Potential Applications of Poly(vinyl alcohol)-Congo Red Aqueous Solutions and Hydrogels as Liquids for Hydraulic Fracturing

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ABSTRACT: The authors report on the viscoelastic characterization of guar hydrogels obtained through complexation reactions with borax ions. These gels are compared with hydrogels obtained from poly(vinyl alcohol) of different degree of hydrolysis through complexation reactions with congo red. The effect of the degree of hydrolysis and both, the concentration of PVA and the concentration of congo red, on the viscoelastic properties of the hydrogels is analyzed. The potential use of the PVA-based hydrogels as hydraulic fracturing liquids is discussed in relation to the commonly used fracturing liquid based on the guar–borax system. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 695–700, 2008

Key words: PVA; guar; hydrogels; viscoelastic properties; fracturing liquids

INTRODUCTION

Hydrogels have many applications in the industry.[1–4] One of the main usages is the suspension of solids in these systems to carry particles to specific sites, avoiding them to settle down.[5] In the particular case of hydraulic fracturing,[6–8] a fluid is used to create a fracture in a reservoir, and then to transport sand particles through the fractured formation. The sand particles, when placed and uniformly distributed in the fracture, keep it open after the fracturing treatment, allowing oil, gas, or soil contaminants to easily flow to the surface. Because of the importance of keeping the solids in suspension during their transport to the fracture site, an accurate design of the carrier fluid is critical for the success of a fracturing treatment.

A great variety of fracturing gels have been developed with many modifications,[9] always trying to adjust the gel properties to the needs found in field of fracturing liquids, that is, gels with sufficient viscosity to transport a propping agent and to resist temperature variations of reservoirs; that exhibit low friction pressure during pumping; that provide good fluid-loss control; and that break and clean up rapidly once the hydraulic treatment is over.

Guar gum suspensions crosslinked with borate ions are the most widely used fracture fluid systems available today.[6,10–13] These gels exhibit viscoelastic fluid characteristics. Guar is a natural polymer derived from the seed of the guar plant that has high affinity for water, however, it presents about 6–10% insoluble residues, therefore, guar gels can produce a reduction of rock permeability in the long run, due to the formation of insoluble residues in the rock pores.

The most important attribute of the guar polymer that allows its crosslinking with borate ions is the presence of a large amount of hydroxyl groups in its structure. The same structural feature is found in poly(vinyl alcohol). PVA is a polymer obtained from the hydrolysis of poly(vinyl acetate).[14–18] The degree of hydrolysis of the polymer determines its gelation properties. Stiff gels of PVA can be obtained from aqueous solutions of the polymer by addition of specific hydrogen bonding agents, as for example congo red.[19,20] This molecule is suitable to act as a crosslinking agent for PVA due to its rather linear and flat architecture, and the presence of azo and amino groups capable to form hydrogen bonds with the hydroxyl groups of the polymer. Complexation might lead to weak or strong gels depending on the concentration of polymer and crosslinking agent.

The objective of this work is to characterize the viscoelastic properties of a guar–borax hydrogel commonly used as fracturing liquid and to reproduce the same type of rheological behavior with a PVA-based hydrogel, trying to achieve the improvement of some properties of the fracturing fluid as the ability to suspend and transport the proppant agent and the reduction of polymer residue in the pore of the rocks due to the use of the fracturing liquid.

EXPERIMENTAL

Materials

PVAs with degree of hydrolysis 88 and 99% used in this study were kindly supplied by Erkol Industries (Spain). Congo Red and sodium tetraborate decahydrate were purchased from Aldrich, and Guar polymer was purchased from Sigma. All the products were used as received.

Borate crosslinked guar gel preparation

The Borate crosslinked guar gel was prepared by mixing 3.12 g of guar per 1 L of distilled water. The solution was allowed to hydrate for 1 h at room temperature under magnetic stirring. Then, the pH was adjusted to 11 with hydrochloric acid. After that, the sample was crosslinked with the appropriate amount of a 13 mg/mL borate crosslinker solution at room temperature.

