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Interaction of hydrocolloid networks with mono- and oligosaccharides

Pawel Ptaszek (✉), Marcin Lukasiewicz, Bohdan Achremowicz, Miroslaw Grzesik

University of Agriculture, Department of Food Technology, 30-149 Krakow, ul.Balicka122, Poland
E-mail: ptaszekp@op.pl

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Summary

The presented research covers the investigation on the interaction of basic mono- (D-glucose, D-fructose) and a disaccharide (saccharose) with two of the most used hydrocolloids, i.e. guar gum and xanthan. As a basic model the 50 % water solution of an appropriate carbohydrate with 1 %wt. of a hydrocolloid was chosen. Viscoelastic measurements were carried out at different temperatures. The analysis covered the time-temperature superposition method and fitting the continuous Maxwell model to the experimental data.

Introduction

Carbohydrates of different plant origin have become one of the most investigated polymeric systems. The phenomenon occurs mainly due to a broad spectrum of different physicochemical properties as well as its biodegradability, one of the most important technical factors nowadays. Food industry uses many carbohydrates including monosaccharides (glucose), oligosaccharides (maltose, cyclodextrins) and polymeric carbohydrates (cellulose, starch). There is also a quite big group of compounds – hydrocolloids, which often serve as food additives to create or keep the structure of final products [1].

The name hydrocolloids refers to a wide range of proteins and in particular polysaccharides which play an important role as thickeners and gelling agents in aqueous solution. They are also very useful as foam, emulsion and dispersion stabilizers, crystallization inhibitors for ice and low-molecular-weight carbohydrates, flavours realising agents, active substances and in many other fields. Even though hydrocolloids are present in a food systems only at a level of ca. 1 %wt. they have a significant influence on its textural and organoleptic properties.

One of the most common applications of hydrocolloids is thickening of food products, so the clear understanding of their rheological behaviour has main gained a growing

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Presented at 44th P.M.M. Microsymposium “Polymer Gels and Networks”, Prague, 10–14 July 2005 interest. The rheological researches are divided into two groups depending on the solution concentration. In a dilute solution macromolecules are relatively free to move independently without significant interactions. In more concentrated systems molecule crowding gives rise to the overlap of polymer coils and strong penetration could occur.

A great number of hydrocolloid solutions behave as viscoelastic, so they can be characterised by the magnitude and frequency dependence of the storage and loss moduli (G' and G''). Both factors are strongly frequency-dependent. G' is proportional to ω^2 and G'' to ω. For dilute systems where macromolecules can freely move in solution, G'' is greater than G' [2]. The situation changes in more concentrated solutions or in cases when intermolecular entanglement can occur.

Most hydrocolloids form so called physical gels originating by physical interactions, for example hydrogen bonding, hydrophobic interactions, ionotropic interactions. This is one of the most characteristic differences between hydrocolloid and synthetic polymer systems.

Because of a very complex composition of food there is also a growing interest in the investigation of its rheological properties in both technological and scientific meaning. Mono- and oligosaccharides are one the most common food ingredients so their interaction with hydrocolloids seems to be a very important factor. This made us conduct the investigation.

Out of large group of hydrocolloids, two examples were taken. We have chosen guar gum and xanthan because of their applications and interesting physicochemical properties.

The production of guar gum is based on its extraction from the leguminous shrub *Cyamopsis tetragonoloba* which utilize them as a food and/or water store. Chemically, compound guar is a galactomannan with (1,4)-linked β-D-mannopyranose backbone with branchpoints at positions 6 linked to α-D-galactose (*i.e.* 1,6-linked-α-D-galactopyranose). It is known that for every galactose unit there is 1,5 to 2 mannose residues [1].

The properties of guar gum strongly depend on the degree of substitution of galactose. Higher mannose amounts increase the stiffness of the polymer but, on the other hand, reduces the extensibility and the radius of gyration for every isolated chain. The galactose residues prevent chain interactions. If the galactose residues were perfectly randomized, it would hardly give molecules with more than one area capable of acting as a junction, thus disallowing gel formation. A block substitution pattern, for which some experimental evidence exists, would allow junction formation if the blocks were of sufficient length.

