Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information for

Additive Manufacturing: Modular Platform for 3D Printing Fluid-containing Monoliths

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Experimental Details

Materials

Graphite (7782-42-5), sulfuric acid (7664-93-9, ACS reagent 95.0–98.0%), potassium permanganate (7722-64-7, ACS reagent), isopropyl alcohol (200-661-7, ACS reagent), ethylenediamine-15-3, ReagentPlus), and 1,6-hexanediisocyanate (822-06-0, puriss.) were purchased from Millipore Sigma. Montmorillonite was purchased from Silky Scents through Amazon. Poly(α-olefin)$_{432}$ (PAO) was received from ExxonMobil and Chevron Phillips Chemical Company. Thermoplastic polyurethane pellets (TPU WHT-1585) were purchased from Wanhua Chemical Group, and N,N-dimethylformamide (68-12-2) was purchased from Fisher Scientific. Elastic resin was purchased from Formlabs.

Instrumentation

Emulsification was completed using a handheld emulsifier (model number 985370) from BioSpec Products, Inc. Centrifugation was carried out using a Thermo Scientific Sorvall ST 8 centrifuge, sonication was carried out using a Fisherbrand CPX3800 Ultrasonic Bath 5.7 L, and vortex mixing was performed using a Fisherbrand vortex mixer. Optical microscopy samples were prepared by putting a drop of emulsion on a glass slide and then visualized using an AmScope 150C-2L microscope equipped with an 18 MP USB 3.0 camera. Scanning electron microscopy (SEM) samples were sputter coated with 5 nm of Pd, and SEM images were collected on either a JEOL JSM-7500F with an acceleration voltage of 3 kV and emission voltage of 20 kV or a TESCAN FERA3 with an acceleration voltage of 1 kV and beam intensity of 6. Particles were filtered using a 120 mesh (125 µm) Fieldmaster® sieve. Particle size analysis was carried out on a HORIBA Partica LA-960 particle size distribution analyzer equipped with a fraction cell, with particles suspended in methanol. Inks were homogenized using a Thinky AR-100 planetary mixer. Rheological properties were analyzed using an Anton Parr MCR 302 rheometer with a 25 mm parallel plate. 3D printing was performed on a Hyrel 3D Engine SR with an SDS-10 syringe extrusion head and 365 nm UV Pen. Compression testing was performed on a TA Instruments DMA 850 equipped with a compression clamp. Optical images of the printed inks and printed objects were recorded using an iPhone 11 Pro.

Preparation of Graphene Oxide

Graphene oxide (GO) was synthesized via a previously reported modified Hummer's method.[1] 1.0 g of graphite flakes were dispersed in ~150 mL of concentrated sulfuric acid at room temperature with constant stirring. 1.0 g of potassium permanganate was added to the graphite/sulfuric acid mixture, and stirring continued for 24 h. This addition was repeated 3 times to add a total of 4.0 g potassium permanganate over 96 h. The solution was quenched via addition to ~750 mL of an ice-water bath, and 30 v/v% aqueous hydrogen peroxide was added dropwise until a color change from pink to yellow was observed, indicating successful quenching of excess potassium permanganate. Centrifugation was used to isolate crude GO as a yellow-brown solid. Crude GO was washed with isopropyl alcohol to neutral pH by centrifuging and discarding the supernatant repeatedly. Purified GO was dried under reduced pressure at room temperature. GO stock solutions were prepared by vortex mixing and sonication of solid GO in distilled water at a concentration of 2 mg/mL.

Preparation of PAO-in-Water Pickering Emulsions

Graphene oxide (GO) nanosheets were used as surfactants to form Pickering-type PAO-in-water emulsions due to their demonstrated use as surfactants in oil-in-water emulsions.[2–5] Nanosheets were prepared via modified Hummer's method and characterized as previously reported.[6–8] Emulsions were prepared by dispersing GO in distilled water via vortex mixing and sonication at a concentration of 2 mg/mL, then adding an appropriate amount of PAO, and agitating the systems with a handheld emulsifier for three cycles of 20 s of emulsification and 15 s of rest. Emulsion formation and stability were verified via optical microscopy imaging at various time points.

Preparation of PAO Capsules

PAO was encapsulated by interfacial polymerization in a Pickering emulsion template via modified procedure as previously reported.[6,9] 1,6-hexanediisocyanate (6.50 mmol) was added to 1 mL of PAO in a flask, followed by a solution of 25 mL of 2 mg/mL aqueous GO or 2 mg/mL aqueous MMT and 0.050 mL of saturated sodium chloride (to flocculate the GO/MMT nanosheets). The mixture was emulsified using a handheld emulsifier for three consecutive cycles of 60 s of emulsification followed by a 55 s break. 6.25 mL of a solution of ethylenediamine in water (6.65 mmol/mL) was added dropwise to the emulsion while swirling by hand. This mixture was left unagitated for 72 h before quenching via addition of propylamine (35 mL) in water (500 mL) for 24 h. Solid capsules were isolated via gravity filtration and washed with distilled water to neutral pH. Capsules were sieved to ≤ 125 μm in diameter and dried under reduced pressure at 30 °C overnight, yielding the light brown powder GO-C or light gray powder MMT-C. PAO weight percent in the capsules was determined by extracting PAO from a capsule sample of known mass with hexane via sonication and removing shell fragments with a syringe filter. Hexane was removed under reduced pressure, and the resulting residue was weighed, allowing the wt% PAO comprising the capsules to be calculated.

