



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.

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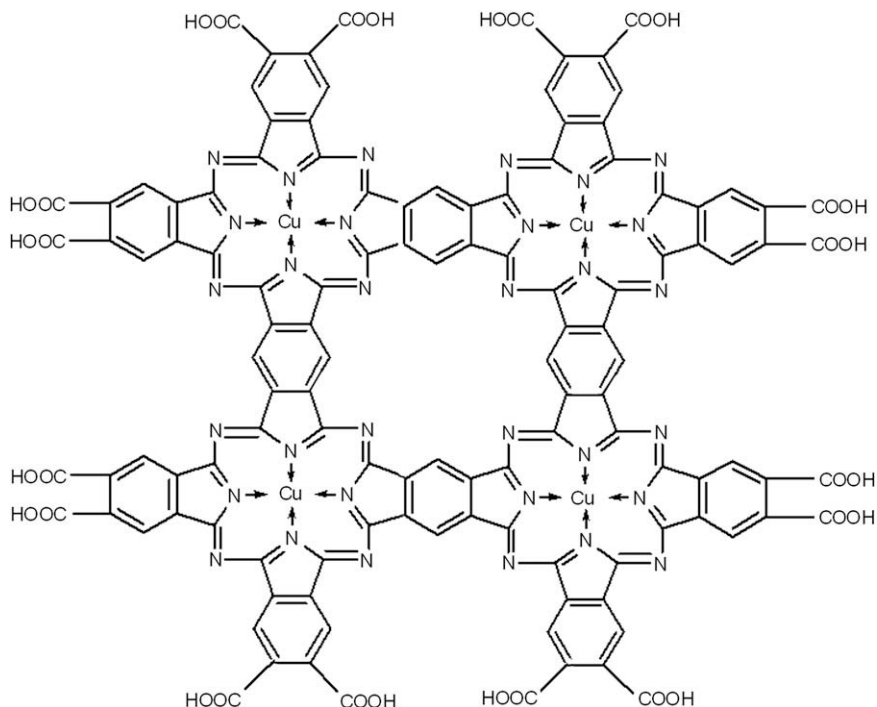
1. Introduction

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 ~1 μm) 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

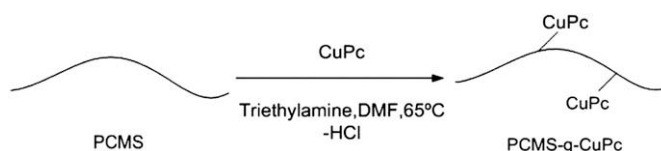
followed by distillation in vacuo prior to use. The PVDF with a weight average molecular weight of 400,000 was purchased from Shanghai 3F New Materials Co., Ltd., China. Other reagents were of analytical grade and used without further purification.

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.

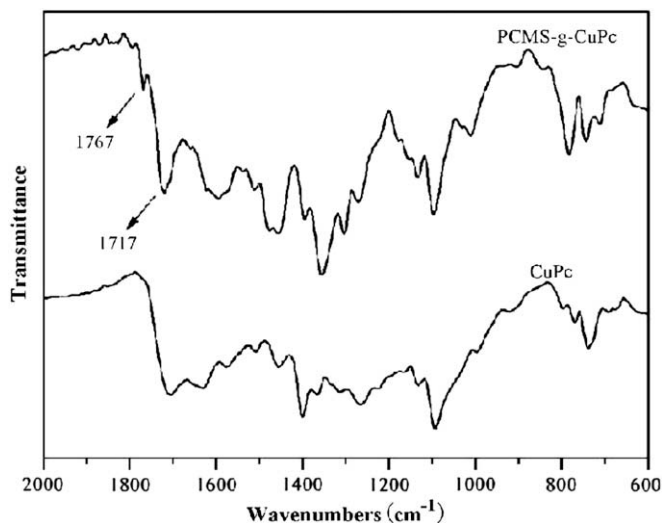


Fig. 1. FT-IR spectra of CuPc and PCMS-g-CuPc.

solution was poured onto a clean glass slide and dried in air at 70 °C for 5 h, then in vacuo at 50 °C for 12 h to remove DMF. Finally, the film was annealed at 120 °C for 12 h and then slowly cooled to room temperature. The preparation procedure of the film of the blend of PVDF and CuPc (PVDF/CuPc) containing 15 wt% CuPc was the same as that of PVDF/PCMS-g-CuPc. The typical film thickness was 30 μm. For the electric characterization, the films were cut into small pieces of about 10 × 10 mm, and circular gold electrodes with 2.5 mm radius were sputtered in the center of both surfaces.

