Photo-thermal polymerization of nanotube/polymer composites: Effects of load transfer and mechanical strength

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The authors report a method where *in-situ* photon assisted heating of multi-wall carbon nanotubes was utilized for enhanced polymerization of the nanotube/polydimethylsiloxane interface that resulted in significant load transfer and improved mechanical properties. Large Raman shifts (20 cm^{-1} wavenumbers) of the 2D bands were witnessed for near-infrared light polymerized samples, signifying increased load transfer to the nanotubes for up to $\sim 80\%$ strains. An increase in elastic modulus of $\sim 130\%$ for 1 wt. % composites is reported for photon assisted crosslinking.

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One of the important applications of carbon nanotubes is their use as nanoscale fillers to improve mechanical properties of polymeric materials. The high aspect ratio, elastic modulus, and tensile strength of carbon nanotubes make them attractive as nanoscale fillers to enable increased load transfer and improved mechanical strength of polymer nanocomposites. The nanotube/polymer interface has been demonstrated to play an important role in efficient stress transfer to the nanotube and determination of overall nanotube/polymeric composite mechanical properties.¹ Ajayan *et al.* demonstrated the load transfer in a multi-wall carbon nanotube (MWNT)/epoxy system using Raman spectroscopy.² The enhanced shift in Raman G' mode during compression demonstrated higher interfacial shear stress and load transfer to the nanotubes.² Since then, numerous reports have demonstrated enhanced load transfer to nanotubes utilizing strategies, such as surface functionalization of nanotubes,^{3–5} refluxing carbon nanotubes with nitric acid to create carboxyl, carbonyl, and hydroxyl groups,^{6,7} sidewall functionalization for better dispersion of nanotubes in the matrix,⁸ alignment of nanotubes in the matrix,⁹ *in-situ* melting and polymerization,^{10,11} melt compounding,¹² and more recently using flexible spacers at the nanotube/polymer interface.¹³ The work by Zhang *et al.* is notable in that it achieved an impressive elastic modulus increase of $\sim 214\%$ for just 2 wt. % of MWNTs in a polymer matrix.¹²

Single wall and multi-wall carbon nanotubes have been known to absorb significant amounts of near-infrared (NIR) light, resulting in photo-thermal heating.¹⁴ Applications of such nanoscale photo-thermal heating include bio-nanotechnology to kill cancer cells,^{14,15} targeted drug delivery,¹⁶ photo-mechanical actuators,¹⁷ and laser assisted photo-thermal imprinting in polymeric materials.¹⁸ Irradiation of nanotube/polymer composites using NIR photons during crosslinking could potentially result in significant heating of nanotubes inside the polymer, thus enhancing the crosslinking process and strengthening the nanotube/polymer interface. This is a paradigm in polymerization of the

samples by enabling crosslinking to start at the nanotube/polymer interface using photo-thermal heating of nanotubes. This type of polymerization and strengthening is not possible using oven based heating methods as heat flows into the sample from the outside. We compare the load transfer and elastic modulus of our NIR light treated samples with a conventional oven crosslinking method of heating to 125°C for 30 min.

This letter reports simple photon assisted heating of nanotubes inside the polymer during crosslinking. Samples were comprised of small amounts (0.01–1 wt. %) of MWNTs (cheap tubes) dispersed within polydimethylsiloxane (PDMS, Sylgard 184), a widely available commercial polymer. Homogenous dispersions of MWNTs in PDMS were prepared using a recently developed evaporative mixing fabrication process which involved sonicating a MWNT and isopropyl alcohol (IPA) solution for 4 h, evaporative mixing of PDMS base compound with the MWNT-IPA suspension for 24 h at 65°C , addition of crosslinker (base compound: curing agent ratio is 10:1) and subsequent degas, crosslinking and polymerization, spin coating and baking, and finally post-bake relaxation for $\sim 12\text{ h}$.¹⁹ In conventional curing, samples are heated in a vacuum oven at 125°C for 30 min following addition of crosslinker and degasing (Figure 1(a)). At this time and temperature, elastic modulus values saturate indicative of the end of the crosslinking process. For NIR light treatment, samples were exposed to varying levels of NIR radiation following crosslinker addition and degasing (Figure 1(b)). Process times and NIR dose were optimized to achieve saturation in elastic modulus values of pure PDMS. Following sample preparation, scanning electron microscopy (SEM) was used to investigate sample cross-sections and the nanotube/polymer interface. In order to compare load transfer between conventional baking and NIR light treated polymerization, Raman spectroscopy was used to ascertain shift in the wavenumbers with increasing strains. The 632.8 nm line beam of a helium-neon laser in an inVia RENISHAW micro-Raman spectrometer was focused onto the sample surface through a $\times 50$ objective lens, forming a laser spot $\sim 3\text{ }\mu\text{m}$ in diameter. Strains were applied to the sample under the micro-Raman spectrometer by stretching the sample to a

