Aligning carbon nanotubes using ultrasound to reinforce composite materials

Michael Dean Haslam
MS Candidate
Dept. of Mechanical Engineering
University of Utah
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Introduction (1)

- **Carbon nanotubes (CNTs)** exhibit extraordinary mechanical properties and have a large surface-to-volume ratio making them ideal for use as **filler material**

- CNTs are most effective as filler when their tube axis is **aligned** in the direction of the applied load

- While many techniques exist to align CNTs they are **limited** by their **scalability** to align large amounts of CNTs

- A new **scalable technique** needs to be developed that can align CNTs in macroscale volumes of polymer
Introduction (2)

• Current Applications:

Sports equipment
baseball-bat.com
whatsalltheracquet.com

Performance bicycles
xpa-cycling.com

Headphones
sears.com
Introduction (3)

- CNTs are monolayer carbon sheets rolled into a tube and come in several varieties based on:
  - The chirality of the carbon bonds
  - The number of concentric tubes

single-walled nanotube (SWNT)

multiwalled nanotube (MWNT)
Introduction (4)

- Examples of alignment techniques:

  **Fiber Processes:**
  - wet spinning
  - direct spinning
  - melt spinning

  **Bulk Processes:**
  - mechanical stretching
  - high-strength magnetic fields

  **Other Processes:**
  - mechanical slicing
  - liquid crystal alignment
  - plasma enhanced CVD

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Objective

- Demonstrate a new method for aligning CNTs using bulk acoustic waves (BAWs)

- Quantify the degree of alignment achieved with this new method on both the macroscale and the nanoscale

- Use this new method to fabricate macroscale composite materials with aligned CNTs

- Measure the mechanical properties of these composite materials under static loading
Overview

• Acoustic manipulation
• Fabrication of composite material samples
  o Experimental apparatus and materials
  o Fabrication procedure
  o Types of specimens
• Results
  o Degree of alignment
  o Degree of dispersion
  o Mechanical properties
• Summary
ACOUSTIC MANIPULATION
Acoustic manipulation theory (1)

- An ultrasound pressure wave exerts a radiation force on objects in its path
- There are two basic types of waves
  - Progressive waves which move objects toward infinity
  - Standing waves which move objects toward the nodes/antinodes of the wave, depending on the sign of the acoustic contrast factor

\[
\Phi = \frac{5\rho_p - 2\rho_m}{2\rho_p + \rho_m} - \frac{\beta_p}{\beta_m} \quad \Phi > 0 \quad \rightarrow \text{Nodes}
\]

\[
\Phi < 0 \quad \rightarrow \text{Antinodes}
\]
Acoustic manipulation theory (2)

- Standing pressure wave
  \[ P = P_a \cos(kx) \]

- Acoustic radiation force acting on a cylinder
  \[ \frac{F}{L} = F_a \sin(2kx) \]

- The acoustic radiation force drives the structures in the direction of the arrows
- The structures accumulate at the nodes of the standing pressure wave
Acoustic manipulation theory (3)

- Theoretical derivations of the acoustic radiation force on spheres and cylinders have been documented in the literature.
- Manipulation of microscale features such as cells or particles have been documented in the literature.
- Manipulation of nanoscale cylinders using BAWs has not been demonstrated.
- We hypothesize that the carbon nanotube can be displaced and aligned driven by the acoustic radiation force associated with a standing pressure wave.
Standing pressure wave between acoustic sources

Piezoelectric (PZT) material is used

Governing equation:

$$f = \frac{c}{\lambda} = \frac{cn}{2d}$$
Nodal locations (2)

- The synchronization of the two PZT plates partially determines the number of nodes obtained.
- The synchronization is controlled by the polarization of the PZT plates:
  - Simultaneous expansion/contraction = even # of nodes
  - Offset expansion/contraction = odd # of nodes
Manipulation of CNTs in water (1)

- Acoustic sources driven at 1135 kHz
- Image size is 4.5 mm x 6 mm
- Shown in real-time
Manipulation of CNTs in water (2)

- Acoustic sources driven at 1135 kHz
- Image size is 4.5 mm x 6 mm
- Shown in real-time
Manipulation of CNTs in water (2)

- Optical microscopy is used to image the alignment of CNTs in water. The expected nodal locations are overlaid in gray.
- Scanning electron microscopy (SEM) is used on a separate sample after the water is evaporated and the CNTs deposit on a glass substrate.

