

Original Paper

Zwitterionic-hydrophobic associating polymer for enhanced rheology and fluid-loss control in high-temperature, high-salinity water-based drilling fluids



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ABSTRACT

In deep oil and gas drilling, high-temperature and high-salinity conditions have posed severe challenges to water-based drilling fluids. These harsh environments can impair the performance of drilling fluids, increase fluid loss, and lead to frequent downhole accidents. In view of the above problems, this study combines the advantages of zwitterionic and hydrophobic association to prepare a zwitterionic hydrophobic association polymer (P-DADL) with high temperature and salt resistance. The chemical structure and properties were characterized and evaluated by in-situ infrared spectroscopy, nuclear magnetic resonance, thermogravimetry, SEM and other experimental methods. The results show that the thermal decomposition temperature of P-DADL is greater than 297 °C, and it has a spatial network structure in aqueous solution, which exhibits strong clay-particle adsorption and suspension stability. After aging at 180 °C for 16 h, the apparent viscosity of the drilling fluid containing 2 wt% P-DADL is 62 mPa·s, the viscosity retention rate is 70.86%, and the FL_{API} is only 7.4 mL. Under the conditions of 180 °C and 35 wt% NaCl, the FL_{API} was further reduced to 6.4 mL, reflecting the salt synergistic filtration reduction characteristics. In addition, the suspension stability of saturated brine drilling fluid is greater than 98% within 48 h. P-DADL can effectively enhance the temperature resistance and salt resistance of water-based drilling fluid. Compared with commercial products, P-DADL exhibited a 78.4% improvement in filtration performance relative to commercial products. These findings highlight the potential of P-DADL as a multifunctional additive for high-salinity, high-temperature drilling operations.

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1. Introduction

As a primary energy source in human production activities, petroleum is an indispensable fundamental resource for ensuring people's livelihoods and driving industrial development (Li et al., 2024; Sun et al., 2024). With the surging demand for petroleum energy and the depletion of shallow oil and gas resources, the

focus of oil and gas exploration and development has shifted to deep and ultra-deep formations (Guo et al., 2019; Dong et al., 2024; Wang et al., 2025). China possesses abundant deep oil and gas resources, but the drilling process faces numerous challenges, such as high temperature, high pressure, high salinity, and other complex conditions (Sun et al., 2022). These extreme drilling conditions pose higher requirements to the performance of drilling fluids. Conventional rheology modifiers for drilling fluids struggle to meet the requirements for temperature and salt resistance, leading to the deterioration of drilling fluid properties during operations. This deterioration results in increased fluid loss, frequent drilling accidents such as lost circulation, pipe sticking,

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and formation collapse, which severely hinder the development and utilization of deep oil and gas resources (Li et al., 2015; Liu et al., 2016; Moghaddam et al., 2021; Wang et al., 2024). Therefore, maintaining the stability of water-based drilling fluid performance under high-temperature and high-salinity (HTHS) conditions is crucial.

Drilling fluids, often referred to as the “blood” of drilling engineering, have rheological properties closely related to key performances such as hole cleaning, wellbore stability, and drill string lubrication (Luo et al., 2017). Common types of drilling fluids include water-based drilling fluids (WBDFs), oil-based drilling fluids (OBDFs), and synthetic-based drilling fluids (Sadeghalvaad and Sabbaghi, 2015; Ghaderi et al., 2020; Moghaddam et al., 2021). Due to the advantages including low preparation cost, good performance, easy maintenance, and environmental friendliness, bentonite water-based drilling fluids have been widely used in the drilling of various formations (Davoodi et al., 2021; Sun et al., 2023). During deep/ultra-deep drilling operations, conventional additives (such as PAC and starch) are highly prone to failure under formation conditions characterized by HTHS, which leads to the flocculation of bentonite in the drilling fluid, deterioration of drilling fluid properties, downhole complications, and increased drilling costs (Song et al., 2016a, 2016b; Liu et al., 2022). To address the performance degradation of water-based drilling fluids, key materials such as fluid loss reducers, rheology modifiers, and structure-building agents are typically added during drilling fluid formulation. As one of the core additives in water-based drilling fluid systems, rheology modifiers serve to improve the viscosity and yield point of the drilling fluid, optimize the yield point to plastic viscosity ratio and shear-thinning behavior, and minimize fluid loss. Common types of rheology modifiers include natural or synthetic polymers (Warren et al., 2003; Noor et al., 2025), modified starch (Zhang et al., 2021; Zhong et al., 2021), carboxymethyl cellulose (Rasheed et al., 2023), partially hydrolyzed polyacrylamide (Moghaddam et al., 2021), polyacrylate (Xie et al., 2024), polyanionic cellulose (Jia et al., 2022), hydrophobically associating polymers (Xie et al., 2016; Sun et al., 2023), and nanomaterials such as SiO₂ (Lai et al., 2023), carbon nanotubes (Lysakova et al., 2023), nanoscale laponite (Yang et al., 2023), and graphene oxide (Kusrini et al., 2020). However, due to the irregular glycosidic bonds (with low bond energy) in natural macromolecular materials, they are only suitable for formations below 180 °C (Sun et al., 2022). Although synthetic polymers improve the temperature resistance of materials in drilling fluids, in high-salinity environments, high temperature tend to exacerbate the aggregation of clay particles, thereby exerting an adverse impact on drilling fluid performance and fluid loss control (Kazemi-Beydokhti and Hajiabadi, 2018). Therefore, the further development of novel, multi-functional drilling fluid rheology modifiers with enhanced temperature and salt tolerance is urgently needed.

The properties of polymers originate from the molecular structures of the specific monomers they contain (Yuan et al., 2023). Acrylamide-based monomers exhibit high polymerization activity, significant hydration effects, and strong adsorption onto clay surfaces (Luo et al., 2020; Gao et al., 2021). Anionic monomers provide strong hydration, preventing the aggregation of clay particles under HTHS conditions (Quan et al., 2022). Cationic monomers offer multiple adsorption sites, enhancing clay stability (Wang et al., 2024). Zwitterionic monomers possess excellent salt/calcium tolerance and strong hydration capabilities (Wang et al., 2025). Cyclic monomers enhance the temperature and salt resistance of polymers by reinforcing the rigid structure of the polymer backbone (Yang et al., 2023). Organosilicon monomers can form

thermally stable siloxane bonds with clay, strengthening adsorption capacity at high temperatures (Liu et al., 2021). Consequently, the incorporation of temperature-resistant and salt-tolerant monomers into the molecular design of synthetic polymers has become a hotspot in the development of new additives for petroleum engineering (Li et al., 2024). Huang et al. synthesized an AM/AMPS/DMDAAC/SSS copolymer via aqueous solution polymerization, which improved the rheological and fluid loss properties of drilling fluids at high temperatures (Huang et al., 2019). Hou et al. prepared an SSS/AM/AMPS polymer based on inverse emulsion polymerization; its addition to drilling fluids resulted in significant shear-thinning behavior and good temperature resistance up to 160 °C (Huo et al., 2018). Liu et al. synthesized an NVP/AMPS/DVB rheology modifier using micellar polymerization. The formulated clay-free drilling fluid system achieved temperature resistance up to 160 °C with stable rheology and filtration properties (Liu, 2022). Wang et al. synthesized a salt-responsive amphiphilic hydrophobically associating polymer (PAADS) based on free radical micellar polymerization, which functioned well as a viscosifier in saturated sodium chloride drilling fluids with good temperature resistance (Wang et al., 2024). Furthermore, studies by Li et al. showed that cellulose nanoparticles (CNP) provide good fluid loss control in drilling fluids (Li et al., 2015). Chang et al. prepared grafts of monomers like AMPS onto lignin, enhancing the high-temperature and salt tolerance of the polymer (Chang et al., 2019). However, due to the inherent limitations of grafted or modified polymers, they often fail to adequately meet the demands of deep well drilling when faced with the dual challenges of HTHS.

Hydrophobically associating polymers, leveraging dynamic physical cross-linking via hydrophobic groups, offer unique advantages such as viscosity enhancement, salt tolerance, and shear-thinning behavior. They are widely used in high-temperature, high-salinity reservoirs and enhanced oil recovery (Jiang and Pu, 2020; Shi et al., 2020; Wang et al., 2022). The unique charge-balanced structure along the molecular chain of zwitterionic polymers grants them excellent salt resistance and environmental adaptability. Due to the anti-polyelectrolyte effect, the polymer chain conformation transforms from collapsed to expanded in the presence of salt ions (Gao et al., 2014; Ranka et al., 2015; Xiao et al., 2018). For instance, the zwitterionic polymer DADN developed by Liu et al. (2022), the comb-shaped polymer P-TPEG synthesized by Yang et al. (2023), and the hydrophobically associating polymers ASML and PAADS researched by Sun et al. (2022) and Wang et al. (2024), respectively, have demonstrated the feasibility of these structures through their excellent performance in high-temperature, high-salinity drilling fluids. However, few studies have simultaneously optimized charge balance and hydrophobic association to maintain polymer stability in highly saline environments above 150 °C. Therefore, this study integrates the characteristics of hydrophobically associating polymers and zwitterionic polymers. A novel zwitterionic hydrophobically associating polymer, designated P-DADL, was synthesized via free radical aqueous solution polymerization using N,N-dimethylacrylamide (DMAM), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), diallyl dimethyl ammonium chloride (DMDAAC), and lauryl methacrylate (LAM) as monomers. It was evaluated as a rheology modifier and fluid loss reducer in water-based drilling fluids. Results indicate that P-DADL has a thermal decomposition temperature exceeding 297 °C. The API filtration loss (FL_{API}) of a saturated saltwater drilling fluid formulated with P-DADL was 6.4 mL. The high-temperature high-pressure fluid loss (FL_{HTHP}) of a drilling fluid containing 15 wt% NaCl, after aging at 180 °C, was 24 mL. P-DADL exhibits excellent viscosity-building characteristics, suspension stability, and salt-responsive fluid loss control under HTHS, providing a new

approach for developing salt-resistant drilling fluid additives for deep and ultra-deep drilling operations.

2. Materials and methods

2.1. Materials

The experimental materials included: N,N-dimethylacrylamide (DMAM, 98%) was purchased from China Shanghai McLin Biochemical Technology Co., Ltd., 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, 98%), diallyldimethylammonium chloride (DMAAC, 60 wt% aqueous solution), lauryl methacrylate (LAM, 97%), sodium dodecyl sulfate (SDS, 98%) were purchased from China Beijing Minda Technology Co., Ltd. Ammonium persulfate (APS, 98%), sodium hydroxide, anhydrous ethanol, sodium chloride and acetone were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Bentonite was purchased from China Huaian Tengfei Bentonite Development Co., Ltd. Deionized water was prepared in the laboratory.

2.2. Synthesis method of P-DADL

The hydrophobic associative polymer P-DADL was synthesized by referring to the experimental methods reported in Sun et al. (2022). The preparation process is shown in Fig. 1. In short, dissolve 6.42 g AMPS (0.0648 mol) in deionized water and stir thoroughly. Adjust the pH to 7–8 with NaOH. Then add 9.79 g DMAM (0.0473 mol), 7.4 g DMAAC (0.0457 mol), and 0.5 g SDS in sequence, and stir until completely dissolved. Add 1.38 g LAM (0.0054 mol) and stir continuously for 10 min. Transfer the above solution to a three necked flask, heat it up to 55 °C in a water bath under N₂ atmosphere, add 0.4 wt% APS and continue the reaction for 5 h to obtain a viscous polymer. At the end of the reaction, the product was purified three times with ethanol and acetone to remove unreacted monomers, dried at 70 °C for 24 h, and crushed to obtain the final product (P-DADL).

