

The preparation, mechanical and dielectric properties of PEN/HBCuPc hybrid films

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Abstract Polyarylene ether nitriles (PEN)/hyperbranched copper phthalocyanine (HBCuPc) hybrid films have been successfully fabricated via PEN mixing with HBCuPc in *N*-methylpyrrolidone solution, solution-casting and then co-crosslinking at high temperature. The dielectric properties of the films were measured to find that dielectric constant as well as dielectric loss of the hybrid films increased linearly with the increasing HBCuPc content without sacrificing dielectric breakdown strength compared to that of the pristine polymer. These results shows PEN/HBCuPc hybrid films have a high dielectric constant and low dielectric loss at a high operational frequency (>1 kHz). The tensile strength and elongation at break of the hybrid films were increased with the increase of HBCuPc content and the thermal stability was improved with the increase of HBCuPc content.

1 Introduction

Recent interests in the use of novel polymeric materials for high dielectric constant effects have increased owing to their possible application in high-energy density and pulsed capacitors [1–3]. In particular, materials which demonstrate desired dielectric properties at high operational frequencies (>1 kHz) are highly sought after. Existing polymeric dielectrics, such as ceramic-polymers [4–7] and metal-polymeric composites [8], typically exhibit a strong

interfacial polarization (Maxwell–Wagner effect [9]), and this effect results in a strong dispersion of the dielectric constant. Polymeric materials mixed with phthalocyanine (Pc) tetramers have been reported with good dielectric response which is heavily related to a space charge effect [10]. However, the dielectric loss of these percolative systems is generally large [4–8] and efforts are still necessary to improve the stability and flexibility of these systems. The use of Pc systems is an intriguing approach, and Pc polymer coated nanoparticles have been prepared and suggested as good candidates for dielectric applications [11]. However, Pc particles are susceptible to be agglomerated in the polymer matrix due to incompatibility of CuPc with the polymer matrix, which will reduce the breakdown field strength and increase the dielectric loss.

As an excellent engineering thermo-plastic resins, PEN is well known for its outstanding properties such as thermal and thermo-oxidative stability and chemical inertia [12–14]. The introduction of CN group enhances the polarizability of polymer compared to that of polyarylether. PEN copolymer can be processed by solution blending and cast, which provide the possibility of hybrid films preparation through sol–gel method, but there are few reports on the properties of dielectric materials use. The PEN/TiO₂ hybrid films were successfully prepared through sol–gel method and solution cast in our previous works [15]. These hybrid films present exciting avenues toward creating large dielectric responses in primarily organic materials, but there has not been much attention to the intrinsic dielectric high-frequency response of all-organic systems.

In order to combine the property of high dielectric constant of Pc with the excellent mechanical and thermal properties of PEN copolymer, the hyperbranched CuPc/PEN hybrid films were prepared by solution-mixing, casting and co-crosslinking at high temperature, and provided a strategy

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toward this aim utilizing an organic multichromophore structure such as a Pc dendritic system could be cured with reactive CN groups of PEN for enhancing the compatibility. A new technical approach would be obtained to prepare high strength, high thermal stability, high dielectric properties, low dielectric loss and flexibility polymer composite for dielectric high-frequency response in this paper.

2 Experimental

2.1 Materials

1,2-Bis(3,4-dicyanophenoxy)biphenylene was synthesized in our laboratory. PEN was provided by Union Laboratory of Special Polymers of UESTC-FEIYA, Chengdu, China. It is a copolymer derived from 2,6-difluorobenzonitrile with hydroquinone and resorcin with the inherent viscosity of 0.88 dL/g (in *N*-methylpyrrolidone, 0.005 g/mL). *N*-methylpyrrolidone ($\geq 99\%$), CuCl ($\geq 99\%$) were obtained from TianJin BODI chemicals.

2.2 Preparation of hyperbranched CuPc

To a flask, 1.31 g (3 mmol) of 1,2-bis(3,4-dicyanophenoxy)biphenylene and 0.099 g (1 mmol) of CuCl were dissolved in 40 mL of NMP and then the mixture was stirred at 200 °C for 4 h [16]. The reaction mixture was poured into 800 mL of water. The crude product was collected by filtration, washed with water, and dried in vacuo. After refluxing in methanol twice, the product was filtrated and washed using cold methanol for three times. The dark blue powdery product was dried in vacuo. The synthesized procedures are shown in Scheme 1.