![Optical microscope](image1.png)  
**Optical microscope**

![SEM](image2.png)  
**SEM – 503 μm expected**

529.41 μm
FABRICATION OF COMPOSITE MATERIAL SAMPLES
Manipulation of CNTs in resin

- To fabricate composite materials reinforced with aligned CNTs, manipulation of CNTs in resin is imperative.
- Difficulties:
  - The increased viscosity of the resin medium
  - The increased power to overcome drag created by the viscosity
  - The sound speed of the resin is unpublished making resonant frequencies more difficult to find
  - The curing of the resin disrupts any established pattern
  - Optical detection of alignment is impaired by the transparency of the resin
Materials

- Polymer: Smooth-Cast 300 polyurethane (thermoset) resin
  - Two-part liquid resin
  - Ultra-low viscosity of 80 cps at room temperature
  - Pot life of 3 minutes at room temperature
- Carbon nanotubes: MWNTs from Cheap Tubes, Inc.
  - 50-80 nm in diameter
  - 10-20 μm in length
  - Quality and purity are not critical for these experiments
Sound speed measurement

- The sound speed $c$ of the liquid medium (resin) is required to accurately predict the resonant frequencies to establish a standing wave between the acoustic sources.
- $c$ is measured using a “time-of-flight” approach, with $c = \frac{d}{\Delta t}$.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Published $c$ [m/s]</th>
<th>Measured $c$ [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1506</td>
<td>1495</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>1170</td>
<td>1172</td>
</tr>
<tr>
<td>Smooth-Cast 300</td>
<td>-</td>
<td>1353</td>
</tr>
</tbody>
</table>
The experimental apparatus is cut from HDPE using a water-jet cutter. HDPE reduces adhesion with the polymer. An anti-stiction layer is placed between the reservoir and the glass slide to eliminate adhesion of the polymer to the glass slide. The dimensions are similar to a D638 Type V plastic sample with a larger gauge length and width to provide ample space for the manipulation of CNTs.
Fabrication procedure (1)

- A six-step procedure is followed to fabricate dog-bone samples of composite materials reinforced with (aligned) CNTs.
Fabrication procedure (2)

- Pure resin samples and randomly oriented CNT samples are also produced.
- Amount and type of samples produced:

<table>
<thead>
<tr>
<th>CNT loading rate (wt%)</th>
<th>0</th>
<th>0.15</th>
<th>0.50</th>
<th>1.00</th>
<th>2.00</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aligned</td>
<td>-</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Random</td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>16</td>
</tr>
<tr>
<td>Total</td>
<td>9</td>
<td>10</td>
<td>9</td>
<td>5</td>
<td>6</td>
<td>39</td>
</tr>
</tbody>
</table>

- The composite material samples are used to quantify:
  - the degree of alignment
  - the degree of CNT dispersion
  - the elastic modulus and ultimate tensile strength

Typical composite material sample with aligned CNTs
RESULTS

Degree of alignment
Degree of dispersion
Mechanical properties
Degree of CNT alignment (1)

- Alignment is quantified using the Hermans’ orientation factor $H$
- $H$ is based on the average angle between each CNT axis and the composite axis
  \[ H = 0.5 \left( 3 \cos^2 \phi - 1 \right) \]

Examples: $H = 1$  

Composite axis

CNTs

Fiber axis

Composite material sample with CNTs
Degree of CNT alignment (2)

Macroscale alignment (optical microscopy)

- Optical images are manually overlaid with lines over the CNT clusters
- $H$ is computed for five samples with loading rates of 0.5, 1, and 2 wt%
- Average macroscale alignment factor = 0.988

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi$ [deg]</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 wt%</td>
<td>2.51</td>
<td>0.997</td>
</tr>
<tr>
<td>1.00 wt%</td>
<td>7.38</td>
<td>0.975</td>
</tr>
<tr>
<td>1.00 wt%</td>
<td>3.45</td>
<td>0.995</td>
</tr>
<tr>
<td>2.00 wt%</td>
<td>5.02</td>
<td>0.989</td>
</tr>
<tr>
<td>2.00 wt%</td>
<td>5.66</td>
<td>0.985</td>
</tr>
<tr>
<td>Average</td>
<td>4.80</td>
<td>0.988</td>
</tr>
</tbody>
</table>
Micro- and nanoscale alignment (scanning electron microscopy)

- $H = 0.97$ (micro) and 0.78 (nano) are obtained
- The quality of nanoscale alignment is similar to other methods:
  - Mechanical stretching ($H=0.70$) – produces small strips
  - Wet spinning ($H=0.85$) – produces fibers
The ASTM dispersion standard (D2663-08) describes a method and index to quantify dispersion of carbon in a compound.