2.4. Characterization

FT-IR spectra were recorded with the sample/KBr pressed pellets using a Bruker Vector-22 FT-IR spectrometer. ¹H NMR spectra were obtained in DMSO-*d*₆ and collected on a Bruker DRX-500 spectrometer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the graft ratio of CuPc in the synthesis of PCMS-g-CuPc. The unreacted CuPc in samples for test was removed by soaking PCMS-g-CuPc in 50 mL of 0.1 mol/L NaOH aqueous solution, followed by distilled water to get rid of NaOH. The resulting product was dried in vacuo at 50 °C, and then was soaked in a crucible which contained a mixture of 3 mL of 70% nitric acid and 0.6 mL of 70% perchloric acid for 12 h. After all of the liquids were slowly evaporated off in air at 80 °C for about 2 h, the organic components were burned up in the crucible. The residues were diluted by 5% nitric acid to a 10 mL solution, and the

metal contents were measured by a Jarrell-Ash J-A1100. For thermal analysis, a Perkin-Elmer DSC-2C calorimeter was used at a heating rate of 20 °C/min. TEM was performed using an H-7650 Transmission Electron Microscope. The specimen was prepared by placing a drop of a solution with about 1.0 wt% of composite in DMF on carbon film coated copper grid and then dried in air at 75 °C before observation. To elucidate the microstructure inside the PCMS-g-CuPc, an ultramicrotomed sample of PVDF/PCMS-g-CuPc was particularly observed. X-ray study was carried out using a D8Advance X-ray generator with a copper target. The wavelength used was 1.5406×10^{-10} m. For the characterization of frequency dependence of the dielectric properties, an Agilent 4194A Impedance Analyzer was used.

3. Results and discussion

3.1. Characterization of PCMS-g-CuPc

CuPc with 16 carboxyl groups (–COOHs) can easily react to PCMS with highly reactive chlorines in the presence of TEA that acts as an acceptor to take in resulting hydrochloric acid in the solution, consequently the esterification is promoted. The FT-IR analysis of CuPc and PCMS-g-CuPc is shown in Fig. 1. The absorption band at 1767 cm^{−1} corresponds to carbonyl band of an ester linkage, which proves the successful esterification [17,18]. The strong absorption band at 1717 cm^{−1} is intrinsic to the stretching vibration of carbonyl group of –COOH, indicating some unreacted –COOHs in PCMS-g-CuPc. Evidence of the successful grafting of CuPc to PCMS can also be obtained from ¹H NMR spectrum of PCMS-g-CuPc. The methylene of Cl–CH₂–C₆H₄– and CuPc–CH₂–C₆H₄– resonances occurred at 4.65 ppm and 5.32 ppm respectively, which confirms that the CuPc was grafted onto PCMS. The resonances at 6.8–7.4 ppm are assigned to aromatic hydrogen in –C₆H₄– of PCMS, and the peak lies at 8.14 ppm is attributed to hydrogen in >C₆H₂< of CuPc. According to the ICP-AES analysis, it is estimated that the grafted CuPc in the synthesis procedure of PCMS-g-CuPc is as much as 96.8%.

3.2. Microstructure of the composites

Fig. 2 shows the TEM micrographs of PVDF/CuPc (with 15 wt% CuPc) and PVDF/PCMS-g-CuPc (with 30 wt% PCMS-g-CuPc, accordingly the content of CuPc is also 15 wt%). Due to the incompatibility of CuPc (also PCMS) with PVDF, the CuPc and PCMS-g-CuPc aggregated in nearly spherical shape particles in polymer matrix. The size of PCMS-g-CuPc in PVDF/PCMS-g-CuPc is ~80 nm, while the CuPc particle size in PVDF/CuPc is ~500 nm, because CuPc has a strong tendency to form stack assemblies and microaggregates due to its planar shape and aromatic nature [28].

