Досліджено вплив органічних пластифікаторів (сечовина, глюкоза, фруктоза, сорбіт, сахароза, гліцерин) на органолептичні властивості біодеградабельних плівок на основі нативного або модифікованого крохмалю та желатину за допомогою комплексного показника якості, а також на відносне подовження та міцність. ІЧ-спектроскопією встановлено, що сечовина вступає у хімічну взаємодію, що позитивно впливає на показник міцності досліджуваних плівок. Результати дозоляють прогнозувати властивості плівки залежно від її складових

Ключові слова: біодеградабельні плівки, органічні пластифікатори, відносне подовження, міцність, ІЧ-спектроскопія

Исследовано влияние органических пластификаторов (мочевина, глюкоза, фруктоза, сорбит, сахароза, глицерин) на органолептические свойства биоразлагаемых пленок на основе нативного или модифицированного крахмала и желатина с помощью комплексного показателя качества, а также на относительное удлинение и прочности. ИК-спектроскопией установлено, что мочевина вступает в химическое взаимодействие, что положительно влияет на показатель прочности исследуемых пленок. Результаты позоляют прогнозировать свойства пленки в зависимости от ее составляющих

Ключевые слова: биоразлагаемый, пластификатор, относительное удлинение, прочность, ИК-спектроскопия

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INFLUENCE OF ORGANIC PLASTICIZERS ON SENSORY, PHYSICAL-MECHANICAL PROPERTIES AND CHEMICAL CHANGES OF BIODEGRADABLE FILMS

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1. Introduction

The following components as filmformer, plasticizer and solvent are constituents of biodegradable films [1]. Each group mentioned above contains a number of substances that are used for the production of films nowadays. There are some studies on filmformers of different nature [2]. Water or alcohol are usually used as solvents. However, there is no comparative analysis on the use of plasticizers, both of organic (carbohydrates, polyols, carboxylic acids, acid amides, etc.) and inorganic (salt) nature. Different nature of plasticizers is a prerequisite for chemical reaction in film making that has a positive or negative impact on the quality of biodegradable films.

Main characteristics that define properties of biodegradable films are organoleptic and physico-mechanical properties, namely tensile strength and elongation.

Given the wide range of plasticizers used, there is a need to study the most common and affordable plasticizers on the quality of films based on starch or modified starch and gelatin.

The aim of the research is to obtain comparative characteristics of main organoleptic and physico-mechanical properties depending on the organic plasticizer in order to predict the properties of new raw materials for making of biodegradable films based on natural polymers.

2. Literature review and problem statement

Plasticizers are an important class of compounds that are widely used for the production of polymeric materials as additives, which improve flexibility and elasticity of biodegradable films, including edible ones. They are located between the chains of film-forming material, reducing the intermolecular force that leads to better flexibility and elasticity of the films. The introduction of plasticizers can increase the diffusion coefficients for gases or water vapour permeability, as well as reduce the cohesion and tensile strength of polymer films. The degree of plasticity of polymers is largely dependent on the chemical structure of plasticizer, its chemical composition, molecular weight and functional groups.

Plasticizers for films based on biopolymers can be divided into two groups-soluble and insoluble in water. The type and amount of plasticizer influence the formation of the film made of polymer aqueous dispersions. Hydrophilic plasticizers are soluble in water, when they are added to the polymer dispersion and when in high concentrations they can lead to an increase in the diffusion of water in the polymer. In contrast, hydrophobic plasticizers can close the micropores in the film, which reduces water absorption. However, water-insoluble plasticizers can cause the phase distribution, which leads to loss of plasticity or also to the formation

of gaps in the film during drying. As a result, the level of vapour increases. Full absorption of insoluble plasticizer can be achieved by optimal speed of mixing of the polymer dispersion with plasticizer.

The most common food plasticizers used in films are: monosaccharides (glucose), disaccharides (sucrose), oligosaccharides, polyols (such as sorbitol, glycerol, mannitol, glycerol derivatives, polyethylene glycol) and also some lipids and their derivatives (phospholipids, fatty acids, surfactants).

Table 1 shows the main components of films and all kinds of plasticizers, which are mostly used nowadays [2].

