

Synthesis and performance evaluation of high temperature drag reducing agent for deep shale gas[#]

Zijia Liu¹, Xinfang Ma^{2*}

1 College of Petroleum Engineering, China University of Petroleum (Beijing), Beijing 102249, China

2 College of Petroleum Engineering, China University of Petroleum (Beijing), Beijing 102249, China

(Corresponding Author: Email: maxinfang@cup.edu.cn)

ABSTRACT

Employing inverse emulsion polymerization with acrylamide (AM) as the principal monomer and acrylic acid (AA) as the functional comonomer, an AM-AA emulsion polymer was successfully synthesized under optimized reaction conditions, including polymerization temperature. The structure of the resulting copolymer was characterized using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA), confirming the incorporation of both AM and AA repeating units. The emulsion displayed an average particle size of 222.4 nm with a polydispersity index (PDI) of 0.075, indicating a uniform and narrow size distribution. The AM-AA copolymer exhibited favorable water solubility and thermal stability. It also demonstrated moderate resistance to temperature and shear: after exposure to 90°C the viscosity retention rate of a 3000 mg/L AM-AA polymer solution reached 47.52%. Furthermore, the drag reduction rate of AM-AA polymer is relatively high when the shear rate is 12000s⁻¹, reaching 64.8%.

Keywords: inverse emulsion polymerization ; AM-AA drag reduction agent ; high temperature resistance ; drag reduction rate

1. INTRODUCTION

Shale gas is primarily stored in dense shale through adsorption and free states [1], characterized by extremely low porosity and permeability. These properties cannot provide adequate flow channels for efficient extraction, making it necessary to employ fracturing techniques to enhance reservoir conductivity [2]. Slickwater is one of the key working fluids used in shale gas fracturing, and drag-reducing agents serve as its core additive. The ability to construct a high-temperature-resistant and performance-stable fracturing fluid system has become critical to the success of fracturing operations [5].

Acrylamide polymers commonly used in oilfields generally suffer from poor thermal stability and shear resistance, rendering them inadequate for stimulating deep shale gas reservoirs. Therefore, enhancing the temperature resistance of copolymers requires modifying the molecular structure by introducing temperature- and salt-tolerant monomers into the acrylamide polymerization process to achieve chemical modification. In 2018, Zhang Rusheng et al. [3] proposed several monomers capable of improving the thermal and salt resistance of polymers, such as sodium p-styrenesulfonate (SSS), vinyl sulfonic acid, and acrylic acid (AA)—all containing sulfonic acid groups. The sulfonic acid group is highly polar; its strong hydrophilicity and electrostatic repulsion impart good water solubility to the copolymer, increase the hydrodynamic volume of the molecular chains [4], and provide excellent thermal stability. Aqueous solution polymerization is the most widely applied method in the industrial production of acrylamide-based polymers, but it has drawbacks such as low product molecular weight and poor polymer solubility [3]. Inverse emulsion polymerization involves dispersing highly water-soluble monomers into an oil-soluble organic solvent with the aid of an emulsifier to form a water-in-oil emulsion, which is then initiated by adding an initiator. This method allows efficient dissipation of reaction heat, facilitating the growth of polymer molecular chains and resulting in a high polymerization rate [6]. The synthesized product exhibits fast dissolution and good stability.

This study focuses on enhancing the temperature and shear resistance of polymer molecular chains. Acrylic acid (AA), a functional monomer containing thermally stable groups, was selected, and a novel temperature and shear-resistant polymer was synthesized via inverse emulsion polymerization. By optimizing the synthesis process and reaction

[#] This is a paper for the 17th International Conference on Applied Energy (ICAE2025), December 8-12, 2025, Bangkok, Thailand.

conditions, the preferred polymerization formulation and parameters were determined. The properties of the polymer product, including viscosity-building capacity, temperature resistance, shear stability, and viscoelasticity, were systematically evaluated.

2. EXPERIMENTAL SECTION

2.1 Reagents and instruments

Acrylamide (AM), acrylic acid (AA), sorbitan monooleate (Span-80), octylphenol polyoxyethylene ether (Op-10), white oil, ammonium persulfate, sodium bisulfite, sodium hydroxide, anhydrous ethanol, disodium ethylenediaminetetraacetate (EDTA • 2Na), sodium formate, urea.

