UDC 621.798:628.473.62 DOI: 10.33273/2663-9726-2020-53-2-80-87

METHODICAL APPROACHES TO ASSESSMENT OF THE CAPABILITY OF BIOCHEMICAL DECOMPOSITION OF POLYMERIC MATERIALS AND THEIR WASTES (REVIEW OF PUBLICATIONS)

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ANSTRACT. Actuality. The urgency of the topic is due to the fact that recently the problem of environmental safety in connection with the generation of large quantities of waste has become particularly acute. A separate aspect of this problem is the accumulation of polymeric material wastes, in particular packaging and packaging waste. Preventing packaging and packaging waste with a view to ensuring a high level of protection of the environment and human health is a major goal of regulation in the field of packaging and packaging management, both nationally and internationally.

Materials and Methods. The purpose of the work is to analyze the existing requirements for packaging and its waste in the EU and Ukraine and to systematize the methods used in the process of evaluation and certification of polymeric packaging according to biodegradation criteria.

It is stated that the manufacture of packaging must be carried out in such a way that the level of toxic and other harmful substances and materials that are components or components of the packaging is minimized. Packaging to be recovered through energy recovery must have the minimum required calorific value for energy recovery. Organic recovery packaging should be characterized by its ability to decompose under the influence of micro-organisms, which should not interfere with its separate collection. The use of biodegradable materials for packaging and packaging is a new step in the field of packaging and packaging waste management, which will prevent waste generation. The characteristic of the main types of biodegradable polymeric materials is given.

DSTU EN 13432: 2015 "Packaging. Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging" and DSTU EN 14995: 2018 "Plastics. Evaluation of compostability. Test scheme and specifications", which sets out the basic requirements and procedures for determining the biodegradability of packaging and packaging materials, which will allow the assessment and certification of packaging according to biodegradation criteria both for the internal market and for export.

Conclusions. The introduction of methods and test schemes for assessing the biochemical degradation capacity of packaging will accelerate the introduction of biodegradable materials in the consumer market of Ukraine, reduce the total amount of packaging and packaging waste, and help meet the goals set by the 2030 National Waste Management Plan.

Key Words: packaging waste, EU Directives, biopolymer materials, biodegradability, methods for determining biodegradation.

Actuality. Accumulation of waste of polymeric materials, in particular packaging, is a global environmental problem for all mankind. The world produces about 300 million tons of polymeric materials annually [1].

Review of publications

Polymers accumulate in the environment due to low biodegradability. The world's oceans are turning into a huge dump of polymer waste, in which polymers can form microparticles, which are called "microplastics". Microplastics can enter the environment directly, for example from polymer granules used in cosmetics, from clothing fibers that are formed during washing, as well as during mechanical degradation of polymeric materials. Due to its small size, microplastics are easily consumed by a number of organisms at almost all levels of the food chain, especially in marine environments: zooplankton, corals, fish, birds and marine mammals. Microplastic accumulates in their body, clogging the stomach, lungs and gills, leading to the death of animals [2].

In addition, microplastic, as a rule, acts as a carrier of hydrophobic organic compounds (for example, polychlorinated biphenyls, pesticides and agrochemicals), which accumulate in the porous structure of the particles. Thus, not only microplastics but also toxic chemicals that can be desorbed in the anaerobic environment of the intestine and absorbed by animal body tissues enter the food chain [3-5].

Reuse of polymeric materials is one way to reduce the amount of polymer waste. But even in the European Union (EU), only 30% of plastic waste is reused. At the same time, about 25.8 million tons of plastic waste is generated in the EU every year, 59 percent of which comes from packaging.

Recycling of such waste requires appropriate preparation and should include the following measures:

- creation of a reliable system of waste collection from the population with sorting and volume reduction;
- development and implementation of perfect and cost-effective technology for their processing;
- creation of appropriate production facilities;
- the presence of markets for products from this type of secondary raw materials.

The prevention of tare and packaging waste in order to ensure a high level of protection of the environment and human health is the main goal of regulation in the field of packaging and packaging management at both national and international levels. In accordance with the requirements of Directive 94/62/EC of the European Parliament and of the Council "On packaging and packaging waste" management in the field of packaging and waste from it should, first of all, ensure the prevention of packaging waste and be guided by such basic principles as its reuse, recycling and other forms of reuse of packaging waste and, ultimately, reducing the volume of final waste disposal [6].

