Tunable Electromechanical Liquid Crystal Elastomer Actuators

Tyler Guin,* Holly E. Hinton, Eric Burgeson, Christopher C. Bowland, Logan T. Kearney, Yuzhan Li, Ilia Ivanov, Ngoc A. Nguyen, and Amit K. Naskar*

Liquid crystal elastomers (LCE) are soft materials which anisotropically shape morph in response to external stimuli. Herein, a method to produce large-area carbon nanotube–LCE nanocomposite films with exceptional electrostrictive properties is examined. A methodology to produce telechelic precursor oligomeric composites at scale (>100 g) is presented along with the continuous casting and photocuring process. The carbon nanotubes are well-aligned and well-dispersed in the films, which exhibit exceptional anisotropic thermomechanical, optical, and thermal shape change characteristics. When an electric field is applied through the film thickness, the material quickly and reversibly contracts along the alignment direction. As an example, a compliant carbon nanotube–LCE film contracts >4% against a 140 kPa load, roughly comparable to the blocking force of many natural muscular tissues. Furthermore, it is demonstrated that this tunable contraction is dependent upon the electric field strength, and that the contraction mimics the form function of the input electric field (e.g., a sine wave). These compliant actuators are excellent candidates for incorporation into soft and/or biological systems.

Force transductions usually rely on motion of rigid objects, propelled by external source of energy such as pressure or electromagnetic fields. However, when these rigid devices need to be incorporated in a soft-matter system, such as biological tissue or rubbery substrate, significant engineering challenges arise. Soft actuators, which are compliant materials for the conversion of energy into useful mechanical motion, are highly desired for soft robotic devices and their applications. Soft actuators, such as those based on shape-memory polymers and dielectric elastomers, can deliver large strain without use of an electrical motor and enable systems without stark material contrast between the body of the device and the actuator, eliminating aforementioned engineering difficulties.

Liquid crystal elastomers (LCEs) with inherently anisotropic building blocks (known as mesogens) in crosslinked rubbery matrix are produced from liquid crystalline macromolecular precursors. These materials display impressive shape changes (>400% strain) in the direction of their alignment and can be actuated by a variety of stimuli, including heat, light, and solvent. LCEs are rubbery materials, and their anisotropic nonlinear mechanical properties can be rationally controlled in many ways, including through chemistry, through process-aided control of alignment direction, or even via exposure to light. This facile control of localized materials properties has enabled the construction of a variety of devices, such as optical arrays, out-of-plane lifters, lenses, and even biomimetic devices such as artificial cilia or grippers. Advancements in chemistry and formulation have enabled facile synthesis that allows for highly tunable control of the polymer mechanical properties, which can be used to match the LCE to the material system it is incorporated into.

Despite the tunable properties via controlled chemical synthesis, the various stimuli that induce shape change in LCEs are not readily incorporated into modern control devices, which nearly exclusively rely on electrical signals for both control and sensing. This limitation requires that prototypical devices have complicated experimental control schemes in which the stimulus is controlled by expensive, inefficient external apparatuses. Commonly, these external control systems are powerful UV or IR lights or carbon-based resistive heating elements. In contrast, almost all commercial small-scale...
actuators utilize electric fields as their stimulus, and those actuators are usually based on piezoelectrics, magnetic coils, and shape memory alloys.\[20\] Therefore, we believe that electrical sensitization is required for the wide-spread adoption of LCEs as a viable material for soft actuators. Recently, Guin et al. examined the ability of single-walled carbon nanotubes (SWCNTs) to sensitize LCEs to through-plane DC electrical fields, enabling a large (\(\approx 18\%\) strain) electrostrictive response.\[21,22\] This mechanism is not electrothermal in nature\[19,22\] but relied upon the unique dielectric response of the nanocomposite system to translate molecular motion into bulk material movement. However, the work was greatly limited by lack of its scalable synthesis and extreme difficulty in material handling, which greatly limited experimental probing into both the material properties and the cause of the electrostrictive behavior.\[21\]