Electronic balance, Ubbelohde viscometer, contact electronic thermometer, heat-gathering constant-temperature magnetic stirrer, six-speed rotational viscometer, constant-temperature drying oven, analytical balance, laser particle size analyzer, infrared spectrometer, thermogravimetric analyzer.

2.2 Synthesis and Structural Characterization of AM-AA Emulsion Polymer

2.2.1 Synthesis of AM-AA Emulsion Polymer

Oil phase: White oil and the Span-80/Op-10 composite emulsifier were weighed in a beaker at a mass ratio of 25:2. This mixture was then transferred into a four-necked flask equipped with a stirring apparatus and stirred at 1500 rpm for 20 minutes to ensure thorough and uniform mixing of the oil phase.

Aqueous phase: Acrylamide (AM) and acrylic acid (AA) were mixed at a mass ratio of 4:1 to prepare an aqueous solution. The pH of this solution was adjusted to approximately 7 using an equimolar amount of sodium hydroxide. Subsequently, a 0.5% ammonium persulfate solution, ethylenediaminetetraacetic acid disodium salt (EDTA·2Na), urea, and sodium formate were added to the aqueous phase. The aqueous phase was then introduced into the oil phase, and the combined mixture was subjected to high-speed stirring at 1500 rpm to achieve complete emulsification, resulting in a stable emulsion system. Deionized water was used for all experimental procedures.

Initiation: High-purity nitrogen gas was purged through the four-necked flask, with one neck left open to vent air. The flask was cooled in an ice-water bath. Nitrogen purging to remove oxygen commenced when the water bath temperature reached 10°C. After approximately 30 minutes of purging, an appropriate amount of sodium bisulfite solution was added

dropwise slowly. The reaction was allowed to proceed for 2-3 hours, after which an inversion agent was introduced to yield the inverse emulsion-type friction reducer. The product is shown in Fig.1.



Fig.1 AM-AA emulsion polymer

2.2.1 Structural characterization

The polymeric product was repeatedly washed with anhydrous ethanol to remove impurities and then dried in a constant-temperature oven. Fourier transform infrared (FTIR) spectroscopy (Nicolet, USA) was employed to qualitatively identify the functional groups on the polymer chains. Particle size analysis was performed using a Malvern Zetasizer Nano ZS90 laser particle size analyzer (Malvern, UK) to determine the particle size distribution. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449 instrument (NETZSCH, Germany) to evaluate the thermal stability of the polymer molecules.

2.3 Performance Evaluation of AM-AA Polymer Solutions

2.3.1 Evaluation of the Viscoelasticity of Polymer Solutions

Viscoelasticity is a crucial characteristic of polymer solutions, referring to their simultaneous possession of both viscous and elastic properties [7]. The viscoelastic behavior of the AM-AA polymer solution was measured using an Anton Paar rheometer. Under room temperature conditions, at a fixed stress of 0.2 Pa and with a shear rate range set from 0.01 to 1000 s⁻¹, a frequency sweep test was performed on a 3000 mg/L AM-AA drag-reducing polymer solution. Additionally, a stress sweep was conducted at a fixed frequency of 0.5 Hz to obtain two key indicators for evaluating viscoelastic behavior: the storage modulus (G') and the loss modulus (G'').

2.3.2 Evaluation of the Temperature and Shear Resistance of Polymer Solutions

At room temperature, AM-AA polymer was prepared into solutions with mass concentrations of 3000 mg/L, 5000 mg/L, and 8000 mg/L, respectively.

The apparent viscosity of the polymer solutions at different temperatures was measured using a six-speed rotational viscometer. Furthermore, the shear resistance of the polymer solutions at mass concentrations of 3000 mg/L, 5000 mg/L, and 8000 mg/L was evaluated using an Anton Paar rheometer.

2.3.3 Evaluation of the Drag Reduction Performance of Polymer Solutions

Drag reduction rate refers to the percentage reduction in the initial frictional resistance of a fluid after the addition of a drag-reducing agent [8]. The drag reduction performance of the AM-AA polymer was evaluated using a pipeline friction tester. The test section of the pipeline friction tester consists of a smooth circular pipe with a length of 6 m and an inner diameter of 0.64 cm. Deionized water was first pumped through the test section to measure the pressure drop (P_0). Subsequently, a polymer aqueous solution was prepared, stirred uniformly, and allowed to dissolve completely for 20 minutes. The test solution was then pumped through the same pipe section. The real-time flow rate was monitored using a flow meter, and the pressure drop (P_1) after fluid passage was recorded. By comparing P_1 with the pressure drop of water (P_0), the drag reduction rate of the polymer was calculated .

