



Article

The Influence of Technological Factors and Polar Molecules on the Structure of Fibrillar Matrices Based on Ultrafine Poly-3-hydroxybutyrate Fibers Obtained via Electrospinning

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Abstract: The article examines the regularities of structure formation of ultrafine fibers based on poly-3-hydroxybutyrate under the influence of technological (electrical conductivity, viscosity), molecular (molecular weight), and external factors (low-molecular and nanodispersed substances of different chemical natures). Systems with polar substances are characterized by the presence of intermolecular interactions and the formation of a more perfect crystalline fiber structure. Changes in technological and molecular characteristics affect the fiber formation process, resulting in alterations in the morphology of the nonwoven fabric, fiber geometry, and supramolecular fiber structure. Polymer molecular weight, electrical conductivity, and solution viscosity influence fiber formation and fiber diameter. The fiber structure is heterogeneous, consisting of both crystalline and non-equilibrium amorphous phases. This article shows that with an increase in the molecular weight and concentration of the polymer, the diameter of the fiber increases. At the same time, the increase in the productivity of the electrospinning process does not affect the fiber geometry. The chemical structure of the solvent and the concentration of polar substances play a decisive role in the formation of fibers of even geometry. As the polarity of the solvent increases, the intermolecular interaction with the polar groups of poly-3-hydroxybutyrate increases. As a result of this interaction, the crystallites are improved, and the amorphous phase of the polymer is compacted. The action of polar molecules on the polymer is similar to the action of polar nanoparticles. They increase crystallinity via a nucleation mechanism. This is significant in the development of matrix-fibrillar systems for drug delivery, bioactive substances, antiseptics, tissue engineering constructs, tissue engineering scaffolds, artificial biodegradable implants, sorbents, and other applications.

Keywords: poly-3-hydroxybutyrate; fibers; electrospinning; solution parameters; dipyrindamole; Fe(III)Cl tetraphenyl porphyrin complex; nanoparticles; structure



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1. Introduction

Today, it is necessary to develop materials with a low density and high specific surface area for the creation of new medical devices (polymeric matrices, implants, etc.) characterized by a high biodegradation rate in living organisms (bioresorption) [1].

The best and optimal solution is nonwoven fibrous materials composed of nanoscale and micron-scale fibers obtained through the electrospinning method [2]. The electrospinning (ES) of ultrafine polymeric fibers represents a complex multiparametric process,

influenced by numerous characteristics that affect both the geometry and structure of individual filaments and the performance of the resulting nonwoven fibrous material [3]. The key parameters of electrospinning that determine the phase and physicochemical state of the polymer solution are electrical conductivity and viscosity, which are influenced by the concentration and molecular weight of the polymer [4]. The electrospinning process and the resulting morphology of the nonwoven material are also affected by environmental factors such as temperature, humidity, pressure, oxygen concentration, etc. [5], as well as the technological parameters of the process, including the production rate, electrode distance, electrode shape, capillary diameter, flow rate of the polymer solution, and others [6].

Therefore, the aim of this study was to create highly porous biopolymeric materials based on ultrathin fibers (diameter 0.5–3 μm) obtained through the modern technological process of electrospinning a polymer solution. This method allows the formation of fibrous nonwoven material layers with a specific thickness, density, and specific surface area. The incorporation of additional functional components into the polymer solution can also influence the structural organization of the fibers. It is essential to investigate how the characteristics of the structural hierarchy impact the performance properties of the materials, as it will play a crucial role in the kinetics of diffusion transport and degradation processes (oxidative, photo-oxidative, biodegradation, etc.).

To achieve the desired set of properties for polymeric materials, various types of chemical, physical, or physicochemical modifications are applied in the preparation stage or during the forming process, leading to radical changes in the polymer material's structure on different levels of structural organization.

Hence, it becomes necessary to establish a correlation between external factors and changes in the parameters of the polymer material's structure. This correlation allows for the targeted adjustment of the properties of the polymer system based on the intended application of the product.

For example, the addition of polyvinylpyrrolidone (PVP) to natural quercetin makes it possible to obtain fibers via the electrospinning of a given geometry. The authors found that with an increase in the PVP content, the diameter of the fibers increases significantly. This is undoubtedly associated with an increase in the viscosity of the blends due to intermolecular interactions [7]. Other scientists have found that increasing the concentration of quercetin in a PVP solution has the opposite effect. The fiber diameter is reduced. In this case, the fiber diameters lie in the nanoscale range [8].

One of the most promising polymers used in medicine is poly(3-hydroxybutyrate) (PHB). This bacterial biopolymer exhibits high crystallinity [9]. By modifying the polymer's crystalline structure during the film or fiber formation process, its transport properties can be regulated to a great extent [10].

Usually, elevated temperatures negatively affect the structure of most biopolymers, which is why the formation of products from their solutions is preferred. This is particularly crucial for medical devices, such as matrices for controlled drug release, since only a limited number of drugs can withstand relatively high temperatures.

This study will investigate the structural organization of nonwoven fibrous PHB materials depending on the technological parameters of the electrospinning process, as well as the influence of low-molecular-weight polar substances and nanoparticles that impart functional properties to the materials.

2. Materials and Methods

2.1. Materials

Polyhydroxybutyrate (PHB) from "Biomer" (Taunus, Germany) with molecular weights of 3.0×10^5 , 4.6×10^5 and 8.5×10^5 was used in this study. The pure chemical solvents used were dioxane, chloroform, formic acid and dichloroethane. Tetrabutylammonium iodide (TBAI) $\{[\text{CH}_3(\text{CH}_2)_3]_4\text{N}\}$ was added to the forming solution to increase its electrical conductivity during the electrospinning process. The electrospinning of nonwoven fibrous materials based on PHB was carried out using an experimental laboratory setup (Figure 1).

The process involved a dynamic viscosity of the solution of 9 Pa·s, electrical conductivity of $\sim 10^{-3} (\Omega \cdot \text{m})^{-1}$, volumetric flow rate of the forming solution of $10\text{--}12 \cdot 10^{-5} \text{ g/s}$, electric field voltage of 15 kV, electrode distance of 18 cm, and capillary diameter of 0.1 mm. The model drug used was dipyridamole—(2,2',2'',2''')-(4,8-di-1-piperidinylpyrimido [5,4-d]pyrimidin-2,6-diyl) dinitrilo] tetraethanol (“hdh”) with a molecular weight of 504.53 g/mol.

