Supplementary Information for

On-demand modulation of 3D printed elastomers using programmable droplet inclusions

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Supporting Information Text

Methods and Materials

Formulation of PDMS Outer Phase. PDMS outer phase was generated by mixing 11 parts Dow Corning SE1700 with 9 parts silicone oil (20 cSt) containing 13 wt.% Dow Corning 749 fluid as a surfactant. For optimal mixing, the SE1700 elastomeric base and silicone oil were homogenized by hand prior to adding the SE1700 curing agent. Upon addition of the curing agent and subsequent mixing, the PDMS ink had a final appearance of a light grey opaque paste and a shelf life of 24 hours.

Design of Microfluidic Printhead. A generic glass capillary microfluidic device made from borosilicate glass capillary tubes was used as the droplet microfluidic printhead. The injection capillary consisted of a round 1-mm diameter glass capillary that is pulled using a glass pulling device (MicroData Instruments Inc.) to form a tapered tip. The tip was subsequently polished using fine sandpaper (grit > 1500) to a final diameter of around 20 µm under an optical microscope. The collection capillary consisted of a round 1-mm diameter glass capillary whose length was limited to 0.75" to limit pressure build-up in the device. Both capillaries were aligned coaxially within a square glass capillary with 1.05 mm long sides and secured in place using Loctite clear epoxy glue. Blunt dispensing needles and polyethylene tubing were used to couple the glass capillary with a syringe pump (Harvard Technologies).

Inner Phase Formulation. Pure glycerol, fluorescein sodium salt, eutectic gallium-indium (eGaIn), poly(ethylene glycol) diacrylate (PEGDA) MW = 700 and diethoxyacetophenone (DEAP) were purchased from Sigma-Aldrich. The glycerol solution was generated by mixing pure glycerol into DI water at 62 wt.%. Fluorescein salt was added into the glycerol solution and DI water, giving them a strong green hue that fluoresces under UV light. The PEGDA solution was generated by dissolving 50 wt.% of PEGDA in deionized water, followed by addition of fluorescein salt. 3 wt.% of photoinitiator (DEAP) was added into the PEGDA solution to generate PEGDA particles upon UV exposure. The final appearance of the PEGDA solution with and without PI was a translucent grey liquid with a slight green hue.

Printing and Processing of Emulsion Inks. PDMS and the aqueous dispersed phase were supplied into the microfluidic printhead using a syringe pump (Harvard Technologies). The selected flow rate for PDMS was fixed at 1.50 mL/hr, and 2.00 mL/hr when dispersing eGaIn, while the flow rate of the inner phase was adjusted to obtain the desired Q* values. Once the fluid phases in the microfluidic printhead reach hydrodynamic equilibrium, the devices were visually inspected for successful emulsion generation. Next, the printhead was mounted on a 3D printer machine, moved along the x, y and z directions to deposit the emulsion in 3D space according to the print path defined by the .gcode file used. The printhead travel speed was set to be equal to the velocity of the emulsion exiting the printhead (i.e. flow rate of PDMS and inner phase divided by cross sectional area of collection capillary). Upon successful printing of the emulsion inks, the printed constructs were then subjected to further processing that varied depending on the emulsion ink system. For glycerol and liquid metal droplets in PDMS, the constructs were heated at 75°C for 24 hours to facilitate curing of the PDMS outer phase. For porous PDMS, the constructs were heated at 75°C for 48 hours to both cure PDMS and evaporate the encapsulated water droplets. For PEGDA particles in PDMS, the constructs were first exposed to UV radiation from a 120 W mercury lamp to photopolymerize the PEGDA particles before being heated at 75°C for 48 hours in Fig. 3E. All constructs in Fig. 4 experiments were exposed to UV if PI was present and subjected to heating at 75°C for only 24 hours.