Congo red crosslinked PVA gel preparation

Aqueous solutions of PVA of different hydrolysis degree were prepared under magnetic stirring at 100°C until complete dissolution of the polymer. After that, different amounts of a Congo red aqueous solution were added to obtain samples with different polymer-crosslinker ratios. After homogenization, the sample was allowed to gel at room temperature.

Viscoelastic measurements

Oscillatory viscoelastic measurements were performed in a TA Instruments AR1000 rheometer, using the 40 mm parallel-plate shear mode to measure the storage modulus, G', the loss modulus, G'' and the loss tangent, tan δ. To avoid the influence of aging on the moduli, all the measurements were performed 24 h after the gels were formed. Also, samples were thermostatized at the experimental temperature for 10 min (until stabilization is reached) prior to the beginning of the experiments. The operational conditions were as follows: temperature ramp from 10 to 80°C with a heat rate of 10°C/

min, frequency of 1 Hz and torque of 30 μN m. The linear viscoelasticity region was determined by means of torque sweeps between 0.1 and 100 μN m. Frequency sweeps from 0.01 to 100 Hz at 20 and 50°C were also performed. To avoid solvent evaporation, when the experiment was carried out at moderately high temperature, a solvent trap from TA Instruments was used.

To determine the gel point time, sweeps at a constant frequency of 1 Hz and 30 μN m of constant torque were performed.

RESULTS AND DISCUSSION

Guar–borax hydrogels

The rheological behavior of a typical hydraulic fracturing liquid system, consisting of a guar hydrogel of polymer concentration 30 mg/mL and borax concentration 30 mg/mL, is presented in Figure 1. Figure 1(a) shows the evolution of the storage and loss moduli as a function of the oscillation stress at 25°C and 1 Hz of frequency. The linear viscoelastic region (LVR) can be observed at oscillation stresses lower than 3 Pa. The solid-like behavior of the system under these experimental conditions can also be observed, with G' higher than G''. The dependency of the storage and loss moduli with frequency is presented in Figure 1(b). The guar–borax aqueous system exhibits the characteristic behavior of a viscoelastic fluid in which the terminal flow region can be observed. Below a critical frequency (around 0.3 Hz) that is related to the relaxation time of the system (3.3 s), the system behaves as a viscoelastic liquid with: $G' < G''$ and a frequency dependence of $G' \sim \omega$ and $G'' \sim \omega^2$. At frequencies higher than 0.3 Hz the system exhibits a solid-like behavior with $G' > G''$. Finally, Figure 1(c) shows the viscoelastic behavior of the guar–borax aqueous system as a function of temperature. As can be observed, the storage modulus presents a pseudoequilibrium plateau at lower temperatures, being G' rather independent of temperature. This pseudoequilibrium plateau is probably associated to the interactions between guar particles, through borax bridges, responsible for hydrogel formation. As the temperature increases, the borax-guar interaction weakens and the elastic modulus decreases with temperature up to the complete disappearance of the interactions conducting to the melting of the hydrogel (crossover of G' and G'').

