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DEGRADATION OF POLY(3-HYDROXYBUTYRATE) AND ITS DERIVATIVES: CHARACTERIZATION AND KINETIC BEHAVIOR

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Abstract. We focused on hydrolytic degradation kinetics at 310 and 343 K in phosphate buffer to compare PLA and PHB kinetic profiles. Besides, we revealed the kinetic behavior for copolymer PHBV (20 % of 3-hydroxyvalerate) and the blend PHB-PLA (1:1). The intensity of biopolymer hydrolysis is characterized by total weight lost and the viscosity-averaged molecular weight (MW) decrement. The degradation is enhanced in the series PHBV < PHB < PHB-PLA blend < PLA. Characterization of PHB and PHBV includes MW and crystallinity evolution (X-ray diffraction) as well as AFM analysis of PHB film surfaces before and after aggressive medium exposition. The important impact of MW on the biopolymer hydrolysis is shown.

Keywords: poly(3-hydroxybutyrate), polylactide, non-enzymatic hydrolysis, crystallinity, weight loss.

1. Introduction

The bacterial polyhydroxyalkanoates (PHA)s and their principal representative – poly(3-R-hydroxybutyrate) (PHB) create a competitive option to conventional synthetic polymers such as polypropylene, polyethylene, polyesters, *etc*. These polymers are nontoxic and renewable. Their biotechnology output does not depend on hydrocarbon production and their biodegradation intermediates and resulting products (water and carbon dioxide) do not provoke the adverse actions in environmental media or living systems [1-3]. Being environmentally friendly [4], the PHB and its derivatives are used as the alternative packaging materials, which are biodegradable in the soil or different humid media [5, 6].

The copolymerization of 3-hydroxybutyrate entities with 3-hydroxyoctanoate (HO), 3-hydroxyheptanoate (HH) or 3-hydroxyvalerate (HV) monomers modifies the physical and mechanical characteristics of the parent PHB, such as ductility and toughness to depress its processing temperature and embrittlement. Besides, copolymers PHB-HV [7], PHB-HH [8] or PHB-HO [9] and other have improved thermophysical and/or mechanical properties and hence they expand the spectrum of constructional and medical materials/items. For predicting the behavior of PHB and its copolymers in an aqueous medium, *e.g. in vitro*, in a living body or in wet soil, it is essential to study kinetics and mechanism of hydrolytic destruction.

Although such-like investigations have about 25 years of history, the problem of (bio)degradation in semicrystalline biopolymers is too far from final resolution. Moreover, in the literature the description of hydrolytic degradation kinetics during long-term period is comparatively uncommon [10-14]. Therefore, the main object of this paper is the comparison of long-term degradation kinetics for the PLA, PHB and its derivatives, namely its copolymer with 3-oxyvalerate (PHBV) and the blend PHB/PLA. The contrast between degradation profiles for PHB and PLA makes it possible to compare the degradation behavior for two most prevalent biodegradable polymers. Besides, a significant attention is devoted to the impact of molecular weight (MW) for the

above polymer systems upon hydrolytic degradation and morphology (crystallinity and surface roughness) at physiological (310 K) and elevated (343 K) temperatures.

2. Experimental

2.1. Materials

In this work we have used poly-L-lactide (PLA) with different molecular weights: 67, 152, and 400 kDa (Fluka Germany); chloroform (ZAO EKOS-1, RF), sodium valerate (Sigma-Aldrich, USA), and mono-substituted sodium phosphate (NaH_2PO_4, ChimMed, RF).

2.2. PHAs Production

The samples of PHB and copolymer of hydroxybutyrate and hydroxyvalerate (PHBV) have been produced in A.N. Bach's Institute of Biochemistry. A highly efficient strain-producer (80 wt % PHB in the dry weight of cells), *Azotobacter chroococcum 7*Б, has been isolated from rhizosphere of wheat (the sod-podzol soil). Details of PHB biosynthesis have been published in [15]. Under conditions of PHBV synthesis, the sucrose concentration was decreased to 30 g/l in medium and, after 10 h incubation, 20mM sodium valerate was added. Isolation and purification of the biopolymers were performed *via* centrifugation, washing and drying at 333 K subsequently. Chloroform extraction of BPHB or BPHBV from the dry biomass, as well as precipitation, filtration, washing again, and drying have been described in our previous work [15]. The monomer-content (HB/HV ratio) in PHBV has been determined by nuclear magnetic resonance in accordance with the procedure described previously in [16]. The percent concentration of HV moiety in the copolymer was calculated as the ratio between the integral intensity of methyl group of HV (0.89 ppm) and total integral intensity of the same group and HB group (1.27 ppm). This value is 21 mol %.

