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Stimuli-responsive transformation in carbon nanotube/ expanding microsphere-polymer composites

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Abstract

Our work introduces a class of stimuli-responsive expanding polymer composites with ability to unidirectionally transform physical dimensions, elastic modulus, density, and electrical resistance. Carbon nanotubes and core-shell acrylic microspheres were dispersed in polydimethylsiloxane, resulting in composites that exhibit a binary set of material properties. Upon thermal or infrared stimuli, liquid cores encapsulated within the microspheres vaporize, expanding the surrounding shells and stretching the matrix. Microsphere expansion results in visible dimensional changes, regions of reduced polymeric chain mobility, nanotube tensioning, and overall elastic to plastic-like transformation of the composite. Here we show composite transformations including macroscopic volume expansion (>500%), density reduction (>80%), and elastic modulus increase (>675%). Additionally, conductive nanotubes allow for remote expansion monitoring and exhibit distinct loading-dependent electrical responses. With ability to pattern regions of tailorable expansion, strength, and electrical resistance into a single polymer skin, these composites present opportunities as structural and electrical building blocks in smart systems.

1. Introduction

Due to potential applications in smart systems, materials that sense external stimuli and execute responses that enhance overall system functionality are attractive areas for research [1]. While some of these materials undergo *reversible* changes upon application of an external stimulus, others undergo *irreversible* changes. Well-known stimuli-responsive materials include piezoelectrics [2], ferroelectrics [3], shape-memory alloys [4], electrostrictive materials [5], dielectric elastomers [6, 7], liquid crystal elastomers [8], and conducting polymers [9]. Despite, and in part because of individual strengths and weaknesses, these materials have been implemented to fulfill various sensing and actuation roles in industrial smart systems [1].

A decade of nanotube/polymer composite research has yielded interesting insights in molecular design and mechanical properties of nanocomposites. Carbon nanotube fillers have been used to increase strength [10]; as stress recovery agents in thermoplastic elastomers and infrared (IR) actuators [11–16]; to improve damping capability [17]; as shape/temperature memory composites [18]; as space durable films for electrostatic charge mitigation [19]; to improve flammability resistance [20]; as conductive scaffolds for printable composites and gels [21, 22]; as electro-responsive chromatic materials [23]; and as skin-like pressure and strain sensors [24]. The combination of high strength, light weight,

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Author contributions

J.L. and B.P. designed the experiments and wrote the manuscript. J.L. performed the experiments, calculations, and application development/fabrication. P.X. performed the stress-strain testing with J.L.

and large elastic energies in these composites have been proposed for diverse applications ranging from high-end sports equipment [25] to artificial muscles in humanoid robots [26]. While important, many of these applications merely incorporate nanotubes to accentuate already existing host matrix features (such as strength, toughness, conductivity), there has been little success in development of stimuli-responsive composites that exhibit dynamic changes in strength, conductivity, density, and volume (visible on macroscopic scales).

We report a stimuli-responsive ternary composite with the ability to unidirectionally transform from an initial elastic state to a more rigid plastic-like state upon thermal or IR stimuli. Addition of thermally expanding microspheres (TEMs) and single-wall carbon nanotubes (SWNTs) in a polydimethylsiloxane (PDMS) elastomer matrix resulted in a material with ability to on-demand undergo volume expansion (>500%), density reduction (>80%), elastic modulus increase (>675%), and resistance changes. Volume expansion is achieved through dispersion of core-shell microspheres in the composites. Consisting of a gas-tight acrylic copolymer shell encapsulating liquid hydrocarbon, TEMs have two states – *initial* (unexpanded) and *expanded* (Figure 1a shows to-scale cutaway). Heating the copolymer shell above its glass transition temperature softens the shell and vaporizes the encapsulated hydrocarbon. The subsequent internal pressure rise plastically deforms the shell, resulting in permanent volume increase [27] (Figures 1b and 1c). While TEMs are commercially available in a range of expansion temperatures, we selected those at the lower end of the spectrum in order to facilitate use of low intensity IR illumination to induce remote expansion ($T_{start} \sim 105^{\circ}\text{C}$ and $T_{max} \sim 140^{\circ}\text{C}$). Using scanning electron microscopy (SEM), initial microsphere diameter was determined to be $7.1 \pm 1.9 \mu\text{m}$, and expanded $17.8 \pm 3.8 \mu\text{m}$ (yielding 150% diameter, 500% surface area, and 1,500% volume increases). Dispersion of SWNTs and TEMs in PDMS was accomplished using an evaporative mixing method developed by our group [14] (Figure 2a), and resulted in interesting stimuli-responsive mechanical and electrical property transformations discussed in the following sections. Figure 2b shows the relationship between SWNT loading and composite resistivity (ρ).

