

In situ thermoresistive characterization of multifunctional composites of carbon nanotubes

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The thermoresistive behavior of nanocomposites with electrically conductive networks of carbon nanotubes (CNTs) in a vinyl ester polymer matrix were characterized using an *in situ* electrical resistance measurement during thermomechanical analysis. A series of specimens above the electrical percolation threshold ranging from 0.10 to 1.00 wt% CNT were studied. The results show the thermoresistive behavior is strongly dependent on the CNT concentration, thermal expansion and polymer segmental motion. At higher concentrations of carbon nanotubes the temperature coefficient of resistance (TCR) varied with temperature and could either be positive or negative while specimens with low CNT concentrations near the percolation threshold showed a near-zero but negative TCR. Since the nanocomposite bulk resistivity of the specimens is dominated by the tunneling resistance at CNT/CNT junctions the nanotubes effectively act as a network of sensors that can detect thermal transitions and other thermochemical changes *in situ*.

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1. Introduction

In the last decade there has been a large focus on the research and development of nanoparticle reinforced polymers. Among the nanoparticles with the greatest potential to improve the mechanical properties of polymer matrix composite materials are carbon nanotubes (CNTs), because of their high aspect ratio (length/diameter) and large axial stiffness [1]. It was found that CNTs can be used to modify matrix-dominated properties of fiber reinforced composite materials, including in-plane and interlaminar properties [2], because of the selective scales of reinforcement possible (macro, micro and nano). In thermosetting polymers, CNTs were found to improve stiffness, strength and fracture toughness given good dispersion and matrix–particle interaction [3]. However, the expected large improvement of overall mechanical properties has not been realized.

One of the most unique properties of CNT composites has been the formation of electrically conductive networks at low carbon nanotube concentrations, often below 0.1 wt% CNTs. This unique ability to form networks has enabled their use as materials where piezoresistivity, the change of resistivity/conductivity with applied deformation that is higher than expected based on simple

dimensional change, can be exploited in a variety of applications. Thostenson and Chou [4] developed approaches for sensing of microcracks using a percolating network of CNTs in the polymer matrix of a fiber reinforced composite. Sensing was realized by measuring the direct current (DC) electrical resistance of the composite during various loading regimes. A combination of linear and non-linear piezoresistive behavior was observed, with the non-linearity resulting from material damage, i.e. matrix cracking. The piezoresistivity and damage sensing functionality is thought to have its origin in the changes occurring in the CNT/CNT interphase, or tunneling gap [5]. Intense interest remains in the sensing applications for these composite materials.

Fiber-reinforced composite materials often experience extreme service environments, for example, in aerospace and marine structures. Such applications have dramatic temperature and humidity fluctuations which, over time, can result in degradation that leads to poor performance and premature failure. *In situ* sensing based on the electrical resistance measurements of a network of dispersed CNTs offers much potential in meeting the needs of critical structures. Composites of dispersed CNTs have already demonstrated the ability to sense micro-scale damage under quasi-static, impact and cyclic loading conditions in glass fiber reinforced composites and bonded joints [6–9]. However, the effect of temperature on multifunctional composites is of both scientific and practical importance and has not been fully investigated.

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Several researchers have attempted to experimentally measure the effect of temperature change on the electrical properties of CNT filled polymers [10–19]. Typical experimental approaches measure DC resistance across a thin film or plate sandwiched between two cylinders with electrical contacts made within the material or on the cylinders. These methods may be an appropriate way to measure the electrical resistance of neat polymers at room temperature, but these methods fail to account for geometric factors such particle size and dispersion, or thermal expansion. Because the specimens are typically constrained between two cylinders, the material is not able to expand and contract freely in all directions during heating or cooling. Furthermore, CNTs have very large aspect ratios and it is possible that a small number of CNTs or CNT agglomerates could span the thickness of these specimens, bringing into question the validity of using thin plates or films as test specimens in a through-thickness measurement. The results produced using these methods do not accurately represent the bulk electrical properties but are instead the result of statistically spanning clusters of CNTs. As a consequence there is wide variation in results reported in the scientific literature. In order to accurately measure bulk electrical properties, the specimen geometry and factors influencing electrical resistance should be considered. In previous research [20] the parallel plate method per ASTM D257 [21] was found to be unreliable for dispersed CNT composites and a rectangular specimen was adopted. Other researchers have also adopted the use of rectangular specimens [10,16] to get accurate bulk resistivity measurements.

In this research, we evaluate the thermoresistive behavior of CNT/vinyl ester nanocomposites and establish an experimental approach where electrical resistivity is measured with volumetric expansion. The thermoresistive behavior of particle filled polymers or composites was assumed to be affected by the particle geometry and dispersion, particle electrical properties, polymer/interphase electrical properties and thermal expansion. The contribution of CNT thermoelectrical properties was expected to be minor given the distribution of metallic and semi-conductor behaviors recorded in the literature [22–24]. In order to confirm this assumption, a CNT film/buckpaper was tested for electrical resistance using a four-wire measurement over a temperature range of 25–165 °C. A very small, linear change in resistance over the temperature range was observed and is in general agreement with the literature [25,26]. To characterize the thermoresistive behavior of CNT/vinyl ester composites the DC electrical resistance was measured *in situ* during thermomechanical analysis. The experiment was designed to allow for near-free volumetric expansion of the specimen while accommodating proven thermomechanical and electrical resistance measurements. Specimens ranging from 0.1 to 1 wt% CNT were thermally cycled for several hours in order to quantify the effect of temperature, thermal expansion, and thermal transitions in the polymer, as well as to observe any transient effects.

