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Constructing conductive multi-walled carbon nanotubes network inside hexagonal boron nitride network in polymer composites for significantly improved dielectric property and thermal conductivity

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ABSTRACT

With the rapid development of high performance capacitors for energy storage, materials with both giant dielectric constant and low dielectric loss are urgently needed. Adding conductive filler could largely enhance the dielectric constant of polymer matrix but also greatly increase the dielectric loss. In this study, we provide a new strategy by using hybrid fillers to construct a segregated double network, where conductive multi-walled carbon nanotubes (MWCNT) network is wrapped by insulating hexagonal boron nitride (h-BN) network to destroy the continuity of embedded MWCNT network. To do this, pre-fabricated micron-sized PS/MWCNT particles were completely coated by h-BN through π-π interaction. As a result, the MWCNT network inside h-BN network provides good conductivity while h-BN network provides the isolation effect but do not increase the distance between two adjacent MWCNT agglomerations, which together can maintain the high dielectric constant and decrease the dielectric loss. Therefore, a high dielectric constant of 123 is achieved while a relatively low dielectric loss is also kept as 0.36. More importantly, this special structure of segregated double network also leads to obviously enhanced thermal conductivity which is 2.23-fold of that of the composites with randomly dispersed hybrid fillers. This high thermal conductivity is ascribed to the high synergistic efficiency between segregated h-BN network and dense MWCNT network. We believe that these good comprehensive performances promise this structure to offer a unique and effective way to prepare high-performance dielectric materials with not only high dielectric constant and low dielectric loss, but also good capability of heat dissipation.

1. Introduction

High dielectric constant materials (high-k) have drawn wide attention because of their wide appealing applications, such as capacitors for energy storage and electromechanical actuators [1–9]. Compared with the conventional ceramic high-k materials, polymer composites become more fascinating owing to their outstanding properties including high electric breakdown strength, good flexibility, easy processing and low density [10–12]. In spite of numerous merits, majority of neat polymers have low dielectric constant. Hence, it is a key issue to increase the dielectric constant of polymer composites via introducing high-k fillers.

One is to introduce high-k inorganic ceramic fillers, such as $BaTiO_3$ and TiO_2, into a polymer matrix [13–19]. However, the enhancement of dielectric constant usually requires a high concentration, which inevitably causes the sacrifice of mechanical properties and economic benefit. Another approach is to prepare electrical percolative composites by using conductive fillers, including graphene, carbon nanotubes, metal particles, conductive polymers, etc. [20–29] It was reported that much high dielectric constant can be achieved as the volume fraction of the conductive fillers gets close to the percolation threshold. In this case, taking carbon nanotubes (CNTs) for example, it was reported that a giant dielectric constant enhancement can be achieved by preparing poly(vinylidene fluoride) (PVDF) composites with uniform dispersion of CNTs via melt mixing [30]. However, in general, the composites also exhibit high dielectric loss for the occurrence of the large leakage current near the percolation threshold, leading to

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performance reduction, heat accumulation and early failure of the dielectrics. Thus, it still remains a great challenge to reduce the dielectric loss of conductive filler/polymer composites into capacitor-tolerated value ($\tan\delta \leq 1$) while remaining high dielectric constant in a simple and efficient way. Hence innovative strategies are imminently needed to prepare high-k conductive fillers/polymer composites with well-suppressed dielectric loss.

In order to address this issue, many significant methods have been tried to prevent the conductive fillers from directly contacting each other. Among these methods, the most popular is the surface modification of conductive fillers, including polymer encapsulation and inorganic coating [14,22,28,31–36]. For example, Huang reported that poly(methyl methacrylate) encapsulated carbon nanotubes (PMMA@CNTs) were prepared by using surface-initiated atom transfer radical polymerization [32]. It was found that insulating PMMA could exert isolation effect on the CNTs to hinder the direct electrical contact between adjacent CNTs, resulting in much lower dielectric loss than that of PMMA/CNTs composites. However, these chemical modification methods through insulating layer-encapsulation also have their own limitation. Although the non-conductive coating layer on the surface of fillers could prevent them from contacting each other to reduce the dielectric loss, the distance between two adjacent filler agglomerations was inevitably increased, thus resulted in much lower capacitance. For example, it was reported that graphene oxide (GO) coating on CNTs was beneficial to reduce the dielectric loss of composites, but the dielectric constant was also largely reduced [22]. For non-encapsulated CNTs filled TPU composites, the dielectric constant could achieved about 204 at only 10 wt%. However, dielectric constant of only 56 was obtained as the GO-encapsulated CNTs content achieved as high as 20 wt%. This largely increased filler loading may lead to mechanical performance degradation and cost increase. Another approach to prevent conductive filler from forming network was introducing hybrid fillers in which one filler served as the non-conductive particle [37,38]. In this case, there were two different situations. When the insulating filler content was low, the conductive particles were inclined to be excluded from insulating filler dominated areas, leading to much higher electrical conductivity owing to the volume exclusion effect. However, when the non-conductive filler content was high enough to form the percolated network, they can serve as the insulating walls to isolate the conductive pathways, resulting in much reduced electrical conductivity. Unfortunately, the dielectric constant of the composites was still low because of the obviously increased filler-filler distance, thus resulted in much reduced capacitance.