2.3. Characterization of P-DADL

Fourier transform infrared spectroscopy (FTIR). The functional groups and structural characteristics of P-DADL were analyzed using FTIR (Nicolet iS50, USA). The drilling fluid

containing P-DADL was vacuum-dried, ground into a fine powder and subjected to infrared analysis to investigate the interaction between P-DADL and bentonite. The sample was prepared using the potassium bromide pellet method, and spectra were recorded in the range of 4000–500 cm^{−1} with a resolution of 4 cm^{−1} and 32 scans. Meanwhile, in-situ FTIR spectra were collected using an in-situ FTIR testing device (INVENIO S, German Bruker, Harrick transmission in-situ chamber) within the temperature range of 25 to 250 °C.

Proton nuclear magnetic resonance (¹H NMR) spectroscopy. The chemical structure of P-DADL was characterised by ¹H NMR spectroscopy (Bruker 600 MHz, Germany). The sample was dissolved in D₂O for analysis.

Thermogravimetric analysis (TGA). The thermal stability of P-DADL was evaluated using TGA (NETZSCH STA 449, Germany). The analysis was performed under a continuous nitrogen purge (flow rate: 20 mL/min), with the sample heated from 30 to 700 °C at a constant heating rate of 10 °C/min. Mass loss was monitored throughout the heating process.

Environmental scanning electron microscopy (ESEM). The microstructure of P-DADL was examined using ESEM (TESCAN CLARA, Czech Republic). Different types of drilling fluids were freeze-dried using liquid nitrogen, followed by vacuum treatment for 8 h and gold sputtering. The microstructure of the polymer solution was characterized by ESEM. Meanwhile, in the ESEM characterization process, the surface element content of the mud cake was obtained using an energy dispersive spectrometer (EDS) with a spectral model of Bruker XFlash616 and an area scanning resolution of 129 eV, high voltage of 15 kV.

Elemental composition analyser (EA). The elemental composition of P-DADL was detected using an EA (Elementar Vario E1 III, Germany), and the CHNS mode was selected for testing to obtain the mass ratios of the four elements C, N, S, and H in the sample.

Gel permeation chromatography (GPC). The average molecular weight and molecular weight distribution of polymer P-DADL were measured by GPC (HLC-8420 GPC, Japan), and the water phase was used as mobile phase at room temperature.

X-ray photoelectron spectrometer (XPS). The surface elemental composition of the mud cake was analyzed by XPS (ESCALAB 250Xi, Thermo Fisher, USA), and the results were mutually verified with EDS. The working voltage is 12.5 kV, the full energy spectrum is 100 eV, the narrow spectrum is 30 eV, the step

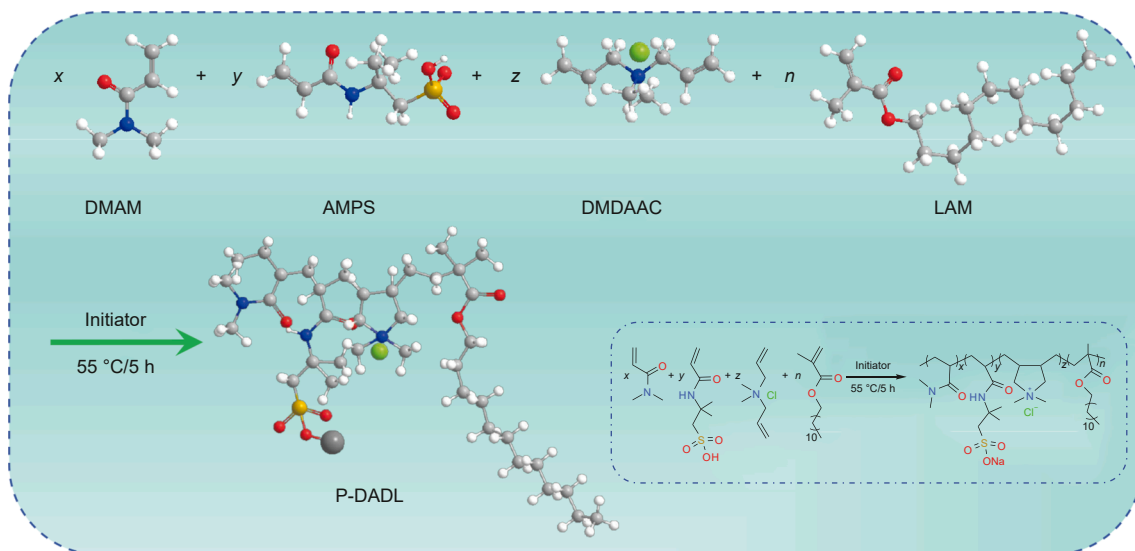


Fig. 1. The translation of P-DADL.

size is 0.05 eV, the residence time is 40–50 ms, and the work function is 4.7 eV.

2.4. Preparation and performance test of drilling fluid

Water-based drilling fluids (WBDFs). 16 g of bentonite and 0.56 g of anhydrous sodium carbonate were added to 400 mL of deionized water, followed by high-speed shear mixing for 30 min. The mixture was then kept under airtight conditions for 24 h for subsequent use.

P-DADL copolymer-modified drilling fluids (P-WBDFs). Add an appropriate amount of polymer P-DADL (2–8 g) to the WBDFs under high-speed stirring for 30 min to obtain P-WBDFs.

Salt-containing polymer drilling fluids (S/P-WBDFs). 0–35 wt% NaCl were added to P-WBDFs (2 wt% P-DADL), followed by high-speed shear mixing for 30 min.

According to the American Petroleum Institute (API) recommended standards (API RP 13I, 2004; API RP 13B-1, 2009), the rheological properties of drilling fluid before and after aging were measured using a six-speed rotational viscometer (Tong Chun, Qingdao ZNN-D6B) at 25 °C. The aging condition is 180 °C and 16 h. The FL_{API} of drilling fluid was tested using an atmospheric medium pressure filter loss meter (Tong Chun, Qingdao SD-3 model) at 25 °C and 0.69 ± 0.03 MPa. The FL_{HTHP} was measured using a GGS42-type apparatus (Qingdao Tong Chun Machinery Petroleum instrument, China), under fixed pressure of 3.5 MPa for 30 min. The drilling fluid rheological parameters of apparent viscosity (AV), plastic viscosity (PV), dynamic shear force (YP), and dynamic plastic ratio (YP/PV ratio) were calculated according to Eqs. (1–4) (Zhang et al., 2016; Chang et al., 2019; Liu et al., 2022; Li et al., 2024).

$$AV = 0.5 \times \theta_{600} (\text{mPa}\cdot\text{s}) \quad (1)$$

$$PV = \theta_{600} - \theta_{300} (\text{mPa}\cdot\text{s}) \quad (2)$$

$$YP = 0.511 \times (\theta_{300} - PV) (\text{Pa}) \quad (3)$$

$$\text{Dynamic plastic ratio} = YP/PV (\text{Pa}/\text{mPa}\cdot\text{s}) \quad (4)$$

where θ_{600} and θ_{300} are the dial readings at 600 and 300 rpm, respectively.

Drilling fluid performance evaluation was carried out in accordance with the API procedures, and the experiments were repeated three times to obtain the average.

The rheological properties of P-DADL aqueous solution and polymer containing P-DADL-modified drilling fluid were analyzed using Bingham plasticity, power law, and Herschel-Burkley model (Wisniewski et al., 2020; Yang et al., 2022; Wang et al., 2025). The analysis is as follows:

$$\text{Bingham model: } \tau = \tau_0 + \mu_p \gamma, \quad (4)$$

$$\text{Power law model: } \tau = K \gamma^n, \quad (5)$$

$$\text{Herschel-Bulkley model: } \tau = \tau_0 + K \gamma^n, \quad (6)$$

where τ is the shear stress (Pa), γ is the shear rate (s^{-1}), τ_0 is the yield point (Pa), μ_p is the plastic viscosity (Pa·s), n is the flow behaviour index, and K is the consistency index (Pa·s ^{n}).

The stability of the drilling fluid system was analyzed using a zeta potential analyzer (Malvern Zetasizer Nano Z, UK). The drilling fluid was diluted 10-fold, and the zeta potential values were

measured. The average of three consecutive measurements was calculated for data analysis.

The suspension stability and cuttings-carrying capacity of the polymer within the drilling fluid system were evaluated by conducting sedimentation stability experiments.

3. Results and discussion

3.1. Molecular structural characterization

3.1.1. FTIR and ¹H NMR spectrum

The FTIR spectrum of P-DADL is shown in Fig. 2(a), the absorption peaks at 3380 and 3324 cm^{-1} belong to the stretching vibrations of N–H and O–H bonds in AMPS. The absorption peak at 2930 cm^{-1} is affiliated to the stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ in the polymer molecules. The absorption peak at 1636 cm^{-1} corresponds to the stretching vibration of C=O in DMAM, AMPS and LAM. The display peak at 1544 cm^{-1} belongs to the bending vibration of N–H in amides. The absorption peak at 1450 cm^{-1} is consistent with the bending vibration of $-\text{CH}_2-$. The absorption peaks at 1403 and 1363 cm^{-1} are subordinate to the stretching vibration of the C–N bond in the five-membered heterocycle formed by DMDAAC, the peak shown at 1222 cm^{-1} corresponds to the asymmetric stretching vibration of the C–O–C bond in LAM (Huang et al., 2019; Maarof et al., 2019). The peaks shown at 1160 and 1040 cm^{-1} belong to the S=O bond stretching vibration and 626 cm^{-1} is attributed to the absorption vibration of C–S bond in AMPS (Huang et al., 2019).

A sample solution of P-DADL was prepared with D₂O as the dispersant for NMR hydrogen (¹H NMR) spectroscopic characterization. As shown in Fig. 2(b), the chemical shifts of the characteristic peaks of the polymer molecular structure have been labeled accordingly in ¹H NMR spectrum. The chemical shift peak of the D₂O solvent was 4.702 ppm. The 1.433, 2.148, and 2.942 ppm peaks were assigned to the chemical shifts of H in the main chain of P-DADL, and the proton peak of methyl ($-\text{CH}_3$) on the side chain is located at 1.185 ppm. The typical chemical shift peaks of 1.185–3.846 ppm corresponded to DMAM, AMPS, DMDAAC, and LAM. The characteristic chemical shift peak of methylene ($-\text{COO}-\text{CH}_2$) in LAM was observed at 3.794–3.846 ppm. Combining FTIR and ¹H NMR spectrum results, the synthesized polymer P-DADL was the designed target product.

