Nanoscale

COMMUNICATION

Magnetoelectric CoFe₂O₄/polyvinylidene fluoride electrospun nanofibres

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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 D is ~ 325 nm, independently of nanoparticle content, and the amount of 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.

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 [1-3]. Giant magnetoelectric voltage coefficients, ≈300 V cm⁻¹ Oe⁻¹ at the ≈50 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 [4], and larger values, ≈750 V cm⁻¹ Oe⁻¹ at the ≈22 kHz resonance, have been reported in 2-1 laminate composites consisting of piezoelectric Pb(Zr,Ti)O₃ 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) at 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 in 0-3 composites comprising magnetic nanoparticles and fluorinated-polymer matrices are relatively large both at moderate [5, 6] and high [6, 7] magnetic fields. In this work, the range of geometries available for polymer-based magnetoelectric composites is extended by fabricating 0-1 nanofibres comprising CFO ferromagnetic particles and PVDF matrix, as such one-dimensional structures undergo an increasing demand and applicability as biomaterials for cell culture, drug delivery systems, electro-optic devices, heterogeneous catalysis, polymer powder impregnation of inorganic fibers in composites and energy harvesting [8-10]. To our knowledge there are no previous reports on polymer-based ME nanofibers, that can be an innovative and disruptive solution for applications in which multifunctional active response is needed (either magnetic to electrical or mechanical to electrical responses, due to the ME, magnetostrictive and piezoelectric effects) at a micro and nanoscale levels, such as in non-invasive control of cell growth and differentiation, active drug release and tissue stimulation [10, 11].

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. The relation between the contents of polymer and solvent has been previously optimized in order to obtain fibers with the desired morphology, degree of crystallinity and crystal phase [12]. For such reason the relations was kept 20/80 (20% PVDF + 80% DMF by w/w) ; (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.

CFO contents ranging from 5wt.% to 20wt.% were chosen since it is expected to obtain fibres with proper micro and nanomorphological features and high ME coupling. Lower CFO contents will have as a result an abrupt decrease in the ME response[6], higher contents, on the other hand, will cause substantial changes on polymer solution properties such as surface tension, conductivity and viscosity, thereby hindering the electrospinning process and affecting the desired fibre morphology[13, 14].

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], 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

$$F_β = A_β / [(K_β/K_α)A_α + A_β] \qquad (eq. 1)$$

where $A_β = T_β^{-1} = 840$ cm^{-1} and $K_β = 7.7×10^4$ cm^2 mol^{-1} are the absorbance and absorption coefficients for the β phase, and $A_α = T_α^{-1} = 764$ cm^{-1} and $K_α = 6.1×10^4$ cm^2 mol^{-1} are the absorbance and absorption coefficients for the α phase [15].

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[16, 17].

Results

The studied CFO/PVDF electrospun nanofibres have an average diameter $\bar{D} ≈ 325$ nm, and are randomly distributed in the aluminium-foil collector (Figure 1).
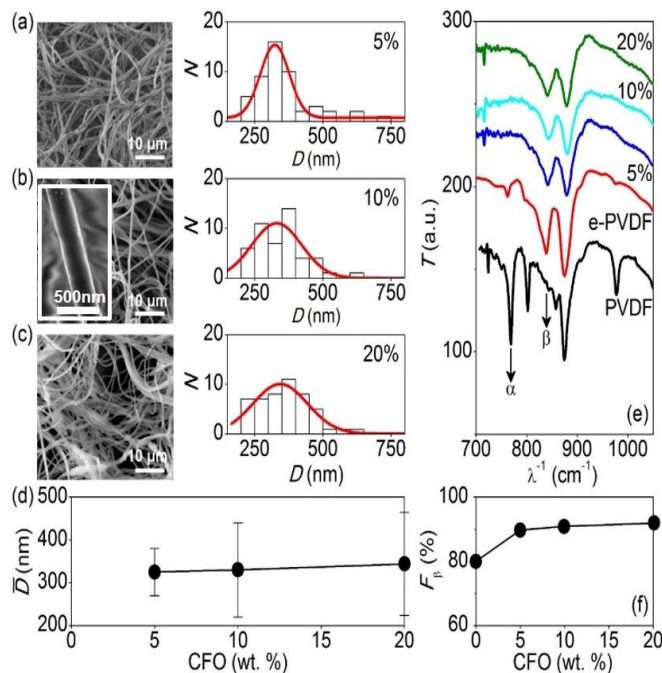

Figure 1. SEM image and corresponding distribution of nanofibre diameter D for CFO/PVDF nanofibres with (a) 5 wt. % CFO, (b) 10 wt. % CFO (inset: detail of a single composite fiber) and (c) 20 wt. % CFO. Red lines are Gaussian fits, which were used to estimate the average diameter $\bar{D}$. (d) Nanofibre 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.

