

Viscoelastic properties of a high temperature cross-linked water shut-off polymeric gel

Ghaithan A. Al-Muntasheri^a, Ibelwaleed A. Hussein^{b,*},
Hisham A. Nasr-El-Din^a, Mohamed B. Amin^b

^a *Research and Development Center, Saudi Aramco, Dhahran 31311, Saudi Arabia*

^b *Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

Received 23 April 2005; accepted 26 April 2006

Abstract

This is the first published study that investigates the viscoelastic properties of an organically cross-linked polymeric gel used in water shut-off treatments. A copolymer of acrylamide and *t*-butyl acrylate was cross-linked with polyethylene imine. The effects of various parameters on the rheological properties of the gel were addressed. Experimental results indicated that the storage modulus of the gel decreases with the increase in the salinity of mixing water. Also, higher gel elastic modulus was obtained at higher cross-linker concentrations. A highest elastic modulus of 3.4 kPa was obtained for a gel with a composition of 7 wt.% polymer and 1.2 wt.% cross-linker. However, syneresis was observed in gel samples with 1.2 wt.% cross-linker concentration. The gel lost 53% of its elastic modulus after 1 month of ageing at 150 °C. Based on the trends noted with the elastic modulus, two different mechanisms for gel formation were identified below and above 100 °C.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Water shut-off; Organic cross-linker; Polyacrylamide gels; Improved oil recovery; Viscoelasticity

1. Introduction

Polymeric gels are obtained by cross-linking high and/or low molecular weight polymers with a suitable cross-linker. These materials exhibit a wide range of rheological properties. This makes polymeric gels suitable for a variety of applications including controlled drug recovery, soft contact lenses and gelatin foods (Kesavan and Prud'homme, 1992). In the oil industry, larger water handling facilities are needed

when water cut in the produced oil and gas increases. This may reach to a level where production from a certain well is no longer feasible. Gels are utilized to minimize water production. They are injected as a solution and then cross-linked at reservoir conditions into a 3-dimensional (3-D) structure. This 3-D structure should be stable at high reservoir temperatures and pressure gradients.

Cross-linked partially hydrolyzed polyacrylamides (PHPA) gels are the most widely applied type of polymeric gels. They can be cross-linked either organically or inorganically. Organically cross-linked polymers are known to have a higher thermal stability (Moradi-Araghi, 2000). Rheological testing of water

* Corresponding author. Tel.: +966 3 860 2235; fax: +966 3 860 4234.

E-mail address: ihussein@kfupm.edu.sa (I.A. Hussein).

shut-off gels was reported in the literature from two aspects. The first aspect is the study of kinetics in which the time needed to form the 3-D structure is measured; hence, gelation parameters such as gelation time and activation energy are extracted. This is achieved by performing either steady (Broseta et al., 2000; Vasquez et al., 2005; Al-Muntasheri et al., submitted for publication) or dynamic shear measurements (Prud'homme et al., 1983; te Nijenhuis et al., 2003; Romero-Zeron et al., 2004). The second aspect is the measurement of the gel elasticity (after gel formation) that is related to the gel cross-link density (Laurent et al., 1980; Pearson and Graessley, 1980; Prud'homme and Uhl, 1984):

$$G' = G'_{en} + qBTN \quad (1)$$

where G' is the elastic modulus (Pa), G'_{en} is the elasticity due to temporary chains entanglement (Pa), N is the cross-link density (mol/m^3), B is the Boltzmann constant (J/K), T is the temperature (K) and q is a constant between 0.4 and 1 (1/mol).

A copolymer of acrylamide and *t*-butyl acrylate (PATBA) cross-linked with polyethylene imine (PEI) was used in the present study. This system is reported to be stable at high temperatures (Hardy et al., 1998). The first field application of this system was on a fractured chalk reservoir with a temperature of 130 °C (Hardy et al., 1999). It was also successfully applied in fractured carbonaceous reservoirs with temperatures up to 129 °C and in sandstone reservoirs with temperatures of 82 °C (Polo et al., 2004). Experimental investigation of this system was previously reported in literature. Hoek et al. (2001), conducted core flooding experiments with this gel and a reduction in permeability was achieved. They reported that the displacement of the gel from the porous medium started when the applied pressure drops exceeded a critical pressure. This critical pressure is the pressure at which the gel starts yielding. When the permeability of the cores (porous rock) is high, lower pressure drops are needed to yield the gel. At low polymer concentrations, no polymer adsorption on the cores was observed. These observations were reported for sandstone cores with clay content ranging from 0.9 to 7.3 wt.%.

Alqam et al. (2001) tested the ability of this gel to reduce permeability of fractured cores. Their results on carbonate cores showed a reduction in permeability from 2,116 to 0.135 mD at 93 °C (200 °F) and 24.15 MPa (3500 psi). In their study, the brine permeability was reported to decrease with time for the first 6 days after treating the core with this gel. Zitha et al. (2002) performed theoretical analysis of the yield

behavior of PATBA/PEI gels. Their study focused on the displacement of the gel from the porous media as a three-stage process. The first stage included compression of the porous medium and the gel. During this stage, the pressure at the inlet of the core increases linearly with time at a constant flow rate. The second stage was the microscopic flow within the gel system before the yield point. Finally, the third stage includes macroscopic flow beyond the yield point during which gel displacement occurs. Their theoretical work was compared to the experimental data of Hoek et al. (2001). They showed that the critical yield stress scales with the square root of the energy of the cross-links, which is represented mathematically as follows:

$$P_c \sim \sqrt{\frac{X\varepsilon YL}{R^2}} \quad (2)$$

where P_c is the critical yield pressure (Pa), X is the number of cross-links in a gel sample(-), ε is the energy needed to break a single crosslink (J), Y is the Young modulus (Pa), L is the cylindrical pore length (m) and R is the cylindrical pore radius (m). Eqs. (1) and (2) indicate that the gel strength is directly proportional to the elastic modulus obtained from oscillatory rheological measurements. Hence, elastic storage modulus measurements can be used to qualitatively describe the effect of various parameters on gel elasticity and hence its strength.

