Graphene Nanoplatelets: A Nanomaterial Additive for Multifunctional Polymers and Composites

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‘Lightweighting’ Structures

Aerospace, Military, Truck, Automotive, Wind

Composites offer superior strength and stiffness giving unparalleled weight reduction potential.

The most likely scenario for substantial vehicle weight reduction is a mixed materials solution utilizing metals, standard polymers and composites.

Greater gains by using MULTIFUNCTIONAL MATERIALS

Source: Autocomposites Workshop Pre-Read, November 2012, Rocky Mountain Inst.
i. Introduction to (few layer) Graphene Nanoparticles
   Synthesis, Characterization, Properties,

ii. ‘Multifunctionality’ in Fiber Reinforced Polymer Matrix Composites - Thermoset and Thermoplastic

iii. Nano-Structuring in 1D, 2D and 3D
# Multifunctional Carbon Based Nano-Materials

<table>
<thead>
<tr>
<th>Physical Structure</th>
<th>Carbon Nanotube</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder</td>
<td>~1nm X 100nm</td>
<td>~1nm X 100nm</td>
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</table>

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(chair, zigzag, chiral)</td>
<td>Graphene</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Interactions</th>
<th>π - π</th>
<th>π - π</th>
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</thead>
</table>

<table>
<thead>
<tr>
<th>Tensile Modulus</th>
<th>1.0-1.7 TPa</th>
<th>~1.0 TPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>180 Gpa</td>
<td>~(10-20 GPa)</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Electrical Resistivity</th>
<th>~ 50 x 10^{-6} (\Omega) cm</th>
<th>~ 50x10^{-6} (\Omega) cm(\parallel)</th>
<th>~ 1 (\Omega) cm(\perp)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Thermal Conductivity</th>
<th>3000 W/m K (\parallel)</th>
<th>3000 W/m K</th>
<th>6 W/m K (\perp)</th>
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</thead>
</table>

<table>
<thead>
<tr>
<th>Coef Thermal Exp.</th>
<th>-1 x 10^{-6} (\parallel)</th>
<th>-1 x 10^{-6}</th>
<th>29 x 10^{-6} (\perp)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Density</th>
<th>1.2 – 1.4 g/cm³</th>
<th>~2.0 g/cm³</th>
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</table>

**Single and Multiwall Carbon Nanotubes**
Synthesis of Graphene & NanoPlatelets

- Mechanical Exfoliation of Graphite
  

- Monolayer Synthesis
  

- Few Layer Exfoliation via Graphite Oxide and Reduction to Graphene
  
  M. Hirata et al., Carbon 42(14), 2929-2937, 2004

- Few Layer Intercalation and Direct Exfoliation of Graphite
Few Layer Intercalation and Direct Exfoliation of Graphite

- Graphite can be a host material for chemicals
  
  *Brodie BC. Ann Chim Phys; 45:351–3, 1855*
  
  *Schafhauztnl C. J PraktChem; 21:129–57, 1840*

- Typical intercalates include:
  - alkali metals (Li, Na, K, Rb, Cs),
  - metal halides (FeCl₃, CrO₃, TiCl₃, PtCl₄, etc.),
  - acids (nitric acid, sulfuric acids, phosphoric acid, perchloric acid, chromic acid, etc)
  - combinations of alkali metal/organic molecule (K/THF, Cs/benzene, Cs/ethylene, Cs/styrene, Cs/butadiene, etc.)

- Some of the GICs can be exfoliated by rapid heating.
Stacks of 10-20 lamellae are less affected by out-of-plane bending forces and retain their platelet structure during processing.

