High Dielectric Constant Composite of P(VDF−TrFE) with Grafted Copper Phthalocyanine Oligomer

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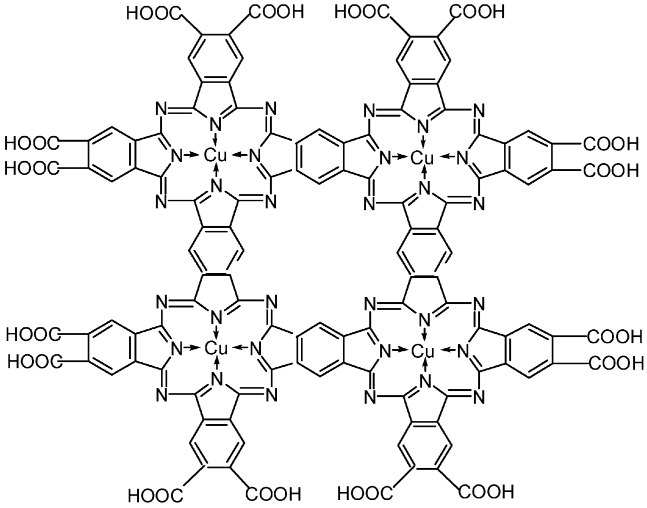
ABSTRACT: Chemically modified copper phthalocyanine (CuPc) oligomer with active vinyl groups was successfully bonded to poly(vinylidene fluoride-trifluoroethylene) (P(VDF−TrFE)) backbone via free radical graft reaction in solution. Improvement of the dispersibility of CuPc oligomer in polymer matrix was confirmed by TEM-observed morphologies. The size of CuPc particulates in the polymer matrix is in the range of 60−120 nm. This nanocomposite (with 25 wt % CuPc) is very flexible with an elastic modulus of 912 MPa, which is nearly the same as that of the polymer matrix, and presents a breakdown field of 37.7 V/μm, while for the blend of P(VDF−TrFE) and CuPc oligomer, it is 29.7 V/μm. The dielectric constant reaches about 100 at 100 Hz and room temperature, representing a more than 6 times increase compared with the matrix. The grafted nanocomposite exhibits a weaker dielectric dispersion in comparison with the blend of P(VDF−TrFE) and CuPc oligomer, particularly at low-frequency range. The low-frequency dielectric dispersion can be attributed to the Maxwell−Wagner−Sillars polarization mechanism.

Introduction

High dielectric constant polymers with excellent electric properties, proper mechanical strength, and good processing properties are of great importance for applications such as super capacitors, on-chip capacitors, and electromechanical devices including artificial muscles, smart skins for drag reduction, and microelectromechanical systems.[1−4] However, for one-component systems, it is hard to realize all these properties. Conventional polymers are easy to process but generally suffer from a low dielectric constant (less than 10). In the past several decades, the composite approach, in which high dielectric constant particulates (most of which are ferroelectric ceramics) were added to a polymer matrix, has been employed to raise the dielectric constant of polymer based materials.[2,4−6] However, because ceramic materials have an elastic modulus much higher than that of polymers, the increased dielectric constant comes at the cost of losing flexibility and significant increase of the elastic modulus.

Recently, Zhang reported an all organic composite approach where high dielectric constant organic particulates were dispersed in a polymer matrix.[1] Copper phthalocyanine (CuPc) oligomer,[7] whose molecular structure is shown in Scheme 1, was selected as a high dielectric constant filler. Its dielectric constant can reach 10^6 due to so-called nomadic polarization mechanism.[8] An all-organic composite of poly(vinylidene fluoride−trifluoroethylene) copolymer (P(VDF−TrFE)) and CuPc oligomer displays high electromechanical properties. Under a field of 13 V/μm a strain near −2% can be induced and the elastic energy density can reach 0.13 J/cm^3. At the same time, the composite film remains flexible. However, this approach suffers from the adversely excessive agglomeration of the CuPc oligomer particulates due to incompatibility of CuPc oligomer with the polymer matrix, which will reduce the breakdown field and increase the dielectric loss. An ideal high-dielectric composite should be mechanically robust and easy to process; i.e., the dispersibility of filler particulates in the material can be easily controlled. Obviously, chemically bonding the CuPc oligomer to P(VDF−TrFE) backbone can improve the compatibility of filler and polymer matrix.

