Piezo-active composite systems based on porous polyvinylidene fluoride films and conducting polymer layers as electrodes

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Abstract. The study has obtained composite systems containing porous polyvinylidene fluoride films and electroconducting polymers—polyaniline and polypyrrole. Porous supports were prepared by melt extrusion. It was shown by scanning electron and atomic force microscopy that porous PVDF films have a relief surface, and a higher surface roughness improves hydrophilicity of supports. The layers of conducting polymers on the surface of porous supports were formed by oxidative polymerization in situ in monomer solution. It was found that conducting coatings have high adhesion of conducting layers to the porous films due to the relief surface of the PVDF film. Composites have surface and volume conductivity on the order of 10^1 S/cm and 10^{-6}–10^{-5} S/cm, respectively. The layers of conducting polymers were used as electrodes to polarize the composites and to measure piezomodulus d_{31}. The maximum value of d_{31} was 18 pC/N.

Keywords: polyvinylidene fluoride, polyaniline, polypyrrole, porous films, electrical conductivity, piezoelectric modulus.

Introduction

Composite systems based on polyvinylidene fluoride (PVDF) and conducting polymers such as polyaniline and polypyrrole draw attention because they combine piezoelectric properties of a PVDF support and high electroactivity of conductive components. Therefore, these materials may find an effective application in energy harvesting, conversion and storage devices. The materials may be used as sensors and transducers in hydroacoustics, as effective membranes in filtration and separation processes as well as as separators in electric batteries (Bar-Cohen, Zhang 2008; Chang et al. 2007; Dang et al. 2013; Lebrun et al. 2009; Salimi, Yousefi 2003). PVDF is one of the promising polymer piezoelectric materials due to its chemical stability and outstanding mechanical characteristics. It also has important advantages over inorganic piezoelectrics such as high processibility, low density, elasticity and environmental safety of production.

Piezoelectric properties of PVDF-based materials are related to the polymorphic character of its crystal phase which contains nonpolar and polar modifications (α, β, γ и δ). Among these modifications the polar β-form has the best piezoelectric characteristics (Branciforti et al. 2007). Research in the

development of PVDF-based piezo elements focuses on increasing the content of piezoactive β-crystallites and deposition of electrode layers on the surface of piezoelectric films. One of the promising ways to improve the transducer parameters is the formation of a porous film structure. It was shown (Gerhard-Multhaupt 2002; Yarysheva et al. 2012) that porous materials demonstrate higher piezo constants in comparison with nonporous electrets.

To use PVDF piezo materials as transducers of mechanical energy to electric energy, it is necessary to deposit contacts (electrodes). Here, the main challenge is to activate the hydrophobic surface of PVDF to ensure adhesion of conducting layers. In addition, electrodes have to meet several requirements: the uniformity of the layer, no direct contact between two layers on the film surfaces, good electroconductivity along the surface and elasticity of the composite. Current methods for depositing electrodes are expensive, ineffective or/and labor-intensive. Traditionally, metallic coatings are used as electrodes. However, the formation of conducting polymer layers is a much more effective technology than vacuum deposition of metals (Dang et al. 2013). Due to electrical, magnetic, optical and oxidation/reduction properties, conducting polymers (polyaniline, polypyrrole, polythiophene, etc.) have a wide application in membranes, electrochemical sensors, pressure transducers and other devices (Liu et al. 2011; Merlini et al. 2014; Ozkorucuklu et al. 2012).

The purpose of the research is the development of effective methods to form electroconducting polymer layers (polyaniline and polypyrrol) as electrodes on the surface of PVDF porous films as supports. It also aims to investigate the structure and surface morphology of the prepared samples, as well as polarization and measurements of piezoelectric modulus for composites.

