IMPROVING MECHANICAL PROPERTIES OF NANOCOMPOSITES USING CARBON NANOTUBES

Richard Fink
Applied Nanotech, Inc.
3006 Longhorn Blvd., Suite 107
Austin, TX 78758
Phone 512-339-5020 x130ext.
Fax 512-339-5021
Email: dfink@appliednanotech.net

Applied Nanotech, Inc.

September, 2009

Applied Nanotech, Inc. (ANI)

Applied Nanotech specializes in research and development of innovative nanotechnology applications. We have more than 150 issued patents and about 100 patents pending. Our focus is creating innovations in the following areas:

- **CNT electron emission**
- **Sensors**
- **Nanoelectronics**
- **Nanoecology**
- **Functionalized nanomaterials**

ANI 3006 Longhorn Blvd. Austin TX
Employees: 35, Founded: 1997

www.appliednanotech.net
512-339-5020

Applied Nanotech, Inc.

ANI at a Glance

ANI

Divisions	Expertise	Applications
Nanomaterials	➢ Enhancing the mechanical and physical properties of materials for improved products.	➢ CNT/nanoclay composites ➢ Metalic nano particles ➢ CarbAl™ for thermal management ➢ Carbon/glass fiber composites
Nanoelectronics	➢ Exploiting nanoscale phenomena for emerging electronics applications	➢ Metalic nanoparticle inks ➢ Other technical inks ➢ Printable electronics ➢ CNT inks and TFTs
Nanosensors	➢ Developing sensors, sensor networks and sensor applications for Industrial, Defense and Medical applications.	➢ Hydrogen ➢ Sono-photonic ➢ Ion mobility ➢ Enzyme coated CNTs
Nanoecology	➢ Developing nanotechnology-based products for a healthier and greener environment.	➢ PhotoScrub™ air filtration ➢ Nanosafety ➢ Electrochromic solid state films
CNT Electron Emission	➢ Developing new applications of electron emission from carbon nanotubes.	➢ Electron sources ➢ Gas ionization sources ➢ Neutron generators ➢ Lighting devices/displays

Applied Nanotech, Inc.

Contents of the presentation

- **Introduction**
- **Experimentation**
- **Results and discussion**
  - **Carbon fiber prepreg**
  - **Glass fiber prepreg**
- **Conclusions**
- **Acknowledgement**

Applied Nanotech, Inc.

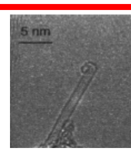
Motivation and goal

- ANI has a long history of applications using CNTs.
  - Field emission displays, lamps
  - Electron and ion sources
- Contracted by sporting goods company to improve CFRP (stronger, lighter, given specific performance goals) within the constraints of their manufacturing process.

CFRP = carbon fiber reinforced prepreg

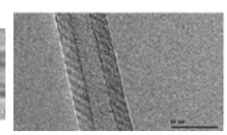
Applied Nanotech, Inc.

Unique properties of carbon nanotubes (CNTs)



SWNT

DWNT



MWNT

Elastic modulus: ~ 1 TPa;

Tensile strength: ~ 50 GPa;

Thermal conductivity: > 1,500 W/mK, much higher than Cu – 400 W/mK;

Electrical conductivity: Better than Cu;

Elongation: >30%;

Density: < 1.2 g/cm^3 for single-wall CNTs, 2.0 g/cm^3 for multi-wall CNTs.

→ **More and more CNT-related high-tech products are shown on the market.**

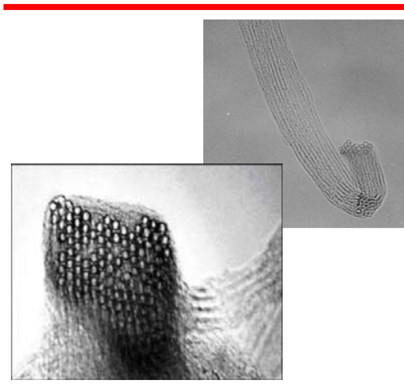
Applied Nanotech, Inc.

Key issues solved for substantially improved mechanical properties by CNT reinforcement

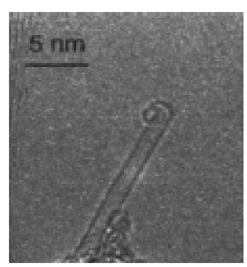
- Dispersion of CNTs in polymer is required to uniformly distribute load - not easily solved;
- Functionalization of the CNTs required to form strong covalent bonding between the CNTs and the polymer matrix;
- Translating the improved properties of the resin to improving the properties of the CFRP.

