DOI: 10.1002/anie.201201689

Polymer/Boron Nitride Nanocomposite Materials for Superior Thermal Transport Performance**

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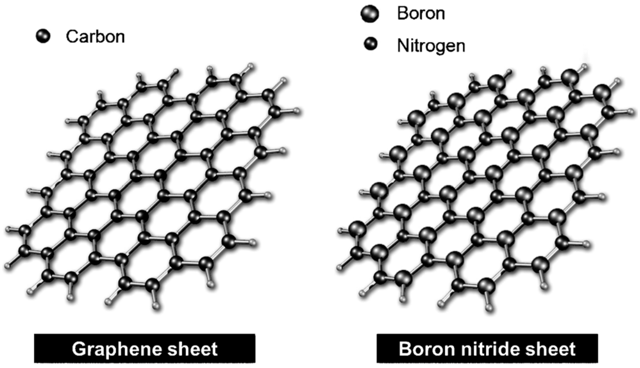
Lightweight nanocomposites with superior thermal transport properties promise great application potential,[1–4] for which there has been extensive development effort.[5–8] Among widely pursued nanoscale fillers in such composites are carbon nanomaterials. For example, carbon nanotubes are extremely thermally conductive at the individual-nanotube level.[9,10] More recently, single- and fewer-layer graphene sheets have been shown to be even more advantageous than carbon nanotubes,[11–15] especially for their uses in polymeric nanocomposites of high thermal conductivity.[16–25]

Hexagonal boron nitride (BN) is structurally analogous to graphite (Scheme 1) and has equally good thermal transport properties.[26,27] In fact, bulk BN has traditionally been considered as a material of choice in thermal-management applications.[28–37] In recent years both BN nanotubes and sheets have attracted growing attention for thermal transport and other uses. For example, Li and Hsu prepared composite films of polyimide with micro- and nanosized BN, including BN "nanoflakes", for which thermal conductivities of up to $1.2\,\mathrm{W\,m^{-1}K^{-1}}$ at 30 wt % BN loading were obtained.[28,29] Sato et al. also studied polyimide composites with hexagonal BN as filler, and films containing 30 and 60 vol % BN exhibited thermal conductivities of 3 and $7\,\mathrm{W\,m^{-1}K^{-1}}$, respectively.[30] Wattanakul et al. found similar thermal conductivities in epoxy composites with 33 vol % hexagonal BN.[31] These results suggest that the thermal transport performance of polymer composites with BN is generally poorer than with graphene sheets as filler. Therefore, there are major challenges and also opportunities in the development of polymer/BN nanocomposites with much improved performance, especially with respect to the need for lightweight composite materials with extreme ratios of thermal to electrical conductivity to exploit the electrically insulating nature of BN.



Scheme 1. Illustration of the structural similarity between graphene (left) and boron nitride (right) sheets.

In this study we exfoliated hexagonal BN in organic medium to give sheets of nanoscale thickness and dispersed the resulting BN nanosheets in poly(vinyl alcohol), PVA, and epoxy matrices. Superior thermal transport performance was achieved in the polymer/BN nanocomposite films thus fabricated, and substantial performance enhancement through mechanical alignment of BN nanosheets embedded in PVA was found. The results demonstrate that BN sheets of nanoscale thickness may indeed hold promise for polymer nanocomposites with metal-like thermal transport performance, similar to what has already been achieved in polymer nanocomposites with fewer-layer graphene sheets.[23,25]

Commercially acquired hexagonal BN was sonicated vigorously in isopropyl alcohol for both dispersion and exfoliation. An aliquot of the resulting suspension was used to prepare specimens for characterization of the BN sheets by microscopy and other techniques. Representative SEM images (Figure 1 a,b) suggest lateral sizes (edge-to-edge) of the sheets on the order of 1 μm or larger. Larger sheets were found under a confocal optical microscope (Figure 1 d). The powder XRD pattern of the BN sheets was typical of that hexagonal BN in the MDI Jade database, though the peaks were obviously broadened, consistent with the expected nanoscale thickness. Applying the Scherrer equation to the diffraction-peak broadening gave a sheet thickness on the order of 10–20 nm. Transmission electron micrographs of sheet edges (Figure 1 c) gave a thickness consistent with the XRD results. Thus, the aspect ratios of the exfoliated BN sheets are on the order of 100 and larger.

For fabrication of PVA nanocomposites with exfoliated BN sheets, PVA was dissolved in hot water, and a separately

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[**] Financial support from the Air Force Office of Scientific Research (AFOSR) through the program of Dr. Charles Lee is gratefully acknowledged. W.-L.S. was a visiting student from School of Materials Science and Engineering (the group of Prof. Mao-Sheng Cao) at Beijing Institute of Technology with a fellowship provided by the China Scholarship Council. L.C. was supported by a Susan G. Komen for the Cure Postdoctoral Fellowship, and A.A. and A.J.F. by South Carolina Space Grant Consortium through a Graduate Research Fellowship and the Palmetto Academy Program, respectively. M.J.M. was on leave from Department of Chemistry/Physics, Northwest Missouri State University.

