

INFLUENCE TEMPERATURE TIME MODE OF CRYSTALLIZATION ON THE STRUCTURE AND PROPERTIES OF NANOCOMPOSITES BASED ON POLYVINYLIDENE FLUORIDE (PVDF) AND ZIRCONIUM OXIDE NANOPARTICLES (ZrO₂)

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The paper studied the effect of temperature time mode of the crystallization on photoluminescent properties and supramolecular structure of nanocomposites based on polyvinylidene fluoride and zirconium dioxide nanoparticles. It has been found that the PL intensity at all wavelengths increases sharply at the cooling mode of film $\beta_1 = 2000^\circ/\text{min}$, as compared with the samples obtained at the cooling mode $\beta_2 = 200^\circ/\text{min}$, and in the case of cooling film $\beta_3 = 2^\circ/\text{min}$. It has been found that the surface roughness of PVDF + 1% ZrO₂ compositions depending on β varies, i.e. for samples prepared in modes $\beta_1 = 2000^\circ/\text{min}$ the roughness is 15-30nm, for samples obtained in the modes $\beta_2 = 200^\circ/\text{min}$ - 20-50 nm, and for the sample obtained at $\beta_3 = 2^\circ/\text{min}$ the roughness is 60-100 nm. It is shown that the variation of the photoluminescence intensity at all wavelengths depending on temperature-time regime of crystallization is explained by the activation of the luminescent centres on zirconium dioxide ZrO₂ nanoparticles due to increasing the interfacial interactions between the nanoparticles with the polymer.

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1. Introduction

The introduction of nanoscale inorganic particles in the polymer can control the structure of the material from the simple composite with volume fillers to systems with a given supramolecular architecture and spatial distribution of filler that contributes to the emergence of a number of new technological and operational properties of obtained composite. Despite significant advances that have been done in the field, the general interconnections characteristics between patterns of nano filler and polymer matrix with the properties of the final composite material is still not studied in details. Still it is unclear the problem of determining the optimal concentration of nanoparticles and their uniform distribution in the polymer matrix [1].

The most promising objects for obtaining of purposive construction nanomaterials are nanocomposites with metal oxides nanoparticles of narrow size distribution, definite morphology and composition, in particular the nanocomposite, containing the ZrO₂ nanoparticles, having high thermomechanical properties, optical transparency, chemical and corrosion resistance, high coefficient of thermal expansion and a low thermal conductivity [2,3]. In the development of nanocomposites the most promising are the polymers that are fundamentally different in term of structure and functionality, such as carbon-chain thermoplastic polymers-polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE) and etc.

Nanocomposites based on these polymers and ZrO₂ nanoparticles have not been previously obtained and are of great interest for the purposive construction of organic-inorganic materials, from a fundamental point of view - the identification of properties of composite materials based on the individual characteristics of their components, and practical - to obtain nanocomposites with practically important properties. The relevance of this work is determined by

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the need to develop new polymer nanocomposites based on carbon-chain thermoplastic polymers with introduction of ZrO_2 nanoparticles in order to improve their thermo-mechanical, electroluminescent properties.

It is known that the supramolecular structure is determined by the molecular structure of the polymer and the conditions of its production (cooling rate, dwell time in the melt and the number of remeltings). The dimensions of the structural elements substantially affect the mechanical properties of polymers; the greater they are, the greater the stress of recrystallization, larger sample brittleness and lower its elongation.

Almost all methods for obtaining nanocomposites are accompanied by a profound interaction with the matrix phase-in substances, especially at the interfaces, which are formed in situ. The introduction of even such small particles causes significant irregularities in the polymer structure.

Nano-sized particles (NSP) introduced into the polymer matrix solution or into a crystalline polymer melt, are able to exert influence on the ratio of the crystalline and amorphous phases. Therefore, developed crystalline structure is formed in the transition regions of the polymer boundary layer in the nanocomposite, wherein the structuring NSP activity improve the thermodynamic conditions of the crystallization of molecular chains in the boundary layer [4].

