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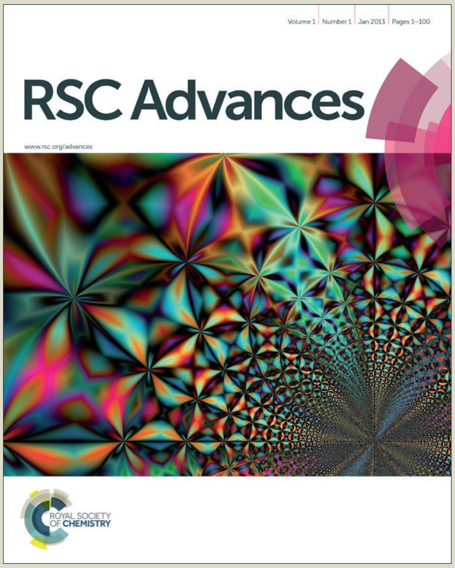

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ARTICLE

An Effective Compound Thermal Diffusivity Characterization Method for Polymer Nanocomposites

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Polymer composites with layered structures are always prepared and applied for ranges of potential applications owing to their excellent thermal properties. This brings in the 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 is employed to fabricate 20nm and 200nm 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 is introduced for measurement verification. The theoretically predicted results accord well with the experimental results, where the in-plane thermal diffusivity of AAO substrate is reduced by 34.7% and 41.7% respectively from 20nm and 200nm HDPE nanowire arrays fabrication. The characterizaion results also reveal 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.

Keywords: Polymer composite, Layer structure, Thermal diffusivity, Compound thermal diffusivity model, Infrared sequence transformation technique

Introduction

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

Literature reported so far [10, 11] gives various ideas of evaluating the thermal diffusivity of polymer composites on experimental basis. Theoretical models from plentiful researches concentrate 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 well-dispersed and not touching each other only at low loadings. Behrens E [15] developed methods to predict the thermal property of two-phase composites with cubic symmetry. Agrawal [16] established the model to predict the thermal diffusivity of spherical shaped particulate filled polymer composites. Theoretical models above mostly concentrate on particulate dispersed composites, few researches have been reported regarding theoretical characterization method for the thermal diffusivity of layer-structured polymer composites. Herein aim of our study is to develop an effective characterization method to theoretically predict the thermal diffusivity of double-layer structured polymer composites.

In this work, 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 contents. To validate the model, double-layer structured polymer composites are synthesized where 20nm and 200nm high density polyethylene (HDPE) nanowires

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x are fabricated within the porous anodic alumina (AAO) substrates using an improved nanoporous template wetting technique. An infrared sequence transformation technique is then employed for experimental verification. The measured in-plane thermal diffusivities of HDPE/AAO composites are compared with results from the predictive model.

Samples preparation and characterization

The double-layer structured HDPE/AAO composites are developed for study. The HDPE nanowires were prepared by the nanoporous template wetting technique developed and improved respectively by Steinhart [17] and Bing-Yang Cao[18]. AAO templates (a ready-made porous template for preparing nano-scaled filling composites for its low cost and variety in specifications) with 20 nm and 200 nm pores were chosen as substrates which were purchased from Whatman, Inc. All the AAO substrates are standard circular plates with diameter of 13mm and thickness of 60μm as well as homogeneous through-hole pores providing a template for HDPE nanowires. The HDPE film is melted by the 160°C heating springs and infiltrated into the through-hole pores[18] under capillary pressure. Then, the sample is taken out of the hot chamber and cooled down to room temperature. To prepare the HDPE/AAO composites for subsequent characterization, the HDPE nanowires are supposed to fill in the pores as much as possible. Therefore the length of the nanowires need to approximately approach the substrate's thickness. The wetting time should be 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, as to the nanoconfinement of nanopores, the viscosities of polymer melts always decrease in their flows through nanopores [21]. The calculated fill-in time for the 200nm AAO is 8.86h according to LWE. Empirically, we prepared two samples with wetting time of 9h and 10h respectively and studied them using scanning electron microscopy (SEM, QUANTA 200 FEG).

