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**Fabrication and magnetoelectric investigation of flexible PVDF-TrFE/cobalt ferrite nanocomposite films**

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**Abstract**

Flexible nanocomposite films, with cobalt ferrite nanoparticles (CFN) as the ferromagnetic component and polyvinylidene fluoride–trifluoroethylene (PVDF-TrFE) copolymer as the ferroelectric matrix, were fabricated using a blade coating technique. Nanocomposite films were prepared using a two-step process; the first process involves the synthesis of cobalt ferrite (CoFe₂O₄) nanoparticles using a sonochemical method, and then incorporation of various weight percentages (0, 2.5, 5, and 10%) of cobalt ferrite nanoparticles into the PVDF-TrFE to form nanocomposites. The ferroelectric polar β phase of PVDF-TrFE was confirmed by x-ray diffraction (XRD). Thermal studies of films showed notable improvement in the thermal properties of the nanocomposite films with the incorporation of nanoparticles. The ferroelectric properties of the pure polymer/copolymer films were studied, showing a significant improvement of maximum polarization upon 5wt% CFN loading in PVDF-TrFE composite films compared to the PVDF-TrFE film. The magnetic properties of as-synthesized CFN and the polymer nanocomposites were studied, showing a magnetic saturation of 53.7 emu g⁻¹ at room temperature, while 10% cobalt ferrite-(PVDF-TrFE) nanocomposite shows 27.6 emu/g. We also describe a process for fabricating high optical quality pure PVDF-TrFE and pinhole-free nanocomposite films. Finally, the mechanical studies revealed that the mechanical strength of the films increases up to 5 wt% loading of the nanoparticles in the copolymer matrix and then decreases. This signifies that the obtained films could be suited for flexible electronics.

**Introduction**

Ferroelectric polymers, such as polyvinylidene fluoride (PVDF) and its copolymers polyvinylidene fluoride–trifluoroethylene (PVDF-TrFE) and polyvinylidene fluoride hexafluoropropylene (PVDF-HFP), have been attracting a growing research interest due to low-temperature processing methods to fabricate flexible materials of lower leakage current and dielectric loss [1–4]. Moreover, these materials offer unique advantages, such as they can be fabricated into different shapes, on molded structures and curved surfaces, thus, making them suitable for applications such as sensors, transducers, actuators, data storage, spintronics, and miniature antennas [5–10]. Magnetoelectric coupling in such polymers can be formed with the incorporation of ferromagnetic nanoparticles, and the coupling properties can be tuned by varying content and shape of nanoparticles in the composite systems [11, 12].

PVDF copolymers such as PVDF-TrFE and PVDF-HFP can crystallize in four different crystalline phases, namely α, β, γ, and δ [13]. The existence of these phases depends on the processing conditions or synthesis processes [14]. The α and β phases are the most interesting ones for technological applications and are widely studied. The α phase is known as the non-polar stable phase, and the β phase is the polar phase. In the β phase, all-trans planar zig-zag conformation results in a non-zero dipole moment, thus exhibiting remarkable ferroelectric properties [15]. The β phase is the only one that possesses a spontaneous polarization and therefore piezoelectricity [16]. Due to multifunctional properties such as ferroelectric, pyroelectric, and piezoelectric,
PVDF and its copolymers demonstrate increasing applications for sensors, actuators, batteries, and nanogenerators [17–20].

Recently, many attempts have been made to produce magnetolectric coupling between ferroelectric PVDF and ferromagnetic nanoparticles with good dispersion of nanoparticles [12, 21]. However, little attention has been dedicated to developing the magneto-electric coupling in the copolymers. One way to introduce magneto-electric coupling in the electroactive PVDF-TrFE copolymer is the embodiment of spinel ferrite $AFe_2O_4$ ($A = \text{Co, Ni, Zn, Cd, Mn, Cu, Mg}$) nanoparticles with good magnetization. Here, sonochemically synthesized cobalt ferrite nanoparticles were infused into a ferroelectric PVDF-TrFE copolymer so that the coupling and synergetic interaction between ferromagnetic CoFe$_2$O$_4$ and ferroelectric PVDF-TrFE could lead to the development of magneto-electric nanocomposites with numerous technological applications. Furthermore, by incorporating ferrite nanoparticles with the nucleation of ferroelectric $\beta$ phase of PVDF-TrFE, thermal properties may be altered or improved, which can extend the application range of the materials. For this, understanding how thermal/magnetic/electric properties are changed due to the physical and chemical interaction between nanoparticles and copolymer is essential. Moreover, by addressing how nanoparticles induce variations in the thermal properties and thermal degradation of copolymers, valuable information on the nature of the particle-copolymer interactions can be understood. Some recent papers also reported using non-magnetic nanoparticles as filler in PVDF matrix, such as PVDF–BaTiO$_3$ [22], PVDF–ZnO [23], PVDF–Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ [24], PVDF–GeO$_2$ [25], PVDF–SiO$_2$ [25] for the enhancement of dielectric properties of PVDF. However, the applications of those studies are restricted to energy storage devices.

