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Experimental characterization of material structure of piezoelectric PVDF polymer

V. Ostaševičius*, I. Milašauskaitė*, R. Daukševičius*, V. Baltrušaitis, V. Grigaliūnas**, I. Prosyčevas****

**Kaunas University of Technology, Institute of High-Tech Development, Studentų str. 65, 51369, Kaunas, Lithuania, E-mail: vytautas.ostasevicius@ktu.lt*

***Kaunas University of Technology, Institute of Material Science, Savanorių av. 271, 50131 Kaunas, Lithuania, E-mail: viktoras.grigaliunas@ktu.lt*

1. Introduction

Nowadays, with technologies rushing to an age of miniaturization based on microelectromechanical systems (MEMS), batteries become a critical juncture between macro and micro worlds. Even the smallest conventional batteries may be much larger than the MEMS system being supplied by power. This, in turn, limits the extent to which the size of overall device can be shrunk. Most of MEMS ideally have to work for long periods, and it is not always easy to replace or recharge their batteries. Thus, alternatives for MEMS long - lasting energy harvesting must be sought for.

These alternatives may include microfuel cells that consume hydrogen to produce electricity, or - on-chip combustion engines, which actually burn a fuel like gasoline to drive a tiny electric generator. Yet the idea of this research is to harvest energy using piezoelectric structure made of polyvinylidene fluoride (PVDF).

Piezoelectric PVDF polymer due to its perfect elastic properties and high piezoelectric constant can be good candidate for energy microgenerators instead of well-known pulsed laser deposited piezoelectric nanocrystalline lead zirconate titanate (PZT) thin films or barium titanate thin films [1]. Creation of energy microgenerators requires good realization of bendable piezoelectric film, which imposes a practical value on experimentation. Many methods of PVDF formation have already been described [2-9], however, some of them require intricate equipment or special formation conditions that are not applicable in micro-manufacturing. Thus the authors made a series of experimental PVDF formations and this paper presents a thorough investigation of two PVDF thin films, which were formed according to the best practice selected by authors.

2. Polyvinylidene fluoride

PVDF is a long chain, semicrystalline polymer having the repeat unit (CH_2-CF_2). It is approximately 55% crystalline and has a molecular weight of typically 4×10^5. Many investigations have been carried out to characterize the structure of PVDF [2-4], since the extraordinary electrical properties of PVDF are a direct result of its crystalline structure. To date, at least four crystal modifications with a permanent dipole moment, denoted as β, γ, δ, and ε have been described for PVDF. In all these crystal forms, the chains are packed in the unit cell in such a way that the dipoles associated with individual molecules are parallel, leading to a nonzero dipole moment of the crystal. Both the molecular and crystal dipoles are perpendicular to the chain axis.

In the fifth known crystal modification, α, the chains are packed in the unit cell in such a way that the molecular dipoles are antiparallel and there is no net (crystal) dipole [5] (Fig.1). The piezoelectricity in such a material may be due to several effects, thus research into the mechanism of piezoelectricity and the enhancement of activity by new forming and poling processes and synthetic methods is still required.

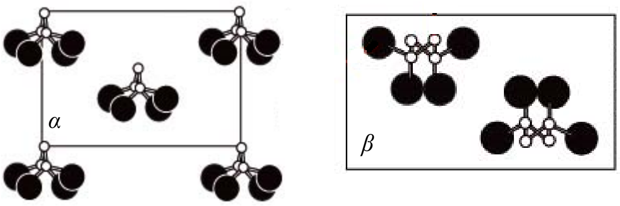


Fig. 1 Crystalline structure of forms α and β of PVDF unit cell. Fluorine atoms are shown as large circles, carbon atoms as small circles and hydrogen atoms are omitted [6]

Table 1

Properties of PVDF [7]

Properties	PVDF
MECHANICAL PROPERTIES	
Elongation %	300~450
Tensile strength (psi)	4500-6200
Flexural strength (psi)	8600-9500
Compressive strength	11,600
Young's modulus (psi)	160,000
Flexural modulus (psi)	90,000~168,000
Coefficient of friction on steel	0.4
Abrasion resistance 1000 revs.	5~15
THERMAL PROPERTIES	
Melting point (°C)	171
Upper service temperature (°C)	129
ELECTRICAL PROPERTIES	
Dielectric constant	7.72
Volume resistivity ohm-cm	2×10^{14}

The piezoelectric responses of PVDF are the highest known for any homopolymer and this is partly related to its high dielectric constant. The piezoelectric coefficients of poled PVDF vary: d_{31} 18-20 pcN^{-1}, d_{32} 2.8-3.2 pcN^{-1}, g_{31} 0.12-0.14 VmN^{-1}, g_{32} 0.018-0.022 VmN^{-1}. Tensile strength of the PVDF at break may be $180 - 220 \times \times 10^6$ Nm^{-2} in machine direction for 9±1 μm film thickness, while tensile modulus 1800-2200 x 10^6 Nm^{-2} for the same thickness. The dielectric constant of the material is 12±1 at 1 kHz, while heat shrinkage comprises 5.5% for the film thickness of 9±1μm [6]. More properties of PVDF may be found in Table 1.

