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Synthesis of Biodegradable Polymer-Based on Starch for Packaging Films: A Review

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ABSTRACT
Due to their crucial qualities and functionalities, polymers have received a lot of attention in recent years as food packaging materials. These characteristics include non-toxicity, ease of availability, biocompatibility, and biodegradability, showing their promise as an alternative to traditional plastic packaging, which has long been under investigation for its environmental impact. Given the present emphasis on sustainable development, research into biopolymers as eco-friendly and sustainable food packaging materials is critical. The synthesis of biodegradable polymers-based on starch represents a significant stride towards sustainable packaging solutions. As the global demand for eco-friendly materials continues to grow, ongoing research and innovation in this field are poised to lead to the development of starch-based packaging films with improved properties and widespread commercial applications. As a result, the primary goal of this review is to create a biodegradable polymer based on corn-starch and PVA with strong physicomechanical characteristics for usage in plastic bags.

Keywords: Polymers, biodegradability, packaging, plastic bags.

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Introduction

Synthetic polymers and products made from them have a high demand for attributes of human life, but their use creates a lot of problems. Synthetic polymer materials are yielded from non-renewable raw materials, and their accumulation and problematic disposal lead to a deterioration of the environmental situation and the creation of a global problem. The volume of production of synthetic plastic materials, mainly polyolefin, is more than 300 million tons per year. Polyolefin is polyethylene and polypropylene, which can be obtained by petroleum organic synthesis. It is worth emphasizing that up to 98% of the world's plastics are produced from non-renewable raw materials such as oil, gas, and coal processing products. Their stocks are limited [1]. Nowadays, the scope of use of plastic materials is extensive and is used in almost all areas of human activity. The largest share of processing of synthetic polymers falls on the manufacture of containers and packaging. The volume of this sector is approximately 60% of the total volume of plastics processing. About 40% of plastic is used for food packaging and the bottling of drinks. A large mass of used goods is made of synthetic polymers, and only about 20% are recycled [[2], [3], [4]]. According to data from the World Bank organization, about 2.01 billion tons of solid household waste are generated annually in the world, and around 242 million tons (12%) of the total amount of solid waste is related to plastic materials [5]. The problem of solid waste management is relevant in the world and the Republic of Kazakhstan is not excluded. In 2021 the amount of solid household waste in Kazakhstan was estimated at 125 million tons for what we used 3 200 official landfills and only 18.3% of solid household waste is recycled [6].

Utilization is a possible solution to reduce the volume of waste of artificial plastics. The utilization process can include recycling, combustion, pyrolysis, and recirculation. Combustion and pyrolysis can contribute to the reduction of waste but worsen the environmental situation. In addition, highly toxic compounds such as furans and dioxins are formed during combustion [7].

Plastic considerably pollutes the air, water, and soil because it contains harmful compounds (lead and cadmium pigments, which are frequently used as additives in low-density polyethylene, high-density polyethylene, and polypropylene), and because it is not biodegradable. Plastic bags have the potential to harm the environment in three different ways. Firstly, natural resources that need to be protected are mainly used for the manufacture of plastic bags: oil, natural gas, or coal. Secondly, during the production of plastic, many harmful pollutants are formed, which production companies need to properly deal with. According to market research, the plastic bags of Kazakhstani manufacturers, which produce them mainly based on petrochemical products, do not decompose quickly because of mineralization and can remain in microscopic form indefinitely [8]. Numerous illnesses, including blood and renal ailments, immunological and brain system abnormalities, and birth defects in children, can be brought on by these compounds [9]. In addition to being extremely poisonous, the primary chemicals utilized in the production of plastic bags include certain carcinogens including benzene and vinyl chloride, as well as gaseous and liquid hydrocarbons that harm the environment. It was found that some synthetic plastics used for the manufacture of plastic containers increase the risk of cancer. Since a moderately dangerous substance for the human body is used for their production - bisphenol A (diphenyl propane A). Bisphenol A dissolves well in an aqueous medium; therefore, it can get into food and directly into the human body through the blood [1].

A more effective and popular way to accelerate the biological degradation of the polymer matrix of synthetic polymers is to add various natural additives to the polymer structure that serve as a nutrient medium for microorganisms and accelerate the destruction of the polymer composition. Polysaccharides (starch, dextrin, chitosan, cellulose, wood processing waste) have become the most widespread in the production of biodegradable packaging [[10], [11]]. Despite a significant amount of work devoted to the production of biopolymer materials, their characteristics, and applications, the issue of creating biodegradable systems to reduce the time of biological decomposition has not been fully resolved [12]. The development of new plastic polymer materials that decompose due to microorganisms in soil and water is one of the urgent and priority directions of science development [13]. Polymer degradation can also be caused by exposure to ultraviolet and thermal radiation, sunlight, hydrolysis, and oxidation of air [14].

The addition of poly (ethylene glycol) methyl ester methacrylate [PEGMA] to polymer compositions filled with natural fillers to create biodegradable compositions has not been previously carried out, which is a novelty of this work. In this regard, studies on the effect of poly (ethylene glycol) methyl ether methacrylate in polymer compositions based on polyvinyl alcohol and natural starch filler for the creation of biodegradable polymers are of both scientific and practical interest.

To achieve this goal, the following scientific tasks were set:

1) Selection of certain components and their ratio.

2) Study technological parameters in the production of materials with high-performance characteristics, such as physical, mechanical, and technological properties.

3) Observe the ability to rapidly biodegrade, considering the regulation of degradation processes.

4) Study the solubility of [PVA-b-S]-g-PEGMA biofilms in water, tea, coke, and soil.

Consequently, PEGMA was grafted onto a PVA/S mix copolymer with potassium persulfate acting as the initiator. By using elongation and tensile strength tests, the impact of the blend ratio ([PVA]:[S]:[PEGMA]) and the molecular weight (300, 500, and 950 g/mol) of PEGMA on the physicomechanical characteristics of PVA/S blends was investigated. It was discovered that the water phase is the best environment for the biodegradability of the produced PVA/S/PEGMA mix films. Additionally, the study aims to offer a quick and affordable way to create biodegradable starch/PVA/PEGMA mix films with better physical qualities, which may find potential uses in the disposable packaging industries [15].

Biodegradable Polymers

The biodegradability of polymers is the ability of a material to decompose without residue under the influence of bacteria, fungi, UV radiation, light, solar radiation, and other natural factors in natural conditions on environmentally friendly substances [16]. The main concept of biopolymer production is to create methods close to the natural cycles of nature. To obtain them, renewable raw materials are used, containing in their composition substances that arise in plants during photosynthesis. Biopolymers are being developed, which are later used as fertilizers, and thanks to microbes and hornbeams, water and carbon dioxide are converted in natural conditions.

Biodegradation is a chemical process caused by biological activity that changes the chemical structure of a material and contributes to the production of natural end products of metabolism.

Synthesis of Biopolymers

Currently, there are three possible directions to produce biopolymers:

1. Synthesis of plastics based on renewable polymers. The synthesis of biodegradable plastics based on natural high-molecular polymers, such as starch, cellulose, chitosan, protein, etc. is used to create composite materials with a variety of natural fillers. Today, biodegradable materials based on cellulose and its derivatives are the most common source of raw materials to produce disposable tableware, packaging material, and other products.

2. Giving the ability to biodegradate plastic materials popular today from petrochemical raw materials. To give biodegradation to plastics, molecules with certain functional groups are introduced into the structure of the main polymer, accelerating its photo-destruction. Composite materials with biodegradable additives that initiate the decomposition of the initial polymer are also obtained. Or purposefully synthesize biodegradable plastics based on petrochemical polymers. For example, a mixture of cellulose, alkyl ketones or compounds containing carbonyl groups accelerates the photodecomposition and biodegradation of polyethylene, polypropylene, or polyethylene terephthalate.