A review of the literature on the rheological testing of water shut-off gels showed that most of previous work focused on PHPA cross-linked with chromium (Han et al., 1996; Kakadjian et al., 1999; Liu and Seright, 2000; te Nijenhuis et al., 2003). To the best knowledge of the authors, this is the first attempt to examine the viscoelastic properties of organically cross-linked water shut-off polymers. Therefore, the objective of the present study is to examine the effect of temperature, gel composition, gel age and salinity of mixing water on the viscoelastic properties of mature gels.

2. Dynamic Mechanical Analysis (DMA)

In the DMA technique, a sinusoidal shear strain (or shear stress) is applied and the resulting stress (or strain) is measured. These oscillatory measurements were used to monitor the gelation without affecting the 3-D structure of the gel (Prud'homme et al., 1983; Macosko, 1994). In controlled strain tests, the governing equation of applied strain, γ , is

$$\gamma = \gamma_0 \sin(\omega t) \quad (3)$$

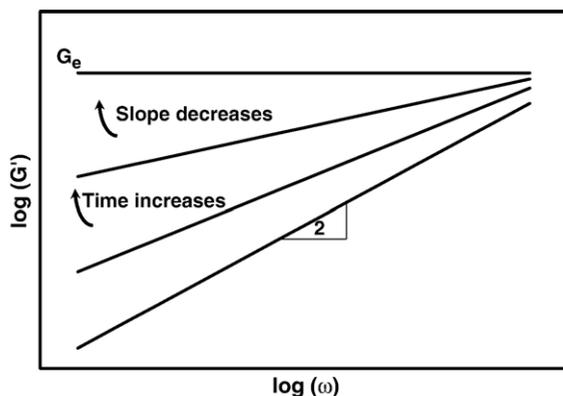


Fig. 1. Gradual formation of gel network followed by frequency sweeps.

where γ_0 is the applied strain amplitude while ω is the frequency of the strain wave.

The measured stress, τ , is described by:

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (4)$$

where the phase angle, δ , is zero for an elastic solid and 90° for a Newtonian fluid. Hence, whenever the tested material is viscoelastic, the phase angle will lie between zero and 90° . In the case of controlled stress tests, stress is applied and the strain is then measured. The expressions for the applied stress and the measured strain in this case are similar to Eqs. (3) and (4), respectively. The mathematical analysis of the produced wave is well known and results in the elastic modulus, G' , and the loss modulus, G'' , which are related through the following equation:

$$\tan(\delta) = \frac{G''}{G'} \quad (5)$$

At the beginning of forming a cross-linked network, the slope of $\log G'$ vs. $\log \omega$ is 2 and then it starts to decrease until G' becomes a very weak function of ω and reaches a plateau value, G_e , as shown in Fig. 1 (te Nijenhuis, 1996). It should be mentioned that the value of 2 originates from the fact that the system starts

Table 1
Properties of the polymer and the cross-linker

Variable	Polymer	Cross-linker
Molecular weight, g/mol	250,000–500,000	70,000
pH	4	12
Density, ^a g/cm ³	1.06	1.05
Active content, wt.%	20	30

^a Measured at room temperature.

Table 2
Chemical analysis of field water

Variable	Value
Ca ^a	126
Mg	53
Na	228
K	14
Cl	361
SO ₄	233
CO ₃	171
TDS ^b	1,186
pH	7.8

^a Ion concentrations are expressed in mg/l.

^b TDS is determined by addition.

initially as a liquid-like material where G' scales with ω^2 at low frequency ranges (Macosko, 1994).

3. Experimental studies

3.1. Materials

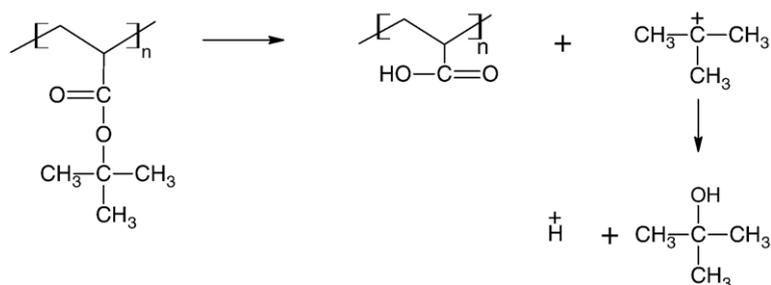
Properties of the polymer and the cross-linker are shown in Table 1. Field water was filtered using 0.22 μm filter papers. Results of chemical analysis of this water are given in Table 2. The active content of the polymer and the cross-linker was measured by TGA as 20 and 30 wt.%, respectively. In order to examine the effect of individual cations on the final gels elasticity, laboratory brines were prepared by dissolving the needed amounts of salts in deionized water such that the final gelling solutions contained 5000 mg/l of Na and K (row 5 of Table 3). KCl and NaCl salts were used to prepare synthetic brines. All salts were ACS grade. Filtered field water was used to prepare all gelling solutions, unless otherwise stated.

