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Abstract

Magnetoelectric 0-1 composites comprising CoFe₂O₄ (CFO) nanoparticles in a polyvinylidene fluoride (PVDF) polymer-fibre matrix have been prepared by electrospinning. The average diameter of the electrospun composite fibres is ~325 nm, independent of the nanoparticle content, and the amount of the crystalline polar β phase is strongly enhanced when compared to pure PVDF polymer fibres. The piezoelectric response of these electroactive nanofibres is modified by an applied magnetic field, thus evidencing the magnetoelectric character of the CFO/PVDF 0-1 composites.

Keywords

electrospun, fluoride, magnetoelectric, nanofibres, cofe₂o₄, polyvinylidene

Disciplines

Engineering | Science and Technology Studies

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Magnetoelectric CoFe₂O₄/polyvinylidene fluoride electrospun nanofibres

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Abstract

Magnetoelectric 0-1 composites comprising CoFe₂O₄ (CFO) nanoparticles in polyvinylidene fluoride (PVDF) polymer-fibre matrix have been prepared by electrospinning. The average diameter of the electrospun composite fibres \bar{D} is ~ 325 nm, independently of nanoparticle content, and the amount of polar crystalline β phase is strongly enhanced when compared to pure PVDF polymer fibres. The piezoelectric response of these electroactive nanofibres is modified by an applied magnetic field, thus evidencing the magnetoelectric character of the CFO/PVDF 0-1 composites.

Introduction

Strain-mediated magnetoelectric composites that exhibit large direct magnetoelectric effects have emerged in recent years as promising candidates for e.g. the development of magnetic-field sensors and energy-harvesters, due to their high sensitivity, simple fabrication, low cost, and room temperature operation [1,2]. Giant magnetoelectric voltage coefficients, $\sim 300 \text{ V cm}^{-1} \text{ Oe}^{-1}$ at the $\sim 50 \text{ kHz}$ resonance, have been observed in 2-2 laminate composites of high-magnetic-permeability Fe-Si-Co Metglas and piezoelectric PVDF polymer layers bonded using epoxy resin [3], and larger values, $\sim 750 \text{ V cm}^{-1} \text{ Oe}^{-1}$ at the $\sim 22 \text{ kHz}$ resonance, have been reported in 2-1 laminate composites consisting of piezoelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$ fibres bonded between Fe-B-Si-C Metglas layers using epoxy resin [4]. However, these strong magnetoelectric effects are non-linear and occur only at very low magnetic-field bias, such that they are not suitable for use as sensors (or harvesters) of moderate and high magnetic fields, and moreover the performance of these composites is compromised by the relative brittleness of the epoxy bonding.

Magnetoelectric composites comprising magnetic nanoparticles embedded in a ferroelectric polymer matrix can overcome these problems: strain coupling typically does not deteriorate with operation, as the magnetic material is in direct contact with, and completely surrounded by, the ferroelectric material, and magnetoelectric voltage coefficients 0-3 composites comprising magnetic nanoparticles and fluorinated-polymer matrices are relatively large both at moderate [5,6] and high [7,8] magnetic fields. Here we extend the range of geometries available for polymer-based magnetoelectric composites by fabricating 0-1 nanofibres comprising CFO ferromagnetic particles and PVDF matrix, as such one-dimensional structures may permit the development of new magnetoelectric devices [9].

Experimental

PVDF powder (Solef 1010) was purchased from Solvay Solexis, CFO nanoparticles (35–55 nm) were purchased from Nanoamor, and pure grade *N,N*-dimethylformamide (DMF) solvent was purchased from Merck. All materials were used as provided by the suppliers. Composite fibres, with nanoparticle content 5, 10 and 20 wt. %, were prepared using the following procedure: (i) CFO nanoparticles were added to the DMF and the solution was placed in an ultrasonic bath; (ii) PVDF powder was added and the resultant solution was mixed using a Teflon mechanical stirrer and an ultrasonic bath until the polymer was completely dissolved; (iii) the CFO/DMF/PVDF solution was introduced into the electrospinning deposition setup, using a plastic syringe connected to a flux regulator; in order to create a jet, high voltage was applied between the syringe needle and an aluminium foil, where the electrospun fibres are collected, forming a mat; deposition conditions were 20 kV bias, 0.5 mm needle inner diameter, 0.5 ml h⁻¹ flow rate, and 20 cm needle-collector distance.

