

## Nematic elastomers with aligned carbon nanotubes: New electromechanical actuators

S. COURTY, J. MINE, A. R. TAJBAKHSH and E. M. TARENTJEV

*Cavendish Laboratory, University of Cambridge - Cambridge CB3 0HE, UK*

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**Abstract.** – We demonstrate, for the first time, the large electromechanical response in nematic liquid-crystalline elastomers filled with a very low ( $\sim 0.01\%$ ) concentration of carbon nanotubes, aligned along the nematic director at preparation. The nanotubes create a very large effective dielectric anisotropy of the composite. Their local field-induced torque is transmitted to the rubber elastic network and is registered as the exerted uniaxial stress of order  $\sim 1$  kPa in response to a constant field of order  $\sim 1$  MV/m. We investigate the dependence of the effect on field strength, nanotube concentration and reproducibility under multiple field-on and -off cycles. The results indicate the potential of the nanotube-nematic elastomer composites as electrically driven actuators.

*Introduction.* – The direct conversion of electrical energy to mechanical work through a material response is critically important for a great number of applications ranging from robotics and microscopic pumps/valves, to biological muscle replacements. Over the years, different kinds of actuators have been developed, with a very broad range of characteristics of generated stress and stroke, as well as the mechanism of actuation [1].

Liquid-crystalline elastomers [2] have only recently entered the actuator arena; with strains of up to 3-400% and characteristic stress of up to 1 MPa, nematic elastomers offer a range of new engineering possibilities. In all cases studied so far, the mechanism of actuation, represented as spontaneous uniaxial extension/contraction of the nematic rubber along the director axis, has been the coupling of the elastic network to the underlying nematic order parameter  $Q$ , see [2] for details. Changing the order can be achieved by heating the material, leading to thermal actuators [3–5], by light in photochromic materials [6, 7], or by other means such as dilution by solvents. Electrically driven actuation in nematic elastomers has so far been impossible, for a very simple reason. Assuming the electric field  $E$  interacts with a dielectrically anisotropic nematic medium, causing the director to rotate, the characteristic energy density could be estimated as  $\sim \varepsilon_0 \Delta\varepsilon E^2$  [8]. For a field  $E \sim 10^6$  V/m and typical dielectric parameters of nematic liquid crystals, this gives a density of  $\sim 10^3$  J/m<sup>3</sup>. The rubbery elastic network resists any such rotation with a characteristic energy density of the order of rubber modulus  $\mu \sim 10^5$  J/m<sup>3</sup> or higher; clearly, no effect could be expected. In this paper we propose a new approach to this problem, in essence, producing a composite material with an effective dielectric anisotropy many orders of magnitude higher than in usual liquid crystals. We achieve this by embedding a low concentration of carbon nanotubes, aligned along the uniaxial director of a monodomain nematic elastomer network. As a result, we demonstrate a significant electromechanical response and study its basic properties.

Since their discovery by Iijima in 1991 [9], carbon nanotubes (CNTs), representing the fourth allotrope of carbon, after diamond, graphite and fullerene, have been the subject of a great number of studies in all imaginable walks of science. Not going into detail of this field, very well covered in the literature [10, 11], we only need to emphasize the large mobility of  $\pi$ -electrons along the cylinder axis, leading to an extremely high anisotropy of polarizability. The mechanical strength and toughness of CNTs, especially their multiwall variety, have been much celebrated in the literature too, with a Young modulus of  $\sim 1$  TPa and surviving elastic bending by up to  $70^\circ$ . CNTs have been demonstrated to act as thermally, chemically or electrically driven actuators on their own [12, 13], individually or in macroscopic sheets and bundles [14]. An interesting early report of mechanical actuation of an isotropic CNT-polymer composite on changing of temperature [15] echoes much of our work reported here. However, we aim at the electrical stimulation and explore the “internal degree of freedom” end of this problem, using multiwall CNTs as passive enhancers of the natural dielectric anisotropy of a nematic rubber shape-memory actuator.

The effective utilization of CNTs in polymer composite applications depends strongly on the ability to homogeneously disperse them throughout a polymer matrix without destroying their integrity [16]. Another key problem is the alignment in the polymer matrix. There are reports of alignment achieved by electric fields [17], confirming our expectation of high effective dielectric anisotropy. In our case, the nanotubes were dispersed at very low concentration in a gel network, which was uniaxially stretched and then crosslinked further, to freeze in the monodomain orientation of the nematic director. Naturally, the CNTs were aligned in this direction as well. After this preparation, the samples of nematic elastomer-CNT composite were subjected to a constant and an oscillating electric field perpendicular to the initial director/CNT alignment, fig. 1(a). As a result of strong dielectric torque on individual nanotubes, the whole polymer network structure experienced a significant mechanical shape change. In the fixed-length (isostrain) conditions, we registered an actuator force of sample contraction along the initial alignment axis.