• Layers can be intercalated and exfoliated into platelets with high aspect ratios (dia ~0.3µ to 50µ and t~ 1nm to 5nm)
• Basal Plane is hydrophobic
• Functional groups at GnP edges
• Covalent bond formation at edge sites
• Surface areas from 100m²/g to 750m²/g
• Some reduction in properties from monolayer graphene
• Inexpensive to produce (retail ~$35/Kg)

XPS C/O atomic ratio

26.2º graphitic peak

Graphitic crystalline domain

$L_a = (2.4 \times 10^{-10}) \lambda_{laser}^4 \left( \frac{I_G}{I_D} \right)$
GnP Dispersion: Aqueous, Thermosets, Thermoplastics

- Water
  - Coatings, Paints, Inks
- Thermoset Resin
  - Epoxy, PU, Vinyl Ester
- Thermoplastic resin
  - PP, PE, Nylons

GnP Edge Functionalization

Surfactants

- Cationic
- Nonionic
- Anionic

Polyelectrolytes

- PEI: Polyethyleneimine
- PAA: Polyacrylic acid
- PVP: Polyvinylpyrrolidone

- PVP is known to interact noncovalently with carbon nanotubes, wrapping around it
i. Introduction to (few layer) Graphene Nanoparticles
   i. Synthesis, Characterization, Properties,

ii. ‘Multifunctionality’ in Fiber Reinforced Polymer Matrix Composites - Thermoset and Thermoplastic

iii. Nano-Structuring in 1D, 2D and 3D
Mixing & Dispersion - (Random) Nanocomposites

- Epon 828
- Jeffamine T403
- Reinforcement

Outgas in vacuum → Pour into mold → Outgas in vacuum → Cure

85°C for 2hrs
150°C for 2hrs

- Ultrasonication
- 3 roll Milling
- Multi Axis Mixing
GnP/Epoxy Nanocomposite Flexural Properties:

Effect of Surface Treatments on Modulus:

- No Treatment
- P2 Plasma
- Amine Grafting
- Acrylamide Grafting

Effect of Surface Treatments on Strength:

- No Treatment
- P2 Plasma
- Amine Grafting
- Acrylamide Grafting

Effect of Size on Flexural Modulus:

- Heat-exfoliated Gr.(15um)
- Heat Milled Gr.(1.1um)
- MW-exfoliated Gr.(15um)
- MW Milled Gr.(0.86um)

Effect of Size on Flexural Strength:

- Heat-exfoliated Gr.(15um)
- Heat Milled Gr.(1.1um)
- MW-exfoliated Gr.(15um)
- MW Milled Gr.(0.86um)

Effect of Surface Treatments on Modulus:

- No Treatment
- P2 Plasma
- Amine Grafting
- Acrylamide Grafting

Effect of Surface Treatments on Strength:

- No Treatment
- P2 Plasma
- Amine Grafting
- Acrylamide Grafting

Optimization of GnP edge chemistry, lateral diameter and surface area enhance stiffness and strength

~100m²/g GnP
Randomly oriented GnP ‘percolates’ at concentrations of from 0.3 to 2 wt% depending on aspect ratio and surface area.

* AC Impedance decreases $\sim 10^9$

* Polymers become electrostatically dissipative, can be electrostatically painted and used for EMI shielding

$\rho_{\text{eff}} = \rho_0 (p - p_c)^{-t}$

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>pc (Vol%)</th>
<th>pc (Wt%)</th>
<th>$\rho_0$ (ohm*cm)</th>
<th>t</th>
</tr>
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<tbody>
<tr>
<td>CF</td>
<td>5.90</td>
<td>9.76</td>
<td>0.4</td>
<td>3.26</td>
</tr>
<tr>
<td>VGCF</td>
<td>1.09</td>
<td>1.87</td>
<td>0.03</td>
<td>3.03</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>1.29</td>
<td>2.00</td>
<td>0.01</td>
<td>3.03</td>
</tr>
<tr>
<td>Exfoliated Gr.</td>
<td>1.13</td>
<td>1.93</td>
<td>0.001</td>
<td>3.12</td>
</tr>
</tbody>
</table>
GnP/Epoxy Thermal Properties

* Random GnP dispersed in polymers Increases thermal conductivity ~10X at concentrations of 3 wt% ~35X at 20 wt% function of aspect ratio and surface area
* Coef Thermal Expansion (CTE) decreases ~50% at 3 wt%
* Thermal Stability Increases and Flammability Decreases

![Graph showing thermal conductivity vs. exfoliated graphite content](image1)

