Bending Actuation of a Composite Liquid Crystal Elastomer via Direct Joule Heating.

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Abstract — In this work a new bi-layered composite actuator based on a polysiloxane-based monodomain nematic Liquid Crystal Elastomer (LCE) and on a conductive PEDOT:PSS thin layer is proposed. The basic idea is to integrate electro-conductive properties in the LCE and to validate the feasibility of direct actuation of the LCE by Joule heating of the conductive (and compliant) PEDOT:PSS layer. The fabrication of the actuator is achieved by depositing a thin conductive polymer layer by drop casting a PEDOT:PSS waterborne solution after having increased the LCE surface wettability with an air plasma treatment. The excellent stability of PEDOT:PSS and its mechanical properties, better matched with LCE ones compared to metals or inorganic nanoparticles used in other approaches, allowed to develop an all-organic reliable actuating composite based on thermoresponsive properties of LCE. Thermal actuation via direct Joule heating of the composite has been verified and prototypes of LCE/PEDOT:PSS bending actuators have been preliminary tested.

I. INTRODUCTION

The development of artificial muscles and actuating microsystems based on monodomain liquid crystal elastomers (LCE) has been the object of increasing interest during the past decade. [1] In a nematic LCE in which mesogen pendant moieties are attached to an elastomeric backbone, thermal cycles around nematic to isotropic phase transition temperature $T_{NI}$ cause the reversible elongation/compression of LCE along mesogens alignment direction (n director). Thermal and electrostatic triggers have been employed so far to control LCE actuation. Such methods generally suffer from poor rate, e.g. because of limited heat transfer rates. One possible approach to develop LCE-based actuators is through the addition of conductive properties or coupling of suitable electrodes to LCE surface. In the recent years several approaches have been attempted in order to achieve the combination of conductive properties with thermoresponsive properties of LCE. Recent studies proposed the realization of surface conducting layers (e.g. carbon coated LCE in which heating is generated by absorption of infrared laser radiation[2]) or the use of LCE-based nanocomposites, incorporating conductive nanomaterials into a LCE matrix, as e.g. CNTs, nanoparticles, nanowires, etc.[3]-[5] In the case of nanocomposite materials electromechanical actuation or indirect thermal actuation by Joule heating could be achieved by exploiting the conductive properties of a surface layer in which nanoparticles are embedded. However, difficulties arose in the fabrication of such conductive layers and the intrinsic larger stiffness of metals and nanocomposite, if compared to the very soft and compliant LCE materials, limited the performances of this kind of actuators.

In order to overcome these problems we present here a bi-layered composite material in which the conductive surface layer is produced adding on the surface of a monodomain nematic LCE (based on a poly-siloxane backbone with chemical composition as in [6]) a thin conductive polymer layer. Coupling of the two layers was achieved by drop casting a waterborne solution of the conductive polymer poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) [7]-[8], after having increased the wettability of the LCE surface with an air plasma treatment. The basic idea is to validate the feasibility of direct actuation of the LCE by Joule heating of the conductive (and compliant) PEDOT:PSS layer. The excellent stability of PEDOT:PSS and its mechanical properties, better matched with LCE ones compared to metals or inorganic nanoparticles used in other approaches, allowed to develop an all-organic reliable actuating composite based on the thermoresponsive properties of LCE. Thermal actuation via direct Joule heating of the composite has been verified and prototypes of LCE/PEDOT:PSS bending actuators have been tested.

The development of compliant and lightweight artificial muscles and bending actuators based on LCE could be beneficial in biomimetic robotics and micro robotics. LCE indeed are promising biomimetic materials due to the fact that their typical stress and strain values are similar to those of natural skeletal muscle. [2]

The paper is organized as follows: in section II the pure LCE material is presented, including fabrication and experimental details about the characterization of LCE mechanical properties. In Section III the actuator idea based on LCE / PEDOT:PSS composite material is introduced as well as the experimental details related to its fabrication and characterization. In Section IV the characterization results and the discussion for both LCE substrate and composite actuator are finally reported.
II. LIQUID CRYSTAL ELASTOMERS OVERVIEW

