High Dielectric Constant Composites Based on Metallophthalocyanine Oligomer and Poly(vinylidene fluoride-trifluoroethylene) Copolymer

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ABSTRACT: Using a solution casting method, a high dielectric constant composite based on a copper-phthalocyanine (CuPc) oligomer and a poly(vinylidene fluoride-trifluoro-ethylene) copolymer is developed. The experimental data show that the low field dielectric constant of the composites (with 55 wt % CuPc) can reach 1000 and the loss is ~0.5 at room temperature and 100 Hz. Because of the long-range electron delocalization in CuPc, which results in a strong space charge response of the composite to the external field, there is a strong frequency dispersion of the dielectric properties. In addition, the dielectric properties exhibit a nonlinear behavior with electric field. At a field of 10 kV/cm, the dielectric constant at 10 Hz reaches 4500; meanwhile the dielectric loss is also high. One of the unique attributes of the composite is its mechanical properties that remain very much the same as those of the polymer matrix. Even for a composite with 55 wt % CuPc (the volume fraction of CuPc in the composite is also in the similar range), the composite film is still flexible, with a Young's modulus of 1.2 GPa at room temperature. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 70–75, 2001

Key words: dielectric property; metallophthalocyanine; poly(vinylidene fluoride-tri-fluoroethylene); composites

INTRODUCTION

Electroactive polymers are of great interest for a broad range of applications, such as electromechanical and dielectric devices, because of their many attractive features, such as light weight, high mechanical flexibility, and conformability.[1,2] On the other hand, compared with ceramic materials, the electroactive properties of polymers, such as the dielectric constant and electrome-

chanical response, are not very high. In the past several decades, there has been a great deal of effort to develop polymers with improved functional properties. One of the focuses of these research and development efforts is to raise the dielectric constant of polymers substantially. In addition to applications directly related to capacitors and charge storage devices, a high dielectric constant polymer is also required for high electromechanical responses. The reason behind this requirement is that in the electromechanical transformation process, the mechanical energy output of an electroactive material cannot exceed the input electric energy due to the principle of en-

ergy conservation. Furthermore, the input electric energy is directly proportional to the dielectric constant of the material and also the square of the applied field. Therefore, to develop high-performance electroactive polymers for electromechanical applications, one of the key issues is how to raise the dielectric constant of the polymer substantially. Recently, by making use of high-energy electron irradiation, it has been shown that the room temperature dielectric constant of poly(vinylidene fluoride-trifluoroethylene) copolymer P(VDF-TrFE) can be increased to near 50, a marked improvement compared with the currently available polymers.[3] However, how to raise the dielectric constant to a much higher level without stiffening the polymers is still a challenge. For example, using high dielectric constant ceramics as the filler, the room temperature dielectric constant of the so-called 0–3 composites (ceramic powder polymer matrix composites) can reach 300.[4] One of the consequences of this ceramic filling process to the 0–3 composites is to increase the elastic modulus of the composites significantly above that of the polymer matrix. It is the objective of this research to investigate alternative 0–3 composite approaches to achieve high dielectric constant while maintaining the high flexibility of the matrix. We will show that by making use of organic solids that possess high dielectric permittivity through the mechanism of nomadic polarization[5–8] as the fillers, at room temperature and 100 Hz, a composite material with dielectric constant >1000 and dielectric loss <0.5 can be realized. The composite film is also mechanically flexible, with the elastic modulus nearly the same as that of the polymer matrix.

The organic solid used in this investigation is a metallophthalocyanine oligomer, copper-phthalocyanine (CuPc), which has a room temperature dielectric constant at 100 Hz of >1000 and the dielectric loss is also high.[7] Because of the nomadic polarization mechanism (delocalized electrons lead to the space charge phenomenon), these oligomers suffer high dielectric loss. In addition, they are brittle and difficult to process.[9] The P(VDF-TrFE) 50/50 mol % copolymer, which has a relatively high room temperature dielectric constant ($\sim$ 18), was chosen as the matrix. Compared with CuPc, the copolymer has very low dielectric loss and as the matrix, it can provide an insulation layer to CuPc particles to significantly reduce the dielectric loss in the composite. In

addition, the process developed here to prepare the composite is relatively simple and of low cost.

