3D Printing of Liquid Crystal Elastomeric Actuators with Spatially Programed Nematic Order

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Liquid crystal elastomers (LCEs) are soft materials capable of large, reversible shape changes, which may find potential application as artificial muscles, soft robots, and dynamic functional architectures. Here, the design and additive manufacturing of LCE actuators (LCEAs) with spatially programed nematic order that exhibit large, reversible, and repeatable contraction with high specific work capacity are reported. First, a photopolymerizable, solvent-free, main-chain LCE ink is created via aza-Michael addition with the appropriate viscoelastic properties for 3D printing. Next, high operating temperature direct ink writing of LCE inks is used to align their mesogen domains along the direction of the print path. To demonstrate the power of this additive manufacturing approach, shape-morphing LCEA architectures are fabricated, which undergo reversible planar-to-3D and 3D-to-3D’ transformations on demand, that can lift significantly more weight than other LCEAs reported to date.

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during drying. Changes and residual stresses that arise from solvent loss of an H-shaped layer (top, 100 µm thick) and a square-shaped layer (bottom, 100 µm thick, 12 mm × 12 mm wide) patterned on a glass substrate using a nozzle diameter of 250 µm and a print speed of 4 mm s⁻¹ at 50 °C (Figure 2a). The H-shaped layer consists of an array of LCE filaments printed in a meanderline pattern using a 90° (from horizontal) print path, while the square layer is printed using a diagonal (45° from horizontal) print path. Using polarized optical microscopy, one clearly observes the spatial control of the director along the direction of print path, i.e., only the H-shaped layer is bright when the cross-polarizers are oriented at 45°/135° (Figure 2a, top), while only the square layer is bright (Figure 2a, bottom) when they are oriented at 0°/90°. To determine the effect of temperature on director alignment, we printed samples (125 µm height) both below (50 °C) and above (105 °C) TNI using a 250 µm nozzle and printing speeds between 2 and 10 mm s⁻¹. Note, different applied pressures are used to ensure that the printed filament width (100 µm width × 125 µm height) is approximately the same in all cases. LCE samples printed at 50 °C had better director alignment along the print path, i.e., a higher order parameter (Figure 2b; see also Figure S3, Supporting Information) than samples printed at 105 °C. The LCE ink is subjected to both shear and extensional flow during the HOT-DIW process, which induces alignment of their mesogenic domains. As expected, the order parameter of LCEA samples printed at 50 °C increases with print speed due to enhanced director alignment (Figure 2c; see also Table S1, Supporting Information).

To investigate their actuation performance, we printed LCEA bilayers (15 × 3 × 0.25 mm) using a nozzle diameter of 250 µm, average print speed of 4.8 mm s⁻¹ and a meanderline horizontal print path. The printed LCEA bilayers are then cycled 20 times between −26 and 105 °C (Figure 3a; Movie S2, Supporting Information). For these experimental conditions,
we measured an average repeatable actuation contraction of $-43.6 \pm 6.7\%$ along the print direction and an average expansion of $29.8 \pm 5.9\%$ normal to that direction (Figure 3b). We note that these LCEAs can be successfully cycled up to 100 times (Figure S4, Supporting Information). Full actuation of these printed LCEAs occurs in $\approx 180$ s, while relaxation back to their original dimensions requires $210$ s (Figure S5, Supporting Information). Hence, a conservative estimate of the cycle time required to “reversibly switch” these printed LCEAs is $\approx 390$ s for the thermal cycling conditions used. We note that longer cooling times are needed due to the lack of active cooling. Next, we printed LCEAs (1 mm thick) using a nozzle diameter of 250 $\mu$m, average print speed of 3.7 mm s$^{-1}$, and a meanderline print path and explored their ability to contract when tethered to different weights (Figure 3c; Movie S3, Supporting Information). In these weight-lifting experiments, strain is calculated using the unloaded LCEA length (Figure 3c, left) as the initial length, rather than the elongated length when loaded (Figure 3c, middle) below $T_{NI}$, and its final length after the loaded LCEA is heated above $T_{NI}$ (Figure 3c, right). Importantly, these thick LCEAs can lift roughly 1000 times their own weight of 106 $\pm$ 1.5 mg. With increased weight loading, the actuation strain for the LCEAs decreases and the actuator work increases, with a maximum energy density of 39 J kg$^{-1}$ (Figure 3d). Since they are not composed of a single domain, the LCEAs can elongate upon heating to a more ordered state$^{32,33}$ prior to contraction (Movie S3, Supporting Information). If the contraction does not surpass the original length, the actuation strain is noted as a positive value and negative work (Figure 3d). Upon cooling, the LCEAs return to within 11% of their initial length. To impart larger contractile strains at an even larger bias stress, one can simply print thicker actuators. Based on the stress–strain measurements reported in Figure S6 (Supporting Information), these printed LCEAs exhibit an elastic modulus of 3.1 $\pm$ 0.3 MPa at room temperature when loaded along the print direction.

