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# Heat conduction in graphite-nanoplatelet-reinforced polymer nanocomposites

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Heat transport in polymer nanocomposites reinforced with graphite nanoplatelets (GNPs) is studied using high-precision thermal conductivity measurements. The resistance to heat conduction across interfaces between GNPs and the polymer matrix has a strong effect on energy transport in the nanocomposites. The thermal conductivity is observed to increase when GNPs are pretreated with nitric acid to improve interfacial bonding. The improvement in the thermal conductivity, however, is much smaller than the corresponding improvement in mechanical properties. The thermal interface resistance extracted from the present thermal conductivity data is comparable to that obtained from the previously reported data on carbon nanotube suspensions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2221874]

Heat conduction across surfaces of nanostructures embedded or suspended in a continuous dielectric medium is of great fundamental and practical interest.[1] Such nanostructures can serve, for example, as localized heat sources for thermal processing of polymers or hyperthermic cancer treatment. Polymer composites incorporating nanoscale fillers may also offer superior thermal, mechanical, and electrical characteristics and are attractive for multifunctional structure applications.

One promising candidate as a nanoscale filler is graphite nanoplatelets (GNPs). GNPs are disk-shaped graphite particles of nanometer scale thickness produced through exfoliation.[2,3] GNPs are very attractive as fillers because they may offer high strength, stiffness, and exceptional electrical and thermal conductivities of graphite. Compared with unidirectional carbon nanofibers or nanotubes, GNPs provide reinforcement in two directions and are expected to be more efficient in improving mechanical properties.

Interfacial bonding between GNPs and a polymer matrix can be readily tailored by chemically or physically modifying the surface of GNPs. As-produced GNPs have smooth and chemically inert surfaces, which lead to weak interfacial bonding. A recent work[3] showed that by modifying the surface of GNPs via a nitric acid oxidation process one can substantially increase both the tensile strength and the modulus of resulting nanocomposites. It is of great interest to examine how such surface treatment influences heat transport in GNP-reinforced nanocomposites.

In the present letter, we report high-precision measurements of the thermal conductivity of GNP-reinforced polymer nanocomposites. Our data show that the resistance to heat conduction across interfaces between GNPs and their polymer matrix has a very strong effect on energy transport in the nanocomposites. The thermal conductivity is higher for nanocomposites with nitric-acid-treated GNPs than for nanocomposites with untreated GNPs. This demonstrates that the thermal transport properties and mechanical properties of nanocomposites are linked to each other through interfacial effects.

Details of GNP fabrication methods and their optical and scanning electron microscopy (SEM) characterization results were reported elsewhere.[2,3] Briefly, graphite intercalation compounds (GICs) were synthesized by intercalating potassium into graphite (Asbury Graphite Mills Inc.) and letting the mixture react with dehydrated benzene in an evacuated Pyrex tube. Some of the exfoliated GICs were chemically treated with 67% of nitric acid ($HNO_3$) at 100 °C. The platelets were then rinsed in de-ionized water and dried in an oven at 200 °C for 24 h to remove residual acid and water. The GNPs produced were approximately 3 $\mu$m in diameter and 25 nm in thickness. The polymer matrix used in the present study is made of a commercially available resin (Epon 862 from Shell Chemical Inc.) and a curing agent (Epicure from Shell Chemical Inc.) mixed at a weight ratio of 100/26.5. GNPs are incorporated into the resin mixture using a shear mixer to eliminate agglomeration and then a sonicator to achieve uniform dispersion. The mixtures are poured into silicon rubber molds and cured at 120 °C for 4 h. The samples used in the thermal conductivity characterization are approximately 1 mm thick and contain a 1% volume fraction of GNPs.