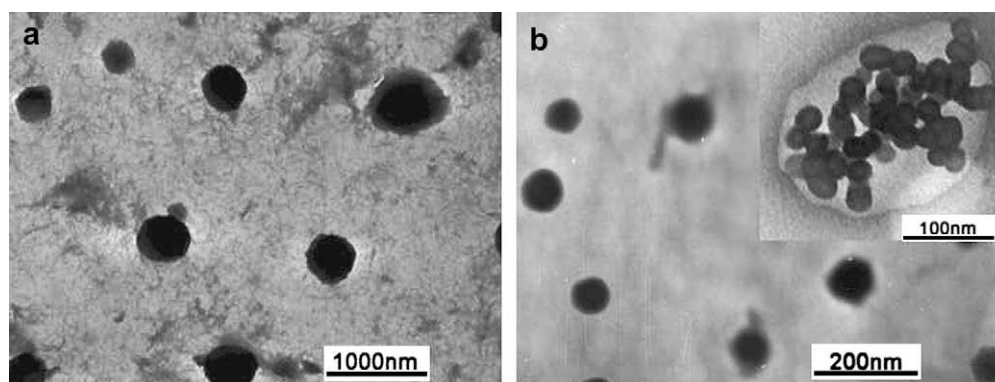


Fig. 2. TEM photographs of (a) PVDF/CuPc and (b) PVDF/PCMS-g-CuPc. Inset in (b) shows the image of ultramicrotomed sample of PVDF/PCMS-g-CuPc.

To reveal the detailed microstructure of PCMS-g-CuPc, TEM was used to observe the ultramicrotomed sample of PVDF/PCMS-g-CuPc. From the inset in Fig. 2(b) we can observe that within the PCMS-g-CuPc particles the CuPc inclusion with an average diameter of ~25 nm, about 20 times smaller than that of CuPc in PVDF/CuPc, was dispersed in PCMS. Suggested reason is that, in the PCMS-g-CuPc, part of CuPc oligomers attached onto PCMS can act as nucleation centers, which further induced the growth of CuPc crystallite. Since the pendent CuPc groups were distributed separately along the PCMS backbone, the size of crystallite was restricted by the accessibility of adjacent CuPc molecules. On the contrary, aggregation of CuPc can hardly be prevented in PVDF/CuPc. In a word, in the nanocomposite PVDF/PCMS-g-CuPc, the grafted CuPc forms nanophase crystallites (~25 nm) in PCMS-g-CuPc particles, and the PCMS-g-CuPc inclusion (~80 nm) is dispersed in PVDF matrix.

Fig. 3 shows the DSC curves of PVDF and two composites. The melting point of pure PVDF is 172.30 °C, and for PVDF/CuPc and PVDF/PCMS-g-CuPc the melting points are 169.25 °C and 168.50 °C, respectively. The decrease in the melting point of the composites compared with the pure PVDF can be explained by the presence of heterogeneity of CuPc and PCMS-g-CuPc which hindered the crystal perfection and the reduced lamellar thickness of PVDF crystallites [17,18,29,30].

The degree of crystallinity (χ) can be calculated according to equation [31]:

$$\chi(\%) = \left(\frac{\Delta H_m}{W \Delta H_m^0} \right)$$

where ΔH_m is the enthalpy of fusion of the melting transition, W is the PVDF content in the composites, ΔH_m^0 is the enthalpy of fusion of 100% crystalline PVDF which is 90.40 J/g [31]. The ΔH_m of PVDF/CuPc and PVDF/PCMS-g-CuPc is 44.68 J/g and 35.06 J/g, respectively, corresponding to the crystallinity degree of 58.2% and 55.4% which are higher than that of pure PVDF (35.9%). The increase in ΔH_m of the two composites can be attributed to the fact that nanofillers can favor the nucleation of PVDF crystalline phase [32,33].

