Structural, Dielectric, and Magnetic Studies on Electrospun Magnesium Ferrite-Polyvinylidene Fluoride Core–Shell Composite Fibers

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Abstract   The sub-micron (of the order of 150 nm) thick core–shell composite fibers of magnesium ferrite-polyvinylidene fluoride are prepared by electrospinning. The loading of magnesium ferrite is varied from 1 to 10 wt%. The study results by X-ray diffraction, scanning electron microscope, and infra-red spectroscopy indicate the formation of core–shell structure and an enhancement in the amount of β-phase compared to α-phase in the polyvinylidene fluoride. The particle size of the magnesium ferrite in the fiber is evaluated to be 30 nm. The low frequency dielectric studies indicate that the addition of the magnesium ferrite increases the polarization resulting in the increase in the dielectric constant but decreases the dielectric loss. The magnetization measurements indicate an increased value of coercivity compared to bulk due to the nano-size of the magnesium ferrite. The microwave absorption at the ferromagnetic resonance increases with the increase in the concentration of magnesium ferrite. The resonance field is found to vary with the loading of MFO.

KEY WORDS: **Electrospinning; Polymer composites; Dielectric properties; Magnetic properties; X-ray diffraction (XRD); Microwave absorption**

1 Introduction

Polymer based magnetic composites are attractive due to their flexibility, good mechanical strength, and ease of fabrication which makes it advantages over other traditional materials. It is useful for novel applications including the miniature of electronic devices like filters and antennas and also for electromagnetic shielding, planar inductive devices,

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etc. [1–4]. After the discovery of giant magnetoelectric coupling in ferroelectric-ferromagnetic composites, much attention has been given in developing such composites and their application in the state-of-the-art devices [5]. When the spinel ferrites that have good ferromagnetic and magnetostrictive properties are made into composite with the ferroelectric polymers, they are expected to have very good magnetoelectric coupling properties. Among the prominent ferroelectric polymers, ferroactive polyvinylidene fluoride (PVDF) is used due to high piezo electric coefficient [6]. PVDF is available in various crystalline forms such as α, β, and γ. Among them β phase shows stronger ferroelectric properties. Though the PVDF as such is a dielectric, usually stretching and poling of the PVDF membrane make it ferroelectric by inducing β phase in it [7]. Other observations show that the process of electrospinning also polarizes the PVDF making it to be ferroactive [8, 9], and the addition of ferrite nanoparticles also improves the ferroelectric properties in PVDF [10]. PVDF has attracted many researchers in making magnetoelectric composites due to its simple

fabrication and flexibility for device application. Recently, giant magnetoelectric effect is observed in PVDF based flexible laminate composite [11]. Similarly, a tri-layered magnetoelectric device is developed at microwave frequencies [12].

The synthesis of new class of $BiFe_2O_3$ and PZT based multiferroic fibers by electrospinning leads to the preparation of PVDF based composites fibers [13]. When the ferrite as a core is surrounded by the ferroelectric polymer shell, the striction caused in the ferrite will cause ripples in the ferro-active polymer thereby giving a good coupling coefficient. Also, filling PVDF with magnetic particles is expected to enhance the electromagnetic wave properties due to the elevated magnetic activity [14]. It is known that magnesium ferrite ($MgFe_2O_4$) possesses high resistivity and is a soft magnetic material with cubic normal spinel structure. It is useful for its application in memory and microwave based devices [15]. Therefore, an attempt is made to produce the core–shell structure of magnesium ferrite-PVDF composite fibers by electrospinning method.

The formation of the core–shell structure is verified using X-ray diffraction (XRD) and scanning near field optical microscopy. The formation of ferroelectrically active β-phase PVDF is examined by the infra-red spectroscopy. The low frequency dielectric study with temperature is undertaken to understand the effect of loading of magnesium ferrite in the PVDF. The ferromagnetic resonance (FMR) absorption can be used to obtain the gyromagnetic ratio of the samples. In this paper, an attempt is made to obtain the FMR at microwave frequency at 9.12 GHz using a reflection type rectangular cavity [16].

