

Fabrication and characterization of thin piezoelectric β -poly(vinylidene fluoride) films

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received 31 January 2023

Summary. — The polymer polyvinylidene fluoride (PVDF) has four phases, each characterized by different molecular configurations of the polymer chains. In its β phase it arranges in an all-trans configuration with dipolar symmetry, exhibiting piezoelectric effects. During the production of thin PVDF films by spin-coating, the polymer chains are not aligned and the dipoles are not oriented. To achieve the desired piezoelectric behavior, it is necessary to optimize both the chain alignment and the dipole orientation processes. We here present an easy procedure to maximize the percentage of the β phase in the polymer production. The efficiency and reliability of such method has been assessed through Fourier-Transform Infra-Red and Raman spectroscopies, while the morphological differences of the two phases have been analyzed through Scanning Electron Microscopy. The results confirm the efficiency of this method.

1. – Introduction

Poly(vinylidene fluoride) (PVDF) is a polymer that has gained significant importance over time, thanks to its physical properties [1]. Since the discovery of its piezoelectricity [2], several research efforts have been focused on the development of a simple and effective method to maximize this effect [3]. It was discovered that when PVDF crystallizes in its β phase, it shows an all-trans (TTT) configuration [4], creating dipoles consisting of fluorine (–) and hydrogen (+) atoms at the ends, with carbon atoms at the center. Of all the possible phases in which this polymer can crystallize,

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the β phase is the one that maximizes piezoelectric effects [5]; for this reason, many studies have been addressed to maximize the β configuration in PVDF films experimental manufacturing. However, the descriptions of the experimental steps leading to such achievements are not always coherent in the literature, and often incomplete. Thin PVDF films of controlled thickness can be obtained by spin-coating [6, 7]; critical to their accomplishment are the spin velocity, which promotes an initial orientation of the polymer chains in a radial direction, and the process temperature, which determines the correct rate of solvent evaporation to obtain the desired polymer phase [8]. Once thin films (in the range 5–20 μm) are obtained, two basic steps are required to achieve piezoelectric properties: alignment of the polymer chains and orientation of the dipoles [9, 10]. The former is generally obtained by mechanical stretching of the sample, while the latter implies application of an intense electric field in the thickness direction of the film. In this work, to evaluate the percentage of the β phase obtained, the samples were analyzed by Fourier-Transform Infra-Red (FTIR) and Raman spectroscopies, looking at the relative intensities of the absorption bands of the different phases. Finally, Scanning Electron Microscopy (SEM) images have been collected to supply a surface characterization and analyze the morphological differences between the α and β phases.

2. – Materials and methods

PVDF films were produced from polymer powder (Sigma Aldrich, average MW $\sim 534,000$). Films were obtained according to the following procedure: PVDF powder (1 g) was dispersed in a 30:70 v/v solution of dimethylformamide/acetone (10 mL). The mixture was then sonicated using a sonic dismembrator (Fisherbrand 120) for 1 h to allow the PVDF to completely dissolve. The resulting solution was cast onto the spin-coater plate and spun at 1000 rpm for about 1 min, thus obtaining films predominantly in the α phase. The presence of the β phase can be maximized by raising the temperature to 60 °C to increase the evaporation rate after casting the polymer solution on the spin-coater plate. The films were slowly cooled to room temperature, detached from the wafer and dissected to obtain 35 mm \times 35 mm samples. To achieve the alignment of the polymer chains, the samples were stretched up to 300% of their length at a speed of 1 mm/min to ensure the rearrangement of the molecular structure following each micro-elongation; the samples were left at maximum elongation for 1 h. To obtain the polarization of the dipoles, the samples were placed in an electric field of 600 V/ μm along their thickness for 1 h to ensure the permanent alignment of all dipoles. FTIR spectra were collected on a Nicolet iS20 FTIR spectrometer equipped with an ATR detector. Confocal Raman Microscopy measurements, performed with a Horiba Xplora Plus equipped with a 100 \times objective and a laser with 638 nm excitation wavelength, were carried out by cutting 2 cm \times 2 cm squares from the entire sample. SEM micrographs were obtained by a Tescan Vega electron microscope. Secondary electron images were collected in high-vacuum conditions and with beam energies in the 10–20 keV range selecting the best trade-off in terms of electron penetration in the samples and image spatial resolution. Before SEM scans, because of their non-conductive nature, the composites were sputter coated with a gold layer of about 10 nm to prevent artifacts due to charge accumulation.

