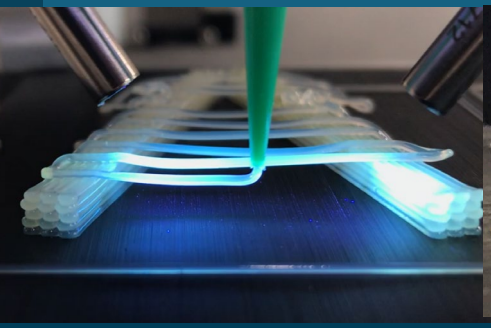
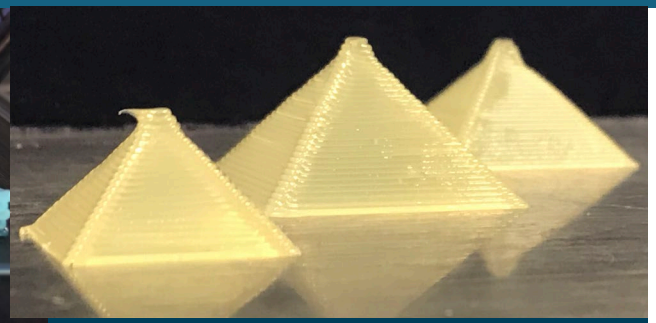
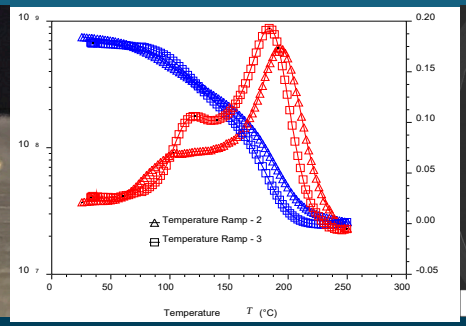
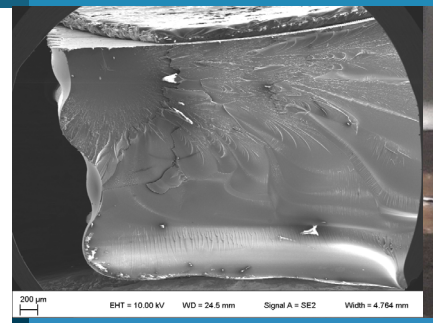
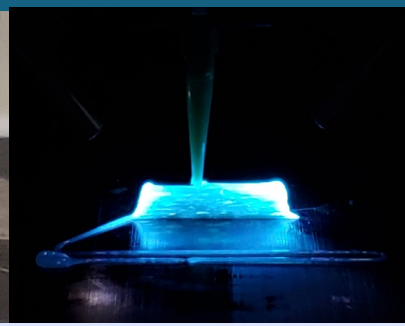
SAND2021-8449PE

Application of Photorheology to the Characterization of UV-Curable Resins for DIW AM





PRESENTED BY

Leah Appelhans, Sandia National Laboratories

Sam Leguizamon, Jessica Kopatz, Adam Cook

August 25, 2021

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Adam Cook, Derek Reinholtz

Current and former Dept. 1853

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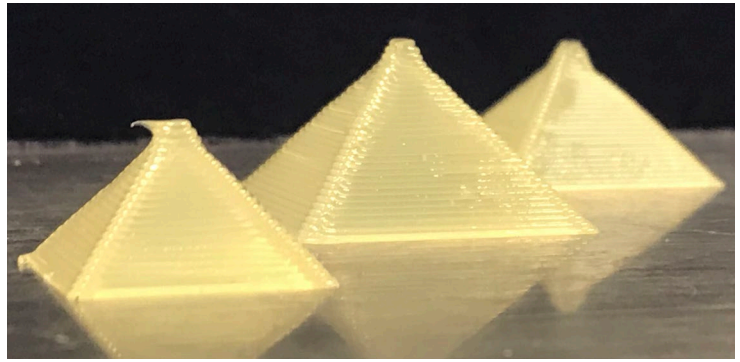
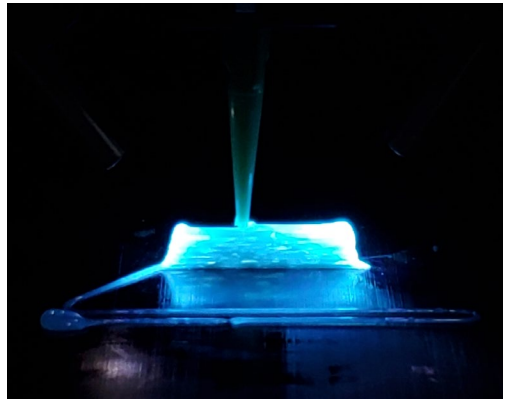
SNL DIW Thermosets Research

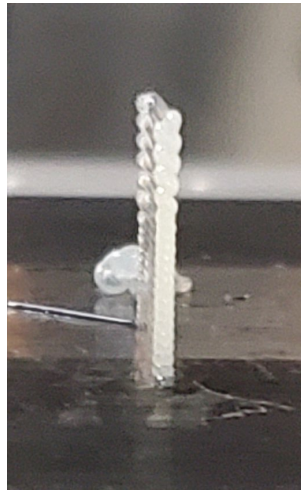


Printing of acrylate/epoxy UV/thermal dual-cure system

Development of thermoset resins for DIW

- Develop ***thermoset systems*** to target specific materials requirements.
- 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.
- Develop ***printability metrics and optimize print techniques*** for varied thermoset systems.





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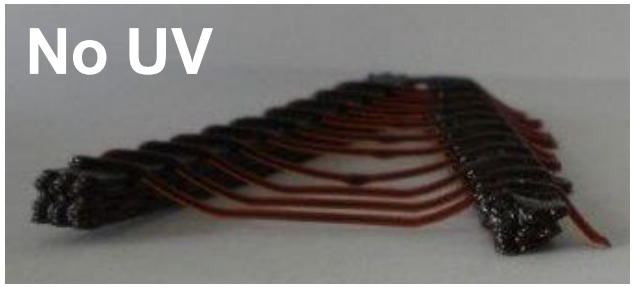
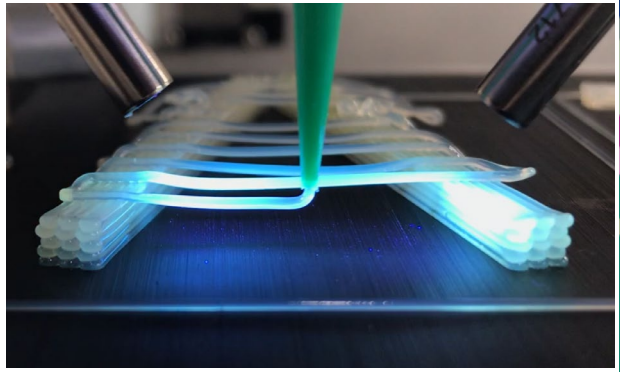


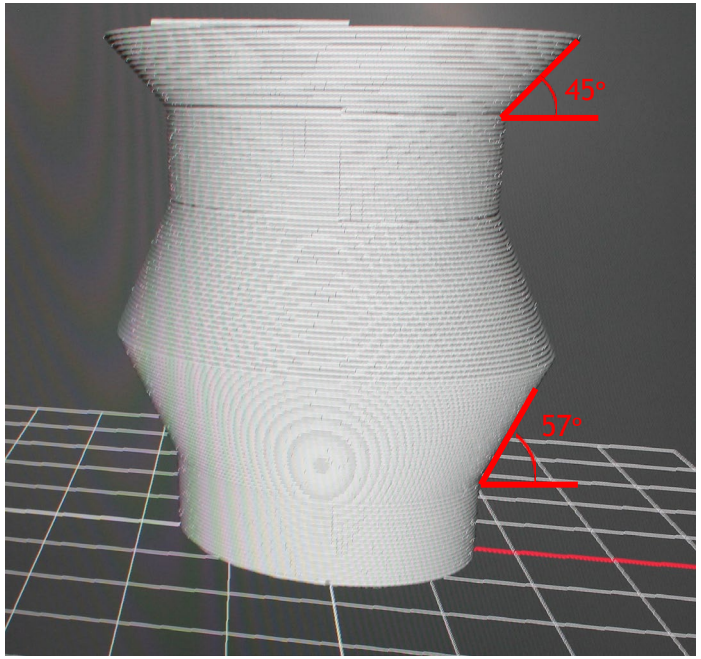


Application of Photorheology to the Characterization of UV-Curable Resins for DIW AM

OR

Taking the Fun Out of 3D Printing

Proposed rendering



Resin Optimization for AM Printing

- Stereolithography (SLA)
  - Layer-by-layer photopolymerization of flowable liquid resins
- Fused deposition modelling (FDM)
  (fused filament fabrication, FFF)
  - Extrusion of thermoplastic filaments
- Direct ink write (DIW)
  - Extrusion of an ink or resin
  - Shear-thinning, reactive, or *in situ* cure

Langmuir **2002,** *18,* 5429−5437

Colloidal Inks for Directed Assembly of 3-D Periodic Structures

James E. Smay,[†,‡] Joseph Cesarano III,[‡] and Jennifer A. Lewis*[,†]

Journal of Manufacturing Processes 35 (2018) 526–537

What makes a material printable? A viscoelastic model for extrusion-based 3D printing of polymers

Chad Duty[a,b,*], Christine Ajinjeru[a], Vidya Kishore[a], Brett Compton[a], Nadim Hmeidat[a], Xun Chen[b], Peng Liu[b], Ahmed Arabi Hassen[b], John Lindahl[b], Vlastimil Kunc[a,b,c]

International Journal of Mechanical Sciences 137 (2018) 145–170

Mechanical performance of wall structures in 3D printing processes: Theory, design tools and experiments

A.S.J. Suiker

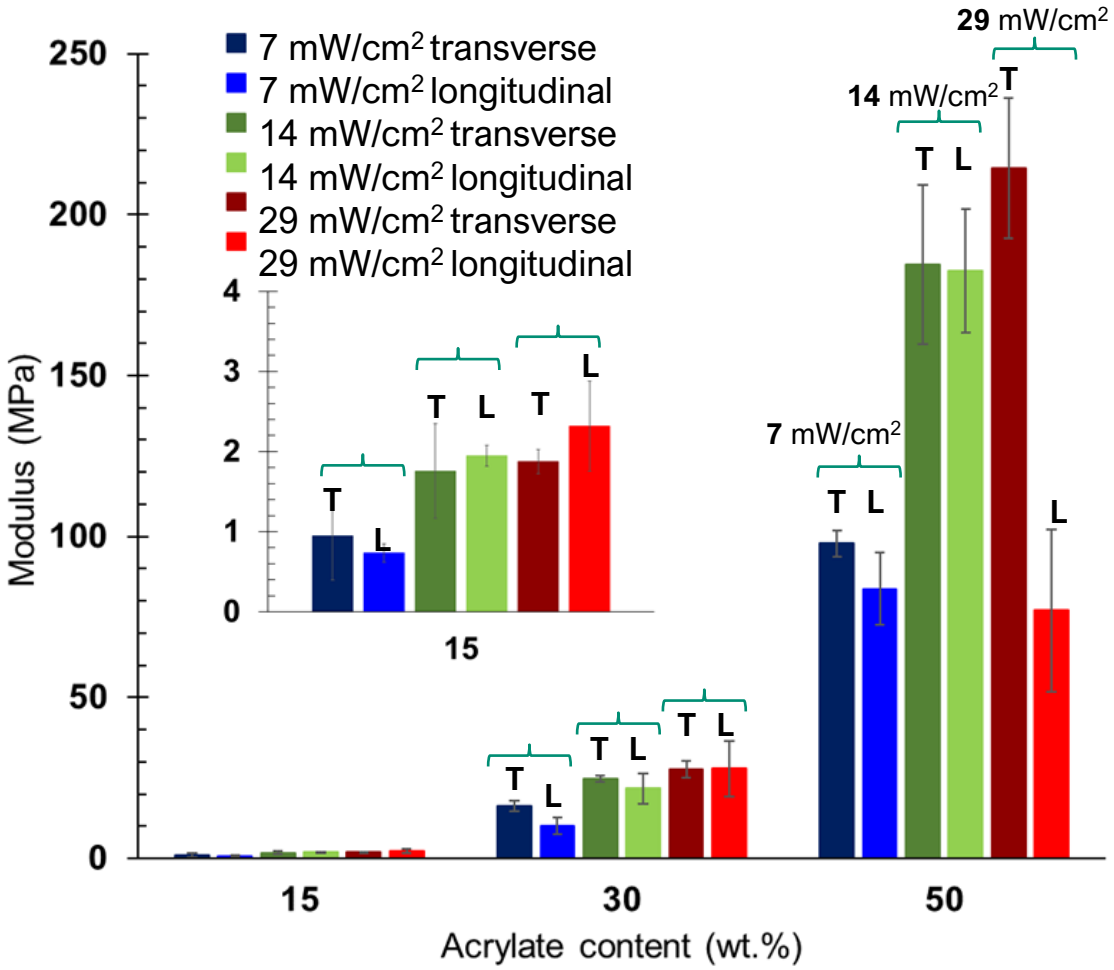
Additive Manufacturing 35 (2020) 101177

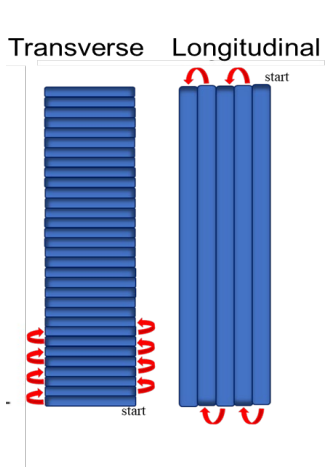
A comprehensive review of the photopolymerization of ceramic resins used in stereolithography

Setareh Zakeri*, Minnamari Vippola, Erkki Levänen

Epoxy/Acrylate Dual Cure: Determine Printability by Printing

UV Print Intensity vs Modulus (Print Cure Only)

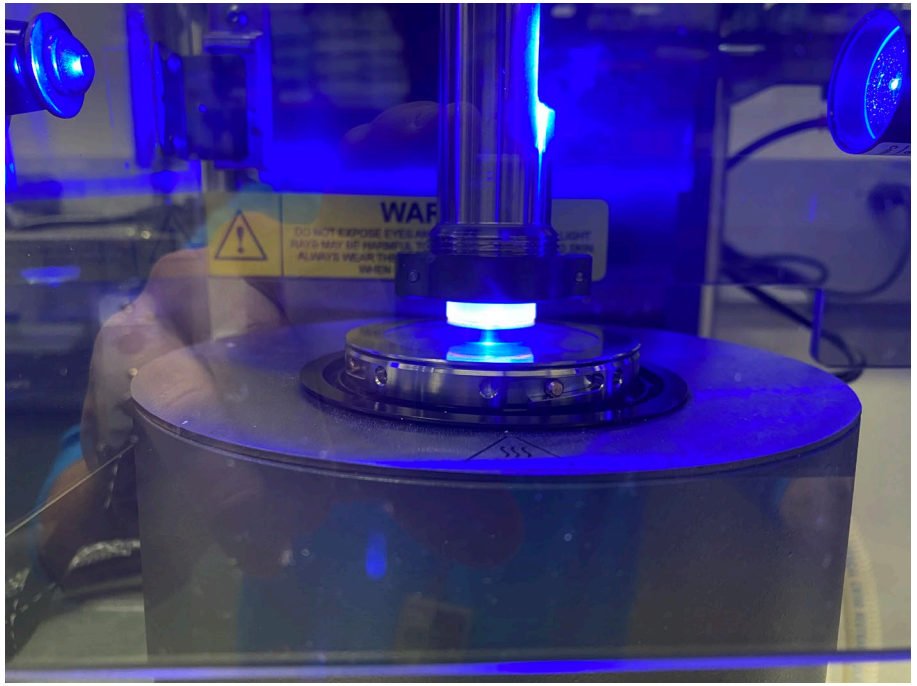


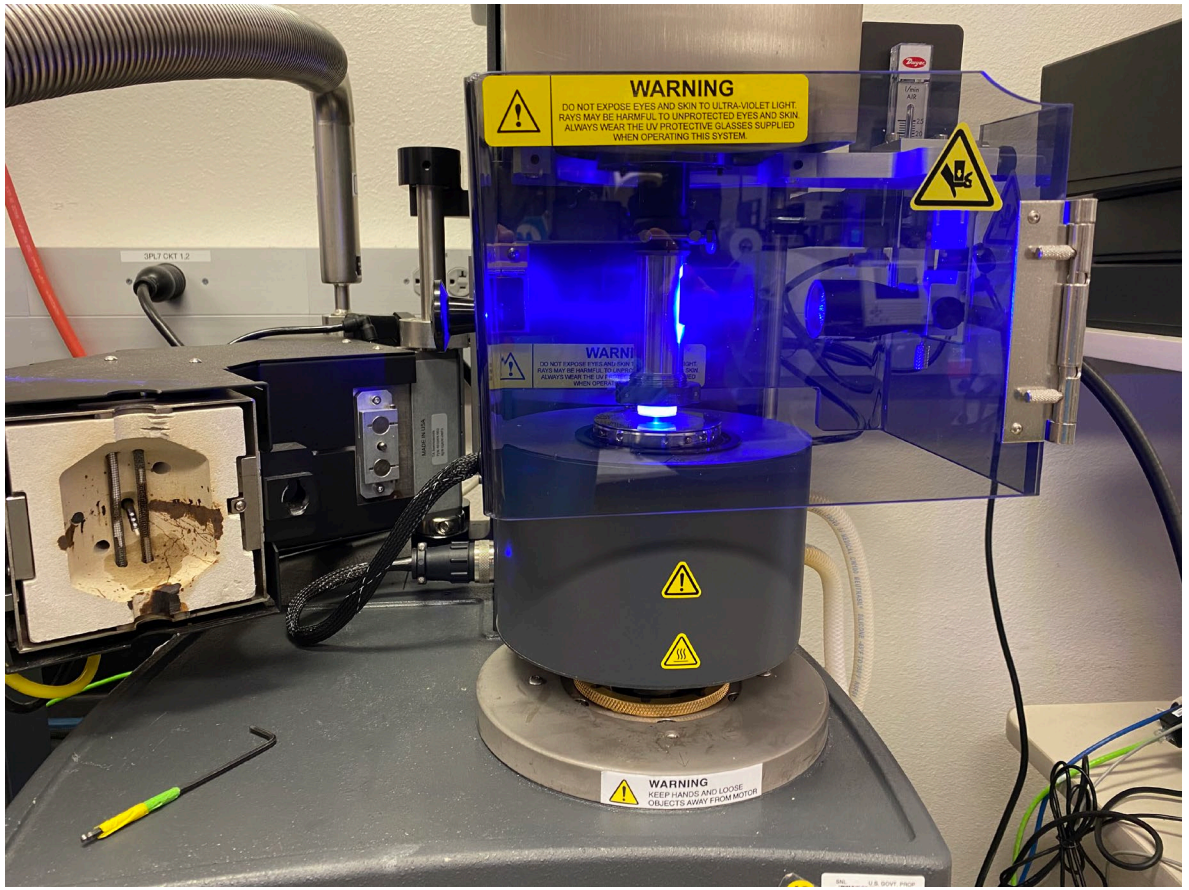


Acrylate network controls the green strength, print parameters optimized for each formulation.

