

Interaction between Starch Paste and Gellan Gum Mixtures Part A: Wheat Starch

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Abstract: *The impact of two forms of gellan gum on the viscoelastic properties of starch pastes obtained from starch grain i.e. wheat starch, is discussed. The evaluation of the pastes structure in the company of low- and high-acyl gellan gum was made with rheological model based on fractional Maxwell-Wiechert approach on how to combine the mechanical components. Rheological parameters were determined and their modification related to the gellan gum content in wheat starch paste was discussed. It was found that the wheat starch pastes containing both forms of gellan gum are the media whose structure represents typical behavior of quasi-solid viscoelastic bodies.*

Keywords: *fractional rheological model, wheat starch paste, gellan gum, viscoelastic behavior*

I. INTRODUCTION

Soft materials are very important in a wide range of technological applications. They may appear as foams and adhesives, detergents and cosmetics, lubricants and fuel additives, paints and food additives. Moreover, a number of biological materials, like blood, muscle, milk, yogurt and jelly are classifiable as soft matter, too. Particularly important are food additives because they are out of shape, the structure and texture of food products. One of them is a starch.

Starch is one of the most important plant polysaccharides. It is a biodegradable, non-toxic and fully biocompatible natural polymer. It is a supplementary material in plants and is deposited in their tissues in the form of grains, so-called granules, whose size and shape depends on the starch botanical origin. A number of specialized applications of starch and its derivatives allow manufacturers to develop a range of products connected with technical applications. As a functional material, starch proved to be irreplaceable in many industries and, at the same time, as one of the most common organic compounds, it is a hydrocolloid with a specific nutritional value. It is the predominant carbohydrate in all major types of food used by humans. Out of many types of starch corn starch and potato starch, followed by wheat, rice and tapioca starches, have the largest share in the world production. Large-scale research is also being conducted on obtaining starch from an increasing number of sources such as starch extracted from kiwifruit (*Actinidia deliciosa*) [1], banana (*Musa paradisiaca*) [2], pea (*Pisum sativum*) [3], acorn (*Quercus ilex L.*) [4] or the chestnut (*Castanea sativa Mill.*) [5-7]. Thus, the prevalence of starch and its wide application in many different industries, with particular emphasis on food industry, makes research on the properties of starch of different botanical origin one of the most rapidly developing areas in terms of production technology and food technology in particular. Gellan gum, a polysaccharide produced by aerobic fermentation of *Sphingomonas elodea* bacteria, is also a hydrocolloid. This polysaccharide molecule consists primarily of repeating units of a tetrasaccharide composed of glucose, glucuronic acid and rhamnose in a 2:1:1 molar ratio, substituted with acyl (glyceryl and acetyl) groups like esters with O-glycosidic bonds [8-10]. Depending on the method of precipitating gellan gum from broth fermentation two gum forms can be obtained: high-acyl gellan gum which, depending on the configuration and chain entanglement, creates viscous, soft and flexible gels, and low-acyl gellan gum that forms hard and brittle gels of low viscosity. Possibility of modification of the gum particles by controlling the number of acyl groups can thus influence both the rheological properties of the final product, such as its viscosity, and the texture of the product, depending on its intended use.

Figure 1 shows the images obtained by scanning electron microscopy, showing the structure of the surface topography formed by the gellan gum [11] – cf. Fig. 1a and xanthan gum – cf. Fig. 1b. The structure formed by gellan gum is a polymer network with relatively low porosity, its appearance resembling a spider's web. By contrast, the structure of xanthan gum resembles a porous honeycomb construction. This example shows how important a role non-starch polysaccharide hydrocolloids play in structuring food products, especially those containing starch.

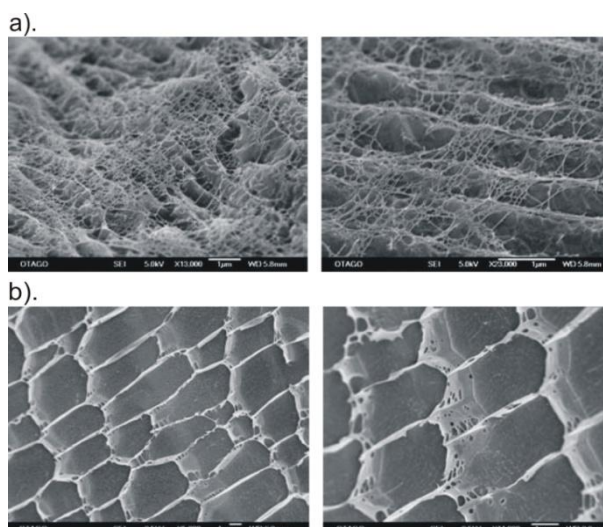


Fig. 1. Scanning Electron Microscopy structure of the surface topography [11]:
a). gellan gum, b). xanthan gum.

It should also be noted that, in general, native starches do not possess such properties that are ideal enough to prepare a desired food product. Most native starches are chemically modified to improve their process parameters (heat, shear) so as to obtain the appropriate gel texture, to ensure a sufficient level of cooling or defrosting and to control the amount of water in the product. A similar effect can also be produced by adding the appropriate polysaccharide hydrocolloid which may affect the behavior of native starch by its grain protection against shear, the product texture improvement, moisture retention and syneresis prevention thereby avoiding interference with starch chemical composition and preventing it from chemical modifications as a result [12]. Accordingly, mixtures of starch and non-starch polysaccharide hydrocolloids are often used together in the food industry to ensure proper structure and texture of the food produced. It is therefore important to understand the interactions (in the system) between starch and added polysaccharide hydrocolloids [12,13].