Compression Testing of PDMS Constructs. 5-mm cube CAD files were converted into .gcode files to guide the motion of the printhead. Upon successful printing and curing of the printed cubes, the cubes were trimmed by hand to obtain flat surfaces and dimensioned prior to compression loading (Instron 1005, 10N load cell). The compressive extension rate and maximum applied compressive strain were set at 1.0 mm/min and 50%, respectively. The mean and standard deviation of compressive elastic moduli were taken by calculating the stress-strain slope between 49 to 50% strain from three samples. The stress-strain curve whose elastic modulus is closest to the average was reported as the representative curve for its sample set (n = 3).

Surface Nanoindentation of PDMS Constructs. Samples were designed as 5-mm squares with a height of 2 mm. Samples were submerged in phosphate buffer solution and probed with a cantilever (OMCL-TR400PB) with a spring constant of 0.02 N/m at an indentation rate of 5 µm/second up until an indentation force of 5 nN is registered. For each sample, four force maps were obtained by selecting four 40 µm by 40 µm probing areas at random and obtaining 100 equally spaced points of data from each probing area. The 100 points were then fitted to a Gaussian distribution to determine a mean and standard deviation that was then reported on the plot in Fig. S3.

Swelling Ratio and Gel Fraction Determination. Printed 5-mm cubes (n = 3) were first weighed to record their original weights. Next, each individual sample was immersed in 5 mL of chloroform inside separate 20 mL glass vials for 48 hours. The samples were then dried for 1 minute under room ambient conditions before being weighed to record their swollen weight, which was then divided by the dry weight to obtain the swelling ratio. The samples were then left to dry for another 48 hours before being weighed once more to record their dried weight. The gel fractions were obtained by dividing the dried weight with the original weight.

Tensile Testing of Multi-Domain PDMS Samples. Tensile testing samples were generated by printing PEGDA-in-PDMS using a printpath that was designed according to the dimensions of ASTM D638 type V test specimens. All testing samples (shown in Fig. 5) were only one layer thick (approximately 580 µm) and printed on a flattened sheet of aluminium foil. After thermal curing of the PDMS, the aluminium foil was dissolved in a 5.0M NaOH bath to liberate the tensile samples with minimal damage. To generate a step-change in the PEGDA particle content in PDMS, the feed of the inner phase was abruptly stopped at approximately halfway down the gauge length of the sample. Tensile stress-strain curves were obtained by subjecting the tensile samples to an extension rate of 25 mm/min until failure on a tensile testing machine (Instron 1028, 50 lb. load cell). The mean tensile elastic modulus was determined by taking the stress-strain slope up to 5% strain from three samples. The stress-strain curve reported in Fig. 5B. is derived from averaging the stress-strain data across different samples within each set.

Printing Magnetically-Actuated Soft Robotic Arm. The magnetically-actuated soft robotic arm in Fig. 5 was printed in several stages corresponding to the distinct compositional/functional domains. The pure PDMS and flexible PEGDA in PDMS segment was printed first using the PEGDA solution described earlier. Prior to printing the ferrofluid-in-PDMS segment, the microfluidic printhead was disconnected from the syringe pumps and the inner phase channel was rinsed once with deionized water. For the magnetically responsive segment, aqueous ferrofluid was dispersed in PDMS at a $Q^* = 0.05$, which corresponds to $Q_{in} = 75$ µL/hr when $Q_{out} = 1.5$ mL/hr. The finished print was then subject to heating at 75°C for 24 hours. To minimize damage to the finished prints, all objects were printed on aluminum foil substrates and subsequently liberated using NaOH same as before.

