

# EFFECT OF PLASTICIZERS ON MOISTURE ABSORPTION AND MECHANICAL PROPERTIES OF AGAR FILMS

O.N. Pozharitskaya<sup>1</sup>, PhD, A.N. Shikov<sup>1\*</sup>, Dr.Sci.,  
D.V. Demchenko<sup>1</sup>, PhD, E.V. Flisyuk<sup>2</sup>, Dr.Sci., V.G. Makarov<sup>1</sup>, Dr.Sci.

<sup>1</sup>Saint-Petersburg Institute of Pharmacy,  
Leningrad region, Vsevolozhsky district, 188663, Kuzmolovo P 245, Russia

<sup>2</sup>Saint-Petersburg State Chemical-Pharmaceutical Academy,  
197376, St. Petersburg, Prof. Popova, 14, Russia

**Introduction.** Polysaccharide-based polymers have a great potential of using in pharmaceutical industry and biotechnology. The advantages of agar versus other gelling agents are its higher stability at low pH values and elevated temperatures. Plasticizers increase the flexibility of the film and prevent its crack during processing and storage.

**Objective:** to investigate the effects of different types of plasticizers and their concentration on the kinetic and static absorption of moisture and on the mechanical properties of agar films.

**Methods.** The effect of plasticizers (glycerol, sorbitol, citric acid, sodium citrate, and mixtures thereof) and their mixtures on the absorption of moisture and the mechanical properties of agar films was investigated when the plasticizers were used at various concentrations according to the experiment design.

**Results.** Addition of glycerol to the films increased the rate of absorption and the amount of absorbed moisture when stored under conditions of higher relative humidity. At the same time, the films containing citric acid and sodium citrate absorbed moisture more slowly and in smaller quantities, especially at a lower relative humidity. There was the thinnest water monolayer (0.035-0.036 g water/g film) on the films containing citric acid and sodium citrate as a plasticizer. When 3.6 wt.-% glycerol and 0.6 wt.-% sorbitol were added to the films, the monolayer thickness increased to 0.065 g water/g film. The highest thickness of the water monolayer (0.158 g water/g film) was observed when 4 wt.-% sorbitol was added. The addition of citric acid to the agar films lowered their strength. While the higher levels of glycerol (up to 5 wt.-%) and sodium citrate (up to 2.5 wt.-%) increased the strength of the films. The strength of agar films with sodium citrate increased by adding of citric acid.

**Conclusion.** The results of the investigation can be used in the pharmaceutical and biotechnological industries when manufacturing agar capsules or an agar-agar pack.

**Key words:** agar films, citric acid; glycerol, sodium citrate, sorbitol.

E-mail: alexs79@mail.ru

## INTRODUCTION

Polysaccharides based biopolymers have a large potential for application in pharmaceutical industry, biotechnology, consumer packaged goods, etc. since they meet a number of specific functional requirements as such as moisture barrier, solute and/or gas barrier, water solubility, color and appearance, good mechanical and rheological characteristics, non-toxic [1].

Red marine seaweeds (*Rhodophyta*) are the source of promising biopolymer agar, which has a unique structure. Agar is a gel-forming polysaccharide, with the main chain consisting of alternating 1,3-linked  $\beta$ -D-galactopyranose and 1,4-linked 3,6 anhydro- $\alpha$ -L-galactopyranose units [2].

Most applications for agar are based on its gelling ability and the fact that it is more stable to low pH and high-temperature conditions compared to other gelling systems. This thermoplastic, biodegradable and biocompatible polysaccharide has shown high mechanical strength with moderate water resistance as packaging material [3,4] and has been used in blends with other biopolymers such as gelatin, starch, soy or milk protein to improve the mechanical and water barrier properties [5-7]. Agar was proposed as gelatin substitute for the preparation of soft capsules [8].

Recently, a number of works dealt with the addition of plasticizers to biopolymer films [9,10]. Plasticizers increase film flexibility since they work as spacers between polymer chains, decreasing intermolecular forces. Plasticizers are generally small molecules such as polyols like sorbitol, glycerol, xylitol, maltitol. They avoid cracking of the film during handling and storage [11], affect gas, water vapor and solute permeability and absorption characteristics [12]. Other plasticizers such as oleic acid, citric acid, tartaric acid, malic acid were also applied to gelatin films, modifying their mechanical and barrier properties [13]. Citric acid has been used as an additive in corn starch films to promote crosslinking [14]. It contributes to the production of a material with increased tensile strength and reduced elongation [15]. The addition of citric acid to thermoplastic starch resulted in considerably lower diffusion coefficients and lower moisture absorption [16].

