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RHEOLOGICAL PROPERTIES OF CHITOSAN EDIBLE FILMS

Zsivanovits Gabor Ivan

Associate Professor, Scientific secretary of Institute of Food Preservation and Quality. Plovdiv, Bulgaria. E-mail: g.zsivanovits@canri.org

Marudova Maria Georgieva

Associate Professor, Faculty of Physics and Technology. Paisii Hilendarski University of Plovdiv. Plovdiv, Bulgaria. E-mail: margo@uni-plovdiv.bg

РЕОЛОГИЧЕСКИЕ СВОЙСТВА СЪЕДОБНОЙ ПЛЕНКИ ИЗ ХИТОЗАНА

Живанович Габор Иван

Доцент, Ученый секретарь. Институт переработки и качества пищевых продуктов. Пловдив, Болгария. E-mail: g.zsivanovits@canri.org

Марудова Мария Георгиева

Доцент, физико-технологический факультет. Пловдивский университет им. Паисия Хилендарского. Пловдив, Болгария. E-mail: margo@uni-plovdiv.bg

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Abstract. The increased requirements for high quality and extended shelf life of fresh and minimally processed fruits in the recent years has helped forward the development of some innovative techniques to keep the natural and fresh look of the food for as long as possible while ensuring it's safety. In this context formulation of new composite edible coating is a promising way to ensure fruit quality for a longer period.

In this study hydrophilic and mechanical properties of composite edible films from chitosan and grape seed oil have been determined. Due to its biocompatibility, nontoxicity and antibacterial activity, chitosan is a preferred polysaccharide for the production of edible films and coatings. Grapeseed oil is high in vitamin E and phenolic antioxidants. It is also a rich source of omega-6 polyunsaturated fats.

Mechanical experiments of the edible films were done in tensile mode at constant deformation rate using the LS 1 (Lloyd Instruments) Universal Testing Machine. The break point, mechanical losses and relaxation parameters were determined.

It was found that the increase of the grape seed oil content reduces the water holding capacity of the edible films, hence their hydrophobic properties are enhanced. At the same time the oil addition reduces the film strength and they become more brittle. Adding oil at concentrations up to 2% results in an increase in the Young's modulus. At higher concentration a decrease of the Young's modulus is noticed. When the oil content increases, it plays a role of plasticizer, which enhances the viscosity properties of the material. As a result of the plasticizing effect of the oil, the stress and the relative deformation at rupture decrease, the equilibrium stress values decrease after the relaxation process, therefore, the visco-elastic behaviour with full relaxation of the tension is increased. The broadness of the relaxation time spectrum decreases when the oil content increases.

Key words: edible film, composite film, chitosan, essential oils, grape seed oil, hydrophilic properties, rheology.

Аннотация. Повышенные требования к качеству и продлению срока годности свежих и минимально обработанных фруктов в последние годы помогли продвинуть разработку некоторых инновационных методов, чтобы как можно дольше сохранять натуральный и свежий вид пищи при обеспечении ее безопасности. В этом контексте разработка нового композитного съедобного покрытия является многообещающим способом обеспечения качества фруктов в течение более длительного периода.

В этом исследовании были определены гидрофильные и механические свойства полимерных съедобных пленок из хитозана и масла виноградных косточек. Благодаря своей биосовместимости, нетоксичности и антибактериальной активности хитозан является предпочтительным полисахаридом для производства пищевых пленок и покрытий. Масло виноградной косточки богато витамином Е и фенольными антиоксидантами. Это также богатый источник полиненасыщенных жиров омега-6.

Механические эксперименты с пищевыми съедобными пленками проводились в режиме растяжения при постоянной скорости деформации с использованием универсальной испытательной машины LS 1 (Lloyd Instruments). Были определены: точка разрушения, механические потери и параметры релаксации.

Было обнаружено, что увеличение содержания масла виноградных косточек снижает влагоемкость пищевых пленок, следовательно, их гидрофобные свойства улучшаются. В то же время добавление масла снижает прочность пленки, и она становится более хрупкой. Добавление масла в концентрации до 2% приводит к увеличению модуля Юнга. При более высокой концентрации наблюдается уменьшение модуля Юнга. Когда содержание масла увеличивается, оно играет роль пластификатора, который улучшает вязкостные свойства материала. В результате пластифицирующего действия масла, уменьшения напряжения и относительной деформации при разрыве значения равновесного напряжения уменьшаются после процесса релаксации, поэтому вязкоупругое поведение при полной релаксации растяжения увеличивается. Широта спектра времени релаксации уменьшается при увеличении содержания масла.

