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O.S. Kabat^a, *O.O. Naumenko*^a, *K.V. Heti*^b**OPTIMIZATION OF PARAMETERS OF POLYLACTIDE PROCESSING ON A 3D PRINTER**^a **Ukrainian State University of Chemical Technology, Dnipro, Ukraine**^b **Oles Honchar Dnipro National University, Dnipro, Ukraine**

The paper examines the main advantages and disadvantages of modern methods for recycling of polymers and polymer composites based on them, which to a certain extent allow preventing environmental pollution by products made of them at the end of their life cycle and after failure. The most progressive and efficient method of polymer waste recycling has been determined, that consists in using biodegradable materials as a polymer base, the products made of them being decomposed into environmentally safe compounds. Polylactide as one of the most widespread biodegradable polymers was considered as a very promising material. It was processed into a product by using 3D printing. The optimal processing temperature (210°C) was determined, at which the maximum level of physical-mechanical properties of polylactide products is observed. We studied the effect of the degree of products infilling, which were obtained on a 3D printer, on their main strength characteristics. The mathematical dependences describing this effect were derived.

Keywords: polylactide, recycling, polymer processing temperature, degree of infilling, density, impact strength.

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Introduction

In the modern world, polymers and polymer composites (PC) based on them are gaining more and more distribution in all industry branches and are displacing such “traditional materials” as metals and their alloys, woods, etc. [1–3]. According to the analysis of the BCC Research Report Overview “Engineering Resins, Polymer Alloys and Blends: Global Markets” (April 2022), the global market for structural polymers and composites based on them will increase from \$70.7 billion in 2021 to \$94.0 billion by 2026. Thus, spending on polymer products in the world will grow by 25% during this period. At the same time, this growth is not related to an increase in the products price made of polymers and PC based on them, but to an increase in the number of products made of them. Accordingly, a rather important problem of their disposal at the end of the life cycle after operation or failure is actualized. Moreover, taking into account the fact that most polymers and PC based on them are rather inert materials that

decompose into elementary compounds for tens and sometimes hundreds of years, it can be argued that they have become the materials that extremely pollute the environment.

The following methods of recycling polymers and PC based on them are known [4,5]: burial in landfills; burning; and recycling.

Despite the increased development of methods of utilization and disposal of plastic waste, a very large proportion of waste is buried in landfills or landfills. Even in developed countries up to 70% of all plastic waste becomes a subject to landfill. Despite the fact that in many countries strict measures have been introduced for the preliminary disposal of waste before burial, this method is a serious source of environmental pollution (especially groundwater). For example, according to the analytical portal «Слово і Діло» and the media agency «ACC», there are more than 5,500 landfills in Ukraine which occupy up to 7% of its total area [6,7].

In accordance with the above, the disposal

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Optimization of parameters of polylactide processing on a 3D printer

method of polymers and PC based on them by means of disposal in landfills is inefficient and not relevant.

In recent years, the incineration has been increasingly used to solve the problem of disposal and disposal of solid waste [8]. This method is especially widespread in those cases where the waste does not find practical use and cannot be disposed of by other methods. At the same time, together with the utilization of polymer waste, it is also possible to obtain a fairly large amount of energy that can be used for industrial and household needs.

However when polymers are burned, a large amount of harmful gases are released (NH_3 , nitrogen oxides, cyanide compounds, etc.) that pollute the air quite strongly. Therefore, this method does not allow to fully disposing the problem of polymer wastes without harming the environment.

The methods of disposal of polymer waste by landfilling and incineration have more disadvantages than advantages, therefore nowadays, there is a tendency of using methods of disposal and disposal of polymer waste, the impact of which on the environment is insignificant [9]. One of these methods is the reprocessing of individual polymer waste into finished products. Recycling allows not only protecting the environment from polymer waste, but also reducing the cost of manufacturing products from polymer materials due to the use of recycled polymer waste as raw materials. It is quite widespread in the developed countries of the world, where the population is engaged in sorting polymer waste already at the stage of its disposal. In Ukraine, sorting is still not widespread enough, that significantly limits the use of the method of reprocessing polymer waste into products.

Thus, according to the literature, landfilling, incineration and recycling into products contribute to environmental pollution and do not manage to dispose the problem of all polymer waste.

