Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):517–527
ISSN 2686-7575 (Online)

Synthesis and processing of polymers and polymeric composites
Синтез и переработка полимеров и композитов на их основе

UDC 617-089.844+544.03
https://doi.org/10.32362/2410-6593-2024-19-6-517-527
EDN ZWXRLX

RESEARCH ARTICLE

Influence of modifying additives on the structure and properties of biodegradable mixtures based on poly-3-hydroxybutyrate and nitrile butadiene rubber

Pavel A. Povernov[1], Lyudmila S. Shibryaeva[1, 2, ✉], Sergei M. Anshin[3]

[1] *N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119334 Russia*

[2] *MIREA — Russian Technological University, Moscow, 119454 Russia*

[3] *Plekhanov Russian University of Economics, Moscow, 117997 Russia*

✉ *Corresponding author, e-mail: lyudmila.shibryaeva@yandex.ru*

Abstract

Objectives. To investigate polymer composite materials based on poly-3-hydroxybutyrate (PHB) of microbiological origin and the synthetic nitrile butadiene rubber NBR-28. The biodegradability of PHB implies the possibility of its use for invasive medical purposes; however, this is significantly limited by its brittleness. The aim of this work was to search for approaches to altering the molecular structure of PHB-based composites, in order to impart them with sufficient physical and mechanical characteristics and increase their compatibility without violating biodegradability.

Methods. Reaction mixtures contained the elastic material NBR-28, various modifiers (sorbitan oleate, epoxidized soybean oil, siloxane rubber), and additional polymer components (ethylene–vinyl acetate copolymer and polybutylene adipate terephthalate). The mixtures were prepared in a PL 2200-3 plasticorder (*Brabender*, Russia) by pressing, holding the material at 180°C under pressure for 3 min followed by quenching in cold water. The surfaces of the films and plates of the mixtures were studied using an Axio Imager Z2m optical microscope (*Carl Zeiss*, Germany) with the Axio Vision software at 50× and 200× magnification in reflected light. The mechanical properties of materials under tension were measured using an Instron 3365 universal tensile testing machine (*Instron*, United Kingdom).

Results. The role of modifiers and polymer additives in the PHB–NBR-28 composites and their influence on the morphology of mixtures, crystallinity, and mechanical characteristics were established. The introduction of modifiers made it possible to reduce the average particle size of the NBR-28 phase in the PHB matrix by 30–50%, additionally changing their morphology. In this case, the uniformity of particle distribution increased, having a positive effect on the mechanical characteristics of the systems.

Conclusions. It was shown that the modifiers change the morphology of mixtures, reduce the average particle size of the NBR phase by 30–50%, and positively affect the strength of the systems. Owing to changes in the structure of their interfacial layers and, as a consequence, physical and mechanical characteristics, the resulting composites render suitable for use in reparative bone and dental surgery, as well as for creating wound healing materials.

Keywords

polyhydroxyalkanoates, bone implants, osteogenesis, biodegradable polymer composite materials, osteoplastic materials

Submitted: 06.04.2023
Revised: 17.09.2024
Accepted: 16.10.2024

For citation

Povernov P.A., Shibryaeva L.S., Anshin S.M. Influence of modifying additives on the structure and properties of biodegradable mixtures based on poly-3-hydroxybutyrate and nitrile butadiene rubber. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2024;19(6):517–527. https://doi.org/10.32362/2410-6593-2024-19-6-517-527

НАУЧНАЯ СТАТЬЯ

Влияние модифицирующих добавок на структуру и свойства биоразлагаемых смесей на основе поли-3-гидроксибутирата и бутадиен-нитрильного каучука

П.А. Повернов[1], Л.С. Шибряева[1, 2, ✉], С.М. Аншин[3]

[1] *Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук, Москва, 119334 Россия*

[2] *МИРЭА — Российский технологический университет, Москва, 119454 Россия*

[3] *Российский экономический университет им. Г.В. Плеханова, Москва, 117997 Россия*

✉ *Автор для переписки, e-mail: lyudmila.shibryaeva@yandex.ru*

Аннотация

Цели. Изготовить и исследовать полимерные смесевые материалы на основе поли-3-гидроксибутирата (ПГБ) микробиологического происхождения и синтетического бутадиен-нитрильного каучука (БНКС) марки БНКС-28. Биоразлагаемость ПГБ предполагает возможность его применения в инвазивных медицинских целях, однако это в значительной степени ограничивается его хрупкостью. В связи с этим, целью данной работы являлось нахождение способов изменения молекулярной структуры композитов на основе ПГБ для придания им достаточных физико-механических характеристик и увеличения их совместимости без нарушения биоразлагаемости.

Методы. В работе использовался эластичный материал БНКС-28, а также различные модификаторы (сорбитан олеат, эпоксидированное соевое масло, силоксановый каучук) и дополнительные полимерные компоненты: сополимер этилена и винилацетата и полибутиленадипинаттерефталат. Смеси были получены в пластикордере PL 2200-3 (*Брабендер*, Россия). Пленки смесей готовили прессованием, выдерживая материал при 180°C под давлением в течение 3 мин с последующей закалкой в холодной воде. Поверхности пленок и пластин смесей изучали с помощью оптического микроскопа Axio Imager Z2m (*Carl Zeiss*, Германия) с программным обеспечением Axio Vision при увеличении 50× и 200× в отраженном свете. Упруго-прочностные свойства материалов при растяжении измерялись на универсальной разрывной машине Instron 3365 (*Instron*, Великобритания).

Результаты. Установлена роль модификаторов и полимерных добавок в композиции ПГБ–БНКС и их влияние на морфологию, кристалличность и механические характеристики смесей. Введение модификаторов позволило снизить средний размер частиц фазы БНКС в матрице ПГБ на 30–50%, а также изменило их морфологию. Равномерность распределения частиц при этом увеличилась, что позитивно повлияло на механические характеристики систем.

Выводы. Показано, что модификаторы меняют морфологию смесей, уменьшают средний размер частиц фазы БНКС на 30–50% и положительно влияют на прочность систем. Полученные композиции ввиду изменения структуры их межфазных слоев и, как следствие, физико-механических характеристик пригодны для применения в репаративной костной и зубной хирургии, а также для создания ранозаживляющих материалов.

