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Microstructure and Dielectric Properties of P(VDF−TrFE−CFE) with Partially Grafted Copper Phthalocyanine Oligomer

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ABSTRACT: A new class of nanocomposites in which the high dielectric constant copper phthalocyanine oligomer (o-CuPc) was partially grafted to the poly(vinylidene fluoride−trifluoroethylene−chlorofluoroethylene) (P(VDF−TrFE−CFE)), a relaxor ferroelectric polymer, was developed. The new approach developed allowed for higher degree of grafting of o-CuPc to the polymer backbone and resulted in a nanocomposite [P(VDF−TrFE−CFE)-*g*-CuPc/CuPc] with o-CuPc inclusion size at about 60−100 nm. Compared with simple blend of the terpolymer and o-CuPc, a lower dielectric loss and higher breakdown field were achieved in the grafted nanocomposite which can be attributed to a more uniform distribution of o-CuPc particles in the polymer matrix as well as much reduced inclusion size. Moreover, the dielectric constant of the grafted nanocomposite at frequencies above 1 kHz is much higher than that of the simple blend, indicating an increased interface effect such as the exchange coupling which can enhance the dielectric response, as suggested recently by Li.[28] It is also interesting to note that at high frequencies (∼1 MHz), in addition to the improved dielectric constant, the grafted nanocomposite also exhibits a much lower dielectric loss than the matrix.

Introduction

Electroactive polymers (EAPs), responding to external electrical stimulation by displaying a significant shape or size change, are attractive for a broad range of electromechanical device applications.[1] How to raise the electric energy density in these EAPs is crucial for electromechanical devices generating high elastic energy densities and capacitive devices for efficient electric energy storage. In the past, inorganic ceramic or metal particulates have been used to enhance the dielectric permittivity of these systems.[2−5] However, these approaches often result in a significant increase in the elastic modulus and hence reduced electromechanical response. A recent work of all organic composites by incorporating copper phthalocyanine oligomer (o-CuPc)[6] (Scheme 1) into the electrostrictive poly(vinylidene fluoride−trifluoroethylene) (P(VDF−TrFE)) matrix represents a major improvement over previous systems,[7] which enhances both the dielectric response and electromechanical response. The o-CuPc represents a family of molecules which has proven to be of remarkable interest for both its chemical and physical properties. An important characteristic of o-CuPc molecule is the pliant response of highly delocalized electrons moving on long molecular domains under electric fields and results in a high dielectric constant (>1000).[6,8] On the other hand, since the o-CuPc molecules are incompatible with the fluoropolymer matrix, the o-CuPc particles are susceptible to be agglomerated in the copolymer matrix, causing reduced breakdown field and increased dielectric loss of the composites.

Recently, we reported an improved approach to prepare an nanocomposite of P(VDF−TrFE) and o-CuPc by partially grafting chemically modified o-CuPc with active vinyl groups to the P(VDF−TrFE) backbone via free radical graft reaction in solution.[9] Improvement of the dispersibility of o-CuPc in the copolymer matrix was achieved, and the dielectric constant of the nanocomposite reaches nearly 100 at 100 Hz with lower dielectric loss. In that nanocomposite, the polymer matrix used P(VDF−TrFE) copolymer with a dielectric constant less than 15. We note that when a termonomer such as chlorofluoroethylene (CFE) is introduced into the P(VDF−TrFE), the normal ferroelectrics can be converted into a relaxor ferroelectric with a dielectric constant above 40 at 100 Hz.[10−13] For these composites, a polymer matrix with higher dielectric constant is preferred.

A further aspect of the present work is to apply an alternative method for grafting copper phthalocyanine oligomer to fluoropolymers (Scheme 2). Ozone-treated P(VDF−TrFE−CFE) was grafted with poly(chloromethylstyrene) (PCMS), followed by in situ reaction with o-CuPc in solution. It imparts several advantages over conventional solution radical grafting polymerization. Anchoring of o-CuPc to polymer backbone can be carried out in an elevated temperature which ensures the completion of the graft reaction. A further benefit is that grafting content can be varied depending upon the concentration of reactive chloride atom in the polymer backbone as well as the feeding ratio of the esterification reaction mixture. All these will lead to a nanocomposite with better controlled process conditions and improved dielectric response.

