Interaction between Starch Paste and Gellan Gum Mixtures Part B: Potato Starch

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Abstract: *The impact of two forms of gellan gum on the viscoelastic properties of starch pastes obtained from potato 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 potato starch paste was discussed. It was found that the potato 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, potato starch paste, gellan gum, viscoelastic behavior*

I. INTRODUCTION

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. Native starches do not possess the properties that are irreplaceable to produce a desired food product. Therefore, most native starches are chemically modified to improve their process parameters 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 prevent it from chemical modifications as a result [1]. Gellan gum, a polysaccharide produced by aerobic fermentation of Sphingomonas elodea bacteria, is one of many polysaccharide hydrocolloids available on the food market. 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 [2-4]. The hydrocolloid occurs in two forms: 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 affect both the rheological properties of the final product, such as its viscosity, and the texture of the product, depending on its intended use. Consequently, synergistic effect of such a hydrocolloid system as starch- non-starch polysaccharide hydrocolloid is commonly found in food industry. It is therefore important to understand the interactions between starch and hydrocolloid polysaccharide [1,5].

In the available literature, there are several studies on the interaction of potato starch with non-starch polysaccharide hydrocolloids. Mandala et al. [6] conducted research on the texture of the gels composed of soluble potato starch and xanthan gum. The solutions of potato starch and xanthan gum were prepared separately at 75^0C and 90^0C and then mixed. The observations revealed that the solutions prepared at 75^0C were a mixture of starch granules surrounded by a continuous phase of amylose, whereas the solutions prepared at 90^0C contained parts of granules or their agglomerates suspended in a continuous phase of amylose, amylopectin, and xanthan gum. Khanna and Tester [7] assessed the impact of Konjac flour on the gelation and retrogradation of potato starch and corn starch with different amylose content. Their analysis revealed that the addition of Konjac flour expands the scope of gelatinization and also increases the final temperature of gelatinization. Fiedorowicz et al. [8] and Sikora and Kowalski [9] conducted studies on the interactions between potato starch and hydrocolloids such as arabic gum, carob gum, guar gum, karaya gum, xanthan gum and carrageenans. On the basis of the rheological measurements, they concluded that the type of hydrocolloid reduces or increase the temperature of gelatinization and may also contribute to the reduction or increase of such mixtures pseudoplasticity. Sikora et al. [10] and Baranowska et al. [11] investigated the properties of potato starch pastes containing hydrocolloids such as arabic gum, carob gum, guar gum, karaya gum, xanthan gum and carrageenans using low field NMR. The study showed that the course of gelatinization in the presence of non-starch polysaccharide hydrocolloids was dependent on the availability of water molecules, which depended on the properties of the hydrocolloids.

Research on the interactions between starch and non-starch polysaccharide hydrocolloid did not involve the analysis of the viscoelastic properties of such mixtures. The fractional derivative rheological models and the fractional calculus are particularly useful for this purpose. The advantages of fractional rheological models have been described in the study by Dinzart and Lipinski [12] as well as in the study by Orczykowska and Dziubiński [13-17], who discussed the dynamic behavior of a variety of biomaterials including, among others, the chestnut and acorn starch, linen gum as well as rice and maize starches in the presence of sugars. Determination of rheological parameters of standard Zener model (FSLSM) by Alcoutlabi and Martinez-Vega and Friedrich-Braun model allowed Orczykowska and Dziubiński for precise determination of biomaterials utility by evaluating the mechanical condition of their structure which was based on the understanding of such characteristics as the elasticity of the network, the structure cross-linking power and cross-linking density of gel.

The authors of the paper have undertaken to analyze the mechanical structure of pure starch paste obtained from potato starch and and the starch containing low- and high-acyl gellan gum and to explain the influence of gellan gum concentration and form 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 structure of the analyzed medium.

II.   MATERIALS AND METHODS

2.1. Materials
Native potato starch (produced by PEPEES S.A. Food Plant, Łomża, 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 amylose content in potato starch was identified and the amylose level was identified by spectrophotometry with iodine by Morrison and Laignelet [18]. The absorbance measurements were made at a wavelength of $\lambda=640$ 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 300rpm for 30min. 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±1°C for 30min. with continuous stirring at 300rpm. 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 50mm diameter, 1^0 angle of inclination and the measuring gap between the cone and the plate equal to 0.048mm. 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 25^0C.

