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Sandia National Laboratories

# Development of Thermoset Resins for Additive Manufacturing

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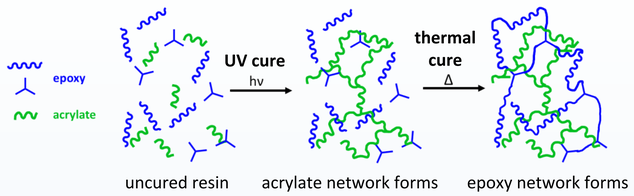
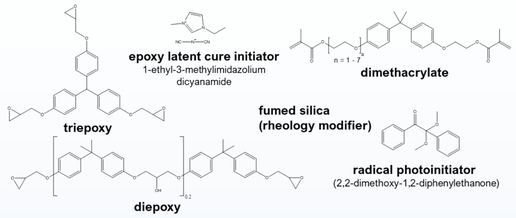
**Objective: Develop printable thermoset resins with a range of chemistries and performance properties and a fundamental understanding of structure-property-performance to enable rational design of AM materials.**

## Dual-cure Epoxy/Acrylate Systems

Dual-cure systems[1-3] use a rapidly curing component to maintain structure during printing in combination with a second component that is cured post-print to impart the final properties. Dual-cure systems form interpenetrating polymer networks (IPNs) which can produce unique thermomechanical properties. Our system uses a photopolymerized dimethacrylate as the rapid-curing component with a thermally cured homopolymerized epoxy.




The printing performance and print fidelity of dual-cure systems depend on the kinetics of acrylate cure and the "green strength" of the as-printed part. We investigated the effects of acrylate wt% and UV dose on the acrylate cure kinetics and green part properties to determine optimum printability.

*Green part modulus for transverse and longitudinal prints at different light intensities.*










Print optimization will depend on composition, intensity, part geometry, print path, nozzle size, print speed, etc.

**Less labor-intensive approaches for optimization are needed!**

*Empirical optimization of light intensity to print high aspect ratio walls for varying acrylate wt% resins.*

*UV rheology and UV FTIR are used to determine correlation between acrylate conversion and development of modulus.*







*Pulsed exposure profiles mimic in situ exposures for different print paths, showing extensive dark cure.*




Final properties of thermally cured parts can be tuned by composition and are comparable to other common engineering materials. IPN phase separation is observed in 50 wt% acrylate formulations.

*Glass transition*

| Acrylate (wt%) | $T_g$ (°C) |
|---|---|
| 0 | 215 |
| 5 | 215 |
| 10 | 221 |
| 15 | 210 |
| 30 | 189 |
| 50 | 121, 186 |
| 100 | 165 |

**Torsional Modulus vs Acrylate Wt%**




**Flexural Modulus (GPa)**

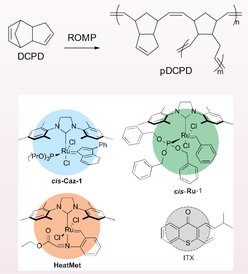



**Flexural Strength (MPa)**

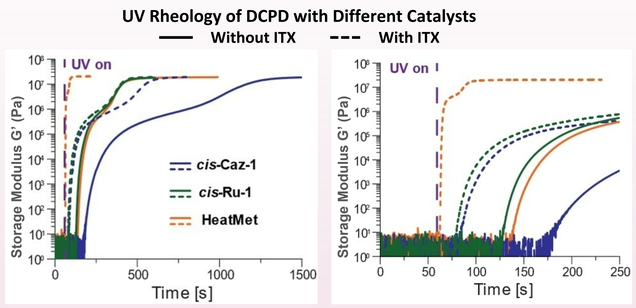



## PhotoROMP DIW pDCPD

The majority of approaches for DIW of thermosets utilizing *in situ* cure use photoinitiated radical or cationic polymerizations. In order to extend DIW printing to a broader range of resins we investigated photoinitiated ring-opening metathesis polymerization (photoROMP) for DIW, inspired by the development of numerous photolatent ROMP catalysts[4-6] and the demonstration of DIW printing via thermally initiated frontal ROMP (FROMP).[7-8]