3. RESULTS AND DISCUSSION

3.1 Effect of Synthesis Conditions on the Polymer Product

3.1.1 Reaction temperature

Upon initiation of the reaction system, the temperature gradually increased, leading to a higher concentration of free radicals, enhanced monomer reactivity, and an accelerated chain propagation rate. The temperature variation during the polymerization process can be divided into three stages: a heating phase after initiation, a constant-temperature phase upon reaching a certain degree of reaction, and a cooling phase upon reaction completion [9].

As shown in Fig.2, when the reaction temperature was around 35 °C, the viscosity of the polymer aqueous solution was relatively low. As the temperature increased to 41 °C, the viscosity reached a peak value of 111 mPa·s. In contrast, the conversion rate exhibited a slow but continuous increasing trend with the rise in polymerization temperature. This phenomenon indicates that temperature significantly influences the initiator activity. At lower temperatures, the initiator activity is insufficient, which inhibits the generation of

active free radicals.

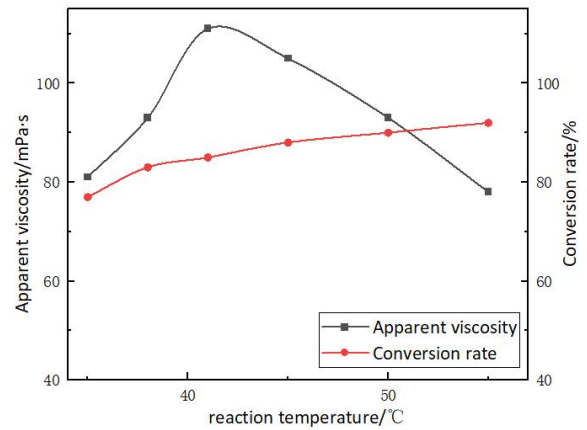


Fig. 2 Influence of reaction temperature on viscosity of polymer solution

When the temperature exceeds a certain threshold, the accumulated reaction heat cannot be dissipated in time, leading to premature termination of the reaction [10]. Therefore, it can be inferred that 41 °C is the optimal polymerization temperature.

3.1.2 Dosage of acrylic acid

With the emulsifier dosage fixed at 6%, the pH of the reaction system at approximately 7, the total monomer mass fraction at 25%, and the polymerization temperature at 41 °C, the effect of acrylic acid dosage on the intrinsic viscosity of the polymer was investigated. The results are shown in Fig.3.

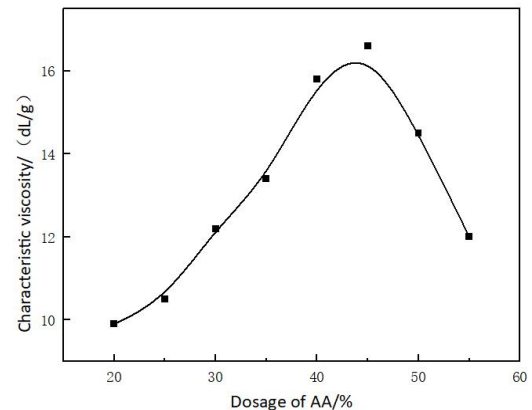


Fig.3 The effect of the dosage of AA on the characteristic viscosity of the polymerization product.

As shown in Fig.3, the intrinsic viscosity of the polymerization product first increases and then decreases with the variation in the dosage of acrylic acid. The intrinsic viscosity reaches its maximum when the dosage of acrylic acid is 45%. Excessive acrylic acid content enhances intermolecular interactions [12], leading to a reduction in solution viscosity. On the other hand, when the acrylamide content is too high, its

higher reactivity [11] promotes self-polymerization, making the polymerization reaction difficult to control and resulting in lower intrinsic viscosity of the polymerization product [13].

3.1.3 The pH value of the reaction system

With the emulsifier dosage fixed at 6%, the total monomer concentration at 30%, the acrylic acid dosage at 45%, and the polymerization temperature at 41°C, the reaction samples were prepared as 1% solutions to investigate the effect of aqueous phase pH on the apparent viscosity and conversion rate of the polymer aqueous solution. The results are shown in Fig.4.

