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INFLUENCE OF TEMPERATURE AND POLYMER CONCENTRATION ON RHEOLOGICAL PROPERTIES OF RHAMSAN

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Abstract. Microbial polysaccharide rhamsan imparts high solution viscosity at very low polysaccharide concentration and forms weak gels. The rheological behaviour, in particular the viscoelastic properties of aqueous rhamsan systems were investigated by using controlled stress rheometer HAAKE RS150, equipped with two sensor systems: cone-plate and double cone. The effects of temperature and polymer concentration on the rheological properties of rhamsan systems were examined under steady shear and oscillatory conditions. Variation in polymer concentration and environmental conditions results in changes of the consistency and the elastic response, which is very important for practical use. The viscoelastic data were described by applying the generalized Maxwell model.

Introduction

Microbial polysaccharides obtained from microbial fermentations can be produced under controlled conditions so that problems of property variations can be avoided [1]. They also present high structural regularity and offer a wide spectrum of rheological characteristics and potentially useful biological, chemical and physical properties. Biopolymers are widely employed in medicine, in agricultural, food, paint, ceramics, cosmetics, pharmaceutical, and textile industry, and for many others applications. They are used commercially as thickeners, film formers, gelling agents, suspending agents, stabilizers, flocculants, binders, lubricants, friction reducers, and as matrices [2].

Rhamsan gum is an anionic extracellular microbial polysaccharide produced by a strain of bacteria Alcaligenes spp. ATCC 31961 under aerobic fermentation conditions. Rhamsan greatly enhances the viscosity of aqueous media, leading with increasing polymer concentration to thermally stable systems with peculiar rheological properties [3]. Even at low polymer concentrations sol-gel transition can be attained.

We studied the rheological behaviour of aqueous rhamsan systems at different concentrations of polymer and examined the influence of temperature on the rheological properties of the investigated systems.

Experimental

Material: Rhamsan (R) produced by Monsanto company was dissolved in distilled water at polymer concentrations in the range of 0.1 - 1.0 wt.%. The measurements were carried out at three different temperatures in the range of 8°C - 45°C.

Instrument: The rheological behaviour of aqueous rhamsan systems was investigated by using the rotational controlled stress rheometer HAAKE RS150, equipped with cone and plate (6 cm, 2°) and double cone (6 cm, 4°) sensor systems.

Temperature was controlled by circulator HAAKE DC5-K20.

Procedure: Prepared rhamsan systems were investigated under continuous and oscillatory shear conditions.

Under destructive shear conditions the flow curves were determined from the shear stress ramps in the stress range of 0.03 Pa - 20 Pa, depending on the polymer concentration. Each sample was left at rest for 10 minutes before the shear stress ramp was carried out in order to ensure the same starting conditions for all the systems examined. After that, the stepwise procedure with sequential changes of shear stress was applied to examine the flow behaviour under equilibrium shear conditions.

The stress sweep tests at a frequency of 1 Hz were carried out in order to determine the range of linear viscoelastic response (the stress range of 0.005 Pa - 17 Pa, depending on the polymer concentration) under oscillatory shear conditions. The frequency sweep measurements under conditions of linear viscoelastic response were performed at a constant stress or constant strain amplitude in the range of 0.02 Hz - 10 Hz.

Analysis of viscoelastic data: The mechanical spectra obtained from the frequency sweep measurements were described by the generalized Maxwell model.

The relaxation spectra were derived on the basis of viscoelastic data analysis.

Results and discussion

Continuous shear conditions

The investigated aqueous rhamsan systems exhibit detectable reversible time dependent behaviour of thixotropic type. The appearance of Newtonian plateau in the low shear stress (or shear rate) range is observed for all samples (Fig. 1).