Scheme 1. Chemical Structure of the CuPc Oligomer



In this paper, we introduce a new approach in which CuPc oligomer was chemically modified by attaching it with highly reactive functionals—vinyl groups. Then via a free radical grafting reaction in solution, the resulting product was grafted to P(VDF−TrFE) copolymer backbone, thus improving the compatibility of the two components, as well as offering the potential of obtaining good dielectric properties and increasing the break-

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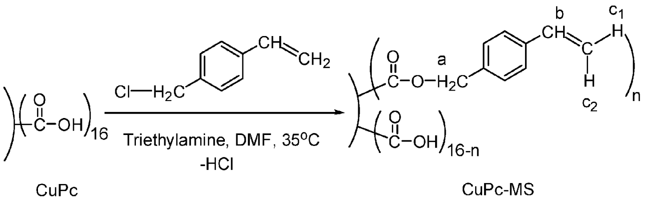
Scheme 2. Schematic Drawing of the Synthesis of CuPc-MS



down field. Furthermore, we also prepared the composite in which the CuPc oligomer particulates were physically blended with P(VDF−TrFE) copolymer and show that indeed the grafted composites exhibit better electric properties as well as more finely dispersed morphology.

Experimental Section

Materials. The CuPc oligomer was synthesized following a procedure reported in ref 9. *p*-Chloromethylstyrene (*p*-CMS) (97%) was purchased from Aldrich and used without further purification. Benzoyl peroxide was recrystallized from methanol before use. The P(VDF−TrFE) 70/30 mol % copolymer with a weight-averaged molecular weight of 200 000 was purchased from Solvay and Cie, Bruxelles, Belgium. Triethylamine (TEA) is of analytical grade and was dried with NaOH, then distilled before use. Dimethylformamide (DMF) is of analytical grade and was dried with CaH_2 followed by distillation in vacuo prior to use.

Synthesis of CuPc—MS. Scheme 2 shows the synthetic route to CuPc−MS, a chemically modified CuPc oligomer with highly reactive vinyl groups. A 100 mL three-neck round-bottom flask fitted with a magnetic stirrer, a thermometer, and a condenser was used as the reactor. *p*-CMS (0.93 mL, 0.0064 mol) was added to a solution of CuPc oligomer (1.0 g, 0.352 mmol) and TEA (1.2 mL, 0.0087 mol) in DMF (50 mL). The solution was stirred at 35 °C for 48 h under nitrogen atmosphere. After the TEA and DMF were eliminated by reduced pressure distillation, the as-solid resulting mixture was washed with benzene to remove unreacted vinylbenzyl chloride, followed by distilled water to get rid of triethylamine hydrochloride. The product was dried in vacuo at room temperature.

In Situ Synthesis of P(VDF—TrFE)-*g*-CuPc. Benzoyl peroxide (0.040 g) was added to a solution of P(VDF−TrFE) 70/30 (0.90 g) and CuPc−MS (0.42 g) in DMF (15 mL) in a three-neck round-bottom flask fitted with a magnetic stirrer, a thermometer, and a condenser. The solution was stirred at 65 °C for 18 h under nitrogen atmosphere. After removal of DMF, the resulting mixture was dried in vacuo. The composite was labeled as P(VDF−TrFE)-*g*-CuPc. For determination of the content of CuPc−MS grafted onto the P(VDF−TrFE) backbone, the unreacted CuPc−MS was removed by soaking P(VDF−TrFE)-*g*-CuPc film in 0.05 mol/L of NaOH aqueous solution for 2 weeks, and then it was extracted with distilled water using a Soxhlet apparatus for 5 days. The resulting product was dried in vacuo.

Preparation of Films for Electric and Mechanical Measurement. Composite films were prepared using the solution cast method. For the blend of P(VDF−TrFE) and CuPc oligomer (P(VDF−TrFE)-*b*-CuPc), the P(VDF−TrFE) copolymer was dissolved in DMF and then a proper amount of CuPc oligomer was added to the solution. The solution was ultrasonically stirred until the CuPc oligomer was dissolved. Afterward, the solution was poured onto a glass slide and dried in air at 70 °C for 5 h, then under vacuum at 70 °C for 12 h. Finally, the composites were annealed at 140 °C in a vacuum for 12 h and slowly cooled to room temperature. For the P(VDF−TrFE)-*g*-CuPc film, the resulting reaction mixture was used directly and the procedure was the same as that of the preparation of P(VDF−TrFE)-*b*-CuPc film. The typical film thickness is 20 μm. For the electric characterization, the films were cut into small pieces of 10 × 10 mm, and circular gold electrodes with 2.5 mm radius were sputtered in the center on both surfaces of each sample.