Experimental Section

Materials. The o-CuPc was synthesized following a procedure reported in ref 14. P(VDF−TrFE−CFE) (66.3/26.4/7.3 mol

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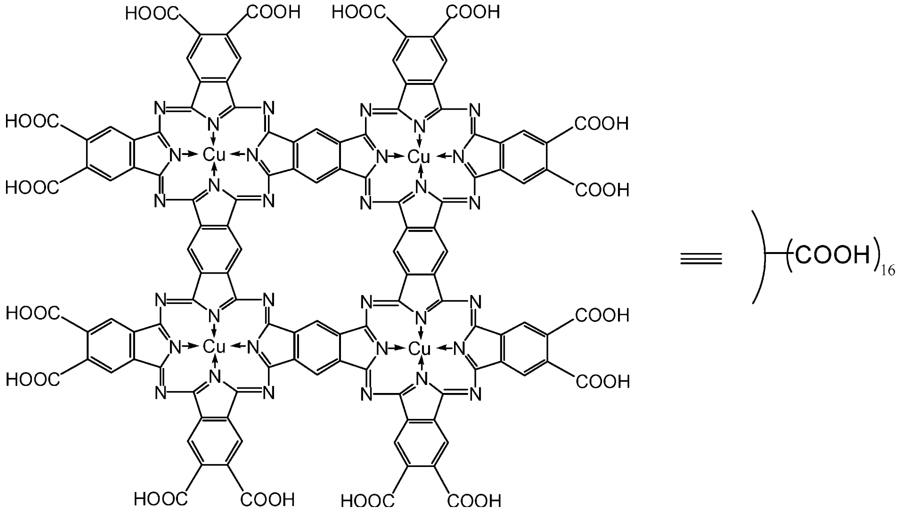
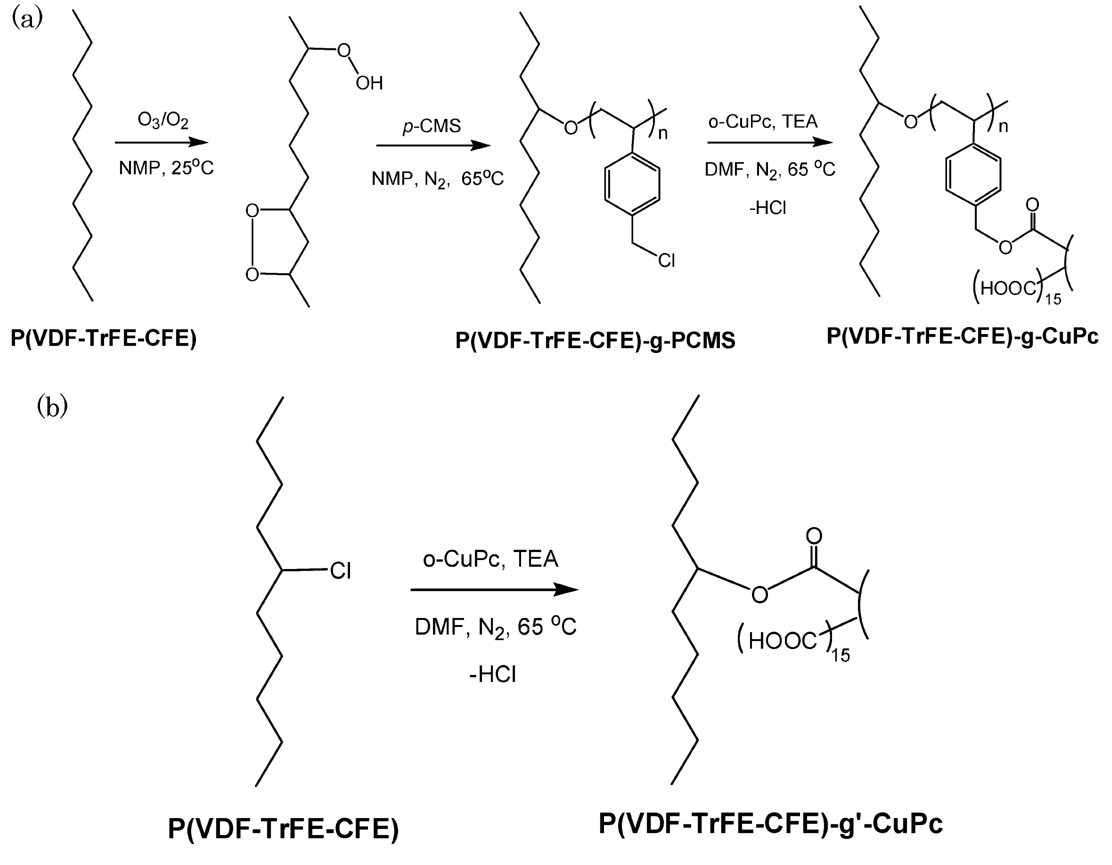
Scheme 1. Chemical Structure of the O-CuPc; Shown on the Right Is a Label to It



Scheme 2. Synthetic Route of (a) P(VDF−TrFE−CFE)-*g*-PCMS, P(VDF−TrFE−CFE)-*g*-CuPc, and (b) P(VDF−TrFE−CFE)-*g*′-CuPc



%) was synthesized by a suspension method.[15] *p*-Chloromethylstyrene (*p*-CMS) (97%) was purchased from Aldrich and used without further purification. *N*-Methyl-2-pyrrolidone (NMP) was distillated in vacuo prior to use. Triethylamine (TEA) was dried with NaOH and then distilled before use. Dimethylformamide (DMF) was dried with CaH_2 followed by distillation in vacuo prior to use.

