\beta\, I(x,t)\, C_I(x,t)$$

β : photodecomposition rate

$$\dot{\blacksquare} = \frac{\partial \blacksquare}{\partial t}$$

- Evolution of the free radicals C_R

$$\dot{C}_R(x,t) = -m\,\dot{C}_I(x,t) - m\,k_t(x,t)[C_R(x,t)]^2$$

+ -

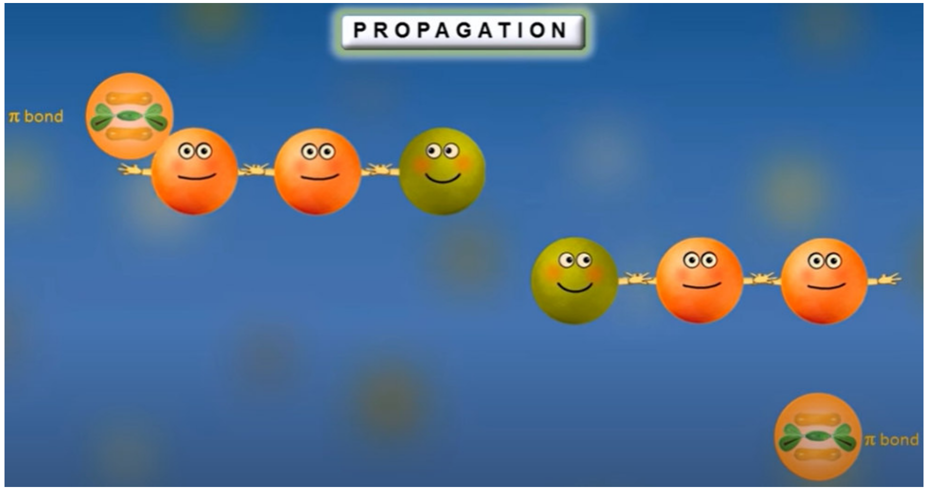
m : number of radicals generated in the photodecomposition (e.g. $m = 2$)

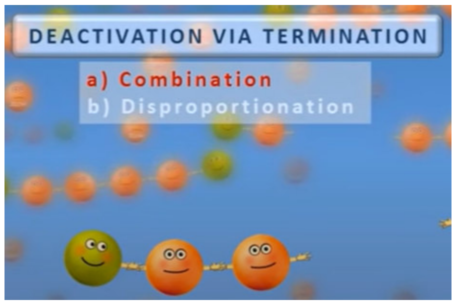
k_t : termination rate

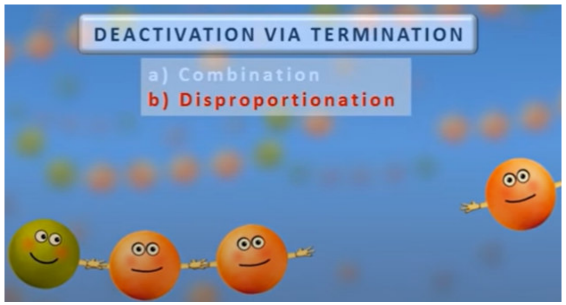
- As the combination with radicals proceeds, the monomers C_M in the solution are gradually consumed, allowing the polymer chains initiation and propagation to occur:

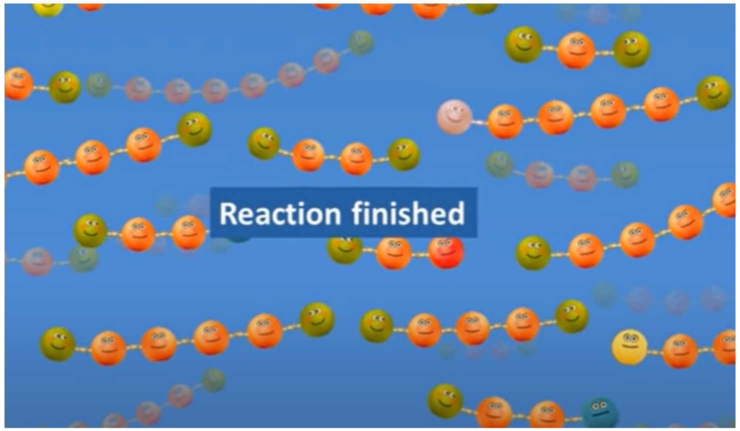
$$\dot{C}_M(x,t) = -k_p(x,t)C_M(x,t)C_R(x,t)$$

k_p : propagation rate constant









2) Simulations

1) Light propagation (Beer-Lambert law):

