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Insulating polymer nanocomposites with high-thermal-conduction routes via linear densely packed boron nitride nanosheets

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ABSTRACT

Electrically insulating polymeric nanocomposites with high thermal conductivity have great potential for use as thermal-management materials in increasingly high-power-density electronics and optoelectronics. Conventional composite materials require a large amount, over 70 vol%, of electrically conducting fillers such as carbon allotropes to attain thermal conductivities of 1–5 W/mK, [Balandin, 2011] [1] which restricts the utility of these materials to applications that require both electrical and thermal conductivities. Here, we introduce a strategy to achieve the strongest enhancement of thermal conductivity to date at a low level of filler loading ($\leq$15 vol%) in insulating polymer nanocomposites with hexagonal boron nitride (BN) nanosheets. The combination of electric-field switching and the application of fillers with various aspect ratios enables the rearrangement of the BN nanofillers into linear densely packed BN structures (LDPBNs). Flexible nanocomposite films with LDPBNs exhibit electrical resistivity greater than 1.50×10^{-6} MΩ cm and a thermal conductivity of 1.56 W/mK, a dramatic enhancement over that of pristine polysiloxane with the same BN loading (0.4 W/mK). Our strategy of electric-field-induced BN nanosheet assembly offers insight into the possibility of solving thermal-management problems using ideal thermal interface materials, thus enabling improved next-generation integrated circuits and nanoelectronics.

1. Introduction

Polymer-based nanocomposites have recently attracted significant interest because the ability to achieve a refined structure with a proper orientation of hard inorganic particles enables the control of the deformation, failure, heat resistance, and thermal properties of a polymer [2,3]. Organic-inorganic composite materials that contain small amounts of insulating nanoceramics could potentially be used as thermal interface materials (TIMs), which require high thermal conductivity and electrical resistivity. Because of the rapidly increasing power density in electronics such as next-generation integrated circuits, 3-dimensional integrated circuits, and ultra-high-power-density transistors, the efficient removal of heat is becoming crucial to the performance and reliability of these devices. [6] However, the very low thermal conductivity of polymers and the thermal boundary resistance (TBR) [7] between the polymer and the filler are the two major obstacles to effective thermal conduction in polymer-based composites. Although polymers are excellent electrical insulators, and their flexible nature offers easy workability, they are the worst heat-conducting bulk solids, and phonon-phonon interactions in isotropic polymers cannot achieve thermal conductivities in excess of ~0.3 W/mK. [8] Because a high TBR is the result of an interface that constitutes an interruption in the regular crystalline lattice in which phonons propagate, [9] a potentially effective approach is to orient the filler along the direction of thermal flow. [10]

Boron nitride (BN) ceramics are excellent conductors of heat, comparable to aluminum nitride, as well as electrical insulators, and they exhibit thermal conductivities that are among the highest of all electrical insulators. [11] Furthermore, hexagonal BN (h-BN) with a graphite-like layered structure exhibits anisotropic thermal

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conductivity; its in-plane thermal conductivity is 600 W/mK, which is 20 times higher than its out-of-plane value of 30 W/mK [12]. A polymer nanocomposite whose in-plane direction is perpendicularly oriented in the polymer matrix can attain a higher thermal conductivity at a low filler content [13,14].

The alignment of nanosheets, or 2-D fillers, via reorientation in the polymer matrix is a crucial technique for such composites, and shear forces [15], magnetic forces [16], and electric fields [15,17] have been widely used to tune the anisotropic orientations of nanosheets in polymer matrices. Recently, the shear-induced extrusion of a mixture of epoxy resin and BN nanosheets has been demonstrated to cause the longitudinal axes of the nanosheets to become highly oriented in the polymer matrix, resulting in a thermal conductivity of up to 38 W/mK (85 vol% BN) [18]. This approach permits the dramatic improvement of the thermal properties of such composites, but their practical applications are limited because of material redundancy, economic inefficiency, and low workability.

It has been demonstrated that reorienting and relocating filler particles such that end-to-end attachment occurs in the polymer matrix is an effective means of enhancing the thermal conductivity using a relatively small amount of thermally conducting fillers, less than 20 vol% [19–22]. In previous studies, to facilitate the conduction of heat along 1-D or 2-D thermally conducting fillers instead of the polymer [23,24], the anisotropy and distribution of the fillers has typically been controlled by applying the first two of the four steps depicted in Fig. 1. Orienting the longitudinal direction of the thermally conducting filler particles parallel to the direction of the heat flux can effectively increase the thermal conductivity of a composite (step 1). The use of 1-D aligned nanotubes in a polymer matrix can allow the conditions the percolation transition of conductivity to be satisfied at a remarkably low volume fraction compared with the use of pristine powder (step 2) [25]. The linear structure produced by the end-to-end attachment of filler particles constitutes an easier heat-conduction route through the filler particles, avoiding the route through the polymer. This structure can be further developed into a more dense arrangement of the filler particles (step 3) through the application of ON-OFF cycles of an applied electric field [26] using conducting carbon nanotube (CNT) fillers prepared via surface functionalization with tetraoctylammonium. In our previous work, the fabrication of filament-like linear structures of BN nanosheets (steps 2 & 3) was accomplished by controlling the polymer viscosity and the electric field [27]. The stretched assemblies of BN nanosheets (5 vol%) formed through end-to-end attachments exhibited an elevated thermal conductivity compared with samples with an anisotropic orientation of BNs. The facilitation of longer filler assemblies to establish thermal-conduction pathways in polymers using the lowest possible filler contents (steps 3 & 4) may be the most ideal approach to fabricating highly thermally conductive composite materials for use as TIMs; however, these technologies remain an unexploited field.