3. – Results and discussion

Both FTIR [11, 12] and Raman [13, 14] spectroscopies can be used to quantify the temperature-induced increase of the β phase in PVDF films. The β phase fraction can

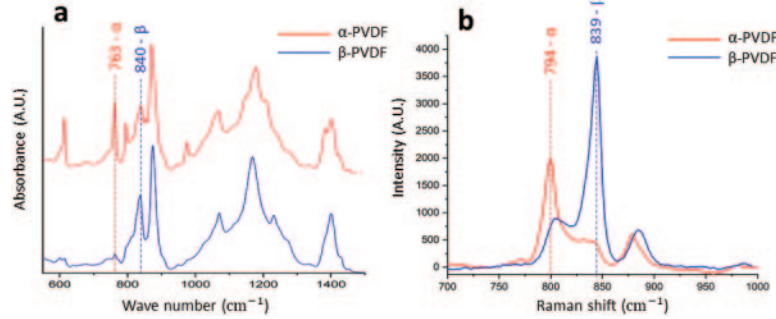


Fig. 1. – (a) FTIR spectra of the α -PVDF (red) and β -PVDF (blue) samples. The spectra have been shifted along the y -axis for easy comparison; (b) Raman spectra of the α -PVDF (red) and β -PVDF (blue) samples.

be calculated from FTIR spectra using the relationship:

$$(1) \quad F(\beta) = \frac{A_{\beta}}{1.26A_{\beta} + A_{\alpha}},$$

where A_{α} and A_{β} are, respectively, the intensities of the 763 cm^{-1} (skeletal bending) and 840 cm^{-1} (CH_2 rocking) peaks. Figure 1 shows the FTIR spectra for two different samples: the red one belonging to the α -PVDF film and the blue one to the β -PVDF film. In the blue spectrum, the α peak at 763 cm^{-1} does not appear, while the β one at 840 cm^{-1} has a higher intensity with respect to the same peak in the red spectrum. SEM was also used to evaluate PVDF morphological changes in the transition from α to β phase [15, 16]. Micro Raman spectra, reported in fig. 1(b), confirm the temperature induced transition from the α to the β phase, showing an inversion of the $837/839 \text{ cm}^{-1}$ and $879/881 \text{ cm}^{-1}$ bands intensities [17]. Figure 2 shows the SEM images relative to films where either the α or the β phase is dominant. The surface morphology is different for the two different samples: the one in the α phase (fig. 2(a)) shows “smallpox” microstructures of $3 \mu\text{m}$ typical size homogeneously distributed on the surface of the sample, while the other in the β phase (fig. 2(b)) is characterized by an almost completely smooth surface.

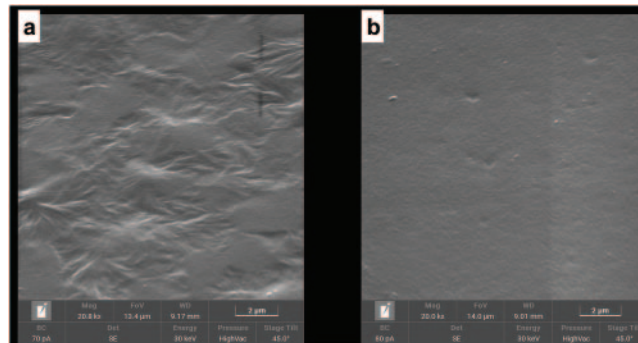


Fig. 2. – (a) SEM images of the α -PVDF surface showing “smallpox” structures of $3 \mu\text{m}$ typical size; (b) β -PVDF sample with an almost completely smooth surface.

surface. The disappearance of the “smallpox” micro-structures is probably due to the heating process immediately after thin film preparation by spin-coating, and therefore to a faster evaporation of the solvent.

