Influence of Molecular Orientation Direction on the In-plane Thermal Conductivity of Polymer/Hexagonal Boron Nitride Composites

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ABSTRACT: The effect of the molecular orientation direction of a polymer matrix on the in-plane thermal conductivity (TC) of injection-molded polymer/hexagonal boron nitride (h-BN) composites is investigated. In this system, the h-BN platelets align in the in-plane direction owing to injection shear flow. Three molecular orientations (perpendicular, random, and parallel to the h-BN plane) are achieved using liquid crystalline polyesters and the in-plane TCs are compared. Although a parallel orientation of the polymer chains provides the highest TC of the matrix in the injection direction, the TC of the composites is the lowest of the three systems for this orientation. The highest in-plane TC is found in the perpendicularly oriented system, irrespective of the in-plane direction. These results reveal that perpendicularly oriented molecular chains serve as effective heat paths between h-BN platelets that are arranged one above the other, and consequently, a continuous thermal network is created in the in-plane direction. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 39768.

INTRODUCTION

Thermally conductive thermoplastics have attracted attention as heat dissipative materials for numerous electronic devices such as automobile parts, communication equipment, and lighting systems. Polymers are excellent electrical insulators and are easy to process. However, their thermal conductivity (TC) is very low ($0.1–0.5$ W m^{-1} K^{-1}).[1–3] Even with large concentrations of thermally conductive fillers, it is difficult to enhance the TC of polymer composites. Moreover, a high filler content leads to undesirable weight gain and poor processability. One solution for these issues would be to enhance the TC of polymer matrices according to Bruggeman's theory[4] (Figure S1, Supporting Information). This theory suggests that the TC of polymer composites can be significantly increased if the polymer matrices serve as good heat conductors between the filler particles. Previously, we found that a main-chain smectic liquid crystalline (LC) PB-10 polyester [Figure 1(a)] acts as an effective thermally conductive matrix in a composite with hexagonal boron nitride (h-BN).[5] PB-10 polyester forms a smectic I LC phase[6] with 47-nm-thick lamellae stacked regularly along the polymer chain direction.[5–9] Shear flow during injection molding induces lamel-

lar crystal alignment, in which the polymer chains are aligned in the normal direction (ND) with respect to the molding surface [Figure 1(b)], thus leading to a high TC (1.2 W m^{-1} K^{-1}) in the ND [Figure 1(c)]. In contrast, the TCs in both the machine direction (MD) and the transverse direction (TD) are only modest at 0.30 W m^{-1} K^{-1}. However, the composites with h-BN exhibit a dramatic enhancement of the TC in not only the ND but also the MD and TD. Thus, we proposed a heat conductive model involving polymer chains aligned in the ND that serve as effective heat paths between the h-BN platelets,[5] which mainly conduct heat in the in-plane direction at a high TC of 400 W m^{-1} K^{-1}.[10]

