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An effective compound thermal diffusivity characterization method for polymer nanocomposites

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Polymer composites with layered structures are easily prepared and applied for a range of potential applications due to their excellent thermal properties. This introduces significant demands to characterize the thermal properties of these nanocomposites. In this study, we report an effective compound thermal diffusivity characterization method to predict and furthermore to help regulate the thermal diffusivity of polymer nanocomposites. As a case study, an improved nanoporous template wetting technique was employed to fabricate 20 nm and 200 nm high-density polyethylene (HDPE) nanowires within porous anodic alumina (AAO) substrates. A compound thermal diffusivity model for double-layer structural nanocomposite is proposed to predict the effective overall thermal diffusivity of the HDPE/AAO samples. An infrared sequence transformation technique was introduced for measurement verification. The theoretically predicted results are in accordance with the experimental results, where the in-plane thermal diffusivity of the AAO substrate was reduced by 34.7% and 41.7%, respectively, from 20 nm and 200 nm HDPE nanowire arrays fabrication. The characterization results also revealed that the thermal diffusivity of the polymer nanocomposites could be quantitatively regulated *via* adjusting the polymer content, which could potentially provide a theoretical basis for thermal management and thermal structure design.

Introduction

Polymer composites are extensively applied for their corrosion stability, low density and cost-effective characteristics.[1,2] Various structures and manufacturing methods exist. The layer-structured polymer composites have recently attracted great attention in the electrical,[3] acoustics,[4] medical,[5] and space[6,7] fields for their ease of processability and desirable electrical, thermal and mechanical properties. In particular, layered polymer composites with tailored thermal properties have always been applied for a range of potential applications, since both conductive[8] and insulative[9] polymer fillers were developed. Increased use of these layered polymer composites for various applications creates a need for thermal property analysis and characterization. Thermal diffusivity is one such important thermal property that needs to be evaluated.

Literature reported to date[10,11] gives various ideas of evaluating the thermal diffusivity of polymer composites on an experimental basis. Theoretical models from many research efforts have concentrated on the intrinsic thermal properties of polymers accounting for variation in size and morphology.[12,13] As for composites, the Maxwell–Eucken[14] equation was originally applied to the thermal conductivity of composites requiring the fillers to be well dispersed and not touching each other only at low loadings. Behrens[15] developed methods to predict the thermal property of two-phase composites with cubic symmetry. Agrawal[16] established a model to predict the thermal diffusivity of spherical shaped particulate filled polymer composites. The theoretical models mentioned above mostly concentrated on particulate dispersed composites and few studies have been reported regarding theoretical characterization methods for the thermal diffusivity of layer-structured polymer composites. Herein, the aim of our study was to develop an effective characterization method to theoretically predict the thermal diffusivity of double-layer structured polymer composites.

In this study, a compound thermal diffusivity characterization model is proposed to predict the composite's effective thermal diffusivity perpendicular to layers. The overall thermal diffusivity could be determined by each component's thermal properties and volume content. To validate the model, double-layer structured polymer composites have been synthesized where polyethylene (HDPE) nanowires with high densities of 20 nm and 200 nm have been fabricated within the porous anodic alumina (AAO) substrates using an improved nanoporous template wetting technique. An infrared sequence transformation technique has been employed for experimental verification. The measured in-plane thermal diffusivities of

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HDPE/AAO composites have been compared with results from the predictive model.

Samples preparation and characterization

The double-layer structured HDPE/AAO composites were developed for study. The HDPE nanowires were prepared by the nanoporous template wetting technique developed and improved by Steinhart[17] and Bing-Yang Cao,[18] respectively. AAO templates (a ready-made porous template for preparing nano-scaled filling composites for its low cost and variety of specifications) with 20 nm and 200 nm pores were chosen as substrates, and were purchased from Whatman, Inc. All the AAO substrates were standard circular plates with a diameter of 13 mm and thickness of 60 μm containing homogeneous through-hole pores that provided a template for the HDPE nanowires. The HDPE film was melted by the springs heated at 160 °C and infiltrated into the through-hole pores[18] with capillary pressure. Then, the sample was taken out of the hot chamber and cooled to room temperature. To prepare the HDPE/AAO composites for subsequent characterization, the HDPE nanowires were supposed to fill in the pores as much as possible. Therefore, the length of the nanowires was selected such that it approximately approached the substrate's thickness. Wetting time was properly controlled. According to the Lucas–Washburn law (LWE),[19] which is considered to be able to model the flows of polymer melts through nanopores,[20] the penetration length is always proportional to the square root of wetting time. Actually, according to the nanoconfinement of nanopores, the viscosities of polymer melts always decrease when flowing through nanopores.[21] The calculated fill-in time for the 200 nm AAO was 8.86 h according to LWE. Empirically, we prepared two samples with wetting time of 9 h and 10 h, and studied them using scanning electron microscopy (SEM, QUANTA 200 FEG).

