Exfoliated Graphite Nanoplatelets (xGnP)
A Carbon Nanotube Alternative for Modifying the Properties of Polymers and Composites

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Why the Interest in NanoComposites?

- **PROPERTY ENHANCEMENT**
  - Mass Reduction (low density, low concentration)
  - Increased Stiffness (high aspect ratio)
  - Increased Toughness (engineered adhesion)
  - Improved Appearance (nano size, scratch and mar resistance)
  - Electrical Conductivity (electrostatic dissipation, electrostatic painting, electromagnetic shielding)
  - Thermal Conductivity, lower C.T.E., higher $T_{ult}$
  - Reduced Flammability (less combustible material)
  - Barrier to Permeants (platelet)
Structure of Clay Platelet Minerals

- Original Nanoreinforcement (Toyota)
- Layered structure - natural mineral
- Metal cations occupy the galleries
- Metal cations can be replaced by ammonium ions
- Existence of hydroxyl groups which can form hydrogen or covalent bonds
- Layers can be exfoliated into platelets with a high aspect ratio
Single Wall Carbon Nanotube (SWNT) and Vapor Grown Carbon Fibers (VGCF)

- Nanotubes produced in single wall and multiwall structures
  - High Aspect Ratio
- VGCF entangled network 0.1-1.0 µ
- Nanocomposite Properties
  - Stiffness, Strength
  - Electrical Conductivity
- Applications
  - Automotive (VGCF-Nylon-PPE) Mirror Housings, Fuel Lines
  - Electrical Disc Drive Housings
- ~ $100/g (Nanotube)
  - $80-100/lb (milled VGCF)
  - $40-50/lb (fibril VGCF)
Cellulose Nanowhiskers

- Cellulose Iβ
- Highly crystalline-95%
- Highly aligned
- Dimensions
  - 2-5 nm
  - “Several μm” length
  - Aspect ratio: 100+
- Estimated $5-10/lb

monocrystalline cellulose domains parallel to the microfibril axis composed of cellulose chains in a cellulose lattice bonded laterally and surrounded by surface chains forming a paracrystalline envelope

Eichhorn et al. 2001
Graphite NanoPlatelets (xGnP*)

- Layered Natural Mineral
- Layers can be intercalated with alkalis, acids, salts, etc. and exfoliated into nanosize platelets with high aspect ratio
- Basal Plane is a graphene sheet and inert (sp² + π)-identical to the wall of a carbon nanotube
- Existence of functional groups at the edges can lead hydrogen or covalent bond with polymer matrix
- xGnP + Polymer = Nanocomposite property improvement expected: mechanical, electrical, thermal and barrier properties

*xGnP = Exfoliated Graphite Nano Platelets*
## Comparison of Nanoreinforcement Properties