EXPERIMENTAL

Synthesis of Copper-Phthalocyanine Oligomer

The copper-phthalocyanine oligomer was synthesized by the solution method.[9] Copper sulfate pentahydrate, pyromellitic dianhydride urea, ammonium chloride, and ammonium molybdate were ground together and then placed in a three-necked flask with a thermometer, condenser, and mechanical stirrer. Nitrobenzene was used as solvent, and the temperature of reaction solution maintained at 185°C for 12 h. The as-synthesized solid materials was finely ground and washed with methanol to remove nitrobenzene completely. The powder was boiled with 2 N hydrochloric acid saturated with sodium chloride and filtered after cooling to room temperature. The product was neutralized by 2 N potassium hydroxide solution containing sodium chloride at 90°C. After centrifugation, the product was dried at room temperature under vacuum. The typical particle size of CuPc used in this investigation, as measured by SEM, was $\sim$1 μm.

Sample Preparation

The P(VDF-TrFE) 50/50 mol% copolymer (purchased from Solvay and Cie, Belgium) was used for the polymer matrix. The composite film was prepared by solution casting method. P(VDF-TrFE) copolymer was first dissolved in dimethyl formamide (DMF), and then a proper amount of CuPc powder was added into the solution. After stirring for 12 h at room temperature, the suspension was then poured onto a glass plate and dried at 70°C for 4 h in air, followed by further drying under vacuum at the same temperature for an additional 12 h to remove any remaining traces of the solvent. After drying, the glass plate with film was immersed into alcohol to make it easy to peel off the composite film. The final composite film thickness was $\sim$70 μm. Composites with 30–80 wt % CuPc were prepared. The samples for the electric characterization were sputtered with gold electrodes with 5-mm radius on both surfaces.

Measurement

The dielectric properties of these composites were characterized as a function of frequency, temper-

ature, and electric field strength. The frequency dependence of the dielectric properties from 100 Hz to 100 kHz was measured with an HP 4192A Impedance Analyzer, and the measuring AC voltage was 0.1 V. In the frequency range from 1 to 100 Hz, a dielectric analyzer (DEA; TA instrument, Model No. 2970) was used for characterization of the dielectric properties. For the measurement of the electric field dependence of dielectric constant, a special set-up was designed in which the composite was electrically in series with a 1 kΩ resistor. A high-voltage AC signal was applied to this circuit, and the current passing through the composite was measured through the voltage drop across the 1 kΩ resistor. By recording both the amplitude and phase of this current signal with respect to the applied voltage using a lock-in amplifier, the complex impedance Z^* of the composite can be determined and from

$$Z^* = \frac{1}{j\omega C^*} \tag{1}$$

where $C^* = (\varepsilon' - j\varepsilon'')\varepsilon_0 A/t$, and both the real part of the dielectric constant and loss ($= \varepsilon''/\varepsilon'$) can be obtained. Here, ω is the angular frequency of the measuring field, A and t are the sample area and thickness, respectively, and ε_0 is the vacuum dielectric permittivity.

RESULTS AND DISCUSSION

Free standing composite films of CuPc oligomer and P(VDF-TrFE) copolymer with different weight percentage of CuPc, from 30 to 80%, were prepared. Because the density of CuPc is close to that of P(VDF-TrFE) copolymer, the weight percentage is also close to the volume percentage of the CuPc in the composite. The films prepared are flexible, and the Young's modulus of the composite with 55 wt % CuPc was 1.2 GPa at 25°C, which is close to the Young's modulus of the polymer matrix. Therefore, the 0–3 composites developed here have very attractive mechanical properties compared with the 0–3 composites made of ceramic fillers.

