Graphene Nanoplatelets: A Multifunctional Nanomaterial for Polymers and Composites

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‘Lightweighting’ Structures
Aerospace, Military, Truck, Automotive, Wind

[Graph showing CO₂ emissions over time for different regions and targets.]

[Bar chart showing material distribution in vehicles from 1977 to 2035.]
• Lightweighting Structures and Higher Power and Energy Densities are gaining increasing importance

• “Do More with Less” leads to...

• Multifunctional Fiber Reinforced Polymer Composites

• Solution is... ’engineering’ of Nano-Particles into structures and energy devices
  
  • Dispersion and Nano-structuring

  • Use of Few layer graphene nanoplatelets (GnP)
i. Introduction to (few layer) Graphene Nanoparticles
   i. Synthesis, Characterization, Properties,
   ii. ‘Multifunctionality’ in Fiber Reinforced Polymer Matrix Composites - Thermoset and Thermoplastic
   iii. Processing and Nano-Structuring in 1D, 2D and 3D
   iv. Applications
Nano-Materials Portfolio

- Nanoclay
- Halloysite Nanotubes
- Cellulose Nanowhiskers
- Boron Nitride NanoPlatelets
- Single and Multiwall Carbon Nanotubes
- Vapor Grown Carbon Fibers
- Boron Nitride Nanotubes
- Fullerene
- Boehmite
- Halloysite Nanotubes
- Graphene
- Cellulose Nanowhiskers
## Multifunctional Carbon Based Nano-Materials

#### Single and Multiwall Carbon Nanotubes

<table>
<thead>
<tr>
<th></th>
<th>Carbon Nanotube</th>
<th>Graphene NanoPlatelets</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical Structure</strong></td>
<td>Cylinder ~1nm X 100nm</td>
<td>Platelet ~1nm X 100nm</td>
</tr>
<tr>
<td><strong>Chemical Structure</strong></td>
<td>Graphene (chair, zigzag, chiral)</td>
<td>Graphene</td>
</tr>
<tr>
<td><strong>Interactions</strong></td>
<td>$\pi - \pi$</td>
<td>$\pi - \pi$</td>
</tr>
<tr>
<td><strong>Tensile Modulus</strong></td>
<td>1.0-1.7 TPa</td>
<td>~1.0 TPa</td>
</tr>
<tr>
<td><strong>Tensile Strength</strong></td>
<td>180 Gpa</td>
<td>~(10-20 GPa)</td>
</tr>
<tr>
<td><strong>Electrical Resistivity</strong></td>
<td>$\sim 50 \times 10^{-6} , \Omega , \text{cm}$</td>
<td>$\sim 50 \times 10^{-6} , \Omega , \text{cm} \parallel$ $\sim 1 , \Omega , \text{cm} \perp$</td>
</tr>
<tr>
<td><strong>Thermal Conductivity</strong></td>
<td>3000 W/m K</td>
<td>3000 W/m K $\parallel$ 6 W/m K $\perp$</td>
</tr>
<tr>
<td><strong>Coeff Thermal Exp.</strong></td>
<td>$-1 \times 10^{-6}$</td>
<td>$-1 \times 10^{-6} \parallel$ $29 \times 10^{-6} \perp$</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>1.2 – 1.4 g/cm$^3$</td>
<td>~2.0 g/cm$^3$</td>
</tr>
</tbody>
</table>
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
  
  *Schafhaeutl 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 \( \sim 0.3\mu \) to 50\( \mu \) and t\( \sim 1\)nm to 5nm)

- Basal Plane is hydrophobic
- Functional groups at GnP edges
- Covalent bond formation at edge sites
- Surface areas from 100m\(^2\)/g to 750m\(^2\)/g
- Some reduction in properties from monolayer graphene
- Inexpensive to produce
GnP Applications and Dispersion Strategies

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

GnP Edge Functionalization

**Surfactants**

**Polyelectrolytes**

Intercalation

Exfoliation

Conventional Composite

Intercalated Composite

Long Range Ordering (LRO) Composite

Disordered Composite

- Water

- Coatings, Paints, Inks

- Thermoset Resin
  - Epoxy, PU, Vinyl Ester

- Thermoplastic resin
  - PP, PE, Nylons

- GnP Applications and Dispersion Strategies

- GnP Edge Functionalization

- Surfactants

- Polyelectrolytes

Intercalation

Exfoliation

Conventional Composite

Intercalated Composite

Long Range Ordering (LRO) Composite

Disordered Composite
i. Introduction to (few layer) Graphene Nanoparticles

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

iii. Processing and Nano-Structuring in 1D, 2D and 3D
Thermoset Matrix NanoComposites

Mixing & Dispersion - (Random) Nanocomposites

Epon 828
Jeffamine T403
Reinforcement

- Ultrasonication
- 3 roll Milling
- Multi Axis Mixing

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

85°C for 2hrs
150°C for 2hrs
GnP/Epoxy Nanocomposite Flexural Properties:

Size and Surface Chemistry Effect of GnP

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 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

~100m²/g GnP
GnP/Epoxy Electrical Resistivity

Percolation Analysis

\[ \rho_{eff} = \rho_0 \left( p - p_c \right)^{-t} \]

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>pc (Vol%)</th>
<th>pc (Wt%)</th>
<th>( \rho_0 ) (ohm*cm)</th>
<th>t</th>
</tr>
</thead>
<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>

\~100m²/g GNP
GnP/Epoxy Thermal Conductivity and CTE

Thermal Conductivity

- Exfoliated Graphite Content (Wt%)
- W/m*K

CTE below Tg

- Control
- Epoxy
- 3 vol% MW Ex.Gr
- 3 vol% CF
- 3 vol% VGCF
- 3 vol% Carbon Black
- Acrylamide Grafted Nanographite

~100m²/g GnP
CTBN Functionalized GnP/Vinyl Ester Composites

GnP-Graphite Nanoplatelets

- Microwave-processed using intercalated graphite compound and then pulverized

Functionalized Elastomer

- Carboxyl-Terminated poly(Butadiene-co-Acrylonitrile) (CTBN)
  - (Acrylonitrile 26%, carboxyl 32%, MW=3,150)

Vinyl Ester

- DERAKANE 411-350
- Initiator: Methyl Ethyl Ketone Peroxide
- Accelerator: Cobalt Octoate
CTBN Functionalized GnP/Vinyl Ester Composites

- Carboxyl-Terminated poly(Butadiene-co-Acrylonitrile) (CTBN)
  - Acrylonitrile 26%, carboxyl 32%, MW=3,150
Thermoset NanoComposite

Epon 828
Jeffamine T403
Reinforcement

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

Ultrasonicate & Mix

Thermoplastic NanoComposite

GNP
TP

Extrude
Injection Mold

Extr/InjMold

GNP
TP Powder

Coat Powder
Compression Mold

PreMix
GnP/PP Nanocomposite Flexural and Impact Properties

**Impact Strength of xGnP-PP Nanocomposites**

- xGnP-1
- xGnP-15

<table>
<thead>
<tr>
<th>Vol%</th>
<th>Impact Strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>8</td>
</tr>
<tr>
<td>0.01%</td>
<td>13</td>
</tr>
<tr>
<td>0.05%</td>
<td>18</td>
</tr>
<tr>
<td>0.1%</td>
<td>23</td>
</tr>
<tr>
<td>1%</td>
<td>28</td>
</tr>
<tr>
<td>2%</td>
<td>33</td>
</tr>
<tr>
<td>3%</td>
<td>38</td>
</tr>
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</table>

**Modulus of Elasticity of xGnP-PP Nanocomposites**

- xGnP-1
- xGnP-15

<table>
<thead>
<tr>
<th>Vol%</th>
<th>Modulus of Elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>1.2</td>
</tr>
<tr>
<td>0.01%</td>
<td>1.4</td>
</tr>
<tr>
<td>0.05%</td>
<td>1.6</td>
</tr>
<tr>
<td>0.1%</td>
<td>1.8</td>
</tr>
<tr>
<td>1%</td>
<td>2</td>
</tr>
</tbody>
</table>

**Flexural Strength of xGnP-PP Composites**

- xGnP-1
- xGnP-15

<table>
<thead>
<tr>
<th>Vol%</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>35</td>
</tr>
<tr>
<td>0.01%</td>
<td>40</td>
</tr>
<tr>
<td>0.05%</td>
<td>45</td>
</tr>
<tr>
<td>0.1%</td>
<td>50</td>
</tr>
<tr>
<td>1%</td>
<td>55</td>
</tr>
<tr>
<td>2%</td>
<td>60</td>
</tr>
<tr>
<td>3%</td>
<td>65</td>
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</table>

**XRD Pattern of xGnP1/PP**

- α <040>
- β <300>
- β <301>
- α <040>

- 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 oC (1 to 10vol% of xGnP)
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iii. Processing and Nano-Structuring in 1D, 2D and 3D
Nano-Structuring

Utilization of graphene nanoplatelets (GnP) fabricated into 1D, 2D and 3D Morphologies to enhance multifunctional properties and applications
E-field Intensity: ~10-25KV/cm

(a) (b) (c)
GnP Modification of Fiber Reinforced Composites

Fiber Direction:
- High modulus
- High strength
- Electrical conductivity,
  thermal conductivity, etc.

