

PAPER



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Thermal conductivity improvement of surface-enhanced polyetherimide (PEI) composites using polyimide-coated h-BN particles

Hoing Lae Lee,^a O Hwan Kwon,^a Sung Min Ha,^a Byoung Gak Kim,^a Yong Seok Kim,^a Jong Chan Won,^a Jooheon Kim,^b Jong Han Choi^c and Youngjae Yoo^{*a}

In this study, we investigated the thermal conductivities and mechanical properties of polyetherimide (PEI) composites using polyimide (PI)-coated h-BN (PI-BN) particles. We found that PI-coated h-BN effectively increased adhesion with the PEI matrix, imparting enhanced mechanical and thermal stability and thermal conductivity with increasing BN content. The thermal conductivity of the PEI composite containing 60 wt% PI-BN was $3.3 \text{ W m}^{-1} \text{ K}^{-1}$, while the thermal conductivity of the PEI/BN composite without modification was $2.6 \text{ W m}^{-1} \text{ K}^{-1}$. The PEI/PI-BN composites show higher impact strengths than the PEI/BN composites because of less BN particle agglomeration and good wettability between PEI and h-BN. The results indicate that the PI-coated BN incorporated into the PEI matrix effectively enhances the thermal conductivity and mechanical properties of the PEI composites.

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1. Introduction

Recently, there has been tremendous progress in the field of electronic devices. With increasing demands for devices with high performance, fast operation and continually smaller sizes, the heat generated by the devices has increased, resulting in reduced device life time and performance.^{1–5} The heat dissipation in electronic packaging is becoming increasingly important. To overcome heat dissipation problems, conductive fillers such as metal powders,^{6–10} carbon materials,^{11–14} and ceramic particles^{15–17} have been introduced into polymer matrices.

Among these various fillers, hexagonal boron nitride (h-BN)^{18–20} has attracted increased attention due to its low density, high thermal conductivity (up to $400 \text{ W m}^{-1} \text{ K}^{-1}$), excellent electrical resistance and relatively low dielectric constant. h-BN is flake-shaped and has excellent resistance to oxidation and chemical corrosion; however, its surface is very inert, leading to poor interfacial adhesion between BN and composite matrices. In a composite, the efficiency of heat transfer depends strongly on the contact point between the filler and matrix. A good contact between these two phases is critical for the efficiency of heat flow.²¹ It has been shown that

treating the filler surface to improve the interfacial adhesion between the filler and polymer matrix (*e.g.*, by silane treatment) significantly improves the heat transfer capability of the composites.^{22,23} Wattanakul *et al.*²⁴ recently used admicellar polymerization to coat two different polymers, polystyrene (PS) and polymethyl methacrylate (PMMA), on BN particles to improve their interfacial adhesion with the epoxy matrix and studied the effect of the treatment on the thermal conductivity of the composites.

Polyetherimides (PEI) possess good mechanical properties, high thermal stabilities, and good solvent resistance. Therefore, they are widely used in electronic packaging, adhesives, films, aerospace and aircraft parts, *etc.* The flexibility of PEI can be improved by designing the molecular structure of the polymer. PEIs that incorporate flexible functional groups such as ethers and amides can demonstrate enhanced flexibility properties. However, the adhesion between the inorganic filler and the polymer matrix is usually poor, resulting in phase separation.

In this paper, we attempt to improve the thermal conductivity, mechanical and electrical properties of PEI composites with polyimide (PI) coated BN particles. The mechanical, electrical and thermal properties of the unmodified and modified structures of PEI/PI-BN composites were investigated and compared.

2. Experimental section

2.1. Materials

Pyromellitic dianhydride (PMDA, Daicel Ind. Co.) and 4,4'-oxydianiline (ODA, Wakayama Co. Ltd.) were used without

^a Advanced Functional Materials Research Group, Korea Research Institute of Chemical Technology, Daejeon 305-600, Republic of Korea.

