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Characterization of Pure Photopolymers and Suspensions for Digital Light Processing (DLP)

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Prof. Carlo Antonini
Raziyeh Akbari

31st October 2022
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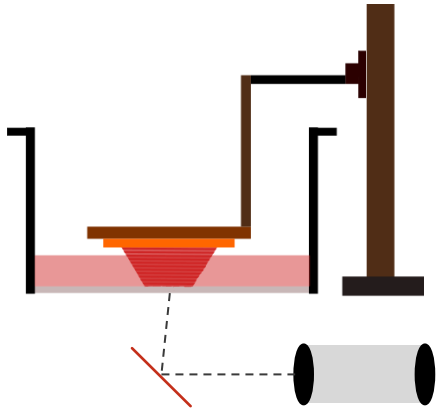
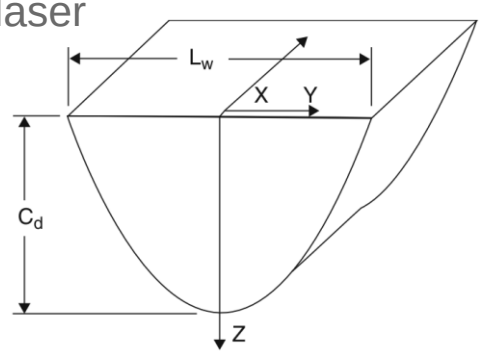
Contents

AM Process: Vat Polymerization

Stereolithography (SLA)

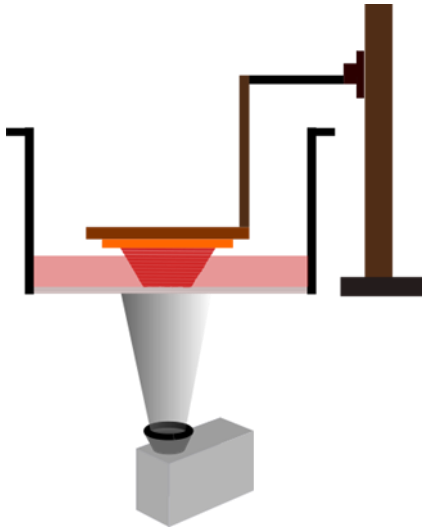


- Scanning with a Gaussian laser



Digital Light Processing

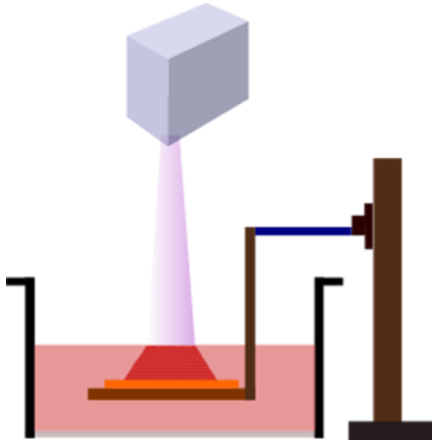
- Bottom-up

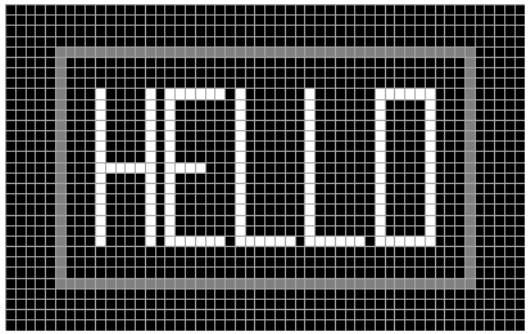


- Grayscale 2D image with array of pixels is projected

Digital Light Processing

- Top-down





Bean AJ (1992) Radiation Curing. In: Radiation Curing. pp 301–332

AM: Vat Polymerization

Pre-printing

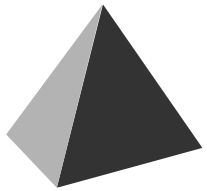
- CAD Modelling
- Slicing software

Printing

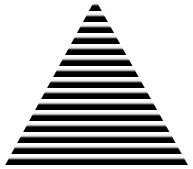
- Photopolymerization

Post-printing

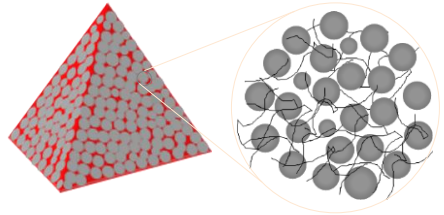
- Cleaning of part
- Removal of support structure
- UV curing
- **Thermal treatment (Debinding and Sintering)**