Experimental methods

PVDF porous films were prepared in five stages: melt extrusion, isometric annealing of extruded films at the temperature close to polymer melting point (170°C), two stages of uniaxial extension— a "cold" stage at room temperature and "hot" stage at 100°C (pore formation stages), and thermal fixation of porous structure at 100°C. Polymer Kynar-720 (Atofina Chemicals Inc., USA), $M_w = 1.9 \times 10^5$, was used for in the preparation process (Elyashevich et al. 2019).

Porous structure of the samples was characterized by the value of overall porosity (P) measured gravimetrically. The value P was calculated as

$$P = [(\rho\text{-}\rho_{p)} / \rho] \cdot 100\%,$$

where ρ is the density of a monolithic PVDF film (1.78 g/cm^3) and ρ_p is the density of porous film, determined by weighing.

Composite samples were prepared by the deposition of conducting polymers (polyaniline, polypyrrol) in oxidative polymerization *in situ* directly on the surface of PVDF porous films. The content x of conducting polymer in the prepare d composites was calculated as

$$x = \Delta W_{cond} / (W_{PVDF} + \Delta W_{cond}) \cdot 100\% ,$$

where W_{PVDF} is the mass of initial porous PVDF film and ΔW_{cond} is the mass difference between the composite sample and PVDF support.

Vertex 70 spectrometer (Bruker, USA) recorded Fourier transform infrared (FTIR) spectra.

The surface morphology of samples was studied by scanning electron microscopy (SEM) using SUPRA-55VP tool (ZIESS, Germany) and atomic force microscopy (AFM) using Nanotop NT-206 (Mikrotestmashin, Gomel, Belarus). The measurements were carried out in semi-contact and contact modes under atmospheric conditions using NSC11/AlBS silicon cantilevers with a stiffness coefficient of $k = 1.5$–5.0 N/m and the radius of curvature of the tip less than 10 nm. The experimental data were processed with the Surface Explorer software.

Wettability of the sample surface was determined by the contact angle technique on DSA30 (KRUSS, Germany).

Electrical conductivity was measured at room temperature by the DC four-probe van der Pauw method using a P-30 potentiostat (Elins, Russia).

PVDF supports were polarized by the contact high voltage DC polarization in the electric field of 80–90 V/μm at temperature of 90°C for 1 h.

Piezoelectric modulus d_{31} was determined from static tension applied along the orientation direction of the polarized film. The potential difference arising on the contact electrodes (the conducting polymer layers) during the sample deformation was measured using the P-30 potentiostat.

Results and discussion

Characteristics of PVDF supports

The prepared porous structure of PVDF supports is controlled by orientation parameters at the extrusion stage (melt draw ratio λ) and at the stages of uniaxial extension (degrees of extension ε_1 and ε_2). It was observed (Dmitriev et al. 2017) that crystalline structure of extruded and annealed films is formed by the stacks of lamellar crystals located parallel to each other and perpendicular to the melt orientation direction. The lamellae are connected by the "bridges" of stressed tie chains. Orientation efforts at uniaxial stages lead to the separation of lamellae and the appearance of the voids (pores) between them. When the number and size of pores is growing bigger due to stronger orientation efforts, the through channels are formed in the film. It is the result of a percolation mechanism when the value of overall porosity reaches the percolation threshold (P = 23% for these samples). The obtained porous films vary in porosity and size of pores due to the parameter-controlled preparation process (Table 1).

Table 1. Characteristics of PVDF porous films

Thickness	10–25 microns
Overall porosity	12–30%
Average size of pores	33 nm
Maximal size of pores	60–80 nm
Surface roughness (R_a and R_q)	45–55 nm and 60–90 nm
Specific surface	25–37 m^2/g
Breaking strength	125–145 MPa
Elongation at break	30–50%

The porous films are marked by a strongly developed relief-like surface (Elyashevich et al. 2019). It is the result of stress release to the surface which leads to the development of through pores. It was shown that the scale of relief increases when orientation parameters are higher—λ and ε, i.e. bigger overall porosity provides an increase in height in a particular surface area (S) (Table 1). Note that the value S for these porous films is on the order of several tens of m^2/g, while for nonporous (i.e., initially extruded and annealed) films it is approximately 10^{-4} m^2/g.