3.1.2. Thermal stability analysis

The thermal stability analysis results of P-DADL are shown in Fig. 3. It can be seen that the thermal decomposition of polymer P-DADL can be roughly divided into three stages (Fig. 3(a)). In the first stage, the mass loss of P-DADL from 30 to 297.3 °C is 9.73%, which is due to the evaporation of free and bound water adsorbed by strongly polar hydrophilic groups on polymer molecules (such as amides, sulfonic acids, and quaternary ammonium salts) at high temperatures (Huang et al., 2019; Yang et al., 2022). In the second stage, the quality loss of P-DADL from 297.3 to 372.1 °C was 34.56%, and the quality loss rate reached its peak at 323.7 °C. As shown in Fig. 3(c) and (d), this may be caused by the thermal degradation of amide group in the polymer molecular chain. The third stage occurs within the temperature range of 372.1 to 491.1 °C, with a mass loss of 31.1%, corresponding to the thermal decomposition of the five membered ring of the polymer molecule side chain and the C–C main chain at high temperatures. Fig. 3(b) shows the infrared spectrum under the conditions of 25–250 °C. As the temperature increases, the intensity of each characteristic absorption peak of polymer P-DADL slowly decreases. Among them, the absorption peak intensities at 3380 and 3324 cm^{-1} were relatively significantly reduced, which was due to the volatilization of adsorbed

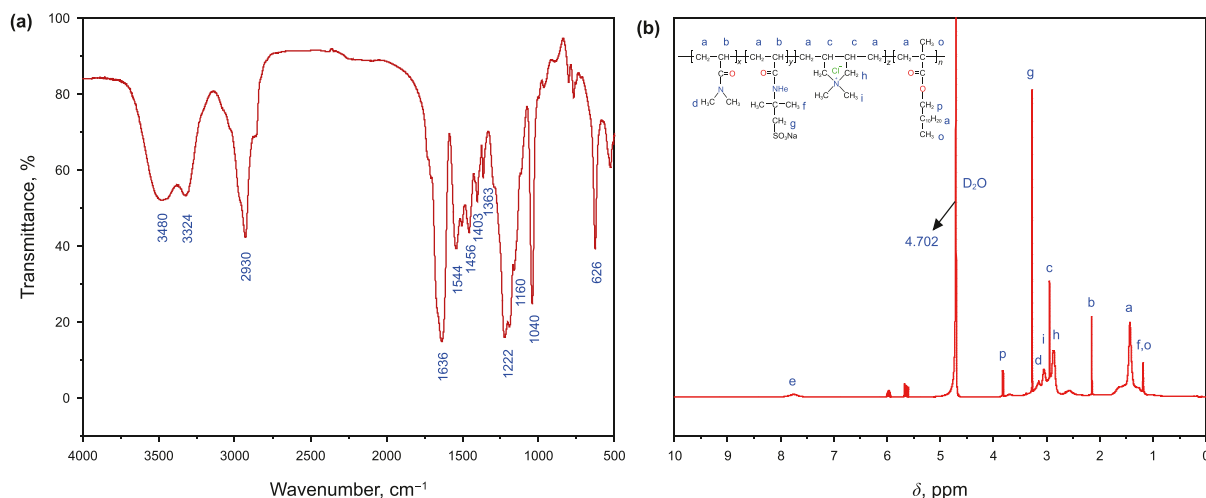


Fig. 2. Characterization of P-DADL: (a) FTIR spectra, (b) ^1H NMR spectra.

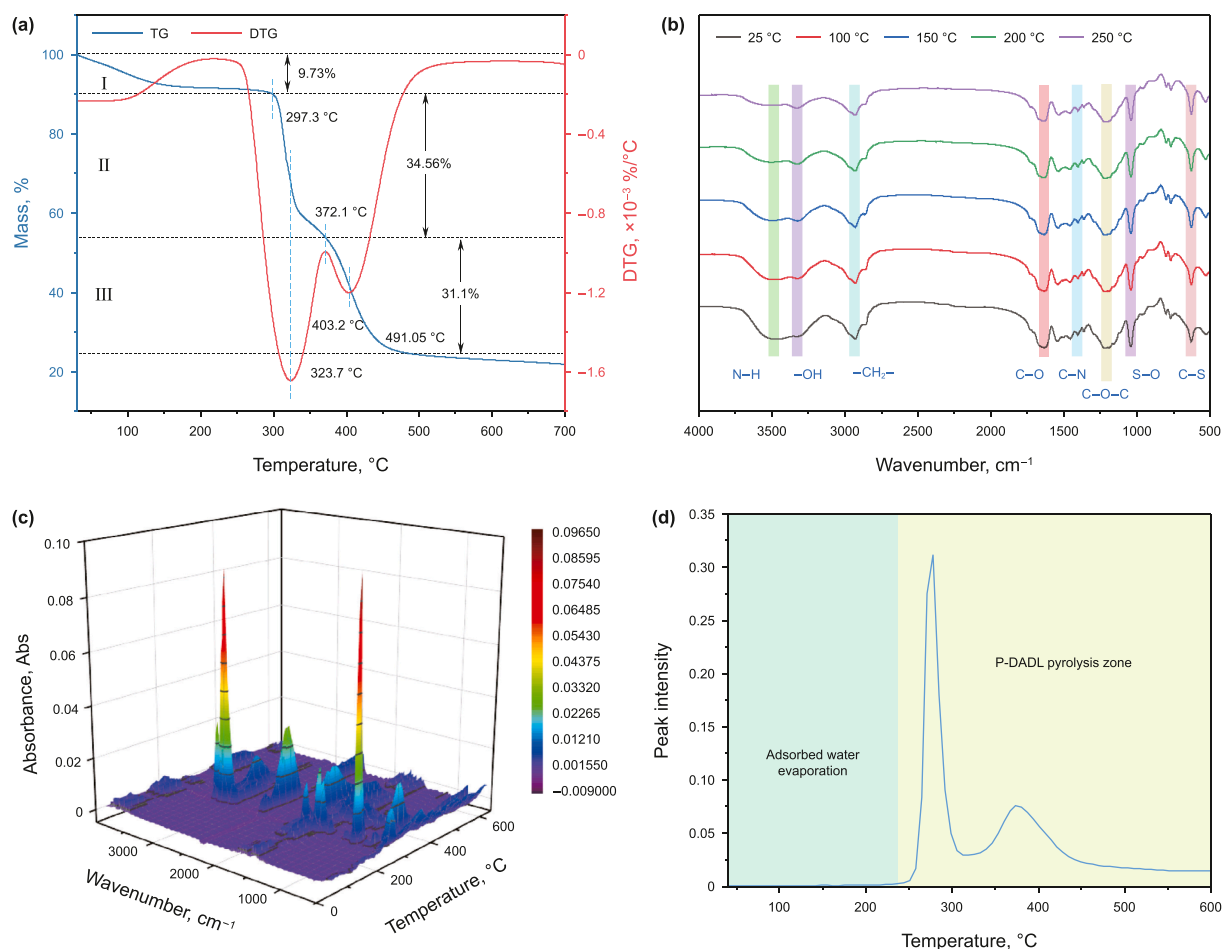


Fig. 3. Thermal stability of polymer P-DADL: (a) TG-DTG curve, (b) in situ FTIR spectra at 25–250 °C, (c) TG-IR curve, (d) peak strength curve of polymer decomposition.

water and bound water containing hydroxyl groups ($-\text{OH}$), while the characteristic peaks did not disappear or shift (Yang et al., 2023). Overall, the degradation of copolymer P-DADL was not significant before 297.3 °C, indicating that P-DADL has good high-temperature resistance.

3.1.3. Analysis of polymer average molecular weight and elemental content

The analysis of the molecular weight and element content of the polymer is helpful to understand the structure and properties of the polymer (Hanton, 2001). The number-average molecular

weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of P-DADL were measured by GPC. The test results demonstrate that the polymer possesses a relatively high molecular weight ($M_n = 721548$, $M_w = 1448056$) and demonstrates adequate solution thickening behavior owing to its good water solubility. The PDI is 2.007, indicating that the molecular weight distribution of the polymer is relatively uniform, which is conducive to the adsorption of the polymer on the surface of the clay particles and improves the performance of the drilling fluid.

The composition of C, N, S and H elements in the P-DADL product was obtained by elemental analysis, as shown in Table 1. It can be calculated from the table that the actual molar ratio of each monomer in the polymer is 28.1:21:19.7:2.7, which is close to the theoretical design. In addition, the content of AMPS and DMDAAC is relatively high, which is beneficial to improve the temperature resistance and salt resistance of the polymer.

3.2. Performance evaluation of P-DADL in WBDF

3.2.1. Effect of concentration

In order to study the effect of P-DADL dosage on the performance of WBDFs, the rheological properties of P-WBDFs with different concentrations after aging at room temperature and 180 °C were evaluated. The results are shown in Fig. 4. The viscosity and shear force of the base slurry before aging was low. With the increase of P-DADL concentration, the rheological parameters (AV, PV, YP) of P-WBDFs showed an upward trend. When the amount of P-DADL was 1.2 wt%, the AV increased from 8 to 57.5 mPa·s, the PV increased from 4 to 34 mPa·s, and the YP increased from 4 to 23.5 Pa. With the increase of concentration to 2.0 wt%, the AV, PV and YP are 87.5 mPa·s, 50 mPa·s and 37.5 Pa, respectively, indicating that the polymer has good viscosity increasing and shearing ability. This is because the polymer P-DADL molecule has strong adsorption groups such as amide and cation, and there is adsorption bridging between the polymers in the drilling fluid and between the polymer and bentonite (Ahmad et al., 2017; Davoodi et al., 2019). By forming an interwoven network structure (Li et al., 2020), the viscosity of the drilling fluid is effectively improved. In addition, the experimental results show that the low addition of P-DADL also improves the rheological properties of drilling fluid.

After thermal rolling at 180 °C for 16 h, the AV, PV and YP of P-WBDFs decreased slightly. The reason is that under high temperature conditions, the adsorption properties of amide groups and cationic groups on the side chain of polymer P-DADL molecule are weakened in the thermal environment, accompanied by a small amount of polymer main chain and side chain fracture and degradation, which is intuitively manifested as the decrease of drilling fluid viscosity and shear force. However, the AV, PV and YP are still 62 mPa·s, 38 mPa·s and 24 Pa after aging with P-WBDFs (2 wt% P-DADL), indicating that P-DADL has excellent temperature resistance. This is due to the fact that the polymer P-DADL molecule has a temperature-resistant structure such as sulfonic acid groups, five-membered heterocycles and longer side chains (Zamir et al., 2021; Sun et al., 2022; Liu et al., 2022), which allows P-DADL to play the role of adsorption and bridging even at high

temperatures. Furthermore, it can be known from Fig. 4(d) that the YP/PV ratio of the aged drilling fluid is 0.33–0.63 Pa/mPa·s, which meets the rheological requirements of the drilling fluid and has suspension stability and rock-carrying capacity at high temperatures.

3.2.2. Effect of salinity

During drilling operations in salt rock and salt-gypsum formations, salt ions in the formations tend to invade the drilling fluid system. This invasion not only interferes with the interaction mechanism between polymers and bentonite but also compresses the diffuse double layer of bentonite particles, ultimately leading to the deterioration of the drilling fluid's rheological properties (Cione et al., 2000). In order to study the salt resistance of P-DADL in drilling fluid, the rheological properties of S/P-WBDFs before and after aging at 180 °C were evaluated, the results are shown in Fig. 5. With the increase of NaCl, the viscosity of drilling fluid shows a decreasing trend. When the NaCl concentration is 5 wt%, the apparent viscosity of the drilling fluid is 71 mPa·s, and the viscosity retention rate is 81.14%. When the concentration of NaCl is 15 and 25 wt%, the drilling fluid still maintains good rheological properties, and the apparent viscosity after aging is 34.5 and 29 mPa·s, respectively. It is attributed to the hydrogen and ionic bonding of cationic, sulfonic and amide groups in the polymer P-DADL molecule in the drilling fluid, which enhances the salt resistance of P-DADL at high temperature. This indicates that P-DADL can weaken the negative impact of NaCl on clay particles. The quaternary ammonium salt structure and bentonite produce strong adsorption through ionic bonds, which hinders the aggregation of bentonite particles. Therefore, under the conditions of 180 °C and 35 wt% NaCl, P-DADL-modified drilling fluid still has good rheological properties (AV 22 mPa·s, PV 17 mPa·s, YP 5 Pa).