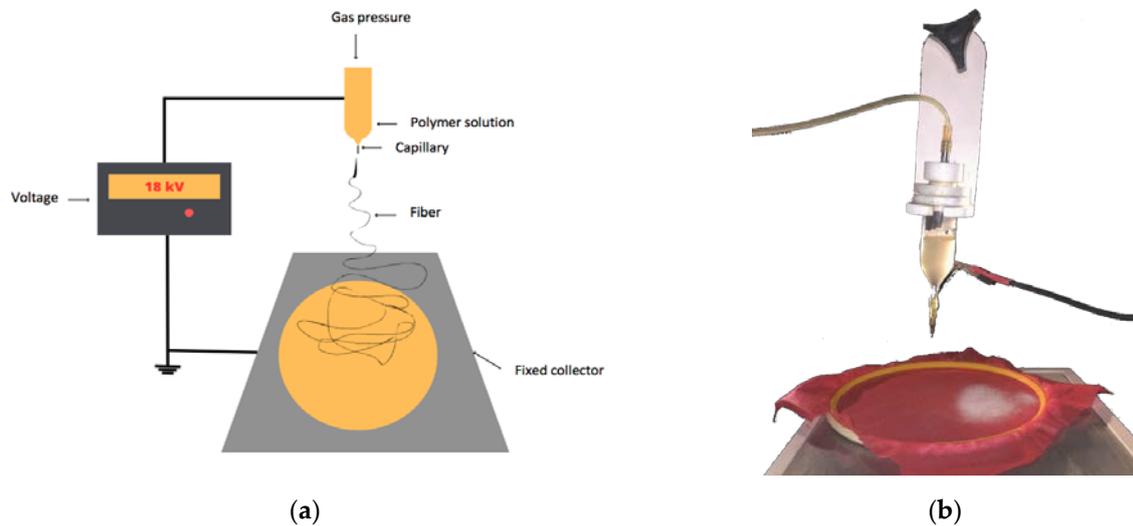


Figure 1. Scheme of the electrospinning process (a) and the working section of a single-capillary electrospinning unit (b).

The iron chloride complex with tetraphenylporphyrin (FeCl-TFP) was obtained according to the method described in [11]. The modifying additives included titanium dioxide (TiO₂-anatase) with an average particle size of 28 nm and a specific surface area of 171 m²/g [12] and a nanocrystalline silicon composition nc-Si/protective shell (SiO₂) with an average particle diameter of 5–7 nm (silicon core diameter 1.5–3.5 nm) and a specific surface area of 260–300 m²/g. The iron chloride complex with tetraphenylporphyrin (FeCl-TFP) was obtained according to the method described in [11]. The modifying additives included titanium dioxide (TiO₂-anatase) with an average particle size of 28 nm and a specific surface area of 171 m²/g [12] and a nanocrystalline silicon composition nc-Si/protective shell (SiO₂) with an average particle diameter of 5–7 nm (silicon core diameter 1.5–3.5 nm) and a specific surface area of 260–300 m²/g [13].

2.2. Methods

Electron paramagnetic resonance (EPR) spectra (X-band) were recorded using an automated EPR spectrometer EPR-V (IHFM RAS, Russia, Moscow). The microwave power in the resonator was kept below 7 mW to avoid saturation effects. The modulation amplitude during spectrum recording was always significantly less than the width of the resonance line and did not exceed 0.5 Gs. A stable nitroxyl radical, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), was used as the probe. The radical was introduced into the fibers from the gas phase at a temperature of 50 °C for an hour. Differential scanning calorimetry (DSC) analysis was performed using a Netzsch DSC 204 F1 instrument in an argon (Ar) inert environment with a heating rate of 10 °C/min. The fibrous materials' geometry was investigated using optical microscopy (MBI-6) and scanning electron microscopy with a “Hitachi TM-1000” scanning electron microscope (Japan) at an accelerating voltage of 20 kV. A layer of gold with a thickness of 100–200 Å was sputtered onto the surface of the nonwoven fibrous material samples. The crystalline structure of the samples was examined via X-ray diffraction using HZG-4 (Ni-filter) and DRON-3M (Russia) diffractometers (graphite flat monochromator) with CuK α radiation (reflection mode). The experimental data were processed using the Profile Fitting V 4.0 program. The qualitative phase analysis of the samples was conducted using the JCPDS PDF-2 database and the ICSD structural database.

3. Results

3.1. Effect of Solvent Parameters on the Structure of Poly-3-hydroxybutyrate Matrices

One of the most important technological aspects of the formation of polymeric films or fibrous materials is the choice of solvent for the base polymer. Solvents differ not only in their boiling point and molecular weight but also in their degree of polarity. Let us consider the influence of solvent polarity on the supramolecular structure of polyhydroxybutyrate (PHB) matrices. For this purpose, we used the method of differential calorimetric analysis.

Figure 2 shows typical heating thermograms of PHB films.

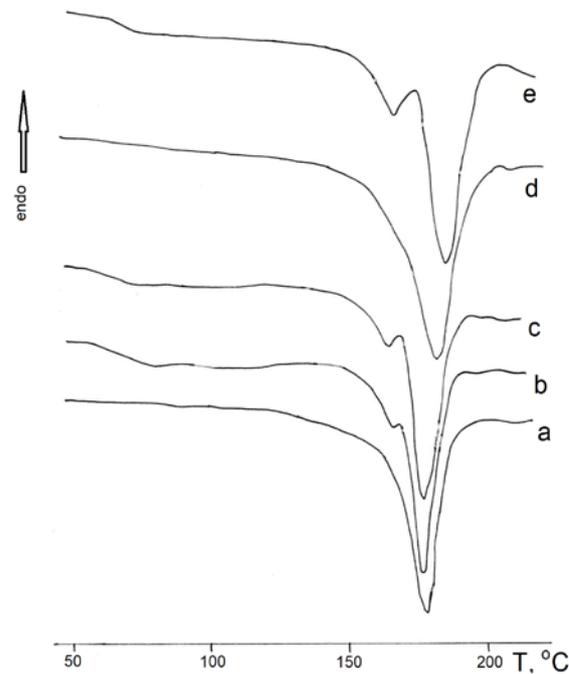


Figure 2. Heating thermograms of PHB-based films: a—pristine polymer; b—cast from dioxane; c—cast from chloroform; d—cast from formic acid; e—cast from dichloroethane.

From the analysis of the thermograms, it can be observed that the original structure of PHB is disrupted after treatment with the solvents: an amorphous phase appears, characterized by a distinct glass transition, and a fine crystalline modification or regions with disrupted crystallinity emerge. This is evidenced by the appearance of a low-temperature melting peak.

Table 1 presents the thermophysical properties of the PHB films with different solvents and solvent parameters. From the table, it can be seen that with an increase in the solvent's dipole moment, the crystalline phase of PHB improves (becomes more ordered). This is evidenced by the increase in the polymer's melting temperature (T_m), as shown in Figure 3.

Table 1. Thermophysical characteristics of PHB films with different solvents.

Solvent	DGm, J/g	T_m , °C	T_g , °C	DCp, J/g·K	Solvent Parameters	
					m, D	e 1/2
Polymer Material Parameters						
Dioxane	−0.076	174	63.0	0.39	0.45	10.05
Chloroform	−0.140	175	53.9	0.24	1.15	9.3
Formic acid	−0.106	176	-	-	1.4	13.5
Dichloroethane	−0.173	179	74.0	0.1	2.06	9.0

Where: DGm, J/g—Gibbs melting energy; T_m , °C—melting temperature; T_g , °C—glass transition temperature; DCp, J/g·K—specific heat capacity; e 1/2—cohesion energy density; m, D—dipole moment.

