Nanotube liquid crystal elastomers: photomechanical response and flexible energy conversion of layered polymer composites

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Received 23 April 2014, revised 29 June 2014
Accepted for publication 14 July 2014
Published 12 August 2014

Abstract
Elastomeric composites based on nanotube liquid crystals (LCs) that preserve the internal orientation of nanotubes could lead to anisotropic physical properties and flexible energy conversion. Using a simple vacuum filtration technique of fabricating nanotube LC films and utilizing a transfer process to poly (dimethyl) siloxane wherein the LC arrangement is preserved, here we demonstrate unique and reversible photomechanical response of this layered composite to excitation by near infra-red (NIR) light at ultra-low nanotube mass fractions. On excitation by NIR photons, with application of small or large pre-strains, significant expansion or contraction of the sample occurs, respectively, that is continuously reversible and three orders of magnitude larger than in pristine polymer. Schlieren textures were noted in these LC composites confirming long range macroscopic nematic order of nanotubes within the composites. Order parameters of LC films ranged from $S_{optical} = 0.51–0.58$ from dichroic measurements. Film concentrations, elastic modulus and photomechanical stress were all seen to be related to the nematic order parameter. For the same nanotube concentration, the photomechanical stress was almost three times larger for the self-assembled LC nanotube actuator compared to actuator based on randomly oriented carbon nanotubes. Investigation into the kinetics of photomechanical actuation showed variation in stretching exponent $\beta$ with pre-strains, concentration and orientation of nanotubes. Maximum photomechanical stress of $\sim 0.5$ MPa W$^{-1}$ and energy conversion of $\sim 0.0045\%$ was achieved for these layered composites. The combination of properties, namely, optical anisotropy, reversible mechanical response to NIR excitation and flexible energy conversion all in one system accompanied with low cost makes nanotube LC elastomers important for soft photochromic actuation, energy conversion and photo-origami applications.

Online supplementary data available from stacks.iop.org/NANO/25/355501/mmedia

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Keywords: carbon nanotube, liquid crystals, energy conversion, order parameter, self-assembly, photomechanical actuation

(Some figures may appear in colour only in the online journal)

1. Introduction

Materials that flow like liquids and yet can order themselves macroscopically like crystals are called liquid crystals (LCs) and hold great technological and commercialization potential [1]. LCs can also be found in nature, such as tobacco mosaic virus [2], proteins [3] and cells [4, 5]. Modern day applications of LCs include polymers such as Kevlar for bullet proof jackets [6], and electro-optics in digital and computer displays [7, 8]. The uniqueness of LC is their tendency to align in specific directions with macroscopic and long range ordering. In recent years, with the synthesis of nanotube LCs by Windle et al [9], organization of nanotubes as LCs has become an interesting and attractive area of study to realize low cost commercial applications based on self-aligned nanotubes. LC nematic self-assembly of nanotubes, as well as graphene and other 2D nanomaterials, presents opportunities in developing novel macroscopic composites with long range order and unique anisotropic properties. Energy efficient photomechanical systems based on nanotube LC-elastomers that combine anisotropic optical and thermal properties of the nanotube LCs and elasticity of the polymer network are yet to be explored. In the recent past, we reported LC of carbon nanotube films using simple vacuum filtration and their subsequent applications as high performance transistors [10]. Thin films of nanotube LCs with order parameters ranging from δ = 0.1–0.5 were patterned into conducting channels of transistor devices which showed high on/off ratios ~20 000 and electron mobility values up to $\mu_e = 79 \text{ cm}^2 \text{Vs}^{-1}$, hole mobility values up to $\mu_h = 287 \text{ cm}^2 \text{Vs}^{-1}$ [10]. Herein we demonstrate elastomeric compositions based on ultra-small amounts of single wall nanotube (SWNT) LC films in poly(dimethyl) siloxane (PDMS) with high orientational order, optical anisotropy, reversible and macroscopic mechanical response to near infra-red (NIR) excitation. Further, we report strain dependent flexible energy conversion based on change in microscopic order parameters of nanotubes and stress to nanotube mass ratio larger than all the nanotube/graphene based nanocomposite based light driven actuators reported to date [11–13]. The amount of nanotube used in this work is also ~10 000 times smaller than past reported electro-mechanical actuators based on nanotube-polymer compositions [14], suggesting the high importance of spontaneous nanotube order for low cost commercial applications. Further, the methods used here may enable standardization of nanotube composite fabrication processes in general, the lack of which has hindered commercialization.

