SAND2020-2950C

Cure Behavior and Thermo-Mechanical Properties of Dual-Cure Thermoset Resins Containing Functionalized Fillers

Center 1800:
Material, Physical and Chemical Sciences

PRESENTED BY

Jessica Kopatz

J. Kopatz, D. Reinholtz, A. Cook, L.N. Appelhans

SAND # HERE

Why is there an interest in using thermoset materials for additive manufacturing?

Thermosets

Pros	Cons
More resistant against high temperatures	Can not be recycled
Hard and rigid	Can not be remolded/reshaped
Excellent dimensional stability	

Thermoplastics

Pros	Cons
Can be recycled	Soften when heated
Can be remolded/reshaped	Not a liquid at room temperature
Can be crystalline	

credit: https://www.modorplastics.com/plastics-learning-center/thermoset-vs-thermoplastics/

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Excellent dimensional stability	

Thermosets are more dimensionally, thermally, and mechanically robust compared to thermoplastic materials

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Additive manufacturing offers the ability to design low-volume, high complex geometric parts

Fused Filament Fabrication

- **Thermoplastic materials**
- Strengths: material $, print speed
- Disadvantages: Accuracy, **porous, anisotropic mechanical properties**

Stereolithography

- **Any photocurable polymer freely flowing at room temperature**
- Strengths: **dimensional accuracy,** Disadvantages: **material flexibility**, print speed

Selective Laser Sintering

- **Metals**, thermoplastic polymers
- Strengths: accuracy, material $ and flexibility
- Disadvantages: **amount of material**

Direct Ink Writing

- Ceramic and/or metal suspensions, **thermosets**
- Strengths: material flexibility, **minimal porosity**
- Disadvantages: print speed, printer limitations based on viscosity range

Melchels et al. *Biomaterials,* vol. 31, no. 24, pp. 6121-30, Aug 2010
Dizon et al. *Additive Manufacturing,* vol. 20, pp. 44-67, 2018.
Feeney et al. sd3d. FFF vs SLA vs SLS 3D printing. 2013.
Lewis et al. *Materials Today*. July/August 2004

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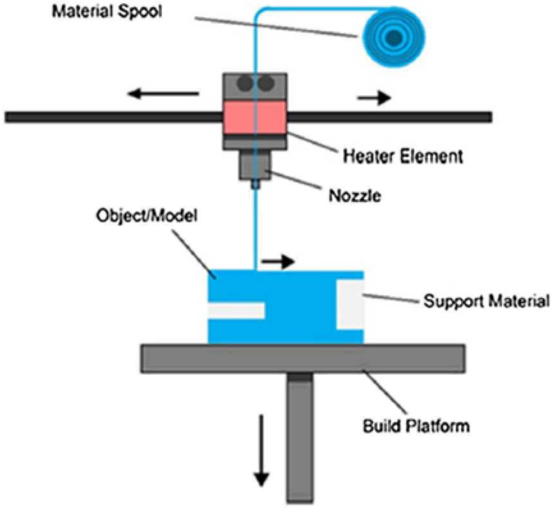

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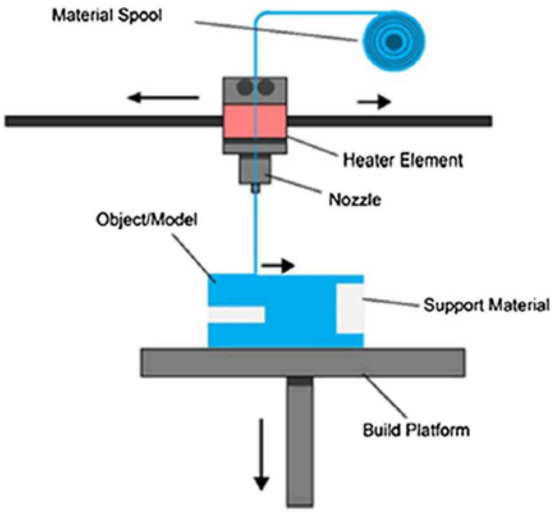

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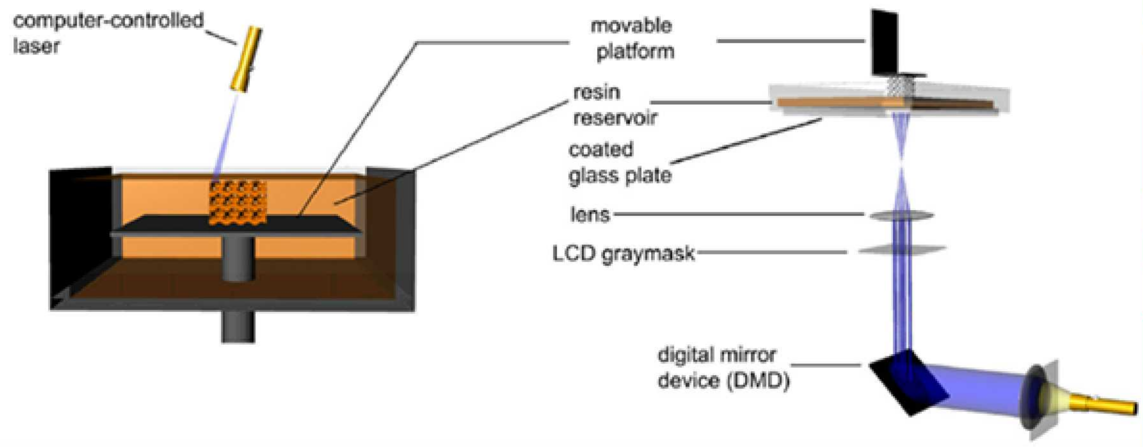

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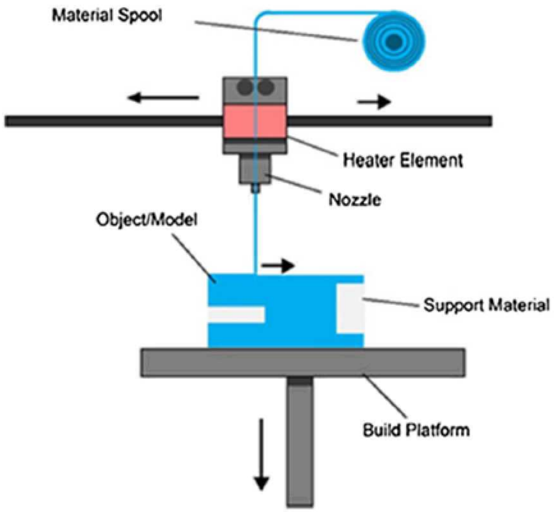

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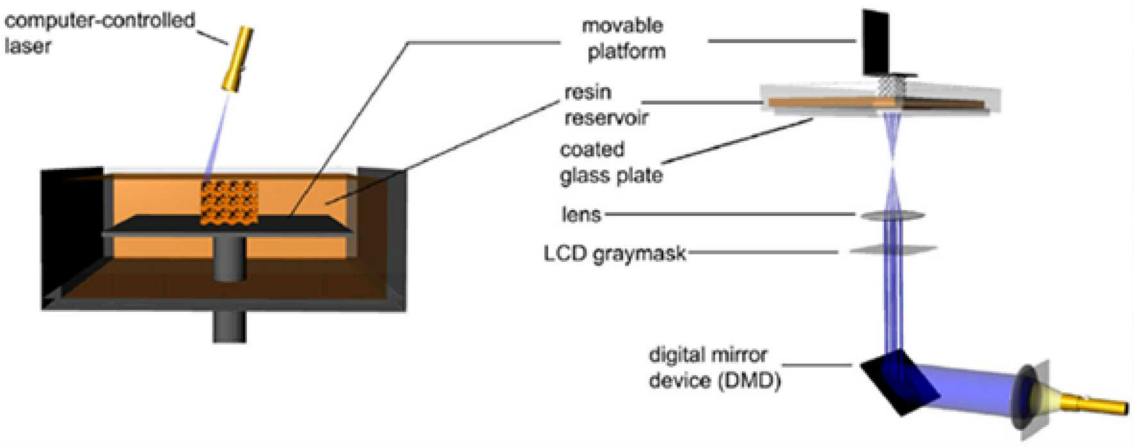

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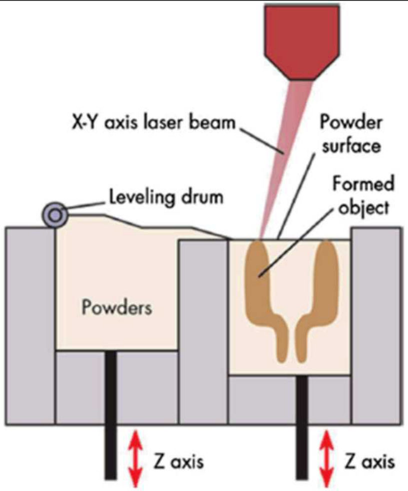

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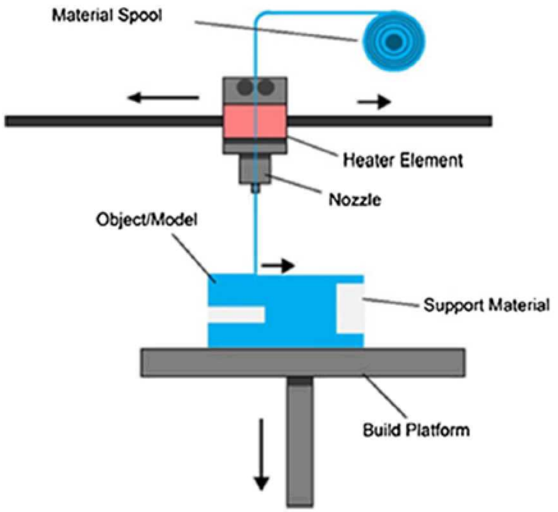

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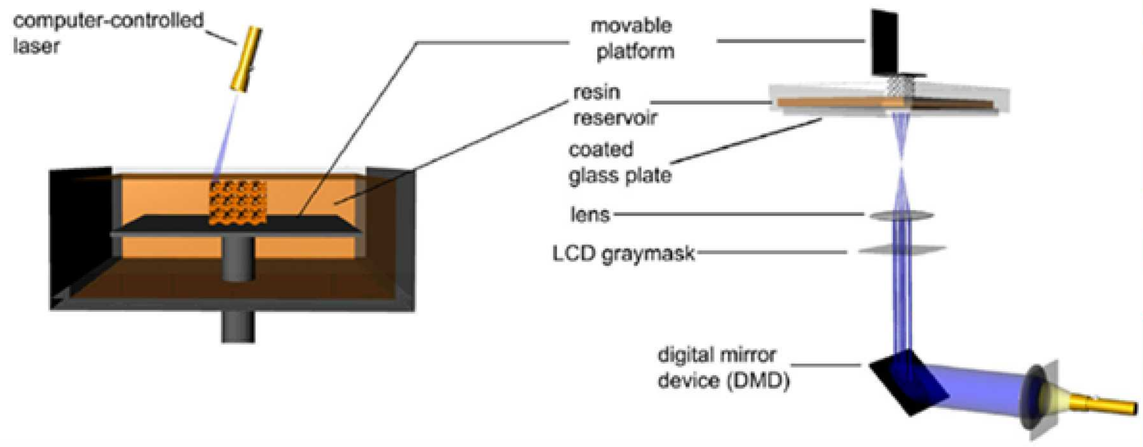

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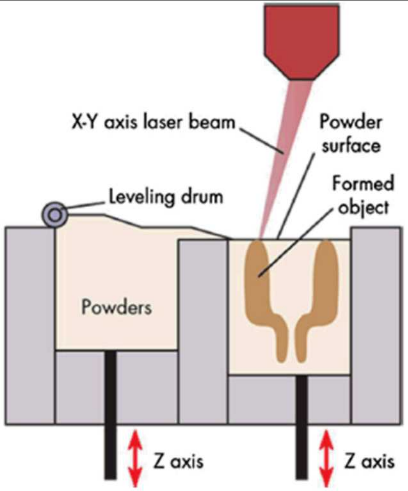

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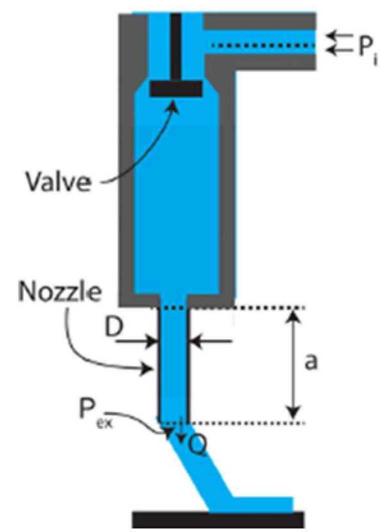

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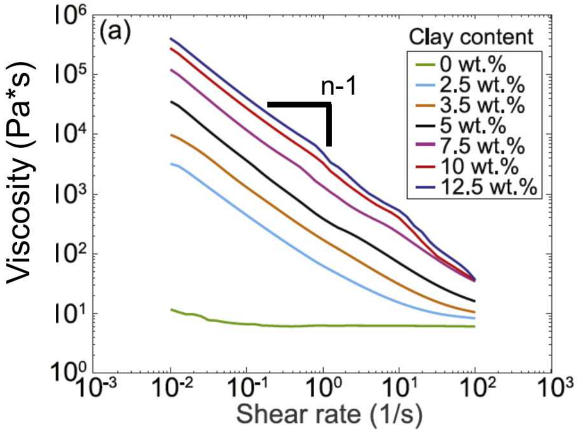
Approaches to DIW printing thermosets

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*
    - Dependent on filler type
- Clogging
- Interlayer inhomogeneity

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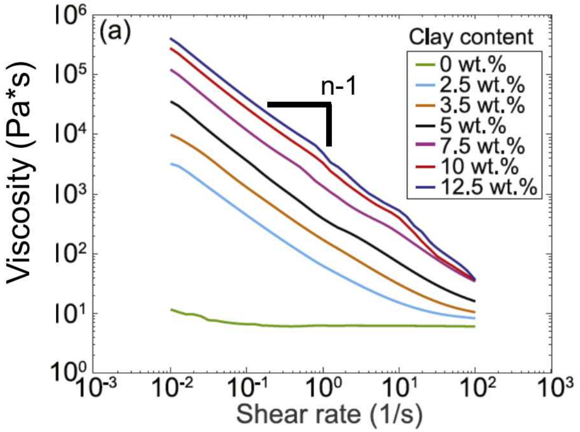

