



Original Article

The Study of the Physical and Chemical Properties of Biopolymer Gel as a Drying Object

Safa Y. Taha¹, Ayat Mohammed Yahya¹, Yassamin Sadk Khalf², Zainab H. Omran¹, Ali M. Ahmed², Ali Hussein Al-Hilali³, Russul Mohammed Shehab^{1*}

¹Department of Radiology and Sonar Techniques, Al-Esraa University College, Baghdad, Iraq

²Medical Instrumentation Engineering Department, Al-Esraa University College, Baghdad, Iraq

³Medical Technical College, Al-Farahidi University, Baghdad, Iraq

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ABSTRACT

This paper aims to investigate and generalize the structural, mechanical, thermophysical, hygroscopic, and field-specific features of biopolymer gel to create biodegradable packaging materials. Therefore, the mathematical dependences of thermophysical, structural-mechanical, hygroscopic, and specific characteristics of a biopolymer gel that have been established for this field of research can be utilized in engineering practice when designing production processes and devices in the field of packaging materials technology. The findings of this research are necessary for the scientific study of the kinetics and dynamics of processes involving the transfer of heat and mass, in particular drying, modeling, and optimization, to conserve energy and resources during the processing and storage of food-related materials.

GRAPHICAL ABSTRACT



* Corresponding author: Russul Mohammed Shehab

✉ E-mail: Email: russul.mohammed@esraa.edu.iq

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Introduction

The study, systematization, and generalization of the structural, mechanical, thermophysical, and hygroscopic characteristics of biopolymer gel are necessary for the scientific analysis of the kinetics and dynamics of heat and mass transfer processes for the production of packaging films, their mathematical modeling, and solving the problems of rationalizing drying equipment. Present day food bundling has made life simpler from various perspective broadened item timeframe of realistic usability, partition control, improved food appropriation (dealing with, opening, reclosing, use, and reuse), takeout food, prepared to-eat food. So forth, Shockingly, this comfort has added to a fast expansion in the amount of bundling waste in landfills [1-4]. The monetary and specialized issues related to reusing plastic bundling waste, like the slow consumption of world oil, have created the need to develop harmless ecosystem bundling. Bundling can be given an assortment of ecologically supportable materials, primarily inexhaustible biopolymers. Combining the detailing and creation strategy, bio-based bundling can be compostable / biodegradable or consumable, empowering new application prospects. Eatable bundling can be utilized where engineered materials are restricted [5-10].

This research examines biopolymer gel's structural, mechanical, thermophysical, hygroscopic, and field-specific properties of biopolymer gel to construct biodegradable packaging. The mathematical dependences of thermophysical, structural-mechanical, hygroscopic, and particular features can be used in engineering practice when designing production processes and devices in packaging materials technology. This research is needed to examine the kinetics and dynamics of heat and mass transfer processes, such as drying, modeling, and optimization, to conserve energy and resources during food processing and storage.

Characteristics of the research object

The investigated object is a gel of biopolymer material (BM). It is a structured system composed of natural polysaccharides and excipients.

Typically, a gel has a three-dimensional polymer framework (mesh) and has the mechanical properties of solids: lack of fluidity, the ability to maintain shape during deformation, and a particular strength (plasticity and elasticity). The gel has biodegradable properties due to natural organic components that decompose under environmental conditions [11, 12]. The process of BM formation has the following stages: 1) quality control or inspection of the original components; 2) insertion of components, according to a rational patented recipe [9], in an aqueous solution broth powder with the required concentration, heated to a temperature of 80 °C; 3) mixing of ingredients: powdered sodium alginate, gel-like glycerin, antioxidant, gel-like or powder dyes, and a flavor base in the form of a powder-concentrated broth; 4) stirring in an apparatus with a stirrer, the rotation frequency of which is set in the range of 250 ÷ 270 rpm with temperature control; 5) quality control of BM. In the process of laminar mixing with small turbulence zones at a given temperature, the formed fluid gel-like medium affects the hydrodynamics of the liquid flow. It necessitates introducing the polymerizing material as a powder into the central funnel formed under the action of centrifugal forces. In presenting the powder, sodium alginate particles are displaced with the solution when it is saturated with air in the peripheral zones of turbulence, which reduce the effect of lump formation and adhesion of particles to working bodies. This achieves the effective dissolution of alginate and its contact with other components of the final film material under the technology [9]. After forming a solid gel, additional components are introduced, which are necessary to provide the desired properties to the polymer: food liquid glycerin, calcium chloride, salt, and food crystallized citric acid. This stage is characterized by a decrease in the rotation frequency of the stirring device to values of 80 ÷ 83 rpm. The complete dissolution of all components determines its completion and the formation of a homogeneous solution (Figure 1). Depending on the quality indicators of the ingredients used, the duration of the mixing process in the first stage of

Figure 1. Homogeneous mixture of tapa is $18 \div 20$ minutes, and on the second - $7 \div 10$ minutes.

