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To cite this article: Chensha Li, Ye Liu, Xuezhen Huang, Chenhui Li & Hongrui Jiang (2015) Light Actuation of Graphene-Oxide Incorporated Liquid Crystalline Elastomer Nanocomposites, Molecular Crystals and Liquid Crystals, 616:1, 83-92, DOI: 10.1080/15421406.2014.990256

To link to this article: http://dx.doi.org/10.1080/15421406.2014.990256
Light Actuation of Graphene-Oxide Incorporated Liquid Crystalline Elastomer Nanocomposites

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The authors demonstrate high-performance photo-actuation of nematic liquid crystal elastomer (LCE) nanocomposites incorporating graphene oxide (GO). The nematic LCE serves as the matrix with reversible thermomechanical response. The incorporated GO absorbs photons and converts the photonic energy to heat, thus actuating the LCE nanocomposite. Both infrared and visible lights of wide spectrum (white light) or various wavelength ranges irradiations are able to effectively actuate the LCE nanocomposites, thus proves that they can fully utilize the photo energy of a light source for their mechanical actuation. Attributed to the well dispersity of GO in LCE matrix, sensitive (in seconds) and reversible photo-induced strain of LCE nanocomposites with consistent shape-changing ratio and significantly enhanced mechanical properties are observed. The contraction of the LCE nanocomposite films under light irradiation is about one third of the original length. The effective load-actuation capability is elevated about 50%.

Keywords Graphene-oxide; liquid crystalline elastomer; nanocomposite; photo-thermo-mechanical actuation

1. Introduction

Photo-induced actuators are attractive to researchers since they offer an effective means to couple photonic energy remotely into the actuator structures, which brings advantages of simplified systems without wires, remote control, and high-level integration [1]. Recently, there has been active research on polymer-based light-driven actuation materials owing to their novel characteristics [2–4], including their stroke, force, and efficiency. Nematic liquid crystal elastomers (LCEs) [5–8] are especially promising because they are equilibrium

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reversible actuating systems that can return to the equilibrium state once the stimulus is removed. However, some nematic LCEs have low response to external stimuli, including light irradiation, due to their low ability of transferring external energy to the molecular switch unit [9], thus being difficult to be actuated remotely. Nowadays, the photo-actuation of nematic LCEs were performed mainly by two ways: one is incorporating photoisomerizable molecules or molecular chromophores into the LCE network, the change in shape of the photoisomerizable molecules or molecular chromophores inducible by light can effect powerful changes of a host material [10,11]. However, their photo-actuation can only be induced by filtered light to specific wave-lengths. Another way is incorporating nano-phase materials to LCE matrix. Adding distinctly different nanofillers to polymeric actuator matrix could exploit the synergy between the nanofillers and the polymers, effectively enhancing the actuation performances [2,3]. For example, carbon nanotubes (CNTs), due to their outstanding electrical, thermal, mechanical, and optical properties, can be used in polymer nanocomposites, including LCE nanocomposites. The photo-actuation of CNT-LCE nanocomposites are activated by the photo-thermal conversion from the CNTs [9,12–16]. However, their poor dispersibility in nanocomposites due to the agglomeration may hamper their practical application [4]. Sometimes surfactants were used to improve their dispersity in LCE matrices [9,12,13,15,17]. It was also reported incorporating dyes to LCEs and actuating LCEs by the photo-thermal conversion of the dyes [17], but the dyes can only absorbing the lights of limited wavelength range and transform them to thermal energy, thus cannot fully utilize the energy from light sources with wide-spectrum, such as natural sunlight, for mechanical actuation.

