Dielectric properties of polyarylene ether nitrile composites based on modified boron nitride

Shuning Liu¹,², Chenchen Liu¹,², Xiaofang Feng¹,², Guo Lin¹,², Zhongxiang Bai¹,² and Xiaobo Liu¹,²*

¹School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, China
²Sichuan Province Engineering Technology Research Center of Novel CN Polymeric Materials, Chengdu 611731, China
*Corresponding author: liuxb@uestc.edu.cn

Abstract. Polyarylene ether nitrile (PEN) is a new type of super engineering polymer with excellent high-temperature resistance, radiation resistance, good electrical insulation, and mechanical properties. In this work, boron nitride (BN) and copper phthalocyanine (CuPc) hybrids were integrated as fillers, which were further dispersed into PEN matrix by solution casting method to obtain a series of PEN composite films. The successful preparation of hybrid fillers was proved by means of X-ray photoelectron spectroscopy and scanning electron microscopy. The test results of the dielectric properties of the composite films show that the CuPc-BN/PEN films exhibit good dielectric properties. When the mass fraction of filler reaches 10 wt%, the dielectric constant of the PEN composite film increases by 17%. This study shows that the composites composed of modified BN and PEN has excellent dielectric properties and has great application potential in heat-resistance thin-film capacitors.

1. Introduction

In order to meet the needs of the electronics industry, high dielectric constant materials show broad application prospects in capacitors and energy storage, etc. [1]. Compared with traditional high-dielectric ceramic materials, polymer composite dielectric materials are widely used in energy storage capacitors and other electronic devices because of their lightweight and easy handling. Polyarylene ether nitrile (PEN) is a novel super engineering polymer with heat resistance, radiation resistance, chemical corrosion resistance as well as excellent mechanical performance and insulation [2-4]. These characteristics indicate that polyarylene ether nitrile is a promising matrix to realize the application of polymer composites in the field of dielectrics.

In order to improve the dielectric constant of polymer dielectrics, high dielectric constant fillers and/or conductive fillers are introduced into polymeric matrix to obtain polymer composite dielectric materials with higher dielectric constant. However, the compatibility between the inorganic filler and organic polymeric matrix is usually poor. The resultant aggregation of the filler would lead to the inhomogeneous electric field and the degraded dielectric loss. Surface modification toward the fillers is an effective strategy to improve the compatibility between fillers and matrix and reduce the dielectric loss of polymer composites [3]. In this paper, copper phthalocyanine (CuPc) was used as interfacial layer to modify boron nitride (BN). The modified BN hybrids were further incorporated into PEN matrix for enhanced dielectric properties.
2. Experimental section

2.1. Preparation of CuPc-BN hybrids
A certain amount of CuPc and BN were added to the beaker that had been rinsed with 10 mL of DMF, mechanically stirred at room temperature for 24 h, washed three times with DMF and then dried. Subsequently, the obtained CuPc-BN was sintered at 350 °C, 450 °C, 550 °C, and 800 °C for 2 hours.

2.2. Preparation of CuPc-BN/PEN composite films
A certain amount of CuPc-BN was uniformly dispersed in NMP solvent and sonicated for half an hour, then 1 g of PEN powder was added and stirred at 80 °C for about 20 min until completely dissolved in the mixture. After that, the mixed solution was cast onto a glass plate leveled in advance, dehydrated in the programmed oven, and cooled to room temperature to obtain the CuPc-BN/PEN composite film.

2.3. Characterization
Scanning electron microscopy (SEM) was conducted to investigate the structure of BN, CuPc, and CuPc-BN using a JEOL JSM-5900LV. The surface of CuPc-BN was examined by X-ray photoelectron spectroscopy (XPS) using an ESCA 2000 from VG Microtech. The dielectric properties were measured by a TH 2819A LCR meter.

3. Results and discussion

To visually observe the microstructure of the prepared nanofillers, the prepared CuPc-BN fillers with different mass ratios were characterized by scanning electron microscopy. As shown in Figure 1(a)–(b), pure BN exhibits oblate spheroids, while CuPc exhibits a multilayer sheet-like structure. Figure 1(c)–(e)
shows the morphologies of fillers with different mass ratios of CuPc and BN. It can be seen that with the increase of BN content in the filler, the adhesion of BN on the CuPc sheet becomes more and more uniform. After sintering, the lamellar structure of CuPc was slightly damaged as shown in Figure 1(f).

XPS analysis was used to ascertain the composition of CuPc-BN. It can be seen from Figure 2(a) and 2(b) that CuPc-BN exists in CuPc and all elements in BN, and the existence of the phthalocyanine ring is proved, which proves the successful preparation of CuPc-BN. As shown in Figure 2(c)-(d), the spectrum of CuPc-BN after sintering is generally the same as that before sintering, which proves that sintering does not change the composition of CuPc-BN.

To study the effect of each component content in CuPc-BN on the dielectric properties of CuPc-BN/PEN composite films, the dielectric constant and loss of the composite films containing 5% of each filler were characterized. As shown in Figure 3(a), the dielectric constant of the polymer film was enhanced after introducing CuPc-BN into the PEN matrix regardless of the kind of CuPc-BN. Compared with pristine PEN, the dielectric constant of the composite film was increased by 12.8%-17.9% at an electric field frequency of 1 kHz. With the increase of the frequency, the polarizability of the polymer film gradually cannot keep up with the change of the electric field frequency, and the dielectric constant exhibits a decreasing trend[5]. Has good dielectric stability. The change in dielectric loss is similar to that of the dielectric constant. Figure 3(b) indicates that the dielectric loss increases with the introduction of CuPc-BN. When the content of CuPc in CuPc-BN reaches 90%, the dielectric loss of the polymer composite film significantly increases. Combining the dielectric properties of PEN composites with different CuPc-BN, we choose 7:3 to carry out the next step in the research on the dielectric properties of polymer films with filler content.

Figure 2. (a) XPS survey spectrum and (b) XPS C1s core-level spectrum of 7:3; (c) XPS survey spectrum and (d) XPS C1s core-level spectrum of 7:3*.
As shown in Figure 4(a), with the increase of filler content in the polymer composite film system, the dielectric constant of the composite film rises rapidly. When the filler content was improved from 5 wt% to 15 wt%, the dielectric constant increased by 31%. As the electric field frequency rises, the dielectric constants of the polymer films all decrease but remain at a small level. When the electric field frequency is from 100 Hz to 1000 kHz, the decrease in the dielectric constant of the composite films can be maintained at about 4%. As shown in Figure 4(b), with the increase of CuPc-BN content in the dielectric film, the dielectric loss also increases accordingly. However, the increase of dielectric loss is much smaller than that of dielectric constant. When the filler content reaches 15 wt%, the dielectric loss can remain below 0.015, which reflects the excellent dielectric properties of CuPc-BN/PEN.

4. Conclusion
In this work, several CuPc-BN fillers with different CuPc mass fractions were prepared, and it was proved by XPS and SEM that BN was successfully modified on CuPc. After introducing CuPc-BN into the PEN matrix, the dielectric properties were improved. When the introduction amount of CuPc-BN reaches 15%, the dielectric constant of CuPc-BN/PEN increases by 76.3% compared with pure PEN film, which reaches 6.72 when the electric field frequency is 1000 Hz. Meanwhile, the dielectric loss of CuPc-BN/PEN can be kept at a low level. When the introduction of CuPc-BN reaches 15%, the dielectric loss can still be kept below 0.015. The excellent dielectric properties of CuPc-BN/PEN composite dielectric films make them have broad application prospects in the field of dielectrics.
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