2. Stimuli responsive transformation

Incorporation and subsequent thermal expansion of TEMs in SWNT/polymer composites results in interesting changes to the polymer matrix. Upon application of thermal or IR stimuli, microsphere expansion results in an eye-observable transformation of the initial (as-fabricated) elastic polymer composite into a plastic-like state. Figure 3a shows the smooth surface of an initial fabricated (0.3 wt% SWNT, 31.2 wt% TEM) unexpanded composite. In this image, neither SWNTs nor TEMs are discernible from the bulk polymer matrix; however, post expansion (Figure 3b) individual microspheres are clearly seen bulging out of the bulk polymer. Examination of the area between adjacent microspheres shows the matrix has been stretched into local thin ($<1 \mu\text{m}$) polymer films, the thickness of which was observed to be inversely proportional to microsphere loading.

In composite materials, observations have demonstrated that at the filler-polymer interface – chain mobility is restricted (confirmed via nuclear magnetic resonance measurements [28]) resulting in a thin region of glassy-like behavior [29–32]. Chain mobility restriction decreases as distance from the filler increases, following a gradient back to the bulk matrix [31]. In initial composites, glassy regions surrounding unexpanded microspheres are relatively small compared to the bulk polymer (as Figure 3c shows). Since the majority of bulk polymeric chain mobility remains unaffected, macroscopic composites retain elastic properties. As TEMs expand, however, the matrix between adjacent microspheres stretches into local submicron polymer films, emulating substantially greater filler loading. Due to TEM surface area increasing on expansion, corresponding polymer chain restrictions also

increase (Figure 3d), resulting in macroscopic transformation of the entire system from an elastic to plastic-like state. Resulting polymer mobility between adjacent filler particles is hindered, possibly forming glassy-like flexible bridges [31]. Such expansion-induced alteration of the polymeric chain conformations observed here could be useful in adaptive and responsive interface development.

3. Binary mechanical properties

Because reinforcing materials are uniformly distributed and randomly oriented in the PDMS matrix, fabricated composites exhibited isometric dimensional and volumetric expansion. Figure 4a shows percent change of these quantities as a function of increasing TEM *wt%*. Theoretical as well as $\pm 1\sigma$ volume expansion curves (based on average TEM unexpanded/expanded size analysis) are also included. Since composite mass is constant but volume increases upon TEM expansion, there is a corresponding decrease in density. Figure 4b compares initial and expanded density as a function of TEM loading, with theoretical curves included here as well. Because theoretical and $\pm 1\sigma$ curves were determined based on measurements of loose TEMs not in a matrix, slight underperformance of experimental results compared to theoretical values is expected. While volumetric expansions up to >900% were witnessed (45 *wt%* TEM), subsequent experimental work was done with 31.2 *wt%* samples. This loading still yields an impressive volume increase of >500% and density reduction of >80% while maintaining composite integrity. Figure 4c is an expanded composite cross-section showing morphology detail of several hollow microspheres and polymer-coated SWNTs.

While high TEM *wt%* is desirable from an expansion perspective, there are associated drawbacks. Increased microsphere loading lowers the PDMS matrix to reinforcing material ratio. Since the PDMS matrix provides polymeric chains responsible for binding the composite, filler loading can be large enough such that resulting structures are not stable and tend to break apart or crack upon expansion. This response was observed to occur above ~50 *wt%* TEM loading. While volumetric expansions up to >900% were witnessed (45 *wt%* TEM), subsequent experimental work was done with 31.2 *wt%* samples. This level yields an impressive volume increase of >500% and density reduction of >80% while maintaining composite integrity. A side-by-side comparison of initial and expanded composites at various TEM loadings is shown in Figures 5a and 5b.

While we used SWNT *wt%* as the standard throughout our work (which remains constant regardless of TEM state), it is interesting to note the decrease in volume fraction (V_f) of SWNTs due to microsphere expansion. Equations (1) and (2) were used to transform *wt%* to V_f (converted to *Vol%* for plotting purposes). Variables ρ_{SWNT} and $\rho_{TEM/PDMS}$ are the densities of the SWNTs and TEM/PDMS matrix, respectively. We used a SWNT density of 2.1 g/cm³ (per manufacturer's documentation), and TEM/PDMS densities of 1.045 g/cm³ and 0.178 g/cm³ for initial and expanded samples, respectively (based on experimental data). Figure 5c shows the relationship between *wt%* and *Vol%*. For a given SWNT loading, microsphere expansion results in no change in *wt%*, but ~80% reduction in *Vol%*.

$$V_f = \frac{\frac{wt\%_{SWNT}}{\rho_{SWNT}}}{\frac{wt\%_{SWNT}}{\rho_{SWNT}} + \frac{100 - wt\%_{SWNT}}{\rho_{TEM/PDMS}}} \quad (1)$$