E-mail: yjyoo@kriict.re.kr; Fax: +82-42-861-4151; Tel: +82-42-860-7216

^b School of Chemical & Materials Science, Chung-Ang University, Seoul 156-756, Republic of Korea

^c Department of Chemical & Biomolecular Engineering, Sogang University, Seoul 121-742, Republic of Korea

further purification. Anhydrous dimethylacetamide (DMAc) was purchased from Aldrich; it was purified by distillation under reduced pressure from calcium hydride (CaH_2) and stored under nitrogen atmosphere prior to use. Boron nitrides (BN) with average particle sizes of 15 μm (KBN20) was obtained from Changsung Co. Chloroform (CHCl_3 , Aldrich Chemical Co.) was used as received.

2.2. Synthesis of BN/poly(amic acid) solution

BN-poly(amic acid) (PAA) solution was prepared by *in situ* polymerization. ODA (5.95 g, 12 mmol) was dissolved in 280 mL of DMAc in a 500 mL 3-neck round flask under nitrogen flow. A pre-calculated amount of BN (100 g) nanoparticles was added into the solution. The mixture was ultrasonicated for 1 h to disperse the particles homogeneously. PMDA (6.75 g, 12 mmol) was added, and the homogeneous mixture was then vigorously stirred under ultrasonication bath for 6 h.

2.3. Preparation of PI-BN particles with core-shell structures

The synthesized BN-PAA solution (280 mL) was slowly dripped into 1000 mL of CHCl_3 over 1 h. This solution was then maintained at room temperature for 6 h. As shown in Fig. 1, the BN-PAA solution and CHCl_3 phases were initially separated. PAA-adsorbed BN nanoparticles gradually sank into CHCl_3 due to high density of BN. After 6 h, PAA-adsorbed BN nanoparticles were completely precipitated, and a layer of excess PAA that was not adsorbed on the surface of BN was formed at the interface of the CHCl_3 phase. The excess PAA layer was removed by suction using a disposable pipet. PAA that was adsorbed on the surface of BN nanoparticles was converted into PI by chemical imidization. The white precipitate in CHCl_3 was stirred vigorously at room temperature. For chemical imidization, a mixture of pyridine and acetic anhydride (1 : 1 molar ratio, 2 mL) was added to the dispersion of PAA-adsorbed BN nanoparticles. After 4 h, the chemically-imidized PI-adsorbed BN nanoparticles were centrifuged and washed three times with ethanol. The formed PI-BN nanocomposite particles were dried in a convection oven at 60 $^\circ\text{C}$.

2.4. Preparation of PEI/PI-BN composites

For comparison between PI-coated BN and pristine BN filler particles, PEI composites containing 20, 40 and 60 wt% of each of the two BN particles were prepared. All composites were prepared using a DSM Xplore micro-compounder with a net barrel capacity of 15 mL, a screw speed of 60 rpm and a barrel temperature of 350–400 $^\circ\text{C}$; all the composite components were added at the same time. Test bars were formed using a DSM Xplore micro-injection molding machine with a barrel temperature of 350–400 $^\circ\text{C}$ and a mold temperature of 120–190 $^\circ\text{C}$. The dimensions of the molded specimen for thermal conductivity testing were $2 \times 2 \times 8 \text{ mm}^3$. The other specimens for mechanical property testing were molded into standard tensile (ASTM D638, Type I) and Izod (ASTM D256) bars (0.318 cm thick). The injection molding pressure and holding pressure were both set at 16 bar. The resulting specimens were tested 'dry as-molded'. The experimental details for the preparation of all PEI composites are shown in Fig. 1.

2.5. Characterization

The PI coated structures of PI/BN nanocomposite particles were examined using scanning electron microscopy (SEM, JEOL JSM-6700F).

Tensile tests were performed according to ASTM D638 using an Instron model 8516 testing machine upgraded for computerized data acquisition. The tensile modulus values were determined using an extensometer. Modulus and yield strength data were determined at a crosshead rate of 0.51 cm min^{-1} . Elongation at break results were collected at 5.1 cm min^{-1} . Izod impact tests were conducted with a 6.8 J hammer and a 3.5 m s^{-1} impact velocity at room temperature using a Tinius Olsen Impact tester (Model 92T). Standard notches were made according to ASTM D256. Typically, data from at least five specimens were averaged to determine mechanical properties.

