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Analytic modeling for the anisotropic thermal conductivity of polymer composites containing aligned hexagonal boron nitride

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ABSTRACT

Polymer composites containing two-dimensional hexagonal boron nitride (h-BN) can achieve enhanced thermal conductivity (TC), and such enhancement is more pronounced along the orientation direction of h-BN platelets. In this paper, an analytical model was developed for simultaneously calculating the anisotropic TC of polymer composites containing aligned h-BN platelets. A unit cell was first abstracted based on the morphological observation in the literature. Then the thermal resistance method and co-ordinate transformation were used to derive the TC of the composites. The model was successfully validated by the experimental data from two independent literature studies over a large range of filler contents. The dependence of TC on the key parameters of the model, including the orientation angle and geometric dimension of the h-BNs, and the interfacial thermal resistance, were quantitatively analyzed and discussed.

1. Introduction

Polymers have been widely used in almost all aspects of modern industrial field because they are light, anticorrosive and easy to process [1]. However, most of polymers have the thermal conductivities (TCs) of only around 0.1–0.3 W/mK [2], limiting their applications in the areas including thermal interface materials [3,4], anti-corrosion heat exchanger [5,6] and heat sinks in electronic devices [7,8]. In order to improve the TC of a polymer material, different kinds of thermally conductive fillers, such as metals, metal oxides and carbon materials, have been utilized to manufacture polymer composites [9,10]. However, the TCs of the resulting polymer composites were still below expectation, which were explained by the poor filler dispersion and the high interfacial thermal resistance (TR) [11–13].

A structural analog of graphite, hexagonal boron nitride (h-BN), also appears as one of the most promising fillers in the preparation of thermally conductive and electrically insulative composites, due to its unique properties [8,14–18]: on the one hand, it is a good thermal conductor with the in-plane TC ranging from 200 W/mK [14] to 400 W/mK [15]; on the other hand, it is an excellent electrical insulator [14]. In addition, the two dimensional h-BN is expected to confer the anisotropic feature on the TCs of composites. When the h-BN micro-platelets were applied as fillers, the in-plane TC of PVA composites [17] was greatly improved and reached 1.45 W/m K, 3.92 W/m K and 4.41 W/m K at the filler loading of 1 wt %, 10 wt% and 30 wt%, respectively. In comparison, the through-plane TC of PVA composites was significantly lower than the in-plane TC because the h-BN platelets were mostly oriented towards the in-plane direction. Tanimoto et al. [14] prepared PI composites with h-BNs of different sizes. For the composites containing the flake-type h-BN with the median diameter of 8 μm, the in-plane TC can be 17.5 W/mK with the corresponding through-plane TC of 2.2 W/mK. The thermal conduction behavior of h-BN filled polymer composites has been qualitatively associated with the geometric dimension, orientation and dispersion of h-BNs observed morphologically [14,17]. To further understand the impact of anisotropic h-BN platelets on the TCs of polymer composites, quantitative analysis by the theoretical model is needed.

As the simplest models for calculating the composites TCs, the Series model and the Parallel model proposed by Voigt-Reuss [19]

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give the lower and upper bounds respectively for a two-phase composite, which is considered to consist of the layers of two phases connected in either series or parallel with regard to the heat flow direction [9,19,20]. By assuming the composites contain the very diluted dispersion of non-interacting spheres within a continuous matrix, Maxwell developed an analytical expression for the effective TC [19,21], which was later modified by Rayleigh, McKenzie and Bruggeman [19,22–24] to extend to higher filler concentration. Among other numerous models that describe the composite TCs [9,19,21,23,25], the Nielsen model includes the effect of the shape and the orientation of the particles by introducing empirical parameters [26,27] and the Agari model considers the effect of formed conductive chains between the fillers [20]. Meanwhile, the composite TCs could also be derived by using the variational approaches [28–30]. Hashin and Shtrikman obtained the narrowest possible conductivity bounds for isotropic two-phase material in terms of phase volume fractions and phase properties [28], and the expressions for these bounds mathematically coincide with the Maxwell model [25,28]. Regardless of the components' volume fractions or TC, these so-called Hashin-Shrtikman bounds always lie within the Series-Parallel bounds [25]. Duan et al. also used the variational principle to derive the explicit expressions for effective conductivity of heterogeneous media, reflecting the joint effect of four factors including the location, orientation and shape of the fillers, and the interface bonding condition [29,30]. Their results are numerically close to those of Nan et al. [31] for the composites with small volume fraction of fillers.