Table 1

Plasticizers used for forming films

Type	Components	Plasticizers	References
Films based on poly-saccharides	Citric acid-modified pea starch and citric acid-modified rice starch	Glycerol	[3]
	γ-carrageenan edible film	Glycerol and water	[4]
	Tapiok starch, oat starch	Glycerol, sorbitol	[5, 6]
	Chitosan films	Glycerol, ethylene glycol, polyethylene glycol, propylene glycol	[7]
	Hydroxypropyl methylcellulose-beeswax	Glycerol and mannitol	[8]
	Cellulose made of sugarcane bagasse and cellulose acetate	Residue xylan acetate	[9]
	Glucomannan	Sorbitol and glycerol	[10]
	Alginate/pectin	Glycerol	[11]
Films based on proteins and lipids	Caseinate-pullulan	Water and sorbitol	[12]
	β-lactoglobulin	Sorbitol, glycerol, polyethylene glycol, ethylene glycol, propylene glycol, sucrose	[13]
	Keratin	Glycerol	[14]
	Fish skin protein	Fatty acid, esters of sucrose, glycerol, sorbitol	[15]
	Gelatin	Sucrose, oleic, citric, tartaric, malic, fatty acids, polyethylene glycol, sorbitol, mannitol, ethylene glycol, diethylene glycol, diethanolamine, glycerol	[16, 17]

The properties of biodegradable films based on oat starch in combination with various plasticizers were investigated. Hydrophilic plasticizers (glycerol, sorbitol and urea) increase permeability and moisture absorption properties of such films, without changing their mechanical properties.

In another study, the same team of researchers studied the effect of sucrose and a mixture of glycerol/sorbitol, glycerol, urea and sorbitol as plasticizer on the microstructure, absorption of moisture, vapor permeability and mechanical properties of oat-starch films aged at different conditions of relative humidity [6]. The type of plasticizer has no significant effect on the moisture content of the films. The films were the most fragile when adding sucrose and at a low relative humidity, while the films with glycerol were the most hygroscopic ones. Films without plasticizer absorb less moisture and show high vapor permeability, indicating the effect of antiplasticity.

Scientific publications don't contain research on urea as a plasticizer for biodegradable films and comparative analysis of the most common plasticizers (sucrose, sorbitol, glycerin and others) hasn't been done. Besides, analysis of publications showed that chemical reaction between plasticizer and filmformer hasn't been studied yet. The use of infrared spectroscopy to study the properties of the film in the cited literature [18] does not explain chemical reaction between film constituents.

3. Research aim and tasks

The aim of the research is to determine the effect of organic plasticizers (such classes of compounds as carbohydrates, polyols, acid amides) on the quality of biodegradable films.

To achieve this aim it is necessary to:

– develop a complex organoleptic characteristic of quality;

– determine changes in tensile strength and elongation depending on the plasticizer;

– ascertain a fact of chemical reaction of the film constituents with plasticizer using infrared spectroscopy.

4. Materials and Methods

4. 1. Materials and equipment used in the experiment

The films were made of corn starch and chemically modified starch made of high-amylose corn (E1420), instant gelatin (E441) (Fig. 1).

a *b*

Fig. 1. Samples of filmformers:
a — corn starch; *b* — modified starch

Glycerol (E422), sorbitol (E420), glucose, fructose, sucrose, urea (E927b), as well as their different combinations: urea and glycerol, sorbitol and glucose, urea and sorbitol, sucrose and urea were selected as plasticizers. Samples were made in the same conditions: film-forming material in solutions was heated separately for dissolution (gelatin, modified starch) or gelatinization (corn starch), and then plasticizer

was added. The films (Fig. 2) were placed on teflon surface and were kept indoors to dry completely (24–36 h.).

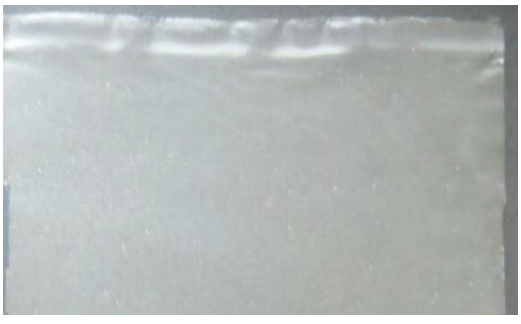

Fig. 2. Sample of film made of starch, gelatin and one of studied plasticizers

4. 2. Method of determining the performance properties of samples

Qualimetric assessment was done according to the methodology [19].

