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SAND2018-3423C

Self-Assembly Assisted Additive Manufacturing of an Epoxy-Amine Resin



PRESENTED BY

Kylie Manning

Additive Manufacturing of Thermosets

3D printing technology that builds object by adding layer-upon-layer of a material

SLA, FDM, SLS, DIW

-Many examples of thermoplastics and UV curable resins

-Limited examples of 3D printed composites and high T_g , high performance thermosets, especially two-part

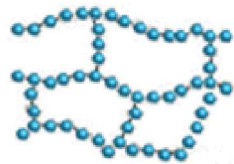
-Slow kinetics, restrictive rheology profiles

-Direct-Ink Writing (DIW), high-speed, extrudes continuous ink filaments

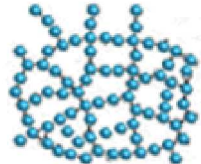
-Need shear-thinning behavior + moderate yield stress



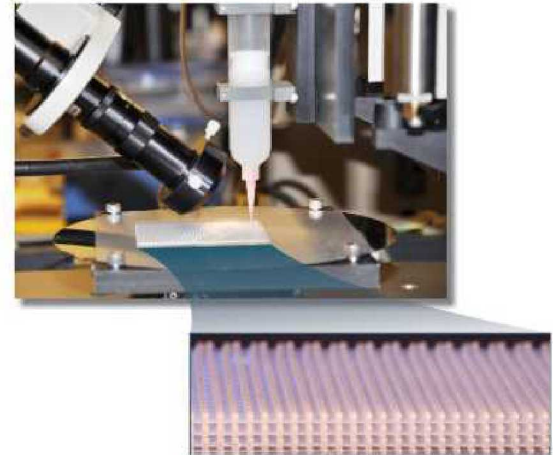
Thermoplastic



Elastomer



Thermoset



3 3D Printed Epoxies by DIW

Printable via fiber fillers- Epon826, nanoclay, imidazole-based ionic liquid as latent curing agent

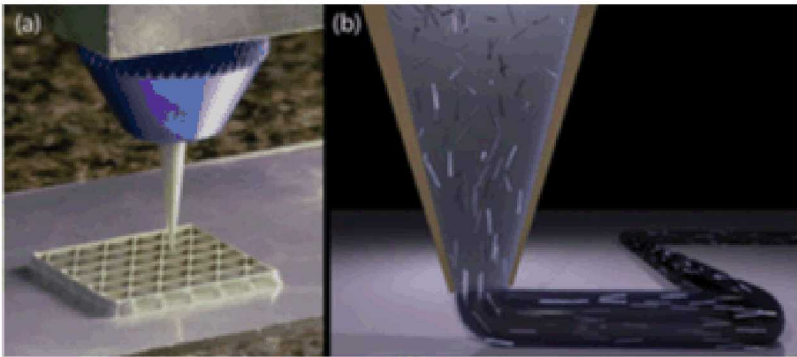


Figure 1. (a) Optical image of 3D printing of a triangular honeycomb composite. (b) Schematic illustration of the progressive alignment of high aspect ratio fillers within the nozzle during composite ink deposition.

Adv. Mater., 2014, 26, 5930-5935.

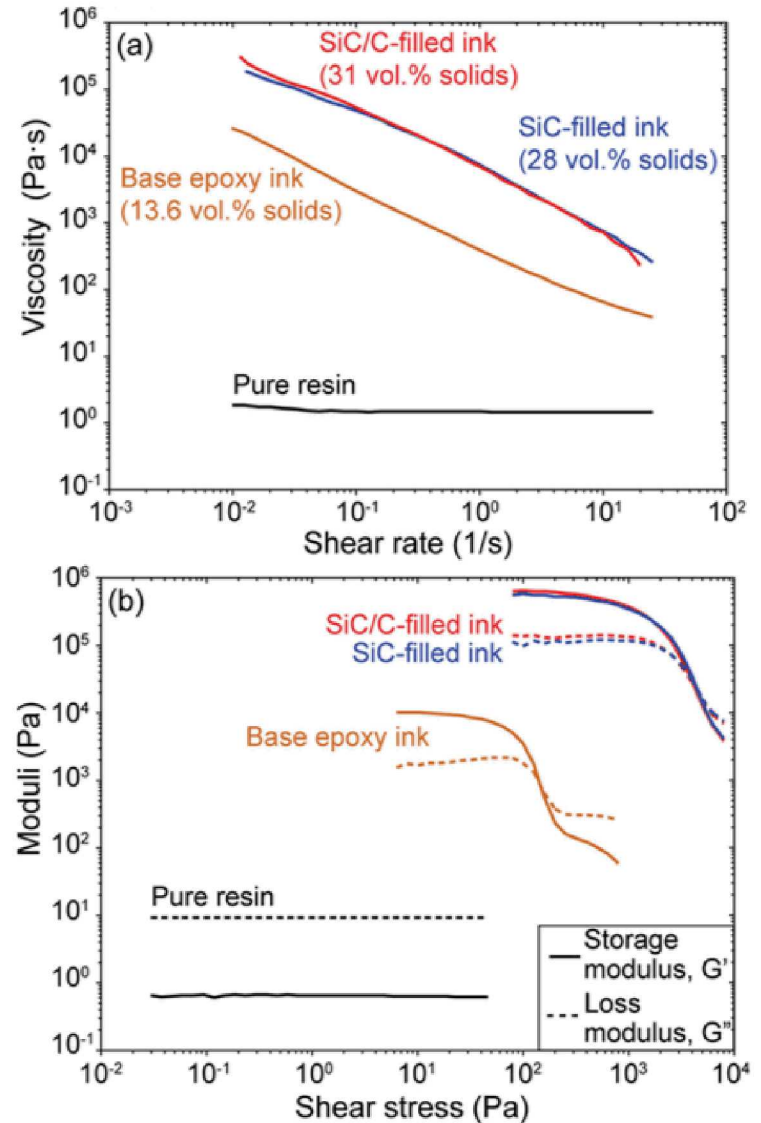


Figure 2. Log-log plots of (a) apparent viscosity as a function of shear rate and (b) shear storage and loss moduli as a function of shear stress for epoxy-based inks of varying composition.

