Thermal and physico-mechanical properties of biodegradable materials based on polyhydroxyalkanoates*)

Igor Semeniuk[1), 3)] (ORCID ID: 0000-0002-8481-4807), **Viktoria Kochubei**[2)] (0000-0003-1537-3953),
Elena Karpenko[1)] (0000-0002-1943-8673), **Yuriy Melnyk**[2)] (0000-0002-8516-9926),
Volodymyr Skorokhoda[2), **)] (0000-0002-2352-5964), **Natalia Semenyuk**[2)] (0000-0002-1112-8486)

DOI: https://doi.org/10.14314/polimery.2022.11.3

Abstract: Thermal and physico-mechanical properties of polyhydroxyalkanoates of *Rhodococcus erythropolis* Au-1, *Pseudomonas* sp. PS-17, *Azotobacter vinelandii* N-15 and polyhydroxybutyrate/polylactide (PHB/PLA) blends were investigated. The addition 5 wt% PLA improved PHB properties, such as thermal resistance and stiffness. However, higher PLA content led to a decrease in thermal stability, while increasing elongation. PHB/PLA blends are recommended as packaging materials for food, agricultural and pharmaceutical products.

Keywords: polyhydroxyalkanoate, polyhydroxybutyrate, polylactide, blends, thermal properties, physical and mechanical properties.

Właściwości termiczne i fizykomechaniczne materiałów biodegradowalnych na bazie polihydroksyalkanianów

Streszczenie: Zbadano właściwości termiczne i fizykomechaniczne polihydroksyalkanianów *Rhodococcus erythropolis* Au-1, *Pseudomonas* sp. PS-17, *Azotobacter vinelandii* N-15 oraz mieszaniny PHB/PLA. Dodatek 5% mas. PLA poprawił właściwości PHB, takie jak odporność termiczna i sztywność. Jednak przy większej zawartości PLA nastąpiło zmniejszenie stabilności termicznej, przy jednoczesnym zwiększeniu wydłużenia. Mieszaniny PHB/PLA są zalecane jako materiały opakowaniowe produktów spożywczych, rolniczych i farmaceutycznych.

Słowa kluczowe: polihydroksyalkanian, polihydroksymaślan, polilaktyd, mieszaniny, właściwości termiczne, fizyczne i mechaniczne.

Polymers and polymer-based plastics are an integral part of modern life and are used as packaging, structural, electrical insulation, and other materials [1]. The amount of non-degradable plastic waste is increasing every year, which poses a threat to the environment. One of the promising areas of modern bioengineering and polymer synthesis technology is the production of polymers which are biodegradable and suitable for use in various fields of human life, in particular, in biomedicine, pharmacy, and the packaging industry [2, 3]. The terms "biobased polymers" and "biodegradable polymers" are widely used in the literature, but there is a significant difference between them. Biodegradable polymers are completely destroyed under the influence of microorganisms, carbon dioxide, methane, and water. Biobased polymers can be biodegradable (e.g., lactic acid polymers) or non-degradable (e.g., biopolyethylene). The limitation of oil resources and the growth of environmental problems cause interest in biodegradable polymers for various industries. Biopolymers are able not only to replace synthetic polymers but allow to obtain new combinations of properties for new applications [4, 5].

In recent decades, much attention has been focused on the production of polyesters – products of bacterial biosynthesis. There is a growing number of developments aimed

---

[1)] Department of Physical Chemistry of Fossil Fuels, L.M. Lytvynenko Institute of Physical Organic Chemistry and Coal Chemistry of the NAS of Ukraine, 3a, Naukova Str., 79060 Lviv, Ukraine.

[2)] Lviv Polytechnic National University, Department of Chemical Technology and Plastic Processing, 12, Bandery Str., 79013 Lviv, Ukraine.

[3)] Foshan Tianheng New Material Technology Co., Ltd, Foshan, China.

[*)] Material contained in this article was presented at the 4th International Scientific Conference Advanced Polymer Material and Technologies "APMT 2022", 11 October 2022, Kyiv and Lviv, Ukraine.

