

## THE STUDY OF RHEOLOGICAL BEHAVIOR AND SAFETY METRICS OF NATURAL BIOPOLYMERS

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**Abstract:** Traditionally, plastics are made from artificial synthetic polymers. These polymers have an unnatural structure, that's why they are not biodegradable. Based on the latest advances in polymers structure studies, the article sets forward new biodegradable materials highly competitive with base plastic. Biodegradable films were received by fill-and-drain method from agar-agar, carrageenan and hydroxypropyl methylcellulose with glycerol, used as a plasticizer. Various compositions of biodegradable films based on natural polysaccharides have been analyzed for their rheological behavior and stress-strain properties, as well as for their safety and ecotoxicity index. It is found that all compositions of received polymer films are biodegradable and relatively bio-safe (III-IV class of danger). The strength characteristics tests revealed that the compositions with carrageenan have higher strength (2.84 MPa) than polymers containing only agar-agar (1.64 MPa). Also biopolymers with the content of carrageenan have the elevated chemical resistance (prolonged time of dissolution in hydrochloric acid). The melting point of the samples narrowly varies from 35.3 to 35.9°C. The study of the received polymers showed no cracks and no serious heterogeneities of composition. According to the testing results the compounds have been selected, which have optimum characteristics for use of biodegradable polymers in various industries. The biopolymers obtained in the future will replace artificial polymers that can solve problems of non-biodegradable polymer systems waste.

**Keywords:** biodegradable polymers, rheology, diffusing, deformation, safety, ecotoxicity, ecology, bioconversion

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### INTRODUCTION

At the present there have come a new approach to polymeric materials making, opposite to the traditional one [1, 2]. The purpose of this approach is the production of polymeric materials which retain producing characteristics only during the consumption period, and then go through physicochemical, chemical and biological transformations under the influence of environmental factors and easily join in processes of a metabolism of natural biosystems [3].

Biodegradable polymers is a class of the high-molecular compounds containing products of biological organisms (cellulose, protein, starch, nucleic acid, natural resin, etc.), and they are capable to decay on neutral for environment substances under corresponding conditions. In biologically active medium biodegradable polymers undergo significant changes in molecular weight and mechanical characteristics or give the nutrients providing growth of microorganisms. In such mediums there are processes of hydrolysis and photochemical destruction of biopolymers. Finally biopolymers decay on the

components participating in a natural cycle – water, carbon dioxide, a biomass, etc. The basic advantage of biopolymers is their ability to biodegradation during rather short time, unlike the traditional analogues received from petrochemical raw materials [4, 5].

The market of biodegradable polymers is one of most emerging economic segments. Their production is already an integral part of national agrochemical complexes of Japan, the USA, European Union countries [6]. Biodegradable polymers possess more ample opportunities of utilization in comparison with traditional polymers, because they solve a problem of dependence on petrochemical raw materials as well as recycling problems. In Russia production of biodegradable polymers is in an incipient state, the overwhelming number of fabricators use basically the foreign workings out [7, 8].

In connection with the aforesaid the working out of Russian analogues of biodegradable films in packaging, food and pharmaceutical industry is considered to be actual.

Polymeric materials' ability to biological degradation is caused, mainly, by their chemical composition, structure and qualities of macromolecules [9, 10]. The great influence on polymers' stability to biodegradation is rendered by some macrostructural characteristics (pore volume, additives equality in polymeric mass, features of surfacing of products, etc.), and also by technological parameters [11, 12, 13].

The purpose of the this research was to investigate films samples made on the basis of natural polysaccharides, and also to choose of tailored composition of films, and conditions of polymers productions, by biodegradability and stress-strain properties.

## OBJECTS AND METHODS OF STUDY

The objects of investigations were biodegradable polymers, produced from vegetable polysaccharides agar-agar, carrageenan and hydroxypropyl methylcellulose with glycerol by fill-and-drain method. 8% of glycerin, as a plasticizer, was added in each sample. Without addition of glycerin the films were rigid and curled at drying. The film-former solution was transferred to a dish with (1–2) mm high bead. The dish was covered with a glass cap. It was cooled at normal temperature. The film drying was carried out in various ways:

- at normal temperature;
- at air convection in a draught cupboard;
- in a vacuum drying chamber (with varied drying temperature);
- in a drying chamber (with varied drying temperature).