To estimate the scale of the surface relief, the porous PVDF films were investigated by AFM method (Fig. 1). Figure 1 shows AFM images of the film prepared at λ = 76, ε_1 = 50% and ε_2 = 40%. In the 3D image (a) and the image of the surface height (b), oriented lamellae with a thickness of ~100–200 nm are clearly visible. By analyzing the profile of the selected surface area (c), it is possible to estimate the pore depth, which reaches a value of 400 nm relative to the ridge of the lamella. The values of the arithmetic mean (R_a) and root-mean-square (R_q) surface roughness for the 30×30 μm scanning matrix are 78.8 nm and 97.9 nm, respectively.

The analysis of AFM pictures of the porous films evidences that roughness of the surface increases along with an increase of orientation parameters and, as a result, it impacts the porosity of the samples. It is known that PVDF is a rather hydrophobic material, it is poorly wetted by water: dense PVDF films have a contact angle (θ) of nearly 75°. If porosity increases from 12 to 30%, the values of θ for the porous films decrease from 71 to 65° (Fig. 2b and 2c), i.e., higher roughness of the surface positively impacts hydrophilicity of the samples. This result is consistent with commonly accepted conception concerning the influence of surface relief on wettability of material (Boinovich, Emelyanenko 2008).

The preparation of composite PVDF/conducting polymers

The PVDF/conducting polymer samples were obtained by *in situ* oxidative polymerization of monomer directly on the surface of a PVDF support. To prepare the PANI/PVDF composites the support was placed into a reaction mixture containing the solution of aniline hydrochloride in 1 M HCl; then the
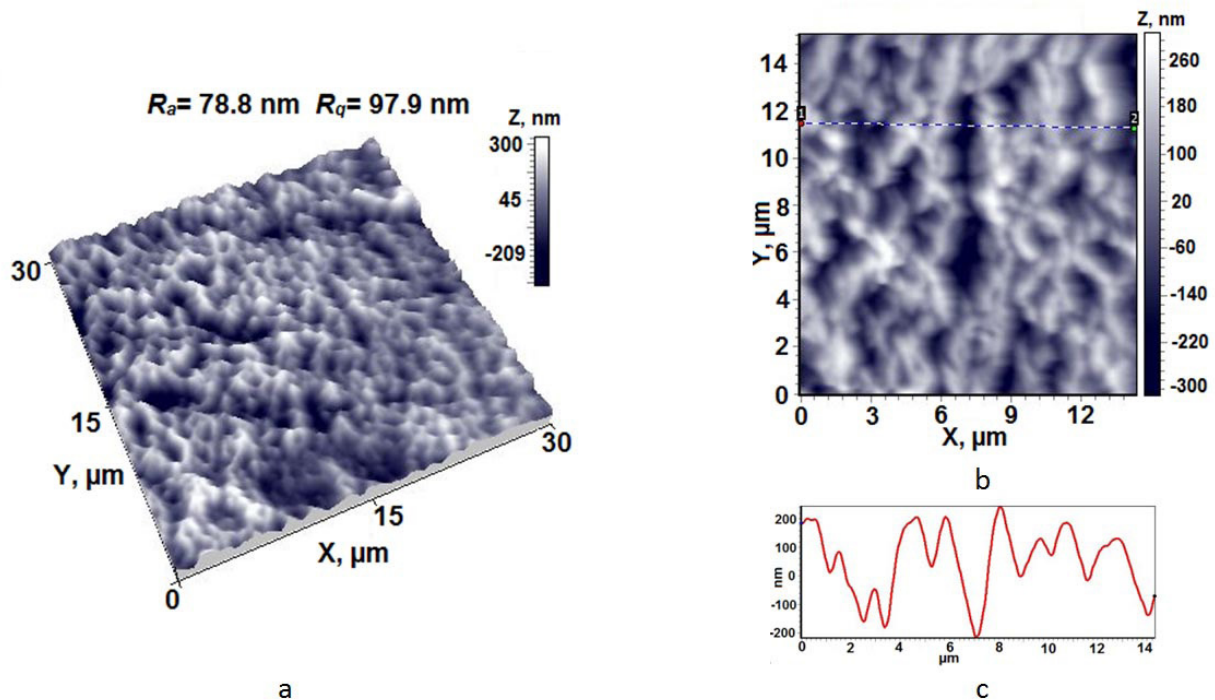
Fig. 1. AFM images of the surface for the porous PVDF film (P = 28%): a—surface topography, b—3D image, c—profile of the selected surface area
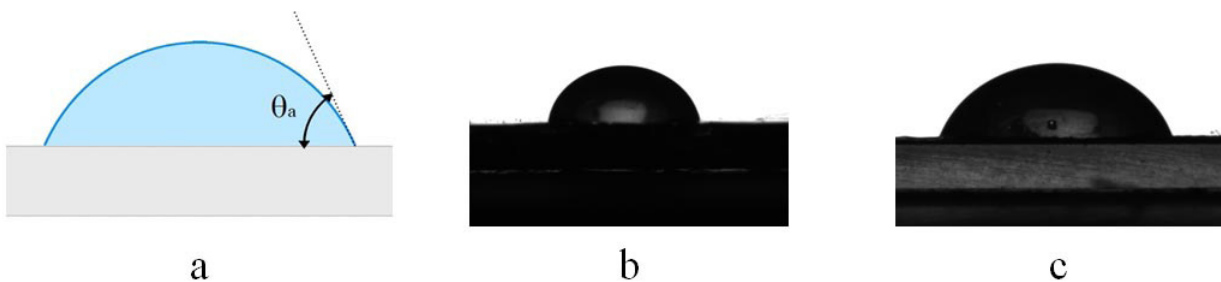