There is another approach to combating polymer waste, which consists in the use of biodegradable polymers as a polymer base, and after the end of their service life, decomposition into low-molecular products that are assimilated in the soil, entering into a closed biological cycle [10–14]. These polymers retain their properties throughout the entire service life and only decompose after the end of this period. According to the research of the German Nova-Institute (Hurth), to date, the total volume of production of such polymers is up to 2% of the volume of petrochemical-based polymers production. At the same time, according to the analysis of the BCC Research Report Overview “Biodegradable Polymers: Global Markets and Technologies” the global market for biodegradable polymers will increase from 3.7 to

9.5 billion US dollars within the period from 2022 to 2027. Thus, such a significant increase in the biodegradable polymers costs indicates the relevance of their use in the present and future.

One of the most widespread biodegradable polymers is polylactide (PLA), that is synthesized from renewable resources such as corn, sugar cane, etc. [15,16]. PLA is used to produce products with an adjustable service life: food packaging, disposable tableware, bags, etc. This polymer is one of the most advanced biodegradable polymers due to its rather high level of physical-mechanical and thermophysical properties. Its products are obtained by injection molding, extrusion, 3D printing, and so on. The most modern and the one that is intensively developing is the method of obtaining products using 3D printing [17]. This method makes it possible to obtain PLA products of a rather complex design without the use of additional equipment (casting mold, strippers, etc.). The disadvantages of this method include its low level of productivity. However, the modern development of 3D printers is constantly reducing this disadvantage. In addition, 3D farms are used for more productive production of products on 3D printers [18].

In accordance with this fact, an urgent task is to determine the optimal processing modes PLA and the design features of its products which are obtained by means of the 3D printers.

Experimental

Materials

Polylactide brand “Devil Design” produced in Poland was chosen as the material for manufacturing products. In its original form, it is a filament in the form of a round wire with a diameter of 1.75 mm.

Polylactide samples were produced on a Creality Ender-3 3D printer (Fig. 1) manufactured by Creality (China).

Samples were obtained at different processing temperatures and with different degree of infilling. The degree of infilling varied from 100 to 10%. Examples of samples with different degrees of infilling are shown in Fig 1.

Methods

The temperature resistance of the research objects was measured using the method of thermogravimetric analysis in accordance with ISO-11358 by temperature scanning methods on a TGA Q50 derivatograph.

The density of products and PC based on them was determined according to ISO 1183-3 using the measuring and weighing method. To measure products, we used PROTESTER electronic calipers with a measurement accuracy of 0.02 mm. The weighing of products was carried out on analytical scales “BJP-200”.

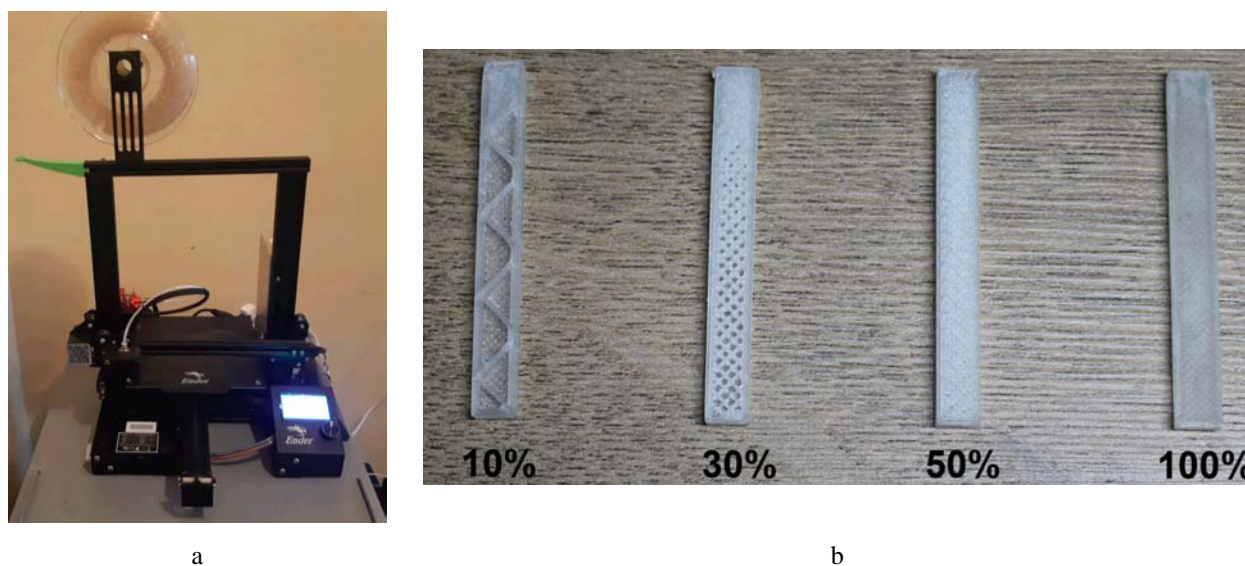


Fig. 1. General view: a – 3D printer Creality Ender-3; and b – samples for studies with different degree of infilling