[**)] Author for correspondence: vskorohoda@yahoo.com

at improving existing biodegradable materials, such as polyhydroxyalkanoates (PHA) and polylactides (PLA) [6, 7]. Among the known commercial biopolymers, polyhydroxyalkanoates are known as a sustainable alternative to synthetic polymers due to their complete degradability [8, 9].

The advantages of PHA over polymers produced from petroleum raw materials are the possibility of synthesis from renewable carbon sources, biodegradability, and biocompatibility [10]. The most common representative of PHA is polyhydroxybutyrate (PHB), discovered in 1923 by Lemoyne. PHB is a thermoplastic polymer with physical properties similar to polypropylene. PHB processing does not require large amounts of additional materials, it is easily formed from solutions and melts, and can be used to obtain films of various thicknesses, sheets, threads, hollow products, and packaging containers.

PHB, which is synthesized by bacteria from renewable raw materials, is an environmentally friendly, fully biodegradable, highly hydrophobic, and partially crystalline thermoplastic polyester material [11, 12]. This isotactic polymer without chain branching does not contain catalyst residues like other synthetic polymers. PHB does not dissolve in water but it is completely biodegradable. Due to its high crystallinity, PHB has relatively high glass transition and melting temperatures, but its rigidity, brittleness and low impact resistance limit PHB use [13–16].

For improving of the PHB technological properties, it is mixed with other polymers, which may be not biodegradable. It is known that various monomers and polymers are used to develop biodegradable compositions with different properties. Among them are mixtures of PHB with copolymers of ethylene propylene and ethylene vinyl acetate, polyvinyl acetate, polyethylene oxide, polypropylene [17]. To improve the mechanical properties of biopolymers, they are also modified with natural fibers, nanomaterials [18] or compatible biodegradable polymers with plasticizing properties [19, 20]. Modified biopolymers are promising for various industries.

The aim of the work was to investigate thermal and mechanical properties of polyhydroxyalkanoates synthesized by *Rhodococcus erythropolis* Au-1 and *Pseudomonas* sp. PS-17 strains, and polyhydroxybutyrate (PHB) synthesized by *Azotobacter vinelandii* N-15 strain as well as the properties of PHB/PLA blends.

EXPERIMENTAL PART

Materials

Polyhydroxyalkanoate (PHA_1) synthesized by *Rhodococcus erythropolis* Au-1 strain, polyhydroxyalkanoate (PHA_2) of *Pseudomonas* sp. PS-17 strain, and polyhydroxybutyrate (PHB) of *Azotobacter vinelandii* N-15 strain were used for this study. Polymers were obtained according to the procedures described in [21–23]. Polylactide (PLA) Ingeo Biopolymer was purchased from NatureWorks (USA).

Research objects: 1 – PHA_1; 2 – PHA_2; 3 – PHB; 4 – PLA; 5 – PHB/PLA (95/5 wt%/wt%); 6 – PHB/PLA (50/50 wt%/wt%); 7 – PHB/PLA (5/95 wt%/wt%).

Methods

Complex thermal analysis of polymeric materials was carried out using a Q-1500D derivatograph at the temperature range of 20–700°C with free air access to the furnace. The mass loss of samples during heating (TG), the rate of mass loss (DTG), and thermal effects (DTA) were determined. The experiments were conducted in a dynamic mode with a heating rate of 7°C/min in an air atmosphere. The weight of the samples was 200 mg on average. The standard was aluminum oxide.

The melt flow index of the obtained materials was measured according to ASTM D1238 using an IIRT-A plastometer at 190°C (PHB) and 210°C (PLA and PHB/PLA mixture) under a load of 2.16 kg. The density of the materials was measured according to ASTM D 792. Shore D hardness was measured according to ASTM D 2240 using a Shore D Durometer digital hardness tester under a load of 5 kg.

The mechanical properties of the films during the tensile test were determined according to ASTM D 638 on a RT-601U universal testing machine (Kimura Machinery) with a rate of 50 mm/min.