Thus, in particular, packaging should be made taking into account the possibility of its reuse and / or disposal. Manufacturing should be carried out in such a way as to minimize the level of toxic and other harmful substances and materials that are elements or components of packaging. Packaging to be disposed of by energy recovery must have the minimum required calorific value for the energy recovery process. Packaging recycled by organic recovery should be characterized by the ability to decompose under the influence of microorganisms, which should not interfere with its separate collection.

Directive 94/62/EC also lays down requirements for packaging that is considered to be renewable. Organic recycling of used packaging is one of the options for recovery during its overall life cycle, which will help reduce the total amount of waste [6].

According to the draft Law of Ukraine "On packaging and packaging waste", organic waste processing is a process of aerobic or anaerobic fermentation of components of such waste, capable of biochemical decomposition under controlled conditions, using microorganisms to obtain stabilized organic residues or methane. Disposal of packaging waste in the ground is not considered a form of regeneration of organic matter.

In January 2018, the European Commission published its report "European Strategy for Plastics in the Closed Cycle Economy" ("EU Circular Economy") [7]. In the Commission's view, this proposal is an ambitious step to make the European polymer management system more resource efficient and to facilitate the transition from a linear to a closed system. Biopolymer materials provide a crucial impetus for innovation and the development of a sustainable closed-cycle economy for polymeric materials, using alternative raw materials and offering a wider range of applications and end-of-life options for plastic products.

The purpose of creating and using biodegradable polymeric materials is to obtain the following economic and environmental benefits:

- utilization and / or processing of polymer waste;
- lower cost of polymers from renewable raw materials;
- reducing the need for synthetic polymers that adversely affect the environment;
- reduction of greenhouse gas emissions by 15 60% when replacing polymeric materials of the previous generation with biodegradable polymers.

According to European Bioplastics e. V. The production of polymeric materials that are biodegradable and meet the requirements of EN 13432 in the EU in 2018 amounted to 912 thou-

Table 1

An example of the classification of polymeric materials by origin and biodegradability according to lwata T. [9]

Biodegradable plastic materials	Plastics based on biopolymers derived from natural plant materials	Examples of use	Plastics based on petroleum hydrocarbons	Examples of use
	Polylactides (PLA)	Medical use	Poly(ε-caprolac- tone) (PCL)	PVC glue
	Polyhydroxyalka- noates (PHAs)	Medical use	Poly(butylene suc- cinate / adipate) (PBS/A)	Agriculture
	Derivatives of polysaccharides	Food packaging	Poly(butylene adi- pate terephthalate) (PBA/T)	Paper cups
	Poly(amino acids)	Medical use		
Non- biodegradable plastic materials	Polyethylene (bio-PE)	Packaging	Polyethylene (PE)	Packaging
	Polyol- polyurethane	Tires	Polypropylene (PP)	Packaging
	Derivatives of polysaccharides	Food packaging	Polystyrene (PS)	Packaging
	Poly(ethylene terephthalate) (bio-PET)	Bottles for drinking water	Poly(ethylene terephthalate) (bio-PET) (PET)	Bottles for drinking water
			Poly(methyl methacrylate)	Optical materials, etc.

sand tons, according to forecasts in 2023 will reach 1,228 million tons. Currently, the main types of biodegradable polymeric materials used, including for the production of packaging, are polybutylene adipate terephthalate (PBAT) – ester of adipic acid, 1,4-butanediol and terephthalic acid, polybutylene (polytetramethylene) succinate (PBS) and succinic acid, polylactide (PLA) – aliphatic polyester, the monomer of which is lactic acid and cyclic diester lactide, polyhydroxyalkanoates (PHAs) and starch derivatives [8].

An example of the classification of polymeric materials by origin and biodegradability is shown in Table 1.

The main requirements and procedures for determining the ability to compost and anaerobic treatment of packaging and packaging materials are set out in DSTU EN 13432:2015 and in DSTU EN 14995:2018 [10, 11]. The adoption of these standards in Ukraine allows for the assessment

and certification of packaging according to biodegradation criteria for both the domestic market and for export, first of all, to the countries of the European Union.

In November 2019, the Verkhovna Rada of Ukraine adopted the bill in the first reading "On restricting the circulation of plastic bags on the territory of Ukraine", which from 2022 proposes to ban the distribution of ultralight, light and oxodecomposable (oxo-biodegradable) plastic bags in retail and restaurant facilities. At the same time, this ban does not apply to biodegradable plastic bags that decompose with the participation of microorganisms into elements of natural origin and meet the criteria established by the national standard DSTU EN 13432:2015.

