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Modification of Natural Polymers for Synthesis of Biodegradable Materials

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Abstract

Methods for obtaining biodegradable films based on protein-carbohydrate components by varying their content and establishing optimal physical and mechanical characteristics depending on the ratio of protein components were developed. The resulting films possess integral structure, strength and ability to biodegradation under natural environmental conditions. Singularity of the obtained copolymer films consists in the fact that their destruction leads to the formation of ecologically safe products being a mixture of carbohydrates and amino acids.

Key words: biopolymer materials, biodegradation, copolymers

INTRODUCTION

The constant increase in the amount of the polymer materials which are used in various fields of national economy, requires a solution of the further utilization problem. Some times the use of polymer materials and burning of waste results in toxic compounds hazardous to the people health [1]. That is why along with a solution of the problem of increase in service life of polymeric materials it is necessary to pay attention to studying of the processes occurring at biodegradation, to develop and let out special types of polymers with adjustable service life, including biodegradable products for various application areas.

The study of mechanisms and optimization of processing biodegradable materials inducing phase transitions of complete structure formation and destruction, can promote creation of new materials with tailor made properties.

The purpose of this work is development of technology for creating the tailor made biodegraded polymers on the basis of a renewable natural polysaccharide – methylcellulose (MC) which can be considered as the general concept for mixed-esterified cellulose ethers. MC is modified by molecules of gelatine by covalent binding of the polypeptide side-chain amino acid residues of gelatine with MC functional groups. It provides not only strength and rigidity of a material, but also its ability to a biodegradation under natural environmental conditions.

The structural and logic model of synthesis of biodegraded tailor made polymers is developed, their physical and chemical and biochemical properties are investigated, biological tests of the received materials are carried out.

EXPERIMENTAL

We used for the work MC (MTs-100), molecular mass $(162.14)_n$ (Technical conditions TC 2231-107-05742755–96, Usolyekhimprom Ltd., Russia). To obtain the structure plasticity the composites were modified by glycerine (State Standard GOST 6259–75, Glitserin.ru Ltd., Russia), its mass fraction is correlated according to its thermodynamic compatibility with a biodegradable material. Strength and rigidity of material was provided by addition of a natu-

ral gelatine protein complex (GOST 11293–89, Minvod Gelatine Plant Ltd., Russia).

The films 3 mm thick were formed by 3–5 % MC water solution by method of free spreading on the smooth glass surface of designated form with solvent evaporation during 2–3 days at the temperature of 20–24 °C. The content of methoxy groups in MC was 26–33 %. The higher the initial water saturation and the reservoir rock permeability, the larger the permeability reduction. The higher the degree of methylation, the larger MC hygroscopicity and it well dissolves in water. This because the cross-saturation of the majority of hydroxyl groups with formation of hydrogen bonds takes place in cellulose macromolecules. With further increase in the content of methoxy groups (to 38 % and above) MC becomes insoluble.

To receiving MC solution it was added to the water heated up to the temperature of 50–60 °C. The mixture was left to stand for 1.5–2 h. The temperature mode is conditioned by the following limitations: at the temperature below 50 and above 60 °C the gelation process slows down. To exclude formation of air bubbles in 5 % MC solution the received solution is necessary to hold at the temperature of 8–10 °C during 12–15 h.

The addition of glycerine plasticizer, natural gelatine protein complex to the films structure was carried out by emulsification in MC solution [2]. The operation sequence, factor selection, a range and number of variation levels are based on the results of preliminary researches consistent with a literature.

Thickness of the obtained films was measured by means of Electro MC Digital Micrometer, graduation scale is 0.001 mm.

The analysis of physical properties of the obtained films includes research of the ranges of absorption spectra in UF region, strength and moisture absorption. These characteristics of the synthesized samples presume to expand their area of use.

The absorption spectra of the films were analysed in a range of $\lambda = 185–400$ nm. The sample size was 10×17 mm, cross section area was 0.6–0.7 mm^2. The spectrophotometer SF-26 (GOST 15150–69) was used for the measurements.

The ultimate length and width strength of biodegradable films was determined according to GOST 17035–86 with use of tensile and universal testing electric drive machine (GOST 7855–84).

Moisture absorption of films was estimated according to the swelling rating at presence of water vapour at the temperature of 18–25 °C during 48 h in dessicator.

