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Dielectric and thermal properties of epoxy/boron nitride nanotube composites*

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Abstract: We report the fabrication of and investigations into the dielectric and thermal properties of epoxy/boron nitride nanotube (BNNT) composites. It was found that BNNT fillers can effectively adjust the dielectric constant of epoxy. Moreover, the thermal conductivity of epoxy was improved by up to 69 % with 5 wt % BNNTs. Our studies indicate that BNNTs are promising nanofillers for polymers, to obtain and control an adjustable dielectric property and improved thermal conductivity.

Keywords: glass transition; particle synthesis; recommendations; sampling; temperature-modulated differential scanning calorimetry (DSC).

INTRODUCTION

In recent years, the strong need for electronics packaging has provided an ongoing incentive to develop new materials possessing novel dielectric and thermal properties [1,2]. Dielectric properties are the measure of how easily a material is polarized in an external electric field. These properties of packaging materials play an important role in device performance. For example, high dielectric constant materials are needed because they are attractive as potential materials for high charge-storage capacitors, electrostriction artificial muscles, and smart skins for drag reduction, etc. [3]. On the other hand, materials possessing low dielectric constant are primarily important for decreasing capacitance between wire interconnections in integrated circuits [4].

In addition, the heat produced by modern electronic components is greater and more highly concentrated as a result of higher clock speeds and reduced size [5]. Metal materials were used in integrated circuit packages to provide thermal paths for removal of heat. However, this mechanism has reached its maximum potential. In recent years, the polymeric materials in the components are increasingly important as heat-releasing paths for the removal of excess heat that may cause failure. Unfortunately, polymeric materials are intrinsically poor thermal conductors, and they must be modified to improve heat removal from electronics. One approach to highly thermo-conductive polymeric materials is to embed inorganic ceramic fillers with intrinsically high thermal conductivity into polymers, providing heat-conducting paths through the composite to increase mean thermal conductivity. Conventional fillers for this application include silicon nitride (Si_3N_4), alumina (Al_2O_3), aluminum nitride (AlN), and boron nitride (BN) microsize particles, etc. [6]. In the past two decades, lots of methods have been developed to synthesize nanomaterials, including nanowires, nanotubes, nanosheets, etc. They are obvi-

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ously more effective fillers for thermal conductivity improvement of polymeric materials because, empirically, fillers with a high aspect ratio may be particularly effective in providing good particle-to-particle contact to efficient transfer heat. However, only in very recent years have the quantity and quality of synthesized nanomaterials marginally met the requirements of studies of their composite materials.

Boron nitride nanotubes (BNNTs) are novel nanofillers due to their constant wide bandgap (~5.5 eV) [7,8], super thermal stability [9,10], high thermal conductivity [11–14], and superior mechanical properties [15–17]. These properties make it possible to use BNNTs as a component in those composite materials where high thermal conductivity, low coefficient of thermal expansion, mechanical reinforcement, and flexible dielectric properties are sought [18]. Moreover, in contrast to conventional BN microsized particles, the one-dimensional morphology, high aspect ratio, and nanoscale size of BNNTs make them more effective in contributing to improvements in the properties of the matrix, and also introduce fewer defects according to well-established theoretical modes for predicting the properties of composite materials [19–24].

In this paper, we report the first usage of BNNTs to adjust dielectric properties of polymer. The epoxy-BNNT composites were fabricated by an in situ polymerization method. Investigations into the dielectric properties of the composite materials have revealed that a decreased dielectric constant is achieved by embedding BNNTs in epoxy. We have also studied the thermal properties of the composites. An effective improvement of thermal conductivity is disclosed and analyzed, and we have also discovered a decreased glass transition temperature for composites, which is attributed to the interaction between epoxy molecules and BNNTs.