4 patents submitted to USPTO, in prosecution.

Dispersion of CNT required for reinforcement



Rope of Single-wall CNTs (www.cnanotech.com)

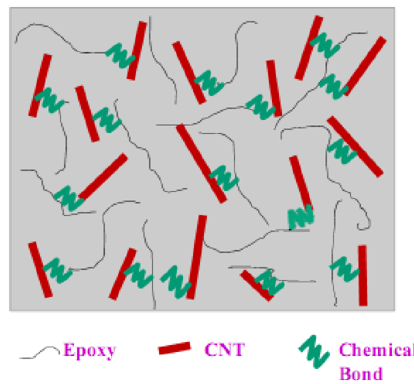


Individual Single-wall Carbon Nanotube

Functionalization of CNTs

- Need to control the interactions between the CNTs and the polymer chains.
- These interactions govern the load-transfer efficiency from the polymer to the CNTs.
- Functionalization of CNTs is needed in order to improve the mechanical properties of the composites
  - Improvement in dispersion
  - Linkage directly to the host matrix

(J. Zhu et al, Advanced Functional Materials 14, 643(2004); A. Romov et al, Journal of Materials Chemistry 15, 3334(2005).)



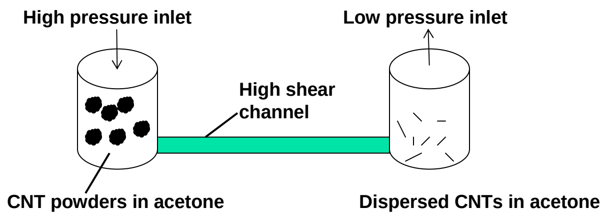
Applied Nanotech, Inc.

Our solution

- Functionalized CNTs to substantially reinforce the nanocomposites
  - amino (NH2-) groups
  - carboxyl (COOH-) groups
  - other functional groups tried but not as successful
- Developed a process for preparing dispersions for incorporation into CNT-epoxy nanocomposites using a microfluidic processor
  - Generates high shear forces to effectively break up CNT ropes and bundles
  - Can be scaled to large volume production

Applied Nanotech, Inc.

ANI's dispersion of CNTs – Microfluidic process



- Microfluidic processor uses high-pressure streams that collide at ultra-high velocities in precisely defined micron-sized channels.
- Combined forces of shear and impact act upon the mixture to create uniform dispersions.
- CNT ropes and clusters can be dispersed into small ropes or even individual CNTs using this process.

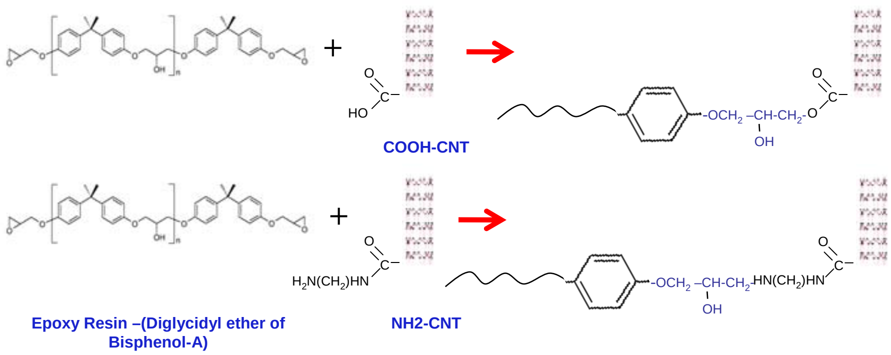
Applied Nanotech, Inc.

Result of the CNT dispersion in solvent

- Each solution contains 0.5g NH_2-DWNTs + 200ml acetone
- The picture was taken 1hr after the dispersion process

Applied Nanotech, Inc.

Reaction between COOH-CNT/NH_2-CNT with epoxy matrix



Cross-linked Epoxy Polymer – CNT composite

Applied Nanotech, Inc.

Composite resin preparation (Epon 828-based)

- DWNT-COOH – 1.2 wt.%;
- DWNT-NH_2 – 0.5, 1.2, 1.8 wt.%;
- MWNT-COOH – 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 wt.%;
- Neat resin as control/reference for comparison.

Applied Nanotech, Inc.

