Rheological Investigation of Xanthan Gum–Chromium Gelation and Its Relation to Enhanced Oil Recovery

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ABSTRACT: Xanthan gum–water solutions with polymer concentrations 0.05–1% w/w and chromium ion content 30–1200 ppm were being gelled at temperatures from 25 to 90°C. A control deformation test (CD test) at a constant shear rate 0.05 s^{-1} was performed for all the specimens. Shear moduli of elasticity and in some cases yield stresses and yield strains were determined from these tests. The energy of activation $E_a = 93 \pm 6$ kJ/mol was obtained. The dependence of the gelation rate on the ionic concentration followed a power law with a coefficient of 1.8. There was relatively small dependence of the gelation rate on the xanthan gum concentration. Surprisingly, the maximum obtainable moduli at complete gelation do not depend on xanthan gum concentration in the range 0.2–1% w/w and are about 2400 Pa. The number of the bound chromium ions per monomer unit of xanthan gum is changed from 0.64 to 0.16 for the above measured concentrations of the polymer. High moduli gels on the base of the lower concentrations of xanthan gum were practically not recoverable after mechanical destruction. The assumption was made that the main reason for the profile modification of the flow for enhanced oil recovery in porous media is the yield stress of the gels. The smaller capillaries can even be closed if the yield stress is higher than the maximum shear stress existing in the capillary. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 160–166, 2007

Key words: xanthan gum; hydrogels; rheology; metal-polymer complexes; oil recovery

INTRODUCTION

Xanthan gum is a biopolymer synthesized by *Xanthomonas* sp.[1] Rheological behavior of its aqueous solution is pseudoplastic in nature and forms "weak gels."[2] Because of these properties, xanthan gum is used as a thickener, emulsion stabilizer, and agent, which prevents the sedimentation in suspensions, preliminary in food, pharmaceutical, and cosmetic industries.[3]

It is well known that xanthan gum–water solutions form gels in the presence of trivalent metal ions such as Al, Fe, and Cr.[4] These systems are a subject of great interest primarily due to their industrial applications. Xanthan gum–chromium gels are commonly used in the drilling industry for tertiary oil recovery,[5,6] and preliminary investigations into the application of xanthan gum combined with ferric ions for the food industry have been conducted.[7]

The gelation process itself is not well understood and there are different theories, explaining this phenomenon. A number of different experimental techniques has been used to extract information related to the mechanism and kinetics involved in these types of reaction systems NMR,[8,9] dynamic light scattering,[10] small amplitude oscillatory rheometry,[7,11] etc.

There is a hypothesis about the gelling mechanism as a formation of dimeric or polymeric ionic bridges.[12] Hansen and coworkers suggested a first-order two-step reaction mechanism between the chromium ions and the xanthan gum molecules.[9] They determine the rate constants and the activation energy E_a of this chemical reaction. They find the apparent rate constant to be independent of the initial chromium concentration and slightly dependent on the xanthan gum concentration. On the contrary, Nolte et al.[4] suggested a power law dependence of the gelation rate on the ionic concentration with a coefficient of 1.7. In his investigation of xanthan gum–ferric gels, Ma[7] assumed a strong dependence of storage modulus (G') on xanthan gum concentration. According to Rodd and coworkers,[10] gelation in xanthan gum–Al is not possible below $T_g = 28°C$.

The present study investigates the gelation of xanthan gum–water solutions with Cr^{3+} ions with the rheological device HAAKE VT 550 (shear flow deformations) by determining the dependences of shear modulus G on time, temperature, xanthan gum, and chromium concentrations. Yield stress was determined and interpreted in relation to enhanced oil recovery.

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EXPERIMENTAL

Source of materials

Xanthan gum RHODIGEL 200, kindly provided by P.I.C.O. (Sofia, Bulgaria) was used as received without further purification. $CrCl_3 \cdot 6H_2O$ was used as a source of chromium ions.

Preparation of gels

Gels with different xanthan gum concentration (0.05–1% w/w) and chromium concentration (30–1200 ppm) were prepared. $CrCl_3 \cdot 6H_2O$ was dissolved in 0.1% w/w solution of NaCl in distilled water. Xanthan gum solutions in distilled water were prepared by vigorous stirring for 1 h with a magnetic stirrer at 1000 cpm. $CrCl_3 \cdot 6H_2O$ and xanthan gum solutions were stored in a refrigerator (at temperature, 4°C). The two solutions were mixed immediately before the gelling process. Gelation was carried out in the testing cylinder of the rheometer, heated to the test temperature in advance.

