

VISCOELASTIC PROPERTIES OF WELAN SYSTEMS - PRACTICAL APPLICATIONS

Andreja Zupanèè

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerèeva 5,
1001 Ljubljana, Slovenia

Abstract

A detailed rheological characterization of aqueous welan systems was performed in the concentration range from 0.1 to 0.5 %w/w of the polymer. In order to illustrate the practical application of aqueous welan systems, the rheological investigations were extended to alumina dispersions in aqueous welan matrices where the polymer concentrations in the disperse medium were of the same range (0.1-0.5 %w/w). The dependence of the viscoelastic properties of aqueous welan systems and alumina-welan dispersions on polymer concentration was examined and discussed in the light of fractional constitutive equations and in the view of practical applications. The experimental data of aqueous welan systems, as well as the results of modeling were compared with those obtained for alumina-welan dispersions.

1. INTRODUCTION

Aqueous polymer solutions, especially those of natural biopolymers, are very important material source in various industrial branches because they exhibit a high stability level and good compatibility and because they are biodegradable. In recent years, the production and the application of such environmentally friendly materials has increased. Industrial uses of polysaccharide systems centre on their ability to increase their weight in the water by several times when it thickens or structures, thus controlling the rheology of hydrated systems. The solution properties of these carbohydrates are of

considerable interest for a number of practical commercial applications such as thickening, suspending and gelling agents[1]. Such properties can be profitably exploited for many industrial applications, in particular in the food, pharmaceutical and ceramic industries.

Hydrophilic polymers and their aqueous dispersions exhibit some specific rheological properties. The structural conditions of these systems, which are influenced by various environmental conditions and polymer concentration, can be determined from detailed rheological examination. Rheological characterization of aqueous polysaccharide systems deals with a wide range of mechanical responses, from pure liquids to elastic solids. These systems in general exhibit the rheological behavior characteristic for polymers or polymer solutions, but under certain circumstances also some specific rheological properties. The transport properties and, specifically, the rheological behavior of real and complex materials such as aqueous polysaccharide systems can be significantly affected by several factors, mainly related to molecular and supermolecular features. Most of these factors are common to all polymeric systems, others are peculiar to carbohydrate polymers. Since the mechanical properties of aqueous polysaccharide dispersions depend on their physical and chemical conditions, their network structural formations depend on polymer concentration, ionic strengths, presence of organic solvents, pH, temperature, etc. In general, hydrophilic polymers are able to form three-dimensional network structures or gel structure already at very low polymer concentrations. The gel structure exhibits elastic solid behavior under the conditions of small deformations. Through a rheological study it is possible to evaluate not only the time evolution of the macroscopic properties of a given system, but also its structural and /or molecular characteristics.

The structural conditions of aqueous polysaccharide dispersions can be classified as: dilute polymer solutions, weak gels, micro gels and strong gels. Above the critical polymer concentration, overlapping and associations of polymer molecules result in the formation of extended junction zones, or in other words, in the formation of a continuous three-dimensional network, where the junction zones play the part of point crosslinks in covalent gels[2]. Strong gel behavior can be observed when the polymer association is strong. Under small deformation conditions the mechanical spectra of strong gels closely approximate solid-like behavior. When subjected to large deformation or continuous flow conditions, the gel network ruptures into small gel regions. The flow conditions then become heterogeneous. This is not the case for weak gels, which may flow homogeneously, even under continuous shear conditions. They exhibit marked non-

Newtonian properties, strictly connected to the progressive disruption of the network into smaller flow units as the shear rate increases. Also weak gels exhibit elastic solid behavior under the conditions of small deformations, but the elastic contribution to the viscoelastic response in this case is not so predominant as for strong gels. When polymer aggregation is favored, segregation into two phases may take place or interchain association may be restricted to small microgel clusters dispersed in a macromolecular solution[2]. The rheological behavior of the microgels depends on the polymer concentration. At a high concentration of the aggregates they exhibit solid like behavior at low stresses and their rheological properties cannot be easily distinguished from those of weak gels. Correlation of rheological data and modeling constitutes a complementary step, necessary for the exploitation of the experimental results.