2.3. Molecular Weight Determination

The viscosity-averaged molecular weight (*MW*) was determined by the viscosity (h) measurement in chloroform solution at 303 K. The calculations of *MW* have been made in accordance with Mark-Houwink equation [17]:

$$[h] = 7.7 \cdot 10^{-5} \cdot M^{0.82}$$

2.4. Preparation of PHAs, PLA Films and their Blends

The films of parent polymers (PHB, PHBV and PLA) and their blends with the thickness of about 40 μm were cast on a fat-free glass surface. We obtained the set of films with different *MW* = 169 ± 9 (defined as PHB 170), 349 ± 12 (defined as PHB 350), 510 ± 15 kDa (defined as PHB 500), and 950 ± 25 kDa (defined as PHB 1000) as well as the copolymer PHBV with *MW* = 1056 ± 27 kDa (defined as PHBV). Additionally we prepared the set of films on the base of PLA with the same thickness of 40 μm and *MW* = 67 (defined as PLA 70), *MW* = 150 and 400 kDa. Along with them we obtained the blend PHB/PLA with the weight ratio 1:1 and *MW* = 950 kDa for PHB, and *MW* = 67 kDa for PLA (defined as PHB+PLA blend). Both components mixed and dissolved in common solvent, chloroform and then cast conventionally on the glass plate. All films were thoroughly vacuum-processed for removing of solvent at 313 K.

2.5. Hydrolytic Degradation *in vitro* Experiments

Measurement of hydrolytic destruction of the PHB, PLA, PHBV films and the PHB-PLA composite was performed as follows. The films were incubated in 15 ml 25 mM phosphate buffer, pH 7.4, at 310 or 343 K in a ES 1/80 thermostat (SPU, Russia) for 91 days; pH was controlled using an Orion 420+ pH-meter (Thermo Electron Corporation, USA). For polymer weight measurements films were taken from the buffer solution every three day, dried, placed into a thermostat for 1 h at 313 K and then weighed with a balance. The film samples weighed 50–70 mg each. The loss of polymer weight due to degradation was determined gravimetrically using a AL-64 balance (Acculab, USA). Every three days the buffer was replaced by the fresh one.

2.6. Wide Angle X-ray Diffraction

The PHB and PHBV chemical structure, the type of crystal lattice and crystallinity was analyzed by wide angle X-ray scattering (WAXS) technique. X-ray scattering study was performed on a device on the basis of 12 kW generator with rotating copper anode RU-200 Rotaflex (Rigaku, Japan) using CuK radiation (wavelength λ = 0.1542 nm) operated at 40 kV and 140 mA. To obtain pictures of wide angle X-ray diffraction of polymers two-dimensional position-sensitive X-ray detector GADDS (Bruker AXS, Germany) with flat graphite monochromator installed on the primary beam was used. The collimator diameter was 0.5 mm [18].

2.7. Atomic Force Microscopy of PHB Films

Microphotographs of the surface of PHB films were obtained be means of atomic force microscopy

(AFM). The AFM imaging was performed with Solver PRO-M (Zelenograd, Russia). For AFM imaging a piece of the PHB film (~2×2 mm^2) was fixed on a sample holder by a double-sided adhesive tape. Silicon cantilevers NSG11 (NT-MDT, Russia) with typical spring constant of 5.1 N/m were used. The images were recorded in semi-contact mode, scanning frequency of 1–3 Hz, scanning areas from 3×3 to 20×20 μm^2, topography and phase signals were captured during each scan. The images sized 512×512 pixels were captured. Image processing was carried out using Image Analysis (NT-MDT, Russia) and FemtoScan Online (Advanced technologies center) software.

3. Results and Discussion

The *in vitro* degradation of PHB with different molecular weight (*MW*) and its derivatives (PHBV, blend PHB/PLA) prepared as films was observed by the changes of total weight loss, MW, and morphologies (AFM, XRD) during the period of 91 days.