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 [19] and Alcoutlabi and Martinez-Vega model [20]. 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 models are an extension of a standard solid body model, and they are shown schematically in Figure 1.
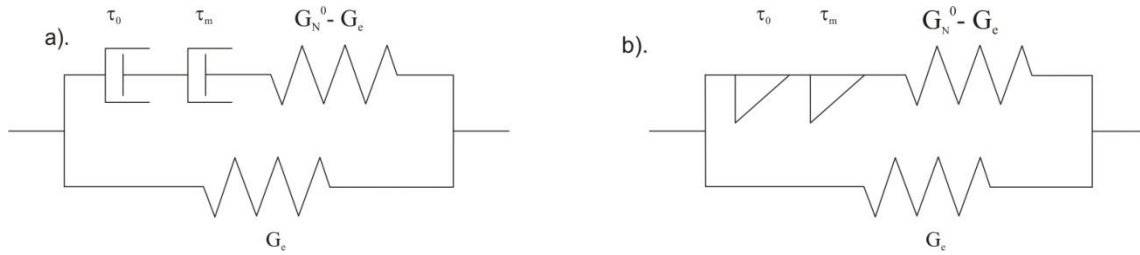
Fig. 1. Graphical representation of:
a). Friedrich and Braun model [19]
b). Alcoutlabi i Martinez-Vega model [20].

A satisfactory description of the collected experimental data showing mechanical spectrum of starch pastes with gellan gum has not been obtained using Friedrich and Braun model [19]. 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 mathematically represented by the relaxation strength ΔG. 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'. 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*|. van Gurp-Palmen plot [21] 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 Gurp-Palmen plot. The values differed by an order of magnitude. Thus, model curve fit of the curves resulting from Friedrich and Braun model [19] and experimental curves from rheological measurements was not obtained.

Similarly, the application of Alcoutlabi and Martinez-Vega model [20] to describe the experimental data on the mechanical spectrum of starch pastes with gellan gum lead to comparable discrepancies. The construction of Alcoutlabi and Martinez-Vega model resembles the model by Friedrich and Braun [19] – cf. Fig.1., with the difference lying in two Newton's viscous elements replaced by two viscoelastic Scott-Blair's elements or 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 rheometric measurements. Neither was the model curve fit obtained of experimental curves and model curves from Alcoutlabi and Martinez-Vega [20] model.

Consequently, neither Friedrich-Braun [19] nor Alcoutlabi and Martinez-Vega's model [20] was considered to be appropriate to describe the dynamic behavior of pure potato 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 [22] to the 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 2 was compiled on the basis of two parallel Maxwell models, each of which has two built-in viscoelastic Scott-Blair's elements and parallel elastic Hook's element.

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

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

(1)

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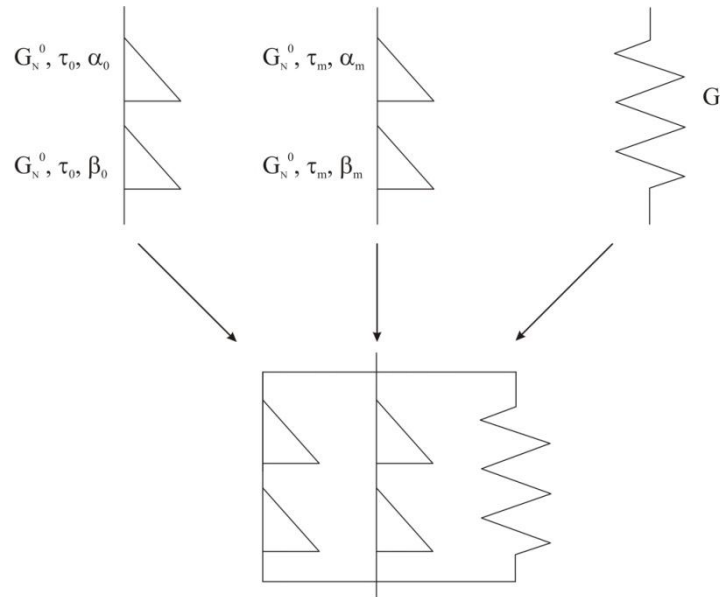
(2)

Fig. 2. Proposed own rheological model.