Several industrial products and biomaterials are composed of solid particles dispersed in polymeric gel matrices. The rheological properties of filled gels are strictly governed by those of the polymeric matrix. The influence of particle addition can become very important, depending on the effective volume concentration of the disperse phase and the type and extent of particle-gel matrix interactions. Weak gel matrices are frequently preferred for many practical purposes, particularly when remarkable concentration levels of the disperse phase must be reached in the filled gel, since their viscous and elastic properties are favorably combined to ensure easy manipulation and transportation, as well as good stability. Among several polysaccharides giving rise to more or less weakly structured systems when dissolved in water under proper conditions, welan can be considered a good candidate to form weak gel matrices, since the sol/gel transition can be attained at low polymer concentrations and their gel properties are only slightly dependent on environmental conditions. Welan gum is produced by *Alcaligenes* spp. ATCC 31555 and has the same basic backbone repeating units as gellan gum, another microbial polysaccharide of widespread industrial use, but with a single α -L-rhamnose or α -L-mannose as side groups in the ratio of 2:1 per repeating unit[2]. Even if the primary structure of these two bacterial polysaccharides differ basically only for the side chains, significant differences can be noted in their viscoelastic properties in aqueous media. Thus, whereas gellan can form stable gels in salt aqueous solutions, welan systems often behave as weak gels, so standing between solutions and chemical gels, and their thermal stability represents an important characteristic for oilfield applications.

The present paper reports the results of experimental studies carried out on aqueous welan systems under small and large deformation conditions. Furthermore, the paper deals with the problems related to the preparation of concentrated aqueous

dispersions of ceramic powders in welan matrices. High purity alumina powder is selected in order to prepare ceramic dispersion in gel matrices. The specific objective of this work is to examine the influence of welan concentration on the structural conditions of aqueous alumina-welan systems.

2. EXPERIMENTAL

The materials used for the preparation of polysaccharide matrices, alumina suspensions, and alumina dispersions in welan matrices were: welan K1A96 (Monsanto) high purity alumina powder A16 SG (Alcoa) ($d_{50} = 0.5 \mu\text{m}$), distilled water and anionic dispersant Duramax D3021 (modified polyacrylic acid, Mw 5000 Rohm&Haas).

The powdered polymer (welan) was dissolved at different concentrations (0.1 - 1 %w/w) in distilled water by mechanical stirring at ambient temperature and stored for two days in order to ensure a complete wetting of the polymer. Alumina-welan dispersions were prepared in two steps. Highly concentrated aqueous alumina suspensions were used as a source of particle addition in the gel matrices. Alumina suspensions were prepared at the same solid volume fraction of 0.55 by dispersing the alumina powder in aqueous - dispersant solution. The dispersant concentration was 0.3 %w/w as calculated on the alumina powder, solid dry weight basis. The suspensions were prepared by ball milling in 0.5 litre polypropylene jars filled with 500 g of Si_3N_4 milling balls for 16 hours at a speed of 70 rpm. The two components (alumina suspensions and welan systems) were blended together in proper quantities by hand mixing. For all the systems the final solid volume fractions were, 0.38 and 0.48 with welan concentration ranging from 0 to 0.5 %w/w. The rheological characterization was carried out two days after the preparation.

The rheological tests were performed under steady and oscillatory shear conditions at 20, 25 and 30°C using mainly the controlled stress rheometer Haake, RheoStress RS 150, equipped with a double cone sensor system (DC 6/4). Some additional tests were done by a controlled rate rheometer Haake CV100, equipped with coaxial cylinder sensor system ZB15. The rheological properties were studied under small and large deformations, as well as in flow conditions, by applying different procedures: stress and frequency sweeps, stress ramps and multistep sequences.

3. RESULTS AND DISCUSSION

Flow curves - large deformation conditions

The rheological behavior of aqueous welan systems strongly depends on the polymer concentration. At 0.1 wt % of welan the linear and non-linear properties are quite similar to those of polymer solutions. Shear thinning behavior and negligible time dependent effects are observed in continuous shear. With increasing polymer concentration, above 0.2 wt % of welan, more pronounced shear thinning behavior and detectable thixotropic time dependent effects are observed. The rheological properties in this case resemble those peculiar for structured liquids or weak gels. Figure 1. demonstrates the influence of welan concentration on the flow properties of aqueous welan systems.