Characterization. IR spectra were recorded with a Bruker Vector-22 FTIR spectrometer. ^{1}H 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 CuPc oligomer content in the composites. Samples for test were decomposed with a mixed solution of 70% nitric acid and 70% perchloric acid at a volume ratio of 5 to 1. After all of the liquids were slowly evaporated off, the organic components were burned up in a 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 to characterize thermal transitions of the pure P(VDF−TrFE) and composites. Each composite solid sample was prepared by drying the corresponding 8.8% DMF solution. All the samples for testing were annealed at 140 °C under vacuum for 12 h, and cooled slowly to room temperature. The data were recorded at heating rate of 20 °C/min, and the sample mass was typically 5 mg. TEM was performed using a JEOL JEM-100S 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, then the specimen was dried by infrared lamp in air before observation. The elastic modulus was determined with a dynamic mechanical thermal analyzer (Rheometric Scientific, Inc., DMTA-V). X-ray study was carried out using a Rigaku D/Max-RA rotating anode X-ray generator with a copper target. For the characterization of frequency dependence of the dielectric properties from 100 Hz to 100 kHz, an Agilent 4194A Impedance analyzer was used, and the dielectric constant *K* of the film was calculated by the formula of a parallel plate capacitor as

$$K = \mathrm{C}t/\epsilon_0 A$$

where *C* is the capacitance of the metal−insulator−metal element, ϵ_0 is the vacuum dielectric permittivity, *A* is the area of the electrode, and *t* is the thickness of the capacitor, respectively.

Results and Discussion

Synthesis and characterization of CuPc—MS and P(VDF—TrFE)-*g*-CuPc. CuPc oligomer has 16 peripheral carboxyl groups (−COOHs) in itself and is hard to react with the P(VDF−TrFE) backbone. To overcome this problem, introducing proper active groups into CuPc oligomer should be an effective and feasible method. In this study, the vinyl group, a typically highly reactive functional group, is introduced to CuPc oligomer. *p*-Chloromethylstyrene (*p*-CMS), with an active chlorine and a vinyl group, was selected as the active group provider. As shown in Scheme 2, *p*-CMS was introduced to CuPc oligomer in the presence of TEA in DMF. The TEA acted as an acceptor to take in resulting hydrochloric acid from the solution, consequently the esterification was promoted. The evidence of existence of CuPc−MS in the resultant product was provided by FTIR and ^{1}H NMR. Figure 1 compares the infrared spectra of CuPc oligomer and CuPc−MS. The absorption band at 1767 cm^{-1}, characteristic of carbonyl band of an ester linkage, proves the successful esterification. The strong absorption band at 1717 cm^{-1}, intrinsic to the stretching vibration of carbonyl group of −COOH, indicates that there are unreacted −COOHs in CuPc−MS. The ^{1}H NMR spectrum gives further evidence. The observed resonances at 4.47 ppm (s, 2H), 6.76 ppm (s, 1H), 5.33 ppm (s, 1H), and 5.90 ppm (s, 1H) are attributed to protons a, b, c_1, and c_2 respectively

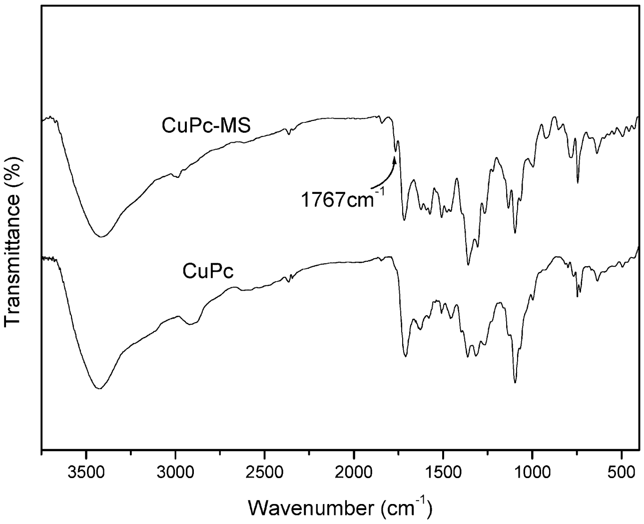


Figure 1. FTIR spectra of CuPc oligomer and CuPc−MS.

