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RHEOLOGICAL AND MECHANICAL BEHAVIOR OF DUAL-CURE DIW THERMOSET RESINS

Center 1800:
Material, Physical and Chemical Sciences

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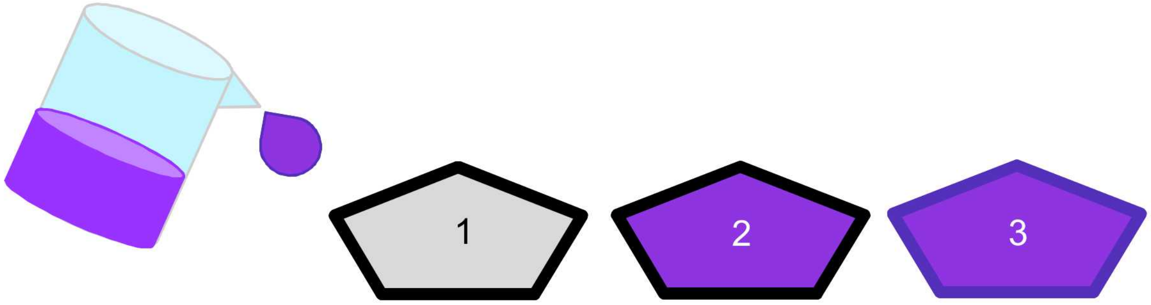
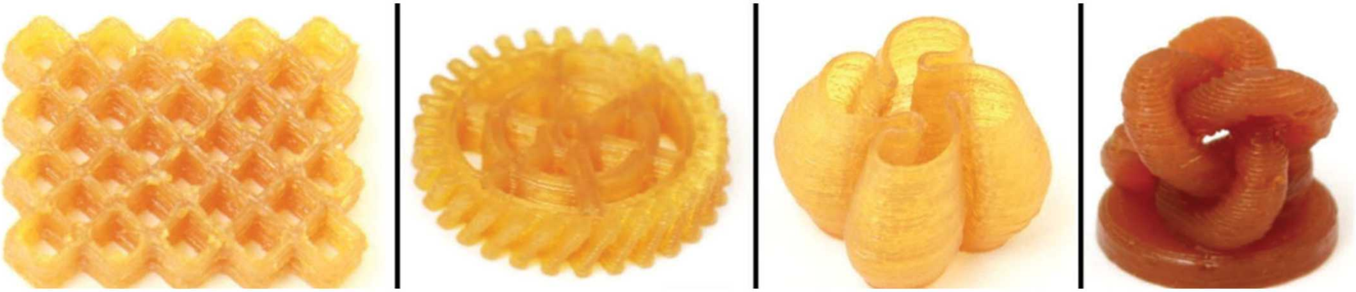
Why DIW thermosets?

Thermoset parts are traditionally fabricated via casting into a mold, but molds have limitations

- Mix curing agent + epoxy resin
- Pour
- Wait to cure
- Limitations: geometry, uniform thickness, high aspect ratio parts