3.1. The Hydrolysis Kinetics of PLA, PHB, and its Derivatives

The hydrolytic degradation of the biopolymer and the derivatives (the copolymer PHBV, and the blend PHB/PLA 1:1) has been monitored for 3 months under condition, which is realistically approximated to physiological conditions, namely, *in vitro*: phosphate buffer, pH 7.4, temperature 310 K. The analysis of kinetic curves for all samples shows that the highest rate of weight loss is observed for PLA with the smallest *MW* ≈ 70 kDa and for PHB with relatively low *MW* ≈ 150 kDa (Fig. 1). On the base of the data in this figure it is possible to compare the weight-loss increment for the polymers with different initial *MW*. Here, we clearly see that the samples with the higher *MW*s (300–1000 kDa) are much stabler against hydrolytic degradation than the samples of the lowest *MW*. The total weight of PHB films with *MW* = 150 kDa decreases faster compared to the weight reduction of the other PHB samples with higher *MW*s = 300 and 450 or 1000 kDa. Additionally, by the 91st day of buffer exposition the residual weight of the low-*MW* sample reaches 10.5 % weight loss that it is essentially higher than the weight loss for the other PHB samples (see Fig. 1).

After establishing the impact of *MW* upon the hydrolysis, we have compared the weight-loss kinetic curves for PLA and PHB films with the relatively comparative *MW* = 400 and 350 kDa, respectively, and the same film thickness. For the PLA films one can see the weight depletion with the higher rate than the analogous samples of PHB. The results obtained here are in line with the preceding literature data [8, 12, 19-21].

Having compared destruction behavior of the homopolymer PHB and the copolymer PHBV, we can see that the introduction of hydrophobic entity (HV) into the PHB molecule *via* copolymerization reveals the hydrolytic stability of PHBV molecules. For PHBV hydrolysis induction time is the longest among the other polymer systems and over a period of 70 days its weight loss is minimal (< 1 wt %) and possibly related to desorption of low-molecular fraction of PHBV presented initially in the samples after biosynthesis and isolation. The kinetic curves in Fig. 1 show also that the conversion of the parent polymers to their blend PHB-PLA decreases the hydrolysis rate compared to PHB (*MW* = 1000 kDa) even if the second component is a readily hydrolysable polymer: PLA (*MW* = 70 kDa).

For the sake of hydrolysis amplification and its exploration simultaneously, polymer exposition in aqueous media has usually been carried out at elevated temperature [11, 19]. To find out the temperature impact on degradation and intensify this process we have elevated the temperature in phosphate buffer to 343 K. This value of temperature is often used as the standard in other publications, *e.g.* in [11]. As one should expect, under such condition the hydrolysis acceleration is fairly visible, which is presented in Fig. 1b. By the 45^{th} day of PLA incubation its films turned into fine-grinding dust with the weight-loss of 50 % (*MW* = 70 kDa) or 40 % (*MW* = = 350 kDa). Simultaneously the PHB with the lowest *MW* = 170 kDa has the weight loss of 38 wt % and the film was markedly fragmented while the PHB samples with higher *MW*s 350, 500 and 1000 kDa have lost the least of their initial weight, namely 20, 15 and 10 %, respectively. Additionally, for 83 days the weight drop in the PHB-PLA blend films is about 51 wt % and, hence, hydrolytic stability of the blend polymer system is essentially declined (cf. Figs. 1a and 1b).

At elevated temperature of polymer hydrolysis (343 K) as well as at physiological temperature 310 K we have demonstrated again that the PHBV films are the most stable because by the 95^{th} day they lost only 4 wt %. The enhanced stability of PHBV relative to the PHB has been confirmed by other literature data [21]. Here it is worth to remark that during biosynthesis of the PHBV two opposite effects of water sorption occur, acting reversely to each other. On the one hand, while the methyl groups are replaced by ethyl groups, the total hydrophobicity of the copolymer is enhanced, on the other hand, this replacement leads to decrease of crystallinity in the copolymer [22]. The interplay between the two processes determines a total water concentration in the copolymer and hence the rate of hydrolytic degradation. Generally, in the case of PHBV copolymer (HB/HV = 4:1 molar ratio) the hydrophobization of its chain predominates the effect of crystallinity decrease from 75 % for PHB to ~60 % for PHBV.