2 Experimental

Magnesium ferrite, $MgFe_2O_4$ (MFO), is prepared by molten salt method [17]. $MgSO_4$, $Fe(NO_3)_3$, NaOH, and NaCl are taken in molar ratio of 1:2:8:10, ground well in an agate mortar for 90 min to get a smooth paste. The dried powder is filtered and washed with deionized water; the residue is calcined at 800 °C for 2 h. It is again calcined at 1,100 °C for 2 h. A PVDF/acetone/dimethyl formamide (DMF) solution of concentration 12 wt% is sonicated for around 3 to 4 h at room temperature to form a homogenous solution. Desired concentration of MFO with respect to PVDF is taken, and a solution with DMF of calculated amount is prepared. The two solutions are then mixed slowly, stirred continuously, and sonicated for 2 h to get a homogeneous solution. The polymer composite fibers are spun at a flow rate of 0.7 mL/h, on an aluminum substrate (kept as the ground). The applied electric field for the spinning is 1 kV/cm. Sheets of composite fibers are obtained for 1, 2, 3, 5, and 10 wt% of MFO with PVDF (12 wt%).

The formation of core–shell MFO/PVDF composite fiber is characterized by XRD, scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectroscopy. XRD is taken using PAnalytical X'pert Pro with CuK_α radiation. Scanning electron microscopy (FEI Quanta FEG 200) is used to examine the morphology and the thickness of the fiber. The vibrational spectra of the polymer composite fiber are studied using FT-IR Perkin-Elmer FT-IR spectrometer in the range of 450–2,000 cm^{-1}. The dielectric measurements are performed using N4L impedance analyzer. The magnetization measurements are taken using Lakeshore VSM7410.

FMR absorption studies are carried out by cavity perturbation technique using Agilent vector network analyzer N5230A for the fibers at the room temperature. The PVDF-MFO fibers collected on the aluminum foil are peeled out in the form of thin film. This film is rolled out into a cylindrical shape of average diameter of 1.5 mm. A TE_{106} mode reflection type rectangular cavity operating at 9.12 GHz is chosen for the present studies. A coaxial to waveguide adaptor along with the coupling iris is used to couple the microwave power from Agilent N5230A to the cavity. The sample is kept at the maximum magnetic field position of the cavity. The external DC magnetic field is applied in a direction perpendicular to the microwave magnetic field. The cavity resonance is observed as function of the external DC magnetic field. The resonant frequency and the quality factor of the cavity along with the voltage standing wave ratio are noted. Since the amount of the ferrite sample in the PVDF is small, the variation of the power absorption with magnetic field will be very small. Therefore to evaluate the power absorption, a method proposed by Subramanian and Sobhanadri [18] is followed. A MATLAB program is written to obtain the quality factor of the cavity as a function of the external DC magnetic field.

3 Results and Discussion

X-ray diffraction pattern of electrospun MFO-PVDF composite shows an increase in the intensity of the characteristic main peak of MFO at $2\theta = 35.6^\circ$ (311) with the addition of MFO indicating the formation of the composite, as shown in Fig. 1. The peak at $2\theta = 20.8^\circ$ indicates the formation of β-phase PVDF. The application of the electric field and spinning process followed in the electrospinning method inherently results in the formation of β-phase in PVDF [19]. Moreover, the presence of the magnetic particle enhances the alignment and polarization of the PVDF resulting in the reduction in the α-phase of the PVDF. The conversion of α to β-phase of PVDF due to the addition of ferrites in films and fibers had also been reported earlier
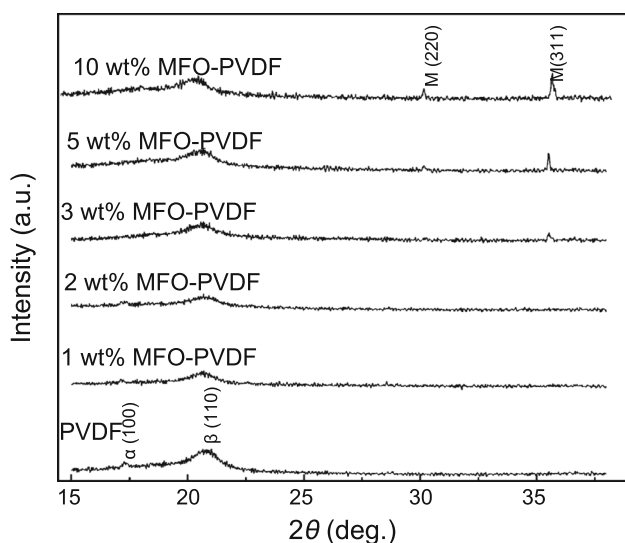
Fig. 1 XRD patterns of pure PVDF and MFO-PVDF with various MFO concentrations