Fig. 2. Wettability by water of PVDF porous films: a—schematic image of a water drop on the film surface and contact angle θ; b—porous film with P = 13%, c—porous film with P = 28%

solution of ammonium persulfate was added as an oxidant. As a result, a PVDF film covered by green polyaniline layer was obtained. We also performed second polymerization of aniline hydrochloride on the surface of the obtained film to increase the content of conducting polymer and to form a PANI layer with higher density and homogeneity. It was carried out by placing the prepared sample in a fresh polymerization mixture.

The layers of polypyrrole (PPy) were formed on the surface of a PVDF support by polymerization of monomer (pyrrole) in the mixed solution of methanol and water in equal volumes. The solution used $FeCl_3$ as an oxidant. The mixture of methanol/water was chosen as an optimal solvent which ensures the best wettability of a PVDF surface and the formation of a homogeneous defect-free PPy layer.

It was observed that the content of conducting polymer in the composite grows along with an increase in overall porosity (Fig. 3). Figure 3 also shows that the dependence becomes stronger at the value of porosity that corresponds to the appearance of through channels (more than 23%). This provides better conditions for the PPy layer formation.
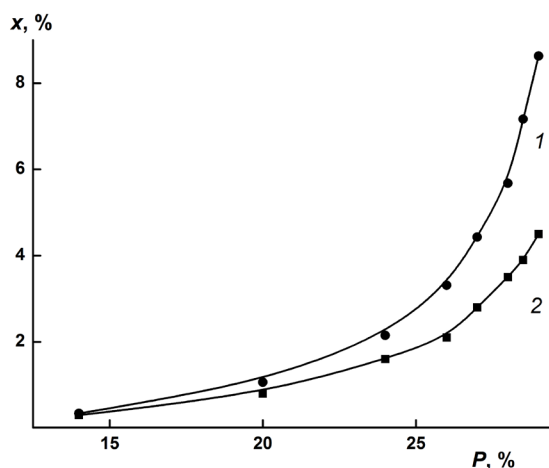
Fig. 3. Content of PPy (1) and PANI (2) in composites vs porosity of a PVDF support