2. Experimental

2.1. Materials synthesis and specimen preparation

Composites of highly dispersed multi-walled CNTs and vinyl ester were prepared in a four step process developed previously [20]. First, vinyl ester monomer was synthesized by reacting bisphenol-F type epoxy monomer (EPON Resin 862, Momentive, USA) and methacrylic acid with triphenylphosphine and triphenylantimony (III) (99%, Sigma–Aldrich, USA) at 0.25 and 0.75 wt%, respectively. The esterification reaction took place between 90 and 95 °C for 2 h while stirring. The dispersion of CNTs (95% purity, Hanwha Nanotech, Korea) into vinyl ester monomer, the second

step, was achieved using a calendering approach with a three-roll mill so as to yield the desired final concentrations in the nanocomposites of 0.1, 0.5, 0.75 and 1 wt%. The high-shear mixing process utilizing a three-roll mill (EXAKT 80E, EXAKT Technologies, USA) ensured a high degree of dispersion of individual CNTs by untangling agglomerates as the CNT/monomer mixture was sheared between the roller gaps at progressively smaller settings using previously established processing protocols [4]. Electron microscopy was used in Refs. [4,20] as well as by other authors [27] to confirm the dispersion quality achieved using this method. The final steps prior to casting parts were the addition of styrene monomer ($\geq 99\%$, ReagentPlus, Sigma–Aldrich, USA) at 40 wt% with a hand-held homogenizer (Tissuemiser Homogenizer, Fisher Scientific, USA) followed by hand mixing of accelerator, cobalt naphthenate (6% in mineral spirits, Sigma–Aldrich, USA) and initiator (Trigonox 239, AzkoNobel, USA) at 0.2 and 1.0 wt%, respectively.

The prepared resin mixture was poured into aluminum molds to be cast into specimen geometries and allowed to cure at room temperature overnight. After demolding and post-curing at 165 °C for 2 h, the specimens were surface ground to 3 mm thickness. Test specimens were cut to final dimensions of $3 \times 3 \times 13$ mm using a diamond saw. To ensure that absorbed moisture did not influence the results, the specimens were dried under vacuum at elevated temperature for 48 h and then stored in the presence of desiccant.

2.2. *In situ* electrical resistance measurements and thermomechanical analysis

Thermomechanical/thermoresistive analysis was conducted using a thermomechanical analyzer (TMA) (TMA/SDTA841e, Mettler Toledo, USA) with a multifunctional data acquisition device (NI-6218, National Instruments, USA) controlled using customized LabVIEW software and an external PC. A minimum of 3 nanocomposite specimens of each nanotube composition were tested in order to ensure repeatability of the observed response. The specimens were designed specifically to meet the requirements of the TMA and also to accommodate an *in situ* electrical resistance measurement. Electrodes and lead wires were attached by first applying silver paint followed by silver filled epoxy to secure the lead wires to either end of the specimen. The conductive epoxy was cured at 60 °C for 2 h.

Fig. 1 shows the test configuration where the electrical resistance is measured along the length of the specimen and the TMA probe measures thermal expansion. As observed in Fig. 1, the electrodes are not in contact with the TMA stage or probe and allow sufficient clearance from the environmental chamber when lowered into place. Specimens were then subjected to a total of nine cycles between 25 and 165 °C at a ramp rate of 3 °C/min. The electrical resistance was monitored during the entire testing period. The normal force exerted by the TMA probe was set to 1 N and 5 min isothermal segments were programmed for 25 and 165 °C to enable the specimen to reach thermal equilibrium. The coefficient of linear thermal expansion (CLTE) given by the normalized derivative of specimen height (h) with temperature (T) given by $(10^6/h_0)dh/dT$ where h_0 is the initial specimen height at room temperature and the units are expressed as $10^{-6}/^\circ\text{C}$.

A diagram of the electrical circuit for the specimen resistance measurement and interface with the data acquisition device is shown in Fig. 2. The electrical resistance was determined through Ohm's Law by measuring the voltage drop across the specimen and the reference resistor wired in series with an excitation voltage of 5 V. A two-probe measurement was used because the specimen resistance values were extremely large as compared to the lead wire contact resistance. The reference resistors (VFR Series, Vishay



Fig. 1. Photograph of nanocomposite specimen mounted on the TMA stage for thermoresistive characterization.