Films and samples preparation

Individual polymers PHB, PLA as well as PHB/PLA blends were dissolved in chloroform (polymer content 3%) at 70°C under stirring for 1 h. Then they were applied with a universal applicator AU1-65 over silicate glass plates mounted on a horizontal surface. The solvent evaporated at room temperature within 48 hours. The resulting films with a thickness of 50 ± 5 μm were dried in a VSH-0.035 vacuum oven at 60°C for 2 hours.

Samples in the form of cylinders with a diameter of 9.40 ± 0.05 mm and a height of 7.0 ± 0.1 mm were made using a MLV-32 vertical casting machine at 175°C.

RESULTS AND DISCUSSION

Thermograms of individual biopolymers are represented in Figs. 1–4; the results of biopolymer thermal analysis are shown in Table 1. On the DTA curves of polyhydroxyalkanoates of *Rhodococcus erythropolis* Au-1 and *Pseudomonas* sp. PS-17 endothermic effects at 28–70°C (Fig. 1, Table 1) and 36–53°C (Fig. 2, Table 1) can be observed, which are not accompanied by a loss of mass and correspond to the samples melting. The maximum melting endo effect of sample 2 (46°C), compared to sample 1 (42°C), is shifted to the region of higher temperatures, which may indicate a higher crystallinity degree of sample 2. The samples 1 and 2 mass loss in the temperature range of 164–264°C and 180–240°C cor-