3.2.3. Effect of temperature

Fig. S2 shows the change rule of rheological parameters (AV, PV, YP, YP/PV ratio) of P-DADL (2 wt%) drilling fluid after aging at different temperatures. From Fig. S2, it can be seen that as the temperature increases, the AV, PV, and YP of the drilling fluid show a decreasing trend. After aging at 180 °C for 16 h, the apparent viscosity of the drilling fluid remained at 62 mPa·s, with a viscosity retention rate of 70.86%. This is because the presence of sulfonic acid groups, pentagonal heterocycles, and long side chains in polymer P-DADL molecules gives it excellent temperature resistance. Therefore, drilling fluid can still maintain good rheological properties after high-temperature aging.

3.2.4. Suspension stability analysis

The suspension stability of drilling fluid is crucial, which is the macroscopic expression of rock-carrying capacity. Prepare DADL-modified drilling fluids of different concentrations and after aging them at 180 °C for 16 h. 50 mL of drilling fluid was taken into a 60 mL sample bottle and left to stand for 48 h, and photos were taken at regular intervals during the experiment (0, 6, 12, 24, 36, 48 h) to observe the suspension stability of the drilling fluid system, as shown in Fig. 6 and Table S4. It is found that the dispersion system of bentonite base slurry is unstable, and stratification will

Table 1
The results of elemental analysis.

Reaction mole ratio of polymer DMAM:AMPS:DMDAAC:LAM	Elemental analysis, (mass fraction, %)				Actual mole ratio of polymer DMAM:AMPS:DMDAAC:LAM
	C	N	S	H	
30.96:22.63:21.80:2.59	58.71	9.633	6.728	9.24	28.1:21:19.7:2.7

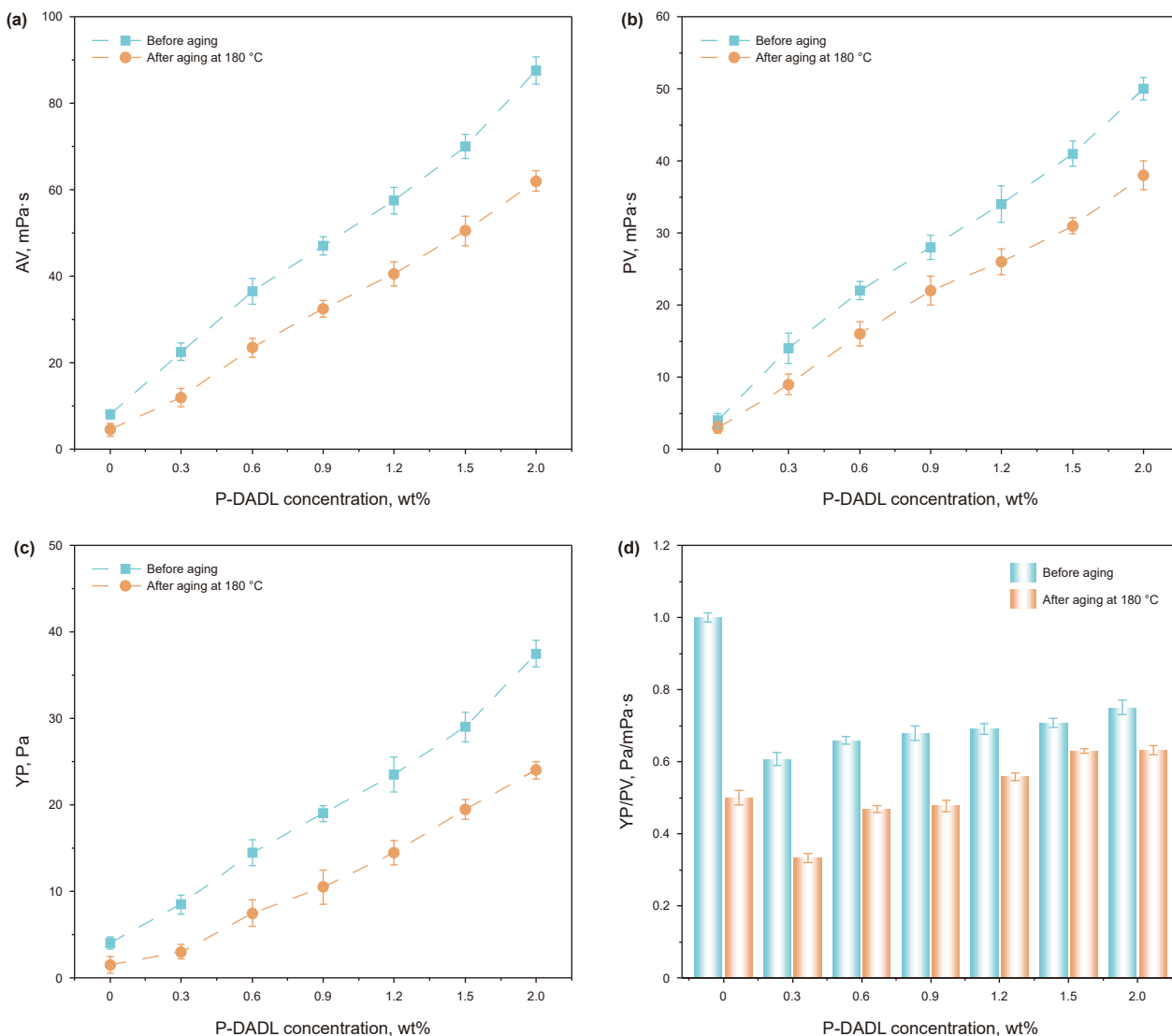


Fig. 4. Rheological properties of the P-WBDs before and after aging at 180 °C: (a) AV, (b) PV, (c) YP, (d) YP/PV ratio.

occur under long-term static state. The supernatant is 2 cm after 6 h (Fig. 6(b)). With the extension of standing time, the layered sedimentation phenomenon of bentonite base slurry is aggravated. After standing for 24 h, the sedimentation is >3 cm (Fig. 6(c)) and after 48 h, the sedimentation is 3.5 cm (Fig. 6(f)), and the settlement degree of bentonite slurry is 35%. Compared with the sedimentation law of different time periods, the drilling fluid system containing polymer P-DADL can maintain the dispersion and suspension stability for a long time. For example, the 2[#] system disperses and stabilizes within 48 h, 3[#] system after 48 h settlement layer (less than 0.1 cm) is negligible. For the 4[#] system, due to the pollution of 35 wt% NaCl, layered sedimentation began to occur after standing for more than 24 h. As shown in Fig. 6(e) and (f), the settlement layer is 0.1 cm at 24 h and 0.2 cm at 48 h, and the suspension stability is more than 98%, which indicates that the P-WBDFs are still stable in high salt environment, with good rock-carrying performance and suspension stability. Having the same pattern as before aging (Fig. S3 and Table S3). Therefore, the addition of P-DADL can offset the aggregation of bentonite particles and the negative impact of salt on the drilling fluid system. There amide group on the polymer molecular chain and the hydroxyl group on the surface of the bentonite particles to form a

hydrogen bond, which enhances the adsorption stability of P-DADL on the surface of the clay particles. Meanwhile, the electrostatic interaction between the polymer molecules forms a stable network structure in the solution, hindering the aggregation of bentonite particles. In addition, when there is a large amount of NaCl in the system, Na⁺ destroys the 'internal salt bond' in the polymer molecular chain, so that the molecular chain extends. The released anionic sulfonic acid group and cationic quaternary ammonium salt can adsorb small molecular branches and clay particles (Liu et al., 2022), hinder the influence of clay particles by NaCl, and maintain the dispersion stability of the drilling fluid system.

3.2.5. Fitting of drilling fluid rheological model

The relationship between shear stress and shear rate of P-DADL aqueous solution and bentonite drilling fluid was fitted by the Bingham model, power-law model and Herschel-Bulkley model (Wisniewski et al., 2020; Yang et al., 2022). The determination coefficient R^2 reflects the degree of fitting. The closer R^2 is to 1, the higher the degree of fitting is. The simulation results are shown in Fig. 7 and Table S3. Fig. 7(a–c) shows the fitted relationship between shear stress and shear rate for 1 wt% and 2 wt% P-DADL

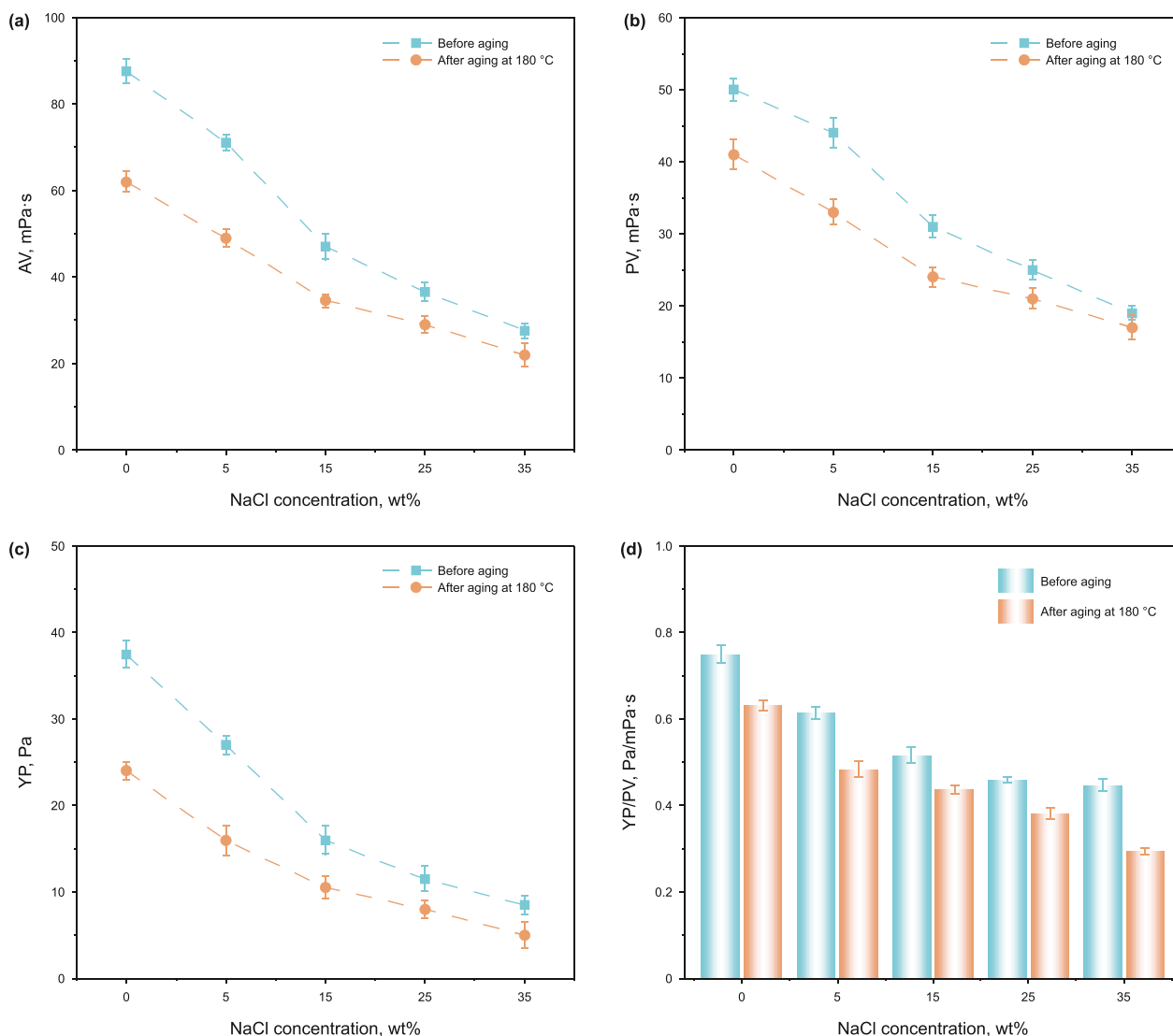


Fig. 5. Rheological properties of S/P-WBDFs before and after aging at 180 °C: (a) AV, (b) PV, (c) YP, (d) YP/PV ratio.

