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Thermally conductive polybutylene terephthalate/hexagonal boron nitride composites with bimodal filler size distribution

Yanting Guo, Siu Ning Leung*

Multifunctional Materials | Micro-and-Nanostructuring Laboratory, Department of Mechanical Engineering, Lassonde School of Engineering, York University, 4700 Keele Street, Toronto, M3J 1P3, Canada

HIGHLIGHTS

- Investigated k_{eff} of PBT composites contain spherical and platelet-shaped hBN.
- PMC filled with spherical hBN of relatively small size possessed the highest k_{eff}.
- Hybrid hBN fillers showed synergistic effect on PMC's k_{eff}.
- Platelet-shaped hBN of significant size difference exhibited most increase in k_{eff}.

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ABSTRACT

Thermally conductive polymer matrix composites (PMC) are promising alternatives to traditional electronic packaging materials to enhance the heat dissipation of integrated circuits, due to polymer's superior electrical insulating property, low cost, and light weight. This work aims to investigate the potentials of using synergy effects of hexagonal boron nitride (hBN) platelets and spherical hBN particulates or those of hBN platlets with bimodal size distribution to promote PMC's effective thermal conductivity (k_{eff}). PMC consists of polybutylene terephthalate (PBT) and hBNs with different geometries and size distributions were used as case examples. Experimental results reveal that PMC filled with solely hBN spherical agglomerates of fine diameters possess the highest k_{eff}, owing to its isotropic thermal conductivity and compact filler-filler interaction. Moreover, two-dimensional hBN platelets, which have anisotropic thermal conductivity, of bimodal size distribution show synergistic effect on PMC's k_{eff}. To maximize PMC's k_{eff} with a minimum filler loading, an optimal mixture of hBN platelets with bimodal size distribution would help to overcome the trade-off between enhanced filler networking and increased thermal contact resistance at the filler-filler interfaces. The findings in this study provide some insights to design and fabricate thermally conductive PMC with reduced filler loading for thermal management applications.

1. Introduction

The worldwide market of semiconductors reached $338.9 billion in 2016, representing a 16.3% increase over that in 2012 [1]. The stunning increase in transistor density on an integrated circuit of the semiconductor industry has marched at the pace of the Moore's Law over the past five decades [2]. With the emerging three-dimensional (3D) chip architecture, this trend will continue until 2021 [3]. Complimentary metal-oxide-semiconductor (CMOS) technology has become indispensable for our life and its advance provides an opportunity to fabricate high-performance processors (e.g., multi-functionality, high operation speed, simultaneously multi-tasking) with smaller footprints. The shrinking of integrated circuit feature size results in several hundred million transistors on a single chip. Miniaturized chips with dense 3D architectures will generate tremendous heat. However, there is a limit on the heat dissipation per unit surface area [4]. Excessive heat generated during a processor's operation causes overheating, potentially leading to system failure and permanent damage. In other words, the future development of 3D integrated circuits requires new solutions for heat removal. Therefore, innovative thermally conductive materials and composites with fast heat dissipation for

* Corresponding author.
E-mail address: sunny.leung@lassonde.yorku.ca (S.N. Leung).

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electronic packaging and other thermal management applications are in high demands.

Owing to the advantages of polymers, including light weight, low cost, superior electrical insulation property, and good processability, they become potential alternatives to traditional electronic packaging materials of integrated circuits [5,6]. However, the drawback of polymers is their low intrinsic thermal conductivity that hinders the heat transfer rate. To address this, it is imperative to develop thermally conductive but electrically insulating polymer matrix composites (PMC). The effective thermal conductivity (k_{eff}) of PMC can be enhanced by establishing networking of thermally conductive fillers. Conventional fillers include ceramic [7–9], metal [10,11], and carbon-based fillers [12–15]. PMC's k_{eff} relies on the intrinsic thermal conductivity and content of conductive fillers. Although metal fillers can dramatically enhance PMC's k_{eff}, their high electrical conductivity and density would impede their applications in electronic packaging. The superior thermal conductivity of carbon-based fillers when compared to ceramic and metal fillers make them promising fillers for thermally conductive PMC [16]. However, similar to metal fillers, their high electrical conductivity limits their uses in electronic packaging. Moreover, if these carbon fillers are nanosized (e.g., carbon nanotubes or graphene), the extremely large surface area to volume ratio would lead to large interfacial thermal resistance between them and surrounding polymer matrix. This would increase phonon scattering for heat conduction. In contrast, ceramic fillers, due to their high thermal conductivity and low electrical resistivity, have gained increasing attentions and been widely used in electronic packaging applications [17]. Nevertheless, because of the phonon scattering at unsatisfactory connections of filler-polymer and/or filler-filler interfaces [18,19], PMC were not able to take full advantage of the filler's high intrinsic thermal conductivity. Significant increase in PMC's k_{eff} were reported by the addition of more than 60 vol% of thermally conductive fillers [20–23]. Such high filler loading would significantly increase the processing difficulty, material cost, as well as density of thermally conductive PMC, and thereby sacrificing some benefits of polymer matrix. Thus, it is vital to develop new strategies to design and fabricate thermally conductive PMC with reduced filler loadings.

