Supplementary Information for

Elastomers Filled with Exfoliated Graphite as Compliant Electrodes

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Reference numbers in the Supplementary Information refer the same references as in the main text.

1. Comparison of PDMS/EG to Similar Compliant Electrode Materials

Table S1 specifies the host material and provides the references for the data in Figure 5 in the main text.

Table S1. Host materials and references for Figure 5 in the main text. Reference numbers are those used in the main text.

Filler material	Host material	Reference
SWNT	PDMS	[15]
SWNT	epoxy	[18]
SWNT	polystyrene	[14]
SWNT	PEDOT-PSS	[21]
MWNT	PDMS	[3]
MWNT	epoxy	[17]
MWNT	polystyrene	[11]
MWNT	polyurethane-urea	[10]
EG	polystyrene	[12]
EG	NBR	[5]
silver particles	PDMS	[1]
CB	polystyrene	[16]
CB	polyurethane	[2]

2. Basis of Using EG for Conductive Composites with Low Modulus

There has been theoretical work on predicting the mechanical and electrical properties of composites. Starting with the mechanical properties, the Guth equation [30] predicts a strong increase in the modulus of the composite with increasing aspect ratio and volume fraction of the filler material:

(1) $E = E_0 (1 + 0.67 f\varphi + 1.62 f^2 \varphi^2)$,

where f is the filler aspect ratio, φ is the filler volume fraction, E_0 is the modulus of the unfilled polymer, and E is the modulus of the composite. Similarly, the Halpin-Tsai model [31] predicts that the modulus of composites with fiber-shaped fillers will be much higher than that of the host polymer:

(2) $E = E_0 (1 + 2 f\varphi) / (1 - \varphi)$.

The dependences of the two models on aspect ratio are shown in Figure S1. From equations 1 and 2, it would *not* appear to be promising to use EG, which has a high aspect ratio. This conclusion has been supported in systems such as polymer/fiber composites and elastomers filled with carbon nanotubes.
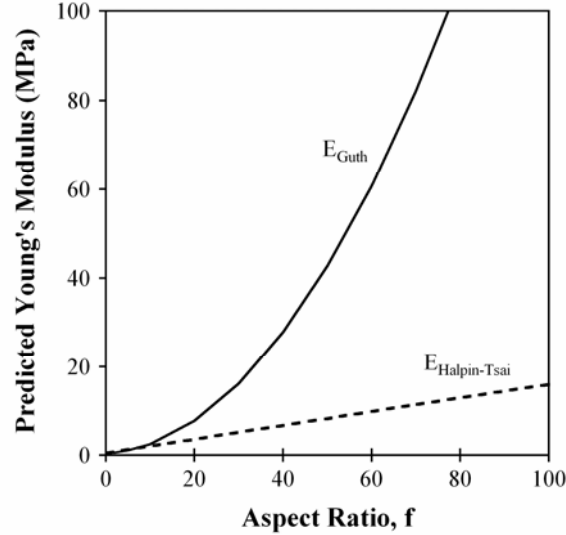

Figure S1. Guth and Halpin-Tsai model predictions for the Young's modulus as a function of aspect ratio f for $E_0 = 0.44$ MPa and $\varphi = 0.15$.

Turning to the electrical properties, Celzard *et al.* [32] developed a model to predict the percolation threshold for composites with randomly-oriented, disk-shaped particles in an insulating matrix. They concluded that there would be a linear relationship between the percolation threshold and the aspect ratio:

(3) $\varphi_C \propto t/r,$

where φ_C is the critical concentration at which a conductive pathway is formed (in vol%), t is the particle thickness, and r is the particle radius. This equation shows that a percolative network is formed at lower loadings for particles with higher aspect ratios, with a factor of 10 reduction in loading for each factor of 10 reduction in particle thickness. Thus, graphene should form a conductive material at much lower loadings than graphite. Based on these relationships, the question is, then, does the material become conductive before the modulus rises significantly?

