Fast Relaxation of Carbon Nanotubes in Polymer Composite Actuators

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Silicone elastomer composites containing multiwalled carbon nanotubes have been irradiated with near-infrared light to study their mechanical actuation response. We show that the speed of the stimulated response is faster than Debye relaxation, instead following a compressed-exponential law. However, the relaxation after switching off the light source follows the simple-exponential relaxation, as does the stimulated response at very low nanotube concentration. We discuss possible models and explanations to account for the fast photomechanical response.

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Carbon nanotube-polymer composites attract a lot of academic and commercial interest. Expectations of unusual material responses are borne out of the fundamentally unique nanotube characteristics that can be transferred to the bulk polymer material with spectacular effect [1–3]. Beyond the more traditional elastic modulus or conductivity enhancements, a rich landscape of functional materials based on nanoscale units (of which carbon varieties are just one) is yet to be explored. Possible photoactuation mechanisms in nanotubes are still debated [4,5], while recent studies of other π-conjugated systems show that large conformational changes could be optically induced if a torque imbalance in the bonding structure is achieved [6].

Very little information is available on nanotube photomechanical behavior when embedded in a host polymer matrix, to a large degree because no noninvasive and nondestructive technique is available to monitor their state. Recent reports show that a polymer film can be made to mechanically deform under light when a small percentage of nanotubes is dispersed and aligned in the matrix [7]. The large photoelastic response of these nanocomposites can be fine-tuned by changing tube concentration and orientation, and leads to a new effect of equilibrium (two-way) actuation [8]. The results did not depend on the host matrix, suggesting that the nanotube filler units are indeed the origin of the observed actuation response. Photon absorption produced a response from the tubes, which directly translated into the macroscopic effect in an otherwise benign polymer system. This macroscopic response of the composite provides the possibility to conjecture the light-actuation properties of the nanotubes themselves and the fascinating physics therein.

In this Letter we report experimental investigations of the response kinetics and relaxation of such polymer nanocomposites under near-infrared (IR) illumination, and show that it is much faster than the canonical Debye (exponential) relaxation. On the other hand, the light-off relaxation is a decidedly classical simple-exponential process.

Multiwalled nanotubes (Nanostructured & Amorphous Materials, Inc., Houston, TX) were used with purity verified as >95% using scanning electron microscopy (SEM. The polymer matrix was polydimethylsiloxane (PDMS) (Sylgard 184$^{\mathrm{TM}}$ elastomer from Dow Corning, USA). In pristine condition this polymer crosslinks with a hydrosilane curing agent (supplied by Dow Corning), forming a uniform solvent-free elastomer. The PDMS matrix is an ideal polymer system for this study as it has a very low glass-transition temperature and displays linear elasticity over a broad range of temperatures and strains, therefore allowing one to study the connection between filler-particle excitations and the polymer-composite relaxation.

Sample fabrication is straightforward. We must flag the difficult issue of nanotube dispersion in polymers [9], which we cannot go into in detail in this short Letter. The commonly used surface modification (by oxidation or surfactants) is undesirable for us as it can alter the tube electronic properties [3]. Our tubes were not surface modified in any way. A viscous fluid containing measured nanotubes in PDMS was mixed in a high-shear laboratory mixer for a minimum of 24 h. Crosslinker was added to the mixture after 24 h. The sample was then further mixed for another 30 sec before being placed in vacuum for 5 min to degas. It was then deposited in a specially designed centrifuge reactor at 5000 rpm and 80 °C to crosslink homogeneous films of the composites. The tube dispersion was verified with SEM on freeze-fractured surfaces. Samples were identified by the wt % of nanotubes mixed with the PDMS: most experiments have been conducted with the 0, 0.02, 0.5, 1, 2, 3, and 7 wt % nanotube loading. In all cases the sample dimensions were kept approximately the same, 30×1.5 mm, with the film thickness 0.2 mm. For comparison, a sample with 3 wt % carbon black, instead of nanotubes, has also been made using identical procedures. Parameters of semiflexible nanotubes (length $\sim 10\ \mu$m, diameter ~ 80 nm, and persistence length $\geq 0.5\ \mu$m) indicate that the overlap concentration (equivalent to the percolation threshold) in our case is $\phi_c \sim 0.5$ wt % [9].

Experiments were conducted with the dynamometer (Pioden Controls Ltd) housed in a custom made thermal-control box with an open front. Distance between the clamps was controlled using a micrometer with ±0.001 mm accuracy. The rig was calibrated with weights to give a measure of stress and (fixed) strain. The cold light source (Schott KL1500 LCD) was positioned ~20 mm from the sample. The peak power density, at 675 nm, was determined as 1.5 $\mathrm{mW/cm^2}$ at this distance.