2. Results

Figure 1 presents the schematic of the SWNTs LCs and the resulting photomechanical composite actuator. Vacuum filtration was used to make the nanotube LC films. The nanotube-surfactant solution, when filtered through the membrane, creates a concentration gradient due to change in fluid velocity across the membrane [10]. As the solution is filtered off and the concentration of nanotube increased, nematic domains form. As presented in figure 1 schematic, nanotube LCs are formed on an anodic filter membrane. The LCs from the membrane are then subsequently transferred to a PDMS surface that is spin coated on a glass slide. The membrane is then gently peeled off the PDMS surface leaving the oriented nanotubes on the surface. A second PDMS layer is then spin coated and polymerized to preserve the internal orientation of the film. Our work also removes impediments in nanotube dispersion and fabrication process such as shear mixing [13], evaporative cross-linking [15, 16], functionalization in acids [17], all of which are challenging and can affect the overall mechanical properties of the composites. Further, the lack of standards in preparing CNT based composites to date makes them prohibitively expensive and hampers commercialization [18]. Composites based on nanotube LCs may become commercially viable owing to the self-assembly of nanotubes as LCs with high anisotropic properties and order parameters. Anodisc alumina filter was used owing to the low interaction energy between SWCNTs and the porous alumina surface, which enables the film to be transferred completely from the alumina filter surface to PDMS (PDMS has a low surface energy of ~19.8 mJ m$^{-2}$ [19]). While such films have been used in the past to transfer random nanotube networks [19], we have now used this technique for transferring the nanotube LC films and preserve the internal orientation of nanotubes in film. The full transfer of the film as shown is quite important for preserving the LC state of the film to accomplish the anisotropic properties. Since films of differing concentration also have slightly differing order parameters above the isotropic to nematic transition, the method used here can produce composites with specific order parameters based on the film concentrations and therefore specific properties. This may potentially be helpful in standardizing nanotube based composite fabrication process.

Figure 2 presents the photographic images of the samples. Figure 2(a) presents the LCs on the alumina membrane. The numbers 0–5 represent plain alumina membrane and nanotubes at concentrations of ~0.01 μg ml$^{-1}$, ~0.03 μg ml$^{-1}$, ~0.05 μg ml$^{-1}$, ~0.1 μg ml$^{-1}$, ~0.3 μg ml$^{-1}$ and ~0.5 μg ml$^{-1}$ respectively. The concentrations mentioned above are the starting solution concentrations to make the film using vacuum filtration process. Figure 2(b) presents the film after full transfer from membrane to PDMS. Cut photomechanical actuators are presented in figure 2(c). The NIR source, power meter, linear actuators for applying pre-strains, precision balance and sample is integrated in an light evacuated black box and the controlled through LabView software as
presented in figure 2(d). Figure 3 presents the cross-sectional SEM images of the composites. The actual thicknesses of the films were between \( \sim 126-865 \) nm for the different concentrations mentioned. The thickness of the LC layer increased with concentration. At these measured thicknesses, the starting concentration needed to make a single layer LC films is anywhere between \( 58-79 \) pg ml\(^{-1} \). Such ultra-small concentrations with the ability to create ordered films could be highly useful in scalable manufacturing of LC nanotubes for high performance commercial applications.

Figure 4 presents the SEM images of the nanotube LC films. Three rows of images show the evolution of the microstructure at different concentrations. The columns represent the same concentration at different length scales. It is observed that at low magnification (figure 4(a-1), the lowest concentration film \( \sim 0.01 \) μg ml\(^{-1} \) consisted of sets of nucleated nematic islands that were loosely connected by few isotropic nanotubes in between. This is a characteristic two phase behavior of a lyotropic nematic LC [1]. The minimum concentration required for formation of nematic liquid crystals was \( \sim 0.0075 \) μg ml\(^{-1} \). Below this concentration, the films were isotropic. As the concentration of the nanotube in solution increased, nucleated nematic regions grow as seen with the increase number of island in figures 4(b-1), (c-1). In figure 4(d-1), the nucleated nematic islands become larger domains thereby closing the gap between adjacent islands. Finally in figure 4(e-1), the films are continuous and bridge all the gaps forming large nematic domains as in refining its own structure/self-healing to achieve final film morphology. Row 2 and Row 3 are the images at 1 μm and 200 nm scale respectively. In Row 2, the nematic like LC texture of film is clearly observed with nanotubes oriented along a specific nematic director. It is evident that \( \pm \frac{\pi}{2} \) disclinations are formed, as in [9], confirming the topology of the nematic phase. In Row 3, the morphology of all the films looks similar after the isotropic-nematic transition. For clarity one of the images is enlarged to show the ordered arrangement of nanotubes. The insert in the image shows the concentration dependence of the local order parameters above the isotropic-nematic transition. There are pores in between the bundles across all the concentrations and there is a twisting pattern of individual nanotubes due to rotation of the nanotube. The competing scenario between translational and rotational entropy of nanotubes thus determines LC texture and order parameters. It is also seen that the orientation of the nanotubes during vacuum filtration occurs in bundles and not individual tubes due to the inter-tube attraction between the nanotubes. These bundles are 10–20 nm in diameter. In Row 3, it is observed that irrespective of the concentration at nano-meter length scales most films have similar orientation in their nematic domains with slight changes in the order parameters. Any LC anisotropy is defined by its order parameter. In two dimensions, the order parameter is given by:

$$ S = < 2 \cos^2 \theta - 1 > , $$

where the brackets denote the average over the ensemble of all angles. \( S \) is therefore at a maximum of 1 when all CNT are aligned in the direction of \( \theta \), and a minimum of \(-1\) when all CNT are perpendicular to \( \theta \). Order parameter was calculated for individual domains from the SEM images with the aid of 2D Fourier analysis similar to one used by Bayan, et al for collagen fiber orientation [20]. These yielded values of

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**Figure 1.** Nanotube liquid crystal elastomer composite. (1) Vacuum filtration is used to deposit carbon nanotubes (CNTs) onto an inorganic filter membrane. (2) PDMS is spin coated on top of a glass slide. (3) The membrane consisting of LCs is pressed against the PDMS that resulted in complete transfer. (4) A second PDMS layer is spin coated and polymerized to enable LC being part of the polymeric network resulting in ‘Nanotube LC Elastomer’.
S = 0.77–0.88 for the different LC films. These were also compared to the randomly oriented films which yielded average order parameters of S = 0.06–0.24 (≈4–13 times smaller) for the same concentration (table S1, suppl.).

