

# Photomechanical Response in Graphene Nanoplatelet Composites

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## ABSTRACT

Large light-induced reversible and elastic stress responses in graphene nanoplatelet (GNP) polymer composites are reported. Homogeneous mixtures of GNP/polydimethylsiloxane (PDMS) composites (0.1–5 wt%) were prepared and their near-infrared (NIR) mechanical responses studied with increasing pre-strains. Using NIR illumination, a photomechanically induced change in stress of four orders of magnitude as compared to pristine PDMS polymer was measured. Actuation responses of graphene polymer composites depended on applied pre-strains. At low levels of pre-strain (3–9%) the actuators showed reversible expansion while at high levels (15–40%) actuators exhibited reversible contraction. For the same fabrication method, GNP/PDMS composites exhibited higher actuation stresses compared to all other forms of nanostructured carbon/PDMS composites tested.

**Keywords:** graphene, photomechanical, actuation, functional materials, carbon nanostructures

## INTRODUCTION

Both in natural and synthetic systems, actuator materials change their shape or dimensions upon external stimulus. The best-known materials for actuation are piezoelectrics [1], ferro-electrics [2], shape-memory alloys [3], electrostrictive materials [4], liquid crystal elastomers [5], and conducting polymers [6]. Recent additions include carbon nanotubes (CNTs) [7] and porous metallic nanoparticles [8] as they exhibit large stresses and strains from low voltage electromechanical actuation. Similarly, both single and multi-wall CNTs (MWNTs) composites have been reported to undergo photomechanical actuation [9, 10]. Compared to electrically/thermally/ionically/phase-transition driven actuators, light driven actuators have several advantages including wireless actuation, electromechanical decoupling (and therefore low noise), elimination of electrical circuits at the point of use, and massive parallel actuation of device arrays from a single light source. Photomechanical actuators already show possible applications encompassing photonic switches [11],

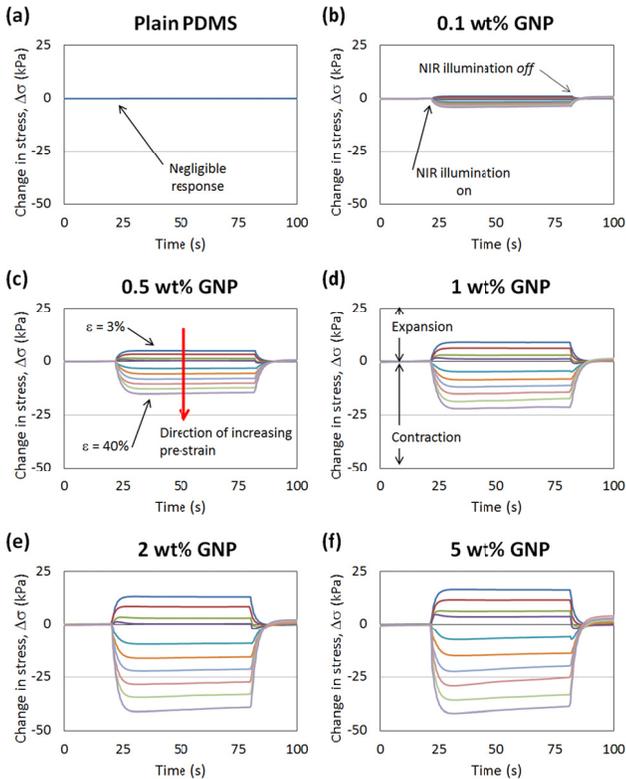
robotics [12], plastic motors [13], and adaptive micro-mirrors [14], thus creating renewed interest in photomechanical actuation.

This work introduces a simple polymer composite system whose photomechanical responses to near-infrared (NIR) light are realized solely by incorporation of homogeneous dispersion of graphene nanoplatelets (GNPs) within a polydimethylsiloxane (PDMS) elastomer matrix. Similar to CNT/PDMS composites, actuation responses of GNP/PDMS composites depend on initial applied pre-strain: at low levels (3–9%), samples showed reversible expansion; at moderate levels (~10%), samples yielded negligible effect; and at high levels (15–40%), samples exhibited reversible contraction. For GNP/PDMS composites, these correspond to a photomechanical stress change 2.4 to 3.6 times greater than any other carbon form tested.