<table>
<thead>
<tr>
<th></th>
<th>Exfoliated Clay</th>
<th>Carbon Nanotube VGCF</th>
<th>Exfoliated h-BN BN Nanotubes</th>
<th>Cellulose Nanowhisker</th>
<th>xGnP-Graphite NanoPlatelets</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PHYSICAL STRUCTURE</strong></td>
<td>Platelet (~1nm x 100nm)</td>
<td>Cylinder NT (~1nm X 100nm) VGCF (~20nm X 100um)</td>
<td>Layer</td>
<td>Needle-Whisker</td>
<td>Platelet (~1nm X 100nm)</td>
</tr>
<tr>
<td><strong>CHEMICAL STRUCTURE</strong></td>
<td>SiO₂, Al₂O₃, MgO, K₂O, Fe₂O₃</td>
<td>Graphene (chair, zigzag, chiral)</td>
<td>Boron Nitride</td>
<td>Cellulose</td>
<td>Graphene</td>
</tr>
<tr>
<td><strong>INTERACTIONS</strong></td>
<td>Hydrogen bond Dipole-Dipole</td>
<td>π-π</td>
<td>Hydrogen bond</td>
<td>Hydrogen Bond</td>
<td>π-π</td>
</tr>
<tr>
<td><strong>TENSILE MODULUS</strong></td>
<td>0.17 TPa</td>
<td>NT 1.0-1.7 TPa VGCF 0.25-0.5 TPa</td>
<td>~1 TPa</td>
<td>~ 130 GPa</td>
<td>~1.0 TPa</td>
</tr>
<tr>
<td><strong>TENSILE STRENGTH</strong></td>
<td>~1 GPa</td>
<td>(NT 180 GPa) VGCF 3-7 GPa</td>
<td>?</td>
<td>10 GPa</td>
<td>~(10-20 GPa)</td>
</tr>
<tr>
<td><strong>ELECTRICAL RESISTIVITY</strong></td>
<td>10¹⁰ – 10¹⁶ Ω cm</td>
<td>NT ~50 x 10⁻⁶ Ω cm VGCF 5-100 x 10⁻³ Ω cm</td>
<td>insulator</td>
<td>10¹⁰ – 10¹⁶ Ω cm ~50 x 10⁻⁶ Ω cm</td>
<td></td>
</tr>
<tr>
<td><strong>THERMAL CONDUCTIVITY</strong></td>
<td>6.7 x 10⁻¹ W/m K</td>
<td>3000 W/m K (NT) 20-2000 W/m K (VGCF)</td>
<td>~3000W/m K</td>
<td>insulator</td>
<td>3000 W/m K</td>
</tr>
<tr>
<td><strong>COEF. THERMAL EXP.</strong></td>
<td>8 – 16 x 10⁻⁶</td>
<td>-1 x 10⁻⁶</td>
<td>~1 x 10⁻⁶</td>
<td>8 – 16 x 10⁻⁶</td>
<td>-1 x 10⁻⁶</td>
</tr>
<tr>
<td><strong>DENSITY</strong></td>
<td>2.8 – 3.0 g/cm³</td>
<td>NT 1.2 – 1.4 g/cm³ VGCF 1.8-2.1 g/cm³</td>
<td>~2.0 g/cm³</td>
<td>1.5 g/cm³</td>
<td>~2.0 g/cm³</td>
</tr>
</tbody>
</table>

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Typical Conversion Process to produce NanoPlatelet Reinforced-Polymer Composites

**INTERCALATION**

Conventional Composite

**EXFOLIATION**

Intercalated Composite

Long Range Ordering (LRO) Composite

Disordered Composite

e.g. Nanoclay
‘Ex-Situ’ Exfoliation and Pulverization of Graphite into NanoPlatelets

Intercalated Graphite (300-500 um) → Expanded Graphite (300-500 um) → Lightly pulverized Graphite (50-100 um) → Fully pulverized Graphite (15 um) → Milled Graphite (1 um)
‘As-received’ (left) and ‘expanded’ graphite at 900ºC (right). (Bar = 500 um)
X-Ray Diffraction of xGnP

As Received Graphite

Heat Exfoliated Graphite

*MSU Exfoliated Graphite
*MSU patent pending
xGnP Morphology

10-20nm
### BET Surface Area and Thickness of xGnP

#### Surface Area of Exfoliated Graphite Samples

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m²/g)</th>
<th>Diameter (μm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio (d/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received Graphite</td>
<td>0.2</td>
<td>300</td>
<td>5172.4</td>
<td>58.0</td>
</tr>
<tr>
<td>Heat Exfoliated</td>
<td>10.5</td>
<td>15</td>
<td>96.5</td>
<td>155.5</td>
</tr>
<tr>
<td>Heat Milled Graphite</td>
<td>24</td>
<td>1.1</td>
<td>45.1</td>
<td>24.4</td>
</tr>
<tr>
<td>MSU xGnP 15μm</td>
<td>105</td>
<td>15</td>
<td>9.5</td>
<td>1573.0</td>
</tr>
<tr>
<td>MSU-xGnP 1μm</td>
<td>94</td>
<td>0.86</td>
<td>10.9</td>
<td>78.8</td>
</tr>
</tbody>
</table>