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 [13-17, 23]:

- 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 [21] 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:

$$f = \frac{G_N^0}{G_e} \tag{3}$$

- 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:

$$k = \frac{G_N{}^0 - G_e}{G_e} \tag{4}$$

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

$$\Delta G = \left(G_N{}^0 - G_e\right) \tag{5}$$

- ω_o [s^{-1}] - cross-linking density of gel, described by the following equation:

$$\omega_o = \frac{1}{\tau_o} \tag{6}$$

- η_o [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:

$$\eta_o = \frac{\tau_m}{J_e} \tag{7}$$

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

$$S = G_N{}^0 \cdot \tau_0{}^{\frac{2 \cdot \alpha_0 \cdot \beta_0}{\alpha_0 + \beta_0}} \tag{8}$$

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

$$L = \frac{\tau_m}{\tau_o} \tag{9}$$

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:

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

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

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

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

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

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

$$EF = \frac{\sum_{i=1}^{N} \left(tg\,\delta_{exp} - tg\,\delta_{exp\,śr}\right)^2 - \sum_{i=1}^{N} \left(tg\,\delta_{mod} - tg\,\delta_{exp}\right)^2}{\sum_{i=1}^{N} \left(tg\,\delta_{exp} - tg\,\delta_{exp\,śr}\right)^2} \tag{13}$$

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

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

where tgδ_{exp} designates experimental value obtained directly from rheological measurements, tgδ_{mod} - is the model value obtained from the fitting of model equations (1) and (2) in the proposed own rheological model, tg$\delta_{expśr}$ - 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 potato starch pastes with low- and high-acyl gellan gum was 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 the mean percentage error (MPE), the mean bias error (MBE), the root mean square 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.

Figure 3a and 3b 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 potato starch paste (with amylose content equal to 22.6%) and potato starch paste with the addition of low- and high-acyl gellan gum in the classical system of coordinates - cf. Fig. 3a and 3b - shows the flat course of the storage modulus G' corresponding to the elastic plateau of "gum" as well as an indistinct minimum occurring in the curve of the loss modulus G", which is present at $10^{-1}s^{-1}$ oscillation frequency. The above characteristics are typical of cross-linked polymers with a structure of unknown nature. In high frequency oscillations the curves of G' and G" moduli approached each other but their intersection was not detected whereas in low frequency oscillations, no approach of the curves of G' and G" moduli was shown. At the oscillation frequency corresponding to the minimum G" the absolute values of the G' and G" moduli differed from each other by about a decade and a half and the phase angle δ for , e.g. pure potato starch paste rached the value of 5.85^0 whereas for the same paste with the addition of low-acyl gellan gum at 0.05% concentration the value amounted only to 5.54^0 and for the paste with added high-acyl gellan gum of 0.05% concentration he value merely reached 5.40^0. Figures 4a and 4b 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 reached the lowest value is the viscoelastic plateau modulus G_N^0 representing the structure cross-linking power. The data presented in Figure 4a and 4b demonstrate that low values of phase angle δ for both pure potato starch paste and the paste containing low- and high-acyl gellan gum in the entire analyzed concentration extent of gellan gum already indicate strong elastic properties of the analyzed media.
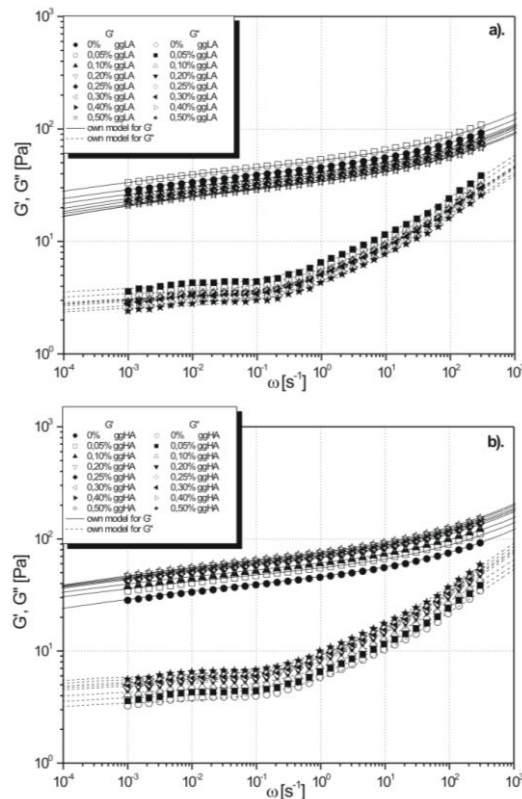

Fig. 3. Mechanical spectra of pure potato paste and potato paste with:
a) low-acyl gellan gum
b) high-acyl gellan gum

Table 1. Parameters of the proposed rheological model designated for pure potato starch paste and potato starch paste with the additive of low-acyl gellan gum at 25^0C.