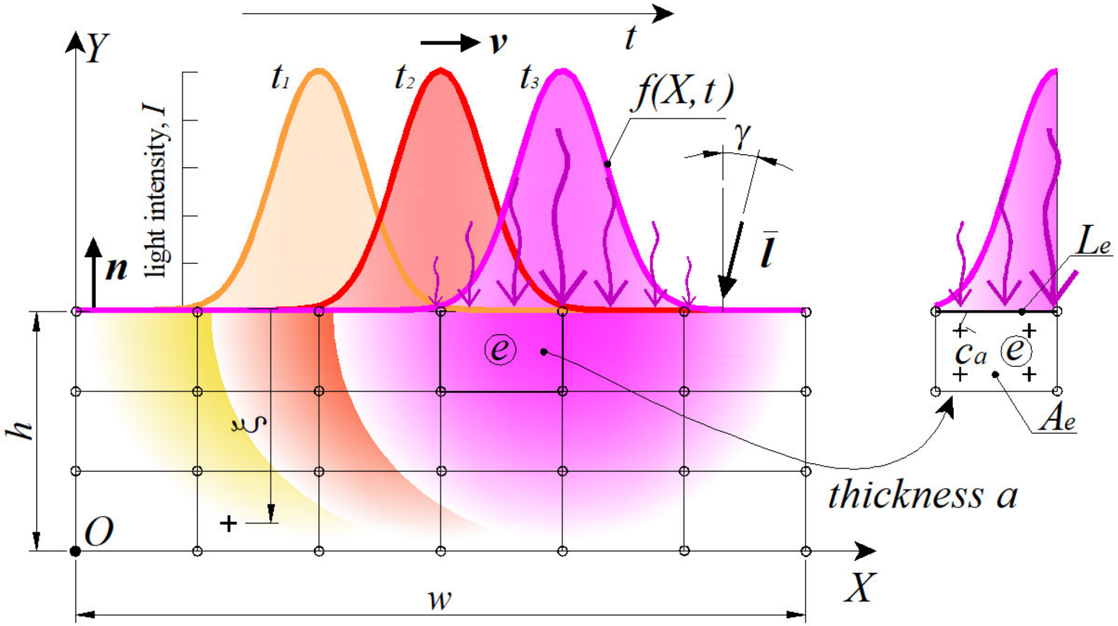
Governing field equations

$$\boldsymbol{l}(\boldsymbol{X},t)\cdot\nabla_X I(\boldsymbol{X},t) = -A(\boldsymbol{X},t)\, I(\boldsymbol{X},t)$$

for $\boldsymbol{X} \in \Omega_0$

Boundary conditions:

$I(\boldsymbol{X},t) = I_0(\boldsymbol{X},t)$ for $\boldsymbol{X} \in \partial\Omega_0$



The solution for the light intensity field in time can be obtained by **FEM implementation** of the above equations

depletion matrix

$$[\,\boldsymbol{E}_e(t) + \boldsymbol{A}_e(t)\,]\,\tilde{\boldsymbol{I}}_e(t) = \boldsymbol{P}_e(t)$$

light gradient matrix

$\tilde{\boldsymbol{I}}_e(t)$ Nodal values of the light intensity

$\boldsymbol{P}_e(t)$ nodal values of the distribution of the incoming light intensity

FEM coding

$$[\ \boldsymbol{E}_e(t) + \boldsymbol{A}_e(t)\ ]\ \tilde{\boldsymbol{I}}_e(t) = \boldsymbol{P}_e(t)$$

or, equivalently:

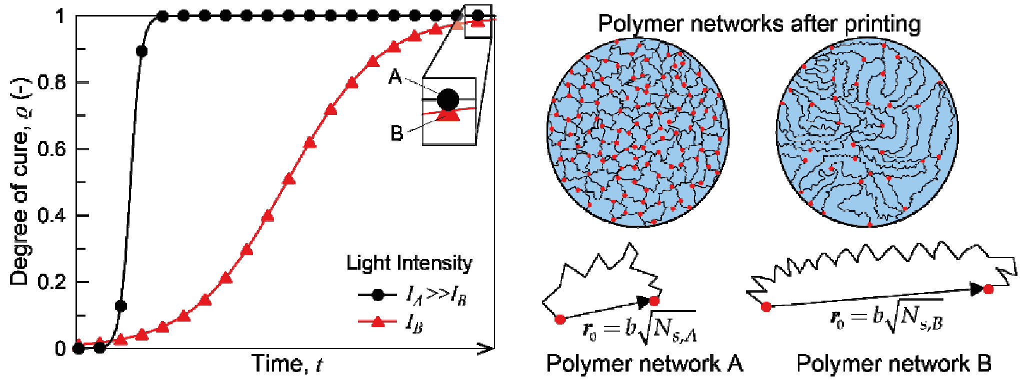
$$\left[\int_{V_e} [B]^T\ \bar{\boldsymbol{l}}(t)[N]dV - \int_{V_e} [N]^T A(\boldsymbol{X},t)[N]\,dV + Qh_e \int_{V_e} [B]^T [B]dV\right]\tilde{\boldsymbol{I}}_e(\tau)$$
$$= \int_{S_e} [N]^T\ f_n(\boldsymbol{X},t)\ dS$$

Explicitly, the above matrices are obtained as follows:

$$\boldsymbol{E}_e(t) = \int_{V_e} [B]^T\ \bar{\boldsymbol{l}}(t)\ [N]\ dV, \quad \boldsymbol{A}_e(t) = -\int_{V_e} [N]^T A(\boldsymbol{X},t)[N]\ dV,$$

$$\boldsymbol{D}_e = Qh_e \int_{V_e} [B]^T [B]\ dV \qquad \text{and} \qquad \boldsymbol{P}_e(t) = \int_{S_e} [N]^T f_n(\boldsymbol{X},t)\ \ dS$$