Sample preparation

- Functionalized CNTs / acetone solution
  - ← Dispersed by microfluidic processor
- CNT / acetone gel
  - ← Epoxy added
- Epoxy / CNT / acetone solution
  - ← Ultrasonicated in bath sonicator
- Epoxy / CNT / acetone suspension
  - ← Stirrer mixing
- Epoxy / CNT / acetone gel
  - ← Hardener added (4.5 PHR)
- Epoxy / CNT / hardener gel
  - ← Degassing
- Cast in mold
  - ← Curing (160°C for 120 minutes)
- Specimens polished and characterized

Applied Nanotech, Inc.

Characterization

- Flexural strength and modulus - ASTM D790;
- Compression strength - ASTM D695;
- Impact strength – ASTM D256;
- Vibration damping – ASTM E756;
- SEM – Hitachi S4800 FEI XL50 High Resolution SEM/STEM system for SEM imaging of fracture surface of both CNT-epoxy and CFRP nanocomposites.

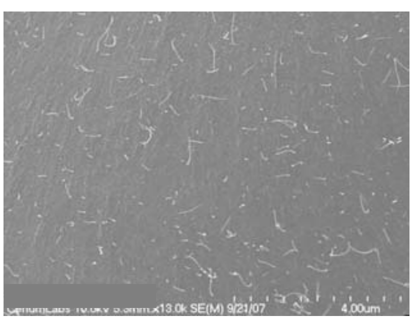
Applied Nanotech, Inc.

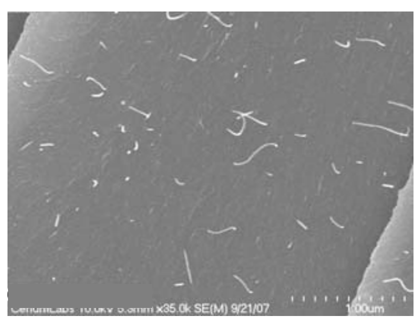
Mechanical property results of the CNT-reinforced epoxy nanocomposites

Material	Compression strength (MPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (J/m)	Vibration damping
Neat Epon 828	125	116	3.18	270	0.331
DWNT (1.2 wt.%)/Epon 828		120	3.56		
COOH-DWNT (1.2 wt.%)/Epon 828		137	3.70		
NH_2-DWNT(1.2 wt.%)/Epon 828		155	3.70		0.466
NH_2-DWNT(0.5 wt.%)/Epon 828		139	3.26		
NH_2-DWNT(1.8 wt.%)/Epon 828	172 (39%↑)	165 (42%↑)	3.70 (16%↑)	355 (31%↑)	0.476 (44%↑)
COOH-MWNT (0.5 wt.%)/Epon 828	131	144	3.38		
COOH-MWNT (0.75 wt.%)/Epon 828	138	151	3.57		
COOH-MWNT (1.0 wt.%)/Epon 828	158	159	3.61		
COOH-MWNT (1.25 wt.%)/Epon 828	170	162	3.70		
COOH-MWNT (1.5 wt.%)/Epon 828	180 (44%↑)	168 (44%↑)	3.72 (16%↑)		
COOH-MWNT (2.0 wt.%)/Epon 828	147	150	3.68		

Applied Nanotech, Inc.

Flexural surface of NH_2-DWNT reinforced epoxy at 1.8 wt.% loading

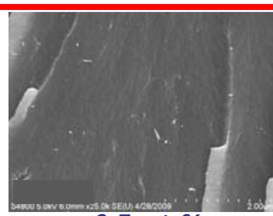




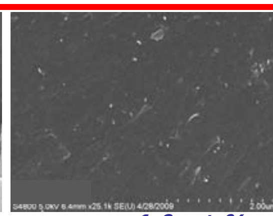
Excellent dispersion of DWNT in epoxy matrix achieved

Applied Nanotech, Inc.

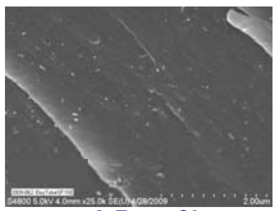
Flexural surface of COOH-MWNT reinforced epoxy at different loadings – Excellent dispersion seen



