Near-Infrared Light Induced Mechanical Responses in Single-to-Few Layer Graphene

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ABSTRACT

Layer dependent physical responses of graphene-based polymer composites to near-infrared (NIR) light are reported. Thin film polymer composites were fabricated and compared utilizing both single layer graphene and few layer graphene (~5 layers). NIR-induced axial stress and kinetics were measured and found to exhibit three distinct pre-strain dependent response states. Composite stress responses, elastic moduli, and efficiencies were observed to depend on the number of graphene layers in the two-dimensional crystal.

Keywords: graphene, photomechanical, actuation, functional materials

Materials that change shape or dimensions in response to external stimuli are widely used in actuation devices. While plenty of materials respond to heat, light, electricity, and magnetism, there is an emerging class of light driven actuators based on carbon nanostructure/polymer composites [1-8]. Photomechanical actuation offers a variety of advantages over traditional devices, including wireless actuation, electromechanical decoupling (and therefore low noise), electrical circuit elimination at point of use, and massive parallel actuation of device arrays from single light source. Applications of photoresponsive materials encompass robotics [9], plastic motors [10], photonic switches [11], micro-grippers [12, 13], and adaptive micro-mirrors [14].

Graphene-based polymer composites have shown remarkable increases in polymeric composite properties, such as mechanical strength [15] and thermal conductivity [16]. Two-dimensional graphene crystals have shown unique layer dependent properties, such as saturable absorption [17], linear monochromatic optical contrasts [18], and electric field-assisted band gaps for graphene bilayers [19]. Recently, few layer graphene polymeric composites comprised of graphene nanoplatelets (GNPs, ~5 layers) were investigated as photomechanical actuators [20]. However, photoresponsive difference between multi versus single layer graphitic crystal polymer composites is unknown. Optical absorption of graphene is ~2.3% per layer over the visible spectrum [21]. Rigid stack-like morphology and lack of inter-plate interactions of GNPs could mean that their dispersion properties and eventual photomechanical response could be different in polymer composites compared to single-layer graphene (SLG).

Photomechanical responses in composites comprised of small quantities (0.01-1 wt%) of SLG dispersed within polydimethylsiloxane (PDMS) are reported. To evaluate layer dependency of responses, GNP/PDMS composites were fabricated and used as a basis for comparison. SLG was prepared through complete reduction of graphite oxide using the modified Hummer’s method. GNPs were synthesized using plasma exfoliation of high purity graphite. Both forms of graphene were studied extensively with scanning electron microscopy (SEM) and Raman spectroscopy to characterize the number of layers prior to fabrication.

![Figure 1](image_url)

**FIGURE 1.** (a) SEM image of pristine SLG sheet; (b) SEM image of pristine GNP stack; and (c) Layer dependent shift of $G$ and $2D$ peaks at 633 nm excitation.

Figures 1(a)–(b) show SEM images of a SLG sheet and GNP stack, respectively. Figure 1(c) compares layer dependent shifts of $G$ (graphite) and $2D$ ($G'$) Raman peaks at 633 nm excitation. While clearly able to distinguish SLG, greater than ~5 graphene layers the Raman signatures can become indistinguishable from that of bulk graphite [22]. Therefore, atomic force microscopy (AFM) step height...
measurements were also utilized in estimation of ~5 graphene layers. A fabrication procedure was developed to homogeneously disperse SLG within PDMS (Figure 2(a)). Test samples were mounted between test dynamometer upper and lower clamp assemblies (Figure 2(b)). Testing was completed as in Ref [20].

**FIGURE 2.** (a) Evaporative mixing fabrication sequence; and (b) Layout of test dynamometer.

Figure 3(a) presents the photomechanical stress response during a test of 1 wt% SLG/PDMS composite at 3% pre-strain. A +17 kPa change in actuator stress is clearly observed. Both actuation and relaxation of the SLG/PDMS polymer were found to follow simple exponential function \( \exp[-(t/\tau)] \) with \( \tau \approx 1.5 \) s, following Debye relaxation for polymers. This is similar to the GNP/PDMS polymer composites, which also followed a Debye relaxation. This suggests that for the macroscopic sample composites used in testing, actuation and relaxation times were not layer dependent. Optical absorption in SLG or GPNs is a fast event with characteristic time scales of femtoseconds. Therefore, actuation and relaxation time scales are limited by absorbed energy transduction to the polymeric chains. Both SLG/PDMS and GNP/PDMS exhibited nearly identical actuation and relaxation photokinetics. However, it is possible that at the nanoscale these events are slower for GNP/PDMS compared to SLG/PDMS composites. Future single chain AFM studies can elaborate on the kinetics of energy transduction from graphene layers to polymeric chains.

