Unique Thermal Conductivity Behavior of Single-Walled Carbon Nanotube−Polystyrene Composites

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Introduction. Carbon nanotubes have extremely high thermal conductivities; single-walled carbon nanotubes (SWCNTs) have been predicted through molecular dynamics modeling to have a thermal conductivity up to 6600 W/(m K).[1] This value is more than 10 times the value for copper and 2 times more than the highest thermally conductive diamond. An obvious SWCNT application would therefore be a high thermally conductive dispersion for applications such as heat conducting composites[1] or heat transfer fluid suspensions.[2] Using Maxwell's mixing theory, SWCNTs should increase a polymer's thermal conductivity by 50-fold at a volume fraction of ∼1 vol %. Experiments have shown that such improvements do not happen in practice, and improvements, if any, are at least an order of magnitude less than expected.[3−5]

This lack of improvement is due to the presence of an interfacial resistance to heat transfer between the solid nanotubes and the surrounding matrix termed the Kapitza resistance. This name has been given because Kapitza first measured such interfacial resistances in 1941 with experiments on metal−liquid helium interfaces.[6] A complete description of the cause of this resistance is beyond the scope of this paper, but in short, the Kapitza resistance occurs because of modulus mismatch between the matrix and the inclusion; the greater the mismatch, the greater the resistance.[7,8] The Kapitza resistance becomes more significant with increasing filler surface area and is extremely high in composites with carbon nanotubes because of their high stiffness as well as their high surface area.[9,10]

Because of its importance, this type of resistance is still being studied today through experiments and computational models.[11] Duong et al.[3,12] reported Monte Carlo simulation results for heat transfer through carbon nanotube composites that produced conductivity improvements similar to experimental results. Work by Gonnet et al.[1] showed that magnetically aligned carbon nanotube mats (bucky paper) have a relatively high thermal conductivity (42 W/(m K) at ambient temperature). However, after incorporating them in epoxy, the thermal conductivity drops to that of random composites.[1]

Although we do not doubt the correctness of the theory, experimental verification of the Kapitza resistance in polymer−matrix nanocomposites is not a trivial task. Work by Yodh et al.[5] found a difference in thermal conductivity for composites processed with and without surfactant and attributed the larger increase in thermal conductivity for the surfactant-processed samples to the surfactant layer modifying this interfacial resistance; however, there was no way to know that the dispersion quality was the same. The work by Gonnet et al.[1] described briefly above is certainly persuasive; however, the bucky paper network might have been affected by infusion and curing of the epoxy. One obvious direct comparison would be to measure the thermal conductivity of two polymers with differing moduli filled to identical levels with nanotubes or some other high conductivity large surface area filler. However, obtaining the same dispersion in both materials is essentially impossible. Our approach was to change the modulus of a polymer by going from the solid state to a viscous melt. To be sure that the dispersion did not change, it is only necessary to show that the thermal conductivity shows no hysteresis; i.e., it is the same before and after melting.

In this study, the thermal conductivity is measured in polystyrene−nanotube composites. A previous study using the same dispersion method but with styrene−isoprene copolymers yielded a very low percolation threshold of 0.2 wt %,[13] indicative of quite good dispersion; the percolation threshold in this material should be quite similar. Finally, a small-molecule dispersing agent was used and only partially removed, and the implications of this contamination are discussed.

Experimental Section. *Materials.* Latex was produced by emulsion polymerization of styrene as described by Ha et al.[13] Styrene monomers, purchased from Sigma Aldrich, were passed through an inhibitor removal column twice and then stored no longer than 60 days at 5 °C before use. 2,2′-Azobis(isobutyronitrile) (AIBN) from Sigma Aldrich and SDBS, 95% purity, were used as received. SWCNTs produced by the CoMoCAT method, grade S-P95-03-GEL, were provided by Southwest Nanotechnologies. These nanotubes have an average diameter ∼0.8 nm. All solutions were prepared with 18 MΩ water.