3.2. Procedure

Gelling solutions were prepared at room temperature. All solutions were prepared by adding the polymer to the mixing water while applying gentle stirring. Then, the cross-linker was added in drops and stirring was

Table 3
Range of parameters examined

Parameter	Range
Temperature	100–150 °C
Polymer concentration	3–7 wt.%
Cross-linker concentration	0.3–1.2 wt.%
TDS of mixing water	0 and 1186 mg/l
Na and K concentrations in synthetic brines	0 and 5000 mg/l
Gel age	0.5–30 days



where n = Number of repeating units of t-butyl acrylate groups on the copolymer chain

Fig. 2. Hydrolysis of PATBA at low pH and low temperature.

continued fast enough to avoid formation of micro gels but without entrapping air bubbles. Then, the sample (30 mL in volume) was transferred to a high temperature/high pressure cell. After the sample loading, nitrogen gas was used to pressurize the system to 3.45 MPa (500 psig). After that, heating started through a surrounding electrical tape for 12 h. The temperature was kept constant using a temperature controller. Samples were given at least 12 h to cure. Previous work (Al-Muntasheri et al., submitted for publication) ensured that the gelation time of all formulations examined in this paper is well less than 12 h at all temperatures examined. Hence, all tests were performed on already gelled samples with the same thermal history except for the case where the temperature is the parameter under investigation. In that case, all parameters are fixed and temperature was varied. Table 3 gives the range for each parameter investigated in this study.

3.3. Instrument

All rheological measurements were performed in a controlled strain ARES rheometer equipped with a force rebalance transducer (0.002–100 Nm torque). This machine is not equipped with a high pressure cell

allowing measurements at high temperatures. Hence, gels had to be cured in an external high temperature/high pressure cell. Then, cured samples were transferred to the rheometer and tests were conducted at room temperature (23.5 °C). If these experiments were done at higher temperatures and pressures, the measured quantities may have increased. Frequency sweep tests were performed in the range of 0.1 to 100 rad/s using a 25 mm diameter cone and plate geometry. The cone angle was 1° and the truncated gap was 48 μm. Gelled samples were placed on the lower cone and the upper plate was brought slowly to the 48 μm gap. Dynamic measurements were performed at 5% strain at which the material response of all gels was in the linear viscoelastic range following separate strain sweep tests.

3.4. Gelation mechanism

Some aspects of the cross-linking chemistry of the PATBA/PEI system were reported previously in the literature (Morgan et al., 1997; Hardy et al., 1998, 1999; Reddy et al., 2003). Hence, a brief summary will be presented in this section. The ester groups (R–COO–R') on the PATBA polymer provide masked cross-linking sites. These groups either hydrolyze or thermolyse according to pH and temperature. At conditions of low

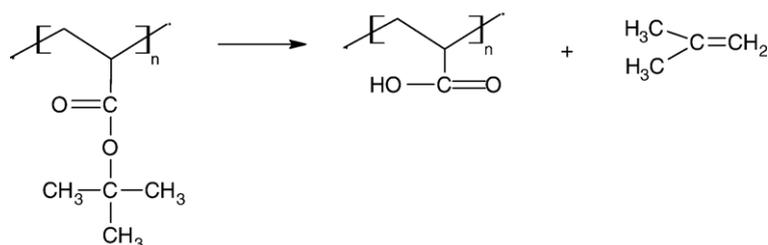


Fig. 3. Thermolysis of PATBA at high pH and high temperature.

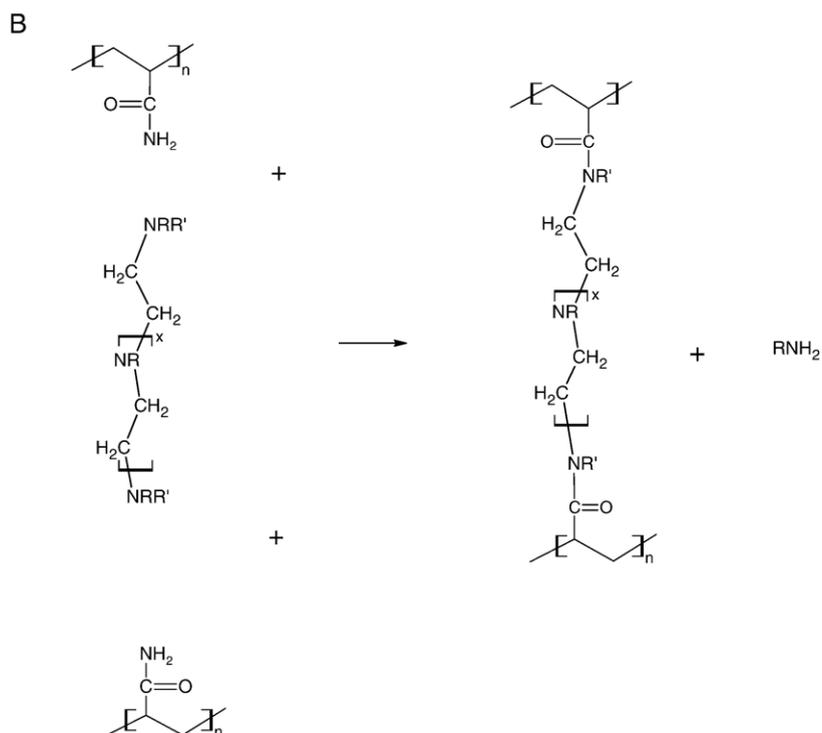
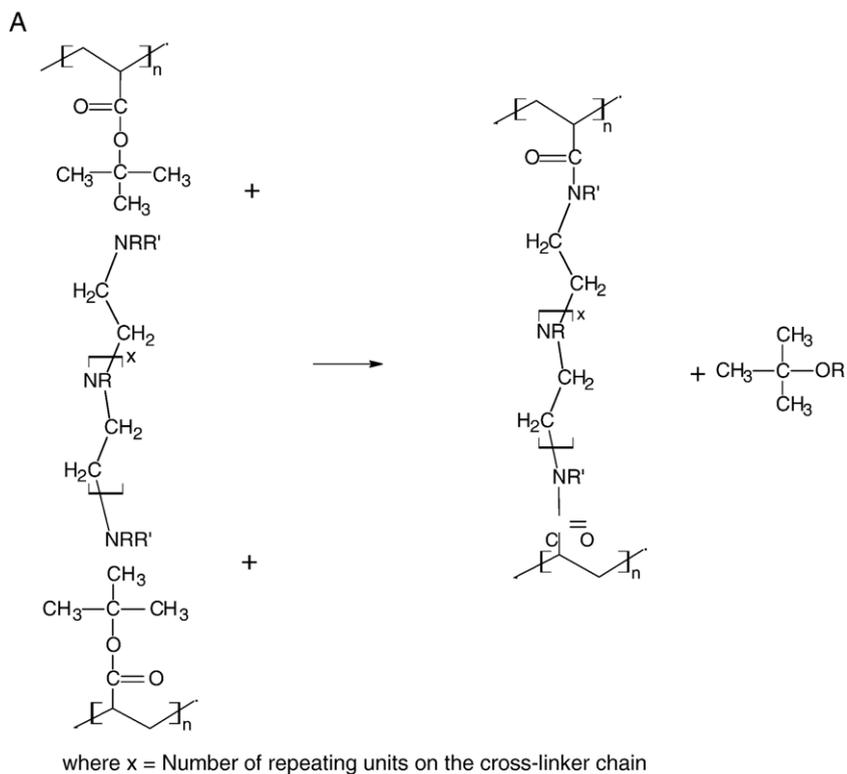


