Optimized magnetodielectric effect on high-temperature polymer-based nanocomposites

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#Equal contribution

CoFe₂O₄ (CFO) ferrite nanoparticles with an average size of 15 nm were synthesized by a hydrothermal method and used to develop magnetodielectric (MD) composites with the piezoelectric diamine 2CN/diamine 0CN as polymer matrix . It is shown that the dielectric constant, dielectric loss, and saturation magnetization values of the composites increase with the increasing CFO content, being 4.4, 0.01, and 12 emu.g⁻¹, respectively, for the sample with 20 weight percentage (wt.%) of ferrite. Additionally the large MD response (MD (%)=10.15 and magnetodielectric coefficient (γ)=5.8x10⁻²) demonstrates the effective magneto-mechano-electrical interaction between magnetostrictive CFO and the polymer matrix. Such high MD response, the highest reported for polymer-based composite materials, can support innovative applications in the areas of sensors, actuators, and filters, among others.

1. Introduction

Aromatic polyimides (PI) are characterized by a high dielectric response, thermal stability, and chemical/radiation resistance¹. They are widely used as high-temperature insulators ($T \leq 200^\circ\text{C}$), circuit boards, packaging materials and dielectric interlayers in microelectronics. In addition, they are also applied in fuel cells or battery separation membranes. Another interesting feature is related with their photophysical properties (absorption and fluorescence), with many applications in photovoltaic, electrochromic, photochromic, thermo-optical, and/or electroluminescent devices²⁻⁴.

However, aromatic polyimides show certain characteristics such as stiffness, toughness, low resistance to fire/ignition and also their barrier properties that are inadequate unless they are modified through addition of fillers leading to the development of composite or nanocomposite materials⁵. In particular, nanoparticles have been proved to be effective additives for introducing useful new properties or characteristics in aromatic polyimides⁶.

The variety of polyimide nanocomposites reported in the literature is very wide, due to the high number of potential applications. It is possible to find examples with carbon nanotubes (CNTs)⁷, clays⁸, graphene⁹ and with nanoparticles, such as copper (Cu)¹⁰, silver (Ag)⁶, barium titanate (BaTiO_3)¹¹, silicon dioxide (SiO_2)¹², titanium oxide (TiO_2)¹³ or calcium carbonate (CaCO_3)¹⁴. Nevertheless, it is difficult to find reports on the use of ferrite nanoparticles in polyimides for magnetism-based applications^{15,16}. This type of composites is of particular interest, since ferrites are important magnetic materials with applications in the areas of sensors, electronics, communication, magnetic recording, microwave absorption-based devices, electrical and automobile industries as well as an increasing applicability in the biomedical and biotechnology fields^{17,18}. Interestingly, ferrites can be used as magnetostrictive phase in magnetoelectric (ME) composites, due to their high magnetostrictive coefficient (up to 200 ppm) and high Curie ($\approx 550^\circ\text{C}$) temperatures among magnetic oxides¹⁹⁻²¹. A ME material is characterized by the variation of the electrical polarization as a response to an applied magnetic field or by the variation of the magnetization by the application of an electric field²². Since ME materials show an interesting interplay between the magnetic and electric properties of matter, those materials have drawn increasing interest due to its potential applications in areas such as information storage, spintronics, sensors and actuators, among others.²² ME materials can also reveal an important

magnetodielectric (MD) coupling, allowing the control of the dielectric properties by an applied magnetic field, expanding the range of applications to tunable filters or four-state memories, among others¹⁶.

In this work, composite films with 0–3 connectivity were prepared via in-situ polymerization, using spherical cobalt ferrite nanoparticles (CoFe_2O_4) as fillers and amorphous copolyimides, 3-bis(3-aminophenoxy)benzene (diamine 0CN) and 1,3-bis-2-cyano-3-(3-aminophenoxy)phenoxybenzene (diamine 2CN), as polymer matrix (Figure 1).

Figure 1. Schematic representation of the two repetitive units of the copolyimide with the polar groups (above) and of a cobalt ferrite nanoparticle (below).