Tensile strength (TS, MPa) and elongation percentage (Ɛ, %) were valued according to ASTM standard method D 882-88 on F-1000 tensile testing machine in the Institute of Chemistry of High-molecular Compounds of the National Academy of Sciences of Ukraine [20].

IR spectra of the samples were recorded by Bruker Tensor 37 spectrometer with Fourier transformation in wave numbers 4000–400 cm^{-1} with 4 cm^{-1} resolution. The film spectra were recorded by the total reflection method.

5. The results of study how organic plasticizers influence organoleptic, physical and mechanical properties and chemical changes of biodegradable films

Plasticizer is a very important component that affects the physical and mechanical properties of the films. A film is easily removed from the surface with the help of plasticizer. When plasticizer is added, intermolecular forces along the polymer chains are reduced and this improves flexibility, elasticity, and reduces strength and breaking strength of the film. On the other hand, to provide barrier properties of the film, the polymer should have high crosslinking density. When adding plasticizer, intermolecular force decreases, film structure gets thinner and softer effectively and mobility of the chain and intermolecular distances increase [21]. Thus, the addition of plasticizer can lead to a relative increase of diffusion coefficients for gas or steam and reduce adhesion, breaking strength and temperature of film glazing [22]. Plasticizer should be compatible with polymer and, if possible, be well soluble in the solvent (to avoid premature separation of film during drying). In other words, effective plasticizers must be close to the structure of polymers [23].

The plasticizers, chosen in the experiment, meet the requirements.

The experimental films were investigated by the organoleptic characteristics by calculating the complex indicator (K).

Table 2 shows the input data for calculation of complex indicator of film quality.

All experimental films are colourless; transparent and have a neutral odor. Complex indicator of quality is the worst (0.7) for films where urea is plasticizer, which gives a slightly bitter flavour to samples. The films, where plasticizers are glucose, sucrose and fructose, the complex indicator is 0.9, have a sweet flavour. All other films have the highest complex indicator – 1.

Table 2

Organoleptic indicators of edible films

Indicator	Characteristics	Coefficient of significance
Flavour	Neutral, without strange favour	0.5
Odour	Corresponds to the odour of raw material used, strange odour is not allowed	0.2
Surface	Smooth, glossy or lustreless	0.1
Colour	Colourless	0.1
Transparency	Transparent	0.1

Physical and mechanical properties of sucrose films are fragile and cannot be measured on a tension testing machine, this fact is supported by literature sources [2]. Glucose makes the film friable, but no so much, as water absorption of this substance is higher and, it consequently better retains moisture, which, in its turn, also acts as a plasticizer. The films with glucose on chemically modified food starch with high-amylose corn are less fragile comparing to the films on corn starch. Amylopectin in the corn starch does not swell fully, creating a less extensive film matrix. Branched amylopectin structure comprises 1.6-glucosidic bond and needs more time to absorb water compared to unbranched amylose structure containing only 1.4-glucosidic bond.

The results of changes in film strength and stretch dependent on plasticizer are shown in Fig. 3. The value for sucrose plasticizer is not displayed on the graph because these films are fragile, as was noted above.