PVA (88% hydrolyzed)–Congo red hydrogels

The rheological properties of the system PVA (88% hydrolyzed)—Congo red for a polymer concentration of 100 mg/mL were analyzed and the results
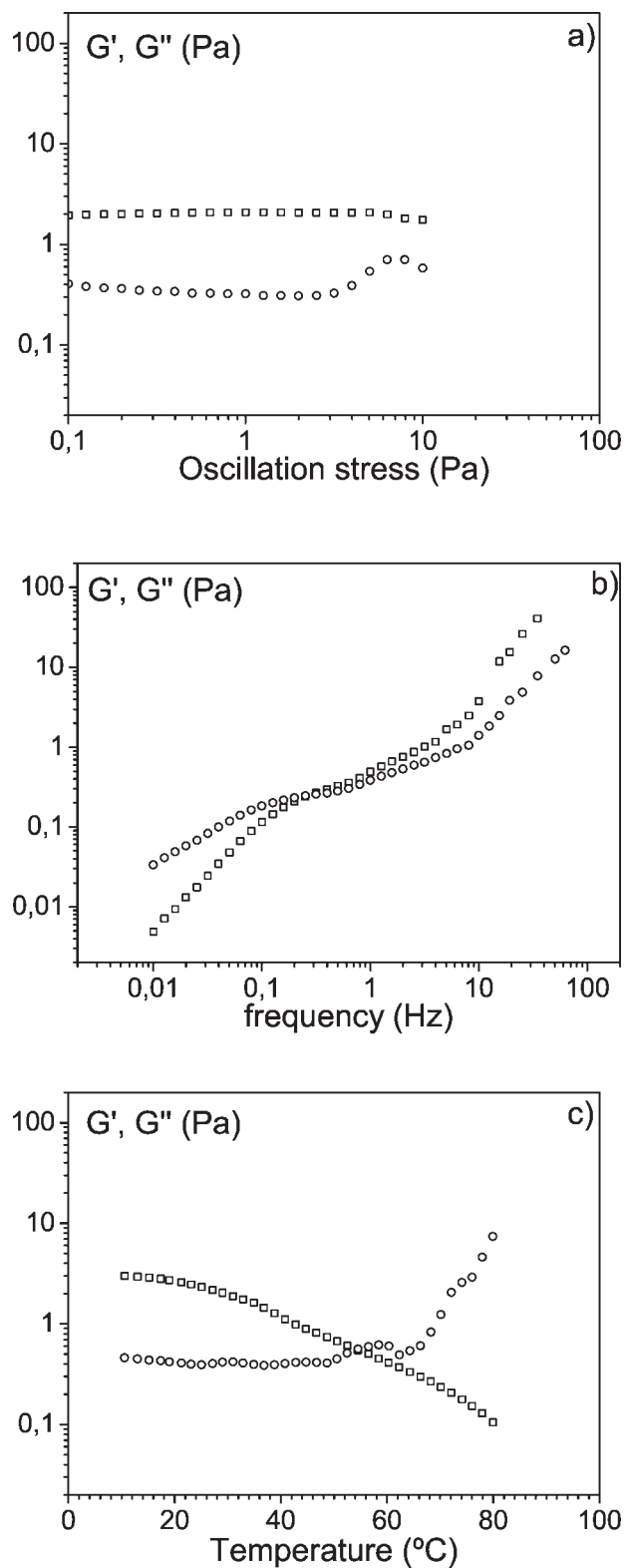
are presented in Figure 2. Figure 2(a) shows the evolution of the storage modulus, corresponding to the LVR plateau at 25°C and 1 Hz of frequency, as a function of the Congo red concentration. The storage modulus value for the guar system under the same experimental conditions is also presented for comparison. As can be observed, all the studied samples exhibit elastic modulus values lower than the guar system except for the sample of concentration 14 mg/mL. To check whether the rheological behavior of this sample is similar to that of the guar–borax system, the dependency of the elastic modulus with frequency is presented in Figure 2(b). As can be observed, the behavior of the PVA system is completely different from that of the guar system. For the PVA based hydrogel, G' is lower than G'' for all the frequencies studied, which means that this
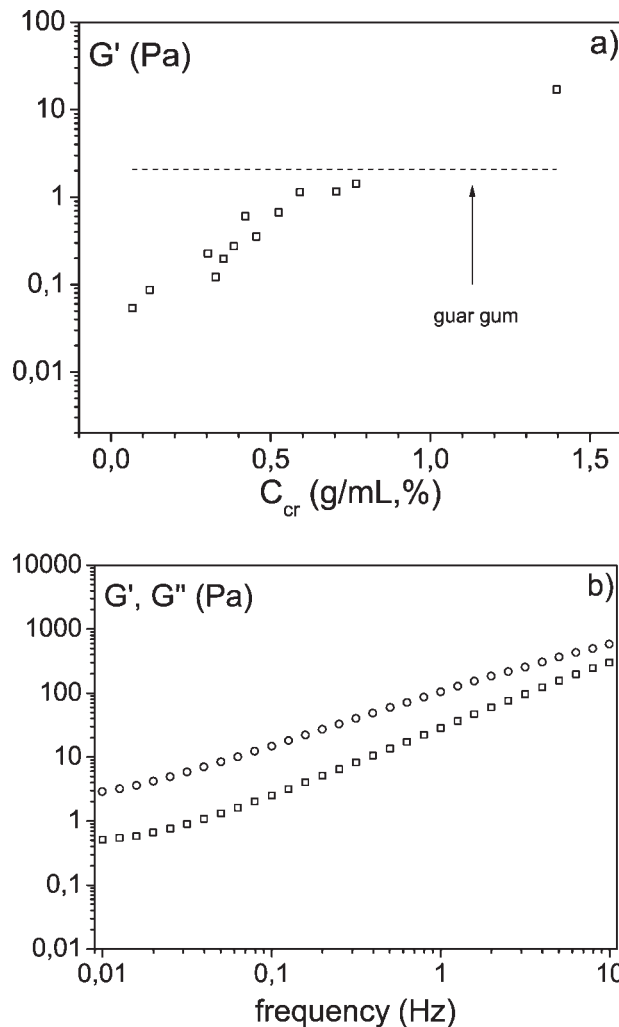

