

Self-assembly networks of wormlike micelles and hydrophobically modified polyacrylamide with high performance in fracturing fluid application

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Abstract Dynamic rheology and steady shear viscosity of an aqueous salt solution of 2 wt% viscoelastic gemini surfactant 1,2-*N,N'*-bis (dimethyloctadecyl) ethene ammonium bromide and its mixture with low molecular weight hydrophobically modified polyacrylamide (HMPAM) were investigated. The solution of surfactant in the presence of potassium chloride exhibited typical Maxwellian fluid behavior with a single stress relaxation time, indicating the formation of transient networks of entangled wormlike micelles (WLMs). Polymer profoundly affected the rheological properties of WLMs. The WLMs/HMPAM system demonstrated higher plateau modulus and zero-shear viscosity than the single WLMs system by self-assembling into common networks which was identified by scanning electron microscopy morphology. In contrast to the WLMs system, the WLMs/HMPAM system exhibited better temperature and shear resistance while retaining complete responsiveness to hydrocarbons. Based on the fracturing fluid application evaluation, the WLMs/HMPAM system had an applicable temperature, which was 30 °C higher than the WLMs system, and the core damage rate showed that the WLMs/HMPAM system was very promising in clean fracturing fluid application.

Keywords Wormlike micelles · Hydrophobically modified polymer · Self-assembly effect · Fracturing fluids

Introduction

With the synergy of some specific additives such as hydrotropes, inorganic salts or surfactants, viscoelastic surfactants (VES) can self-assemble into elongated flexible wormlike micelles (WLMs). The entanglement of WLMs can form transient networks displaying remarkable viscoelastic properties, which is similar to the solutions of flexible polymers. In contrast to the polymer macromolecules, WLMs can incessantly break and recombine, which makes the viscoelastic properties highly responsive to the variation of external conditions such as temperature and shear stress, hence they are also called as “living polymers” [1–9]. Because of their remarkable viscoelasticity, WLM solutions are very promising in many industrial applications, particularly as hydraulic fracturing fluids to enhance oil recovery. One of the unique characteristics of the VES fracturing fluids is that when contacted with hydrocarbons, the gel-like solutions would spontaneously transform into low viscosity fluids without any insoluble residuals which are more easily and thoroughly able to flow back from the propped fractures. Therefore, because of the high permeability and conductivity as well as low damage rate, the VES fracturing fluids are also called as “clean fracturing fluids” [10–14]. However, the VES fracturing fluids have also shown disadvantages that their rheological characteristics significantly deteriorate at high temperature and the high price and consumption of surfactants have also restricted their large-scale applications.

Recently, researches on the self-assembly effects between hydrophobically modified polymers (HMP) and WLMs reported a pronounced increase in both the linear viscoelastic modulus and steady shear viscosity upon the addition of a small amount of HMP, such as hydrophobically modified hydroxypropyl guar (hm-HPG) [15], hydrophobically modified polyacrylamide (HMPAM) [16–20], and hydrophobically end-capped PEO (hm-PEO) [21, 22], into the WLMs aqueous

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solutions. Meanwhile, the WLMs/HMP systems also remained responsive to hydrocarbons [16, 18].

Although the WLMs/HMP self-assembly systems have been carried out in some researches, relative applications in fracturing fluids have been less reported. Erucyl *bis* (hydroxyethyl) methyl ammonium chloride (EHAC)/hm-HPG and EHAC/HMPAM systems were suggested as fracturing fluids because of their higher temperature resistance than the single component system [15, 16]. However, these two systems were not completely responsive to hydrocarbons due to their high proportion of polymers, so that the viscosities of these two systems were much higher than those of the pure WLMs systems after contacting with hydrocarbons. Thus extra treatments were required to degrade the polymers when used as fracturing fluids. Therefore, we put forward an idea to investigate a novel self-assembly system composed of WLMs and low molecular weight HMPAM which is expected to exhibit complete hydrocarbon responsiveness and better performance in temperature and shear resistance, so that it can be further applied as clean fracturing fluids.

In the present work, gemini surfactant 1, 2-*N,N'*-bis (dimethyloctadecyl) ethene ammonium bromide (GS-18, seen in Fig. 1.) in the presence of KCl was applied to construct the WLMs system. Dynamic rheology and steady shear viscosity of the WLMs solution and its mixture with low molecular weight HMPAM were detailedly compared to identify the formation of self-assembly common networks in the WLMs/HMPAM system. SEM morphologies were further applied to confirm the enhancement of networks in the WLMs/HMPAM system. Effects of temperature, shear stress, and hydrocarbons on the rheological properties of the two systems were also researched. At last, relative properties of the WLMs system and the WLMs/HMPAM system as fracturing fluid were also investigated and discussed.

Materials and methods

Materials

Acrylamide, cetyltrimethylammonium bromide (CTAB), potassium chloride, ammonium persulfate (APS), anhydrous ethyl alcohol were all analytical grade, purchased from Kelong chemical reagent factory (Chengdu, China). Gemini surfactant GS-18 (over 99 %) and cetyl dimethyl allyl ammonium bromide (SD-16, over 99 %) were received from Titaning Chemical Technology Co., Ltd. (Henan, China) and were both recrystallized twice with ethyl acetate before using. Kerosene was commercially available. Sand stone core ($\phi 2.5 \times 8$ cm) was provided by State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (Chengdu, China).

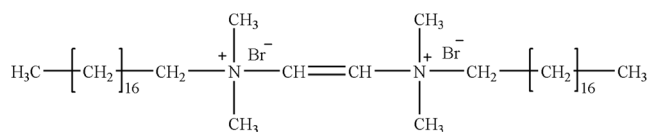


Fig. 1 The chemical structure of gemini surfactant 1, 2-*N,N'*-bis (dimethyloctadecyl) ethene ammonium bromide

Polymer synthesis

HMPAM was synthesized by free-radical copolymerization of acrylamide (99.4 mol %) and SD-16 (0.6 mol %) with APS (0.3 g/L) as initiator. CTAB with a mole ratio to SD-16 of 2:1 were added as co-surfactants to form mixed micelles to control the length of the microblocks of the hydrophobic monomers [23, 24]. The polymerization was preceded for 7 h at 55 °C under nitrogen atmosphere, and then the polymer was precipitated in ethanol several times. Finally, the copolymer was cut into small particles and dried in a vacuum oven. The molecular weight of HMPAM was determined by a gel permeation chromatography (GPC) in solvent containing 70 vol% 0.1 mol/L NaNO₃ (aq) and 30 vol% methanol that the HMPAM has a molecular weight of 5.2×10^5 g/mol [16]. The chemical structure and ¹H NMR spectra of the HMPAM (D₂O, TMS) are shown in Fig. 2.

