Composites: Part A 98 (2017) 184–191

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Synergistic effect of spherical Al_2O_3 particles and BN nanoplates on the thermal transport properties of polymer composites

Young-Kuk Kim [a],*, Jae-Yong Chung [a], Jung-Goo Lee [a], Youn-Kyung Baek [a], Pyoung-Woo Shin [b]

[a] Korea Institute of Materials Science (KIMS), #797 Changwondaero, Changwon, Kyungnam 641-010, South Korea
[b] Changwon National University, #9 Sarimdong, Changwon, Kyungnam 641-773, South Korea

ARTICLE INFO

Article history:
Received 25 October 2016
Received in revised form 8 February 2017
Accepted 26 March 2017
Available online 27 March 2017

Keywords:
Al_2O_3
Hexagonal boron nitride
Nanoplatelets
Surface

ABSTRACT

Efficient heat transport along through-plane direction is one of the primary requisites for thermal interface materials (TIMs) to relieve heat accumulation at the interface between chip and heat sinks. We report enhanced thermal conduction of Al_2O_3-based polymer composites by surface wetting and texturing of thermally conductive hexagonal boron nitride (h-BN) nanoplatelets with large anisotropy (diameter <500 nm, thickness <30 nm) in morphology and physical properties. The thermally conductive polymer composites are prepared with hybrid fillers of Al_2O_3 macrobeads and surface modified h-BN nanoplatelets. Here, the clustering or assembly of h-BN nanoplatelets is analyzed based on depletion interaction of colloidal particles. In addition, further addition of minimal amount of SiO_2 nanoparticles shows a drastic improvement of thermal transport properties, which is attributed to the depletion interaction between nanoplatelets mediated by spherical nanoparticles. Here, the benefits of surface wetting for thermal management composite materials are illustrated.

1. Introduction

With development of modern microelectronic technology, power density of electronic devices is rapidly increasing due to miniaturization or integration of device elements, operation at high frequency, high power conditions [1–3]. Thermal problems are known to cause power leakage, device failure and deterioration of performances [3,4]. Thus, efficient removal of accumulated heat is essential to maintain device efficiency and to ensure long lifetime span. To meet the requirement, various thermal management materials have been devised and employed as a part of electronic packaging. Among the various thermal management materials for electronic devices, thermal interface material (TIM) which fills the air gap between chips and heat sinks suppresses the thermal bottleneck at the interface [4–6]. To fill the interfacial gaps and to extract heat generated from electronic devices, composites consisting of ceramic fillers and polymer matrix are popularly selected as TIMs owing to their moderate thermal conductivity, gap-filling capability and easy processing ability with low cost. To reinforce thermal and mechanical properties of polymers with poor thermal conducting ability but high flexibility, ceramic fillers with high thermal conductivity and excellent electrical resistivity are often employed [5–7]. Numerous inorganic particles such as diamond, alumina (Al_2O_3), aluminium nitride (AlN), boron nitride (BN), etc. have been employed as thermally conductive fillers and BN particles with hexagonal crystal structure (h-BN) are among the most effective fillers for thermally conducting polymer composites due to their high chemical stability and unique physical properties including high thermal conductivity and electrical resistivity. In addition, h-BN belongs to the group of crystals with 2D layered structure and manifests a significant anisotropy in physical properties including thermal conductivity, coefficient of thermal expansion [8]. As in graphene-based polymer composites, high in-plane thermal conductivity exceeding 100 W/mK was already reported for BN-containing polymer sheet [9].

Typically, h-BN is supplied as powders of crystalline platelet having high aspect ratio and h-BN fillers in polymer composites often exhibit preferential alignment along in-plane axis of the composites, resulting in large in-plane thermal conductivity [10]. However, many applications of thermally conductive composites such as thermal interface materials, substrates, etc. popularly require efficient through-plane heat transfer. So, highly conductive axis of h-BN fillers is required to be aligned along through-plane direction and various attempts have been tried to align h-BN platelets in the polymer composite by applying external electric or magnetic field [10–13]. However, only small through-plane thermal diffusivity less than 0.5 mm^2/s was reported by h-BN containing

---

* Corresponding author at: Korea Institute of Materials Science (KIMS), #797 Changwondaero, Changwon, Kyungnam 641-010, South Korea.

E-mail address: voice21@kims.re.kr (Y.-K. Kim).

http://dx.doi.org/10.1016/j.compositesa.2017.03.030
1359-835X/

polymer composites assisted by external field. Recently, highly improved thermal diffusivity of ~1 mm^2/s along plane-normal direction of h-BN/silicone rubber composites were reported using aligned BN plates induced by directionally growing ice front [14].

Multi-component fillers with different morphology, dimension and size are often used to improve thermal transport properties of polymer composites due to their capability of forming formation of efficient thermal networks [15–17]. In this study, we demonstrate highly enhanced through-plane thermal conductivity of polymer composites by surface wetting or segregation of BN nanoplatelets with high thermal conductivity on the surface of spherical Al_2O_3 particles. Additionally, further improvement in the thermal diffusivity of polymer composite with multi-component fillers is achieved by adding small amount of silica nanoparticles, which can be ascribed to enhanced colloidal interaction between nanoplatelets.

2. Experimental approach

Spherical Alumina (Al_2O_3, 45 μm, DAW-45) particles were purchased from Denka (Japan) and BN powders (~1 μm, purity 98%) were purchased from Sigma-Aldrich (USA). Polydimethylsiloxane (PDMS, Sylgard 184 elastomer kit) was obtained from Dow cornings (USA) and methyl ethyl ketone (MEK) was purchased from Daejung chemicals (Korea). The epoxy resin (diglycidyl ether of bisphenol F-DGEBF, YD-170, E.E.W = 167.5 g/eq) was kindly donated by Kukdo chemicals (Korea) and 4,4-diamino diphenyl methane (DDM, TCI) was purchased from Sejin chemical (Korea).