Ink Preparation and 3DP

Thermoplastic polyurethane inks

In a 20 mL scintillation vial, 2 g of thermoplastic polyurethane (TPU) pellets were added to 20 mL of N,N-dimethylformamide (DMF), then heated at 60 °C overnight to dissolve the TPU. The 1:10 w:v TPU/DMF solution was cooled to room temperature. GO-C were added to the solution at a weight ratio of 1 g capsules:1.1 g solution. This mixture was thoroughly homogenized by mixing in a Thinky AR-100 at 2000 rpm for 1 min to produce the ink GO-T.

Resin inks

In a 20 mL scintillation vial wrapped with aluminum foil, GO-C or MMT-C were added to Formlabs Elastic resin at a weight ratio of 1 g capsules:1.5 g resin. The mixtures were thoroughly homogenized by mixing in a Thinky AR-100 at 2000 rpm for 1 min to produce the inks GO-R and MMT-R.

3D Printing

Each ink was loaded into a 10 mL syringe equipped with an 18G nozzle (0.840 mm inner diameter). The loaded syringes were then placed on the extrusion cartridge of the 3D printer, and lattices were printed onto a glass bed with a fixed layer height of 0.1 mm, extrusion rate of 20 mL/h, and infill of 10%. Resin-based inks GO-R and MMT-R were crosslinked via *in situ* UV exposure after each layer. GO-T was cured after printing by washing with water to remove DMF. Printed layer heights were varied from 0.1 to 0.5 mm for GO-R and MMT-R. A block T Texas A&M logo (designed by Jackson Mika, open-source model from Thingiverse) was printed using GO-T with a layer height of 0.1 mm and infill of 0%, as only the walls were needed for the design.

Rheometry Experiments

All rheological experiments were performed using an Anton Parr MCR 302 rheometer with a 25 mm parallel plate at 25 °C, with a gap distance of 1 mm. A shear rate ramp from

1 to 1000 s^{-1} was performed for each matrix material and ink three times, and viscosity was measured. A stress amplitude sweep was performed on each matrix material and ink three times from 0.001 to 100 Pa at a frequency of 1 s^{-1}, and storage and loss moduli were measured.

Depth of Cure Experiments

In a 2 mL vial, 1 mL of GO-R or MMT-R was added from the extrusion syringe and defoamed by low-speed centrifugation (1000 rpm). The vial was then positioned 2.5 cm above a 365 nm UV Pen and exposed to radiation at 100% intensity for 5 30-second intervals, and allowed to cool between each interval to 35 °C. The vial was broken to retrieve the samples, and then the samples were cut in half vertically. The samples were then measured at the midpoint of the cured ink using calipers 3 times each. 1 cm square outlines of GO-R and MMT-R were also printed using layer heights ranging from 0.1 to 0.5 mm and crosslinked via *in situ* UV exposure after each layer. Tweezers were used to separate uncured layers to evaluate delamination.

Compression Tests

Cylindrical compression samples 4 mm tall and 4 mm in diameter were prepared from GO-T, MMT-R, bulk TPU, the 1:10 TPU/DMF solution, and the photopolymer resin. GO-T, MMT-R, TPU/DMF, and resin were cast into silicone molds and cured by either soaking in water or irradiation with UV light. Samples of bulk TPU were prepared by hot pressing TPU pellets at 150 °C to form a TPU sheet. After the sheet cooled, 4 x 4 mm cylinders were hole punched out of it. For all samples, stress-strain profiles were collected on a TA Instruments DMA 850 at room temperature. The compression clamp applied a preload force of 0.001 N, and samples were compressed at a rate of 1 mm/min until the maximum allowable force (18 N) was reached on the instrument. Five samples of each type were measured.

Mass Loss Experiments

Three 1 x 1 x 1 cm samples each of GO-T and MMT-R were printed, cured, and allowed to equilibrate to ambient conditions for 24 hours, after which the samples were weighed. The samples were then placed onto Kimwipes to absorb oil leakage. The mass of each sample was recorded over 14 days.