The dielectric constant and loss as a function of the frequency (100 Hz–100 kHz) measured at room temperature for the composite films containing different CuPc weight percentages are shown in Figure 1. These results show that the
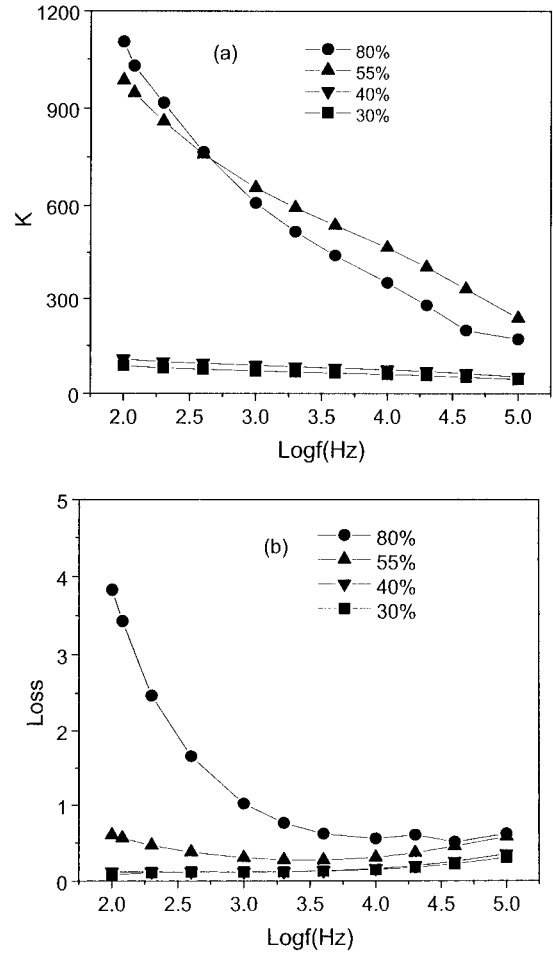

Figure 1   Low field dielectric properties of the composite films measured at room temperature with different weight percentage of CuPc filler as functions of frequency: (a) dielectric constant; (b) dielectric loss.

composite films possess high dielectric constants. At 100 Hz and room temperature, the dielectric constant of the composite with 55 wt % CuPc is ~1000. Even up to 10 kHz, the dielectric constant of the composite with 55 wt % CuPc is still >500. In the same frequency range, the dielectric loss varies ~0.5, a significant reduction compared with pure CuPc. For the composite film with 80 wt % CuPc, the loss is high at lower frequencies and then decreases as the frequency increases. The results suggest that the conduction behavior of CuPc also contributes to the dielectric response and, for composites at high CuPc weight percentage, there exists resistance percolation. Further studies will be carried out in our lab to verify these suggestions.

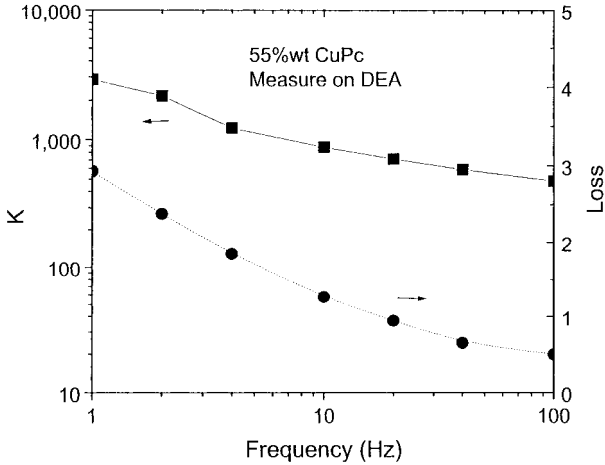The dielectric constant of the composite with 55 wt % CuPc was also characterized at lower

Figure 2   Dielectric properties of the composites with 55 wt % CuPc measured at room temperature in the frequency range from 1 to 100 Hz.

