



Viscoelastic properties of waxy maize starch and selected non-starch hydrocolloids gels

A. Ptasek *, W. Berski, P. Ptasek, T. Witczak, U. Repelewicz, M. Grzesik

Department of Food Technology, Agricultural University, Krakow PL-30-149, ul. Balicka 122, Krakow, Poland

ARTICLE INFO

Article history:

Received 11 June 2008

Received in revised form 13 November 2008

Accepted 18 November 2008

Available online 27 November 2008

Keywords:

Starch

Hydrocolloids

Time-temperature superposition

Relaxation spectra

Regularization

Continues Maxwell model

AFM

ABSTRACT

Polysaccharides play a significant role in food systems as texture forming agent. Their solutions possess some peculiar rheological behaviors. Some information about structure of these biopolymers and relaxation processes occurring in their solutions may be obtained by investigation of linear viscoelasticity properties. The aim of this research was to investigate viscoelastic properties of systems consisting of waxy maize starch–hydrocolloid–water. To achieve this aim two techniques were applied: rheological measurements in frequency domain and structural studies by means of AFM method. The results were interpreted on basis of time–temperature superposition principle and phenomenological theory of viscoelasticity. Thermal stability of analyzed systems allowed applying time–temperature superposition principle. Calculation of a_T parameter enabled to obtain the master curves. Continuous Maxwell model was applied to analyze phase separation in examined systems. Relaxations spectra obtained by Tikhonov regularization method were heterogeneous, indicating on non-homogeneous structure of system.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. Starch and non-starch hydrocolloids

Hydrocolloids and starch are used in food systems as texture and stability improvers (Whistle & Bemiller, 1994). Starch is plant storage material, deposited in plant's storage organ in the form of granules, which size and dimensions are determined by botanical origin. It is composed of two alpha glucans: essentially linear amylose, and branched amylopectin. The amylose has a small degree of branching but it is predominantly regarded as a single chain. Its chain length (500–6000 glucose units) can vary with the botanical origin of the starch. The chain of amylopectin contains only up to 30 glucose units. However, the multitude of branching in amylopectin gives it a molecular weight that is 1000 times greater than that of amylose. Amylopectin is one of the largest biomacromolecules with a molecular weight of 400 MDa (Tester, Karkalas, & Qi, 2004; Whistle & Bemiller, 1994). In starch pastes can occur phase separation phenomenon. It resulting from thermodynamics incompatibility of system creating compounds (Alloncle & Doublier, 1991). Starch pastes are clearly thermal unstable and behave as viscoelastic object. This instability is attributed to amylose crosslinking and crystallization. Adding another biopolymer, like guar (GG) or xanthan

(XG) gum, carboxymethylcellulose (CMC) into starch–water system, it modifies its structure. One on the hydrocolloids widely used in food industry is galactomannan: guar gum (GG). Its production bases on extraction from seeds of the leguminous shrub *Cyamopsis tetragonoloba*. Guar is a galactomannan with backbone consisting of linear chain of mannose units linked by 1–4- β -glycosidic bonds, with several branch points at C6, where single α -D-galactose unit is attached by 1–6- β -bonds. It is soluble both in hot and cold water, but some caking may occur due to fast water absorption. Their water solutions are stable at pH 3.0–10.5. Alone GG creates no gel, but has synergistic effect on agar and κ -carrageenan gelling (Phillips & Williams, 2000). Other hydrocolloid is xanthan gum (XG). It is extra cellular polysaccharide of bacterial origin produced by *Xanthomonas campestris*. It comprises of linear 1–4 linked β -D-glucose units, identical as in cellulose, with a trisaccharide branch containing one glucuronic acid unit between two mannose units linked to every other glucose unit at 3 position. In recent years a broad application in many industrial branches found cellulose derivatives, such as carboxymethylcellulose (CMC). It is produced from cellulose by reaction with alkali and chloroacetic acid. It consists of cellulose chain substituted, at different level, with carboxylic groups at position 6. Usually CMC molecules are shorter than cellulose. Depending on degree of substitution CMC may vary in its solubility and viscosity. Usually it is well soluble both in hot and cold water to give clear and colorless solutions with neutral flavor, and found application as food stabilizer (Dumitriu, 2005).

* Corresponding author. Tel.: +48 126624768; fax: +48 126624761.

E-mail address: aptasek@ar.krakow.pl (A. Ptasek).

Nomenclature

G^*	complex modulus [Pa]	t	time [s]
G'	real part of complex modulus [Pa]	α	regularisation parameter
G''	imaginary part of complex modulus [Pa]	λ	relaxation time [s]
G_e	equilibrium modulus [Pa]	η	viscosity [Pa s]
g	spring constant [Pa]	ω	frequency [Hz]
$H(*)$	relaxation spectra [Pa]		
j	complex unit		

1.2. Viscoelasticity

1.2.1. Maxwell model

In the viscoelasticity science usually there are performed two relaxation experiments: step function, where deformation is constant in time and oscillatory, where deformation is sinusoidally changed in function of time. As a result of experiment conducted in such way, the most often the complex viscoelastic modulus is obtained ($G^*(j\omega)$ Eq. (1)). It consists of real part G' , representing amount of energy stored by system, and by imaginary part G'' , amount of energy dissipated by the system.

$$G^*(j\omega) = G'(\omega) + jG''(\omega) \quad (1)$$

Basing on these results the parameters of rheological model can be estimated. The most basic and often used model describing viscoelastic system was proposed by Maxwell (Ferry, 1980; Tschoegl, 1989). It consists of such elements like dashpot and spring, joined together in series. Dashpot represent Newtonian viscosity, spring on the other hand elastic Hook's element. Its mathematical form depends on domain (time or frequency), which was select to perform experiment and to analyse obtained data. In this work analysis of Maxwell model was performed in frequency domain Eq. (2).

$$G^*(j\omega) = G_e + h \cdot \frac{(\lambda\omega)^2}{1 + (\lambda\omega)^2} + j \cdot h \cdot \frac{(\lambda\omega)}{1 + (\lambda\omega)^2} \quad (2)$$

Relaxation time λ is a value directly resulting form Maxwell model. It is defined as relationship of dashpot viscosity (η) vs. spring constant (g):

$$\lambda = \frac{\eta}{g} \quad (3)$$

This value is called the most probable relaxation time, and it is specific for given material and temperature, and h represents its intensity. But single Maxwell's element could not represent behavior of real material. For that reason there is a need to approximate properties of viscoelastic material by higher number of parallel joined Maxwell elements. In such case relaxation times (λ_i) create discrete spectrum, and (h_i) values represent its intensity:

$$G^*(j\omega) = G_e + \sum_{i=1}^n h_i \cdot \frac{(\lambda_i\omega)^2}{1 + (\lambda_i\omega)^2} + j \cdot \sum_{i=1}^n h_i \cdot \frac{(\lambda_i\omega)}{1 + (\lambda_i\omega)^2} \quad (4)$$

Value G_e appearing in Eq. (4) is called equilibrium elasticity modulus and it characterizes viscoelastic solid state (additional spring attached in series into Maxwell elements). Even better approximation of viscoelastic properties of real materials is given, when continuous Maxwell model was applied. In such case, Maxwell's elements create *continuum*, and it has effect on relaxation time ($\lambda + d\lambda$). Eq. (5) presents continuous Maxwell model for oscillation experiment:

$$G^*(j\omega) = G_e + \int_0^{+\infty} H(\lambda) \cdot \frac{(\lambda\omega)^2}{1 + (\lambda\omega)^2} d\lambda + j \cdot \int_0^{+\infty} H(\lambda) \cdot \frac{(\lambda\omega)}{1 + (\lambda\omega)^2} d\lambda \quad (5)$$

Continuous function $H(\lambda)$ in Eq. (5), describing distribution of relaxation times, is called relaxation spectrum, and completely describes investigated material in aspect of viscoelasticity in linear area. This spectrum is interpreted as continuous distribution of relaxation times (λ) with proper intensity (H). Area of peak gives impression about number of Maxwell elements creating relaxation time. If the peak is narrow with the small area, Maxwell elements have similar relaxation time. But in case when peak is flattened and its area is quite big, it means that system behavior can be described by Maxwell elements with different relaxation times. Moreover, having relaxation spectrum it is possible to calculate any rheological function in linear range of viscoelasticity (Ferry, 1980). To estimate parameters of discrete Maxwell model the most often the least square method is used. It is performed by looking for minimum of properly defined non-linear target function. When continuous relaxation spectrum $H(\lambda)$ is searched, it is not possible to apply directly the least square method, because searched integrated function is not described by analytical formula. So it is found as set of points, and as result it leads to so called *ill-posed* problem (Engl, Hanke, & Neubauer, 1996). It used to say about such type problems, that even very small experimental noise can lead to obtaining absolutely different estimators than for raw data. It requires to apply the proper methods to estimate parameters. One of the estimation methods is Tikhonov's regularization (Tikhonov, Goncharsky, Stepanov, & Yagola, 1995). This method can be described as the case of least square method. It relies on minimization of adequate target function (Honerkamp & Weese, 1990) and connects parametric and nonparametric estimations. Regularization method was used to estimate parameters of relaxation and retardation spectrum for synthetic polymers (Tan, Tam, & Jenkins, 2000; Weese & Friedrich, 1994) and also for biopolymers (Mao, Tang, & Swanson, 2000; Ptaszek, Lukasiewicz, Achremowicz, & Grzesik, 2007) but this problem is still open.