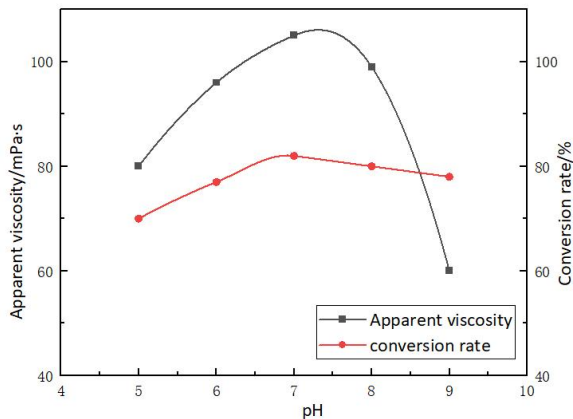


Fig.4 Effect of polymerization system pH value on viscosity of polymer solution

As shown in Fig.4, both the apparent viscosity of the polymer aqueous solution and the conversion rate initially increase and then decrease as the system pH changes from acidic to alkaline. This behavior can be explained as follows: when the polymerization system is highly acidic, imidization is likely to occur, leading to a decrease in the apparent viscosity of the polymer aqueous solution. As the pH increases, the ionization of carboxyl groups generates more -COO^- , enhancing electrostatic repulsion between chains. Simultaneously, numerous carboxyl groups form hydrogen bonds with water molecules, increasing the hydrodynamic volume of the polymer chains. Additionally, the solubility of the product improves [9]. Under alkaline conditions, however, acrylamide is prone to hydrolysis, resulting in a decreased conversion rate [14]. Therefore, a reaction pH between 7 and 8 is considered favorable.

3.2 Structural characterization of polymers

3.2.1 FT-IR test of AM-AA polymers

As shown in Fig.5, the absorption peak at 3192 cm^{-1} is attributed to the stretching vibration of the primary amide -NH_2 group. The characteristic absorption peak at 2934 cm^{-1} corresponds to the -CH_2 group, while the

peak at 1453 cm^{-1} is assigned to the -CH group. These observations confirm the presence of amide groups in the polymer. The peak at 1321 cm^{-1} represents the C–O stretching vibration of the carboxylic acid group, and the characteristic C=O absorption peak of the carboxylic acid group appears at 1704 cm^{-1} . The absorption at 1555 cm^{-1} is attributed to the C=C stretching vibration of the alkene segment. The absence of a distinct C=C double bond absorption peak in the spectrum indicates that the double bonds were cleaved during the reaction, confirming the occurrence of polymerization.

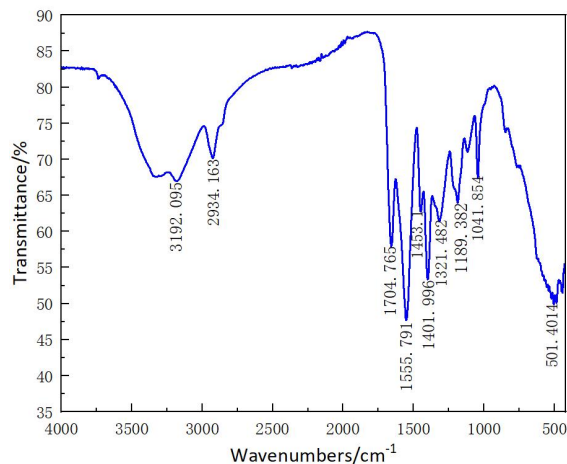


Fig.5 Infrared absorption spectrum of AM-AA polymer on viscosity of polymer solution

3.2.2 Particle Size Analysis of AM-AA Polymer Emulsion

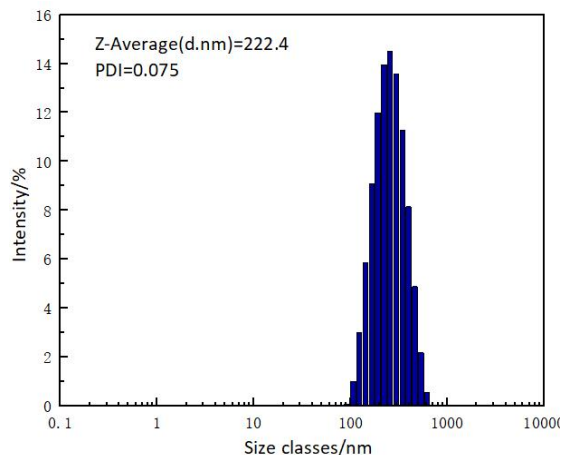


Fig.6 Particle size distribution of AM-AA polymer emulsion on viscosity of polymer solution

As shown in Fig.6, the AM-AA polymer emulsion exhibits an average particle size of 222.4 nm and a polydispersity index (PDI) of 0.075. The uniform particle size and narrow size distribution indicate a highly homogeneous emulsion. The low PDI value further confirms the uniformity of the emulsion particles,

suggesting that the emulsion system remained stable during the polymerization process.