aqueous solutions. It can be seen from Fig. 7(b) and (c) that P-DADL aqueous solution exhibits non-Newtonian characteristics, and Herschel-Bulkley model has the highest fitting R^2 , which can better reflect the rheological properties of polymer P-DADL aqueous solution. Fig. 7(d–f) shows the relationship between shear stress and shear rate for base slurry, P-DADL concentrations of 1 wt% and 2 wt%, and drilling fluids containing 15 wt% NaCl, with the best Herschel-Bulkley model fit (maximum R^2). Fig. 7(f) shows that the drilling fluid has shear thinning characteristics after adding polymer P-DADL to the base slurry, and the flow pattern index (n) decreases with the increase of P-DADL dosage. According to the yield stress (τ_0) and consistency coefficient (K) of Herschel-Bulkley model (See Table S5), P-DADL-modified drilling fluids has excellent shear thinning and rock carrying capacity. P-DADL adsorbed with bentonite particles to form a mesh structure through hydrogen bonding, electrostatic and long hydrophobic side chains. Meanwhile, due to the introduction of sulfonic acid, quaternary ammonium salt and five-membered heterocyclic groups, P-DADL still has good rheological properties and rock-carrying capacity under high salt environment.

3.2.6. Filtrate loss reduction performance of P-DADL in WBDFs

The effect of P-DADL on drilling fluid filtration loss is shown in Fig. 8. The fluid loss of P-WBDFs before and after aging is shown in Fig. 8(a). It can be seen that the blank WBDFs exhibits relatively high FLAPI values before and after aging, which are 18 and 28.4 mL, respectively. As the concentration of P-DADL increased, the FL_{API} of the P-WBDFs gradually decreased. When the dosage is 2 wt%, the filtration loss is reduced to 7.4 mL. The FL_{API} of S/P-WBDFs with different NaCl concentrations before and after aging is presented in Fig. 8(b). It is noteworthy that with the addition of salt, the drilling fluid filtration loss decreased instead, with the FL_{API} decreasing from 6.4 to 3.6 mL before aging, and from 7.4 to 6.4 mL after aging. In response to the above, the author makes the following assumptions. The addition of P-DADL to the WBDFs introduces amide groups, sulfonic acid groups, quaternary ammonium salt groups, five-membered heterocycles and hydrophobic side chains. These phenomena are that strongly adsorbed groups adsorbed on the surface of bentonite, positive and negative ionic groups and associations within the molecular chain will occur simultaneously, which is conducive to the formation and

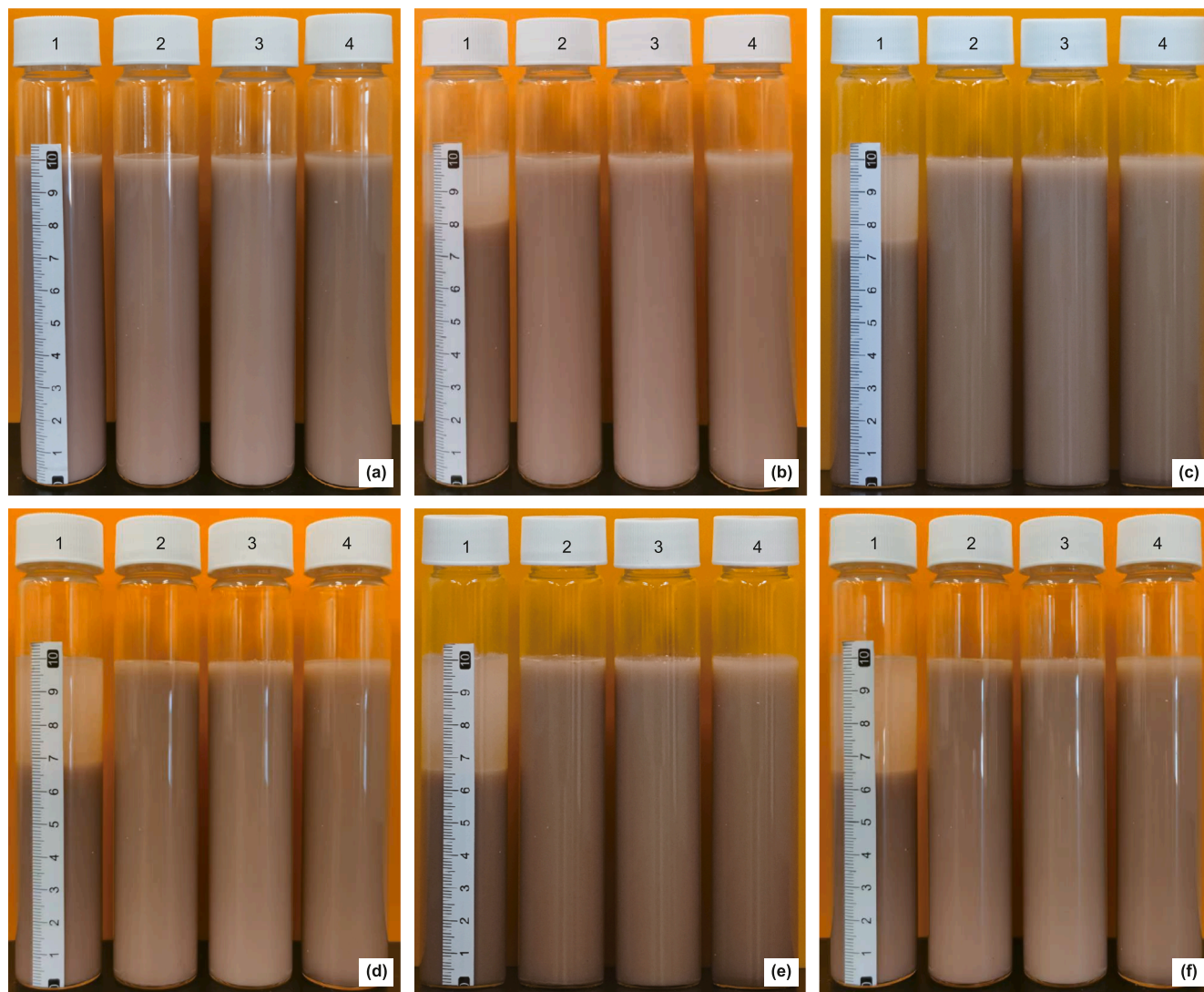


Fig. 6. The suspension stability and cuttings carrying capacity of the P-WBDFs: (a) 0 h, (b) 6 h, (c) 12 h, (d) 24 h, (e) 36 h, (f) 48 h; 1: WBDFs, 2: 0.5 wt% P-WBDFs, 3: 1 wt% P-WBDFs+10 wt% NaCl, 4: 2 wt% P-WBDFs+35 wt% NaCl.

stabilization of the network structure. Although the shear force that increases the viscosity of the drilling fluid is increased, it results in the molecular chains appearing as curled-up agglomerates due to intramolecular polymerization. However, with the addition of NaCl, the polymer molecular chains become extended from curling up in the brine (Wang et al., 2024). The polymer is effectively adsorbed on the bentonite surface through hydrogen and ionic bonding, and is subjected to pressure difference to form a dense and smooth membrane structure, which enhances the polymer adsorption capacity on the clay surface under high temperature environment, thus reducing the filtration loss. Although tested only in NaCl systems, the observed improvement in rheology and filtration suggests electrostatic shielding and zwitterionic charge compensation as key contributors.

3.3. Mechanism analysis of P-DADL in WBDFs

3.3.1. Characterization of microstructure of drilling fluid

To further elucidate the underlying working mechanism of the polymer P-DADL in water-based drilling fluids, the microstructure of the polymer aqueous solution and P-WBDFs systems were systematically characterized and analyzed. The microstructure of the

aqueous solution of polymer P-DADL is shown in Fig. 9. Due to the presence of amphoteric ions and hydrophobic side chains on the molecular chain of P-DADL, the solution forms an obvious mesh structure/house of cards structure by the action of “internal salt bonds” and “hydrophobic bonding” after dissolving in water, which is the key to improve the rheology of drilling fluids and the ability of rock cuttings to be suspended. In addition, the 2 wt% aqueous solution of P-DADL has stronger spatial reticulation property (Fig. 9(b)). The presence of “tentacle-like” branched structure on the reticulation structure, which may be the amino, sulfonic, quaternary ammonium salt and hydrophobic side chain of the P-DADL molecular side chain. The branched chain can interact with bentonite particles and enhance the adsorption strength.