The best way of drying was chosen for each type of the sample, allowing to provide uniformity of drying and to exclude deformation of the sample (overdrying, formation of cracks).

### *Evaluation of thickness and density*

Thickness of films was measured with an electronic micrometer “MK gladkii N 26591” by direct measurement method. At least 10 parallel meterages were carried out on 5 various sites of a film, and the midrange value was counted.

### *Water absorption measurement*

Water absorption measurement was held in accordance with GOST 4650-80. Samples in the form of a square with the side of 50 mm were taken for tests. Before test samples were exsiccated at 50°C in a drying chamber within 24 h, and then were cooled in a desiccator over phosphorus pentoxide at 23°C. After cooling samples were weighed. Further samples were dipped in distilled water and maintained at temperature 50°C within 24 h. After that, samples were taken out from water, wiped with filter paper and were being weighed during 1 minute.

### *Chemical durability evaluation*

For evaluation of chemical durability squares in the size of 10/10 mm were cut out for each sample. The received squares were dipped in the reactive mediums preliminarily prepared in glassware, and by means of a stop watch the time of sample degradation was defined.

### *Research of strength characteristics of the films*

The load at tearing up was defined with desktop electromechanical testing machine Instron 3343 in accordance with GOST 14236-81. The parameters of

measurements: a gross capacity is 50 kN, speed of movement of cross-arm is 100 mm/min, the sizes of the sample, a clamping length of 150 mm. The size of samples was 170/10/0.2 mm/mm/mm with equal edges without defects. The test was made at temperature 23°C and relative humidity of 50%.

### *Evaluation of melting point of films*

Evaluation of melting point of films was made by method of differential scanning calorimetry on DSC 204 F1 Phoenix device at heat rate of 10 °C/minutes in air atmosphere by method STO TGU 074-2010 “Thermal analysis of film composite polymeric materials on the basis of polyolefins”.

### *Estimation of biodegradability*

Biodegradability degree was defined by method ISO 846:1997. Agar-agar was prepared without nutrients and was poured to Petri dish. Samples were sterilized before test by submergence in 70% ethanol during 1 minute, and then exsiccated within 72 h at a constant air адщц. Then samples were put in Petri dishes, and the suspension of viable fungus spores was put on a surface in number of 100 mkl. The suspension of fungus microorganisms was represented by *Aspergillus niger*, *Penicillium funiculosum*, *Paecilomyces variotii*, *Aspergillus terreus*, *Aureobasidium pullulans*, *Penicillium ochrochloron* in number of 10<sup>6</sup> spores in ml for each kind. The selected microorganisms are specific for growth on biodegradable plastics and inhabit in natural biocenosis. The samples were incubated in a thermostat within 28 days at temperature 29°C and relative humidity of ≥90% and were weighed on reference points.

### *Evaluations of ecotoxicity*

For estimation of influence of films samples ecotoxicity we used the influence on phyto- and zooplankton. The first variant used an algological pure diurnal growth of seaweed *Chlorella vulgaris* Beijer, with optical density 0.625 according to FR 1.39.2011.10993 “Technique of evaluation of an index of ecological toxicity of concentrated aqueous disperse systems of nanoparticles on growth inhibition of test culture seaweed chlorella”. 2 ml of the diurnal growth of seaweed was placed in each of 6 prepared glassfuls containing 48 ml of blank and test samples. The test samples were spilt for 5 ml in sample vial, in triplicate. Escalating of growth of seaweed chlorella was defined after 22 hours of cultivation. Toxicity estimation was carried out by measurement of optical density of test sample and by comparison of a diurnal gain of seaweed cells in blank and test samples (if the optical density in test vials were not lower than 0.120).

In the second variant the lower crustaceans were used, by technique FR 1.39.2010.09102 “Technique of evaluation of an index of toxicity nanopowders, products from nanomaterials, nanocoatings, waste and sludge containing nanoparticles, according to the mortality the test-organism *Daphniamagna Straus*” with modification STO TGU 137-2015 “Nanomaterials and superfine materials, waste and sludge containing nanoparticles. The evaluation index of toxicity on mortality the test-organism *Daphniamagna Straus*”. The experiment took 72 h. The criterion of sharp toxicity was the death at least of 50%

daphnids in test sample for 48 hours, while in a blank sample all the bions keep the germinating power. The daphnias mortality account in blank and test samples was made by each 24 hours. The experiment was stopped, if the death of more than 50% bions was observed in all test tubes within 24 hours. Motionless bions considered to be dead if they did not start to move within 15 seconds after light rocking of a test tube. Besides, the behavior of daphnias (activity and character of movement), filling of bowels, the dumped ephippiums number were considered.