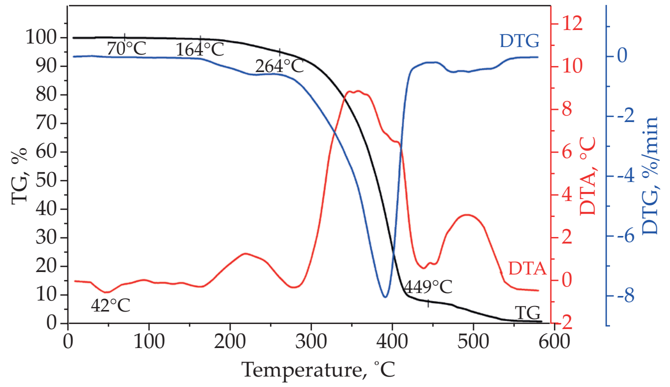

Fig. 1. TGA thermogram of PHA$_1$ of *Rhodococcus erythropolis* Au-1 strain

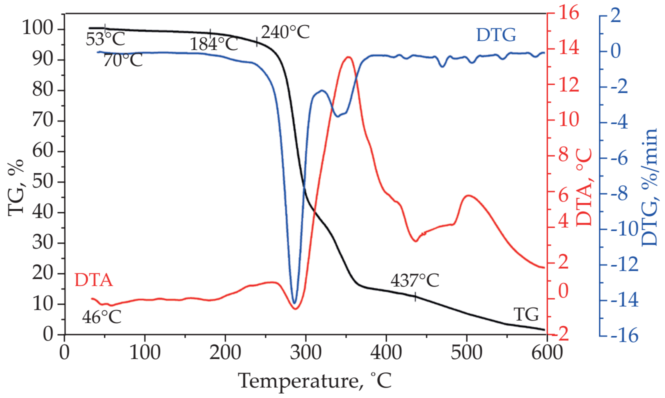

Fig. 2. TGA thermogram of PHA$_2$ *Pseudomonas* sp. PS-17 strain

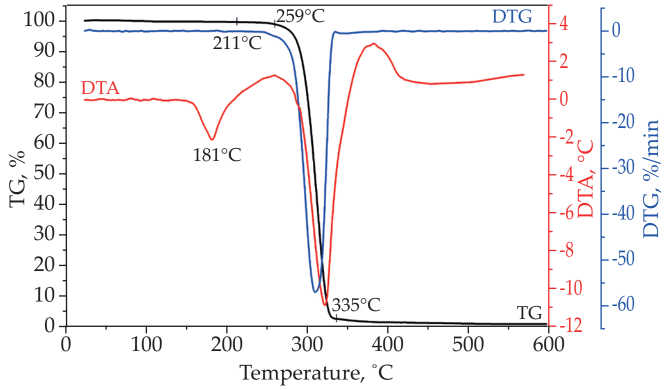

Fig. 3. TGA thermogram of PHB of *Azotobacter vinelandii* N-15 strain

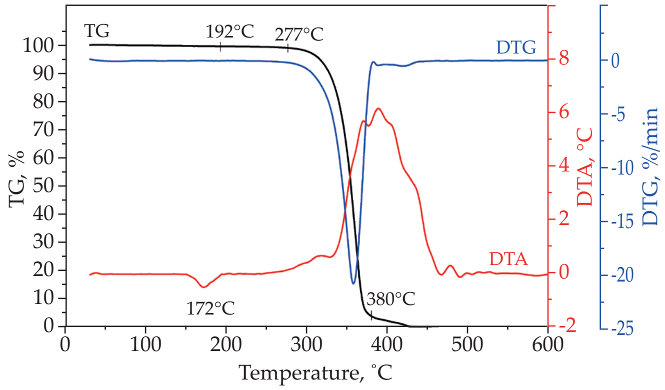

Fig. 4. TGA thermogram of PLA

T a b l e 1. Thermal analysis of individual biopolymers

Sample	Temperature range, °C	Mass loss, %
Polyhydroxyalkanoate of *Rhodococcus erythropolis* Au-1 (sample 1)	28–70	–
	70–164	0.5
	164–264	4.4
	264–449	87.1
	449–585	6.8
Polyhydroxyalkanoate of *Pseudomonas* sp. PS-17 strain (sample 2)	36–53	–
	53–180	1.5
	180–240	3.0
	240–437	83.0
	437–600	11.4
Polyhydroxyalkanoate of *Azotobacter vinelandii* N-15 strain (sample 3)	150–211	–
	211–259	0.7
	259–335	96.3
	335–700	2.3
Polyactide (PLA) (sample 4)	152–192	–
	192–277	1.0
	277–380	95.0
	380–500	4.0

responds to the initial thermal oxidation processes with slight extrema on the DTG curves and the appearance of exothermic effects on the DTA curves.

At the temperatures of 264°C and 240°C, the destructive and thermooxidative processes with intensive mass loss are observed for samples 1 and 2, as well as the appearance of sharp extrema on the DTG curves. The endo effects, which are observed on the DTA curves of biopolymers, turn into strongly exothermic effects with increasing temperature. At temperatures higher than 449°C and 437°C, pyrolytic residue combustion in samples 1 and 2 takes place. With regard to PHB of *Azotobacter vinelandii* N-15 strain, it is characterized by higher heat resistance and thermal stability. The melting thermal effect of this sample is deeper and is manifested on the DTA curve at 150–211°C with a maximum temperature of 181°C.

For sample 3 the initial thermal oxidation processes are shifted to the region of higher temperatures (211–259°C). They are accompanied by a slight loss of sample mass (0.7%) and DTA deviation toward the region of exothermic effects. Intensive destructive processes in sample 3 begin to develop at temperatures higher than 259°C. They are accompanied by a sharp extremum on the DTG curve and a deep endothermic effect on the DTA curve. At tempera-

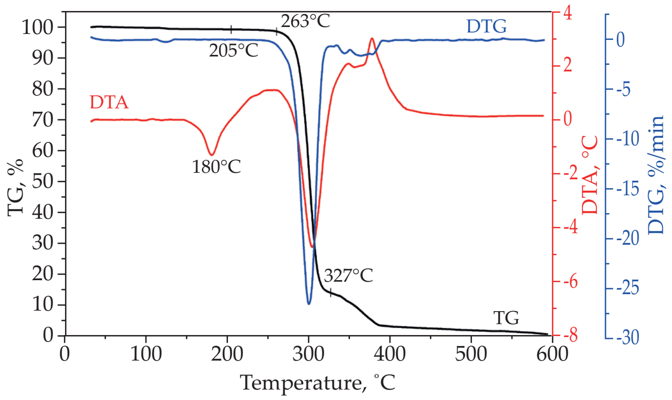

Fig. 5. TGA thermogram of PHB/PLA (95/5)