	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]	4.83	5.37	4.08	3.57	3.08	2.18	2.36	3.71
G_N^0 [Pa]	39.10	46.04	36.19	33.30	31.87	30.09	29.71	28.74
ω_0 [s^{-1}]	27.28	38.57	35.88	30.29	28.01	25.87	31.15	32.63
α_m [-]	0.189	0.177	0.181	0.192	0.198	0.203	0.190	0.187
α_0 [-]	0.436	0.526	0.525	0.522	0.520	0.518	0.522	0.523
β_m [-]	0.016	0.018	0.019	0.021	0.021	0.022	0.020	0.020
β_0 [-]	0.387	0.347	0.348	0.349	0.350	0.351	0.349	0.348
f [-]	8.09	8.57	8.87	9.32	10.34	13.80	12.58	7.74
S [Pas]	10.08	9.99	8.08	7.99	7.90	7.71	7.04	6.69
k [-]	7.095	7.574	7.870	8.328	9.347	12.803	11.589	6.747
L [-]	$2.269\cdot10^5$	$3.382\cdot10^5$	$3.059\cdot10^5$	$2.419\cdot10^5$	$2.173\cdot10^5$	$1.947\cdot10^5$	$2.515\cdot10^5$	$2.682\cdot10^5$
η_0 [Pas]	$4.017\cdot10^4$	$4.708\cdot10^4$	$4.478\cdot10^4$	$2.851\cdot10^4$	$2.388\cdot10^4$	$1.641\cdot10^4$	$1.905\cdot10^4$	$3.049\cdot10^4$
α_m-β_m [-]	0.173	0.158	0.162	0.172	0.176	0.181	0.170	0.168
α_0-β_0 [-]	0.049	0.179	0.177	0.173	0.170	0.167	0.174	0.175
ΔG [Pa]	34.27	40.67	32.11	29.73	28.79	27.91	27.35	25.03
R^2	0.9993	0.9993	0.9994	0.9993	0.9992	0.9991	0.9992	0.9992
MPE	0.0423	-0.0540	-0.0233	0.0584	0.0773	0.0663	-0.0224	0.0680
MBE	-0.0023	0.0028	0.0013	-0.0034	-0.0046	-0.0041	0.0013	-0.0038
RMSE	0.0136	0.0165	0.0073	0.0196	0.0268	0.0237	0.0074	0.0222
EF	0.9998	0.9996	0.9999	0.9995	0.9991	0.9993	0.9999	0.9994
X^2	0.0002	0.0004	0.0001	0.0005	0.0009	0.0007	0.0001	0.0006

Table 2. Parameters of the proposed rheological model designated for pure potato starch paste and starch paste with the additive of high-acyl gellan gum at 25^0 C.

	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]	4.83	7.19	8.06	8.48	8.28	8.26	7.74	6.27
G_N^0 [Pa]	39.10	47.16	51.67	57.02	58.96	60.62	63.40	65.70
ω_0 [s^{-1}]	27.28	41.15	38.92	36.23	35.31	34.52	33.26	25.61
α_m [-]	0.189	0.173	0.176	0.181	0.182	0.184	0.186	0.192
α_0 [-]	0.436	0.527	0.526	0.525	0.525	0.524	0.524	0.417
β_m [-]	0.016	0.018	0.018	0.019	0.019	0.019	0.020	0.016
β_0 [-]	0.387	0.346	0.347	0.348	0.348	0.348	0.348	0.401
f [-]	8.09	6.55	6.41	6.72	7.12	7.33	8.19	10.47
S [Pas]	10.08	9.96	11.17	12.70	13.26	13.78	14.64	17.45
k [-]	7.095	5.559	5.411	5.724	6.121	6.339	7.191	9.478
L [-]	$2.269\cdot10^5$	$3.700\cdot10^5$	$3.424\cdot10^5$	$3.101\cdot10^5$	$2.992\cdot10^5$	$2.900\cdot10^5$	$2.754\cdot10^5$	$2.096\cdot10^5$
η_0 [Pas]	$4.017\cdot10^4$	$6.465\cdot10^4$	$7.090\cdot10^4$	$7.257\cdot10^4$	$7.014\cdot10^4$	$6.937\cdot10^4$	$6.407\cdot10^4$	$5.129\cdot10^4$
α_m-β_m [-]	0.173	0.155	0.158	0.162	0.163	0.164	0.166	0.176
α_0-β_0 [-]	0.049	0.181	0.180	0.178	0.177	0.176	0.176	0.015
ΔG [Pa]	34.27	39.97	43.61	48.54	50.68	52.36	55.66	59.43
R^2	0.9993	0.9991	0.9990	0.9990	0.9992	0.9992	0.9994	0.9994
MPE	0.0423	-0.0052	0.0330	0.0543	0.0493	0.0529	0.0409	0.0008
MBE	-0.0023	0.0003	-0.0017	-0.0029	-0.0027	-0.0029	-0.0023	-0.00005
RMSE	0.0136	0.0016	0.0100	0.0170	0.0156	0.0169	0.0132	0.0003
EF	0.9998	1.0000	0.9999	0.9996	0.9997	0.9996	0.9998	1.0000
X^2	0.0002	0.0000	0.0001	0.0004	0.0003	0.0004	0.0002	0.0000