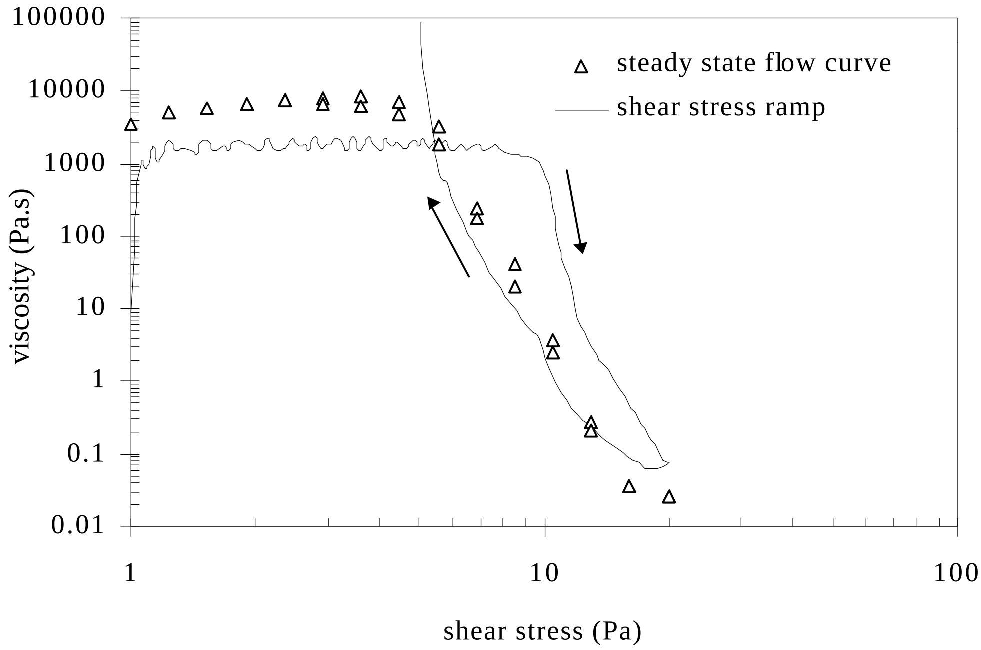

Figure 1. The comparison of the experimental data obtained from the steady shear flow and the shear stress ramp: 1 wt.% of rhamsan in distilled water at 25°C.

In the range of higher shear stresses the viscosity values obtained by using the stepwise procedure are comparable with the viscosity values arising from down curves of the shear stress ramps, whereas in the low shear stress range the down curves exhibit an asymptotic increase of viscosity, characteristic for plastic behaviour.

The shear dependent behaviour of the examined systems is strongly influenced by polymer concentration (Fig. 2). The most significant difference in the flow curves appears between the samples with 0.1 and 0.3 wt.% of rhamsan in distilled water.