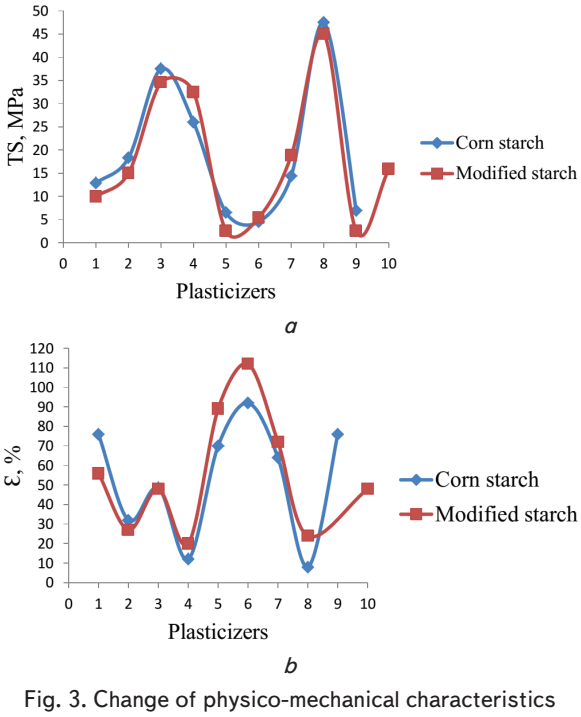

Fig. 3. Change of physico-mechanical characteristics dependent on plasticizer: *a* – tensile strength; *b* – elongation; 1 – glycerol, 2 – sorbitol, 3 – glucose, 4 – fructose, 5 – urea, 6 – urea+glucose, 7 – urea+sorbitol, 8 – sorbitol+glucose, 9 – urea (tap water), 10 – urea+saccharose

The films in combination of sorbitol and glucose, fructose and glucose are the strongest. The most stretching are samples in combination of urea and glucose. The least strong are the films of urea as the other experimental plasticizers are composed of OH-groups that contribute to the formation of hydrogen bonds which hold the film. Films with sucrose plasticizer are very fragile.

The experimental results (Fig. 3) indicate that different types of plasticizers have the same effect on the strength and stretch regardless the type of starch (corn starch or chemically modified food starch from high amylose corn) as correspondent curves are parallel on the diagram.

According to Fig. 3 different types of starch have no significant effect on the physical and mechanical properties of the films. Different strength of samples of films with urea plasticizer can be explained by its chemical interaction that is confirmed by IR spectroscopy.

Mentioned plasticizers, except urea, don't react with the constituents (starch and gelatin), as confirmed by IR spectroscopy: the example is films with sorbitol and fructose (Fig. 4) compared with the output substances Fig. 5. IR spectrum of high amylose starch is not shown, as it does not contain other functional groups compared with corn starch.

IR spectra are obtained for all films with experimental plasticizers.

