Multifunctional Graphene Polyimide Nanocomposites

Mitra Yoonessi, Matthew A. Dittler, Daniel Scheiman, Marisabel Lebron-Colon, James Gaier, John Peck, Michael A. Meador

Ohio Aerospace Institute, Cleveland, OH
NASA Glenn Research Center, Cleveland, OH
ASRC, Cleveland, OH

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
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
Aerospace Composites: Micro to Nano

Nanoparticles: CNTs

- 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

Composite Nanoparticles

Magnetic graphene
Graphite 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.

Actuation and morphing

Multifunctional

Stiffness and modulus
and reinforcement

Electrical performance
and EMI shielding

Thermal performance
and stability

• Space
• Aero
• Electronics

Continuous operating range between -65 ºC to +357 ºC

Quartz fabric–polyimide 815 ºC

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

\[ \text{Bisphenol A diglycidyl (BADIA)} \]
\[ \text{2,2-Bis[4-(4-aminoxy)phenyl] propane (HAPP)} \]

+ Polyimide solution

Solvent casting

0.025 wt% graphene/PI


www.nasa.gov 5
Polyimide Graphene Nanocomposites

Electrical Performance

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

<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>0.01 S/cm</td>
</tr>
<tr>
<td>PS Gr, Latex method</td>
<td>0.6 wt%</td>
<td>0.15 S/cm</td>
</tr>
<tr>
<td>PET graphene</td>
<td>0.47 vol.%</td>
<td>0.021 S/cm</td>
</tr>
<tr>
<td>PC graphene, emulsion</td>
<td>0.14 vol.%</td>
<td>0.512 S/cm</td>
</tr>
<tr>
<td>PC graphene, solution</td>
<td>0.38 vol.%</td>
<td>0.226 S/cm</td>
</tr>
<tr>
<td>PS CCG</td>
<td>0.19 vol.%</td>
<td>0.722 S/cm</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


www.nasa.gov
Dispersion of graphene in polyimide

TEM

Graphene vol. %

Conductive path

0.25 vol.%

1.1 vol.%

Conductivity, S/cm

0 1 2 3 4 5

Graphene vol. %

1E-15 1E-14 1E-13 1E-12 1E-11 1E-10 1E-9 1E-8 1E-7 1E-6 1E-5 1E-4 1E-3 1E-2 1E-1 10

10 micron

200 nm

500 nm

10 micron
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 $T_g$.
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>
</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

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

Conductivity, S/cm vs. Graphene weight percent, %

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

www.nasa.gov
Anisotropic Properties

Mechanical properties

Graphene wt%

Tensile Modulus, MPa

Highly oriented
Medium Orientation
Random Orientation
Neat Polyimide

Stress

Tensile Modulus, MPa vs Mild Magnetic Field

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 $\varepsilon-2$ 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