- ~100m²/g GnP

![Graph showing CTE below Tg](image2)
Ex. GnP-CTBN Functionalized in Vinyl Ester Composites

* CTBN Functionalized GnP dispersed in vinyl ester Increases Impact Strength ~250% with only slight reduction in modulus and strength
Thermoset NanoComposite

- Epon 828
- Jeffamine T403
- Reinforcement

Thermoset NanoComposite

- Outgas in vacuum
- Pour into mold
- Outgas in vacuum
- Cure
  - 85°C for 2hrs
  - 150°C for 2hrs

Thermoplastic NanoComposite

- Ultrasonicate & Mix

Thermoplastic NanoComposite

- Extr/InjMold
- GNP
- TP

Thermoplastic NanoComposite

- Injection Mold
- Extrude
- GNP
- TP

PreMix

- Coat Powder
- Compression Mold
- GNP
- TP Powder
**GnP** surface is a superb nucleating agent
* e.g. GnP in Polypropylene Increases Stiffness, Strength and Impact Properties
* Spherulite Size Decreases by >10X
* Crystallization Temperature increase ~20°C

**xGnP promotes the formation of β phase crystals (at low %)**

**β-phase crystals of PP have higher impact strength and toughness**

No change in the degree of crystallinity

Tc increases by 10-20 °C (1 to 10vol% of xGnP)
* GnP dispersed in N66 Increases Stiffness 300% Strength 60% at 20 v%  
* Increases Thermal Conductivity 700% Electrical Conductivity ~10^{10} at 20 v%  
* Reduces Oxygen Permeability 70% at 3 v%
Multifunctional GnP Modified SMC

Apply GnP to fibers and filler with a sizing
Mix fibers and filler with UPE
Add Initiator and Promoter Ultrasonicate
Cast and Cure

28% (glass fiber) + 47% (CaCO₃) + 23% (UPE)
A = (GnP 0%)
B = (GnP 0.3%)
C = (GnP 1.0%)
D = (GnP 1.5%)
E = (GnP 2.0%)
F = (GnP 3.8%)

D = 28% (glass fiber) + 47% (CaCO₃ / 3.2% GnP-1)
+ 23% (UPE) = composite (GnP™ 1.5%)

20% Modulus
10% Strength

80% Impact

10⁹ increase conductivity

28% (glass fiber) + 47% (CaCO₃) + 23% (UPE)

D = 28% (glass fiber) + 47% (CaCO₃ / 3.2% GnP-1)
+ 23% (UPE) = composite (GnP™ 1.5%)
Bipolar plates account for approximately 80% of the fuel cell volume, 70% of the fuel cell weight and as much as 60% of the entire stack cost.

**DOE Goals:** Bipolar must exhibit:
- in-plane electrical conductivity > 100 S cm⁻¹
- thermal conductivity > 10 W/m°K
- chemical stability < 16 mA/cm²
- gas permeability: < 2 × 10⁻⁶ cm³ (cm² s)⁻¹
- mechanical strength: flexural strength > 25 MPa

**GnP 40w% + CB 20w% + HDPE or PPS – Compression Molded**
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Nano-Structuring

Utilization of graphene nanoplatelets (GnP) fabricated into 1D, 2D and 3D Morphologies to enhance multifunctional properties and applications
Ex. Conductive Adhesives

High voltage source

Voltage detector

Copper plates
Plastic dish

Voltage divider

E field Intensity: ~10-25KV/cm
2w% GnP Nanoparticles Applied to Carbon Fiber Surfaces in Epoxy Composites

- Dispersion of GnP in a ‘fugitive’ sizing
- Sizing ‘swells’ during impregnation
- Nanoparticles are ‘released’ in the interphase
- Apply to ANY reinforcing fiber
- Dry, handlable sized fibers
2D Multilayer GnP ‘Paper’

Superior Electrical and Thermal Conductivity, InPlane Strength

- Highly Aligned GNP
- Controllable size
  35 cm x XXX
- Controllable thickness
  (~3μ to ~1000µ)
- Simple process
- Scalable to large sheets
  2m+ XXX