Precision Foil, Israel) used were ultra-precise and extremely stable under varying conditions. A hermetically sealed reference resistor (VHP Series, Vishay Precision Foil, Israel) was used when measuring the 0.1 wt% specimens to improve the ultra-low current measurement stability. The reference resistor value was chosen to match the resistance range of the specimen type being tested. For example, the 0.1 wt% CNT/vinyl ester specimens had an average resistance of about 800 k Ω and the reference resistor was chosen to be 1 M Ω . By selecting a reference resistor within an order of magnitude of the specimen resistance, an accurate measurement was ensured. Table 1 shows the specimen resistance range and reference resistor used in the measurements. Electrical resistance is represented in normalized form by $\Delta R/R_0$ in %. The temperature coefficient of resistance (TCR) was calculated in a similar way to CLTE and is the normalized derivative of resistance (R) with temperature given by $(10^6/R_0)dR/dT$ where (R_0) is the initial resistance at room temperature and the units are expressed as $10^{-6}/^\circ\text{C}$.

The specimen volume resistivity (ρ_v) at ambient temperatures can be calculated using the measured resistance, specimen cross sectional area (A) and specimen length (l), which represents the distance between the two electrodes.

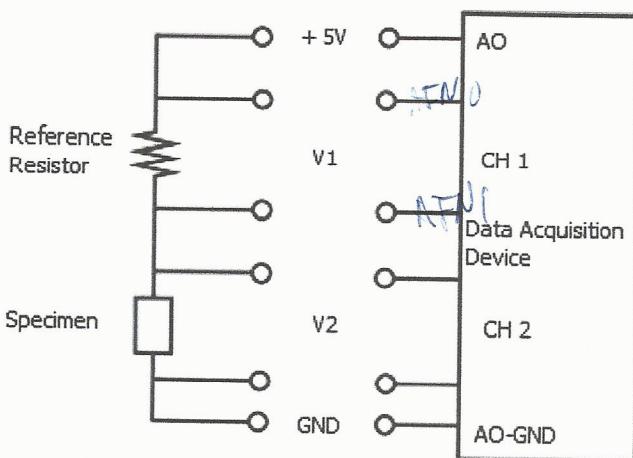


Fig. 2. Electrical circuit and data acquisition interface diagram.

Table 1

Average electrical resistance range during thermal cycling and value of reference resistor used for each specimen group.

Carbon nanotube concentration (wt%)	Specimen resistance range (Ω)	Reference resistor (Ω)
1.00	11,167–12,018	10,000
0.75	15,401–16,365	10,000
0.50	118,970–125,067	100,000
0.10	805,467–805,667	1,000,000

$$\rho_v = R \frac{A}{l} \quad (1)$$

In the TMA measurement the height of the specimen is measured as the temperature is changed. Assuming that the thermal expansion coefficients (α) of the nanocomposites are isotropic, the specimen will expand proportionally in all directions and the area and length can be expressed as:

$$A = w_0(1 + \alpha(T - T_0))h \quad (2)$$

and

$$l = l_0(1 + \alpha(T - T_0)) \quad (3)$$

where w_0 is the initial specimen width, l_0 is the initial specimen length and T_0 is the initial specimen temperature. For all specimens l_0 and w_0 are 13 and 3 mm, respectively. Substituting Equations (2) and (3) into Equation (1) we can calculate the volume resistivity based on the measured specimen height at any temperature.

$$\rho_v = R \frac{w_0 h}{l_0} \quad (4)$$

Note that the coefficient of thermal expansion and temperature change are eliminated in Equation (4) since the proportional change in specimen width and length is the same with temperature.

3. Results and discussion

3.1. Thermoresistive response under thermal cycling

Previous research [20] showed that the electrical percolation threshold for CNT/vinyl ester nanocomposites was below 0.1 wt%. For the thermal cycling experiments the compositions were chosen to examine the thermoresistive response both near the percolation threshold and well as far above the electrical percolation threshold. Fig. 3 shows the typical observed transient electrical response under thermal cycling for the different nanocomposite compositions. The nanocomposite specimens that are well above the percolation threshold, 0.5–1 wt% showed fluctuations in the electrical resistance during the ramp up and ramp down segments of the thermal cycles but the trend observed is an increase in electrical resistance with increasing temperature and a decrease in resistance upon cooling. In contrast, the 0.1 wt% CNT/vinyl ester specimens showed a decrease in the electrical resistance with increasing temperature, but the magnitude of the resistance change with temperature is orders of magnitude smaller than the other specimens. In addition, the 0.5 through 1 wt% CNT/vinyl ester nanocomposites showed an increase in average electrical resistance over time.

