Carbon nanotubes and graphene nanoplatelets for multi-functional composites

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1. Brief introduction to carbon nanotubes (CNTs) and graphene nanoplatelet

2. Single walled carbon nanotubes (SWNTs)- Nylon 6 composite fiber

3. Graphene-epoxy composite

4. CNTs/carbon fiber 3D matrix composite

5. Work @ Sabic Innovative Plastics

6. Work @ UW
Carbon nanotube & graphene nanoplatelet

- High mechanical strength and tensile modulus (Young’s modulus ~1TPa, carbon fiber: 400-600 MPa)
- Unique electrical properties (~1*10^5 S/cm)
- Exceptional thermal conductivity (~3000 W/mK)
- Low density (~1.3-2g/ml) high aspect ratio (L/D~1000)
Synthesis of carbon nanotubes

Chemical vapor deposition

Arc-discharge
Applying SWNTs & GNPs to polymers

High mechanical properties
Antistatic
EMI shielding
Against lighting strike

Nano-materials will bring revolution to industry
Brief example—strongest polymer composite ever made

Tensile strength matches spider silk and modulus (80 GPa) is much higher than spider silk

*R. Baughman, 290,1310, Science, 2000*
Nylon 6/SWNT Advanced Composites --- mechanical/electrical enhancement

Yu, A. et al., J. of American Chemical Society 2005, 127
Motivation and challenges

- Nylon is a widely used thermoplastics owing to its good strength high elongation, excellent abrasion resistance, etc.
- There is need to improve the mechanical strength, toughness and electrical conductivity.

- Lack of functionality resulting chemical incompatibility with the polymer matrix and the self-aggregation of SWNTs into bundles due to van der Waals attraction.
- Homogeneous dispersion & SWNTs not pull out from polymer
Ensure efficient load transfer from the matrix to the fiber, the **interfacial bonding** between the polymer matrix and the carbon nanotubes is necessary to prevent fiber pull out.

Controlled HNO$_3$ treatment of SWNTs, brings –COOH to the end of SWNT

In-situ grafting PA6 chain to SWNT surface
Step one: HNO₃ treatment

1. SWNT surface hydrophilic

2. Removed catalyst particles

Atomic Force Microscopy
Step 2: In-situ grafting nylon 6 to SWNT

\[ \text{NH}_2(CH_2)_5COOH \]

initiator
6-aminocaproic acid

\[ \text{ON} \]

\[ \text{H}_2N(CH_2)_5COO^- + \text{H}_2\text{N}(CH_2)_5COO^- \]

sonication, 80 °C

Advantages:
No solvent
PA6 grafted to SWNT
Characterization of SWNTs with grafted Nylon 6

AFM of SWNT

IR spectra samples prepared using different initiator concentrations

1640 cm\(^{-1}\)→C=O group of the amide functionality
1540 cm\(^{-1}\) combination of N-H bond C-N bond of the amide group
In situ polymerization setup & fiber preparation

- Lab reactor
- Fiber spinneret
- Cross-section

Composite fibers
Characterization of SWNTs-Nylon 6 composite

SEM

TEM

Differential thermal analysis.

Thermal decomposition T.

Differential thermal analysis (DTA) and differential thermal gravimetric analysis (DTG) graphs for different wt% of SWNT in Nylon 6. The graphs show the temperature range from 150 to 300 °C for DTA and 420 to 460 °C for DTG, with various wt% of SWNT in Nylon 6 marked on the graphs.
Results of electrical conductivity

<table>
<thead>
<tr>
<th>Samples @ 1wt % loading</th>
<th>Electrical conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6 grafted SWNT composite</td>
<td>1.1E-6</td>
</tr>
</tbody>
</table>

Electrical conductivity data show:
The composites are in the anti-static range
1 wt % SWNT loading
The PA6 grafted leads to 84% increased tensile strength and 170% Young’s modulus (1.5 wt% loading)
Modeling calculation of SWNTs-Nylon 6 composite

**Halpin–Tsai model**

Is widely used to predict the modulus of unidirectional or randomly distributed filler-reinforced composites

\[
E_c = \left[ \frac{3 + 2 \left( \frac{l_{NT}}{d_{NT}} \right) \eta_L V_{NT}}{8 \left( 1 - \eta_L V_{NT} \right)} \right] \left[ \frac{5 + 2 \eta_L V_{NT}}{8 \left( 1 - 2 \eta_L V_{NT} \right)} \right] E_m
\]

\[
\eta_L = \frac{\left( \frac{E_{NT}}{E_m} \right) - 1}{\left( \frac{E_{NT}}{E_m} \right) + 2 \left( \frac{l_{NT}}{d_{NT}} \right)}
\]

\[
\eta_L = \frac{\left( \frac{E_{NT}}{E_m} \right) - 1}{\left( \frac{E_{NT}}{E_m} \right) + 2}
\]
Summary

- The PA6 chains are found to be grafted to the SWNTs by a condensation reaction between the –COOH groups of the SWNTs and the terminal amino group of PA6.

