DOI: https://doi.org/10.15688/jvolsu10.2016.4.3

УДК 620.3(076)
ББК 24.7

STRUCTURE AND PARAMETERS OF POLYHYDROXYBUTYRATE NANOFIBRES

Anatoliy Aleksandrovich Olkhov

Candidate of Technical Sciences, Associate Professor, Senior Researcher,
Laboratory of Prospective Compositional Materials and Technologies,
Russian University of Economics named after G. V. Plekhanov
Stremyanny Pass., 36, 117997 Moscow, Russian Federation;
N. N. Semenov Institute of Chemical Physics, RAS
aolkhov72@yandex.ru
Kosygina St., 4, 119991 Moscow, Russian Federation

Olga Valeryevna Staroverova

Fellow,
N. N. Semenov Institute of Chemical Physics, RAS
aolkhov72@yandex.ru
Kosygina St., 4, 119991 Moscow, Russian Federation

Aleksey Leonidovich Iordanskiy

Doctor of Chemical Sciences, Professor,
Head of Laboratory of Diffusion Phenomena in Polymer Systems,
N. N. Semenov Institute of Chemical Physics, RAS
aolkhov72@yandex.ru
Kosygina St., 4, 119991 Moscow, Russian Federation

Gennadiy Efremovich Zaikov

Doctor of Chemical Sciences, Professor,
Head of Department of Biological and Chemical Physics of Polymers,
Institute of Biochemical Physics named after N. M. Emanuel, RAS
chembio@sky.chph.ras.ru
Kosygina St., 4, 119334 Moscow, Russian Federation

Abstract. This research work focuses on process characteristics of polymer solutions, such as viscosity and electrical conductivity, as well as the parameters of electrospinning using poly-3-hydroxybutyrate modified by titanium dioxide nanoparticles, which have been optimized. The structure of materials has been examined by means of X-ray diffraction, differential scanning calorimetry (DSC), IR-spectroscopy, and physical-mechanical testing. The fibrous materials obtained can find a wide application in medicine and filtration techniques as scaffolds for cell growth, filters for body fluids and gas-air media, and sorbents.

Key words: spolymer solutions, **t**itanium dioxide nanoparticles**,** X-ray diffraction, IR-spectroscopy, physical-mechanical testing.

Introduction

This research work focuses on process characteristics of polymer solutions, such as viscosity and electrical conductivity, as well as the parameters of electrospinning using poly-3-hydroxybutyrate modified by titanium dioxide nanoparticles, which have been optimized. Both physical-mechanical characteristics and photooxidation stability of materials have been improved. The structure of materials has been examined by means of X-ray diffraction, differential scanning calorimetry (DSC), IR-spectroscopy, and physical-mechanical testing. The fibrous materials obtained can find a wide application in medicine and filtration techniques as scaffolds for cell growth, filters for body fluids and gas-air media, and sorbents.

Development of materials with revolutionary characteristics is closely connected with obtaining nanosized systems. Of greatest interest today are compositions derived from polymers and nanosized objects which show a unique set of characteristics, have no counterparts, and drastically change present ideas about a polymer material.

Titanium dioxide nanoparticles are the most attractive because of the developed surface of titanium dioxide, the formation of surface hydroxyl groups with high reactivity resulted from reacting with electrolytes as crystallite sizes decrease down to 100 Å and lower, and a high efficiency of oxidation of virtually any organic substance or many biological objects.

Many modern applications of TiO_2 are based on using its anatase modification which shows the minimum surface energy and greater concentration of OH-groups on sample surface compared with other modifications. According to Dadachov's patents [4; 5], the nanosized η-modification of TiO_2 is considerably superior to anatase in the above mentioned properties. The main characteristics of titanium dioxide modifications in use are sample composition, TiO_2 modification, nanoparticle size and crystallite size, specific surface area, pore size and pore volume.

Polyhydroxybutyrate (PHB) is the most common type of a new class of biodegradable termoplasts, namely polyoxyalkanoates. It demonstrates a high strength and the ability to biodegrade under natural environmental conditions, as well as a moderate hydrophilicity and nontoxicity (biodegrades to CO_2 and water) [7]. PHB shows a wide range of useful performance characteristics [3]; it is superior to polyesters which are the standard materials for implants, can find application in different branches of medicine, and is of great importance for cell engineering due to its biocompatibility [2].