In conclusion, a simple and non-expensive method was provided to fabricate and polarize thin films of β -PVDF. The β phase maximization was evaluated by FTIR spectroscopy and, from SEM micrographs, morphological differences between samples of the two phases were shown, possibly providing a visual way to recognize the presence of one of the two phases in any PVDF sample.

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The authors gratefully acknowledge the support of the JRU ISIS@MACH ITALIA, Research Infrastructure hub of ISIS Neutron and Muon Source (UK) (MUR Official Registry 0013837-04-08-2022).

REFERENCES

- [1] SAXENA P. and SHUKLA P., *Adv. Compos. Hybrid Mater.*, **4** (2021) 8.
- [2] KAWAI H., *Jpn. J. Appl. Phys.*, **8** (1969) 975.
- [3] KIM G. H., HONG S. M. and SEO Y., *Phys. Chem. Chem. Phys.*, **11** (2009) 10506.
- [4] KALIMULDINA G., TURDAKYN N., ABAY I., MEDEUBAYEV A., NURPEISSOVA A., ADAIR D. and BAKENOV Z., *Sensors*, **20** (2020) 5214.
- [5] AHN Y., LIM J. Y., HONG S. M., LEE J., HA J., CHOI H. J. and SEO Y., *J. Phys. Chem. C*, **117** (2013) 11791.
- [6] CARDOSO V. F., MINAS G. and LANCEROS-MÉNDEZ S., *Smart Mater. Struct.*, **20** (2011) 087002.
- [7] RAMASUNDARAM S., YOON S., KIM K. J. and LEE J. S., *Macromol. Chem. Phys.*, **209** (2008) 2516.
- [8] PRAMOD K. and GANGINENI R. B., *Bull. Mater. Sci.*, **38** (2015) 1093.
- [9] KIM H., TORRES F., WU Y., VILLAGRAN D., LIN Y. and TSENG T. L. B., *Smart Mater. Struct.*, **26** (2017) 085027.
- [10] YOUSRY Y. M., YAO K., CHEN S., LIEW W. H. and RAMAKRISHNA S., *Adv. Electron. Mater.*, **4** (2018) 1700562.
- [11] LANCEROS-MENDEZ S., MANO J. F., COSTA A. M. and SCHMIDT V. H., *J. Macromol. Sci.*, **40** (2001) 517.
- [12] KABIR E., KHATUN M., NASRIN L., RAIHAN M. J. and RAHMAN M., *J. Phys. D: Appl. Phys.*, **50** (2017) 163002.
- [13] RIOSBAAS M. T., LOH K. J., O'BRYAN G. and LOYOLA, B. R. , *Sens. Smart Struct. Technol. Civ., Mech. Aerospace Syst.*, **9061** (2015) 235.
- [14] CONSTANTINO C. J. L., JOB A. E., SIMÕES R. D., GIACOMETTI J. A., ZUCOLOTTO V., OLIVEIRA JR O. N., GOZZI G. and CHINAGLIA D. L., *Appl. Spectrosc.*, **59** (2005) 275.
- [15] MAHALE B., BODAS D. and GANGAL S. A., *Bull. Mater. Sci.*, **40** (2017) 569.
- [16] SENCADAS V., GREGORIO FILHO R. and LANCEROS-MENDEZ S., *J. Non-Cryst. Solids*, **352** (2003) 2226.
- [17] CONSTANTINO C. J. L., JOB A. E., SIMÕES R. D., GIACOMETTI J. A., ZUCOLOTTO V., OLIVEIRA JR O. N., GOZZI G. and CHINAGLIA D. L., *Appl. Spectrosc.*, **59** (2005) 275.