Fig. 4 presents the XRD results of the pristine PVDF, PVDF/PCMS-g-CuPc, PVDF/CuPc and CuPc acquired at room temperature. For PVDF the diffraction peaks at 20.2° and 26.8° correspond to (110)

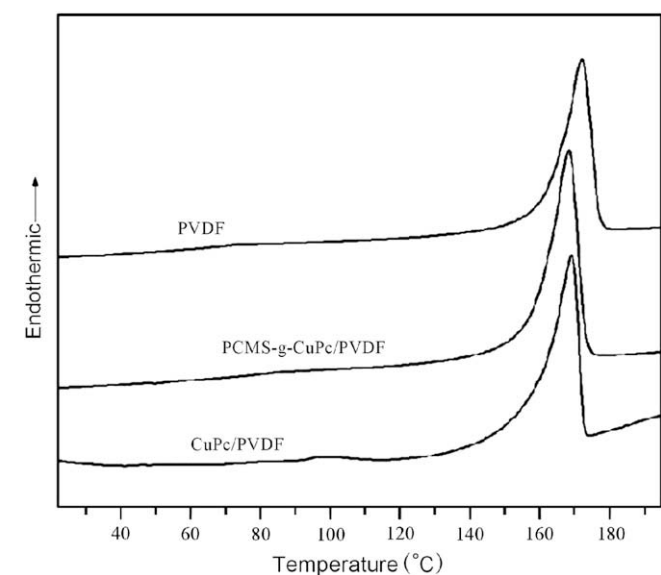


Fig. 3. DSC curves of pure PVDF, PVDF/PCMS-g-CuPc (with 15 wt% CuPc) and PVDF/CuPc (with 15 wt% CuPc).

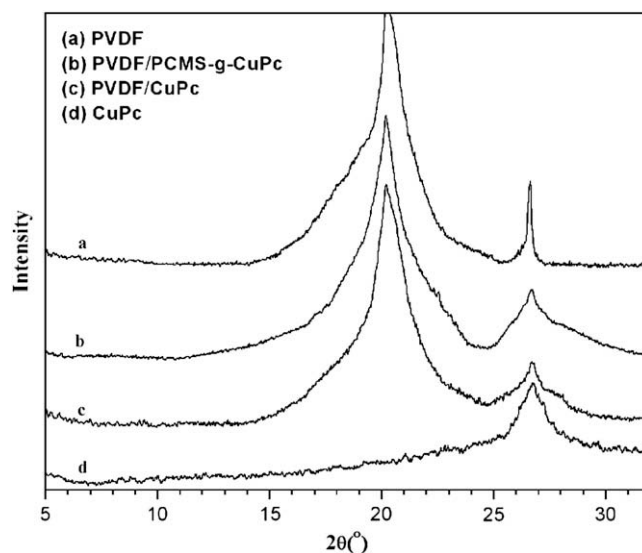


Fig. 4. X-ray data of PVDF, PVDF/PCMS-g-CuPc, PVDF/CuPc and CuPc.

and (021) reflections [34]. For the composites, the peak positions corresponding to (110) reflection almost do not change, and the wider diffraction peaks at ~27° are the (021) diffraction peak of PVDF overlapped with that of CuPc at ~27°.

By employing the Scherrer equation, the Miller Index L_{hkl} can be estimated [35]:

$$L_{hkl} = 0.9\lambda / (B \cos \theta)$$

where λ is the X-ray wavelength, B is the full width at half-maximum of the diffraction peak in 2θ , and θ is the peak angular position. The Miller Index L_{hkl} in the direction perpendicular to the crystal planes can be deduced. For each sample except the CuPc, L_{110} is about 4.8 nm. These results lead to the conclusion that the bulky CuPc oligomer is totally excluded from the crystalline regions [17,18].

