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Short communication

Electrospun poly(vinylidene fluoride-trifluoroethylene) based flexible magnetoelectric nanofibers

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ABSTRACT

Flexible multiferroic nanofibers of poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) containing 20% w/w of bismuth ferrite doped with neodymium and cobalt ($Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$) nanoparticles were fabricated by electrospinning. SEM micrographs show well aligned nanofibers with average diameter of 420 nm, X-Ray diffraction revealed R3c crystalline structure corresponding to $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$ and crystallinity β phase of PVDF-TrFE polymer. FTIR spectra and DSC thermogram were used to investigate the crystallization behavior of PVDF-TrFE and showed pure β phase crystals and high degree of crystallinity. Dielectric measurements determined a low conductivity was found (3×10^{-6}–1×10^{-9} S) together with a piezoelectric coefficient of 35 pm/V ($-d_{33}$) and low permittivity (ε_r = 30–42). Obtained nanofibers displayed a ferromagnetic hysteresis loop, with coercivity of 140 mT and remnant magnetization of 0.580 Am^2/kg at room temperature. The coexistence of magnetic hysteresis and ferroelectric properties in $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$/PVDF-TrFE nanofibers indicates magnetoelectric performance and hint for potential applications on technological devices.

1. Introduction

Multiferroic materials have attracted much attention in recent years, due to their outstanding applications in technological devices. These materials couple at least two ferroic properties (antiferro-ferromagnetism, ferroelectricity and ferroelasticity) simultaneously [1].

The coupling of the ferroic properties of ferromagnetism and ferroelectricity produce the magnetoelectric effect. The magnetoelectrical effect occurs as a product of mechanical deformation from magnetostriction and results in dielectric polarization due to the piezoelectric effect, allowing coupling of ferroic properties at room temperature [2]. There are few single-phase materials that couple at least two ferroic properties with high magnetoelectric values. Due to this, manufacture of magnetoelectric composites using ferromagnets and piezoelectric materials has become popular.

The most common magnetic materials used to fabricate magnetoelectric composites are metals, alloys and ceramics [3–5]. On the other hand, piezoelectric materials commonly used are ceramics [6–8]; however, polymers have been gaining interest due to the appearance of ferroelectric polymers such as PVDF, which not only grant ferroelectric property, but also ferroelastic properties [9–12]. However, polyvinylidene fluoride can present three crystalline phases, Fig. 1, α phase with alternate conformations trans - gauche (TGTG), β phase only with trans conformations (TTTT) and γ phase (TTTG), from these three phases, only β-phase is relevant for electrical applications due to his polarization (ferroelectric properties). The co-polymer PVDF-TrFE crystallizes preferentially in β phase with all trans structural conformation (TTTT) due to the trifluoroethylene structure that prevents the ordering in gauche [13–15]. In addition, the confinement of the polymer due to the nanofibers, forces the compacting of the structure and crystallizes in β-phase [16–19].

By combining a polymeric matrix with magnetic nanoparticles, result in flexoelectric material that may be manufactured on a large scale, allowing for a wide array of applications, sensors [20], actuators [21],

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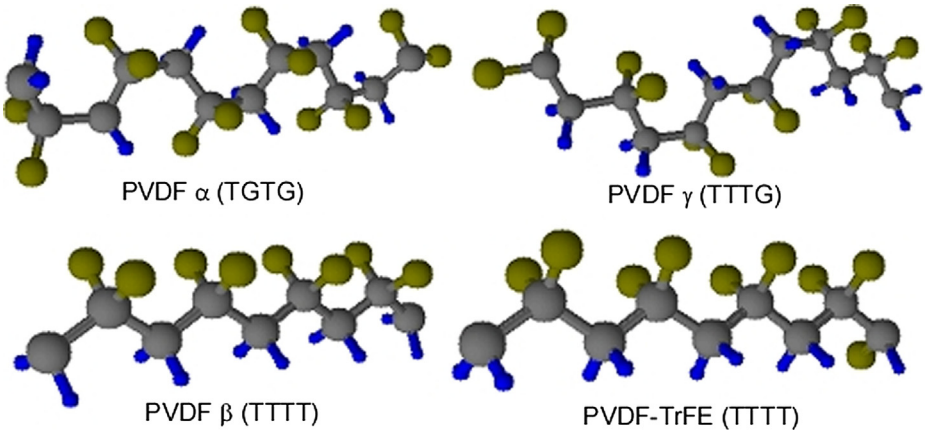

Fig. 1. PVDF and PVDF-TrFE conformations.

energy conversion and storage [22], magnetoelectric memory devices [23], batteries [24,25], distillation [26], tissue engineering [27], etc.

An effective coupling of these properties is nonetheless not always present in composites. This is because the coupling depends on the magnetostriction capacity of the magnetic material and the capacity of the ferroelectric material to respond to the mechanical stimulation of the magnetostrictive material. Thus, a material based on $BiFeO_3$, known to have both ferroelectricity and anti-ferromagnetism, is used in this work as aggregated in nanofibers due to its particle size smaller than 62 nm (Cycle size of spin cycloydal for $BiFeO_3$ is 32 nm) [28,29], this allows the material to change from antiferromagnetism to ferromagnetism [30,31]. In this work, nanometric fibers of PVDF-TrFE were loaded with magnetic particles of $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$ in order to obtain flexible magnetoelectric materials.