A number of preparation methods have been reported for PVDF-based nanocomposites films using magnetic nanoparticles, such as PVDF–BiFeO$_3$ [26], PVDF–CoFe$_2$O$_4$ [27, 28], PVDF–NaNbO$_3$–Ni [12], PVDF–HFP/crystal/NaF [29], and PVDF–NiFe$_2$O$_4$ [30, 31], using either a solution casting, hot press, or electrospinning to improve the magneto-electric coupling. In those studies, enhancements in magneto-electric coupling and dielectric constant with the increase in filler nanoparticles were reported. However, because of the stochastic nature of the processes, it is challenging to prepare large films and control thickness using those methods. Additionally, nanocomposite films are often encountered with voids and aggregated ferrite particles in the polymer matrix. In contrast, microelectronic applications require thinner and pinhole-free films to operate at low-voltage and to prevent electrical shorts, respectively. To address aforementioned issues, herein, we report a straightforward route for the fabrication of flexible and highly smooth pure PVDF-TrFE and CoFe$_2$O$_4$–(PVDF-TrFE) nanocomposites films using doctor blade technique, wherein the thickness of the films can be controlled using thickness adjustable film coater or casting blade. Additionally, using this technique, the coating speed, and substrate temperature can be controlled in between 20 to 110 °C. We observe that voids present in the films due to the exchange of solvent (DMF) and non-solvent (water vapor from ambient humidified air) can be avoided by raising the substrate temperature at or above 95 °C.

Materials and methods

All chemicals used in the reaction were of analytical grade and were purchased from Sigma–Aldrich. PVDF–TrFE (C$_2$H$_4$F$_2$)$_3$(C$_3$F$_7$H)$_2$, and N, N-dimethylformamide (DMF) (C$_2$H$_7$NO, 99.9% purity) were used for the fabrication of the films. Cobalt nitrate (99.99% purity) and iron acetate (99.99% purity) precursors which were used to synthesize cobalt ferrite nanoparticles were purchased from Sigma–Aldrich.

Synthesis of cobalt ferrite nanoparticles
CoFe$_2$O$_4$ nanoparticles (CFN) were synthesized from cobalt nitrate and iron acetate precursors with the assistance of ultrasound irradiation. A reaction mixture of cobalt nitrate (0.5 g) and iron acetate (1 g) in 60 mL of solvent (50 mL of water and 10 mL of DMF) was prepared. The mixture solution (pH 7) was then sonicated for 2 h by employing a probe sonicator (Sonics vibra cell ultrasound, modeled as VCX 750) with an ultrasonic liquid processor of 750 W output with 20 kHz, 100 W cm$^{-2}$ converter and a flat titanium horn of 19 mm in diameter was used. It was driven at a frequency of 20 kHz and operated at 62% amplitude. The cavitation produced by intense ultrasonic waves was strong enough to drive oxidation, reduction, decomposition, hydrolysis, and dissolution reactions [32–34]. A solid brown precipitate was obtained after 2-h irradiation and was separated by centrifugation. The resulting precipitate was dried overnight in an oven at 80 °C, and the final product was calcined at 650 °C for 5 h.

