ANALYSIS OF THE STRUCTURAL AND MECHANICAL PROPERTIES AND MICROMORPHOLOGICAL FEATURES OF POLYMERIC FILMS BASED ON HYDROCOLLOIDS OF VEGETABLE ORIGIN USED FOR THE PRODUCTION OF BIODEGRADABLE POLYMERS

L. S. Dyshlyuk

Kemerovo Institute of Food Science and Technology,
bul'v. Stroitelei 47, Kemerovo, 650056 Russia
phone: +7 (951) 600 96 32; e-mail: soldatovals1984@mail.ru

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Abstract: Modern research and technology approaches to the production of biodegradable polymeric materials based on renewable resources have been reviewed. It has been found that films prepared of cellulose, chitosan, gelatin, polypeptides, casein, soy, wheat, corn, rice, and maize are being commonly used at present. The structural and mechanical properties and micromorphological features of hydrocolloids of vegetable origin promising for the production of biodegradable polymers—starches, pectins, carrageenans, and agar—have been studied. It has been determined that, with respect to strength and suitability for use in films of individual components, all the studied hydrocolloids can be arranged in ascending order as follows: starches, carrageenans, pectins, agar. According to analysis of the structural and mechanical properties of the films, it has been shown that the best parameters are found for the samples based on pectin P1 and agar A2. The breaking stress for these materials is 52 and 77 MPa, respectively. The breaking strain is 11.5 and 8.0%, respectively. Analysis of the micromorphology has revealed the formation of surface microdiscontinuities in the films based on high methoxyl pectins P1 and P4 and unmodified corn starch S3 and the formation of wavy folds in the case of the films of kappa-carrageenan C1; these folds are formed during drying and decrease the tensile strength of the respective films. The found features will be used in the development of technologies for the production of biodegradable polymeric materials based on hydrocolloids of vegetable origin with enhanced performance and processing characteristics.

Keywords: biodegradable materials, hydrocolloids, starch, pectin, agar, carrageenan, micromorphological properties, mechanical properties

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INTRODUCTION

The important environmental issues that are extensively discussed at the present day include the salvation of nature from debris, the direction of development of the industry of biodegradable polymeric materials, and the rates of annual output [1–4].

It is known that most of the plastics used in the global production are based on products of processing of hydrocarbon-containing raw materials (propylene, ethylene, and other organic compounds). However, the further focusing on these technologies is attributed to the rise in prices for hydrocarbon-containing raw materials and negative impacts on the environment. In addition, the amount of plastic waste also increases; the waste disposal requires studies on the development of technologies for the production of stable biodegradable plastics for various purposes. This direction is consistent with the modern concept of improvement and development of the production of useful goods from waste. These raw materials include biological waste; prior to use, it must be processed and modified by physicochemical methods [5].

The previous studies were primarily focused on the design of polymeric materials that are resistant to environmental factors. At present, there is a new approach to the development of polymeric materials; it is based on maintaining their performance characteristics only in the period of their use. Despite all the difficulties faced by scientists, this direction of polymer materials science is part of their research interests, as evidenced by recent publications [6].

Modern biopolymers can be produced from both renewable natural resources and conventional raw materials, i.e., petrochemicals [7]. At present, films based on natural biodegradable polymers, such as cellulose, chitosan, gelatin, polypeptides, casein, and soybean, are commonly used in the food industry [8–11]. Of particular interest is starch because it is the cheapest raw material and the main sources of its industrial production are potatoes, wheat, corn, rice, maize, and some other plants [12–14].

Russian scientists have developed approaches to the preparation of biodegradable polymers based on enzymatic hydrolysate of keratin waste [15].

A research trend of high priority is the development of new approaches to the production of biodegradable polymers exhibiting a high rate of biodegradation, enhanced performance characteristics, and a low cost.

The aim of this study is to analyze the structural and mechanical properties and micromorphological features of polymer films based on hydrocolloids of

vegetable origin that are used for the production of biodegradable polymers.

OBJECTS AND METHODS OF RESEARCH

The objects of research are listed in Table 1.

The films of the studied components were prepared by drying solutions of the test substances. The solutions at a temperature of 60°C were poured onto preformed Teflon substrates (Fig. 1). Drying was conducted under gradual cooling for a few hours. To this end, the samples were placed in a TS-1/20-SPU thermostat (SKTB, Russia) heated to 60°C; after that, the heat supply was turned off and the samples were left in the thermostat overnight. In 10 h, the door of the thermostat was slightly open and the samples were dried for 2 days until the cessation of weight loss. The resulting films were cut in strips measuring 6 cm in length and 1 cm in width. The film thickness was measured using an MSC 25 electronic micrometer (Matrix, China). The thickness of the different films varied from 0.15 to 0.5 mm; this fact was taken into account in the calculations.