In the available literature, there are several studies on the interaction of wheat starch with polysaccharide hydrocolloids. Funami et al. [14] demonstrated that the addition of 0.5 ÷ 1.0% of non-ionic polysaccharide hydrocolloids in the form of guar gum, tara gum, locust bean gum and konjac gum to 13% concentration of wheat starch solution resulted in lowering the gelatinization temperature. Of all the hydrocolloids used guar gum appeared to have the greatest impact on lowering the temperature during the starch-hydrocolloid gelatinization. Mandala and Bayas [15] investigated the effect of the addition of chestnut gum on the properties of wheat starch in relation to two different methods for sample mixtures preparation. They concluded that the differences in rheological properties of the analysed starch-hydrocolloid systems resulted from the techniques of sample mixture preparation, gelatinization temperature as well as the size of the macromolecules. Alloncle et al. [16] investigated the rheological properties of the mixtures of wheat and maize starch with guar gum and locust bean gum. They found that the addition of hydrocolloids in starch caused an increase in energy thixotropy and pseudoplasticity of starch-hydrocolloid systems. Moreover, intensive research was conducted on the gelatinization of wheat starch in the presence of polysaccharide hydrocolloids such as xanthan gum, locust bean gum, carboxymethyl cellulose, hydroxypropyl methylcellulose, carrageenans and alginates, arabinoxylan and β -glucan [17-22]. As a result, the so-called synergistic effect manifested by a significant increase in the viscosity of the starch-hydrocolloid system was observed.

However, none of these experiments involved the analysis of viscoelastic properties of starch pastes obtained. Yet, the study of viscoelastic properties allows us to explore such features of these pastes as total elasticity of the network, the structure cross-linking power and cross-linking density of gel or network mesh size, persistence length and entanglement length [23]. This is possible by using the description models which consist of a suitable combination of Hooke's law-satisfying springs and viscous dampers operating in accordance with Newton's law, which, in turn, allows the visualization of both the resilient and the viscous characteristics of the analyzed paste. Consequently, the viscoelastic behavior of starch pastes can be described using the so-called fractional rheological model and fractional calculus. The advantage of the fractional rheological models is that dynamic behaviors can be described by a single equation which has a number of constant parameters defining viscoelastic properties of the tested material. When the fractional rheological model is applied, it is very important to identify the model parameters on the basis of experimental data while the identification process itself is called a reciprocal problem i.e. first, the experimental results are approximated by trigonometric functions and then the rheological parameters of the model are determined. Dinzart and Lipinski [24] described

several fractional rheological models which allow us to specify viscoelastic characteristics of the analyzed media whereas Orczykowska and Dziubiński [25-29] discussed the dynamic behavior of biomaterials using the fractional Zener model (FSLSM) by Alcoutlabi and Martinez-Vega and Friedrich and Braun model. Determination of rheological parameters of these models allowed for precise determination of biomaterials utility by evaluating the mechanical condition of their structure. Moreover, the models provided the opportunity to identify the direction and the changes which occurred in the structure and to determine their cause.

Due to continued interest in both native starch and hydrocolloids polysaccharide, the author of this paper has undertaken to analyze the mechanical structure of the pure starch paste obtained from wheat starch and the paste in the presence of both low- and high-acyl gellan gum and to explain the influence of gellan gum form and concentration on the rheological properties of the related biomaterials by applying fractional rheological model. The proposed method of interpreting the results of rheological measurements enabled a comprehensive assessment of the analyzed medium structure.

II. MATERIALS AND METHODS

2.1. Materials

Native wheat starch (produced by CARGILL, Germany, delivered via Bosto, Katy Wroclaw, Poland), low-acyl - ggLA (Kelcogel) and high-acyl gellan gum - ggHA (Kelcogel LT100) (produced by CP KELCO U.S. Inc., Atlanta, USA) were used as the study material.

2.2. Methods

The wheat starch amylose content was determined. Amylose level was identified by spectrophotometry with iodine by Morrison and Laignelet [30]. The absorbance measurements were made at a wavelength of $\lambda=640\text{nm}$ using Specord M 42 spectrophotometer (Carl Zeiss, Germany). Test solutions were prepared as described: a starch aliquot was or was not mixed with an appropriate amount of gellan gum and distilled water so that the starch concentration in the dispersion amounted to 4% (m/v), while the concentration of gellan gum additive was 0.05% - 0.1% - 0.2% - 0.25% - 0.3% - 0.4% and 0.5% (m/v) respectively. The sample was stirred using a mechanical stirrer at 300 rpm for 30 min. at room temperature in order for the grains to swell. Afterwards, the prepared dispersion was placed in the vessel with the column condenser to prevent water evaporation and heated in a water bath at $95\pm 1^\circ\text{C}$ for 30 min. with continuous stirring at 300 rpm. The obtained starch paste was then cooled down in a water bath at 20°C , and after cooling it was stored in a closed glass container in a refrigerator at 5°C for 24 hours. After 24 hours the rheometric measurements were performed.

2.2.1. Rheological measurements

After 24 hours of the pastes formation their rheological properties were determined using a rotational rheometer Physica MCR 501 by Austrian Anton Paar company and a cone - plate measuring system, with the cone of 50 mm diameter, 1° angle of inclination and the measuring gap between the cone and the plate equal to $0.048\mu\text{m}$. After placing the sample in the rheometer it was left at rest for 1 hour for stress relaxation generated while establishing the measurement gap. Basic research which constitutes the subject of the analysis performed was conducted in dynamic conditions in a controlled mode of deformation, determining the mechanical spectra by measuring the storage G' and loss G'' moduli. The tests were performed in a wide range of oscillation frequency ω changes i.e. 0.001s^{-1} - 200s^{-1} , collecting five measurement points for each decade. The same value of relative deformation of 3%, determined in previous studies of the linear viscoelastic range of the materials tested, was adopted for all frequencies of oscillation. Rheometer tests were carried out at 25°C .

