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COMPARATIVE DYNAMIC CHARACTERISTICS OF ELECTROSPUN ULTRATHIN FIBERS AND FILMS BASED ON POLY(3-HYDROXYBUTYRATE)

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Received: January 16, 2015 / Revised: May 25, 2015 / Accepted: December 12, 2015

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Abstract. The dynamic of polymer chains for electrospun poly(3-hydroxybutyrate) (PHB) fibers and the PHB films was studied with spin probe characteristics obtained by ESR technique. The ESR data combined with DSC analysis reveal the presence of two TEMPO probe populations with different correlation times indicating the heterogeneous structure of intercrystalline areas in the films, fibers and the cold rolled fiber mats. The ESR data are in agreement with the 2-mode model of amorphous state in semicrystalline polymers. The difference in peak intensities shows that effective correlation time in the electrospun fibers exceeds the same characteristic in the film, that also indicates the slower molecular mobility in the low-dense amorphous fraction of PHB fibers as compared to the film. The impact of potential aggressive factors such as water, temperature and ozone upon probe mobility allows suggesting that both the fiber electrospinning and the cold-rolling procedure lead to rearrangement in the intercrystalline fields of PHB that contribute to the progress in the fiber stabilization against the aggressive factors.

Keywords: poly(3-hydroxybutyrate), electrospinning, ultrathin fibers, film, ESR, TEMPO, chain dynamics, aggressive media.

1. Introduction

For conventional fiber technologies there are significant challenges in arranging fibers and threads with the diameter in submicron range [1]. Currently the alternative manufacture of ultrathin fibers is the unconventional technology based on electrospinning of polymer solutions and melts that enables one to produce fibers and nonwoven materials (mats) in the nano-sized range. Electrospinning presents technologically uncomplicated but multivariate process for ultrathin fibers formation that promotes their wide applications [2]. The process is based on the combination of mechanical and electrodynamic forces affecting polymer solution (or melt) which is aligned in electric field [3]. Therefore a number of technological parameters such as electric potential, distance between collector and electrode, solution conductivity, *etc.* influence morphology, surface properties, functionality, porosity, and fiber diameter [4].

Recently, for poly(3-hydroxybutyrate) (PHB) and a number of its composites [5-7] we have studied physical-chemical, dynamic and transport characteristics of macroscopic biodegradable matrices and microparticles of PHB which were designed for controlled drug release [7, 8]. High biocompatibility, controlled biodegradation and appropriate mechanical properties allow one to consider

this biopolymer as one of the most promising biomedical polymers. Besides therapeutic aims, PHB is widely used as bone implants, nervous conduits, matrices in cell engineering, filters and membranes, in cardiology and in other areas [5, 9, 10].

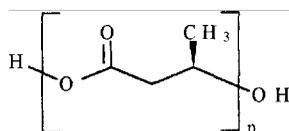
A large number of methods for polymer structure orientation, such as extrusion, blow molding, hot shaping, drawing, nozzle extrusion, *etc.* is currently known. All of them dominate in polymer technology but unfortunately the stretching processes of this type are accompanied by the undesirable effect of microcavitation development [11]. The fibers obtained by electrospinning in electric field are less prone to defect formation. To arrange an additional orientation of macromolecules in fibers, we used the cold rolling belonging to the grope of compression methods that likewise minimizes the probability of defect cavities forming in the fibrillar mats [12]. In spite of a number of limitations, mechanical rolling does not demand high energy expenses and therefore it remains one of the most economical processes in metal- and polymer-technologies.

The transition from films to ultrathin fibers and unwoven fiber materials is accompanied by the changes of physical-chemical and transport characteristics related to spatial confinements modulating dynamics of polymer molecules [13]. In this relation, at the molecular level the comparison of structure-dynamic characteristics will be performed for PHB matrices, ultrathin fiber mats and the same mats after rolling process to elucidate the specific behavior of diffusion and chemical degradation proceeding under spatial confinement conditions. The study of local segmental dynamics in ultrathin fibers plays a significant role in understanding structure-property relationships shown by biodegradable polymers.