## RESULTS AND DISCUSSION

For each pre-strain value (3–40%), test composites underwent 5 cycles of NIR illumination *on* for 60 seconds, followed by NIR illumination *off* for 30 seconds. The magnitude of actuation was found to be highly repeatable for each test sample. Photomechanical responses started at time ( $t$ ) = 0 s and became saturated at  $t$  = 5 s. Similarly, once the light is switched *off*, actuators undergo relaxation in  $t$  = 5 s. This is significantly fast actuation compared to past reports on CNT/PDMS actuators where actuation achieved saturation at  $t$  = 10–15 s [15]. Dependency of actuation and relaxation responses as a function of time were also examined, with experimental data fit to simple exponential functions by incorporation of a fitting parameter ( $\tau$ ). The experimental actuation data was fitted with a simple exponential function of  $1 - \exp[-(t/\tau)]$ , while the relaxation data was fitted with  $\exp[-(t/\tau)]$ . Both actuation and relaxation responses followed Debye characteristics [15]. When normalized to account for the magnitude of change in stress, actuation and relaxation responses for all GNP/PDMS test composites were nearly identical. Unlike CNT/PDMS actuators which follow a compressed exponential function for actuation [15],

GNP/PDMS actuators were found to not only follow a simple exponential function during both actuation and relaxation, but also exhibit about a 3 times faster response. Secondly, actuation kinetics of the CNT/PDMS actuators followed a compressed exponential function only above the percolation threshold [15]. For values lower than the percolation threshold, at  $\sim 0.02$  wt% concentration of nanotubes in the PDMS matrix, actuation was far slower with time constants of actuation greater than 20 s for achieving saturation [15]. This shows dependence of actuation kinetics on the number of interconnected nanotubes in the matrix.



**Figure 1.** Increasing photomechanically-induced stress response in GNP/PDMS composites for increasing GNP concentrations: (a) Plain PDMS, (b) 0.1 wt%, (c) 0.5 wt%, (d) 1 wt%, (e) 2 wt%, and (f) 5 wt%.

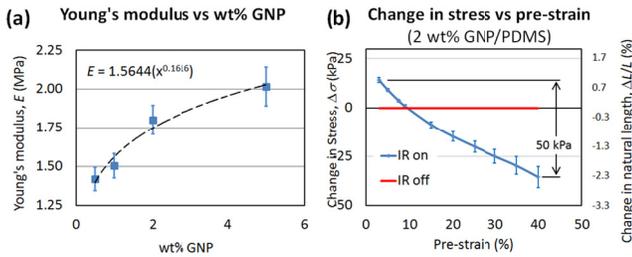
Starting with a plain PDMS elastomer (Figure 1(a)) and progressing from 0.1 to 5 wt% concentration GNP/PDMS composites (Figure 1(f)), each plot shows photomechanical response to 808nm NIR illumination for a single 60-second cycle. Since the optical loss of PDMS in the NIR region is  $< 0.5$  dB/cm [16], negligible response in the plain PDMS sample (Figure 1(a)) was expected. However, by a concentration of 0.1 wt% GNP (Figure 1(b)), the photomechanical effect is clearly visible through telltale expansion and contraction of the actuator. Due to rubbery elasticity properties of the PDMS matrix, all composites exhibited expansion at low pre-strains (positive-induced stress) and contraction at high pre-strains (negative –

induced stress). From GNP concentrations of 0.1 wt% to 2 wt%, (Figures 1(b)–(e)), magnitude of photoinduced stress was observed to increase, reaching almost four orders of magnitude greater than the pristine PDMS polymer. By a concentration of 2 wt%, however, photomechanical response of the GNP/PDMS composites had become saturated. Comparison with higher GNP concentration of 5 wt% (Figure 1(f)) showed only a marginal increase in magnitude of the stress. Therefore, photomechanical response of the 2 wt% GNP/PDMS composite sample was used as the benchmark for comparison. As applied pre-strains increase overall test sample length, GNPs within the PDMS polymer become more aligned/re-arranged with respect to one another. As a result, the macroscopic magnitude of photomechanical response is amplified.