Typically homopolymerized epoxy (or other moiety)

Latent curing agents

Fiber fillers/fillers (carbon fibers, silicon carbide whiskers, nanoclay, silica nanoparticles, nanocellulose)

Mechanical properties depend on loading, fiber length, orientation (alignment), distribution, fiber-matrix interfacial adhesion, fiber-polymer interactions

Lack of two-part amine-epoxy resins (desired physical properties, slow kinetics, limited rheological profiles)

Hypothesis: Incorporation of strong, yet reversible non-covalent physical crosslinks will yield epoxy-amine pre-polymer resins with DIW amendable properties

Characteristics of Supramoleculars

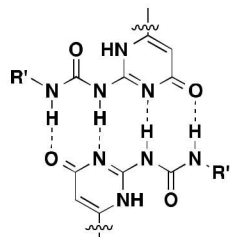
Self-assembly involves the aggregation of molecules and macromolecules to thermodynamically stable structures which are held together by weak and noncovalent interactions

Reversible and Self-repairing

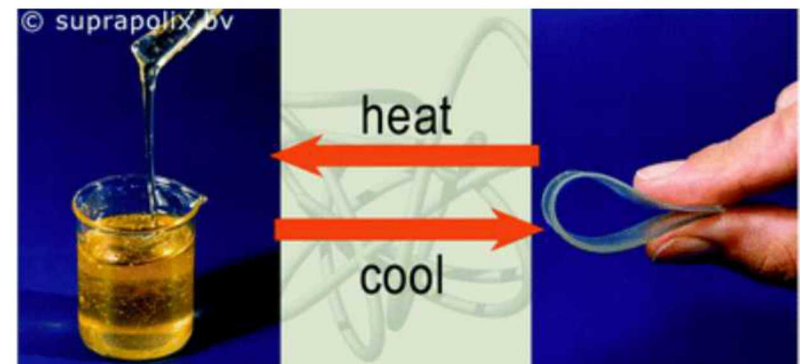
-Reversible aggregates that can break and recombine typically on experimental time scales

Stimuli-Responsive

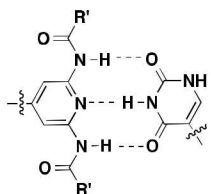
-Noncovalent interactions are sensitive to stimuli such as solvent, temperature, and pH



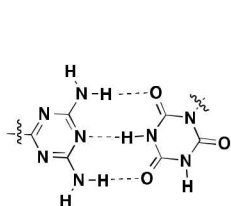
Ureidopyrimidinone
Dimer



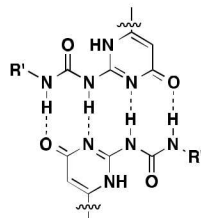
6 Exploiting Self-Assembling/Supramolecular Moieties in AM



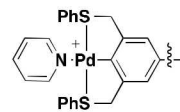
DAP/THY
 $K_a \approx 10^3 \text{ M}^{-1}$



DAT/CA
 $K_a \approx 10^2 \text{ M}^{-1}$

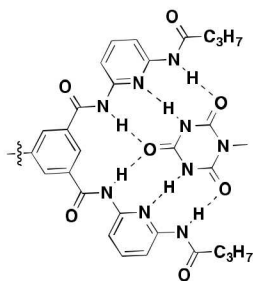


UPy dimer
 $K_a \approx 10^7 \text{ M}^{-1}$

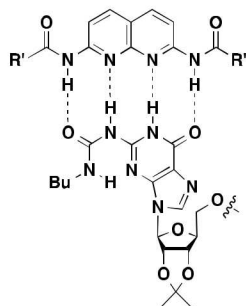


SCS-Pd^{II} pincer
 $K_a \approx 10^9 \text{ M}^{-1}$

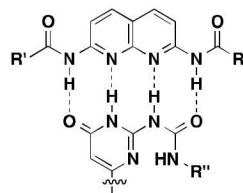
- Vary strength
- Stimuli-responsive
- Vary architectures



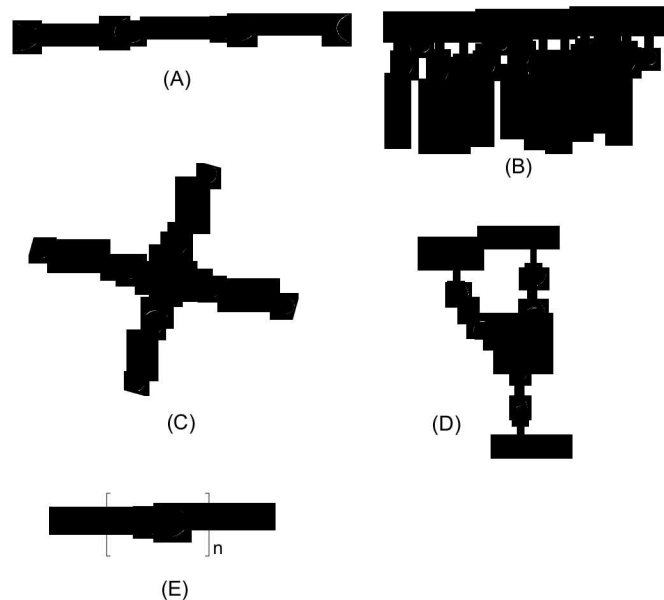
Hamilton Wedge HW/CA
 $K_a \approx 10^5 \text{ M}^{-1}$



DAN/UG
 $K_a \approx 10^7 \text{ M}^{-1}$

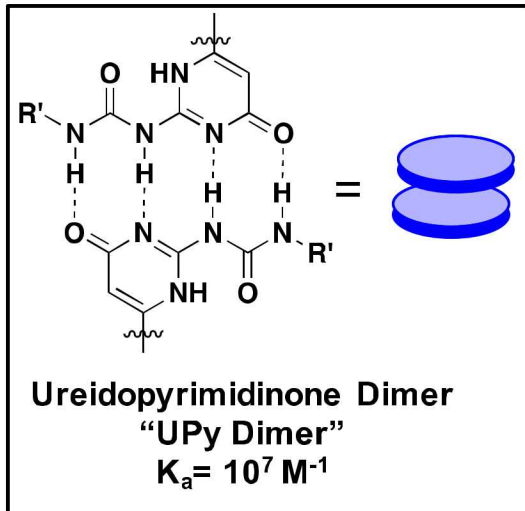


DAN/UPy
 $K_a \approx 10^6 \text{ M}^{-1}$



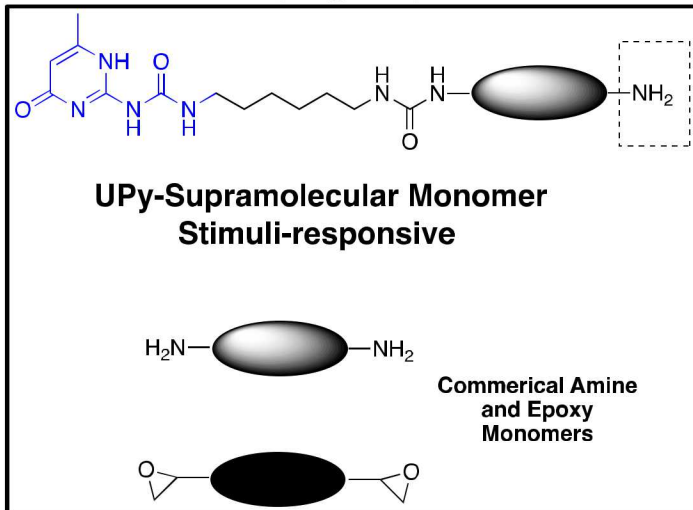
- Change rheology
- Shear effects
- Reprocessable

