

VINYL ESTER NANOCOMPOSITES FOR DAMAGE SENSING IN NAVAL APPLICATIONS

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SUMMARY

This paper reports recent work in processing and characterization of carbon nanotube / vinyl ester nanocomposites. The high aspect ratio of the carbon nanotubes are preserved during processing, enabling the formation of electrically conductive networks at concentrations as low as 0.1 wt% nanotubes. Formation of electrically-conductive networks in glass fiber composites enables sensing of damage *in situ*.

Keywords: Carbon Nanotubes, Electrical Properties, Structural Health Monitoring

INTRODUCTION

Because of their unique material properties carbon nanotubes have generated widespread interest in the development of polymer nanocomposites reinforced with nanotubes [1, 2]. Their unique mechanical and electrical properties have opened-up new applications as sensing materials [3]. Recent research has established carbon nanotubes as *in situ* sensors for detecting damage in fiber composites [4-8].

As compared to advanced structural fiber reinforcement, such as carbon or glass fibers, carbon nanotubes are three orders of magnitude smaller. As a consequence, carbon nanotubes are able to penetrate the matrix rich regions within fiber bundles and also between the layers of the composite. If the nanotubes are able to form electrically conductive pathways around the structural fiber reinforcement the networks can act as nerve-like sensors for detecting the formation and accumulation of matrix cracks. In addition to the sensitivity of the technique for detecting cracks *in situ*, the technique is minimally invasive since these conductive networks are formed at very low nanotube volume fractions.

Crucial to the ability of carbon nanotubes to sense the formation of damage in fiber composites is the ability to adequately disperse carbon nanotubes in the polymer without substantially reducing the carbon nanotube aspect ratio (length/diameter). Recently a calendaring approach using a three-roll-mill has been established that enables nanotubes to become untangled from their as-grown state and is also potentially scalable for industrial applications [9-11].

Vinyl ester resins are frequently utilized in large-scale structural applications due to their low viscosity, enabling processing using resin infusion techniques, and ability to cure at ambient temperatures. Vinyl ester resins contain both vinyl ester and styrene monomers. Styrene content for commercially available vinyl ester resins is typically 40-50%. Because styrene is volatile it is a significant technical challenge to disperse carbon nanotubes using many techniques due to the evaporation of styrene during processing. Evaporation results in variability in the concentrations of the constituent materials.

In this research we demonstrate that it is feasible to disperse carbon nanotubes in vinyl ester resins using a calendaring approach by first dispersing the nanotubes in vinyl ester monomer followed by addition of styrene. Electrical percolation thresholds for the nanocomposites were achieved at concentrations of less than 0.1 wt%. Carbon nanotube / glass fiber / vinyl ester composites were produced using a conventional vacuum-assisted resin transfer molding technique and electrical percolation was achieved in the as-processed composites. The sensitivity to detection of cracks was investigated using direct-current resistance changes coupled with acoustic emission.

EXPERIMENTAL

Dispersion of Carbon Nanotubes

As discussed in the preceding section, the evaporation of styrene results in substantial processing challenges for dispersion of carbon nanotubes in vinyl ester resins. In order to overcome the difficulty presented by the volatility of styrene a vinyl ester monomer was first synthesized from a commercially-available low-viscosity epoxy resin as a precursor (bisphenol-F epichlorohydrin epoxy resin; EPON 862 Hexion Specialty Chemicals, Inc.). The vinyl ester monomer was synthesized by reacting stoichiometric amounts of methacrylic acid with the epoxy in the presence of catalyst to convert the epoxy groups to vinyl groups [12, 13].

Once the monomer was produced nanotubes were then dispersed directly in the vinyl ester monomer by using the calendaring approach described in our earlier research on carbon nanotube / epoxy composites [11]. The nanotube / vinyl ester monomer dispersion was passed through the calendaring mill at progressively smaller gap settings down to a final setting of 5 μm . After calendaring styrene monomer (Aldrich) was added at a concentration of 40 wt%. In order to cure the nanocomposite cumene hydroperoxide initiator (Trigonox 239A, Akzo-Nobel Industries) at a concentration of 1 wt% and cobalt naphthenate accelerator at a concentration of 0.2% were mixed into the nanotube dispersion.

For the fabrication of nanocomposite test specimens the mixture was de-gassed under vacuum for 10 minutes followed by curing in an aluminum specimen mold at room temperature for three hours. In order to minimize styrene evaporation prior to gelation, the mold was covered with a plastic film. After curing at room temperature the specimens were then postcured at 160°C for one hour. The processing steps for vinyl ester nanocomposites are highlighted in Figure 1.