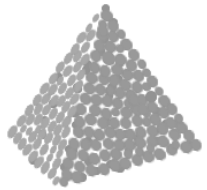
3D design



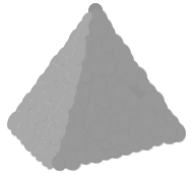
Slicing



Printing

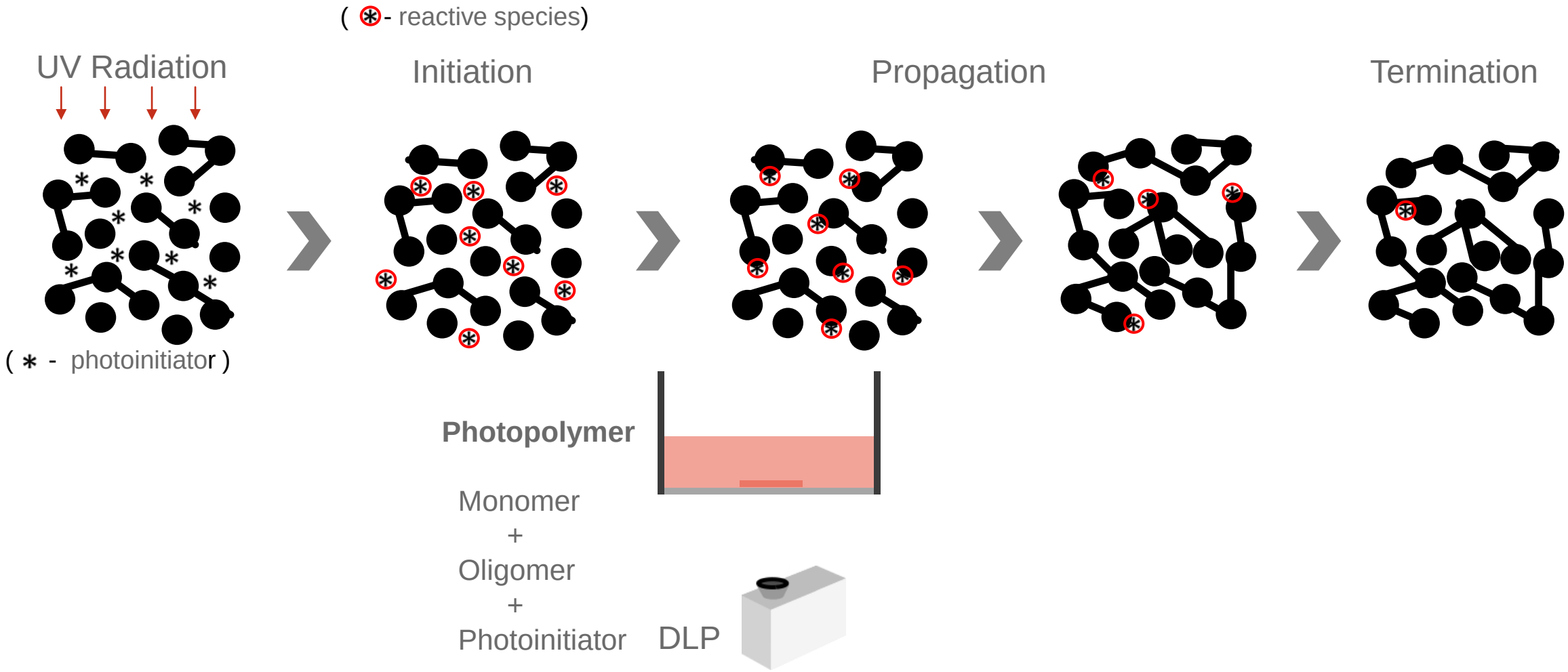


Debinding



Sintering

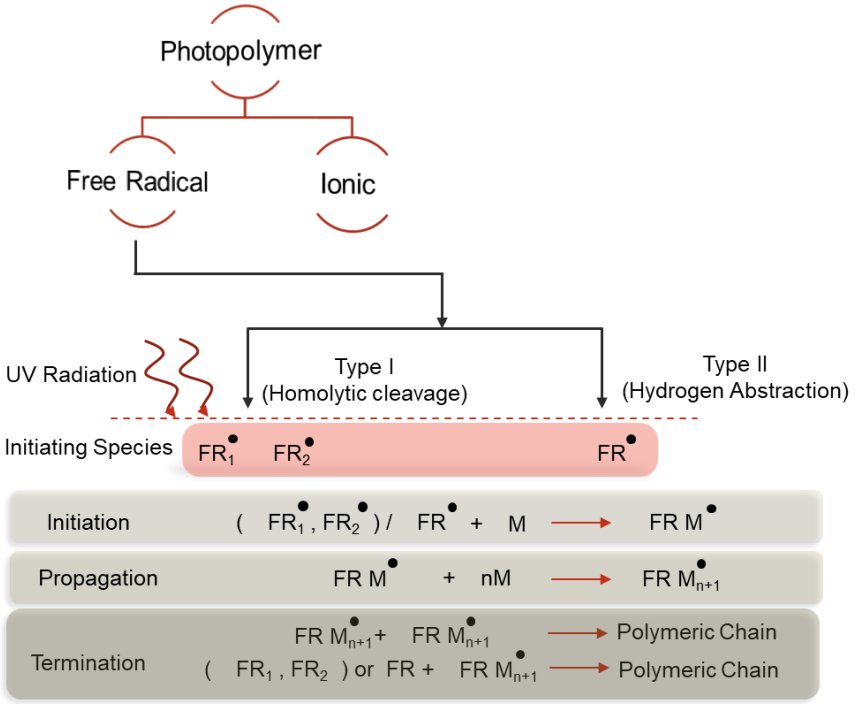
Photopolymerization



Yagci Y, Jockusch S, Turro NJ (2010) Photoinitiated polymerization: Advances, challenges, and opportunities. Macromolecules 43:6245–6260

Photopolymerization

Reactions



Photopolymer (Resin) characteristics

Penetration Depth & Critical Time (energy)

According to Beer's Law,

$$I(z) = I_0 e^{-z/D_p}$$

Corresponding dose,

$$D(z,t) = t.I_0 e^{-z/D_p}$$

Critical dose at distance z_p,

$$D_c(z,t) = t_p.I_0 e^{-z_p/D_p} \quad \ldots. (1)$$

Critical time to reach critical dose,

$$T_c = \frac{D_c}{I_0} \quad \ldots. (2)$$

$$z_p = D_p \ln(t_p / T_c)$$

Penetration depth

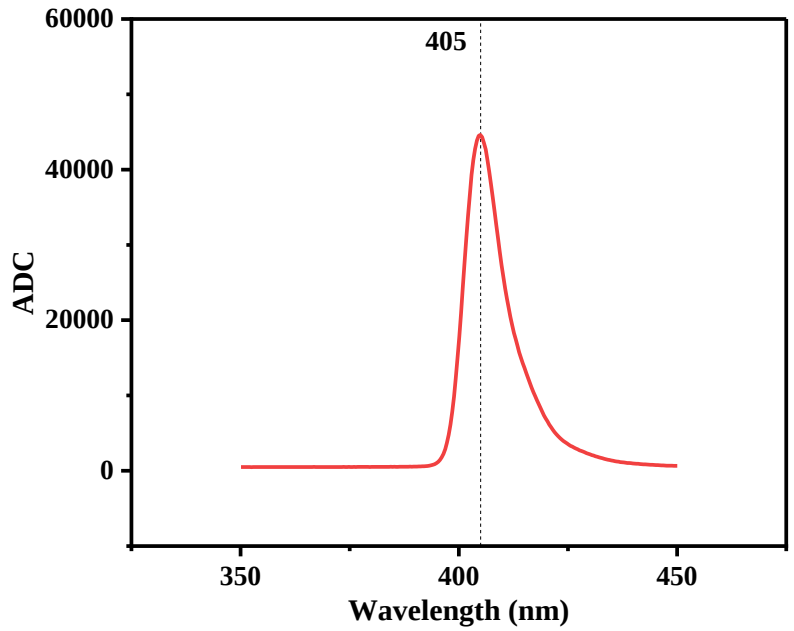
Critical time to reach critical dose

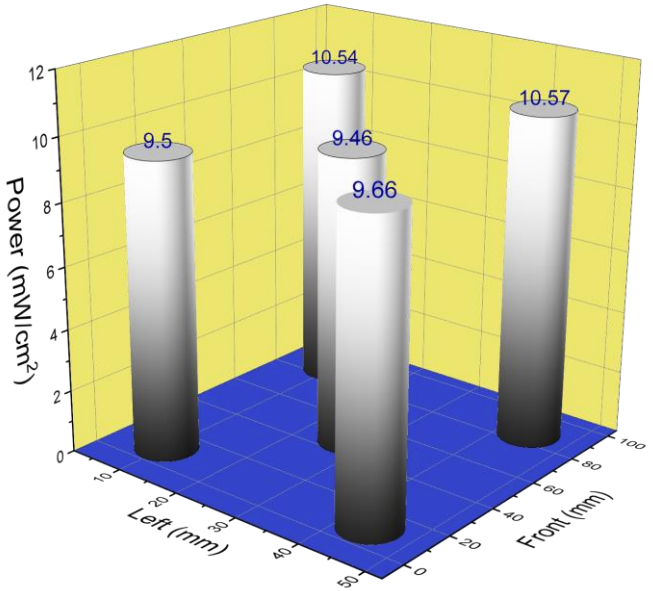
Gong H, Beauchamp M, Perry S, et al (2015) Optical approach to resin formulation for 3D printed microfluidics. RSC Adv 5:106621–106632.

Characterization: Why?