Synthesis of P(VDF−TrFE−CFE)-*g*-PCMS. The ozone treatment or ozonization of PVDF-based polymers had been well reported in the literature.[16−19] The synthetic route to chemically modified P(VDF−TrFE−CFE) grafted with *p*-CMS, P(VDF−TrFE−CFE)-*g*-PCMS, is shown in Scheme 2a. P(VDF−TrFE−CFE) (1.8 g) was dissolved in NMP (24 mL) in a three-necked round-bottom flask equipped with a magnetic stirrer, a thermometer, and a condenser. A continuous stream of O_3/O_2 mixture was bubbled through the solution for 60 min at 25 °C. The O_3/O_2 mixture was generated from an ozone generator (BX-9, Beijing Environmental Science Institute). The gas flow rate was adjusted to 12 L/h to give rise to an ozone production rate of about 1.4 g/h. After the ozone treatment, about 1/4 of the solution was poured in excess dichloromethane at 0 °C to obtain the precipitate of the ozone-treated terpolymer for determination of the content of peroxides. The resulting mixture was centrifugated, and then the product was dried under reduced pressure at ambient temperature. To the remaining solution in the flask, 1.3 mL of *p*-CMS (8.95 mmol) was introduced, and the solution was saturated with purified nitrogen for 30 min under stirring. The flask was then placed in an oil bath at 65 °C to initiate the grafting reaction. A constant flow of purified nitrogen was maintained during the thermal grafting polymerization for 5 h. The grafted terpolymer was collected by precipitation from excess dichloromethane, followed by centrifugation. The obtained product was redissolved in 10 mL of acetone and then reprecipitated in 200 mL of dichloromethane. The above procedure was repeated another two times to remove the residual *p*-CMS homopolymer, if any. The product was dried in vacuo at room temperature.

Determination of Peroxide Concentration. Determination of peroxide concentration was carried out following the procedures reported in the literature.[20,21] The ozone-treated terpolymer (100 mg) was dissolved in a mixture of DMF (4.0 mL) and isopropyl alcohol (4.0 mL) and kept in darkness for 5 min. Then 0.5 g of potassium iodide and 2.0 mL of glacial acetic acid were added. The solution was kept in darkness at 95 °C under stirring for 2 min, and then it was titrated with a standard sodium thiosulfate aqueous solution (0.0056 mol/L) until disappearance of the yellow color.

Synthesis of P(VDF−TrFE−CFE)-*g*-CuPc. The synthetic route is also illustrated in Scheme 2a. Triethylamine (TEA) (0.35 mL, 2.54 mmol) was added to a solution of P(VDF−TrFE−CFE)-*g*-PCMS (0.80 g) and o-CuPc (0.27 g) in DMF (13.5 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 purified nitrogen atmosphere. After removal of TEA by reduced pressure distillation, the resulting mixture was poured into excess distilled water to get rid of triethylamine hydrochloride as well as to precipitate the product. The product was dried in vacuo at 50 °C and was labeled as P(VDF−TrFE−CFE)-*g*-CuPc/CuPc. For determination of the content of o-CuPc grafted onto the P(VDF−TrFE−CFE)-*g*-PCMS, the unreacted o-CuPc was removed by soaking P(VDF−TrFE−CFE)-*g*-CuPc/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 at 50 °C and termed P(VDF−TrFE−CFE)-*g*-CuPc.

Synthesis of P(VDF−TrFE−CFE)-*g*′-CuPc. Scheme 2b shows another synthetic route to P(VDF−TrFE−CFE)-*g*′-CuPc, i.e., P(VDF−TrFE−CFE) grafted with o-CuPc directly. TEA (0.13 mL, 0.94 mmol) was added to a solution of P(VDF−TrFE−CFE) (0.30 g) and o-CuPc (0.10 g) in DMF (5.0 mL) in a three-neck round-bottom flask fitted with a magnetic stirrer, a thermometer, and a condenser. The remaining procedures were the same as that of P(VDF−TrFE−CFE)-*g*-CuPc.