Ключевые слова

полигидроксиалканоаты, костные имплантаты, остеогенез, биодеградируемые полимерные композиционные материалы, остеопластические материалы

Поступила: 06.04.2023
Доработана: 17.09.2024
Принята в печать: 16.10.2024

Для цитирования

Повернов П.А., Шибряева Л.С., Аншин С.М. Влияние модифицирующих добавок на структуру и свойства биоразлагаемых смесей на основе поли-3-гидроксибутирата и бутадиен-нитрильного каучука. *Тонкие химические технологии*. 2024;19(6):517–527. https://doi.org/10.32362/2410-6593-2024-19-6-517-527

INTRODUCTION

Currently, great importance is attached to the research and development of materials with applications in medicine, in particular, in osteoplasty and dental implant surgery [1–5]. An active search is underway for materials and composites which would have an osteoplastic effect while at the same time be resistant to bacteria [6–8]. However, due to their high degree of biodegradability, polymeric materials suitable for this application have a number of disadvantages in physical and mechanical characteristics and thus require modification.

The literature describes some possible variants of modification of polymers, such as hydrophilization of the polymer surface by plasma-chemical treatment in order to increase adhesive properties [9], or modification by introducing a mineral component, nanosized hydroxyapatite, in order to form porous calcium phosphate composites with a controlled structure [10]. In addition, research is underway to synthesize modifiers specifically for biodegradable polymers based on polyester polyols, and surfactants with a hyperbranched structure [11, 12]. Furthermore, research is being conducted to create fibrous materials from poly-3-hydroxybutyrate (PHB) with modifiers based on metal complexes with tetraphenylporphyrin [13, 14].

This paper examines the modification of PHB by introducing nitrile butadiene rubber and various compatibilizers and elasticizers in its composition with the purpose of improving the compatibility of the composite, its adhesion and strength, while maintaining the required degree of biodegradability.

EXPERIMENTAL

The main polymer under study was PHB synthesized by the microbiological method (*Biomer*, Germany) with a molecular weight of $2.1 \cdot 10^5$ and a crystallinity of 65%. Elasticity to the composite was imparted by adding NBR-28 AMN nitrile butadiene rubber (*SK Sibur*, Russia), a synthetic polymer, a product of the radical copolymerization of butadiene with acrylonitrile in an aqueous emulsion.

The following components were used as modifiers and compatibilizers.

1. Epoxidized soybean oil (ESO) (*Novokhim*, Russia) acts as a plasticizer and a heat and light stabilizer. The use of ESO is to increase the flexibility of the finished product without changing its chemical properties, reduce the melting point, and improve its heat and light stability [15].
2. Ethylene–vinyl acetate copolymer (EVA) (*Rusplast*, Russia). The addition of EVA increases the elasticity of the polymer composite material by 15–25% and improves the physical and mechanical properties. EVA helps to reduce the interfacial tension between the components and increase the thermodynamic compatibility of the polymer and rubber [16]. It is likely that the introduction of a hydroxyl-functionalized EVA copolymer (EVA-F) may further improve the interaction of the components thanks to hydrogen bonds between the terminal hydroxyl groups of PHB and EVA-F. Functionalization can be carried out by alkaline alcoholysis of EVA-F in a 30% KOH solution [17, 18].
3. Siloxane rubber (*Ekotek*, Russia) is an inert elastomer which does not affect biological processes and is suitable for use in medical implants. It is a biocompatible, hypoallergenic, chemically stable component, and can be used as a compatibilizer for the mixture during plasticization.
4. Polybutylene adipate terephthalate (PBAT) (*Anhui Juhong Trading Co.*, China) is a random polymer with a disordered structure that cannot crystallize. Therefore, this polymer can impart such characteristics to the composite as high flexibility, high impact toughness, low stiffness, and low elastic modulus, as well as a wide range of melting temperatures. It is important to note that this is a completely biodegradable polymer [19].
5. Oleic acid polyethylene glycol ester PEG-7 (*PCC Exol SA*, Poland) can serve as a compatibilizer for PHB and NBR-28. This is due to good compatibility with both components according to literature data [20]. At the same time, PEG-7 is a biodegradable substance, soluble both in water and in most organic solvents, allowing it to be used in the preparation of composite materials using both high-temperature and solution technologies. PEG-7 is safe and approved for indirect contact with food products and medicines.

Samples of the original polymers and mixtures containing 10, 20, 30, 40, 50, 60, 70, 80, and 90 wt % NBR-28 in PHB were studied. In addition, we also examined three-component mixtures based on PHB and NBR-28 with the addition of modifiers (ESO, EVA, siloxane rubber, oleic acid ester) or additional polymers (EVA and PBAT).

The composites were produced in a PL 2200-3 plasticorder (*Brabender*, Russia), which models a closed-type rubber mixer. This device provides a wide range of temperatures and operating speeds, allowing the composites to be studied over a wide range of shear rates. Mixing of the composites for this work was performed for 5 min at a temperature of 160 to 180°C, depending on the ratio of components and the type of modifier.

For samples with increased rubber content, the mixing of PHB and NBR-28 was also carried out on

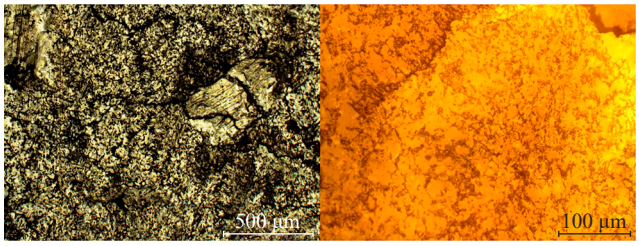
PD-240 laboratory rollers (*GDW*, Germany) with heating to 60°C, preliminary plasticization of rubber for 10 min, and subsequent introduction of a PHB powder.

Films of the mixtures were prepared by pressing on a laboratory press. The material was maintained at 180°C under pressure for 3 min with subsequent quenching in cold water. The surfaces of the films and plates of the mixtures were studied with an Axio Imager Z2m optical microscope (*Carl Zeiss*, Germany) with Axio Vision software at 50× and 200× magnification in reflected light.

RESULTS AND DISCUSSION

Figures 1–6 show macrophotographs of various three-component mixtures with modifiers at 50× and 200× magnification.

An analysis of the macrophotographs of these samples determined that siloxane rubber (Fig. 1) significantly affected the size distribution of NBR-28 particles in the PHB phase. The large particle size adversely affected the uniformity of particle distribution and can cause the sample properties to vary with the thickness of the product and the degree of its unevenness, as well as could increase the brittleness of the composite because of the presence of large foreign particles in the matrix, which serve as centers for the growth of defects and cracks in the sample.