$$Vol\% = 100V_f \quad (2)$$

While volumetric and density changes are the most visual effects, they are merely a façade for interesting synergistic effects between SWNTs, TEMs, and the polymer matrix. Just as microsphere expansion causes macroscopic dimensional changes, expansion also alters loading distribution within the composites. To examine these effects, we looked at engineering stress (σ_e) versus engineering strain (ϵ_e) for an initial and expanded 0.3 wt% SWNT, 31.2 wt% TEM sample (Figure 6a). Because expansion induced volume increase (and correspondingly cross-sectional area increase) was due to void generation in the TEMs, the initial (unexpanded) area provides a reasonable value to use for both initial and expanded stress calculations. Interestingly, not only did the composites exhibit elastic stress responses in the initial (unexpanded) state, but they also followed Hooke's law ($\sigma_e \approx E_{ee}$) up to ~25% strain. After microsphere expansion however (upper curve), significant variations in composite strength existed and Hooke's law applied in a much smaller region, reaching the proportional limit at ~1% strain. Expansion of a 0.3 wt% SWNT, 31.2 wt% TEM composite resulted in a remarkable 675% increase in Young's modulus (E) as compared to the same wt% unexpanded sample (4.7 MPa initial, 37 MPa expanded), greater than most nanotube/polymer composites to date [33]. Furthermore, microsphere expansion also transformed the classic elastic stress-strain responses seen in the unexpanded composites into something more indicative of a plastic material. Hence, we refer to expanded composites as "plastic-like".

After initial fabrication, carbon nanotubes were randomly oriented and untensioned, resulting in minimal effect on elastic properties. However, microsphere-induced expansion and subsequent thin film formation in composites was observed to result in nanotube tensioning. Figures 6b and 6c are SEM images of 0.3 wt% SWNT, 31.2 wt% TEM samples at 40% strains. Crease lines imparted from the polymer onto the TEMs are clearly visible in Figure 6b, with several circled for clarity. Figure 6c shows a polymer-covered SWNT stretched across an expanded microsphere acting as a nanotether and providing strength to the expanded composite. Additional examples are shown in Figures 7a and 7b, which are SEM images clearly showing carbon nanotubes acting as tethers in an expanded composite. While still randomly oriented, it is believed that nanotube tensioning will result in enhanced load transfer. Furthermore, due to random orientation, the strengthened bulk composites will retain beneficial isotropic properties, vice anisotropic properties typically associated with aligned carbon nanotube composites [34]. These results are supported by past reports that show composites with aligned as opposed to random nanotube distributions are three times more effective as reinforcement materials [35]. Expansion-induced tensioning of carbon nanotubes has not been reported in previous studies and could represent a paradigm in stimuli-responsive composites.

4. Electrical changes due to shifting nanotube junctions

Effects of microsphere expansion are not limited solely to transformations in mechanical properties. Because of SWNTs' 1D-morphology, microsphere expansion-induced rearrangement of nanotube junctions causes corresponding electrical property shifts. IR-induced TEM expansion was used to alter amount of overlap, or electrical junctions, between adjacent SWNTs. Composite samples were exposed to 45 s of IR point source illumination [850 nm light emitting diodes (LEDs)] while continuously monitoring resistance and expansion rate (Figure S1 in the supplementary information presents test setup). The ratio of post-expansion (R_f) resistance to initial (R_0) resistance (R_f/R_0) as a function of SWNT loading (represented by resistivity, ρ) was utilized to evaluate electrical relationships. Note that low ρ results from high SWNT wt%, and vice versa. In all experiments, TEM loading was kept at 31.2 wt%, while SWNT ratios were varied. Intriguingly, we found R_f/R_0 exhibited four different wt% dependent electrical responses,

including becoming *more* conductive, *less* conductive, *transitioning* from conductive to insulating, or *remaining* insulating.

Figure 8a is a plot showing R/R_0 versus initial sample resistivity. Near the plot center, a percolation threshold region is shown as the vertical pink bar; resistivities lower than this are conductive, and higher are insulating. At high $w\%$ (low ρ), SWNT loading is much greater than the percolation threshold. Here (region 1), TEM expansion and subsequent nanotube junction rearrangement results in composites becoming *more* conductive ($R/R_0 < 1$). As SWNT loading lowers and ρ increases (region 2), amount of conductive overlap between adjacent nanotubes decreases as the microspheres expand. Even after expansion, however, there is still enough nanotube contact to retain conductivity; therefore, region 2 loading results in samples becoming slightly *more* resistive and therefore *less* conductive ($1 < R/R_0 < 10$). As SWNT loading is further lowered to just greater than the percolation threshold (region 3), microsphere expansion again stretches junctions between adjacent nanotubes. SWNT loading is low enough, however, that as microspheres expand, electrical contact between nanotubes is either broken or greatly reduced. This reduction in contact area results in substantial resistance increase ($R/R_0 > 10$). Expansion of these composites can essentially be thought of as an *off* switch. Finally for insulating composites where SWNT loading is less than percolation threshold (region 4), there was no observed change in electrical properties. Conductive sample data was fit to the exponential function $R/R_0 = 0.8e^{0.15\rho}$ while insulating data fit to $R/R_0 = 1$.