Based on these observations, the principal aim of the present paper is twofold: i) using ESR spectroscopy, to study the dynamic of polymer chains for electrospun PHB ultrathin fibers and ii) to compare the obtained results with preliminary obtained data on PHB matrices [14] at earlier stages of interactions between aggressive components (water and ozone) and polymer molecules.

2. Experimental

The PHB was kindly presented by Biomer Co (Krailling, Germany) as lot 16F. The PHB chemical formula is designed as:



The initial polymer was in the form of white powder with particle size of 5–20 μm , $MW = 2.06 \cdot 10^5 \text{ Da}$. Ultrathin fibers were obtained by electrospinning from 5 to 9 % PHB chloroform solutions. The details of this procedure were described earlier in [15]. Physical modifications of PHB structure was produced by cold rolling at $295 \pm 1 \text{ K}$ at rolling rate of 30 s^{-1} and compression of 200 kg/cm^2 [16]. As the result of compression the film thickness decreased from 120 ± 15 to $95 \pm 10 \mu\text{m}$.

Segmental mobility was studied by probe ESR method with Radiopan spectrometer. The probe was 2,2,6,6-tetramethylpyperidin-1-oxil (TEMPO), that was incorporated from vapour phase at 298 K. Correlation times, τ , were calculated from ESR spectra [17] using the formula:

$$t = 6.65 \cdot 10^{-10} \cdot \Delta H^+ \left[\left(\frac{I^+}{I^-} \right)^{1/2} - 1 \right]$$

where ΔH^+ – the weak-field peak on the half height; I^+/I^- is the ratio of peaks in weak and stark magnetic field areas. Standard deviation of measuring was 7 %.

Ozone oxidation was performed in oxygen-ozone atmosphere at $5 \cdot 10^{-5} \text{ mol/l}$ (for O_3). The oxidation degree was controlled by FT-IR spectrum on the Bruker IFS 48 spectrometer (Germany) in the area of $1650\text{--}1700 \text{ cm}^{-1}$. DSC thermograms were obtained by DSC 204 F1 calorimeter (Netzsch) in inert atmosphere of Ar at heating rate 10 K/min . The averaged standard deviation of polymer fusion was 2 %.

3. Results and Discussion

Under electrospinning a number of polymer solution characteristics affect both morphology of ultrathin fibers and such important indicator as their diameter. In Fig. 1 we have illustratively shown that relatively small increase of spinning solution from 5 to 9 wt % changes the diameter distribution in the PHB fibers. It is reasonable to note that when developing medical sensors and chemical detectors, a challenge issue to decrease a fiber diameter in the nanometer range but in the case of biomedical applications (*e.g.* scaffold performance in tissue engineering) such reduction results in poor cell adhesion and dysregulation of tissue growth [18]. The possibility of control in ultrathin fiber geometry by the variation of solution characteristics was described in the recent publication [19]. In this paper we have chosen 7 % PHB solution in chloroform as a basic option due to the good reproducibility of geometry and quality of the fibers.