While the order parameter is easy to calculate from SEM images using the 2D FFT analysis, it is important to validate this method through measuring order parameters using polarization optical microscopy [21]. The order parameter of the nanotube LCs was ascertained using polarization microscopy [21]. Films were transferred to a glass sample and the order parameter of the films was calculated using both FFT analysis and polarization microscopy. The order parameter using polarized microscopy was evaluated by using dichroic ratio Δ given as the ratio of absorbance that is parallel and perpendicular to the director. The absorbance is measured in parallel (A∥) and perpendicular (A⊥) configuration using the Lambert–Beers Law:

\[ A = \log \frac{I_o - I_{dark}}{I - I_{dark}} \]  

where \( I_o \) is the intensity of light without any sample, \( I \) is the intensity of light with nanotube on the glass, and \( I_{dark} \) is the intensity with light blocked. The dichroic ratio was calculated

Figure 2. Film transfer, actuators and test setup. (a) Single wall nanotube (SWNT) liquid crystal films on membrane after vacuum filtration; (b) fully transferred film onto PDMS; (c) SWNT LC photomechanical actuators. The numbers represent concentrations of CNTs as follows: 0–plain PDMS; 1–0.01 μg ml⁻¹; 2–0.05 μg ml⁻¹; 3–0.1 μg ml⁻¹; 4–0.3 μg ml⁻¹; 5–0.5 μg ml⁻¹; (d) test set up with the sample between the clamps mounted on a precision balance, laser used for excitation and manual positioner with linear actuator to apply pre-strains [13].
using the equation
\[ \Delta = \frac{A || A_L}{A_L}. \] (3)

The order parameter is then given by the equation:
\[ S_{\text{optical}} = \frac{\Delta - 1}{2 + \Delta}. \] (4)

Figure 5 presents the linear correlation between the order parameters from both the methods. The order parameters measured using polarization microscopy was smaller than the 2D FFT by factor of ~1.5. A linear relation between order parameters from both techniques was established:
\[ S_{\text{FFT}} = 1.49 \times S_{\text{optical}} + 0.01. \] (5)

The FFT technique although produced a higher order parameter is easier to quantify based on SEM images of the nanotube LCs without additional experiments. The relationship is useful in calculating any future order parameters of nanotube films for their alignment and one can get a realistic estimate of order parameter without resorting to transferring films onto glass slides and additional polarization microscopy experiments. All the data reported from hereon has the corrected order parameter based on the optical measurements. Thus the order parameter mentioned above using FFT for LC films can be corrected to \( S_{\text{optical}} = 0.51-0.58 \) and for randomly oriented film \( S_{\text{optical}} = 0.04-0.16 \).

Figure 6(a) presents the Schlieren textures of nanotube LC films suggesting nematic orientational order in the macroscopic composite. At 2.5 degree rotation of the polarizer, due to enhanced contrast, the domain walls are visible with each domain aligned along a specific director. Measuring domain size as a function of concentration yielded dramatic results which are presented in figures 6(b)–(g). The domain counts and size were calculated based on the particle analysis function in NIH Image J software for the polymer composites from the binary images [22]. The size of these domains were anywhere from 1 \( \mu \text{m}^2 \) to 150 \( \mu \text{m}^2 \). It is seen that with increase in concentration, the domain size decrease significantly. The number of domains per mm\(^2\) (~5–10 \( \mu \text{m}^2 \) size) is seen to increase from 260 domains mm\(^{-2}\) at ~0.01 \( \mu \text{g} \text{ml}^{-1} \) to 14 367 domains mm\(^{-2}\) at ~0.5 \( \mu \text{g} \text{ml}^{-1} \). As the concentration increases, the film also spreads over a large area however making the domain size smaller suggesting large number of directors for formation of LCs in subsequent layers. As the nanotubes arrange in different layers, some of these nanotubes spontaneously become directors for the formation of individual domain thereby making the process more localized resulting in smaller domains as the film spreads over large area.

While there are hundreds of papers in the literature showing measurements of nanotube composite mechanical properties, most of them are nanocomposites prepared using shear mixing, functionalization, acid treatments or other mixing methods. Here we show that our layered nanotube LC polymer composites have order dependent mechanical properties. Figure 7 presents the elastic modulus versus weight fraction of nanotubes in polymer composites. The elastic modulus is seen to increase with concentration of nanotubes at these ultra-small concentrations (~1.4 \( \times 10^{-2} \text{ wt.\%} \)). At low mass fractions (~0.5 \( \times 10^{-2} \text{ wt.\%} \)), the elastic modulus of the
composite is seen to be only dependent on the nanotube fillers. Insert presents the change in elastic modulus of such ordered LC composites. The change in elastic modulus $E \sim 20\%$ was seen for the concentrations used which had high order parameters between $S_{\text{optical}} = 0.5-0.6$ (above the isotropic-nematic transition). It should also be noted that the $\sim 20\%$ change in $E$ was achieved for just $\sim 3 \times 10^{-3}$ wt.% of nanotube and $\sim 90\%$ change in elastic modulus of composite was achieved for mere $<1.4 \times 10^{-2}$ wt.% of nanotube, about 100 times smaller weight fractions than past reports [23]. The use of surfactant enabled nanotube LCs thus presents a more environmentally benign approach (no acid treatment or functionalization), easier sample preparation, order dependent elastic modulus for low mass fraction of nanotubes to prepare composites.