3.2.3 Thermogravimetric Analysis of AM-AA Polymer

Fig.7 presents the thermogravimetric analysis (TGA) curve of the copolymer, from which it can be observed that the first mass loss of 4.38% in the range of 40–150°C corresponds to the evaporation of water in the system, followed by a second mass loss of 2.57% between 150–300°C due to the thermal decomposition of amide bonds; upon further heating, the carboxylic acid groups start to decompose, resulting in an increased mass loss rate, and the corresponding derivative thermogravimetry (DTG) curve shows a significant endothermic peak at 319.236°C within 300–340°C. Based on the above analysis, it is concluded that the glass transition temperature of the AM-AA copolymer is higher than that of polyacrylamide (188°C), and the copolymer exhibits a relatively high decomposition temperature and improved thermal resistance, which can be attributed to the introduction of large side chains containing carboxyl groups into the molecular structure [15], enhancing both intermolecular and intramolecular interactions and thereby improving the thermal stability.

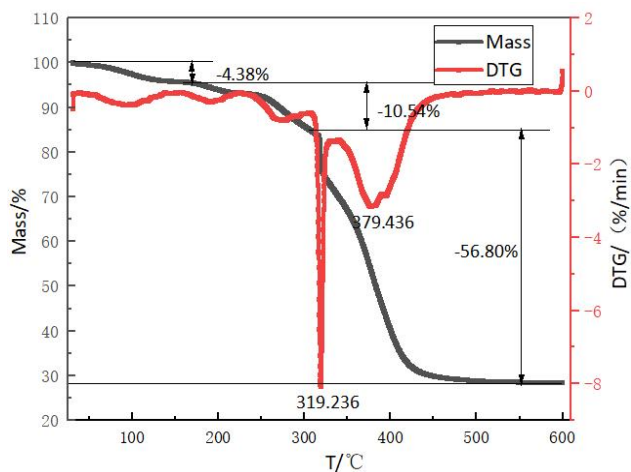


Fig.7 Polymer TG-DTG test solution

3.3 Performance evaluation of AM-AA polymer solution

3.3.1 Evaluation of solubility of polymer solutions

Polymer solutions with concentrations of 1000 mg/L and 2000 mg/L were prepared, and the viscosities of the systems at different dissolution times as well as the viscosity after complete dissolution at 4 hours were measured using a capillary viscometer. The results are presented in Table 1. For the AM-AA polymer product at a concentration of 1000 mg/L, the solution viscosity reached 93.09% of that after complete dissolution within 120 seconds, indicating favorable dissolution performance of the AM-AA polymer product.

Wang Haiyan et al. [22] employed the same method to test the 2-minute dissolution rates of HPG drag reducer, YS-108 drag reducer, and FA-30 drag reducer, obtaining their dissolution rates at a concentration of 1000 mg/L. The dissolution rates of the two polymer drag reducers in this study were compared with these values (Fig.8). Analysis indicates that the 2-minute dissolution rates of the AM-AA polymer products are higher than those of the three drag reducers—HPG, YS-108, and FA-30—demonstrating excellent dissolution performance.

3.3.2 Visco-elastic evaluation of polymer solutions

As shown in the frequency sweep curve of the AM-AA polymer (Fig.9), the storage modulus (G') is consistently higher than the loss modulus (G''), indicating that the elastic behavior dominates over the viscous behavior at this concentration.