[10]. Therefore, one may find the near total β-phase PVDF in the fiber. Andrew and Clarke [9] reported similar findings when nickel zinc ferrite-PVDF composite was electrospun. From the well known Scherrer formula, the XRD of the 10 wt% MFO loaded PVDF fiber indicates the particle size of the MFO as around 30 nm.

Typical SEM images for the pure PVDF and 3 wt% MFO-PVDF composite fibers are presented in Fig. 2. The thickness of the pure PVDF fiber is around 90 nm and that of MFO-PVDF composite fiber is around 150 nm. The dimension of the fiber remains almost same for other concentrations of MFO (1 to 10 wt% MFO-PVDF) since the particle size of MFO remains the same. The increase in

the thickness for the MFO loaded fiber is due to the encapsulation of the MFO particles by PVDF. This indicates a typical core shell formation, where the core is the ferrite material, and the shell is the polymer.

Typical FT-IR spectra of the PVDF fiber and for the 10% loaded MFO-PVDF composite are shown in Fig. 3. It is observed from the transmittance spectra that the absorptions at 511, 842, 1,073, 1,277, and 1,400 cm^{-1} indicate the formation of β-phase PVDF. One can also observe the presence of absorption at 880 cm^{-1} indicating γ-phase. The absorptions at 532, 612, 763, 796, 854, 870, and 970 cm^{-1} corresponding to α-phase are not prominent. Once the polymer is loaded with the ferrite and electrospun, the diameter of the fiber increases, and the radius of gyration is improved, resulting into an increase in the β-phase. It may also be noted that the absorption lines indicating that α-phase decreases with increase in the addition of the ferrite.

The electrospun fibers are collected and made as a thin disk of 13-mm diameter. The variation of the dielectric constant (ε_r) is presented in terms of ε_r/d, where d is the thickness of the sample. The variation of ε_r/d with frequency at 70 °C under different loadings of MFO is shown in Fig. 4. The decrease in the dielectric constant indicates a dielectric relaxation process. When the loss tangent (tanδ) variation is plotted as a function of frequency (Fig. 5), it clearly shows the absorption around 2×10^5 Hz for pure PVDF. There is no appreciable change in the frequency at which the absorption is maximum even when loaded with MFO. The relaxation time is evaluated to be 0.8 μs.