The analysis of the experimental data described by the proposed rheological model showed that high values of viscoelastic plateau modulus G_N^0 revealed that in all the analyzed cases, the medium obtained displayed the structure whose behavior is typical of viscoelastic quasi-solid bodies. For pure potato starch paste viscoelastic plateau modulus G_N^0 responsible for the structure cross-linking power equaled 39.1 Pa.

In order to compare the effect that the form of gellan gum has on potato 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 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.
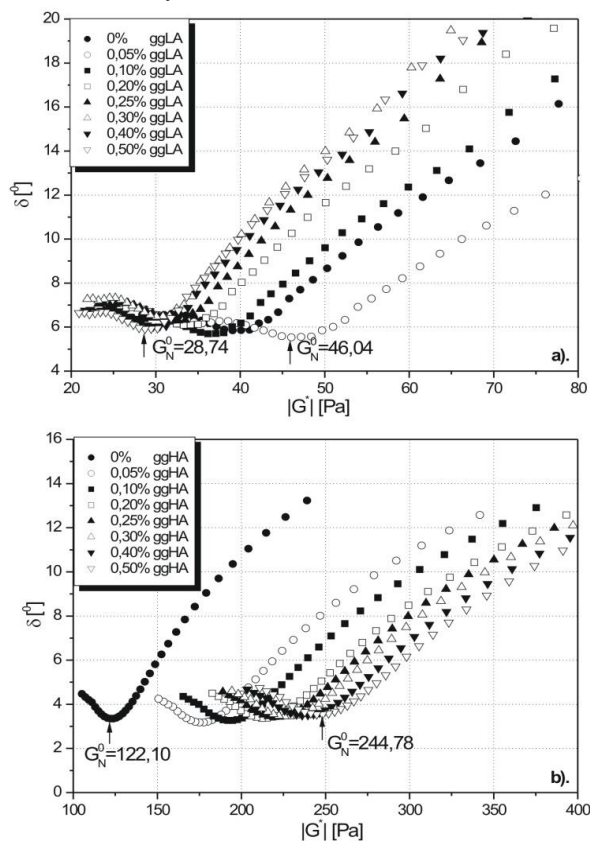

Fig. 4. van Gurp-Palmen plot for pure potato starch paste
and potato starch paste with the addition of:
a.) low-acyl gellan gum, b). high-acyl gellan gum