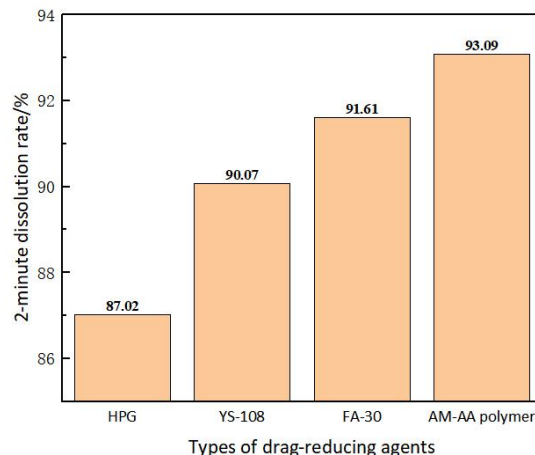


Fig.8 Comparison of solubility of different resistance reducers after 2min in water

Table 1 Test experiment of solubility of two resistance reducing agents

Drag reduction agent	Concentration mg/L	Solution viscosity at different dissolution times /mPa·s					2-minute dissolution rate
		10s	30s	60s	120s	4h	
AM-AA	1000	2.11	2.28	2.34	2.40	2.57	93.09%
	2000	5.05	5.16	5.23	5.51	5.93	92.91%

From the stress sweep curve (Fig.10), the linear visco-elastic region (LVR) of the AM-AA polymer solution is determined to be 0.01–0.55 Pa. Based on this, a stress value of 0.1 Pa was selected for the frequency sweep measurements. Further observation of Fig.9 reveals that at a stress of 0.1 Pa, the storage modulus exceeds the loss modulus, demonstrating the dominance of elastic properties in the polymer solution system [15].

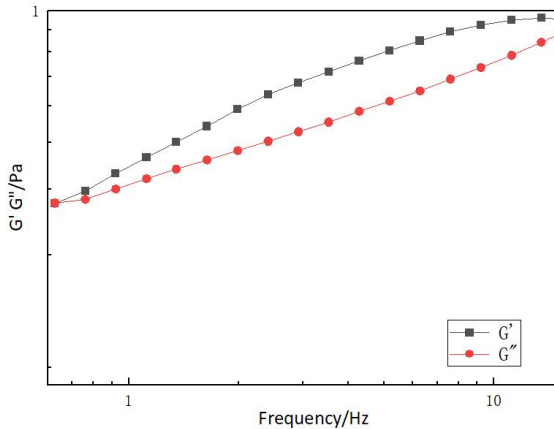


Fig.9 3000mg/L AM-AA polymer frequency scan curve

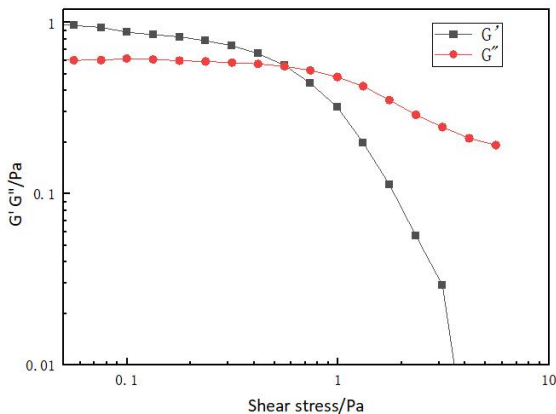


Fig.10 3000mg/L AM-AA polymer frequency stress curve

In summary, the AM-AA polymer solution exhibits low viscosity and high elasticity. According to the visco-elastic drag reduction mechanism [16], when fluid flows through a pipeline, polymer macro-molecules absorb part of the energy and convert it into elastic energy, thereby reducing frictional resistance.

3.3.3 Evaluation of the heat resistance and shear resistance of polymer solutions

Fig.11 shows the apparent viscosity changes of AM-AA polymers with different mass concentrations under temperatures ranging from 30 to 90°C. As can be seen from the figure, the apparent viscosity of the polymer decreases with increasing temperature for all three

concentrations. As the polymer concentration increases, the viscosity retention values also rise, measuring 12.5 mPa·s, 27.3 mPa·s, and 36.9 mPa·s, respectively. The viscosity retention rate increases from 47.52% to 52.57%. This behavior can be attributed to the introduction of functional monomers, which modifies the molecular structure of the polymer and enhances the thermal resistance of the polymer molecular chains [17].

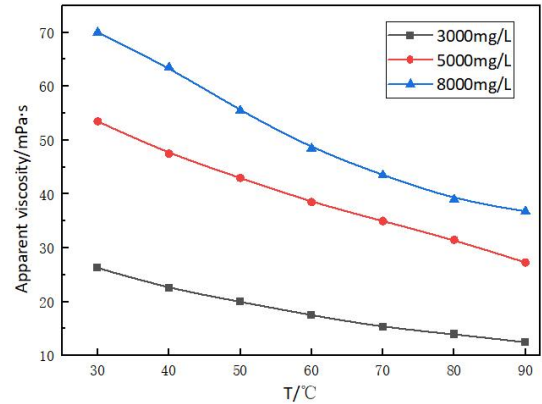


Fig.11 Influence of temperature on the properties of AA polymers with different concentrations

The relationship between shear stress and shear rate for the AM-AA polymer is plotted in Fig.12. As shown in the figure, the dependence of shear stress on shear rate is nonlinear, indicating that the AM-AA polymer exhibits non-Newtonian fluid behavior [19].