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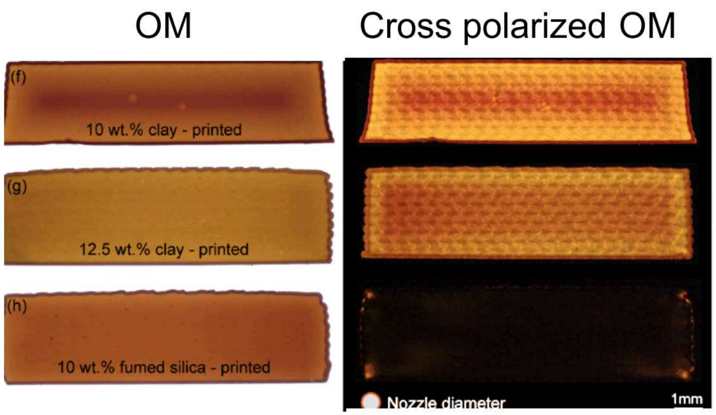

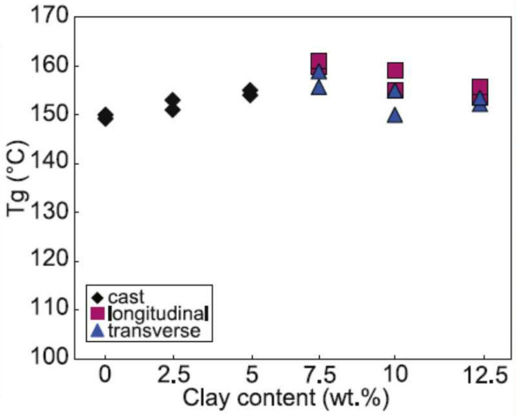

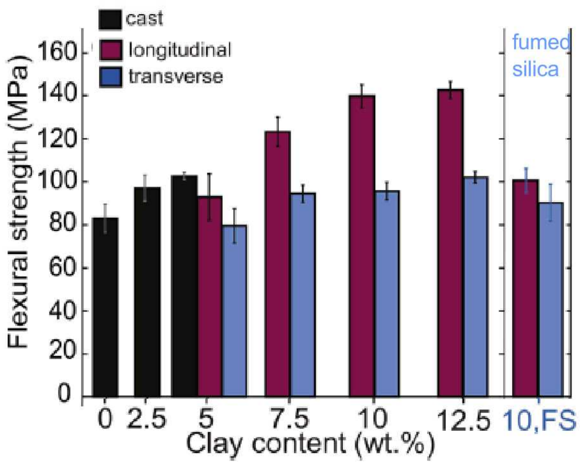

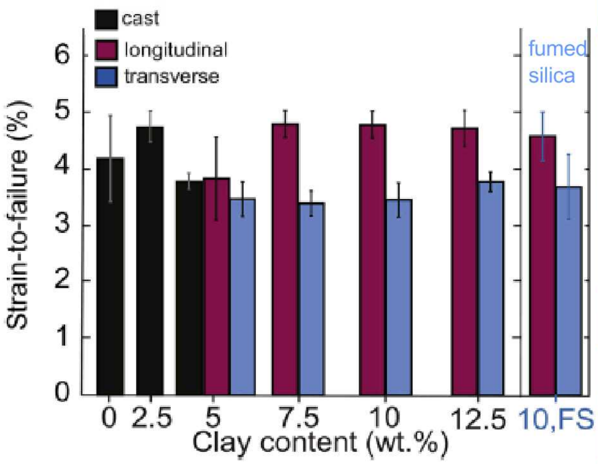

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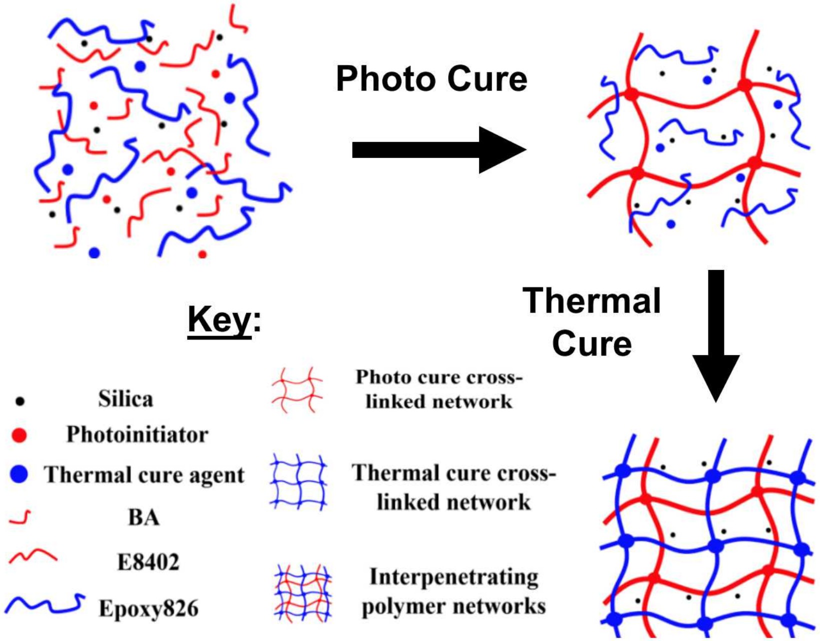
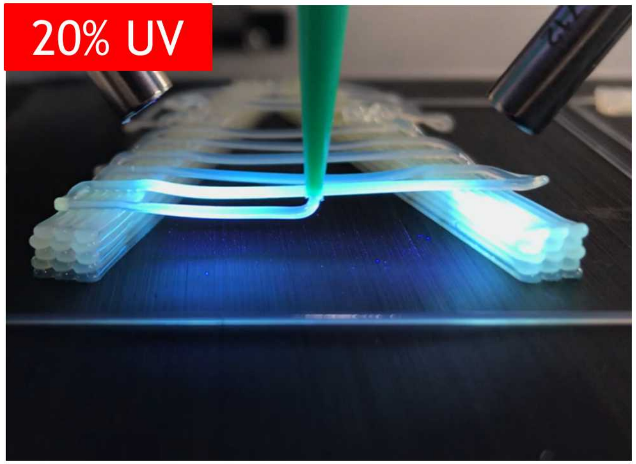
Approach 2: Dual-cure networks



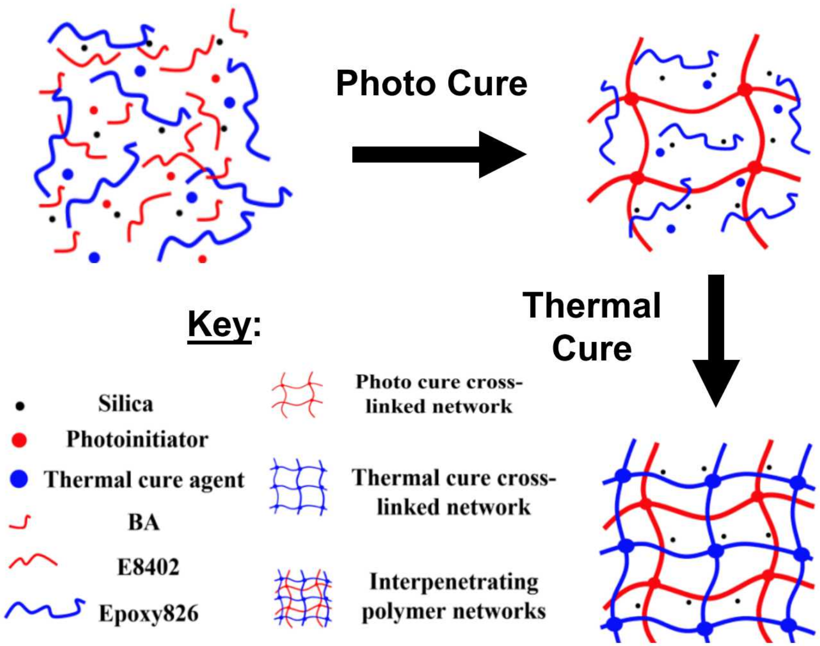
Chen et al. *Soft Matter.* 2018. Vol 14.

Limitations:
- Photocurable acrylates
- May require ex-situ UV individual layer cure



Approaches to DIW printing thermosets

Approach 2: Dual-cure networks



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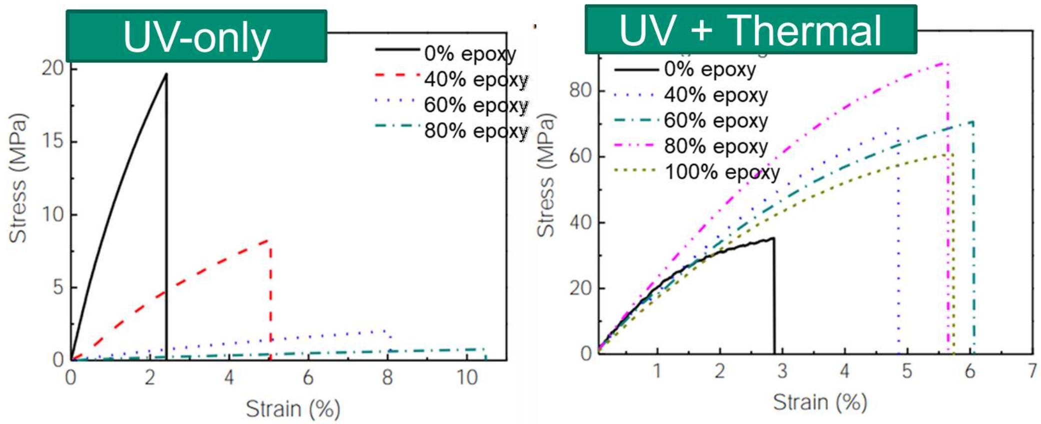
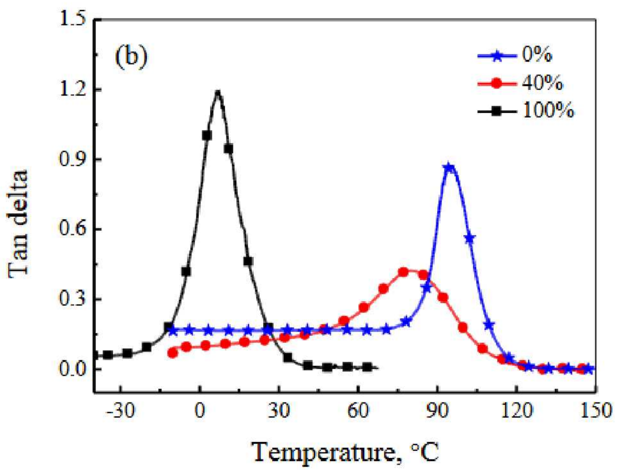


Tensile stress-strain curves of dual-cure photopolymer-epoxy samples with varying amounts of epoxy after 1st stage (green part) and 2nd stage (fully cured) cure exposures

Kuang et al. Macromol. Rapid. Commun. 2018. vol 39



Variable temperature DMA of fully cured resins ranging from 0-100% acrylate

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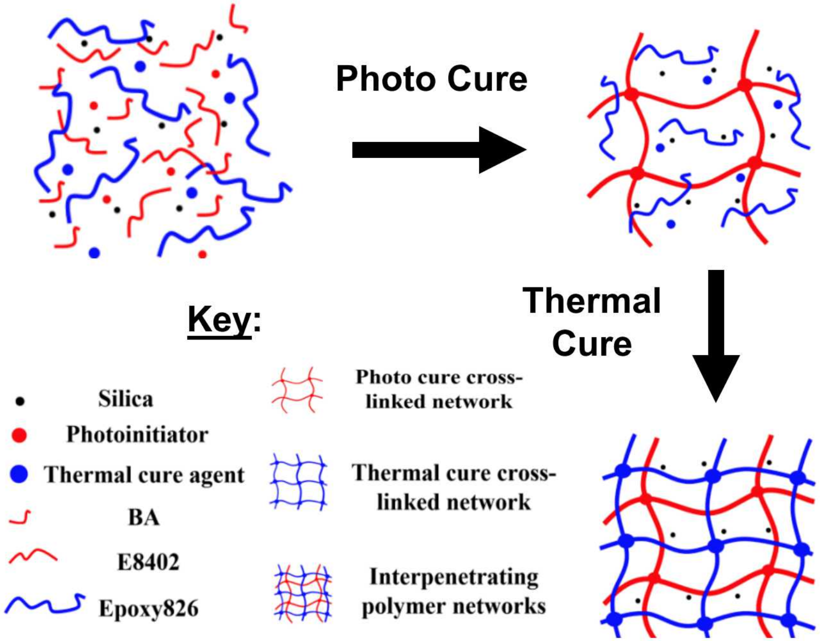

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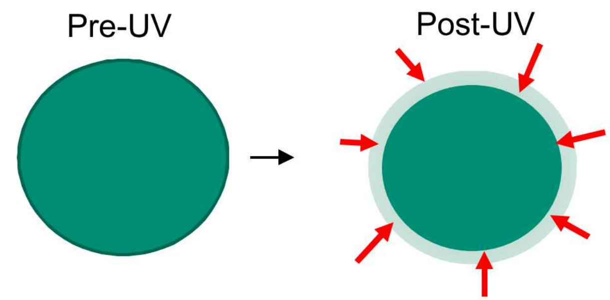
Shrinkage