2.2.2. Fractional rheological model

In order to describe the experimental data on the mechanical spectrum of pure starch pastes and their mixtures with gellan gum in a wide range of changes in the oscillation frequency ω fractional rheological models, involving both fast and slow processes of dissipation, i.e. the models with their mathematical descriptions containing the shortest τ_0 and the longest τ_m relaxation time respectively, were applied. Two such models are known in the literature: Friedrich and Braun model [31] and Alcoutlabi and Martinez-Vega model [32]. The models contain six rheological parameters: the equilibrium modulus G_e , the viscoelastic plateau modulus G_N^0 , the shortest relaxation time τ_0 , the longest relaxation time τ_m , and the relaxation coefficients α and β . These moduli are an extension of a standard linear solid model, and they are shown schematically in Figure 2. A satisfactory description of the experimental data in the form of mechanical spectrum of starch pastes with gellan gum was not obtained by Friedrich and Braun model [31]. Friedrich and Braun model is based on the difference between the viscoelastic plateau modulus G_N^0 and the equilibrium modulus G_e and the difference is represented by the relaxation strength ΔG in the mathematical description of the model. When determining rheological parameters in Friedrich and Braun model, firstly, the value of relaxation strength ΔG is established from the curve of the loss modulus G'' , and secondly, the value of the equilibrium modulus G_e is determined from the curve of the storage modulus G' .

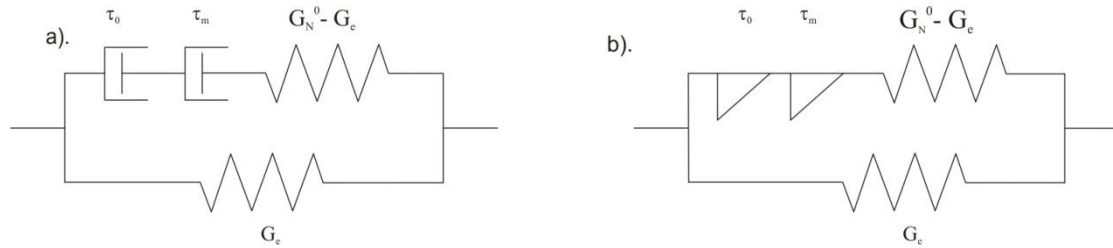


Fig. 2. Graphical representation of :
 a). Friedrich and Braun model [31],
 b). Alcoutlabi and Martinez-Vega model [32].

The value of the viscoelastic plateau modulus G_N^0 is represented by the sum of the values of the relaxation strength ΔG and the equilibrium modulus G_e . However, the viscoelastic plateau modulus G_N^0 can be experimentally determined directly from rheological measurements using the dependence of the phase angle δ as the modulus function $|G^*|$. Plot of van Gorp-Palmen [33] is a graphical representation of this dependence. The value of the viscoelastic plateau modulus G_N^0 was represented by such a value of function modulus $|G^*|$ at which phase angle δ was the smallest i.e. when the minimum manifested by a characteristic peak occurred. The viscoelastic plateau modulus obtained from Friedrich and Braun model was not numerically equal to the module obtained from the rheological measurements - from van Gorp-Palmen plot. The values differed by an order of magnitude. Thus, model curve fit of the curves resulting from Friedrich and Braun model [31] and experimental curves from rheological measurements was not obtained.

Similarly, the application of Alcoutlabi and Martinez-Vega model [32] to describe the experimental data on the mechanical spectrum of starch pastes with gellan gum led to a comparable discrepancies. The construction of Alcoutlabi and Martinez-Vega model resembles the model by Friedrich and Braun [31] – cf. Fig. 2, with the difference lying in two Newton's viscous elements replaced by two viscoelastic Scott-Blair's elements - two springpots. However, the mathematical description of Alcoutlabi and Martinez-Vega model is also based on the difference between the viscoelastic plateau modulus G_N^0 and the equilibrium modulus G_e . Therefore, the viscoelastic plateau modulus G_N^0 from Alcoutlabi and Martinez-Vega model did not correspond to the experimental value of the module obtained directly from the rheological measurements. Neither was the model curve fit obtained of experimental curves and model curves from Alcoutlabi and Martinez-Vega model. Consequently, neither Friedrich and Braun [31] nor Alcoutlabi and Martinez-Vega's model [32] was considered to be appropriate to describe the dynamic behavior of pure starch pastes and their mixtures with gellan gum in a wide range of oscillation frequency changes with rapid and slow dissipation processes.

Therefore, in order to describe the mechanical spectrum of the pure starch pastes and their mixtures with gellan gum Maxwell-Wiechert approach [34] to methods of joining mechanical elements was applied. A new model was proposed as a generalized version of Maxwell-Wiechert model. The model outlined in Figure 3 is based on two parallel Maxwell models, each of which has two built-in viscoelastic Scott Blair 's elements and parallel elastic Hook's element.

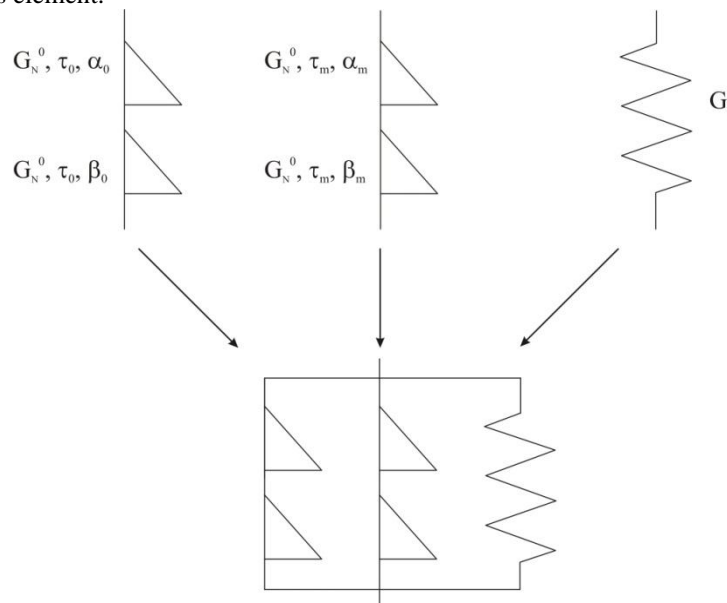


Fig. 3. Proposed own rheological model.