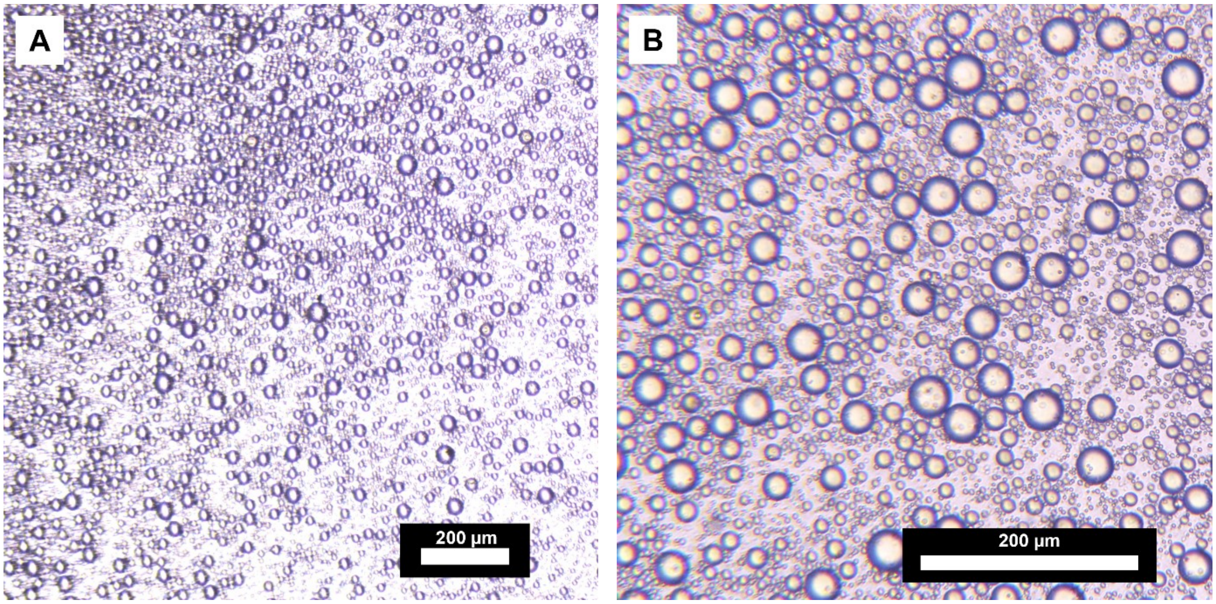

Figure S1. Optical microscopy images of GO-stabilized Pickering emulsion at (A) 4x and (B) 10x magnification.

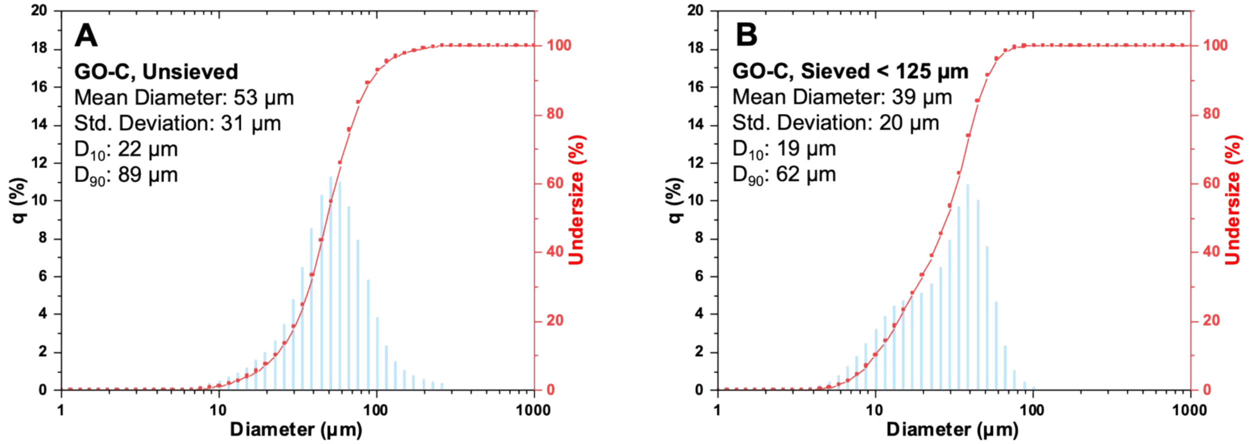

Figure S2. Particle size distributions for GO-C (A) before and (B) after sieving to remove particles > 125 µm.

Table S1. Wt% PAO within GO-C before and after sieving.

	Wt% PAO			Average	Std. Dev.
Unsieved GO-C	75.2	73.9	76.2	75.1	1.2
Sieved GO-C	81.9	78.5	80.5	80.3	1.7

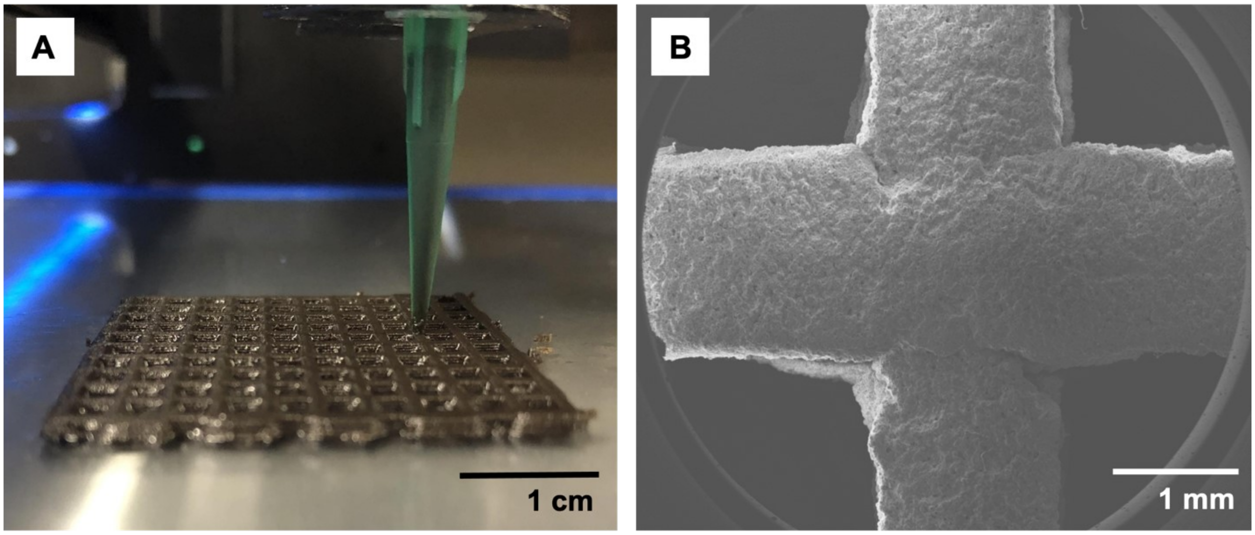

Figure S3. (A) Printing of lattice using GO-T. (B) SEM image of GO-T printed and cured lattice.