Ключевые слова: съедобная пленка, композитная пленка, хитозан, эфирные масла, масло виноградных косточек, гидрофильные свойства, реология.

Introduction. Edible coatings can be defined as a thin layer of material that covers the surface of the food and can be consumed as a part of the product. Their composition should be in conformity with the regulations applicable to foodstuffs [1], European Commission Directives [2], and US Federal Resource Code [3].

Packaging is an important element in the concepts for providing appropriate (mechanical and functional) goods protection during the

storage. As conventional packaging of synthetic materials leads to environmental pollution, there is a tendency for the development of bio-packages that are edible together with the packaged food product — edible packaging. Biodegradable and edible coatings are made from natural polymers, and functional ingredients and are formed on the surface of food products [4].

Edible packages have a number of advantages over the other packaging techniques. They can act as barriers to moisture and gases, to control the microbial growth, to preserve the colour, texture and moisture of the product and in this way to prolong effectively its shelf life. The two most important benefits of the edible packaging are the reduction of synthetic waste, and the possibility of incorporating functional components that increase the nutritional value and functional properties of the packaged product.

The concept of edible packaging as a protective layer has been developed since 1800. The first used edible packaging is wax in China. Extensive research in this area trace the way for various effective edible films and coatings derived from a variety of natural polymers or their mixtures [5].

Chitosan is a widely used natural polymer that is obtained by deacetylation of chitin, the second most common biopolymer after the cellulose. Chitosan possesses many valuable properties such as biocompatibility, biodegradability, low toxicity, that make it applicable to biomedical engineering and pharmacy. Chitosan is known for its good film-forming properties and antimicrobial activity [6], which is also used in the food industry [7]. A major drawback of chitosan is its sensitivity to moisture. One of the strategies to overcome this disadvantage is mixing chitosan with hydrophobic materials, thereby preserving the overall biodegradability of the composite material [8].

One of the new technologies for development of edible coatings consists in the formulation of multilayer films based on the electrostatic self-assembly (9).

In this study hydrophilic and mechanical properties have been determined for composite edible film of chitosan and grape seed oil. Along with improving antibacterial activity, incorporating into minimal concentrations in the chitosan matrix essential oils may improve the barrier properties of the coating and reduce weight loss.

Materials and methods.

Materials

Low molecular weight water-soluble chitosan with deacetylation degree: ≥90%, molecular mass 1.6 kD and viscosity 100 mPa.s was bought from «Lyphar Biotech Co., LTD», China. As emulsifier inulin-palmitate ester was used. It is produced in University of food technology- Plovdiv, Bulgaria. The degree of polymerization is DP ≥ 23, the level of sweetness is 0% in comparison with the sucrose. Grape deed oil was purchased from the local market.

Formulation of edible films

The films were casted from 1% chitosan solution in distilled water, to which 0.5% glycerol, 0.5% emulsifier inulin palmitate and grape seed oil at different concentrations: 0.5%, 1%, 2%, 3% and 5% were added. These concentrations are selected on the basis of preliminary studies, and literature review [10], which showed, that oil at concentrations greater than 5%, migrated to the surface and the film became «greasy». The resulting emulsions are homogenized with a 30 kHz ultrasonic stirrer for 15 min and then degassed in an ultrasonic bath for 30 min. The emulsions are poured into glass Petri dishes in such a volume that after drying the film thickness was 100 μm. The films are dried at room temperature until a constant mass is obtained.

Determination of moisture content of edible films [11]

To determine the moisture content of edible films, the following procedure was applied:

The samples were dried in a desiccator at 0% relative humidity for 24 hours, then their mass — m_0 was measured.

The samples were placed in a desiccator with the desired humidity — 34%, 55%, 75% and 100% for 24 hours, then its mass — m was measured.

The moisture content was calculated by the formula:

$$moisture\ \ content = \frac{m - m_0}{m_0} \qquad (1)$$

Rheological tests

The tests were conducted in uniaxial tensile deformation mode using the LS 1 (Lloyd

Instruments) Universal Testing Machine. The sample was clamped to the instrument sensor by means of pneumatic locks with a rubber seal, thus not disturbing its surface. The sample deformation rate was 0.1 mm/s. 7 samples were measured from each type of edible film for the purpose of good statistics.

