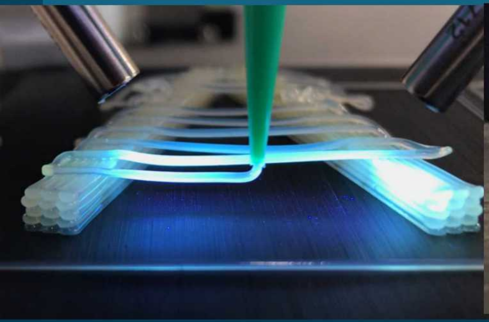
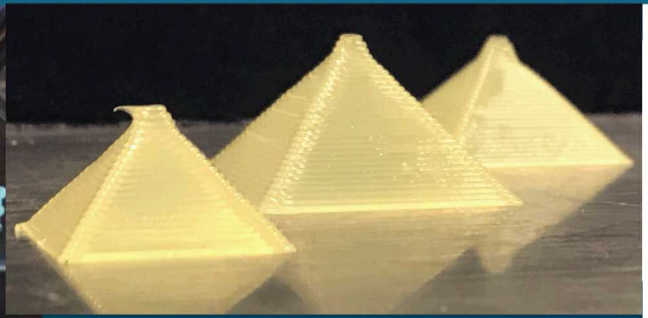
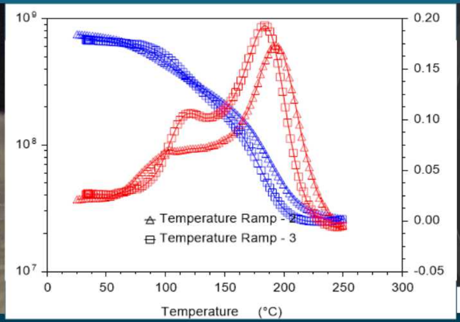
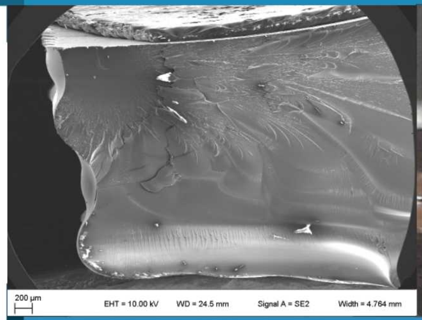
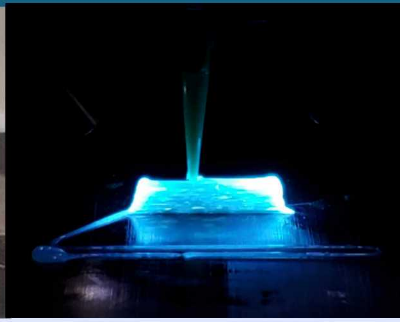
SAND2020-2596C

Polymer Network Formation in Epoxy/Acrylate Dual-Cure Thermoset Resins for Direct Ink Write Additive Manufacturing



PRESENTED BY

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Adam Cook, Jessica Kopatz, Jackie Unangst, Derek Reinholtz

APS March Meeting, Denver 2020

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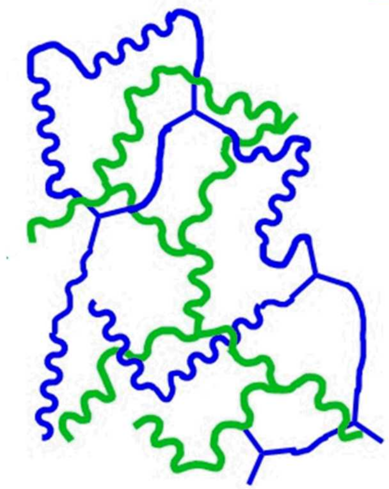
Interpenetrating Polymer Networks (IPNs)

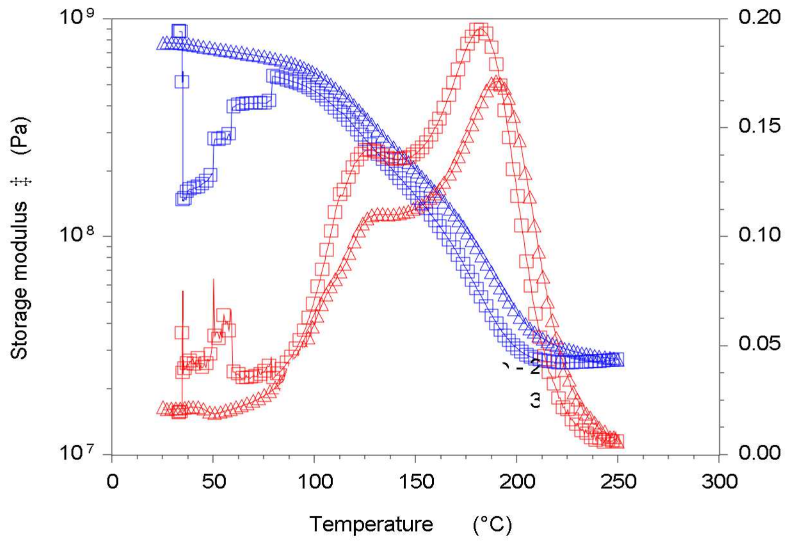
How do different resin components change IPN formation, printability, mechanical properties, and cure kinetics?



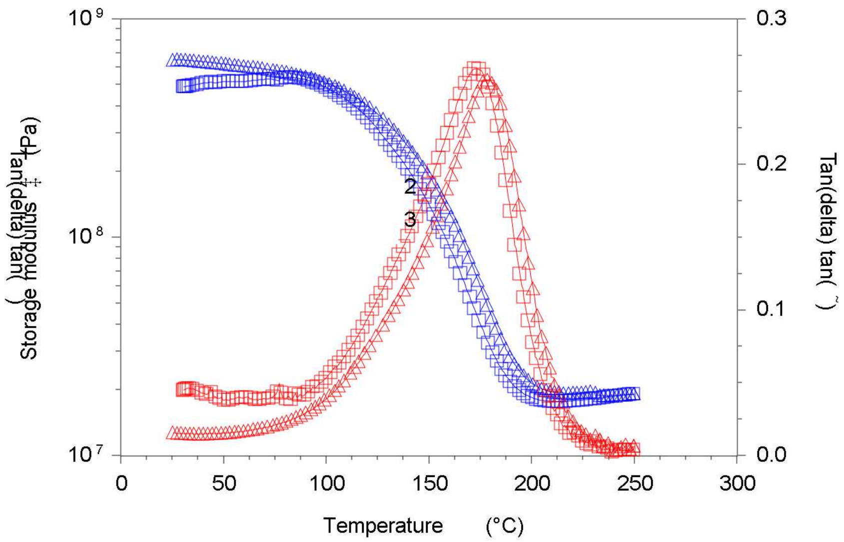
IPN

Phase separation and domain sizes depend on:

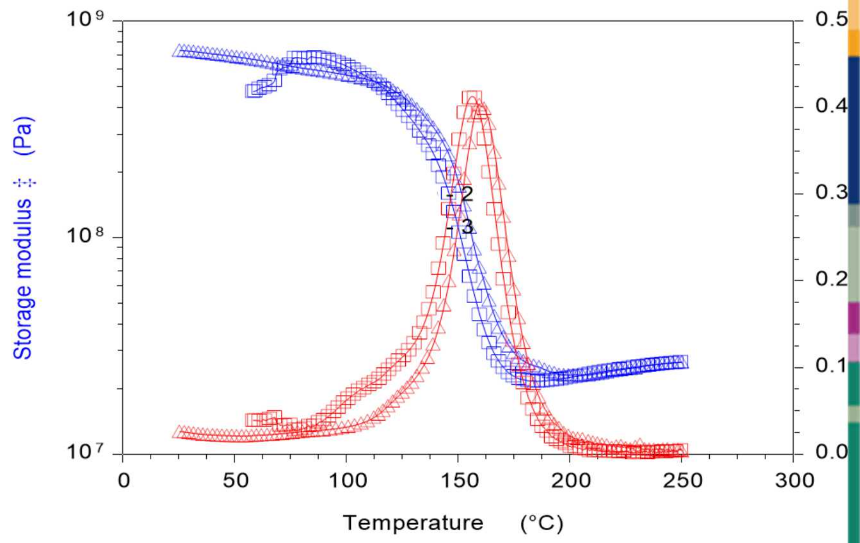
$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$ **cure order** **cure kinetics**



Phase-separated systems exhibit multiple T_gs



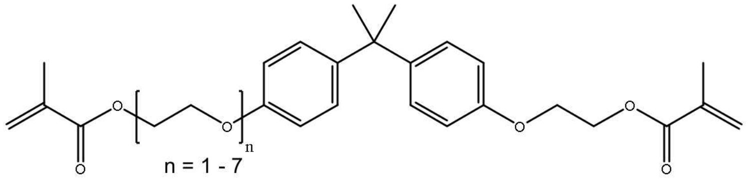
T_g broadness correlates to distribution of compositions in interphases



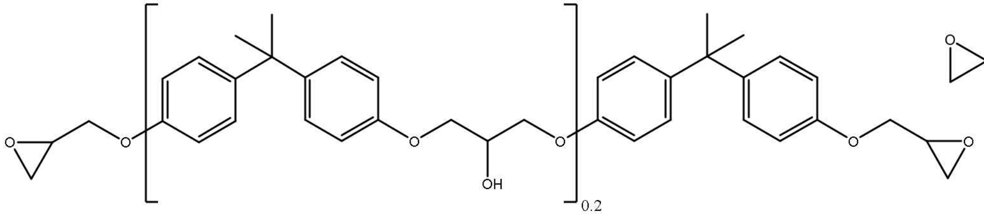
Homogeneous* IPNs exhibit single T_g

UV-Thermal Dual Cure Resin Formulation

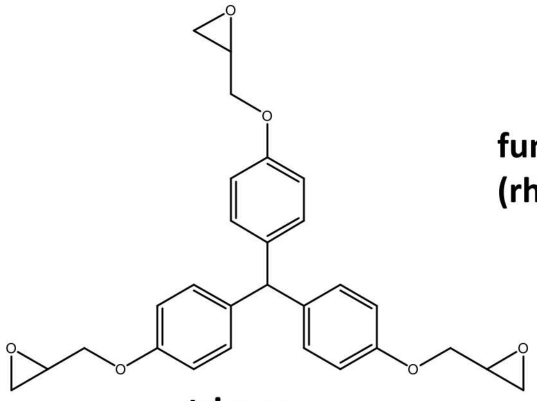
UV-thermal Epoxy/acrylate Formulation



dimethacrylate

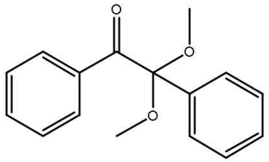


diepoxy

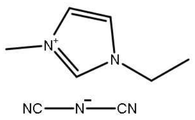


triepoxy

fumed silica
(rheology modifier)

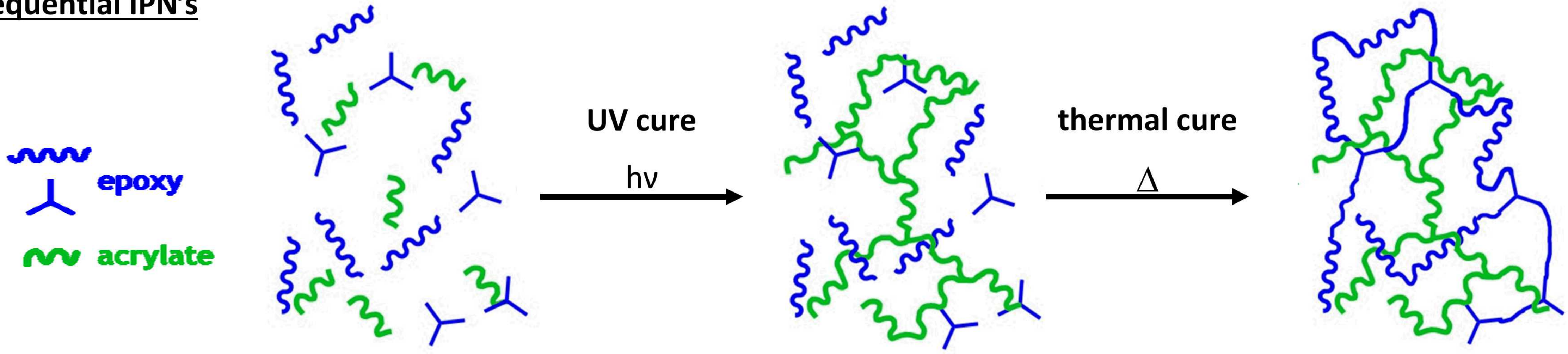


radical photoinitiator
(2,2-dimethoxy-1,2-diphenylethanone)