Figure 1 Storage modulus (□) and loss modulus (○) as a function of: (a) oscillation stress at 25°C and 1 Hz; (b) frequency at 25°C and oscillation stress 1 Pa; and (c) temperature at 1 Hz and oscillation stress 1 Pa for a guar gum hydrogel of polymer concentration 3 mg/mL and borax concentration 3 mg/mL.

Figure 2 (a) Storage modulus versus Congo red concentration for PVA hydrogels of polymer concentration 100 mg/mL and (b) Storage modulus (□) and loss modulus (○) versus frequency for a PVA hydrogel of polymer concentration 100 mg/mL and Congo red concentration of 14 mg/mL. The degree of hydrolysis of PVA was 88% in both figures.
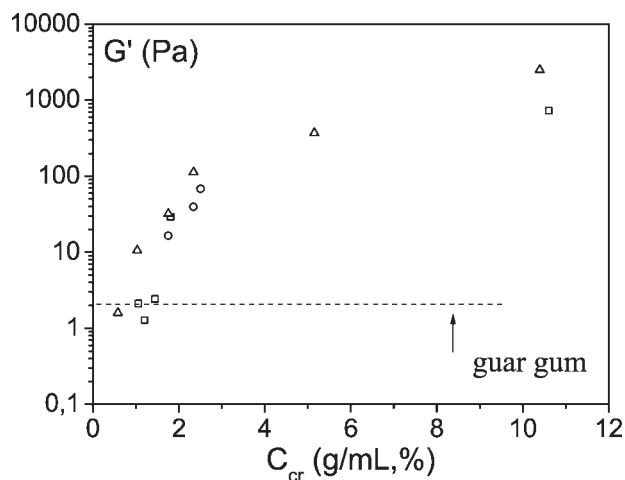
Figure 3 Storage modulus as a function of Congo red concentration for PVA hydrogels of polymer concentrations: 70 (○); 80 (□); and 100 (△) mg/mL. Degree of hydrolysis of PVA 99%.

system exhibits a liquid-like behavior in all the frequency range. Therefore, the systems exhibit a different behavior from the point of view of the terminal relaxation times.

Other samples with higher PVA concentrations were analyzed and in no case, the rheological behavior characteristic of the guar system could be reproduced.

PVA (99% hydrolyzed)–Congo red hydrogels

Hydrogels based on PVA with a higher degree of hydrolysis (99%) were prepared and their rheological properties studied. In Figure 3 the storage modulus values (determined in the LVR plateau at 25°C and 1 Hz) are depicted as a function of the Congo red concentration for hydrogels with different polymer concentration. The storage modulus value for the guar–borax system under the same experimental conditions is presented for comparison purposes. As can be observed, the storage modulus value of the guar system can be achieved for all the PVA concentrations even at small Congo red concentrations.

