Texture-controlled hybrid materials fabricated using nanosecond technology

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The controlled assembly of micro- and nano-ceramic fillers in polymer nanocomposites provides robust properties such as wetting, adhesion, thermal conductivity, electrical insulation and optical activity, and enable the extended application of these hybrid materials as thermal interfacing materials in microelectronics and for energy conversion. However, the required properties can only be obtained either by homogeneous mixing or by anisotropic orientation of a large amount (>50 vol.%) of expensive fillers, which is economically inefficient. Here we propose a strategy for tuning the orientation and assembly of ceramic boron nitride nanofillers in a polymer nanocomposite using a small amount (<5 vol.%) of filler to enhance thermal conduction. The texture of the BN fillers is tuned by application of a nanosecond pulse electric field and a superconductor magnetic field (10 T); the three-dimensional structure of the products was analyzed using 3-D X-ray CT scanning. The enhanced anisotropic orientation and thermal properties of the products were assessed as a function of the structural variation of the boron nitride fillers in the polymer.

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1. Introduction

Polymer nanocomposites with high electrical insulation and thermal conductivity properties are promising materials for micro- and nano-electronics applications such as sensors, actuators, and solar cells.¹⁻³⁾ However, the ongoing miniaturization and integration of power-intensive devices results in thermal management problems affecting the performance, reliability and stabilization of devices.⁴⁾ For example, the temperature rise in photovoltaic solar cells reduces the produced power by ~20% due to heat build-up and corresponds to an efficiency loss of 0.5% per 1°C increase in the temperature of the cell.⁵⁾

Materials ideal for effective thermal management should have high thermal conductivity and high electrical insulation. Thermal interface materials (TIM) are positioned between the heat generating source and the heat sink and minimize thermal build-up by effectively transferring the generated heat to the heat sink. TIMs with these properties have been generated either by homogeneous mixing or by anisotropic orientation of large amounts (>50 vol %) of expensive fillers,⁶⁾ and their extended application is limited due to the decreased workability of the composite films and the high cost of the fillers.

Aligned one-dimensional (1-D) or two-dimensional (2-D) nanofillers in a polymer matrix exhibit conductivity percolation using a smaller amount of fillers compared to composites with

randomly distributed fillers.^{7,8)} Furthermore, the physical, electrical and thermal properties of pristine polymers can be modified by tuning the orientation and assembly of inorganic inclusions. Vertical double percolation (VDP),⁹⁾ a honeycomb-like structure,¹⁰⁾ and self-assembly¹¹⁾ techniques have been applied to the controlled assembly of 1-D and 2-D nanofillers. VDP and self-assembly alter the interactions between fillers by controlling their electrical or chemical properties, whereas the honeycomb-like technique uses polymer balls as a matrix to facilitate the physical separation of domains between the polymer and inorganic boron nitride (BN) fillers prior to thermal treatment.¹⁰⁾ Electric fields,¹²⁾ shear forces¹³⁾ and magnetic fields¹⁴⁾ have been applied as external torque sources for the anisotropic orientation of nanofillers.

Electrophoresis, polarization, Coulombic attraction, surface modification and aspect ratio have been used to determine the anisotropic orientation and assembly of 1-D/2-D nanofillers in polymer matrices in an electric field.¹⁵⁾ The electric field should be as high as possible in order to control the alignment and assembly of the insulating ceramic fillers in an amorphous polymer matrix. However, the intensity of the electric field that can be applied to the composite system is limited by electrical breakdown and burnout of the material caused by application of an electric field intensity higher than the breakdown voltage.¹⁵⁾ We recently reported that a nanosecond pulse electric field does not cause electrical breakdown, yet orients insulating BN nanosheets.^{15,16)} electrical breakdown caused by application of 1 kV DC did not occur when up to a 40 kV nanosecond pulse electric field was applied. The anisotropic orientation of the BN nanosheets was demonstrated by activating the diamagnetic

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susceptibility of the *c*-axis of the BN using a high (10 T) magnetic field.¹⁷⁾ The combination of nanosecond pulse electric field application coupled with diamagnetic susceptibility measurements showed that the insulating ceramic BN fillers can be oriented without the need for surface modification. However, structural variations of the BN fillers in the polymer, and the effect of these variations on the thermal conduction properties during application of both nanosecond pulse electric fields and magnetic fields, need to be understood before these materials can be used for practical applications.

