

RHEOLOGICAL SCALING PROPERTIES OF STARCH SOLUTIONS IN DIMETHYLSULFOXIDE

Paweł Ptaszek^{1*}, Marcin Łukasiewicz¹, Anna Ptaszek¹, Mirosław Grzesik²

¹Agricultural University of Krakow, Faculty of Food Technology, Balicka 122, 30-149 Kraków, Poland

²Institute of Chemical Engineering of Polish Academy of Sciences, Bałtycka 5, 44-100 Gliwice, Poland

The possibility of scaling viscoelastic properties of starch solutions in relation to biopolymer concentration was presented in this study. An application of this empirical method enabled to widen the observation horizon of viscoelastic properties. It was also determined that the scope of its applicability is limited by amylose content in the solution. In high amylose solutions, for which up to 40% (w/w) concentration was the highest one obtained, calibration caused the formation of master curve in the widest frequency range. Determined values of scaling coefficients a_C changed exponentially in starch concentration function in the solution. For waxy starch solutions of maximum concentration equal to 20% (w/w), scaling did not significantly widen the observation window. Based on master curves constructed in such way, continuous relaxation spectra $H(\lambda)$ were determined using Tikhonov regularisation method. Their structure indicates advantageous of viscous elements in the process of viscoelastic phenomena formation.

Keywords: viscoelasticity, Maxwell model, continuous relaxation spectra, starch

1. INTRODUCTION

Starch which is produced and stored in seeds and tubers is one of the most important plant polysaccharides. Most of all, it is the main ingredient of human food. Moreover, starch and its derivatives function differently in the formation of functional properties of food, among which structure stabilisation and gelling can be considered as the most important ones (BeMiller and Whistler, 2009; Eliasson, 2004).

Because of its biodegradability, non-toxicity and complete biocompatibility an increasing interest in this biopolymer is observed nowadays. Starch and its derivatives are increasingly used in the production of new, biodegradable materials (Crini, 2005; Sashiwa and Aiba, 2004; Yarema, 2005). There are two kinds of biopolymers which are the main ingredients of starch. The first of them, amylose is a linear fraction composed of α -D-glucose connected with α -(1-4) bonds and its molecular mass varies between 10^5 and 10^6 g/mol. Amylopectin has a higher molecular mass of 10^6 - 10^7 g/mol and is highly branched by α -(1-6) bonds (BeMiller and Whistler, 2009; Eliasson, 2004). Such a different molecular structure of starch fractions results in some processing problems. During modification the appropriate solvents for both fraction should be used. There are only a few known systems, which allow to dissolve starch with water, dimethyl sulfoxide (DMSO) or N,N-dimethylacetamid combined with LiCl (Cao et al., 2000). DMSO is well known and easy to use due to its relatively polar nature,

*Corresponding author, e-mail: p.ptaszek@ur.krakow.pl

capacity to accept hydrogen bonds and small and compact structure. Other features, such as miscibility with water are also important (Smallwood, 1996).

Starch and most of all amylose and amylopectin behavioural features in different solvents still remains in the area of interest of researchers. Attempts to clarify the nature of polysaccharide- solvent interaction are carried out using such methods as SLS, DLS, HPSEC or intrinsic viscosity (Bello-Perez et al., 1998; Jordan and Brant, 1980; Radosta et al., 2001; Ring et al., 1985). A selection of conducted studies includes determination of radius of geration (R_G), hydrodynamics radius (R_H) or second virial coefficient A_2 for pure amylose and amylopectin in such popular solvents as water or DMSO. Obtained results indicate extreme behaviour of these two polysaccharides. Amylose in water solutions shows a very small inertial radius, as opposed to branched amylopectin. Water is not a good solvent for amylose. This phenomenon is observed because of the botanical origin of amylose (Radosta et al., 2001; Ring et al., 1985). On the contrary, in DMSO R_G , R_H values are much higher. In binary water/DMSO mixtures an increase of value of the second virial factor for amylose is caused by an increase of DMSO contribution in binary solvent (Jordan and Brant, 1980). Values of R_G i R_H determined on the basis of static and dynamic light dispersion in amylopectin solutions in DMSO (Bello-Perez et al., 1998) suggest a spherical or globular structure of this polysaccharide. One consequence of such complex solvent- polysaccharide interactions is that their mixtures hale rheological properties. One of methods of studying them is to determine the viscoelastic properties (Ferry, 1980). Viscoelasticity is a very important phenomenon in analysis of mechanical properties of polymer solutions (Weese and Friedrich, 1994; Tan et al., 2000) and biopolymers (Mao et al., 2000; Ptaszek and Grzesik, 2007; Ptaszek et al., 2009; Sodhi et al., 2010). Results obtained based on G' and G'' measurements in a linear range can serve in the immediate analysis of mechanical properties of the studied material. An important area of interest of researches is also the estimation of parameters of rheological functions based on experimental data. Knowledge of linear rheological functions describing viscoelastic properties of a material enables to evaluate the structure of relaxation and retardation phenomena. Continuous rheological functions are of the most general character. Their form is dependent on the type of source experiment providing the experimental data (Ferry, 1980; Tschoegl, 1989). For data originating from dynamic experiments using stress, continuous Maxwell model is the most one:

$$G^*(j\omega) = G_e + \int_0^{+\infty} H(\lambda) \frac{(\lambda\omega)^2}{1 + (\lambda\omega)^2} d\lambda + j \int_0^{+\infty} H(\lambda) \frac{\lambda\omega}{1 + (\lambda\omega)^2} d\lambda \quad (1)$$

In the equation, function $H(\lambda)$ is called the relaxation spectrum, and its argument λ the relaxation time, G_e value is described as equilibrium module This parameter specifies the value of the modulus of elasticity for the time approaching infinity. For viscoelstic liquids the parameter takes the value of 0. It results from the presented approach that relaxation times form *continuum* ($\lambda + d\lambda$). Relaxation spectrum $H(\lambda)$ describes the intensity of given relaxation time in the whole of the phenomenon. Moreover, the function shows a character of typical distribution by analogy with, for example, density distribution of probability. $H(\lambda)$ carries extremely important information regarding rheological behaviour of the tested systems, because it represents the intensity of the given relaxation processes (relaxation times) in the phenomenon. An accumulation of relaxation processes showing similar parameters is manifested by the occurrence of characteristic peaks in the spectrum $H(\lambda)$.

The presence of peaks in the range of short relaxation times indicates a participation of viscous contributions in the formation of the phenomenon. Similarly, the accumulation of peaks in the range of long times can indicate a phenomenological advantage of elastic properties. Knowledge of distribution of relaxation times gives an insight into the structure of relaxation phenomena occurring in real materials. This knowledge can be used directly in the modeling of technological process or be the starting point in the discussion regarding molecular interactions.

Important information about the nature of relaxation phenomena is provided by the analysis of

viscoelastic functions at various temperatures and/or concentrations. The empirical principle of superposition of time and temperature can be of help here, which was the most often used to determine the influence of temperature on viscoelastic properties of synthetic polymers (Weese and Friedrich, 1994; Tan et al., 2000) as well as systems of biopolymers (Mao et al., 2000; Ptaszek and Grzesik, 2007). As a general rule, it amounts to transfer to the area of scientific study the advantages resulting from the application of *the theorem of complementary states* (successfully used in the discussion of properties of gases) (Ferry, 1980). From the prediction point of view of mechanical properties of biopolymers (also their solutions) the principle of calibration of time (frequency) to molecular mass or concentration is of the greatest importance.