Such composition has been chosen to tackle the main challenge of the polymer-based nanocomposite with the highest magnetodielectric response reported in the literature¹⁶, namely, to increase the temperature range of application above 100°C ^{1,16}. The amorphous copolyimide, 2CN/2CN can be used as an alternative to the semicrystalline poly(vinylidene fluoride), PVDF, and family polymers²³, allowing the use of polymer-based MD materials in higher-temperature applications.

Experimental

All chemicals were used as received from the suppliers, while CFO nanoparticles were synthesized as reported elsewhere²⁴. The CFO particles are characterized by....

Synthesis

CFO/OCN2CN films were prepared from 4,4'-oxydiphthalic anhydride (ODPA) and a mixture of two aromatic diamines, 1,3-bis-2-cyano-3-(3-aminophenoxy)phenoxybenzene (diamine 2CN) and 1,3-Bis(3-aminophenoxy)benzene (diamine OCN) with cobalt ferrite magnetic nanoparticles (CoFe_2O_4 , CFO) following the procedure schematically indicated in Figure 2. Firstly (step 1), the nanoparticles were introduced into a vial containing dimethylacetamide (DMAc), and the vial was placed in an ultrasonic dispersion reactor for 60 min to ensure the uniform dispersion of the CFO on DMAc. Then (step 2), a mixture of the two aromatic diamines (50% mole percentage) was added and stirred until the complete dissolution of the diamines. The content of ferrite nanoparticles ranged from xxx to xxx.

Figure 2. Schematic representation of the polyimide based nanocomposites fabrication procedure.

Later, 4,4'-oxydiphthalic anhydride (ODPA) was introduced to the mixture and (step 3) stirred at room temperature for 24h in a dry nitrogen atmosphere resulting in a viscous polyamic acid (PAA)

solution containing CFO nanoparticles (Figure 3). Finally, (step 4), the mixture was cast in 150 μm thick films and (step 5) thermally imidized according to the thermal treatment presented in Figure 3.

Figure 3. a) Thermal treatment used in the preparation of the CFO/P0CN2CN ME nanocomposites. b) TEM image of the synthesized CFO nanoparticles.

The ferrite nanoparticles (15 nm diameter, Figure 3)) content was varied from 0 to 20 in weight percent (wt.%), 0 to 0.1 in volume fraction aiming to avoid losses in the flexibility of the material, large agglomerates and increased fragility.

Sample characterization

Transmission electron microscopy (TEM) images were obtained with a Titan ChemiSTEM transmission electron microscope (FEI Company), operated at 200 kV and having a resolution of 0.24 nm. The sample was prepared by dropping ultrasonically dispersed NPs onto a holey Cu carbon grid, followed by the evaporation of the solvent.

Measurements of the electrical capacity and dielectric loss ($\tan \delta$) were performed with an automatic Quadtech 1929 Precision LCR meter with an applied voltage of 0.5 V in the frequency range from 1 Hz to 1 MHz. Such frequency range was selected to contain the resonance frequency of the polymer-based nanocomposites. In order to obtain a plane parallel condenser geometry, Au contacts with 5 mm diameter were deposited on both sides of the samples using a Polaron SC502 sputter coater. The real part of the dielectric constant, ϵ' , was determined from the electrical capacity (C) taking into account the geometry of the sample (thickness (d) and electrode area (A)) (equation 1):

$$\epsilon' = \frac{C \times d}{A} \quad (1)$$

Room-temperature magnetic hysteresis loops were measured at room temperature using a Microsense 2.2 Tesla Vibrating Sample Magnetometer.

With the purpose of obtaining the out-of-plane MD coefficient, a *DC* magnetic field was applied by an electromagnet, with a maximum value of 0.5 T, along the perpendicular direction of the electric polarization of the aromatic polyamides, i.e., parallel the surface of the composites. The induced change in the dielectric response of the composites was measured with an automatic Quadtech 1929 Precision LCR meter. The MD coupling was studied at magnetic fields up to 0.5 T, once for higher fields the piezomagnetic coefficient of CoFe_2O_4 decreases, leading to a decrease in the MD response.

Results and discussion

The dielectric response and magnetic properties were studied first to investigate the effect of CFO loading within the nanocomposite (Figure 4).