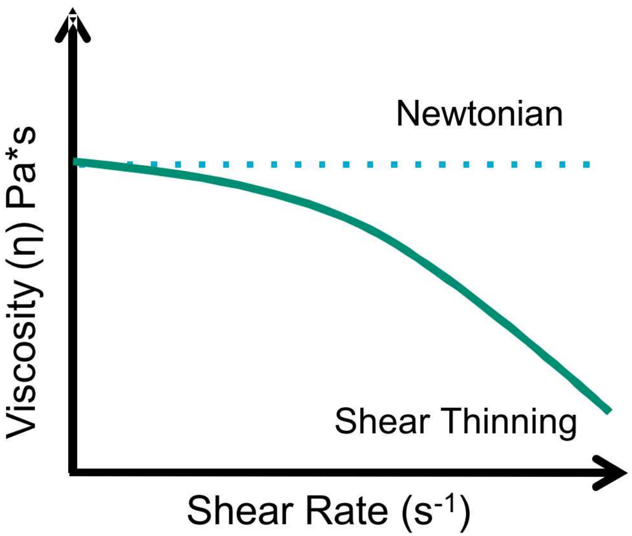


DIW facilitates the design of more complex geometries



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

Shear thinning behavior is required for DIW

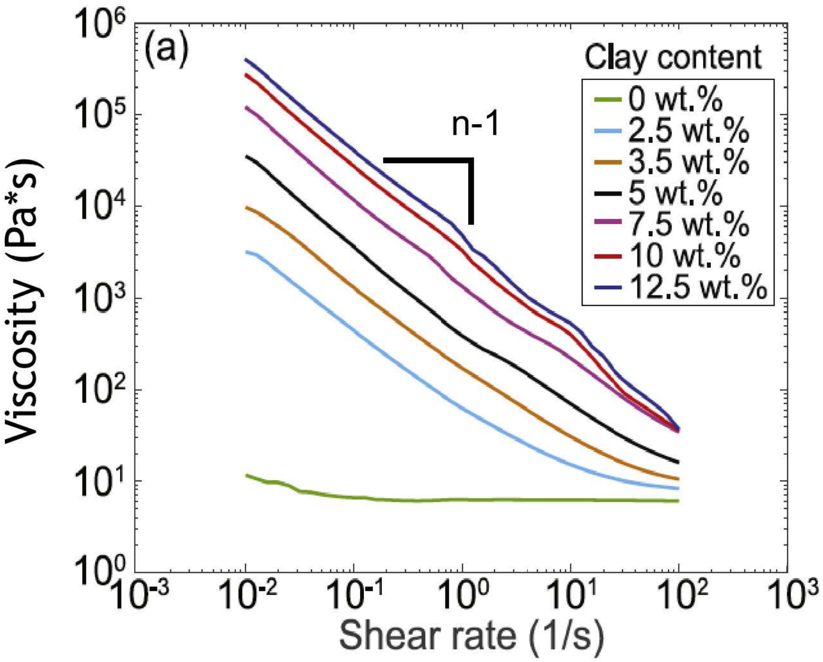


Vlachopoulos et al. Role of Rheology in Polymer Extrusion. 2003

Power law

$$\eta = K\dot{\gamma}^{n-1}$$

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

Dual-cure mechanisms enable printing of thermoset systems

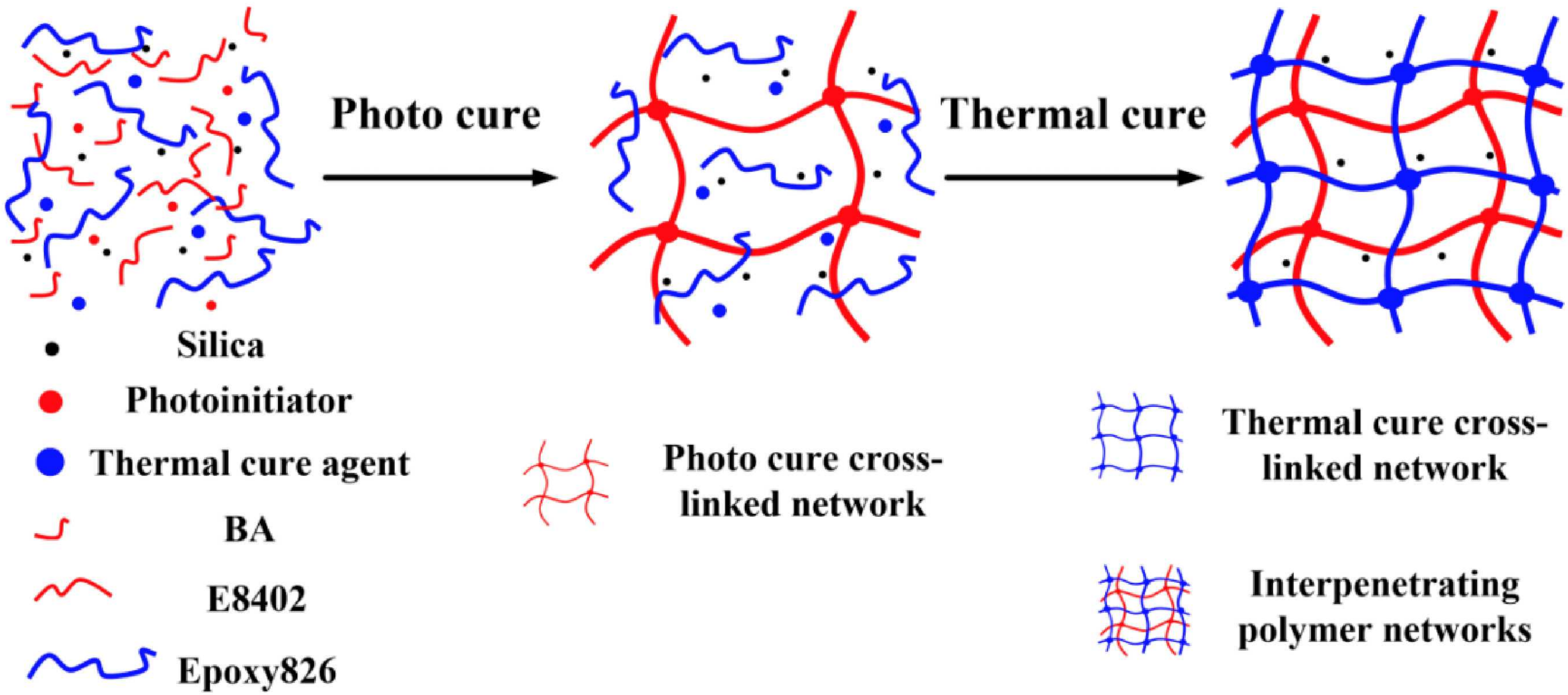


Illustration of the chemical reaction with a dual-cure process by Chen et. al using UV assisted DIW

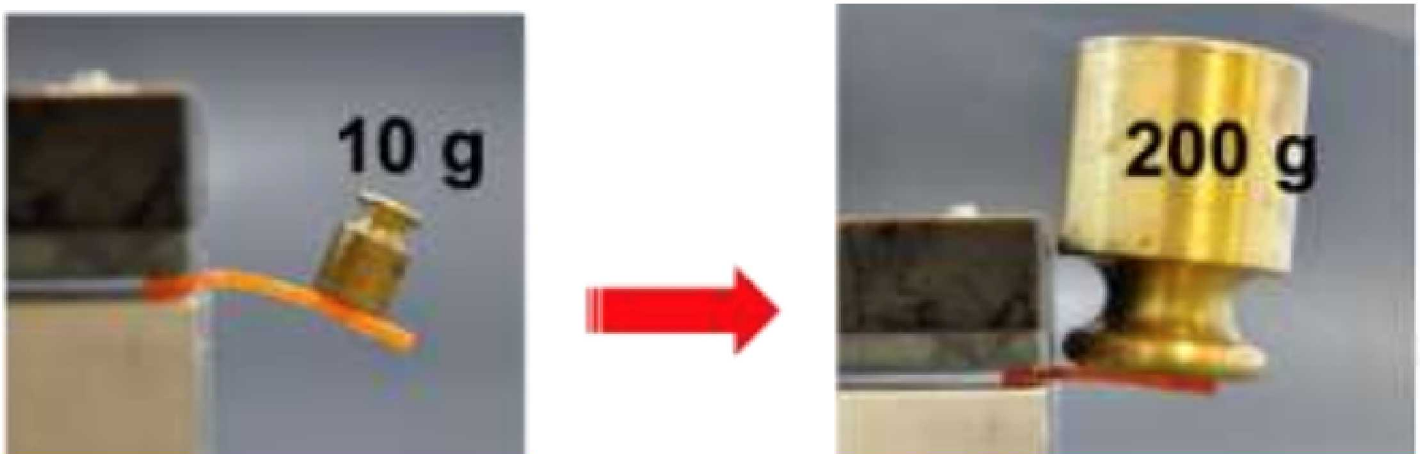
Chen et al. *Soft Matter.* 2018. Vol 14.