Graphene is emerging as a promising material because of its prominent intrinsic properties [18,19]. Specifically, the perfect sp² carbon-network structures of graphene materials lead to high thermal conductivity and excellent photo-thermal conversion capability [20]. Theoretical [21] and experimental [22–24] results have revealed that graphene is the strongest material developed so far [24]. Thus, nanocomposites utilizing graphene materials as nanofillers are offering opportunities to impart unprecedented enhancing mechanical and thermal properties to polymers. Moreover, the efficacious use of nanofiller in polymer nanocomposites is strongly correlated with the ability to disperse them homogeneously in a polymer matrix. Graphene materials, with the basic structure of one atom thick and two-dimensional single layer, generally have well dispersibility for reason that there are general no inherent bundling, intrinsic impurities from catalysts and amorphous carbon [25]. Among the graphene materials, graphene oxide (GO) demonstrates excellent processability and dispersion in solutions [19,26], and exhibits extraordinary physical properties when mixed with polymers to form nanocomposites [19].

We here report on a light responsive LCE nanocomposite which is based on thermoresponsive nematic LCE incorporating GO. We take advantage of the giant photo absorption band in GO [27] and its effective thermal conductivity to absorb light energy and to trigger the nematic-isotropic transition within the LCE matrix. It was demonstrated that the GO-LCE nanocomposites could be reversibly and sensitively actuated by infrared (IR) irradiation and visible light of wide spectrum (white light) or various wavelength ranges, this proved that our GO-LCE nanocomposite can fully utilize the energy from light sources for mechanical actuation. In addition, the material’s mechanical performance was significantly enhanced by incorporating GO into the nematic LCE matrix. The effective load-actuation capability during photo-thermo-mechanical actuation with large contraction ratio was elevated about 50%, this should increase the practicality of the applications of LCE materials in the field of actuators.
2. Experimental Procedures

GO was synthesized in our laboratory from natural graphite powder by a modified Hummers method [28,29]. The synthesis of the LCE network was based on the hydroisilation cross-linking reaction of the polysiloxane backbone (poly-dimethylhydrosiloxane), the mesogenic rod-like molecule (4-methoxyphenyl-4-(1-buteneoxy) benzoate) and the two-functional crosslinker (1,4 alkeneoxybenzene) [5,30]. The GO-incorporated side-chain nematic LCE with polysiloxane backbone aligned in uniaxial orientation was obtained via a two-stage cross-linking coupled with a drawing process, leveraging a method we previously reported [14]. Here, GO-LCE nanocomposite film samples were prepared with GO weight contents of 0.1%, 0.3%, and 0.7%, respectively, as well as blank nematic LCE without GO.

The physical characteristics of the materials were investigated by using differential scanning calorimetry (TA Instruments Q100 modulated DSC, New Castle, DE, heating/cooling rate: 10 K/min), scanning electron microscope (SEM, Zeiss LEO 1530, Thornwood, NY) and polarizing optical microscopy (POM, NIKON, SMZ 1500, Melville, NY).

The photo-actuation measurements of LCE nanocomposite films were performed by using a white light source (New Port, Oriel Productline, Model 66885, USA) and an IR source (HOT SPOT: HS 250.3, 250 Watt), the measured spectrum of their emitted light are shown in our previous reported work [14,29]. Stress meters were employed to measure the mechanical property of the LCE materials. All reported data were taken at the environment temperature of 25°C.

3. Results and Discussions

The LCE mesomorphic property was evaluated by measuring the transmittance of a probe light through two crossed polarizers with an LCE film between them. The POM images of the GO-LCE nanocomposite film are shown in Fig. 1. The highest transmittance appeared when the angles between the axial direction of the films and the polarization direction of either polarizer were approximately ±45° (Figs. 1(a) and (b)), while the lowest appeared when the axial direction was parallel with one of the polarization directions (Figs. 1 (c) and (d)). Periodic changes of dark and bright images were observed by rotating the film with an interval of ∼45°. The result proved an LCE nematic-phase texture with the side-chain units being well uniaxially aligned.

Graphene materials have the ability of being readily dispersed in solution to form a stable dispersion composed of completely exfoliated individual graphene sheets [4,31], which allows them to be intimately blended with polymer matrix through solution mixing processing and lead to homogeneous dispersion in polymer matrix. From POM observation in Fig. 1, it was not found that obvious aggregation areas of GO existed in LCE matrix. SEM examination, as shown in Fig. 2, indicates that the GO nanoparticles are well dispersed in LCE matrix without agglomeration.