Table 1. Objects of research

Designation	Denomination
	Starches
S1	Acetylated distarch adipate C'Tex 06201 food supplement, Cargill B.V.
S2	Modified corn starch C'Tex 06205 food supplement, Cargill B.V.
S3	Corn starch, MP Biomedicals, CAS 9005-25-8
S4	Modified corn starch, Thermtex
	Pectins
P1	Pectin ARA 103, Yantai Andre Pectin
P2	Pectin ARA 104, Yantai Andre Pectin
P3	Pectin ARS 105, Yantai Andre Pectin
P4	Pumpkin pectin, ZAO NPO Evropa-Biofarm
	Carrageenans
C1	Refined kappa-carrageenan E-407, CAS 9000-07-1
C2	Semirefined iota-carrageenan, OOO Nord Plus
	Agar
A1	QP agar-agar, Panreac
A2	Agar, Helicon

To determine the structural and mechanical properties, the prepared films of hydrocolloids with given sizes were fixed using clamps with rubber heads and placed in an LR50KPlus universal tensile testing machine (Lloyd, United Kingdom). The measurement was conducted by uniaxial tension with breaking of the sample. Stress–strain diagrams were recorded in the experiment. The parameters of the diagrams were calculated using the software of the instrument.

The micromorphology of the films based on components for the production of biodegradable polymers was examined by atomic force microscopy in the tapping mode. The scanning of the samples was conducted on a SmartSPM atomic force microscope (AIST-NT, Russia) using fpN01S cantilevers (Nanotyuning, Russia); the radius of curvature was ≤10 nm. The resulting images were analyzed using the Gwiddion software (Czech Metrology Institute, Czech Republic).

For each scan of the film surface, two images are shown below: the surface topography and the image recorded in the amplitude registration mode. Since the film surface is extremely heterogeneous and characterized by a large height difference, the image based on the amplitude registration is more informative because it reveals more details.

RESULTS AND DISCUSSION

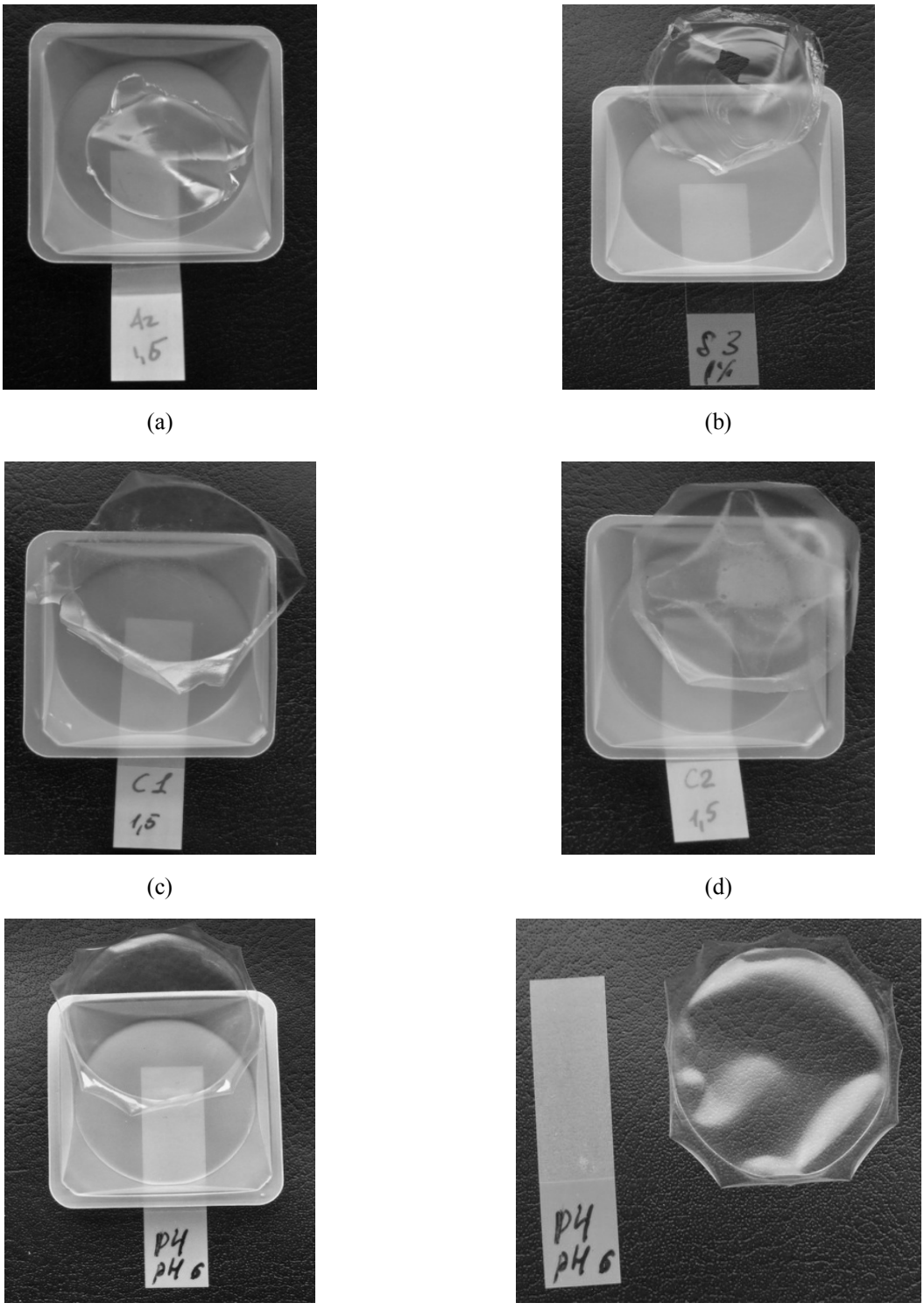
The mechanical properties of the films are among the most important characteristics of gelling agents used in mixtures for producing biodegradable materials. The substances used in the study are capable of forming their own films during drying of the solution. The parameters of the films determined in this study are Young's modulus, breaking stress, and breaking strain. These parameters can be used in predicting the properties of the final biodegradable polymers comprising the test substances.