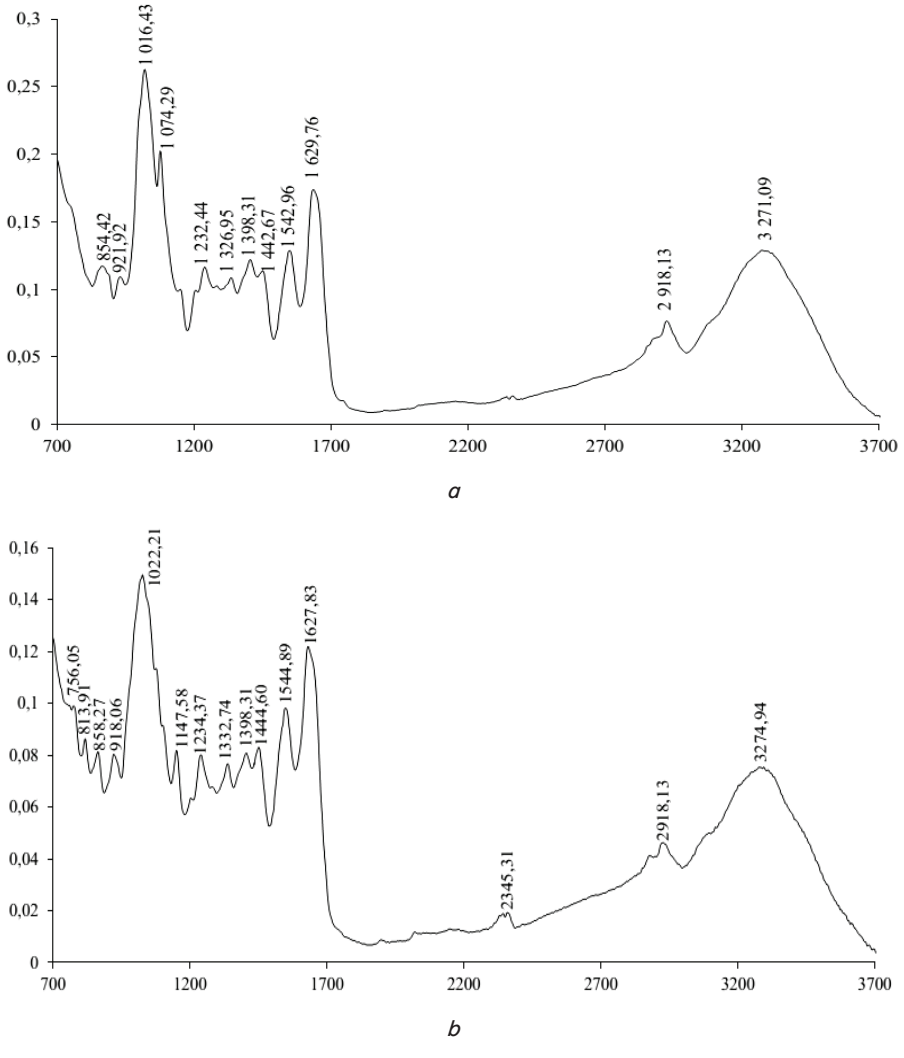

Fig. 4. IR spectra of samples of films on corn starch with gelatin and plasticizer: *a* — sorbitol, *b* — fructose

For the film with sorbitol (Fig. 4, *a*) characteristic bands are at 3271,09 cm^{-1} (stretching vibrations of OH- and NH-groups), which due to association of hydrogen bonds of these groups are shifted in a weaker field compared with the spectra of starch (Fig. 5, *b*) and sorbitol (Fig. 5, *d*), where the stretching vibrations of OH-groups are at 3409,95 cm^{-1} and 3313,52 cm^{-1}, respectively. Characteristic bands of NH-groups of gelatin are at 3415,74 cm^{-1} (Fig. 5, *a*).

It should be noted that the CH-group stretching vibrations in the spectrum of film with sorbitol (Fig. 4, *a*) are at 2918,13 cm^{-1}, and in the spectrum of starch at 2923,92 cm^{-1} (Fig. 5, *b*) and in the spectrum of sorbitol at 2927,78 cm^{-1} (Fig. 5, *d*).

The similar situation is for the film with fructose (Fig. 4, *b*). Characteristic bands of OH-, NH-groups are at 3274,94 cm^{-1} and fructose – 3375,24 cm^{-1}, they are shifted towards weak field, as in the previous film. As for the CH-groups stretching vibrations, they are constant, in this case at 2918,13 cm^{-1} for the film and at 2929,70 cm^{-1} for fructose (Fig. 4, *c*). The presence of vibrations of each of the above groups indicates that the chemical interaction between them doesn't occur.

The similar situation is observed for other film compositions based on corn starch, chemically modified high amylose corn, glycerol, glucose, sucrose and double combinations of these plasticizers.

Another situation is observed in films with urea as a plasticizer. IR urea spectrum shows a double peak (Urea range Fig. 5, *e*), which is at 3340,52; 3436,95 cm^{-1}, which is typical for the primary amino group [21]. In the spectrum of the film, which consists of starch, gelatin and urea there is no evident double peak there, there are only traces of it of low intensity at 3317,37; 3421,52 cm^{-1}, that confirms the chemical interaction of urea with carboxylic groups of gelatin. The strength of this film is 7 MPa (Fig. 3, *a*). While the strength of the corn starch, gelatin and urea films is 5.5 MPa, because the urea amino group didn't react in full, as it is evident from the spectrum of the film having peaks at 3238,30 and 3415,74 cm^{-1} (Fig. 6, *a*).

There are the most intensive peaks on the film with corn starch (Fig. 6, *b*) at 3323,16 and 3423,45 cm^{-1}, indicating a lower degree of interaction with gelatin and urea that is confirmed by strength, which is only 2.5 MPa (Fig. 3, *a*).