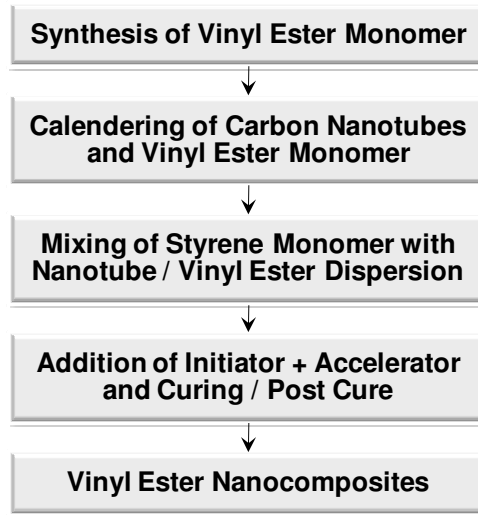


Figure 1. Processing steps for vinyl ester nanocomposites [13].

Fabrication of Nanotube / Glass Fiber / Vinyl Ester Composites

Carbon nanotube / E-glass / vinyl ester composite laminates were manufactured using a conventional vacuum assisted resin transfer molding (VARTM) technique. The nanotube dispersions were first produced using the calendaring approach described above. Prior to infusion the viscosity of the resin and other components was measured using a rotational viscometer to ensure a suitable viscosity for the VARTM process. Unidirectional non-woven fiber mats in unidirectional and cross-ply configurations were sealed in a vacuum bag with a resin distribution layer and the nanotube / vinyl ester mixture drawn through the specimens under vacuum (Figure 2). After infusion the composite was allowed to cure at room temperature followed by post-cure.

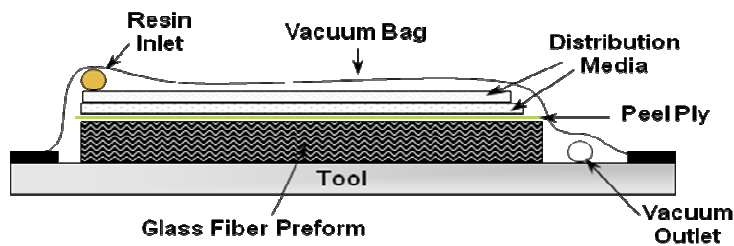


Figure 2. Schematic of the VARTM process.

Electrical and Mechanical Characterization

Test specimens for both the nanocomposite and nanotube/fiber composites were machined for electrical and mechanical characterization. The volume resistivity of the nanocomposites was measured following ASTM D257 using long rectangular strip

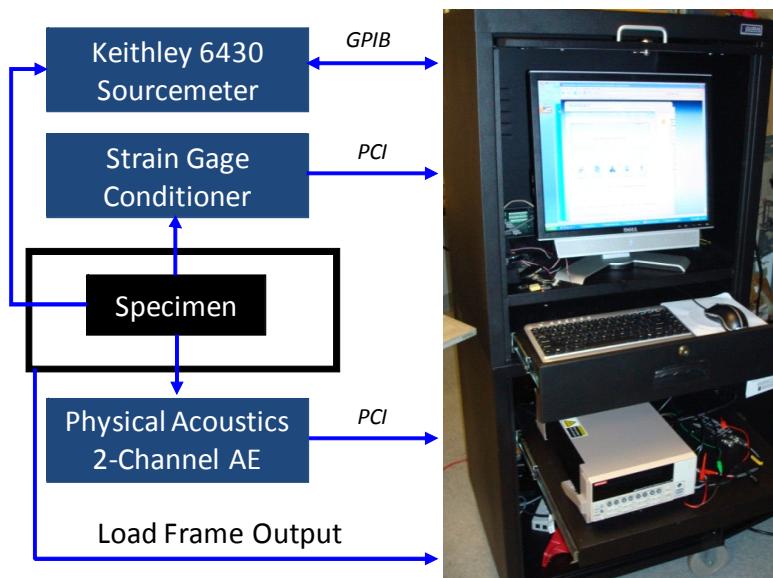


Figure 3. Schematic showing inputs into the mechanical/electrical/acoustic emission data acquisition system.

specimens with electrodes applied to the ends of the specimen using conductive silver paint (Structure Probe, Inc.). A constant voltage was sourced and the current measured using a highly-sensitive sourcemeter (Keithley 6430). The volume resistivity of the vinyl ester without nanotubes was measured using a parallel plate fixture (Keithley 8009). For the fiber composites with electrically conductive nanotube networks the composites were machined into strips along the fiber direction and at different locations in the laminate. The resistivity of the composite was measured using the sourcemeter with electrodes applied to the ends of the specimen.