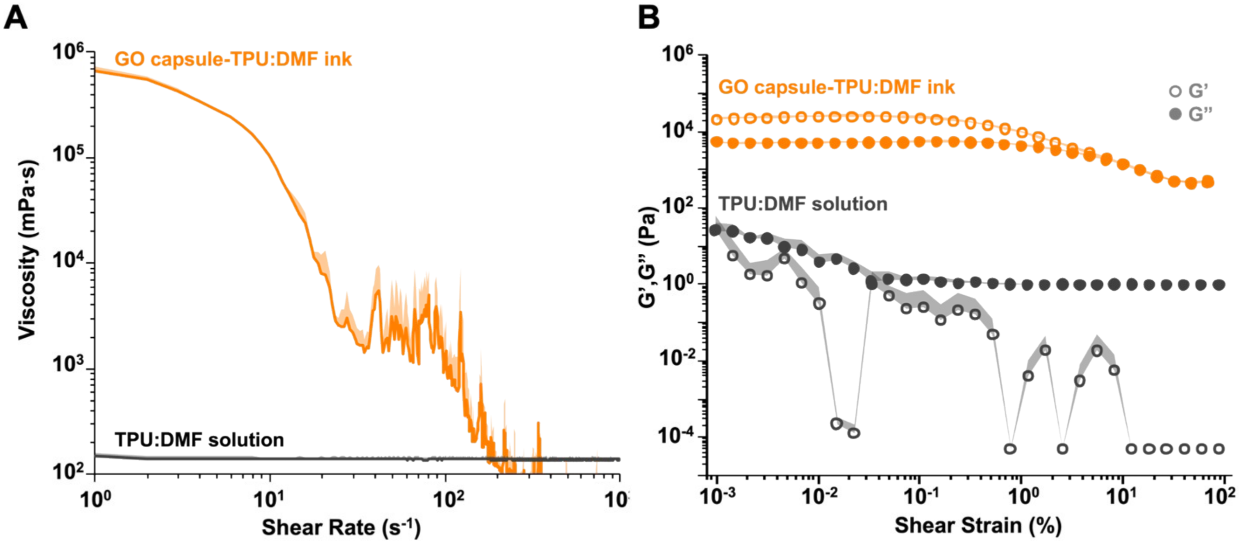

Figure S4. (A) Viscosity of TPU:DMF solution (gray trace) and GO-T (orange trace) as shear rate was increased. (B) G' and G" of TPU:DMF solution (gray markers) and GO-T (orange markers) as shear strain was increased. Shaded areas indicate standard deviation (n=3).

