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Facile orientation of unmodified BN nanosheets in polysiloxane/BN composite films using a high magnetic field

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Abstract Composite films consisting of highly oriented boron nitride (BN) nanosheets in polysiloxane were fabricated without modifying the BN surface by applying a high magnetic field generated by a superconducting magnet. The hexagonal BN nanosheets were dispersed by sonication in a prepolymer mixture of polysiloxane. The homogeneous suspension was then cast on a polyamide spacer of microscale thickness and a magnetic field was applied before the mixture became crosslinked. The BN nanosheets in the polysiloxane were aligned with high anisotropy either parallel or perpendicular to the composite film plane depending on the magnetic flux direction. The fabricated composite films exhibited enhanced thermal conductivity by controlling the anisotropy of the BN nanosheets in the film. The mechanisms for rotation of BN nanosheets and heat diffusion across the composite film are discussed.

Introduction

Recently, polymer/nanosheet composites have attracted considerable interest [1–8] because refined structures of polymer microcomposites and nanocomposites exhibit enhanced physical properties when they are appropriately ordered. In particular, deformation, failure, heat resistance, and thermal properties of the polymer can be controlled by adding small quantities of hard inorganic particles. Well-aligned nanosheets with a one-dimensional orientation in a polymer matrix exhibit a conductivity percolation transition at a much lower volume fraction than those of other powders [9–11]. Graphite nanosheets have been attracting a lot of interest for achieving anisotropic alignment in polymers since such composites exhibit high thermal and electrical conductivities [9, 10]. However, since the electrical properties of graphite range from metallic to semiconducting, these composites have limited application as electrical insulators. Boron nitride (BN) is promising for compensating the limited application of graphite. It exhibits exceptional semiconducting properties with high band gap energies in the range 5.5–6.4 eV depending on the polymorph. It is not only an excellent heat conductor (it has one of the highest thermal conductivities of all electric insulators [12]), but also a good electrical insulator. Nanoscale BN has the potential to be used in nanoscale electronic devices and nanostructured ceramics [13–15]. Hexagonal BN nanosheets have a graphite-like structure and their thermal conductivity increases with increasing anisotropy: the thermal conductivity of BN nanosheets aligned perpendicular to the *c*-axis is almost 20 times greater than that when they are aligned parallel to the *c*-axis [12, 16]. Aligning nanosheets by reorienting them in the polymer is a critical technique. Shear forces [17], magnetic forces [1–3, 18–20], and electric fields [4, 17] have been widely used to reorient nanosheets in a polymer matrix. Shear-induced assembly can be used to align nanosheets in a polymer matrix without surface modification, but it cannot orient nanosheets perpendicular to the composite film surface [17]. When orienting nanosheets using normal electric fields and magnetic forces, the nanosheet surface must be modified by metallic nanopowders such as iron nanoparticles to achieve better

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orientation of the nanosheets [2, 3]. Higher torques, such as those generated by electrical nanopulses with amplitudes up to 40 kV, have been used to avoid surface modification of BN nanosheets [21]. The orientation of objects such as nanoparticles [22], nanotubes [23] and nanosheets [9, 10] in a polymer matrix in the presence of an electric field has been investigated to determine the orientation mechanism in terms of structure variation. However, there have been few studies of ordered BN nanosheet–polymer composite films [18, 24] because BN has a wide band gap and low wettability [12, 16] making it difficult to control the nanosheet alignment by applying an electric field or modifying the surface.

The aims of this study are to control the BN nanosheet arrangement to achieve a high anisotropy by applying a magnetic field generated by a superconducting magnet, to enhance the thermal conductivity of the composites, and to determine the heat diffusion mechanisms due to the different BN anisotropies. We exploited the fact that the *c*-axis of hexagonal BN is diamagnetic [25] to control the alignment of nanosheets using a superconducting magnet. Polysiloxane was used as the polymer matrix because it is widely used as a coating material to produce electronic devices with low electrical conductivities and high thermal resistances [26, 27]. The amount of BN nanosheets was varied to investigate the effect of the composite viscosity on the anisotropy of the BN nanosheets. Highly ordered polysiloxane/BN composite films were produced by applying a high magnetic field before the suspensions of the prepolymer and BN nanosheets became cross-linked. X-ray diffraction (XRD), scanning electron microscopy (SEM), digital microscopy and thermal conductivity measurements were used to characterize the fabricated composite films.