UV Rheology: A “New” Characterization Tool

- Correlate UV exposure profiles and conversion to rheological behavior
- Design printable resins w/o printing*

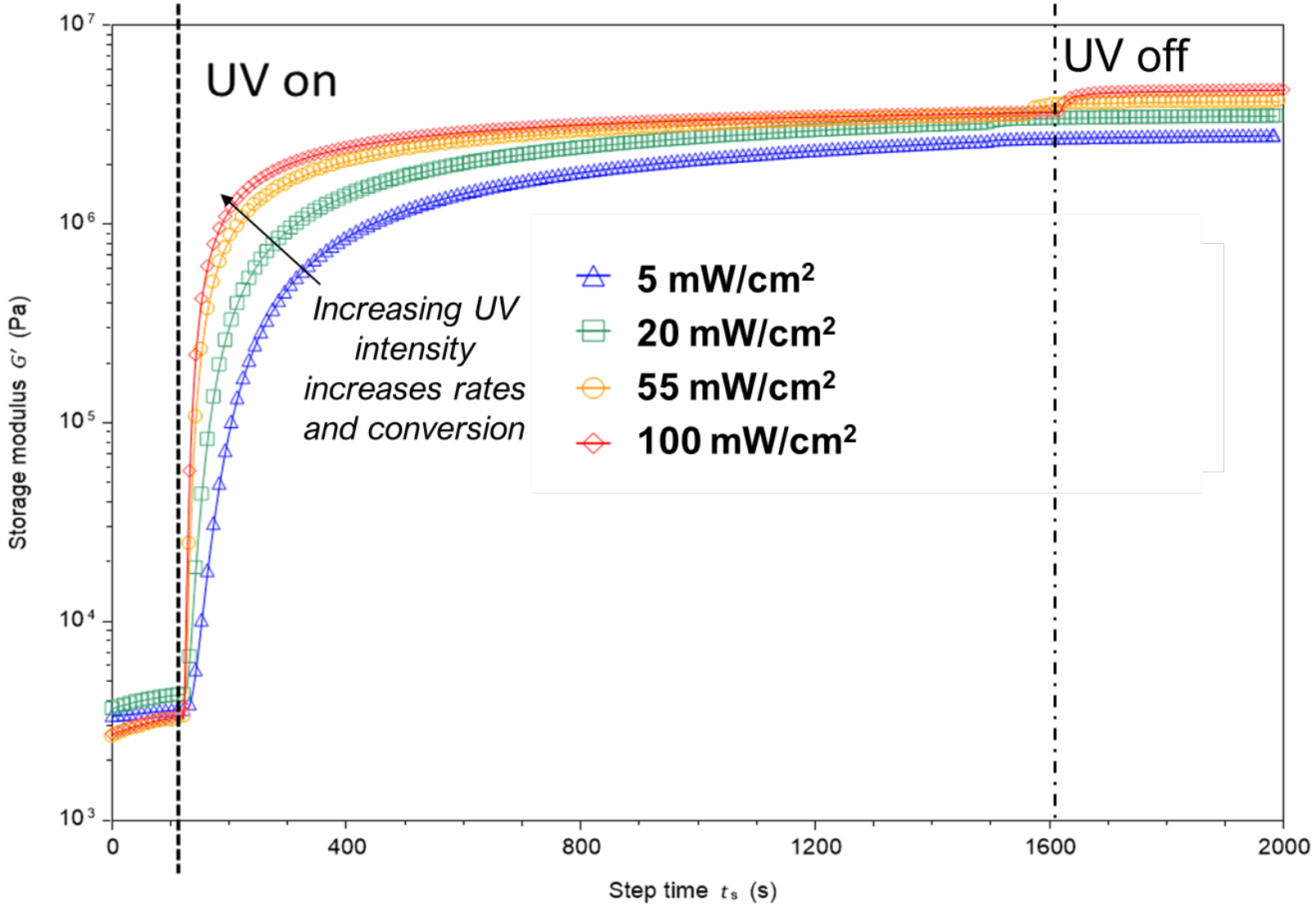




- Peltier oven allows control of lower plate temperature
- 365 nm filter to mimic printing conditions

UV Rheology: Basic Measurements

Continuous exposures at varying intensity for **15wt% acrylate resin**. Irradiation time = 25 min



Continuous exposures can be used to:

Investigate effects of:

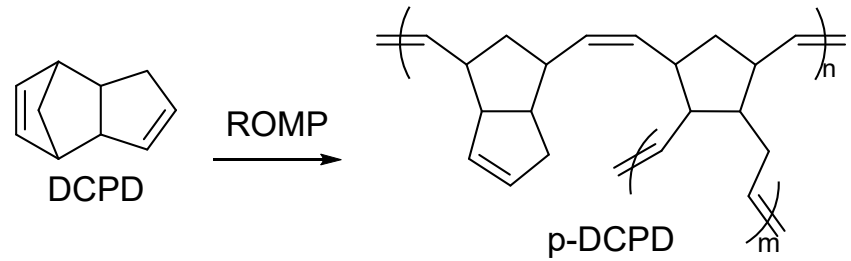
- **Intensity**
- **Formulation**
- **Fillers**

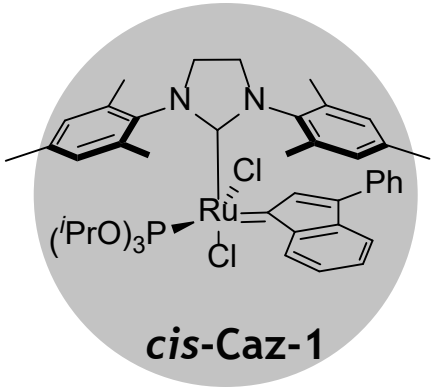
On:

- **Reaction rates**
- **Gel point/modulus crossover**
- **Plateau moduli**
- **t = x moduli**

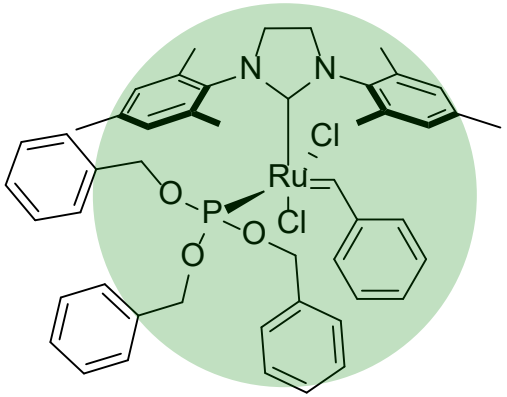
UV Rheology Applied: Photo-ROMP AM

Used UV rheology to easily investigate photopolymerization reaction rates with minimal catalyst/resin.

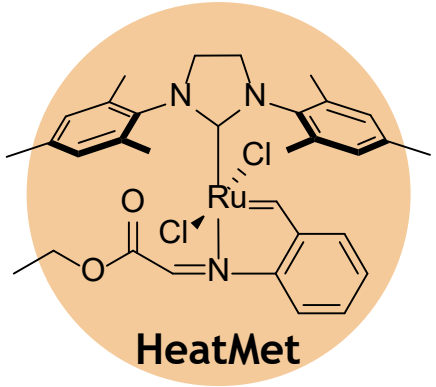




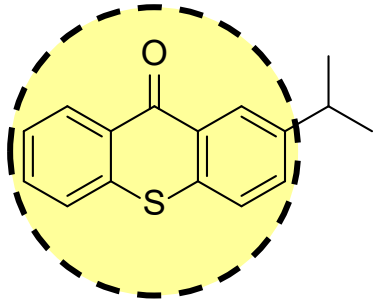
cis-Caz-1



cis-Ru-1

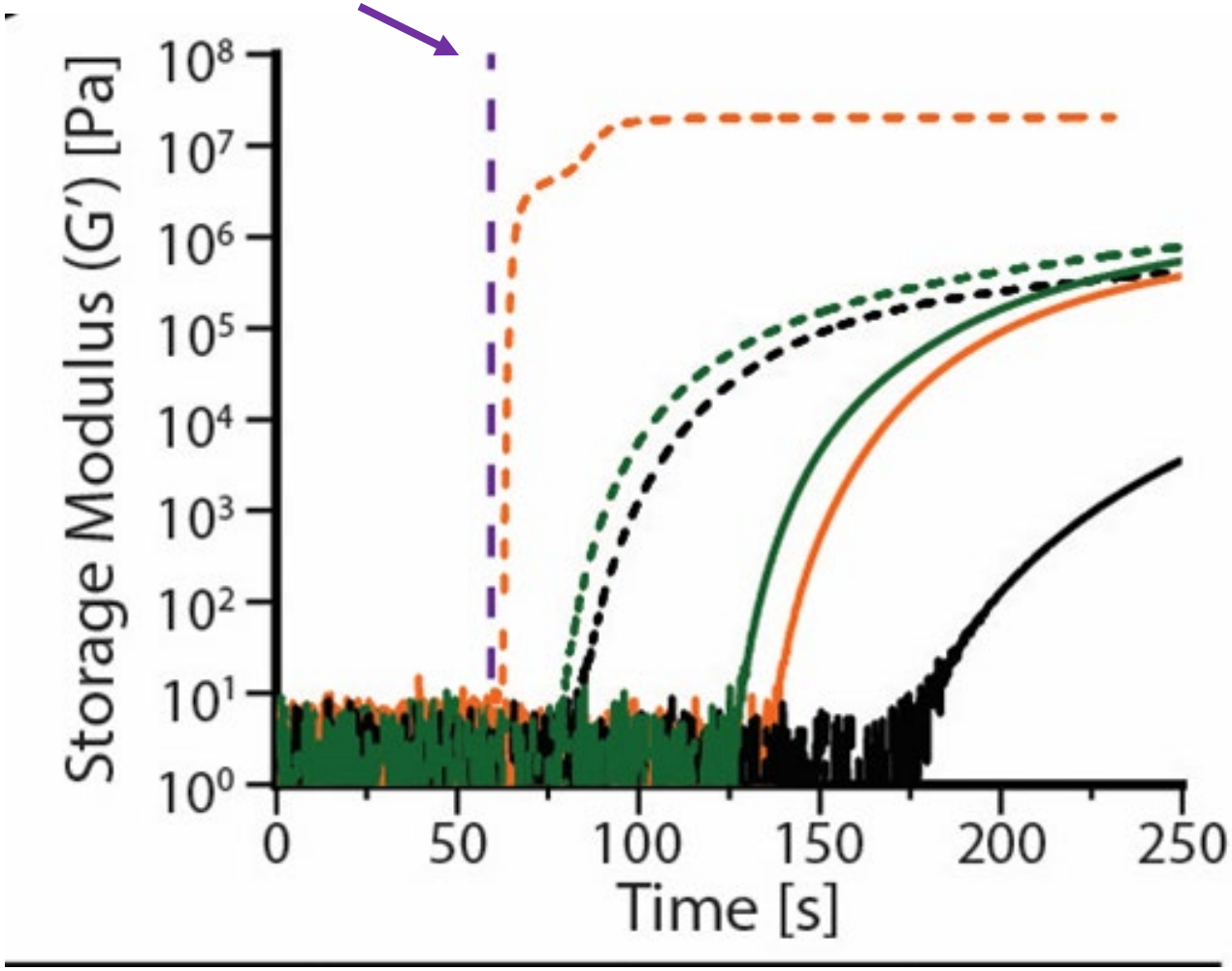


HeatMet



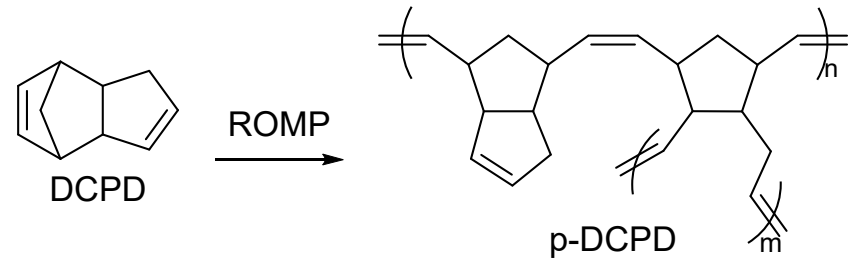
2-isopropylthioxanthone (ITX)

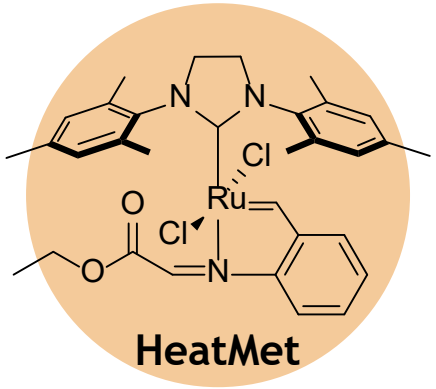
UV on (365 nm @ 120 mW/cm^2)

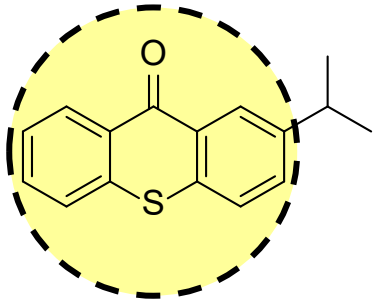


UV Rheology Applied: Photo-ROMP AM

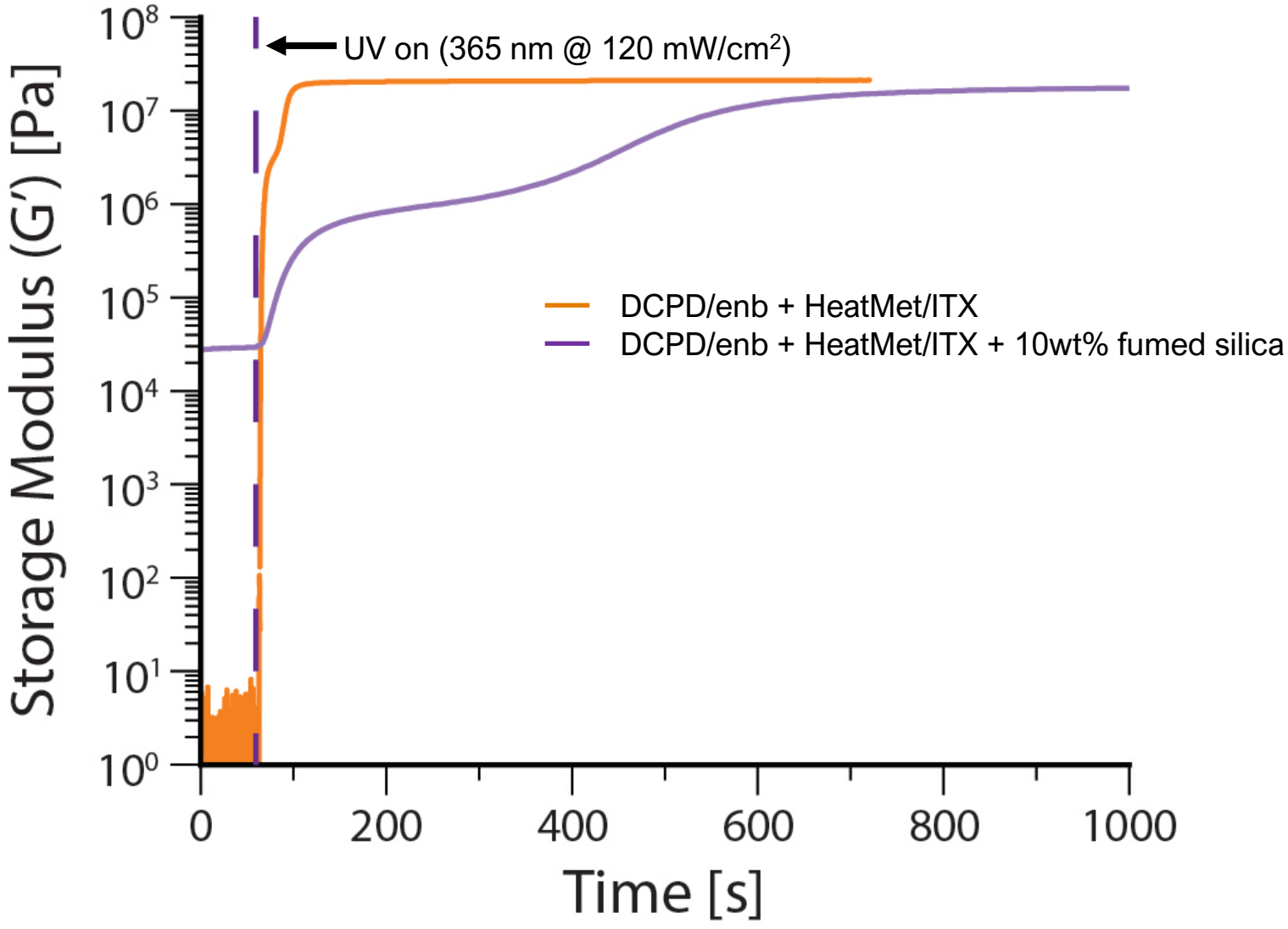
Investigate the effect of silica (rheology modifier) on photopolymerization rates and modulus evolution.