Fabrication of composite magnetolectric films
PVDF-TrFE was dissolved in DMF as PVDF-TrFE crystallizes in the $\beta$ phase when the films are fabricated using DMF as the solvent. A 15 wt% of PVDF-TrFE homogeneous solution was prepared by continuously heating and stirring PVDF-TrFE in DMF at 85 °C. It is noted that very small crystallites are still present in the solution at low
temperatures due to partial dissolution or refolding of the polymer chain, which could act as nuclei when the solution is recrystallized. We observe that complete dissolution of PVDF-TrFE can be achieved only by raising the temperature but not by a longer dissolution time. Once the complete dissolution of the PVDF-TrFE was achieved, an appropriate amount of cobalt ferrite was added to the solution to prepare a series of various content (0, 2.5, 5, and 10 wt%) of cobalt ferrite in the solution while magnetically stirring for 30 min. The reaction solutions were then sonicated for at least an hour to attain a uniform distribution of cobalt ferrite nanoparticles in the copolymer solution. The homogeneous dispersion thus obtained was used to prepare films using a film coater. The PVDF-TrFE films were prepared at room temperature and various substrate temperatures up to 95 °C. At 95 °C, we observe smooth and void-free films; thus, all the nanocomposite films were prepared at 95 °C. As-fabricated pure PVDF-TrFE and nanocomposites films were then heated at 130 °C for an hour to facilitate the formation of β-phase in the PVDF-TrFE and (PVDF-TrFE)–cobalt ferrite nanocomposites. It was then allowed to cool down to room temperature, forming pure PVDF-TrFE and (PVDF-TrFE)–cobalt ferrite nanocomposite films, which were then stored for characterization and thin-film analysis.

Characterization of nanoparticles/PVDF-TrFE and nanocomposite films:

The x-ray diffraction analysis was accomplished using a Rigaku SmartLab powder XRD with a Cu-Kα radiation (λ = 1.54 Å) operating at a voltage of 40 kV and current of 30 mA. Data were collected over a range from 5 to 80° 2θ angle at a rate of 2° min⁻¹ with a step size of 0.02°.

The cobalt ferrite nanoparticles and polymer/nanocomposite films were morphologically characterized by scanning electron microscopy (SEM) utilizing a JEOL JSM-7200F field emission scanning electron microscope (FESEM, JEOL USA) at 10–20 kV. Before the SEM characterization, a thin layer of gold/palladium (Au/Pd) was deposited on the surface to avoid charging using a Hummer sputter coater for 3 min at 10 mA. Also, the elemental analysis was performed using a Bruker energy dispersive x-ray spectrometer (EDX) coupled with the JEOL FESEM.

The structural characterization of the samples at the nanoscale was performed by utilizing transmission electron microscopy (TEM) using a JEOL 2010 operating at an accelerating voltage of 200 kV. TEM samples were prepared by dispersing the cobalt ferrite nanoparticles (CFN) in ethanol in an ultrasonic bath, then drop-casting the nanoparticles solution on a carbon-coated 200 mesh copper grid under ambient conditions.

Thermal stability analysis of polymer/composites was done using a Thermogravimetric analysis (TGA) with TA Instruments’ Q-500, which was purged with dry nitrogen at a rate of 90 ml min⁻¹. The samples were analyzed within the scanning range of 30 to 1000 °C at a ramp rate of 10 °C min⁻¹. The TGA thermogram reveals the samples’ stability parameters and percentage weight loss with respect to the temperature.

A non-isothermal mode with a scanning range of 30 to 200 °C at a heating rate of 5 °C min⁻¹ and a nitrogen flow rate of 50 cm³ min⁻¹ was used to perform the differential scanning calorimetric measurements (TA Instruments Q2000 DSC machine). The samples weighing 10–15 mg were sealed in an aluminum pan before the measurements. Also, an empty pan made with aluminum was used as a reference. In order to determine the melting/curee crystallization temperature of polymers/composite films, a TA-analysis software package was used.

A precision multiferroic II ferroelectric tester (Radiant Technologies) was employed to execute the ferroelectric hysteresis measurements of pure polymer/composite films with applied standard bipolar excitation signal at a maximum field strength of 2000 kV cm⁻¹ and different periods (50 to 1000 ms).

The magnetic properties of the CFN and composites were measured at room temperature with vibrating sample magnetometry using a Quantum Design VersaLab between −30 kOe and +30 kOe. The saturation magnetization was calculated for each sample by plotting the magnetization as a function of 1/H² and extrapolating the curve back to zero. The coercivity was determined using a linear fit to the demagnetization data, and when this curve crossed the abscissa (i.e., when the magnetization was zero).

In order to study the mechanical properties of the pure PVDF-TrFE and (PVDF-TrFE)–CoFe₂O₄ nanocomposite films, we perform the uniaxial tensile tests by following the ASTM D3379 standard using a Zwick/Roell Z2.5 universal Mechanical Testing Machine with displacement control mode at a speed of 5 mm min⁻¹, preload of 0.01 N, and a load cell of 20 N. A crosshead displacement is used to measure the strain values, and a TestXpert data acquisition and analysis software was used to find the tensile strength/elongation at a breakpoint.