In addition to tunable R/R_0 resistance relationships, distinct time-dependent (and IR illumination-induced) resistivity patterns were observed. Figures 8b–8d show change in resistance (plotted as R/R_0) versus time for the first three regions. Region 4 is not shown as there are no R/R_0 changes. Red lines indicate IR illumination signals. Prior to IR illumination *on*, resistance level is steady in regions 1–3 ($R/R_0 = 1$). At 20 s, IR LEDs are energized. Immediately for all three regions, IR-induced heating begins and thermally generated electron-hole ($e-h$) pair generation begins to occur in the conductive samples, resulting in resistance decrease (dip in R/R_0). As the composites quickly reach microsphere expansion temperature (~ 3 s), composite dimensions start to increase in the area of IR illumination. While $e-h$ pair generation continues to dominate, by ~ 5 s after illumination, composite expansion rate is significant enough to dictate response. For region 1, high SWNT loading, junction stretching plays a minor effect and only a slight bump up is seen before $e-h$ pair generation continues to dominate. For region 2, SWNT loading is lower, and junction stretching causes an increase in R/R_0 as microsphere expansion reduces SWNT conductive overlap. As expansion reaches $\sim 80\%$, $e-h$ pair again dominates and R/R_0 trend reverses. In region 3, TEM expansion causes a significant (or “open circuit” depending on $w\%$) reduction of nanotube junctions. Follow-on $e-h$ pair generation effect is not observed. After IR illumination is turned *off* (65 s) all regions show an increase in R/R_0 as $e-h$ pairs recombine and resistance increases to an overall higher steady state value.

We noticed two additional interesting effects. First, for the same IR illumination time and intensity, samples with higher SWNT $w\%$ exhibited larger regions of microsphere expansion. This expansion indicates that associated increase in composite thermal conductivity resulted in a larger portion of the sample expanding in response to IR point source heating. More concisely, as electrical and thus thermal conductivity increase, microsphere expansion transitions from local to global effect. Second, we noticed that the presence of nanotubes was required for a composite to exhibit IR-induced expansion as well as photon-induced resistance change. Regardless of illumination time, plain 31.2 $w\%$ TEM samples (0 $w\%$ SWNT) exhibited negligible expansion – indicating nanotubes were efficient at photon absorption and subsequent energy transduction, and required for IR-induced expansion (Figures 9a and 9b show relationship). It is remarkable that nanotubes

with diameters almost three orders of magnitude smaller than the microspheres result in IR-induced TEM expansion.

4.1. Electrical applications

Since R_f/R_0 is controllable via SWNT wt%, these results can be used for creating embedded thermally actuated polymer circuits or switches with dynamically controllable electrical properties. Expansion start and stop positions can be controlled via IR modulation or selection of TEMs with either higher or lower expansion temperatures. A TEM/SWNT/PDMS circuit can be embedded within a larger plain PDMS structure, heating and subsequent expansion will only occur within the patterned circuit (IR absorption by the SWNTs [36]), while the bulk PDMS (optically clear [37]) remains cool (Figure 10).

4.1.1 Embedded circuit response calculations—While many different combinations are possible, the following calculations show an example of using IR-induced expansion of the embedded parallel resistor network shown in Figure 10 to either *raise*, *lower*, or *maintain* total resistance. We assume a circuit fabricated with two TEM-based resistors (R_1 and R_2) of identical microsphere wt% but different nanotube loading. Initially, total resistance of the circuit (R_{total}) is given by equation (3).

$$R_{total} = \frac{R_1 R_2}{R_1 + R_2} \quad (3)$$

Because we want the circuit to respond as described, careful resistor selection and design is required. Based on results from Figure 8a, R_1 will be chosen with a SWNT wt% that falls into region 1, likewise R_2 will be from region 2. Because region 1 selection results in $R_f/R_0 < 1$ when resistor R_1 (and R_1 only) is subjected to IR-induced expansion, R_1 and therefore R_{total} will decrease. Similarly, since region 2 results in a $1 < R_f/R_0 < 10$, IR illumination of R_2 (and R_2 only) will result in an associated rise in R_{total} . If both R_1 and R_2 are illuminated, the circuit can be balanced such that expansion-induced resistance changes cancel each other out, and R_{total} remains constant.

4.1.2 Selection of SWNT wt%—Figure 8a gives us equation (4), which rearranged to solve for ρ yields equation (5).

$$R_f/R_0 = 0.8e^{0.15\rho} \quad (4)$$

$$\rho = \frac{1}{0.15} \ln\left(\frac{R_f}{0.8R_0}\right) \quad (5)$$

In order to create a balanced circuit, we will chose R_1 such that $R_f/R_0 = 0.9$ (region 1), and R_2 such that $R_f/R_0 = 1.125$ (region 2). Solving for ρ for each resistor results in ρ of 0.785 k Ω -m 12 (R_1) and 2.273 k Ω -m (R_2). Equation (6) is the ρ -wt% relationship derived from our evaporative dispersion method (Figure 2b). Rearranging to solve for wt% yields equation (7).

$$\rho = 1.7 \times 10^{-5} e^{\left(\frac{2.75}{wt\% + 0.025}\right)} + 0.2 \quad (6)$$

$$wt\% = \frac{2.75}{\ln\left(\frac{\rho - 0.2}{1.7 \times 10^{-5}}\right)} - 0.025 \quad (7)$$

Solving for R_1 and R_2 gives loadings of 0.24 and 0.21 wt%, respectively.