The anisotropic TC property observed in polymer/h-BN composites exhibits strong correlation with the orientation and the size of h-BN platelets. Ando and co-worker reported that polyimide (PI)/h-BN films filled with large plate-shaped particles exhibited a large anisotropy in TC because of the strong in-plane orientation of h-BN platelets, whereas smaller anisotropy was observed in films filled with aggregates and small flakes which are less likely to orient in the in-plane direction during film processing.[11] When the in-plane TC of a polymer/h-BN
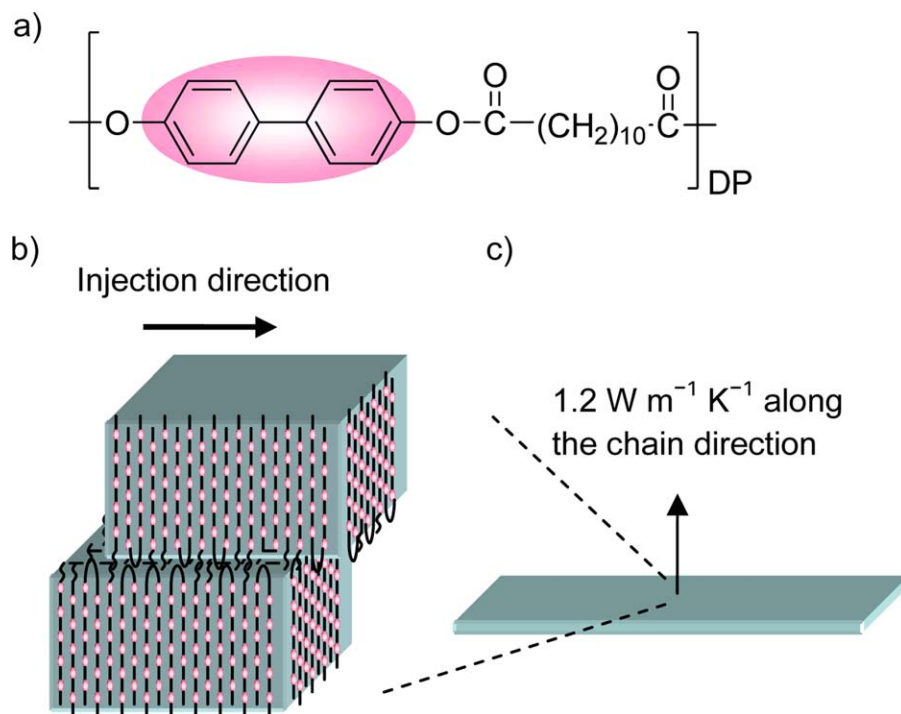
Figure 1. Characteristics of PB-10. (a) Chemical structure of PB-10. (b) Alignment of the LC lamellae induced by injection shear flow, leading to molecular orientation in the ND. (c) High thermal conductivity of molded PB-10 in the ND. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite must be increased, thus, in-plane orientation of heat-conducting basal plane of h-BN should be utilized. For the same purpose, in addition, a polymer matrix with a high in-plane TC is thought to be more effective. Ando and co-worker also showed that PI matrix with higher in-plane TC effectively enhanced the in-plane TC of PI/h-BN composites using two different PI specimens, which exhibit the TC value of 1.22 and 0.526 W m^{-1} K^{-1} in the in-plane direction, respectively, whereas the out-of-plane TCs are similar (0.248 and 0.277 W m^{-1} K^{-1}).[11] From the point of view, aligned PB-10 polyesters are not efficient but isotropic PB-10 polyesters should be better because the TC of isotropic PB-10 polyesters is 0.52 W m^{-1} K^{-1} in all directions.[5] Moreover, it is well known that conventional fully aromatic thermotropic LC polyesters (LCP) can readily provide molecular orientation in the MD under injection shear. Choy and co-worker reported that the highly oriented structure of the resultant materials results in a high TC of more than 1 W m^{-1} K^{-1} in the MD.[12] Therefore, LCPs might be the optimum matrix to achieve a higher in-plane TC in h-BN composites.

Herein, we report that a polymer matrix with high TC in the ND enhances the in-plane TC of the polymer/h-BN composites more effectively than a matrix with high in-plane TC. In this study, three LC polyesters were used: PB-10-I and PB-10-II with different molecular weights and a commercially available LCP (Ueno LCP A-8000). As 45-μm-sized h-BN platelets were used, the injection shear flow induced in-plane orientation of h-BN. PB-10-II is always isotropic even after injection molding owing to its high molecular weight.[5] The LCP exhibited the highest TC in the MD. However, the order of the

composite TC in the MD was PB-10-I > PB-10-II > LCP. These findings revealed that molecular chains oriented in the ND serve as the most effective heat paths between h-BN platelets stacked closely, leading to the formation of a continuous thermal network.
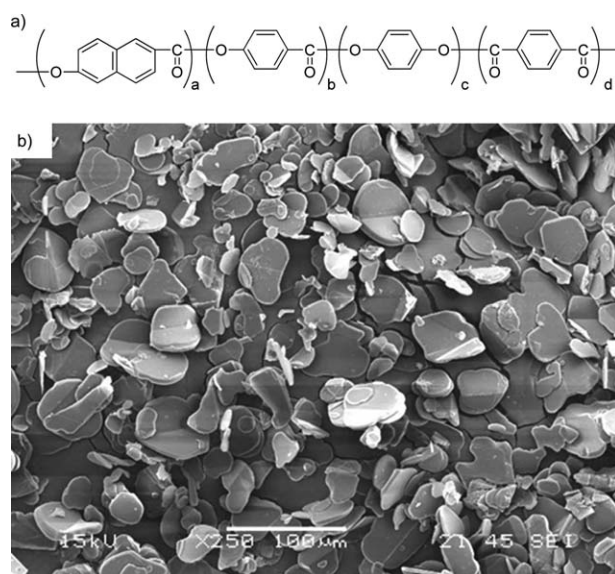

