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Endowing the high efficiency thermally conductive and electrically insulating composites with excellent antistatic property through selectively multilayered distribution of diverse functional fillers

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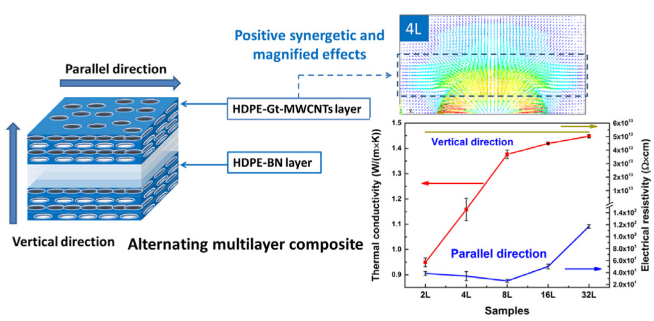
HIGHLIGHTS

- The alternating multilayered composites with 2 to 32 layers were obtained.
- The multilayered structure was constructed through the melt extrusion method.
- The contradiction between antistatic property and electrical insulation was resolved.
- Thermally conductive enhancement mechanism of structure was in-depth investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

To fabricate thermally conductive while electrically insulating composites with excellent antistatic property is a huge challenge in the region of packaging materials of electronic devices due to the contradiction between the electrical insulation and the antistatic property. In the present work, the peculiar multilayer structures with alternating high efficiency thermally, electrically conductive layers and thermally conductive, electrically insulating layers were constructed successfully through a simple, one-step melt extrusion method. Such thermally conductive and electrically insulating composites possessed significant anisotropic electrical resistivity; for example, the in-plane electrical resistivities (parallel to the layer direction) were below $117\ \Omega \times \text{cm}$, while the through-plane electrical resistivities were over $5 \times 10^{13}\ \Omega \times \text{cm}$. Meanwhile, with increasing the layer number, thermal conductivity of the composite with the same filler loading was improved monotonously, and reached as high as $1.45\ \text{W}/(\text{m} \times \text{K})$ in the composite with 32 layers. In addition, tensile strength and elongation at break of the composites were also enhanced due to the different deformation mechanisms of separate layers. Furthermore, to give a deep insight into the enhancement mechanism of thermally conductive property, finite element analysis was applied and the results indicated that high efficiency thermally, electrically conductive layers possessed magnified effects on the heat dissipation. Therefore, the multilayer structure with alternating high efficiency thermally, electrically conductive layers and thermally conductive, electrically insulating layers can endow the composite with excellent comprehensive properties effectively, and it also sheds light on the design and fabrication of high performance materials for the applications of thermal management or other energy harvesting fields.

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1. Introduction

Thermally conductive and electrically insulating polymer-matrix composites have become increasingly important with the rapid development of high-speed, high-power electronic devices and other energy harvesting equipment [1–5]. Traditionally, the most common way to fabricate such composites is to introduce thermally conductive while electrically insulating fillers into polymer matrix, such as aluminum nitride (AlN) [6–8], alumina (Al_2O_3) [9,10], silicon carbide (SiC) etc [11,12]. However, due to their relatively low intrinsic thermal conductivities, the thermally conductive properties of the final composites always cannot meet the increasing requirements.

In recent years, carbon based fillers, which possess much higher intrinsic thermal conductivities, have attracted much more attentions in this region [13–18]. For example, thermal conductivities of graphites (Gt) and carbon nanotubes (CNTs) are as high as 2000 and 3000 W/(m $\times$ K), which are several tens times larger than those of conventional thermally conductive while electrically insulating fillers [19–22]. As a result, thermally conductive properties of the filled composites are always much higher, which has already been proved by other researchers [23,24]. However, how to keep the high electrical resistivity of the final composite filled with large amount of carbon based fillers is a critical issue for resolution. The most popular method is coating insulating layers onto carbon based fillers to restrain their electrically conductive properties, for example, AlO(OH)-coated MWCNTs [25], BN-coated MWCNTs [26], and graphene oxide (TRGO)-based silica nanofillers [27], etc. The high electrical resistivity is indeed achieved with such core-shell structures, but thermal conductivity of the composite is decreased undesirably due to the introduction of other interfaces [2,25]. Therefore, finding a proper method to fabricate the thermally conductive while electrically insulating composites without surface treatment is important to take further advantage of carbon based fillers.