3. Production of biodegradable polyesters by chemical or biological methods. According to literary sources, this direction has been actively developing recently. The direction is based on the biotechnological or chemical synthesis of biopolymers based on hydroxycarboxylic acids, such as glycolic, lactic, valerian, and others [1].

The biodegradability and non-toxicity of bioplastics are the fundamental requirements for purchasing them. Standards for polymaterials are used for this purpose, and they provide for testing of all additives and polymers to prevent environmental harm [17].

The biodegradation of polymer materials is significantly influenced by the size and chemical structure of the molecule, the presence and type of replacements, and supramolecular micro- and macrostructure [18].

There are certain fragments in the structure which enhance the biodegradation of plastic [18]:

1) heteroatoms;

2) double bonds R = CH2; R = CH–R1; hydroxyl groups R–CH2–OH; R–CH(OH)–R; ether bonds R–CO–H; R–CO–R1, etc.;

3) less than five CH2 groups;

4) volumetric substituents;

5) Natural products of microorganisms, such as starch, cellulose, lactose, magnesium, and urea.

The main mechanisms of polymer biodegradation are biological hydrolysis, which begins with the adsorption of microorganisms on the surface and biological oxidation depends on the chemical composition of the monomer link [18].

Types of Bioplastic Materials

The two categories of raw materials used to create bioplastics are renewable and non-renewable raw materials. Polymer materials are also distinguished by spontaneous decomposition in the natural environment, that is, by biodegradation: biodegradable and non-biodegradable [18]. Based on the above characteristics, all plastics are divided into the following groups as shown in Table 1.

Table 1 - Classification of plastics by raw materials

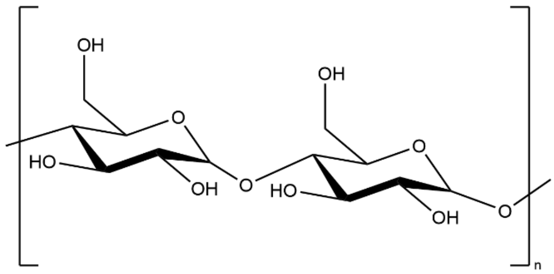
The raw material	Type of plastic
Non-biodegradable plastics from non-renewable raw materials.	Some examples of these include polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene, polybutylene terephthalate, polycarbonate, and polyurethane.
Biodegradable plastics from non-renewable raw materials.	These are synthetic, non-natural materials derived from petrochemical hydrocarbon raw materials; yet, due to specific structural properties, they are biodegradable. Polybutyrates (adipic acid, dimethyl terephthalate, and 1,4-butanediol copolymers (PBAT), polybutylene succinates (PBS), polyvinyl alcohol (PVA), polycaprolactones (PCL), and polyglycolic acid (PGA) are examples of this category.
Non-biodegradable plastics are based on natural raw materials.	These include biopolyethylene, biopolyvinyl chloride, terephthalic PET biopolyesters, etc.
Biodegradable plastics from natural raw materials:	- with the formation of a polymer chain in a natural way. These are biopolymers based on starch, cellulose, etc. - with the formation of a polymer chain with the help of microorganisms in a certain environment. These are polyhydroxyalkanoates; - with the formation of a polymer chain, during the synthesis of a monomer due to a biological process. This is polylactic acid. In this work, the type of biodegradable plastics from natural raw materials prepared by a new biopolymer is examined and studied for degradability.

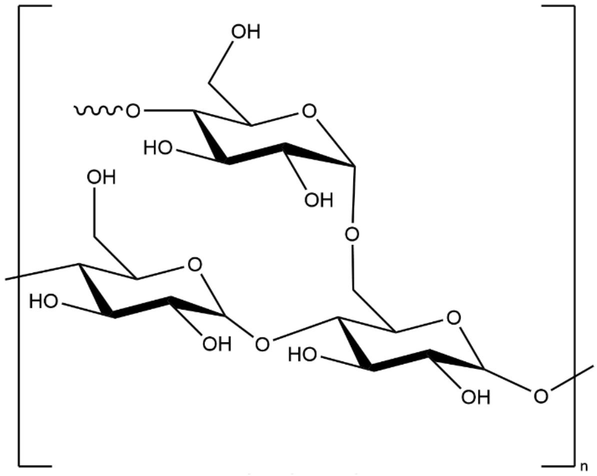
Natural Biopolymers
Bioplastics from Biomass

Polysaccharides are the most famous natural macromolecules. These are high-molecular carbohydrates consisting of glycoside bonds. They are often one of the important structural elements of the framework of plants and animals. Plants such as potatoes, wheat, legumes, sunflowers, beets, and a variety of wood serve as raw materials to produce a variety of biodegradable polymer products. Now, natural polymers such as polysaccharides, cellulose, rubber, polypeptides, chitin, epoxidized oil, lignin, pullulan, polyesters, etc. are used. The most popular is starch because it is less expensive and obtained from potatoes, wheat, corn, and rice [19].

Starch is a white amorphous powder, tasteless and odorless. Starch does not dissolve in cold water but swells in hot water and forms a paste. In industry, starch is obtained from potatoes (starch content - up to 24%) or corn kernels (57-72%).

Amylopectin (Figure 1), is a highly branching polymer composed of short chains of -1,4 linked by -1,6-links. Connections, and amylose, an essentially linear polysaccharide comprised of -1,4-anhydroglucose units, make up starch. Due to the valence angles between the glucose atoms, amylose molecules have between 200 and 20,000 glucose units and are made up of them in a spiral shape. The polymer amylopectin contains a significant amount of branching. Thirty glucose units are connected along the length of a short-side chain. The starch source affects the relative ratio of the two elements. The usual concentration of amylose is between 15 and 25 percent and is often present as a secondary component. As a raw material for biodegradable goods, starch is currently readily accessible at a cost that is far lower than that paid even for commercial polymers. However, because pure starch has an excessive amount of hydroxyl groups that may absorb water, items created from it have two severe drawbacks: fragility and susceptibility to moisture. The economic potential of starch-based polymers is considerably reduced by these two characteristics; however, research is already underway to enhance starch-based materials. Starch-based materials' rather low mechanical qualities were traditionally overlooked by combining them with other





a) Molecular structure of amylose

b) Molecular structure of amylopectin

Figure 1 - Chemical structure of amylose (a) and amylopectin (b)

biopolymers, adding a lot of plasticizers like glycerin or ethylene glycol, or altering the chemical makeup of starch itself. The ratio of amylose to amylopectin, the ability of the starch to form films, the size and shape of the grain, and the temperature at which the starch becomes gelatinous are all influenced by the source of the starch. The overall structure, shape, and thermal properties of starch are influenced by the ratio of amylose and amylopectin [18].

The decomposition of biopolymers is facilitated by hydroxyl groups that bind water. Starch is a polymer with functional (-OH) hydroxyl groups in the structure, which consist of D-glucose. When a small amount of acid is added to the starch solution as a catalyst, its hydrolysis occurs. Macromolecules break down into smaller molecules (dextrin, maltose), and the final product of the hydrolysis reaction is alpha glucose. The reaction mechanism proceeds as follows: a positively charged ion is attracted to an oxygen bridge between two alpha-glucose residues, and connects with an oxygen atom, thereby breaking the connection. On the atom of the second fragment of the starch molecule, it forms a positive charge, which attracts the water molecule to itself. The oxygen in the water molecule is attached to a carbon atom, and one of the hydrogen molecules is separated from the water molecule. As a result, dextrin molecules are formed, which are hydrolyzed by the same mechanism to form maltose molecules. The final product of starch hydrolysis is an alpha-glucose molecule. Starch is a very popular vegetable polysaccharide with excellent film-forming properties. However, some hydroxyl groups can be replaced with ether or ester groups. In this case, water will not be able to easily affect the polymer. To increase the heat resistance of polymers, acid resistance, and shearing force, additional chemical treatment is required, which makes it possible to create additional bonds between different parts of the polymer - starch [20].