The advantages of PVDF over piezoceramics include lower cost, larger area coverage, flexibility, low acoustic impedance, and high-frequency operation. Moreover, very thin, self supporting films are easily produced; electrodes can be attached on the films in a virtually unlimited variety of patterns; the polymer is very flexible and tough, and hence can be molded or stretched to conform to a surface [7].

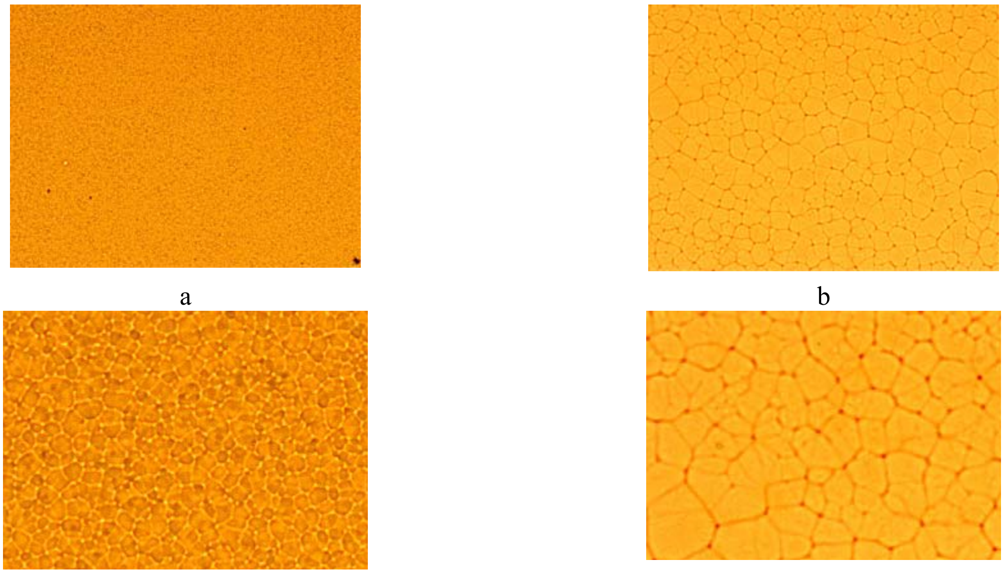
3. PVDF thin films formation

(PVDF) polymer is commercially available as powder, pellets or semitransparent films (ranging from 8 to 110 μm in thickness). With a melting temperature of approximately 170°C and reasonable melt viscosity it is suitable for melt processing without the need for processing aids, stabilizers or additives. The polymer can also be dissolved due to its solubility in common polar solvents. For the research, PVDF pellets (M_r~180,000, Aldrich) and PVDF granules (M_w~534,000, Aldrich) were dissolved in various solvents, namely dimethyl formamide (DMF), dimethoxy – tetrahydrofuran, methyl pentanone and a mixture of dimethyl formamide with acetone. The concentration of PVDF ranged from 5% wt to 20 % wt in the solutions. All solutions were stirred at 100° C for half an hour to ease the dissolution. It was noted that PVDF pellets dissolve better in polar solvents, thus films formed out of them possessed higher quality (less porous, less opaque and less fragile). Since dimethoxy – tetrahydrofuran and methyl pentanone were the poorest swelling agents, they were eliminated from further study. The most suitable concentration of PVDF was found to be 5% and 10% wt.

PVDF thin films were formed on silicon as well as on finely polished Al_2O_3 substrates. First of all, the substrates were immersed in distilled water, later boiled in acid cleaner, ultrasonically cleaned in acetone, and finally treated with plasma. The first batch of films was formed by means of spin coating, however it was determined that the spin speed of available spin coater was too high, and the films formed were too thin, thus the second batch of films was produced by dip coating. In all cases the solvents were dried out at 110°C for 10 minutes and the produced films were melted at 220 °C for another 10 min. According to the described procedure, films ranging in thickness of 10 – 20 μm were obtained.