To further elucidate the interaction mechanism between P-DADL and bentonite, the microstructure of the P-DADL-modified drilling fluids was observed, as shown in Fig. 10. Fig. 10(a) and (b) display the microstructure of the bentonite-based slurry before and after contamination with NaCl. The addition of NaCl disrupted the “card house” structure of the bentonite matrix, causing bentonite particles to transition from surface-to-edge adsorption to surface-to-surface adsorption. Under the influence of cations, the particles aggregated with each other, leading to a deterioration

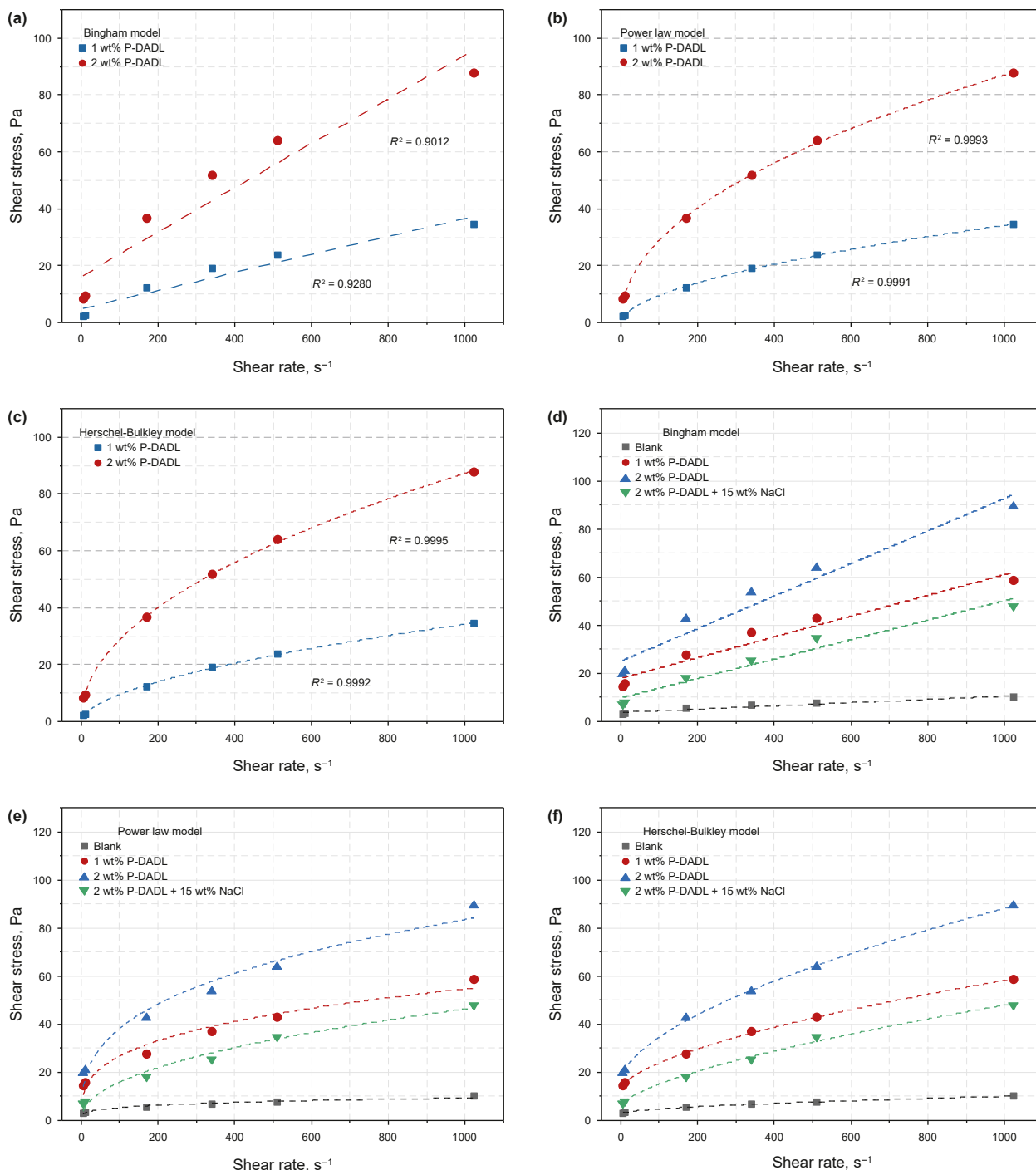


Fig. 7. Rheological model fitting of polymer WBDFs: (a, d) Bingham model, (b, e) Power law model, (c, f) Herschel-Bulkley model.

in drilling fluid performance. After the incorporation of polymer P-DADL, the card house structure of the bentonite slurry was maintained and strengthened, while the negative effects of cationic monomers on the drilling fluid were eliminated, as shown in Fig. 10(c) and (d). The interaction between P-DADL and bentonite particles resulted in a coarser mesh skeleton structure in the drilling fluid. Within this coarse skeleton, finer scaffold-like structures were filled, forming an alternating pattern of large and small skeletons, which further enhanced the rheological properties and suspension capacity of the drilling fluid (Yang et al., 2022; Liu et al., 2022; Li et al., 2024). In the presence of NaCl, the molecular chains of P-DADL become more extended. Due to the

anti-polyelectrolyte effect and electrostatic shielding, the amino groups, cationic groups, anionic groups, and hydrophobic side chains on the P-DADL molecular chains are exposed, providing more adsorption sites to interact with bentonite particles. This promotes the full dispersion of clay particles and maintains the network structure of the drilling fluid. This explains the relatively dispersed yet networked microstructure of the solution observed in Fig. 10(d).

3.3.2. Influence of P-DADL on drilling fluid mud cake

During the drilling process, the mud cake quality not only affects the filtration loss of drilling fluid, but also is closely related to

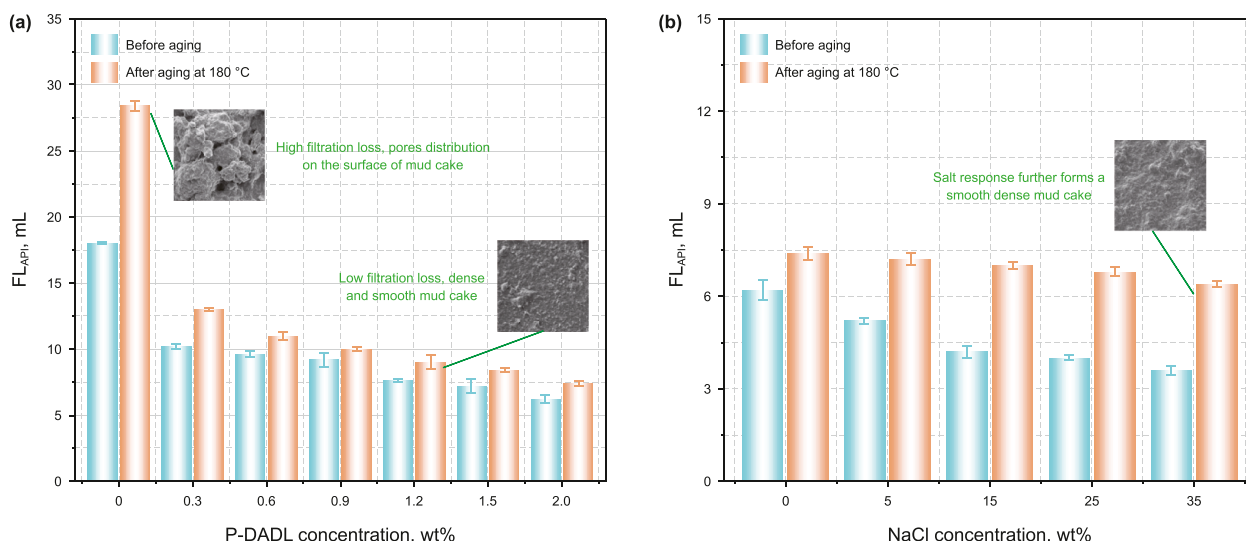


Fig. 8. FL_{API} of P-DADL-modified drilling fluids: (a) Polymer concentrations, (b) NaCl concentrations.

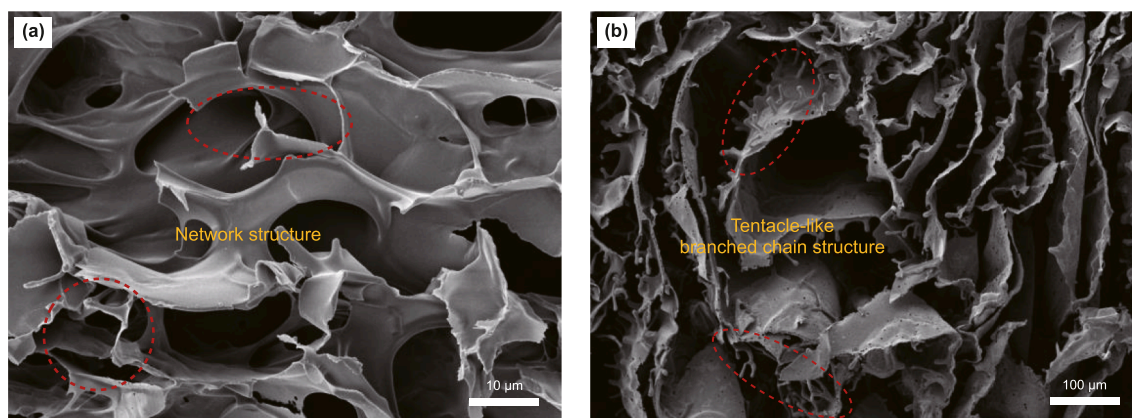


Fig. 9. The microscopic structure of P-DADL aqueous solution: (a) 1 wt%, (b) 2 wt%.

the stability of well wall and reservoir protection. The macroscopic morphology and microstructure of drilling fluid mud cake after aging at 180 °C are shown in Fig. 11. From Fig. 11(a) and (b), it can be seen that the thickness of base slurry mud cake is 1.7 mm and the surface is smooth, while the quality of filter cake is poorer after the base slurry is contaminated by salt, which is not only thickened (4.2 mm), but also has more pores on the surface. The polymer P-DADL significantly enhanced the mud cake quality. As can be seen from Fig. 11(c) and (d), the drilling fluid filter cake containing P-DADL is characterized as thin, smooth and dense, and the presence of NaCl further thins the mud cake (mud cake thickness of 0.21 mm). The above results are consistent with previous results on the amount of filtration loss, indicating that the polymer P-DADL has good resistance to temperature and salt, and also has a filtration loss reduction effect.

The micromorphology of the base slurry mud cake surface is shown in Fig. 11(e). The hydration film of bentonite particles is extremely sensitive to temperature: under high-temperature conditions, the hydration film on the clay particle surface becomes thinner, and the clay particles aggregate and stack in an edge-to-edge and face-to-face manner. This results in a raised mud cake surface with distinct pores, which further form filtration channels. The quality of the mud cake after the bentonite-based

slurry was contaminated by NaCl was even worse (shown in Fig. 14(b)), with the surface of the cake being uneven and having a large number of obvious holes. This is attributed to the weakening of bentonite hydration capacity at high temperatures, and the thinning of the hydration film leads to a decrease in the interparticle repulsion, triggering the phenomenon of high-temperature aggregation. At the same time, the presence of Na^+ compresses the clay diffusion bilayer, which further reduces the repulsive force between clay particles and makes the mud cake loose and porous. In addition, as a large amount of free NaCl in the drilling fluid accumulates and crystallizes on the surface of the filter cake, it leads to a further increase in the pore seams of the mud cake, which increases the amount of filtration loss. The addition of polymer P-DADL effectively improved the mud cake quality. As shown in Fig. 11(f) the surface of the mud cake was thin and smooth with no pore generation. This is attributed to the interaction between P-DADL and bentonite. The polymer P-DADL and bentonite are tightly adsorbed through electrostatic interaction, hydrophobic side chains, hydrogen bonding and ionic bonding, which prevents agglomeration of clay particles from occurring, and forms a smooth, thin and dense hydration film under pressure. The microstructure of polymer P-DADL-modified drilling fluid mud cake after NaCl contamination is shown in