To compare photomechanical responses of GNP/PDMS composites with other forms of carbon/PDMS composites, test samples were fabricated for graphite oxide (GO)/PDMS, CNT/PDMS, and pyrolytic carbon black (CB)/PDMS using identical fabrication methods. All samples underwent identical testing procedures to the GNP/PDMS composites. All forms of carbon displayed similar photomechanically induced expansion/contraction stress responses as the GNPs, although with varying magnitudes. Of these samples, GO/PDMS showed the smallest amount of actuation, from +2 kPa (3% pre-strain) to –9 kPa (40% pre-strain). This result also shows that studies of graphene-composites derived from GO materials are quite different from single, bi-layer, or few layer graphene. The magnitude of induced stress change in CNT/PDMS was slightly higher, from +4 kPa (3% pre-strain) to –10 kPa (40% pre-strain). Finally, CB/PDMS exhibited a stress change from +7 kPa (3% pre-strain) to –14 kPa (40% pre-strain). The GNP/PDMS response magnitude of stress-induced change ranged from +14 kPa to –36 kPa, an average of 4.5 times larger than that of GO/PDMS, 3.6 times CNT/PDMS, and 2.4 times CB/PDMS for the same fabrication methods. The similar magnitude of stress change seen in CNT/PDMS and CB/PDMS demonstrate the lack of dispersion of CNTs in the PDMS matrix acting like particles similar to CB rather than tubular filaments is due to short mixing times. Past reports have shown much larger stress increases for MWNTs than seen here [15]. In those studies, MWNTs were shear mixed in a high shear laboratory mixer for minimum of 24 hours in the PDMS base compound before fabricating the actuator. In the present study, graphene was only shear mixed for 5 minutes before fabricating actuators.

The same short-time shear mixing procedure was followed for all carbon/PDMS composites, to enable a standardized comparison between different types of carbon/PDMS actuators. This procedure shows the relative ease at which the plate-like GNPs disperse in an elastomeric matrix such as PDMS compared to other carbon forms. The plate-like structure of GNPs may enable the

individual layers to slide against the polymer, thus achieving rapid and uniform dispersion compared to filament-like CNTs that tend to roll up into particles in the short mixing time. For the GNP/PDMS actuators, when the actuation is translated into a stroke, this corresponds to a total strain of  $\sim 2\text{--}5\%$ , significantly larger than lattice expansion or contraction alone [17]. It is clear that the photomechanical actuation of graphene is quite impressive compared to its other carbon counterparts.



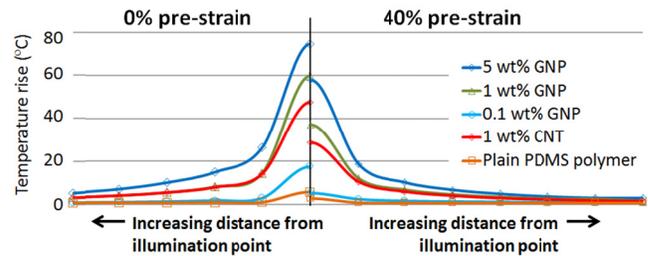
**Figure 2.** Average actuation response versus pre-strain with  $\pm 1$  standard deviation error bars, (b) Increase in Young's modulus of the actuator with increase in GNP fraction.

Figure 2(a) presents change in Young's modulus ( $E$ ) as a function of GNP fractions dispersed in the polymer. A Young's modulus increase of almost twice that of pristine PDMS elastomer was obtained [18], and thus higher wt% GNP actuators are also stiffer. These results suggest that GNPs in PDMS produced not only a stiffer actuator but also an extraordinary optical-to-mechanical energy conversion. Figure 2(b) shows photomechanical stress response versus applied pre-strain, with  $\pm 1$  kPa standard deviation error bars. At low pre-strains (under 15%), the standard deviation is less than 1.5 kPa, as pre-strain increases, so does the standard deviation, reaching a maximum of  $\pm 5.4$  kPa at 40% pre-strain. This suggests that as pre-strains increase, combined effects of GNP orientational ordering and elastic forces result in larger contractions.