4. PVDF thin films investigation

One of the most important parameters affecting the piezoelectric properties of PVDF is the level of crystallinity. Without crystallinity or defined morphology, PVDF would not exhibit any piezoelectric properties since it could not sustain a net dipole. Crystallinity also defines the mechanical, chemical and thermal properties of semicrystalline polymers. To analyse the crystallinity of formed PVDF thin film and evaluate its quality, a wide range of techniques were used in this research including microcopy, X-ray and infrared spectroscopy methods.



a b

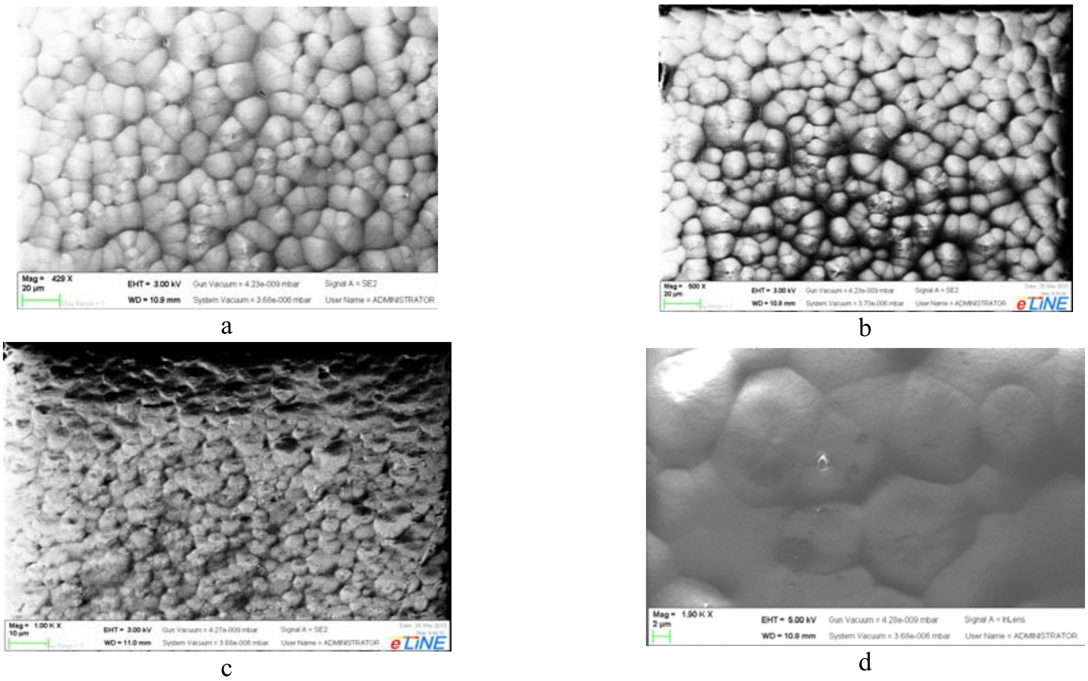
c d

Fig. 2 PVDF thin films on silicon substrates a) PVDF (10% wt) film on silicon substrate (magn. 10×); b) PVDF (10% wt) thin on silicon substrate (magn. 100×); c) PVDF (5% wt) film on silicon substrate (magn. 10×); d) PVDF (5% wt) film on silicon substrate (magn. 100×)

4.1. Microscopy

Firstly, the morphology of the PVDF thin film samples from various solvents was derived by means of industrial microscope NIKON ECLIPSE LV150. The PVDF thin film surfaces in Fig. 2 illustrate the distinct spherulitic structure, yet the films are smooth and uniform, which indicates that films are stable and homogeneous. It was noted that this structure renders whitish translucent films becoming milky opaque when thicker. This occurs because the cavities between the solid/air interface reflects and refracts the visible radiation.

The surface topography of the films can also be clearly seen in the scanning electron microscope (SEM) micrographs (Fig. 3) of PVDF thin films obtained by means of Raith e-line - a versatile electron beam lithography and nanoengineering workstation's SEM. These micrographs are obtained at different magnification 429×, 500×, 1000× and 1900× correspondingly. The speriulities (3 - 5 µm) present on the top surface of the film refer to β - phase, as also demonstrated by FTIR and X - ray analysis.



a b

c d

Fig. 3 SEM of PVDF (5% wt) thin film on silicon substrate magnified: a - 429×, b - 500×, c - 100×, d - 1900×