Figure 4. SEM images of LC-CNTs. (a-1)–(a-3): 0.01 µg ml$^{-1}$; (b-1)–(b-3): 0.05 µg ml$^{-1}$; (c-1)–(c-3): 0.1 µg ml$^{-1}$; (d-1)–(d-3): 0.3 µg ml$^{-1}$; (e-1)–(e-3): 0.5 µg ml$^{-1}$; scale bars: row 1: (a-1)–(e-1): 10 µm; row 2: (a-2)–(e-2): 1 µm; row 3: (a-3)–(e-3): 200 nm, (g) order parameter versus concentration and (f) magnified 100 nm image of (e-3).
 Photomechanical responses of nanotube LC-polymer composites are presented in figures 8(a)–(f). In figure 8 starting with a plain PDMS elastomer (figure 8(a)) and progressing from ~0.01 μg ml⁻¹ to ~0.5 μg ml⁻¹ concentrations of nanotube-LC/PDMS composites (figure 8(f)), each plot shows the photomechanical response to ~808 nm NIR illumination for five consecutive cycles each one being 60 s. Since the optical loss of PDMS in the NIR region is <0.5 dB cm⁻¹ [24], the negligible/zero response in the plain PDMS sample (figure 8(a)) was expected. However, by a concentration of ~0.01 μg ml⁻¹ (figure 8(b)), the photomechanical effect becomes clearly observable through expansion and contraction of the actuator. Inset in figure 8(b) clearly shows the expansion for low pre-strains and contraction for moderate to high pre-strains. All the composites exhibited that low pre-strain values resulted in positive film expansion and thus positive-induced stress, while high pre-strain values resulted in contraction (negative thermal expansion) and thus negative change in stress. More concisely stated, weakly stretched composites show reversible expansion while highly stretched composites show reversible contraction suggesting rubbery elasticity. At ~9% pre-strain, the samples exhibited zero stress or no photomechanical actuation [12]. This cross-over from small positive expansion to large negative expansion suggests rubbery elasticity at the thermo-elastic inversion point [12]. The magnitude of the photomechanical response was negligible (no movement) for plain PDMS, +0.10 kPa to ~0.25 kPa for ~0.01 μg ml⁻¹, +0.7 kPa to ~2.2 kPa for ~0.05 μg ml⁻¹, +2.8 kPa to ~7.2 kPa for ~0.1 μg ml⁻¹, +5.5 kPa to ~14.7 kPa for ~0.3 μg ml⁻¹ and +8.0 kPa to ~22.8 kPa for ~0.5 μg ml⁻¹ concentrations of nanotube LCs. Each plot in figure 8 also shows the entire 5 cycle response and shows reproducibility from one cycle to the next. Such photomechanical actuators have been operated continuously in our laboratory for more than 3000 cycles without degradation [15].

One interesting question that arises is the effect of nanotube ordering on the photomechanical response. In order to investigate this, films with exact concentrations (~0.5 μg ml⁻¹) and same nanotube purity were processed into both randomly oriented bucky papers (S_{optical}=0.16) and surfactant processed LC films (S_{optical}=0.58). The thickness of the sample was quite similar after vacuum filtration and film transfer. Figures 9(a) and (b) presents the SEM images of the randomly oriented and LC films respectively. The difference in morphology is easily seen with ordered arrangement of nanotube in figure 9(b). Subsequent testing for photomechanical response suggested almost three times smaller in photomechanical response for randomly oriented sample compared to the LC sample as presented in figures 9(c), (d). This unambiguous result suggest that for same concentration, the photomechanical response, the kinetics and the energy transduction all depend on the order of the nanotube in film. This may suggest that the overall photomechanical response may be sum of individual nanotube-polymer response around the light spot. Using high quality randomly oriented films only resulted in lower response. The result in figure 9(c) (0.5 μg ml⁻¹ randomly oriented) can be compared to figure 9(c) (~0.05 μg ml⁻¹ LC nanotubes), ten times small amount of mass. The use of randomly oriented films thus leads to higher cost and moderate performance compared to self-assembled LC films which can access the superior nanotube properties.

