Polymer Testing 48 (2015) 199–205

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Product performance

High performance electromechanical actuators based on ionic liquid/poly(vinylidene fluoride)

J.C. Dias [a, b], A.C. Lopes [a, **], B. Magalhães [a], G. Botelho [b], M.M. Silva [b], J.M.S.S. Esperança [c], S. Lanceros-Mendez [a, *]

[a] Centro/Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal
[b] Centro/Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal
[c] Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157, Oeiras, Portugal

ARTICLE INFO

Article history:
Received 12 September 2015
Accepted 15 October 2015
Available online 26 October 2015

Keywords:
PVDF
Actuators
Ionic liquids
Sensors

ABSTRACT

Due to the increasing need of low voltage actuators, independent from electrochemical processes, electroactive actuators based on poly(vinylidene fluoride) composites with 10, 25 and 40% of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_2mim] [NTf_2], ionic liquid are prepared by solvent casting and melting. We show that the charge structure of [C_2mim] [NTf_2] induces the complete piezoelectric β-phase crystallization of the PVDF within the composite and decreases its crystallinity fraction significantly. [C_2mim] [NTf_2] also works as a plasticizer of PVDF, reducing the elastic modulus down to 12% of the initial value. Moreover, the composites show significant displacement and bending under applied voltages of 2, 5 and 10 Vpp. The displacement and bending of the composite membranes are also evaluated as a function of [C_2mim] [NTf_2] content and sample thickness. Increasing amounts of ionic liquid result in larger deformations independently of the applied voltage.

1. Introduction

The development of smart polymer materials for advanced technologies [1] presents increasing potential for applications in areas such as printable electronics [2] or wearable and bio-integrated devices [3]. The ability of electroactive polymers, EAP, to develop an electrical signal under mechanical excitation and/or to deform in response to suitable electrical stimuli, along with its simplicity, versatility and scalability makes them the highest promising material for the development of novel applications. Significant achievements are related to the development of sensors based on EAP, including chemical, force, deformation and biological sensors [4,5]. In contrast, the advances in the area of actuators are still modest.

EAP are commonly divided into ionic or electronic [6,7], the former being the most commonly used in the development of actuators due to their low driving voltage response [8]. Most ionic electroactive polymer, iEAP, actuators are based in the use of conducting polymers, ionic polymer-metal composites, IPMCs [9], or carbon nanotubes, CNTs, using ionic liquids, ILs, as electrolytes [10]. Different ILs ([C_2mim][Tf], [TES][NTf_2], [BMP][NTf_2] and [C_2mim][CI]) have been used as dopant of Nafion ionomeric membranes, showing that cations with larger Van der Walls volume results in the enhancement of cationic strain [11], while [C_2mim][PF_6] and [C_6mim][PF_6] integration in block copolymer electrolytes induces a large generation of strain (up to 4%) with millimetre-scale displacements for the actuators at high frequency and sub-1-V conditions [12]. Similar studies with poly(butadiene-co-acrylonitrile), 3,4-ethylenedioxythiophene, PEDOT [13], were also performed. The incorporation of ionic liquids in nano-structured sulphonated block copolymers causes greatly improved actuation performance without signs of back relaxation due to the fast and efficient ion transport thought the polymer layers [12]. Poly(vinylidene fluoride), PVDF, as well as its copolymers, is one of the most used polymers for actuators applications due to its thermoplastic characteristics. PVDF and its copolymers are usually used to store the ionic electrolyte in ionic electroactive polymer actuators based on nano-carbon electrodes. Their combination with ionic liquids is attracting large interest from the scientific community. Different ionic liquids such as [C_2mim][BF_4] and [C_2mim][NTf_2] have been tested [8,10] as well as the effect of average molecular

* Corresponding author.
** Corresponding author.
E-mail addresses: clopes@fisica.uminho.pt (A.C. Lopes), lanceros@fisica.uminho.pt (S. Lanceros-Mendez).

http://dx.doi.org/10.1016/j.polymertesting.2015.10.012
0142-9418/

weight of the polymer and the hexafluoropropylene, HFP, content in poly(vinylidene fluoride – hexafluoropropylene), P(VDF-HFP), on the electrochemical and electromechanical properties of actuators [14].

Nevertheless, despite the large application possibilities of these materials for the development of biomimetic devices, such as artificial muscles, most of them are based on electrochemical processes, resulting in large response times and limiting their use over time. Moreover, the use of electronic EAP has been poorly explored for large strain applications since its electrostatic nature results in the requirement of high driving electric fields for the activation of the actuation response. However these polymers present high actuation forces, fast responses and long lifetimes [8].

Novel approaches in order to improve performance of polymer based actuators include the introduction of ionic mobile species into polymers [15] and, in particular, into highly polar matrixes [16]. This can be reached by the inclusion of ionic liquids into a PVDF matrix [16,17]. PVDF is an electronic EAP with one of the highest piezoelectric responses among polymers and a high dielectric constant (being typically between 6 and 12, depending on the polymer phase [18]) as well as a very high thermal and chemical stability and biocompatibility [18]. Ionic liquids are organic salts with low melting point, resulting from the incorporation of a bulky asymmetric cation in the same structure of a weakly-coordinating cation [19]. Ionic liquids present negligible vapour pressure and flammability as well as high ionic conductivity and a wide electrochemical stability window. The extensive structural possibilities of ionic liquids allows their design to reach specific applications in a myriad of distinct areas, *e.g.* energy generation and storage, sensor and actuators or biomedical devices [15].