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

Sequential IPN's



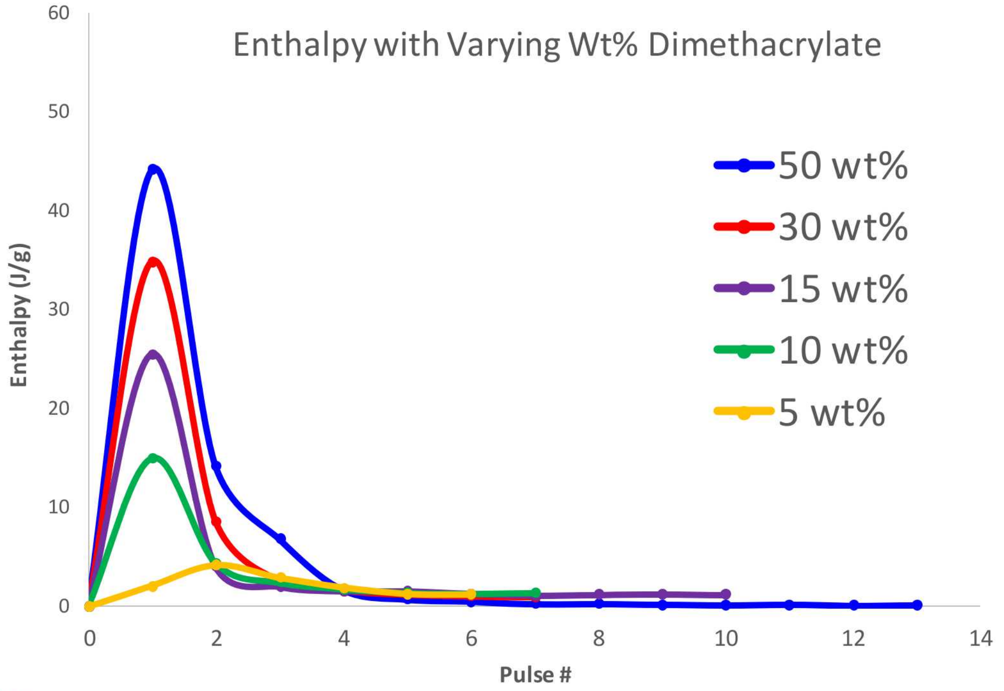
uncured resin mixture | acrylate network forms | epoxy network forms

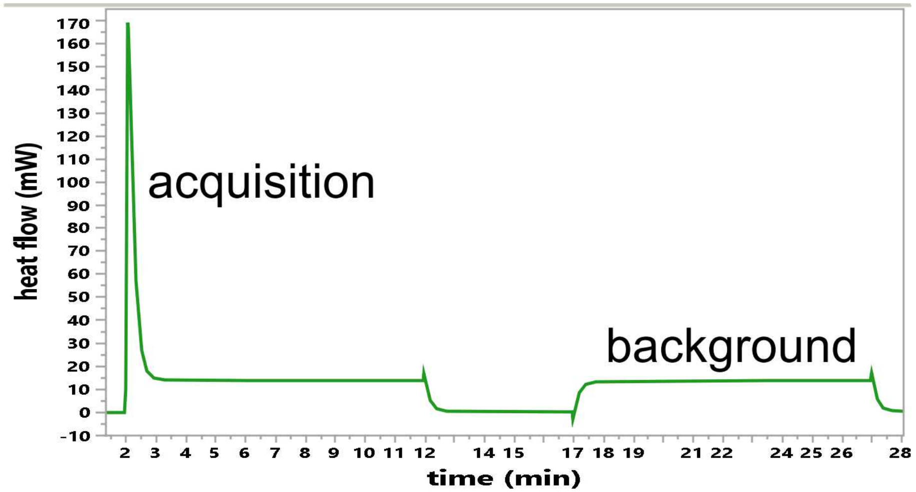
UV-Thermal Dual Cure: Acrylate Network Formation

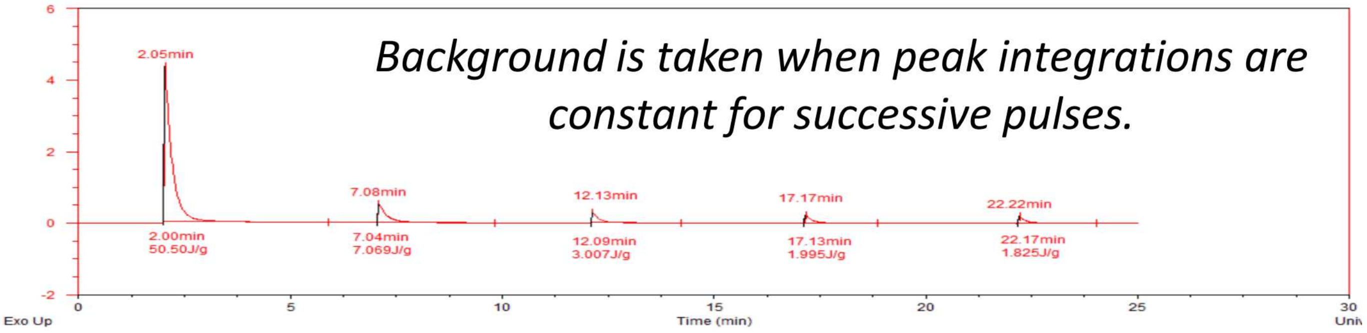
Characterizing UV-cure kinetics by UV-Differential Scanning Calorimetry (UV-DSC): Different wt% diacrylate

Pulsed UV-DSC: 2.4s pulses followed by 5 min. equilibration 109mW/cm^2(10% UV-DSC intensity)

Continuous UV-DSC: 10 min UV exposure followed by 5 min. equilibration and 10 min background







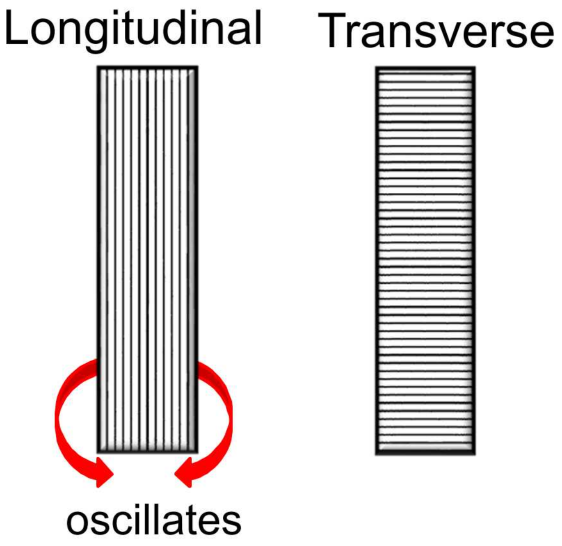
Background is taken when peak integrations are constant for successive pulses.

wt% dimethacrylate	Pulsed kJ/mol methacrylate FG	Continuous kJ/mol methacrylate FG
50	36	53 (4)
30	47	45 (3)
15	50	44 (1)
10	49	54 (1)

ΔH_{poly} (methacrylate) = ~56 kJ/mol

Dual-cure Components: Acrylate Network

Storage modulus measurements by torsional DMA at 30°C



UV-cure profile

In situ UV during printing (varying exposure time 6.9 mW/cm^2)

30-minute flood cure (5.7 mW/cm^2)

UV Cure Only (Print Only)

Resin Formulation	Storage Modulus (MPa)	
Print Direction	L	T
15 wt% dimethacrylate	4 (1)	9 (1)
30 wt% dimethacrylate	30 (1)	24 (7)
50 wt% dimethacrylate	184 (25)	199 (6)

UV Cure Only (Print + UV Flood)

Resin Formulation	Storage Modulus (MPa)	
Print Direction	L	T
15 wt% dimethacrylate	6 (1)	9 (4)
30 wt% dimethacrylate	41 (5)	31 (6)
50 wt% dimethacrylate	240 (12)	281 (20)

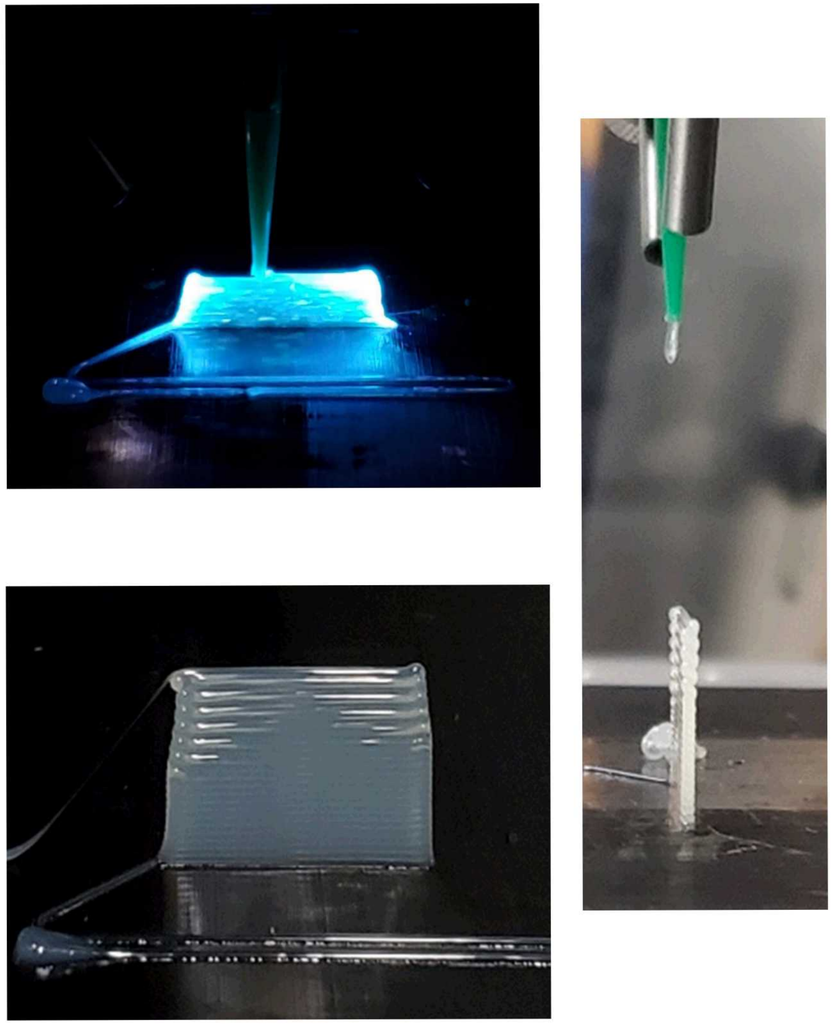
Acrylate network controls the green strength

No consistent L vs T differences in modulus

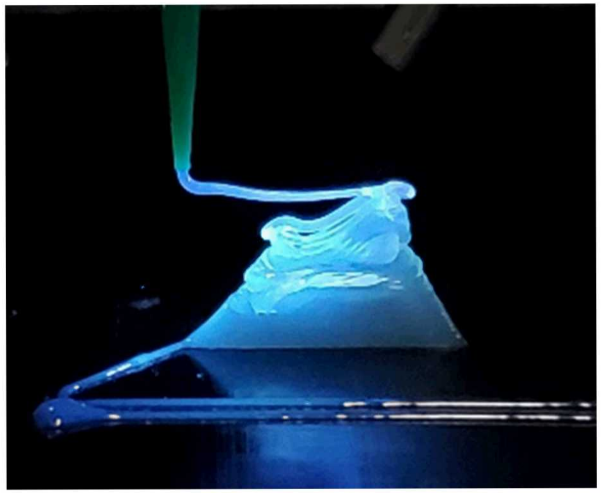
Modulus increases after flood cure.

Dimethacrylate conversion incomplete after UV cure.

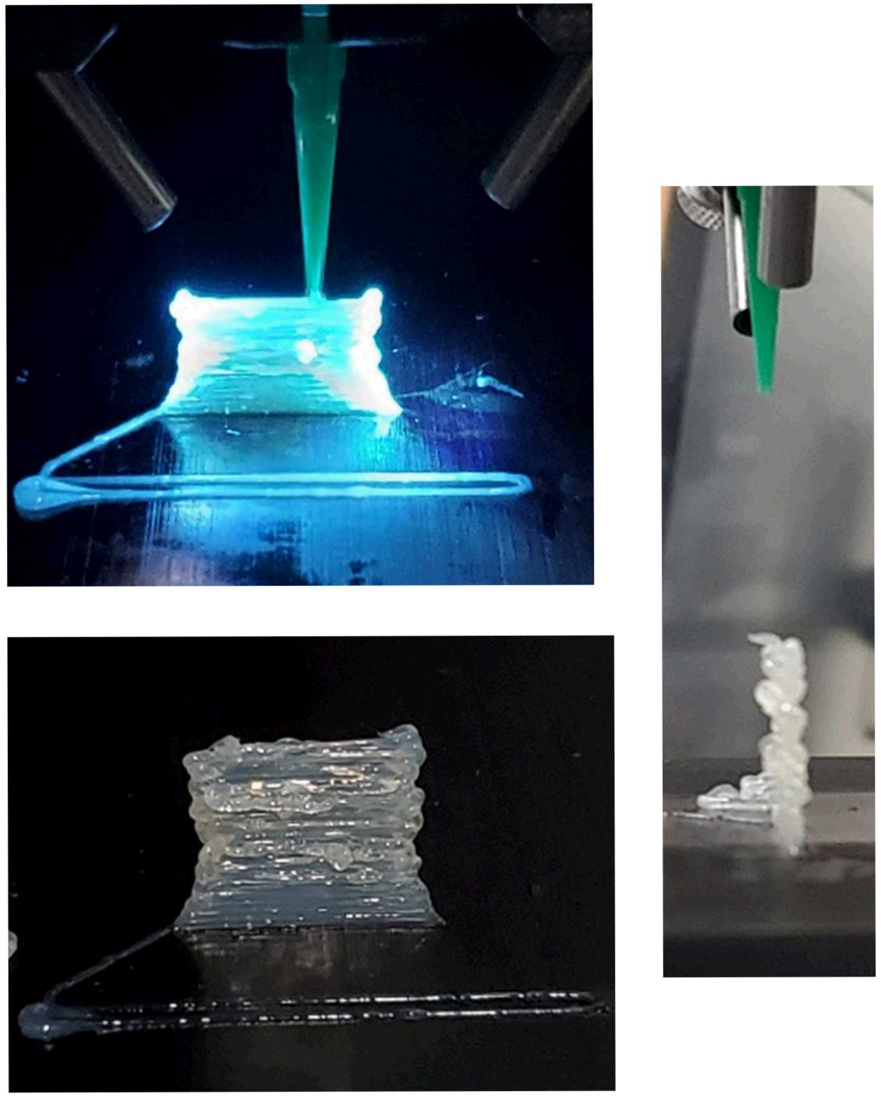
Acrylate Network and UV Power Determine Printability



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



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



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

Thermal Cure and IPN Formation

Resin composition and cure profile determine post-thermal cure properties.

