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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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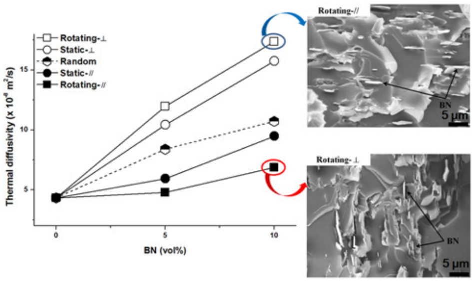
HIGHLIGHTS

- ► 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 ~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 (10*T*) 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.

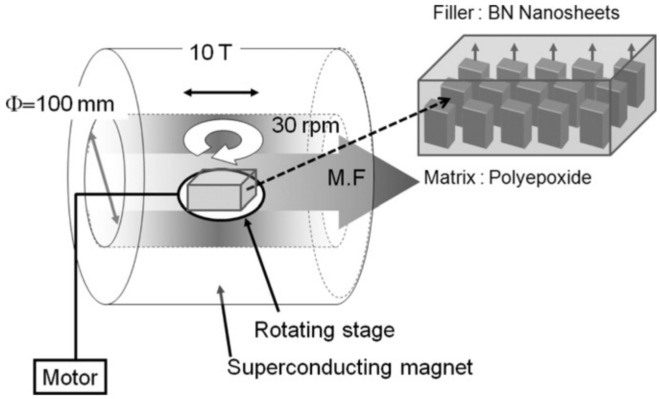

Fig. 1. Schematic illustration of experimental setup to the apply a rotating magnetic field (Notice: the prepolymer suspension is introduced in a stage, which is located inside a cylinder with a 100 mm inner diameter, and the stage rotates using a motor outside the superconducting magnet so that the 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 10*T* superconducting magnet for

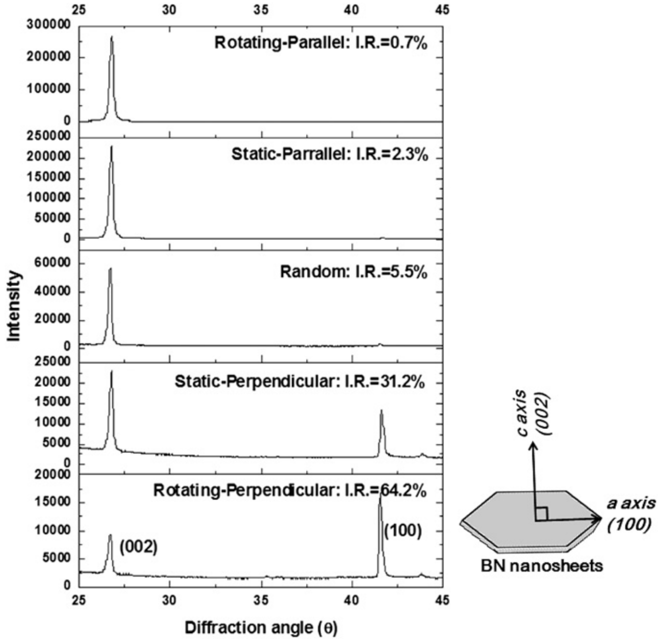

Fig. 2. X-ray diffraction of nanocomposite films as a function of magnetic field (10 vol% BN); I.R. = intensity ratio.

16 h to orient the BN nanosheets before the composite cured. The composites were placed on stages in the center of the superconducting magnet cylinder, and their planes were aligned either parallel or perpendicular to the magnetic field under two different conditions. The samples were either placed on a stationary stage (static magnetic field) or on a stage rotating at 30 rpm (rotating magnetic field), as shown in Fig. 1. Finally, the prepared composites were dried for 0.5 h at 80 °C to ensure complete curing. The prepared composite films were 200–220 μm thick.

The anisotropic alignment of BN nanosheets in the polymer films was analyzed by X-ray diffraction (XRD; RINT 2500, Rigaku Co.). Reflections from the BN nanosheets were observed at $2\theta = 26.76^\circ$ for the (002) plane and at $2\theta = 41.60^\circ$ for the (100) plane. The degree of orientation of the BN nanosheets either parallel or perpendicular to the film plane was evaluated in terms of the intensity ratio (I.R), I.R. = *a*-axis/(*a*-axis + *c*-axis) × 100 (%), of the fabricated nanocomposites. The cross-sectional surface morphologies of the composites were observed by scanning electron microscopy (SEM; JSM-6700F, JEOL Ltd.), and the thermal diffusivity of the prepared composites was measured in the plane of the films using temperature wave analysis (ai-Phase Mobile 1).