The moisture content in agar films can affect significantly its physical and barrier properties. Agar-based films tend to absorb water at elevated relative humidity (RH) conditions. Although there are studies focused on absorption properties of edible films [13, 17, 18], little information is available on the effect of type of plasticizer on absorption characteristics of agar films.

The objective of this study was to evaluate the effect of plasticizer type and concentration on kinetic and static moisture absorption characteristics and on mechanical properties of agar films.

## EXPERIMENTAL

### Materials

An agar powder (agar-agar 900, Proagar S.A., Chile) was used for film preparation. Glycerol, sorbitol, citric acid, and sodium citrate were purchased from Vekton (St.-Petersburg, Russia).

### Film casting

Agar film-forming solution was prepared by dissolving agar (5 g/100 ml) in distilled water. Four types of plasticizer (glycerol, sorbitol, citric acid and sodium citrate) were added to the solution in concentration as shown in Table 1. Composition 1 without plasticizers was served as control. The mixtures were stirred to obtain a good blend and the films made by casting and drying afterward at 40°C in a drying oven model SNOL 58/350 (AB Umega, Lithuania) to constant weight (about 20 h). For each experiment, the quantity of mixture poured into the glass plates was calculated to obtain a constant weight of dry matter of approximately 9 mg/cm<sup>2</sup>, and the resulting films had a thickness of 0.08±0.01 mm, as measured by a micrometer Micromar 40 EW (Mahr GmbH, Esslingen, Germany).

### Moisture absorption characteristics

#### Moisture curve and rates

Agar film specimens (30 mm x 30 mm) were pre-dried for 7 days over phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) and then were placed at 25±2°C over saturated salt solutions in separated desiccators having desired relative humidity (33, 52 and 75% RH) conditions [19]. Weights of film specimens were measured as a function of time and moisture content of the films was determined by oven drying at 105°C. Moisture absorption data were fitted according to a mathematical model suggested by Peleg:  $M(t) = M_0 + t/(k_1 + k_2 t)$ , where  $M(t)$  is the moisture after time,  $M_0$  is the initial moisture content and  $k_1$  and  $k_2$  are constants [20]. All tests were conducted in triplicate.

#### Absorption isotherms

The moisture absorption isotherm was determined at 25±2°C. Film samples were conditioned in a desiccator for 7 days at ≈0% RH to reduce the initial moisture content. Samples were then placed over saturated salt solutions having the desired 33, 53, and 75% RH conditions [19]. The equilibrium conditions were reached when the two consecutive weighings were equal. Equilibrium moisture content was calculated from the increase in mass of the sample after equilibration reported to the dried mass obtained after drying in an oven at 103°C for 10 h. The Guggenheim-Anderson-de Boer (GAB) model was used to fit film absorption isotherm data:

$M = m_0 C K a_w / (1 - K a_w)(1 - K a_w + C K a_w)$ , where  $M$  is the equilibrium moisture content at a water activity ( $a_w$ ),  $m_0$  is the monolayer value (g water/g solids), and  $C$  and  $K$  are the GAB constants [21]. GAB equation parameters were calculated from the Water Analysis software (ver. 97.4).

### Tensile properties of the agar films

The tensile strength of the agar films was measured using a texture analyzer (TA-XT2, Stable Micro Systems Ltd., UK), based on standard method ASTM D882-02 (ASTM, 2002). Films were cut into 1.5 cm wide and 8 cm long strips and conditioned at 23°C and 50% RH for three days before testing. All measurements were replicated five times.

### Statistical analysis

The data were analyzed using Statistica version 6.0 (Statsoft, Moscow, Russia). Differences among groups were analyzed using ANOVA for unequal variance, and those with  $p < 0.05$  were accepted as statistically significant.