*Materials and preparation.* – The side-chain polysiloxane nematic polymers and their elastomer networks, aligned in the uniaxial monodomain orientation, were prepared in the Cavendish Laboratory following the procedure pioneered by Finkelmann [2, 18]. The polysiloxane backbone chains ( $\sim 60$  monomer units long) had the mesogenic rod-like groups 4-methoxyphenyl)-4'-buteneoxy benzoate (MBB) attached end-on and crosslinked using the two-functional 1,4-di-11-undeceneoxy benzene (11UB). The molar ratio 18 : 1 (or 9 : 1 for substituted groups on each chain) results in the 10% crosslinking density.

To separate CNTs from their solid aggregates, we initially stirred the aggregates in toluene, using alternating high-power sonication and mechanical stirrer at 2000 rpm for at least 24 hours. The sample was then transferred into the polymer reacting mixture and stirred for a further 4-6 hours. Finally, the crosslinking was initiated by adding the catalyst and heating to  $80^\circ\text{C}$ . The subsequent procedure of two-stage crosslinking [18], with an intermediate stretching, induces good director and CNT alignment. We prepared three samples from the same batch, with identical chemical composition and alignment, and with CNT concentration of 0, 0.0085 and 0.02 weight%. At such low amount of loading, shown by conductivity measurements to be well below the percolation limit,  $\sim 0.1\%$  [19], one should expect each nanotube to act on its own, embedded in a rubber elastic medium and providing a very strong local anchoring to the nematic director.

*Experimental details.* – The materials were characterized with differential scanning calorimetry and optical microscopy, confirming that no phase other than the nematic was present below the clearing point  $T_c \approx 100^\circ\text{C}$ . The spontaneous uniaxial thermal expansion

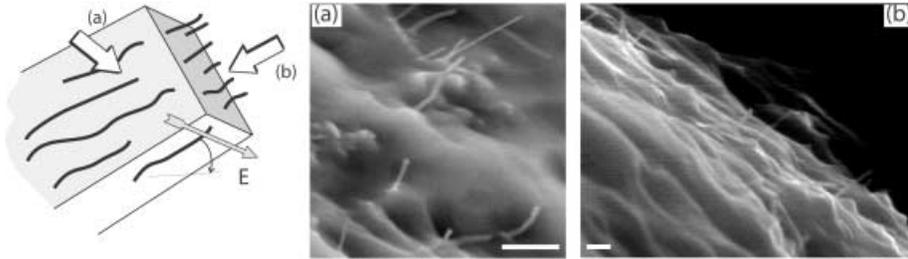


Fig. 1 – The sketch of a plane strip of nematic elastomer with embedded aligned CNTs. Applying electric field  $E$  across the sample causes a local torque and a small nanotube rotation. The arrows indicate two planes of freeze-fracture, shown in electron microscopy images of 0.02% CNT sample: (a) in the plane parallel to the nematic director and the nanotube alignment axis, viewed from the top; (b) in the plane perpendicular to this axis, viewed edge-on. The scale bar in both images is  $0.5 \mu\text{m}$ .

measurements were performed with a travelling microscope focused on a sample heated in the glass-fronted oven.

All mechanical measurements were carried out at a fixed temperature of  $24^\circ\text{C}$  ( $\pm 0.3^\circ$ ), sufficiently far from the glass, or nematic-isotropic transition points. The dynamometer setup measured the force exerted in extension, with the accuracy  $\pm 4 \cdot 10^{-5} \text{ N}$  ( $\pm 0.4 \text{ mg}$ ). The rectangular samples ( $\sim 7 \times 15 \times 0.4 \text{ mm}$ ) were mounted with insulating plastic clamps, without any pre-stress, and not allowed to change shape during the force-actuation experiments. The tensile stress was calculated as the force divided by the fixed cross-section area. The electric field was generated between two aluminium plates separated by  $1.56 \text{ mm}$  and surrounding the flat strip of clamped elastomer sample, with no contact. With this setup, in order to generate a substantial electric field, we needed a high voltage (we used up to  $3500 \text{ V}$ ) and so safety against discharges was ensured by additional electronic circuits.