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FIG. 1. Schematic of the two different polymerization techniques: (a) oven based heating; (b) NIR light treatment method.

pre-determined length using a linear actuator. Finally, samples containing various fractions (0.01-1 wt. %) of MWNTs in PDMS were prepared and tested for their elastic moduli using both oven heated and NIR photon irradiated samples. The Young's moduli of the samples were determined by measuring the stress change with application of increasing pre-strains to the samples from 0% to 5% in increments of 1%.²⁰ The effect of improvement in elastic modulus for different weight fractions of MWNTs and different levels of NIR radiation were studied. The change in elastic modulus was calculated based on the elastic modulus of the pure PDMS for both the methods and calculating the percentage change based on increasing weight fractions of MWNTs for the same time and NIR power.

Figure 2(a) presents the cross-sectional SEM of the nanotube/polymer interface for various weight fractions of

MWNTs (0.01-1 wt. %) in PDMS. Raman spectra for both pure PDMS and MWNT/PDMS composites are presented in Figure 2(b). SEM images clearly show dispersion of MWNTs with increasing nanotube density with increasing wt. % of the samples. In all the three SEM images, one end of the MWNT was stretched out of the matrix while the other end was embedded firmly in the matrix. This is indicative of strong interfacial adhesion between the nanotubes and PDMS/polymer.¹² The SEM images of both oven heated samples (not shown) and the NIR photon irradiated samples qualitatively exhibited similar results. In the Raman spectrograph of Figure 2(b), one can see all the nine peaks associated with the PDMS in both the samples. The radial breathing mode (RBM, 219.3 cm^{-1}), the disorder induced D band (1328 cm^{-1}) tangential mode G band (1588 cm^{-1}), and 2D or G' (2657 cm^{-1}) bands of the MWNT are clearly seen in the nanotube/polymer sample, demonstrating high purity of sample preparation, subsequent crosslinking, and polymerization methods. Based on the RBM mode of the nanotube/polymer samples, the diameter of the nanotubes was calculated using equation $\omega_{\text{RBM}} = A/d_t + B$, where constants $A = 233\text{ cm}^{-1}\text{ nm}$ and $B = 10\text{ cm}^{-1}$ result in an inner MWNT diameter $\sim 1.06\text{ nm}$. This diameter value based on the RBM mode in the nanotube/polymer samples demonstrates lack of bundling of MWNTs and excellent dispersion of MWNTs in the polymer samples using evaporative mixing. The lack of bundling and smaller diameter may also indicate higher interaction of nanotubes with the polymer providing better interfacial adhesion and strength for both methods.

Raman spectroscopy has been used by many groups in the past to measure strains in nanoscale fillers such as carbon nanotubes.^{2,21-28} When a strain is applied, interatomic distances change resulting in a shift in the vibrational frequencies. The G' band around 2700 cm^{-1} in the Raman spectra for MWNTs is highly sensitive to strain. The larger shift in Raman G' band peak position is indicative of a larger load carried by nanotubes. Since the SEM images and Raman signatures of the samples look qualitatively similar before applying strain, characterizing wavenumber shift in G' peak in both the samples indicates strength of the nanotube/polymer interface for both samples. Figure 3 presents the shift in

FIG. 2. SEM images of MWNT/PDMS samples, scale bar 500 nm; (a) 0.01 wt. %; (b) 0.1 wt. %; (c) 1 wt. % MWNT fractions; (d) Raman spectra of pure PDMS and 1 wt. % MWNT/PDMS sample. The peaks labeled 1-9 are the different vibrational peaks of Si-O-Si and CH₃ groups. The peaks labeled (RBM) is radial breathing mode (219.3 cm^{-1}), (a) is disorder-induced D band (1329 cm^{-1}), (b) is the tangential mode G band (1588 cm^{-1}), and (c) is the second-order G' band (2657 cm^{-1}).