#### *Electronic microscopy*

The system with electronic and focused bunches Quanta 200 3D was used for electronic microscopy. The samples were analyzed according to TGU 041-2009 "Technique of carrying out researches of surface structure of a solid body by method of raster electronic microscopy". Researches were made on the samples extended before deformations, corresponding to a proportional limit, to a lower limit of fluidity and to ultimate strength.

#### *Research light transmittance*

The research is made on equipment CARY 100 SCAN. Light transmittance of polysaccharide films is measured in a range 180–780 nm. The samples have been preliminarily nonfatted with 70% ethanol and exsiccated.

## RESULTS AND DISCUSSION

The work was made to two stages. At the first stage samples of films are made from natural polysaccharides of different composition (Table 1). Agar-agar, carrageenan and hydroxypropyl methylcellulose were used as the substances possessing a high potential to formation of hydrogels with stable chemical and a physical structure.

**Table 1.** Composition of probed films

No. n/n	Quantity of ingredient. mass, %			
	agar-agar	carrageenan	hydroxypropyl methylcellulose (HPMC)	water
1	5.0	-	-	95.0
2	20.0	-	-	80.0
3	-	2.5	-	97.5
4	-	5.0	-	95.0
5	-	-	2.5	97.5
6	-	-	10.0	90.0
7	5.0	2.5	-	92.5
8	20.0	2.5	-	77.5
9	5.0	5.0	-	90.0
10	5.0	10.0	-	85.0
11	5.0	-	2.5	92.5
12	20.0	-	2.5	77.5
13	5.0	-	5.0	90.0
14	5.0	-	10.0	85.0
15	-	2.5	2.5	95.0
16	-	10.0	2.5	87.5
17	-	2.5	5.0	92.5
18	-	2.5	10.0	87.5
19	5.0	2.5	2.5	90.0
20	10.0	5.0	5.0	80.0

**The sample No. 1:** small enough concentration of agar-agar in suspension allows to pulpify it on a magnetic stirrer with function of maintenance of temperature.

Stirrer temperature – 150°C.

Speed of rotation – 800 rpm.

After the solution became transparent, it was poured out on a substrate with 2 mm bead height.

Drying was made in a drying chamber at temperature 85°C.

**The sample No. 2:** Because of the big concentration of agar-agar the dry-mix which cannot be pulpified on a magnetic stirrer is formed. This sample was pulpified in an autoclave on a blowdown mode within 15 minutes.

The received solution poured out on a substrate with 1 mm bead height.

Drying was made in a drying chamber at temperature 90°C.

**The sample No. 3:** too small concentration of carrageenan. It was not possible to receive a film.

**The sample No. 4:** too small concentration of carrageenan. It was not possible to receive a film.

**The sample No. 5, the sample No. 6:** It was not possible for HPMC to dissolve completely. It was not possible to receive a film.

**The sample No. 7:** the mixture at dissolution in water forms moderately dense suspension that allows to weld it on heating mantle.

Agitator temperature – 150°C.

Speed of rotation – 800 rpm.

The received solution was poured out on a substrate with 2 mm bead height.

Drying was made in a drying chamber at temperature 85°C.

**The sample No. 8:** the big concentration of agar-agar with carrageenan. The sample was pulpified in an autoclave on a blowdown mode within 15 minutes.

The received solution poured out on a substrate with 1 mm bead height.

Drying was made in a drying chamber at temperature 90°C.

**The sample No. 9:** the yielded mixture was pulpified on heating mantle.

Agitator temperature – 150°C.

Speed of rotation – 800 rpm.

The received solution was poured out on a substrate with height of shoulders by 2 mm.

Drying was made in a drying chamber at temperature 85°C.

**Sample No. 10** was pulpified in an autoclave on a blowdown mode within 15 minutes.

The received solution was poured out on a substrate with height of shoulders 1 mm.

Drying was made in a drying chamber at temperature 90°C.

**The sample No. 11, Sample No. 12, Sample No. 13, Sample No. 14, Sample No. 15, Sample No. 16, Sample No. 17, Sample No. 18, Sample No. 19, Sample No. 20:** it was not possible to receive a quality film, there are undissolved particles of HPMC.

