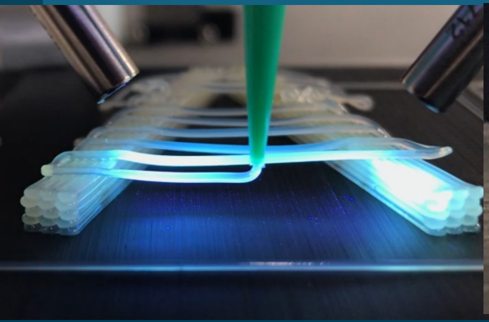
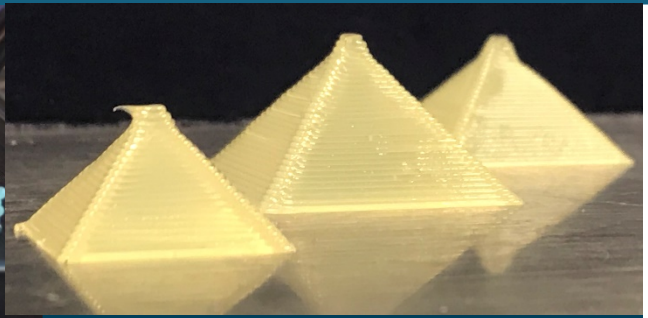
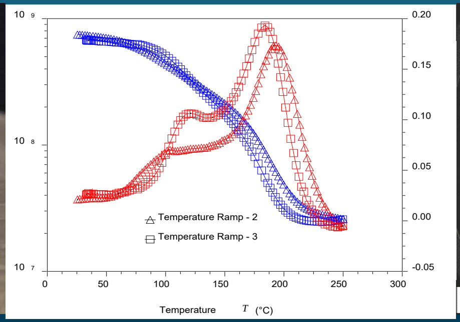
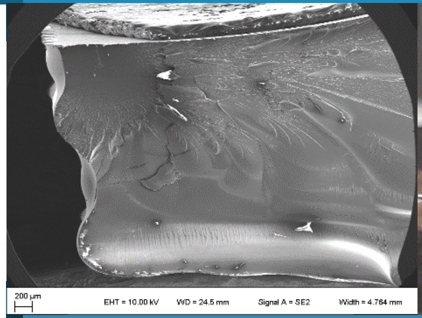
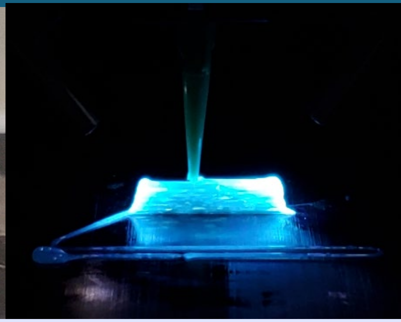
SAND2021-9845PE

Approaches to Thermoset Resins for Direct-Ink-Write Additive Manufacturing

Sandia National Laboratories



PRESENTED BY

Leah Appelhans, Sandia National Laboratories

Jessica Kopatz, Samuel Leguizamon, Adam Cook

DIW Dense Paste Workshop, August 2021

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Acknowledgements

Thanks to:

Jess Kopatz (epoxy/acrylate)

Sam Leguizamon (DCPD)

Adam Cook, Derek Reinholtz (DIW tool design)

Jackie Unangst

Mat Celina, Brad Jones, Erica Redline, Nick Wyatt, Lindsey Hughes,

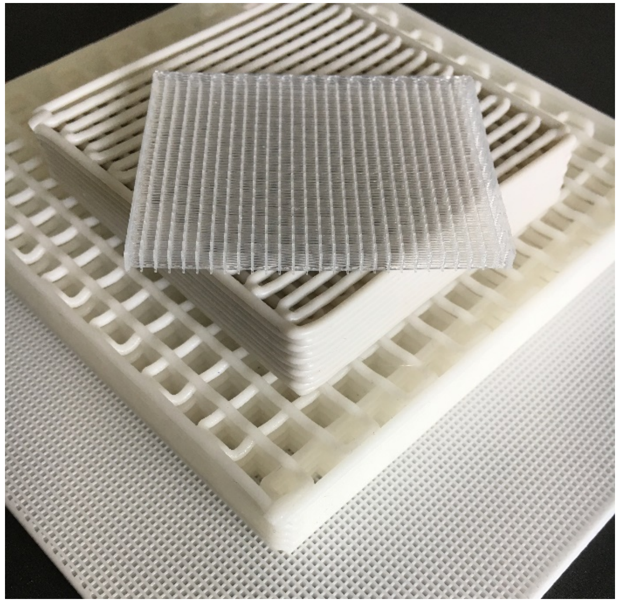
Patti Sawyer, Mark Stavig, Sarah Russell, Nick Monk, Liz Zapien

$$$ NNSA NA-115 Additive Manufacturing

Development Program

Approaches to DIW Printing of Thermoset Resins

Filled silicone DIW compression pads.

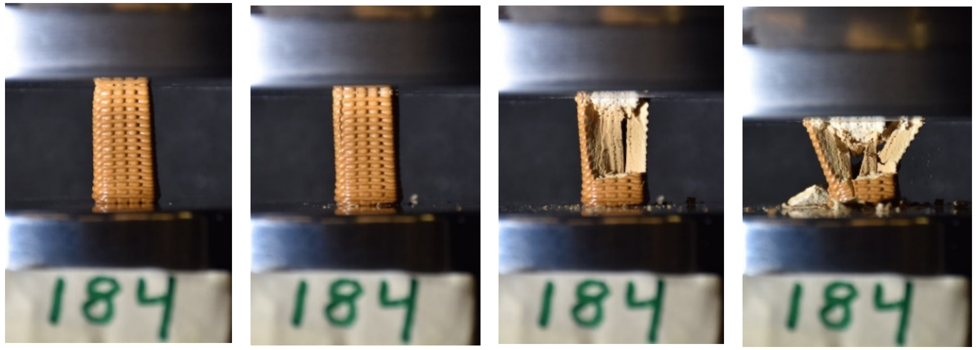


Adam Cook and team (SNL)

1) Increase zero-shear viscosity

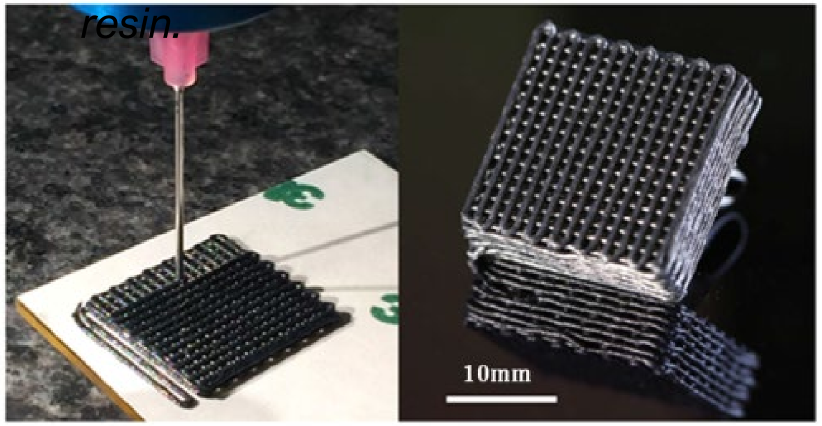
- Moderate-to-high filler loadings
- B-staging
- Shear thinning
- High zero-shear viscosity maintains printed shape

Compression test of printed epoxy/GMB foams.



Collaboration between Jamie Messman (KCNSC) and Brett Compton (UTenn, Knoxville)

Carbon fiber filled printed epoxy resin.



Jim Lewicki and team (LLNL)

Lewicki et al. Scientific Reports, **2017**, 7, 43401

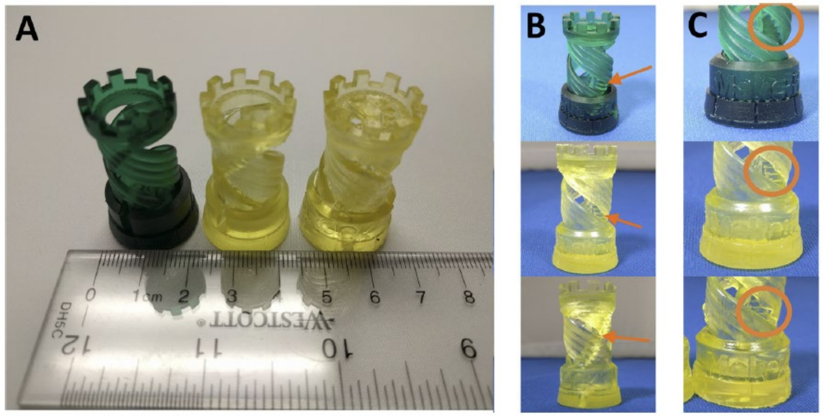
Approaches to DIW Printing of Thermoset Resins

2) *In situ* cure

Single cure for rapidly polymerizing single component systems

- UV or thermal initiation
- Rapid RT polymerization

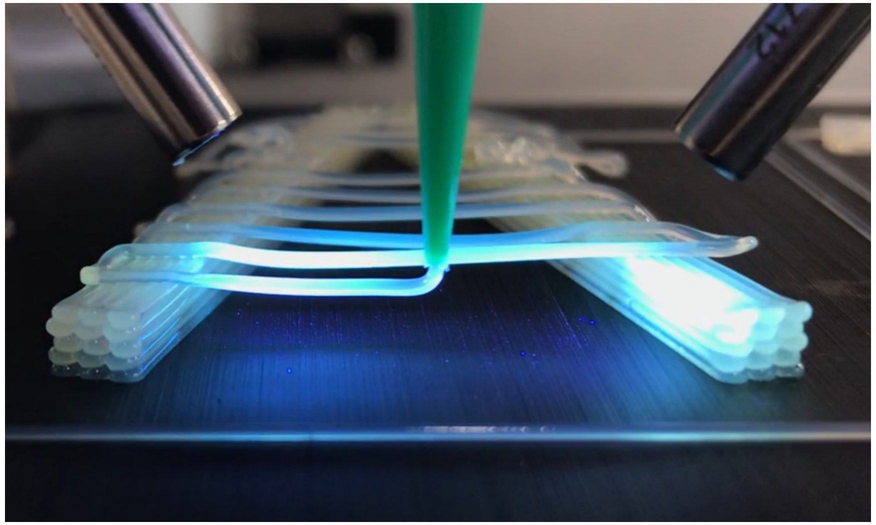
Thermally initiated frontal polymerization (FROMP) of poly(DCPD) thermoset
Robertson et al. *Nature*, **2018,** *557*, 223

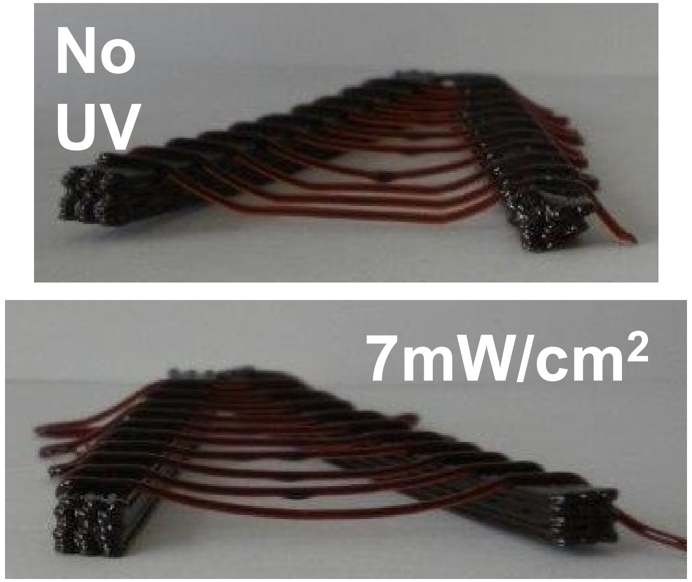


Additive Manufacturing 23 (2018) 374–380

Dual-cure

- **UV/thermal**
  - **Acrylate/epoxy most common**
- Thermal/thermal
- UV/UV



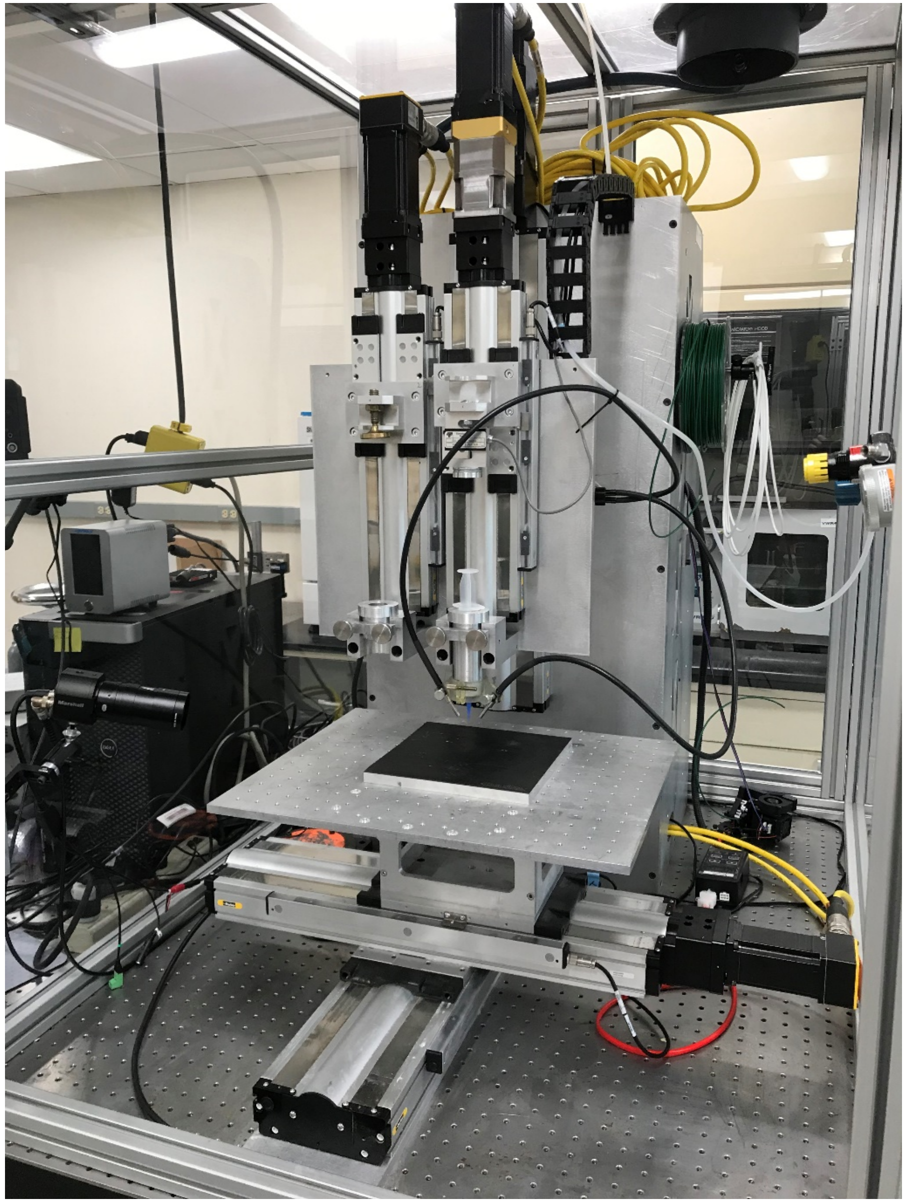


Printing of acrylate/epoxy UV/thermal dual-cure system

Sandia's UV-assisted Direct-Ink Write Capability

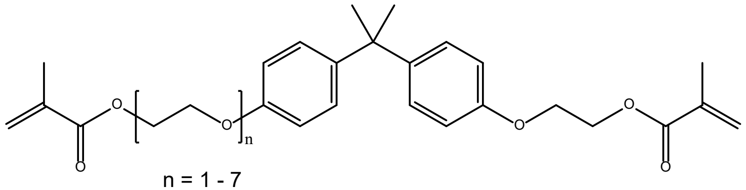
Adam Cook/Derek Reinholtz

- **LED spot-curing system, 365 nm**
- **Controllable UV intensity (max ~450 mW/cm^2)**
- Print nozzle diameter from 0.15-1.55 mm
- Table speed 0.01 mm/s to ~60mm/s
- Print dimensions 300x300x200 mm
- **Constant volume extrusion**