4.1.3 Designing R_1 and R_2 for a balanced circuit—When both resistors are expanded, we want the circuit to maintain its original R_{total} . While the two resistors have different R_f/R_0 and thus different ρ values, to achieve a balanced response we need equal original resistances ($R_{10} = R_{20}$). Additionally, we impose a constraint of equal cross-sectional areas ($A_1 = A_2$). Setting R_1 and R_2 equal to each other [equation (8)], substituting Pouillet's law [equation (9)], and solving for a length relationship yields equation (10).

$$R_{10} = R_{20} \quad (8)$$

$$\rho_1 \frac{L_1}{A} = \rho_2 \frac{L_2}{A} \quad (9)$$

$$L_1 = 2.9L_2 \quad (10)$$

Therefore, resistor R_1 should be comprised of 0.24 wt% SWNT, 31.2 wt% TEM, and length $2.9L_2$. Resistor R_2 should be 0.21 wt% SWNT, 31.2 wt% TEM, and length L_2 .

4.1.4 Circuit response: IR illumination of R_1 only—With resistor parameters determined, evaluate circuit response upon expansion of R_1 only. Note that since $R_{10} = R_{20}$, initial total resistance [equation (3)] simplifies to $R_{total,0} = 0.5R_0$. Additionally, because of our region 1 selection, we know $R_{1f}/R_0 = 0.9$. Therefore $R_{1f} = 0.9R_0$. Substituting this into equation (3) and solving yields equations (11) and (12):

$$R_{total,f} = \frac{(0.9R_0)R_2}{(0.9R_0) + R_2} \quad (11)$$

$$R_{total,f} = 0.47R_0 \quad (12)$$

Since $R_{total,f} < R_{total,0}$, illumination of R_1 only causes a *decrease* in overall circuit resistance.

4.1.5 Circuit response: IR illumination of R_2 only—Similar to preceding calculations, circuit response upon expansion of R_2 only is determined. Because of our region 2 selection, we know $R_{2f}/R_0 = 1.125$, therefore $R_{2f} = 1.125R_0$. Again, substituting this into equation (3) and solving yields equations (13) and (14):

$$R_{total,f} = \frac{R_1(1.125R_0)}{R_1 + (1.125R_0)} \quad (13)$$

$$R_{total,f} = 0.53R_0 \quad (14)$$

Since $R_{total,f} > R_{total,0}$, illumination of R_2 only causes an *increase* in overall circuit resistance.

4.1.6 Circuit response: IR illumination of both R_1 and R_2 —The final possible circuit response is obtained when both R_1 and R_2 are IR expanded. Substituting known values into equation (3) and solving yields equations (15) and (16):

$$R_{total,f} = \frac{(0.9R_0)(1.125R_0)}{(0.9R_0)+(1.125R_0)} \quad (15)$$

$$R_{total,f} = 0.5R_0 \quad (16)$$

Since $R_{total,f} = R_{total,0}$, illumination of both R_1 and R_2 serves to *maintain* overall circuit resistance.

5. Outlook

Even though carbon nanostructure/TEM composites only allow for one-time expansion/actuation, the innovative combination of filler materials in an elastomer matrix and resulting binary set of material properties presents a plethora of research and industrial applications. Possible applications encompass fields such as structural health monitoring of aircraft [38] and ships [39], deformable elements for flight control surfaces [40], deformable mirror and antennae surfaces on spacecraft [41], strain sensing for roads and bridges [42], machinery vibration control systems [43], and biomedical applications including micropumps [44] and targeted drug delivery [45].

Elastic to plastic-like transformation allows for incorporation of sensing and actuation into a single coherent functional material thereby minimizing complexity and maximizing reliability. Furthermore, benefits of IR-induced microsphere expansion include wireless actuation, electromechanical decoupling (and therefore low noise), and massive parallel actuation of device arrays from a single light source. Focused IR illumination can be used to expand a specific area or the entire composite. Ability to pattern various filler compositions into a single polymer skin allows for a diverse set of properties (such as regions of variable expansion, conductivity, and strength) in one continuous composite, and then change these properties on-demand for structural and/or electrical components. For example, thin unexpanded flexible elastic polymer films can be incorporated into vehicle and/or equipment skins, and later expanded to provide on-demand structural elements preventing system failure. In biomedical applications, carbon nanostructure/TEM composites provide a possible stent material. Although TEMs cause overall system expansion, contractive forces can be obtained through selective microsphere patterning (Figures 11 and 12). In applications where volume is critical, such as aerospace and space travel, thin elastic polymer films can be fabricated (Figure 13a) and subsequently rolled-up for shipping or launch. Once on station, these films can be expanded (Figure 13b) to function as electrical, mechanical, and structural components. Finally, such composites could be highly useful in lab-on-a-chip, flexible bioelectronics and sensor applications. Flexible skins could include microfluidic channels that could expand and increase in volume on demand to create reaction chambers for live analysis of captured rare cells such as circulating tumor cells.