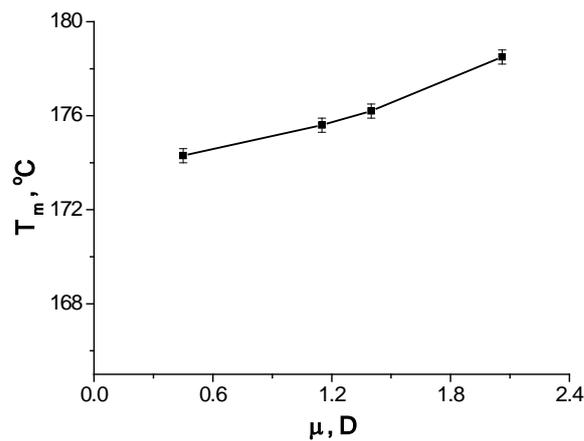


Figure 3. Dependence of PHB melting temperature (T_m) on the solvent's dipole moment (μ).

Concurrently, the specific heat capacity (DC_p) of PHB decreases. This may be related to a decrease in the proportion of the amorphous phase in the polymer.

The PHB molecule contains a complex ester group in its main chain that is capable of interacting with polar solvent molecules. As a result, the conformation of macromolecules in both the crystalline and amorphous regions of the polymer can change under the influence of solvent molecules. The structure of the crystallites is stabilized, and the macromolecules in the amorphous phase lose their flexibility. These effects were observed by other authors [14], who studied the influence of water molecules on PHB films. It was found that the interaction with polar water molecules leads to the formation of hydrogen bonds between neighboring chains, resulting in the stabilization of the polymer's crystalline structure. The hydrogen bonding network formed at the crystallite boundaries enhances the orientation of crystallites in the polymer matrix.

In the present study, among the considered solvents, which have a dipole moment lower or higher (dichloroethane) than that of water (1.84 D) [15], these effects may occur to a lesser extent due to the presence of PHB films with defective crystalline structures, which exhibit lower melting temperatures, as shown in Figure 1.

In conclusion, an increase in solvent polarity corresponds to an increased ability of the solvent to interact with polar groups of PHB. As a result of this interaction, the crystallites are improved, and the amorphous phase of the polymer is densified during film formation.

This study also revealed that the changes in the Gibbs melting energy of the PHB crystalline phase and the cohesion energy density of the solvent molecules are well-correlated in a certain sequence, as shown in Table 1.

Cohesion energy density is known to characterize the degree of intermolecular interaction in a substance [16]. From Table 1, it follows that decreased intermolecular interaction in the solvent leads to an increase in disorder in the crystalline phase of the PHB films, characterized by a decrease in the Gibbs melting energy. In other words, the lower the level of intermolecular interaction in the solvent is, the higher the mobility of its molecules is, and consequently, the higher their rate of transition to the vapor phase (evaporation) is. Due to the different rates of phase transition of molecules in the considered solvents, the formation of PHB films proceeds differently. This is reflected in the degree of completion of the crystallization process and the parameters of the polymer's crystalline structure.

Based on the conducted research, it can be concluded that with an increase in the polarity of the solvent, there is an increase and improvement in the crystalline structure, and the proportion of the amorphous phase of PHB decreases. With a decrease in the degree of intermolecular interaction in the solvent, the proportion of defective crystalline phase in PHB films increases. It was found that the highest-quality films are obtained from chloroform. Films obtained from dioxane have a non-homogeneous, heterogeneous structure. In the course of the experimental work on solvent combination, it was found that high-quality films can be obtained from dioxane by re-dissolving the films from chloroform.

Films from dichloroethane were characterized by increased brittleness and heterogeneity. Combining solvents did not improve the quality of the films. The films based on formic acid were not cohesive and disintegrated into fragments after the desorption of the solvent. Additionally, formic acid accelerates the hydrolysis processes of PHB. Therefore, based on the analysis of the film morphology, chloroform was chosen as a good solvent for obtaining homogeneous film materials for the study of water sorption–diffusion properties. In addition to solvent characteristics, important factors for fiber structure formation include polymer solution parameters. The fiber morphology primarily determines the geometric parameters of the monofilament nonwoven fibrous material. Furthermore, in this study, we attempted to summarize the influences of the main technological characteristics of the polymer solution on the electroforming and structure of polyhydroxybutyrate (PHB) fibers.

3.2. Influence of the Main Technological Characteristics on the Structure of the Fibrous Matrices of Poly-3-hydroxybutyrate

As a large number of factors are responsible for various stages of electrospinning, researchers and technologists are faced with the task of identifying the most significant and dominating characteristics that have the greatest impact on the fiber's structure, morphology, porosity, and geometry. This is typical of various polymer systems. For example, a solution of natural chitosan or chitosan lactate with polyethylene oxide is perfectly formed with the addition of ethyl alcohol, but the technological parameters of electrospinning have little effect on the morphology of the material. The viscosity of the spinning solution is determined by the polymer concentration as well as the interpolymer interactions [17]. In this regard, we will now consider some key physicochemical characteristics of polymer solutions of PHB intended for electrospinning.

The geometric parameters of monofilaments primarily determine the morphology of the nonwoven fibrous material (packing density, filament orientation, defectiveness, etc.). At the same time, they affect a number of performance properties, including diffusion, physical–mechanical and biomedical properties, etc. The geometry of the fiber mainly depends on the polymer's molecular weight, viscosity, electrical conductivity, and solution flow rate (productivity).

In Figure 4a,b, the dependencies of the PHB fiber diameter on the productivity of the electroforming process are presented for 5% and 7% polymer solutions in chloroform.

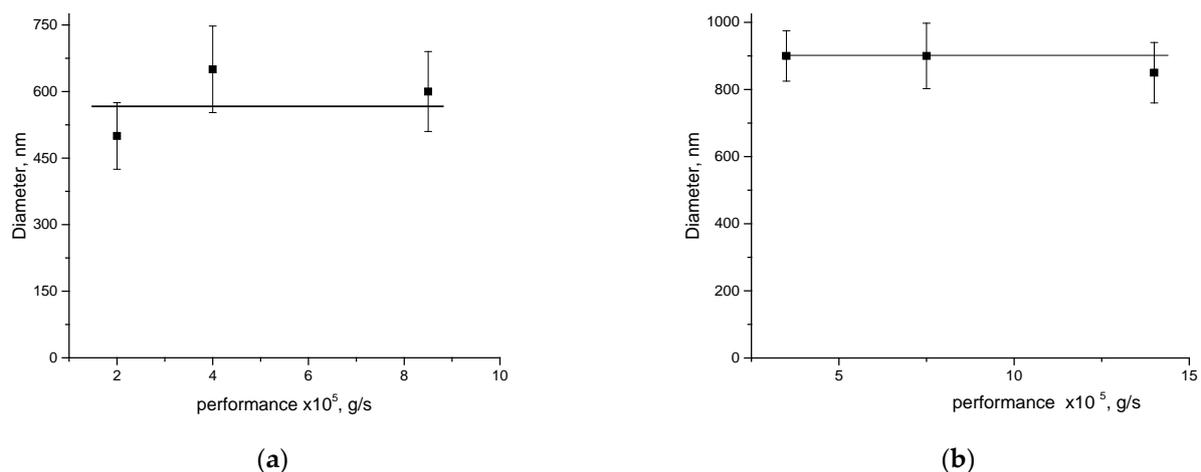


Figure 4. The dependence of the fiber diameter on the performance of the electrospinning process of 5% PHB (a) and 7% PHB (b) in chloroform.