Mixing Latex and Nanotubes. Methods for mixing the latex and SWCNTs are as described by Ha et al.[13] SDBS was mixed with water to a concentration of 8.4 mM, and SWCNTs were added to produce a concentration of 0.1 mg/mL SWCNT solution with a surfactant concentration of ∼0.9 mM (0.75·cmc) after adsorption according to the adsorption isotherm.[14] 25 mL of the mixture was sonicated for 1 h; many mixtures were required to produce the necessary amount of material. The latex, before drying, was mixed with the SWCNT dispersion in a beaker and stirred at room temperature for 20 min. The SWCNT content of the final composite was controlled by varying the volume ratio of the SWCNT solution to the latex. Water was evaporated, and the solid polymer remaining was extracted with isopropanol using a Soxhlet apparatus to remove surfactant. The resulting product was then dried in vacuo to remove isopropanol. The amount of surfactant was measured for selected samples using elemental analysis for sulfur (Galbraith Laboratories). A similar styrene−isoprene latex at 2% NT content had 5% SDBS, while the 10% and 30% samples from this study had 15.5 and 37.4 wt % surfactant after extraction.

DSC Methods. A TA Instruments Q-1000 heat-flux DSC with Peltier cooling was used in these experiments with nitrogen flowing through the cell. Indium, tin, and biphenyl were used for temperature calibration. On the basis of the fit to the heat capacity of polystyrene to the published heat capacity,[15] sapphire was found to be a better enthalpy (heat capacity) calibrant than indium, so sapphire was used. The heat capacity was calibrated over a range from −25 to 200 °C. Both hermetically sealed and normal crimped pans were used in the sapphire procedure, and within experimental error, the two agreed. In all cases, calibration was performed at a heating rate of 10 °C/min.

Thermal conductivity was determined using a modulated differential scanning calorimeter (MDSC) as described by

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Marcus et al.[16] Samples were formed into right, circular cylinders using a thermal press and mold; typical dimensions were 0.4 cm length and 0.5 cm diameter. A modulating period of 80 s and a modulation temperature of 1 °C were used to measure the apparent heat capacity at a given temperature. This heat capacity of the long cylinders is significantly smaller than the actual heat capacity because of the nonuniform temperature of the sample, which in turn causes heat flow from hot parts of the sample to cold parts of the sample, as opposed to only flow between the DSC and the sample.

The specific mathematics used to derive eq1 are beyond the scope of this paper, but this expression comes from the solution of one-dimensional heat flow from high to low temperature with one side being exposed to a sinusoidal temperature profile. With the assumption of no heat flow from the sides or the exposed face of the cylinder, as well as the assumption of low thermal conductivity, the thermal conductivity can be calculated as[16]

$$K_o = (8LC^2)/(C_pMd^2P) \qquad (1)$$

where K_o = the observed thermal conductivity (W/(m °C)), L = sample length (m), d = sample diameter (m), M = mass (g), C_p = actual heat capacity (J/(g °C)), C = apparent heat capacity (J/°C), and P = the period of temperature modulation (s). Measurement of the thermal conductivity requires knowledge of the actual heat capacity; to find the actual heat capacity of the unknown material, the same procedures and a typical thin sample were used with a diameter of about 0.5 cm.

To account for heat loss through the sides and one end of the specimen, a thermal conductivity calibration constant was used. This calibration constant, D, is found by using the literature value for thermal conductivity with the observed value of a known material in the following equation:[16]

$$D = (K_{o,ref}K_r)^{0.5} - K_r \qquad (2)$$

where D = thermal conductivity constant, $K_{o,ref}$ = observed (i.e., from eq 1) reference material thermal conductivity (W/(m °C)), and K_r = true reference material thermal conductivity (W/(m °C)). Of course, the sample that is used for this calibration should have the same dimensions as the unknown sample. Even in the Soxhlet extracted pure polystyrene there is about 0.5% surfactant measured using elemental analysis. Hence, just to be sure, PS purchased from Aldrich (M_n = 140 000; M_w = 230 000) was used for the calibration; later measurements indicated that the synthesized sample and the purchased PS had identical heat capacities as a function of temperature within experimental error. For a material with unknown thermal conductivity, the following equation converts the thermal conductivity (K_o) from eq 1 to the actual thermal conductivity (K):[16]