Rupture test

The rupture test allows the determination of the breaking point, which is characterized by the normal tensile stress and strain at breaking point, as well as the Young modulus, which is calculated as the gradient of the linear section of the stress-strain dependence.

Mechanical hysteresis test

The test is carried out till 20% strain is reached [12].

The mechanical hysteresis test is used to determine the coefficient of elasticity, which is defined according to the dependence:

$$coefficient\ of\ elasticity = \frac{A_2}{A_1} \qquad (2)$$

where A_1 is the area under the loading curve, and A_2 is the area under the unloading curve. The physical meaning of A_1 is the work required to deform the film, and A_2 represents the work of the elastic forces performed to restore the original state of the film. The degree of elasticity is a number varying between 0 and 1. When the material is absolutely elastic, no hysteresis is realized. Then $A_1 = A_2$ and the degree of elasticity is 1. There is no irreversible deformation and the sample completely restores its original size. Therefore, the less the degree of elasticity, the more plastic deformation occurs.

Relaxation test

The relaxation test was performed at 20% strain, realized by a constant deformation rate, after which the deformation was held constant for 180 s. The relaxation test shows the change of the force overtime.

Experimental data were fitted with the following equation:

$$\sigma = \sigma_\infty + \sigma_1 \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \qquad (3)$$

where σ_∞ is the normal stress at equilibrium, σ_1 is the difference between the initial and the equilibrium stress, t is the average relaxation time, and τ is the value of the stretched exponent parameter [13]. The value of β is between 0 and 1. As the value is smaller, the wider the range of relaxation times. The approximation with this function has a very good correlation between the experimental data and the theoretical curve and a uniform distribution of the residuums [14].

Results and discussion. *Examination of the hydrophilic properties of the edible films*

One hypothesis when mixing chitosan with a hydrophobic material, such as grape seed oil, is to reduce its hydrophilic properties. The characterization of these properties determines the moisture content of the films at room temperature at different humidity and different oil contents — Fig. 1.

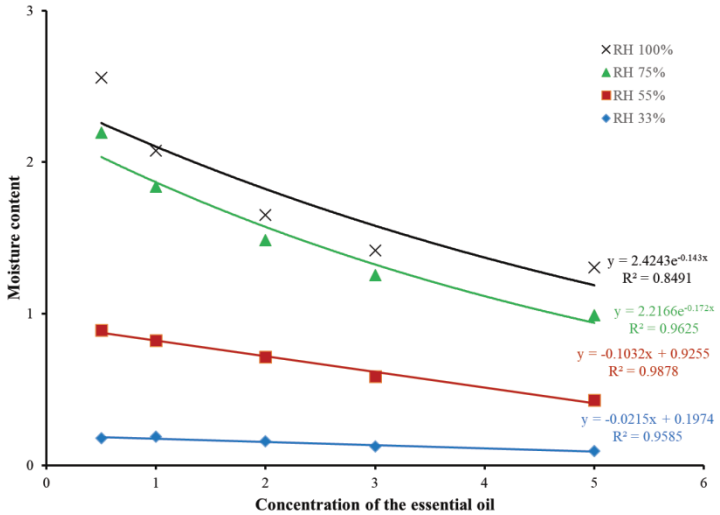

Fig. 1. Dependence of moisture content on relative humidity and oil concentration

A decrease in moisture content is observed, with decreasing the relative humidity of the air and increasing the oil content of the chitosan matrix. This result is expected and can be interpreted based on the hydrophobic properties of grape seed oil and the hydrophilic nature of chitosan. At lower relative humidity (33% and 55%), the moisture content of the oil concentration is linear while it is exponential at a higher relative humidity (75% and 100%).

Rheological parameters

Determination of the tensile strength of edible films

The dependence of the tensile stress at break on the incorporated oil concentration is shown in Fig. 2.

