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Surface modification of boron nitride by reduced graphene oxide for preparation of dielectric material with enhanced dielectric constant and well-suppressed dielectric loss

Kai Wu [a], Chuxin Lei [a], Weixing Yang [a], Songgang Chai [b], Feng Chen [a, **], Qiang Fu [a, *]

[a] College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China
[b] Guangdong Shengyi Technology Limited Corporation, Dongguan, 523039, China

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ABSTRACT

Adding conductive filler is an effective way to enhance the dielectric constant while usually also increases the dielectric loss of polymer. In this study, we demonstrated that polymer composites with much improved dielectric constant while maintaining ultra-low dielectric loss could be achieved via using hybrid filler and controlling the dispersion of conductive filler in polymer matrix. To do this, the graphene oxide was designed to be immobilized on the surface of large-sized insulating hexagonal boron nitride (h-BN) via electrostatic self-assembly, and afterwards introducing this hybrid filler into epoxy accompanied with chemical reduction. In this case, since the reduced graphene oxide (rGO) sheets were fixed on the surface of h-BN, rGO sheets were well separated from each other even at high loading. Hence not only significantly enhanced dielectric constant was observed, but also a very low dielectric loss comparable to that of neat epoxy was achieved. This low dielectric loss was believed to be ascribed to both embedded insulating network of h-BN to inhibit the mobility of charge carrier and well-separated rGO sheets via immobilization. In addition to obviously improved dielectric properties, the nanocomposites also exhibited good thermal conductivity. We believe that this special structure will provide a new thought for fabricating dielectric materials with much enhanced dielectric constant as well as well-suppressed dielectric loss.

1. Introduction

Polymer composites with high dielectric constant and low dielectric loss have attracted tremendous attention for their fascinating applications in electromechanical actuators, high-density electronic packaging technology and capacitors for energy storage [1–4,53,54]. Additional to the excellent dielectric property, good thermal conductivity is also very important, since the heat generated during service will cause shortening of life time and performance degradation [5–8]. However, most polymers exhibit low dielectric constant and insufficient thermal conductivity, hence multifunctional fillers should be introduced to enhance both the properties [9–15].

Graphene, an ultrathin and flexible layer of sp^2-hybridized carbon atoms arranged in a two-dimensional hexagonal lattice, has shown attractive prospects for preparing polymer based nanocomposites owing to its extraordinary carrier mobility, excellent mechanical properties and unique thermal conductivity [16–19]. It was reported that graphene or reduced graphene oxide (rGO) nanocomposites can obtain high dielectric constant at the extremely low graphene loading [20,21].

However, it should be noted that as increase of graphene content, the dielectric loss which degrades the discharged energy density and the charge-discharge efficiency will upgrade sharply. Hence innovative strategies are imminently needed to reduce the dielectric loss of graphene nanocomposites [13,22,23]. Recent studies have shown that encapsulating conductive fillers with insulating layers, such as polyaniline (PANI) [13] and titanium dioxide@titanium diboride [24], was beneficial to prevent the direct contact of conductive filler, leading to repressed dielectric loss. For example, Li reported insulating PANI decorating rGO in poly(methyl methacrylate) (PMMA) matrix [13]. It was found that insulating PANI could exert isolation effect on the rGO sheets in

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* Corresponding author.
** Corresponding author.
E-mail address: qiangfu@scu.edu.cn (Q. Fu).

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PMMA to hinder the direct electrical contact between rGO, thus resulting in much lower dielectric loss than that of PMMA/rGO. However, compared to that of neat PMMA, the dielectric loss of PMMA/PANI@rGO still increased to 0.12, over 2.4-fold higher than that of neat PMMA. Thus fabricating polymer/graphene or rGO composites with much improved dielectric constant while maintaining ultra-low dielectric loss (comparable to or lower than that of neat polymer matrix) remains great challenge.

Recently, embedded hexagonal boron nitride (h-BN) and exfoliated h-BN in polymer matrix were reported to be effective to inhibit the mobility of the charge carrier, thus resulting in dramatic decrease of dielectric loss [8,25]. Meanwhile, due to its extraordinary antioxidation stability, high thermal conductivity, good mechanical properties and high breakdown strength (around 800 MV m-1), h-BN is considered as one of the best choice for preparation of polymer composites with enhanced thermal conductivity and decreased dielectric loss [5,26–29,55]. To further improve the dielectric constant, the simple way is directly mixing h-BN and graphene or rGO in polymer matrix. In this case, only a small amount of graphene could be used to maintain the low dielectric loss. Otherwise, graphene sheets will contact with each other to degrade the dielectric loss. Thus the key is to find a way which could well separate graphene sheets even at high loading. This need a careful design of interaction between h-BN sheets and graphene sheets, and special structure and combination between these two fillers to control the distribution of graphene sheets in polymer matrix.