In this paper, we studied the effect of temperature time mode of crystallization on the structure and photoluminescence properties of polymer nanocomposites based on PVDF + ZrO_2 .

2. Experimental part

2.1. Synthesis of polymer nanocomposites.

Polymer nanocomposite PVDF+ ZrO_2 was prepared as follows: polyvinylidene fluoride powders at room temperature were dissolved in an organic solvent-dimethylformamide. Nanoparticles ZrO_2 added to the polymer solution at different volume contents and mixed for an hour to obtain a homogeneous mixture. The mixture was transferred to a Petri dish and dried in a vacuum oven during the day. Then, from these samples by hot pressing at a melt temperature of polyvinylidene fluoride and a pressure of 10 MPa obtained the thin film of nanocomposite.

Cooling of the film after hot pressing was carried out at 3 modes: cooling by liquid nitrogen (cooling rate $2000^\circ/\text{min}$); cooling in water (cooling rate $200^\circ/\text{min}$) and the slow cooling under press for 24 hours (cooling rate $2^\circ/\text{min}$).

2.2. Research methods of polymer nanocomposites

IR study

IR spectra of the samples were recorded on a spectrometer FT-IR Varian-3600 Excalibur Series, allowing to record the spectra in the range of $4000\text{-}400\text{ cm}^{-1}$.

SEM analysis

Distribution of zirconium oxide nanoparticles in the polymer matrix was studied by scanning electron microscopy (SEM, Jeol JSM-7600 F). Scanning was conducted in the SEI mode at an accelerating voltage of 15 keV and working distance of 4.5 mm.

AFM analysis

The morphology of the nanocomposites was studied using atomic force microscopy Integra Prima (NT-MDT, Zelenograd). For the scan used special silicon cantilevers fabricated by plasma etching method with the needle radius of curvature of 20 nm and the resonance frequency of 1-5 Hz. Scan size was $2 \times 2\text{ mm}$. The measurements were performed in the semicontact microscopy mode in air, needle change of the cantilever oscillation amplitude was fixed, determining the surface topography. The scanning speed and the number of scanned lines of the image are respectively 256 and 1,969 Hz.

Photoluminescent analysis of nanocomposites

Luminescent properties of nanocomposite films were examined using a spectrofluorometer Varian Cary Eclipse at wavelength range 200-900 nm.

3. Results and discussion

Fig. 1 shows the IR spectra of PVDF and nanocomposites based on PVDF + ZrO₂. The infrared spectroscopy study of the PVDF samples indicated the existence of two crystalline forms of the polymer: α and β . In the α - form the chain molecules are in helical conformation with the period of the identity of 4.64 Å, comprising two monomer units. The β -form macromolecules are planar zigzag chains, with the period of the identity - 2.56 Å and include one monomer unit. The characteristic bands of PVDF with helical conformation reveal at 1385, 1146, 997, 768, 600 and 535 cm⁻¹, whereas planar zigzag chains have the characteristic bands at 510, 488 and 445 cm⁻¹. In the IR spectrum of the PVDF there are two bands at 3020 and 2980 cm⁻¹ relating to the asymmetric and symmetric vibrations of CH₂ groups correspondingly. This is a “doublet” band pair usually occurring near 2926 and 2980 cm⁻¹, but occurs here at 3020 and 2980 cm⁻¹ owing to the presence of fluorine on the adjacent carbon atom [5]. Vibrational bands at 615 and 763 cm⁻¹ (CF₂ bending and skeletal bending) and 795 cm⁻¹ (CH₂ rocking) refer to α -phase. Vibrational bands at 509 cm⁻¹ (CF₂ bending), and 840 cm⁻¹ (CH₂ rocking) correspond to β -phase. The α -phase had a characteristic infrared absorption at 763 cm⁻¹ and assumed that the 840 cm⁻¹ absorption band is uniquely characteristic of the β -phase[6].