Investigating the kinetics of actuation and relaxation, nanotube LC elastomer composites demonstrated actuation kinetics that was fitted as per the Kohlrausch–Williams–Watts (KWW) function for actuation Δσ_{actuation} (t) = 1 - exp[-(τ/τ')^β] and relaxation Δσ_{relax} (t) = exp[-(τ/τ')^β] [25]. Figures 10(a) & (b) presents the actuation and relaxation kinetics fitted to the KWW functions for both expansion and contraction respectively. The time constants τ_{actuation} = 7 s and τ_{relaxation} = 5 s for relaxation is seen with stretching exponent β_{actuation} = 0.91 and β_{relaxation} = 1.04. The stretched exponential function contains just two free parameters: the relaxation time τ and the fractional ‘stretching’ exponent β, which satisfies 0 < β < 1. The upper limit of β = 1 corresponds to simple exponential decay or Debye relaxation, while lower values of β are indicative of a more complicated non-exponential relaxation process or viscoelasticity [26]. The results here suggest that on NIR excitation, heating the nanotubes and subsequent movement of polymer chains is a highly dynamic process. While τ is a material sensitive parameter, we investigated how β varies with nanotube concentration and pre-strains to investigate the topographical origin of β. We assumed it would be constant and independent of nanotube concentrations and pre-strains. Figures 10(c) & (d) presents the stretching exponent β as a function of nanotube concentration and pre-strains respectively. Several interesting things can be seen. The stretching exponent β is almost constant (β < 1) with increase in nanotube concentration for relaxation. For actuation, β is seen to decrease, reach a minimum (β = 0.8 at 0.2 μg ml⁻¹) and then go back up (β = 0.9 at 0.5 μg ml⁻¹) suggesting both short and long range interactions. With increase in pre-strains, the variation of β is also seen in
Figure 6. Schlieren textures and domain size analysis: (a) Schlieren textures of nanotube LCs; rotation of the polarizer by 2.5 degrees (92.5 degrees) resulted in enhanced contrast and better imaging of the Schlieren textures and domain walls suggesting long range order. Scale bar: 2 mm. (b)–(g) Domain size measurements as a function of concentration inside the LC-polymer composites: (b) \(\sim 0.01 \mu g/ml\); (c) \(0.05 \mu g/ml\); (d) \(\sim 0.1 \mu g/ml\); (e) \(0.3 \mu g/ml\); (f) \(\sim 0.5 \mu g/ml\); (g) average domain size versus CNT concentration showing almost twice the decrease in domain size with increasing concentration. Line is shown for eye guidance only.
actuation. This variation of $\beta$ may be due to change in microscopic order of the nanotubes after stretching resulting in more complex chain movements and longer range of interactions of the disordered polymer when excited by NIR light. However, in both cases of relaxation $\beta$ almost tries to approach unity at high concentrations and pre-strains. The case of randomly oriented sample is even more interesting. While the relaxation patterns look similar, the actuation is flat at all pre-strains at the same concentration as the LC actuator. The variations in $\beta$ may also infer dynamic changes in rheological properties of the sample with light excitation, pre-strains and nanotube concentrations. We tried to fit the actuation and relaxation with $\beta=2$ as in the past which was far worse compared to past nanotube photomechanical actuators [27]. While past studies did throw some light on the stretching exponent and fast relaxation [27], the variation of $\beta$ with mixing methods such as shear, evaporative, functionalization and other methods is not well understood and could be subject of future investigation. Therefore this study shows that design of photomechanical actuators whether layered composite or nanocomposite encompassing the same material can have two different responses and therefore is a highly complex but interesting system to study.

Nanotube-LC addition to elastomers not only creates high mechanical strength composites and photomechanical actuation, but also could potentially be viable system for energy harvesting. We calculated some optical to mechanical conversion factors. Figure 11(a) presents the optical to mechanical conversion factor versus concentration. This number is a measure of stress generated to the power absorbed by the actuator light spot and has been reported in the past as a measure of photomechanical actuator performance [13, 28]. Maximum opto-mechanical conversion factor of $\sim$0.5 MPa W$^{-1}$ was measured for the nanotube LC elastomeric actuator. These numbers are similar to past carbon nanotube and more recently graphene based photomechanical actuators 0.5–10 MPa W$^{-1}$ [12, 13]. However, in contrast to all previous work, the amount of carbon nanotube used in the present work was $\sim$100–1000 times smaller and our design is a layered composite unlike past nanotube/graphene photomechanical actuators which were nanocomposites [12, 13]. The mass fractions used were also $\sim$10 000 times smaller than past electro-mechanical actuators based on nanotube polymer nanocomposites [14]. This may suggest that instead of mixing nanotubes into polymer resulting in nanocomposites, high quality nanotubes at ultra-low concentrations that are self-assembled into LC with layered design may potentially lower the cost for commercial applications. This may especially be true for thin film transistors where accessing the extraordinary properties of nanotube LC may result in high electron mobility. We therefore believe the commercialization of nanotube products is thus one of design and understanding the trade-offs between performance and material utilization.

An important aspect of any actuator is the energy efficiency at converting external stimulus into useful work. Therefore, efficiency ($\eta$) of the nanotube-LC composites to a known IR illumination source was evaluated. Figure 11(b) presents the efficiency as a function of nanotube-LC loading. The efficiency increased with increase in concentration which ranged from $\sim$0.0015% (0.01 $\mu$g ml$^{-1}$ at 50% pre-strains) to $\sim$0.0045% ($\sim$0.5 $\mu$g ml$^{-1}$ at $\sim$50% pre-strains), about three times increase at such small nanotube-LC concentration. Further, efficiencies were also observed to be tunable with respect to strains. Stretching the rubber composite increases the efficiency due to the increase in entropic force (rubber elasticity) [29]. However, the increase in efficiency is also related to increase in order parameters of self-assembled nanotubes after stretching. Past nanocomposite photomechanical actuators based on carbon nanotubes have shown change in induced order parameters using x-ray diffraction measurements upon stretching [12]. For instance, for pre-strain value of $\varepsilon=0.6$ (60%), the induced orientational order $S$ in nanotube-PDMS composite reaches as high as $S_{\text{stretched}}=0.29$ from an unstretched value of $S_{\text{unstretched}}=0.005$. Although the change in order is large, these values are $\sim$4–5 times smaller than present work suggesting true LC actuators presented here [12]. Therefore, we believe that the order parameters of the stretched composites in our case should also further increase as high as $S_{\text{stretched}}=0.7$–0.8 from a starting unstretched value of $S_{\text{unstretched}}=0.5$. Maximum energy conversion efficiencies of $\sim$0.0045% was measured All these observations show that as we stretch the composites, the self-assembled nanotubes should undergo further ordering in the direction of strain. Parallel and perpendicular autocorrelation (figure S1 suppl.) from 0% strain to 92% strain suggest the domain size increase along y (direction of strain) while decrease along the x-
direction suggesting change in bundle size and orientation of the nanotube within the domain. This deformation of the individual domains suggests localized change in distance between nanotube bundles and increase in order in direction of strain in the viscoelastic PDMS matrix. This change in microscopic order of nanotube LC domains coupled with rubbery elasticity of the matrix should result in large contraction when excited by NIR light and thus a unique actuation mechanism.

