Multifunctional Graphene Polyimide Nanocomposites

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Engineered Materials and Structures

- Multifunctional
- Adaptive Materials
- Self Healing Materials

Light Weight 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.

Electronics and packaging

Multifunctional

Stiffness and modulus and reinforcement

Actuation and morphing

Electrical performance and EMI shielding

Thermal performance and stability

• Space
• Aero
• Electronics

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

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

**Percolation**
- Chemically graphene PS nanocomposites: 0.1 vol.%
- PS Gr, Latex method: 0.6 wt%
- PET graphene: 0.47 vol.%
- PC graphene, emulsion: 0.14 vol.%
- PC graphene, solution: 0.38 vol.%
- PS CCG: 0.19 vol.%

**Max. Conductivity**
- Chemically graphene PS nanocomposites: 0.01 S/cm
- PS Gr, Latex method: 0.15 S/cm
- PET graphene: 0.021 S/cm
- PC graphene, emulsion: 0.512 S/cm
- PC graphene, solution: 0.226 S/cm
- PS CCG: 0.722 S/cm

**CNT/nanocomposites**
- t = 1.2 – 2
- CNF/polyimide
  - t ~ 3.1
- PET graphene
  - t ~ 3.47 ± 0.64
- PS graphene
  - t ~ 2.74 ± 0.2

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>
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S \sim 0.99 \rightarrow \text{hopping}
S \sim 0.72 \rightarrow \text{3D material}
S \sim 0.58 \rightarrow \text{anomalous diffusion in fractal cluster exist}

Dispersion of graphene in polyimide

TEM

0.25 vol.%

Conductive path

1.1 vol.%

Conductivity, S/cm

Graphene vol. %

500 nm

200 nm

10 micron
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)
2.8 wt% Ni-Graphene polyimide nanocomposite
Anisotropic Properties

Electrical properties

Conductivity, S/cm

Graphene weight percent, %

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

- Highly oriented
- Medium Orientation
- Random Orientation

Stress

Neat Polyimide

-0.5 0.0 0.5 1.0 1.5 2.0

Graphene wt%

-0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4

Tensile Modulus, MPa

-0.5 0.0 0.5 1.0 1.5 2.0

Graphene wt%

Neat PI

14

www.nasa.gov
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.
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