In 50wt% acrylate systems there is distinct phase separation.

	UV + 150 °C Thermal Cure	
wt% dimethacrylate	**Tg ramp up (°C)**	**Tg ramp down (°C)**
5	**213**	**197**
30	**195**	**183**
50	**94** **190**	**115** **183**

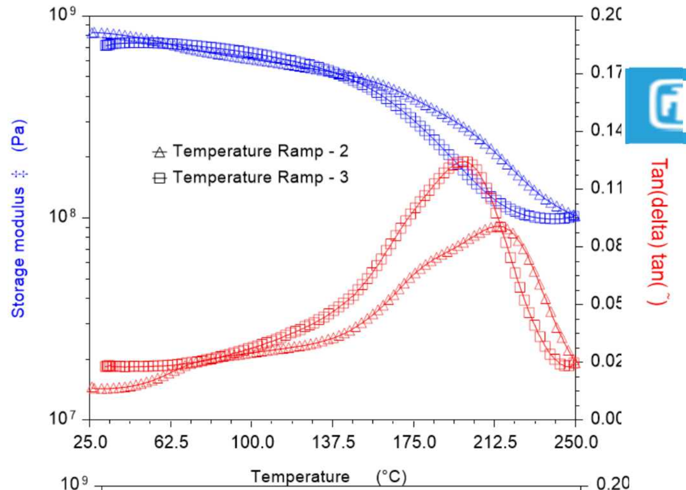
<u>UV cure</u>
in situ cure
30 min flood

<u>Thermal Cure</u>
100°C/4hrs
150°C/2hrs

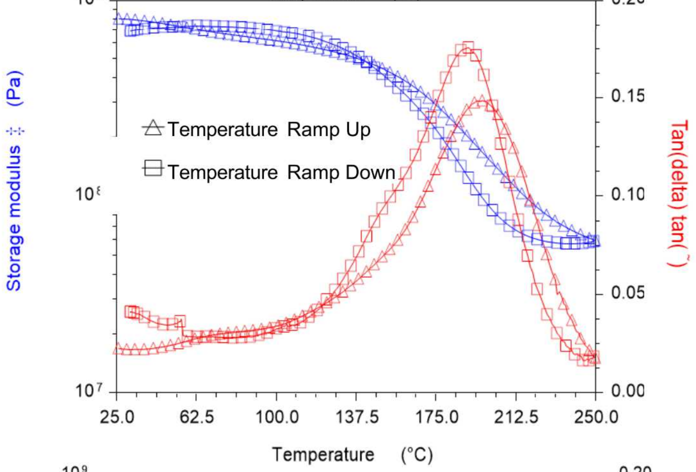
Resin composition: varying diacrylate, remainder 1:1 diepoxy:triepoxy

<u>varying wt% acrylate resin</u>

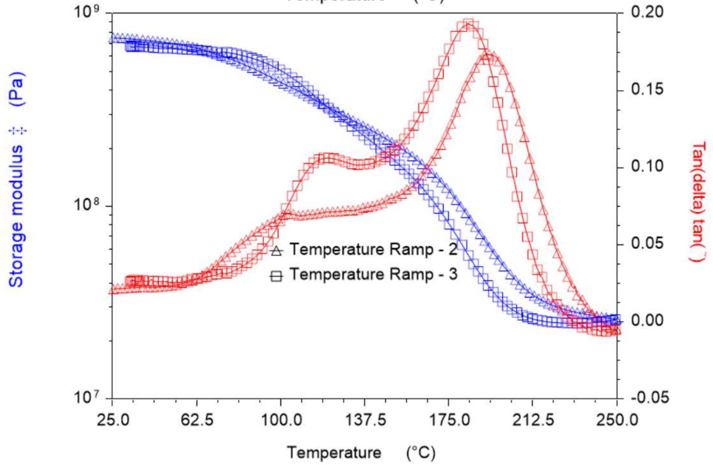
5 wt%



30 wt%



50 wt%



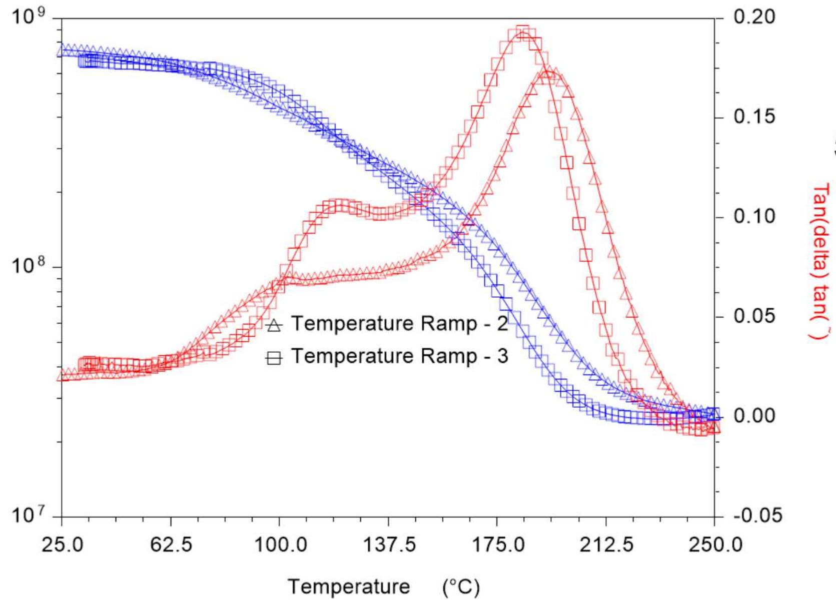
Dual-cure Components: Varying wt% Acrylate Resins

Phase separation depends on thermodynamic miscibility and **cure kinetics.**

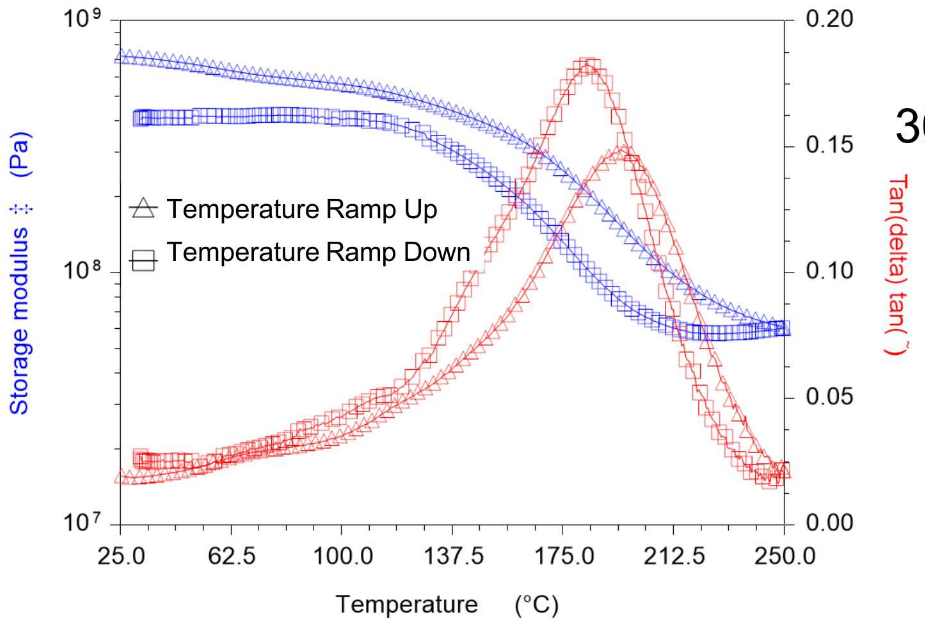
50wt% acrylate: **Epoxy gelation is slow** due to inhibition by the acrylate network. Allows **time for phase separation**.

Lower wt% acrylate: **Epoxy gelation is faster** and **phase separation is reduced**.

Weight % Sartomer	5	30	50
Onset Time of Gelation (s)	821	910	2106



50wt% acry.
UV cure
100°C/4hrs
150°C/2hrs



30wt% acry.
UV cure
100°C/4hrs
150°C/2hrs

Dual-cure Components: 50wt% Acrylate Resin

Phase separation and stability depends on thermodynamic miscibility and cure kinetics.

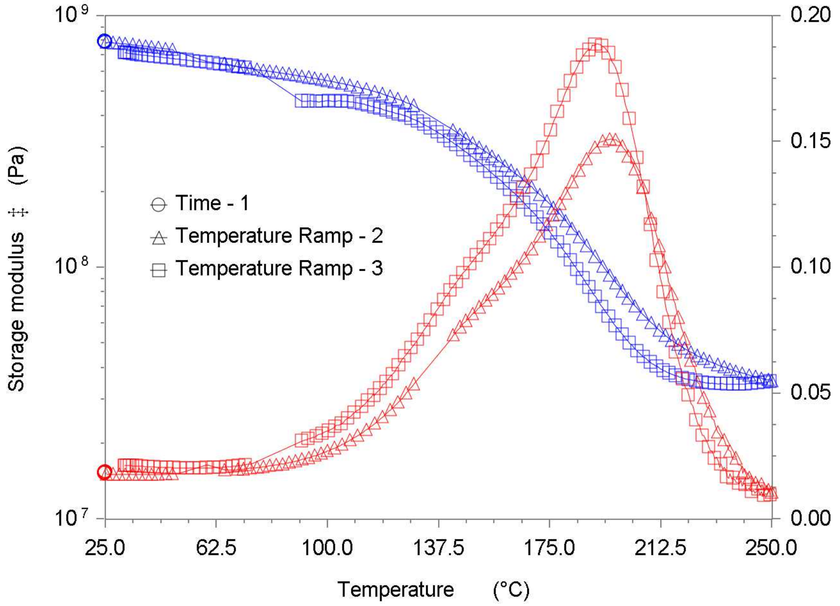
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

At low curing temperatures ($T\Delta S_{mix}$) smaller than unfavorable ΔH_{mix}

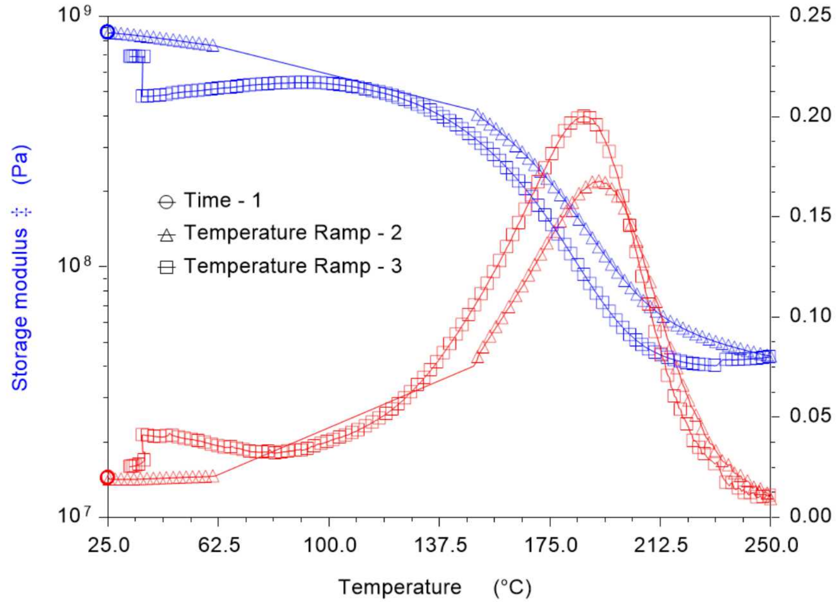
At higher cure temperature ($-T\Delta S_{mix}$) contribution overcomes unfavorable ΔH_{mix}

Kinetics at higher curing temperature are faster, trap system before phase separation.

Additional cure increases acrylate network Tg and phase separation cannot be detected by Tg.