Aim of the Research. Given the importance of the problem of determining the ability of packaging to biodegrade, it is urgent to introduce methods and test schemes to assess the ability to biochemical degradation. Taking into account the above,

the aim of the work was to systematize the methods used in the process of evaluation and certification of packaging made of polymeric materials according to the criteria of biodegradation.

Materials and Methods.To establish the compliance of packaging with the requirements of organic reduction (biochemical decomposition), it is necessary to conduct detailed studies of four main processes [10-13]:

- biodegradation;
- decomposition during biological treatment;
- impact on the process of biological treatment;
- impact on the quality of the obtained compost.

It is important to emphasize that the peculiar biodegradation test and further evaluation of the obtained compost should be preceded by evaluation of packaging formulation, determination of weight reduction during incineration at 550°C, content of heavy metals and other hazardous substances, including zinc, copper, nickel, cadmium, lead, mercury, chromium, molybdenum, selenium, arsenic and fluorine (Table 2).

The presence of these substances in the packaging in quantities exceeding the maximum content set in DSTU EN 13432:2015, does not allow at this preliminary stage of research to classify the packaging as one that can be biodegradable.

The actual biodegradation test is a study of aerobic biodegradation and anaerobic degradation. The percentage of aerobic biodegradation for packaging, including polymeric materials, should be at least 90, and for anaerobic – based on the release of biogas should be 50 or more of

Table 2

Maximum content of hazardous chemicals in packaging materials

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Name of the substance	Dry matter content, mg / kg			
Zinc	150,0			
Copper	50,0			
Nickel	25,0			
Cadmium	0,5			
Lead	50,0			
Mercury	0,5			
Chrome	50,0			
Molybdenum	1,0			
Selenium	0,75			
Arsenic	5,0			
Fluorine	100,0			

the theoretical value for the material.

Indicators of aerobic biodegradation are determined by oxygen uptake or carbon dioxide release according to ISO 14851:1999, ISO 14852:1999 and ISO 14855-2007 [14-16].

In the method described in ISO 14851:1999. the biodegradation of a plastic material takes place under the influence of aerobic microorganisms in an aqueous medium. The test mixture contains inorganic components, organic test material (the only source of carbon and energy) with a concentration of organic carbon from 100 mg / I to 2,000 mg / I, activated sludge or a suspension of active soil or compost as a source of microorganisms. The mixture is placed in closed flasks in a respirometer for a period not exceeding 6 months and the level of biochemical oxygen demand (BOD) is determined by measuring the amount of oxygen required to maintain a constant volume of gas in the respirometer flasks, or by measuring volume or pressure combinations thereof) automatically or manually. The level of biodegradation is determined by comparing the level of BOD with the theoretical amount of oxygen consumption (ThOD) and is expressed as a percentage. It is also necessary to take into account the influence of possible nitrification processes on BOD. The test result is the establishment of the final level of biodegradation determined on the plateau phase of the biodegradation curve. A carbon balance can also be calculated to obtain additional information about the biodegradation process [14].

According to ISO 14852:1999, the process of biodegradation of plastic material also takes place under the influence of aerobic microorganisms in the aquatic environment. The mixture contains inorganic components, organic test material (the only source of carbon and energy) with a concentration of organic carbon from 100 mg / I to 2,000 mg / I, activated sludge or a suspension of active soil or compost as a source of microorganisms. The mixture is incubated in flasks, purged with carbon dioxide-free air, depending on the biodegradation kinetics for a period not exceeding 6 months. The carbon dioxide released during microbial degradation is measured by an appropriate analytical method. The level of biodegradation is determined by comparing the amount of carbon dioxide emitted with the theoretically possible amount of carbon dioxide (TCO2) and expressed as a percentage. The test result is the final level of biodegradation determined on the plateau phase of the

biodegradation curve. A carbon balance can also be calculated to provide additional information on the biodegradation process [15].

