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Bifunctional organic/inorganic nanocomposites for energy harvesting, actuation and magnetic sensing applications

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ABSTRACT

The fabrication of a single material being a competitive actuator as well as an electric current generator is no longer a challenge. This article presents novel nanocomposites based on a polyurethane (PU) matrix containing (0–5 wt.%) iron carbide-based nanofillers (Fe_3C@C) fabricated by electrospinning. Such materials have both electrostrictive and magnetoelectric properties. The introduction of conductive fillers in PU, which is a good candidate for actuating applications, improved the electro-mechanical coupling due to an increase in the composite permittivity. A significant increase of the dielectric permittivity and an almost 7 fold gain for the deflection strain under 17 V/μm were measured on a diaphragm-type actuator for the PU-2.5 wt.% Fe_3C@C nanocomposite. It was shown that a higher loading led to reduced actuation properties, probably due to the presence of Fe_3C aggregates in the composite as shown by Focused Ion Beam characterization. The magnetoelectric (ME) properties of the nanocomposites still showed an increase for contents over 2.5 wt.%. The current generated by the nanocomposite, when subjected to a magnetic field, was comparable or higher than several ceramic materials and at least 100 times higher than polymer-based systems studied for their ME behavior.

1. Introduction

One of the current and the future challenges in materials science is to develop specific materials by considering simultaneously several parameters such as human health, the environment and the production costs.

In microtechnology, the conversion of energy into motion is carried out by actuators which are widely used in automated systems. Compared to ceramics, polymer-based materials are very interesting for their lightweight and pliable properties for actuating applications. Moreover they are easy to process under different shapes and large surfaces. In this case the actuation is possible with an electrostrictive effect in the material.

Concerning actuation, the total electric field-induced strain (S) is a combination of electrostriction and Maxwell strains, see Eq. (1) [1].

$$S = S_{\text{electrostriction}} + S_{\text{Maxwell}} = M_{33}^{*} E^2 \tag{1}$$

where M_{33}^{*} is the apparent electromechanical coefficient and E the applied electrical field.

The Maxwell stress effect comes from the interaction between charges on the electrodes; from the electrostatic stress it follows a mechanical stress on the electrode and as a consequence a thickness contraction of the polymer (Eq. (2)).

$$S_{\text{Maxwell}} = \frac{\varepsilon_r' \varepsilon_0}{Y} E^2, \tag{2}$$

where ε_0 and ε_r' are the free space permittivity and relative permittivity of the polymer respectively. The electrostriction is the change in dimensions of a dielectric material occurring as an elastic strain when an electric field is applied. It is the direct coupling between the polarization and mechanical response in the material.

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By assuming a linear relationship between the polarization P and the electrical field E, $S_{\text{electrostriction}}$ can be expressed by Eq. (3).

$$S_{\text{electrostriction}} = QP^2 = Q\varepsilon_0^2(\varepsilon_r' - 1)^2 E^2 \quad (3)$$

where Q is the electrostrictive coefficient.

Finally, the apparent electromechanical coefficient M_{33}^* may be expressed as;

$$M_{33}^* = -\frac{\varepsilon_0 \cdot \varepsilon_r}{Y} + Q \cdot \varepsilon_0^2(\varepsilon_r - 1)^2 \quad (4)$$

Electroactive polymers (EAP) are classified depending on the mechanism responsible for electromechanical coupling, thus, there are two major EAP families: ionic and electronic polymers. Among the electronic polymers demonstrating high potentialities in actuation, polyurethane (PU) presents a segmented structure organized into a mixture of soft and hard segments. A good choice of the hard on soft segments ratio leads to great electromechanical performances [2].

It has been previously published that electrostriction is the main mechanism involved for PU.[3] As actuation capabilities depend on the dielectric and mechanical properties of the polymer, one way to improve these properties is to fill the polymer matrix with nano objects. Due to the nanoscale dimensions of these objects, a great change of the properties can be obtained with relatively low amount of fillers. An improvement of the electromechanical capabilities was shown on polystyrene-coated SiC nanowires-based PU [4]. The effect can be enhanced with the use of conductive fillers to induce a higher increase of the permittivity [5].

The magnetoelectric (ME) effect is defined as the dielectric polarization induced by an applied magnetic field or an induced magnetization in an external electric field [6]. Here, ME effect represents the coupling between an applied magnetic field and a change in electric polarization in a solid. Intensive research has been devoted to the ME effect during the last decade because of the interesting transduction properties of the magnetoelectric materials. The first observation of the ME effect [7] triggered considerable excitement because of the obvious potential of the cross-correlation between the magnetic and electric properties of matter for technical applications [8].