The studies have revealed that the starch films are the most brittle; they are partially transparent, solidify nonuniformly and form a wavy surface (Fig. 1b). An increase in the starch concentration results in an increase in the brittleness of the material. The films of agar A1 and A2 are thick and dense; they are not brittle and undergo strong deformation during drying (Fig. 1a). The films of carrageenans C1 and C2 differ in properties (Figs. 1c, 1d). Kappa-carrageenan C1 forms very thin cellophane-like films, which are transparent and exhibit a fairly high tensile strength. Iota-carrageenan C2 forms thick brittle varicolored turbid films. Pectins, except for P3 (Fig. 1e), are dried to form smooth thin transparent films. The films of P1 are tinted; however, they preserve transparency. The pectin films, in common with the films of agars, are not brittle.

Despite the mild conditions of drying, some of the film samples were declared unfit for further examination after complete drying. This is primarily attributed to the fact that these compounds cannot retain water as a natural plasticizer. Thus, the films of most starches are extremely brittle; the films of some pectins and agars undergo strong deformation during drying; the carrageenan films do not dry uniformly.

The stress–strain diagrams were recorded for all classes of the test compounds: starches, pectins, agars, and carrageenans (Fig. 2). In general, the stress–strain diagrams derived for agar (A1 and A2) and pectin (P4) were typical for that sort of studies. This is indicative of the correct sample preparation and the possibility in principle to use solutions of these substances for preparing films suitable for research. The diagram for carrageenan C1 is not typical, which can be indicative of the nonuniform drying of the sample.

Some parameters of the resulting films, such as Young's modulus, breaking stress, and breaking strain, can be estimated from the stress–strain diagrams (Table 2).



(a) (b) (c) (d) (e)

Fig. 1. Examples of films of the test substances: (a) 1.5% agar-agar A1, (b) 1% starch S3, (c) 1.5% carrageenan C1, (d) 1.5% carrageenan C2, and (e) 1.5% pectin P4 prepared in a universal buffer solution with a pH of 6.