Instead of distilled water, artificial seawater was used as a solvent for some gels. It was made by dissolving 1060 g NaCl, 218 g $CaCl_2 \cdot 2H_2O$ and 128 g $MgCl_2 \cdot 6H_2O$ in 20 kg distilled water,[5] and contained about 6% total dissolved solids.

Experimental techniques

The rheological measurements were performed with the rheological device, HAAKE ViscoTester 550, produced by Thermo Electron (Germany). It is a rotational viscometer for automated quality control, suitable for the complete characterization of fluids in the rotational mode, e.g., the determination of yield points in the CD (controlled deformation) mode. The experiments were done with coaxial cylinder sensors SV DIN, which are recommended for high viscosity liquids (viscosities in the range 50–10^5 mPa are able to be measured). The sample volume is 14 cm^3 and the gap between the coaxial cylinders is 0.9 mm. The exact temperature control can be provided by the use of a circulator. The CD test at a constant shear rate $\dot{\gamma} = 0.05$ s^{-1} was applied to all gels. A shear stress-time dependence (stress-strain dependence) was obtained from this kind of measurements. The module of elasticity G was determined from Hook's law ($\tau = G\gamma$) by using the linear part at the maximum slope of the $\tau(\gamma)$ curve, where $\gamma = \dot{\gamma}t$, as described elsewhere.[13] The yield stress τ_0 was defined as the curve peak value of the shear stress-time dependence. The yield strain (the strain at which gels are destroyed) is the strain, corresponding to the peak of the curve $\gamma_0 = 0.05t_{peak}$.
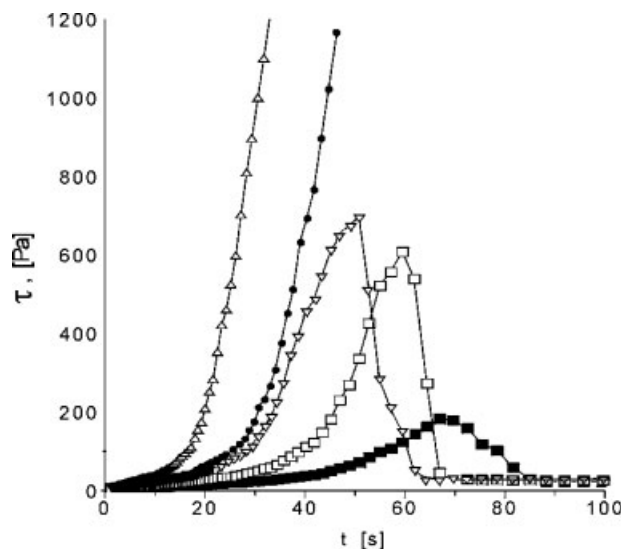
Figure 1 CD test: Shear stress-time dependence, for 1% w/w xanthan gum gels with 150 ppm Cr^{3+} at 40°C. Tests were conducted after different times of gelation: ■, 60 min; □, 80 min; ▽, 90 min; ●, 120 min; △, 200 min. All tests were performed at a constant shear rate $\dot{\gamma} = 0.05$ s^{-1}.

RESULTS AND DISCUSSION

Xanthan gum solutions formed elastic gels on addition of Cr^{3+}.

Kinetics of gelation

Gel development during/with time at a fixed temperature was monitored by the CD test (Fig. 1). Shear modulus G (the slope of the experimental curves) and yield stress increase with time, while the yield strain decreases, that is to say, during storage, gels loose their visco-elasticity and become stiffer and more elastic.

The development of the gelation process with time was studied in detail at five temperatures, 40, 45, 50, 55, and 60°C (Fig. 2). The curves, which present the development of the shear modulus during the gelation time, can be divided into three ranges: a latent period (range I), when the shear modulus G has in practice the same value as in xanthan gum–water solution without Cr^{3+} and the same xanthan gum concentration (for the 1% w/w solution this value is about 11 Pa); range II is characterized by a strong increase of G and plateau range III, where saturated values are observed. It can be seen that the latent period decreases when temperature increases, but the final values of the shear modulus are almost the same, which concerns also the values of the modulus in the plateau range at room temperature and 90°C.