2) Simulations



- Evaluation of the degree of cure

$$\dot{\varrho}(\boldsymbol{x},t) = \frac{k_p(\boldsymbol{x},t)C_M(\boldsymbol{x},t)C_R(\boldsymbol{x},t)}{C_{M0}} \quad \rightarrow \quad \varrho(\boldsymbol{X},t) = 1 - \frac{C_M(\boldsymbol{X},t)}{C_M(\boldsymbol{X},t=0)}$$

- Evaluation of chain concentration

Shear modulus
(Fully cured polymer)

$$c_a(\boldsymbol{X},t) = \frac{\mu(\boldsymbol{X},t)}{k_B T} = \frac{\bar{\mu}}{k_B T} \cdot \exp[\alpha(\varrho(\boldsymbol{X},t) - 1)]$$

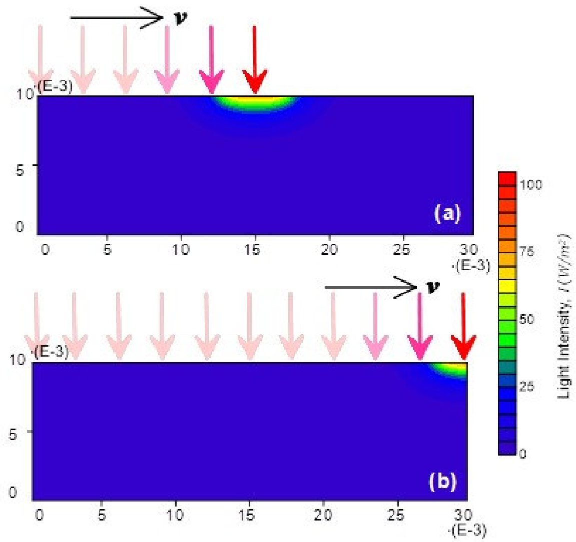
$$c_a(\boldsymbol{X},t_c) = c_{a0}(\boldsymbol{X}) + \int_0^{t_c} \dot{c_a}(\boldsymbol{X},t)\, dt$$

$$\mu(\boldsymbol{X},t) = G(\boldsymbol{X},t) = c_a(\boldsymbol{X},t)\, k_B\, T$$

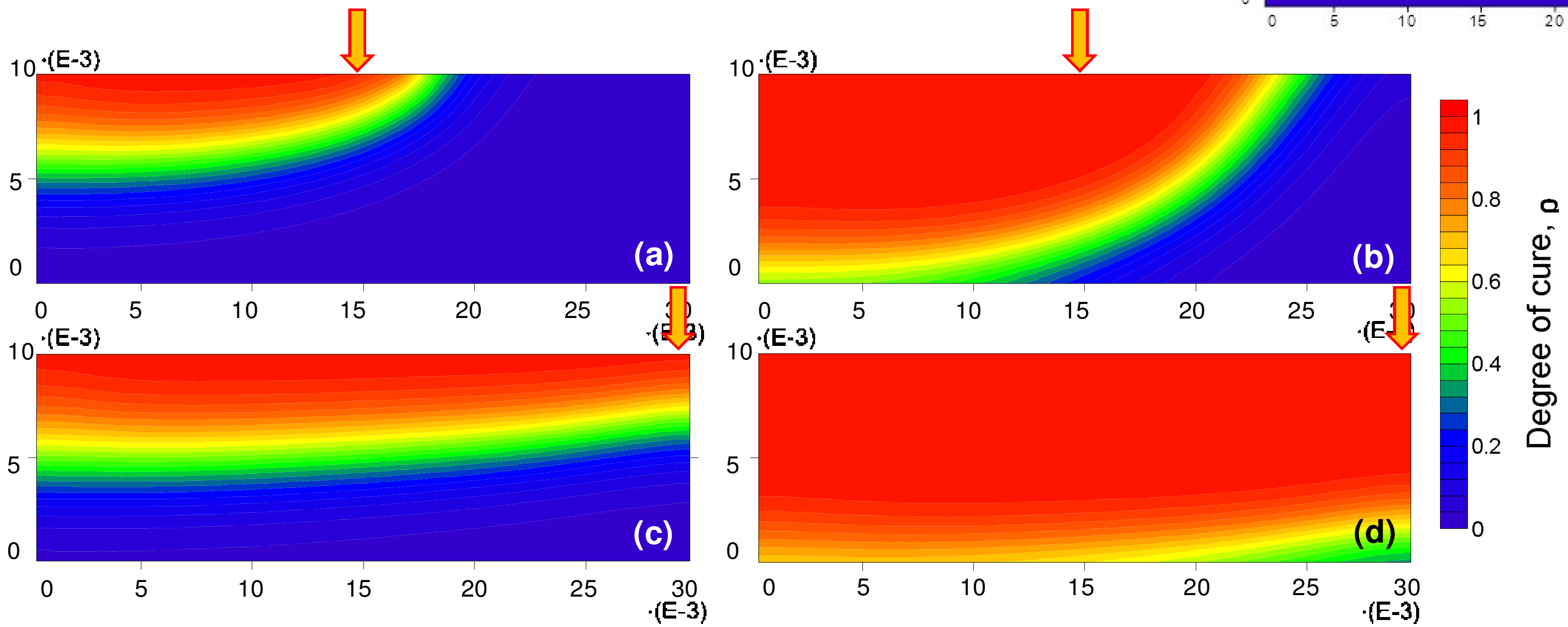
Polymer shear modulus distribution at time t

Wu J, Zhao Z, Hamel CM, et al (2018) Evolution of material properties during free radical photopolymerization. **Journal of the Mechanics and Physics of Solids** 112:25–49.