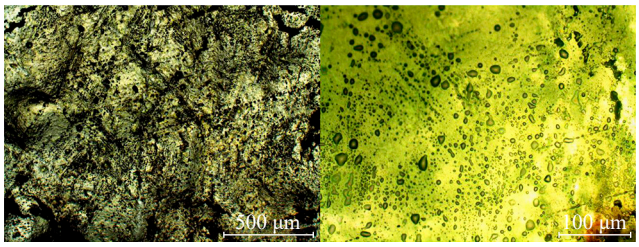


(a) (b)

Fig. 1. PHB–NBR-28 + siloxane rubber (90/10% + 3%) at (a) 50× and (b) 200× magnification

The microphotographs at 200× magnification show that, although the morphology of these mixtures is heterogeneous, the NBR-28 particles (dark inclusions in the matrix) are finely dispersed fibrous aggregates which form bundles and ribbons, in contrast to spherical aggregates in the case of the PHB–NBR-28 mixture without the use of a compatibilizer [21]. The particle size in the two-component mixture is 60–100 μm, whereas the length of the NBR-28 bundles using a compatibilizing agent reaches 20–40 μm.

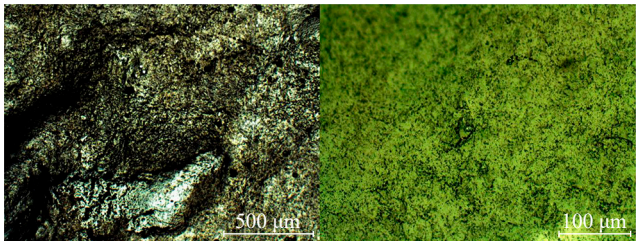
In order to increase the elasticity and biodegradability of the mixtures, the possibility of using PBAT as a component to replace rubber was explored. As can be seen in Fig. 2, mixing of PBAT and PHB in the presence of small amounts of ESO can give uniformly distributed dispersed PBAT particles in the PHB matrix. In this work, drop-shaped PBAT inclusions with sizes from 10 to 30 μm were obtained. At the same time, due to the high biodegradability of both components [19, 22], the ratios of the components can be varied over a wide range. This allows the parameters of the decomposition rate and the mechanical characteristics of the polymer composite material for the required medical application to be varied (dental implant, bone implant for low or high mechanical load, biodegradable suture material, etc.).



(a) (b)

Fig. 2. PHB–PBAT + ESO (70/30% + 3%) at (a) 50× and (b) 200× magnification

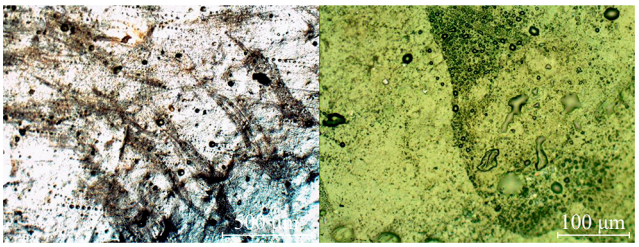
An interesting composite to study was the three-component mixture PHB–NBR-28–PBAT with a low rubber content and PHB as the main matrix-forming component (Fig. 3). In this case, since the compatibilization of both PHB with PBAT and NBR with PBAT was quite successful, PBAT served as a compatibility agent for the other two components. Based on the micrographs, in the case of three components, both PBAT and NBR were uniformly distributed both in the PHB matrix as a whole and relative to each other. The sizes of NBR and PBAT particles in the matrix were even smaller than in the case of siloxane rubber and ESO. The thickness of the aggregates did not exceed 20 μm, and the length was <40 μm. The average calculated equivalent diameter of such particles was 125 μm.



(a) (b)

Fig. 3. PHB–NBR-28–PBAT (60/10/30%) at (a) 50× and (b) 200× magnification

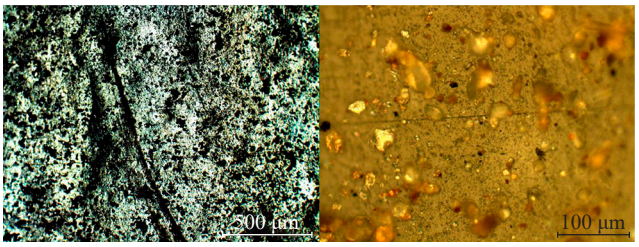
The combination of PHB and NBR-28 with EVA also proved to be relatively successful (Fig. 4), but the question of the biodegradation of these composites in dynamics remained open.



(a) (b)

Fig. 4. PHB–NBR-28–EVA (60/10/30%) at (a) 50× and (b) 200× magnification

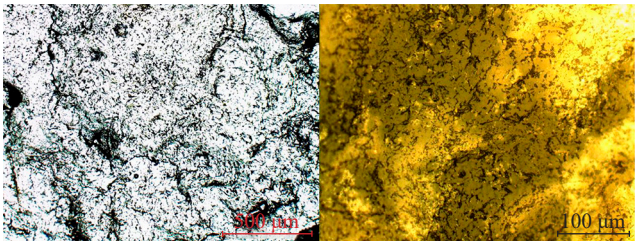
Figure 5 presents the micrographs of the sample containing 30 wt % EVA after biodegradation in soil for 1 month. It can be seen that volume defects and cavities in the structure of the material formed during this time. However, it is currently unknown whether all components decompose in this mixture or the main mass loss occurs due to the destruction of PHB. At present, studies are being conducted on the biodegradation of composites with EVA. They preliminarily show that, at a sufficient degree of biodegradability of these composites, the use of EVA improves the thermodynamic compatibility of the polymer matrix and rubber and reduces the interfacial tension between them.



(a) (b)

Fig. 5. PHB–NBR-28–EVA (60/10/30%) after biodegradation in soil for 1 month at (a) 50× and (b) 200× magnification

The introduction of PEG-7 as a compatibilizer (Fig. 6), as in the case of siloxane rubber and ESO, produced the expected effect of dispersing the components in each other and facilitated the processing of the composite in the plasticorder.



(a) (b)

Fig. 6. PHB–NBR-28 + PEG-7 (90/10% + 3%) at (a) 50× and (b) 200× magnification

The effect of additives taken in small amounts (up to 3%) on the crystalline and amorphous regions and the degree of crystallinity of the composite was studied by means of X-ray fluorescence analysis of the samples (Figs. 7a–7c) with the same content of NBR-28. A statistical analysis showed that the average calculated degrees of crystallinity of the samples with siloxane rubber and PEG-7 additives were 54% and 56%, respectively, whereas the degree of crystallinity of the composite without a modifier was 61%. We believe that the decrease in the size of inclusions of the NBR-28 phase upon the introduction of a modifier gives rise to strong interphase interactions. Modifiers behave as crystallization nuclei. The growth of small crystallites increases segmental mobility. This leads to an increase in the free volume, the porosity, and the number of physical entanglements.

In pure PHB without either additives or rubber, the degree of crystallinity was 70%. The lowest degree of crystallinity for the PHB–NBR-28 composite was observed at an equimass ratio of the components of 36% (Fig. 7d). This indicates that the addition of NBR-28 to PHB changes the phase and molecular structure by the intermolecular interaction of the components. In any further study of these composites, it is advisable to apply methods for studying the free surface energy and other surface properties of polymer composite materials, e.g., the methods used to study the effect of additives on the surface properties of NBR-based composites described previously [23, 24].