According to the two-step reaction mechanism of the first-order described by Hansen,[9] this experimental
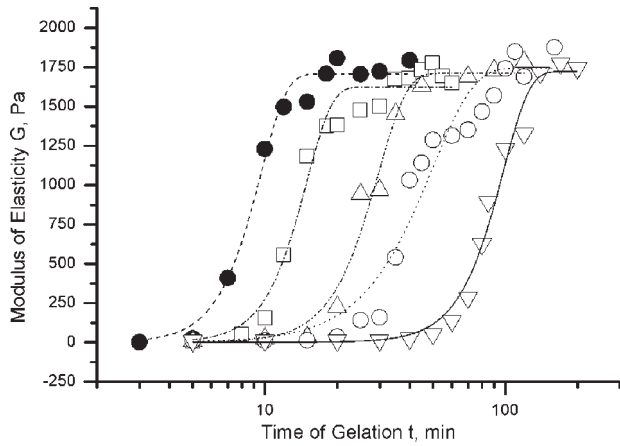
Figure 2 Time development of 1% w/w xanthan gum gels with 150 ppm Cr^{3+} at different temperatures: ●, 60°C; □, 55°C; △, 50°C; ○, 45°C; ▽, 40°C. Each point on the curves was measured by CD test at a constant shear rate $\dot{\gamma} = 0.05 \text{ s}^{-1}$.

curve should be referred to the following equation (double exponent equation):

$$G(t) = G_\infty \left(\frac{k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} + 1 \right), \quad (1)$$

where G_∞ is saturated (plateau) value of shear modulus, k_1 and k_2 are the rate constants for each step of reaction.

A fitting of the experimental data with this equation did not show a sufficient accuracy (Table I). Another fitting with the Avrami equation,

$$G(t) = G_\infty (1 - \exp(kt)^n), \quad (2)$$

concerning polymer crystallization at a constant temperature was conducted. G_∞ is saturated (plateau) value of shear modulus, k is the rate constant, and n is the Avrami exponent. A better fitting in that case has been attained (Table I). We use this equation only for good phenomenological descriptions of the experimental data, yet we do not assert that the observed gelation is a crystallization process.

TABLE I
Kinetics of Gelation of Xanthan Gum Water Solutions in the Presence of Cr^{3+} Ions, Examined by the Avrami Equation

	Double exponent equation		Avramy equation		
T (K)	G_∞ (Pa)	R^2	G_∞ (Pa)	$k \times 10^4$ (s^{-1})	R^2
313	3056	0.917	1723	1.697	0.99
318	1982	0.934	1625	3.800	0.96
323	1875	0.907	1712	5.595	0.98
328	1792	0.912	1672	11.127	0.97
333	1893	0.907	1707	17.297	0.99

Contrary to the double exponent equation, eq. (2) predicts a latent period for gelation. This can be interpreted as time necessary for the initial binding of Cr ions to the xanthan gum macromolecule before the formation of a three-dimensional network. Parameter $1/k$ in eq. (2) corresponds to the inflection point in the experimental curve and k could be considered as a rate constant of gelation.

Assuming that Arrhenius-type temperature dependence of the rate of gelation

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right), \quad (3)$$

the activation energy E_a was calculated: $E_a = 93 \pm 6$ kJ/mol (Fig. 3). The correlation coefficient was $R^2 = 0.99$. This value of activation energy is about two times larger than reported before.[4,9] If one uses the value of activation energy reported in Ref. 9 ($E_a = 47.5 \pm 10$ kJ/mol), the rate constant should increase about 1.7 times per every 10°. It is evident from the experimental curves (Fig. 2) and Table I that the decrease of k (and the corresponding increase of time of gelation) is about three times per every 10°.

The value of activation energy was used to calculate the time for reaching a plateau modulus of 1% w/w xanthan gum gels with 150 ppm Cr^{3+} at 90°C and room temperature (25°C), which are 1.25 and 1033 min, respectively. The plateau moduli at these temperatures are practically the same as the plateau moduli in the temperature range 40–60°C.