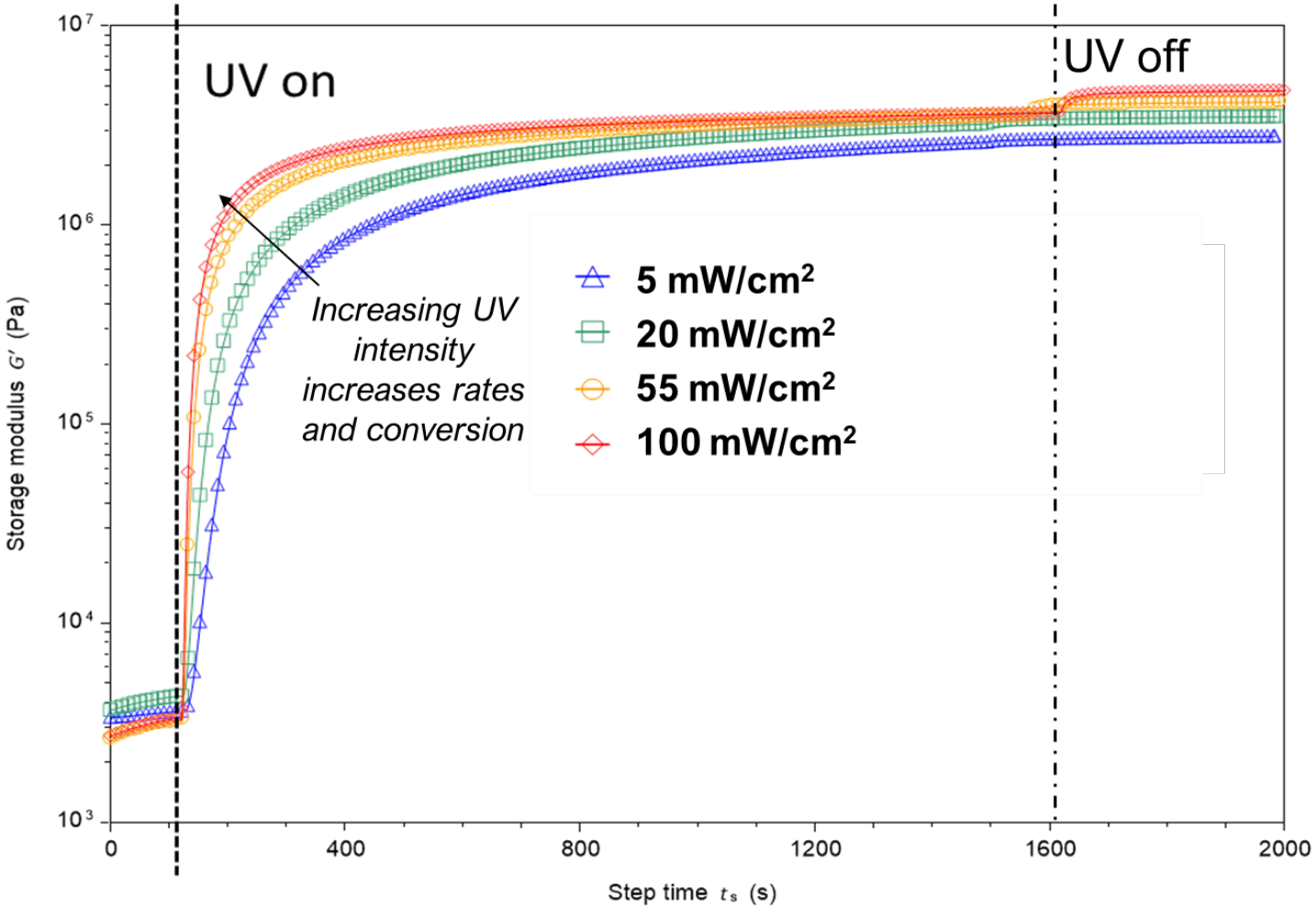


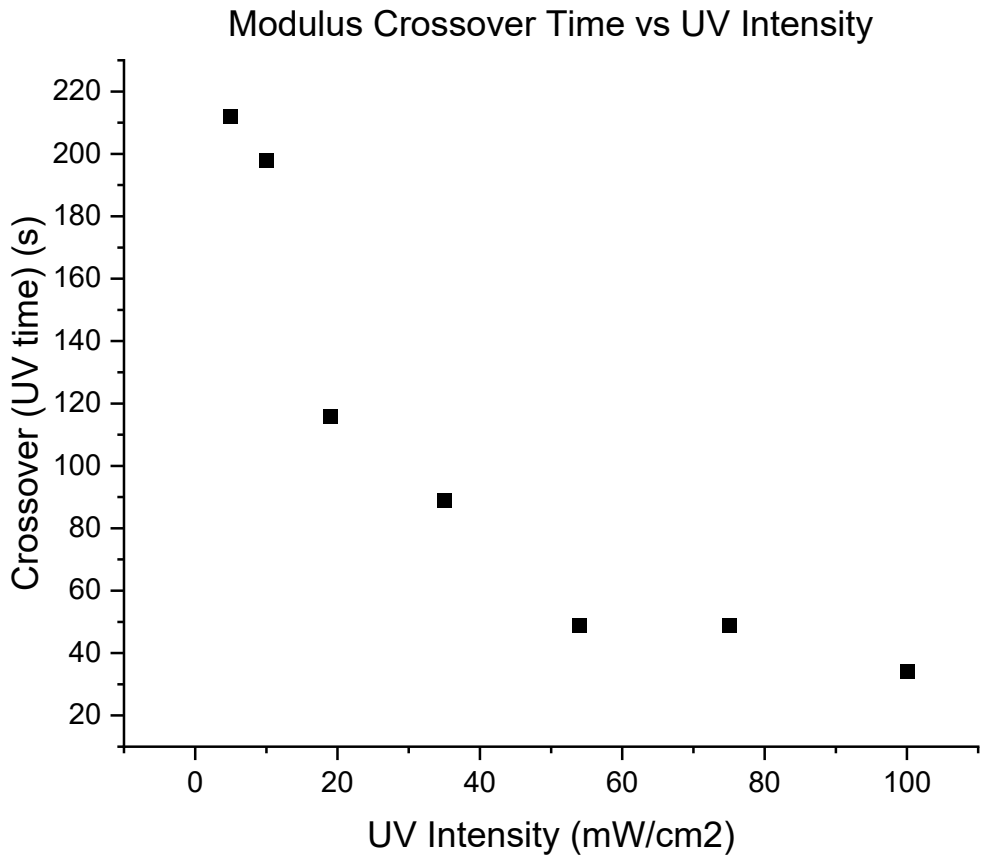
2-isopropylthioxanthone (ITX)



UV Rheology: Basic Measurements

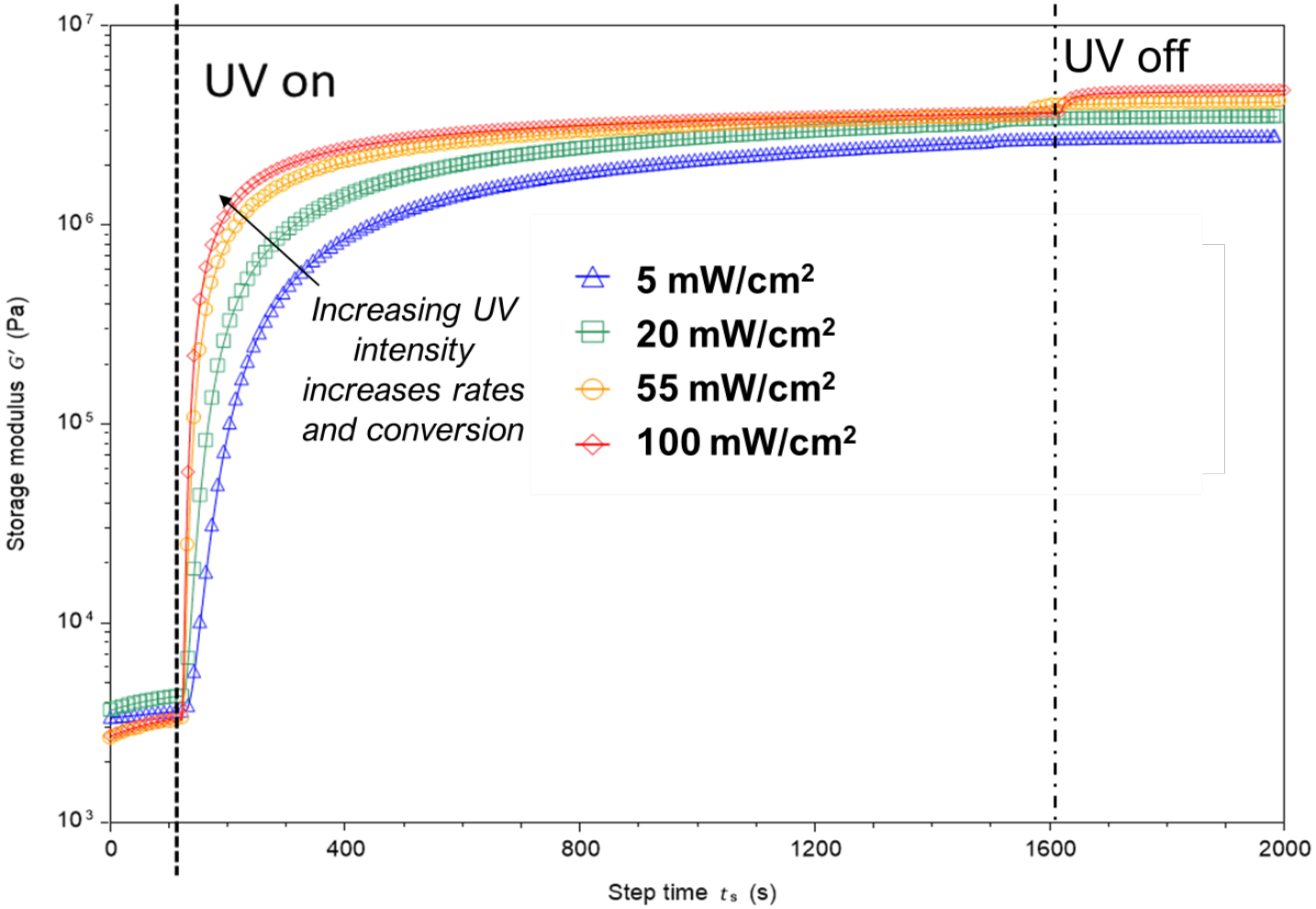
Continuous exposures at varying intensity for **15wt% acrylate resin**. Irradiation time = 25 min

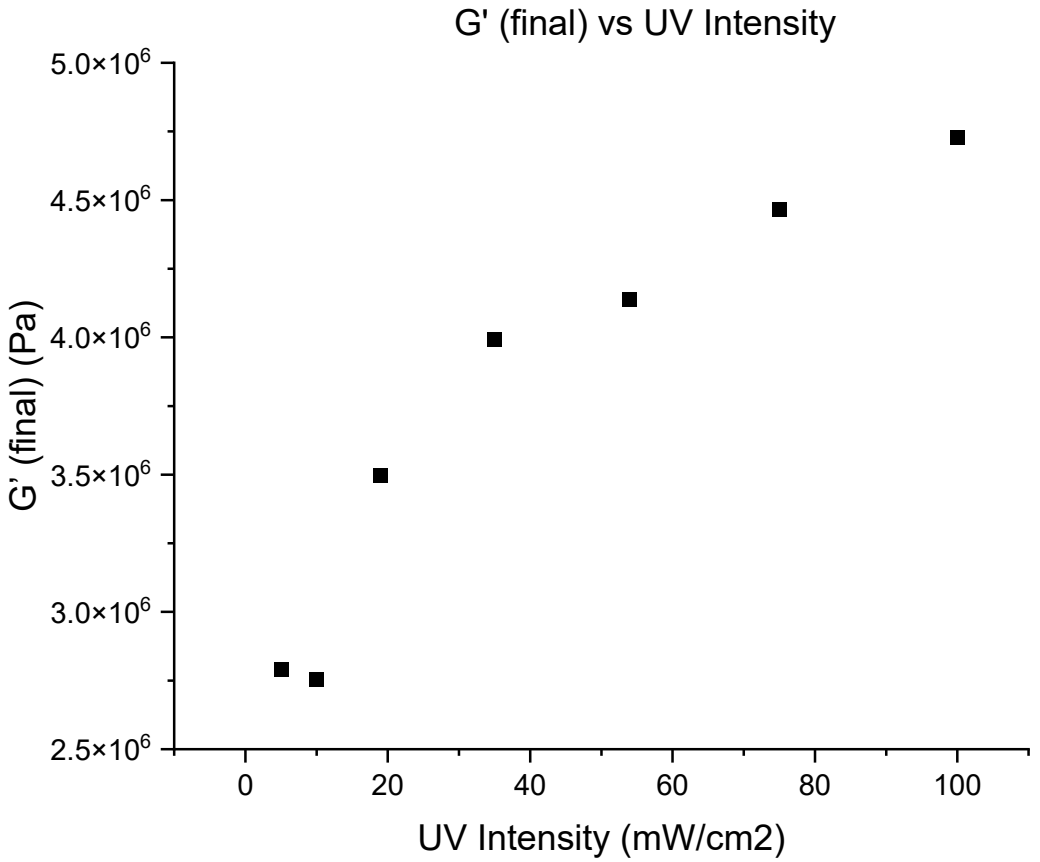




UV Rheology: Basic Measurements

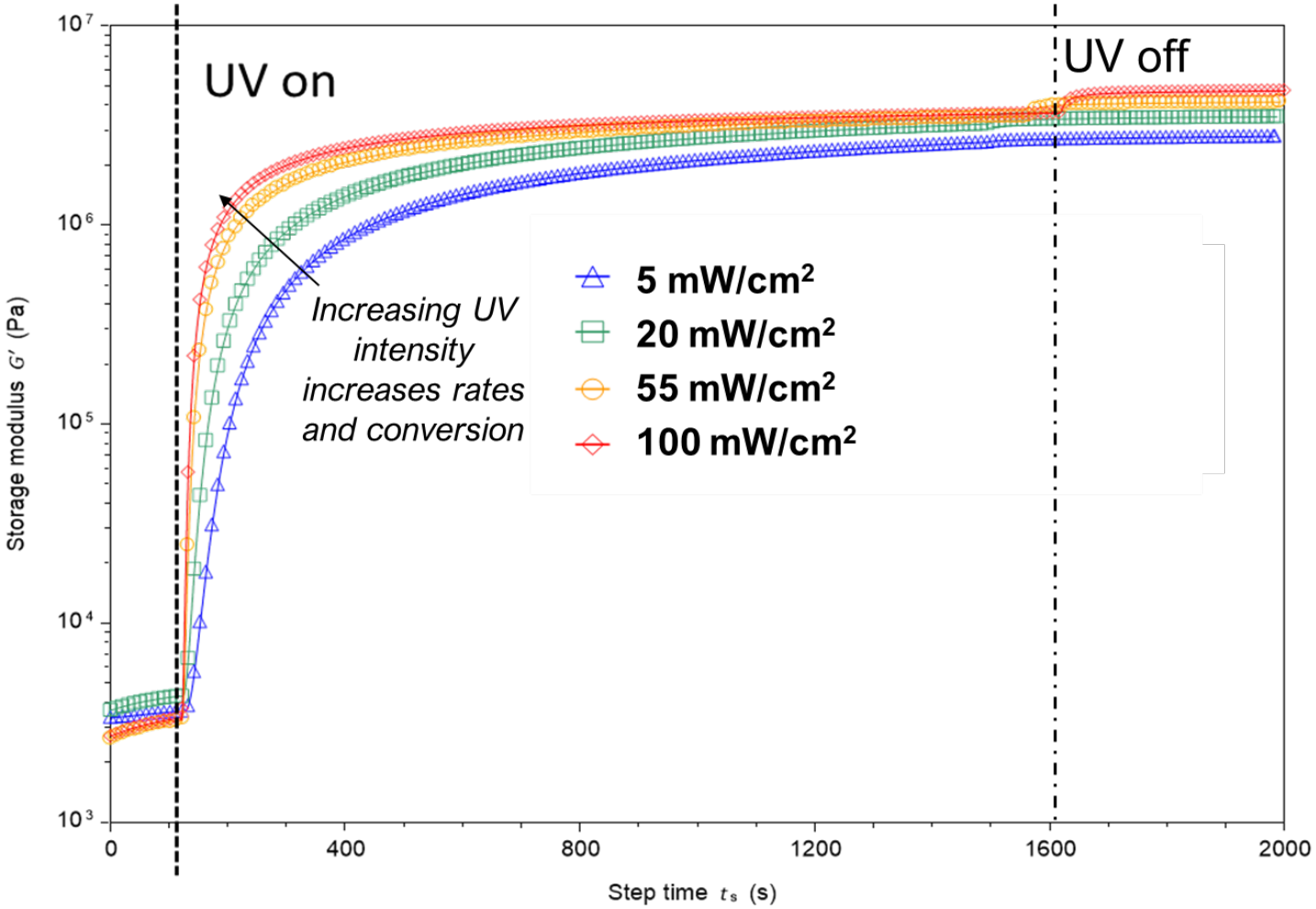
Continuous exposures at varying intensity for **15wt% acrylate resin**. Irradiation time = 25 min