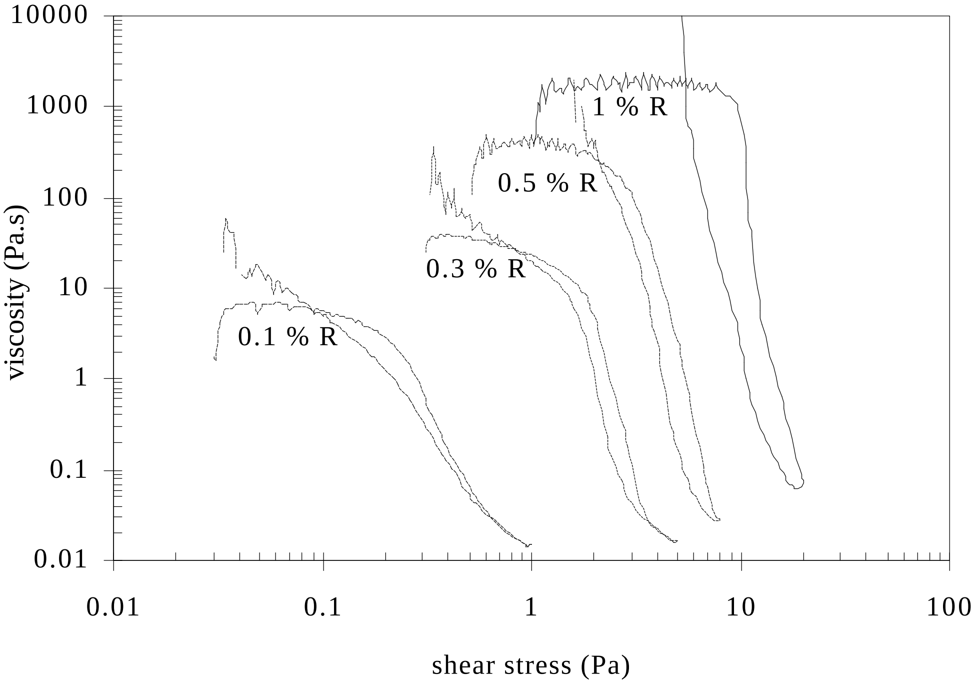

Figure 2. The effect of polymer concentration on the viscosity profiles at 25°C.

In the temperature range examined, the rheological properties of the samples prepared in distilled water are not influenced by the temperature (Fig. 3).

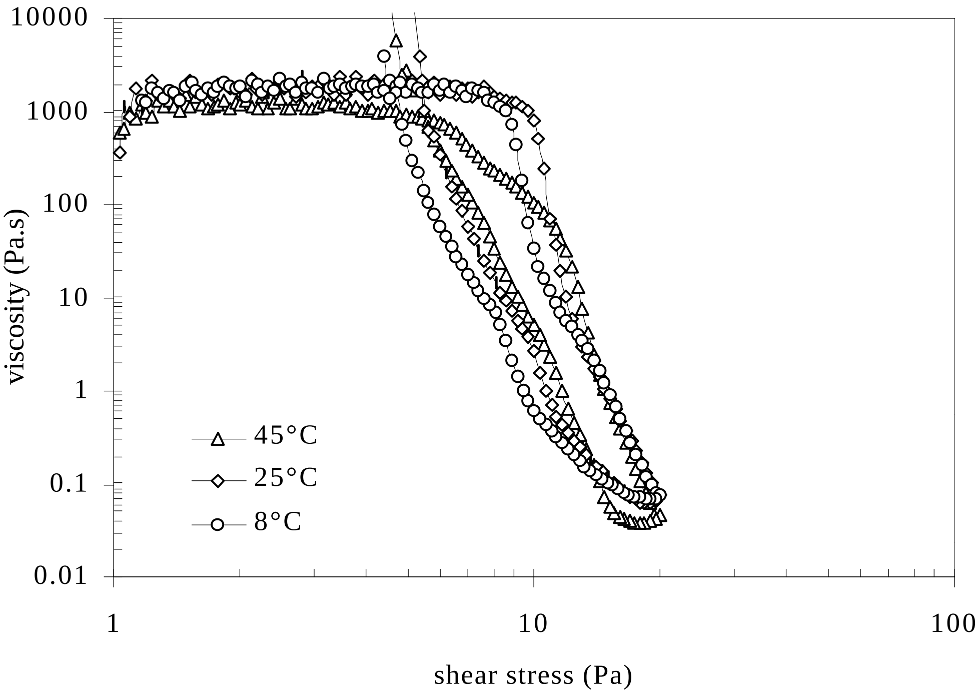

Figure 3. The effect of temperature on the viscosity profiles: 1 wt.% of rhamsan.

Detective difference is observed only for the samples of 0.1 wt.% of rhamsan in distilled water (Fig. 4).

