The fractional derivative rheological model and the linear viscoelastic behavior of hydrocolloids

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This study was aimed at evaluating the possibility to use the Friedrich-Braun fractional derivative rheological model to assess the viscoelastic properties of xanthan gum with rice starch and sweet potato starch. The Friedrich-Braun fractional derivative rheological model allows to describe viscoelastic properties comprehensively, starting from the behaviour characteristic of purely viscous fluids to the behaviour corresponding to elastic solids. The Friedrich-Braun fractional derivative rheological model has one more virtue which distinguishes it from other models, it allows to determine the relationship between stress and strain and the impact of each of them on viscoelastic properties on the tested material. An analysis of the data described using the Friedrich-Braun fractional derivative rheological model allows to state that all the tested mixtures of starch with xanthan gum form macromolecular gels exhibiting behaviour typical of viscoelastic quasi-solid bodies. The Friedrich-Braun fractional derivative rheological model and 8 rheological parameters of this model allow to determine changes in the structure of the examined starch – xanthan gum mixtures. Similarly important is the possibility to find out the trend and changes going on in this structure as well as their causes.

Keywords: hydrocolloids, xanthan gum, fractional derivative rheological model

1. INTRODUCTION

Hydrocolloids, i.e. food gums are commonly used substances added to food. These are water soluble polysaccharides exhibiting thickening and/or gelling properties. As food components they reduce its energetic value, and owing to binding considerable amounts of water they may be used as a substitute of fat. Used as food additives, they improve the quality and durability of food products, assuring their stability while they are stored. Owing to such a comprehensive range of possibilities of using hydrocolloids in the production of food, in recent years a lot of attention was paid to the group of polysaccharides isolated from marine plants (alginates, carrageens), rare terrestrial plants (guar gum, locust bean gum), and from bacteria cultures grown on industrial scale in bioreactors (xanthan, dextran, curdlan, gellan, welan, pullulan).

Special attention should be paid to xanthan gum, usually called xanthan. Xanthan is a polysaccharide synthesised by bacteria of *Xanthamonas* genus - *X. campestris*, *X. fragaria*, *X. oryzae*. In 1969 FDA (Food and Drug Administration, USA) acknowledged this biopolymer as a compound which does not unnecessary space pose any risk to human health and admitted it to common use in the United States. Xanthan replaced then polysaccharides obtained from plants and algae through extraction. In the food concentrates industry xanthan may be used as a thickening and stabilising agent. In the technology of the production of sauces for salads or „dressing"-like products this polysaccharide may prevent the dispersion of insoluble particles of external oil phase and facilitate binding of particular components of

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the products concerned. Xanthan of microbiological origin gives solutions high viscosity, and products obtained with it are durable in a wide spectrum of pH, temperature and ionic strength of the medium. In bakery and confectionery industry, xanthan through cohesion with starch particles may improve the structure and prolong the storage of finished products. Besides, this extracellular polysaccharide by binding free water, responsible for synersis, stabilises and improves the quality of frozen products. As a sweetening and texturing agent, xanthan forms an appropriate consistency, aroma and taste of low-calorific beverages and products for diabetics (Myszka and Czaczyk, 2004).

Another hydrocolloid is starch which exhibits specific nutritive values. In food industry, starches of various botanical origin are used, such as e.g. starch of potato, maize, wheat, oat, barley, rye, rice, amaranth, tapioca or sago, differing in shape and size of grains or the content of amylose and amylopectin. Depending on the application, starch undergoes technological processing, such as e.g. pasting. Swelling of starch grains during heating in water and partial dissolution of macromolecules contained in the grains constitutes the essence of the pasting process. It is on the scope of these two phenomena that the rheological properties of the formed suspension depend. Starches exhibit two stages of morphological changes connected with swelling and solubility. A starch paste is created whose structure and functional properties of starch as a result of a further technological treatment may be destroyed due to changes in environmental *pH*, temperature or strong shearing. Such a sensitive structure of this biopolymer requires stabilisation, therefore more studies on interactions between hydrocolloid pairs are conducted, e.g. starch – polysaccharide hydrocolloid.