According to appearance and structure from the received samples the greatest interest for the further research was introduced by samples:

– The film sample No. 1 consisting of 5.0 mass. Agar-agar %; 95.0 mass. water %;

- The film sample No. 2 consisting of 20.0 mass. Agar-agar %; 80.0 mass. water %;
- The film sample No. 7 consisting of 5.0 mass. Agar-agar %; 2.5 mass. % carrageenan; 92.5 mass. water %;
- The film sample No. 8 which composition includes 20.0 mass. % of agar-agar and 2.5 mass. % carrageenan, 77.5 mass. water %;
- The film sample No. 9 which composition includes 5.0 mass. % of agar-agar and 5.0 mass. % carrageenan; 90.0 mass. water %;
- The film sample No. 10 which composition includes 5.0 mass. % of agar-agar and 10.0 mass. % carrageenan; 85.0 mass. water %.

At the second stage various compositions of biodegradable films made of natural polysaccharides were probed on rheological behavior, stress-strain properties, and also on safety and ecotoxicity.

The received results on biodegradability are shown in Table 2.

From Table 2 it follows, that the samples of the film No.1 had the maximum degree of biodegradability (78.0% for 3 days, 86.0% for 28 days) consisting of 5.0 mass. agar-agar %; and the sample of the film No. 8 which composition includes 20.0 mass. % of agar-agar and 2.5 mass. % carrageenan had the minimum degree (54.0% for 3 days, 68.0% for 28 days). All probed samples correspond to the research problems on creation of biodegradable films, possessing high speed of biodegradation. According to the results of experiment the speed of biodegradability is in inversely proportional dependences on concentration of raw materials. Agar-agar possesses higher firmness to action of micro-organisms, than carrageenan, that is explained by the feature of a molecular structure of carrageenan which under the influence of microbial enzymes breaks up to low molecular weight complexes easier and assimilates living organisms.

Data of thickness and density of biodegradable films are shown in Table 3.

From Table 3 it follows, that the maximum thickness (1.518 mm) is typical for a film consisting of 20.0 mass. % of agar-agar and 2.5 mass. % carrageenan, minimum (0.593 mm) – for a film consisting of 5.0 mass. agar-agar %. The maximum density (1.4284 g/cm<sup>3</sup>) characterizes a film consisting of 5.0 mass. % of agar-agar and 5.0 mass. % carrageenan, the minimum density (1.2344 g/cm<sup>3</sup>) – a film consisting of 5.0 mass. % of agar-agar and 10.0 mass. % carrageenan. As a result of researches interrelation between thickness and density has not been registered, and also between these characteristics and composition of films. However the regularity was found, according to which is revealed at the maintenance of ingredients more than 10% mass. it is impossible to receive a sample with a thickness less than 1 mm in the bulk way (a demanded thickness  $0.6 \pm 0.1$ ).

The results of evaluation for strengthening characteristics of biodegradable films on the basis of natural polysaccharides are introduced in Table 4. The extension strength is measured in MPa, it is the force enclosed to the area, i.e. kg/cm<sup>2</sup>. The higher this value is, the more stable against efforts to a stretching the material is.

From Table 4 it is seen, that the maximum magnitude of tensile stress (2.84 MPa) is typical for a film which composition includes 20.0 mass. % of agar-agar and 2.5 mass. % carrageenan, minimum (1.64 MPa) – for a film consisting of 5.0 mass. % of agar-agar and 2.5 mass. % carrageenan. There is an implicit correlation between thickness of films and tensile stress, besides carrageenan attaches thickness to a finished product, and so also the tensile stress.

**Table 2.** Degree of films biodegradability on the basis of natural polysaccharides

Sample number	Average proportion of a weight loss of degraded samples, %				
	3 days	7 days	14 days	21 days	28 days
1	78.0 ± 0.3	79.0 ± 0.2	80.0 ± 0.3	82.0 ± 0.7	86.0 ± 0.1
2	63.0 ± 0.4	64.0 ± 0.3	66.0 ± 0.3	70.0 ± 0.6	74.0 ± 0.5
7	71.0 ± 0.5	72.0 ± 0.9	74.0 ± 0.9	79.0 ± 0.3	82.0 ± 0.3
8	54.0 ± 0.4	56.0 ± 0.8	58.0 ± 0.4	62.0 ± 0.5	68.0 ± 0.8
9	64.0 ± 0.5	65.0 ± 0.7	66.0 ± 0.4	69.0 ± 0.5	73.0 ± 0.5
10	52.0 ± 0.3	57.0 ± 0.7	58.0 ± 0.3	62.0 ± 0.5	69.0 ± 0.3