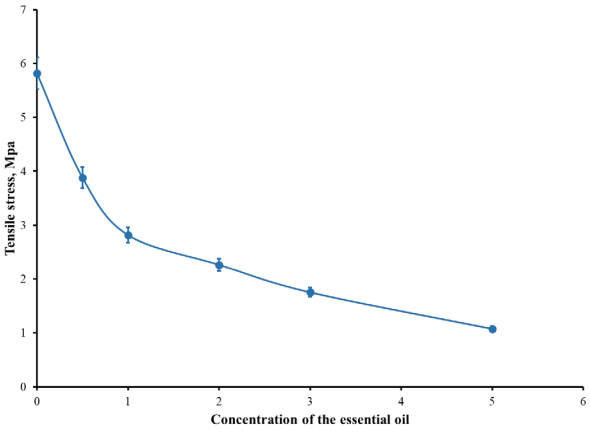

Fig. 2. Dependence of normal tensile stress on grape seed oil concentration

The zero point corresponds to a film containing 1% chitosan, 0.5% glycerol and 0.5% emulsifier. For comparison, all film parameters were determined from 1% chitosan, 0.5% glycerol without added emulsifier. This sample is considered to be the control.

The normal tensile stress at break for the control film is 40.3 MPa. Addition of an emulsifier results in a reduction of the tensile stress nearly 7 times. A probable cause is the plasticizing effect of the emulsifier, which is a low molecular mass compound, and results in a decrease of the glass transition temperature in the system and, consequently, the deterioration of the films strength. The addition of oil further reduces the normal tensile stress.

A similar trend is observed in the other strength parameter, namely the strain at break. For a chitosan film, it is approximately 100%, while at oil concentrations greater than 2%, it decreases about 10 times — Fig. 3.

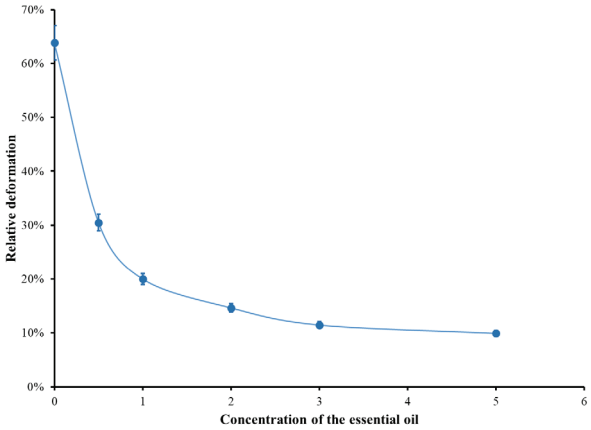

Fig. 3. Dependence of relative deformation at the tensile stress on the concentration of the grape seed oil

Determination of the hardness of the edible films

The elasticity of the edible films is characterized by the Young modulus — Fig. 4. The higher values of the Jung module correspond to the higher elasticity of the studied material.

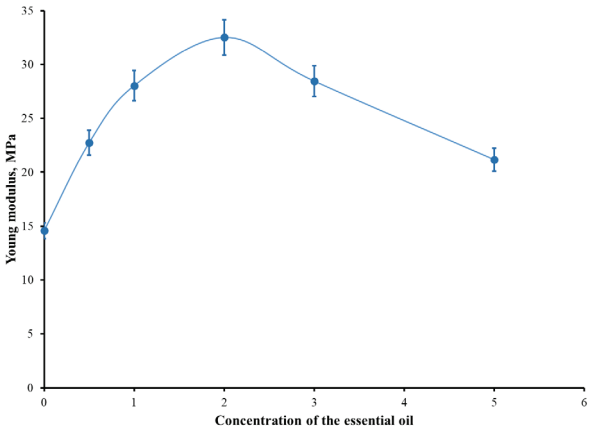

Fig. 4. Dependence of Young's modulus on the concentration of the grape seed oil

The value of the Young modulus for the control film is 37.92 MPa, which is in the same range with synthetic polymers, like polyethylene and polytetrafluoroethylene (Teflon) [15].

The addition of an emulsifier to the edible film results in a drastic reduction in the Young's modulus — approximately 2.6 times. Incorporation of a low molecular compound

such as an inulin-palmitate ester into the polymer matrix and the formation of an emulsion results in a disruption of the entanglement between the macromolecules, and decreasing of the film elasticity modules. The addition of oil in concentrations up to 2% increases the Young's modulus more than 2 times. The probable cause for the observed trend is the possibility that the oil phase will act as a filler that stabilizes the emulsion and increases its strength. Incorporation of larger quantities of oil results in a reduction of the Young modulus, since micro-unheterogenity may occur in the system and aggravation of physico-mechanical parameters.

Determination of the elastic (hysteresis) properties of the edible films

The main parameters characterizing the elasticity of the films are the elasticity coefficient and final relative deformation determined by the mechanical hysteresis test.