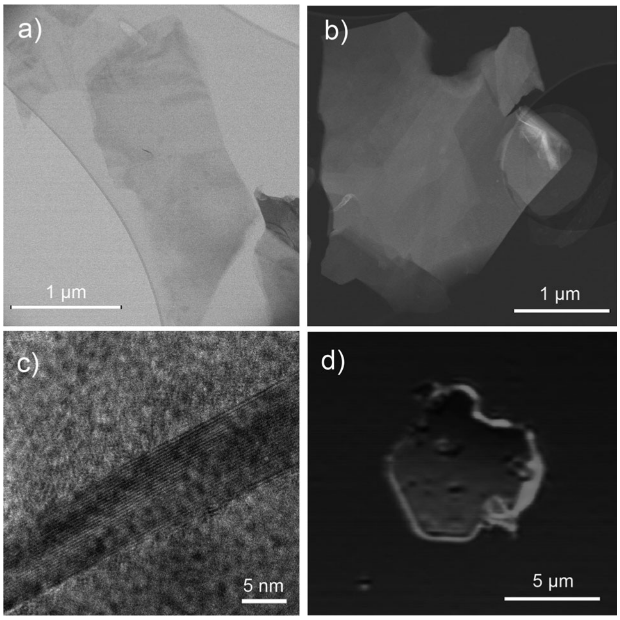

Figure 1. SEM (a, b), TEM (c, view on sheet edge), and optical microscopy (d) images of BN nanosheets.

prepared suspension of BN sheets in isopropyl alcohol was added dropwise to the aqueous polymer solution at room temperature. The mixture was concentrated by evaporating water with vigorous stirring. The resulting polymer blend with dispersed BN sheets was cast into a thin film with a targeted thickness of about 50 µm on an etched glass slide, and then the free-standing film (Figure 2, inset) was peeled off for subsequent characterization and measurements.

The PVA/BN nanocomposite films were microtomed to obtain thin slices (targeted thickness < 100 nm) for cross-sectional TEM imaging of the BN sheets embedded in the polymer matrix. The representative TEM images shown in Figure 2 suggest that the BN sheets in the composite films are largely similar to those in the isopropyl alcohol suspension, with sheet thicknesses of generally 10 nm or less, that is, the large aspect ratios are retained.

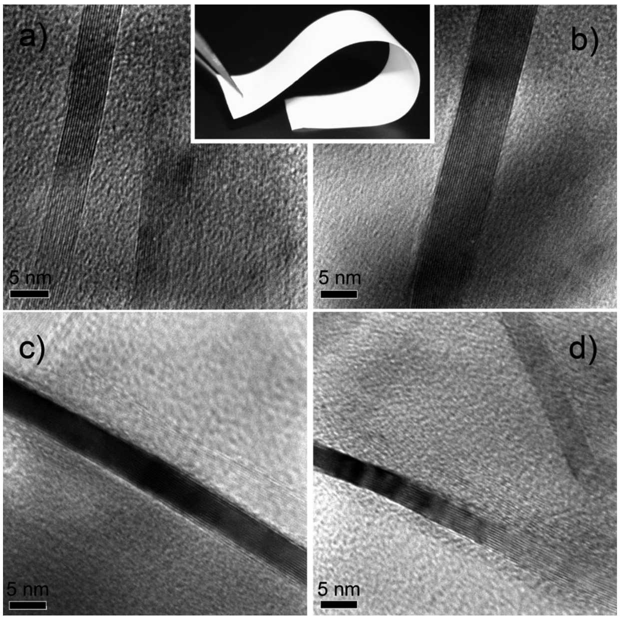

Figure 2. TEM images of cross-sectional microtomed slices of PVA/BN (a, b; inset: photo of a piece of film) and epoxy/BN films (c, d).

The thermal transport properties of PVA thin films with various loadings of BN sheets were evaluated by measurements of in-plane thermal diffusivity (TD). The TD increases monotonically with BN loading and reaches 6 $mm^2 s^{-1}$ at 50 vol% BN (Figure 3). The performance is at the upper end of those achieved in various polymer/BN composite materials.[28–37] For further improvements in thermal transport performance, the PVA/BN nanocomposite films were mechanically stretched to take advantage of the known ability of PVA polymer matrix to align molecular and nanoscale species.[38,39] For example, carbon nanotubes could be aligned in stretched PVA polymer films for much enhanced anisotropic characteristics in optical absorption and photoluminescence emission.[39] In this study, alignment of the BN sheets in the PVA polymer matrix by mechanical stretching of the composite film dramatically enhanced TD, which reached almost 9 $mm^2 s^{-1}$ at 15 vol% BN, many times higher than that of the unstretched film (Figure 3). For films with even higher BN loadings, mechanical stretching became rather difficult, and presented a significant challenge for further investigations. Nevertheless, the results obviously demonstrated a simple way to align BN nanosheets in PVA to achieve record-setting thermal transport performance with relatively low BN loadings, while largely preserving the morphological characteristics of the PVA/BN thin film (Figure 3).[23,25]

