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Modeling and analysis of synergistic effect in thermal conductivity enhancement of polymer composites with hybrid filler

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ABSTRACT

Hybrid filler with proper filler ratio can remarkably improve the thermal conductivity of polymer composites by the synergistic effect. However, there is a lack of an effective mathematical model that could describe such effect or predict the optimal ratio of the hybrid filler. In this paper, a two-step analytical model was developed for calculating the effective thermal conductivity (k_{eff}) of epoxy composites containing hybrid single-walled carbon nanotubes (SWCNTs) and graphite nanoplatelets (GNPs) filler. Based on the experimental observation in the literature, a unit cell containing a GNP–SWCNTs–GNP sandwich structure was abstracted, and thermal resistance method and effective medium approach were used to derive the model with the assumption that the effective height of the SWNCTs in the unit cell follows the normal distribution. The modeling results were highly consistent with the experiment results in the literature. The synergistic effect was clearly observed and the optimal ratio of hybrid filler could be predicted from the model. Effect of the key parameters on the k_{eff} in the model were also analyzed and discussed.

1. Introduction

Polymers have many advantages over metals, including lighter weight, much better anti-corrosion property, and improved processability [1]. However, low thermal conductivities of polymers, usually less than 0.3 W/mK [2], have limited their applications in many areas, such as thermal interface materials [3–6], electronic devices heat dissipation [7,8], anti-corrosion heat exchanger [9,10]. One of the ways to improve the thermal conductivity of a polymer is adding thermally conductive fillers to the polymer matrix. When the micro-sized fillers, such as metal powders, ceramic powders and carbon fibers, were used [11], the thermal conductivity of the polymer composites were usually below 4 W/mK even with the filler contents as high as 50 wt%, which would raise the processing difficulty and cause the degradation of mechanical properties of the composite materials. Carbon nanotube (CNT) and graphene, with remarkably high thermal conductivities, are regarded as the promising fillers to produce polymer composites with high thermal conductivities [12]. However until now, most of the polymer composites containing the CNT or graphene still have quite low thermal conductivities, usually less than 5 W/mK, which are mainly explained by poor filler dispersion and high interfacial thermal resistance in the composites [11,13,14].

Combination of several types of fillers, i.e., hybrid filler, has also been attempted in the preparation of the polymer composites in order to better improve the thermal conductivity [15]. Weber et al. [16,17] used the combinations of three carbon fillers, including carbon black, synthetic graphite and carbon fiber, to prepare the polymer composites based on nylon 6,6 and polycarbonate. A synergistic effect was discovered when the synthetic graphite-carbon fiber hybrid filler was used, causing a statistically significant enhancement of the composite thermal conductivity. It was suggested that the additional thermally conductive pathways were formed, with the carbon fiber connected with the synthetic graphite. Yu et al. [18] observed a synergistic effect between 1D single-walled carbon nanotubes (SWCNTs) and 2D graphite nanoplatelets (GNPs) for the improvement of thermal conductivity of the epoxy composites. For the same total filler content of 10 wt%, the hybrid filler with a weight ratio of ~3:1 (GNPs: SWCNTs) surpassed the performance of individual SWCNT or GNP fillers.

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Nomenclature

A	area
a_K	Kapitza radius
D	diameter
δ	thickness
Φ_m	mass fraction
Φ_V	volume fraction
H	height
H_a	expectation of bridging height
k	thermal conductivity
L	length
m	mass
n	number of certain substance
Q	heat flow
R	thermal resistance
ρ	density
θ	mass fraction ratio of the GNPs to the SWCNTs
V	volume
σ	standard deviation of bridging height

Subscripts

b	bridging
eff	effective
equ	equivalent
G	GNP
hf	hybrid filler
M	matrix
non	non-bridging
opt	optimal
S	SWCNT
v	vertical

Later on, several other research groups also reported similar synergistic effect in the thermal conductivity enhancement of composites by using hybrid filler [19–23].

As suggested by the above-mentioned results in the literature, the synergistic enhancement with hybrid filler could provide a promising way to achieve high thermal conductivity of composites at relatively low filler loading. However, there is a lack of mathematical or analytical models that describe such synergistic effect of thermal conductivity enhancement caused by hybrid filler. Although there are many models describing or predicting the composite thermal conductivities [17,24–30], only a monotonic relationship between the composite thermal conductivity and the filler content was generally observed in these models. Moreover, at a certain total filler loading, there could exist an optimal ratio of the componential fillers at which a highest composite thermal conductivity is attained. Yet none of the current models could predict such an optimal ratio.

