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Thermal anisotropy of epoxy resin-based nano-hybrid films containing BN nanosheets under a rotating superconducting magnetic field

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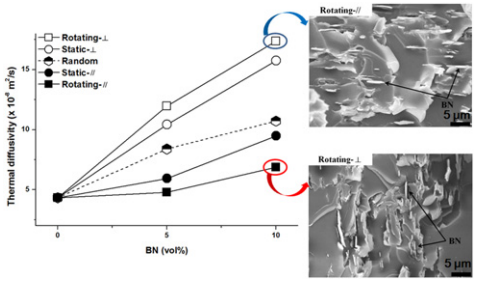
HIGHLIGHTS

- Fabrication of thermally anisotropic polyepoxide/BN nanosheet nanocomposites films.
- Controlled assembly of diamagnetic fillers in polymer under rotating magnetic fields.
- High thermal anisotropy of composites without necessitating modification of the BN.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrated that the orientation of unmodified BN nanosheets can be controlled in a polymer matrix either perpendicular or parallel to the nanocomposite film surface with high anisotropy triggered by a rotating superconducting magnetic field (10*T*) while the prepolymer suspension of polyepoxide was cross-linked. The resulting polymer nanocomposite had outstanding thermal anisotropy, and the increased thermal diffusivity was proportional to the anisotropic orientation of the BN nanosheet. This research provides a method to effectively control diamagnetic 1D or 2D nanofiller particles in polymer-based nanocomposites, and may provide enhanced dielectric thermal interface materials for the semiconductor industry.

1. Introduction

Boron nitride (BN) has a thermal conductivity among the highest of all electrically insulating ceramics, and close to aluminum nitride (AlN) [1,2]. While AlN readily reacts with moisture in air to form Al_2O_3, resulting in a deterioration of thermal conductivity [3], BN has remarkable chemical stability. Furthermore, hexagonal BN (h-BN), which has a graphite-like layered structure, is thermally anisotropic in heat transfer. When heat is conducted in the plane of h-BN, its thermal conductivity is 60 W mK^{-1}, 20 times higher than thermal conductivity out of the plane (3 W mK^{-1}) [4,5]. This high thermal anisotropy along with a wide band gap, 5.5–6.4 eV (depending on the polymorph), enables extended application of BN nanosheets to research the controlled orientation of 2-D fillers in polymer-based

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nanocomposites [6,7]. The orientation of 1-D or 2-D nanofillers in composites with their longitudinal direction normal to the electrical and thermal flux can enhance the electrical and/or thermal conductivity of the composites at remarkably low volume fractions compared to the pristine powder [8,9]. Exfoliated graphite nanosheets (GNs) have attracted significant attention as representative 2-D nanofillers, because their high aspect ratio allows a filler-to-filler network in a polymer matrix and also enables a percolation threshold using low filler content rather than graphite flakes [10]. Soft polymer nanocomposites with oriented GNs have finger-pressure sensitive properties as sensor materials due to the electrical properties of graphite, which range from metallic to semiconducting [11]. The electrical conductivity of oriented GNs may enable their application as thermal interface materials (TIMs) requiring antistatic properties, while restricting them to applications that require both thermal conductivity and electrical insulation [12]. The demand for composite materials with these properties is increasing because they may help solve heat emission problems resulting from scale-minimization and the compact integration of numerous components in semiconductor devices. However, the low thermal conductivity of amorphous polymers [13] and the thermal boundary resistance (TBR) [14] between polymers and fillers can prevent effective thermal conduction through highly thermally conductive fillers. While polymers are excellent electrical insulators, and their flexible nature makes them easily workable, they have the worst heat conduction of the bulk solids, and phonon–phonon interactions in isotropic polymers cannot exceed thermal conductivities of $\sim$1 W mK^{-1} [13,15]. Furthermore, an exceptionally high TBR exists between polymers and inorganic fillers. A temperature drop (ΔT) occurs at the interface between two materials when a heat flux (J, W m^{-2}) flows through the interface boundary. This TBR phenomenon is also called Kapitza resistance, defined as $R_k = \Delta T/J$ [14,16]. An interface constitutes an interruption in the regular crystalline lattice on which phonons propagate [17], which can result in a high TBR. Orienting the filler along the thermal flow direction, however, effectively mitigates this effect and can reduce the TBR [18]. Orienting the longitudinal ends of BN nanosheets perpendicular to the composite surface is one promising approach to minimize those factors. The alignment of nanosheets and 2-D fillers by reorientation in a polymer matrix is a critical technique that has been accomplished using shear force [19], magnetic force [20–22], and electric field [23].

