



Multilayer spin-coating deposition of poly(vinylidene fluoride) films for controlling thickness and piezoelectric response

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ARTICLE INFO

Article history:

Received 3 June 2012

Received in revised form

15 December 2012

Accepted 15 December 2012

Available online 21 December 2012

Keywords:

Electroactive polymers

Transducers

Piezoelectric

Functionally graded materials

ABSTRACT

Poly(vinylidene fluoride), PVDF, films have been processed by spin-coating with controlled thickness by multilayer film deposition. Films with thickness ranging from 300 nm to 25 μm , β -phase content up to 80%, piezoelectric coefficient d_{33} up to ~ -20 pC/N and an optical transmittance in the visible range higher than 70%, were obtained with a one to three layer deposition process. The influence of the annealing temperature in the different layers is discussed as well as the possibility of obtaining functionally graded electroactive polymers though controlling spin-coating deposition parameters and thermal annealing of the different layers.

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1. Introduction

Poly(vinylidene fluoride) (PVDF) is an extensively studied and applied polymer material due to its outstanding electroactive properties among polymers, which allow the development of sensor and actuator applications [1]. Further, PVDF shows an excellent combination of processability, moldability, lightness, mechanical strength, chemical stability and low mechanical and acoustic impedance [2]. The latter two properties are important when acoustic impedance of the transducer needs to match that of water or living tissue, as it is the case of ultrasonic transducers for lab-on-a-chip applications [3] or ultrasound diagnosis/therapy [4]. Therefore, PVDF becomes an excellent candidate for a wide range of applications [5]. Also interesting in PVDF is its unusual polymorphism among the polymers, featuring at least four crystalline phases, commonly known as α , β , γ and δ [6]. The α -phase is non polar and is the most common and stable when the crystallization from the solution takes place at temperatures higher than 80 °C or when crystallized from the melt at moderate or high speeds. The β -phase is the most interesting for sensor and actuator applications as it presents the best electroactive properties [7]. The achievement of different

phases and the interconversion between them strongly depend on the processing conditions, including thermal, mechanical and electrical treatments applied to the material [6,8]. Usually, the β -phase is obtained by mechanical stretching of the α -phase with a stretch ratio equal to or higher than 3 at temperatures lower than 100 °C [9]. Therefore, this method does not allow the deposition of the film on the desire substrate, requiring intermediate adhesion layers to adapt the film to the substrate, which can limit the efficiency of the transducer. Further, this method hinders microfabrication and therefore many microtechnological applications. Methods to overcome this limitation include the inclusion of different fillers such as ferrites [10] and clays [11] in order to nucleate the electroactive phases of PVDF without the need of the stretching step. Recently, the use of spin-coating has been reported for the deposition of films of PVDF in the electroactive β -phase [8,12]. This technique allows a highly controlled and reproducible deposition of films on the desire substrate, e.g. without any coupling layer, and on large areas with high structural uniformity. The adhesive forces at the polymer solution/substrate interface, the rapid solvent evaporation conditions and the rotational forces acting on the polymer solution result on the preferential formation of the β -phase of PVDF.

The morphology and crystalline phases of PVDF films deposited by spin-coating strongly depend on the thermal annealing temperature [8]. Despite the higher β -phase content being obtained for samples prepared at room temperature without further thermal annealing, the obtained films are porous and therefore difficult to pole and to deposit electrodes without causing short circuit.

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Moreover, the optical transmittance strongly decreases, limiting the range of applications of the material. Applying a thermal annealing to the PVDF films promptly after the spin-coating deposition allows removing porosity. On the other hand, the higher the thermal annealing temperature, the smaller is the β -phase content and therefore the piezoelectric effect of the PVDF film [13]. At thermal annealing temperatures equal to or higher than 80 °C, the β -phase content disappears. In this way, the piezoelectric response can be tailored depending on the application by applying controlled thermal annealing to the sample. However, deposition by spin-coating imposes limits in the possible film thicknesses that can be obtained. With a PVDF/DMF mass fraction of 20%, a maximum thickness of 4.5 μm is obtained [8]. The purpose of this paper is to show that multiple spin-coating depositions allow establishing larger film thicknesses in a controlled way. The effect of multiple depositions on the morphology, crystalline phases and piezoelectric response of the obtained films has been studied. Further, the possibility of fabrications of layered films with graded electroactive properties along its thickness or along its length [14] is discussed for functionally graded materials (FGM) applications.

2. Experimental procedures

Poly(vinylidene fluoride), PVDF (Solef 1010) powder and N,N-dimethylformamide (DMF) solvent were purchased from Solvay and Merck, respectively. A defined amount of the polymer was dissolved in the solvent with the help of a magnetic stirrer until a transparent and homogeneous solution was obtained. In the first 15 min, a slight warming at 30 °C was used to help dissolving and preventing agglomerates. Then, PVDF thin films were deposited by spin-coating (Laurell WS-6505-6NPP/A1/AR2) on highly polished and cleaned glass substrates. The films were immediately submitted to thermal annealing temperature equal to or higher than 30 °C, using a hot-plate (Präzitherm) to increase the solvent evaporation rate and avoid the formation of pores [8]. In the case of multiple films deposition, only the last layer was submitted to thermal annealing, the previous layers being dried at room temperature. The room temperature and humidity were 20 °C and ~50%, respectively, in all the experiments.