PHB is a unique sample of a moderate hydrophobic polymer being biocompatible and biodegradable at both high melting and crystallization temperatures. However, its strength and other characteristics, such as thermal stability, gas permeability, and both reduced solubility and fire resistance, are insufficient for its large-scale application.

The objective of the research was to prepare ultra-fine polymer composition fibres based on polyhydroxybutyrate and titanium dioxide and to determine the role played by nanosized titanium dioxide modifications in achieving special properties of the compositions.

Experimental

The nanosized η-TiO_2 and anatase (S12 and S30) were prepared by sulfate process from the two starting reagents, $(TiO)SO_4 \cdot xH_2SO_4 \cdot yH_2O$ (I) and $(TiO)SO_4 \cdot 2H_2O$ (II) correspondingly [8].

Samples of titanium dioxide and its compositions with polymers were analyzed by X-ray diffraction technique, using HZG-4 (Ni filter) and (plane graphite monochromator) diffractometers, CuK $_{\alpha}$ radiation, diffracted beam, in the range of 2θ 2–80°, rotating sample, stepwise mode (the impulse accumulation time is 10 s, by step of 0.02°). Experimental data array was processed with PROFILE FITTING V 4.0 software. Qualitative phase analysis of samples was carried out by using JCPDS PDF-2 database, ICSD structure data bank, and original papers.

Particle sizes (coherent scattering region) of TiO_2 samples were calculated by the Selyakov – Scherrer equation $L = \frac{k\lambda}{\beta \cdot \cos\theta_{hkl}}$, where $\beta = \sqrt{B^2 - b^2}$ is physical peak width for the phase under study (diffraction reflections were approximated by Gaussian function), B is integral peak width, b is instrument error correction ($b \sim 0.14°$ for α-Al_2O_3 as a reference), $k \sim 0.9$ is empirical coefficient, λ is wavelength. Calculations were based on a strongest reflection at 2θ~25°. Standard deviation was ± 5 %.

Starting PHB with molecular weight of 450 kDa was prepared through microbiological synthesis by BIOMER (Germany). Chloroform (CFM) was used as solvent for preparing polymer solution. Both HCOOH (FA) and $[CH_3(CH_2)_3]_4N$ (TBAI) were used as special additives.

Electrostatic spinning of fibres based on PHB and titanium dioxide was carried out with original laboratory installation [6].

The dynamic viscosity of polymer solutions of various compositions was measured as a function of PHB concentration with Heppler and Brookfield viscosimeters. The electrical conductivity of polymer solutions was calculated by the equation $\lambda = \alpha/R$, $Ohm^{-1}cm^{-1}$; the electrical resistance was measured with E7-15 instrument.

The fibre diameter distribution was studied by microscopy (optical microscope, Hitachi TM-1000 scanning electron microscope). Fibre orientation was studied by using birefringence and polarization IR-spectroscopy (SPECORD M 80 IR-spectrometer). Crystalline phase of polymer was studied by differential scanning calorimetry (DSC) (differential scanning calorimeter). The packing density of fibrous materials was calculated as a function of airflow resistance variation with a special manometric pressure unit [1].

Physical-mechanical characteristics of fibrous materials were determined with PM-3-1 tensile testing machine according to TU 25.061065-72. Kinetics of UV-aging was studied with Feutron 1001 environmental test chamber (Germany). Irradiation of samples was carried out with a 375 W high pressure Hg-lamp, at a distance of 30 cm.

For *in vitro* biodegradation studies, the materials were incubated in test tubes filled with 10 ml of 0.025 M phosphate buffer solution (pH = 7.4) at 70 °C for 21 days. At regular time intervals the materials were removed from the buffer and rinsed with distilled water, then placed into incubator at 70 °C for 3 hours, and finally weighed within 0.001 g.