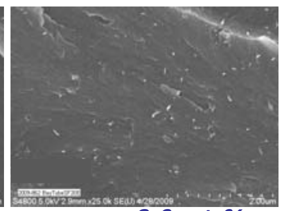
0.5 wt.%



1.0 wt.%



1.5 wt.%

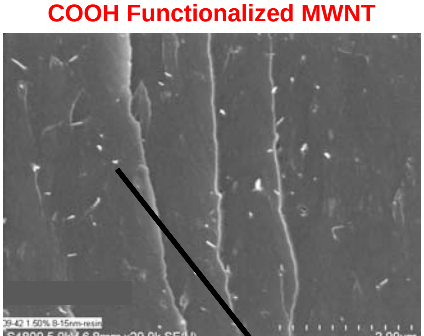


2.0 wt.%

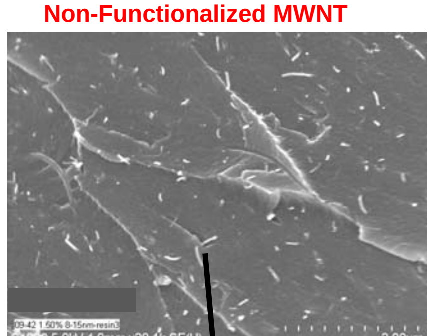
Applied Nanotech, Inc.

Flexural surface of 1.5 wt.% MWNT reinforced epoxy

COOH Functionalized MWNT



Non-Functionalized MWNT



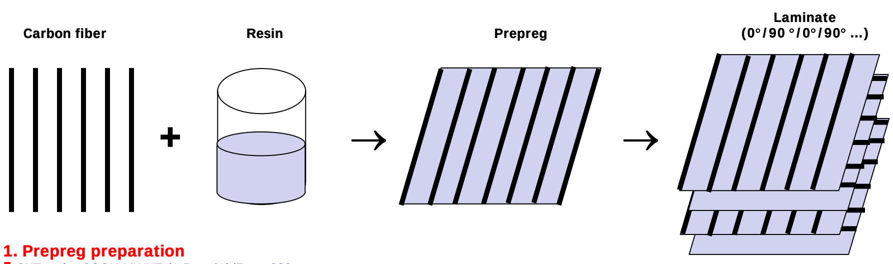
Applied Nanotech, Inc.

Summary of the results for epoxy/CNT composites

- **Achieved excellent dispersion of CNTs in the epoxy matrix.**
- **Proper functionalization of CNTs has great effect on the mechanical properties.**
- **NH_2-functionalization is more effective for the improvement of the mechanical properties of the epoxy matrix than COOH-functionalization.**
  - **The NH_2-functional groups are terminated at the open end of the DWNTs, as a result, the DWNTs can be integrated easily into the epoxy matrix.**
- **COOH functionalized CNT affects the wettability of the CNTs in the matrix;**
  - **Improves their dispersion in the epoxy matrix,**
  - **COOH-functional groups offer an opportunity for chemical interactions with the epoxy matrix.**
  - **COOH-MWNT is a cheaper, simpler process ($MWNT = 10% $DWMNT, fewer process steps)**
- **The performance of the MWNT COOH-functionalize epoxy nanocomposites met target goals of program.**
  - **The mechanical properties were improved with increasing loading of CNTs and then started to degrade at loading above 1.5 wt.%.**
  - **Higher loading of the CNTs leads to higher viscosity, which may leave voids in the specimens after the curing process.**

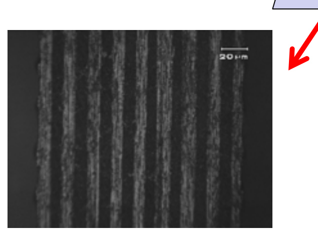
Applied Nanotech, Inc.

Prepreg preparation using CNT-reinforced epoxy



1. Prepreg preparation
- CNT resin: COOH-MWNT (1.5 wt.%)/Epon 828;
- Hardener content: 4.5 PHR;
- Carbon fiber: 60 Vol.%;
- FAW: 125 g/m^2;
- Process temperature: 70°C;

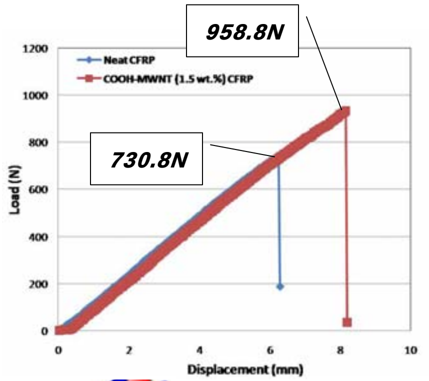
2. Curing
- Method: Autoclave;
- Pressure of autoclave: 0.49 MPa;
- Number of lay up: 17 (direction: 0°/90°/0°/90°...;)
- Cure condition: 160 °C x 120 min.