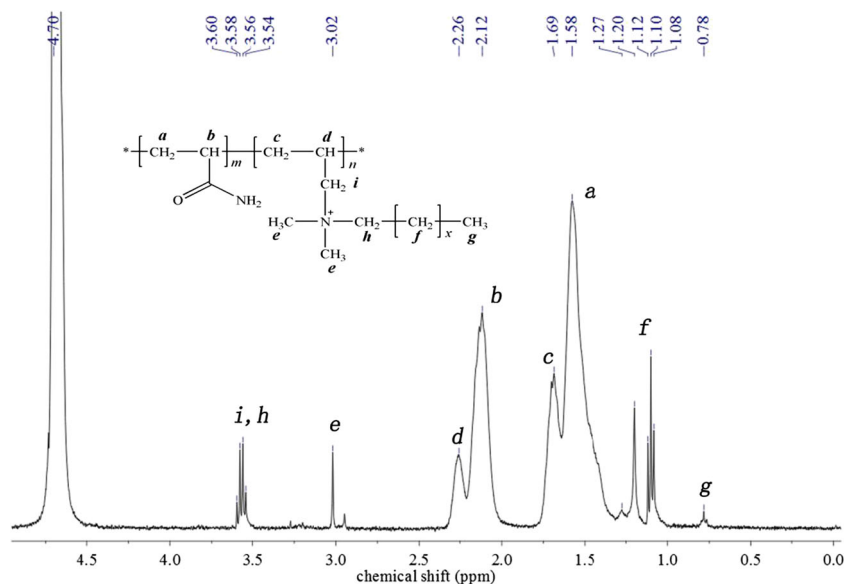
Sample preparation

WLMs solutions were prepared by dissolving 2 wt% GS-18 and 4 wt% KCl in deionized water. The WLMs/HMPAM systems were obtained by dissolving the same amount of GS-18 and KCl in the HMPAM solutions which were prepared in advance. The HMPAM concentration was kept at 0.3 wt%, except any specific statement. All the samples were gently stirred and left to equilibrate at 50 °C for at least 1 day to eliminate the air bubbles before testing.

Rheology test

Rheological properties were determined on a HAAKE MARS III Rheometer (Thermo Scientific, Germany). Dynamic rheology were performed with a parallel-plate geometry P35 Ti L (the gap is 1 mm) and the stress amplitude were checked beforehand in order to ensure that all measurements were performed within the linear viscoelastic region. Steady shear viscosity was measured using a cone-plate geometry C60 1° Ti L or a Couette geometry DG41 Ti according to the fluid viscosities. Sufficient time was allowed before data collection at each shear rate to ensure the viscosities reached their steady values. A solvent trap was used to minimize sample evaporation. Viscosity under high temperature and high shear rate were measured on a sealed PZ38 geometry. All samples were equilibrated for at least 20 min at certain temperature prior to conducting measurements.

Fig. 2 Chemical structure and ^1H -NMR spectrum of the synthesized HMPAM



SEM morphology

The morphologies of WLMs and WLMs/HMPAM systems were imaged with a Quanta 450 scanning electron microscope (FEI, Netherlands). The samples were prepared by freezing a small drop of the solutions on a clean wafer with liquid nitrogen so that the microstructures of the mixtures in aqueous solution can be well retained. After that, the frozen sample was dried under vacuum at about $-50\text{ }^{\circ}\text{C}$ and then coated with Pt.

Core flooding test

The permeability of the sand stone core was measured on a YSF-1 core laboratory unit (Jiangsu Haian Scientific Research Device Co., Ltd.) according to Chinese Oil and Gas industry standard SY/T 5107-2005. The pore volume of the core was determined beforehand by dividing the weight difference of the saturated core and the dry core by the density of standard brine. The core was loaded in a core holder system with an overburden pressure fixed at 15 MPa. An electric heating device was applied to keep the core holder system at a constant temperature of $80\text{ }^{\circ}\text{C}$. Standard brine, gel-breaking fluid of the WLMs and WLMs/HMPAM system were injected into the core in sequence. The injection rate Q was 1 ml/min, controlled by an advection pump to ensure laminar flow and applicability of Darcy's law. Pressure sensors were connected to a computer to monitor and record the pressure difference (ΔP) across the core during the measurements. When the pressure difference became stable, the permeability K can be calculated by Darcy's law:

$$K = Q\mu L / A\Delta P$$

Where μ is the fluid viscosity, L is the length of the core and A is the fluid cross area. The core damage rate (Φ) can be calculated by:

$$\Phi = (K_0 - K) / K_0$$

Where K_0 is the initial permeability of the core measured by standard brine and K is the permeability measured by gel-breaking fluid.

Results and discussions

Rheology of GS-18/KCl solution

The viscoelastic behavior of the aqueous salt solution of 2 wt% GS-18 at $50\text{ }^{\circ}\text{C}$ is illustrated in Fig. 3a. It is seen that the frequency dependent loss modulus or viscous modulus $G''(\omega)$ went through a maximum whereas the storage modulus or elastic modulus $G'(\omega)$ showed a plateau. In the range of low and medium frequencies, the data points of the GS-18 solution well fit to the single stress relaxation time Maxwellian model (represented by the solid lines) which has been widely applied to characterize the viscoelastic behavior of WLMs systems [1, 4, 5]. For the Maxwellian fluid, the storage modulus G' and loss modulus G'' relate to the shear frequency, ω , and relaxation time τ_R by the following relations:

$$G'(\omega) = \frac{G_0 \omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2}$$

$$G''(\omega) = \frac{G_0 \omega \tau_R}{1 + \omega^2 \tau_R^2}$$

Where G_0 is the plateau of storage modulus at middle and high frequency [1]. This behavior strongly indicates the formation of networks by entangled WLMs. The upturn of G'' from the model at high frequencies is another evidence of the WLMs, which corresponds to the fact that WLMs are in a dynamic equilibrium and exist in rapid breaking and recombination processes [1, 9]. The shape of the Cole-Cole plot (Fig. 3b) follows perfectly a semicircle in the range of low and medium frequencies, indicating again that the present systems obey Maxwellian model with a single stress relaxation time [1, 8, 9].