Figure 3(a) exhibits a characteristic X-Ray diffraction pattern of the GO-LCE nanocomposite with the GO content of 0.7 wt%. It indicates a monodomain aligned nematic liquid crystal [32] with a pronounced azimuthal distribution of intensity at 2θ = 20.15°, corresponding to a dimension of lateral packing mesogenic units ∼0.44 nm. The uniaxially ordered LCE matrix creates two areas of high intensity, which can be confirmed by the two peaks in the azimuthal integration of wide-angle diffraction arc, as shown in Fig. 3(b). Some smectic fluctuations can bring weak small angle reflections on the equator in the X-Ray diffraction pattern [32], which result in the weak shoulder peaks between two large peaks in Fig. 3(b). Other GO-LCE nanocomposite samples and the blank LCE sample
Figure 1. POM images of the GO-LCE nanocomposite film (GO concentration: 0.7 wt%). (a) and (b) The angles between the uniaxial direction of the GO-LCE film and the polarization directions are $\pm 45^\circ$, i.e., highest transmittance. (c) and (d) The uniaxial direction of the GO-LCE film is parallel to one of the crossed polarization directions, i.e., lowest transmittance.

Figure 2. A SEM image of the GO-LCE nanocomposite, showing the distribution state of GO in LCE matrix (GO concentration: 0.7 wt%).
exhibited consistent result of X-Ray diffraction pattern and X-Ray intensity distribution. By analyzing the X-Ray diffraction data, the obtained nematic order parameters of every sample are listed in Table 1. It indicates that the nematic order parameters of the blank LCE and the GO-LCE nanocomposites with different GO content are basically consistent, and weakly influenced by the incorporated GO, it can be considered as the effect of the good dispersion of GO in LCE matrix.

DSC measurement of phase transformations of the LCE nanocomposite films was performed to obtain the nematic-isotropic transition temperature \( T_{ni} \) and the glass transition temperature \( T_g \) of the samples (Table 1). \( T_{ni} \) and \( T_g \) of the blank nematic LCE are about 82°C and 5.41°C, respectively, while those of the GO-LCE nanocomposites are similar. Thus, the thresholds of phase transition of the LCE matrix were weakly affected by the incorporated GO. In our previous work using SWCNTs as the nanofiller in the same LCE matrix [14,16], the \( T_{ni} \) was obviously decreased. The reason lies in that CNTs have one-dimension nanostructure with high length/diameter ratio, especially curved even curly parts.

**Table 1.** The properties and photo-actuation performances of the blank LCE (only be actuated by IR) and GO-LCE nanocomposite films. The maximum axial contraction ratio is the contraction ration from nematic to isotropic transition. The measured final temperatures of the films under photo irradiation were above 85°C, which was above the \( T_{ni} \).

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_g ) (°C)</th>
<th>( T_{ni} ) (°C)</th>
<th>Nematic order parameter</th>
<th>Maximum axial contraction ratio (%)</th>
<th>Load-actuation* (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank LCE</td>
<td>5.41</td>
<td>81.98</td>
<td>0.637</td>
<td>32.8</td>
<td>&lt;110</td>
</tr>
<tr>
<td>LCE 0.1 wt% GO</td>
<td>3.21</td>
<td>81.72</td>
<td>0.640</td>
<td>33.1</td>
<td>&lt;131</td>
</tr>
<tr>
<td>LCE 0.3 wt% GO</td>
<td>4.08</td>
<td>82.15</td>
<td>0.638</td>
<td>32.9</td>
<td>&lt;148</td>
</tr>
<tr>
<td>LCE 0.7 wt% GO</td>
<td>4.94</td>
<td>80.74</td>
<td>0.637</td>
<td>32.6</td>
<td>&lt;163</td>
</tr>
</tbody>
</table>

*If the loads are above these range, the LCE or GO-LCE nanocomposites prone to be fractured during photo-actuation processes.

