



SCALABLE PROCESSING TECHNIQUES FOR NANOTUBE-BASED POLYMER COMPOSITES

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Abstract

Toward the establishment of high volume, high rate techniques for cost-effective manufacturing of nanocomposites it is important to develop techniques that are scalable. In this research we have investigated the use of a calendaring approach for dispersion of multi-walled carbon nanotubes in epoxy and vinyl ester. Vinyl ester monomer was synthesized from the epoxy resin to overcome processing challenges associated with volatility of the styrene monomer in vinyl ester resin. The high aspect ratios of the carbon nanotubes were preserved during processing and enabled the formation of a conductive percolating network at low nanotube concentrations. The formation of percolating carbon nanotube networks at low concentration holds promise for the utilization of carbon nanotubes as sensors for detecting deformation and damage in advanced fiber composites.

1 Introduction

Advanced naval structures and other military applications often require complex, multifunctional components. These structures are exposed to a variety of conditions, including impact, shock loading and extreme changes in temperature. Toward the development of advanced naval composites, there is an increasing need to integrate multifunctionality in these material systems where both the structural and functional requirements, such as EMI shielding or IR and RCS signatures, can be tailored at the micro- and nano-scales.

Carbon nanotubes are known to have exceptional mechanical and physical properties. These properties have stimulated considerable research in attempting to utilize carbon nanotubes as a structural reinforcement in polymer nanocomposites [1, 2]. Carbon nanotubes are

inherently multifunctional and the coupling between mechanical and physical properties makes them ideal candidates as sensors. Our recent research has demonstrated that carbon nanotubes can be utilized as a network of sensors in traditional fiber composites to detect deformation and damage *in situ* and is particularly sensitive to the onset of matrix damage [3]. If a microscopic crack forms it breaks the pathway of the sensors and the response can be measured using electrical techniques. *In situ* monitoring using carbon nanotubes offers potential as both a tool for evaluating the damage during testing and in-service structural health monitoring.

Crucial to the capability to create *in situ* sensors that are minimally invasive to the properties of the composite laminate is the ability to achieve electrical percolation at extremely low carbon nanotube concentrations. Furthermore, many existing approaches to nanocomposite processing are limited in scalability and not amenable to high volume production. Calendaring using a three-roll mill has been recently introduced as a potential solvent-free, scalable technique for processing nanocomposites [4-6].

Large-scale composite structures often use vinyl ester as a primary resin system because of its relative low cost and low viscosity, making it suitable for vacuum assisted resin transfer molding (VARTM) processing. The potential of nanotube-reinforced vinyl ester composites has been largely unexplored. Fan *et al.* [7, 8] examined the influence of different dispersion techniques on the dispersion of carbon nanotubes in vinyl ester. They reported that acid oxidized nanotubes were dispersed homogeneously in the matrix because the nanotube length was reduced during the acid reflux, but no mechanical or physical properties of the as-manufactured nanocomposites were reported. More recently, Gryshchuk and co-workers investigated vinyl ester nanocomposites through the use of mechanical stirring and ultrasonic mixing [9]. Poor

nanotube dispersion was noted in the vinyl ester system due to nanoscale entanglement. Minor increases in the elastic properties and fracture toughness at varying nanotube concentrations as well as an increase in electrical conductivity were reported.

The styrene monomer in vinyl ester resin results in substantially reduced viscosity, making vinyl ester suitable for the VARTM process, but substantial nanocomposite processing challenges are encountered with vinyl ester systems because of the volatility of the styrene monomer. In this research we process carbon nanotube/epoxy and carbon nanotube/vinyl ester nanocomposites using a calendaring approach and characterize the resulting electrical properties.

2 Processing of Carbon Nanotube-Based Composites

A wide variety of techniques have been developed to process nanotube composites as highlighted in a recent review [1]. We have recently explored the calendaring approach using a three-roll mill as a potential scalable technique for processing nanocomposites. CVD-grown carbon nanotubes have substantial nanoscale entanglement (Figure 1) which is a barrier to achieving a high degree of dispersion. With the calendaring approach adjacent cylinders rotating at different velocities are utilized to impart high shear stresses, illustrated in Figure 2. The narrow gap, δ_g , combined with mismatch in adjacent roll angular velocity, $\omega_1 < \omega_2$, results in high shear rates. Unlike other mills, which rely on compressive impact as well as shear, calendaring results in nearly pure shear. Because the mixture must pass through the gap the process also uniformly shears the entire volume. For dispersing nanotubes, high shear stresses break-up and untangle nanotubes while short residence time limits nanotube breakage.