Figure 6 shows the variation of dielectric constant in terms of ε_r/d with temperature measured at 10 kHz under different loadings of MFO. The increase in the temperature
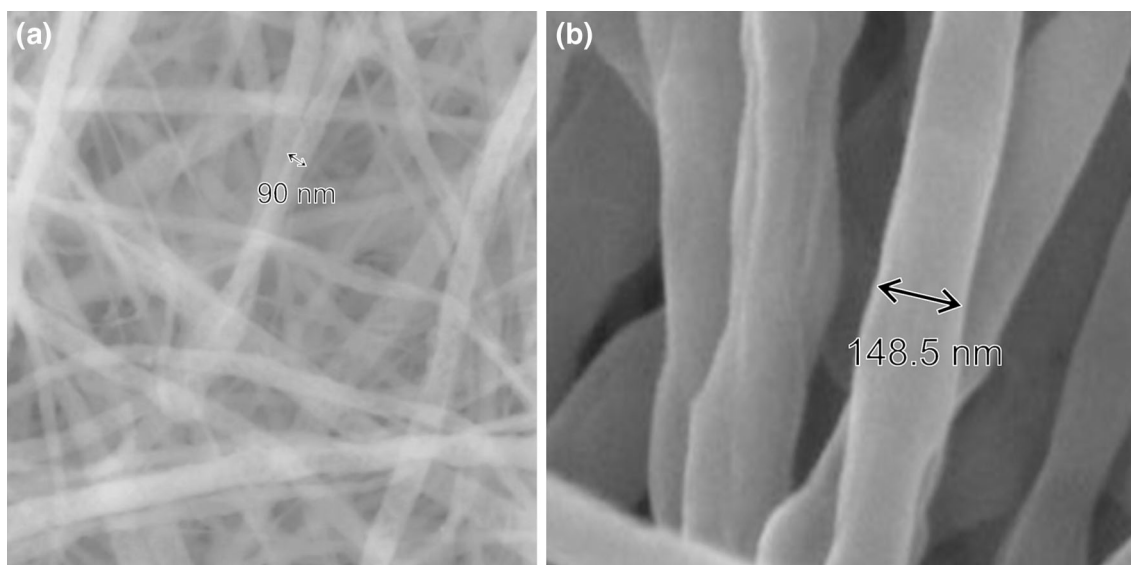
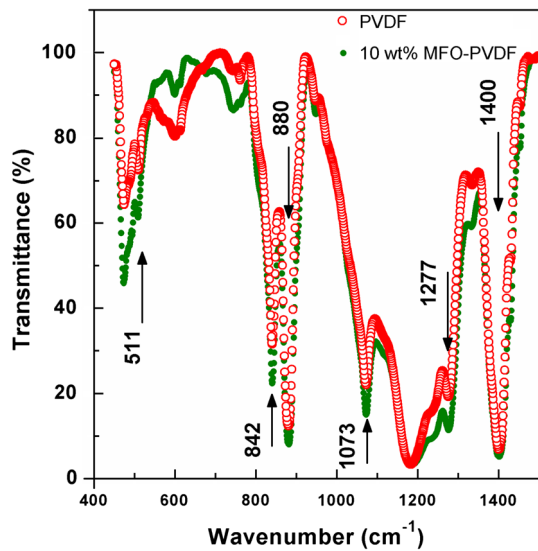

Fig. 2 SEM images of **a** pure PVDF, **b** 3 wt% MFO-PVDF

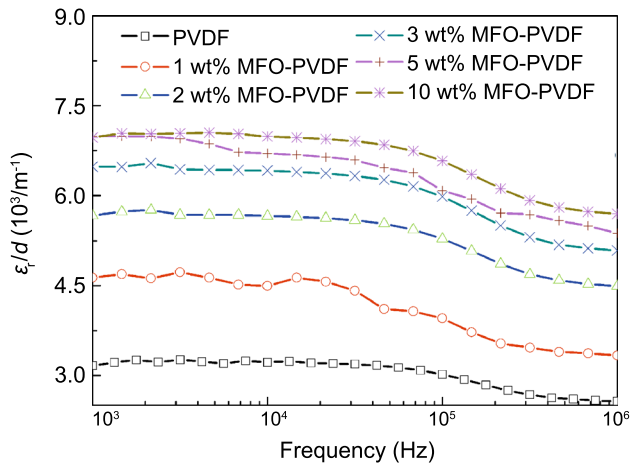**Fig. 3** FT-IR transmittance spectra for pure PVDF and 10 wt% MFO-PVDF

Fig. 4 Variation of dielectric constant (ε_r/d) versus frequency ($\lg F$) at 70 °C

Fig. 5 Variation of loss tangent with frequency at 70 °C for various loading of MFO

Fig. 6 Variation of dielectric constant (ε_r/d) with temperature measured at 10 kHz for various loading of MFO

increases the free volume thereby enhancing the polarization of the PVDF resulting in an increase in the dielectric constant. The presence of MFO further assists in the polarization as evident from a marginal increase in the slope of the curve when percentage of MFO is increased. This also explains the increase in the ac conductance (expressed in terms of σ_{AC}/d (mS/m^2)) with temperature, as shown in Fig. 7.

