Carbon nanotube composites for thermal management

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Single-wall carbon nanotubes (SWNTs) were used to augment the thermal transport properties of industrial epoxy. Samples loaded with 1 wt % unpurified SWNT material showed a 70% increase in thermal conductivity at 40 K, rising to 125% at room temperature; the enhancement due to 1 wt % loading of vapor grown carbon fibers was three times smaller. Electrical conductivity data showed a percolation threshold between 0.1 and 0.2 wt % SWNT loading. The Vickers hardness rose monotonically with SWNT loading up to a factor of 3.5 at 2 wt %. These results suggest that the thermal and mechanical properties of SWNT-epoxy composites are improved, without the need to chemically functionalize the nanotubes. © 2002 American Institute of Physics.

We fabricated SWNT-epoxy composites and measured a thermal conductivity enhancement greater than 125% at 1.0 wt % nanotube loading. Composites loaded with vapor grown carbon fibers (VGCF) at 1.0 wt % show considerably weaker enhancement of 45%. As is typical for composite materials, both measurements are well below the “law of mixtures” prediction (10 W/m K and 20 W/m K, respectively), even with a conservative estimate of 1000 W/m K for the SWNT thermal conductivity, and the published value of 1900 W/m K for the VGCF. The electrical conductivity sharply increases by nearly 10^5 between 0.1 and 0.2 wt % SWNT loading but not until 1–2 wt % for VGCF composites. This suggests easier formation of a percolation network of SWNTs due to their larger aspect ratio. We used microindentation testing (Vickers hardness or VH) to evaluate the mechanical properties because of limited material quantity. There is a monotonic increase in VH with SWNT loading that reaches a factor of 3.5 at 2 wt %.

Samples were based on Shell Chemicals Epon 862 epoxy resin and Air Products Ancamine 2435 dimethane-amine curing agent. Composites were loaded with raw SWNT soot grown by the HiPCO (high pressure carbon monoxide) method12 or VGCF from Applied Sciences, Inc. The SWNT material contained 15–25 wt % Fe catalyst in the form of isolated nanoparticles. Quoted loading values are based on the mass of as-grown SWNT material and are not reduced to account for Fe impurities. Transmission electron microscopy (TEM) revealed that the SWNT material had a broad tube diameter distribution peaked at 1.1 nm and tube lengths from several microns to over 10 mm. During sample production (mixing, sonication; see next) VGCF tend to break to lengths below 100 μm. The fiber thermal conductivity is 1900 W/m K at room temperature,14 nearly that predicted for

Rapid advance in bulk synthesis of single wall carbon nanotubes (SWNTs), coupled with their remarkable mechanical properties, are positive signs for application in a host of composite materials. First, the high Young’s modulus and strength-to-weight ratio of SWNTs are extremely promising for enhanced strength in mechanical composites. Second, and only more recently appreciated, because phonons dominate thermal transport at all temperatures in carbon materials,1 and since phonon thermal conductivity (\( \kappa \)) is roughly \( \kappa = C_P v_s l \) (where \( C_P \) is the specific heat, \( v_s \) the speed of sound, and \( l \) the mean free path), SWNTs should be ideal for high-performance thermal management.2 Indeed, theory predicts an extremely high value (~6000 W/m K) for the room temperature thermal conductivity of an isolated SWNT.3 The measured \( \kappa(T) \) for bulk SWNT samples agrees with predictions for one-dimensional phonon systems,4,5 while a recent measurement of 3000 W/m K for the room temperature thermal conductivity of an individual multiwall nanotube6 shows directly that the superior thermal properties of the graphene plane are realized in its related nanomaterials.

Despite this great promise, progress in mechanical composites has proved difficult. Enhanced strength was observed in SWNT-poly(methylmethacrylate) (PMMA) composites,7 but SWNT-epoxy and MWNT-epoxy composites are typically weaker or barely stronger than the pristine epoxy.8–10 This has been attributed to weak nanotube–matrix interaction but may also reflect processing difficulties and poor SWNT dispersion.11 We report here our results on the thermal and mechanical properties of SWNT-epoxy composites.

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SWNTs. Control samples of pristine epoxy were also measured.

Care was taken to disperse carbon material uniformly through the composite. Carbon materials were dispersed ultrasonically for as long as 48 h in an organic solvent (dichloroethane or N–N dimethylformamide) to form a stable suspension. The epoxy resin was subsequently dissolved in the carbon/solvent mixture; high quality dispersal was indicated by the formation of a smooth emulsion. The solution was placed under a vacuum to remove trapped air. After degassing, samples were heated to 130 °C for 1 h to completely evaporate the solvent. The curing agent was added, and the samples left at room temperature for two to four days followed by a 2 h postcure bake at 120 °C. Loading was studied up to 5 wt %; Fig. 1 shows that the SWNTs were fairly well dispersed in the material on the micrometer scale, with random tube/rope orientation. Samples were black, however, indicating that the dispersal was still not ideal.

