SAND2019-9478C

Center 1800:
Material, Physical and Chemical Sciences

Rheological and Mechanical Behavior of Dual-Cure DIW Resins

PRESENTED BY

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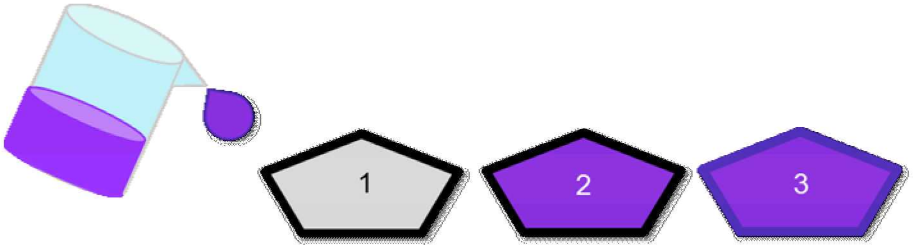
SAND

Why Direct-ink write printing of thermosets?

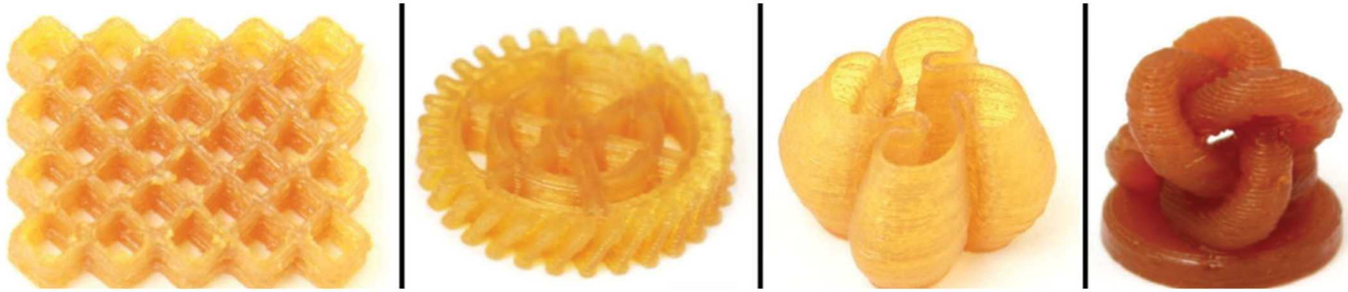
- Thermosets have good mechanical properties thermal and chemical stability
- Traditionally fabricated using molds

Limitations of traditional fabrication methods :

- Geometry
- Non-uniform thickness
- No high aspect ratio parts

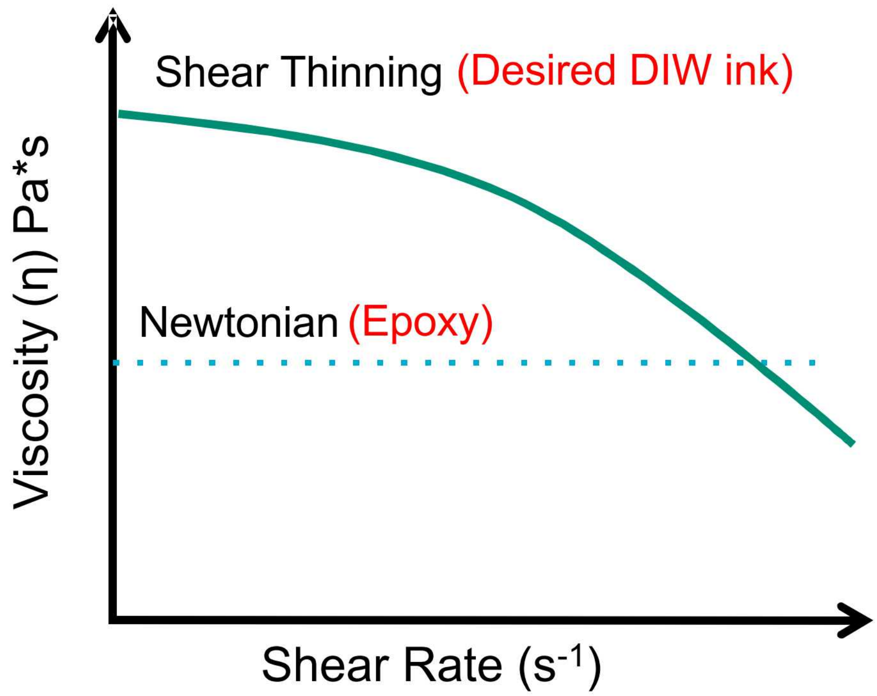


Solution: DIW facilitates the design of more complex geometries



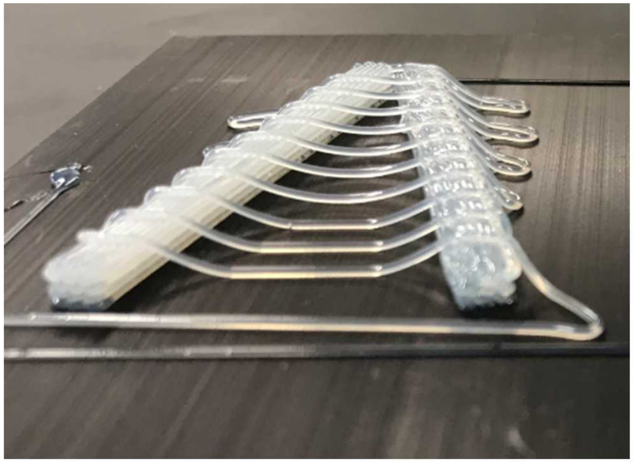
Chen et al. *Soft Mater*. J 2018. vol. 14

Challenges of DIW printing thermosets



Vlachopoulos et al. Role of Rheology in Polymer Extrusion. 2003

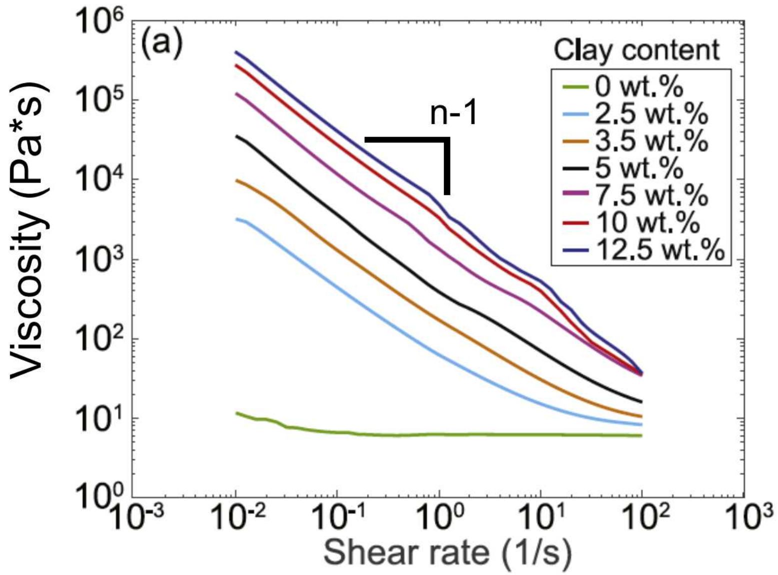
- Shape retention/deformation while printing
- Post-print processing
  - Requires thermal cure
    - Part deformation/distortion



Approaches to DIW printing thermosets

Approach 1: Incorporation of fillers

Plot of log-log apparent viscosity vs. shear rate of DGEBPA epoxy (EPON 826) + Garamite 7305 clay



Hmeidat et al. *Compos. Sci. & Tech*. 2018. vol. 160

Limitations:

- Requires high zero shear viscosity
- Property anisotropy
- Filler type

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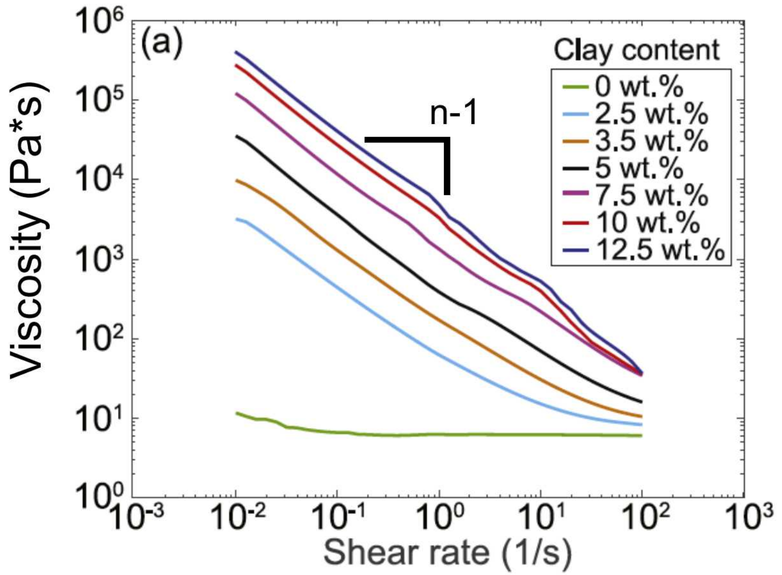
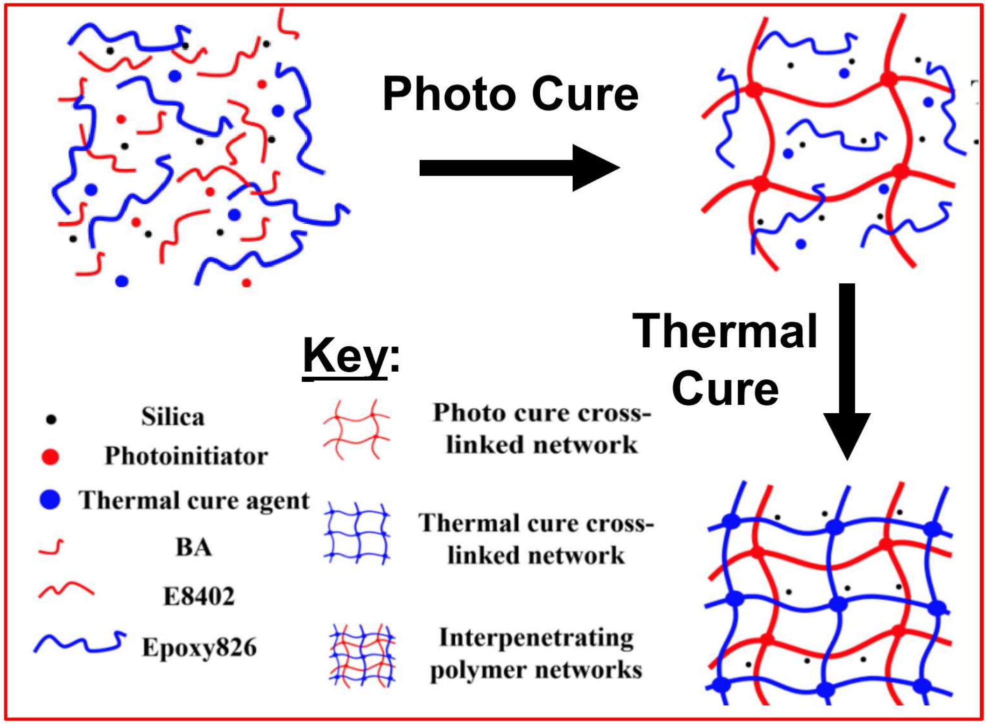
Plot of log-log apparent viscosity vs. shear rate of DGEBPA epoxy (EPON 826) + Garamite 7305 clay



Hmeidat et al. *Compos. Sci. & Tech*. 2018. vol. 160

Limitations:
- Requires high zero shear viscosity
- Property anisotropy
- Filler type

Approach 2: Dual-cure networks



Chen et al. *Soft Matter.* 2018. Vol 14.