Specialist literature contains many papers explaining interactions of starch with polysaccharide hydrocolloids. Survey articles (Sikora and Kowalski, 2003; Sikora and Krystyjan, 2008) are particularly interesting.

One of the most frequently used polysaccharide hydrocolloids for stabilisation of starch of various botanical origins is xanthan gum. Interactions between starch and xanthan gum give rise to gel. Xanthan gum, surrounding starch granules with a thin film, causes detachment of starch granules, disturbing diffusion of macromolecules (Mandala and Palogou, 2003). The category of such macromolecular gels is characterised by extraordinary diversity and their viscoelastic properties comprise a vast scope of rheological behaviour – from viscoelastic quasi-solid bodies to typical viscoelastic fluids resembling polymer solutions.

Viscoelastic properties of macromolecular gels, resulting from interactions of starches with xanthan gum may be described using the so-called fractional derivative rheological models and fractional calculus. An advantage of fractional rheological models is the possibility to describe dynamic behaviour with one equation which contains a certain number of parameters which are constants determining viscoelastic properties of a given material (Kilbas et al., 2006). If the fractional rheological model is used, a very important issue is identification of parameters of this model according to experimental data, whereas the identification process itself is the so-called reverse problem. This means that in the identification process first the approximation of experimental results with trigonometrical functions should be made, and then rheological parameters of the applied model are determined.

Two authors Dinzart and Lipiński (2009) presented in their study several fractional rheological models enabling determination of viscoelastic properties of biopolymers according to the above described method. These are: Zener's model (Zener, 1948) having 4 rheological parameters and the Friedrich-Braun five-parameter model (Friedrich, 1991; Friedrich, 1993; Friedrich and Braun, 1992; Friedrich and Braun, 1994; Friedrich and Heymann, 1988).

The Friedrich-Braun five-parameter fractional derivative rheological model is particularly important. This results from the fact that it allows to describe viscoelastic features in a comprehensive range, starting from the behaviour characteristic of purely viscous fluids to the behaviour corresponding to elastic solids.

Details of the model's development can be found in the originals papers (Friedrich, 1991; Friedrich, 1993; Friedrich and Braun, 1992; Friedrich and Heymann, 1988). This derivation, on account of its complexity and extensiveness and complicated records of tensors has not been reported in this work, because it would change its character. Readers interested in this publication are referred to the original work of Friedrich and Braun, in particular to the paper written by Friedrich (1993). In this study, only the final result of the equation of Friedrich-Braun model for oscillatory measurements of rheological properties of the material and biomaterial in the form of presented Equations (2) and (3) was determined. A similar procedure can be found in many papers on the characterisation of rheological properties of materials by means of this model (Fijan et al., 2007; Fijan et al., 2009; Oblonšek et al., 2003; Siddig et al., 2004; Sittikijyothin et al., 2005; Zupančič and Žumer, 2001).

Using the fractional differential calculus, the Friedrich-Braun model can be presented in the following form:

$$\overline{\tau} + \lambda^c D^c \left|\overline{\tau}\right| = G_e \left\{ D^0 \left|\overline{\gamma}\right| + \lambda^c D^c \left|\overline{\gamma}\right| \right\} + \Delta G \lambda^d D^d \left|\overline{\gamma}\right| \tag{1}$$