FIG. 3. Load transfer in conventional (a-1) and NIR light polymerized methods (b-1); change in wavenumber as a function of percentage strain for conventional (a-2) and NIR light polymerized samples (b-2).

Raman peak position of the G' band for both oven polymerized (Figure 3(a-1)) and NIR light polymerized samples (Figure 3(b-1)) as a function of applied tensile strain. It is clear that oven polymerized samples have a smaller shift to the left in Raman peak position compared to NIR light treated samples. There are several interesting characteristics in the Raman spectra as a function of applied strains. For both conventional and NIR photon irradiated methods, at 0% strain, Raman signatures look identical (blue line). As we increase the strain to $\sim 50\%$, oven baked samples undergo only a small shift to the left (red line, Figure 3(a-1)), while NIR light treated method undergoes much larger shift (red line, Figure 3(b-1)). The shift in Raman peak position at $\sim 80\%$ strain is even more predominant for NIR photon polymerized samples (green line). It is clear from Figures 3(a-1) and 3(b-1) that higher load transfer to the nanotubes occurred in samples treated with NIR light compared to oven polymerized samples. This may indicate better crosslinking and polymerization of the nanotube/polymer interface. Figures 3(a-2) and 3(b-2) presents the change in wavenumbers as a function of strain. For both oven baked samples and NIR light treated samples, there is a decrease in G' mode wave-

numbers for 0.5 wt. % and 1 wt. % MWNT/polymer samples. For the oven baked method, there was 3 cm^{-1} change in wavenumber for 0.5 wt. % and 9 cm^{-1} change in wavenumber for 1 wt. % MWNT/polymer composites for the strain values tested. On the other hand, there was 5 cm^{-1} change in wavenumber for 0.5 wt. % and 20 cm^{-1} change in wavenumber for 1 wt. % MWNT/polymer composites for the NIR light treated method at strains from 0% to 80%. Samples strained $>80\%$ lead to complete failure. Past reports on Raman spectroscopy for investigating load transfer on nanotube/polymer composites have only been done in a limited range ($\pm 15\%$ strains) before sample failure.^{2,29} Higher strains used here and larger shifts in the Raman positions (up to $\sim 20\text{ cm}^{-1}$ wavenumbers) show greater load transfer to the nanotubes than past reports. It should be noted that for $\sim 0.5\text{ wt. \%}$ MWNT/polymer samples the wavenumber shift saturates beyond $\sim 40\%$. There is no appreciable change in wavenumbers at 80% strain, and thus strains are not resolvable beyond $\sim 40\%$. This is true for both types of samples, suggesting that saturation of the Raman signal is related to weight fraction of nanotubes in the polymer matrix or number of nanotube/polymer sites that undergo strain. This may be related to the percolation threshold (PT) and requires further exploration. As nanotube wt. % increases in the matrix, not only is there significant increase in load sharing but samples below and above the PT should exhibit different Raman shifts. From our past experience, the PT of nanotube/PDMS composites is $\sim 0.5\text{ wt. \%}$.⁹ Therefore, at 1 wt. % above the PT, load is shared more uniformly and the interpenetrating network of nanotubes in the polymer matrix makes wavenumber shifts resolvable at higher strains.

Figure 4(a) presents Young's modulus as a function of NIR energy dose with increasing fraction of MWNTs in polymer composites. For small fractions (0.01-0.1 wt. %) of MWNTs in PDMS, there is only a small change in elastic modulus values and both curves look similar. However, at $\sim 1\text{ wt. \%}$ MWNTs, Young's modulus values increase by roughly twice for all NIR dose energy levels. This suggests that as NIR dose is increased and with more carbon nanotubes in the matrix, significant strengthening occurs. This can only happen if nanotubes are heating the polymer and strengthening the interface. Figure 4(b) compares the change in elastic modulus as a percentage for both samples. It is clear that for all wt. % MWNTs, change in elastic modulus is higher for NIR treated samples compared to the oven polymerized samples. A $\sim 36\%$ increase in elastic modulus at

FIG. 4. (a) Young's modulus versus NIR light dose for MWNT/PDMS fractions; (b) change in elastic modulus versus weight percentage of MWNT for light treated and oven baked methods.