Preparation of Films for Electric and Mechanical Measurement. Films were prepared using the solution cast method. For the blend of P(VDF−TrFE−CFE) and o-CuPc (labeled as P(VDF−TrFE−CFE)/CuPc), the P(VDF−TrFE−CFE) terpolymer was dissolved in DMF, and then o-CuPc (the wt % of o-CuPc in P(VDF−TrFE−CFE)/CuPc is 25 wt %, which is the same as that in P(VDF−TrFE−CFE)-*g*-CuPc/CuPc) was added to the solution. The mixture was ultrasonically stirred until the o-CuPc was dissolved. Afterward, the solution was poured onto a glass slide and dried in air at 70 °C for 5 h and then under vacuum at 70 °C for 12 h. Finally, the composites were annealed at 110 °C in a vacuum for 12 h and slowly cooled to room temperature. For the P(VDF−TrFE−CFE)-*g*-CuPc and P(VDF−TrFE−CFE)-*g*-CuPc/CuPc films, each composite was ultrasonically dissolved in DMF directly and then followed the same procedures as that for preparation of P(VDF−TrFE−CFE)/CuPc film. The typical film thickness is 20 μm. For the electric characterization, the films were cut into small pieces of 5 × 5 mm, and circular gold electrodes with 0.6 mm radius were sputtered in the center on both surfaces of each sample.

Characterization. FTIR spectra were recorded with a Bruker Vector-22 spectrometer. ^{1}H NMR spectra were obtained in acetone-d_6 and collected on a Bruker DRX-500 spectrometer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the o-CuPc 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 Pyris 1 DSC calorimeter was used. All the samples for testing were annealed at 110 °C under vacuum for 12 h and then cooled slowly to room temperature. The data were recorded at a 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 and then dried with an infrared lamp in air before observation. The elastic modulus was determined with a dynamic mechanical thermal analyzer (Rheometric Scientific, Inc., DMTA-V) at 1 Hz and room temperature. An X-ray study was carried out using a Rigaku D/Max-RA rotating anode X-ray generator with a copper target. The wavelength used was 1.5406 Å. For the characterization of frequency dependence of the dielectric properties from 100 Hz to 4 MHz, an Agilent 4194A impedance analyzer was employed.

Results and Discussion

Characterization of P(VDF−TrFE−CFE)-*g*-CuPc. Peroxide groups were introduced onto terpolymer backbone using ozone treatment in NMP solution. About 1.1 peroxide groups were found in every 100 monomer units. Thermally induced decomposition of the peroxide groups, including five-number peroxide ring, produced free radicals on the chain,[22] which can serve as initiation sites for graft polymerization of *p*-CMS (Scheme 2a).

Evidence of the successful grafting of *p*-CMS to the terpolymer can be obtained from the ^{1}H NMR spectrum. The resonances at 7.0−7.4 ppm are assigned to aromatic hydrogen in $-C_6\mathbf{H}_4-$, and methylene of $-C\mathbf{H}_2-C_6H_4-$ resonance occurred at 4.53 ppm. This confirms that the *p*-CMS was grafted onto P(VDF−TrFE−CFE) backbone. The peak at 6.67 ppm is attributed to hydrogen of methine ($-C\mathbf{H}{=}CF-$, $-C\mathbf{H}{=}CCl-$) in the terpolymer backbone, which are undesirable side effect of the ozone treatment. Other peaks lie at 2.28−3.3 ppm ($-C\mathbf{H}_2$-CF_2-, $-C\mathbf{H}_2CFCl-$) and 5.1−6.0 ppm ($-C\mathbf{H}FCF_2-$).

Copper phthalocyanine oligomers were bonded to chemically modified terpolymer with chloromethyl groups via an esterification reaction in DMF solution (Scheme 2a). The reaction was promoted using TEA as an acceptor to get rid of resulting hydrochloric acid. Only partial of o-CuPc was actually immobilized onto polymer backbone. Unreacted o-CuPc can be removed from P(VDF−TrFE−CFE)-*g*-CuPc/CuPc by the procedures described above. It was estimated by ICP-AES analysis that the content of the oligomers in P(VDF−TrFE−CFE)-*g*-CuPc is 4.1 wt %. Grafting of o-CuPc to P(VDF−TrFE−CFE)-*g*-PCMS results in the appearance of two characteristic absorption bands at 1766 and 1719 cm^{-1} due to carbonyl group of an ester linkage and carboxylic acid groups (Figure 1).