Soft Robotic Arm Characterization. To determine the lifting current of the soft robotic arms with different flexible segment configurations (i.e. different amounts of PEGDA particles), each soft robotic arm was laid flat on surface while a round electromagnet was suspended 10 mm above it. The electromagnet was then supplied with electric current that is gradually ramped up. The current at which the soft robotic arm is lifted up and held against the electromagnet is recorded as the lifting current (or $I_{current}$). Current measurements were performed in triplicate to obtain an average and standard deviation. To characterize the range of motion of the gripper arms in response to an external B-field, the arms were first suspended vertically. A round electromagnet is then placed next to the soft robotic arm at a horizontal distance of 10 mm. The round electromagnet was supplied with 36 Volts and 0.5 Amps, and the resulting deflection from the arms was visually analysed using ImageJ to produce a quantitative measurement of the angular deflection of the soft robotic arm and the contributions from the flexible joints. The angles were recorded from three samples to report an average and standard deviation. The final magnetically-responsive soft robotic arm assembly consisted of 9/32" stainless steel socket and multiple soft robotic arms attached to the round electromagnet using Loctite Plastics Bonding System and standard adhesive putty. The arms had flexible joints ($Q^* = 0.05$) at locations 1 and 4.

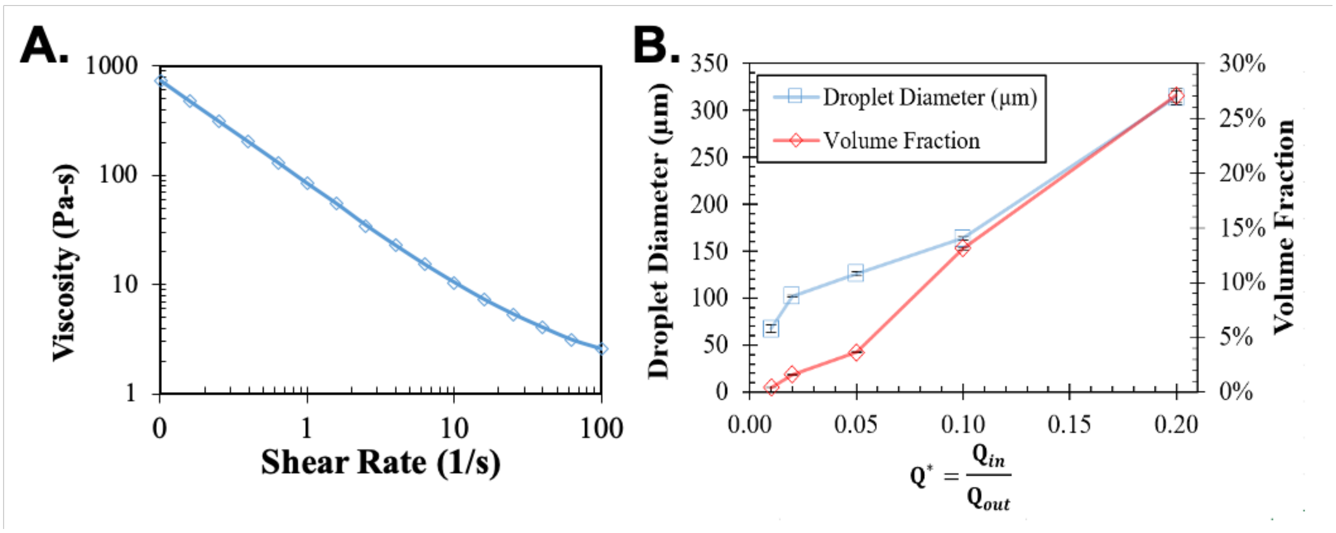

Fig. S1. Rheological and droplet dispersion characterization of the PDMS phase. A. Curves showing the viscosity of the PDMS outer phase (55 wt.% SE 1700, 1:10 ratio of curing agent to elastomer, and 45 wt.% silicone oil) as a function of shear rate. The relevant shear rates in our microfluidic printhead does not exceed $O(100\ s^{-1})$. **B.** Curves characterizing the droplet generation of glycerol in PDMS for a representative device. The relationship between droplet diameter and Q* deviates from perfect linearity due to change in droplet generation frequency with Q*. Volume fraction is determined by calculating the total volume of droplets produced per unit time and dividing that by the total flow rate (i.e. $Q_{in} + Q_{out}$) per unit time.