- **Determined from ESEM observation.**
- **Theoretically Calculated.**
Thermoset Matrix Composite Fabrication

- Epon 828
- Jeffamine T403
- Reinforcement

Ultrasonicate & Mix

Outgas in vacuum

Pour into mold

Outgas in vacuum

Cure

85°C for 2hrs
150°C for 2hrs
Maximum Packing

200um (200,000nm)

$V_f = \sim 9\ \text{vol} \% \text{ for } t=1\ \text{nm}$
$V_f = \sim 49\ \text{vol} \% \text{ for } t=10\ \text{nm}$

- If the average diameter of a polymer chain entanglement is 10nm, a practical limit for 1nm-thick flakes is about 10 vol%.
- Maximum packing factor decreases as thickness decreases.
Effect of xGnP Platelet Size on Properties

Effect of Size on Flexural Modulus

Effect of Size on Flexural Strength
Effect of xGnP Surface Chemistry on Mechanical Properties

Effect of Surface Treatments on Modulus

Effect of Surface Treatments on Strength

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xGnP vs Exfoliated OrganoClay
Flexural Modulus below and above Tg

![Graph showing improvement in flexural modulus vs reinforcement content](image)

- xGnP
- Control Graphite
- ODA-Clay

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Baseline Carbon Reinforcements

1. Chopped Panex-33-MC Carbon Fiber (Zoltek)
3. KETJENBlack EC-600-JD Carbon Black (Akzo Nobel)

Average Diameter = 7um
Average Length = 175um
(Scale Bar = 200um)

Average Diameter = 160nm
Average Length = 50um
(Scale Bar = 5um)

Average size = 20 nm
(Scale Bar = 5um)
Flexural Properties: xGnP vs Carbon Reinforcements

Flexural Modulus

Flexural Strength

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Impedance of xGnP/Epoxy

![Graph showing impedance of different concentrations of xGnP in epoxy](image-url)
Resistivity of Composites

![Graph showing resistivity vs. weight percentage for different composites]

- VGCF
- Carbon Black
- PAN CF
- MSU-xGnP
- Milled Graphite
**Percolation Analysis**

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

<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>MSU-xGnP</td>
<td>1.13</td>
<td>1.93</td>
<td>0.001</td>
<td>3.12</td>
</tr>
</tbody>
</table>
Coefficient of Thermal Expansion

Reinforcement Content = 3 Vol%
Thermal Conductivity --- Carbon Materials

![Graph showing thermal conductivity vs. xGnP content (Wt%)]

- Control Epoxy
- 3 vol% xGnP
- 3 vol% CF
- 3 vol% VGCF
- 3 vol% CB

~3.5
**xGnP in TPO & PP**

**PP** : Profax6301 [Basell]

**TPO** : S7101 Medium Impact Co-polymer
(16-20% rubber phase) [Basell]

- *Mini-extruder*
  - Temperature : 180°C
  - Rotation speed : 200rpm
  - Mixing time : 3min
- Injection Molding
  - Mold Temperature : 80°C

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**Flexural Modulus**

**Flexural Strength**

**Impact Strength (Composites)**
Crystallization of xGnP-PP at $T=130^\circ$C

- PP
- 0.01vol% xGnP-15/PP
- 0.01vol% xGnP-1/P
- 0.1vol% xGnP-15/PP

Images:
- 130\degree C 10min PP
- 130\degree C 10min 0.01vol% xGnP-15/PP
- 130\degree C 10min 0.01vol% xGnP-1/PP
- 130\degree C 12min 0.1vol% xGnP-15/PP
Nylon Nanocomposites

Nylon 66 : Zytel101 NC010 [DuPont]

\[
\left[ \text{NH}\underbrace{\text{CH}_2\text{NH}\text{CO}\text{(CH}_2\text{))}_n\text{CO})_n \right]
\]