Results and discussion

Diffraction patterns of the nanosized anatase and η-TiO_2 prepared are presented in Figs. 1, *a* and 1, *b* correspondingly. The sample S30 referring to anatase contains trace amounts of β-TiO_2 (JCPDS 46-1238) (Fig. 1, *a*).

Analysis of the obtained size values of coherent scattering regions (L-values) of the η-TiO_2 and anatase samples showed that L = 50 (2) Å and L =100 (5) Å, i.e. crystallite sizes for the η-TiO_2 samples are substantially less.

Time dependencies of the dynamic viscosity of PHB solutions are shown in Fig. 2.

Analysis of the dynamic viscosity of polymer solutions showed how the solution viscosity varies with time as the (HCOOH) – (S1) is added. Most probably, the decrease in viscosity results from the decrease in the molecular weight of polymer.

Examination of the electrical conductivity of polymer solutions and choosing solvent mixture allowed the ($[CH_3(CH_2)_3]_4N$) – (TBAI) concentration in solution to be decreased from 5 down to 1 g/l due to adding the S1. The increase in PHB concentration up to 7 wt. % in a new solvent mixture was gained.

The fibre diameter distribution was studied by using fibres from 5 % PHB solution in chloroform/formic acid mixture and 7 % PHB solution as well. It was found that 550-750 nm diameter fibres are produced from 5 % solution, while 850-1250 nm diameter fibres are produced

from 7 % solution, i.e. the fibre diameter increases as the solution concentration rises (Fig. 3). The increase in the process velocity leads to the fibre diameter virtually unchanged.

Examination of fibrous materials by electron microscopy showed that the fibrous material uncovered by the current-conducting layer decomposes in 1-2 min, when exposed by electron beam.

Examination of polymer orientation in fibres by using birefringence showed that elementary fibres in non-woven fabric are well oriented along fibre direction. However, it is impossible to determine the degree of orientation quantitatively because the fibres are packed randomly.

Analysis of fibrous materials by differential scanning calorimetry showed that at low scanning rates a small endothermic peak appears at 190 ÷ 200 °C which indicates the presence of maximum straightened polymer chains (orientation takes place). Upon polymer remelting this peak disappears.

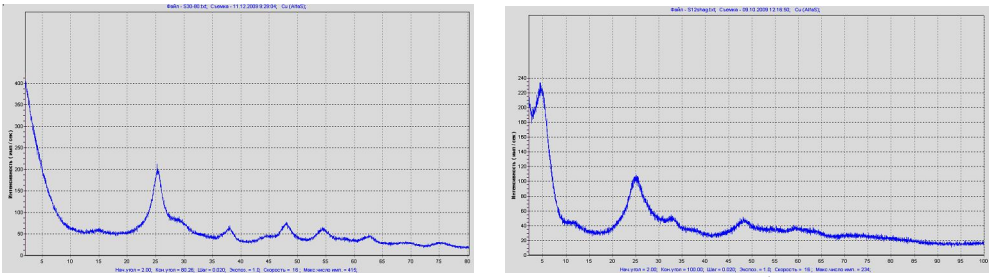
IR-examination showed that this method can be also applied only for qualitative estimation of orientation occurrence.

Measurement of the packing density of fibrous materials showed that the formulation used a day after preparing the solution has the greatest density of fibre packing. Probably, it is concerned with a great fibre diameter spread when smaller fibres are spread between bigger ones. The TiO_2-containing fibres are also characterized by the increased packing density.

The results of powder diffraction analysis of PHB powder (*a*) and PHB fibres obtained from 7 % solution with modifying additives (*b*) and the nanosized TiO_2 modifications (*c*, *d*) are presented in Fig. 4.

The results of physical-mechanical testing of fibrous materials of different formulations are presented in Table 1.

Physical-mechanical tests showed that introducing nanosized TiO_2 into solution substantially alters the properties of the resulting fibrous material.