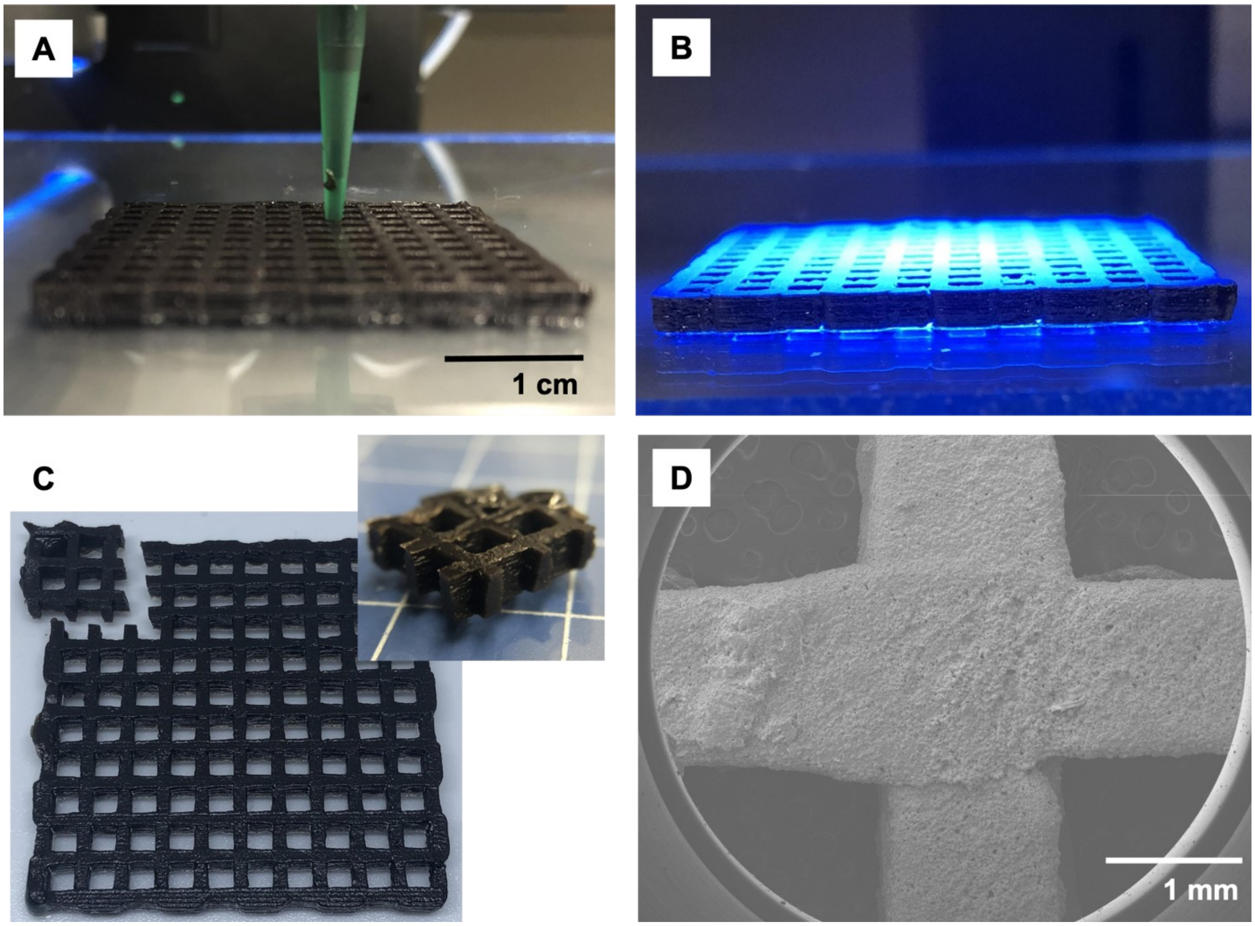

Figure S5. (A) Printing of lattice using GO-R. (B) Curing of GO-R lattice. (C) Printed and cured GO-R lattice with inset showing full curing throughout structure. (D) SEM image of GO-R printed and cured lattice.

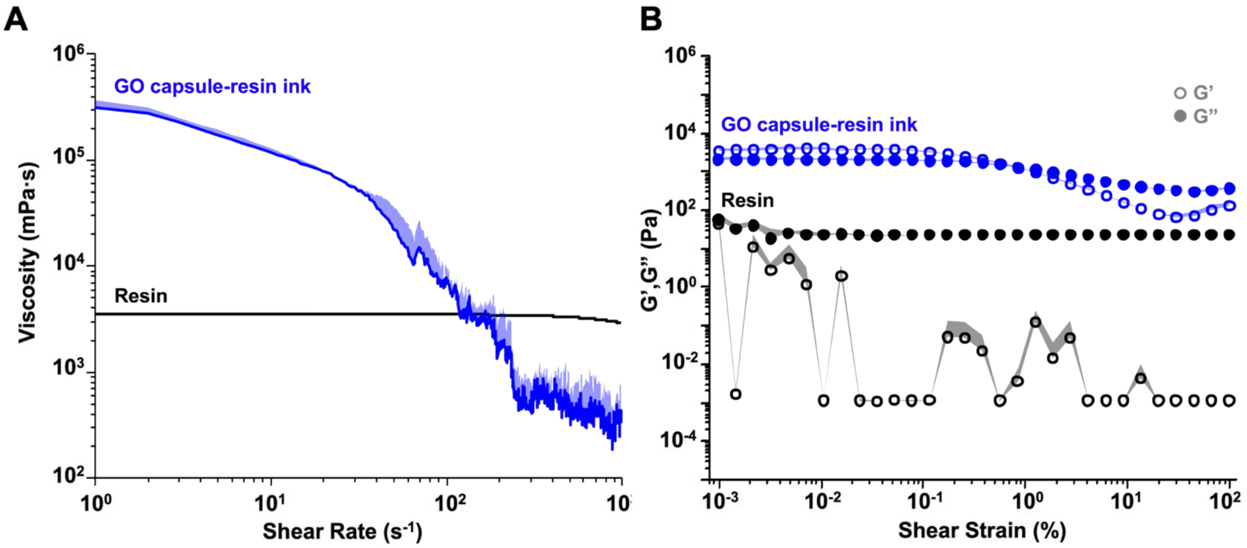

Figure S6. (A) Viscosity of photopolymer resin (black trace) and GO-R (blue trace) as shear rate was increased. (B) G' and G" of photopolymer resin (black markers) and GO-R (blue markers) as shear strain was increased. Shaded areas indicate standard deviation (n=3).