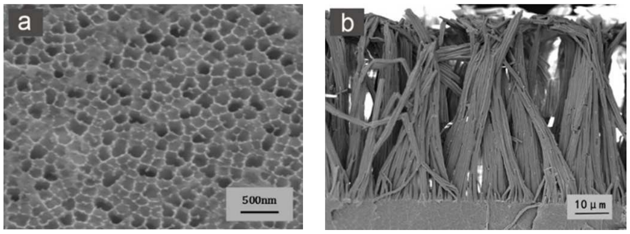


Fig. 1 Scanning electron micrographs of (a) top view of 200nm HDPE nanowires embedded in AAO template (b) cross-section view of 200nm HDPE nanowires after removing the AAO template.

A top-view image of the sample with wetting time of 10h 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. Additionally, the AAO template was removed in NaOH aqueous solution and the HDPE nanowire arrays were rinsed with deionized water and dried at 30℃ 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 overdeposited HDPE film. The x-ray diffraction scans of HDPE nanowires were displayed in Fig. 2, where the two strong peaks correspond to orthorhombic phase of HDPE of (110), (200) compared with the peak positions of standard PDF#40-1995, indicating the synthesis of high-purity nanowire samples with well crystallization. Subsequently composites with 20nm HDPE nanowire arrays were prepared with wetting time of 124h after similar discussion ready for study.

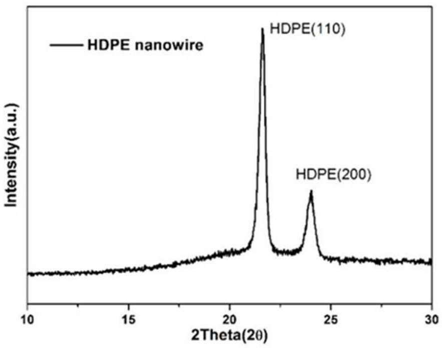


Fig. 2 X-ray diffraction scans of HDPE nanowires

Compound thermal diffusivity model

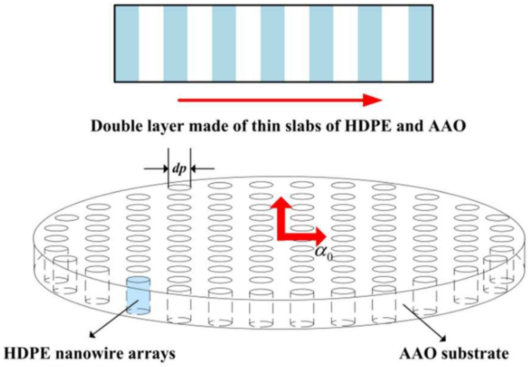


Fig. 3 Compound thermal diffusivity model for double-layer composite

Before experimental investigations, a compound thermal diffusivity model is applied for theoretical prediction. The HDPE/AAO composite can 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 depend 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[22]:

$$\rho_0 c_0 = \sum \varphi_i \rho_i c_i = \varphi \rho_{HDPE} c_{HDPE} + (1-\varphi)\rho_{AAO} c_{AAO} = \varphi \frac{\lambda_{HDPE}}{\alpha_{HDPE}} + (1-\varphi)\frac{\lambda_{AAO}}{\alpha_{AAO}} \quad (1)$$

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, 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]:

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

Assuming that the two components are both equivalent homogeneous in thermal physical effects, the resultant thermal diffusivity depends mainly on the porosity of AAO substrate. Considering $\lambda_0 = \alpha_0 \rho_0 c_0$, the overall thermal diffusivity perpendicular to the layers is obtained as:

$$\frac{1}{\alpha_0} = \frac{\rho_0 c_0}{\lambda_0} = \frac{\varphi^2}{\alpha_{HDPE}} + \frac{(1-\varphi)^2}{\alpha_{AAO}} + \varphi(1-\varphi)\left\{\frac{\lambda_{AAO}}{\lambda_{HDPE}\alpha_{AAO}} + \frac{\lambda_{HDPE}}{\lambda_{AAO}\alpha_{HDPE}}\right\} \quad (3)$$