Thermal expansion tests were conducted according to ASTM D696 using a TA Instruments thermomechanical analyzer (TMA Q400 system). Rectangular specimens were prepared by milling the center part of the injection-molded Izod bars (as-molded) to the following dimensions: 3.175 mm thickness,

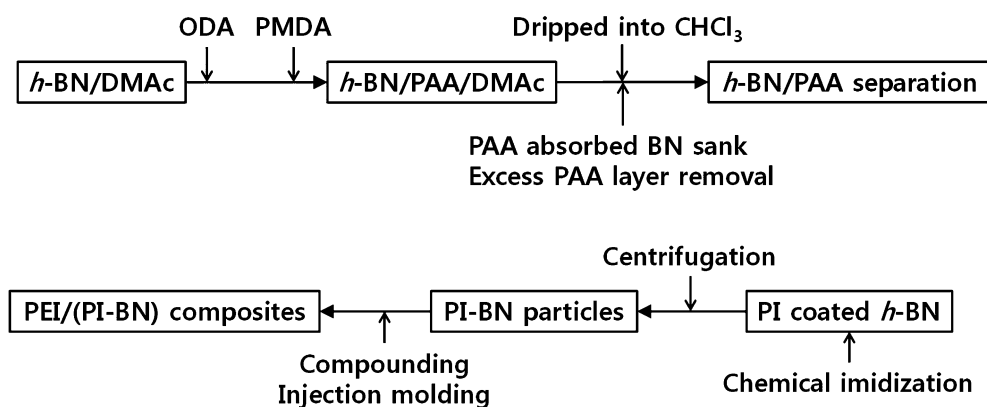


Fig. 1 Preparation of PEI/PI-BN composites.

6.35 mm width, and 12.7 mm height. The measurements were made in the flow direction (FD) and the normal direction (ND). In order to examine the effect of the thermal history, specimens were annealed at 140 °C for 15 h in a vacuum oven. Thermal expansion tests were performed over the temperature range from −30 to 80 °C at a rate of 5 °C min^{−1} in a nitrogen atmosphere.

The thermal diffusivity of the composites was determined by the laser flash method (ASTM E1461) using a Netzsch laser flash thermal diffusivity apparatus (LFA 447 NanoFlash). Thermal conductivity was then calculated from the multiplication of thermal diffusivity, density and specific heat. The density and specific heat were determined from a Protech Gas Pycnometer (Accupyc 1330) and a TA Instruments modulated