CFRP properties
- Fiber direction
  - Compressive strength
  - Interlaminar fracture toughness
- Transverse direction
  - Electrical & Thermal conductivities
  - Damping property

Compressive strength
- Prevent fiber buckling by enhancement of modulus and yield strength of matrix

Interlaminar fracture toughness
- Reduce crack propagation by bridging effect
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
Coating multiple layers of GnP on glass fiber reduces adhesion and the interfacial shear stress between fiber and matrix significantly.
Apply GnNP 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)

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

Need balance of strength and toughness
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/cm^3
  Cu density ~8.9 g/cm^3
- Thermal Conductivity
  ~200 W/m*K - in-plane
  ~5 W/m*K - thru-plane
  Cu is ~400 W/m*K
**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

*Stretching ratio = \( \frac{\text{drawing speed}}{\text{extruding speed}} \)*
<table>
<thead>
<tr>
<th>Loading &amp; xGnP type</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Electrical conductivity (S/cm)*</th>
<th>Thermal conductivity (W/m°K)*</th>
<th>Relative $O_2$ Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injection molding</strong></td>
<td><strong>Companion xGnP type</strong></td>
<td><strong>GnP+PEI</strong></td>
<td><strong>10wt% GnP-5</strong></td>
<td><strong>6.6</strong></td>
<td><strong>98</strong></td>
</tr>
<tr>
<td><strong>Compression molding</strong></td>
<td><strong>GnP+PEI</strong></td>
<td><strong>10wt% GnP-5</strong></td>
<td><strong>5.7</strong></td>
<td><strong>98</strong></td>
<td><strong>E-4.5</strong></td>
</tr>
<tr>
<td><strong>SSBM &amp; Pre-coating GnP+PEI</strong></td>
<td><strong>GnP+PEI</strong></td>
<td><strong>5wt% GnP-15</strong></td>
<td><strong>3.9</strong></td>
<td><strong>65</strong></td>
<td><strong>1.25</strong></td>
</tr>
<tr>
<td><strong>Extrusion cast GnP-PEI film</strong></td>
<td><strong>GnP+PEI</strong></td>
<td><strong>10wt% GnP-5</strong></td>
<td><strong>6.8</strong></td>
<td>106</td>
<td><strong>E-6.1</strong></td>
</tr>
<tr>
<td><strong>Annealed</strong></td>
<td><strong>GnP-PEI film</strong></td>
<td><strong>10wt% GnP-5</strong></td>
<td><strong>Annealed</strong></td>
<td><strong>E-4.3</strong></td>
<td><strong>0.80</strong></td>
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<tr>
<td><strong>Pressed xGnP paper</strong></td>
<td><strong>GnP-15</strong></td>
<td><strong>7.0</strong></td>
<td><strong>2.8</strong></td>
<td><strong>850</strong></td>
<td><strong>246</strong></td>
</tr>
<tr>
<td><strong>GnP-100</strong></td>
<td><strong>2200</strong></td>
<td><strong>313</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>GnP paper -PEI</strong></td>
<td><strong>80wt% GnP-15</strong></td>
<td><strong>19</strong></td>
<td><strong>23</strong></td>
<td><strong>620</strong></td>
<td><strong>0.01</strong></td>
</tr>
<tr>
<td><strong>GnP paper -PEI</strong></td>
<td><strong>70wt% GnP-15</strong></td>
<td><strong>22</strong></td>
<td><strong>32</strong></td>
<td><strong>550</strong></td>
<td><strong>0.01</strong></td>
</tr>
<tr>
<td><strong>GnP paper - epoxy</strong></td>
<td><strong>15wt% GnP-15</strong></td>
<td></td>
<td></td>
<td><strong>20.5</strong></td>
<td><strong>0.02</strong></td>
</tr>
</tbody>
</table>
Blast Impact by shock-tube

Maximum air speed = Mac3 ~ 1000 m/sec = 2,250 miles/hr
80 times high speed than Dynatup!

a) GF 63.0 wt% VE  t=0.124”

b) CTBN coated GnP-15um (t=35 um) 0.6 % GF 61.0 wt% VE, t=0.128”

c) 10% holes (Dia. 6.3mm) GnP-200um (t=40um) 2.3 % GF 60.3% VE, t=0.128”
GnP Film for EMI Shielding

![Graph showing S21 db vs Frequency (GHz)](image)

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

*Tunnel f=2 to 18 GHz
PNA – AGILENT*
• **Graphene Nano-Platelets offer a route to Multifunctional Materials**
• **Direct Intercalation/Exfoliation to produce platelet morphology**
  • Variable Platelet Thickness; Diameter; Surface and Edge Chemistry;
  • Dispersible in water, solvent and thermoset and thermoplastic polymers
  • Reasonable cost ~$15/lb
• **GnP Polymer Nano-Composite Multifunctional Properties**
  • High Modulus, Low Density
  • High Electrical Conductivity and High Thermal Conductivity
  • Optically Transparency
  • Thermo-Oxidative Resistance
  • Barrier Properties
  • Dispersible in Polymers and Water, Variable size
  • Thermoset or Thermoplastic Matrices
• **Nano-Engineering for 1D, 2D or 3D Morphology**
• **Transformational Material for Multifunctional Lightweight Composites**
  • Placement of GnP on Reinforcing Fiber Surface of Between Lamina
  • Increase Adhesion, Toughness, Off-axis properties
  • Blast and Impact Resistance