3. Results and discussion

Fig. 2 shows X-ray diffraction patterns of BN nanosheets in epoxy-resin-based composites as a function of the magnetic field. Note that the *y*-axis scale of each composite is different. The scale expands proportionally with increasing h-BN (002) plane intensity at $2\theta = 26.76^\circ$, which corresponds with the *c*-axis intensity of h-BN. The (100) plane of the BN nanosheet, the *a*-axis, is only detectable when the BN plane was almost exactly perpendicular to the film surface. The (002) plane of BN, however, is easily detectable even when the BN plane is slightly misaligned from parallel to the composite film surface. The low I.R. of composites with a random distribution of BN nanosheets, as low as 5.5%, confirms that the *a*-axis is more intense than the *c*-axis. As BN nanosheets are aligned with high anisotropy perpendicular to the composite surface, the *a*-axis intensity increases while the *c*-axis intensity decreases, increasing the intensity ratio. When BN nanosheets were perpendicular to the film surface, the I.R. of BN increased to 31.2% under a static magnetic field and 64.2% under a rotating magnetic field. In a parallel orientation, the I.R. decreased to 2.3% under a static magnetic field and 0.7% under a rotating magnetic field. The composite

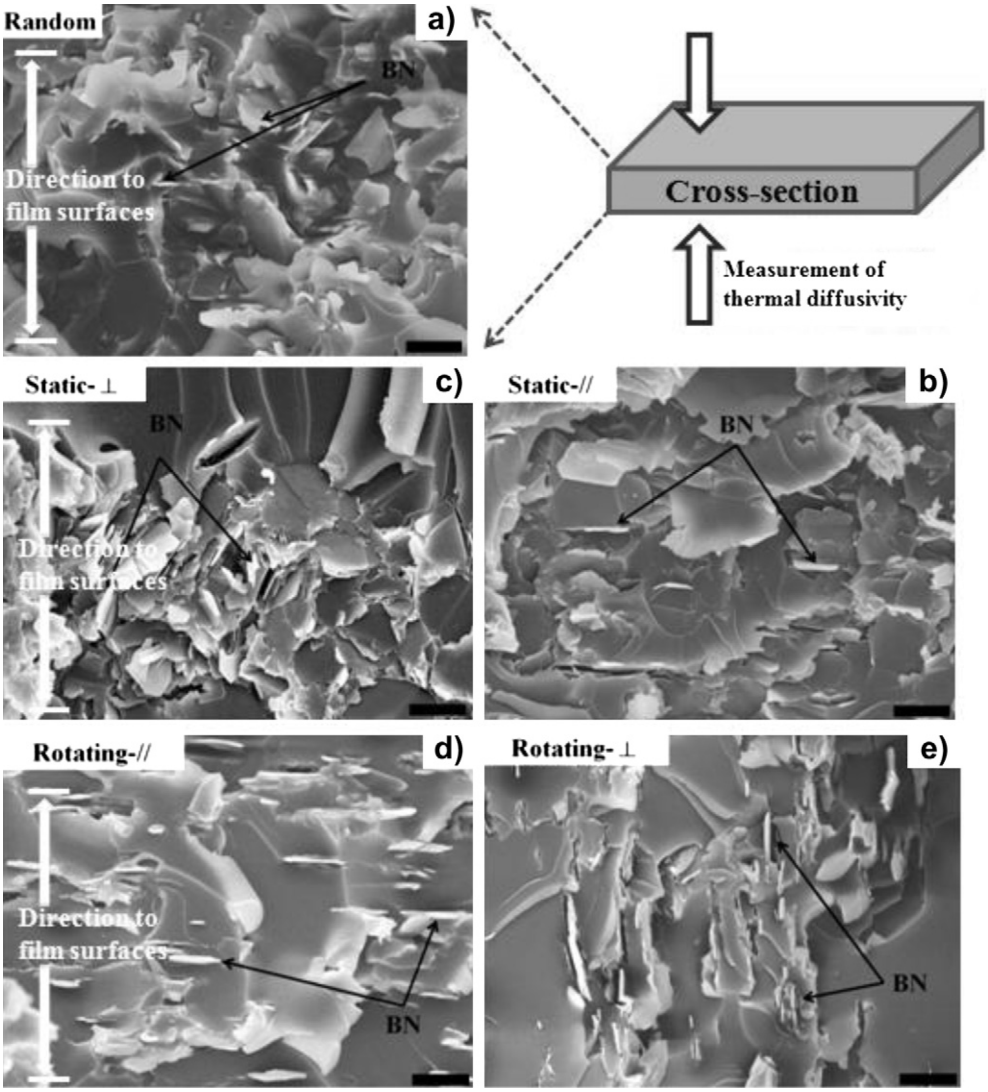

Fig. 3. Cross-sectional SEM micrographs of nanocomposites as a function of magnetic field (5 vol% BN, scale bar: 5 μm): ⊥, the BN plane is perpendicular to the film plane; //, the BN plane is parallel to the film plane.