In our previous work, we reported a new structure named as segregated double network, where MWCNT filler network could be completely segregated by another continuous conductive graphene nanoplates (GNPs) network [39]. It was found that largely enhanced thermal conductivity can be achieved owing to the continuous coated GNPs. Thus it is very interesting to ask if the MWCNT filler network is segregated by non-conductive filler network, could it be possible to increase the dielectric constant while reduce the dielectric loss of the prepared composites. To broaden the application of this structure, in this study, we reported a unique and efficient way to design a segregated double network structure embedded in polystyrene (PS) matrix for preparing high-k polymer ternary composites with not only well-suppressed dielectric loss but also effectively-maintained high dielectric constant. In this double network, robust hexagonal boron nitride (h-BN) network served as the insulating shell and was excluded from polystyrene matrix not to isolate single MWCNT but to destroy the continuity of local MWCNT network within PS phase. To do this, firstly, PS/MWCNT material was simply fabricated by melt mixing PS with different volume content of MWCNT. Then the resultant composites were smashed to get micron-sized PS/MWCNT powders. Finally, different volume content of h-BN was coated on the PS/MWCNT powders under the intense mechanical mixing via π-π self-assembly to obtain the segregated double network (PS/MWCNT@h-BN). The binary composites (PS/MWCNT) and the ternary hybrid network (PS/MWCNT/h-BN) with randomly dispersed fillers were also fabricated by melt mixing for comparative study. Interestingly, for PS/MWCNT/h-BN composites, the dielectric constant is much lower although the dielectric loss is controlled at a low level. But for PS/MWCNT@h-BN composites, a high dielectric constant of 123 is achieved while a relatively low dielectric loss is also kept as 0.36. Even if compared to the optimal dielectric properties of PS/MWCNT composites, the dielectric constant of PS/MWCNT@h-BN composites is 3.36 times of that of PS/MWCNT composites while the dielectric loss is only 46% of that of PS/MWCNT composites. This higher dielectric constant and suppressed dielectric loss are mainly ascribed to the well-maintained distance between adjacent MWCNT and dramatically reduced AC conductivity owing to the segregated effect of insulating h-BN layer. More importantly, another advantage is that this special structure of segregated double network also leads to obviously enhanced thermal conductivity which is usually ignored for dielectric materials but is closely related to the service life and heat dissipation capability of devices [40–43]. We believe that the high thermal conductivity is ascribed to the high synergistic efficiency between segregated h-BN network and dense MWCNT network. These attractive overall properties suggest that this special physical structure could provide a simple way to fabricate high performance dielectric materials with not only high dielectric constant and low dielectric loss, but also good capability of heat dissipation.

2. Experimental section

2.1. Materials

Polystyrene (PS, PG-383) was obtained from Zhenjiang Qimei Chemical Co. Ltd., China. Hexagonal boron nitride (h-BN, 3 μm in lateral size) was purchased from the Eno Material Co. Ltd., China. Multi-walled carbon nanotubes (MWCNT, NC7000, diameter of 9.5 nm, length of 1.5 μm) were supplied from Nanocyl S.A, Belgium.

2.2. Preparation PS/MWCNT micron-sized particles

As is shown in Fig. 1 (c), PS/MWCNT material was simply fabricated by melt mixing PS with different volume content of MWCNT at 190 °C under 60 rpm/min for 20 min in the internal

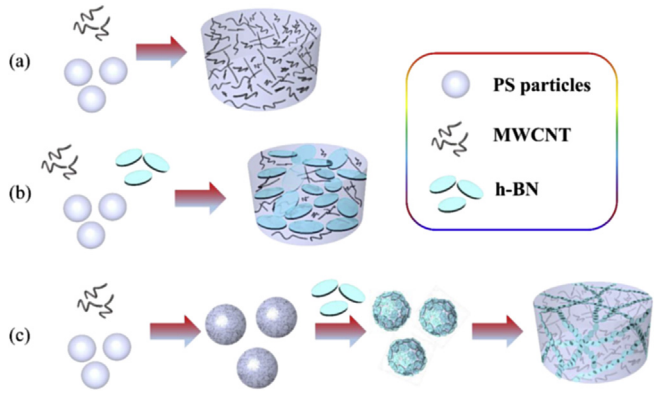

Fig. 1. Preparation procedures and structure diagram of (a) PS/MWCNT, (b) PS/MWCNT/h-BN and (c) PS/MWCNT@h-BN composites.