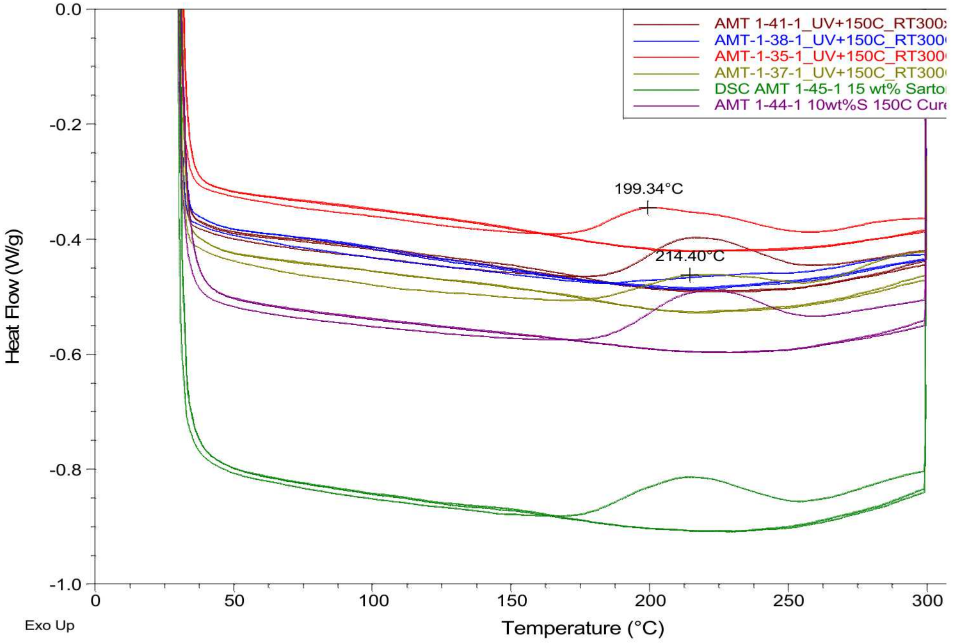
UV cure
100°C/4hrs
200°C/2hrs

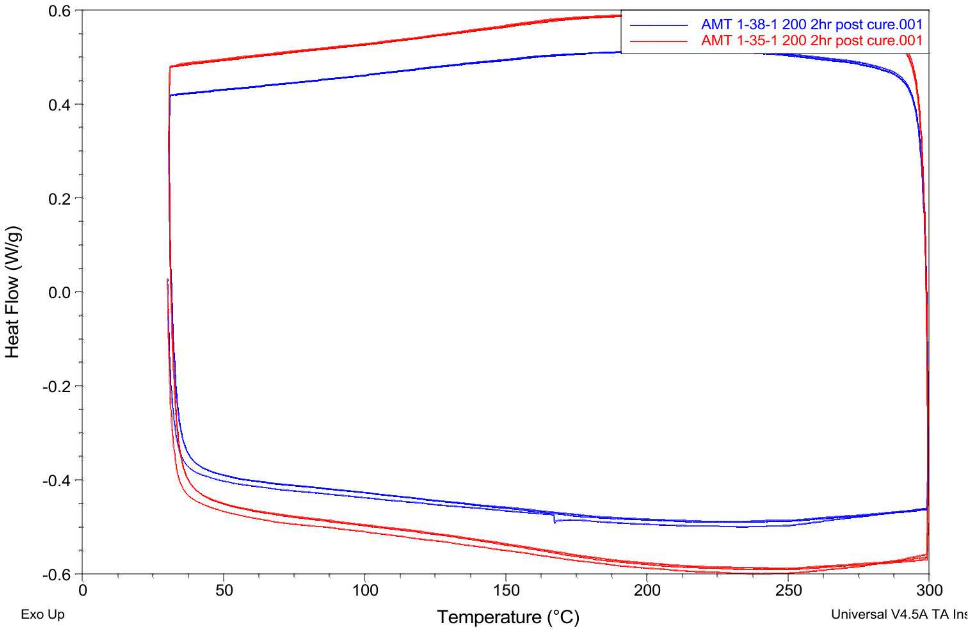


UV cure
200°C/2hrs

Post-cure: additional network conversion

DSC shows significant additional cure after 150°C cure, no additional cure after 200°C cure or post-cure.





FTIR-ATR also shows an increase in % acrylate reacted after thermal post-cures.

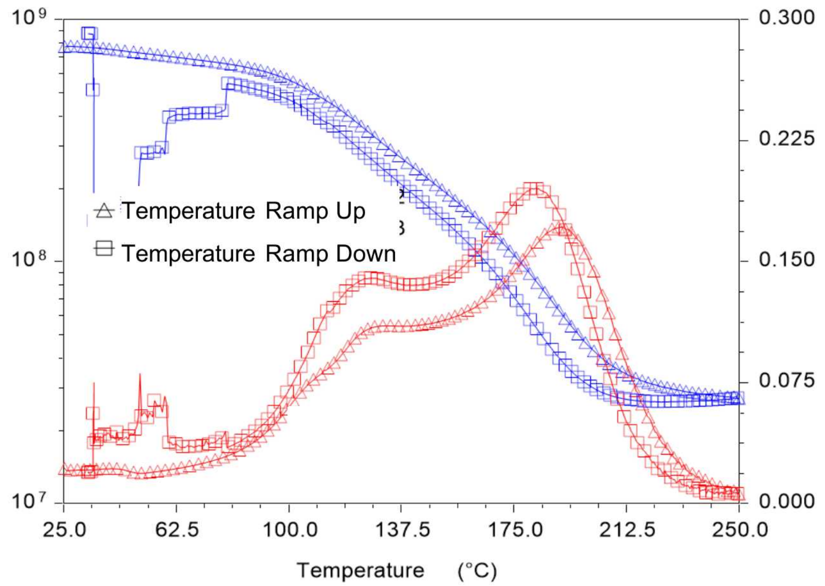
50wt% acrylate: FTIR-ATR	
cure T_{max}	(C=C)/(C=O)
150°C	0.85*
200°C	0.95*
250°C	0.98*

IPN Network Formation: 50wt% Acrylate Formulations

Post-cure can result in a single Tg but post-cure temperature must significantly exceed Tg.

200°C/2hr post-cure

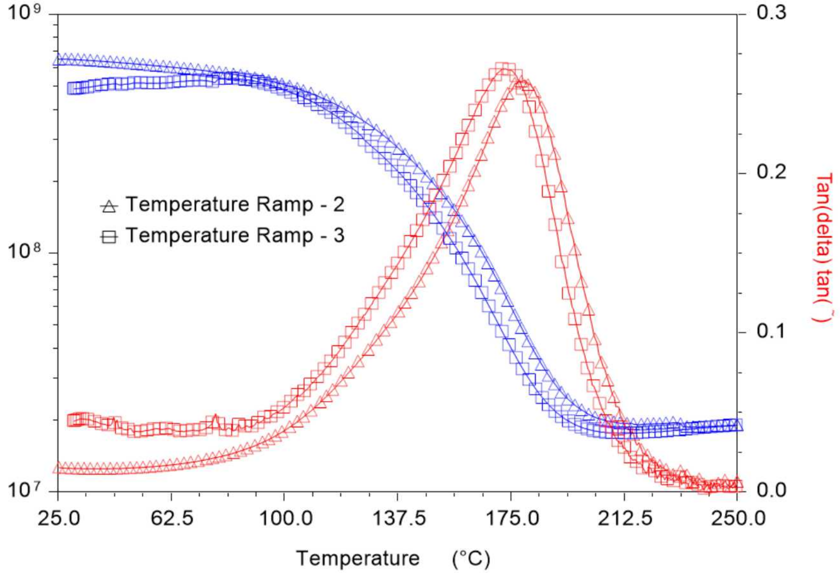
Two Tgs



100°C/4hrs
150°C/2hrs
200°C/2hrs

250°C/2hr post-cure

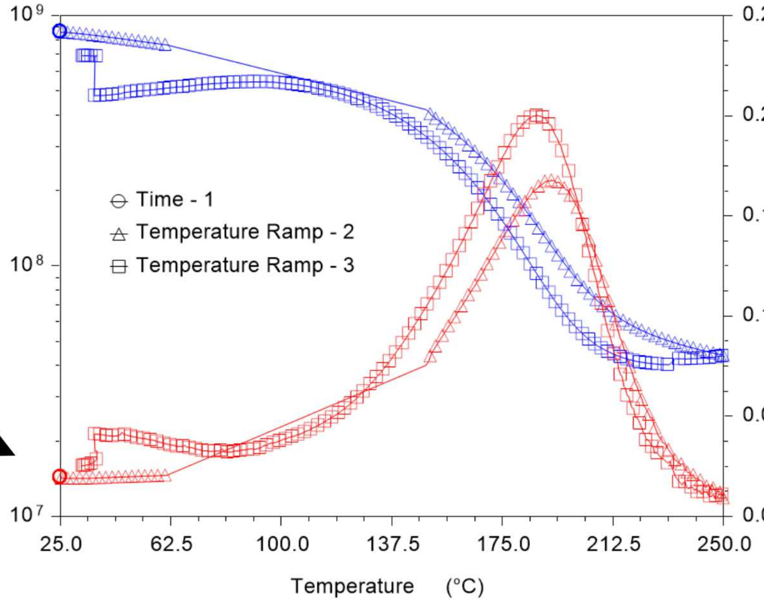
Single broad Tg

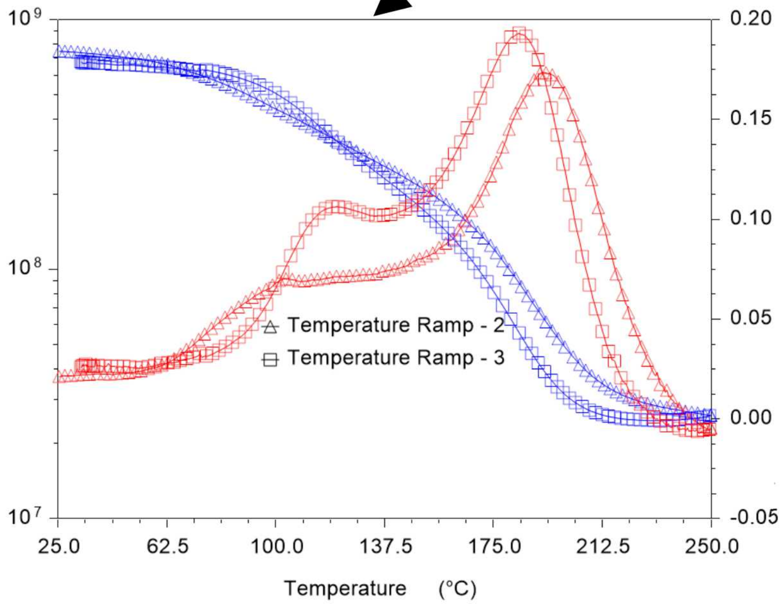


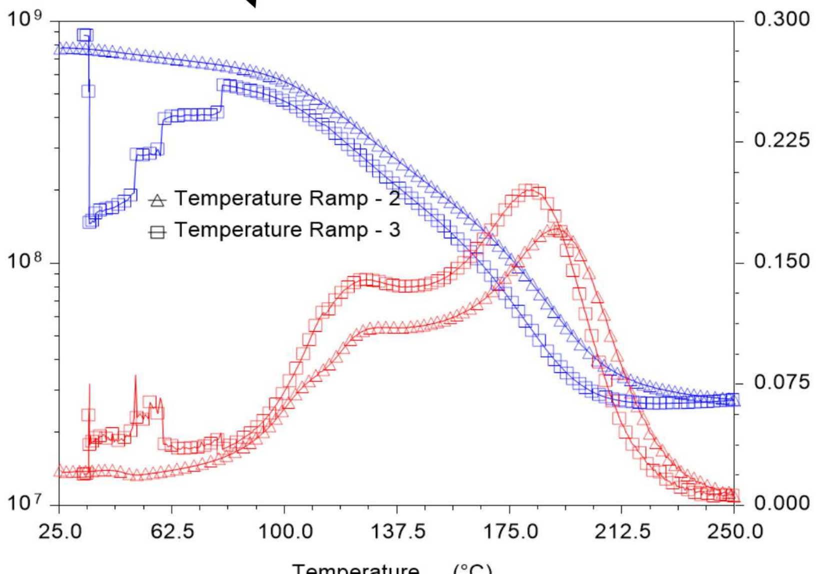
100°C/4hrs
150°C/2hrs
250°C/2hrs

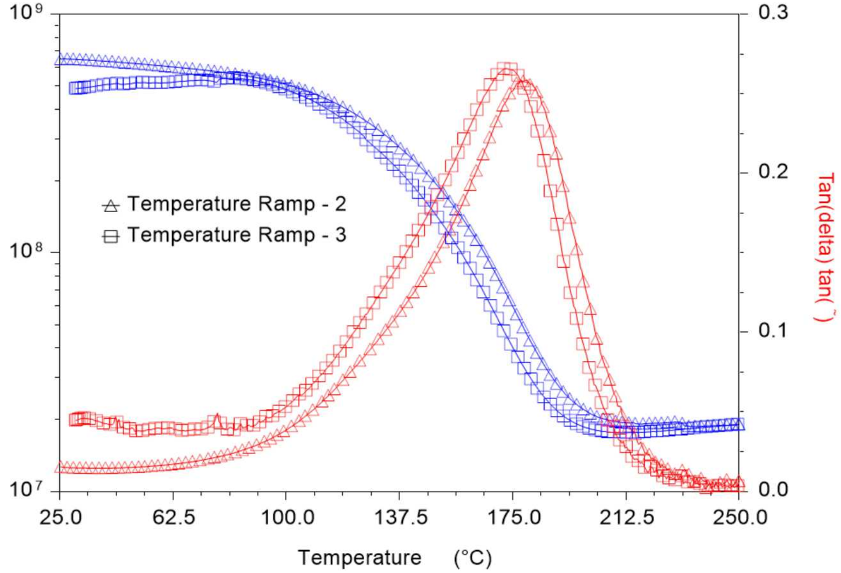
IPN Network Formation: 50wt% Acrylate Formulations

Thermal Post Profile	100C 4h 150C 2h	+150C 6h	+ 200C 2h	+ 250C 2h	100C 4h 200C 2h	200C 2h
Tg Transition (°C)	94 190	119 183	127 182	180	196	192
Storage Mod (MPa)	802	767	777	777	712	859









Summary

For diepoxy/triepoxy/dimethacrylate dual-cure resins developed for DIW thermoset printing:

- For UV cure of the acrylate component the UV exposure profile has a significant impact on conversion.
- Acrylate network formation kinetics and green strength are key to printability.
- In tricomponent diepoxy/triepoxy/dimethacrylate resin systems there is complex IPN phase behavior dependent on *both* thermodynamic miscibility and cure kinetics.