Due to formation of covalent bonds

Aging

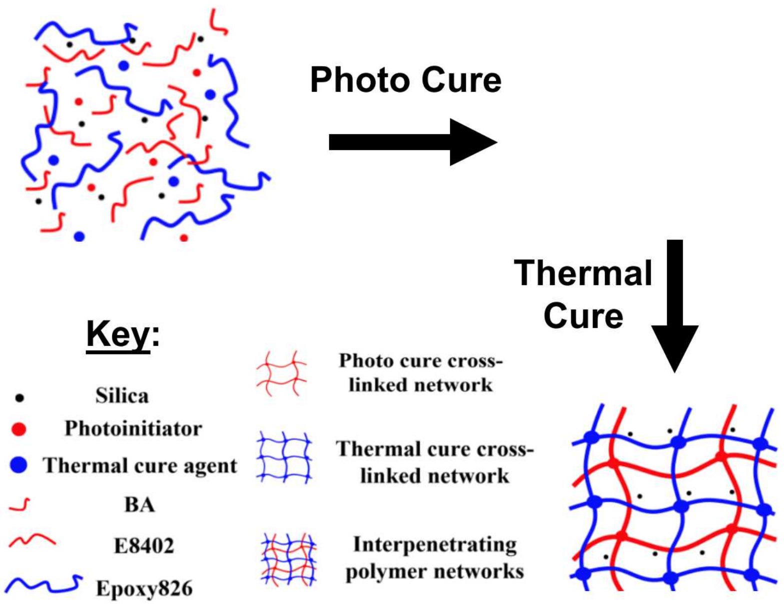
- Degradation of mechanical properties

Mechanical properties

- Variable degree of cure
    - Oxygen inhibition could be an issue
- Tend to be brittle
- Low Tg's

Using functionalized fillers in dual-cure networks

Approach 2: Dual-cure networks



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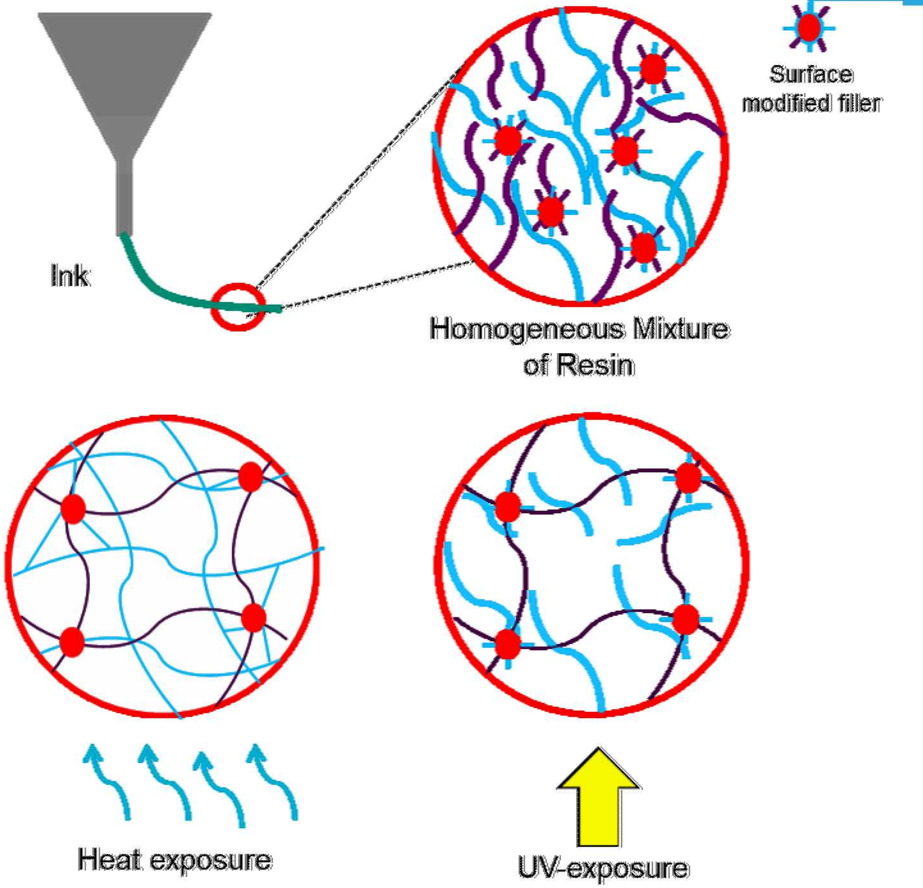


Solution:

- Addition of acrylate-functionalized fillers to decrease overall amount of acrylate necessary to form a stable structure while printing
- Addition of dual-functionalized fillers to tether networks together in a dual-cure system

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

Functionalized Fillers

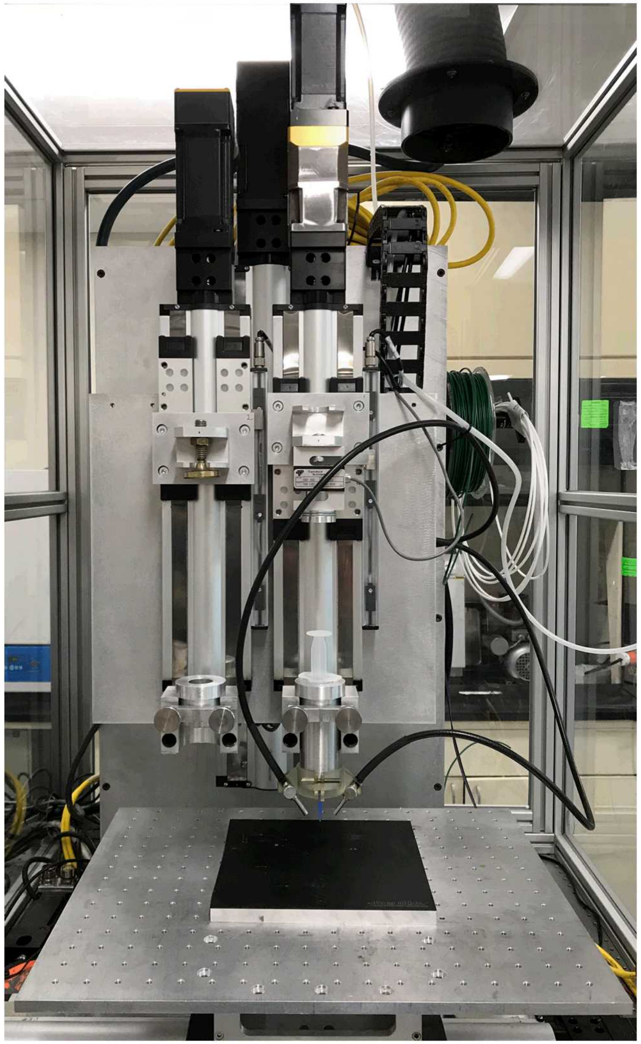
R': epoxy or acrylate
functional group

Goals:

- Replace acrylate resin with acrylate-functionalized fillers
- Add epoxy-functionalized fillers to help form epoxy network
- Dual-functionalized particles to link epoxy and acrylate networks

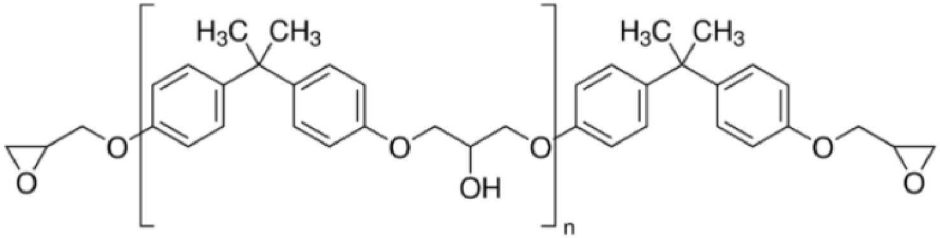
UV-assisted Direct-Ink Write Capability

- Constant volume
  - Allows for better extrusion control of resins having varying rheology
- 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

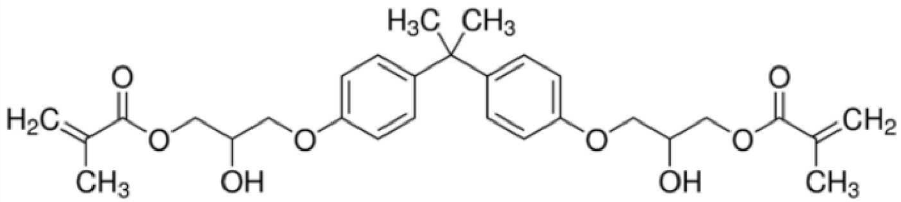


Printer Acknowledgement:
Adam Cook & Derek Reinholtz

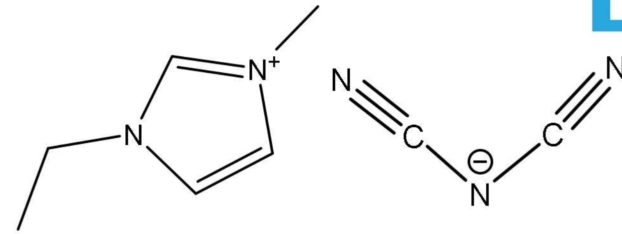
DIW dual-cure formulations



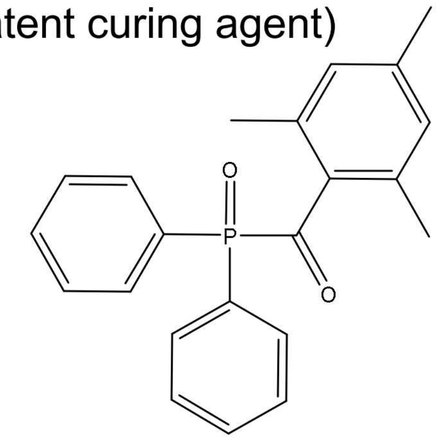
MW= 188/epoxy, n=0.2



MW= 256.3/acrylate



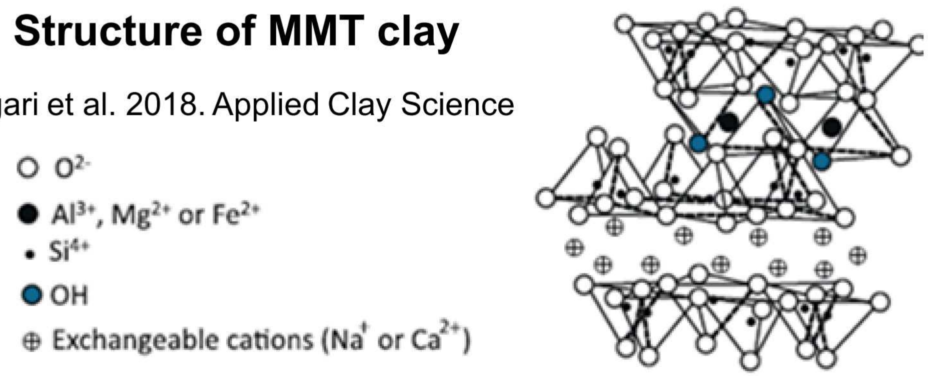
1-ethyl 3-methyl imidazolium dicyanamide
(latent curing agent)



TPO (photoinitiator)

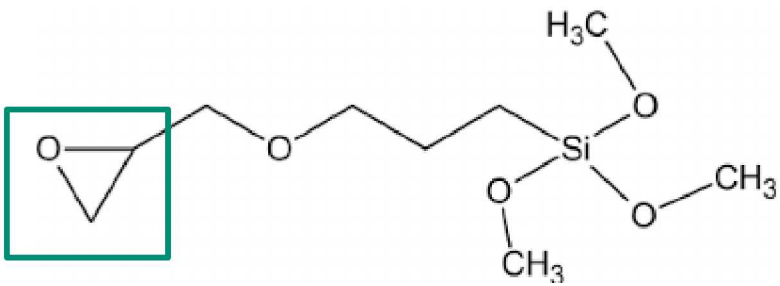
Structure of MMT clay

Asgari et al. 2018. Applied Clay Science

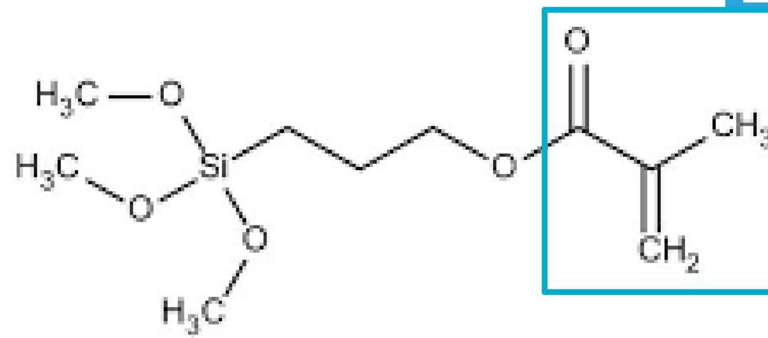


Filler materials: fumed silica and Na^{+} montmorillonite

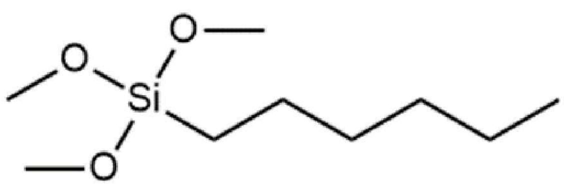
Silanes and filler materials investigated