Results and discussion

Structural characterization

XRD patterns of cobalt ferrite nanoparticles, pure PVDF-TrFE film, and the nanocomposite films are shown in figures 1(a), (b). The diffraction pattern of as-synthesized cobalt ferrite nanoparticles is presented in figure 1(a).
The typical reflections of the (111), (220), (311), (222), (400), (422), (511), and (440) planes were observed, which indicate the cubic spinel structure of the highly crystalline cobalt ferrite nanoparticles. All the observed peaks match well with the standard JCPDS data (card number 022–1086). The crystallite size (L) of the cobalt ferrite nanoparticles was calculated from the most intense diffraction peak, i.e. (311) plane, by using the Debye–Scherrer equation:

$$L = \frac{K\beta}{\cos\theta}$$

Where λ is the wavelength of the x-ray radiation, K is a constant (K = 0.9), θ is the Bragg angle, and β is the full width at half maxima (FWHM) of the diffraction peak. The crystallite size of the cobalt ferrite nanoparticle was calculated as 9 nm. It is reported that calcination temperature influences the crystal size, with an increase in temperature resulting in an increase in crystallite size of cobalt ferrite [35]. As shown in figure 1(b), the neat PVDF-TrFE film has distinct diffraction peaks at 18.27°, 19.95°, 36.22°, and 38.86°. The strong peaks at 18.27° and 19.95° correspond to the (110) and (200) planes of the β phase. The observed strong β phase of the PVDF-TrFE film can be attributed to the preferential crystallization of PVDF-TrFE while using DMF as the solvent [36]. The low-intensity peaks at 36.22° and 38.86° are attributed to the γ and α (002) phases of PVDF-TrFE [31]. This result suggests that the plain PVDF-TrFE film possesses a combination of α, β, and γ crystalline polymorphs with a relatively higher quantity of the ferroelectric β phase. The composite films show the characteristic peaks corresponding to β phase of PVDF-TrFE and CoFe2O4 nanoparticles (figure 1(b)). It is clearly seen that the peaks corresponding to cobalt ferrite become more intense with the increase in cobalt ferrite content in the PVDF-TrFE matrix. The α phase of PVDF-TrFE at 38.86° is slightly shifted to 40.79° with the incorporation of cobalt ferrite, and its intensity decreased gradually above 5 wt% loading of cobalt ferrite. This implies that the higher loading of ferrite nanoparticles might have influenced the crystallization of PVDF-TrFE.

Figure 1(c) shows a photograph of the PVDF-TrFE thin film prepared at 95 °C substrate temperature, revealing a high optical quality and transparent nature of the film. The thickness of the film was measured using a digital screw gauge. The average thickness of the film was found to be (21 ± 2.7) μm, which was obtained by measuring at five different areas of 3 different batches of the films. We observe that the speed of coating, the temperature of the substrate, and physical properties of the solution (viscosity, density) affect the thickness of the film. So, we keep all these parameters constant to control the thickness of the PVDF films.

**Morphology and size analysis of cobalt ferrite nanoparticles**

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to identify the morphology and size of the cobalt ferrite nanoparticles (figure 2). The SEM images show that the prepared cobalt ferrite nanoparticles are slightly aggregated (figures 2(a), (b)), whereas TEM images at higher resolution revealed the particles’ more or less spherical shape (figures 2(c), (d)). The moderately aggregated particles observed in the images could be due to calcination at higher temperatures (650 °C). The increase in average particle size and coalescence nature of the particle due to annealing at higher temperatures was also reported previously [35]. The Moire fringes observed in the TEM image (figure 2(d)) support the crystalline nature of the cobalt ferrite nanoparticles observed in the XRD pattern (see figure 1). The average particle size of the nanoparticles determined from TEM was found to be (23 ± 3.5) nm. This is in contrast to the x-ray diffraction analysis, which
found a grain size of $\sim 9$ nm. The discrepancy is likely due to the fact that the nanoparticles are polycrystalline, with diffracting domains (grains) on the order of 9 nm. Moreover, energy dispersive x-ray Spectroscopy (EDX) is utilized to show the presence of cobalt/iron/oxygen, find the atomic/weight percentage of those elements, and map their distribution in the cobalt ferrite nanoparticles sample. EDX elemental mapping (figure 3(a)–(d)) shows the distribution and confirms the presence of cobalt/iron/oxygen in the sample.

