Sandia National Laboratories

Additive Manufacturing Of Thermoset Polymers

Nicolas T. Monk, Jessica W. Kopatz, Samuel C. Leguizamon*, Leah N. Appelhans** Sandia National Laboratories, Albuquerque, NM

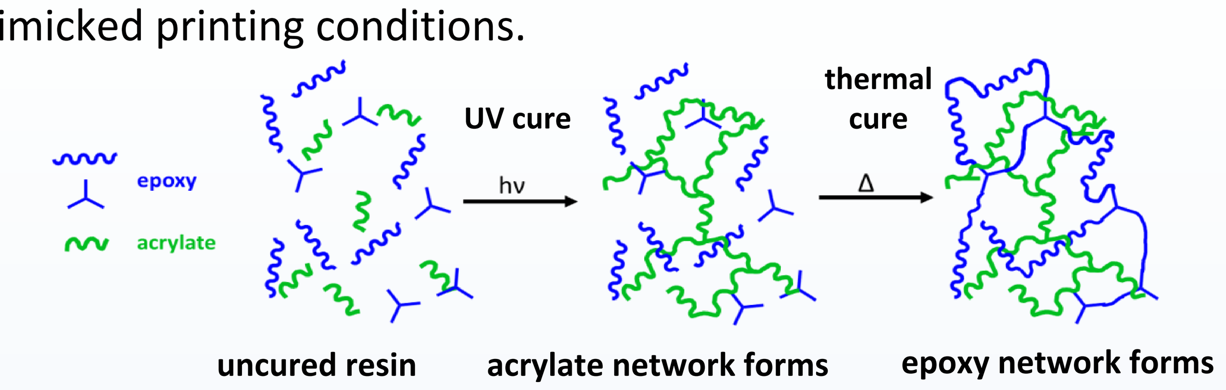
**lappelh@sandia.gov
*sleguiz@sandia.gov

Objective: Using Photorheology with Thermosets for Direct Ink Write and Vat Polymerization Printing

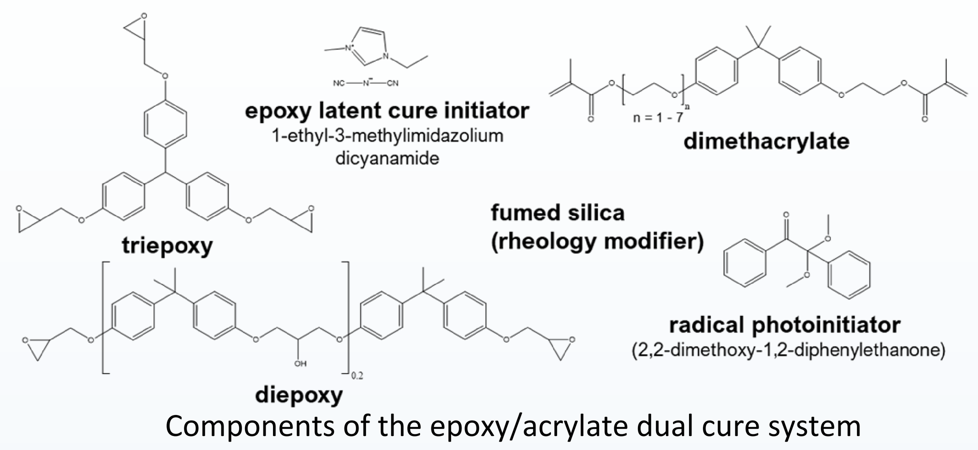
Determine if we can use photorheology to achieve printability of resin formulations as well as see how the kinetics differ when changing stoichiometries, without having to use a significant amount of resin to empirically determine optimal print parameters.

Dual-Cure System Photorheology

INTRO: Dual cure systems contain components cured by UV irradiation and a thermal cure to develop a stronger Interpenetrating Polymer Network (IPN). Our dual-cure system consists of a dimethacrylate that rapidly cures via in situ UV irradiation to help maintain the structure during Direct Ink Write (DIW) printing. The second component is a homopolymerized epoxy which is thermally cured post-print to achieve a stronger IPN. Using different weight percents (wt%) of acrylate, along with UV dose, we can determine the rate of cure and how a formulation will peform under mimicked printing conditions.



