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Effect of inclusion of titanium dioxide microparticles on the properties of PVDF/TiO₂

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Abstract. In the course of the study, a method for obtaining a composite PVDF film with titanium dioxide microparticles was proposed. The work studied the effect of adding different amounts of titanium dioxide microparticles on the surface morphology and roughness of the resulting material. The spectral characteristics of PVDF/TiO₂ films were studied. The electrophysical characteristics of the films were analyzed depending on the concentration of added titanium dioxide microparticles.

Keywords: microparticles, TiO₂, PVDF, composite materials, atomic force microscopy

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Материалы конференции

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Влияние включения микрочастиц диоксида титана на свойства композитных пленок ПВДФ/ТiO₂

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Аннотация. В ходе исследования предложен способ получения композитной пленки ПВДФ с микрочастицами диоксида титана. В работе изучено влияние добавления различного количества микрочастиц диоксида титана на морфологию поверхности и шероховатость полученного материала. Изучены спектральные характеристики пленок ПВДФ/ТiO₂. Проведен анализ электрофизических характеристик пленок в зависимости от концентрации добавленных микрочастиц диоксида титана.

Ключевые слова: микрочастицы, TiO₂, ПВДФ, композиционные материалы, атомно-силовая микроскопия

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Introduction

Polyvinylidene fluoride and its copolymers have excellent piezoelectric properties, which allows to significantly expand the areas of application of PVDF products [1]. The polymer consists of 5 crystalline phases, which differ significantly in properties, primarily mechanical, optical and electrophysical. [2] It is important to note that without polarization or additional post-production processing, products can have extremely low mechanical properties, including an overly developed surface, which can limit the areas of their application [3]. Adding various materials to the polymer matrix can help in structuring PVDF, form intermolecular bonds, and also cause spontaneous polarization of the material [4]. Titanium dioxide is a biocompatible and crystalline material and can be used for structuring and as additional crystal formation points when obtaining films [5]. The main objective of this work is to evaluate the effect of the inclusion of TiO_2 microparticles on the morphology, transparency and phase composition of the polymer, which is important for the creation of various devices based on PVDF and its copolymers. [6, 7].

Materials and Methods

Particle preparation. To obtain composites, titanium dioxide nanoparticles were used, obtained by a standard method [6], in which 21 ml of the mixture (13 ml – isopropyl alcohol and 8 ml of titanium butoxide) was slowly added to 180 g of water heated to 135 °C, after which the mixture was heated for 2 hours at 145 °C, after which the heating was turned off and the mixture was stirred for another 5 days. Then the suspension was concentrated and dried in a drying cabinet at 57 °C.

Obtaining composite films. Weighed portions of titanium dioxide nanoparticles were weighed in falcons (5–20% relative to the amount of PVDF), after which 14 ml of a 5% PVDF solution in DMF were added to them, then the mixture was homogenized by stirring on a multitorator for 2 hours and 10 minutes using ultrasound treatment. After that, the suspensions were cast into Petri dishes and kept at 80 degrees for 28 hours.

Atomic Force Microscopy. The morphology and ferroelectric properties of the PVDF film with TiO_2 nanoparticles were studied using scanning probe microscopy with NTEGRA Prima (NT-MTD, Zelenograd, Russia) using FMG01/Pt cantilevers with platinum coating.

FTIR spectroscopy. FTIR spectra of the films were recorded using an FT-803 FTIR spectrometer with an attenuated total internal reflection attachment manufactured by Simex LLC (Russia, Novosibirsk). Single FTIR attachment, diamond crystal. The range of IR spectra recording was 550–4000 cm^{-1} , resolution 2 cm^{-1} . The IR spectrum of pure TiO_2 particles was recorded in transmission in a NaCl tablet using a PerkinElmer 1760X FTIR spectrometer, range 400–4000 cm^{-1} , resolution 4 cm^{-1} .

Results and Discussion

The morphological and optical (transparency in the visible range) characteristics of films obtained with different contents of titanium microparticles were studied. Scanning probe microscopy data when introducing microparticles reduces the value of the mean square roughness of the film from 220 nm (the value for the outer rougher side of the control film) to 12 nm (Table 1). Spherical particles of micron sizes are observed on the surface of the control film (Fig. 1). From the AFM data it is evident that the inclusion of any amount of titanium dioxide in the polymer matrix significantly reduces the roughness, which may be due to the intermolecular interaction of the polymer and microparticles.