The rheological investigation is extended to examination of alumina dispersions in aqueous welan matrices where the solid volume fraction (Φ) of alumina powder is 0.38. The most significant changes in the flow properties of the dispersions are observed already at the lowest polymer concentration (0.1 %w/w of welan) in the disperse medium. At higher welan concentrations the shape of the flow curves, as well as the viscosity level, become similar to those of aqueous welan matrices.

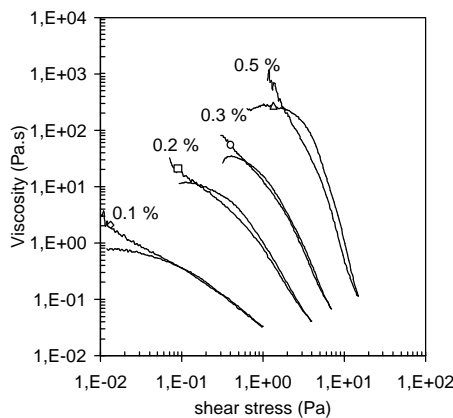


Fig.1: Flow curves of aqueous welan systems at different welan concentrations

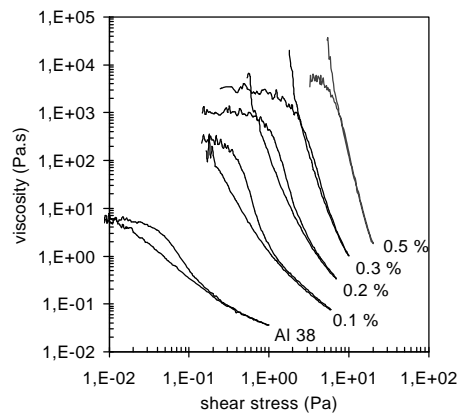


Fig.2: Flow curves of alumina-welan dispersions at $\Phi = 0.38$ and different welan concentrations

Viscoelastic properties - small deformation conditions

The results obtained from stress sweeps at a frequency of 1 Hz show that the critical strain for the linear viscoelastic regime decreases with increasing polymer concentration. Figure 3 illustrates such peculiar features for some aqueous welan systems

at different polymer concentrations. The limit of linear viscoelastic response of all aqueous welan systems ranged up to 10% of strain amplitude, whereas the critical strain amplitude of alumina-welan dispersions is shifted toward lower values of strain amplitude (between 0.7 and 2%) as shown in Figure 4. The numbers beside the symbols in Figures 3 and 4 indicate welan concentrations in %w/w.

Some preliminary tests were performed to check the influence of environmental conditions on the rheological properties of aqueous welan systems. The effects of pH by addition of HCl or NH_4OH , temperature (8 - 45°C) and the presence of dispersant were

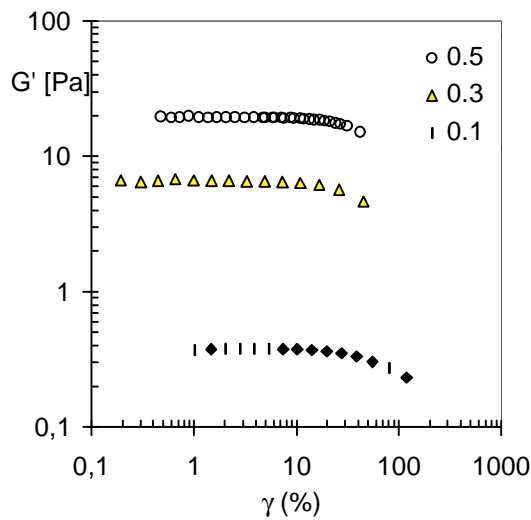


Fig. 3: Stress sweep tests: aqueous welan systems at different welan concentrations