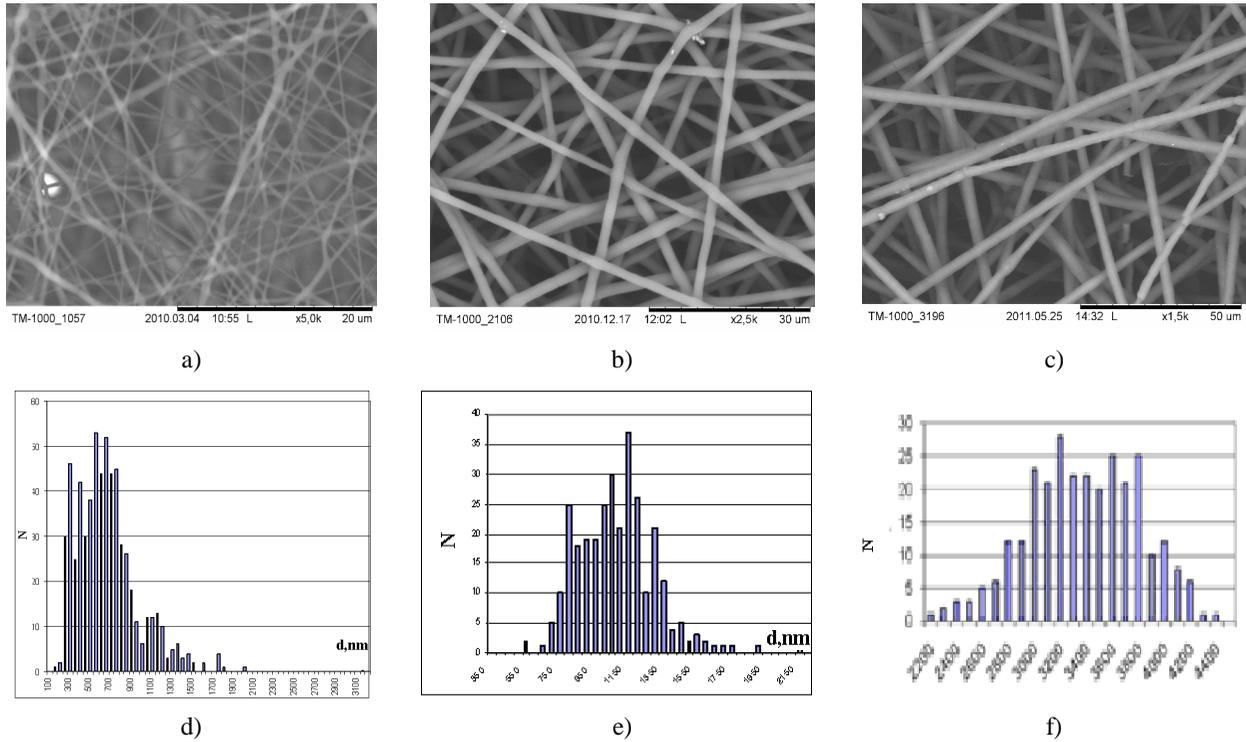


Fig. 1. SEM images of spun PHB fibers obtained from solution at concentrations of 5 % (a); 7 % (b) and 9 % (c) and corresponding fiber diameter distributions with the averaged values of 620 nm (d); 1100 nm (e) and 3350 nm (f).