To standardize the results across all samples, preliminary checks were undertaken to accurately find the zero-strain natural length L_0, for every experimental run. The imposed fixed extensional strain was calculated as $\varepsilon = (L - L_0)/L_0$, with L provided by the micrometer reading. After such a fixed prestrain was applied to each sample, readings of stress were taken for 1 min to verify that the material was equilibrated in its prestrained state, and then the shutter allowed the light at full intensity. After a period of exposure, the light source was shut off and further relaxation data collected. We verified that the effects we observe are not an artefact of the overall light-induced heating by conducting separate experiments with the samples heated to a comparable temperature without any light.

Figure 1 shows key features of the photomechanical actuation response: the step of stress, $\Delta\sigma$ as a function of time, upon switching on the cold light source (at $t = 40$ s), in the isostrain configuration. Positive and negative values of actuation stress indicate the contraction and expansion of the natural length L_0, respectively. The change of the response magnitude and its direction has been firmly associated with the degree of nanotube alignment in the elastomer matrix [7,8]. We find the nonaligned composites expanding their length, while a large uniaxial contraction occurs in the well-aligned state. Wide angle x-ray scattering proves the increasing nanotube orientation in a rubbery matrix, induced by the applied uniaxial stress [10]. Having mapped the tube orientational order on the applied prestrain ε [8], we plot the magnitude of maximum (saturation) stress $\Delta\sigma_{\max}$ against prestrain in Fig. 1(b). In this range of strains, the induced orientational order parameter of nanotubes changes between 0 and ~0.2, with the crossover at ~0.06. The same crossover from expansive to contractive behavior, occurring at $\varepsilon_c \sim 10\%$, was observed for samples with all nanotube concentrations (and in all studied host polymers); see [8] for detail. The same crossover actuation response is also observed for the 3 wt % carbon black in the PDMS sample, however, the magnitude of the effect in such a sample is far smaller in this case.

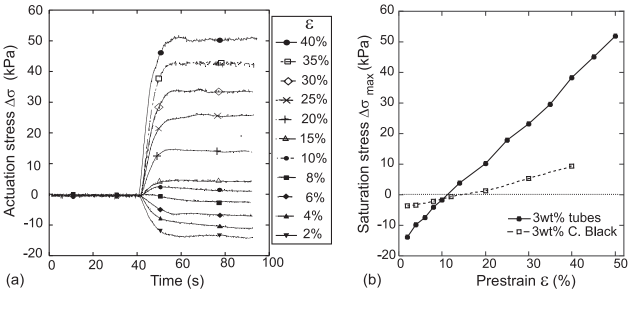

FIG. 1. (a) Typical light-induced stress at different prestrains (ε, labeled on plot), corresponding to the increasing tube alignment. The data for a PDMS sample with 3 wt % nanotubes. (b) The dependence of saturation stress $\Delta\sigma_{\max}$ on the degree of tube alignment, represented here by the applied prestrain ε. Data for a PDMS sample containing 3 wt % carbon black is also presented for comparison.

All studied nanocomposites display a photomechanical response, with the highest amplitude when the tubes are better aligned in the rubbery matrix. In spite of several reports in the literature, there is no clear model of this physical effect. The analysis of tube orientational distribution allows to account for the bimodal actuation and the crossover prestrain ε_c [8], however, we do not know what happens at the microscopic level, when nanotubes embedded in the matrix absorb low-energy infrared photons. In order to reproduce the observed macroscopic photoactuation of the composites, the orientational-averaging model must assume that the individual tube contracts by ~20%, while conserving local volume in its vicinity [8]. Such a large overall contraction cannot be accounted for by lattice strains of tube shells and suggests crumpling of nanotubes. Such instability could be caused by, e.g., polaron excitations leading to high local defect density and generating kinks on originally straight tube segments [11,12]. A different mechanism based on photoinduced charge transfer [4,13,14] has been suggested to account for percolation in concentration, and also the decline in the actuation at very high tube loading, over 10 wt %.

In order to study the kinetics of this response, and the relaxation when switching the light on or off, we shall examine the normalized stress, $\Delta\sigma/\sigma_{\max}$, as illustrated in Fig. 2. Figure 2(a) plots the normalized stress of the same representative 3 wt % PDMS nanocomposite for a range of prestrains ε. The time axis is shifted so that the photomechanical response starts at $t = 0$ s (light on) and reaches saturation at $t \sim 10$–15 s. Actuation becomes marginally quicker as prestrain ε (and tube orientational ordering) increases, however, the different sets of data are very close to each other in spite of the large difference in actual response between, e.g., 2% and 40% prestrain in Fig. 1(a). The simultaneously measured change in sample