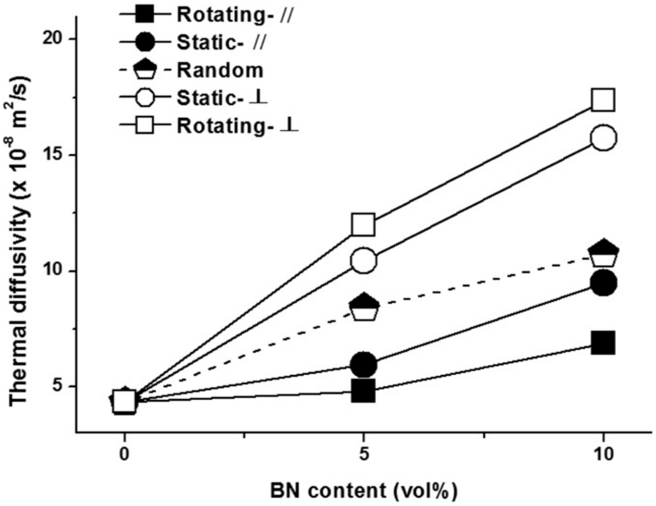

Fig. 4. Thermal diffusivity of nanocomposite films under various magnetic fields: ⊥, the BN plane is perpendicular to the film plane; //, the BN plane is parallel to the film planes.

with parallel BNs had a lower intensity ratio than the composite with randomly distributed BN. This result implies that BN nanosheets can be oriented by applying a strong magnetic field without modifying the BN surface. Additionally, a rotating magnetic field enhanced the anisotropic orientation of hexagonal-BNs, either perpendicular or parallel to the film surface, more effectively than a static magnetic field.

The SEM images in Fig. 3 show the cross-sectional surface morphology of the composite films. Without a magnetic field, BN nanosheets were distributed in random directions (Fig. 3a). Applying a static magnetic field aligned the BNs planes along the direction of the magnetic field. Fig. 3c shows some BN nanosheets, with planes perpendicular to the composite surfaces, but in some domains the fillers are embedded at a slight tilt. Applying a rotating magnetic field (Fig. 3e) obviously decreased population of tilted BN nanosheets by enhancing perpendicular orientation.

Fig. 4 shows how the anisotropic orientation of BN nanosheets affects the thermal properties of the composites. The thermal diffusivity of composites was proportional to the intensity ratio of the BN nanosheets, as shown in the XRD results (Fig. 2). Enhancing the parallel orientation with a rotating magnet decreased the thermal diffusivity to 6.86 × 10^{-8} m^2 s^{-1}, which was lower than the composite with randomly oriented BN nanosheets (10.71 × 10^{-8} m^2 s^{-1}). The thermal diffusivity increased to 17.37 × 10^{-8} m^2 s^{-1} when BN nanosheets were oriented perpendicular to the surface with a rotating magnetic field, which is 300% the parallel orientation. These results imply that the magnetic field, induced by a superconducting magnet, effectively oriented BN nanosheets. Furthermore, using a rotating magnetic field further enhanced the filler anisotropy noticeably increasing the thermal diffusivity of the polymer-based nanocomposites.

The mechanism of BN nanosheet orientation can be explained as illustrated in Fig. 5.

The diamagnetic susceptibility of GN is 1.73 × 10^{-6} Am^2 kg^{-1} [30]. The *c*-axis of hexagonal BN with a similar planer structure has a diamagnetic susceptibility of −0.48 × 10^{-6} Am^2 kg^{-1} [31], which is much lower than GN. Our previous research, demonstrated that, a normal magnetic field, such as 7597 A m^{-1} (=100 Oe), could not actuate the diamagnetic susceptibility [24]. Instead, the orientation of the BN nanosheets could be controlled after modifying the BN surface with pure ferromagnetic by CVD [24]. γ-Fe_2O_3 nanoparticles had this effect because they have a paramagnetic susceptibility of (58.6 ± 0.5) × 10^{-6} Am^2 kg^{-1} [31]. Therefore, the BN filler orientation under a 10*T* magnetic field without surface modification and the pronounced enhancement in thermal diffusivity under a rotating magnet are novel results.