\( \text{Tm}=262^\circ\text{C} \)

Nylon 6 : Durethan B40SK [Bayer]

\[
\left[ \text{NH}\underbrace{\text{(CH}_2\text{))}_6\text{CO}}_n \right]
\]

\( \text{Tm}=222^\circ\text{C} \)

- Mini-extruder
  - Temperature : 290°C [N66], 260°C [N6]
  - Rotation speed : 200rpm
  - Mixing time : 3min

- Injection Molding
  - Mold Temperature : 90°C [N66], 80°C [N6]
xGnP +Nylon 6 and Nylon 66 Nanocomposite Flexural Modulus and Strength

Flexural Modulus of Nylon 6 Composites

Flexural Modulus of N66 Composites

Flexural Strength of Nylon 6 Composites

Flexural Strength of N66 Composites
Electrical and Thermal Conductivity of xGnP-Nylon 66 Nanocomposites

Electrical Conductivity of Nylon 66 Composites

Thermal Conductivity of Nylon 66 Composites
Oxygen Permeability of xGnP-Nylon Nanocomposites

Permeability of Nylon 6 Films

- Control N6
- 3v% xGnP-15um/N6
- 3v% xGnP-1um/N6
- 3v% CF/N6
- 3v% GF
- 3v% VGCF/N6
- 3v% Nanomer/N6
- 3v% Cloisite/N6

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Effect of Platelet Size and Concentration on Permeability

Total path of a diffusing gas

\[ d' = d + \frac{d \cdot L \cdot Vf}{2W} \]

- **d**: thickness of a film
- **L**: length of a clay
- **W**: width of a clay
- **Vf**: volume fraction of a clay

Tortuosity factor

\[ \tau = \frac{d'}{d} = 1 + \frac{L \cdot Vf}{2W} \]

Equation for a permeability coefficient

\[ P_c = \frac{Pp}{\tau} = \frac{Pp}{(1 + L \cdot Vf / 2W)} \]

**Pc**: permeability coefficient of a matrix polymer

**Pp**: permeability coefficient of a matrix polymer
Improved Scratch Resistance

<table>
<thead>
<tr>
<th>Material</th>
<th>Pcritical (mN)</th>
<th>Width (μm) @ Pcrit.</th>
<th>% Recovery @ 600 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6</td>
<td>12.3</td>
<td>13.8</td>
<td>90</td>
</tr>
<tr>
<td>VGCF</td>
<td>12.6</td>
<td>7.8</td>
<td>82</td>
</tr>
<tr>
<td>NC</td>
<td>8.6</td>
<td>7.7</td>
<td>48</td>
</tr>
<tr>
<td>xGnP-1</td>
<td>14.1</td>
<td>12.3</td>
<td>85</td>
</tr>
<tr>
<td>xGnP-15</td>
<td>14.6</td>
<td>12.7</td>
<td>64</td>
</tr>
</tbody>
</table>

LSCM images of the progressive scratch tests conducted on Nylon 6 (left) and xGnP-1 (right).
Nano-Macro Hybrid Structure
xGnP + CF + Epoxy

0° Flexural Modulus

0° Flexural Strength

90° Transverse Modulus

90° Transverse Strength

Short Beam Shear Strength
Property Enhancements and Applications with xGnP

- Mass Reduction (low density, low concentration)
- Increased Stiffness (high aspect ratio)
- Increased Toughness (engineered interfacial adhesion)
- Electrical Conductivity (electrostatic dissipation, electrostatic painting, electromagnetic shielding)
- Thermal Conductivity (lower C.T.E., higher $T_{ult}$)
- Improved Appearance (scratch resistance)
- Barrier to Permeants (platelet morphology)
- Reduced Flammability (less combustible material)
- Surface Conductivity (controlled deposition and alignment)
- Intra and Interlaminar Strengthening and Toughening