**Table 3.** Results of evaluation of thickness and density of biodegradable polymers on the basis of natural polysaccharides

Sample number	Thickness, mm	Density, g/cm <sup>3</sup>
1	0.593 ± 0.030	1.2879 ± 0.0644
2	1.270 ± 0.064	1.3455 ± 0.0673
7	0.711 ± 0.036	1.3857 ± 0.0693
8	1.518 ± 0.076	1.3086 ± 0.0654
9	0.849 ± 0.042	1.4284 ± 0.0714
10	1.220 ± 0.061	1.2344 ± 0.0617

**Table 4.** Results of evaluation for strengthening characteristics of biodegradable films on the basis of natural polysaccharides

Sample number	Tensile stress at a gross capacity, MPa
1	2.09 ± 0.09
2	2.19 ± 0.45
7	1.64 ± 0.24
8	2.84 ± 0.26
9	2.72 ± 0.12
10	2.66 ± 0.08

As the developed biodegradable films are planned to use further for creation of packing materials, it is interesting to find out the measurement of water absorption of considered films. The influence of moisture on polymeric materials there can make essential changes. Moisture diffusion in polymer is accompanied by reduction in it of intermolecular interaction which can appear useful from the point of view of strengthening properties, but the further increase of specific humidity renders deleterious effect. Thus, it is necessary to estimate possibility of influence of external liquid medium on plastic.

The results of experiments on measurement of water absorption of films on the basis of natural polysaccharides are shown in Table 5.

**Table 5.** Results of water absorption evaluation of biodegradable polymers on the basis of natural polysaccharides

Sample number	Weight fraction of absorption of water, %	Water mass, absorbed by the sample, mg
1	3.0 ± 0.6	0.0071 ± 0.0015
2	19.0 ± 0.8	0.0913 ± 0.0036
7	81.0 ± 0.7	0.2039 ± 0.0084
8	72.0 ± 0.3	0.3844 ± 0.0052
9	165.0 ± 0.3	0.4949 ± 0.0090
10	168.0 ± 0.9	0.5369 ± 0.0120

The analysis of data of Table 5 testifies that samples of films No.9 and No.10 (165.0% and 168.0%) are characterized by the maximum water absorption, consisting, accordingly, from 5.0 mass. agar-agar %, 5.0 mass. % carrageenan and 5.0 mass. agar-agar %, 10.0 mass. % carrageenan. The minimum water absorption (3.0%) is observed for the sample of a film No.1 (5.0 mass. agar-agar %).

Along with susceptibility to biodegradability the polymers should possess chemical durability. This concept also falls into to one of the main protective criteria of the films characterizing ability to stand up to the influence of chemical agents of environment among which mineral and organic acids evolve, and also their solutions in water, solutions of alkalis; solutions of salts both other chemicals and their connections possessing strong redox potential. Parametres of chemical durability of polymer allow to receive representation about possibility of its utilization in various industries.

Chemical durability of biodegradable films was probed in relation to acids (sulfuric, saline) and to alkalis (sodium hydroxide). The received results are shown in Table 6.

From Table 6 it follows, that the sample No. 1 dissolves in HCl<sub>conc</sub> during 3 mines, the sample No. 2 – during 17 mines, samples No. 7–10 – within 55 minutes.

**Table 6.** Research results of chemical durability of biodegradable polymers on the basis of natural polysaccharides

Sample	Solvent	Duration of dissolution of the sample				
		H <sub>2</sub> SO <sub>4</sub> , concentration	HCl, concentration	HCl, 0.1 M	NaOH, 2 M	NaOH, 0.1 M
1	22 hours	22 hours	3 min	Fims didn't break down	Films swelled, but didn't break down	Fims didn't break down
2			17 min			
7			55 min			
8						
9						
10						

The best dissolution of films samples occurs in a solution of concentrated muriatic acid that is explained by extreme aggressiveness of medium in which vegetable polysaccharides are exposed to hydrolysis.