Figure 12 presents the nanotube mass fractions comparing our layered LC photo-mechanical actuators to all other nanocomposite photomechanical actuators employing nanotubes and polymers and reported till date in this area [12, 13, 15, 16, 30, 31]. Past reported nanotube/graphene based nanocomposite photomechanical actuators have used anywhere from \(\sim 0.02\) wt.% to \(\sim 7\) wt.% of nanotubes and 0–5 wt.% of graphene in PDMS respectively [12, 13, 15, 16, 30, 31]. These are randomly oriented nanotube/graphene mixed inside the polymers as nanocomposites and do not show any optical anisotropy. Even after stretching no LC ordering was seen in the past actuators. The mass of CNT used in these past actuators for the wt.% mentioned above correspond to \(\sim 22\) μg–1100 μg of nanotube/graphene used to prepare the composites [12, 13, 16, 30, 31]. Compared to that the present LC films reported here use only \(\sim 0.07–3.31\) μg of CNT mass which is \(\sim 100–10,000\) times smaller. Our actuator is a laminate with two layers of PDMS in between self-assembled nanotube LC layer. So while this is different design from a nanocomposite, the amount of high quality nanotube used is significantly smaller for the same response. 1 mg >99% purity nanotubes in100 ml solution today costs \(\sim 799\). Only 1 ml of stock solution is used to prepare these films. We have been able to make 100 films (30–35 mm using anodisc membrane) using the 100 ml stock solution. Each LC film resulted in 5–10 actuators of the size mentioned. Therefore, one can make anywhere between 500–1000 actuators, which costs anywhere between \(\sim 0.8–1.50\) approximately. Since there is no additional processing for aligning the nanotubes, these films may be highly useful for applications such as thin film transistors with high electron mobility [32] and nanopositioning systems utilizing nanotube/graphene photomechanical actuators at low cost [33].

3. Discussion

This work presents novel composite system consisting of nanotube LCs in elastomers and their performance as light driven actuators. The work combines the anisotropic properties of LCs with flexibility of elastomers which has been the approach for photo-chromic actuators in the past [34]. Our work also demonstrates the use of ultra-small amounts of nanotubes to achieve a large mechanical response compared to past reported actuators in this area till date [12, 13, 16, 30, 31]. The transfer process and the ability to
define composites with specific order parameters and relate them to concentration, elastic modulus and photomechanical response could be useful for making standardized nanotube composites based on LCs. Lack of standard processing techniques of carbon nanotube composites have hindered commercialization and the present work shows a novel pathway consisting of simple and low cost vacuum filtration followed by transfer process which preserves the orientation of the LC. The present work could also be of significant interest to electro-mechanical actuation technologies and creating artificial muscles with other polymers employing our processing technique, where high anisotropic SWNT conductivity and percolation pathways are preferred [14]. In the past, large amounts of SWNT was required (almost 0.1–18% w/w in nanofl of randomly oriented HiPco nanotubes [14]) to achieve high conductivity and subsequent electro-mechanical actuation (macroscopic response of 4.5 mm at 18% w/w SWNT) [14]. This makes them prohibitively expensive. Compared to this, our nanotube LC actuators use four orders of magnitude small mass fractions of nanotube. Electro-mechanical actuators and energy conversion devices based on low mass fractions using nanotube LCs could pave the way for commercial development. It is seen that with increasing concentration, the domain size decreases and use of polarization microscopy to image dichroic nanotubes is convenient for creating map of domain size and their counts. In this case, the domain size indicates the size of the aligned carbon nanotubes against a specific director. These domains might be highly interesting in studies concerning strains in composites and their non-destructive evaluation based on polarization microscopy. Manufacturing nanotube LC composites with specific order could also mean specific physical properties thereby enabling standardization of nanotube-polymer composite manufacturing processes.

Figure 9. Disordered versus ordered systems. (a) SEM image of randomly oriented film (~0.5 μg ml⁻¹ concentration); (b) SEM image of LC nanotube film (~0.5 μg ml⁻¹ concentration with order parameter S = 0.6); (c) photomechanical stress change for randomly oriented film based actuator; (d) photomechanical stress change for LC film based actuator.
Eliminating process complexities such as acid treatment and functionalization of nanotubes in polymer composites thus makes our process environmentally benign. It may be possible that structural laminates based on epoxies could use LC nanotubes as fillers enabling super strong composites with order dependent mechanical properties.