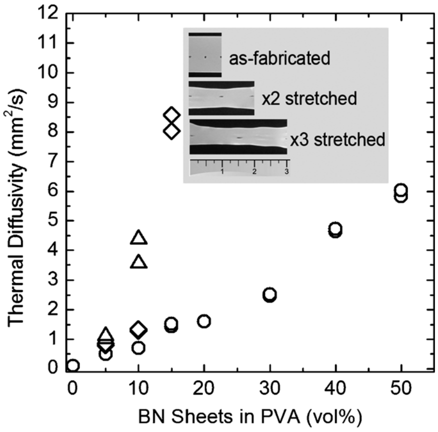

Figure 3. TD values at different BN loadings in PVA/BN films as fabricated (○) and mechanically stretched (×2: ◇; and ×3: △). Inset: photos of as-fabricated and stretched films with 10% BN loading.

The thermal transport performance of polymer/BN nanosheet composites is dependent on the polymer matrix. Epoxy resin, which has been widely used in BN-based composite materials for thermal management applications,[31,33,34] gives polymer/BN thin films with much higher TD values. The fabrication procedures for epoxy/BN films were similar to those for their PVA/BN counterparts, except that a solution of epoxy resin in THF was used. The cast thin films on etched glass slides were detached in free-standing form after immersion in water for about 30 min and dried in a vacuum oven.

The TEM images of microtomed thin slices of the epoxy/BN films did not appear to be meaningfully different from those for PVA/BN specimens (Figure 2). Macroscopically, however, the epoxy-based composite films exhibited much better thermal transport performance. The observed in-plane TD values were also monotonically dependent on BN loading, but consistently higher than those of PVA/BN films (Figure 4). An epoxy/50 vol% BN thin film showed a TD of almost 19 $\mathrm{mm^2\,s^{-1}}$, much higher than those of PVA/BN films (Figure 4) or any other polymer/BN composite materials reported in the literature.[28–37] The corresponding in-plane thermal conductivity (TC) calculated from the equation $\mathrm{TC} = \alpha\mathrm{TD}$ (where $\alpha = \text{density} \times \text{specific heat}$) was higher than $30\,\mathrm{W\,m^{-1}K^{-1}}$ in the films with 50 vol% BN, that is, close to 15% of the TC of aluminum metal.

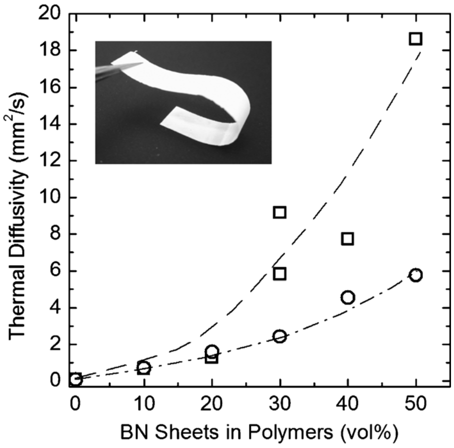

Figure 4. TD values of epoxy/BN nanocomposite films at different BN loadings (□) compared with those for PVA/BN films (○). Inset: photo of a piece of film with 50% BN loading.

The dependence of thermal transport on the polymer matrix in polymer/BN nanocomposites is interesting, as the similarly higher performance with the epoxy resin matrix was also observed in nanocomposites with fewer-layer graphene sheets.[23,40] Possibly, the epoxy resin is structurally more compatible with the nanosheets, so that interfacial resistance to phonon propagation, which is responsible for thermal transport, is reduced. However, the PVA matrix with its special elastic characteristics offers the unique opportunity to align the embedded nanosheets by simple mechanical stretching. The substantial post-alignment enhancement of in-plane TD values provides strong evidence for the expected major role of BN nanosheets with large aspect ratios in thermal transport in nanocomposite films. There is obviously more room for improvements in the mechanical stretching process, especially for composite films with higher BN loadings, with emphasis on balancing the need for the PVA matrix to be sufficiently elastic (e.g., stretching above ambient temperature) and the requirement that the matrix retain the necessary microstructure for filler alignment on stretching. Nevertheless, the mechanically stretched films serve as a unique platform for the facile preparation of highly thermally conductive polymer/BN nanocomposites at lower BN loadings.