The obtained biopolymer gel is cooled to a temperature of $35 \div 40$ °C to increase its viscosity, which contributes to the uniform distribution of BM on the working surface of the dryer or the substrate. Next, a sensory check of the biopolymer gel as a drying object is carried out, which is necessary for an a priori assessment of the structure and complex of specific properties of the obtained polymers. The results of the organoleptic analysis serve as one of the important and, in some cases, determining indicators of the suitability of materials for the drying process [13]. In terms of

organoleptic indicators, the test gel must meet the requirements specified in Table 1. To substantiate the recommended recipes for the production of packaging material [14, 15], in particular the amount of E401 addition, an organoleptic evaluation of semi-finished products with different flavor bases was carried out in comparison with acceptable control grades. In Figures 2, 3, and 4 shows the results of the assessment of the organoleptic characteristics of polymer semi-finished products having as a flavor base mushroom, vegetable concentrated broths, concentrated chicken minced meat broth, and homogenized, cherry juice.



Figure 1: Homogeneous mixture

Table 1: Organoleptic characteristics of a polymer gel solution prepared for drying

Indicator name	Organoleptic assessment (points) maximum score - 10	Score not less
Appearance	The solution is clean and homogeneous. The presence of lumps is not allowed.	9.5
Consistency	Homogeneous, viscous, jelly-like, and flowing.	8
Color	It corresponds to the selected flavoring filler and, depending on the type of broth, varies from light yellow to brown.	8
Scent	Light smell of flavoring filler.	7

