Foam Stabilization Mechanism of a Novel Non-cross-linked Foam Fracturing Fluid

Junjie Xiong, Zhongcong Zhao,* Wenan Sun, and Wei Liu

ABSTRACT: Traditional foam hydraulic fracturing fluids used guar cross-linking technology. However, major production problems, such as high friction and difficulty to accurately control the cross-linking time, have influenced the large-scale application of cross-linked guar foam fracturing fluids. In this study, we developed a novel non-cross-linked foam fracturing fluid using a series of polymers synthesized with acrylamide and hexadecyl trimethylallyl ammonium chloride as monomers and improved the stability of foam by forming structures in solution through association. The results showed that the hydrophobic groups were the key factors that affect the foam stability, and the hydrolysis degree had a significant effect on the elasticity of the polymer solution. The model association polymer with 0.75% hydrophobic group content and 56% hydrolytic degree was optimal. The stability of our proposed foam was comparable to that of the cross-linked guar gum foam. The adsorption of associating polymers on the gas and water interface resulted in a high-stability foam. Our study demonstrates a new avenue to develop high-stability foams to satisfy the current hydraulic fracturing scheme.

1. INTRODUCTION

Hydraulic fracturing is the key stimulation technology that creates fractures in the low-permeable reservoirs to improve the yield of oil and gas.1 The fracturing fluid transports the proppant during hydraulic fracturing to obtain the artificial fracture diversion channel.2 The high-quality hydraulic fracturing fluid aims to create sufficient fractures for oil and gas flow and control the proppant transportation.3 In practice, the water-based fracturing fluid is the most cost-effective choice. However, the residue contents generated by guar gum water-based fracturing may cause damage to low-permeability reservoirs and are difficult to be eliminated.4 The application of the water-based fracturing fluid may also cause environmental problems, such as the consumption of large amounts of water and the pollution of surface water and groundwater.5,6

The first application of foam fracturing was in Lincoln, the United States, in 1968, and began to develop rapidly after 1973.7 In recent years, new foam fracturing fluids, such as viscoelastic surfactant foam fracturing fluid8,9 and nanoparticle-stabilized foam fracturing fluid,10−12 have received much attention. Foam consists of both gas and liquid phases. Because liquid is the external phase of gas, foam has the characteristics of high viscosity and low density. Compared to other types of fracturing fluids, foam fracturing fluids use less water13 and show low damage to the reservoir, easy flowback, and sand-carrying capacity.14

Traditional foam fracturing fluid system is based on cross-linked guar gum fracturing fluid. However, the foam stability of the guar fracturing fluid is insufficient, which needs cross-linking agents to improve its foam stability and strong viscoelasticity.15−17 Thus, the formulation and process can be very complicated. It is challenging to form foam in the field application, and increase in the friction and reduction in the shear resistance may occur when the cross-linking time of the foam fracturing fluid is too short.18,19 On the other hand, long cross-linking time may cause a decreased sand-carrying performance, increased filtration loss, and sand plugging occurrence.

The non-cross-linking fracturing fluids, such as viscoelastic surfactant (VES) fracturing fluids, have become an important development direction of fracturing fluid technology.20−22 VES forms associated structures through rodlike micelles, which is essentially a kind of association.23−25 In 1999, Zhang and Gupta26 first proposed the combination of VES and foam fracturing fluid. In 2006, VES−CO2 foam fracturing fluid technology was first successfully applied in Park, Wyoming.27 Since then, VES−CO2 foam fracturing fluid has rapidly become a hot research topic in the world. However, the use of VES−CO2...
foam fracturing fluid is limited by its high surfactant concentration, high cost, and poor temperature resistance.

This study developed a new water-soluble polymer as a foam stabilizer. A stable structure can be formed by the mutual association between the polymer molecular chains without chemical cross-linking. This self-formed structure is reversible and can meet the stability and viscoelasticity requirements of foam fracturing fluids. The rheological properties and functions of the proposed foam fracturing fluid system are similar to those of the cross-linked guar gum foam fracturing fluid. The different mechanisms compared to chemical cross-linking demonstrate an alternative method to form a highly stable foam.

2. RESULTS AND DISCUSSION

2.1. Characterization of Foam Stability. The foam stability of the associating polymer foam and cross-linked guar gum foam was compared. The foam stability of the associating polymer foam with cross-linked guar gum foams at different temperatures was similar (Table 1). This showed that the space structure formed by association can meet the demand of foam stability, which was similar to the effect of the space structure of cross-linked guar gum.