$$K = [K_o - 2D + (K_o^2 - 4DK_o)^{0.5}]/2 \qquad (3)$$

In this study, polystyrene was used as the known material; values for the thermal conductivity as a function of temperature are given by Kline[17] and Fuller et al.[18] In all cases, samples were premelted in the DSC in order to provide consistent thermal contact. For a given method (see below), an average calibration constant was used for all measurements.

Two types of cylinders were used to measure the thermal conductivity of the samples. Method 1 was used for pure polystyrene samples tested at temperatures near the glass transition temperatures (80 and 150 °C) as well as 25 °C. Method 1 encapsulates the sample in a homemade cylindrical sample container made with a polytetrafluoroethylene (PTFE) wall and an aluminum disk fastened to the bottom with epoxy glue. Polystyrene pellets were melted one at a time at about 150 °C, to avoid bubble formation, into the sample container. The purpose of the sample container is to maintain the sample shape after the sample is heated past the glass transition temperature. Presumably, because the sample containers were custom-made and therefore not identical, there was more scatter in the data collected using this method as described in the Results and Discussion. Method 1 was only used for polystyrene.

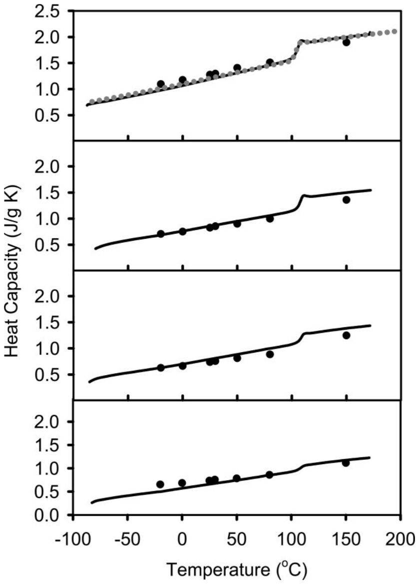

Figure 1. Specific heat capacities. The continuous curve represents heat capacity measured via DSC after a 60 °C/min cool rate followed immediately by a 10 °C/min heat rate, while the data points represent heat capacity measured using the isothermal modulating method. From top to bottom: pure PS, 5% NT, 10% NT, 30% NT. The gray dotted curve in the top plot represents calculated PS heat capacity from the ATHAS database.[15]

All samples, including polystyrene, were tested using method 2. The major difference was that no PTFE wall was present. This method reduced data scatter and could be used only if the samples did not change shape during measurement. Because of the very large low shear viscosity of nanotube samples, samples did not change shape during the 5−10 h time scale of the experiment. Method 2 used a thermal press and mold to form the samples into the desired cylindrical shape; the approximate temperature used was 150 °C. This method likely produced samples with nanotubes oriented in planes perpendicular to the long axis; i.e., the thermal conductivity measured was likely lower than that which would be measured for a truly isotropic sample. The sample was then placed on a flat aluminum disk located on the sample platform in the DSC. A drop of silicone oil was used between the sample and the disk to increase thermal contact.

Results and Discussion. A direct comparison of the specific heat capacities determined via the one-point modulating method on a thin sample and the more typical scanning method is shown in Figure 1. Small differences were expected; the enthalpy and heat capacity calibration are based on a 10 °C/min temperature ramp of indium and sapphire, respectively, in crimped aluminum pans, which is very unlike the conditions used in a modulated experiment. It is well-known that the calibration parameters for a DSC depend on the conditions used to measure those parameters.[19] The modulated values were used in eq 1; the type of calibration errors mentioned in the previous sentences should be very similar for the thick and thin samples and hence should roughly cancel out in the data analysis. The general trend of the heat capacity is that it decreases with the addition of nanotubes—not surprising since the heat capacity of carbon nanotubes[20] is much lower than that of the polymer.