1.2.2. Time temperature superposition

In order to broaden the observations horizon of viscoelastic properties, the method of superposition of time (frequency) and temperature was applied. (Ferry, 1980). This is a basic method for analysis of data originating from rheological measurements of synthetic polymers. It also finds application in food and biopolymers science (Kasapis, 2001; Ptaszek et al., 2007). According to this rule, it is possible to broaden the observation horizon of the given rheological value through sliding over the experimental data obtained at different temperatures into data at the reference temperature. It is done by shifting given measuring data set (collected at selected temperature) for a_T vector in such manner that obtained results will create continuation of rheological function with data from reference temperature (master curve). As a result of this operation, it is possible to observe course of rheological function in broader time or frequency range. Yielded in this manner data set is broaden by experimental points obtained for different temperatures. Application of superposition method for the given system allows for preliminary assessing of system thermal stability (i.e.

lack of phase transitions or chemical reactions). This method relies on simultaneous estimation of all values of a_T coefficient for data from whole temperatures set.

1.3. Viscoelastic properties starch and non-starch hydrocolloids

The presence of hydrocolloids is changing the pasting and rheological properties of systems containing starch (Chaisawang & Supphantharika, 2005, 2006). But their structure is quite complicated, due to presence of two types of glucans. Starch during pasting can be described by two phase model of suspensions of swollen particles in macromolecular medium (Alloncle & Doublier, 1991; Bagley & Christianson, 1982; Evans & Haisman, 1979; Ptaszek & Grzesik, 2007). The swollen particles consist mainly of amylopectin, whereas amylose is leaching from granules and forming a three dimensional network of continuous phase. The presence of hydrocolloids complicates this model, adding interactions with amylose (Christianson, Hodge, Osborne, & Detroy, 1981; Rodriguez-Hernandez, Durand, Garnier, Tecante, & Doublier, 2006). Therefore waxy starch, containing almost only amylopectin, offers a possibility to investigate nature of system without interfering effect of amylose. There are papers describing effect of hydrocolloids addition on properties of waxy starches (Achayuthakan & Supphantharika, 2008; Achayuthakan, Supphantharika, & Rao, 2006; Freitas, Gorin, Neves, & Sierakowski, 2003; Khondkar, Tester, Hudson, & Karkalas, 2007; Ptaszek & Grzesik, 2007; Shi, & BeMiller, 2002). But much less attention has been paid to viscoelastic properties of systems consisting of starch and hydrocolloids and their description by means of rheological models (Kulicke, Eidam, Kath, Kix, & Kull, 1996). This study is trying to broaden the current knowledge in this aspect. The majority of the presented results of oscillatory investigations usually are performed only in one temperature. The interpretation of their results is rather qualitative, not a quantitative. (Kulicke et al., 1996) analyzed the influence of waxy rice starch concentrations on viscoelastic properties of its solution. Also they investigated the effect of galactomannans addition. But they did not analyze the effect of temperature on rheological behavior, and also there were no attempt of mathematical description of the observed phenomena. (Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997) investigated the changes in viscoelastic properties of waxy starches with hydrocolloids in function of time. The analyzes were performed at one frequency and temperature. In conclusions the authors stated, that the most pronounced effect has been the retardation of gelation kinetics of waxy maize starch by the hydrocolloids.

1.4. AFM structure study

Atomic force microscopy (AFM) is quite useful tool to examine structure of both synthetic polymers mixtures, and also widely implied biological material, including foodstuff. The nature of the described method allows to characterize the conformation of the separate molecules, investigations of the surface as well as the properties of the individual phases in the heterogeneous systems. Krok, Szymonska, Tomasik, & Szymoński (2000) investigated by means of AFM changes in the structure of potato starch granules freezed in liquid nitrogen. Lukasiewicz, Ptaszek, Koziel, Achremowicz, and Grzesik (2007) determined structural properties of CMC/polyaniline blends basing on AFM topographical investigation. AFM also enables to evaluate such parameters like range, shape and character of intermolecular interactions (Camesano & Wilkinson, 2001; Decho, 1999; Ikeda et al., 2004), including hydrocolloids responsible for forming of structure of many food products. Morris et al. (2001) studied xanthan, gellan gum and selected proteins using contact mode of AFM. The maximal observed area was not bigger than $1.5 \times 1.5 \mu\text{m}$, and enabled to

characterize the conformation of these biopolymers. AFM also found applications in phase separation phenomena studies in liquid–liquid systems of synthetic polymers conducted by some authors (Karim et al., 1998; Lin, Hung, Chang, & Chen, 1999; Wang, Song, Li, & Shen, 2003) or polysaccharides (Ptaszek et al., 2007). Lin et al. (1999) applied Force Modulation Microscopy (FFM) to examine phase separation in thin layers of polymers blends (ether-PPV:CNPPV) with different shares of constituents. They described the character of individual phases basing on their different elastic properties. As result, they obtained topographical images ($20 \times 20 \mu\text{m}$) of the surface, indicating on different phase behavior of mixtures depending on their composition. In phase separation studies much bigger scanned areas ($40 \times 40 \mu\text{m}$) are analyzed. Such scale/magnification gives a full view of phase behavior, enabling to study gelling systems or emulsions (Patino et al., 2007). At the same time it allows to gain more information than by means of classical light microscopy applied to confirm an existence of such phenomenon.

2. Aim

The aim of the present work was to define the viscoelastic properties of (pasted) mixtures of the selected polysaccharides. As the material waxy maize starch was selected, and then pasted in the water solution of the following hydrocolloids: guar gum (GG), carboxymethylcellulose (CMC) and xanthan gum (XG). Hydrocolloids were chosen in order to represent different properties and source. Guar gum is extracted from plant seeds, xanthan gum represents group of substances produced by microorganisms, and CMC is chemically modified biopolymer. Rheological investigations were performed in frequency domain at different temperatures. Theoretical analysis included adaptation of some achievements of phenomenological theory of viscoelasticity to evaluate the results obtained for the mentioned above biopolymers. The emphasis was focused on description of relaxation behaviors by continuous rheological models (Maxwell model) in frequency domain. Also an attempt was undertaken to apply time–temperature superposition rule to determine the unchanging character of relaxation mechanism for the analyzed mixtures. Moreover atomic force microscopy (AFM) would be applied as a complementary method in order to visualize the surface of the investigated systems in microscale.

3. Experimental

3.1. Gel permeation chromatography

Waxy maize starch used in this research was provided by National Starch (USA). Guar gum, xanthan gum and carboxymethylcellulose were provided by Regis (Poland). Molecular mass distribution was 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 all columns was 16 mm. As eluent Na_2CO_3 solution (0.005 mol l^{-1}) was used, flow rate was $0.125 \text{ ml min}^{-1}$. Sample of starch (0.05 g) was dissolved in 4 ml of 90 wt.% DMSO (Merck, Germany) in 70°C for 24 h.

Chromatographic analyses of hydrocolloids were performed in set of two columns 0.380 and 0.460 m filled with Pharmacia Sephacryl gels S-200 and S-500, respectively. Eluent and its flow rate were as previously described. Hydrocolloids samples (0.05 g) were dissolved in eluent (4 ml) by vigorous agitating during 24 h at ambient temperature. The volume of sample was 1 ml. Knauer K-2300 refractometer was used as detector. All analyses were

performed at 20 °C. Standard calibration was performed using pullulans standards provided by Shodex (Japan) (Achayuthakan & Suphantharika, 2008).