The impact strength (a_n) of polylactide products was determined in accordance with ISO 179-1:2000 (Plastics – Determination of Charpy impact properties) on the MK-30 pendulum tester.

The compressive stress at yield (σ_y) of polylactide samples was determined according to ISO 604 on a 2167 P-50 universal tearing machine.

Results and discussion

The main technological parameters of polymer processing on 3D printers include the processing temperature, degree of infilling products, printing speed, supply of the initial polymer, etc.

It is known [19,20] that one of the main parameters of polymer processing is temperature. To determine the optimal processing polylactide temperature, it is necessary to set the processing temperature interval. The maximum processing temperature can be determined by thermogravimetric analysis of the original polymer. The results of the research are shown in Fig. 2.

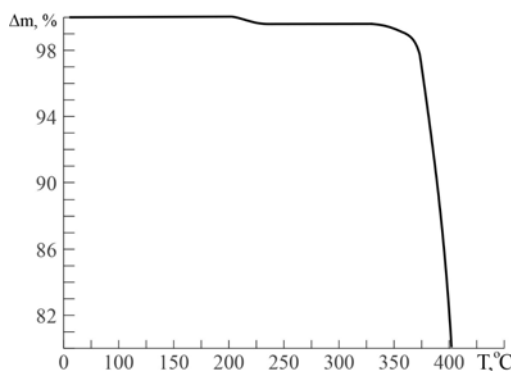


Fig. 2. Thermogravimetric curve of the original polylactide

According to the registered thermogravimetric curve, a decrease in the polymer weight is observed with an increase in temperature from 20 to 400°C due to its thermal destruction. Thus, no weight loss of the investigated polymer is observed in the temperature range of 20 to 230°C. Starting from 230°C, a weight loss of up to 1% is observed; and starting from 330°C, the weight loss increases sharply and reaches 20% at 400°C. According to the conducted investigations, it can be stated that the maximum processing temperature of polylactide should not exceed 230°C when the weight loss of the polymer is observed when it is exposed to a temperature field.

The minimum processing temperature should exceed the transition temperature of polylactide from a highly elastic to a viscous state. According to reference literature [21], it equals to 176–180°C.

Thus, the optimal processing temperature of polylactide will be in the range of 180°C to 230°C. However, when processing polylactide on a 3D printer at a temperature of 180°C, it was impossible to obtain a solid product (Fig. 3), which is due to insufficient viscosity of the polylactide melt. Therefore, the processing temperature range was narrowed to 190–230°C.

Determination of the optimal processing temperature of polylactide was carried out by an indirect method according to the values of the main physical and mechanical properties (density and impact strength) of the obtained products.

Figure 4 shows the investigation results of impact strength (a_n) and density (ρ) as a function of processing polylactide products temperature (T).

