

at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether), bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene; stretching said polymer greater than its original length; and thereafter annealing said polymer at a temperature below its melting point, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross, exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibits an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

Ter-polymers include, but are not necessarily limited to, polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene hexafluoropropylene, polyvinylidene fluoride tetrafluoroethylene hexafluoropropylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

CuPc/PVDF-TrFE composites of the present invention can provide high dielectric constant (~1,000 at 100 Hz with a loss at 0.5 level). In addition, a strain which is proportional to E² of 0.3% can be obtained under a field of 1 V/μm from the composite with 55 wt % of CuPc. And the composite film is flexible with a elastic modulus 1.2 GPa. By further improving the breakdown field, the strain level can be much higher. For example, for a composite with 40 wt % CuPc and irradiated P(VDF-TrFE) polymer as the matrix, a strain of near 2% is induced under a field of 13 MV/m. The elastic modulus of the composite is 0.6 GPa.

A preferred high dielectric constant semiconductor organic solid used in this invention is a metallophthalocyanine oligomer, copper-phthalocyanine (CuPc) oligomer whose molecular structure is shown in FIG. 1. The CuPc has a room temperature dielectric constant at 100 Hz of more than 1,000 and the dielectric loss is also high. 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. The P(VDF-TrFE) based relaxor ferroelectric polymers, which have a relatively high room temperature dielectric constant (~40) after irradiation treatment, is 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.

Synthesis of copier-phthalocyanine oligomer. Copper-phthalocyanine oligomer was synthesized by solution method. 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 2N hydrochloric acid saturated with sodium chloride and filtered after cooling to room temperature. The product was neutralized by 2N potassium hydroxide solution containing sodium chloride at 90° C. After centrifugation, the product was dried at room temperature under vacuum.

Sample preparation. The P(VDF-TrFE) based relaxor ferroelectric polymer, either the high energy irradiated copolymer or non-irradiated terpolymer, 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 additional 12 h to remove any remaining traces of the solvent. Composites with weight percentage of the CuPc from 30–80% were prepared.

The free standing composite films of CuPc oligomer and P(VDF-TrFE) copolymer with different weight percentage of CuPc from 30% to 80% were prepared. Since the density of CuPc is close to that of P(VDF-TrFE) copolymer, the wt % is also close to the volume % of the CuPc in the composite. The films prepared are flexible and the Young's modulus of the composite with 55 wt % CuPc was measured to be 1.2 GPa at 250° 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.

Presented in FIG. 2 is the dielectric constant and loss as a function of the frequency (100 Hz to 100 kHz) measured at room temperature for the composite films containing different CuPc wt %. These results show that the composite films possess high dielectric constant. At 100 Hz and room temperature, the dielectric constant of the composite with 55 wt % CuPc is about 1,000. And even up to 10 kHz, the dielectric constant of the composite with 55 wt % CuPc is still above 500. In the same frequency range, the dielectric loss varies around 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 wt %, there exist resistance percolation.

The dielectric constant of the composite with 55 wt % CuPc was also characterized at lower frequencies (1 Hz to 100 Hz) and the result is shown in FIG. 3. The dielectric constant increases continuously as the frequency decreases, and at 1 Hz it reaches 3,000 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 high dielectric constant of CuPc can be explained in terms of the long-range electron orbital delocalization, also called nomadic polarization. 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