Graphene Polymer Nanocomposites for Aerospace Applications

Mitra Yoonessi, James Gaier

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

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Polymer Nano-Composites for Aerospace Applications

Multi-Functional Materials

- Reinforcements, Mechanical strength in a wide temperature range - Barrier - Toughness

Conductive Polymers

- DC & AC Electrical - Permittivity – Stiffness / Ductility

Smart Adaptive Materials

- Actuation – Thermal, Magnetic, Electrical

- Sensors
  - Static discharge
  - Lightening strike

- Actuators

- Morphing fan casing
- Blended wing body inlet
- Flex. packaging
- Space deployable structures

A two-seat F106B jet made 1,496 thunderstorm penetrations and got struck by lightning 714 times during NASA’s eight-year Storm Hazards Research Program. Credit: NASA

Figure 2. SMP Composite Truss in Packed and Deployed Configurations

Figure 4. 0.5-m Diameter SMP Reflector in Both Deployed and Packed Configurations
Graphite and Graphene

Graphite:
- Advantages: Naturally abundant material, Low cost

Graphene:
- Mechanical peeling
- Acid intercalation, thermal shock, sonication
- Acid intercalation followed by high pressure, high temperature treatments

Graphene:
- In-plane stiffness of 1,060 Gpa
- Resistivity in the range of 50μΩ cm
- 98.7% transmission normal to the incident beam for the first layer, 2.3% reduction for the next layers in vacuum
- Thermal conductivity: ~ 3000 W/mK
- Field effect mobility of 200 000 cm²/Vs

Graphene Surface and Interface

**Tailored Interface**
- Compatibility with the polymer matrix
- Improving dispersion
- Load/stress transfer
- Electron transfer
- Thermal energy transport

**Surface Characteristics:**
- SP² hybridization for electron transport
- van der Waal Interaction (aromatic structures)
- Combination of sp³ and sp² hybridization
  Covalent bonding; -OH, -COOH, -phenolic-OH, -epoxide

**Covalent bonding**
Graphene Polymer Nanocomposites

Conductive Nanocomposites

Electrical Performance

- DC electrical conductivity
- AC electrical conductivity
- Dynamic mechanical analyzer, modulus, Tg
- Morphology:
  - electron microscopy
  - SANS

Polymer+

Dispersion via sonication

Reinforcement, toughness and thermal properties

Multifunctional actuators

Electrical, thermal, mechanical and actuation performance

Polymer+

- DC electrical properties
- Mechanical properties, modulus, Tg
- Morphology: electron microscopy

Polyimide

- Solution mixing

Polycarbonate

- Solution mixing
- Emulsion mixing

Epoxy

Epon 826

- Dynamic mechanical analyzer, modulus, Tg
- Fracture toughness
- TGA
- Morphology; electron microscopy

Epon 826

D 230

- Solution mixing

Dynamic mechanical analyzer, modulus, Tg
- Fracture toughness
- TGA
- Morphology; electron microscopy
Electrical Percolation

Percolating the conductors

- Inherent conductivity of nanoparticle
- Concentration
- Aspect ratio
- Dispersion
- Orientation

Increasing C-nanoparticle concentration

Aggregation and Dispersion of nanoparticles

<table>
<thead>
<tr>
<th>Type of Nanoparticle</th>
<th>van der Waals Interaction Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two spheres (radii $R_1$ and $R_2$) separated by distance $D$</td>
<td>$W = -\frac{A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/3}$</td>
</tr>
<tr>
<td>Two parallel cylinders (radii $R_1$ and $R_2$) separated by a distance $D$ and of length $L$</td>
<td>$W = -\frac{AL}{12V}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/3}$</td>
</tr>
<tr>
<td>Two crossed cylinders (radii $R_1$ and $R_2$) separated by a distance $D$</td>
<td>$W = -\frac{A}{6D}\left(R_1R_2\right)^{1/3}$</td>
</tr>
<tr>
<td>Two parallel plates separated by a distance $D$</td>
<td>$W = -\frac{A}{12\pi \varepsilon D}$</td>
</tr>
</tbody>
</table>

Note: $A$ (Hamaker constant) = $\pi^2 \varepsilon^4 p_1 p_2$, where $C$ is the coefficient in the atom–atom pair potential, and $p_1$ and $p_2$ are the number of atoms per unit volume.