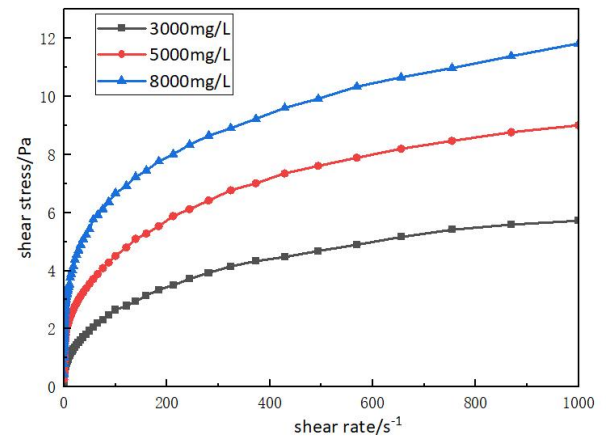


Fig.12 Shear rheological curve of AM-AA

3.3.4 Evaluation of polymer resistance reduction rate

From the two curves at a concentration of 1000 mg/L in Fig.13, it can be observed that the drag reduction rate of both polymers increases with the rising shear rate. At lower shear rates, the drag reduction rate increases rapidly. When the shear rate exceeds 8000 s⁻¹, the polymer chains become highly unstable under high shear conditions, and the

entanglement effect of the macro-molecular linear groups weakens, leading to a slower increase in the drag reduction rate.

It can also be seen from the figure that the drag reduction rate of the AM-AA polymer reaches 64.8% at a shear rate of 12,000 s^{-1} . This is attributed to the addition of polymer macro-molecules into clean water, which enhances the rigidity of the molecular chains and allows full extension of the linear groups [20]. The resulting force counteracts the axial force generated by turbulence, effectively reducing turbulent intensity and minimizing energy loss caused by turbulence itself. As a result, the drag reduction rate of the polymer increases.

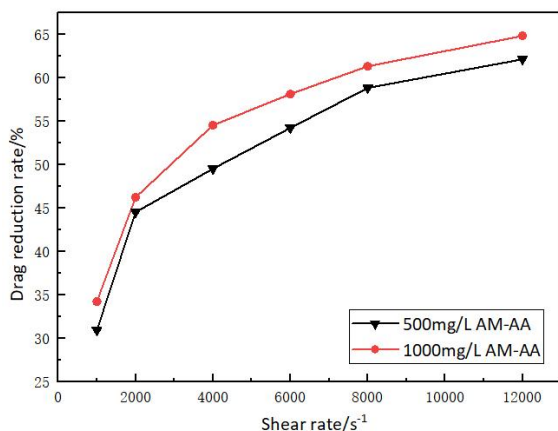


Fig.13 The drag reduction rate of polymers under different concentrations and shear rates

The polymer concentration also influences the drag reduction rate. When the polymer concentration increases, the drag reduction rate rises from 62.1% to 64.8% at a shear rate of 12,000 s^{-1} . The reason for this behavior is that higher polymer concentration enhances the visco-elasticity of the fluid, enabling it to absorb more energy and convert it into elastic energy. This improved energy storage capacity reduces radial forces on the pipe wall during flow, thereby decreasing frictional resistance and increasing the drag reduction rate [21].

4. CONCLUSIONS

This study focuses on the preparation of a temperature-resistant and shear-stable acrylamide-based drag reduction agent. AM-AA emulsion polymer was synthesized via inverse emulsion polymerization. The apparent viscosity and intrinsic viscosity of the polymerization products were investigated under single-factor conditions, and their structures and properties were characterized and evaluated. The following conclusions were drawn:

(1) The optimal synthesis conditions were determined as follows: polymerization temperature of 41°C, acrylic acid dosage of 45%, and reaction system pH of 7–8.