On the basis of the principles of the fractional differential calculus, the values of storage G' and loss G'' moduli may be described using trigonometric functions, which the following equations can yield:

$$G' = G_e + \Delta G \frac{(\lambda_0 \omega)^d \left[\cos\left(\frac{\pi}{2} d\right) + (\lambda_0 \omega)^c \cos\left(\frac{\pi}{2}(d-c)\right) \right]}{1 + 2(\lambda_0 \omega)^c \cos\left(\frac{\pi}{2} c\right) + (\lambda_0 \omega)^{2c}} \tag{2}$$

$$G'' = \Delta G \frac{(\lambda_0 \omega)^d \left[\sin\left(\frac{\pi}{2} d\right) + (\lambda_0 \omega)^c \sin\left(\frac{\pi}{2}(d-c)\right) \right]}{1 + 2(\lambda_0 \omega)^c \cos\left(\frac{\pi}{2} c\right) + (\lambda_0 \omega)^{2c}} \tag{3}$$

The Friedrich-Braun fractional derivative rheological model has one more advantage which distinguishes it from other models, namely that it allows to determine the relationship between stress and strain and the contribution of each of them to viscoelastic properties of the examined material, through the sizes of parameters of models „c" and „d". The forces conditioning elastic responses of polymer or biopolymer mixtures, such as e.g. starch and xanthan gum, have two components: entropic component and the internal energy, i.e. enthalpic component. The entropic component results from the strain of biopolymer chains to the state of a lower probability of existence, and the ability to recover the primary shape is a consequence of increased entropy after elimination of stress. Instead, the enthalpic component results from the direct strain of the chemical bond. Therefore, two mechanisms – entropic and enthalpic, and thus also their related stresses and strains, contribute to the mixture's elastic response (Clark and Ross-Murphy, 1987; Doublier, 1981; Ferry, 1980).

The Friedrich-Braun model is correct if the following conditions are met:

$$G_e \geq 0$$

$$\Delta G \geq 0$$

$$\lambda_0 \geq 0$$

$$0 \leq c \leq d \leq 1$$

These conditions result from the second thermodynamics law and come down to the requirement that the storage modulus G' and loss – dissipation modulus G'', depending on oscillation frequency, should have positive values for all possible oscillation frequencies.

The study determined viscoelastic properties of the mixture of two biopolymers, starch and xanthan gum through estimation of viscoelasticity constants using the Friedrich-Braun fractional derivative rheological model. This study is also aimed at showing that the fractional derivative rheological model of Friedrich-Braun may be used for analysing the structure of biomaterial mixtures, not only to assess properties of elastomers and synthetic polymers.

2. RESULTS

The material for the analysis of viscoelastic properties of macromolecular gels, using the Friedrich-Braun fractional derivative rheological model, was taken from the studies carried out by Kim and Yoo (2006) and Choi and Yoo (2009).

Kim and Yoo examined rheological properties of 5% rice starch pastes with xanthan gum at the concentration of 0.2%, 0.4%, 0.6% and 0.8%. Oscillation tests of these pastes were carried out within the oscillation frequencies from 0.63 to 63 s^{-1} at a constant strain reaching 2%.

Similar studies consisting in the evaluation of rheological properties were carried out by Choi and Yoo. The object of their studies were also starch pastes but these were obtained from sweet potato starch, 5% solutions, in interactions with xanthan gum at the concentration reaching respectively 0.2%, 0.4% and 0.6% within the oscillation frequencies from 0.63 to 63 s^{-1} at the constant 3% strain.

The analysis of these starch pastes flow curves indicates that these are non-Newtonian fluids diluted by shearing, and the obtained rheometrical curves were described by Kim and Yoo (2006) as well as Choi and Yoo (2009) using the Ostwald de Waele power law model.

On the other hand, the curves of the storage *G'* and loss *G''* moduli obtained during oscillation measurements were described by the authors using the power law model of the following equations:

$$G' = k' \cdot \omega^{n'} \tag{4}$$

$$G'' = k'' \cdot \omega^{n''} \tag{5}$$

The values of the parameters of this model for the studies carried out by Kim and Yoo (2006) are presented in Table 1, whereas those for the studies carried out by Choi and Yoo (2009) - in Table 2.