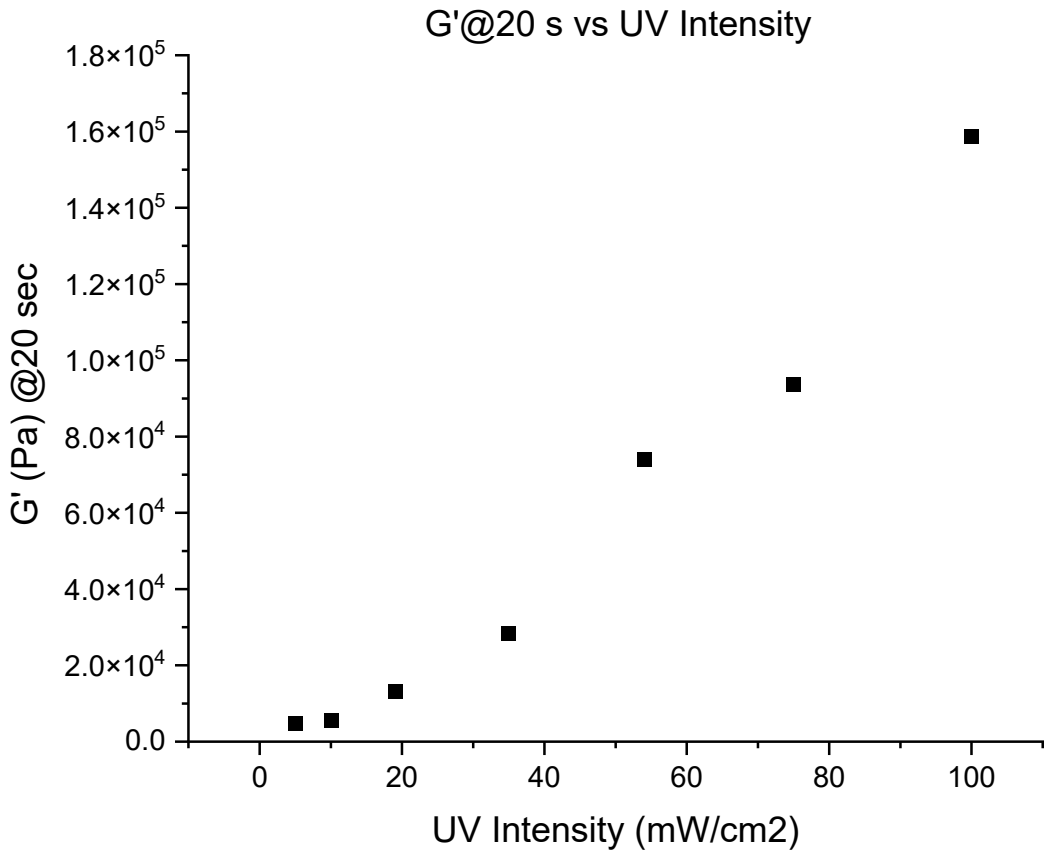




UV Rheology: Basic Measurements

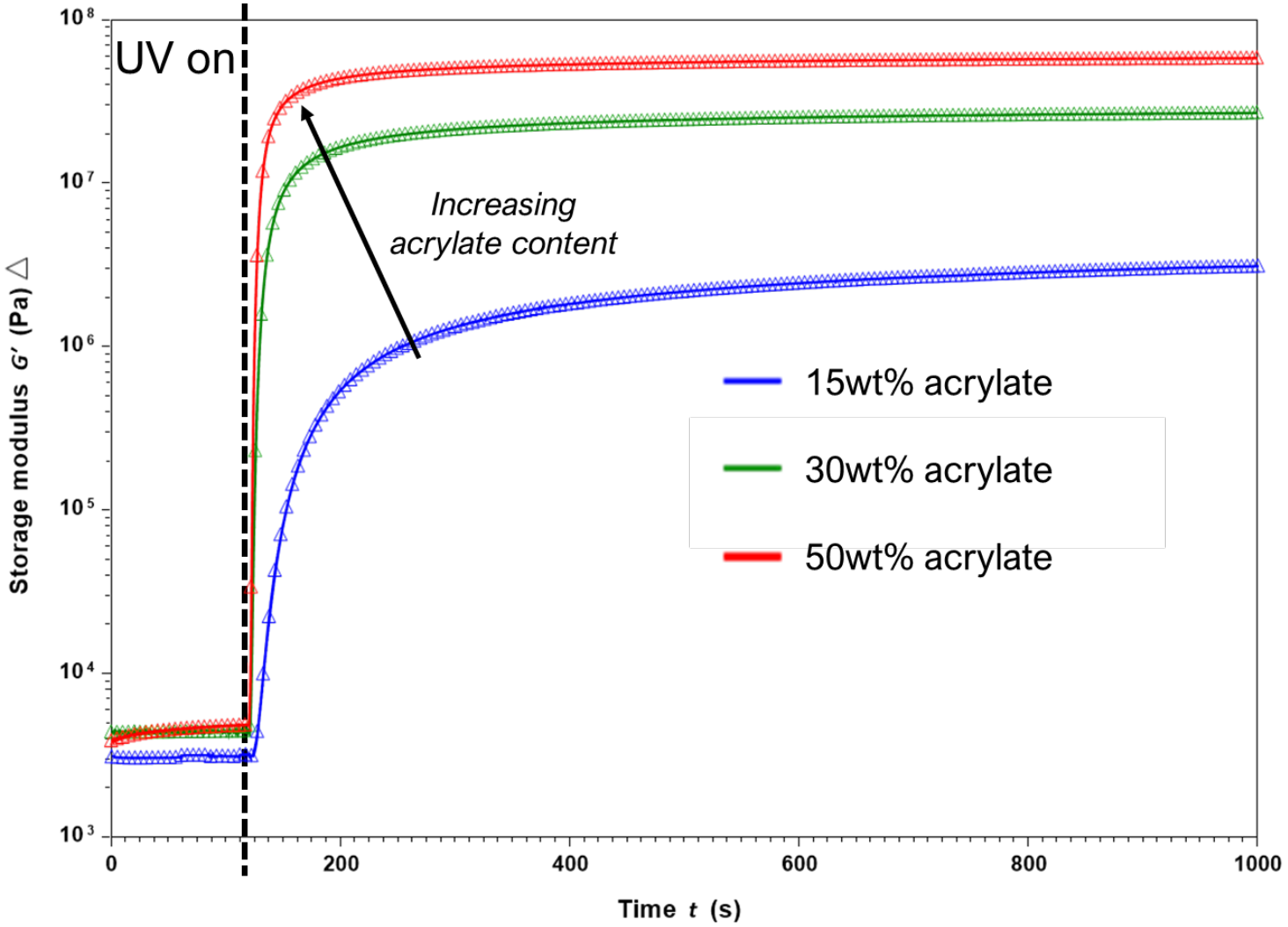
Continuous exposures at varying intensity for **15wt% acrylate resin**. Irradiation time = 25 min

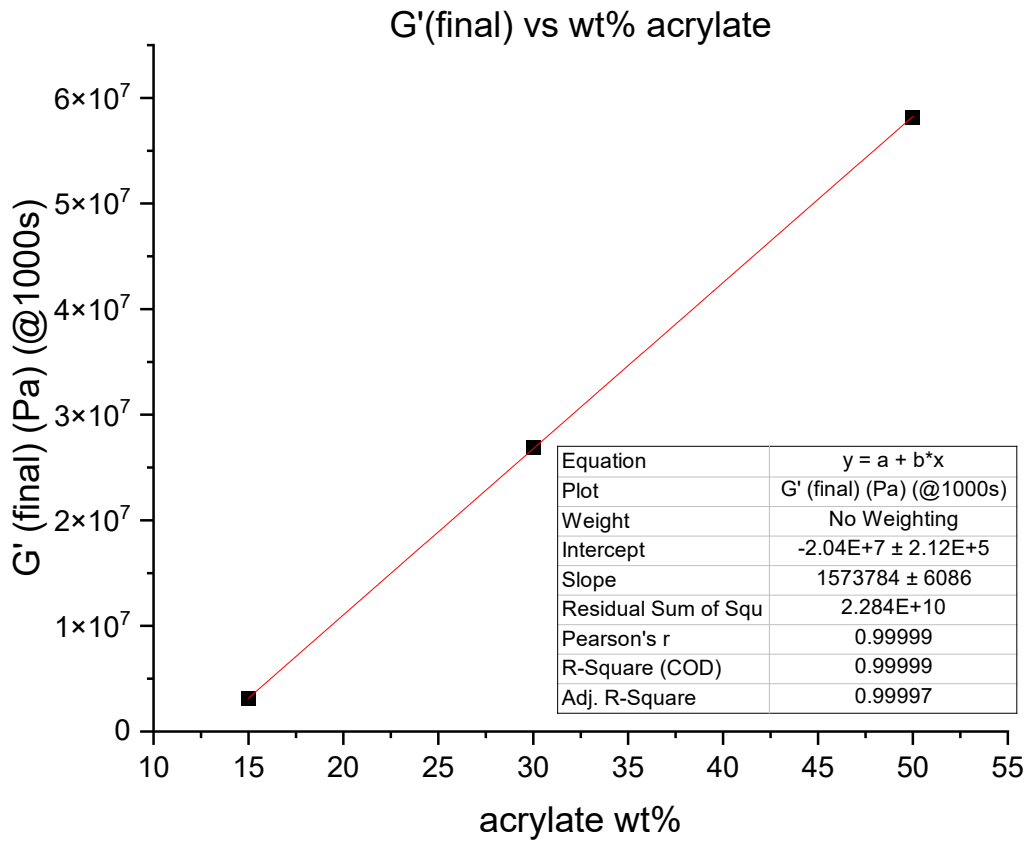




UV Rheology: Basic Measurements

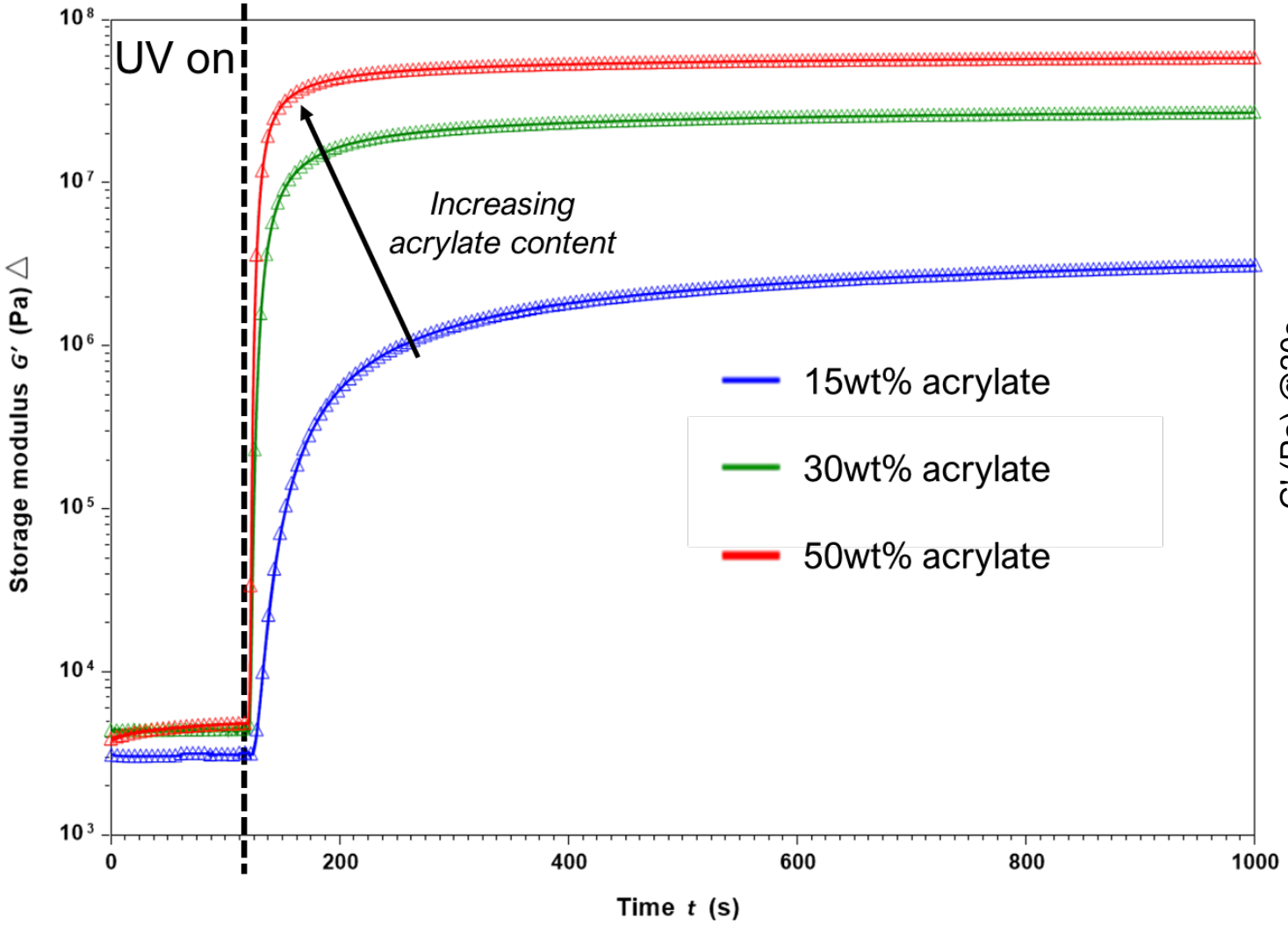
Continuous exposures at **35 mW/cm²** for different acrylate wt% resins.

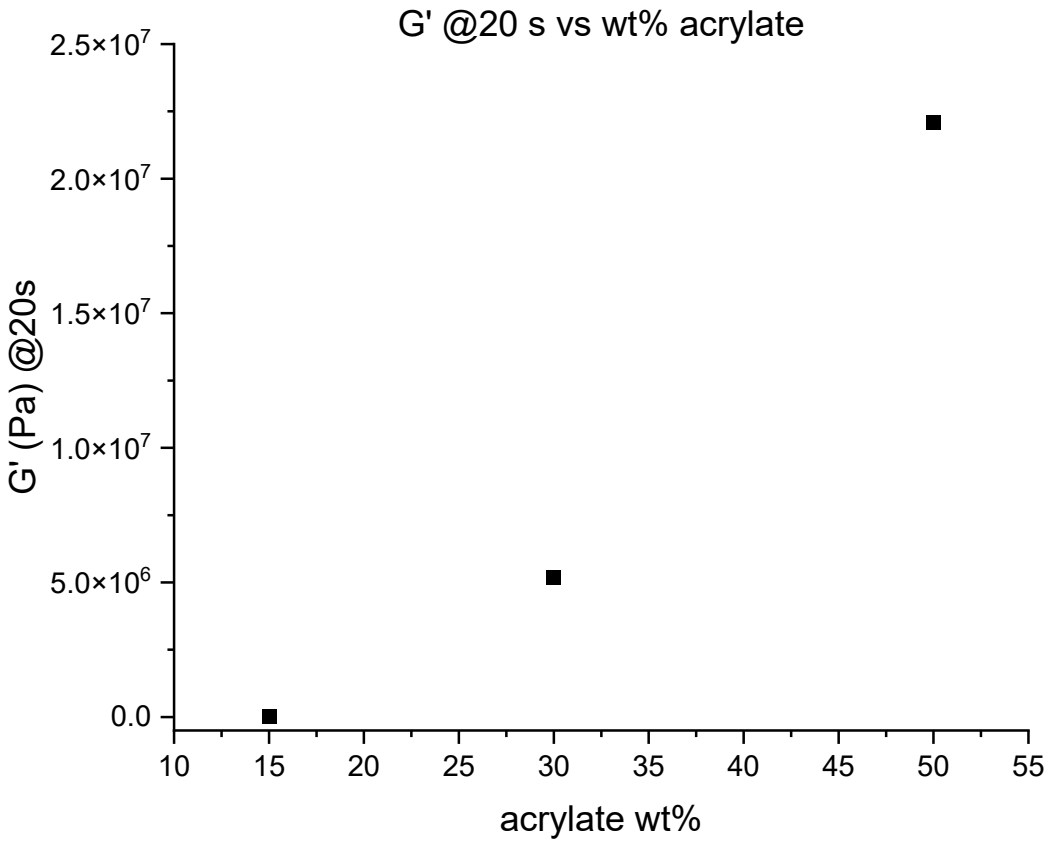




UV Rheology: Basic Measurements

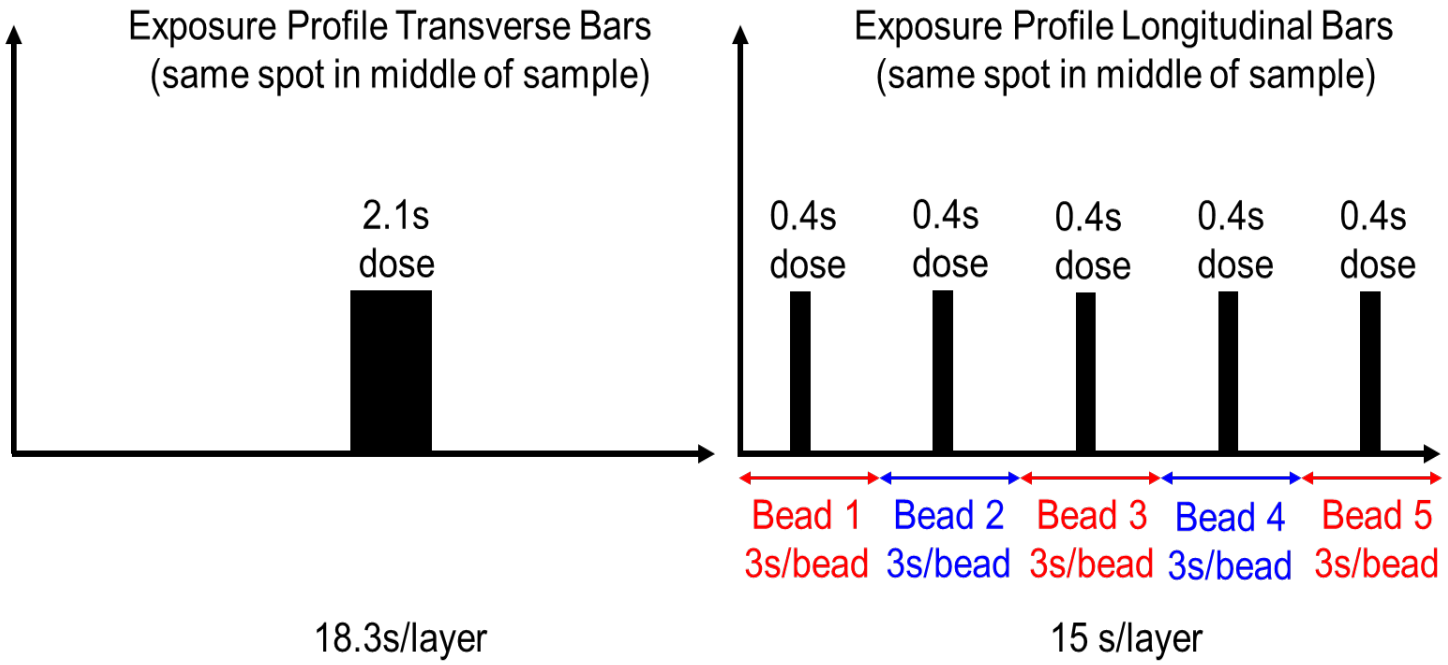
Continuous exposures at 35 mW/cm^2 for different acrylate wt% resins.