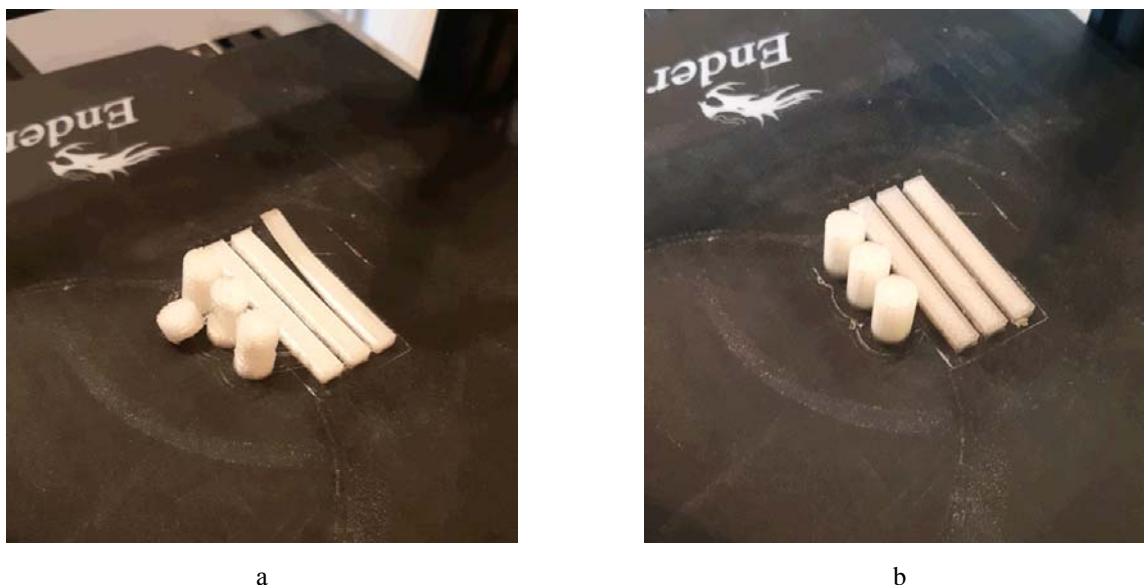


Fig. 3. Polylactide samples obtained at temperatures: a – 180°C; and b – 190°C

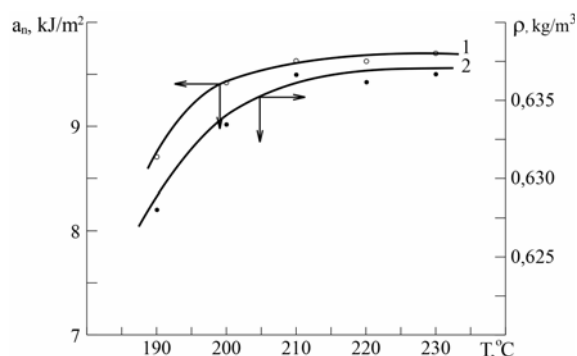


Fig. 4. Dependences of (1) impact strength (a_n) and (2) density (ρ) on processing temperature (T) of polylactide-based products (3D printed with 20% product filling)

According to the obtained results, it can be concluded that there is an increase in the impact strength and density of polylactide products with an increase in temperature from 190 to 230°C. Moreover, the most intensive increase is observed in the area of processing temperatures from 190 to 210°C with further stabilization of the values of impact strength and density up to a temperature of 230°C. Analysis of these results confirms that the optimal processing temperature for polylactide products on a 3D printer is 210°C. At this temperature, the maximum values of impact strength and density of the studied samples are observed with minimal energy costs for their processing.

One of the main characteristics when processing products on a 3D printer is the degree of products infilling. Thus, with this method of processing, both solid products (100% filling) and hollow products (less than 100% filling) can be fabricated. Moreover,

it should be noted that products with a low degree of filling are much lighter in weight than solid ones, which leads to a significant saving of material and is a rather significant factor in the production of parts in aircraft and shipbuilding and the space industry.

Therefore, it is important to determine the dependence of the main strength characteristics of polylactide products on the degree of products infilling.

Figure 5 shows the dependences of impact strength (a_n) and compressive stress at yield (σ_y) on the degree of infilling in polylactide products.

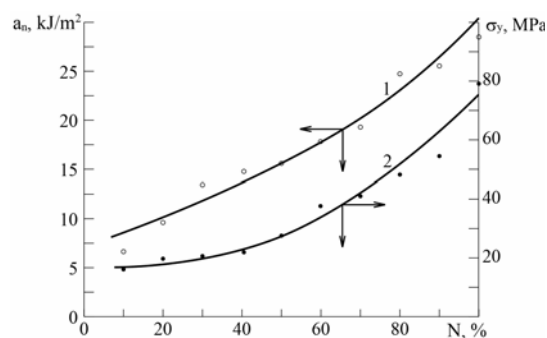


Fig. 5. Dependences of impact strength (a_n) and (2) compressive stress at yield (σ_y) on the degree of infilling (N) of polylactide products (obtained on a 3D printer at a temperature of 210°C)

According to the obtained results, it can be concluded that, the impact strength and compressive stress at yield increase with an increase in the degree of infilling of polylactide products. Moreover, attention should be focused on the non-linear character of the obtained dependence. Thus, the increase in the studied characteristics at degrees of product filling from 10%

to 60% has a lower intensity than in the interval from 60% to 100%. That allows recommending products with optimal filling from the point of view not only of strengthening characteristics but also of material capacity.