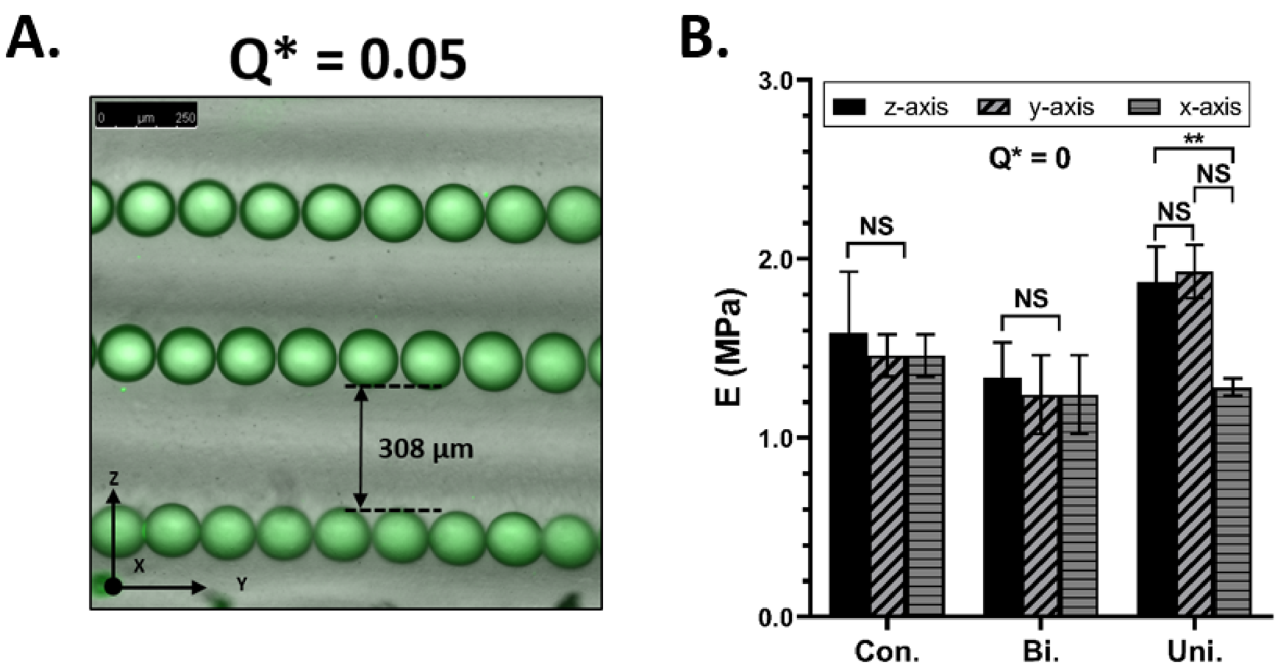

Fig. S2. Mechanical anisotropy in PDMS constructs. A. Micrograph showing multiple PDMS emulsion filaments stacked in the z-axis for Q* = 0.05. **B.** Comparison of the effect of print path and loading orientations when no inner phase is present (i.e. Q* = 0). **p<0.01, using student t-test. Error bars as shown are SD. NS, not significant.