Table 1. Results of oscillation studies carried out by Kim and Yoo (Kim and Yoo, 2006) for rice starch with xanthan gum at temp. $T = 25^{0}$C

Xanthan gum	*G'*		R^2	*G''*		R^2
concentration [%]	*n'* [-]	*k'* [Pas^n]	[-]	*n''* [-]	*k''* [Pas^n]	[-]
0	0.1	73.5	0.99	0.24	8.39	0.99
0.2	0.12	72.2	0.99	0.2	13	0.99
0.4	0.12	95.7	0.99	0.18	17.2	0.98
0.6	0.12	114	0.99	0.18	20.3	0.98
0.8	0.12	130	0.99	0.18	23.3	0.98

Kim and Yoo (Kim and Yoo, 2006) as well as Choi and Yoo (Choi and Yoo, 2009) on the basis of the obtained experimental data from oscillation measurements stated generally that xanthan gum increased viscoelastic properties of rice starch pastes and sweet potato starch.

Table 2. Results of oscillation studies carried out by Choi and Yoo (Choi and Yoo, 2009) for sweet potato starch with xanthan gum at temp. $T = 25^{0}$C

Xanthan gum	G'		R^2	G"		R^2
concentration [%]	n' [-]	k' [Pas^n]	[-]	n" [-]	k" [Pas^n]	[-]
0	0.3	11.7	0.97	0.33	4.66	0.99
0.2	0.26	16.1	0.99	0.27	6.19	0.99
0.4	0.19	38.8	0.99	0.22	10.5	0.98
0.6	0.16	54.5	0.99	0.21	13.2	0.97

However, such an analysis is insufficient for the evaluation of viscoelastic properties and the formed structure. A complete analysis of the material's viscoelastic properties includes fast and slow dissipation processes. Fast dissipation processes result from movements occurring in the network's structural segments between its nodes, whereas slow dissipation processes correspond to movements crosswise the network nodes (Ferry, 1980). The need to determine these processes in the development of macromolecular gel's structure in the starch - xanthan gum mixtures requires determination of additional parameters which will describe them.

The Friedrich-Braun model – equations (2)÷(4) – yields 5 rheological parameters, i.e. G_e, G_0, λ_0, „c" and „d". The interpretation of these parameters in the aspect of evaluation of the properties of a given material is presented as follows:

- the value of equilibrium modulus, elasticity modulus in the steady state flow condition G_e determines the total elasticity of the network, and its reciprocal is the flexibility at the state of equilibrium J_e. High values of modulus G_e point to an increase in the material's elastic behaviours;
- the value of viscoelastic modulus - plateau G_o is equated with the structure's cross-linking power. The higher the value of this modulus, the higher the structure's cross-linking.
- the value of characteristic relaxation λ_0 time determines the time after which stress relaxation occurs. Low values of relaxation times point to strong elastic properties of the material.
- the value of parameters „c" and „d" determine the share of stresses and strains in the structure formation, whereas their values equal to zero indicate behaviour characteristic of elastic bodies, while the values of these parameters equal to one indicate behaviour characteristic of viscous fluids.

However, the knowledge of these parameters allows for much more, i.e. to get to know the values of the dispersion modulus, viscosity in the steady state flow condition which is a measure of conventional flow properties of the network's elementary cells (i.e. a set of elements closed with a minimum number of the network's nodes capable of individual displacement) and the longest retardation time characterising the mixture's polydispersity. The relationships enabling determination of the values of 3 new parameters based on 5 existing parameters from the Friedrich-Braun model are described by the following equations:

- - dispersion modulus f

$$f = \frac{G_0}{G_e} \qquad (6)$$

- - viscosity of fixed flowing η_0

$$\eta_0 = G_0 \cdot \lambda_0 \qquad (7)$$

- - the longest retardation time λ_r

$$\lambda_r = \left(\frac{1}{G_e}\right) \cdot \eta_0 \qquad (8)$$

As a result, 8 rheological parameters are obtained, which allow us to analyse comprehensively the viscoelastic properties of a given material.