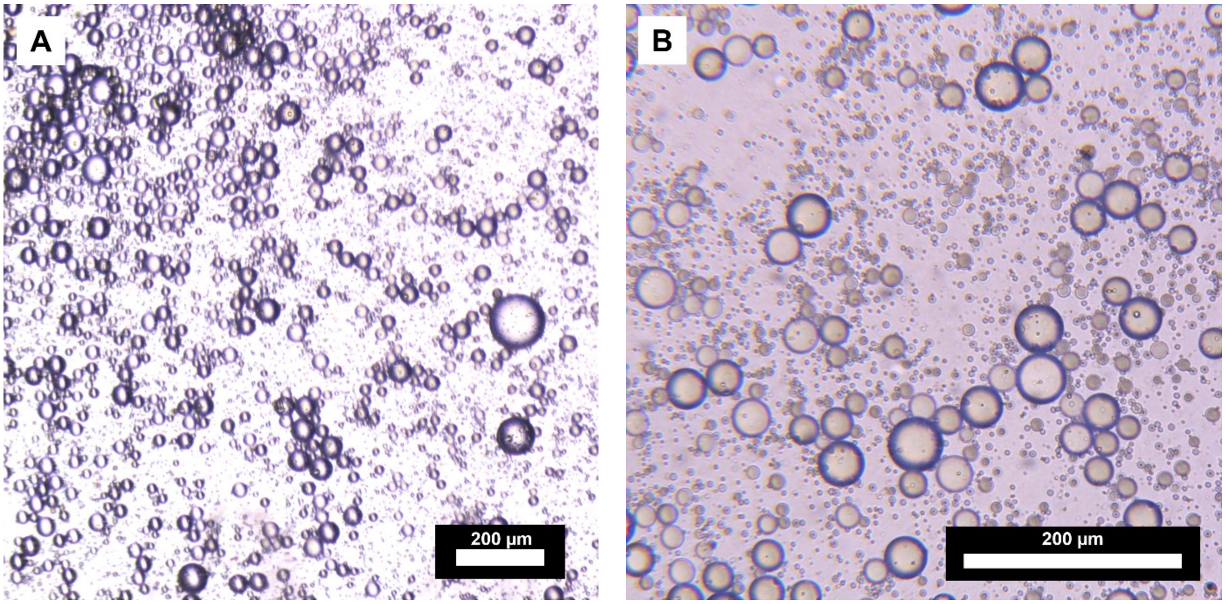

Figure S7. Optical microscopy images of MMT-stabilized Pickering emulsion at (A) 4x and (B) 10x magnification.

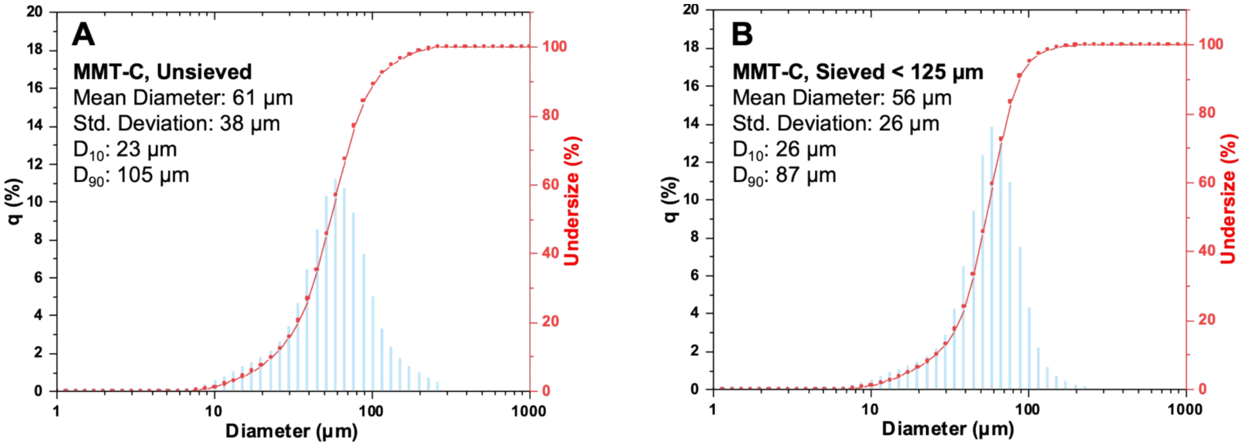

Figure S8. Particle size distributions for MMT-C (A) before and (B) after sieving to remove particles > 125 μm.

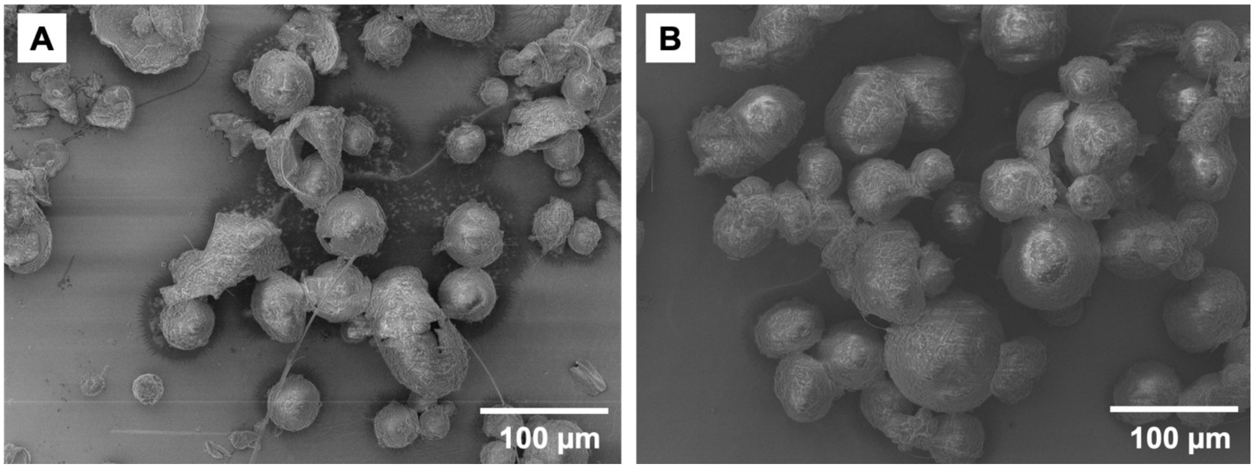

Figure S9. SEM images of (A) GO-C and (B) MMT-C.

