Fabrication of flexible and self-standing inorganic–organic three phase magneto-dielectric PVDF based multiferroic nanocomposite films through a small loading of graphene oxide (GO) and Fe₃O₄ nanoparticles†

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Flexible inorganic–organic magneto-electric (ME) nanocomposite films (PVDF, PVDF-GO, PVDF-Fe₃O₄ and PVDF-GO-Fe₃O₄), composed of well-dispersed graphene oxide (GO 5 wt%) and magnetic Fe₃O₄ nanoparticles (5 wt%) embedded into a poly(vinylidene-fluoride) (PVDF) matrix, have been prepared by a solvent casting route. The magnetic, ferroelectric, dielectric, magneto-dielectric (MD) coupling and structural properties of these films have been systematically investigated. Magnetic (Ms = 2.21 emu g⁻¹) and ferroelectric (P = 0.065 µC cm⁻²) composite films of PVDF-GO-Fe₃O₄ (PVDF loaded with 5% GO and 5% Fe₃O₄) with an MD coupling of 0.02% at room temperature (RT) showed a three times higher dielectric constant than that of the pure PVDF film, with a dielectric loss as low as 0.6. However, the PVDF-Fe₃O₄ film, which exhibited improved magnetic (Ms = 2.5 emu g⁻¹) and MD coupling (0.04%) properties at RT with a lower dielectric loss (0.3), exhibited decreased ferroelectric properties (P = 0.06 µC cm⁻²) and dielectric constant compared to the PVDF-GO-Fe₃O₄ film. MD coupling measurements carried out as a function of temperature on the multi-functional PVDF-GO-Fe₃O₄ film showed a systematic increase in MD values up to 100 K and a decrease thereafter. The observed magnetic, ferroelectric, dielectric, MD coupling and structural properties of the nanocomposite films are attributed to the homogeneous dispersion and good alignment of Fe₃O₄ nanoparticles and GO in the PVDF matrix along with a partial conversion of nonpolar α-phase PVDF to polar β-phase. The above multi-functionality of the composite films of PVDF-Fe₃O₄ and PVDF-GO-Fe₃O₄ paves the way for their application in smart multiferroic devices.

Introduction

Multiferroics are materials that exhibit more than one primary ferroic order parameter like ferromagnetism, ferroelectricity and ferroelasticity simultaneously in a single phase. Further, researchers consider materials to be multiferroic only if they exhibit coupling between primary ferroic order parameters. These multiferroic materials (MFMs) are of great importance due to their potential applications in multi-functional devices.¹,² The key to device functionality is a multiferroic material with strong magneto-electric (ME) and magneto-dielectric (MD) coupling for a simple control of magnetization via polarization or dielectric constant and vice versa. Unfortunately, very few materials have shown the coexistence of magnetism and ferro-electricity (FE) with a reasonable dielectric constant and a low dielectric loss. Materials with magnetism and FE may have a weak ME coupling at room temperature or may not possess desirable dielectric properties.³,⁴ Though there are a few single phase multiferroic materials, their applications are limited, either due to their order parameters existing at low temperatures⁵ or difficulties in synthesizing them in a stoichiometric form with low dielectric loss⁶ or ME coefficients being too weak in these materials.⁷