To fabricate the nanotube/epoxy composites the nanotubes were dispersed in the epoxy resin using a laboratory-scale three-roll mill that enables precise control over the gap down to a minimum of 5 μm . In our previous research we studied the processing/structure relations and developed processing protocols to achieve a high degree of dispersion [6]. By adjusting the processing conditions the relative degree of dispersion can be controlled. When the materials are milled to a final gap setting of 10 μm the structure shows a dispersed/partially agglomerated structure where a large number of individual nanotubes are dispersed

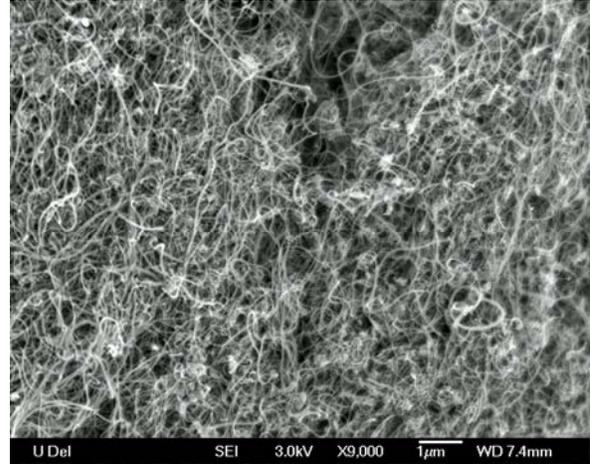


Fig. 1. Scanning electron micrograph showing the nanoscale entanglement of multi-walled carbon nanotubes in their as-grown state.

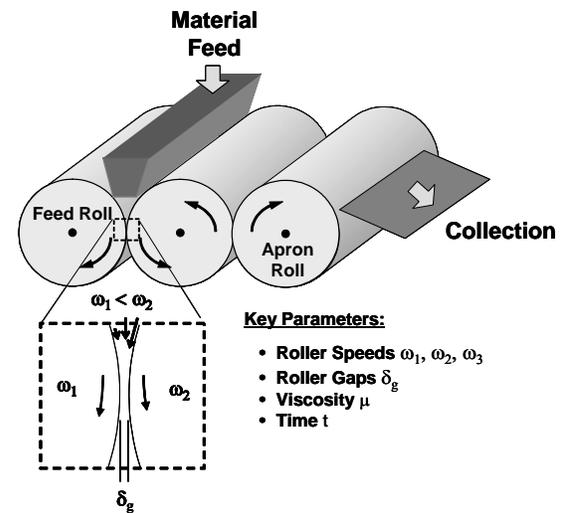


Fig. 2. Schematic of a 3-roll mill and (inset) area of high shear mixing.

in the matrix with some small (sub-micron) agglomerates of nanotubes present. When the suspension of nanotubes is milled to the smallest gap setting of 5 μm the nanotubes are highly dispersed with little or no agglomerates present.

Nanotube/epoxy composites were processed by first direct mixing multi-walled carbon nanotubes in their as-received condition in a bisphenol-F epoxy polymer matrix (EPON 862; Hexion Specialty Chemicals, Inc.). The mixture was then repeatedly passed through the mill at progressively decreasing gap settings.

After processing in the three roll mill the nanotube/epoxy dispersion was heated to 50°C in an

oven to reduce the viscosity. The nanotube/epoxy dispersion was then mixed with an aromatic diamine curing agent (Epi-Kure W, Hexion Specialty Chemicals, Inc.) at ratio of 26.4/100 curing agent to epoxy. The mixtures were placed in aluminum specimen molds and cured for 6 hours at 130°C. After curing, the specimens were cooled and machined into test specimens for characterization.

For processing of vinyl ester nanocomposites a different approach was required. During the calendaring process a thin film of resin is formed on the surface of the rollers. As a consequence, a large amount of surface area per unit volume of resin is exposed to air. Styrene in commercial vinyl ester resin systems, typically 30-50% by weight, is volatile and evaporates during the calendaring process.

In order to avoid evaporation of the styrene monomer, and subsequent variations in both styrene and nanotube concentrations in the final resin mixture, vinyl ester monomers were synthesized from the epoxy resin as a precursor. The vinyl ester monomer was produced following the method used by Robinette and co-workers [10]. Stoichiometric amounts of epoxy and methacrylic acid were reacted using triphenyl antimony and triphenyl phosphine as catalyst. The reaction, shown in Figure 3 was carried out in a hot oil bath under constant stirring at temperatures between 90 to 95°C for two hours. After the reaction the vinyl ester monomer was characterized using fourier transform infrared spectroscopy (FTIR) to ensure the epoxy groups had been reacted to form vinyl ester. After reaction to form the vinyl ester monomer styrene was added at 40% by weight to form the final vinyl ester resin.

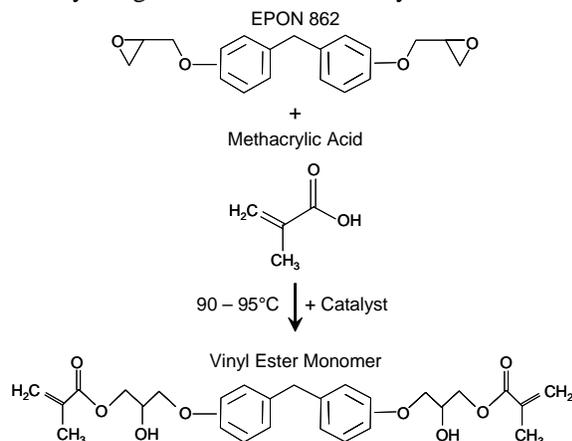


Fig. 3. Reaction of EPON 862 epoxy with methacrylic acid to form a vinyl ester monomer.