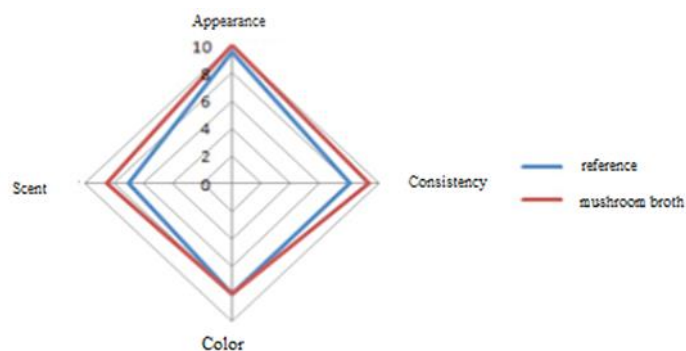


Figure 2: Profilogram of the quality of biopolymer gel based on mushroom broth

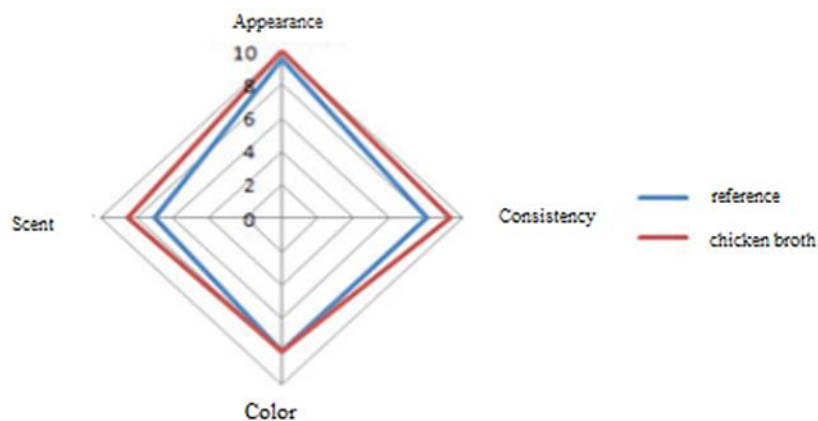


Figure 3: Profilogram of biopolymer gel quality based on chicken broth

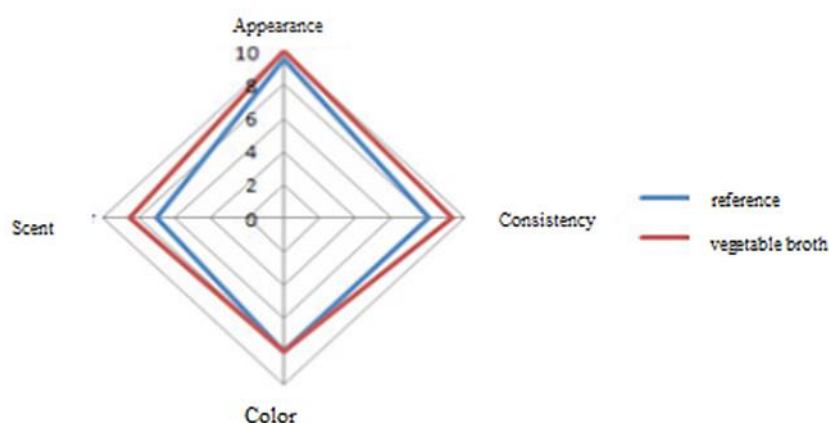


Figure 4: Profilogram of the quality of biopolymer gel based on vegetable broth

The organoleptic characteristics of BM gel make it possible to obtain a film material corresponding to the requirements of TU [14].

Hygroscopic characteristics of biopolymer gel

With dynamic equilibrium, the amount of moisture in the product depends on its type and structure, the type and energy of the binding of moisture with it, and the parameters of the vapor-air environment above the surface of the product, in particular, the temperature and partial pressure of water vapor. The sorption (desorption) isotherm graphically shows the relationship between the equilibrium moisture content of the product and the corresponding relative air humidity under isothermal conditions. This relationship does not have a rigorous analytical description [1], so it must be determined experimentally. This empirical study of the

hygroscopic characteristics of a biopolymer gel (equilibrium moisture content of the product and the environment) was carried out using the tensometric Method of Van Bamelén [1]. According to this Method, samples of a test product with predetermined moisture content were kept in desiccators with a solution of sulfuric acid of various concentrations. In this case, a particular concentration of the solution at a given temperature corresponds to a specific partial pressure of water vapor, i.e., a specific value of the relative humidity of the air φ . The film material is periodically weighed until a constant mass is reached, at which its moisture content corresponds to the equilibrium one [11, 12, 16]. The equilibrium moisture W_p achieved during the experiments was determined by the formula:

$$W_p = \frac{G_2 - G_1(1 - W_{sample})}{G_2} \quad (1)$$

Where G_1 is the initial mass of the test sample, kg; G_2 is the mass of the sample upon reaching hygrothermal equilibrium, kg; W_{sample} the initial moisture content, kg/kg. The relative error of moisture determination samples (at least 3/5 replicates) did not exceed $\varepsilon_{WP}=5\%$.

The experimental study of hygroscopic properties is aimed at characterizing the studied dry product and recommending the choice of the final moisture content of the material, which is the most appropriate for the storage process. Based on the experimental results, isotherms of moisture sorption by a polymer material based on E401 at air temperatures of 313K and 293K are shown in Figure 5. When constructing the sorption curves, it was assumed [1] that the numerical values of the indicator water activity A_w and the relative humidity of air φ coincide, due to the equality of the vapor pressure above the surface of the test material and its force in the closed volume of the desiccator. The obtained sorption isotherm can be

conditionally divided into three sections, which is especially clearly seen when plotting isotherms in semi-logarithmic coordinates modifications (Figure 5). Singular points on curves correspond to critical values of moisture content and information about the transformation of the sorption mechanism. Generalization of the results obtained is usually carried out using the classification of A.V. Lykov, according to which, depending on the colloidal-physical properties, biopolymer materials can be attributed to the group of capillary-porous colloidal bodies, in which liquid is characterized by various forms of moisture-solid skeleton bonding, inherent in both capillary-porous and colloidal bodies. The polymer under study is elastic and swells enormously upon liquid absorption and drying, shrinkage.