We here investigated controlling the texture of insulating BN fillers in a polymer using two torque sources: a nano pulse electric field and a magnetic field. The effects of the two fields on 3-D structural variations of the fillers were determined using X-ray computed tomography and thermal diffusivity was evaluated. This strategy for tuning the insulating and diamagnetic susceptibility of 1-D or 2-D in a polymer matrix may help enhance the thermal and optical properties of hybrid materials using small amounts of nanofillers.

2. Experimental

2.1 Materials

Nano-dimensional hexagonal BN nanosheets (BNNSs) were purchased (DENKA Co., Ltd.) and used as received. Two polysiloxane pre-polymers with different viscosities were used: silicone YE5822(A), 1.2 Pa S, and silicone YE5822(B), 0.2 Pa S (Momentive Co., Ltd.). An indium-tin oxide (ITO) coated glass slide with 8–12 Ω /sq surface resistivity (Sigma–Aldrich Co.) was used as an electrode for application of the electric field. The silicone release agents HD-1101 TH and HD-TH (Harves Co. Ltd.) were used on the surface of the ITO-coated electrode to aid detachment of the composite film.

2.2 Localization control of BN nanosheets in polymer-based nanocomposite films

Polysiloxane/BNNSs hybrid nanocomposites were fabricated by application of a nanosecond pulse electric field as described previously.¹⁸⁾ Briefly, a pre-polymer mixture of silicone YE5820(A) and YE5822(B) was prepared by mixing 3.0 g of silicone YE5820(A), 0.3 g of silicone YE5822(B) and 0.372 g of hexagonal BN (*h*-BN) (10 vol.%) in a high-speed mixer at 1500 rpm for 5 min to produce a homogeneous dispersion. This dispersion was cast onto a glass spacer (15 $\times$ 15 mm² $\times$ 250 μ m) precoated first with the silicone release agent HD-1101 TH, then with HD-TH (soaking for 4 s in the silicone, then drying for 2 min), which was then located between two ITO coated glass electrodes. The cast polymer was kept for 16 h under a nanosecond pulse electric field applied in one direction (single direction). Alternatively, the polarity of the nanopulse electric field was switched once after 8 h to observe changes in the movement of the nanofillers in the polymer; this approach was termed ‘nano pulse-polarity change’. The fabricated composite films are detached from the electrodes and underwent drying for 30 min at 80°C prior to recovery. The orientation of the BNNSs under application of a high magnetic field was conducted as described elsewhere:¹⁷⁾ the pre-polymer suspension was subjected to a 10 T magnetic field (a superconducting magnet) for 24 h to enhance either the perpendicular or parallel alignment of the BN nanosheets in the composite film. The polysiloxane/BN nanosheet composites were dried for 0.5 h at 80°C to complete curing. **Figure 1** illustrates the experimental setup used to apply the electric fields. The amount of BN was varied from 0–15 vol.% whereas the frequency of the nanopulse-wide field was fixed at

10 Hz. The nanopulses were controlled at 50 ns/dV in a 40 kV electric field.

2.3 Analysis and characterization

The anisotropic alignment of BNNSs in the composite films was analyzed using an X-ray diffractometer (XRD, RINT 2500, Rigaku, Co.). The degree of anisotropic alignment of the BNNSs perpendicular to the film plane in the prepared samples was estimated by comparing the percent ratio calculated by *a*-axis/(*a*-axis + *c*-axis) $\times$ 100. The film thickness and surface morphology of the composites were examined using a scanning electron microscope (SEM) (JSM-6700F, JEOL, Ltd.). The 3-D distribution of BNNS in the matrix was observed with a high resolution X-ray micro CT scanner (SkyScan 1172, Bruker micro CT, detail detectability; 0.5 μ m at highest resolution) using the following settings: 60 kV X-ray energy, 1350 ms exposure time, 0.25 deg. rotation step. The 3-D X-ray tomographic images were obtained by reconstructing all the observed X-ray transmission section images.