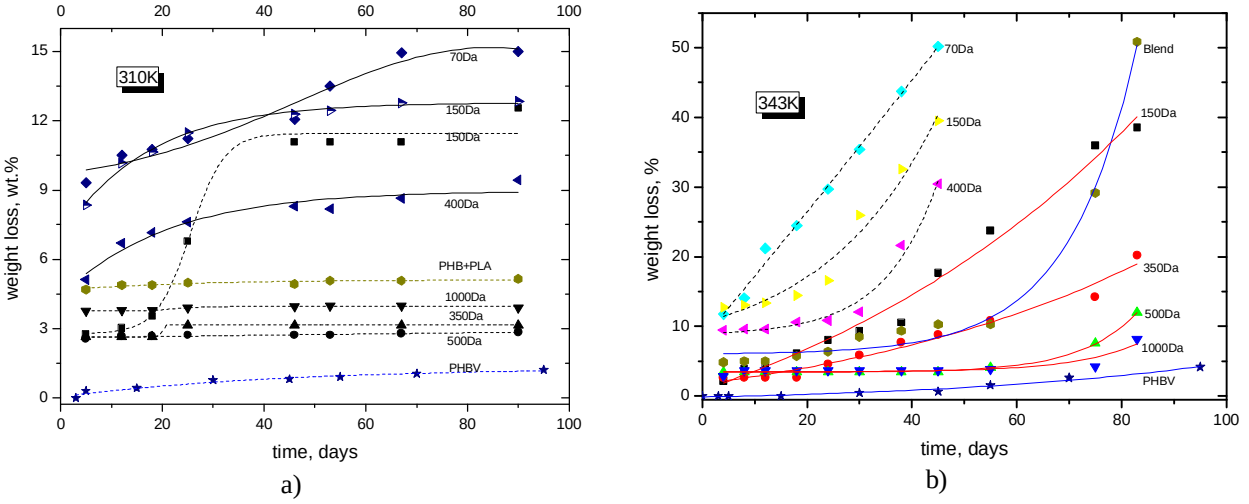

Fig. 1. Weight loss in the phosphate buffer for PHB and its derivatives with different *MW* (shown on the curves in kDa) at 310 K (a) and 343 K (b): ♦,►, and◄ are PLA films with *MW* = 70, 150, and 400kDa, respectively; ■,▲,●, and ▼ are PHB samples with 170, 350, 500, and 1000 kDa, respectively; PHBV 1050 (★); and PHB-PLA blend (**Ã**)

3.2. Change of Molecular Weight for PHB and PHBV

At the exposure of PHB and PHBV films to buffer medium at physiological (310 K) or elevated (343 K) temperatures, we have measured both their total weight loss (Section 1) and the change of their *MW* simultaneously. In particular, we have shown the temperature impact on the *MW* decrease that will be much clearer if we compare the *MW* decrements for the samples at 310 and 343 K. At 343 K the above biopolymers have a more intensive reduction of *MW* compared to the reduction at 310 K (see Fig. 2). In particular, at elevated temperature the initial *MW* (350 kDa) has the decrement 7 times greater than the *MW* decrement at physiological condition. Generally, the final *MW* loss is nearly proportional to the initial *MW* of the sample that is correct especially at 343 K. As an example, after the 83-day incubation of PHB films, the initial *MW* = 170 kDa dropped as much as 18 wt % and the initial *MW* = 350 kDa has the 9.1 wt % decrease.

The diagrams in Fig. 2 show that the sharp reduction of *MW* takes place for the first 45 days of incubation and after this time the *MW* change becomes slower. Combining the weight-loss (Section 1) and the *MW* depletion, it is possible to present the biopolymer hydrolysis as a two-stage process. On the initial stage, the random cleavage of macromolecules and the *MW* decrease without a significant weight loss occur. Within this time the mean length of PHB intermediates is fairly large and the molar ratio of the terminal hydrophilic groups to the basic functional groups in a biodegradable fragment is too small to provide the solubility in aqueous media. This situation is true for the PHB samples with middle and high *MW* (350, 500, and 1000 kDa) when at 310 K their total weight remains stable during all time of observation but the *MW* values decrease to 76, 61, and 51 wt %, respectively. On the second stage of degradation, when *MW* of the intermediate molecules attains some "critical" value and the products of hydrolysis become hydrophilic to provide dissolution and diffusion into water medium, the weight reduction is clearly observed at 343 K. This stage is accompanied by the changes of physical-chemical, mechanical and structural characteristics and geometry alteration. A similar 2-stage mechanism of PHB degradation has been described in other publications [23, 24]. Furthermore, in the classical work of Reush [25] she showed that hydrophilization of PHB intermediates occurs at relatively low *MW*, namely, at several decades of kDa. Our results provide evidences that the reduction of *MW* to "critical" values of about 30 kDa leads to the expansion of the second stage, namely, to intensive weight loss.