The ability of film to biodegradation (biodegradation kinetics) was evaluated by weight loss with account of cellulase and proteolytic activity of microorganisms allocated from the soil medium and placed on the fragments of biodegradable film with initial mass of 0.5–0.6 g, placed in Petri's cups and incubated over the water in the thermostat at the temperature of 35 °C during 14 days. Cellulasic and proteolytic activity was defined according to the techniques given in [3].

RESULTS AND DISCUSSION

Increased threshold of the light absorbance of the polyethylene film in UF region can be used in producing the packing materials providing extended storage period. Data on the light

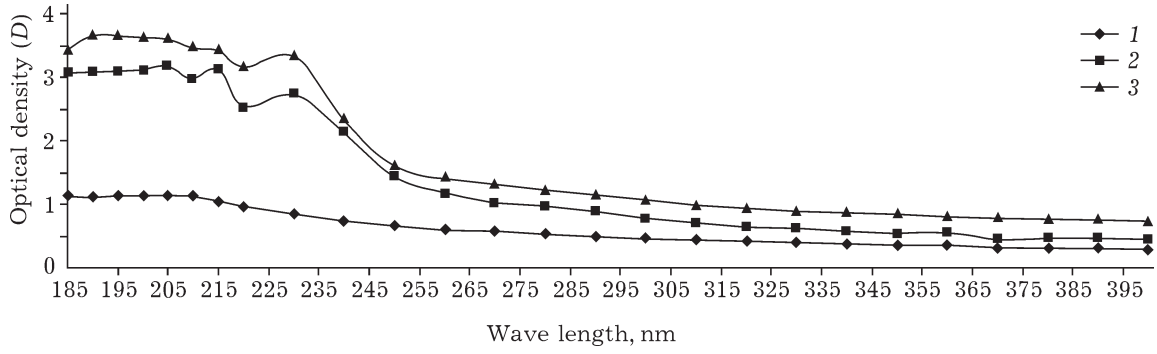

Fig. 1. Influence of the plasticiser content on light absorption ability of biodegradable MC based film in UF region (content of gelatine protein complex is 6 mass %). Content of glycerine, mass %: 0 (*1*), 21.7 (*2*), 54.3 (*3*).

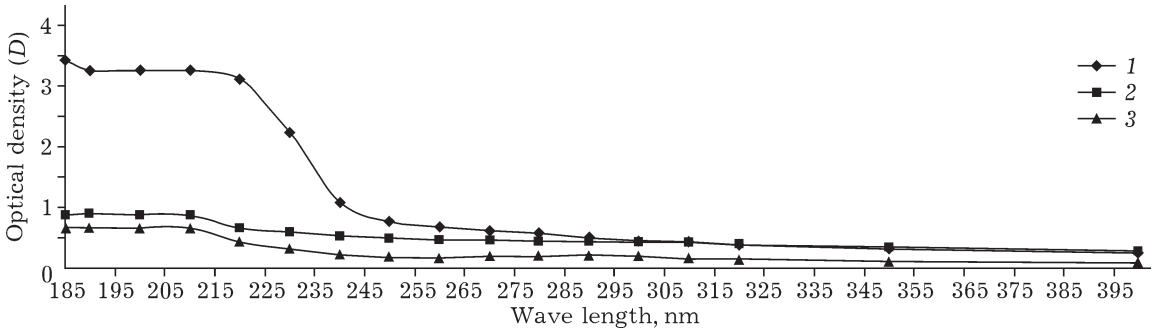

Fig. 2. Comparative analysis of absorption spectra in UF region (content of gelatine protein complex is 6 mass %, glycerine – 21.7 mass %): *1* – the obtained biodegradable film, *2* – polyethylene, *3* – cellophane.

TABLE 1

Comparative characteristic of strength of biodegraded and polyethylene films

Structure of films, mass %	Thickness (h), mm	Length (l_0), mm	Cross section area (A_0), mm^2	Width strength (σ_w), MPa	Length strength (σ_l), MPa
MC 70.67, gelatine 6.0, glycerine 21.7, water 1.63	0.059	15	0.878	14.2	14.8
MC 38.08, gelatine 6.0, glycerine 54.3, water 1.62	0.048	15	0.713	15.2	15.3
Polyethylene	0.040	15	0.600	13.7	14.7

absorbance of the synthesized biodegradable films in UF region are presented in Figs. 1 and 2.