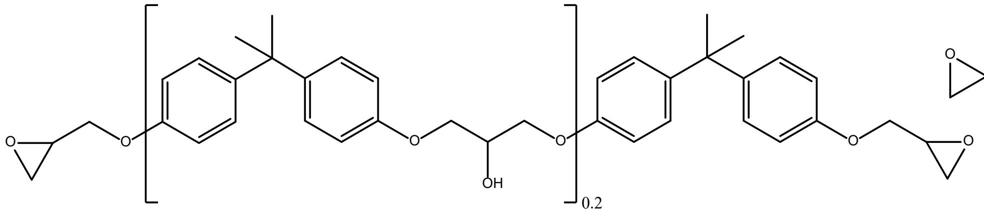
UV-Thermal Dual Cure Resin Formulation

UV-thermal Epoxy/acrylate Formulation

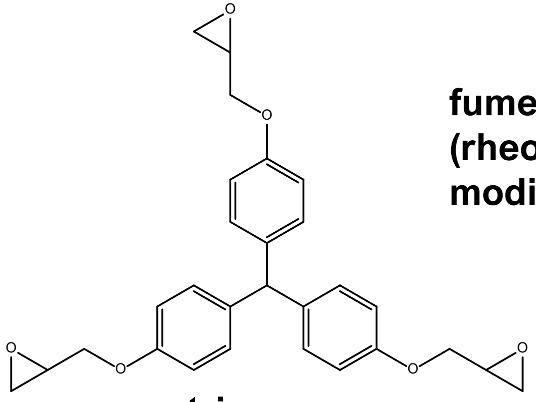


n = 1 - 7

dimethacrylate

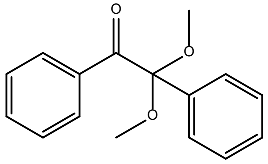


diepoxy

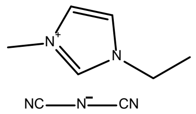


triepoxy

fumed silica (rheology modifier)

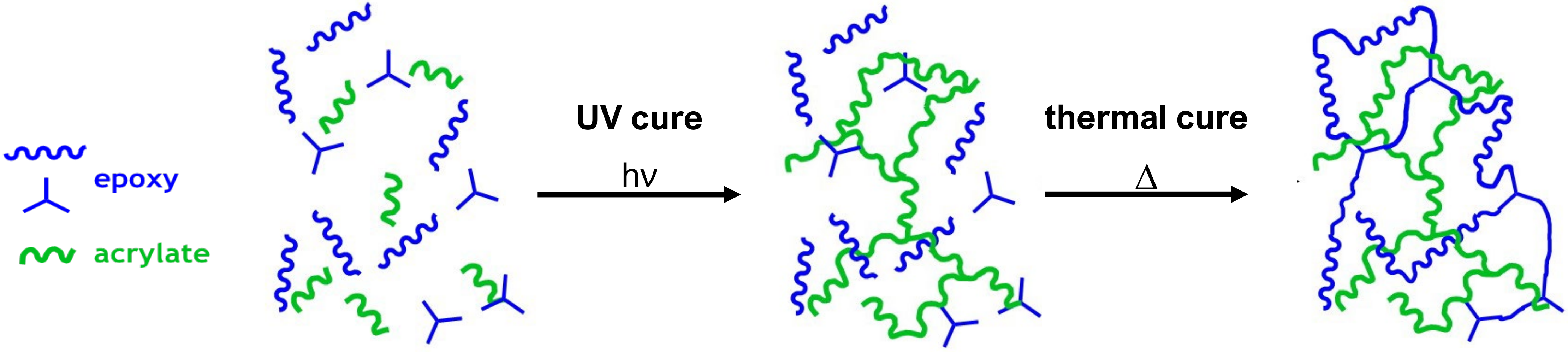


radical photoinitiator
(2,2-dimethoxy-1,2-diphenylethanone)



epoxy latent cure initiator
1-ethyl-3-methylimidazolium dicyanamide

Sequential Interpenetrating Polymer Network



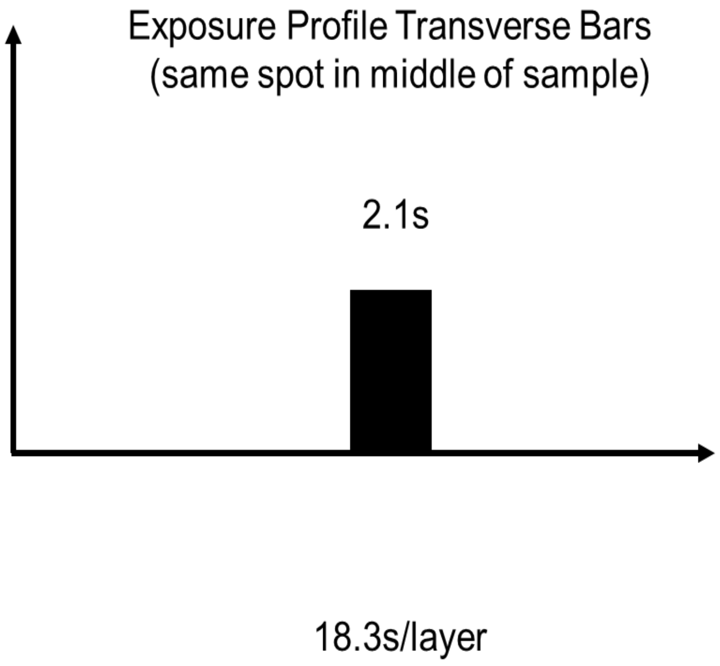
uncured resin mixture

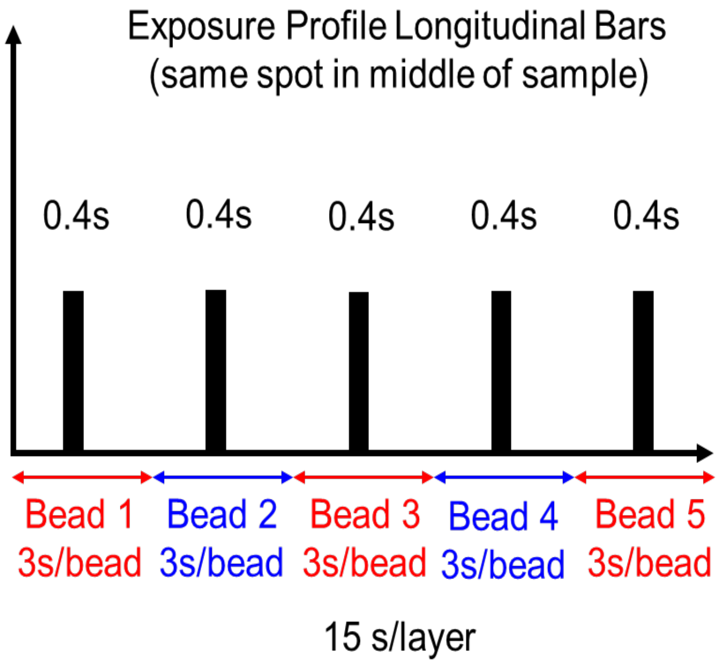
acrylate network forms

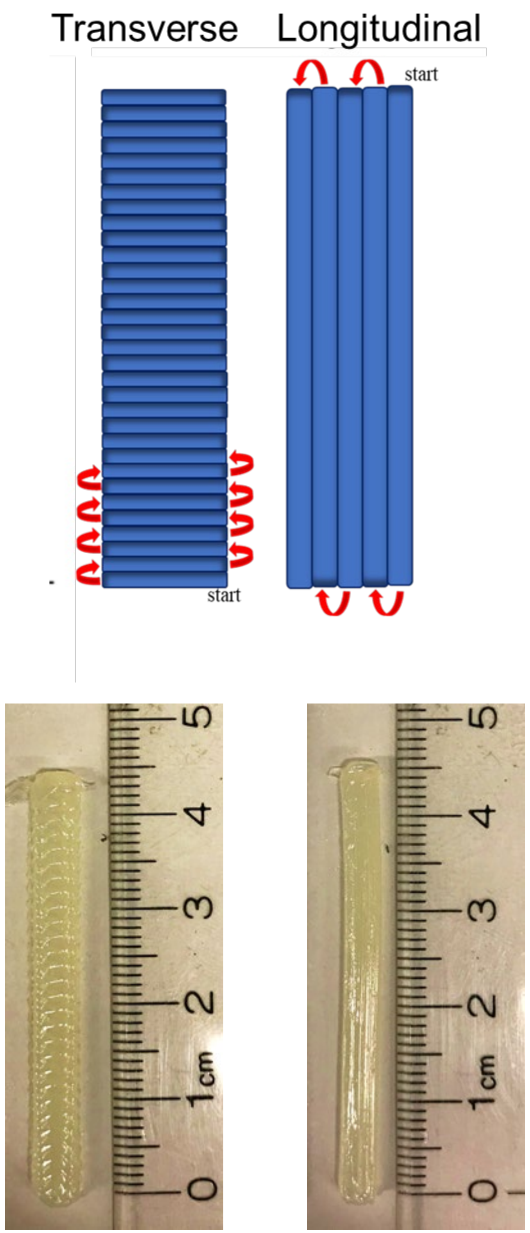
epoxy network forms

Characterize Exposure Profile Effects

Print path determines exposure profile.
- Reciprocity
  - Dose = intensity x duration

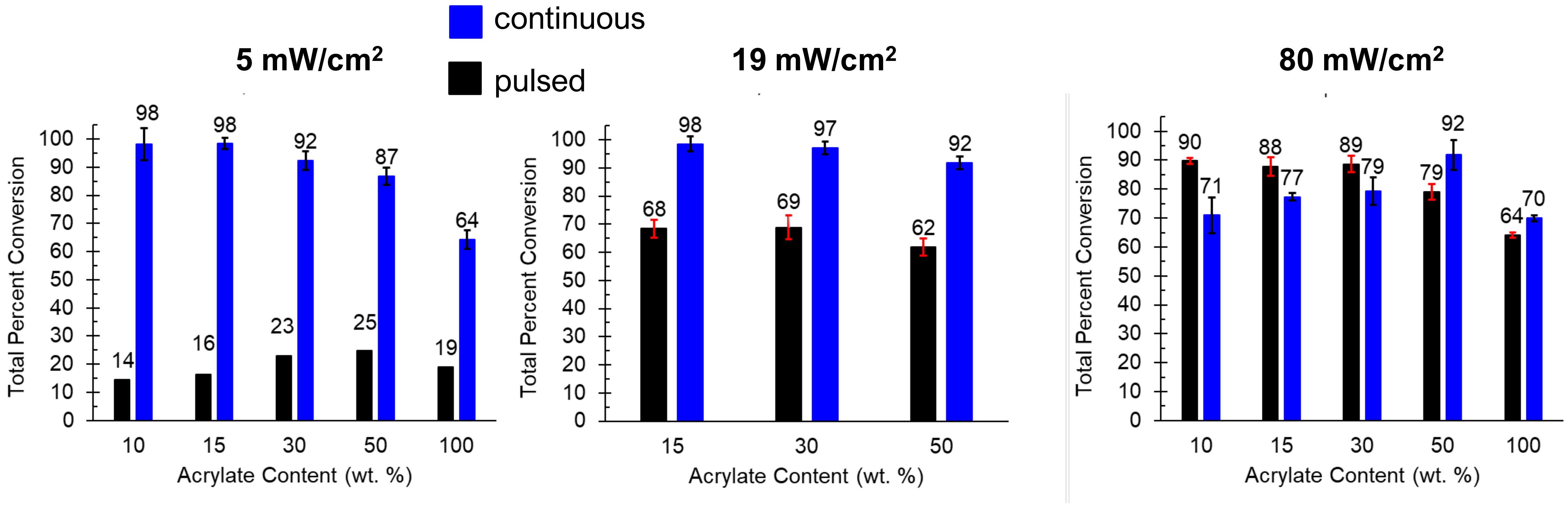






Acrylate Network Formation: Pulsed Exposures

UV-DSC: Determine effects of UV exposure profile and intensity on acrylate conversion.



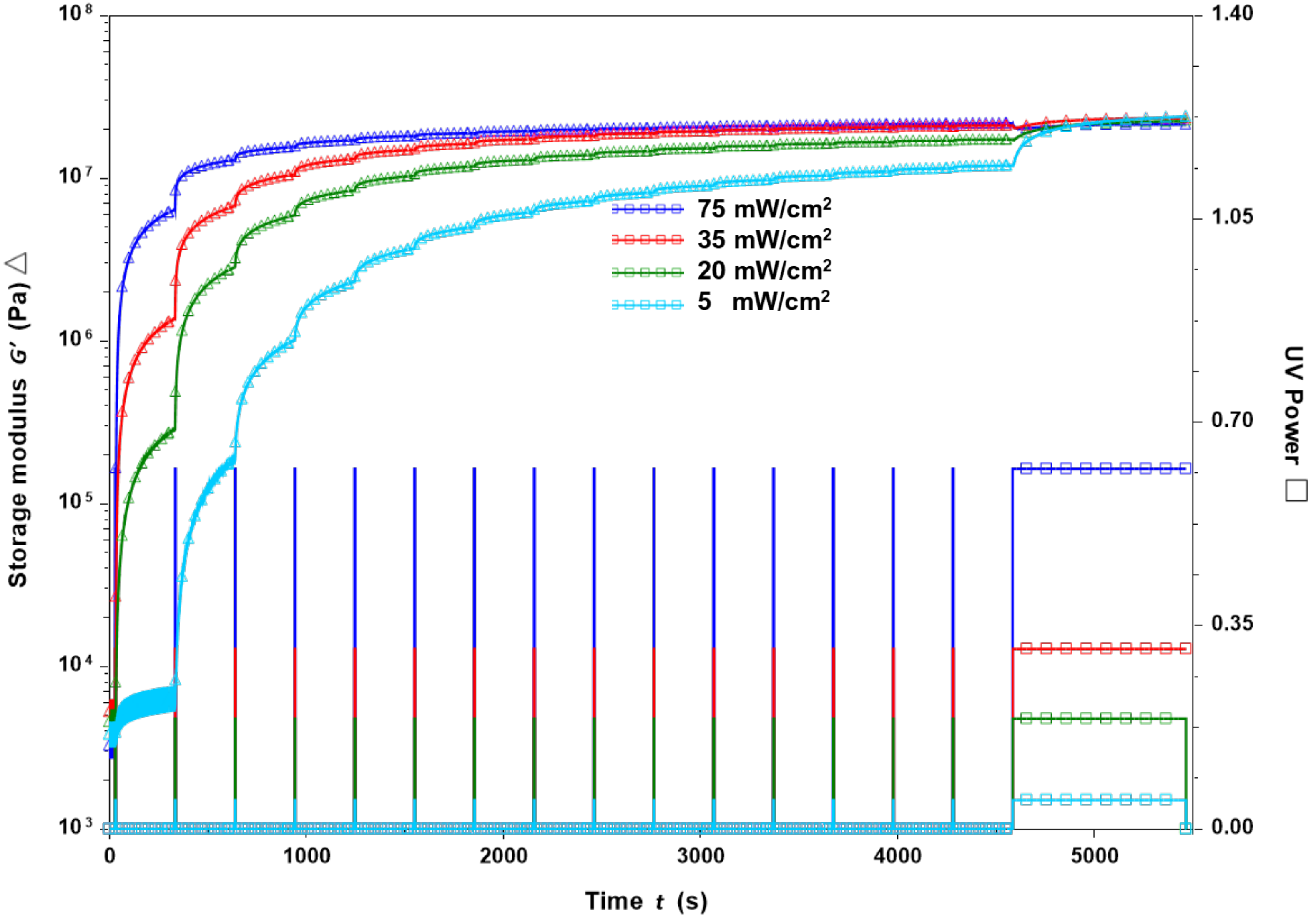
Acrylate conversion vs pulsed/continuous UV exposure at different print intensities

Printing and post-print curing protocols must balance printability, green strength, and conversion.