2.3 Preparation of PEN/HBCuPc hybrid films

PEN/HBCuPc hybrid films were prepared using solution-casting method. For the solution-mixing of PEN and

HBCuPc with the HBCuPc of 10, 20, and 30 wt% in a flask, HBCuPc was added to the solution of PEN in NMP, and then mechanical stirred for 2 h at 160 °C. Afterward, the solution mixture was poured onto a clean glass slide for casting and dried in oven at 80, 100, 120, 160, 200 °C for 2 h, respectively, then at 300 °C for 4 h to cure and then slowly cooled to room temperature. The typical film thickness was 0.1 mm. For the dielectric characterization, the films were cut into small pieces of about 10 × 10 mm, and coated with conductive silver paste on both surfaces.

2.4 Characterization

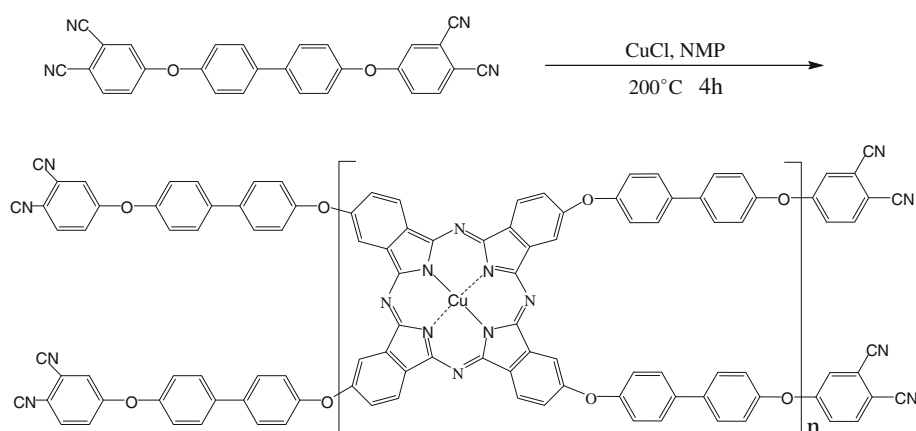
Mechanical properties of the films were measured using SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine and gained as average value for every three samples. The thermal gravimetric (TG) analysis of the films were carried out under N₂ atmosphere at a heating rate of 10 °C min⁻¹ using TA instrument Q50 series analyzer system combination with data processing station. Dielectric measurements for the PEN/HBCuPc hybrid films were performed using a dielectric analyzer (DEA 2970, TA Instruments). The samples were sandwiched between the ceramic parallel plate sensors, and subjected to a force of 200 N. The experiments were performed at frequencies of 0.1, 1, 10, 100, 1,000 kHz at 20 °C with 40% humidity.

3 Results and discussion

3.1 Chemical structure of the films

The chemical structure of the PEN and its hybrid films prepared at different temperature was characterized with FTIR spectra. The typical absorption at 2,231 cm⁻¹ is assigned to the symmetrical stretching of the CN group, and the absorption at 1,247 and 1,287 cm⁻¹ is assigned to -C-O-C-, which are ortho to CN group respectively. They

Scheme 1 Synthesis of hyperbranched copper phthalocyanine



are all the characteristic absorption of polyarylene ether nitriles and appeared in all polymer and hybrid films. The characteristic absorption of phthalocyanine ring of HBCuPc occurred at 1,010 and 1,620 cm^{-1} . The introduction of HBCuPc would decreased the CN group absorption of PEN at 2,231 cm^{-1} , and a new absorptions at 1,360 and 1,520 cm^{-1} was observed, which is triazine structure contributed to co-crosslinking of PEN and HBCuPc at high temperature.