In Figure 4 the evolution of the storage and the loss modulus of PVA-congo red hydrogels is depicted as a function of the oscillatory frequency at different concentrations of polymer and congo red. Figure 4(a) shows the earlier mentioned dependency of the modulus with frequency for the sample with PVA concentration 100 mg/mL and congo red concentration 12 and 21 mg/mL. Both samples have storage modulus values above the value of the guar system. Nevertheless, the rheological behavior of both samples is different. At a congo red concentration of 12 mg/mL, the loss modulus is higher than the storage modulus in all the frequency range and,
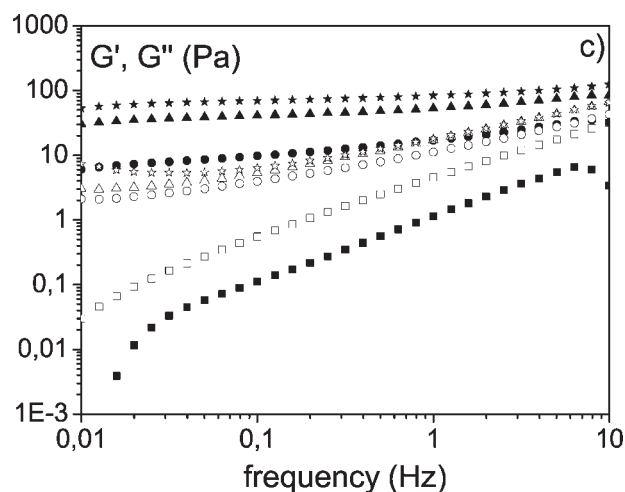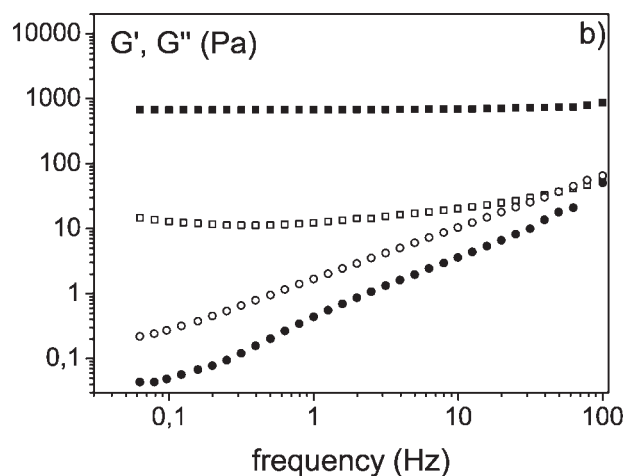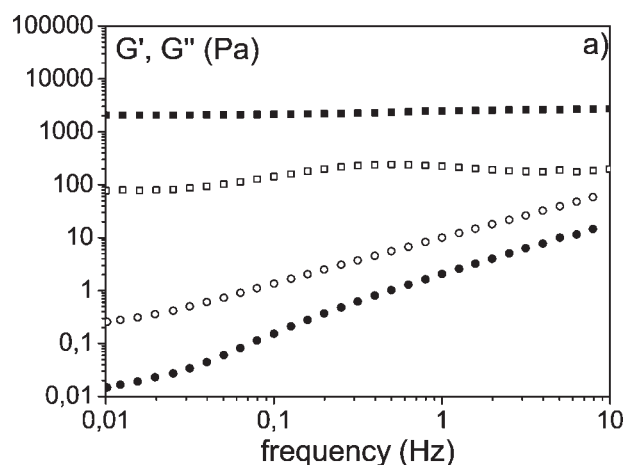