Self-Assembly Assisted AM of an Epoxy-Amine Thermoset

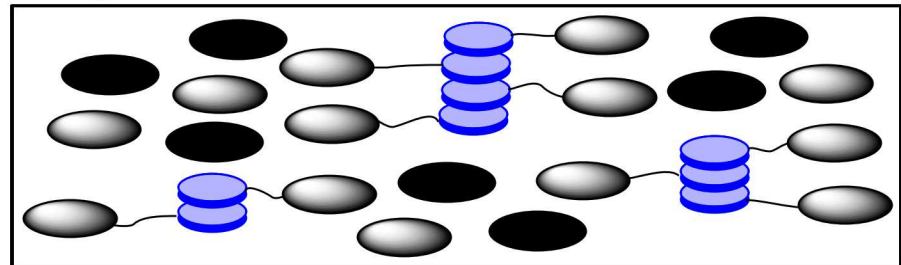


- Rheology modifier
- Toughening agent
- Reversible binding (80 °C, competitive solvent)
- Shear thinning/thickening
- Affects yield stress

Mix with varying UPy Content



Complex Network Structure of “Unreacted” Resin



Serves as 3D printing “ink”

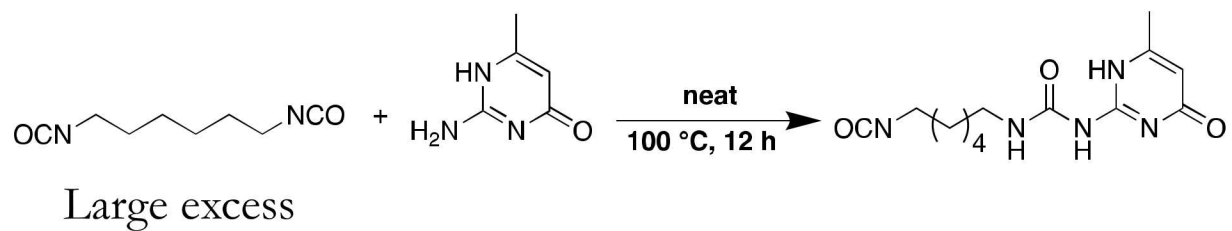
Rheology profile amendable to Direct-Ink Write

Slow Reaction Kinetics → Longer pot life

Print unreacted resin at r.t.

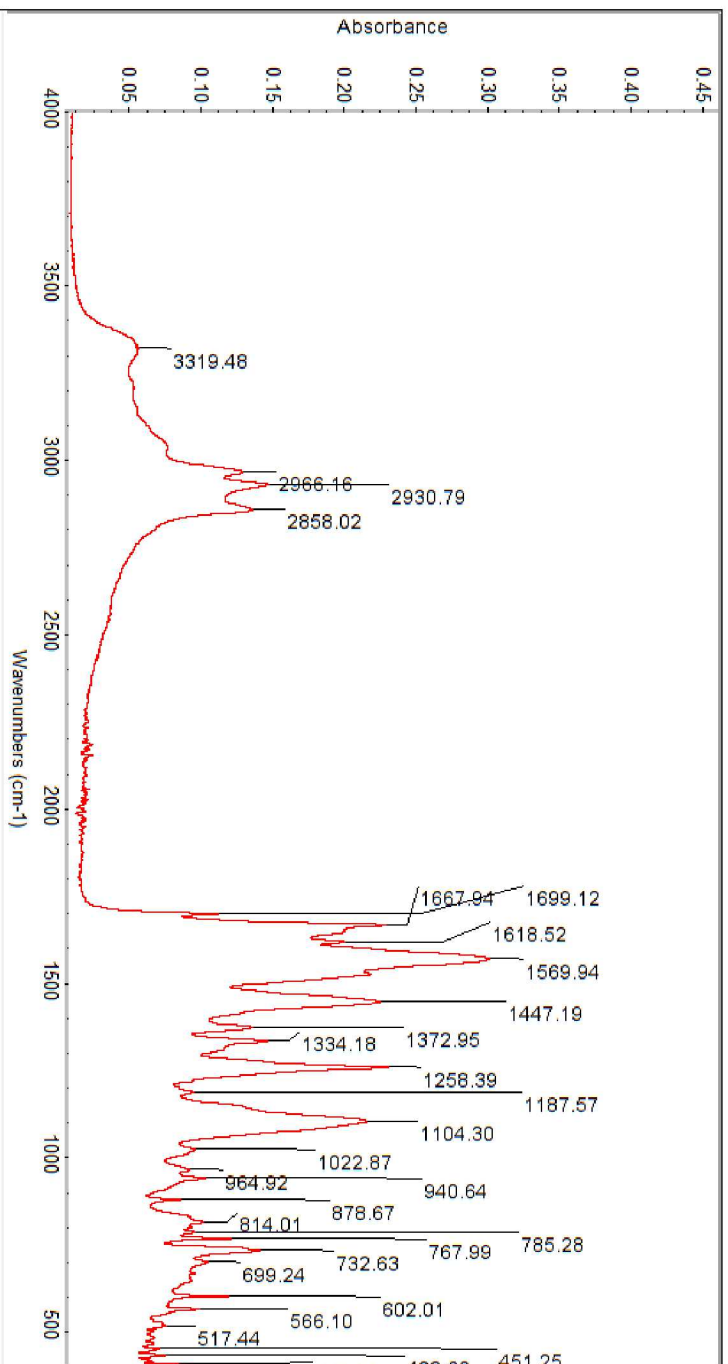
Post-cure to full conversion

Synthesis of UPy-Functionalized Jeffamine® D230- UPyD230

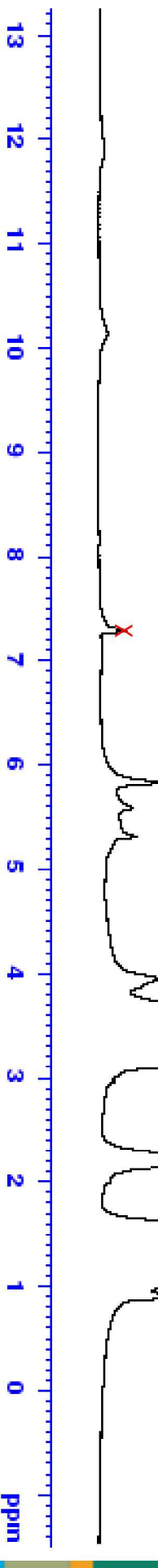
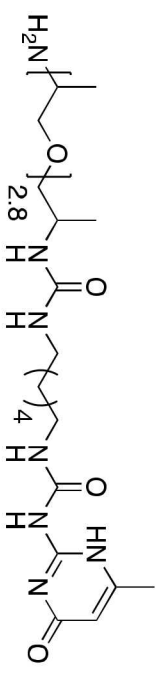