The values of 8 parameters obtained using the Friedrich-Braun fractional derivative rheological model are presented in Tables 3 and 4.

Table 3. Rheological parameters of the Friedrich-Braun model, calculated according to experimental data of Kim and Yoo (2006) for the mixture of rice starch with xanthan gum at temp. $T = 25^0$C

Xanthan gum [%]	G_e [Pa]	G_0 [Pa]	c [-]	d [-]	λ_0 [s]	G_0/G_e [-]	η_0 [Pas]	λ_r [s]	R^2 [-]
0	54.68	75.47	0	0.24	26.32	1.38	1986	36.32	1.000
0.2	31.54	75.08	$4 \cdot 10^{-6}$	0.2	26.93	2.38	2022	64.11	1.000
0.4	36.21	101.01	0.002	0.181	35.77	2.79	3613	99.76	1.000
0.6	44.24	118.86	$8 \cdot 10^{-5}$	0.18	40.22	2.68	4780	108.06	1.000
0.8	84.65	111.28	0.583	0.81	26.94	1.31	2998	35.42	1.000

Table 4. Rheological parameters of the Friedrich-Braun model, calculated according to experimental data of Choi and Yoo (2009) for the mixture of sweet potato starch with xanthan gum at temp. $T = 25^0$C

Xanthan gum [%]	G_e [Pa]	G_0 [Pa]	c [-]	d [-]	λ_0 [s]	G_0/G_e [-]	η_0 [Pas]	λ_r [s]	R^2 [-]
0	4.48	10.89	0.046	0.357	27.34	2.43	297	66.44	0.997
0.2	3.22	15.84	0.005	0.273	25.03	4.91	396	122.86	0.999
0.4	11.03	41.15	0.01	0.225	26.47	3.73	1089	98.76	1.000
0.6	16.05	55.69	0.0002	0.21	30.68	3.47	1708	106.47	1.000

The use of the Friedrich-Braun fractional derivative rheological model was also presented graphically in the form of the curves of storage *G'* and loss *G''* moduli with the curves obtained from Equations (3) and (4) – Fig.1 and Fig. 2.