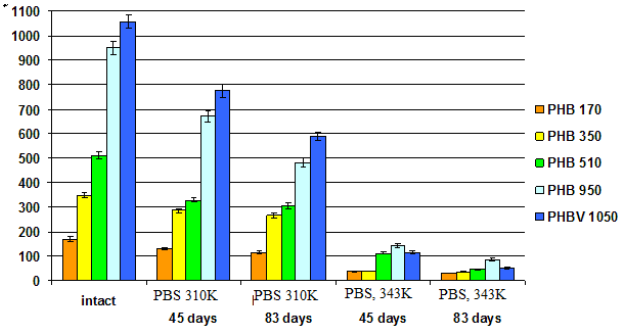

Fig. 2. The molecular weight conversion of PHB and PHBV films during hydrolysis in phosphate buffer (PBS). pH = 7.4, 310K and 343K

3.3. Crystallinity of PHB and PHBV

As it was established above, during hydrolytic degradation PHB and PHBV show *MW* reduction (Section 2) and total weight decrease (Section 1). Additionally, by the X-ray diffraction technique (XRD) we have measured the crystallinity degree of PHB and PHBV that varied depending on time in the interval of values 60–80 % (see Fig. 3a). We have noted that on the initial stage of polymer exposition to the aqueous buffer solution (at 310 K for 45 days) the crystallinity degree has slightly increased and then, under following exposition to the buffer, this characteristic was constant or even slightly decreased showing a weak maximum. When taken into account that at 310 K the total weights for the PHB films with *MW*s equal to 350, 500 and 1000 kDa and the PHBV film with *MW* equal to 1050, are invariable, a possible reason of the small increase in crystallinity is recrystallisation described earlier for PLA [26]. Recrystallization (or additional crystallization) occurs in semicrystalline polymers where the crystallite portion can increase using polymer chains in adjoining amorphous phase [22].

At higher temperature of hydrolysis (343 K) the crystallinity increment is strongly marked and has a progressive trend. The plausible explanation of this effect includes the hydrolysis progress in amorphous area of biopolymers. It is well known that the matrices of PHB and PHBV are formed by alternative crystalline and non-crystalline regions, which determine both polymer morphologies and transport of aggressive medium. Additionally, we have revealed recently by H-D exchange FTIR technique that the functional groups in the PHB crystallites are practically not accessible to water attack. Therefore, the hydrolytic destruction and the weight decrease are predominantly developed in the amorphous part of polymer [22, 27]. Hence, the crystalline fraction becomes larger through polymer fragment desorption from amorphous phase. This effect takes place under the strong aggressive conditions (343 K) and does not appear under the physiological conditions (310 K) when the samples have invariable weight.

Owing to the longer lateral chains in PHBV, copolymerization modifies essentially the parent characteristics of PHB such as decreasing in crystallinity, depression of melting and glass temperatures and, hence, enhancing ductility and improvement of processing characteristics [14, 28, 29]. Additionally, we have found out that the initial crystallinity of PHB films is a monotonically increased function of initial *MW* (see Fig. 3b). For the samples with relatively low molecular weight it is difficult to compose the perfect crystalline entities because of relatively high concentration of terminal groups performing as crystalline defects.