The main problem of the PHB biopolymer is its high brittleness, rendering it impossible to use it in pure form for any biomedical purposes [25]. In the case of the two-component system PHB–NBR, a large amount of rubber in the system (from 30%) significantly increases the elasticity of the system, although sharply reducing its ability to biodegrade and the rate of decomposition. Previous studies have confirmed that the content of NBR-28 in the polymer matrix up to 20% leaves the possibility for biodegradation of the polymer in biological environments at a sufficient rate for the growth of cells and vessels in the polymer matrix. It also enables complete decomposition before the onset of complications caused by the rejection of a foreign body by the organism [26]. Therefore, composites with a content of NBR-28 up to 20% will meet a set of requirements for biodegradable medical devices, provided that they are sufficiently elastic. The introduction of modifiers in this case helps to increase the strength characteristics due to better compatibility of components and dispersion of phase particles in the matrix. In addition, modifiers change the microstructure of the composites and can accelerate the processes of polymer biodegradation.

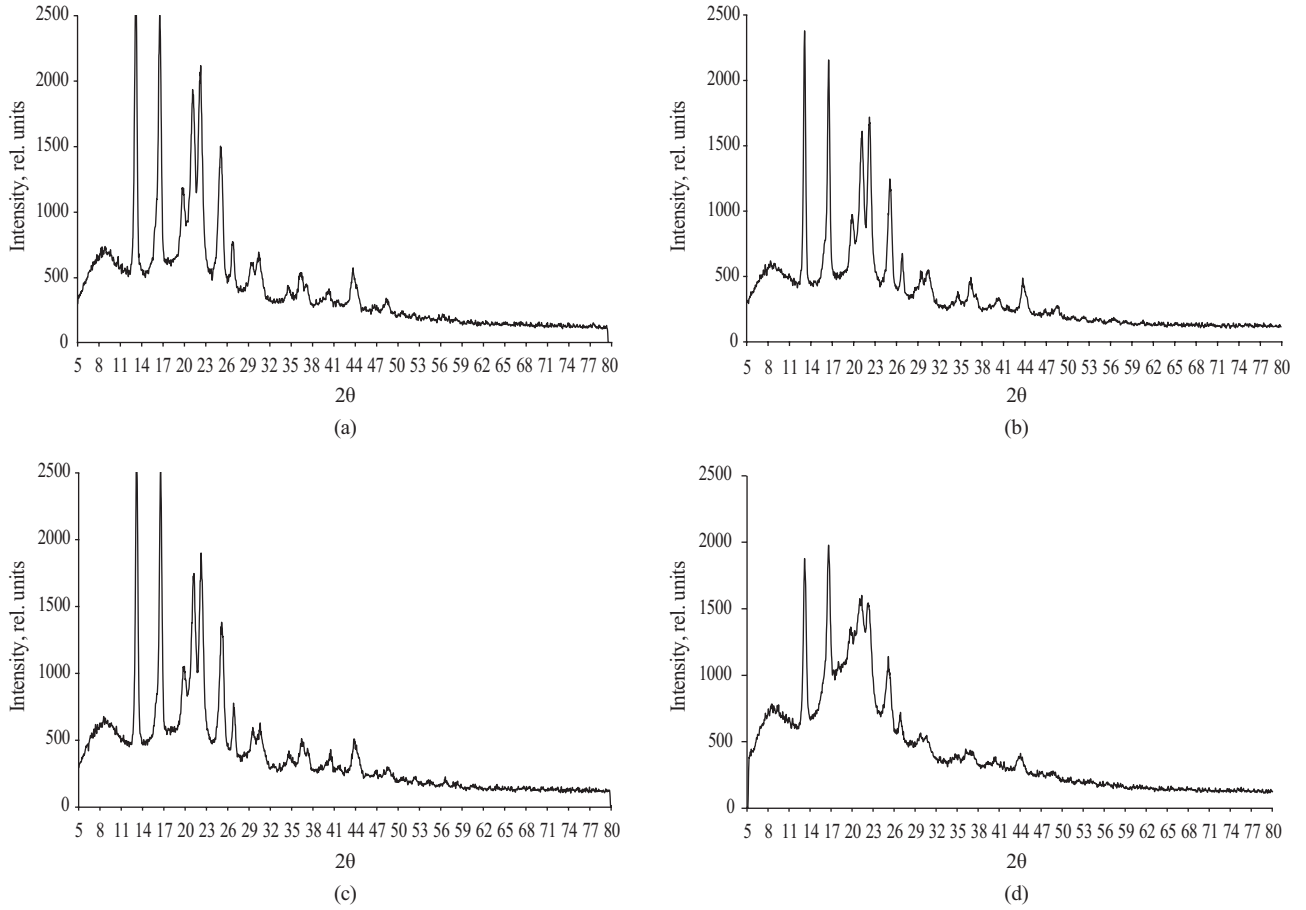


Fig. 7. X-ray fluorescence spectra of the 90% PHB–10% NBR-28 composite (a) without the addition of a compatibilizer, (b) with the addition of 3% siloxane rubber, and (c) with the addition of 3% PEG-7; (d) X-ray fluorescence spectrum of the 50% PHB–50% NBR-28 composite without a modifier

Tests used to determine the elastic strength properties under tension (GOST 270-75[1]) were carried out on an Instron 3365 universal tensile testing machine (*Instron*, United Kingdom). Of the composites studied, pronounced elastic properties were demonstrated by all PHB–NBR-28 two-component composites with a rubber content of 30% and higher, the PHB–NBR-28–EVA (60/10/30%) composite, and, to a lesser extent, the PHB–NBR-28–PBAT (60/10/30%) composite. Some samples modified only with compatibilizing additives (ESO, siloxane rubber), 90% PHB contents, and up to 10% NBR-28 proved to be brittle for testing of this kind. Clearly the strengthening of the composite, as expected, can be carried out in two ways: by increasing the content of NBR-28 to more than 20% in the presence of a compatibilizer; or by introducing an elastic polymer as an additional component, as in the case of the PHB–NBR-28–PBAT and PHB–NBR-28–EVA systems. The following table presents the obtained mechanical characteristics of these composites.

Note that composite 6 (PHB–NBR-28, 10/90%) is not biodegradable to a sufficient degree and serves only for comparative analysis, as does composite 5 with a NBR-28 content of 50%. In turn, sample 4 with a content of NBR-28 of 30% is borderline suitable for certain medical products. However, the degree of its biodegradability and the possibility of enhancing degradation with additives have yet to be studied.