The GS-18 solution had a plateau moduli G_0 of 5.1 Pa and a characteristic relaxation time τ_R of 18 s, determined by the crossover frequency ω_c at which the G' and G'' values are equal by $\tau_R = 1/\omega_c$ [4, 7]. Figure 3c shows the steady shear viscosity profile of GS-18 solution at 50 °C. The GS-18 solution exhibited a considerably high viscosity, and presented Newtonian behavior at low shear rate and shear thinning response when the shear rate exceeded the critical shear rate γ_c about $4 \times 10^{-2}/s$. This behavior was attributed to the alignment and break of the entangled WLMs [8]. Extrapolating the viscosity curve along the plateau in the Newtonian region to zero gave the values of the zero-shear viscosity η_0 for the WLM solution of about 87.4 Pa, which was very closely to the value estimated by $\eta_0 = G_0 \times \tau_R$ [1].

Effect of adding HMPAM

Dynamic rheology of WLMs/HMPAM systems composed of 2 wt% GS-18 and different content of HMPAM is illustrated in Fig. 4a. Apparently, adding a small amount of HMPAM in the WLMs solutions profoundly affected the rheological properties of WLMs solutions. When the HMPAM content was 0.1 wt%, the mixture solution exhibited a plateau moduli G_0 of 8.2 Pa, however, increasing the HMPAM content to 0.3 wt% resulted in an increase by several times to 24.9 Pa, the cross points of G' and G'' shifted to lower frequencies indicating longer relaxation time τ_R . These results were also consistent with the steady shear behavior as shown in Fig. 4b, where the mixtures exhibited an evident enhancement of zero-shear viscosity η_0 and the critical shear rate γ_c shifted to lower values with increasing content of HMPAM, especially for the one containing 0.3 wt% HMPAM, whose first Newtonian plateau and zero-shear rate viscosity could scarcely be observed in the shear rate range studied. The apparent behavior can be ascribed to the formation of common networks of WLMs and HMPAM. Driven by the hydrophobic association effect, the hydrophobic C_{16} groups of SD-16 in HMPAM would spontaneously penetrate into the surfactant WLMs to minimize the free energy and the mixed WLMs were formed in consequence [16, 22]. However, the structures of the WLMs are not appreciably affected by HMPAM which has been identified by small-angle neutron scattering (SANS) [18, 22]. Therefore the HMPAM can be

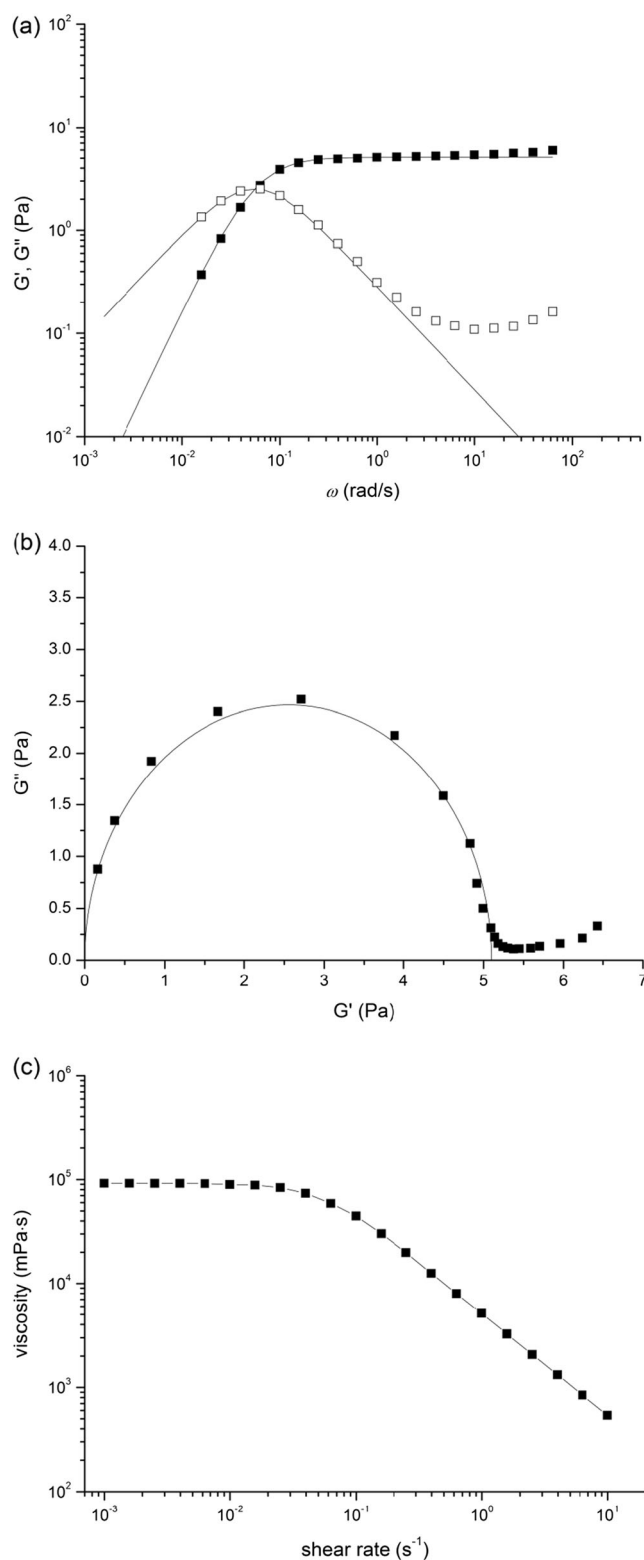


Fig. 3 Frequency dependent viscoelastic spectrum (a) Cole-Cole plot (b) and steady shear viscosity (c) of 2 wt% GS-18 solution at 50 °C. Solvent: 4 wt% KCl in deionized water

figuratively taken as crosslinkers that the entangled WLMs are further physically crosslinked by HMPAM [15, 16, 21],

which implies a profound increase in crosslink density ν and a decrease in average mesh size ζ of the networks, subsequently an increase of the plateau modulus G_0 estimated as follows [1]:

$$G_0 = \nu kT$$

$$G_0 = kT/\xi^3$$

Where T is the temperature, and k is the Boltzmann constant.

It is reported that the VES/HMPAM solutions had a spectrum of relaxation times similar to semidilute polymer solutions rather than the simple Maxwell behavior of the pure WLMs [16, 18]. However, the WLMs/HMPAM studied in the present work still exhibited Maxwell behavior in low and medium frequencies (Fig. 4a, c), and this behavior was also observed in the CTAC/hm-PEO systems [21]. Contribution of HMP networks in the common networks should be responsible for the difference. In the WLMs/HMP system, when the WLMs are physically crosslinked by the HMP, it can also be thought that

the HMP are simultaneously crosslinked by the WLMs as well, which also contributes to the common networks. By the crosslink effect of WLMs, the low molecular weight hm-PEO or HMPAM applied in the present work formed networks which were far weaker than those of the entangled WLMs. Thus, the viscoelastic behavior of the solution would still be mainly dominated by the fast breaking and recombination equilibrium of the WLMs like “living polymers”. However, when the molecular weight of HMP is high enough, such as that of the VES/HMPAM system, the contribution of crosslinked HMP networks are comparable to the WLMs networks, the solution viscoelastic behavior would therefore deviate from the pure WLMs to unbreakable “dead polymers” solutions.