Fig. 4. (A) Cross-linking of PATBA with PEI at temperatures less than 100 °C and reaction times shorter than 20 h. (B) A second mechanism for cross-linking reaction.

pH and temperature, the copolymer hydrolyzes and forms partially hydrolyzed polyacrylamide (PHPA) and *t*-butyl alcohol (Fig. 2). On the other hand, the copolymer thermolyses at high temperatures and pH conditions producing PHPA and isobutene as shown in Fig. 3. After the breakage of the ester groups, carboxylate groups are formed. Hardy et al., 1999 reported the cross-linking mechanism of this system as a nucleophilic attack by an imine nitrogen from the PEI on the carbonyl carbon attached to the ester. That should result in a covalent bond as shown in Fig. 4A. However, this mechanism can only govern the gelation of this system at temperatures less than 100 °C for reactions taking place in less than 20 h. Hardy et al., 1999 showed that these conditions (temperatures below 100 °C and reaction times less than 20 h), ensured that the cross-linking reaction took place only through this pathway shown in Fig. 4A. We noticed the formation of thermally stable gels at temperatures up to 150 °C, which is in agreement with what was reported earlier (Hardy et al., 1999). Hence, indicating a different mechanism of covalent bonding resulting in gel formation. The only different mechanism reported in the literature is the one proposed by Reddy et al., 2003. Namely, where PEI attacks the carbonyl carbon attached to the amide group as shown in Fig. 4B. The mechanism governing this reaction at these high temperatures is beyond the scope of this paper and will be addressed in future publications.

4. Results and discussion

4.1. Effect of polymer concentration

Fig. 5 shows the elastic modulus, G' , measured in the frequency range $\omega=0.1$ –100 rad/s for gelled samples containing polymer concentrations of 3 to 7 wt.%. In

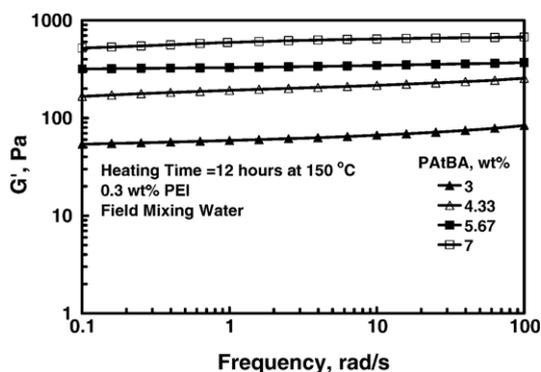


Fig. 5. Frequency sweeps for gel samples with different polymer concentrations.

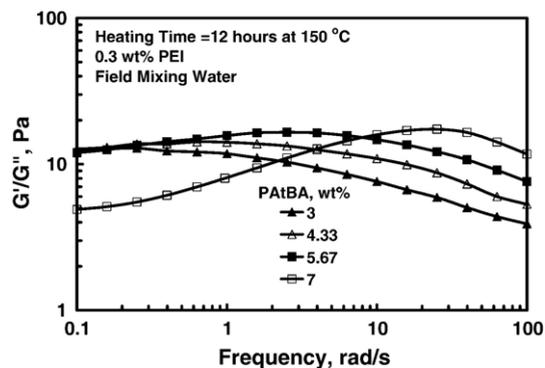


Fig. 6. G'/G'' data as a function of frequency for samples with different polymer concentrations.

order to simulate field conditions, filtered field water was used to prepare the gelling solutions. All samples contained the same amount of cross-linker (0.3 wt.%) and were subjected to the same thermal history (12 h of heating at 150 °C). From Fig. 5, three important notes can be made. The first is that all slopes of $\log G'$ vs. $\log \omega$ were less than 2 indicating the formation of a cross-linked network for all the four samples. The second note is that G' values were larger than G'' over the whole ω range as shown in Fig. 6. The third observation is that G' showed very weak dependency on ω over the range 0.1–10 rad/s and reached a plateau modulus at $\omega < 1$ rad/s. The plateau modulus is concentration dependent. These observations confirm the formation of a gel network of rubbery nature (Michon et al., 1993; Macosko, 1994; te Nijenhuis, 1996). A similar behavior was previously reported by other researchers for polymeric gels used for water shut-off treatments (Prud'homme et al., 1983; Thurston et al., 1985; Kakadjian et al., 1999; Liu and Seright, 2000; Grattoni et al., 2001).