Composites with introduced EVA and PBAT showed a tensile strength exceeding the strength of composites 3 and 4 with a high rubber content without additional additives. Meanwhile, based on the data of reviews [25, 27] concerning methods of strengthening composites with PHB, the comparative strength of the PHB–NBR-28 and PHB–NBR-28–EVA composites is somewhat higher than those of PHB composites with starch, cellulose, and polymer fillers (ethylene–vinyl

[1] GOST 270-75. Interstate Standard. Rubber. Method of the determination elastic and tensile stress-strain properties. Moscow: Standartinform; 2008.

Table. Mechanical characteristics of polymer composites

No.	Composite	Elongation at break, %	Tensile strength, MPa
1	PHB–NBR-28 (90/10%)	0–2 (brittle fracture)	16 ± 1
2	PHB–NBR-28–PBAT (60/10/30%)	21 ± 1	32 ± 1.5
3	PHB–NBR-28–EVA (60/10/30%)	26 ± 1.5	37 ± 2
4	PHB–NBR-28 (70/30%)	33 ± 2	33 ±1.5
5	PHB–NBR-28 (50/50%)	58 ± 3	48 ± 2.5
6	PHB–NBR-28 (10/90%)	85 ± 4	61.5 ± 3

acetate copolymer, polylactide). However, it is lower than those of fibers obtained from mixtures of PHB and ultrahigh-molecular-weight PHB by cold drawing [28] or fibers of a PHB copolymer with poly-3-hydroxyhexanoate [29].

The process of complete degradation of three-component composites with EVA and PBAT is currently being studied. According to the results of biodegradation for 100 days in the soil, preliminary conclusions can be made about a gradual decrease in the weight of samples and a significant degree of crack growth up to 40 and 70 nm thick in the case of EVA and PBAT, respectively. It can also be assumed that the weight loss of the composite during degradation in the case of EVA and PBAT is equal to or even exceeds the weight loss of the PHB–NBR-28 composites without additional additives.

CONCLUSIONS

In this work, the optimal mode of mixing of the PHB–NBR-28–modifier composite was selected. The necessary modifiers were found to improve the compatibility of the components and impart the necessary physical and mechanical properties while maintaining the required degree of biodegradability.

A more extended study into the biodegradability of the components is being conducted elsewhere; however, preliminary findings indicate a sufficient degree of biodegradability of the most promising composites, namely, PHB–NBR-28–EVA (60/10/30%) and PHB–NBR-28–PBAT (60/10/30%). With regard to composites with 90% PHB, 10% NBR-28, and an additive (ESO, siloxane rubber), the modifier in an amount of 1–3% does not adversely affect their biodegradability. A composite with pure PHB and NBR-28 in a ratio of 9 : 1 has already been studied earlier and is suitable for use in biodegradable medical products.

As expected, the introduction of modifiers, allowed the average particle size of the NBR phase in the PHB matrix to be reduced by 30–50% or greater. It also changed their morphology from spherical particles of 60–100 nm to elongated fibers aggregated into bundles and ribbons with a thickness of 5 to 20 nm and a length of 10 to 50 nm for different modifiers. The uniformity of particle distribution increased, beneficially affecting the mechanical characteristics of the systems. However, without the introduction of the second polymer (EVA or PBAT), the brittleness of the systems remained quite high; therefore, modifiers (ESO, siloxane rubber) will be of interest for use at an increased NBR content (presumably 20% or more).

Authors' contributions

L.S. Shibryaeva—concept and management of the work, editing the text of the article.

P.A. Povernov—conducting experiments, discussing the results of the study, and writing the text of the article.

S.M. Anshin—conducting experiments, discussing the results of the study.

The authors declare no conflicts of interest.

REFERENCES

1. Verma M.L., Kumar S., Jeslin J., Dubey N.K. Microbial Production of Biopolymers with Potential Biotechnological Applications. In: *Biopolymer-Based Formulations*. Elsevier; 2020. P. 105–137. https://doi.org/10.1016/B978-0-12-816897-4.00005-9
2. Rebelo R., Vila N., Rana S., Fangueiro R. Poly Lactic Acid Fibre Based Biodegradable Stents and Their Functionalization Techniques. In: Fangueiro R., Rana S. (Eds.). *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*. *RILEM Bookseries*. 2017;12:331–342. https://doi.org/10.1007/978-94-017-7515-1_25
3. Vasilyev I.Yu., Ananyev V.V., Kolpakova V.V., Sardzhveladze A.S. Development of technology for producing biodegradable hybrid composites based on polyethylene, starch, and monoglycerides. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2020;15(6):44–55. https://doi.org/10.32362/2410-6593-2020-15-6-44-55
4. Vasilyev I.Yu., Ananyev V.V., Chernov M.E. Biodegradable packaging materials based on low density polyethylene, starch and monoglycerides. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(3):231–241. https://doi.org/10.32362/2410-6593-2022-17-3-231-241
5. Gomzyak V.I., Demina V.A., Razuvaeva E.V., Sedush N.G., Chvalun S.N. Biodegradable polymer materials for medical applications: From implants to organs. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2017;12(5):5–20 (in Russ.). https://doi.org/10.32362/2410-6593-2017-12-5-5-20
6. Lykoshin D.D., Zaitsev V.V., Kostromina M.A., Esipov R.S. New-generation osteoplastic materials based on biological and synthetic matrices. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2021;16(1):36–54. https://doi.org/10.32362/2410-6593-2021-16-1-36-54
7. Gomzyak V.I., Puchkov A.A., Artamonova N.E., Polyakov D.K., Simakova G.A., Gritskova I.A., Chvalun S.N. Physico-chemical properties of biodegradable hyperbranched polyester polyol based on 2,2-bis(methylol)propionic acid. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2018;13(4):67–73 (in Russ.). https://doi.org/10.32362/2410-6593-2018-13-4-67-73
8. Gordienko M.G., Somov T.N., Yusupova Y.S., Chupikova N.I., Menshutina N.V. Preparation of spherical microparticles from biodegradable natural and synthetic polymers for their application in regenerative medicine. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2015;10(5):66–76 (in Russ.).
9. Luque-Agudo V., Hierro-Oliva M., Gallardo-Moreno A.M., González-Martín M.L. Effect of plasma treatment on the surface properties of polylactic acid films. *Polym. Test*. 2021;96:107097. https://doi.org/10.1016/j.polymertesting.2021.107097
10. Gorshenyov V.N., Ziangirova M.Yu., Kolesov V.V., Krasnopol'skaya L.M., Prosvirin A.A., Teleshev A.T. New additive technologies for forming complex bone structures for medical and biological applications. *RENSIT*. 2019;11(3):369–390 (in Russ). https://doi.org/10.17725/rensit.2019.11.369
11. Gomzyak V.I., Artamonova N.E., Kovtun I.D., Kamyshinsky R.A., Gritskova I.A., Chvalun S.N. Heterophase Polymerization of Styrene in the Presence of Boltorn Polyester Polyol. *Polym. Sci. Ser. B*. 2020;62(1):22–29. https://doi.org/10.1134/S156009041905004X
12. Sedush N.G., Kadina Yu.A., Razuvaeva E.V., *et al.* Nanoformulations of Drugs Based on Biodegradable Lactide Copolymers with Various Molecular Structures and Architectures. *Nanotechnol. Rep*. 2021;16(4):421–438. https://doi.org/10.1134/S2635167621040121