Experimental procedures

Materials

Polysiloxane/BN nanosheet composite films were prepared by introducing BN nanosheets into a polysiloxane prepolymer mixture. Hexagonal BN nanosheets ($D_{90} = 10.6$ μm) of commercial origin (Denka Co., Ltd.) with lateral dimensions in the range 10–20 μm and thicknesses in the range 2–10 nm were used. Two polysiloxane prepolymers with different viscosities were used: YE5822(A) (viscosity: 1.2 Pa.s) and YE5822(B) (viscosity: 0.2 Pa.s) (Momentive Performance Materials Inc.). These two low-viscosity prepolymers were used to ensure that the mixture had a low viscosity when aligning BN nanosheets by applying a magnetic field before the mixture became cross-linked by polymerization.

Fabrication of ordered polysiloxane/BN composite films under a high magnetic field

Polysiloxane/BN nanosheet composites were prepared by the following method. 3 g of silicone YE5820(A) was sonicated for 5 min. 0.3 g of silicone YE5822(B) and 0.372 g of BN (10 vol%) were mixed, introduced into the sonicated silicone YE5820(A) and 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. It was then cast on a glass spacer (1.2 mm × 1.2 mm × 120 μm) and subjected to a 10 T magnetic field for 24 h to enhance either the perpendicular or parallel alignment of the BN nanosheets in the polysiloxane prepolymer mixtures. Finally, the prepared composites were dried for 0.5 h at 80 °C to ensure complete curing. Figure 1a and b illustrate the graphite-like hexagonal BN structure and the experimental setup used to apply the magnetic field, respectively. The amount of BN was varied from 0.5 to 40 vol%.

Characterization and measurements

The anisotropic alignment of BN nanosheets in the polymer films were analyzed by XRD (RINT 2500, Rigaku Co.). Reflections from the BN nanosheets were observed at $2\theta = 26.76°$ for the (002) plane and at $2\theta = 41.60°$ for the

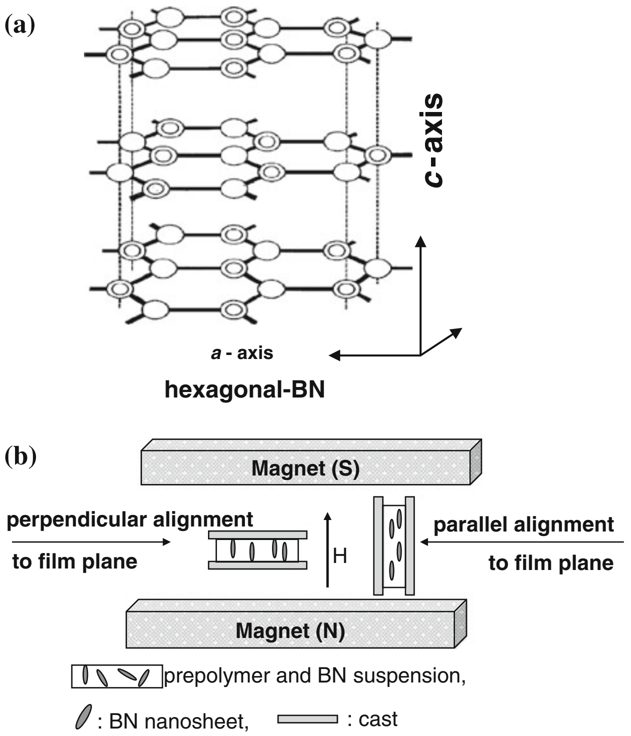

Fig. 1 Schematic illustration of **a** graphite-like hexagonal BN structure and **b** experimental setup

(100) plane. The degree of anisotropy of the BN nanosheets perpendicular to the film plane was estimated by comparing the intensity ratios *a*-axis/(*a*-axis + *c*-axis) × 100(%) of the prepared composites. The transmittances of the composite films, which indicate the anisotropy of the BN nanosheets in the polymer matrix, were measured by UV–Visible spectroscopy (V630, Jasco). The surface morphologies of the composites were observed by SEM (JSM-6700F, JEOL Ltd.) and the thermal conductivities of the prepared composites were analyzed using a system for measuring the thermal diffusivity that is based on temperature wave analysis (ai-Phase Mobile 1, ai-Phase Co.).

Results and discussion

Orientation of BN nanosheets in polysiloxane matrix

Figure 2 shows a typical SEM image of the hexagonal BN nanosheets. The BN nanosheets have diameters in the range 10–20 μm and thicknesses in the range 2–10 nm. The image reveals that some nanosheets are attached to each other, whereas others are single sheets. The nanosheets have smooth surfaces and curved edges.