3.2 Thermal and mechanical properties of the films

The TG profiles of the PEN/HBCuPc hybrid films are shown in Fig. 1. There are obvious increases in the thermal stability of the hybrid films with the increase of HBCuPc content, the initial decomposition temperature (T_{id}) of the hybrid films obviously higher than those of pure PEN films. The hybrid film's initial decomposition temperature of 470 °C increased by about 50 °C, compared to that of pure polymer up to 420 °C. It can also be seen that decomposition of the pure film is more speedy than that of hybrid films, and the char residue of the films increases with the HBCuPc weight content. The film with a 30% HBCuPc content has a 75% char residue at 800 °C, compared to the 42% char residue of pure polymer. From this point of view, the incorporation of HBCuPc enhanced the thermal stability of hybrid films. HBCuPc serving as cross-link points would decrease and limit the segmental mobility of the polymer chain, which results a higher thermal stability for the hybrid films.

The mechanical properties of the hybrid films are listed in Table 1. The pure PEN shows excellent mechanical property as special engineering plastics. The introduction of HBCuPc increases the values of the tensile strength and the elongation at breaking. In this study, the mechanical property of 30 wt% HBCuPc hybrid films was also

Table 1 Mechanical properties of PEN and PEN/HBCuPc hybrid films

PEN/HBCuPc (w/w)	100:0	90:10	80:20	70:30
Tensile strength (Mpa)	91.47	92.63	106.06	115.74
Elongation at breaking (%)	5.26	7.19	7.22	7.93

measured and was found too flexible, the values of the tensile strength and the elongation attained 115.74 MPa and 7.93%, the tensile strength and elongation at breaking of 30 wt% PEN/HBCuPc hybrid film increased approximately 26 and 50% compared to that of pure PEN films, respectively. But the tensile strength of 10 wt% PEN/TiO₂ hybrid film decreased approximately 40% compared to that of pristine PEN films in our previous research [15]. It can be seen that there is a interesting tendency of strength and elongation both increase with the increasing HBCuPc content, which are contributed by the co-crosslinking of PEN and HBCuPc.

3.3 Morphologies of the films

The mechanical, thermal and dielectric properties are all greatly influenced by the miscibility between the organic phase and inorganic phase. The agglomeration of the inorganic particles has great influence on the mechanical property as well as the dielectric property of the films. Figure 2a–c display the SEM morphology of PEN, uncured and cured hybrid films containing 10 wt% HBCuPc, respectively. It can be seen from the SEM micrographs, there are the better compatibility between PEN and HBCuPc to provide a good mechanical properties and greatly decrease interface loss. For cured hybrid films, no phase-separated was observed and the morphological profiles was very compact. This condensed structure would increase mechanical properties and dielectric properties of hybrid films.

3.4 Dielectric properties of the hybrid films

The dielectric constant can be increased by introduced of a polar group, such as CN group. Cyano group can result to dipole polarization and make CN substituted PEN possess a higher dielectric constant than the corresponding polyarylether polymer. The incorporation of HBCuPc changed the chemical environment of the polymer, and it was necessary to characterize the influence of it on the value of dielectric constant and dielectric loss. Dielectric properties of hybrid films with different weight fractions of HBCuPc measured at room temperature are shown in Fig. 3. As generally expected, the dielectric constants of hybrid films are increased linearly with the increasing HBCuPc content and reach 4.8 for hybrid film with 20 wt% HBCuPc, 45%