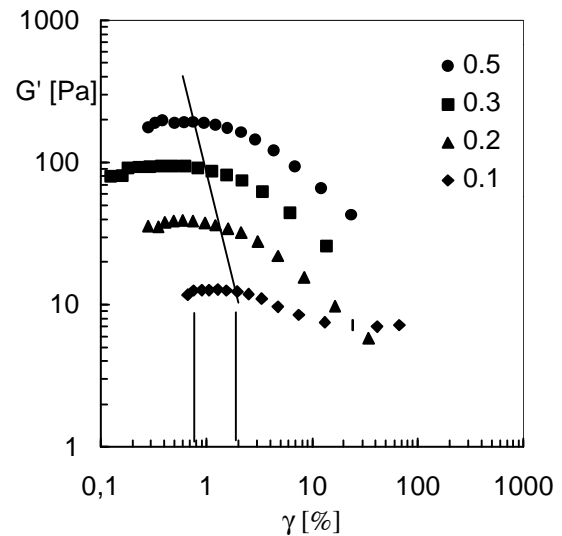


Fig. 4: Stress sweep tests: alumina-welan dispersions at $\Phi = 0.38$ and different welan concentrations

checked in the range of polymer concentration between 0.3 and 1 %w/w of welan. It was found that the systems were almost insensible to the investigated environmental conditions. This is confirmed in Figure 5 which illustrates the mechanical spectra of aqueous welan systems at different pH (2 – 9.5) and the same polymer concentration of 0.5 %w/w.

The mechanical spectra of aqueous welan systems at different polymer concentrations (at 25 °C) are reported in Figure 6. For the lowest polymer concentration (0.1 %w/w) the viscous component exceeds the elastic one under low amplitudes of oscillatory shear strains, below i.e. 10%. At >0.2 %w/w of welan the elastic component becomes predominant and both moduli are less sensitive to the applied frequency. When polymer concentration exceeds 0.1%, a net change is observed in the profiles of both moduli, suggesting the appearance of a sol/gel transition.

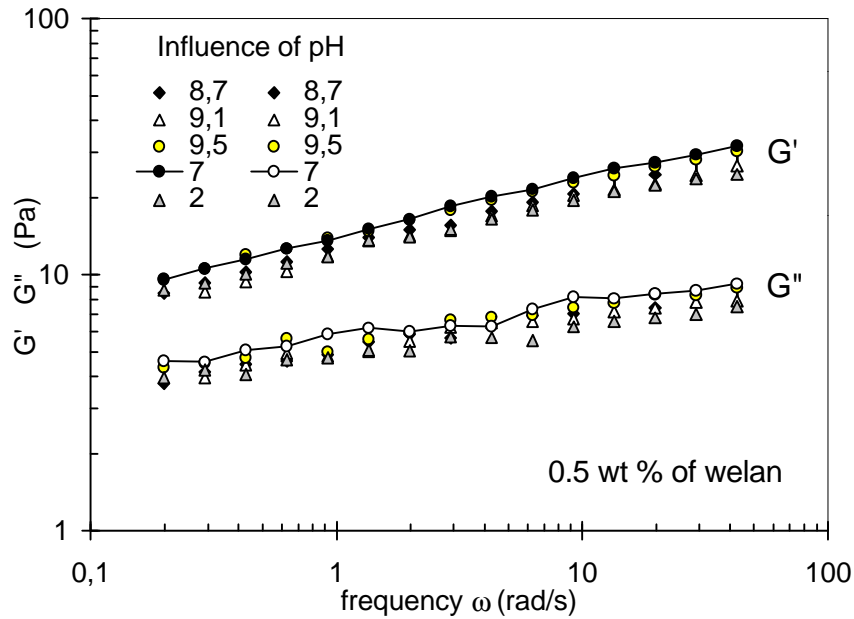


Fig. 5: The influence of pH on the mechanical spectra of aqueous welan systems

At above 0.1 % of welan the increase of polymer concentration (C), G' and G'' scale as $C^{1.9-2.3}$ and $C^{1.7-1.95}$, respectively (both exponents increase with decreasing frequency). A C^2 dependence of the storage modulus (G') is often observed for gelling systems, in accordance with theoretical models proposed for biopolymers with high functionality [3].