The results of the comparative analysis of absorbance spectrum in UF region of the elaborated and traditional film materials demonstrate increase in light absorbance threshold that can be related with increase in packaging density in the MC amorphous regions at the expense of structure modification by glycerine and gelatine molecules. MC modification by molecules of gelatine is by covalent binding of the lateral amino acid residues of polypeptide chains of the latter with the MC functional groups.

The mechanical properties of polymeric material depend on the durability of the structure under ultimate tensile stress. According to the data in Table 1, the elaborated biodegradable polymeric films do not yield to commonly used polyethylene in durability.

The integral structure of biodegradable materials and their moisture absorption ability depend not only on the mechanisms of interaction of the components the films are based on, but also depends on their quantitative relation. Moisture absorption was estimated by swelling rating of investigated samples (Fig. 3).

Destruction took place under natural conditions with direct soil to film contact. Data on

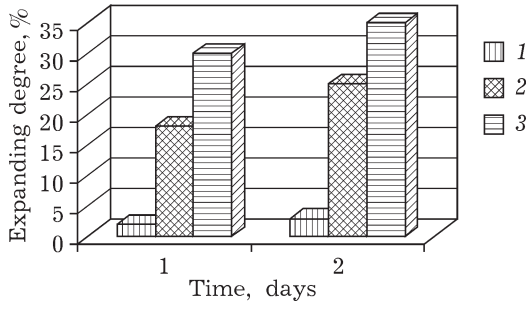

Fig. 3. Expanding kinetics of biopolymer films (MC–gelatine–glycerine, content of gelatine protein complex is 6 mass %) each 12 days. Content of glycerine, mass %: 0 (*1*), 21.7 (*2*), 54.3 (*3*).

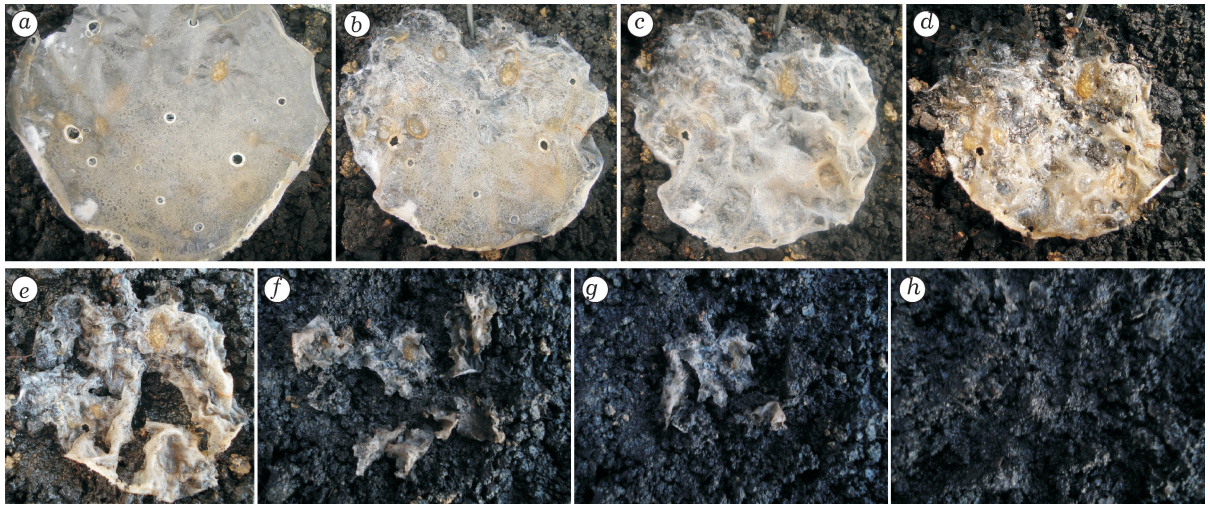

Fig. 4. Time dependent destruction of MC based films contacting to the soil under natural conditions, days: 1 (*a*), 2, 3 (*b*), 4 (*c*), 6 (*d*), 9 (*e*), 11(*f*), 14 (*g*).

destruction of the MC based films are presented in Fig. 4. Complete decomposition of the MC based films under natural conditions occurred in two weeks.

CONCLUSION

Biodegradable films based on the protein-carbohydrate components are characterized by integral structure, which does not yield in durability to polyethylene films, and there are biodegraded under natural conditions.

The singularity of the obtained copolymer films is formation of non-polluting products which enriching the soil and appearing in the course of films destruction during the contact to the soil.

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