Acrylate Network Formation: Pulsed Exposures

UV Rheology: Determine effects on modulus of pulsed exposure profiles.

Pulsed exposures at varying intensity for 30 acrylate wt% resin.



Pulsed exposures can be used to mimic print conditions.

Investigate effects of:

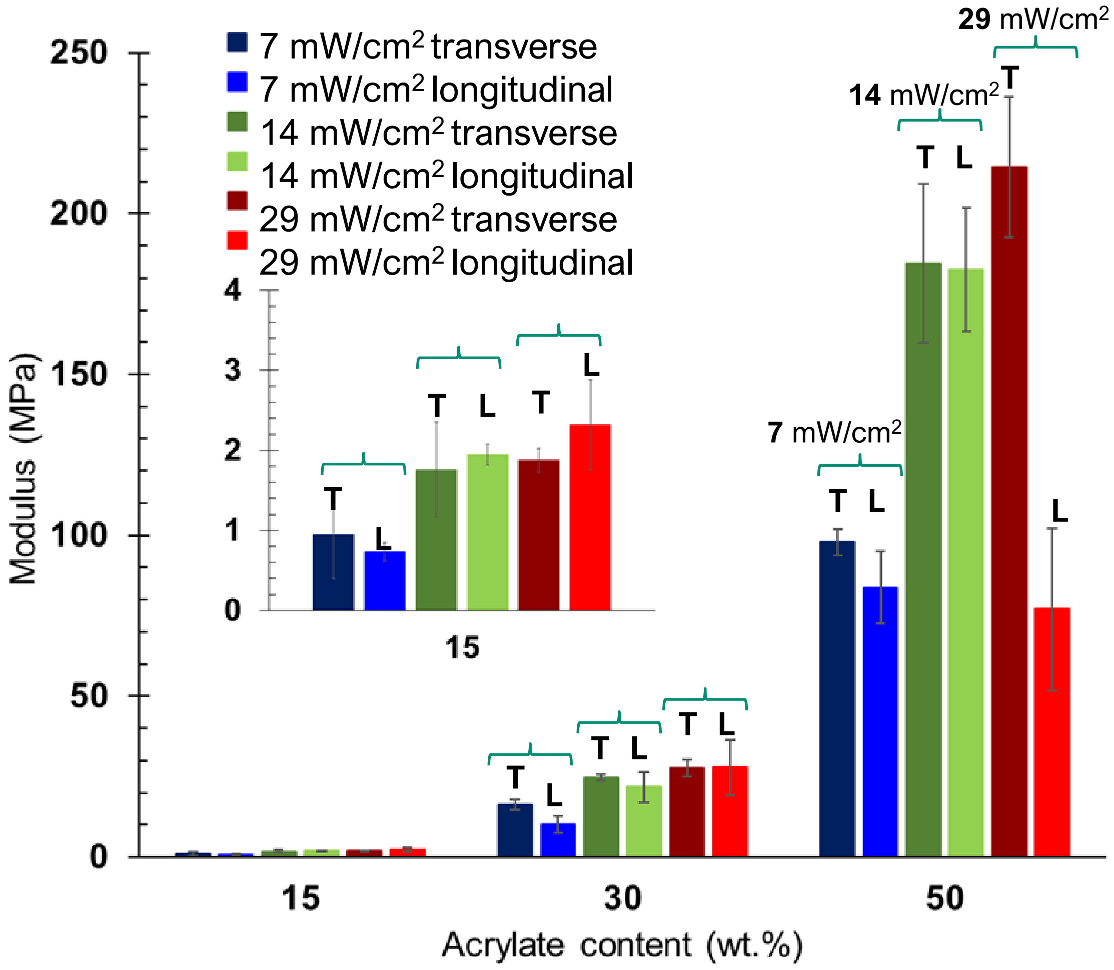
- **Dark cure**
- **Exposure times**
- **Exposure profiles**

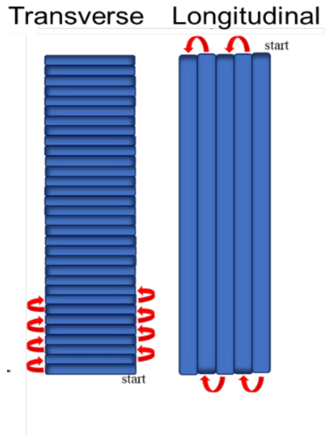
On:

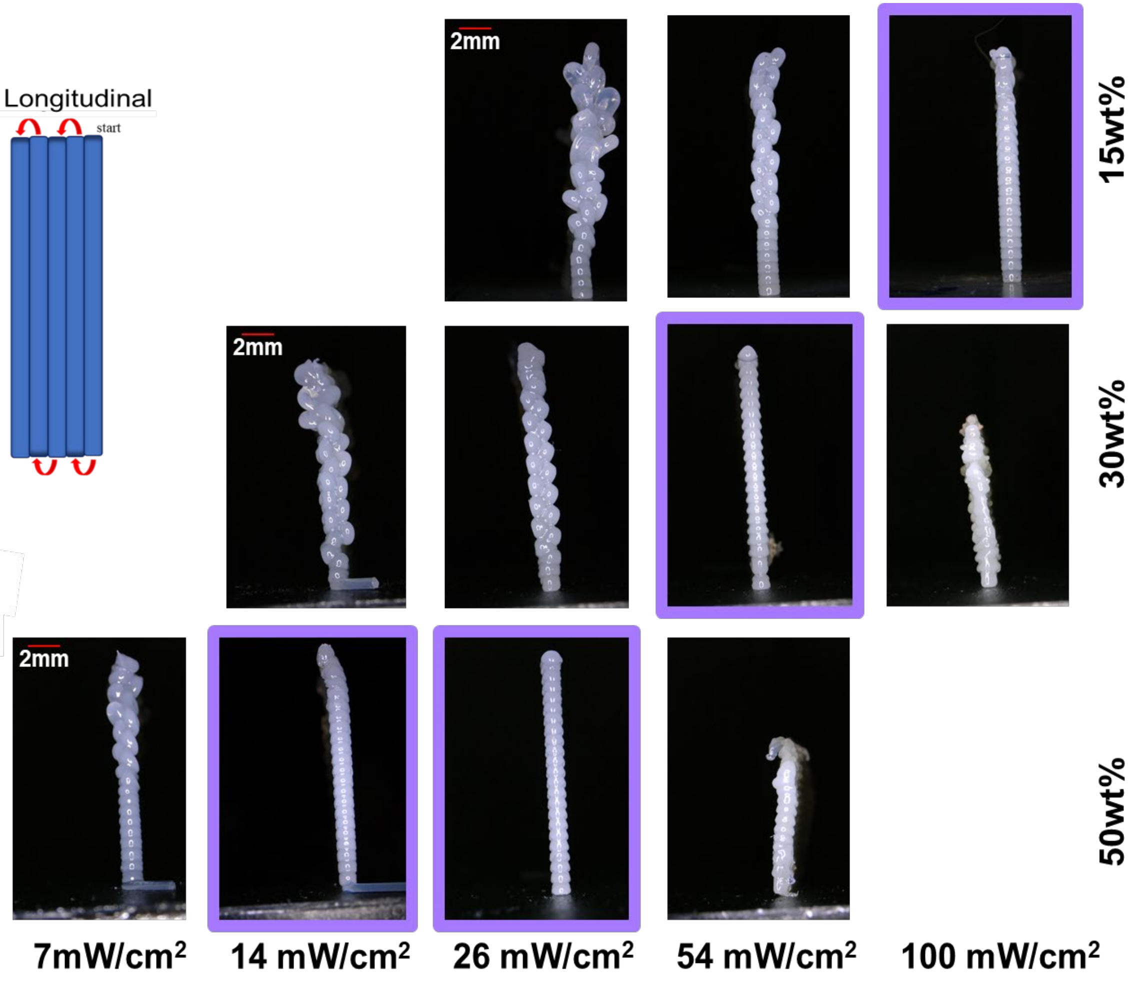
- **Gel point**
- **Plateau moduli**
- **t = x moduli**

UV/Thermal Dual Cure: Printability

UV Print Intensity vs Modulus (Print Cure Only)



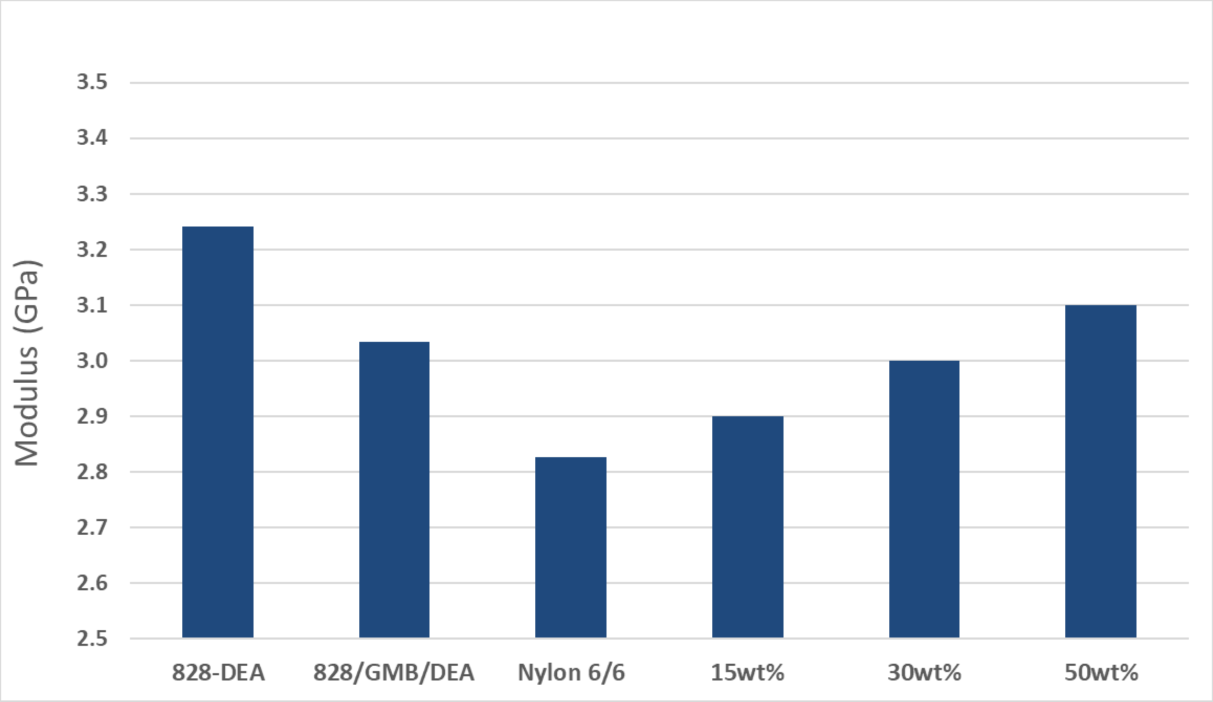




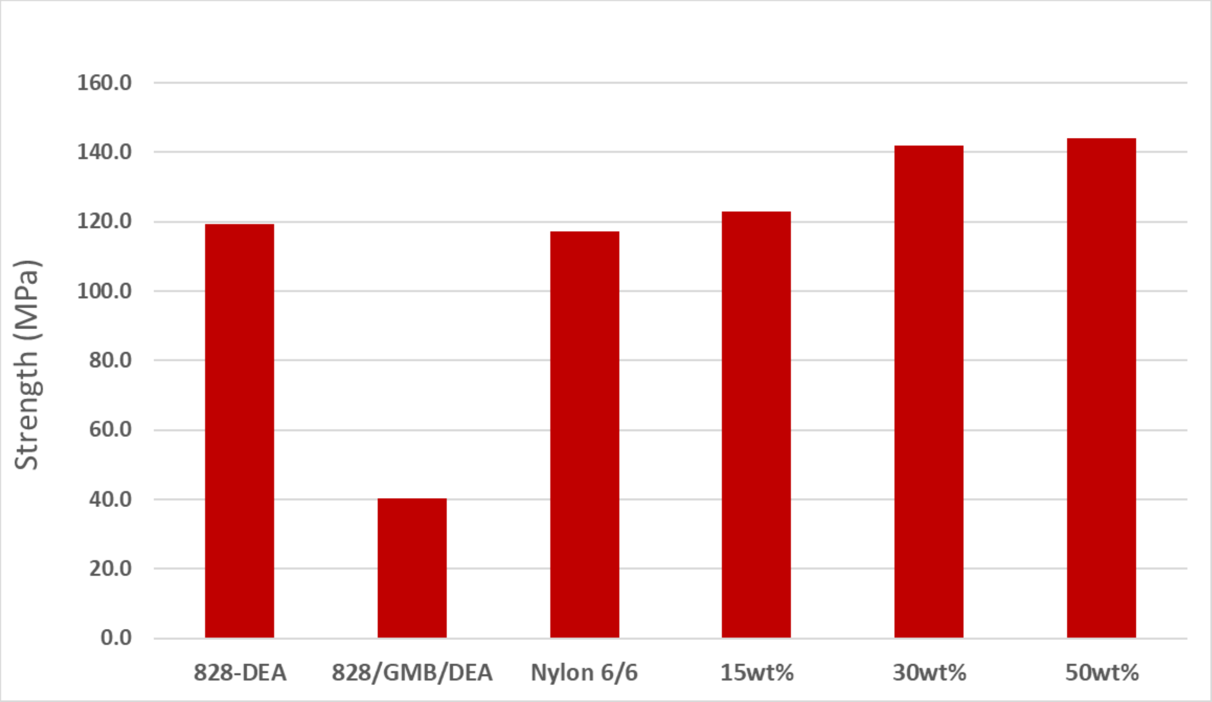
Acrylate network controls the green strength

UV/Thermal Dual Cure: Final Properties Comparisons

Flexural Modulus (GPa)



Flexural Strength (MPa)



Modulus and strength performance comparable to thermoset and thermoplastic alternatives.

* Nylon and 828 formulations data provided by Mark Stavig.