2) Simulations



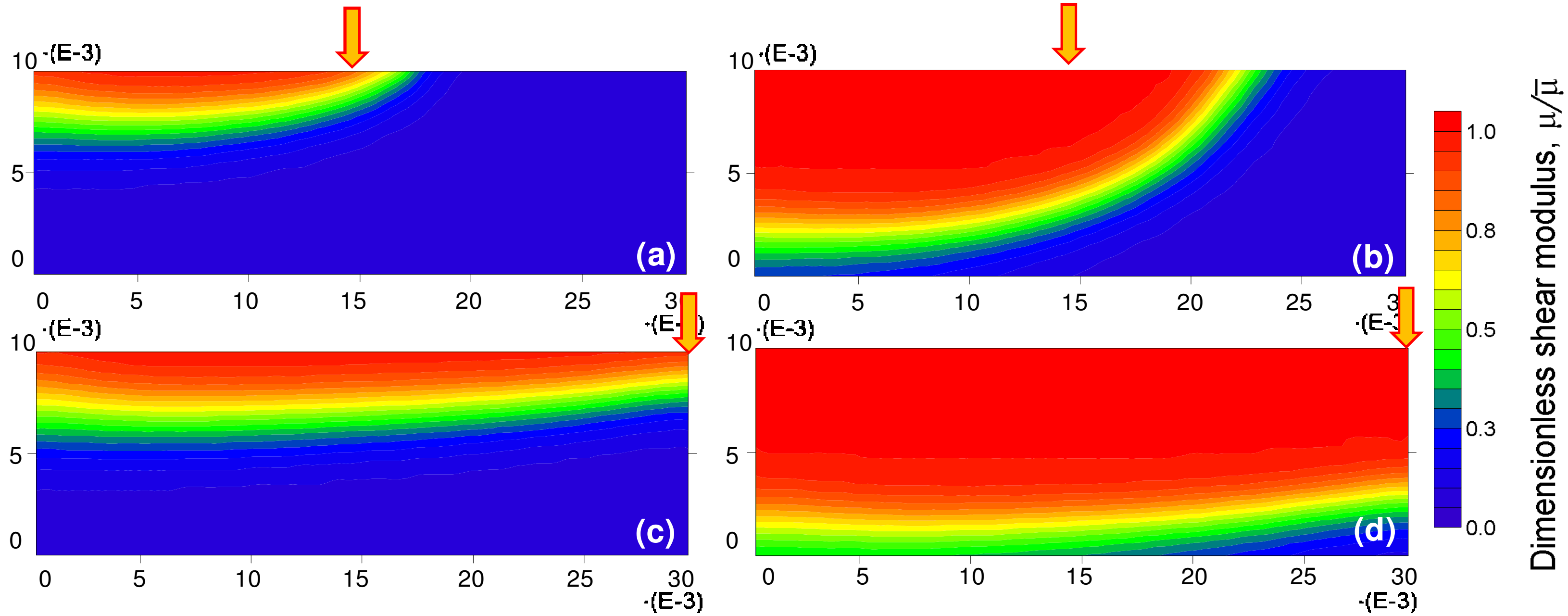
Distribution of the degree of cure



$v = 10^{-3} \mathrm{m/s}$ $\qquad$ $v = 10^{-4}\ \mathrm{m/s}$

2) Simulations

Final distribution of the shear modulus



$v = 10^{-3}\text{m/s}$ $\qquad$ $v = 10^{-4}\ \text{m/s}$

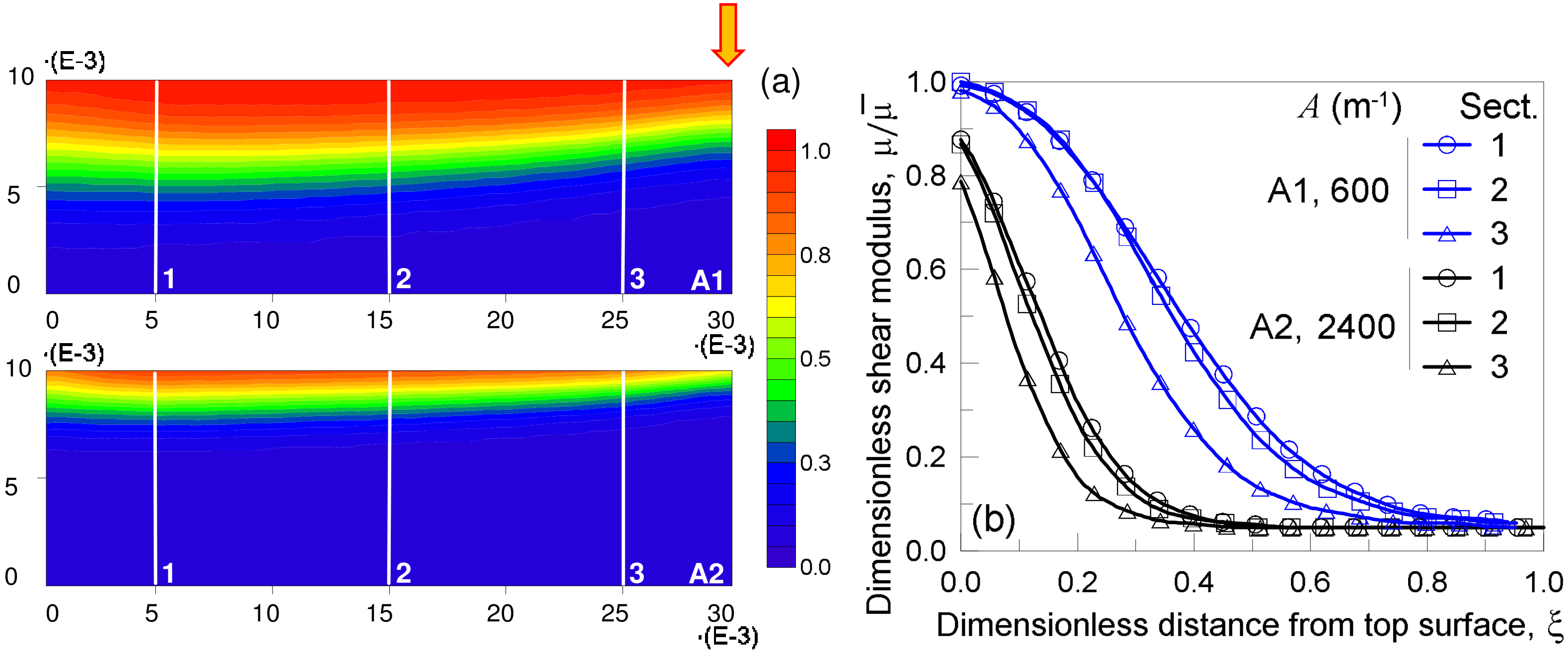
2) Simulations