(Scheme 2). To characterize how many −COOHs of a CuPc−MS have reacted with *p*-CMS, titrimetric analysis was used. These peripheral −COOHs were titratable with standardized aqueous alkali in a back-titration procedure. It was calculated that about 5 out of 16 −COOHs in a CuPc oligomer have been capped with *p*-CMS.

Grafting of CuPc−MS was accomplished by introducing free-radicals onto P(VDF−TrFE) backbone, which served as initiation sites for free-radical polymerization of CuPc−MS. Under the grafting condition used in this study, a mixture of graft polymer and unreacted CuPc−MS was expected. Unreacted CuPc−MS can be removed by the procedures described above. The degree of graft was estimated by ICP-AES analysis. It was found that about 9.6% of CuPc−MS was grafted onto P(VDF−TrFE) backbone. After extraction of unreacted CuPc−MS from P(VDF−TrFE)-*g*-CuPc, the grafted copolymer was characterized by ^{1}H NMR spectra. The resonances at 7.0−7.4 ppm are assigned to aromatic hydrogen in $-\mathrm{C_6}\mathbf{H}_4-$ and $>\mathrm{C_6}\mathbf{H}_2<$, and methylene of $\mathrm{CuPc{-}C}\mathbf{H}_2-\mathrm{C_6H_4}-$ resonance occurred at 4.65 ppm. This confirms that the CuPc−MS was grafted onto P(VDF−TrFE) backbone. The peak at 6.63 ppm is attributed to hydrogen of methine ($-\mathrm{C}\mathbf{H}{=}\mathrm{CH_2}$), which reveals that partial of the vinyl groups still remains unreacted. Other peaks lie at 2.7−3.4 ($-\mathrm{C}\mathbf{H}_2\mathrm{CF_2}-$) and 5.3−6.2 ($-\mathrm{C}\mathbf{H}\mathrm{FCF_2}-$, $-\mathrm{CH{=}C}\mathbf{H}_2$).

Microstructure of CuPc Oligomer and P(VDF−TrFE) Composites. Figure 2 compares the TEM photographs of P(VDF−TrFE)-*b*-CuPc and P(VDF−TrFE)-*g*-CuPc. The data show that the CuPc oligomer particulates in both composite samples have spherical shape, and in the P(VDF−TrFE)-*g*-CuPc sample, relatively uniformly sized CuPc oligomer particulates were produced. The size of CuPc oligomer in P(VDF−TrFE)-*g*-CuPc is in the range of 60−120 nm, which is about 5 time smaller than that of the P(VDF−TrFE)-*b*-CuPc sample. In the P(VDF−TrFE)-*g*-CuPc, CuPc oligomer attached on the main chain can act as a nucleation center, which further induced the growth of CuPc oligomer crystallite. Since the pendent CuPc oligomer groups were distributed separately along the polymer backbone, the size of crystallite was restricted by the accessibility of adjacent CuPc oligomer molecules. On the contrary, aggregation of CuPc oligomer can hardly be prevented in P(VDF−TrFE)-*b*-CuPc.