Parameters

- **Radiation Properties**
  - Wavelength
  - Intensity

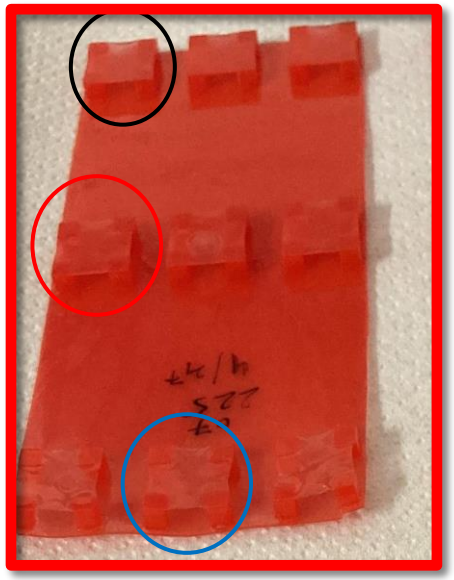


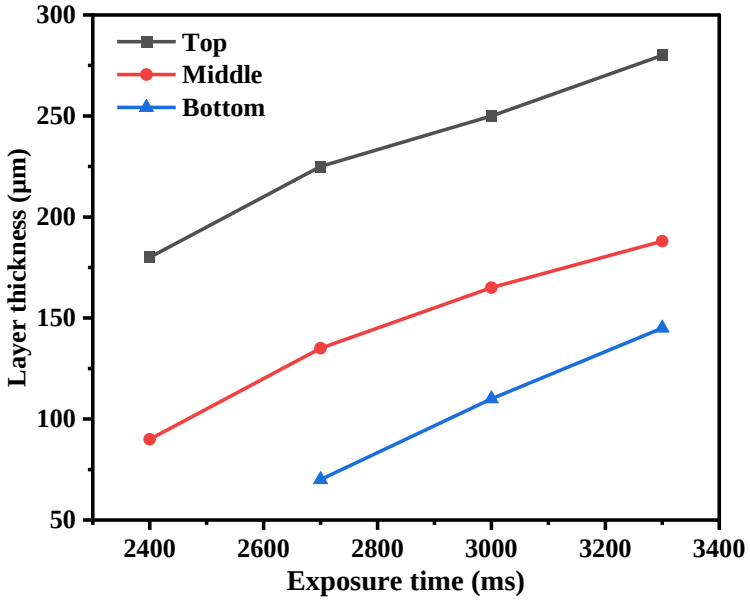


Characterization: Why?

Parameters

- **Radiation Properties**
  - Wavelength
  - Intensity
- **Material Properties**
  - Exposure time
  - (Composition)
  - Layer thickness





Photopolymers

Pure photopolymers

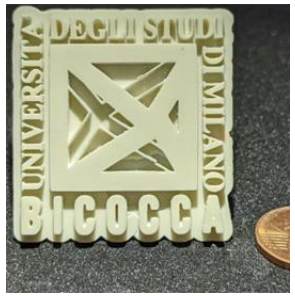
- Dental clear

- Model black

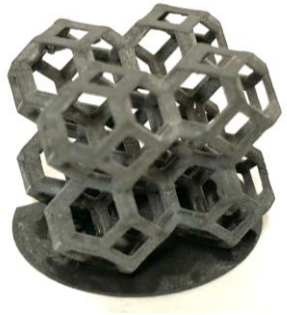
- Gstrong

Suspensions

- Procelite

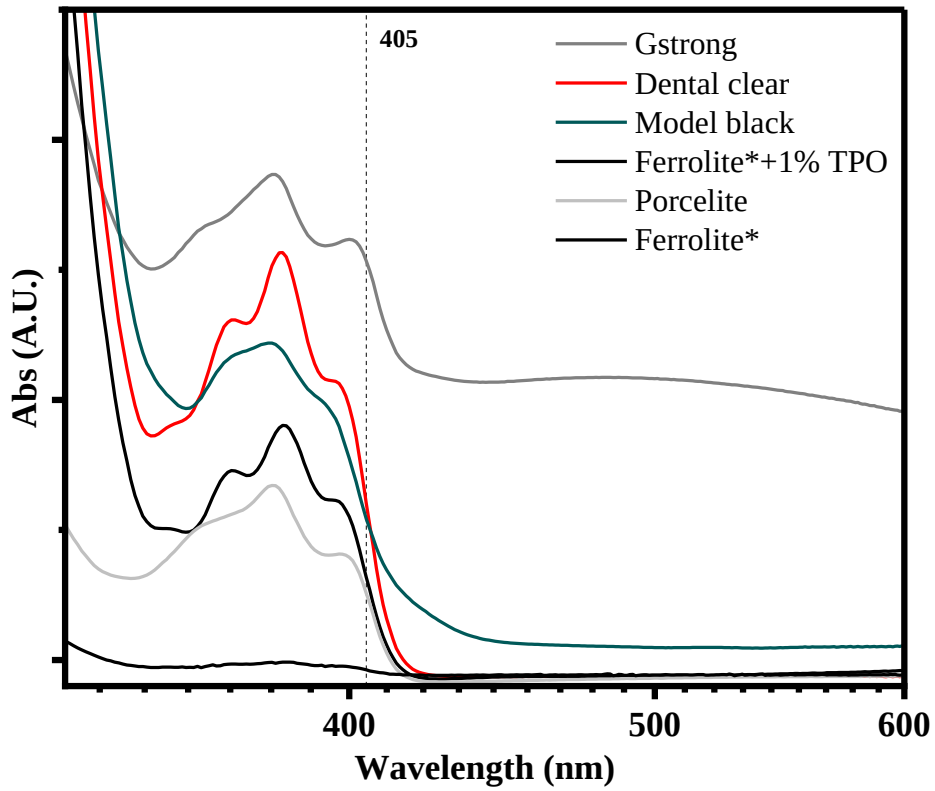


- Ferrolite* (+1% Photoinitiator)

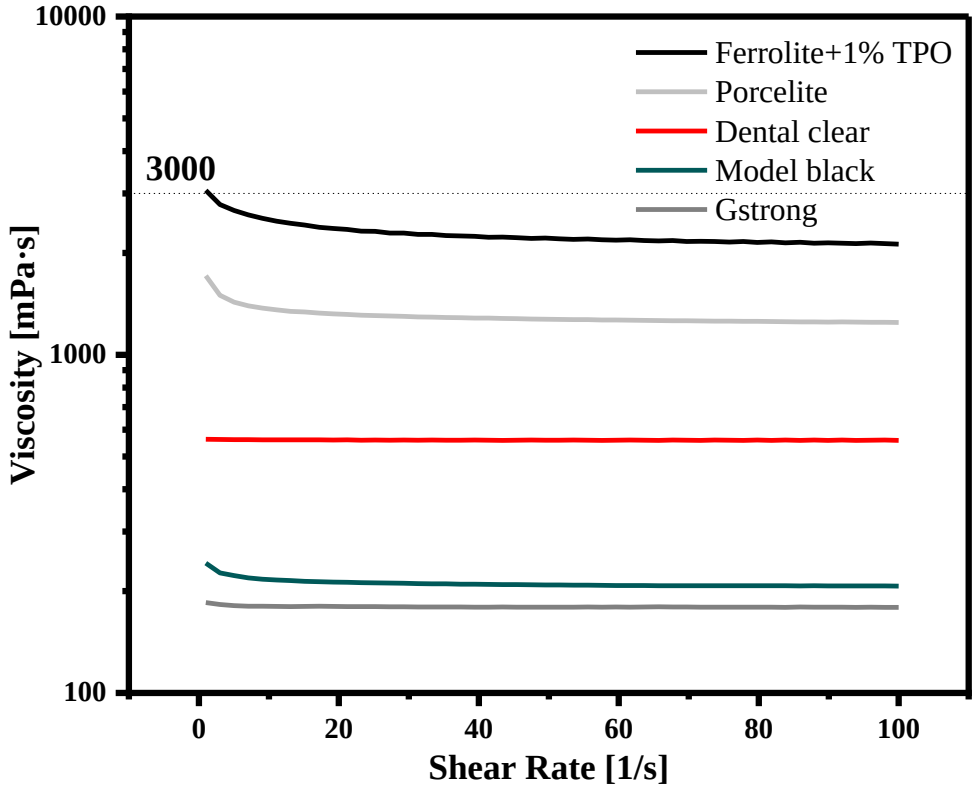


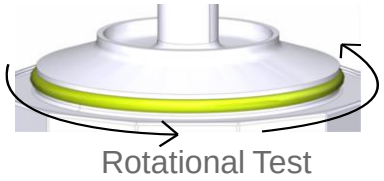
Characterization

UV-Vis spectroscopy



Rheology





Komissarenko, D., Sokolov, P., Evstigneeva, A., Shmeleva, I., & Dosovitsky, A. (2018). Rheological and Curing Behavior of Acrylate-Based Suspensions for the DLP 3D Printing of Complex Zirconia Parts. Materials, 11(12), 2350.