The least square multiple regression methodology was used to enquire the relationship between the tensile strength and  $X_1$  – glycerol,  $X_2$  – sorbitol,  $X_3$  – sodium citrate and  $X_4$  – citric acid concentrations. The multiple regression equations were used to fit the polynomial equation based on the experimental data.

The model was compared based on the coefficient of determination ( $R^2$ ), adjusted coefficient of determination ( $R^2$ -adj) and predicted coefficient of determination ( $R^2$ -pred). The coefficient of determination ( $R^2$ ) is defined as the regression of sum of squares proportion to the total sum of squares which illustrates the adequacy of a model.  $R^2$  ranges from 0 to 1.  $R^2$  values closer to 1, means the model is more accurate. The high adjusted and predicted coefficient of determination also illustrate whether the model adequately fits the data [22]. After selecting the most accurate model, Pareto analysis of variance (ANOVA) was used to investigate the statistical significance of the regression coefficients by conducting the Fisher's F-test at 95% confidence level. The interactive effects of the factors were observed using surface plots, derived from the chosen model.

## RESULTS AND DISCUSSION

### Moisture absorption kinetics of agar films

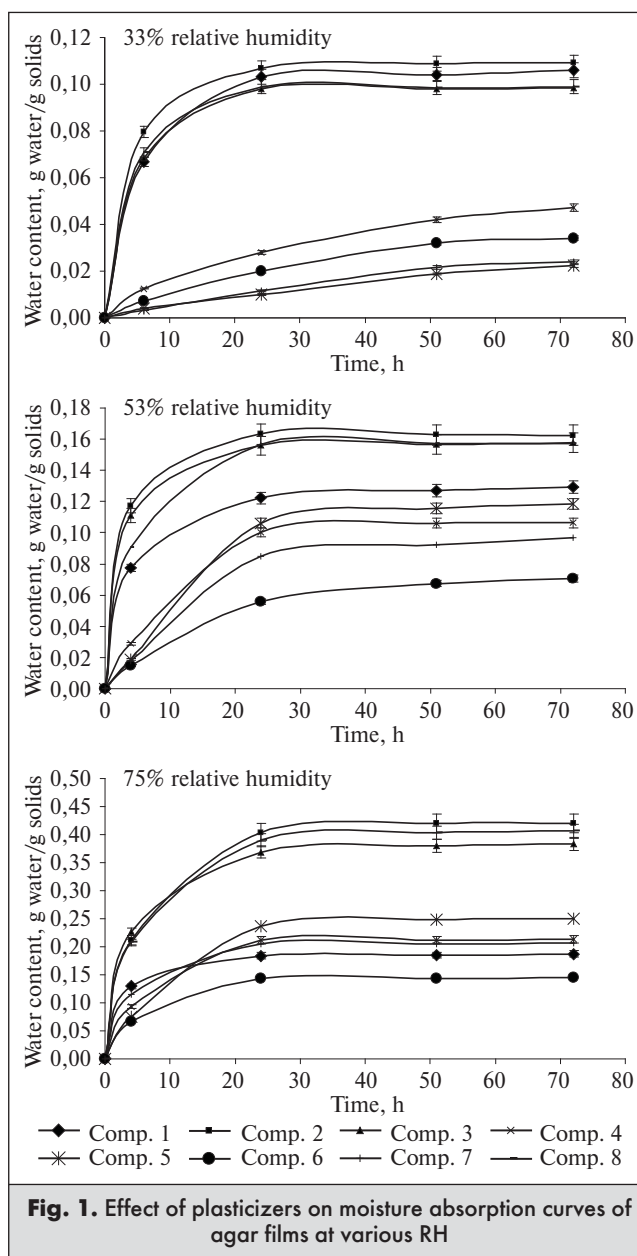
The main composition of materials used in film composition is presented in Table 1. Moisture absorption curves of agar films are shown in Fig. 1.