- Understanding resin structure-function relationships and reaction and cure kinetics is required to tune final properties and printability.
- In-depth knowledge of UV cure kinetics is necessary to enable print-process scale-up and successful translation to more complex geometries.
- The effects of thermal cure and subsequent thermal exposures on microstructure formation and evolution are key to understanding environmental performance limits, property stability, and aging.

Acknowledgements

Jess Kopatz, PhD candidate (Penn State)

Jackie Unangst, post doc

Also thanks to:

Adam Cook, Derek Reinholtz

Kylie Manning (now at Dow), Mat Celina

Brad Jones, Erica Redline, Nick Wyatt

Lindsey Hughes, Patti Sawyer, Mark Stavig

$$$ NNSA NA-115 Additive Manufacturing Development Program

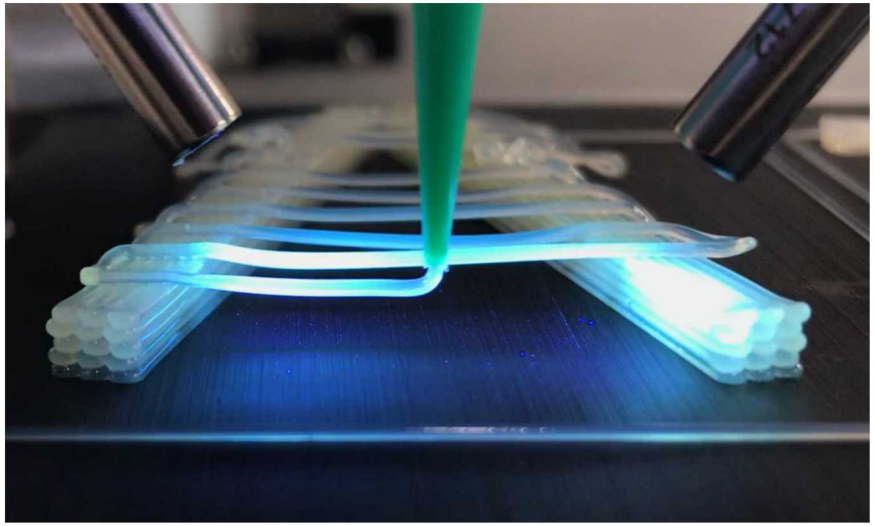
Questions?

Supplementary Slides

Approaches to DIW Printing of Thermoset Resins

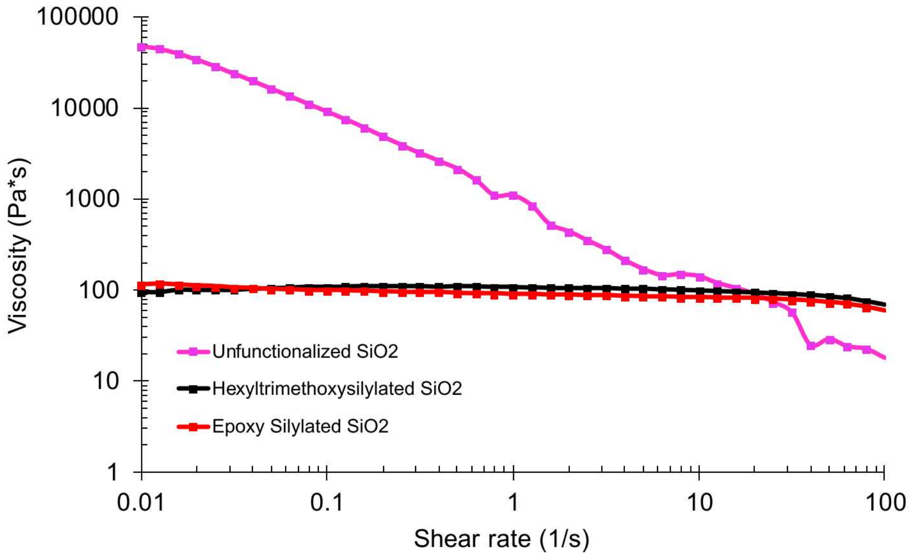
1) In situ cure – full or partial cure during printing

- Single mechanism cure (e.g. UV curable)
- **Dual-cure** (**UV/thermal**, UV/UV, thermal/thermal)
  - Printed shape maintained by 'green strength' of partially cured resin



2) Increase zero-shear viscosity

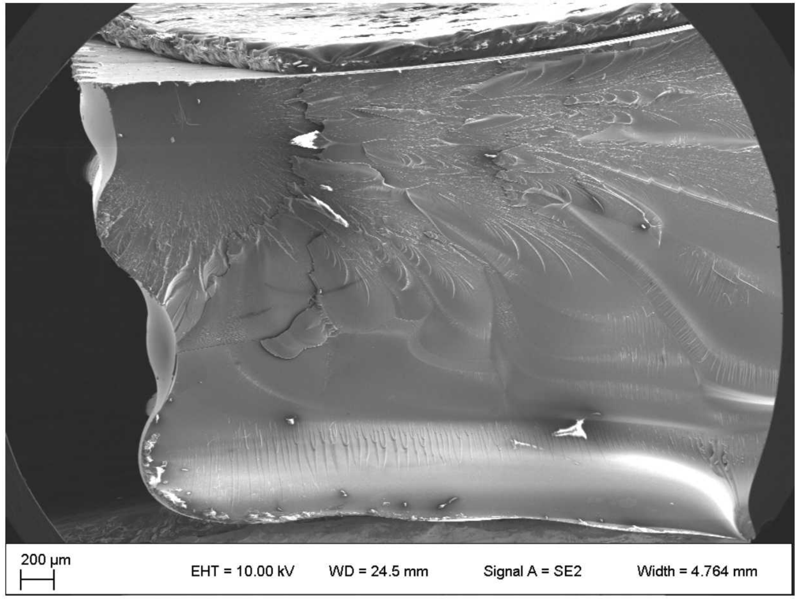
- Moderate-to-high filler loadings
- B-staging
- Shear thinning
- High zero-shear viscosity maintains printed shape



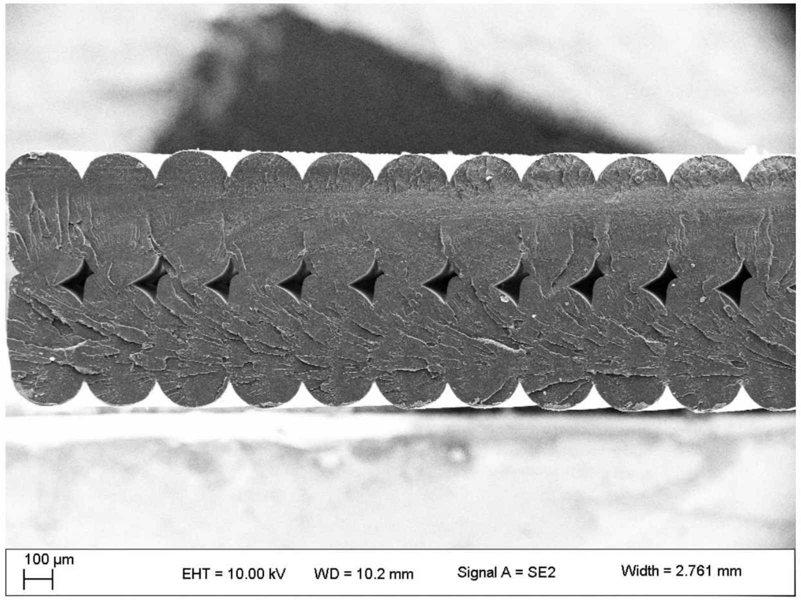
Why AM Printing of Thermosets?

May offer specific AM advantages relative to thermoplastics

- **Interlayer adhesion/homogeneity**
- **Key for mechanical and dielectric properties**



SEM of cross section of DIW printed thermoset resin

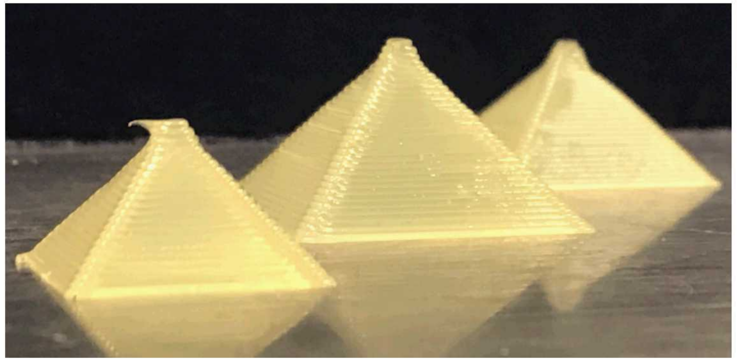


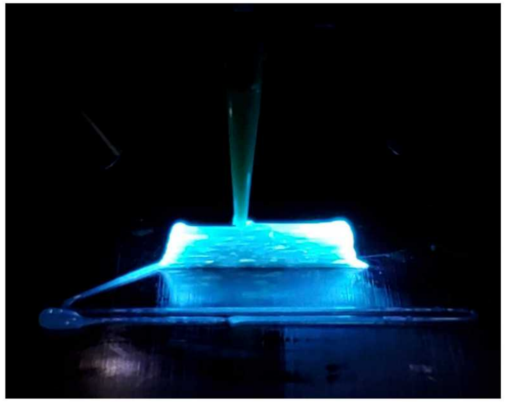
SEM of cross section of FFF printed Nylon

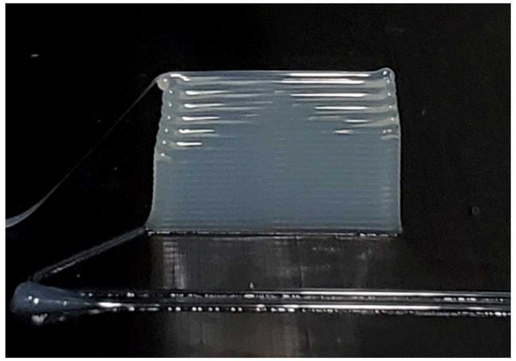
Sandia’s Approach

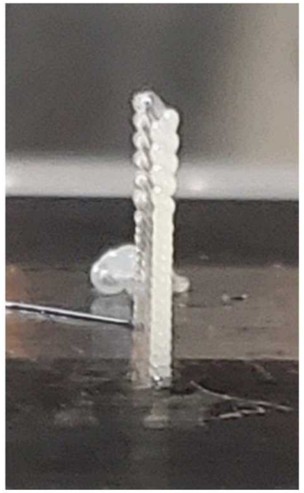
Development of thermoset resins for DIW

- 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 thermoset systems.







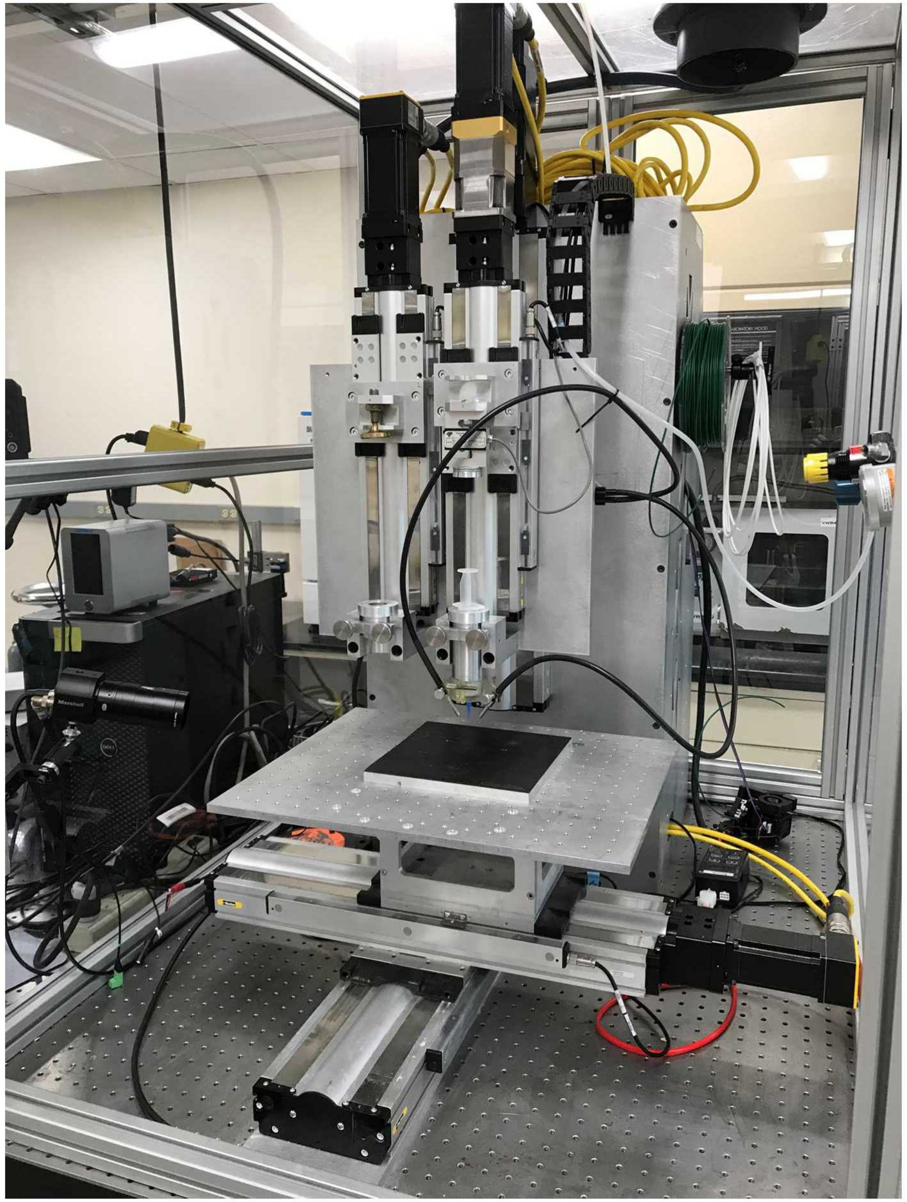


>10:1 w:h

Sandia's UV-assisted Direct-Ink Write Capability

Adam Cook/Derek Reinholtz

- LED spot-curing system, 365 nm, max power 40 W/cm^2
- Controllable UV intensity (0-100%)
- Print nozzle diameter from 0.15-1.55 mm
- Table speed 0.01 mm/s to ~60mm/s
- Print volume 300x300x200 mm