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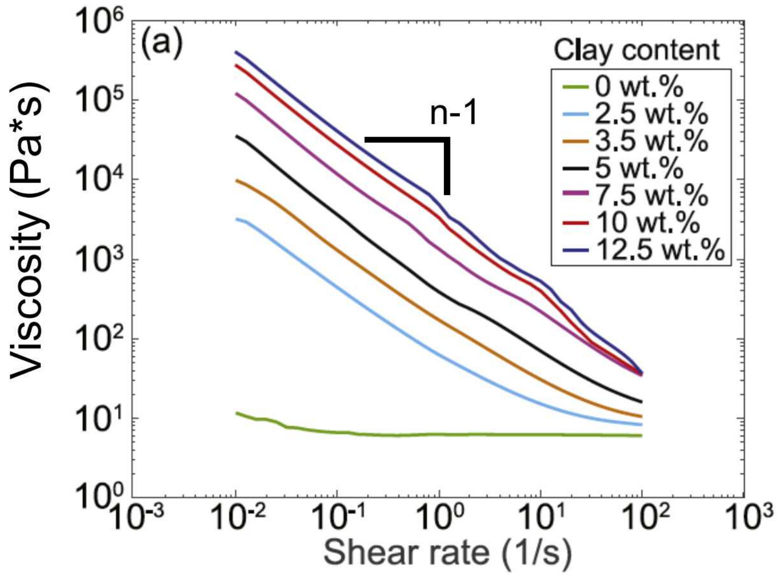
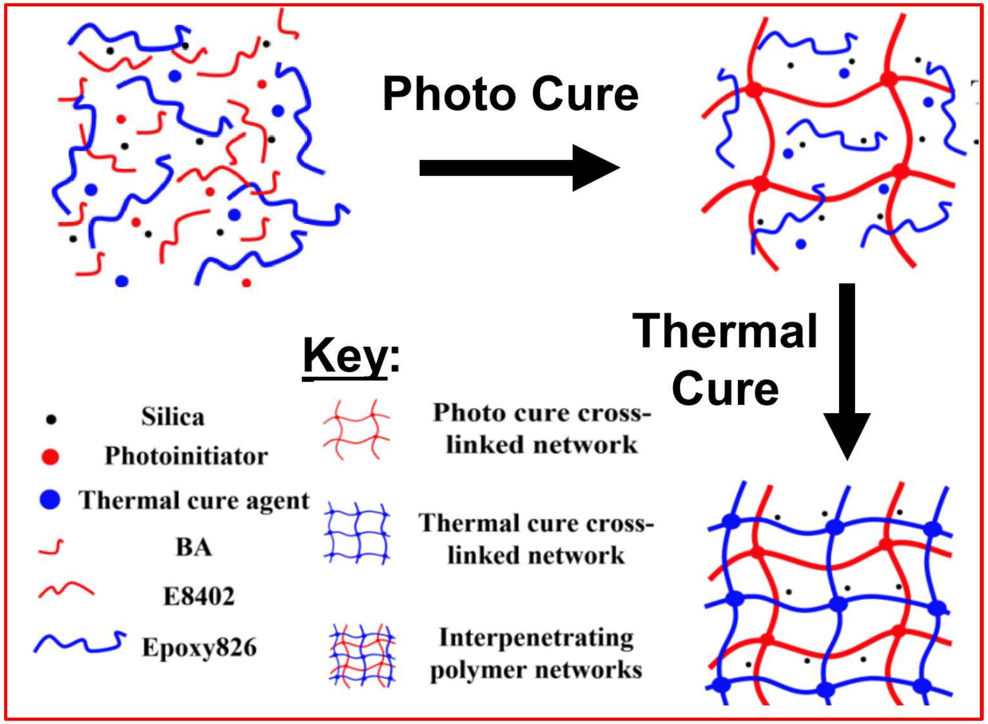


Hmeidat et al. *Compos. Sci. & Tech*. 2018. vol. 160

Approach 2: Dual-cure networks



Chen et al. *Soft Matter*. 2018. Vol 14.

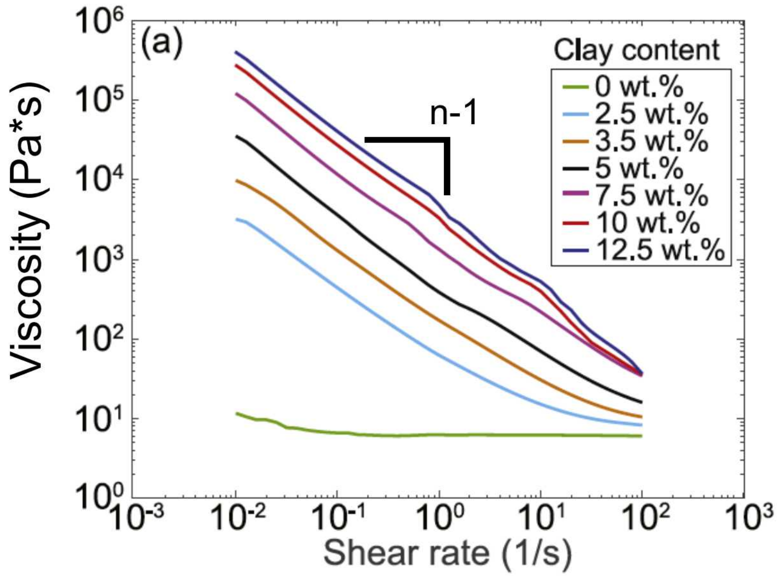
Limitations:
- Requires high zero shear viscosity
- Property anisotropy
- Filler type

Limitations:
- large amounts of acrylate
- Ex-situ layer cure

Approaches to DIW printing thermosets

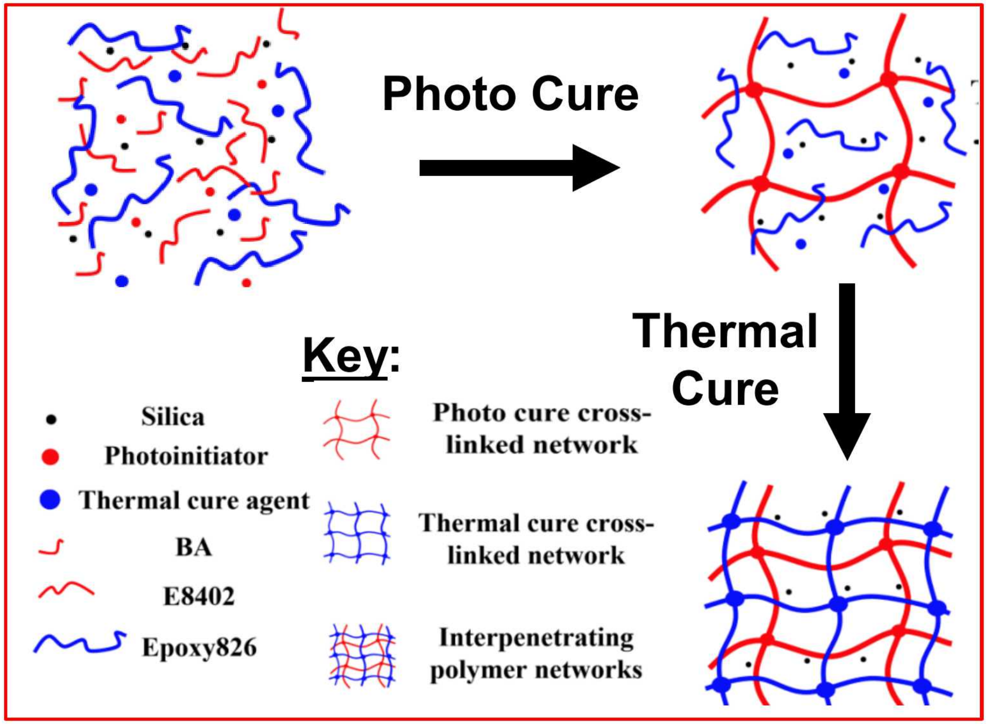
Approach 1: Incorporation of fillers

Plot of log-log apparent viscosity vs. shear rate of DGEBPA epoxy (EPON 826) + Garamite 7305 clay



Hmeidat et al. *Compos. Sci. & Tech*. 2018. vol. 160

Approach 2: Dual-cure networks



Chen et al. *Soft Matter.* 2018. Vol 14.

Solution: Addition of acrylate-functionalized silica and clay to decrease overall amount of acrylate necessary to form a stable structure while printing

This project is working towards understanding the impact of functional additives on the cure kinetics and mechanical properties of dual-cure formulations for direct ink write of thermosets

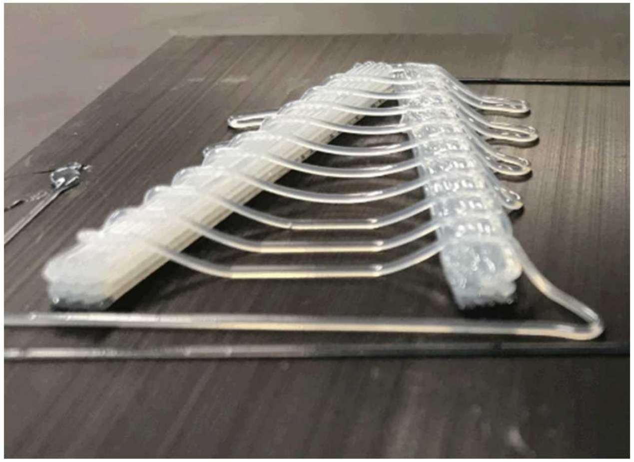
Dual-cure mechanisms enable printing of thermoset systems

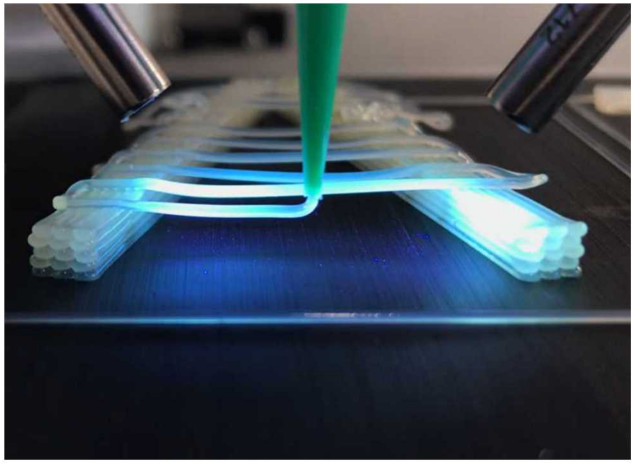
Kuang et al. *Macromolecular Rapid Commun.* 2018. Vol 39.