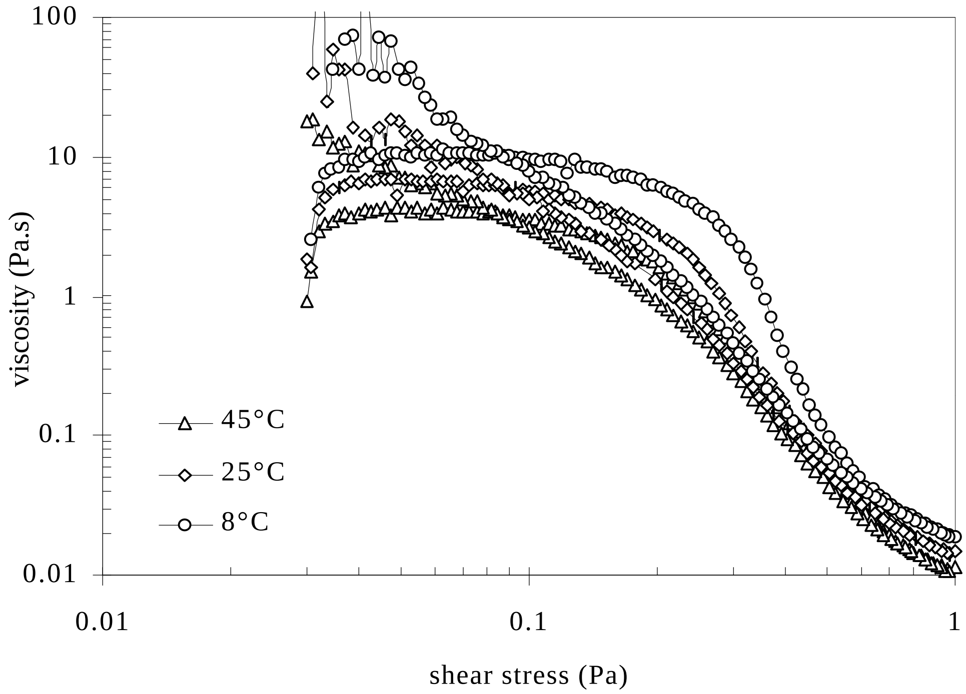

Figure 4. The effect of temperature on the viscosity profiles: 0.1 wt.% of rhamsan.

Oscillatory shear conditions

Under oscillatory shear conditions, stress sweep tests and frequency sweep experiments were performed in order to study the viscoelastic behaviour of the examined systems. All observations resulting from the continuous shear tests are confirmed with the results of oscillatory measurements.

The results of the stress sweep tests show an increase of the loss modulus, G', followed by a sharp decrease when the system passes from linear to non-linear viscoelastic regime (Fig. 5). The storage modulus, G', starts to decrease continuously at slightly higher stresses or strain amplitudes than those where the loss modulus starts to change. When polymer concentration increases, such overshoot of the loss modulus becomes more pronounced.