COMPOSITE FABRICATION

The multi-walled BNNTs were fabricated by a chemical vapor deposition method (CVD) using boron and metal oxide as reactants, as we reported before [25,26]. The epoxy-BNNT composites were fabricated by in situ polymerization methods. Briefly, in order to make the composites with a 1 wt % BNNT fraction, 8.8 g epoxy resin was mixed with 100 mg BNNTs. The BNNTs were dispersed by grinding the mixture for 30 min. Then, 1.1 g of a curing agent, diethylenetriamine, was added and the resultant mixture was ground over 30 min for the complete BNNT dispersion. The obtained paste was poured into a Teflon model. The sample was cured at 0 °C for 12 h to avoid appearance of bubbles and then at 80 °C for 5 h and at 100 °C for 5 h.

DIELECTRIC PROPERTIES

The surface morphology of the obtained epoxy-BNNTs composites was investigated by scanning electron microscopy (SEM), as shown in Fig. 1. The appearance of BNNTs (white-colored stripes) in the epoxy matrix is obvious. The BNNTs keep straight morphology and are uniformly dispersed within the epoxy. It should be noted that the straight shapes are peculiar to BNNTs as opposed to curled and entangled morphologies of conventional CVD-grown carbon nanotubes (CNTs) [27]. No obvious alignment was observed because model curing instead of casting was utilized during the sample fabrication.

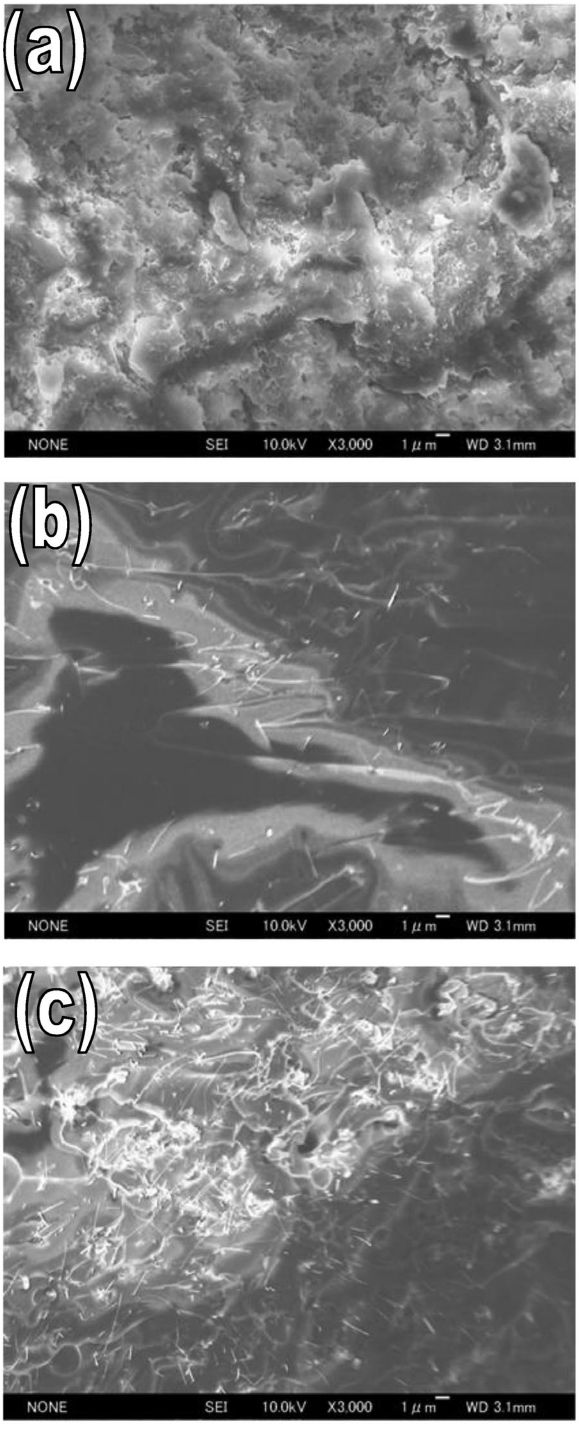

Fig. 1 Cross-sectional SEM images of (a) epoxy, (b) a composite with 1 wt % BNNT fraction, and (c) a composite with 5 wt % BNNT fraction.