As can be seen in Figure 4, the fiber diameter does not depend on the performance of the electrospinning process at different concentrations of PHB in solution. Apparently, as a result of the presence of strong intermolecular interaction in the PHB solution, as evidenced

by a high degree of crystallinity (60–80%), an increase in the productivity of fiber formation does not lead to a change in the degree of crystallinity or free intermolecular volume.

Figure 4 shows the dependence of the fiber diameter on the molecular weight of PHB for the 7% solutions in chloroform.

As shown in Figure 5, there is an increase in the diameter of the fiber with an increase in the molecular weight of the medium-viscosity PHB. The increase in diameter with an increase in the length of the macromolecular chains of PHB is quite natural and is explained by the increase in the number of intermolecular engagements in the polymer solution, which prevent the stretching of the jet during electroforming. The mesh of physical meshes formed in the solution interferes with orientation processes and increases the viscoelastic properties of the polymer system. The formation of a network of intramolecular entanglements, as well as the growth of the crystalline phase, will lead to an increase in the mechanical characteristics of the fibers. This aspect will be considered by us in a separate scientific publication.

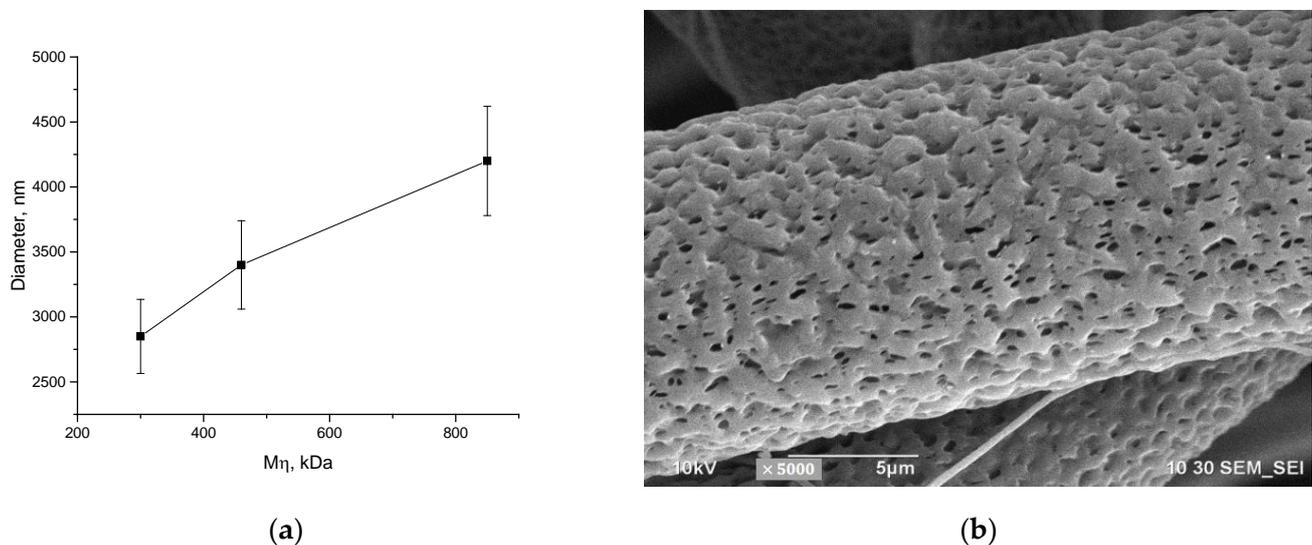


Figure 5. (a) The dependence of the fiber diameter on the molecular weight of PHB (for 7% solutions in chloroform); (b) SEM microphotograph of fiber surface.

In the process of electrospinning, the electric field creates free ionic charges that migrate along the polymer solution jet from one electrode to another. In organic nonionic polymer solutions with low dielectric permittivity, the concentration of such ions is extremely low, which determines the low values of the electrical conductivity of the molding system. Such systems include solutions of PHB, which is known to be highly soluble in chloroform, dichloroethane and some other nonionic organic solvents [18].

The flow of the primary jet of the polymer solution between two oppositely charged electrodes is associated with two processes: the interaction of an electric field with the polymer solution and the evaporation of the solvent, resulting in the formation of an ultrathin fiber. The first process is largely determined by the electrical conductivity of the polymer solution. In this case, the electromechanical effect on the formed polymer jet sets the conditions for changing the diameter and degree of defect of the resulting ultrathin fiber [19]. The second process is determined by the intermolecular interaction between the polymer and the solvent, as well as the cohesion energy of the solvent. When the solvent diffuses from the fiber, micro- and nanoporous systems are usually formed (Figure 5b).

The effect of electrical conductivity and viscosity on the electrospinning process of a binary solution of PHB in chloroform was studied (Figure 6). In particular, it was found that the low electrical conductivity of the PHB solution prevents the formation of fibers of uniform thickness, as demonstrated in Figure 6a.

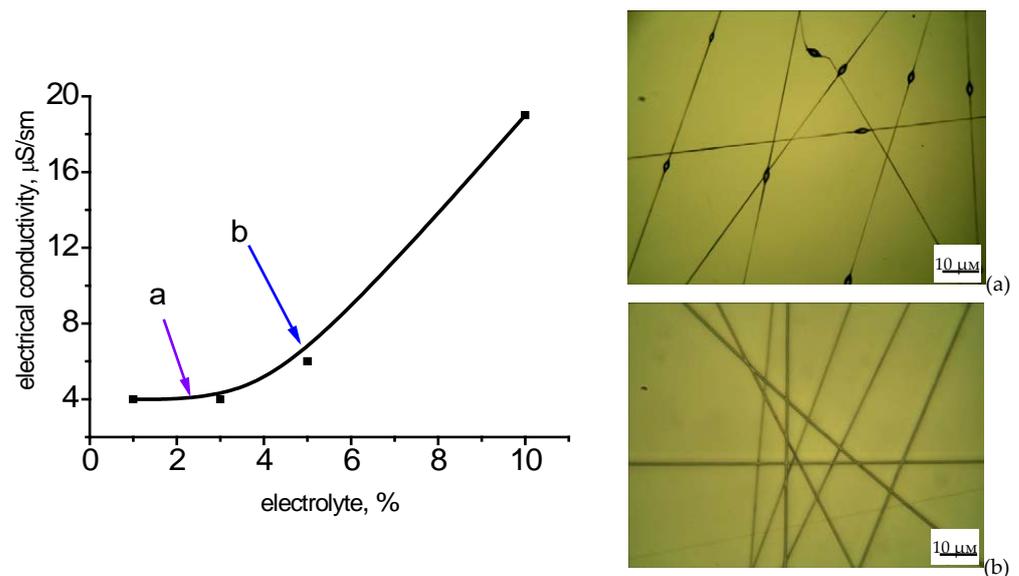


Figure 6. The dependence of the electrical conductivity of the PHB solution in chloroform on the concentration of the electrolyte. Microphotographs of the fibers formed at low electrical conductivity (a). Optimal electrical conductivity (b). Left subfigures show microphotographs with low (a) and optimal (b) electrical conductivity.