Epoxy/Acrylate Dual Cure Summary

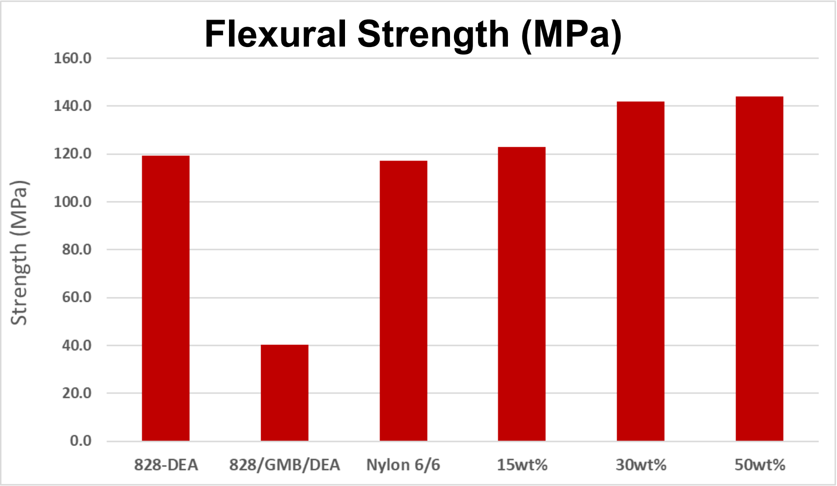
- **Acrylate conversion depends on UV exposure profile (not reciprocal!)**
- **Green strength depends on acrylate content and conversion**
- **Tune green strength and printability with formulation and print conditions**
- **Cured mechanical performance similar to amine/epoxy formulations**

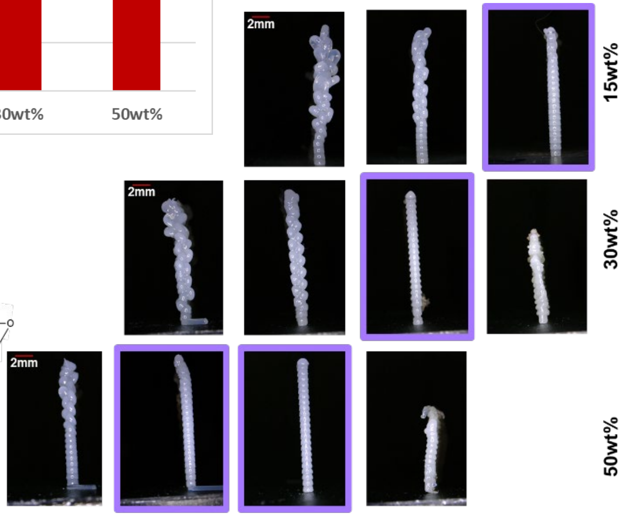
ELSEVIER

Additive Manufacturing
Available online 3 July 2021, 102159
In Press, Journal Pre-proof

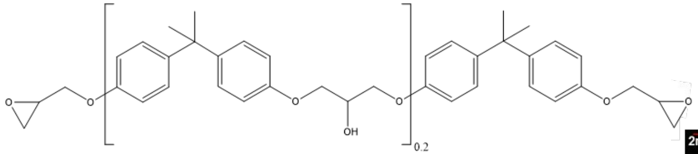
Compositional Effects on Cure Kinetics, Mechanical Properties and Printability of Dual-Cure Epoxy/Acrylate Resins for DIW Additive Manufacturing

Jessica W. Kopatz, Jaclynn Unangst, Adam W. Cook, Leah N. Appelhans

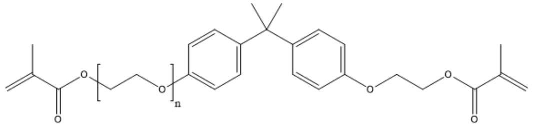




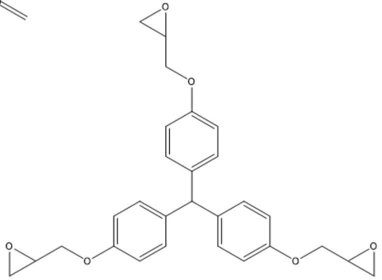
7mW/cm² 14 mW/cm² 26 mW/cm² 54 mW/cm² 100 mW/cm²



diepoxy



dimethacrylate



triepoxy

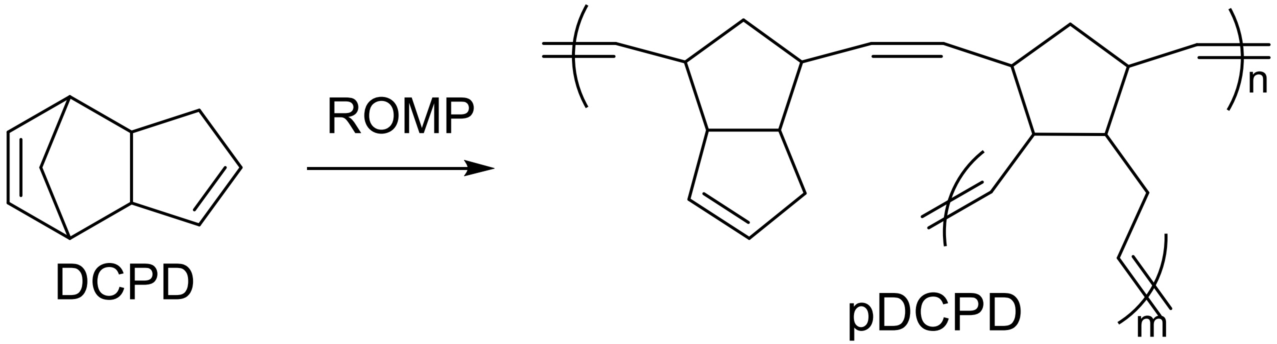
Additional DIW Thermoset Chemistries

Alternative dual-cure systems: Ring Opening Metathesis Polymerization (ROMP)

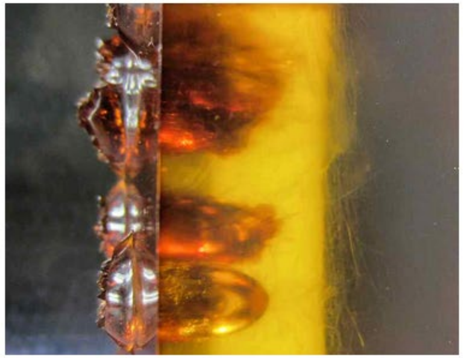
Poly(dicyclopentadiene) (pDCPD)
Thermoset polyolefin

- High impact strength
- Excellent chemical resistance
- High heat distortion temperature
- High T_g (>150°C)
- Excellent dielectric properties
- Commercial resin supplier*

- **ROMP DCPD compatible with epoxy/anhydride as dual-cure system**



https://www.materia-inc.com/products/thermoset-resins



THERMOSET RESINS

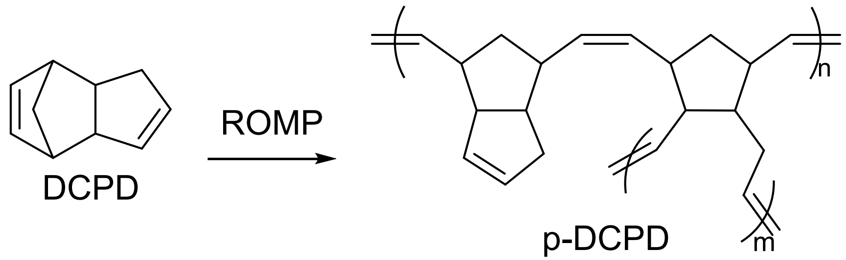
The Next Generation of Thermoset Resins

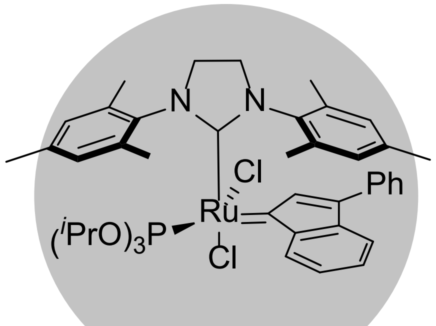
Proxima® Thermoset Resins

*not compatible with latent catalysts

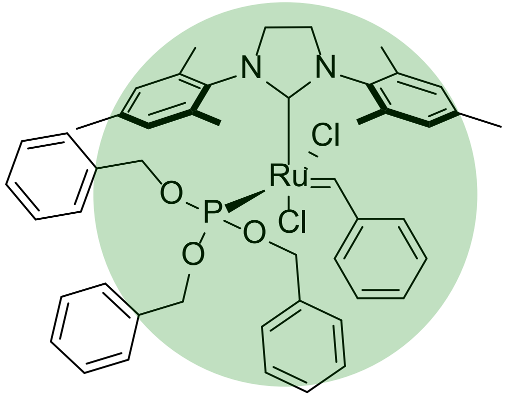
Photo-ROMP AM

- **Access to wide-range of metathesis-active monomers**
- **Rapid printing rates with optimized formulation**

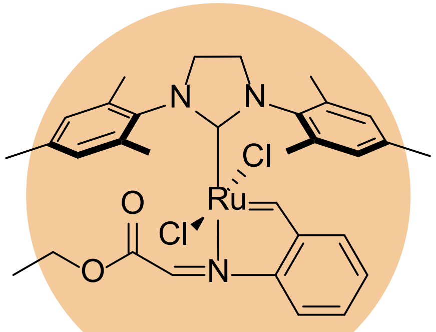




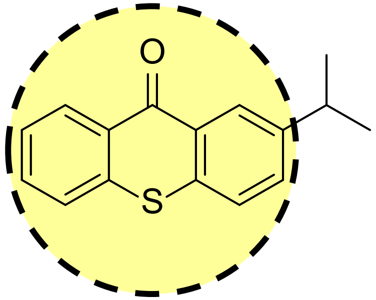
***cis*-Caz-1**



***cis*-Ru-1**

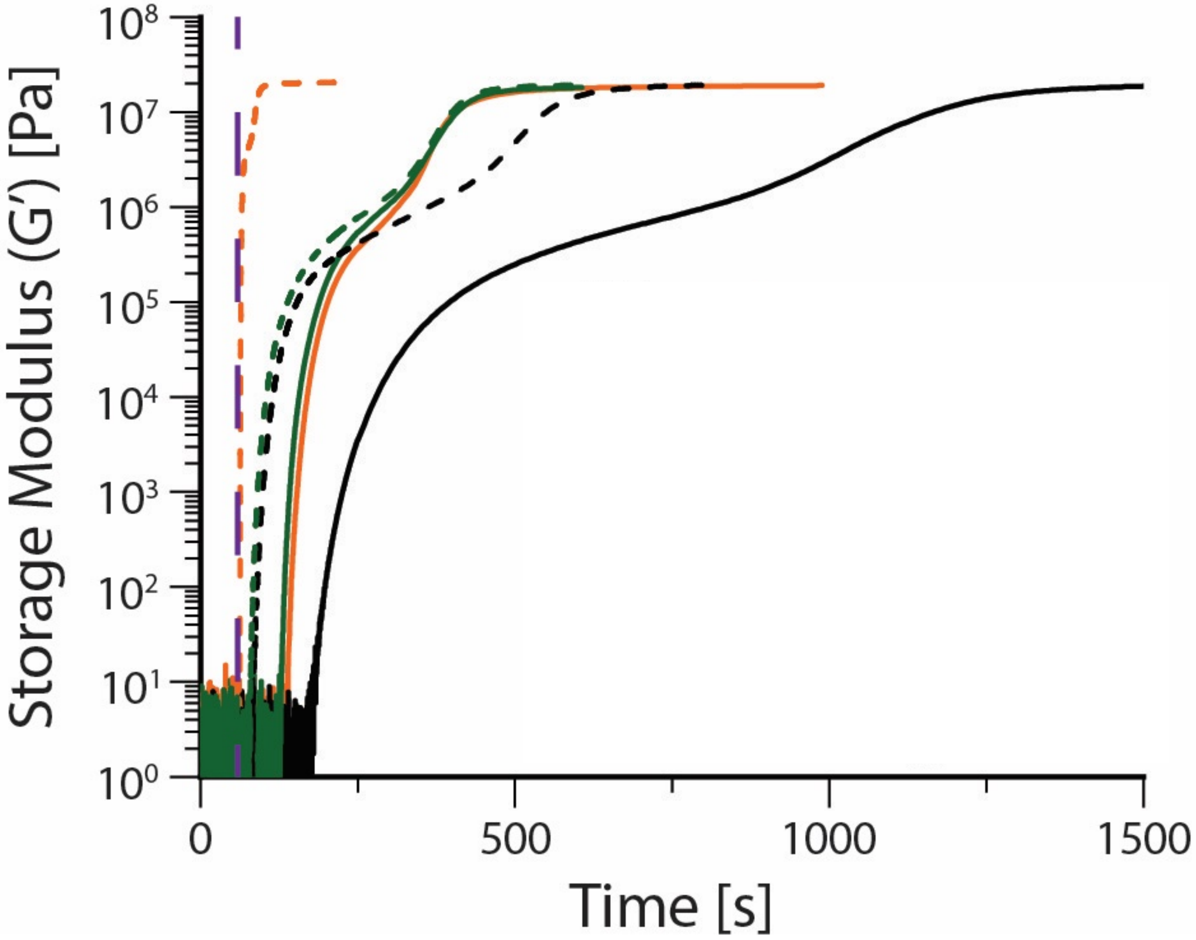


HeatMet



2-isopropylthioxanthone (ITX)

UV on (365 nm @ 120 mW/cm^2)



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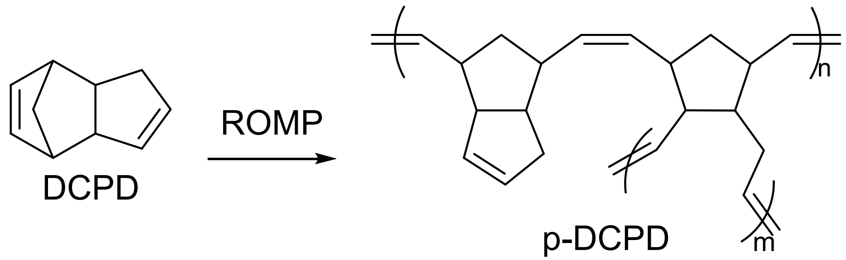
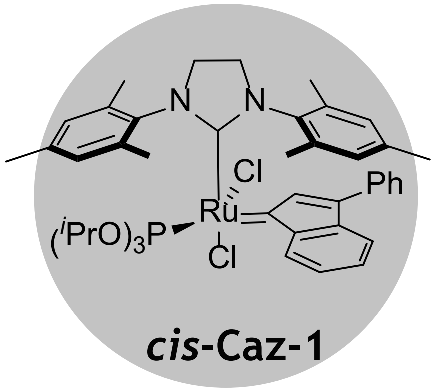
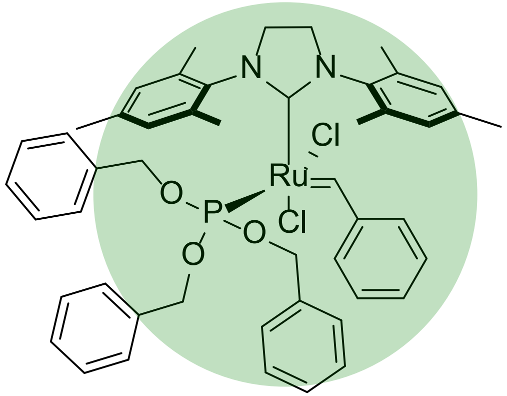




***cis*-Caz-1**



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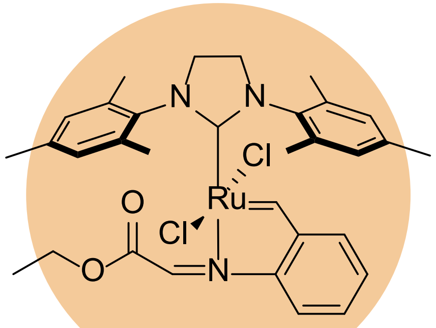
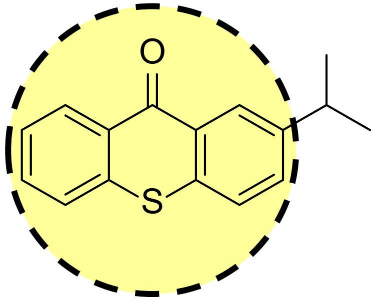