A top-view image of the sample with wetting time of 10 h is shown in Fig. 1(a). It can be seen that most of the nanowires have exactly filled in the pores, forming a suitable sample for thermal study. In addition, the AAO template was removed in an aqueous solution of NaOH and the HDPE nanowire arrays were rinsed with deionized water and dried at 30 °C in vacuum. Fig. 1(b) is the cross-section view of HDPE nanowires after removing the AAO template, which shows the uniformly distributed nanowires on the over deposited HDPE film. The X-ray diffraction scans of the HDPE nanowires are displayed in Fig. 2, where the two strong peaks correspond to the (110) and (200) orthorhombic phases of HDPE, when compared with the peak positions of standard PDF#40-1995, indicating the synthesis of high-purity nanowire samples with good crystallization. Subsequently, composites with 20 nm HDPE nanowire arrays were prepared with a wetting time of 124 h.

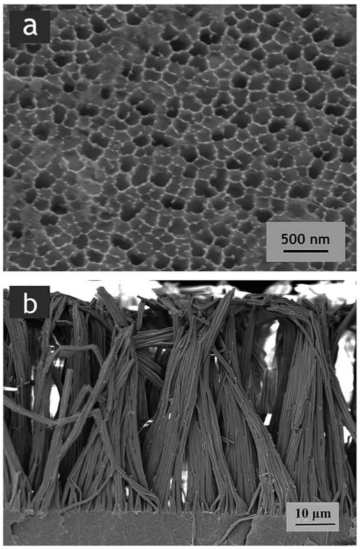


Fig. 1 Scanning electron micrographs of (a) top view of 200 nm HDPE nanowires embedded in AAO template and (b) cross-section view of 200 nm HDPE nanowires after removing the AAO template.

Compound thermal diffusivity model

Before the experimental investigation, a compound thermal diffusivity model was applied for theoretical prediction. The HDPE/AAO composite could be abstracted to a porous media model with double-layer structures, as shown in Fig. 3. The overall thermal diffusivity parallel and perpendicular to the layers are generally anisotropic, which depends on the respective thermal properties of the two components. In the direction perpendicular to the layers, the effective overall specific heat follows the mixture rule as follows:[22]

$$\begin{aligned}\rho_0 c_0 &= \sum \varphi_i \rho_i c_i = \varphi \rho_{\mathrm{HDPE}} c_{\mathrm{HDPE}} + (1-\varphi)\rho_{\mathrm{AAO}} c_{\mathrm{AAO}} \\ &= \varphi \frac{\lambda_{\mathrm{HDPE}}}{\alpha_{\mathrm{HDPE}}} + (1-\varphi)\frac{\lambda_{\mathrm{AAO}}}{\alpha_{\mathrm{AAO}}} \end{aligned} \tag{1}$$

where φ is the porosity of AAO substrate. c_{HDPE}, c_{AAO}, λ_{HDPE}, λ_{AAO}, α_{HDPE}, α_{AAO}, ρ_{HDPE} and ρ_{AAO} are the specific heat, thermal conductivity, thermal diffusivity and the density of two components, respectively. ρ_0 and c_0 are the overall density and specific heat perpendicular to the layers.

