

Elastomeric nanocomposites with high dielectric response

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Abstract

Dielectric elastomers (DE) are one of the best-performing kinds of electroactive polymers which are highly desirable for use in a broad of electromechanical applications. At present, the need for high-driving electric fields limits the use of DE of potential applications. Increasing the dielectric constant of DE is a feasible approach to overcome this drawback. In this study, high dielectric constant nanocomposites were developed by bonding copper phthalocyanine oligomer (CuPc) to polyurethane (PU) chains. Transmission electron microscope (TEM) images revealed that the sizes of CuPc particles in nanocomposite of PU bonded with 8.78 vol% of CuPc were in the range of 10-20nm, much smaller than the sizes (250-600nm) in PU with the same volume fraction of CuPc. At 100Hz, the nanocomposite film exhibited a dielectric constant of 391, representing a ca sixtyfold increase with respect to the pure PU. The enhanced dielectric response of the nanocomposites makes it possible to induce a high electromechanical response under a much reduced electric field (a strain of 17.7% was achieved under a field of 10V/ μm).

1. Introduction

Electroactive polymers, responding to external electrical stimulation by displaying a significant shape or size change, are attractive for a broad range of electromechanical device applications [1-6] According to their operational mechanism, Electroactive polymers can be divided into two main classes: ionic, which are activated by electrically induced transport of ions in a liquid medium, and electronic, which are activated by electric fields or Coulomb forces in general. The former generally require low voltage but high currents, while the latter need high voltage but low currents. [6] Among electronic EAPs, dielectric elastomers (DE), as well as various actuators developed with them, have been intensely studied in recent decade. Dielectric elastomer actuators consist of a polymer film sandwiched between two compliant electrodes. When a voltage is applied, the elastomer film reduces its thickness and expands its area, converting electrical energy into mechanical energy. This field is growing rapidly, whether measured by number of research papers, performance of the technology, or diversity of potential applications including micropumps, energy harvesters, space robotics, positioners, and bioinspired robotic systems, due to attractive features of dielectric elastomer actuators including large strain, fast response, high efficiency, high power-to-mass ratio, facile processibility, and affordability. [1-7]

In earlier years, much of the research focus was on actuator configurations, and in more recent years the focus has turned to investigating material properties that are critical for the enhancement of actuator performance. At present, one of the major challenges in the development of dielectric elastomer actuators is the high electric field requirement. Driving voltages up to 150 MV/m are required to actuate these elastomeric films, because the dielectric constants of elastomers used are very low (<7.0). [3,6,8] As a result, these polymers usually require high electric fields to generate high elastic energy density which limits their applications, especially in the biomedical field. [8] Composite methods, in which high dielectric constant particulates were added to a polymer matrix, have been carried out to fabricate high dielectric constant polymeric materials. [3,9] Dielectric fillers increase the dielectric constant of polymeric materials so that the required field for a certain strain can be reduced. In this study, we selected copper phthalocyanine oligomer (CuPc) as dielectric filler to enhance the high dielectric constant of polymeric materials. CuPc, a planar multiring organic semiconductor, exhibits a very high dielectric constant ($>10^5$) due to the electron delocalization within the giant conjugated molecule. [10] As expected, when dispersed in a polymer matrix, the resulting composite can exhibit increased dielectric constant. Furthermore, as an organic material, CuPc has a modulus which is much smaller than that of inorganic counterparts (such as piezoelectric ceramics). Therefore, a high dielectric constant can be achieved in their composite without losing the flexibility of the polymeric material.