9 Characterization of UPyD230

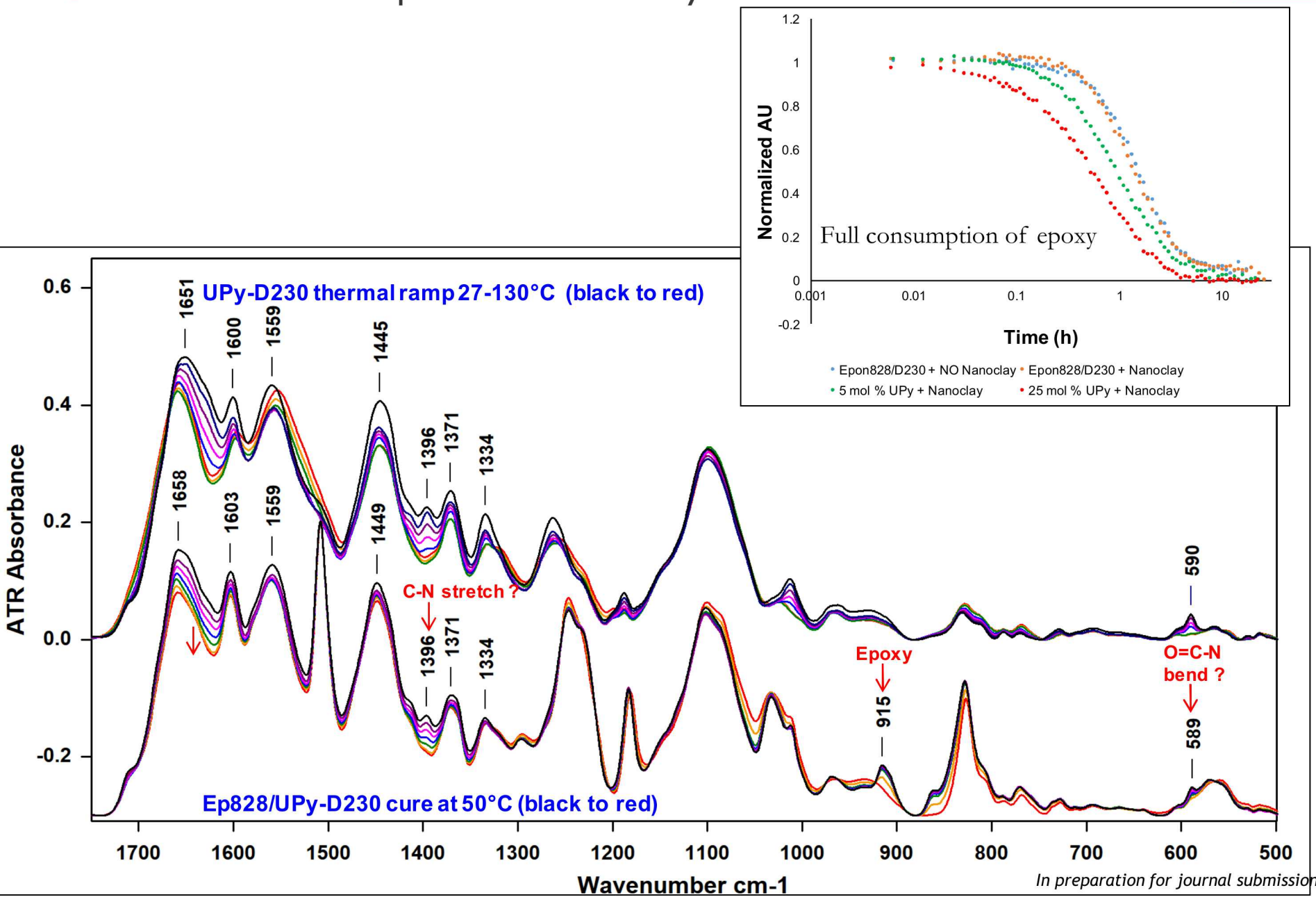
MID-IR



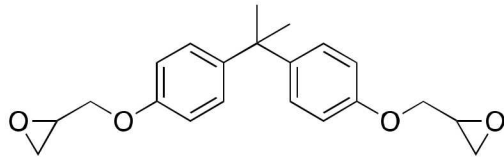
¹H NMR in CDCl₃



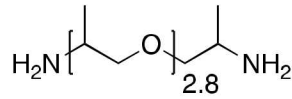
Full Cure and Temperature Effects by Near- and Mid-IR