Final distribution of the shear modulus

$$I_0 = 150 \ W/m^2$$

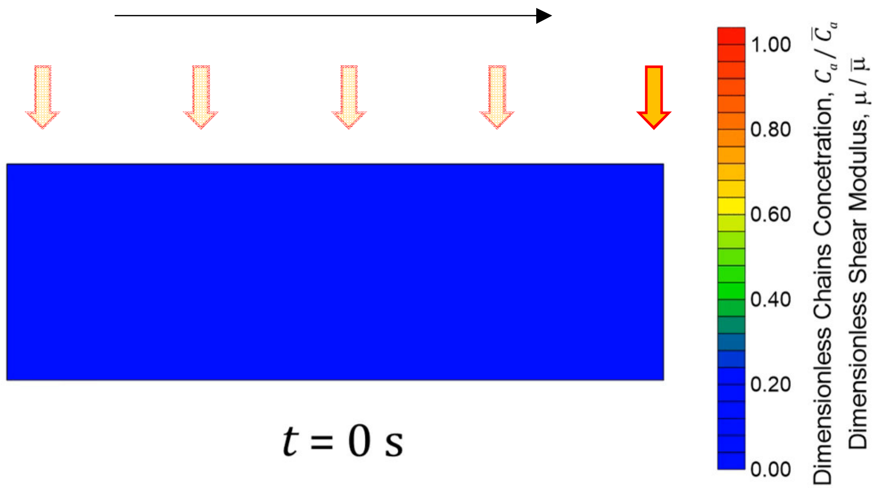
$A = 600 \ m^{-1}$

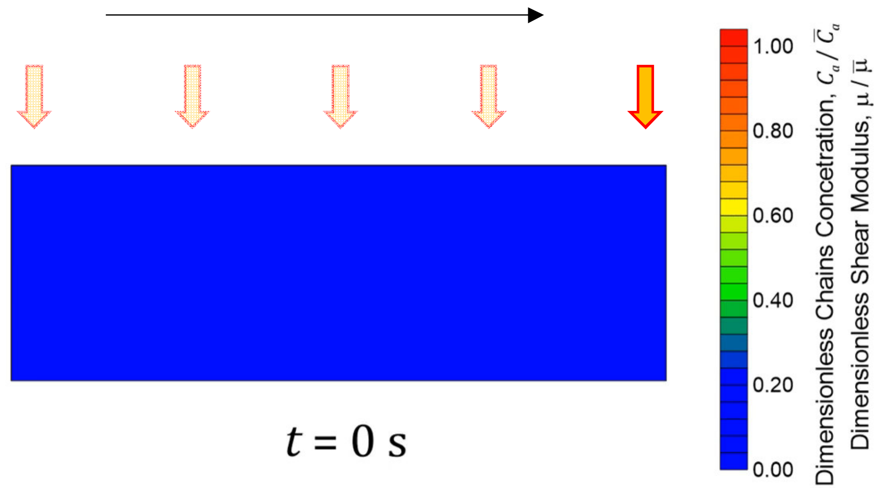
$A = 2400 \ m^{-1}$



2) Simulations

Real-time evolution of the shear modulus in SLA





$v = 10^{-3}\text{m/s}$

$I_0 = 150\ W/m^2$

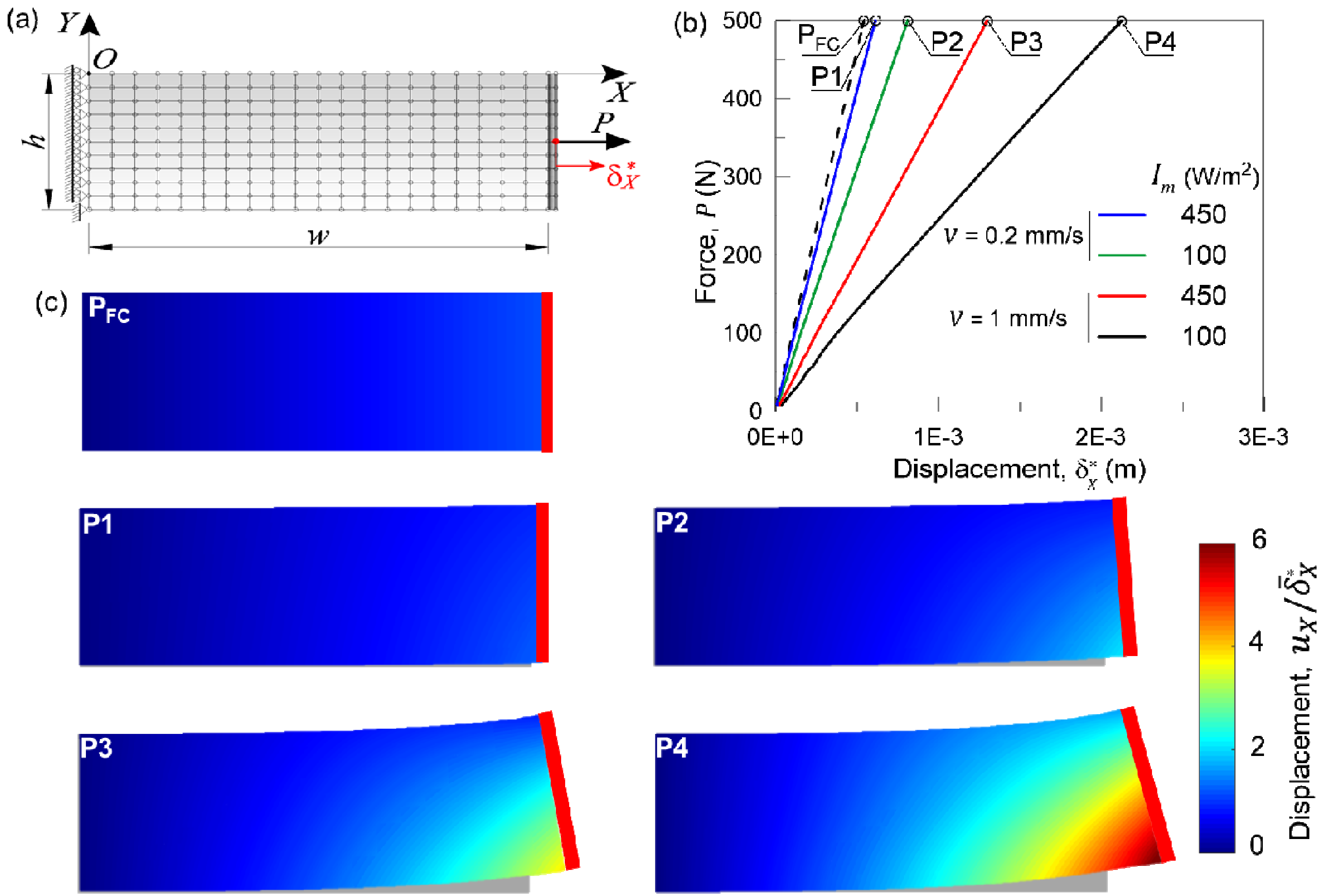
$A = 600\ m^{-1}$