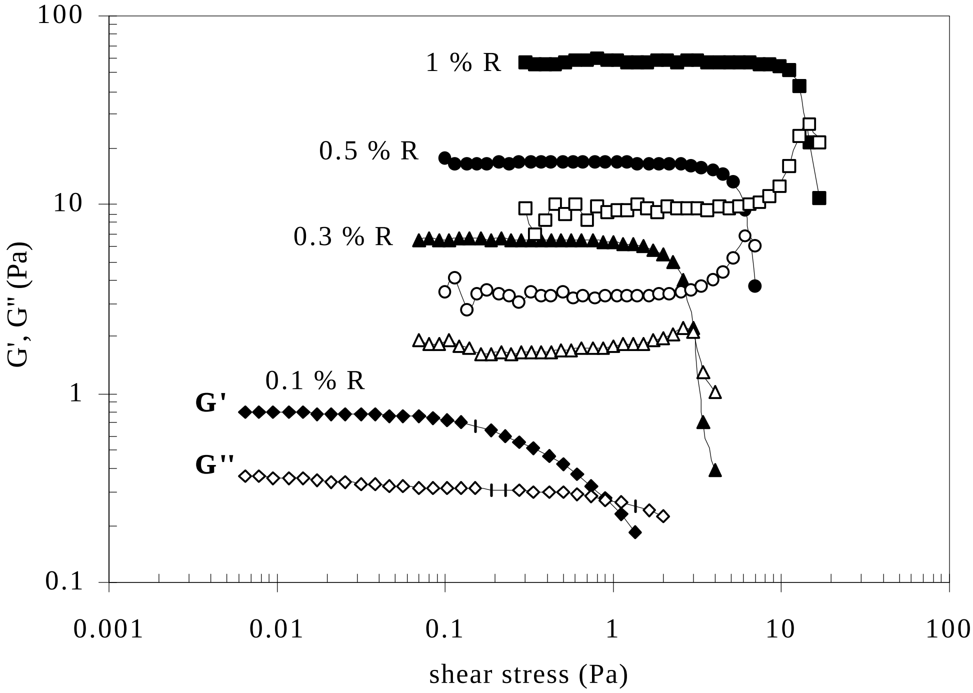

Figure 5. The effect of polymer concentration on dynamic functions G' and G'' obtained from the stress sweep tests at a frequency of 1 Hz and temperature of 25°C.

The critical strain characterizing the limit of the linear viscoelastic regime is around 10 % and is not strongly dependent on the polymer concentration (Fig. 6).

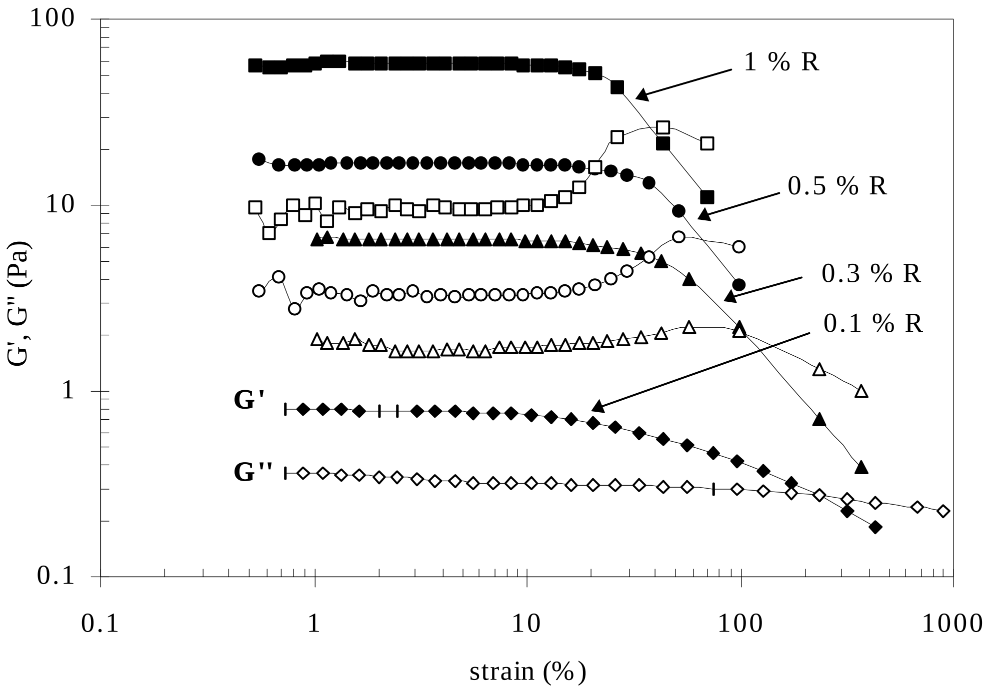

Figure 6. The effect of polymer concentration on G', G'', and the critical strain obtained from the stress sweep tests at a frequency of 1 Hz and temperature of 25°C.

The examination of temperature influence on dynamic functions shows that only at the lowest polymer concentration G’ slightly decreases with increasing temperature, but G’’ remains the same (Fig. 7 and Fig. 8).