*Sample structure.* – The presence of CNTs in the rubbery network can be immediately seen by the color of the otherwise transparent material. At  $0.0085\%$  loading the elastomer is lightly grey and at  $0.02\%$  the material is dark grey and nearly opaque. Other samples, at much higher nanotube loading, were completely black. We do not present studies of these materials here because we could not verify the quality of dispersing or the alignment of CNTs at higher concentrations. Figure 1 shows the scanning electron microscopy (SEM) images of freeze-fractured composite samples. Note that SEM-imaging of nanotubes embedded in an insulating polymer matrix is a challenge: traditional methods of gold-coating to prevent surface charging would mask the nanotubes; the alternatives include lower energies and the atmosphere for ionic cascades—all resulting to strictly surface imaging and lower resolution. Two fractured planes shown in fig. 1(a,b) illustrate the low CNT concentration and their good alignment. Image (b) shows several nanotubes protruding perpendicularly out of the fracture surface, while image (a) gives an opportunity to see a few nanotubes that showed out of the fractured polymer surface, nearly parallel or at a small angle to it.

It is interesting to see the effect of low-concentration highly anisotropic aligned filler on the nematic behavior of elastomer network. Figure 2(a) shows “classical” thermal expansion measurements (the thermal actuation of nematic rubbers), making comparison between the pure and the nanocomposite samples. Clearly, the qualitative behavior is not changed, with a constant sample length in the isotropic phase and a rapid elongation in the nematic phase. This transition is frequently reported in the literature as a diffuse increase, while we see a nearly critical response: in fact, both curves in fig. 2(a) are fitted with the same law  $L/L_0 - 1 =$

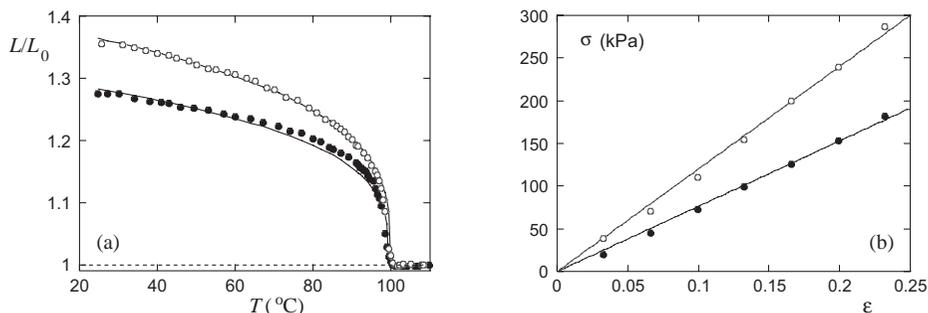


Fig. 2 – (a) Uniaxial thermal expansion of nematic elastomers: the comparison between the pure network ( $\bullet$ ) and the 0.02% CNT composite ( $\circ$ ). The solid lines are the critical fit described in the text. (b) Equilibrium stress-strain variation on uniaxial extension  $\varepsilon = \Delta L/L$  along the director (and CNT alignment) axis, for the pure network ( $\circ$ ) and the 0.02% CNT composite ( $\bullet$ ). A linear fit provides the Young moduli  $Y_0 \approx 0.76$  MPa and  $Y_{\text{CNT}} \approx 1.2$  MPa.

$C(1 - T/T_c)^{0.29}$ . Surprisingly, and unexpectedly to us, the overall expansion/contraction magnitude (measured by the constant  $C$  in the above fit) was lower for the aligned CNT composite elastomer. Since the nanotubes provide local sources of extra alignment, we cannot attribute this to a reduction in nematic order due to added impurities (in fact, their effect is probably minor since the transition temperature has hardly changed). Our explanation for the reduction in overall thermal expansion is based on the assumption that nanotubes, which remain rigid and aligned while embedded in the rubbery network, prevent the latter from excessive shape changes along the alignment axis. Clearly, this conclusion is only preliminary and the phenomenon has to be investigated further, with varying concentration and length of CNTs, as well as the natural capacity for expansion of the network. One cannot exclude a possibility of rigid CNTs locally rupturing the network, if its polymer chains are too highly anisotropic; this was not the case in our studies because all reported effects were reproducible after many cycles of temperature, or later —electric field.

The important characteristic of any rubber elastic material is its modulus. For a uniaxial nematic elastomer one may find it difficult to identify a single value for the rubber modulus: the matters of so-called “soft elasticity” form a central part of their unique mechanical properties [2]. However, for our main experiments we need the particular geometry of uniaxial extension along the axis of director (and CNTs) alignment. Figure 2(b) shows that the linear stress-strain regime persists up to strain of at least 25% and thus the linear (Young) modulus can be unambiguously defined. Clearly the presence of aligned CNTs makes the polymer composite stiffer. At the low concentrations we are working at, the Young modulus remains within the same order of magnitude,  $Y \sim 1$  MPa.