Morphology of composites

Morphology of composite films was studied using scanning electron microscopy. Fig. 4 shows the surfaces of PANI/PVDF and PPy/PVDF composites in comparison with a PVDF support. The SEM picture of the PVDF support demonstrates its developed relief structure: surface comb-like peaks and cavities between them. The SEM image of PVDF/PANI shows that polyaniline fills the pores and forms the so-called cauliflower structure on a PVDF surface. Fig. 3c shows that the surface of a PPy layer has a globular structure typical of PPy, and the conducting coating fully masks the support relief (as is seen in Fig. 3, the content of PPy in the composite is twice higher than the content of PANI).
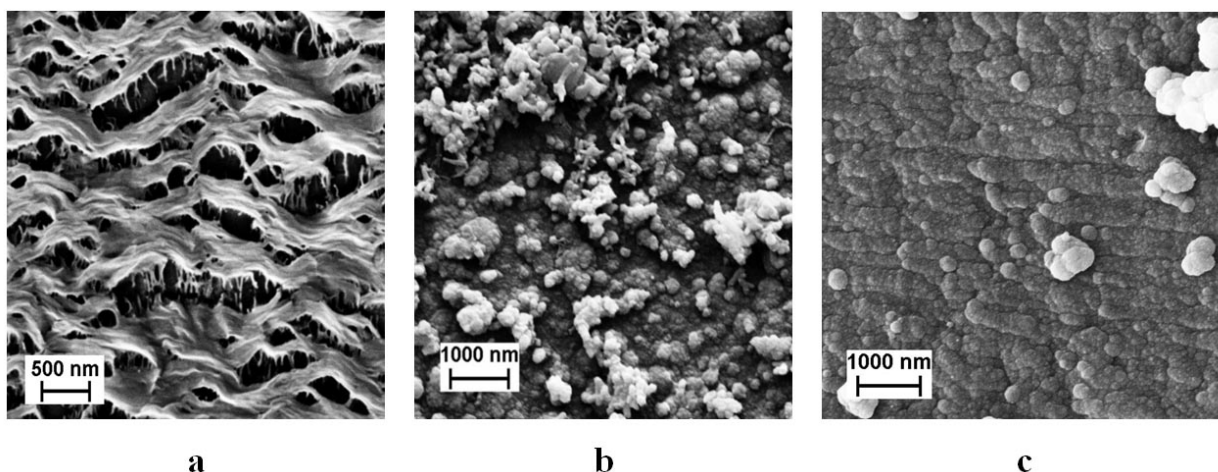

a **b** **c**

Fig. 4. SEM pictures (surface) of PVDF films (a) and PVDF/PANI (b) and PVDF/PPy (c) composites

