GRAPHENE BASED IMPACT MODIFIED POLYPROPYLENE NANOCOMPOSITES FOR AUTOMOTIVE APPLICATIONS

Alper Kiziltas, Alex Duguay, Behzad Nazari, Esra Erbas Kiziltas, Douglas J. Gardner and Habib J. Dagher

Advanced Structure and Composites Center, University of Maine, Orono, ME 04469, USA

SPE Automotive Composites Conference & Exhibition (ACCE) - September 11, 2013
Allotropic Forms of Carbon

- **Diamond**: highly transparent, hardest of all materials, abrasive, electrical insulator, the best thermal conductor.

- **Amorphous carbon**: carbon atoms in non-crystalline irregular state.

- **Carbon nanotubes**: discovered in 1991.

- **Graphite**: good electrical conductivity, highly stable, require high temperatures to react with oxygen, the most thermodynamically stable.

- **Graphene**: was developed practically in 2004, although it was theoretically studied during the last sixty years.

Graphenebiz 2013, Shepelev and King 2010
What is Graphene/Graphite? Why are they unique?

- A two-dimensional atom size thick layer produced mainly by exfoliating of a three-dimensional graphite structure. Consists of a hexagonal array of sp2 bonded carbon atoms.

<table>
<thead>
<tr>
<th>Physical Structure</th>
<th>Exfoliated Clay</th>
<th>Carbon Nanotube</th>
<th>Graphite Nanoplatelets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platelet</td>
<td>Platelet</td>
<td>Cylinder</td>
<td>Platelet</td>
</tr>
<tr>
<td>~1nm x 100 nm</td>
<td>~1nm x 100 nm</td>
<td>~1nm x 100 nm</td>
<td>~1nm x 100 nm</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>SiO₂, Al₂O₃, MgO</td>
<td>Graphene</td>
<td>Graphene</td>
</tr>
<tr>
<td>K₂O, Fe₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>~ 1 GPa</td>
<td>~ 180 GPa</td>
<td>~10 – 20 GPa</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>10¹⁰ – 10¹⁶ Ohm cm</td>
<td>~50×10⁻⁶ Ohm cm</td>
<td>~ 50×10⁻⁶ Ohm cm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>6.7×10⁻¹ W/mK</td>
<td>3000 W/m K</td>
<td>3000 W/m K</td>
</tr>
<tr>
<td>CTE</td>
<td>8 – 16×10⁻⁶</td>
<td>-1×10⁻⁶</td>
<td>-1×10⁻⁶</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>2.8 – 3.0</td>
<td>1.2 – 1.4</td>
<td>~2.0</td>
</tr>
</tbody>
</table>

- Cost Comparison
  - Exfoliated Clay ~ 3-5/ lb
  - SWCNT ~ 100 $ / g
  - MWCNT ~ 300$/Kg
  - VGCF ~ 40 – 100 $ / lb
  - xGnP ~ 5 – 10 $ / lb

Shepelev and King 2010, Drzal 2012
Graphene-Based Research and Applications

- Fuel tank and fuel line coatings
- Electronic enclosures
- Automotive parts
- Aerospace
- Appliances
- Sporting goods
- Coatings and paints
- Batteries
- Fuel cells

Graphene has been the subject of a wealth of scientific research and received much media attention because of the early paper by Geim and Novoselov in 2004 and huge research funding initiatives.
xGnP = Exfoliated Graphite Nano Platelets

- Very thin, typically 5 nm thick (corresponding to more than 16 layers of graphene). Flat particles with large diameters – 100 – 1000 nm.

- Particles are sensitive to Van der Waals attractive forces and tend to re-aggregate.

- Layers can be intercalated with alkalis, acids, salts, etc. and exfoliated into nanosize platelets with high aspect ratio.

- Existence of functional groups can lead hydrogen or covalent bond with polymer matrix.