2.2. Effect of Associative Structure on Foam Stability. The temporal conductivity changes for polymer foams with different hydrophobic group contents (A1, A2, A3, and A4) are shown in Figure 1. For hydrolyzed polyacrylamide (HPAM) without the hydrophobic group, the foam conductivity decreased linearly with time, and HPAM near-completely defoamed within 15 min. A1 polymer contained a small number of hydrophobic groups, and the drainage speed of the liquid film was reduced compared with that of HPAM. With the further increase of the hydrophobic group content, the binding effect of the association structure on water was further enhanced, and the stability of A2 polymer foam was also further improved. At the initial stage of foam formation, both A3 and A4 polymer foams had a significant rapid drainage stage, which was about 5 min. The associative structure was likely destroyed under high shear rates, which gradually recovered under static conditions. When the associative structure attained a certain strength, the drainage speed of the liquid film slowed down significantly. The hydrophobic group content of the A4 polymer was the largest, and the foam conductivity changed to be the slowest and the foam was the most stable. The results of higher hydrophobic group contents in the polymer corresponding with a slower change rate of foam conductivity indicate that the association structure can significantly improve the stability of the foam.

The stability of cross-linked guar gum foam was lower than that of the A4 associating polymer foam at 60 °C under the conditions of the same concentration and similar foam quality. When the hydrophobic group content reached 1%, the stability of non-cross-linked foam formed by association was superior to that formed by cross-linked guar gum. The stability of the associating polymer foam was very good because the foam volume could continue to grow under continuous high-speed stirring. In comparison, the shear resistance of cross-linked foams was poor, and the volume of foams decreased significantly due to continuous stirring. Thus, the hydrophobic group content was a key factor that can influence the foam stability (Tables 2 and 3).

Table 1. Results of Foam Stability Tests

| temperature (°C) | C3 associating polymer foam | cross-linked guar gum foam |
|------------------|-----------------------------|---------------------------|
|                  | foam volume (mL) | half-life for drainage (min) | foam volume (mL) | half-life for drainage (min) |
| 25               | 348            | 232                        | 353            | 229                        |
| 60               | 352            | 196                        | 358            | 172                        |

Figure 1. Effect of hydrophobic group content on foam stability.

Table 2. Parameters of HPAM, A1, A2, A3, A4, and Cross-Linked Guar Gum

|                  | hydrophobic group content (%) | degree of hydrolysis (%) | foam quality (%) | slope of the curve |
|------------------|-----------------------------|--------------------------|------------------|-------------------|
| HPAM             | 0                           | 28.7                     | 55.55            | −1.03             |
| A1               | 0.25                        | 26.28                    | 55.06            | −0.53             |
| A2               | 0.5                         | 25.00                    | 54.55            | −0.24             |
| A3               | 0.75                        | 28.01                    | 56.06            | −0.051            |
| A4               | 1                           | 26.26                    | 54.49            | −0.016            |
| cross-linked guar gum | 0.047                      | 0.049                    | 0.24             | 1.03              |

Table 3. Parameters of A3, B3, and C3

|                  | hydrophobic group content (%) | degree of hydrolysis (%) | foam quality (%) | slope of the curve |
|------------------|-----------------------------|--------------------------|------------------|-------------------|
| A3               | 0.75                        | 28.01                    | 56.06            | −0.051            |
| B3               | 0.75                        | 40.77                    | 55.88            | −0.049            |
| C3               | 0.75                        | 56.99                    | 58.33            | −0.047            |

The degree of hydrolysis had little effect on foam stability. The trend lines of the conductivity curves of polymer foams with different degrees of hydrolysis were nearly parallel under the condition of the same hydrophobic content (Figure 2). From the slope of the curve, it can be seen that the degree of hydrolysis increased and the foam stability increased slightly.

2.3. Effect of Associative Structure on Foam Viscoelasticity. The viscoelasticity of 0.3% associating polymer solution with different hydrophobic group contents and different degrees of hydrolysis was compared (Figure 3). The viscoelasticity of the polymer solution increased with increased hydrophobic group contents under the same degree of hydrolysis. The energy storage modulus (G’), which was less than the energy dissipation modulus (G’’), and the polymer solution was mainly viscous when the hydrophobic group content was less than 0.5%. When the hydrophobic group content was more than
Before cross-linking, the molecular chains were distributed in layers without forming a three-dimensional network structure. The cross-linking between boron and guar gum cis-hydroxyl groups formed a very dense network structure in guar gum solution after the addition of the boron cross-linking agent. In comparison, the structure formed by association (Figure 4B) is similar to that of cross-linked guar gum (Figure 4C). Notably, the structure network of the associating polymers was formed due to the physical reaction, while that of guar cross-linking agents was due to the chemical reaction.

