Monthly Progress Report

For the project (CCRP 2002-03):

**Nanocomposite Materials**

By

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Accomplishments
The work performed in the past month is outlined below. Different approaches for functionalization and an approach for alignment are being tried.

**Task 1: Nanotube Synthesis (~6% effort)**
The focus of our current work is on the other tasks. In related work, MgO powder was used as substrate to prepare a catalyst. The MgO was prepared two ways. One is decomposition from Mg(NO₃)₂. Another is decomposition from MgCO₃. The substrate powder was immersed into Fe(NO₃)₃ solution and dried at 100 °C for 5 hours. The processing is similar to regular processing. The difference this time was using high power ultrasound to disperse the MgO first. A use higher temperature and lower gas flow ratio were used to grow nanotubes.

**Task 2: Coating and Dispersion of Nanotubes (~47% effort)**
Work on functionalization and dispersion is outlined below.

**Magnetic Coating.**
Coating experiments using Co(NO₃)₂ and Ni(NO₃)₂ were performed to increase the magnetic property of PR-24 nanotubes and make it much easier to align the nanotubes in a magnetic field. The magnetic property of PR-24 is weak. The processing steps are;
1. PR-24 was dispersed in water in ultrasonic condition for 4 hours,
2. Co(NO₃)₂ or Ni(NO₃)₂ was added in solution and totally dissolved,
3. the solution was stirred and heated up to 100 °C until the solution was totally dry,
4. the powder was heated to 400 °C for 2 hours until the cobalt nitride totally discomposed into cobalt oxide,
5. this was ground it to fine powder and used as substrate in plasma treatment.
We are awaiting the TEM pictures to show the structure. It is evident that the magnetic property is stronger than the uncoated PR-24 by magnetically testing the material.

**Plasma Polymerization.** Not done this month.

**No-Solvent Functionalization.** Additional PR-24 nanotubes were functionalized using the no-solvent method.

**Surfactant Approach.** Not done this month.

**Opening Nanotubes.**
Carbon nanotubes were treated by concentrated nitride acid to open the ends of the nanotubes and to functionalize the surface. PR-24 5 grams were added into 300 ml concentrated nitride acid. The solution was refluxed for 24 hours. Then solution was diluted and the nanotubes were filtered out from the solution. The purpose of this treatment is to:
1. functionalize the surface of the nanotubes to get good bonding between the surface of nanotube and the polymer matrix. The PR-24 concentration was 0%, 1%, 2%, 3%, 5%. The polymer matrix is polystyrene.
2. the open end nanotubes can be further used with the in-situ polymerization method to make a composite. The idea is. (a) absorb some initiator inside of the open end nanotube; (2) the initiator will cause the polymerization reaction in the monomer to form a polymer chain; at the same time, we can form the bulk composite material. In this way, no solvent is needed and the dispersion will be good. We will try this method next month.
Dispersing Nanotubes with Combined Shear Mixing and Ultrasound. (some info from manuf web)

We are starting to investigate in more depth the use of ultrasound and shear mixing for dispersing and deagglomerating nanotubes and homogenizing the nanocomposite. The use of a longer sonotrode in combination with high speed rotary shear mixing may improve dispersion of the nanotubes. Ultrasound possibly can be used to form amorphous nanostructured materials by modification of nanotube surface morphology and nanotube length by high velocity interparticle collisions. Sonochemistry is the application of ultrasound to chemical reactions and processes. Sonochemistry can be used for the degradation and modification of polymers, synthesis of polymers, polymerization, and for the acceleration of curing reactions or dissolving processes. The sonochemical effects in liquids are caused by acoustic cavitation. Sonochemical effects in chemical reactions and processes can increase the reaction speed, increase the reactivity of reagents or catalysts, and other effects.

Cavitation is the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation collapse produces intense local heating (~5000 K), high pressures (~1000 atm), very large heating and cooling rates (>10^9 K/sec), and liquid jet streams (~400 km/h). Cavitation bubbles are vacuum bubbles created by a fast moving surface on one side and an inert liquid on the other. The resulting pressure differences serve to overcome the cohesion and adhesion forces within the liquid. Cavitation is produced using ultrasonic transducers in which the input energy is transformed into friction, turbulences, waves and cavitation. The fraction of the input energy that is transformed into cavitation depends on several factors describing the movement of the cavitation generating equipment in the liquid.

The acceleration of the fluid is one of the most important factors influencing the efficient transformation of energy into cavitation. Higher acceleration creates higher pressure differences. This in turn increases the probability of the creation of vacuum bubbles instead of the creation of waves propagating through the liquid. Thus, the higher the acceleration the greater the energy that is transformed into cavitation. In case of an ultrasonic transducer, the intensity of acceleration is described by the amplitude of vibration of the probe. Higher amplitudes result in a more effective creation of cavitation. Sonicators can create amplitudes of 115 µm. These high amplitudes allow for high power densities of up to 100 W/cm³. In addition to the intensity, the liquid should be accelerated in a way to create minimal losses in terms of turbulence, friction and wave generation. For this, the optimal way is unidirectional movement. Combining the effect of shear mixing and ultrasonication in the epoxy resin alone, and then with nanotubes is being studied. The temperature and viscosity of the resin, the size of nanotubes, the power level of the rotary mixer, the power level of the sonicator, and the pressure of the fluid (e.g. in a vacuum or at high pressure) need to be studied to improve the dispersion without degrading the material.

Task 3: Fabrication and Characterization of Nanocomposites (~47% effort)

The processing results are discussed below.