Shepelev and King 2010, Drzal 2012
Objectives

- Fabricate xGnP-filled impact modified polypropylene (IMPP) nanocomposites via melt compounding and injection molding.

- Characterize the effect of particle diameter, filler loading and the addition of coupling agents on the mechanical, rheological and thermal properties of xGnP-filled IMPP nanocomposites.

- Utilize electron microscopy techniques as well as traditional mechanics models to draw conclusions regarding degree of xGnP dispersion within the matrix IMPP.

- Correlate mechanical results with rheological behavior to gain insight into optimizing nanocomposites formulations.
### Materials and Formulations

- Maleic anhydride (MA) content differs by over an order of magnitude

<table>
<thead>
<tr>
<th>Material</th>
<th>Product Name</th>
<th>Supplier</th>
<th>Density (g/cm³)</th>
<th>Maleic Anhydride Content (%)</th>
<th>Mw</th>
<th>Acid Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>FHR Polypropylene AP5135-HS</td>
<td>Polystrand Co.</td>
<td>0.90</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Exfoliated Graphite Nanoplatelets xGnP5</td>
<td>XGSciences</td>
<td></td>
<td>0.18-0.25</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Exfoliated Graphite Nanoplatelets xGnP15</td>
<td>XGSciences</td>
<td></td>
<td>0.18-0.25</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Exfoliated Graphite Nanoplatelets xGnP25</td>
<td>XGSciences</td>
<td></td>
<td>0.18-0.25</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PP-g-MA</td>
<td>427845-Polypropylene-graft-maleic anhydride</td>
<td>Sigma-Aldrich</td>
<td>0.934</td>
<td>8-10</td>
<td>9,100</td>
<td>47</td>
</tr>
<tr>
<td>PP-g-MA</td>
<td>Epolene E-43</td>
<td>West Lake Chemical</td>
<td>0.934</td>
<td>&lt;0.7</td>
<td>9,100</td>
<td>45</td>
</tr>
</tbody>
</table>

- **Filler:Compatibilizer = 2:1**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Compatibilizer</th>
<th>Filler</th>
<th>Filler Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMPP</td>
<td>None</td>
<td>xGnP5</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>WL9100 SA9100</td>
<td>xGnP15</td>
<td>4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>xGnP25</td>
<td>6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8%</td>
</tr>
</tbody>
</table>
Experimental Approaches

**Mechanical Properties**
- Tensile and Flexural Strength
- Tensile and Flexural MOE
- Elongation at Break
- Notched Izod Impact Strength
- Storage and Loss Modulus
- Tan Delta
- Fracture Initiation Resistance

**Thermal Properties**
- Glass Transition Temperature
- Melting Temperature
- Crystallization Temperature
- Crystallinity
- Thermal Stability
- DTGA Temperature
- Residual Mass

**Rheology and Density**
- Viscosity
- Shear Stress
- Melt Flow Index
- Density
- Density versus MOE
Composites formulated with xGnP5 and WL9100 have consistently higher tensile strength.
Tensile MOE vs. Filler Loading

- Composites formulated with xGnP5 and WL9100 have superior tensile MOE.
- All composites exhibited a decrease in strain at failure with the addition of xGnP. Compatibilizer slightly magnifies this decrease in strain at failure (i.e. creates a more brittle composite).
Composites formulated with xGnP5 and WL9100 have consistently higher flexural strength.
Compatibilized composites filled with xGnP5 tend to perform best in terms of flexural MOE.
Izod Impact Testing: Fracture Initiation Resistance

“A characteristic property of the material which defines the energy required for crack initiation”

Unnotched Impact Strength - Notched Impact Strength = Fracture Initiation Resistance
Correlation of impact properties with MFI