3D surface morphology pictures (Fig. 4, a) obtained by means of Atomic Force Microscope NT-206 (AFM NT-206) and data reveal that average roughness (R_a) values are high, indicating that the surface is quite rough. This is also confirmed by high root mean square roughness (R_q) – statistical parameter that defines width of the amplitude distribution function. Negative skewness coefficient (R_{sk}) – parameter determining change of surface symmetry with respect to mean height - indicates that surface is porous, dominated by deep valleys. Since asymmetry parameter, R_{sk}, is not greater than absolute value 1.5, surface is of usual shape and average roughness parameter, R_a, is adequate for surface profile characterization. It is also very important to note, that 3D phase pictures (Fig. 4, b) clearly indicate at least two phases appearing in the PVDF thin film. Comparing obtained results with other scientific papers [8-10], it becomes obvious that α - phase is predominant over β -phase.

a b

Fig. 4 Lateral force microscopy on PVDF thin films: a - 3D surface morphology of PVDF thin film; b - 3D phase identification of PVDF thin film

4.2. X – Ray analysis and IR spectroscopy

The diffraction pattern created when X-rays impinge on a polymer sample can be used to determine the crystalline phases and also the level of absolute crystallinity. XRD spectra usually contain sharp peaks due to the crystallites, while the amorphous regions give rise to a much broader background scattering. For the study, the diffractograms of PVDF samples were acquired on a Dron-3 X-ray Powder Diffractometer using Cu Kα radiation. The values of 2Θ and respective d spacing observed in diffractograms are presented in the Table 2 and Fig. 5.

The spectra of sample from 5% wt PVDF solution and 10% wt PVDF solution on Si substrate are seen to have well defined peaks at $2\Theta = 20.2°$ (20.14° for 10% wt PVDF respectively), referent to the sum of the diffractions in plane (110) and (200) characteristic of the β phase. Peaks at $2\Theta = 18.40°$ (18.30°) and 26.56° (26.52°) referent to the diffractions in planes (020) and (021) respectively, are characteristic of α phase.

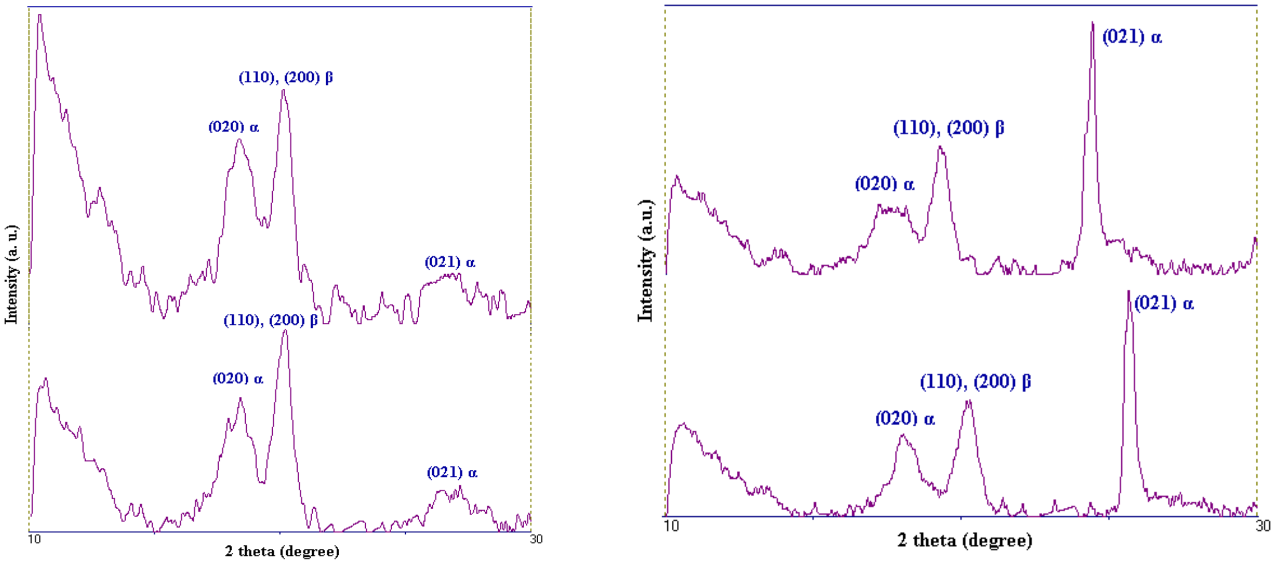
Table 2

Values of 2Θ and respective d spacing observed in diffractograms of Fig. 5

	2Θ	d(Å)
Phase β	20.20 20.14	4.405 4.405
Phase α	18.40 18.30	4.818 4.848
Phase α	26.56 26.52	3.352 3.352

The spectra of sample from 5% wt PVDF solution and 10% wt PVDF solution on polycorodium substrate are also seen to have well defined peaks at 2Θ=20.3°, referent to the sum of the diffractions in plane (110) and (200) characteristic of the β phase. Peaks at 2Θ=18.02° and 26.64° referent to the diffractions in planes (020) and (021) respectively, are characteristic of α phase.