To do this, in this study, we designed a structure through immobilizing rGO sheets on the surface of large-scale planar lamellar h-BN for the purpose of inhibiting agglomeration of rGO as well as preventing rGO sheets from directly contacting with each other to form conductive network in the polymer matrix. This combination needs chemical stable h-BN to be highly surficial oxidized and functionalized, thus guaranteeing enough absorbed content of rGO. So far, some methods including plasma treatment [30], using reagents which can generate radicals [31] and hydrothermal oxidation [32], were considered to be effective to introduce hydroxyl groups (-OH). But the oxygen content was limited and most of these modifications were complex or time-consuming. Hence not only intricate the fabricating procedure will be, but also the loading of fixed rGO will be restricted. Recently, our group found an efficient route to oxidize h-BN or exfoliated h-BN to obtain the highly oxidized product whose oxygen content can achieve as high as 10.26%. This modification was carried out through a simple ultrasonication treatment in nitric acid (HNO_3), followed by a rapid neutralization to generate −OH, accompanied with the obvious change in color from white to brown yellow. The related work will be published elsewhere. In this work, we mainly utilized this highly hydroxylated h-BN which was grafted by 3-aminopropyltriethoxysilane (APS) in order to introduce $-NH_2$ on the surface. Afterwards, modified h-BN was mixed with GO in the aqueous solution in order to make GO be fixed on the h-BN by mutual electrostatic interactions. The successful modification, self-assembly and immobilization were confirmed by XPS, Zeta potential, Raman spectra, SEM and TEM characterizations as well as elemental mapping. Afterwards, this hybrid filler (h-BN@GO) was introduced into epoxy, subsequently being reduced into epoxy/h-BN@rGO by the amine curing agent as the epoxy was cured at the high temperature. Due to the excellent thermal conductivity of h-BN and high dielectric constant of rGO, this incorporated filler combined both the properties together. On the one hand, it was found that the dielectric constant for epoxy/h-BN@rGO (up to ~15) is much higher than that of epoxy filled with h-BN as well as epoxy filled with directly mixed h-BN and rGO at the same filler concentration. On the other hand, of particular note is that the dielectric loss decreased as increase of h-BN@rGO loading, resulting in obviously lower dielectric loss (0.0068) than that of neat epoxy (0.0092) at the frequency of 100 Hz when the hybrid filler content was 30 wt%. The phenomenon of extremely low dielectric loss is interesting and the mechanism for the well-improved dielectric properties is concluded as inhibited mobility of charge carriers due to embedded insulating network of h-BN as well as suppressed direct contact and agglomeration of rGO sheets due to immobilization. In addition to obviously improved dielectric properties, the nanocomposites also exhibited good capability of heat dissipation with thermal enhancement factor of 390% at 30 wt% loading in comparison with neat epoxy. This result was much higher than polymers filled with same volume content of common dielectric fillers such as barium titanate [7].

Our method is simple and it provides the new thoughts for preparation of dielectric materials with not only high dielectric constant, ultra-low dielectric loss, but also good capability of heat dissipation.

2. Experimental section

2.1. Materials

Graphite powders were purchased from Qingdao Black Dragon graphite Co., Ltd. Micron sized hexagonal boron nitride (average lateral size: 30 μm) was supplied by Qinhuangdao Eno Material Co., Ltd. 3-aminopropyltriethoxysilane (APS) was purchased from Aladdin Chemicals Co., Ltd. Potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4 98%), hydrogen peroxide (H_2O_2), Nitric acid (HNO_3), 4, 4-diamino diphenyl methane (DDM), ethanol, tetrahydrofuran (THF) and epoxy (E-44) were supplied by Kelong Chemical reagent plant (Chengdu, China).

2.2. Surface modification of h-BN

500 mg h-BN was dispersed in 500 ml HNO_3 solution (65% w/w), followed by sonication for 5 h using an output power of 120 W and a rapid neutralization, as was shown in Fig. 1 (1). Then the product was collected by three washing steps by centrifugation and dried at 60 °C under vacuum. This procedure was designed to introduce −OH groups on the surface of h-BN through oxidation, named h-BN (HNO_3).

Secondly, modified h-BN by HNO_3 (500 mg) was mixed with 5 wt% of silane coupling agent APS in the 500 ml ethanol solution (ethanol: $H_2O = 95:5$). Then, the solution was kept at 60 °C overnight for reaction. After that, the obtained product named h-BN-NH_2 was washed by deionized water and ethanol for 2 times, and dried under vacuum.

2.3. Electrostatic self-assembly of h-BN-NH_2 and GO

Before electrostatic self-assembly, GO was fabricated via the exfoliation of natural graphite by Hummers method [33]. Then the exfoliated GO was collected by centrifugation to remove the non-exfoliated graphite. After that, steady GO aqueous solution was achieved by sonication in deionized water for 2 h.

From Fig. 1 (2), the electrostatic self-assembly between GO and h-BN-NH_2 was achieved through a simple procedure: 500 ml GO aqueous solution (0.15 mg/ml) and 500 ml h-BN-NH_2 suspension (5 mg/ml) were mixed together under mild magnetic stirring for 2 h. Then, the h-BN@GO powder was collected by centrifugation and dried under vacuum.