Considering that the double-layer structure is arranged similarly in serial connections, the overall thermal conductivity perpendicular to the layers λ_0 follows the in-serial model:[23]

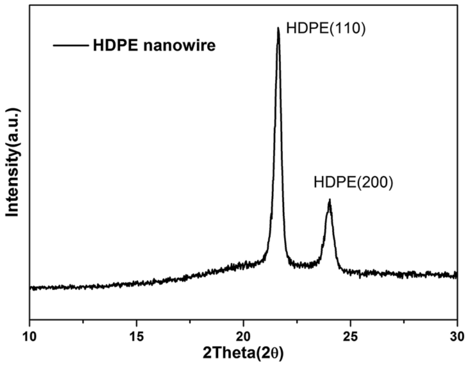


Fig. 2 X-ray diffraction scans of HDPE nanowires.

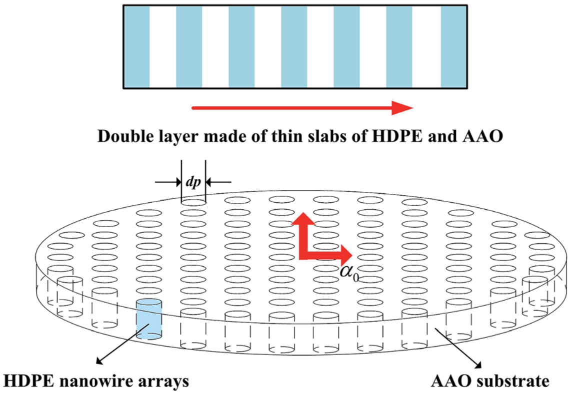


Fig. 3 Compound thermal diffusivity model for double-layer composite.

$$\frac{1}{\lambda_0}=\left[\sum\frac{\varphi_i}{\lambda_i}\right]^{-1}=\frac{\varphi}{\lambda_{\mathrm{HDPE}}}+\frac{1-\varphi}{\lambda_{\mathrm{AAO}}} \tag{2}$$

Assuming that the two components are both equivalently homogeneous in thermal physical effects, the resulting thermal diffusivity depends mainly on the porosity of the AAO substrate. Considering $\lambda_0 = \alpha_0\rho_0c_0$, the overall thermal diffusivity perpendicular to the layers is obtained as follows:

$$\begin{aligned}\frac{1}{\alpha_0}&=\frac{\rho_0c_0}{\lambda_0}\\&=\frac{\varphi^2}{\alpha_{\mathrm{HDPE}}}+\frac{(1-\varphi)^2}{\alpha_{\mathrm{AAO}}}+\varphi(1-\varphi)\left\{\frac{\lambda_{\mathrm{AAO}}}{\lambda_{\mathrm{HDPE}}\alpha_{\mathrm{AAO}}}+\frac{\lambda_{\mathrm{HDPE}}}{\lambda_{\mathrm{AAO}}\alpha_{\mathrm{HDPE}}}\right\}\end{aligned} \tag{3}$$

Eqn (3) is a compound thermal diffusivity model for the nanocomposites with double-layer structures. The effective overall thermal diffusivity can be predicted by the thermal properties of the AAO substrate and HDPE nanowires.

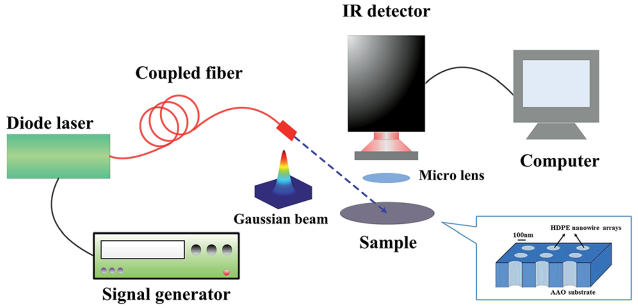


Fig. 4 Experimental set-up for thermal diffusivity measurements.

Experimental investigations

The overdeposited HDPE layer on the rear surface of the substrate was polished before measurement. An infrared sequence transformation technique[24] was applied for the in-plane thermal diffusivity measurement. Fig. 4 shows the measurement system. A semiconductor laser (BWT DS2-50.00W) with a pulse width of 62.5 ms and a power of 25 W was used to irradiate the nanocomposite surface. An IR camera (FLIR A315) with a spectral range from 7.5 μm to 13 μm was used for the temperature field detection. In addition, to achieve the local heat flow detection of the tiny HDPE/AAO samples with a specific diameter of 13 mm, both the IR camera lens and the irradiating Gaussian beam radius were adjusted. In particular, a macro lens was placed in the IR detection optical path at a distance of 79 mm from the sample surface, and the Gaussian beam radius was focused to 0.4 mm by a self-focusing lens. Through the configuration mentioned above, the local temperature field could be recorded with a special resolution of 100 μm. Theoretically, the temperature field evolution $T(r,\theta,t)$ is given as follows:

$$T(r,\theta,t)=f(\varphi)\frac{1}{0.5{R_{\mathrm{C}}}^2+4\alpha_0t}\exp\left[-\frac{r^2}{0.5{R_{\mathrm{C}}}^2g(\varphi,\theta)+4\alpha_0t}\right] \tag{4}$$

where r and θ are the radial distance and polar angle, respectively, R_{C} is the radius of the laser beam, φ is the laser's incident angle, and $f(\varphi)$ and $g(\varphi,\theta)$ are the functions of φ and θ, respectively. To study the properties of the thermal diffusing peak, $\partial T(r,\theta,t)/\partial t = 0$ was set and the maximum temperature curve $r_{T_{\max}}(\theta)$ was approximately derived as follows:[24]

$$r_{T_{\max}}(\theta)=\sqrt{\frac{{R_{\mathrm{C}}}^2g(\varphi,\theta)}{2}+4\alpha_0t} \tag{5}$$

Then, the diffusing area s was derived from the integral of $r_{T_{\max}}(\theta)$[24] as follows:

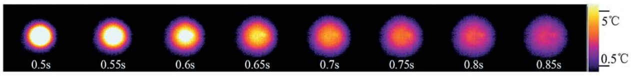
$$s=\frac{\pi{R_{\mathrm{C}}}^2}{2\cos\varphi}+4\pi\alpha_0t \tag{6}$$

where s could be described and divided from the extracted thermal images. Then, α_0 could be consequently calculated from the s–t curve according to eqn (6).

Results and discussion

During the experiment, efforts were made to avoid the potential influence[25] from the central temperature rise upon the measured thermal diffusivity. The recorded temperature field evolutions were selected for analysis in the time range of $0.5\ \mathrm{s} < t < 0.85\ \mathrm{s}$ and at certain distances from the heat centre ($1\ \mathrm{mm} < r < 2\ \mathrm{mm}$).

The experimental results were extracted and analyzed using the abovementioned measurement system. Fig. 5(a) shows the raw IR images of the 200 nm HDPE/AAO sample in the range of 0.5–0.85 s. It can be seen that the temperature of the whole sample was below 7 °C, which is considered to not introduce extra measurement errors. The binary thermal diffusing sequences were obtained through the proposed method, as shown in Fig. 5(b), where the boundary (red curves) between the black region ($T' < 0$) and the grey region ($T' > 0$) indicate the thermal diffusing edge. It is clear that the thermal diffusing



(a) Raw IR camera images in the time range of 0.5 s–0.85 s

(b) Binary thermal diffusing sequences

Fig. 5 IR sequence transformations for the 200 nm HDPE/AAO composite during thermal diffusing process. (a) Raw IR camera images in the time range of 0.5–0.85 s. (b) Binary thermal diffusing sequences.

edge spreads as time increases and the spreading speed is the slope according to eqn (6).

The area s surrounded by the thermal diffusing edge was calculated by a DRLSE formulation.[20] The (s_i, t_i) sequences were therefore extracted and the slopes of the s–t curves were calculated with linear regression. The results for 20 nm and 200 nm HDPE/AAO composites are shown in Fig. 6, where the thermal diffusivities of the 20 nm and 200 nm HDPE/AAO composites were calculated to be 5.92×10^{-7} m^2 s^{-1} and 5.29×10^{-7} m^2 s^{-1}, respectively, according to eqn (6).