- It is oftentimes used in the literature to quantify the dispersion of CNTs in polymer composites.
  - The index is calculated by a count of carbon pixels $U$ in 5 of 9 defined fields.
  - The count is then compared to the volume percentage of carbon $L$.

\[
D = 100 - \frac{SU}{L}
\]
Quantifying dispersion (2)

- The ASTM dispersion index was determined for all composite samples made
  - An image of the fracture surface after tensile testing was used to calculate the index
  - Only 8 of the 30 samples received an index value > 0
  - Not a reliable measure to quantify dispersion
Quantifying dispersion (3)

- The ASTM dispersion index is inaccurate:
  - It excludes 4 of the 9 fields
  - It averages the count of black pixels with no regard for the location of those pixels
  - It does not account for the size of the carbon agglomerates
  - **Example:**
    These two images visually convey a similar level of dispersion
    The ASTM index ranks them entirely opposite
Quantifying dispersion (4)

- To improve on the ASTM index, the composite index \( \text{compIndex} \) is developed.
- It is the arithmetic average of two separate indexes:
  - The dispersion distribution index – accounts for the location of black pixels
  - The size distribution index – accounts for the size of the carbon agglomerates
- It does not exclude any fields
- It utilizes a 3 x 4 grid to correspond to a standard image size
- **Example:** Typical image divided in a 3 x 4 grid to determine the \( \text{compIndex} \)
The dispersion distribution index \((dIndex)\) is a measure of the consistency of black pixels among all 12 fields of the image.

It requires the set of all 12 black pixel percentages \(b\) (one for each field)

\[
dIndex = \frac{1}{2} \left[ 1 - \frac{s(b)}{0.5222} + \frac{\bar{b}}{\max(b)} \right]
\]

The size distribution index \((sIndex)\) is a measure of the distribution of particle sizes.

It requires the set of all particle sizes \(a\), expressed in pixels

\[
sIndex = \frac{1}{2} \left[ \frac{l}{N} + 1 - \frac{\max(a)}{\sum a} \right]
\]
Quantifying dispersion (6)

- The \( \text{compIndex} \) assigns a value > 0 for all 30 samples.
- The results are averaged by CNT loading rate for all 30 samples.
- The dispersion index decreases for increasing CNT loading rate.
Mechanical properties (1)

- The effect of CNT alignment on the material properties of the composite material is evaluated:
  - Elastic modulus ($E$)
  - Ultimate tensile strength (UTS)
- Tensile testing is performed in an Instron load frame
Mechanical properties (2)

- Average results over all samples are shown, error bars represent 90% confidence interval.
- Elastic modulus increases significantly when adding CNTs to the resin matrix.
- Alignment of the CNTs seems to increase the elastic modulus, if sufficient dispersion can be obtained.
Mechanical properties (3)

- Average results over all samples are shown, error bars represent 90% confidence interval
- UTS increases slightly when adding CNTs to the resin matrix, but decreases with increasing CNT loading rate
- Alignment of the CNTs did not seem to increase the UTS in the experiments performed
Mechanical properties (4)

- The technique of aligning CNTs using BAWs effectively increases the elastic modulus of the composite material.
- With 0.15 wt% CNT loading, the elastic modulus of the composite material with aligned CNTs:
  - is 44% larger than the composite material with randomly oriented CNTs.
  - Is 51% larger than the pure resin materials.
- Increasing the loading rate beyond 0.15 wt% results in:
  - an insignificant change in elastic modulus beyond what is obtained at 0.15 wt%.
  - a decrease in UTS.
- The experimental results at loading rates > 0.15% are likely corrupted by insufficient dispersion of the CNTs in the resin matrix. Dispersion is critical for shear transfer between the resin matrix and the CNT filler.
- Bath sonication is not the most effective method to disperse CNTs, in particular in a viscous medium.
Mechanical properties (5)

- Evaluating the UTS versus dispersion substantiates that a decrease in UTS may result from insufficient dispersion.
Conclusion

• CNTs were **successfully aligned** in a macroscale volume of thermoset polymer using BAWs. This provides a **scalable method** to aligning CNTs.

• The **degree of alignment** achieved \( H = 0.78 \) is **comparable to other alignment methods** reported in the literature such as mechanical stretching \( H \approx 0.70 \) and wet spinning \( H = 0.85 \).

• The composite material samples fabricated using the acoustic manipulation technique, demonstrated an **increase in ultimate tensile strength of 5% and elastic modulus of 51%** at a CNT loading rate of 0.15 wt% compared to the pure resin material.

• **Poor dispersion of CNTs** was found to be the reason higher loading rates displayed no further increase in elastic modulus and a decrease in ultimate tensile strength.
Acknowledgements

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Questions?