3.3. Dielectric properties of the composites

Dielectric properties of PVDF/PCMS-g-CuPc with different weight fractions of CuPc measured at room temperature as a function of frequency are plotted in Fig. 5. As generally expected, the dielectric constants (K) of composites are remarkably enhanced compared with that of the pure PVDF (8.4 at 100 Hz), and increased with weight percentage of CuPc inclusion. However, compared with PVDF/PCMS-g-CuPc with 15 wt% CuPc, the composites with more CuPc exhibit quite slow increase of dielectric constant. Furthermore, at frequencies above 3250 Hz, the dielectric constant of PVDF/PCMS-g-CuPc with 25 wt% CuPc is even lower than that of the sample with 15 wt% CuPc. Similar results were observed previously [6,36]. This phenomenon is probably arising from the Maxwell–Wagner–Sillars (MWS) polarization mechanism [18,24,37] which is caused by the large difference in dielectric constant between the polymer matrix and the filler. Bobnar et al. [38–40] have reported that, the high dielectric response of the CuPc/PVDF based copolymer/terpolymer composites is not due to the intrinsic high dielectric constant of CuPc oligomers but is rather governed by MWS interfacial effect. For composites with high CuPc concentrations discussed here, the strong MWS relaxation results in large low frequency dielectric dispersion. We will come back to this aspect later. Due to its relatively high dielectric constant and lower dielectric dispersion compared with composites with higher

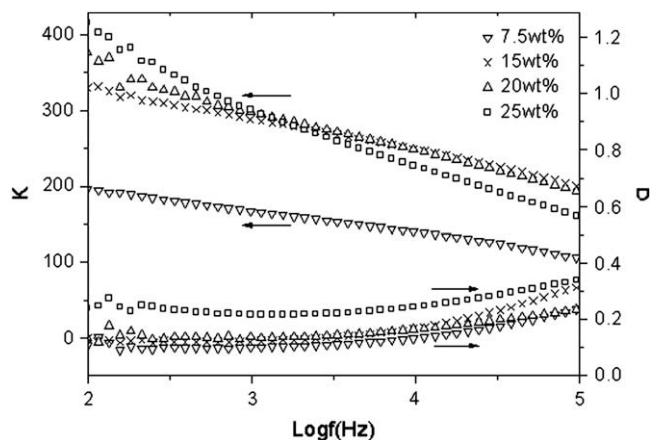


Fig. 5. Dielectric properties of PVDF/PCMS-g-CuPc with different weight fractions of CuPc (7.5 wt%, 15 wt%, 20 wt%, and 25 wt%) measured at room temperature as a function of frequency.

loading of CuPc, sample with 15 wt% CuPc was selected for further investigation.

Fig. 6 shows the comparison of dielectric constant and dielectric loss (D) of composites and pure PVDF as a function of frequency from 100 Hz to 100 KHz at room temperature. The dielectric constant of the two composites is substantially increased compared with the pure PVDF. The PVDF/PCMS-g-CuPc film shows a dielectric constant of more than 325 at 100 Hz, nearly 40 times higher than that of pure PVDF, meanwhile, the dielectric constant of PVDF/CuPc is ~ 50 at the same frequency. It should be pointed out that the dielectric constant of the composites is much higher than that derived from various models, especially for PVDF/PCMS-g-CuPc. For example, according to the model in Ref. [41], if we consider the composites as random mixture of PVDF matrix and nearly spherical inclusions of CuPc and PCMS-g-CuPc, respectively, logarithm of the dielectric constant ($K_{\text{composite}}$) of such composites is linearly proportional to the volume fraction of the filler (φ_{filler}) with the slope dependent on the dielectric properties of both components:

$$\log K_{\text{composite}} = \varphi_{\text{filler}} \log \left(\frac{K_{\text{filler}}}{K_{\text{polymer}}} \right) + \log K_{\text{polymer}}$$

The dielectric constants of CuPc and PCMS-g-CuPc are $\sim 4 \times 10^5$ and $\sim 6.6 \times 10^3$ separately. It is estimated that, the dielectric constants of PVDF/CuPc (with 15 wt% CuPc) and PVDF/PCMS-g-CuPc (with 30 wt% PCMS-g-CuPc) can only reach 42 and 62, respectively.