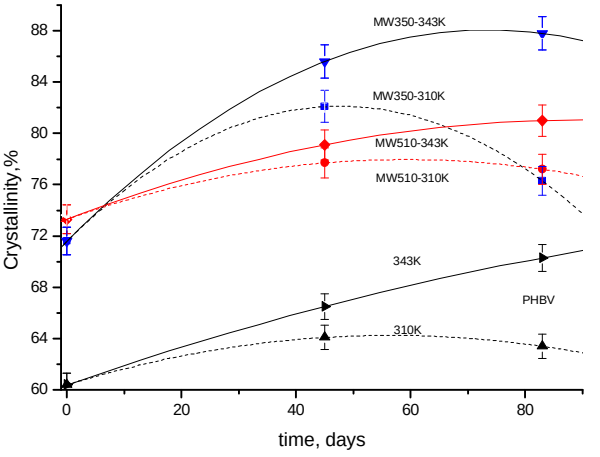

Fig. 3a. Crystallinity evolution during the hydrolysis for PHB and PHBV films (denoted values of temperature and *MW*)

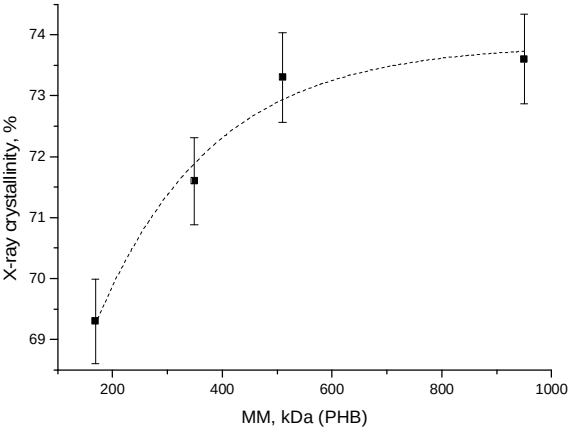

Fig. 3b. Crystallinity as function of initial *MW* for PHB films prepared by cast method

Thus, at physiological temperature the crystallinity measured during degradation by XRD technique has a slightly extreme character. On the initial stage of PHB degradation the crystalline/amorphous ratio increases owing to additional crystallization through involvement of polymer molecules situated in amorphous fields. In contrast, at 343 K after reaching the critical *MW* values (see Section 2), the following desorption of water-soluble intermediates occurs. On the following stage, as the degradation is developed till film disintegration, the crystallinity drop takes place as the result of crystallite disruption.

3.4. Analysis of Film Surfaces for PHB by AFM Technique

Morphology and surface roughness of PHB film exposed to corrosive medium (phosphate buffer) have

been studied by the AFM technique. This experiment is important for surface characterization because the state of implant surface determines not only mechanism of degradation but the protein adsorption and cell adhesion, which are responsible for polymer biocompatibility [30]. As the standard sample we have used the PHB film with relatively low *MW* = 170 kDa. The film casting procedure may lead to distinction in morphology between two surfaces when one plane of the polymer film was adjacent to glass plate and the other one was exposed to air. Really, as it is shown in Fig. 4 the surface exposed to air has a roughness formed by a plenty of pores with the length of 500–700 nm. The opposite side of the film contacted with glass (Fig. 4b) is characterized by minor texture and by the pores with the length as small as 100 nm. At higher magnification (not presented here) in certain localities the stacks of polymer crystallites with the width of about 100 nm and the length of 500–800 nm can be observed.

