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BIODEGRADATION OF WASTED BIOPLASTICS

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ABSTRACT

Bioplastic is plastic made from renewable biological material, usually plants, bio-waste or microorganisms, rather than petroleum or natural gas. Most bioplastics are environmentally friendly compared to plastics that are made from fossil fuels. But this is not always the case - a lot depends on how bioplastic is produced and disposed of.

The bioplastics industry is young—accounting for only 1% of global plastics production in 2019. Standardization of raw material sources, types of plastic, or labeling of what is biodegradable or compostable is poorly developed. This often confuses consumers because not everything made from plants is biodegradable. However, growing awareness of the dangers of overuse of plastics and increased government regulation of plastic waste have led to a surge of interest and investment in bioplastics, an industry expected to grow 10-14% in the next few years. It is possible that this will partially help solve one of the most serious environmental problems in the world: plastic pollution.

Marine plastic pollution is a growing global problem. The most striking example is the Great Pacific Garbage Patch. According to the EPA (U.S. Environmental Protection Agency), of the approximately 36 million tons of plastic produced annually in the United States, less than 1% is recycled. Globally, only about 9% of plastic waste is recycled. About 11 million tons of plastic waste are dumped into the world's oceans every year. Even more comes from land-based sources, where plastic slowly breaks down into smaller and smaller particles. According to some estimates, there are up to 51 trillion microplastic particles floating in our oceans. Scientists estimate that the average adult ingests approximately 883 microplastic particles every day, which accumulate in our body tissues. Ingestion of plastic by marine and terrestrial animals can have extremely adverse effects on their health, including death.

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Introduction.

Bioplastics are a type of plastic that is obtained from renewable sources of biomatter: vegetable oils and fats, starch or microbiometa. Bioplastics can be made from secondary agricultural products or polymer by-products using microorganisms. Simple plastics are mainly derived from gas and oil, but their production requires the use of huge amounts of fossil fuels, and the greenhouse gas emissions that are a by-product of their production are much higher than those of bioplastics. Bioplastics can include various elements: starches, celluloses, biopolymers and many others. Interestingly, some types of bioplastics are biodegradable, which makes them attractive to all humanity. Every year the volume of their use is only growing. They are already used for the manufacture of biodegradable tableware, children's toys, packaging and packaging materials, the medical industry, electronics, and also as raw materials for polymer 3D printing. Degradable bioplastics are also widely used in medicine. Polymers made from biomolecules are better compatible with human tissue and are more easily absorbed than “traditional” plastics. For example, German surgeons tested polylactide surgical screws. They resolve within two years, and patients do not need to be operated on again, as is now the case with metal pins. In the United States, medical implants made from mixtures of biodegradable polymers are being studied, for example, to restore knee cartilage. And the Japanese recently released onto the market an almost transparent adhesive film tens of nanometers thick. It is made from chitosan and is designed to quickly heal internal wounds. Theoretically, it could replace medical threads or staples.

Bioplastics can be divided into three groups depending on their source of origin and ability to biodegrade:

• plastics made from renewable raw materials but not biodegradable, e.g. polyamide (PA), polyethylene terephthalate (PET),

• biodegradable plastics, but not made from renewable raw materials – for example, polybutyrate adipine terephthalate (PBAT) or polycaprolactone (PCL),

• bioplastics obtained from renewable raw materials (biodegradable polymers), biodegradable - for example, polylactide, i.e. plastic based on a biopolymer of lactic acid (PLA), polyglycolide based on glycolic acid (PGA) or modified starch.