The XRD analysis was used to compare the anisotropic arrangements of BN nanosheets in the polysiloxane/BN composite films (Fig. 3). When no magnetic field was applied, the intensity of the *c*-axis peak of BN (at $2\theta = 26.76°$) was higher than that of the *a*-axis peak (at $2\theta = 41.60°$); the intensity ratio of these two peaks was 4.6%, which implies that the sensitivity of the (002) plane of BN is significantly higher than that of the (100) plane. When a magnetic field of 10 T was applied perpendicular to the film plane, the *a*-axis peak intensity increased significantly, whereas the *c*-axis peak intensity decreased greatly, so that the intensity ratio increased to 91.3%. In contrast, when a magnetic field was applied parallel to the film plane, the *c*-axis peak intensity increased drastically, whereas the *a*-axis peak intensity was almost zero (intensity ratio = 0.7%). The composite fabricated without applying a magnetic field had a higher intensity ratio than that prepared with parallel alignment, but it had a lower intensity ratio than that prepared with perpendicular alignment. This demonstrates that the anisotropy of the BN nanosheets can be well controlled without modifying the surface. The nanosheets rotate to minimize the magnetostatic energy and overcome the free energy of the system; in this manner, they reorient themselves into a stable configuration [1]. We found that BN nanosheets modified by γ-Fe_2O_3 nanoparticles (results not shown) exhibited an intensity ratio of 80% in polysiloxane under a magnetic field of 7957 A/m (=100 Öe). The BN nanosheets were oriented due to the paramagnetic susceptibility of γ-Fe_2O_3. In previous studies, the alignment induced when a high (100 T) magnetic field was applied to graphite nanosheets in epoxy resin was enhanced by modifying their surfaces with metal nanoparticles (e.g., Fe nanoparticles) [5]. The rotation mechanism of the graphite nanosheets depends on the paramagnetic susceptibilities of the iron oxides coated on the graphite nanosheet surfaces. However, since BN nanosheets do not have a paramagnetic susceptibility and have not been modified by a metal or a metal oxide, they must be rotated by a different mechanism. Hexagonal BN contains both single and double bonds; the nitrogen atoms in the double bonds possess a positive charge due to the π-bonds that contribute to the diamagnetic susceptibility of BN through π-electron flow [28]. The diamagnetic susceptibility along the *c*-axis of hexagonal BN is -0.48×10^{-6} Am^2/kg [13], which is much lower than

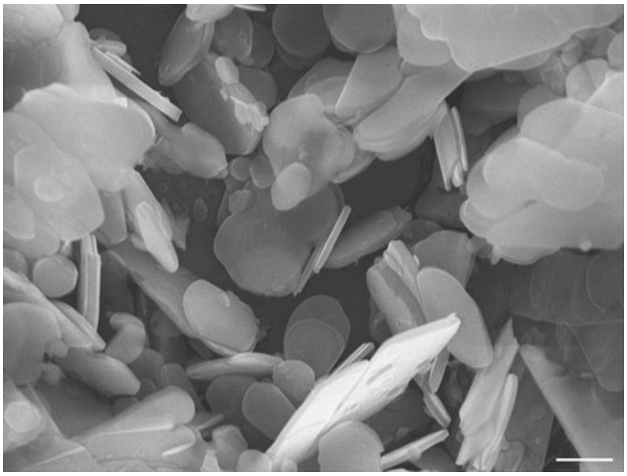

Fig. 2 Scanning electron micrographs of hexagonal BN nanosheets (*scale bar*: 1 μm)

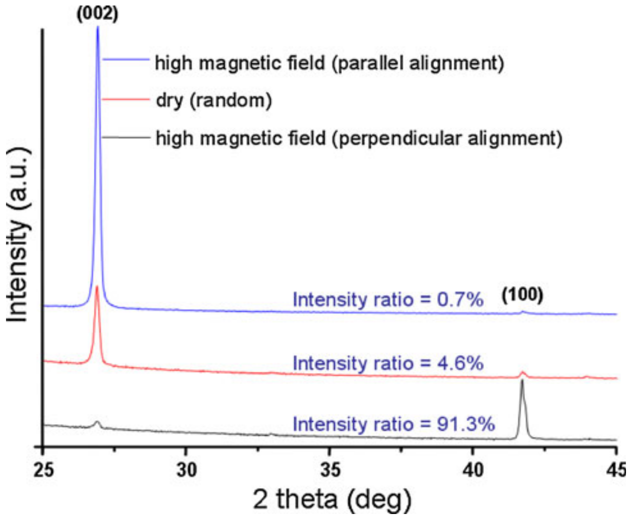

Fig. 3 XRD patterns of polysiloxane/BN nanosheet composites produced by applying a high magnetic field (BN content: 5 vol%)