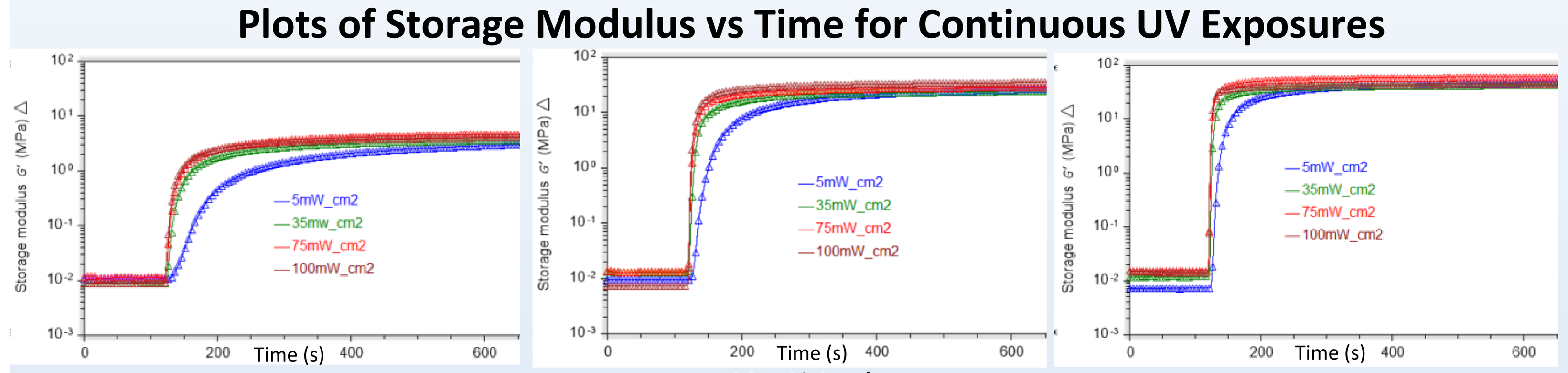
IPN formation via a UV Cure and a Thermal Cure



Components of the epoxy/acrylate dual cure system

RESULTS: Using photorheology we can determine how the UV irradiation step is forming the acrylate network, which is needed for DIW. The intensity of UV (@365 nm) determines the rate of cure. Using photorheology we can use a very small amount of resin to determine the kinetics and change stoichiometries to find the optimal resin for DIW printing.

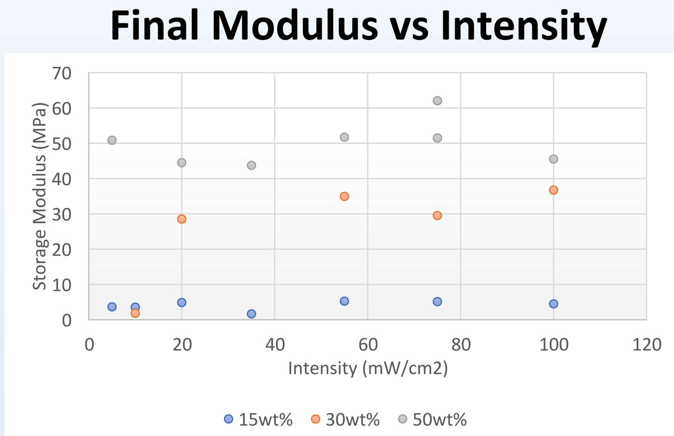
Plots of Storage Modulus vs Time for Continuous UV Exposures



15wt% Acrylate | 30wt% Acrylate | 50wt% Acrylate

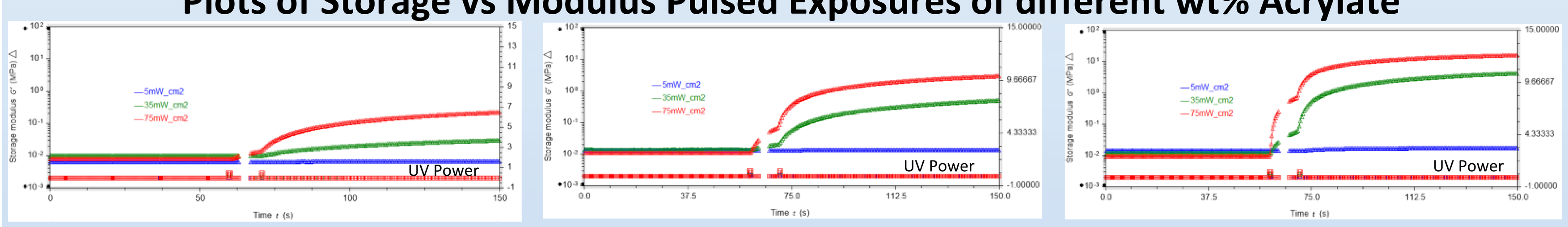
With photorheology we can see how using different UV intensities effects the cure kinetics and final modulus of each of our wt% formulations. Each test is run with a 25 min continuous UV exposure.