The dielectric properties of the epoxy-BNNT composites were studied by a Wayne Kerr Precision Component Analyzer. Figure 2 shows the dielectric constant-frequency curves. With an increase in frequency, the dielectric constants of all three samples decrease slightly. This is because, in the range of frequencies applied, instead of relaxation polarization, the displacement polarization is in effect, which is responsible for the regarded changes in the dielectric constant at optical frequencies [1,2]. It is also clear that with more BNNTs added, the dielectric constants of the composites effectively decrease.

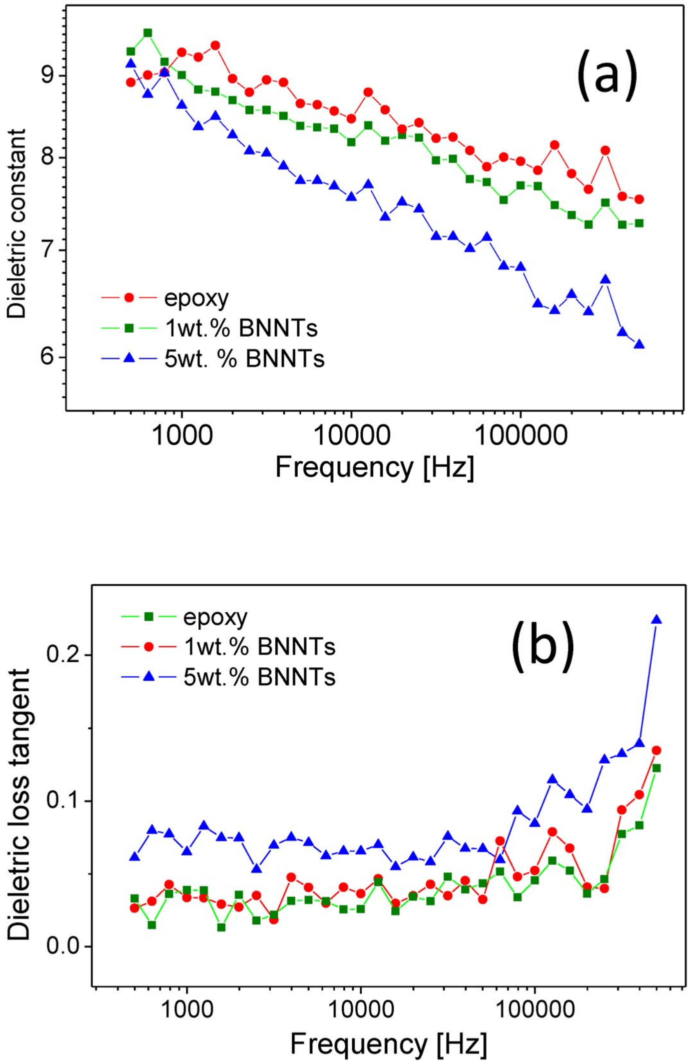

Fig. 2 Frequency-dependent (a) dielectric constant and (b) loss tangents of epoxy and its BNNT composites.