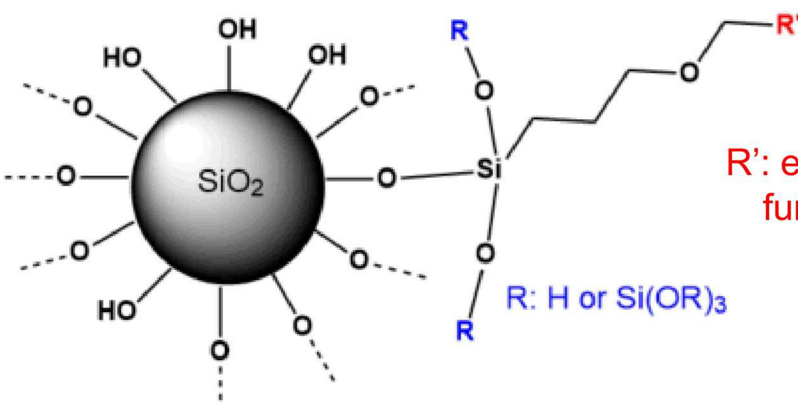
Glycidoxypropyltrimethoxy silane



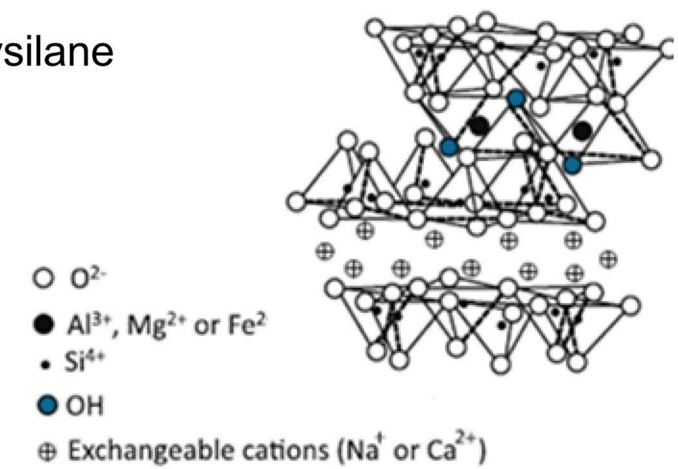
methacryloxypropyltrimethoxy silane



Hexyltrimethoxysilane



R': epoxy or acrylate functional group



Structure of MMT clay

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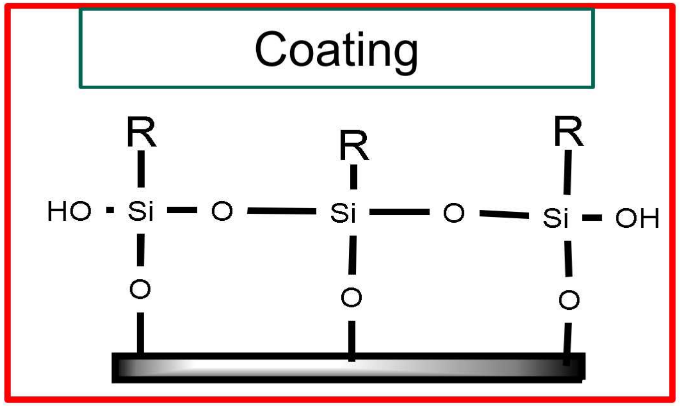
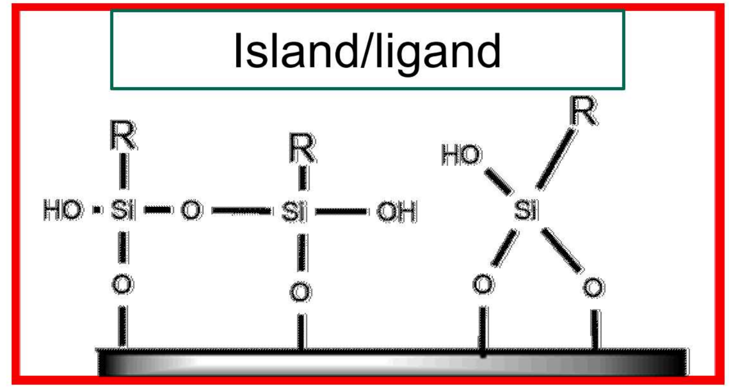
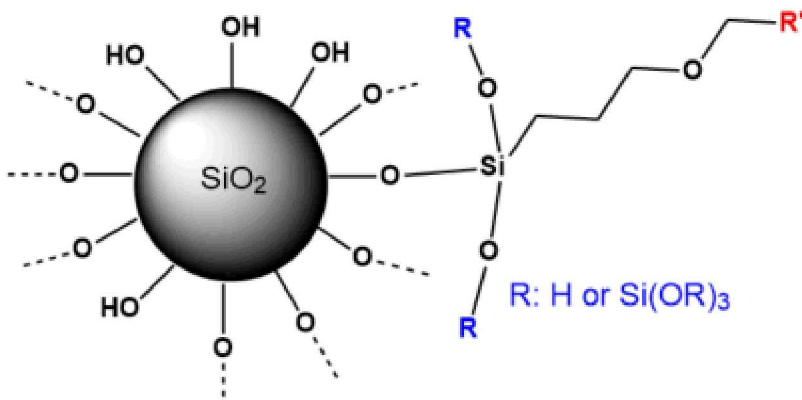
Silane grafting mechanisms







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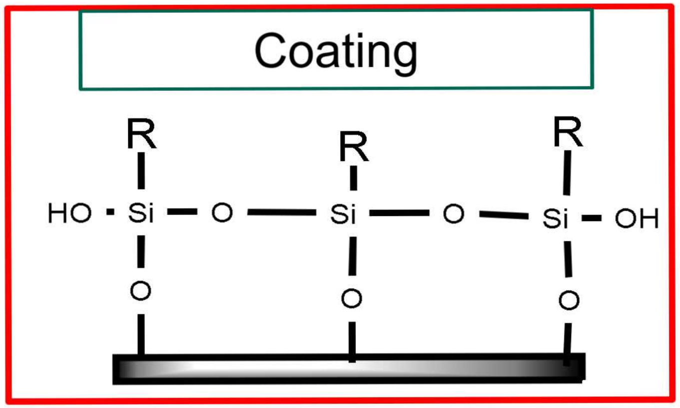
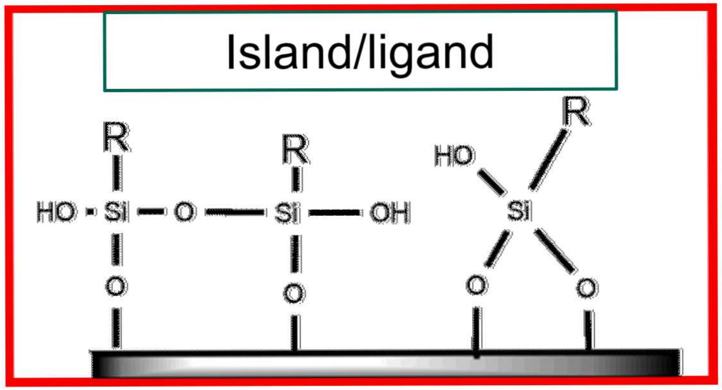
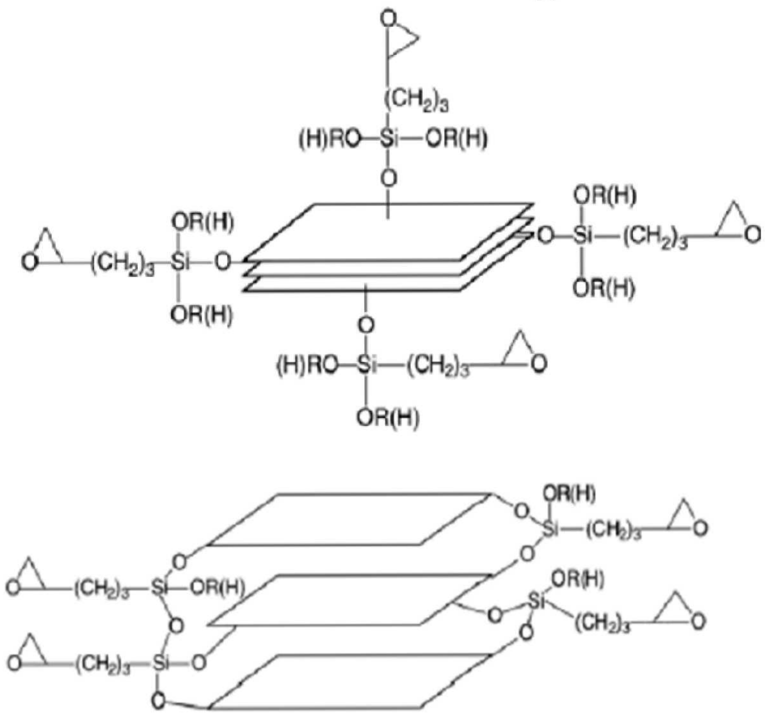
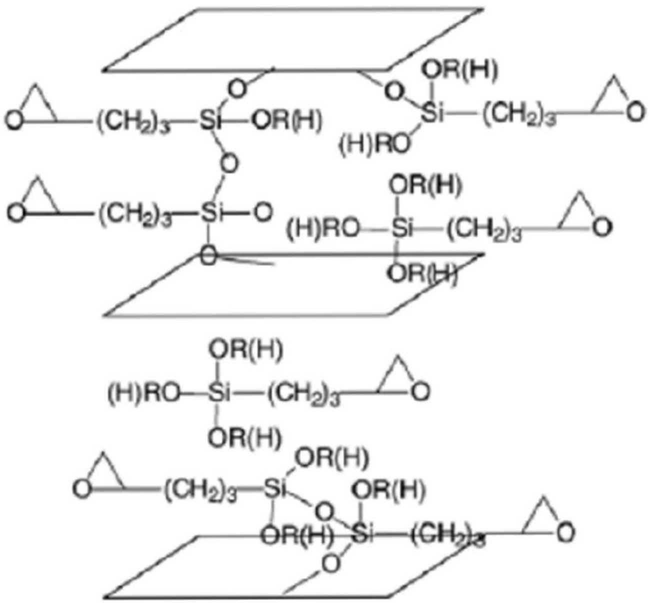