Figure S2 shows the conductivity and Young's modulus in our composites as a function of EG loading. Surprisingly, their stiffness did *not* increase significantly with loading, deviating from both the Guth and Halpin-Tsai equations. This is most likely due to the formation of voids in our material (Figure 8b), which neither model takes into account.
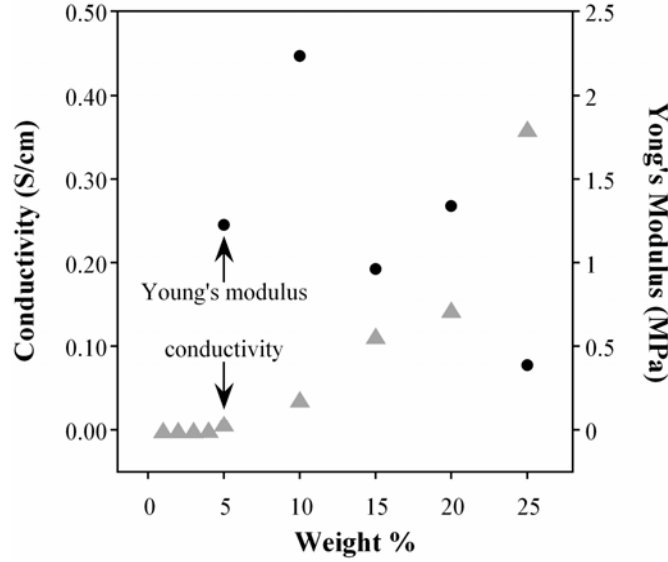
Figure S2. Conductivity and Young's modulus vs. weight % of EG for PDMS/EG composites.

3. Geometry Calculations

To ensure proper calculation of electrical conductivity (from the measured voltage, known current, and original dimensions), the changing dimensions of the sample under strain should be accounted for. Sample dimensions for a given strain were calculated from known mechanics of materials equations to conserve the sample volume as follows.

(4) $\quad L_{actual} = L_0 + L_0\,\varepsilon_x$

(5) $\quad W_{actual} = W_0 - \{W_0\,[1 - (1 + \varepsilon_x)^{-\upsilon}]\}$

(6) $\quad t_{actual} = t_0 - \{t_0\,[1 - (1 + \varepsilon_x)^{-\upsilon}]\}$

L_0, W_0, and t_0 are the initial length, width, and thickness (respectively), L_{actual}, W_{actual}, and t_{actual} are the calculated length, width, and thickness (respectively), υ is Poisson's ratio (assumed to be 0.5), and ε_x is the strain in the x-direction. A Poisson's ratio of 0.5 is found in perfectly incompressible materials, an assumption commonly used for polymers above the glass transition temperature at small strains.

The resistance R of the PDMS/EG samples were calculated using Ohm's law:

(7) $\quad R = V / I,$

where V was the potential difference measured across the inner pair of electrodes in Volts and I was the current applied across the outer pair of electrodes in Amperes.

Resistance is related to resistivity ρ by

(8) $\quad R = \rho\,L/wt.$

Electrical conductivity is defined as

(9) $\quad \sigma = 1/\rho = L/Rwt.$

The conductivity was thus calculated by combining equations 4-7 and 9:

(10) $\sigma = L_{actual} / (W_{actual} \cdot t_{actual} \cdot R)$,

where V was the voltage drop between the two innermost contact pads and I was the current applied to the outermost two contact pads.

Example

If the sample is at rest ($\varepsilon_x = 0\%$) and $L_0 = 1.0$ cm, $W_0 = 1.0$ cm, $t_0 = 0.01$ cm, and $R_0 = 100$ Ω, then $\sigma_0 = 1$ S/cm. If the sample is then strained 50% ($\varepsilon_x = 0.5$) and R increases to 500 Ω then:

$L_{actual} = L_0 + (L_0 \cdot \varepsilon_x) = 1.0 + (1.0 \cdot 0.5) = 1.5$ cm,
$W_{actual} = W_0 - (W_0 \cdot (1 - (1 + \varepsilon_x)^{(-\upsilon)})) = 1.0 - (1.0 \cdot (1- (1 + 0.5)^{(-0.5)})) = 0.816$ cm,
$t_{actual} = t_0 - (t_0 \cdot (1 - (1 + \varepsilon_x)^{(-\upsilon)})) = 0.01 - (0.01 \cdot (1 - (1 + 0.5)^{(-0.5)})) = 0.00816$ cm,

and

$\sigma_{actual} = 0.45$ S/cm.

If only the changing length were being considered in these calculations, the resulting conductivity would be calculated as only 0.3 S/cm.