It was expected that the chloride atoms in CFE unit are also reactive. To distinguish the o-CuPc grafted directly to CFE units from that to chloromethyl groups, P(VDF−TrFE−CFE)-*g*′-CuPc was synthesized as a parallel product (Scheme 2b). The reaction condition is the same as that of the P(VDF−TrFE−CFE)-*g*-CuPc. The infrared spectrum of P(VDF−TrFE−CFE)-*g*′-CuPc is also shown in Figure 1. The absorption band at 1763 cm^{-1} arises from carbonyl group of an ester linkage. But the grafting ratio is relatively low. By ICP-AES analysis, the content of o-CuPc in P(VDF−TrFE−CFE)-*g*′-CuPc is 0.96 wt %. Consequently, most of the copper phthalocyanine oligomers in P(VDF−TrFE−CFE)-*g*-CuPc was directly linked to the PCMS segment.

Microstructure of the Composites. As revealed by the TEM micrographs, the o-CuPc particulates in composites are nearly spherical in shape (Figure 2). In

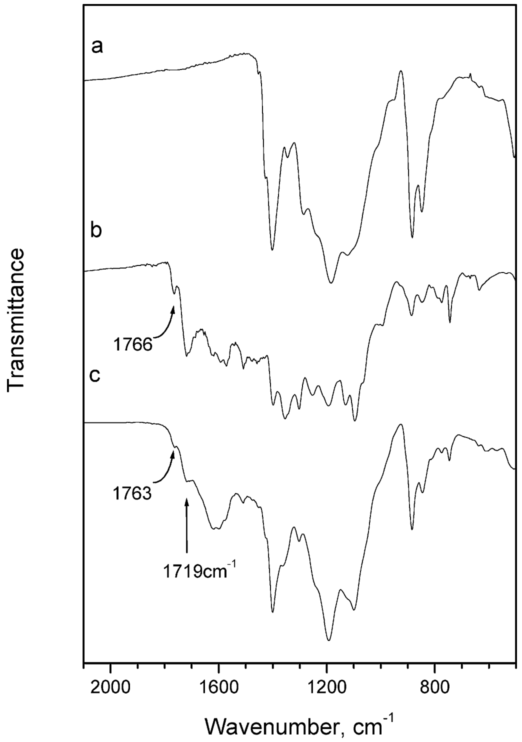


Figure 1. FTIR spectra of (a) P(VDF–TrFE–CFE), (b) P(VDF–TrFE–CFE)-*g*-CuPc, and (c) P(VDF–TrFE–CFE)-*g*′-CuPc.

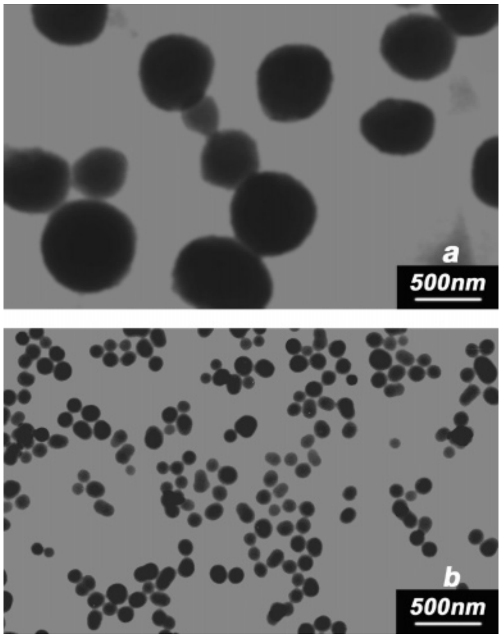


Figure 2. Transmission electron microscope pictures of (a) P(VDF–TrFE–CFE)/CuPc and (b) P(VDF–TrFE–CFE)-*g*-CuPc/CuPc.

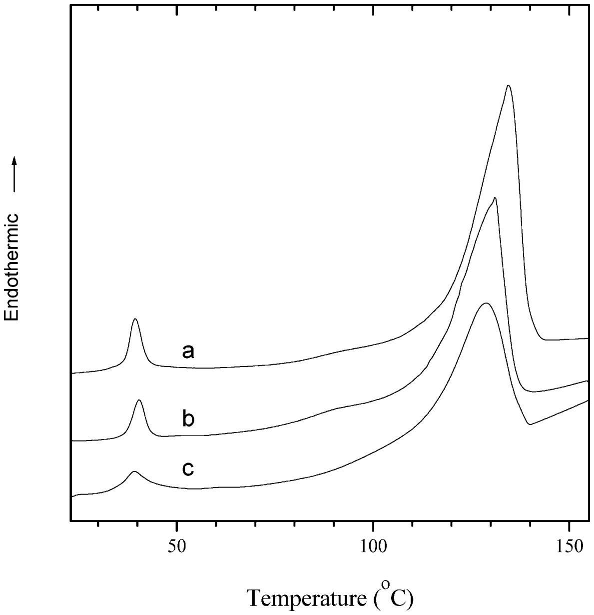


Figure 3. DSC curves taken during heating for (a) P(VDF–TrFE–CFE), (b) P(VDF–TrFE–CFE)-*g*-CuPc, and (c) P(VDF–TrFE–CFE)-*g*-CuPc/CuPc.