Size and morphology of the CFO/PVDF nanofibres were studied by scanning electron microscopy (SEM) using a Quanta 650 FEI electron microscope with acceleration voltage of 10 kV. Prior to SEM, the nanofibre mats were coated with gold. SEM image analysis was performed using Image J software.

Volume fraction of electroactive β -phase in the nanofibre PVDF matrix was determined via Fourier transform infrared spectroscopy (FTIR) [6,10], performed using a Jasco FT/IR-4100 type A that was operated in attenuated total reflectance mode, with 2 cm⁻¹ resolution. For each sample, sixty four spectra were averaged, and then values of volume fraction F_{β} were obtained as $F_{\beta} = A_{\beta} / [(K_{\beta}/K_{\alpha})A_{\alpha} + A_{\beta}]$, where $A_{\beta} = T_{\beta}^{-1} = 840 \text{ cm}^{-1}$ and $K_{\beta} = 7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ are the absorbance and absorption coefficients for the β phase, and $A_{\alpha} = T_{\alpha}^{-1} = 764 \text{ cm}^{-1}$ and $K_{\alpha} = 6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ are the absorbance and absorption coefficients for the α phase [11].

Magnetization loops $M(H)$ were measured up to 10 kOe using an Oxford Instruments vibrating sample magnetometer. Piezoelectric coefficients d_{33} were determined using a Digital Instruments Dimension 3100 for piezoresponse force microscopy (PFM), with conductive Cr/Pt-coated tips of stiffness 40 N m^{-1} . d_{33} measurements were performed using a 2 V peak-to-peak ac bias at 13 kHz, with and without a 1 kOe magnetic field that was applied using a permanent magnet. Prior to local measurements of the nanofibres piezoresponse, the cantilever deflection amplitude was calibrated via force-distance measurements.

Results and discussion

The studied CFO/PVDF electrospun nanofibres have an average diameter $\bar{D} \sim 325 \text{ nm}$, and are randomly distributed in the aluminium-foil collector (Figure 1). CFO nanoparticle content has no significant impact on the nanofibre average diameter [Figure 1 (a-d)]. The CFO/PVDF nanofibres show a strong enhancement in the volume fraction of electroactive β phase F_β [11,12] when compared to pure PVDF electrospun nanofibers [Figure 1(e) and (f)], as the interaction between the negatively charged surface of the CFO nanoparticles (whose zeta potential is -22 mV) and the positively charged polymer CH_2 groups promotes nucleation of the polar β phase, as seen in CFO/PVDF films [10]. The increase in β phase volume fraction is also assisted by the low evaporation temperature of the solvent ($\leq 60 \text{ }^\circ\text{C}$) and the stretching that occurs during jet formation [13].

The magnetization of the nanofibres increases with increasing CFO content (Figure 2), as expected [2,5,6]. The shape of the magnetization loops is determined by the mixture of single-domain and multidomain nanoparticles [14], and the magnetization does not saturate at the maximum applied magnetic field of 10 kOe, due to the strong magnetic anisotropy ($> 30 \text{ kOe}$) of the CFO nanoparticles [15].

To establish the magnetoelectric character of the nanofibre composites, we performed piezoresponse force microscopy with and without applied magnetic field [Figure 3(a)]. Piezoelectric coefficient d_{33} increases with applied magnetic field, due to the strain-mediated coupling between the magnetostrictive CFO nanoparticles and the piezoelectric PVDF matrix, which shows reduced piezoelectric coefficients when compared to bulk polymers, possibly due to clamping by the surrounding material (which may reduce significantly the local deformation of the nanofibers) [6,16,19].

To conclude, we studied the structural, magnetic and piezoelectric properties of low-temperature processed 0-1 nanofibre composites of CFO and PVDF. Magnetic-field-induced changes in the piezoelectric response of the nanofibres demonstrated the magnetoelectric character of these 0-1 composites, which may be useful for the development of micro and nanoscale magnetoelectric devices.