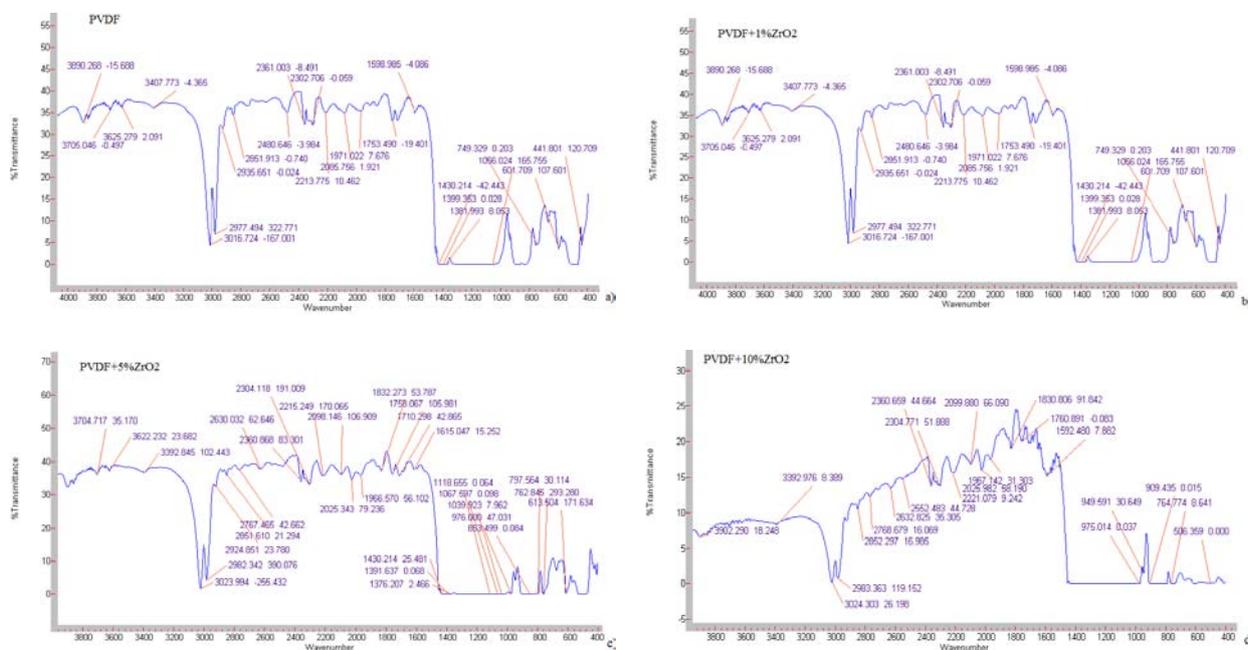


Fig.1 IR-spectra of PVDF+ZrO₂ nanocomposites
a) PVDF; b) PVDF+1% ZrO₂; c) PVDF+5%ZrO₂; d) PVDF+10%ZrO₂

With increasing of ZrO₂ nanoparticles concentration in polymer matrix the characteristic peak is shifted to longer wavelengths (3016 cm⁻¹ → 3016 cm⁻¹, 3023 cm⁻¹, 3024 cm⁻¹; 2977 cm⁻¹ → 2977 cm⁻¹, 2982 cm⁻¹, 2983 cm⁻¹). Consequently, we can assume that the ZrO₂ nanoparticles are distributed in the volume of the polymer and there are non-covalent interactions between them and CH₂ and CF₂ groups of polymer matrix [7,8].

Fig. 2 shows SEM images of polymer-based nanocomposites PVDF+ZrO₂ with 10% volume content of ZrO₂ nanoparticles. It has been found that at the introduction of ZrO₂ nanoparticles in PVDF matrix the agglomeration and aggregation of nanoparticles not depend of the cooling rate, and the nanoparticles have approximately the same size at about 20 nm. In EDS spectrum of nanocomposite there are lines related to C, Zr, F and O atoms.