3. Results and discussion

3.1 Structural variation in BNNS assembly due to different external torque sources

Figure 2 shows magnified images of hexagonal BNNSs and a fabricated polysiloxane/BNNS composite. The graphite-like layered structure of BN has a smooth, round shape and the longitudinal length ranges from 5 to 20 μ m [Fig. 2(a)]. The thickness of the BN ranges from 5 to 15 nm, depending on the number of the *h*-BN layers [Fig. 2(b)]. The inset shows the fabricated polymer/BNNS nanocomposite film (15 $\times$ 15 mm² $\times$ 250 μ m). The flexibility of the composite allows its extended application on various protrusions micro- and nano-electronic surfaces.

The X-ray diffraction patterns of polysiloxane/BNNS composite films as a function of fabrication conditions are shown in **Fig. 3**. Random distribution of the BNNSs provides a high BN intensity of (002) at $2\theta = 26.75^\circ$ in the polymer matrix; this intensity decreases as the BN plane is oriented perpendicular to the composite film plane, providing an increase in the (100) intensity at $2\theta = 41.58^\circ$. The intensity ratio (I.R.) is calculated by comparing the intensities of the *c*-axis, (002) plane and *a*-axis, (100) plane, and describes the degree of BNNS plane orientation vertical to the film planes under conditions of high BNNS anisotropy. The composite with random BNNS distribution shows an I.R. of 4.43%, which decreases to 3.19% when the BNNSs are oriented parallel to the film plane. When the BNNSs are oriented perpendicular to the film plane under a magnetic field, the I.R. becomes maximum (49.21%) compared to other external orientation sources, electric fields. The nanosecond pulse electric field in one direction increased I.R. to 30.56% (described as Nano pul.-single direction) and to 44.41% upon polarity change of the nanosecond pulse electric field (described as Nano pul.-polarity change). Thus, by changing the direction of the nanosecond pulse for the 16 h electric field application, the I.R. was enhanced by 14% compared to single-direction application. The low I.R. value obtained for the parallel orientation and the high I.R. value obtained for the perpendicular orientation of BNNSs indicates that application of a high magnetic field (10 T) is more effective for controlling the orientation of BNNSs in polysiloxane matrix under a given condition compared to the application of a nanosecond pulse electric field. The orientation of *h*-BN under a high magnetic field relates to the diamagnetic susceptibility of *h*-BN along the *c*-axis, which is $-0.48 \times 10^{-6} \text{ Am}^2/\text{kg}$.¹⁹⁾ The nitrogen atoms engaged in double bonds in *h*-BN carry a positive charge due to π -

Fig. 1. Schematic diagram of the experimental setup for a) preparation of polysiloxane/BNN nanocomposites, b) electrode coating and c) application of electric & magnetic fields and sample analysis.

bonds, and these bonds contribute to the diamagnetic susceptibility of BN through π -electron flow.²⁰⁾

The fabricated composite films were cross-sectioned and observed under a digital microscope; images are shown in Fig. 4. In the absence of orientation, the randomly distributed BNNSs show as bright domains in Fig. 4(b), indicating that the nanofillers are homogeneously distributed throughout the polymer matrix. The application of nanosecond pulses [Figs. 4(c) and 4(d)] results in the bright BNNS domains assembling into different structures. Application of a Nano pul.-single direction field during sample preparation results in most BNNSs relocating to the right, towards the positive electrode. Furthermore, several BNNS branches developed perpendicular to the film plane. Linear BNNS branches developed into a bridged structure, anchoring the film planes inside the composites. The length of these linear bridged BNNS (LBBN) structures are the same as the composite film thickness (250 μm), and the thickness of the LBBNs increased from 6–9.5 to 40–56 μm under application of a nano pul.-single direction field. Comparison of composites prepared under application of a nanosecond pulse and composites prepared under a magnetic field [Figs. 4(e) and 4(f)] showed that those prepared under a magnetic field did not show any characteristic changes in the relocation or localization of the BN fillers: the BNNSs were as homogeneously distributed as in composites with randomly distributed BNNS, indicating that the

nanosheet planes were oriented either perpendicular or parallel to the composite planes induced by the diamagnetic susceptibility without relocation in the polymer matrix.