Dependence of the rate of gelation on Cr^{3+} concentration

A kinetic study (shear module G versus gelation time) at 60°C of 1% w/w xanthan gum gels with
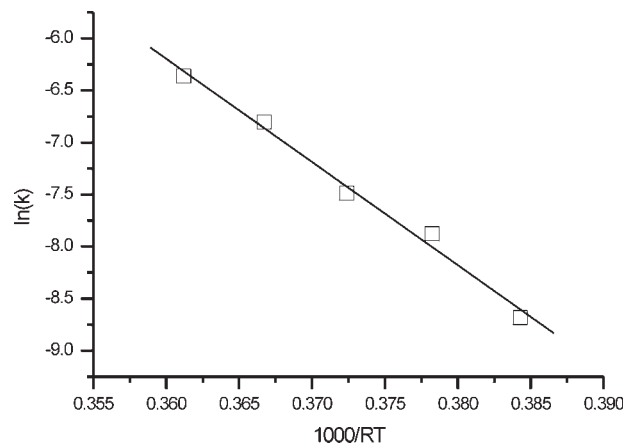
Figure 3 Determining of activation energy E_a, logarithm of rate constant at different temperatures versus the inverse of the absolute temperature for 1% w/w xanthan gum gels with 150 ppm Cr^{3+}. The solid line represents the best fit to the Arrhenius model.
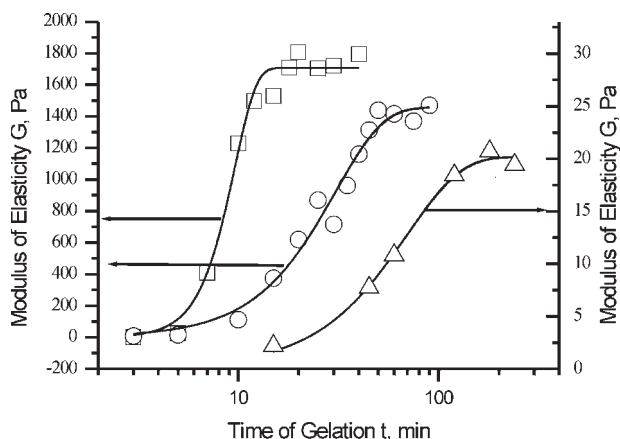
Figure 4 Gel formation of 1% w/w xanthan gum gels with different Cr³⁺ concentrations: □, 150 ppm; ○, 100 ppm; △, 60 ppm. All tests were conducted at temperature 60°C and a constant shear rate $\dot{\gamma} = 0.05$ s⁻¹.
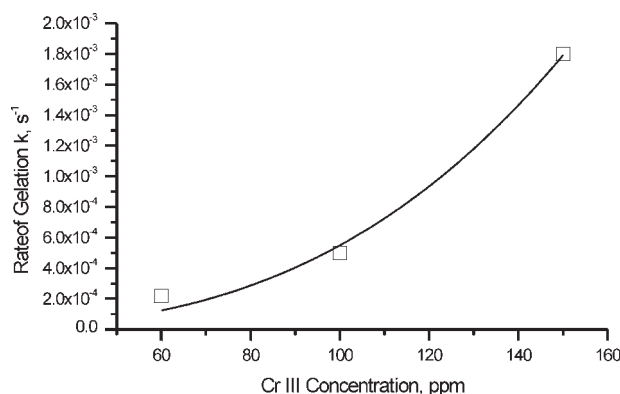
Cr³⁺ concentrations 60, 100, and 150 ppm, similar to these used in Ref. 5, was carried out (Fig. 4). It is evident that the Cr³⁺ concentration influences the plateau values of the shear modulus and gelation rate as well. The dependence of the rate constant on Cr³⁺ concentration was fitted to a power law equation:
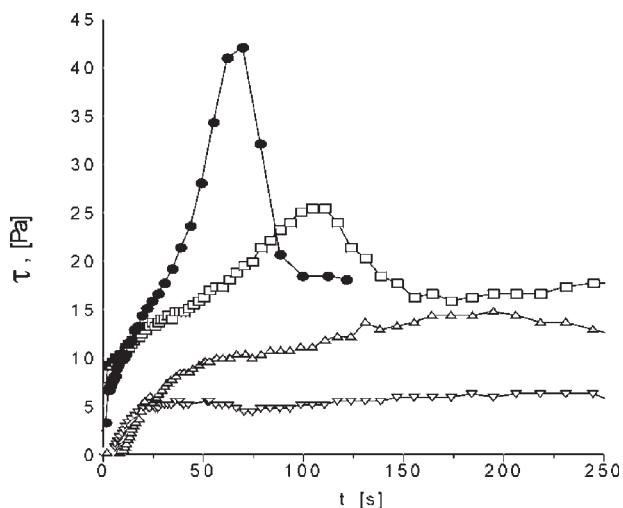
$$k = k_0' c_{Cr}{}^{\alpha}, \qquad (4)$$

where c_{Cr} is chromium concentration, measured in ppm (Fig. 5). The power coefficient is $\alpha = 1.8$, which is in good agreement with previous works.[4]