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

Dual-cure mechanisms enable printing of thermoset systems



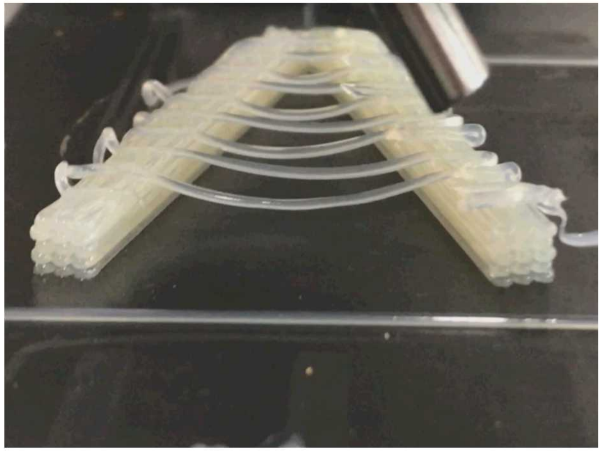
1st stage cure

2nd stage cure

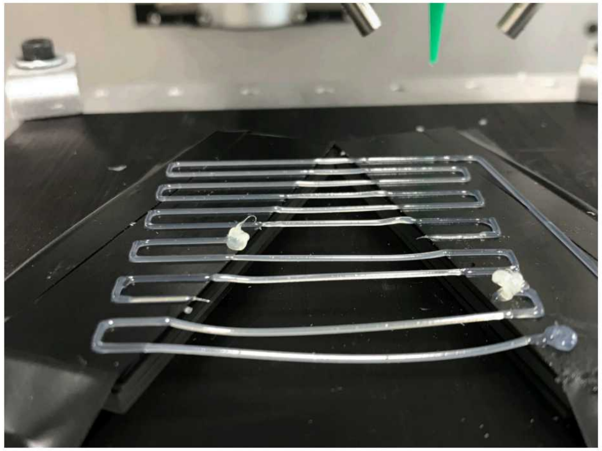
- First stage cure locks-in structure during print
- Second stage cure enhances mechanical properties

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

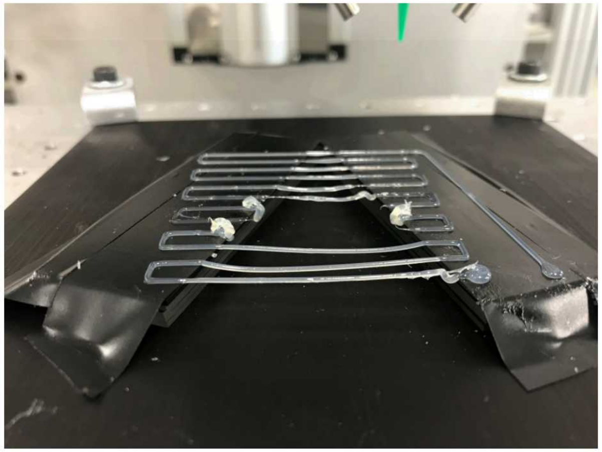
Dual-cure mechanisms enable printing of thermoset systems



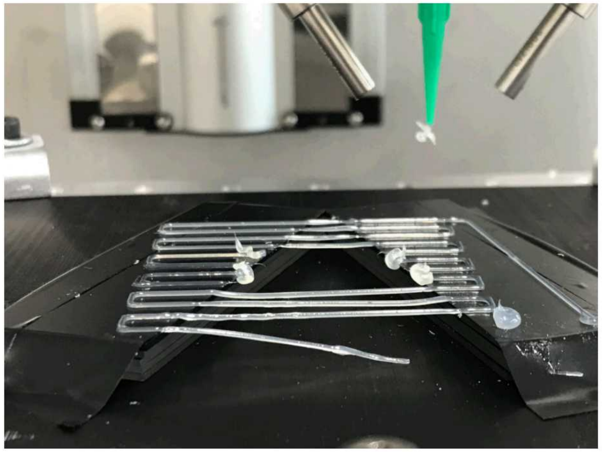
10% UV power



25% UV power



50% UV power



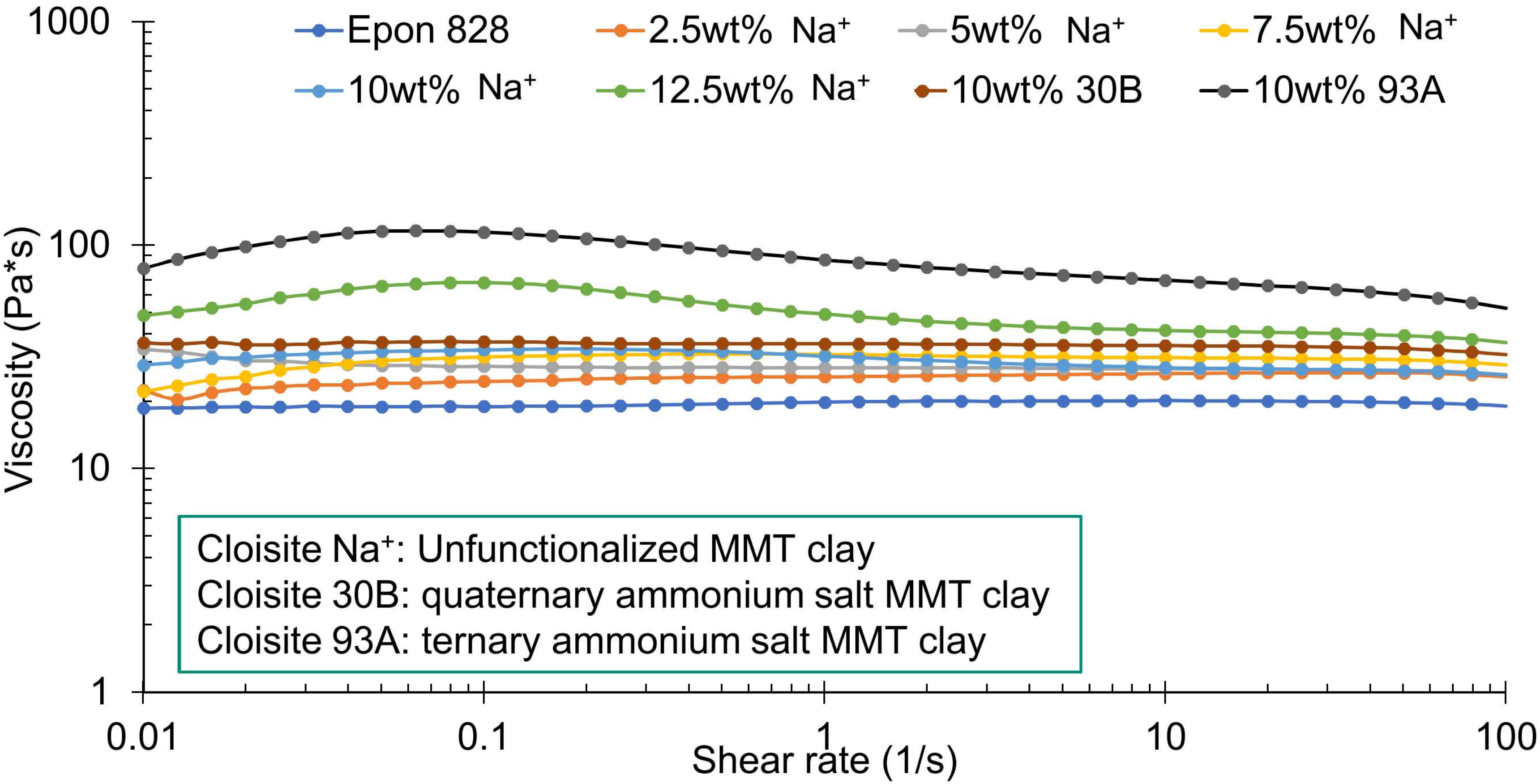
75% UV power

Base formulations being investigated

Original	Modified
30wt% Tri-functional epoxy	
30wt% Di-functional epoxy	60wt% Di-functional epoxy
30wt% Ethoxylated Bisphenol A dimethacrylate	30wt% Bisphenol A (BPA) dimeth- or di- acrylate
0.5wt% Photoinitiator	0.5wt% Photoinitiator
3wt% Latent curing agent	3wt% Latent curing agent
varying wt% Filler material	varying wt% Filler material