Moisture absorption was more rapid at the initial stages of the storage and lower amounts of water were absorbed as time increased. Then, the moisture content of agar films reached a plateau indicating that they became equilibrated with storage RH. Moisture equilibrium time was influenced by storage RH and plasticizer type and concentration; films plasticized with glycerol showed a trend to absorb more water than other plasticized films (Fig. 1). To improve the investigation about water absorption

Table 1

**CONCENTRATION OF THE PLASTICIZERS  
IN THE FORMULATIONS**

Formulations	Concentrations (wt%)			
	glycerol	sorbitol	sodium citrate	citric acid
Comp. 1	0.0	0.0	0.0	0.0
Comp. 2	5.0	0.0	0.0	0.0
Comp. 3	4.0	1.0	0.0	0.0
Comp. 4	0.0	2.0	0.0	0.0
Comp. 5	0.0	0.0	2.0	0.0
Comp. 6	0.0	0.0	0.0	1.0
Comp. 7	0.0	0.0	1.0	0.5
Comp. 8	3.6	0.6	1.1	0.5



**Fig. 1.** Effect of plasticizers on moisture absorption curves of agar films at various RH

behavior, the moisture content data obtained at different times were fitted using Peleg model [20].

The Peleg parameters [20],  $k_1$  and  $k_2$ , are shown in Table 2. As  $k_1$  is a constant related to mass transfer, the lower  $k_1$ , the higher the initial water absorption rate;  $k_2$  is a constant related to maximum water absorption capacity and the lower the  $k_2$ , the higher the absorption capacity [23]. Films plasticized with glycerol and stored at highest RH had lower  $k_1$  and  $k_2$  values (Table 2), indicating that these films absorbed faster and more water during its storage.

Films with sorbitol showed intermediate  $k_1$  and  $k_2$  values generally nearly that of films containing glycerol, citric acid, and sodium citrate (Table 2). According to Sothornvit and Krochta [24], molecular differences between glycerol and sorbitol are probably responsible for the different absorption rate of films plasticized with them. Glycerol and sorbitol are polyols with similar straight-chain molecules; however, glycerol molecule is smaller (molecular weight of 92) and has three hydroxyl groups while sorbitol molecule (molecular weight of 182) has six hydroxyl groups. Although sorbitol presented more hydroxyl groups to interact with water by hydrogen bonds, glycerol presented higher water affinity demonstrated by absorption and desorption isotherms [25]. According to Garcia et al. [26], since sorbitol is more similar to the molecular structure of glucose units than glycerol, the chances of sorbitol to interact with polymeric agar chains are higher, thus, sorbitol-containing films presented higher intermolecular forces and showed a lower capacity to interact with water.

Films plasticized with citric acid and sodium citrate had higher  $k_1$  and  $k_2$  values (Table 2), indicating that these films absorbed slower and less water during its storage especially at low RH.

#### *Moisture absorption isotherms of agar films*

The moisture absorption isotherms of agar films were estimated and the GAB model parameters are shown in Table 3.

Films without plasticizer presented the medium monolayer value (0.066 g water/g solids) while the highest monolayer value (0.158 g water/g solids) was observed when 4 wt.% sorbitol was incorporated. The monolayer value indicates the maximum amount of water that can be absorbed in a single layer per gram of dry film. Films with citric acid and sodium citrate as plasticizer presented the lowest monolayer values (0.035–0.036 g water/g solids), while higher monolayer value (0.065 g water/g solids) was observed when additionally 3.6 wt.% glycerol and 0.6 wt.% sorbitol were incorporated.

It was previously shown that the agar-based film absorbs higher amounts of moisture than starch films in the same RH conditions. This trend is due to the most hydrophilic characteristics of agar compared to starch. The agar-based film was recognized as the most hydrophilic film. Its water vapor permeability was comparable with that of cassava

starch film and significantly lower than that of normal rice starch and waxy (glutinous) rice starch films. The hydrophilic nature of the film-forming substance limits their ability to form films with good moisture barrier ability [1]. The addition of plasticizer provides more active sites by exposing its hydrophilic hydroxyl groups in which the water molecules could be absorbed [12].

The C parameter is related to the difference of the magnitude in the upper layers and in the monolayer [27]. This parameter decreased with increased polyols plasticizer concentration and glycerol-containing and sorbitol-containing films showed the lower values (Table 2). Our result was according to findings of other authors, who also stressed that K parameter is effectively independent of composition [28]. Sodium citrate and citric acid in agar films do not affect the C parameters. Compared to thermoplastic starch films plasticized with glycerol, the addition of citric acid resulted in considerably lower diffusion coefficients and lower moisture content over the entire RH ranges [16].

