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 Road map Technology Area 10
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 Road map 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

Composite Nanoparticles

- Magnetic graphene
- Boron nitride graphene

Processing:
- Solution blending
- Direct mixing
- In-situ polymerization

Magnetic graphene
Polyimide
High Performance Polymer

Satellite
Aromatic polyimide:
- Low color
- Flexibility
- High thermal stability
- Dimensional stability
- Low dielectric constant
- High T<sub>g</sub>
- Radiation resistance
- Low coefficient of thermal expansion

General Ind.
Stiffness and modulus and reinforcement

Electrical performance and EMI shielding

Multifunctional

Actuation and morphing

Thermal performance and stability

• Space
• Aero
• Electronics

Electronics and packaging

Quartz fabric–polyimide 815 °C

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

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

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

- Conductivity vs. Graphene vol. %
  - 0.036% 0.938 S/cm

- Log (\((\phi - \phi_C)/(1 - \phi_C)\)) vs. Log (\(\sigma_{DC}\))
  - \(t = 3.8 \pm 0.29\)

Percolation
- Chemically graphene PS nanocomposites
- PS Gr, Latex method
- PET graphene
- PC graphene, emulsion
- PC graphene, solution
- PS CCG

Max. Conductivity
- 0.1 vol.% 0.01 S/cm
- 0.6 wt% 0.15 S/cm
- 0.47 vol.% 0.021 S/cm
- 0.14 vol.% 0.512 S/cm
- 0.38 vol.% 0.226 S/cm
- 0.19 vol.% 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

\[ \sigma(\omega) / \sigma_{DC0} = 1 + k(\omega / \omega_c)^s \]

<table>
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<th>Vol.%</th>
<th>(\sigma_{DC0}), S/cm</th>
<th>(\omega_c), Hz</th>
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\(S \sim 0.99 \rightarrow \) 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

0.25 vol.%

200 nm

10 micron

1.1 vol.%

Conductive path

500 nm

Graphene vol. %

Conductivity, S/cm

0 1 2 3 4 5

0 1E-15 1E-13 1E-11 1E-9 1E-7 1E-5 1E-3 1E-1 10

www.nasa.gov
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 $T_g$. 

![Graphene wt% vs. $T_g$ and $T_d$ graphs]
Ni-Tethered Graphene

Composites Nanoparticles
Thermal decomposition of Ni(acac)₂ in the presence of O-graphene

First-order reversal curve (FORC)

Hc = 17.34 mT
Ms = 4.795 Am²/Kg
Controlled Directionality

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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, %

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](image)

- Highly oriented
- Medium Orientation
- Random Orientation

Stress

- Neat Polyimide

Mild Magnetic Field

Graphene wt% vs. Tensile Modulus, MPa
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 \textit{in-plane} conductivity and insulating in the \textit{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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