$v = 10^{-4}\text{m/s}$

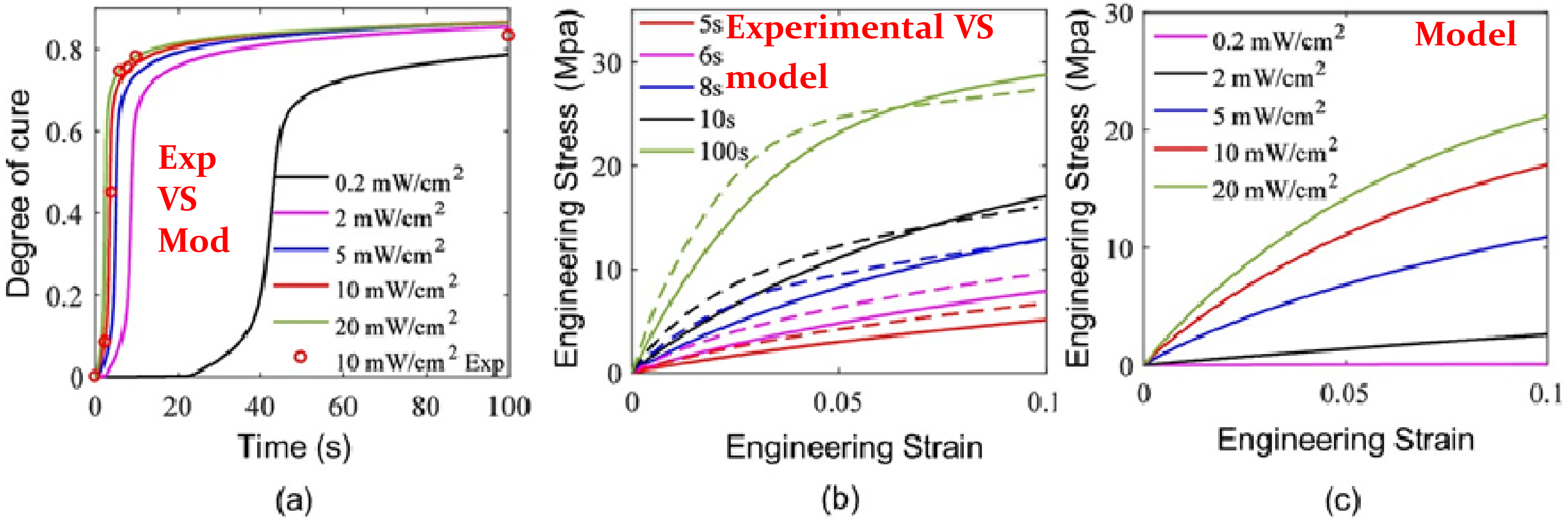
$I_0 = 150\ W/m^2$

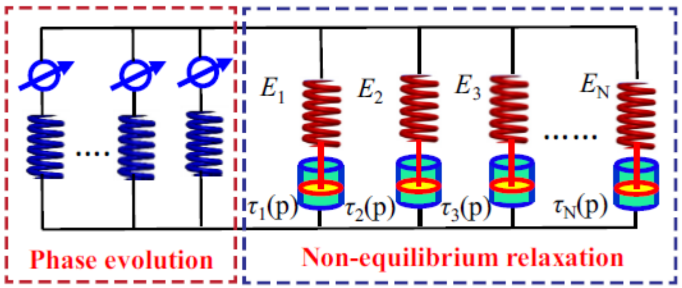
$A = 600\ m^{-1}$

Influence of the AM setup on the mechanical response of a tensile bar



2) Simulations (literature models)





$$\boldsymbol{\sigma}_{eq} = J^{-1}(\mu_{eq} J^{-\frac{2}{3}} \boldsymbol{F}\boldsymbol{F}^T + k_{eq} \ln J \boldsymbol{I})$$