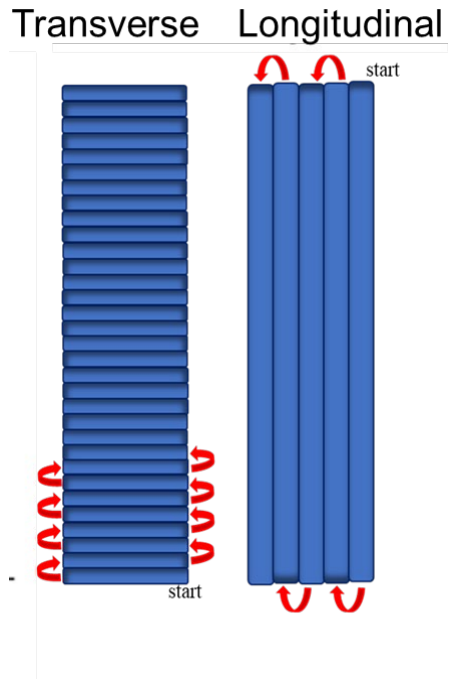


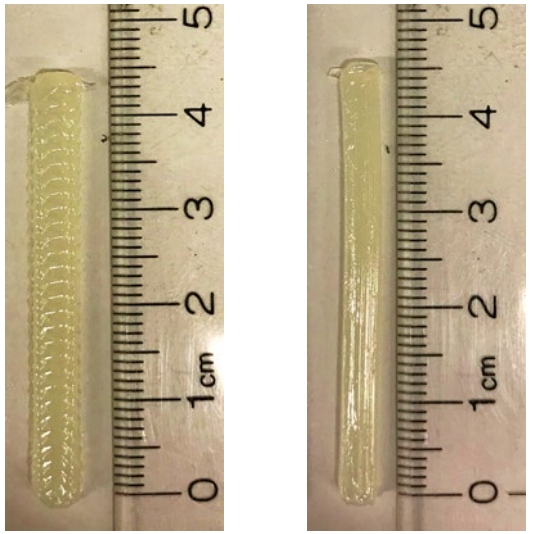


UV Rheology: Pulsed exposures

Print path determines exposure profile.

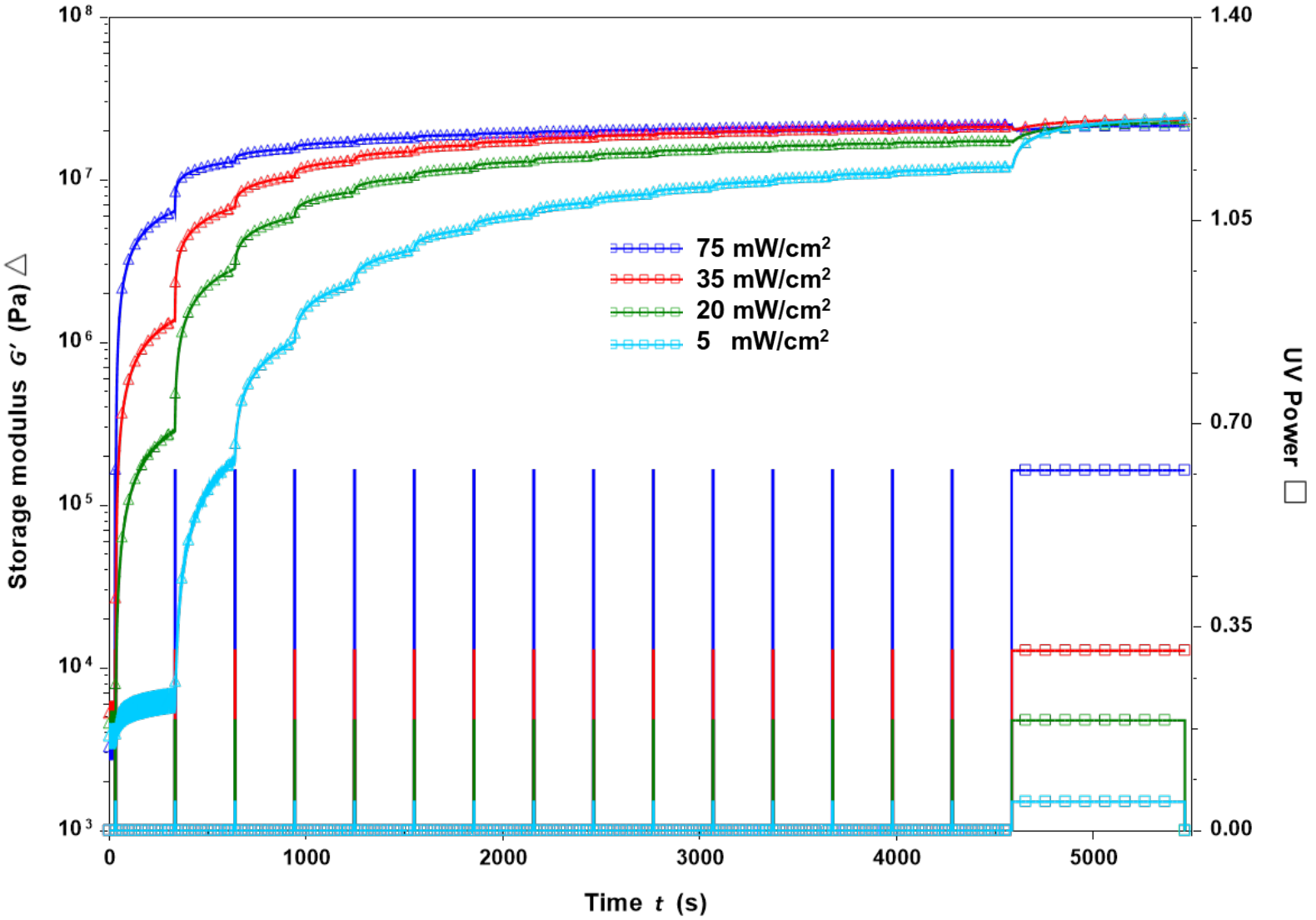






UV Rheology: Pulsed exposures

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



Pulsed exposures can be used to mimic print conditions.

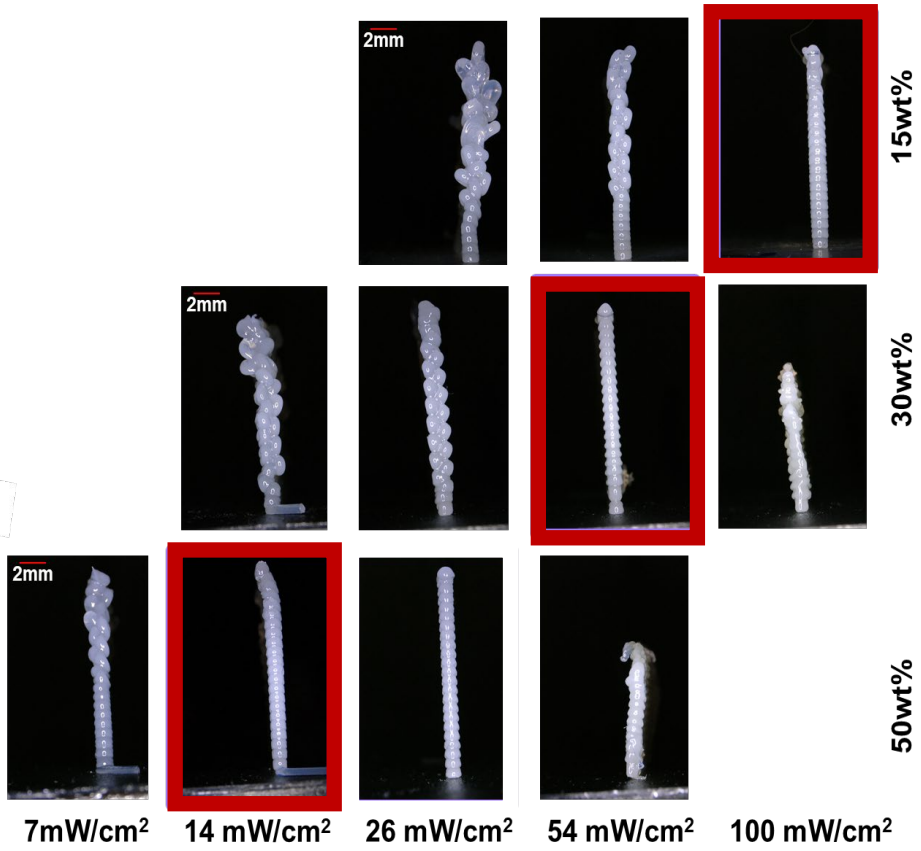
Investigate effects of:

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

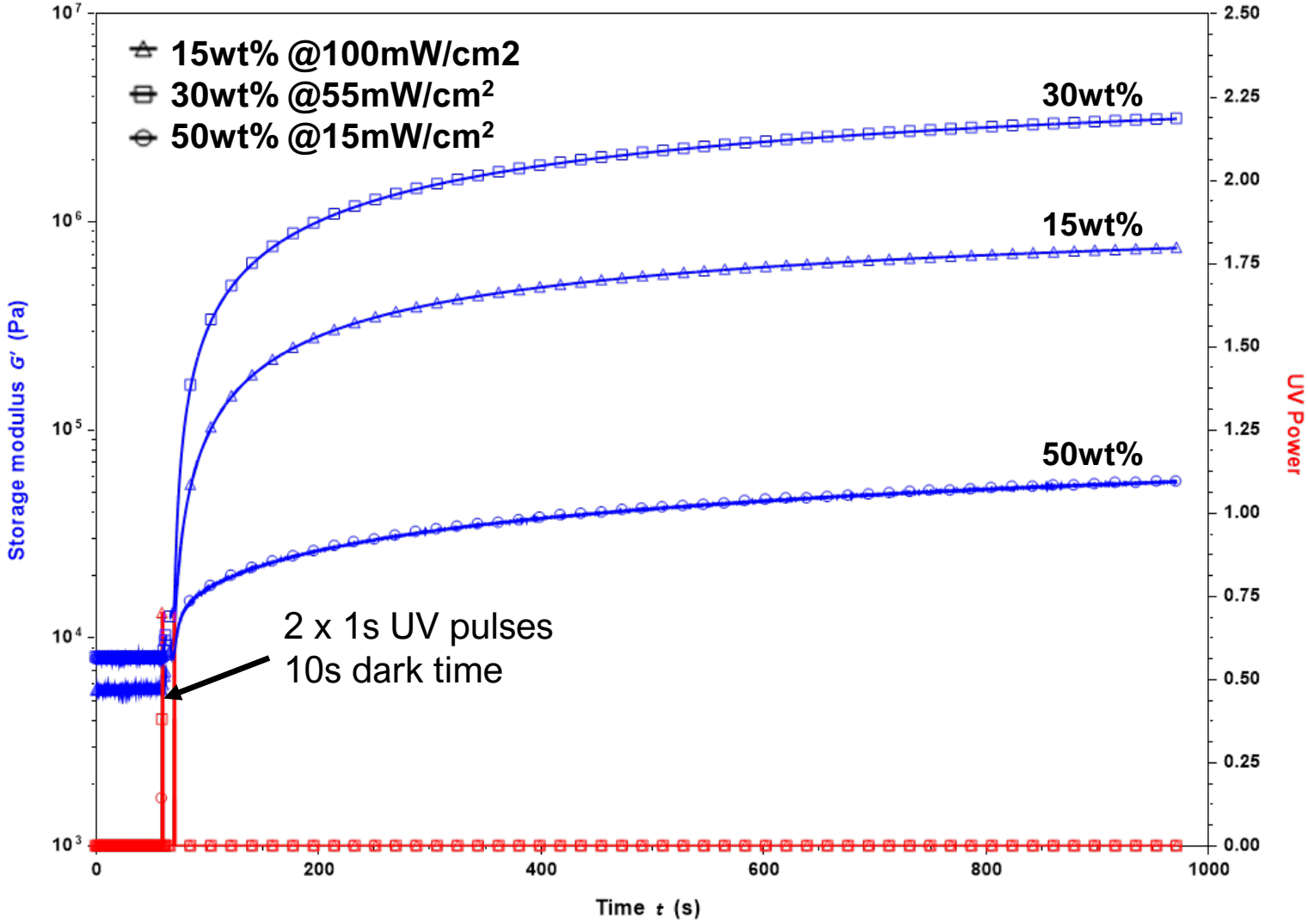
On:

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

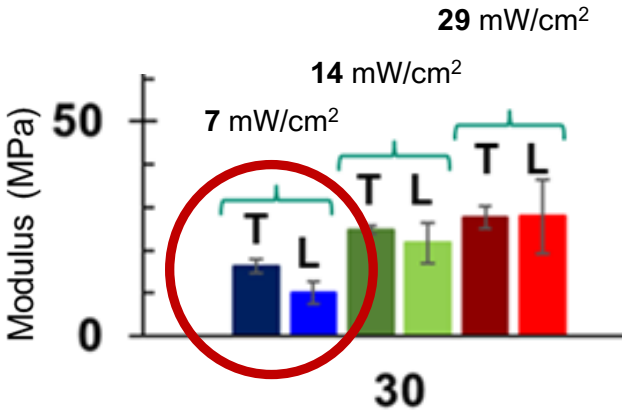
UV Rheology: Can pulsed exposures predict printability?

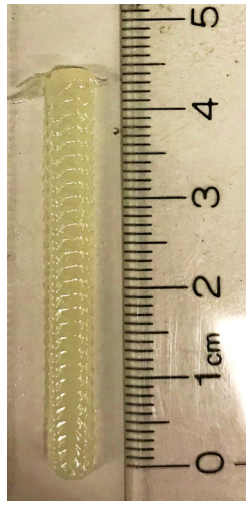


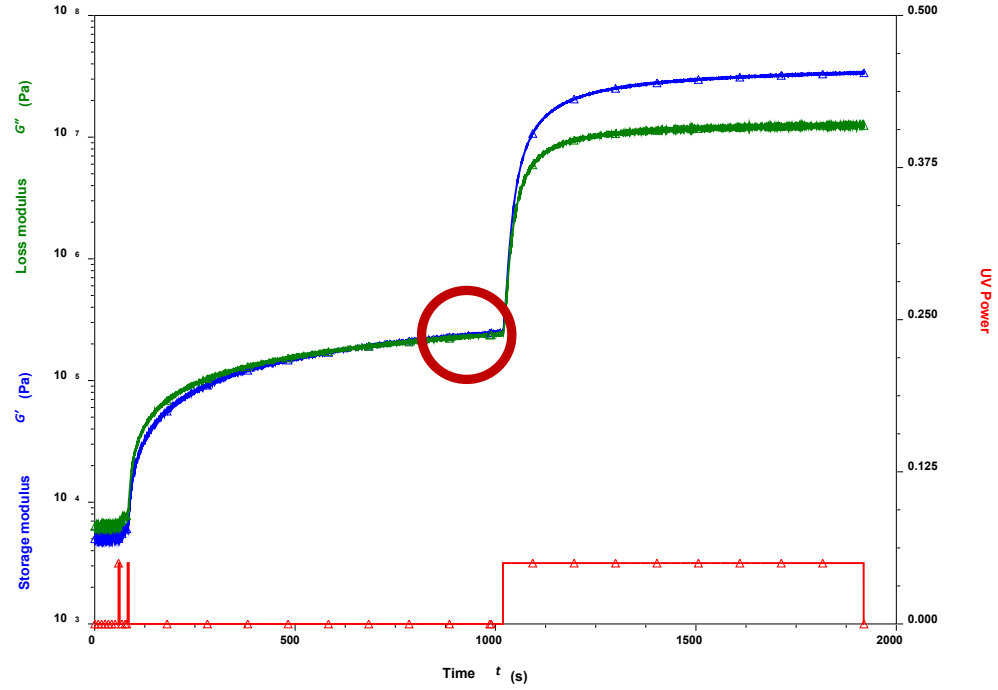
2 x 1s pulsed exposures (walls), then continuous exposure