СПИСОК ЛИТЕРАТУРЫ

1. Verma M.L., Kumar S., Jeslin J., Dubey N.K. Microbial Production of Biopolymers with Potential Biotechnological Applications. In: *Biopolymer-Based Formulations*. Elsevier; 2020. P. 105–137. https://doi.org/10.1016/B978-0-12-816897-4.00005-9
2. Rebelo R., Vila N., Rana S., Fangueiro R. Poly Lactic Acid Fibre Based Biodegradable Stents and Their Functionalization Techniques. In: Fangueiro R., Rana S. (Eds.). *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*. *RILEM Bookseries*. 2017;12:331–342. https://doi.org/10.1007/978-94-017-7515-1_25
3. Васильев И.Ю., Ананьев В.В., Колпакова В.В., Сарджвеладзе А.С. Разработка технологии получения биоразлагаемых композиций на основе полиэтилена, крахмала и моноглицеридов. *Тонкие химические технологии*. 2020;15(6):44–55. https://doi.org/10.32362/2410-6593-2020-15-6-44-55
4. Васильев И.Ю., Ананьев В.В., Чернов М.Е. Биоразлагаемые упаковочные материалы на основе полиэтилена низкой плотности, крахмала и моноглицеридов. *Тонкие химические технологии*. 2022;17(3):231–241. https://doi.org/10.32362/2410-6593-2022-17-3-231-241
5. Гомзяк В.И., Демина В.А., Разуваева Е.В., Седуш Н.Г., Чвалун С.Н. Биоразлагаемые полимерные материалы для медицины: от импланта к органу. *Тонкие химические технологии*. 2017;12(5):5–20. https://doi.org/10.32362/2410-6593-2017-12-5-5-20
6. Лыкошин Д.Д., Зайцев В.В., Костромина М.А., Есипов Р.С. Остеопластические материалы нового поколения на основе биологических и синтетических матриксов. *Тонкие химические технологии*. 2021;16(1):36–54. https://doi.org/10.32362/2410-6593-2021-16-1-36-54
7. Гомзяк В.И., Пучков А.А., Артамонова Н.Е., Поляков Д.К., Симакова Г.А., Грицкова И.А., Чвалун С.Н. Физико-химические свойства биоразлагаемого сверхразветвленного полиэфирполиола на основе 2,2-бис(метилол)пропионовой кислоты. *Тонкие химические технологии*. 2018;13(4):67–73. https://doi.org/10.32362/2410-6593-2018-13-4-67-73
8. Гордиенко М.Г., Сомов Т.Н., Юсупова Ю.С., Чупикова Н.И., Меньшутина Н.В. Получение микрочастиц из биодеградируемых природных и синтетических полимеров для применения их в области регенеративной медицины. *Тонкие химические технологии*. 2015;10(5):66–76.
9. Luque-Agudo V., Hierro-Oliva M., Gallardo-Moreno A.M., González-Martín M.L. Effect of plasma treatment on the surface properties of polylactic acid films. *Polym. Test*. 2021;96:107097. https://doi.org/10.1016/j.polymertesting.2021.107097
10. Горшенёв В.Н., Зиангирова М.Ю., Колесов В.В., Краснопольская Л.М., Просвирин А.А., Телешев А.Т. Новые аддитивные технологии формирования сложных костных структур для медико-биологических применений. *РЭНСИТ*. 2019;11(3):369–390. https://doi.org/10.17725/rensit.2019.11.369
11. Gomzyak V.I., Artamonova N.E., Kovtun I.D., Kamyshinsky R.A., Gritskova I.A., Chvalun S.N. Heterophase Polymerization of Styrene in the Presence of Boltorn Polyester Polyol. *Polym. Sci. Ser. B*. 2020;62(1):22–29. https://doi.org/10.1134/S156009041905004X
12. Седуш Н.Г., Кадина Ю.А., Разуваева Е.В., Пучков А.А., Широкова Е.М., Гомзяк В.И., Калинин К.Т., Кулебякина А.И., Чвалун С.Н. Наносомальные лекарственные формы на основе биоразлагаемых сополимеров лактида с различной молекулярной структурой и архитектурой. *Российские нанотехнологии*. 2021;16(4):462–481. https://doi.org/10.1134/S1992722321040117

[Original Russian Text: Sedush N.G., Kadina Yu.A., Razuvaeva E.V., Puchkov A.A., Shirokova E.M., Gomzyak V.I., Kalinin K.T., Kulebyakina A.I., Chvalun S.N. Nanosomal dosage forms based on biodegradable lactide copolymers with different molecular structure and architecture. *Rossiiskie Nanotekhnologii*. 2021;16(4):462–481 (in Russ.). https://doi.org/10.1134/S1992722321040117]