ISO 14855-2007 describes a method for determining the ultimate aerobic biodegradation and the degree of decomposition of a plastic material under conditions that mimic the intensive aerobic composting process. The test material is mixed with the inoculum obtained from mature compost of the organic fraction of municipal solid waste, placed in composting vessels and composting at optimal concentrations of oxygen, humidity and temperature for not more than six months under controlled composting conditions. The end products of biological decomposition of the studied material are carbon dioxide, water, mineral salts and newly formed microbial cellular components (biomass). The emitted carbon dioxide is constantly monitored or measured at regular intervals in test and control vessels to determine the level of carbon dioxide accumulation. The percentage of biodegradation is determined by the ratio of carbon dioxide formed from the test material to the maximum theoretical amount of carbon dioxide that can be formed from the test material. The maximum theoretical amount of carbon dioxide formed is calculated based on the measurement of the total organic carbon content (TOC). This percentage of biodegradation does not include the amount of carbon converted to new cellular biomass that is not metabolized to carbon dioxide during testing. Additionally, the degree of decay of the test material is determined at the end of the test by measuring the decrease in mass of the test material. Instead of mature compost, the method allows the use of vermiculite, which improves the reproducibility of the method [16].

Anaerobic biodegradation rates are determined by the formation of methane and carbon dioxide in accordance with ISO 14853:2005 and ISO 15985:2004 [17, 18].

According to ISO 14853:2005, the determination of the final anaerobic biodegradation of plastic materials is carried out in an aqueous medium under anaerobic conditions. The test material with a concentration of from 20 mg / I to 200 mg / I of organic carbon (OC) is incubated at (35+2)°C in sealed vessels with activated sludge for a period not usually exceeding 60 days. Before use, the activated sludge is washed so that it contains a small amount of inorganic carbon (NC) and diluted to a concentration of solid particles of 1-3 g / I.

The increase in pressure or volume increase in gases is measured (depending on the method used to measure biogas emissions) in test vessels resulting from the formation of carbon dioxide and methane. A significant amount of carbon dioxide dissolves in water or is converted to bicarbonate or carbonate under test conditions. This inorganic carbon is measured at the end of the test. The amount of microbiological carbon released is calculated as the sum of the released biogas and the formed NC, taking into account the control. The percentage of biodegradation is calculated as the ratio of the total amount of carbon converted to biogas and NC, and the measured or calculated amount of carbon added as test material. The course of the biodegradation process can be controlled by intermediate measurements of biogas release [17].

The test method described in ISO 15985:2004 is intended for optimized modeling of the intensive process of anaerobic conversion and determines the final biodegradation and the degree of decomposition of the test material in a solid medium under anaerobic conditions. Methanogenic inoculum includes anaerobic microorganisms isolated from the organic fraction of decomposed solid waste. The test material is mixed with the inoculum and introduced into a vessel, where the decomposition process takes place at the optimum temperature and humidity for 15 days or longer until the plateau of biodegradation is reached. During anaerobic biodegradation, the studied material, methane, carbon dioxide, water, mineral salts and new microbial cellular components (biomass) are the end products of biodegradation. The biogas (methane and carbon dioxide) emitted is constantly monitored or measured at regular intervals in the test and in the control to determine the total biogas release. The percentage of biodegradation is determined by the ratio of the amount of biogas formed from the test material and the maximum possible theoretical amount of biogas that can be released from the test material. The maximum theoretical volume of isolated biogas is calculated from the measured total organic carbon. This percentage of biodegradation does not include the amount of carbon that is converted to new cellular biomass, which is not metabolized, in turn, to biogas during the test. Additionally, the degree of decay of the test material at the end of the test is determined by measuring the weight loss of the test material [18].

Decomposition rates in aerobic composting and anaerobic gasification are determined by reducing the particle size of the waste. Thus, after feeding into the composting process for a maximum of twelve weeks, not more than 10% of the original dry weight of the test material should not pass through a sieve fraction ≤ 2 mm. Decomposition tests are performed under standardized composting conditions (temperature, pH, humidity and oxygen content). The test material is ground, mixed with fresh biological waste and added to the composting medium. The ratio of carbon to nitrogen should be in the range from 20 to 30 (if necessary, add urea), humidity of about 50%, no free water, volatile substances (about 50% in terms of dry weight), pH about 5.0 units. During the testing process, the compost is regularly mixed (once a week for the first four weeks of composting, and then once every two weeks). The oxygen content in the compost is measured every working day during the first month, and then once a week. The oxygen concentration must be at least 10%, if necessary, blown 15 I / kg per hour. During mixing, humidity and pH are measured, the structure, development of fungi, particle size of test material are analyzed. Every working day the temperature in the middle part of the compost is measured and compared with the norms [19-21].