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Recently, the ME effect has been observed and investigated in a range of single-phase materials like Co$_3$B$_7$O$_{13}$Br, Bi$_4$FeTi$_3$O$_{15}$, and LiCoPO$_4$. Such single-phase ME materials, however, are not suitable for use in ME devices due to their low Neel temperatures and weak ME effect. Achieving strong ME coupling between net magnetization and net electric polarization is particularly important for device applications. This problem can be partially circumvented by fabricating multiiferroic composite materials or hybrid materials with diverse properties. For example, ferrite–piezoelectric (PE) ceramic composites, such as CoFe$_2$O$_4$–BaTiO$_3$, ferrite–lead zirconate–titanate (PZT), and Tb–Dy–Fe alloys (Terfenol-D)–PZT, have been found to exhibit much higher ME coupling than the mono-phase multiiferroics. In such composites, the ME effect is known to be an extrinsic “product property”, resulting from the interaction of the elastic components of the ferrite and FE constituents. However, these ceramic composites have some limitations including chemical reaction, inter-diffusion and differential thermal expansion during high temperature processing (>1000 K), which make them unsuitable for device applications. One way to simplify the preparation process as well as avoid the problem of inter-diffusion between the FE and magnetostrictive phases is by fabricating polymer based composite materials made by filling polymers with magnetic, dielectric and FE component phases which have lower processing temperatures. In this context, stimuli-responsive polymers like PVDF are among the most important polymers due to their FE and PE properties. PVDF is a semi-crystalline polymer exhibiting at least four crystalline phases, namely, α, β, γ, and δ. Among these, polar β-phase is the most desirable phase with high permittivity or FE value. PVDF has been chosen as the polymer matrix in the present study due to the above mentioned desirable properties and its low cost, good mechanical properties, and chemical and electrical resistance. PVDF is easy to process and can be cast into any desirable shape by simple methods.

The addition of nano-fillers to PVDF is often performed to initiate the nucleation of the electro-active β-phase. In most of the studies graphene oxide (GO) has been selected as a nano-filler in a polymer matrix, because of its high surface area, aspect ratio, mechanical strength and thermal conductivity. Further, GO is an electrically insulating material due to its disrupted sp$^2$ bonding networks. It has abundant surface groups such as epoxy, hydroxyl and carboxylic acid and can be easily dispersed in an organic solvent via sonication in the form of individual GO nanosheets. In addition, GO can uniformly disperse in a polymer matrix because of hydrogen bonds or strong and specific interactions between oxygen-containing functional groups. Kuwahara et al. demonstrated that the dielectric constant of the PVDF composites can be increased by loading it with GO by the solvent casting method. Sigumani et al. used a co-solvent approach involving water and DMF to dissolve GO and PVDF to obtain the GO/PVDF composites with increased electrical conductivity. However, studies on polymer based multiiferroic or functional composites having reasonable magnetic, ferroelectric, and dielectric responses with low dielectric loss and MD coupling are mostly centered on two phase materials, except for a few isolated reports on three phase (ternary) composites. Guo et al. prepared the 0–3Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (NZFO)–PVDF composite films with low dielectric loss, and giant magneto-dielectric coupling effect. Composites like La$_{0.5}$Sr$_{0.3}$MnO$_3$–PVDF and Fe$_3$O$_4$ loaded PVDF exhibit multiiferroic properties with significant ME coupling. Despite the studies on a variety of multiiferroic materials mentioned above, to the best of our knowledge, complete studies of a three or two phase multifunctional material encompassing magnetic, ferroelectric, dielectric, magneto-dielectric and structural properties are scarce.

Herein, we report the synthesis of flexible and self-standing ternary phase multiiferroic polymer composite films of PVDF-GO-Fe$_3$O$_4$ and binary phase PVDF-Fe$_3$O$_4$ films exhibiting magnetic, FE, dielectric, and MD coupling properties with low dielectric loss. These functional films were prepared using GO, PVDF and Fe$_3$O$_4$ nanoparticles by a simple solvent casting method. Films of PVDF-GO and PVDF have also been made for comparison and completeness.

**Experimental**

**Synthesis of Fe$_3$O$_4$ nanoparticles**

FeCl$_2$·4H$_2$O (99.9% Sigma), FeCl$_3$·6H$_2$O (99.9% Sigma), and ammonium hydroxide solution were used as the starting materials. Fe$_3$O$_4$ nanoparticles were synthesized by using a co-precipitation method. 0.5515 g of FeCl$_2$·4H$_2$O and 1.5 g of FeCl$_3$·6H$_2$O were dissolved in distilled water at 50 °C. Aqueous ammonium hydroxide solution was slowly injected into the above solution under magnetic stirring until the pH was 12. After 1 h, the entire solution was neutralized with dilute HCl and the black color precipitate obtained was separated using a permanent magnet and washed three times with distilled water and finally with alcohol.

