

FIG. 4 shows the induced strain of a composite with 40 wt % CuPc filler and the relaxor ferroelectric P(VDF-TrFE) copolymer matrix measured at room temperature and 1 Hz applied field

FIG. 5a and FIG. 5b are graphs of the dielectric constant and dielectric loss, respectively, of the composite with 55 wt % CuPc filler at different frequencies.

FIG. 6 shows the molecular structure of ClAn/Cl₄ and Pyrene/o-iodoBA.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a polymer based material with preferred, but not necessarily limited to, dielectric constant of higher than 400 while still retaining the flexibility of the polymers, with elastic modulus in the range of polymers (~1 GPa). This class of material has been shown to exhibit high electromechanical properties under low applied field (<20 V/ μ m).

In electroactive materials, it is well known that when an electric field E is applied to a material with the dielectric constant K and elastic modulus Y, there is an electrostatic force (Maxwell stress) generated strain S:

$$S=K\epsilon_0 E^2/Y$$

where $\epsilon_0=8.85\times 10^{-12}$ F/m. In addition, the electromechanical conversion efficient of a Maxwell stress based material is also proportional to KE^2/Y . In current polymers, because of low dielectric constant (<10), in order to generate large Maxwell strain with high energy conversion efficiency, a material which is very soft (low elastic modulus and in most of the current soft polymers with high strain, the modulus is at or below 10 MPa level) and a very high electric field (>100 V/ μ m) are required. For almost all practical device applications, it is necessary to reduce the applied field and use polymer systems with a reasonable elastic modulus (~1 GPa). In order, to reach those goals, it is clear from eq. (1) that one should significantly raise the dielectric constant of the material.

Recently, it was also discovered that in modified poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) based polymers, a high electrostrictive strain with high elastic energy density can be achieved (for example 5% strain under 150 V/ μ m field). One of the issues to further improve the performance of the material is to reduce the driving electric field markedly while still maintain the high strain and high elastic energy density.

Metallophthalocyanine oligomers such as copperphthalocyanine (CuPc) oligomers have been shown to exhibit high dielectric constant (>1,000) and high dielectric loss while elastically is relatively compliant. One of the problems with CuPc is the poor processibility. Recently, it has also been shown that poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) based polymers, through proper modifications such as high energy irradiation and terpolymers with selected ter-monomers, exhibit relatively high room temperature dielectric constant (>50) which is by far the highest among the all polymers known and high electrostrictive strain. Therefore, by forming CuPc/PVDF-TrFE composites, one can make use of the very high dielectric constant of CuPc while blocking the dielectric loss due to the high insulation nature of PVDF-TrFE. Furthermore, PVDF-TrFE as the matrix material can also provide good processing capability which also has relatively high dielectric constant and high field induced strain.

Modified poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) based polymers. Ferroelectric polyvinylidene

fluoride polymer, that has been processed to exhibit an electrostrictive strain of 4% or more when an electric field strength of 50 megavolts per meter or greater is applied thereacross, has been developed. The processing of the polymer preferably involves subjecting it to either electron beam radiation or gamma radiation. The polyvinylidene fluoride polymer is selected from the group of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene tetrafluoroethylene P(VDF-TFE), polyvinylidene trifluoroethylene hexafluoropropylene P(VDF-TFE-HFE) and polyvinylidene hexafluoropropylene P(VDF-HFE). Such ferroelectric polymers can be prepared by a process comprising the steps of annealing a polyvinylidene fluoride polymer at a temperature at or about 130° C. to about 140° C. for about 16 hours; and irradiating said polyvinylidene fluoride polymer in an oxygen free atmosphere with an energy in the range from about 500 KeV to about 3 MeV to produce a relaxor ferroelectric polymer which exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of about 100 megavolts per meter or greater is applied thereacross. The irradiating step is preferably at a temperature from about 25° C. to about 120° C.

Relaxor ferroelectric polymers (polyvinylidene fluoride polymers) are preferably selected from the group consisting of: polyvinylidene fluoride homopolymer, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene fluoride-tetrafluoroethylene P(VDF-TFE), polyvinylidene fluoride trifluoroethylene-hexafluoropropylene (VDF-TFE-HFE) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE). In a preferred relaxor ferroelectric polymer the molar percentages of polyvinylidene fluoride/trifluoroethylene are from about 30/70 to about 75/25 mol %.

Preferred relaxor ferroelectric polymers of electrostrictive polyvinylidene fluoride exhibit 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. Such relaxor ferroelectric polymers generally exhibit the following properties: a dielectric constant, at room temperature, of greater than 40 at 1 kHz or higher; and an elastic energy density, at room temperature, of greater than 0.3 Joules/cm³ or 160 Joules/kg, which enables avoidance of breakdown at applied field levels thereacross of at least 350 megavolts per meter.

Terpolymers exhibiting high room temperature dielectric constant and high strain. Polymers are prepared by polymerizing a mixture of three monomers comprising: at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene (if not already present), vinyl fluoride, perfluoro (methyl vinyl ether); bromotrifluoroethylene, chlorotrifluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene. Polymers of the invention exhibit 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; exhibit a dielectric constant, at room temperature, of 20 or higher at 1 kHz; and exhibit an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

Terpolymer process. Also, terpolymers may be prepared by a process comprising: polymerizing a mixture of three monomers comprising at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and