Figure 4 Storage modulus (full symbols) and loss modulus (open symbols) as a function of frequency for PVA hydrogels: (a) PVA concentration 100 mg/mL and Congo red concentrations 12 mg/mL (●, ○) and 21 mg/mL (■, □); (b) PVA concentration 80 mg/mL and Congo red concentrations 12 mg/mL (●, ○) and 106 mg/mL (■, □); and (c) PVA concentration 70 mg/mL and Congo red concentrations 14 (■, □), 17.5 (●, ○), 23.4 (▲, △) and 25.1% mg/mL (★,☆). Degree of hydrolysis of PVA 99%.
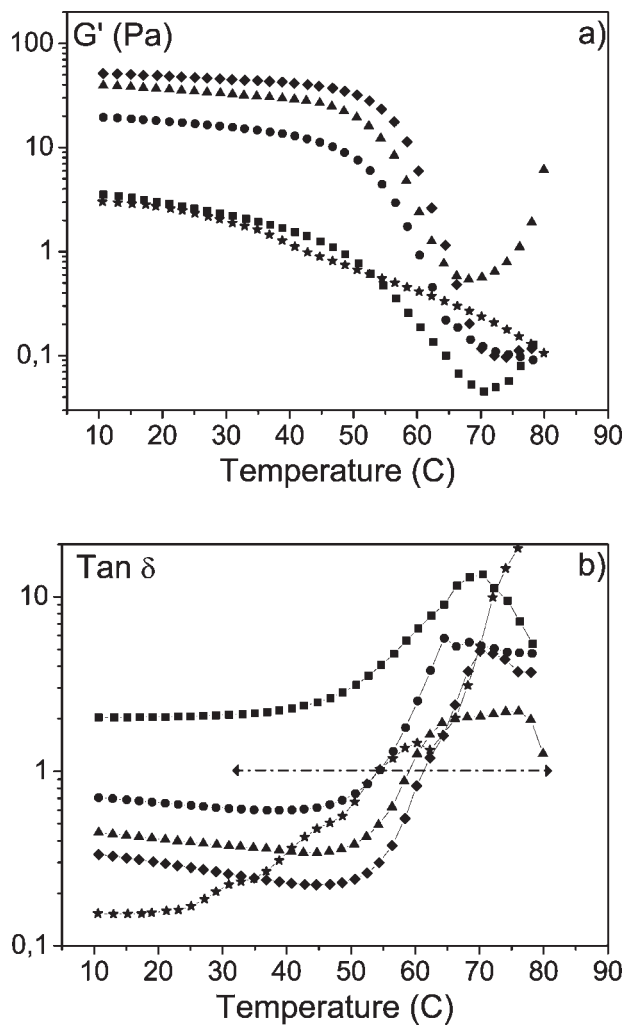
Figure 5 Storage modulus (a) and loss tangent (b) as a function of temperature for PVA hydrogels of PVA concentration 70 mg/mL and Congo red concentrations 14 (■); 17.5 (●); 23.4 (▲), and 25.1 (◆)% mg/mL; and for a guar gum hydrogel of concentration 3 mg/mL (★).

in addition, there is a strong dependence of the modulus with frequency, typical of a liquid-like behavior. The situation is the opposite for the sample with a congo red concentration of 21 mg/mL. In this case, the storage modulus is always higher than the loss modulus and, the dependency of the modulus with frequency is almost zero, as corresponds to a gelled system. A similar behavior is found for samples with different PVA concentration [see Fig. 4(b and c)]. The main conclusion that can be drawn from these figures is that the storage modulus values depend mainly on the PVA concentration of the samples, because the storage modulus increases with the polymer concentration. Nevertheless, the transition from a liquid-like to a solid-like behavior depends mainly on the congo red concentration: At low congo red concentrations, the system behaves as a liquid in all the frequency range investigated,

whereas at intermediate and high congo red concentrations the gelation of the systems takes place and a solid-like behavior is observed. This is the main difference with respect to the guar system, as in this case the transition from a liquid to a solid-like behavior can be observed within the frequency range investigated (terminal flow region observed).