Currently, the development and creation of composite polymer materials (CPMs) is one of the most promising areas of modern polymer materials science [1]. An analysis of the scientific literature has demonstrated the advantages of CPM over traditional thermoplastic polymer materials. The reason for their popularity is the steady trend that has emerged in recent years of replacing traditional plastics with compositions of thermoplastic polymers with various types of fillers. Their properties can vary widely depending on the type of filler matrix used, its dispersion, concentration and combination of several fillers. Of particular interest lately have been the so-called biodegradable and biocompostable plastics and composite materials, which, after their use under special conditions, decompose into environmentally friendly components. The rapid growth in the consumption of bioplastics in the world is the main trend in the development of the raw material base for the production of biodegradable packaging, tableware, various types of containers, parts of construction equipment, medicine, automobile, aircraft and shipbuilding. Biodegradable polymers, especially those produced from biological feedstocks, make up a fairly small share of the global plastics market. A recent report on biodegradable materials released by the European Commission's Advanced Technology Research Institute concluded that these materials will account for around 5% of the European polymer market by 2020. Major applications for biodegradable plastics include food packaging. Containers, films and foams made from these polymers are used to package meat, dairy, baked goods and other products. Other common uses include disposable bottles and cups for water, milk, juices and other drinks, plates, bowls and trays. Another market for such materials is the production of bags for collecting and composting food waste, as well as bags for supermarkets. A growing application for these polymers is the market for agricultural films, including those used for soil mulching. Unlike most plastics, biodegradable polymers can be broken down in the environment by microorganisms such as bacteria or fungi. More than 99% of all polymers and plastics are made from oil, gas or coal. This means that everything that surrounds us - packaging, building materials, car parts, fabrics, electronic devices - is made from non-renewable resources. However, polymer materials back in the 60s. XX century They learned how to obtain it from corn, potato starch, wheat, sugar cane, etc., but in terms of technological properties they were inferior to polymers from hydrocarbons, and they were expensive. However, in recent years, the production of polymers from plants has increased sharply, and there are several reasons for this [2]. Biopolymers are long molecules consisting of identical units that are found in nature and are part of living organisms - proteins, nucleic acids, polysaccharides and others. But now we will not talk about them, but about polymers made from plant materials, they are called bioplastics.

However, their “natural” origin and name with the prefix “bio” do not mean that they are all biodegradable and safe for the environment. From hydrocarbon raw materials, they have learned to produce both durable polymers that do not decompose in the soil for more than 200 years, and biodegradable ones - they contain special additives, thanks to which, in accordance, they decompose in 180 days into components that are non-toxic to plants (therefore they are often also called bioplastics).

The prevailing area of consumption of PM is the production of containers, packaging (flexible and rigid) and disposable tableware: about 40% of the total volume of manufactured PM is used as containers and packaging of food (47%) and non-food (53%) products. Back in the mid-70s of the last century, PM came in third place in consumption after glass and paperboard materials in these applications. But if glass containers, like is usually in the consumer cycle, and paper decomposes in natural conditions, then packaging made of PM, amounting to more than 40 % of household waste is practically “eternal” - it does not undergoes decomposition within 30–80 years, and the questions of “what to do” and “what to do” with polymer “garbage” become a global environmental problem. From solving the problem of polymer waste. The environmental situation in the world in the 21st century and, apparently, the pace and direction of development of PM production will largely depend. Otherwise humanity is on its own will bury polymer “garbage” in the form of waste from the production of products made from PM (waste in the form of separated gates, allowances for manufacturing products, etc.) and actually used PM products (in hereinafter – waste from PM).

Currently known and mostly lesser extent, the following are actively developing PM waste management methods:

-disposal (storage in landfills and composting);
-burning;
-pyrolysis;
-recycling;
-creation of biodegradable (in natural conditions) materials.

These methods have both advantages and shortcomings, sometimes significant. For example, disposal of waste from PM is a temporary measure, which leads to the alienation of large areas of land for many decades and, in fact, is shifting today's problems onto one's shoulders future generations.

Combustion and pyrolysis of PM waste does not fundamentally improve the environmental situation due to a large number of emissions of gases and aerosols harmful to living organisms. Secondary processing (recycling) solves this issue to a certain extent, but it also requires significant labor and energy costs: selection of polymer containers from household waste and packaging, separation by type of PM, washing, drying, grinding and only then processing into final products. To activate the direction of recycling waste from PM, a number of countries are adopting legislative standards for the mandatory collection and recycling of polymer containers and packaging. For example, directives of a number of countries in Western Europe provide for the use of at least 15% of recycled PM in the manufacture of polymer packaging, and in Germany this quota is 50% and should increase to 60%. Some experts believe that this is technically impossible, since only for transport and non-food packaging it is possible to use up to 25% recycled PM, but not for food products. It should be noted that the situation with the cost of products obtained from a mixture of primary and secondary PM is ambiguous. On the one hand, there is a constant increase worldwide the cost of primary PM, on the other hand, additional costs for the collection and recycling of waste from PM in general can lead to an increase in the cost of the original mixed PM, and their quality is, as a rule, lower than that of primary PM. In addition, psychologically, not every consumer agrees to use products made from similar, albeit certified, PM (for example, as food packaging). Even if we assume that a significant part of containers and packaging made from PM will be reused, the question arises as to what frequency of recycling is acceptable, after which the time will come to solve this problem in another way. In any case, the environmental situation in the surrounding world is becoming more and more aggravated, not least due to the accumulation of polymer “garbage”.

