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A large enhancement in dielectric properties of poly(vinylidene fluoride) based all-organic nanocomposite

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ABSTRACT

A nanocomposite was fabricated using poly(vinylidene fluoride) (PVDF) as matrix and poly(*p*-chloromethyl styrene) (PCMS) grafted with high dielectric constant copper phthalocyanine oligomer (CuPc) (PCMS-*g*-CuPc) as filler. Transmission electron microscopic morphologies reveal that the PCMS-*g*-CuPc particle size of ca. 80 nm in average are dispersed in PVDF matrix, while in PCMS-*g*-CuPc particles the PCMS acts as "matrix" which contains dispersed CuPc balls with a average size of ca. 25 nm [1/20 of that of CuPc in simple blend of PVDF and CuPc (PVDF/CuPc)]. The nanocomposite with only 15 wt% CuPc can realize a dielectric constant of 325 at 100 Hz, about 7 times larger than that of PVDF/CuPc, and nearly 40-fold enhancement with respect to that of the pure PVDF. The significant enhancement of dielectric response can be attributed to the remarkably strengthened exchange coupling effect as well as the Maxwell–Wagner–Sillars polarization mechanism.

1. Introduction

Electroactive polymers (EAPs) with high dielectric constant play important roles in electromechanical fields such as high performance sensors, actuators, artificial muscles, as well as bypass capacitors in microelectronics and energy-storage devices [1–9]. The dielectric constant of pure polymers is relatively low (<10). Consequently, a great deal of effort has been focused on the development of polymer/ceramics 0–3 composites in which ferroelectric ceramics are selected as fillers to increase dielectric constant of continuative polymers in the past several decades [10–13]. High loading of the ceramic fillers needed in the composite, usually over 50 vol%, can increase dielectric constant by about ten times relative to the polymer matrix. However, this approach usually suffers from the increase of the modulus of the polymer matrix, the loss of the flexibility, and the deterioration of processibility at the same time [3]. Furthermore, most ferroelectric fillers used in the composites are lead-based ceramics, which are not environmentally friendly [2].

In recent years, two kinds of all-organic composite approaches were used to fabricate high dielectric constant polymer composites [5]. One approach is to use the percolation phenomena observed in polymer/conductive polymer composites [3,5,7,14]. Dielectric constant enhancement of ca. 10–100 times that of polymer matrix has been observed in several such percolative composites. However, simultaneously, these composites also exhibit relatively high dielectric loss due to the insulator–conductor transition near the percolation threshold. The other approach is to increase the dielectric constant of the polymer matrix by dispersing some organic semiconductors with super-dielectric constant in it. In 2002, Q. M. Zhang [15] reported a high dielectric constant all-organic composite of copper phthalocyanine oligomer (CuPc, 40 wt%) (Scheme 1) and poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)]. CuPc has a very high dielectric constant ($>10,000$) due to the electron delocalization within the giant conjugated molecule [16]. As an organic material, CuPc has a modulus comparable to that of the P(VDF-TrFE). Therefore, a high dielectric constant can be achieved in their composite without increasing the material modulus [5,15,17,18]. The composite exhibits excellent electromechanical properties. However, CuPc particles are susceptible to be agglomerated in the polymer matrix (the size of CuPc particles is $\sim 1\ \mu m$) due to incompatibility of CuPc with the polymer matrix, which will reduce the breakdown field and increase the dielectric loss. It is well known that in polymer composite the compatibility between the filler and the polymer matrix can be enhanced by addition of dispersant [19], the formation of intermolecular hydrogen bonding [20–22], cross-linking [23], or grafting [17,18], etc. In 2005, we developed a grafting approach to prepare a composite in which CuPc (25 wt%) was partially grafted to poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] [18]. Improvement of the dispersibility of CuPc in the terpolymer matrix was achieved (the CuPc inclusion size is

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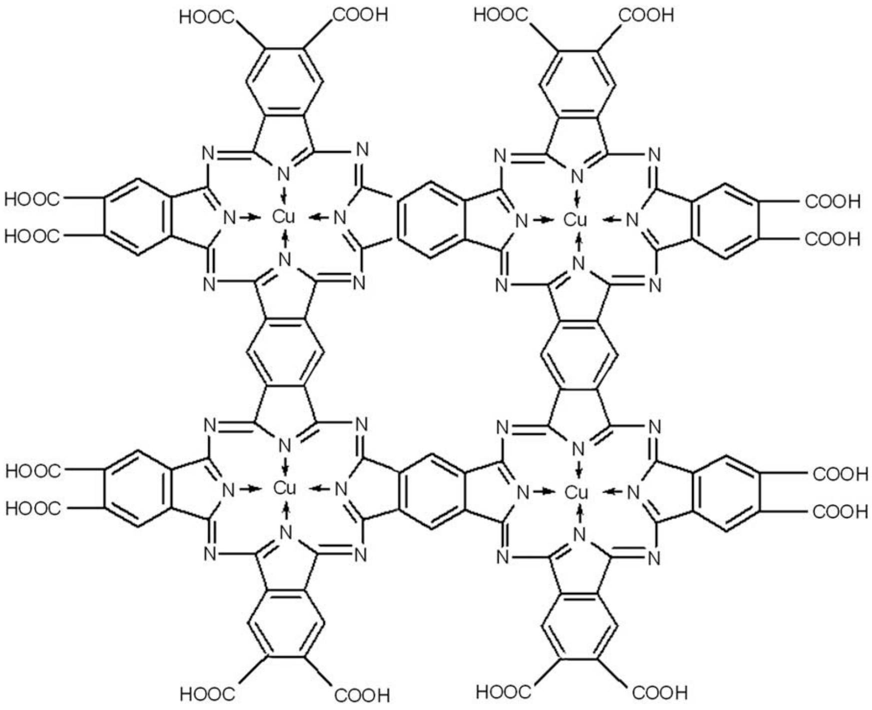