Nanocomposite liquid crystal elastomers (n-LCEs) were prepared via photo-crosslinking of a liquid crystalline oligomeric (LCO) mixture containing single-walled carbon nanotubes (SWNT). The LCO mixture was synthesized via a thiol-Michael addition reaction using a commercially available diacylate (RM257) monomer and ethanedithiol, with structures shown in Figure 1A. This reaction requires mild conditions, does not yield any by-product, and is highly robust; therefore, the reaction was readily scaled to produce over 100 g of oligomer with no special equipment or precautions. Separation of the oligomer from the reaction mixture was readily achieved via precipitation into water, followed by vigorous rinsing. The overall yield was over 94\%, indicating that very little material was left in the aqueous phase. The oligomer had a molecular weight (\(M_n\)) of 20 000 Da (PDI = 1.7), as determined by gel permeation chromatography, and was end-capped by acrylate groups as excess diacylate (RM257) was used (see Fourier-transform infrared spectroscopy data Figure S1, Supporting Information). The molecular weight was kept deliberately low to increase the potential end-groups that can be crosslinked in the final elastomeric product. The oligomer was completely odorless, indicating almost no residual thiol, and only slightly colored, though it was extremely tacky at room temperature. To disperse SWNT into the mixture, the solid reaction product was dissolved into DMF, mixed with SWNT, and then ultrasonicated at a power of 1.5 W g\(^{-1}\) for 1 h in an ice bath. Afterward, the mixture was gently centrifuged (2000 rpm for 15 min) to remove poorly dispersed material. The oligomeric nanocomposite was readily recovered by precipitation into water, yielding a pitch-black viscous material. Control mixtures containing no nanoparticles were prepared via solubilization of the oligomer, ultrasonication, followed by precipitation. The incorporation of nanotubes darkened the specimens. A diagram of the blade-coating and

![Figure 1. A) Reaction scheme for the production of the LCO, B) diagram of the blade-coating and curing of the LCO to LCE, C) cross-polarized image of the n-LCE with 0.2 wt% SWCNTs with the axis of orientation 45° to the analyzer and D) 0° to the analyzer, E) photograph of the cured n-LCE being held and stretched by hand, and F) Raman signal intensity of the G’ band of the SWNT (black) and mesogenic peak (red) of the LCE as a function of crystal alignment direction relative to incoming laser polarization. The Raman signal intensity is maximized when the nanotube alignment is parallel to the laser polarization.\[23\]](image)
crosslinking process is shown in Figure 1B. The blade-coating method produced large samples (>10 cm in width, >100 cm in length) on the bench. No obvious aggregations of nanotubes were observed in optical microscopy at loadings below 0.5 wt%, and aggregations were not present throughout the mixture until 1 wt% SWNT loading.

As expected, incorporation of nanotubes affected the thermal and optical properties of the LCO mixtures. Dynamic scanning calorimetry (DSC) traces are shown in Figure S2, Supporting Information. The nematic-isotropic transition temperature ($T_{ni}$) is increased from 46 to 54 °C (Table 1) by the incorporation of SWNT, irrespective of its loading. Similarly, the glass transition temperature ($T_g$) is also significantly increased, from −12 to −7 °C. The rigid SWNT reduces the molecular mobility of the LCO and shifts the thermal transitions. It is likely that the mixture is nearly saturated by 0.2 wt% SWNT; thus, further SWNT loading does not affect the thermal transitions of the nanocomposite LCO. From polarized optical microscopy (Figure S3, Supporting Information), there is little qualitative difference between the LCO with and without SWNT, except for a slight darkening effect. This confirms the well-dispersed nature of the nanocomposite mixture.

Alignment of the liquid crystalline mixture is induced by simple blade-coating, which aligns the oligomer in a uniaxial manner. To increase the crosslink density, 15 wt% liquid crystalline monomer (RM257) was added to the oligomer, along with photo-initiator (dimethylamino)benzophenone (DMABP) and inhibitor tert-butylhydroquinone (t-BHQ). At 15 °C, the LCE precursor mixture did not readily align with shear. As shown in Figure S4, Supporting Information, the mixture at this temperature does not readily flow. However, at 35 °C, the viscous mixture could be readily sheared. Upon shearing, the material aligns, as confirmed visually by a loss of scatter and by uniaxial birefringence observed through cross-polarized microscopy (Figure S5 and S6, Supporting Information). To produce the n-LCEs and LCEs via free-radical crosslinking, the LCO mixture was heated to ≈35 °C, blade coated to a thickness of 100–150 μm at a speed of 50 mm s$^{-1}$ (330–500 s$^{-1}$), then immediately cooled to room temperature (≈15 °C) and cured by exposure to 365 nm UV light for 30 min.