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 $F_β$ [15, 18] when compared to pure PVDF electrospun nanofibres [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 [6]. The increase in β phase volume fraction is also assisted by the low evaporation temperature of the solvent (≤ 60 °C) and the stretching that occurs during jet formation [12].

The magnetization of the nanofibres increases with increasing CFO content (Figure 2), as expected [2, 5, 6].
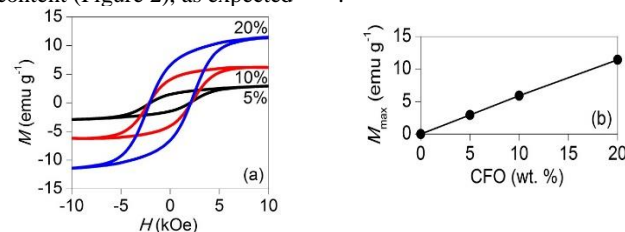

Figure 2. (a) Room-temperature magnetization M(H) of CFO/PVDF nanofibre composites with different CFO concentration. Magnetization was measured along the out-of-plane direction of the nanofibre mats [complementary in-plane M(H) measurements (not shown) evidenced the isotropic magnetic character of the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

The shape of the magnetization loops is determined by the mixture of single-domain and multidomain nanoparticles [19], and the magnetization does not saturate at the maximum applied magnetic field of 10 kOe, due to the strong magnetic anisotropy (> 30 kOe) of the CFO nanoparticles [20].

To establish the magnetoelectric character of the nanofibre composites at a single fiber level, as required in many application at the micro and nanoscale levels, piezoresponse force microscopy experiments were performed with and without applied magnetic field [Figure 3].
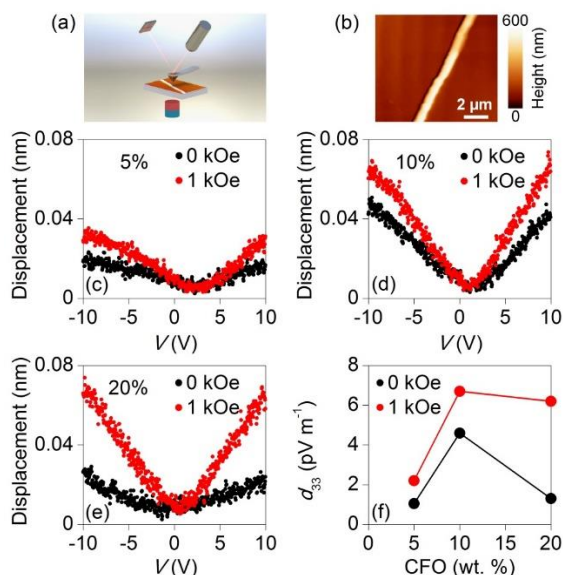

Figure 3. (a) Schematic representation of the piezoresponse force microscopy setup in applied magnetic field used to establish the magnetoelectric character of the CFO/PVDF nanofibres. (b) One of such nanofibres, as seen via atomic force microscopy. Displacement as a function of voltage, with and without 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 ~30 MV m-1, which is smaller than the coercive field of PVDF films (~50-120 MV m-1) [21]. (f) Piezoelectric coefficient d33 as a function of CFO content and magnetic field.

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, 22-25].

Conclusions

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.

Notes and references

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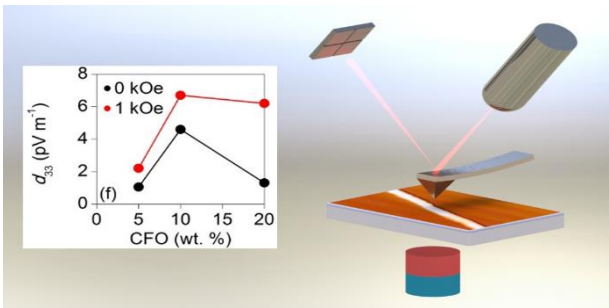
Magnetoelectric CFO/PVDF electrospun fibers and fiber matts have been prepared for multifunctional active response applications.

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