We employ the transient hot-wire method to measure the thermal conductivity of the polymer nanocomposites. Details of the hot-wire method and its advantages are described by Gustafsson *et al.*[4] and will not be repeated here. A 25 $\mu$m diameter Au or Pt wire is bonded to each composite sample using a 20-$\mu$m-thick insulating adhesion layer. The wire is

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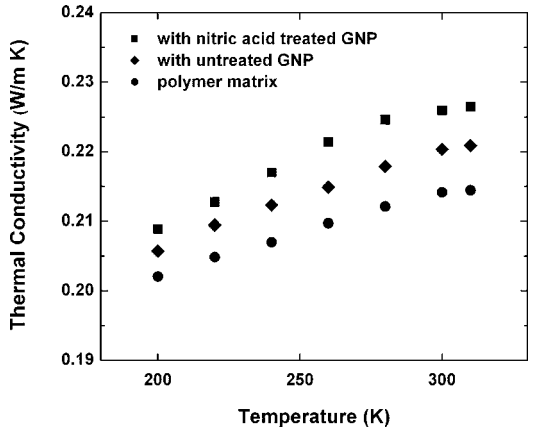


FIG. 1. The thermal conductivity of polymer composites reinforced with graphite nanoplatelets (GNPs) as a function of temperature. The thermal conductivity of the polymer matrix is also shown.

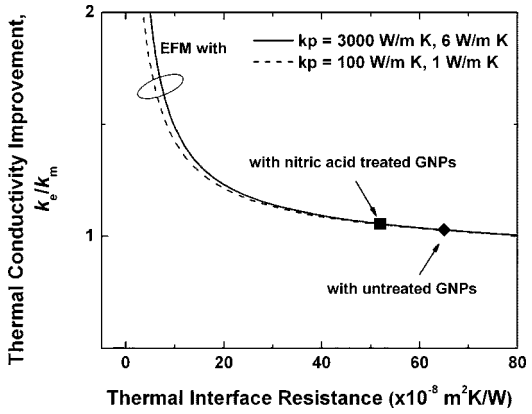


FIG. 3. Thermal conductivity improvement predicted using the effective medium model as a function of thermal interface resistance. Since no independent data are available, two different sets of anisotropic thermal conductivity are assumed for graphite nanoplatelets (solid line and dashed line). The symbols correspond to the experimental data.

subjected to a current pulse of precisely known amplitude, and the resulting temperature rise is determined as a function of time. By analyzing the temporal temperature profile using solutions to the heat conduction equation, we determine the thermal conductivity of each sample. All measurements reported here are conducted in an evacuated ($<5 \times 10^{-6}$ Torr) cryostat.

Figure 1 shows the thermal conductivity of the polymer matrix without GNPs (sample I), the nanocomposite with untreated GNPs (sample II), and the nanocomposite with nitric-acid-treated GNPs (sample III) as a function of temperature. The thermal conductivity of all three samples increases monotonically with temperature over the temperature range investigated, which is consistent with the general trend for highly disordered dielectric materials.

The improvement in the thermal conductivity (see Fig. 2) increases with temperature and is approximately 2%–3% for sample II and 3%–6% for sample III. A previous study on polymer composites incorporating alumina nanoparticles reported comparable increase in the thermal conductivity.[5] In contrast, polymer composites with carbon nanotubes showed substantially larger improvement at similar volume concentrations.[6,7] Direct comparison with data from carbon-nanotube-based nanocomposites, however, is not appropriate since the percolation threshold for carbon nanotubes is well below 1%. There remains disagreement among theoretical studies, but heat conduction along percolated networks of nanotubes appears to play a significant role in heat conduction in nanotube composites.[8]

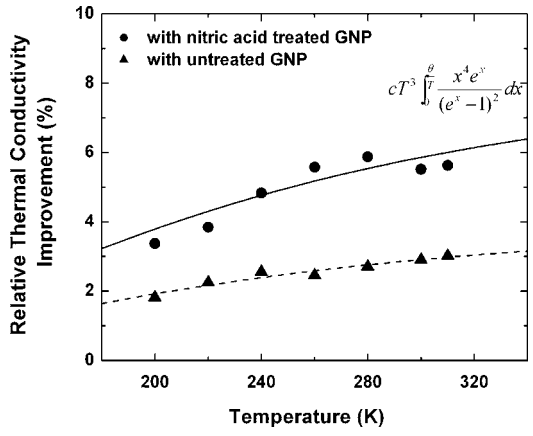


FIG. 2. Relative improvement in the thermal conductivity of two different polymer nanocomposites, one with nitric acid-treated GNPs and the other with untreated GNPs. The solid and dashed lines are best fits based on Eq. (1).