Figure 8 shows the variation of magnetic moment with loading of MFO. Care was taken to load same amount of the sample for all the measurements. The mass of the sample was roughly around one hundredths of a milligram. Since it is difficult to evaluate the actual mass of the MFO present in the PVDF, the plot shows the magnetic moment. It is clear that with the increase in the loading of MFO, the
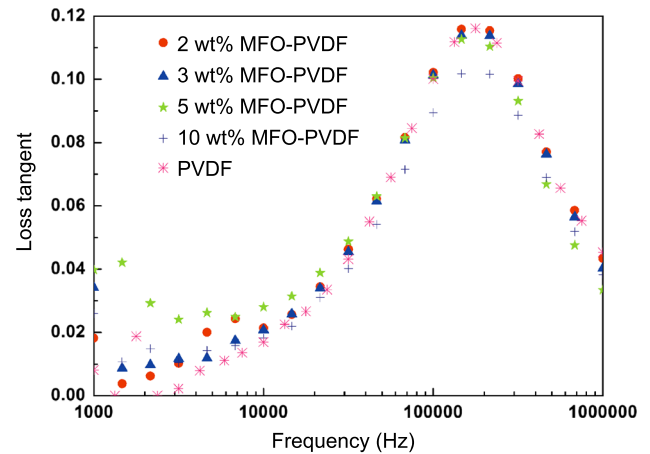
magnetic moment increases. As expected, the coercive field H_c remains the same with the loading of MFO. It may be noted that H_c is around 40 Oe (3.183 kA/m). Earlier reports indicate that the coercive field depends on the critical diameter, aniosotropy, and the domain structure [8]. Rashad [20] reported an initial increase and then a decrease in the coercive field with particle size. For the particle size between 27.2 and 49 nm, the coercive field increased from 58 Oe (4.616 kA/m) to 68 Oe (5.411 kA/m) and further decreased to 45 Oe (3.581 kA/m). In the present case, the size of the MFO is around 30 nm, and therefore the obtained value of 40 Oe (3.183 kA/m) agrees well with the earlier reports.

The microwave power absorption at the FMR is evaluated from the area under the resonance curve [18]. Figure 9 shows the variation of percentage of microwave power absorption with DC magnetic field at the FMR. The power absorption is less compared to bulk since the amount of
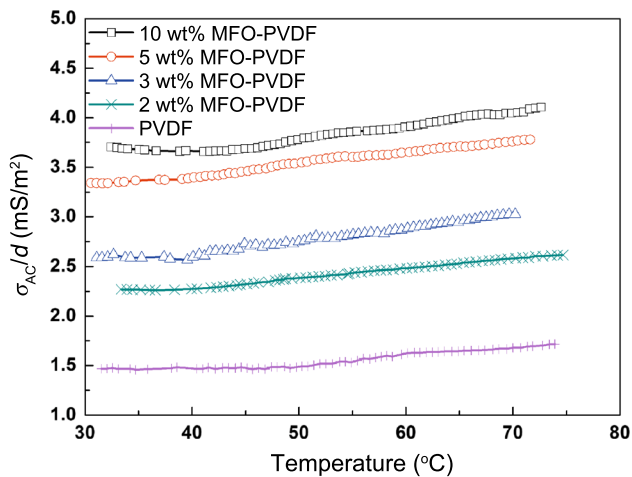
Fig. 7 Variation of ac conductivity in terms of σ_{AC}/d with temperature measured at 10 kHz for various loading of MFO
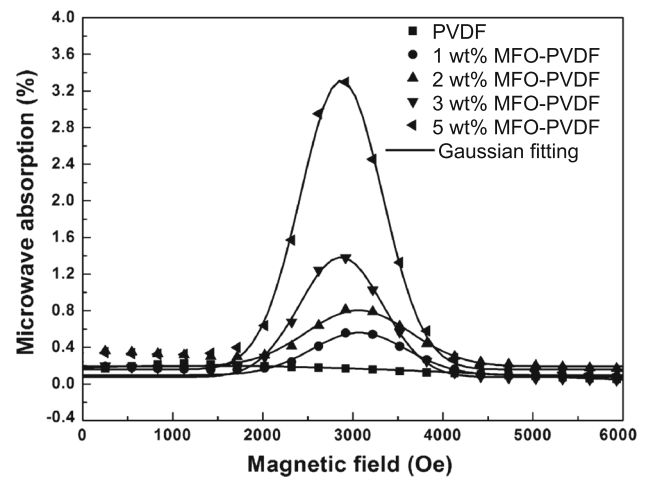

