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## Experimental investigation of viscoelastic polymers for stabilizing foam

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### ABSTRACT

Foam stability can be significantly improved by adding a polymer in foam system, mainly due to the reduction of liquid drainage and the enhancement of interfacial adsorption behavior. In this paper, we combined rheological properties with surface properties to investigate the effect of different polymers on the stability of polymer enhanced foam, and then analyzed the foam stability from microscopic viewpoint. From the results, the liquid drainage of polymer enhanced foam was highly depending on the solution viscosity with a high shear-rate ( $200 \text{ s}^{-1}$ ) instead of the initial thickening ability of polymer, and the stability of liquid films was improved by increasing solution elasticity or interfacial viscoelasticity or by reducing surface tension. Finally, the micro-experiment revealed that the XG (xanthan gum) enhanced foam possessed the dense and uniform gas bubbles and the thick and multi-layered liquid films, which contributes to the reduction of coalescence and the increase of film strength.

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### Introduction

A patent on gas flooding in reservoir was claimed in 1958, in which foam was first introduced to restrict the gas mobility [1]. When the gas and surfactant liquor are injected together, foam can be self-generated in porous media [2,3] and thus control the gas mobility. Concretely speaking, gas mobility is reduced due to the plenty of gas bubbles trapped in pores and throats, and these stationary fractions are prone to block the gas flowing by producing the Jamin effect [4,5]. Meanwhile, foam is crucially dependent on its texture (i.e., bubble density or lamella packing density) to control the gas mobility in porous media [6,7]. It is confirmed that finely textured foams has a greater ability to control the mobile gas than coarsely textured foams [8]. However, foam, formed only by surfactant adsorption, tends to be probably unstable and coarsely textured in reservoir [9]. To achieve the stronger foam, the addition of a stabilizer is the most common approach in the petroleum industry. Over recent decades, water-soluble polymers (e.g., hydrolyzed polyacrylamide, xanthan gum) has been extensively used additives to foam stability and already

applied to oilfield site of China (e.g., Daqing oilfield, Shengli oilfield) [10–13].

The most striking feature of polymer in foam system is its significantly viscoelastic behavior brought to the aqueous phase compared to the other stabilizers (e.g., nanoparticle). The specific performance of this behavior is embodied in an increase of the viscosity in aqueous phase and thus leads to a slowing down of the liquid drainage [14], and the foam stability increases with the increase of solution viscosity [15]. Moreover, polymer–surfactant mixtures can produce a polymeric network formation in the liquid films which control the liquid drainage and reduce the film permeability [16]. Furthermore, the composition and properties of the adsorbed layer at the gas–liquid surface give rise to the strong foam [17]. On the one hand, polymer molecules can act as surfactant molecules to adsorb at the gas–liquid interface and thus modify the surface coating [18]. On the other side, polymer can increase and accelerate the adsorption quantity at the interface because of synergistic interaction (i.e., electrostatic interaction) and thereby create the packed adsorption layers [19]. Therefore, according to previous researches, the focus on stabilizing mechanisms of polymer–surfactant foam can be classified as two basic types on the whole: (i) by retarding the liquid drainage of liquid films; (ii) by enhancing the adsorption behavior of film surface.

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Therefore, the rheology behavior and the surface characterization of polymer–surfactant mixtures play a crucial role in foam stabilizing, which has rarely been researched simultaneously at present. In this paper, we chose practical and feasible polymers in petrochemistry: hydrophobically associating water-soluble polymer (HAWP), comb like polymer (CP) and xanthan gum (XG). The rheological properties of these polymer solutions were first investigated, and followed by the evaluation of surface properties, afterwards, the foam properties were studied. Finally, to investigate the stability of polymer enhanced foam from microscopic viewpoint, the microstructure of gas bubbles and liquid films were observed respectively by using the electron microscopy (EM) and the environmental scanning electron microscope (ESEM).

## Experimental section

### Materials

Foaming agent: Lauramidopropyl Hydroxy SulfoBetaine (LHSB) was supplied by Kelong (Chengdu, China). Foam stabilizer: hydrophobically associating water-soluble polymer (HAWP, with a molecular weight of  $800\text{--}1100 \times 10^4$ ) was supplied by Grangya (Chengdu, China), Comb like polymer (CP, with a molecular weight of  $1800\text{--}2100 \times 10^4$ ) was supplied by Hengju (Beijing, China) and xanthan gum (XG, with a molecular weight of  $50\text{--}100 \times 10^4$ ) was supplied by Zhengmin (Shijiazhuang, China). In this study, the concentration of surfactant and polymer was fixed at 0.2 wt%. Brine water used in this experiment is about  $2 \times 10^4$  mg/L, and calcium and magnesium is about 770 mg/L.

### Methods

#### Rheological analysis

The rheological properties of polymer solution (i.e., XG + LHSB, HAWP + LHSB and CP + LHSB) were measured by using high-temperature rotary rheometer (HAAK MARSIII, Thermo Fisher Scientific Ltd., America). The frequency was 0.1–10 Hz, elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) of polymer solution were tested at 80 °C. Meanwhile, the viscosity of polymer solution was measured as a function of shear rate ( $7.5\text{--}200 \text{ s}^{-1}$ ).