Our proposed mechanism for foam stabilization is shown in Figure 5. The liquid film’s spatial network structure greatly improved the liquid film’s strength and elasticity by the interaction between the molecular chains of the associating polymer and the surfactant micelles. This structure may obstruct the plateau channel, which reduces the degree of freedom of water molecules and improves foam stability.

2.5. Foam Stabilization Mechanism of Associating Polymers. The fluorescence stain was evenly distributed in the whole polymer solution, as seen from the confocal fluorescence image of the C3 associating polymer solution (Figure 6). When the foam was formed, the concentration of fluorescent dye on the surface of the foam was higher than that in the liquid phase, indicating that the associating polymer tended to separate toward the gas—liquid interface in an aqueous solution. The improved foam stability is likely because the polymer was concentrated on the gas—liquid interface, which made the foam difficult to generate polymerization and drainage.

The transmittance of the SDS solution foam was better but that of the C3 associating polymer solution foam was greatly weakened (Figure 7). The surface of the foam was wrapped by the associating polymer in the C3 associating polymer solution, resulting in decreased transmittance. The associating polymer adsorbed on the gas—liquid interface provided a protective film, which SDS did not provide.

3. CONCLUSIONS

The main conclusions of this study are as follows:

1) It is feasible to improve the stability of foam by association, and the stability of the associating polymer foam was equivalent to that of cross-linked guar gum foam.

2) Associating polymer had the characteristic of enrichment at the gas—liquid interface, and it wrapped the foam and improved the airtightness. The association formed a spatial network structure through winding and side-chain association in the liquid phase, which improved the strength and elasticity of the liquid film, thus improving the stability of the foam.

3) Shear thickening and shear dilution were beneficial to the formation and stability of the foam. The problem of uncontrollable cross-linking time of cross-linking foam fracturing fluid was avoided by association.

4. EXPERIMENTAL SECTION

4.1. Materials. Acrylamide (AM, AR), SDS (AR), sodium hydrogen sulite (NaHSO₃, AR), ammonium persulfate ([NH₄]₂S₂O₈, AR), potassium chloride (KCl, AR), and sodium hydroxide (NaOH, AR) were purchased from ChengDu Chron Chemicals Co., Ltd. Hexadecyl trimethylallyl ammonium chloride (C16DMAAC) was purchased from Chengdu BaiChun Petroleum Technology Co., Ltd.
4.2. Synthesis of the Hydrophobic Associating Polymer. The hydrophobic associating polymers were prepared by aqueous free-radical solution polymerization and posthydrolysis techniques. AM and C16DMAAC were dissolved in deionized water and then poured into a small jacketed reaction kettle. Oxygen was removed by fluxing nitrogen at 20 °C for 30 min. While the solution was heated to 40 °C, polymerization was initiated by adding the initiator solution (NaHSO3-(NH4)2S2O8). Nitrogen bubbling was stopped when the viscosity of the monomer solution increased. Polymerization was finished after 6 h at 40 °C. The polymerized gelatin was cut into small pieces, mixed with sodium hydroxide powder, and hydrolyzed at 80 °C for 3 h. The hydrolyzed polymer was purified with ethanol and dried in a vacuum oven at 60 °C.
series of polymers with different numbers of hydrophobic groups (A1, A2, A3, and A4) and degrees of hydrolysis (A3, B3, and C3) were prepared by changing the proportion of C16DMAAC and the weight of NaOH. In this paper, the content of the hydrophobic group in the associating polymer is expressed by the feeding ratio (Figure 8).

![Molecular structure of the associating polymer](https://example.com/molecular_structure.png)

**Figure 8.** Molecular structure of the associating polymer.

### 4.3. Degree of Hydrolysis Tests of Polymers

The degree of hydrolysis of the synthetic polymer was measured by the conductivity method. 100 mL of 0.04% polymer solution was prepared and placed on a magnetic stirrer. 0.5 mL of hydrochloric acid standard solution was added each time until the conductivity value exceeded 1500 μs. The curves of the two sections before and after the jump point were fitted using the consumed volume of hydrochloric acid as the vertical coordinate and the corresponding conductivity value as the horizontal coordinate. The horizontal coordinate corresponding to the intersection of the two fitting lines was used as the endpoint of titration to calculate the degree of hydrolysis.