The electrical conductivity can be regulated by the introduction of an electrolyte into the solution for electrospinning. Figure 6 shows the dependence of electrical conductivity on the concentration of the electrolyte and that of the diameter of the fibers on the electrical conductivity of the PHB solution in chloroform. The concentration of the electrolyte has a great impact on the electrical conductivity of the solution, which leads to changes in the diameter of fibers (Figure 7). These dependencies are exponential. The initial section is characterized by a low level of indicators, which is reflected in the formation of a defective fiber structure (thickening). In the case of low electrical conductivity, the fiber is not formed at all, but droplet formation occurs. When the optimal level of indicators is reached, smooth fibers are formed. These dependencies are quite closely correlated with the dependence of the viscosity of the PHB solution on the concentration of the polymer (Figure 8). This correlation is primarily related to the properties of the polymer solution at the polymer–air interface. The surface tension determines the conditions for the extraction of the jet and its disintegration into separate fragments (droplets).

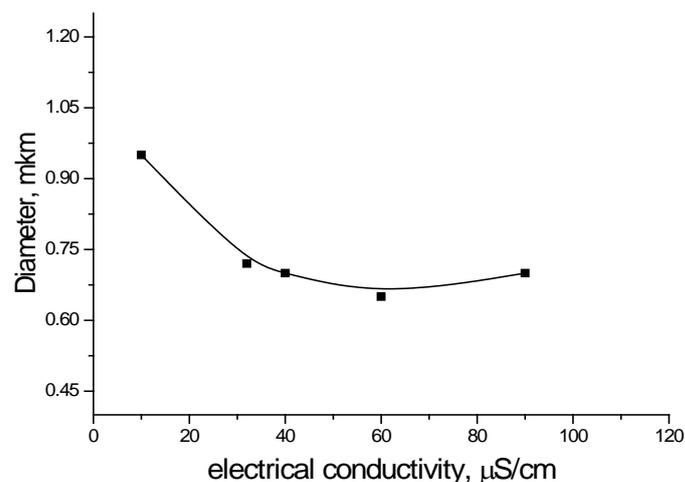


Figure 7. The dependence of the diameter of the fibers on the electrical conductivity of the PHB–chloroform–electrolyte system.

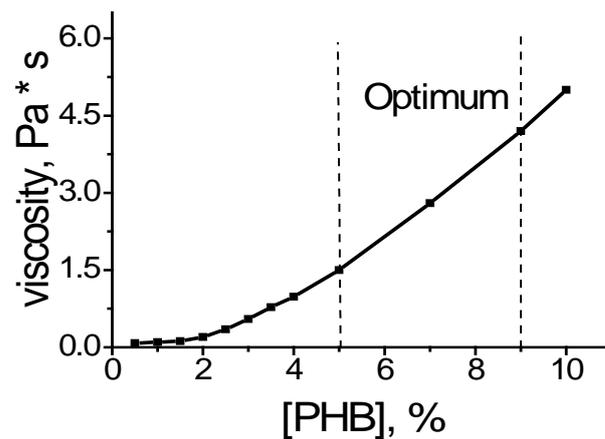


Figure 8. Dependence of the viscosity of the solution on the concentration of PHB.

The dependence of the average diameter on the electrical conductivity is characterized by an exponential descending curve (Figure 7). With increasing electrical conductivity, the average diameter decreases to a certain value, and then there is a tendency towards some growth. This growth is determined by an increase in the viscosity of the solution due to the high concentration of the electrolyte.

A gradual increase in the concentration of PHB in the solution leads to the emergence and increase in the number of intermolecular knots of engagement and interlacing of the polymer chains, which allows the polymer solution to stretch into a thin jet and form a fiber at an appropriate concentration (Figure 9). At a low polymer concentration, the intermolecular entanglements are not sufficient to form a stable jet, and it breaks up into individual droplets. As shown in Figure 9, this occurs in the concentration range of 1–3 wt.% PHB. In the transition region of concentrations of 3–6 wt.% PHB, the lack of molecular meshing does not lead to the disintegration of the jet but to the formation of fibers of complex geometry with alternating cylindrical sections and teardrop-shaped thickenings. At these concentrations, the polymer solution exhibits a sufficiently high value of surface tension, which does not cause the jet to disintegrate into separate fragments. At an optimal concentration of PHB in solution over 6 wt.%, the number of molecular meshes is large enough to form smooth cylindrical fibers. It should be noted that with an increase or decrease in the molecular weight of the polymer, this dependence shifts to the region of lower or higher concentrations.

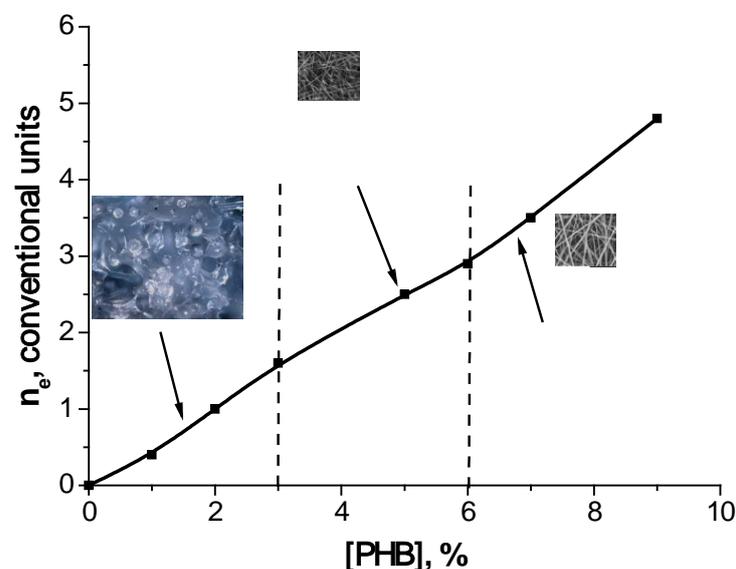


Figure 9. Dependence of the number of engagements and artefacts on the polymer concentration.

Since the studied fibrous materials are recommended for use in medicine as matrices for the prolonged delivery of drugs, antiseptics and tissue engineering, next, we will consider the effects of these substances on the fiber structure. For the model experiment, we selected substances with terminal hydroxyl groups and a complex containing a metal halide. Intermolecular interactions of these components with the polar groups of PHB can be expected in the process of fiber formation.

3.3. Influence of Polar Molecules on the Structure of the Fibrous Matrices of Poly-3-hydroxybutyrate

The presence of polar functional groups or complexes with metal in a chemical compound (medicinal, biologically active and antiseptic substances) should affect not only the technological characteristics of the molding solution but also the processes of fiber structure formation. As an illustration, we chose two different substances: dipiuidamol (DPD), containing terminal -OH groups, and the iron (III) chlorine terrafenylporphyrin (FeCITPP), containing ferric chloride (3+) as part of the complex. Figure 10 shows the structural formulas of these compounds.

