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Studying Physical Properties of a Polyvinylidene Fluoride/Lead Zirconate Titanate Piezoelectric Composite

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Abstract—The authors studied the effect of the percent fraction of microscopic lead zirconate titanate particles in a polyvinylidene fluoride-based composite material on its mechanical, piezoelectric, and structural properties. We found that an additional 10% of lead zirconate titanate particles enhances the piezoelectric response by increasing the degree of polymer crystallinity for this concentration while the ultimate stress values of the material remain in the range used for obtaining mechanical impact sensors.

Keywords: polyvinylidene fluoride, lead zirconate titanate, composite material, piezoelectric effect, constant d_{33}

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INTRODUCTION

Polyvinylidene fluoride (PVDF) is a polymer actively used in the production of smart materials because it is capable of converting mechanical action into electric energy. It is characterized by strong resistance to wear, chemical inertness, biocompatibility, and other properties. PVDF is widely used in the manufacture of electrical sensors, nanogenerators, and sensors in medical devices [1–3]. However, the values of a piezoelectric signal generated in the polymer are quite low, relative to ceramic piezoelectric materials [4]. Therefore, an active search for ways to increase the piezoelectric response in polymer materials is in progress. One approach involves creating multi-layer composite materials [5] and designing composites that contain piezoelectric ceramic particles [6].

Piezoelectric properties of PVDF can be improved through long-term polarization of a sample at high temperatures (40–80°C) in an electric field of 30–100 kV/cm [7]. However, this requires long periods of time for polarization and the PVDF itself imposes a limit on the increase in signal, which is determined by the saturation polarization of the dielectric. Another method to enhance the piezoelectric response in PVDF involves adding inclusions to the composite that then become centers of the crystallization of the electroactive PVDF phase. Lead zirconate titanate (PZT) is one possible material for such inclusions.

In this work, we studied the effect of microscopic PZT particles added to a PVDF polymer matrix on the polymer's piezoelectric response. It was found that adding microscopic particles significantly increases the polymer's degree of crystallinity. The value of the piezoelectric constant d_{33} in our PVDF/PZT composites was increased by an order of magnitude while keeping the ultimate stresses in the composite within the range used for designing mechanical impact sensors based on them.

EXPERIMENTAL

Polyvinylidene fluoride produced by Sigma-Aldrich ($M_w \sim 534000$, France) in the form of white powder was used to manufacture our composite films. The powder was dissolved in *N*,*N*-dimethylformamide (≥98%; Ekos-1, Russia) with a polymer mass concentration of 14.3%. Lead zirconate titanate produced by Aurora–Elma (Volgograd, Russia) was used as a type 0–3 filler.

Synthesis of Samples

Films formed from a solution were used to synthesize piezoelectric composite films based on polyvinylidene fluoride with added PZT particles. The raw PZT material was subjected to mechanical grinding to obtain a homogeneous powdered state. Amounts of PVDF and PZT were precisely weighted in different percentage mass ratios of 0, 5, 10, 20, and 30%. Solvent (dimethylformamide, DMF) was added to the resulting dry mixture in a ratio of 1 : 6 (PVDF : DMF).