For more convenient use of the research results, mathematical dependences were obtained using the MathCAD program to determine the values of the impact strength and compressive stress at yield point in compression of the degree of infilling of polylactide products. The derived formulae are given below:

$$a_n = 3.8 \cdot 10^{-5} \cdot N^2 + 0.23 \cdot N + 4.583;$$

$$\sigma_y = 8.1 \cdot 10^{-3} \cdot N^2 - 0.297 \cdot N + 22.833.$$

Conclusions

According to our findings, the optimal processing temperature, at which the maximum level of physical and mechanical properties of polylactide products is observed, is 210°C.

The influence of the degree infilling of polylactide products obtained on a 3D printer on their main strength characteristics was determined and mathematical dependences were derived to describe it.

REFERENCES

1. *Determining* the influence of the filler on the properties of structural thermal-resistant polymeric materials based on phenylone C1 / Kabat O., Makarenko D., Derkach O., Muranov Y. // *East. Eur. J. Enterprise Technol.* – 2021. – Vol.6. – No. 113. – P.24-29.
2. *Polymeric* composite materials of tribotechnical purpose with a high level of physical, mechanical and thermal properties / Kabat O., Sytar V., Derkach O., Sukhyy K. // *Chem. Chem. Technol.* – 2021. – Vol.15. – No. 4. – P.543-550.
3. *Kabat O., Sytar V., Sukhyy K.* Antifrictional polymer composites based on aromatic polyamide and carbon black // *Chem. Chem. Technol.* – 2018. – Vol.12. – No. 3. – P.326-330.
4. *Sytar V.I., Burmistr M.V., Kabat O.S.* Promyslova ekolohiia pry vyrobnytstvi ta pererobtsi polimernykh materialiv. Dnipropetrovsk: DVNZ “UDKhtU”, 2011. – 161 p.
5. *Overcash M.R., Ewell J.H., Griffing E.M.* Life cycle energy comparison of different polymer recycling processes // *J. Adv. Manuf. Process.* – 2020. – Vol. 2. – Art. No. e10034.
6. *Electronic* resource. Slovoidilo.ua. Available from: <https://www.slovoidilo.ua/2020/12/04/infografika/suspilstvo/najbilshe-smittyezvalyssh-vinnyczkij-ta-poltavskij-oblastyax>.
7. *Electronic* resource. Acc.cv.ua. Available from: <https://acc.cv.ua/news/ukraine/yaku-kilkist-zemel-zaymayut-smittiezvalischa-v-ukrayini-video-19416>.
8. *Shaklein A.A.* Numerical study of the external heat source effect on polymer burning // *Combust. Sci. Technol.* – 2022. – Vol.14. – P. 2864-2879.
9. *Radovenchuk V.M., Homelia M.D.* Promyslova ekolohiia pry vyrobnytstvi ta pererobtsi polimernykh materialiv. – K.: Kondor, 2010. – 552 p.
10. *CO₂-based* biodegradable supramolecular polymers with well-tunable adhesive properties / Li X.-J., Wen Y.-F., Wang Y., Peng H.-Y., Zhou X.-P., Xie X.-L. // *Chinese J. Polym. Sci.* – 2022. – Vol.40. – P.47-55.
11. *The preparation* of biodegradable composite materials based on polyvinyl alcohol / Sytar V.I., Sukhyy K.M., Mitina N.B., Garmash S.M., Lisichenko B.O. // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2020. – No. 1. – P.86-91.
12. *Biodegradable* composite materials based on poly(3-hydroxybutyrate) for 3D printing applications / Mencik P., Melcova V., Kontarova S., Prikryl R., Perdochova D., Repiska M. // *Mater. Sci. Forum.* – 2019. – Vol.955. – P.56-61.
13. *Development* of new biodegradable composites materials from polycaprolactone and wood flour / Cintra S.C., Braga N.F., de Melo Morgado G.F., do Amaral Montanheiro T.L., Marini J., Passador F.R., et al. // *Wood Mater. Sci. Eng.* – 2022. – Vol.17. – No. 6. – P.586-597.
14. *Varghese J.T., Sarath Raj N.S., Jiji G.* Development of biodegradable composites and investigation of mechanical behavior // *Mater. Today Proc.* – 2021. – Vol.38. – P.3378-3385.
15. *Evaluating* and modeling the degradation of PLA/ PHB fabrics in marine water / Bao Q., Zhang Z., Luo H., Tao X. // *Polymers.* – 2023. – Vol.15. – Art. No. 82.
16. *Kukhar V.P.* Bioresursy – potentsialna syrovyna dlia promysloвого orhanichnoho syntezy // *Catal. Petrochem.* – 2007. – Vol.15. P.1-15.
17. *Wang J.* The design research analysis of 3D printer based on FDM // *J. Phys. Conf. Ser.* – 2021. – Vol.1992. – Art. No. 022143.
18. *Siena F.L., Forbes C., Truman K.* Democratic manufacturing: a student manufactured & operated 3D printer farm // *Proceedings of the 24th International Conference on Engineering and Product Design Education.* London. – 2022. – P.DS117.
19. *Kabat O.S., Sytar V.I., Sukhy K.M.* Bioresursy – potentsialna syrovyna dlia promysloвого orhanichnoho syntezy // *Technol. Syst.* – 2017. – Vol.4. – P.248-252.
20. *Kabat O.S., Dusheiko M.V.* Polimerni kompozytsiini materialy spetsialnoho pryznachennia na osnovi fluoroplastu // *Technol. Syst.* – 2017. – Vol.4. – No. 81. – P.63-67.
21. *Kabanov V.A.* Entsiklopediia polymerov. Tom 2. – M: “Soviet encyclopedia”, 1974. – 1082 p.