When a magnetic material is placed under a magnetic field, the driving force for filler orientation minimizes the magnetization energy [21]. The magnetization energy *U* for a diamagnetic material can be calculated using the following equation [27];

$$U(\theta) \cong -\frac{1}{4\mu_0} V B^2 (2\chi + \Delta\chi \cos\theta) \tag{1}$$

where μ_0, V, B, and θ are the magnetic permeability of vacuum, the volume of the particle, the magnetic field, and the angle between the magnetic field and the crystal axis, respectively. Δx is the anisotropic susceptibility of the diamagnetic material [32];

$$\Delta x = x(\perp) - x(//) \tag{2}$$

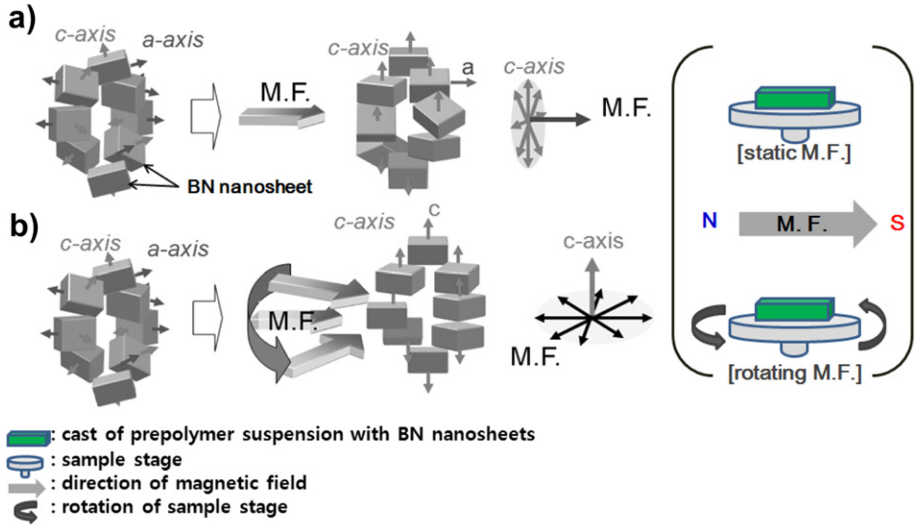

Fig. 5. Schematic illustration of mechanisms for enhanced anisotropic orientation of BN nanosheets under magnetic fields (M.F.): a) static magnetic field, b) rotating magnetic field.

Therefore, a diamagnetic material with the least diamagnetic susceptibility tends to align parallel to the magnetic field [27]. For diamagnetic hexagonal BN nanosheets, the *a*-axis, $x(//)$, is parallel to the magnetic field and the *c*-axis, $x(\perp)$, is perpendicular to the magnetic field. Thus, BN nanosheets could be oriented in a polymer matrix without modification by ferromagnetic nanoparticles, because the diamagnetic susceptibility of the *c*-axis of BN was actuated under a 10*T* magnetic field. Compared to a static magnetic field, a rotating magnetic field seems to intensify the magnetic flux, as shown in Fig. 5. In a static magnetic field, the diamagnetic susceptibility of *c*-axis of BN is actuated by one-directional magnetic flux (Fig. 5a). When the magnetic field is rotating (Fig. 5b), however, the magnetic flux acts as if the magnetic field radiates around the sample, more strongly actuating the diamagnetic susceptibility of BN nanosheets. In addition, the magnetic-field-induced orientation of unmodified BN nanosheets was accomplished while the epoxy resin matrix had low viscosity [33], and the suspension cured under continued application of the magnetic field. Fabricating polymer-based nanocomposites with a magnetic field was comparable to our previous research, which used a sintering process to fabricate grain-oriented titania ceramics [34] or *c*-axis oriented $Ksr_2Nb_5O_{15}$ ceramics [26]. Orientating highly thermally conductive filler particles perpendicular to the composite planes enables heat conduction through the filler rather than through the polymer [35]. Orientating diamagnetic filler particles while fabricating polymer-based nanocomposite films under a rotating magnetic field induced by a superconducting magnet is, therefore, an attractive option for manufacturing thermal interface materials in the semiconductor industry.

4. Conclusions

Thermally anisotropic polyepoxide/BN nanosheet nanocomposites were successfully fabricated by modulating the orientation of the filler particles using a rotating magnetic field. The diamagnetic susceptibility of the *c*-axis of BN nanosheets can be actuated under a strong magnetic field, such as 10*T*, orientating BN particles in a polymer matrix without modifying the BN surface with magnetite. Rotating the magnetic field increased the magnetic flux, which acts in one direction under a static magnetic field, to radially surrounding the BN nanosheets and pre-polymer suspension (see Fig. 5). This radial magnetic field intensified the diamagnetic susceptibility of the BN nanosheets and enhanced the anisotropic filler orientation. The better control of the anisotropic orientation of BN particles resulted from a rotating magnetic field and also increased both the thermal diffusivity and thermal anisotropy of the nanocomposite films. Depending on the anisotropy of the BN nanosheets in the polymer, the thermal diffusivity of these nanocomposites increased by as much as 300%, because the high anisotropy provided a thermal conduction route through the thermally conductive BN particles rather than through the polymer matrix.

Acknowledgments

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