In order to better visualize the effect of temperature and cycle iteration on electrical resistance, the electrical response is shown with respect to temperature in Fig. 4. Note that the data for the

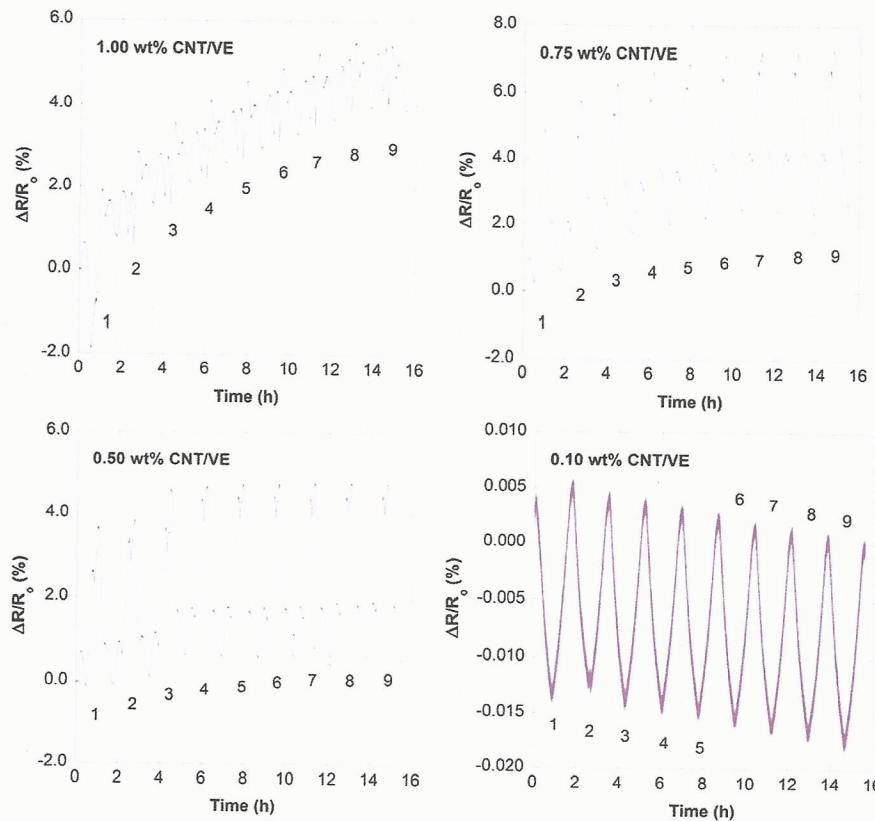


Fig. 3. Normalized electrical resistance change of CNT/vinyl ester composites during iterative thermal cycling from 25 to 165 °C; dashed lines and numbering indicating the thermal cycle iterations.

0.1 wt% CNT/vinyl ester specimen was filtered in order to clearly resolve the small cycle-to-cycle changes. In this case, additional signal processing was required because the relative noise amplitude was large compared with the resistance changes. For all other specimens the raw data is presented. In Fig. 4 the 0.1 wt% nanocomposite shows an extremely small decrease in the electrical resistance with increasing temperature whereas the other nanocomposite compositions show a distinct shape to the resistance change/temperature curves with local maxima near 70 °C and 150 °C. In addition, the 1 through 0.5 wt% CNT/vinyl ester specimens clearly show increasing resistance during the 5 min isothermal segments at 165 °C. This magnitude of the resistance change corresponds to an offset in the resistance change at 25 °C. As the number of thermal cycle iterations increased, the transient increase in resistance at 165 °C diminished. This transient behavior indicates that some permanent material changes are taking place at the high temperature isothermal segments. In order to show the permanent changes in resistance observed for 0.50 through 1.00 wt % CNT/vinyl ester specimens, the data from the 5 min isothermal segments at 165 °C are plotted against total isothermal time in Fig. 5. While some of the changes in resistance during each isothermal segment are due to thermal effects of the specimen reaching equilibrium, there is a clear overall trend in the data in a diffusion-like fashion.

After gelation, the later stages of cure become diffusion-limited and the reaction slows because the mobility of unreacted monomer is hindered by the formation of crosslinks. The post-cure cycle for the vinyl ester matrix was determined by a previous kinetic study [28] using differential scanning calorimetry (DSC). The slight

increase in degree of cure at much later stages is difficult to measure during DSC because little exothermic heat is generated from the reaction during this time. For the vinyl ester system it is likely that styrene conversion continues to increase after most of the vinyl ester has reacted. As discussed earlier, the carbon nanotube network electrical conductivity is dominated by the tunneling resistance at the CNT/CNT junctions. The ability to detect this transient response during the isothermal segments is likely due to the local changes in the ionic conductivity of the polymer in the regions of the CNT/CNT junctions as material continues to react. As a result, the numerous CNT/CNT junctions in composites well above the electrical percolation threshold become a distributed network of *in situ* cure sensors throughout the polymer matrix allowing the opportunity to detect chemical changes in the matrix. Although the specimens were post-cured for 2 h these results indicate that the cure cycle determined by DSC results in an incomplete reaction.