Laser irradiation on the GNP/PDMS composites was found to increase actuator temperature at the irradiation spot. The temperature decrease as a function of distance from the illumination source, therefore, was characterized for various GNP/PDMS composite concentrations. Figure 3 details this temperature rise for 0% pre-strain (sample length 50 mm) as well as 40% pre-strain (sample length 70 mm). As expected, the highest temperature increase also occurs at the highest GNP concentration (5% GNP, 0% pre-strain). A  $\sim 75^\circ\text{C}$  temperature rise quickly diminishes as distance from the illumination point increases. As pre-strain and thus sample length increase, the amount of graphene exposed to the fixed size irradiation spot decreases due to orientational ordering; and, therefore, thermal effects also start to diminish. At 40% pre-strain, the maximum temperature increase has fallen to  $\sim 60^\circ\text{C}$ , a  $15^\circ\text{C}$  change compared to the unstrained sample. It should be pointed out

that at large pre-strain, the overall magnitude of the actuation increase, while the temperature rise in the actuator decrease. This outcome possibly indicates that thermal effects may not be the only effect contributing to the overall actuation mechanism. We believe that this response is a result of contributions from electrostatic, elastic, polaronic, and thermal effects that cause this impressive overall photoresponse of GNP/PDMS composites similar to CNT/PDMS composites [9, 10, 15].

While it is understandable GNPs performed better than CB and GO/PDMS mixtures, questions linger as to the reason for smaller amplitudes of photomechanical stress for CNT/PDMS. There are several likely reasons for this which warrants further research. First, the two-dimensional (2D) nature of GNPs enables sliding of individual platelets on top of one another and thus resulted in homogenous sample dispersions within a relatively short time ( $\sim 5$  minutes) shear mixing process. GNPs act like discrete 2D rigid plates. Due to similar atomic arrangement of carbon and crystal-like behavior, friction and interaction effects between the graphene platelets is expected to be negligible. However in CNT/PDMS composites, the short time shear mixing was not long enough to overcome the natural tendency of nanotubes to form bundles due to their enhanced inter-tube interactions, thus giving rise to smaller amplitudes of photomechanical stress. In other words, nanotubes exhibited "particle-like" behavior for short mixing times rather than that of a matrix of dispersed 1D tubes. Hence the photo-mechanical stresses exhibited by CNT/PDMS actuators were quite similar to CB/PDMS actuators for the short mixing time. Therefore, both matrix orientation and percolation threshold is crucial for enabling high amplitudes of photomechanical stress and faster kinetics for CNT/PDMS actuators [17]. Longer mixing times and more sophisticated dispersion methods are needed to separate the nanotubes from the bundles as well as rendering them oriented in the PDMS matrix.



**Figure 3.** Steady-state temperature rise in GNP/PDMS composites as a function of distance from illumination point for 0% and 40% pre-strain.

This study demonstrated intrinsic photomechanical actuation of graphene-based polymer composites. Actuation was witnessed only through the presence of graphene. Dispersion of GNPs into a PDMS silicone elastomer matrix resulted in a novel GNP-based photomechanical actuator

that showed reversible light-induced elastic expansion and contraction. For a 2 wt% sample, a photomechanically induced change in stress of +14 kPa at low pre-strains, and -36 kPa at high pre-strains was successfully demonstrated. For the same fabrication method, GNP/PDMS composites outperformed all other carbon forms tested.

Looking forward into a variety of possible future applications of photomechanical actuators, one can develop skins that can undergo either expansion or contraction. On a small scale, this could be used for assembling surfaces to study mechanical forces on soft matter, such as biological materials such as cells, where the forces are delivered in non-contact manner using photo-mechanical actuation. On a large scale, thin films of GNP/PDMS polymer could be utilized as functional smart materials for adaptive skins. The temperature decrease with increase in pre-strains of the actuators could be useful for developing a new type of strain gauge owing to linear temperature change with strain. We believe that further development of graphene based polymer composites will extend the promising potentials of graphene based actuation technologies and will serve as a catalyst to inspire continued research into energy conversion devices and systems.

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