а б

Fig. 1. Diffraction patterns of anatase (*a*) and h-TiO_2 (*b*):
a – S30; *b* – S12

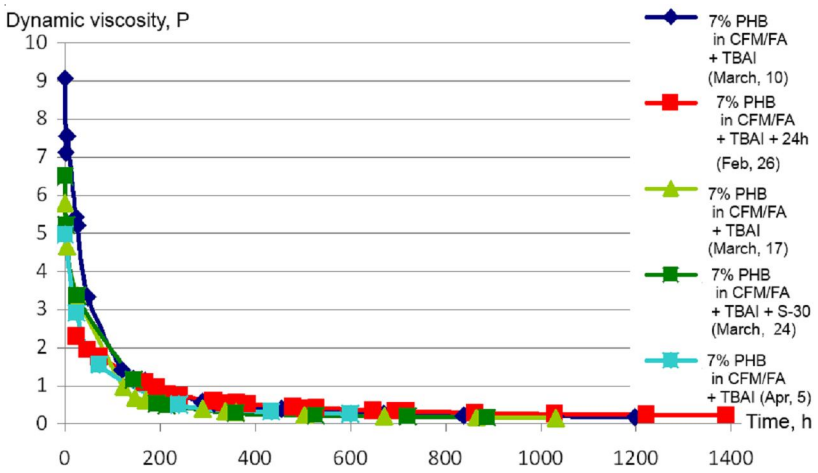


Fig. 2. Dynamic viscosity of PHB solutions as a function of time

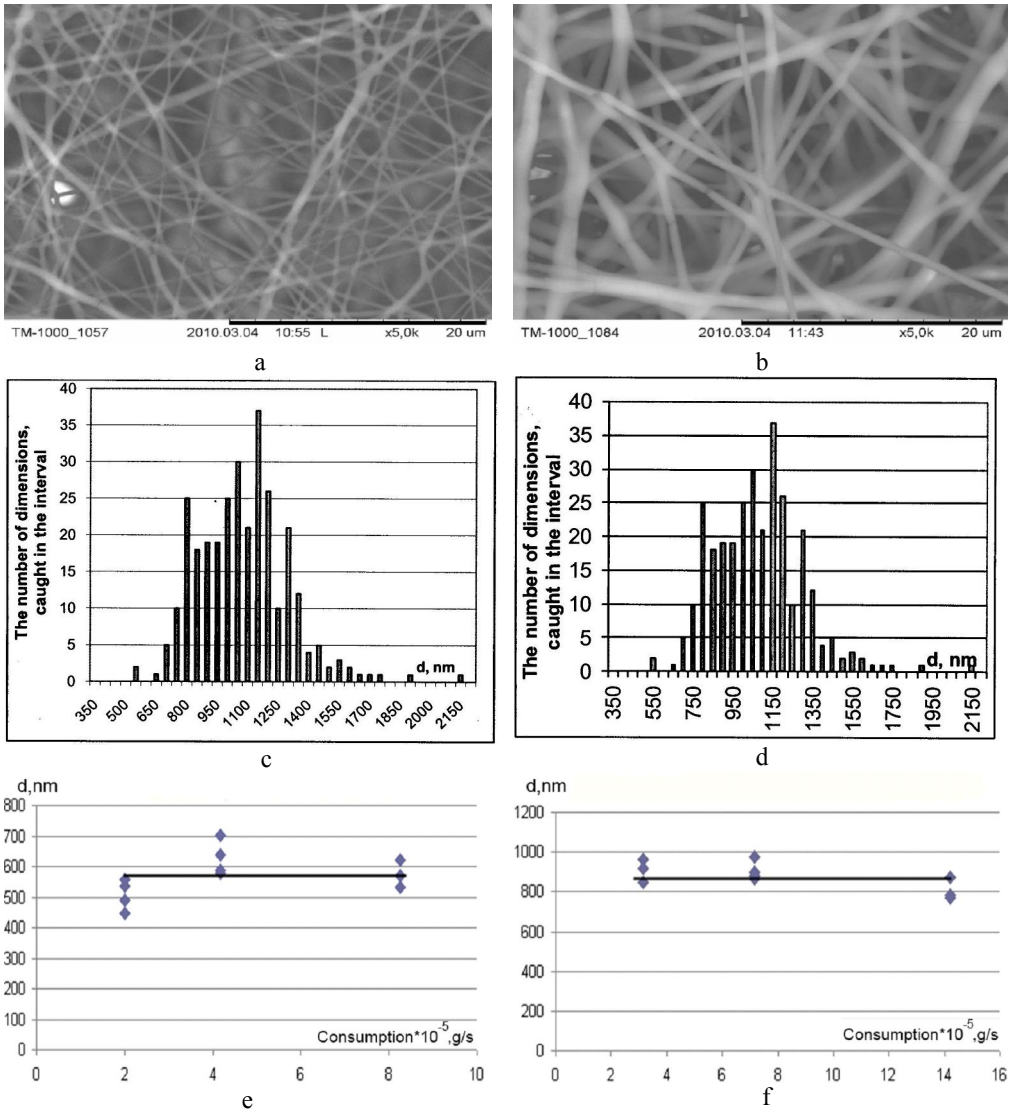


Fig. 3. Microscopic images of fibrous material as a function of PHB solution concentration:
a – 5 %, *b* – 7 %; fibre diameter distributions: *c* – 5 %, *d* – 7 %;
the fibre diameter as a function of the process velocity (flow rate): *e* – 5 %, *f* – 7 %

Non-woven fibrous material contains randomly packed fibre layers. Actually, its deformation can be considered as a "creeping", and more and more fibres while straightening during deformation contribute to the breaking stress growing up to its maximum. In other words, the two processes take place simultaneously, namely fibre straightening and deformation of the fibres straightened.

Obviously, as the TiO_2 content increases the fibre flexibility rises due to the decreased crystallinity. This results in a greater amount of fibres simultaneously contributing to the breaking stress and, consequently, the greater slope of the curve.

Moreover, the addition of both S-12 and S-30 is likely to cause the formation of a firm fibre bonding at crossing points, possibly due to hydrogen bonding. Figuratively speaking, a network is formed. At the beginning, this network takes all the deformation stress. Finally, network breaking occurs followed by straightening and "creeping" of fibres which does not affect the stress growth.