Effect of clay filler type on viscosity

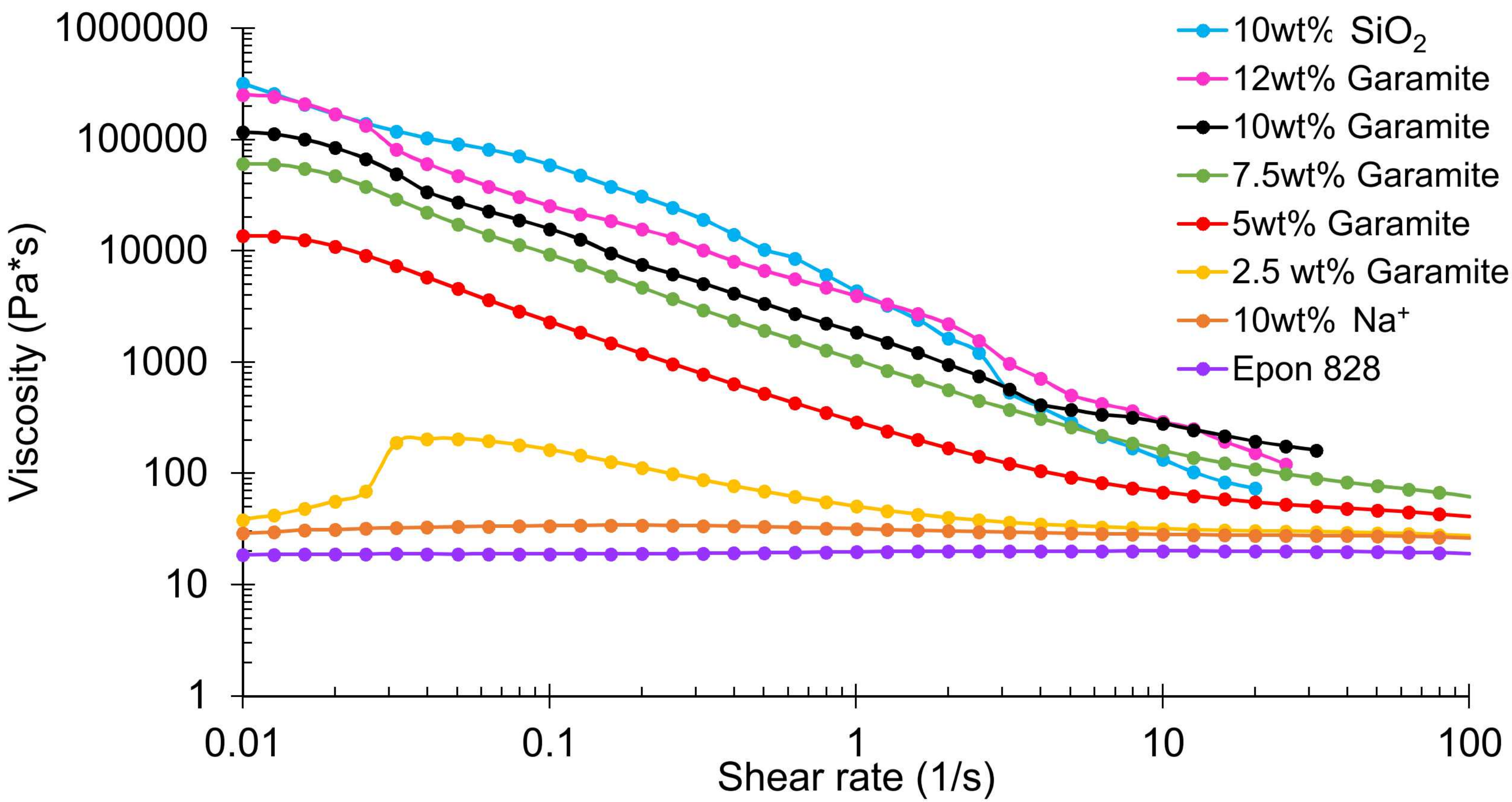
Formulation: 15g EPON 828, 0.75g curing agent, 'x'wt% filler material



The addition of clay moderately increases the viscosity, but no significant shear-thinning behavior is observed up to 12wt%.