Grafting

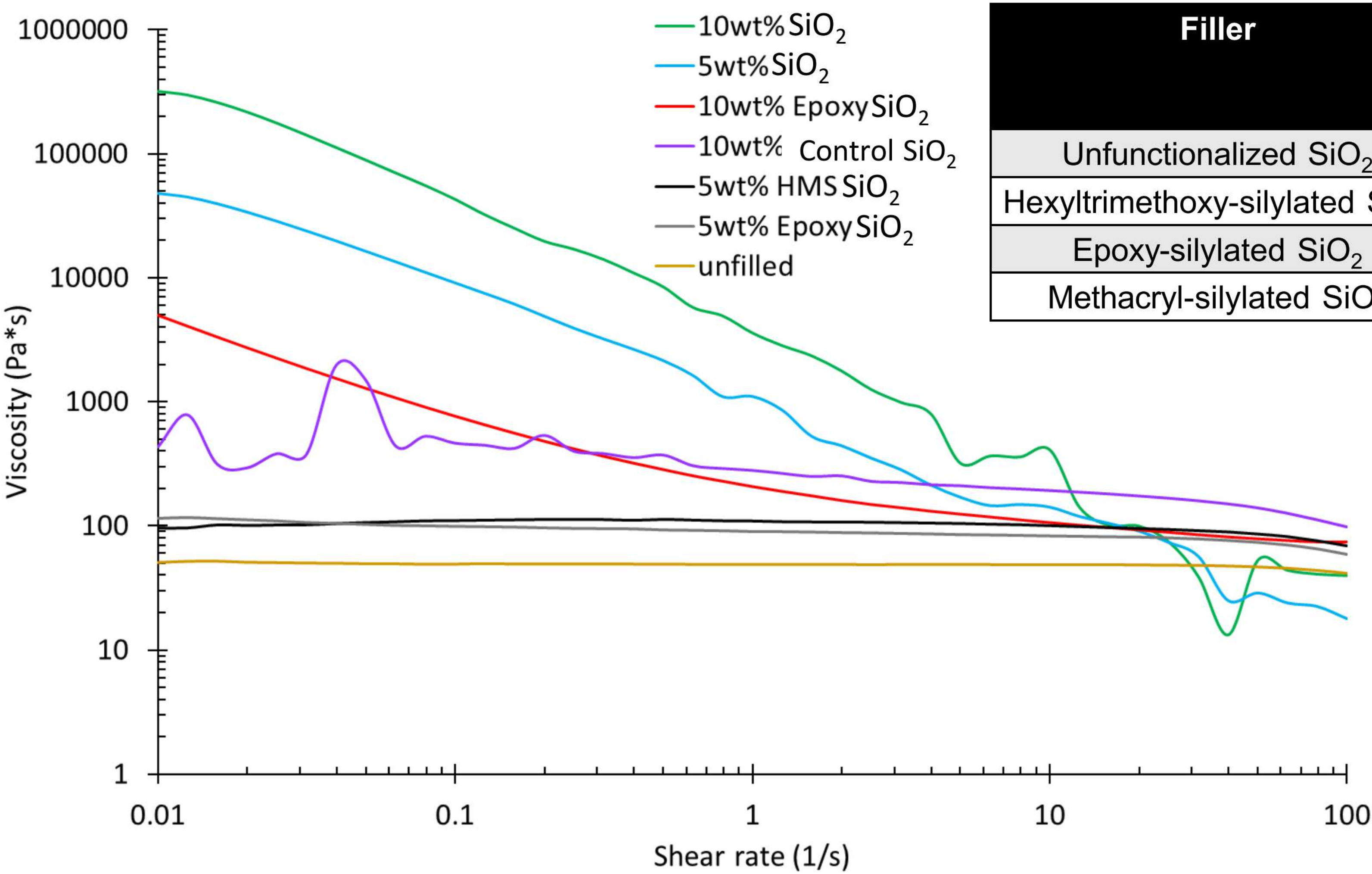


Intercalation &/or Grafting



Gianni et al. 2008 Appl.ClaySci. (42) pp. 116-124

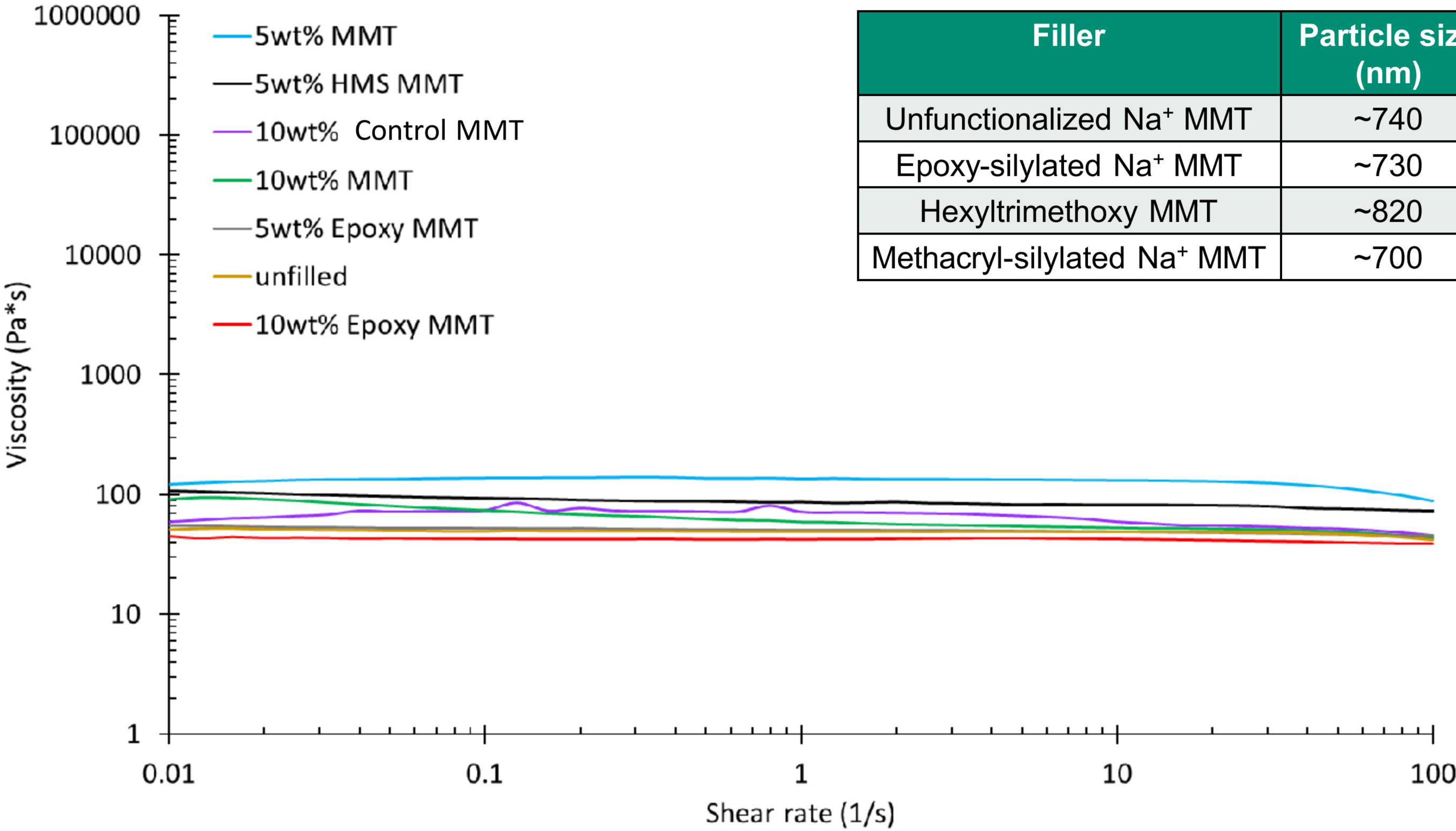
Effect of silica functionalization on viscosity



Filler	Particle size (nm)
Unfunctionalized SiO_2	~554
Hexyltrimethoxy-silylated SiO_2	~450
Epoxy-silylated SiO_2	~340
Methacryl-silylated SiO_2	~210

- Formulations with functionalized SiO_2 do not exhibit shear thinning behavior due to surface polarity changes
- Settling of particles is not observed
- All formulations are printable using a higher UV intensity

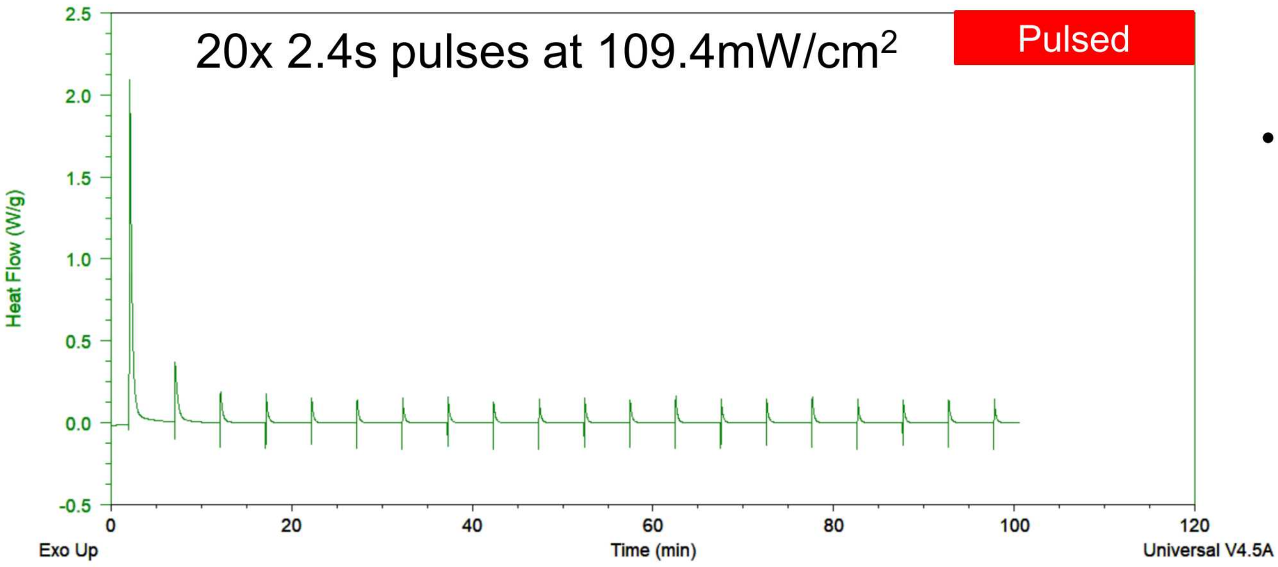
Effect of functionalized clay on viscosity



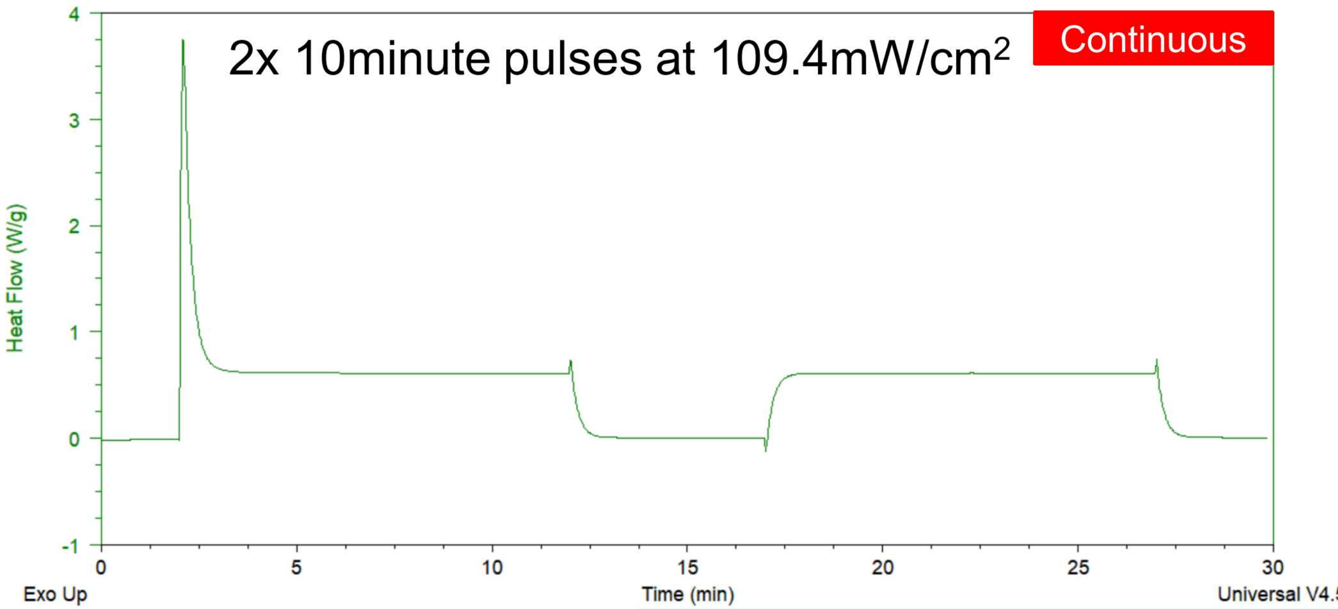
Filler	Particle size (nm)
Unfunctionalized Na^+ MMT	~740
Epoxy-silylated Na^+ MMT	~730
Hexyltrimethoxy MMT	~820
Methacryl-silylated Na^+ MMT	~700

- 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

Studying acrylate cure kinetics and conversion



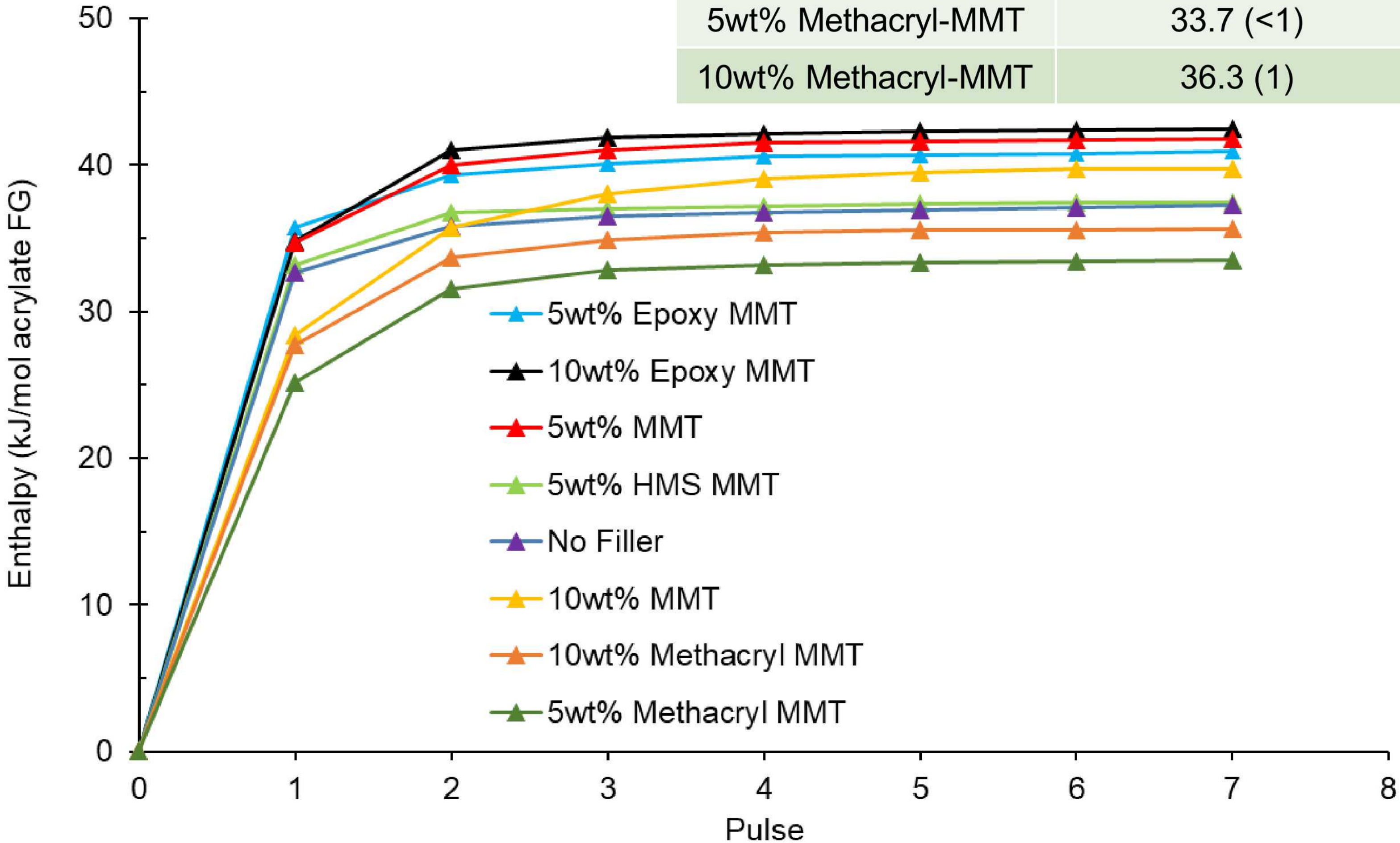
- Representative of cure kinetics observed while part is being printed



- Representative of cure observed post-print during the flood cure
- Gives idea of 'final' conversion