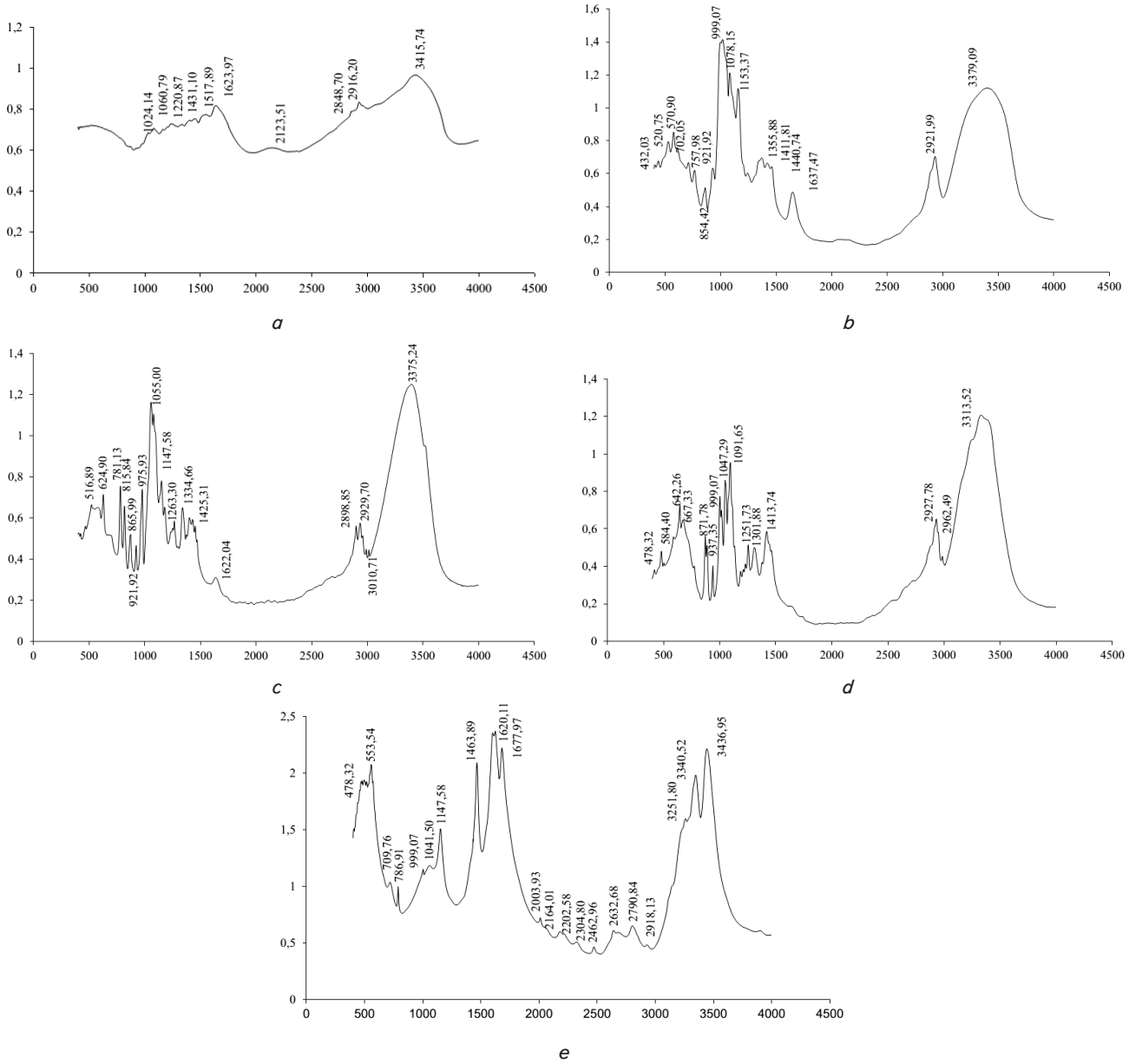

Fig. 5. IR spectra of some output substances for the film with different plasticizers:
a — gelatin, *b* — corn starch, *c* — fructose, *d* — sorbitol, *e* — urea