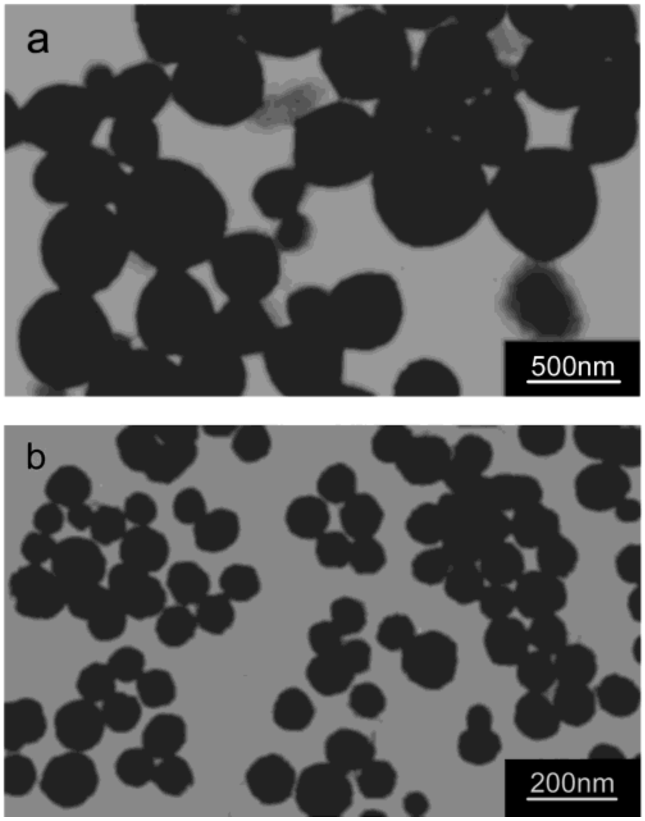


Figure 2. TEM photographs of (a) P(VDF−TrFE)-*b*-CuPc and (b) P(VDF−TrFE)-*g*-CuPc.

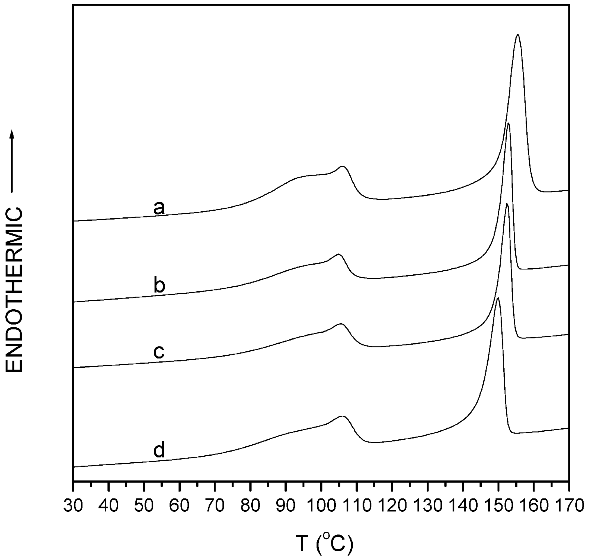


Figure 3. DSC curves of (a) P(VDF−TrFE), (b) P(VDF−TrFE)-*b*-CuPc (with 25 wt % CuPc oligomer), (c) CuPc−MS-filled blend (with 32 wt % CuPc−MS, corresponding to 25 wt % of CuPc oligomer), and (d) P(VDF−TrFE)-*g*-CuPc (with 32 wt % CuPc−MS, corresponding to 25 wt % of CuPc oligomer).

Figure 3 shows the DSC curves for composites as well as for the copolymer matrix. It is observed that compared with that of pure P(VDF−TrFE), the melting points of P(VDF−TrFE)-*b*-CuPc and CuPc−MS filled blend decrease by 2.7 and 3 °C, respectively, while for the P(VDF−TrFE)-*g*-CuPc, a further decrease by 2.8 °C is observed compared with the P(VDF−TrFE)-*b*-CuPc. In addition, for the three composites, the enthalpies of fusion are reduced to roughly two-third of the neat P(VDF−TrFE). The decreasing of the melting point in

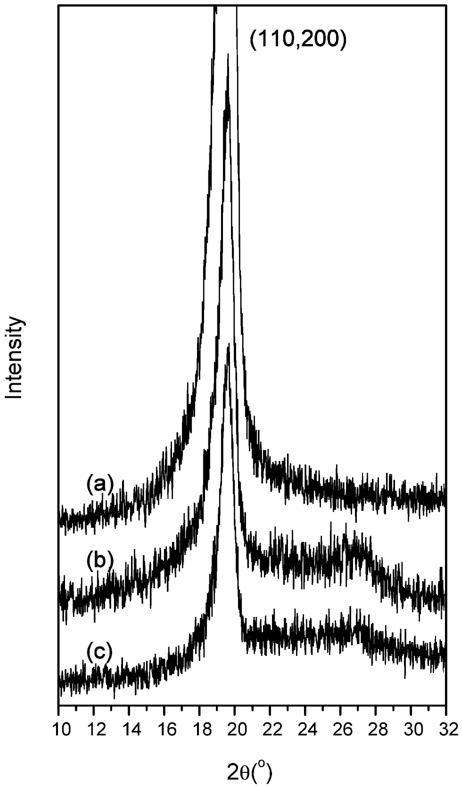


Figure 4. X-ray data of (a) P(VDF−TrFE), (b) P(VDF−TrFE)-*g*-CuPc, and (c) P(VDF−TrFE)-*b*-CuPc.

the composites can be explained by the presence of heterogeneity.[10] In the composites, in particular P(VDF−TrFE)-*g*-CuPc, the lamellar thickness of the crystallites will also be reduced, which can cause reduction of the melting temperature.