Final Modulus vs Intensity



The final modulus after 25 min continuous UV exposure increases with increasing wt% acrylate.

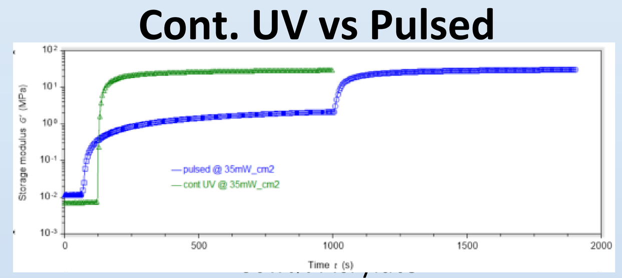
Plots of Storage vs Modulus Pulsed Exposures of different wt% Acrylate



15wt% Acrylate | 30wt% Acrylate | 50wt% Acrylate

Using photorheology we are able to mimic printing exposure profiles, which vary based on geometry and print path. Plots show the first 150 seconds of a pulsed exposure with two 1 second pulses of UV light separated by 10 second dark times followed by a 15 min dark time.

Cont. UV vs Pulsed

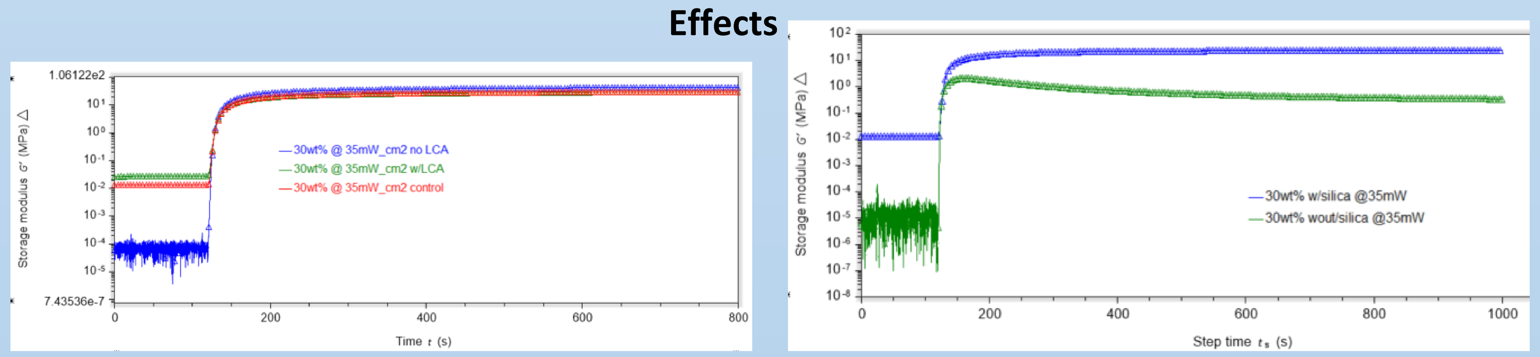


Above is a continuous test compared to a pulsed UV test with 2x1s pulses followed by 15 min dark and 15 min continuous UV exposure. The final modulus is the same for both cure profiles.

The addition of fumed silica increases the viscosity of our formulation to enable DIW printing, which is a versatile form of additive manufacturing. With dual cure systems we can improve interlayer adhesion better then single cure formulations due to the IPN forming between layers which improves the overall strength.

Interlayer Adhesion of Acrylate wt% @ Differing Intensities

Using Photorheology to Determine Component Effects



Removal of the epoxy atent cure initiator lowers the initial viscosity, but does not impact the cure or final modulus.

The removal of silica reduces the initial viscosity and the final modulus, but does not significantly impact the cure kinetics.

After successfully developing this dual cure formulation for DIW we are now looking at unfilled formulations for Vat Polymerization (VP). We are also interested in printing with a single cure system using photorheology to screen formulations.