High-molecular compounds such as chitosan are characterized by visco-elastic properties, which, along with the instantaneous deformation, also give rise to irreversible plastic deformations leading to the occurrence of mechanical hysteresis. For this reason, the coefficient of elasticity decreases and the value determined for the film control is 0.4.

Addition of oil to concentrations of 2% results in an increase in the coefficient of elasticity about 2 times, i. e. increasing the elastic properties of the material (fig. 5).

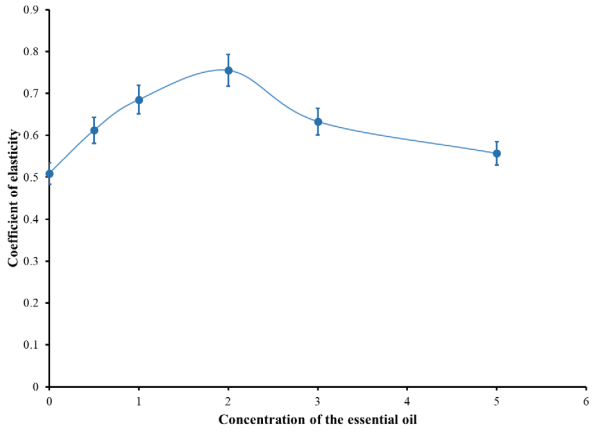

Fig. 5. Dependence of the coefficient of elasticity on the grape seed oil concentration

In this case, the oil phase involved in the emulsion system, acts as a filler and reduces the viscosity properties of the polymer matrix. The material becomes more brittle (its strength decreases), but at the same time harder (Young's modulus grows) and more elastic (the coefficient of elasticity increases — fig. 5).

A further increase in the oil concentration above 2% results in a decrease of the elasticity coefficient. The same tendency is observed for the rigidity of the films. At the same time, however, the strength continues to decrease. Therefore, it can be suggested that the inclusion of a large amount of oil phase leads to disruption of the homogeneity and integrity of the matrix of chitosan due to sharply deteriorate physical and mechanical performance.

The observed elastic behaviour of the films is also confirmed by the dependence of the final relative deformation on the oil concentration — Fig. 6.

At oil concentrations up to 2% the final relative deformation decreases, the material becomes more elastic. At higher oil concentrations, the final deformation increases and the plastic properties also increase.

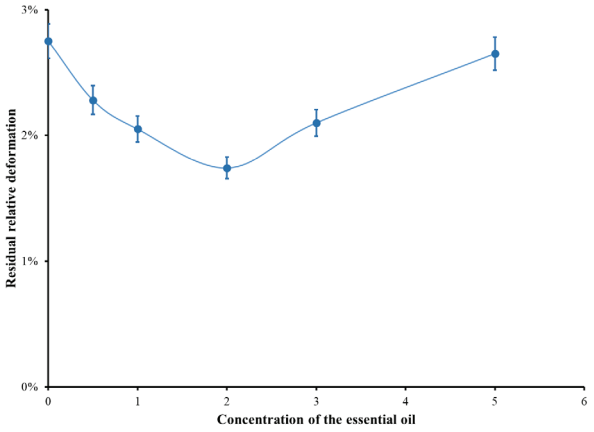

Fig. 6. Dependence of the final relative deformation on the oil concentration

Relaxation properties of edible films

The relaxation properties of the films are characterized by the relaxation time, the relaxation time spectrum, and the equilibrium normal stress, which is the tension that is reached after termination of the relaxation process and reaching the equilibrium state.

The dependence of the relaxation time on the oil concentration is shown in Fig. 7.

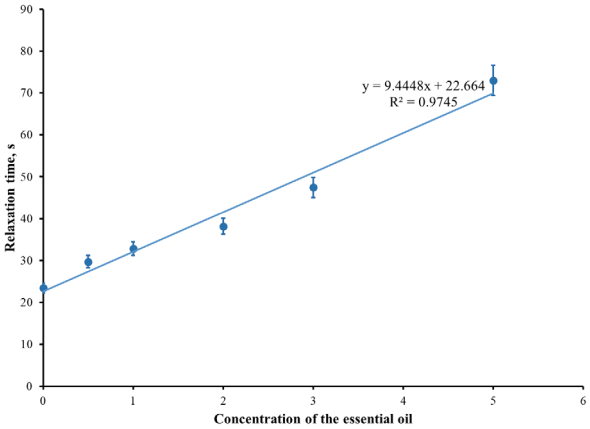

Fig. 7. Dependence of the relaxation time on the oil concentration

For the chitosan control film the relaxation time is 17.5 s. Addition of oil to the polymer matrix results in a delay in the relaxation process and an increase in relaxation time. The reason for this can be found in the creation of a two-phase system, the dispersed phase in which prevents the movement of macromolecules of chitosan and slows down their reorganization. This makes relaxation more difficult in the system.