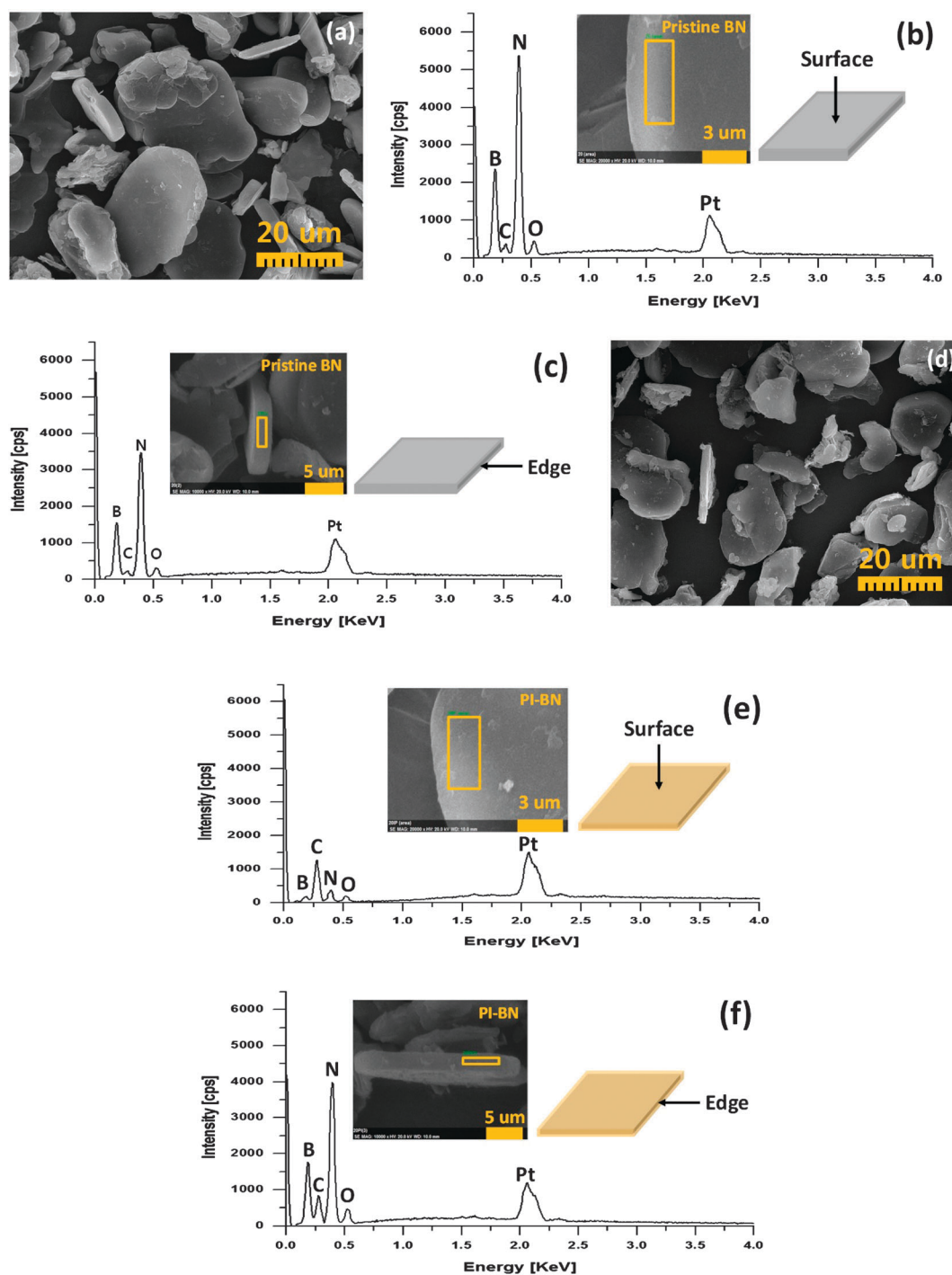


Fig. 2 SEM image of (a) pristine BN powder, (b) magnified image of BN surface and corresponding EDS spectrum, (c) magnified image of BN edge and corresponding EDS spectrum, (d) PI coated BN powder, (e) magnified image of PI coated BN surface and corresponding EDS spectrum, (f) magnified image of PI coated BN edge and corresponding EDS spectrum.

differential scanning calorimeter (MDSC Q200), respectively. Thermal imaging was also performed using an FLIR infrared camera (T300).

3. Results and discussion

3.1. Characterization of PI–BN particles

SEM micrographs of the pristine BN and PI-coated BN surfaces are shown in Fig. 2. The PI-coated BN surfaces (Fig. 2(d–f)) are quite different from the clean surface of pristine BN (Fig. 2(a–c)). The micrographs show clear evidence of the deposition of a relatively thin layer of polymer on the BN surface. At magnification, the PI-coated BN surface was hardly distinguishable from the pristine BN surface. To ensure that PI coated the BN surface, we conducted energy dispersive X-ray spectroscopy (EDS) to analyse the composition of pristine BN and PI-coated BN; the corresponding spectra are shown in Fig. 2(b, c) and (e, f), respectively. The elemental signatures of B, C, N and O are seen in the PI–BN spectra, indicating that both the top and bottom surface of BN was successfully coated with PI.