3.2. Sample preparation

As the control samples are used: waxy maize starch paste (4.00 wt.%) and guar gum (1.00 wt.%), xanthan gum (1.00 wt.%), carboxymethylcellulose (1.00 wt.%) water solutions. The starch paste and hydrocolloids water solutions were prepared: in water bath (95 °C) with constant agitating (200 rpm) for 30 min. The starch (concentrations range 3.00–3.75 wt.%) hydrocolloid (1.00–0.25 wt.%) blends were prepared in the following way: first water solution of hydrocolloid was prepared, agitating by mechanical stirrer during 24 h, and then starch was added. This range of starch and hydrocolloid concentrations is typical in technologies practice. Next it was placed for 30 min. in water bath (95 °C) with constant agitating (200 rpm).

Rheological measurements were performed using RS-150 rheometer (Haake, Germany). Temperature was controlled by means of F-6 ultrathermostat (Haake, Germany) with accuracy of 0.1 °C. All measurements were done using co-axial cylinders measuring system with 75 cm³ volume (rotor type Z40Ti DIN). This system was chosen due to better thermal stability. Based on previous comparison experiments it may be concluded, that for investigated systems there were observed no important differences between data obtained with two different measuring sensors (co-axial cylinders and cone-plate).

3.3. Rheological measurement

First step was to determine the area of linear viscoelasticity (Ferry, 1980). This test relies, in case of frequency domain measurements, on measurements of the absolute value of complex modulus as $|G^*(\gamma_0)|$ function of deformation amplitude at constant frequency. Linear viscoelasticity region determines the range of deformation amplitude (γ_0), for which $G^*(\gamma_0)$ values are parallel to axis of abscissa (γ_0 axis). For all analyzed systems, the measurements of linear viscoelasticity range were done at extreme values of temperature and frequency. It allowed to determine, common for all systems, range of ($\gamma_0 = 0.01$), and to select one value of deformation amplitude used in the following investigations. Basing on value of amplitude from linear range, there were performed measurements of changes in complex modulus in function of frequency (0.1–10.0 Hz), at temperature range 60.0–0.0 °C (cooling).

3.4. Estimation of master curves and relaxation spectra

For estimation of master curves the algorithm proposed by (Honerkamp & Weese, 1993) was applied. Basing on regularization method proposed by Tikhonov (Honerkamp & Weese 1990; Tikhonov et al., 1995; Weese, 1992) it was created numerical procedures in C++ enabling the estimation of relaxation spectra $H(\lambda)$ (Eq. (5)) of the viscoelastic materials in frequency domain. The references temperature was set to 20 °C.

3.5. Atomic force microscopy research

Images of blends films were obtained by means of Atomic Force Microscope (AFM) “Nomad” (Quesant, USA). This equipment enables to perform the surface scanning in two modes. First, non-contact, relies on examination of van der Waals attraction forces. Scanning probe is moving over the surface of sample in constant distance of only few nanometers. In second, contact mode, the probe is located so close to sample, that allows to measure repulsions forces. Work in this mode gives possibility to determine

topography of the investigated system under layer of water absorbed on its surface. Due to this reason all analyses were done in contact mode. Samples were prepared in the same manner like for rheological measurements, and next sample was prepared by smearing the paste in thin layer over the surface of microscopic slide, (previously) heated to 95 °C. For each paste two preparations were done. Then it was cooled down to 20 °C in dry air, and scanning of surface was performed. The selection of this temperature was favorable due to fact, that this temperature was reference for rheological examinations. It enabled for coherent analysis of results obtained by two different methods. Phase separation phenomenon was observed on 40 × 40 μm images (resolution 1024 dots per line), but at least two repetition were executed for single sample.

4. Results

4.1. Gel permeation chromatography

Molecular masses and polydispersity of the investigated hydrocolloids are presented in Table 1. Additionally molecular mass distributions are given on Fig. 1 (for GG, XG, CMC) and on Fig. 2 for waxy starch. Molecular mass distributions of GG and XG consist of one multimodal peak. In case of CMC, which is chemically modified hydrocolloid, the molecular mass is in broader range. Waxy maize starch is predominantly composed of highly branched amylopectin chains. Molecular mass distribution of amylopectin is bimodal (Fig. 2). Content of linear amylose is very low.

4.2. Rheological measurement

4.2.1. Non starch hydrocolloids

Master curve for 1.00 wt.% solution of guar gum was presented on Fig. 3. Basing on presented data it may be concluded, relaxation mechanism is the same for given concentration of guar gum in the investigated range of temperatures. It may be a proof, that superposition rule of time and temperature can find application in analysis of experimental data. Value of a_T coefficient is included in the area of unity in sense of reference temperature data. Relaxation spectrum calculated for data from master curve (presented on Fig. 3) consists of one peak stretched in wide window of relaxation times. Analysis of this system indicates that the highest shares of relaxation times were concentrated about small values of λ . It is supported by the biggest in whole distribution values of $H(\lambda)$ creating a well defined maximum in the second decade (0.1–0.01 s). Concentration of relaxation processes in this area indicates that stress relaxation phenomenon occurs very fast in guar gum solution. Moreover the system exhibits features of viscoelastic liquid ($G_e = 0$). Relaxation spectrum calculated for guar gum solution is homogenous. It results from the presence in the system the only one type of polymer chains, with different length, that was shown by molecular mass distribution (Fig. 1). Each of these chains contributes into global relaxation process. Relaxation of investigated system is created by mutual interaction between chains and solvent. It results in homogenous relaxation process manifested by uniform relaxation spectrum. Similar interpretation was proposed

Table 1
Molecular masses of the investigated hydrocolloids.

Hydrocolloid	Waxy starch	GG	XG	CMC
Batch number	ABH 305/0405	020118	020435	020312
$M_w, g \cdot mol^{-1}$	14.7×10^6	7.47×10^5	19.6×10^5	2.31×10^5
$M_n, g \cdot mol^{-1}$	1.30×10^4	3.21×10^4	0.22×10^4	0.005×10^4
Polydispersity	585	23	871	417

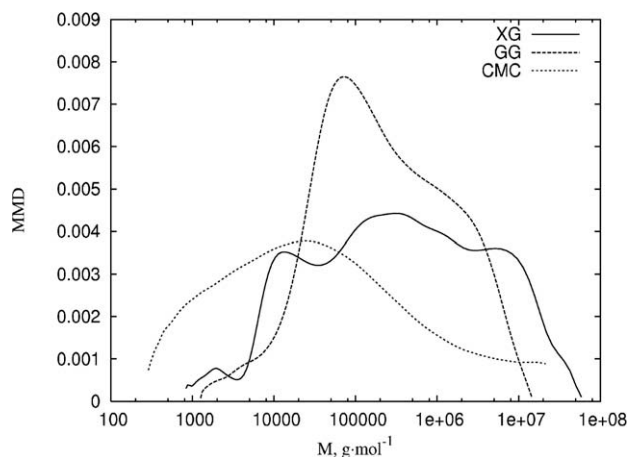


Fig. 1. Molecular mass distributions of non-starch hydrocolloids.

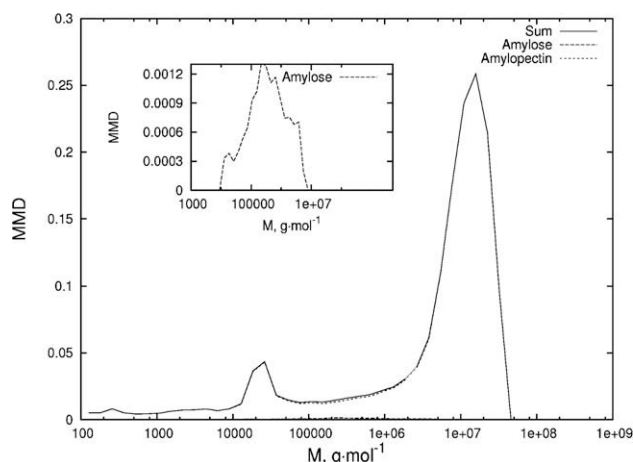


Fig. 2. Molecular mass distribution of waxy starch.