Figure 2. Components of polymer composites. (a) Chemical structure of Ueno LCP A-8100. (b) SEM image of the hexagonal boron nitride platelets (h-BN). Scale bar, 100 μm.
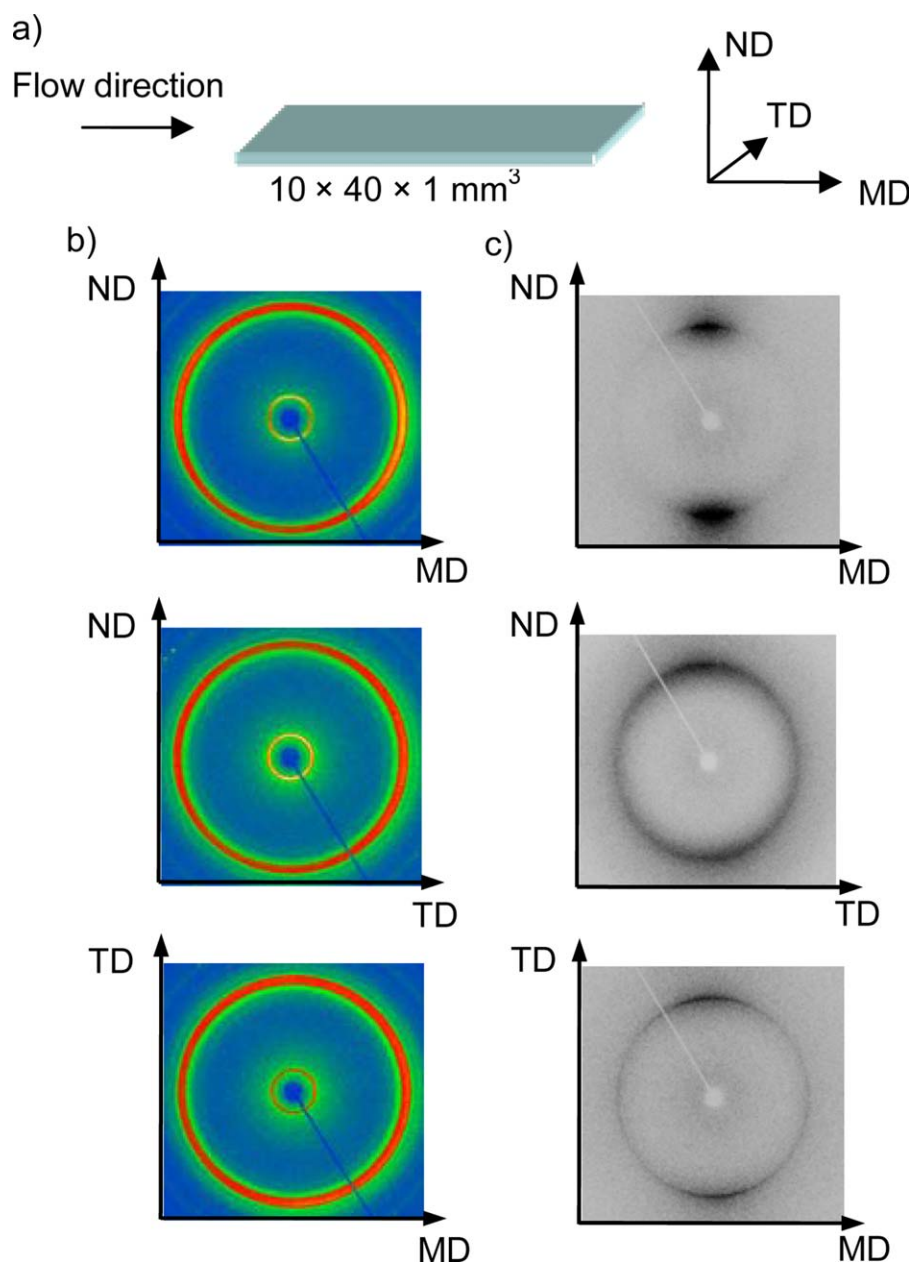
Figure 3. Characterization of injection-molded polymer plates. (a) Shear geometry. (b) and (c) 2D-WAXD patterns along the MD, TD, and ND for PB-10-II and the LCP, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
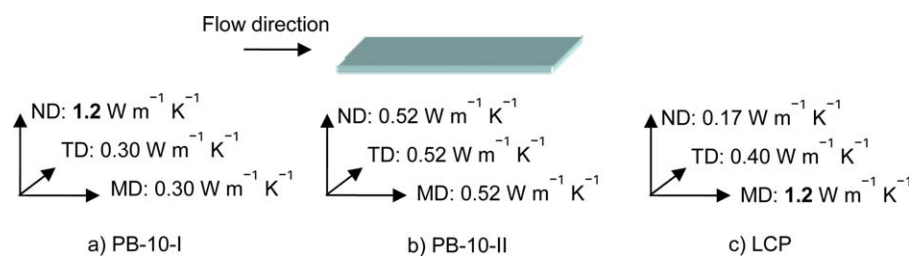
Figure 4. Thermal conductivity measured in three characteristic directions for each polymer plate: (a) PB-10-I, (b) PB-10-II, and (c) the LCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Characterization of injection-molded composite plates (40 vol%). (a) Crystal structure of h-BN. (b) and (c) 2D-WAXD patterns along the MD, TD, and ND for PB-10-II and the LCP, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
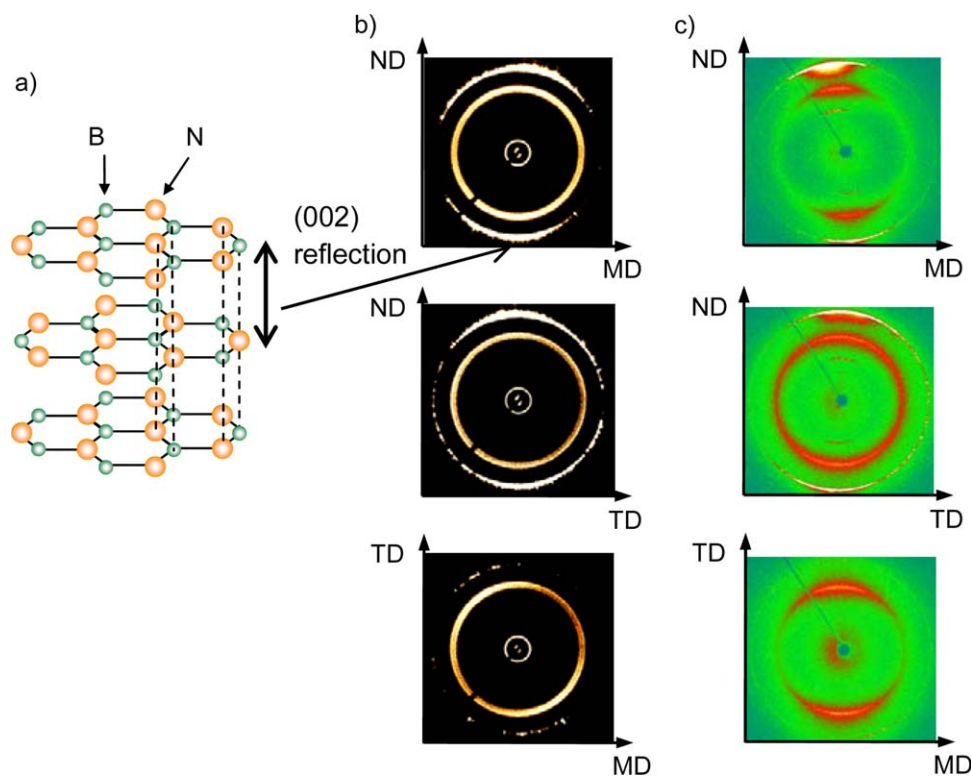
EXPERIMENTAL