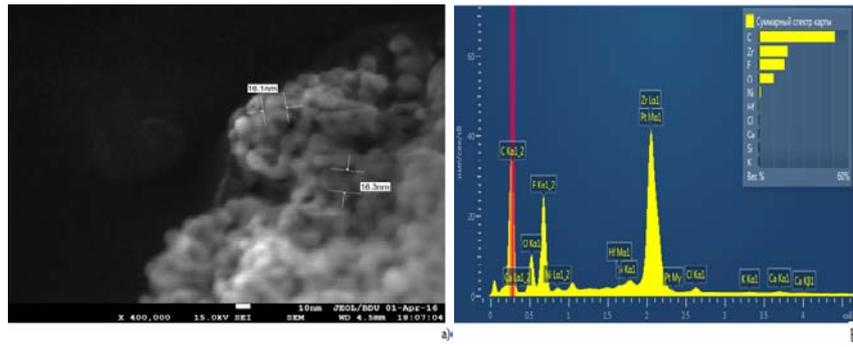


Fig.2 SEM image (a) and EDS spectra (b) of nanocomposite PVDF+ZrO₂.

Fig. 3 shows photoluminescence spectra of PVDF+ZrO₂ nanocomposites, obtained at slow cooling mode (1), at cooling mode in water (2) and at cooling mode in liquid nitrogen (3). As can be seen in the photoluminescence spectra of PVDF+ZrO₂ nanocomposites observed peaks at wavelengths of 443 nm, 456 nm, 495 nm, 530 nm and 565 nm. It also shows that with the change of the temperature time mode of crystallization of nanocomposite films the photoluminescence intensity strongly varies. Thus in the case of cooling mode in liquid nitrogen the photoluminescence intensity sharply increases as compared with the cooling mode in water and slow spontaneous cooling. Figure 4 shows the excitation and emission spectra for PVDF+ZrO₂ nanocomposites at various excitation wavelengths.

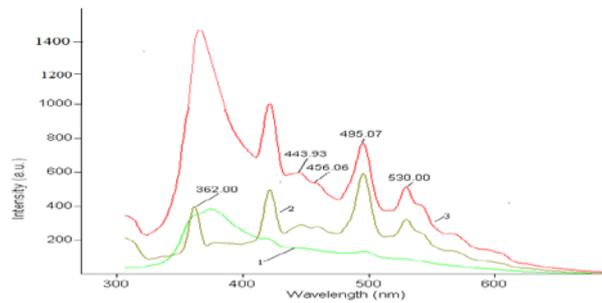


Fig.3 Photoluminescent spectra of PVDF+1%ZrO₂ nanocomposite at slow cooling mode (1), cooling mode in water (2), cooling mode in liquid nitrogen(3)