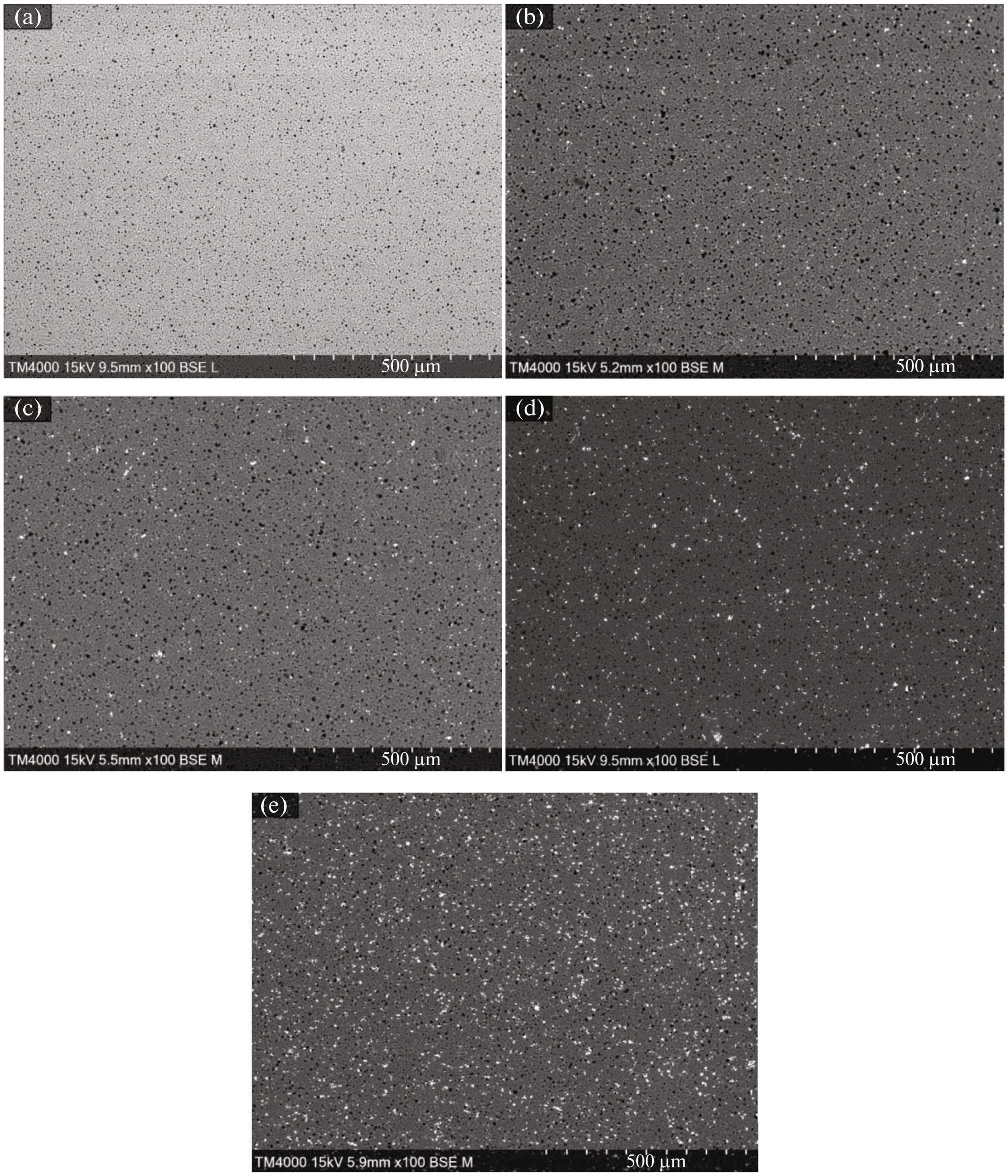

Fig. 1. Images of PVDF/PZT composites obtained on the scanning electron microscope at PZT contents of (a) 0, (b) 5, (c) 10, (d) 20, and (e) 30%.

The container with the reaction mixture was placed on a magnetic stirrer and stirred for 1.5 h until a homogeneous solution formed. After obtaining the homogeneous mixture, it was applied to a glass substrate and uniformly distributed over it using a squeegee with a special blade [8]. The resulting composite films were placed into a dry heat sterilizer at a temperature of 65°C and dried for 20 h until the solvent had completely evaporated. After the drying stage was complete, the films were cooled to room temperature and separated from the glass substrates with distilled water.