Dual-cure Components: 50wt% Acrylate Resin

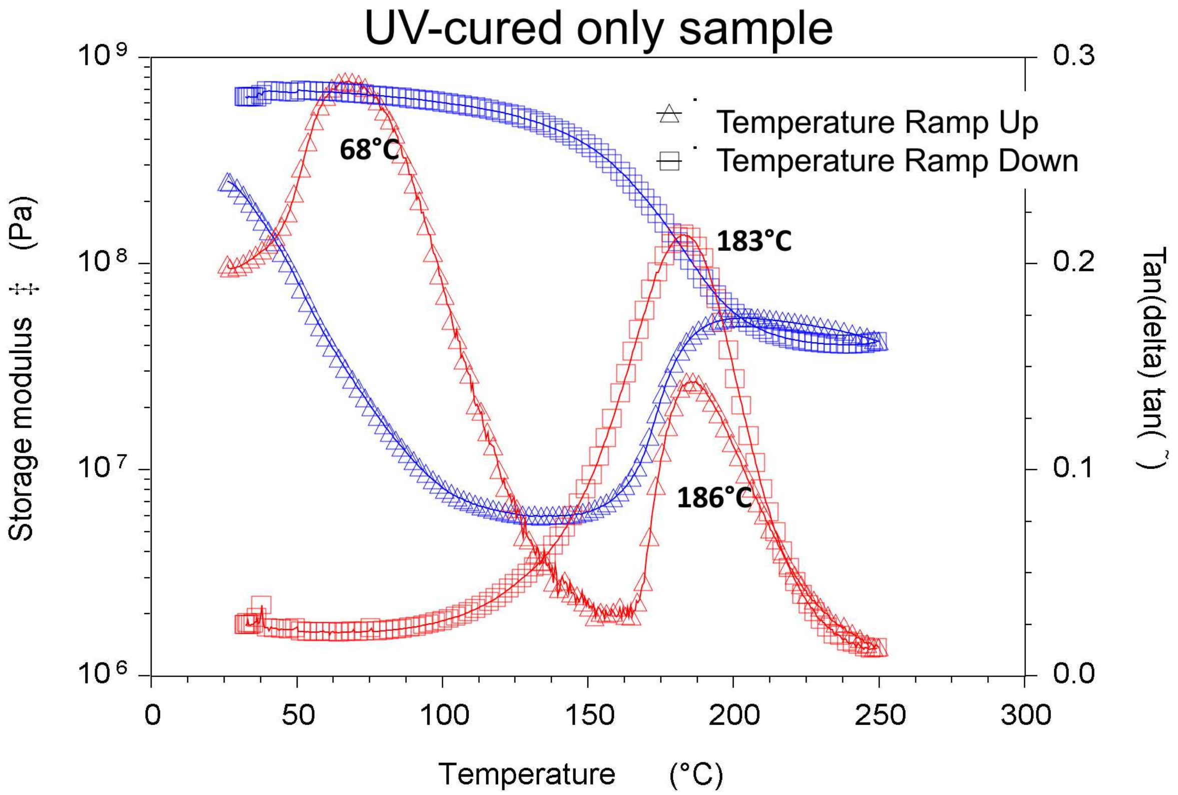
Resin composition: 50wt% diacrylate, 23wt% diepoxy, 19wt% triepoxy

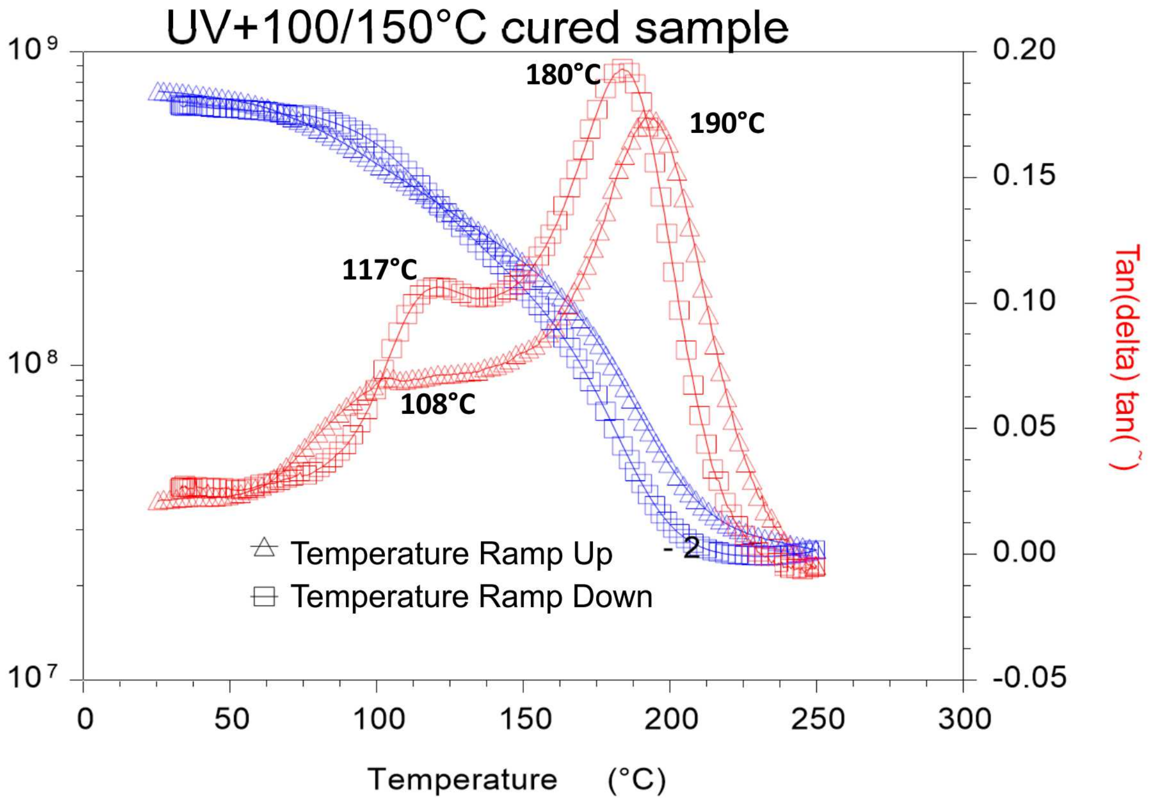
UV-cured only samples cycled to 250°C show only one T_g on ramp down.

100/150°C UV+thermal cured samples have two T_gs, which evolve but do not coalesce with short duration temperature cycle.

100/150 °C thermal-cure profile

100 °C for 4 hours
150 °C for 2 hours





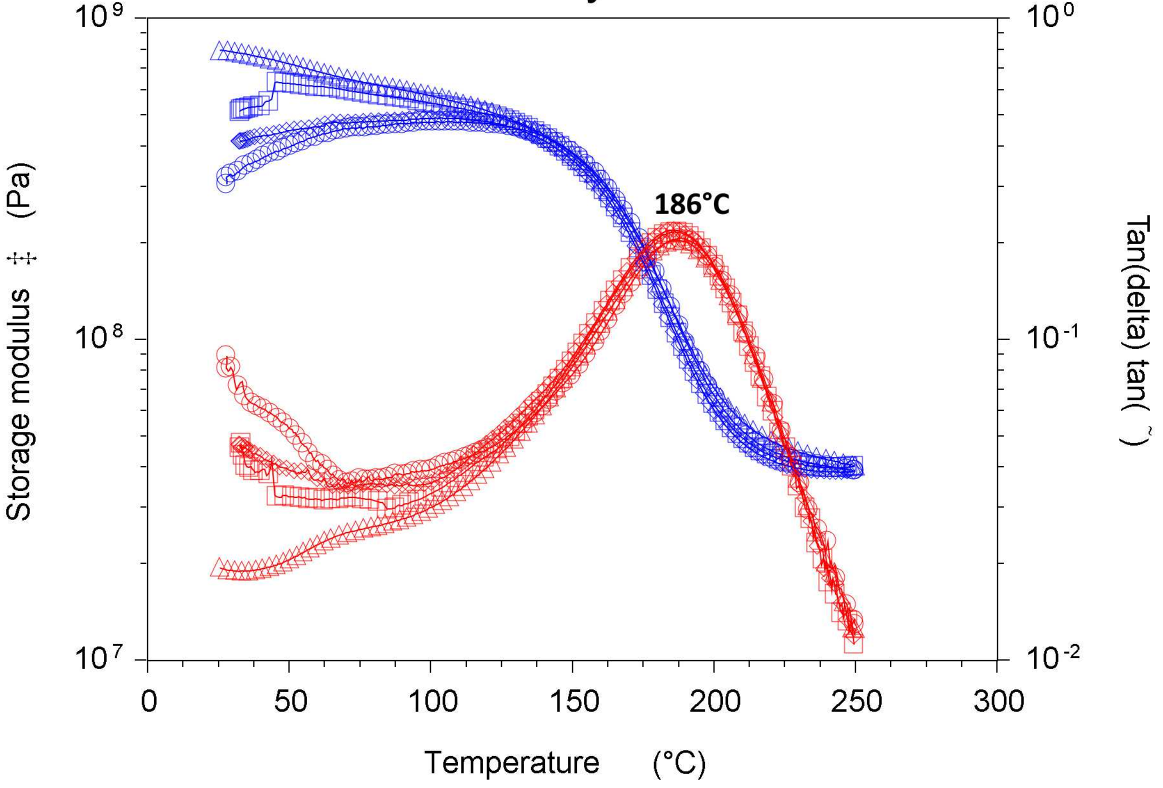
Dual-cure Components: 50wt% Acrylate Resin

For cycling to 250°C for short dwell times no further evolution of Tg is observed.

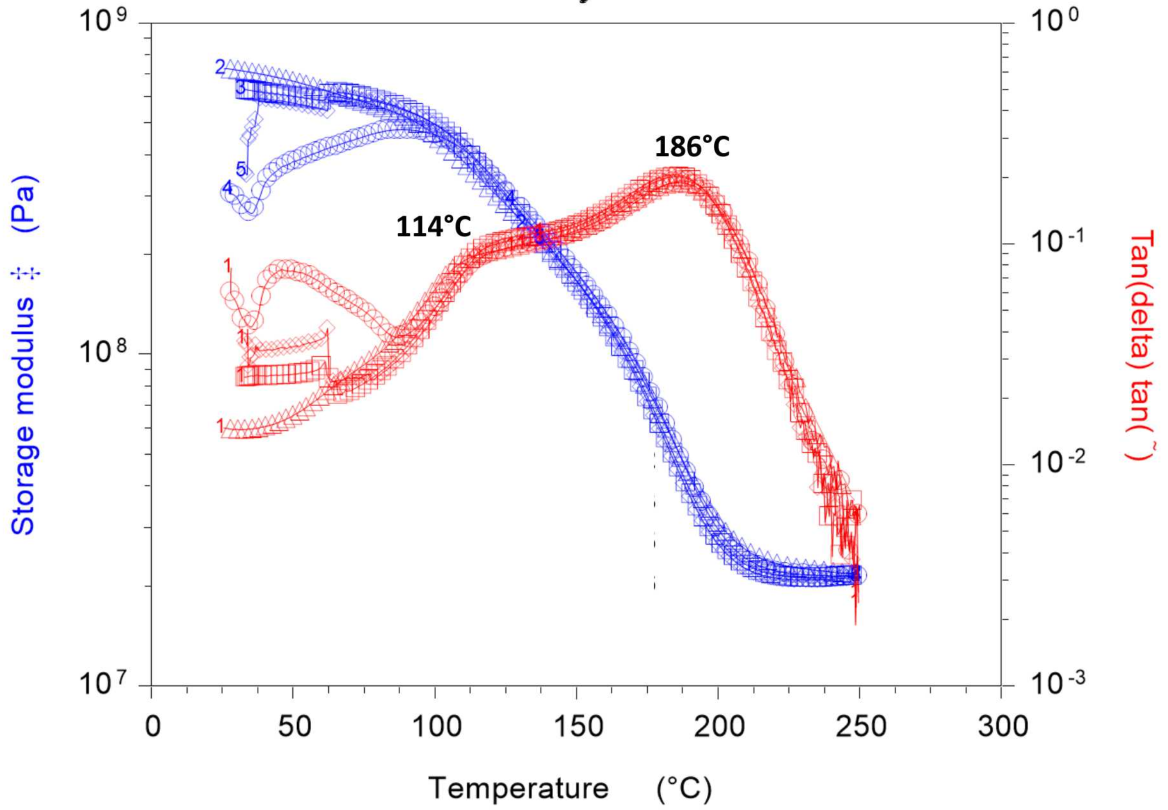
Thermal-cure profile
100 °C for 4 hours
150 °C for 2 hours