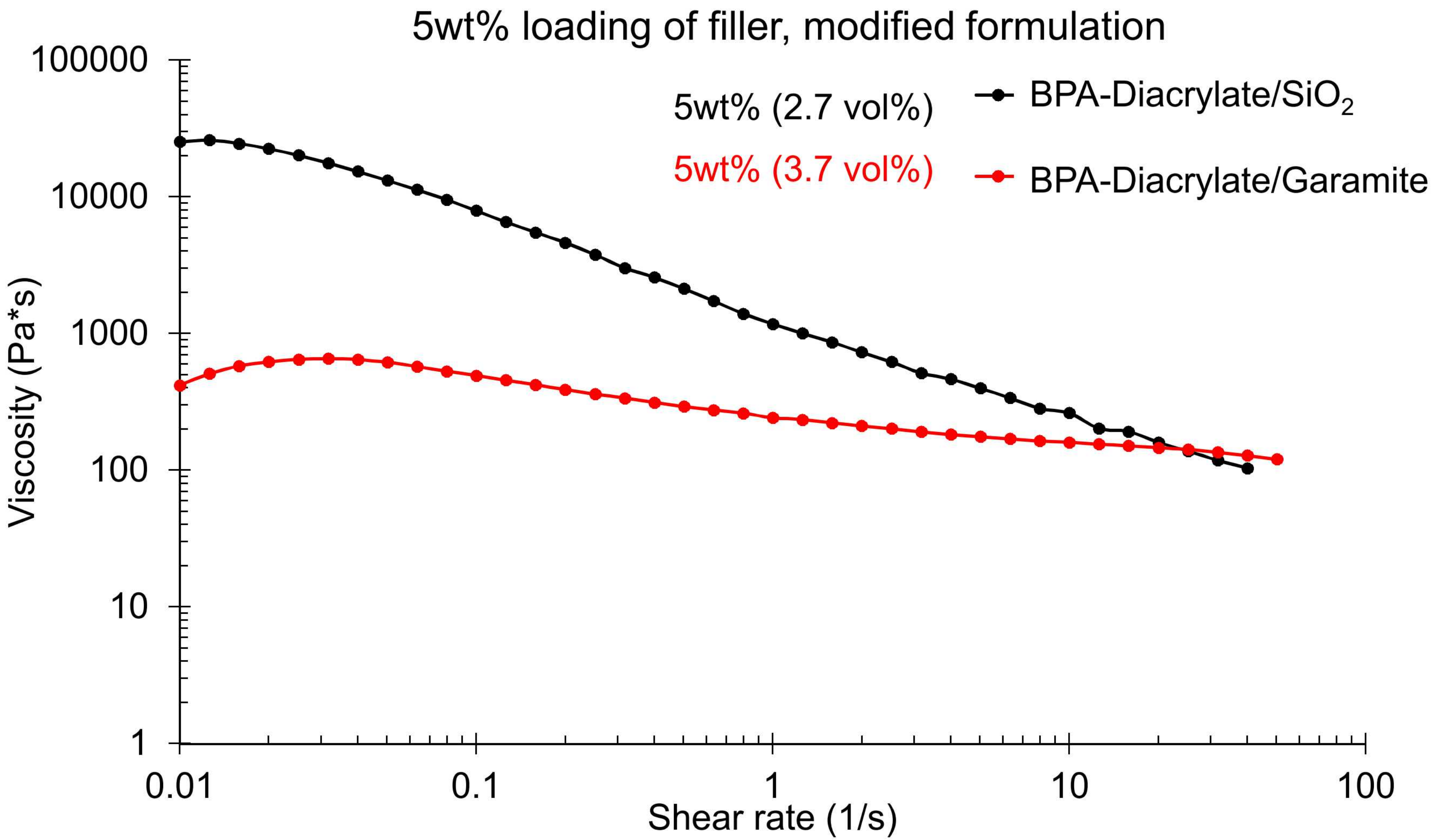
Effect of different filler types on viscosity

Formulation: 15g EPON 828, 0.75g curing agent, ‘x’wt% filler material



- Garamite 7305 is a blend of MMT and bentonite clays that are functionalized to disperse in polar solvents
  - Also has a wide distribution of particle geometries, i.e. rods, plates, etc.
- Garamite 7305 increases viscosity more than clay and also induces strong shear-thinning behavior, although a higher wt% is needed than silica.

Rheological effects of Silica vs Garamite



- Silica leads to a higher zero-shear viscosity and higher degree of shear thinning compared to Garamite 7305, at the same wt% loading