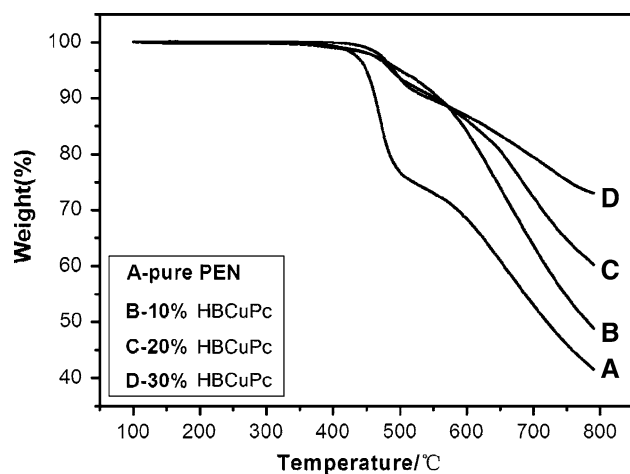


Fig. 1 TGA curves of PEN and PEN/HBCuPc hybrid films

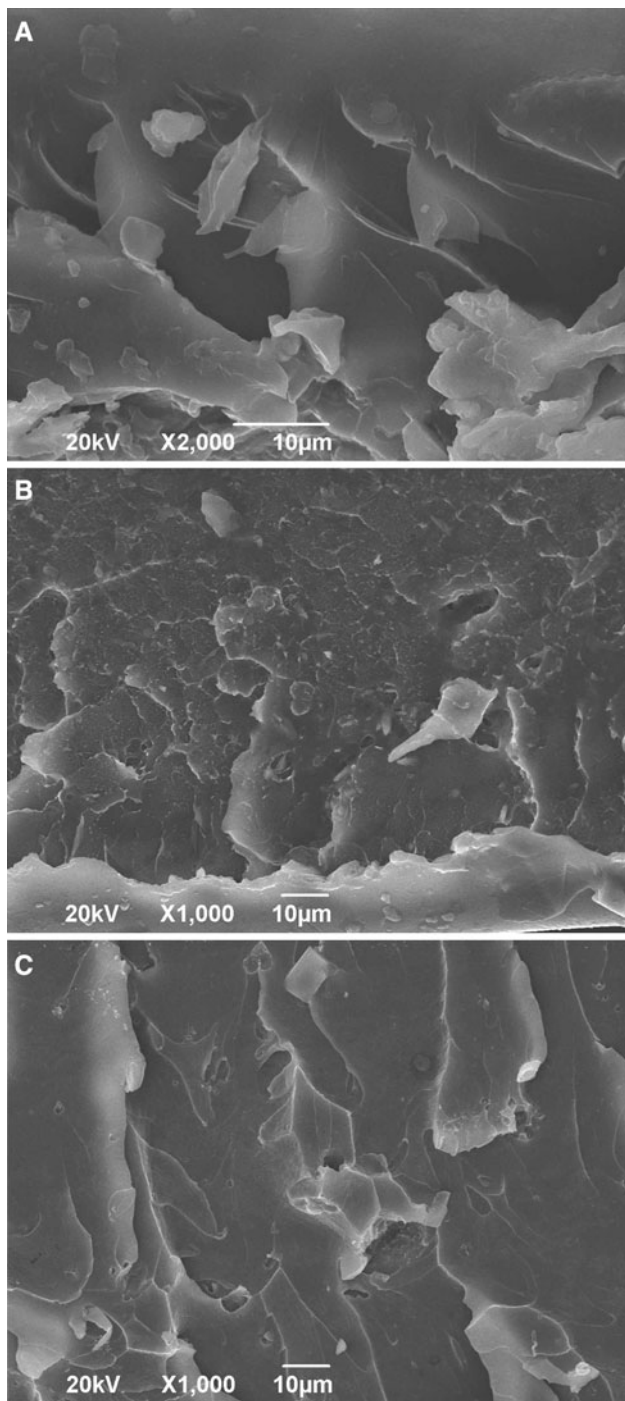


Fig. 2 SEM images for PEN, uncured and cured hybrid films containing 10 wt% HBCuPc, respectively: **a** PEN, **b** uncured, **c** cured

increase compared to that of the pure polymer. This is mainly because the CuPc component was contained in HBCuPc has a very high dielectric constant due to the electron delocalization within the giant conjugated molecule [19]. Figure 3 also demonstrates that the dielectric losses of hybrid films are increased linearly with the increasing HBCuPc content, which is due to HBCuPc

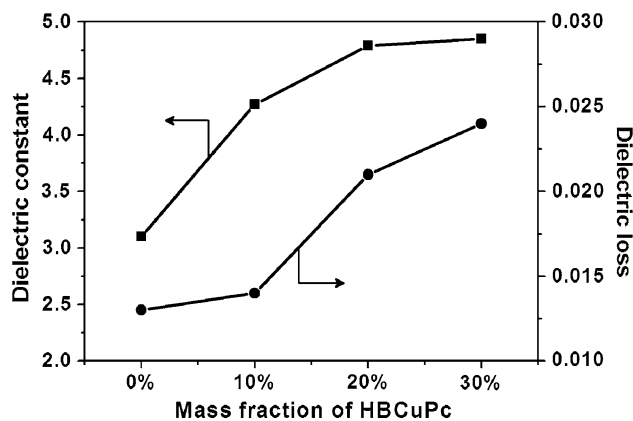


Fig. 3 Influence of HBCuPc content on dielectric constant and dielectric loss at 100 Hz