The firmness of polymers to = various chemical reagents and solvents changes over a wide range not only from polymer to polymer, but in some cases and within various grade numbers of the same polymer. Generalizations concerning chemical durability of this or that polymer should be held with big care because of exceptions. Nevertheless, certain structural and chemical properties of polymer can be used for the approached estimation of firmness to various chemical reagents.

Films with carrageenan are marked by better firmness in concentrated muriatic acid, than the films including only agar-agar. This results from the fact that

in sour mediums agar-agar is less stable, than the majority of polysaccharides, because 3,6-angidro- $\alpha$ -L-glycosidic bonds containing in agar-agar are decomposed by acids low fidelity in 100 times lighter than  $\beta$ -glycosidic bonds with carrageenan.

It is important to have the optimum indexes of melting temperature providing stability of a material to environmental conditions and thus not causing big expenses by production. Melting is a process of polymer transferring from the ordered state to the liquid one. Melting process has diffuse and relaxation character; its passing and result are defined by a parity of melting and heating speeds.

In Table 7 the evaluation results of melting point of biodegradable films on the basis of natural polysaccharides are resulted.

**Table 7.** Evaluation results of melting point of biodegradable films on the basis of natural polysaccharides

Sample number	Fusion temperature, °C
1	35.7 ± 0.2
2	35.5 ± 0.2
7	35.9 ± 0.4
8	35.3 ± 0.5
9	35.7 ± 0.5
10	35.4 ± 0.5

The data from Table 7 proves that melting temperature of all probed samples varies in a narrow range from 35.3 to 35.9°C.

A special value of biodegradable plastics is in ecological compatibility of production and utilization, in comparison with traditional polymers. Safety parameters are the important index for all types of biodegradable polymers. One of such indexes is ecotoxicity which shows hazard of studied substance to corresponding biocenosis. The ecotoxicity parameters of biodegradable films samples are shown in Table 8.

From Table 8 it follows, that the influence on environment (toxicity for natural biocenosis), according to a principle of an estimation of toxicity on the most expressed reaction, is the following: the sample No. 2 falls into to V class of hazard, samples No. 7 and No. 10 – to IV class of hazard, samples No. 1, No. 8 and No. 9 – to III class of hazard.

The micromorphology of films on the basis of natural polysaccharides was probed by method of scanning electronic microscopy as working with materials is important to define size and form of their particles, degrees of uniformity of particles distribution in a solution, interrelation of the form and particle size with other characteristics of a material. The received results are introduced in Fig. 1.