- The grafted PA6 chains enhance the SWNT-nylon6 interfacial interaction and improve their compatibility, leading to a homogeneous dispersion of the SWNTs in the nylon matrix.

- The Young’s modulus, tensile strength, and thermal stability of nylon 6 fibers are greatly improved by the incorporation of SWNTs via the process.

- The composite is also anti-static in the pursued concentration range.
Graphene/ Epoxy Resin Composites
--- Thermal Interface Materials


With continued scaling of devices, heat-transport problems will most likely be aggravated at all levels.
GNPs as fillers in epoxy matrix for TIMs

Requirements of TIMs:
Thermal conductivity $\geq 2 \text{ W/mK}$
Low thermal expansion

Thermal conductivity of polymer matrix: 0.2-0.4 W/mK

Conventional Particles:
$\text{SiO}_2$, $\text{AlN}$, Ag

Disadvantages:
Low aspect ratio
High loading

Advantages of GNPs
• High thermal conductivity
• High aspect ratio
• Low CTE
• Low density

Using GNPs as filler
Schematic process to obtain GNPs

Natural graphite

Intercalation
\[ \text{H}_2\text{SO}_4/\text{HNO}_3 \]

Thermal shock

Exfoliated graphite

Physical process
Microscopic observation of GNPs

Optical Microscopic

(a) Natural graphite

(b) Exfoliated graphite

Scanning Electron Microscopic
AFM of GNPs

Statistic size:

L ~ 1.1 μm, t ~ 1.7 nm, AR = 200; 4 layer graphene (G4)
GNP/epoxy composite

**Challenges:** High loading nano-material dispersion

**Epoxy:** Diglycidyl ether of bisphenol A

![Chemical structure of epoxy resin]

Even in lab scale, mechanical stirring is not enough

**Curing agent:** Diethyl-toluenediamine

**Homogenizer:** Shear mixing

**Three roll mill**
Schematic show of the composite process

Shear mixing & sonication in acetone

Exfoliated graphite

Cross section TEM image of GNP-Epoxy

Shear mixing
Cross-linking epoxy

Three-roll mill curing

GNP-Epoxy
High resolution TEM of GNP in epoxy matrix

$L \sim 1.1 \mu m$, $t \sim 1.7$ nm, $AR = 200$; 4 layer graphene (G4)
Thermal conductivity measurements: heat flow two thickness testing

Designed according to ASTM C518-98
From Lasercomp. Inc.
Thermal conductivity of the GNP/epoxy composites

**Thermal Conductivity vs GNP Ratio**

- Linear increase of thermal conductivity with filler loading
- Thermal conductivity up to (10.12 W/mK-40 Vol%) - suitable for electronic packaging, superior than conventional fillers
- In the T range of computer run, performance is good
Comparison of carbon fillers

GNPs filler perform better than other carbon fillers

GNP shows: **130% enhancement / 1 vol.%** – efficient filler

Whereas it is 20-30% for conventional fillers

**Reason:** High aspect ratio and rigid 2D structure of

**Diagram:**
- CB - carbon black
- GMP - graphite microplatelet
- MWNT - Multi-Walled Carbon Nanotubes
- SWNT - Single-Walled Carbon Nanotubes
- GNP - graphite nanoplatelet
Modeling prediction & discrepancy

1. Inverse Rule of Mixtures

\[ \frac{K_c}{K_p} = \frac{1 + A B \phi_f}{1 - B \psi \phi_f} \]

2. Nielsen’s model accounts for the geometry of the fillers

\[ A = k_e - 1 \]

\[ B = \frac{K_f / K_p - 1}{K_f / K_p + A} \]

\[ \psi = 1 + \left( \frac{1 - \phi_m}{\phi_m^2} \right) \phi_f \]