A. Properties of LCE

Liquid crystal elastomers (LCEs) are crosslinked liquid crystalline polymers with unique physical properties due to the combination between the elasticity of crosslinked polymer network and the ability of liquid crystals (LCs) to form self-organized and ordered structures [9]-[11]. The increased interest in LCEs in the last ten years is due to their potentialities for several technological applications, such as artificial muscles, microvalves, smart surfaces and propulsion systems [12]-[14] in the field of biomedicine and robotics. The crucial feature of LCEs is indeed their large shape variation in response to external stimuli, such as temperature, light irradiation and electric/magnetic fields. [15] Once the stimulus is off (i.e. zero electric voltage) or reversed (i.e. the temperature is increased), the initial shape is completely recovered. For this reason, LCEs are also known as “shape-memory” polymer materials [16-17]. In LCEs the macroscopic deformation can be also induced by a molecular-level change. This additional property of LCEs is related to the transition between a state where the LC molecules are isotropically distributed (isotropic phase) and a state where the LC molecules are aligned along a preferred direction, namely the nematic director \( \mathbf{n} \) (nematic phase). [18]. The monomodomain LCEs prepared according to the so-called “Finkelmann” procedure, also referred as Liquid Single Crystal Elastomers (LSCEs) [19], show a very large macroscopic contraction by heating the sample from the isotropic to the nematic phase above the nematic to isotropic phase transition temperature \( T_{NI} \). The initial extended length is fully retrieved by cooling the sample down to room temperature (RT < \( T_{NI} \)), that is, by restoring the isotropic phase. The largest macroscopic deformation of LCEs has been observed in polysiloxane main-chain nematic LSCEs [9], however, almost all mimetic elastomers prepared in different ways [9-11] show a macroscopic change induced by a molecular-level one.

B. Fabrication of LCE

The structure of the basic components of the LCE film employed in this study, named EV1-0.15-M11-0.48 are shown in Fig.1. Two benzoic acid phenyl ester-based mesogens (1 and 2) and the crosslinker (3) are typical constituents of conventional side-chain liquid crystalline elastomers [18]. Components 1-3 were used as reactants in the hydroxylation reaction with dimethylsiloxane polymer 4 also shown in Fig.1. Synthesis of components 1, 2 and 3 was performed as described in Ref. [20]. All reagents and solvents were purchased from Sigma-Aldrich and used as received or purified using standard procedures.

The pre-polymerization mixture was prepared adding to 2 ml of anhydrous toluene: the poly(methylhydrosilane) (1 mmol), the crosslinker 3 (0.15 mmol), the mesogen 1 (0.38 mmol) and the mesogen 2 (0.48 mmol). The Pt-catalyst was then added and the pre-polymerization mixture was filtered. The first step of the reaction was carried out in a special cylindrical form under centrifugation (spinning rate 4500 rpm) at a temperature of 75°C. After a period of 1 hour, a partially crosslinked, gel-like film network of dimensions 1 x 20 cm² and thickness of about 200 \( \mu \)m was removed from the form. The second step of reaction was performed at room temperature by mechanically loading the film with variable weights (up to 3 g) and then completing the crosslinking reaction in the oven at 75°C. During this second step, uniform uniaxial alignment of liquid crystal nematic domains was reached with the local director oriented along the vertical direction. The prepared films were swollen in toluene and dried in the oven at about 320 K. This procedure was repeated several times in order to ensure that the non-reacted mesogens or crosslinkers did not remain in the network.

Fig. 1. Chemical structure of the main components of the LCE film EV1-0.15-M11-0.48: (a) mesogen 1 (with \( n=2 \) and mesogen 2 (with \( n=8 \)); (b) crosslinker 3 and (c) polysiloxane chain 4.

C. Mechanical characterization of LCE

In order to perform quantitative mechanical characterization of the LCE materials and of the related composites a dedicated test platform was developed. The platform could be used for samples with very small length (4-20 mm) and it was able to measure low forces down to 0.003 N, as those generated by the “active” elastomers. The platform was essentially composed by a Translation Stage with sub-micrometric resolution (model M-126.CG1, PI, Germany) connected to a mini-clip for specimen holding, and by a high precision load cell (model LRF 400 FSH00259, Futek, US) connected to a second mini-clip for specimen holding. The relative control and conditioning electronics was connected with a dedicated PC through a multichannel DAQ Board (model USB-6218, National Instruments, US) as reported in the scheme in Fig. 2. The setup was completed by a controlled current source, a Peltier module (for specimen temperature control) and two thermocouples (for specimen temperature monitoring).

The control software, developed in C#, managed all the components, timing and acquisition. The data samples were acquired at 10 Hz and stored as .csv files. The acquired data included: time, slider position, force, temperatures and...
voltage/current supplied to the Peltier module by the driver. The main measurements that could be performed by the platform were:
- Stress vs. Strain (at controlled temperature)
- Force (Stress) vs. Temperature (at controlled Strain)
- Strain vs. Temperature (at controlled Force)

The platform could also integrate other devices, such as a LCR meter (LCR E4980A, Agilent, USA), to perform strain dependent impedance measurements, as well as other electromechanical measurements.