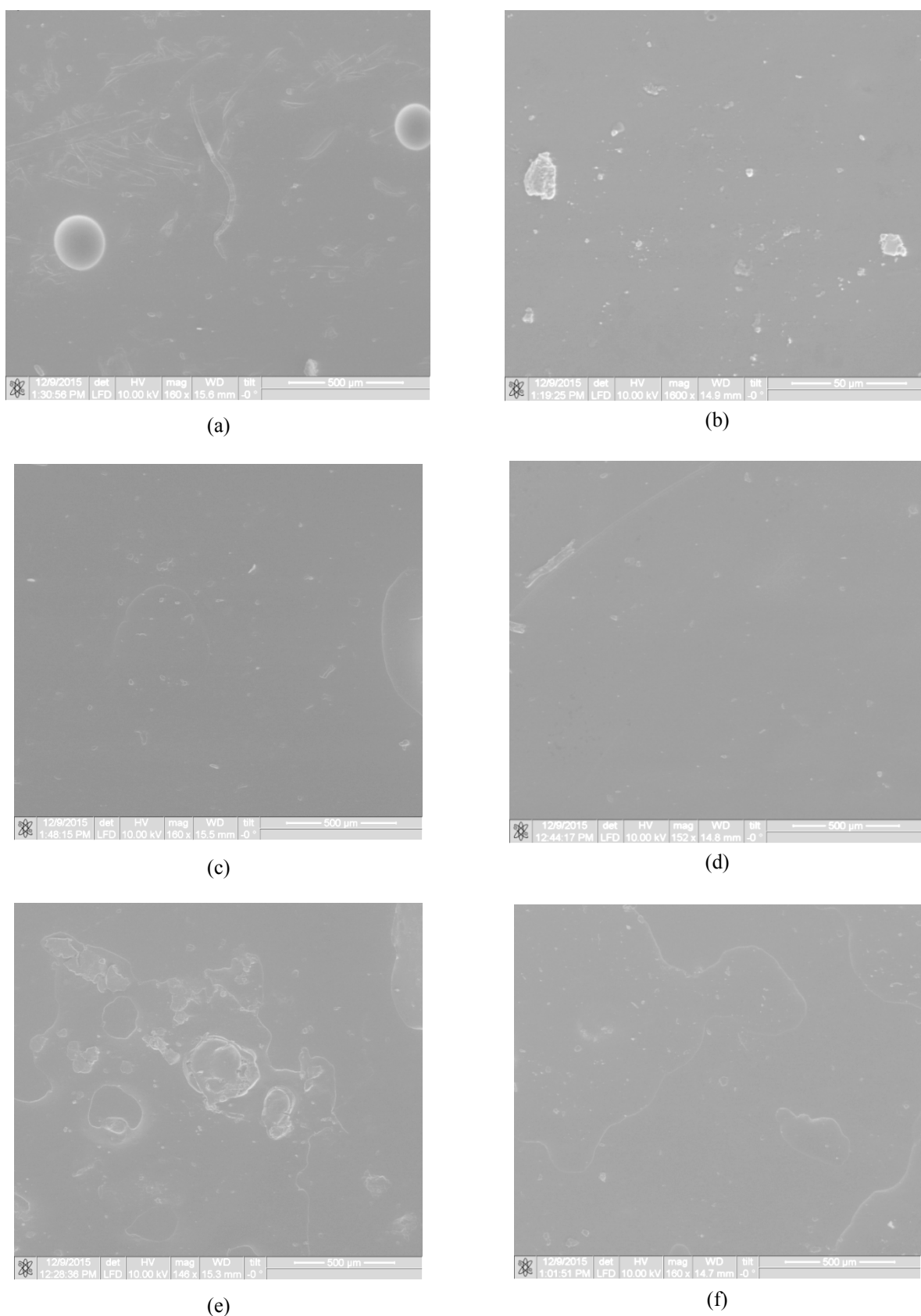
The research of films has not revealed cracks and serious inhomogeneities of composition, however samples No. 7, No. 8, No. 10 have more uniform structure in comparison with the others.

One of the major protective attributes of packing is property to detain a luminous flux, as ultraviolet and visible light are the reason of photodegradation and other changes in a product.

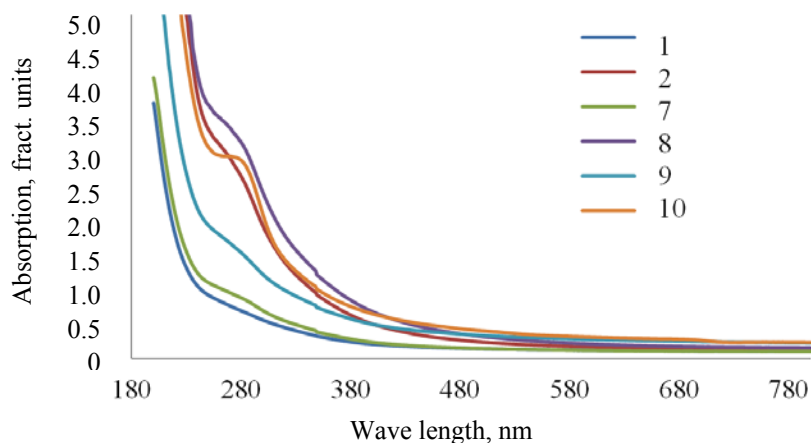
The received results on light transmittance of films are shown in Fig. 2.

**Table 8.** Ecotoxicological indexes of biodegradable films samples on the basis of natural polysaccharides

Sample number	Test-organism	Test-reaction	Frequency rate of deluting to safe level	Class of hazard	General class of hazard
1	<i>Chlorella vulgaris Beijer</i>	Inhibition of test culture growth	60.00	III	III
	<i>Daphnia magna</i>	Mortality	2.21	IV	
2	<i>Chlorella vulgaris Beijer</i>	Inhibition of test culture growth	1.00	V	V
	<i>Daphnia magna</i>	Mortality	0.88	V	
7	<i>Chlorella vulgaris Beijer</i>	Inhibition of test culture growth	5.55	IV	IV
	<i>Daphnia magna</i>	Mortality	3.13	IV	
8	<i>Chlorella vulgaris Beijer</i>	Inhibition of test culture growth	535.70	III	III
	<i>Daphnia magna</i>	Mortality	2.69	IV	
9	<i>Chlorella vulgaris Beijer</i>	Inhibition of test culture growth	352.20	III	III
	<i>Daphnia magna</i>	Mortality	5.20	IV	
10	<i>Chlorella vulgaris Beijer</i>	Inhibition of test culture growth	25.40	IV	IV
	<i>Daphnia magna</i>	Mortality	28.90	IV	



**Fig. 1.** Photomicrography of films on the basis of natural polysaccharides: (a) sample No. 1; (b) sample No. 2; (c) sample No. 7; (d) sample No. 8; (e) sample No. 9; (f) sample No. 10.