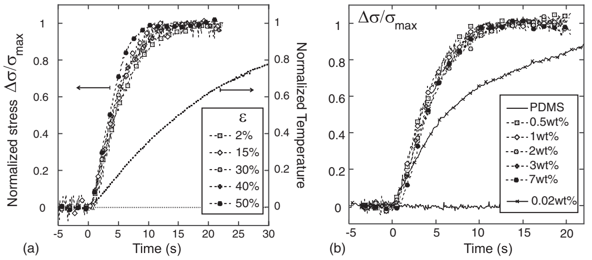

FIG. 2. Normalized stress, $\Delta\sigma/\sigma_{\max}$ vs time, which allows comparison of the response kinetics: (a) The light-on response of 3 wt % composite at different values of prestrain ε. The right y axis shows the simultaneously measured, similarly normalized, change in temperature on irradiation. (b) The light-on response of different composites, all measured at the same 20% prestrain.

temperature (also normalized, $\Delta T/T_{\max}$) is shown on the same plot to highlight the difference in the response speed.

The behavior is repeatable for all nanotube-polymer concentrations, as the results in Fig. 2(b) demonstrate. By using $\varepsilon = 20\%$ for all samples we ensure the nanotubes are relatively well aligned in the soft crosslinked elastomer matrix. For reference, Fig. 2(b) also presents the results for the pristine PDMS sample (as expected, no photomechanical response is observed) and the nanocomposite with very low tube concentration, 0.02 wt %. The notably slower response of this sample is in marked contrast to all other nanocomposites. This discrepancy will present the greatest difficulty when we attempt to offer an explanation for the observed effects. Apart from the lowest-concentration sample, the data in Fig. 2(b) strongly suggest that the photomechanical actuation kinetics remains independent of nanotube alignment and concentration (above the percolation threshold).

Examining the time dependence of the photoresponse, we fit the data with a compressed-exponential function $1 - \exp[-(t/\tau)^{\beta}]$. The quality of this fit, as well as the important comparison with the classical exponential behavior, are shown in Fig. 3. The two fitting parameters are the relaxation time, $\tau \approx 5$ s and the exponent $\beta \approx 2$. These values were obtained nearly the same for all aligned composites with nanotube concentrations above the percolating threshold. At this point we would like to focus on the main effect and disregard a weak dependence of τ and β on the applied prestrain, suggested by Fig. 2(a). Such a fast response of the system is a striking result and the main focus of this Letter. One must appreciate that the individual photomechanical response of a freestanding nanotube must proceed within a nanosecond time scale, if one assumes polaron excitation and relaxation [11]. The kinetics at the scale of our observations is certainly due to the rubbery matrix constraints. The polymer would usually be expected to follow the classical Debye relaxation ($\beta = 1$), if not slower due to the mode coupling and viscoelasticity. This is not the case in our experiments where the compressed exponent $\beta \approx 2$, with the characteristic time scale of ~13 s. Moreover, the fast cooperative response is reproduced in both expansive (unaligned) and contractive (aligned) modes of photoactuation, suggesting a unique underlying mechanism for the bimodal photomechanical actuation.

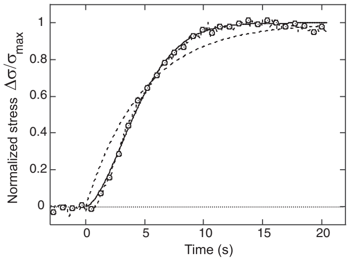

FIG. 3. Illustration of the data fit, for 3 wt % composite at 20% prestrain. Experimental data (○) is fitted by the compressed-exponential (solid line) and the simple-exponential (dashed line) functions to demonstrate the discrepancy.

When the light source is switched off, Fig. 4(a), all the nanocomposite materials in our range relax normally, following the classical $e^{-t/\tau}$ law with $\tau \approx 5$ s. The same normalized kinetics of the light-off relaxation is obtained at all different values of prestrain ε. As a more detailed comparison to the fast light-on response illustrated in Figs. 1–3, the plot in Fig. 4(b) shows results from an identical experiment conducted on PDMS samples with trace amounts of nanotubes (0.02 wt %) and also with 3 wt % carbon black. The response is evidently much slower in this case. Importantly, these curves superpose and also follow a simple-exponential fit, $1 - e^{-t/\tau}$, with $\tau \sim 10$ s here. Evidently, for the faster response to take place, nanotube (and not carbon black) concentration needs to remain above the percolating threshold.

Apart from the ideas based on the electronic structure of nanotubes, there is one more possibility to account for their large local deformation in a polymer matrix. A large (and fast) local tube heating is inevitable on photon absorption. In fact, there are reports of such an effect [5,15], presumably based on the incomplete reradiation of the absorbed energy. Assuming the polymer chains are highly aligned in the vicinity of nanotubes due to the boundary anchoring on their surface, the local heating should generate local contracting strain along the alignment axis. This is a classical thermodynamic effect of uniaxial contraction of a stretched rubber. Such a local strain could lead to an Euler buckling instability of a rigid nanotube embedded in the elastic matrix, which would account for many features of photoactuation.