13. Karpova S.G., Ol'khov A.A., Krivandin A.V., *et al.* Effect of zinc–porphyrin complex on the structure and properties of poly(3-hydroxybutyrate) ultrathin fibers. *Polym. Sci. Ser. A.* 2019;61(1):70–84. https://doi.org/10.1134/S0965545X19010140
[Original Russian Text: Karpova S.G., Ol'khov A.A., Krivandin A.V., Shatalova O.V., Popov A.A., Lobanov A.V., Iordanskii A.L. Effect of zinc–porphyrin complex on the structure and properties of poly(3-hydroxybutyrate) ultrathin fibers. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2019;61(1):67–81 (in Russ.). https://doi.org/10.1134/S2308112019010164]
14. Karpova S.G., Ol'khov A.A., Zhul'kina A.L., *et al*. Nonwoven Materials Based on Electrospun Ultrathin Fibers of Poly(3-hydroxybutyrate) and Complex Tin Chloride–Porphyrin. *Polym. Sci. Ser. A.* 2021;63(4):369–381. https://doi.org/10.1134/S0965545X21040040
[Original Russian Text: Karpova S.G., Ol'khov A.A., Zhul'kina A.L., Popov A.A., Iordanskii A.L. Nonwoven Materials Based on Electrospun Ultrathin Fibers of Poly(3-hydroxybutyrate) and Complex Tin Chloride–Porphyrin. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2021;63(4):249–262 (in Russ.). https://doi.org/10.31857/S2308112021040040]
15. Pour-Esmaeil S., Sharifi-Sanjani N., Khoee S., Taheri-Qazvini N. Biocompatible chemical network of *α*-cellulose-ESBO (epoxidized soybean oil) scaffold for tissue engineering application. *Carbohydr. Polym*. 2020;241:116322. https://doi.org/10.1016/j.carbpol.2020.116322
16. Zhang H.-C., Huang J., Zhao P.-F., Lu X. Bio-based ethylene-co-vinyl acetate/poly (lactic acid) thermoplastic vulcanizates with enhanced mechanical strength and shape memory behavior. *Polym. Test*. 2020;87:106537. https://doi.org/10.1016/j.polymertesting.2020.106537
17. Emmanuelle M., Yves C., Nathalie I., Franck E., Laurent G., Philippe F. The Controlled Solvolysis of Ethylene−Vinyl Acetate Copolymers. *Macromolecules*. 2001;34(17):5838–5847. https://doi.org/10.1021/ma0102666
18. Sukhikh E.S., Silant'eva M.E., Lirova B.I., Suvorov A.L., Nadol'skii A.L., Tyukova I.S., Suvorova A.I. Synthesis of copolymers of ethylene and vinyl alcohol (EVA), their structure and membrane properties. In: *Problems of Theoretical and Experimental Chemistry:* Abstracts of reports of the 20th Russian Youth Scientific Conference. Yekaterinburg: 2010. P. 406–408 (in Russ.).
19. Zhang J., Hirschberg V., Rodrigue D. Mechanical fatigue of biodegradable polymers: A study on polylactic acid (PLA), polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT). *Int. J. Fatigue*. 2022;159(2):106798. https://doi.org/10.1016/j.ijfatigue.2022.106798
20. Povernov P.A., Shibryaeva L.S., Lyusova L.R., *et al.* The Influence of Mixing Conditions on the Morphology of Poly-3-hydroxybutyrate and Nitrile-Butadiene Rubber Polymer Compositions. *Polym. Sci. Ser. D.* 2022;15(4):628–632. https://doi.org/10.1134/S1995421222040220
21. Zhorina L.A., Rogovina S.Z., Prut E.V., *et al*. Biodegradable compositions based on poly-(3-hydroxybutyrate) and polylactide polyesters obtained from vegetable raw materials. *Polym. Sci. Ser. A.* 2020;62(4):361–367. https://doi.org/10.1134/S0965545X20040136
13. Карпова С.Г., Ольхов А.А., Кривандин А.В., Шаталова О.В., Лобанов А.В., Попов А.А., Иорданский А.Л. Влияние комплекса цинк–порфирин на структуру и свойства ультратонких волокон поли(3-гидроксибутирата). *Высокомолекул. соединения. Сер. А.* 2019;61(1):67–81. https://doi.org/10.1134/S2308112019010164
14. Карпова С.Г., Ольхов А.А., Жулькина А.Л., Попов А.А., Иорданский А.Л. Нетканые материалы на основе ультратонких волокон поли(3-гидроксибутирата) с комплексом хлорид олова–порфирин, полученных электроформованием. *Высокомолекул. соединения. Сер. А.* 2021;63(4):249–262. https://doi.org/10.31857/S2308112021040040
15. Pour-Esmaeil S., Sharifi-Sanjani N., Khoee S., Taheri-Qazvini N. Biocompatible chemical network of *α*-cellulose-ESBO (epoxidized soybean oil) scaffold for tissue engineering application. *Carbohydr. Polym*. 2020;241:116322. https://doi.org/10.1016/j.carbpol.2020.116322
16. Zhang H.-C., Huang J., Zhao P.-F., Lu X. Bio-based ethylene-co-vinyl acetate/poly (lactic acid) thermoplastic vulcanizates with enhanced mechanical strength and shape memory behavior. *Polym. Test*. 2020;87:106537. https://doi.org/10.1016/j.polymertesting.2020.106537
17. Emmanuelle M., Yves C., Nathalie I., Franck E., Laurent G., Philippe F. The Controlled Solvolysis of Ethylene−Vinyl Acetate Copolymers. *Macromolecules*. 2001;34(17):5838–5847. https://doi.org/10.1021/ma0102666
18. Сухих Е.С., Силантьева М.Э., Лирова Б.И., Суворов А.Л., Надольский А.Л., Тюкова И.С., Суворова А.И. Синтез сополимеров этилена и винилового спирта (ЭВС), их структура и мембранные свойства. В сб.: *Проблемы теоретической и экспериментальной химии:* тезисы докладов XX Российской молодежной научной конференции. Екатеринбург. 2010. С. 406–408.
19. Zhang J., Hirschberg V., Rodrigue D. Mechanical fatigue of biodegradable polymers: A study on polylactic acid (PLA), polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT). *Int. J. Fatigue*. 2022;159(2):106798. https://doi.org/10.1016/j.ijfatigue.2022.106798
20. Povernov P.A., Shibryaeva L.S., Lyusova L.R., *et al.* The Influence of Mixing Conditions on the Morphology of Poly-3-hydroxybutyrate and Nitrile-Butadiene Rubber Polymer Compositions. *Polym. Sci. Ser. D.* 2022;15(4):628–632. https://doi.org/10.1134/S1995421222040220
21. Жорина Л.А., Роговина С.З., Прут Э.В., Кузнецова О.П., Грачев А.В., Иванушкина Н.Е., Иорданский А.Л., Берлин А.А. Биоразлагаемые композиции на основе полиэфиров поли-(3-гидроксибутирата) и полилактида, получаемых из растительного сырья. *Высокомолекул. соединения. Сер. А.* 2020;62(4):263–270. https://doi.org/10.31857/S2308112020040136
22. Тарасенко А.Д., Дулина О.А., Буканов А.М. Влияние неполимерных компонентов резиновой смеси на поверхностные свойства эластомерных композиций. *Тонкие химические технологии*. 2018;13(5):67–72. https://doi.org/10.32362/2410-6593-2018-13-5-67-72
23. Дулина О.А., Еськова Е.В., Тарасенко А.Д., Котова С.В. Влияние различных факторов на поверхностные свойства эластомерных материалов на основе бутадиен-нитрильных каучуков. *Тонкие химические технологии*. 2022;17(2):152–163. https://doi.org/10.32362/2410-6593-2022-17-2-152-163
24. Yeo J.C.C., Muiruri J.K., Thitsartarn W., Li Z., He C. Recent advances in the development of biodegradable PHB-based toughening materials: Approaches, advantages and applications. *Mater. Sci. Eng.: C*. 2017;92:1092–1116. https://doi.org/10.1016/j.msec.2017.11.006