Extensive studies have been conducted to promote PMC's k_{eff} by various techniques to facilitate the filler network formation, such as doctor blading [24], extrusion [25], electric field [26], and foaming [27]. In addition, researchers found that hybrid fillers with different shapes and/or sizes promoted PMC's k_{eff} by maximizing filler packing fraction and effectively forming thermally conductive paths in PMC. The hybrid filler systems investigated include spherical and fibrous fillers [28,29], fibrous and platelet-shaped fillers [30,31], spherical and platelet-shaped fillers [32], and spherical filler with different sizes [33]. It was revealed that the high aspect ratio of platelet-shaped filler and fibrous filler promoted the interconnectivity among fillers, and consequently the establishment of filler network in PMC. In order to seek for in-depth understanding about the synergistic effect of hybrid fillers of the same type but different geometries (i.e., shapes and sizes) on PMC's k_{eff}, this article employs hybrid fillers consisting of platelet-shaped and spherical fillers as well as platelet-shaped fillers with bimodal size distribution. Using polybutylene terephthalate (PBT) as the polymer matrix, PMC filled with a single type of hexagonal boron nitride (hBN) and hybrid hBNs are fabricated and examined. Three grades of platelet-shaped hBNs with different lateral sizes and aspect ratios and two grades of spherical hBNs with different diameters are used in this study. The effects of filler content, filler geometry (i.e., size and shape), filler property (i.e., isotropic and anisotropic thermal conductivity), and size difference between hybrid fillers on PMC's k_{eff} are investigated. Although many analytical models are often used to preliminarily estimate the dependence of PMC's k_{eff} on the filler volume fraction and aspect ratio, these models have two types of limitations [34]. First, the phase morphologies of fillers are usually assumed to have idealized shapes (e.g., monodisperse spherical filler or perfectly aligned or isotropic monodisperse cylinders). Second, these models are only semi-quantitatively or unable to capture the effects of thermal contact resistance. Therefore, the experimental studies conducted in this work are required to elucidate the mechanism behind the synergistic effects of hybrid fillers of the same type but different geometries on PMC's k_{eff} and to provide a more complete picture of hybrid fillers induced enhancement of PMC's k_{eff}.

2. Experimental

2.1. Materials

Commercially available PBT (Celanese, Celanex 2002-2) was used as the matrix material in this work. Five grades of hBN fillers (Momentive Performance Materials, PolarTherm, AC6041, PT120, PT110, PTX25 and PTX60), which have different shapes and/or sizes, were embedded in the matrix to prepare PBT/hBN composites. Among the five grades of hBN fillers, AC6041, PT120 and PT110 are two-dimensional (2D) platelets with mean lateral sizes of 6, 12 and 45 μm, respectively. PTX25 and PTX60 are 3D spherical agglomerates with mean diameters equal to 25 and 60 μm, respectively. All materials were used as received without further modification. The 2D hBN platelets possess high aspect ratios ranging from 16 to 23. This would likely promote the development of thermally conductive network when these platelets are dispersed in a polymer matrix. Their graphite-like molecular structures lead to their anisotropic thermal conductivity. In contrast, the 3D hBN spherical agglomerates consisted of randomly oriented hBN platelets that contributed to their isotropic thermal conductivity and good localized filler-filler connectivity. With the same number density of hBN particles, larger filler size would lead to higher filler loading and increase PMC's k_{eff}. With the same filler content, larger hBNs have better filler continuity that would minimize the detrimental effect of phonon scattering for heat transfer. In contrast, smaller hBNs would lead to a higher population density and facilitate the establishment of filler network. In this context, composites with both 2D and 3D hBNs or 2D hBNs with bimodal size distribution were fabricated to investigate the potentials of using synergy effects of hybrid fillers to promote PMC's k_{eff}. Tables 1 through 3 summarize the physical properties of PBT and hBN fillers. PBT is an engineering thermoplastic that possesses excellent mechanical properties and superior heat-deflection temperature (i.e., 160 °C at 0.46 MPa, ASTM D648). Enhancement of the thermal conductivity of this material would contribute to various thermal management applications that demand high structural and thermal stabilities.

2.2. Sample preparation

The overall procedures to prepare PBT-hBN composite samples are illustrated in Fig. 1. PBT pellets were first ground into fine powders with particle sizes ranging from 250 to 500 μm by a mill

Table 1
Physical properties of PBT.

Property	Value	Unit
Density	1310	kg/m^3
Melting temperature	225	°C
Thermal conductivity	0.29	$W \cdot m^{-1} \cdot K^{-1}$
Dielectric strength	23	MV/m