The second chosen hydrocolloid is xanthan gum which is a biopolymer produced by microorganism *Xanthomonas campestris* in an aerobic submerged fermentation process. Chemical composition of xanthan can be interpreted as a cellulose backbone (i.e. glucose units linked with β-1,4 glycoside bond) with branching at carbon-3 atoms. The branches contain D-mannopyranose-(2,1)-β-D-glucuronic acid-(4,1)-β-D-mannopyranose. Additionally, less than 40 % of terminal mannose units appears as 4,6-pyruvated and the inner mannose units are acetylated at carbon 6 atom. The branching is not regular and some of the branches could be missing. According to the rheological investigation it could be pointed out that xanthan solutions are highly pseudoplastic. It seems to be a result of the ability of xanthan macromolecules making aggregates. The phenomenon occurs due to hydrogen bonding or polymer entanglement. The viscosity of xanthan solutions is also salt-, pH- and temperature-dependent. One of the known xanthan properties is also the interaction with galactomannans, which leads to the enhanced viscosity and gelation [1].

Experimental

Sample preparation

The research covers the rheological experiments with concentrated (50 %wt.) D-glucose, D-fructose or saccharose solutions with 1 %wt. of guar gum or xanthan (commercial grade). Solutions for viscoelasticity measurements of guar gum-saccharide-water systems were prepared in a water bath at room temperature by dissolving a 50 g of desired carbohydrate in water to give 100 g of final solution. In the experiment with a solution of both glucose and fructose 25 g of each sugar was used. To the each solution of low-molecular-weight carbohydrate 1.01 g of a hydrocolloid was added and the mixtures were homogenized by vigorous stirring for ca. 2 h.

Rheological measurements

Rheological measurements were performed using a RS-150 rheometer (Haake, Germany), in a coaxial cylinder sensor system in a temperature range of 0 °C – 40 °C. The range of linear viscoelasticity was estimated in a frequency domain as reported earlier, by changing the amplitude of deformation at constant frequency and observing changes in the absolute value of complex relaxation modulus. The amplitude was set to 0.01 at 40 °C. Changes of complex modulus were registered as the function of frequency 0.01-10 Hz and temperature and master curve were estimated [3]. Complex continuous Maxwell model (**1**) was fitted to the experimental data [4], [5]. Calculations were carried out using Tikhonov regularization method [6].

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

Gel permeation chromatography analysis

Molecular weight, polydispersity and molecular weight distribution were determined by gel permeation chromatography (GPC). The following system was used: two columns were connected in a series and filled with Sephacryl gels (Pharmacia, Sweden): S-200, 380 mm; S-500, 460 mm. The internal diameter of all columns was 16 mm. As eluent an Na_2CO_3 solution (0.003 mol/L) was used, with the flow rate 0.128 ml/min. A hydrocolloid (10 mg) was dissolved in 5 mL of the eluent at room temperature within 24 hours. The sample volume was 1 mL. Knauer K-2300 refractometer was used as detector. All analyses were performed at 20 ºC. Standard calibration was performed using pullulans provided by Shodex.

Results and Discussion

Rheological properties of polymer solutions strongly depend on molecular weight of the compound and its distribution. GPC of hydrocolloids was performed depending on their MW. As we have used commercial-grade compounds, the polydispersity was relatively high (Table 1). Comparing the weight-average molecular weight of the investigated system we can confirm higher value for xanthan gum. On the other hand, the number-average molecular weight of this polymer is slightly lower than those observed for guar gum.

Table 1. Molecular weight and polydispersity of investigated biopolymers.

	Guar gum	Xanthan
M_w [g/mol]	$7.47 \cdot 10^5$	$19.6 \cdot 10^5$
M_n [g/mol]	$3.21 \cdot 10^4$	$0.22 \cdot 10^4$
Pd	23	871

Figure 1 shows the molecular weight distributions of guar gum and xanthan. Both of them show one multimodal broad peak. In the case of guar the peak is bimodal and for xanthan three maxima could be detected. Discussing the phenomenon we can point out that there is no dominant single fraction present in the sample; however it is possible to isolate the fraction with higher concentration. The broad-distribution of molecular weight is the result of manufacture technology of hydrocolloids.