As a result, the suggested rheological model could be described by the following equations:

$$G' = G_e + G_N^0 \left\{ (\omega\tau_0)^{\alpha_0} \frac{\cos\left(\frac{\pi\alpha_0}{2}\right) + (\omega\tau_0)^{\alpha_0-\beta_0} \cos\left(\frac{\pi\beta_0}{2}\right)}{1 + 2(\omega\tau_0)^{\alpha_0-\beta_0} \cos\left[\left(\alpha_0 - \beta_0\right)\frac{\pi}{2}\right] + (\omega\tau_0)^{2(\alpha_0-\beta_0)}} + (\omega\tau_m)^{\alpha_m} \frac{\cos\left(\frac{\pi\alpha_m}{2}\right) + (\omega\tau_m)^{\alpha_m-\beta_m} \cos\left(\frac{\pi\beta_m}{2}\right)}{1 + 2(\omega\tau_m)^{\alpha_m-\beta_m} \cos\left[\left(\alpha_m - \beta_m\right)\frac{\pi}{2}\right] + (\omega\tau_m)^{2(\alpha_m-\beta_m)}} \right\} \quad (1)$$

$$G'' = G_N^0 \left\{ (\omega\tau_0)^{\alpha_0} \frac{\sin\left(\frac{\pi\alpha_0}{2}\right) + (\omega\tau_0)^{\alpha_0-\beta_0} \sin\left(\frac{\pi\beta_0}{2}\right)}{1 + 2(\omega\tau_0)^{\alpha_0-\beta_0} \cos\left[\left(\alpha_0 - \beta_0\right)\frac{\pi}{2}\right] + (\omega\tau_0)^{2(\alpha_0-\beta_0)}} + (\omega\tau_m)^{\alpha_m} \frac{\sin\left(\frac{\pi\alpha_m}{2}\right) + (\omega\tau_m)^{\alpha_m-\beta_m} \sin\left(\frac{\pi\beta_m}{2}\right)}{1 + 2(\omega\tau_m)^{\alpha_m-\beta_m} \cos\left[\left(\alpha_m - \beta_m\right)\frac{\pi}{2}\right] + (\omega\tau_m)^{2(\alpha_m-\beta_m)}} \right\} \quad (2)$$

The suggested model – see eqs. (1)÷(2) – has eight rheological parameters, i.e., G_e , G_N^0 , τ_0 , α_0 , β_0 , τ_m , α_m , β_m . These parameters represent the following properties of tested materials [25-29,35]:

- G_e [Pa] is an equilibrium modulus, modulus of elasticity in the steady state flow condition which represents total elasticity of the medium. High values of modulus G_e indicate significant elastic properties of the material. Its reciprocal, J_e , is a susceptibility limit in the state of equilibrium.

- G_N^0 the viscoelastic plateau modulus identified with the structure of cross-linking power. High values of this modulus indicate high structure of cross-linking and potential slowing down of the process of physical ageing in time. The reciprocal of this modulus is susceptibility of the structure at cross-linking J_N^0 . It should be noted here that the value of viscoelastic modulus G_N^0 was determined experimentally i.e. directly from rheological measurements on the basis of van Gurp-Palmen plot [33] reflecting the dependence of phase angle δ as a function of relative greatest stress to the greatest strain. The value of the viscoelastic plateau modulus G_N^0 was represented by such a value of function modulus $|G^*|$ at which phase angle δ was the smallest i.e. when the minimum manifested by a characteristic peak occurred.

- τ_0 [s] is the shortest relaxation time value in high frequency oscillations,

- τ_m [s] is the longest relaxation time value in high frequency oscillations,

The times define the time after which stress relaxation will occur and short relaxation times indicate strong elastic properties of the material.

- α_0 and β_0 [-] are relaxation coefficients directly associated with the shortest relaxation times in the high frequency of oscillation,

- α_m and β_m [-] are relaxation coefficients directly associated with the longest relaxation times in the high frequency of oscillation,

Relaxation coefficient values range from 0 to 1. If the value is equal to zero it is characteristic of elastic bodies and when it is equal to one, the behavior is characteristic of viscous liquids. The difference between the two relaxation coefficients (α - β) responsible for the deformation results from the stress impact on the structure formation of the tested medium, in low and high values of the oscillation frequency respectively.

The knowledge of eight rheological parameters in the model which includes two relaxation times, thereby covering both fast and slow dissipation processes, allows for a comprehensive evaluation of the rheological properties of viscoelastic materials through the knowledge of other parameters determining their properties. In this model, the parameters include:

- f [-] - dispersion modulus which indicates how many times a structure reorganization occurred over the analyzed oscillations frequencies ω and is described by the following equation:

$$f = \frac{G_N^0}{G_e} \quad (3)$$

- k [-] - the damping factor of network oscillations which indicates to what extent the structure of the medium is resistant to vibration from the outside, described by the equation:

$$k = \frac{G_N^0 - G_e}{G_e} \quad (4)$$

- ΔG [Pa] - relaxation strength, described by the following equation:

$$\Delta G = (G_N^0 - G_e) \quad (5)$$

- ω_0 [s⁻¹] - cross-linking density of gel, described by the following equation:

$$\omega_0 = \frac{1}{\tau_0} \quad (6)$$

- η_0 [Pas] - Newtonian viscosity in a steady state which is a measure of the flow properties of the contractual

elementary cells of the network, i.e. a set of elements closed by a minimum number of network nodes with the ability for individual movement, described by the equation:

$$\eta_o = \frac{\tau_m}{J_e} \quad (7)$$

- S [Pas] - gel stiffness, described by the following equation:

$$S = G_N^0 \cdot \tau_o^{\frac{2\alpha_0 \cdot \beta_0}{\alpha_0 + \beta_0}} \quad (8)$$

- L [-] - the width of the viscoelastic plateau which combines fast and slow processes of dissipation, described by the following equation:

$$L = \frac{\tau_m}{\tau_o} \quad (9)$$

2.2.3. Statistical analysis

In order to assess the accuracy of the description of the experimental models with model equations (1)÷(2) in the proposed rheological model statistical analysis [36] was done by curve fitting of the model curves and the experimental curves in relation to the tangent of the loss angle δ , which is the ratio of the loss modulus G'' to the storage modulus G' . The evaluation was conducted by estimating:

- MPE – the mean percentage error, described by the following equation:

$$MPE = \frac{1}{N} \sum_{i=1}^N \left[\frac{(tg \delta_{exp} - tg \delta_{mod})}{tg \delta_{exp}} \right] \cdot 100 \quad (10)$$

- MBE – the mean bias error, described by the following equation:

$$MBE = \frac{1}{N} \sum_{i=1}^N (tg \delta_{mod} - tg \delta_{exp}) \quad (11)$$

- RMSE – the root mean square error, described by the following equation:

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (tg \delta_{exp} - tg \delta_{mod})^2 \right]^{\frac{1}{2}} \quad (12)$$

- EF – modelling efficiency, described by the following equation:

$$EF = \frac{\sum_{i=1}^N (tg \delta_{exp} - tg \delta_{exp_{sr}})^2 - \sum_{i=1}^N (tg \delta_{mod} - tg \delta_{exp})^2}{\sum_{i=1}^N (tg \delta_{exp} - tg \delta_{exp_{sr}})^2} \quad (13)$$

- χ^2 – chi-square test described by the following equation:

$$\chi^2 = \frac{\sum_{i=1}^N (tg \delta_{exp} - tg \delta_{mod})^2}{N - n_{mod}} \quad (14)$$

where $tg\delta_{exp}$ designates experimental value obtained directly from rheological measurements, $tg\delta_{mod}$ - is the model value obtained from the fitting of model equations (1) and (2) in the proposed own rheological model, $tg\delta_{exp_{sr}}$ - is the average experimental value obtained directly from rheological measurements, N - is the number of experimental points obtained by rheological measurements, n_{mod} - is the number of rheological parameters of the proposed own rheological model.

III. RESULTS AND DISCUSSION

The experimental data obtained by dynamic measurements on the rheological properties of wheat starch pastes with low- and high-acyl gellan gum were described by proposed rheological model - eqs. (1)÷(2) and the parameter values obtained are shown in Tables 1 and 2.

Results of statistical evaluation presented in Tables 1 and 2 indicate low values of mean percent error (MPE), mean bias error (MBE), root mean squared error (RMSE) and standard error (X^2) but also show very high values of the model fit efficiency (EF), which, together with high values of correlation coefficient (R^2), reflect a very good fit of the proposed rheological model with the experimental data obtained directly from dynamic measurements.

Table 1. Parameters of the proposed own rheological model designated for pure wheat paste and wheat starch paste with the addition of low-acyl gellan gum at 25⁰C.

	0.00%LA	0.05%LA	0.10%LA	0.20%LA	0.25%LA	0.30%LA	0.40%LA	0.50%LA
G _e [Pa]	8.43	6.21	5.78	5.93	8.29	9.37	11.79	11.17
G _N ⁰ [Pa]	51.30	49.27	47.35	47.01	78.86	81.95	89.79	92.46
ω ₀ [s ⁻¹]	34.75	33.54	33.50	38.14	24.91	23.33	24.60	20.54
α _m [-]	0.239	0.241	0.241	0.235	0.254	0.257	0.255	0.263
α ₀ [-]	0.449	0.447	0.447	0.455	0.426	0.422	0.427	0.413
β _m [-]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
β ₀ [-]	0.238	0.239	0.239	0.236	0.244	0.245	0.244	0.247
f [-]	6.08	7.93	8.19	7.92	9.51	8.74	7.61	8.27
S [Pas]	17.00	16.51	15.88	15.14	29.06	30.85	33.21	36.27
k [-]	5.085	6.934	7.192	6.927	8.513	7.746	6.616	7.278
L [-]	2.788·10 ⁵	2.669·10 ⁵	2.665·10 ⁵	3.119·10 ⁵	1.866·10 ⁵	1.725·10 ⁵	1.781·10 ⁵	1.453·10 ⁵
η ₀ [Pas]	6.761·10 ⁴	4.941·10 ⁴	4.598·10 ⁴	4.849·10 ⁴	6.208·10 ⁴	6.926·10 ⁴	8.533·10 ⁴	7.897·10 ⁴
α _m -β _m [-]	0.239	0.241	0.241	0.235	0.254	0.257	0.255	0.263
α ₀ -β ₀ [-]	0.211	0.208	0.208	0.218	0.182	0.176	0.184	0.166
ΔG [Pa]	42.87	43.06	41.57	41.08	70.57	72.58	78.00	81.29
R ²	0.9992	0.9996	0.9996	0.9995	0.9995	0.9994	0.9995	0.9992
MPE	0.0745	-0.0054	-0.0152	-0.0423	0.0276	0.0680	0.0525	0.0934
MBE	-0.0033	0.0002	0.0007	0.0018	-0.0013	-0.0032	-0.0024	-0.0045
RMSE	0.0191	0.0014	0.0039	0.0106	0.0076	0.0189	0.0143	0.0265
EF	0.9993	1.0000	1.0000	0.9998	0.9999	0.9994	0.9997	0.9989
X ²	0.0005	0.0000	0.0000	0.0001	0.0001	0.0005	0.0003	0.0009

Table 2. Parameters of the proposed own rheological model designated for pure wheat paste and wheat starch paste with the addition of high-acyl gellan gum at 25⁰C.