3.2. Thermomechanical/thermoresistive analysis

Considering the transient phenomena observed during the thermal cycling experiments, the data from the final ramp-up segment was isolated for further analysis. The resistance change/temperature curve for the final thermal cycle are shown in Fig. 6. Denoted on the plots are the locations of the local minima of interest. It was found that, for composites of 1 wt% CNT/vinyl ester, the electrical resistance increased from 25 to 80 °C, then decreased until 118 °C and increased again until 145 °C before decreasing steeply to 165 °C. This behavior was similar for the 0.75 and 0.5 wt% CNT/vinyl ester specimens, although less exaggerated. The

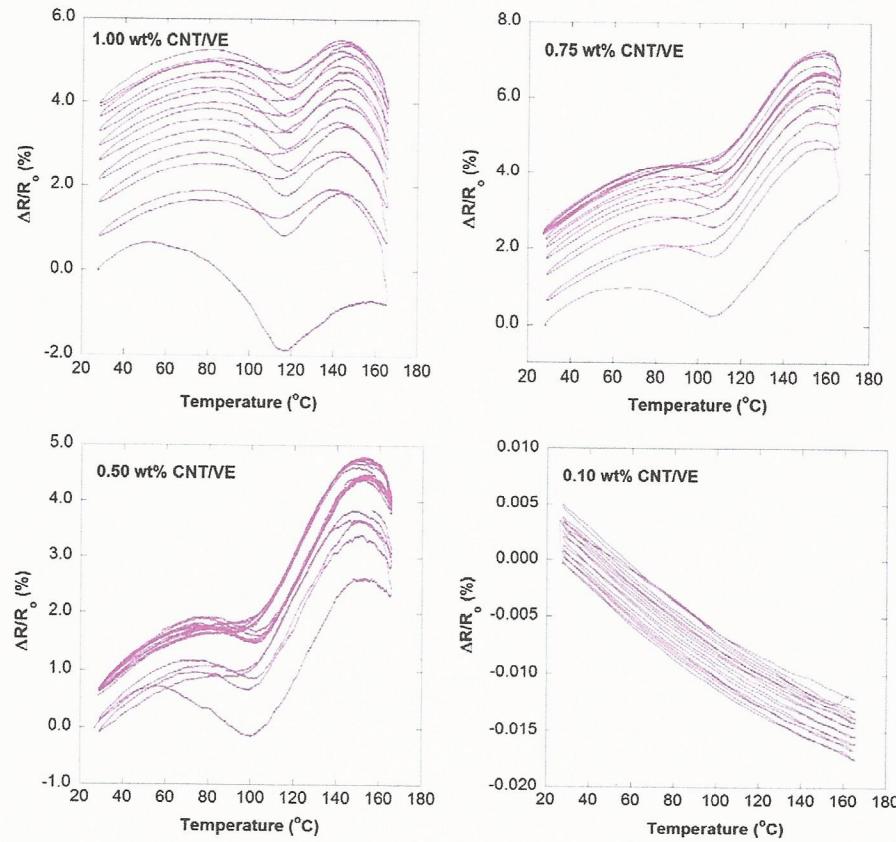


Fig. 4. Normalized electrical resistance change versus temperature of CNT/vinyl ester composites during thermomechanical testing.

resistance of 0.1 wt% CNT/vinyl ester specimens decreased monotonically with temperature, very different than composites with higher CNT content. Given that the percolation threshold has been experimentally observed to be less than 0.1 wt% CNT content for highly dispersed systems [20] as well as predicted by three-

dimensional modeling [29], this difference in behavior indicates that as the number of CNT/CNT junctions increase with nanotube content, the thermoresistive behavior becomes increasingly sensitive to the polymer interphase or tunneling medium. This supports the predictive modeling work on CNT-reinforced composites which indicated a tunneling-dominant resistance response [5].

It was expected that thermal expansion is a major factor in the thermoresistive behavior of composites of dispersed CNTs. The data presented in Fig. 6 does not account for dimensional changes in the specimen upon heating. The CLTE of the specimen changes as the polymer undergoes thermal transitions, particularly at the glass transition temperature (T_g). Fig. 7 shows the dimensional change and CLTE for the 1 wt% nanocomposite. Around 120 °C there is a significant change in the slope of the expansion curve resulting at the glass transition temperature. In TMA, T_g is taken to be at the location where the dimension curve increases slope dramatically (inflection point in CLTE curve) and is considered to be the onset of polymer segmental or main chain motion [30]. This is the transition from the glassy to rubbery state. The local minima in electrical resistance shown in the left of Fig. 6 corresponded very closely with the glass transition measurements from the thermomechanical method. This was observed for all specimens with CNT concentrations well above the percolation threshold. To summarize the difference in T_g sensing methods, the values determined from the TMA and thermoresistive methods are presented in Table 2. The thermoresistive method yielded average glass transition temperatures 2–6 °C higher than the TMA approach, but had similar precision.

Based on the coupled measurement of thermal expansion and resistance the volume resistivity of the nanocomposite can be

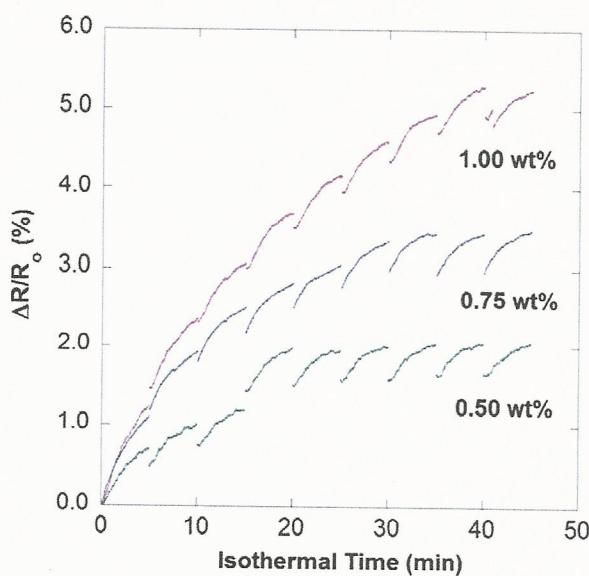


Fig. 5. Normalized electrical resistance change during the isothermal segments at 165 °C showing diffusion-like increase in overall resistance.