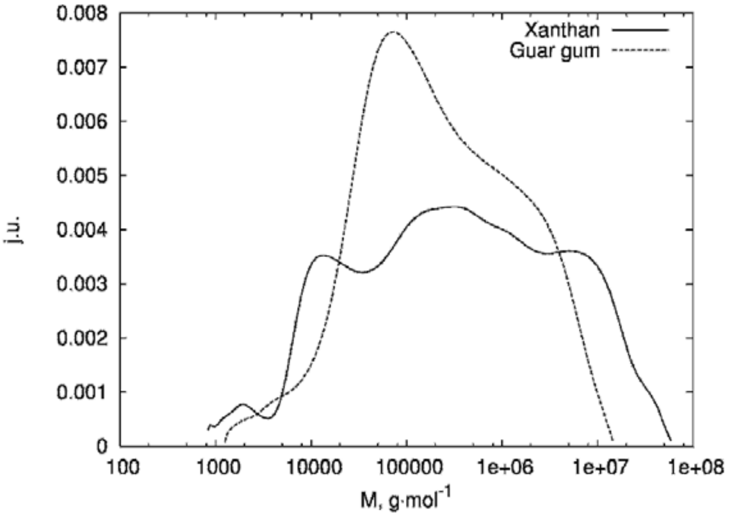

Figure 1. Molecular weight distribution of investigated hydrocolloids.

Figure 2 presents a cumulative curve for 1 %wt. water solution of guar gum and the corresponding relaxation spectra *H(λ)*. The viscoelastic behavior of the described system is characteristic of the network containing from the entanglements of single macromolecules. Such phenomenon is easily proved by intersection of *G'* and *G"* plots. The relaxation spectrum consists of three separate peaks but for the discussed phenomenon only the times with the greatest intensity are responsible. The presence of one distinct big peak and other smaller ones gives the information about the uniform structure of the system. Additionally, it is worth pointing out that the system is a viscoelastic liquid, which is confirmed by the lack of G_e parameter.

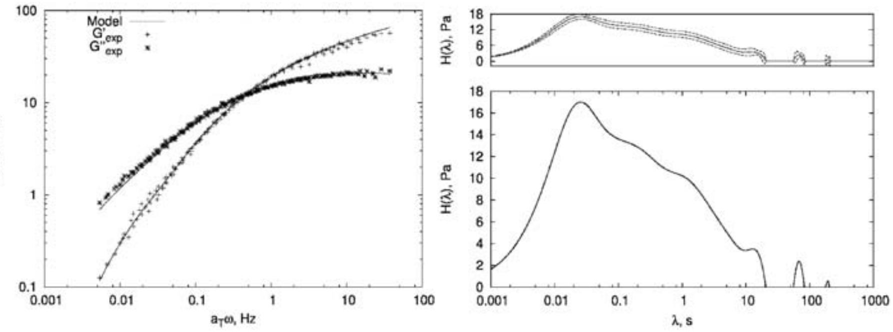

Figure 2. Master curve (left) and stress relaxation spectra (right) for guar-water system.

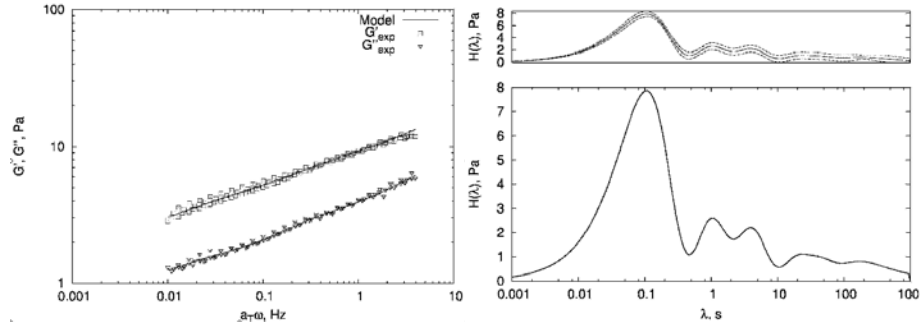

Figure 3. Master curve (left) and stress relaxation spectra (right) for xanthan-water system $G_e = 1.54 \pm 0.04$ Pa.

