YERMEKOV YERNAZ YERMEKOVICH

Production of new starch-based biodegradable film materials

ANNOTATION

for the dissertation work of Yermekov Yernaz Yermekovich for the degree of Doctor of Philosophy (PhD)

in specialty 8D07201 – " Food Technology"

The relevance of the work. The food industry occupies a key place in the modern economy, and packaging materials play a vital role in ensuring the safety, security and quality of food products. Plastic packaging is widely used for packaging bakery products, dairy products, frozen foods and beverages due to its properties such as moisture resistance, mechanical strength and hermeticity. Research shows that about 40% of plastic waste is associated with food and beverage packaging. However, the use of petroleum-based plastic packaging is accompanied by significant environmental damage due to its long period of decomposition and insufficient recycling. According to research, a significant portion of packaging waste ends up in the environment, where it creates barriers to sustainable development and food safety. Annual plastic production is expected to reach 1.1 billion tons by 2060, and the accumulated amount of non-degradable plastic waste in the world will reach 12 billion tons by 2050, which will entail significant destruction of marine and terrestrial ecosystems. In the food industry, where plastic is used primarily to preserve and protect food products, such materials pose a particular threat to the environment. One of the by-products of plastic degradation, microplastics , is found in all layers of the ecosystem, including food products. These plastic particles enter the food chain through contaminated water, soil and air, posing a serious threat to human health. Microplastics pose the greatest risk to food products such as seafood, vegetables and salt. Consuming these products can lead to the accumulation of toxic substances in the body, including pesticides and heavy metals. This makes the development of biodegradable alternatives to synthetic plastics one of the most important tasks facing national and global science.

In the context of global environmental threats, including requirements for biodegradable packaging materials, Kazakhstan faces the need to develop its own technologies for the production of biodegradable packaging. The proposed work is relevant in the context of solving the problem of plastic pollution and creating domestic biodegradable materials with a high share of localization for the food industry of Kazakhstan. In particular, the emphasis in this work is on the use of renewable raw materials - grain starch, to create materials that can decompose into safe components.

The purpose of the dissertation work is to develop composite granules based on wheat starch for the production of biodegradable films for use in the food industry.

In accordance with the goal, the following tasks were set:

1. Study of the physicochemical properties of native and modified wheat starch.

2. Determination of optimal compositions for obtaining granules and biodegradable film based on compositions of modified starches with PCL – poly-(ε- caprolactone)

3. Study of biodegradability properties of the obtained films

4. Development of technology for obtaining biodegradable materials

Objects of study: Native corn starch; wheat starch; potato starch, samples of composite biodegradable film consisting of modified wheat A and B starch and PCL, control samples in the form of films made of pure PCL.

Research methods. Theoretical and experimental studies were conducted in accordance with the set scientific tasks. Experimental studies include physical and chemical methods, microbiological methods, biotechnological methods, technological experiments. The results of the studies were processed by statistical analysis and mathematical optimization methods.

The scientific novelty of the work. For the first time in domestic practice, a technology has been developed for producing biodegradable film materials based on modified wheat A and B starch and poly(ε- caprolactone) (PCL), providing improved mechanical and barrier properties, as well as a high degree of biodegradation.

The author's personal contribution. The author is a direct participant in the development of research methods, the laying down and conducting of experiments, the development and optimization of the technology being developed, as well as in obtaining laboratory data on physicochemical and mechanical studies of the obtained samples of packaging material films, the author also performed mathematical processing of the data and co-authored the obtained results.

The main provisions submitted for defense:

- The morphological, thermodynamic and physicochemical properties of native and modified wheat starch types A and B as raw materials for the production of biodegradable materials are substantiated, their differences in the degree of substitution, solubility, swelling and ability to undergo thermoplastic processing are established.

- The formulations of composite granules and films based on acetylated wheat starch and poly(ε- caprolactone) have been developed and optimized, providing improved mechanical, barrier and technological properties of biopolymer materials.

- The patterns of biodegradation of film materials under composting conditions have been established, and a high degree of decomposition of films (up to 43.75%) has been confirmed

depending on the composition and type of modified starch, which indicates their environmental safety.

- A technology has been developed for the production of biodegradable films based on compositions of modified starch and PCL, including the stages of modification, granulation and molding.

The practical value of the work.

The developed films can be used as an alternative to traditional plastic packaging. Experimental data confirm their sufficient mechanical and barrier properties, as well as a high degree of biodegradability . The technology used allows the production process to be adapted to an industrial scale and offers an effective solution for environmentally sustainable packaging material.

The optimal compositions of starch-polymer films, including acetylated starch and PCL, were selected and substantiated, contour maps of the influence of the composition of composite films on their strength were constructed, which made it possible to achieve an optimal balance between mechanical strength from 15 to 30 MPa.