Let us now consider the effects of welan concentration on viscoelastic properties of alumina-welan dispersions at a solid volume fraction of 0.38. The mechanical spectra of alumina-welan dispersions at different polymer concentrations in the disperse medium are shown in Figure 7. As already mentioned, the most significant changes in the rheological properties are observed for the systems containing 0.1 %w/w of welan. Under linear oscillatory shear conditions the elastic component appreciably predominates over the viscous one for all alumina-welan systems and both moduli strongly increase in the presence of polymer in the disperse medium. When polymer concentration exceeds 0.1%, the dispersions behave like structured liquids or weak gels. With increasing polymer concentration (> 0.2 %w/w) in the disperse medium the traces of $G'(\omega)$ and $G''(\omega)$ become parallel to each other and G' is at least one order of magnitude higher than G'' . Such a condition corresponds to an apparent sol/gel transition according to the criterion suggested by Winter and Chambon [4].

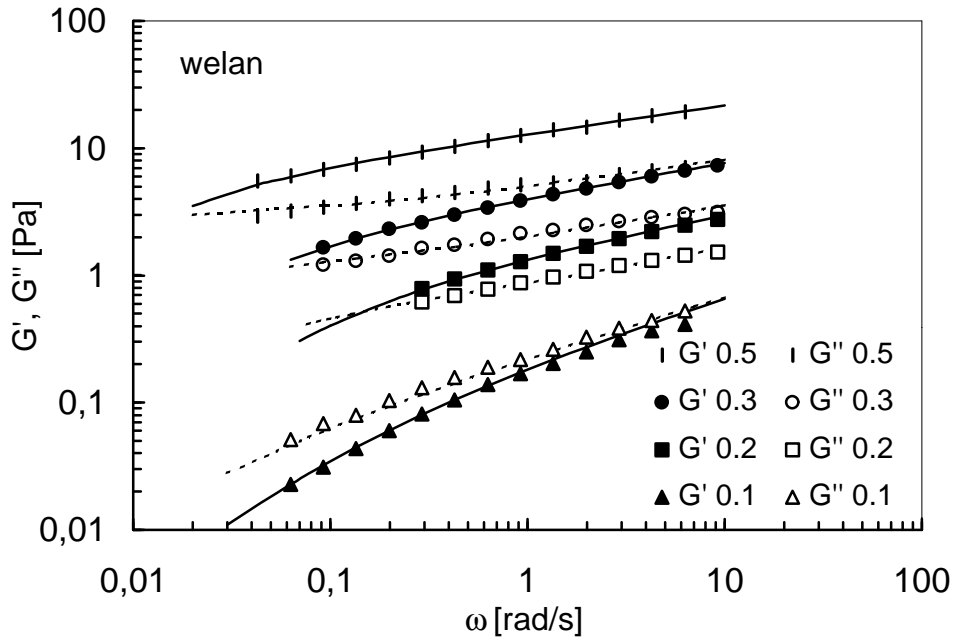


Fig. 6: Frequency dependence of G' and G'' for aqueous welan systems, numbers beside the symbols indicate welan concentrations in %w/w and curves calculated from the Friedrich model.