HeatMet



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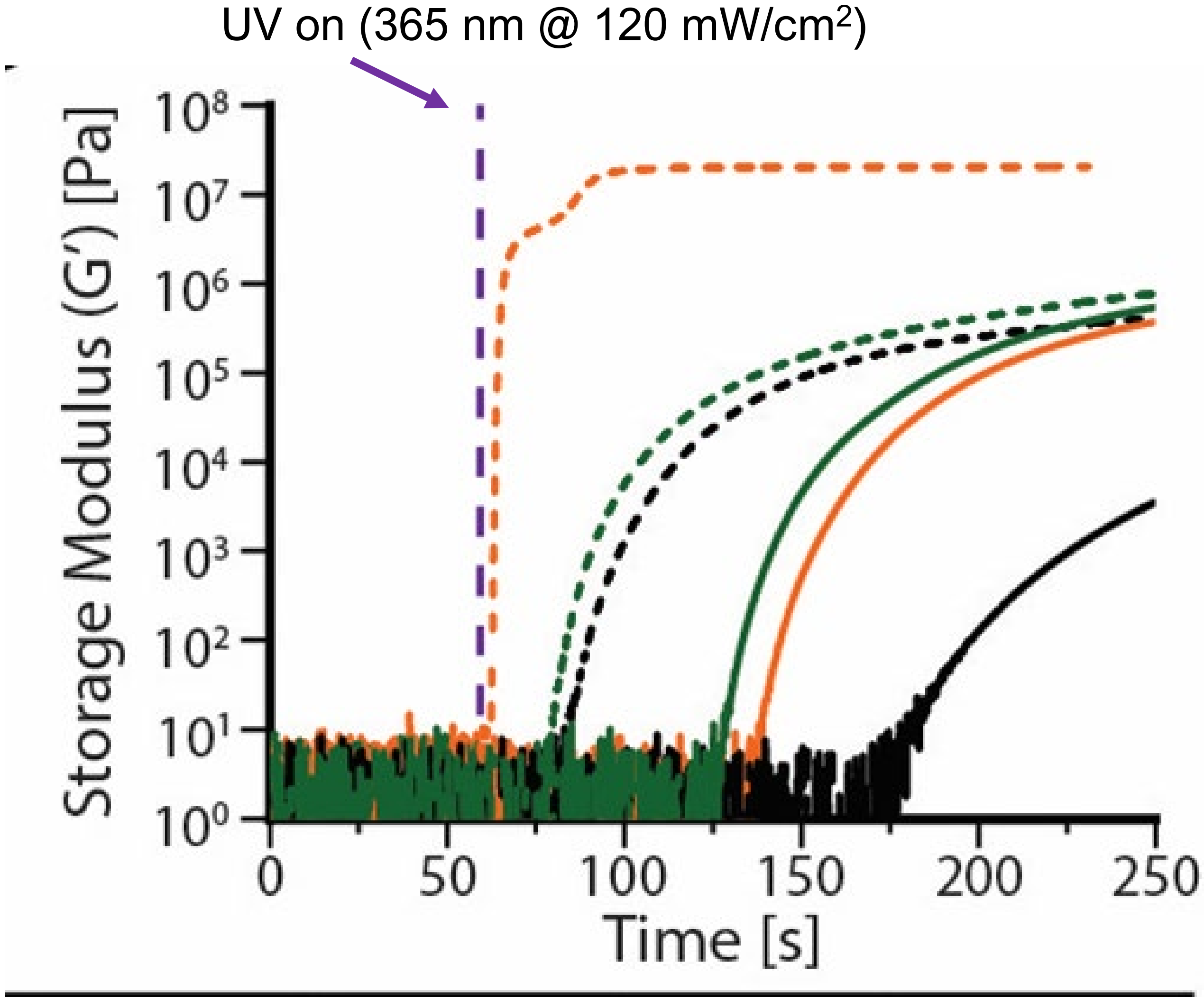
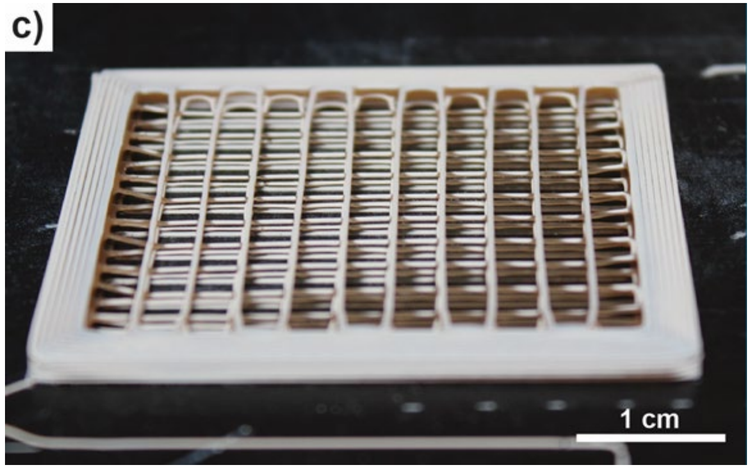
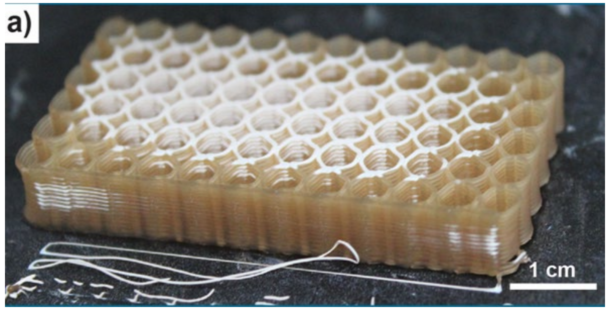
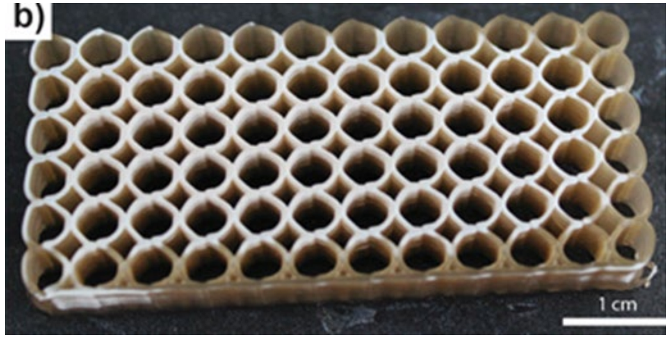
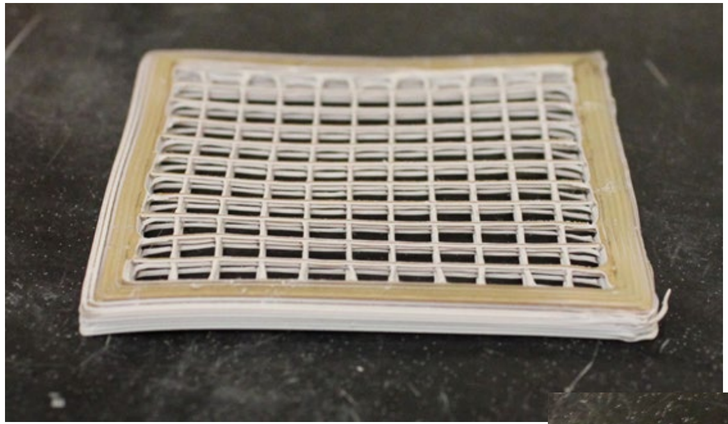


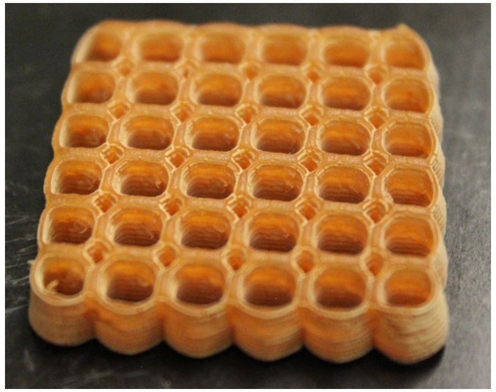


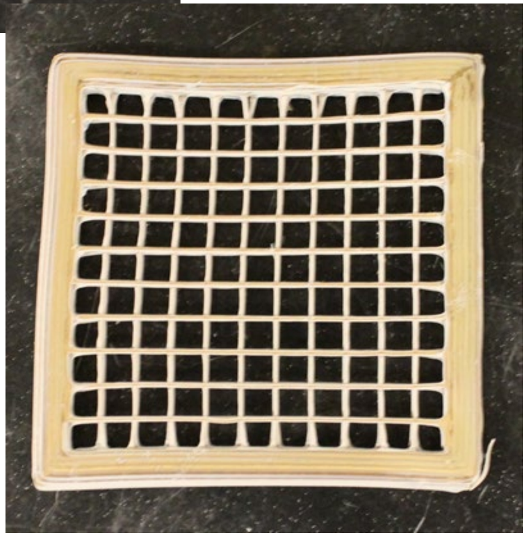


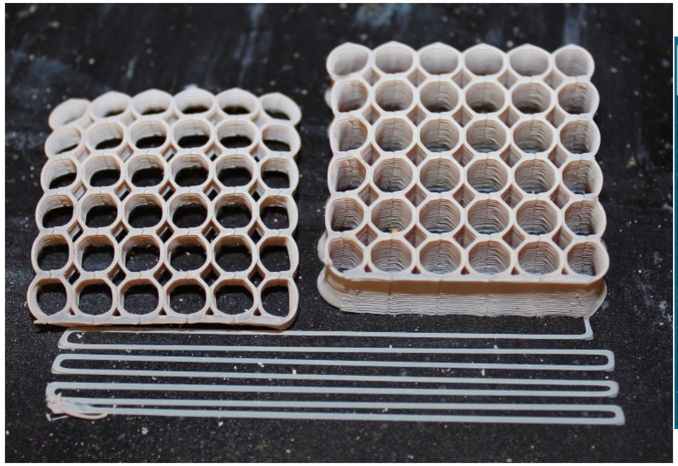


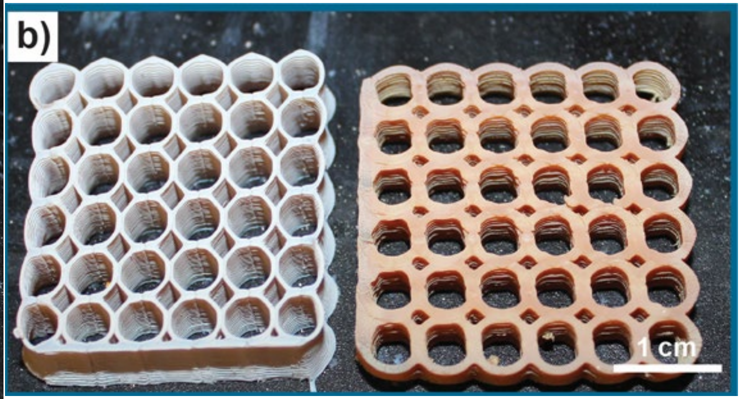


DIW Printing of photoROMP DCPD + 10wt% fumed silica



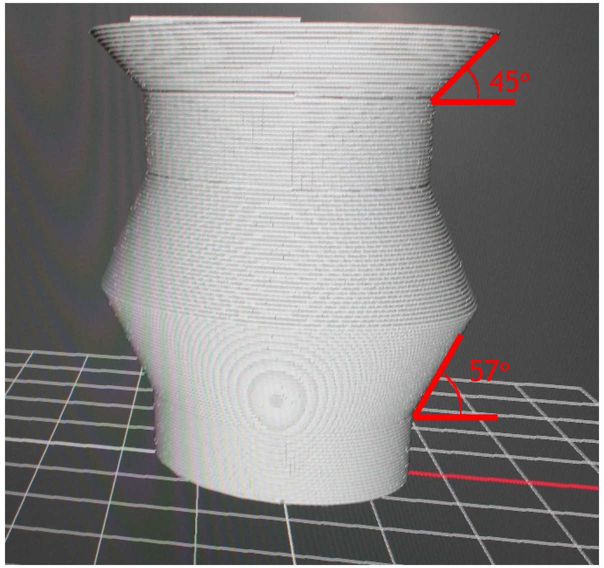


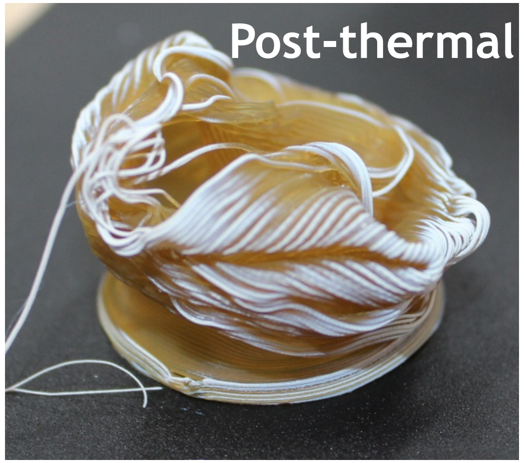




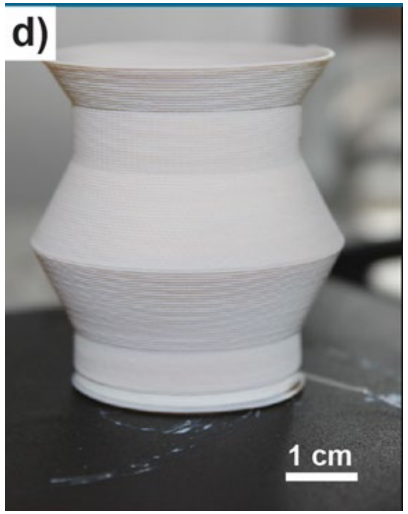
DIW Printing of photoROMP DCPD + 10wt% fumed silica