**Figure 3.** (a) An X-Ray diffraction pattern obtained from a GO-LCE nanocomposite sample. (b) Azimuthal intensity distribution of the X-Ray diffraction pattern of the GO-LCE nanocomposite sample. (GO concentration: 0.7 wt%).
often exist on their tube walls. These factors may enable a remarkable thermal-deformation effect of CNTs, and create thermal–mechanical effect of CNTs in the polymer matrices [2,3]. Such thermal-deformation stress of CNTs can promote the transition of the mesogenic groups from the nematic state to the isotropic state, leading to the lowering of $T_{ni}$.

The graphene materials have one-layer carbon-network structure, the aspect ratio in the other two dimensions is also not high, result in a low thermal-deformation effect and weak influence to the movement of the mesogenic groups. Therefore the $T_{ni}$ of LCE was weakly affected by the incorporated GO. The LCE and GO-LCE nanocomposite films showed reversible deformation when undergoing temperature change above and below their $T_{ni}$, consistent with previous literature [5,6].

The GO-LCE nanocomposite films further demonstrated attractive photo-induced actuation characteristics. They undergo maximum contraction under a white-light irradiation (intensity $\sim 100$ mW/cm$^2$), or under an IR irradiation (intensity $\sim 1$ W/cm$^2$). For example, Figs. 4(a) and (b) shows the contraction of a GO-LCE film (left) and a blank LCE film (right) under a 3.0 W/cm$^2$ IR irradiation, while Figs. 4(c) and (d) shows the contraction of the same pair of films under a 265 mW/cm$^2$ white light irradiation. The GO-LCE nanocomposite films started conspicuous uniaxial contraction and reached the maximum contraction within several seconds under the white light irradiation, and then restored to their initial length also in several seconds after the light source was switched off, indicating completely reversible photo-actuation. On the contrary, the blank LCE film showed no response to white light even with an intensity of 10 W/cm$^2$ (maximum output from our light source). Meanwhile, the GO-LCE film contracted to about its maximum under an IR intensity of 3.0 W/cm$^2$, while the blank LCE film only exhibited a contraction of 8% under the same condition.

The reason behind the distinctively inferior photo response of the blank LCE film to the GO-LCE nanocomposite films lies in that the blank film is essentially photo transparent with low photo-thermal energy conversion efficiency, therefore, being difficult to respond to photo irradiation. However, some molecular groups in LCE network can absorb some spectral spectrum of IR to create vibrations, such as Si–O–Si absorbs the IR of 1125 cm$^{-1}$ and 1133 cm$^{-1}$, C–H in –CH$_3$ absorbs the IR of 1390 cm$^{-1}$, C–H in –CH$_2$– absorbs the IR of 1446–1466 cm$^{-1}$, C=O absorbs the IR of 1723 cm$^{-1}$, C–O ether bond absorbs the IR of 1000–1300 cm$^{-1}$, etc. [33]. These vibrations of molecular groups created thermal...