- In general, MFI was found to increase with decreasing xGnP particle diameter for both neat and xGnP-filled composites containing coupling agent.
- In nearly all cases, MFI increased with the addition of coupling agent.
- The correlation of impact properties with MFI was extremely linear.
Figures illustrate the obvious improvement in quality of dispersion in properly compatibilized composites.
## Recommendations Based On M.P.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Compatibilizer</th>
<th>Filler</th>
<th>Filler Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPP Impact Copolymer</td>
<td>None</td>
<td>xGnP5 xGnP15 xGnP25</td>
<td>2% 4% 6% 8%</td>
</tr>
</tbody>
</table>

- Tensile MOE increase of 25.1%
- Tensile strength increase of 1.8%
- Flexural MOE increase of 28.5%
- Flexural strength increase of 13.8%
## DSC of Composites

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMPP</td>
<td>164.3 (0.7)</td>
<td>122.6 (0.4)</td>
<td>61.0 (4.0)</td>
<td>-91.5 (4.6)</td>
<td>29.5 (1.9)</td>
</tr>
<tr>
<td>SA9100</td>
<td>156.0 (0.9)</td>
<td>105.0 (1.9)</td>
<td>62.6 (12.1)</td>
<td>-99.7 (14.9)</td>
<td>30.2 (5.9)</td>
</tr>
<tr>
<td>WL9100</td>
<td>154.0 (1.2)</td>
<td>104.0 (1.9)</td>
<td>67.3 (1.2)</td>
<td>-109.1 (5.1)</td>
<td>32.5 (0.6)</td>
</tr>
<tr>
<td>IMPP_SA9100_2%</td>
<td>163.2 (0.6)</td>
<td>116.1 (1.3)</td>
<td>54.4 (1.6)</td>
<td>-84.1 (0.8)</td>
<td>26.3 (0.8)</td>
</tr>
<tr>
<td>IMPP_WL9100_2%</td>
<td>163.9 (0.6)</td>
<td>116.8 (1.0)</td>
<td>58.2 (6.0)</td>
<td>-88.0 (3.4)</td>
<td>28.1 (2.9)</td>
</tr>
<tr>
<td>IMPP_xGnP5_4%</td>
<td>165.5 (0.3)</td>
<td>126.5 (1.4)</td>
<td>56.3 (3.5)</td>
<td>-84.2 (0.6)</td>
<td>28.3 (1.7)</td>
</tr>
<tr>
<td>IMPP_xGnP15_4%</td>
<td>165.5 (1.5)</td>
<td>125.8 (2.3)</td>
<td>59.3 (2.5)</td>
<td>-86.0 (1.2)</td>
<td>29.8 (1.3)</td>
</tr>
<tr>
<td>IMPP_xGnP25_4%</td>
<td>165.0 (0.2)</td>
<td>126.1 (0.2)</td>
<td>57.1 (2.0)</td>
<td>-86.2 (0.5)</td>
<td>28.7 (1.0)</td>
</tr>
<tr>
<td>IMPP_SA9100_xGnP5_4%</td>
<td>164.8 (0.6)</td>
<td>124.6 (0.4)</td>
<td>55.0 (3.5)</td>
<td>-87.1 (6.2)</td>
<td>27.7 (1.0)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_2%</td>
<td>165.9 (0.0)</td>
<td>124.3 (0.2)</td>
<td>61.5 (1.9)</td>
<td>-84.0 (2.8)</td>
<td>30.3 (0.9)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_4%</td>
<td>165.2 (0.5)</td>
<td>124.9 (0.3)</td>
<td>56.7 (2.4)</td>
<td>-85.1 (3.3)</td>
<td>28.5 (1.2)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_6%</td>
<td>165.3 (1.0)</td>
<td>125.1 (0.4)</td>
<td>59.1 (1.9)</td>
<td>-81.9 (2.9)</td>
<td>30.3 (1.0)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_8%</td>
<td>165.2 (0.9)</td>
<td>125.6 (0.3)</td>
<td>55.7 (1.5)</td>
<td>-78.7 (1.2)</td>
<td>29.2 (0.8)</td>
</tr>
</tbody>
</table>