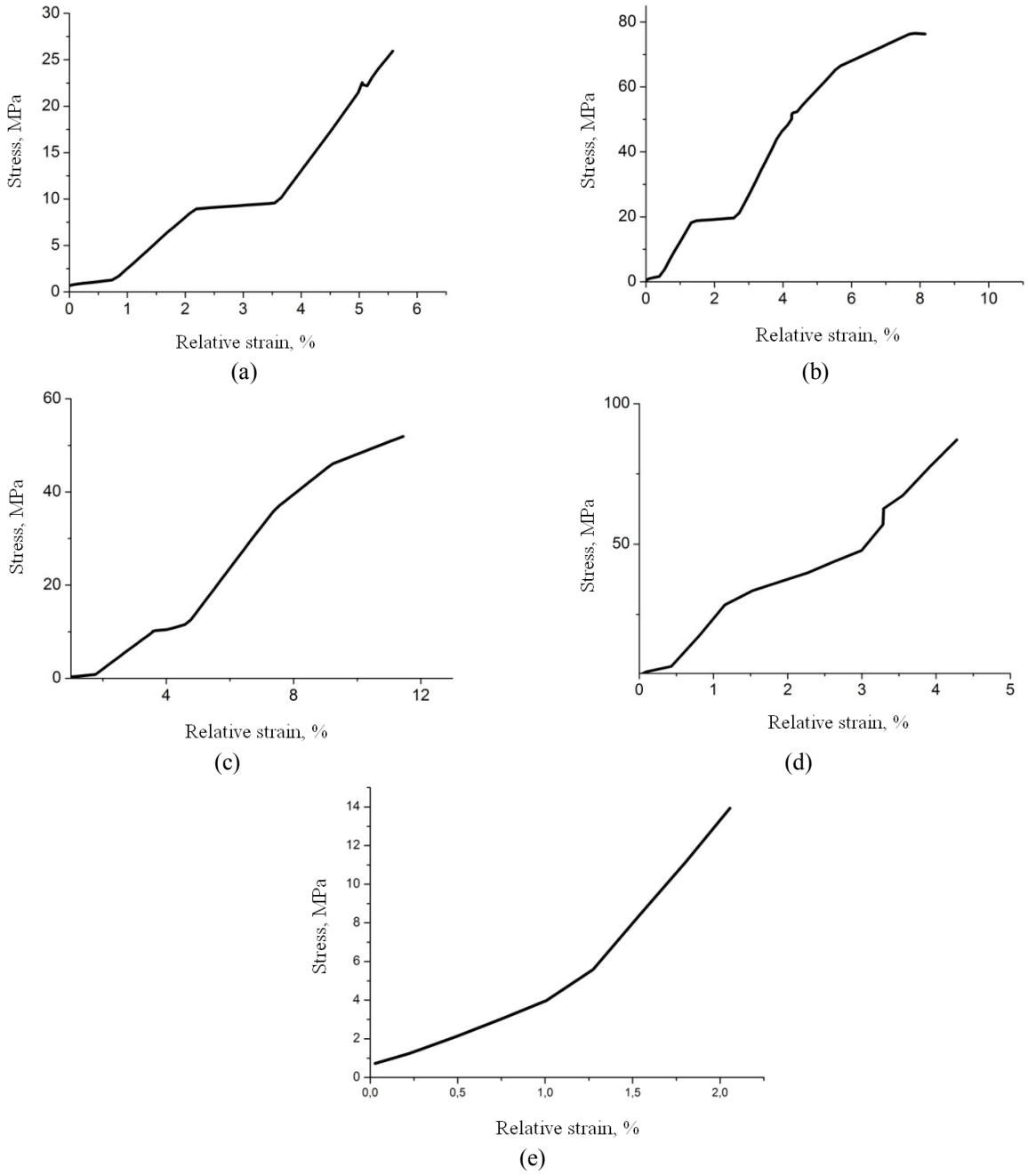


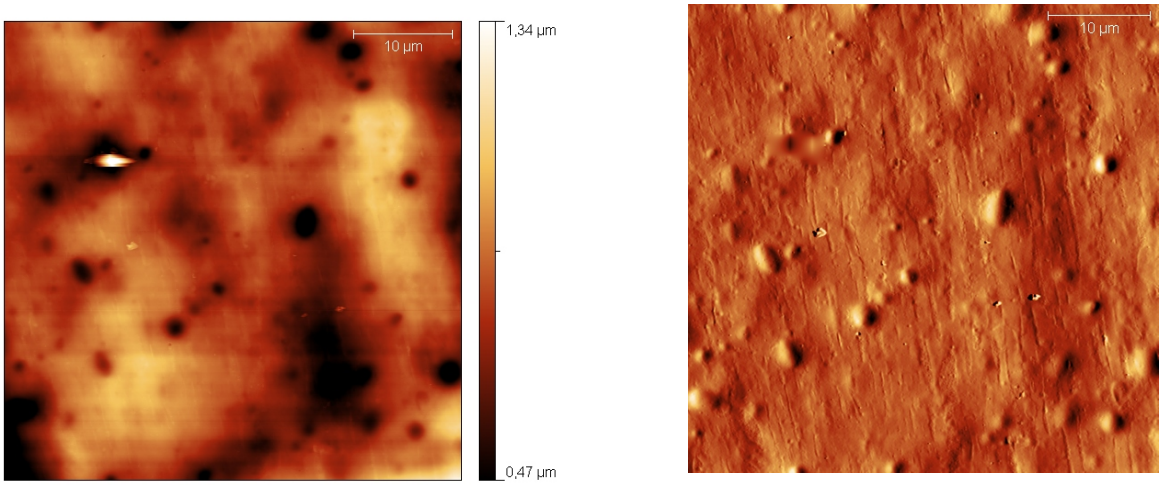
Fig. 2. Examples of stress–strain diagrams for the studied substances: (a) 1.5% agar A1, (b) 1.5% agar A2, (c) 1.5% pectin P1, (d) 1.5% pectin P4, and (e) 1.5% carrageenan C1.

Table 2. Structural and mechanical properties of films based on the components for the production of biodegradable polymers

Sample	Breaking stress σ_p, MPa	Breaking strain ε_p , %	Young's modulus *E*, MPa
C1-1	14.0	2.10	1025
C1-2	8.0	2.10	1250
C2-1	4.2	0.44	1600
C2-2	12.6	2.20	3800
A1-1	26.6	6.00	923
A2-2	77.0	8.00	2203
P1-3	52.0	11.50	904
P4-3	90.0	4.30	2200

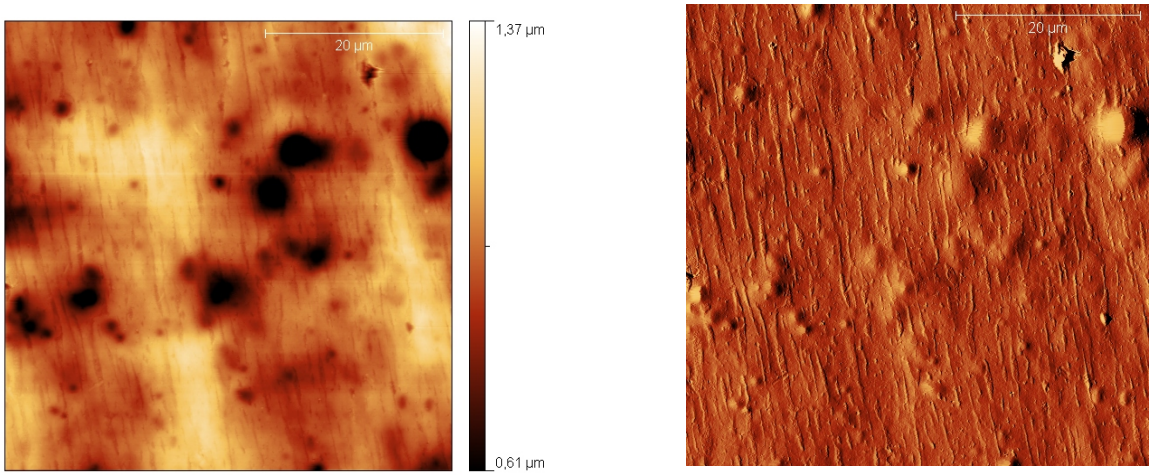
Films with the highest strength are formed from solutions of agar A2 and pectin P4; the breaking stress of these samples is greater than 75 MPa. The films of pectin P1 withstand the highest deformation before breaking; the breaking strain of these films is more than 10%. The lowest strength is exhibited by the films of carrageenans C1 and C2; for these samples, the breaking stress is lower than 15 MPa and the breaking strain is less than 2.5%.