**Surface morphology analysis of PVDF-TrFE and nanocomposite films:**
The microstructures of pure PVDF-TrFE and nanocomposite films prepared at a 95 °C substrate temperature were studied using FE-SEM and are shown in figure 4 a–d. Our previous studies showed a highly rough PVDF film surface and voids due to DMF and water (from humidified air) phase separation. It was reported that the unwanted rough surface at room temperature was transformed into a very smooth and pore-free surface upon heating the substrate at 95 °C. All the films were prepared at a 95 °C substrate temperature to avoid unwanted
voids. It is noted that microelectronic applications require thinner and pin-hole-free film to operate at low-voltage and prevent electrical shorts.

The microstructures and distribution of cobalt ferrite nanoparticles in the PVDF-TrFE matrix are shown in figures 4(b), (d). The roughness on the film surface increases with an increase in the content of the nanoparticles in the PVDF-TrFE matrix. It is noted that the microstructures of our PVDF-TrFE films do not show tree-like spherulite structures as reported previously with solution casting or spin coating method \cite{31, 36, 37}. This could be due to the predominant ferroelectric $\beta$ phase in our PVDF-TrFE films, as evidenced by XRD result (figure 1(b)). The spherulite structures are formed with the $\alpha$ nucleation process of PVDF, and this unfavorable structure is reported to diminish with an increase in nanoparticle content in PVDF polymer due to improvement in $\beta$ phase \cite{36}. Additionally, unlike previous reports, where significant aggregation of filler particles or formation of voids in PVDF nanocomposite films due to the addition of nanoparticles is reported \cite{1, 30}, our nanocomposite films show a uniform distribution of nanoparticles. As shown in figures 4(b)–(d), our nanocomposite films are highly smooth and pore-free in nature.

Melting/Crystallization peak characterization

DSC measurements on neat PVDF-TrFE and various wt% of cobalt ferrite incorporated nanocomposites (PVDF-TrFE–2.5% CoFe$_2$O$_4$, (PVDF-TrFE–5% CoFe$_2$O$_4$, and (PVDF-TrFE–10% CoFe$_2$O$_4$ films were performed (figure 5) to understand the effect of the cobalt ferrite nanoparticles on the melting temperature and the degree of crystallinity of the nanocomposites. The DSC analysis reveals the Curie temperature ($T_{c1}$) at 127 °C corresponds to the Ferro- to paraelectric transition upon heating (figure 5(a)), and $T_{c2}$ at 65 °C represents the para- to ferroelectric transition upon cooling (figure 5(b)) for neat PVDF-TrFE film whereas the melting and crystallization temperature of the same films are observed at 151 and 120 °C during the heating and cooling cycle, respectively, which are consistent with previous work\cite{38, 39}. The $T_{c1}$ temperature of the polymer films loaded with CoFe$_2$O$_4$ nanoparticles appears at a lower temperature, whereas $T_{c2}$ temperature shows up at a higher temperature than the pure PVDF-TrFE film. Also, the melting temperature decreases (figure 5(a)), and the crystallization temperature increases (figure 5(b)) upon incorporating cobalt ferrite nanoparticles into the polymer matrix. Unlike the pure PVDF-TrFE sample, which shows broad crystallization/melting/$T_{c2}$ peaks, relatively a much sharper response at a slightly different temperature is observed for polymer nanocomposites which can be attributed to a stronger domain separation with the incorporation of CFN\cite{40}. Similar results were also previously reported with the addition of boron nitride nanotubes into the PVDF-TrFE copolymer matrix \cite{41}.
Thermal stability analysis

Thermal degradation and the nucleation of the ferroelectric phases of PVDF-TrFE can be significantly impacted by the geometrical factor such as the size of the nanoparticles and the interaction at the interface between nanofillers and copolymer \[42\]. We use thermogravimetric analysis (TGA) to study the thermal behavior of PVDF-TrFE with the various amount of cobalt ferrite loading. TGA thermograms for various cobalt ferrite nanoparticle loading, ranging from 0 to 10 wt%, are shown in figure 6. The typical one-step thermal degradation characteristic of PVDF-TrFE changes to two-step degradation with 10 wt% loadings of CFN. This additional degradation step in the presence of nanoparticles can be linked to the interaction between the polymer matrix and the nanoparticles \[15\]. Interestingly, the loading of cobalt ferrite nanoparticles significantly improved the thermal stability of the PVDF-TrFE, showing the change of weight percent from \(~3.70\) to \(38\%\) at \(980\) °C upon the incorporation of 10 weight percent of cobalt ferrite nanoparticles. As shown in figure 5, the first step of degradation of the polymer takes place within the range of \(465\)–\(500\) °C, indicating the polymer’s maximum degradation temperature is affected by the percentage of loading of nanoparticles in the nanocomposite. In this first degradation step, the decomposition mechanism is related to chain-stripping where carbon-hydrogen and carbon-fluorine scission occurs, and the presence of both hydrogen and fluorine radicals leads to the formation of hydrogen fluoride \[15, 43\].