Figure 5 shows 2-D X-ray topographies and 3-D analyses obtained by 3-D X-ray CT scanning of BN assemblies in polysiloxane/BNNS composite films. Three samples prepared using different alignment conditions are viewed from three directions: I) y-z plane, II) x-z plane and III) x-y plane tomographies [Fig. 5(a)]. BN nanofillers in BNNSs with random distribution [Fig. 5(b)] show no sign of localization or agglomeration in the three images and confirm that the BNNSs are homogeneously distributed in the polymer matrix. This observation is consistent with that of the parallel and perpendicular orientation of BNNSs induced using a magnetic field (data not shown). In contrast, alignment of the nanosheets under application of a nanosecond pulse electric field resulted in linear branches of BNNSs induced by nano pulse-single direction application [Fig. 5(c)] and LBBNs induced by nano pulse-polarity change [Fig. 5(d)]. Both results are consistent and confirm the results shown in Fig. 3. The views from x-y plane tomography shown in Fig. 5(c) indicate linear branches of BNNSs (domains indicated by arrows) scattered from the y-z plane tomography (circled domains). Figure 5(d) shows that the linear branches of BNNSs developed into LBBNs and that the gaps between the LBBNs narrowed (x-y plane tomography). Furthermore, the population of anchoring structures and

domains in the LBBNs (x-z plane tomography) increased if the nanosecond pulse electric field changed polarity. Comparison of the 3-D images in Figs. 5(c) and 5(d) confirms the development LBBNS from linear branches of BNNSs.

3.2 Thermal properties

Figure 6 shows the thermal diffusivity of composite films as a function of the fabrication conditions. The influence of the degree of orientation and the structural variation of BNNSs on the

thermal properties of the polymer/BNNS composites were compared. The thermal diffusivity of pristine polysiloxane is $1.66\text{E-}07$ (m^2s^{-1}); this increased to $1.97\text{E-}07$ (m^2s^{-1}) by the addition of 5 vol.% BN, but decreased to $1.82\text{E-}07$ (m^2s^{-1}) under application of a nano pulse-single direction electric field and to $1.75\text{E-}07$ (m^2s^{-1}) under application of a magnetic field, causing the BNNSs to orient parallel to the film plane. The thermal diffusivity increased to $2.33\text{E-}07$ (m^2s^{-1}) following perpendicular orientation of the BN planes and to $5.32\text{E-}07$ (m^2s^{-1}) by application of a nano pulse-polarity change electric current. This later value [$5.32\text{E-}07$ (m^2s^{-1})] is 320% higher than that of pristine polysiloxane and 252% higher than that of the corresponding composite with randomly distributed BNNs. The highest thermal

Fig. 2. Micrographs of BNNSs by a) SEM (inset: fabricated nano-composite film with flexibility with incorporation of BNNSs [$15 \times 15 \text{ mm}^2 \times 250 \mu\text{m}$ (BN 15 vol.%)] and by b) TEM.

Fig. 3. X-ray diffraction patterns of polysiloxane/BNNS composite films as a function of fabrication conditions. {Intensity ratio (%) = $[a \text{ axis}/(a \text{ axis} + c \text{ axis})] \times 100$ (%)}

Fig. 4. Cross-sectional 2-D analysis of polysiloxane/BNNS composite films using a digital microscope (BN, 5 vol.%; scale bar, $50 \mu\text{m}$): a) polysiloxane, b) random distribution, c) nano pulse-single direction, d) nano pulse-polarity change, e) magnetic field-vertical and f) magnetic field-parallel.