Exposure time vs layer thickness

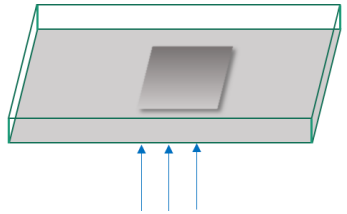
Pure photopolymers

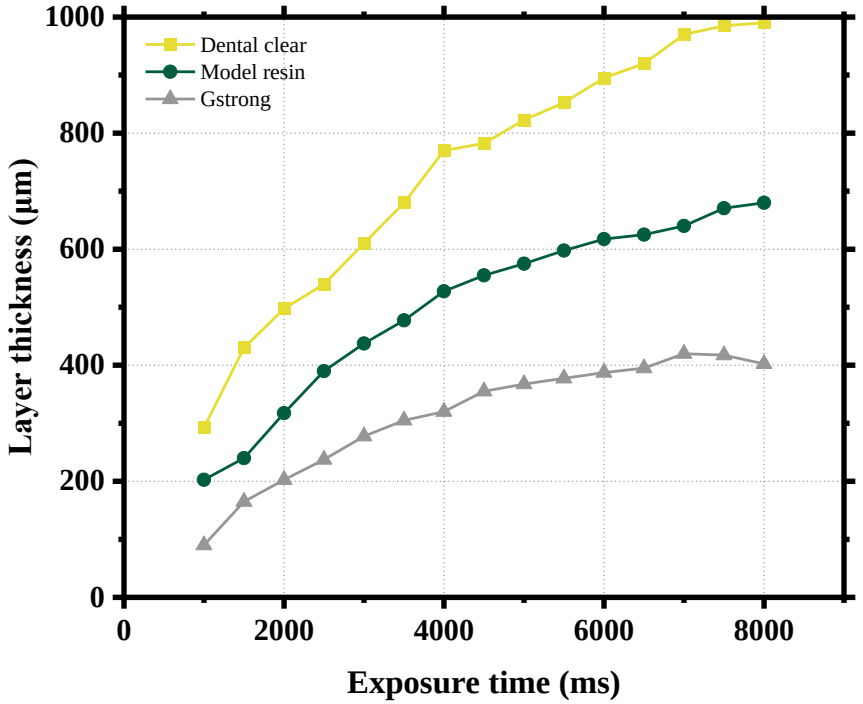
- Dental clear

- Model resin

- Gstrong

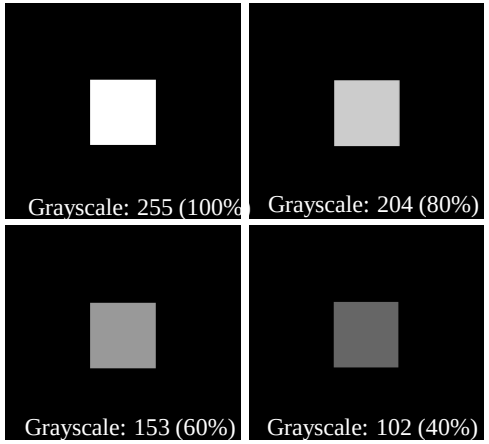
Unconstrained



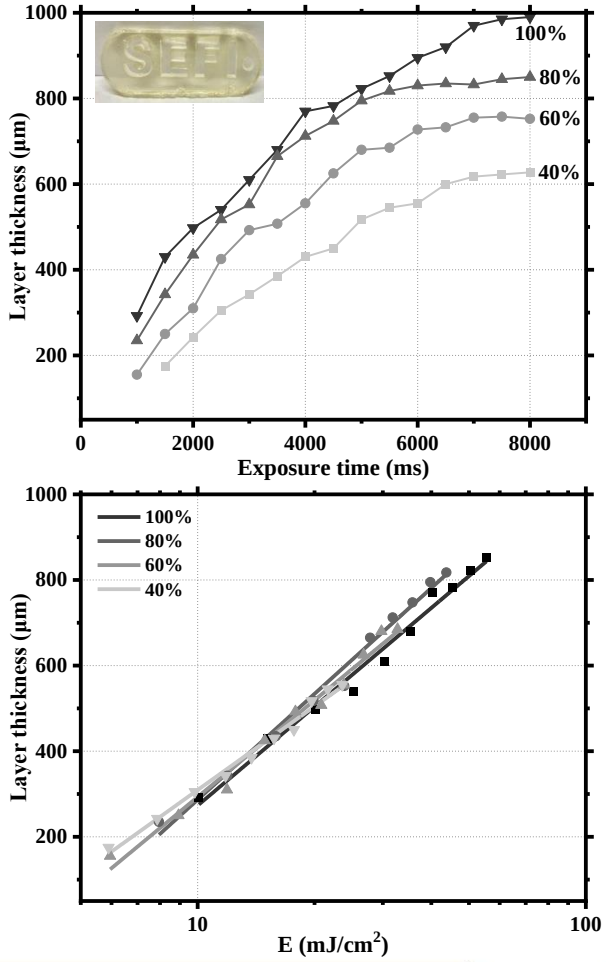


Exposure time vs layer thickness

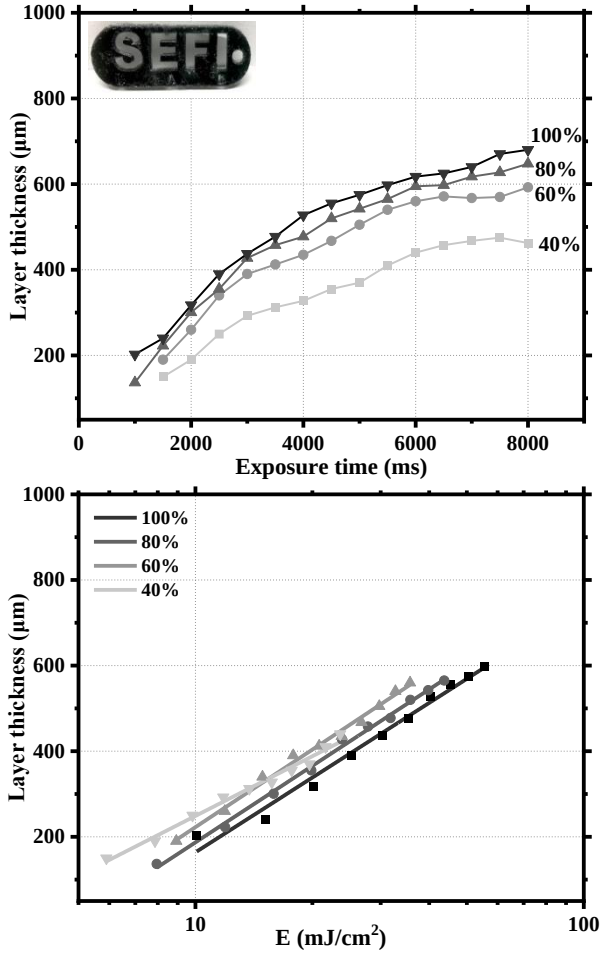
Projections (Diff. intensities)