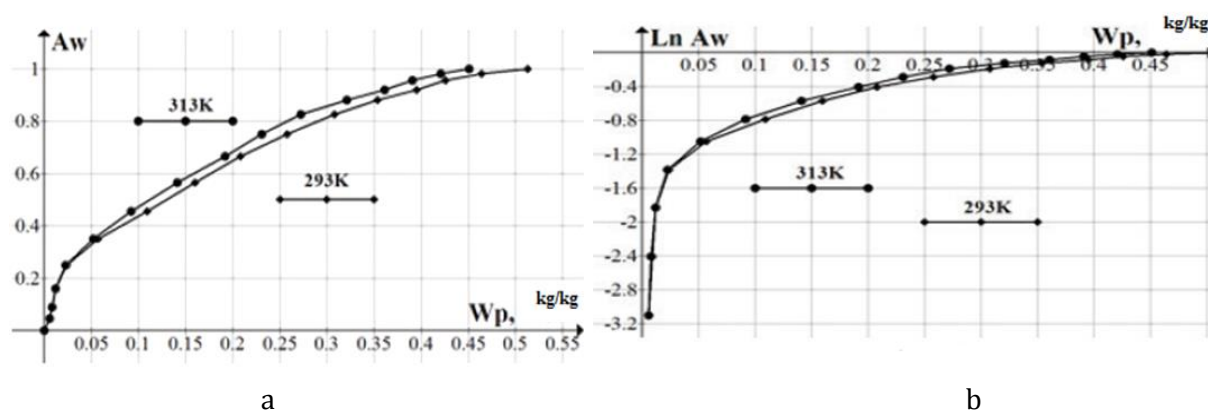


Figure 5: Isotherms of sorption by a polymer material based on E401, at temperatures of 313K and 293K, a - in conventional, b - semilogarithmic coordinates

According to the classification developed by S. Brunauer, L. Deming, W. Deming, R. Emmet, and B. Teller [1], the obtained isotherms can be classified as type III, which are characteristic of systems with a fragile sorbent-sorbate interaction. This is because sodium alginate, the main structure-forming component, consists of salt of alginic acid, a linear polysaccharide. It usually consists of 100-3000 monomeric residues connected in a flexible chain and has the following formula: $(C_6H_8O_6)_n$. When interacting with polar groups, electron pairs of hydrogen H are displaced to electronegative oxygen atoms O, creating an electric field at the

surface of polymer molecules. Volumetric filling of sorption centers begins, and upon completion, a conditional "monomolecular" layer is formed, which "crosslinks" the molecular structure and includes a crosslinked polymer [1].

As a result, bonds in the alginate structure are weakened. It should be noted that in the first section, at low moisture content is the formation of a "monolayer" of moisture, which is most strongly associated with the product, which leads to low microbiological activity. Therefore, for the dried biodegradable polymer material, the suitable final moisture content is that which

corresponds to the range of water activity in the range $0.045 \leq A_w \leq 0.250$

In Figure 5, there are quite clear transitions from one conditional area to another, which correspond to the predominance of one of the forms of moisture connection with the dry residue of the material (osmotic, immobilization, and structural). The logarithm facilitates the interpretation of the obtained isotherms due to the linear approximation of the obtained dependences. The calculated error between approximated and empirically obtained values is

1.5%. The experimental dependencies of the logarithm of water activity on temperature and moisture content are as follows:

$$\ln A_w = (a_i T + b_i) W_p + (j_i T + d_i) \quad (2)$$

Where a_i, b_i, c_i, d_i are empirical coefficients; i is the serial number of the isotherm section. Coefficient values a_i, b_i, j_i and d_i for each zone are summarized in Table 2.

The values of the coefficients a_i, b_i, c_i, d_i for each zone A_w

Table 2:

Empirical coefficients	$0,045 \leq A_w \leq 0,250 \quad i = 1$	$0,250 \leq A_w \leq 0,825 \quad i = 2$	$0,850 \leq A_w \quad i = 3$
a_i	0	-0.0037	0.000285
b_i	-5.69	1.1731	-0.0682
j_i	0	1.176	0.458
d_i	0.386	-37.06	-13.769

Thermophysical and structural-mechanical characteristics of the gel

To perform calculations for dryers, it is necessary to know the product's thermophysical characteristics (TPC), on which the choice of a rational method for drying the material depends. Studies of heat and mass transfer [1] show that the thermal characteristics of wet dispersed materials depend on the chemical nature of the constituent components of the medium, the structure of the material, its moisture content, the forms and energy of the connection of moisture with the material, density, temperature, etc. The main TPH includes the coefficients of thermal conductivity λ , thermal diffusivity a , and specific heat c_m . The structural and mechanical properties of drying objects characterize their resistance to external energy due to the product's structure, the quality of the final products, and when choosing the conditions for their production and storage.