**Synthesis of nanocomposite films**

The studied nanocomposite films were prepared by a solvent casting method. In a typical synthesis of PVDF-GO-Fe$_3$O$_4$ composites, a required amount of PVDF was dissolved in DMF at room temperature and the synthesized Fe$_3$O$_4$ nanoparticles (5 wt%) and GO (5 wt%) powder (prepared indigenously) were added into the PVDF + DMF solution and stirred at room temperature for 1 h. After 1 h sonication, the mixture was poured on a cleaned glass slide and heated at 80 °C to ensure the evaporation of DMF to obtain self-standing and flexible polymer composite films. The same procedure was followed when using GO, PVDF and Fe$_3$O$_4$ to prepare PVDF, PVDF-GO and PVDF-Fe$_3$O$_4$ films.

**Characterization**

The phase purity of all the samples was confirmed by XRD using a Rigaku X-ray diffractometer, which was operated at 40 kV and 15 mA. The morphology of PVDF based films was
studied using a field emission scanning electron microscope (JEOL JSM7600). Transmission electron microscopy imaging was carried out with a JEOL JEM 2010 transmission electron microscope (TEM). FTIR spectra of the films were recorded by using a Perkin-Elmer Spectrum Two spectrometer operating in the ATR mode and a Bomem MB102FTIR spectrometer operating in the transmission mode. Raman spectra were recorded using 532 nm lines from a diode-pumped Nd-YAG laser (power 15 mW) focused on a spot size of about 20 μm. The scattered light was analyzed using a home-built 0.9 m single monochromator coupled with a supernotch filter and detected using a cooled charge coupled device (CCD, Andor Technology). The entrance slit was kept at 50 μm, which gave a resolution of ~3 cm⁻¹.

The room-temperature magnetization measurements were carried out using a Quantum Design Physical Property Measurement System (PPMS). The zero-field-cooled (ZFC) measurements were performed by cooling the sample in zero field to 10 K, and then the magnetization was measured while warming in a field of 1000 Oe. In field-cooled (FC) measurements, the sample was cooled in a field of 1000 Oe to 10 K, and the moment was measured while warming to 300 K. The FE measurements were performed on a commercial FE test system (aixACCT: TF-2000). All the ferroelectric hysteresis loops were measured at room temperature at 100 Hz. A thin layer of Ag paint was applied to the top and bottom of the films to which Au wires were attached to make a parallel plate capacitor. An Agilent 4284A LCR meter was used to measure the frequency dependent (1–10⁶ Hz) dielectric properties at 1 volt excitation, while the PPMS was used to provide the magnetic field (0–10 kOe) for magneto-dielectric coupling measurements at 30 kHz. Background correction was performed to extract the magneto-dielectric data.

Results and discussion

Fig. 1 depicts the XRD pattern of pristine PVDF and different composite films made by adding 5 wt% GO and 5 wt% Fe₃O₄ to PVDF dissolved in DMF. As can be seen from the figure, the pristine PVDF film is dominated by the nonpolar α-phase with characteristic peaks at 2θ = 18.1°, 19.7°, 26.5° and 39.1°. The addition of GO or Fe₃O₄ or both to PVDF decreases the α-phase and partially converts it into β-phase PVDF in composite films. The XRD patterns of GO and Fe₃O₄ nanoparticles are also shown for comparison with the characteristic peak of GO at 2θ = 9.6°. As the concentrations of both GO and Fe₃O₄ are only 5% in the composite films, their corresponding peaks in the XRD pattern are very weak, specifically for GO (inset, Fig. 1). The average particle size obtained for Fe₃O₄ nanoparticles by using the Scherrer formula is ~10–12 nm.