*Electromechanical response.* – The samples, mounted on an insulating (thermally and electrically) frame which keeps the natural length of the sample fixed but measures the contractile force exerted on the clamps, were subjected to a constant electric field perpendicular to the initial director (and CNT) orientation. With the applied voltage of 3000 V, the field was  $E \approx 1.9 \cdot 10^6$  V/m. Figure 3(a) shows a typical sequence of “field-on” and “field-off” cycles applied in a successive 1-hour sequence, demonstrating the dependence of actuation stress on the elapsed time. The response is clearly significant. The on-cycle shows an immediate step rise in exerted stress, which then reaches a plateau level  $\sigma_{\text{max}}$  that depends on CNT concentration as well as the field strength; the latter is illustrated in fig. 3(b). There is no electromechanical response in the elastomer without nanotubes, which confirms our estimates

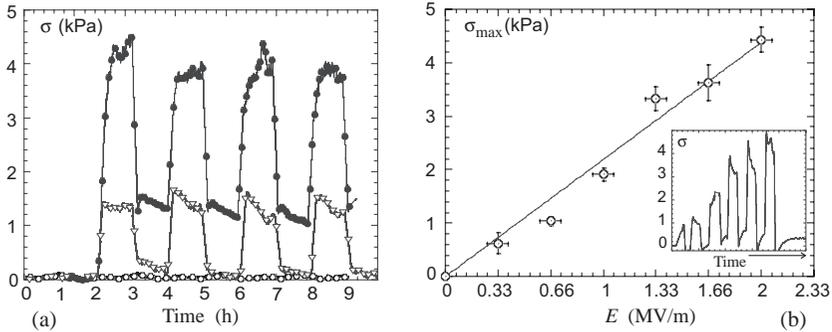


Fig. 3 – (a) Field cycles ( $E \approx 1.9$  MV/m), for samples with increasing CNT concentration: 0% (non-filled elastomer ( $\circ$ )), 0.0085% ( $\nabla$ ) and 0.02% ( $\bullet$ ). (b) Dependence of the plateau stress  $\sigma_{\max}$  on the applied field strength, for the 0.02% composite sample. The inset shows the elapsed time dependence, with each cycle at increasing constant field  $E$ . The linear fit gives  $\sigma_{\max}(\text{kPa}) = 2.3E(\text{MV/m})$ .

about the relative strength of dielectric and elastic torques.

The mechanism of the electromechanical response seems to be clear: the highly polarisable nanotubes experience a high torque to rotate towards the direction of constant field, proportional to  $\Delta\epsilon_{\text{CNT}}E^2$ . Nanotubes respond, and take the elastic network with them, causing the measurable stress on the clamped sample. It is possible that, at high enough field, the nanotubes would rupture the local polymer network in their vicinity. In our case the actual rotation of CNTs is small, which is indicated by the field dependence of plateau stress  $\sigma_{\max}$ , fig. 3(b). If a full  $90^\circ$ -rotation was achieved one would see a plateau, whereas the linear increase  $\sigma_{\max} = \text{const} \cdot E$  clearly indicates the regime of “small fields”.

The fact that the stress on the off-cycle does not quite return to the initial zero level is an indication of how much we do not understand about the underlying mechanism. This feature is unambiguously reproduced for the 0.02% sample, as the response at each cycle reaches the same maximum level and falls down to the same non-zero level when the field is off, thus confirming that no sample degradation occurs. (The fact that we see no such effect for the 0.0085% sample could be simply due to the overall lower amplitudes —or possibly due to the cooperative effects of CNT motion showing more prominently at their higher loading.) A possible explanation is that, after spending an hour in the strained state with the field on, in the  $E$ -off state the viscoelastic polymer network has a very slow relaxation mode and takes a much longer time to return to its initial equilibrium (with zero stress).

An important feature of any actuator is the reproducibility and the speed of its response. Figure 4 demonstrates the effect, for the 0.02% composite, under a field of  $1.9 \cdot 10^6$  V/m (as in fig. 3(a)) switching on and off every 30 seconds. Clearly, the stress responds very fast, to both “on” and “off” cycles. The initial spike at each cycle is an artefact of our power supply electronics that produces a voltage surge before settling at the required constant value. Both the short-time and the long-time representations in plots (a) and (b) illustrate a good reproducibility of response speed and the plateau stress amplitude  $\sigma_{\max}$ . This is practically useful for any actuator application.