(2) The viscosity retention rate of a 3000 mg/L AM-AA polymer solution reached 47.52% at 90°C. The drag reduction rate of both polymers increased with rising shear rate. The drag reduction rate of the AM-AA polymer was high at a shear rate of 12,000 s^{-1} , reaching 64.8%.

REFERENCE

- [1] Zhao, J., Ren, L., Jiang, T., et al. China's shale gas fracturing decade: Review and prospects. *Natural Gas Industry*, 2021, 41(8): 121-142.
- [2] Zhang, W., Yi, Z., Zhu, L., et al. Synthesis and properties of a drag reducer for emulsion fracturing fluid. *Petrochemical Technology*, 2015, 44(3): 607-611.
- [3] Zhang, R., Zhang, P., Tian, Y. Preparation of a slickwater friction reducer with temperature resistance, salt tolerance, and shear resistance. *Applied Chemical Industry*, 2018, 47(4): 834-838.
- [4] Ram P S, Pal S, Krishnamoorthy S, et al. High-technology materials based on modified polysaccharides. *Pure Appl Chem*, 2009, 81: 525-547.
- [5] Ding, F., Dai, C., Sun, Y., et al. Research and application status of temperature-resistant polyacrylamide drag reducing agent. *Petrochemical Technology*, 2022, 51(12): 1502-1507.
- [6] Zhao, Y., He, B., Ha, R. Synthesis and properties of hydrophobically associating polyacrylamide in inverse microemulsion. *Acta Polymerica Sinica*, 2000, (5): 550-553.
- [7] GARY P, JEREMY H. Hydraulic fracturing under extreme HPHT conditions: successful application of a new synthetic fluid in South Texas gas wells[C]. SPE132173, 2010.
- [8] Chen, Z. Performance evaluation and characterization of polymer drag reducing agents. Master's Thesis, Xinjiang University, 2007, pp. 20–25.
- [9] Yan, R., Wan, J. Inverse microemulsion polymerization of nano-sized amphoteric polyacrylamide. *Polymer Materials Science & Engineering*, 2010, 26(4): 9-12.
- [10] Liu, L., Meng, J., Yang, W. Inverse emulsion polymerization of acrylamide initiated by redox system. *Journal of Beijing University of Chemical Technology*, 2002, 29(2): 59-62.
- [11] Luo, C. Synthesis and performance evaluation of temperature- and salt-resistant emulsion polymers.

Master's Thesis, China University of Petroleum (Beijing), 2017.

[12] Ibrahim A F, Nasr-El-Din H A, Rabie A, et al. A new friction-reducing agent for slickwater-fracturing treatments[J]. *SPE Prod Oper*, 2018,33(3): 583-595.

[13] Xu, X., Zhang, Z., Fei, B., et al. Inverse emulsion polymerization of sodium acrylate. *Acta Polymerica Sinica*, 1998, (2): 134-138.

[14] Cao, Z. Study on emulsion polyacrylamide profile control agent. Master's Thesis, China University of Petroleum, 2008.

[15] Jin, Z. Synthesis and properties of temperature- and salt-resistant acrylamide copolymers. Master's Thesis, Zhejiang University, 2023.

[16] Jiang, S., Chen, F., Zhang, H., et al. Development and evaluation of a novel polymer fracturing fluid. *Journal of Southwest Petroleum Institute*, 2004, 26(4): 44-47.

[17] Che, E. Study on the preparation and application of water-in-oil polyacrylamide by inverse emulsion polymerization. Master's Thesis, Shaanxi University of Science & Technology, 2020.

[18] Liu, Q., Guan, B., Liu, Y., et al. Research and application progress of drag reducers for slickwater fracturing fluid. *Oilfield Chemistry*, 2020, 37(3): 545-551.

[19] Yang, C. Testing and evaluation of drag reduction performance of slickwater fracturing fluid. Master's Thesis, China University of Petroleum (Beijing), 2019.

[20] Liu, H., Zhu, H., Luo, J., et al. Elongational rheological behavior of polyacrylamide and its copolymer aqueous solutions. *Acta Petrolei Sinica*, 2010, 31(5): 806-809.

[21] Wei, J., Liu, J., Du, K. Development and application of an inverse emulsion drag reducer and slickwater system. *Petroleum Drilling Techniques*, 2015, 43(1): 27-32.

[22] Wang, H. Y., Huo, B. X., Guo, L. M., et al. Performance study of a fast-viscosifying slick water drag reducer[J]. *Applied Chemical Industry*, 2016, 45(12): 2229-2233+2237.