4. Elastic Behavior of the Composites

To probe the elastic behavior and determine the Young's moduli of the composite samples, stress-strain tests were performed. The Young's moduli reached a steady state after the first few strain cycles for loadings below 15 wt%, as shown in Figure S3a for a 5 wt% PDMS/EG sample. However, for samples containing 20 and 25 wt%, the modulus kept decreasing with increasing strain cycle number, as shown in Figure S3b.
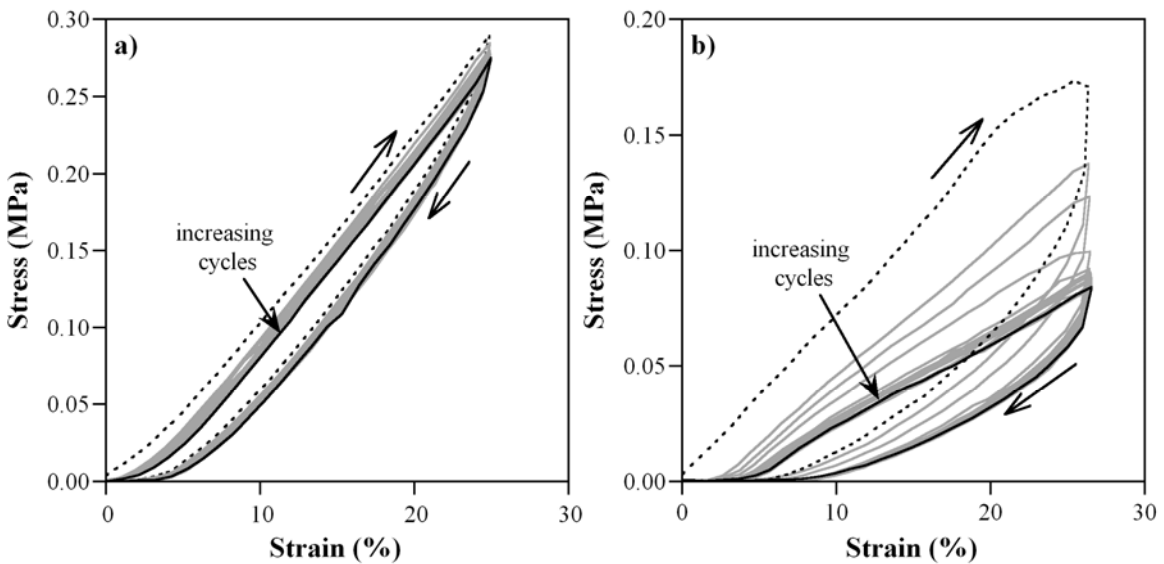

Figure S3. a) Stress vs. strain for a sample with 5 wt% loading. b) Stress vs. strain for 25 wt% loading.

5. Sample Fabrication

The fabrication process for forming an individual PDMS/EG sample was as follows.
1) In a 23 ml glass vial, combine 0.05 g of the filtered/dried EG with 6.0 g hexane.
2) Sonicate the solution until the worm-like structures have broken apart (3+ hrs).
3) Evaporate off 4.5 g of the hexane in the mixture on a hot plate at 150 °C.
4) Add the desired amount of PDMS resin and sonicate for 30 min.
5) Add the corresponding amount of PDMS curing agent and sonicate for 10 min.
6) Cast the solution in a polyethylene dish and vacuum desiccate for 2 hrs.
7) Bake on a hot plate at 75 °C overnight.
8) Cut the sample into strips 38 mm long and 10 mm wide.
9) Attach a 14 mm length of the sample to 1" x 3" x 1.2 mm glass slides using a photo-curable adhesive (such as Loctite 3108) leaving 24 mm of the sample unattached. This is the fixed end of the sample.
10) Glue a 16 mm long, 12 mm wide transparency sheet to the unattached end of the sample so that 2 mm of the transparency sheet remains unattached and there are 1 mm edges on either side of the 10 mm wide sample. This will leave a 10 mm wide, 10 mm long section of the PDMS/EG sample (active area) between the glass slide and the transparency sheet. This is the free end of the sample.
11) Punch a small hole in the center of the 2 mm unattached area of the transparency sheet. Thread this hole with one end of a piece of suture thread and tie off with a knot. Connect the other end of the thread to the hole in the force/strain transducer arm the same way.
12) Add 4 electrical connections for 4-point probe resistance measurements by painting conductive silver epoxy (Chemtronics, CircuitWorks CW2400) across the surface of the PDMS/EG sample. The contact pads should be 2 mm wide and have a 10 mm spacing between them. Before the epoxy sets, place 10 mm of a 200 mm length of fine stainless steel wire (43 gauge, California fine Wire co.) into each of the pads; 200 mm is long enough not to impede the stress/strain tests. Allow the silver epoxy to cure for 24 hrs.