The excellent properties of starch as a natural multi-tonnage polymer arouse the interest of researchers and large manufacturers for the development and production of various starch-based products.

The main advantages of starch as a natural polysaccharide [21]:

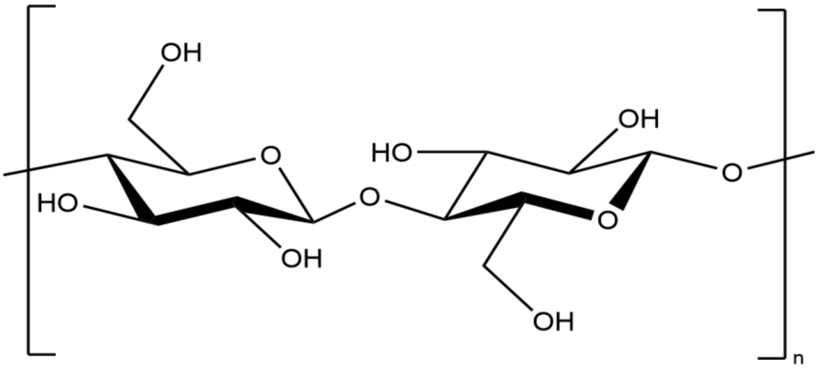


Figure 2- The chemical structure of Cellulose

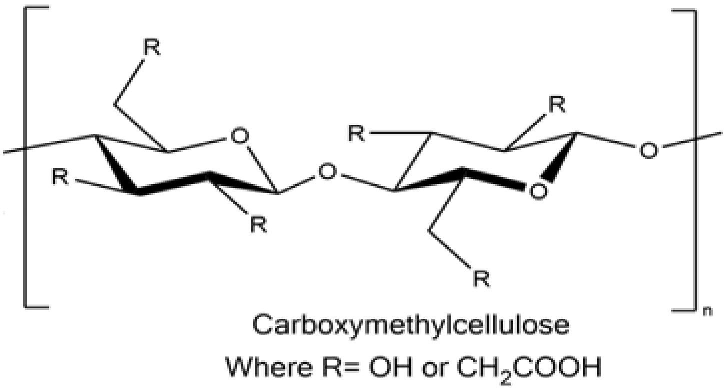


Figure 3 - The chemical structure of Carboxymethylcellulose

– the renewability and inexhaustibility of raw materials from year to year, such as potatoes, corn, wheat, rye, etc. This raw material has a huge advantage over cellulose obtained from wood, which takes at least 17-20 years to grow.

– easy modification and giving valuable characteristics through chemical, physical, biological, or combined interaction.

– a wide range of reactions with starch related to the chemistry of low molecular weight compounds.

– the ability to give biodegradable properties to synthetic polymers using starch.

– environmental friendliness, no toxicity and convenience of working with starch.

Cellulose (Figure 2) is a fascinating natural polymer that contains reactive OH groups. The molecular structure of starch and cellulose are identical; cellulose is a polysaccharide. The d-glucose units in starch are connected to -glycosidic bonds, but they are not present in cellulose.

Cellulose has high mechanical strength, does not dissolve in water and organic solvents, and also does not melt. Cellulose, when interacting with acid, is easily hydrolyzed. It is known that to obtain cellulose gum, it is necessary to dissolve cellulose in a solution of sodium hydroxide and carbon disulfide. Then it is converted to sulfuric acid and a cellophane film is obtained [22]. The simplest cellulose derivative is methylcellulose. It has high film-forming properties, good solubility, and low oxygen permeability. Methylcellulose has all the prospects as a raw material for biodegradable materials [23]. The characteristics of edible films made of methylcellulose were studied with the introduction of special extracts saturated with polyphenols and antioxidants into the mixture [24]. A film packaging made of cellulose glued with starch, with high resistance to fats, allowed for direct contact with food products, was obtained. This packaging is resistant to high or low temperatures and is used when baking products in the oven or microwave [25].

A method is known for producing biopolymers by the interaction of cellulose with an epoxy compound and dicarboxylic acid anhydrides. As a result, the obtained biomaterials are completely biodegraded in compost in 4 weeks. Products such as disposable tableware, films, bottles, etc. are made by molding [26].

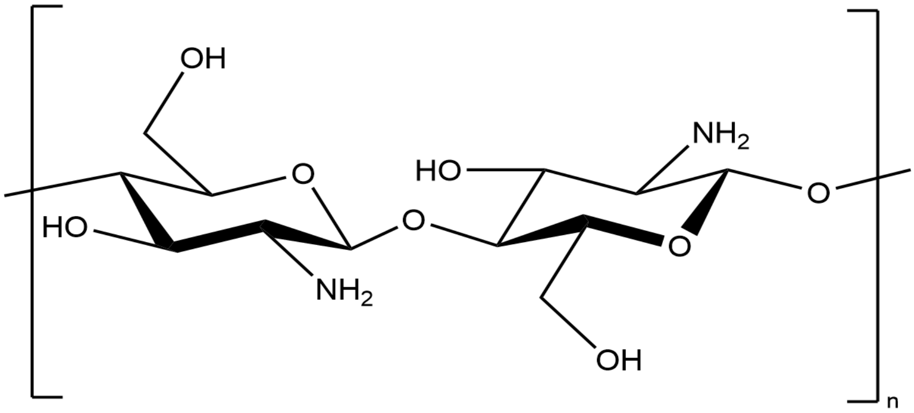


Figure 4- The chemical structure of Chitosan

The carboxyl methyl group (-CH_2-COOH) of carboxymethylcellulose (CMC; Figure 3) is linked by the hydroxyl groups of glucose monomers. CMC is readily soluble in water, possesses strong film-forming abilities, and gets along well with other biomolecules [22].

There is a nitrogen-containing polysaccharide from the residues of n-acetyl glucosamine, interconnected by β-glycoside ties which are called chitin. It can be obtained by fungi or in the sea (the shells of shrimps, crabs, and lobsters). The predominant characteristics of chitin are low density, layered structure of the polysaccharide, high ability to form a film, selectivity of interaction with bacteria, and radio-absorbing and radioprotective properties. All these important properties of chitin make it possible to develop biodegradable materials based on it when interacting with polyethylene [27]. Chitosan is an amino sugar, a linear polysaccharide derivative, whose macromolecules are made up of randomly bound β–(1-4) D-glucosamine units and N-acetyl-D-glucosamine (Figure 4). It is a chitin derivative.

The main advantages of Chitosan to produce edible films are non-toxicity, environmental friendliness, biocompatibility, biodegradability, and the ability to form films [28]. It has been established that chemical and physical modifications are used to improve the technological properties of chitosan in the manufacture of biofilms. For example, mixing chitosan with starch or protein [29]. Starch is the most suitable biopolymer for mixing with chitosan because it is available as a raw material and has excellent physical characteristics (tasteless, odorless, and transparent) [30].