Any mixture tested in the present study can be selected as a reference state. For all the systems there is an intended rheological function determined in the same frequency/ time range. The possibility of shifting/ reducing the value of this function in the linear direction in respect of rheological data obtained for the system at reference concentration allows to obtain a curve illustrating the behaviour of a polymer, in a very wide time/ frequency range. In case of concentrated solutions of polymers/ biopolymers of large molecular mass, which can form the structure based on net of entanglements, calibration of rheological functions to concentration indicates proportional dependence of friction (viscosity) factor on the biopolymer concentration. At lower polymer/ biopolymer concentrations or small molecular masses the mechanism of friction is complex: the motions of free ends of chains greatly contribute to the process of forming the phenomenon of friction. Rheological studies of starch solutions are predominantly related to *time-dependent* properties of aqueous starch solutions (Dewar and Joyce, 2006; Dzuy Nguyen et al., 1998; Tarrega et al., 2005; Tecante and Doublier, 1999) and their viscoelastic properties in linear range (Ptaszek et al., 2009). The subject literature regarding the rheology of starch solutions in DMSO is slightly scarcer (Chamberlain and Rao, 1999; de Vasconcelos et al., 2000). Extensive results of studies on rheological properties of starch in aqueous mixtures with DMSO were presented by Kapoor and Bhattacharya (2000). They investigated three maize starches: amylostarch *Hylon VII*, waxy and the normal one. They determined properties of starch solutions at 2%- 8% concentrations in mixture of 90% DMSO and 10% water at 21-23°C temperature. They concluded about the nature of rheological behavior based on the course of $G'(\omega)$ and $G''(\omega)$ relationship. On the basis of molecular theory of Rouse they discussed the behaviour of starch solutions extrapolated to zero concentration. The authors, however, did not estimate the parameters of discrete Maxwell model. It was concluded that in case of all starch solutions the values of loss modulus (G'') were greater than those of storage modulus (G'). Rheological properties of studied solutions were highly dependent on the type and concentration of starch in DMSO. Behaviour characteristic for viscoelastic liquid as well as for solid substance was observed. In the next publication from 2001 Kapoor and Bhattacharya included considerations on steady shear and transient properties of the same solutions, as previously of starch in mixture of DMSO and water. They noticed a relationship between the content of amylopectin in starch and the phenomenon of shear dilution. They concluded that complex behaviour of 8% starch solutions can contribute to further studies on their structural properties.

Results of studies presented in the discussed publications form a starting point for further considerations of viscoelastic properties of starch solutions in pure DMSO. Extremely different behaviour of amylose and amylopectin in DMSO can suggest very complex rheological properties of starch solutions. Further analysis of viscoelastic phenomena can be helpful, supported by reduced variables and estimation of continuous relaxation spectra based on Maxwell model.

2. EXPERIMENTAL

All starches used in research were provided by *National Starch* (USA). Starch with different amylose content i.e. waxy starch (*Amioca*), normal maize starch and high amylose starch (*Hylon VII*) were used

for all the experiments. Each starch was investigated by means of amylose content (Gilbert and Spragg, 1964) as well as molecular mass and its distributions. Molecular mass distributions were performed by means of Gel Permeation Chromatography (GPC). The following chromatographic system was used: four columns connected in series, filled with *Sephacryl* gels (*Pharmacia*, Sweden): S-200, 0.470 m; S-200, 0.940 m; S-500, 0.860 m; S-1000, 0.830 m. Internal diameter of the columns was 16 mm. As eluent Na_2CO_3 water solution (5 mmol/L) was used, flow rate was estimated at 0,128 mL/min. A sample of starch (50 mg) was dissolved in 4 mL of 90 wt% DMSO (*Merck*, Germany) at 70°C for 24 h and then diluted by 4mL of the eluent. The volume of the sample was 2 mL. The molecular mass and molecular mass distribution was estimated using anthron method (Morris, 1948) applied for every single fraction collected after elution. The values for amylose and amylopectin were also estimated using colourimetric method applied for every fraction as well (Praznik et al., 1983). All analyses were performed at 20°C. Calibration was done using pullulans standards provided by *Shodex* (Japan).

Sample preparation was carried out as follows. The calculated amount of starch was dried at 130°C until a constant mass was achieved. The samples were then dissolved by suspending them in hot (95°C) dimethylsulfoxide (*Merck*, Germany) until a clear solution was obtained. Solubilisation was supported by mechanical stirring (200rpm). The resulted solution was kept free from the air atmosphere until rheological measurements were done. The following concentrations of starch (according to % w/w) were prepared: 10, 20, 30, 40% for *Hylon* starch, 10, 20, 30% for regular starch and 10 and 20% for *Amioca*. In each case it was impossible to obtain more concentrated solutions.