Upon blade-coating and curing, the material becomes optically clear, insoluble (87% gel fraction in dichloromethane), changes color to yellow, and is obviously solidified (Figure 1E). There was minor scatter, likely due to mild phase separation during quenching. The n-LCE or LCE is readily released from the substrate by submerging in distilled water and peeling from the glass. We note that the n-LCE can also be cast on a flexible polymer substrate, such as polypropylene. Both n-LCEs and LCEs are highly birefringent, and the uniaxial alignment is confirmed optically by observation through cross-polarizers (Figure 1C,D). Even though the SWNT could act as defect sites, no optically detectable disclinations or misalignments were observed in n-LCEs for the SWNT at loadings <0.5 wt%. At loadings >1 wt%, the SWNT aggregated to such a point that the material was difficult to handle, breaking readily when peeled from the substrate. Raman spectroscopy was used to determine the orientation of both the SWNT and the LCE mesogens simultaneously, as the Raman scattering intensity is a function of molecular orientation relative to the Raman laser polarization angle. Polarized Raman spectroscopy (full scan shown in Figure S7, Supporting Information) confirms that the SWNT follows the alignment of the LCE (Raman intensity as a function of orientation relative to excitation laser polarization angle shown in Figure 1F), whereas wide-angle X-ray scattering (image plates shown in Figure S8, Supporting Information) confirms the alignment of the LCE mesogens ($S_{SWNT-LCE} = 0.40$, $S_{SWNT-0.2% n-LCE} = 0.45$).

The alignment of LCEs translates to highly anisotropic mechanical and thermomechanical behavior. In the direction of alignment, the material displays a linear response to a mechanical field, whereas perpendicular to the direction of alignment, the material displays nonlinear “soft elasticity,” which is due to the rotation of the rigid mesogens in the lightly crosslinked material. We hypothesized that the inclusion of rigid, relatively large SWNT into the LCE matrix would reinforce the flexible segment of the LCE and inhibit the large strain soft elastic response. However, as shown in Figure 2A, we see very little difference in the mechanical behavior due to the inclusion of SWNT in the LCE matrix. Raw mechanical data and replicates are shown in Figure S9, Supporting Information. We do not believe that SWNT are simply not dispersed—there is significant evidence that the nanotubes are not significantly aggregated. For example, there is no significant change in the Raman spectra of the nanotube radial breathing modes (RBM) after incorporation into the LCE matrix (Figure S8, Supporting Information). Additionally, the thermal characteristics of the n-LCE (Table 1) were modified by the incorporation of SWNT, which would not be the case if the SWNT were exclusively aggregated. Although the $T_{ni}$ of the LCO was higher after incorporation of SWNT, the transition temperature of the n-LCE decreased with 0.2% SWNT content. Further increase in SWNT content lowers the original $T_{ni}$ with gradual appearance of a second $T_{ni}$ peak at higher temperature. This suggests that a secondary structure with a higher transition temperature is formed in the LCE matrix by the SWNT. Additionally, the SWNT greatly affects the thermomechanical shape change in the LCE, reducing the magnitude of the shape change significantly as shown in Figure 2B. We believe that the SWNT, which are very rigid, restrict the macroscopic shape change behavior. However, above the $T_{ni}$, both the n-LCEs and LCEs lose the overwhelming majority of their birefringence, (Figure S10, Supporting Information) indicating that while the shape-change was quenched, the molecular loss of order still occurs.