Agar — a mixture of agarose polysaccharides and agaropectin obtained by extraction from red algae (Rhodophyta) is an excellent alternative for obtaining biodegradable polymers. Agar compositions with synthetic polymers (polybutylene adipate-terephthalate (PBAT), low-density polyethylene (LDPE) and polyvinyl alcohol (PVA)) have been studied [31].

Pectin is a polysaccharide formed mainly by galacturonic acid residues. High-strength and flexible films with heat resistance up to 180 °C are obtained from a mixture of citrus pectin components and high-amylose starch [32]. The structure of galacturonic acid is shown in Figure 5.

Protein is a high molecular weight organic substance consisting of alpha-amino acids connected to a chain of peptide bonds. It is a natural polymer made from vegetables and animals. Soy protein, gluten, etc. are also of interest to produce biopolymers [33]. The cohesiveness of the protein, its adhesiveness, the ability to absorb water and fat, as well as the ability to texture, give a high degree of film formation to biodegradable polymers [34]. Soy products such as soy milk, soy flour and fractionated soy proteins have also been studied [35]. There are two main factors in the production of biopolymers based on soy: this is the concentration of protein and the pH of the film-forming mixture. When casting the film, the protein concentration is 4-5%, when using the "dry" technology; the protein concentration is 80% [36].

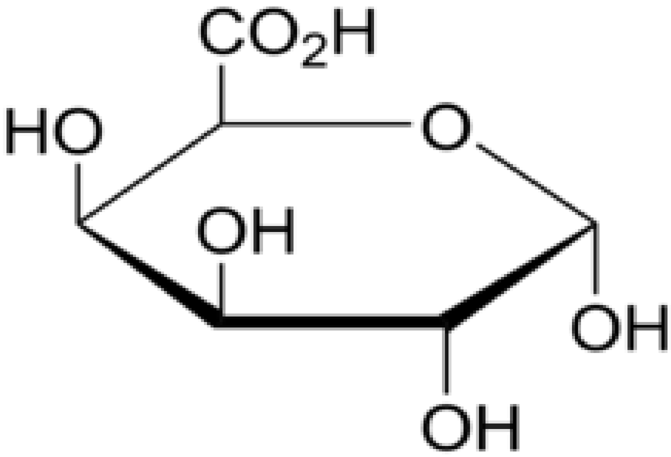


Figure 5 - The chemical structure of Galacturonic acid

Figure 6 - Microorganism: a) Paracoccus, b) Bacillus, c) Spirullum

Bioplastics from Naturally Occurred or Genetically Engineered Microorganisms

Biopolymers, such as Paracoccus, Bacillus, and Spirillum (Figure 6), are created by living microbes. One such biopolymer is poly (3-hydroxybutanoic acid), which is produced from glucose by certain microorganisms. PHB is a biopolymer with similar properties as synthetic polymers, but under aerobic conditions, it can completely decompose to water and carbon dioxide molecules. This biopolymer is obtained by fermentation of glucose strains or wastewater. Cane sugar and starch are the most affordable and suitable carbon sources to produce PHB. According to the LCA categories, the production of PHB is less environmentally harmful than the production of polypropylene (PP). The demand for crude oil in the production of PHB is much lower; accordingly, this significantly reduces the impact on the environment. If we consider the production of PE and PHB, then PE has a lower environmental impact in terms of acidification and eutrophication, but if we consider the utilization of polymers - the burning of synthetic polymers, this will significantly increase the environmental burden [22]. Within 9 months after disposal, PHB can be broken down by microorganisms in the soil and natural water sources. PHB costs 15 times as much as polyethylene, though.

Poly(3-hydroxybutyrate)-hydroxy valerate (PHBV) is a copolymer comprising hydroxybutyrate (PHB) and hydroxy valerate (HV). It crystallizes strongly. The tensile strength and crystallinity of polymers decrease while the impact strength increases with the development of HV, the melting point, and the glass transition temperature. PHB is more delicate than PHBV. PHBV breaks down more quickly than PHB [24].

Light-sensitive functional groups, such as carbonyl groups, are integrated into the polymer chains of photodegradable polymers. These groups will collect solar energy and use it to disrupt the polymer's chemical connections, resulting in tiny pieces that break down more quickly than lengthy strands. However, these polymers and synthetic biodegradable polymers have the same problem - both are obtained from materials that were derived from fossil fuels [23]. Photodegradable plastic bags are shown in Figure 7.

Figure 7 - Photodegradable plastic bags

A significant role is played by the issue of giving biodegradable properties to existing industrial polymers such as Polyethylene (PE), Polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). The strategy to get photo-degradable or oxo-biodegradable plastics is to add to standard conventional plastics such as PE, PP, PET etc. some photodegrading additives. These additives are added in at the extrusion stage, they help to attack free radicals on the polymer and initiate degradation. The chain breaks with the formation of smaller fragments, where bacterial degradation starts. Polymers can be decomposed within a few months [24].

These additives are mainly based on transition metals of cobalt (Co), magnesium, manganese, zinc, iron, or nickel. These metal ions have a high susceptibility to light, heat, and moisture. These factors lead to mechanical stress and weaken the tensile strength of the chain [24].

Synthetic Biodegradable Plastics

Synthetic biodegradable materials can be obtained by polymerization, such as aliphatic polyesters, polylactic acid-based polylactic acid copolymers, and others [26]. Polylactic acid is linear aliphatic polyester. Polylactic acid is obtained by polymerization of lactic acid made on the basis of fermentation of corn sugars or other biological mass. The breakdown of polylactic acid proceeds in two stages. In the first stage, the ester groups are hydrolyzed with water to form lactic acid and other small molecules. Next comes their decomposition in the presence of advising microorganisms in a certain environment. Polylactic acid reaches 72% decomposition within 45 days under favorable composting conditions [37]. To date, polylactide is one of the promising bios-destructive polymaterials for use as a packaging material. Polycaprolactone is biodegradable synthetic aliphatic polyester with a low melting point and high mechanical strength, as well as high barrier properties to water and fats. Biodegradation of this polymer occurs by 75% after 28 days of contact with relevant microorganisms and fungi [38]. Shtilman and other authors obtained biodegradable copolymers of the product of the co-polymerization of ethylene with caprolactone using the grafted copolymerization method [39]. There are companies “El-Batyr Biopolymer” LLP and “Eco Products” LLP which produce biodegradable bags based on PLA in Astana (Kazakhstan).

PVA is a synthetic polymer with biodegradable properties, high mechanical characteristics, good film-forming properties, and high thermal stability, and PVS has the property of high bonding. PVA has mainly C-C connections in its chain. They activate rapid biodegradation [40].

PVA is produced worldwide on an annual basis in quantities of several hundred tons. It is the largest quantity of water-soluble polymer currently manufactured. PVA is produced by hydrolysis of poly (vinyl acetate) in an alkaline medium, with a possibility of fluctuating the degree of hydrolysis as shown in Figure 8 [19].