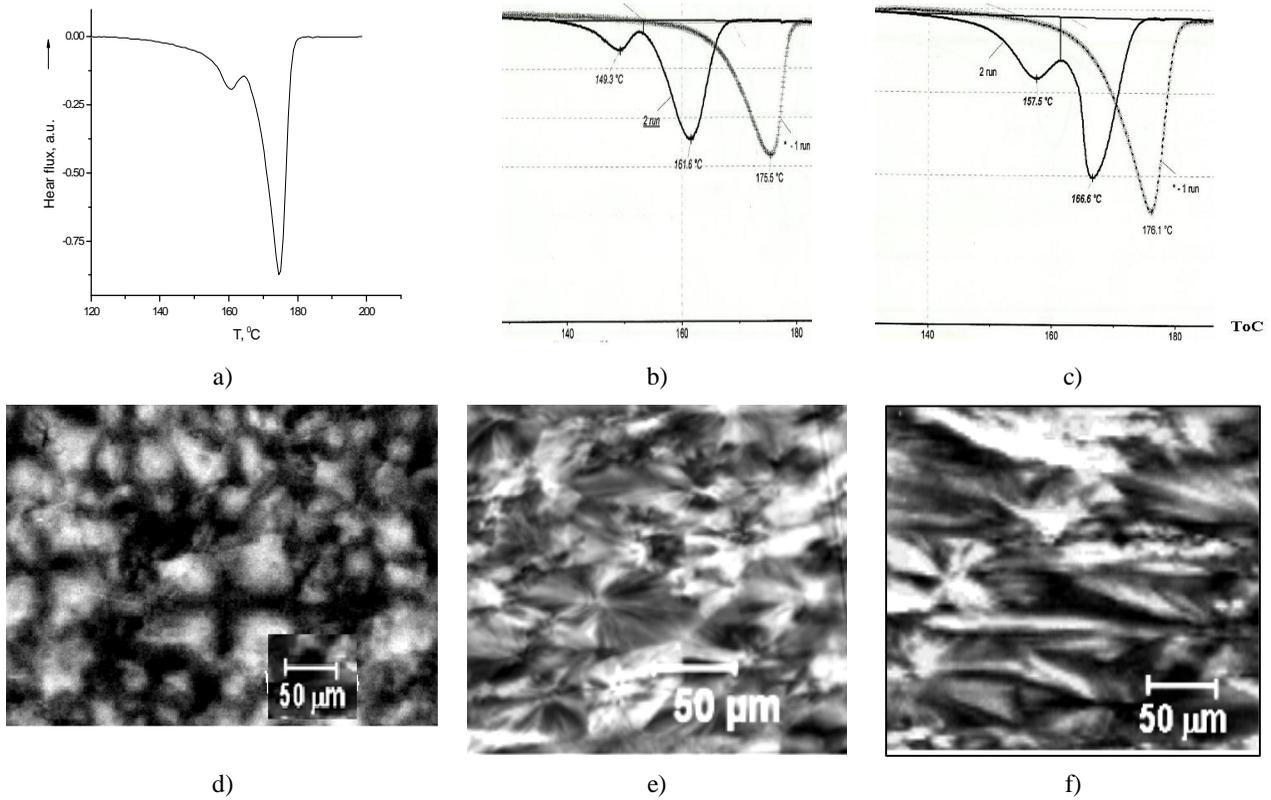


Fig. 2. DSC melting thermograms (a-c) and optical microphotographs (d-f) of PHB for the film (a, d); the spun fibrillar mat (b, e) and the analogous mat after cold-rolling (c, f). The microphotographs were obtained after the first DSC scan

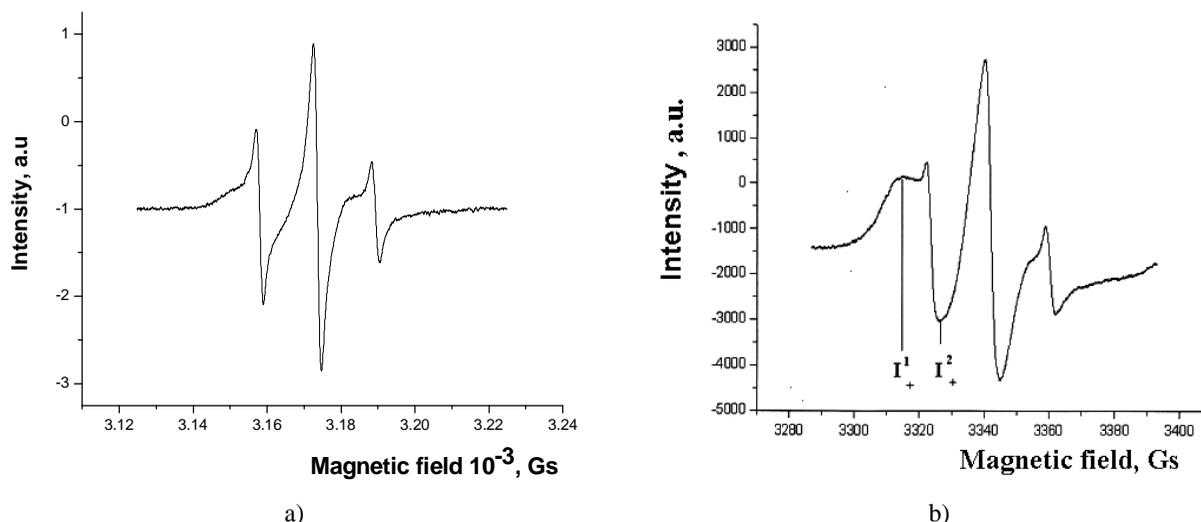


Fig. 3. The ESR spectra of the probe TEMPO in the PHB film (a) and the PHB fiber mat (b) at 298 K. The spectrum (b) shows the features of superposition for two rotating populations: slow (I_+^1) and fast (I_+^2) modes