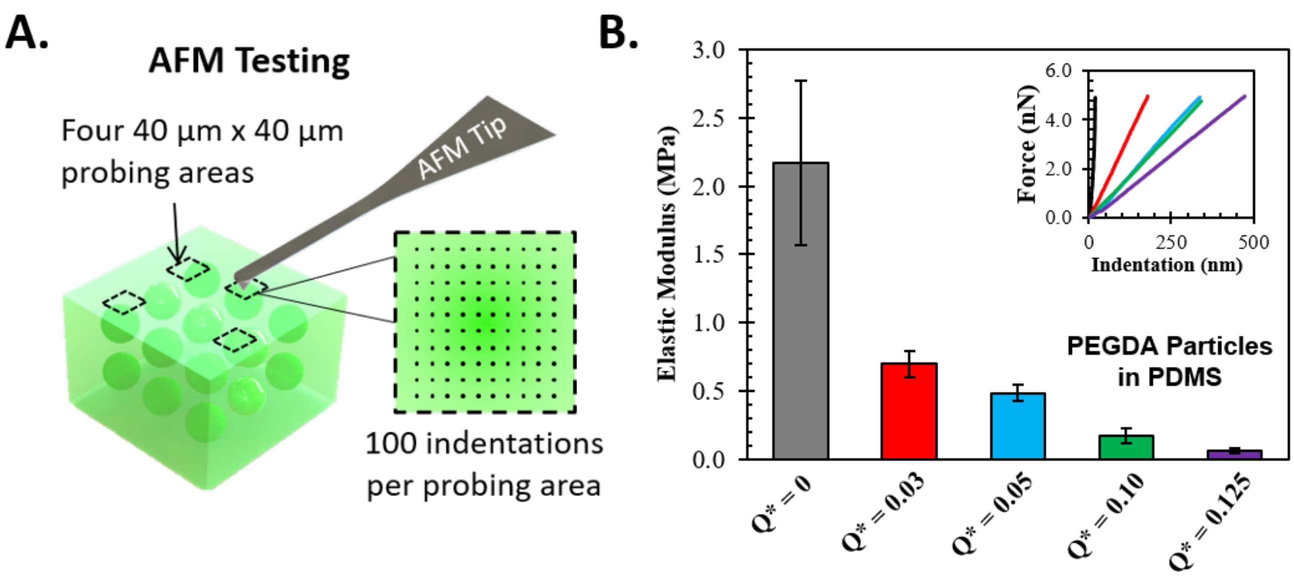

Fig. S3. Surface nanoindentation confirms intrinsic softening of PDMS elastomer. A. Schematic of atomic force microscopy (AFM) surface nanoindentation of different 3D-printed PDMS constructs with PEGDA particle inclusions. **B.** Plot of calculated from AFM force-indentation of various Q* in PEGDA particles-in-PDMS. Inset shows the representative force-indentation curves. Samples were indented with a pyramidal tip (k = 0.10 kN/m) until a force of 5 nN was registered and the corresponding indentation depth was measured. Note, the maximum recorded indentation depth is 466 nm. Error bars as shown are SD.