those of graphite (1.73×10^{-6} Am^2/kg) [13] and paramagnetic Fe_2O_3 (58.6×10^{-5} Am^2/kg) [29, 30]. We thus conclude that the BN nanosheets are affected only by the *c*-axis diamagnetic susceptibility, which rotates them perpendicular to the direction of the magnetic flux (i.e., parallel to the *a*-axis when a high magnetic field (10 T) is applied). The rotational resistance experienced by a nanosheet in a viscous polymer when an external torque is applied is greater than that experienced by a one-dimensional nanorod or nanofiber. Thus, in this case, the rotational torque generated by the magnetic flux was sufficiently large to overcome the rotational resistance, enabling the BN nanosheets to be highly aligned without modifying their surfaces with magnetic nanoparticles.

The BN nanosheet content was varied and the effect of applying a 10 T magnetic field was observed (see Fig. 4). Perpendicular alignment gave the highest XRD intensity ratio when the BN content was 5 vol%; it decreased drastically to 5% as the BN content increased to 40 vol%. In contrast, the intensity ratio was 0.7% for parallel alignment. It did not change up to a BN content of 20 vol%, but it increased slightly up to a BN content of 30 vol%; this intensity ratio is very close to that of a composite with a random alignment of BN nanosheets. A sudden reduction in the intensity ratio to become close to that of a composite with a random alignment of BN nanosheets was also observed for composites prepared with perpendicular alignment and with BN contents of over 30 vol%. This indicates that a composite containing over 30 vol% BN has little anisotropic alignment. The higher viscosities of composites with higher BN contents is considered to provide the main resistance to the rotational torque generated by the magnetic field because the BN nanosheets will encounter a greater rotational resistance in the polymer matrix. This explanation is consistent with the results obtained using nanosecond pulsed electric fields [21]. The higher rotational torque of nanosheets relative to those of nanofibers or produces a higher anisotropy, whereas the viscosity of the prepolymer solution reduces the anisotropy with increasing filler content.

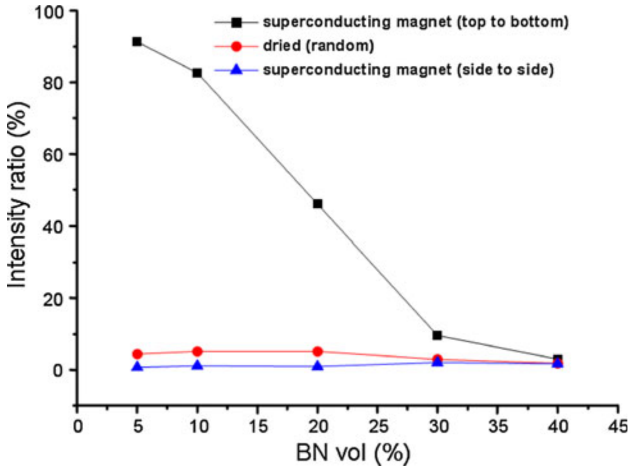

Fig. 4 Intensity ratio of BN nanosheets in polysiloxane/BN composite films as a function of BN content

Anisotropic alignment of BN nanosheets was verified by observing the surface morphologies of the composites by cross-sectional SEM (Fig. 5). The SEM images obtained reveal that randomly distributed BN nanosheets are reoriented perpendicularly or parallel with high anisotropy relative to the surface of the composite film.

Optical and thermal properties of the films

When the nanosheets are aligned perpendicular to the film plane (i.e., parallel to the direction of light propagation), the area of obstacles that inhibit light transmission is less than that when the nanosheets are aligned parallel to the film plane [5, 18] since more light is reflected when the BN nanosheets are aligned parallel to the film plane. Transmission spectra in the range 400–800 nm of the polysiloxane/BN composite films were measured (see Fig. 6). The composite containing perpendicularly aligned BN nanosheets has the highest transmittance, whereas the composite with BN nanosheets aligned parallel to the film plane has the lowest transmittance. A composite with a higher anisotropy perpendicular to the film plane has a higher transmittance since less light is reflected compared with the composite in which the BN nanosheets are parallel to the polymer matrix plane. This is further evidence that the BN nanosheets in the polysiloxane matrix have a high anisotropy.