Fig. 2 shows the photographs of films of PVDF, PVDF-GO, PVDF-Fe₃O₄ and PVDF-GO-Fe₃O₄, which depicts the flexible and free-standing nature of PVDF and their composite films. Fig. 3(a and b) show the TEM image and the selected area diffraction pattern of Fe₃O₄ nanoparticles used in making the
composite films. From the TEM images it is clear that the Fe3O4 nanoparticle size is ∼10–12 nm and they are crystalline in nature (Fig. 3(a and b)) in agreement with XRD results. The SEM of GO (Fig. 3(c)) shows that they are of sheet type morphology with micrometer dimensions.

To investigate the influence of Fe3O4 and GO on the microstructure of the composite films, FESEM pictures of composite films along with the pure PVDF film were obtained. Fig. 4(a) shows the microstructure of pure PVDF, where it can be seen that the morphology of the pure PVDF layer is dense and smooth with no visible voids, but small fold lines appear on the surface. From the figure, a good dispersion of GO in the PVDF matrix can be clearly observed. It is the strong interaction between oxygen-containing groups, especially carbonyl groups (–C=O) on the GO surface and fluorine groups in PVDF, that led to the homogeneous dispersion of GO in the PVDF matrix. Compared to the pure PVDF film, the PVDF-GO, PVDF-Fe3O4 and PVDF-GO-Fe3O4 composite films have rough surfaces and contain some granular particles distributed nearly homogeneously in the films (Fig. 4). The composition and elemental mapping (Fig. S1, ESI†) confirm the homogeneous distribution of the nanofillers in the PVDF matrix.

FTIR spectra

Fourier Transform Infrared (FTIR) spectroscopy is an effective method to study crystalline phase transformation in PVDF. Fig. 5(A) shows the ATR-IR spectra of PVDF, PVDF-GO, PVDF-Fe3O4 and PVDF-GO-Fe3O4 films in the 400–1800 cm⁻¹ region while Fig. 5(B) shows the IR spectra of PVDF-GO and PVDF-GO-Fe3O4 films in the 400–3600 cm⁻¹ region. Details of peak assignment are given in ESI Table S2.† As can be seen in this figure, pure PVDF crystallizes mainly in the α-phase (with a small quantity of β phase) with characteristic peaks at 490, 530, 615, 760, 795, 854 and 975 cm⁻¹. The peaks at 440, 510, 840, 1170 and 1275 cm⁻¹ correspond to the β-phase.40–45

It is clear from the IR spectra that the addition of GO, Fe3O4 or both GO and Fe3O4 to PVDF causes the intensity of those peaks corresponding to the α-phase to decrease with a concomitant increase in the intensity of the peaks characteristic of the β-phase. This confirms that the addition of GO or Fe3O4 or both leads to crystal transformation of PVDF from the α-phase to the β-phase. The increase in the β-phase in the composite films could be due to the Fe3O4 nanoparticles and GO providing additional nucleation sites for the crystallization of the β-phase. It is known that the strong interaction between carbonyl groups in graphene oxide and fluorine groups in PVDF causes a transformation of the α-phase’s trans-gauche–trans-gauche conformation into the trans-trans conformation characteristic of the β-phase.46 The presence of GO in composite films of PVDF-GO and PVDF-GO-Fe3O4 is confirmed by the peaks at 1725 cm⁻¹ (carboxyl or carbonyl stretching vibration) and 1620 cm⁻¹ (C–O stretching) in PVDF-GO and PVDF-GO-Fe3O4 (Fig. 5(B)). The presence of GO in PVDF-GO and PVDF-GO-Fe3O4 films is further confirmed by the Raman spectra of these films which is discussed below.
Raman spectroscopy studies