Constitutive parameters
(Functions of the degree of cure)

<u>Rheological model</u>

- Mechanistic kinetic model
- Degree of cure as a function of time and space
- Correlation with mechanics: constitutive model

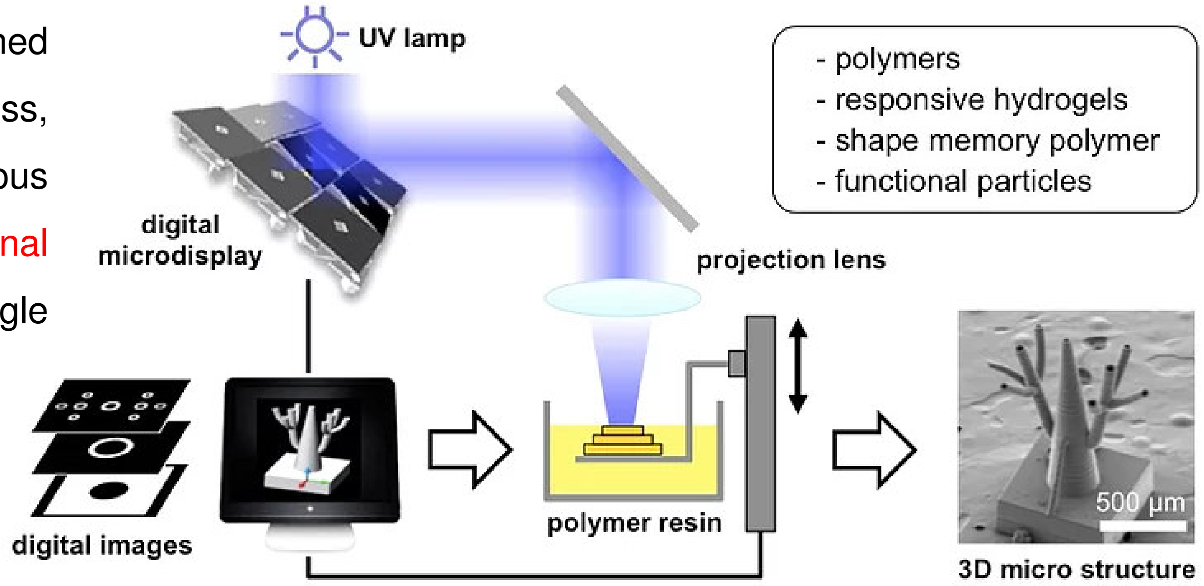
Wu J. *Journal of the Mechanics and Physics of Solids* **2018**, *112*, 25-49