Effect of functionalized MMT on UV-cure kinetics

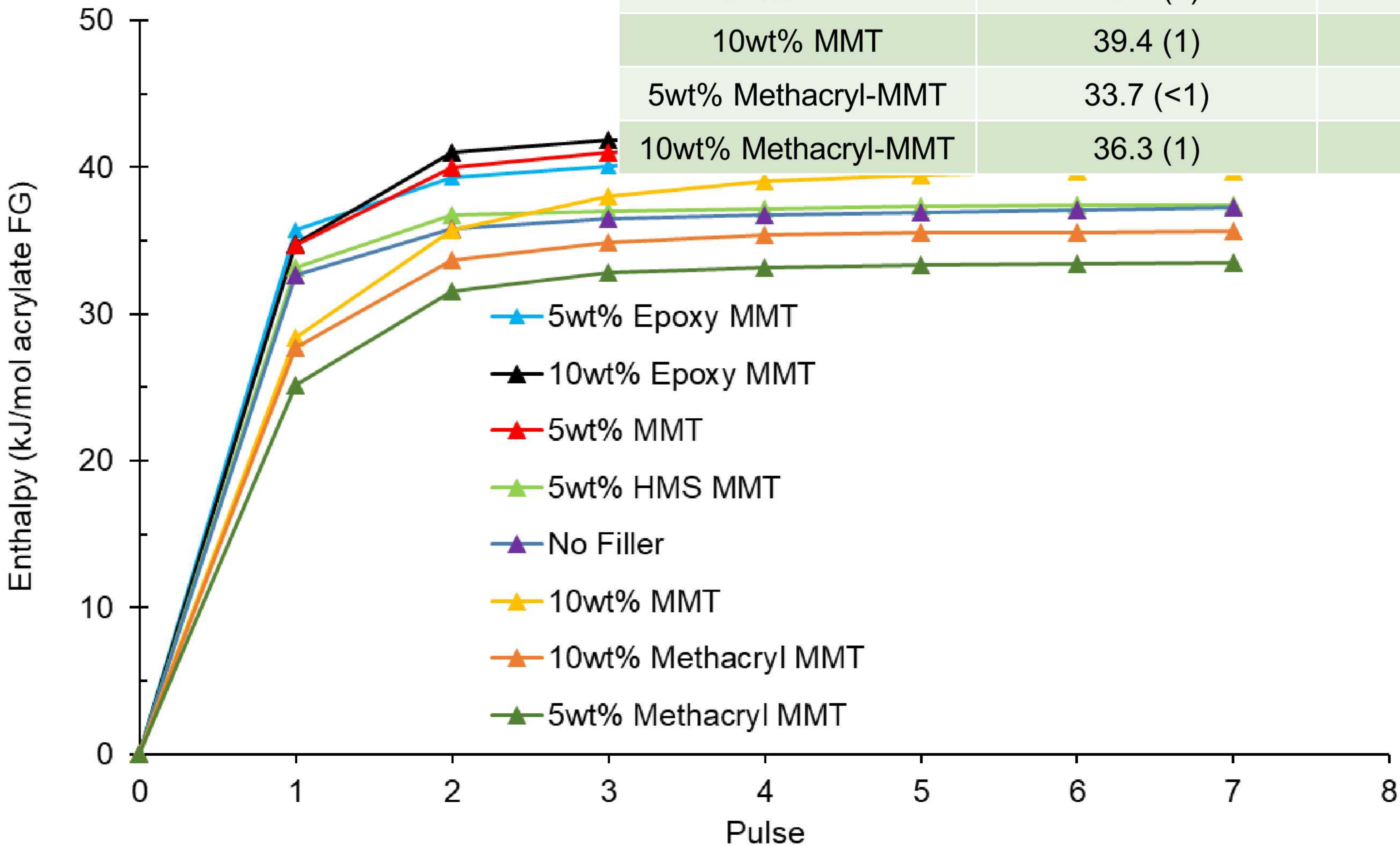
Composition	Enthalpy / mol acrylate (kJ/mol ac)	% conversion
No filler	37.3 (<1)	66
5wt% MMT	40.7 (1)	72
10wt% MMT	39.4 (1)	70
5wt% Methacryl-MMT	33.7 (<1)	59
10wt% Methacryl-MMT	36.3 (1)	64



Effect of functionalized MMT on UV-cure kinetics

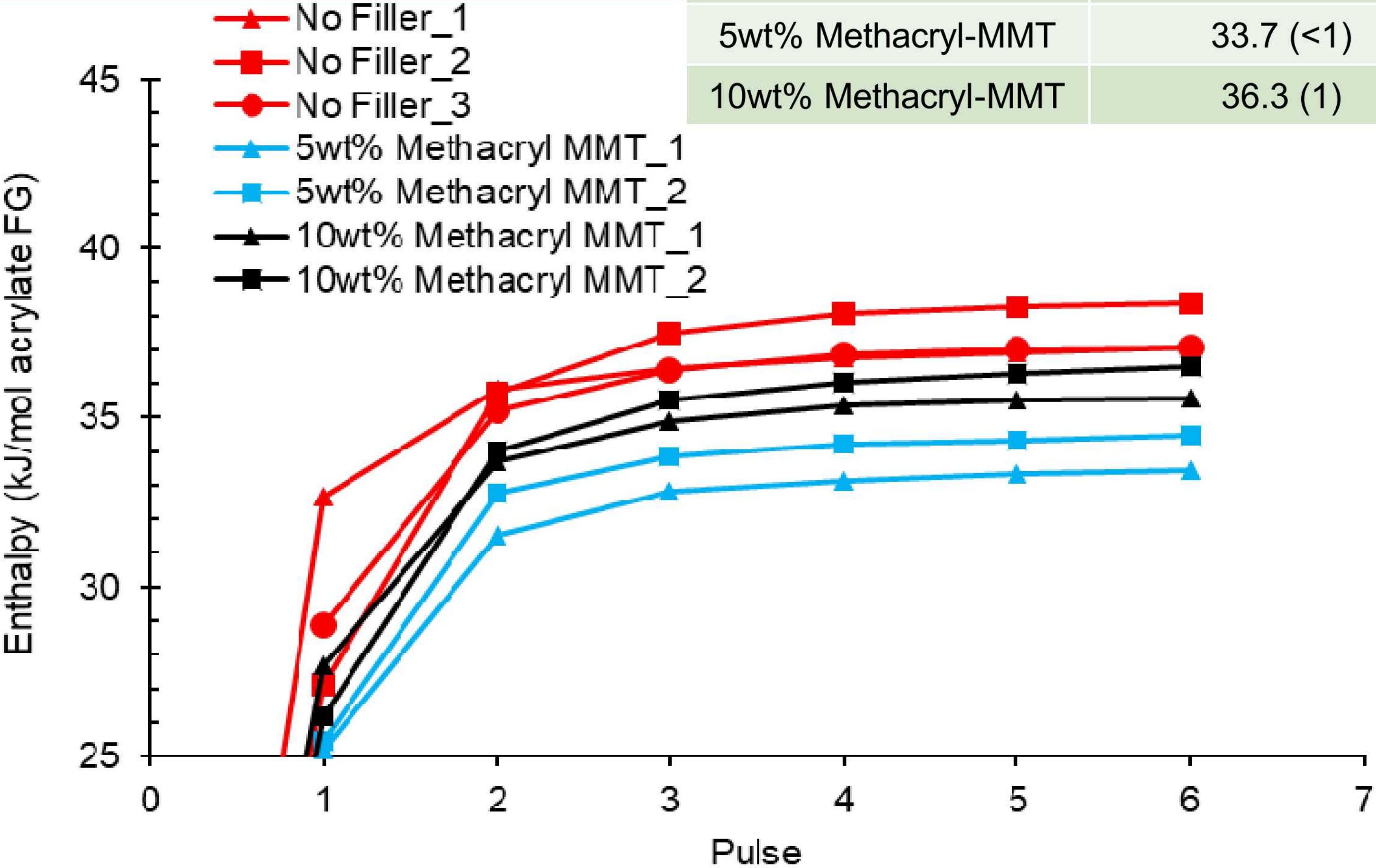
- The total enthalpy is dependent upon formulation
- The methacrylate-functionalized MMT results in the lowest total enthalpy, this could be due to vitrification

5wt% MMT	40.7 (1)	72
10wt% MMT	39.4 (1)	70
5wt% Methacryl-MMT	33.7 (<1)	59
10wt% Methacryl-MMT	36.3 (1)	64



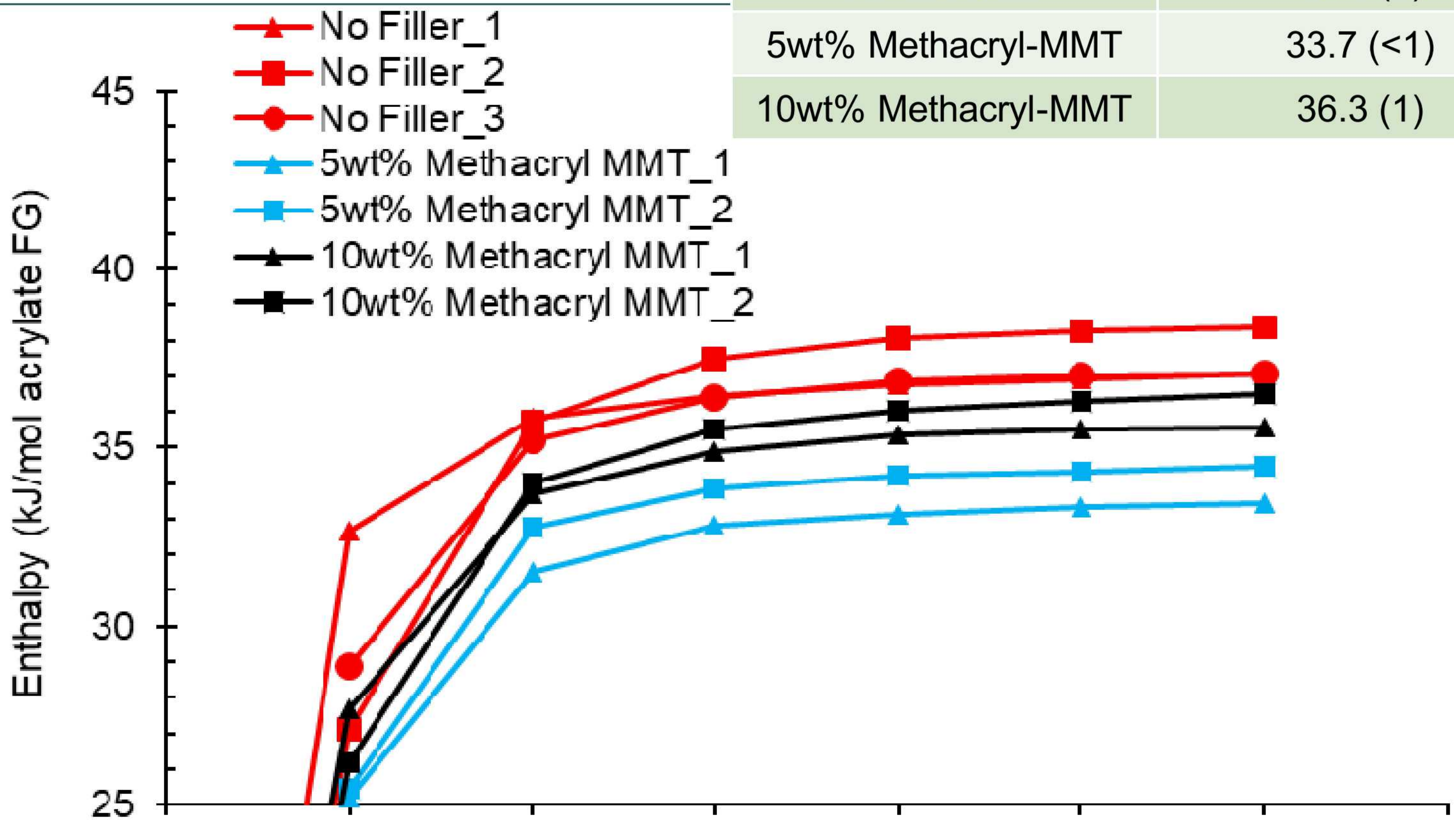
Effect of functionalized MMT on UV-cure kinetics

Composition	Enthalpy / mol acrylate (kJ/mol ac)	% conversion
No filler	37.3 (<1)	66
5wt% MMT	40.7 (1)	72
10wt% MMT	39.4 (1)	70
5wt% Methacryl-MMT	33.7 (<1)	59
10wt% Methacryl-MMT	36.3 (1)	64



Effect of functionalized MMT on UV-cure kinetics

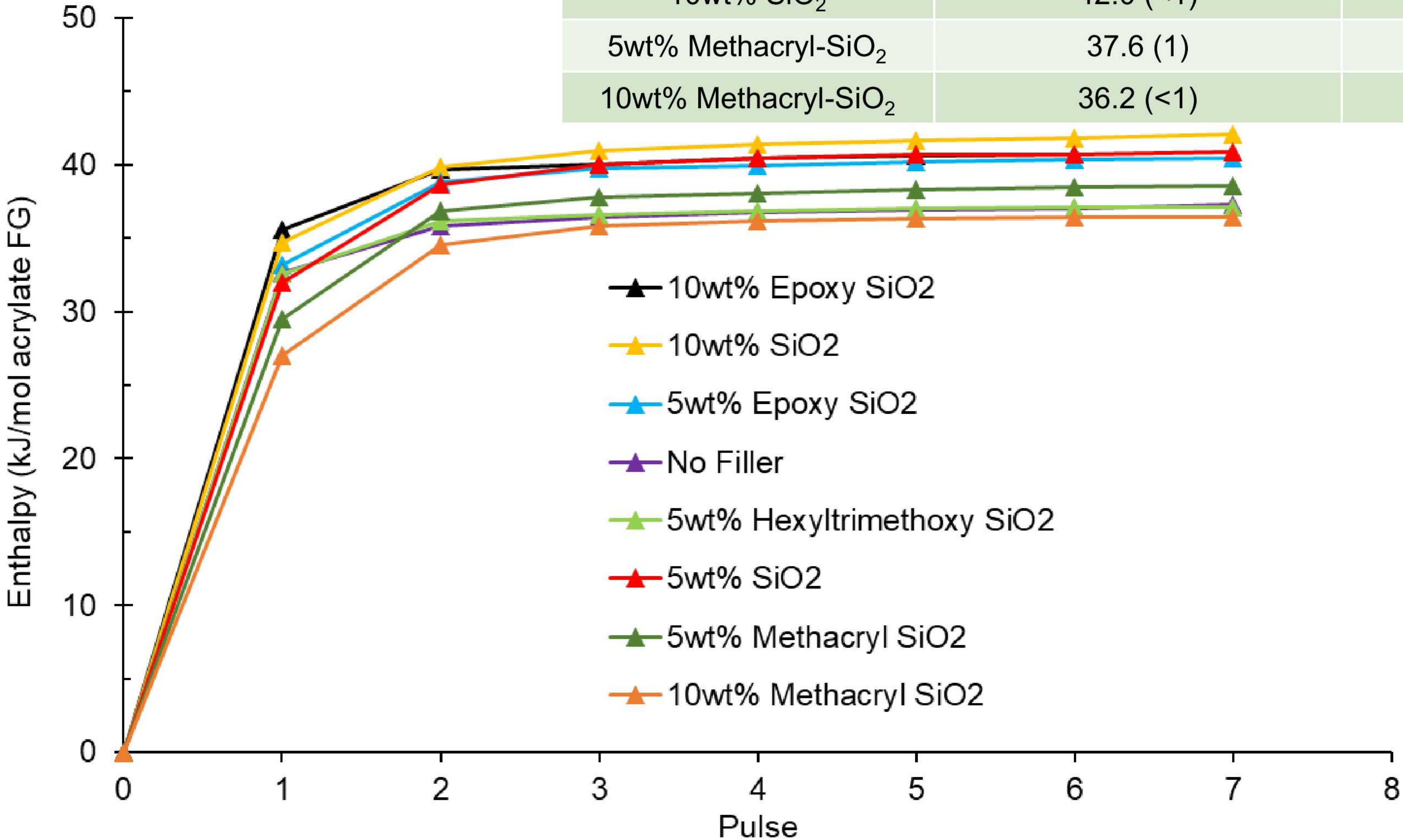
Composition	Enthalpy / mol acrylate (kJ/mol ac)	% conversion
No filler	37.3 (<1)	66
5wt% MMT	40.7 (1)	72
10wt% MMT	39.4 (1)	70
5wt% Methacryl-MMT	33.7 (<1)	59
10wt% Methacryl-MMT	36.3 (1)	64