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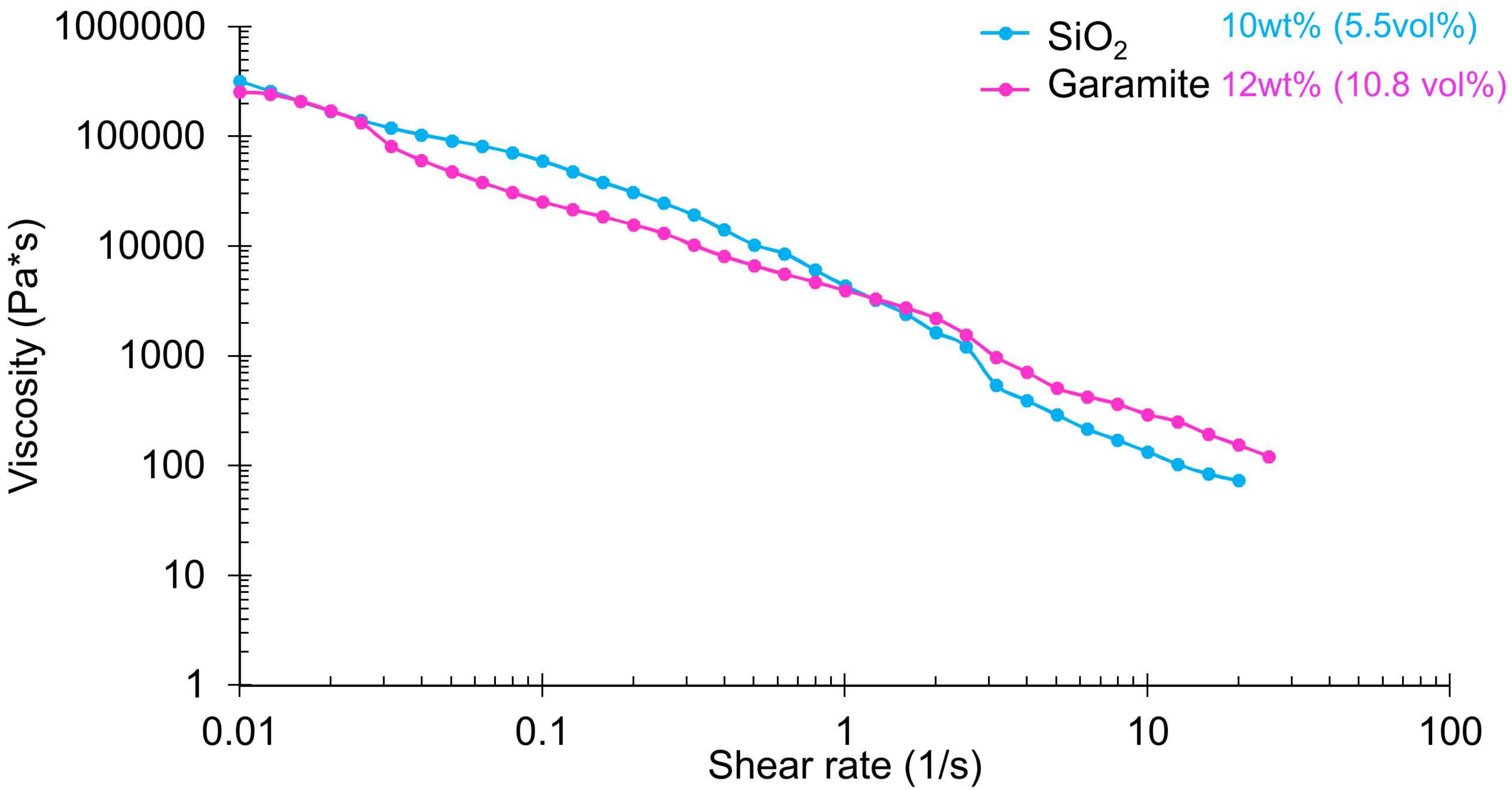
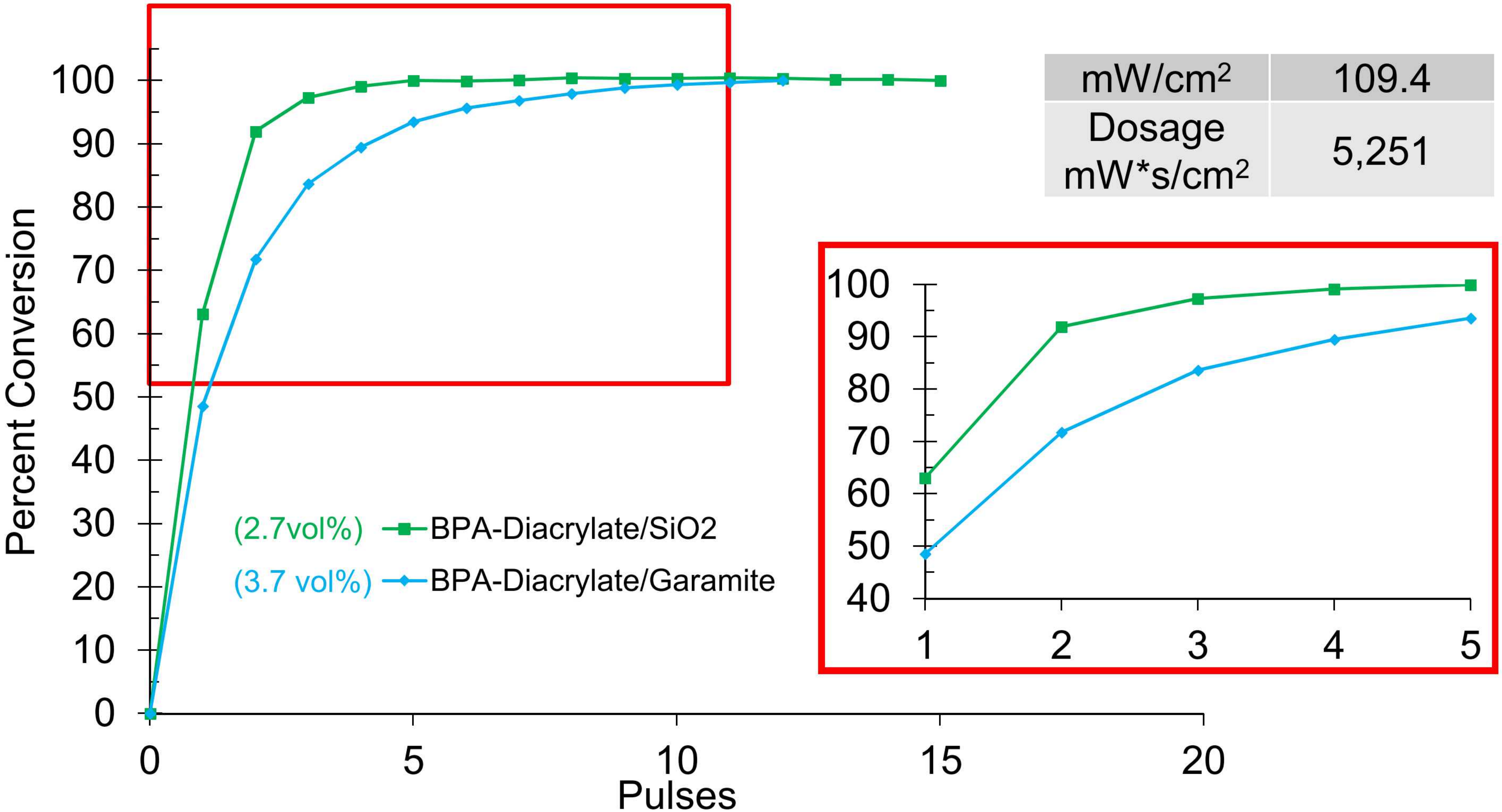


- By increasing the wt% of Garamite 7305, the apparent viscosity and shear-thinning behavior matches that of 10wt% SiO_2

UV DSC comparing different filler materials

At 10% UV power, 5% loading of filler, modified formulation

mW/cm^2	109.4
Dosage $mW*s/cm^2$	5,251



Formulations with Garamite have slower UV-cure kinetics than with SiO_2

Photocalorimetry: resin, each DSC pan received 20 x 2.4s flashes of UV

The impact of filler material on the moduli & Tg

5wt% loading of filler, original formulation

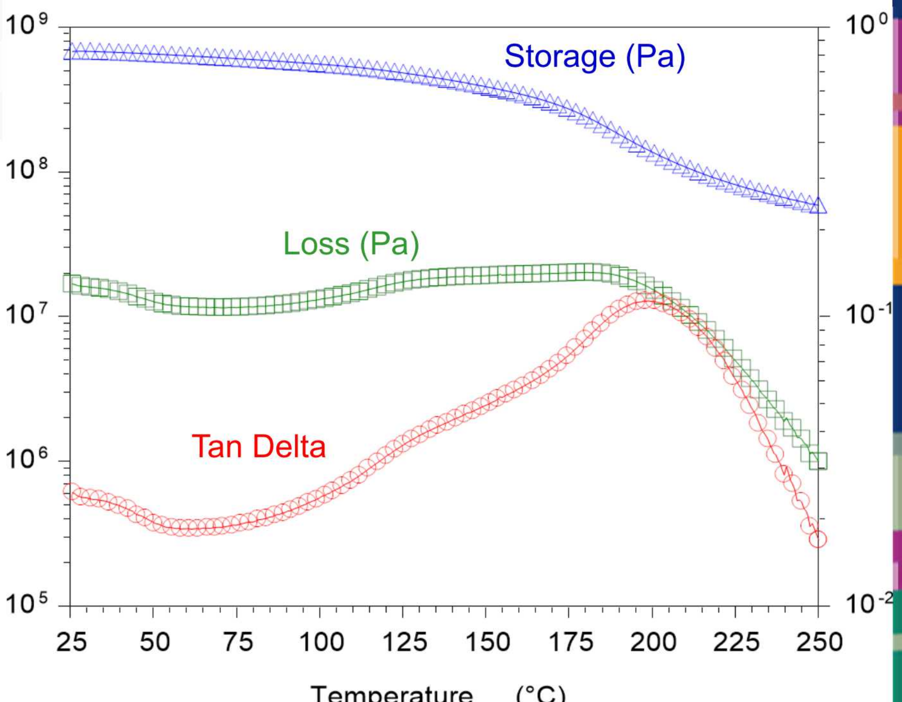
Room Temperature Measurement, Torsional DMA