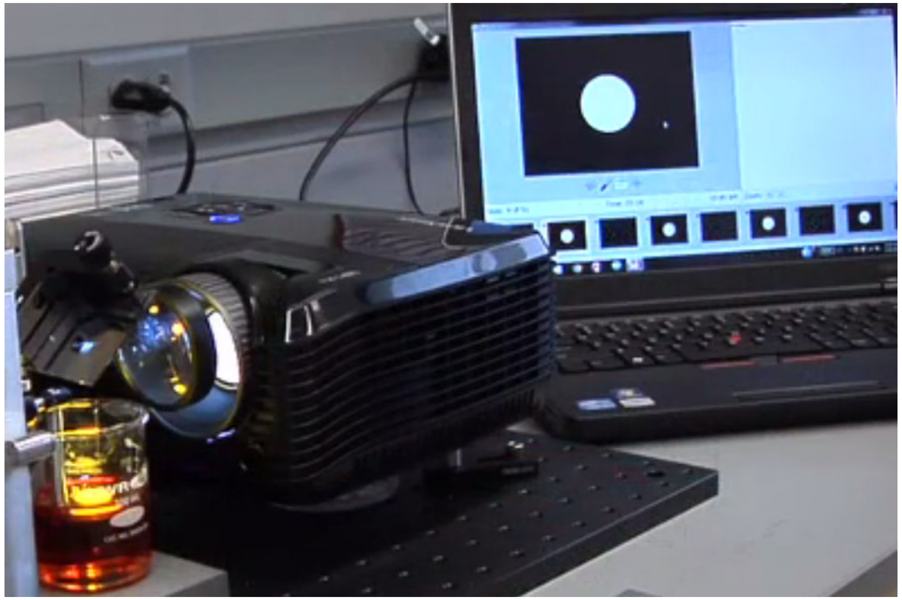
Latest technology in photopolymerization

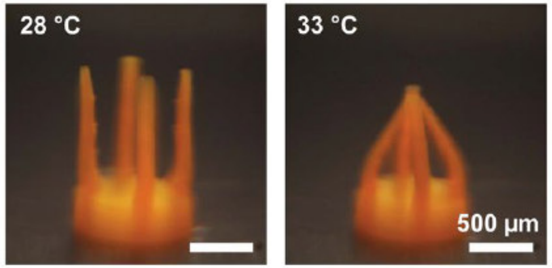
Projection Micro-StereoLithography (PμSL)

- PμSL utilizes the most advanced digital micro display technology as a dynamic mask generator.
- This technique combines advantages of conventional stereolithography (SLA) and projection lithography, allowing for rapid photo-polymerization of the entire layer with a flash of UV illumination at micro scale resolution.
- Light intensity is controlled at a single pixel level → crosslinking density and thus material properteis of the fabricated structure can be tailored with desired spatial distribution.

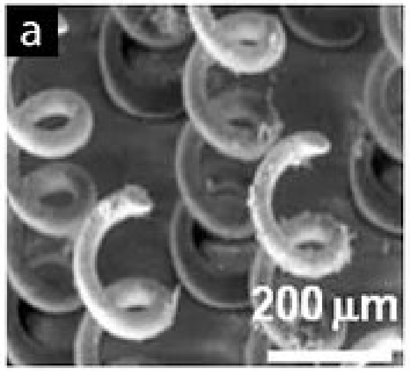
- Materials can be easily switched during the fabrication process, which enables heterogeneous integration of multiple functional material elements in a single process



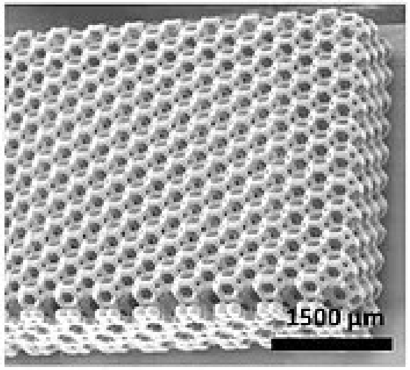




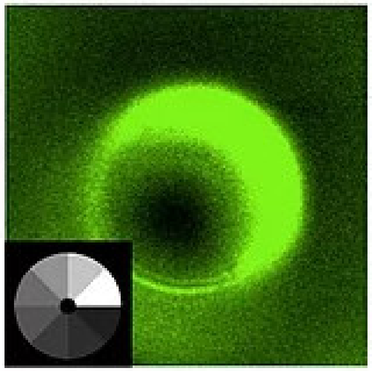
Responsive hydrogels



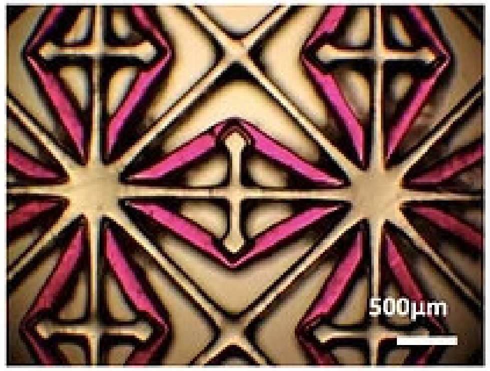
3D micro-structures



Scalable (µm to cm)



Functionally graded



Multi-material

- D. Han et al., Multimaterial Printing for Cephalopod-Inspired Light-Responsive Artificial Chromatophores, *ACS Appl. Mater. Interfaces* 2021, Jan. 3, 2021. https://doi.org/10.1021/acsami.0c17623

6. Conclusions

- Polymers are particularly suitable to be Additively Manufactured
- Several technologies are available
  - powder bed fusion
  - photopolymerization
  - material extrusion
  - material jetting, binder jetting
  - sheet lamination
- The size of the printed object can range from macro to micro
- Many different polymers can be printed; also multimaterial AM is possible
- The printing process can be often precisely controlled
- New AM technologies are emerging, allowing to obtain unprecedented materials

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