**UV Rheology of DCPD with Different Catalysts**

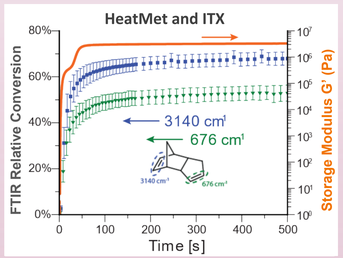



*We found the addition of the photosensitizer ITX greatly increased rates for all catalysts, but most significantly for HeatMet.*

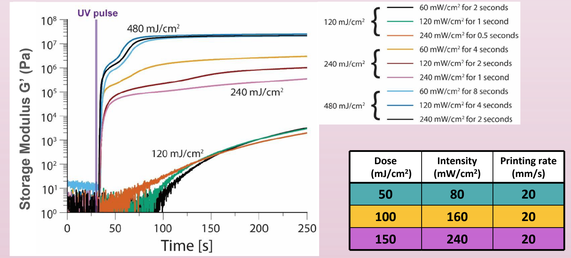
*UV rheology enables rapid screening of catalysts and sensitizers to downselect formulations without printing.*

Conversion, dose dependence and reciprocity were investigated with UV-FTIR and UV rheology. The effect of UV intensity and dose on print fidelity and interlayer adhesion were also examined. DCPD ROMP polymerization is intensity/time reciprocal, but effects on print fidelity and interlayer adhesion occur at higher printing doses.

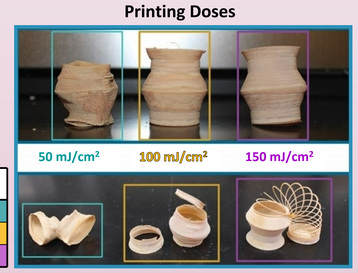
**UV FTIR: ROMP of DCPD**




**UV Rheology: Intensity/Time Reciprocity for DCPD/HeatMet/ITX**



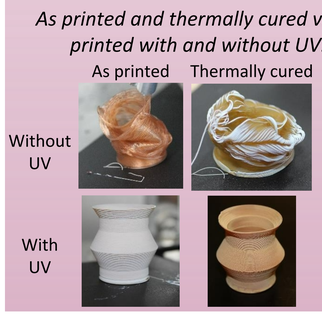

**Interlayer Adhesion at Different UV Printing Doses**

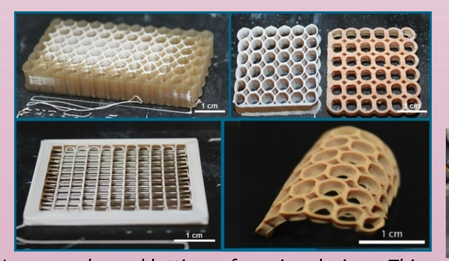



| Dose (mJ/cm²) | Intensity (mW/cm²) | Printing rate (mm/s) |
|---|---|---|
| 50 | 80 | 20 |
| 100 | 160 | 20 |
| 150 | 240 | 20 |

A printing formulation was developed with 10wt% fumed silica as a rheology modifier. Printing requires optimization for different geometries and print paths but with optimized parameters a wide range of technically challenging form factors are accessible. Incubating the resin overnight enables free-space printing or "skywriting".

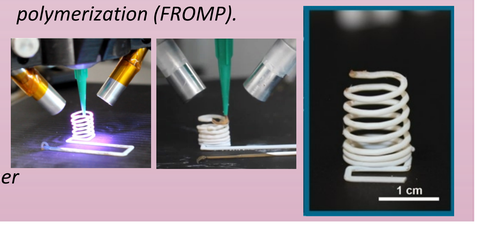
*As printed and thermally cured vases printed with and without UV.*




*Honeycombs and lattices of varying designs. Thinner prints sometimes warp during thermal cure.*

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




**Conclusions and Future Work:** Two thermoset resins were developed for DIW additive manufacturing, a dual-cure epoxy/acrylate resin and a photoinitiated ROMP resin. The development of both resins has been greatly facilitated by understanding and optimizing the photochemistry and cure kinetics for print-specific requirements via photorheology and photo-FTIR. **Future work includes:** 1) investigating varied acrylate/epoxy monomers in dual-cure formulations 2) investigating fiber fillers and effects on epoxy/acrylate formulation kinetics and final properties, 3) optimizing ROMP resins for printing and final properties, and extending to additional AM methods and 4) better understanding ROMP kinetics and latent catalyst photochemistry relevant to printing applications.

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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

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