Dependence of plateau values of modulus of elasticity on Cr³⁺ concentration

Because the plateau moduli in Figure 4 continue to rise with the increase of the chromium concentration, it is useful to know how the plateau modulus
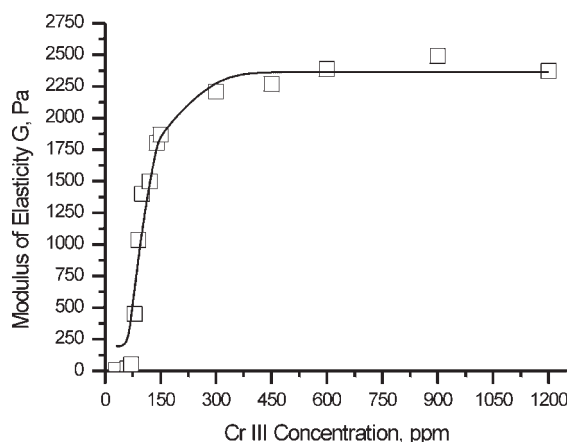

Figure 6 CD tests for 1% w/w xanthan gum gels with different Cr³⁺ concentrations: ●, 60 ppm; □, 40 ppm; △, 30 ppm; ▽, pure xanthan gum. All tests were conducted at 60°C and a constant shear rate $\dot{\gamma} = 0.05$ s⁻¹.

will develop with further increase of the Cr³⁺ concentration. Dependence of modulus of elasticity on chromium concentration of 1% w/w xanthan gum gels at 60°C was studied within a large range from 30 to 1200 ppm of chromium concentration. At 30 and 40 ppm Cr³⁺, very low modulus and extremely soft and speadible gels were developed (Fig. 6). From 60 to 300 ppm, a very strong increase in the plateau moduli is observed (Fig. 7). With a further increase of the chromium concentration up to 1200 ppm, the moduli are practically the same about 2400 Pa.

The observed results in Figure 7 can be interpreted with the existence of a limited ratio of chromium ions that can bind to a xanthan gum monomer. According to Hansen and Lund,[9] when positive Cr³⁺ binds to a negative site (COO⁻) on the side chain of the xanthan gum monomer, a positive charge on that

Figure 5 Rate of gelation versus Cr³⁺ concentration for 1% w/w xanthan gum gels at 60°C. The solid line represents the best fit with power law.
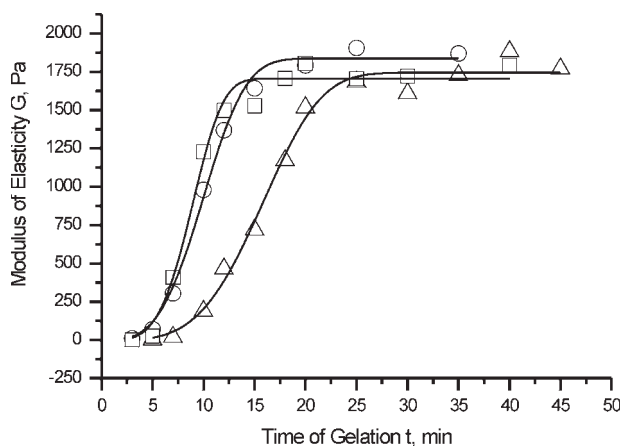

Figure 7 Dependence of modulus of elasticity in plateau range on Cr³⁺ concentration for 1% w/w xanthan gum gels at 60°C.