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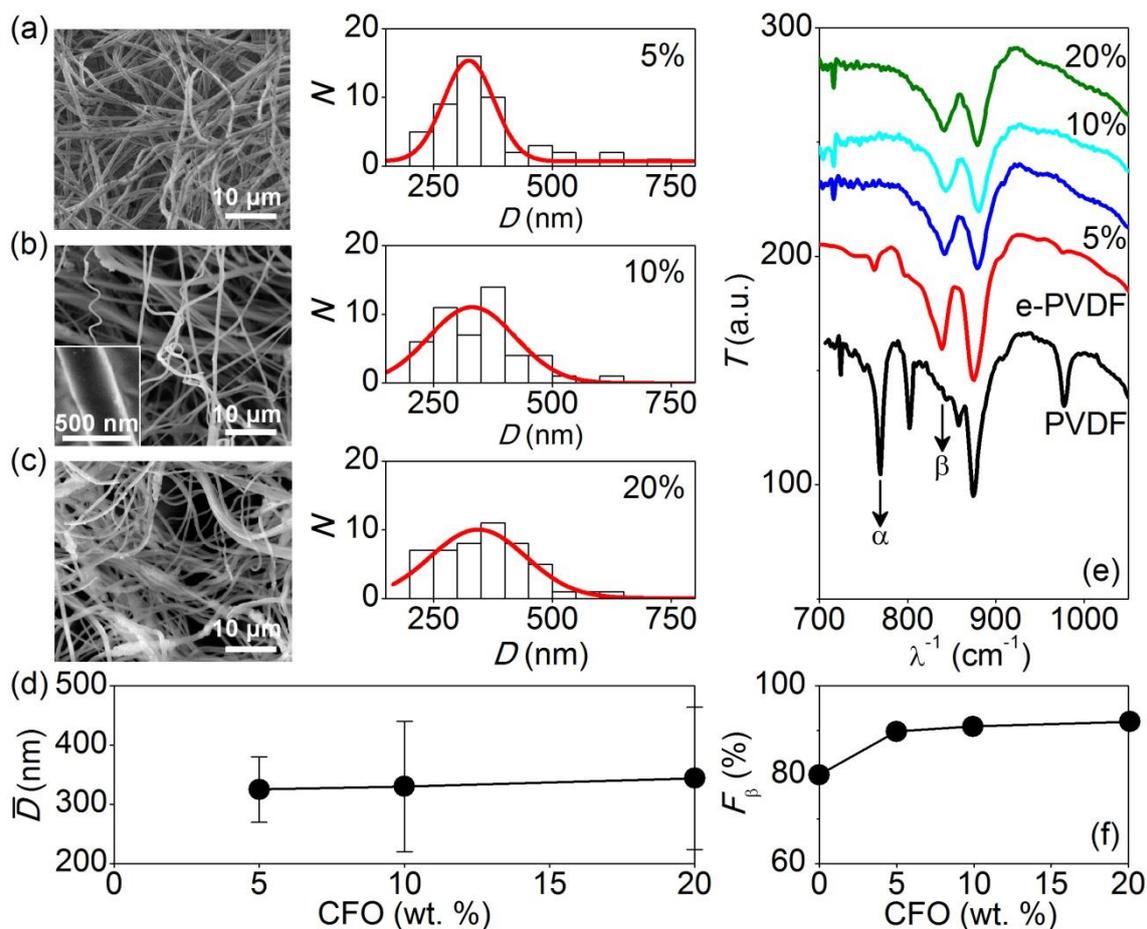


Figure 1. SEM image and corresponding distribution of nanofibre diameter D for CFO/PVDF nanofibres with (a) 5 wt. % CFO, (b) 10 wt. % CFO and (c) 20 wt. % CFO. Red lines are Gaussian fits, which were used to estimate the average diameter \bar{D} . (d) Nanofibre average diameter \bar{D} as a function of CFO content. (e) FTIR spectra for CFO/PVDF nanofibres, and two pure polymer samples in film (PVDF) and nanofibre (e-PVDF) form. Vertical arrows indicate the traces for the α (766 cm^{-1}) and β (840 cm^{-1}) phases. (f) β -phase volume fraction F_{β} as a function of CFO content.