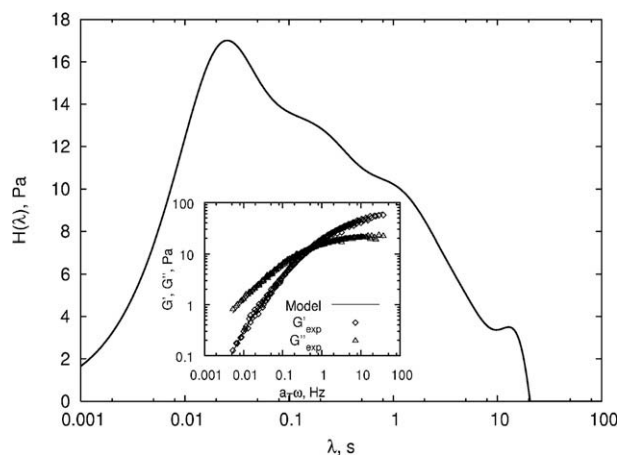


Fig. 3. Master curve and relaxation spectrum for 1.00 wt.% water based guar gum solution.

by (Weese & Friedrich, 1994) for synthetic polymers. The authors analyzed stress relaxation spectra for melt poly(styrene-acrylonitrile) copolymer. Investigated system created uniform constant phase that determined its mechanical properties. Calculated by author's relaxation spectra were homogenous in aspect of its structure. The implication of the mentioned above consideration is

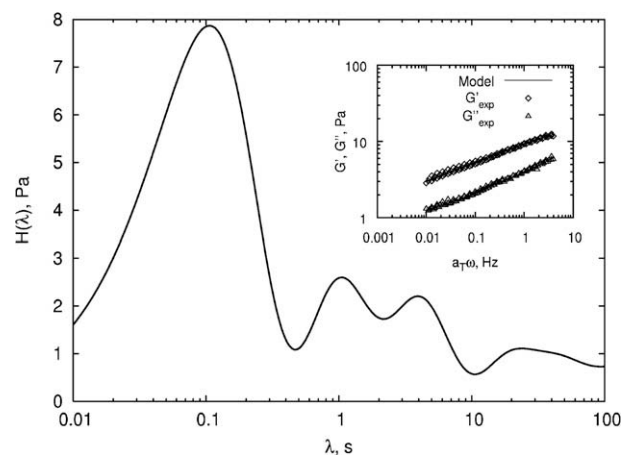


Fig. 4. Master curve and relaxation spectrum for 1.00 wt.% xanthan (gum) solution.

conclusion, that homogenous systems will generate homogenous relaxation spectra.

Master curve and relaxation spectrum for water based 1.00% xanthan solution is presented on Fig. 4. Behavior of such type could not be easily interpreted. It may be only suppose that it is part of plateau region. In the case of xanthan gum rheological measurements were performed only in 60 and 40 °C. For data obtained at temperatures below 40 °C it was not possible to calculated master curve. Superposition method in this case gives only chance to evaluate thermal stability, because extending of observation window is not possible due to the presence of strong disturbances. Relaxation spectrum (Fig. 4) is composed of single multimodal peak filling whole window of material time scale. It is proved by different from zero value of $G_e = (1.54 \pm 0.04)$ Pa in Maxwell model. Calculated relaxation spectrum has homogeneous character, and it consists of four-modal peak spreading out over whole window of analyzed relaxation times. In case of xanthan gum (XG) rheological behavior is complex, and it is an evidence of complicated structure. It may be an evidence of high heterogeneity of chains present in solution, and it is reflected by multimodal peak of relaxation. They are predominantly responsible for creating rheological behavior of the investigated mixture: relaxation spectrum consists of single peak (with one maximum). It is worth to note, that molecular mass distribution is described by multimodal peak, and three of four maximums have the highest, very similar value.

On Fig. 5 is presented master curve and relaxation spectrum for 1.00% water based solution of CMC. Scaling allowed to extend

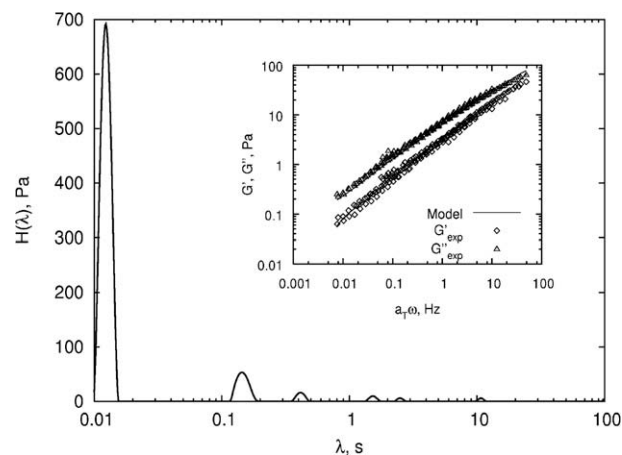


Fig. 5. Master curve and relaxation spectrum for 1.00 wt.% water based CMC solution.

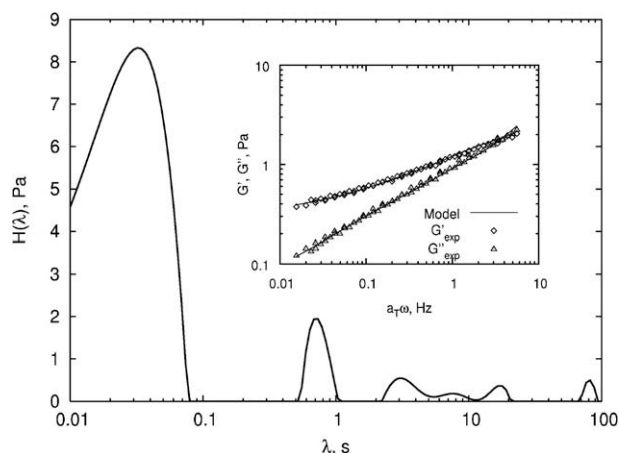


Fig. 6. Master curve and relaxation spectrum of 4.00% waxy starch paste.

observation window almost by decade, in higher frequency region. It was also observed, G' value is lower than G'' , that allow to place investigated system in flow region. Relaxation spectrum consists of six peaks located in every decades of the observed time scale. Peak with highest intensity is present in the first decade, and it is forming relaxation phenomenon in the discussed system. Small width and high intensity of the discussed peak can be caused by high number of similar contributing elements creating the relaxation phenomenon.

4.3. Waxy starch

Fig. 6 depicts relationship of G' and G'' modulus values in frequency function, and relaxation times distribution for 4.00% water based solution of waxy starch. To analyze thermal stability it is possible to apply the rule of time and temperature superposition. Calculated values of a_T coefficient are close to unity, and therefore

scaling has almost no effect on extending the frequency window. Also some problems with data interpretation occurred due to presence of disturbances at higher frequencies. It was caused by liquid character of investigated system. Relaxation spectrum consists of four peaks. Peak with highest intensity is located in second decade of the material time scale, and lack of G_e parameter in Maxwell model reveals that analyzed system is viscoelastic liquid. It is worth to notice, that character of relaxation spectrum consisting of four separated peaks, is closely related to complex, heterogeneous molecular mass distribution of waxy starch.

4.4. Starch–non-starch hydrocolloids

Viscoelastic behavior of waxy starch paste with addition of GG is presented on Fig. 7a–d. Fig. 7a depicts master curve for 0.25% GG and 3.75% waxy starch paste. The nature of the analyzed system is typical for transition between plateau region and rubber-like area. It is clearly seen a overlapping of G' and G'' values at higher frequencies. Master curve for system consisting of GG (0.50%) and waxy starch (3.50%) is presented on Fig. 7b and looks quite interesting. Such behavior is typical for rubber-like region, precisely at the moment of intersect of G' and G'' curves. This area is stretched on whole frequency window, and discussed structure is thermally stable. Further increase of hydrocolloids concentration (GG 0.75% – waxy starch 3.25%) gives no clear answer about area of viscoelastic behavior (Fig. 7c). It may be assumed, that it is rubber-like region. Values of real part of complex modulus of elasticity are greater than imaginary. Curves, depicted on Fig. 7c are ascending, and at higher frequencies they close to each other, that may lead to contact and next to separate. Substitution of waxy starch by higher amount of GG does not lead to any dramatic changes in G' and G'' values in relation to previous concentration, that is illustrated on Fig. 7d. All discussed cases enabled to apply the superposition rule of time and temperature. It allowed to construct master curves, and values of a_T coefficients for selected temperatures were close to unity. It not allowed to predict the viscoelastic properties at wider frequency