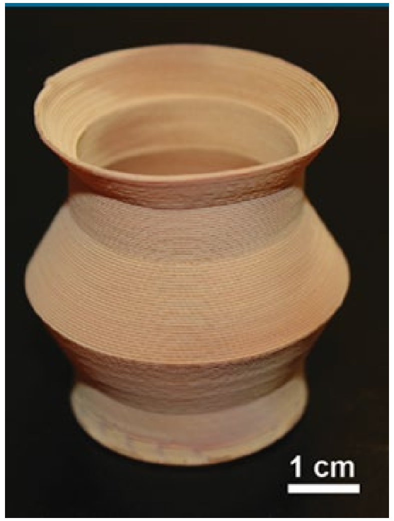
Proposed rendering





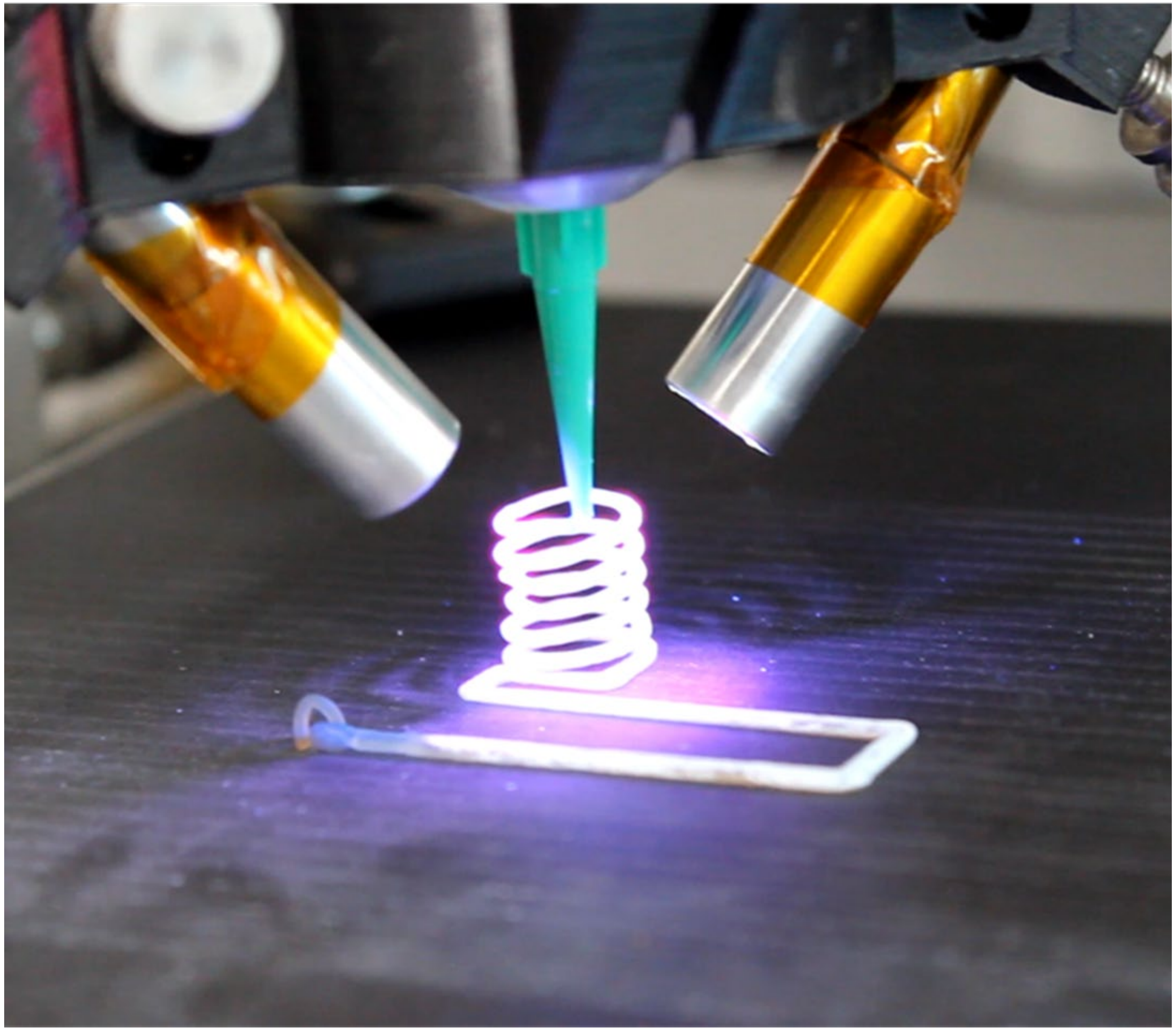
No Print Irradiation

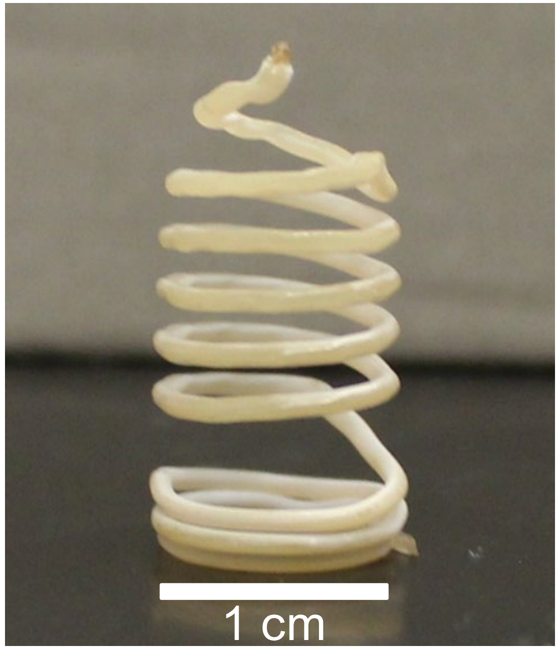




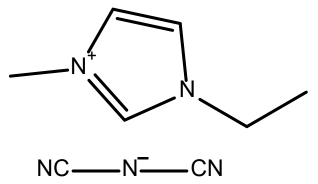
Irradiated

DIW DCPD Photo-Skywriting





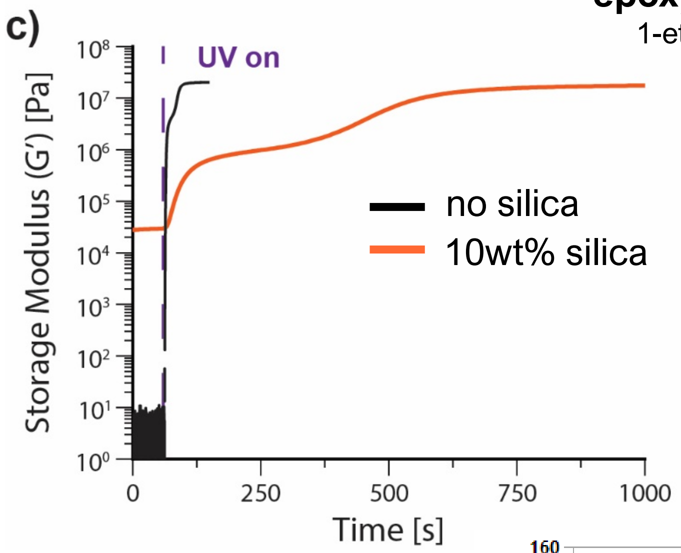
Application to Dense Paste DIW



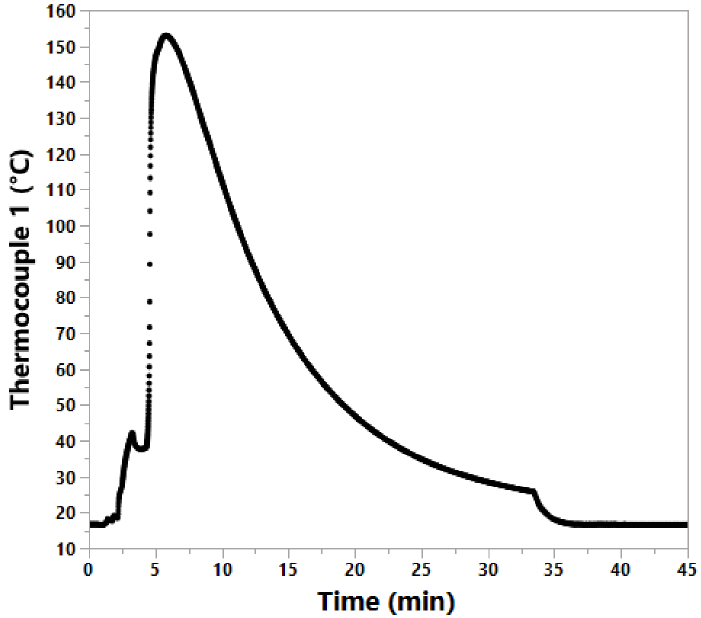
epoxy latent cure initiator
1-ethyl-3-methylimidazolium
dicyanamide

Potential Challenges

- Light penetration depth with highly filled resins (dark cure/dual-cure can mitigate)
- Filler inhibition of reaction kinetics/network formation
- Epoxy/acrylate – latent cure agent chemical compatibility
- DCPD – polymerization exotherm



UV Rheo for photoROMP on filled and unfilled DCPD resins

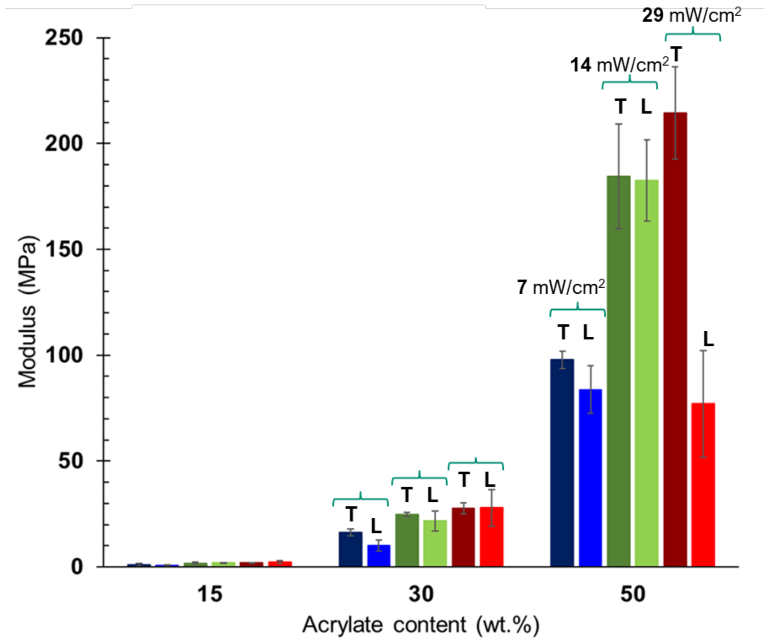


Resin temp vs time for bulk cure of Proxima DCPD resin

Application to Dense Paste DIW

Potential Advantages

- Improved print complexity, print fidelity, and aspect ratios
- Long pot lifes
  - Epoxy/acrylate – 1 year+ ?
  - PhotoDCPD – 16 hrs*
- DCPD – very low viscosity
- DCPD – compatible with epoxy/anhydride dual-cure system (in progress)
- Epoxy/acrylate – tunable resin properties with formulation

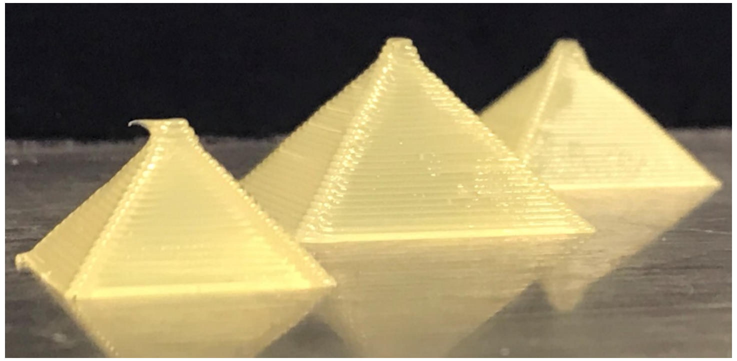


Supplementary Slides

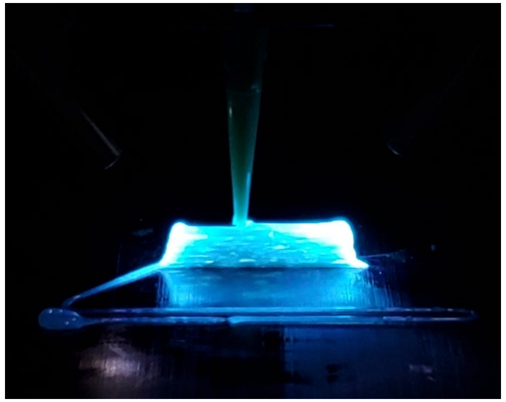
ACT Thermosets Research

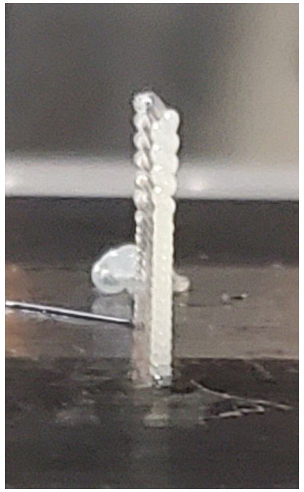
Development of thermoset resins for DIW

- Develop ***dual-cure systems*** to target specific materials requirements.
  - Epoxy/acrylate (UV/thermal)
  - Other dual-cure mechanisms and polymer systems
- Characterize resin component contribution to physical properties and cure kinetics to enable ***design of tunable resin systems***.
- Characterize ***DIW-unique factors*** that impact network formation, extent of cure, and final properties.
- Characterize thermoset ***stability and aging characteristics.***
- Develop ***printability metrics and optimize print techniques*** for varied thermoset systems.
- Develop new approaches to ***qualification*** for AM methods.

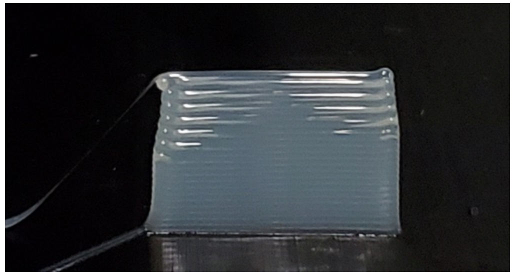


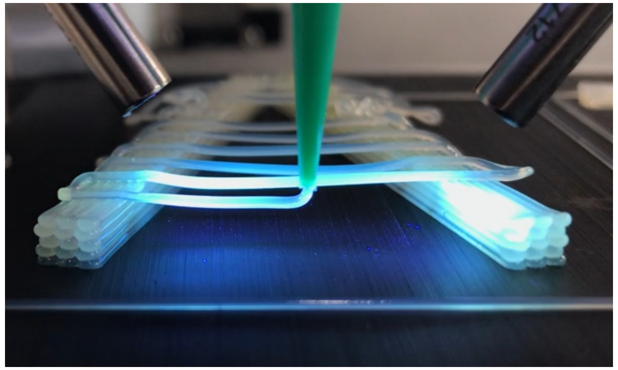
Printing of acrylate/epoxy UV/thermal dual-cure system