The data presented in Figure 5 indicate that high-acyl gellan gum additive in potato starch pastes clearly leads to an increase in the network elasticity G_e as well as in Newtonian viscosity in a steady state η_0 which is a measure of the flow properties of the contractual elementary cells of the network; both of these parameters are higher in pastes with high-acyl gellan gum when the gum concentration in the pastes does not exceed the concentration limit of 0.3%. Above the concentration of 0.3%, the increase in the gum concentration results in a slight increase in these parameters. Low-acyl gellan gum content in potato starch pastes causes the changes of a different character. After the initial rise of the two parameters at 0.05% gum concentration in the paste, further increase in low-acyl gellan gum in potato starch pastes causes both the network elasticity and Newtonian viscosity in a steady state to decrease at concentrations of up to 0.3%. The two parameters can be observed to rise again when low-acyl gellan gum concentration continues to increase. However, the values are lower than in the case of potato starch pastes with high-acyl gellan gum. The viscoelastic plateau modulus undergoes an identical pattern of changes. The values of viscoelastic plateau modulus G_N^0 representing the structure cross-linking power of potato starch pastes with low- and high-acyl gellan gum are lower than the cross-linking power of pure potato starch pastes but the values are higher in the pastes with high-acyl gellan gum than with low-acyl gum additive – cf. Fig. 5.
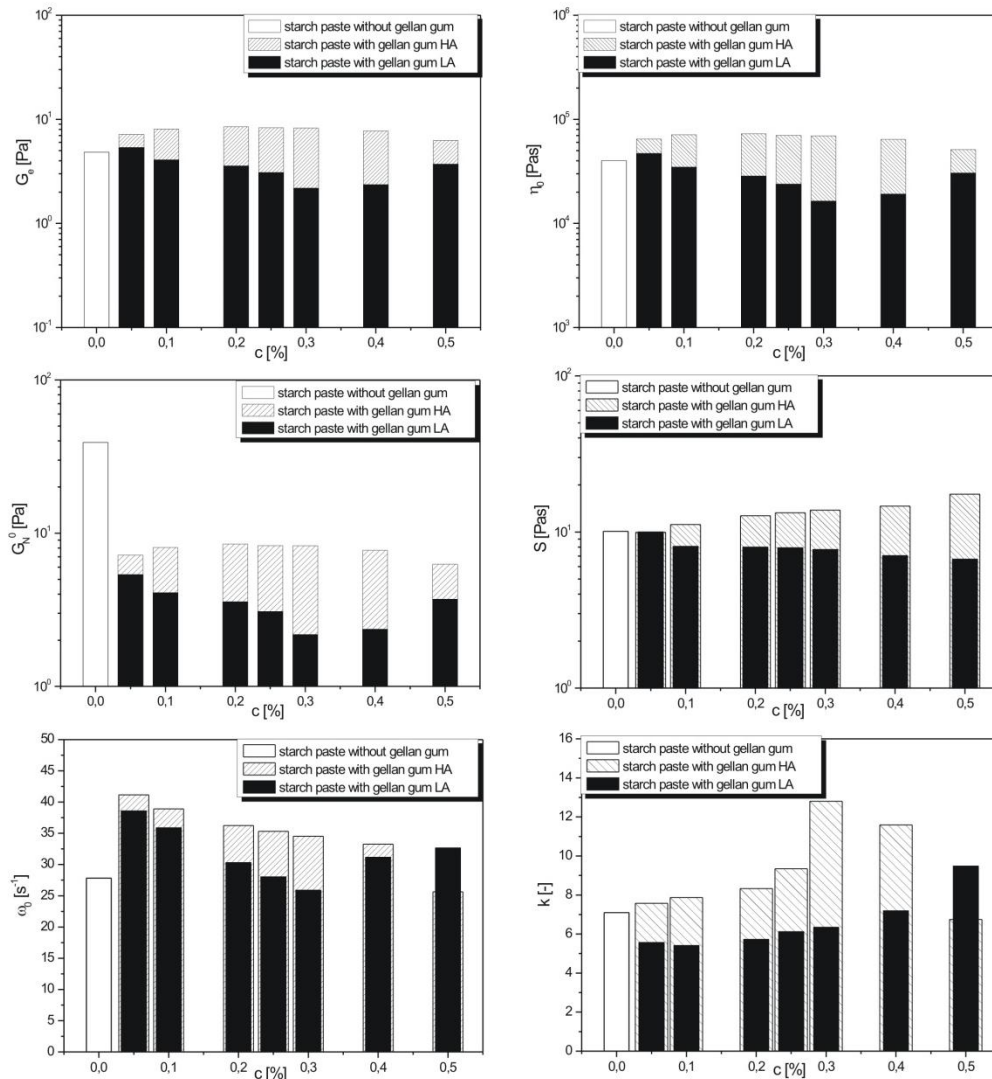
Fig. 5. Comparison of viscoelastic properties of potato starch pastes
with low- and high-acyl gellan gum additive.

The same tendency in cross-linking density of gel ω_0 changes was observed with only one difference: both low- and high-acyl gellan gum additive typically results in the increase in cross-linking density in comparison with pure potato starch pastes.