Determination of the coefficient of thermal conductivity of the gel.

Thermal conductivity coefficient λ is a thermophysical parameter characterizing the ability of a body to conduct heat, depending on the nature of the substance, its structure, temperature, and other parameters. It should be

noted that biopolymer materials, like most food products, are not solids in a sense given to this word in physics and the theory of heat transfer, and are capillary-porous structures in the form of a gel with pores or cells of various sizes and shapes. They are filled with gas or liquid or their mixture. In this regard, thermal energy transfer occurs through thermal conductivity through the solid skeleton, thermal conductivity and convection through cells filled with fluid or gas, and radiation between the walls of the pores. The heat energy transmitted by any of these methods can be approximately proportional to the temperature difference between two adjacent thermal surfaces. Therefore, Fourier's law can be used for a mathematical description of the total heat transfer process by all of the above methods, in which the proportionality coefficient will be the equivalent, or practical, coefficient of thermal conductivity λ [10]. The thermal conductivity of polymeric materials was determined according to the Method described in GOST 7076-99, "Method for determining thermal conductivity and thermal resistance at stationary heat vom mode." Based on the data obtained from the experiment, an approximated dependence thermal conductivity coefficient $\lambda, W / (m \cdot K)$ of polymer gel from temperature T, K and humidity $W, kg / k$ in the dehydration process.

The general view of the approximating dependence of λ , of the gel on the temperature in the range $300\text{K} \leq T \leq 333\text{K}$ and humidity in the range of $0.1 \text{ kg/kg} \leq W \leq 1 \text{ kg/kg}$ has the form:

$$\lambda(w, T) = (aT + b)w^2 + (cT + d)w + (eT + f) \quad (3)$$

The values of the coefficients a , b , c , d , e , and f are presented in Table 3.

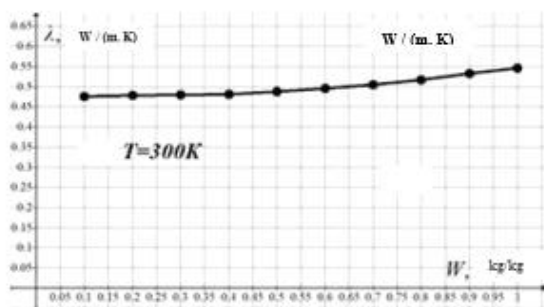
Table 3 coefficients a , b , c , d , e

An analysis of empirical curves (Figure 6) shows that an increase in material moisture leads to a change in the thermal conductivity coefficient towards an increase, which is due to the effect of

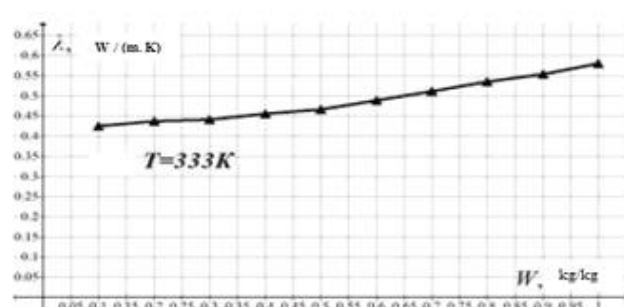
the action of water on the expansion of the polymer lattice of the material and, as a result, to its partial destruction. With a decrease in moisture content in the initial gel, the thermal conductivity of the material decreases because, during the formation of the polymer lattice, pores are formed in the material, which is filled with air, the thermal conductivity of which is much lower than the thermal conductivity of the liquid, which is quantitatively reduced in the polymer. When the bound moisture is removed in the process of drying, the strengthening of the molecular lattice of the polymer begins, including due to the partial displacement of air from its structure.