Dental clear

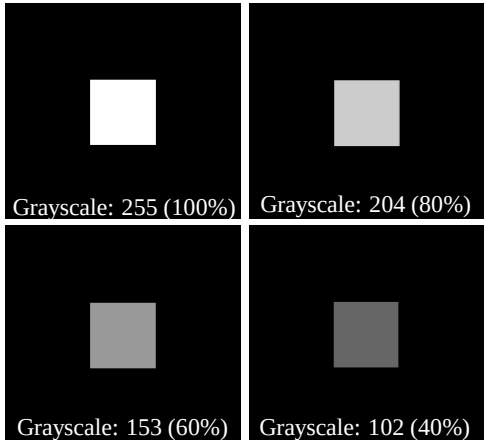


Model resin

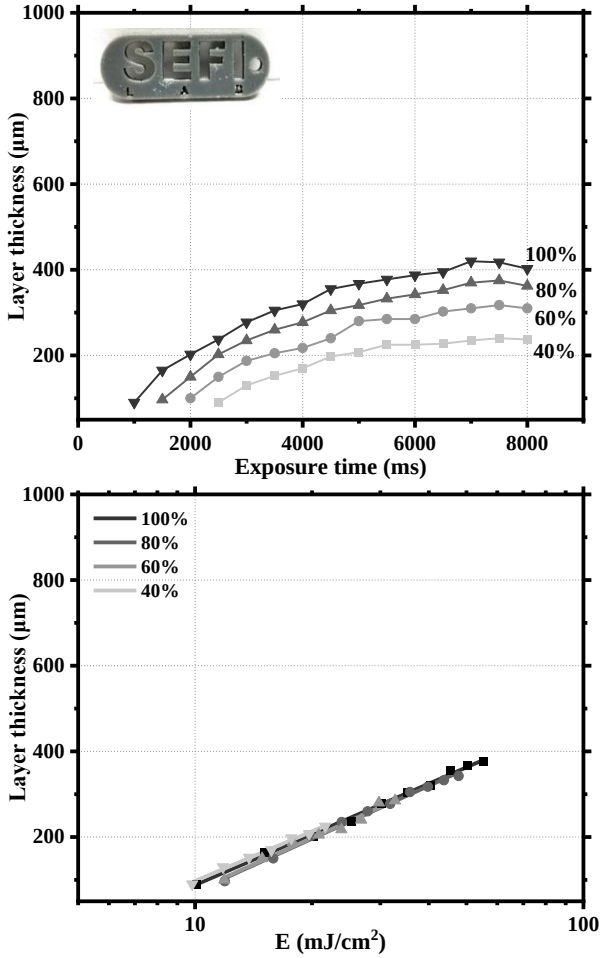


Exposure time vs layer thickness

Projections (Diff. intensities)