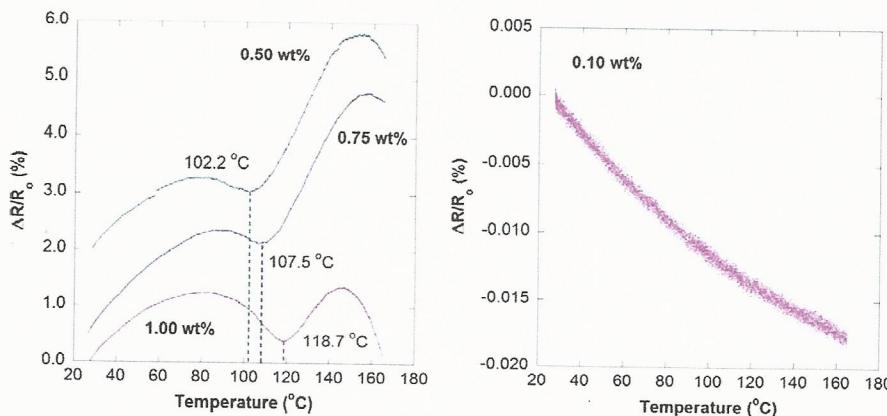


Fig. 6. Electrical resistance change of CNT/vinyl ester composites during the final ramp-up segment; right: unfiltered data for 0.1 wt% specimen, left: local minima indicating T_g locations for specimens with greater than 0.1 wt% CNT (note that 0.5–0.75 wt% data are offset by 2 and 0.5% resistance change, respectively, to clearly show the curves).

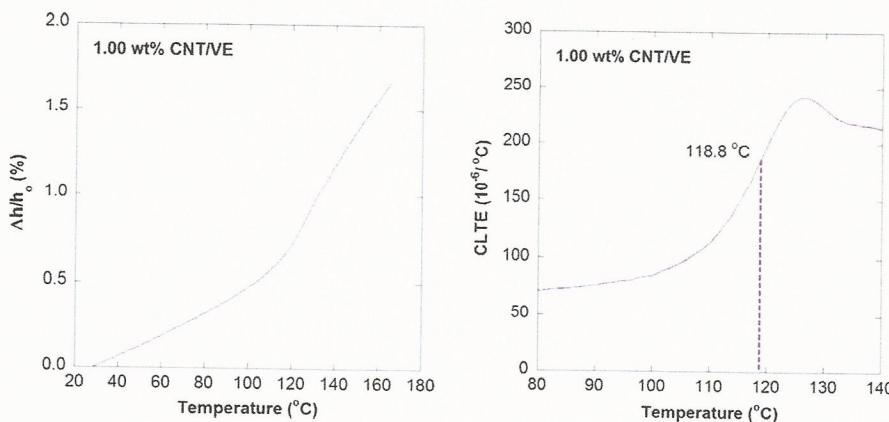


Fig. 7. TMA results for 1 wt% CNT/vinyl ester specimen showing dimensional changes during heating and the calculated linear thermal expansion curve showing the T_g location.

evaluated as a function of temperature. Fig. 8 shows the volume resistivity and expansion of the nanocomposites during the ramp-up segment of the last cycle. The importance of thermal expansion is illustrated by comparing the shapes of the resistivity and expansion curve. Essentially, the larger the effect of thermal expansion, the more closely the resistivity curve resembles the expansion curve. The plot in Fig. 8 for the 0.1 wt% CNT/vinyl ester specimen is a good example. Here, the resistance change with temperature was nearly constant; therefore, the resistivity was nearly proportional to the thermal expansion. For the nanocomposites well above the electrical percolation threshold the overall shape of the curve is similar to the measured resistance, with clearly defined maxima and minima. When volumetric expansion is taken into account it is clear that other mechanisms are contributing to the change in the material electrical properties with temperature. The local minima in both the resistance and resistivity curves in Figs. 6 and 8 correlate strongly to the T_g measured by TMA (see also, Table 2). As a result, the thermoresistive analysis of the carbon nanotube network enables *in situ* measurement of glass transition in a bulk material without the use of complex thermal analysis instrumentation.