1st stage cure

2nd stage cure

- First stage cure locks-in structure during print
- Second stage cure enhances mechanical properties





Dual-cure resin with no UV (left), print with 20% UV (right)

DIW using functionalized fillers

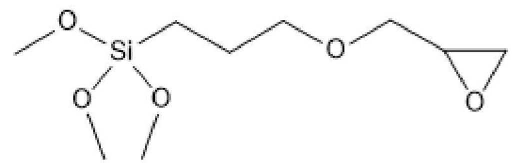
Di-functional epoxy

Bisphenol A (BPA)
dimeth- or di- acrylate

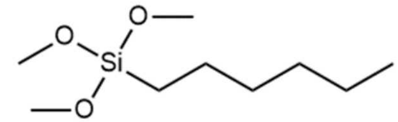
Photoinitiator

Latent curing agent

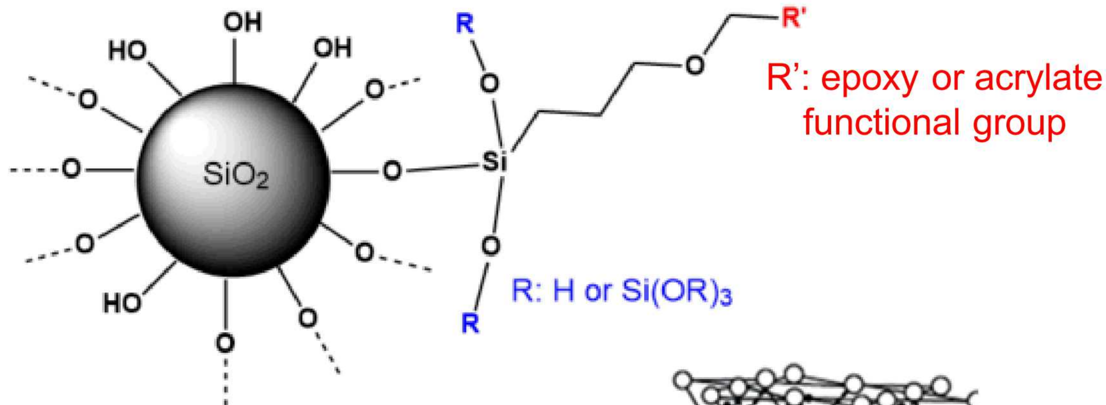
Filler



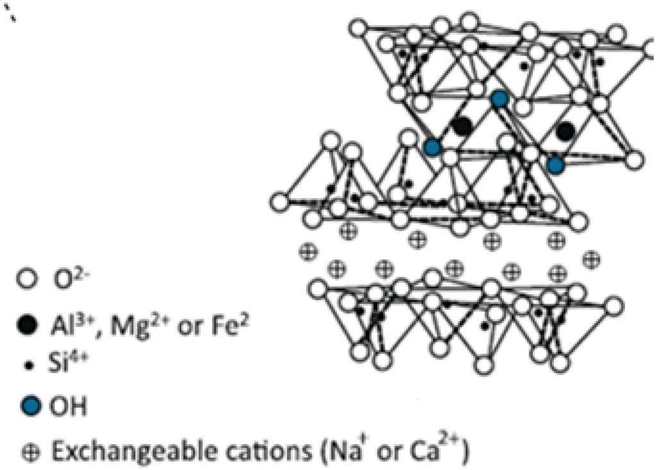
Glycidoxypropyltrimethoxysilane



Hexyltrimethoxysilane



Goals:
- Replace acrylate content with acrylate-functionalized fillers
- Dual-functionalized particles to link epoxy and acrylate networks

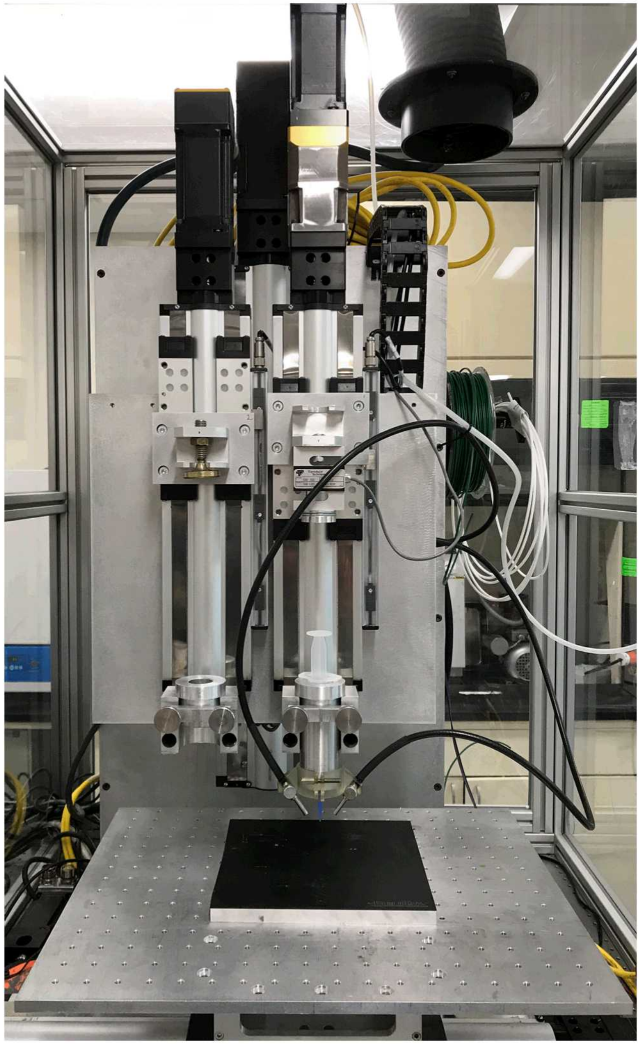


Structure of MMT clay

Asgari et al. 2018. Applied Clay Science

UV-assisted Direct-Ink Write Capability

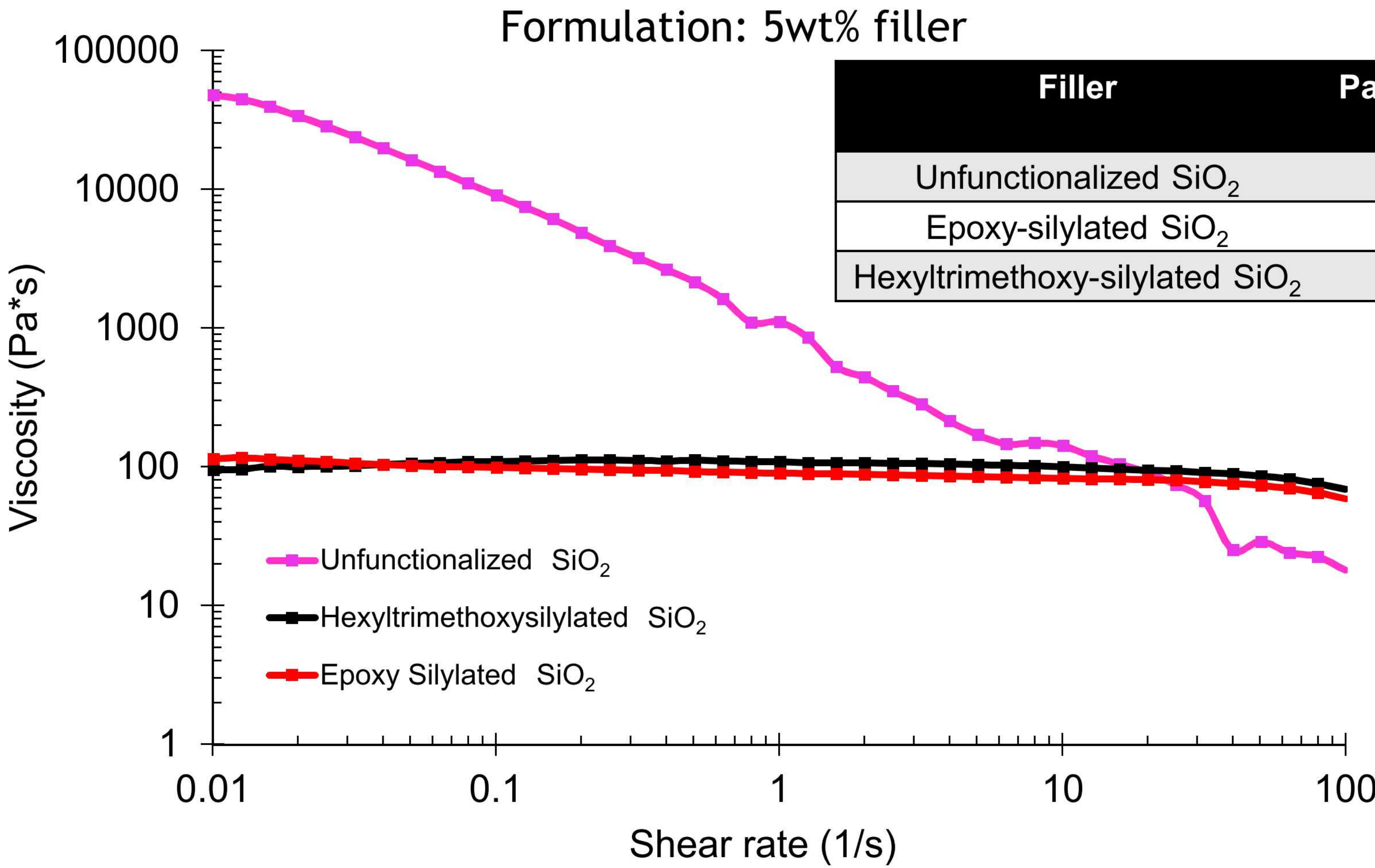
- 2 x 365nm Dymax BlueWave MX150 LED UV light sources
- Controllable UV intensity (0-100%)
  - Intensity: ~200-20,000 mW/cm^2
- Print nozzle diameter from 0.15mm to 1.55mm
- Table speed from 0.01mm/s to 50mm/s
- Print volume of 300x300x200mm