The curves presented in Figures 1 and 2 show a very good compliance of the experimental data of Kim and Yoo (2006) as well as Choi and Yoo (2009) with the curves obtained using the Friedrich-Braun fractional derivative rheological model. The maximum error of the description of experimental data using the Friedrich-Braun model amounted to ±8% and referred only to the storage modulus curve for pure sweet potato starch paste. The average error of the description of experimental data for all the other mixtures of starch with xanthan gum was at the level of ±2%.
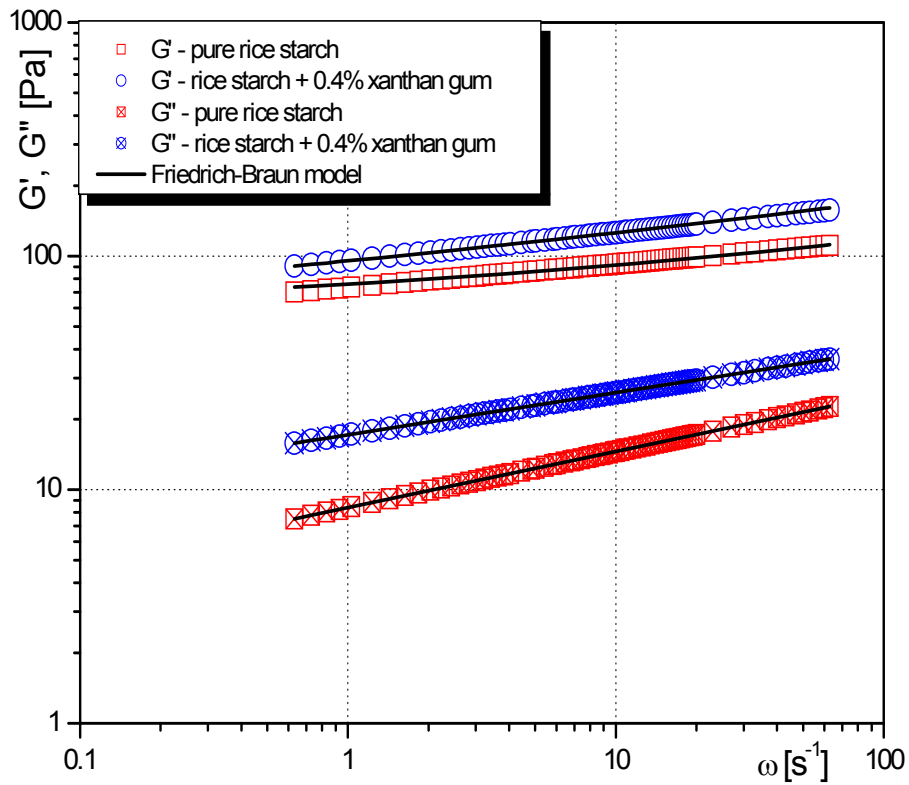
Fig. 1. Frequency dependence of *G'* and *G''* for rice starch – xanthan gum mixtures.
The curves throughout the experimental data are calculated using the Friedrich-Braun model
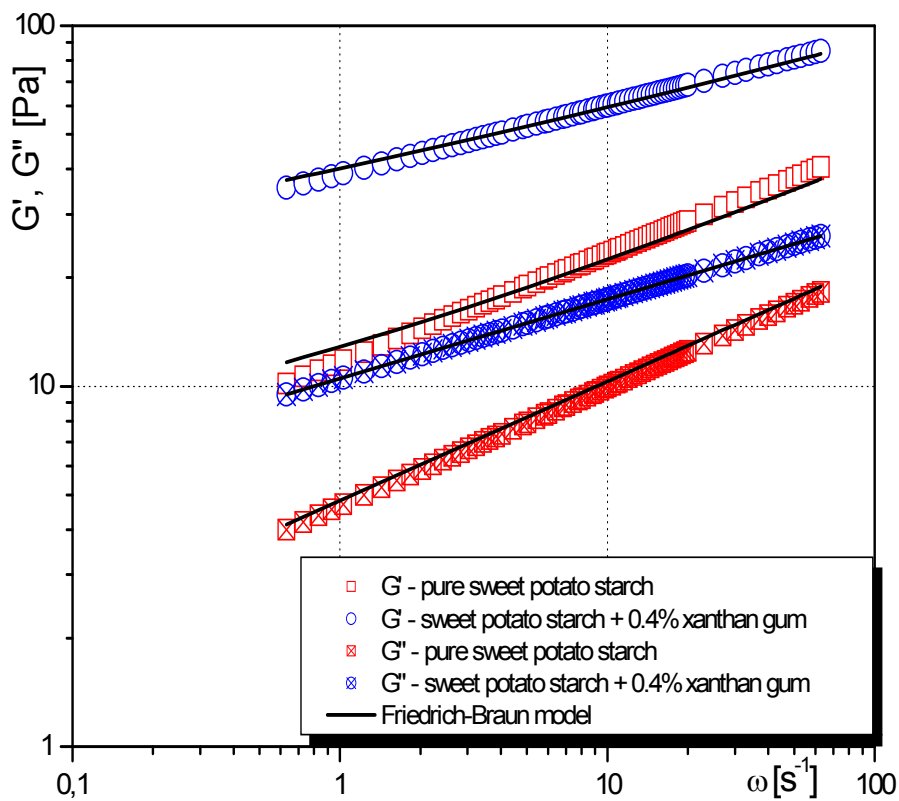