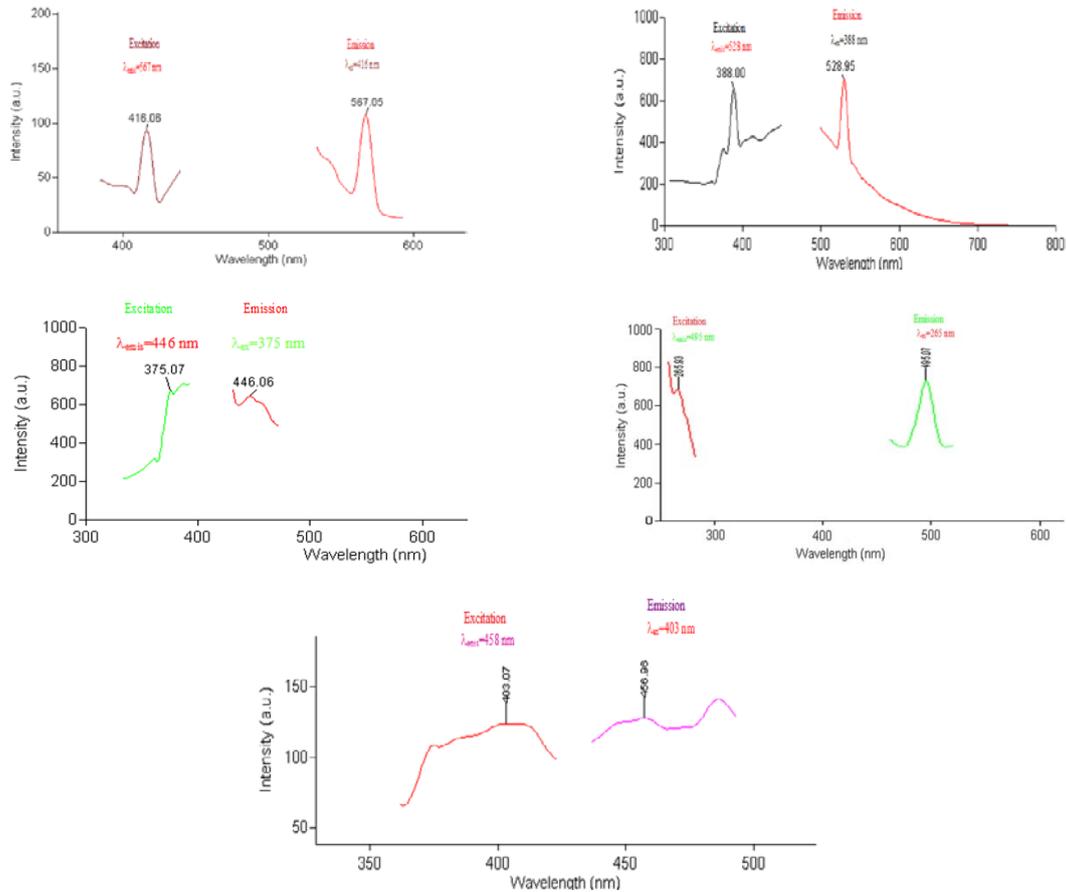


Fig.4. Excitation and emission spectra for PVDF+ZrO₂ nanocomposites at various excitation wavelengths.

In our opinion the photoluminescence intensity change at all wavelengths depending on temperature-time mode of crystallization is explained with the activation of the luminescent centers in zirconium dioxide nanoparticles by increasing the interfacial interactions between the nanoparticles with the polymer. At the slow cooling $\beta_3 = 2^0/\text{min}$ there form larger molecular structures, and this leads to weakening of the interaction with the nanoparticles. At the rapid cooling mode in liquid nitrogen the smaller crystallites are formed and nanoparticles play role of nucleation centre of crystallization. As a result, between the polymer and nanoparticles increases interfacial interactions and the photoluminescence intensity increases. Consequently, it was found that the PVDF is not merely a passive matrix, but there occur strong interfacial interactions between nanoparticles and PVDF and this, in turn influences the luminescent properties of nanocomposite[9,10].

Figure 5 shows the AFM 2D image of PVDF+ZrO₂ nanocomposites, depending on the temperature timemode of crystallization. Figure 6 shows a histogram of the surface roughness of the PVDF+ZrO₂ nanocomposites.