On the other hand, considering that the specific heat and the density of the nanofibers are the same as those of bulk materials for both parameters and are not sensitive to the crystallinity at room temperature,[26] the specific heat and the density of HDPE nanowires are $\rho_{\text{HDPE}} = 945$ kg m^{-3} and $c_{\text{HDPE}} = 1900$ J kg^{-1} K^{-1}. Knowing that the thermal conductivity of bulk HDPE is $\lambda_{\text{HDPE}} = 0.5$ W m^{-1} K^{-1}, the thermal diffusivity of HDPE nanowires is calculated to be $\alpha_{\text{HDPE}} = 2.78 \times 10^{-7}$ m^2 s^{-1}. Moreover, the thermal conductivity of AAO is $\lambda_{\text{AAO}} = 1.02$ W m^{-1} K^{-1} and the measured thermal diffusivity is $\alpha_{\text{AAO}} = 9.03 \times 10^{-7}$ m^2 s^{-1}. Given that the porosities of the 20 nm and 200 nm AAO substrates were 31% and 42%, the overall thermal diffusivity values for the 20 nm and 200 nm HDPE/AAO composites were 5.76×10^{-7} m^2 s^{-1} and 5.03×10^{-7} m^2 s^{-1}, respectively, which was calculated using eqn (3).

The experimental and the theoretically predicted results are listed and compared in Table 1, where the experimental and theoretical results are consistent. It can be seen that the in-plane thermal diffusivity of the AAO substrate is reduced by 34.7% and 41.7% from the 20 nm and 200 nm HDPE nanowire arrays fabrication, respectively. The results indicate that the overall thermal diffusivity of the composites could be quantitatively modulated *via* adjusting the polymer content, which demonstrates that polymer nano-filling is a promising effective thermal control method for base materials. Furthermore, it is interesting to note that the theoretical results from the compound thermal diffusivity model were slightly lower than the experimental results for both the 20 nm and 200 nm HDPE/AAO composites.

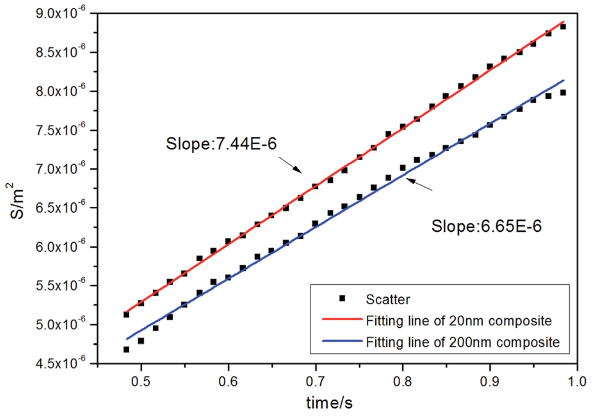


Fig. 6 The area surrounded by the thermal diffusing edge *versus* time.

Table 1 Experimental and theoretical thermal diffusivity results for HDPE/AAO composites

Sample	Experimental results (m^2 s^{-1})	Theoretical results (m^2 s^{-1})
AAO template	9.03×10^{-7}	—
HDPE/AAO (20 nm)	5.92×10^{-7}	5.76×10^{-7}
HDPE/AAO (200 nm)	5.29×10^{-7}	5.03×10^{-7}

The difference between the theoretical and experimental results is probably due to several reasons. First, polymers could probably exhibit scale effects in thermal transport. It was investigated by molecular dynamics simulations[27] that a single chain or aligned polymer chains may have enhanced thermal conductivity. The thermal diffusivity of HDPE nanowires could be slightly above that of bulk materials, which was applied in the model. The crystallinity of the polymer nanofibers during the fabrication process, such as pore size and cooling rate, could probably affect the resulting difference.[28] Other potential unpredictable factors, such as the extent and quality of thermal contact between the nanofibers and pores in alumina caused during fabrication, could also possibly contribute to the experimental results.

Conclusions

The compound thermal diffusivity characterization method has been proposed to predict the effective thermal diffusivity of layered polymer composites. Composites composed of AAO and HDPE nanowires with diameters of 20 nm and 200 nm have been prepared using the nanoporous template wetting technique. The infrared sequence transformation technique has been applied for experimental verification. The experimental results showed 34.7% and 41.7% reduction in the thermal diffusivity of the substrates, which are consistent with the theoretical results, indicating that HDPE nano-filling is an effective method to reduce the thermal diffusivity of base materials. It can be also concluded that the overall thermal diffusivity of layered polymer nanocomposites could be quantitatively regulated by adjusting the polymer content based on the abovementioned characterization method. This study could potentially offer specific guidance for thermal design in nano-integration devices.

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