- The results are very repeatable/reproducible between formulations as well as between runs

Effect of functionalized SiO_2 on UV-cure kinetics

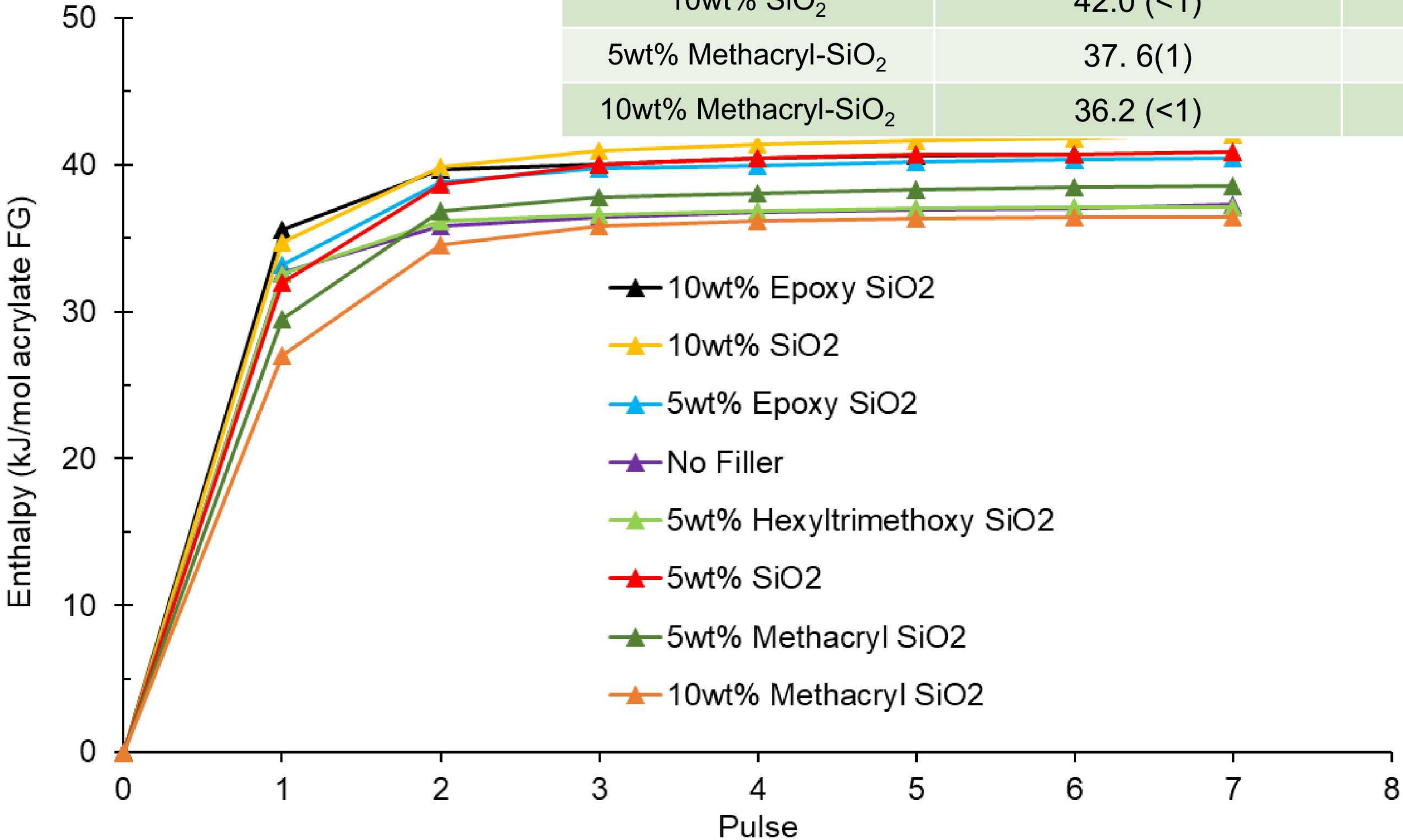
Composition	Enthalpy / mol acrylate (kJ/mol ac)	% conversion
No filler	37.3 (<1)	66
5wt% SiO_2	41.5 (1)	73
10wt% SiO_2	42.0 (<1)	74
5wt% Methacryl-SiO_2	37.6 (1)	66
10wt% Methacryl-SiO_2	36.2 (<1)	64



Effect of functionalized SiO_2 on UV-cure kinetics

- The total enthalpy is dependent upon formulation
- The methacrylate-functionalized SiO_2 results in the lowest total enthalpy, this could be due to vitrification

5wt% SiO_2	41.5 (1)	73
10wt% SiO_2	42.0 (<1)	74
5wt% Methacryl-SiO_2	37. 6(1)	66
10wt% Methacryl-SiO_2	36.2 (<1)	64



Effect of acrylate functionalization on conversion

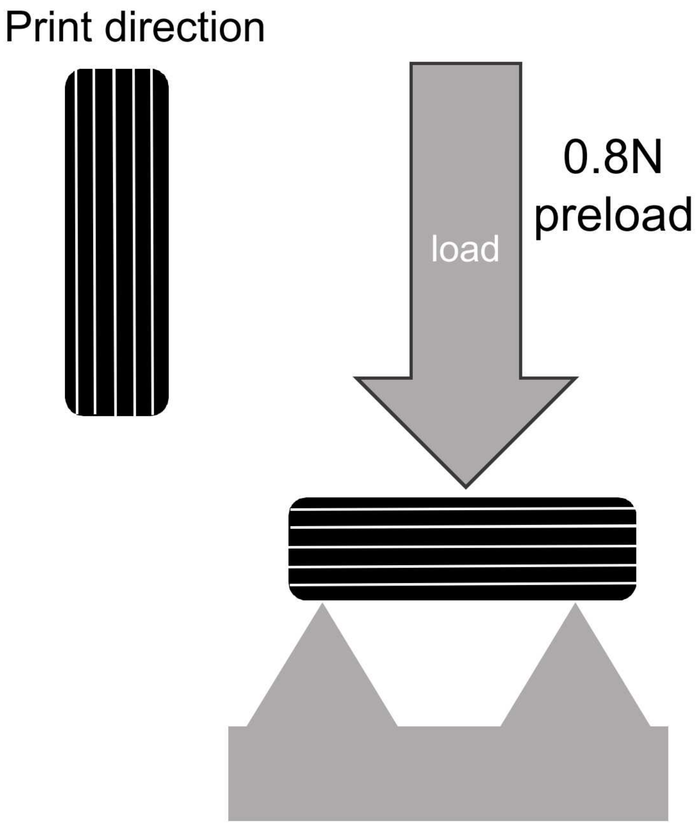
	Continuous	Pulsed
Composition	Enthalpy / mol acrylate (kJ/mol ac)	Enthalpy / mol acrylate (kJ/mol ac)
No filler	54.3	37.3 (<1)
5wt% SiO_2	52.4	41.5 (1)
10wt% SiO_2	58.9	42.0 (<1)
5wt% Methacryl-SiO_2	58.4	37. 6(1)
10wt% Methacryl-SiO_2	41.8	36.2 (<1)

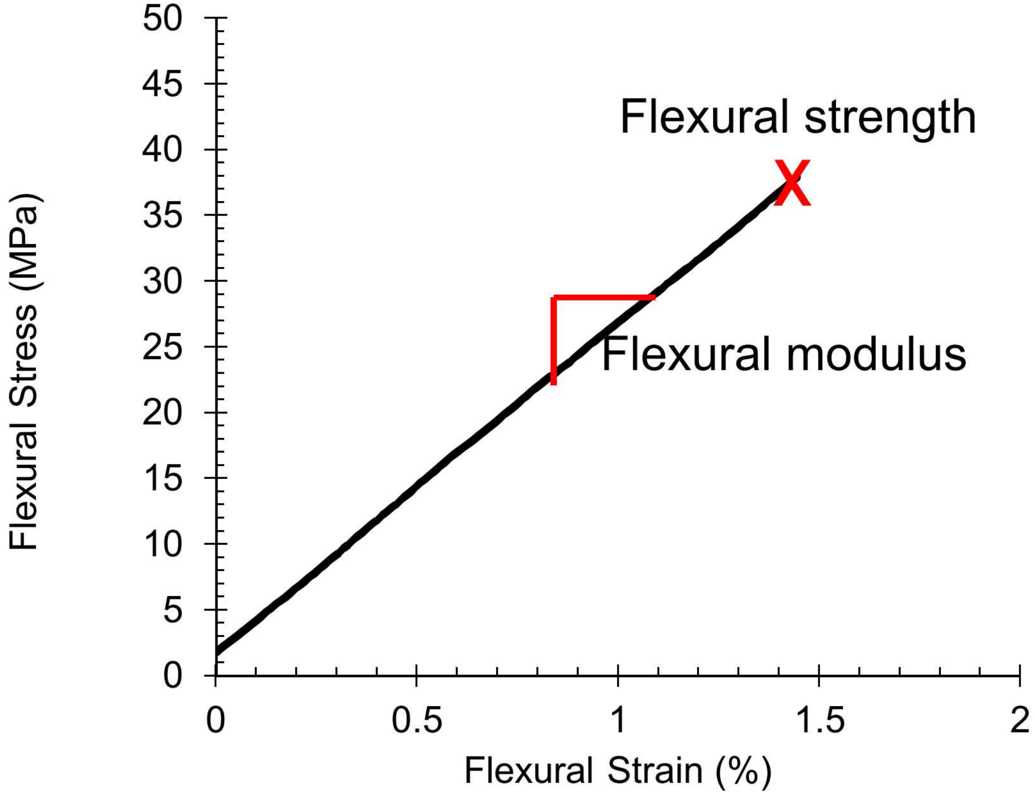
Composition	Enthalpy / mol acrylate (kJ/mol ac)	Enthalpy / mol acrylate (kJ/mol ac)
No filler	54.3	37.3(<1)
5wt% MMT	56.8	40.7 (1)
10wt% MMT	54.4	39.4 (1)
5wt% Methacryl-MMT	45.4	33.7 (<1)
10wt% Methacryl-MMT	40.6	37.1 (1)

Heat of polymerization for dimethacrylate: 56.6 kJ/mol acrylate

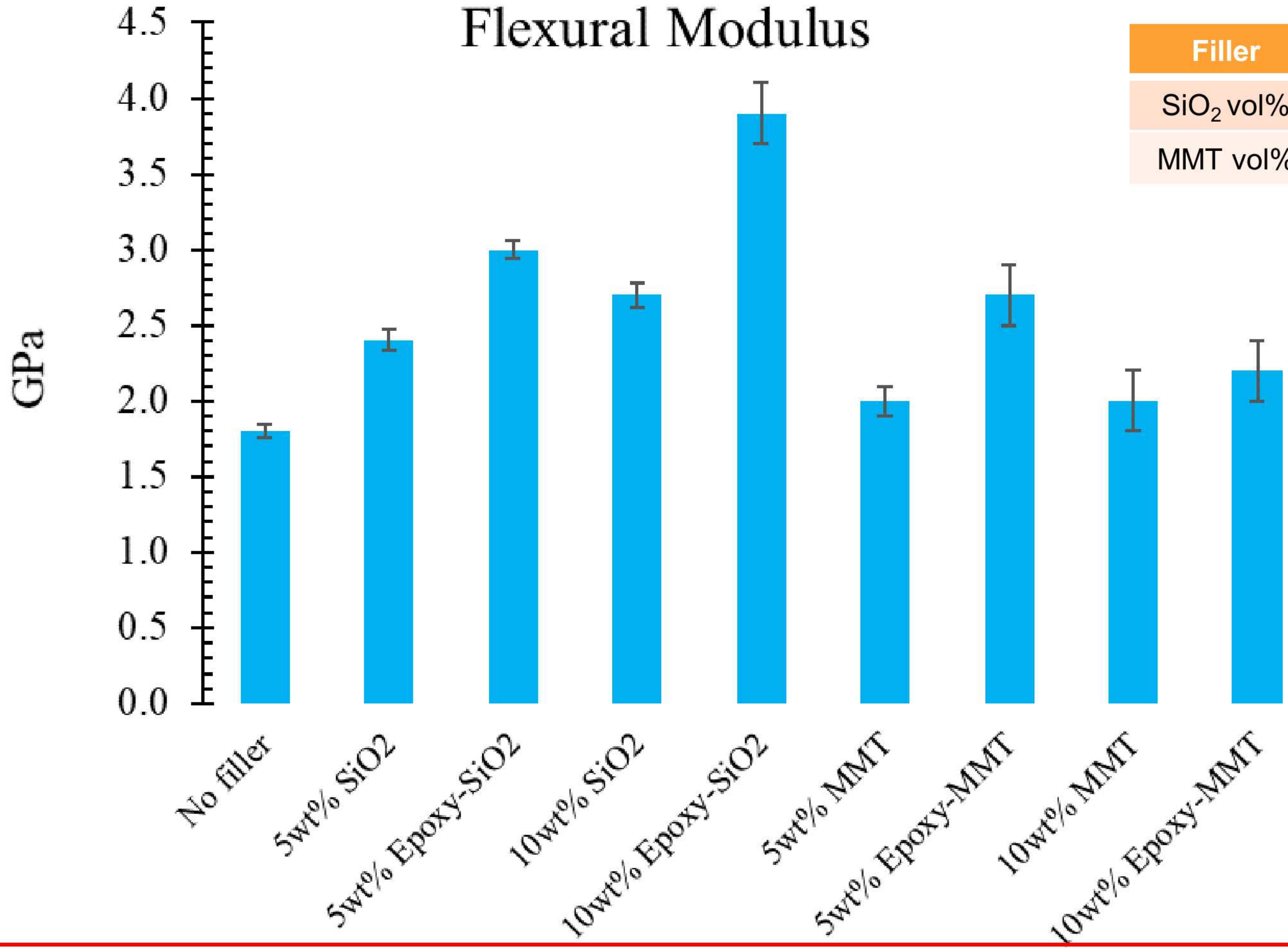
- The addition of acrylate functionalized MMT and 10wt% acrylate functionalized SiO_2 decreased the total conversion
- The enthalpy values for pulsed UV exposure is much lower than that of the continuous exposure