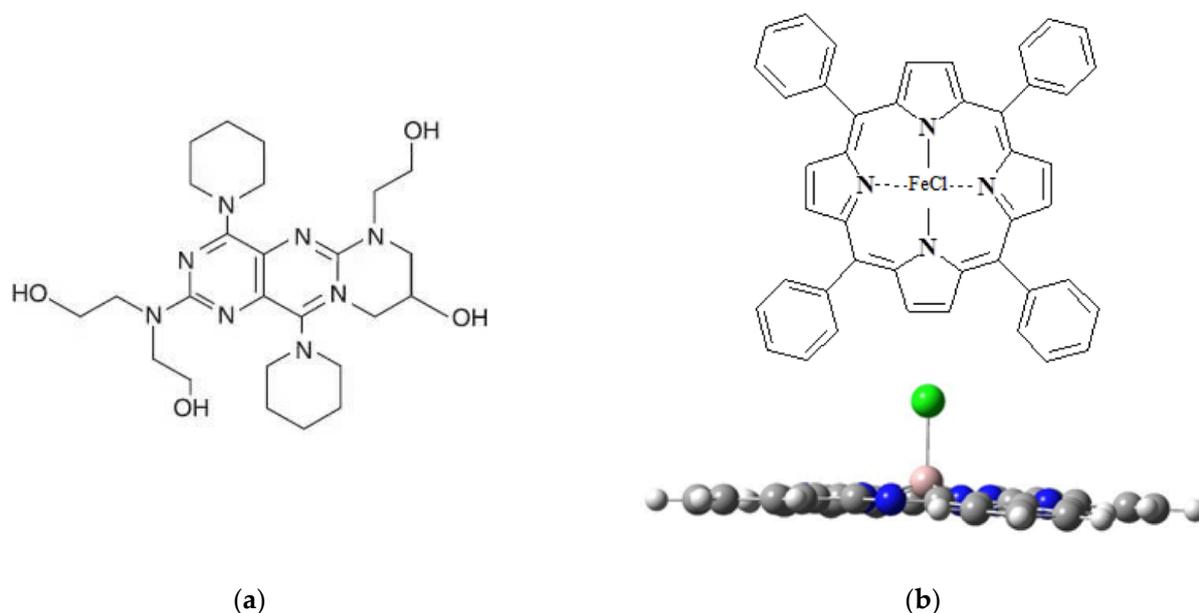


Figure 10. Structural formulas of DPD (a) and FeCITPP (b).

Since the presence of foreign substances is prohibited in biomedical materials, the electrolyte was not introduced into the molding solution. However, as our research has shown, the introduction of a medicinal substance, antiseptic or other ingredient containing polar groups of atoms into the molding solution can improve the technological parameters of the solution. This was demonstrated on the PHB-DPD and PHB-FeCITPP fibrous matrices.

Figure 11 shows that with an increase in the concentration of DPD, the geometry of the fibers changes from transitional (cylinders-drops) to smooth and cylindrical. At the same time, the fibers themselves have a porous structure. The average diameter of the fiber is 2–5 microns, and the pore size ranges from 0.05 to 0.2 microns.

The supramolecular structure of PHB changes with the increasing DPD concentration. Figure 12a shows the dependence of the enthalpy of melting of PHB on the concentration of DPD (DSC method). With an increase in the content of DPD, an increase in the enthalpy of melting of PHB is observed, which indicates an increase in the degree of crystallinity. DPD particles are effective nuclei of crystallization. At the same time, the average size of the crystallites practically does not change, as indicated by the invariance of the melting temperature (168–169 °C).

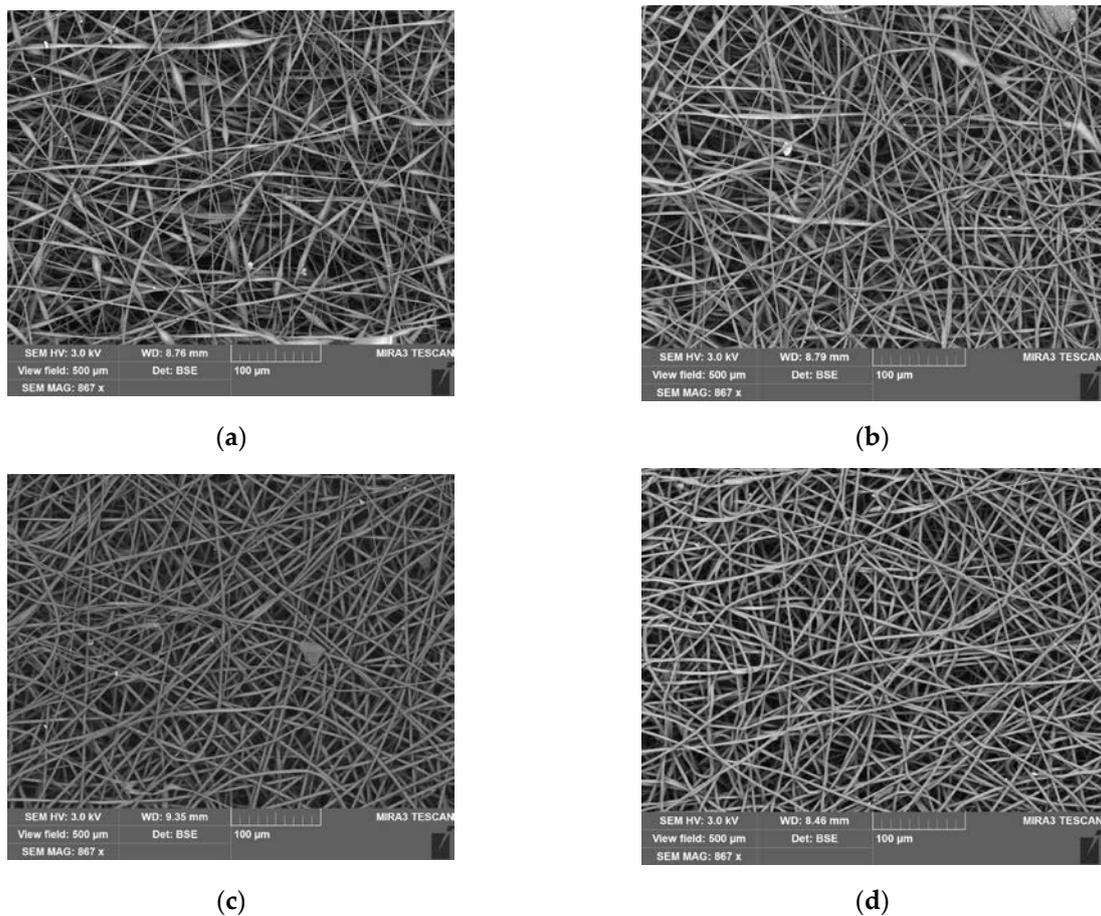


Figure 11. SEM images: PHB (a); PHB + 1% DPD (b); PHB + 3% DPD (c); PHB + 5% DPD (d).