Figure 4   The field dependence of the dielectric properties measured at room temperature and 10 Hz.

frequencies (1 Hz to 100 Hz), and the result is shown in Figure 2. The dielectric constant increases continuously as the frequency decreases, and at 1 Hz it reaches 3000, although the dielectric loss also becomes quite high (~3). These results indicate that the dielectric properties of the composite have strong frequency dispersion, which is a result of the space charge polarization mechanism in CuPc.

The dielectric constants measured at 100 Hz for the composite as a function of the weight percentage CuPc are summarized in Figure 3. As is
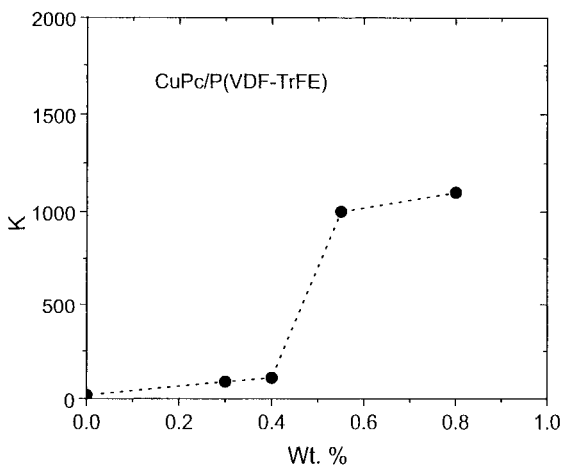

Figure 3   Variation of the low field dielectric constant and dielectric loss of the composites with the weight percentage of the filler measured at room temperature and 100 Hz.
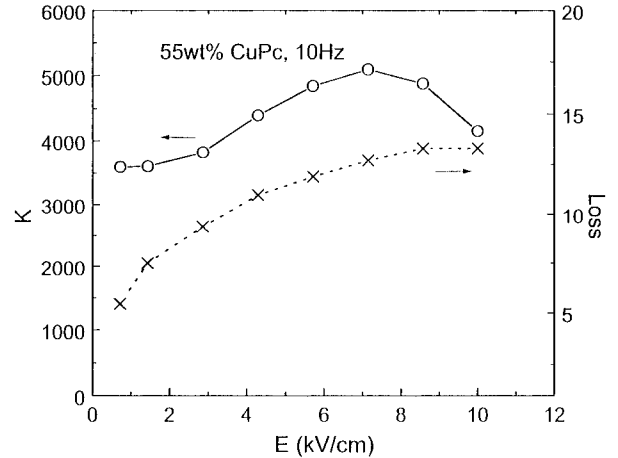
expected, the dielectric constant increased with the weight percentage of CuPc. However, the data can not be fitted with any models describing the dielectric behavior of 0–3 composites, such as the Yamada model,[10] which implies that there exist other effects in the composites studied here; for example, the percolation of resistive network of CuPc at high weight percentage of the filler and the Maxwell–Wagner relaxation space charge phenomenon.

The dielectric constant of the composite also exhibits a nonlinear behavior with field, as shown in Figure 4, which was measured at room temperature and 10 Hz on a composite film containing 55 wt % CuPc with thickness of 70 μm. Apparently, the dielectric constant becomes quite high as the field increases and, at a field of 10 kV/cm, the dielectric constant reaches 4500, and the dielectric loss is also high (~13). The dielectric breakdown was observed at ~10 kV/cm field level for this film and near that field level, a thickness strain of 0.3% was observed (the strain is approximately to the square of the applied field). This large strain is very attractive because with improved breakdown field, a high strain can be induced with a field much lower than those used in current electroactive polymers. The nonlinear behavior observed in Figure 4 originates from each component in the composite. It is understandable that the dielectric loss increases continuously with the electric field. P(VDF-TrFE) copolymer is a typical ferroelectric material that exhibits a polarization hysteresis loop. The dielectric constant of a ferroelectric material increases with electric
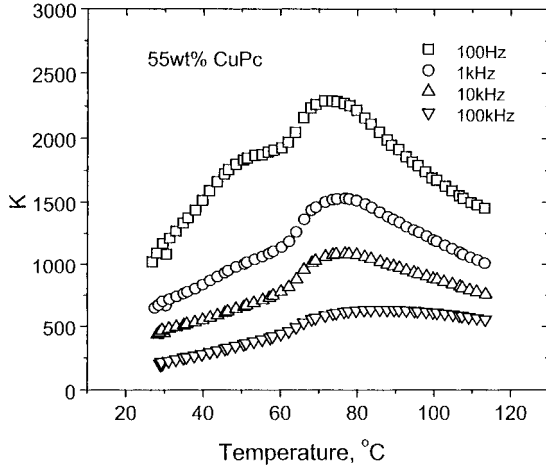
Figure 5 Temperature dependence of dielectric properties of the composite with 55 wt % CuPc filler at different frequencies.