In consequence, both forms of gellan gum in potato starch pastes can be concluded to reduce the cross-linking power of the medium but increase its structure cross-linking density. The presence of high-acyl gellan gum in potato starch paste leads to gel stiffness enhancement while low-acyl gellan gum additive produces the opposite result i.e. its increasing concentration in the paste increasingly reduces gel stiffness.

In potato starch pastes with low-acyl gellan gum the values of the damping factor of network oscillations *k* are considerably higher – cf. Fig. 5. When low-acyl gum concentration in the paste falls within the range of up to 0.3% , the gum causes the factor to rise. When the gum concentration exceeds 0.3%, the paste capacity to damp network oscillations decreases although it is still fairly high. By contrast, high-acyl gellan gum diminishes the ability of potato starch pastes to damp network oscillations and the values of the damping factor of network oscillations *k* are lower in comparison with low-acyl gellan gum.

Interestingly, the values are also lower than the ones reflecting the capability of pure potato starch paste. A change can be detected only when the gum concentration reaches 0.5%. This probably results from starch granules getting blocked by the network of „advancing" high-acyl gellan gum, which, in consequence, leads to the structure stiffening and creating gel of a reduced ability to damp network oscillations and harder than with low-acyl gellan gum.

The graph in Fig. 6 demonstrates the impact of the form of gellan gum on the stress relaxation strength in potato starch pastes.
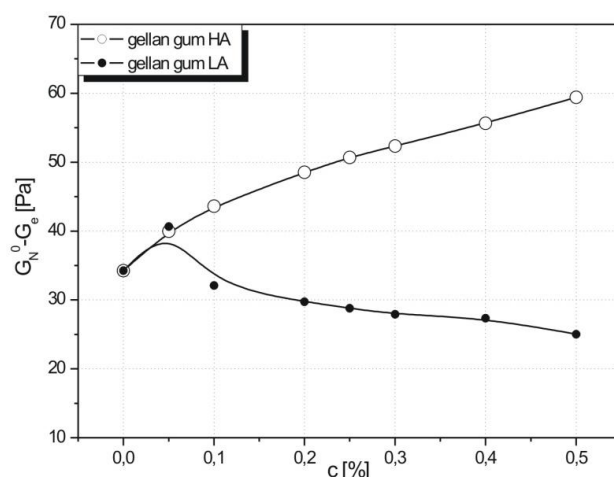

Fig. 6. Changes in the stress relaxation strength in potato starch pastes
with low- and high-acyl gellan gum.

High-acyl gellan gum present in potato 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. An entirely different efect is produced by low-acyl gellan gum added to such pastes. After the initial increase in stress relaxation triggered by low-acyl gellan gum appearance in the paste i.e. at its concentration of 0.05%, further concentration rise leads to stress relaxation decrease in potato starch pastes, which results from reduced gel stiffness and greater ability to damp network oscillations. Both starch and low-acyl gellan gum networks coexist.

IV.   CONCLUSIONS

The structure of potato starch pastes with low- and high-acyl gellan gum was assessed. Viscoelastic properties of pastes obtained from potato starch with low- and high-acyl gellan gum were 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 include a number of constant parameters defining viscoelastic properties of the mixtures composed of potato starch paste with low- and high-acyl gellan gum. The analysis of the data obtained by the proposed rheological model based on Maxwell-Wiechert approach revealed that the pastes obtained from potato starch with the additive of low- and high-acyl gellan gum are the media 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, potato starch pastes' cross-linking power is weaker than the power of pure potato starch paste but, at the same time, the cross-linking power is greater in the paste with high-acyl than low-acyl gellan gum,
- the additive of low- and high-acyl gellan gum in potato starch pastes resulted in higher elasticity of the network G_e in pastes with high-acyl gellan gum than with low-acyl gellan gum,
- low- and high-acyl gellan gum added to potato starch pastes resulted in reduced cross-linking power and density of the medium but enhanced cross-linking density of its structure, smaller reduction of cross-linking power and more substantial increase in cross-linking density were demonstrated by the potato pastes with high-acyl gellan gum,
- when mixed with potato starch, high-acyl gellan gum creates harder gels than high-acyl gellan gum does.

Mixtures of starch with non-starch polysaccharide hydrocolloid are commonly applied in food industry. Fractional rheological models can play a substantial role in production and processing of this type of biomaterials. The presented analysis of the mechanical conditions of the biomaterials' structure shows how helpful they can prove in control and suitable structure and texture formation of such biomaterials which are determined by the utility of the manufactured product.

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