Morphology of Samples

A Hitachi TM4000Plus scanning electron microscope was used to estimate the uniformity of the distribution of PZT particles in the PVDF polymer matrix. From the images in Fig. 1, it is evident that the particles were uniformly distributed in all the synthesized composites. The average size of PZT particles did not vary from composite to composite and was 4.20 ± 1.03 μm. No particle agglomerates or large microparticles were observed. The added particles also did not affect the

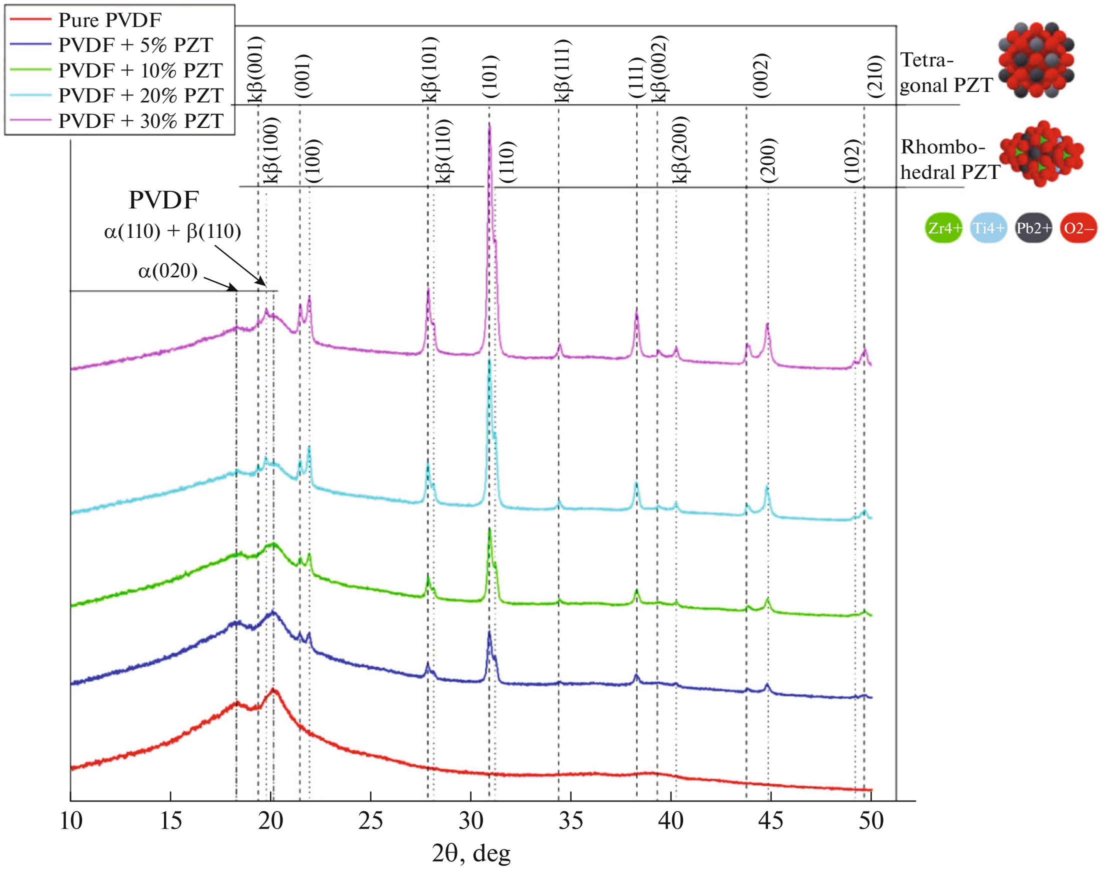

Fig. 2. X-ray diffraction patterns of the PVDF/PZT composites.

porosity of the polymer. The density of the pore distribution remained the same, and the average pore size was still 5.20 ± 1.55 μm.

Structural Properties

The degree of crystallinity (see Table 1) of the composites was determined by analyzing curves obtained on a Phoenix 204 F1 differential scanning calorimeter (NETZSCH) at a heating rate of 10°C/min. Calculations were based on the heat of fusion (E_{exp}) of a sample, relative to the heat of fusion of a polymer with a 100% degree of crystallinity ($E_{100\%}$) [9]:

$$X_{\text{c}}(\%) = E_{\text{exp}}/E_{100\%} \times 100\%. \qquad (1)$$

Our data show that the degree of PVDF cristallinity increased abruptly by 8.6% upon raising the mass fraction of PZT microparticles to 10%. It remained virtually the same after another increase in the fraction of particles in the composite. Such abrupt growth could be attributed to the PZT particles inside the polymer acting as the nuclei of a new phase in the drying process and the formation of crystalline phases.