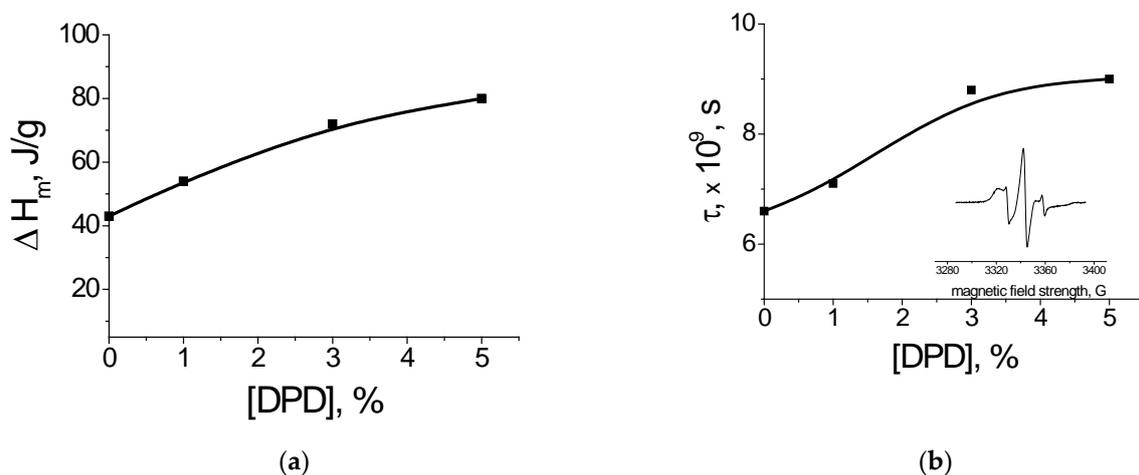


Figure 12. The dependence of: (a) the enthalpy of melting; (b) the correlation time of PHB on the concentration of DPD.

The analysis of the amorphous phase of PHB fibers via the EPR method using a probe (TEMPO) (Figure 12b) showed the presence of a superposition of the spectra of the probe rotation speeds, showing a disequilibrium of the structure of the amorphous phase in the fibers: the presence of regions with different packing densities of macromolecule segments. The dependence of the average correlation time on the concentration of DPD is shown in Figure 12b. It can be seen that with an increase in the concentration of DPD, the correlation time increases. This allows us to highlight the compaction of the amorphous phase in

the fibers. This dependence correlates with the DSC data, which show an increase in crystallinity (Figure 12a).

For comparison, we examined the structure of heterogeneous fibrous matrices based on PHB and FeCITPP with high antibacterial properties. This compound is a derivative of chlorophyll and has a high antibacterial effect due to its specific reaction with oxygen [20]. Figure 10b shows the structural formulas of one of the FeCITPP samples. Figure 13 shows SEM images of the electrospun PHB-FeCITPP materials.

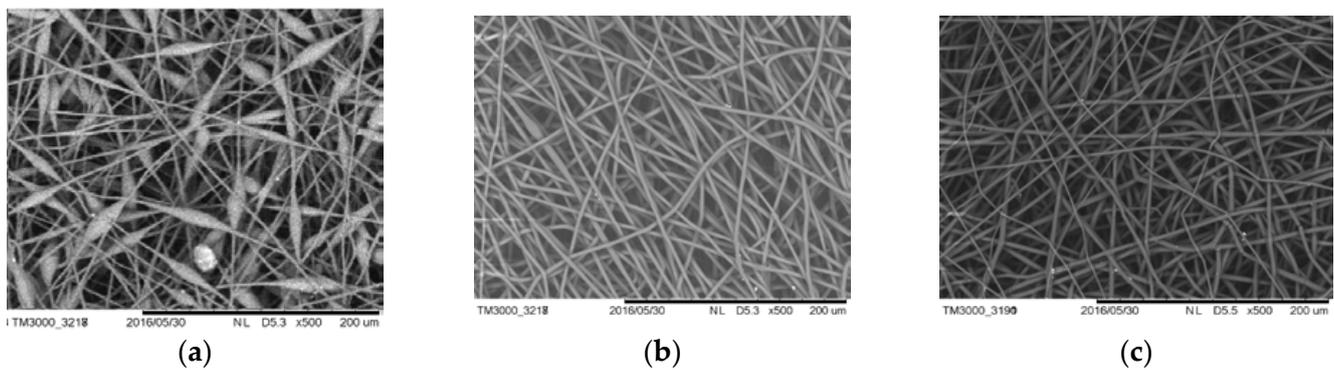


Figure 13. SEM images PHB (a); PHB + 3% FeCITPP (b); PHB + 5% FeCITPP (c).

As in the case of DPD, the addition of 1–5 wt.% FeCITPP improves the quality of the polymeric solution for electrospinning process, which leads to the formation of smooth fibers with an average diameter of 2–4 microns. The strong polarity of this complex may cause its active interaction with oxygen-containing groups of PHB during the formation of fibers. Table 2 shows the results of the study of the fibers using the DSC method.

Table 2. Characteristics of the crystalline phase of PHB fibers with FeCITPP.

Content of FeCITPP, %	Heating		Cooling	
	X of Melting, %	T _m °C (±10)	X of Crystallisation, %	T _{cr} °C (±10)
0	65	175	68	94
1	66	170	45	68
3	68	169	59	89
5	85	169	58	76

Where (X) is the degree of crystallinity, with the melting point (T_m) and crystallization (T_{cr}).

Table 2 shows that the increase in the concentration of FeCITPP leads to an increase in the degree of crystallinity of PHB. In this case, a typical mechanism of nucleation of the crystalline phase is observed. Upon the cooling of the material, the inhibition of crystallization processes in PHB is visible, which is associated with the strong intermolecular interaction and high viscosity of PHB in the melted state.

Studying the crystalline structure of PHB via the X-ray method showed that with an increase in the concentration of FeCITPP, the longitudinal size of the crystallites and the long period of the crystalline phase of PHB increased (Figure 14). This observation is consistent with the overall increase in the degree of crystallinity measured using the DSC method (Table 2). This is in good agreement with the patterns obtained earlier when adding the DPA.