Fig. 5. 2-D and 3-D analysis of polysiloxane/BNNS composite films by 3-D X-ray CT scanning (BN, 5 vol.%): a) schematic of 2-D tomographic images (All three images; I, II and III planes, are cross-sectional views of each sample using 3-D X-ray CT scanning from three different planes), b) random distribution, c) nano pulse- single direction and d) nano pulse-polarity change.

Fig. 6. Thermal diffusivity of polysiloxane/BNNS composite films (BN, 5 vol.%; measurement, out-of-plane direction): a) polysiloxane, b) random distribution, c) nano pulse-single direction, d) magnetic field-vertical, e) magnetic field-parallel and f) nano pulse-polarity change.

diffusivity was obtained for composites prepared using a nano pulse-polarity change current.

3.3 Techniques for texture control of hybrid nano-composites in relation to enhanced thermal properties

The anisotropic orientation of the BNN planes either parallel or perpendicular to the film plane was confirmed using a 10 T magnetic field. The magnetic field was more effective at aligning the BNN planes than the nanosecond electric pulse technique. The application of a nano single-direction pulse facilitated

localization of the BNNSs to the positive electrode and formation of linear branched BNNSs which developed into LBBNs connecting the film surfaces. Importantly, electrophoresis and controlled orientation of BNNSs was achieved without the need to modify the BN surface with magnetic metal nanoparticles²¹⁾ or by chemical functionalization.²²⁾ It is noteworthy that the breakdown of polysiloxane-based composite 250 μm thick occurred using an electric field of less than DC 3.5 kV, which was verified to be overcome by applying electric field with nano-pulse intervals,¹⁸⁾ as is the demonstration of the morphological changes of *h*-BN nanofillers into the linear branched structure and the thicker branched structure using further modified techniques. The generation of the linear bridged structure of BN by polarity change may be explained by coordinated effects of dipolarization, Columbic attraction, electrophoresis, and surface charge influenced by static electricity, as mentioned in related research on the incorporation of micro-diamond fillers into polymer matrices.²³⁾ Despite the very low dielectric constant of insulating *h*-BN (≈ 2.3)²⁴⁾ and the requisite very high electric voltage required compared to conducting graphite nanosheets (dielectric constant ≈ 13.5),²⁵⁾ a 40 kV electric field pulsed at 50 ns intervals is sufficient to drive filler-to-filler contact, resulting in the fabrication of a thicker and denser LBBN structure by nano pulse-polarity change.

Thermal conduction in the out-of-plane direction of the composite due to vertical orientation of the BNNSs was higher than when the BNNSs were randomly distributed, indicating that higher, more efficient thermal conduction might be realized by further facilitating filler-to-filler connections, as demonstrated by application of nano pulse-polarity change.

4. Conclusion

The texture of insulating BN nanofillers in a polymer-based hybrid material was controlled using either a nano-pulse electric field or superconducting magnetic fields. The analytical results

of XRD and digital microscope exhibited that application of a 10 T magnetic field tuned the anisotropic alignment of BNNSs to either perpendicular or parallel to the composite film surface, and the additional coordination of 2-D and 3-D structural analysis by 3-D X-ray CT scanning revealed that application of a nano-pulse electric field with polarity change facilitated the formation of a linear bridged structure of BNNSs (LBBNs) in the polymer without causing electrical breakdown. The presence of LBBNs in the composites increased the thermal diffusivity to $5.32\text{E-}07\text{ (m}^2\text{s}^{-1}\text{)}$, which is 2.5 times higher than that of the composite exhibiting the highest perpendicular anisotropic orientation to the film under application of a magnetic field-inducement ($2.33\text{E-}07\text{ m}^2\text{s}^{-1}$). This demonstrated that inducing contacts between fillers with a linear structure is a more straightforward approach for enhancing thermal dissipation to out-of-plane composite films than enhancing the perpendicular orientation of fillers with no inter-particle connections. Thus, alignment technology using polarity change of a nanosecond pulse electric field holds potential for tuning the orientation and assembly of insulating or diamagnetic nanofillers in a polymer matrix, and thus may be promising for application in the electronics, optoelectronics and semiconductor industries for the generation of photonic devices and systems.

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