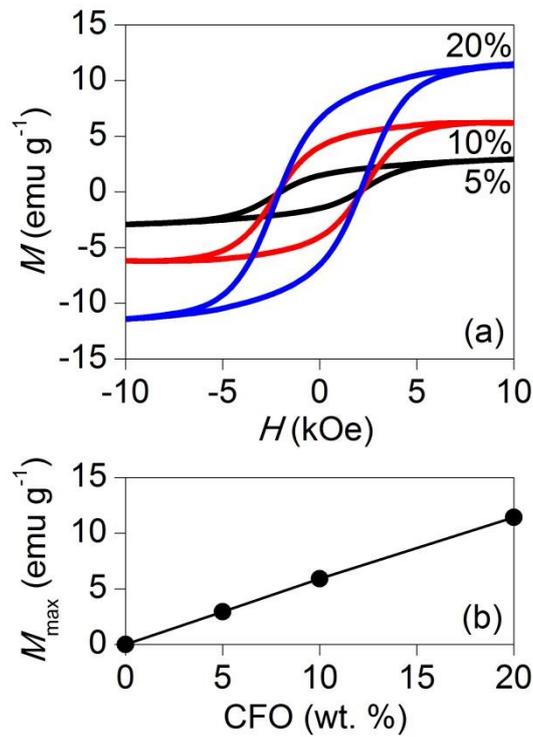


Figure 2. (a) Room-temperature magnetization $M(H)$ of CFO/PVDF nanofibre nanocomposites with different CFO concentration. Magnetization was measured along the out-of-plane direction of the nanofibre mats [complementary in-plane $M(H)$ measurements (not shown) evidenced the isotropic magnetic character of the nanofibre composites]. (b) Magnetization M_{max} measured at 10 kOe as a function of CFO content.

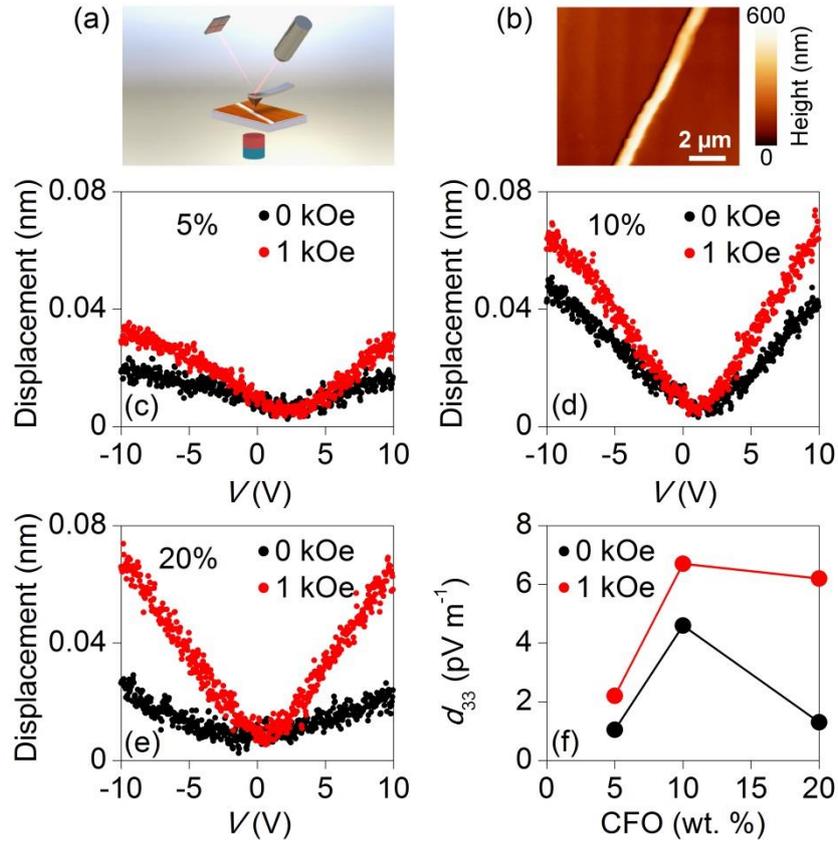


Figure 3. (a) Schematic representation of the piezoresponse force microscopy setup in applied magnetic field used to establish the magnetoelectric character of the CFO/PVDF nanofibres. (b) One of such nanofibres, as seen via atomic force microscopy. Displacement as a function of voltage, with and without magnetic field, for CFO/PVDF nanofibres with (c) 5 wt. % CFO, (d) 10 wt. % CFO and (e) 20 wt. % CFO. The maximum electric field applied was $\sim 30 \text{ MV m}^{-1}$, which is smaller than the coercive field of PVDF films ($\sim 50\text{-}120 \text{ MV m}^{-1}$) [20]. (f) Piezoelectric coefficient d_{33} as a function of CFO content and magnetic field.