Rheological measurements were performed using RS6000 rheometer (*Haake*, Germany). Temperature was controlled with accuracy of 0.1°C by means of F-6 ultrathermostat (*Haake*, Germany). All measurements were done using cone-plate sensor and performed at 25°C.

The initial condition for a proper determination of linear rheological functions allow to perform measurements in linear viscoelasticity area (Ferry, 1980). This test relies, in case of frequency domain measurements, on determination of the complex modulus G^* as a function of deformation amplitude at constant frequency. Linear viscoelasticity region determines the range of deformation amplitude (γ_0), for which G^* is independent of the amplitude γ_0 . For all analysed systems, the measurements of linear viscoelasticity range were done at extreme values of concentration and frequency. It allowed to determine and select one value of deformation amplitude used in all the investigations i.e. $\gamma_0 = 0.01$. Based on amplitude derived from linear range experiments, the measurements of changes in complex modulus as a function of frequency (0.1-100 Hz) and selected concentrations were performed.

The method of reduced variables was used in interpretation of experimental data. Values of calibration coefficients a_C and b_C were determined based on algorithm presented in Honerkamp and Weese studies (1993). As a reference system, rheological properties of 20% starch solutions were chosen (in case of waxy starch this was the highest concentration obtained). Relaxation spectra were determined by estimating subintegral function $H(\lambda)$ in complex Maxwell function (Eq. 1) using Tikhonov regularisation method. Algorithm and methodology were described in Honerkamp and Weese (1990) as well as in Ptaszek and Grzesik (2007) publications.

3. RESULTS AND DISCUSSION

For starch solutions of the highest *Hylon VII* amylose content (Table 1) it was possible to carry out calibration of rheological functions in full concentration range. As a result very high broadening of rheological observation horizon was observed in relation to initial frequency range of 10-1-102 Hz (Fig. 1). Calibration caused reposition of G' and G'' curves in the range of 10^{-3} to 10^4 Hz. For low frequencies G' values are definitely lower than G'' value. With an increase of frequencies, the difference between them decreases until they are equal in the last decade.

Table 1. Composition and rheological parameters of investigated systems

Sample	Fraction content, %		Concentration, % wt.	G_e , Pa	a_c
	Amylose	Amylopectin			
<i>Hylon</i>	52	48	10	-*	0.045
			20	0.09 +/-0.04	1.0
			30	4.53 +/-0.11	19.0
			40	15.41 +/-0.53	200.0
Normal	24	76	10	0.82 +/-0.08	0.24
			20	6.20 +/-0.13	1.0
			30	28.43 +/-3.32	0.54
<i>Amioca</i> (waxy)	1	99	10	-*	-
			20	-*	-

* Not estimated

This indicates that viscoelastic properties of high-amylose starch solutions belong to *flow* region and crossing the point between *flow* and *plateau* zones. The possibility of calibrating these properties also indicates an invariable mechanism of phenomenon of friction. Values of a_c coefficients in concentration function increase exponentially (0.045, 1.0, 19.0, 200.0 for a corresponding increase of starch concentrations in DMSO at 20% reference solution) Such monotonous changes indicate predominance of viscous elements. The relaxation spectrum determined based on this summary curve has a complex structure (Fig.1). In the area of short relaxation times 10^{-4} to 10^{-2} s formation of a polymodal peak can be observed. This means that the most characteristic relaxation time lies in this time interval.