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

Experimental investigations

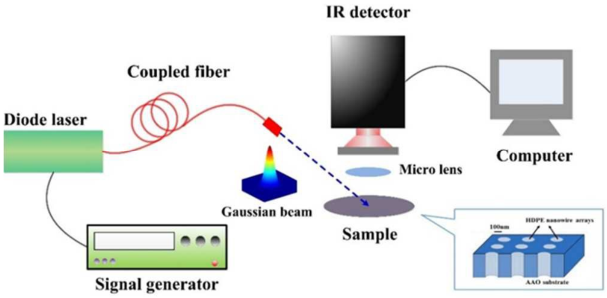


Fig. 4 Experimental set-up of thermal diffusivity measurements

The overdeposited HDPE layer on the rear surface of the substrate is polished before measurement. An infrared sequence transformation technique[24] is 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 62.5ms and a power of 25W is used to irradiate the nanocomposite surface. An IR camera (FLIR A315) with a spectral range from 7.5µm to 13µm is used for the temperature field detection. In addition, to achieve the local heat flow detection of the tiny HDPE/AAO samples with specific diameter of 13mm, both the IR camera lens and the irradiating Gaussian beam radius are supposed to be adjusted. Specifically, a macro lens is placed in the IR detection optical path with a distance of 79mm from the sample surface, and the Gaussian bean radius is focused to be 0.4mm by a self-focusing lens. Through the configuration above, the local temperature field can be recorded with a special resolution of 100µm. Theoretically, the temperature field evolution $T(r,\theta,t)$ follows:

$$T(r,\theta,t) = f(\varphi)\frac{1}{0.5R_C^{\,2} + 4\alpha_0 t}\exp\left[-\frac{r^2}{0.5R_C^{\,2} g(\varphi,\theta) + 4\alpha_0 t}\right] \quad (4)$$

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

$$r_{T\max}(\theta) = \sqrt{\frac{R_C^{\,2} g(\varphi,\theta)}{2} + 4\alpha_0 t} \quad (5)$$

Then the diffusing area s is derived from integral of $r_{Tmax}(\theta)$ [24]:

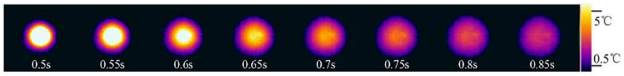
$$s = \frac{\pi R_C^{\,2}}{2\cos\varphi} + 4\pi\alpha_0 t \quad (6)$$

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 Eq. (6).

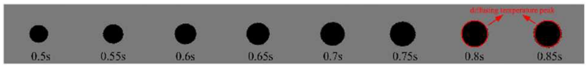
Results and discussion

During the experiment, in order 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 time range of 0.5s<t<0.85s and in certain distances from the heat centre (2mm<r<3mm).

The experimental results are extracted and analyzed using the above established measurement system. Fig. 5(a) shows the raw IR images of the 200nm HDPE/AAO sample within 0.5s~0.85s It can be seen that the temperature of the whole sample is below 7℃ which is considered not to introduce extra measurement errors. The binary thermal diffusing sequences are 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 ($T' > 0$) indicates the thermal diffusing edge. It is clear that the thermal diffusing edge spreads as time increases and the spreading speed is the slope according to Eq. (6).