Materials

PB-10 polyesters [Figure 1(a)] were synthesized by melt condensation of 4,4′-diacetoxy biphenyl and 1,10-dodecanedioic acid with sodium acetate as the catalyst. These chemicals were purchased from Wako Pure Chemical Industries, and were used as received. The PB-10 polyesters showed crystal-smectic transformations at T_m and smectic-isotropic transformations at T_i, which were measured by differential scanning calorimetry (DSC) at a heating rate of $10°C$ min^{-1} (PerkinElmer Pyris 1 DSC). Two specimens with different molecular weights, PB-10-I (M_n: 10,000, M_w: 19,000, T_m: 204°C, T_i: 246°C) and PB-10-II (M_n: 24,000, M_w: 58,000, T_m: 206°C, T_i: 256°C) were prepared by controlling the reaction period of the melt condensation. After polycondensation, the molten polymer was discharged onto a stainless plate. An LCP sample (Ueno LCP A-8000) was provided by Ueno Fine Chemicals Industry. It showed a solid-LC transition temperature (T_m) at 220°C. Kimura and co-worker reported the chemical structure [Figure 2(a)] and the molecular weight (M_n: 10,000, M_w: 31,000).[13] Plate-shaped h-BN (PT110) with a mean particle size of 45 μm in diameter and 2 μm in thickness was purchased from Momentive Performance Materials (Figure 2b). The h-BN platelets have electrical insulation properties, density of 2.25 g cm^{-3} and out-of-plane and in-plane TC values of 2 and 400 W m^{-1} K^{-1}, respectively.[10,14]