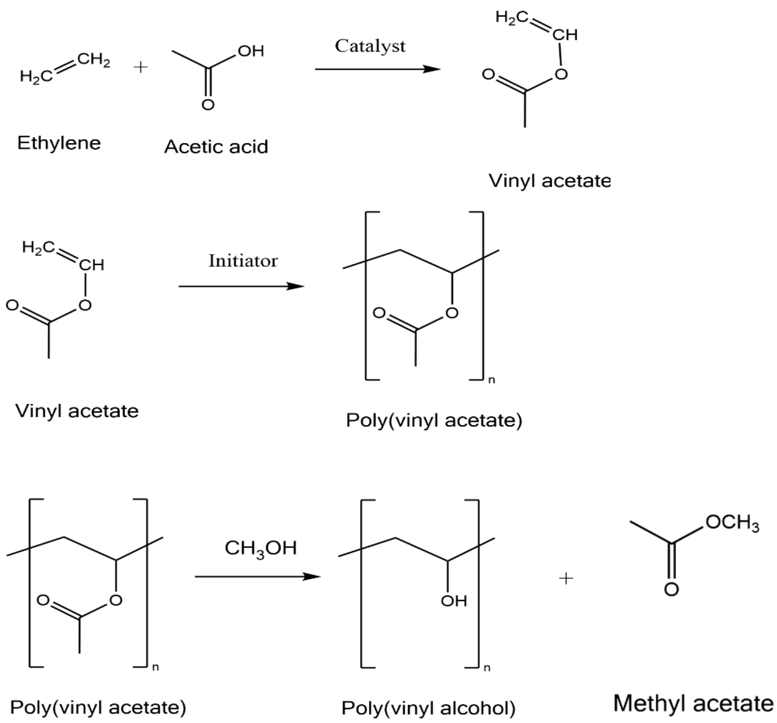


Figure 8 - Scheme of PVA production

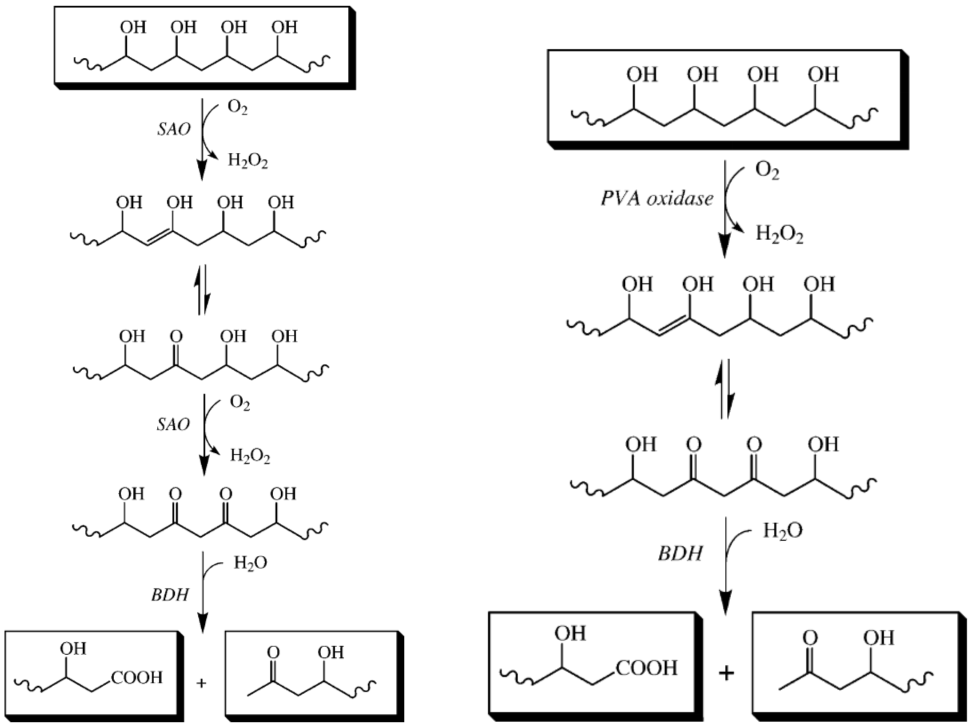
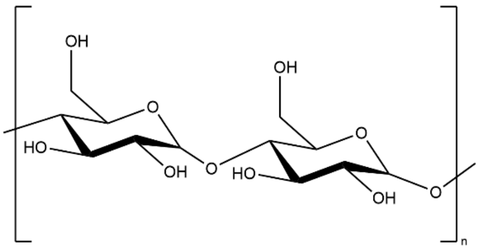
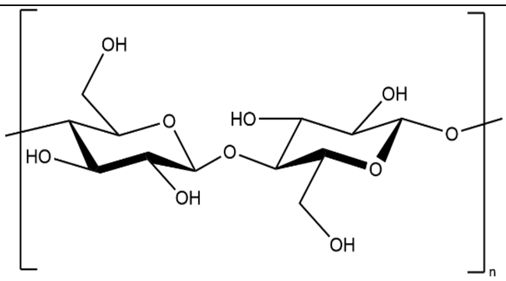
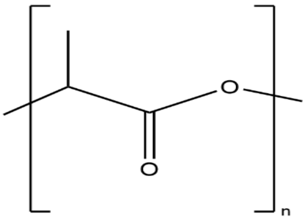
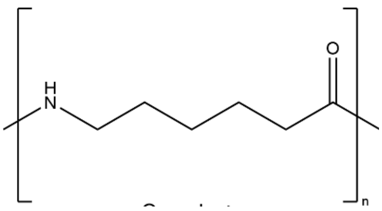
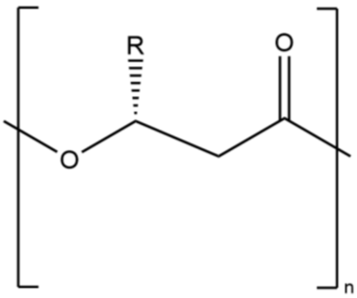


Figure 9 - Metabolic pathways of PVA degradation

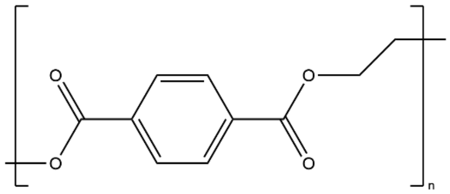
PVAc is obtained by free radical polymerization. Fully hydrolyzed PVA has higher performance characteristics compared to partially hydrolyzed PVA. The molecular weight of PVA is regulated by the time of polymerization in the reactor, the rate of supply of vinyl acetate, the amount of solvent (methanol), the concentration of the radical initiator, and the temperature of polymerization. The degree of PVAc hydrolysis is regulated by the time of presence, the concentration of the catalyst, and temperature [41].

Watanabe and his associates explored the PVA depolymerization mechanism in the 1970s. Their

Table 2 - Characteristics of the main biodegradable polymers.

Starch-based biopolymers		
	In terms of mechanical properties, they are close to conventional polymers and resistant to fats and alcohol. A significant difference in properties depends on the ratio of amylopectin and amylose, as well as other additives. Subject to composting	Packaging of food and personal hygiene products, medical and sports products
Cellulose-based biopolymers		
	They have a sufficiently high mechanical strength; they are easily hydrolyzed under the influence of acids. Varieties: acetyl cellulose, carboxymethyl cellulose, celluloid, etc.	Products for household use, construction and sports purposes, toys
Polylactic acid, polylactide (PLA)		
	The properties depend on the stereochemical composition and may approach the properties of polypropylene, polystyrene, polyvinyl chloride	Packaging for household and construction purposes, biocomposites
Polycaprolactam, polycaproamide, Capron (PCL)		
	High mechanical strength and good barrier properties (concerning water and fats), low melting point (50 °C). It can be composted or recycled.	Packaging, fibers for textiles
Polyhydroxyalkanoates (PHA)		
	The physicochemical properties depend on the composition. The presence of properties characteristic of both thermoplastics and elastomers. High barrier properties. They are subjected to composting.	Packaging of food and personal care products, biocomposites, foams

Continued Table 2

Aliphatic-aromatic Copolymer (AAC)		
	Combines the biodegradability properties of aliphatic parts with the high mechanical properties of aromatic parts.	Packaging, laminates, and material for storing products in agriculture and construction.
Modified Polyethylene terephthalate (pet)		
	High mechanical strength and good barrier properties (in relation to water and fats). It can be subjected to composting and recycling.	Packaging, agricultural products

further investigation revealed that the compound's bonds cleave at random, thus grafting won't significantly affect the polymer chain's biodegradability. Numerous metabolic pathways exist, some of which are depicted in Figure 9. Typically, neither the degree of polymerization nor the degree of hydrolysis affects how quickly PVS degrades [33].