A radical solution to this problem, according to experts, is the creation and development of a wide range of PMs that, under the influence of environmental factors, can self-decompose after a given period of time into components that are harmless to living and inanimate nature. It is the biodegradability of high molecular weight compounds and will be the priority direction of development that will eliminate a significant number of waste management problems from PM. From a terminological point of view, it should be noted that in literary sources there are different definitions of the same concept in principle - "biodegradation", "biodegradation", "biodegradation" and "biodegradation" of PM, of which, for clarity, the most accepted one is chosen in this article - "biodegradation". Assessment of the current situation regarding development and development and degradable PM allows us to identify two main directions for the development of search and applied work in this area: development of biodegradable PMs themselves based on reproducible sources of raw materials of natural origin (hereinafter referred to as natural PMs or biopolymers) - starch, chitosan, polyhydroxyalkanoates, cellulose derivatives, etc.; imparting biodegradability to industrial high-molecular synthetic materials. In recent years, the direction of producing biopolymers based on reproducible plant and animal raw materials has been increasingly developing all over the world. The main raw materials for the production of polymer products capable of subsequent controlled biodegradation in nature are lactic acid, hydroxyalkanoates, cellulose derivatives, chitosan, starch, etc. Under the influence of water and soil microorganisms, these polymers decompose mainly into carbon dioxide and water [3].

Products based on chitosan are obtained from raw materials in the form of crushed shells and other parts of sea crabs, shrimp, etc. The production of products from cellulose and derivatives based on it dates back more than a hundred years. One of the most important advantages of using biopolymers instead of synthetic ones is the possibility of using substances and products that are constantly reproduced in nature as raw materials, such as sugar and its production waste, in contrast to oil, coal and gas, which have a limited supply in nature.

Products made from polylactide (PLA), a transparent thermoplastic that is a polycondensation product of lactic acid, decompose in compost within one month and a little longer in seawater. An important advantage of PLA is the possibility of its processing using traditional equipment. Disposable tableware, films, fibers, and implants for medicine are formed from PLA.

When an appropriate plasticizer is added, PLA becomes elastic and can compete in properties with polyethylene (PE), polypropylene (PP) or lastified polyvinyl chloride. The service life of the polymer increases with a decrease in the size of the monomer unit in its composition, as well as after orientation drawing, causing an increase in the elastic modulus and thermal stability of PLA. By fermenting corn dextrose, the American company Cargill Inc. has mastered the production of PLA under the Eco-Pla trademark, sheets of which are comparable in impact resistance to polystyrene (PS). The films have high strength, transparency, gloss, low friction coefficient and good weldability. However, PLA is not without its drawbacks, the main of which is the ability to swell and dissolve during prolonged contact with water. Moreover, the higher the temperature, the faster these processes proceed. Another disadvantage hindering the widespread use of PLA as a polymer for household and general technical purposes is its high cost. Another example of polymers of natural origin that can quickly decompose under the influence of soil and water microorganisms are polyhydroxyalkanoates, derivatives of polyhydroxybutyric acid. The most promising polymer of this group at present is poly-3-hydroxybutyrate or polyhydroxybutyrate (PHB), discovered by microbiologists back in 2012. In nature, this polymer is synthesized by some types of microorganisms and plays the role of an intracellular energy reserve, like glycogen and polyphosphates in other microorganisms. The polymer is found in the cytoplasm of microbial cells in the form granules and usually accounts for more than 40% of their dry weight [4].