The crystalline structure of the composite was studied using a PROTO AXRD Benchtop X-ray diffractometer with a copper X-ray tube and no Ni filter. In the X-ray diffraction pattern (Fig. 2), we can see peaks corresponding to the tetragonal and rhombohedral phases of PZT, peaks of the alpha and beta phases of PVDF, and the amorphous halo corresponding to the amorphous phase of the PVDF polymer. In the estimated value of the occupied area under the peaks indicates that, the fraction of the tetragonal phase of PZT is larger than that of the rhombohedral one. The coexistence of phases in PZT is explained by the chosen sintering temperature and fractions of raw powders during sintering [10].

Table 1. Degree X_{c} of crystallinity, constant d_{33}, and ultimate stress σ in the composite films, depending on the percent of PZT particles

PZT, %	X_{c}, %	d_{33}, pC/N	σ, MPa
0	36.3	0.30	35.0
5	37.3	0.60	25.0
10	45.9	1.91	19.0
20	43.0	2.12	12.5
30	46.9	2.51	10.5

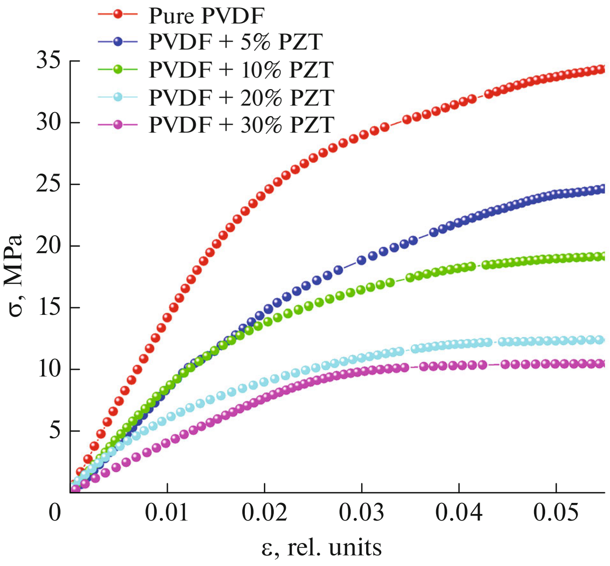

Fig. 3. Dependence of transverse stress σ in the composite on relative elongation ε of the sample.

Our diffraction patterns show that the area of the amorphous halo was reduced at the line of 20.2° for samples with PZT contents of 0, 5, and 10% with an increase in the PZT fraction. This agrees with the DSC data on the degree of crystallinity of the obtained composite. The tendency of a growing degree of PVDF crystallinity was disrupted upon reaching a PZT content of 10%. The areas of the amorphous halo for the PZT weight contents of 10, 20, and 30% are close. This also aligns with the data on the estimated degrees of crystallinity for these samples, which differ little from one another.

It is difficult to determine the ratio of the α, β, and γ-phases of the PVDF from the XRD data, since the most intense peaks are in close proximity to one another in the range of small angles and cannot be resolved. However, the higher value of the peak intensity at the line of 20.2° (relative to the peak on the line of 18.2°) indicates the presence of an electroactive phase inside the composite in all samples of the analyzed series [11].

Mechanical Properties

The mechanical properties of our PVDF/PZT films were estimated by measuring the dependencies of transverse stress σ in the composite on relative elongation ε (Fig. 3) using a Deben Microtest TM200 measuring setup.