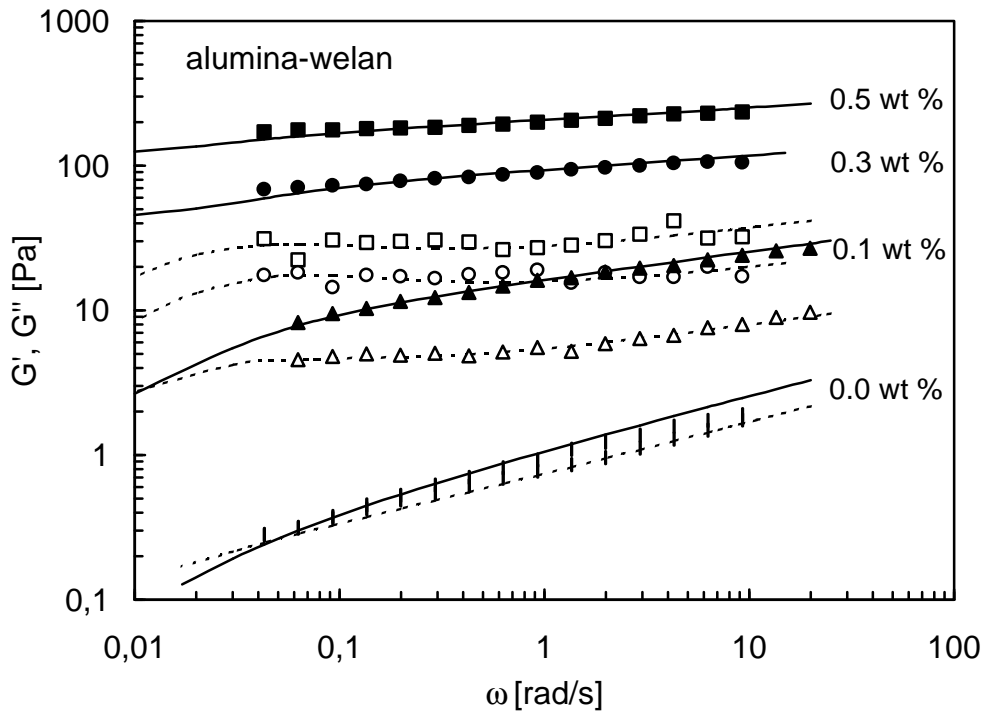


Fig. 7: Frequency dependence of G' (filled symbols) and G'' (open symbols) for alumina-welan dispersions with $\Phi=0.38$ at 25°C , and curves calculated from the Friedrich model

In the case of such structured fluids the analysis of experimental data must necessarily be performed by resorting to phenomenological models instead of molecular approaches, particularly when we aim to describe effects of polymer concentration or sol/gel transitions. Satisfactory data fitting of mechanical spectra is provided by the fractional derivative (per time) Maxwell model suggested by Friedrich and Braun [5].

$$\bar{\tau} + D^c [\bar{\tau}] = G_\infty \left\{ D^0 [\bar{g}] + D^c [\bar{g}] \right\} + \Delta G D^d [\bar{g}] \quad (1)$$

where $\bar{\tau}$ and \bar{g} are the stress and strain tensors, respectively, and c and d are the derivation orders. When $c = d = 1$, the equation corresponds to the ‘solid model’ for $G_\infty > 0$, whereas the canonical Maxwell ‘liquid model’ is obtained for $G_\infty = 0$. The fractional derivative model was selected because it is able to describe a wide range of viscoelastic responses, from viscous liquid to elastic solid, by a limited number of parameters. Under oscillatory shear conditions the linear viscoelastic response can be expressed by the following equations:

$$G'(\omega) = G_\infty + \Delta G \frac{(\mathbf{I}\omega)^d \left[\cos\left(d\frac{\omega}{2}\right) + (\mathbf{I}\omega)^c \cos\left((d-c)\frac{\omega}{2}\right) \right]}{1 + 2(\mathbf{I}\omega)^c \cos\left(c\frac{\omega}{2}\right) + (\mathbf{I}\omega)^{2c}} \quad (2)$$

$$G''(\omega) = \Delta G \frac{(\mathbf{I}\omega)^d \left[\sin\left(d\frac{\omega}{2}\right) + (\mathbf{I}\omega)^c \sin\left((d-c)\frac{\omega}{2}\right) \right]}{1 + 2(\mathbf{I}\omega)^c \cos\left(c\frac{\omega}{2}\right) + (\mathbf{I}\omega)^{2c}} \quad (3)$$

where G_∞ represents the equilibrium modulus when the frequency tends to zero, and hence the model describes liquid-like responses if $G_\infty = 0$. Parameter \mathbf{I}_0 is a characteristic time of a material which determines the role of the relative contribution of elastic and viscous components in the viscoelastic response. Figures 6 and 7 report a comparison between experimental data and the curves calculated from equations (2) and (3). Apparently, the model provides an adequate correlation of loss and storage moduli as the function of frequency in the whole range of polymer concentration for both aqueous welan systems and alumina-welan dispersions. In order to obtain reasonable values of the parameters in equations (2) and (3), the yielding conditions: $0 < c \leq d \leq 1$ and $G_\infty \geq 0$ should be satisfied. As an objective function in the minimization procedure the mean square relative deviation was used. Evaluation of the model parameters by applying the fitting procedure simultaneously for both $G'(\omega)$ and $G''(\omega)$ showed that for almost all studied systems exponent d converged to the limiting conditions $d = 1$. Consequently, the influence of polymer concentration on the frequency dependence of the dynamic moduli