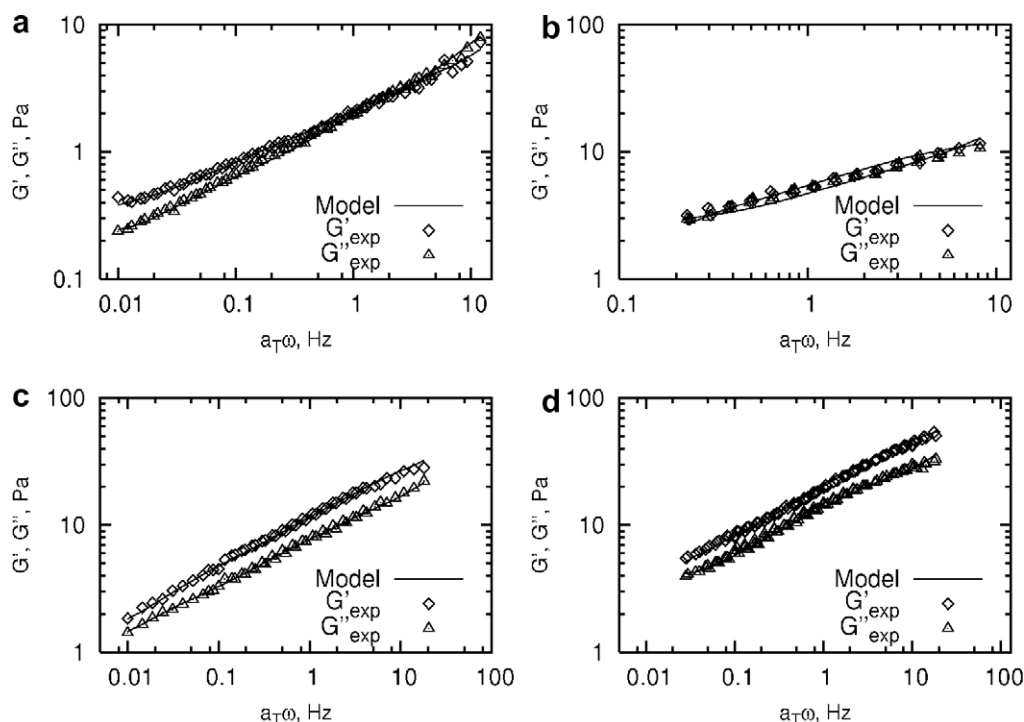


Fig. 7. Master curves of systems: (a) 0.25 wt.% GG–3.75 wt.% starch, (b) 0.50 wt.% GG–3.50 wt.% starch, (c) 0.75 wt.% GG–3.25 wt.% starch, (d) 1.00 wt.% GG–3.00 wt.% starch.

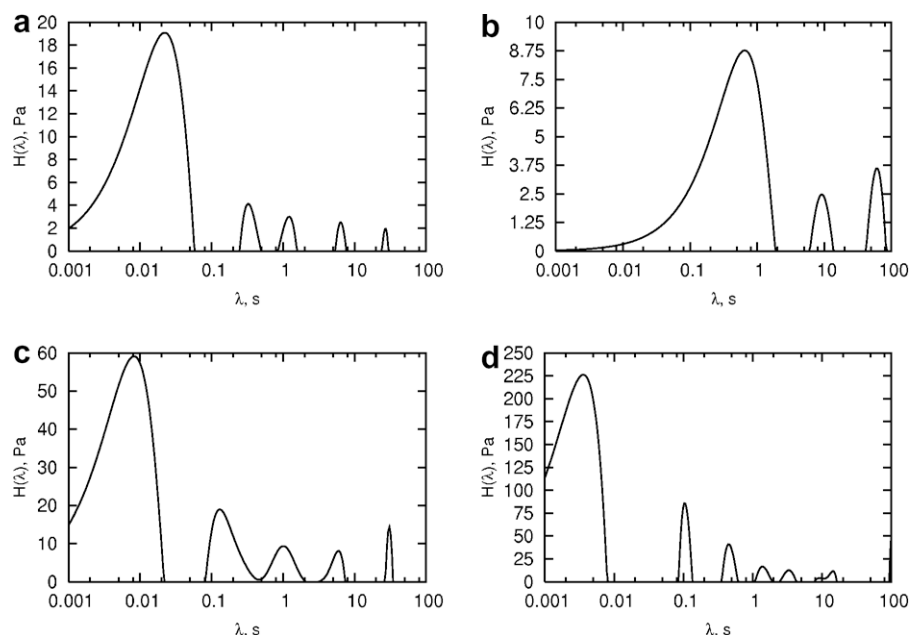


Fig. 8. Relaxation spectra of systems: (a) 0.25 wt.% GG-3.75 wt.% starch, (b) 0.50 wt.% GG-3.50 wt.% starch, (c) 0.75 wt.% GG-3.25 wt.% starch, (d) 1.00 wt.% GG-3.00 wt.% starch.

window. Behavior of waxy starch – GG system is typical for viscoelastic liquids. It is confirmed by the lack of G_e parameter in continuous Maxwell model fitted to experimental data. Liquid nature of mixture can also explain the presence of disturbances in the results from oscillatory investigations. The most possible source of these disturbances is thermal fluctuation of biopolymer chains. It is caused because of loose structure of paste (relatively small values of G' and G''). Stress relaxation spectrum for GG – waxy maize starch system is presented on Fig. 8a–d. In all discussed cases relaxation spectrum consists of few peaks. The highest intensity of phenomenon is observed at first two decades. It means, that observed viscoelastic

phenomenon is the mostly influenced by fast relaxation processes. Remaining peaks are very small, that suggests small effect of longer lasting processes. Such shape of spectrum and its intensity of the observed peaks may indicate on transitory character of the created structure. Calculation of relaxation spectra for GG 0.50% – waxy starch 3.50% system (Fig. 8d) proved to be extremely difficult, so range of frequency window used for calculations was narrowed to 0.2–10 Hz. Obtained result is presented on Fig. 8b. Analyzed spectrum consists of three peaks. The highest intensity (of phenomenon) is observed at third decade. It can be observed the growing importance of longer lasting relaxation processes in

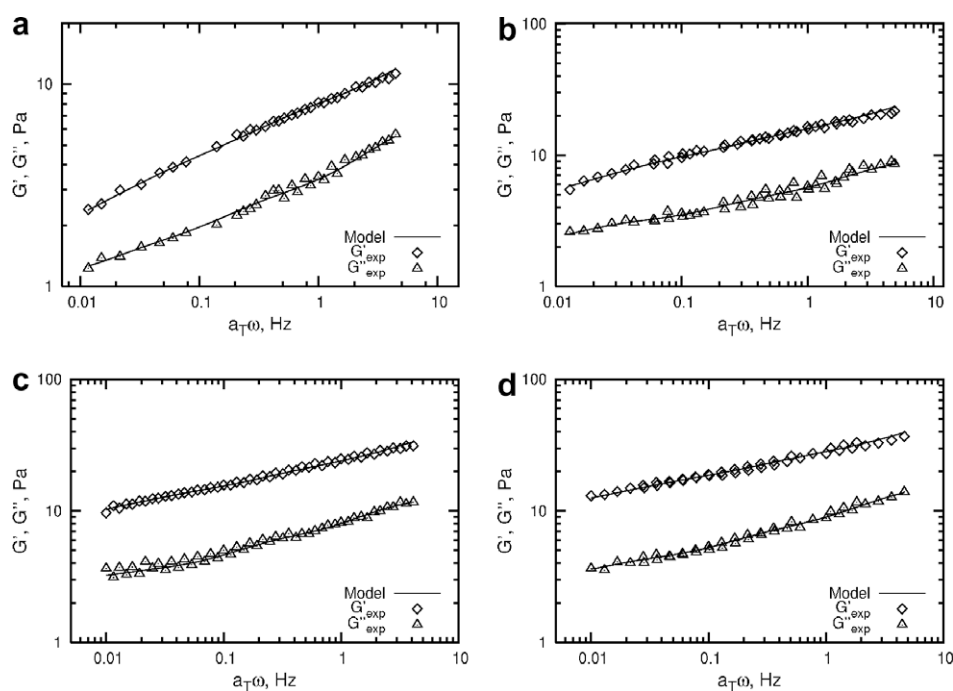


Fig. 9. Master curves of systems: (a) 0.25 wt.% XG-3.75 wt.% starch, (b) 0.50 wt.% XG-3.50 wt.% starch, (c) 0.75 wt.% XG-3.25 wt.% starch, (d) 1.00 wt.% XG-3.00 wt.% starch.