The effect of temperature on the viscoelastic properties of both, guar and PVA systems can be observed in Figure 5. Figure 5(a) shows the evolution of the storage modulus as a function of temperature for the guar–borax hydrogel and the PVA-congo red hydrogels of PVA (70 mg/mL) and different congo red concentrations. Figure 5(b) shows the evolution of the tan δ as a function of temperature for the same systems. As can be observed, all the systems show a pseudoequilibrium plateau at low temperatures and a sharp decrease in the storage modulus at high temperatures, where the melting of the hydrogels take place. The value of the plateau modulus increases, and the melting temperature of the hydrogel (temperature at which tan δ becomes 1, that is, G' becomes lower than G'') increases with the concentration of congo red.

The PVA-congo red sample (congo red concentration 14 mg/mL) presents a similar storage modulus value to that of the guar system. However, the evolution of the viscoelastic properties with temperature of these samples seem very different: The guar sample shows a solid-like behavior with $G' < G''$, at low temperatures and the melting of the hydrogel at around 55°C, whereas the PVA sample shows a liquid like behavior for all temperatures (with G'' always higher than G', that is tan δ > 1).
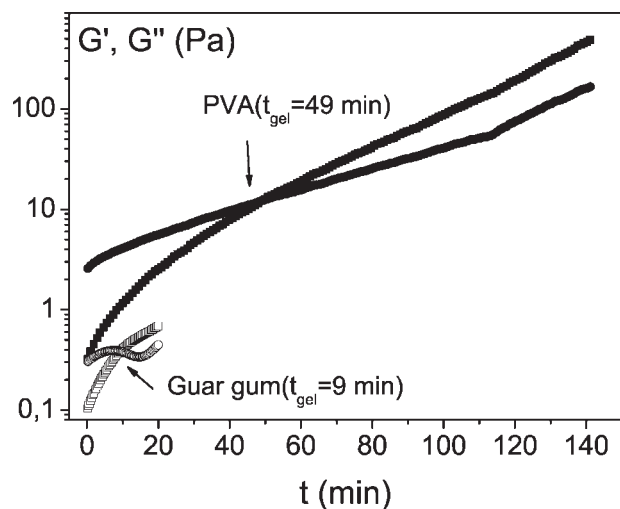

Figure 6 (a) Storage modulus (■, □) and loss modulus (●, ○) as a function of time for a PVA-Congo Red hydrogel of polymer concentration 70 mg/mL and Congo Red concentration 17.5 mg/mL (full symbols) and a guar gum hydrogel of concentration 3 mg/mL and borax concentration 3 mg/mL (open symbols).

The gelation kinetics of the guar–borax system was studied and compared with the gelation process of the PVA-congo red system of PVA concentration 70 mg/mL and congo red concentration 17.5 mg/mL), as these systems present similar storage modulus values and the same viscoelastic behavior. Figure 6 shows the evolution of the storage and the loss modulus with time at 20°C for the guar and the PVA systems. As can be observed, at low times $G'' > G'$ for both systems. As time increases, both G' and G'' increase, being the rate of increase of G' higher than G''. Consequently, at a certain time G' and G'' crossover defining the gelation point (around 9 min for the guar system and 49 min for the PVA system).

CONCLUSIONS

The rheological behavior of a typical hydraulic fracturing liquid system, consisting of a guar–borax hydrogel, has been reproduced with PVA-congo red hydrogels. Varying the degree of hydrolysis of the polymer, and the concentration of both, the polymer and the Congo-red crosslinker, it is possible to obtain a system with a similar overall rheological behavior to the guar–borax system. Some improvements can be achieved by using the PVA-Congo red system from the point of view of their applications as hydraulic fracturing liquids: (i) an increase in the gelation time that allows a better diffusion of the liquid through the rock pores; (ii) an increase in the elastic modulus that favors the suspension and therefore the transport of sand to the fracture zone; and (iii) the ease of removing the fracturing liquid after its use, because the PVA-Congo red hydrogel is based on a linear polymer (not crosslinked as it is the case of the guar polymer) that undergoes a thermoreversible gelation process.

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