Commercial polymers such as polyvinylidene fluoride (PVDF) have calculated opto-mechanical conversion factor $(\eta_{m})$ of $\sim 97$ kPa W$^{-1}$ is five times smaller than the value of $\sim 0.5$ MPa W$^{-1}$ reported for nanotube-LC actuators [13]. Further, the energy conversion efficiencies were $\sim 50$ times lower ($8.5 \times 10^{-5}$% for PVDF versus 0.0045% for nanotube-LC) compared to PVDF [28]. Polymers containing cinnamic groups were reported to be deformed and fixed into predetermined shapes such as elongated films and tubes, arches or spirals by ultraviolet light illumination [35]. However, they can only be recovered to their original shape by irradiating UV light of different wavelength for 60 min [35]. Compared to this the nanotube LC actuators relax to their original configuration after light is switched off and are thus reversible. The strain dependent energy conversion would also be useful in energy scavenging using vibrational effects. Nanotube LC actuators as presented here show optical anisotropy, unique photomechanical response and tunable energy conversion in one system making this important for smart applications.

4. Materials and methods

4.1. General setup

Semiconducting SWNT (also called IsoNanotubes-STM) and HiPCo SWNT was purchased from NanoIntegris, and used without any further modification. Sodium dodecyl benzene sulfonate (NaDDBs) was purchased from Sigma Aldrich Company. WhatmanR Anodisc 47 inorganic filter membrane was purchased from VWR Scientific International. Fisherbrand 75 mm x 50 mm glass slides were used extensively for fabricating the LC-CNT PDMS composites. An 808 nm NIR laser of $\sim 160$ mW served as the illumination source. All experiments were conducted in a climate-controlled laboratory. Test equipment was operated inside a light-isolated enclosure mounted on an active-air suspension table. Webcams inside the testing enclosure were continuously monitored to ensure all control gear operated properly.

4.2. Sample preparation

IsoNanotubes in aqueous solution (1 mg in 100 ml) was prepared by mixing pre-determined volume of nanotube stock solution ($\sim 0.1$ ml) with known volume of surfactant sodium dodecyl benzene sulfonate ($\sim 14.9$ ml). Then DI water is added ($\sim 85$ ml) to make the entire contents to 100 ml. The
volume of nanotube stock solution and the surfactant is changed to make the five different nanotube solutions with concentrations namely \( \sim 0.01 \, \mu\text{g ml}^{-1} \), \( \sim 0.05 \, \mu\text{g ml}^{-1} \), \( \sim 0.1 \, \mu\text{g ml}^{-1} \), \( \sim 0.3 \, \mu\text{g ml}^{-1} \), and \( \sim 0.5 \, \mu\text{g ml}^{-1} \) respectively. Then the contents are ultrasonically agitated for 4 h. The separated nanotubes well coated with NaDDBS is then filtered using vacuum filtration. WhatmanR Anodisc 47 inorganic filter membrane is used as filter for collecting the nanotube LCs films. PDMS silicone elastomer obtained from Dow Corning (Sylgard 184) was used as the host matrix. PDMS is a two-part solvent-free flexible silicone organic polymer in the form of a base compound with a separate hydrosilane curing agent that acts as a cross-linker. A cross-linker was added at a ratio of 1:10 and mixed for 5 min to remove trapped air pockets, the prepared polymers were degassed for 30 min Small amounts of liquid polymer mixtures were deposited on the glass slides. A standard spin coating process at 750 rpm for 90 s successfully produced nominally \( \sim 75 \, \mu\text{m} \) thick films. High temperature curing at 125 C for 20 min was employed to finish the cross-linking process in the polymer. The nanotube-LCs on the filter membrane is then transferred to the PDMS layer by gently pressing the nanotube layer on the PDMS for 5 min and peeling the filter off. Then a second PDMS layer is then spun coat at 750 rpm for 90s. A final high temperature curing at 125 C for 20 min is employed to finish the cross-linking process of the second PDMS layer. The samples are then allowed to relax for 12 h at room temperature. The sample are then cut to 25 mm (L) \times 3 mm (W) strip, and test area is to 20 mm (L) \times 3 mm (W) (5 mm is used for clamp). The thickness of the sample is \( \sim 150 \, \mu\text{m} \) (two PDMS layer with nanotube-LC layer in between).

### 4.3. Stress test experimentation

PDMS composite test samples were mounted vertically between two clamps. The bottom clamp was attached to a weighted (\( \sim 68.6 \, \text{g} \)) base and placed on a high accuracy balance (Acculab ALC-80.4). The upper clamp was attached to an automated linear actuator that was in turn mounted to a
high accuracy manual positioning stage. The laser diode was placed ∼75 mm from the middle of the test strip such that illumination impacted normal to the PDMS surface. Deformation in the composite strips as a result of NIR illumination caused a change in weight readings on the balance. Once the light was turned off, both the actuator and balance returned to their original length/reading, respectively. Actuation was quite repeatable from cycle to cycle with nearly the same displacement amplitude. Stress test standardization was accomplished by finding the zero strain value of each sample and zeroing the balance. Stress test on each sample was conducted with pre-strain values ranging from 3% to 50%. The timing sequence for each pre-strain value was 1 min relaxation wait followed by five cycles of NIR illumination on for 60 s, and then off for 30 s. Engineering stress calculations (referred to as stress throughout the paper) were made by dividing the change in force between illumination on and off by the cross-sectional area of the test samples.

4.4. Polarized optical microscopy

Olympus IX-71 Inverted Research Microscope with PixeLink Camera (3.0 MP) was used for the polarized image analysis. All the specimens were brought to focus in the bright field (BF) observation (with no optical element engaged in the light path). IX2-AN polarizer was then employed for polarized light observation. Rotational polarization was done by rotating the polarizer knob t horizontally to get a different angle polarization light (0° and 5°). The characteristic of the domain configuration in the composite strips as a result of NIR illumination was obtained by the cross-sectional area of the test samples.