*Conclusions.* – In this paper, for the first time, we have reported the observation of a significant electromechanical effect in liquid-crystal elastomer system filled with aligned carbon nanotubes. A question may reasonably be raised, whether a similar effect would be seen in an ordinary isotropic rubber if the embedded CNTs were similarly aligned. This is not a subject of our current work; here we focus on the nematic elastomer, where on the one

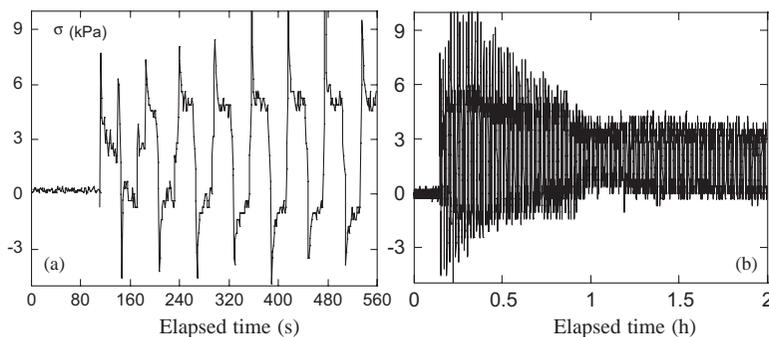


Fig. 4 – The response of 0.02% CNT composite to an alternating field, switching on and off every 30 seconds. The short initial period of this test, plot (a), illustrates the high speed of the stress response which closely follows the field spike produced by our power supply on both switching on and off. The long-time representation (b) cannot resolve each individual cycle, but demonstrates the overall stability of the response.

hand, the actuation is an established feature and, on the other, the electric stimulation is much sought after by analogy with low-molar-mass liquid crystals.

We used multiwall CNTs with no special purification, at very low concentration (below the percolation limit, so that samples remain electrically insulating). The presumed mechanism of the response is the very large anisotropy of polarizability of CNTs, which results in a high local torque when an electric field perpendicular to their equilibrium orientation is applied to the sample. Small rotation of nanotubes is transmitted to the nematic elastomer network—even a small re-alignment of the director induced by the CNT rotation generates a uniaxial mechanical response of the whole sample, which we register as the actuation stress.

The response stress is demonstrated to follow a linear dependence on applied field, at least in the range of fields studied. This, in fact, is puzzling because if one assumes the angle of local CNT rotation,  $\theta$ , to be linearly proportional to the dielectric torque (which in turn is  $\propto \Delta\epsilon_{\text{CNT}}E^2$ ), then the uniaxial strain induced in the rubbery network along the initial director axis should be  $\propto (1 - \cos\theta) \propto \theta^2$ , which means the strain (or in the isostrain conditions of our experiments, the exerted stress  $\sigma_{\text{max}}$ ) could be expected to follow  $\propto E^4$ ; this is very clearly not the case.

Another difficulty we have is explaining the stress not returning to zero after the field is switched off. This is most likely a result of complex relaxation of polymer network with embedded CNTs, after spending a long time (1 hour in fig. 3) under the applied field. However, simply claiming the slow relaxation as the explanation of non-zero “off”-stress may not be enough: if the nanotubes start each following field-on cycle with a non-relaxed pre-tilt angle, one might expect the “on”-stress to increase. The results of Fig. 3 clearly demonstrate that this is not the case and that  $\sigma_{\text{max}}$  is a unique and reproducible function of applied field, but not the field application history. Note that in the fast-alternating field experiment on the same material under the same field, fig. 4, we see no residual stress in the field-off state. If anything, the “off”-stress is below zero during the first hour of testing, perhaps due to a reactive effect in the elastic network. Figure 4(b) shows that after the initial settling period, the response becomes very regular, returning to zero on every 30-second cycle.

We only studied composite materials with aligned CNTs at two low concentrations. The main difficulty in preparation of samples with higher loading was the CNT dispersal, which in our case was not fully successful at higher concentrations. One may not be able to exploit this electromechanical effect in this situation anyway because above the percolation threshold

(which is still very low,  $\sim 1\%$  for highly anisotropic multiwall CNTs) the composite would become a conductor.

Notwithstanding many shortcomings in our preparation techniques, sample characterization and our understanding of the underlying fundamental physical mechanisms, the effect of large electromechanical actuation is demonstrated unambiguously and its speed and reproducibility make it an attractive system for new applications. The uniaxial stress, of the order  $\sim 1$  kPa (or the corresponding strain of 0.1%, from the rubber modulus  $\mu \sim 1$  MPa), is induced by an electric field of the order  $\sim 1$  MV/m. There are many systems that generate higher stress, and strains well above 50% are common in nematic elastomers. However, the ability to produce a mechanical response by an electrical stimulus is invaluable for many practical applications. Carbon nanotubes provide such a capacity in liquid-crystal elastomers.

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