Results of examination of the micromorphology of the films show that the samples of pectins with the highest degrees of esterification form films with transverse striations (Figs. 3, 4), which apparently results from the drying of the film.



(a) (b)

Fig. 3. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of pectin P1 in the amplitude registration mode.



(a) (b)

Fig. 4. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of pectin P4 in the amplitude registration mode.

A reduction in the size of the scanned surface, in the case of the samples of pectins P1 and P4, made it possible to visualize individual chains of polysaccharides (Figs. 5b, 6b). These images recorded in the amplitude registration mode show branched molecules of rhamnogalactouronan, which is one of the components of pectins. The size of the rhamnogalactouronan molecules varies in a range of up to 400 nm, which is consistent with published data [16, 17].

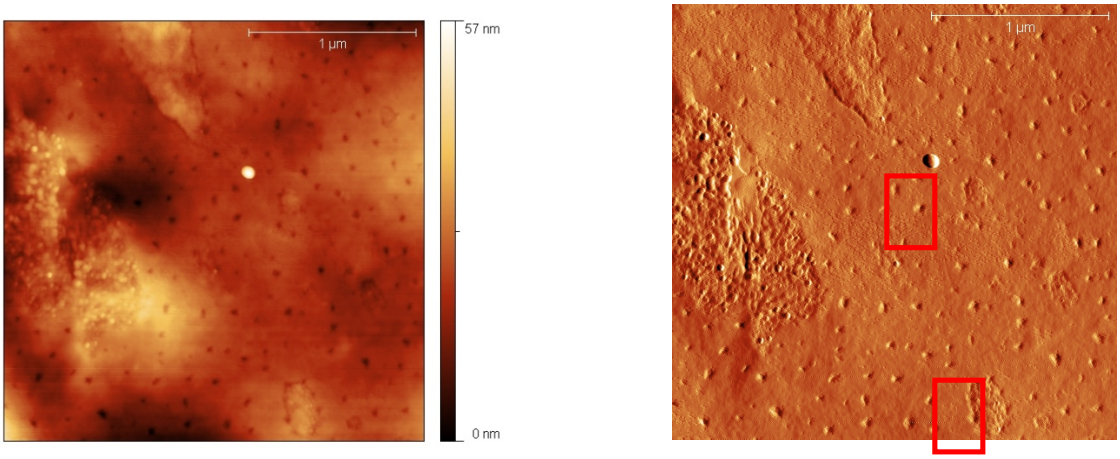
Unlike the samples of pectins P1 and P4, pectin P2 with a lower degree of esterification forms films with a grained surface (Fig. 7) in which individual chains of polysaccharides are not visualized.

The drying of a 1% aqueous solution of unmodified corn starch S3, similarly to pectins P1 and P4, results in the formation of a film with transverse striations caused by the formation of surface discontinuities (Fig. 8). At the same time, all the studied samples of modified corn starches are characterized by the formation of films in which smooth surface regions alternate with rough regions (Figs. 9–11). Apparently, modification of corn starch leads to an increase in the stability of the respective films and to the formation of surface microdiscontinuities during drying.

Analysis of the micromorphology of the films resulting from drying of a 1% aqueous solution of

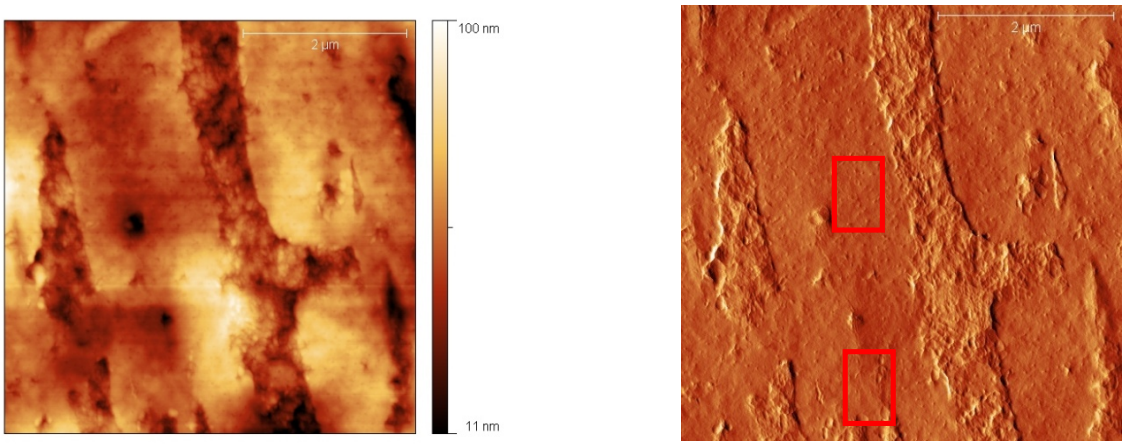
kappa-carrageenan C1 revealed wavy contractions; this fact explains why the films are readily torn off after tearing from the edge (Fig. 12).