Table 3:

a	b	c	d	E	f
0.00048	-0.0434	0,0024	-0.753	-0.0018	1.024



a



b

Figure 6: Graph of the dependence of the thermal conductivity coefficient of a biopolymer gel on its moisture content at a temperature of 300K (a) and 313 (b)

Determination of the specific heat of the gel. When determining the clear heat C_M , it is assumed that the moisture and dry matter of the product are neutral. That is, their mixing occurs without a thermal effect. Then, the value C_M of biopolymer gel is defined as the weighted average specific value between the heat capacities of moisture c_w and dry matter $C_{c.o.}$ under normal conditions. To determine the specific heat capacity of the investigated material at a given temperature T , it is necessary to know the specific heat of its dry residue at the same temperature and mass fraction of moisture in the product. The equation for calculating the heat capacity of the investigated polymer C_M at temperatures from 0°C to 70°C it looks like this:

$$c_M = 4187W + (1 - W)c_{c.o.} \quad (4)$$

Where W is the humidity of the research object, kg/kg ; $C_{c.o.}$ - specific heat of dry residue, $\text{J} / (\text{kg K})$; 4187 is the value of specific heat capacity of water, $\text{J} / (\text{kg K})$. The temperature range $273 \div 350 \text{ K}$ practically does not change worries. Based on the analysis of methods for determining C_M [7], a method based on the determination of constant calorimeter - K , taking into account the loss of thermal energy, as well as the creation of a susceptible measurement circuit small (up to 2 K) changes in T sample, which allows you to get a result within a few minutes (Figure 7).

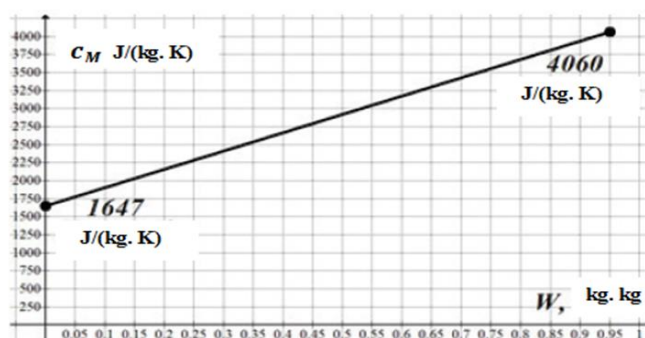


Figure 7: Dependence of c_M gel on moisture at $T = 273 \div 363$ K

The thermal diffusivity a , (m^2/s) is determined from the known relation $a = \lambda/c_p$

Determination of the density of the gel

The thickness of polymeric materials in the temperature range from 273 K to 363 K remains constant. Therefore, for this range, we can apply the psychometric Method of research in detail described in [6]. For the polymer under study, the experimental mean values were obtained as true density ρ , (kg/m^3) at its prescription moisture content $W = 0.95$ kg/kg in a given temperature range, and its additively determined values, in the case of lowering the moisture content of the gel to zero. In Figure 8 shows a graphical interpretation of the dependence of the actual density ρ of a

biopolymer from sodium alginate in the temperature range 273 ÷ 363 K and humidity from 0.1 to 0.95 kg/kg. The physical density of the polymer is determined by taking into account the volume of gases contained in the product. Considering that the final moisture content of the biodegradable material corresponds to water activity in the range of $0.0450.250 A_w \leq A \leq$, moisture removal from the original gel is carried out to a moisture content of 0.2 kg/kg. The drying process, as a rule, proceeds with a significant change in the volume of the structure, which, with a constant decrease in crushing volume, leads to the reduction in the physical density of the product, which in the resulting film material with appropriate moisture content can also be determined by psychometric Method.

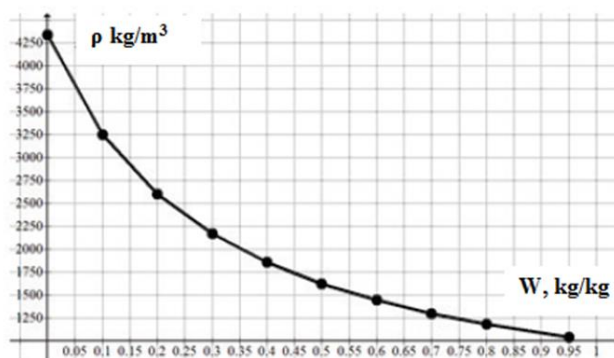


Figure 8: Dependence of the density of the gel on its moisture content at $T = 273 \div 363$ K

The experimentally obtained average value of physical density ρ_0 (kg/m^3) at its final moisture content $W = 0.2$ kg/kg in a given temperature range is equal to $\rho_0 = 971$ kg/m^3 . This is consistent with the data on the physical density of such polymers since the percentage of air in the

material is less than 0.1%, with a density of 1.3 kg/m^3 . Based on the film technology, the formation of an elastic gel from a liquid one occurs at a moisture content of the base composition of 0.45 kg/kg (Figure 9), while during the formation of the polymer lattice, the air is captured by the

resulting low-porous structure of the material. Therefore, using the additivity rule to calculate the density of a biopolymer gel in the moisture range of $0.95 \div 0.75$ kg/kg, two components are taken

into account, namely water and dry substances, and in the range from 0.1 to 0.75 kg/kg is added the third component is air.