The characteristic properties of bacterial PHB are its optical activity, thermoplasticity, piezoelectric properties, and the ability for "pure" biodegradation, as a result of which the polymer is completely converted into carbon dioxide and water. Products from this polymer can be obtained both from the melt and from its solutions in organic solvents - pyridine, dioxane, NaOH, higher alcohols, camphor and chloroform, in which, however, PLC is limitedly soluble. The polymer is practically insoluble in water, ether, lower alcohols, and acetone, which are used as precipitants for PHB from its solutions. PHB has a number of useful properties - biocompatibility with living organisms, rhomboresistance, good elastic-strength properties. The ability of PHB to biodegrade is the defining property on which its widespread use is based both in pure form and as a component of mixtures and copolymers based on it. Therefore, products made from PHB are environmentally friendly and do not require special disposal after use. In addition, the possibility of burying PHB products after their use in soil or seawater is attractive, where their complete biodegradation is ensured, which eliminates environmental pollution.

The environmental aspect of these developments is so important that abroad, PHB, along with some other biopolymers, are already classified as strategic materials. The low energy intensity of the fusion process is also unique and deserves attention in the context of the energy crisis. In world practice, PHB has now found its use in medicine as absorbable suture threads, bandages and tampons, plates and rods in orthopedics. In the form of a film material, it can be used for packaging and storing food products, for prolonged action of medicines, plant growth stimulants, mineral fertilizers, for which capsules are made from PHB. Encapsulating (enveloping) the seeds of cereal plants with this polymer, intended for their pre-sowing treatment, makes it possible to localize vital substances on the seeds, protect the seeds from exposure to low temperatures, and also reduce sowing rates by 4 times and increase seed germination and yield by 7-10%.

Due to its rapid biodegradation in the gastrointestinal tract of mammals, PHB can be used for the production of hay twine to replace the currently used PP. The feasibility of using PHB is also determined by the fact that its technological properties are practically no different from synthetic thermoplastics and therefore can be processed on standard industrial equipment of chemical plants where threads, films and other products from PM are formed. In industry, PHB can be used in production to create biodegradable polymer compositions with a controlled service life.

Thus, from the above it is clear that wide opportunities are opening up for the use of PHB in various fields, which will undoubtedly stimulate increased demand for this polymer and its further research.

However, the synthesis of biopolymers today is expensive, since it is associated with complex technology for washing the polymer. In this regard, biopolymer developers are currently paying special attention to the issues of reducing the cost of products by creating high-performance technological processes and/or using biopolymers as components to impart special properties to traditional materials, for example, to obtain self-degrading multicomponent or, otherwise, biosynthetic PM (BSPM), which are created, as a rule, from mixtures of natural and synthetic polymers with the subsequent use of traditional technologies for molding products from filled PM.

Since products made from natural biopolymers, which decompose relatively easily and quickly in the environment as their service life expires, are relatively expensive, and their production volume is not comparable with the need and production of synthetic polymers. For the optimal course of the biodegradation process, a certain set of environmental factors is needed: temperature, pressure, humidity in the liquid or gas phase, the type and concentration of salts, the presence or absence of oxygen (aerobic or anaerobic decomposition), the availability of alternative electron acceptors, the presence of trace elements and nutrients, pH value, redox potentials, stability or change in environmental conditions, microorganisms “opponents”, inhibitors, alternative carbon sources, light intensity and wavelength. In this case, a necessary condition is the presence of a minimum water content.

The most pressing task at present is the creation of compositions (mixtures) from synthetic (derived mainly from oil) and natural (organic and inorganic) materials - BSPM, in which the continuous (matrix) phase is a synthetic polymer [8].