- Electrical conductivity: 2128 S/cm
  Surface resistivity: 0.1 ohm/sq
  OFHC Copper: 5.8*10^5 S/cm
- GnP paper density ~2g/cm³
  Cu density ~8.9 g/cm³
- Thermal Conductivity
  ~200 W/m°K -in-plane
  ~5 W/m°K -thru-plane
  Cu is ~400 W/m°K
GnP Paper

Stage I  Porous structure

Stage II  GnP paper
Continuously Extruded GnP-5/Polymer film

Material: extrusion cast film

10wt% GnP-5/PEId composite film, stretching ratio=2, 0.3mm thickness, 16 layers

Neat PEId film, stretching ratio=3, 0.22mm thickness, 15 layers

\[
\text{stretching ratio} = \frac{\text{drawing speed}}{\text{extruding speed}}
\]
GnP ‘Paper’ for EMI Shielding

Frequency (GHz)

S21 (dB)

Sheet 1U
Sheet 2U
Sheet 7P
Sheet 9P
Brass Plate+

Tunnel f = 2 to 18 GHz
PNA – Agilent
• Polyurethene
• Silicone
• SCO$_2$
• Syntactic
• Resilience
• Barrier
• Heating
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<tbody>
<tr>
<td>Loading &amp; xGnP type</td>
<td>10wt% GnP-5</td>
<td>10wt% GnP-5</td>
<td>5wt% GnP-15</td>
<td>10wt% GnP-5</td>
<td>GnP-15</td>
<td>GnP-15</td>
<td>GnP-15</td>
<td>GnP-15</td>
</tr>
<tr>
<td>GnP+PEI</td>
<td>10wt% GnP-5</td>
<td>10wt% GnP-5</td>
<td>5wt% GnP-15</td>
<td>10wt% GnP-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>6.6</td>
<td>5.7</td>
<td>3.9</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>98</td>
<td>98</td>
<td>65</td>
<td>106</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical conductivity (S/cm)*</td>
<td>E-6.7</td>
<td>E-4.5</td>
<td>1.25</td>
<td>E-6.1</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Thermal conductivity (W/m°K)*</td>
<td></td>
<td></td>
<td>0.85 (t-plane, 3.3 @ 10wt%)</td>
<td>0.29 (t-plane)</td>
<td></td>
<td></td>
<td></td>
<td>20.5</td>
</tr>
<tr>
<td>Relative O₂ Permeability</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.35</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*The values indicate the conductivity or thermal conductivity at specific conditions.
GnP for Multifunctional Composites

• Graphene Nano-Platelets: a low-cost Additive for Multifunctional Materials
• GnP Polymer Nano-Composite Multifunctional Properties
  • High Modulus, Low Density
  • High Electrical Conductivity and High Thermal Conductivity
  • Optically Transparent Conductive Coatings
  • Dispersible in Polymers and Water, Variable size
  • Thermoset or Thermoplastic Matrices
  • Reduced Flammability and Thermo-Oxidative Resistance
  • Enhanced Barrier Properties for gases (O2, H2O, H2)
  Liquids (gasoline, ethanol)
• GnP for Multifunctional Lightweight Composites
  • GnP on Reinforcing Fiber Surface of Between Lamina
  • Increase Adhesion, Toughness, Off-axis properties
  • Impact Resistance, Conductive Glass Fibers
Graphite (Graphene) NanoPlatelet (GnP) Group

- Hiroyuki Fukushima, PhD
- Dana Miloaga, PhD
- Sanjib Biswas, PhD
- Jinglei Xiang, PhD
- Anchita Monga, PhD
- Yan Li
- Keith Honaker
- Nick Kamar
- Fuzhong Wang
- Wanjun Liu, PhD
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- Jue Lu, PhD
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- Kyriaki Kalaitzidou, PhD, Prof.
- InHwan Do, PhD
- Xian Jiang, PhD
- Huang Wu, PhD
- Debkumar Saha, PhD
- Diandra Rollins
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- Zeyang Wu
- Donghwan Cho, Prof.
- Xiaobing Li, PhD
- Frederick Vautard, PhD
- Saswata Bose, PhD

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