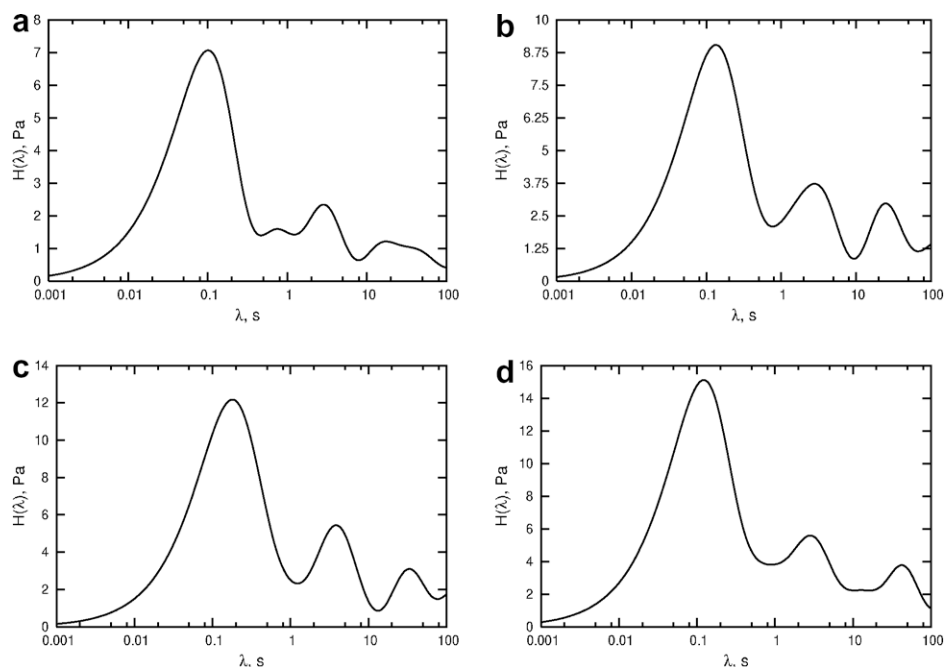


Fig. 10. Relaxation spectra of systems: (a) 0.25 wt.% XG-3.75 wt.% starch, (b) 0.50 wt.% XG-3.50 wt.% starch, (c) 0.75 wt.% XG-3.25 wt.% starch, (d) 1.00 wt.% XG-3.00 wt.% starch.

structure of phenomenon. It is manifested, as compared to previous case, by higher intensity of peaks. It may suggest creation of more complicated structure. For mixture consisting of 1.00% GG and 3.00% waxy starch, relaxation time at which the highest intensity is observed, is located at the first decade. So relaxation process is very rapid. Intensity of peaks representing longer lasting relaxation processes was significantly lowered. Created structure can be more elastic. On Fig. 9a–d master curves for system containing xanthan

gum were depicted. Created structure is thermally stable, that allowed to apply time-temperature superposition rule. Values of a_T coefficients are close to unity, preventing the prediction of viscoelastic properties in wide range of frequencies. The presence of disturbances is also seen, especially for imaginary part of complex viscoelasticity modulus. Such behavior is related to liquid character of the investigated systems. Important feature of the investigated pastes, except thermal stability, is stable character of

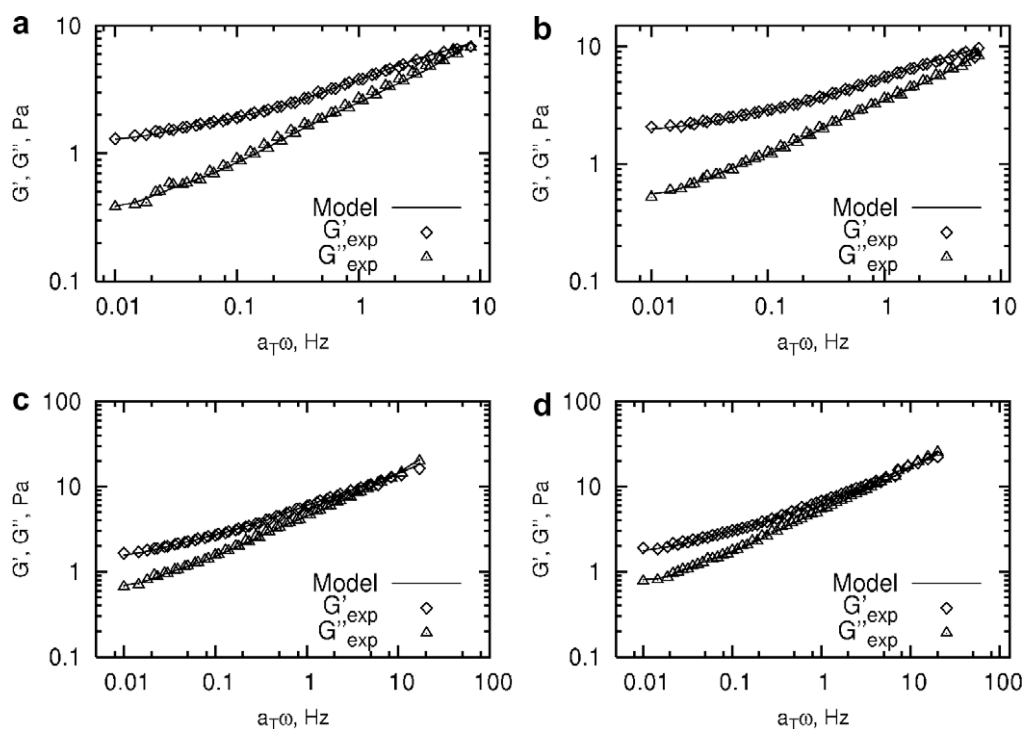


Fig. 11. Master curves of systems: (a) 0.25 wt.% CMC-3.75 wt.% starch, (b) 0.50 wt.% CMC-3.50 wt.% starch, (c) 0.75 wt.% CMC-3.25 wt.% starch, (d) 1.00 wt.% CMC-3.00 wt.% starch.

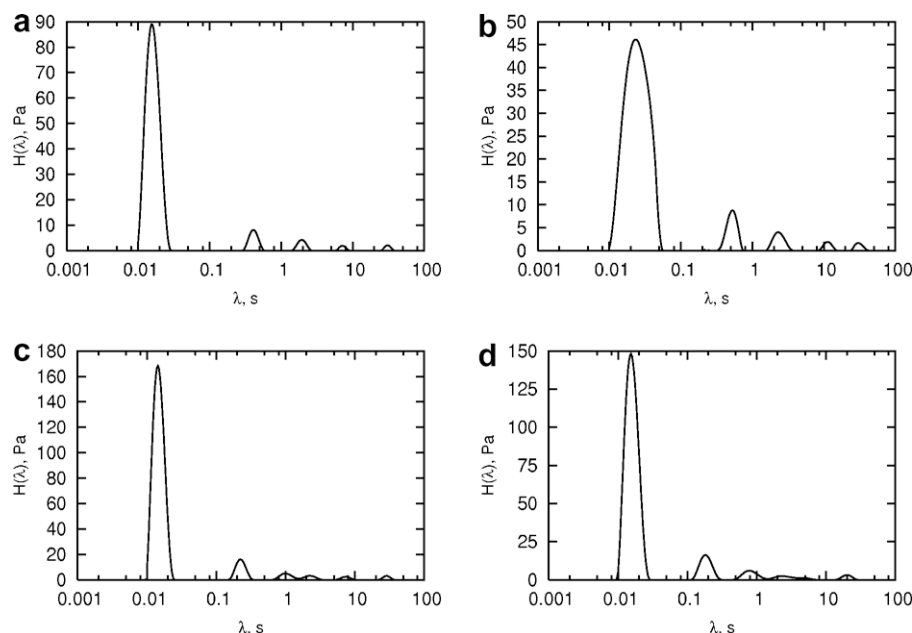


Fig. 12. Relaxation spectra of systems: (a) 0.25 wt.% CMC-3.75 wt.% starch, (b) 0.50 wt.% CMC-3.50 wt.% starch, (c) 0.75 wt.% CMC-3.25 wt.% starch, (d) 1.00 wt.% CMC-3.00 wt.% starch.

structure with growing amount of hydrocolloids in the system. The system becomes more elastic, that is depicted on Fig. 9d. Pastes are also very similar each other. The relaxation spectra for xanthan gum and waxy starch water solutions are presented on Fig. 10a–d. All of them are consisting of single peak with many maximums. In this case the highest intensity is located close to 0.1 s. Stable character of structure is illustrated by increase of relaxation spectrum intensity for higher concentrations of xanthan gum. Such behavior can be explained by growing number of elastic elements with constant parameters. Increasing concentration of non-starch hydrocolloid results only in increased intensity of peaks, but not in their drift on material time scale. Similar shape of particular relaxation spectra is proving about constant qualitative character structure, in sense of interaction. Observed regularity is related only to quantitative changes. Viscoelastic behavior of pastes composed of waxy starch and CMC was depicted on Fig. 11a–d. To analyze data, the rule of time and temperature superposition was applied. It enabled to evaluate thermal stability of structure, and for higher content of CMC, slightly extend frequency window. All discussed cases may be classified as terminal area of plateau region. Despite such clear similarities, two types of viscoelastic behavior can be observed. First, for two lower concentrations (Fig. 11a and b), which are systems with higher elasticity. Curves are approaching to intersect, but distance between them is bigger than for relation from Fig. 11c and d (second type of rheological behavior). Analysis of parameters of the continuous Maxwell model fitted to the curves reveals that, discussed systems are viscoelastic liquid. It is confirmed by lack of G_e parameter. Relaxation spectra are presented on Fig. 12a–d. Their structure is similar. The common trait is a single big peak (located) at 0.001–0.1 s and few smaller at higher time. It may suggest the presence of one, main source of relaxation. Moreover small width of peaks is typical for large number of similar elements creating relaxation phenomenon.