Scheme 1. Chemical structure of CuPc.

about 60–100 nm), and the dielectric constant of the resulting nanocomposite reaches nearly 175 at 100 Hz. According to a theoretical modeling by Li [24] on such kind of composites, the interface exchange coupling effect can result in a significant change in the local polarization level. Since the exchange coupling exists only in the near interface region, if we further decrease the size of CuPc, dramatically improved dielectric properties can be achieved [5,18]. Furthermore, content of the filler should also be taken into consideration in view that low loadings of the filler will benefit the reduction of the amounts of voids/defects in the final composite and result in improvement of mechanical properties [22,25].

In this paper, we introduce a novel avenue to fabricate nanocomposite of PVDF and PCMS grafted with CuPc. PVDF is a commercially easily available piezoelectric polymer which possesses good performance and widely used in electromechanical application [1,26]. To further decrease the size of CuPc particles, poly(*p*-chloromethyl styrene) (PCMS) was selected for grafting. It imparts several advantages over the above mentioned grafting polymerization [18]. Anchoring of CuPc to PCMS backbone is much easy, thus the grafting ratio is very high compared with the above mentioned one, which will lead to much decreased CuPc inclusion size in PCMS "matrix". A further benefit is that the dispersion of PCMS itself or PCMS-*g*-CuPc in PVDF is much better than that of CuPc in PVDF, which was found during our study. By grafting CuPc to PCMS, then blending with PVDF using the solution cast method, we developed a nanocomposite (with only 15 wt% CuPc) in which the improvement of dispersion and decrease of size level of CuPc were achieved, consequently a large enhancement in dielectric response of PVDF based all-organic nanocomposite is realized.

2. Experimental section

2.1. Materials

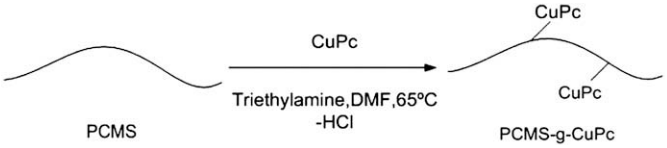
The CuPc (Scheme 1) was synthesized following a procedure reported in Ref. [27]. PCMS ($M_n = 55{,}000$) was purchased from Aldrich. Triethylamine (TEA) was dried with NaOH and distilled before use. Dimethylformamide (DMF) was dried with CaH_2 followed by distillation in vacuo prior to use. The PVDF with a weight average molecular weight of 400,000 was purchased from Shanghai 3F New Materials Co., Ltd., China. Other reagents were of analytical grade and used without further purification.

2.2. Synthesis of PCMS-g-CuPc

Scheme 2 shows the synthetic route of PCMS-*g*-CuPc. A 100 mL three-necked round-bottom flask fitted with a magnetic stirrer, a thermometer and a condenser was used as the reactor. TEA (3.0 mL) was added to a solution of PCMS (0.5 g) and CuPc (0.5 g) in DMF (40 mL). The solution was stirred at 65 °C for 12 h under purified nitrogen atmosphere. After TEA and DMF were removed by reduced pressure distillation, the mixture was washed with methylene dichloride to remove unreacted PCMS, if any, followed by distilled water to remove triethylamine hydrochloride. The final product was dried in vacuo at 50 °C, and labeled PCMS-*g*-CuPc.

2.3. Preparation of films for electric measurement

Films were prepared using solution cast method. For the blend of PVDF and PCMS-*g*-CuPc (PVDF/PCMS-*g*-CuPc) with the PCMS-*g*-CuPc of 15 wt%, 30 wt%, 40 wt%, and 50 wt% (accordingly the contents of CuPc are 7.5 wt%, 15 wt%, 20 wt%, and 25 wt%, respectively), PCMS-*g*-CuPc was added to the solution of PVDF in DMF, and then ultrasonically stirred for at least 2 h. Afterward, the



Scheme 2. Schematic drawing of the synthesis of PCMS-*g*-CuPc.