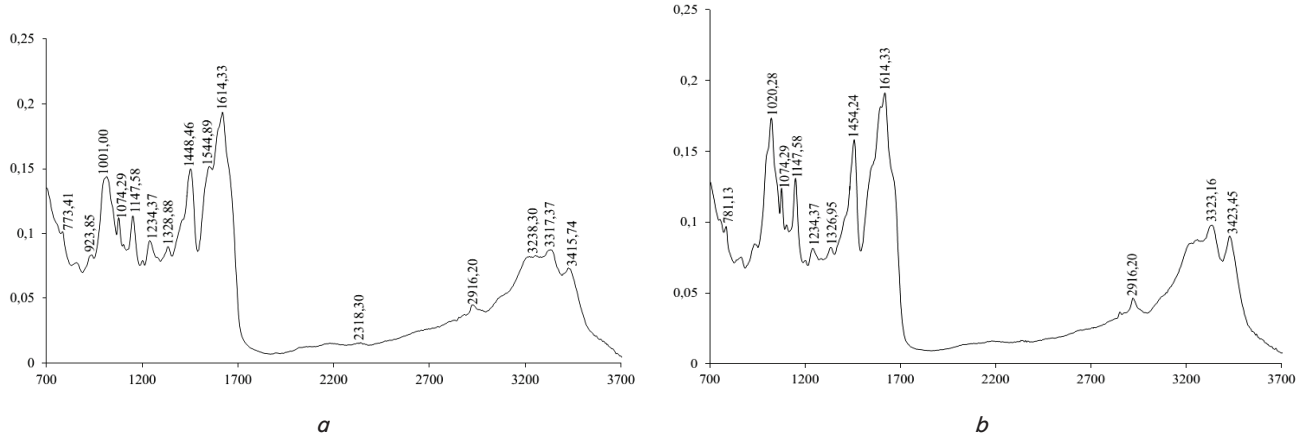

Fig. 6. IR spectra of films with different types of starches, gelatin and urea:
a — on chemically modified starch made of high-amylose corn, *b* — on corn starch

6. Discussion if organic plasticizers influence the properties of biodegradable films

In determining the impact of organic plasticizers on the quality of biodegradable films, it is found that sucrose makes films more friable that is supported by published articles [2]. That is why there is no data on physical and mechanical properties of films with this plasticizer on Fig. 3, *a, b*.

As film constituents are food stuffs, the film is also edible. Calculation of complex indicator of quality based on qualimetric assessment showed that film with urea scored the lowest (0.7) grade. However, if the edible film with urea is considered as a constituent of food, it tastes less bitter in the product than in the film.

The chemical changes in films that occur in their making are studied by IR spectroscopy. Previous studies made by this method [1, 18], unfortunately, do not give a full interpretation of the spectra. The detailed analysis of the spectra showed the presence of chemical reaction between the primary urea amino group and carboxylic group of gelatin (Fig. 5, *e*; 6, *a*). Chemical reaction resulted in film hardening: values of tensile strength increased to 7 MPa unlike 5.5 MPa in the film where chemical reaction did not occur (Fig. 3, *a*).

So, it is possible to control physico-chemical properties of the films choosing such chemically active substances that will react with the film formers.

The use of complex compositions of plasticizers in order to eliminate the shortcomings of each separate organic plasticizer is grounded by the authors in the research. The developed compositions of urea+glucose, sorbitol+urea, urea+sucrose, decrease the total concentration of urea in the system that prevents chemical reaction between gelatin and urea. The sorbitol+glucose combination didn't influence positively on the quality of the film. That's why urea is the most effective plasticizer for biodegradable films, in spite of the lowest complex organoleptic characteristics. Firstly, such film is not always edible, and secondly, the light bitter taste can be easily concealed behind the taste of the product. However, these assumptions require further research.

The obtained results allow to predict the properties of the films depending on the type of raw material, that will also extend the range of ingredients used.

The detailed analysis of IR spectra of films and raw materials allows to collect data for further analysis of qualitative changes in the film constituents.

The research on organic plasticizers should be continued in selecting of substances that have biological value. Special attention should be paid to hydrophobic organic plasticizers.

7. Conclusions

1. The complex organoleptic indicator of quality is the highest score 1 for organic plasticizers such as glycerin and sorbitol; 0.9 for films with such plasticizers as glucose, sucrose and fructose; 0.7 for films with urea as plasticizer.

2. The changes in tensile strength and elongation depending on the plasticizer are calculated. The strongest are the films with such plasticizers as sorbitol and glucose, fructose and glucose. The highest elongation is observed in samples combinations of urea and glucose plasticizers. The least strong are the films with urea as plasticizer. The obtained results can be explained by properties of organic compounds used as plasticizers.

3. IR Spectroscopy was used to determine that carbohydrates (fructose, glucose, sucrose) and polyhydric alcohols (glycerin, sorbitol) did not enter into chemical reaction with film forming agents (starch and gelatin). Only acid amides (urea) react with gelatin strengthening biodegradable films.

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