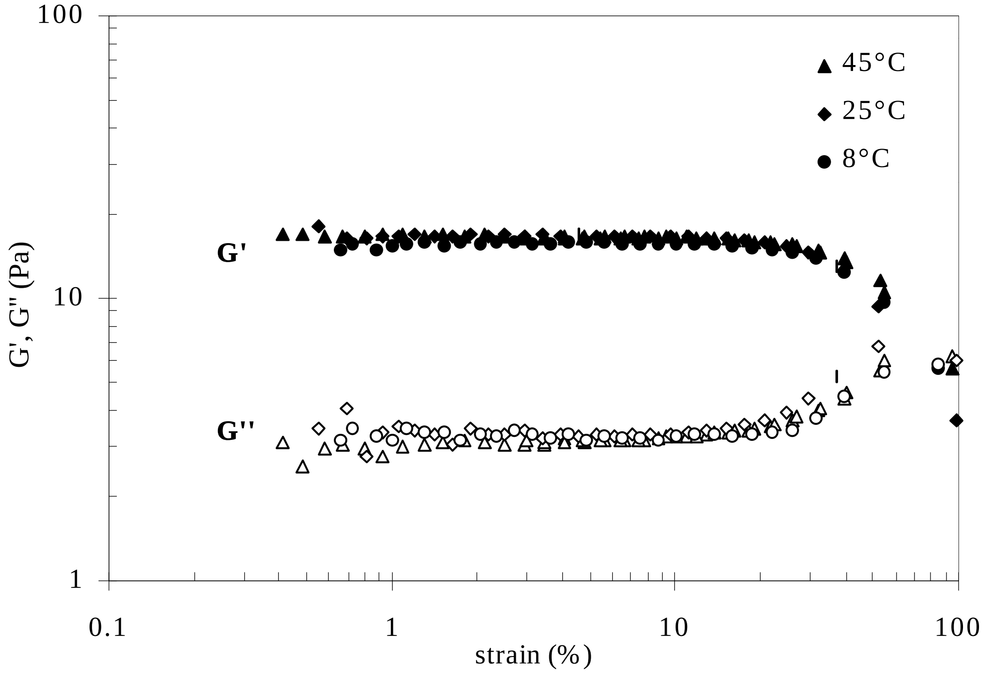

Figure 7. The effect of temperature on dynamic functions G’ and G’’ obtained from the stress sweep tests at a frequency of 1 Hz: 0.5 wt.% of rhamsan in distilled water.

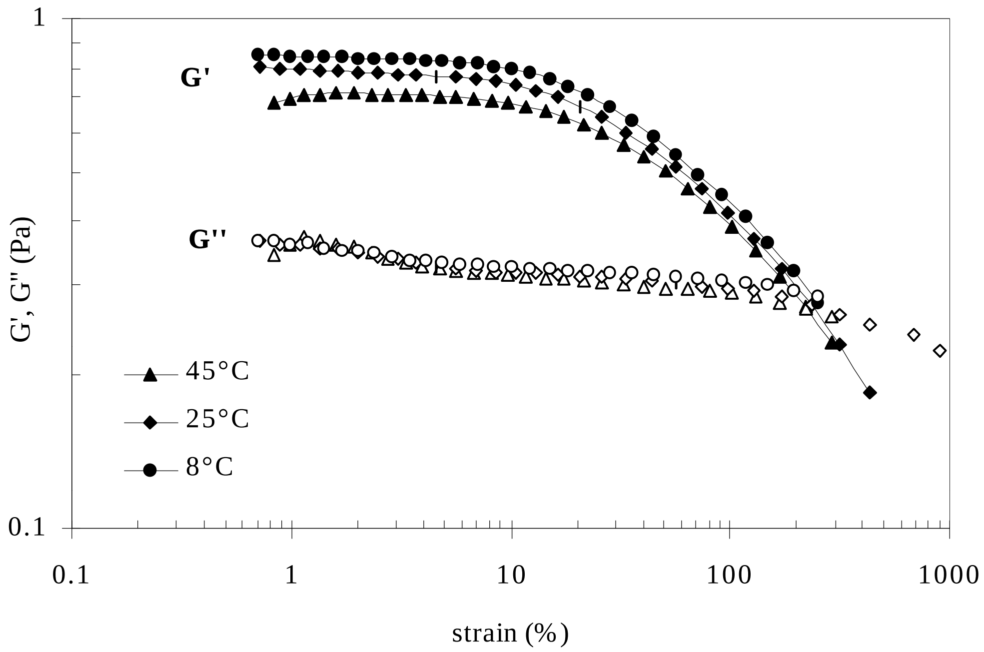

Figure 8. The effect of temperature on dynamic functions G’ and G’’ obtained from the stress sweep tests at a frequency of 1 Hz: 0.1 wt.% of rhamsan in distilled water.