3.2. Mechanical properties

The mechanical properties of particulate-filled polymer composites are known to depend on the efficiency of stress transfer at the filler–matrix interface, which in turns depends on the adhesion strength between the two phases. An improvement in the interfacial adhesion generally leads to an increase in the mechanical properties of the composite. In this study, the compatibility between the BN particles and the PEI matrix was enhanced by the PI-coated BN. Fig. 3 shows that the Izod impact strength of PI-coated BN–PEI and pristine BN–PEI composites decreased with increasing BN content. When comparing the mechanical properties of the PI-coated BN/PEI and pristine BN–PEI composites in Fig. 3, it can be seen that PI-coated BN exhibited a higher impact strength than pristine BN, in accordance with the greater wettability of PEI resin on PI-coated BN surfaces.

3.3. Thermal expansion behaviour

The coefficients of thermal expansion (CTE) of the composites were evaluated by thermomechanical analysis (TMA) conducted in the flow and normal directions over the workable temperature ranges of 0–30 °C, 60–90 °C and 120–150 °C for various BN contents.

The specimens for measurement were annealed at 140 °C for 15 h in a vacuum oven. The PEI, PEI–BN and PEI–PI–BN composites in this work show non-linearity during thermal expansion as the temperature increases. The thermal expansion coefficient of the composites decreased slightly for the pristine BN–PEI composites. When the PI-coated BN was added to the polymer matrix, the thermal expansion coefficients improved significantly compared to those of pristine BN (Fig. 4).

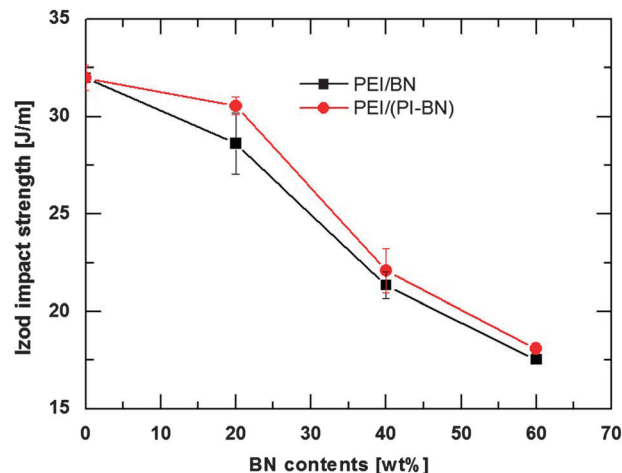


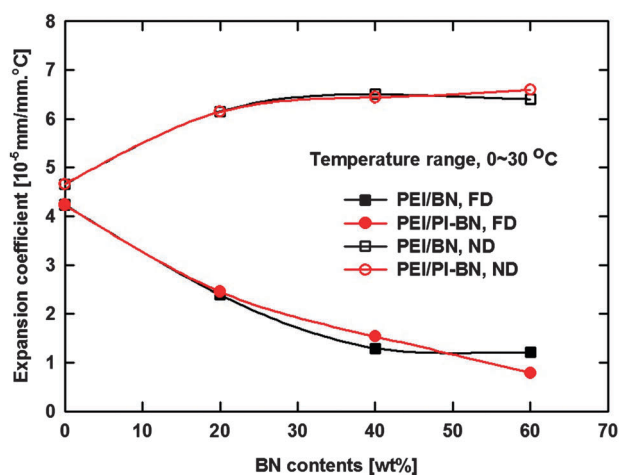
Fig. 3 Izod impact strength of the PEI/BN composites with various BN contents.