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



(b) Binary thermal diffusing sequences

Fig. 5 IR sequence transformations for thermal diffusing process of 200nm HDPE/AAO composite

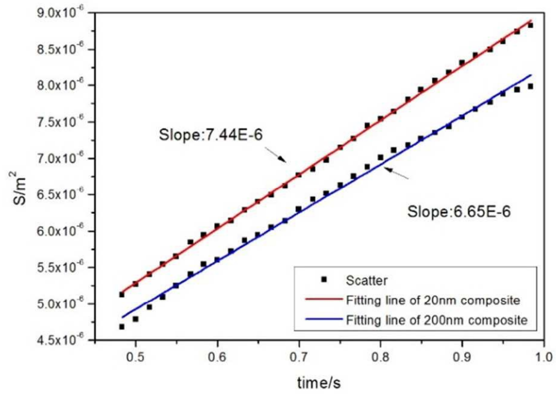


Fig. 6 The area surrounded by the thermal diffusing edge versus time

The area s surrounded by the thermal diffusing edge is calculated by a DRLSE formulation[20]. The (s_i, t_i) sequences are therefore extracted and the slopes of s-t curves are calculated with linear regression. Results for 20nm and 200nm HDPE/AAO composites are shown in Fig. 6, where the thermal diffusivities of 20nm and 200nm HDPE/AAO composites are calculated to be 5.92×10-7 m^2s^{-1} and 5.29×10-7 m^2s^{-1} from the fitting curves respectively according to Eq. (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 are not sensitive to the crystallinity at room temperature[26], the specific heat and the density of HDPE nanowires are $\rho_{HDPE} = 945 kgm^{-3}$ and $c_{HDPE} = 1900 Jkg^{-1}K^{-1}$. Knowing that the thermal conductivity of bulk HDPE is $\lambda_{HDPE} = 0.5 Wm^{-1}K^{-1}$, the thermal diffusivity of HDPE nanowires is calculated as $\alpha_{HDPE} = 2.78\times10^{-7} m^2s^{-1}$. Moreover the thermal conductivity of AAO is $\lambda_{AAO} = 1.02 Wm^{-1}K^{-1}$ and the measured thermal diffusivity is $\alpha_{AAO} = 9.03\times10^{-7} m^2s^{-1}$. Given that the porosities of 20nm and 200nm AAO substrates are respectively 31% and 42%, the overall thermal diffusivity of 20nm and 200nm HDPE/AAO composites are 5.76×10^{-7} m^2s^{-1} and 5.03×10^{-7} m^2s^{-1} calculated from Eq. (3).

The experimental and the theoretically predicted results are listed and compared in Table 1, where the experimental results are well consistent with the theoretical results. It can be seen that the in-plane thermal diffusivity of the AAO substrate is reduced by 34.7% and 41.7% respectively from the 20nm and 200nm HDPE nanowire arrays fabrication. 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‘s interesting to note that the theoretical results from compound thermal diffusivity model are slightly lower than the experimental results for both 20nm and 200nm HDPE/AAO composites.

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

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

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

Conclusions

The compound thermal diffusivity characterization method is proposed to predict the effective thermal diffusivity of layered polymer composites. Composites composed of AAO and HDPE nanowires with diameters of 20nm and 200nm are prepared using the nanoporous template wetting technique. The infrared sequence transformation technique is applied for experimental verification. The experimental results show 34.7% and 41.7% reduction of the substrate's thermal diffusivity, which are well consistent with the theoretical results, indicating that HDPE nano-filliing 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 above characterization method. The study could potentially offer specific guidances for thermal design in nano-integration devices.

Acknowledgements

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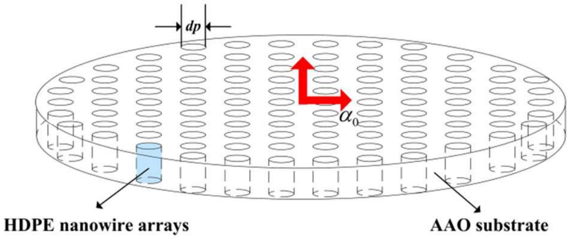

An effective compound thermal diffusivity characterization method is proposed for layer-structured polymer composites.