6. Power Law Model for Conductivity vs. Loading

Conductivity vs. loading data are often fit with a power law model [4, 8, 13, 14, 28, 41, 42]:

(11)
$$\sigma = \left(\frac{V - V_c}{1 - V_c} \right)^t,$$

where V is the volume fraction of the filler, V_c is the percolation threshold, and t is the critical exponent. Figure S4 shows such power law fits for both the strained and unstrained samples, giving $t = 3.0$ and 3.5, respectively.
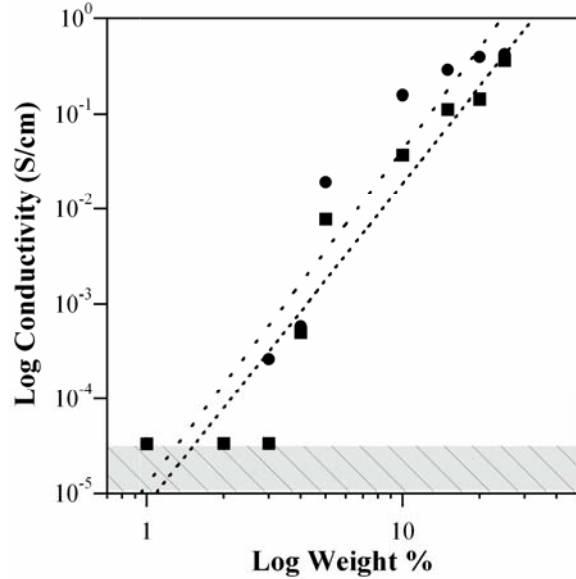
Figure S4. Power law fit to the conductivity vs. loading data, with the dotted line representing the fit for unstrained samples (squares) and the dashed line representing the fit for strained samples (circles). Each point represents one sample.

The exponent *t* has been postulated to depend on the dimensionality of the conductive network, with values ranging from 1.30 to 1.43 for two dimensional systems [10, 17, 43] and 1.5 to 2.0 for three dimensional systems [8, 10, 13, 17, 43-45]. Values of t > 2 (so called non-universal values) have also frequently been reported [8, 12-14, 22, 44]. Non-universal values of *t* have been attributed to high aspect ratio filler particle geometries (i.e. as found in CNTs and graphene) [13], the formation of voids in the material [14], and tunneling through insulating coatings on the particles [13, 44-47].

Some experimentally obtained values of *t* from prior work are compared to the results from this research in Table S2. The exponents range from 1.2 to 3.8 and appear to be uncorrelated with performance parameters such as conductivity and modulus. The merit of the critical exponent is therefore unclear. The values of *t* obtained in this investigation are similar to those reported for PS/EG, PMMA/EG, and PS/graphite composites.

Table S2. Critical exponents *t* for PDMS/EG compared with results from prior work on unstrained elastomers with conductive fillers.

Filler Material	Host Polymer	*t*	Reference
This Work			
EG	PDMS	3.50 3.00 (strained)	
Prior Work			
MWNT	epoxy	1.20	[17]
SWNT	epoxy	1.30	[18]
MWNT	polyvinylalcohol	1.33	[43]
graphite powder	PMMA	1.82	[13]
MWNT	polyurethane-urea	1.98 1.60 (strained)	[10]
SWNT	PS	2.20	[14]
EG	epoxy	2.50	[22]
EG	PS	3.07	[12]
EG	PMMA	3.47	[13]
graphite particles	PS	3.50	[44]
CB	ethylene-octene	3.80	[8]

The decrease in the exponent *t* after straining shown in Figure S4 was also observed in MWNT/polyurethane-urea elastomer composites [10]. In that work, the decrease was attributed to either a change in the dimensionality of the system or to a decrease in the width of the distribution of tunneling resistances [10]. Also, as mentioned earlier, the voids shown in Figure 8b may contribute to the high values of the exponent *t* found in the power law fit.