Aerobic composting is carried out in experimental-industrial conditions or in laboratory conditions. Priority is given to conducting research in experimental-industrial conditions (pilot-scale test). Relevant research methods are described, in particular in ISO 16929:2002 and ISO 20200:2004 [20, 21].

After composting, the following is measured [10]:

- particle size of the test material;
- volatile substances;
- pH;
- ammonium nitrogen;
- nitrite and nitrate nitrogen;

- total nitrogen.

The effect of the investigated polymeric materials on the quality of the obtained compost is also evaluated by ecotoxicity indicators for at least two species of plants from the list given in OECD 208 [22]. Moreover, the germination rate and plant biomass must be at least 90% of the indicators for the control sample of compost [10].

Since its founding in 1964 as the All-Union Scientific-Research Institute of Hygiene and Toxicology of Pesticides, Polymers and Plastics (AUSRIHTPPP), our Research Center has paid special attention to the problem of polymeric materials intended for use in various industries and agriculture.

Conclusions

1. The problem of accumulation and management of polymer waste requires the development and implementation of special management, technological and organizational solutions.

2. One of the ways to solve this problem is the use of biodegradable polymers and, accordingly, the introduction of methods that determine the ability of packaging to biodegrade.

3. The Research Center has begun preparations for the implementation of the necessary methods and test schemes to assess the ability of polymers to biochemical degradation. The availability of qualified personnel, the necessary material base and experience of accreditation in accordance with the requirements of DSTU ISO/IEC 17025:2017 [23] and GLP [24], will allow to conduct research at an internationally recognized level.

4. The introduction of methods and test schemes for assessing the ability of packaging to biochemical degradation will accelerate the introduction of biodegradable materials in the consumer market of Ukraine, which will reduce the total amount of packaging and packaging waste and contribute to the goals set by the National Waste Management Plan until 2030 [25].

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МЕТОДИЧНІ ПІДХОДИ ЩОДО ОЦІНЮВАННЯ ЗДАТНОСТІ ДО БІОХІМІЧНОГО РОЗПАДУ ПОЛІМЕРНИХ МАТЕРІАЛІВ ТА ЇХНІХ ВІДХОДІВ (Огляд літератури)

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РЕЗЮМЕ. Актуальність. Об'єми промислових і побутових відходів, зокрема використаної полімерної тари і упаковки значні, внаслідок інтенсивного розвитку виробництва полімерних матеріалів постійно збільшуються.

Матеріали та методи. В Україні поступово вводяться обов'язкові вимоги до упаковки і пакувальних відходів, які мають відповідати Європейському законодавству. Розглянуто основні аспекти вимог до тари та упаковки, що містяться в нормативних актах вітчизняного та європейського законодавства. Визначено і оцінено основні види біодеградабельних полімерних матеріалів.

Висновки. Проведено порівняльний аналіз методів щодо визначення здатності до компостування, анаеробної та аеробної обробки упаковки та пакувальних матеріалів.

Ключові слова: відходи тари та упаковки, Директиви ЄС, біополімерні матеріали, біодеградабельність, методи визначення біодеградації.

МЕТОДИЧЕСКИЕ ПОДХОДЫ ОЦЕНИВАНИЯ СПОСОБНОСТИ К БИОХИМИЧЕСКОМУ РАЗЛОЖЕНИЮ ПОЛИМЕРНЫХ МАТЕРИАЛОВ И ИХ ОТХОДОВ (Обзор литературы)

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РЕЗЮМЕ. Актуальность. Объемы промышленных и бытовых отходов в виде использованной полимерной тары и упаковки значительны, вследствие интенсивного развития производства полимерных материалов постоянно увеличиваются.

Материалы и методы. В Украине постепенно вводятся обязательные требования к упаковке и упаковочным отходам, которые должны соответствовать Европейскому законодательству. Рассмотрены основные аспекты требований к таре и упаковке, изложенные в нормативных актах отечественного и европейского законодательства. Дана характеристика основных видов биоразлагаемых полимерных материалов.

Выводы. Произведен сравнительный анализ методов по определению способности к компостированию, анаэробной и аэробной обрабатке упаковки и упаковочных материалов.

Ключевые слова: отходы тары и упаковки, Директивы ЕС, биополимерные материалы, биодеградабельность, методы определения биодеградации.

Received March 27, 2020