[Original Russian Text: Zhorina L.A., Rogovina S.Z., Prut E.V., Kuznetsova O.P., Grachev A.V., Ivanushkina N.E., Iordanskii A.L., Berlin A.A. Biodegradable compositions based on poly-(3-hydroxybutyrate) and polylactide polyesters obtained from vegetable raw materials. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2020;62(4):263–270 (in Russ.). https://doi.org/10.31857/S2308112020040136]
22. Tarasenko A.D., Dulina O.A., Bukanov A.M. The effect of non-polymeric components of a rubber mixture on surface properties of elastomer compositions. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2018;13(5):67–72 (in Russ.). https://doi.org/10.32362/2410-6593-2018-13-5-67-72
23. Dulina O.A., Eskova E.V., Tarasenko A.D., Kotova S.V. Influence of various factors on surface properties of elastomeric materials based on nitrile butadiene rubbers. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(2):152–163. https://doi.org/10.32362/2410-6593-2022-17-2-152-163
24. Yeo J.C.C., Muiruri J.K., Thitsartarn W., Li Z., He C. Recent advances in the development of biodegradable PHB-based toughening materials: Approaches, advantages and applications. *Mater. Sci. Eng.: C*. 2017;92:1092–1116. https://doi.org/10.1016/j.msec.2017.11.006
25. Povernov P.A., Shibryaeva L.S. Scientific approaches to the development of materials based on compositions of poly-3-hydroxybutyrate and polylactide for bone implants. In: *Innovatsii v sozdanii materialov i metodov dlya sovremennoi meditsiny* (*Innovations in the Creation of Materials and Methods for Modern Medicine*): Proceedings of the regional conference. 2020. P. 173–179 (in Russ.).
26. Povernov P.A., Shibryaeva L.S., Lusova L.R., Popov A.A. Modern polymer composite materials for bone surgery: Problems and prospects. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(6):514–536. https://doi.org/10.32362/2410-6593-2022-17-6-514-536
27. Kabe T., Tsuge T., Kasuya K., Takemura A., Hikima T., Takata M., Iwata T. Physical and Structural Effects of Adding Ultrahigh-Molecular-Weight Poly[(*R*)-3-hydroxybutyrate] to Wild-Type Poly[(*R*)-3-hydroxybutyrate]. *Macromolecules*. 2012;45(4):1858–1865. https://doi.org/10.1021/ma202285c
28. Kabe T., Hongo C., Tanaka T., Hikima T., Takata M., Iwata T. High tensile strength fiber of poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] processed by two-step drawing with intermediate annealing. *J. Appl. Polym. Sci*. 2014;132(2):41258. https://doi.org/10.1002/app.41258
25. Повернов П.А., Шибряева Л.С. Научные подходы к разработке материалов на основе композиций из поли-3-гидроксибутирата и полилактида для костных имплантатов. *Инновации в создании материалов и методов для современной медицины:* материалы региональной конференции. 2020. С. 173–179.
26. Повернов П.А., Шибряева Л.С., Люсова Л.Р., Попов А.А. Современные полимерные композиционные материалы для костной хирургии: проблемы и перспективы. *Тонкие химические технологии*. 2022;17(6):514–536. https://doi.org/10.32362/2410-6593-2022-17-6-514-536
27. Kabe T., Tsuge T., Kasuya K., Takemura A., Hikima T., Takata M., Iwata T. Physical and Structural Effects of Adding Ultrahigh-Molecular-Weight Poly[(*R*)-3-hydroxybutyrate] to Wild-Type Poly[(*R*)-3-hydroxybutyrate]. *Macromolecules*. 2012;45(4):1858–1865. https://doi.org/10.1021/ma202285c
28. Kabe T., Hongo C., Tanaka T., Hikima T., Takata M., Iwata T. High tensile strength fiber of poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] processed by two-step drawing with intermediate annealing. *J. Appl. Polym. Sci*. 2014;132(2):41258. https://doi.org/10.1002/app.41258

About the authors

Pavel A. Povernov, Postgraduate Student, Junior Researcher, Laboratory of Physico-Chemistry of Compositions of Synthetic and Natural Polymers, N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences (4, Kosygina ul., Moscow, 119334, Russia). E-mail: pav3444@yandex.ru. Scopus Author ID 57210264564, ResearcherID ABC-5732-2021, RSCI SPIN-code 1408-2867, https://orcid.org/0000-0003-3017-4397

Lyudmila S. Shibryaeva, Dr. Sci. (Chem.), Professor, Leading Researcher, Laboratory of Physico-Chemistry of Compositions of Synthetic and Natural Polymers, N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences (4, Kosygina ul., Moscow, 119334, Russia); Professor, F.F. Koshelev Department of Chemistry and Technology of Processing of Elastomers, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: lyudmila.shibryaeva@yandex.ru. Scopus Author ID 7003539026, ResearcherID A-7634-2014, RSCI SPIN-code 3664-7997, https://orcid.org/0000-0001-6805-4492

Sergey M. Anshin, Junior Researcher, Department of Chemistry of Innovative Materials and Technologies, Plekhanov Russian University of Economics (36, Stremyannyi per., Moscow, 115054, Russia). E-mail: asm51@bk.ru

Об авторах

Повернов Павел Алексеевич, аспирант, младший научный сотрудник, лаборатория физико-химии композиций природных и синтетических полимеров, ФГБУН Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук (199334, Россия, Москва, ул. Косыгина, д. 4). E-mail: pav3444@yandex.ru. Scopus Author ID 57210264564, ResearcherID ABC-5732-2021, SPIN-код РИНЦ 1408-2867, https://orcid.org/0000-0003-3017-4397

Шибряева Людмила Сергеевна, д.х.н., профессор, ведущий научный сотрудник, лаборатория физико-химии композиций природных и синтетических полимеров, ФГБУН Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук (199334, Россия, Москва, ул. Косыгина, д. 4); профессор, кафедра химии и технологии переработки эластомеров им. Ф.Ф. Кошелева, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: lyudmila.shibryaeva@yandex.ru. Scopus Author ID 7003539026, ResearcherID A-7634-2014, SPIN-код РИНЦ 3664-7997, https://orcid.org/0000-0001-6805-4492

Аншин Сергей Михайлович, младший научный сотрудник, кафедра химии инновационных материалов и технологий, ФГБОУ ВО «Российский экономический университет им. Г.В. Плеханова» (115054, Россия, Москва, Стремянный переулок, д. 36). E-mail: asm51@bk.ru

Translated from Russian into English by V. Glyanchenko
Edited for English language and spelling by Dr. David Mossop