6. Experimental

Raw materials

TEMs (Expancel 461 DU 20) were obtained from AkzoNobel. Depending on hydrocarbon and outer shell material selection, commercially available TEMs have expansion temperatures ranging from 100 – 200°C, initial (unexpanded) diameters as small as 6 μm, and final (expanded) diameters as large as 150 μm. The TEMs chosen for this study consisted of a poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate) acrylic copolymer shell encapsulating an isobutane liquid hydrocarbon. Unexpanded SEM images (Figure 1b) and diameter measurements were taken on loose TEMs deposited on a silicon

wafer. TEMs were then thermally expanded at 125°C for 10 min, and SEM images (Figure 1c) and diameter measurements taken again. In each case, a sample size of 500 microspheres was used to determine average diameter and standard deviation. Sylgard 184 silicone elastomer (Fisher Scientific) was chosen as the matrix because this polymer is commonly used in industrial/scientific research and biocompatible. SWNTs (>99% purity) were obtained from Cheaptubes.com, primarily selected as their small diameters (1–2 nm) and long lengths (3–30 µm) were found to have several beneficial properties over other graphitic carbon forms initially tested, including high aspect ratios and ability to achieve conductivity in resulting composites at a relatively low *wt%* loading.

Evaporative mixing fabrication

A 1 mg/mL concentration SWNT/ isopropanol (IPA) solution was sonicated for ~4 h. Separately, PDMS base compound was heated to 160°C, while a magnetic stir bar (60 rpm) provided agitation. Approximately ~1 mL/min of SWNT/IPA solution was added to the PDMS mixture. As the IPA boiled/evaporated off, dispersed SWNTs were transferred to the PDMS base compound. After securing SWNT/IPA addition, the mixture was heated for additional 2 h (~12 h total heating time). The PDMS base compound/SWNT mixture was then removed from heat and allowed to cool. The mixture was divided and diluted with pristine PDMS base compound (which also went through the evaporative mixing process, but with plain IPA – no SWNTs) as necessary in order to obtain desired lower *wt%* concentrations. As opposed to the SWNTs that were difficult to disperse, TEMs are well suited for shear mixing. Additionally, as evaporative mixing would have resulted in microsphere expansion, TEMs were added to the mixture following dilution. Equations (17) and (18) were used to determine grams of SWNTs and TEMs needed, respectively (m_{SWNT} and m_{TEM}), depending on *wt%* desired (m_{base} and m_{cross} are amount of PDMS base and crosslinker).

$$m_{SWNT} = \frac{SWNT_{wt\%}(m_{base} + m_{cross})}{(100\% - SWNT_{wt\%} - TEM_{wt\%})} \quad (17)$$

$$m_{TEM} = \frac{TEM_{wt\%}(m_{base} + m_{cross} + m_{SWNT})}{(100\% - TEM_{wt\%})} \quad (18)$$

Crosslinker was added to the mixture at a ratio of 10:1 (PDMS base compound/crosslinker) and shear mixed for a further ~5 min. Finally, mixtures were placed in a vacuum chamber and degassed for ~30 min to removed trapped air bubbles.

Spin coating

Standard 50 mm × 75 mm microscope slides were cleaned and dried. SWNT/TEM/PDMS was then deposited onto the slides, and spun to achieve nominal 300 µm thick films (various spin speeds were used due to different mixture viscosities). In order to not expand the microspheres, spin-coated sliders were polymerized at 65°C for 12 h. As SWNT *wt%* increased, reliability of spin casting to produce consistent film thickness diminished. Therefore, SWNT composites were limited to <0.45 *wt%* (this issue was not noticed with TEMs). Following polymerization, composites were allowed to cure for an additional 12 h at room temperature prior to testing.

Expansion testing

For expansion testing, in order to minimize measurement errors, relatively large samples (50 mm diameter × 5 mm height) were fabricated. After polymerization and removal from molds, mass and initial dimension measurements were taken. Next, samples were thermally

expanded in an oven at 125°C for 10 min and post expansion measurements made. Percent volume ($V\%$) change was calculated according to equation (19).

$$V\% = 100\% \times \left(\frac{V_{\text{expanded}} - V_{\text{initial}}}{V_{\text{initial}}} \right) \quad (19)$$

Similarly, percent change in diameter ($d\%$), and density ($\rho\%$) were calculated. Theoretical volume and density curves (Figures 4a and 4b) were calculated according to simplified equations (4) through (6), where $V\%_{\text{theory}}$ is theoretical percent change in volume, m_{PDMS} is mass of the PDMS component (including crosslinker), m_{total} is total composite mass, ρ_{PDMS} and ρ_{TEM} are PDMS and unexpanded TEM densities, r_i and r_f are initial and expanded TEM diameters, and $\rho_{i \text{ theory}}$ and $\rho_{f \text{ theory}}$ are initial and expanded composite densities, respectively.