Raman spectroscopy is widely used to characterize the crystal structure, disorder and defects in graphene-based materials. Fig. 6(a) shows the Raman spectra of pristine PVDF and its composite films. The presence of GO in the PVDF film leads to changes in the relative intensity of two main peaks in the Raman spectra viz. D and G. The D peak of GO located at 1350 cm$^{-1}$ stems from a defect-induced breathing mode of sp$^2$ rings. It is common to all sp$^2$ carbon lattices and arises from the stretching of the C–C bond. The G peak at around 1595 cm$^{-1}$ for GO is due to the first order scattering of the E$_{2g}$ phonon of sp$^2$ C atoms. The intensity of the D peak is related to the size of the in-plane sp$^2$ domains. The relative intensity ratio of both peaks ($I_D/I_G$) is a measure of the degree of disorder and is inversely proportional to the average size of the sp$^2$ clusters. Normally, the $I_D/I_G$ intensity ratio of GO is larger than that of $I_D/I_G$ of GO. However, in this study, $I_D/I_G \approx 1$ for both PVDF-GO-Fe$_3$O$_4$ and PVDF-GO films (Fig. 6(a)) indicating the presence of only GO without a noticeable reduction of GO to RGO in both composite films. There are reports of using the intensity ratio $I_D/I_G$ to estimate the size of the domains. The size of the GO domains estimated using this intensity ratio is of the order of 20 nm which may be related to the thickness of the GO sheets.

Raman spectroscopy also provides information about the conjugated structure and the chain skeleton of polymers. The weak Raman bands at 794 cm$^{-1}$ and 839 cm$^{-1}$ in pristine PVDF films (Fig. 6(a and b)) correspond to $\alpha$- and $\beta$-phases, respectively. These features appear with a strong luminescence background and hence it is difficult to comment on the changes in $\alpha$- and $\beta$-phases from the Raman data, even though the band at 794 cm$^{-1}$ corresponding to the $\alpha$ phase broadens and shifts towards a higher frequency (839 cm$^{-1}$) of the $\beta$-phase with the insertion of GO or Fe$_3$O$_4$ as shown in the inset of Fig. 6(b). One possible reason for this may be due to the possible conversion of a part of the $\alpha$-phase into the $\beta$-phase as confirmed by XRD patterns and IR spectra. This is also reflected in the dielectric and ferroelectric studies, as discussed in the following sections.

XPS studies

We have recorded the XPS spectra of Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films and the results are depicted in Fig. S3 (ESI†). Binding energies 711.1 eV (Fe 2p$_{3/2}$) and 724.5 eV (Fe 2p$_{1/2}$) correspond to the XPS spectrum of Fe$_3$O$_4$ (Fig. S3, ESI†). The presence of GO is also confirmed by the C 1s XPS spectrum of the PVDF-GO-Fe$_3$O$_4$ film. We tried to record the XPS spectra of the PVDF-GO-Fe$_3$O$_4$ sample in the Fe 2p region, to show the presence of Fe 3O$_4$ in the PVDF-GO-Fe$_3$O$_4$ film. However, the samples did not give any Fe signal in this region. This may be due to the fact that XPS probes only a small depth (≈100 angstroms) and the particles may be well below that distance in the films.

Magnetism

Fig. 7 shows the magnetization vs. field ($M$ vs. $H$) measurements of PVDF, PVDF-GO, PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films at room temperature. Fe$_3$O$_4$ nanoparticles embedded composite films of PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ show superparamagnetic behavior with a very small coercivity of 35 Oe (Fig. 7, inset). The saturation magnetization ($M_s$) values for PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films are 2.61 and 2.21 emu g$^{-1}$.

Fig. 6 (a) Raman spectra of PVDF, PVDF-Fe$_3$O$_4$, PVDF-GO and PVDF-GO-Fe$_3$O$_4$ films; (b) Raman spectra of PVDF and PVDF-GO-Fe$_3$O$_4$ films and the inset shows a selected range of spectra.