Printing of Pre-Polymers at r.t. with Direct-Ink Write 3D printing

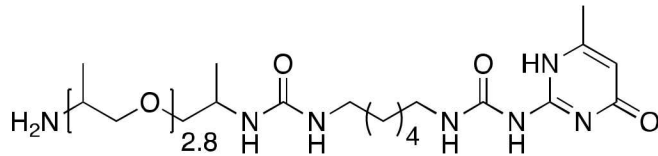


Epon828

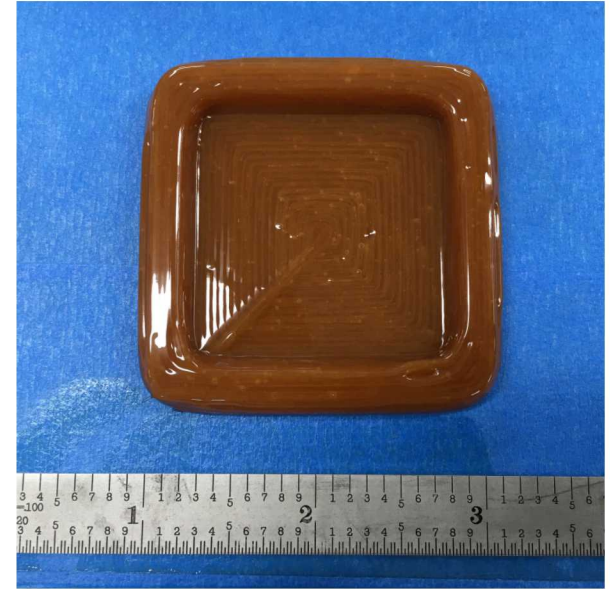


D230

10-20 wt%
nanoclay

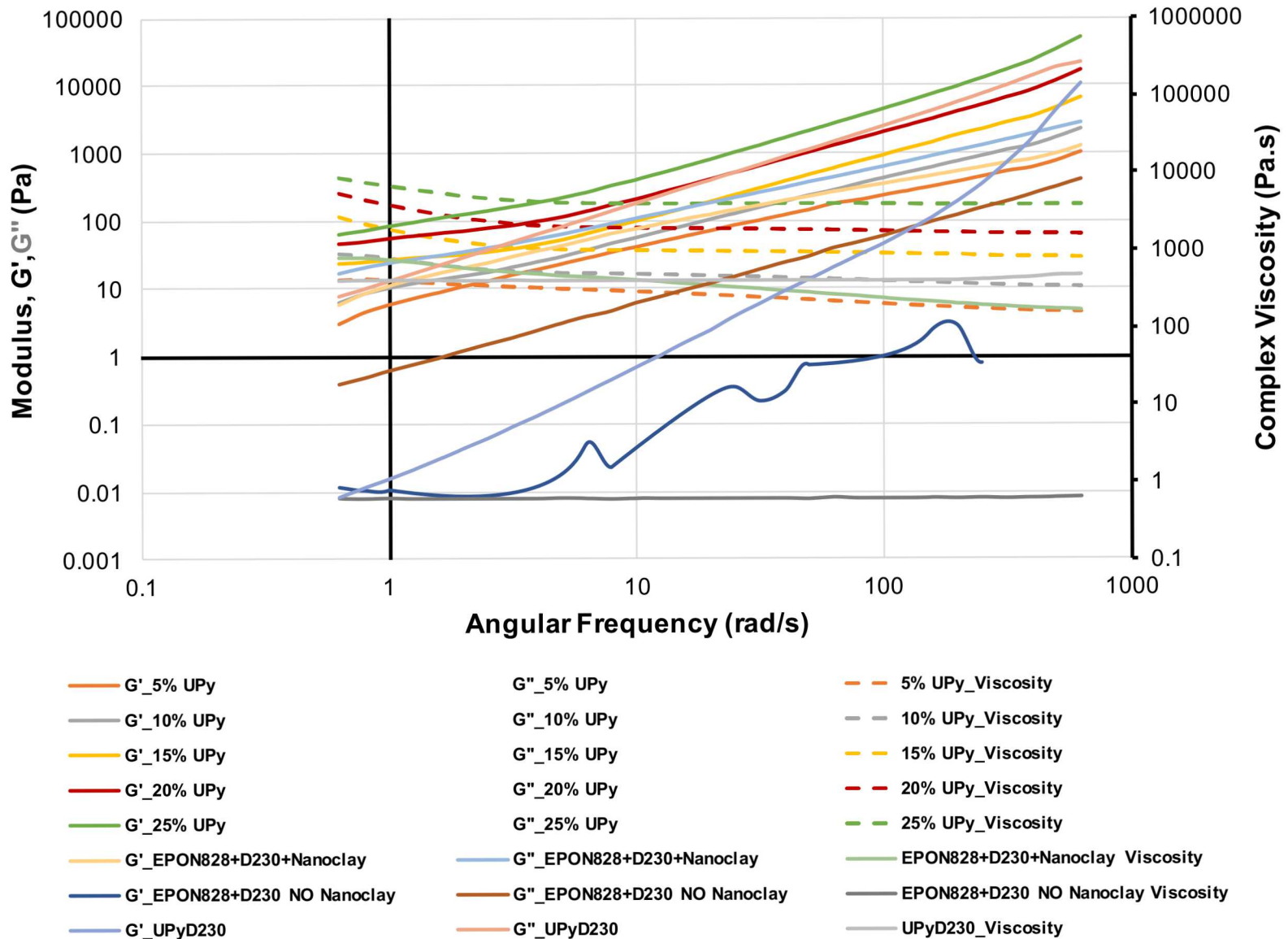


MonoUPY-D230

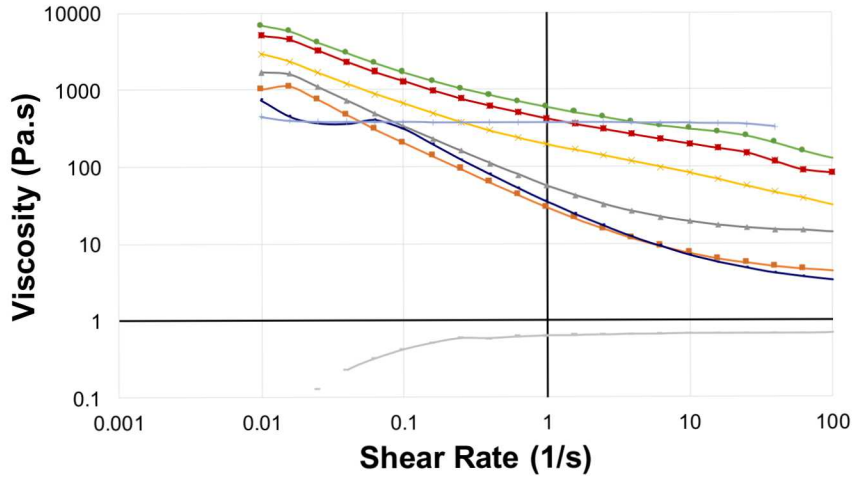


- Ink is shear-thinning due to nanoclay
- Increased yield stress due to hydrogen bonding monomer (holds shape)
- Complex shear rheology

Rheological Response to Oscillation Frequency is Predominately Viscous



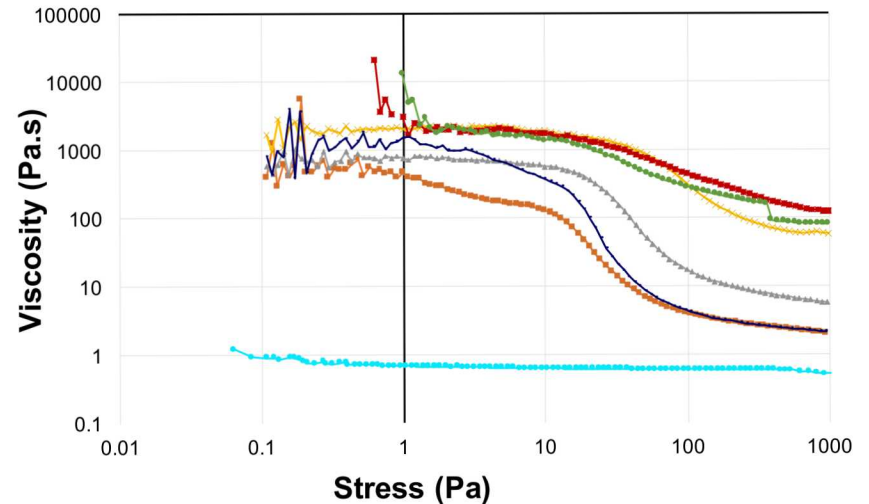
Rheological Behavior is Amendable to DIW