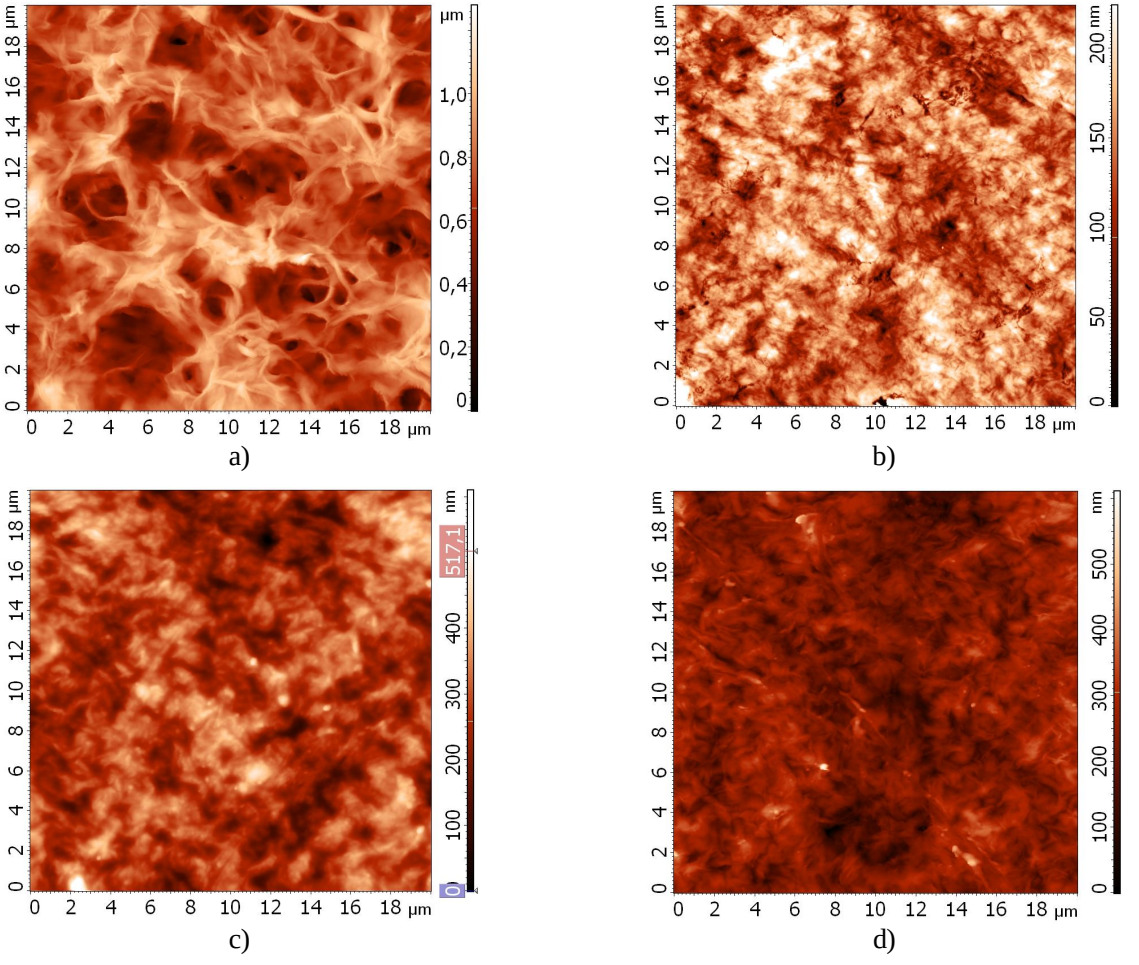

Fig. 4. AFM topographic images of PHB films (170 kDa) with a scan size of 18×18 μm: the rough surface of fresh-prepared sample (exposed to air) (a); the smooth surface of fresh-prepared sample (exposed to glass) (b); the sample exposed to phosphate buffer at 310 K for 83 days (c) and the sample exposed to phosphate buffer at 343 K for 83 days (d). Magnification 300×

The difference in morphology of the two surfaces gets clearly evident when quantitative parameters of roughness (r_n) are compared. A roughness analysis has shown that averaged value of this characteristic

$$R_a = \frac{1}{N}\sum_{n=1}^{N}|r_n|$$

and a root mean square roughness

$$R_q = \sqrt{\frac{1}{N}\sum_{n=1}^{N} r_n^{\,2}}$$

for surfaces exposed to glass and air differ about ten times.

The variance of characteristics is related to the conditions of solvent evaporation during the film cast. During chloroform evaporation the flux forms additional channels (*viz.* the pores), which are fixed as far as the film

is solidified and crystallized. Simultaneously, during evaporation the morphology and texture on the opposite side of film exposed to the glass support are not subjected to the impact of solvent transport. The morphology of the latter surface depends on energy interaction conditions (interface glass-biopolymer tension) predominantly. The exposition of PHB films to the buffer for a long time (83 days) leads to a threefold growth of roughness characteristics (see Table) for glass-exposed surface and practically does not affects the air-exposed surface. It is interesting that the temperature of film degradation does not influence the roughness change. The surface characteristics of film surface have the same values after treatment at 310 and 343 K (see again Table).

Table

Roughness of PHB 170 kDa films

Sample	Side of film	R_a, nm	R_q, nm
control	"rough*"	130±10	165±10
control	"smooth**"	15±2	20±1
PBS buffer, pH 7.4, 310 K	"rough*"	135±5	166±7
PBS buffer, pH 7.4, 310 K	"smooth**"	46±2	59±1
PBS buffer, pH 7.4, 343 K	"rough*"	138±6	167±7
PBS buffer, pH 7.4, 343 K	"smooth**"	41±3	52±3

Notes: PBS – acronym of phosphate buffer, * – film surface exposed to air, ** – film surface exposed to glass.