Our group modified the surface of BN nanosheets with γ-Fe_2O_3 nanoparticles to demonstrate that 2-D fillers can be oriented with a normal magnet of 100 Oe [24]. Furthermore, the c-axis of BN nanosheets has a diamagnetic susceptibility that can be actuated when the BN is under a high magnetic field (10T) without requiring modification of the BN surface [25]. Recently, we reported that a rotating magnetic field can align the axis of ceramic incursions having the largest diamagnetic susceptibility [26,27], suggesting potential applications for multilayer piezoelectric devices. Since our result used the diamagnetic susceptibility of the fillers, we compared our results to a report on fabricated magnetic field-oriented polymer structures, using the diamagnetic susceptibility of the aromatic ring of a polymer matrix, (a poly[ethylene terephthalate]) instead of fillers [28].

This study developed a new application for a rotating magnetic field to control the orientation of BN nanosheets in polymer-based nanocomposites, and demonstrated the effectiveness of this system in fabricating thermal anisotropic nanocomposites as a potential application of TIMs. The orientation mechanism of BN nanosheets was elucidated by investigating the relationship between the c-axis diamagnetic susceptibility of BN and the intensified magnetic flux by magnetic field rotation.

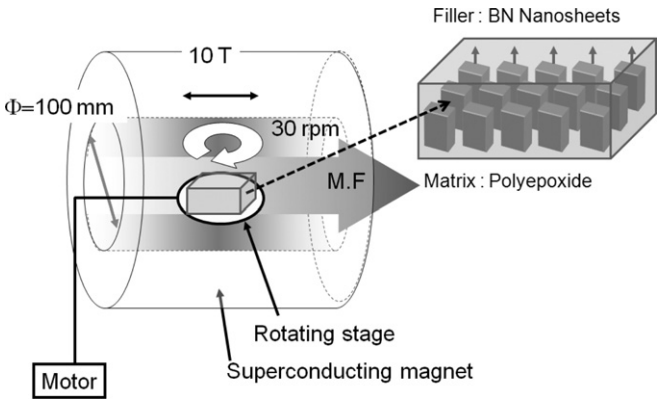

Fig. 1. Schematic illustration of experimental setup to the apply a rotating magnetic field (Notice: the prepolymer suspension is introduced in a stage, which is located inside a cylinder with a 100 mm inner diameter, and the stage rotates using a motor outside the superconducting magnet so that the motor is not affected by the magnetic field.)

2. Experimental

Polyepoxide/BN nanosheet nanocomposites were prepared by suspending BN nanosheets in bisphenol A diglycidyl ether (BADGE) and curing with 1,2-ethylenediamine (EDA). Commercially available hexagonal BN nanosheets (D_{90} = 10.6 μm, Denka Co., Ltd.) 10–20 μm across and 2–10 nm thick were used. Ten grams of BADGE (Tokyo Chemical Industry Co., LTD.) was diluted with 1.50 mL of acetone. BN nanosheets (1.31 g) were introduced into the diluted resin as filler, and the mixture ultrasonicated for 1 h at 50 °C. EDA (0.8 g; Wako Pure Chemical Industry Co., LTD.) was added to the suspension and stirred using a high-speed mixer at 1500 rpm for 5 min to produce a homogeneous dispersion, which was then cast on a polyimide spacer (1.2 mm × 1.2 mm × 120 μm). The spacer, was attached to the surface of two cover glasses using 80 μm-thick double-sided tape [29]. Then, the specimen was placed under a high magnetic field induced by a 10T superconducting magnet for

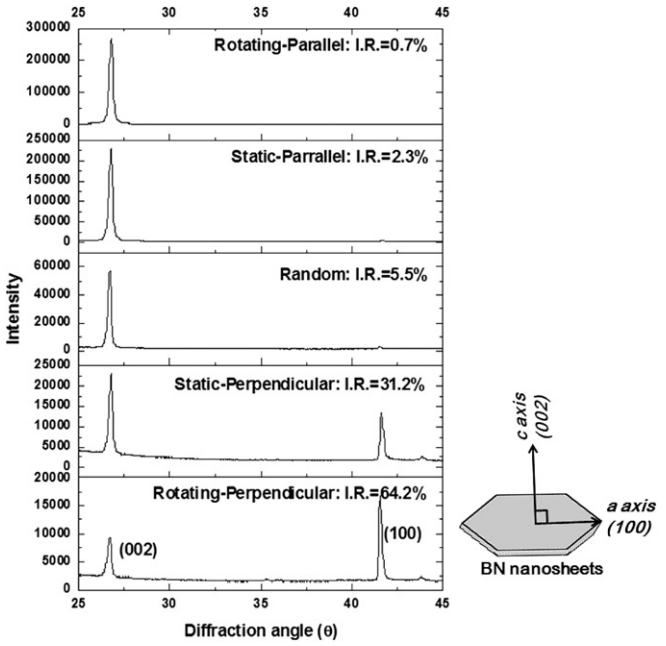

Fig. 2. X-ray diffraction of nanocomposite films as a function of magnetic field (10 vol% BN); I.R. = intensity ratio.