Figure 3(b) presents the increase in Young’s modulus \( (E) \) starting with ~1.6 MPa for pristine polymer and increasing 25% to ~2 MPa in 1 wt% of SLG. Using a forecasting equation derived from experimental data, \( E \) is expected to double at an impressively low ~5 wt% SLG loading. Even the 25% increase observed within the experimental regime is remarkable, however, considering the low SLG concentration. Past results on GNP actuators report a ~60% rise in \( E \) for 5 wt% loading, thus showing a layer dependent effect [20]. Figure 3(c) presents change in stress of 1 wt% SLG/PDMS as a function of increasing pre-strains and shows three distinct response states. At low pre-strains (~3–9%) actuators expand, with maximum observed change in stress of ~17 kPa (1 wt% SLG). At moderate pre-strains (~10–15%), actuators have negligible stress response. At high pre-strains (>15%) actuators contract, exhibiting maximum value of ~32 kPa (1 wt% SLG). It is expected that similar to GNP/PDMS, photomechanical stress of SLG/PDMS will saturate beyond 2 wt% loading [20]. However, the amplitude of stress response at saturation should be greater for SLG/PDMS than GNP/PDMS.

**FIGURE 3.** (a) SLG/PDMS at 3% applied pre-strain; (b) Young’s modulus as a function of SLG loading; and (c) Single NIR cycle for 1 wt% SLG/PDMS at pre-strains from 3–40% with NIR off stress normalized to zero.

Saturation in the composites is a result of light absorption and subsequent energy transduced to the polymer matrix, and percolation threshold. Past reports have shown saturable absorption in graphene due to Pauli blocking [23], with absorption dependent on the number of layers, each absorbing \( \pi \alpha \) (~2.3%) [21]. A second important factor in saturation of photomechanical response is percolation threshold of the graphene/polymer composite. Overall photomechanical response is a result of local interaction between graphene and polymer, which can
easily saturate at the point of NIR illumination. Crossing the percolation threshold results in a connective network where energy transfer extends beyond the illumination point, resulting in a globalized response. Experimental composites were fabricated at wt%’s less than the percolation threshold. Therefore, macroscopic stress responses seen were the summation of localized disconnected microscopic events happening at the graphene-polymer interface within the area of NIR illumination. It is remarkable these disconnected networks can give rise to such collective macroscopic responses as seen in the SLG and GNP-based composites. Repeatability over 24 h period of cycling near-infrared (NIR) on/off was measured and found to be stable in expansive and contractive modes. Maximum total observed change in stress from expansion to contraction in 1 wt% SLG/PDMS was ~50 kPa. Translated into a stroke, this corresponds from ~0.8% expansion to ~1.6% contraction.

FIGURE 4. (a) NIR-induced stress dependency as a function of concentration and laser power for a fixed wt%; and (b) Efficiency vs. concentration and pre-strain.

Figure 4(a) presents relative change in stress (from 3–40% pre-strain) of SLG and GNP composites as function of both wt% concentration and NIR laser power. Across the board, SLG-based composites exhibit more than twice the recoverable stress compared to their multilayered GNP counterparts. With respect to concentration, upward correlation between increasing stress response with increasing wt% carbon loading was observed. As opposed to upward trend with concentration, above ~50 mW/mm² SLG/PDMS composites exhibited saturable mechanical response. For identical wt% loading and NIR intensity, stress response was seen to decrease ~20% with each additional layer of graphene. Next, optical-to-mechanical energy conversion efficiencies ($\eta$) were calculated based on stored potential energy to incident light energy, following methodology in Ref [24]. Figure 4(b) presents optical-to-mechanical energy conversion efficiency as function of both concentration and pre-strain. Efficiency increased linearly with concentration for both SLG and GNP/PDMS composites. Note that laser spot size was only 3 mm × 3 mm. As the entire test sample was 50 mm × 3 mm, not only was just 6% exposed to NIR illumination, but graphene contained in this small section was also responsible for the entire photomechanical response. Higher responses and efficiencies can be obtained by increasing illumination to sample area ratio. Finally, efficiency with respect to pre-strain for SLG/PDMS was evaluated. As actuators changed state from expansion to contraction (>15% pre-strain), however, magnitude of stress response, and therefore efficiency, increased as well. Again, layer dependency on efficiency was witnessed, with each additional graphene layer lowering efficiency ~30%. Decrease in stress as well as efficiency with number of layers depends on a few factors such as optical absorption, surface area increase for SLG versus decrease for stack-like GNP in contact with the polymer, “rigid rod-like” (GNPs) versus “flexible ribbon-like” (SLG) behavior affecting overall dispersion, and finally percolation threshold. Lower photomechanical response of multilayer composites may be due to the relationship of decreasing surface area to volume for polymer interaction with increasing number of layers. The GNP and SLG should have same amount of carbon content for same wt% loading. Photomechanical response is therefore determined by the amount of carbon in contact with polymer. SLG due to its high surface area can weave itself within the polymer creating a continuous matrix, while GNPs with rigid stacked sheet-like morphology cannot; and effective surface area for photon absorption, elastic modulus, and actuation therefore decreases. Due to this, GNPs may only use a fraction of absorbed energy to create localized heating causing expansion or contraction of polymeric chains. In other words, for the same wt% loading, increasing each additional graphene layer in the crystal loses a layer of contact with the polymer.

In summary, layer dependent physical responses of graphene-based polymer actuators are reported, with SLG and GNP composites tested to determine photomechanical responses. Layer dependent stress and efficiency responses were witnessed, with a decrease of 20% and 30%, respectively, per additional graphene layer. These results suggest that dispersion of number of graphene layers in contact with polymer is a critical consideration in designing graphene-based composites.
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REFERENCES