There are different additives used in solutions. By purpose, all additives can be divided into process additives and production additives. The first ones are used to control both viscosity and electrical conductivity of spinning solutions as well as the velocity of fibre formation. The

second ones are intended for obtaining fibrous products with desired properties.

Examination of the crystallinity of fibrous materials, films, and PHB powder showed that main crystallite modification of both PHB powder and fibres and films melts at 175-177 °C, i.e. the morphology of crystals remains unchanged.

For fibres, the low-melting shoulder at 160-163 °C appears which confirms either the presence of smaller crystallites or their imperfection. For the S-12 based formulation, the low-melting peak disappears which is the evidence of more uniform distribution of the additive within the material.

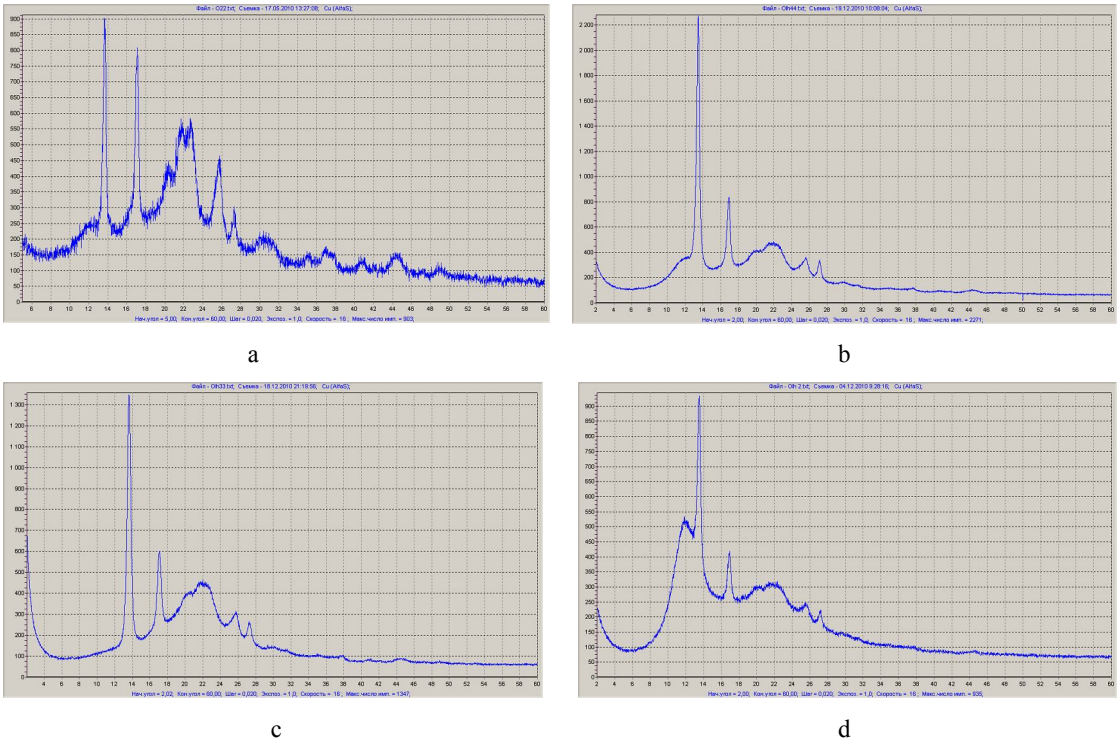
The broadened crystallization peak is observed for the S-12 based samples. The increased friction and decreased chain mobility lead to the obstructed crystallization and the decreased crystallization rate.