No-Solvent Method Sample Testing. The elastic modulus and strength of the no-solvent samples tested was lower than the clear epoxy. It is planned to do FTIR analysis to try to determine which kind of function groups are attached to the surface. This will aid in understanding the change in elastic properties. A high functionalization density is necessary for high solubility and dispersion because the attached organic molecules are small compared to the tube length, particularly when using the larger nanofibers. The techniques for functionalization of SWCNT also may not readily apply to CNF because of their lower crystallinity.

Dispersion. The combined ultrasonication and shear mixing steps in the procedure for dispersion of nanotubes in epoxy are being tested. This combined ultrasonication and shear mixing may shorten the time of sample preparation. A hot plate is being used for larger samples to reduce viscosity. A literature survey has indicated that too aggressive of mixing and sonication may reduce the length of the polymer chains in the epoxy. This would reduce the viscosity and also reduce the elastic modulus and strength of the cured epoxy. Carl Glezen from Tec-Epon said the resin should not be degraded by sonication and mixing unless the hardener is added. Testing of the clear epoxy without and with the sonication and
mixing step will be done to determine if there is an adverse effect on the epoxy due to sonication and mixing.

Alignment of nanotubes in the Cylindrical Mold. A liner is being put into the cylindrical mold and this will be tested. Removing the film from the mold is a difficult problem.

Nanotube Epoxy Testing. Samples were tested in the past month under different conditions and a summary is given in Table 1. The relative elastic modulus relative to pure epoxy (E=2.3 GPa) and the strength relative to pure epoxy (S=65MPa) are given in the table. The relative value is computed as: \( \frac{E_{\text{nanotube}}}{E_{\text{clear}}} \) or \( \frac{S_{\text{nanotube}}}{S_{\text{clear}}} \). The results are for a single sample. Our results indicate the no-solvent method degrades the elastic properties of the Carbon Nanofiber (CNF) PR-24. The acid treated sample with no coating also did not improve properties. The PR-19 CNF (larger diameter with carbon coating) improved the properties for the one sample tested. SEM images of the PR-19 nanocomposite are shown at the end of the report.

Table 1. Results of Single/Multiple Tension Tests of Nanofibers in Epoxy for Different Conditions.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Processing Condition</th>
<th>Relative Elastic Modulus Er</th>
<th>Relative Strength Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear Epoxy W Curing</td>
<td>No vacuum degassing, 250 F cure 4 hr</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Acid Treated PR-24 CNF, 1wt%</td>
<td>No vacuum degassing, 250 F cure 4 hr, no coating</td>
<td>0.91</td>
<td>1</td>
</tr>
<tr>
<td>No-solvent method, PR-24 CNF, 1wt%</td>
<td>Vacuum at 110C, vent, evacuate, close 1.5 hr and cure 250 F 4 hr.</td>
<td>0.9</td>
<td>0.62</td>
</tr>
<tr>
<td>PR-19 CNF, no coating, 1wt%</td>
<td>Vacuum degass 8 hr RT, 250 F cure 4 hr., rotary mixing</td>
<td>1.3</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Other Activity.
Web Site. The monthly updates and other reports for the project are on the project web site: [http://www.min.uc.edu/~mschulz/smartlab/smartlab.html](http://www.min.uc.edu/~mschulz/smartlab/smartlab.html). To use, click on restricted, and enter the password: getmein.

Electromechanical Testing. The acid treated CNF PR-24 were tested for electrochemical actuation and the material did not actuate. It appears the strong acid treatment changed the electrical properties of the CNF. This is a disadvantage of the acid functionalization for some applications. On the other hand, noncovalent attachment by plasma polymerization is advantageous because it improves solubility and the nanotube structure and electronic properties are not altered significantly.

Collaborations.
- Michael A. Meador, Chief, Polymers Branch, Materials Division, NASA John H. Glenn Research Center is processing the paperwork to seek permission for the visit.
- Professor Shankar Mall at the AFIT is going to collaborate on AFM and possibly mechanical testing of our samples. We plan to cast epoxy with SWCNT, MWCNT, and CNF and compare. This will start in another month or so.

New Equipment. As discussed at the last review meeting, we are ordering a glove box, vacuum oven and other equipment and will be setting up a new vacuum processing system for nanocomposite materials fabrication. It is anticipated that the equipment will begin arriving in March.
Figure 1. Image of the fracture surface of the uncoated PR-19 nanofiber in epoxy. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)

Figure 2. Image of uncoated PR-19 nanofiber, fine carbon particles are used to prevent charging of sample. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)
Figure 3. Image of side of uncoated PR-19 nanofiber, fine carbon particles are used to prevent charging of sample. (Image by Rob Gilliland, UC student using Sirion SEM from W.P.A.F.B.)

Figure 4. Image of uncoated PR-19 nanofiber pulling out of the epoxy matrix indicating weak bonding between the fiber and matrix. (Image by Rob Gilliland, UC student using Sirion SEM from W.P.A.F.B.)
Figure 5. Image of an uncoated PR-19 nanofiber in epoxy fracture surface. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)

Figure 6. Image of an uncoated PR-19 nanofiber in epoxy side view of fracture surface. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)
Figure 7. Image of uncoated PR-19 nanofiber in epoxy fracture surface top view. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)

Figure 8. Image of an uncoated PR-19 nanofiber in epoxy at fracture. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)
Figure 9. Image of an uncoated PR-19 nanofiber, after fracture. (Image by Rob Gilliland, UC student; Instrument: Sirion SEM from W.P.A.F.B.)