3-point bend it utilized to measure mechanical properties





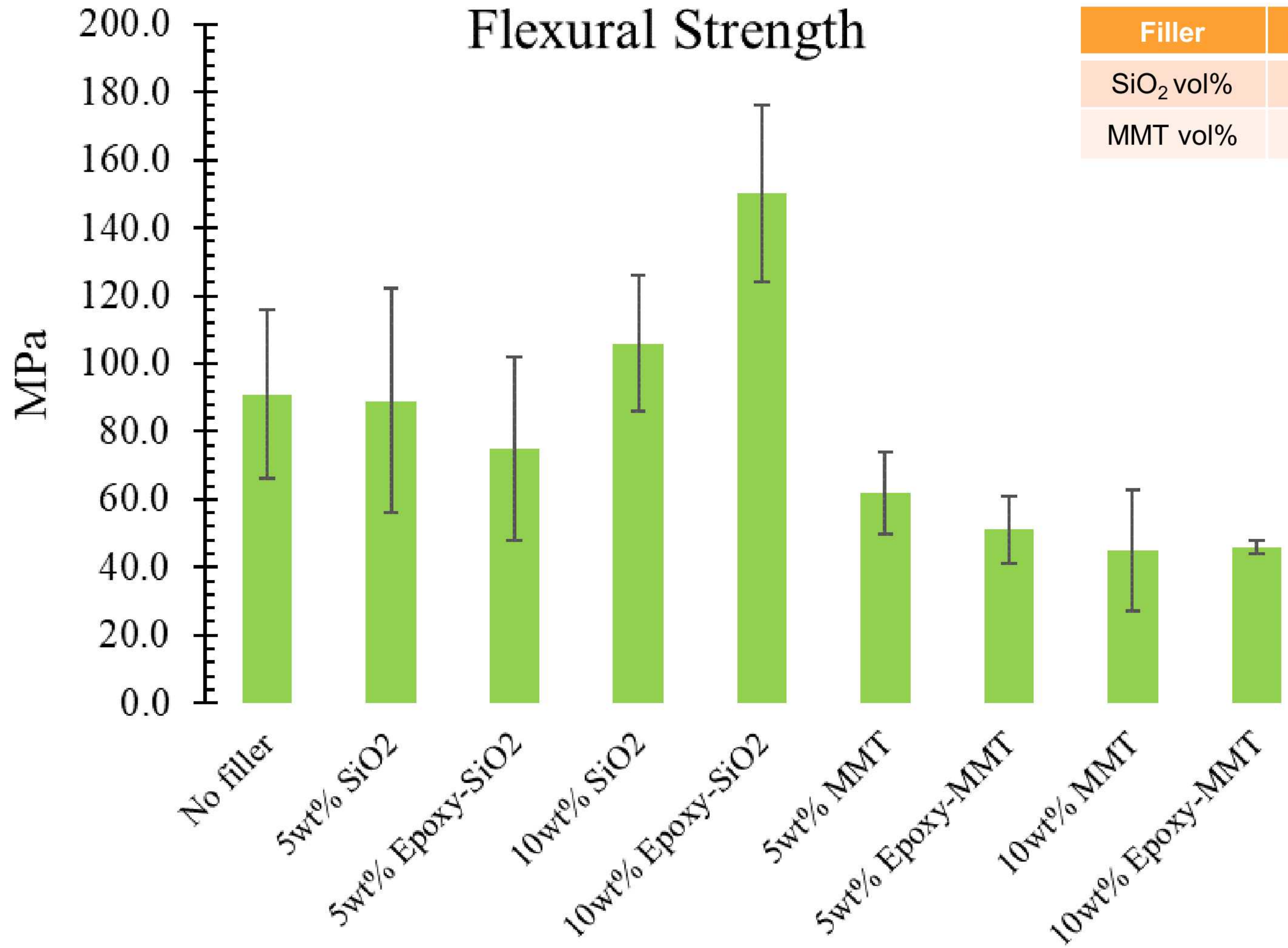
Impact of particle functionalization on mechanical properties



Filler	5wt%	10wt%
SiO_2 vol%	3.3	6.6
MMT vol%	2.6	5.2

- The presence of fillers alone increases the flexural modulus
- Epoxy functionalized fillers increases the flexural modulus, with the exception of 10wt% epoxy MMT
  - This is believed to be caused by aggregation
- SiO_2 has a greater impact on flexural modulus than MMT
  - This could be due to better dispersion. SEM currently being utilized

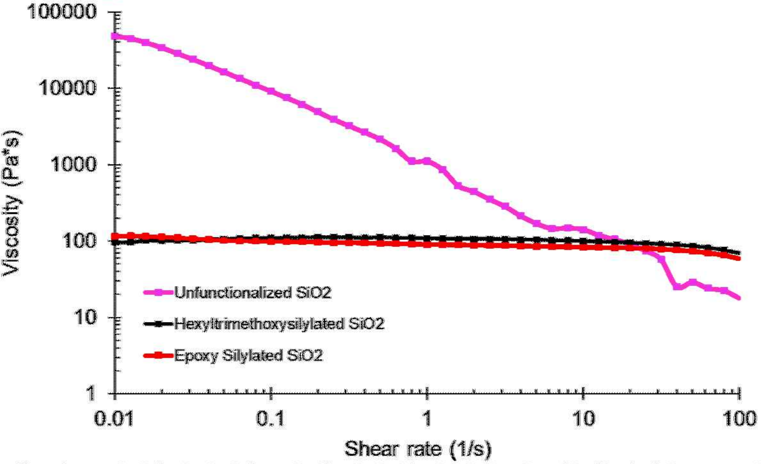
Impact of particle functionalization on mechanical properties

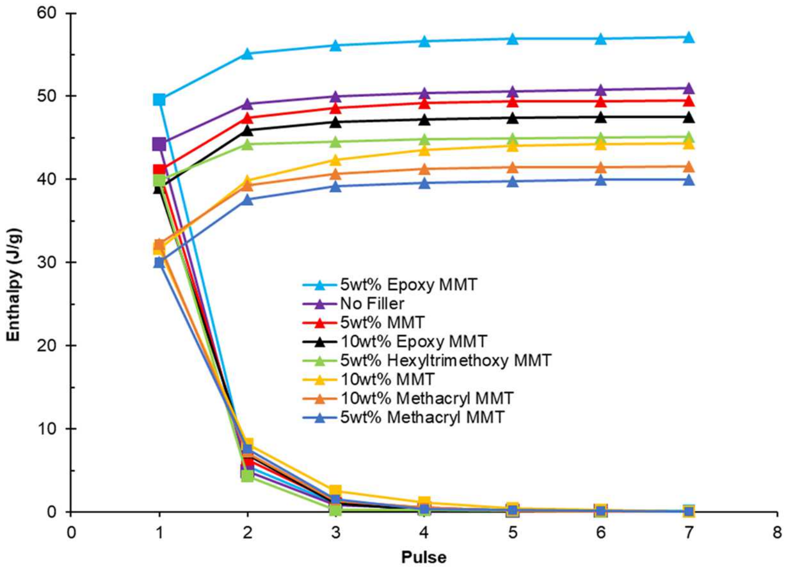


Filler	5wt%	10wt%
SiO_2 vol%	3.3	6.6
MMT vol%	2.6	5.2

- There are no statistically significant differences between fillers and surface functionalization on flexural strength

Conclusions





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

2. Methacrylsilane functionalized particles results in lower total enthalpy than unfilled and unfunctionalized fillers

3. The presence of fillers increases the flexural modulus of printed parts compared to unfilled resins. SiO_2 has a greater impact than MMT, possibly due to dispersion

Thank You!

Acknowledgements:

Leah Appelhans, Adam Cook, Jackie Unangst, Derek Reinholtz

Patti Sawyer, Shelby Beasley

$$$ NNSA NA-115 Additive Manufacturing Development Program

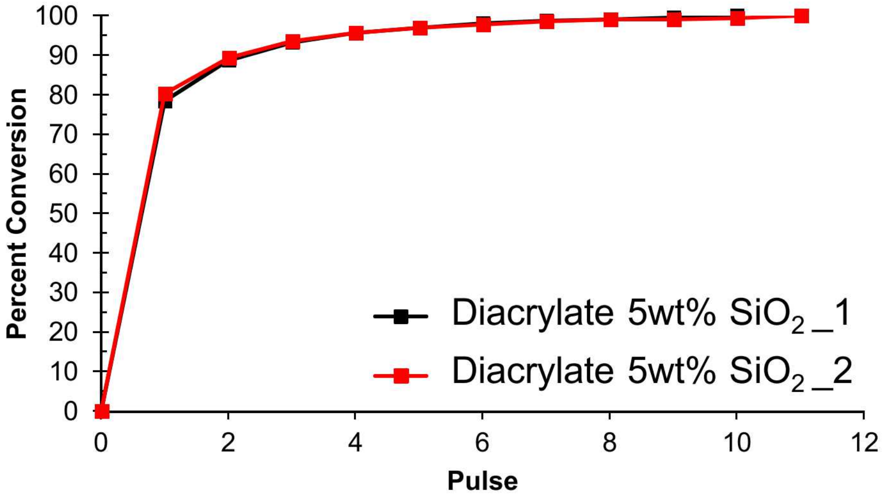
Dosage calculations

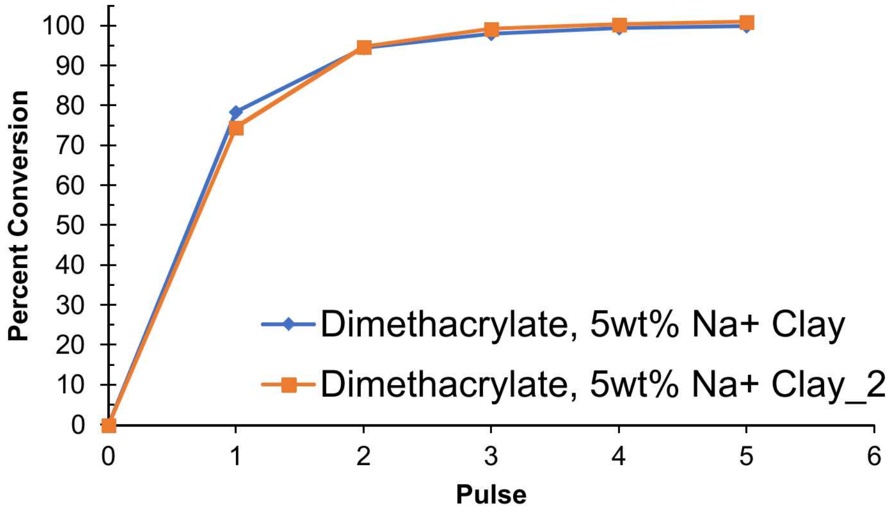
Device	Wavelength & Dosage	power % 1	5	10	20	40	80	
Dual UV probes at AML	365nm	1.2	6.9	14.3	29	57.3	106.3	Measured intensity (mW/cm^2)
	Dosage (190s)	228	1,311	2,717	5,510	10,887	20,197	
Bulk UV cure light at AML	365nm	5.7						
	Dosage (1800s)	10,260						
Photocalorimetry DSC	365nm	-	44.9	109.4	207.2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

Dosage: Intensity*time of exposure

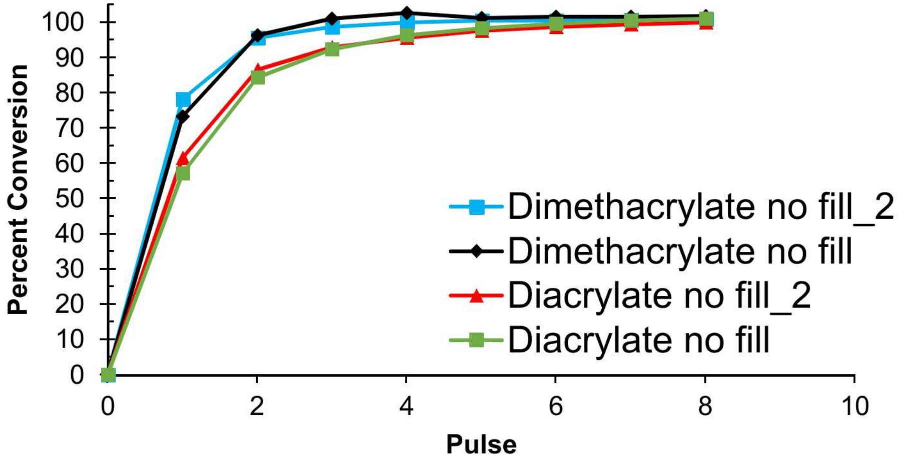
UV probes: continuous coverage for 190s
Bulk UV: continuous coverage for 1800s
Photocalorimetry: 5 x 2.4s flashes

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