Polyvinyl alcohol dissolves well in water, and successfully undergoes final biodegradation due to the corresponding microorganisms. Therefore, great interest is shown in the production of environmental materials based on polyvinyl alcohol, and their use in a wide range of applications. The main characteristics of the most popular biodegradable polymers are shown in Table 2.

The Dependence of the Structure and Properties of Polymers on Biodegradation

The dependence of the structure and properties of polymers on biodegradation based on:

- Molecular weight. It was found that with a decrease in the molecular weight of macromolecules, the ability of polymer biodegradation increases.
- Crystallinity of polymers. It has been proved that by increasing the degree of crystallinity, the ability of biodegradation of polymers decreases, i.e., polymers with an amorphous structure are destroyed better than polymers with a crystalline structure. Also, the biodegradability of low-molecular polymers with a crystalline structure is better than high-molecular polymers. The ability to biodegrade is higher when branching in polymer macromolecules is formed. The introduction of various modifying additives into polymers significantly affects the ability to biodegrade [21].

For example, ester plasticizers increase the biodegradability of PVC on the one hand, however, uneven dispersion on the polymer surface of a biodegradable plasticizer -dibutyl phthalate can lead to a low biodegradability of PVC. The rate and outcome of polymer biodegradation are complicated processes that are influenced by environmental factors such as humidity, temperature, pH, light, contact with soil, and type of soil, in addition to the polymer's structure and qualities [21].

Oxybiorestructive Additives

There are special oxybiorestructive additives based on modified starch, lactic acid, and cellulose, which contain metal ions - carboxylates, which accelerate photo- and thermal oxidation in polymer materials (Table 3). The main difference between these additives from conventional ones is the high efficiency at low doses of concentration from 1 to 3%, as well as their decomposability by two factors: UV radiation and the action of microorganisms.

The mechanism of biodegradation due to oxybioregosing additives is that salts of transition metals (cobalt, zinc, iron, etc.) contribute to the appearance of free radicals that create hydroxides and peroxides as esters, aldehydes, ketones, alcohols, and carboxylic acids. These compounds are easily biodegradable. Microbes and fungi spread on the folds of the film and throughout its thickness. In the process of biodegradation of polymers, three stages are distinguished: stage 1 – oxidative processes (exposure to UV light, high temperature); Stage 2 – reduction of physical characteristics (fragility and size reduction); stage 3 – decomposition into molecules and a further chain of transformations to carbon dioxide and water.

Table 3 - Characteristics of oxybiorestructive additives

Name	**Properties**
PDQ-H	An additive whose principle of operation is based on the reduction of the molecular weight of the main polymer (to improve biological decomposition) under the action of UV radiation and oxidizing media. Decomposes by UV radiation and microorganisms
ECM	The additive is decomposed by microorganisms
Bio-Batch	The additive is decomposed by microorganisms
Renatura	It contains a unique iron-based ingredient (the company's development) and is mainly used for the biodegradation of polyolefins
Reverte	Additives and masterbatch mixtures containing prodegradants from metal ions impart photo- and thermal decomposition to the base polymer. It also contains a unique biodegradation booster of the second stage, which uses a reaction rate modifier to control
D2w	the initiation and timing of oxybioregradation
P-Life	Prodegradant additives based on masterbatch polyester, polypropylene, or polystyrene. The company also supplies fully degradable polymer materials

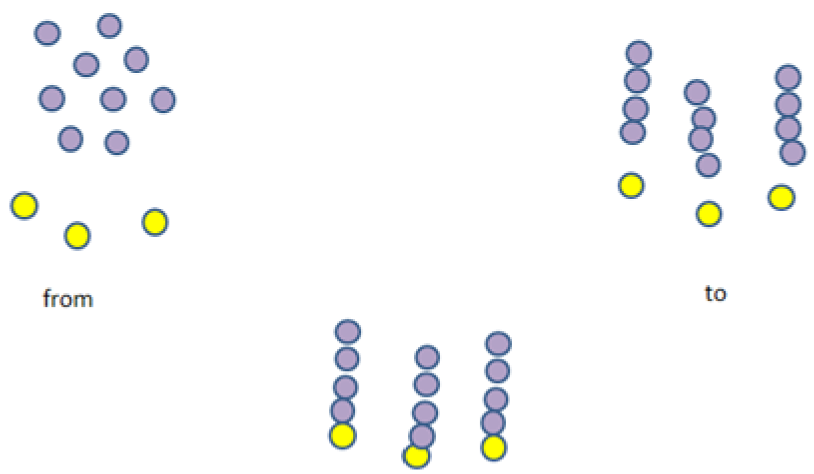


Figure 10- Schematic illustration of two types of graft-copolymerization

Grafting Copolymerization

Grafting copolymerization is a type of polymerization, where one or several blocks of homopolymer are grafted onto a main backbone like branches. This approach of modification of polymer allows upgrading properties of main chain with growing of grafted chain of another polymer.

There are the most popular grafting techniques: “grafting from” and “grafting to” techniques. The schematic illustration of two types of graft copolymerization is shown in Figure 10. The “Grafting from” method is the initiation of polymerization of the main chain with monomer solution by the special catalyst and the “grafting to” technique uses a special coupling agent [27].

Synthesis of Biodegradable Starch-Based Materials

Obtaining biodegradable starch-based materials boil down to several principles [30]:

– the creation of thermoplastic starch and its derivatives.

– the creation of a mixture of synthetic and natural polymers.

– the creation of starch products by extrusion method.

Methods of obtaining and characteristics of the obtained materials are widely covered in many publications and reviews. Thanks to the processing, starch is modified, can decompose in the environment, and has the properties of the necessary thermoplastics. The equipment to produce modified starch is the same as to produce ordinary plastic. Modified starch can be dyed, and it can also be printed using all standard technologies. This material is antistatic. The physical properties of modified starch are still inferior to the properties of resins – low and high-pressure polyethylene, and polypropylene. Starch decomposes at a temperature of 30 °C in two months [[30], [31], [32]].

Methods of producing extrusion-blown and injection-molded films containing 50% starch have been studied. The water resistance of these films was achieved by applying polyvinyl chloride to the surface of the film [40]. Mixing urea with polyols helped to improve starch plasticization and obtain high-quality films [41]. It has been established that to improve the technological properties of starch for the manufacture of biofilms, various modifications are used, such as mixing with other compounds, and grafting-copolymerization [42]. Due to intermolecular and intramolecular hydrogen interactions between the amino and hydroxyl groups of the major chains of the two components, chitosan/starch combinations produce films with a high degree of film formation. The physicomechanical, water-barrier, and miscibility characteristics of biodegradable films are influenced by the ratio of starch and chitosan [43]. Films based on starch and agar were investigated. It was found that the addition of agar improves the microstructure Mirzoerova et al. used calcium carbonate as a plasticizer to produce a film based on starch and polyvinyl alcohol (60:40 wt. %) by mechanical mixing. It is revealed that with an increase in the concentration of calcium carbonate, the mechanical properties of the film increase, in particular, the tensile strength. The degrees of biodegradation of films in the soil were determined. It turned out that with an increase in the percentage of the plasticizer - calcium carbonate in the mixture, the degree of biodegradation increases [42].