30 min UV-cure only	
Sample	**Storage Modulus MPa**
SiO_2 (2.7vol%)	47.9 ± 3.6
Na^+ clay (2.1vol%)	68.7 ± 15.7
Garamite (3.7vol%)	-

Fully cured	
Sample	**Storage Modulus MPa**
SiO_2	511.4 ± 11.9
Na^+ Clay	663.5 ± 25.3
Garamite	552.5 ± 42.3

Room temperature → 250C → Room temperature Torsional DMA

Fully cured	
Sample	**Tan Delta (Tg) °C**
SiO_2	183.1 ± 1.8
Na^+ Clay	**198.4 ± 1.4**
Garamite	**199.2 ± 0.5**



The addition of clay results in a greater Tg compared to silica
Unfunctionalized clay also appears to increase the storage modulus

The impact of filler material on the moduli & Tg

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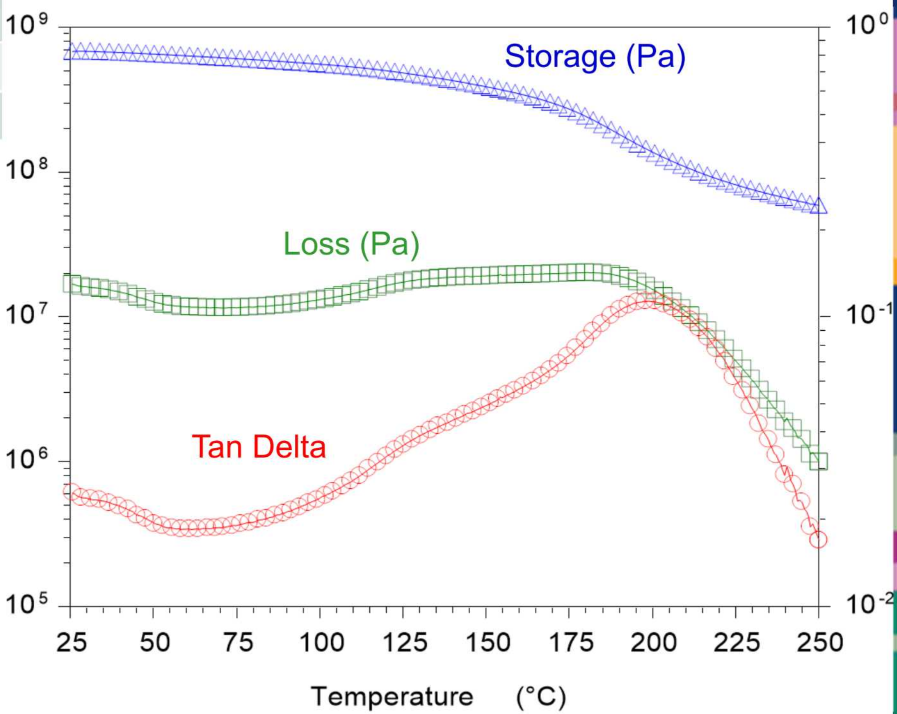

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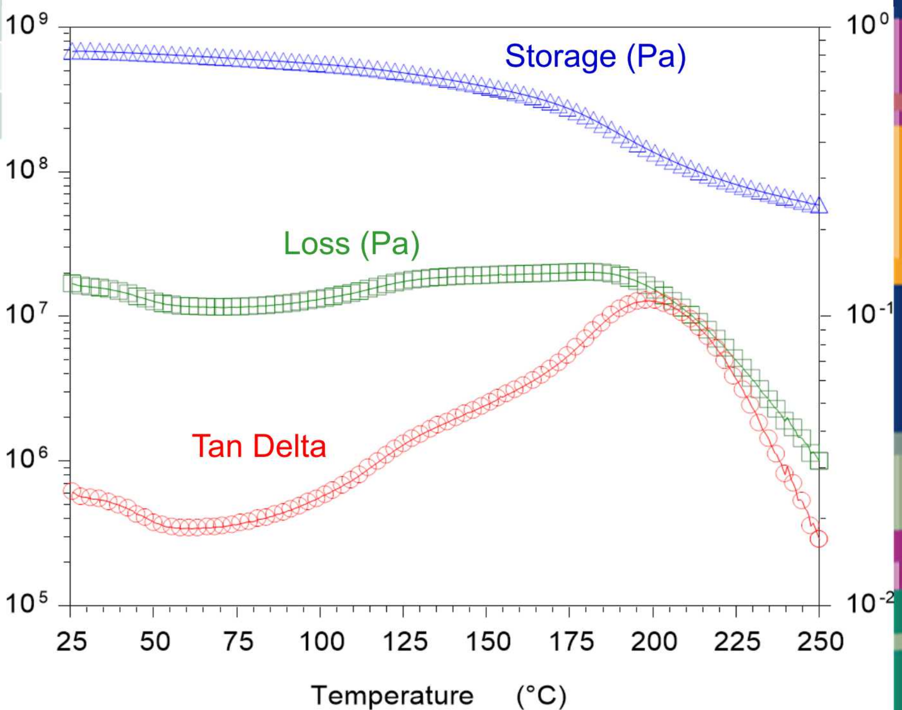

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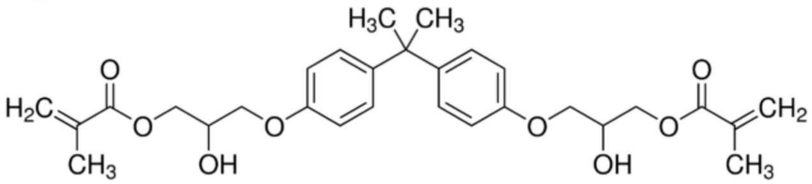
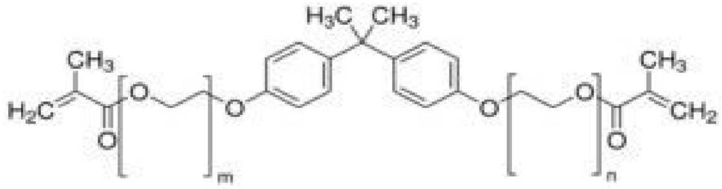
Unfunctionalized clay also appears to increase the storage modulus