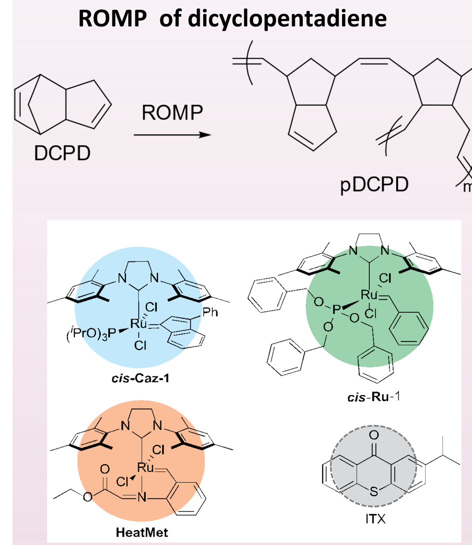
Single Cure System Photorheology

INTRO: Our second system uses Ring Opening Metathesis Polymerization (ROMP) of dicyclopentadiene (DCPD) with photoinitiated catalysts. This system has a high strength and toughness but the rate of polymerization with Ru catalysts alone is too slow for practical DIW and Vat Polymerization printing (VP). With the addition of a photosensitizer, isopropylthioxanthone (ITX), we are able to achieve a high rate of polymerization perfect for DIW and VP. UV Rheology allows us to screen catalysts and photosensitizers without actually having to print.

RESULTS: The addition of photosensitizer ITX increases the rate of reaction dramatically with each catalyst, especially **HeatMet**. However the HeatMet system has a potlife of only about 3 hours which is not ideal for VP.

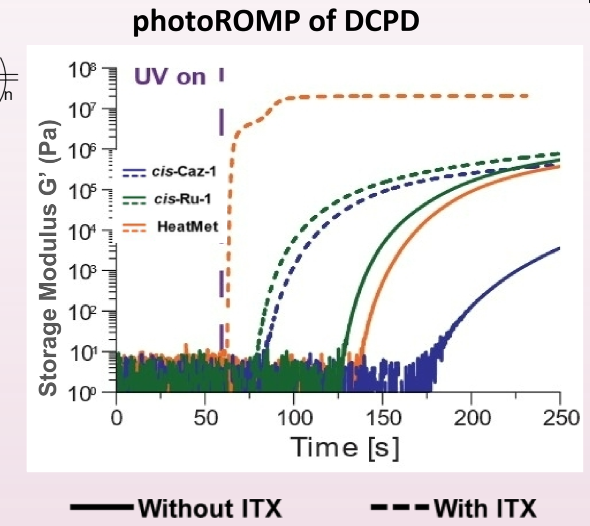
Catalyst Screening

ROMP of dicyclopentadiene

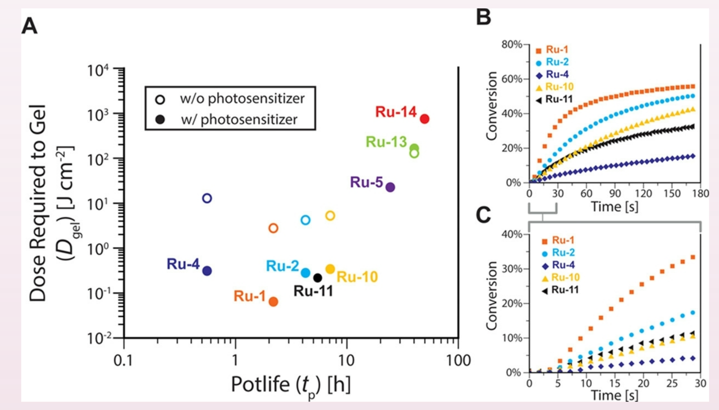


Catalysts screened for DIW printing (with ITX)