Applied Nanotech, Inc.

Flexural testing of the MWNT-COOH reinforced epoxy CFRP

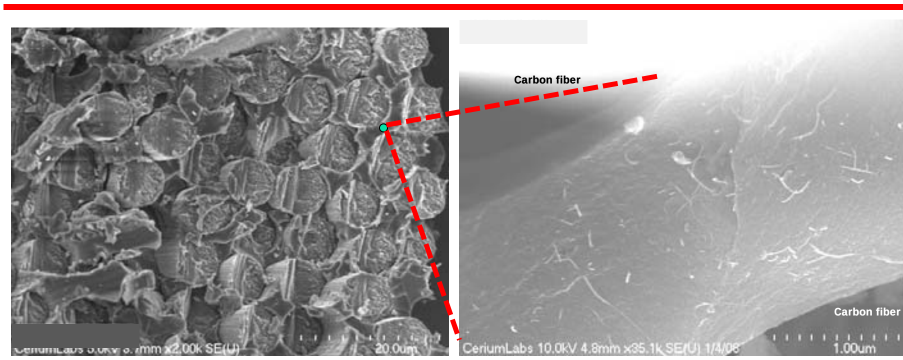
Average carbon fiber weight: 125 g/m²;
Content of the carbon fiber: 60 Vol.%;
Content of the MWNT-COOH in the resin: 1.5 wt.%.



- **30% increase in load for COOH-MWNT (1.5 wt.%) CFRP compared to neat epoxy CFRP.**
- **18 % increase in flexural modulus.**

Applied Nanotech, Inc.

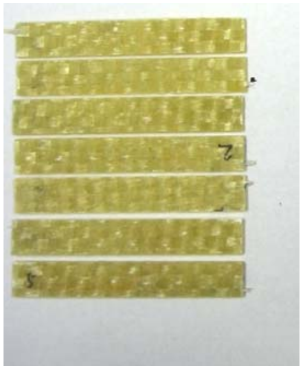
SEM images of the COOH-MWNT(1.5 wt.%) reinforced CFRP



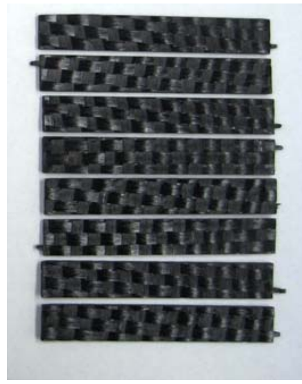
- SEM images show that the MWNTs are well dispersed in-between the carbon fibers

Applied Nanotech, Inc.

Glass fiber reinforced composite using COOH-MWNT resin



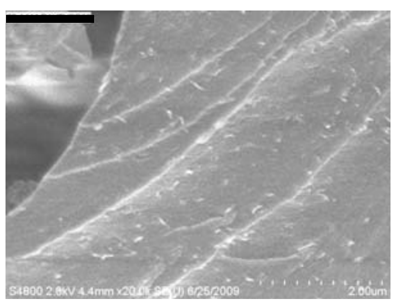
Neat epoxy/glass fiber



MWNT-epoxy/glass fiber

Applied Nanotech, Inc.

Flexural surface of glass fiber composite with functionalized MWNT epoxy



Functionalized MWNT were very well dispersed in the matrix

Result: Functionalized MWNT epoxy/glass fiber composite achieved over 40% improvement of the flexural strength over the neat epoxy glass fiber composite.

Applied Nanotech, Inc.

Conclusions

- Mechanical properties of both functionalized DWNT- and MWNT-epoxy nanocomposites were evaluated.
- NH_2-functionalization of CNTs is more effective than COOH-functionalization.
- At NH_2-DWNT loading of 1.80 wt.% (compared to neat epoxy):
  - compression strength improved 39%,
  - flexural strength improved 42%,
  - modulus improved 16%,
  - impact strength improved 31%,
  - vibration damping factor improved 44%.
- At COOH-MWNT loading of 1.5 wt.%:
  - compression strength improved 44%,
  - flexural strength improved 44%,
  - modulus improved 16%.
- The flexural strength of COOH-MWNT (1.5 wt.%) Carbon Fiber Reinforced Prepreg was **improved over 30%** as compared with CFRPs of neat epoxy.
- The flexural strength of COOH-MWNT (2.0 wt.%) Glass Fiber Reinforced Prepreg was **improved over 40%** as compared with GFRPs of neat epoxy.

Applied Nanotech, Inc.