The locations of T_g were consistent within each batch, as expected, but generally increased with increasing CNT loading. Given the size and chemical nature of CNTs, it is possible that they may affect the polymerization process and influence morphology, which has been reported recently in the literature for several material

systems [27,31,32]. Kim et al. [31] observed that, when reacted under ultrasonication, CNTs covalently bonded with styrene chains and consumed initiator during the polymerization of styrene monomer to form CNT/polystyrene nanocomposites. In an epoxy system, El Sawi et al. [32] showed that CNTs increased the initial reaction rate, although T_g was not significantly affected. Seyhan and co-workers [27] found that T_g increased slightly with CNT content in a vinyl ester system. They suggest that, in addition to a possible increase in the degree of polymerization, the CNT/polymer interface has reduced polymer mobility which results in an increase in T_g for the bulk composite. The effect of nanotube loading on the curing kinetics of vinyl ester resin is the subject of another study.

The temperature coefficient of resistance (TCR) is analogous to the thermal expansion coefficient and is a measure of a material's electrical resistance response to temperature change. Fig. 9 shows the variation in TCR with temperature for the various

Table 2

Comparison of the thermoresistive and thermomechanical methods for sensing T_g showing the average of three specimens.

Carbon nanotube concentration (wt%)	T_g – Thermoresistive method (°C)	T_g – Thermomechanical method (°C)
1.00	115 ± 2	113 ± 3
0.75	109 ± 2	105 ± 2
0.50	102 ± 3	96 ± 3

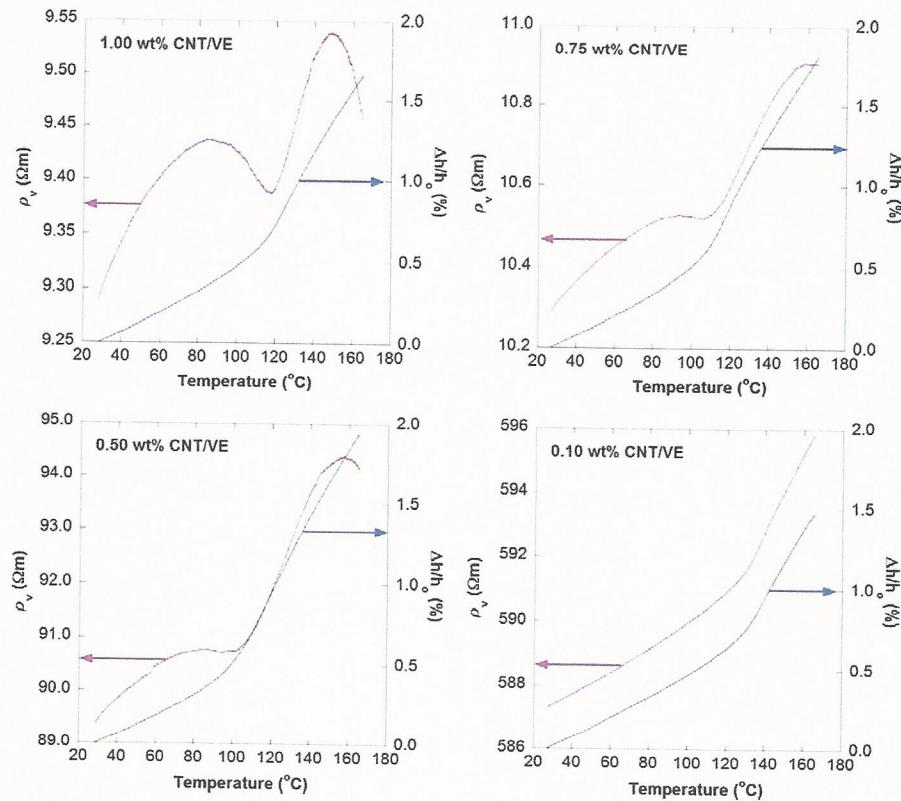


Fig. 8. Comparison of volume resistivity and dimensional change curves for CNT/vinyl ester composites during final ramp-up segment.