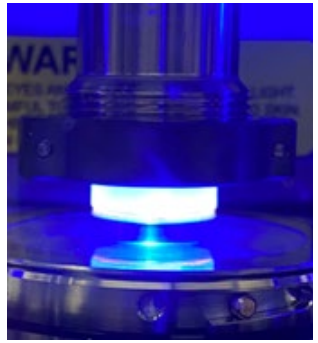


Where predictions fall short: Modulus prediction









G' for UV rheo vs printed bars
5 mW/cm² for varying acrylate wt%

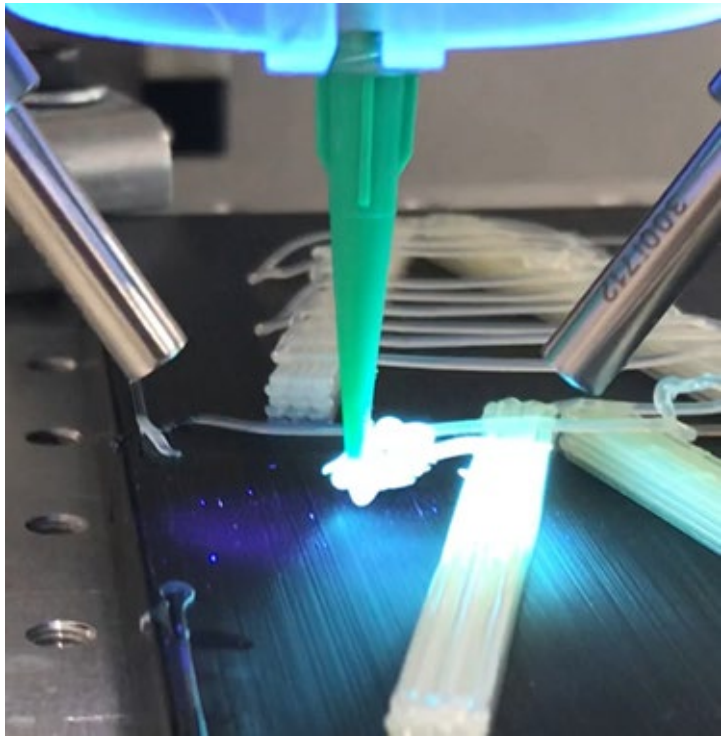
wt% acrylate	G' (plateau) (UV rheo)	G' (plateau) (printed)
15	0.03	0.16
30	0.22	25.2
50	1.15	125.9

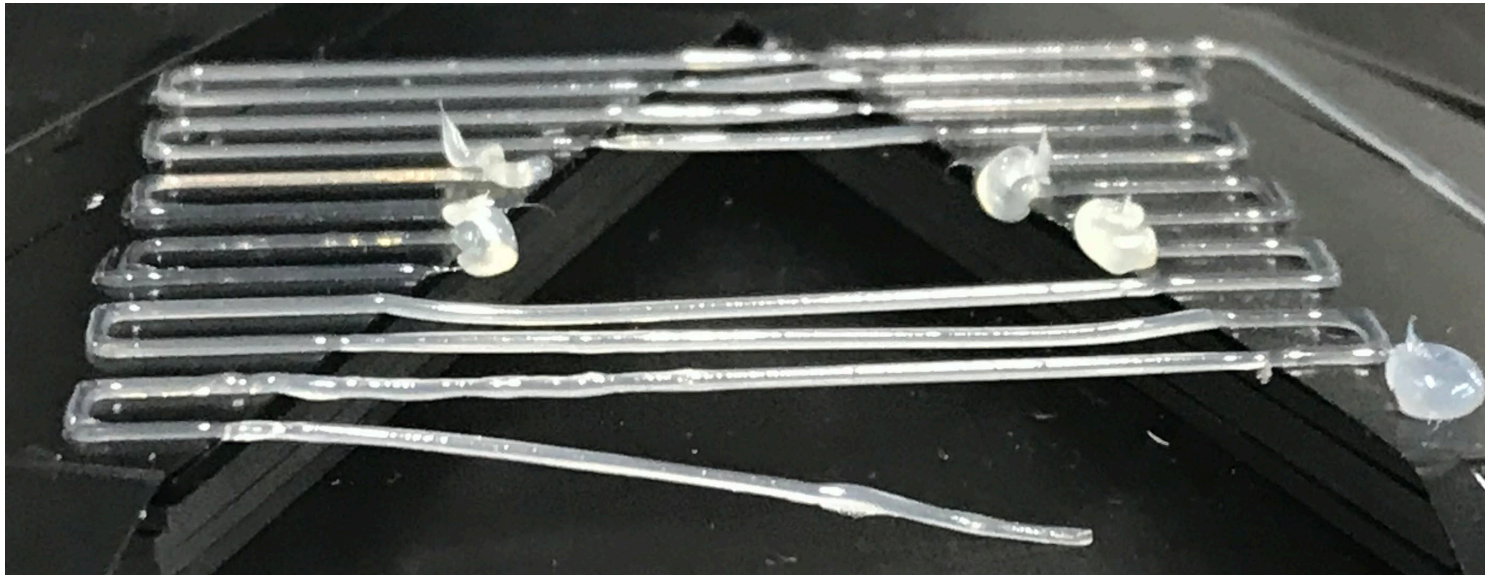
G' for UV rheo vs printed bars **15wt% acrylate** varying intensity

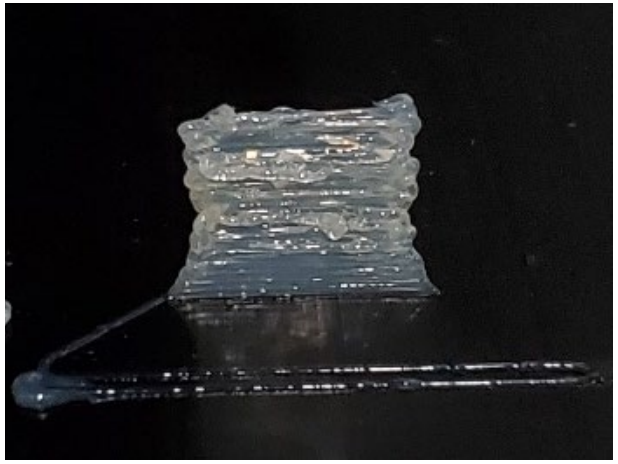
Intensity (mW/cm²)	G' (plateau) (UV rheo)	G' (plateau) (printed)
5/7	0.03	0.16
20/26	0.81	2.74
75/NA	2.57	-

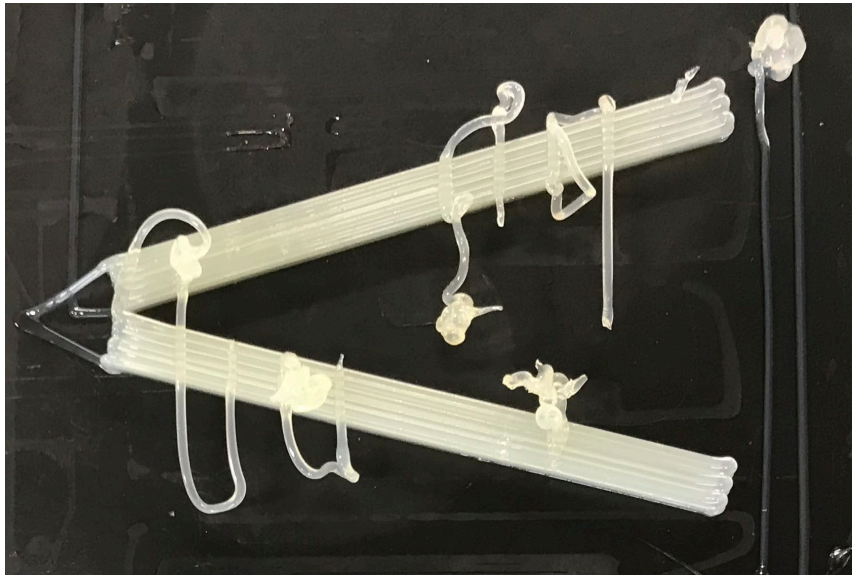
Where predictions fall short: Interlayer adhesion

Where predictions fall short: Clogging/cure effects on extrusion









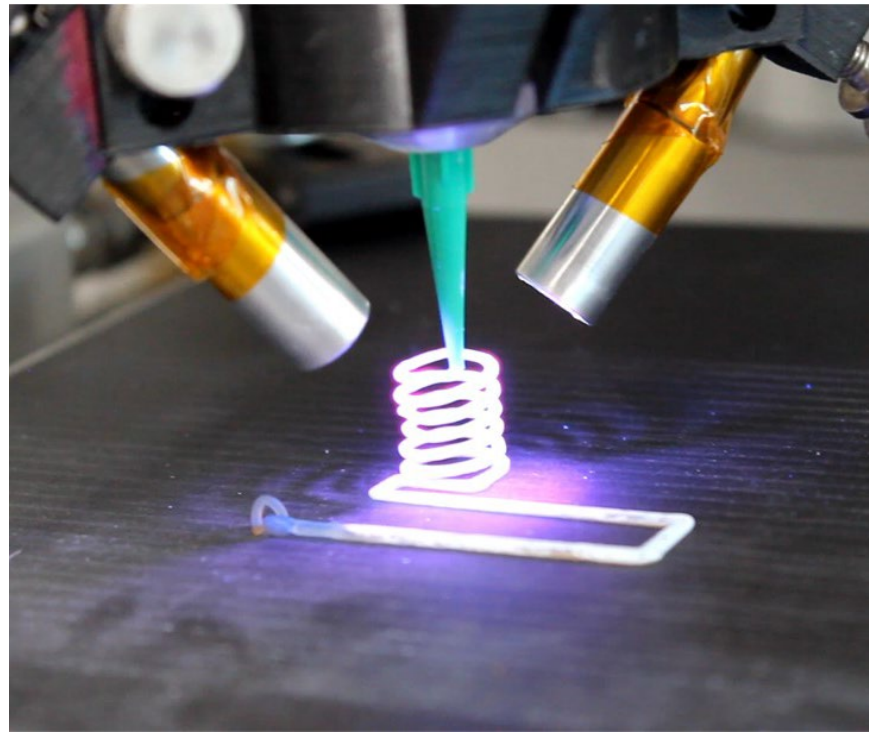
Conclusions

Successes:

- Downselect resin formulations based on photokinetics
- Interrogate effects of formulations, UV intensity, UV dose, and exposure profiles (pulse length/dark times)

Needs future work:

- Correlation between photorheology measurements and printed properties is not 1:1
- Translate models for thermoplastics, inert thermosets, and reactive resins to photocatalyzed dual-cure resins
- Topology optimization-like predictive print design



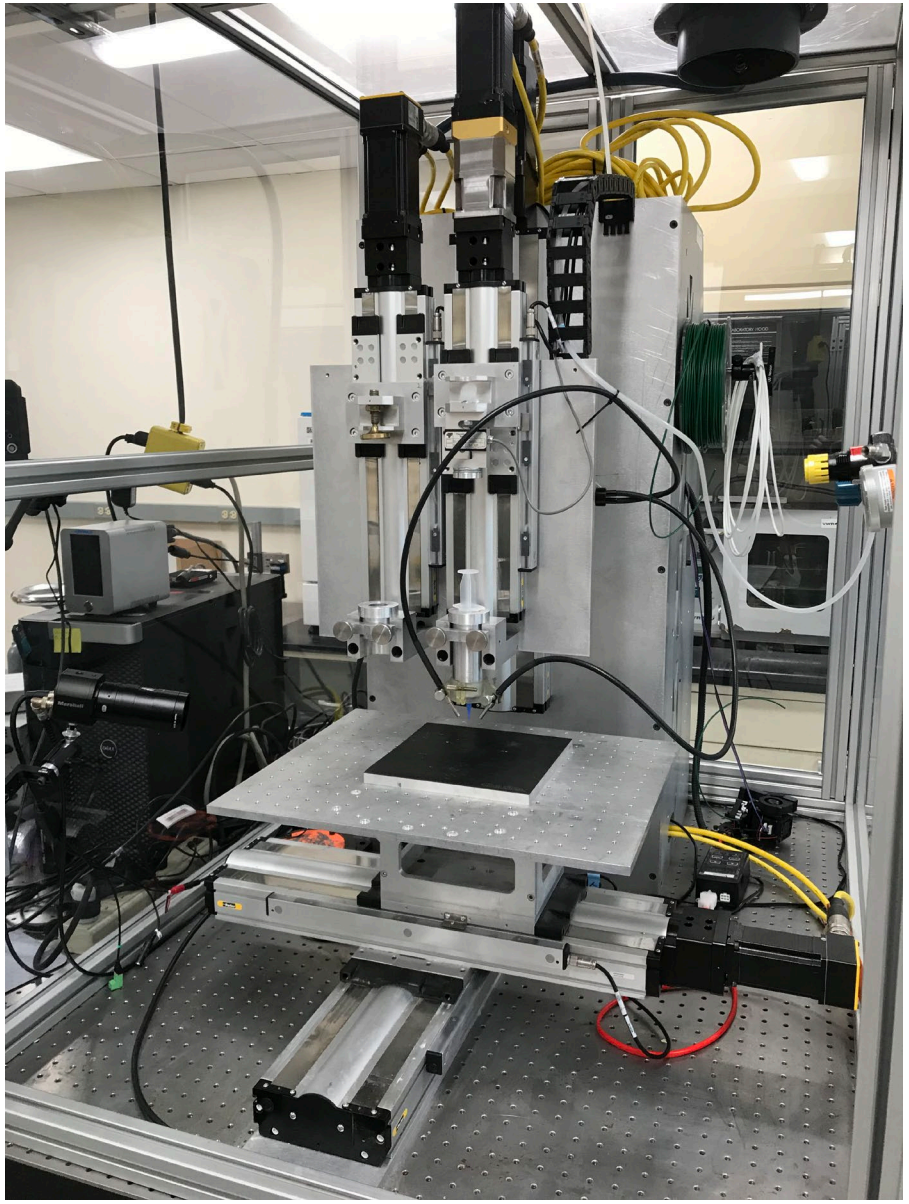
DCPD Photo-skywriting

Supplementary Slides

Sandia's UV-assisted Direct-Ink Write Capability

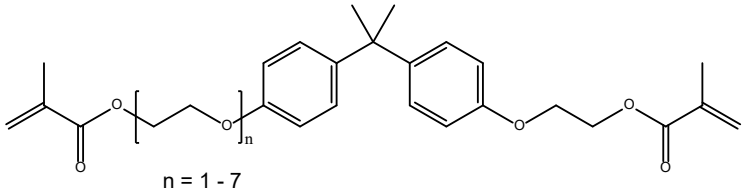
Adam Cook/Derek Reinholtz

- **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**

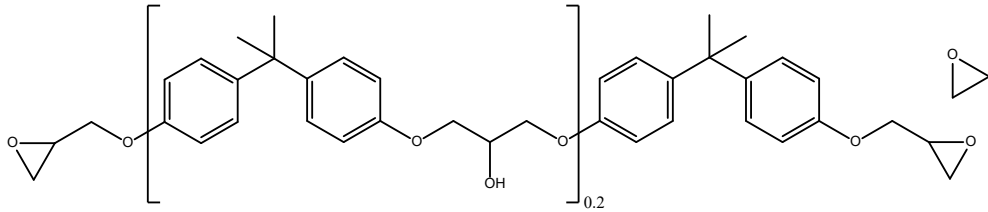


UV-Thermal Dual Cure Resin Formulation

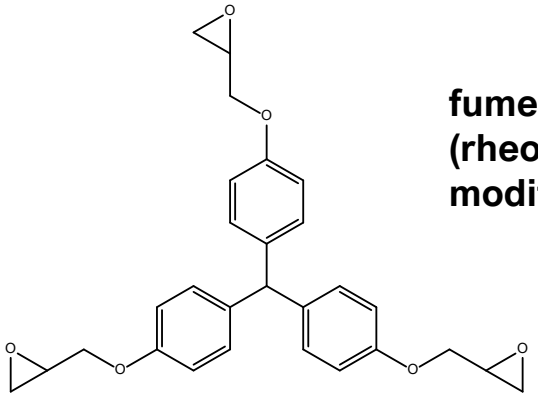
UV-thermal Epoxy/acrylate Formulation



dimethacrylate

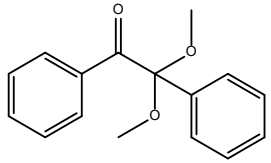


diepoxy

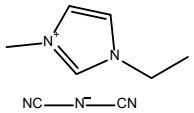


triepoxy

fumed silica (rheology modifier)

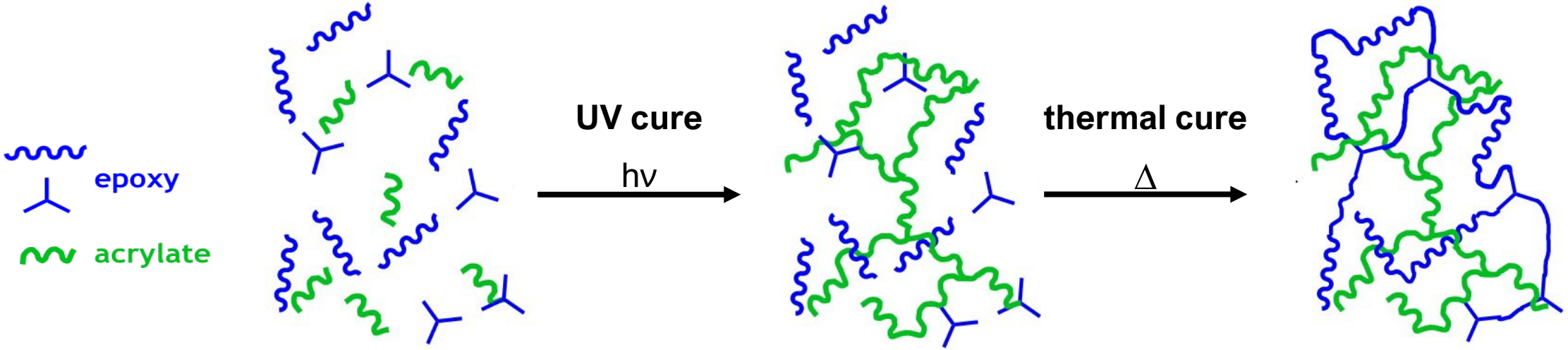


radical photoinitiator
(2,2-dimethoxy-1,2-diphenylethanone)