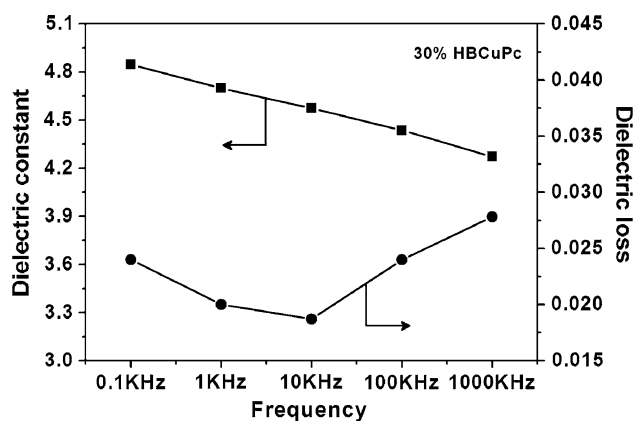


Fig. 4 Influence of frequency on dielectric constant and dielectric loss

possesses a relatively high dielectric loss [17, 18]. But in the PEN/HBCuPc hybrid films, PEN matrix acts as insulation layers to reduce the dielectric loss of HBCuPc. Moreover, the well dispersion of HBCuPc in PEN matrix reduces the dielectric loss of hybrid films. So even if the HBCuPc content of 30 wt%, the dielectric loss of hybrid film is also lower than 0.025 at 100 Hz.

For high energy density films, it should possess such typical characteristics as high dielectric constant and low dielectric loss. Figure 4 shows that the dielectric loss of hybrid film are decreased with the increasing frequency under 10 kHz, which is 0.02 at 1 kHz and 0.017 at 10 kHz. While 10 kHz to 1 MHz the dielectric loss are increased with the increasing frequency, but it's still remained at 0.017 to 0.027, within fully meet the application needs. It can be seen that the dielectric loss of the hybrid film with high HBCuPc content also lower than 0.027 at relatively high frequency. The dielectric strength of hybrid films is independent of HBCuPc content shown in Fig. 5. The electric conductivity of hybrid film increased with the increase of HBCuPc content, but the electric conductivity

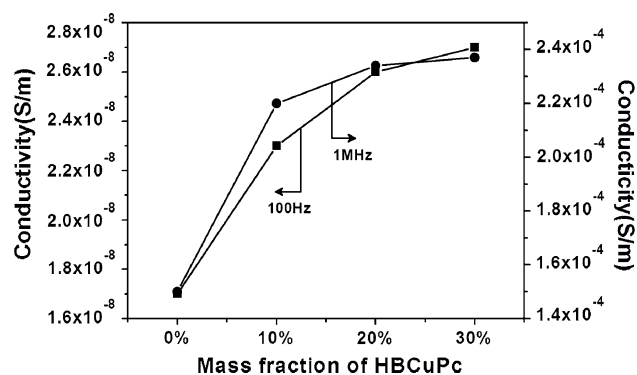


Fig. 5 Influence of HBCuPc content on conductivity

is strongly dependent on its chemical structure and the values of electric conductivity is same quantitatively compare pure PEN. That is largely because the chemical structure of HBCuPc hindered the formation of conductive channels of CuPc. Limited incorporation of HBCuPc has no obvious influence on conductivity and this phenomenon is consistent with that observed in mechanical strength, revealing that HBCuPc and PEN phase has a favorable miscibility.

4 Conclusions

A novel approach to fabricate high dielectric constant hybrid films by using polyarylene ether nitriles cross-linking with hyperbranched copper phthalocyanine. PEN/HBCuPc hybrid films have a high dielectric constant and low dielectric loss at a high operational frequency, which is reached 4.8 of dielectric constant and 0.017 of dielectric loss. The tensile strength and elongation at break of the hybrid films were increased with the increase of HBCuPc content as well as the thermal stability was improved with the increase of HBCuPc content, which is demonstrated this is flexible and thermostable hybrid film.

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