Fig. 7 Magnetization vs. field ($M$ vs. $H$) at 300 K of PVDF, PVDF-GO, PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films. The inset shows an enlarged view of $M$ vs. $H$ at 300 K.
respectively, with remanence ($M_r$) $\sim$ 0.16 emu g$^{-1}$. As expected, both PVDF and PVDF-GO films show weak diamagnetic behavior. Fig. 8 shows the magnetization versus temperature of the PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ composite films which also confirms the superparamagnetic ($T_B \sim$ 90 K) nature of the composite films containing Fe$_3$O$_4$ nanoparticles.

$P$–$E$ loop

The room temperature ferroelectric ($P$–$E$) loops of PVDF, PVDF-GO, PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ composite films are shown in Fig. 9. For comparison, all the samples were polarized in the range of 70 kV cm$^{-1}$. The plots of polarization versus electric field ($P$–$E$ responses) are obtained at a frequency of 100 Hz at room temperature for all the samples. PE hysteresis clearly shows the effect of adding Fe$_3$O$_4$ and GO to the PVDF which is the FE component. In the presence of an electric field, pure PVDF shows polar $\beta$-phase dependent polarization ($P$). The strength of polarization in PVDF depends on the amount of $\beta$-phase present. In our current study, the pristine PVDF film is dominated by nonpolar $\alpha$-phase with a small amount of polar $\beta$-phase and hence the PVDF film shows a weak $P$ vs. $E$ curve (Fig. 9). It is worth mentioning here that all the samples show somewhat lossy ferroelectric behavior. The definable area under the curve, which is caused by the internal heterogeneous charge, gives the charge storage ability of the material. The area under these curves increases upon introduction of dielectric materials, GO and Fe$_3$O$_4$ into the polymer matrix PVDF. This is reflected in the $P$–$E$ curve shown in Fig. 9, from which it is clear that the addition of GO or Fe$_3$O$_4$ or both into PVDF causes an increase in $P$ values of the respective composite films. Hence the increase in $P$ values of composite films (Fig. 9) PVDF-GO, PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ can be due to the accumulation of charges at the interface of the conducting and dielectric Fe$_3$O$_4$ and GO, which facilitates the heterogeneous polarization in the systems, which further enhances the ferroelectric behavior of the sample. The maximum polarization obtained in the PVDF film filled with GO is 0.1 $\mu$C cm$^{-2}$ (Fig. 9) which is higher than that of the pure PVDF with a polarization of 0.038 $\mu$C cm$^{-2}$. In the case of PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films, the saturation polarization values are around 0.058 and 0.065 $\mu$C cm$^{-2}$, respectively, which are higher than that of the pristine PVDF film. A small decrease in polarization values observed in PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films compared to the PVDF-GO film may be due to the presence of Fe$_3$O$_4$ nanoparticles with conducting nature. The increase in saturation polarization upon the addition of Fe$_3$O$_4$ to PVDF is due to (1) the introduction of free charges to stabilize the polarization domain and (2) Fe$_3$O$_4$ nanoparticles acting as a nucleating agent for the stabilization of the $\beta$-phase. The remnant polarization and coercive field increase with the addition of dielectric materials. This confirms that the presence of dielectric materials significantly influences the polarization response of the polymer matrix.

Dielectric properties

The dielectric properties of the studied composite films are shown in Fig. 10(a). The relative permittivity of dielectrics (dielectric constant) increases with decreasing the frequency, and a significant drop in permittivity is observed in the higher frequency range ($10^3$–$10^6$ Hz). This is because the dipole relaxation of the composites cannot catch up with the frequency changes of the external field. The relative permittivity of all the samples shows a similar frequency dependence. It is well known that PVDF has a strong dipole moment due to the presence of electronegative fluorine atoms in its molecular structure and also the interface polarization which is observed at the $\alpha$- and $\beta$-phase interface of the PVDF. The relative permittivity of all the samples shows a similar frequency dependence. It is well known that PVDF has a strong dipole moment due to the presence of electronegative fluorine atoms in its molecular structure and also the interface polarization which is observed at the $\alpha$- and $\beta$-phase interface of the PVDF. The relative permittivity of all the samples shows a similar frequency dependence.