Before describing the results on the thick sample, it should be noted that this method of measuring thermal conductivity is not without controversy. Any thermal conductivity method has an issue with thermal contact between the sample and the DSC cell because the effect of finite thermal resistance is similar to that of finite thermal conductivity. (A method was recently published that claims to separate thermal resistance from thermal conductivity using the differences in response time, although the assumptions made in that model make it somewhat unsuitable for low thermal conductivity polymers.[21]) The ideal procedure is to eliminate thermal resistance between the sample and the DSC cell; the purpose of the silicon oil used in our experiments is to reduce this resistance as much as possible. In fact, the constant *D* in eq 2 and the associated procedure are designed to account for finite heat transfer to the purge gas; however, *D* also contains a contribution from finite thermal resistance. In our experiments, a single value of *D* was used for a given method, and the average thermal conductivities were no more than 3% removed from the literature values, a deviation similar to what was reported previously,[16] suggesting that the assumption of neglecting the effect of thermal resistance is a good one.

Perhaps a more relevant objection was described in a paper by Simon and McKenna;[22] these authors argue that the use of eqs 1−3 for certain materials is not appropriate. According to this paper as well as the original derivation, the value *f* represented by the equation below must be about 1 for the procedure given in the Experimental Section to be valid.

$$f = \frac{1 - 2e^{2ZL}\cos(2ZL) + e^{4ZL}}{1 + 2e^{2ZL}\cos(2ZL) + e^{4ZL}} \tag{4}$$

$Z = (\omega/2 \times \text{thermal diffusivity})$ and L is the length of the sample. Using the appropriate values of $\omega = 2\pi/80$, $L \approx 5$ mm, and thermal diffusivity $\approx 1.5 \times 10^{-7}$ m^2/s for polystyrene and 5 times this value for the nanotube-filled material gives a negligible error for polystyrene and about a 7% underestimation in thermal conductivity according to the analysis presented in the Simon and McKenna paper. Since the thermal conductivities are all about the same for a given sample, the overall effect would be to shift the curves upward. Hence, the qualitative behavior around the glass transition that is the focus of this analysis would not be affected.

Both methods to measure thermal conductivity were first performed on pure polystyrene samples to determine the constant *D*. For method 1 the measured thermal conductivity value at 25 °C was 0.079 ± 0.025 W/(m °C) as compared to the literature value of 0.133 W/(m °C), while for method 2 the values at 0 °C were 0.102 ± 0.005 and 0.131 W/(m °C). The calibration correction factor from eq 2 was then applied to the measured value as shown in eq 3 to yield the observed thermal conductivity. Composite samples, measured using method 2, show significantly more scatter than pure polystyrene samples measured using that same method. We believe larger data scatter is not due to measurement scatter but is a result of small differences in the arrangement of nanotubes in a particular sample, which in turn can give different thermal conductivities. The thermal conductivity did not change greater than experimental error upon successive heating and cooling cycles for a given sample.

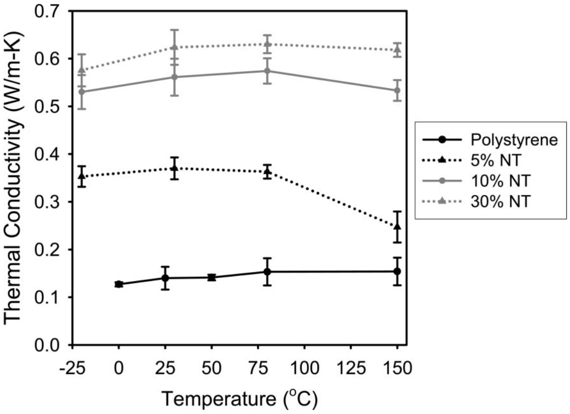

Figure 2. Thermal conductivities as measured using modulating temperature cycle around a single temperature. For polystyrene, data at 25, 80, and 150 °C represents method 1 while method 2 data are presented for 0 and 50 °C. Lines are drawn to guide the eye.