In the frequency range examined, the elastic component is predominant for all samples. With increasing rhamsan concentration both dynamic functions becomes less sensitive to the applied frequency (Fig. 9). Such viscoelastic behaviour is usually found for structured systems and weak gels.

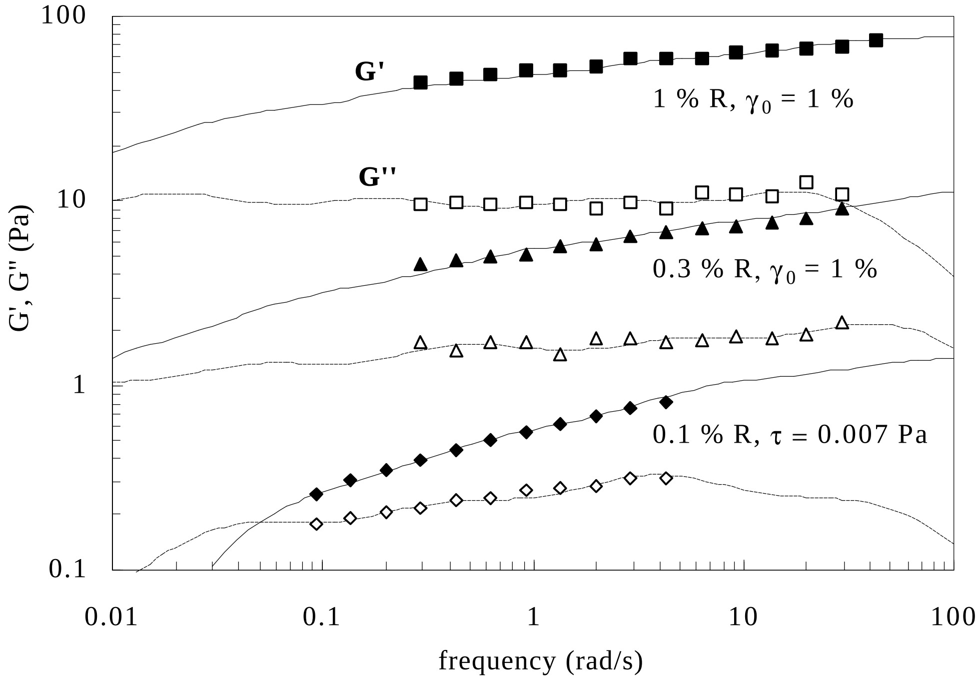

Figure 9. The comparison of experimental data from frequency sweep tests at 25°C with calculated values (curves) by using the generalized Maxwell model.

On the basis of viscoelastic data analysis by the generalized Maxwell model [1]:

$$G'(w) = \sum \frac{g_i \cdot l_i^2 \cdot w^2}{\left(1 + l_i^2 \cdot w^2\right)},$$

$$G''(w) = \sum \frac{g_i \cdot l_i \cdot w}{\left(1 + l_i^2 \cdot w^2\right)},$$

where ω is frequency, λ_i is the relaxation time of the i^{th} Maxwell element and g_i is the elastic modulus, the discrete relaxation time spectra are derived.

The comparison of the oscillatory and the continuous shear behaviour (Fig. 10) shows a failure of the Cox-Merz rule [1]. The empirical Cox-Merz rule states that the magnitudes of the complex viscosity η^* and the steady shear viscosity η must be equal at equal values of frequency and shear rate. Parallel dependencies of viscosity on shear rate and complex viscosity on frequency are obtained, with the values of complex viscosity higher than the viscosity values from continuous shear ramps. The rheological properties of the investigated systems differ from those of the polymer solutions and are more similar to those of the structured systems. Therefore the structural conditions of these systems can be described as a dispersion of gel micro domains in the polymer solution matrix.