The main stages of biodegradation of BSPM Based on numerous studies of such systems, the following sequential stages of biodegradation of products from BSPM have been established. Initial formation of microcracks and subsequent destruction of products into fragments. The mechanism of these processes is based on photodestruction of system components under the influence of ultraviolet (UV) radiation with the formation of radicals, which in turn activate photooxidative processes in the PM [5]. When large and small fragments of a product enter the soil, they are exposed to intense microorganisms. The formation of microfungal colonies is facilitated by the biocomponent included in the PM. In the process of fouling of BSPM fragments with soil microorganisms, destruction of BSPM occurs and a significant drop in their strength. and only slightly erode on the surface. Microbial enzymes and metabolites, together with water and chemical components of the soil, cause further biodegradation of product residues [6]. However, as the authors of this publication have established, PHB combines two functions: an initiator-accelerator of photodestruction of the main (matrix) polymer, as well as a component that promotes the development of microfungal colonies on the surface of the product. Depending on the content and activity of components from the group of biodegradable natural polymers at the first stage, it is possible to regulate the time and intensity of the destruction processes of the product, as evidenced by the following experiment, in which LDPE and

LDPE-based films, intended mainly for coverings of greenhouses and greenhouses and serving as one of the main sources of environmental pollution [7]. Samples of films from pure (unfilled) LDPE and from BSPM (PE + PHB) with different PHB contents (from 2 to 90%) were kept for various times in an artificial weather chamber under conditions simulating natural factors - humidity, air, solar radiation, temperature conditions.

Under the influence of enzymatic systems present in living organisms, polymer fragments are involved in hydrolytic and redox reactions, as a result of which the formation of new free molecules continues radicals. Thanks to them, the macromolecules of the synthetic polymer are intensively destroyed, as a result of which its molecular weight is significantly reduced [9].

Fragments of a synthetic polymer with a molecular weight reduced to 5,000 and below can be absorbed by some soil microorganisms, releasing CO2, H2O and other compounds, which in turn are a nutrient medium for soil microflora. To activate and accelerate the stage of photodestruction of BSPM, salts of metals of variable valence (copper, iron, etc.) are often used. When these substances are exposed to UV radiation, mobile radicals are formed, which interact with the polymer chains, breaking them. Further destruction of the polymer occurs via a chain free radical mechanism. After complex climatic exposure (O2, H2O, UV radiation), the formation of microcracks is observed on the surface of only BSPM films, and the average length of microcracks, other things being equal, increases with increasing relative PHB content. Thus, as a result of the initial act of destruction of products made from BSPM under the influence of UV radiation, oxygen and water, particles of material enter the soil, which are subsequently exposed to soil microorganisms. Moreover, pre-photoinitiated films are destroyed much more intensely. The sizes of spores of microfungi and soil bacteria are smaller than the characteristic sizes of cracks on the surface of product fragments. Therefore the presence surface microcracks promotes the penetration of spores of microfungi and soil bacteria into the material, which, assimilating PHB, develop on fragments of used products, releasing various metabolites, enzymes and other products, which in turn are chemically aggressive for PE environments and significantly accelerate in the future processes of oxidative destruction of the polyethylene matrix (up to a molecular weight of 5,000 and below). This is evidenced by the size of microfragments of products, commensurate with the size of soil particles, which contributes to their complete further decomposition [10-11].

Conclusions.

As a result of my research, I solved the problems and obtained various samples of starch-based bioplastics, examined their organoleptic properties and changes in their structure in various environments and conditions of use. Of course, today plastic is indispensable in all areas of life; it is light and durable, can be of any color and shape, allowing you to create shapes and objects that would be impossible without it. Plastic is made from oil, gas, coal, but the main problem is not what this plastic is made from, but that it is produced in huge quantities and people have not established processes for recycling it. A huge amount of waste ends up in landfills, in the oceans, in the air, etc. but there is an excellent alternative - bioplastic. The direction of biodegradable PM and, first of all, BSPM based on natural self-degradable ingredients that decompose the main synthetic polymer is interesting primarily due to the complete reproducibility and practical unlimitedness of raw materials, which is becoming increasingly promising due to the intensive consumption of raw material sources throughout the world (oil and gas) for the production of traditional synthetic polymers. The main task of researchers of biodegradable PM is to provide the required level of cost, as well as technological and performance properties at a level close to or corresponding to synthetic polymers. The need for biodegradable PM is growing, as evidenced by the fact that in economically developed countries, for example, a fairly large share of disposable packaging is already made from such materials. New directions are being created and research is being conducted to develop a wide range of materials based on various types of starches, lignins, cellulose proteins, polyoxyalkanoates and polylactides.

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