### 4.4. Foam Stability

150 mL of 0.3% C3 associative polymer solution with 1% KCl and 0.03% SDS solution was added into a Warring mixer. The speed of the mixer was adjusted to get about 350 mL foam, and the stirring time was controlled to be 2 min. The foam volume and half-life for drainage were recorded in a measuring tube. Similarly, 150 mL of 0.3% guar gum solution and 0.2% foaming agent was added into the Warring mixer. The speed of the mixer was adjusted to get about 350 mL foam, and the stirring time was controlled to be 2 min. The foam volume and half-life for drainage were recorded in a measuring tube. Similarly, 150 mL of 0.3% guar gum solution and 0.2% foaming agent was added into the Warring mixer.

Foam stability is the most critical parameter. Foam is a thermodynamically unstable system, and its decay mechanism includes liquid film drainage and coalescence. These are the key to studying foam’s stability from the liquid film because these two mechanisms are directly related to the film. As the liquid film of the external phase conducts electricity while the gas—liquid interface. The total concentration of rhodamine B in the aggregate increases when the polymer aggregates in an aqueous solution. 0.1% C3 associating polymer solution with 1% KCl and 0.025% SDS was prepared. After full dissolution, the solution was kept for 24 h. The conductivity method was used to observe the foam. 0.3% C3 associating polymer solution containing 0.025% SDS and 1% KCl was prepared with deionized water, which was kept for 24 h. The C3 associating polymer solution and 3% SDS solution were added into two beakers separately. The solutions were stirred slowly to generate foam. The foams on the glass slides were observed and imaged.

### AUTHORS INFORMATION

**Corresponding Author**

Zhongcong Zhao — Petroleum Engineering College, Yangtze University, Wuhan 430100 Hubei, China; Email: xjjkk@163.com

**Authors**

Junjie Xiong — Petroleum Engineering College, Yangtze University, Wuhan 430100 Hubei, China; CNOOC EnerTech-Drilling & Production Co., Tianjin 300452, China

Wenan Sun — Petroleum Engineering College, Yangtze University, Wuhan 430100 Hubei, China; orcid.org/0000-0001-8124-4936

Wei Liu — Petroleum Engineering Technology Research Institute, Sinopec Jianghan Oilfield Company, Wuhan 430035 Hubei, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04861

### Notes

The authors declare no competing financial interest.

### REFERENCES

(1) Zhong, C.; Zolfaghari, A.; Hou, D.; Goss, G. G.; Lanoil, B. D.; Gehman, J.; Tsang, D. C. W.; He, Y.; Alessi, D. S. Comparison of the Hydraulic Fracturing Water Cycle in China and North America: A Critical Review. *Environ. Sci. Technol.* 2021, 55, 7167−7185.

(2) Zhu, J.; Yang, Z.; Li, X.; Song, Z.; Liu, Z.; Xie, S. Setting Behavior of the Proppants in Viscoelastic Foams on the Bubble Scale. *J. Pet. Sci. Eng.* 2019, 181, 106216.

(3) Kim, J. Y.; Zhou, L.; Morita, N. Study of Degradable Fibers With and Without Guar Gum As A Proppant Transport Agent Using A Large Scale Slot Equipment. *Study of Degradable Fibers With and Without Guar Gum As A Proppant Transport Agent Using A Large Scale Slot*
(4) Ishii, M.; Murata, S.; Ishitsuka, K.; Lin, W. Stability of Novel Cellulose-Nanofiber-Containing Foam as Environmentally Friendly Fracturing Fluid. J. Pet. Sci. Eng. 2022, 208, 109512.

(5) Vengosh, A.; Jackson, R. B.; Warner, N.; Darrah, T. H.; Kondash, A. A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States. Environ. Sci. Technol. 2014, 48, 8334–8348.

(6) Zhong, C.; Nesbo, C. L.; Goss, G. G.; Lanoil, B. D.; Alesi, D. S. Response of Aquatic Microbial Communities and Bioindicator Modelling of Hydraulic Fracturing Flowback and Produced Water. PEMS Microbiol. Ecol. 2020, 96, fiaa068.