The segmental mobility measurements performed by the ESR technique, which will be shown beneath, were combined with thermophysical measurements obtained by the DSC method. The melting endotherms for the PHB mats before and after cold rolling reveal similar melting behavior but their phase transitions are located at the different temperatures. In spite of the fact that single peaks for first melting (1^{st} run) of samples before and after cold rolling are very close to each other: 448 and 449 K, respectively, the positions in melting temperatures (bimodal peaks) after 2^{nd} run are displaced quite significantly. First, for both samples the single peak is transformed to the bimodal peaks located respectively at 434.6 and 422.3 K for initial mats and 439 and 430.5 K for mats after cold rolling. Second, as the result of repeated heating the high-temperature peaks are displaced to area of lower temperatures on decrement ~ 10 K, that attests nonperfect organization of crystalline structure of PHB after its controlled cooling (10 K/min) to room temperature. Additionally, by comparing the initial and mechanically treated mats the cold-rolled mats are characterized by two melting peaks at higher temperatures. The main conclusions that could be obtained from the analysis of thermograms (Fig. 2) are: i) mechanical treatment of the mats leads to bimodal distribution of crystalline entities including more perfect and less perfect spherulites; ii) if comparing the peak temperature positions for the bulk film and the fiber mat unrolled or cold-rolled, the temperature shift for PHB increased in the set film > unrolled mat > cold-rolled mat under approximately constant degree of crystallization ($\sim 79\%$); iii) the two-modal crystalline structure would be most likely conjugated with two modes of amorphous phase. To

confirm the last suggestion we have used the probe ESR method that enables to estimate not only dynamic characteristics of segment mobility τ but the difference of amorphous densities in the framework of modern dual-mode model of amorphous phase in semicrystalline polymers, considering the intercrystalline space as combination of denser and less dense fields [20].

In Fig. 3 the typical ESR spectra of the TEMPO probe encapsulated in the PHB film and the PHB mat, respectively, are shown. The spectral characteristics of the mats and the films such as the ratio of intensities for low-field and high-field components of spectra and effective time correlations are essentially distinguished. Irrespective of the production method (film casting, electrospinning or cold rolling) all PHB spectra represent superposition of two single spectra pertaining to individual radicals with different correlation times (τ_1 and τ_2). The inherent correlation time τ_1 determines the state of the probe in denser amorphous fields with slow rotation and τ_2 does the fast probe rotation in less dense amorphous fields of the polymer. The presence of two TEMPO populations in amorphous phase of PHB with distinct rotation frequencies indicates heterogeneous structure of intercrystalline areas which could be approximated by 2-mode model of amorphous state in semicrystalline polymers such as PHB, polylactides, and poly(ethylene terephthalate) proposed earlier [20, 21]. The quality analysis of ESR spectra was pursued by using the ratio of intensities of two first low-field peaks, I_+^1 and I_+^2 , belonging to slow and fast rotation, respectively (see Fig. 3b). Additionally the spectrum characteristic was selected as the distance between the first peak and the third one (L) in single triplet that identifies mobility in denser areas of

amorphous phase. In ESR spectra comparison the value L for the bulk film of PHB (50 Gs) was slightly less than for the fibers (62 Gs) that allows one to suggest slower rotation of the probe in denser field of the fiber mat than in the same field of the PHB film. The distinction between behaviors of two probe populations in the film is more noticeable than in the fiber mats. In fact, the ratio I_+/I_-^2 in the rolled mats has higher value (0.52) as compared with the initial fiber mats (0.37). The difference in peak intensities shows that effective correlation time in the fibres ($3.5 \cdot 10^{-9}$ s) exceeds the same characteristic in the film ($1.36 \cdot 10^{-9}$ s) that also indicates the slow molecular mobility in the low-dense amorphous fraction of PHB rolled fibers as compared to the film.

Additionally to dynamic measurements the static sorption experiments performed by integration of ESR spectra were carried out to determine the TEMPO concentration in equal mass quantities of PHB prepared as the film, the fiber mat, and the fiber mat after cold rolling. Integration spectra calculations show that the radical contents in the PHB items are $4.6 \cdot 10^{18}$ (the film), $2.9 \cdot 10^{18}$ (the fiber mat) and $2.3 \cdot 10^{18}$ spin/cm³ (the cold-rolled mat). Taking into account the identical temperature (298 K), time of sorption (24 h) and relatively equal polymer crystallinity for all types of samples (~79 %), these results point out the decrease in specific volume of PHB being available to absorb the probe, namely, the decrease in the denser amorphous fraction in the sequence: the film > the mat after electrospinning > the same mat after cold rolling. Thus, comparative study of ESR spectra in differential and integration forms indicates that all three samples are estimably different in amorphous phase organization. This effect leads to the change of effective segmental mobility that influence rate of radical rotation in the samples of different origin (different conditions of stretching).