Starch can serve as a filler to produce reinforced plastics. For this, a little starch is added to the synthetic polymer, giving these polymer biodegradable properties. Starch is modified in various ways to produce plastic masses based on it. The starch solution is cast to create the film. However, this method has not been widely applied due to the high expense of manufacturing starch solutions. The thermomechanical processing techniques (wet starch compression, extrusion, and injection molding) have received most of the attention in studies related to starch products. The article shows the results of research and characteristics of polymer compositions based on starch and calcium chloride. It has been known the thermal stability of this composition reduced with the rising of calcium chloride [44]. According to the publication [45], starch was modified directly in extruders, starch esters and esters, grafted copolymers, and oxidized and cationic starches were obtained.

To produce biodegradable polymers, starch is mixed with aliphatic polyesters or polyvinyl alcohol. Main et al. synthesized polyesters as polyhydroxyalkanoates by microbes and polylactide by chemical polymerization [46]. It is noted that among the above-mentioned synthetic polymers, polyvinyl alcohol is the most popular in use. PVA has excellent qualities such as high compatibility with starch, ease of preparation, absence of carcinogens, relative cheapness, good biocompatibility, and biodegradability in nature. It was found that the usual mixing of polymers strongly affects the quality of the resulting films. PVA and starch interact well with each other, forming intermolecular and intramolecular hydrogen bonds due to the excess of hydroxyl groups in both polymers (Figure 11).

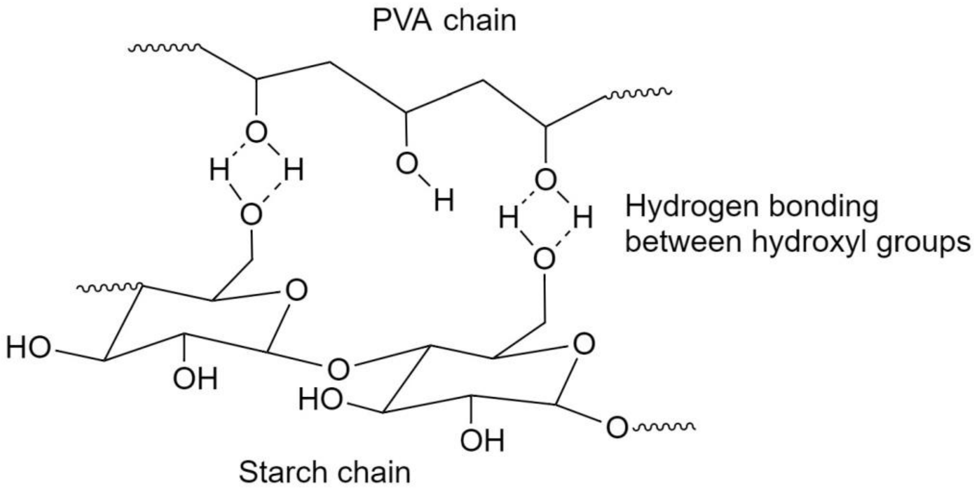


Figure 11 - Hydrogen bonding between PVA and Starch chains.

This contact causes the films to absorb more water. However, chemical starch modification can be used to enhance the water-resistant qualities of films made of a PVA/Starch (PVA/C) combination. The most popular technique for enhancing the qualities of natural polymers like starch is grafting. In addition, it is assumed that the film from the PVS/K mixture is biodegradable since both components easily degrade in the bacterial environment. In this regard, scientists are faced with the task of improving the structural integrity of the polymer mixture. There are various crosslinking agents for starch crosslinking [21]. A method is known for producing a biofilm-based on starch and PVA, a mixture of which was modified with silicon dioxide nanoparticles. The results were improved mechanical properties, water resistance, and light transmission of the films [47].

Crosslinking agents are not safe and toxic, respectively, and have limitations for their use both in everyday life and for medical purposes. In scientific work, maleic acid was used as a crosslinking agent between starch and PVA using esterification to increase the physical and mechanical properties and to create a high-quality polymer. Maleic acid is a common food additive, nontoxic, and biologically pure. These characteristics are favorable for obtaining biomaterial being a dicarboxylic acid, the starch esterification reaction with PVA proceeds through the substitution of carboxyl groups of maleic acid with free hydroxyl groups of starch and PVA [48].

Plasticizers, namely their carboxyl and hydroxyl groups, are utilized to increase molecular dynamics and provide flexibility. Additionally, crosslinking changes significantly enhance the tensile strength, elastic modulus, heat, and water resistance, swelling capacity, and antibacterial activity of biofilms. Gas tightness, mechanical rigidity, transparency, and thermal stability are enhanced thanks to the filler. Chemical and physical modifications make it possible to improve films by changing the molecular structure during esterification, esterification, due to the formation of hydrogen bonds and oxidation [22].

Gulati et al. analyzed the effect of carboxymethyl cellulose (CMC) on the thermal and mechanical properties of PVS/starch films, which were synthesized and obtained by casting. Glycerin is a plasticizer. Citric acid is a crosslinking agent. It was revealed that with an increase in the concentration of CMC, the thermal stability of PVS/starch films increased. The PVA/starch/CMC film had a maximum tensile strength of 36.56 ± 1.54 MPa and was used for testing when adding walnut shell flour (WSF). The PVA/starch/CMC films reinforced with WSF have improved thermal stability and water resistance. However, this also led to a decrease in the film's biodegradability [23].

Incorporating -polylysine into maize starch/polyvinyl alcohol (PVA)/glycerin films was studied by Bin Liu et al. The hydroxyl group of the starch/PVA combination and the amino group of -polylysine interacted, according to FTIR studies. The films' thermal stability increased with the addition of -polylysine. It was also looked at if adding -polylysine produced a flatter surface. The tensile strength and elongation at the break of films, as well as other strength characteristics, have improved. The films' antibacterial and water absorption capacities have also improved [24].

Intelligent Films Based on Starch

Today, starch-based packaging materials are being developed with new features that control the quality of the food packaged inside or determine the environment of the food. This is how packaging is called smart packaging. For this, natural active substances with antibacterial and antioxidant activity are used.

In comparison to other biodegradable polymers, the fundamental benefit of starch-based film is its lack of color and transparency. Changes in factors like color can be visibly identified thanks to the content of indicators in intelligent packaging. The freshness indicator reacts with some of the gases released during food storage to reveal the shelf life of food goods. The shelf life of food goods is also shown by a temperature-time indicator, which considers the effects of both time and temperature accumulation [30].

Films constructed of PVA and starch were deemed sensible packaging by Abedi-Firoozjah et al. Due to the chemicals found in PVA/starch films' antioxidant and antibacterial properties, these films can be utilized as a sign of the quality and safety of food. It should be emphasized that the source, kind, quantity, and composition of the active chemicals determine how effective these packing sheets are. The way different polymers and components interact inside the film structure is also crucial. The PVA/starch film is given colorimetric characteristics by the addition of natural food dyes. Products containing food may benefit from such clever packaging [25].

Indicator of Freshness

The biopolymer is in a great position to create intelligent colorimetric films thanks to starch's high capacity for film formation. These days, there is a lot of interest in the creation of intelligent pH-sensitive starch-based films. Changes in pH are the main indicators of food freshness. When food begins to rot due to microbial action, the environment begins to change, and therefore the freshness and quality of food can be determined by changing pH values. The environment and the human body are both safe around organic pH monitors. Curcumin (CR), carotenoids, anthocyanins (ATH), and others are some of the well-known natural markers. Electrochemical and colorimetric methods are used to determine the pH values [31].