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

Sequential Interpenetrating Polymer Network



uncured resin mixture

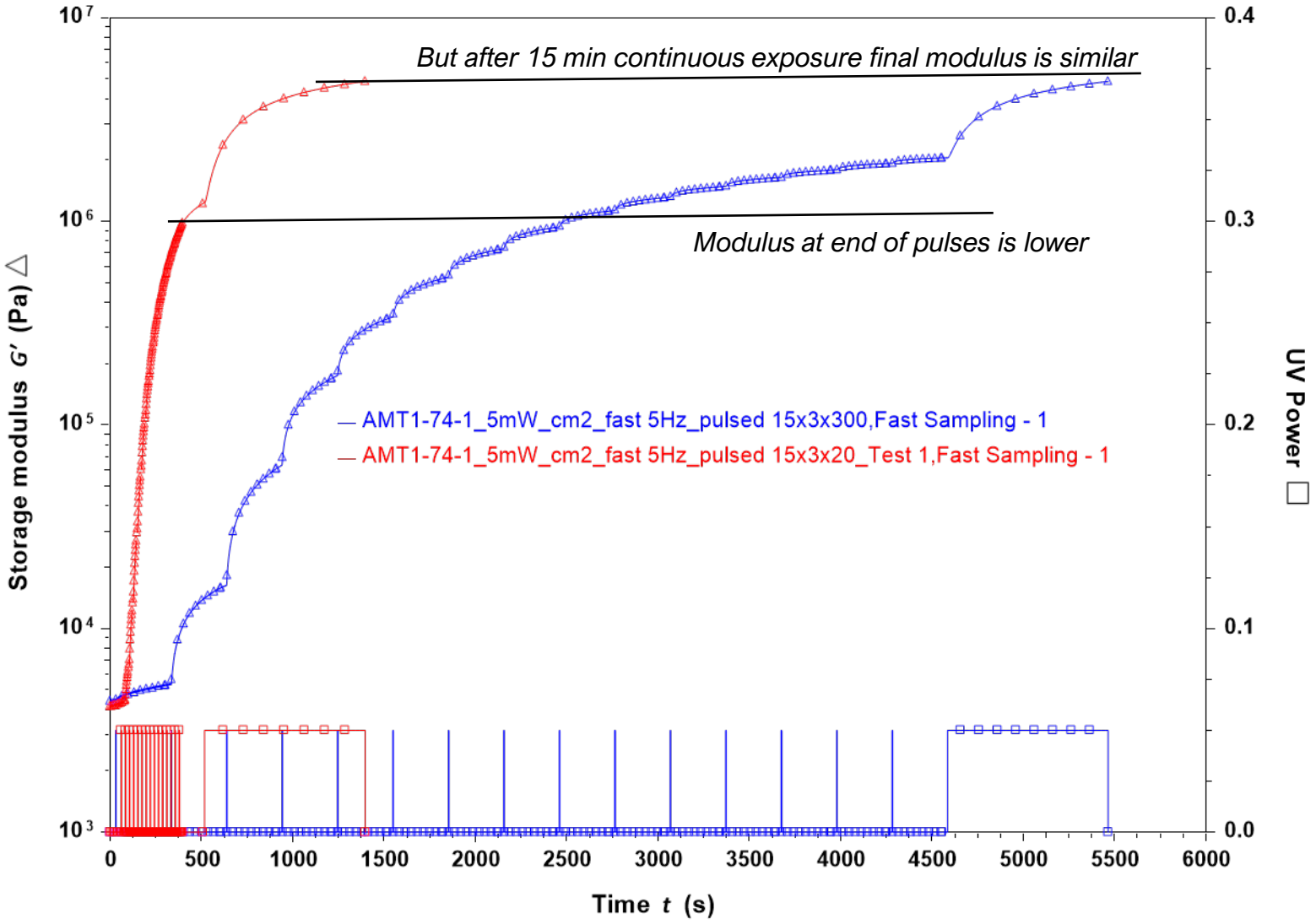
acrylate network forms

epoxy network forms

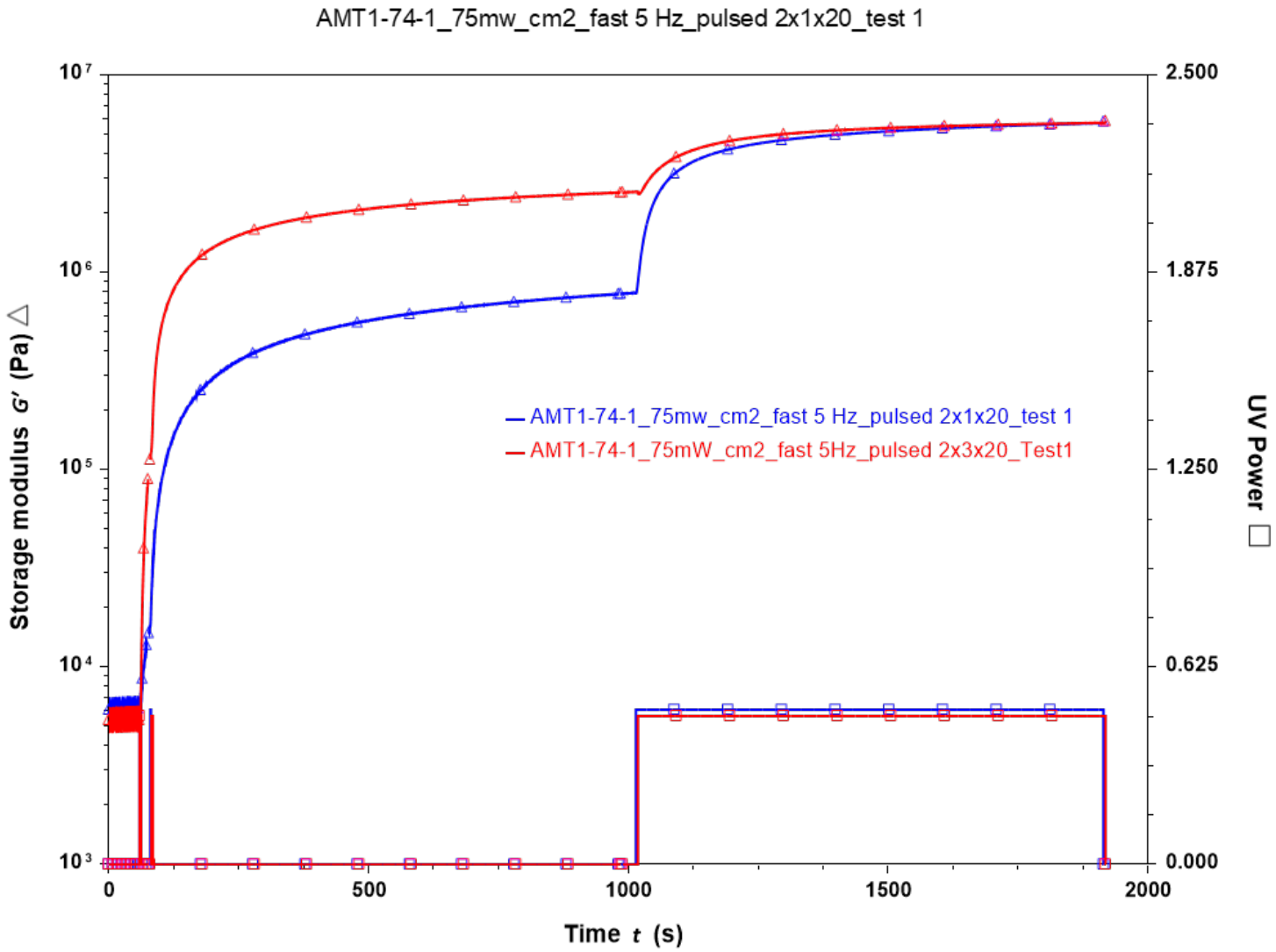
Pulsed exposures comparing 300 s and 20 s dark times

15 pulses
3 s UV, X s dark time

15 min continuous UV exposure at end



Pulsed exposures with 3 s vs 1 s pulse lenghts



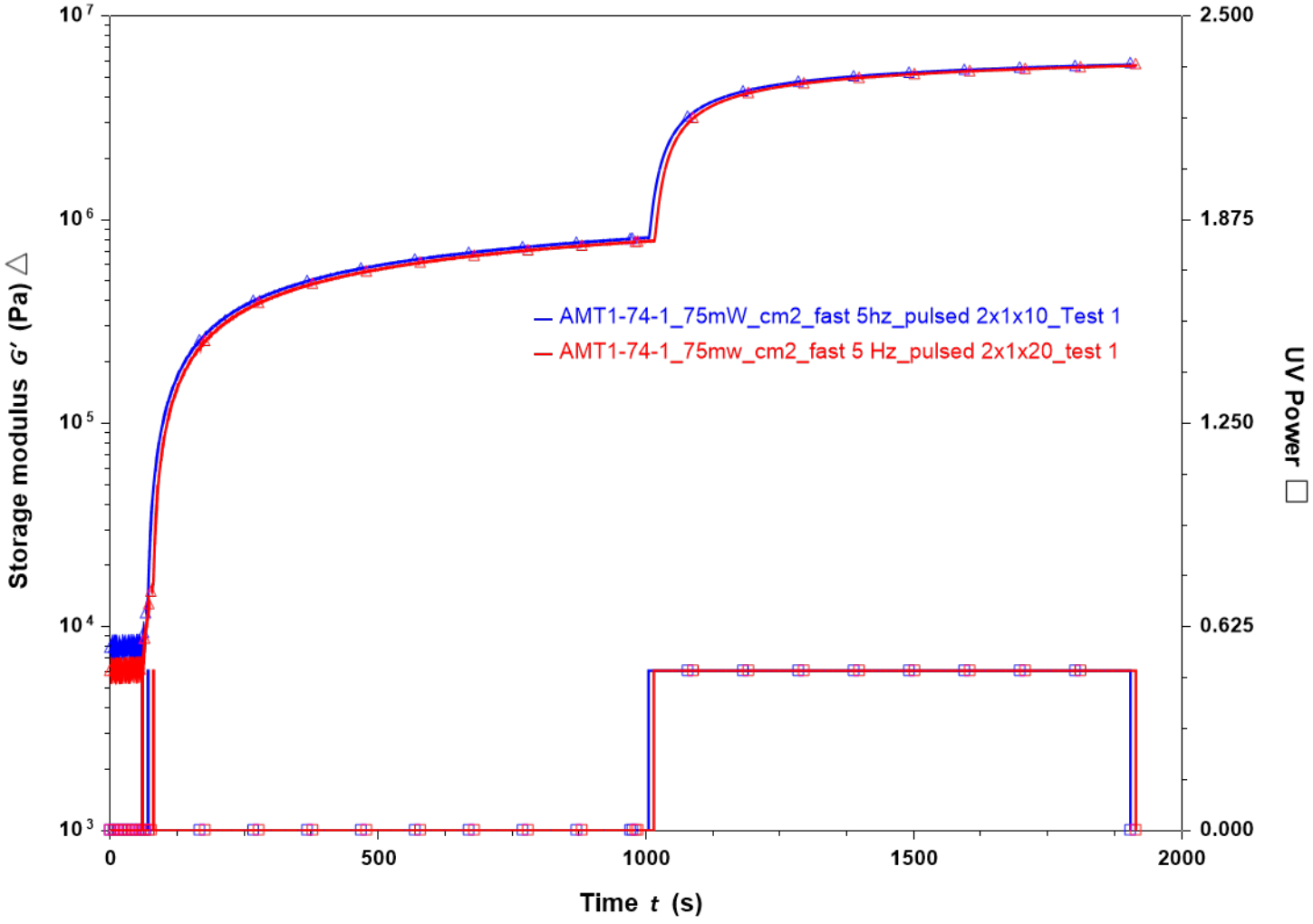
2 pulses
1 s vs 3 s
20 s dark time

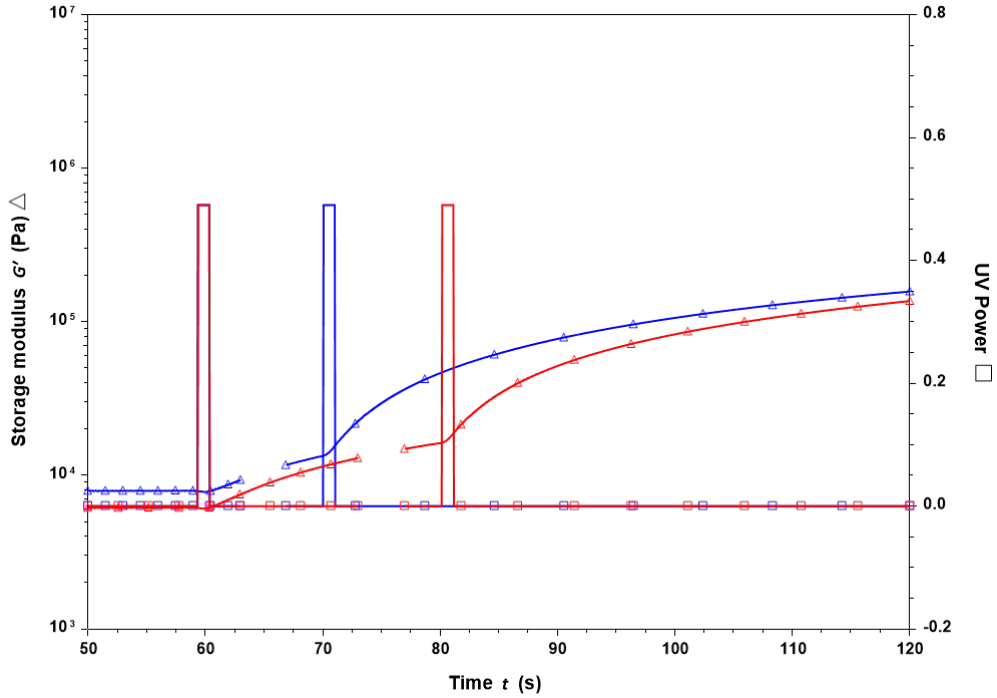
Modulus before 15 min continuous UV exposure is significantly different.

After continuous exposure similar final moduli.

Pulsed exposures comparing 10s and 20 s dark times

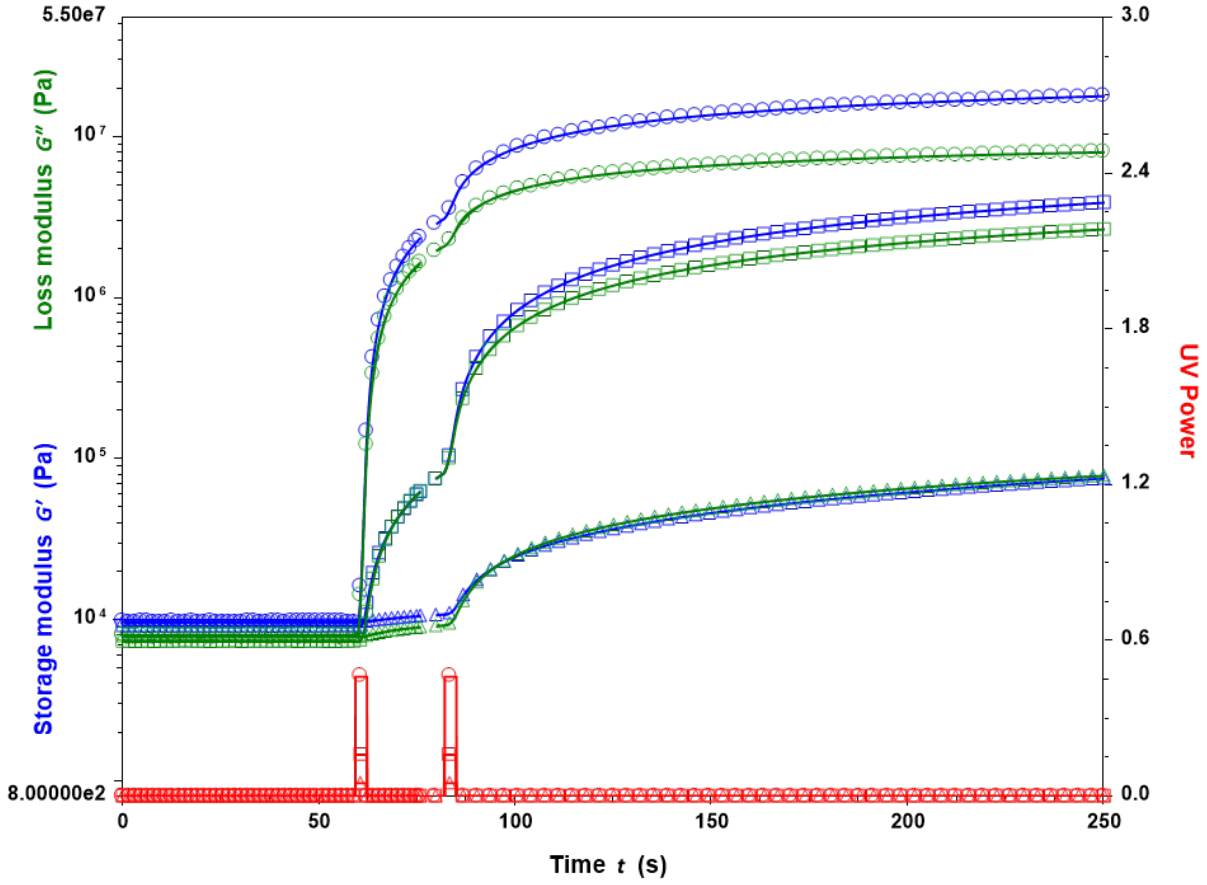
For short dark times negligible differences for plateau modulus (before and after continuous exposure) but there are short-time differences.