It was observed however that blending also causes a decrease in the breakdown field and an increase in the dielectric loss of the resulting composites due to the agglomeration of CuPc to form large spherical particulates (~500nm). [10] As a result, the size of filler particles in composites like polymer/CuPc should be substantially reduced to a proper level. In our previous investigations, grafting approach was employed to reduce CuPc particle size in polymer matrix. [10,11] However, satisfied dispersibility of CuPc oligomer was still not achieved. It should be pointed out that, a significant aspect of such kind composite is the size effect of the CuPc particles when dispersed in polymer matrix, since the filler-polymer interface plays a relatively important role on the enhancement of dielectric response of the composites. [12]

In this research, we developed high dielectric elastomeric nanocomposites for electromechanical applications. Three composites, i.e. PU chemically bonded with CuPc (PU-CuPc), with chemically bonded and blended CuPc (PU-CuPc/CuPc), and blended with CuPc (PU/CuPc), were fabricated. PU was synthesized as matrix since it is a ferroelectric polymer and exhibits excellent flexibility, and PU with isocyanate end groups can easily react with CuPc with $-COOHs$. Morphology of the above composites differs from each other, which leads to different dielectric response. As will be pointed out later, by bonding CuPc to PU backbone, the dispersion of CuPc in PU-CuPc nanocomposite was remarkably improved. And for the resulting nanocomposite film with tailored morphology, which was fabricated by a solution-cast technique, an enhanced dielectric response was realized, and a large electric field induced strain was achieved.

2. Experimental

2.1. Materials

CuPc was synthesized following a procedure reported in Ref. 13. The soft segment, polyether N220 ($M_n=2000$) was purchased from Nanjing Oswald chemical company and was dehydrated and degassed under vacuum at 120 °C for 3 h and stored under dried nitrogen. The hard segment, 2,4-diisocyanatotoluene was purchased from BASF company and distilled

in vacuo and stored under dried nitrogen. 1,4-Dihydroxybutane (BDO) was of analytical grade and was dried with MgSO₄ followed by distillation under reduced pressure before use. Dimethylformamide (DMF) was of analytical grade and was dried with CaH₂, then distilled in vacuo. Other chemicals are of analytical grade and used as received.

2.2. Synthesis of PU-CuPc

A 100mL three-neck round bottom flask fitted with a magnetic stirrer, an addition funnel, a condenser and a nitrogen inlet was used as the reactor. TDI (1.554 g, 8.93 mmol) was dissolved in 5 mL of DMF, added to the three-neck flask, and stirred. N220 (5.0 g, 2.5 mmol) was dissolved in 15 mL of DMF and added to the funnel. The N220 solution was slowly (about 0.5 h) dripped into the TDI solution. The reaction mixture was then stirred at 70 °C for 2 h under a purified nitrogen atmosphere to form the pre-polymer. The pre-polymer was then chain extended to form a high molecular weight polymer by adding BDO (0.54 g, 6.0 mmol) to the reaction mixture and stirring at 80 °C for 5.0 h. Then, a predetermined amount of CuPc oligomer solved in DMF (the concentration is 0.02 g/mL) was added to the solution of pre-polymer through constant pressure drops of liquid funnel. The solution was stirred at 80 °C for 8 h under purified nitrogen atmosphere. The reaction mixture was precipitated into a large excess of distilled water. The resulting PU-CuPc was washed with methanol and dried under vacuum until constant weight. To obtain pure PU, the reaction mixture after chain extension was precipitated into a large excess of distilled water. The resulting PU was washed with methanol and dried under vacuum until constant weight.

2.3. Preparation of films for electric and mechanical measurement

The films were prepared using solution cast method. For the PU/CuPc films, a calculated amount of CuPc was added to the solution of PU in DMF, and then the mixture was ultrasonically stirred for about 2 h in order to obtained a homogeneous solution. Afterwards, the mixture was cast onto a polytetrafluoroethylene mold and dried in air at 70 °C for 12 h, followed by thorough removal of solvent residue under vacuum at 70 °C for 12 h. Finally, the film was annealed at 120 °C in vacuum for 12 h and slowly cooled down to room temperature (10 °C/h). For the PU-CuPc films with different CuPc content, each composite was ultrasonically dissolved in DMF directly and then followed the same procedure used for the PU/CuPc film. To fabricate a composite with CuPc particulate size between those in PU/CuPc and PU-CuPc, PU-CuPc with 3.58 vol % CuPc and neat CuPc (label the resulting nanocomposite with 8.78 vol % of total CuPc as PU-CuPc/CuPc) were ultrasonically dissolved in DMF, and then followed the same procedures used for the PU/CuPc film.