#### Surface analysis

Using the spinning drop video tensiometer (SVT20, Dataphysics Ltd., Germany), and the rotate speed was set to 6000 RPM and temperature was fixed at 80 °C. Surface tension of each solution was measured three times as function of time and the averaged value was recorded. Interfacial viscoelastic modulus ( $E^*$ ) was measured as function of time under frequency 0.05 Hz and amplitude 1000 RPM. Meanwhile, interfacial viscoelastic modulus was also measured as function of frequency (0.02–0.1 Hz)

#### Bulk foam analysis

Using Waring Blender (7012S, Waring Ltd., America), 100 mL solution was prepared and blended at 6000 rpm for 1 min. Foam was then poured into a measuring cylinder and taken into visualization thermostat (UF110, Memmert Ltd., Germany). Finally, the liquid drainage and bulk foam volume were measured foam properties as a function of time at 80 °C.

#### Foam microstructure analysis

Foam was first generated by using Waring Blender, and then the microstructure of gas bubbles was measured by using Leica microscope (LM) (DMLB2, Leica Ltd., Germany) and the liquid films of foam were investigated by using environmental scanning electron microscopy (ESEM) (Quanta 450, FEI Ltd., America).

## Results and discussion

### Rheological properties

The elastic modulus ( $G'$ ) and the viscous modulus ( $G''$ ) of polymers (i.e., HAWP, CP and XG) were studied. From Fig. 1(a) and (b), both  $G'$  and  $G''$  increase as the frequency increases. At low frequencies,  $G''$  is higher than  $G'$  in the solutions of HAWP and CP indicating the viscous modulus played a dominating role and the aqueous solutions are more viscous rather than elastic. Accompanying the frequency increases, the growth of  $G'$  is more significant and the curves of  $G'$  and  $G''$  crossed each other at a specific frequency (i.e., the crossing frequency), especially in CP solution (its  $G'$  exceeded  $G''$ ). It indicates that the elasticity of CP solution is highlighted gradually at the elevated frequency. From Fig. 1(c), obviously, the variation value of  $G'$  is higher than that of  $G''$  and the gap between them generally widens with the increasing of frequency, which indicates that XG solution presents a significant elasticity and becomes more elastic at the elevated frequency. Consequently, the elasticity of three polymers, from more to less in proper order: XG > CP > HAWP. In other words that the viscosity of them followed by: HAWP > CP > XG.

As shown in Fig. 2, the viscosities of polymer solutions (CP, XG and HAWP) decrease obviously at the elevated shear-rate, which presents a pseudoplastic behavior. Rheological parameters (i.e.,  $K$  and  $n$ ) were calculated by using the Power-law model and shown in Table 1. It can be observed that, with the values of  $n$  less than 1, the solution has a stronger pseudoplastic behavior when  $n$  is smaller, indicating a significantly stretched conformation of polymer molecule (followed by CP > HAWP > XG). A higher value of  $K$  exhibits a stronger thickening ability (followed by HAWP > XG > CP). Meanwhile, XG solution presents the largest viscosity at high shear-rate ( $200 \text{ s}^{-1}$ ). This is mainly because that, for CP, the shear thickening is hardly observed at higher shear rate, resulting from the disentanglement effect and oriented behavior of long-chain molecules; for HAWP, due to the cross-linking structures are developed by intra- and inter-molecular associations between the hydrophobic units [20], the shear thickening effect is considerable at a low shear-rate; As for XG, its molecular main-chain is composed of sugar units and grafted by side-chain with polar groups [21], and thus promotes forming a branched and rigid rod structure and increase shear-resistant.

### Surface properties

The surface properties of polymer–surfactant mixtures are fairly important for foaming ability and foam stability, and the surface tension of three polymer–surfactant solutions were investigated in this section. As shown in Fig. 3, the surface tension of polymer–surfactant solutions is immediately reduced to 28–31 mN/m and does not change obviously over time. Comparing with the initial value of solutions without surfactants (61 mN/m), these mixtures can absorb at the interface at a fast rate and low the surface tension, which presents the intense interaction between polymers and surfactants that stated by Petkova et al. [19]. This is mainly because that the interaction is entirely up to electrostatic and hydrophobic forces [22–24], meanwhile, the surfactant (LHSB) with strongly hydrophilic groups (i.e. sulphonate ( $\text{SO}_3^-$ ), hydroxyl ( $\text{OH}^-$ ) and amino ( $\text{N}^+$ )) interacts positively with polymers. Therefore, these polymers have great potential to preserve the good foam formation. It should be noted that the equilibrium surface tension follows the order: HAWP > CP > XG, indicating the most dense adsorption layer is formed in XG solution.

In order to further study the surface properties of polymer–surfactant mixtures, the viscoelasticity of liquid film was evaluated by measuring the interfacial viscoelastic modulus. As shown in

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