According to the micromorphological studies, the surface of the films based on agars A1 and A2 was characterized by almost uniformly distributed roughnesses and the absence of transverse striations (Figs. 13, 14).



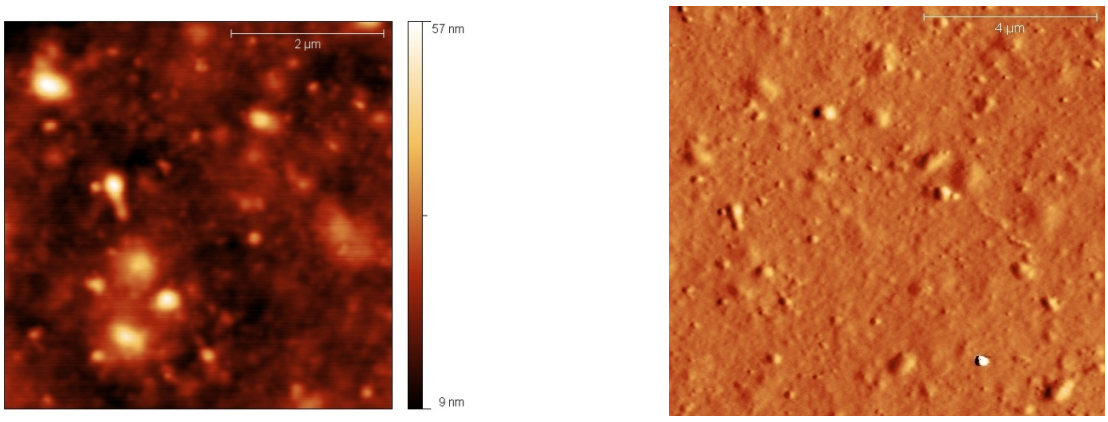
(a) (b)

Fig. 5. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of pectin P1 in the amplitude registration mode.



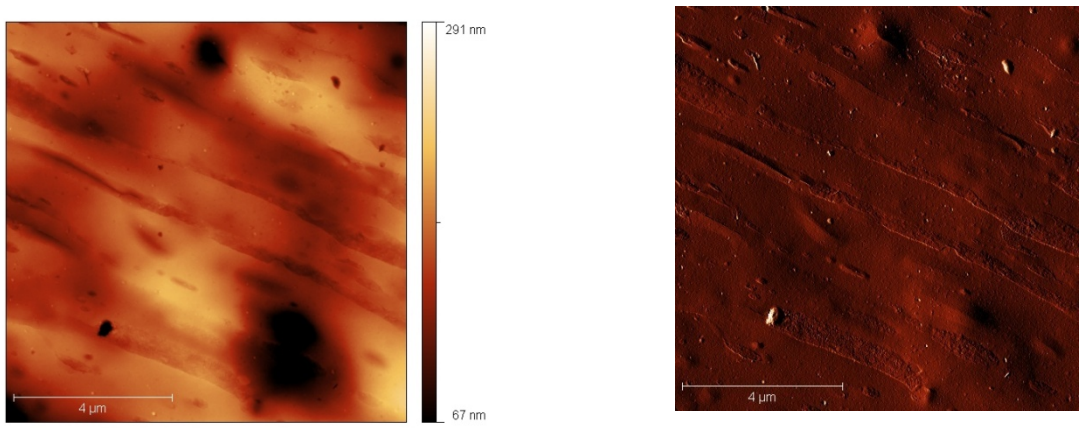
(a) (b)

Fig. 6. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of pectin P4 in the amplitude registration mode.



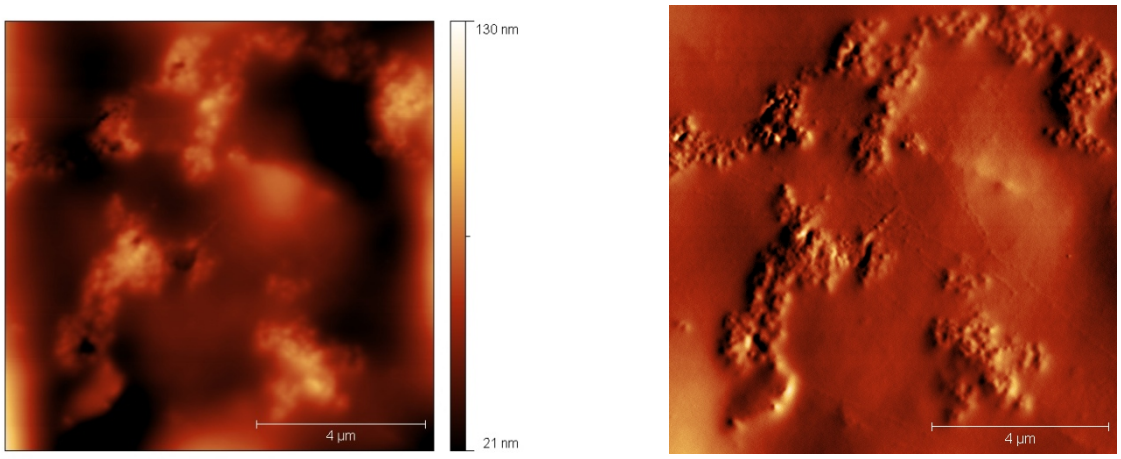
(a) (b)

Fig. 7. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of pectin P2 in the amplitude registration mode.