2.4. Characterization

FT-IR spectra were recorded with the sample/KBr pressed pellets using a Bruker Vector-22 FT-IR spectrometer. A combination of inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the bonding ratio of CuPc in PU-CuPc. The unreacted CuPc in sample for test was removed by soaking PU-CuPc with 50mL 0.1mol/L NaOH aqueous solution, followed with distilled water to wash out NaOH. The resulting sample was dried in vacuo at 50°C. 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 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. For the characterization of frequency dependence of the dielectric properties, an Agilent 4194A impedance analyzer was used. The films for test 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 film sample. Strain measurements were made with films stretched on a circular rigid frame. The bidirectional prestrain was 100%. Carbon based conducting grease were brushed on the top and bottom of the films. A digital video optical system was used to measure the lateral areal strain upon actuation. The corresponding transverse strain (along the specimen thickness direction) was computed from the measured lateral strain by assuming isochoric deformation and isotropic lateral displacement.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

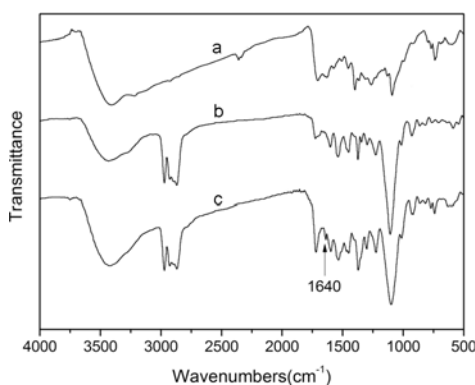


Figure 1. FT-IR spectra of CuPc, PU and PU-CuPc with 8.78 vol % of CuPc.

To substantially reduce the CuPc particle size in PU-CuPc, the bonding ratio of CuPc molecules to PU chains should be high enough. As a result, in order to realize successfully the chemical reaction between the two components, it is preferred that PU chains should bearing active functional groups that can easily react with carboxyl groups (-COOHs) around CuPc molecules. To this end, PU end capped with active -NCOs was synthesized here. The FT-IR spectra of CuPc, PU, and PU-CuPc with 8.78 vol % of CuPc are shown in Figure 1. For PU-CuPc, the absorption peak at 1640 cm^{-1} corresponds to the stretching vibration of carbonyl group in amide group (-NHCO-), and the absorption band at 935~918 cm^{-1} corresponds to the -C-O-C- nonsymmetric stretching overlapped with the vibration of coordinate bonds between copper ion and nitrogen atoms of each pyrrole ring in CuPc, all of which prove that the CuPc molecules were successfully attached to PU chains. According to the ICP-AES analysis, it was estimated that the chemically bonded CuPc in the synthesis procedure of PU-CuPc is as high as 96.8%.

3.2. Transmission electron microscopy

TEM micrographs of the three composites with a same CuPc content of 8.78 vol % are shown in Figure 2. For the PU-CuPc/CuPc, both grafted CuPc (3.58 vol %) and blended (5.20 vol %) CuPc are included. It is evident that the dispersibility of CuPc differs in the three composites. For PU/CuPc, due to the incompatibility of CuPc with PU, the CuPc molecules aggregated in nearly spherical shape particles with about 250-600 nm in diameter in the polymer matrix (Figure 2a), because CuPc has a strong tendency to form stack assemblies and

microaggregates due to its planar shape and aromatic nature [10]. While within the PU-CuPc sample, the CuPc inclusions with diameters in the range of about 10-20 nm (Figure 2c), much smaller than those in PU/CuPc, were dispersed in PU matrix. Suggested origin is that in the PU-CuPc part of CuPc oligomers attached onto PU chains can act as nucleation centers which further induced the growth of CuPc oligomer crystallite. However, since the movability of bonded CuPc groups was hindered by the PU backbone, the accessibility of adjacent CuPc molecules was restricted, and the growth of crystallite was markedly limited. On the contrary, aggregation of CuPc can hardly be prevented in PU/CuPc. Furthermore, within the PU-CuPc/CuPc nanocomposite the sizes of CuPc particulates ranged from 30-70 nm, (Figure 2b) and were much larger than those in PU-CuPc, but much smaller than those in PU/CuPc. This can be explained that, in the PU-CuPc/CuPc sample, the presence of PU-CuPc with 3.58 vol % CuPc enhances the compatibility between PU and CuPc. Consequently, the CuPc particle sizes were remarkably decreased as compared with those in PU/CuPc. [10,11] Nevertheless, the blended CuPc molecules can move more easily toward nucleation centers than the bonded molecules can. Therefore, compared with PU-CuPc, PU-CuPc/CuPc includes larger sized CuPc particles. It should be pointed out that the smaller CuPc particle size will further increase the interface exchange coupling effect and the dielectric properties of the composite. We will come to this aspect in the next section.