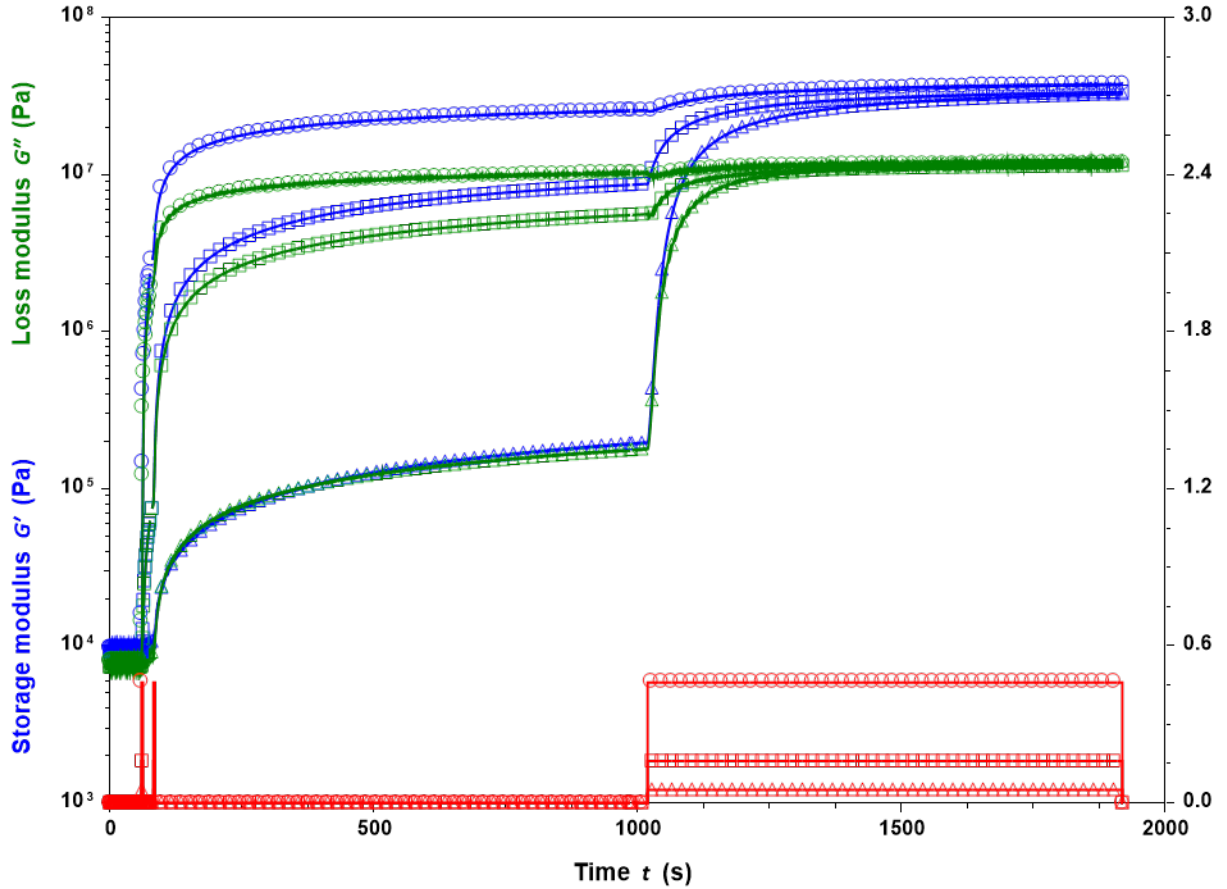




Pulsed exposures mimicking transverse bar prints (30wt% acrylate)

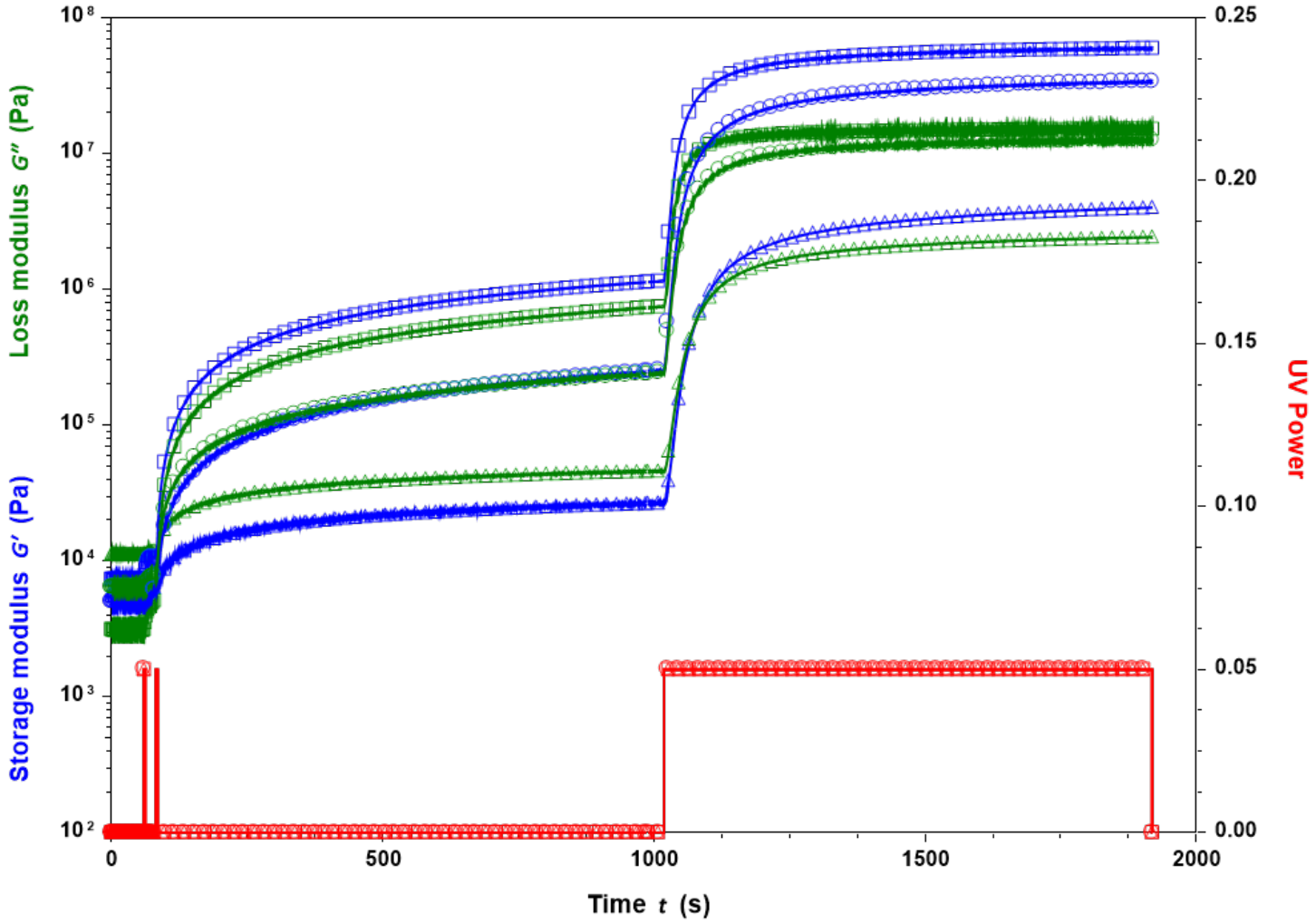
2 x 3s pulsed exposure (transverse)
varying intensities, 30wt% acrylate resin.





UV Rheology

2 x 3s pulsed exposure, 20 s dark (transverse)
5mW/cm2, varying wt% acrylate resin.



Approaches to DIW Printing of Thermoset Resins

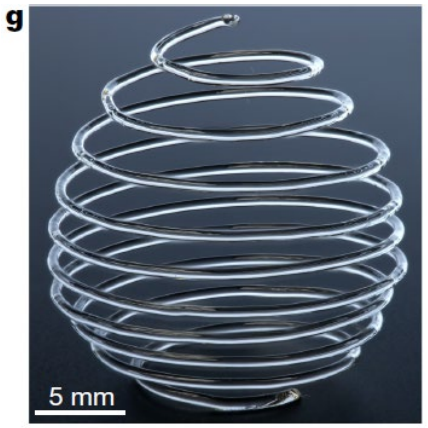
2) *In situ* cure

Single cure for rapidly polymerizing systems

- UV initiated
- Thermally initiated
- Rapid RT polymerization

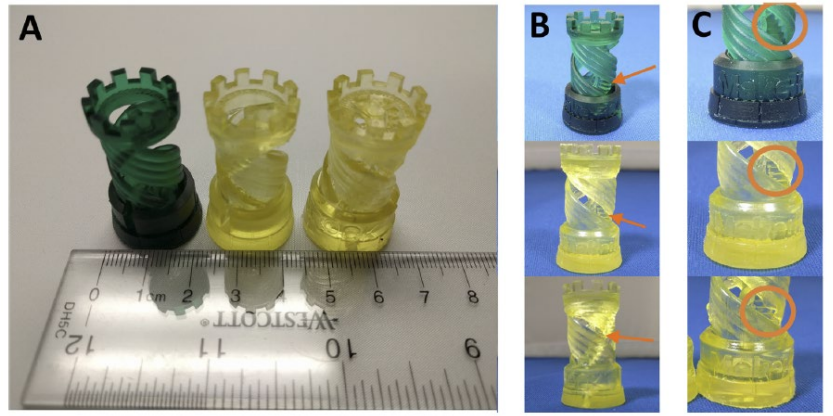
Dual-cure

- UV/thermal
  - Acrylate/epoxy most common
- Thermal/thermal
  - Different initiation temperatures
  - Kinetic differentiation
- UV/UV
  - Different initiation wavelengths
  - Kinetic differentiation

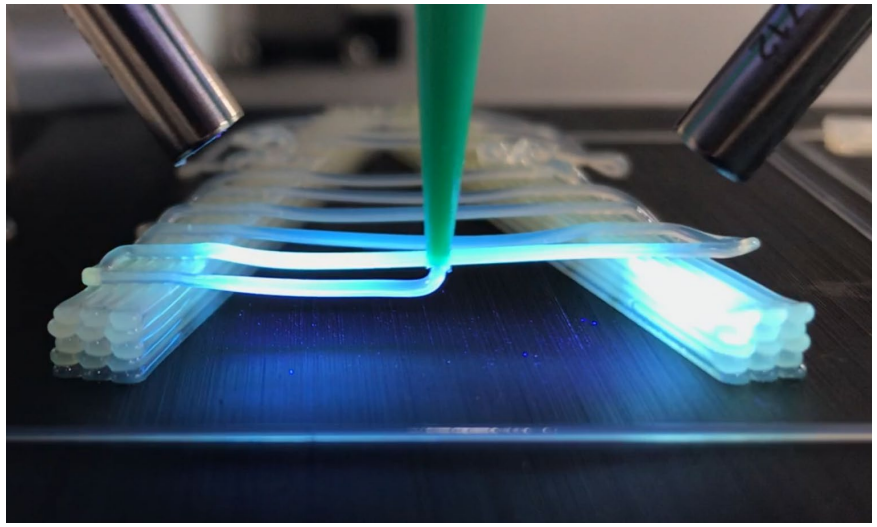


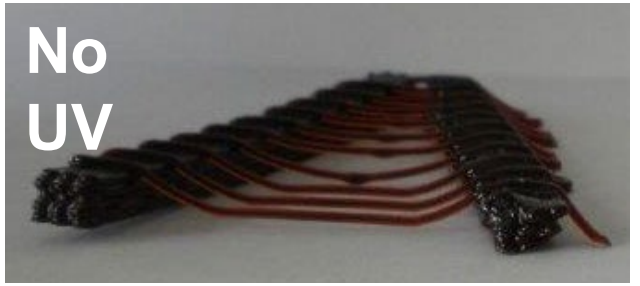
Thermally initiated frontal polymerization (FROMP) of poly(DCPD) thermoset

Robertson et al. *Nature*, **2018,** *557*, 223



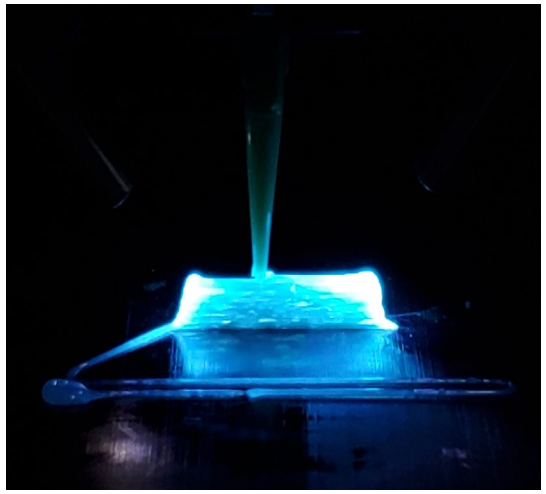
Additive Manufacturing 23 (2018) 374–380

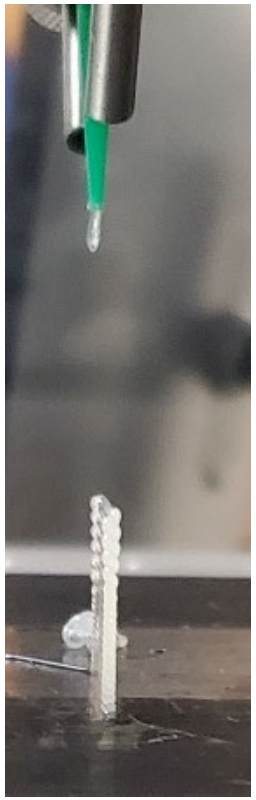


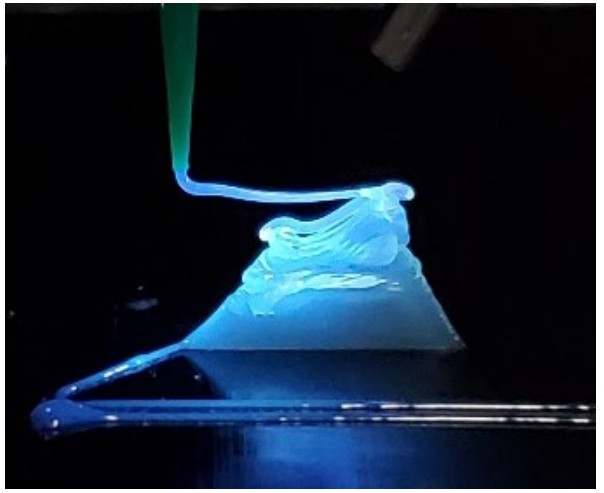


Printing of acrylate/epoxy UV/thermal dual-cure system

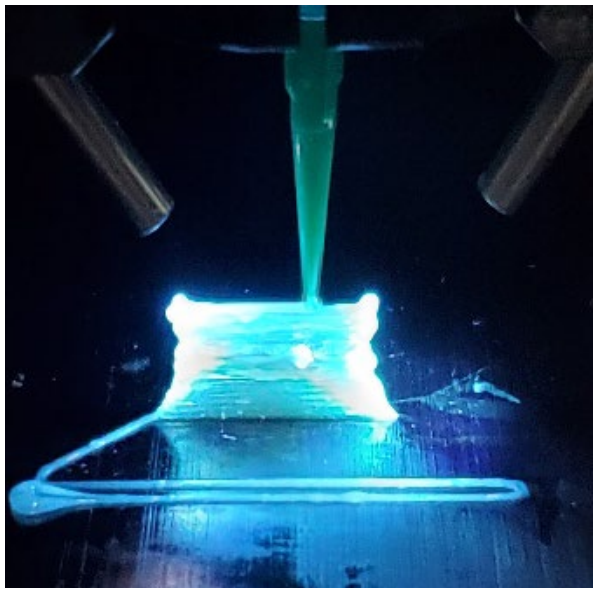
Acrylate Network Formation and UV Power Determine Printability

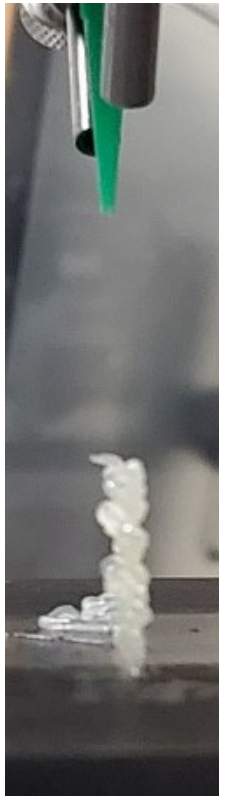


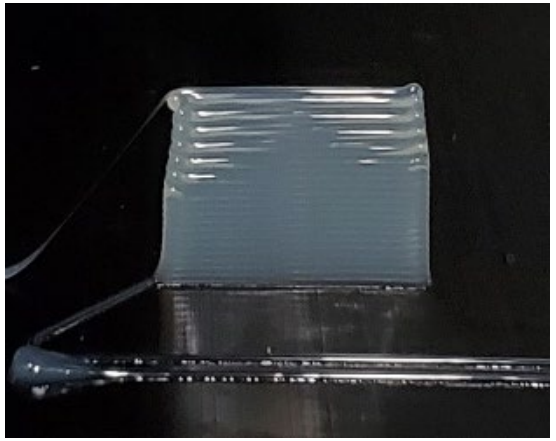




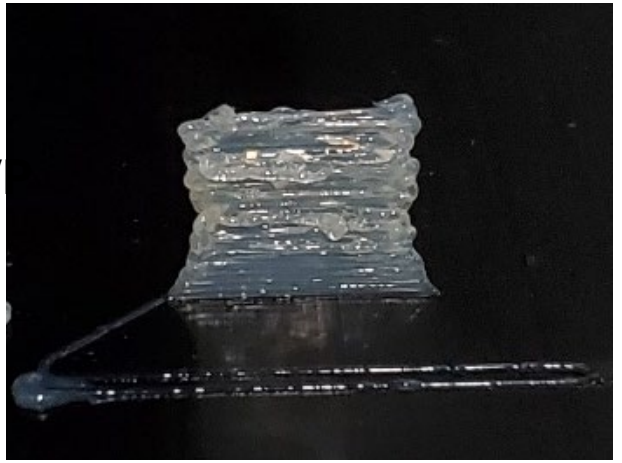
15 wt% dimethacrylate at 5% UV (7 W/cm²)







15 wt% dimethacrylate at 25% UVP (35 W/cm²)



10 wt% dimethacrylate at 85% UVP (115 W/cm²)