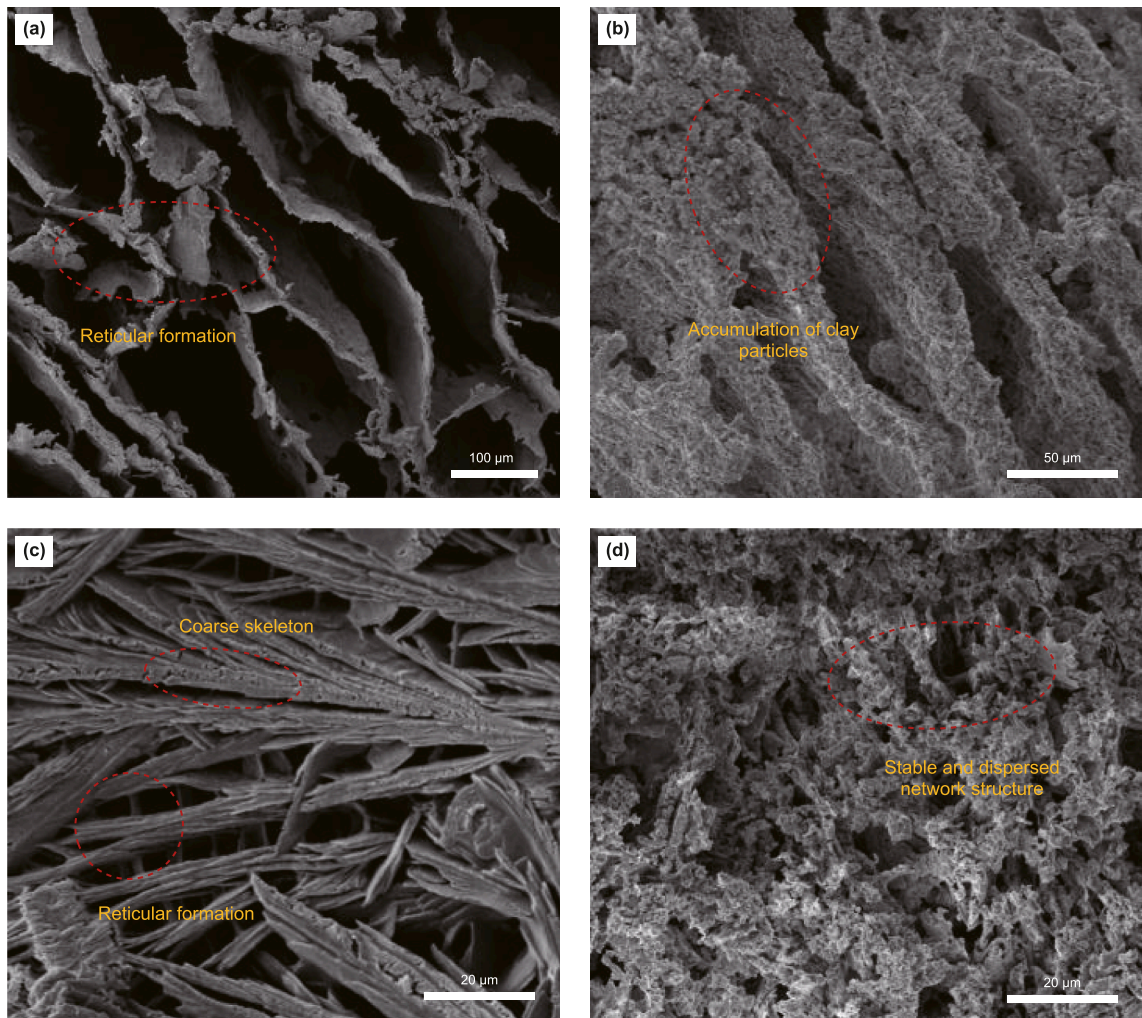


Fig. 10. The microscopic structure of P-DADL in the WBDFs: (a) based slurry, (b) based slurry+15 wt% NaCl, (c) based slurry+1 wt% P-DADL, (d) based slurry+2 wt% P-DADL+15 wt% NaCl.

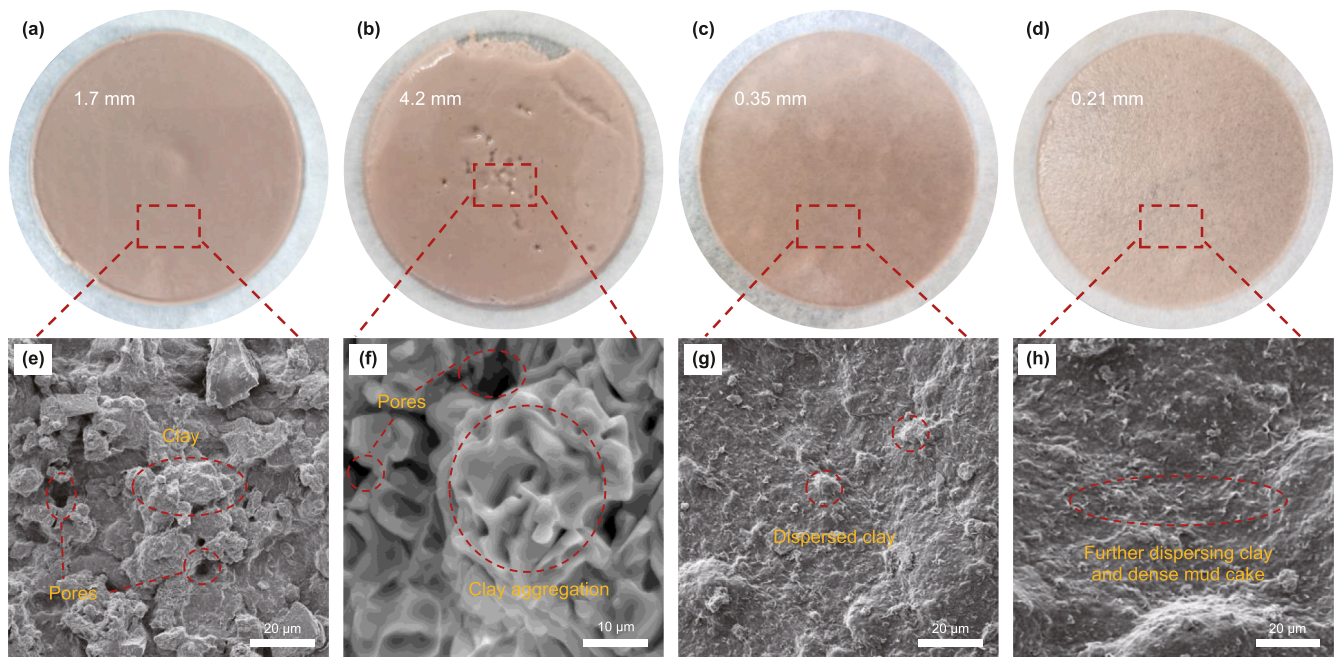


Fig. 11. Surface topography of drilling fluid mud cake: (a, e) based slurry, (b, f) based slurry+15 wt% NaCl, (c, g) based slurry+1 wt% P-DADL, (d, h) based slurry+2 wt% P-DADL+15 wt% NaCl.

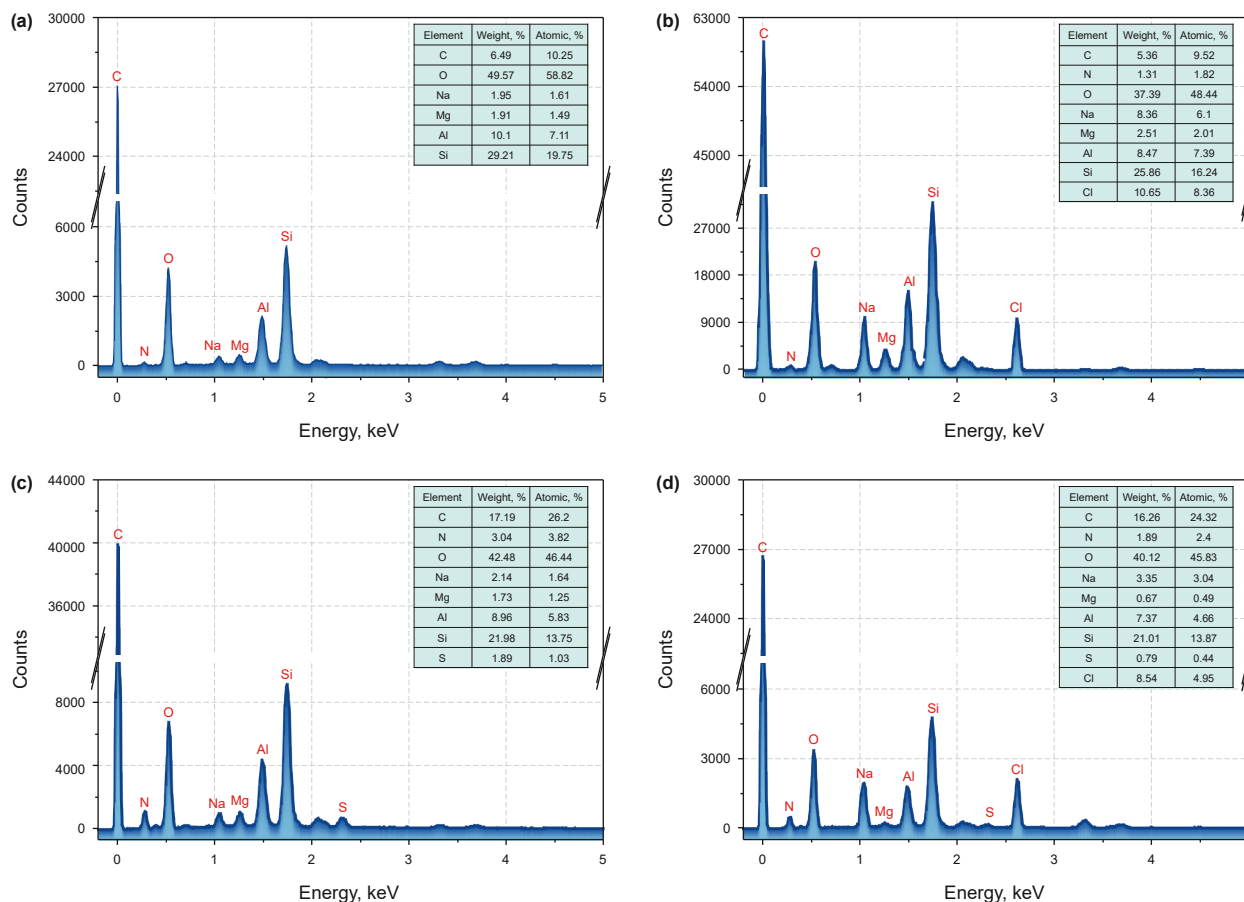


Fig. 12. Analysis of the elemental content of the drilling fluid mud cake: (a) based slurry, (b) based slurry+15 wt% NaCl, (c) based slurry+1 wt% P-DADL, (d) based slurry+2 wt% P-DADL+15 wt% NaCl.

Fig. 11(h). The drilling fluid mud cake is denser and smoother compared with Fig. 11(g). The SEM results show that polymer P-DADL can maintain the stable dispersion of bentonite particles under HTHS conditions, form a smooth, thin and dense membrane structure, and reduce the filtration loss.