The impact of acrylate on the moduli & Tg



Bisphenol A (BPA) glycerolate dimethacrylate



SR348: Ethoxylated bisphenol A dimethacrylate

Room Temperature Measurement, Torsional DMA

30 min UV-cure only	
Sample	**Storage Modulus MPa**
SR348	47.9 ± 3.6
BPA- dimethacrylate	81.6 ± 6.4

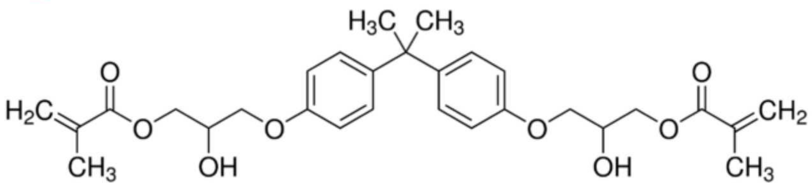
Fully cured	
Sample	**Storage Modulus MPa**
SR348	511.4 ± 11.9
BPA- dimethacrylate	844.0 ± 62.9

Room temperature → 250C → Room temperature, Torsional DMA

Fully cured	
Sample	**Tan Delta (Tg) °C**
SR348	183.1 ± 1.8
BPA-dimethacrylate	200.9 ± 3.4

BPA-dimethacrylate results in a higher Tg and storage modulus than Sartomer SR348

The impact of acrylate on the moduli & Tg



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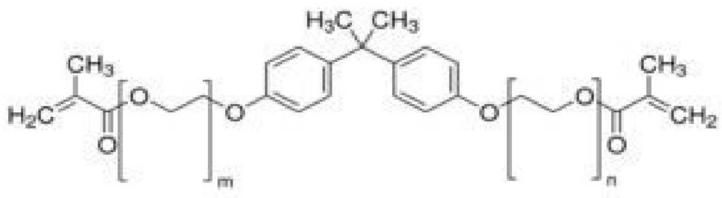

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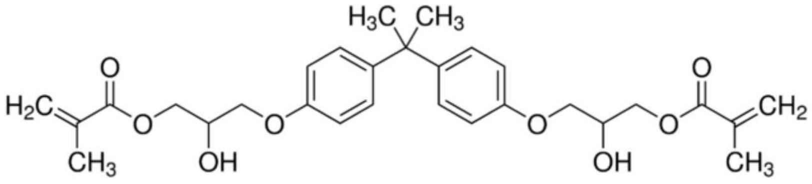

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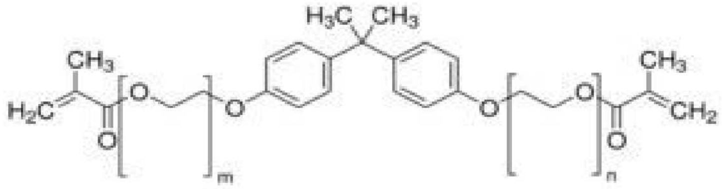

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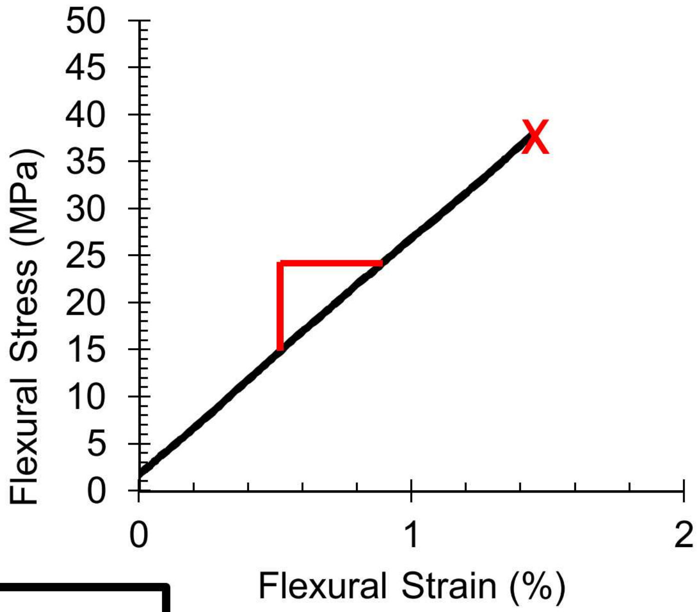
BPA-dimethacrylate results in a higher Tg and storage modulus than Sartomer SR348

Flexural testing – 3pt bend

Original Formulation, 5wt% loading of filler

Sample Fully Cured	Flexural Modulus (GPa)	Flexural Strength (MPa)	n
SiO_2*	4.2 ± 0.1	116.0 ± 34.7	22
Na^+ clay	3.1 ± 0.2	64.3 ± 4.2	3
SiO_2, dimethacrylate in place of Sartomer SR348	3.7 ± 0.1	135.6 ± 25.2	6



Modified Formulation, 5wt% loading of filler

Sample Fully Cured	Flexural Modulus (GPa)	Flexural Strength (MPa)	n
BPA-dimethacrylate, SiO_2	3.6 ± 0.1	105.2 ± 39.9	4
BPA-dimethacrylate, Garamite 7305	2.9 ± 0.4	60.4 ± 27.5	3
BPA-diacrylate, SiO_2	3.7 ± 0.1	178.9 ± 11.6	4
BPA-diacrylate, Garamite 7305	2.9 ± 0.2	65.4 ± 15.7	3

- Silica leads to a higher flexural modulus and flexural strength at break
- The type of acrylate appears to have minimal impact on modulus or stress

* These are cut from printed coupons

n= sample size

Conclusions

- Pure MMT clay fillers do not induce shear-thinning
- Silica and Garamite (modified clay for rheological purposes) induce shear thinning and increase zero-shear viscosity
- Formulations with Garamite have slower UV-cure kinetics than with silica
- Clay filler increases the Tg relative to silica filler
- The BPA-dimethacrylate increases the storage modulus and Tg relative to Sartomer SR348
  - This may be due to the higher crosslink density of shorter-chained BPA-dimethacrylate
- The type of acrylate used has minimal impact on the flexural modulus or strength of the printed parts
- Silica filled samples have higher flexural modulus and strength than Garamite filled samples

Next Steps:

- Further analyze impact of fillers on mechanical properties
- Investigate the impact of functionalized clay on the epoxy network formation via isothermal cure measurements

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