Figure 2 shows that the thermal conductivity of the pure polystyrene samples increases monotonically with temperature as expected and measured elsewhere. However, there is a different trend for the composites. The thermal conductivity increases with temperature until the glass transition temperature is approached. At this point, the thermal conductivity decreases with increasing temperature, which is very unique behavior. The decrease is not overly large, except for the 5% sample, but is noticeable for all samples. It should be noted again that for the nanotube samples only method 2 was used and hence only one *D* was used; i.e., the decrease is not a function of the *D* used.

Since neither the carbon nanotubes nor the polystyrene has a decreasing thermal conductivity with temperature, the only logical explanation is that the Kapitza resistance is increasing. In other words, the modulus of a molten polymer is orders of magnitude less than the modulus of a glassy polymer, and hence a decrease in thermal conductivity as the polymer goes through its glass transition was observed. The transition appears gradual, which also is expected since the modulus of a polymer typically drops over a 20−30 °C range in the glass transition region.

Using the Maxwell equation modified by Rayleigh for long cylindrical inclusions in a composite material, the expected increase in heat conductivity with the increase in percent filler can be calculated. The effective thermal conductivity, K_{eff}, of the composite in the case of SWCNTs oriented parallel and perpendicular to the direction of heat flux can be calculated by eqs 5a and 5b, respectively:[23]

Parallel:

$$K_{\text{eff}} = (1 - \phi)K_{\text{m}} + \phi K_{\text{SWCNT}} \tag{5a}$$

Perpendicular:

$$K_{\text{eff}} = K_{\text{p}} \left[1 + \frac{2\phi}{\left(\frac{K_{\text{SWCNT}} + K_{\text{p}}}{K_{\text{SWCNT}} - K_{\text{p}}}\right) - \phi + \left(\frac{K_{\text{SWCNT}} - K_{\text{p}}}{K_{\text{SWCNT}} + K_{\text{p}}}\right)(0.30584\phi^4 + 0.013363\phi^8)} \right] \tag{5b}$$

where K_{SWCNT} and K_{p} are the thermal conductivities of the SWCNTs [$K_{\text{SWCNT}} \approx 3000$ W/(m °C)] and of the polystyrene [$K_{\text{p}} \approx 0.1$ W/(m °C)], respectively, and ϕ is the volume fraction of the SWCNT in the composite. Furthermore, we assume that randomly oriented cylinders can be approximated as cylinders perfectly aligned with an angle θ relative to the direction of the heat flux such that $\cos^2 \theta = 1/3$. In that case, the thermal conductivity of the composite should double when the wt % of SWCNTs increases from 5 to 10% (4% to 8.2 vol %) and by about 3.5 times when the wt % of SWCNTs increases from 10% to 30% (8.2% to 25.7 vol %). However, the experimental measurements presented in Figure 2 indicate that the increase in thermal conductivity is very small for the 30% sample relative to the 10% sample. There might be two reasons for this observation: (a) this difference is evidence of poorer SWCNT dispersion in the former relative to the latter sample, and (b) an increase in % SWCNTs introduces an additional resistance to heat transfer, i.e., the resistance to transfer heat from one SWCNT to another. Preliminary molecular dynamics results from Maruyama's group have shown that the resistance to heat transfer from a SWCNT to another is higher than the resistance to heat transfer between a SWCNT and a polymer.[24] At high % SWCNTs the contact points between SWCNTs increase, adding another resistance to heat transfer that can possibly dominate the process at very high % SWCNTs.

Conclusions. The thermal conductivity of SWCNT−polystyrene composites was increased up to 4.5 times relative to that of pure polystyrene in 10 wt % nanotube composites, but there was not a significant increase at higher weight fractions indicative of poorer dispersion and, possibly, of an additional resistance to heat transfer that might be dominant at high % SWCNT. The thermal conductivity of SWCNT composites decreases when the polymer matrix becomes less stiff as a result of heating above the T_g, indicating that the Kapitza resistance increases when the matrix surrounding the CNTs becomes less stiff.

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