Fig. 2. Frequency dependence of *G'* and *G''* for sweet potato starch – xanthan gum mixtures.
The curves throughout the experimental data are calculated using the Friedrich-Braun model

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The analysis of the experimental data obtained using the Friedrich-Braun fractional derivative rheological model – Tables 3 and 4 – allows to state that all the analysed systems of starch with xanthan gum form macromolecular gels which exhibit behaviour typical of viscoelastic quasi-solid bodies. This is evidenced by quite high values of viscoelastic modulus plateau G_0. With an increase in the concentration of xanthan gum in the solution, the structure's cross-linking power is increased; it is higher for xanthan gum – rice starch mixtures than for xanthan gum – sweet potato ones. Analogical dependence is observed when analysing the values of equilibrium modulus G_e. The total elasticity of the network grows in both starches with an increase in the concentration of xanthan gum, but elasticity of the network is definitely higher in the case of rice starch. In both the investigated mixtures, responsible for the formation of the structure are strains, i.e. entropic changes, which is best seen when analysing the values of parameters „c" and „d", and particularly the values of parameter „d", which are formed at the level 0.2. The value of parameter "d" corresponds to elastic behaviours of the tested materials. The only exception is an addition of 0.8% xanthan gum in the rice starch solution, which can indicate a more intense coating and thereby the pressure of xanthan gum on starch granules, which induces their inhibition. This contradicts the synergistic effect described by Christianson (Christianson, 1982) referring to an increase in the pressure force exerted on the swelling starch granules. This fact is additionally confirmed by the value of viscosity in the steady state flow condition η_0 for this concrete case. The viscosity decreases to 2998 Pas, which indicates that we deal with viscosity induced by a higher concentration of xanthan gum itself, as compared to the interaction of rice starch – xanthan gum. This is additionally confirmed by the value of dispersion modulus f and a low value of the longest retardation time λ_r, these values determine the mixture's polydispersedness and indicate the existence of a structure which is xanthan gum. The increases in the dispersion modulus and the longest retardation time as well as the viscosity in the steady state flow condition show how with an increased concentration of xanthan gum in the solution the structure of the tested mixture changes and when the structure formed by adding xanthan gum begins to dominate.
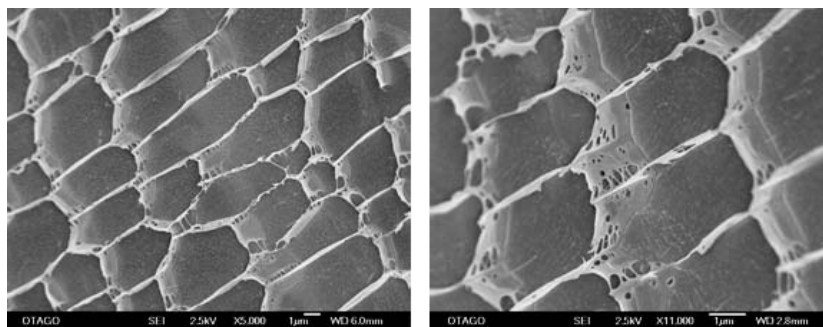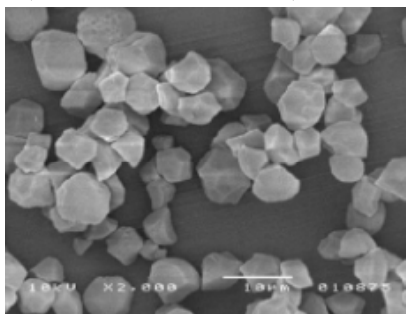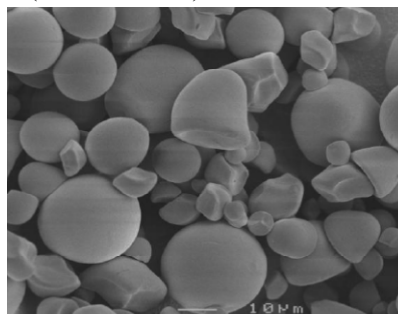
a) xanthan gum (Rupenthal, 2008)

b) rice starch granules
(Koroteeva et al., 2007)

c) sweet potato granules
(Mweta, 2009)