3.4. Thermal conductivity

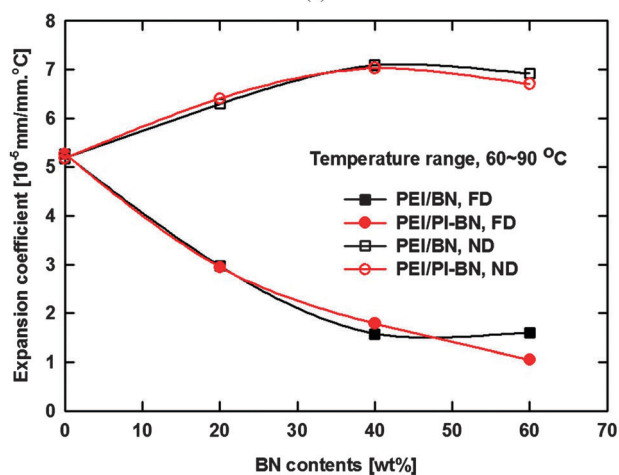
The thermal conductivity of neat PEI was $0.22 \text{ W m}^{-1} \text{ K}^{-1}$, which is in exact agreement with the value quoted in the brochure. Fig. 5 compares the thermal conductivity of 20, 40, and 60 wt% BN-filled PEI composites using PI coated BN and pristine BN particles. The results show that the thermal conductivity of both the PI coated BN and pristine BN-filled PEI composites increased with increasing BN content. When the loading of BN was 60 wt%, the thermal conductivity of the composite reached $2.55 \text{ W m}^{-1} \text{ K}^{-1}$. Thus, the thermal conductivity was improved significantly by 11.6 fold compared to that of neat PEI ($0.22 \text{ W m}^{-1} \text{ K}^{-1}$). When the PI-coated BN content was 60 wt%, the thermal conductivity was increased to $3.32 \text{ W m}^{-1} \text{ K}^{-1}$. Based on these results, it can be concluded that PI-coated BN exhibits higher thermal conductivity than pristine BN. Improvements in the dispersion and the interface through filler surface treatment would lead to increased thermal conductivity; both of these were improved by modifying the BN surface, which led to the observed enhancements in thermal conductivity. Since the PI-coated BN surface lowers the thermal barrier of the interface between the polymer matrix and the BN particles, heat is more easily transferred within the composite, resulting in the increased thermal conductivity. Fig. 6 shows the k_{\perp} , k_{\parallel} value observed for the 20, 40 and 60 wt% PEI/BN and PEI/PI–BN composites.

3.5. Thermography

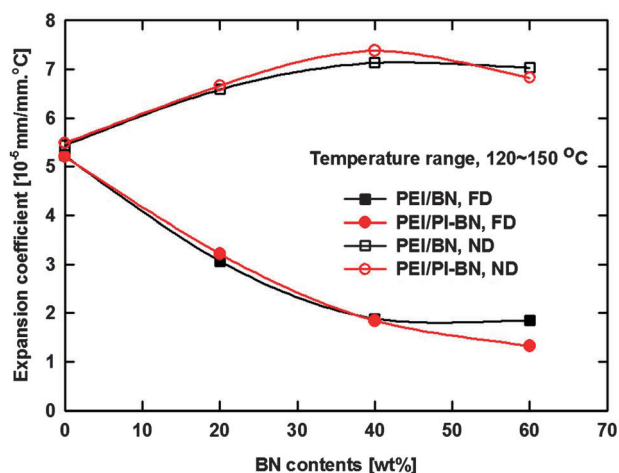
Fig. 7 shows the thermographic images of the PEI/BN and PEI/PI–BN composites. For comparison between PI-coated BN and pristine BN, filler contents of 0, 20, 60 wt% were tested for each of the composites. Samples were mounted on a hot-plate with the surface temperature set to 100 °C, and the temperature changes of the composites were then traced. Because the thermal transport proceeds through the flow direction of the specimen, these thermographic images are closely related to in-plane thermal conductivity. After 240 s,



(a)



(b)



(c)

Fig. 4 Linear thermal expansion coefficients of PEI/BN composites as a function of filler concentration determined in the range of (a) 0–30 °C, (b) 60–90 °C and (c) 90–120 °C.

pure PEI does not show any significant heat transfer from the hot plate surface to the composites, as typical polymeric materials are generally thermal insulators. However, the PEI/BN and PEI/PI-BN composites show noticeable color changes,