A profilometer (Veeco Dektak 150) and a digital micrometer (Fisher Dualscope 603-478) were used to measure the thickness of the films. The surface and cross-sectional morphology of the PVDF films were studied by scanning electron microscopy (SEM – nanoSEM-FEI Nova 200). The UV–vis transmittance spectra were obtained using an optical spectrophotometer (Shimatzu UV-3101 PC). The β -phase content was determined by Fourier Transformed Infrared Spectroscopy (FTIR) in Attenuated Total Reflectance mode (Spectrum 100) with 16 scans in the range between 650 and 4000 cm^{-1} . The electrical poling of the PVDF films was performed by corona discharge. The applied voltage was 10 kV at a constant current of 15 μA . The distance between the sample and the tip was 2 cm and the poling temperature was 100 °C. The films were subjected to the corona field for 45 min and were cooled down to room temperature with the electrical field applied. The piezoelectric response was measured with a d_{33} meter APC YE2730A.

3. Results and discussion

As referred previously, a single layer deposition by spin-coating limits the maximum film thickness that can be obtained, which can be an important issue when lower resonance frequencies, for example, have to be achieved. In fact, lower frequencies are generally achieved with higher material thicknesses. For some applications, low resonance frequencies are required to simplify the actuation

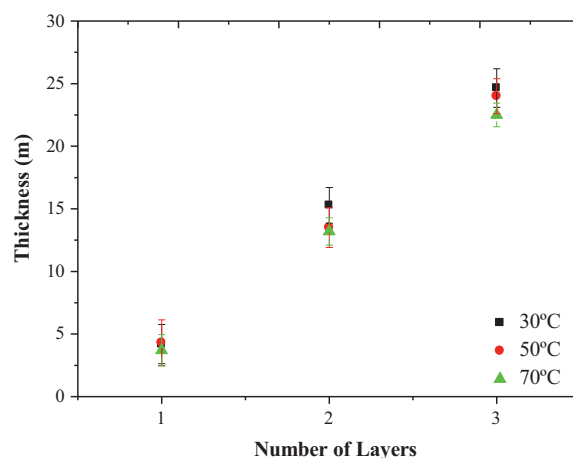


Fig. 1. Film thickness as a function of the number of layers deposited by spin-coating at an angular velocity of 1000 rpm, a PVDF/DMF mass fraction of 20% and various thermal annealing temperatures after top layer deposition.

and/or readout electronics for actuator and sensor applications, respectively.

With a PVDF/DMF relative mass fraction of 20%, a maximum thickness of 4.5 μm is obtained [8]. Films with increasing thickness are obtained by increasing number of depositions and submitting the top layer to thermal annealing at a temperature equal to or higher than 30 °C. The lower layers are dried at room temperature during 60 min each. With this procedure, higher thicknesses are obtained comparatively to submitting all layers to thermal annealing, with no loss of material performance. One layer of 20 wt% PVDF/DMF deposited at a rotational speed of 1000 rpm, acceleration of 750 rpm/s and time of 30 s shows a thickness of 11.9 μm and 4.5 μm , without thermal annealing and independently of the thermal annealing temperature between 30 °C and 70 °C, respectively (Figs. 1 and 3a).

Two layers of 20 wt% PVDF/DMF deposited with the same spin-coating parameters but just with the top layer submitted to thermal annealing shows a final thickness of 13.5 μm . The layers dried at room temperature exhibit high porosity (~80%) and with white appearance (Figs. 2a and 3a) due to the slow evaporation rate of the DMF solvent. The deposition of a top layer submitted to thermal annealing promptly after the spin-coating deposition removes the porosity of the lower layers and increase the solvent evaporation rate, resulting in transparent (Fig. 2c), compact and smooth and flat surface films (Fig. 3b) than can be poled and used in electromechanical applications. The cross-sectional cut of the samples (Fig. 3b, inset) shows that the pores are effectively filled by the deposition of the top layer submitted to thermal annealing. Notice that during the first moments of the thermal annealing procedure of the top layer the solution has a relatively low viscosity, allowing the penetration within the pores. Varying the PVDF/DMF mass ratio between 10 and 20 wt%, the angular velocity between 1000 and 8000 rpm and the number of layers deposited between 1 and 3, PVDF films with thickness between 300 nm and 25 μm were obtained. The thermal annealing temperature used on the top deposited layer does not affect, within experimental error, the final thickness of the film (Fig. 1).

With respect to the optical transmittance spectra of the films, Fig. 4 demonstrates that a PVDF film dried at room temperature shows a poor transmittance due to the porous structure (Figs. 2a and 3a). A slight thermal annealing at 30 °C allows the removal of the porosity, obtaining films with optical transmittance in the visible range higher than 70%. Further, the transmittance does not vary significantly independently of the number of layers. On the other hand, an increase of the thermal annealing temperature to

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