Consider now the dynamics of such a response, assuming the relaxation process is controlled by the overdamped balance of an elastic force against viscous friction. To understand the fast response one must take the observed time dependence $x \sim \exp[-\alpha t^2]$, where $x(t)$ is the relevant strain variable, and work backwards to isolate the nature of the forces involved. Taking $\ln x = -\alpha t^2$ and differentiating,

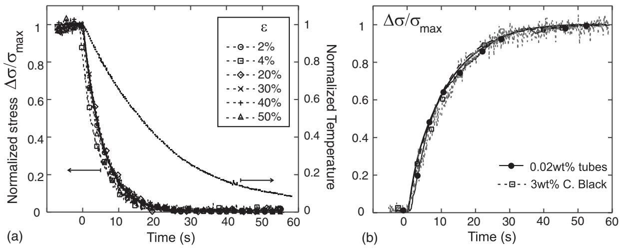

FIG. 4. (a) The normalized stress relaxation of a 3 wt % nanocomposite illuminated at different prestrain, when the light source is switched off. The right y axis shows the simultaneously measured, similarly normalized, change in temperature on irradiation. (b) The light-on response of the composite with very low tube loading, and also that of a sample with 3 wt % carbon black, both at $\varepsilon = 20\%$. The Debye relaxation is found in both cases, with the fit curve shown by the solid line in both plots.

one obtains the "kinetic equation" in the form $\dot{x} = -(2\alpha t)x$. The effective relaxation time has to be the ratio of the elastic modulus G to the viscous coefficient η, from the force balance $Gx + \eta\dot{x} = 0$. In order to generate the compressed exponential, this ratio $[G/\eta]$ has to be a linear function of time since the moment the light was switched on.

On sudden local heating, the equilibrium balance between the chain alignment and the boundary conditions on the tube surface is distorted: the entropy cost for chain stretching increases, resulting in a uniaxial contracting force exerted on the tube along its axis. The magnitude of this force, in the leading order, is a linear function of the local temperature increase $\Delta T = T(t) - T_0$. If the temperature increases, then the contracting force would increase as a function of time, too (initially—linearly with time). In small increments at $t \rightarrow 0$ we can write $G = g_0 t$ and the kinetic equation becomes $\dot{x} = -[g_0/\eta]tx$, exactly reproducing the results of our observations, with the effective relaxation time $\tau = \eta/g_0 t$. Of course, there are many complications to this simple model. For instance, the viscosity in the dissipating medium is also a function of temperature (in simplest terms, proportional to the Arrhenius activation, $\eta \propto e^{E/kT}$); this will introduce an additional time dependence $\eta \approx \eta_0(1 - at)$. The real viscoelasticity of a polymeric system would make all of these arguments much more involved. However, in the leading order, we would still expect to see the contraction dominated by the linear (or near-linear) time dependence of the local rubber modulus.

The fast compressed-exponential response was not found in the light-off relaxation, which agrees with our basic logic. After the illumination period, the temperature equilibrates through the whole sample, giving the average temperature that we detect. The new balance of forces is reached, maintained by the steady flux of heat from the irradiated tubes. When the light is turned off, both the viscosity and the modulus remain roughly constant (only weakly dependent on time), resulting in the simple Debye relaxation towards the original local conformation of the elastomer which was established at the crosslinking.

The attempted explanation based on the sharp local heating of nanotubes captures many key features of our findings, but also has some difficulties. The light-on compressed-exponential response was not found in two cases; (a) at concentrations below overlap ϕ_c, and (b) at $\varepsilon \approx \varepsilon_c$, around the transition from compressive to contractive actuation. In (a) the kinetics could be dominated by the bulk isotropic matrix between sparsely distributed nanotubes, while in (b) the tubes of different orientation in effect compensate each other's local action, including the principal relaxation modes.

Several phenomena, including the photoinduced polaron excitations concentrated near the tube defects or photogenerated charge redistribution, may well coexist during irradiation and differentiating which mechanism is dominant is not experimentally trivial. Electron microscopy techniques might be inherently unsuitable due to flooding of the π-conjugated tubes with beam electrons. A definitive measurement of individual nanotube photoresponse would involve irradiating a tube in a setup similar to single-chain atomic force microscope studies [16].

In conclusion, we have shown that elastomers filled with nanotubes respond to light much faster than classical relaxation predicts, following a universal compressed-exponential law once above percolation. The favored explanation considers nanotubes as photon absorbers that locally redistribute the energy as heat causing contraction of anisotropic polymer chains aligned near the nanotube walls. This demonstrates how nanotubes can impart photomechanical properties in otherwise benign materials; the role of the nanotube-polymer interface is of great interest and the speed of the photoactuation response warrants much further experimental and theoretical investigation.

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