is described through the variation of only four parameters: G_{∞} , ΔG , I_0 and c . The variation of relaxation time I_0 and exponent c with increasing welan concentration in aqueous welan systems and alumina-welan dispersions is shown in Figure 8. Increase of I_0 with polymer concentration in aqueous welan systems indicates that the elastic contribution becomes more important. The value of I_0 evaluated for the reference aqueous alumina suspension is quite different from those of the alumina-welan dispersions (Figure 8). Noticeable increase of exponent c is observed only at low polymer concentrations. At higher welan concentrations c values ranges around 0.8 for both welan and alumina-welan systems. The most significant differences in parameter ΔG , which control the level of the dynamic moduli, is observed between 0.1 and 0.2 %w/w, where sol-gel transition can be expected for aqueous welan systems, whereas ΔG exhibits a strong increase as soon as welan is present in the alumina-welan dispersions (Figure 9). The differences in structural conditions between aqueous welan systems and alumina-welan dispersions are indicated also with the appearance of G_{∞} , (G_e in Figure 9) for the alumina-welan dispersions. For aqueous welan systems the values of G_{∞} converge to limit conditions, $G_{\infty} = 0$. When sol-gel transition is observed for the aqueous systems, alumina dispersions exhibit ‘solid like’ response under non-destructive conditions of small deformations.

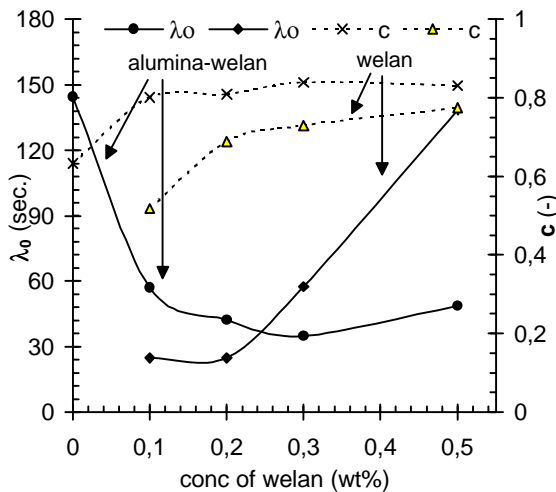


Fig. 8: Parameters I_0 and c of the Friedrich model vs. welan concentration for aqueous systems and alumina-welan dispersions at 25°C

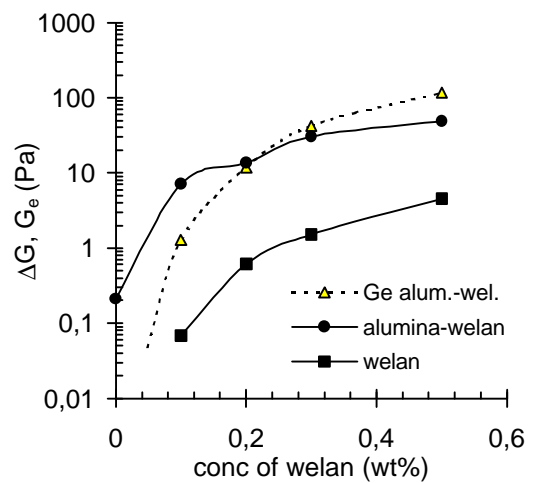


Fig. 9: Parameters ΔG and G_{∞} of the Friedrich model vs. welan concentration for aqueous systems and alumina-welan dispersions