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ОПТИМІЗАЦІЯ ПАРАМЕТРІВ ПЕРЕРОБЛЕННЯ ПОЛІЛАКТИДУ НА 3D ПРИНТЕРІ

О.С. Кабат, О.О. Науменко, К.В. Гети

У роботі розглянуті основні переваги та недоліки сучасних методів утилізації полімерів і полімерних композиційних матеріалів на їх основі, які дозволяють певною мірою запобігати забрудненню навколишнього середовища виробами з них наприкінці життєвого циклу після експлуатації чи виходу із ладу. Визначено найбільш прогресивний та ефективний метод утилізації відходів полімерів, що полягає у використанні біодеградабельних матеріалів як полімерної основи, виробу з яких розкладаються на безпечні для навколишнього середовища сполуки. Як такий матеріал розглянуто полілактид, що є одним із найбільш розповсюджених біодеградабельних полімерів. Перероблення його у виріб виконано за допомогою 3D принтерінгу. Визначено оптимальну температуру перероблення (210°C), при якій спостерігається максимальний рівень фізико-механічних властивостей виробів із полілактиду. Досліджено вплив ступеня заповнення виробів, одержаних на 3D принтері, на їх основні міцнісні характеристики та виведено математичні залежності, що описують цей вплив.

Ключові слова: полілактид, утилізація, температура перероблення полімеру, ступінь заповнення, густина, ударна в'язкість.