On the other hand, the xanthan solution is a typical crosslinked system demonstrating the solid-state character (estimated G_e parameter 1.54 ± 0.04 Pa). The corresponding dependences are presented in Figure 3. In this case the relaxation spectra consist of one multimodal peak which covers the whole frequency window.

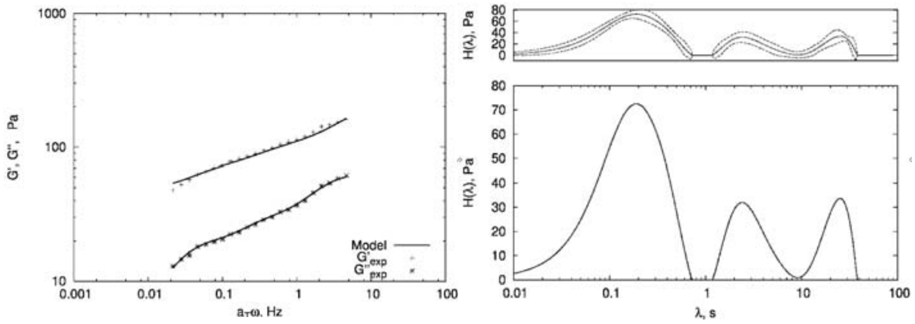

Figure 4. Master curve (left) and stress relaxation spectra (right) for guar-glucose-water system.

Figure 4 and 5 present the results for the system with glucose as a monosaccharide. Cumulative curves show the plateau zone and the relaxation spectra consist of many small peaks, which leads to the conclusion about heterogeneity of the described systems [7].

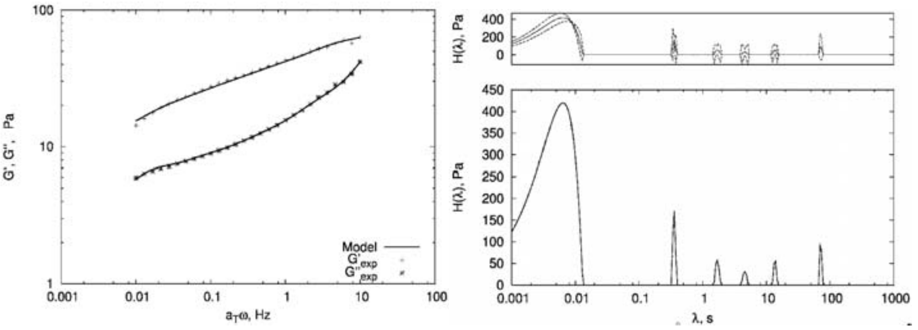

Figure 5. Master curve (left) and stress relaxation spectra (right) for xanthan-glucose-water system $G_e = 12.17 \pm 0.18$ Pa.

Fructose based systems (Figures 6 and 7) are different from those with glucose by due to their viscoelastic character. The fructose-guar pattern can be classified as transitional zone between a plateau and rubber-like material. In the case of fructose-xanthan system we can state that it definitely belongs to the plateau region. In both cases the relaxation spectra give the information about good homogeneity of investigated mixtures. On the basis of the spectra we can assume that in the presence of fructose both hydrocolloids are the main factors causing viscoelastic properties.