Experimental data are significantly lower than modeling prediction;
The model needs modification for nanomaterials
Summary of 2D-GNP/epoxy composite

- Thermal conductivity of GNP-epoxy resin composite is high up to 10.12 W/mK, which is excellent for thermal interface material application.
- Cost effective production: Graphite $50/Kg
- Highest filler efficiency using rigid 2D fillers
3 D Multi-functional Composites

- Biaxial Weave
- Triaxial Weave
- Knit
- Multiaxial Multilayer Warp Knit
- 3-D Cylindrical Construction
- 3-D Braiding
- 3-D Orthogonal Fabric
- Angle-Interlock Construction


**Boeing 787 Dreamliner**: composite materials for half of the parts, next generation Airplane material is not metal, will be carbon fiber matrix
Motivation and Objective

Motivation:
Matrix rich regions form defect in the carbon fiber - polymer composite
Cracking and failure usually start and propagate from these defect sites

Approach:
Carbon nanotube to reinforce matrix regions and void the defect in composite
Increase the carbon fiber – polymer interfacial interaction and load transfer

T. W. Chou, F. Ko, Textile Structural Composites, 1988
Bridging the scale from Nano to Macro

Atomic Interactions
- Stretching
- Bending
- Torsion
- van der Waals

Carbon Nanotubes
- Armchair
- Zig-Zag

Epoxy Matrix

Nanocomposite

Carbon Nanocomposite

Multi-Scale Composite

Modeling Hierarchy – Bridging the Scale from Nano to Macro
CNT reinforcement increases the interfacial interaction and the loading transfer and can avoid fiber pull-out.
CVD Deposition of CNTs on Carbon Fiber/Fabrics

- deposition of iron (Fe) for selective growth of CNTs

![Diagram showing the process of CVD deposition of CNTs on carbon fibers. The diagram includes the following steps:

1. Iron chloride (FeCl₃) solution is placed on the carbon fibers.
2. Hydrogen (H₂) is introduced to facilitate the reduction of iron oxide to form iron (Fe) and facilitate the growth of CNTs.
3. Ferrocene, mixed with p-xylene solution, is vaporized at a temperature of ~180°C, and the vaporized mixture is introduced into the reactor.
4. At a temperature of 700°C, multi-walled carbon nanotubes (MWNTs) grow on the iron-coated carbon fibers.

The diagram also highlights the iron-coated carbon fibers as a result of the deposition process.]
SEM of Carbon Fibers Coated with CVD-grown CNTs
Epoxy resin system

EPON 862 – EPI-Cure W Curing Agent
(Resolution Performance Products, Inc.)

Bisphenol-F Epichlorohydrin Epoxy

Aromatic Diamine (diethyltoluenediamine)

Amine hydrogen equivalent wt (AHEW) 43-46
Vacuum assisted infusion

Diagram showing Peel Ply, Vacuum Bag, Distribution Media, Resin Inlet, Vacuum Outlet, Tool, Layers of Glass Fabric, and Nanotube-Coated Carbon Fiber Bundles.
SEM observation of the composite

Carbon fiber

CNTs
Both in-plane and out-plane electrical conductivity increased about 17 % @ 0.5 wt% CNTs loading
Mechanical properties enhancement

Flexural strength and stiffness of CF/epoxy composites with and without CNTs were slightly improved.

Shear strength of CF/epoxy composites with and without CNT was enhanced at 35% (loadings of 0.2 and 0.5 wt %).
Summary

- CNTs had been deposited on carbon fiber surface

- Both in-plane and out-plane electrical conductivity increased about 17% 

- Flexural strength and stiffness were slightly improved and shear strength of the carbon fiber epoxy was enhanced at 35% with 0.5 wt % of CNTs.
My work in SABIC Innovative Plastics

Aiping Yu
My work @ uwaterloo
My work @ uwaterloo

Super capacitor: a new energy storage device
My work @ uwaterloo

High loading multi-functional graphene/polycarbonate composite

Infiltration with polycarbonate → Sandwitch → Multilayer composite

Graphite → Oxidizing agent → Graphitic oxide

Graphene

Reducing agent

SEM

Cross-section

2 μm
Recent publications of graphene

![Graph showing publications in graphene field and polymer composite area](chart.png)
Welcome collaborations and suggestions for applying carbon nanotubes and graphene to polymer composites

Thanks a lot for your attention