SEM morphologies

Figure 5a-d illustrate the SEM morphologies of the pure WLMs and WLMs/HMPAM solutions with different

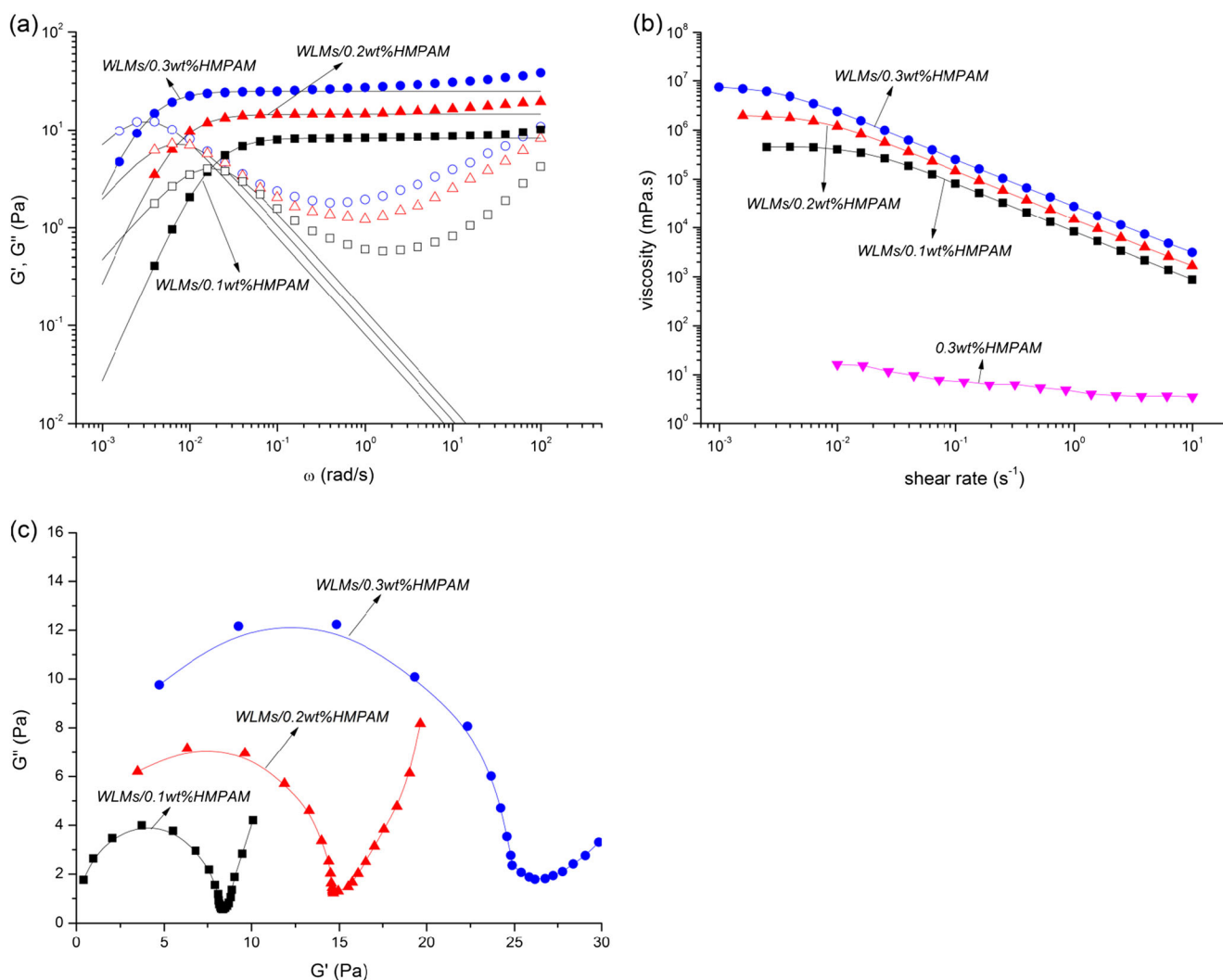


Fig. 4 Dynamic viscoelastic spectra (a), steady shear plots (b) and Cole-Cole plots (c) of WLMs/HMPAM system composed of 2 wt% GS-18 and different content of HMPAM at 50 °C. Solvent: 4 wt% KCl in deionized water