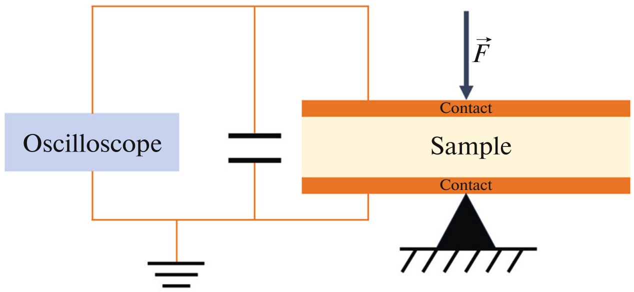

Fig. 4. Schematic image of the setup for measuring constant d_{33} quasistatically.

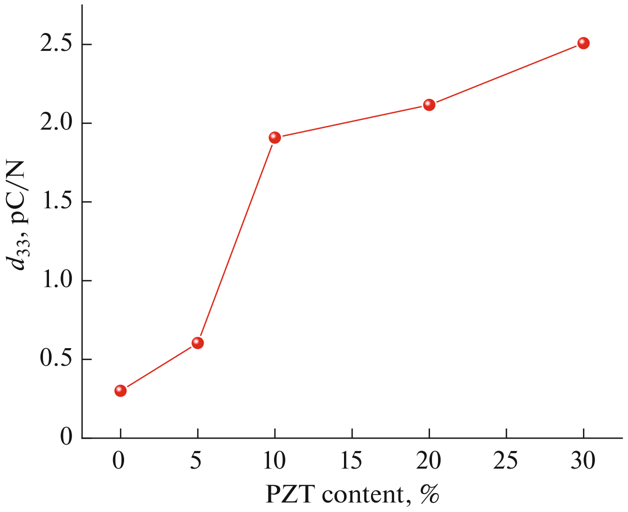

Fig. 5. Dependence of constant d_{33} on the percent of PZT particles in the composite.

The resulting patterns indicate that adding PZT particles significantly reduces the peak stresses that emerge in the composite: from 35 MPa for pure PVDF to 10 MPa for PVDF with a PZT particle content of 30%. However, the material with a peak stress of 10 MPa could still be used in designing mechanical impact sensors, despite the dilution of its mechanical characteristics. The values of the piezoelectric coefficient d_{33} were obtained quasistatically to estimate the piezoelectric response of the analyzed films. A scheme of the experimental setup is shown in Fig. 4.

The obtained dependence of the value of d_{33} on the percentage of PZT particles in the film (Fig. 5) shows that the optimum value of this content is 10%, as an increase in the value of d_{33} by an order of magnitude is observed at this value, relative to the pure unpolarized PVDF. The growth of d_{33} was significantly reduced upon a further increase in the percentage of PZT particles. The polymer's degree of crystallinity also experienced a significant jump of 8.6% for the composite with a 10% mass fraction of PZT particles and remained unchanged after a further increase in the number of particles. These data indicate that the primary contributor to the increase in constant d_{33} was the greater degree of polymer crystallinity caused by the PZT particles added to the composite, acting as centers of polymer crystallization during the drying process.

CONCLUSIONS

A way of amplifying a piezoelectric signal in polyvinylidene fluoride (by adding microscopic PZT particles to the polymer) was studied as an alternative to polarization. For composite films with mass contents of PZT microparticles of 5, 10, 15, and 20%, it was found that raising the mass fraction of PZT particles improves the piezoelectric response of the material. However, it also reduces the ultimate mechanical stresses that the material can tolerate. An increase in constant d_{33} on the order associated with the jumpwise growth of the degree of polymer crystallinity was observed for a 10% mass fraction of PZT particles in the composite. Raising the mass fraction of particles again did not result in significant growth of a sample's piezoelectric response. Lowering the peak stresses from 25 MPa for pure PVDF to 10 MPa for PVDF with a PZT particle content of 30% is not critical for potential applications, as the value of ultimate stresses of 10 MPa remains within the range characteristic of materials used in designing mechanical impact sensors. Thus, the optimum mass fraction of PZT particles in a PVDF/PZT composite that is needed to increase the piezoelectric response while retaining the mechanical properties required for designing mechanical impact sensors was determined.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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