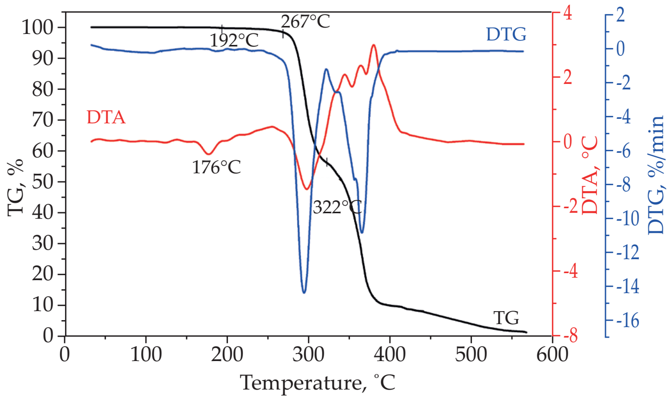

Fig. 6. TGA thermogram of PHB/PLA (50/50)

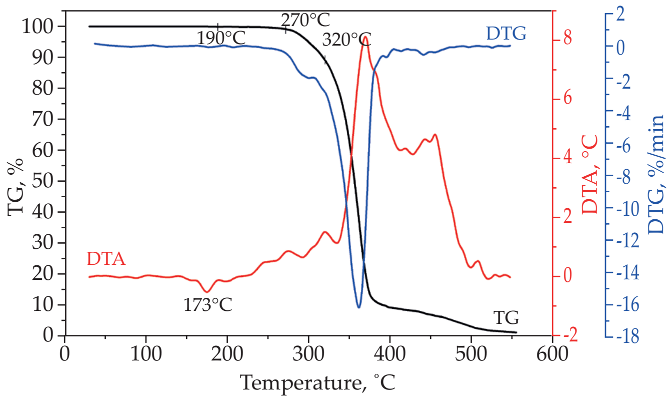

Fig. 7. TGA thermogram of PHB/PLA (5/95)

Table 2. Thermal analysis of PHB/PLA blends

Sample	Temperature range °C	Mass loss %
PHB/PLA (95:5, w/w) (sample 5)	150–205	–
	205–263	0.6
	263–327	84.8
	327–600	13.9
PHB/PLA (50:50, w/w) (sample 6)	160–192	–
	192–267	1.6
	267–322	42.2
	322–600	56.3
PHB/PLA (5:95, w/w) (sample 7)	160–190	–
	190–270	0.9
	270–320	10.0
	320–550	88.2

tures higher than 335°C, the pyrolytic residue combustion of sample 3 occurs. Taking into account the sample 3 higher values of heat resistance and temperature stability compared to samples 1 and 2, it was sample 3 that was used for the development and research of polymer compositions. The high melting point of *Azotobacter vinelandii* N-15 PHB may indicate its crystallinity high degree, which causes the low resistance of the biopolymer to impacts, rigidity and brittleness. To improve the mechanical properties, PHB was modified with polylactide – a biodegradable biopolymer with plasticizing properties.

The endothermic effect on the DTA curve of PLA thermogram (Fig. 4) in the range of 152–192°C with a maximum of 172°C corresponds to the sample melting. A slight loss of mass (1%) in the range of 192–277°C (Table 1) with a DTA deviation toward the exothermic effects region corresponds to initial thermooxidative processes. Intense mass loss (95%) of the PLA sample at the temperatures of 277–380°C with a sharp exothermic effect on the DTA curve corresponds to deep thermooxidative and destructive processes.

Figures 5–7 represent thermograms of PHB/PLA blends with different content of the components; the samples' thermal analysis results are shown in Table 2. DTA results show that the increase of the PLA content in the samples promotes the decrease of the melting thermal effect and a shift of the maximum endo effects toward the lower temperatures region. Thus, the temperature 181°C corresponds to the maximum of the melting endothermic effect of PHB. The temperatures 180°C, 176°C and 173°C correspond to the maximum melting endo effects of samples 5, 6 and 7. Such changes in the melting thermal effects of compositions with increasing PLA content indicate a decrease in crystallinity. This is in accordance with the physical and mechanical properties of the PHB biopolymer and blends with PLA (Table 3).