The modest improvement in the thermal conductivity we observe is rather surprising since the thermal conductivity of graphite ($\sim$3000 W/m K) is orders of magnitude higher than that of the polymer matrix. We hypothesize that finite resistance to heat conduction across interfaces between GNPs and the polymer matrix strongly impedes heat conduction in the present nanocomposites. The importance of the interfaces is further highlighted by the fact that the thermal conductivity of sample III is higher than that of sample II. This is consistent with the observation that the tensile modulus of sample III is approximately twice that of the nanocomposite with untreated GNPs (sample II). It is believed that the nitric acid oxidation process generates polar functional groups on the GNP surfaces and thereby improves interfacial bonding with the polymer matrix.

We next analyze the thermal conductivity data using the effective medium model (EFM).[9] We expect this model to be a reasonable approximation for the present nanocomposites at a filler volume concentration of 1%. GNPs are approximated as flat disks. We do not have independent data for the thermal conductivity of the platelets $k_{GNP}$, which can be smaller than bulk values due to the size effect or high concentrations of defects. A parametric study, however, shows (see Fig. 3) that the composite thermal conductivity does not depend sensitively on $k_{GNP}$ when the thermal interface resistance is large. The prediction also considers anisotropy in the thermal conductivity of GNPs, but it is not expected to have a significant effect due to the high diameter-to-thickness ratio of the platelets.

Figure 3 shows the predicted thermal conductivity of the GNP-reinforced nanocomposites as a function of thermal interface resistance. A typical value of the thermal interface resistance between dissimilar solids is of the order of $10^{-8}$ m$^2$ K/W near room temperature. At such a low value of interface resistance, the relative thermal conductivity enhancement is predicted to be more than 200%. The thermal interface resistance extracted from the present data is, however, significantly larger, approximately (65 and 52)

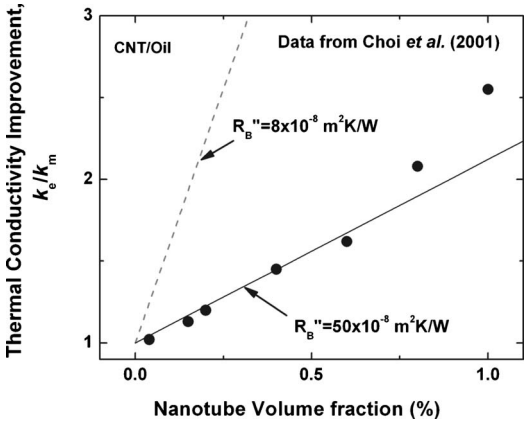


FIG. 4. Extraction of the thermal boundary resistance from the thermal conductivity of carbon nanotube suspensions using the effective medium model.

$\times 10^{-8}$ m$^2$ K/W at room temperature for samples II and III, respectively.

To put our data in perspective, we compare the present thermal interface resistance with that observed in carbon nanotube suspensions. We apply the effective medium model[10] to analyze the thermal conductivity of synthetic poly ($\alpha$-olefin) oils with suspended carbon nanotubes[11] shown in Fig. 4. At low volume concentrations, a best fit is obtained using the thermal interface resistance of $50\times 10^{-8}$ m$^2$ K/W, which is comparable to that of the GNP nanocomposites. At high concentrations, the thermal conductivity of the nanotube suspensions deviates from the effective medium model prediction due presumably to heat conduction through percolation networks. Published data from nanotube-based polymer composites vary greatly, and the thermal interface resistance as small as $0.2\times 10^{-8}$ m$^2$ K/W is estimated.[7,12] It is not clear whether such large variations reflect intrinsic phenomena, inhomogeneity in samples, large experimental uncertainties, or limitation of the effective medium model.