From Fig. 5, in general, gels with higher polymer concentrations exhibited higher values of G' . The sample with the highest polymer concentration produced the highest G' value (500–700 Pa depending on ω). It should be mentioned that this is the first value reported for organically cross-linked polyacrylamide copolymers. Previous studies reported data for inorganically cross-linked systems only (Thurston et al., 1985; Kakadjian et al., 1999; Liu and Seright, 2000).

The ratio of G'/G'' for the above mentioned samples is given in Fig. 6. At low ω , G' is generally higher than G'' by a factor of 10. The unusual trend for the 7 wt.% polymer sample in Fig. 6 is due to the different trend of G'' at low ω (see Fig. 7) at this polymer concentration. This indicates the presence of more free coils (uncross-linked chains), which increases the viscous contribution

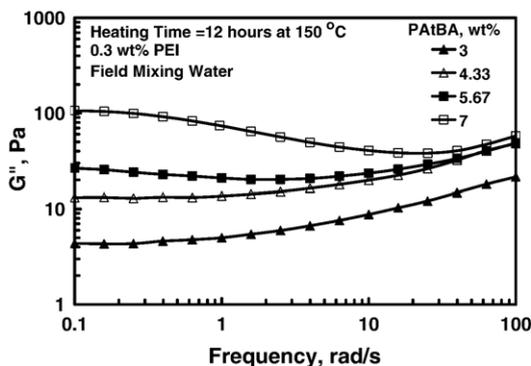


Fig. 7. Effect of polymer concentration on loss modulus.

of the sample. This is likely due to the consumption of the cross-linker which acts as the limiting reactant at such high polymer concentrations. Also, results of Fig. 6 suggest that the quantity G'/G'' is frequency independent at low ω for polymer concentrations up to 5.67 wt.%. At 3 wt.% polymer concentration, G' values were significantly lower than the 4.33 wt.% case unlike other samples with 7 and 5.67 wt.% polymer concentrations. This result suggests that the intensity of cross-links is the lowest at this level of polymer concentration. At the same time, G'' showed a different dependency on ω as shown in Fig. 7.

Fig. 8 shows the equilibrium elastic modulus, G_e , and G'' as a function of polymer concentration extracted from Figs. 5 and 7, respectively. G_e is defined as the plateau modulus. There is a strong dependence of both G_e and G'' on polymer concentration. Both G_e and G'' followed the form $[G = a \exp(bx)]$ where x is the polymer concentration in wt.%, a and b are constants. A similar behavior of G' and G'' vs. concentration was observed in inorganically cross-linked polyacrylamides (Grattoni et al., 2001).

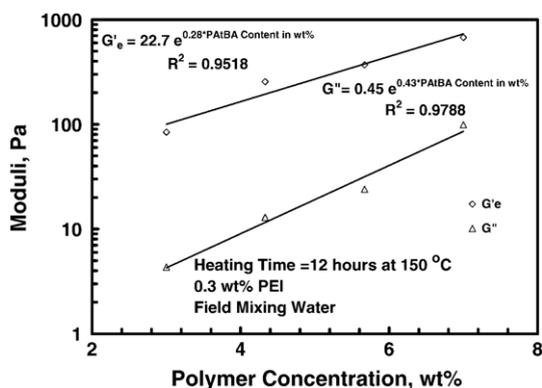


Fig. 8. Equilibrium storage modulus and loss modulus as a function of polymer concentration ($\omega = 0.25$ rad/s).

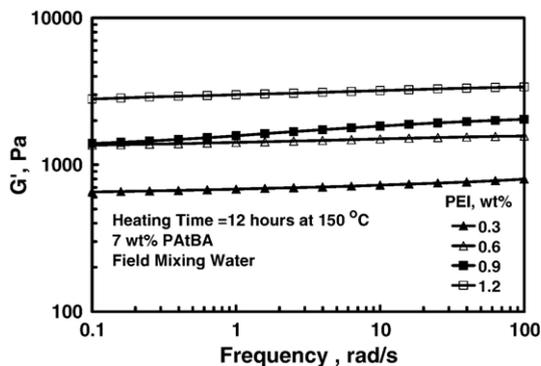


Fig. 9. Effect of cross-linker concentration on elastic modulus.

4.2. Effect of cross-linker concentration

Fig. 9 shows storage modulus as a function frequency for samples with different cross-linker concentrations. Namely, PEI contents of 0.3, 0.6, 0.9 and 1.2 wt.% were used. Samples were prepared according to the procedure outlined in the experimental section. The polymer concentration was kept constant at 7 wt.%. All data were typical of rubbery like materials since G' values were independent of ω over a wide range of ω . Clearly, addition of cross-linker results in a proportional increase in the gel elastic nature. No drop in modulus as a function of PEI concentration was observed. This supports our previous hypothesis that PEI was the limiting reactant when PEI and the polymer were used at 0.3 wt.% and 7% concentrations, respectively. Values of G_e were extracted from Fig. 9 and then fitted in Fig. 10. Hence, the influence of polymer concentration on G_e discussed earlier is similar to that of cross-linker on G_e . However, proper ratios should be adjusted according to the available cross-linking sites in the polymer and the active sites in the cross-linker.

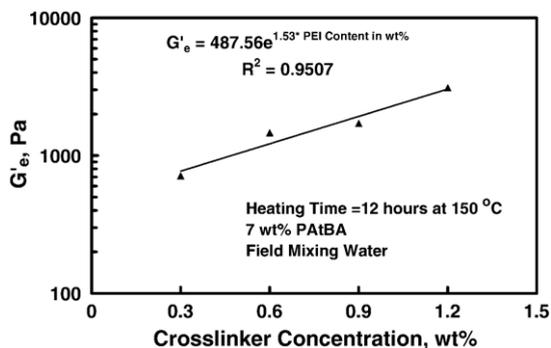


Fig. 10. Equilibrium storage modulus as a function of cross-linker concentration.