Resin composition: 50wt% diacrylate, 23wt% diepoxy, 19wt% triepoxy

UV-cured only sample:
VT to 250 °C cycles 2 and 3



UV+100/150°C thermal cure sample:
VT to 250 °C cycles 2 and 3

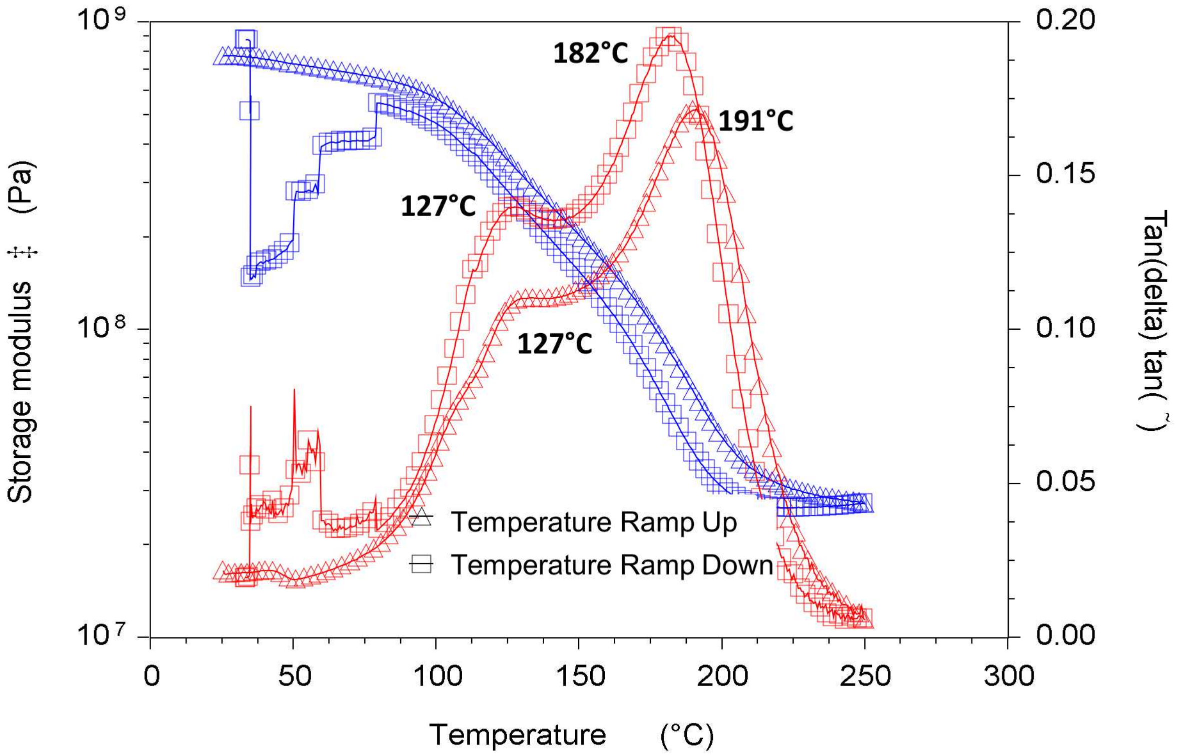


Dual-cure Components: 50wt% Acrylate Resin

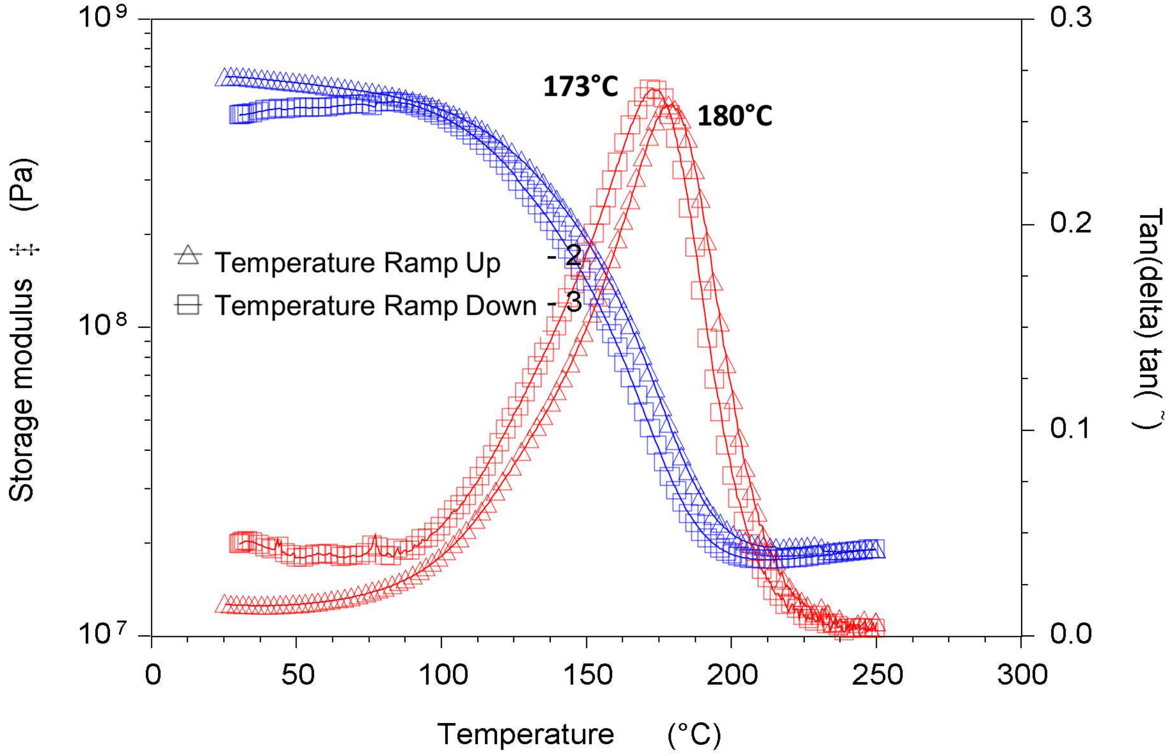
The dynamic evolution of the epoxy/acrylate interpenetrating polymer network is observed during thermal cure.

Longer post-cure does lead to Tg/microstructure evolution, depending on T_{max} of post-cure.

Microphase-separated 100/150°C system stable with 200°C/2hr post cure



Microphase-separated 100/150°C sample homogenizes with 250°C/2hr post cure



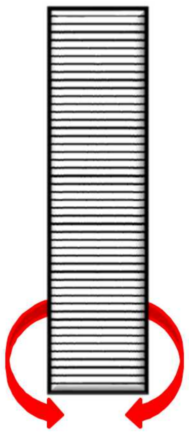
Dual-cure Components: Acrylate Resin

Storage modulus measured at RT *before* thermal cycling on samples printed in a *transverse* geometry.

Tg measured by VT DMA to 250°C.
No significant differences between *transverse* and *longitudinal* Tg.

	30 min UV Cure 150˚C Thermal Cure		
wt% dimethacrylate	Storage Modulus (MPa)	Tg up (˚C)	Tg down (˚C)
5 wt%	870 (40)	213	197
30 wt%	779 (173)	195	183
50 wt%	700 (20)	94 190	115 183

T

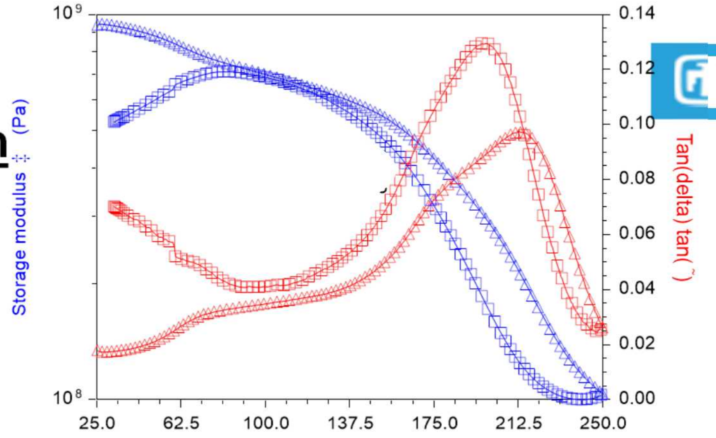


oscillates

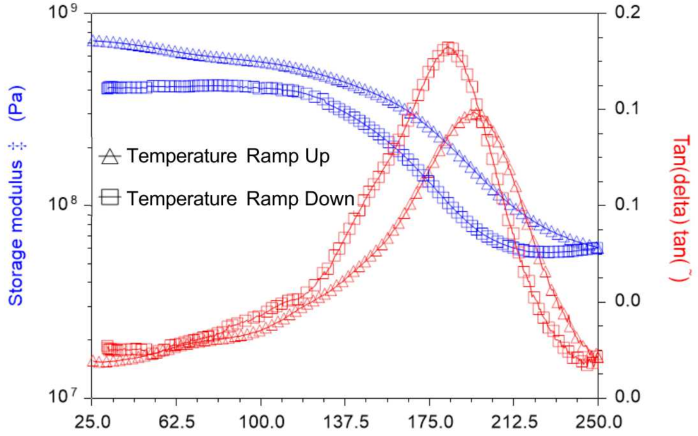
Resin composition: varying diacrylate, remainder 1:1 diepoxy:triepoxy

varying wt% acrylate resin

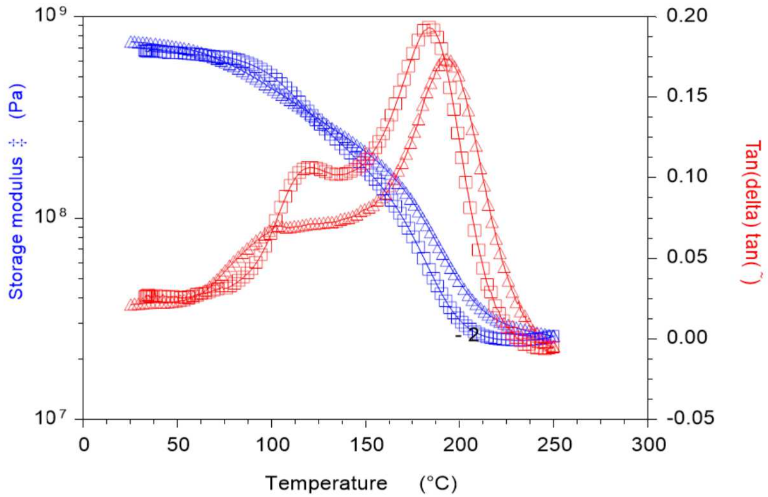
5 wt%



30 wt%



50 wt%



Dual-cure Components: Triepoxy Resin

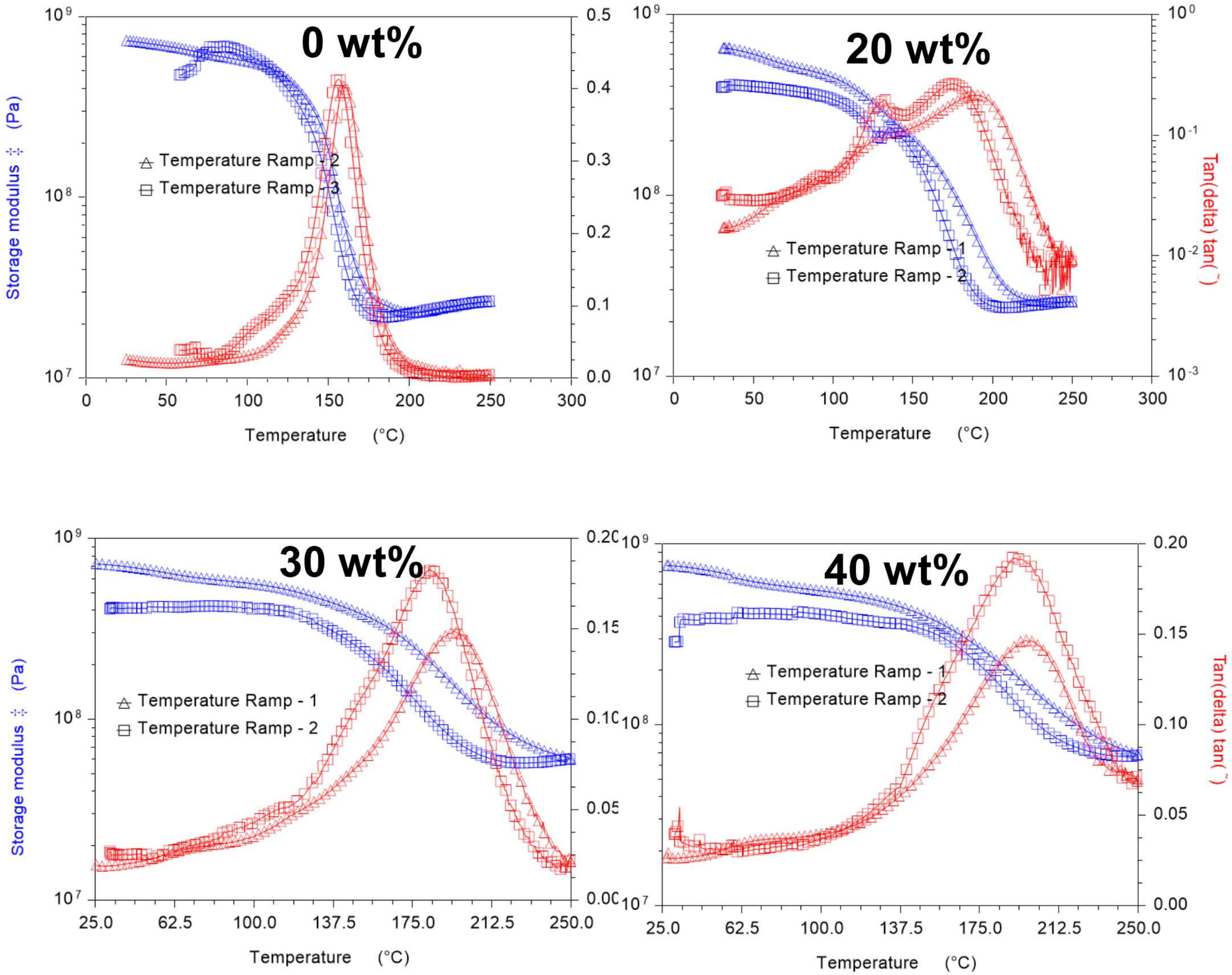
~30wt% acrylate, 63wt% epoxy (di/tri).