2. Experiments

Ceramic material $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$, was prepared using a method previously published by our research group [30]. The copolymer PVDF-TrFE 80/20 (80% of PVDF and 20% of TrFE) was purchased from PIEZOTECH ARKEMA group. It was dissolved in 10 mL of N,N-dimethylacetamide (DMAc) and stirred/heated for 3 h to allow all the polymer chains to extend. Once the polymer was dissolved, 20% weight of the ceramic material was added to the polymer and sonicated for 15 min to allow the dispersion of particles in the medium until stability was achieving. The solution was poured into a 5 mL syringe with a blunt ended needle of 21 gauge. Electrospinning experiment were performed in a non-commercial equipment at room temperature applying a voltage of 12 kV, with a DC power supply ES30 by *Gamma High Voltage Research Inc.*; and using a constant PVDF-solution flow rate of 1 mL h^{-1}, controlled by a syringe pump NE-300 by *New Era Pump Systems*. The fibers obtained were dried under vacuum at 40 °C to remove solvent.

All experiment characterization was made without any further heat or electric treatment. The composite fiber mats were subjected to thermal analysis in order to determine the crystallization temperature with a *Q100* differential scattering calorimetry system (DSC) *by TAInstrument*. These mats were then characterized using X-ray diffraction (XRD) with a *Siemens D-500 diffractometer* with Cu Kα radiation (λ = 0.154178 nm) at 35 kV and 25 mA at a scan rate of 0.025° (2θ)/s. Infrared spectra was also measured at room temperature using a *8400S FT-IR spectrometer by Shimadzul*. Scanning electron microscopy (SEM) images were obtained on a *Jeol 6490-Link 10000AN scanning electron microscope* at an acceleration voltage of 15 kV. SEM was used to study the diameter and morphology of the fibers. For the SEM analysis, sampling was carried out by collecting the obtained fibers on sample holder next to collector to prevent differences on samples.

Dielectric measurements were performed using a *Keysigth E4980A presicion LCR meter*, and piezoelectric coefficient were determined in a *Wide-Range d33 tester*. Finally, magnetic properties were measured at room temperature using a *Microsense Vibrating Sample Magnetometer* (VSM) in field up to 2 Tesla.

3. Results and discussion

Intense and well-defined bands in the IR spectrum were due to the presence of the fluorine atoms of the polymer. The IR spectrum of the composite $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$/PVFF-TrFE obtained by electrospinning is shown in Fig. 2. The characteristic vibrational modes of the "β" phase of PVDF-TrFE are observed in 850 and 1295 cm^{-1} and can be assigned to asymmetric stretching of CF_2, symmetric stretching of CF_2 coupled to CCC scissoring, these vibrational modes are associated with three or more trans units that indicated the presence of "β" phase [32–34]. Bands at 615, 764 and 976 cm^{-1}, are associated with the "α" phase (TGTG) [35–45], highlighting as useful in the calculation of the "α" and "β"phase content in the absence of the "γ" phase the bands at 764 cm-1 ("α" phase) and 848 cm^{-1} ("β" phase), for which the respective absorption coefficients (Kα = 6.1 × 104 y Kβ = 7.7 × 104) have been calculated, resulting in Eq. (1) [36,37,41]. The C-C band of PVDF-TrFE was observed at 1185 cm^{-1} [46]. The peaks at 878 and 840 cm^{-1} were related to C-C-C asymmetrical stretching vibration and CF stretching vibration of PVDF [47]. It can be observed that for wave number higher to 1500 cm^{-1} presented two doubled peaks at 3022 and 2980 cm^{-1} corresponding to symmetrical and asymmetric vibrations CH_2. The peak at 1403 cm^{-1} was attributed to CH_2 wagging vibration. No additional vibrational modes of the polymer or of solvents or additives used to manufacture the fibrillary material were observed. From

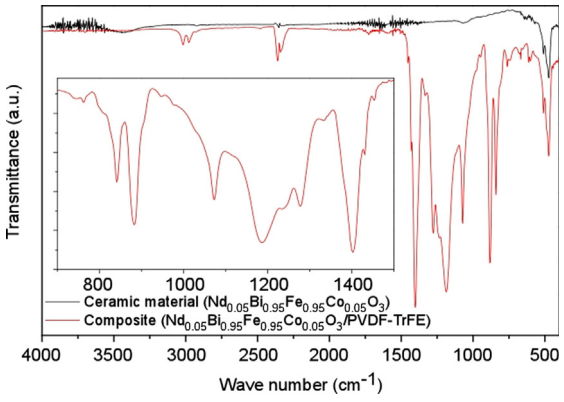

Fig. 2. IR spectrum of the ceramic material $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$ and composite $Nd_{0.05}Bi_{0.95}Fe_{0.95}Co_{0.05}O_3$/PVDF-TrFE.