Using the measurements of ESR spectra at different temperatures, the effective time correlation τ dependences on temperature are presented to calculate activation energy of radical rotation in the samples after different stretching treatment, namely, after electrospinning and cold rolling (see Fig 4). Corresponding calculations reflected in semilogarithm coordinates gave the activation energies 27 for films, 42 for the electrospun mats and 55 kJ/mol for the same mats after cold rolling. In passing from the conventional films to the cold-rolled mats the progressive increasing in the activation energy testifies the increase in activation energy barrier of TEMPO rotation that is related to rendering segmental mobility in dense fields of amorphous phase. The tendency to mobility decreasing is manifested in the same sequence as the radical concentration sequence: in the film > in the fiber mat > in the cold-rolled fiber mats.

The semilogarithmic relation ($\lg(\tau) - 1/T$) for the cold-rolled mats has shown the anomalous behavior that was observed at elevated temperatures (~343 K) as deviation from the function linearity (Fig. 4b). This phenomenon could be interpreted as the result in bimodal distribution of the probe in the oriented samples with two individual mobilities for each population. While the temperature decreases below 343 K, the dense amorphous fraction increases (see also [22]), that leads to the decline of effective mobility in intercrystalline area of cold-rolled PHB. For such samples the beginning of dense fraction formation precedes cold crystallization of PHB observed by DSC method at about 333 K and slightly higher [20]. Under dynamic measurements by ESR technique the segmental ordering in PHB as the process preceding cold crystallization is detected at slightly higher temperature ~343 K, when the probe correlation time begins to deviate from the $\lg(\tau) - 1/T$ function linearity as it is shown in Fig 4b.

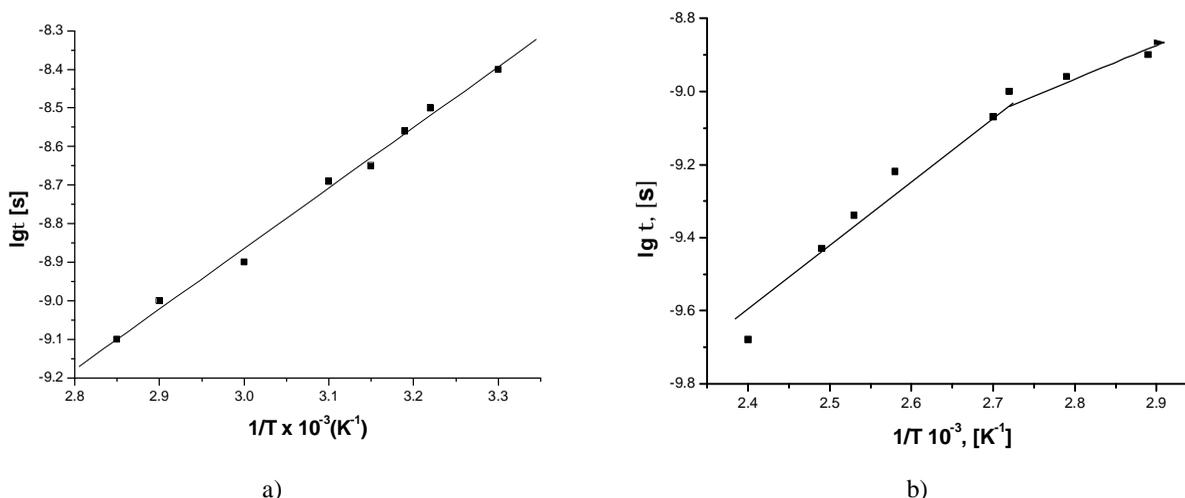


Fig. 4. Time correlation dependence on the reciprocal temperature for the PHB mat (a) and the same mat after cold-rolling (b). The solid lines reflect approximation for energy activation calculations

For the same reason the polymer exposure in liquid water, that is the moderate PHB plasticizer [23], does not enhance molecular dynamics but leads to opposite effect, namely, to some reduction in segmental mobility. In Fig. 5 the dependences of effective time correlation on water contact duration for the PHB mats at 313 K, *i.e.* in the vicinity of physiological temperature are shown. From the Figure it is seen that with increasing in contact duration the correlation time is increased as well. This trend attests decreasing in segmental mobility due to segmental redistribution between denser fields and less dense fields in amorphous phase similarly as it has occurred at temperature impact (see the previous paragraph) when the concentration of polymer segments with low mobility is raised. The additional orientation of polymer molecules after cold-drawing produces the concentration rise in the dense amorphous fields and, hence, leads to the increase of effective time correlation as compared with characteristic of the initial mats that is demonstrated for all times of water contact in Fig. 5.