Nevertheless, too much cross-linker can lead to syneresis. Syneresis is defined as repulsion of water out of the gel structure due to shrinkage in gel volume. This reduction in gel volume was suggested by some researchers (Moradi-Araghi and Doe, 1984). We visually observed that the sample with the highest cross-linker content (1.2 wt.%) exhibited syneresis. Then, the liquid was discarded and the gel structure was tested. The maximum G' value was 3.4 kPa measured for the sample with the 1.2 wt.% cross-linker. This is more than four times larger than G' for the 0.3 wt.% polymer sample. It is important to note that syneresis was found to enhance the gel permeability reduction in porous media in certain instance (Eggert et al., 1992; Bryant et al., 1996). Since G' is qualitatively proportional to the expected yield behavior of the gel, the significant increase in G' for the syneresis sample (1.2 wt.%) explains the extra permeability reduction in cores. That is syneresis results in extra elasticity which in turn gives more permeability reduction. However, additional work is needed to correlate yielding behavior to quantitatively relate the yield behavior in porous media to the elastic storage modulus obtained from rheometry.

4.3. Effect of gel age

Fig. 11 shows the storage modulus as a function of frequency for samples containing 7 wt.% polymer and 0.3 wt.% cross-linker prepared in field mixing water aged at 150 °C. The ageing time (time during which the gelling solution was kept at 150 °C), was varied from 12 h to 1 month. From Fig. 11, it can be seen that there is a 53% loss of the gel storage modulus after heating for 1 month. The storage modulus reached a plateau of 250 Pa (at $\omega=0.25$) after 1 month of heating. The gel has almost stabilized at this value in the first 4 days. This value is still higher than what was previously published

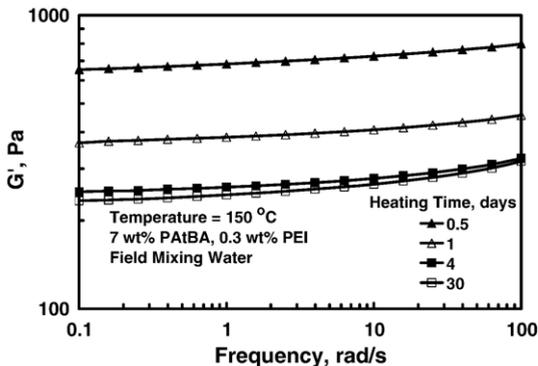


Fig. 11. Frequency sweeps for gel samples with different gel ages.

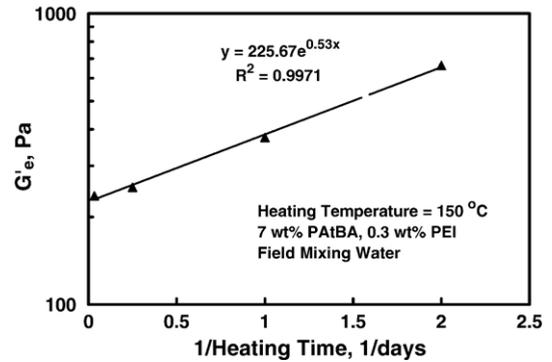


Fig. 12. Equilibrium storage modulus as a function of gel age.

for gels formed by using inorganic cross-linkers (Prud'homme et al., 1983; Thurston et al., 1985; Kakadjian et al., 1999 Grattoni et al., 2001; Liu and Seright, 2000). Moreover, data shown in Fig. 11 after 1 month of heating still shows a typical cross-linked network behavior. The effect of gel age on the equilibrium storage modulus is fitted in Fig. 12. It should be mentioned that this system was reported to have good permeability reduction on sandstone cores even after heating treated cores for more than 2 months at 177 °C (350 °F) (Vasquez et al., 2003). That indicates that the 250 Pa might be still more than the G' corresponding to the critical yield pressure in porous media.

4.4. Effect of gelation temperature

Four gelling solutions were prepared using field mixing water with 7 wt.% polymer, 0.3 wt.% cross-linker and aged for 12 h. The ageing temperatures were 100, 120, 130 and 150 °C. The elastic modulus increased with the increase in temperature as shown in Fig. 13. One possible explanation for this observation is the increase in the formation of cross-links due to the

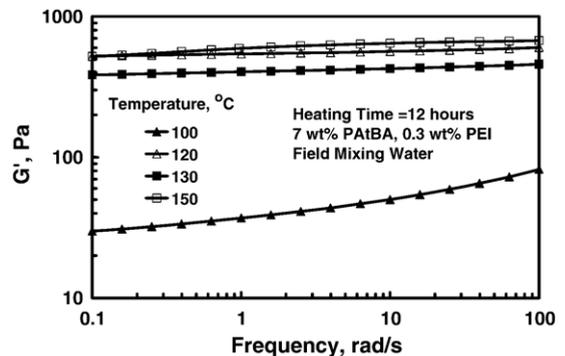


Fig. 13. Effect of temperature on elastic modulus.