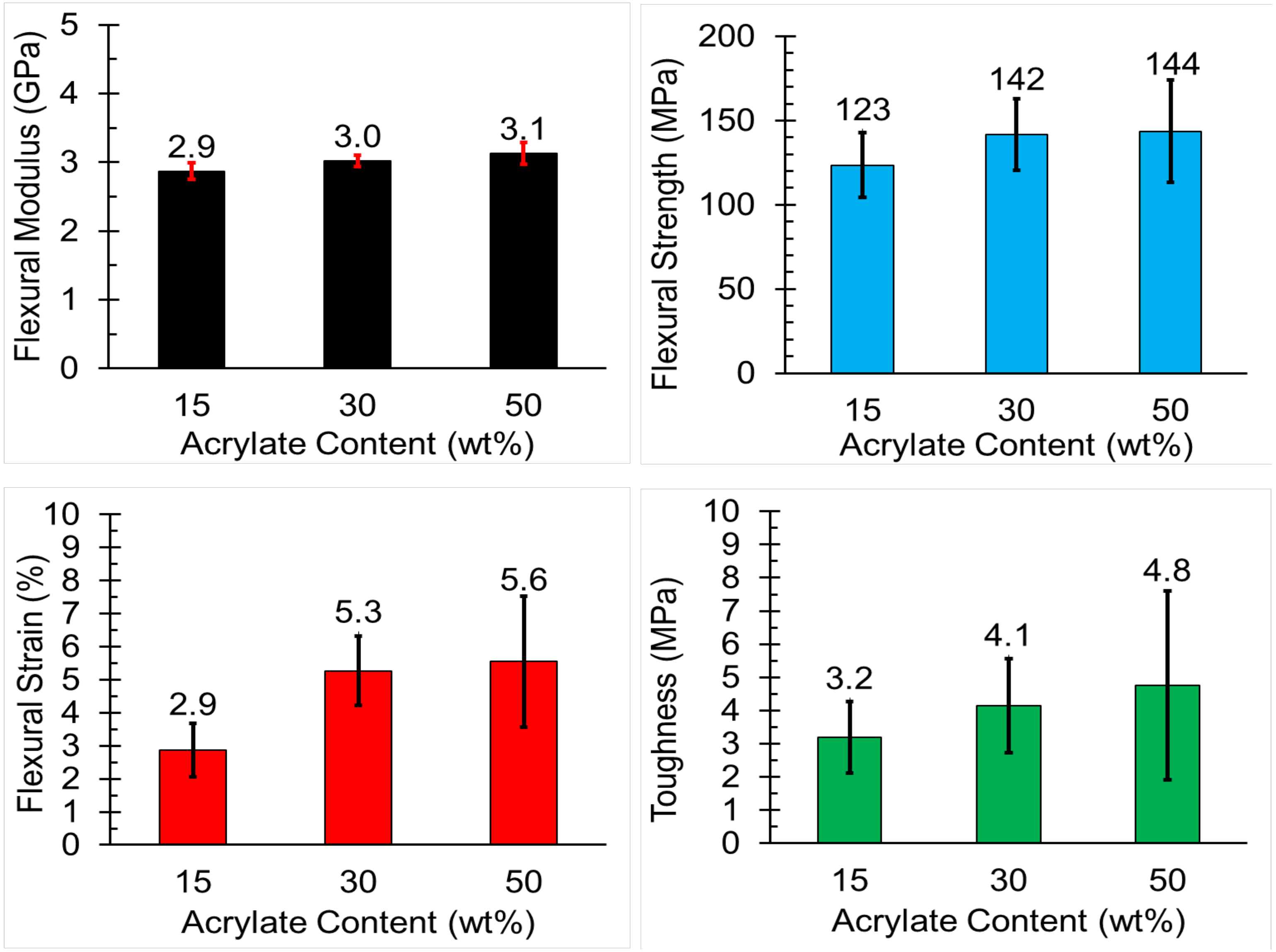
>10:1 w:h





UV/Thermal Dual Cure: Final Properties

Flexural Properties



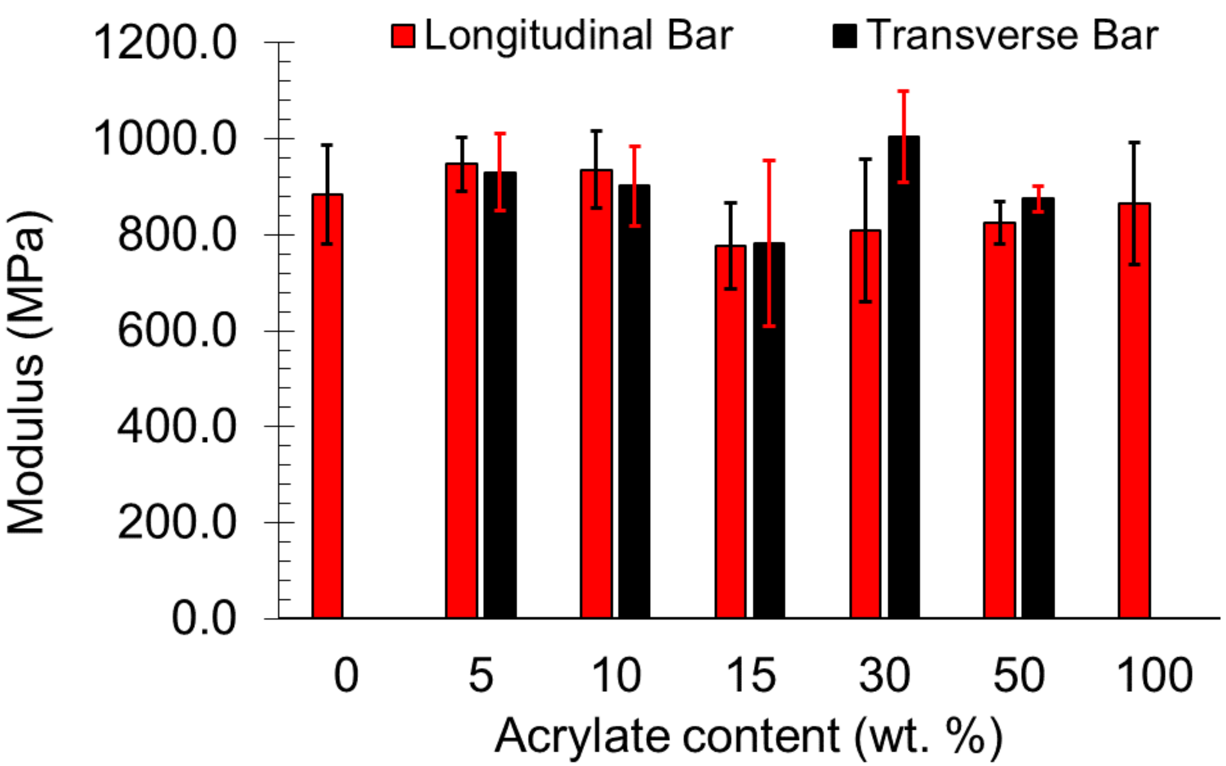
Mechanical properties after thermal cure are relatively independent of acrylate content, allowing design flexibility.

UV/Thermal Dual Cure: Final Properties

T_g vs Composition (150°C max cure)

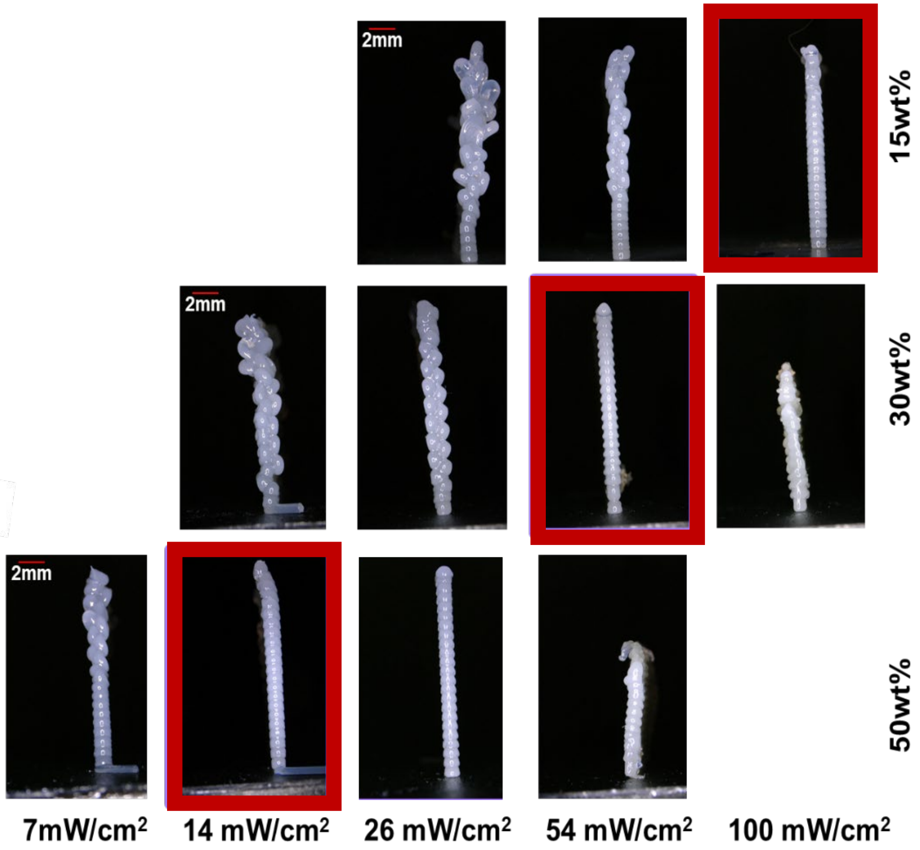
Acrylate Content	Tg
wt%	°C
0	215
5	215 (2)
10	221 (1)
15	210 (6)
30	189 (6)
50	121 (4), 186 (5)
100	165

Torsional Modulus vs Composition

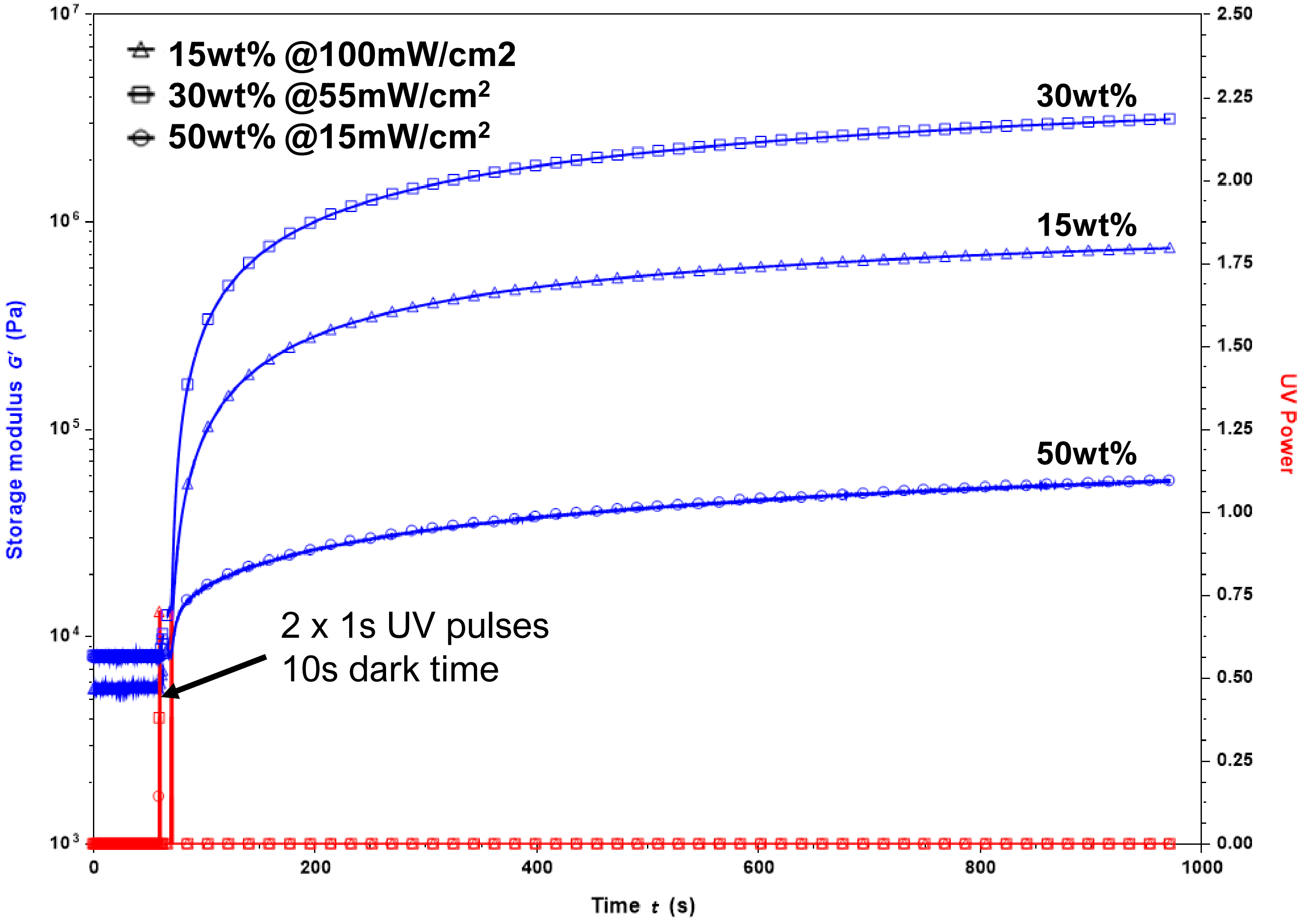


Mechanical properties after thermal cure are relatively independent of acrylate content, allowing design flexibility.

UV Rheology: Can pulsed exposures predict printability?

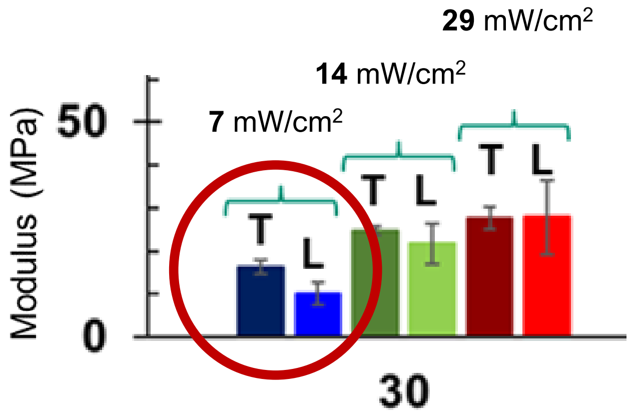


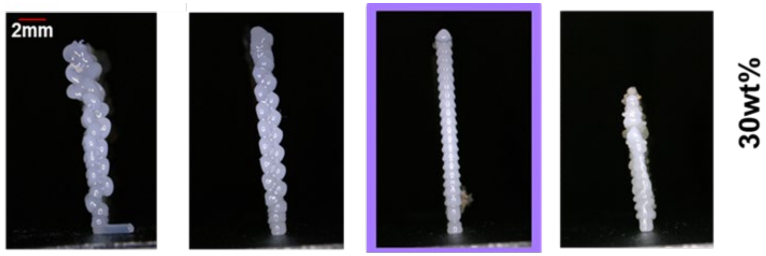
2 x 1s pulsed exposures (walls), then continuous exposure



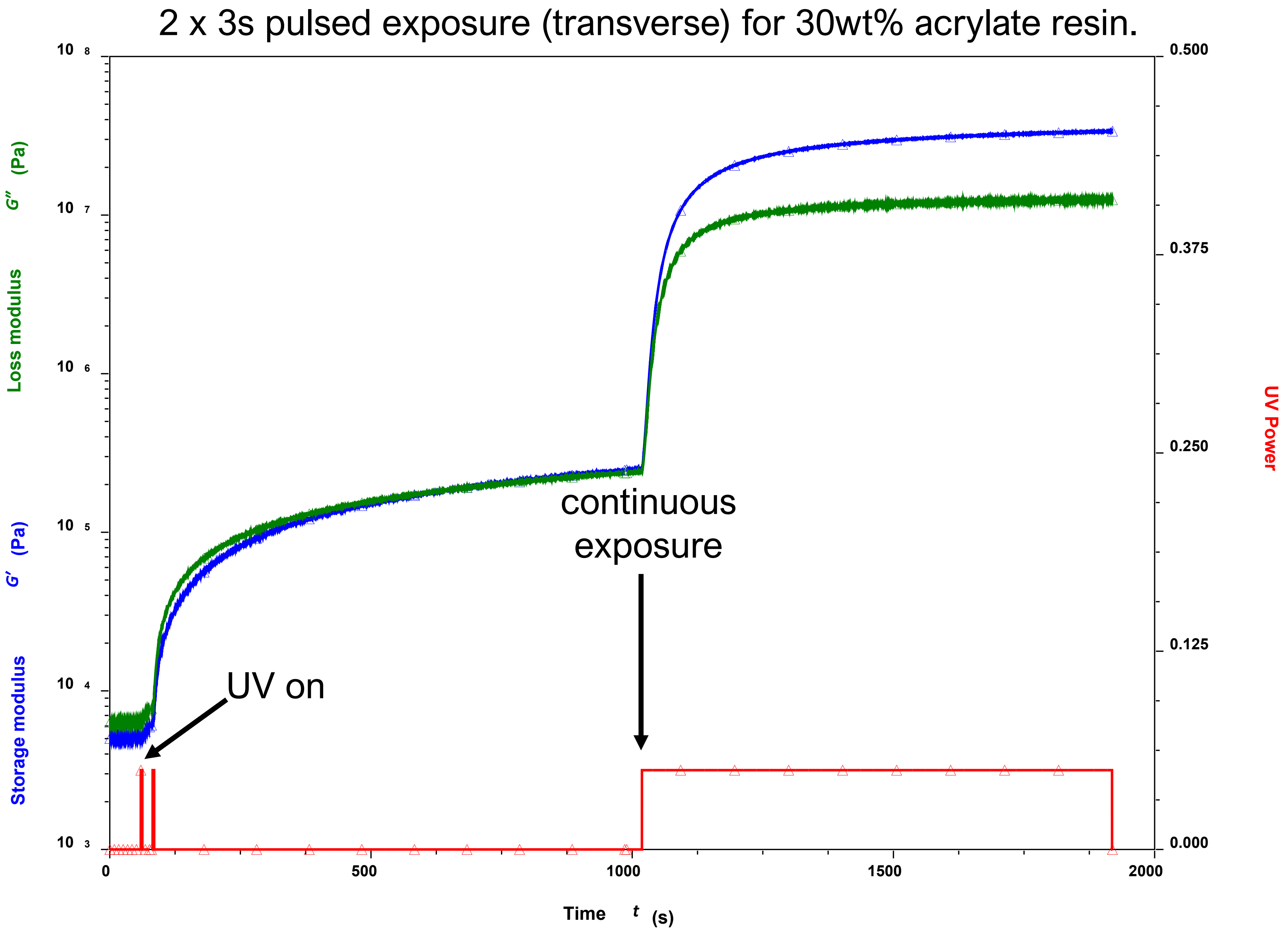
UV Rheology

Can you predict green strength from rheology?