2.1. Preparation of polymer composites

Spherical alumina particles and BN powders were used as fillers for polymer composites. Spherical Alumina was used as received and BN nanoplatelets were prepared by thermal treatment at 900 °C in air to remove adsorbed organic contaminant and to introduce —OH groups to improve surface properties. After thermal treatment, BN powders were rinsed with deionized water to remove excess boron oxide. Typically, diameters of final BN powders are below 500 nm as characterized with TEM images. In polymer composites, PDMS was used as polymer matrix. To prepare uniform polymer composites, initially, mixture of silicone resin containing base resin and curing agent (containing Pt-catalyst) in weight ratio of 10:1 was simultaneously dissolved in MEK and mixed with inorganic fillers using a planetary mixer (ARM-310, Thinky, Japan) with 2000 rpm in rotation speed for 3 min. After mixing, the solvent was removed by evaporation in vacuum desiccator for 1 h. The dried mixture of polymers and fillers was casted with a Teflon mold and subsequently, it was cured at 80 °C for 1 h in drying oven. Sometimes, colloidal silica was added to improve colloidal interaction between particles and resultant thermal properties of composites. BN nanoplatelets are mixed with colloidal solution of silica nanoparticles (colloidal silica HS-40, Sigma-Aldrich) having average size of ~12 nm in diameter. Subsequently, the mixture was dried in air for further processing to prepare polymer composites.

2.2. Characterization

The bulk density (ρ) of the specimens was measured from the ratio of actual mass of specimen to difference in between mass of specimen and apparent mass measured with the sample fully immersed in distilled water based on Archimedes' principle. The thermal diffusivity (D_T) was measured at room temperature with disk samples using laser flash method (LFA467, Netzsch Instruments Co.). The specific heat (C_p) was measured with the same instrument by scanning various temperatures from 25 °C to 50 °C using pyroceram 9606 as a standard reference material. C_p of test sample was obtained by comparing properties of test sample of under investigation to known physical properties of reference material from the following equation:

$$C_{p,means} = \frac{\Delta T_{ref}(\rho_{ref} l_{ref}) C_{p,ref}}{\Delta T_{means}(\rho_{means} l_{means})} \tag{1}$$

where ΔT, l and ρ are temperature change during laser flash, thickness and density, respectively. Here, the subscript of "ref" and "meas" refer to the reference material and test sample under measurement. The thermal conductivity (K) was calculated with formula: $K = D_T \times C_p \times \rho$. The shape and the crystal structure of BN nanoplatelets were checked with transmission electron microscopy (TEM) on a JEOL 2100F. Fourier transform infrared spectroscopy (FT-IR) measurements were carried out with a Nicolet iS5 spectrometer (Thermoscientific, USA) ranging from 4000 to 400 cm^{-1} at room temperature using ZnSe pellets. In order to characterize spatial distribution of BN nanoplatelets in the polymer composites, polymeric composites with the same composition were prepared using epoxy polymer which was prepared by mixing diglycidylether of bisphenol F (YDF-170, Kuk-do chemicals) and 2-ethyl-4-methyl imidazole (95%, Sigma-Aldrich) in weight ratio of 4:1. The specimens were cut and polished with diamond slurry to prepare flat surface for microscopy and spectral characterization. We employed a Raman spectrometer with confocal microscopy (Lab-Ram HR, Horiba-Jovin Yvon) operating with accumulation time of 30 s and aperture having 50 μm pinhole through a 100x objective lens and a diffraction grating of 1800 grooves/mm. A Raman spectrum of BN-containing polymer matrix was obtained between two Al_2O_3 particles using a 514 nm-laser. The intensity variation of the characteristic spectrum at 1360 cm^{-1} for BN was collected with scanning increment of 0.2 μm and the spatial resolution was approximately 1 μm. Polarized optical microscopy was done with optical microscope (Eclipse MA200, Nikon) equipped with CCD and images were captured with software.

3. Results and discussion

3.1. Morphology and thermal properties of polymer composites containing macroscopic Al_2O_3 spheres as thermally conductive fillers

Polymer composite containing spherical α-Al_2O_3 as thermally conductive fillers were prepared by simple casting. Here, polydimethylsiloxane (PDMS) is adopted as matrix for polymer composites. The through-plane thermal conductivity of polymer composites increases as filler loading increases and is analyzed with theoretical expectation to check the change in thermal conductivity. Among the various theoretical model regarding to effective thermal conductivity of polymer composites, Hashin-Shtrikman (HS) model provides upper (HS+) and lower boundary (HS−) of thermal conductivity of mixtures which can be described as [18]

$$K_{HS+} = \frac{2K_f + K_p - 2\phi_p(K_f - K_p)}{2K_f + K_p + \phi_p(K_f - K_p)} K_f \tag{2}$$

$$K_{HS-} = \frac{2K_p + K_f - 2\phi_f(K_p - K_f)}{2K_p + K_f + \phi_f(K_p - K_f)} K_p \tag{3}$$

where K_p, K_f denote thermal conductivity of polymer matrix and fillers, respectively. In addition, ϕ_p, ϕ_f denote volume fraction of polymer matrix and fillers. Both upper and lower boundary of thermal conductivity of Al_2O_3–containing composites are calculated from HS formula is shown in Fig. 1 and compared with experimental data. The measured thermal conductivity of polymer composite is