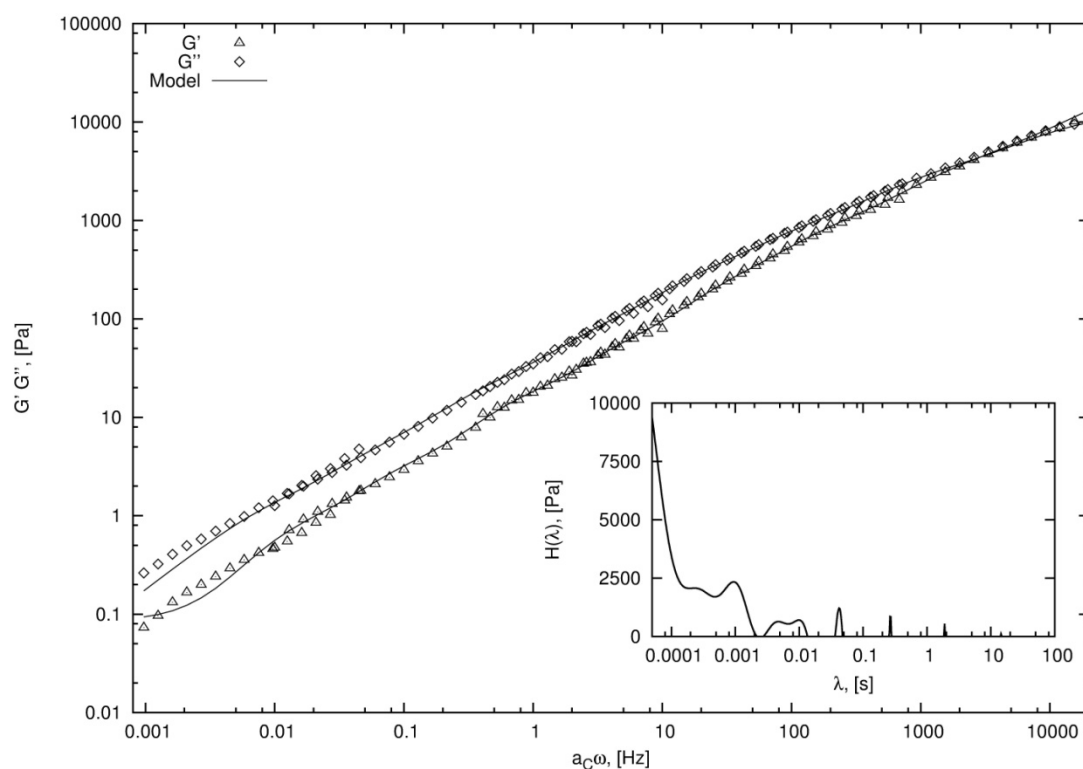


Fig. 1. G' and G'' as a function of frequency for *Hylon*/DMSO system (relaxation spectra inside)

This conclusion is strictly related to relaxation time $\lambda = 1.89 \cdot 10^{-4}$ s estimated by Kapoor and Bhattacharya (2000) based on literature data and results from their own rheological studies for non-concentrated, high-amylose starch solutions in aqua DMSO. It supports the suggestion about the invariable mechanism of friction during shear flow. The accumulation of short relaxation times observed in the spectrum is the result of advantage of viscous effects. Other peaks present in the range of higher relaxation times ($10^{-2} - 10^1$ s) are characterised by a small area and indicate weak influence of elastic phenomena in the whole range of the studied viscoelastic phenomenon.

The peaks' presence can be related to the tendency of the system to reach the crossing point (flow area), observed on the master curve. What is interesting, the possibility of estimation of G_e parameter indicates that from the rheological point of view the system behaves like a viscoelastic solid material in the flow area. The value of this parameter is small and equals to $(0.854 \pm 0.038) \cdot 10^{-1}$ Pa. Literature reports about conformation of amylose in diluted DMSO solutions indicate its helical structure (Aberle and Burchard, 1997). In concentrated solutions (up to 40%) amylose can form a chaotic net of entanglements, which is penetrated by solvent molecules and amylopectin. In these conditions, amylopectin takes a conformation of a bundle, which can additionally stiffen the obtained amylose matrix. Such a solution structure would explain the behaviour typical to viscoelastic solid substances. Nevertheless, the net of entanglements created by amylose is not able to permanently store energy in the conditions of shear. This energy can be lost as a result of friction of a deformed net, including free ends of chains. Highly branched amylopectin chains forming 'spiky' bundles in solution deepen this phenomenon, moving in irregular amylose matrix.