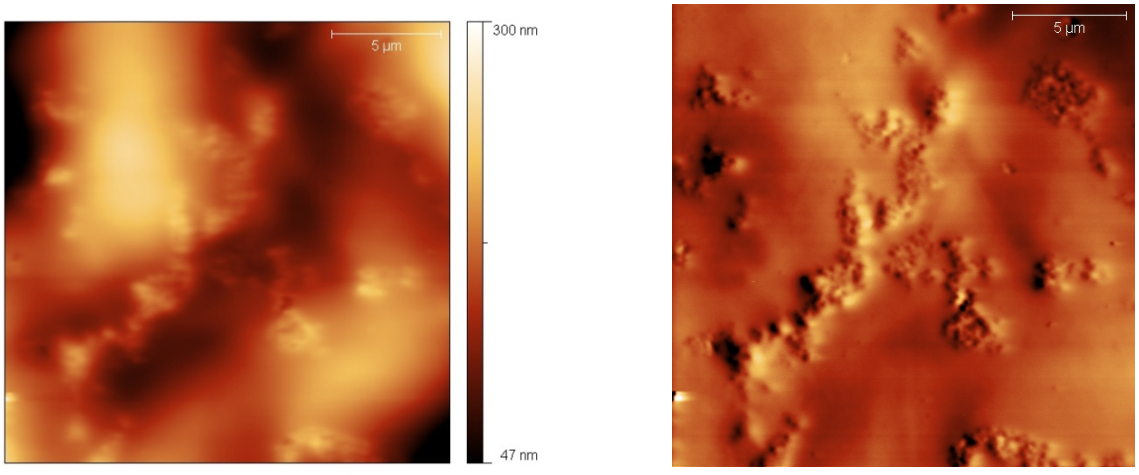
(a) (b)

Fig. 8. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of native corn starch S3 in the amplitude registration mode.



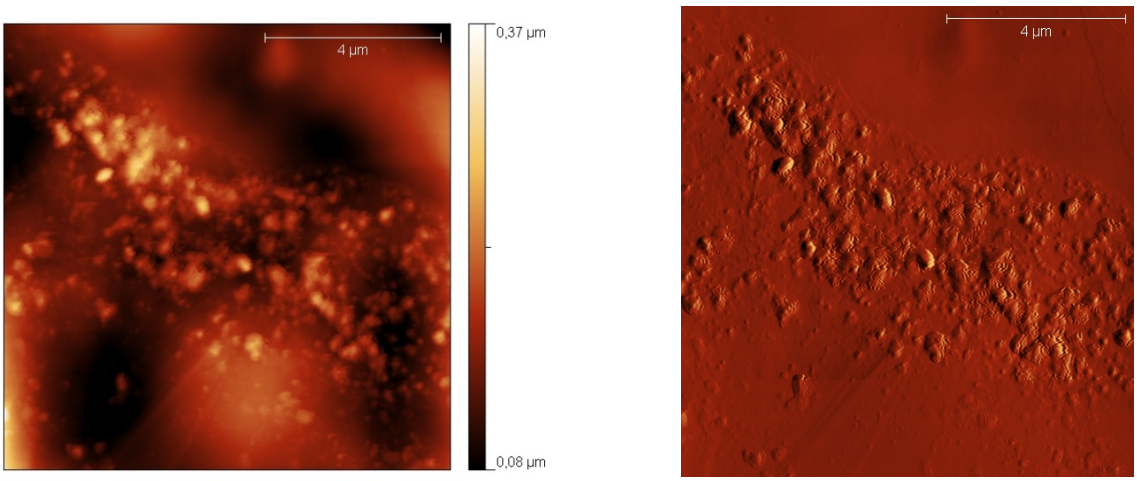
(a) (b)

Fig. 9. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of modified corn starch S1 in the amplitude registration mode.



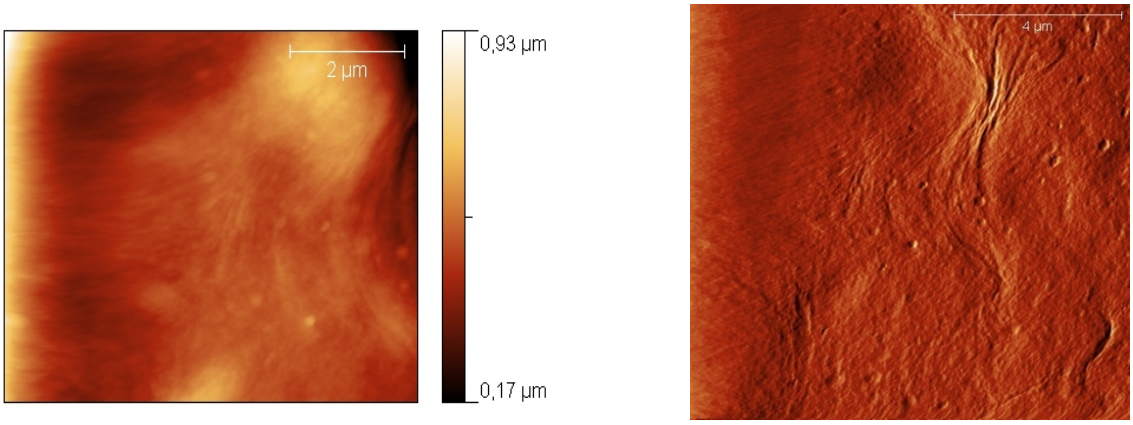
(a) (b)

Fig. 10. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of modified corn starch S2 in the amplitude registration mode.