Table S2. Wt% PAO within MMT-C before and after sieving.

	Wt% PAO			Average	Std. Dev.
Unsieved MMT-C	74.8	73.9	74.3	74.4	0.5
Sieved MMT-C	81.5	83.3	83.5	82.8	1.1

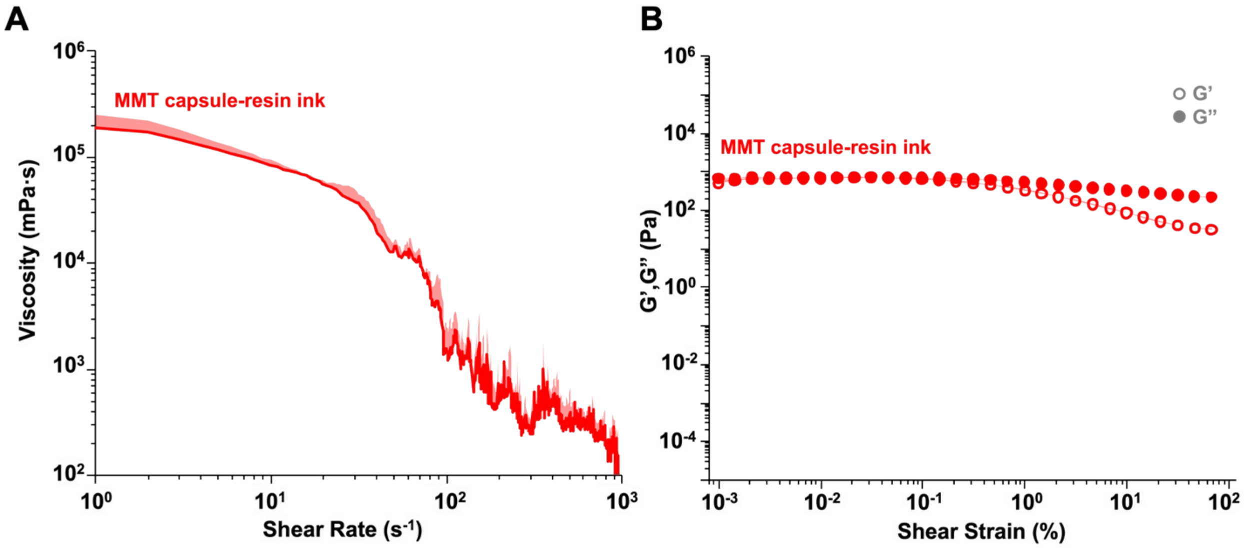

Figure S10. (A) Viscosity of MMT-R as shear rate was increased. (B) G' and G" of MMT-R as shear strain was increased. Shaded areas indicate standard deviation (n=3).