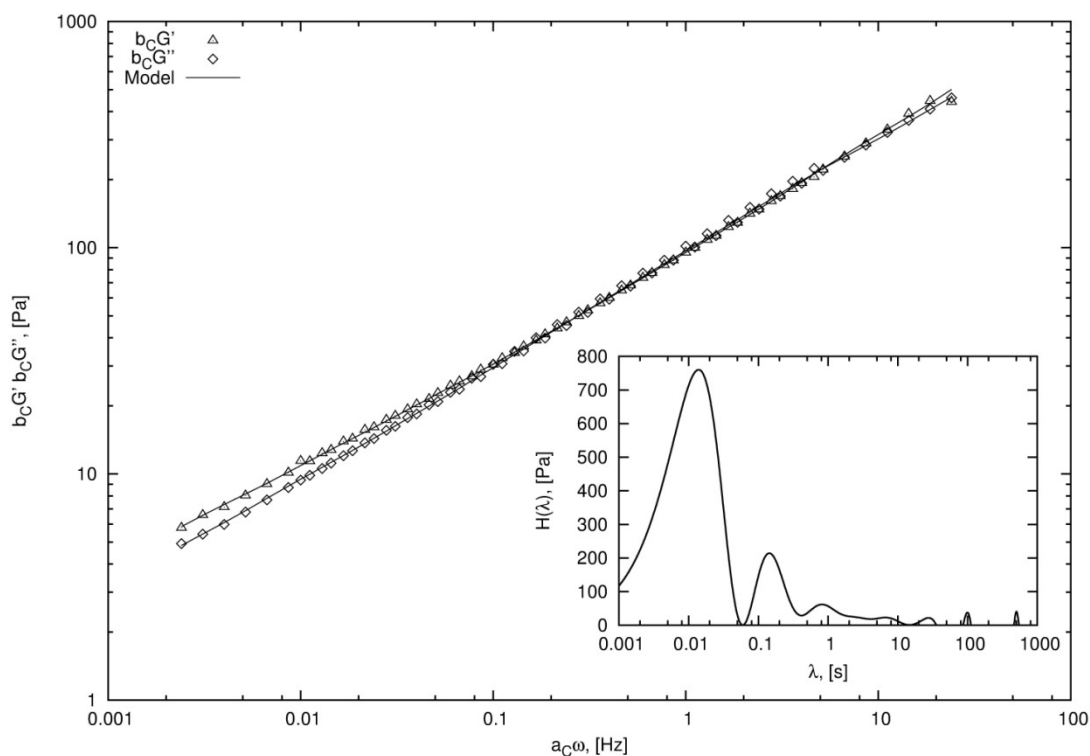


Fig. 2. G' and G'' as a function of frequency for maize/DMSO system (relaxation spectra inside)

The maximum obtained concentration of maize solution in DMSO was smaller than that for *Hylon* and was equal to 30%. In the range of obtained concentrations it was possible to carry out calibration (Fig.2). However, it required additional procedures. They comprised calibrating to coordinate axis the values of G' and G'' using b_c factors (Honerkamp and Weese, 1993).

Thanks to immediate calibrating of these rheological functions it is possible to obtain complete information regarding viscoelastic properties of the studied solutions. The observed course of summary G' and G'' curves corresponds to the crossing point of *flow* zone with *plateau* zone: experimental points interweave. Calibration of viscoelastic properties caused widening of the horizon by two decades in the direction of lower frequencies. The values of calibration coefficients a_c were lower than one (0.24 for 10% solution and 0.54 for 30%). Unlike high-amylose starch there were no monotonous changes in the values of a_c coefficients observed in the function of solution concentration, which is possible in case of using, in the strict sense, the empirical method (Ferry, 1980). This fact can suggest that the mechanism of friction is complex. The shape of the master curve (Fig.2) indicates, however, that there is a significant participation of viscous phenomena in the formation of viscoelastic properties. Similar behaviour was observed for diluted maize starch solutions in aqua DMSO (Kapoor and Bhattacharya, 2000), while it definitely belonged to fluidification zone. The shape of G' and G'' curves is supported by the structure of relaxation spectrum of stress values (Fig.2). It is composed of several peaks, while the peak with the greatest area lies in the interval of short times (range 10^{-3} - 10^{-1} s). Similar to previously discussed solutions of high-amylose starch, the tested system behaves like viscoelastic solid substance, while the value of equilibrium modulus is higher ($G_e = 3.00 \pm 0.37$ Pa).