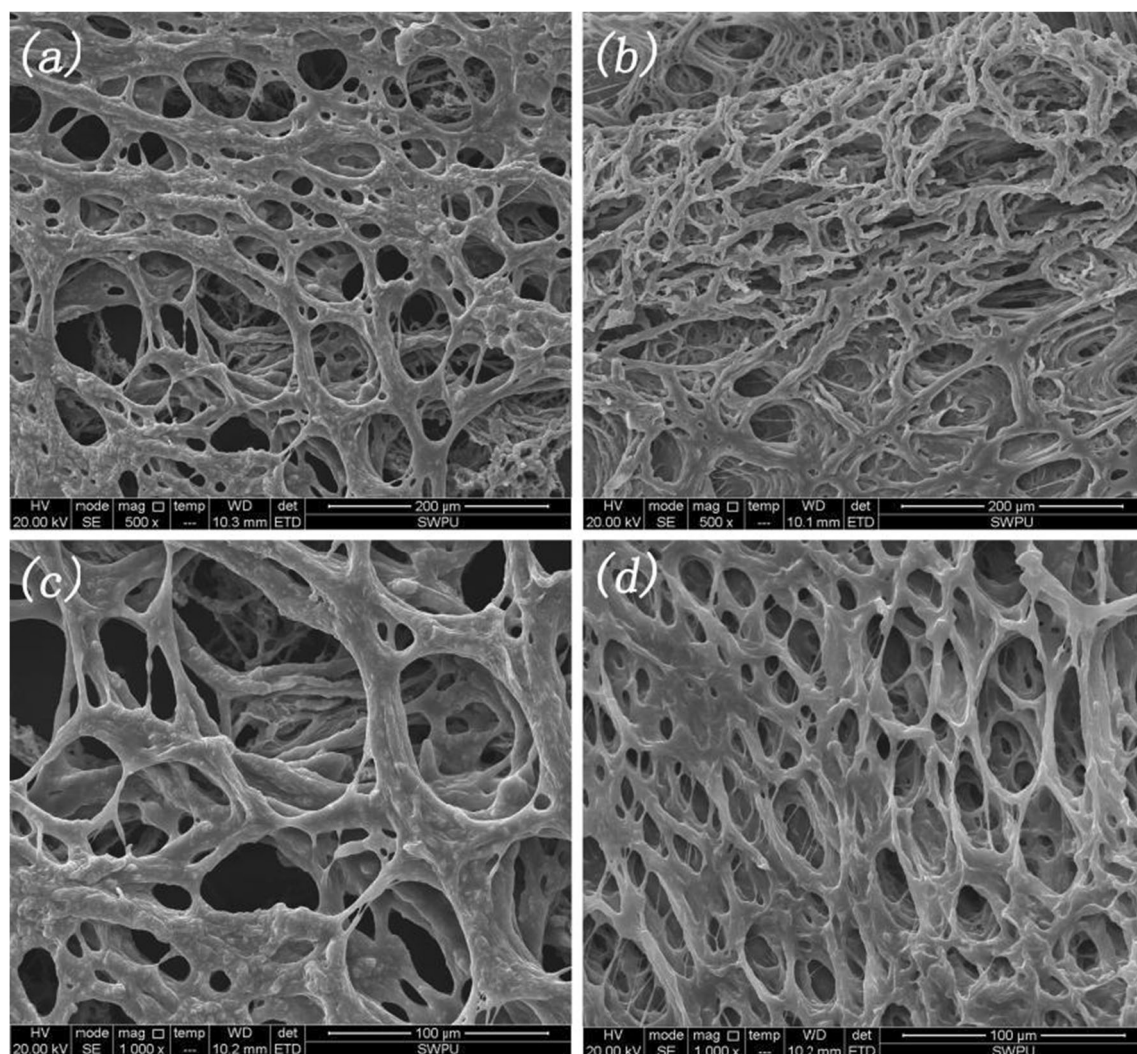


Fig. 5 SEM morphology of the pure WLMs system (**a** $\times 500$ and **c** $\times 1000$) and the WLMs/HMPAM system (**b** $\times 500$ and **d** $\times 1000$)

amplification factor. Three-dimensional networks could be clearly observed in the solutions. The formation of three-dimensional network structure attributes to the entanglement of WLMs and the further physical crosslink of WLMs by HMPAM in the WLMs/HMPAM, which greatly improves the solution viscosity. It is seen that upon the addition of a small amount of HMPAM, the networks in the WLMs/HMPAM solutions (**b** and **d**) become much more intensive than that in the pure WLMs solutions (**a** and **c**) and the size of the meshes of the WLMs/HMPAM networks is smaller than the WLMs networks. Therefore, the SEM morphologies provide an apparent evidence that the addition of HMPAM implied profound increases of the crosslink density ν and decreases of the average mesh size ζ of the WLMs networks, which could be applied to explain the increase of plateau modulus G_0 and zero-shear rate η_0 in the self-assembly systems as discussed above.

Effect of temperature

Figure 6a shows the effect of temperature on the dynamic rheology of the WLMs system. It is seen that as the temperature increased, the minimum value of the loss modulus $G''_{\min}$ increased as well and shifted to higher frequency, while the value of plateau modulus G_0 showed a very slightly decrease. Since the plateau modulus G_0 were almost independent of temperature, the mesh size ζ and hence the entanglement length l_e were independent of temperature as well. This indicates an expected decrease of the average contour length $\bar{L}$ of micelles according to the equation [1, 5]:

$$\frac{G''_{\min}}{G_0} \approx \frac{l_e}{\bar{L}}$$

Mean-field result for the variation in $\bar{L}$ with surfactant volume ϕ and temperature can be applied to further quantify the effect of temperature [1]:

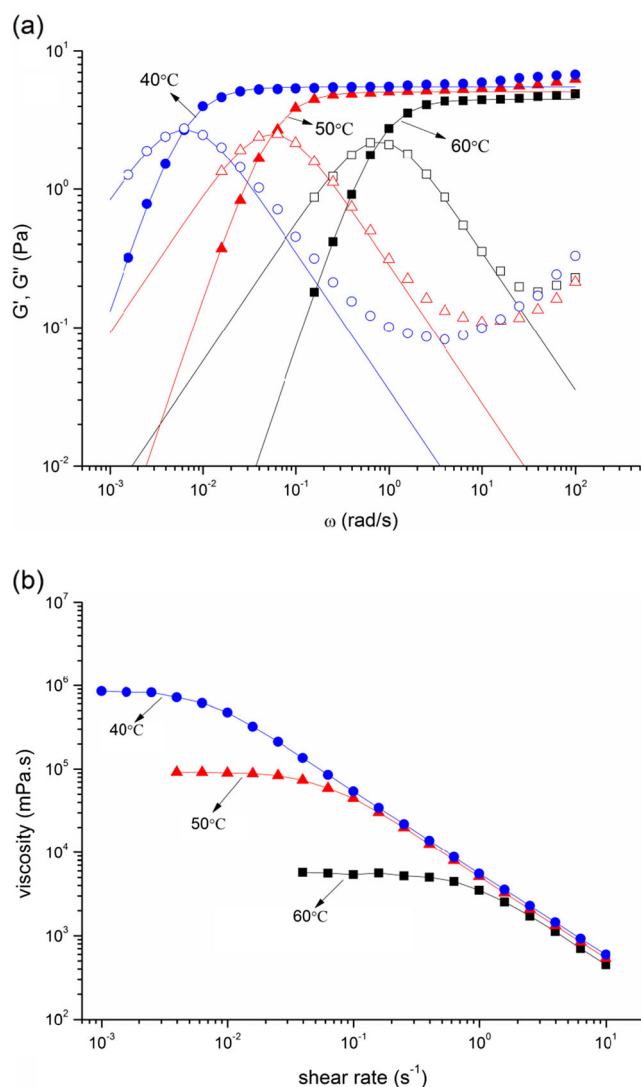


Fig. 6 Effect of temperature on the dynamic viscoelastic spectra (a) and steady shear plots (b) of the WLMs system

$$\bar{L} \sim \phi^{1/2} \exp[E_c/2kT]$$

The shortening of average contour length $\bar{L}$ with increasing temperature would subsequently affect the relaxation time τ_R and zero-shear viscosity η_0 [25]. Therefore, the cross frequency ω_c of G' and G'' shifted to higher frequency in Fig. 6a and zero-shear viscosity in Fig. 6b decreased sharply as the temperature increased.