In general, the moisture absorption isotherms for films showed a sigmoidal shape and were influenced by the concentration and by type of plasticizer. Higher levels of plasticizer increased the films moisture affinity and these results could be attributed to the hydrophilicity of the plasticizers, which presented hydroxyl groups capable to interact with water by hydrogen bonds. In general, glycerol films showed a higher capacity to absorb water. Glycerol molecules are small and present high capacity to interact with starch chains, enhancing the molecular mobility and increasing free volume in the film matrix, besides, glycerol had a more hydrophilic character than sorbitol and these combined effects contributed to the higher water affinity of glycerol films [24].

#### *Tensile properties of the agar films*

After stored at 50% RH for 48 h, the tensile properties of the samples were tested. On the basis of the experimental design presented in Table 1, a second-order polynomial equation (1) in terms of actual factors was found more adequate than others. It demonstrated the empirical relationships between the  $X_1$ -glycerol,  $X_2$ -sorbitol,  $X_3$ -sodium citrate and  $X_4$ -citric acid concentrations (all in wt.%) and the response Y – tensile strength (MPa):

$$Y = 0.14509X_1 + 0.06585X_2 + 0.06323X_3 - 0.37965X_4 - 0.03371X_1X_3 + 0.01738X_3X_4 - 0.00956X_1^2 - 0.00955X_2^2 + 0.01292X_3^2 + 0.11141X_4^2 \quad (1)$$

Table 2

**CONSTANT VALUES ( $k_1$  and  $k_2$ ) AND COEFFICIENT OF DETERMINATION ( $R^2$ ) FOR ABSORPTION CURVE EQUATIONS (Peleg model) OF AGAR FILMS AT SELECTED RH**

Formulations	33 % RH			53 % RH			75 % RH		
	$k_1$	$k_2$	$R^2$	$k_1$	$k_2$	$R^2$	$k_1$	$k_2$	$R^2$
Comp. 1	0.28	0.09	0.999	0.19	0.08	0.999	0.08	0.05	0.999
Comp. 2	0.17	0.09	0.999	0.07	0.06	0.999	0.08	0.02	0.999
Comp. 3	0.08	0.10	0.999	0.09	0.06	0.999	0.06	0.03	0.999
Comp. 4	4.61	0.21	0.970	0.83	0.10	0.988	0.18	0.05	0.997
Comp. 5	15.33	0.45	0.897	1.52	0.09	0.951	0.29	0.04	0.988
Comp. 6	7.27	0.29	0.998	2.05	0.10	0.995	0.26	0.07	0.998
Comp. 7	16.49	0.41	0.980	1.58	0.11	0.964	0.12	0.05	0.999
Comp. 8	0.19	0.10	0.998	0.14	0.06	0.999	0.08	0.02	0.999

An analysis of variance (ANOVA) indicated that experimental data had a determination coefficient ( $R^2$ ) of 0.9694 with the calculated model and no significant lack of fit at  $p > 0.05$ . This finding means that the calculated model was able to explain 96.94% of the results. The results indicated that the model used to fit response variables was significant ( $p < 0.001$ ) and adequate to represent the relationship between the response and the independent variables. An F-test suggested that the model had a high model F-value ( $F = 19.02$ ), indicating that this model was highly significant. The  $R^2_{adj}$  (adjusted determination coefficient), which is the correlation measure for testing the goodness-of-fit of the regression equation, was 0.9235.

To further evaluate the quantitative effect of four variables on the tensile strength of agar films, the p-values were calculated. The concentration of  $X_1$ -glycerol,  $X_2$ -sorbitol, the synergistic effect of  $X_1$ -glycerol and  $X_3$ -sodium citrate, the synergistic effect of  $X_3$ -sodium citrate and  $X_4$ -citric acid, and the second-order effect of  $X_4$ -citric acid are highly significant parameters with p-values  $< 0.01$ . Furthermore, the effect of  $X_3$ -sodium citrate, second-