The intense mass loss of the investigated mixtures in the range of 263–327°C is caused mainly by the PHB destructive processes. In the same temperature range, thermal oxidation processes begin in PLA macromolecules. There is an endothermic effect on the DTA curves of samples 5–7, the depth of which decreases with increasing PLA content.

An increase in the PLA content in the blends affects their thermal stability. The confirmation is the observed

T a b l e 3. Properties of biodegradable polymeric materials

Polymer Property	PHB	PLA	PHB/PLA (95/5)	PHB/PLA (50/50)	PHB/PLA (5/95)
Density, kg/m^3	1220 ± 0.5	1240 ± 0.5	1222 ± 0.5	1230 ± 0.5	1239 ± 0.5
Melt flow index, g/10 min	14.0 ± 0.5	8.0 ± 0.5	12.5 ± 0.5	11.0 ± 0.5	9.5 ± 0.5
Shore hardness, °ShD	82 ± 2	66 ± 2	80 ± 2	75 ± 2	68 ± 2
Tensile strength, MPa	33.0 ± 2	25.0 ± 2	31.5 ± 2	30.0 ± 2	27.0 ± 2
Elongation at break, %	3.3 ± 0.2	11.0 ± 0.2	4.5 ± 0.2	7.0 ± 0.2	9.5 ± 0.5

shift of the destruction beginning toward the region of higher temperatures. Destructive processes for the PHB sample begin at 259°C, for blend 5 – at 267°C, and for blend 6 – at 270°C. Such regularities regarding the dependence of the blends thermal stability on the heat-resistant PLA content can be explained by the formation of bonds between components due to the van der Waals force action, hydrogen bonds, etc. The mass loss of PHB/PLA blends in the range of 320–600°C is probably caused by active thermo-oxidative processes of PLA and combustion of the samples pyrolytic residue. This process is accompanied by the appearance of exothermic effects on the DTA curves, the value of which increases with an increase in the PLA content in the mixture composition.

The results of the technological, physical and mechanical properties studies of the developed polymer materials (Table 3) show that with increased PLA content in the blend the tensile strength slightly decreases but the materials elasticity increases. At the same time, the melt flow index remains at a high level and is only slightly lower compared to PHB. The values of PHB/PLA hardness are lower than those of pure PHB, which is obviously due to the reduction of the crystalline region in the obtained polymer mixtures.

CONCLUSIONS

It was established that the obtained biopolymers of *R. erythropolis* Au-1 and *Pseudomonas* sp. PS-17 strains were characterized by low heat resistance. The melting point of biopolymers PHA_1 and PHA_2 is 42°C and 46°C, respectively. Polyhydroxybutyrate of *Azotobacter vinelandii* N-15 strain has higher heat resistance, its melting point is 181°C. This is due to the presence of an aliphatic fragment in the macromolecule with a molecular weight smaller compared to biopolymers PHA1 and PHA2. Modification of PHB with PLA promotes to reduce the heat resistance of the blends and their crystallinity degree. The melting of the PHB/PLA (5/95) occurs at 180°C, the PHB/PLA (50/50) and PHB/PLA (95/5) – at 176°C and 173°C, respectively. PHB/PLA blends are characterized by better thermal stability compared to PHB – the beginning of their thermal destruction shifts to the region of higher temperatures. Intensive thermo-oxidative and destructive processes are observed at temperatures above 259°C for PHB, and 263–270°C for PHB/PLA blends. The results of thermal analysis are confirmed by the properties of materials obtained from PHB/PLA blends, which are characterized by bigger elasticity compared to PHB. Their tensile strength and hardness remain at a high level. Such properties of the obtained PHB/PLA blends confirm the compatibility of their components. Thus, by changing the composition of PHB/PLA blends, it is possible to obtain thermoplastic biodegradable materials with a wide range of thermo-physical, technological and physico-mechanical properties, which will be suitable for various purposes, in particular for packaging.