14 mW/cm² 26 mW/cm² 54 mW/cm² 100 mW/cm²

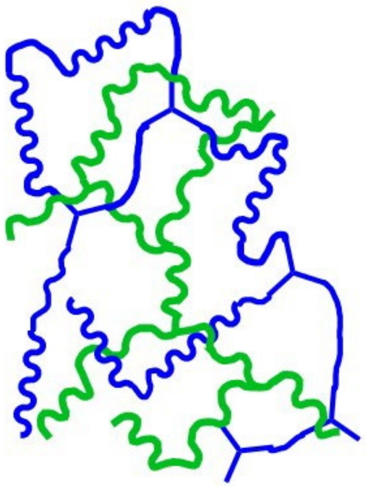


Thermomechanical Properties of UV+Thermally Cured Resins

Phase separation occurs in 50wt% acrylate resins. Can be controlled by thermal cure profile.

Glass transition temperatures varying acrylate content

Acrylate (wt%)	Tg (°C)
0	215
5	215 (2)
10	221 (1)
15	210 (6)
30	189 (6)
50	**121 (4)** **186 (5)**
100	165



IPN

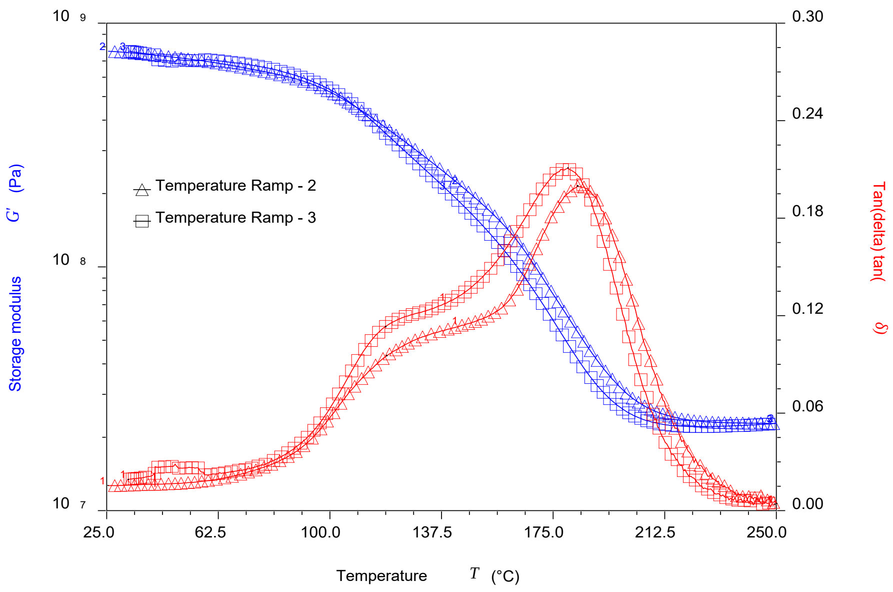
Phase separation and domain sizes depend on:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

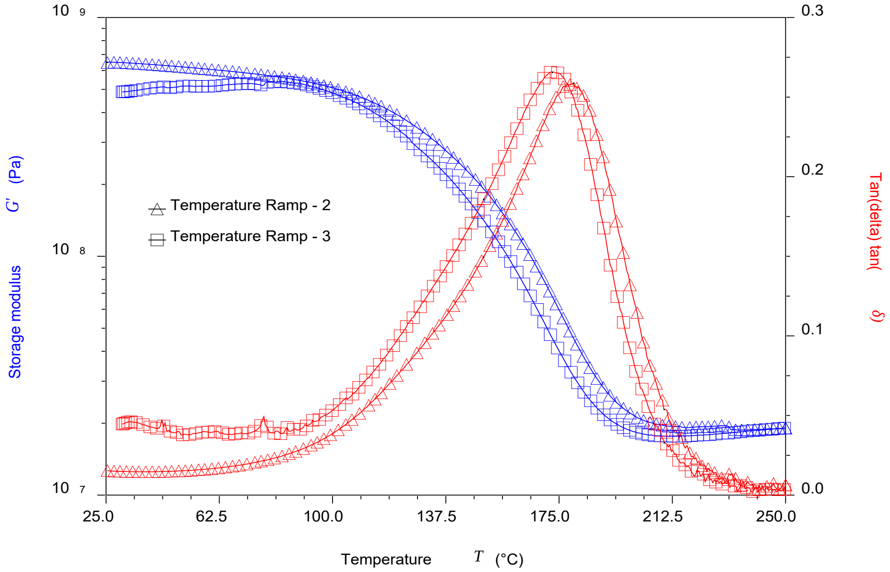
cure order

cure kinetics

UV
100°C 4 hrs
150°C 2 hrs



UV
100°C 4 hrs
150°C 2 hrs
250°C 2 hrs

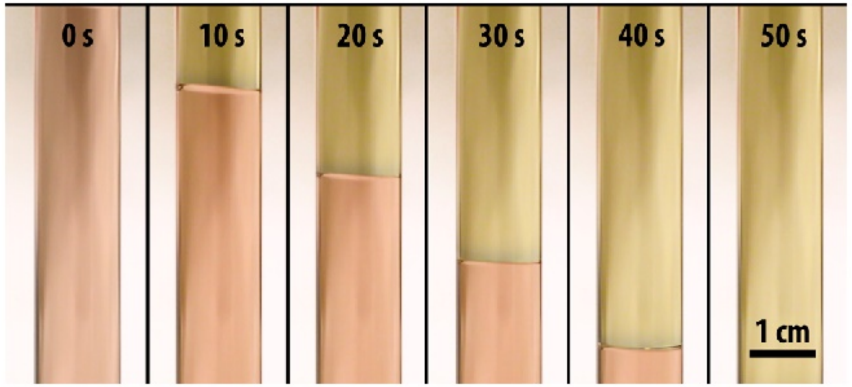


Previous AM with DCPD

AM with DCPD previously demonstrated using frontal ROMP (FROMP)

Limitations:

- *Undesirable operation window*
- *Single bead geometries – overlapped beads absorb exotherm*
- *FROMP may be sensitive to fillers*



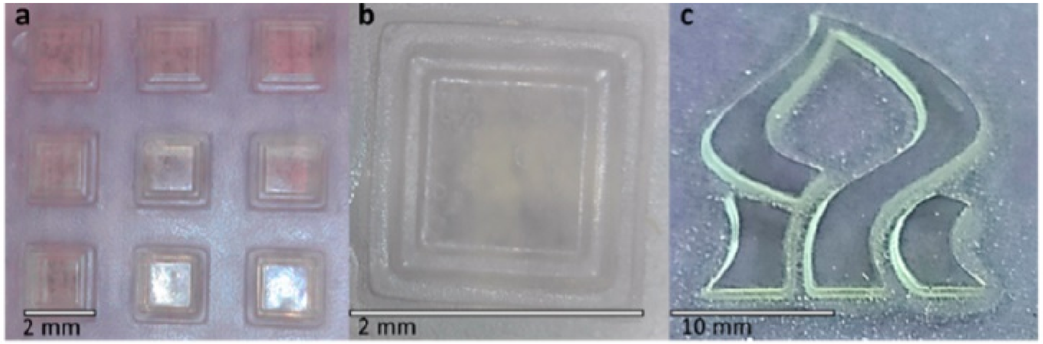
Robertson et al. ACS Macro Lett., 2017, 6, 6

Robertson et al. Nature, 2018, 557, 223

Layer-by-layer AM previously demonstrated using photoROMP/masking

Limitations:

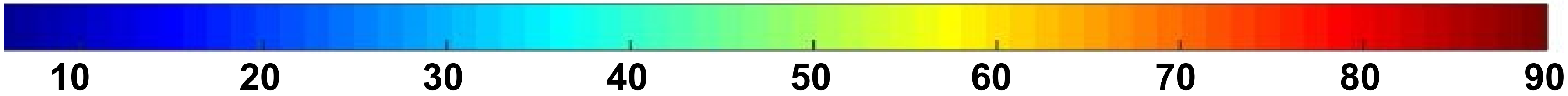
- *Poor polymerization rates*
- *Few available photo-latent catalysts*
- *Demonstrations limited to <5 layers*



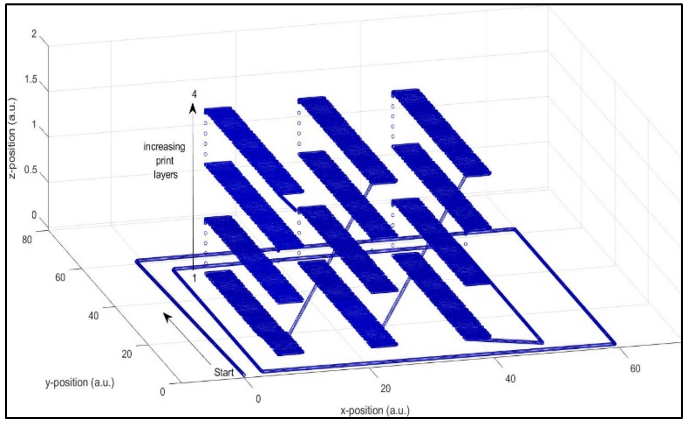
Eivgi *et al.* ACS Catal. **2020**, 10, 2033−2038

In situ Process Monitoring

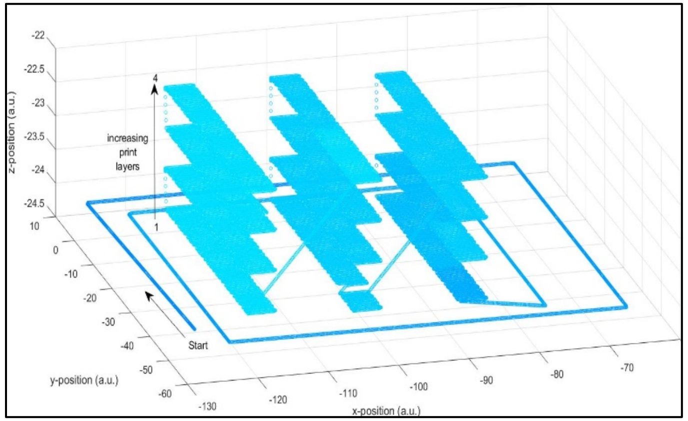
6.6vol% filler



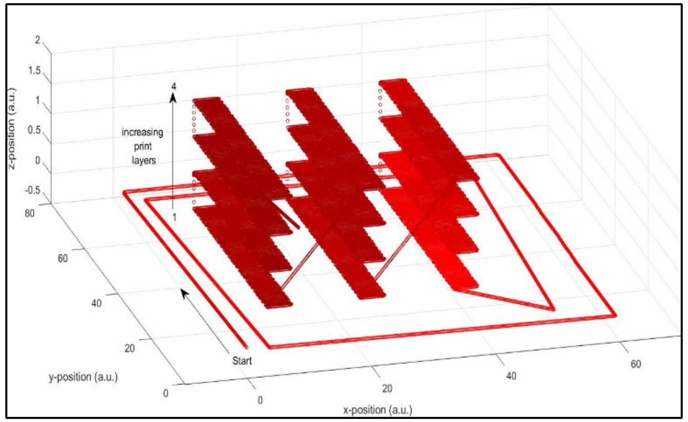
Platelet Montmorillonite (MMT)

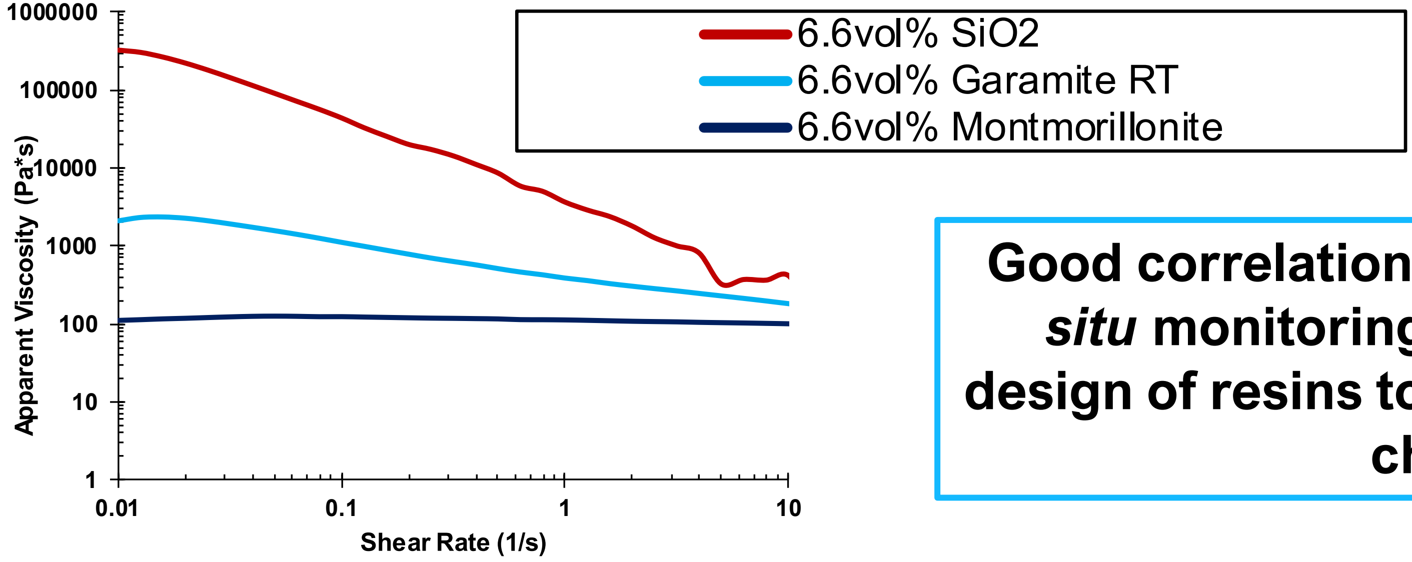


Rods/plates (Garamite)



Spherical SiO_2





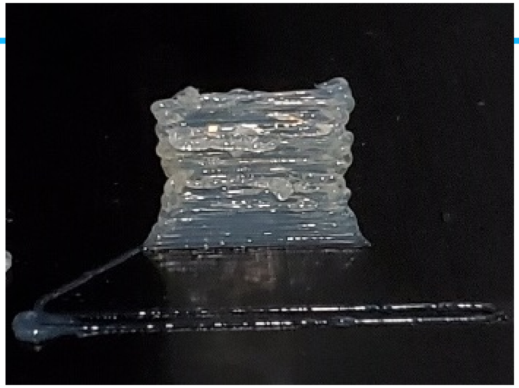
All printed at 5% UV
(6.9 mW/cm^2)

Good correlation between rheological properties and *in situ* monitoring of printing performance will enable design of resins to target specific print characteristics for challenging applications.

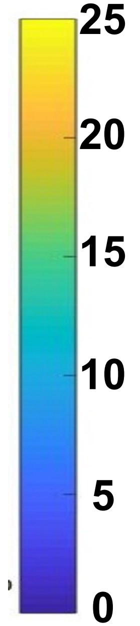
In situ Process Monitoring

- *In situ* pressure monitoring
- Raman/IR spectroscopy
- Process loop feedback control
- Defect identification and screening

***In situ* pressure monitoring enables monitoring of blockages due to UV back cure or high filler loadings and identification of location in the printed part.**



Example of print defects from a "too high" in situ UV intensity



Force (lbs)

15wt% MMT (8vol%) in 2:1 diepoxy:diacrylate