Gel Permeation Chromatography

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the PB-10 polyesters were

determined by gel permeation chromatography (GPC) in a *p*-chlorophenol/toluene (3/8 volume ratio) solution (Viscotek Ht-GPC with a RI detector). The molecular weight was calibrated as a relative value to a polystyrene standard.

Morphology Characterization

Two-dimensional wide-angle X-ray diffraction (2D-WAXD) patterns were recorded on an imaging plate at 25°C using Cu Kα radiation, which was generated by a Rigaku-Denki UltraX18 X-ray generator equipped with a graphite crystal monochromator and a pinhole collimator. The 2D-WAXD patterns for the PB-10-II/h-BN composite were recorded at 25°C with a Bruker AXS D8 Discover using Cu Kα radiation. Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 SEM microscope. To observe the dispersion of h-BN in composites, each specimen with the surface smoothed using a microtome was subjected to platinum–palladium deposition. To observe the crystalline lamellae of PB-10, the specimen with the surface smoothed using a microtome was exposed to RuO$_4$ vapor before platinum–palladium deposition. To observe the LCP fibrils, the specimen was first fractured and then subjected to platinum–palladium deposition.

Compounding and Injection Molding Conditions

The polymers and h-BN were mixed using a twin-screw extruder (TECHNOVEL, KZW15TW). The screw rotation speed was 90 revolutions per minute. The temperature was set at 220°C for PB-10-I, 230°C for PB-10-II, and 250°C for LCP. The actual filler content of the composites was determined from their densities and residual content after a burn-out test at 450°C. The polymers and composites were molded by a mini

injection molder (DSM Xplore, Micro Injection Moulding Machine 5.5 mL) to plates with dimensions of $10 \times 40 \times 1$ mm^3. The cylinder and mold temperatures were 240°C and 170°C for the PB-10s and their composites and 250°C and 170°C for the LCP and its composites, respectively. The injection pressure was 0.7 MPa.

Thermal Conductivity Measurements

TC (λ) was evaluated using thermal diffusivity (α) data according to the following equation:

$$\lambda = \alpha \rho c, \tag{1}$$

where ρ and c are the density and heat capacity, respectively. The thermal diffusivities of the samples in the ND, MD, and TD were measured in triplicate for each direction at 25°C in accordance with the American Society for Testing and Materials (ASTM) E-1461 using a Netzsch LFA 447 NanoFlash instrument with ±5% accuracy. Figure S2 (Supporting Information) outlines the sample preparation process for the thermal diffusivity measurements. The samples were polished with sand paper and coated with a carbon spray (Black Guard Spray FC153, Fine Chemical Japan). The density and heat capacity were determined by the Archimedean and DSC methods, respectively.

RESULTS AND DISCUSSION

Morphology and TC of the Neat Polymers after Injection Molding

The orientation direction of the polymer chains at each injection-molded polymer plate center was determined using 2D-WAXD [Figure 3(a)]. In a previous report,[5] the 2D-WAXD patterns for PB-10-I were shown, indicating that the polymer chains were well aligned perpendicular to the (MD, TD) plane. Figure 3(b) shows the patterns for PB-10-II and indicates a random chain orientation. We speculate that this flow behavior results from the inhibition of lamellar sliding derived from the inter-lamellar connectivity by the higher M_n polymer.[5] Figure 3(c) shows the patterns for the LCP, in which the peaks from the inter-mesogen reflections (5.34 Å) are observed. In both the (ND, MD) and (TD, MD) patterns, the peaks strongly appear on the meridian. These profiles indicate a polymer chain orientation in the MD. In the (ND, TD) pattern, the inter-mesogen reflection is somewhat concentrated on the meridian, indicating that the molecules also lie slightly in the TD.