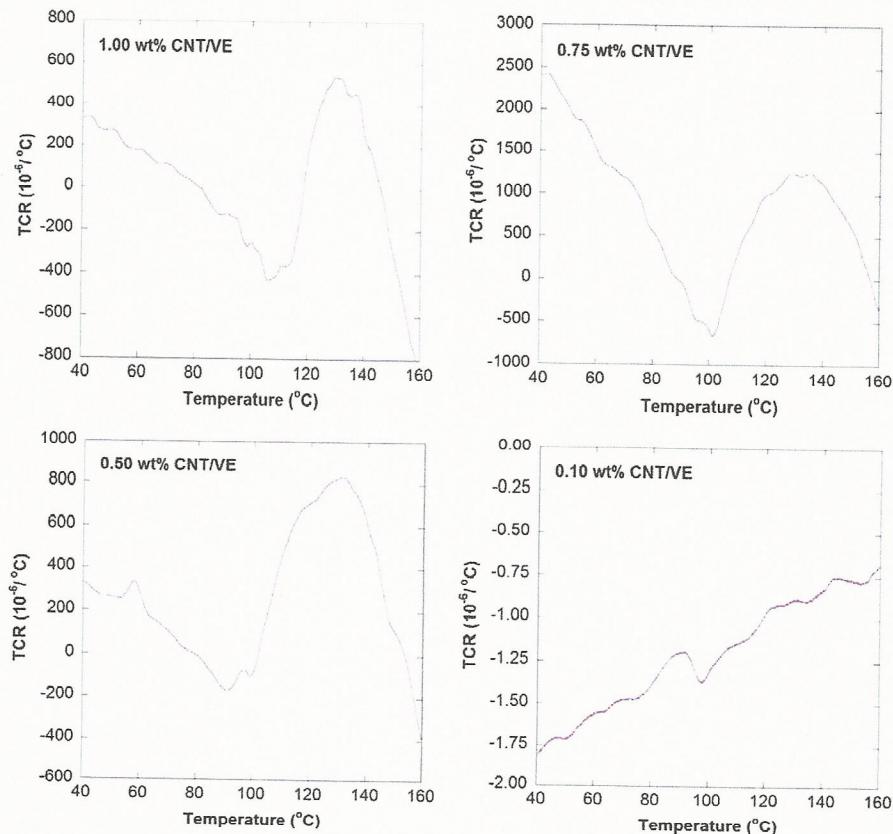


Fig. 9. TCR curves for composites of CNT and vinyl ester during final ramp-up segment showing difference in thermoresistive trends for 0.5–1 versus 0.1 wt% composites.

nanocomposites. Note that the 0.5 through 1 wt% CNT/vinyl ester nanocomposites share a common shape of the resistance change versus temperature curve (Fig. 6). This is reflected in the similarity between their respective TCR curves. Clearly, for these material types, TCR varied widely over the temperature range and is positive or negative over the span from 40 to 160 °C. The 0.75 wt% CNT/vinyl ester specimens had the highest degree of sensitivity to temperature, a peak TCR of roughly $2400 \text{ } 10^{-6}/\text{C}$. The TCR range of the 1 and 0.5 wt% CNT/vinyl ester materials had similar values. In contrast, the 0.1 wt% CNT/vinyl ester specimens had an extremely low and negative TCR, an average value of $-1.2 \text{ } 10^{-6}/\text{C}$ over a 120 °C span. There were no significant changes in the TCR trend in the T_g region for this material.

The results show that for the specimens far above the percolation threshold that influences other than thermal expansion strongly affects the electrical resistance signal. For the 1 wt% CNT composite the variations in electrical properties are most pronounced while composites with lower concentrations of CNTs show electrical responses that are more influenced by thermal expansion. With volumetric expansion of the polymer matrix the tunneling gap between the individual nanotubes expands while, on the other hand, an increase in temperature increases the electron mobility. At lower nanotube concentrations there are fewer tunneling gaps and the thermal expansion more strongly dominates this effect. At higher nanotube concentrations there are not only more CNT/CNT junctions but it is likely that, on average, the tunneling gap between nanotubes is smaller enabling thermally-activated hopping of the electrons. As a consequence the resistance measurements are more sensitive to thermal transitions in the polymer where changes in segmental mobility affect the tunneling of electrons.

In the study of thermoelectrical properties of polymers, electro-thermic analysis methods such as the thermally stimulated discharge current method (TSD or TSDC) have been used to study carbon black-filled polymers [33] and more recently to study nanocomposites [34]. TSDC is very sensitive to variations in the dielectric properties which are related to specific side-chain and segmental processes including the γ , β , α (T_g) and ρ processes [35]. Goel and co-workers [36] used TSDC to investigate the electrical properties of vinyl ester and observed similar trends in local maxima in the dielectric constant to peaks observed in thermoresistive analysis using CNTs. The CNT/CNT junctions with a thin region of vinyl ester between the contacts act much like a nanoscale electro-thermic sensor. As a result the percolating structure of the nanotubes may also act as a distributed network to sense polymer transitions.

4. Conclusions

The thermoresistive behavior of composites of CNTs and vinyl ester was determined by measuring electrical resistance *in situ* during thermomechanical analysis. The thermomechanical analyzer allowed for the thermal expansion to be accounted for in the calculation of volume electrical resistivity which provided additional insight that would otherwise have been ignored. Of the factors assumed to affect the thermoresistive behavior of CNT filled polymers, the results showed that CNT concentration, polymer/interphase electrical properties and thermal expansion had the greatest effects. The latter two of these factors are strongly dependent on temperature and polymer thermal transitions. The 0.1 wt% CNT nanocomposite had a near-zero and negative TCR whereas specimens with greater CNT loading had positive and negative TCR. Specimens with 0.5–1 wt% CNT (well above the percolation threshold) showed sensitivity to changes in the polymer interphase apart from thermal expansion. The glass transition was accurately detected in these specimens by taking the local minimum in the electrical resistance/temperature curve.

It was shown that tunneling-based sensing using CNTs could detect transient effects resulting from further cure even beyond that of the DSC method. Thermoresistive analysis using CNTs was found to be similar to a much more complicated electrothermic analysis technique, the TSDC method. In composites of dispersed CNTs, the tunneling of electrons across CNT/CNT junctions gives rise to a network of sensors formed by a percolating network of nanotubes.

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