Gstrong



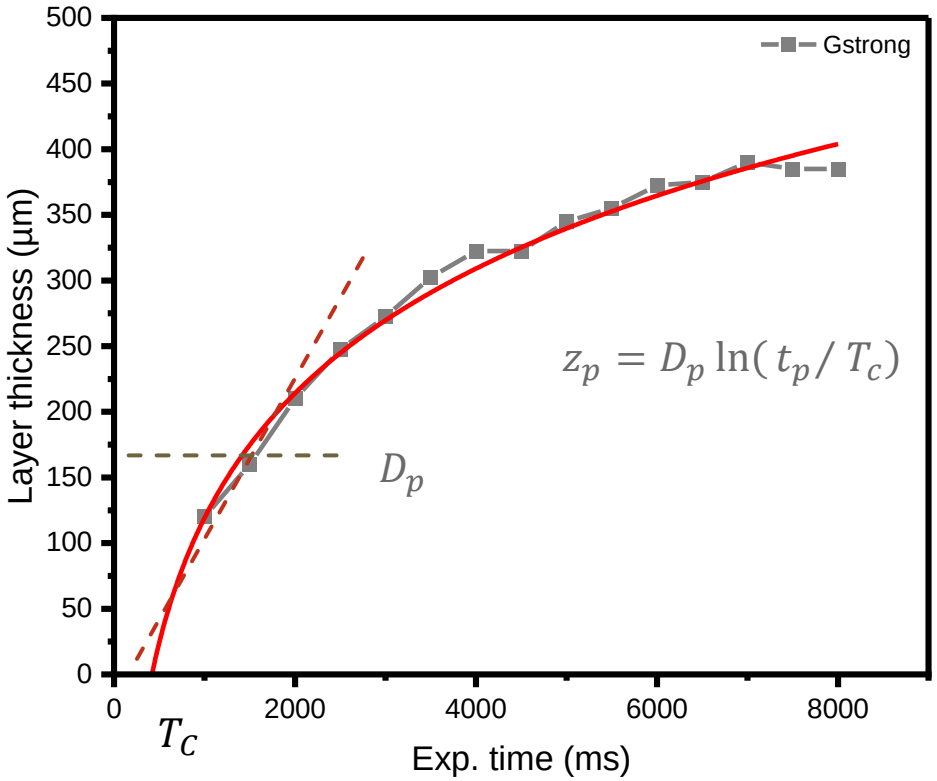
$$z_p = D_p \ln(t_p / T_c)$$

Penetration depth

Critical time to reach critical dose

Characteristic parameters

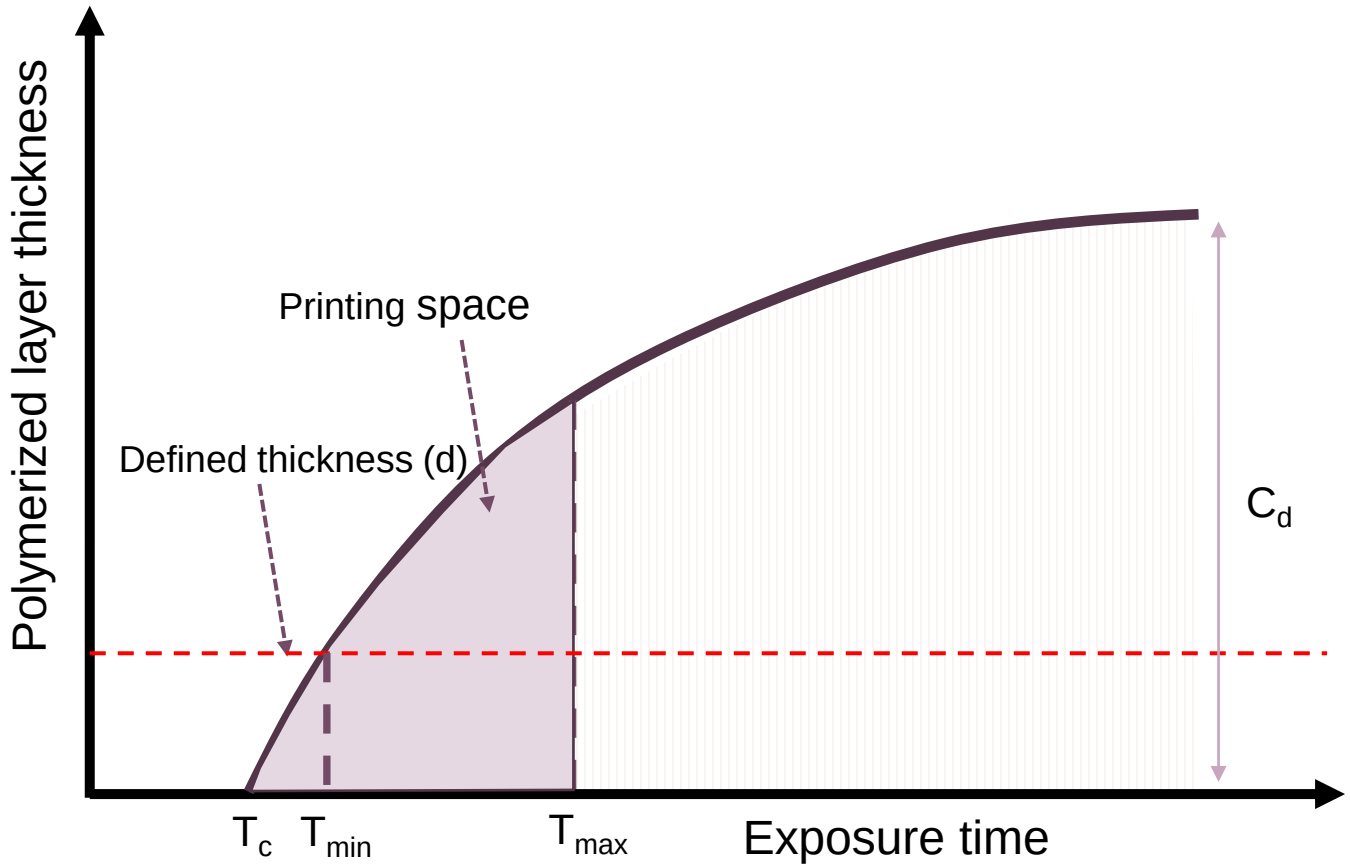
Gstrong



Characteristic parameters (Gstrong)

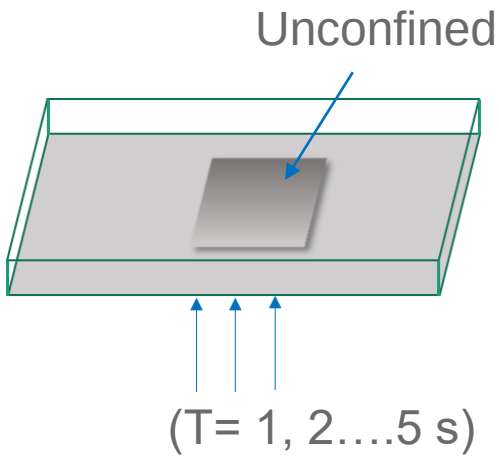
Intensity	Parameters	
	D_p	E_c
100	170.9 ± 3.5	5.9 ± 0.2
80	178.3 ± 4.7	6.5 ± 0.4
60	177.7 ± 9.9	6.5 ± 0.4
40	167.0 ± 6.1	5.5 ± 0.2

3D printing map

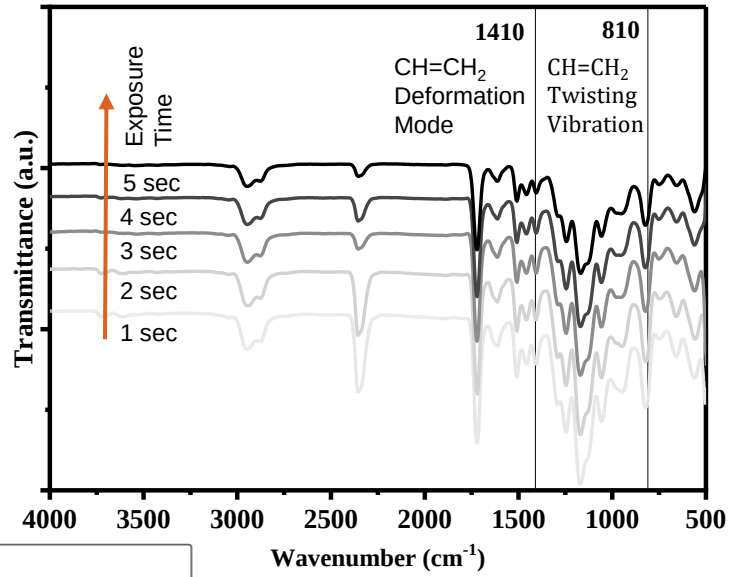


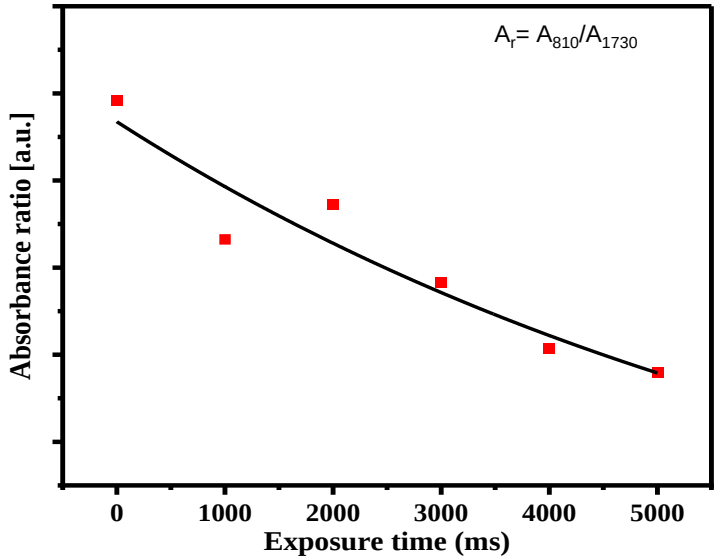
Characterization (FTIR-ATR I)

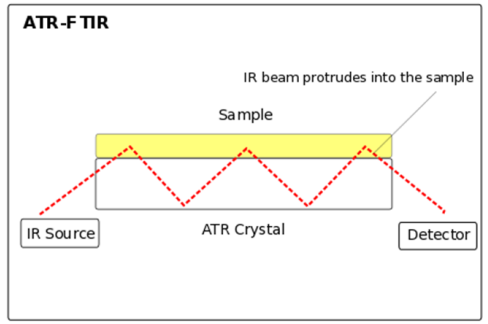
Method



FTIR (Gstrong)