field increasing initially and then reaches its maximum at a field near the coercive field (E_c). At higher field, the dielectric constant decreases with field increasing. From the data in Figure 4, one can observe that the dielectric constant reaches its maximum at the field of 7 kV/cm, which is much lower than the coercive field of the pure P(VDF-TrFE) copolymer. The reason is that high conductivity in CuPc makes the local electric field in P(VDF-TrFE) copolymer much higher than the applied electric field on the composite.

The high dielectric constant of CuPc can be explained in terms of the long-range electron orbital delocalization, also called nomadic polarization.[6] Metallophthalocyanine oligomers are highly conjugated and have a large planar structure. The π-electrons are completely delocalized over the entire molecule. In addition, with increased field, there is also an increased probability of electron tunneling between molecules, resulting in a higher dielectric constant and loss. After mixing with P(VDF-TrFE) matrix, the nomadic polarization of CuPc still plays an important role in the composite film, especially for the composite with high percentage of CuPc.

The temperature dependence of the low field dielectric constant of the composite with 55 wt % CuPc was also investigated and the results are shown in Figure 5. The data show that over a relatively broad temperature range, the dielectric constant is quite high, especially at lower frequency (e.g., 100 Hz). A dielectric maximum of ~2300 (at 100 Hz) was observed at 70 °C, which is

near the Curie temperature of P(VDF-TrFE) copolymer. For the copolymer, the dielectric constant is 18 at room temperature and 100 Hz and increases with temperature. At the ferroelectric–paraelectric phase transition temperature, which is ~70 °C for the copolymer studied in this article, the copolymer exhibits a dielectric maximum, which is ~50. Therefore the dielectric constant of the composite, which is determined by copolymer and CuPc, also shows a dielectric maximum. This result is consistent with the data in Figure 5.

It should be pointed out that the dielectric properties of the composites depend on the homogeneity of the composite film. For example, it has been observed that for composites with 40 wt % CuPc, if CuPc is not uniformly distributed in the composite films across the thickness, both the dielectric constant and the dielectric loss can be high (at 100 Hz, a dielectric constant of 300 and a loss of 1.2). In comparison, for the composite with the same wt % CuPc, the dielectric constant is 100 and loss is 0.15 if CuPc is uniformly distributed in the film. It is believed that the particle size of the CuPc powder is a factor that affects the homogeneity. The scanning electron microscope (SEM) pictures showed that the particle size of CuPc used in this investigation is ~1 μm. Reducing the particle size will favor a more uniform distribution of the CuPc in the composite.

CONCLUSIONS

A flexible composite film with high dielectric constant based on CuPc oligomer and P(VDF-TrFE) copolymer was prepared by a solution casting method. The dielectric constant of the composites can reach >1000 at room temperature and 100 Hz, when the weight percentage of CuPc in the composite is >55%. Because of the space charge polarization (de-localized electrons) in CuPc, the composite exhibits strong frequency dispersion. The dielectric constant and dielectric loss also show nonlinear behavior with the electric field and increases with field. The temperature dependence of dielectric constant of composite shows a dielectric maximum that is close the curie temperature of P(VDF-TrFE) copolymer.

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