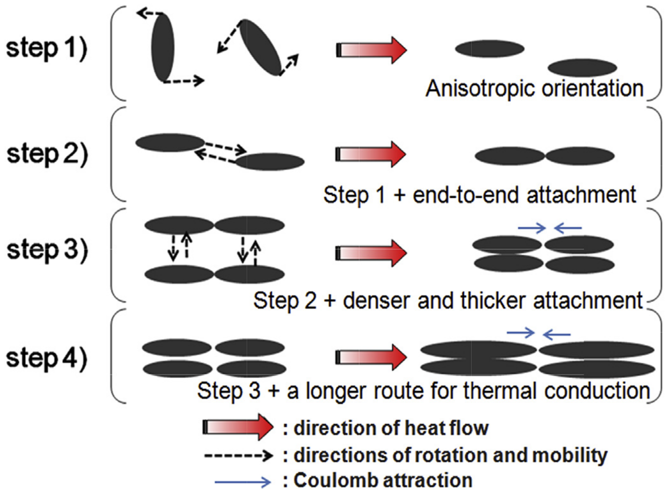

Fig. 1. Schematic illustration of the development of 1-D and 2-D fillers in polymers induced by various rotation sources: *step 1)* Orientation parallel to the longitudinal direction, *step 2)* End-to-end attachment of fillers (linear structure), *step 3)* Denser localization of fillers to form a linear structure, and *step 4)* A longer route for thermal conduction.

Here, we report a straightforward route for the direct assembly of highly thermally conductive BN nanosheets into linear densely packed bundles in a nanocomposite film, in which the structural and thickness variations and the filler-to-filler gaps are controlled using applied electric fields. The combination of electrostatic and Coulombic attraction present in an assembly of BN nanosheets can drive the end-to-end assembly of different linear bundle structures. Our robust strategy of constructing thermal-conduction routes using LDPBNs allows for a sharp increase in the thermal conductivity of insulating nanocomposites at noticeably lower filler contents.

2. Material and methods

2.1. Materials and sample preparation for ordered polysiloxane/BN nanocomposites

Polysiloxane/BN-nanosheet nanocomposite films were prepared by introducing BN nanosheets into a poly (dimethylsiloxane) elastomer [28,29]. Three types of hexagonal boron nitride (BN) nanosheets of commercial origin (Denka Co., Ltd, Japan), ranging from 10 to 20 μm in diameter and from 2 to 10 nm in thickness, were used (See Fig. 2): BN-HGP (particle diameter $D_{90} = 10.6$ μm, aspect ratio = 141.3) and BN-GP ($D_{90} = 17.1$ μm, aspect ratio = 228.0) were used as sheet-type fillers, and BN-SP2 ($D_{90} = 14.2$ μm) was used as a powder-type filler with agglomerated nanosheets [14]. The inset image reveals that the BN nanosheets, BN-HGP, had a planar graphite-like structure with smooth surfaces and curved edges and a layered structure with a thickness of less than 10 nm that was composed of several BN layers.

The amount of BN nanosheets that was added was 5, 10, or 15 vol%. The samples were prepared using a commercially available silicone elastomer (YE5822) manufactured by Momentive Performance Materials Inc., New York, USA. Two liquid components of YE5822 with different viscosities were used: YE5822(A), with a viscosity of 1.2 Pa s and Mw_{av} of 21,000, and YE5822(B), with a viscosity of 0.2 Pa s and Mw_{av} of 16,000. An indium-tin-oxide (ITO)-coated glass slide (2.5 × 7.5 × 1.0 mm^3, Sigma-Aldrich), with a surface resistivity of 8–12 Ω/sq, was used as an electrode for the application of the electric field. First, 3 g of silicone YE5820(A) was sonicated for 5 min; a mixture of 0.3 g of silicone YE5822(B) and 0.416 g of BN (5 vol%) was then introduced into the sonicated silicone YE5820(A), and the resulting mixture was further sonicated for 10 min. The mixture was stirred using a high-speed mixer at 1500 rpm for 5 min to produce a homogeneous dispersion, which was then cast onto a polyimide spacer (1.5 mm × 1.5 mm × 120 μm), which was placed between the two electrodes (Fig. 3) and subjected to a 1.0 kV AC (50 Hz), DC, or switching DC electric field for 16 h to orient and relocate the BN nanosheets in the mixtures. The polarity of the DC electric field was changed at 4-h intervals during the experiment. Finally, the prepared composites were dried for 0.5 h at 80 °C to ensure complete curing.