the P(VDF–TrFE–CFE)-*g*-CuPc/CuPc, the diameter of particulates is relatively uniform and is in the range of 60–100 nm, which is about 6 time smaller than that of the P(VDF–TrFE–CFE)/CuPc. In the P(VDF–TrFE–CFE)-*g*-CuPc/CuPc, o-CuPc grafted to the main chain can act as a nucleation center, which further induce the growth of o-CuPc crystallite. Since the pendent o-CuPc groups were distributed separately along the polymer backbone, the size of crystallite was restricted by the accessibility of adjacent o-CuPc molecules. On the contrary, aggregation of o-CuPc can hardly be prevented in P(VDF–TrFE–CFE)/CuPc. For the P(VDF–TrFE–CFE)-*g*-CuPc, the TEM micrograph show no sign of aggregation of o-CuPc in the composite.

Figure 3 shows the DSC curves for grafted composites as well as for the parent terpolymer. It is observed that compared with that of pure P(VDF–TrFE–CFE) the melting points of P(VDF–TrFE–CFE)-*g*-CuPc and P(VDF–TrFE–CFE)-*g*-CuPc/CuPc decrease by 3.6 and 6.1 °C, respectively, and the enthalpies of fusion are reduced to 17.2 and 14.7 J/g from 20.4 J/g, indicating reduced crystallinity due to the inclusion of o-CuPc, which is expected. In these composites, the lamellar thickness of the crystallites will be reduced, causing reduction of the melting temperature.

The DSC data also show a weak peak at a temperature near 40 °C, and the peak position is nearly the same for the three samples. This peak is assigned to be the transition of the local polar regions (all-trans chain conformation) in the crystalline phase of the terpolymer to a nonpolar ones (TGTG′ and T_3GT_3G').[10,23,24] The result is consistent with the total exclusion of o-CuPc from the crystalline regions, and therefore, compositing the terpolymer with the o-CuPc does not have marked effect on the phase changes in the crystalline region, which was also observed in our previous work.[9]

For terpolymer and its composites the wide-angle X-ray diffraction peaks at 18.3° are characteristic of the (110, 200) reflection (Figure 4). They are nearly identical in terms of both peak position and width. The coherence length of the crystal lattice perpendicular to a particular crystallographic plane can be deduced using the Scherrer equation:[25]

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

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. For these samples, the $L_{110/200}$ = 26 nm, which corresponds to the crystallite size of terpolymer matrix in perpendicular to the polymer chain direction. These results lead to the conclusion that o-CuPc is totally excluded from the crystalline regions,

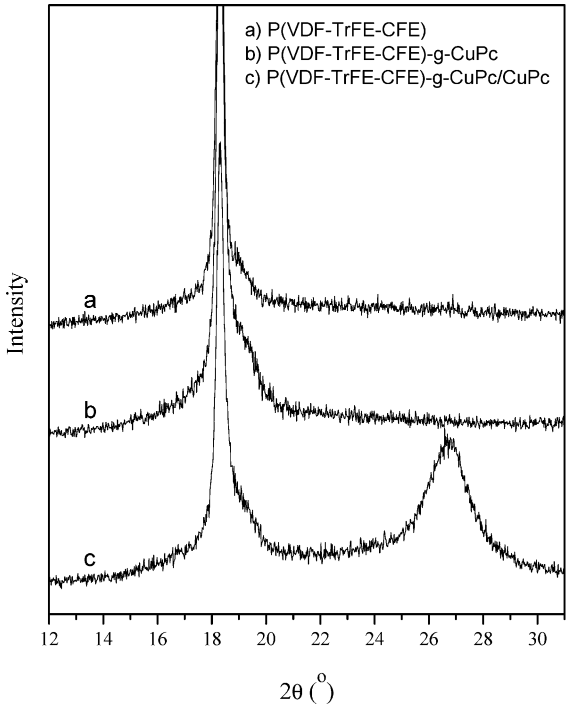


Figure 4. X-ray diffraction data for terpolymer and composite films.

which is consistent with the TEM and DSC results. For P(VDF−TrFE−CFE)-*g*-CuPc/CuPc, the diffraction peak at 27° arises from o-CuPc crystalline phase in the terpolymer matrix,[9] while for P(VDF−TrFE−CFE)-*g*-CuPc, there is no such peak observed.