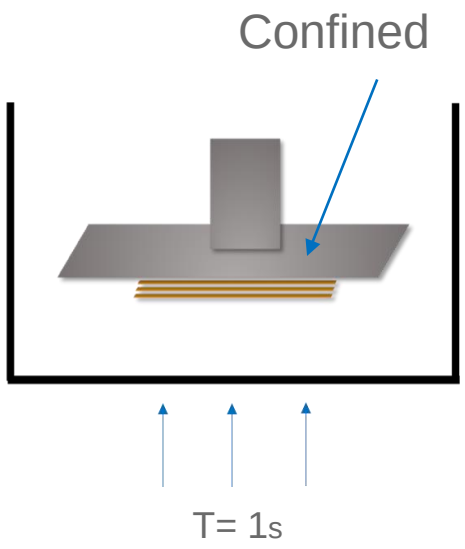


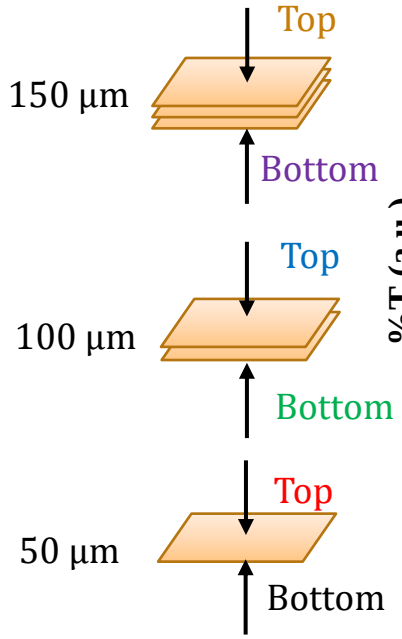


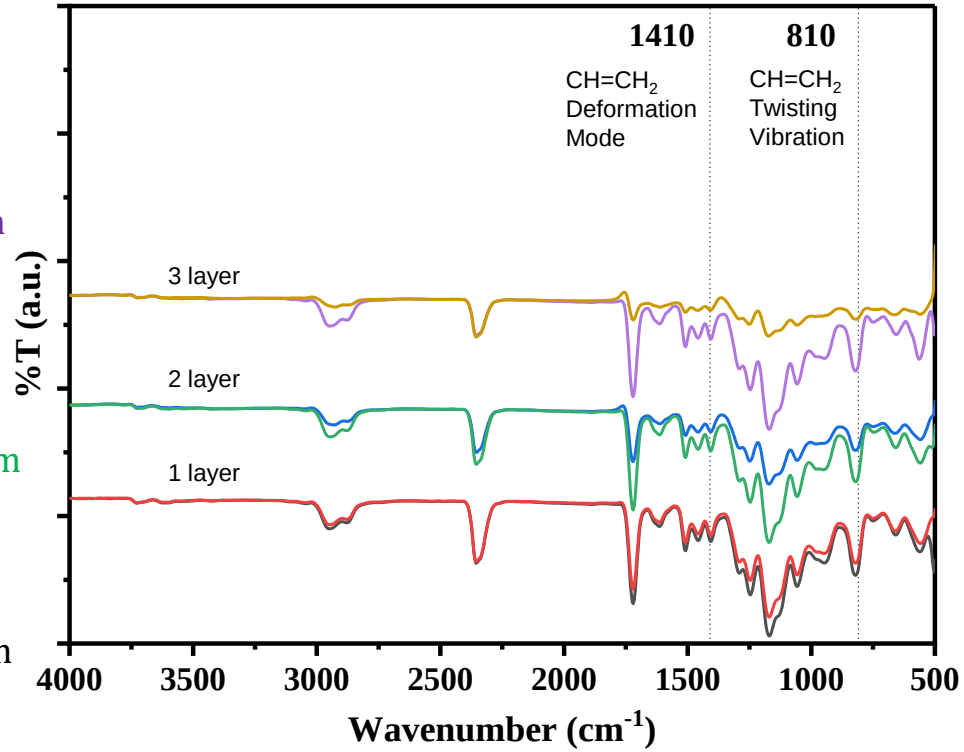
T. Scherzer, U. Decker, Vib. Spectrosc. 19 (1999) 385–398.; D. Kunwong, N. Sumanochitraporn, S. Kaewpirom, Songklanakarin J. Sci. Technol. 33 (2011) 201–207.

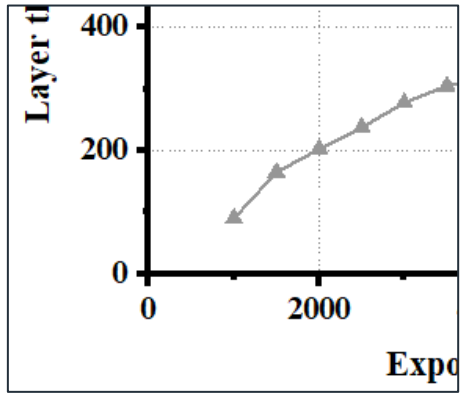
Characterization (FTIR-ATR II)

Method









Printing and characterization

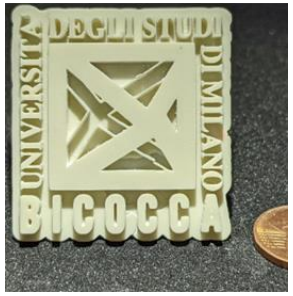
Suspensions

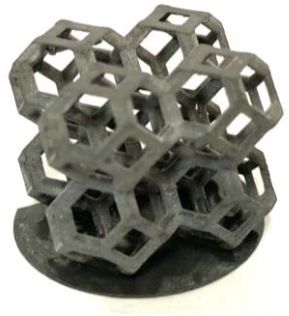
- Porcelite
- Ferrolite* (+1% Photoinitiator)

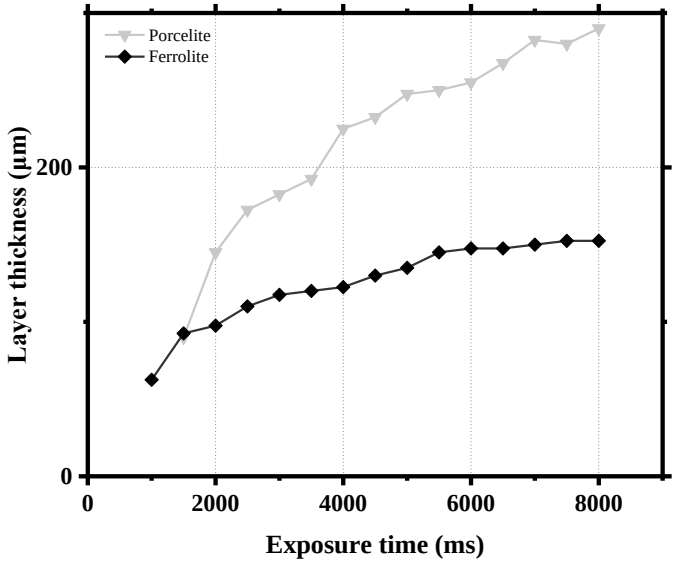
Critical dose at distance z_p,

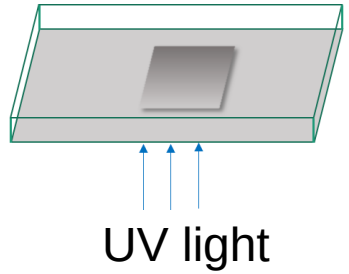
$$z_p = \frac{2\langle d \rangle}{3\tilde{Q}} \frac{n_0^2}{\Delta n^2} \ln\left(\frac{T_0}{T_{crit}}\right)$$

<d> = average particle size
$\Delta n^2 = (n_p - n_0)^2$; square of refractive index difference
$\tilde{Q}$ = scattering efficiency term





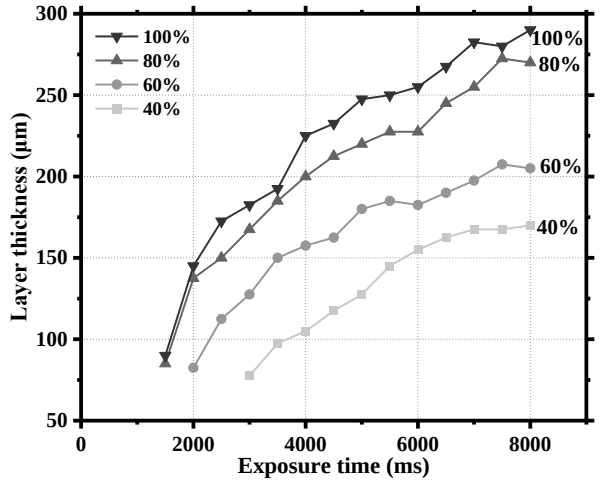


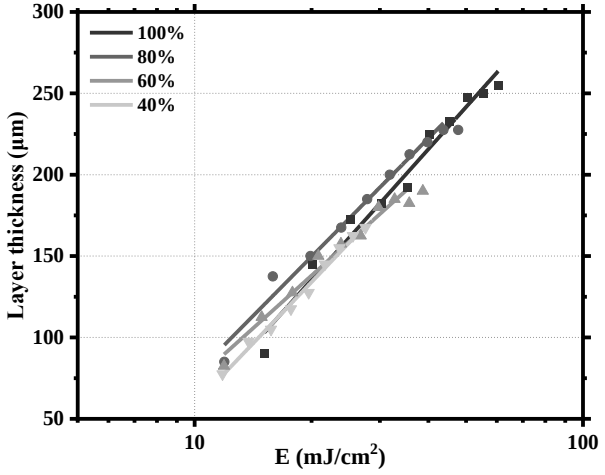


Gentry SP, Halloran JW (2015) Light scattering in absorbing ceramic suspensions: Effect on the width and depth of photopolymerized features. J Eur Ceram Soc 35:1895–1904.