	0.00%HA	0.05%HA	0.10%HA	0.20%HA	0.25%HA	0.30%HA	0.40%HA	0.50%HA
G _e [Pa]	8.43	12.61	13.76	14.27	15.34	15.63	13.85	12.79
G _N ⁰ [Pa]	51.30	78.04	84.56	92.32	95.12	97.53	101.58	104.91
ω ₀ [s ⁻¹]	34.75	45.01	40.98	36.31	34.70	33.38	27.84	26.46
α _m [-]	0.239	0.227	0.231	0.237	0.239	0.241	0.249	0.252
α ₀ [-]	0.449	0.465	0.459	0.452	0.449	0.446	0.434	0.431
β _m [-]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
β ₀ [-]	0.238	0.233	0.235	0.237	0.238	0.239	0.242	0.243
f [-]	6.08	6.18	6.14	6.47	6.20	6.24	7.33	8.20
S [Pas]	17.00	23.90	26.64	30.19	31.55	32.74	36.12	37.92
k [-]	5.085	5.189	5.144	5.470	5.201	5.240	6.334	7.203
L [-]	2.788·10 ⁵	3.814·10 ⁵	3.403·10 ⁵	2.938·10 ⁵	2.782·10 ⁵	2.654·10 ⁵	2.132·10 ⁵	2.006·10 ⁵
η ₀ [Pas]	6.761·10 ⁴	1.068·10 ⁵	1.143·10 ⁵	1.155·10 ⁵	1.229·10 ⁵	1.242·10 ⁵	1.061·10 ⁵	9.694·10 ⁴
α _m -β _m [-]	0.239	0.227	0.231	0.237	0.239	0.241	0.249	0.252
α ₀ -β ₀ [-]	0.211	0.231	0.224	0.215	0.211	0.208	0.192	0.188
ΔG [Pa]	42.87	65.43	70.79	78.05	79.78	81.90	87.73	92.12
R ²	0.9992	0.9995	0.9995	0.9995	0.9993	0.9993	0.9994	0.9995
MPE	0.0745	-0.0022	0.0266	0.0407	0.0687	0.0771	0.0710	0.0510
MBE	-0.0033	0.0001	-0.0011	-0.0018	-0.0030	-0.0034	-0.0033	-0.0024
RMSE	0.0191	0.0005	0.0066	0.0103	0.0176	0.0199	0.0190	0.0138
EF	0.9993	1.0000	0.9999	0.9998	0.9994	0.9993	0.9994	0.9997
X ²	0.0005	0.0000	0.0001	0.0001	0.0004	0.0005	0.0005	0.0002

Figure 4a and 4b show the experimental relations of storage G' and loss G'' moduli as the function of ω and curves representing these values which result from the proposed rheological model - eqs. (1) and (2). Mechanical spectrum of pure wheat starch paste (with amylose content equal to 24.3%) and wheat starch paste with the addition of low- and high-acyl gellan gum in the classical system of coordinates - cf. Fig. 4a and 4b - shows the flat course of the storage modulus G' corresponding to the elastic plateau of "gum" as well as a minimum occurring in the curve of the loss modulus G'' , which is present in the range of $10^{-2} \div 10^0 \text{ s}^{-1}$ oscillation frequency. These are the characteristics of cross-linked polymers with a structure of unknown nature. Both in low frequency and high frequency oscillations the curves of G' and G'' moduli approached each other but their intersection was not detected. At the oscillation frequency corresponding to the minimum G'' the absolute values of the G' and G'' moduli differed from each other by more than a decade and the phase angle δ for, e.g. pure wheat starch paste, reached the value of 4.58° whereas for the same paste with the addition of low-acyl gellan gum of 0.05% concentration the value amounted only to 4.62° and for the paste with added high-acyl gellan gum of 0.05% concentration the value merely reached 4.33° .

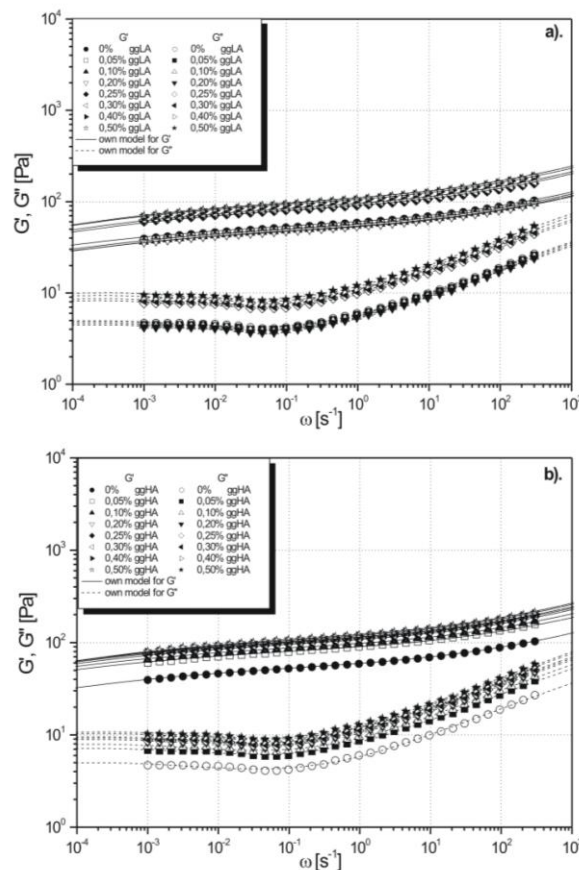


Fig. 4. Mechanical spectra of pure wheat paste and wheat paste with:
 a). low-acyl gellan gum,
 b). high-acyl gellan gum

Figures 5a and 5b show the dependence of the phase angle δ as a function of absolute values of the G' and G'' moduli; the dependence is referred to as van Gurp-Palmen plot. The value of the modulus $|G^*|$ at which the phase angle reaches the lowest value is the viscoelastic plateau modulus G_N^0 , representing the structure cross-linking power. The data presented in Figures 5a and 5b demonstrate that the values of phase angle δ for both pure wheat starch paste and the paste containing low- and high-acyl gellan gum in the entire analyzed concentration extent of gellan gum ranged from 4.33° to 5.12° , which at this stage already indicates a strong elastic properties of the analyzed media. Simultaneously, the value of this angle is a quantitative measure of the biopolymer chain branching. The analysis of the experimental data described by the proposed rheological model - eqs. (1) and (2) - showed that high values of viscoelastic plateau modulus G_N^0 revealed that in all analyzed cases, the medium obtained displayed the structure whose behavior is typical of viscoelastic quasi-solid bodies. For pure wheat starch paste viscoelastic plateau modulus G_N^0 responsible for the structure cross-linking power equaled 51.3Pa.