For the WLMs/HMPAM self-assembly system, however, the plateau modulus G_0 showed an evident decrease with increasing temperature rather than a very slight decrease in the WLMs system as well as the relaxation time τ_R (Fig. 7a) and steady shear viscosity (Fig. 7b). Though the crosslink density ν of the WLMs may not be affected by temperature as expressed before, in the self-assembly systems, the decrease of $\bar{L}$ which can be taken as a break of micelles, would

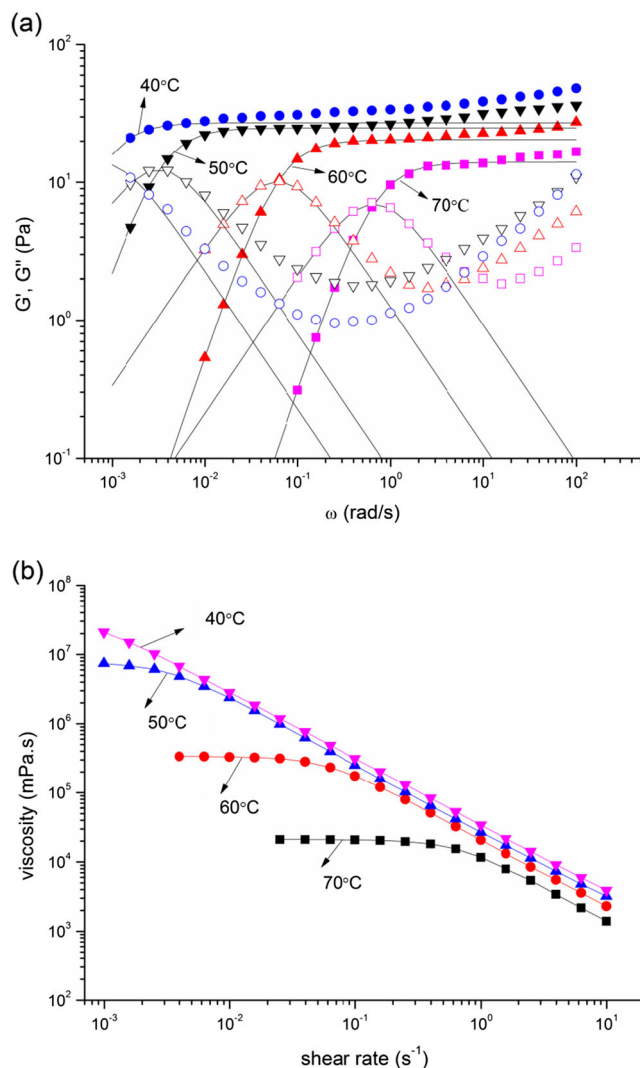


Fig. 7 Effect of temperature on the dynamic viscoelastic spectra (a) and steady shear plots (b) of the WLMs/HMPAM system

dramatically affect the crosslink density of the common networks. Adding HMPAM to physically crosslink the WLMs promote to the formation of more meshes with decreased mesh size ζ , thus would result an increase in crosslink density ν ; while a break of WLMs would on the contrary destroy the meshes and reduce the crosslink density of the networks. Meanwhile, elevated temperature would promote the thermo motion of the hydrophobic substitute of HMPAM which accelerates the hydrophobic stickers to separate from the mixed WLMs that also weakens the self-assembly effects. Within the two possible reasons, heating would result in a more pronounced effect on the network structure of the self-assembly systems.

From the steady shear viscosities of the WLMs system and WLMs/HMPAM system presented in Figs. 6b and 7b, it was observed that the WLMs/HMPAM system showed a more pronounced decrease in the zero-shear viscosities η_0 than the WLMs system with the same temperature increase. Here,

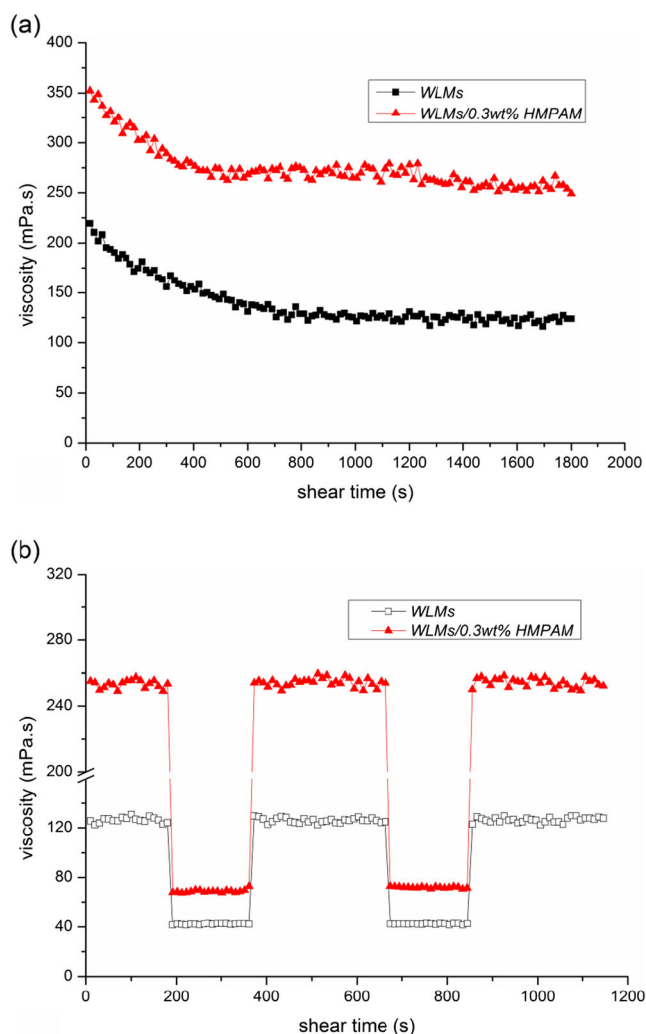


Fig. 8 Effect of constant shear (a) and alternant shear (b) on the viscosity of the WLMs and WLMs/HMPAM system