- **Incorporation of xGnP increases the crystallization temperature** ($T_c$) **of IMPP by about 2 to 3 °C attributed to the heterogeneous nucleation of xGnP.**
- **Increasing the xGnP content in the IMPP results in smaller** $\Delta H_m$ **and** $\Delta H_c **values.**
TGA of Composites

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>DTGA Temp. (°C)</th>
<th>Weight Loss (%)</th>
<th>Residual Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMPP</td>
<td>459.9 (1.3)</td>
<td>63.0 (3.1)</td>
<td>1.6 (0.1)</td>
</tr>
<tr>
<td>SA9100</td>
<td>458.3 (1.1)</td>
<td>69.8 (1.9)</td>
<td>4.0 (0.4)</td>
</tr>
<tr>
<td>WL9100</td>
<td>453.8 (1.9)</td>
<td>65.3 (2.7)</td>
<td>4.0 (0.6)</td>
</tr>
<tr>
<td>IMPP_SA9100_2%</td>
<td>458.9 (0.8)</td>
<td>74.0 (5.5)</td>
<td>2.3 (0.4)</td>
</tr>
<tr>
<td>IMPP_WL9100_2%</td>
<td>461.1 (0.9)</td>
<td>68.8 (2.4)</td>
<td>2.0 (0.1)</td>
</tr>
<tr>
<td>IMPP_xGnP5_4%</td>
<td>463.7 (0.3)</td>
<td>58.9 (0.8)</td>
<td>5.5 (0.1)</td>
</tr>
<tr>
<td>IMPP_xGnP15_4%</td>
<td>463.9 (0.7)</td>
<td>60.2 (1.2)</td>
<td>5.4 (0.3)</td>
</tr>
<tr>
<td>IMPP_xGnP25_4%</td>
<td>462.5 (0.6)</td>
<td>55.9 (1.0)</td>
<td>5.0 (0.3)</td>
</tr>
<tr>
<td>IMPP_SA9100_xGnP5_4%</td>
<td>464.8 (0.9)</td>
<td>63.8 (3.0)</td>
<td>5.1 (1.4)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_2%</td>
<td>461.2 (1.0)</td>
<td>60.2 (2.5)</td>
<td>4.3 (0.6)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_4%</td>
<td>462.6 (0.2)</td>
<td>55.4 (1.2)</td>
<td>6.1 (0.3)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_6%</td>
<td>467.2 (0.4)</td>
<td>58.1 (1.1)</td>
<td>7.7 (0.3)</td>
</tr>
<tr>
<td>IMPP_WL9100_xGnP5_8%</td>
<td>469.1 (0.1)</td>
<td>58.2 (1.1)</td>
<td>10.0 (0.2)</td>
</tr>
</tbody>
</table>

- TGA shows at 4% loading level xGnP particle diameter did not have significant influence on the thermal degradation behavior.
- The onset temperature of rapid thermal degradation was shown to increase with xGnP loading.
Conclusions

- The smallest diameter filler investigated in this study (5µm) performed the best in terms of mechanical properties of xGnP-filled IMPP composites.

- Tensile and flexural moduli and strengths both increased with xGnP filler loading for compatibilized composites.

- A correlation study to determine a relationship between impact properties and MFI was explored and showed impact properties to increase with MFI linearly.

- Particle diameter had no significant effect on the $T_m$ and $T_c$ as well as $\Delta H_m$ and $\Delta H_c$ of the composites.

- The increase in thermal stability is believed to originate from the more thermally stable graphite.
Acknowledgements

- U.S. Army ERDC, MAFES and USDA WUR Special Grant for support.
- Prof. Gardner’s team: Dr. Yousoo Han and Chris West
- Donald Gjeta and Alex Nash.
- SPE Automotive Division, especially Peggy Malnati.
THANK YOU
QUESTIONS?