4.5. AFM results

AFM research of guar gum solution and waxy maize starch paste indicates on homogenous nature of the investigated systems at temperature 20 °C. The obtained pictures of topography (40 × 40 μm) were covered by continuous phase. Similar phase

behavior could be observed for waxy maize starch – xanthan gum mixtures. Uniform structures were observed for whole concentrations range at 20 °C. Compounds incompatibility phenomenon was only observed in the case of waxy starch – GG mixture in whole analyzed concentration range (Figs. 13–16). It consequence is phase separation observed at images/windows 20 × 20 and 40 × 40 μm. Intensity of this phenomenon is related to concentration of the investigated mixture: increase in hydrocolloids concentration causes greater incompatibility between compounds.

5. Conclusions

In case of water based hydrocolloids solutions, waxy starch paste and also all mixtures with hydrocolloids it is observed

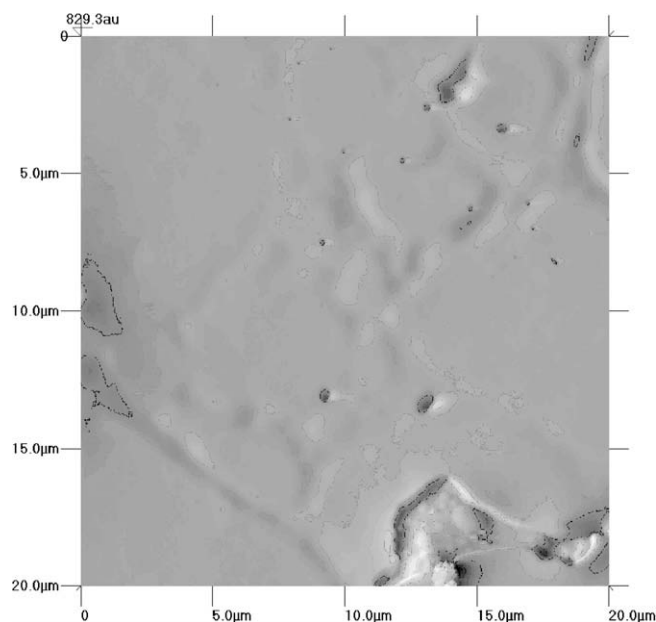


Fig. 13. AFM image of 0.25 wt.% GG-3.75 wt.% starch water system.

temperature scaling phenomenon. As a result, it was possible to analyze master curves. It enabled to calculate stress relaxation spectra. Their shape was strongly influenced by the composition of mixture. Calculated on their basis relaxation spectra are, depending on compounds concentration, homogenous (consisting of one multimodal peak) or heterogeneous which are created by few separates peaks. Type of rheological behavior finds reflection in structure of system, observed by means of AFM. System with uniform structure were characterized by homogeneous relaxation spectra. In the case of systems where heterogeneous structure was observed, they relaxation spectrum consisted of few peaks. So rheological behavior is formed by relaxation phenomena occurring in individual phases. Conclusions drawn on this foundation about structure corresponds with AFM scans. Structure analysis at reference temperature leads to important conclusion. Change of temperature (increase or decrease) did not change quantity

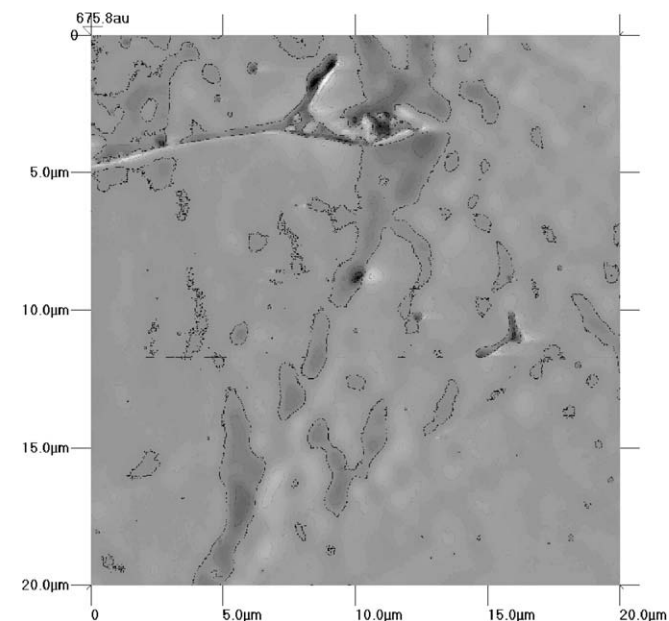


Fig. 14. AFM image of 0.50 wt.% GG-3.50 wt.% starch water system.

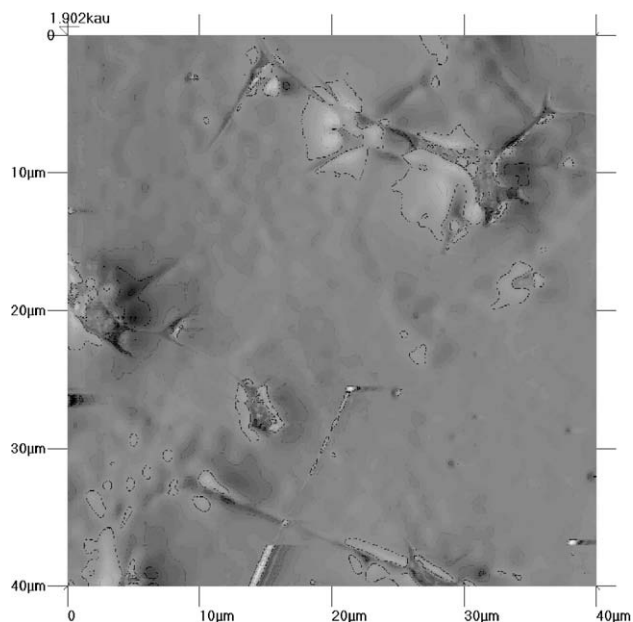


Fig. 15. AFM image of 0.75 wt.% GG-3.25 wt.% starch water system.

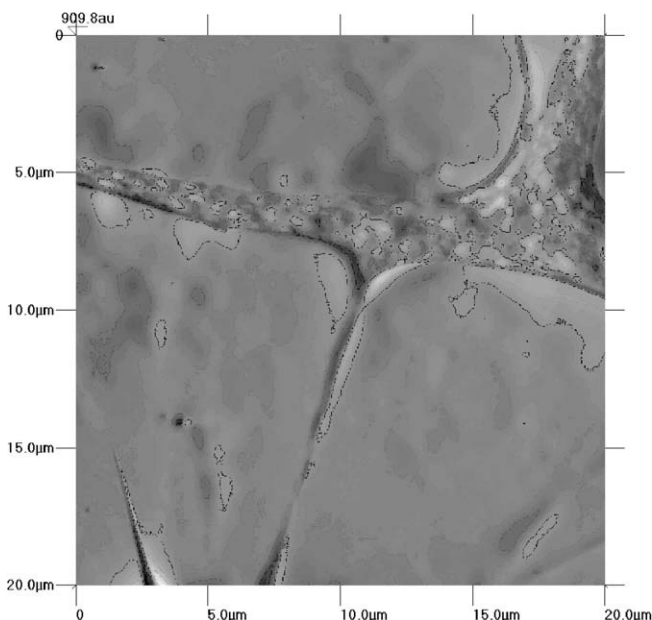


Fig. 16. AFM image of 1.00 wt.% GG-3.00 wt.% starch water system.

changes of structure for the blend with specified composition. It means that shares of individual phases stay constant, only their mechanical properties will change. Viscoelastic behavior of guar gum maize waxy starch system is much riversid, and has base in incompatibility of components. This effect highlights through very complicated structure and relaxation spectra. Moreover there is area where heterogeneity is minimal, or there is no occurrence of this phenomenon. In this range scaling can be performed easily and precisely, that is proved by smooth shape of master curves, and moreover substantial extending of frequency window. Moreover large addition of guar gum to the system is causing transition from solid to liquid state of aggregation.