Figure 4. (a) Frequency-dependent dielectric response for CFO/0CN2CN nanocomposites and; (b) Room-temperature variation of the dielectric constant (squares) and dielectric loss ($\tan\delta$ - circles) of the polymeric composites as a function of CFO content for a frequency of 5 kHz; (c) Room temperature hysteresis loops for the pure ferrite nanoparticle powder and the CFO/0CN2CN nanocomposites; (d) Saturation magnetization values as a function of CFO content.

Figure 4a shows that the dielectric constant first decreases fast with increasing frequency, and, later, remains almost constant for frequencies higher than 10 kHz. This behavior at the lower frequencies range can be explained by the Maxwell–Wagner type polarization, in agreement with Koop's phenomenological models²⁵.

For all measured frequencies it is observed an increase of the real part of the dielectric permittivity for the composites with respect to the neat 0CN2CN, reaching the maxim value for the composite with 20 wt.% of CFO content. The dielectric losses also increase with increasing nanoparticle content reaching the maximum value 0.01 at 5 kHz in the 20 wt.% composite sample. Figure 4b exhibit the variation of the dielectric properties to the nanocomposites with CoFe₂O₄ wt.% at a frequency of 5 kHz and reveals that the addition of CFO nanoparticles in the 0CN2CN matrix leads to a gradual increase of the real part of dielectric constant (from 2.8 to 4.4) and dielectric losses (from 0.006 to 0.010). The observed increase of both the dielectric constant and the dielectric loss is related to the accumulation of interfacial charges in the nanoparticle-polymer

interface, which is known as the Maxwell–Wagner–Sillars interfacial polarization phenomenon^{26,27}.

Regarding magnetic properties, all CFO/0CN2CN composite develop a ferromagnetic hysteresis loop with a coercivity of ≈ 0.20 T. Moreover an increase of the remanence and saturation magnetization values with increasing CFO loading is observed.

The maximum magnetization values and shape of the measured hysteresis loops for the CFO/0CN2CN composite (Figure 4c) demonstrate that magnetic particles are randomly oriented within the polymer matrix. Additionally, the measured maximum magnetization of $12. \text{ emu} \cdot \text{g}^{-1}$ reveals that CoFe_2O_4 nanoparticles are well distributed and dispersed in the 0CN2CN matrix and that the maximum magnetization value is directly proportional to the amount of nanoparticles loaded into the polymer-based composite.

The simultaneous existence of dielectric and ferromagnetic orders allows the coupling between electric polarization and magnetization. The coupling was measured by monitoring the variation of the dielectric constant with increasing magnetic field for the different composites (Figure 5).

Figure 5. (a) Dielectric constant as a function of the DC magnetic field at 500 Hz; (b) MD (%) as a function of the frequency ; (c) MD (%) as a function of the CFO content at 400 mT and 500 Hz; (d) Parabolic curve fitting of the MD (%) as a function of the DC magnetic field.

Figure 5a shows a decrease of the dielectric constant with increasing DC magnetic field modulus that reflects a decrease of the dipolar mobility as a consequence of increasing hardness of the composite resulting from the mechanical compressing induced by the magnetostrictive strain. Similar to what happens on ME composites, there is an electromechanical resonance frequency at which the magnetodielectric effect (MD) coupling is optimized²², that was found to be 500 Hz (Figure 5b) for the CFO/0CN2CN MD composites.

Such variation in the dielectric response with the applied magnetic field is usually quantified by the MD constant, defined as $MD (\%) = (|e_H - e_0| / e_0) \times 100$, where e_H and e_0 are the dielectric constants with and without the applied magnetic fields, respectively¹⁶.

The additional mechanical force that emerges from the magnetostrictive response of the CFO nanoparticles and decreases the dielectric response of the composite films is higher for higher CFO loadings, resulting in the increase of the MD (%) from 15.6 (for the wt.% sample) to 19.2 (for the 20 wt.% sample).