The thermal conductivities of the prepared composites were measured to evaluate their relationship with the anisotropic alignment (see Fig. 7). The polysiloxane film prepared by cross linking the prepolymer mixture without adding BN nanosheets had a thermal conductivity of 8.6×10^{-2} W/m K; this increased to 10.3×10^{-2} W/m K when 5 vol% BN nanosheets were added (Fig. 7). Moreover, the thermal conductivity increased with increasing XRD intensity ratio. This demonstrates that the thermal conductivity of the polysiloxane/BN nanosheet composite increases as the anisotropic alignment of the BN nanosheets in the polymer matrix increases. The thermal conductivity of the composite film containing 5 vol% BN has a low anisotropy due to the low thermal conductivity of the polymer matrix (95 vol%). However, it demonstrates that the addition of a small amount of BN nanosheets can cause the thermal properties of a composite film to vary depending on the orientation of the nanosheets in the polymer. The increase in the thermal conductivity depends on the thermal diffusion path lengths in the BN nanosheets and the polysiloxane matrix and on the orientation of the

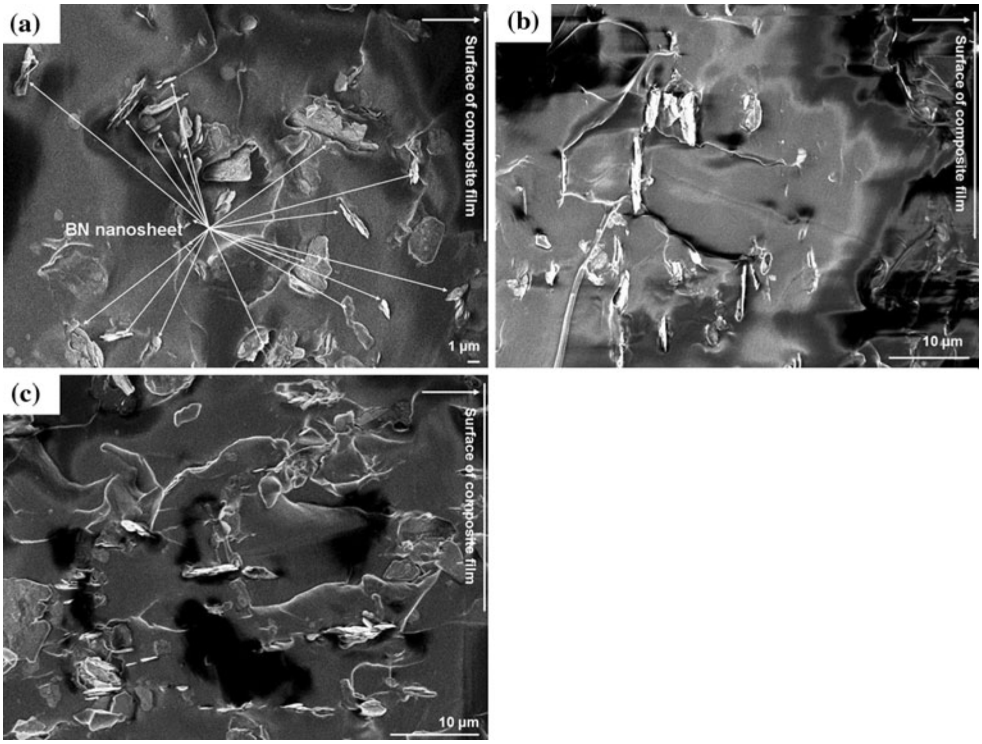

Fig. 5 Cross-sectional SEM images of **a** random, **b** parallel and **c** perpendicular alignments of BN nanosheets in polysiloxane/BN nanosheet composite (film thickness: 255 μm; BN content: 5 vol%)

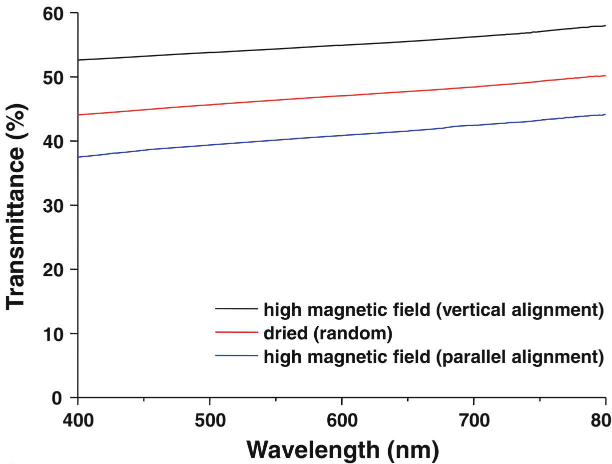

Fig. 6 UV–Visible transmission spectra of polysiloxane/BN nanosheet composites produced by applying a high magnetic field (BN content: 5 vol%)