Although the SWNT may restrict thermomechanical shape change, they enable electromechanical shape change of the LCE matrix. Prior work has demonstrated that small loadings of SWNT sensitize LCEs to through-thickness DC electric

### Table 1. Glass transition temperatures ($T_g$) and nematic-isotropic transition temperatures ($T_{ni}$), as determined by DSC, for LCOs and LCEs with various SWNT loadings.

| SWNT Loading | $T_g$ Oligomer (°C) | $T_g$ Oligomer (°C) | $T_{ni}$ Oligomer (°C) | $T_{ni}$ Oligomer (°C) | $T_g$ Elastomer (°C) | $T_{ni}$ Elastomer (°C) |
|--------------|---------------------|---------------------|------------------------|------------------------|---------------------|------------------------|
| No SWNT      | −11 ± 2             | 46 ± 3              | 9 ± 1                  | 86 ± 3                 |                     |                        |
| 0.2% SWNT    | −7 ± 2              | 54 ± 3              | 14 ± 1                 | 80 ± 5                 |                     |                        |
| 0.5% SWNT    | −7 ± 2              | 53 ± 4              | 14 ± 2                 | 81 ± 3, 94 ± 3         |                     |                        |
| 1% SWNT      | −7 ± 2              | 54 ± 3              | 14 ± 4                 | 70 ± 4, 96 ± 5         |                     |                        |
The materials reported here display a similar response. Fabricating free-standing actuators has proven to be elusive for n-LCEs, due to the difficulty of producing high-quality, zero-pore films across large areas.\cite{21,22} Carbon grease is a common electrode material for soft actuators, as it can maintain conductivity despite large areal changes, and it is cheap and commercially available.\cite{30} However, due to its viscous nature, it is likely to short, especially if the film has any defects.\cite{31} We also found that any aggregation of SWNT produced an electrical short circuit if the voltage was sufficiently high, which could be hazardous. To prevent these shorts, two LCE or n-LCE films were laminated together using a room-temperature liquid crystalline nematic adhesive described in previous work.\cite{10,11} The adhesive takes on the orientation of the n-LCE films and forms an effective seal without greatly disrupting the anisotropic mechanical properties of the film. We found that this bilayer stack—n-LCE film, LCE adhesive, n-LCE film—was not prone to shorting and could be handled with little effort. However, the carbon grease was prone to wicking around the edges of the film, and therefore great care was taken to keep the grease from the edge of the films during coating.

**Figure 2.** A) Stress–strain curves for LCEs and n-LCEs, parallel and perpendicular to the axis of orientation, and B) unloaded (floating on oil) thermal shape change along the axis of orientation for LCEs and n-LCEs when heated to the isotropic transition.

**Figure 3.** A) Diagram of the experimental setup for monitoring the electromechanical response of n-LCE films. The film is clamped between metal clamps with wires leads, suspended vertically in a TMA. Carbon grease applied to both sides of the film, with care taken to prevent the grease from contacting both leads. B) Constriction of a 0.2 wt% n-LCE film along the orientation director as a function of through-thickness electrical field, loaded with 140 kPa, and C) constriction along the n-LCE orientation as a function of field strength and film tension. The film broke upon electric field application at loadings above 300 kPa.
Electrostriction of n-LCE stacks was tested in a thermo-mechanical analyzer (Q400 TMA) using a quartz film-and-fiber stage. The outside surfaces of the films were coated in a thin layer of carbon grease, and thin wires were fed from a high voltage DC amplifier and function generator. The film resistance and supply voltage and amperage were monitored online. The experimental apparatus is diagramed in Figure 3A. When an electric field is applied through the LCE without SWNT, there is a very small electrostrictive response that is difficult to measure, far less than \(\approx 0.01\%\) contraction (Figure S11, Supporting Information). However, when a field is applied to a 0.2% SWNT n-LCE, a distinctive, large magnitude electromechanical response is observed (Figure 3 and 4). The n-LCE quickly contracts in the direction of alignment, reaching a plateau that does not change with time. When the field is released, the n-LCE relaxes to the original length. It should be noted that at higher \(E\) field values (\(>1.2\) VDC \(\mu\)m\(^{-1}\)), there was significant plastic deformation. Figure 3B compares the input DC electric field to the measured constriction at 140 kPa stress. The film displays no response at low field strengths (\(<0.2\) VDC \(\mu\)m\(^{-1}\)). With increasing \(E\) field, the stroke of the n-LCE constriction increases, approaching 4% strain at 1.4 VDC \(\mu\)m\(^{-1}\). It should be noted that at higher field strengths, the n-LCE trilayer stack can short, and the film can no longer be actuated. Constrictions of higher \(E\) fields are therefore not reported due to this difficulty. The electromechanical response is very strong, as shown in Figure 3C, nearly reaching 25% of the tensile strength of the film itself (\(\approx 1200\) kPa). This is comparable to the blocking force of mammalian skeletal muscle (\(\approx 200\) kPa).\(^{12}\) As the external mechanical load is increased on the film, the stroke of the n-LCE decreases. The magnitude of the stroke versus force curve can be modulated by adjusting the electric field (Figure 3C). The clamp and electrical leads contributed a significant load to the system, and therefore stresses lower than 48 kPa could not be tested.