The triepoxy component moderately increases the Tg but has no significant effect on the storage modulus of the 150°C cured samples.

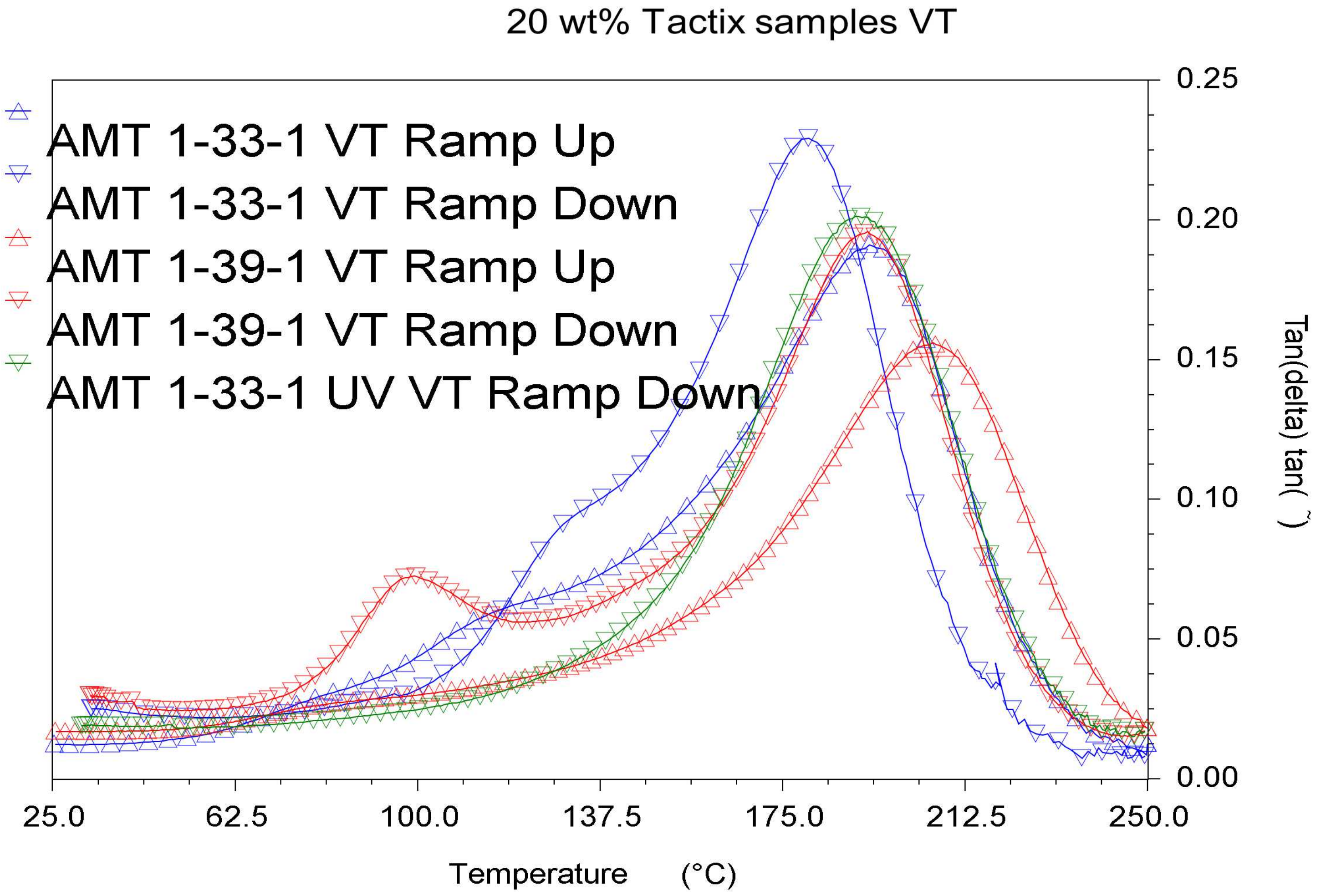
	30 min UV Cure + 150°C Thermal Cure		
Triepoxy	Tg Up (°C)	Tg Down (°C)	Storage Modulus (MPa)
0 wt%	159	156	776 (156)
20 wt%	191	177*	771 (125)
30 wt%	195	184	836 (116)
40 wt%	199	192	643 (113)

Tg measured by torsional VT DMA to 250°C.
Storage modulus at room temperature.
*additional peaks in loss modulus plot due to sample slipping

varying wt% triepoxy resin



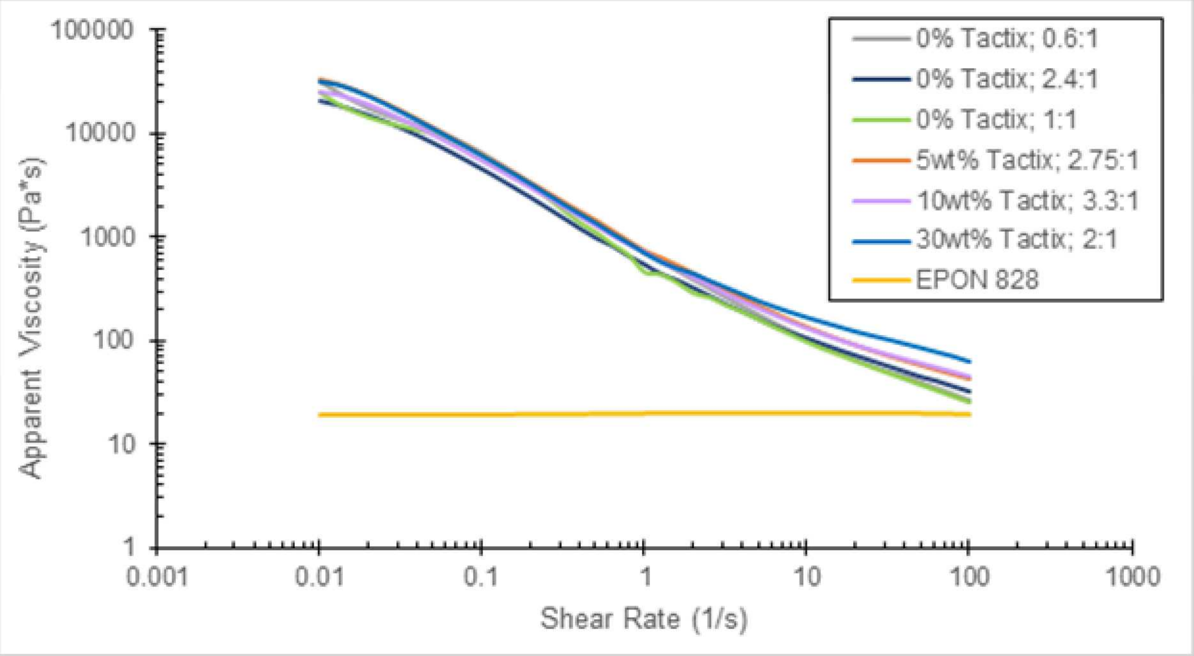
20 wt% Tactix comparison of VT 1st cycle from 2 the different batches with UV sample



Sandia's UV-Thermal Dual Cure: Rheology

Rheology of resins is not highly sensitive to monomer compositions.

Allows broad variation of resin compositions while maintaining printability.



Supplementary: UV Exposure and Dose for Different Sources

Device	Wavelength & Dose	power %						Measured Intensity
		1	5	10	20	40	80	
Dual UV source (printer)	**365nm**	**1.2**	**6.9**	**14.3**	**29.0**	**57.3**	**106.3**	Measured intensity (mW/cm^2)
	Dose (190s)	228	1,311	2,717	5,510	10,887	20,197	
Post-print UV cure	365nm	5.7						
	Dose (1800s)	10,260						
Photo-DSC	**365nm**	**-**	**45**	**109**	**207**	**327**	**413**	
	Dose (12s)	-	539	1313	2,486	3,918	4,958	
	Dose (2.4s)	-	108	263	497	784	992	

Dosage: Intensity*time of exposure

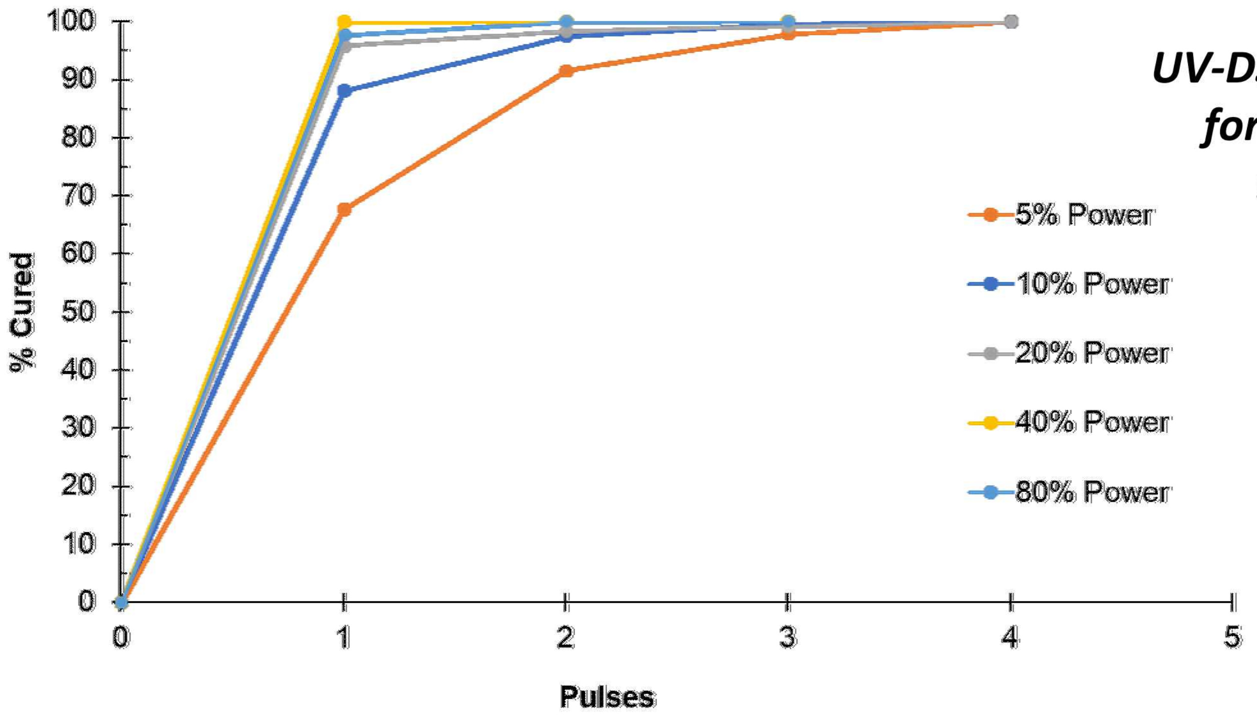
Dual UV source: continuous coverage for 190s
Post-print UV: continuous coverage for 1800s (30 min)
Photo-DSC: 5 x 2.4s flashes

UV-Thermal Dual Cure

Characterizing UV-cure kinetics by UV-DSC

Photo-DSC @365nm	5%	10%	20%	40%	80%
Measured intensity (mW/cm^2)	45	109	207	327	413
Dose (5 pulses, 12s)	539	1313	2,486	3,918	4,958
Dose (1 pulse, 2.4s)	108	263	497	784	992

5 pulses at 10% power in UV-DSC matches calculated dose for printing at 5% power



UV-DSC of 2:1 epoxy:acrylate formulation at different irradiation powers

Baseline problem in continuous exposures with low acrylate %?