For *in situ* damage sensing experiments non-conductive end tabs were bonded to laminates and specimens were obtained by cutting the laminate into strips with a width of 12.7mm (0.5 in.). Electrodes were placed directly on the ends of specimens by anchoring a lead-wire to the end tab and applying conductive silver paint across the specimen cross-section. Mechanical tests were performed using a screw-driven load frame (Instron 5567) at a fixed displacement rate of 1.27 mm/min (0.05 in./min). A two-channel acoustic emission system (Physical Acoustics, Princeton Junction, NJ) was used to record acoustic events throughout the test. A 35–100 KHz transducer coupled with a 100 KHz–1 MHz analog filter was mounted on the surface of the specimens. Resistance, strain, load, extension and acoustic emission were measured simultaneously using a custom integrated LabView® data acquisition system, shown in Figure 3.

RESULTS AND DISCUSSION

Figure 4 shows the electrical properties of the carbon nanotube / vinyl ester composites. The neat vinyl ester is an electrical insulator with a volume resistivity on the order of $10^{16} \Omega \text{ cm}$. With the addition of just 0.1 wt% carbon nanotubes the volume resistivity

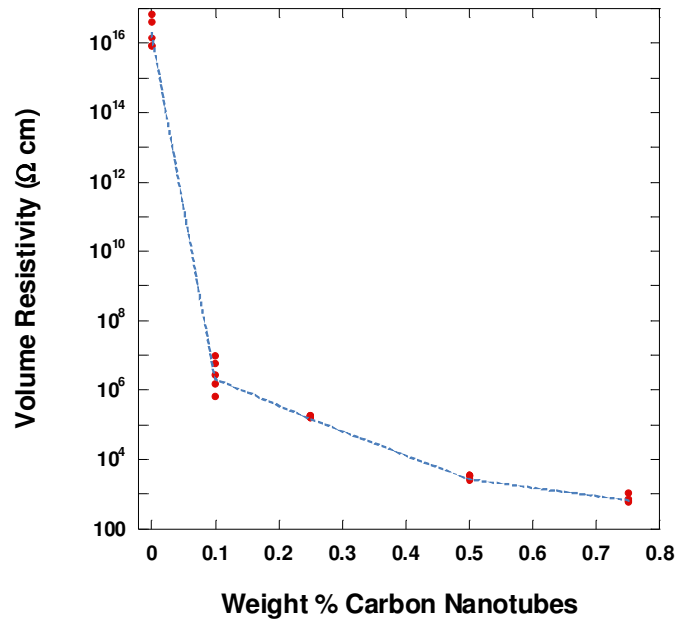


Figure 4. Electrical properties of carbon nanotube / vinyl ester nanocomposites [13].

decreases by almost nine orders of magnitude. The low electrical percolation threshold in these nanocomposites indicates that the aspect ratio of the carbon nanotube was maintained during the dispersion process and is able to form electrically conductive networks throughout the insulating polymer.

Table 1 shows the measured viscosity of the vinyl ester with and without the addition of carbon nanotubes. The vinyl ester monomer synthesized from EPON 862 has a viscosity at ambient temperatures of 3600 cP, but with the addition of 40 wt% styrene to the vinyl ester monomer the viscosity is approximately 15 cP and is a substantially lower than commercially-available vinyl ester resin systems. The dispersion of 0.5% carbon nanotubes results in a substantial increase in the viscosity of the monomer, but after the addition of styrene the viscosity is still below that of commercial vinyl ester resins and suitable for vacuum infusion.

Table 1. Viscosity of components of the as-synthesized vinyl ester system and comparison with a commercially-available vinyl ester resin [14].

Material	Viscosity
Monomer with 0.5 wt% Nanotubes	500,000 cP
Monomer w/out Nanotubes	3600 cP
Resin with 0.5 wt% Nanotubes	130 cP
Resin w/out Nanotubes	15 cP
<i>Derakane™ 411-350</i>	<i>370 cP</i>