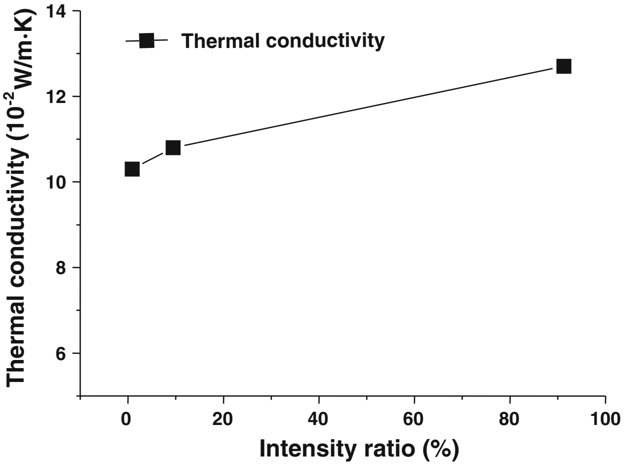

Fig. 7 Thermal conductivities of polysiloxane/BN nanosheet composite film as a function of XRD intensity ratio (BN content: 5 vol%)

BN nanosheets (Fig. 8). For a composite with a high XRD intensity ratio for BN, more heat diffuses through BN nanosheets that are perpendicular to the film plane (straight line) than through the polymer (dotted line) (Fig. 8a). As the number of nanosheets that are parallel to the film plane increases, the thermal diffusion length through BN nanosheets decreases and more heat will diffuse through the polymer matrix (Fig. 8b). The thermal conductivity of BN nanosheets parallel to the *a*-axis (=), 60 W/m K, is 20 times higher than that of BN nanosheets parallel to the *c*-axis (⊥), 3 W/m K, [12, 16], which is another reason why the thermal conductivity of the composite films increases with increasing XRD intensity ratio of the BN nanosheets. This demonstrates that the fabricated polysiloxane/BN hybrid composite films have the potential to be used in semiconductor applications that require electrical insulators with high thermal conductivities.

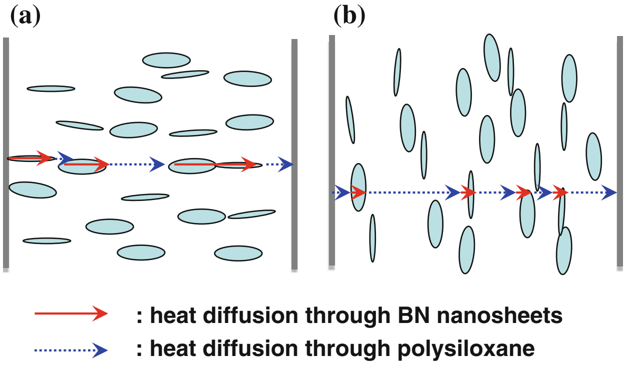

Fig. 8 Schematic illustration showing cause for the increase in the thermal conductivity of composite films between parallel (**a**) and perpendicular (**b**) inducements of BN nanosheets

Conclusions

The alignment of BN nanosheets was controlled in a viscous polysiloxane matrix by applying a magnetic field generated by a superconducting magnet. This method did not require the surfaces of the BN nanosheets to be modified. It enabled them to be aligned parallel to the magnetic field with a high anisotropy (either perpendicular or parallel to the film plane). The rotation of BN nanosheets was attributed to the diamagnetic susceptibility along the *c*-axis of hexagonal BN nanosheets, which was induced by applying a high magnetic field of 10 T. The torque generated the BN nanosheets was sufficiently high to overcome the rotational resistance of polysiloxane and it significantly increased the anisotropy of unmodified BN nanosheets. This is the first time that hexagonal layered nanosheets have been orientated in an organic–inorganic hybrid film using diamagnetism without surface modification. BN nanosheets aligned perpendicular to the composite film facilitated efficient thermal conduction by causing heat to be conducted through the BN nanosheets rather than the polymer matrix.

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