As high molecular compounds are characterized by molecular mass distribution, a spectrum of relaxation times is also characteristic of them. Shorter chains with lower molecular mass are reorganized more quickly when changing external influences, resulting in smaller relaxation times. The movement of the longer chains is hampered by steric hindrances, and they are more difficult to move, so the relaxation time is even greater.

The width of the relaxation time spectrum is characterized by the magnitude of the gradation factor b in the relaxed exponential relaxation model. As the value of b is closer to 1, the narrower the spectrum of relaxation times.

The value of b for the control film is estimated at 0.4, meaning that chitosan films are characterized by a relative wide range of relaxation times. The width of the relaxation time spectrum decreases as the oil content increases Fig. 8.

For dispersion systems such as oil-admixed films, relaxation time is substantially dependent on the dispersed phase concentration as its presence in the system slows down the movement of the continuous phase and prolongs the relaxation time. In this case, the molecular mass distribution characteristic of the polymer systems has less influence.

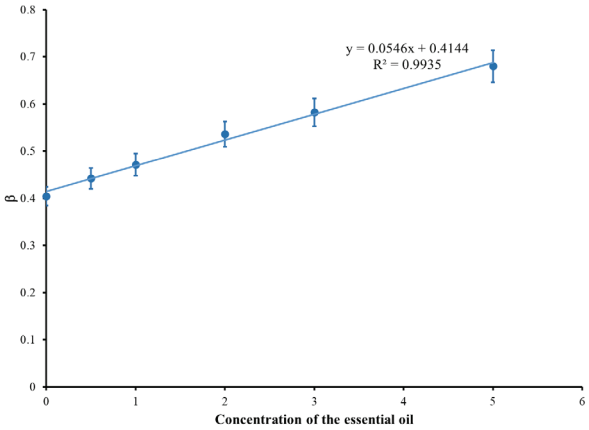

Fig. 8. Dependence of the b parameter on the grape seed oil concentration

When increasing the oil content in the films, the equilibrium stress values after the relaxation process cease to decrease, hence, the visco-elastic behavior with a full relaxation of the tension is enhanced — Fig. 9.

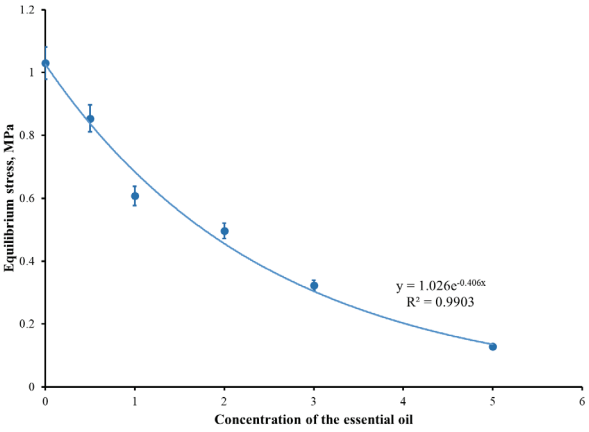

Fig. 9. Dependence of the equilibrium strain on the concentration of grape seed oil

The observed dependence is due to the difficult mobility of the macromolecules of chitosan and the reduction of the probability for formation of a crosslinked polymer system.

Conclusions. On the basis of the experimental results obtained in the research, the following more important conclusions can be drawn:

The increased oil content in the films reduces their water-holding capacity, hence, the hydrophobic properties of the films are enhanced.

Adding oil reduces the strength of edible films.

Adding oil at concentrations up to 2% results corresponds to increase in the Young's modulus.

When the oil content increases above 2%, it also plays a role of plasticizer, which enhances the viscosity properties of the material.

As a result of the plasticizing effect of the oil, the stress and the relative deformation at rupture decrease.

When increasing the oil content in films, the equilibrium stress values decrease after the relaxation process, i. e., the visco-elastic behavior with full relaxation of the tension is increased.

The broadness of the relaxation time spectrum decreases when the oil content increases.

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