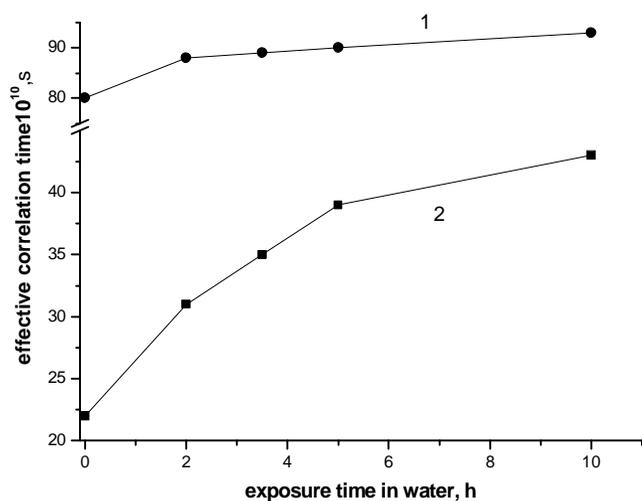


Fig. 5. The time correlation dependence in the fibrillar mats on water contact duration: the initial PHB mat (1) and the same mat after cold-rolling (2)

Special experiments were carried out for the estimation of ultrathin fibers' behavior in ozone atmosphere as in effective oxide-active medium. In Fig. 6 the dependences of effective correlation time for initial and cold-rolled mats on ozone oxidation time are represented. The Figure shows that for the first hour there is a sharp drop of the τ values and then for the next 3 h the decrease of τ is very small, *i.e.* the dynamic characteristic is stabilized. After 4 h of oxidation, the final stage shows the initiation of correlation time decrease. Note that the

initial PHB mats and the cold-rolled mats demonstrate the symbatic probe rotation when in accordance with temperature- and water-influence data the mobility of TEMPO in the cold-rolled oxidised mat is decreased relative to the initial mat after ozonolysis. Taking into account the previous characteristics of crystalline structure and ESR data in amorphous area of the PHB and PHBV films after ozone exposition [14], it can be assumed that at the first stage of oxidation the partial destruction of macromolecules occurs, that leads to the increase of probe mobility. At this stage only more accessible and defect molecules take part in reaction with ozone, which are situated in less dense fields of PHB. After their concentration depletion the PHB-ozone interaction is stabilized for the next 3 h, that could be treated as induction period (the plateau in Fig. 6) and then the oxidation process is enhanced to involve not only the low-dense fields (see above) but the denser fields in intercrystalline space of PHB.

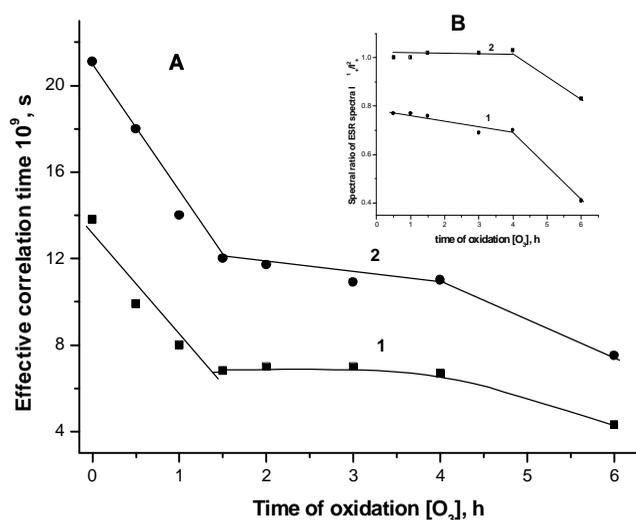


Fig. 6. A: The dependence of effective time correlation of TEMPO probe on time of PHB mat exposition in ozone atmosphere: the initial fiber mat (1) and the same mat after cold-rolling treatment (2). B: The ratio of fast and slow components in ESR probe spectra as function of time oxidation

This mechanism is supported by ESR spectra analysis of oxidated mats based on calculations of the ratio for two first peaks I_+^1 and I_+^2 (Fig. 6b) belonging to slow and fast-rotating fraction of the probe accumulated in denser and less dense amorphous areas, respectively. Fig. 6 shows the constant ratio of the peaks for 4–5 h, that testifies induction period as it was described above.