P(VDF−TrFE) exhibits a ferroelectric−paraelectric (F−P) phase transition.[20] Below the F−P transition, the crystal has an ordered structure with long sequences of all-trans molecular conformation. Above the phase transition temperature (Curie temperature), an increasing number of *gauche* conformations are introduced. Therefore, the polarity in the crystal regions decreases. The DSC data show that the Curie temperature is almost the same for P(VDF−TrFE)-*g*-CuPc (105.8 °C) and P(VDF−TrFE) (106.1 °C). It means that introducing CuPc oligomer into the copolymer matrix has no influence on F−P phase transition of P(VDF−TrFE). Therefore, the CuPc oligomer is not included in the crystalline regions of copolymer.

Figure 4 presents the wide-angle X-ray diffraction data of P(VDF−TrFE), P(VDF−TrFE)-*g*-CuPc, and P(VDF−TrFE)-*b*-CuPc acquired at room temperature. For composites, the diffraction peaks at 27° indicated that CuPc oligomer aggregated in the copolymer matrix. Meanwhile, the peak positions corresponding to (110, 200) reflection[11] does not change. Using the Scherrer equation[12]

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

where λ is the X-ray wavelength, B is the full width at half-maximum of the diffraction peak in question (in 2θ), and θ is the peak angular position, the coherence of the crystal lattice perpendicular to a particular crystallographic plane can be deduced. At room temperature, for each sample, $L_{(110,\ 200)}$ is about 9.0 nm, which corresponds to the ferroelectric domain size of P(VDF−TrFE) copolymer in perpendicular to the polymer chain. These results lead to the conclusion that CuPc oligomer is totally excluded from the crystalline regions, which is consistent with the DSC data.

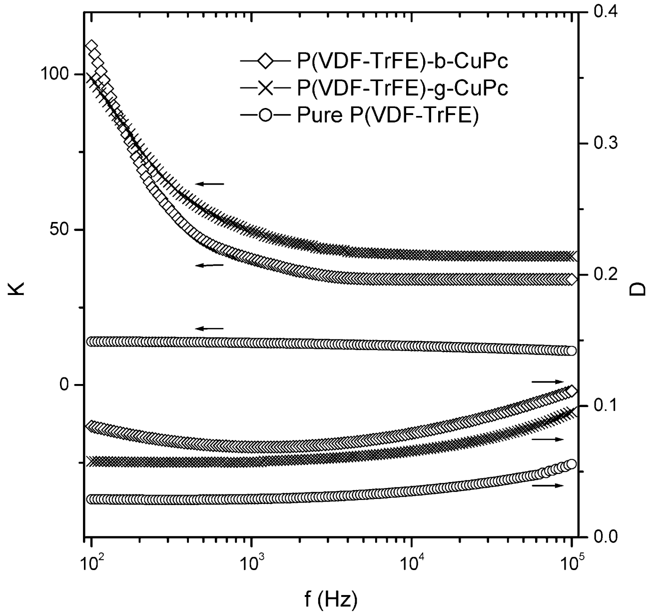


Figure 5. Low-field dielectric properties of P(VDF−TrFE), P(VDF−TrFE)-*b*-CuPc, and P(VDF−TrFE)-*g*-CuPc as functions of frequency ranging from 100 Hz to 100 kHz.

The elastic modulus of samples was measured at 1 Hz and room temperature. The elastic modulus is 900, 912, and 1205 MPa for the copolymer, the P(VDF−TrFE)-*g*-CuPc, and the P(VDF−TrFE)-*b*-CuPc, respectively.