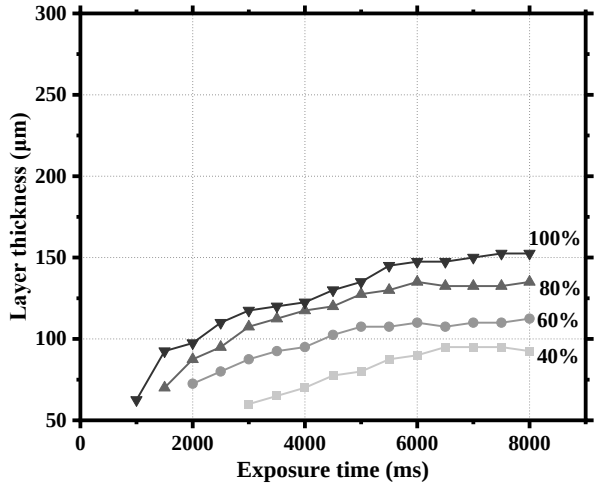
Exposure time vs layer thickness

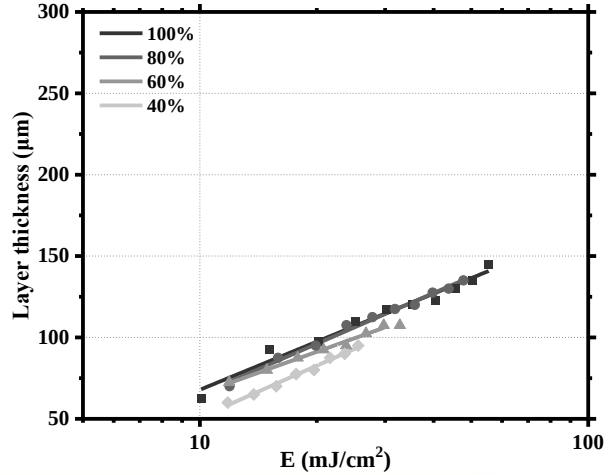
Porcelite





Ferrolite



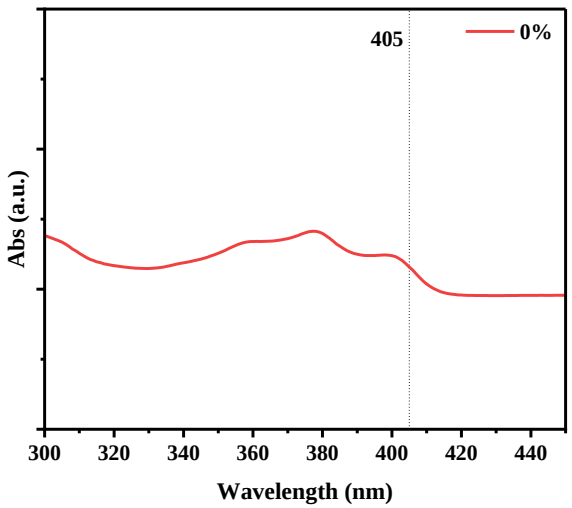


Photopolymer	Parameter	Intensity			
		100	80	60	40
Porcelite	D_p	115.8± 6.4	104.9± 5.1	93.3 ± 5.7	108.6 ± 4.1
	E_c	6.2 ± 0.6	4.8 ± 0.4	4.5 ± 0.4	5.8 ± 0.2
Ferrolite	D_p	42.6 ± 2.5	45.0 ± 1.4	37.1 ± 1.7	46.0 ± 1.9
	E_c	2.0 ± 0.3	2.3 ± 0.1	1.7± 0.2	3.3 ± 0.2

Feedstock preparation

Preparation and characterization

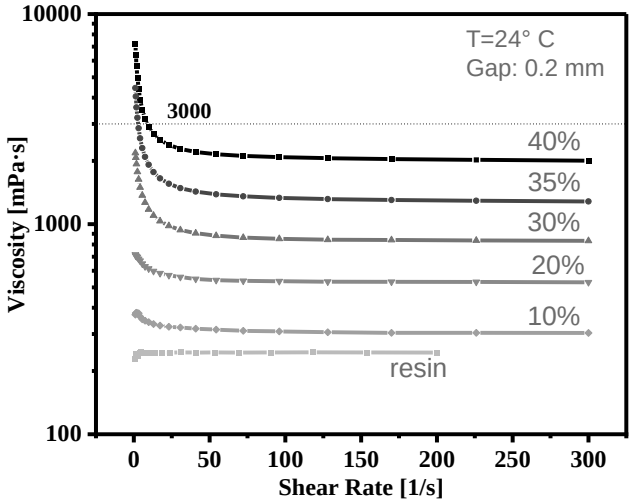
– Five different feedstocks have been prepared by mixing 10%, 20%, 30%, 35% and 40% v/v stainless steel powder (~22µm) into *Tethon high development base resin.*



Base Resin

+

Stainless Steel Powder



Summary & Conclusion

- **Product characterization**
  - Wavelength
  - Intensity
- **Material characterization**
  - UV spectroscopy
  - Rheology
  - FTIR
- **Fundamentals of vat polymerization**
  - Characteristic parameters
- **Printing map**
- **Potential of metal printing by DLP**

Acknowledgements

Surface Engineering And Fluid Interfaces (Est. 2018)

SEFI Lab

SurfICE

surfice-itn.eu
(2021-24)

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Regione Lombardia

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ENEA ,Feanza

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Dott. Enrico Lione
Dott. Paride Fabri

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Research to Standards
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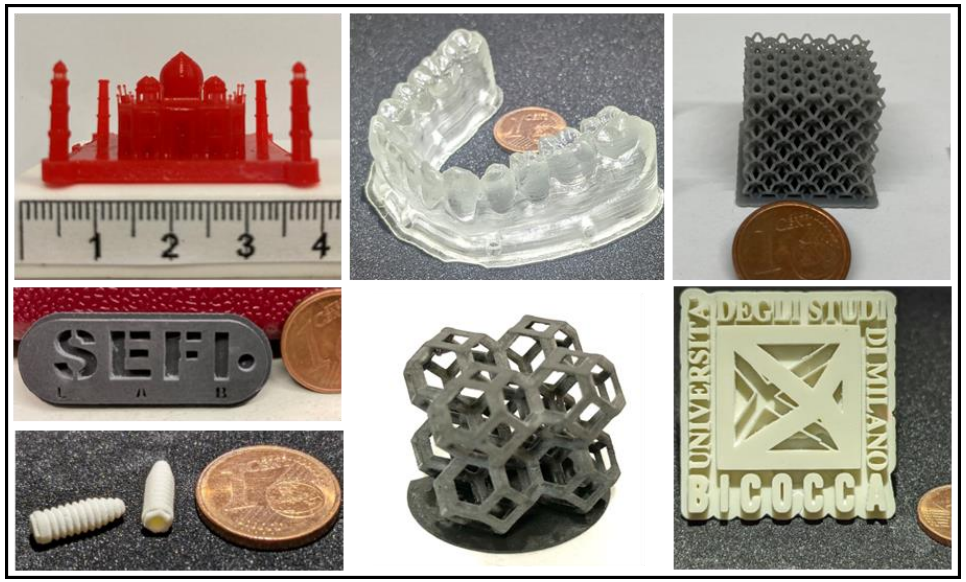
Helping our world work better

Thank you.

Rajat Chaudhary
31st October 2022



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