So far, there have been no reports in regard to dielectric constant of BNNTs since the common powder-like BNNT sample morphology makes it difficult to avoid the effects of air on the measured values. Extensive ab initio finite electric-field calculations revealed a BNNT dielectric constant of 5.9 regardless of their radius and chirality [28], and the frequency dependence was not investigated. Some theoretical models were developed to calculate the dielectric constant of composite materials, including well-known logarithmic mixing rule [29] and Maxwell–Garnett approximation [30]. The logarithmic mixing rule is based on the following formula: $\log \varepsilon_{\text{composite}} = f_{\text{BNNTs}} * \log \varepsilon_{\text{BNNTs}} + f_{\text{epoxy}} * \log \varepsilon_{\text{epoxy}}$, in which ε is the dielectric constant and f is the volume fraction. The Maxwell–Garnett approximation is based on the following equation: $\varepsilon_{\text{composite}} = \varepsilon_{\text{BNNTs}} * [(1 + 3f_{\text{epoxy}}\beta)/(1 - f_{\text{epoxy}}\beta)]$, in which $\beta = (\varepsilon_{\text{epoxy}} - \varepsilon_{\text{BNNTs}})/(\varepsilon_{\text{epoxy}} + 2\varepsilon_{\text{BNNTs}})$. Roughly, herein we consider dielectric constant values at a frequency of 1000 Hz. For the 1 wt % BNNTs in epoxy, the calculated $\varepsilon_{\text{composite}}$ is 9.27 and 9.26 when the Maxwell–Garnett approximation and logarithmic mixing rule are used, respectively, while the experimental data is 9.01. In case of 5 wt % BNNTs, the numbers become 9.10 and 9.09 for two models, respectively, compared with the experimental value of 8.62. The two models give very similar results in both cases, however, the calculated values are always larger than the experimental data. The discrepancy is thought to originate from the two possible reasons: first, although no obvious bubbles were observed in the composite with the naked eye; some absorbed air on BNNTs is supposed to be mixed with the composites; which means that there are three phases in the composites instead of two which the models consider. The second possibility is that the dielectric constant of BNNTs is not as high as suggested, i.e., 5.9 [28]. Keeping in mind that a hexagonal BN has the dielectric constant of only 4, it is possible that the BNNTs' dielectric constant is lower than 5.9. It is worth noting that the two mentioned possibilities may take place simultaneously.

The loss tangents ($\tan\delta$) of the epoxy/BNNT composites are shown in Fig. 2b. As exhibited in Fig. 1, the BNNTs are well dispersed in the epoxy matrix, so a low loss tangent was revealed for the composites, and only a slight increase was observed when BNNTs were added, the latter was due to the interfacial losses. The loss tangent also slightly increased with an increase in applied frequency. This is believed to be caused by existent porosities in the composites. These data reveal that after mixing with BNNTs, epoxy is still dielectric, but its dielectric constant becomes finely adjustable.

In other studies, many types of inorganic powders were used to modify dielectric properties of epoxy. In most cases, higher dielectric constants were achieved. For example, by utilizing chelating agent to assist, a very high dielectric constant (>50) was obtained by adopting only 5 wt % barium titanate particles as fillers [31]. However, in Cho et al.'s studies, a maximum dielectric constant of around 60 were obtained by embedding 50–60 vol % barium titanate particles in epoxy [32]. With more barium titanate embedment, the dielectric constant even decreased due to introduction of pores or voids. In addition, some modified barium titanate materials, such as $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ particles were also studied, but the effect was not as good as expected. A maximum dielectric constant of 23.6 was obtained with 70 wt % inorganic particles filled [33]. The most impressive data for high dielectric constant of epoxy is obtained in polyanline/epoxy composites: a super high dielectric constant of 3000 was obtained, and a dielectric loss tangent less than 0.5 at 10 kHz was kept [34]. Instead of composites, modifying epoxy's molecular chains is also useful for adjusting dielectric properties of epoxy. For example, the introduction of trifluoromethyl (CF) groups into the chain of the epoxy resin resulted in a decreased dielectric constant due to polarization effects of CF groups [35].