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Graphene Polycarbonate

Lexan 121, Mw = 26,301 g/mol, PDI=1.72

- Excellent thermal properties
- Good mechanical properties
- High impact strength and toughness
- Good processability

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

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

S-G PC series \( t = 4.18 \pm 0.26 \)
\( \sigma_f = 106.55 \pm 0.69 \) S/cm

E-G PC series \( t = 4.04 \pm 0.58 \)
\( \sigma_f = 106.39 \pm 1.32 \) S/cm

Chemically modified graphene PS nanocomposites 0.1 vol.% Conductivity of 0.001 S/cm at 1 vol.%


Graphene Polycarbonate

Tunneling

Charge carrier can travel through the barrier insulating polymer gap, a distance longer than the nanoparticle length.

\[ \omega_c \sim \sigma_{DC}^b \]

Yoonessi, M.; Gaier, J. R. ACS Nano, 2010

Objectives:

- To determine the effects of graphene addition and surface modification on the thermal and dynamic modulus, fracture toughness of the low content graphene nanocomposites.

Epoxy: Epon 826

Low viscosity resin

Transparent

Jeffamine D230: a polyetheramine, (an amine terminated PPG)

MW 230, X~ 2.5

Reduced graphene sp² hybridized

Highly oxygenated graphene, sp², and sp³

Amino propyl polydimethyl siloxane graphene, sp², and sp³

2500 – 27000 g/mol
Epoxy Graphene Nanocomposites

Graphene loading 0.05 - 0.5 wt%

Graphene/epoxy nanocomposite, wt%

Reduced graphene $T_g$

O-graphene $T_g$

PDMS-graphene $T_g$

Neat Epoxy

Glass transition temperature, °C

Graphene epoxy nanocomposites, wt%

Neat Epoxy

Glass transition temperature, °C

Graphene/epoxy nanocomposite, wt%

Neat Epoxy

Neat Epoxy

Neat Epoxy

PDMS-Graphene/epoxy nanocomposite, wt%

Reduced graphene, Modulus @ 60°C

O-graphene, Modulus @ 60°C

PDMS-graphene, Modulus @ 60°C

Neat Epoxy

Neat Epoxy

Neat Epoxy

Graphene epoxy nanocomposites, wt%
Epoxy Graphene Nanocomposites

\[ K_{IC} = \frac{P_{\text{max}}}{B\sqrt{W}} f(x) \]

\[ G_{IC} = \frac{(1 - \nu^2)K_{IC}^2}{E} \]

\[ f(x) = 6x^{1/2} \left[ \frac{1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)}{(1 + 2x)(1 - x)^{3/2}} \right] \]
Good dispersion was obtained in all nanocomposites.
Polyimide, thermal stability >500 °C, T_g > 200 °C, flexible and semi-transparent.\(^2\)

\[\text{Bisphenol A diamide (BPDA)} \quad + \quad \text{2,2-Bis[4-(4'-aminoxyxyloxy)]propylamine (HAPP)} \]

**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

Addition of graphene resulted in composite reinforcement without adverse effect on the $T_g$.

Flexible films at 2wt% with 200 micron thickness.
Dispersion of graphene in polyimide

TEM

Conductive path

0.025 vol.%

1.1 vol.%

Conductivity, S/cm

Graphene vol. %
Reinforcement: O-Graphene Surface Modifications

- Covalent bonding of imide moieties using grafting to method
- Provide compatibility with the polyimide resin matrix
- Generate steric hindrance and promote dispersion

3 units were on the surface:
- 2 anhydride and 1 diamine

P-amino phenyl trimethoxy silane
3,3',4,4'-Biphenyl tetracarboxylic dianhydride (s-BPDA)
2,2'-Dimethyl-4,4'-diaminobiphenyl (m-Tolidine)

After 2 months

O-graphene
Graphene with rigid surface modifier
Graphene with flexible surface modifier
Surface Modification of Graphene with Rigid Imides

Covalent Functionalization of imide structure to Graphene

\[ \text{Intensity} \]

\[ \text{Wavenumber, cm}^{-1} \]

Mw 1058.28 g/mol: 3 unit

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Addition of graphene with rigid surface imide moieties resulted in increase in modulus and $T_g$.
Conclusions

- Incorporation of reduced graphene in both polycarbonate and polyimide resulted in superior electrical conductivity along with reinforcement with none or insignificant adverse effect on the glass transition temperature.

- The plateau electrical conductivity of graphene polyimide nanocomposite reached to 0.92 S/cm with a critical percolation of 0.036 vol. fraction.

- Low graphene content (0.05-0.5 wt%) graphene epoxy nanocomposites exhibited improvements in glass transition temperature, modulus, thermal stability, and fracture toughness.

- Graphene surface characteristics is the key for the target property enhancement in all three resin matrices.
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NASA-University Programs

GRC Lead for the agency nanotechnology

- NRA – Aeronautics
  - NASA inspire web site

- NASA Graduate Student Researchers Program (GSRP)
  - [http://fellowships.hq.nasa.gov/gsrp/nav/](http://fellowships.hq.nasa.gov/gsrp/nav/)

- NASA Undergraduate Student Research Program (USRP)
  - [http://usrp.usra.edu/](http://usrp.usra.edu/)

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