The TCs of the three specimens are shown in Figure 4. The LCP exhibited a high TC of 1.2 W m^{-1} K^{-1} in the MD, but a very low TC of 0.17 W m^{-1} K^{-1} in the ND. The TC in the TD (0.40 W m^{-1} K^{-1}) is attributed to the moderate molecular orientation in this direction. The TC value in the MD was as large as that of PB-10-I in the ND. PB-10-II exhibited a TC of 0.52 W m^{-1} K^{-1} in all directions, which is greater than that of PB-10-I in the in-plane direction.

Morphology and TC of the Injection-Molded Polymer/h-BN Composites

Next, the orientation directions of the polymer chains and h-BN platelets in each composite (40 vol %) were investigated using 2D-WAXD. There are two dimensions in the h-BN, which are the graphite-like structure with strong bonding within the
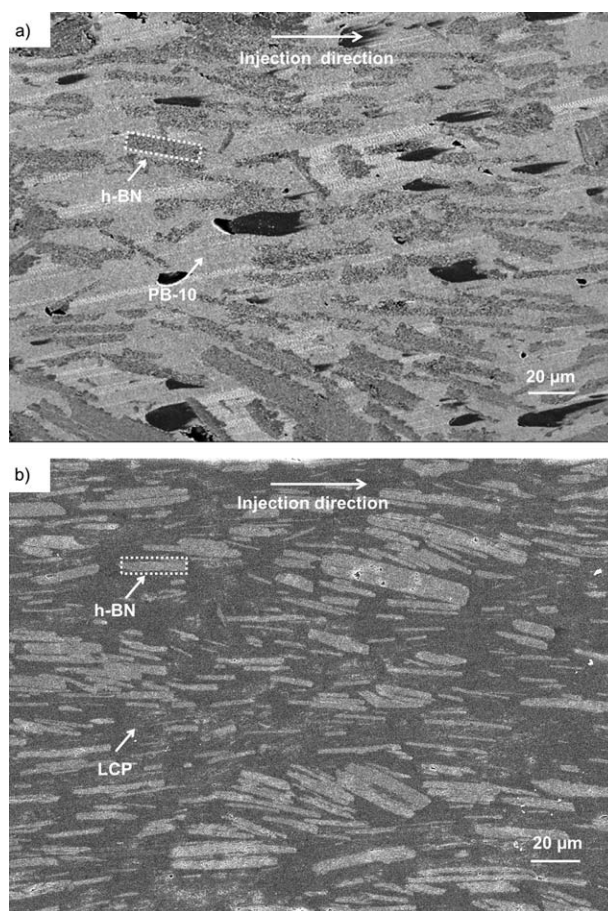

Figure 6. SEM images of the cross-sectional surface (ND, MD) for the (a) molded PB-10-I composite (30 vol %) and (b) molded LCP composite (29 vol %). Scale bar, 20 μm.

planar, fused, six-membered rings (a-axis) and the van der Waals bonding in-between layers (c-axis) [Figure 5(a)]. Figures 5(b,c) show the (002) reflections (3.33 Å) derived from the h-BN in addition to the same reflection patterns from each polymer (PB-10-II and LCP) as seen in Figures 3(b,c). In both the (ND, MD) and (ND, TD) patterns, the (002) reflections are observed on the meridian, and the (MD, TD) pattern shows a weak (002) reflection. These profiles indicate that the h-BN platelets tend to align in the in-plane direction, and the preferred orientation for each polymer is achieved even after incorporation of h-BN. The 2D-WAXD patterns for PB-10-I composite (40 vol %) were previously reported,[5] revealing the in-plane orientation of h-BN platelets and molecular orientation in the ND. Figure 6 shows the SEM images observed on a cross-sectional surface of (ND, MD) plane about PB-10-I and LCP composites at 30 and 29 vol %, respectively, indicating that h-BN platelets are comparatively oriented in the in-plane direction. Moreover, the interface between polymer matrix and h-BN platelets appears to be continuous without voids and the dispersion of platelets are similar between PB-10-I and LCP composites.