Photorheology of Catalysts for photoROMP of DCPD

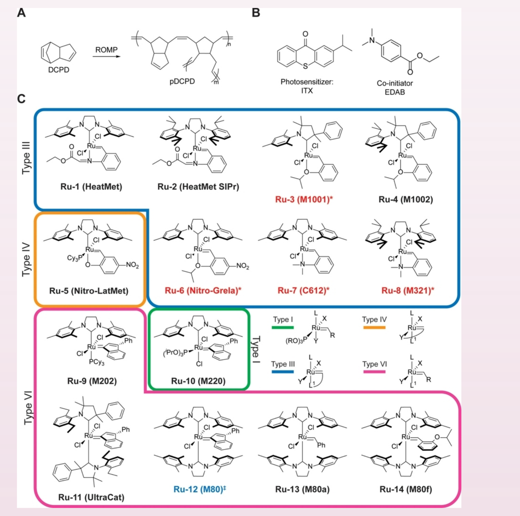


Ruthenium Catalyst Screening for Vat Polymerization



Ru-1: HeatMet, Ru-2: HeatMet SIPr, Ru-4:M1002, Ru-10: M220, Ru-11: Ultra Cat

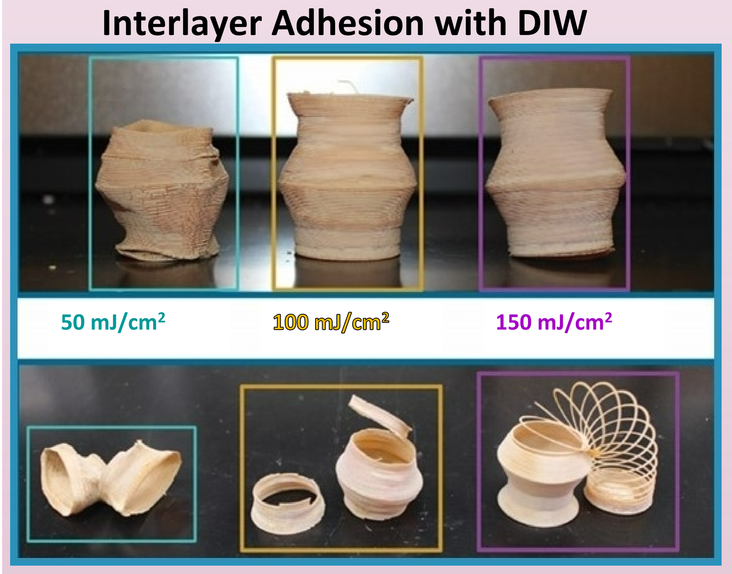
Catalysts Used for Screening



Even though HeatMet has the smallest dose requirement the potlife is relatively short which makes VP printing with HeatMet challenging. By using photorheology to quickly screen many catalysts we have been able to determine that Ru-10 and 11 optimize required dose and potlife for VP printing.

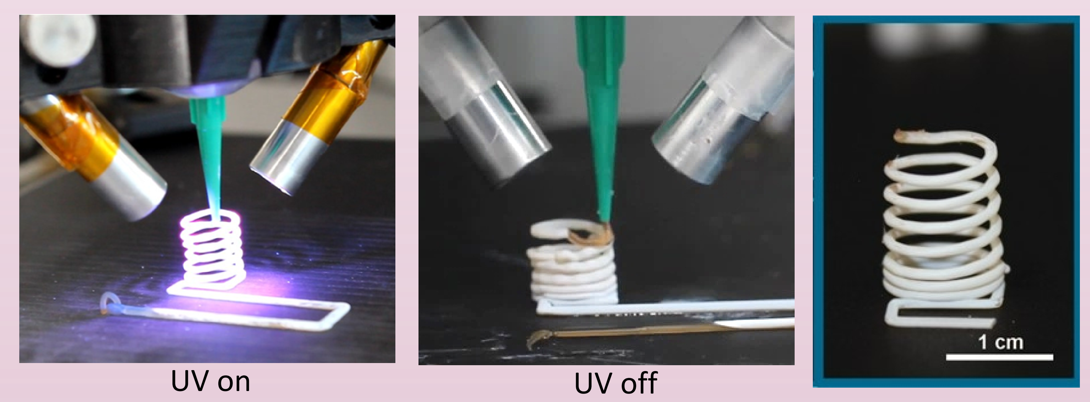
DIW Printing of pDCPD

Interlayer Adhesion with DIW



To the left is an example of the effects of interlayer adhesion during printing via DIW. The far left shows too low a UV dose which made the part not able to hold its own weight. The far right is an example of too high a UV dose which led to no interlayer adhesion, creating the slinky effect. The middle is an example of strong interlayer adhesion with a failure that does not occur along an interlayer boundary.

