Linear viscoelastic retardation phenomena in selected polysaccharides systems
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Abstract

The aim of present study was to determine the viscoelastic properties of the model mixtures of the selected pasted polysaccharides. The initial material was maize starch (SK), mixed with guar gum (GG). Rheological tests were performed in time domain. Theoretical analysis covered adaptation of some achievements of phenomenological theory of viscoelasticity, which were applied during interpretation of results obtained for mentioned above mixtures of biopolymers. The emphasis was placed on description of retardation behaviours with the aim of continuous rheological Burger's model.

Keywords: viscoelasticity, polysaccharides, regularization, continues Burger's model

1. Introduction

Polysaccharides are main constituent of human's food. They are used also as food texturing agents and to grant food with proper resistance. Polysaccharides, due to their biodegrability and renewability found wide applications in pharmaceutical, ceramic, and textile industries, and also in biotechnology. Discussed compounds are characterized by very complicated structure, and exhibit many interesting, from practical point of view, rheological phenomena. Complex hydrodynamic behavior of polysaccharides and their solutions allows to apply them as pilot testing materials in emerging technologies. It seems to be reasonable to undertake researches dealing with viscoelastic phenomena of water based solutions of polysaccharides. It gives unequivocal opportunity to characterize investigated material in linear area, and also it is start point to model phenomena connected with non-linear viscoelasticity and thixotropy.
The aim of present study was to determine the viscoelastic properties of the model mixtures of the selected pasted polysaccharides. The initial material was corn starch (SK), mixed with guar gum (GG).

2. Material and methods

Starch is plant storage material, which is composed of two alpha glucans: essentially linear amylose, and branched amylopectin. The linear amylose (chain length 500 to

6000 glucose units) has a small degree of branching but it is predominantly regarded as a single chain. The chain of amylopectin contains only up to 30 glucose units. Regular corn starch (SK) produced by National Starch was used in this research. The production of guar gum bases on its extraction from the leguminous shrub *Cyamopsis tetragonoloba*. By means of chemical compound guar is a galactomannan with (1-4)-linked β-D-mannopyranose backbone with branch points from their 6-positions linked to α-D-galactose. Guar gum (GG) was supplied by Regis (Poland).

Rheological measurements were performed using rotary rheometer RS-150 (Haake, Germany) equipped with coaxial cylinder system. Temperature was controlled by ultratermostat F9 (Haake, Germany) with 0.1˚C accuracy. The principle of rheological measurements was to search for linear viscoelastic area by step function, and finally to create creeping curves. This investigation relied on conducting few deformation measurements in time function for different stress τ_o values. Next, the function of susceptibility for creeping was calculated according to following formula: $J(t) = \frac{\gamma(t)}{\tau_o}$ and if obtained curves matched each other that indicated on linear viscoelasticity of the system. Obtained in such way curves, also known as creeping susceptibility curves, were used for further analysis. The measurements were executed in the following manner: starch paste or hydrocolloid solution (95^{o}C), prepared in water bath (95^{o}C±1^{o}C) and mixed for 30 min., was placed in measuring cylinder previously heated to 95^{o}C. Next sensor was cooled down to desired temperature during one hour, and was kept at this temperature for the next 30 minutes. Next measurement was performed.

One of the relationships describing retardation phenomenon is continuous Burger model, which can be described as:

$$J(t) = \underbrace{J_g + \frac{1}{\eta}\cdot t}_{\text{Maxwell's element}} + \underbrace{\int_0^{\infty} L(\lambda)\left[1-\exp\left(-\frac{t}{\lambda}\right)\right]d\lambda}_{\text{Kelvin–Voigt's element}} \qquad (1)$$

To estimate function L(λ) and other parameters, regularization method of Tikhonov was used.