Figures 7(a,b) show the TC of composites with different levels of h-BN content in the ND and in the MD, respectively. Table S1 (Supporting Information) lists detailed results for the TC,
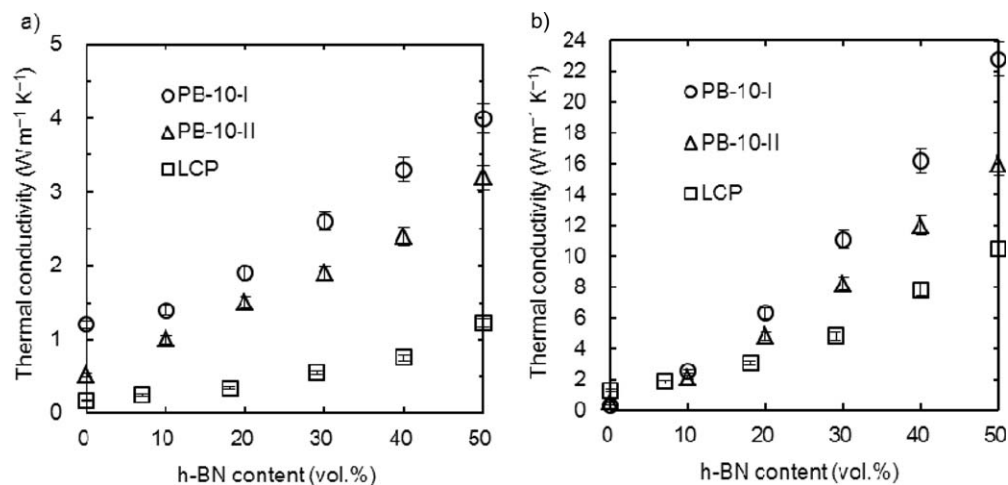
Figure 7. Effect of h-BN filler content on the thermal conductivity of polymer composites in the (a) ND and (b) MD.

thermal diffusivity, density, and specific heat of all of the composites. In the ND, the TC of the PB-10-I composites is the highest of the three systems. This result is a direct reflection of the difference in the TCs of the respective polymer matrices. The TC of PB-10-I composite at 50 vol % was 4.0 W m^{-1} K^{-1}, which is more than out-of-plane TC (2 W m^{-1} K^{-1}) of h-BN platelets. This is due not only to the existence of the a-axis of h-BN along the thickness direction of the molded plates as seen in Figure 6 but also to the molecular orientation in the same direction. Surprisingly, the highest TC in the MD was also observed with the PB-10-I matrix, although PB-10-I is a poor conductor in this direction. Unexpectedly, the TC of the LCP composites in this direction was the lowest. At a 50 vol % loading, the TC value was 10 W m^{-1} K^{-1}, which is the same level as that of a conventional polymer composite at a comparable loading level (see the data based on polybutylene terephthalate in Ref. 5).

Such a difference between in-plane TCs of the composites can be attributed to the difference of the heat conductive functions of the matrices between the h-BN platelets closely stacked. The in-plane-oriented h-BN platelets are arranged "one above the other" or "adjacent to each other" (Figure 8). However, in composites containing plate-shaped particles, it is known that the main thermal or electrical path is the way through the contact of the platelets arranged "one above the other" because of the large contact area of the platelets.[15–17] Therefore, the effective heat path of the matrix between such arranged platelets [Figure 8(a)] is expected to significantly increase the in-plane TC values of the composites. The SEM images in Figure 9 show the morphology between h-BN platelets closely stacked one above the other in composites. In the PB-10-I composite (30 vol %), the crystalline lamellae aligned along the h-BN surfaces [Figure 9(a)].

This arrangement is ideal for the lamellae to behave as effective heat paths between the h-BN platelets. In the LCP composite (29 vol %), the LCP fibrils align well parallel to the MD, and this orientation is responsible for the high TC of the matrix in this direction [Figure 9(b)]. However, the fibrils do not seem to serve as heat paths between the h-BN platelets. The fibrils lie along the h-BN surface, thus causing high thermal resistance. As a result, the TC value along the heat paths between the platelets is thought to be 0.17 W m^{-1} K^{-1} [Figure 4(c)].

On the other hand, the fibrils could serve as effective heat paths between h-BN platelets arranged adjacent to each other. In fact, the TC in the MD of the composites is larger than that in the TD (Table S1, Supporting Information). However, the comparison between composite TCs of PB-10-I and LCP in Figure 7 indicates that the high thermal resistance of LCP in Figure 9(b) has a more powerful effect on the in-plane TC of the composites because of the large contact area of the platelets.