**Figure 5.** DSC thermogram of pure PVDF-TrFE and nanocomposite films loaded with 2.5, 5, 10 wt% of cobalt ferrite nanoparticles upon (a) heating and (b) cooling.

**Figure 6.** TGA plots of PVDF-TrFE and a series of (PVDF-TrFE)-cobalt ferrite nanocomposite films showing cobalt ferrite loading (up to 10 wt%) significantly improved the thermal stability of the PVDF-TrFE at \(~980\) °C.
Ferroelectric properties

In order to investigate the effect of loading CoFe$_2$O$_4$ nanoparticles (CFN) on the ferroelectric properties of the polymer/composite films, we measure the dependence of electric field $E$ on polarization $P$ at room temperature by applying a standard bipolar drive signal with a maximum field strength of 2000 kV cm$^{-1}$ at different periods varying from 50 to 1000 ms (figure 7a) and various CFN weight fractions changing from 0 to 10% (figure 7b). As the structure of a hysteresis loop may change depending on the competition of the ferroelectric dipole switching time and period of the drive signal under an applied field strength [44], we vary the periods of the excitation signal from 50 to 1000 ms at a fixed electric field. At a lower period starting from 50 ms, the hysteresis loops take a form like an ellipse with a low remnant polarization value due to the suppression of ferroelectric switching, whereas the shape of the hysteresis loops become slightly rectangular with an increase in remnant polarization and coercive field at a higher period of the excitation signal corresponds to the more efficient switching of the dipole moments (figure 7a). The ferroelectric hysteresis loops of PVDF-TrFE and PVDF-TrFE loaded with different CoFe$_2$O$_4$ nanoparticles (CFN) weight fractions showed an enhancement of the polarization value upon introducing CFN in the polymer films. The neat PVDF-TrFE film provides a maximum polarization ($P_{\text{max}}$) value of 0.11 $\mu$C cm$^{-2}$, whereas the composite films show an increased polarization with a $P_{\text{max}}$ of $\sim$0.29 $\mu$C cm$^{-2}$ for (PVDF-TrFE)−5%CoFe$_2$O$_4$ sample (figure 7b). The loading of CoFe$_2$O$_4$ nanoparticles may introduce more free charges in the PVDF-TrFE/CoFe$_2$O$_4$ polymeric composite films, which can compensate/stabilize the polarization domain[45, 46]. Moreover, CFN may act as nucleation centers in the ferroelectric domain during the polarization process resulting in an improvement of the ferroelectric properties of the copolymer matrix [47–49]. Additionally, due to the large surface area of CFN filler in the composites, an exchange coupling effect can occur via a dipolar interface layer leading to an enhancement of the dielectric properties and polarization level[50]. The sample loaded with 10% CFN shows a 7% lower $P_{\text{max}}$ value than the sample containing 5% CFN, indicating the existence of a critical point for the CFN loading to optimize the ferroelectric switching response. Any ferrite contents above this critical point may destroy the long-range ordered dipole chains of the polymer phase leading to a decrease of the $P_{\text{max}}$ value[47, 51].