1 wt. % MWNTs was observed for oven polymerized samples versus $\sim 130\%$ increase in elastic modulus for the same wt. % of MWNTs for NIR light polymerized samples. These impressive results suggest that irradiating samples with NIR light caused nanotubes to heat inside the polymer, thereby resulting in enhanced crosslinking and polymerization of the nanotube/polymer interface leading to better mechanical properties and increased load transfer. Macroscopic temperature rise was measured to be $\sim 75^\circ\text{C}$ for NIR photon irradiated samples. However, actual temperature rise at the nanotube/polymer interface must be much higher than this value to enable such exceptional strength and load transfer. As the nanotubes are well dispersed and with increase in weight fraction of MWNTs in the polymer, each nanotube/polymer interface must undergo significant heating and therefore improved the overall load transfer to the nanotubes thereby enabling higher mechanical strength. Materials such as carbon nanotubes or graphene can heat up and cool rapidly (within micro to nano-seconds), and therefore, future time resolved studies at the nanotube/polymer interface can capture the actual fast thermal events that resulted in such exceptional strength of the nanotube/polymer interface.

Looking forward into variety of applications, NIR heating of nanotubes in polymers could be used as a fundamental technique to enable large scale crosslinking and enhanced mechanical properties of nanocomposite materials in general. The method reported here could be useful in improving the interfacial shear strength and mechanical properties of emerging class of light-weight and high-strength nanocomposites based on graphene. While surface chemical functionalization of nanotubes/graphene is quite attractive, recent reports have shown that improvement in interfacial adhesion due to surface functionalization of nanotubes does not always promote substantial improvement in mechanical properties.³⁰ This is due to surface degradation of nanotubes/graphene during functionalization. Compared to these techniques, the use of NIR light is benign and can render high strength nanocomposites as reported here. Looking more closely, it is expected that the structural properties of nanotubes should remain unaffected for both processes. What is being changed is heat flow. In the conventional process, heat flows from outside to insides of the sample. Depending on polymer heat transfer rate and filler thermal conductivity, one can find localized cold and hot spots that can affect crosslinking process and eventual mechanical properties. On the other hand, in the NIR method, exciting the nanotubes to high temperature, each and every nanotube in the matrix should participate in the heating process. As a result, the matrix is crosslinked around the nanotubes more uniformly and results in higher load transfer as suggested by Raman spectroscopy. Since structural properties remain unaffected, so should electron transport properties of the composites.

On a more practical note, nanotubes/graphene functionalized with sulphur and followed by NIR treatment as reported here can enable nano- to macroscopic scale vulcanization of rubber materials that is of significant use to many day to day applications worldwide. Other applications of nanotube/polymer composites could be envisioned in aerospace structures, reinforced laminates, high strength plastics, wear resistant and bullet proof textiles, and electrical cables. All these applica-

tions could benefit the NIR method reported here for enhanced crosslinking that can result in significant load bearing and mechanical strength without damaging the nanotubes.

In summary, we demonstrate photon assisted heating of MWNTs inside a polymer matrix that resulted in better polymerization of the nanotube/polymer interface. Dramatic enhancement in load transfer to the nanotubes and subsequent increase in elastic modulus was observed. Compared to traditional polymerization techniques, NIR method yielded an increase in elastic modulus value of $\sim 130\%$ for just 1 wt. % MWNT in PDMS polymer, greater than most reported to date. Raman spectroscopy suggested shift in wavenumbers of $\sim 20\text{ cm}^{-1}$ for $\sim 80\%$ strain, larger than most past reported values. These results suggest NIR light-induced heating of carbon nanotubes at the nanoscale could potentially be used as a scalable nanomanufacturing technique for increased load transfer and higher mechanical strength for reinforced polymer composites.

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