The elastic modulus is 272 and 356 MPa at ambient condition for the terpolymer and the P(VDF−TrFE−CFE)-*g*-CuPc/CuPc, respectively. The enhancement of elastic modulus for the composite is derived from the physical cross-linking effect of o-CuPc as well as higher elastic modulus of o-CuPc (~2 GPa).[26]

Electrical Properties of the Composites. In a heterogeneous mixture of a relatively high conductive filler and an insulting polymer phase, i.e., o-CuPc particulates in terpolymer, it is generally expected that the breakdown field will be reduced. For the P(VDF−TrFE−CFE)/CuPc film, the breakdown field is 27.6 V/μm. If the particulates are surrounded by a shell of polymer materials, as in the case of the P(VDF−TrFE−CFE)-*g*-CuPc/CuPc, the breakdown field can be improved, and indeed a higher breakdown strength of 36.0 V/μm is obtained for the P(VDF−TrFE−CFE)-*g*-CuPc/CuPc film.

The dielectric constant and loss (*K* and *D*) as a function of frequency (*f*) for the composites along with that from the terpolymer matrix are shown in Figure 5. The dielectric constant of P(VDF−TrFE−CFE)-*g*-CuPc/CuPc reaches 175 (100 Hz), about 4.5 times of that of the terpolymer. The observed frequency dispersion is mainly caused by the frequency dispersion of the o-CuPc (Figure 6). In low frequency (10^2−10^4 Hz), the dielectric constant and loss of the P(VDF−TrFE−CFE)/CuPc increase more rapidly with decreasing frequency in comparison to that of the P(VDF−TrFE−CFE)-*g*-CuPc/CuPc; i.e., the P(VDF−TrFE−CFE)/CuPc exhibits stronger dispersion. This is probably caused by the nonuniform distribution of the o-CuPc inclusion in the matrix, resulting in a stronger Maxwell−Wagner−Sillars (MWS) [27−31] space charge phenomenon, which diminishes at higher frequencies.

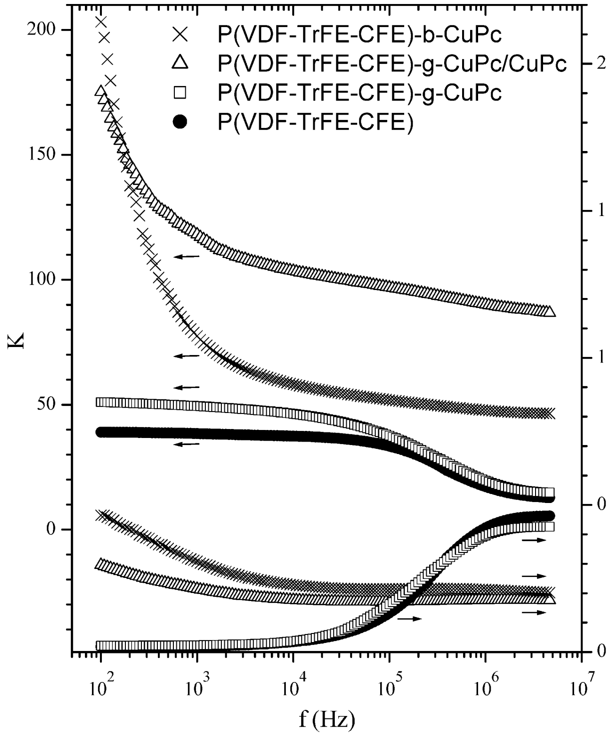


Figure 5. Dielectric properties as functions of frequency measured from 100 Hz to 4 MHz at room temperature.

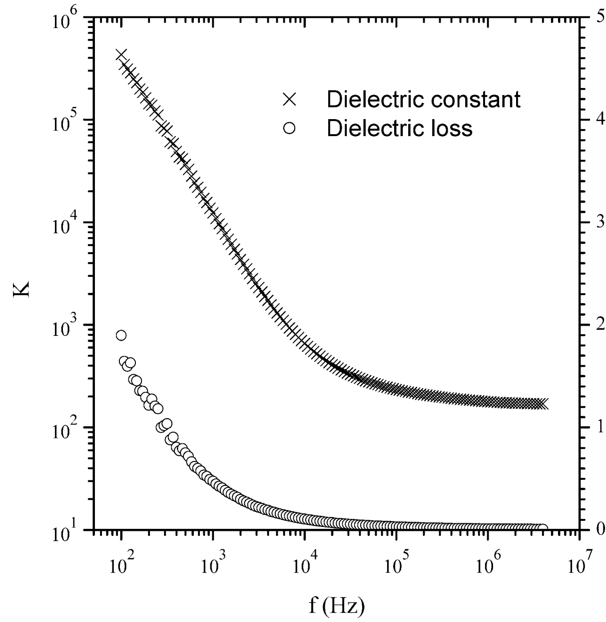


Figure 6. Dielectric response as a function of frequency measured from the pressure compressed pellet of o-CuPc.