Ammonia, dimethylamine, triathalon, and other gases that alter the pH level around the food are produced as a result of rotting food. Additionally, in accordance with its function, the organic indicator present in the packing film will change color in response to the pH shift. A strong color intensity results from the high anthocyanin concentration. The high starch content's porosity results in great sensitivity. The mechanical strength of the sensor increases with cellulose binder concentration. The color of anthocyanins changes from mauve to blue-violet to blue-green as the pH rises. The customer assesses the product's freshness based on the color shift [30].

A colorimetric pH agar/potato starch/anthocyanin indicator film was created by Choi et al. This film was used to package pork, and as the meat's quality declined and the pH altered, the film's color changed from red to green [32]. The pH of logs made from chitosan/cornstarch/purple cabbage extract was examined by Silva-Pereira et al. This is how they established the fish's breakdown [33]. Liu et al. (2017) studied PVA/starch film containing purple yam for quality control of pasteurized milk. They kept the milk in this package for 48 hours, after which the color of the smart film changed from purple to red, indicating spoilage of milk at room temperature [36]. To ascertain the deterioration of pasteurized milk, Mustafa et al. (2020) investigated a film based on PVA/starch/propolis/red cabbage extract. The color of the film quickly and clearly changed from pink to light purple and then to yellow when the pH value changed from an acidic to an alkaline environment [37].

Manufacturers of Biodegradable Plastic Materials

The largest manufacturers of biodegradable plastic materials are Nature Works (USA), BASF (Europe), Novamont (Europe), and Mitsubishi Chemicals (Japan).

Popular brands on bioplastics:

1) Novon™ is a starch-based biopolymer; modified polysaccharide derivatives are often added. Products: disposable tableware, egg packaging, cosmetics, wrapping films for textiles and clothing, medicinal capsules, diapers for children, women's tampons, etc.

2) Biopac™ is a starch-based biopolymer with a content of 87-94%. Products: packaging of bakery products, cereals, eggs, etc.

3) Bioceta™ is a cellulose-based biopolymer with additives. Products: Packaging of batteries for household electrical appliances.

4) Bioflex™ is a starch-based biopolymer with the addition of plasticizers such as alcohols, sugars, fats, wax, and aliphatic polyesters.

Film material decomposes in compost at a temperature of 30 °C in 56 days with the formation of products favorable for plant growth.

Market Development for Biodegradable Polymers

European Bioplastics gave a positive forecast for the world bioplastics industry. There was no dynamic plastics production in 2020, mainly because of Covid-19. But now there is a new impulse for global bioplastics manufacturing. It is a positive outlook for the capacity from 2.23 million tons of bioplastics production in 2022 to 6.3 million tons -in 2027. The data was done with the cooperation of the Nova-Institute (Hürth, Germany) and European Bioplastics [49].

According to data [50]. In 2021 world plastic production increased by 4% and accounted for around 390 million tons. The reason is the growing demand for and development of more sophisticated applications and products. Over the next five years, manufacturing capabilities will continue to rise dramatically and diversify as a result of the strong development of polymers such polyhydroxyalkanoates (PHA), polylactic acid (PLA), and polyamides, as well as the steady expansion of polypropylene (PP).

Nowadays the world produces annually more than 1.1 million tons (51%) of biodegradable plastics based on PLA, PHA, starch blends, and others. The capacity of bioplastic production will increase due to the rapid development of PHA (polyhydroxyalkanoates), polylactic acid (PLA), and others. In 2027 it is predicted to produce more than 3.5 million tons based on these polymers. Global production of non-biodegradable plastic materials such as biobased PE, biobased PET, and biobased PA has amounted to almost 1.1 million tons (48%) annually. In 2027 it is expected decrease in these materials will be around 44% [51]. Bioplastics are widely used in various sectors such as food packaging, children's toys, consumer electronics, auto manufacturing, agriculture, and textiles. In 2022 packaging will be the largest bioplastics application sector with almost 1.1 million tons (48%) of the total bioplastics market [52].

Asia is the largest player in this industry and produces about 41% of eco-plastics. Now, more than 25% of production capacity remains in Europe. According to forecasts, in 2027 the share of Europe and other regions of the world will decrease significantly while production capacity in Asia will grow to almost 63% [53].

In 2022, the world's agricultural area is 5 billion hectares, of which only 0.8 million hectares or 0.015% is allocated to land for the cultivation of renewable raw materials to produce bioplastics. Simultaneously with the forecast of a significant increase in global bioplastics production until 2027, the earth is projected to grow by up to 0.06%. This proves that the production of bioplastics does not interfere in any way with the use of land for growing food and feed [54].

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Қаптама пленкаларына арналған крахмал негізіндегі биологиялық ыдырайтын полимердің синтезі: Шолу

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Қабылданды: *14 қыркүйек 2023*

ТҮЙІНДЕМЕ
Өзінің маңызды қасиеттері мен функционалдық мүмкіндіктеріне байланысты полимерлерге соңғы жылдары азық-түлік орауыш материалдары ретінде көп көңіл бөлініп жатыр. Бұл сипаттамаларға уытты еместігі, қолжетімділігі, биоүйлесімділігі және биоыдырағыштығы жатады. Бұл оларды қоршаған ортаға әсері бұрыннан зерттелген дәстүрлі пластикалық қаптамаға балама етеді. Қазіргі уақыттағы тұрақты дамуды ескере отырып, биополимерлерді тамақ өнімдерін орау үшін экологиялық таза және тұрақты материалдар ретінде зерттеу өте маңызды. Крахмал негізіндегі биологиялық ыдырайтын полимерлерді синтездеу маңызды қадам болып табылады. Экологиялық таза материалдарға жаһандық сұраныс өсіп келе жатқандықтан, осы саладағы үздіксіз зерттеулер мен инновациялар қасиеттері жақсартылған және кең қолданылатын крахмал негізіндегі орау пленкаларын кең өндіруге әкелуі мүмкін. Осыған байланысты, бұл шолудың негізгі мақсаты пластикалық пакеттерде пайдалану үшін жоғары физика-механикалық сипаттамалары бар жүгері крахмалы мен ПВА негізіндегі биологиялық ыдырайтын полимерді жасау болып табылады.

Түйін сөздер: Полимерлер, биологиялық ыдырағыштық, қаптау, пластикалық пакеттер.

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Синтез биоразлагаемого полимера на основе крахмала для упаковочных пленок: Обзор

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Аннотация
Благодаря своим качествам и функциональным возможностям в последние годы полимерам уделяется большое внимание в качестве материалов для упаковки пищевых продуктов. Эти характеристики включают нетоксичность, доступность, биосовместимость и способность к биоразложению, что свидетельствует об их перспективности в качестве альтернативы традиционной пластиковой упаковке, воздействие которой на окружающую

среду уже давно исследуется. Учитывая нынешний упор на устойчивое развитие, исследования биополимеров как экологически чистых и устойчивых материалов для упаковки пищевых продуктов имеют решающее значение. Синтез биоразлагаемых полимеров на основе крахмала представляет собой значительный шаг на пути к экологичным упаковочным решениям. Поскольку глобальный спрос на экологически чистые материалы продолжает расти, текущие исследования и инновации в этой области могут привести к разработке упаковочных пленок на основе крахмала с улучшенными свойствами и широким коммерческим применением. В связи с этим основной целью данного обзора является создание биоразлагаемого полимера на основе кукурузного крахмала и ПВС с высокими физико-механическими характеристиками для использования в пластиковых пакетах.

Ключевые слова: Полимеры, биоразлагаемость, упаковка, пластиковые пакеты.

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