$$V\%_{\text{theory}} = 100\% \times \frac{\left(\frac{r_f}{r_i}\right)^3 - 1}{\left(\frac{m_{\text{PDMS}}\rho_{\text{TEM}}}{m_{\text{TEM}}\rho_{\text{PDMS}}} + 1\right)} \quad (20)$$

$$\rho_{i \text{ theory}} = \frac{m_{\text{total}}}{\frac{m_{\text{TEM}}}{\rho_{\text{TEM}}} + \frac{m_{\text{PDMS}}}{\rho_{\text{PDMS}}}} \quad (21)$$

$$\rho_{f \text{ theory}} = \frac{m_{\text{total}}}{\frac{m_{\text{TEM}}}{\rho_{\text{TEM}}} \left(\frac{r_f}{r_i}\right)^3 + \frac{m_{\text{PDMS}}}{\rho_{\text{PDMS}}}} \quad (22)$$

Mechanical testing

Stress-strain data was taken on a Rheometric Mechanical Analyzer (RMA, TA instruments-Waters LLC). Composites were strained to 25% over 200 s. Initial (unexpanded) composite sample dimensions were 40 mm × 6 mm. Similarly, expanded composite were cut with the identical dimensions and thermally expanded at 125°C for 10 min. In all calculations, initial (unexpanded) cross-sectional area was used, while test length was kept at 40 mm.

Electrical testing

A custom IR LED expansion test station was built that simultaneously illuminated both front and back of a 50 mm × 4 mm composite sample test sample. Total LED radiant flux was 1.8 W, and distance between sample surface and each LED was 10 mm. The entire test station was enclosed within a light isolated “black box”. Electrodes were connected to the top and bottom of each sample and supplied with 1 μ A source current for resistance measurements. A machine vision system monitored composite expansion in real time. Testing sequence for each sample consisted of 5 min stabilization time (which was averaged for R_0), followed by 45 s of IR illumination, and concluded with 5 min post illumination wait (averaged for R_p). Sequencing and data recording was controlled remotely with LabVIEW software, which logged resistance and expansion position measurements every 100 ms and 200 ms, respectively.

SEM spectroscopy

SEM imaging was conducted on a Zeiss SUPRA 35VP field emission scanning electron microscope. Composite and loose TEM samples were mounted/placed on silicon substrates unless otherwise noted.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Expanding microsphere overview

a, To-scale cutaway showing size relationship between initial and expanded microspheres.

b, SEM of loose unexpanded microspheres (average diameter of $7.1 \pm 1.9 \mu\text{m}$), **c**, SEM of

loose expanded microspheres (average diameter of $17.8 \pm 3.8 \mu\text{m}$).

Figure 2. Fabrication details and relationships

a, Evaporative mixing timeline. Approximate fabrication time is ~40 h, however, can vary depending on nanostructure dispersion difficulty (more difficult nanostructures require longer sonication time) and evaporative temperature (higher temperatures result in faster solvent evaporation and thus lower time, yet possibly results in some nanostructure boil off).

b, Plot of resistivity (ρ) versus SWNT wt% loading (data fit to a NIST MGH10 nonlinear regression equation). For the same matrix and reinforcing material, various dispersion methods can be applied in composite fabrication. Resulting ρ -wt% curves associated with each method will give a measure of relative dispersion method efficiency. Curves shifted up or to the right represent less efficient dispersion methods, while curves shifted to the left or down are more efficient.

Figure 3. Effects of microsphere expansion

a, SEM image showing smooth surface of the initial fabricated composites (0.3 wt% SWNT, 31.2 wt% TEM). **b**, SEM of the same composite sample after expansion, with microspheres clearly visible. **c**, Unexpanded TEMs exhibit little influence over bulk composite properties. **d**, The larger surface area associated with expanded TEMs, however, greatly inhibits polymer chain movement and results in macroscopic material property changes.

Figure 4. Expansion and density overview

a, Expansion versus TEM wt% plot including dimensional and volumetric curves. **b**, Density versus TEM wt% plot showing reduction between the initial and expanded composites. **c**, SEM cross-sectional image of the expanded composite, showing large cavities inside the microspheres as well as several polymer-coated SWNTs.

Figure 5. Volume and dimensional expansion plugs

Standard size plugs (45 mm diameter, 8 mm height) were used to determine expansion changes as a function of increasing TEM wt%. **a**, Initial (as-fabricated) expansion plugs, in the initial or elastic state. TEM loading levels from 5 wt% (top plug) to 45 wt% (bottom plug) were evaluated. **b**, Expanded, or plastic-like, plugs. A relationship between increased TEM loading and resulting volumetric increase is clearly visible. Also interesting to note, as TEM wt% increases, color change in the expanded composites is more noticeable compared to the initial plug. While wt% of all constituents remains constant, TEM expansion alters effective volumetric percentage. **c**, Relationship between volume percent and wt% for SWNT loading. Expanded (upper) curve illustrates volumetric increase (and thus density reduction) resulting from microsphere expansion.

Figure 6. Stress-strain overview

a, Composite stress-strain curve (0.3 wt% SWNT, 31.2 wt% TEM). Lower curve is initial (elastic) response, upper curve is expanded (plastic-like) response. **b**, SEM image of expanded composite (0.3 wt% SWNT, 31.2 wt% TEM) at 40% strain. Circled areas highlight several polymer-induced creases on the microspheres. **c**, SEM image of expanded composite (0.3 wt% SWNT, 31.2 wt% TEM) showing polymer-covered SWNT stretched across expanded TEM at strain of 40%. Nanotube is bridging bulk polymer on either side of the microsphere.