The most often used idea in determining of estimators of mathematic models parameters is minimization of square sum of difference between observed value and calculated value based on model. There are many modifications of this method, one of them is called regularization method. It is applied, when analysed problem belongs to group of so called *"ill-posed"*. Such problems are very sensitive to data fluctuation. Even small such event may lead to results diametrically opposed to original data. Such disturbances have no influence on solution of well posed problems. Basing on least square method and regularization idea proposed by Tikhonov the following aim function was obtained:

$$V(\alpha) = \sum_{i=1}^{n} \frac{1}{\sigma_i^2}\left(J_i^{\sigma} - J_i\right)^2 + \alpha\left\|D\,L(\lambda)\right\|^2 \rightarrow \min_{L(\lambda)\geq 0,\, J_g \geq 0,\, \frac{1}{\eta}\geq 0} \qquad (2)$$

where:

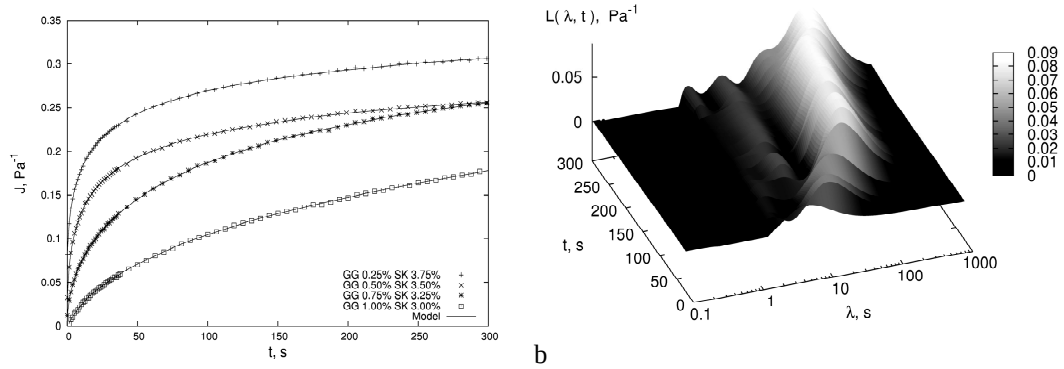
$$J_i = J_g + \frac{1}{\eta}\cdot t_i + \int_0^{+\infty} L(\lambda)\cdot\left[1-\exp\left(-\frac{t_i}{\lambda}\right)\right]d\lambda$$

where function beneath integral $1-\exp\left(-\frac{t_i}{\lambda}\right)$ is called the kernel of equation and function $L(\lambda)$ and $J_g, \frac{1}{\eta}$ coefficients are unknown. In such cases, it really very rare that $L(\lambda)$ function is described by precise analytical equation. Therefore, there is a necessity to look for estimators of this function in the form of set of its values, or to approximate it by proper polynomial. In such case, when values of function should belong to specified interval, the whole problem should be additionally linked to inequalities restrictions. Most often applied restrictions result from interpretation of solution, and they place condition on value of $L(\lambda)\geq 0$ function.

First part of equation (2) results from least square method, and is responsible for error minimization, whereas second one is called stabilizer or regularizer, and its role is to provide the proper shape of the searched function. Parameter α is called regularization coefficient and its value is responsible for "smoothness" of the solution, while *D* is a proper differential operator. Such placing of problem is justified, because selecting, both model and its parameters, one should be guided by rules of moderation and savings, and also to have in mind, that solution have to have physical interpretation. The goal is to produce "smooth" function curve, with as low as possible numbers of extremes. It is particularly important in when particles diameter distribution or molecular masses are searched by means of regularization method. For α=0 problem converts to typical least square problem. There is a still open question with selection of the proper value of a parameter. Several methods for the proper groups of physicochemical problems have been developed basing on differential calculus and mathematical statistics. Basing on regularization method set of numerical procedures was created, allowing to estimate retardation spectra $L(\lambda)$ of viscoelastic materials. Moreover there was possibility to calculate error of estimation.

3. Results

Creeping curves for guar gum–corn starch mixture were presented in Figure 1a. Increasing share of guar gum (GG) was causing decrease of creeping compliance (*J*) value. Basing on susceptibility towards creeping in function of time, the retardation spectra $L(\lambda, t)$ were calculated and presented in Figure 1b. Two distinctive peaks could be observed. Peak observed at range of longer time was characterized by higher intensity. For system containing GG (0.50% wt.) and corn starch (3.50% wt.) (Fig. 1b), entire phenomenon was generated from peak consisting of two maximums. With the passing time maximum located in the third decade was separated into two maximums, and next the new one was emerging from them. This confirmed observation about complex nature of the structure.



a b

Figure 1: a. Creeping curves for mixtures maze starch with guar gum (GG) addition. b. Evolution of retardation spectra for mixtures maze starch with guar gum addition.

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