Table 3

**GAB MODEL FOR AGAR FILMS WITH DIFFERENT PLASTICIZERS**

Formulations	$m_0$	C	K	$r_2$
Comp. 1	0.066	200.0	0.97	0.995
Comp. 2	0.069	200.0	0.99	0.982
Comp. 3	0.071	35.8	0.98	0.986
Comp. 4	0.158	0.54	0.98	0.992
Comp. 5	0.036	0.33	0.97	0.980
Comp. 6	0.036	0.61	0.98	0.883
Comp. 7	0.035	0.43	0.99	0.988
Comp. 8	0.065	200.0	0.99	0.978



order effects of  $X_1$ -glycerol and  $X_2$ -sorbitol are significant with  $p < 0.05$ . More information about the importance of the variables in Eq. (1) was provided by Pareto analysis in the form of Pareto Chart. As shown in Fig. 2, the most important variable for the tensile strength of agar films was the amount of  $X_1$ -glycerol (35.62%), followed by  $X_2$ -sorbitol (17.32%) and then the synergistic effect of  $X_1$ -glycerol and  $X_3$ -sodium citrate (14.71%). In addition, the strength of films was also affected by synergistic effect of  $X_3$ -sodium citrate and  $X_4$ -citric acid (8.48%), second-order effect of  $X_4$  (7.84%),  $X_3$ -sodium citrate (6.69%), second-order effect of  $X_2$  (4.86%), and second-order of  $X_1$  (4.07%).

The three-dimensional surfaces plots were formed for the better understanding of the relationship between the tensile strength of agar films and the independent variables  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$ .

Increasing the content of the glycerol and sodium citrate increases the strength of the agar films (Fig. 3a).

The addition of the sodium citrate to agar increases the strength of the agar films. Moreover, increase in the content of citric acid in the composition decreases the tensile strength of the films with sodium citrate (see Fig. 3b). According to the data, the addition of the citric acid lowers the film strength of the agar while adding glycerol and sodium citrate increases the strength of the films. Increasing the glycerol content increases strength agar film

and decreases only when the content is more than 5 wt.%. Glycerol and sodium citrate have a common influence on the strength of the agar films. When sharing the content in the composition increases the strength of films at a sodium citrate content of 2.5 wt.%. The strength of agar films with sodium citrate increased by adding of citric acid.

Citric acid and sodium citrate had a mutual influence on the agar gel dynamic viscosity. Increasing the citric acid at low sodium citrate concentrations decreased the viscosity and increased it at high concentrations [29].

The citric and tartaric acids contribute to the production of a material with increased tensile strength and reduced elongation when their concentration in the starch/ poly (butylene adipate co-terephthalate) blend is increased. This result is most likely caused by crosslinking reactions, which interconnect the polymeric molecules and restrict their mobility, in agreement with the results of water vapor permeability. The effect of the citric acid and maleic anhydride in the starch/poly (butylene adipate co-terephthalate) blends has already been discussed in a previous study [30]. Shi et al. [31] and Reddy and Yang [14] also reported similar results with the inclusion of citric acid in starch-based materials. Citrate added to the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) films enhanced their thermal and mechanical properties and showed good plasticizing properties [32].

Thus, the result shows that, beyond the crosslinking reactions, sodium citrate interacts with the polymeric molecules of agar and produces strong hydrogen bonds.

## CONCLUSIONS

It was established that water absorption and mechanical properties of the agar films dependent on plasticizers content. 3D response surface plots were constructed from the experimental data in order to represent the relationship between process variables and the responses. It can be concluded that the concentrations of glycerol and sodium citrate significantly affect the properties of agar film. These basic data on the influence of process variables on the water absorption and mechanical properties of agar films are important in assessing the applicability of agar films in food and pharmaceutical industries.

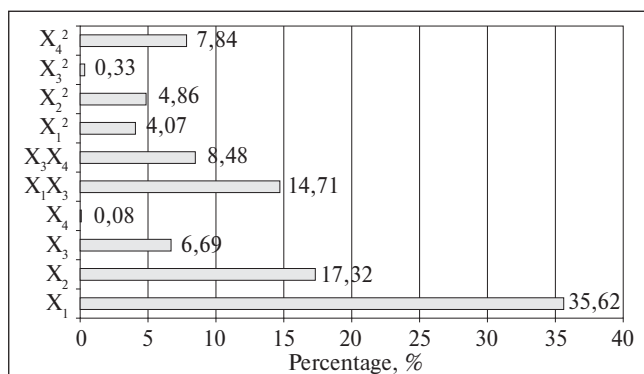


Fig. 2. Pareto graphic analysis for percentage effect of each factor on tensile strength of agar films