(7) Gaydos, J. S.; Harris, P. C. Foam Fracturing: Theories, Procedures And Results. Foams Fracturing: Theories, Procedures And Results; OnePetro, 1980.

(8) Wu, M.; Mohanty, K. K. Rheology of Polymer-Free Foam Fracturing Fluids. J. Pet. Sci. Eng. 2015, 134, 87–96.

(9) Elbag, A. S.; Da, C.; Chen, Y.; Mukherjee, N.; Noguera, J. A.; Alzobaidi, S.; Reddy, P. P.; AliSumaiti, A. M.;HIRASAKI, G. G.; BIWAL, S. L.; NGUYEN, Q. P.; JOHNSTON, K. P. Viscoelastic Diamine Surfactant for Stable Carbon Dioxide/Water Foams over a Wide Range in Salinity and Temperature. J. Colloid Interface Sci. 2018, 522, 151–162.

(10) Fei, Y.; Johnson, R. L.; Gonzalez, M.; Haghhighi, M.; Pokalai, K. Experimental and Numerical Investigation into Nano-Stabilized Foams in Low Permeability Reservoir Hydraulic Fracturing Applications. Fuel 2018, 213, 133–143.

(11) Fei, Y.; Pokalai, K.; Johnson, R.; Gonzalez, M.; Haghhighi, M. Experimental and Simulation Study of Foam Stability and the Effects on Hydraulic Fracture Proppant Placement. J. Nat. Gas Sci. Eng. 2017, 46, 544–554.

(12) Qajar, A.; Xue, Z.; Worthen, A. J.; Johnston, K. P.; Huh, C.; Bryant, S. L.; Prodanovic, M. Modeling Fracture Propagation and Cleanup for Dry Nanoparticle-Stabilized Foam Fracturing Fluids. J. Pet. Sci. Eng. 2016, 146, 210–221.

(13) Mojid, M. R.; Negash, B. M.; Abdulelah, H.; Jufar, S. R.; Adewumi, B. K. A state-of-art review on waterless gas shale fracturing technologies. J. Pet. Sci. Eng. 2021, 196, 108048.

(14) Abdelaal, A.; Aljawad, M. S.; Alyousef, Z.; Almajid, M. M. A Review of Foam-Based Fracturing Fluids Applications: From Lab Studies to Field Implementations. J. Nat. Gas Sci. Eng. 2021, 95, 104236.

(15) Wang, C.; Zhang, Z.; Du, J.; Li, X.; Zhao, M.; Zhang, Z. Titanium-based nanoscale cross-linker for guar gum fracturing fluid: effects on rheological behaviour and proppant-carrying ability. Micro Nano Lett. 2019, 14, 1096–1101.

(16) Wang, C.; Du, J.; Liu, P.; Su, Y.; Li, X.; Zhang, Z. Pentazyriterhitol Encapsulated with Boric Acid: An Efficient Composite Crosslinker for Guarp Gum Fracturing Fluid. J. Appl. Polym. Sci. 2020, 137, 48528.

(17) Zhang, Z.; Pan, H.; Liu, P.; Zhao, M.; Li, X.; Zhang, Z. Boric Acid Incorporated on the Surface of Reactive Nanosilica Providing a Nano-Crosslinker with Potential in Guarp Gum Fracturing Fluid. J. Appl. Polym. Sci. 2017, 134, 45037.

(18) Jiang, T.; Zuo, L.; Huang, J. Development Trends and Prospects of Less-Water Hydraulic Fracturing Technology. Pet. Drill. Tech. 2020, 48, 1–8.

(19) Wei, J.; Liu, T.; Dai, X.; Lin, B.; Teng, Z. Synthesis and Properties of a Flow Accelerator for Non-Crosslinked Fracturing Fluid. Petrochem. Technol. 2021, 50, 332–337.

(20) Yekeen, N.; Padmanabhan, E.; Idris, A. K. A Review of Recent Advances in Foam-Based Fracturing Fluid Application in Unconventional Reservoirs. J. Ind. Eng. Chem. 2018, 66, 45–71.

(21) Li, X.; Xie, S.; Yang, Z.; Zhu, J. Research Progress on Nanoparticles-Containing Foam System and Its Application in Hydraulic Fracturing. Mod. Chem. Ind. 2020, 40, 223.

(22) Almubarak, M.; Alyousef, Z.; Almajid, M.; Almubarak, T.; Ng, J. H. Enhancing Foam Stability Through a Combination of Surfactant and Nanoparticles; OnePetro, 2020.