increase of molecular mobility or formation of new cross-linking sites due to chemical reactions. It should be noted that the elastic modulus increased by almost a factor of 6 upon heating from 100 to 120 °C. This indicates that the cross-linking intensity at 100 °C is significantly lower than that at 120 °C. A possible explanation for this trend is the existence of different gelation mechanism at these two temperatures (120 °C and 100 °C). That is likely the thermolysis of the ester group on the copolymer chain that takes place at high temperatures (Hardy et al., 1998). Our results suggest that this temperature is likely between 100 °C and 120 °C. Therefore, at 100 °C the bulky *t*-butyl group hinders the cross-linking reaction and hence there will be less cross-linking sites on the PATBA backbone. In other words, for the same period of time, there were less cross-links at temperatures of 100 °C and below. On the other hand, at 120 °C, the breakage of the ester group created more accessible sites for cross-linking. Also, the high temperature increases the hydrolysis rate of the available amide groups giving rise to more cross-linking sites and therefore. It should be mentioned that the slope of $\log G'$ vs. $\log \omega$ for the sample heated at 100 °C is ~ 0.1 which is still well below 2 indicating the formation of a gel structure at that lower temperature. Zitha et al. (2002) have shown that the pressure drop during the compression of this system in sandstone cores shows significant increase when the gel is cured inside treated cores at 120 °C. However, their results at curing temperatures of 100° and 80 °C the pressure drops were significantly lower. These observations from measurements in porous media are consistent with the trends of our G' measurements in a rheometer.

This observation was also noted in another work by our group (Al-Muntasheri et al., submitted for publication). We suggested that the temperature at which the ester group broke was below 100 °C and higher than 80 °C in the presence of shearing (8.5 s^{-1}). The breakage of the ester group at a higher temperature in this case is likely due to the absence of shear during the gelation reaction. Hence, shear could have either enhanced the mobility of cross-linkable sites or induced thermo-mechanical degradation of the ester group as observed for other polymers (Hussein et al., 2000).

4.5. Effect of salinity

Gelling polymers are prepared in field mixing waters, seawater or fresh water. Therefore, it is important to examine the effect of salts on the final viscoelastic properties. In order to examine the effect of different

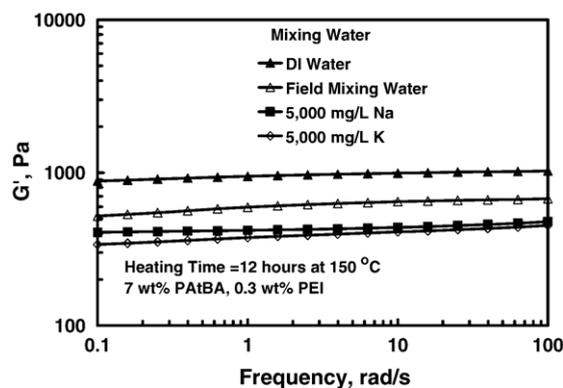


Fig. 14. Effect of salinity of mixing water on equilibrium elastic modulus.

cations on the elastic behavior of this system, samples containing different amounts of salts were prepared. Fig. 14 shows frequency sweeps for samples containing 7 wt.% PATBA and 0.3 wt.% PEI prepared in various saline waters. It is clear that samples prepared in deionized water had the maximum storage modulus. Adding salts may have resulted in shrinkage of the polymer chain or masked the cross-linking sites. Consequently, the number of active cross-linking sites decreased and thus the intensity of cross-links was lowered. It should be noted that field mixing water had a lower equilibrium elastic modulus, 675 Pa, than the deionized water case (1025 Pa). Therefore, the influence of salts on the elasticity of gels is negative.

5. Conclusions

1. The elastic modulus of the organically cross-linked gel examined was found to be higher than the previously reported values for inorganically cross-linked gels used in water shut-off systems.
2. The elastic modulus showed substantial increase when the gel was heated at temperatures higher than 100 °C proposing different reaction pathways leading to higher cross-linking; hence, elasticity.
3. Both G_e and G'' showed an exponential dependence on polymer concentration while only G' showed the same dependence on cross-linker concentration.
4. The elastic modulus increased by a factor of 4.8 upon increasing the cross-linker concentration by a factor of 4 (from 0.3 to 1.2 wt.%). However, syneresis was noticed with the samples of 1.2 wt.% PEI.
5. Low elastic moduli were noted when the salinity of mixing water was increased.
6. G_e decayed at 150 °C with gel age; hence a fast decrease in elasticity was observed.

Acknowledgments

The authors would like to acknowledge KFUPM and Saudi Aramco for their support and permission to publish this work. Mr. Dalrymple, Halliburton, is highly acknowledged for the many useful discussions. Thanks are also due to Mr. Ali Al-Amri who conducted a portion of the experimental work presented in this paper. The Analytical Support Division of the R and DC at Saudi Aramco is appreciated for the analysis of mixing waters and for conducting TGA tests.