Magnetic properties

The $M$ v. $H$ curve of cobalt ferrite nanoparticles and nanocomposite films measured at room temperature are shown in figure 8. The saturation magnetization, obtained by plotting $M$ v. $1/H^2$ and extrapolating to zero, was found to be 47.4 emu/g for the CFN alone. This is in line with previous results on the saturation magnetization reported elsewhere [1, 27, 28, 30, 52, 53]. The coercivity was on the order of 2 kOe, consistent with the hard magnetic cobalt ferrite material. For the composites, the saturation magnetization was proportional to the loading of the CFN in the composites, while the coercivity remained on the order of 2 kOe for all of the compositions. The pure CFN and polymer composites loaded with 2.5, 5, 10% CFN show a saturation magnetization of 51.5, 12.3, 19.8, 27.6 emu g$^{-1}$, respectively [47, 54], indicating the saturation magnetization did not correlate with the CFN content. For instance, the composite loaded with 2.5% CFN did not have a saturation magnetization of 2.5% of the CFN themselves. Further, the values for the 5% and 10% loading were not 2x and 4x that of the 2.5% loading. This may be due to uneven CFN distribution in the composites and samples for magnetic measurements oversampled CFN content.
Mechanical properties

The uniaxial tensile tests were performed to characterize the mechanical properties of pure PVDF-TrFE and PVDF-TrFE-CoFe₂O₄ nanocomposite films. The mechanical properties were measured using a Zwick/Roell Z2.5 universal mechanical testing machine. For the tensile tests, displacement control mode with a constant crosshead speed of 5 mm min⁻¹, preload of 0.01 N, and a 20 N load cell was used. The stress-strain curves of pure PVDF-TrFE and PVDF-TrFE-CoFe₂O₄ nanocomposite films are presented in figure 9a. All the films exhibited thermoplastic behavior. It can be seen that the stress-strain behavior was not affected by the 2.5 wt% loading of the cobalt ferrite, whereas it was found to be significantly improved with the 5 wt% loadings. With 10 wt% loadings, the mechanical properties were observed to be decreased. This decrease in mechanical property can be linked to defect creation in the matrix due to higher than optimal loading of the nanoparticles. The pure PVDF-TrFE film can withstand up to a strain of 7.99% with a good tensile strength of 22.7 MPa. Adding 5 wt% cobalt ferrite nanoparticles in the copolymer matrix remarkably increases the strain value up to 51.8% at a maximum tensile strength of 37.6 MPa. Thus, the mechanical strength of the composite films has not been affected by 2.5 wt% loadings but notably increased by 65.6% with the addition of 5 wt% nanoparticles.

Figure 9b shows a change in tensile strength (left axis) and elongation at break (right axis) as a function of the content of cobalt ferrite nanoparticles in the copolymer matrix. The tensile strength increases with the 5 wt% loadings and decreases with 10 wt% loading of the nanoparticles. Similarly, improve in elongation at break is found to be with the 5 wt% loading of the nanoparticles. Unlike previous studies on films prepared from the solution casting method, where a decrease in mechanical properties of a pure polymer film with the addition of nanoparticles was reported. Our studies show an increase in the mechanical properties of the nanocomposite.
film up to a specific maximum loading of nanoparticles in the polymer matrix, and then a decrease in the properties was observed. This improvement in mechanical properties with nanocomposite could be presumably due to the adopted doctor blading technique and substrate heating at 95 °C, which produces smooth and void-free nanocomposite films as evidenced by SEM images of the films (figure 4).

Conclusion

Cobalt ferrite nanoparticles of average diameter 23 ± 3.5 nm were prepared by using a sonochemical method. As-synthesized cobalt ferrite nanoparticles are highly crystalline in nature and demonstrated the cubic spinel structure with good magnetization properties. Next, we fabricated pure PVDF-TrFE and nanocomposite films by incorporating various weight percentages of as-synthesized nanoparticles in the PVDF-TrFE matrix using a blade coating technique. The highly smooth, good optical quality, and void-free flexible films were obtained by avoiding phase separation between organic solvent and water from humidified air. XRD analysis confirmed the presence of predominant ferroelectric β-crystalline phase in pure PVDF-TrFE and nanocomposite films. The microstructure analysis showed the uniform distribution of cobalt ferrite nanoparticles in the PVDF-TrFE matrix. Furthermore, the investigation of the effect of cobalt ferrite nanoparticles on thermal degradation of PVDF demonstrated an increase in thermal stability of PVDF-TrFE film at 980 °C with the infusion of 10 wt% of cobalt ferrite nanoparticles. Ferroelectric and magnetic measurements confirm the ferroelectric and ferromagnetic nature of the nanocomposite films at room temperature. The mechanical tests revealed enhancement in film strength up to 5% cobalt ferrite loading into the PVDF-TrFE matrix. Finally, the achievement of smooth, pin-hole-free, ultra-thin films of PVDF-TrFE and nanocomposites pave the way to integrate ferroelectric and ferromagnetic properties into flexible microelectronic devices as well as open up the possibilities in photonic applications.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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