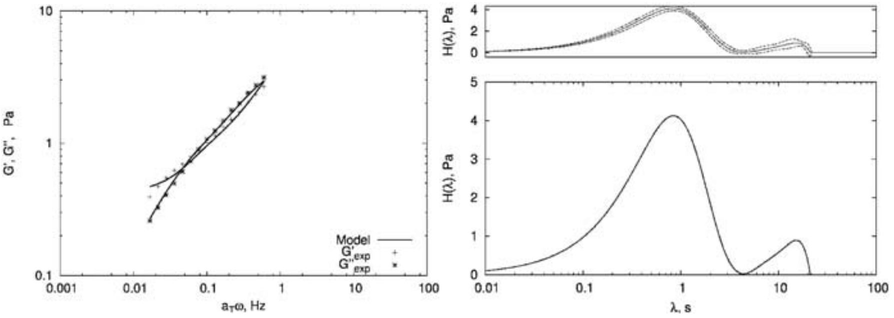

Figure 6. Master curve (left) and stress relaxation spectra (right) for guar-fructose-water system.

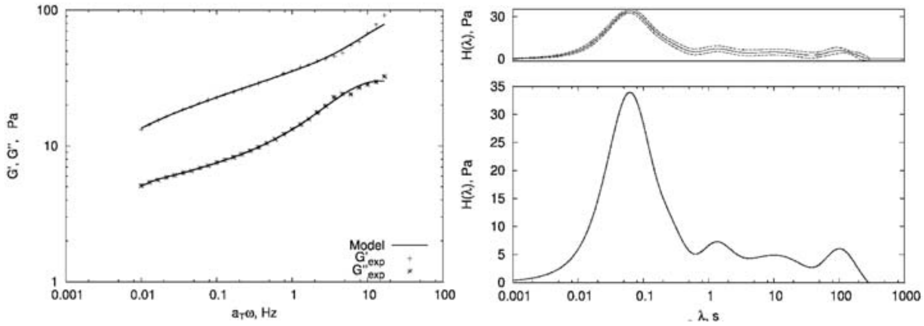

Figure 7. Master curve (left) and stress relaxation spectra (right) for xanthan-fructose-water system $G_e = 9.56 \pm 0.60$ Pa.

Figures 8 and 9 show the corresponding master curves and spectra for the system in which the single monosaccharide was exchanged for the 1:1 mixture of glucose and fructose. The analogy in shape to the results obtained for water solutions of hydrocolloids without low-molecular-weight sugars can be seen.

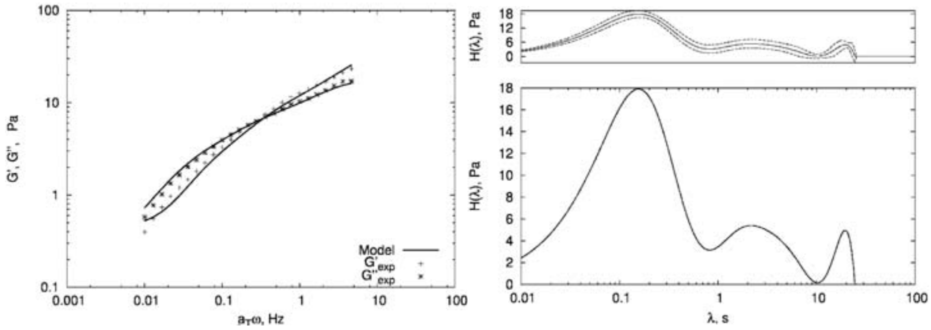

Figure 8. Master curve (left) and stress relaxation spectra (right) for guar-(glucose-fructose)-water system.

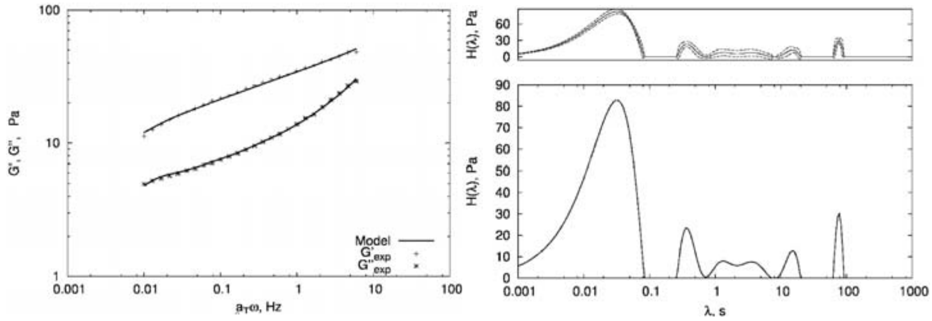

Figure 9. Master curve (left) and stress relaxation spectra (right) for xanthan-(glucose-fructose)-water system $G_e = 9.00 \pm 0.11$ Pa.