The formation of different phases was also confirmed by FTIR spectra, obtained by means of Nicolet 6700 FT-IR spectrometer. A FTIR spectometer Nicolet 6700 allowed spectral measurements in the band of 400 – 1300 cm^{-1} (the finger print region for crystalline phases of PVDF). In Fig. 6 intensive absorbtion band at 480, 530, 612,764, 797, 855, 976 and 1410 cm^{-1} correspond to large amount of α crystal phase, whereas peak at 1226 cm^{-1} indicates β phase and results complying well with those described in literature [11, 12].



a

b

Fig. 5 X- ray diffractograms: a - X - ray diffractograms of 5% wt PVDF and 10% wt PVDF on Si substrate; b - X - ray diffractograms of 5% wt PVDF and 10% wt PVDF on Al_2O_3 substrate

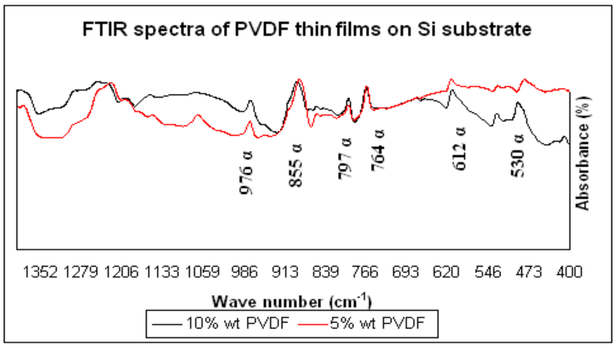


Fig. 6 FTIR spectra of PVDF thin films

5. Conclusions

This paper presents initial results of piezoelectric PVDF thin film fabrication and analysis. The PVDF thin films are fabricated according to the authors' determined best practice. The quality of the obtained films and their material characteristics are evaluated by means of microscopy (optical, SEM and AFM) as well as X-ray and Infrared analysis. As the obtained results comply well with those described in the literature, one may state, had qualitative thin films were obtained, ranging in thicknesses of 10 - 20 μm. SEM, AFM, X - ray and IR analysis results reveal, that all samples indicate distinct craystalline phases, with α - phase dominating in all the samples.

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V. Ostaševičius, I. Milašauskaitė, R. Daukševičius,
V. Baltrušaitis, V. Grigaliūnas, I. Prosyčevas

EKSPERIMENTINIS PJEZOELEKTRINIO POLIMERO PVDF MEDŽIAGOS STRUKTŪROS TYRIMAS

Reziumė

Straipsnyje pristatoma alternatyvi PZT medžiaga – pjezoelektrinis polimeras polivinilidenfluoridas (PVDF), kuris gali būti taikomas mikrogeneratorių gamyboje. Pateikiamas eksperimentinis šios medžiagos formavimo procesas bei pirminiai jos tyrimų rezultatai – SEM, AFM mikrofotografijos, XRD, FTIR spektrai.

V. Ostaševičius, I. Milašauskaitė, R. Daukševičius,
V. Baltrušaitis, V. Grigaliūnas, I. Prosyčevas

EXPERIMENTAL CHARACTERIZATION OF MATERIAL STRUCTURE OF PIEZOELECTRIC PVDF POLYMER

Summary

This paper presents the alternative for well know PZT material – piezoelectric polymer poliviniliden fluoride, which may be applied for microgenerators fabrication. The experimental fabrication process of PVDF is described along with initial investigation results of the material – SEM, AFM micrographs, XRD, FTIR spectrograms.

В. Осташявичюс, И. Милашаускайте, Р. Даукшявичюс,
В. Балтрушайтис, В. Григалюнас, И. Просычевас

ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ СТРУКТУРЫ ПЬЕЗОЭЛЕКТРИЧЕСКОГО ПОЛИМЕРНОГО МАТЕРИАЛА

Резюме

В статье представлена альтернатива материалу ПЗТ-пьезоэлектрический полимер поливинилиден флорид, который может быть использован в производстве микрогенераторов. Приведен экспериментальный процесс формования материала и первичные результаты его исследований – микрофотографии, получены на сканирующем электронном микроскопе и микроскопе атомных сил, также спектральный анализ рентгена и ИК.

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