It was established that the obtained conducting layers have a high adhesion to the porous PVDF films, and no exfoliation was observed during the mechanical bending of the composites. At the same time, PPy and PANI layers were easily separated from the smooth dense support. It means that relief-like surface and porous structure provide adhesion between the components of the composite samples. This conclusion is confirmed by IR spectroscopy investigations. It is clearly seen (Figs. 5 and 6) that at the spectra of the composites the bands of the initial components are presented without any changes or shifting. It means that there are no chemical interactions between the components and conducting layers adhere to the porous support through the so-called mechanical adhesion. Note that high adhesion of the PVDF films under study is also related to the formation of a conducting polymer layer in deep pores opening to the surface (Elyashevich et al. 2002).
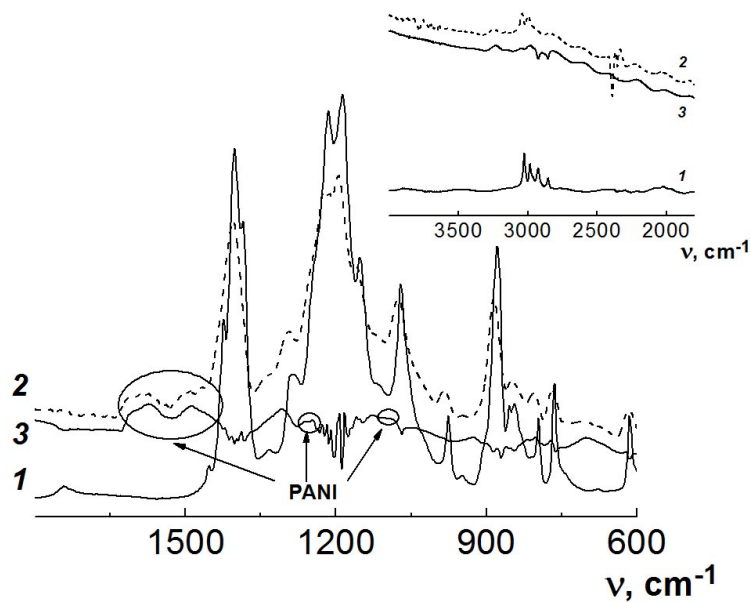
Fig. 5. IR spectra of porous PVDF films (1), PVDF/PANI composites (2), and the resulting difference spectrum (3). Inset: the region of conductivity plateau for PVDF/PANI sample (2) and the difference spectrum (3)
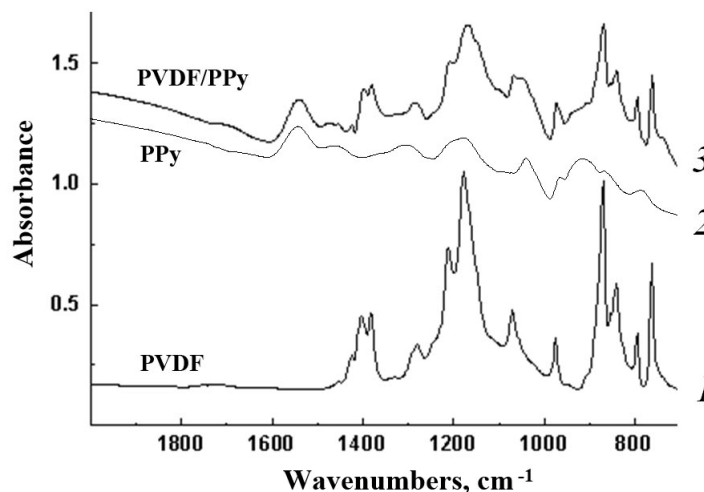

Fig. 6. IR spectra of a PVDF support (1), polypyrrole (2) and PVDF/PPy composites

Fig. 5 shows the IR spectra of a PVDF film, a PVDF/PANI film as well as the spectrum obtained by subtraction of these two spectra. The composite spectrum clearly shows the sample conductivity: absorption bands at 1570 and 1480 cm^{-1} typical for the vibrations of quinoid and benzoid rings that corresponds to protonated (conducting) form of PANI—emeraldine salt. The insert shows the so-called plateau of conductivity where conductive PANI exhibits a weak slope; it is absent in the initial PVDF spectrum. In summary, it is the evidence that PANI is polymerized on the surface of a PVDF porous film to a conductive form.

PANI and PPy are rigid-chain polymers, and their presence in composites often results in their lower mechanical strength and elasticity. However, we did not observe such changes in the prepared composites and they had the same values as the support (Table 1). It is important to note that the composites preserve mechanical integrity during deformation or even a break.