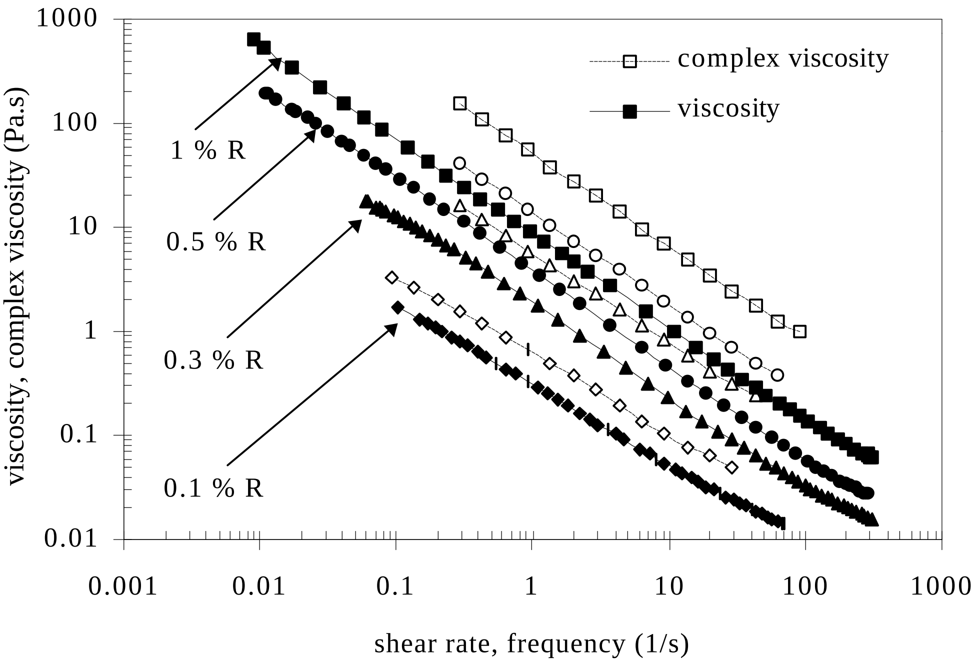

Figure 10. The comparison of the oscillatory and the continuous shear behaviour for samples with different polymer concentration at 25°C.

Conclusions

All investigated samples exhibit detectable reversible time-dependent behaviour of thixotropic type. The examined aqueous rhamsan systems are almost insensitive to temperature in the range of 8°C - 45°C. The most significant changes in the rheological behaviour appear between the samples with 0.1 and 0.3 wt.% of rhamsan. The storage modulus exceeds the loss modulus in the whole frequency range examined.

From the rheological characterisation it can be concluded that the investigated aqueous rhamsan systems behave as structured systems where gel micro domains are dispersed in the polymer solution matrix. Such weak gel matrices can be used for preparation of a highly concentrated stable suspension containing well dispersed solid particles, e.g. in ceramic processing.

References

[1] R. Lapasin, S. Pricl, *Rheology of Industrial Polysaccharides: Theory and Applications*; Blackie Academic&Professional, An Imprint of Chapman&Hall, Glasgow, 1995.
[2] P. A. Sandford et al., *Pure & Appl. Chem.* **1984**, 56(7), 879-892.
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Povzetek. Ramzan je biopolimer, ki ga proizvaja bakterija Alcaligenes spp. ATCC 31961. Po kemijski zgradbi spada med polisaharide. Že nizke koncentracije biopolimera zadošèajo, da viskoznost raztopin moèno naraste in nastanejo šibki geli. Reološko obnašanje v vodi raztopljenega ramzana smo prouèevali z rotacijskim reometrom z nastavljivo strižno napetostjo HAAKE RS150, pri èemer smo uporabili senzorska sistema stožec-plošèa ter dvojni stožec. Vpliv temperature in koncentracije biopolimera na reološke lastnosti prouèevanih sistemov smo raziskovali pri stacionarnih in dinamiènih strižnih pogojih. Viskoelastièno obnašanje vzorcev smo opisali s splošnim Maxwellovim modelom.