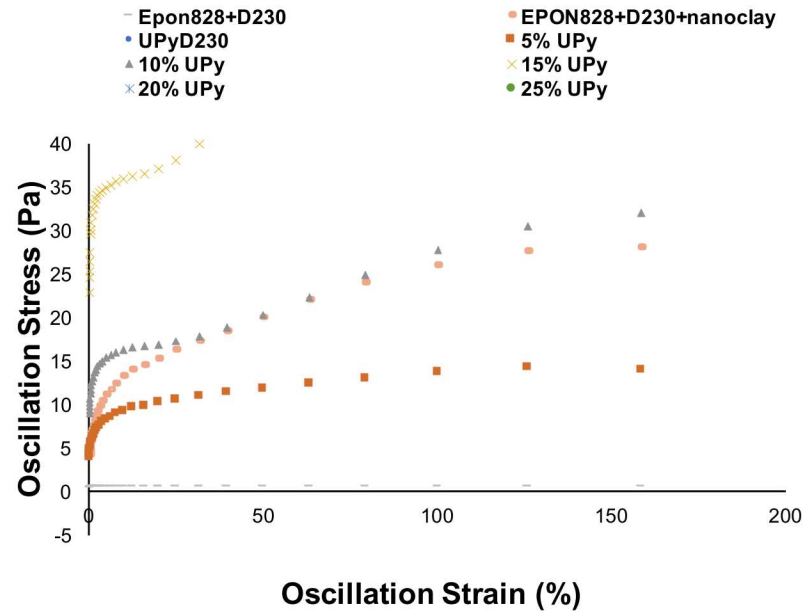
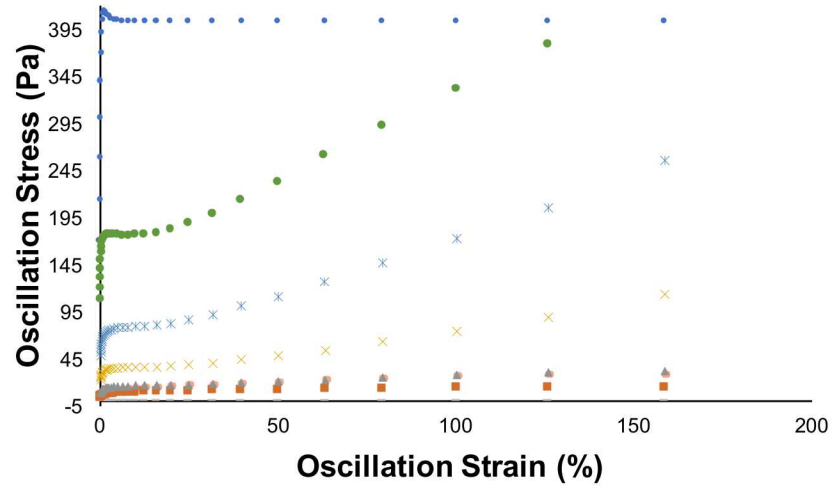
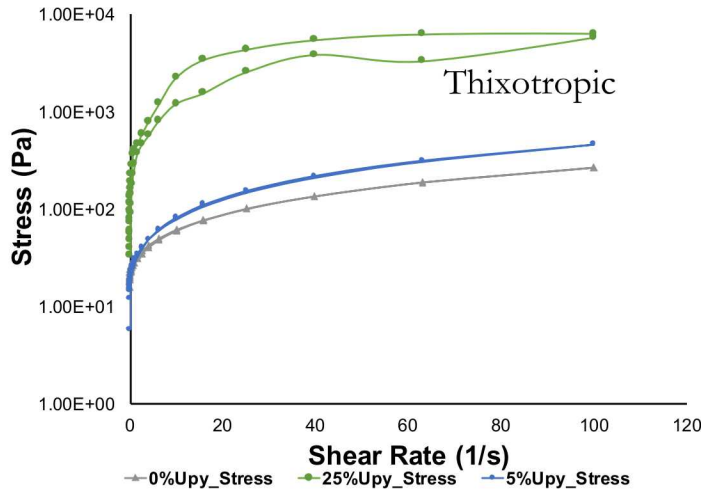
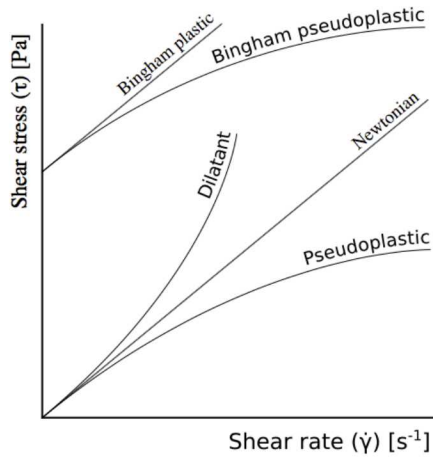
- 5% UPy
- 10% UPy
- 15% UPy
- 20% UPy
- 25% UPy
- EPON828+D230+Nanoclay
- Epon828+D230+NO Nanoclay

-Behaves as yield stress fluid with the addition of nanoclay
 -Increase viscosity and apparent yield stress with increasing UPy content

- Increased initial viscosity due to H-bonded network
- Ink is shear-thinning
- Subtle changes in slope
- Shear-effects due to H-bonds?

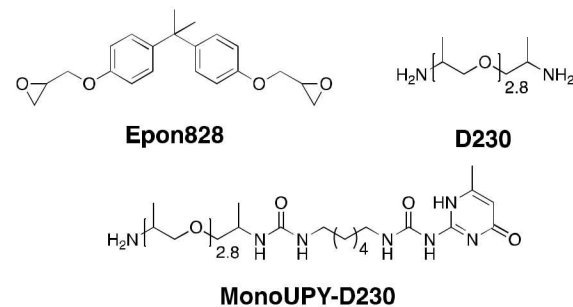


- 5%UPy
- 10%UPy
- 15%UPy
- 20%UPy
- 25%UPy
- EPON828+D230+Nanoclay
- EPON828+D230 NO Nanoclay

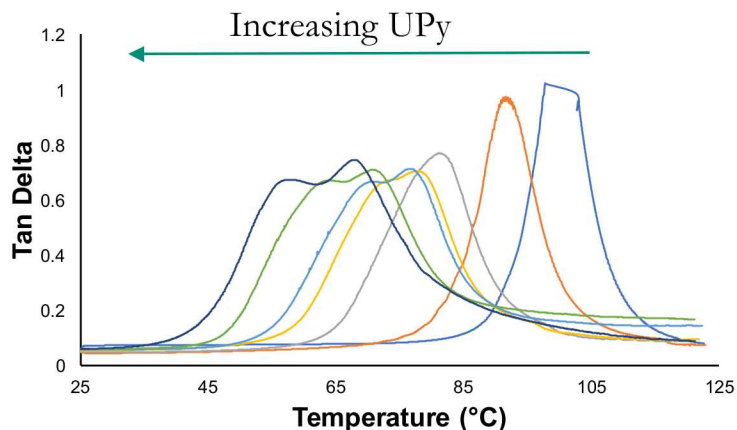


T_g and Evidence of Phase Separation in Cured Resins

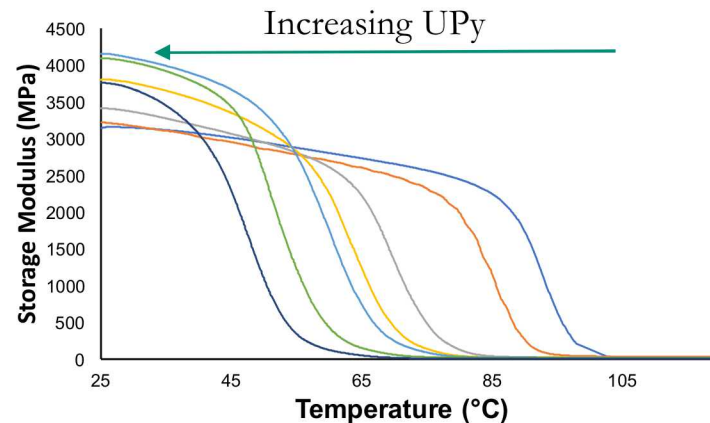
Epoxy Resin	D230	UPyD230	Ratio (E/NH)	Mol % UPyD230 (%)	T _g ¹	T _g ²	T _g ³
Epon828 ³	1	0	1:1	0	≈90.0	97.8	102.7
Epon828	1	0	1:1	0	≈90.0	91.2	84.3
Epon828	0.9	0.1	1:1	5	≈85.0	82.1	69.9
Epon828	0.8	0.2	1:1	10	≈80.0	78.7	63.9
Epon828	0.7	0.3	1:1	15	≈75.0	77.4	59.3
Epon828	0.6	0.4	1:1	20	≈70.0	71.5	52.2
Epon828	0.5	0.5	1:1	25	≈60.0	68.4	47.6