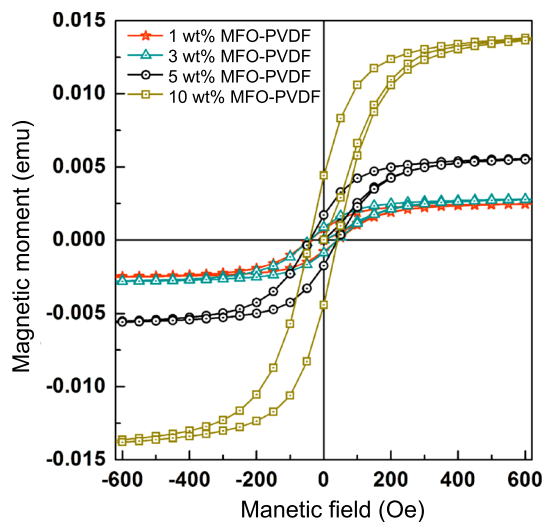**Fig. 9** Variation of fraction of microwave power absorption with MFO loading

Fig. 8 *M-H* loops of MFO-PVDF composites with various loading of MFO

ferrite in the composite is less. It is observed that the FMR shifts toward the lower magnetic field as the MFO content increases. The power absorption increases with the increase in magnesium ferrite. For the 10 wt% MFO-PVDF, the fraction of microwave absorption is close to 5.4% compared to 0.5% for the 1 wt% MFO-PVDF. As the MFO content increases, the maximum absorption field shifts from 3065 Oe (243.9 kA/m) for 1 wt% MFO-PVDF to 2870 Oe (228.4 kA/m) for 5 wt% MFO-PVDF. But further increase in the MFO content to 10 wt%, the maximum absorption shifts to higher magnetic field of 2895 Oe (230.4 kA/m). It may be noted that for the bulk MFO, the resonance happens at 3180 Oe (253.1 kA/m) for 9.12 GHz. As it is difficult to prepare polymer fibers with higher concentration of MFO (>10 wt%), the variation of

resonance field with concentration could not be obtained for the samples with MFO concentration higher than 10 wt%. It is possible that the presence of PVDF and the de-magnetization factor effectively change the gyromagnetic ratio. While gyromagnetic ratio for bulk is 28.68 GHz/T, the value increases to 29.8 GHz/T for 1 wt% MFO and reaches the maximum (to 31.78 GHz/T) for 5 wt% MFO and starts decreasing further. At 10 wt% MFO, the gyromagnetic ratio is around 31.5 GHz/T. More studies on this may be required for further insight into this behavior.

4 Conclusion

Core–shell composite fibers of PVDF-MFO with various MFO concentrations fabricated by electrospinning technique. The presence of MFO in the sub-micron fibers is confirmed by XRD. The formation of β-phase PVDF due to the electrospinning process and its enhancement due to the loading of MFO were confirmed by FTIR. The improvement in the polarization of PVDF due to the addition of MFO increased the dielectric constant. The increase in the dielectric constant with temperature was due to the expansion of the fiber that gave more room for the alignment of the polymer. The dielectric dispersion indicated a relaxation at around 2×10^5 Hz with a relaxation time of 0.8 μs. This value did not vary with the addition of MFO showing the contribution of PVDF alone. The variation of the ac conductivity with temperature indicated the enhancement of conduction process due to the presence of MFO. The magnetization curve indicated a constant coercive field of 40 Oe (3.183 kA/m) for all the studied concentrations. This value is expected to be larger than the

bulk since the size of MFO is around 100 nm. The FMR at 9.12 GHz observed as a function of the loading of MFO, indicates that the resonance magnetic field attains the lowest for the 5% loading, while the amount of microwave absorption increases with the increase in the loading of MFO.

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