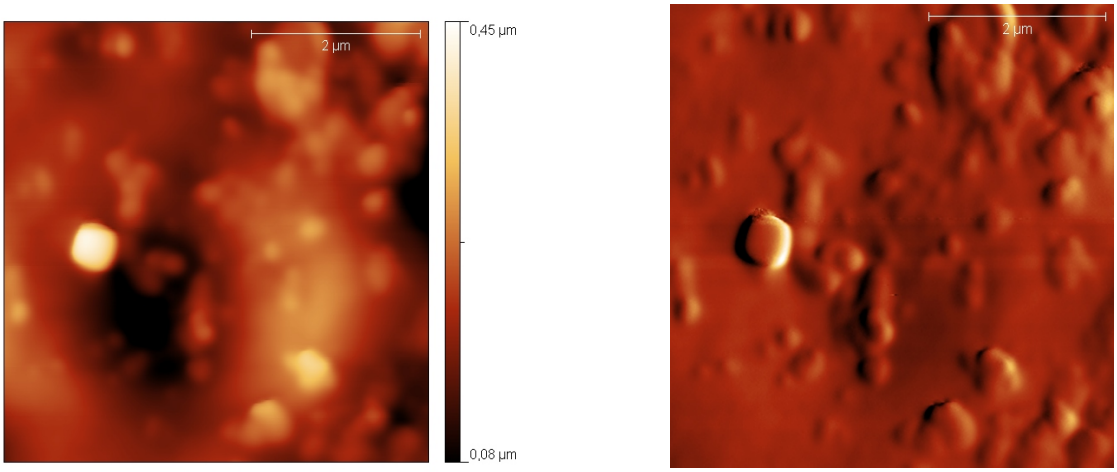
(a) (b)

Fig. 11. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of modified corn starch S4 in the amplitude registration mode.



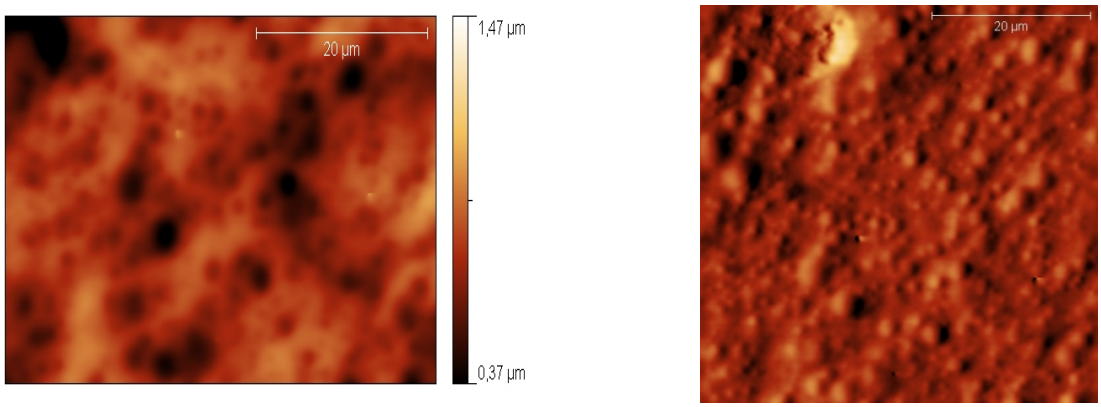
(a) (b)

Fig. 12. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of kappa-carrageenan C1 in the amplitude registration mode.



(a) (b)

Fig. 13. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of agar A1 in the amplitude registration mode.



(a) (b)

Fig. 14. (a) Topography and (b) image of the surface of the film prepared by drying a 1% aqueous solution of agar A2 in the amplitude registration mode.

Results of the structural and mechanical analysis and microscopic studies suggest the following.

1. By drying solutions under mild conditions, films for all the studied components—agar-agar, starches, carrageenans, and pectins—have been prepared. It has been found that some components are incapable of independently forming films suitable for examination of structural and mechanical properties and morphological features. This fact limits their use in the composition of technological mixtures for producing biodegradable polymers.

2. Parameters of the prepared films for all classes of the studied components have been determined. With respect to strength and suitability for use in films of individual components, all the studied components can be arranged in ascending order as follows: starches, carrageenans, pectins, agar.

3. Analysis of the structural and mechanical properties of the films has revealed the best results for the samples based on pectin P1 and agar A2. The breaking stress of these films is 52 and 77 MPa, respectively. The breaking strain is 11.5 and 8.0%, respectively.

4. Analysis of micromorphology has revealed the formation of surface microdiscontinuities in the films based on high methoxyl pectins P1 and P4 and unmodified corn starch S3 and the formation of wavy folds in the case of the films of kappa-carrageenan C1; these folds are formed during drying and decrease the tensile strength of the respective films.

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