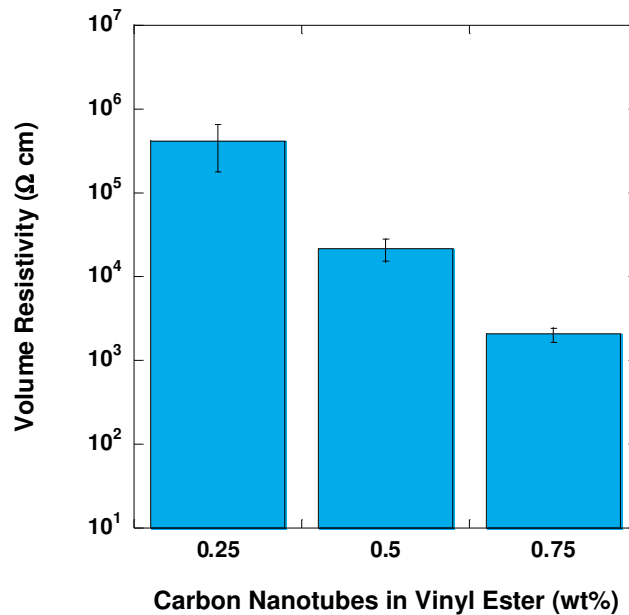


Figure 5. Electrical properties of carbon nanotube / glass fiber / vinyl ester composites.

Figure 5 shows the electrical properties of the nanotube / glass fiber / vinyl ester composites along the axial fiber direction. At concentrations above 0.25 wt% of nanotubes in the vinyl ester resin it is clear that percolation has been achieved in the nanotube / fiber / vinyl ester composite. It is interesting to note that the electrical properties of the nanotube/fiber composite are on the same order of magnitude as the nanocomposites.

In our earlier research we established that the networks of carbon nanotubes in glass/epoxy composites can be utilized as a distributed sensing network that can be utilized for sensing of both deformation and damage *in situ*. The unique aspect of in situ sensing using embedded carbon nanotube networks is the capability to detect the onset and evolution of microstructural damage [4, 5]. As cracks propagate in the composite the conducting pathways are broken in the percolating network. The capability to sense damage is unique to nanostructured materials since a nano-scale conductor is necessary to sense the formation of a micro-sized crack.

In order to establish the technique of in situ sensing for advanced vinyl ester naval composites, cross-ply $[0/90]_s$ composites were manufactured at varying nanotube concentrations and the evolution of microstructural damage examined under tensile loading studied. Figure 6 shows the electrical resistance response of the specimen undergoing tensile loading. There are large increases in electrical resistance with the accumulation of microstructural damage. Also shown in Figure 6 is the acoustic emission measured real-time during testing. It is clear that there are acoustic emission counts that correspond directly to large jumps in the resistance/strain plot, validating that the observed resistance response corresponds directly to the breaking-apart of the percolating network due to the formation of cracks.

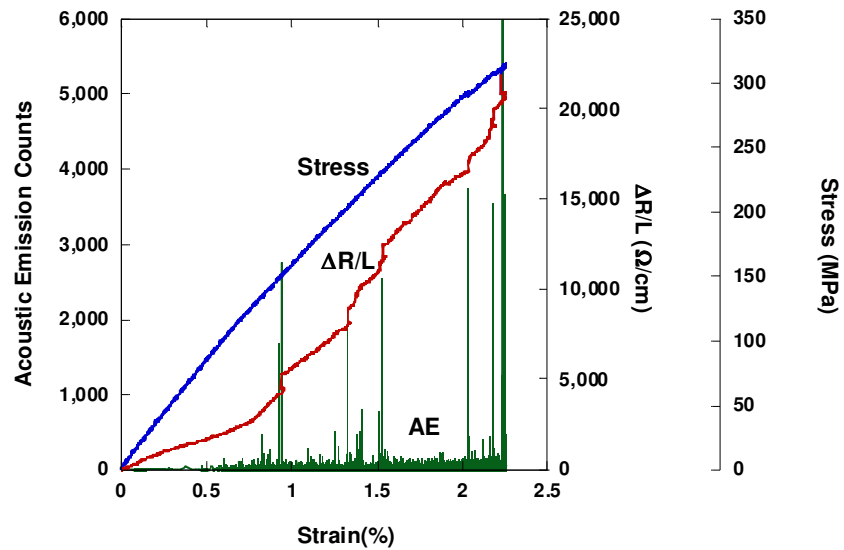


Figure 6. Stress, resistance change per specimen length ($\Delta R/L$) and acoustic emission response of a cross-ply glass fiber / carbon nanotube / vinyl ester composite undergoing quasi-static tensile loading.

CONCLUSIONS

A comprehensive study in the processing and electrical property characterization for nanotube and nanotube/fiber hybrid composites has demonstrated that the high aspect ratios of the carbon nanotubes are preserved during processing. This enables the formation of conductive percolating networks at low nanotube concentrations in both the nanocomposites and the nanotube/fiber composites. Key experiments are ongoing to evaluate the influence of processing condition and fiber orientation on the electrical properties of the composites, and results demonstrate the sensitivity of the vinyl ester composites for *in situ*.

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