In this work, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2mim] [NTf_2])/PVDF samples were prepared with different ionic liquid content and thickness. A morphological, mechanical and thermal study was performed in order to improve the actuation behaviour.

2. Experimental

2.1. Sample preparation

Poly(vinylidene fluoride), PVDF (Solef 6020, Mw = 700000 g/mol, Solvay) was dissolved in N,N-dimethylformamide, DMF, (99.5%, Merck) at room temperature under magnetic stirring in a polymer/solvent 15/85% (v/v) ratio. Then, different quantities of ionic liquid [C_2mim] [NTf_2] (Iolitec, stated purity of 99%) were added to the solution, with the ionic liquid concentration, relative to the polymer, ranging from 0 up to 40% (w/w). This IL is characterized by an almost null volatility, a low melting point (258.15 K) [20] and a relatively low viscosity (32.1–34 cp) [20], which facilitates its dispersion in the polymer [21,22]. Further, its higher decomposition temperature and absence of corrosion problems also make it attractive [23]. Finally, the samples were obtained by spreading the solution at room temperature on a clean glass substrate. Solvent evaporation and sample melting were performed inside an oven at a controlled temperature of 210 °C for 10 min. Samples with final thickness between 6 and 38 μm were obtained.

The effect of IL concentration and sample thickness on the physical properties and performance of the actuators were evaluated.

2.2. Sample characterization

The samples were characterized by SEM (Scanning Electron Microscopy), FTIR (Fourier Transform Infrared Spectroscopy) and DSC (Differential Scanning Calorimetry). The electrical and mechanical response was also performed as well as the characterization through bending actuation experiments.

The SEM analysis was performed in a *Quanta 650 FEG* electron microscope at 3 kV. The samples were previously coated with gold by magnetron sputtering with a *Polaron SC502*.

FTIR measurements were carried out with a *JAS.CO FT/IR-4100* spectrometer in the attenuated total reflection (ATR) mode. 64 scans were performed for each sample with a resolution of 4 cm^{-1} in the range between 650 and 4000 cm^{-1}.

DSC scans were performed on samples of about 4 mg, from 25 °C to 200 °C at a rate of 10 °C min^{-1} in a *Mettler 821e* setup.

The capacity and dielectric loss of the samples was measured with a *Quadtech 1920 LCR* precision meter at room temperature with a 0.5 V signal in the 20 Hz–1 MHz frequency range. Electrodes with 5 mm diameter were placed in each side of the sample by magnetron sputtering (*Polaron SC502*) in order to form a parallel plate capacitor. The a.c. electrical conductivity was then calculated from the imaginary component of the dielectric function, applying $\sigma' = \omega \cdot \varepsilon_0 \cdot \varepsilon''$ and $\tan\delta = \frac{\varepsilon''}{\varepsilon'}$ and taking into account the geometry of the sample.

Quasi-static mechanical stress-strain tests were performed in samples with dimensions of 15 mm × 10 mm. A *Shimadzu AG-IS* set up was used with a load cell of 50 N at a stretching rate of 1 mm min^{-1}.

For the bending test, 12 mm long and 1 mm wide samples were prepared and coated with gold by magnetron sputtering on both sides. They were fixed using two needles with a free length of 10 mm. A function generator *Agilent 33220A* was connected to the needles.

The actuation performance was obtained in a home-made setup by measuring the displacement of the samples after electrical actuation with a driving sinusoidal wave signal at 2, 5 and 10 Vpp with a frequency of 10 mHz and 0.5 Hz. During the tests, a voltmeter was placed in parallel with the excitation circuit to detect short-circuit or damage of the samples. The measurements were registered by filming the sample during the experiments with a *Logitech Hd 1080p* high resolution camera connected to a PC. The bending (ε) was quantified [10] (Equation (1)) with the help of image processing software by measuring the sample displacement along the *x* axes and taking into account the sample free length (L), thickness (d) and displacement (δ), considering no distortion of the cross section, as shown in Fig. 1.

$$\varepsilon = \frac{2d\delta}{L^2 + \delta^2} \tag{1}$$

3. Results and discussion

Representative SEM images of the surface morphology of the IL/PVDF samples prepared with different percentage of IL are shown in Fig. 2. A reduction of the spherulitic microstructure characteristic of neat PVDF is observed, as observed by comparing the large spherulites of the pure polymer (Fig. 2a) with the smaller ones of the composites (Fig. 2b, c and d). Further, the spherulite size does not show a relevant size dependence with IL content. On the other hand, more defined contours are observed with increasing IL content, leading to the appearance of pores.

Fig. 3 shows the FTIR spectra for neat PVDF and the composites of PVDF with 10, 25 and 40% of [C_2mim] [NTf_2]. The characteristic bands of α-PVDF, 766, 795 and 976 cm^{-1}, are present with large intensity just in the neat polymer, undergoing a strong reduction in the PVDF/10%[C_2mim][NTf_2] composite, not being detected in the PVDF/25%[C_2mim][NTf_2] and PVDF/40%[C_2mim][NTf_2] composites. On the other hand, Fig. 3 shows that the characteristic bands of the polar β-phase, 840 and 1279 cm^{-1} are present in all the composite