Printer Acknowledgement:
Adam Cook & Derek Reinholtz

Functionalized Fillers

Effect of silica functionalization on viscosity

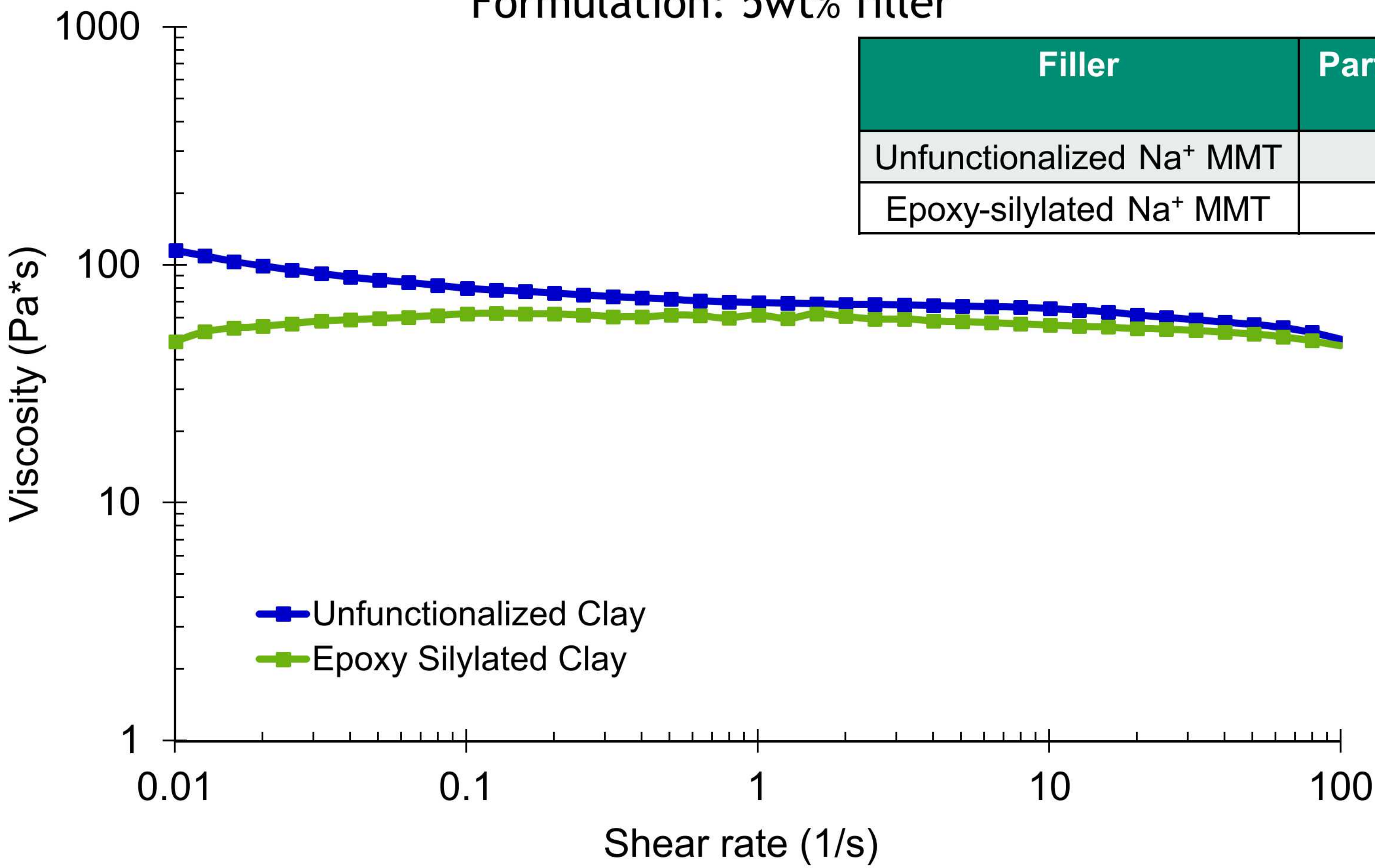


Filler	Particle size (nm)
Unfunctionalized SiO_2	~554
Epoxy-silylated SiO_2	~340
Hexyltrimethoxy-silylated SiO_2	~450

- Formulations with functionalized SiO_2 do not exhibit shear thinning behavior
  - Dispersion and particle size distribution are being investigated
- All formulations are printable using a higher UV intensity

Effect of functionalized clay on viscosity

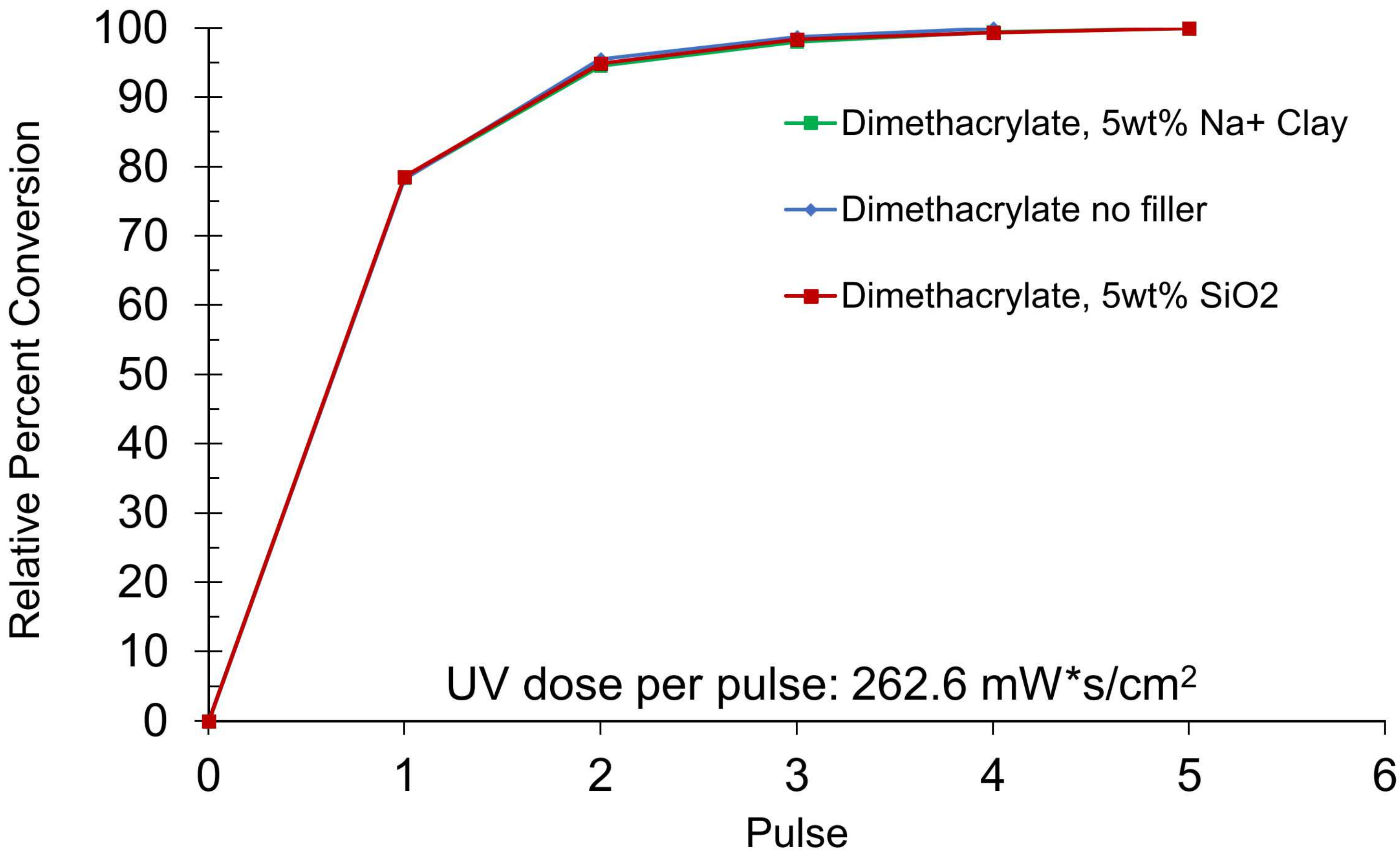
Formulation: 5wt% filler



Filler	Particle size (nm)
Unfunctionalized Na^+ MMT	~740
Epoxy-silylated Na^+ MMT	~730

- Unlike silica, the clay filler does not induce shear-thinning behavior
- Functionalized clay also shows no-shear thinning behavior
- All formulations are printable using a higher UV intensity

Effect of filler on UV-cure kinetics

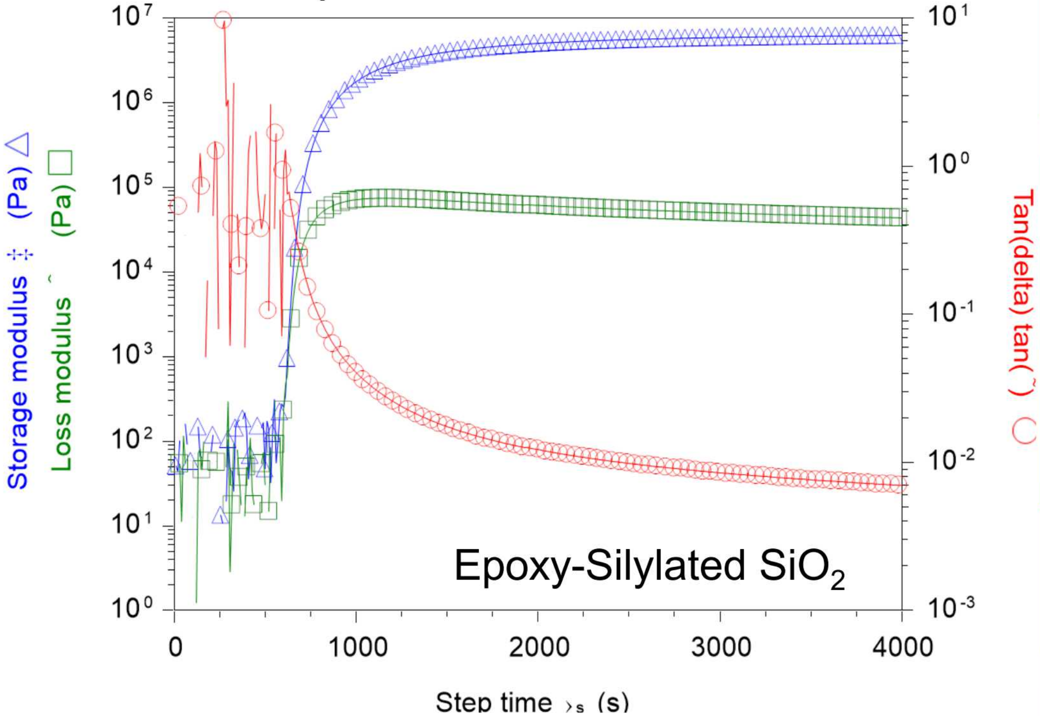


- While the addition of fillers impacts the rheology, the UV-cure kinetics were not impacted by the fillers at 5wt%