Table 1

Data from piezoresponse force microscopy

TiO ₂ concentration, %	Side	<i>d</i> , μm	Rms, nm	VPFM, pA	LPFM, pA
Control	Outer side	7	220	21	52
	Inner side	5	19	28	66
5	Outer side	—	15	−1	51
	Inner side	—	2	6	56
10	Outer side	—	12	−5	−13
	Inner side	—	3	−3	56
20	Outer side	—	6	−5	−59
	Inner side	—	3	27	169

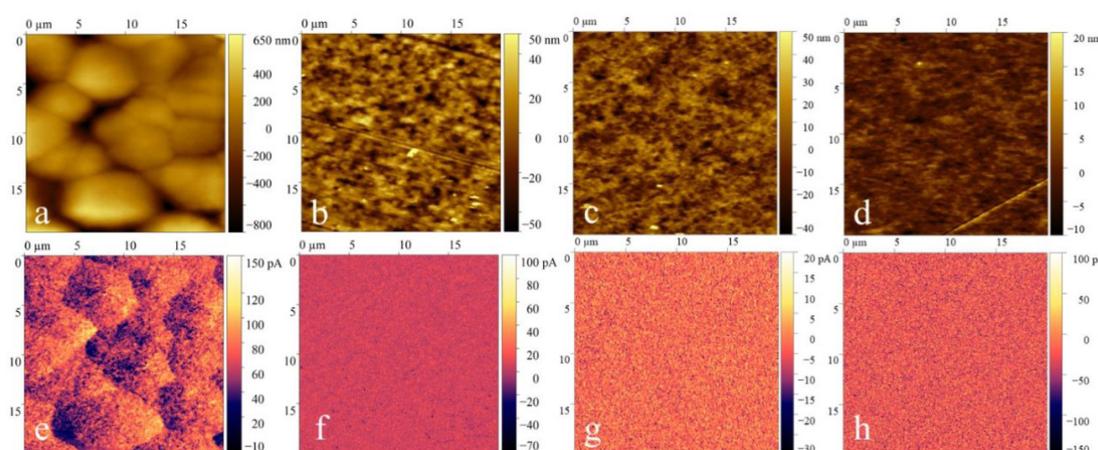


Fig. 1. AFM/PFM images of PVDF/TiO₂ composite films

The optical spectroscopy results demonstrate a significant change in turbidity after the inclusion of titanium dioxide microparticles (see Fig. 1). Turbidity in the visible part of the spectrum decreased from 79% to 9% for the film with 5% titanium dioxide nanoparticles. This effect may be associated with the formation of more compact supramolecular structures, as well as with the predominant content of the transparent γ -phase in PVDF.

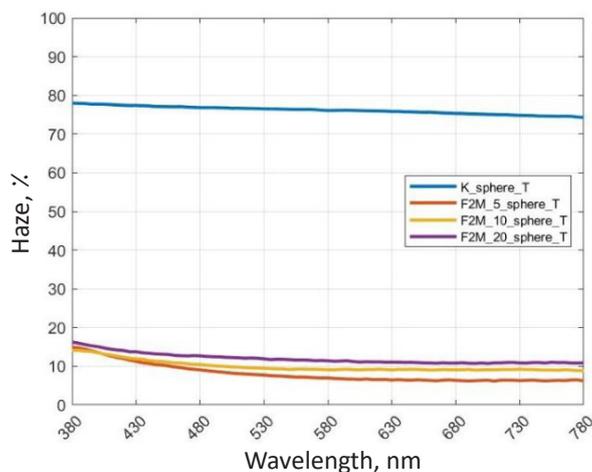


Fig. 2. Wavelength dependence of turbidity of PVDF films with incorporated titanium dioxide

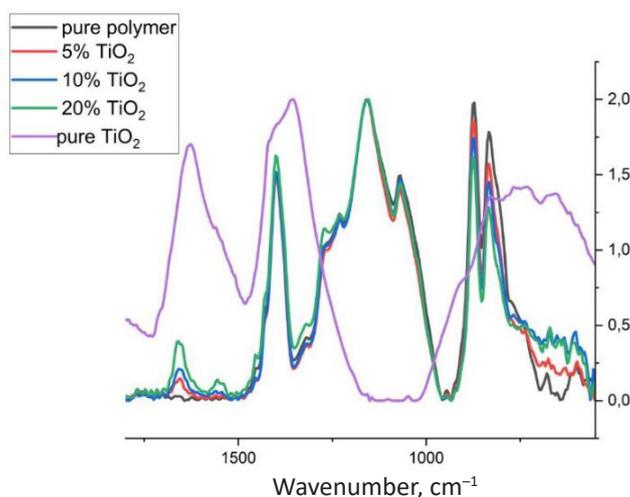


Fig. 3. FTIR spectra of PVDF/TiO₂ composite films, pure PVDF and microparticles TiO₂

The FTIR spectroscopy data (Fig. 3) confirm the formation of a composite material, which is noticeable by the shift of the band at 1650 cm⁻¹, which is characteristic of TiO₂. The shift of the band is associated with the formation of intermolecular bonds of nanoparticles with the CH- and CF- groups. In addition, by changing the intensities of the characteristic CF- vibration bands in the region of 700–840 cm⁻¹, a change in the phase composition and conversion from the α -phase to β and γ -phase are noticeable, which leads to a change in the optical properties.

Conclusion

In this paper, we propose a new method for producing a composite of titanium dioxide and PVDF microparticles. The effect of particle number on the optical characteristics, surface morphology, and electrical properties is determined. The proposed method can be used as a basis for producing composite films of PVDF and its copolymers with specified roughness and phase composition of the composite material.

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