Concerning the present work, the platform was used to perform measurement of the displacement as a function of the temperature at controlled force (virtually null), and of the stress/strain curves at different temperature and speed.

![Diagram](image.png)

**Fig. 2.** (Top, left) Functional scheme of the measurement platform; (Bottom) Picture of the assembled platform; (Top, right) Particular of the specimen clamping system.

### III. LIQUID CRYSTAL ELASTOMERS COMPOSITES

#### A. LCE / PEDOT:PSS Composite Fabrication

Composite bi-layered films comprising a LCE substrate coated with a conductive polymer layer of poly(ethylenedioxythiophene) : poly(styrene sulfonate) (PEDOT:PSS) were prepared for the realization of actuators to be tested in this study. LCE samples were cut in small stripes of ~ 2 mm x 4 mm and exposed to air plasma (80 s, power P = 7 W, PDC-32G Plasma Cleaner, Harrick Plasma) in order to improve the wettability of their surface by aqueous solutions. A commercially available dispersion of PEDOT:PSS in water (Clevios™ PH1000, 1:2.5 PEDOT:PSS ratio; Heraeus, Germany) was employed after filtration and it was deposited with a micropipette dispenser over the LCE substrate (0.4 µl/mm²). The solution is left to dry at room temperature overnight (drop casting), in order to realize a homogenous film of PEDOT:PSS with thickness t ~ 5 µm.

#### B. LCE / PEDOT:PSS Composite for Joule Effect actuation

In the case of composite samples to be employed for direct Joule heating the rather limited conductivity of the pristine PEDOT:PSS layer (~ 0.1 - 1 S cm⁻¹) needed to be improved, in order to match feasible voltage/current characteristics to drive heating via Joule effect. Moreover, while showing excellent chemical stability, PEDOT:PSS is readily overoxidized when driven with voltage exceeding 10 V in the presence of oxygen, losing irreversibly its electronic conductivity. For these reasons, the voltage to be applied to samples needed to be limited (2-3 V typically, in our experiments). Therefore PEDOT:PSS conductivity was improved by the introduction of dimethylsulfoxide (DMSO) in the material formulation. DMSO is known to act as a secondary dopant for PEDOT:PSS, improving its conductivity up to 800-1000 S cm⁻¹. [21] [22]

By following a totally similar recipe as described above, a 5 wt.% content of DMSO was added to Clevios™ PH1000 and the solution was stirred for 2 hours before filtration. The LCE stripe (4x1.5x0.3 mm ) was exposed to plasma as described above and thin copper wires (diameter 50-170 µm) were placed on it in order to provide wiring for applying voltage to the actuator. Deposition of the conductive layer was then provided by drop casting of the solution (0.4 µl/mm²) onto the LCE stripe and wire, providing a good adhesion and electrical contact between the wire and the conductive layer.

#### C. LCE / PEDOT:PSS Composite Characterization

The prepared LCE/PEDOT:PSS composite samples were first characterized in terms of their surface topography, thickness and electrical properties. Thickness of the PEDOT:PSS layer was assessed by depositing identical amounts of the conductive polymer aqueous dispersion on LCE samples and on PDMS samples with identical size and allowing films to dry. Once the PEDOT:PSS layer was dried (after 5-6 hours) it could be easily peeled off from the PDMS surface with the aid of tweezers, due to surface hydrophobic recovery of PDMS that hampered the adhesion. The thin PEDOT:PSS film was then transferred on a clean silicon wafer and its thickness was measured with the aid of a stylus profilometer (P-6 Profilometer, KLA Tencor, USA) along several directions in order to assess the homogeneous deposition of PEDOT:PSS. Electrical resistance of the samples was measured with a LCR meter (LCR E4980A, Agilent, USA) sample stripes with 5x6 mm dimension. Thermal actuation of the composite was assessed by visually inspecting the samples with the aid of a digital microscope setup (KH-7700, Hirox, Japan) while the samples were placed horizontally on the surface of a Peltier Cell that was
controlled in current by means of a DC power supply. Operating Current was monitored throughout the experiments with the aid of a digital acquisition system (DAQ USB-6218, National Instruments). Temperature of the sample was as well monitored continuously with a thermocouple placed next to the sample.

Actuation of the composite systems via direct Joule heating was tested using the same experimental setup and applying the necessary voltage/current to the sample with a dedicated power supply. Actuation has been tested both in horizontal position (one edge of the sample was clamped with a metal clip, providing also the necessary electrical contact) and in vertical position (sample suspended with two wires providing electrical connection). Image analysis on pictures taken with a Hirox digital microscope was performed with an image processing and analysis software (ImageJ) permitting the measurement of total displacement, bending angle, radius of curvature of the samples.