Effect of functionalized fillers on gelation & epoxy network formation

Dimethacrylate, 5wt% filler, 150°C		
Filler	**Onset of Gelation (s)**	**Particle size (nm)**
Unfunctionalized SiO_2	553	~554
Epoxy-silylated SiO_2	**614**	**~340**
Hexyltrimethoxy-silylated SiO_2	522	~450
Unfunctionalized Na^+ MMT	536	~740
Epoxy-silylated Na^+ MMT	824	~730

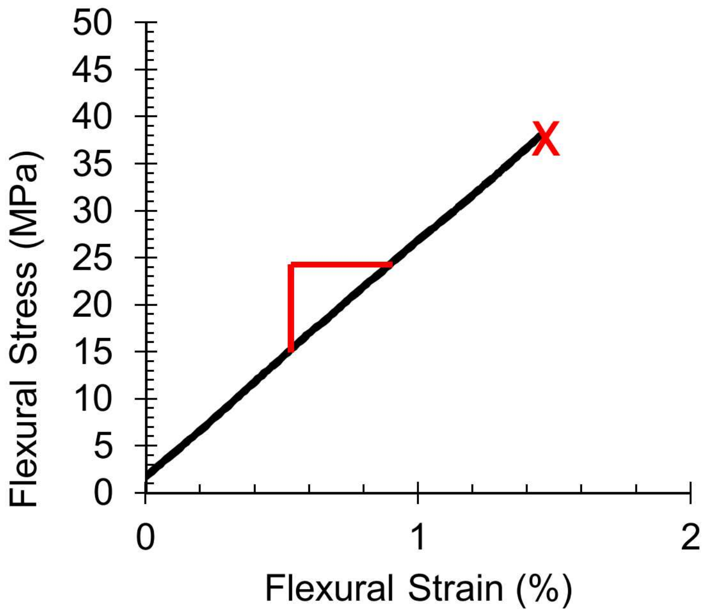
Example of isothermal cure data

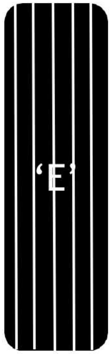


- The formulation with epoxy-silylated Na+ MMT has a slower onset of gelation than other formulations

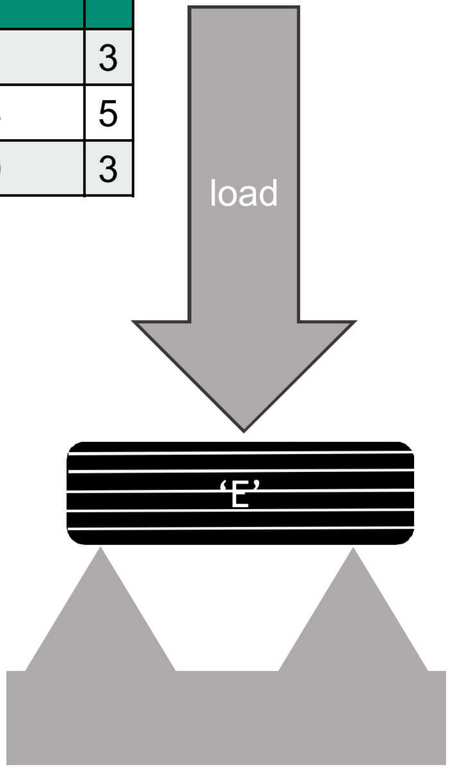
Impact of particle functionalization on mechanical properties

Functionalized vs unfunctionalized fillers, all "E"				
Filler Fully Cured	**Flexural Modulus (GPa)**	**Flexural Strength (MPa)**	**Particle size (nm)**	**n**
No filler	2.3 ± 0.2	35.8 ± 61.9	-	3
Un-silylated SiO_2	3.4 ± 0.2	88.4 ± 49.3	~554	5
Hexyltrimethoxysilylated SiO_2	2.9 ± 0.8	74.2 ± 11.6	~450	3





n= sample size



- The presence of fillers alone increases the flexural modulus
- However, there is no different in flexural modulus between the alkyl-chain functionalized and unfunctionalized fillers
- Have not tested epoxy functionalized fillers yet

Future work on particle functionalization

R': epoxy or acrylate functional group

Goals:

- Replace acrylate resin with acrylate-functionalized fillers
- Dual-functionalized particles to link epoxy and acrylate networks

Hybrid monomers to crosslink epoxy and acrylate networks

DIW using epoxy-acrylate hybrid monomer

Di-functional epoxy

Bisphenol A (BPA)
dimeth- or di- acrylate

Photoinitiator

Latent curing agent

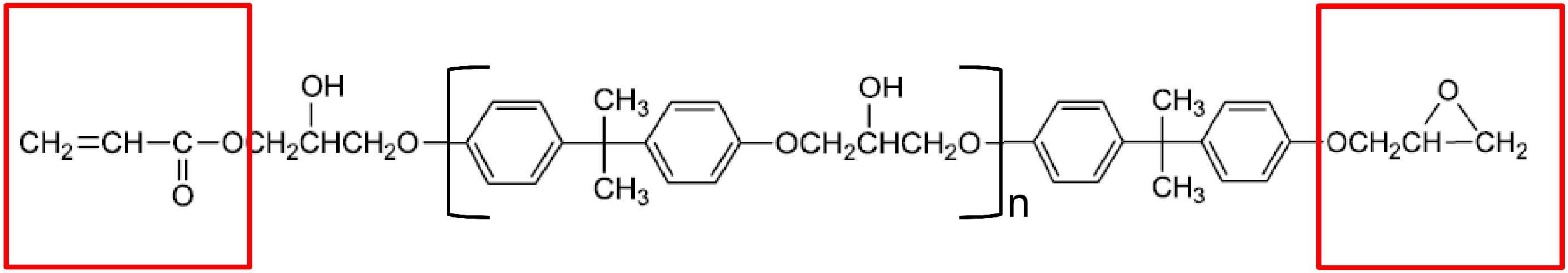
Filler

Epoxy-acrylate hybrid
monomer

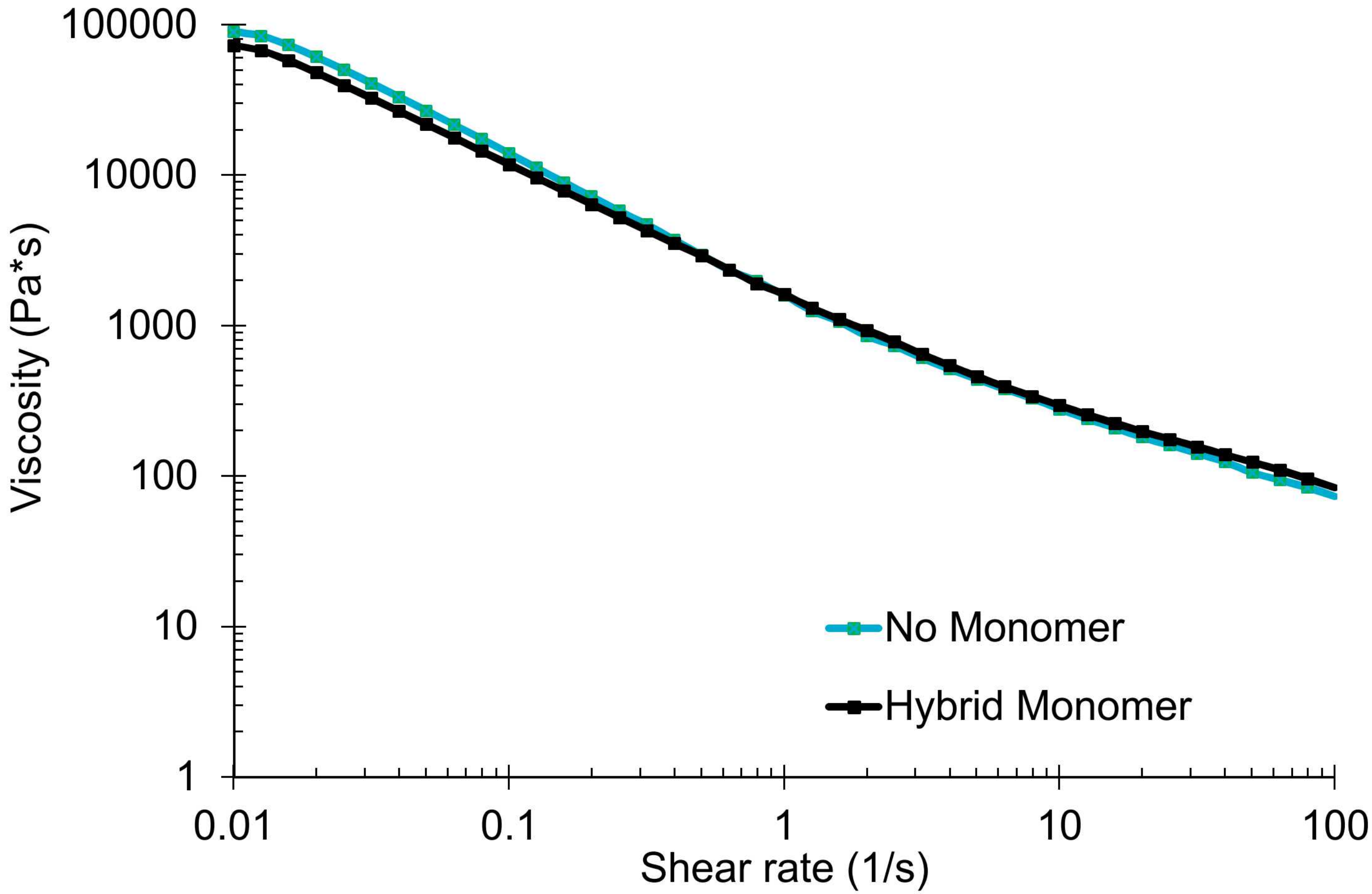
- Goal:
  - study the crosslinking behavior and cure kinetics of the epoxy-acrylate interpenetrating polymer network formation
    - Simpler structure to study before the addition of dual-functionalized filler particles