Summarizing the AMF data we can conclude that during degradation the air-exposed, rough surface remained stable, which is probably related to the volume mechanism of degradation (V-mechanism [31, 32]). The pores on the surface provide fast water diffusion into the bulk of PHB. However, under the same environmental conditions, the change of surface porosity (roughness) for glass-exposed surface is remarkable, showing the engagement of surface into degradation process (S-mechanism [31, 32]). The last findings show that along with the volume processes of polymer degradation the surface hydrolysis can proceed. Several authors [20, 21] have recently reported on surface mechanism of PHB destruction but traditional point of view holds to volume mechanism of degradation [12]. Here, using an advanced method of surface investigation (AMF) we have shown that for the same film under the same exterior conditions the mechanism of degradation could be changed depending on the prehistory of polymer preparation.

4. Conclusions

Having analyzed all results related to hydrolytic degradation of PHB and its derivatives, the consecutive stages of such complicated process are presented as follows. During the initial stage, the total weight is invariable and the cleavage of biomolecules resulting in the *MW* decrease is observed. Within this time the PHB intermediates are too large and hydrophobic to provide solubility in aqueous media. Because the PHB crystallites stay stable, the crystallinity degree is constant as well and even it may grow up due to additional crystallization. On the second stage of hydrolysis, when the *MW* of intermediates attain the "critical" value, which is equal to about 30 kDa, these intermediates can dissolve and diffuse from the polymer into buffer. Within this period the weight loss is clearly observed. The intensity of hydrolysis characterized by the weight loss and the *MW* decrement is enhanced in the series PHBV < PHB < PHB-PLA blend < PLA.

The growth of the initial *MW* (a terminal group reducing) impacts the hydrolysis stability probably due to the increase of crystallite perfection and crystallinity degree. The XRD data reflect this trend (Fig. 3b). Moreover, the surface state of PHB films explored by AFM technique depends on the condition of film preparation. After cast processing, there is a great difference in morphologies of PHB film surfaces exposed to air and to glass plate. It is well known that the mechanism of hydrolysis could include two consecutive processes: a) volume degradation and b) surface degradation. Under essential pore formation (in the surface layer exposed to air) the volume mechanism prevails. The smooth surface of PHB film contacted during preparation with the glass plate is degraded much more intensely than the opposite rough surface (Fig. 4).

In conclusion, we have revealed that the biopolymer *MW* determines the form of a hydrolysis profile (see Fig. 1). For acceleration of this process we have to use small *MW* values of PHB. In this case we affect both the degradation rate and the crystalline degree (Fig. 3b). By contrast, for prolongation of service-time in a living system it is preferable to use the high-MW PHB, that is the most stable polymer against hydrolytic degradation.

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ГІДРОЛІТИЧНА ДЕСТРУКЦІЯ ПОЛІ(3-ГІДРОКСИБУТИРАТА) І ЙОГО ПОХІДНИХ: ХАРАКТЕРИСТИКА ТА КІНЕТИЧНА ПОВЕДІНКА

Анотація. *Наведено порівняльні дослідження стосовно гідролітичної деструкції полі-3-гідроксибутирату (PHB) і поліактиду (PLA) у фосфатному буфері за 310 і 343 К, а також кінетики деструкції кополімеру 3-гідроксибутирату і 3-гідроксивалерату (20 %) та суміші PHB-PLA (1:1). Інтенсивність гідролізу характеризувалась втратою загальної маси та пониженням середньов'язкісної молекулярної маси зразків. Встановлено, що швидкість гідролізу зростає у послідовності PHBV < PHB < суміш PHB-PLA < PLA. З використанням методу РСА визначена еволюція кристалічності та ММ, а із застосуванням методу АСМ показано різницю шороховатості для поверхні PHB до і після контакту з агресивним середовищем. Показано важливу роль ММ полімеру як чинника, що відповідає за гідролітичну деструкцію біополімерів.*

Ключові слова: *полі-3-гідроксибутират, поліактид, неферментний гідроліз, кристалічність, втрата маси.*