As a final demonstration, we printed LCEAs with spatially programed directors that are capable of complex, reversible shape transformations. First, to program shape change into a cone with positive Gaussian curvature, LCEAs (of diameter 10 mm) are printed using a nozzle diameter of 250 $\mu$m and print speed of 4.5 mm s$^{-1}$ with four layers (0.4 mm thick) each of which is based on equivalent Archimedean spiral print paths (Figure 4a; Movie S4, Supporting Information). Using this type of print path$^{34}$ the LCEA transforms into a cone with a maximum height of 6.5 mm when heated above $T_{NI}$, which corresponds to a 1628% stroke out-of-plane. As expected, the LCEA recovers its original dimensions and shape upon cooling (Figure S7a, Supporting Information). We also printed LCEAs capable of morphing into shapes with negative Gaussian curvature with 5 mm s$^{-1}$ print speed (Figure 4b; Movie S5, Supporting Information). In these four-layer LCEAs (0.4 mm thick),
the top and bottom pairs of layers are printed using perpendicularly oriented, in-filled meanders. Upon heating, this LCEA morphs into a saddle form. However, due to residual stresses introduced during inline UV crosslinking, it does not return to its original flat conformation upon cooling, but rather snaps into an inverted saddle configuration (Figure S7b and Movie S6, Supporting Information). When heated again, it snaps back into the programmed saddle configuration, and alternating actuation between both configurations is observed upon thermal cycling. Hence, after the initial actuation, this LCEA exhibits a repeatable 3D-to-3D′ shape transformation. Next, we created in-plane mechanical metamaterials in the form of printed LCEA meshes with an inner strut width of 0.86 mm and thickness of 0.5 mm (Figure 4c; Movie S7, Supporting Information), which shrinks isotropically ≈18% in-plane (i.e., both horizontally and vertically) and recovers to their initial dimensions upon cooling to room temperature (Figure S7c, Supporting Information). Lastly, we printed a larger LCEA (2.5 x 2.5 cm²) capable of out-of-plane shape change (Figure 4d; Movies S8 and S9, Supporting Information) using a print path that consists of a square spiral array (see Figure S8, Supporting Information, which shows the resulting director alignment). This LCEA morphs out-of-plane into an array of cones with a maximum height of 1.92 mm upon heating to 95 °C, returning to its near-initial conformation upon cooling (Figure S7d, Supporting Information).

In summary, we have demonstrated the ability to create LCEAs with programmed director alignment by HOT-DIW. By controlling the ink composition, rheology, and printing parameters, LCEAs were fabricated in multilayered structures with arbitrary thickness and overall dimensions. These LCEAs exhibited large contractions when heated to temperatures above their nematic-to-isotropic phase transition, which enabled their exceptional actuation performance with a maximum energy density of 39 J kg⁻¹, actuation of up to 70 g loads, and complex shape-morphing capabilities, including both 2D-to-3D and 3D-to-3D′ transformations. Additive manufacturing of LCEA architectures opens new avenues for creating artificial muscles, soft robotics, and other dynamic functional structures based on these materials.

Experimental Section

**LCE Ink**: The LCE ink was prepared by a modified one-pot synthesis reported previously utilizing a catalyst-freeaza-Michael addition chemistry. As-received 1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (Synthon, 97%, 2 g), n-butylamine (Sigma-Aldrich, 99.5%), and Irgacure 651 (I651, BASF) were added to a 25 mL round bottom flask in 1:1 molar ratio and 2 wt%, respectively. The mixture was heated to 110 °C, above the melting point of the mesogen and the TNI of the resulting LCE, and stirred vigorously. The reaction was shielded from fluorescent light, and the clear, yellow product was quenched in ice after 18 h.

**3D Printing**: The HOT-DIW setup was a modification on a previously demonstrated custom print setup (Figure S1, Supporting Information). Briefly, it was comprised of a steel barrel surrounded...
by a heater coil (FM Keefe Company Inc., 62H36A5X-1128) with temperature readout by thermocouple (k-type) at the tip of the stainless steel nozzle (TecDia Inc., ARQ-S-2535) and internal temperature readout by thermocouple (K-type) to prevent heating the barrel above the \( T_{NI} \) while printing. The temperature of the nozzle was set to the print temperature of 50 °C and maintained with a temperature controller (Omega, CNi16). HOT-DIW was performed with a custom three-axis motion control stage (Aerotech Inc.) that deposits ink via pressure-driven extrusion with an Ultimus V pressure box (Nordson EFD) according to programed G-code (Mecode). LCEAs were printed on precleaned glass substrates secured to a leveled multiaxis stage (ThorLabs). Each batch of ink (\( \approx 2 \) g) was manually consolidated into large pellets and loaded into the barrel at room temperature. The temperature was increased above \( T_{NI} \), then cooled at \( \approx 10 \) °C min\(^{-1} \) rate until the nozzle temperature reached that of the prescribed printing temperature. The system was held at this temperature (typically 50 °C) for \( \approx 30 \) min prior to printing to allow the system to reach a steady state operating condition. As the ink was extruded, it was exposed to UV light (Omnicure, S2000) at an intensity of \( \approx 12 \) mW cm\(^{-2} \) (Figure S1, Supporting Information). After printing, LCEAs were exposed to higher intensity UV (\( \approx 31 \) mW cm\(^{-2} \)) for 20 min (10 min for the top and bottom sides) to ensure uniform crosslinking. Printed LCEAs that were thicker than two filamentary layers were exposed to UV light every two layers for 400 s (\( \approx 31 \) mW cm\(^{-2} \)).