Figure 4 demonstrates the electromechanical response of a 0.2 wt% n-LCE film in response to DC, square wave, and sine wave electric field. When the n-LCE film is exposed to a DC field (Figure 4A), the material contracts along the alignment direction, reaching a plateau that does not change with time. In the case of a 60 kPa stress and 0.4 V \(\mu\)m\(^{-1}\) electric field, the n-LCE reaches the plateau in roughly \(10\) s (Figure 4B). This response is qualitatively different from the response induced by resistive heating.\(^{19,33}\) By applying a low-frequency sine wave, slower than the response rate of the film, the material will contract in a sinusoidal manner, matching the frequency of the input.

**Figure 4.** Constriction of a 0.2% n-LCE, loaded with 60 kPa, along the alignment direction in response to a through-thickness A) DC field, B) 50 mHz square wave, C) 50 mHz sine wave, and D) 5 Hz sine wave. The black line is the constractive response and the red is the applied through-thickness voltage.
voltage. Figure 4C demonstrates this phenomenon at 50 mHz
frequency. However, if the frequency is much faster than the
response rate (example of 5 Hz in Figure 4D), the n-LCE does
not oscillate with the electric field, but instead approaches a very
shallow plateau (<0.05% strain) until the field is removed.

In summary, we have demonstrated a novel method to pro-
duce large-area LCE nanocomposites in a highly scalable manner
which display the expected anisotropic thermal and mechanical
properties. SWCNTs were dispersed in these elastomers, and
they modify the thermal and thermomechanical nature of
the materials. Importantly, the nanotubes enable electrostriction
in these films, contracting over 4% against a 140 kPa load,
above the blocking force of many natural muscles. The response
occurs at ambient conditions and household available voltages
(<120 volts). We believe that LCE nanocomposites are a promis-
ing new material class for electroactive materials for soft robotics.

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

Acknowledgements
Research was sponsored by the Laboratory Director’s R&D Program of
Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the
US Department of Energy. A portion of this research was conducted at
the Center for Nanophase Materials Sciences, which is a DOE Office of
Science User Facility.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
actuators, electromechanical strain, liquid crystal elastomers,
nanocomposites, scaled-up synthesis

Received: February 3, 2020
Revised: February 27, 2020
Published online: April 26, 2020

[1] M. Spenko, S. Buerger, K. Iagnemma, *The Darpa Robotics Challenge
Finals: Humanoid Robots to the Rescue*, Vol. 121, Springer, Charn 2018.
[2] G.-Z. Yang, R. J. Full, N. Jacobstein, P. Fischer, J. Bellingham, H. Choset, H. Christensen, P. Dario, B. J. Nelson, R. Taylor, Sci. Robot. 2019, 4, 1826.
[3] G.-Z. Yang, J. Bellingham, P. E. Dupont, P. Fischer, L. Floridi, R. Full, N. Jacobstein, V. Kumar, M. McNutt, R. Merrifield, Sci. Robot. 2018, 3, 7650.
[4] C. Laschi, B. Mazzolai, M. Cianchetti, Sci. Robot. 2016, 1, 3690.