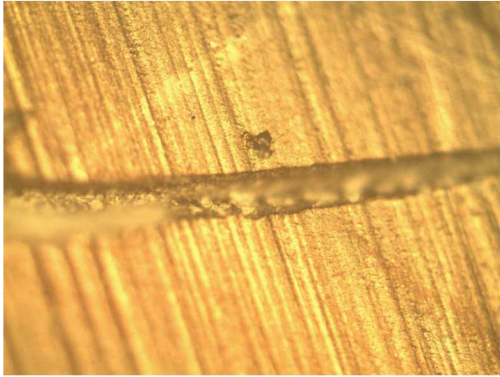
Resins were cured at 60 °C for 15 h, followed by a post-cure at 120 °C for 2 h. Note: (1) T_g¹ is the glass transition temperature based on DSC and (2) T_g² is the tan delta max and T_g³ is the mid-point of E¹ analyzed by DMA (3) This sample does not contain nanoclay.



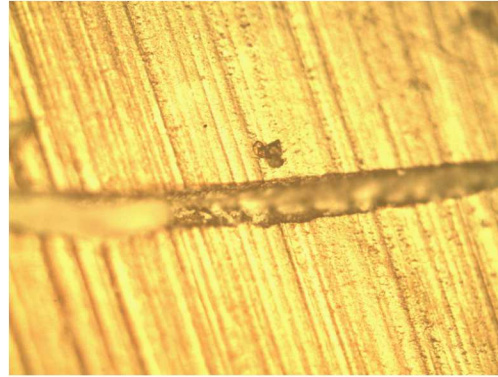
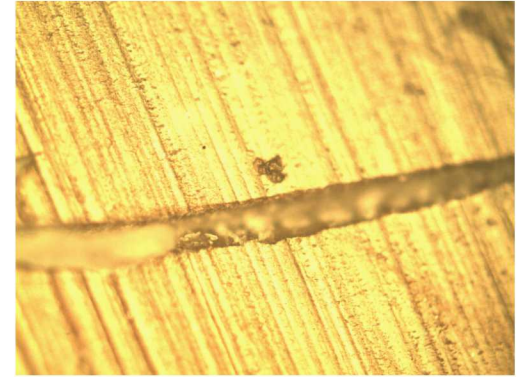
— Epon828+D230
 — 5 mol % UPyD230
 — 10 mol % UPyD230
 — 15 mol % UPyD230
 — 20 mol % UPyD230
 — 25 mol % UPyD230
 — Epon828+D230+nanoclay
 — 10 mol % UPyD230
 — 20 mol % UPyD230



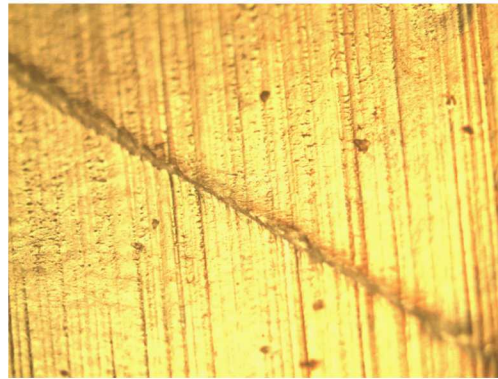
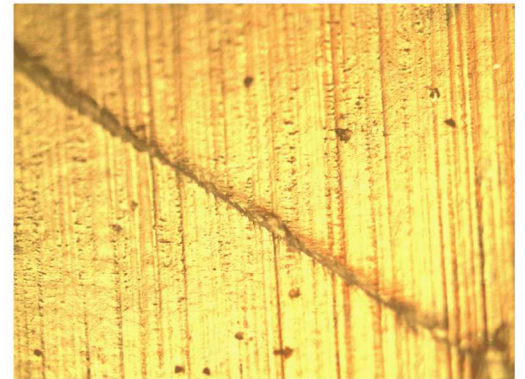
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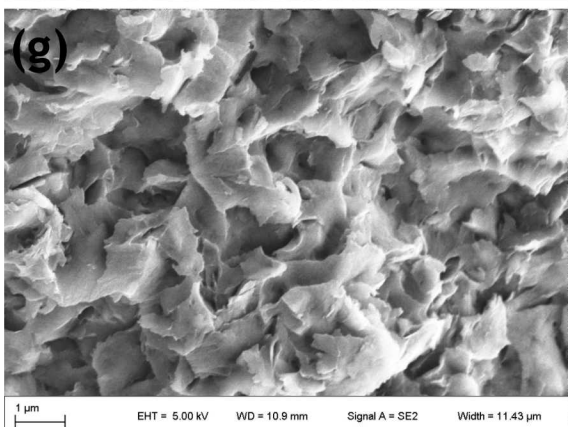
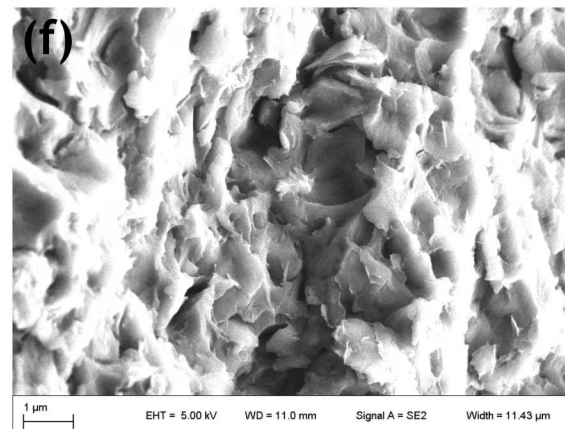
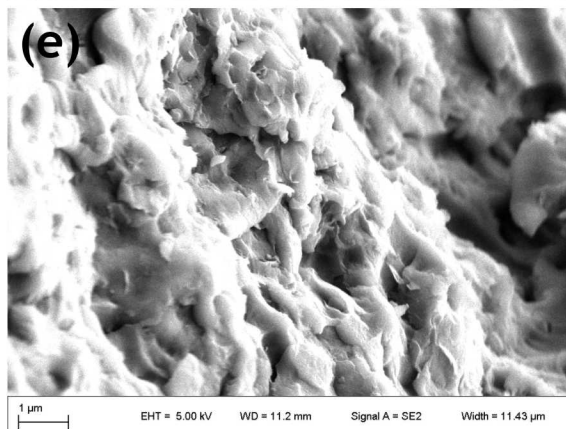
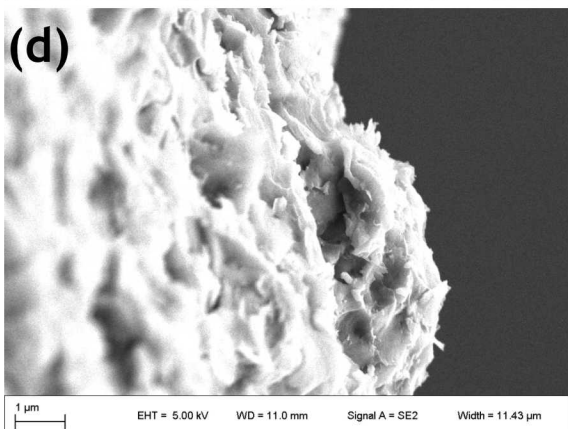
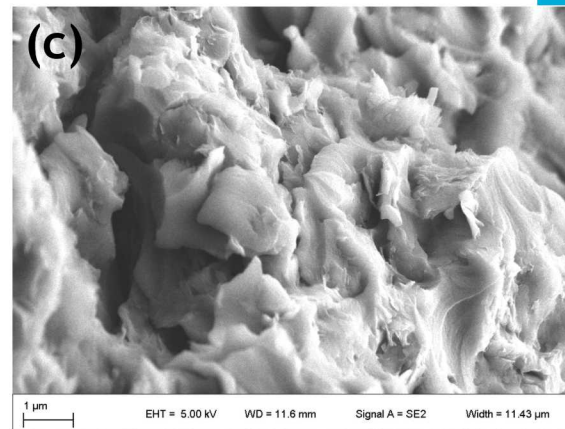
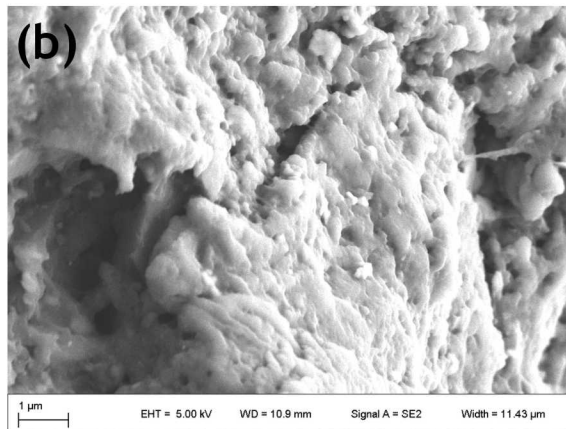
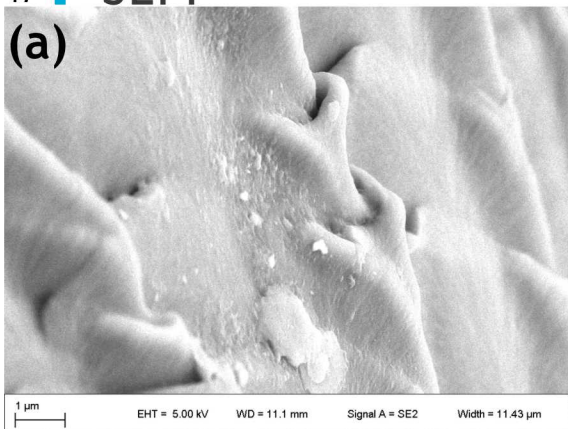
NO UPyD230, r.t.