The obtained MD(%) *vs* H_{DC} curves (Figure 6d) can be fitted with a parabolic equation wherein the MD is proportional to the P²M² term in a symmetry-allowed Ginzburg–Landau free energy (P and M are the electrical polarization and magnetization, respectively)²⁸. Such quadratic dependence is observed in many ME materials²⁸, where their thermodynamic potential (φ) can be written as:

$$\phi = \phi_0 + \alpha P^2 + \frac{\beta}{2} P^4 - PE + \alpha' M^2 + \frac{\beta'}{2} M^4 - MH + \gamma P^2 M^2 \quad (3)$$

where α , β , α' , β' and γ are coupling coefficients. A ferroelectromagnet material is described by a potential ϕ that can be used to quantify the effect of magnetic ordering on the dielectric susceptibility, and the term representing the exchange MD interaction $\gamma P^2 M^2$ is allowed in any ferroelectromagnet^{29,30}. In this way, the change of the relative dielectric constant will be proportional to the square of the magnetic order parameter, i.e., $\Delta\epsilon \approx \gamma M^2$ (Figure 6).

Figure 6. (a) Variation of the dielectric constant versus $(M)^2$ plot for the CFO/PVDF composites; (b) γ as a function of the CFO content at 500 mT and 5 kHz.

Figure 6 shows that the resulting $(|e(H) - e(0)|) / e(0)$ *vs.* M^2 plots are properly fitted ($r^2 \geq 0.96$). The value of the MD interaction coefficient- γ - (slope of $|e(H) - e(0)| / e(0)$ *vs.* M^2 plots) of the

composite samples decreases from 0.058 $\text{emu}^2 \text{g}^2$ to 0.001 $\text{emu}^2 \text{g}^2$ with increasing ferrite content from 5 to 20 wt.%, suggesting a lower magnetodielectric coupling with increasing ferrite content. Similar decrease in the value of γ with the increasing filler content has already been reported in other polymer-based CFO MD composites, and is related to the increase of dielectric losses and the deterioration of mechanical connectivity with the increased ferrite loading that forms agglomerates.

Table I. Type of MD material, composition and highest coupling parameters found in the literature.

Materials composition			Coupling (Temperature, H_{DC})		Ref.
Type	Ferroelectric	Magnetic	MDE (%)	γ ($\text{emu}^{-2}\text{g}^2$)	
Polymer Composite	PVDF	CoFe_2O_4	4.2 (300 K, 0.5 T)	1.5×10^{-2}	¹⁶
	OCN2CN	CoFe_2O_4	19.15 (300K, 0.4T)	5.8×10^{-2}	Our

All in all, Table I compares the highest MD coupling parameters (MDE (%) and γ) reported in the literature with the ones reported in the present study. It was observed that the substitution of PVDF to OCN/2CN not only allows the use of the CFO/OCN2CN composite on high-temperature technological application but also shows improved MD effect (19.15% and $5.8 \times 10^{-2} \text{emu}^{-2}\text{g}^2$).

Conclusion

Composite films were produced from dianhydride ODPA and a combination of two aromatic diamines 3-bis(3-aminophenoxy)benzene (diamine OCN) and 1,3-bis-2-cyano-3-(3-aminophenoxy)phenoxybenzene (diamine 2CN) with 15 nm CoFe_2O_4 (CFO) magnetostrictive nanoparticles. The value of dielectric constant, dielectric loss and saturation magnetization of the polymer-based composites increase with increasing CFO content being maximized to 4.4, 0.01, and 12 emu.g^{-1} , respectively, for the composite film

with 20 weight percentage (wt.%) of CFO. The linear fitting of the variation of the dielectric constant ($\Delta\epsilon$) with the square of magnetization allowed to determine the value of magnetoelectric interaction coefficient (γ)= 5.8×10^{-2} , the highest reported on polymer-based MD materials. Thus, the large MD response and the thermal stability up to xxx °C, as well as due to its simple processability and flexibility, makes this polymeric composite suitable for a wide range of applications.

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Author Contributions

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ABBREVIATIONS

diamine 0CN , bis(3-aminophenoxy)benzene; diamine 2CN, 1,3-bis-2-cyano-3-(3-aminophenoxy)phenoxybenzene; MD, Magnetodielectric; ME, Magnetoelectric.

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