In this paper, based on the experimental results reported in the literature [18], a mathematical model has been developed to calculate the effective thermal conductivity of the epoxy composites containing the hybrid filler of 1D cylinder-like SWCNT and 2D plate-like GNP. A unit cell containing a GNP–SWCNTs–GNP sandwich structure was abstracted [27], in which the effective height of the SWCNTs along the heat flow direction was reasonably assumed to follow the normal distribution. Thermal resistance method [29] and effective medium approach (EMA) [31] were then used to derive a two-step analytical model. The calculated thermal conductivities were found to be consistent with the experimental results reported in the literature [18]. The synergistic effect was clearly observed, and the optimal ratio of hybrid filler predicted by our model matched well with the experimental values.

2. Thermal conductivity modeling

2.1. Unit cell abstraction and basic assumptions

The polymer composites studied in this paper are the epoxy composites containing 1D-SWCNT and 2D-GNP. As observed in the SEM and TEM images of Yu's experiments [18], the end sections of some SWCNTs could be aligned along the GNP surfaces due to the van der Waals attraction between the SWCNTs and GNP. Additional heat flow pathways were therefore formed in the polymer matrix. A schematic hybrid filler structure of the polymer composite, which is similar to that of Fig. 2(c) of literature [18], is shown in Fig. 1(a).

As shown in Fig. 1(b), a unit cell with a GNP–SWCNTs–GNP sandwich structure, which is the periodic structure of the polymer composite, is abstracted to calculate the effective thermal conductivity of the composite [27,29]. The assumptions for the unit cell selection and simplification are made as follows:

(i) The hybrid filler, including both the GNPs and SWCNTs, is uniformly distributed in the epoxy matrix, so the polymer composite is composed of many cuboid unit cells. Considering the symmetry and periodicity, each unit cell contains one half GNP on its top and on half GNP on its bottom, with several SWCNTs lying between these two half GNPs.

(ii) The GNPs and SWCNTs are simplified as cylinders. The geometries and densities of the GNP, SWCNT and epoxy matrix are cited from the work of Yu et al. [18], as listed in Table 1.

(iii) The number of SWCNTs between two half GNPs n_S is determined by Eq. (1),

$$n_S = \frac{\Phi_{m,S}/m_S}{\Phi_{m,G}/m_G} = \frac{\rho_G V_G}{\theta \cdot \rho_S V_S} \tag{1}$$

where m_S and m_G are the masses of a single SWCNT and a single GNP, respectively. $\Phi_{m,S}$ and $\Phi_{m,G}$ are the mass fractions of the SWCNTs and GNPs, respectively. ρ_S and ρ_G are the densities of SWCNTs and GNPs, respectively. V_S and V_G are the volumes of SWCNTs and GNPs, respectively. θ is the mass fraction ratio of the two componential fillers,

$$\theta = \frac{\Phi_{m,G}}{\Phi_{m,S}} \tag{2}$$

The mass fraction of hybrid filler $\Phi_{m,hf}$ equals to the sum of the two mass fractions of the SWCNTs and GNPs,

$$\Phi_{m,hf} = \Phi_{m,G} + \Phi_{m,S} \tag{3}$$

so the mass fraction of SWCNTs and GNPs can be obtained when θ and $\Phi_{m,hf}$ are known, vice versa.

$$\Phi_{m,G} = \frac{\theta}{1+\theta}\Phi_{m,hf}, \quad \Phi_{m,S} = \frac{1}{1+\theta}\Phi_{m,hf} \tag{4}$$

(iv) The cuboid unit cell has the same length and width of L and the height of H, as shown in Fig. 1(b). The volume fraction of the GNPs in the unit cell equals to that in the polymer composites,

$$\Phi_{V,G} = \frac{V_G}{L^2 \cdot H} = \frac{\Phi_{m,G}/\rho_G}{\Phi_{m,G}/\rho_G + \Phi_{m,S}/\rho_S + (1-\Phi_{m,hf})/\rho_M} \tag{5}$$