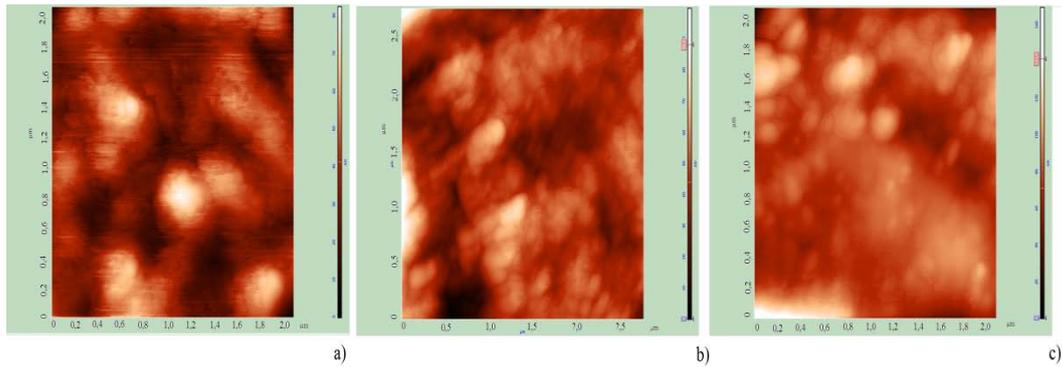


Fig.5 AFM image of PVDF+ZrO₂ nanocomposite a) cooling mode in water; b) cooling mode in liquid nitrogen; c) slow cooling mode

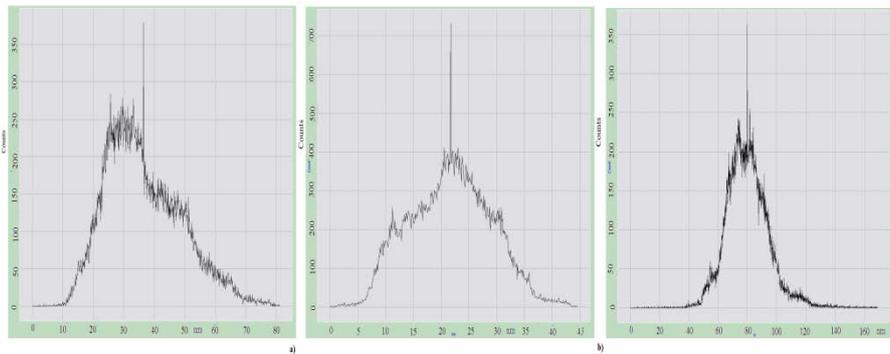


Fig.6 Histogram of the surface roughness of PVDF+ZrO₂ nanocomposite a) cooling mode in water; b) cooling mode in liquid nitrogen; c) slow cooling mode

For obtained nanocomposite films at the cooling mode in water ($\beta_2 = 200^0/\text{min}$), the root mean square surface roughness is 20-50 nm, at the cooling mode in liquid nitrogen ($\beta_1 = 2000^0/\text{min}$) - 15-30 nm; for samples obtained in the slow cooling mode ($\beta_3 = 2^0/\text{min}$) - 60-100 nm. AFM studies again prove that at the cooling mode in liquid nitrogen formed smaller crystallites than in the case of modes of water cooling and slow cooling. Consequently, at the cooling mode in liquid nitrogen the stronger interfacial interactions occur between polymer and zirconium oxide nanoparticles and thus the photoluminescence intensity sharply increases [11,12].

4. Conclusions

The paper studied the effect of temperature-time mode of the crystallization on photoluminescent properties and supramolecular structure of nanocomposites based on polyvinylidene fluoride and zirconium dioxide nanoparticles.

It has been found that the PL intensity at all wavelengths increases sharply at the cooling mode of film $\beta_1 = 2000^0/\text{min}$, as compared with the samples obtained at the cooling mode $\beta_2 = 200^0/\text{min}$, and in the case of cooling film $\beta_3 = 2^0/\text{min}$. It has been found that the surface roughness of PVDF + 1% ZrO₂ compositions depending on β varies, i.e. for samples prepared in modes $\beta_1 = 2000^0/\text{min}$ the roughness is 15-30 nm, for samples obtained in the modes $\beta_2 = 200^0/\text{min}$ - 20-50 nm, and for the sample obtained at $\beta_3 = 2^0/\text{min}$ the roughness is 60-100 nm.

It is shown that the variation of the photoluminescence intensity at all wavelengths depending on temperature-time regime of crystallization is explained with the activation of the luminescent centres on zirconium dioxide ZrO₂ nanoparticles due to increasing the interfacial interactions between the nanoparticles with the polymer.

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