Rational technological modes for obtaining films have been developed and experimentally confirmed, ensuring homogeneity of structure and increasing operational characteristics. It has been established that films with 30% acetylated wheat starch A and B decompose by 35.92–43.75% within 10 days under composting conditions, which confirms their suitability for environmentally safe use.

The dissertation was completed within the framework of the scientific project AR08857439 "Development of new biodegradable film materials based on starch" (2020-2022) under the priority "Sustainable development of the agro-industrial complex" within the framework of subprogram 101 " Grant financing of scientific research" at the Kazakh Agrotechnical Research University named after S. Seifullin.

Approbation of the work. Pilot industrial testing of the developed technology for the production of biodegradable film material was carried out at SP Uly Dala LLP.

Publications. On the topic of the dissertation work, 6 scientific papers have been published: 1 article in a foreign publication indexed in the Scopus database , 5 articles in a journal from the List of publications recommended by the KOKSNVO MNVO RK, as well as a patent for a utility model No. 7307 “Method for producing acetylated starch” dated July 29, 2022 .

The volume and structure of the dissertation. The dissertation consists of an introduction, 3 sections, a conclusion, a list of references and appendices. The list of references consists of 239 titles. The text of the dissertation is illustrated with 28 tables and 25 figures.

essment of the completeness of the solution of the tasks. The data obtained correspond to the purpose of the thesis and allow us to conclude that all the tasks were successfully completed as follows:

1. The physicochemical properties of corn, potato and wheat A- and B-starches as raw materials for further processing were studied. The content of amylose, lipids, proteins, minerals, morphology, thermodynamic and viscosity properties were determined. It was found that wheat A- and B-starches have optimal physicochemical, thermodynamic and rheological characteristics, ensuring their suitability for the formation of biopolymer films. Potato starch showed high hydrophilicity and low thermal stability, which makes it less suitable for use as a base for biodegradable films. Chemical modification of wheat A- and B-starches was performed using acetylation and propionation methods. The optimal acetylation conditions were determined: the ratio of starch to acetic anhydride is 1 to 7, the reaction time is 40 minutes. The obtained modified starches have reduced sensitivity to moisture, which increases their compatibility with poly(ε-caprolactone) (PCL) and solves the problem of starch hydrophilicity. The effect of various plasticizers (glycerin, polyvinyl alcohol) on the mechanical properties of films was assessed. It was found that glycerin provides higher elasticity of films compared to polyvinyl alcohol. The optimal concentration of glycerin is 10% of the dry mass of starch. Increasing the plasticizer content above 15% leads to a decrease in the strength of the films.

2. Optimal compositions of granules and films based on modified wheat starches and PCL have been developed. A three-factor experimental design was used to determine the effect of starch, glycerol, and calcium carbonate content on the mechanical properties of the films. Contour maps of the strength dependence on the compositions of composite films were constructed to show that compositions containing 30–50% acetylated starch have a strength of 15–30 MPa, which is comparable to packaging materials based on petroleum products. Scanning electron microscopy analysis of the film structure showed that the addition of acetylated wheat starch results in a granular surface of the films. This indicates a uniform distribution of starch granules in the polymer matrix, which promotes controlled biodegradation. A study of the thermodynamic characteristics showed that films with acetylated starch have a high decomposition temperature and are resistant to moisture.

Biodegradability of the films has been experimentally confirmed . Composite films with 30% acetylated starch decompose by 35.92–43.75% within 10 days under composting conditions. Films with wheat B-starch demonstrated the highest decomposition rate. This is explained by its high reactive surface and better accessibility for microorganisms. Ecotoxicological studies have confirmed the absence of toxic effects on soil microorganisms.

4. A process flow chart for the production of biodegradable films has been developed, including chemical modification of starch, granulation, extrusion and film blowing. Optimized process parameters make it possible to obtain materials with specified properties and high stability during storage. Optimal film formulations have been selected based on the studies conducted. Films with 30% acetylated starch type A are optimal for packaging materials that require high strength and moderate vapor permeability . At the same time, films with 40% acetylated B- starch are better suited for use in conditions of high humidity and the required high permeability to water vapor . Practical tests have confirmed the possibility of using the films in the food industry. An analysis of the cost of production of biodegradable films has been conducted. It was found that the cost price of 1 kg of packaging material is 15,405.18 tenge, and the market price varies in the range of 33,000–40,000 tenge. Calculations showed that the proposed technology has a high profitability (28%) and is economically advantageous compared to traditional plastic packaging materials. The conducted studies made it possible to create a scientifically sound technology for obtaining biodegradable films based on modified wheat starch and poly(ε- caprolactone) (PCL). The developed films have high mechanical strength, stability and a high degree of biodegradation. The practical tests and economic analysis confirm the possibility of industrial implementation of the proposed technology.