A relaxation spectrum for the guar gum system confirms in this case the homogeneous structure in contrast to heterogeneity in the material based on xanthan [7].
The exchange of the glucose - fructose mixture for saccharide leads to further unification of the structure, which can be observed in relaxation spectra (Figures 10 and 11). However, the spectra differ in the number of peaks; we have detected a single peak for guar solution and two separate bands in the case of xanthan.

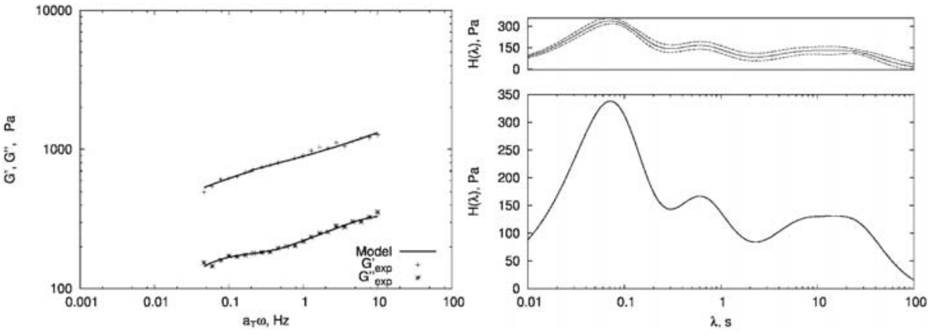

Figure 10. Master curve (left) and stress relaxation spectra (right) for guar-saccharose-water system G_e = 413.00 ±18.00 Pa.

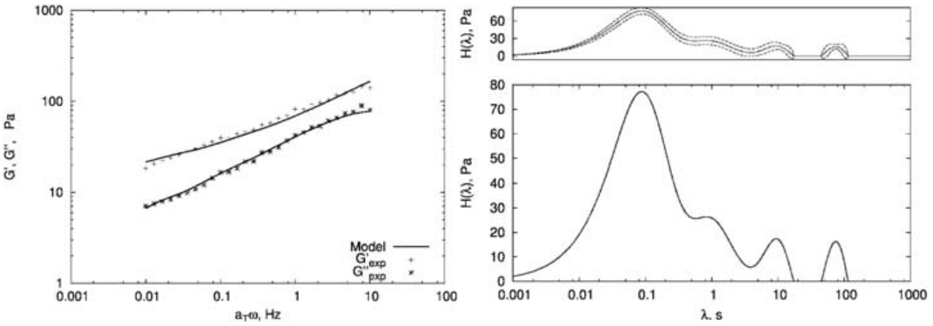

Figure 11. Master curve (left) and stress relaxation spectra (right) for xanthan-saccharose-water system G_e = 17.68 ±0.89 Pa.

Conclusions

The presence of low-molecular-weight carbohydrates has a great influence on viscoelastic behavior of some hydrocolloid solutions. In guar gum systems which contain free glucose, fructose or saccharose an increase in the intensity of relaxation spectra was detected. For the fructose-guar system we have observed that the value of $H(\lambda)$ is falling down. On the other hand, all xanthan-based systems show a higher intensity of relaxation spectra. We do not claim any changes in the state of matter in this situation. The system remains solid-like, independently of the carbohydrate added. Such phenomenon is corroborated by the parameter G_e in the Maxwell model. The change of the state of matter was observed only for the guar-saccharose-water system, which is also proved by the G_e factor.

The complex systems consisting of hydrocolloids and low-molecular-weight saccharides vary in their rheological properties according to the type of the saccharide. The obtained results could be very important for understanding food systems and might by useful for optimization of many food technologies.

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