**Fig. 2.** Absorption spectra in UV, VID-areas for films samples.

It follows from Fig. 2, that all samples displayed similar properties in the analysis of light transmittance. Maximum light absorption was registered at wave length of 180 nanometers. In the process of wave length increase light holding ability of films falls and reaches less than 0.5 fract. units at 480 nanometers.

On a result of experiment the sample 8 possessed the best light barrier properties, and the sample 1 had maximum light transmittance. Also the regularity was revealed that the less thickness of films and concentration of substances in the sample corresponds to bigger light transmittance.

Thus, as a result of the made researches the following results are received:

(1) Six samples of the received films on the basis of the natural polysaccharides are chosen for the further researches, for their elasticity and form constancy. In the samples 5–20 it was not possible to receive qualitative film, as at solutions there were undissolved particles of HPMC and concentration of carrageenan was too low for a stable form of a total film in the samples 3–4.

(2) It is positioned, that all considered samples of films on the basis of natural polysaccharides are biodegradable. According to the results of experiments speed of biodegradability is inversely proportional dependences on concentration of raw materials. Agar-agar possesses higher firmness to action of microorganisms, than carrageenan.

(3) The thickness and density of biodegradable polymers on the basis of natural polysaccharides is defined. The interrelation between thickness and density has not been registered, and also between these characteristics and composition of films on the basis of polysaccharides. However the regularity is revealed according to which at the maintenance of ingredients more 10% mass. It is not possible to receive a sample in the thickness less than 1 mm in the bulk way.

(4) As a result of evaluation of strengthening characteristics of biodegradable films on the basis of natural polysaccharides it is positioned, that maximum magnitude of tensile stress (2.84 MPa) is characteristic for a film which composition includes 20.0 mass. % of agar-agar and 2.5 mass. % carrageenan, minimum (1.64 MPa) – for a film consisting of 5.0 mass. % of

agar-agar and 2.5 mass. % carrageenan. There is an implicit correlation between thickness of films and tensile stress, besides carrageenan attaches to a finished product more thickness, and so also the tensile stress.

(5) Analysis of water absorption of biodegradable polymers on the basis of natural polysaccharides showed, that films samples No. 9 and No. 10 are characterized by maximum water absorption, and the sample of a film No. 1 – by the minimum one.

(6) All received samples of biodegradable polymers are stable against action of the diluted with sulfuric, saline acids and sodium hydroxide. In concentrated sulfuric acid all analyzed samples have dissolved within 22 hours. The probed films display the greatest sensitivity in relation to concentrated muriatic acid. Films with addition of carrageenan differ bigger firmness in concentrated muriatic acid, than the films including only agar-agar.

(7) Evaluation results of melting temperature of biodegradable films on the basis of natural polysaccharides testify that melting temperature of all probed samples varies in a narrow range from 35.3 to 35.9°C.

(8) Analysis of ecotoxicity samples of biodegradable films has shown, that the sample No.2 falls into to V class of hazard (the ecological system practically is not broken), samples No. 7 and No. 10 – to IV class of hazard (low-hazard substances), samples No. 1, No. 8 and No. 9 – to III class of hazard (moderately hazardous).

(9) Research of films has not revealed cracks and serious inhomogeneities of composition, however samples No. 7, No. 8, No. 10 have more uniform structure in comparison with the others.

(10) All samples displayed similar properties in the analysis of light transmittance. Maximum light absorption was registered at wave length of 180 nanometers. In the process of wave length increasing the light holding ability of films falls and reaches less than 0.5 fract. unit at 480 nanometers. On a result of experiment the sample No. 8 possessed the best light barrier properties, and the sample No.1 had maximum light transmittance. Also regularity has been revealed: the smaller thickness of films and concentration of substances in the sample corresponds to the bigger light transmittance.



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