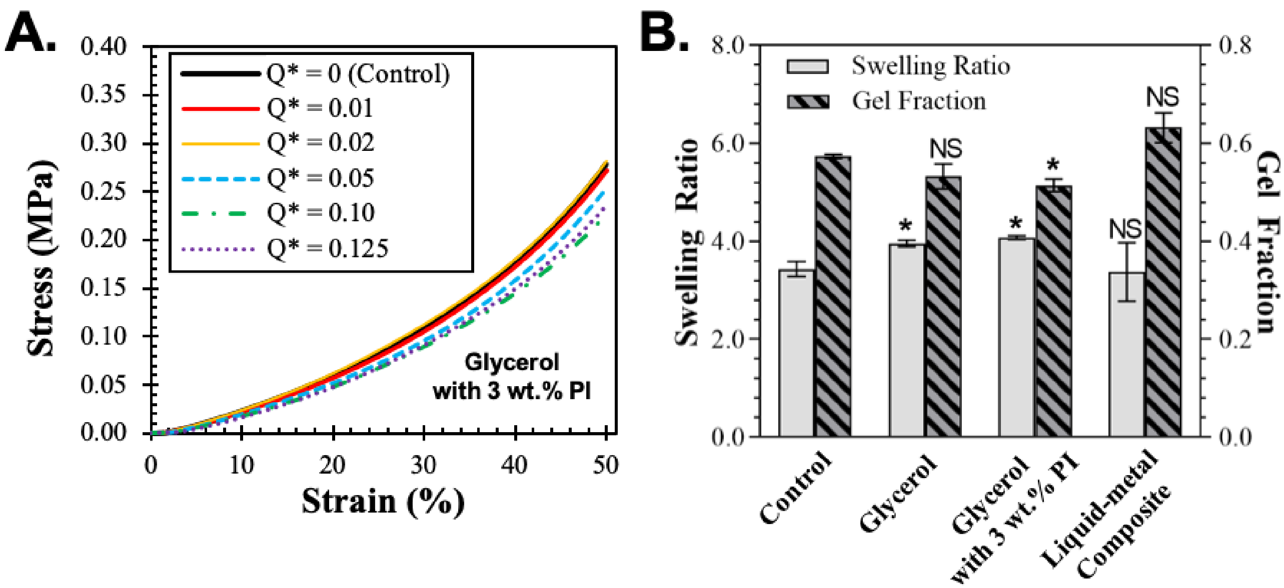

Fig. S4. Investigation of PEGDA-mediated softening of PDMS using mechanical and polymer chemistry characterization. A. Representative compression stress-strain curves of PDMS samples with glycerol droplet inclusions and 3 wt.% PI for various Q* values. The control refers to PDMS with no inner phase (i.e. Q* = 0). **B.** Plot of calculated swelling ratios and gel fractions for PDMS with glycerol (Q* = 0.20), glycerol (Q* = 0.125) with PI and eGaIn inclusions (Q*   0.20). The control refers to PDMS with no inner phase. *p<0.05, student t-test. Error bars as shown are SD. NS, not significant.