IV. RESULTS AND DISCUSSION

Thermo-mechanical characterization was performed on the LCE material in order to measure the important parameters such as the stress strain response around the nematic to isotropic phase transition temperature $T_{NI}$. The transition temperature $T_{NI}$ was estimated simply by the Strain vs. Temperature curve, acquired by applying a constant force. The curve in Fig 3.a reports a typical trend of the contraction of the LCE as the temperature is increased over the $T_{NI}$, that is possible to be roughly estimated at around 70-80 °C, confirming the value of $T_{NI} = 74^\circ$C previously obtained for the same material with different techniques.[20] The Stress vs. Strain curves recorded at different temperatures (Fig 3.b) highlight another peculiar behavior of the LCE material. Since at room temperature the material showed a very strong visco-elastic behavior (with an elastic module in the order of 0.7 - 2 MPa) the behavior changed dramatically when the temperature was increased, losing the viscous properties and showing a pure elastic behavior (with a smaller elastic module, in the order of 70 kPa). This behavior can be explained by taking into account the molecular structure of the material and in particular with the loss of the orientational order due to the rearrangement of the mesogens above $T_{NI}$, that makes it a pure elastomer.

Prototypes of composite actuators have been realized according to the recipes described in Section III A. and B.; an example of a prototype is shown in Fig. 4, in which the stripe of LCE (4.0 x 1.5 x 0.3 mm) covered with a 5 μm-thick layer of PEDOT:PSS is contacted with two thin copper wires that are embedded in the conductive layer during the process. Very good adhesion of the upper PEDOT:PSS layer to the LCE substrate was verified for the composite developed in this study. This is indeed one of the major achievements if compared with different approaches aiming at the integration of conductive properties in thermoresponsive LCE materials.

Usually metal electrodes suffer from cracks and delamination with consequent loss of surface continuity and failure of actuation when they are deposited onto soft, compliant materials that change their shape and length due to strain or active smart behavior. In the present case, however, no sign of surface delamination or cracking is observed, due to the good matching of mechanical properties between PEDOT:PSS and LCE. This behavior is very different from that observed in other polysiloxane materials, as in the case of PDMS onto which PEDOT: PSS is poorly adhered, and it is probably ascribable to the different surface chemistry of LCE. [23] Geometry of the composite LCE/PEDOT:PSS samples was chosen for determining the desired bending actuation. Indeed LCE samples used in this study, were originally produced as stripes with 20 cm of length, 1 cm of width and ~ 0.3 mm of thickness. Because of the process used during preparation of the LCE for the alignment of mesogens (see Section II), the director $n$ is aligned along the length of the samples and characterizes the typical actuation performance of the LCE, that is, reversible contraction/elongation along the length of the sample due to the transition from nematic to isotropic phase occurring at $T_{NI}$. Therefore, as concerns LCE material itself, linear actuation triggered by thermal activation is possible. On the other hand, when dealing with the composite materials prepared in this study, compressive forces due to the contraction of the soft active substrate (LCE) combined with

Fig. 3. (a) Graph of elongation/contraction of LCE as a function of temperature; (b) Stress-Strain curves of LCE at different temperatures.
the relatively stiffer and not compressible passive layer of PEDOT:PSS caused the sample to bend in the isotropic phase, i.e. when heated at $T > T_{NI}$. A schematic picture of the bending actuation mechanism and of the geometry and orientation of the sample shape with respect to director $n$ is depicted in Fig.4.

Samples were cut from the original LCE stripe with the necessary form factor in order to emphasize the bending actuation and maintaining the long side along $n$ direction. It is important to notice that one major role in determining the final actuator performance was played by the thickness of the (mechanically) passive PEDOT:PSS layer. Indeed, a preliminary test performed on samples prepared with different thicknesses of this layer (data not shown here) permitted to appreciate that when a ultrathin layer is deposited with thickness $t \approx 100$ nm, the linear actuation behavior of the LCE is fully retained with the corresponding microwrinkling of the upper PEDOT:PSS layer. On the other hand, thicker and stiffer PEDOT:PSS layers ($t \approx 20-50$ μm) partially hindered the LCE actuation, resulting in poor bending and also inducing a not fully reversible behavior, probably due to plastic deformation of the stiff PEDOT:PSS layer. Moreover, the thickness of the PEDOT:PSS layer strongly influenced its actual electrical resistance, which is of overall importance in determining the voltage/current characteristics for driving the actuator. Actually, the thickness of PEDOT:PSS employed in this study ($t \approx 5$ μm) was selected as the best compromise for obtaining good bending actuation, durability and reliability of the conductive properties, feasible electrical resistance, ease of processing. PEDOT:PSS thickness measurement by stylus profilometry have been performed both on samples prepared with pristine PEDOT:PSS solution and on samples doped with DMSO. Data about thickness and electrical resistance of these samples are listed in Table 1. As reported in Table 1, electrical conductivity of Clevios PH1000 formulation is greatly improved by the addition of the secondary dopant DMSO but also by a post-process thermal treatment provided on samples at $T = 120$ °C for 15 minutes. Both effects have been already described in the recent literature even if a comprehensive rationalization of the basic phenomena causing such effects is still argued [21],[22].