Differential Scanning Calorimetry: The LCE ink was heated to 120 °C to erase any thermal history, cooled to \(-50 \) °C, then heated to 200 °C, all at a rate of 10 °C min\(^{-1} \) (Q200; TA Instruments).

Ink Rheology: The rheological properties of the LCE ink were characterized using a controlled stress rheometer (Discovery HR-3 Hybrid Rheometer; TA Instruments) equipped with 20 mm steel Peltier plate geometry and 0.750 mm gap. Prior to testing, the ink was brought to \( T_{NI} \) to erase the thermal history.

Wide Angle X-ray Scattering (WAXS): X-ray measurements were performed on a SAXSLAB system with a Rigaku 002 microfocus X-ray source (CuK\( \alpha_1 \) = 1.5409 Å) with sample to detector (PILETUS 300K, Dectris) distance of 109.1 mm for 15 min with Osmic staggered parabolic multilayer optics to focus the beam crossover at the second pinhole. It contains two sets of JJ X-ray 4 jaw collimation slits that are 0.9 mm. WAXS samples consisted of one-layer LCEAs printed as unidirectional strips. Their order parameter was calculated from the WAXS data using Equation (1) by numerically integrating (MATLAB function trapz)

\[
S = \frac{1}{2} - N^{-1} \frac{3}{2} \sum_{i=0}^{N/2} \left[ \sin^2 \theta + \left( \sin \theta \cos \theta \right) \log \left( \frac{1 + \sin \theta}{\cos \theta} \right) \right] d\theta
\]

where \( N = \int_0^\infty I(\theta) \, d\theta \)\(^{[39]} \).

Imaging and Image Analysis: Printed LCE architectures were photographed using a camera (Canon 5D Mark III) between crossed polarizers (ThorLabs) keeping imaging conditions constant for both positions of crossed polarizers. Micrographs of unidirectional LCE samples were obtained using an inverted microscope equipped with crossed polarizers (Axio Observer, Zeiss).

Actuation Measurements: Cyclic actuation measurements were performed on a custom three-axis motion control stage. Printed LCEAs were placed on a thin silicone oil layer on top of an anodized aluminum stage and lowered onto and raised off of a hotplate such that their temperature was alternated between room temperature (held for 210 s) and the printing temperature (held for 30 min) for 2 cycles.

Figure 4. Programmable shape morphing LCEAs. a,b) Images of disc-shaped LCEAs (\( \approx 0.4 \) mm thick) printed using layered spiral (a, top) and layered perpendicular meanders (b, bottom) print paths (scale bars = 1 mm). Upon heating above \( T_{NI} \), these LCEAs morph into a cone (a, bottom) and saddle (b, bottom) shape, respectively (scale bars = 1 mm). c) Top-down images of mesh-shaped LCEAs (\( \approx 0.5 \) mm thick) after printing (left) and shrinking into an isotropic form (right) upon heating above \( T_{NI} \) (scale bars = 5 mm). d) Top view (upper row) and side view (lower row) of a LCEA sheet after printing (left) and morphing (right) into a conical array upon heating above \( T_{NI} \) (scale bars = 5 mm).

Photographs of these LCEA samples were taken throughout this process (Canon EOS 5D Mark III) at a frequency of 0.1 Hz. An in-house MATLAB image analysis script was used to determine the dimensions of the actuated samples. To demonstrate their ability to lift weight, mass standards (Spectrum Chemicals) were attached to printed LCEAs with a binder clip (1.19 g) and heated with a heat gun (Milwaukee, MHT3300). To demonstrate their ability to reversibly change shape, printed LCEAs were heated using a hot plate (IKA RET basic) and imaged during this process. The saddle LCEA was actuated on hot plate held at 90 °C, while the spiral, conical array, and mesh LCEAs were actuated on a hot plate held at 95 °C. Note, the spiral actuation was aided by a heat gun that was held above the actuator. All actuators were lubricated with silicone oil to prevent adhesion to the substrate prior to actuation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
Jennifer Lewis has co-founded a startup company, Voxel8, which focuses on multimaterial 3D printing.

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