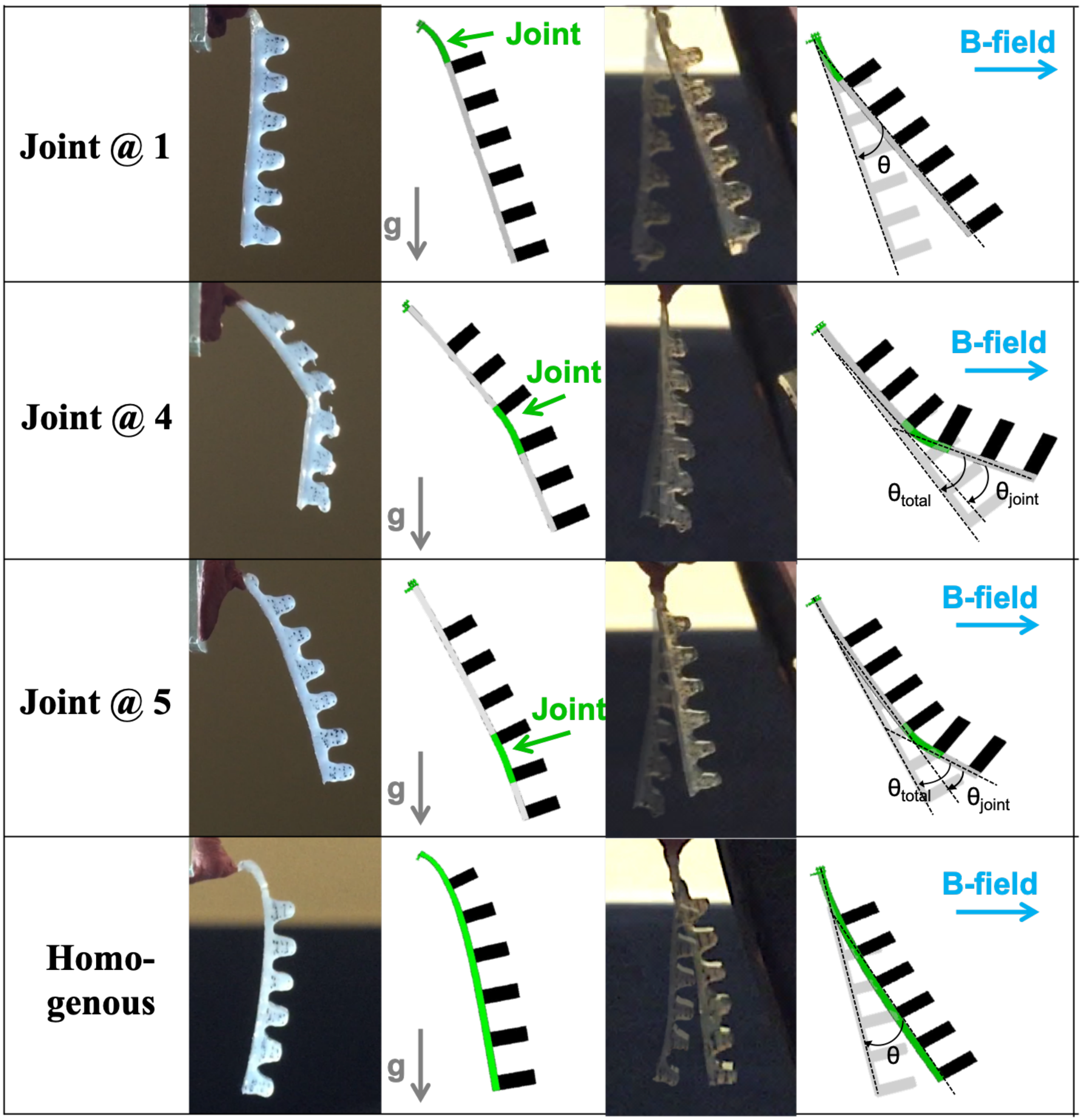

Fig. S5. Design and optimization of softened PDMS joints in a soft-robotic gripper arm assembly. An illustration of the different flexible joint configurations considered for optimizing the deflection/bending response of the gripper arm. Left: experimental images and schematics of the different configurations under the load of gravity. Right: experimental images and schematics of the motion expected when subjected to an external B-field in the transverse direction.

Table S1. List of calculated elastic moduus values for different inner phase constituents, as well as p values comparing the control and max Q* cases. The control refers to when there is no inner phase (i.e. Q* = 0), and the max refers to Q* = 0.20 (or 0.125 in the case of PEGDA). All PDMS constructs used in compression testing were printed using the bidirectional serpentine (or Bi) printpath and loaded in the z-axis. Values are expressed as mean ± SD. SD values are formatted to 2 decimal places. P values are taken from student t-test and formatted to 2 significant figures.

Inner Phase	Control Elastic Modulus (MPa)	Max Q* Elastic Modulus (MPa)	n	P value
62 wt.% glycerol	1.34 ± 0.20	1.13 ± 0.13	3	0.11
Water	2.39 ± 0.06	1.85 ± 0.10	3	0.0020
eGaIn	1.32 ± 0.14	0.96 ± 0.09	3	0.0048
50 wt.% PEGDA + 3 wt.% PI	2.64 ± 0.28	0.42 ± 0.08	3	0.00019

Table S2. List of calculated elastic modulus values for different PI content in 50 wt.% PEGDA droplet inclusions. Values are expressed as mean ± SD, which is formatted to 2 decimal places. P values are taken using student t-test and formatted to 2 significant figures.

Photoinitiator (PI) amount (wt.%)	Elastic Modulus (MPa)	n	P value
0	0.77 ± 0.10	3	-
0.3	0.67 ± 0.10	3	0.14
1.0	0.55 ± 0.11	4	0.016
3.0	0.53 ± 0.12	3	0.028

Table S3. List of calculated elastic modulus values for different PEGDA content with no PI. Values are expressed as mean ± SD, which is formatted to 2 decimal places. P values are taken using student t-test and formatted to 2 significant figures.

PEGDA content (wt.%)	Elastic Modulus (MPa)	n	P value
0	1.23 ± 0.21	3	-
10	0.88 ± 0.06	3	0.055
25	0.71 ± 0.02	3	0.024
50	0.65 ± 0.05	3	0.021
75	0.48 ± 0.04	3	0.013

Movie S1. Timelapse video of printing a hollow tube using water-in-PDMS

Movie S2. Printing ferrofluid-in-PDMS

Movie S3. Toothed magnetically-actuated soft gripper arm holding onto silicone rubber tubing.