Fig. 8 Magnetization vs. temperature ($M$ vs. $T$) of (a) PVDF-Fe$_3$O$_4$ and (b) PVDF-GO-Fe$_3$O$_4$ films.

Fig. 9 Electric field dependent polarization ($P$–$E$ curve) at 100 Hz of PVDF, PVDF-GO, PVDF-Fe$_3$O$_4$ and PVDF-GO-Fe$_3$O$_4$ films at room temperature.
Activity increases on the addition of GO or Fe$_3$O$_4$ to PVDF, due to an increase in the average electric field in the polymer matrix. The relative permittivity observed for all three composite films (PVDF-Fe$_3$O$_4$ $\sim$ 12, PVDF-GO $\sim$ 19 and PVDF-GO-Fe$_3$O$_4$ $\sim$ 18) is larger than that of the pristine PVDF film ($\sim$ 6). The addition of Fe$_3$O$_4$ nanoparticles to the PVDF matrix not only induces interfacial polarization, but also increases the relative permittivity. This is due to the increase in the density of Fe$^{2+}$–O dipoles, which increases the dipolar polarization. The addition of GO to the PVDF-Fe$_3$O$_4$ (PVDF-GO-Fe$_3$O$_4$) composite causes a further increase in the relative permittivity due to the MWS (Maxwell–Wagner–Sillars) polarization. Since the polymer matrix and the inorganic filler have different dielectric constants, a large number of charge carriers accumulate on these interfaces and a strong MWS polarization develops, which has an important role in the enhancement of the dielectric constant. Since GO can form hydrogen bonding and more charges accumulate on the interface, which may enhance the interfacial relaxation.

Dielectric loss

Fig. 10(b) shows the variation of the dielectric loss (tan $\delta$) with frequency, which shows a similar trend to that of the dielectric constant. The observed dielectric losses in these composites are relatively low ($<0.7$), which is lower than that of many other composite systems.$^{56,57}$ The dielectric loss of the studied samples decreases marginally with increasing the frequency. However, in composite films the dielectric losses (tan $\delta$) are marginally higher (with the PVDF-GO-Fe$_3$O$_4$ film showing a maximum loss of $\sim$0.6) than that of the pure PVDF (tan $\delta$ $\sim$ 0.1). Generally, several factors contribute to the dielectric loss in the composite films, including direct current conduction, MWS relaxation and the Debye loss factor ($\delta = \delta_{DC} + \delta_{MW} + \delta_B$). The marginally higher dielectric loss observed in the PVDF-GO-Fe$_3$O$_4$ composite film compared to PVDF-GO and PVDF-Fe$_3$O$_4$ may be due to the interfacial relaxation process.$^{58}$

As stated above, GO can form hydrogen bonding and more charges accumulate on the interface, which may enhance the interfacial relaxation.

Magneto-dielectric coupling

Multiferroic materials with sufficient cross coupling of ferromagnetism and ferroelectricity are desirable for the proposed applications as transducers, multistate data storage devices, etc. The coupling between magnetic and electric polarizations can be calculated by measuring the change in the dielectric constant under an applied magnetic field. The change in the dielectric constant with the applied magnetic field is characterized by the MD coupling constant, defined as $\text{MD} = \left[\frac{\varepsilon_H - \varepsilon_0}{\varepsilon_0}\right] \times 100\%$, where $\varepsilon_H$ and $\varepsilon_0$ are the dielectric constants at a certain applied magnetic field and zero magnetic field, respectively. From Fig. 11, which shows MD at 300 K and 30 kHz,
it can be observed that diamagnetic PVDF and PVDF-GO samples do not show any change in dielectric constant upon the application of the magnetic field, as expected. On the other hand, the samples loaded with magnetic Fe3O4 show variation in dielectric constant upon the application of the magnetic field, with the samples PVDF-Fe3O4 and PVDF-GO-Fe3O4 showing a MD of ~0.035% and 0.02%, respectively, at 300 K. It may be noted that Mandal et al.59 studied the dielectric and magneto-dielectric coupling (MD%) properties of a hydroxylated Ni-PVDF based system and have observed that the magneto-dielectric coupling value of Ni-PVDF samples was about 0.02% at room temperature. Our present sample (PVDF-GO-Fe3O4) shows a higher MD coupling (0.04%) at room temperature compared to the Ni-PVDF sample.