The further exposure of the polymer to ozone leads to the probe mobility increase related to oxidative destruction of PHB. It is worth to note that the drop in rotation mobility for the mats after cold-rolling is less pronounced than for the initial mats. Taking into account the previous ESR data this effect enables one to suggest that the cold-rolling leads to denser field formation in the intercrystalline area of PHB furthering its stabilization against attack of temperature, water and oxidative agent.

4. Conclusions

A coherent study on ESR dynamics for PHB prepared in the forms of matrices and ultrathin fiber mats reveals the presence of two spin probe populations with different rotation mobilities. The presence of two TEMPO probe populations indicates heterogeneous structure of intercrystalline areas in the films, fiber mats and the cold rolled fiber mats which could be approximated by 2-mode model of amorphous state in semicrystalline polymers. The difference in peak intensities shows that effective correlation time in the fibres ($3.5 \pm 0.6 \cdot 10^{-9}$ s) exceeds the same characteristic in the film ($1.4 \pm 0.3 \cdot 10^{-9}$ s), that also indicates the slower molecular mobility in the low-dense amorphous fraction of PHB rolled fibers as compared to the film. The comparative study of ESR spectra after differential and integration treatments revealed that all three samples (cast films, electrospun fibers and the same mats after cold rolling) are estimably different in amorphous phase organization. This effect leads to the change of effective segmental mobility that influences the rate of ESR probe rotation in the samples with different origin. Taking into account the ESR technique data, the analysis of temperature, water and ozone impacts upon probe mobility one can suggest that the cold-rolling procedure for the fiber mats leads to denser field formation in the intercrystalline area of PHB furthering its stabilization against the attack of the exterior aggressive factors.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project No 14-03-01086/14a) and by the Division of Chemistry and Materials Sciences, Russian Academy of Sciences, under the academic research program Creation of Macromolecu-

lar Structures of New Generations (03/OKhM-14). Authors express their thanks to PhD. S.M. Lomakin and N.G. Shilkina for the DSC thermograms performance.

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**ПОРІВНЯЛЬНІ ДИНАМІЧНІ ХАРАКТЕРИСТИКИ
УЛЬТРАТОНКИХ ВОЛОКОН, ОТРИМАНИХ
ЕЛЕКТРОФОРМУВАННЯМ І ПЛІВОК НА
ОСНОВІ ПОЛІ(3-ГІДРОКСИБУТИРАТУ)**

***Анотація.** З метою дослідження динаміки полімерних сегментів методом зондової спектроскопії ЕПР проведено порівняльний аналіз плівок та ультратонких волокон полі(3-гідроксибутирату) (ПГБ). Волокна отримані методом електроформування і додатково досліджені методом ДСК. Показано, що у міжкристалічних областях існують дві популяції молекулярного зонду ТЕМПО, які відрізняються часом кореляції і розташовані у більш або менш щільних облас-*

тях ПГБ, що узгоджується з бімодальною моделлю аморфного стану в частково кристалічних полімерах. Різниця в ЕПР спектрах доводить, що молекулярна рухомість зонду у волокнах сповільнена порівняно з його рухомістю у плівках ПГБ. Додатково розглянутий вплив агресивного середовища (води і озону) за підвищених температур і показано, що в процесах холодної обкатки або витягуванні волокна при електроформуванні відбувається перебудова міжкристалічних областей ПГБ, що сприяє стабілізації фібрилярної структури проти дії зовнішнього агресивного середовища.

***Ключові слова:** полі(3-гідроксибутират), електроформування, ультратонкі волокна, плівка, ЕПР, зонд ТЕМПО, динаміка ланцюга, агресивне середовище.*