In recent studies, dramatic enhancement of thermal transport performance by dispersing graphene sheets in polymers was demonstrated, and metal-like thermal conductivity was observed in some lightweight nanocomposites.[25] The results reported here suggest that exfoliated BN sheets could serve the same purpose for similarly high performance polymer nanocomposites. Further opportunities for improvement include more effective and controllable exfoliation for higher quality BN nanosheets, whereby a significant challenge is that interlayer bonding in hexagonal BN is much stronger than that in graphite. For potential technological applications, polymer/BN nanocomposites have several advantages over those based on graphene sheets, especially when electrically insulating nanocomposites are required.

In summary, hexagonal BN processed and suspended in organic solvent was found to be dominated by sheets of nanoscale thickness and large aspect ratios. The BN nanosheets were dispersed in polymer matrices to give nanocomposite films with superior thermal transport performance. The in-plane thermal diffusivities of epoxy/BN nanocomposites are considerably higher than those found in the literature, and approach the record-setting values achieved in similar nanocomposites based on fewer-layer graphene sheets. The as-fabricated PVA/BN films are somewhat less thermally conductive, but on being mechanically stretched to align the embedded BN nanosheets offered high thermal conductivities at lower BN loadings. These results demonstrate great potential for BN nanosheets in highly thermally conductive polymer nanocomposites, with application potential competitive with or beyond those based on graphene sheets.

Experimental Section

Materials: Hexagonal boron nitride (99.5%) was supplied by Alfa Aesar, and PVA ($M_\mathrm{W} \approx 70000$–$100000$) by Aldrich. The epoxy polymer (EPONOL resin 53-BH-35, $M_\mathrm{W} \approx 26000$) in methyl ethyl ketone/propylene glycol monomethyl ether was obtained from Hexion Specialty Chemicals, and the polymer was recovered by precipitation in water and then complete removal of water. Isopropyl alcohol was purchased from OmniSolv, and THF from Fisher Scientific.

Measurements: XRD measurements were carried out on a Scintag XDS-2000 powder diffraction system. SEM imaging was performed on a Hitachi S4800 field-emission SEM system, and TEM imaging on Hitachi HD-2000 S-TEM and Hitachi H-9500 TEM systems. Carbon- or holey carbon-coated copper grids were used in the imaging experiments. Microtomed specimens were prepared by embedding a film sample in epoxy resin and cutting cross-sectional slices of less than 100 nm in thickness with a Reichert-Jung Ultracut E Microtome with a 30° diamond knife at room temperature. Optical micrographs were obtained on a Leica DMIRE2 microscope (with TCS SP2 SE scanning system and a JDS Uniphase argon-ion laser) in reflective mode. The specimen for imaging was prepared by diluting a sample suspension and then dropping the suspension onto a cover glass slide, followed by drying under ambient conditions.

The in-plane thermal diffusivity (TD) measurements for the free-standing polymer/BN nanocomposite thin films were performed on an Ulvac LaserPIT thermal diffusivity/conductivity meter operated in a vacuum of 0.01 Pa at room temperature.[41] The thin-film specimens were each about 30 × 5 mm in size, with the surface facing the laser in the instrument spray-coated with a thin layer of fine graphite powder. The densities and specific heats of the nanocomposite films were estimated from those of the polymer and filler in terms of the simple mixing rule: Composite $= w_{\text{polymer}}$Polymer $+ w_{\text{filler}}$Filler, where w denotes weight fractions.

Nanocomposite films: A hexagonal BN sample (200 mg) was added to isopropyl alcohol (20 mL), and the mixture sonicated (VWR-250D, 120 W) for 48 h. The relatively stable suspension thus formed was used in subsequent fabrication. PVA was dissolved in hot water (80 °C), and the aqueous solution remained homogeneous on cooling to room temperature. The epoxy polymer was dissolved in THF.

For film fabrication, an aqueous PVA solution (10 mL) or a THF solution of the epoxy polymer (10 mL) was mixed with various volumes of the isopropyl alcohol suspension of BN sheets by dropwise addition of latter to the former with stirring. The mixture was concentrated by solvent removal with vigorous stirring, and the resulting polymer blend with BN sheets was cast as a thin film on an etched glass slide. The PVA/BN films could be peeled off directly in free-standing form, while the epoxy/BN films were released from the glass slides after immersion in water for about 30 min. The free-standing films were dried in a vacuum oven at 80–100 °C for PVA/BN and 22 °C for epoxy/BN before characterization and measurements.

Mechanical alignment: In a typical experiment, a PVA/BN film strip of 35 × 12 mm in size was stretched at room temperature by manually applying a constant load to the long ends of the film strip until the targeted draw ratio was reached. After stretching, the PVA/BN film strips were dried in a vacuum oven at 80–100 °C.

Received: March 1, 2012

Keywords: boron · nanostructures · nitrides · polymer nanocomposites · thermal transport

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