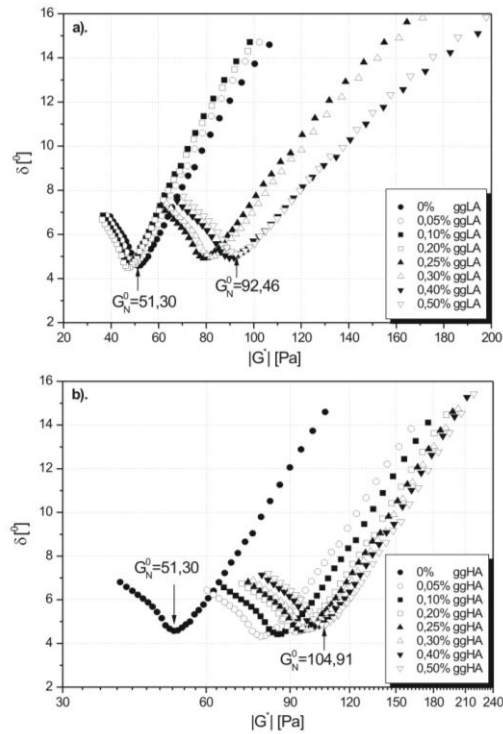


Fig. 5. van Gorp-Palmen plot for pure wheat starch paste and wheat starch paste with the addition of:
 a). low-acyl gellan gum, b). high-acyl gellan gum

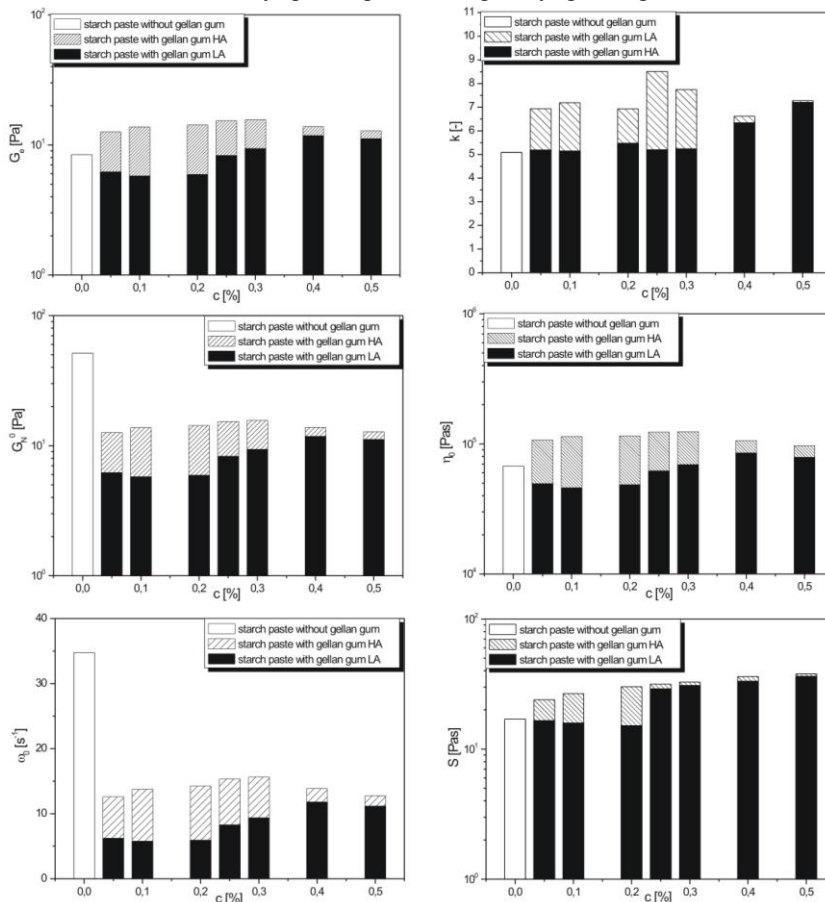


Fig. 6. Comparison of viscoelastic properties of wheat starch pastes with low- and high-acyl gellan gum additive.

In order to compare the effect that the form of gellan gum has on wheat starch pastes, the graphs were compiled with a view to comparing the values of viscoelastic importance in starch pastes as a function of varying concentrations of both low- and high-acyl gellan gum. These values included: equilibrium modulus G_e representing the network elasticity, viscoelastic plateau modulus G_N^0 identified with the structure of cross-linking power, cross-linking density of gel ω_0 , Newtonian viscosity in a steady state η_0 , gel stiffness S , the damping factor of network oscillations k , the relaxation strength representing the difference between the structure cross-linking power G_N^0 and the network elasticity G_e .

The data presented in Fig. 6 indicate that high-acyl gellan gum additive in wheat starch pastes leads to an increase in the network elasticity G_e as well as in Newtonian viscosity in a steady state η_0 ; both of these parameters are higher in pastes with high-acyl gellan gum. On the other hand, low-acyl gellan gum causes the two parameters to rise only when the gum concentration in the paste exceeds 0.3%. The values of viscoelastic plateau modulus G_N^0 reflecting the cross-linking power in wheat starch pastes with low- and high-acyl gums are lower than structure cross-linking power of pure wheat starch paste. Simultaneously, however, these values in the starch paste with high-acyl gellan gum are higher than in the paste with low-acyl gellan gum. In the case of high-acyl gellan gum, an increase in cross-linking power is observed up to 0.3% concentration of gellan gum in the paste, at concentration values exceeding 0.3% the cross-linking power decreases. By contrast, low-acyl gellan gum causes the cross-linking power to decrease when the gum concentration in the paste does not exceed 0.2%, above this value the structure cross-linking power rises. Interestingly, however, both low- and high-acyl gellan gum at their concentrations in starch paste amounting to 0.4% and 0.5% lead to very comparable values of structure cross-linking power. Most likely, these concentrations of both gellan gum forms lead to the "full" cross-linking lock of the structure whose power then stems only from the "tightening" in the gum cross-linking structure on the stiffened starch granules. The nature of the cross-linking density of gel change is the same as in the case of the structure cross-linking power. In practice, this means a clear weakening of the cross-linking power and cross-linking density of gel of wheat starch pastes in the company of low- and high-acyl gellan gum compared to pure wheat starch paste. Nevertheless, it is noteworthy that low-acyl gellan gum has a stronger impact on weakening these wheat pastes characteristics than high-acyl gellan gum. High-acyl gellan gum in wheat starch pastes increases the viscosity of these pastes when its concentration does not exceed 0.3%, above this concentration we observe a decrease in viscosity - cf. Fig. 6.