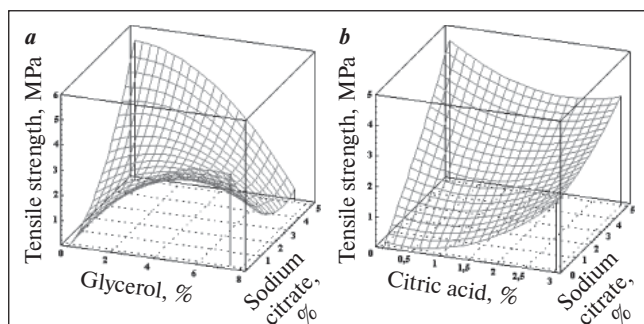


Fig. 3. Response surface plots showing the interaction effects of process variables on tensile strength.

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## ВЛИЯНИЕ ПЛАСТИФИКАТОРОВ НА АБСОРБЦИЮ ВЛАГИ И МЕХАНИЧЕСКИЕ СВОЙСТВА АГАРОВЫХ ПЛЕНОК

О.Н. Пожарицкая<sup>1</sup>, кандидат фармацевтических наук, А.Н. Шиков<sup>1</sup>, доктор фармацевтических наук, Д.В. Демченко<sup>1</sup>, кандидат фармацевтических наук, Е.В. Флисюк<sup>2</sup>, доктор фармацевтических наук, В.Г. Макаров<sup>1</sup>, доктор медицинских наук

<sup>1</sup>Санкт-Петербургский институт фармации, 188663, Россия, Ленинградская обл., Всеволожский р-н, г.п. Кузьмолковский, ул. Заводская, д. 3, корп. 245 e-mail: spbpharm@mail.ru

<sup>2</sup>Санкт-Петербургская государственная химико-фармацевтическая академия; Россия, 197376, Санкт-Петербург, ул. проф. Попова, д. 14 e-mail: elena.flisyuk@pharminnotech.com

### РЕЗЮМЕ

**Введение.** Перспективы применения полимеров на основе полисахаридов в фармацевтической индустрии и биотехнологии очень широкие. Преимущества агара по сравнению с другими желеобразующими системами – его более высокая стабильность при низких значениях pH и повышенных температурах. Пластификаторы улучшают гибкость пленки и предотвращают растрескивание пленки во время ее обработки и хранения.

**Цель** исследования – изучение влияния видов пластификаторов и их концентрации на кинетическую и статическую абсорбцию влаги и на механические свойства агаровых пленок.

**Материал и методы.** Влияние пластификаторов (глицерина, сорбитола, лимонной кислоты, цитрата натрия и их смесей), а также их смесей на абсорбцию влаги и механические свойства агаровых пленок было изучено при различных концентрациях пластификаторов, согласно дизайну эксперимента.

**Результаты.** Добавление глицерина в состав пленок повышало скорость абсорбции и количество поглощаемой влаги при хранении в условиях повышенной относительной влажности. В то же время пленки с добавлением лимонной кислоты и цитрата натрия абсорбировали влагу медленнее и в меньшем количестве, особенно – при более низкой относительной влажности. Самый тонкий монослой воды (0,035–0,036 г воды / г пленки) наблюдался на пленках с лимонной кислотой и цитратом натрия в качестве пластификатора. При добавлении в состав пленок 3,6 мас.% глицерина и 0,6 мас.% сорбита толщина монослоя увеличивалась до 0,065 г воды / г пленки. Наибольшая толщина монослоя воды (0,158 г воды / г пленки) отмечена при включении в состав 4 мас.% сорбитола. Добавление лимонной кислоты в состав агаровых пленок снижала их прочность, а увеличение содержания глицерина (до 5 мас.%) и цитрата натрия (до 2,5 мас.%) повышало прочность пленок. Дополнительное введение лимонной кислоты в состав пленок с цитратом натрия также повышало прочность пленок.

**Заключение.** Результаты исследования могут быть использованы в фармацевтической и биотехнологической промышленности при выпуске агаровых капсул или упаковки из агар-агара.

**Ключевые слова:** агаровые пленки; лимонная кислота; глицерин; цитрат натрия; сорбитол