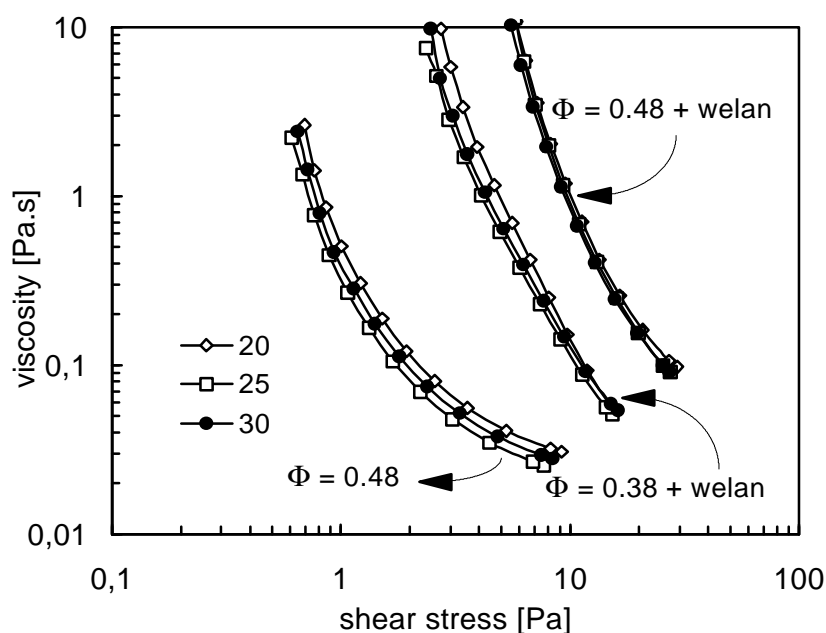


Fig. 10: Flow curves of aqueous alumina suspension ($\Phi = 0.48$) and alumina welan dispersions ($\Phi = 0.38$ and 0.48) at 20 °C, 25 °C and 30 °C.

CONCLUSIONS

Aqueous welan systems exhibit weak gel properties even at low polymer concentration and their behavior does not change appreciably when pH and other environmental conditions are changed. At 0.1 %w/w of welan the rheological properties are similar to those of polymer solution, whereas at higher polymer concentrations the systems exhibit behavior characteristic for structured systems or weak gels. Such rheological properties of aqueous welan systems enable different practical applications under wide range of environmental conditions.

Experimental tests performed with alumina-welan dispersions showed that even a small addition of welan to the disperse medium produces significant changes in the rheological properties of aqueous alumina suspensions. As soon as welan is present in the disperse medium, the rheological properties of alumina-welan dispersions changes significantly. Such systems exhibit the behavior of structured systems. At above 0.1 %w/w of welan in the disperse phase the rheological properties of alumina-welan systems are governed by welan concentration (weak gel behavior). The biopolymer under such conditions provides an essential contribution to particle stabilisation.

The experimental results demonstrate that welan can be used in ceramics as matrices for particle dispersions also in the case when high solid content should be

achieved. We need some additional tests to support these perspectives. Only for illustration, alumina-welan dispersions are possible to prepare at least to the solid volume fractions of 0.48. The effects of temperature (20 - 30 °C) on steady shear viscosity, evaluated from sequential shear rate steps, are studied for aqueous alumina suspensions at $\Phi = 0.48$ and alumina - welan (0.25 %w/w) dispersions at $\Phi = 0.38$ and 0.48. Figure 10 shows that the presence of welan in the disperse medium reduces the temperature effects.

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POVZETEK

Obširna reološka karakterizacija vodnih gelskih sistemov velana je bila izvedena v območju koncentracij 0.1 do 0.5 utežnih % polimera v vodi. Da bi prikazala praktično uporabo vodnih sistemov velana, sem raziskave razširila na disperzije glinice v vodnih gelskih matrikah velana, pri katerih je bila koncentracija polimera v disperznem mediju v enakem območju kot pri vodnih sistemih velana. Odvisnost viskoelastičnih lastnosti vodnih gelskih struktur velana in vodnih disperzij glinice v velanu od koncentracije polimera sem v predstavljenem delu analizirala z uporabo delnih odvodov konstitutivnih enačb. Primerjava eksperimentalnih podatkov in rezultatov modeliranja, pridobljenih na vodnih sistemih velana, z rezultati določenimi za vodne disperzije glinice v gelskih matrikah velana omogoča predvideti pomen vodnih sistemov velana v tudi različnih drugih aplikacijah.