It probably means that above this concentration starch granules are completely blocked by "advancing" gellan network. In contrast, low-acyl gellan gum in wheat starch pastes results in pastes of lower viscosity than that of pure wheat starch paste without this gellan gum. This is the case, however, with up to 0.2% concentration of gellan gum in the paste. When the concentration is higher than 0.2%, low-acyl gellan gum additive leads to increased viscosity of wheat pastes. Generally, lower viscosity is more characteristic of wheat pastes with low-acyl than with high-acyl gellan gum. Low- and high-acyl gellan gums added to wheat starch pastes create stiff gels. The presence of high-acyl gellan gum in wheat pastes leads to systematic enhancement of gel stiffness along with the gum concentration in comparison to pure starch paste - cf. Fig. 6. Meanwhile, low-acyl gellan gum reduces gel stiffness as compared to pure wheat paste only to increase wheat paste stiffness when the gum concentration exceeds 0.2%. Interestingly, at the level of 0.25% concentration of both types of gellan gum in wheat paste these pastes stiffness begins to be comparable, with only a slight advantage of high-acyl gellan gum.

The ability of wheat pastes with high-acyl gellan gum to damp the network oscillations is practically at the same level as in pure wheat paste but only with gellan gum concentration in the paste amounting to 0.3% - cf. Fig. 6. Above this concentration value, such capacity is increasing due to the coexistence of high-acyl gellan gum network.

With low-acyl gellan gum, the ability of the paste to damp the network oscillations in the gum concentration range of up to 0.3% is much better than with low-acyl gellan gum and, at the same time, better than the capability of pure wheat paste. However, at 0.4% and 0.5% concentrations of high-acyl gellan gum in wheat pastes damping the network oscillations is nearly the same as with the additive of low-acyl gellan gum. This is indicative of the gellan gum structure tightening at the starch granules blocked by the gum. In general, low-acyl gellan gum produces softer gels than high-acyl gellan gum does.

Figure 7 demonstrates the effect of the form of gellan gum on the stress relaxation strength in wheat starch pastes. High-acyl gellan gum present in wheat starch paste results in a very systematic increase in the stress relaxation along with the increased concentration of gellan gum in the starch paste. This is the result of blocking starch granules by high-acyl gellan gum from the moment of its appearance in such a paste solution. Two mechanisms of action, however, can be easily detected in the low-acyl gellan gum. Up to 0.2% concentration of low-acyl gellan gum, a linear, albeit very small, decrease in stress relaxation can be detected, whereas above this concentration value, a linear and marked increase in stress relaxation is observed. The low-acyl gellan gum concentration of 0.2% in wheat starch paste is therefore a threshold concentration below which blockage of starch granules is observed and above which the gum's share in affecting the wheat paste's

viscoelastic properties increases.

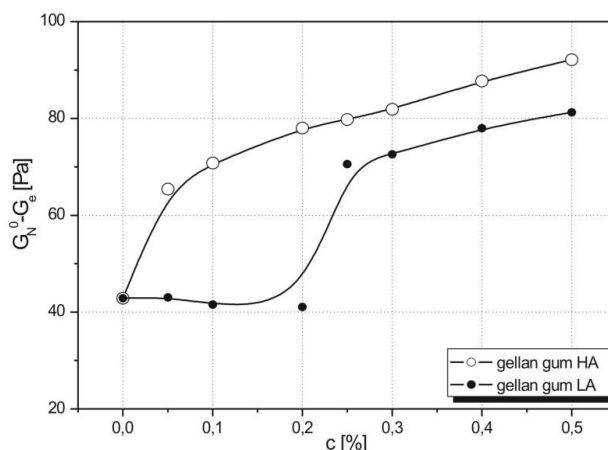


Fig. 7. Changes in the relaxation power in wheat starch paste with the additive of low- and high-acyl gellan gum.

IV. CONCLUSIONS

Viscoelastic properties of pastes obtained from wheat starch can be described using the so-called fractional rheological models. The advantage of the fractional rheological models is that dynamic behaviors can be described by equations which have a number of constant parameters defining viscoelastic properties of the tested material. The analysis of the data obtained by the proposed rheological model revealed that the paste obtained from wheat starch with the additive of low- and high-acyl gellan gum is the medium of the structure displaying typical properties of viscoelastic quasi-solid bodies. The values of the parameters in the applied fractional rheological model indicate that:

- when containing low- and high-acyl gellan gum, wheat starch pastes' cross-linking power was weaker than the power of pure wheat starch paste but, at the same time, the cross-linking power was greater in the wheat paste with high-acyl than low-acyl gellan gum,
- the additive of low- and high-acyl gellan gum in wheat starch pastes increases the elasticity of the network G_e ; starch pastes with high-acyl gellan gum displayed higher elasticity than the pastes with low-acyl gellan gum,
- low- and high-acyl gellan gum added to wheat starch pastes resulted in reduced cross-linking power and density of such pastes in relation to pure starch pastes and low-acyl gellan gum had a stronger impact on weakening these features of starch pastes than high-acyl gellan gum,
- when mixed with wheat starch, low-acyl gellan gum creates softer gels than high-acyl gellan gum does.

It should be emphasized that from the food industry standpoint and its need for mixtures of starch and non-starch polysaccharide hydrocolloid, during production and processing of such biomaterials, fractional rheological models can be very useful for control or suitable formation of the biomaterial structure and texture for the purposes of the manufactured product. It is the criterion identified by technologists that determines the choice of the product for its functional characteristics.

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