Acknowledgments

This work is supported by Grant of Polish Ministry of Science and Higher Education no 2 P06T-08429.

References

- Achayuthakan, P., & Supphantharika, M. (2008). Pasting and rheological properties of waxy corn starch as affected by guar gum and xanthan gum. *Carbohydrate Polymers*, 71, 9–17.
- Achayuthakan, P., Supphantharika, M., & Rao, M. A. (2006). Yield stress components of waxy corn starch-xanthan mixtures: Effect of xanthan concentration and different starches. *Carbohydrate Polymers*, 65, 469–478.
- Alloncle, M., & Doublier, J. L. (1991). Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocolloids*, 5, 455–467.
- Bagley, E. B., & Christianson, D. D. (1982). Swelling capacity of starch and its relation-ship to suspension viscosity-effect of cooking time, temperature and concentration. *Journal of Texture Studies*, 13, 115–126.
- Biliaderis, C. G., Arvanitoyannis, I., Izydorczyk, M. S., & Prokopowich, D. J. (1997). Effect of hydrocolloids on gelatinization and structure formation in concentrated waxy maize and wheat starch gels. *Starch*, 278–283.
- Camesano, T. A., & Wilkinson, K. J. (2001). Single molecule study of Xanthan conformation using atomic force microscopy. *Biomacromolecules*, 2, 1184–1191.
- Chaisawang, M., & Supphantharika, M. (2005). Effects of guar gum and xanthan gum additions on physical and rheological properties of cationic tapioca starch. *Carbohydrate Polymers*, 61, 288–295.
- Chaisawang, M., & Supphantharika, M. (2006). Pasting and rheological properties of native and anionic tapioca starches as modified by guar gum and xanthan gum. *Food Hydrocolloids*, 20, 641–649.
- Christianson, D. D., Hodge, J. E., Osborne, D., & Detroy, R. W. (1981). Gelatinization of wheat starch as modified by xanthan gum, guar gum, and cellulose gum. *Cereal Chemistry*, 58, 513–517.
- Decho, A. W. (1999). Imaging an alginate polymer gel matrix using atomic force microscopy. *Carbohydrate Research*, 315, 330–333.

- Dumitriu, S. (2005). *Polysaccharides: Structural diversity and functional versatility*. New York: Marcel Dekker.
- Engl, H. W., Hanke, M., & Neubauer, A. (1996). *Regularization of inverse problems*. Kluwer.
- Evans, I. D., & Haisman, D. R. (1979). Rheology of gelatinised starch suspensions. *Journal of Texture Studies*, 10, 347–370.
- Ferry, J. D. (1980). *Viscoelastic properties of polymers*. New York: Wiley.
- Freitas, R. A., Gorin, P. A. J., Neves, J., & Sierakowski, M.-R. (2003). A rheological description of mixtures of a galactoxyloglucan with high amylose and waxy corn starches. *Carbohydrate Polymers*, 51, 25–32.
- Honerkamp, J., & Weese, J. (1990). Tikhonovs regularization method for ill-posed problems. *Continuum Mechanics Thermodynamics*, 2, 17–30.
- Honerkamp, J., & Weese, J. (1993). A note on estimating mastercurves. *Rheologica Acta*, 32, 57–64.
- Ikeda, S., Nitta, Y., Kim, B. S., Temsiripong, T., Pongsawatmanit, R., & Nishinari, K. (2004). Single-phase mixed gels of xyloglucan and gellan. *Food Hydrocolloids*, 18, 669–675.
- Karim, A., Slawewski, T. M., Kumar, S. K., Douglas, J. F., Salija, S. K., Han, C. C., et al. (1998). Phase-separation-induced surface patterns in thin polymer blend films. *Macromolecules*, 31, 857–862.
- Kasapis, S. (2001). The use of Arrhenius and WLF kinetics to rationalise the rubber to glass transition in high sugar/ κ -carrageenan systems. *Food Hydrocolloids*, 15(3), 239–245.
- Khondkar, D., Tester, R. F., Hudson, N., & Karkalas, J. (2007). Rheological behaviour of uncross-linked and cross-linked gelatinised waxy maize starch with pectin gels. *Food Hydrocolloids*, 21, 1296–1301.
- Krok, F., Szymonska, J., Tomasik, P., & Szymski, M. (2000). Non-contact AFM investigation of influence of freezing process on the surfach structure of potato starch granule. *Applied Surface Science*, 157, 382–386.
- Kulicke, W.-M., Eidam, D., Kath, F., Kix, M., & Kull, A. H. (1996). Hydrocolloids and rheology: Regulation of visco-elastic characterisits of waxy rice starch in mixtures with galactomannans. *Starch*, 48, 105–114.
- Lin, H.-N., Hung, T.-T., Chang, E.-C., & Chen, S.-A. (1999). Force modulation microscopy study of phase separation on blend polymer films. *Applied Physics Letters*, 19(74), 2785–2787.
- Lukasiewicz, M., Ptaszek, A., Koziel, L., Achremowicz, B., & Grzesik, M. (2007). Carboxymethylcellulose/polyaniline blends synthesis and properties. *Polymer Bulletin*, 58, 281–288.
- Mao, R., Tang, J., & Swanson, B. G. (2000). Relaxation time spectrum of hydrogels by CONTIN analysis. *Journal of Food Science*, 65(3), 374–381.
- Patino, J. M. R., Caro, A. L., Nino, M. R. R., Mackie, A. R., Gunning, A. P., & Morris, V. J. (2007). Some implications of nanoscience in food dispersion formulations containing phospholipids as emulsifiers. *Food Chemistry*, 102, 532–541.
- Phillips, G. O., & Williams, P. A. (2000). *Handbook of hydrocolloids*. Boca Raton: CRC Press.
- Ptaszek, P., & Grzesik, M. (2007). Viscoelastic properties of maize starch and guar gum gels. *Journal of Food Engineering*, 82, 227–237.
- Ptaszek, P., Lukasiewicz, M., Achremowicz, B., & Grzesik, M. (2007). Interaction of hydrocolloid networks with mono- and oligosaccharides. *Polymer Bulletin*, 58, 295–303.
- Rodrguez-Hernndez, A. I., Durand, S., Garnier, C., Tecante, A., & Doublier, J. L. (2006). Rheology-structure properties of waxy maize starch gellan mixtures. *Food Hydrocolloids*, 20, 1223–1230.
- Shi, X., & BeMiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers*, 50, 7–18.
- Tan, H., Tam, K. C., & Jenkins, R. D. (2000). Relaxation spectra and viscoelastic behavior of a model hydrophobically modified alkali-soluble emulsion (HASE) polymer in salt/SDS solutions. *Journal of Colloid and Interface Science*, 231, 52–58.
- Tester, R. F., Karkalas, J., & Qi, X. (2004). Starch composition, fine structure and architecture. *Journal of Cereal Science*, 39, 151–165.
- Tikhonov, A. N., Goncharsky, A. V., Stepanov, V. V., & Yagola, A. G. (1995). *Numerical methods for the solution of ill-posed problems*. Kluwer.
- Tschoegl, N. W. (1989). *The Phenomenological theory of linear viscoelastic behaviour*. Springer.
- Wang, Y., Song, R., Li, Y., & Shen, J. (2003). Understanding tapping-mode atomic force microscopy data on the surface of soft block copolymers. *Surface Science*, 530, 136–148.
- Weese, J. (1992). A reliable and fast method for solution of Fredholm integral equations of the first kind based on Tikhonov regularization. *Computer Physics Communications*, 69, 99–111.
- Weese, J., & Friedrich, Chr. (1994). Friedrich; relaxation time spectra in rheology: Calculation and examples. *Rheology*, 6, 69–76.
- Whistle, R. L., & Bemiller, J. N. (1994). *Starch: Chemistry and technology*. Academic Press.