Figure 8 Gel formation xanthan gum gels with 150 ppm Cr^{3+} and different xanthan gum concentrations: □, 1%; ○, 0.5%; △, 0.2%. All tests were conducted at temperature 60°C and a constant shear rate $\dot{\gamma} = 0.05\ s^{-1}$.

site arises. Because of electrostatic repulsions, not all negative (COO^-) sites could be occupied by Cr^{3+} ions. To study xanthan gum–chromium interaction in gel, it is useful to determine the ratio f, the number of chromium ions that bind to one xanthan gum monomer. From the rubber elasticity theory for crosslinked polymers in solutions,[14] dependence between shear modulus and molecular weight between crosslinks M_c is known:

$$G = \frac{cRT}{M_c}, \qquad (5)$$

where c is polymer concentration in g/L, R, gas constant in J/mol K, and T, absolute temperature in K. For 1% w/w (10 g/L) xanthan gum gels at 60°C, the plateau value of the shear modulus is 2375 Pa. According to eq. (5), the molecular weight M_c is 11,657. The molecular weight of xanthan gum monomer is 937. Consequently, the number of xanthan gum monomers between two crosslinks is 12.44, or the maximum number of chromium ions that bind to one xanthan gum monomer is 0.16. This ratio coincides with the ratio obtained in Ref. 9 by the use of NMR.

Dependence of rate of gelation on xanthan gum concentration

Kinetic studies (shear module G versus gelation time) for gels with 150 ppm and different xanthan gum concentration at 60°C were conducted as well (Fig. 8). The rate constant decreases with the decrease of the xanthan gum concentration. The dependence of the rate constant on xanthan gum concentration was fitted to a power law equation:

$$k = k_0'' c_X^\beta, \qquad (6)$$

where (c_x) is xanthan gum concentration. The power coefficient was calculated to $\beta = 0.368$. The values of α and β show predominant effect of chromium concentration on gelation rate.

### Dependence of shear modulus at complete gelation on the xanthan gum concentration

Shear moduli of xanthan gum gels with different xanthan gum concentrations from 0.05 to 1% w/w with 150 ppm Cr^{3+} gelled at 60°C were measured (Fig. 9). It can be seen that the plateau values of shear moduli were almost the same for the xanthan gum concentrations from 0.2 to 1% w/w. This means that the xanthan gum concentration in this range does not influence the values of the shear moduli. This unanticipated result can be interpreted as an increase of the ratio f. As we use eq. (5), for 0.2% w/w xanthan gum concentration at 60°C, where the plateau modulus is 1883 Pa, molecular weight between two crosslinks is 2914, and the number of monomers between the two crosslinks is 3.1. Consequently, the ratio $f = 0.64$, which seems to be very high, but according to the data presented in Ref. 7, 1% w/w xanthan gum gels with ferric ions have moduli of 13,000 Pa, which corresponds to the ratio $f = 0.983$. Ferric ions are considered as extremely reactive and the binding of every xanthan gum monomer with a ferric ion could be anticipated.

Restoring of xanthan gum gels after mechanical destruction

The development of a shear modulus after mechanical destruction in gels with 150 ppm Cr^{3+} and 1 and 0.2% w/w xanthan gum was investigated. Gels with 1% w/w xanthan gum concentration were tested
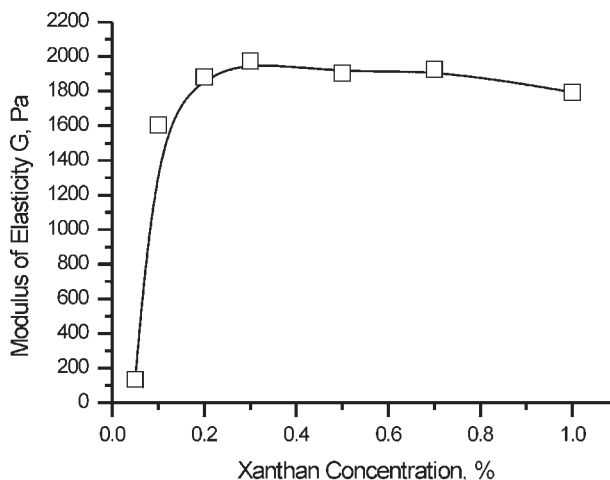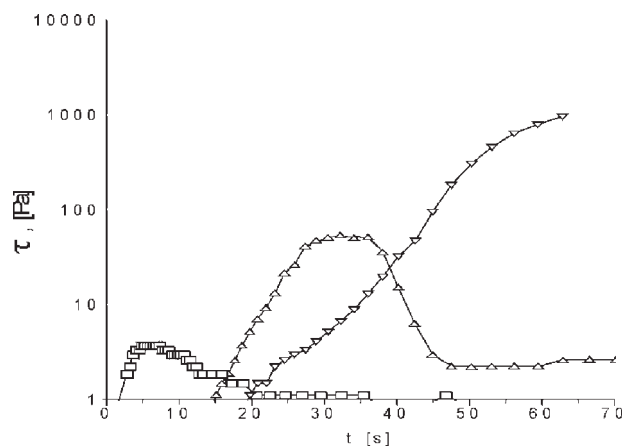