The narrowed crystallization peak is observed for the S-30 based samples. Crystallization proceeds only where no contact with this additive is. Hence, the S-12 and S-30 have different energies of intermolecular interaction of PHB chains and the additive surface (Table 2).

The crystallinity was calculated by the following equation:

$$\alpha_{кр} = \frac{H_{пл}}{146},$$

where $H_{пл}$ is melting heat calculated from melting peak area, *J*/*g*; 146 is melting heat of monocrystal, *J*.



a b c d

Fig. 4. Diffraction patterns of: PHB (*a*), PHB-B (7 % PHB+1 % TBAI) (*b*), PHB-B +S 30 (*c*), PHB-B + S12 (*d*)

Table 1

Physical-mechanical characteristics of fibrous materials prepared from polymer compositions as a function of formulation

Formulation	*L*, *m* *	ε, %
PHB + TBAI	724.43	20.83
PHB + TBAI (after a day)	1001.78	12.48
PHB + TBAI + S-12	1430.45	53.37
PHB + TBAI + S-30	1235.91	62.02

Note. * – *L* is breaking length, ε is breaking elongation.

Table 2

Widths of crystallization peaks at the scanning rate of 20 °C/min

Material	Heating No.	*Tm*, °C	Crystallization peak width (at the onset), °C
PHB (starting)	1	174.90	18.61
	2	173.97	18.02
PHB fibres 1g/l TBAI	1	176.83	20.90
	2	169.27–159.74	20.93
PHB fibres 1g/l TBAI a day after	1	176.94	26.24
	2	171.98–163.14	22.80
PHB fibres 1g/l TBAI based on S-12	1	177.49	34.11
	2	170.33	27.38
PHB film from chloroform solution	1	177.21	18.27
	2	171.95–163.10	18.57

The most loosely packed structure, i.e. the most imperfect, is observed for the formulation prepared a day after.

The S-12 based samples demonstrate excessive fibre bonding; the TiO_2 particles themselves obstruct crystallization. In the case of the S-12 the distribution is good.

The S-30 obstructs crystallization to a lesser extent; the fibres crystallize worse, and the chains are not extended.

Crystallization in fibres occurs upon orientation. The additive is not considered as a nucleating agent.

UV-aging tests showed that TiO_2-modified fibres demonstrate greater UV-aging resistance. Although the induction period for S-30 based samples is less than that for other formulations, the UV-degradation rate for the S-30 based sample is comparable to that for the S-12 based one.

For TiO_2-containing samples the increased thermal degradation heat after UV-aging is characteristic since the UV-treated TiO_2 acts as the initiator of both thermal and thermooxidation degradation due to OH-groups traveling to powder granule surface.