The ME effect has been defined using the Gibbs free energy [9]. Kumar et al. showed that ME can be expressed as Eq. (5),

$$P_i = \alpha_{ij} H_i + \frac{1}{2}\beta_{ijk} H_j H_k \quad (5)$$

where P is the polarization developed at the electrodes of the sample, H is the external ac magnetic field amplitude and α_{ij} is the linear ME coefficient and β_{ijk} is the quadratic ME coefficient.

The most pertinent parameter to quantify the ME effect and thus to compare the ability of ME compounds is the *linear* ME voltage coefficient $\alpha_E = dE/dH$ with E the induced electric field or linear ME polarization coefficient $\alpha_P = dP/dH$. It may be noted that α_E and α_P coefficients are related to each other by $\alpha_P = \varepsilon_r \varepsilon_0 \alpha_E$ where ε_r and ε_0 are the relative permittivity of the material and free-space permittivity, respectively [10].

In this paper, we investigate a new bifunctional nanocomposite presenting both electrostrictive and magnetoelectric properties. It is composed of a PU matrix filled with ferromagnetic nanofilaments, to promote the ME coupling, coated with a thin carbon layer in order to enhance the electrostrictive effect as explained above. The fillers are iron carbide-based materials fabricated by electrospinning. Cementite (Fe_3C) is of great technological importance for its usage in optics, ferro-fluids, catalysis, magneto-optic devices and actuators [11]. This material is expected to show exceptional properties when the size of crystals approaches nanometer range. The present study reveals that suitably controlled incorporation of large aspect ratio Fe_3C fillers in a semicrystalline polyurethane host matrix yields a dramatic improvement in the electrostrictive properties as compared to neat PU in the bending diaphragm mode, which has to the best of our knowledge never been previously reported, to our. The last, but perhaps the most beneficial effect of Fe_3C filling is the appearance of significant room temperature ME coupling in monolayer Fe_3C/PU composite films. In fact, ME voltage coefficient of easily fabricated composite films may reach 2400 mV/(cm Oe), independently of the applied DC bias magnetic field. These results show that these particulate composites are good candidates for magnetic field sensing and energy harvesting applications and their flexibility and lightness are in favor of their easy integration. Finally, they clearly offer a much simpler and more efficient alternative to the classical multi-layered ceramic composites made of piezoelectric and magnetic phases, such as those recently developed consisting of 6 nickel ferrite and 7 lead iron niobate relaxor (PFN) layers, yielding a maximum ME voltage coefficient of ~35 mV/(cm Oe) [12].

2. Experimental

2.1. Fabrication of 1D iron-based fillers by electrospinning

Electrospinning process was chosen in this study since it is the only well established technique capable of producing nanofibrous structures in a continuous way, and we have already demonstrated that Fe_3C filaments with tunable properties can be obtained thanks to this technique [13]. In a conventional electrospinning experiment, an electric field is applied between the tip of a metallic nozzle, which is the spinneret, and a grounded collector. A polymer solution, with suitable properties, is flowing through the needle with a controlled rate. Due to the electrostatic forces the polymer solution is distorted from a spherical pendant drop to a Taylor cone as the electric field (high voltage) is applied. Once these forces overcome the surface tension of the polymer solution a jet is drawn from the tip of the Taylor cone which is subsequently elongated due to bending. As a result a nonwoven material is deposited on the collector substrate.

As mentioned, the fabrication of iron carbide nanofilaments by electrospinning has already been investigated in one of our previous works [13]. Briefly, a raw solution was prepared by with PVP (polyvinyl pyrrolidone) and iron acetate in various solvent amounts.

2.1.1. Preparation of the solution to be spun

A 7 wt.% PVP solution was prepared by dissolving PVP in absolute ethanol and was stirred for 24 h. 7 mL of this solution were then mixed with 1 mL of acetic acid, and iron acetate was added step by step in order to obtain reach a ($FeAc_2$/PVP) weight ratio of 1.75. The presence of acetic acid in the solution to be spun is important to improve the stability of the jet during the electrospinning experiment. Before electrospinning, the solution was systematically centrifuged (Eppendorf 5810, 5 min at 6000 rd/min) to remove possible undissolved iron acetate grains which could have a deleterious effect on the spinning step.

2.1.2. Preparation of the filaments

Fe_3C filaments were produced (i) by shaping the as-prepared polymer solution in filaments before (ii) performing a thermal treatment dedicated to the polymer-to-ceramic conversion.

In the first step, the polymer solution was loaded in a 10 mL plastic syringe linked to a stainless steel needle, inner diameter = 0.5 mm. This needle was connected (alligator clip) to the positive polarity of a high voltage device (ISEG, T1CP 300 304P) and the liquid feeding rate was fixed (1 mL h^{-1}) using a syringe pump (KD Scientific, KDS 100). The electric potential (15 kV) was