References

- Al-Muntasheri, G.A., Nasr-El-Din, H.A., Hussein, I.A., submitted for publication. A rheokinetic study of an organically cross-linked polymeric gel used for water shut-off. *J. Pet. Sci. Eng.*
- Alqam, M.H., Nasr-El-Din, H.A., Lynn, J.D., 2001. Treatment of super k-zones using gelling polymers. Paper SPE 64989, presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, TX, February 13–16.
- Broseta, D., Marquer, O., Blin, N., Zaitoun, A., 2000. Rheological screening of low-molecular-weight polyacrylamide/chromium (III) acetate water shutoff gels. Paper SPE 59319 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, OK, pp. 3–5.
- Bryant, S.L., Rabaioli, M.R., Lockhart, T.P., 1996. Influence of syneresis on permeability reductions by polymer gels. *SPE Prod. Facil. J.* 209–215.
- Eggert, R.W., Willhite, G.P., Green, D.W., 1992. Experimental measurement of the persistence of permeability reduction in porous media treated with Xanthan/Cr (III) gel systems. *Soc. Pet. Eng. Res. Eng.* 29–42.
- Grattoni, C.A., Al-Sharji, H.H., Yang, C., Muggeridge, A.H., Zimmerman, R.W., 2001. Rheology and permeability of cross-linked polyacrylamide gel. *J. Colloid Interface Sci.* 240, 601–607.
- Hardy, M.B., Botermans, C.W., Smith, P., 1998. New organically cross-linked polymer system provides competent propagation at high temperatures in conformance treatments. Paper SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, OK, pp. 19–22.
- Hardy, M.B., Botermans, C.W., Hamouda, A., Valda, J., John, W., 1999. The first carbonate field application of a new organically cross-linked water shutoff polymer system. Paper SPE 50738 presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, pp. 16–19.
- Han, M., Shi, L., Ye, M., Guo, Q., 1996. Characterization of viscoelastic properties of polyacrylamide/Cr(III) hydrogels. *Polym. Bull.* 36 (4), 483.
- Hoek, V., Botermans, C.W., Zitha, P.L.J., 2001. Full blocking mechanism of polymer gels for water control. Paper SPE 68982 presented at the SPE European Formation Damage Conference held in The Hague, The Netherlands, pp. 21–22.
- Hussein, I.A., Kam, H., Goyal, S.K., Karbasheski, E., Williams, M. C., 2000. Thermomechanical degradation in the preparation of polyethylene blends. *Polym. Degrad. Stab.* 68 (3), 381–392.
- Kakadjian, S., Raueo, O., Mejias, F., 1999. Dynamic rheology as a method for quantify gel strength of water shutoff systems. Paper SPE 50751 presented at the International Symposium on Oilfield Chemistry held in Houston, TX, pp. 16–19.
- Kesavan, S., Prud'homme, R.K., 1992. Rheology of guar and HPG cross-linked by borate. *Macromolecules* 25, 2026–2032.
- Laurent, J.-L., Janmey, P.A., Ferry, J.D., 1980. Dynamic viscoelastic properties of gelatin gels in glycerol–water mixtures. *J. Rheol.* 24 (1), 87–98.
- Liu, J., Seright, R.S., 2000. Rheology of gels used for conformance control in fractures. Paper SPE 59318 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, April 3–5, 2000.
- Macosko, C.W., 1994. *Rheology: principles, measurements and applications*. Wiley-Vch, New, pp. 175–378.
- Michon, C., Cuvelier, G., Launary, B., 1993. Concentration dependence of the critical viscoelastic properties of gelatin at gel point. *Rheol. Acta* 32, 94.
- Moradi-Araghi, A., Doe, P., 1984. Stability of polyacrylamides in hard brines at elevated temperatures. Paper SPE 13033 presented at the 59th Annual SPE Conference and Exhibition, Houston, TX, pp. 16–19.
- Moradi-Araghi, A., 2000. A review of thermally stable gels for fluid diversion in petroleum production. *J. Pet. Sci. Eng.* 26, 1–10.
- Morgan, J.C., Smith, P.L., Stevens, D.G., 1997. Chemical adaptation and deployment strategies for water and gas shut-off gel systems. Paper presented at the Royal Chemistry Society's Chemistry in the Oil Industry 6th International Symposium, Ambleside, UK, pp. 14–17.
- Pearson, D.S., Graessley, W.W., 1980. Elastic properties of well-characterized ethylene–propylene copolymer networks. *Macromolecules* 13, 1001–1009.
- Polo, R.P.O., Monroy, R.R., Toledo, N., Eoff, L., Everett, D., 2004. Field applications of low molecular-weight polymer activated with an organic cross-linker for water conformance in South Mexico. Paper SPE 90449 presented at the SPE Annual Technical Conference and Exhibition held in Houston, TX, pp. 26–29.
- Prud'homme, R.K., Uhl, J., Poinsette, J.P., Halverson, F., 1983. Rheological monitoring of the formation of polyacrylamide/Cr⁺³ gels. *SPE* 804–808.
- Prud'homme, R.K., Uhl, J., 1984. Kinetics of polymer/metal-ion gelation. Paper SPE 12640 presented at the SPE/DOE Fourth Symposium on Enhanced Oil Recovery held in Tulsa, OK, pp. 15–18.
- Reddy, B.R., Eoff, L., Dalrymple, E.D., Black, K., Brown, D., Rietjens, M., 2003. A natural polymer-based cross-linker system for conformance gel systems. *SPE J.* 99–106, June.
- Romero-Zeron, L., Manalo, F., Kantzas, A., 2004. Characterization of cross-linked gel kinetics and gel strength using NMR. Paper SPE 86548 presented at the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, pp. 18–20.
- te Nijenhuis, 1996. Calculation of network parameters in thermo-reversible gels. *Polym. Gels Netw.* 4, 415–433.
- te Nijenhuis, K., Mensert, A., Zitha, P.L.J., 2003. Viscoelastic behavior of partly hydrolyzed polyacrylamide/chromium(III) gels. *Rheol. Acta* 42, 132–141.
- Thurston, G.B., Ozon, P.M., Pope, G.A., 1985. The viscoelasticity and gelation of some polyacrylamide and Xanthan gum solutions. Paper SPE, unsolicited.
- Vasquez, J., Civan, F., Shaw, T.M., Dalrymple, E.D., Eoff, L., Reddy, B.R., Brown, D., 2003. Laboratory evaluation of high-temperature conformance polymer systems. Paper SPE 80904 presented at the

- SPE Production and Operations Symposium held in Oklahoma City, OK, USA, pp. 22–25.
- Vasquez, J., Dalrymple, E.D., Eoff, L., Reddy, B.R., Civan, F., 2005. Development and evaluation of high-temperature conformance polymer systems. Paper SPE 93156 presented at the SPE International Symposium on Oilfield Chemistry held in Oklahoma City, OK, pp. 2–4.
- Zitha, P.L.J., Botermans, C.W., v.d. Hoek, J., Vermolen, F.J., 2002. Control of flow through porous media using polymer gels. *J. Appl. Phys.* 92 (2), 1143–1153.