In case of maize starch solutions elastic properties have an increasing participation in the formation of rheological properties, which is also manifested by the increase of number and area of peaks present in longer relaxation times. This is an interesting conclusion, because in the tested solutions, there is higher amount of amylopectin. Paradoxically, amylopectin can stabilise the amylose matrix, but not by increasing the elastic properties of the net of entanglements. Almost twice higher content of amylopectin (Table 1) can counteract deformation of net during shear stiffening of the formed structure.

For waxy starch the illustration of rheological behaviour (Fig. 3) is typical as for the end of shear zone, with a clearly shaped crossing point and the beginning of *plateau* zone. It indicates that the values of equilibrium modulus are lower than the values of loss modulus. Such rheological behaviour is the continuation of the course of G' and G'' curves observed by Kapoor and Bhattacharya (2000) for diluted solutions of waxy starch. The master curve presented in Fig. 3 was obtained on the basis of data for two starch solutions at 10%wt and 20%wt. Calibration was also carried out for both frequencies and values of rheological functions. It allowed to widen the observation horizon by one decade for lower frequencies. During the evaluation of relaxation spectrum for the master curve the G_e value was not estimated, which indicates that the tested system behaved like viscoelastic liquid.

Waxy starch is practically composed of amylopectin, that is large molecules adopting the conformation of statistical bundle in DMSO. This fact can be interpreted as lower affinity of solvent to polymer which results in 'denser' amylopectin bundles. The bundles rub one another, and consequently dissipate mechanical energy which, in turn, is manifested by a higher value of G'' than that of G' . The shape of the obtained relaxation spectrum (Fig.3) is similar to the latter (Fig.2), while its shift in the direction of shorter relaxation times is clear. This indicates the dominance of viscous effects in the formation of the phenomenon of viscoelasticity.

A comparison of results obtained for the tested solutions indicates a double function of amylopectin. On the one hand it is responsible for dissipation of energy during shear flow. This is manifested by a correlation between amylose content and drifting of the main peak in the spectrum towards short relaxation times. On the other hand, in case of solutions with high amylose content, the observed rheological behaviour corresponds to that of viscoelastic solid substances. This is, of course, the consequence of the formation of a net of entanglements by amylose. The presence of amylopectin results in stiffening of this net which, in turn leads to an increase of G_e value with an increase of amylopectin amount in starch.