Figure 9 Dependence of modulus of elasticity in plateau range on xanthan gum concentration for xanthan gum gels with 150 ppm Cr^{3+} at 60°C.
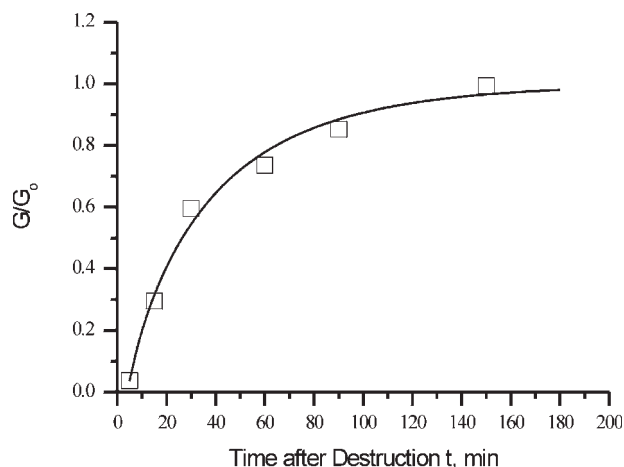
Figure 10 Time development of 1% w/w xanthan gum gels with 150 ppm Cr^{3+} at 50°C after mechanical destruction–shearing 10 min at shear rate $\dot\gamma = 800$ s^{-1}.

after 1 h gelling at 50°C. A CD test was done for each sample and the modulus of elasticity G_0 at the plateau range was determined. Gels were destroyed by shearing for 10 min at shear rate $\dot\gamma = 800$ s^{-1}. The measurements of the shear modulus immediately after shearing showed that the polymer three-dimensional network was totally destructed. Development of a normalized modulus G/G_0 during the time after destruction was presented in Figure 10. One hour after destruction (the time of gelling process), about 70% of the initial shear module was reached, while full restoring is observed after 3 h, that is, three times more than gelling time.

The same experiments were conducted with 0.2% w/w xanthan gum gels at 70°C (Fig. 11). Unlike gels with the higher polymer concentrations, these restore very slowly, only about 10% during a period of time, which is two times longer than the gelling time. Gels with xanthan gum concentrations of 0.2% w/w and lower, which are formed at room temperature for 2–3 days, are practically not recoverable after mechanical destruction.
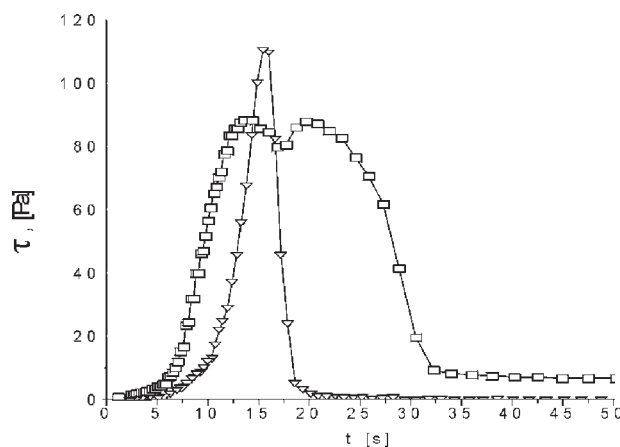
These results show a thixotropic behavior of xanthan gum–Cr^{3+} gels. The thixotropic effect is due to reversibility of the electrostatic interactions between Cr^{3+} ions and COO$^-$ groups in the side chains of xanthan gum molecule. The time of restoring seems to be concentration dependent and decreases with increasing polymer concentration. An increase in polymer concentration leads to increasing of cross-linking and therefore to faster development of gel structure.