Acrylate-functionality

Epoxy-functionality

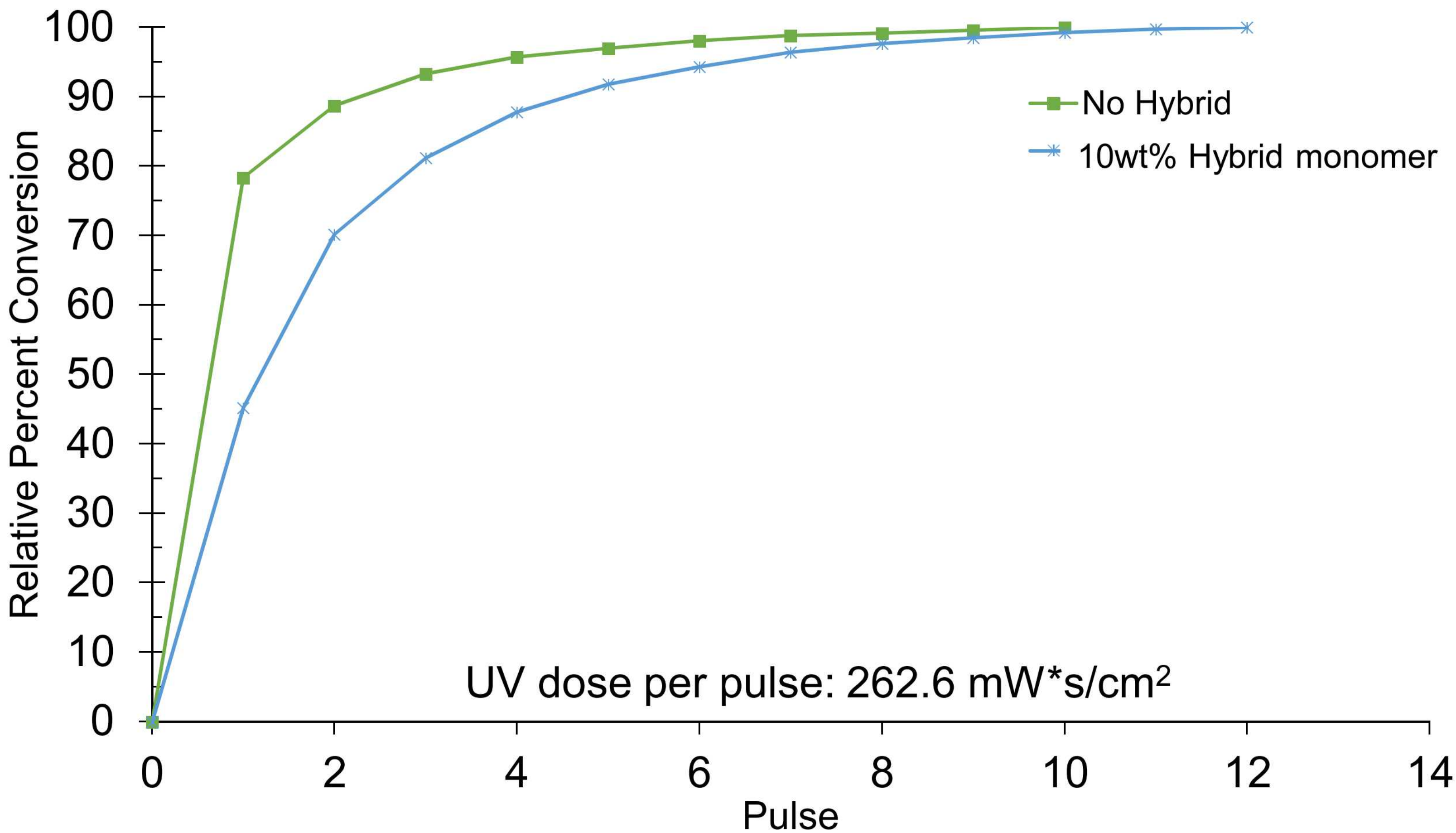


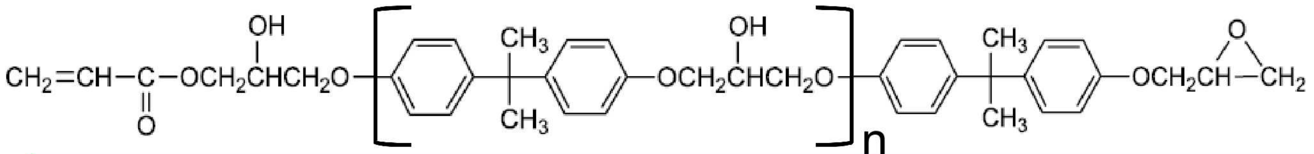
Effect of hybrid epoxy-acrylate monomer on viscosity



- The presence of the hybrid monomer does not change bulk rheological properties

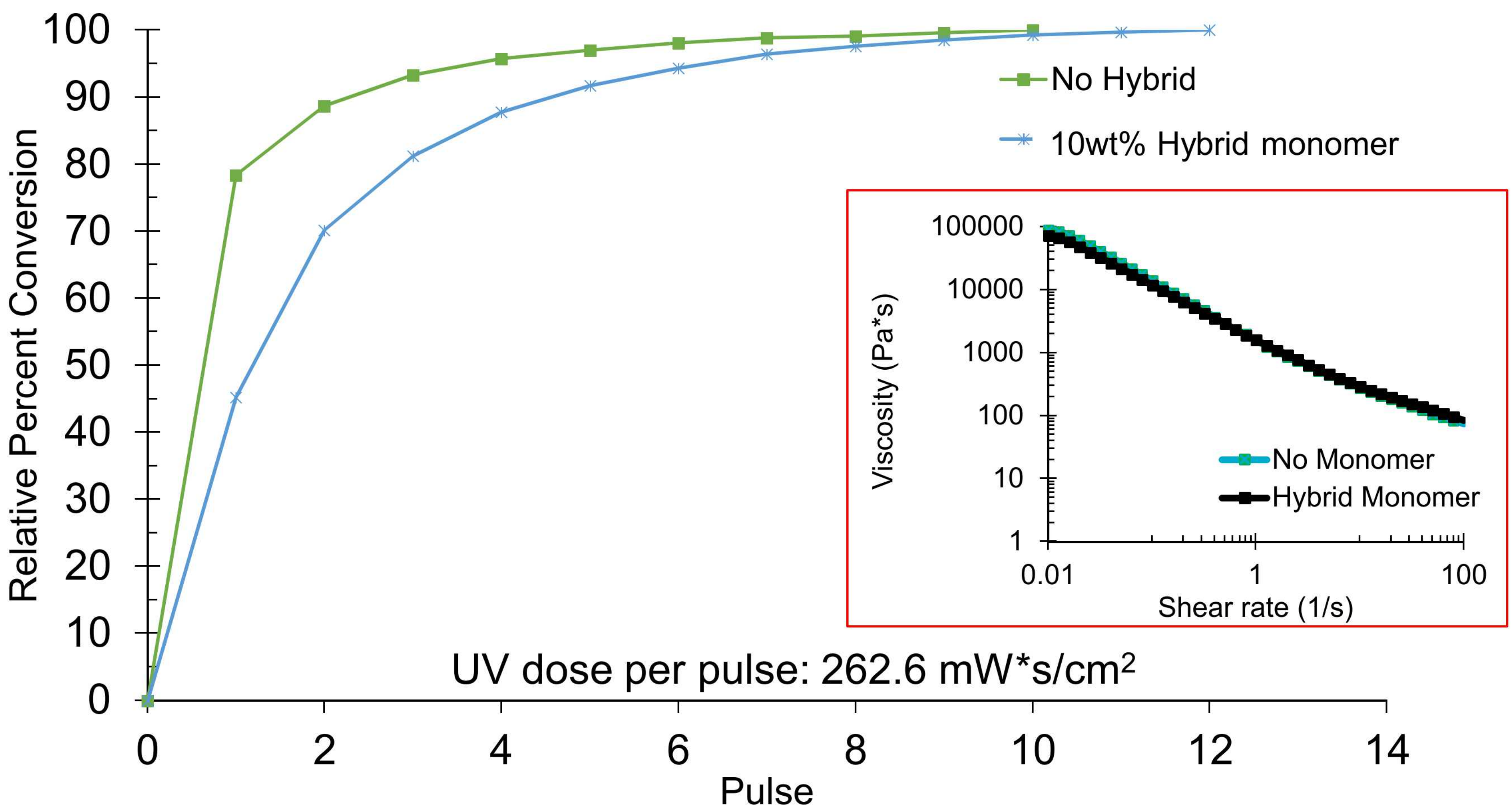
Effect of hybrid epoxy-acrylate monomer on UV-cure kinetics

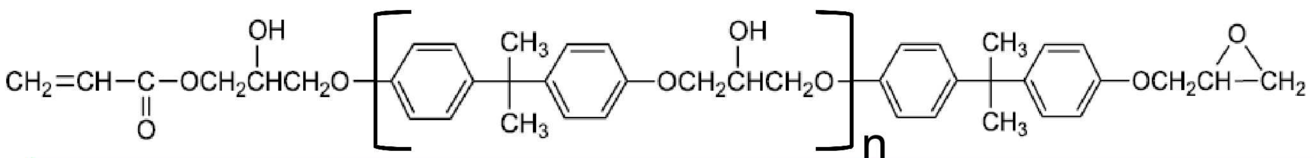




- The presence of the hybrid monomer decreases the rate of UV-cure, possibly due to having only one reactive site

Effect of hybrid epoxy-acrylate monomer on UV-cure kinetics



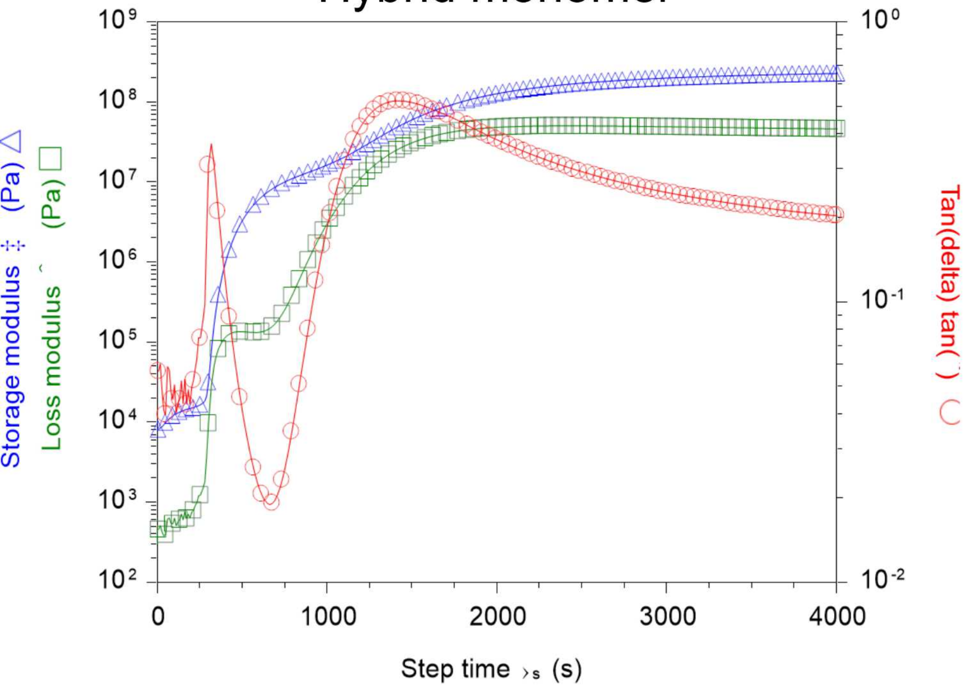


- There could be microstructure level effects even though bulk rheology is the same