**Figure 4.** Optical images of photo-actuation behaviors of the blank LCE film and GO-LCE nanocomposite (GO concentration: 0.7 wt%) film, each film is loaded by 3 g of weights. (a) Before IR irradiation. (b) After 7.0 sec of IR irradiation (intensity: 3.0 W/cm$^2$). (c) Before white light irradiation. (d) After 8.5 sec of white light irradiation (intensity: 255 mW/cm$^2$).
energy in LCE matrix, which was the reason that the IR irradiation can also actuate the blank LCE in some extent. There is no spectrum absorption of molecular groups in visible light range. On the contrary, GO can efficiently absorb and convert photo energy into thermal energy, thus acting as nanoscale heaters embedded in the LCE matrix. Combined good dispersion and effective thermal conductivity, GO served as thermal conduction networks to heat the LCE matrix uniformly and rapidly. The absorbed thermal energy increased the temperature in the LCE matrix above its $T_{ni}$, leading to the nematic–isotropic phase transition and axial strain in the LCE nanocomposite. The maximum axial contraction ratio under light irradiation of the blank LCE (only be actuated by IR) and the GO-LCE nanocomposite films are both around 1/3 (also listed in Table 1) of the original length, this basically consistent shape-changing ratio should be attributed to their basically consistent nematic order parameters, as listed in Table 1. Experiments also indicated that in general, the higher the GO content incorporated in the LCE matrix, the lower the required light irradiation intensity for the film to reach maximum contraction. Since more graphene
nanofillers correspond to more nanoscale heater, higher thermal energy would be generated in the composites, which thus could lead to a lower needed light irradiation intensity. In the following experiment, we measured the photo-actuation performance of the GO-LCE nanocomposites by the lights of various wavelength ranges. The emitted white light with the intensity of 265 mW/cm² was filtered to be different limited wavelength ranges by three optical filters, respectively, the wavelength ranges of the transmitted lights were respective 380–500 nm, 480–580 nm, and 580–720 nm. Experiment indicated that GO-LCE nanocomposites demonstrated consistent photo responsive characteristic when they were respectively irradiated by the lights of three different wavelength ranges with the same intensity, as shown in Fig. 5 and supplementary videos [34], thus verified that the efficiency of photo-actuation has no spectral spectrum dependence. Therefore, different from those photo-responsive LCE materials based on incorporating photoisomerizable molecules or molecular chromophores into the LCE network, or incorporating photo-thermal responsive dyes to LCE matrices whose photo-actuation can only be induced by using lights of specific wavelengths, this GO-LCE nanocomposites can fully utilize the energy from light sources for mechanical actuation.

This axial contraction is due to the change of orientational order during the nematic-isotropic transition [5]. As the orientational order is decreased during the nematic-isotropic transition, the conformational constraint on the LCE network is overcome, and its effect on an elastomer would be to change its shape and generate a retractive force, thus bring an ability of mechanical actuation. But the capability of this mechanical actuation can be limited by the material’s mechanical property. Under a high temperature around \( T_{ni} \), the LCE materials may be fractured during the contraction actuation process by a high load [35]. Experiment indicated that the blank LCE actuated a maximum load without being fractured during photo-actuation was about 110 kPa, while the maximum loads actuated by the GO-LCE nanocomposites were obviously elevated, arrived 163 kPa, a increase of about 50%, as listed in Table 1. This experiment result indicated that GO-LCE nanocomposites also show significant improved mechanical property compared to blank LCE. The increased load-actuation capability of GO-LCE nanocomposites should be led by a enhanced tensile strength during nematic-isotropic transition, which can be considered as the effect of the excellent mechanical characteristics and good dispersion in LCE matrix of GO.

4. Conclusions

Utilizing graphene materials in a novel way of optical-absorption and nanoscale energy transfer unit imparts effective photo-actuation behavior to the nematic LCE matrix. We have demonstrated GO-LCE nanocomposite films that possess reversible and large photo-thermo-mechanical response with a uniaxial contraction of 1/3 of the original length. The GO-LCE nanocomposites can utilize the photon energy of various spectrum simultaneously to realize photo-thermo-mechanical actuation under the irradiation of a broad-spectrum light, fully transfer the photo energy from a wide spectrum light source to mechanical actuation. Utilizing GO as the nanofiller not only enhances the photo-thermo-mechanical energy conversion capability of the LCE materials and improves the uniformity of the LCE nanocomposites, but also significantly improved their mechanical property. The effective load-actuation was increase by about 50% at rather low concentrations of GO in LCE matrix (below 1 wt%). Given these properties and the abundant supply of graphite and the processability of graphene materials with high purity, graphene materials may open new promise for practical applications of actuation materials.
This work was supported by the University of Wisconsin–Madison Vilas Associates Program supported by the Vilas Trustees, and partly by the Wisconsin Institutes for Discovery. This research utilized NSF-supported shared facilities at the University of Wisconsin. The authors thank N. L. Abbott, Z. Q. Yang, and C. Lo for academic communications.

References

[34] Our experiment indicated that CNT-LCE nanocomposites also demonstrated consistent photo responsive characteristic when they were respectively irradiated by the lights of these three different wavelength ranges with the same intensity.