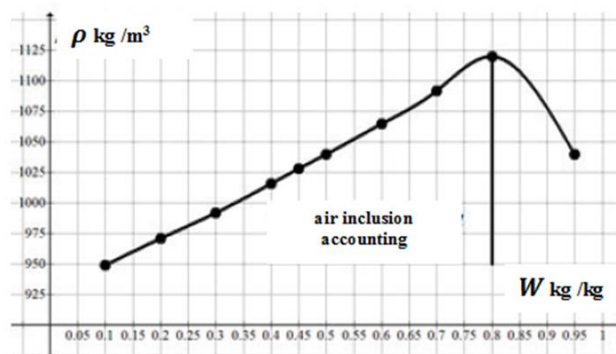


Figure 9: Dependence of the density of the gel on moisture in the temperature range $273 \div 363$ K

For the polymer under study, both the experimental average values of density ρ , (kg / m³) at a moisture content of $W = 0.95$ kg/kg and $W = 0.20$ kg/kg in a given temperature range. It is additively determined values given technology. In Figure 9 shows the dependence of ρ of a biopolymer from sodium alginate in the temperature range $273 \div 363$ K and humidity from 0.1 to 0.95 kg/kg. Linear approximation of this dependence for humidity ranges:

$0.1 \leq W \leq 0.8$ kg / kg and $0.8 \leq W \leq 0.95$ kg / kg in the temperature range from 273 to 363 K has the form:

$$\rho_{rash}(W) = 244W + 924, \text{ for } 0.1 \leq W \leq 0.8 \quad (5)$$

$$\rho_{rash}(W) = -533W + 1546, \text{ for } 0.8 \leq W \leq 0.95 \quad (6)$$

Specific characteristics of the gel for this field of research

The coefficient of dynamic viscosity of a biopolymer gel is the property of a material to resist shear flow. However, some food media still have an apparent significant bulk viscosity [2, 3], which characterizes the intensity of the work expended on the fluid flow. For rate viscosity, an RV-8 rotary viscometer was used. Dynamic viscosity was determined for a 4% solution of sodium alginate, and broth with a temperature of $75\text{--}80^\circ\text{C}$, consistent with the technology [6, 9], and its average value with five repetitions of the experiment was equal to 0.65 Pa s. The obtained

viscosity values do not contradict the known literature data [4, 5, 11]. Using higher temperatures for broths or other flavor components is undesirable because, due to thermal effects, the alginate molecule will be destroyed. The van der Waals adhesion forces will weaken, leading to a decrease in the aggregate stability of the gel and the formation of dense sediment due to the accumulation of colloidal particles. Shear rate $\omega = 115 \text{ s}^{-1}$, which is relatively low for elastic gels, was measured using a Brookfield R / S rheometer to study the effect of the E401 additive on the gel formation process and the strength of the obtained gel system. Gel strength can be measured as the force required to break the gel when its penetration by a cylindrical indenter deforms it at a constant rate [8]. During conducted experimental studies of the strength of biopolymer gel [9], when using the device "Structurometer ST-1M" obtained values of strength F in the range, $0.35 \div 0.37$ N. Liquid fraction) broth (the gel was in the temperature range of $75 \div 80^\circ\text{C}$, and the dosage of alginate was 4%. Melting temperature gel was determined on a Heppler viscometer and was 94°C at a given concentration of sodium alginate. pH = 6.8 was determined with a pH meter pH-013.

Conclusion

Regarding the design of production processes and devices in packaging materials technology, engineers can use the mathematical dependencies

established for thermophysical, structural-mechanical, hygroscopic, and specific characteristics of a biopolymer gel for this area of research. The findings of this research are necessary for the scientific study of the kinetics and dynamics of processes involving the transfer of heat and mass, in particular drying, modeling, and optimization, to conserve energy and resources during the processing and storage of food-related materials.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

The author declared that they have no conflict of interest.

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