**Table 1. Thickness $t$ and electrical resistance $R$ of PEDOT:PSS layers employed in LCE/PEDOT:PSS composite of this study.**

<table>
<thead>
<tr>
<th>Sample/PEDOT:PSS formulation</th>
<th>$t$ (μm)</th>
<th>$R$ (Ω)</th>
<th>$R^*$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clevios PH1000</td>
<td>$5.3 \pm 0.9$</td>
<td>8K</td>
<td>6K</td>
</tr>
<tr>
<td>Clevios PH1000 + 5 wt.% DMSO</td>
<td>$5.4 \pm 0.5$</td>
<td>30</td>
<td>20</td>
</tr>
</tbody>
</table>

* After thermal treatment performed at $T = 120$ °C, 15 minutes.*

The stability of electrical properties during actuation and after many cycles of thermal actuation ($T_0 = 25$ °C, $T_1 = 90$ °C, $T_2 = T_0 = 25$ °C) has been assessed by measuring the variation of resistance $R$ as a function of temperature during the first cycle of actuation and then repeating the measurements at $T_0$ and $T_1$ for many cycles. The results of these experiments are shown in Fig. 5.

Fig. 5. Change of relative electrical resistance ($R/R_0$) as a function of temperature during repeated actuation cycles between 25 and 90 °C.

A significant resistance drop is observed during the first heating cycle (from $T_0$ to $T_1$) that is completely recovered once the sample temperature is restored at $T_0$ (first cooling, from $T_1$ to $T_0$). The same behavior is also observed in repeated cycles, with no sign of degradation of electrical properties due to cracking of the conductive layer.

The bending actuation of the LCE/PEDOT:PSS composite has been tested with an experimental setup in which heating of the sample was provided by a Peltier cell controlled in current. Fig. 6 shows pictures taken during a typical experiment in which a prototype composite actuator is placed horizontally on the surface of the Peltier cell and it changes its shape from a horizontally relaxed state at RT (nematic phase) to a bent state at $T = 90$ °C (isotropic phase). Such behavior is fully reversible, with the recovery of the relaxed state once RT is restored. Image analysis of pictures taken with a digital microscope setup permitted to estimate the bending behavior of the composite. Sample
prototypes with dimension of 4.0 x 2.0 x 0.3 mm and 5 μm thick PEDOT:PSS layer showed typical flexure angle of 118.5° ± 4° (curvature radius 1.67 ± 0.05 mm) at maximum bending. Actuation of the composite via direct Joule heating has been validated and some pictures of a prototype sample of actuator suspended to two copper wires are shown in Fig. 7. Samples tested with Joule heating had dimension of 4.0 x 1.5 x 0.3 mm and electrical resistance of ~ 25 Ω. Actuation was tested by applying typical voltages of 1.5 – 3 V (corresponding to about 60 – 120 mA) for the time needed for heating the composite over its T_{N-I} and so causing the bending. Once the maximum bending was achieved, the applied voltage was turned off and the actuator recovered to its fully relaxed position while cooling down to RT. Preliminary testing permitted to evaluate actuation time in the order of 1-4 s depending on the driving voltage. Similar values were found for the recovery time. When repeated actuation/recovery cycles (up to 50) are applied on samples, very good reproducibility is obtained with no damages in the composite even if a comprehensive and quantitative study of actuation time and reliability is needed in order to better characterize the behavior of these prototypes; this will be the object of future research. On the other hand during these preliminary testing, we could appreciate that actuator failure only occurred in the region where wires are connected to the PEDOT:PSS layer; in this way, if wiring and connection are replaced, the actuator keeps on working. For this reason one of the possible future improvements will regard the establishment of robust and compliant electrical connections that would allow for improving the number of repeated actuation cycles without breaking.

Fig. 7. Direct Joule heating of the prototype. (a) Relaxed state, current off; (b) Bent state, current = 100 mA.