Electrical Properties of the Composites. The breakdown field of the P(VDF−TrFE)-*g*-CuPc film was measured to be 37.7 V/μm, while for the P(VDF−TrFE)-*b*-CuPc film, it is 29.7 V/μm. The higher breakdown field observed in the P(VDF−TrFE)-*g*-CuPc film was expected due to the notably reduced and more uniformly sized CuPc oligomer particulates in P(VDF−TrFE)-*g*-CuPc as compared with the P(VDF−TrFE)-*b*-CuPc. In the latter, the excessive agglomeration of CuPc oligomer particulates can easily lead to conductive paths and lower breakdown field.

Figure 5 shows the dielectric constant (*K*) and loss (*D*) as a function of the frequency (*f*), ranging from 100 to 100 kHz measured at room temperature. The dielectric constant of the composites is substantially increased. For example, in P(VDF−TrFE)-*g*-CuPc, it reaches about 100 at 100 Hz, representing a more than 6 times increase compared with the P(VDF−TrFE) matrix. The dielectric constant of the composites is enhanced by CuPc oligomer, because the easy displacement of the electrons under electric fields through the highly conjugated π-bonds within the entire sheetlike molecule results in a high dielectric response. It is interesting to note that the increase of the dielectric constant of the composite here (more than six times) is comparable or even higher than that reported in ref 1 even though the CuPc oligomer content for the composite here is only 25 wt %, which is much lower than that in ref 1 (40 wt % CuPc oligomer). This enhanced dielectric response in the composite investigated here could be attributed to the reduced particle size (increased interface effect) as well as better dielectric properties of CuPc oligomer used.[14,16] As a semiconductor material, the conductivity of CuPc oligomer can vary over a broad range which will affect the composite dielectric property quite significantly. It is also noted that the dielectric constant of the composite is much higher than those derived from various models, which could be caused by the enhanced interface effect as well as the Maxwell−Wagner−Sillars (MWS) space charge polarization mechanism.[13,14,17−19]

The dielectric constant increases with decreasing frequency and the relatively high dielectric dispersion was observed in both composites, particularly at low frequencies. The low-frequency dielectric dispersion seems to originate from MWS polarization mechanism, which exists in the composites having large differences in both the dielectric constant and conductivity between two components.[7,13] It is noteworthy that, the dielectric constant of the P(VDF−TrFE)-*b*-CuPc increases more significantly with decreasing frequency in comparison to that of the P(VDF−TrFE)-*g*-CuPc, i.e., the P(VDF−TrFE)-*b*-CuPc exhibits stronger dielectric dispersion. The weaker dielectric dispersion of the P(VDF−TrFE)-*g*-CuPc compared with P(VDF−TrFE)-*b*-CuPc can be attributed to more uniform distribution of CuPc oligomer particles.

It is also interesting to note that although the CuPc oligomer content in both composites is the same, the P(VDF−TrFE)-*g*-CuPc exhibits a higher dielectric constant at most of the frequency range, which is probably caused by the interface effect due to the much smaller particle size as observed in TEM micrograph. In a recent publication,[14] Li has shown that in composites such as CuPc oligomer/P(VDF−TrFE) in which there exists very large difference in the dielectric constant between the two components, the interface coupling can lead to a very significant increase in the dielectric response.

CuPc oligomer suffers a high dielectric loss due to the long-range intermolecular hopping of electrons.[15] In composites, copolymer matrix provides insulation layers to significantly reduce the dielectric loss of CuPc oligomer. Over the frequency range observed, the loss of the P(VDF−TrFE)-*g*-CuPc is lower than that of the P(VDF−TrFE)-*b*-CuPc. This can be attributed to the improved dispersion of CuPc oligomer in the former. If the CuPc oligomer was dispersed in polymer matrix as single molecule, a much lower dielectric loss will be expected. However, aggregation of CuPc oligomer is still inevitable in P(VDF−TrFE)-*g*-CuPc, which explained its higher dielectric loss with respect to copolymer matrix.

Conclusions

To improve the compatibility of the two components, we introduced a new approach to prepare CuPc-P(VDF−TrFE) composites, i.e., chemically modified CuPc oligomer was grafted to copolymer main chain. As a result, the CuPc oligomer particle size was reduced significantly, as well as more uniformly distributed in the matrix as compared with the P(VDF−TrFE)-*b*-CuPc. Consequently, the P(VDF−TrFE)-*g*-CuPc exhibits a high dielectric constant, low dielectric loss, and a high breakdown field, all of which are highly desirable for high dielectric constant composites.

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