Multifunctional Graphene Polyimide Nanocomposites

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Nanotechnology Roadmap Technology Area 10

Graphene in Space, NASA’s Spitzer Space Telescope has spotted the signature of flat carbon flakes, called graphene, in space

https://ntrs.nasa.gov/search.jsp?R=20150010366 2020-03-22T04:25:06+00:00Z
Nanotechnology
Engineered Materials and Structures

Light Weight Materials

- Multifunctional
- Adaptive Materials
- Self Healing Materials

Development of nanostructured materials 50% lighter than conventional materials with equivalent or superior properties

Reduced Vehicle Mass

Boeing 787 composite aircraft
Copper mesh 4000 lb of weight

NGST ½-scale Sunshield Demonstration Model Deployment,
Cadogan, D. P. et al.

Meador, M., Files B., Li J., Manohara, H., Powell, D., Siochi, E.J. Nanotechnology Roadmap Technology Area 10
Nanoparticles:
- SWNT ~ 1315 m²/g
- DCNT ~ 700-800

Graphite and Graphene – Giem 2004
- Graphene ~ theoretical: 2600 m²/g, 700-1300 m²/g

Carbon nanofibers
- Alumina silicates – Fukushima, Toyota 1987
  - Montmorillonite ~ 725 m²/g
  - Magadiite, Laponite, Vermiculite

Magnetic Nanoparticles
- Organometallic physical crosslinkers
- POSS

Composite Nanoparticles
- Magnetic graphene
- Oxide graphene
Polyimide
High Performance Polymer

Aromatic polyimide:
- Low color
- Flexibility
- High thermal stability
- Dimensional stability

- Low dielectric constant
- High $T_g$
- Radiation resistance
- Low coefficient of thermal expansion

Satellite

General Ind.

Stiffness and modulus and reinforcement

Electrical performance and EMI shielding

Thermal performance and stability

Actuation and morphing

Multifunctional

Electronics and packaging

Quartz fabric–polyimide 815 °C

Continuous operating range between -65 °C to +357 °C

Polyimide Graphene Nanocomposites

Polyimide, thermal stability >500 °C, T_g > 200 °C, flexible and semi-transparent.

Thermal imidization:

- Mixing and dissolving equi-molar ratio diamine in anhydrous-NMP under dry N_2 followed by addition of dry anhydride and stirring for 24h in flame dried vessels.
- Then, increasing the temperature ~230 °C (NMP reflux) for 3h and precipitating in methanol and drying

Polyimide Graphene Nanocomposites

Electrical Performance

\[ \sigma_{DC} = \sigma_f \left[ \frac{(\phi - \phi_C)}{(1 - \phi_C)} \right]^t \]

Percolation

<table>
<thead>
<tr>
<th>Material</th>
<th>Vol. %</th>
<th>Max. Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically graphene PS</td>
<td>0.1</td>
<td>0.01 S/cm</td>
</tr>
<tr>
<td>PS Gr, Latex method</td>
<td>0.6</td>
<td>0.15 S/cm</td>
</tr>
<tr>
<td>PET graphene</td>
<td>0.47</td>
<td>0.021 S/cm</td>
</tr>
<tr>
<td>PC graphene, emulsion</td>
<td>0.14</td>
<td>0.512 S/cm</td>
</tr>
<tr>
<td>PC graphene, solution</td>
<td>0.38</td>
<td>0.226 S/cm</td>
</tr>
<tr>
<td>PS CCG</td>
<td>0.19</td>
<td>0.722 S/cm</td>
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</tbody>
</table>

Max. Conductivity

<table>
<thead>
<tr>
<th>Material</th>
<th>Max. Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT/nanocomposites</td>
<td>t = 1.2 – 2</td>
</tr>
<tr>
<td>CNF/polyimide</td>
<td>t = 3.1</td>
</tr>
<tr>
<td>PET graphene</td>
<td>t ~ 3.47 ± 0.64</td>
</tr>
<tr>
<td>PS graphene</td>
<td>t ~ 2.74 ± 0.2</td>
</tr>
</tbody>
</table>