4.5. Stress–strain testing

Stress versus strain tests were conducted by Rheometric System Analyzer (RSA-3, TA instruments-Waters LLC) at the room temperature. Multiple extension mode was selected and four zones of separate extension test were performed. The zone time was set at 20 s, 10 s, 30 s and 20 s while the extension rate was set at 0.05 mm s⁻¹, 0 mm s⁻¹, 0 mm s⁻¹ and −0.05 mm s⁻¹ separately, typical for viscoelastic polymers. Stress and strain curve was then plot by Igor and the exponential curve fitting was performed to calculate the elastic modulus (E).

4.6. Scanning electron microscopy

Microscopic characterization was conducted using a Zeiss SUPRA 35VP field emission scanning electron microscope. All the specimens were observed under InLens Detector (WD 3 mm optimal) with 10.0 kV accelerating voltage.

4.7. Optical-to-mechanical energy conversion factor and conversion efficiency

\[ P_{\text{absorbed}} = P_{\text{uninterrupted}} \cdot P_{\text{sample}}, \]
\[ W_{\text{actuation}} = \left[ \Delta \sigma / \text{A cross-section} \right] \times d, \]
\[ E_{\text{absorbed}} = P_{\text{absorbed}} \times t, \]

opto–mechanical factor \( \eta_m = \Delta \sigma_{\text{total}} / P_{\text{absorbed}}, \)
energy conversion efficiency \( \eta = W_{\text{actuation}} / E_{\text{absorbed}}. \)

Newport 1918-C power-meter was employed to measure the power absorbed in the sample. Initially the uninterrupted laser power was measured. Next, LC-CNT composite test sample was mounted in front of the power meter and a value of \( P_{\text{sample}} \) was measured. The difference between \( P_{\text{uninterrupted}} \) and \( P_{\text{sample}} \) gives the actual power absorbed by the sample. The optical-to-mechanical energy conversion factor \( (\eta_m) \) is calculated by dividing the total change in engineering stress \( (\Delta \sigma_{\text{total}}) \) from maximum expansion to maximum contraction by the \( P_{\text{absorbed}}. \) Furthermore, \( W_{\text{actuation}} \) is the work done was calculated by photomechanical stress \( \sigma \) multiplied by \( A_{\text{cross-section}} \) and deformation \( d. \) The total absorbed energy \( E_{\text{absorbed}} \) was obtained by the \( P_{\text{absorbed}} \) multiplied by time \( t \) (in this experiment 60 s).

4.8. Optical characterization of order parameters using dichroic ratio

Carbon nanotube film was transferred to a glass substrate. The film was imaged by SEM (Zeiss Supra 35VP) and optical polarization microscopy. For optical polarization microscopy, an Olympus IX71 microscope was fitted with polarizer and analyzer. The sample was illuminated with a white light source. The objective used was 60×, 0.90 NA. Beyond the output polarizer, a 200 mm focal length lens projected the image directly onto a CMOS camera sensor (Pixelink PL-B776F) mounted 1.2 m from the lens. The polarizer and analyzer were both rotated to the vertical direction of the camera sensor. The parallel configuration of the polarizers was verified by rotating the analyzer to maximize the mean intensity recorded at the camera sensor. Images were recorded of the sample \( (I) \), empty glass substrate \( (I_o) \), and with the light source obstructed \( (I_{\text{dark}}) \). Polarizer and analyzer were both rotated 90° and the same measurements were repeated. Absorbance is then calculated using the formula given in the text.

Acknowledgments

BP acknowledges funding from NSF grants ECCS 1202190, CMMI 1233996 and DMR 1410678. XF and BK acknowledge Grosscurth Graduate Fellowship at the University of Louisville. The authors thank Dr Roger Bradshaw for DMA equipment support.

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SUPPLEMENTARY DOCUMENTATION

Nanotube LC Elastomers: Photomechanical Response and Flexible Energy Conversion of Layered Polymer Composites

Table S1: Order parameter of super purified randomly oriented carbon nanotube versus LC nanotubes for the same concentration.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Order Parameter S of Super Purified (HiPco) randomly oriented nanotube (~0.5 μg/ml) $S_{FFT}$</th>
<th>Order Parameter S of Liquid Crystal Nanotube Film (~0.5 μg/ml) $S_{FFT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.06832</td>
<td>0.82123</td>
</tr>
<tr>
<td>2</td>
<td>0.15643</td>
<td>0.77956</td>
</tr>
<tr>
<td>3</td>
<td>0.24491</td>
<td>0.87968</td>
</tr>
<tr>
<td>4</td>
<td>0.06241</td>
<td>0.85713</td>
</tr>
<tr>
<td>5</td>
<td>0.12722</td>
<td>0.78383</td>
</tr>
<tr>
<td>Average</td>
<td>0.13186</td>
<td>0.82429</td>
</tr>
</tbody>
</table>
Figure S1: Parallel and Perpendicular Autocorrelation from 0% strain to 92% strain suggesting the domain size increases along y (direction of strain) while decreasing along the x-direction. The ratio of the maximum FWHM to the minimum FWHM also called anisotropy increases with strain. The anisotropy ratio and the insert shows this ratio increasing as the strain increases. This suggests increase in order parameters with strain.