We next attempt to interpret the temperature dependence of the interface resistance suggested in Fig. 2 with the aid of the diffuse mismatch model. The diffuse mismatch model accounts for the finite transmission probability of phonons incident on an interface due to mismatch in atomic vibrational properties. The model was originally developed for crystalline solids.[13] The model may not be considered a rigorous quantitative model for the present GNP-polymer interface, but it may still provide useful qualitative insight.

To simplify the analysis, we assume that the thermal conductivity varies in inverse proportion to the interface resistance. The present thermal conductivity data all lie within the linear regions of the predicted thermal conductivity versus thermal interface resistance curves (see Fig. 3). We fit the data shown in Fig. 2 using a functional form suggested by Swartz and Pohl's diffuse mismatch model[13]

$$(R_B'')^{-1} = cT^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx. \quad (1)$$

In both sets of data, the best fits are achieved when the Debye temperature $\theta_D$ is approximately 900 K. This value is comparable to the lower of the two Debye temperatures of in-plane phonon modes in graphite. This is intriguing, but we caution the reader that the agreement should not be regarded as a definitive proof that the diffuse mismatch model indeed captures the correct mechanism of the thermal interface resistance between GNPs and the polymer matrix. We note that there can be alternative explanations for the observed temperature dependence, such as weakening of interfaces due to mismatch in thermal expansion coefficient between GNPs and polymer matrices. Repeated thermal conductivity measurements during heating and cooling cycles, however, do not reveal any noticeable hysteresis. Scattering of phonons at the surfaces of GNPs may also suppress heat conduction within GNPs. The size effect is expected to be stronger at lower temperatures.

In summary, we report a study of energy transport in polymer nanocomposites reinforced with graphite nanoplatelets using high-precision thermal conductivity measurements. Our data show that the thermal interface resistance has a very strong effect on energy transport in the nanocomposites, making the thermal conductivity a useful probe of interfaces between GNPs and their polymer matrix. The thermal conductivity is higher for the nanocomposite with nitric-acid-treated GNPs than for the nanocomposite with untreated GNPs, consistent with the results of mechanical characterization.

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[1] Y. S. Ju, J. Heat Transfer **127**, 1400 (2005).
[2] L. M. Viculis, J. J. Mack, O. M. Mayer, H. T. Hahn, and R. B. Kaner, J. Mater. Chem. **15**, 974 (2005).
[3] O. Choi, H. T. Hahn, S. Gilje, and R. B. Kaner, Proceedings of the Society for the Advancement of Material and Process Engineering (SAMPE) Fall Technical Conference (37th ISTC), Seattle, WA, 31 October–3 November 2005 (CD-Rom).
[4] S. E. Gustafsson, E. Karawacki, and M. A. Chohan, J. Phys. D **19**, 727 (1986).
[5] S. A. Putnam, D. G. Cahill, B. J. Ash, and L. S. Schadler, J. Appl. Phys. **94**, 6785 (2003).
[6] M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson, and J. E. Fischer, Appl. Phys. Lett. **80**, 2767 (2002).
[7] M. B. Bryning, D. E. Milkie, M. F. Islam, J. M. Kikkawa, and A. G. Yodh, Appl. Phys. Lett. **87**, 161909 (2005).
[8] M. Foygel, R. D. Morris, D. Anez, S. French, and V. L. Sobolev, Phys. Rev. B **71**, 104201 (2005).
[9] C.-W. Nan, R. Birringer, D. R. Clarke, and H. Gleiter, J. Appl. Phys. **81**, 6692 (1997).
[10] C.-W. Nan, G. Liu, Y. Lin, and M. Li, Appl. Phys. Lett. **85**, 3549 (2004).
[11] S. U. S. Choi, Z. G. Zhang, W. Yu, F. E. Lockwood, and E. A. Grulke, Appl. Phys. Lett. **79**, 2252 (2001).
[12] S. Shenogin, L. Xue, R. Ozisik, P. Keblinski, and D. G. Cahill, J. Appl. Phys. **95**, 8136 (2004).
[13] E. T. Swartz and R. O. Pohl, Rev. Mod. Phys. **61**, 605 (1989).