Figure 7. SWNTs imparting mechanical strength in expanded composites

a, b, Both SEM images show cross-sectional views of expanded composites (0.3 *wt%* SWNT, 31.2 *wt%* TEM). Polymer-coated SWNTs can be seen bridging, or acting as a nanotether, between expanded TEMs and bulk polymer matrix. Microsphere-induced expansion tensions nanotubes. This results in enhanced load transfer in expanded composites, forming the basis for increases in mechanical strength.

Figure 8. Electrical overview and response regions 1–3 (Region 4 not shown as insulating nature results in no change)

a. Plot of change in sample resistance (R_f/R_0) versus initial resistivity. Response regions (1–4) as well as percolation threshold are indicated on the graph. **b–d.** Detail resistance changes of the first three regions versus time.

Figure 9. Relative IR-induced expansion in various wt% SWNT composites

a, Amount of IR-induced expansion in 0, 0.1, and 0.3 wt% SWNT composite samples (all 31.2 wt% TEM). Increasing relative expansion area shows SWNTs are efficient at IR absorption and subsequent thermal transduction to polymeric chains. As nanotube loading increases, increased thermal conductivity in the composites results in a larger expansion region (starts transitioning from local effect to global one). IR illumination (850 nm) is initiated at time $t = 0$ s. **b**, Image showing IR-expanded composite test samples. SWNT wt% increases from left (no nanotubes) to right (0.3 wt% nanotubes). All strips shown are 31.2 wt% TEM and were subjected to identical IR test conditions. Inclusion of even a small amount of SWNTs allows for some expansion, as is shown when comparing the 0.01 wt% (minor expansion area) to the 0 wt% (no expansion).

a Fabrication sequence

b Final circuit

Figure 10. Embedded circuit fabrication sequence

Sequence presented shows steps required to embed a simple parallel resistor circuit into a flexible polymer skin. **a**, In step 1, a lower encapsulation layer is deposited. Note that arbitrary colors are used to help illustrate different layers in the fabrication process. Next (step 2), SWNT/PDMS with nanotube loading greater than the percolation threshold is deposited to form conductive traces (note equivalent circuit diagram shown in this step). In step 3, two separate regions of different wt% SWNT/TEM/PDMS are patterned forming resistors R_1 and R_2 (note circuit diagram in this step as well). A filler layer (step 4) of plain PDMS is used to equalize the substrate and circuit feature height. Finally in step 5, an upper encapsulation layer seals the circuit. **b**, Rendering of the SWNT/TEM circuit inside of its transparent plain PDMS shell. IR illumination of the structure will cause heating only in the polymer region containing SWNTs (and subsequent microsphere expansion in resistors R_1 and R_2). Upon exposure to focused IR illumination, circuit electrical properties can be altered by expanding either R_1 , R_2 or both R_1 and R_2 . Using results obtained from Figure 2 to tune resistors' electrical responses, this circuit can be designed such that depending on

which resistor element(s) are IR illuminated, the circuit can become *more* conductive, *less* conductive, or *maintain* the same conductance.

Figure 11. Assorted applications

Ternary combination of SWNTs, TEMs, and PDMS allows for design of independently controllable regions of variable mechanical strength, electrical conductivity, and expansion in the same polymer composite. **a**, For example, thin-patterned polymer films can be incorporated into vehicle and/or equipment skins, and expanded to provide on-demand structural elements to prevent system failure. **b**, In biomedical applications, carbon nanostructure/TEM composites provide a possible new stent material. An unexpanded composite on a mold is shown at the left of the figure (future molds can incorporate IR LED elements). These stents can be inserted into region of interest, and LEDs energized to induce

expansion. With the composite expanded, the LED mold is then retracted. **c**, Finally in actuation applications even though the TEMs cause an overall system expansion, contractive forces can still be obtained. This image shows a thin polymer film patterned to curl up on itself, thus generating a contractive force.

a Fabrication sequence

b Expansion detail

Figure 12. Contracting skin fabrication sequence

Four layers are required to achieve the contractive response of the contracting skin shown in Figure 12(c). **a**, First, a lower expansion layer comprised of SWNT/TEM/PDMS is patterned. When heated, these areas will expand. Next, a lower filler layer of SWNT/PDMS (no TEMs) is placed in the regions between expanding strips. When heated, these filler sections will not expand. Third, an upper expansion layer is patterned to align on top of the lower filler layer. When the skin is heated and microspheres expand, these two stacked layers will act as a bimetallic strip, inducing a curling force in the skin. Finally, an upper filler layer is deposited in order to duplicate curling in the opposite direction and obtain a contractive expanding response. **b**, Rendering showing resulting initial and expanded composite skins.

Figure 13. Application example showing use of patterned TEM regions to serve as structural component

a, As-fabricated polymer sheet shown in elastic (unexpanded) state. **b**, Same polymer sheet, but with expanded (plastic-like) honeycomb-patterned TEM regions.