Xanthan gum–Cr^{3+} gelatioin and oil recovery

The only known application of xanthan gum–Cr^{3+} gelation is for modification of the profile of flow through porous media in oil recovery. The flow in the narrowest channels at low-pressure gradients is much more restricted than predicted by the known theories, which is beneficial for the enhanced oil recovery.[5] The authors suggest that elasticity of the fluid should be taken into account to develop a new theory, explaining these results better.

We assume that the main reason for the observed results at low-pressure gradients[5] is the yield stress of the gels. When the maximum shear stress in the capillary is lower than the yield stress, the gel responds elastically and flow cannot be realized. At least qualitatively, one can use the formula for the maximum developed stress in the capillary:[15]

$$\tau_w = \frac{RP}{2L} \tag{7}$$

Figure 11 CD tests at $\dot\gamma = 0.05$ s^{-1} for 0.2% w/w xanthan gum gels with 150 ppm Cr^{3+} different time after destruction: ▽, reference curve (before destruction, 2 h after gelation); □, immediately after destruction; △, 210 min after destruction. Initial gelation and rebuilding were done at 70°C.

Figure 12 CD tests at $\dot\gamma = 0.05$ s^{-1} for 0.2% w/w xanthan gum gels with 500 ppm Cr^{3+} in different solvents: ▽, distilled water; □, artificial seawater. Tests were conducted at 60°C 1 h after gelation.
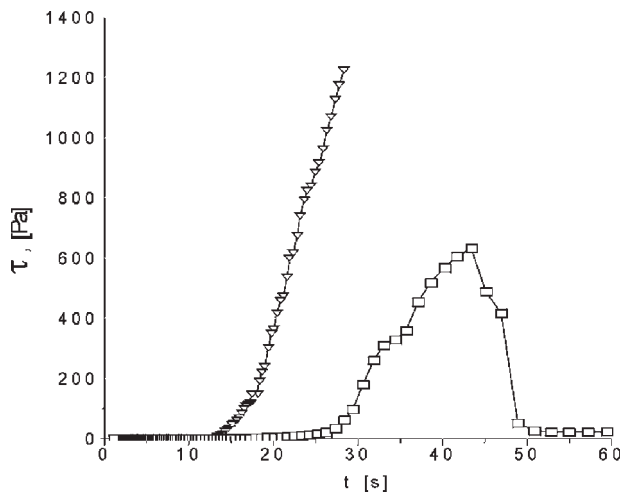
Figure 13   CD tests at $\dot{\gamma} = 0.05$ s^{-1} for 0.05% w/w xanthan gum gels with 500 ppm Cr^{3+} in different solvents: $\triangledown$, distilled water; $\square$, artificial seawater. Tests were conducted at 60°C 1 h after gelation.

where τ_w is the shear stress at the wall of the capillary, P/L is the pressure gradient, and R is the radius of the capillary. The maximum τ_w is proportional to R, which means that for the smaller capillaries, it will be lower than the yield stress and they will be closed and the flow will be realized preferentially by high permeability streaks, which is the aim of the profile modification. If $\tau_w > \tau_0$, the gel at the capillary's walls will be destroyed. The core of the gel will move as a solid cylinder, surrounded by a ''lubricant,'' the liquid, into which the destroyed gel was converted.

Figures 12 and 13 show that the yield stresses and the moduli of elasticity of the completely gelled solutions are different with distilled water and artificial seawater used as a solvent. Most probably this is due to the very different ionic strength. At complete gelation for 0.2% w/w xanthan gum in distilled water, yield stress is more than 1200 Pa. Gels with xanthan gum concentration 0.05% w/w can posses yield stress of 110 Pa. Even if the gelation is far from complete, yield stresses of several tens of Pa are created.

Accepting the important role of the yield stress for the profile modification of the flow through porous media, different possibilities exist for improving the efficiency in practice.

CONCLUSIONS

The present work has shown how the gelation process of xanthan gum with Cr^{3+} ions can be investigated by the control deformation test with a HAAKE VT 550 viscotester. The obtained results present complementary information to the rheological experiments done earlier, conducted by oscillatory rheometry (G' and G'') and viscometry (basic rheological curve). They can be useful for further clarifying of the gelation mechanism of xanthan gum with the trivalent ions of Cr, Al, and Fe. An assumption was made that the gel's yield stress is the main reason for the profile modification of the flow in porous media and even for the closing of the smaller capillaries. The results could be useful for enhanced oil recovery.

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