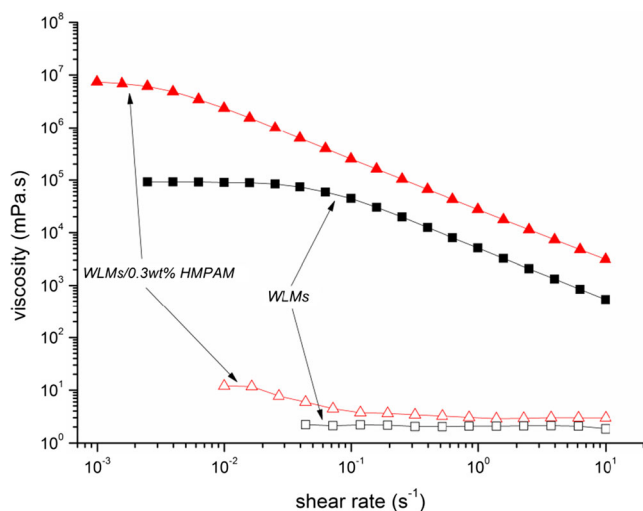


Fig. 9 Steady shear viscosity of the WLMs/HMPAM and WLMs systems before (solid) and after (open) contacting with kerosene

we suppose that the zero-shear viscosity η_0 relates to the temperature by the Arrhenius equation [26] and its logarithmic form can be presented as:

$$\ln \eta_0 = \ln A + \frac{E_a}{R} \cdot \frac{1}{T}$$

Where E_a is the activation energy, R is the gas constant, and A is the pre-exponential factor. So it could be estimated that the WLMs/HMPAM system would exhibit a higher absolute value of slope of $\ln(\eta_0)$ versus $1/T$ than that of the pure WLMs system. Therefore, the WLMs/HMPAM system had a higher value of E_a than the WLMs system, thus the self-assembly systems were more sensitive to temperature than the pure WLMs systems because of higher activation energy.

Though the plateau modulus G_0 and zero-shear viscosity η_0 declined more pronouncedly in the self-assembly system, they still retained higher values than that of the pure WLMs system through the entire temperature range studied indicating that the self-assembly system is more resistant to heating than pure WLMs.

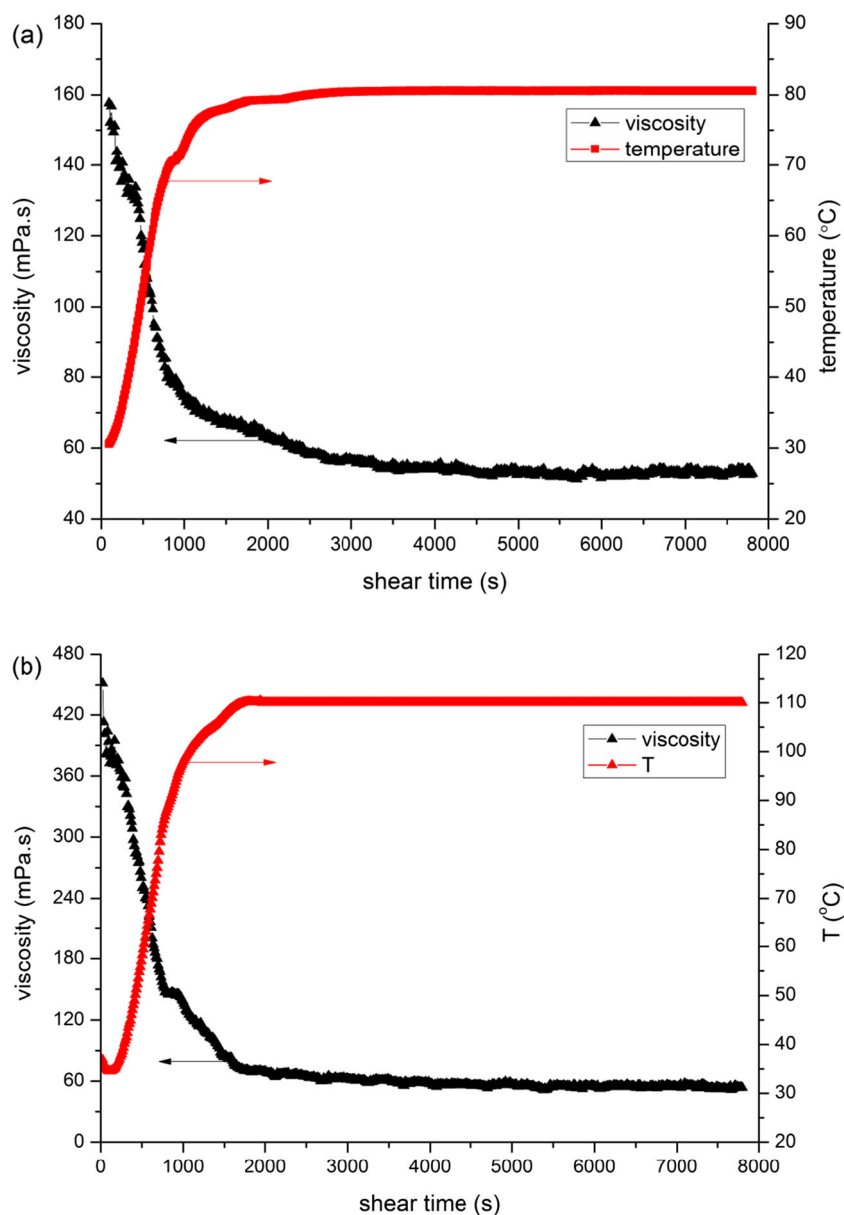
Effect of shear

For many industrial applications of viscoelastic fluids, such as fracturing fluids or drag reducers, high shear rate conditions are more likely encountered. Figure 8 compares the viscosity of pure WLMs and WLMs/HMPAM systems under a constant shear rate of 170/s and alternant shear rate (170 and 1022/s) at 50 °C.

With the constant shear rate of 170/s, both the WLMs and WLMs/HMPAM systems firstly showed shear thinning and then the viscosities remained constant (Fig. 8a). Apparently, the WLMs/HMPAM system maintained a higher value than that of the WLMs system indicating that the self-assembly system was more resistant to shear. In the alternant shear process (Fig. 8b), when the shear rate increased from 170 to 1022/s, the viscosities dropped significantly but rapidly returned to their original values when the shear rate turned back to 170/s. After two rounds of alternant shear, the final viscosities were almost the same with the original values, demonstrating that both systems had a good shear thinning and shear recovery property.

As has been discussed before, the self-assembly interaction between the HMPAM and WLMs resulted in more intensive networks than the single WLMs system, therefore they are more resistant to shear and able to maintain a high level of viscosity. Meanwhile, no chemical bonds were formed in this process, which means the crosslink between HMPAM and WLMs is physically reversible. Therefore, the viscosity showed a very slight change before and after the high shear but the chemical crosslinked polymer gels would be permanently disrupted after a high shear rate process. Shear recover property is a very important feature for fracturing fluids

Fig. 10 Viscosities versus time and temperature plots of WLMs (a) and WLMs/HMPAM (b) as fracturing fluids



because they undergo a high shear rate process when pumped through the pipelines and perforation holes, and the low viscosity helps to reduce the friction. However, the viscosity

needs to be restored to suspend the proppants and control the fracture geometry after entering the formation.