For the existing models, the TCs of polymer composites are mainly a function of the filler content. Many other key parameters, such as the geometric dimension and distribution of the fillers, have been largely overlooked. In the above mentioned polymer composites with high TC [14,17], the h-BN fillers are not only aligned with each other but also tilted against the heat transfer direction due to the processing methods. The anisotropic TCs of the composites have rarely been simultaneously predicted by the existing models [20–23,26–35]. In this paper, a mathematical model was developed to simultaneously calculate the anisotropic TCs of the polymer composites filled with aligned h-BN platelets. After a unit cell was abstracted according to the morphological observation in the literature [17], thermal resistance method and coordinate transformation were used to derive the analytical model. The calculated anisotropic TCs were found to be consistent with the experimental results reported in the literatures [14,17]. The influence of the orientation and geometric dimension of h-BNs and the interfacial thermal resistance on the TCs of polymer composites were also discussed.

2. Unit cell abstraction

2.1. Selection of the unit cell

As observed in the SEM images of Ref. [17], owing to the shear force generated by tape-casting, the micro-sized 2D h-BN platelets in the polymer composites are aligned along the casting direction with a certain orientation angle. A schematic of the filler distribution in the polymer matrix is shown in Fig. 1.

To abstract a unit cell for the TC calculation of a polymer composite [33,34], the h-BN distribution in the polymer matrix is simplified as a parallel array which forms an angle of α with the horizontal direction (i.e., the x axis), as shown in Fig. 2. A unit cell is generally selected as the red rectangle (in dashed line) in Fig. 2(a), which has boundaries parallel to that of the polymer composite. The TC of the unit cell equals to that of the composite if the unit cell has sufficient number of h-BN platelets, and an iterative process is needed to determine the proper number. In addition, such unit cell always contains small portions of h-BN platelets, which makes it difficult to calculate the TC of the unit cell. Alternatively, a unit cell could be selected as the red rectangle (in dashed line) shown in Fig. 2(b), containing only one h-BN platelet in the center. The boundary of the unit cell is parallel to that of the h-BN platelet, rather than that of the polymer composite. The TC calculation of such unit cell is much simplified, and the composite TC can be easily obtained by the mathematic conversion based on the TC of the unit cell. Therefore, the unit cell in Fig. 2(b) is adopted for further calculation and analysis in this work.

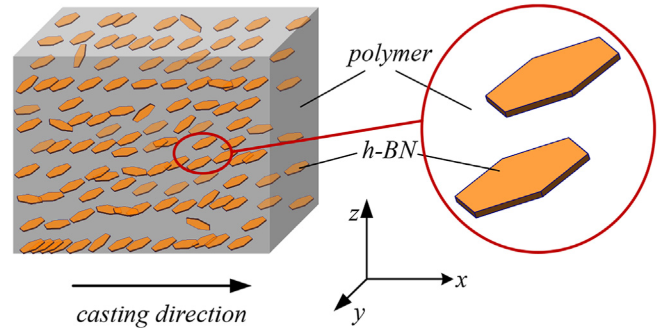

Fig. 1. Distribution of h-BN in the polymer composite prepared by tape-casting method, with a zoom-in image to indicate the filler and the matrix.

2.2. Transformation of coordinate systems

In order to convert the calculated TC of the unit cell into the TC of the polymer composite, a two-coordinate system is utilized, with the x-y-z coordinate fixed with the polymer composite as shown in Figs. 1 and 2, and the $\xi-\zeta-\eta$ coordinate fixed with the h-BN platelet. The two coordinate systems are overlapped at first, as shown in Fig. 3(a). Then the unit cell rotates around the ζ axis by an angle of α, as shown in Fig. 3(b). The parameter α will be used for converting the TC of the unit cell into the TC of the polymer composite.

3. Calculation of the anisotropic thermal conductivity

3.1. Basic assumptions for the unit cell

Fig. 4 is the three-view diagram of the selected unit cell in the $\xi-\zeta-\eta$ coordinate system. The basic assumptions for the unit cell are made as follows.

(i) The h-BN fillers are uniformly distributed, so that the polymer composite is composed of many unit cells with length L, width W and height H. The h-BN is simplified as a hexagonal platelet with a mean diameter (the distance between the parallel sides) of a and a thickness of b, locating in the center of the unit cell. The values of a and b are usually reported in the literature [14,17].

(ii) The volume fraction Φ_V of the h-BN in the unit cell equals to that in the polymer composite, and could be calculated as

$$\Phi_V = \frac{\sqrt{3}}{2}\frac{a^2 \cdot b}{L \cdot H \cdot W} \tag{1}$$

(iii) The distances between the perimeters of the h-BN and unit cell are δ_L, δ_W and δ_H, respectively. Therefore $L = a + 2\delta_L$, $H = b + 2\delta_H$, $W = \frac{2}{\sqrt{3}}a + 2\delta_W$.