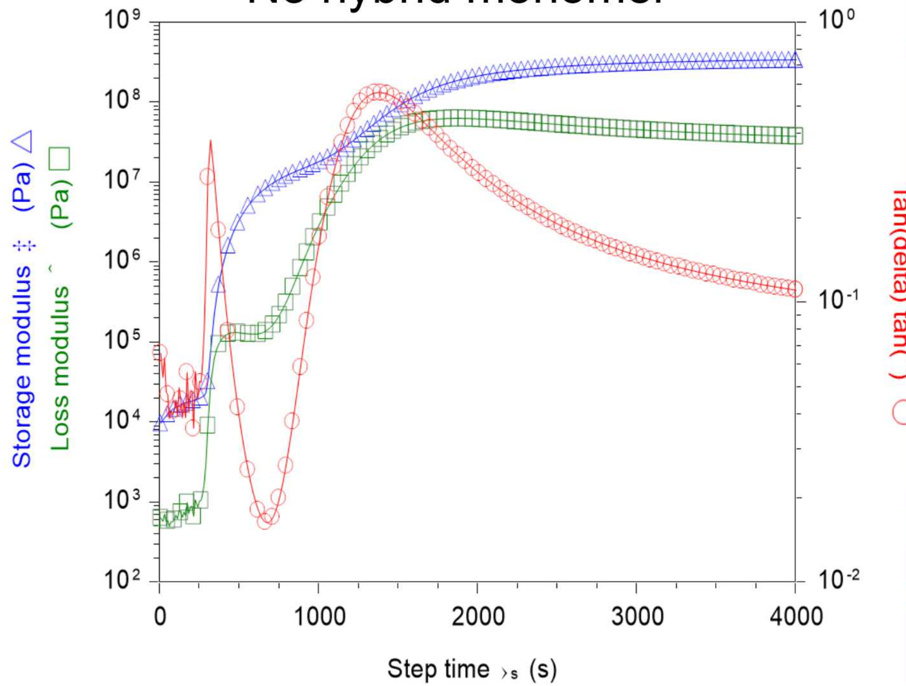
Impact of the hybrid monomer on the onset of gelation and formation of the epoxy network

150°C Isothermal cure, diacrylate, 5wt% filler			
Sample	**Tg (°C)**	**Onset of Gelation (s)**	**Vitrification (s)**
Hybrid monomer (10wt%)	156	319	1421
No hybrid monomer	162	322	1381

Hybrid monomer



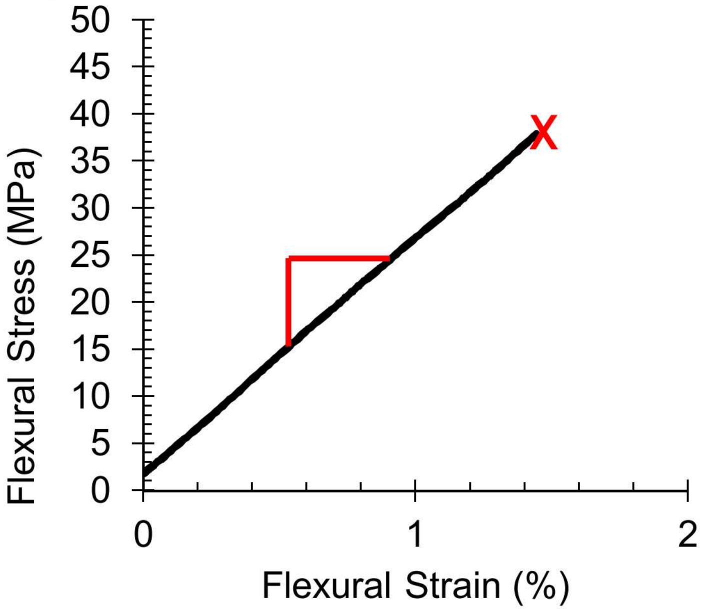
No hybrid monomer

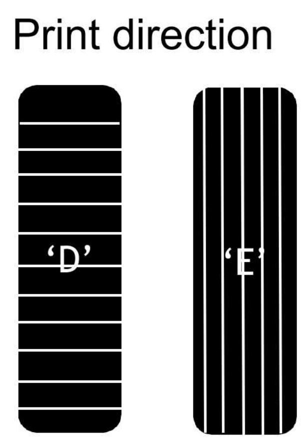


- The hybrid monomer does not impact the onset of gelation

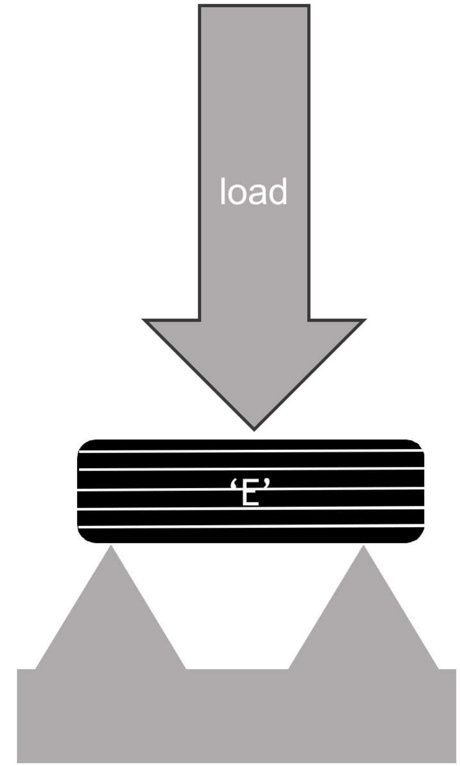
Impact of hybrid monomer on mechanical properties

5wt% loading of SiO_2			
Sample Fully Cured	**Flexural Modulus (GPa)**	**Flexural Strength (MPa)**	**n**
"D" No hybrid monomer	4.2 ± 0.0	151.9 ± 52.6	2
"E" No hybrid monomer	3.4 ± 0.2	88.4 ± 49.3	5
"D" 10wt% Hybrid monomer	3.4 ± 0.1	31.4 ± 0.8	3
"E" 10wt% Hybrid monomer	3.4 ± 0.3	35.7 ± 2.7	4





n= sample size



- Print direction appears to have an impact on the flexural modulus in the 'no hybrid' samples
- In contrast, there is no dependence on print direction for the "with hybrid" samples

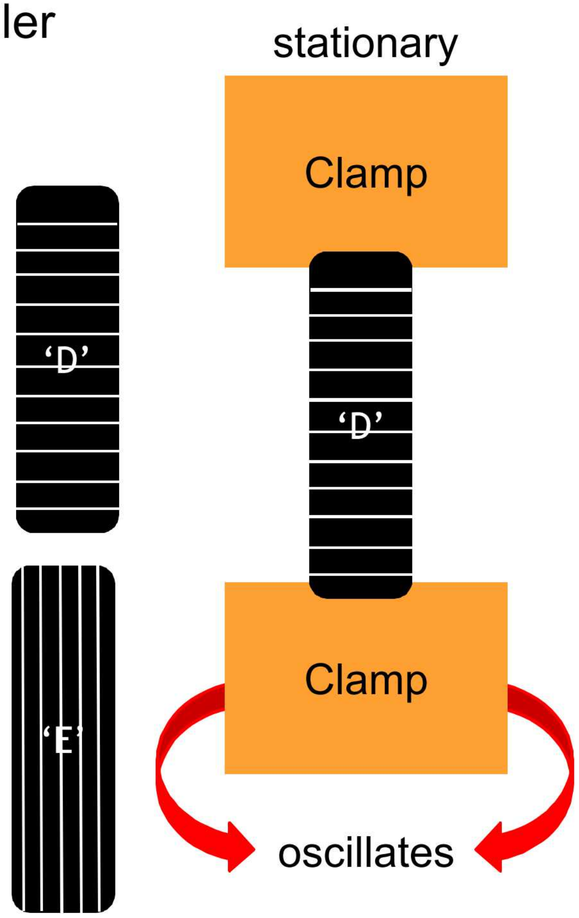
Impact of print direction and 10wt% hybrid monomer on the modulus & Tg

5wt% loading of unmodified SiO_2 filler

Room Temperature Measurement, Torsional DMA

30 min UV-cure only	
Sample "D"	Storage Modulus MPa
No hybrid monomer	12.6 ± 0.3
Hybrid monomer	3.5 ± 1.5

30 min UV-cure only	
Sample "E"	Storage Modulus MPa
No hybrid monomer	8.3 ± 1.3
Hybrid monomer	4.3 ± 1.6



- After UV-cure only, the presence of an epoxy-acrylate hybrid monomer results in a lower modulus of the UV-cured acrylate network
- There are print direction effects in samples not containing the hybrid monomer

Impact of print direction and 10wt% hybrid monomer on the modulus & Tg

5wt% loading of unmodified SiO_2 filler

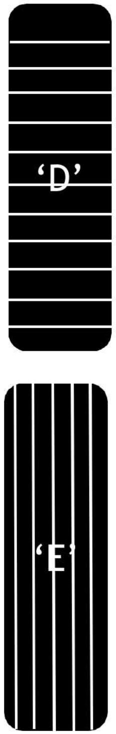
Room Temperature Measurement, Torsional DMA

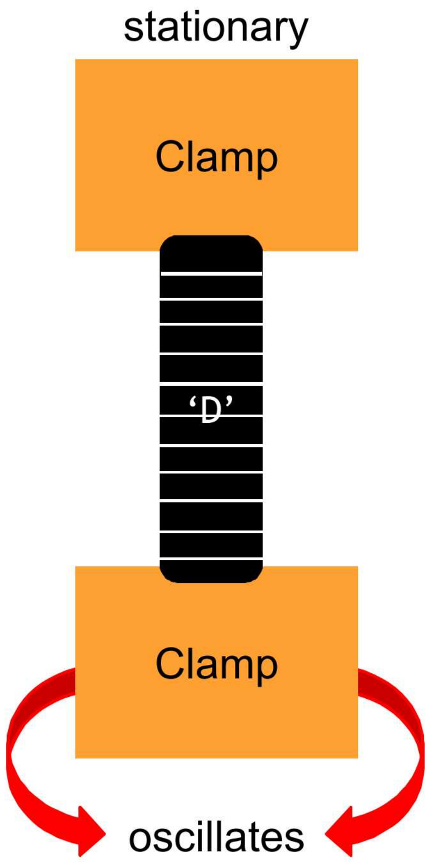
30 min UV-cure only	
Sample "D"	**Storage Modulus MPa**
No hybrid monomer	12.6 ± 0.3
Hybrid monomer	3.5 ± 1.5