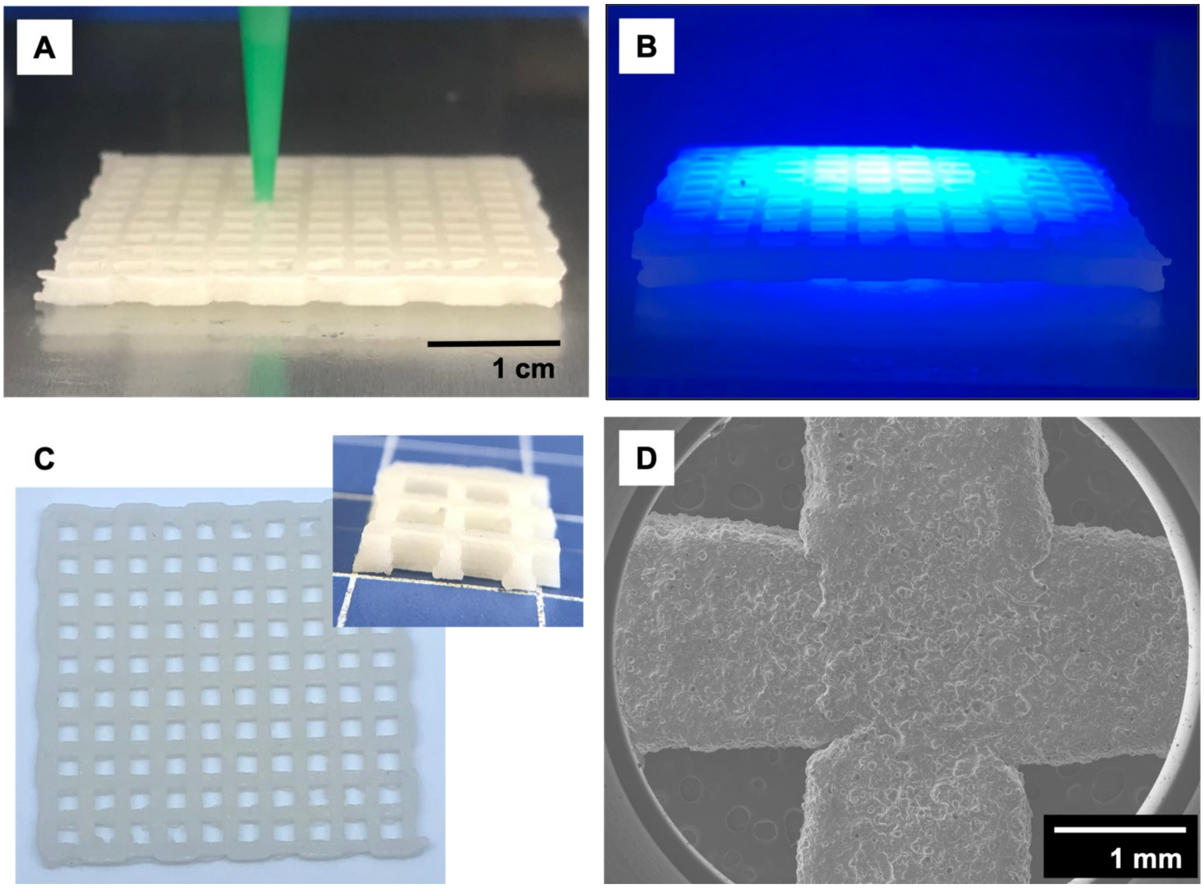

Figure S11. (A) Printing of lattice using MMT-R. (B) Curing of MMT-R lattice. (C) Printed and cured MMT-R lattice with inset showing full curing throughout structure. (D) SEM image of MMT-R printed and cured lattice.

Table S3. DOC results for GO-R and MMT-R.

	Measured Depth of Cure (mm)			Average	Std. Dev.
GO-R	0.66	.072	0.67	0.68	0.03
MMT-R	6.17	6.35	6.37	6.30	0.11

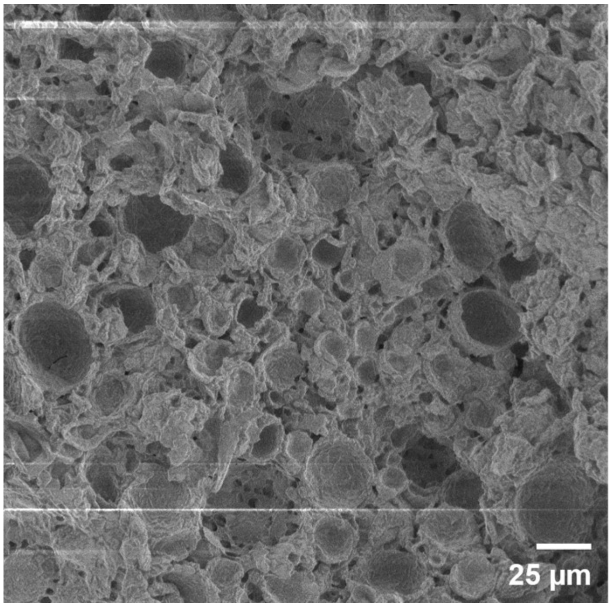

Figure S12. SEM image of GO-T cross-section.

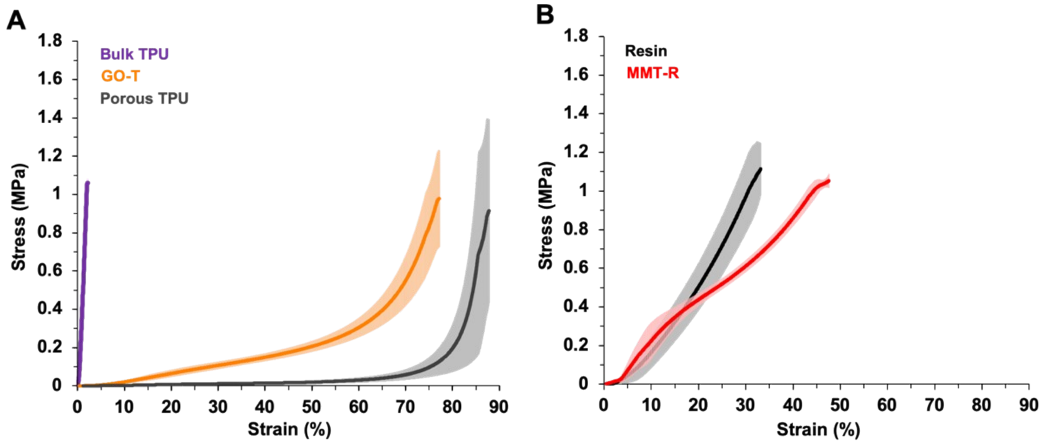

Figure S13. Stress-strain curves from compression tests of (A) bulk TPU, GO-T, and porous TPU, and (B) photopolymer resin and MMT-R. Shaded areas indicate standard deviation (n=5).

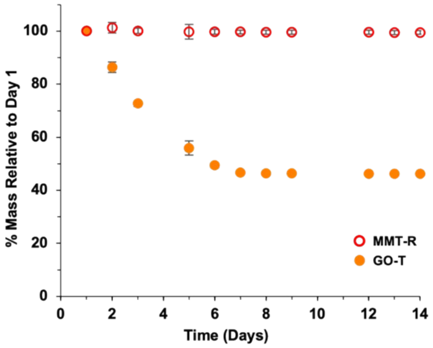

Figure S14. Mass of printed and cured lattices of each ink over time. Error bars indicate standard deviation (n=3).

References

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