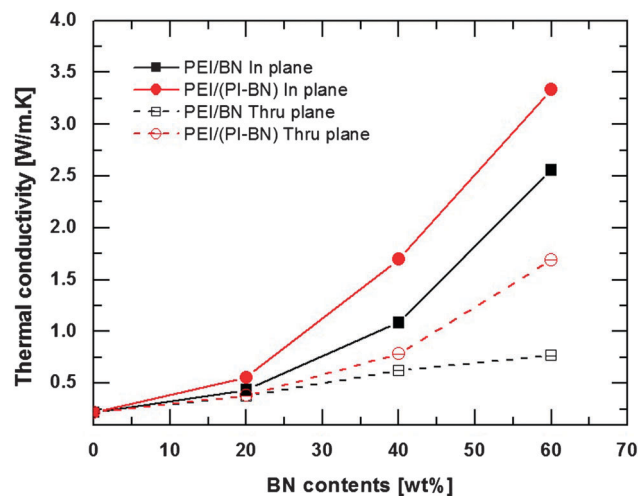


Fig. 5 In-plane and through-plane thermal conductivities of the PEI/BN composites.

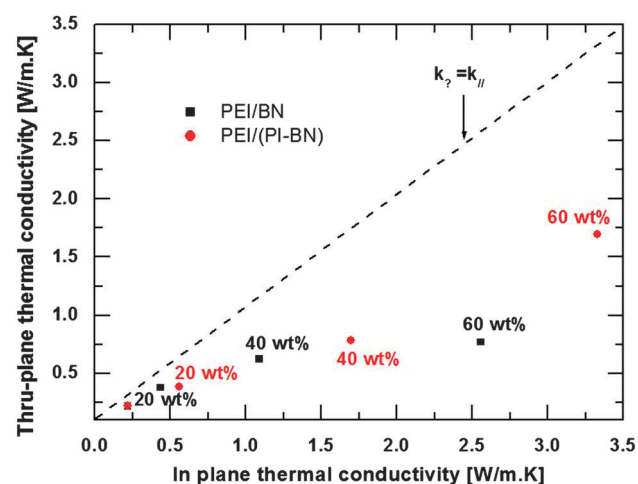


Fig. 6 Anisotropy of thermal conductivity for 20, 40 and 60 wt% PEI/BN and PEI/PI-BN composites.

indicating high thermal conductivity. These results are in good agreement with the thermal conductivity values shown in Fig. 5.

4. Conclusions

PI was successfully coated on BN particles by *in situ* polymerization and chemical imidization. The PI-coated BN and pristine BN were successfully incorporated into a PEI matrix to fabricate composites by melt processing. To explore the effect of the interfacial adhesion between the PEI matrix and PI-coated BN, Izod impact strengths and thermal conductivities were determined. The BN filler shows homogeneous dispersion in the PEI matrix. The PI-coated BN filler is well dispersed and possesses good wettability in the matrix. Test results show that the PI-coated BN incorporated with the PEI matrix can

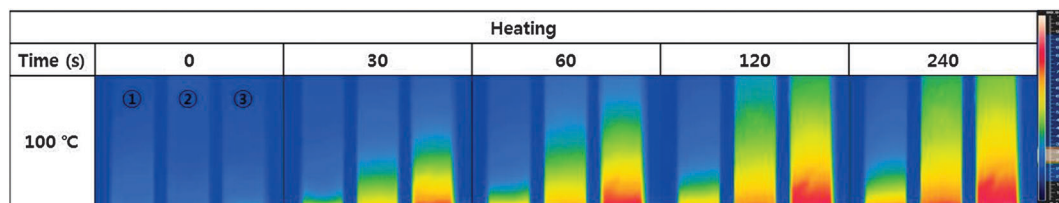


Fig. 7 Sample surface temperatures for PEI/BN composites during thermography testing: (1) PEI; (2) PEI/BN 60 wt%; and (3) PEI/PI–BN 60 wt%/PI.

effectively enhance the mechanical and thermal properties of the composite.

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