Fig. 3. Scanning electron micrographs of xanthan gum, rice and sweet potato granules

The analysis of the experimental data described by the Friedrich-Braun fractional derivative rheological model and the obtained values of 8 rheological parameters of this model allow to determine changes in the structure of the tested starch – xanthan gum mixtures. Furthermore, we should emphasise the importance of the possibility to find the trend and changes going on in this structure and determining their cause.

To depict better the interactions occurring between xanthan gum and rice starch or sweet potato starch, some pictures obtained under the scanning microscope are additionally shown, which present the topography of the surface of the structure formed by xanthan gum, along with the pictures presenting the differences in the shapes and sizes of the granules of the two analysed types of starch – Fig. 3.

3. CONCLUSIONS

Viscoelastic properties of macromolecular gels which arose from the interaction between starch and xanthan gum may be described using the so-called fractional rheological models. An advantage of fractional rheological models is the possibility of describing dynamic behaviour with one equation which contains a certain number of parameters that are constants determining the viscoelastic properties of a given material. The Friedrich-Braun five-parameter fractional derivative rheological model is particularly important, which allows to describe viscoelastic properties comprehensively, starting from behaviour characteristic of purely viscous fluids to behaviour corresponding to elastic solids. The Friedrich-Braun fractional derivative rheological model has one more advantage which distinguishes it from other models: it allows to determine the relationship between stress and strain and the impact of each of them on viscoelastic properties of a given material.

The analysis of the data obtained using the Friedrich-Braun fractional derivative rheological model – Tables 3 and 4, allows to state that all the analysed starch – xanthan gum mixtures form macromolecular gels exhibiting behaviour typical of viscoelastic quasi-solids. This is demonstrated by quite high values of viscoelastic modulus plateau G_0. With an increase in the concentration of xanthan gum in the solution, the structure's cross-linking power grows, being higher for xanthan gum – rice starch mixtures than for xanthan gum – sweet potato starch mixtures. Analogical dependence is observed when analysing the values of equilibrium modulus G_e. The total elasticity of the network is increased in both the analysed types of starch with increasing concentration of xanthan gum, although the network's elasticity is much higher in the case of rice starch - Tables 3 and 4. The analysis of the experimental data described by the Friedrich-Braun fractional derivative rheological model and the obtained values of 8 rheological parameters of this model allow to determine changes in the structure of the tested starch – xanthan gum mixtures. Furthermore, it is important to be able to find the trend and changes occurring in this structure as well as their cause.

Concluding, we should emphasise that determination of rheological parameters of the Friedrich-Braun model is very important practically, because it enables a precise determination of functional properties of the examined biomaterials.

SYMBOLS

c, d parameters, which determine the share of stresses and strains in the structure formation, -
D^c, D^d fractional derivatives of orders c and d, -
f dispersion modulus, -
G' storage modulus, Pa
G'' loss modulus, Pa
G_0 viscoelastic modulus – plateau, Pa

G_e	equilibrium modulus, elasticity modulus in the steady state flow condition, Pa
ΔG	parameter which is a difference between the value of viscoelastic modulus - plateau G_o and the value of equilibrium modulus G_e, Pa
k', k''	rheological parameters in eqn. (4) and (5)
n', n''	rheological parameters in eqn. (4) and (5)

Greek symbols

$\bar{\gamma}$	tensor of strain, %
η_0	viscosity of fixed flow, Pa·s
λ_0	characteristic relaxation time, s
λ_r	longest retardation time, s
$\bar{\bar{\tau}}$	tensor of stress, Pa
ω	oscillation frequency, s^{-1}

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