Multifunctional Graphene Polyimide Nanocomposites

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Graphene in Space, NASA’s Spitzer Space Telescope has spotted the signature of flat carbon flakes, called graphene, in space.
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
Composites: Micro to Nano

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.
Electronics
Stiffness and modulus and reinforcement
Actuation and morphing
Electrical performance and EMI shielding
Thermal performance and stability

• Space
• Aero
• Electronics

Quartz fabric–polyimide 815 ºC

Continuous operating range between -65 ºC to +357 ºC

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**

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

<table>
<thead>
<tr>
<th>Percolation</th>
<th>Max. Conductivity</th>
<th>CNT/nanocomposites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically graphene PS nanocomposites</td>
<td>0.1 vol.%</td>
<td>t = 1.2 – 2</td>
</tr>
<tr>
<td>PS Gr, Latex method</td>
<td>0.6 wt%</td>
<td>CNF/polyimide</td>
</tr>
<tr>
<td>PET graphene</td>
<td>0.47 vol.%</td>
<td>t ~ 3.1</td>
</tr>
<tr>
<td>PC graphene, emulsion</td>
<td>0.14 vol.%</td>
<td>PET graphene</td>
</tr>
<tr>
<td>PC graphene, solution</td>
<td>0.38 vol.%</td>
<td>t ~ 3.47 ± 0.64</td>
</tr>
<tr>
<td>PS CCG</td>
<td>0.19 vol.%</td>
<td>PS graphene</td>
</tr>
<tr>
<td></td>
<td></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>
</thead>
<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>
</tr>
<tr>
<td>0.6115</td>
<td>2.11e-4</td>
<td>1.241e5</td>
<td>0.446</td>
</tr>
</tbody>
</table>

S ~ 0.99 -> hopping
S ~ 0.72 -> 3D material
S ~ 0.58 -> anomalous diffusion in fractal cluster exist

Dispersion of graphene in polyimide

TEM

Conductive path

Graphene vol. %

0.25 vol.%

1.1 vol.%

Conductivity, S/cm

Graphene vol. %

10 micron

200 nm

500 nm
Temperature Dependence Conductivity

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

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

5 vol. % graphene polyimide
Thermal and Mechanical Properties

Addition of graphene resulted in composite reinforcement without adverse effect on the $T_g$
**Controlled Property Direction**

**Ni-Tethered Graphene**

Composites Nanoparticles

Thermal decomposition of Ni(acac)$_2$ in the presence of O-graphene

![Graph showing 2theta, degree and d spacing](image)

<table>
<thead>
<tr>
<th>2theta, degree</th>
<th>d spacing, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.496</td>
<td>2.036</td>
</tr>
<tr>
<td>51.841</td>
<td>1.764</td>
</tr>
<tr>
<td>76.436</td>
<td>1.246</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>hkl</th>
<th>Ni, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>2.035</td>
</tr>
<tr>
<td>200</td>
<td>1.763</td>
</tr>
<tr>
<td>220</td>
<td>1.243</td>
</tr>
</tbody>
</table>

2theta, degree: 26.06, 62.58

<table>
<thead>
<tr>
<th>C, d spacing, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.419, 1.484</td>
</tr>
</tbody>
</table>

Ni: 2.035, 1.763, 1.243

hkl: 111, 200, 220

**First-order reversal curve (FORC)**

Hc = 17.34 mT
Ms = 4.795 Am$^3$/Kg
Controlled Directionality

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>B_x</th>
<th>B_y</th>
<th>B_z</th>
</tr>
</thead>
<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

- Conductivity, S/cm
- Random Orientation
- Mild Magnetic field Orientation
- Strong Magnetic field Orientation

In-plane in the magnetic field direction
- Conductivity, S/cm
- In-plane perpendicular to the magnetic field direction

Graphene weight percent, %

Graphene weight percent, %
Anisotropic Properties

Mechanical properties

- Highly oriented
- Medium Orientation
- Random Orientation

Stress

Graphene wt%

Tensile Modulus, MPa

Neat Polyimide

Mild Magnetic Field

Graphene wt%

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 e-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.
Acknowledgements

• The NASA Aeronautics-Subsonic Fixed Wing Program: Contract NNC07BA13B

• Dr. Dave Kankam, NASA USRP program, NASA GRC
• Dr. Kathy Chuang, NASA GRC
• Dr. Dean Tigelaar, NASA GRC
• Dave Hull, Derek Quade, Terry McCue, NASA/GRC
• Professor Aksay, Princeton University,
• Vorbeck Materials Inc., John Lettow