In order to prepare carbon nanotube/vinyl ester composites two different methods were explored. In one method, the carbon nanotubes were first dispersed in the epoxy using the three-roll mill prior to reaction to form the vinyl ester monomer. In the second method, the carbon nanotubes were dispersed directly in the vinyl ester monomer using the three-roll mill. In both cases, the nanotube/polymer mixtures were milled at progressively smaller gap settings down to a final setting of 5 μm . The final concentration of carbon nanotubes after the addition of styrene was 0.5 wt% for both sets of nanocomposites. The vinyl ester nanocomposites were cured by reacting the vinyl ester resin with a cumene hydroperoxide initiator (Trigonox 239A, Akzo-Nobel Industries) and cobalt naphthenate as the accelerator.

3 Electrical Characterization

The DC volume resistivity was measured following ASTM D257 [11] using a highly sensitive sourcemeter (Keithley 6430 Sub Femtoamp Remote Sourcemeter). Resistivity measurements on the insulating, unreinforced epoxy were performed using a parallel plate resistivity test fixture (Keithley Model 8009). For more conductive materials the contact resistance associated with the parallel plate fixture is significant. Resistivity measurements on all of the nanocomposites were performed using strip specimens and with electrodes applied to the ends using highly-conductive silver paint

Figure 4 shows the influence of nanotube concentration on the volume resistivity of the as-processed nanotube/epoxy composites. For the highly dispersed and partially agglomerated structures the electrical percolation threshold occurs at a concentration below 0.1 weight percent. The low percolation threshold for both sets of nanocomposites indicates that the large nanotube aspect ratio is maintained during processing and the nanotubes form a percolating network throughout the matrix. For the partially agglomerated structure the electrical resistivity is larger than the highly dispersed structure, particularly at lower fractions of carbon nanotubes. Because of local nanotubes agglomeration, the statistical fraction of nanotube participating in conductive percolation is lower, resulting in higher overall resistivity and more scatter in the data at the lower carbon nanotube concentrations.

The nanotube/vinyl ester composites processed by dispersing the carbon nanotubes in both the epoxy precursor and the vinyl ester monomer using

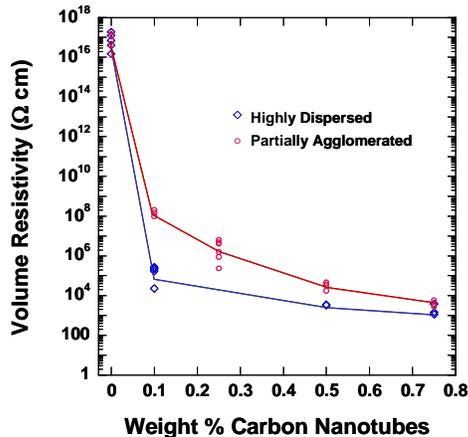


Fig. 4. Influence of nanocomposite structure on the electrical percolation behavior of carbon nanotube/epoxy composites.

the three-roll mill were both above the threshold for electrical percolation. Table 1 summarizes the volume resistivity data for the nanotube/polymer composites at final nanotube concentrations of 0.5 wt%. Both of the vinyl ester nanocomposites show overall volume resistivity values close to that of the highly dispersed epoxy system, which was milled to a final gap setting of 5 μm . The partially agglomerated epoxy system, milled to a gap setting of 10 μm , shows an average volume resistivity that is an order of magnitude higher. The nanoscale structure characterization of the vinyl ester nanocomposites is ongoing, but, with the similarity in electrical properties to the highly dispersed epoxy system, a high degree of nanoscale dispersion is expected.

Table 1 Volume resistivity of 0.5 wt% carbon nanotube / polymer composites

| Resin | Dispersion Condition | Volume Resistivity ($\Omega\text{ cm}$) |
|-------------|-------------------------------|---|
| Epoxy | Milled to 10 μm | 33000 \pm 11300 |
| Epoxy | Milled to 5 μm | 3380 \pm 107 |
| Vinyl Ester | Milled in Vinyl Ester Monomer | 5140 \pm 384 |
| Vinyl Ester | Milled in Epoxy Precursor | 3750 \pm 147 |

4 Conclusions

Toward the establishment of high volume, high rate manufacturing techniques for cost-effective manufacturing of nanocomposites we investigated the use of a calendaring approach for dispersion of multi-walled carbon nanotubes in both epoxy and vinyl ester polymer matrix materials. The high aspect ratios of the carbon nanotubes were preserved

during processing and enabled the formation of a conductive percolating network at concentrations below 0.1% by weight carbon nanotubes in epoxy. In exploratory research in preparing vinyl ester nanocomposites we established a technique of dispersing the nanotubes in a vinyl ester monomer synthesized from the epoxy precursor. Our initial experiments indicate that the percolation threshold in vinyl ester nanocomposites is below 0.5 wt% and the volume resistivity is similar to the highly-dispersed epoxy system.

The low percolation threshold for both the epoxy and vinyl ester composites holds potential for the use of nanotubes as sensors in traditional fiber composites to detect deformation and damage *in situ* while being minimally invasive to the mechanical performance of the laminate.

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