On the other hand, with the further development of electronic devices, fast assembly line speed and stability of the product are also highly demanded, which makes the antistatic property become much more important [28,29]. As a result, endowing the thermally conductive and electrically insulating composites with excellent antistatic property is very necessary to provide a safe packing process and a stable operating environment to electronic equipment. However, it is commonly accepted that the electrical insulation and the antistatic property are significantly contradictory. Therefore, endowing the final composite with these two properties simultaneously is still a challenge in this region.

In order to overcome the barriers mentioned above, the multilayered film with alternating thermally, electrically conductive layers (graphene oxide filled layer) and thermally conductive while electrically insulating layers (boron nitride filled layer) was fabricated initially through layer-by-layer casting in our previous work. With such multilayered structure, excellent thermally conductive property and significant anisotropic electrical resistivity were indeed obtained [30]. Therefore, in practical applications, the outmost electrically insulating and thermally conductive layer, which can prevent short-circuiting in the system, can contact with electronic devices directly. Furthermore, electrically and thermally conductive layers can endow the composite with excellent antistatic property, which could guarantee the stability and safety of electronic devices or other thermal managements.

Subsequently, in the present work, for the purpose of further simplifying the preparation process through a solvent-free method, the multilayer composites with much more layers and more regular structures were obtained through selectively multilayered distribution of diverse functional fillers in one matrix by one-step melt extrusion fabrication. As a result, the interfacial thermal conduction and interaction between adjacent layers could be improved. With increasing the layer number from 2 to 32, the final thickness of the composite was always kept at 2 mm, which was beneficial to investigate the effects of the multilayered structure and the layer number on thermally conductive property of final composites. Moreover, fillers could also be significantly oriented along the melt flow direction, thus mechanical properties of the final composites could also be enhanced sharply.

Based on this idea, boron nitride (BN) was selected as the filler confined in thermally conductive while electrically insulating layers due to its relatively higher thermal conductivity compared with other thermally conductive while electrically insulating fillers and low coefficient of thermal expansion. Meanwhile, because of the peculiar 2-D structure, it was hard to construct through-plane thermally conductive pathways when they were highly oriented along one direction, which made it possible for us to investigate the effect of the multilayer structure on the heat transport performance of the composites clearly [31,32]. Then, graphite (Gt) was chosen as the main filler confined in the thermally and electrically conductive layers due to its high thermal conductivity, great compatibility with polymer matrix and low cost [24]. And multi-walled carbon nanotubes (MWCNTs) were served as the second filler confined in thermally and electrically conductive layers owing to their high electrical conductivity, thermal conductivity and the excellent synergetic effect with graphites on enhancing the thermal conductivity of the composites by improving their dispersion states [33–35]. The thermal conductivity, electrical resistivity, electromagnetic interference shielding and mechanical properties of the composites with different layer numbers were all characterized in the subsequent experiments. Furthermore, finite element analysis was also applied to give a deep insight into the enhancement mechanism of thermally conductive property of the multilayered system.

2. Experimental

2.1. Materials

The polymer used in this work was high density polyethylene (HDPE) (5000 s) supplied by Lanzhou Petroleum Chemical (China), with the melt index of 1.0 g/10 min (2.16 kg, 190 °C) and density of 0.95 g/cm^3. Hexagonal boron nitride with an average particle size of 10–20 μm was purchased from Dandong Rijin Technology Co., Ltd. (China). Graphite with a particle size of 10–15 μm was supplied by Qingdao Xingyuan Shimo Co., Ltd. (China). Multi-walled carbon nanotubes (NC 7000) with the average diameter of 9.5 nm and length of 1.5 μm were purchased from Nanocyl SA (Belgium). All these materials were used as received.

2.2. Specimens preparation

First, HDPE, BN, Gt and MWCNTs were dried in a vacuum oven at 80 °C for 12 h. Then, the polyethylene based thermally and electrically conductive composite containing 22 vol% Gt powders and 1.1 vol% MWCNTs and the polyethylene based thermally conductive, electrically insulating composite filled with 9.5 vol% BN were melt mixed by a co-rotating twin screw extruder, respectively. The temperatures of the extruder were maintained at 155, 195, 195, and 190 °C from hopper to die. After the extrusion, the blends were cut into small particles and dried for another 12 h. In this work, the composites with alternating thermally conductive, electrically insulating layers and thermally, electrically conductive layers were fabricated with 2, 4, 8, 16, 32 layers by using 0, 1, 2, 3, 4 layer multiplying elements (LMEs), separately. The schematic of the composite was shown in Fig. 1. The process was that the dried HDPE-