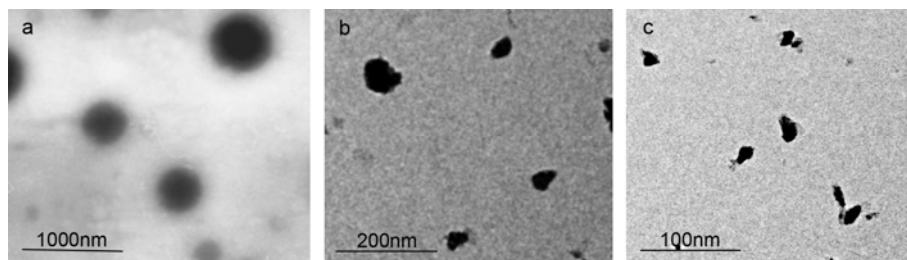


Figure 2. TEM pictures of (a) PU/CuPc, (b) PU-CuPc/CuPc and (c) PU-CuPc. The volume fraction of CuPc in the three composites is 8.78 vol %.

As can also be observed in Figure 2, the three composites display different shape regularity of CuPc particulates. The shape of CuPc particulates in PU-CuPc is irregular. In contrast, in PU/CuPc the CuPc molecules aggregated in nearly spherical shape particles. During the phase separation between PU and CuPc as the minor component, which is driven by a reduction in the surface energy of CuPc particulates, these oligomers spontaneously formed nearly spherical shape particles during the solvent evaporation, which is the case for the PU/CuPc blend. While for the PU-CuPc sample, however, because the movement of bonded CuPc molecules was obstructed by the PU chain, it was hard for them to move freely to form spherical crystallites.

The elastic modulus is 21.7 and 29.6 MPa at ambient condition for the pure PU and the PU-CuPc, respectively. The enhancement of elastic modulus for the composite is derived from the physical cross-linking effect of CuPc as well as higher elastic modulus of CuPc (~2 GPa). [14]

3.3. Electrical properties of the composites

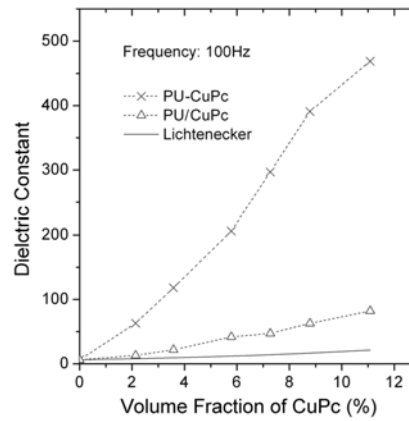


Figure 3. Variation of the dielectric constant of PU-CuPc and PU/CuPc with the volume fraction of CuPc measured at 100 Hz. Dashed curves are a guide to the eye and solid curve is from Eq. 1.

Figure 3 shows the dielectric constants of PU-CuPc and PU/CuPc measured at room temperature and 100 Hz as a function of the volume percentage of CuPc, together with the curve calculated from Eq 1. As expected, the dielectric constants increase with the volume fraction of CuPc. It should be pointed out that the dielectric constants of the composites are much higher than those derived from various models. For instance, if we regard the composites as random mixtures of PU matrix and CuPc particulates, according to the widely used logarithmic dielectric mixing rule proposed by Lichtenecker, the effective dielectric constant (K) of the composites can be estimated as:[3]

$$\ln K = c_1 \ln K_1 + c_2 \ln K_2 \quad (1)$$

where c_i and K_i are the volume fraction and dielectric constant of component i , respectively. Here, K_1 and K_2 are 4.3×10^5 and 6.3 separately. Obviously, this model cannot be used to explain the large enhancement of the dielectric constant as observed in both composites, especially for PU-CuPc (Figure 3). The enhancement of dielectric constant of the composites could be arising mainly from the interface effect. [12] We will discuss this aspect later.