Conductivity and piezoelectric properties of PVDF/conducting polymer composites

Electric properties of the composites were characterized by surface and volume conductivity (Table 2). It was observed that conductivity increases along with an increase in the porosity of the support because the content of conducting polymer increases due to a bigger number and sizes of pores (Fig. 3). The volume conductivity is provided by conducting layers which are polymerized on the walls of pores and in the interlamellar regions. The deeper the monomer penetrates in the volume of a PVDF film (penetration depth also depends on wettability of the support by solvent during polymerization and its chemical nature) and the more content of the conducting component it produces, the higher the value of conductivity.

Table 2. Conductivity of the composites PVDF/conducting polymer

Sample	Content of conducting component, %	Surface conductivity, S/cm	Volume conductivity, S/cm
PVDF/PANI	5	3.0	10^{-6}
PVDF/PPy	8	6.0	10^{-5}

The conducting layers of polyaniline and polypyrrole were used as electrodes during polarization to investigate the piezoelectric properties of the prepared PVDF/PANI and PVDF/PPy composites. The piezo effect was characterized by modulus d_{31}. The value of the modulus is determined by the content of the polar piezo-active β-phase in a PVDF crystal structure. Extruded and annealed films contain only non-polar α-form of crystals. During the preparation of porous PVDF films the β-crystals are formed during uniaxial extension as a result of a polymorphous α - β transition. It was shown in (Elyashevich et al. 2019) that the content of β-phase increases at growth of orientation degrees (ε_1 and ε_2) at uniaxial extension stages. At the same time, it was observed that an increase in orientation at the extrusion stage (λ) leads to a decrease in β-form content formed at the subsequent α - β transformation under uniaxial deformation. The effect of negative influence of melt crystallization at high λ was explained by the data of X-ray investigations: α-crystals in the weakly-ordered spherulite structure which is formed at low λ is more effectively transformed into β-phase than more oriented lamellar structure arising at crystallization in higher oriented melt (Gerasimov et al. 2020).

To realize the piezo effect the composites were polarized in a constant electric field. In this work, the samples were polarized by the contact method at an elevated temperature at electric field E_{pol} = 90 V/μm, temperature T_{pol} = 90°C during 1 hour. The measurements of the modulus were carried out under the load of 5–10 MPa in the direction of film orientation. After the polarization all the samples exhibited piezoelectric properties. The highest values of the piezoelectric modulus d_{31} are presented in Table 3.

Table 3. Piezoelectric properties of PVDF/conducting polymers composites

Sample	Overall porosity, %	Content of β phase, %	d_{31}, pC/N
PVDF/PPy	13	60	18
PVDF/PANI	27	43	12

To compare the efficiency of using conducting polymers as an electrode material, the electrodes of liquid indium-gallium alloy were also used. It was found that the value of d_{31} measured by applying polymer electrodes did not differ from the values obtained for the same PVDF films with metallized surfaces. This is the evidence that conducting polymer layers may be effectively used as electrodes.

Conclusion

In our study, composite piezo-active systems were prepared by the polymerization of conducting polymer layers on the surface of porous PVDF films as supports. During the preparation of PVDF supports the formation of pores during uniaxial extension is accompanied by the development of a pronounced relief on the film surface. This important effect is due to the structure transformation: it is the relief that provides a high adhesion of conducting polymer layers to the support. Owing to the orientation efforts during uniaxial extension the polymorphous transition of PVDF crystals into a piezo-active form also goes at this stage in parallel with the formation of pores. As a result, the prepared films

and the composites based on them are characterized by a unique combination of a porous structure and high content of a piezo-active β-phase. Electric properties of the deposited conducting polymer coatings on the surface of a PVDF support make it possible to use them as electrodes for polarization and measurements of the piezo modulus in the composites. It should be noted that the homogeneous layers of the rigid-chain of conducting polymers make composites mechanically stable during deformation. The very important advantage of the elaborated approach is the ability to produce complete ready-to-use polymer-based piezo elements. Physical and functional characteristics of the prepared composites make them a promising piezoelectric material that may find an application in energy transducers, biosensors and actuators.

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