Effect of hydrocarbons

In the present work, kerosene was applied to investigate the effect of hydrocarbons on the viscosities of the two systems. 100 ml of viscoelastic fluids was mixed with 15 ml kerosene and left to equilibrate for 4 h at 50 °C. During this period, the mixtures separated into two transparent phases (top-kerosene, bottom-aqueous solution). Then, the bottom phases saturated with hydrocarbons were separated out and their rheological behaviors were subsequently measured. Figure 9 shows the steady shear viscosity of the WLMs and WLMs/HMPAM systems before and after contacting with

Table 1 Properties of the gel-breaking fluid of the WLMs and WLMs/HMPAM fracturing fluids

	Viscosity (mPa s)	Surface tension (mN/m)	Interfacial tension with kerosene (mN/m)	Residual content (%)
WLMs	1.85/1.41 ^a	23.03	0.57	Unmeasurable
WLMs/ HMPAM	2.76/2.54 ^a	24.36	0.52	Unmeasurable

^a Conducted at 80 °C and other measurement were all conducted at 50 °C

kerosene. It is seen that in the absence of hydrocarbons, the two systems were viscoelastic and exhibited high viscosity plateau values at low shear rate and shear thinning at high shear rate, such behavior is a typical evidence of entangled chains. By contrast, upon contact with hydrocarbons, the viscosity dropped by orders of magnitude that the gel-like solutions transformed into fluids with very low viscosities of less than 5 mPa s. This behavior indicates that the WLMs/HMPAM system is absolutely responsive to hydrocarbons like the pure WLMs system that no additional treatments should be taken to deal with the HMPAM.

The drop in viscosity induced by hydrocarbons is attributed to the transformation of WLMs to spherical micelles which completely disrupted the common networks [18]. Meanwhile, the HMPAM applied in this work has a very low molecular weight which ensures a limited thickening capacity (3.45 mPa s before contacting with the hydrocarbons, as seen in Fig. 3b) and the HMPAM would be much more coiled when contacted with the hydrocarbons (2.76 mPa s after contacting with the hydrocarbons); on the other hand, the low molecular weight HMPAM can no longer form networks with excess spherical micelles according to the “three stage models” [27, 28].

Fracturing fluids application

Applicable temperature

The applicable temperature for the WLMs and WLMs/HMPAM system as fracturing fluids were evaluated and shown in Fig. 10. Both the systems were heated with an average speed of 3 °C/min to the target temperature in order to simulate the heating process of fracturing fluids from the wellhead to the down hole, and then continuously sheared for 90 min under the target temperature, and the entire process was kept at a constant shear rate of 170/s.

After a 90-min continuous shear under the target temperature, the curves of viscosity values versus time of the two systems were maintained at 50–60 mPa s, which is the minimum viscosity value required for fracturing fluids to suspend the proppants [26], indicating that the highest applicable temperature of WLMs and WLMs/HMPAM systems can reach to 80 and 110 °C, respectively. Compared with the pure WLMs fracturing fluids, the self-assembly ones exhibited higher applicable temperature without increasing the concentration of the surfactant. In other words, the WLMs/HMPAM fracturing fluids would require a lower surfactant concentration if they presented the same temperature resistance property with the pure WLMs systems.

Core damage rate

Table 1 shows the properties of the gel-breaking fluids of the WLMs and WLMs/HMPAM systems. The viscosities of the two gel-breaking fluids were both less than 5 mPa s which meet the requirement of practical application as fracturing fluids. The surface tension of gel-breaking fluids was about 25 mN/m and their interfacial tension with kerosene was about 0.5 mN/m, due to the high concentration of surfactants. Low viscosity and interfacial tension ensures low capillary resistances when flow back from the reservoir. Most importantly, in practical use, people concern more about the plugging of the core and propped fractures caused by insoluble residuals, however, the self-assembly system scarcely contained insoluble residuals as the WLMs which can effectively avoid this disadvantage.

The core damage rate of the gel-breaking fluids is shown in Fig. 11. Original permeability K_0 of the sand stone core measured by standard brine is $63.41 \times 10^{-3} \mu\text{m}^2$. The injection pressure showed a slight increase after the gel-breaking fluid of WLMs system was injected and the permeability dropped to $57.88 \times 10^{-3} \mu\text{m}^2$ with a damage rate of 8.72 % which was far lower than the typically required upper limit value of 20 % for the VES fracturing fluid. After injecting the gel-breaking fluid of the WLMs/HMPAM system, the injection pressure raised again and the permeability descended to $52.1 \times 10^{-3} \mu\text{m}^2$ which dropped by 17.84 % contrasted to the original permeability and 9.99 % to the first damaged permeability. It should be emphasized that the result came from the overlay effect of the two gel-breaking fluids; therefore, the absolute damage rate of the single WLMs/HMPAM system should be lower than the present value. Therefore, the WLMs/HMPAM system can also be taken as a new kind of clean fracturing fluids as the WLMs systems.

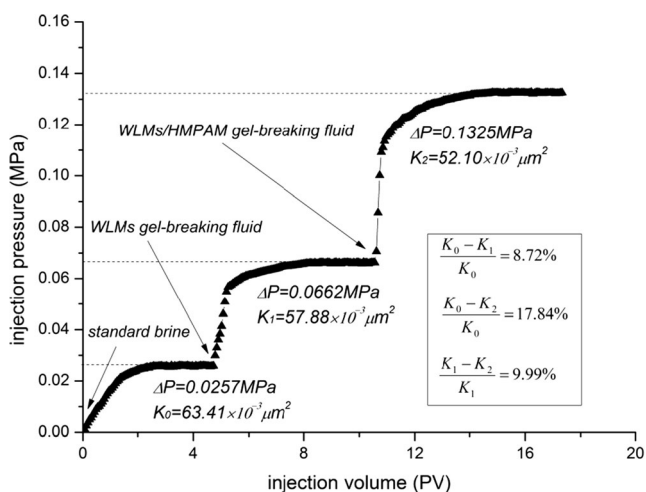


Fig. 11 Core damage rate of the WLMs and WLMs/HMPAM fracturing fluid systems

Conclusions

The addition of low molecular weight hydrophobically modified polyacrylamide in the wormlike micelles system solutions significantly enhances the viscoelasticity by forming self-assembly common networks. The WLMs/HMPAM self-assembly system is more resistant to shear and elevated temperature than the single WLMs system. In particular, the self-assembly system retains the hydrocarbon responsiveness like the WLMs that the viscoelastic system transform into a Newtonian liquid with low viscosity when contacting with hydrocarbons. These unique characteristics make the WLMs/HMPAM self-assembly systems very promising for high-temperature resistance clean fracturing fluid application.

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