OPTIMIZATION OF PARAMETERS OF POLYLACTIDE PROCESSING ON A 3D PRINTER

O.S. Kabat^{a,}, O.O. Naumenko^a, K.V. Heti^b*

^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine

^b Oles Honchar Dnipro National University, Dnipro, Ukraine

* e-mail: Amber_UDHTU@i.ua

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REFERENCES

1. Kabat O, Makarenko D, Derkach O, Muranov Y. Determining the influence of the filler on the properties of structural thermal-resistant polymeric materials based on phenylene C1. *East Eur J Enterprise Technol.* 2021; 6(113): 24-29. doi: 10.15587/1729-4061.2021.243100.
2. Kabat O, Sytar V, Derkach O, Sukhyi K. Polymeric composite materials of tribotechnical purpose with a high level of physical, mechanical and thermal properties. *Chem Chem Technol.* 2021; 15(4): 543-550. doi: 10.23939/chcht15.04.543.
3. Kabat O, Sytar V, Sukhyi K. Antifrictional polymer composites based on aromatic polyamide and carbon black. *Chem Chem Technol.* 2018; 12(3): 326-330. doi: 10.23939/chcht12.03.326.
4. Sytar VI, Burmistr MV, Kabat OS. *Promyslova ekoloziia pry vyrobnytstvi ta pererobtsi polimernykh materialiv* [Industrial ecology in the production and processing of polymeric materials]. Dnipropetrovsk: DVNZ «UDKhTU»; 2011. 161 p. (in Ukrainian).
5. Overcash MR, Ewell JH, Griffing EM. Life cycle energy comparison of different polymer recycling processes. *J Adv Manuf Process.* 2020; 2: e10034. doi: 10.1002/amp2.10034.
6. Slovoidilo.ua [Internet]. Kyiv; [cited 2020 Feb 04]. Available from: <https://www.slovoidilo.ua/2020/12/04/infografika/suspilstvo/najbilshe-smittyezvalyshh-vinnyczkij-ta-poltavskij-oblastyax>.
7. Acc.cv.ua [Internet]. Kyiv; [cited 2016 June 26]. Available from: <https://acc.cv.ua/news/ukraine/yaku-kilkist-zemel-zaymayut-smittezvalischa-v-ukrayini-video-19416>.
8. Shaklein AA. Numerical study of the external heat source effect on polymer burning. *Combust Sci Technol.* 2022; 14: 2864-2879. doi: 10.1080/00102202.2021.1894139.
9. Radovenchuk VM, Homelia MD. *Promyslova ekoloziia pry vyrobnytstvi ta pererobtsi polimernykh materialiv* [Solid waste: collection, processing, storage]. Kyiv: Kondor; 2010. 552 p. (in Ukrainian).
10. Li XJ, Wen YF, Wang Y, Peng HY, Zhou XP, Xie XL. CO₂-based biodegradable supramolecular polymers with well-tunable adhesive properties. *Chinese J Polym Sci.* 2022; 40: 47-55. doi: 10.1007/s10118-021-2641-9.
11. Sytar VI, Sukhyi KM, Mitina NB, Garmash SM, Lisichenko BO. The preparation of biodegradable composite materials based on polyvinyl alcohol. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2020; (1): 86-91. doi: 10.32434/0321-4095-2019-128-1-86-91.
12. Mencik P, Melcova V, Kontarova S, Prikryl R, Perdochova D, Repiska M. Biodegradable composite materials based on poly(3-hydroxybutyrate) for 3D printing applications. *Mater Sci Forum.* 2019; 955: 56-61. doi: 10.4028/www.scientific.net/MSF.955.56.
13. Cintra SC, Braga NF, de Melo Morgado GF, do Amaral Montanheiro TL, Marini J, Passador FR, et al. Development of new biodegradable composite materials from polycaprolactone and wood flour. *Wood Mater Sci Eng.* 2022; 17(6): 586-597. doi: 10.1080/17480272.2021.1905712.

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14. Varghese JT, Sarath Raj NS, Jiji G. Development of biodegradable composites and investigation of mechanical behavior. *Mater Today Proc.* 2021; 38: 3378-3385. doi: 10.1016/j.matpr.2020.10.478.
15. Bao Q, Zhang Z, Luo H, Tao X. Evaluating and modeling the degradation of PLA/PHB fabrics in marine water. *Polymers.* 2023; 15: 82. doi: 10.3390/polym15010082.
16. Kukhar VP. Bioresursy – potentsialna syrovyna dlia promyslovoho orhanichnoho syntezy [Bioresources as potential raw materials for industrial organic synthesis]. *Catal Petrochem.* 2007; 15: 1-15. (in Ukrainian).
17. Wang J. The design research analysis of 3D printer based on FDM. *J Phys Conf Ser.* 2021; 1992: 022143. doi: 10.1088/1742-6596/1992/2/022143.
18. Siena FL, Forbes C, Truman K. Democratic manufacturing: a student manufactured & operated 3D printer farm. In: Bohemia E, Buck L, Grierson H, editors. *Proceedings of the 24th International Conference on Engineering and Product Design Education (E&PDE 2022)*; 8th-9th September 2022; London; DS 117. doi: 10.35199/EPDE.2022.49.
19. Kabat OS, Sytar VI, Sukhy KM. Bioresursy – potentsialna syrovyna dlia promyslovoho orhanichnoho syntezy [Bioresources as potential raw materials for industrial organic synthesis]. *Technol Syst.* 2017; 4: 248-252. (in Ukrainian).
20. Kabat OS, Dusheiko MV. Polimerni kompozytsiini materialy spetsialnoho pryznachennia na osnovi fluoroplastu [Special purpose polymer composite materials based on fluoroplastic]. *Technol Syst.* 2017; 4(81): 63-67. (in Ukrainian).
21. Kabanov VA. *Entsyklopedyia polymerov. Tom 2* [Encyclopedia of polymers. Volume 2]. Moscow: Soviet Encyclopedia; 1974. 1082 p. (in Russian).