Skywriting pDCPD with photoROMP

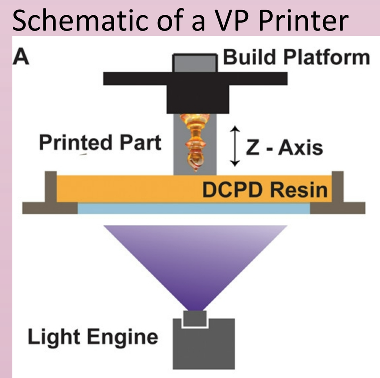


UV on | UV off

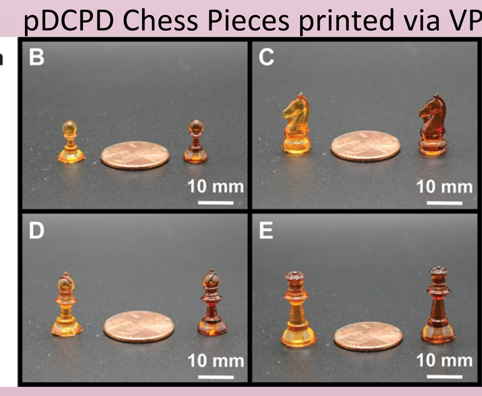
Turning UV on and off during free space printing shows that the ROMP is photocontrolled, and not a photoinitiated frontal polymerization (FROMP).

Vat Polymerization of pDCPD

Schematic of a VP Printer



pDCPD Chess Pieces printed via VP

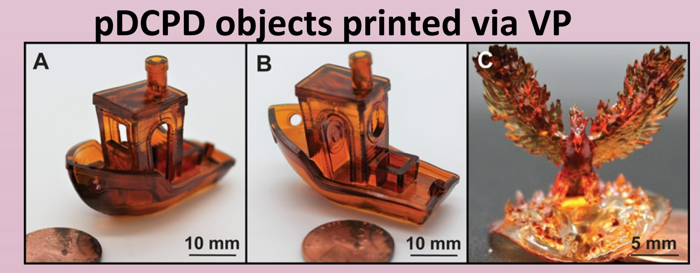


VP printing enables printing of parts with much higher resolution than DIW.

Pieces on the left were VP printed with benzil/Ru-11 and on right with benzophenone/Ru-10

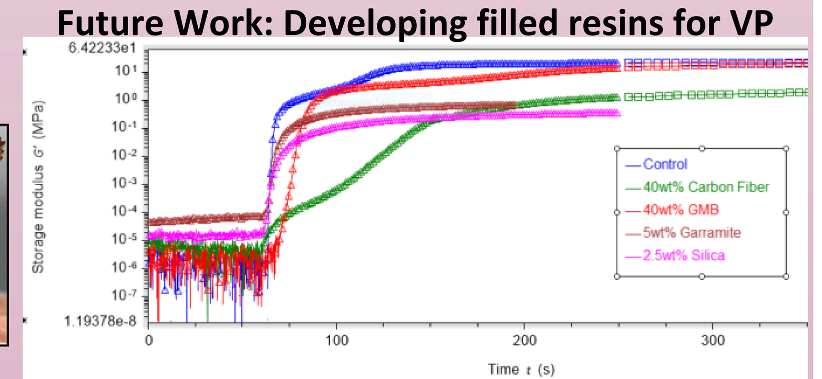
Using the optimized formulations identified by screening with photorheology we were also able to demonstrate vat polymerization printing of pDCPD.

pDCPD objects printed via VP



Boat printed using benzophenone/Ru-10 and phoenix printed using benzil/Ru-11 formulation

Future Work: Developing filled resins for VP



Photorheology allows us to see how different fillers impact our printable resin formulations.

Conclusions and Future Work: Using photorheology we are able to quickly develop our thermoset polymers in order to find the formulations and printing parameters needed for Direct Ink Write and Vat Polymerization printing. With photoROMP of DCPD we were able to achieve a system that could DIW as well as VP print. The development of these formulations would have taken much more time and material without photorheology.

Future work includes: 1) Vat polymerization of pDCPD with fillers to determine how they change our current formulation 2) Vat polymerization with Epoxy/Acrylate formulations

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See also: Epoxy/acrylate dual-cure: J.W Kopatz, J. Unangst, A.W. Cook, L.N. Appelhans* *Additive Manufacturing,* **2021**, 46, 102159
PhotoROMP DIW: Leguizamon, S. C.; Cook, A. W.; Appelhans, L. N.* *Chemistry of Materials* **2021,** *33* (24), 9677-9689
Photoinitiated Olefin Metathesis and Stereolithographic Printing of Polydicyclopentadiene: Leguizamon, S. C*.; Monk, N. T.; Hochrein, M. T.; Zapien, E. M.; Yoon, A.; Foster, J. C.; Appelhans, L. N.**