The obtained curves have been fitted to a quadratic equation in H, as \(\left[\varepsilon_{11} - \varepsilon_0\right]/\varepsilon_0 = \gamma H^2\) which originates from the lowest-order coupling terms polarization \(P\) and magnetization \(H\) in the free-energy term.60 The MD effect in these samples arises from terms proportional to \(P^2M^2\) in a symmetry-allowed Ginzburg–Landau free energy, where \(P\) and \(M\) are electric polarization and magnetization, respectively. In the present samples, the MD showed a quadratic dependence on magnetization, which is observed in other magneto-electric MFMs.61,62

The MD coupling in the composites arises as a result of the product of the magnetostriction of the magnetic phase and the piezo-electricity of the FE phase. The MD coupling takes place through elastic interaction between the magnetic and FE phases. Therefore, the ME effect in these composite systems is extrinsic in nature, which severely depends on the microstructure and coupling interactions between the magnetic and FE interfaces. In these multiferroic hybrids, upon the application of a magnetic field, the magnetic domains of Fe3O4 align in such a way that it can cause stress on the neighboring FE PVDF phase via magnetostriction, which eventually leads to the accumulation of some surface charge due to the PE effect. This accumulated charge changes the dielectric constant of the composite in the presence of a magnetic field.

The magnetic field dependence of the MD coupling response at 30 kHz for different temperatures is shown in Fig. 11(b) for the PVDF-GO-Fe3O4 film. The MD (%) increases with increasing temperature and reaches a maximum value of 0.035% at 100 K in a magnetic field of 1 T. At 150 K, the MD coupling decreases to 0.028 and eventually decreases to 0.02% at 300 K. The increase of the magneto-dielectric response below 150 K, or near the transition temperature of Fe3O4 nanoparticles (~130 K), indicates a direct correlation between magnetism and dielectric properties. This is in agreement with the Ginzburg–Landau phenomenological theory,59 according to which, below \(T_c\), the magneto-dielectric effect is proportional to the spin-pair correlation of neighboring spins, hence the square of the magnetization MD (%) = \(\gamma H^2\). Further, at low temperature the magnetic phase will be in the aligned state and the interaction between the magnetic and FE phases will be strong and this leads to increased MD coupling.

Conclusions

In conclusion, we have demonstrated that self-standing, flexible inorganic–organic three-phase and two phase hybrid composite films of PVDF, GO and Fe3O4 can be made by a solvent casting method by embedding GO or Fe3O4 or both into a PVDF polymer at low temperature, ensuring no chemical reaction or inter-diffusion between the atoms of ferroelectric, piezoelectric and magnetostrictive phases. SEM, TEM, XRD, Raman and FTIR confirm the structure of the films. PVDF-GO-Fe3O4 and PVDF-Fe3O4 films showed excellent magnetic, ferroelectric, dielectric and magneto-dielectric properties with low dielectric loss and increased dielectric constant compared to the pristine PVDF film at room temperature. Temperature dependent MD coupling measurements on the multifunctional PVDF-GO-Fe3O4 composite film showed an increased value below 150 K due to strong coupling interactions between magnetic and FE or FE phases. These observations pave the way for implementing composite films of PVDF, GO and Fe3O4 in magneto-dielectric devices.

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References