REFERENCES

[1] Levyts'kyi V.E., Katruk D.S., Kochubei V.V. *et al.*: *Materials Science* **2017**, *53*(*3*), 385.
https://doi.org/10.1007/s11003-017-0086-7

[2] Narancic T., Cerrone F., Beagan N. *et al.*: *Polymers* **2020**, *12*(*4*), 920.
https://doi.org/10.3390/polym12040920

[3] Jambeck J.R., Geyer R., Wilcox C. *et al.*: *Science* **2015**, *347*, 768.
https://doi.org/10.1126/science.1260

[4] Doug S: Bioplastics: technologies and global markets. BCC research reports PLS050F 2021.

[5] Kumari S.V.G., Pakshirajan K., Pugazhenthi G.: *International Journal of Biological Macromolecules* **2022**, *221*, 163.
http://doi.org/10.1016/j.ijbiomac.2022.08.203

[6] Karamanlioglu M., Preziosi R., Robson G.: *Polymer Degradation and Stability* **2017**, *137*, 122.
https://doi.org/10.1016/j.polymdegradstab.2017.01.009

[7] Masyuk A., Kysil Kh., Katruk D. *et al.*: *Materials Science* **2020**, *56*, 319.
https://doi.org/10.1007/s11003-020-00432-y

[8] Khanna S., Srivastava A.: *Process Biochemistry* **2005**, *40*, 607.
https://doi.org/10.1016/j.procbio.2004.01.053

[9] Mitra R., Xu T., Xiang H. *et al.*: *Microbial Cell Factories* **2020**, *19*, 86.
https://doi.org/10.1186/s12934-020-01342-z

[10] Avérous L., Pollet E.: Environmental Silicate Nano-Biocomposites, Springer, London, UK, 2012, p.13-39.

[11] Zdenko S., Igor L., Elena L. *et al.*: *Polymer Degradation and Stability* **2006**, *91*, 4. 856,
https://doi.org/10.1016/j.polymdegradstab.2005.06.019

[12] Wang L., Zhu W., Wang X. *et al.*: *Journal of Applied Polymer Science* **2008**, *107*(*1*), 166.

https://doi.org/10.1002/app.27004

[13] Lagaron J.M., Lopez-Rubio A. *Trends in Food Science and Technology* **2011**, *22*, 611. https://doi.org/10.1016/j.tifs.2011.01.007

[14] Bashir S. M, Girdhar M, Rehman H. *et al*.: *Biosci Biotech Res Asia* **2014**, *11*(*3*), 1273. https://doi.org/10.13005/bbra/1516

[15] Trakunjae C., Boondaeng A., Apiwatanapiwat W. *et al*.: *Scientific Reports* **2021**, *11*, 1896. https://doi.org/10.1038/s41598-021-81386-2

[16] Pachekoski W., Agnelli J., Belem L.: *Materials Research* **2009**, *12*(2),159. https://doi.org/10.1590/S1516-14392009000200008

[17] Wang L., Du J., Cao D. *et al*.: *Journal of Macromolecular Science, Part A* **2013**, *50*, 885. https://doi.org/10.1080/10601325.2013.802540

[18] Rydz J., Sikorska W., Kyulavska M. *et al*.: *International Journal of Molecular Sciences* **2015**, *16*(*1*), 564. https://doi.org/10.3390/ijms16010564

[19] Mekonnen T., Mussone P., Khalil H. *et al*.: *Journal of Materials Chemistry A* **2013**, *1*(*43*), 13379. https://doi.org/10.1039/C3TA12555F

[20] Reichert C., Bugnicourt E., Coltelli M. *et al*.: *Polymers* **2020**, *12*, 1558. https://doi.org/10.3390/polym12071558

[21] Semeniuk I., Koretska N., Kochubei V. *et al*.: *Journal of Microbiology, Biotechnology and Food Sciences* **2022**, *11*(*4*), 1. https://doi.org/10.55251/jmbfs.4714

[22] Semeniuk I., Kochubei V., Skorokhoda V. *et al*.: *Chemistry and Chemical Technology* **2020**, *14*(*1*), 26. https://doi.org/10.23939/chcht14.01.026

[23] Semeniuk I., Pokynbroda T., Kochubei V. *et al*.: *Chemistry and Chemical Technology* **2020**, *14*(*4*), 463. https://doi.org/10.23939/chcht14.04.463

Received 3 XI 2022.