THERMAL PROPERTIES

In addition to being a reliable dielectric material, BNNTs are excellent thermal conductors [36]. Their one-dimensional morphology makes them even more effective for the thermal conductivity improvement of a matrix material. In the present work, the thermal conductivity of the epoxy/BNNT composites was tested by a hot-disk method. The specific heat, thermal diffusivity, and thermal conductivity of the composites are summarized in Table 1. There is not an obvious change in specific heat. By contrast, the thermal diffusivity of the composites dramatically increases, e.g., a 69 % improvement in thermal conductivity of epoxy/BNNT composites is recorded at a 5 wt % BNNTs fraction. As far as such thermal conductivity improvement is concerned, the closest competing nanomaterial to BNNTs are CNTs. For example, Biercuk et al. reported that under 1 wt % single-walled CNTs embedment in the epoxy, the thermal conductivity was improved up to 100 % [37]. However, two points should be considered here. One is that the pristine epoxy that the authors used possessed a thermal conductivity of 0.2 W/mK compared to the present 0.49 W/mK. Based on many well-established models, the initially lower thermal conductivity of a starting material makes its rise easier [20,21,30]. The other issue is that the regarded authors used single-walled CNTs, which exhibit a higher aspect ratio (~1000) compared with the presently utilized multi-walled BNNTs (aspect ratio of ~100–150). In fact, it was also reported that the thinner nanotubes have higher thermal conductivities [36]. In another work, 20 wt % multi-walled CNTs were found to improve thermal conductivity of PVC (a starting value of 0.318 W/mK) to 0.555 W/mK (~87 % increase), again indicating the importance of quality, aspect ratio, and diameter of nanotubes for the thermal conductivity improvement [38].

Table 1 Summary of thermal properties of epoxy and its BNNT composites.

Sample	Specific heat (MJ/m^3K)	Thermal diffusivity (mm^2/S)	Thermal conductivity (W/mK)
Epoxy	0.0023	202.9	0.49
Epoxy + 1 wt % BNNTs	0.0027	207.6	0.55
Epoxy + 5 wt % BNNTs	0.0028	299.8	0.83

Compared with conventional BN or AlN micro-size particles with low aspect ratio, the advantage of BNNTs can be revealed even more clearly. By the conventional fillers, very limited improvement of thermal conductivity can be obtained at low filler fraction, and remarkable improvement can only be obtained at very high filler fraction. For example, in ethylene vinyl acetate copolymer/BN particle composites, a 20 wt % BN particle induced an improvement of thermal conductivity from 0.3 to 0.8 W/mK along the direction of filler alignment, while no improvement was obtained along the perpendicular direction [39]. In the BN platelet-filled polymers, both experimental and theoretical data indicate that only when the volume fraction is higher than 40 %, can the thermal conductivity be remarkably improved [40]. Thus, at this stage it can be suggested that the single-walled BNNTs could be the best ultimate nanofillers for dielectric highly thermo-conductive polymer composites based on their high aspect ratio and super high thermal conductivity along axis. Regretfully, the presently achievable qualities and quantities of single-walled BNNTs are still far from the demands of composite material fabrication.

In addition, it should be noted that according to the theoretical models [20,21,30], after achieving a certain fraction of BNNTs in the matrix, the BNNTs start to contact each other, forming an effective channeling network for the thermal transfer [19,21]. The thermal conductivity would be dramatically improved after this threshold point. In our experiments, we used not more than 5 wt % BNNTs due to experimental difficulties. As shown in SEM images, Fig. 1, at this fraction, the tubes still do not contact each other to form a continuous channel for the heat transfer. Thus, it is believed that with a much higher fraction of BNNTs embedded in the epoxy, the thermal conductivity would further drastically increase. The related experiments are underway.

The glass transition of a polymer is one of the most interesting topics because many properties, such as mechanical and thermal ones, change dramatically at the glass transition temperature T_g. [41]. Herein, the differential scanning calorimetry (DSC) tests were performed to investigate the influence of the BNNTs' embedment on the epoxy's T_g. The samples were firstly heated to 110 °C and kept for 30 min to remove moisture. Then the temperature was decreased to room temperature and then increased again at a rate of 5 °C/min during the measurements. The second-cycle data are presented in Fig. 3. The BNNTs' embedment effectively decreases T_g. This indicates that the BNNTs interact with the epoxy molecules, inducing their higher mobility and/or a higher time constant for the interfacial healing processes [42–45]. These interactions can be explained in terms of π-stacking noncovalent interactions, which in this case, occur between diglycidyl ether of bisphenol A and the BNNTs' atomic layers [46]. A molecular dynamics simulation is currently being carried out to confirm the regarded interactions.