The onset temperature of both thermal and thermooxidation degradation decreases due to UV-degradation proceeded not only within amorphous phase but also within crystalline phase, as said above.

The TiO_2 acts as the initiator in UV-aging processes.

Conclusions

1. Physical-mechanical characteristics of fibrous materials increase as the TiO_2 is introduced.

2. The morphology of main PHB crystallites in powder and fibres is kept unchanged. However, the fibres show the low-melting shoulder (small and imperfect crystals). The TiO_2 obstructs crystallization.

3. PHB fibres are characterized by strongly pronounced molecular anisotropy.

4. S-12 based samples show the best thermal- and thermooxidation degradation stability as well as UV-aging resistance.

The results obtained can be considered as the ground for designing new biocompatible materials, such as self-sterilizing packing material for medical tools or a support for cell growth.

REFERENCES

1. Barham P.J., Keller A., Otum E.L., Holms P.A. *J. Master Sci.,* 1984, 19 (27), 81-279.

2. Bonartsev A.P., et al. *Journal of Balkan Tribological Association*, 2008, no. 14, pp. 359-395.

3. Boskhomdgiev A.P. *Author's Abstract of Thesis for PhD in Biology*. Moscow, 2010.

4. Dadachov M. *U.S. Patent Application Publication. US 2006/0144793*.

5. Dadachov M. *U.S. Patent Application Publication. US 2006/0171877*.

6. Filatov Yu.N. *Electrospinning of Fibrous Materials (ES-Process)*. Moscow, Khimiya Publ., 2001. 231 p.

7. Fomin V.A., Guzeev V.V. *Plasticheskie Massy*, 2001, no. 2, pp. 42-46.

8. Kuzmicheva G.M., Savinkina E.V., Obolenskaya L.N., Belogorokhova L.I., Mavrin B.N., Chernobrovkin M.G., Belogorokhov A.I. Synthesis, Characterization, and Properties of Nanoscale Titanium Dioxide Modifications with Anatase and Eta-Tio2 Structures. *Crystallogr. Rep.*, 2010, vol. 55, no. 5, pp. 913-918.

СТРУКТУРА И ПАРАМЕТРЫ НАНОВОЛОКОН ПОЛИОКСИБУТИРАТА

Анатолий Александрович Ольхов

Кандидат технических наук, доцент, старший научный сотрудник
лаборатории перспективных композиционных материалов и технологий,
Российский экономический университет им. Г. В. Плеханова
Стремянный пер., 36, 117997 г. Москва, Российская Федерация;
Институт химической физики им. Н. Н. Семенова РАН
aolkhov72@yandex.ru
ул. Косыгина, 4, 119991 г. Москва, Российская Федерация

Ольга Валерьевна Староверова

Сотрудник Института химической физики им. Н. Н. Семенова РАН
aolkhov72@yandex.ru
ул. Косыгина, 4, 119991 г. Москва, Российская Федерация

Алексей Леонидович Иорданский

Доктор химических наук, профессор,
заведующий лабораторией диффузионных явлений в полимерных системах,
Институт химической физики им. Н. Н. Семенова РАН
aolkhov72@yandex.ru
ул. Косыгина, 4, 119991 г. Москва, Российская Федерация

Геннадий Ефремович Заиков

Доктор химических наук, профессор,
заведующий отделом биологической и химической физики полимеров,
Институт биохимической физики им. Н. М. Эмануэля РАН
chembio@sky.chph.ras.ru
ул. Косыгина, 4, 119334 г. Москва, Российская Федерация

Аннотация. В работе исследуются технологические характеристики растворов полимеров, такие как вязкость и электропроводность, а также параметры электроформования с использованием поли-3-гидроксибутирата, модифицированного наночастицами диоксида титана. Структура материалов была исследована с помощью рентгеновской дифракции, дифференциальной сканирующей калориметрии (ДСК), ИК-спектроскопии, а также физико-механических испытаний. Полученные материалы могут найти широкое применение в медицине в качестве фильтров для жидкостей и сорбентов.

Ключевые слова: полимерные растворы, наночастицы диоксида титана, дифракция рентгеновских лучей, ИК-спектроскопия, физико-механические испытания.