Fully cured	
Sample "D"	**Storage Modulus MPa**
No hybrid monomer	813.9 ± 73.0
Hybrid monomer	633.0 ± 83.7

30 min UV-cure only	
Sample "E"	**Storage Modulus MPa**
No hybrid monomer	8.3 ± 1.3
Hybrid monomer	4.3 ± 1.6

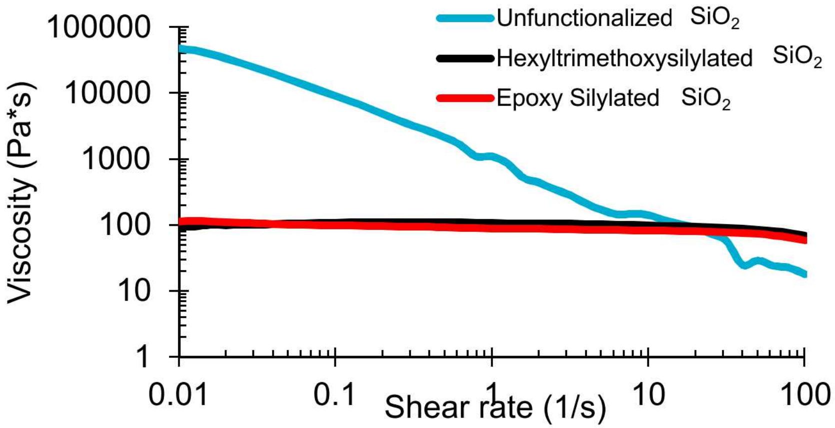
Fully cured	
Sample "E"	**Storage Modulus MPa**
No hybrid monomer	752.2 ± 58.1
Hybrid monomer	869.9 ± 69.6





- After UV and thermal cure, the hybrid monomer shows print direction effects while the "no hybrid monomer" samples do not
  - These results show different behavior than the flexural data
- The underlying mechanism causing these print direction effects is still being investigated

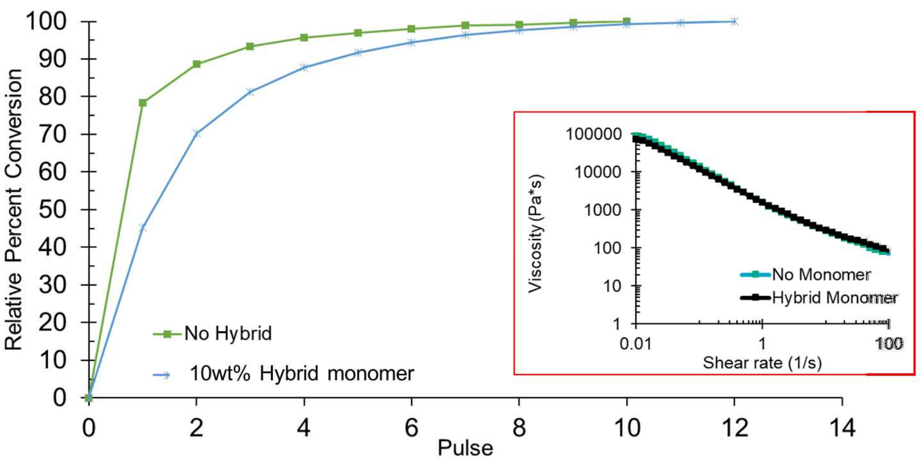
Conclusions



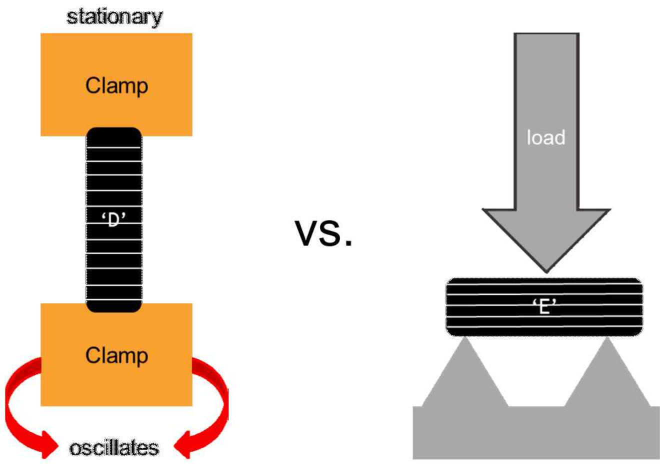
1. Functionalized particles exhibit low zero-shear viscosity and no shear- thinning behavior, but inks are printable at increased UV intensity

Filler Fully Cured	Flexural Modulus (GPa)
No filler	2.3 ± 0.2
Un-silylated SiO_2	3.4 ± 0.2
Hexyltrimethoxysilylated SiO_2	2.9 ± 0.8

2. The presence of fillers increases the flexural modulus of printed parts compared to unfilled resins, but functionalization does not have any impact



3. The epoxy-acrylate hybrid monomer alters the acrylate cure kinetics, but not the viscosity or isothermal gel point



4. Mechanical properties vary depending on print direction, presence of the hybrid monomer, cure profile, and test type

Mechanisms still under investigation

Thank You!

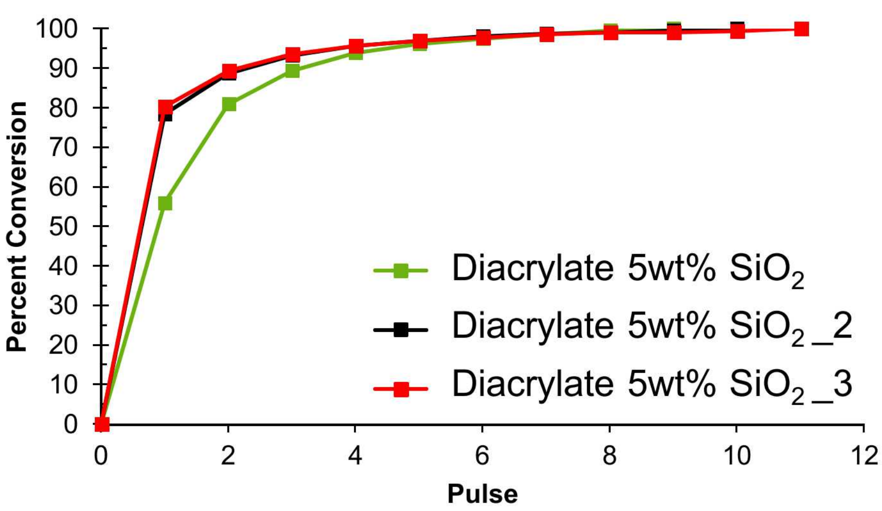
Dosage calculations

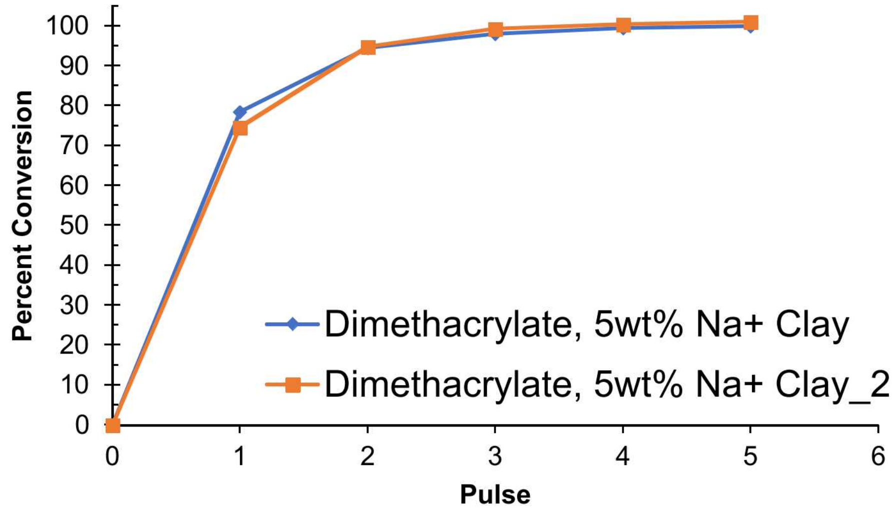
Device	Wavelength & Dosage	power % 1	5	10	20	40	80	
Dual UV probes at AML	365nm	1.2	6.9	14.3	29	57.3	106.3	Measured intensity (mW/cm^2)
	Dosage (190s)	228	1,311	2,717	5,510	10,887	20,197	
Bulk UV cure light at AML	365nm	5.7						
	Dosage (1800s)	10,260						
Photocalorimetry DSC	365nm	-	44.9	109.4	207.2	326.5	413.2	
	Dosage (12s)	-	539	1313	2,486	3,918	4,958	

Dosage: Intensity*time of exposure

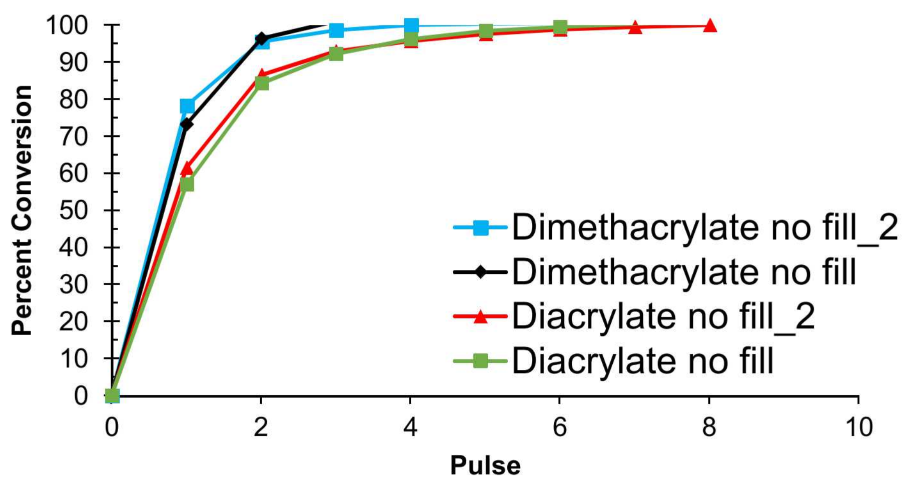
UV probes: continuous coverage for 190s
Bulk UV: continuous coverage for 1800s
Photocalorimetry: 5 x 2.4s flashes

UV-DSC is repeatable, under the same conditions





Run 1 is off because the lamp had not fully warmed up



Regardless of filler-type or acrylate used, the UV-DSC results are repeatable and reproducible across multiple samples and multiple days