At frequencies above 200 Hz, the dielectric constant of P(VDF−TrFE−CFE)-*g*-CuPc/CuPc is higher than that of P(VDF−TrFE−CFE)/CuPc. It is noted that at 1 MHz the dielectric constant of P(VDF−TrFE−CFE)-*g*-CuPc/CuPc is still at 90, which is more than 5 times higher than that of the matrix (~17), while the dielectric constant of P(VDF−TrFE−CFE)/CuPc is 48. The observed enhancement of the dielectric constant in P(VDF−TrFE−CFE)-*g*-CuPc/CuPc is likely caused by the interface effect due to the nanoparticle size as observed in TEM micrograph. In a recent publication,[28] Li has shown that in composites such as o-CuPc/P(VDF−TrFE), in which there exists very large difference in the dielectric constant between the two components, the

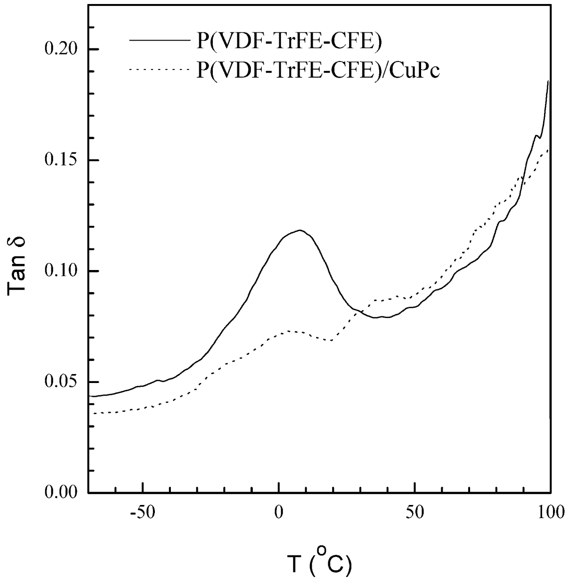


Figure 7. DMTA behavior of terpolymer and P(VDF−TrFE−CFE)/CuPc, tan δ vs T.

interface exchange coupling effect can lead to a very significant enhancement in the dielectric response.

From Figure 5 it is also observed that, for the P(VDF−TrFE−CFE) and P(VDF−TrFE−CFE)-*g*-CuPc, there are loss peaks at frequencies around 1 MHz, which are relaxation processes due to the chain segmental motions in the amorphous regions and dipolar relaxation in the crystalline regions. The nature of this relaxation peak has been extensively studied earlier on P(VDF−TrFE) copolymer and recently terpolymers.[23,32−34] On the other hand, with increased o-CuPc in the composite from 4.1 wt % in the P(VDF−TrFE−CFE)-*g*-CuPc to 25 wt % in P(VDF−TrFE−CFE)-*g*-CuPc/CuPc and P(VDF−TrFE−CFE)/CuPc, this high-frequency dielectric relaxation becomes nearly nonobservable. It is interesting that, as observed by DMTA measurement (Figure 7), incorporation of o-CuPc into terpolymer results in a strong decrease of mechanical loss signal related to the segmental motion process about 8 °C. This can be ascribed to the physical cross-linking effect of o-CuPc fillers which suppresses the mobility of chain segments in disordered region. So o-CuPc may also contribute to the disappearance of the high-frequency dielectric loss peak (Figure 5). As shown in Figure 6, copper phthalocyanine oligomer exhibits a low dielectric loss (0.122) at 1 MHz. Therefore, the dielectric loss of both P(VDF−TrFE−CFE)-*g*-CuPc/CuPc and P(VDF−TrFE−CFE)/CuPc is much reduced from that of the matrix. The much increased dielectric constant and reduced dielectric loss at high frequencies make it very attractive for high-frequency capacitor applications.

Conclusions

We introduce a new approach to obtain a nanocomposite of P(VDF−TrFE−CFE) with high dielectric constant copper phthalocyanine oligomer partially grafted onto the polymer backbone. The o-CuPc particles were more uniformly distributed in the terpolymer, and the particle size was reduced significantly as compared with simple blend of the terpolymer and o-CuPc. Consequently, the grafted nanocomposite exhibits a high dielectric constant, low dielectric loss, and a high breakdown field, all of which are highly desirable for high dielectric constant composites. Furthermore, the enhanced dielectric response in the P(VDF−TrFE−CFE)-*g*-CuPc/CuPc demonstrates the importance of the interface effect in nanocomposites in raising the material responses far beyond that expected by simple mixing rules when there is a large dielectric contrast between the two components in the composite.

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