Viet Hung Pham et al., J. Mater. Chem., 2011, 21, 11312
AC Electrical Performance

Broad band AC impedance spectroscopy

Extended pair approximation model

\[ \frac{\sigma(\omega)}{\sigma_{DC0}} = 1 + k \left( \frac{\omega}{\omega_c} \right)^S \]

<table>
<thead>
<tr>
<th>Vol.%</th>
<th>( \sigma_{DC0}, S/cm )</th>
<th>( \omega_c, Hz )</th>
<th>S</th>
</tr>
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<tbody>
<tr>
<td>0.03046</td>
<td>8.21e-9</td>
<td>150.47</td>
<td>0.499</td>
</tr>
<tr>
<td>0.3051</td>
<td>1.879e-6</td>
<td>7.027e3</td>
<td>0.647</td>
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<tr>
<td>0.6115</td>
<td>2.11e-4</td>
<td>1.241e5</td>
<td>0.446</td>
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</tbody>
</table>

\( S \sim 0.99 \rightarrow \) hopping
\( S \sim 0.72 \rightarrow 3D \) material
\( S \sim 0.58 \rightarrow \) anomalous diffusion in fractal cluster exist

Dispersion of graphene in polyimide

TEM

Conductive path

0.25 vol.%

1.1 vol.%

200 nm

500 nm
Temperature Dependence Conductivity

\[ \sigma = 0.2844T^{0.2177} \]

\[ T = 322.404\sigma^{4.6} \]

5 vol. % graphene polyimide
Addition of graphene resulted in composite reinforcement without adverse effect on the $T_g$.
Composites Nanoparticles
Thermal decomposition of Ni(acac)₂ in the presence of O-graphene

First-order reversal curve (FORC)
Controlled Directionality

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>B_x</th>
<th>B_y</th>
<th>B_z</th>
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<tbody>
<tr>
<td>A</td>
<td>1150</td>
<td>-1150</td>
<td>-237</td>
<td>-50</td>
</tr>
<tr>
<td>B</td>
<td>976</td>
<td>-948</td>
<td>475</td>
<td>50</td>
</tr>
<tr>
<td>C</td>
<td>440</td>
<td>-432</td>
<td>-55</td>
<td>-120</td>
</tr>
<tr>
<td>D</td>
<td>500</td>
<td>-520</td>
<td>-12</td>
<td>42.3</td>
</tr>
</tbody>
</table>

2.8 wt% Ni-Graphene polyimide nanocomposite
Anisotropic Properties

**Electrical properties**

- **Random Orientation**
- **Mild Magnetic field Orientation**
- **Strong Magnetic field Orientation**

Conductivity, S/cm

Graphene weight percent, %

- **In-plane in the magnetic field direction**
- **In-plane perpendicular to the magnetic field direction**

In-plane
Magnetic field
Anisotropic Properties

Mechanical properties

Graphene wt% vs. Tensile Modulus, MPa

- Neat Polyimide
- Highly oriented
- Medium Orientation
- Random Orientation

Stress

Graphene wt% vs. Tensile Modulus, MPa

Neat PI
Transmission Electron Microscopy

1.77 wt% Ni-graphene polyimide
90% parallel and 5% perpendicular
Conclusions

- Addition of graphene resulted in nanocomposites with high conductivity with a percolation as low as 0.036 vol.% and a maximum conductivity of 0.94 S/cm.

- Dynamic moduli of the nanocomposites increased with addition of graphene with no adverse effect on $T_g$ or flexibility.

- Magnetic graphene were synthesized enabled controlled orientation of graphene in magnetic fields.

- Ni-graphene/PI nanocomposites were obtained which has $\leq 2$ S/cm in-plane conductivity and insulating in the through-plane direction.

- Ni-graphene/PI nanocomposites exhibited increased modulus with increasing orientation.

- The orientation was verified by magnetic characterization and TEM studies.
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