Frequency dependent dielectric constant and dielectric loss at room temperature are shown in Figure 4, of both pure PU and the three composites (PU-CuPc, PU-CuPc/CuPc, and PU/CuPc) with a same CuPc content of 8.78 vol %. As generally expected, the dielectric constants (K) of composites are much higher in comparison to that of the pure PU. For instance, at 100Hz, The dielectric constants of PU-CuPc, PU-CuPc/CuPc, and PU/CuPc are 391, 310, and 48, representing nearly 62-, 50-, and 7.6-fold enhancement with respect to that of the pure PU, respectively. In addition, for each composite sample, the phenomenon of dielectric dispersion at low frequencies is observed. This phenomenon is ascribed to interfacial polarization mechanism caused by the large difference in dielectric constant between the polymer matrix and the filler. [15,16] Interestingly observed in Figure 4 is that, although the CuPc content in three composite samples is the same, the dielectric constant of PU-CuPc is higher than that of PU-CuPc/CuPc, while the curve of PU-CuPc/CuPc is above that of PU/CuPc over the observation frequency range. For example, at 100Hz, the dielectric constant of PU-CuPc is more than 1.25 and 8.12 times higher than that of PU-CuPc/CuPc and PU/CuPc, separately. It was suggested that this phenomenon was caused by the so called interface exchange coupling effect. Li [12] has predicted that for composite like polymer with high dielectric constant filler, 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. Therefore, the dramatic enhancement of dielectric response observed in PU-CuPc is probably caused by the stronger exchange coupling effect, as well as the interfacial polarization effect, due to the much smaller CuPc particle size as compared with that of PU-CuPc/CuPc and PU/CuPc samples as observed in TEM micrographs.

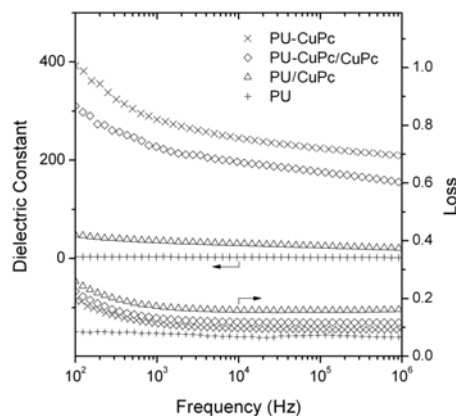


Figure 4. Dielectric properties versus frequency for pure PU, PU/CuPc, PU-CuPc/CuPc and PU-CuPc. The volume fraction of CuPc in the three composites is 8.78 vol %.

The dielectric losses of composites are relatively low (Figure 4). CuPc suffers a high dielectric loss due to the long range intermolecular hopping of electrons. [11,17] 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 PU-CuPc is lower than those of the other two composites, which can be attributed to the reduced particle size and improved dispersibility of CuPc in PU-CuPc. At 100 Hz, the loss of the PU-CuPc is about 0.19.

Due to the large dielectric response in PU-CuPc, the field induced thickness strain of the PU-CuPc film reaches 17.7% under a field of 10V/ μm , which is a large increase of nearly 5.4 times over that of PU/CuPc sample (3.3%).

4. Conclusions

A nanocomposite of PU chemically attached with CuPc was developed. The sizes of the CuPc particles within the nanocomposite with 8.78 vol% of CuPc are in the range of 10~20 nm. Size effect played a very important role in the enhancement of electric performance of the nanocomposite. The nanocomposite exhibits a high dielectric constant (391), low loss (0.19), large electric field induced strain (17.7% under 10V/ μm), all of which are highly desirable for high performance electromechanical actuators and artificial muscles.

Acknowledgements

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