About the difference between the TCs of the PB-10-I and PB-10-II composites, the same discussion is applicable. Figure 7 shows the TC of the PB-10-I composite is higher in both the ND and the MD than those of the PB-10-II composite. In this case, the TC of each matrix must directly contribute to the TC of each composite because the same PB-10-type matrices were used. Based on these findings, it is concluded that the high TC of the matrix in the ND leads to effective heat pathways between h-BN platelets arranged one above the other, resulting in the formation of a continuous thermal linkage in the in-plane direction.

To increase the TC of polymer composites, increasing the TC of polymer itself is important. However, even if such a polymer is successfully developed, whether the polymer functions as an effective heat path between filler particles is another matter. This
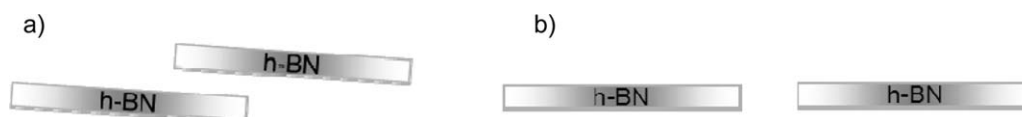

Figure 8. In-plane-oriented h-BN platelets, which are arranged: (a) one above the other, and (b) adjacent to each other.
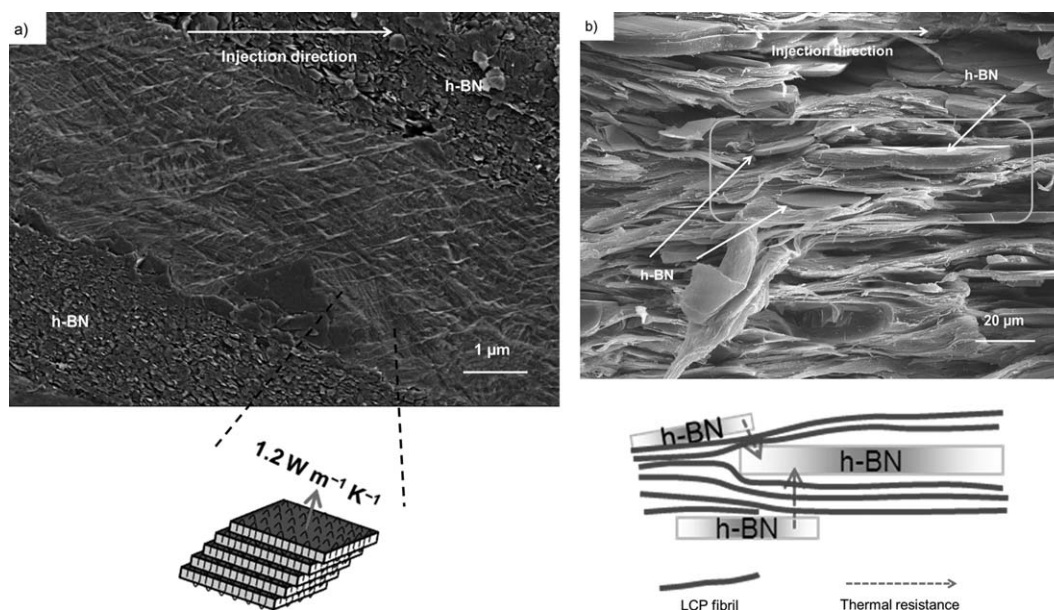
Figure 9. SEM images and schematic illustrations of the polymer morphology between the h-BN platelets arranged one above the other. (a) Molded PB-10-I composite (30 vol %). Scale bar, 1 μm. (b) Molded LCP composite (29 vol %). Scale bar, 20 μm.

function is an essential factor for increasing the TC of the composite. In a composite system with in-plane-oriented h-BN platelets, a perpendicular relationship between the polymer and h-BN orientations results in dramatic enhancement of the in-plane TC.

CONCLUSIONS

In a polymer/h-BN composite system, three types of polymer chain orientations relative to the h-BN plane were investigated to determine if controlling the orientation could lead to enhancement of the in-plane TC. Although the polymer orientation in the in-plane direction was initially thought to be the best condition, polymer chains oriented in the ND led to composites with the highest TCs. As the main thermal path of the composites is the way that heat transfers through the linkage between h-BN platelets arranged one above the other, the matrix serving as an effective heat pass between such arranged platelets can provide composites with high in-plane TC. For this purpose, the molecular chains oriented in the ND were found to be the most ideal.

ACKNOWLEDGMENTS

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