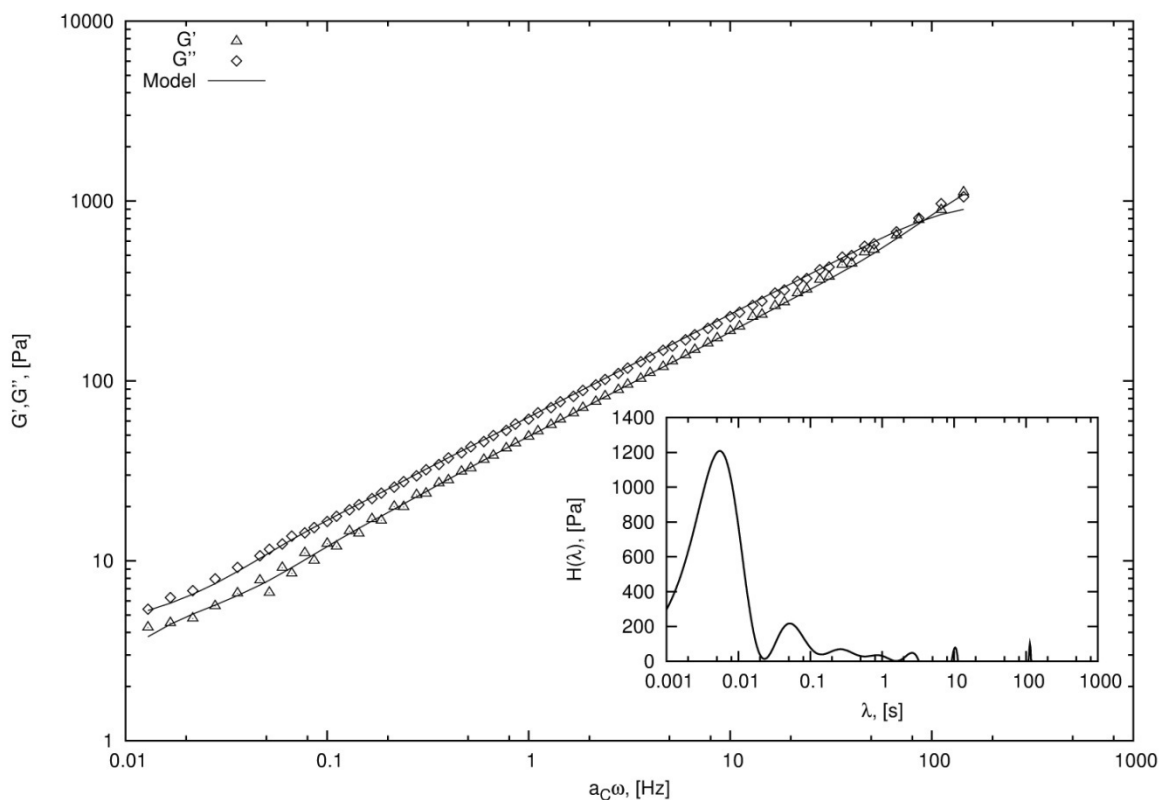


Fig. 3. G' and G'' as a function of frequency for waxy starch/DMSO system (relaxation spectra inside)

4. CONCLUSIONS

Concluding the investigation, we would like to report the very first results on high concentrated starch/DMSO solutions. Nowadays, when new technologies are turning to biodegradable and renewable resources these are precious results with high application potential (e.g. Łukasiewicz et al., 2007).

The solubility of starch in DMSO is independent from the linear/branched fraction ratio up to 20% but even at this level there are plenty of rheological differences. More concentrated systems are able to be obtained only when the amount of the branched fraction is limited. It is a kind of reversion when compared to starch water systems known from the phenomenon of pasting difficulties observed for starches with higher amylose content. Such comparison leads to the conclusion that a lower molecular mass of linear fractions is not the limiting factor for amylose dissolution. The reasons lie probably in the conformation of macrochains in the presence of a solvent but for a full understanding of the phenomenon further study is needed.

Concluding all the remarks it is also important to make some general rheological statements. First of all the scaling of rheological properties of starches may be done by means of linear fraction content. Hence, the prediction of the rheological function in a wide range of frequency and time values becomes possible.

Secondly, may be successfully applied for high concentrated non aqueous (DMSO) starch solutions. As a result of estimation, continuous relaxation spectra $H(\lambda)$, as well as G_e were obtained. Looking at the relaxation spectra of all the investigated starch compositions the one dominant peak may be detected. It testifies to accumulation of similar relaxation contributions. All isolated peaks that may be seen on the relaxation spectra evidence and prove the testify on complicated heterogeneous composition of

relaxation course in starch dispersed in DMSO. Furthermore, the higher concentration of the biopolymer, the more the systems starts to behave like a viscoelastic solids – gels. Such a phenomenon may be tracked by raising G_e parameter.

The applied procedure can successfully be used to calculate absolute relaxation times. Contrary to that, as it is known from the literature, the application of discrete models gives only an estimation of the relaxation time. Additionally a complete structure of relaxation times for the investigated systems was obtained.

For high-amylose starch the superposition of time and concentration allows to extend the field of viscoelastic phenomena observation. The presence of nonzero G_e parameter might be the very first criterion of viscoelastic solid (i. e. gels). The non-zero G_e was detected for almost all *Hylon* based suspensions. Conversely, all *Amioca's* as well as 10% of *Hylon* systems looked like a viscoelastic liquid and did not possess G_e at all. Likewise, the viscoelasticity of 20% of *Hylon* solutions may be questionable due to a rather high error of estimation which is placed near the border of the estimator.

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SYMBOLS

G^*	complex modulus, Pa
G'	storage modulus (real part of G^*), Pa
G''	loss modulus (imaginary part of G^*), Pa
G_e	equilibrium modulus, Pa
$H(*)$	relaxation spectra, Pa
j	complex unit
λ	relaxation time, s
ω	frequency, Hz

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