The much higher dielectric constant of our composites could be arising from at least two characteristics of such composites. First, the MWS space charge phenomenon results in strong low frequency dielectric dispersion, especially for the PVDF/PCMS-g-CuPc due to the large interface-to-volume ratios of CuPc particles, as observed in Fig. 2. Second, the exchange coupling effect may play a much important role in the prominent enhancement of dielectric constant of composite. As the heterogeneity in the composite becomes smaller and smaller, the influence of the exchange layer, an interface layer in which the polarization is strongly affected by both phases, becomes more and more important, and eventually dominates when the heterogeneity size and the exchange length become comparable [24]. Although the CuPc content in both composites is the same, the dielectric constant of PVDF/PCMS-g-CuPc with CuPc nanoparticles is more than 7 times higher than that of PVDF/CuPc. Moreover, in one of our previous work, P(VDF-TrFE-CFE) with 25 wt% partially grafted CuPc (the particle size is ca. 60–100 nm) has a dielectric constant of only 175 at 100 Hz. Although the dielectric constant of PVDF (8.4) is much less than that of P(VDF-TrFE-CFE) (~ 40), the dielectric constant of PVDF/PCMS-g-CuPc is nearly one time higher than that of P(VDF-TrFE-CFE) based composite. In consequence, the dramatic enhancement of dielectric response observed in PVDF/PCMS-g-CuPc is probably caused by the strong exchange coupling effect, as well as the MWS interface effect, due to the much smaller CuPc particle size as observed in TEM micrographs [5,17,18,24].

Fig. 6 also demonstrates that the dielectric losses of composites are relatively low. CuPc suffers a high dielectric loss due to the long-range intermolecular hopping of electrons [6,42]. In composites, polymer matrix acts as insulation layers to significantly reduce the dielectric loss of CuPc. Over the frequency range observed, the loss of the PVDF/PCMS-g-CuPc (about 0.10 at 100 Hz) is lower than that of the PVDF/CuPc which can be attributed to the reduced particle size and improved dispersibility of CuPc in PVDF/PCMS-g-CuPc.

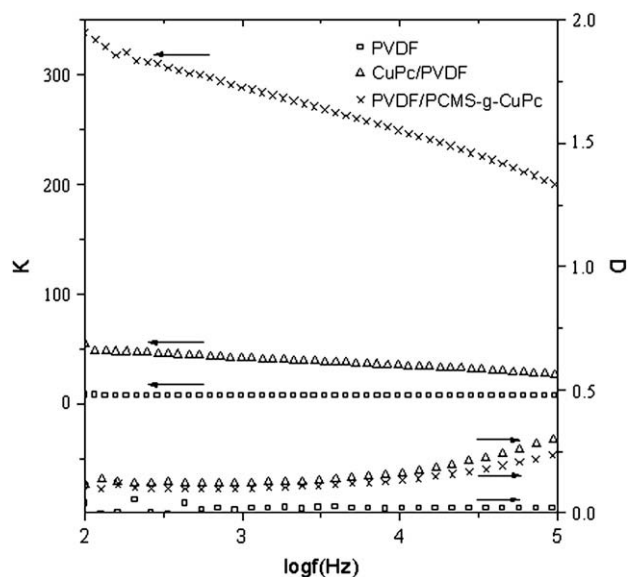


Fig. 6. Dielectric properties of PVDF/CuPc (with 15 wt% CuPc), PVDF/PCMS-g-CuPc (with 15 wt% CuPc) and pure PVDF as a function of frequency at room temperature.

4. Conclusions

A novel approach to fabricate high dielectric constant nanocomposite using PVDF as matrix and chemically modified CuPc as filler was introduced. The size of the CuPc particles within the nanocomposite is ca. 25 nm, representing a 1/20 decrease in comparison with that of CuPc in the simple blend of PVDF and CuPc. The nanocomposite exhibits a high dielectric constant (325, nearly 40 times that of the pure PVDF, and about sevenfold enhancement with respect to that of the simple blend), low loss (0.10), all of which are highly desirable for high dielectric constant composites. Further property improvement can be expected through the amelioration in the nanocomposite fabrication process, especially by using high dielectric constant organic fillers with further reduced particle size (such as on the order of 10 nm) [43] as well as increasing the distribution uniformity of the filler particles in polymer matrix.

Acknowledgements

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