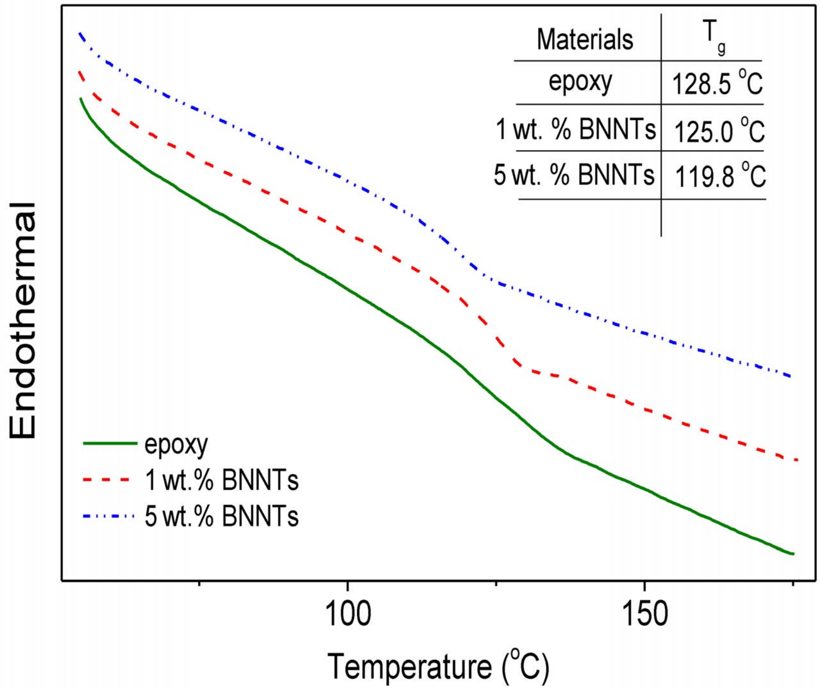

Fig. 3 Typical DSC curves of epoxy and its BNNT composites and their glass transition temperatures.

SUMMARY

In this paper, we fabricated epoxy/BNNT composites and investigated their dielectric and thermal properties. It was found that the embedment of BNNTs effectively reduced the epoxy's dielectric constant, whereas it only slightly increased the loss tangent, indicating BNNTs might be useful for making composite materials possessing low dielectric constant. In addition, thermal conductivity improvements of epoxy/BNNT composites were investigated. With only a 5 wt % BNNT fraction, the thermal conductivity of the epoxy was improved by 69 %, which is comparable with data produced by CNTs, and better than conventional BN microsize particle fillers. Our studies indicate that BNNTs, as a dielectric highly thermo-conductive nanomaterial, are prospective fillers for polymers fully capable of their thermal and dielectric properties adjustment/tuning.

Actually, ceramic particles have been used as fillers for polymeric composites to obtain improved or tunable properties for many years. In recent years, many nanomaterials have been invented and synthesized. As fillers for composite materials, nanomaterials possess advantages such as high aspect ratio, low defect concentration introduction to matrix, etc. Unfortunately, the yield and quality of nanomaterials were problematic for a long period. For example, conventional BN particles were used to improve thermal conductivity and tune dielectric properties of polymers for many years. However, the problems for BN particles are as follows: (1) only the (002) plane possesses very high thermal conductivity, while along other atomic planes, the thermal conductivity is low; (2) the microsize particles may easily introduce some defects, voids in the matrix. A tubular BN nanostructure can solve these problems well with maximized surface area of (002) plane and low defect introduction. However, the studies on BNNT's polymeric composites were only initiated from 2005 due to difficulties of synthesizing large quantities of highly pure BNNTs. Multi-walled BNNTs were used in all composite-related studies, while the quality and yield of single-walled BNNTs are still not good enough for composite fabrication. In fact, the current challenges of nanocomposites is still fabrication of large quantities of nanofillers with high quality. Although the nanocomposites are still far from real applications, they are very promising due to their intrinsic advantages. For example, single-walled BNNTs can be the ultimate nanofillers for highly thermo-conductive insulating composite materials with adjustable dielectric properties.

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