From the bulk product, we cut samples (typically 1 mm x 1 mm x 2 mm), excluding regions with macroscopic air inclusions. We verified that different samples cut from the same composite gave identical measurement results. Thermal conductivity was measured from 20–300 K with a comparative technique. Briefly, a sample is mounted between two constantan rods of known thermal conductivity. A heat current is passed through this thermal “circuit” to thermal ground (sample stage). Temperature drops are measured across each rod and the sample with differential thermocouples, giving the relative thermal conductivity of the sample. The second standard is used to monitor heat current loss to radiation and other sources; care is taken to minimize these negative effects. To calibrate the method, we accurately reproduced the known thermal conductivity of many different samples of metals and carbon fibers.

For room temperature data as a function of carbon loading (Fig. 2), five to ten measurements were averaged for each sample. The thermal conductivity enhancement in SWNT-epoxy samples rises much more rapidly than in VGCF-epoxy samples. There is a 125% enhancement in $k$ at 1 wt % SWNT loading while equal loading of VGCF produces but a 45% increase. Data for $k(T)$ were collected in a closed-cycle helium-cooled system; typical raw data and the enhancement in $k(T)$ are presented in Fig. 3. SWNT-epoxy composites show a markedly higher $k$ enhancement at all temperatures than VGCF-loaded samples.

Room temperature electrical conductivity of the composites was measured to characterize the extent of the carbon material network. For both carbon materials, low-loading samples display a factor of 2 or 3 change in conductivity followed by a sudden jump by more than $10^4$, consistent with the formation of a percolating network. The percolation threshold, where the sharp onset in conductivity is observed, is between 0.1 and 0.2 wt % for SWNT-epoxy samples, while VGCF requires loading between 1 and 2 wt %. These values are reasonable in light of experimental, numerical, and theoretical work indicating that the percolation threshold in dilute, random rod systems is approximately equal to the inverse of the aspect ratio, roughly 1000 for SWNTs and 100 for VGCF. Our measured critical loading for SWNT epoxy is four times smaller than that found by others for SWNT-epoxy.
PMMA composites. This difference reflects the fact that their samples were formed by spin coating which preferentially aligns nanotubes in the plane of the sample, normal to the current direction in their experiment. An even more extreme case is presented by SWNT-PMMA fibers of Ref. 7. They were made with a very large draw ratio, leading to high SWNT alignment, and are electrical insulators even at loadings as high as 5 wt %. In sharp contrast to these cases, the SWNTs in our samples are oriented randomly, and the percolation network forms at lower loading.

Resistance to plastic flow for HiPCO-epoxy samples was measured using a Tukon Microhardness Tester with a Vickers indenter. Epoxy samples were mechanically polished to ensure a smooth sample surface, and VH measured using a 100 gram load. The VH increased almost linearly from 0.4 for the pristine epoxy to 1.4 at 2 wt % loading.

These experiments demonstrate convincingly that a small fraction of SWNT material dramatically enhances the thermal properties of an epoxy matrix, and that they are more effective than larger diameter carbon fibers for this purpose. It is likely that SWNTs are superior to VGCFs because their nanoscale diameter and larger aspect ratio enable a more extensive network to form at the same weight loading, as indicated by theory and the lower critical loading for percolation seen in electrical conductivity. The observed increase in VH is intriguing. First, it implies that SWNT-based thermal composites do not suffer mechanical degradation, a fact that argues well for applications. Second, the increase in VH suggests that SWNT dispersion is an important factor for enhanced strength of SWNT-epoxy composites. Ongoing TEM imaging to characterize the SWNT dispersion on the nanometer scale, and mechanical tests that directly measure the elastic moduli of the composites will further illuminate this point.

In summary, we demonstrated that SWNT-epoxy composites have enhanced thermal conductivity, and SWNTs are much more effective for this than larger-diameter carbon fibers. We observed an increase in Vickers hardness with increasing SWNT loading that will be the subject of additional investigation. Future improvements might result from chemical functionalization of the SWNTs to enhance the SWNT–matrix interaction and the creation of anisotropic thermal management composites via nanotube alignment.

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15. Solvent evaporation was considered complete when the remaining sample mass was within 0.1% of the original mass of resin plus carbon material.