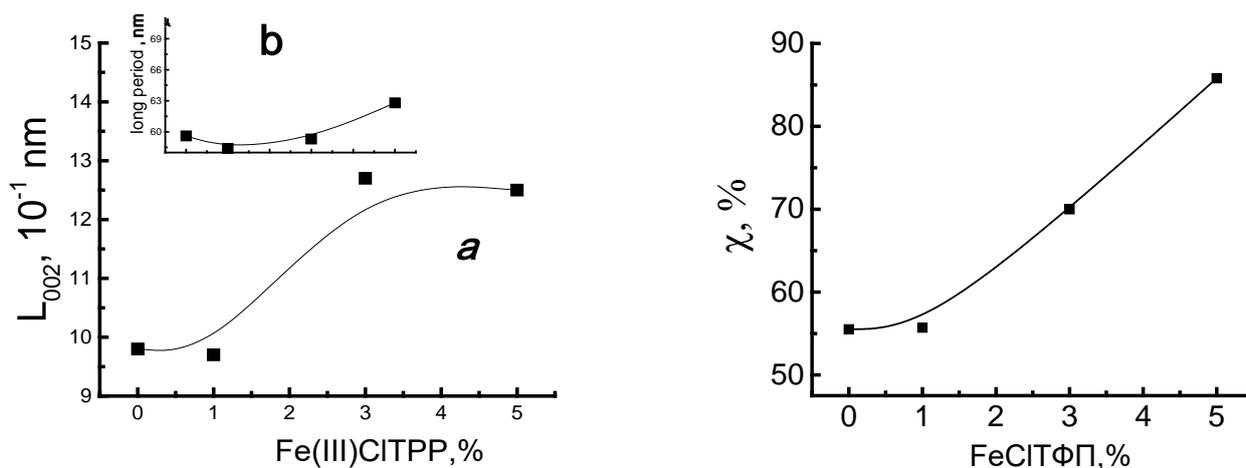


Figure 14. Dependence of the longitudinal size of crystallites (a) and the long period (b) of PHB on the content of FeCITPP (left) and dependence of the crystallinity degree on the content of FeCITPP (right).

The results of the EPR study of the PHB- FeCITPP fibers are shown in Figure 15.

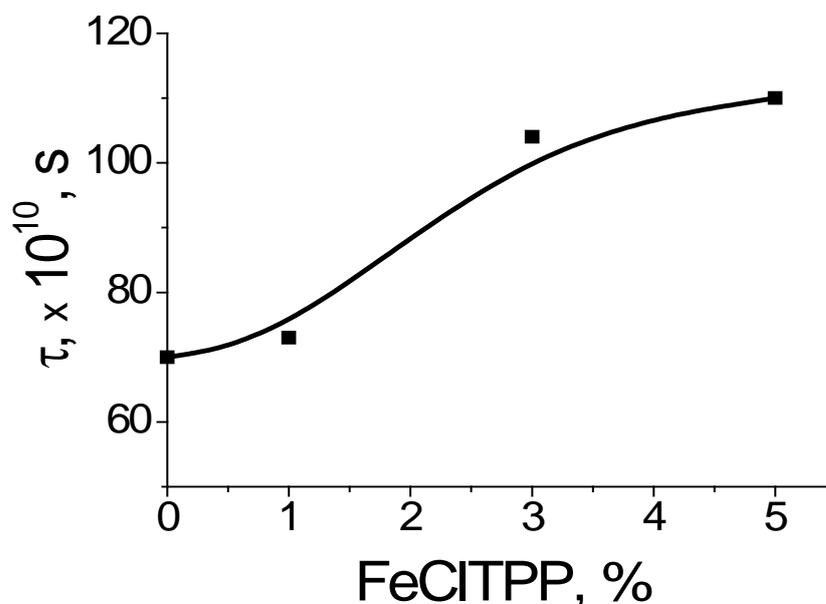


Figure 15. Dependence of the correlation time of the probe on the concentration of FeCITPP.

The introduction of FeCITPP into PHB leads to the compaction of the amorphous phase of the polymer during the formation of the fiber. The proportion of dense regions increases with an increase in the concentration of FeCITPP. Apparently, the disequilibrium of the fiber is caused by a large number of mesomorphic structures (unfinished crystals), the formation of which occurs as a result of the intermolecular interactions of polar groups of PHB with strongly polar FeCITPP complexes. Adhesive bonds prevent the realization and complete passage of the crystallization process of the polymer matrix.

Both DPD and FeCITPP are highly soluble in chloroform and are distributed evenly in the fiber on the molecular level. In the case of polar nanoparticles, a different structural formation of PHB can be expected due to the insolubility of the particles in chloroform and their agglomeration in the fiber during the formation of the supramolecular structure. Our task was to study the effects of titanium and silicon oxide nanoparticles on the formation of the crystal structure of the fiber.

3.4. Effect of Polar Nanoparticles on Poly-3-hydroxybutyrate Fibers

It is known that nanoparticles in crystallizing polymers can act as crystallite nuclei [21]. However, the question of how ultra-low concentrations of polar nanoparticles will behave in a moderately hydrophobic and weakly polar biopolymer of PHB [22] requires clarification. The data of the DSC studies are presented in Table 3.

Table 3. Characteristics of PHB fibers with nanoparticles at a concentration of 0.1 wt.%.

Sample	T _m , °C	T _{cr} , °C	χ, %	d, μm
PHB	175	94	65	3.0–5.0
PHB + TiO ₂	176	88	66	2.0–3.0
PHB + SiO ₂	177	87	67	0.8–1.5

T_m—melting temperature, °C; T_{cr}—crystallization temperature, °C; χ—crystallinity degree (obtained from DSC), %; d—average fiber diameter, μm.

It can be seen from the data (Table 3) that the polar nanoparticles in the PHB matrix contribute to an increase in the number and size of crystallites, according to the known mechanism of crystallization, which is indicated by an increase in the melting temperature and the degree of crystallinity. At the same time, we can observe a decrease in the crystallization temperature and the size of the average diameter of the fibers. This effect can be explained by the intermolecular interaction between the polar carbonyl and terminal hydroxyl groups of PHB with the polar surface of the nanoparticles as a result of electrostatic forces of attraction. At the same time, during the cooling of the material, the crystallization processes are inhibited, and the amorphized plastic fiber, under the action of tensile stresses, is capable of additional extraction.

4. Conclusions

In this paper, fundamental studies of the structural organization of heterogeneous fibrillar matrices based on poly-3-hydroxybutyrate containing low-molecular polar and nanodispersed substances were carried out. Polar substances create conditions for a uniform charge flow and the formation of an even fiber geometry. The medical substance DPD, the antibacterial substance FeCITPP and the nanoparticles SiO₂ and TiO₂ were selected as modifying additives. The determining role of the polarity of a soluble, low-molecular substance in the formation of the supramolecular structure of PHB fibers was demonstrated. The addition of insoluble inorganic nanoparticles to the polymer matrix led to the changes in the supramolecular structure. Intermolecular interaction was observed between the polymer and additives. This interaction led to the improvement of the crystalline structure of PHB, regardless of the chemical nature of the low-molecular-weight or nanodispersed component in the fiber structure. The polarity of the molecules and nanoparticles led to the appearance of electrostatic forces of attraction in the intermolecular space of the amorphous phase of a weakly polar crystallizing polymer. Due to this, crystallization took place on a deeper level.

It was also observed that the characteristics of the polymer solution largely determine the geometry and morphology of the ultrathin fibers based on PHB. SiO₂ and TiO₂ nanoparticles lead to a decrease in the crystallization rate and, as a consequence, to a decrease in the diameter of the polymeric fibers. The introduction of FeCITPP and DPD complexes into the PHB matrix leads to significant changes in the geometry and morphology of polymer fibers due to introduction of the metal. The action of polar molecules on the polymer is similar to the action of polar nanoparticles. They increase crystallinity via a nucleation mechanism.

The polymer fibrous materials considered in the study can be successfully used to create matrices for the controlled release of drugs, scaffolds for tissue engineering and compounds.

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