NO UPyD230, 80 °C, 15 min
Observed at r.t.NO UPyD230, 80 °C, 45 min
Observed at r.t.

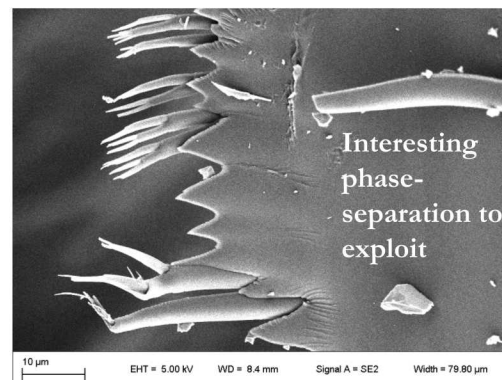
25% UPyD230, r.t.

25% UPyD230, 80 °C, 15 min
Observed at r.t.25% UPyD230, 80 °C, 45 min
Observed at r.t.

*Cured at 60 °C for 15 h and 120 °C for 2 h

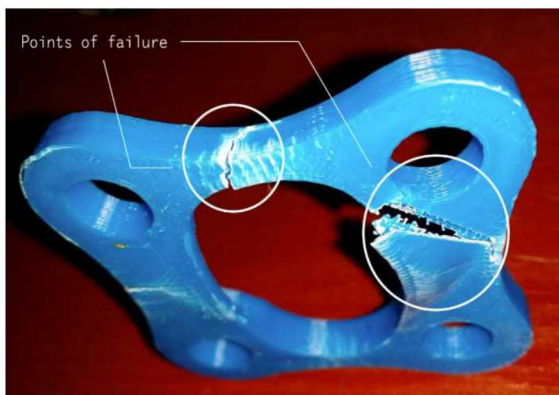
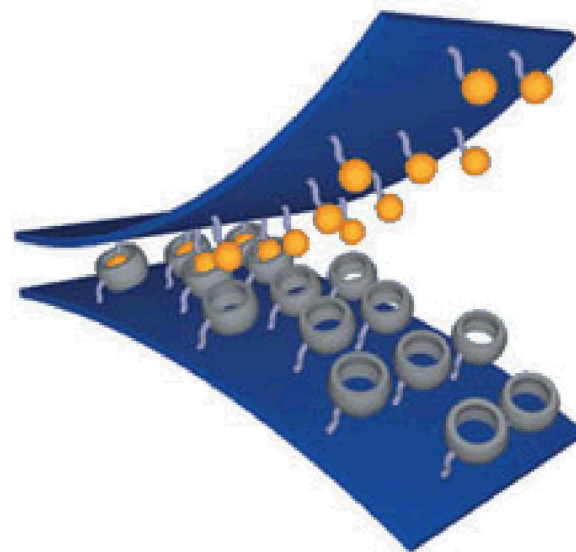
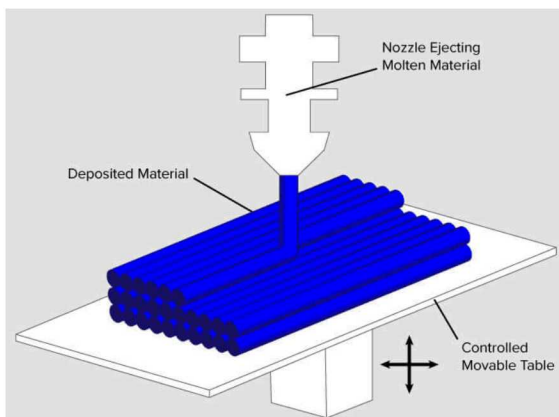


- (a) Epon828/D230
- (b) Epon828/D230 + Nanoclay
- (c) 5% UPy + Nanoclay
- (d) 10% UPy + Nanoclay
- (e) 15 % UPy + Nanoclay
- (f) 20 % UPy + Nanoclay
- (g) 25 % UPy + Nanoclay



Improvement of Interlayer Adhesion?

- Mechanical test along and against printing axis
- Compare to molded samples
- Mechanical properties may be very similar



Angew. Chem., Int. Ed., **2013**, *52*, 3140-3144.

Acknowledgements

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*Adam Cook: Direct-Ink Write

Bonnie McKenzie: SEM

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