3.3.3. Analysis of elemental content in mud cake

The interaction mechanism between polymer P-DADL and bentonite was further explored by energy spectrum analysis, and the results are shown in Fig. 12. Comparison of Fig. 12(a) and (c) shows that the elemental content of C, N, O and Al on the surface of the drilling fluid filter cake containing polymer P-DADL increased significantly, while the distribution of S element appeared, indicating that P-DADL is still firmly adsorbed on the surface of clay particles after aging at high temperature and maintains the stable dispersion of bentonite. Fig. 12(b) shows that the elemental content of Na and Cl on the surface of the filter cake under high salt conditions increased significantly, while the peaks of N, O and Si elements decrease, indicating that NaCl acts on bentonite, resulting in flocculation of bentonite and increased filtration volume. As can be seen from Fig. 12(d), the Na and Cl elemental peaks in the filter cake decreased significantly after adding P-DADL to the brine-based slurry, which may be due to the anti-polyelectrolyte effect in P-DADL. The addition of P-DADL protects the hydration of bentonite and inhibits the effect of NaCl on bentonite. Therefore, the residual amount of NaCl on the surface of mud cake is small (i.e., the relative content of Si increases), which not only maintains the stability of drilling fluid performance, but also reduces the

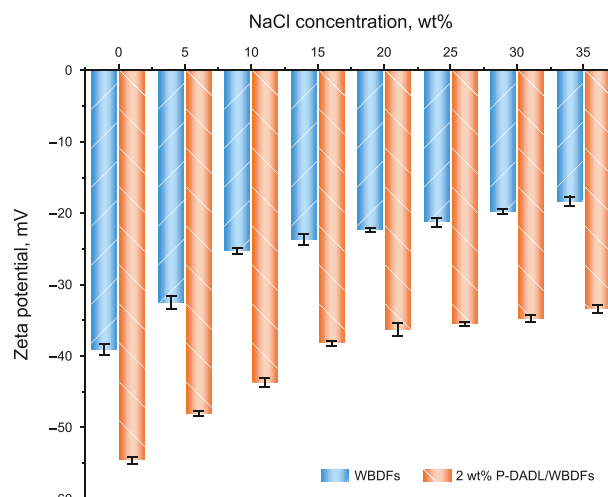


Fig. 13. Effect of P-DADL on zeta potential of WBDFs.

filter loss. The XPS experimental results further demonstrate the positive impact of P-DADL on drilling fluids (Fig. S10).

3.3.4. Zeta potential analysis of drilling fluids

The zeta potential of WBDFs after aging at 180 °C/16 h was measured at 25 °C, and the results are shown in Fig. 13 and Table S6. Compared with WBDFs, the absolute value of zeta

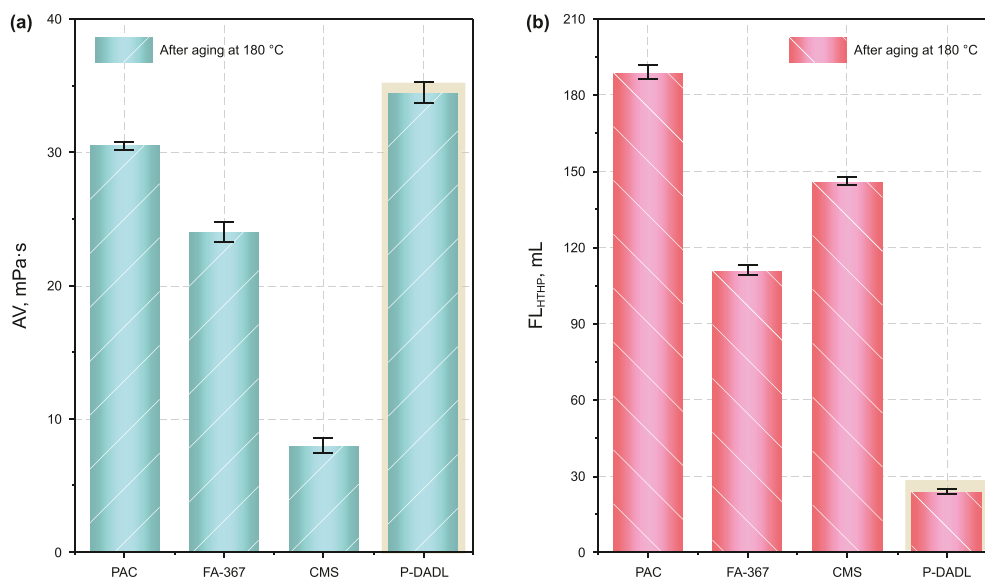


Fig. 14. Performance comparison between P-DADL and commercial filtrate reducer: (a) AV of drilling fluid, (b) FL_{HTHP} at 180 °C and 500 psi).

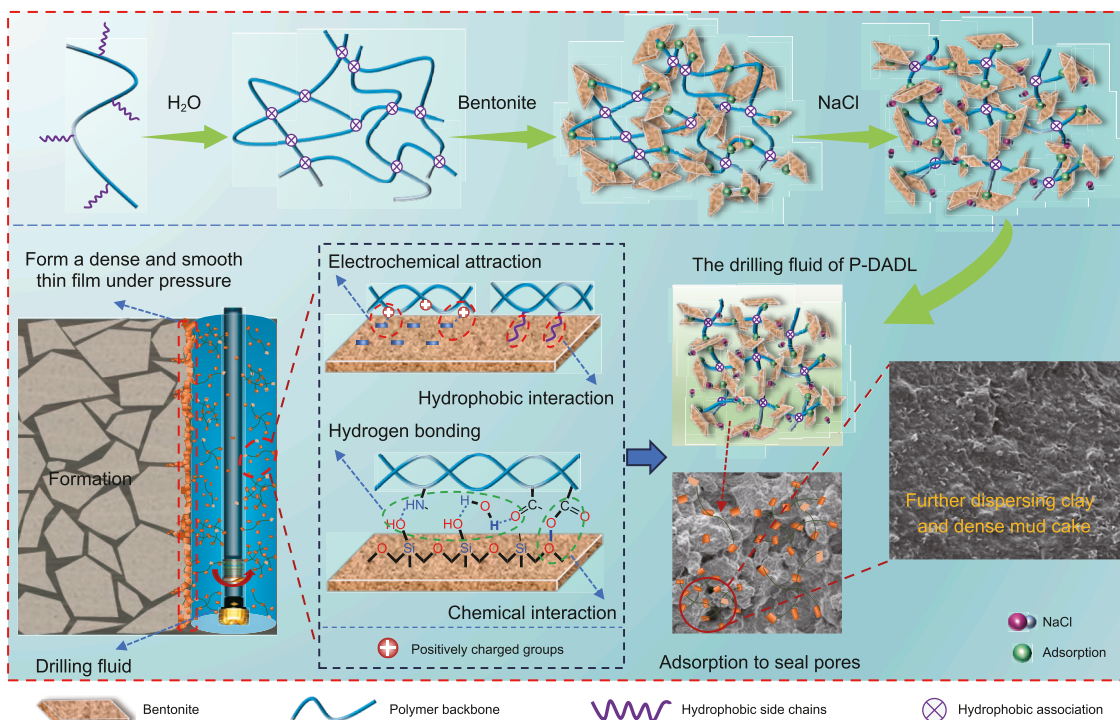


Fig. 15. Action mechanism diagram of P-DADL.

potential increased from 39.1 to 54.6 mV after adding P-DADL, which is due to the increased thickness of clay particle hydration film adsorbed by P-DADL on the clay surface. The addition of NaCl compresses the diffusion double layer of bentonite, reduces the electrostatic repulsion between clay particles, and leads to a decrease in the absolute value of zeta potential. However, in the case of saturated salt, the zeta potential of 2 wt% P-DADL/WBDFs remained at -33.4 mV, indicating the stability of the drilling fluid system. This is consistent with the results of the rheological properties of the drilling fluid and the results of the filter loss reduction in Figs. 5, 6 and 8.

3.3.5. Comparison with similar commercial products

According to the survey, commercial flow regulators (PAC, carboxymethyl starch, FA-367) are widely used in oilfield drilling (Minaev et al., 2016; Xia et al., 2023; Saadi et al., 2025). Through experimental comparison, we can more accurately evaluate the novelty and practicality of P-DADL. During the experiment, the polymer dosage was 2 wt% and the NaCl concentration was 15 wt%, the experimental results are shown in Fig. 14. The results showed that the performance of P-DADL polymer was significantly better than that of commercial products, with an AV improvement of 13.31% and a FL_{HTHP} of only 24 mL, resulting in a 78.4%

improvement in performance. In addition, as shown in Fig. S5, compared with commercial products, the mud cake after P-DADL testing is denser and smoother. The reason is the thermal stability and salt resistance of P-DADL, which tightly adsorbs with clay particles through hydrogen bonds, electrostatic and chemical bonds.

3.4. Comprehensive analysis of P-DADL action mechanism

The mechanism of P-DADL action in WBDFs is shown in Fig. 15. Due to the introduction of cationic groups, anionic groups and hydrophobic groups on the P-DADL molecular chain, P-DADL undergoes intramolecular aggregation under electrostatic and hydrophobic association, forming an irregular network spatial structure. When P-DADL is added to WBDFs, a large number of polymer molecules adsorb onto the surface of clay particles. Under the action of “internal salt bonds” and “hydrophobic association”, the polymer main chains intertwine with each other, and the side chains adsorb onto the clay surface, further constructing a spatial network structure. Macroscopically, this is manifested as an increase in drilling fluid viscosity and enhanced suspension stability. In addition, due to the anti-polyelectrolyte effect, when NaCl is added, the curled molecular chains of the polymer gradually stretch, releasing more interaction sites with clay particles. The drilling fluid forms a relatively regular spatial network structure, maintaining the rheological properties of the drilling fluid. Therefore, P-DADL tightly adsorbs with clay particles through electrostatic interactions, hydrophobic side chains, hydrogen bonds, and ionic bonds, forming a smooth, thin, and dense mud cake under pressure differential, reducing the amount of drilling fluid loss. NaCl promotes a more regular and distinct grid structure of P-DADL-modified drilling fluids, and the bentonite particles are uniformly and stably dispersed in the drilling fluid system, further enhancing the filtration reduction effect.

4. Conclusions

In order to meet the drilling needs under HTHS conditions, this study prepared a temperature and salt resistant zwitterionic-hydrophobic associating polymer (P-DADL). The performance of P-DADL in water-based drilling fluids was systematically evaluated, and its mechanism of action was analyzed using various characterization methods. The results indicate that P-DADL has a thermal decomposition temperature higher than 297 °C and excellent rheological improvement and filtration control ability under HTHS conditions. When the dosage is 2 wt%, and the drilling fluid has good performance after aging at 180 °C. The apparent viscosity is 62 mPa·s, and the FL_{API} is 7.4 mL. In saturated saline mud, the FL_{API} further decreases to 6.4 mL, demonstrating the synergistic filtration reduction characteristics of P-DADL and NaCl. P-DADL enhances the stability of drilling fluid in high-temperature and high salt environments through adsorption and bridging with clay particles, maintained >98% suspension stability over 48 h in saturated brine. In addition, P-DADL can promote the formation of dense mud cake in drilling fluid, effectively controlling filtration. With the addition of 2 wt% P-DADL, the 15 wt% NaCl salt-based drilling fluid achieved an HTHP fluid loss of 24 mL, representing a 78.4% performance enhancement over analogous commercial products. Future work will focus on validating P-DADL in multi-ion brines and field-scale WBDFs formulations, further clarifying its application potential.

CRediT authorship contribution statement

Qi-Bing Wang: Writing – review & editing, Writing – original draft, Visualization, Validation, Data curation. **Wan-Jing Luo:**

Writing – review & editing, Supervision, Conceptualization. **Li-Fang Pan:** Validation, Investigation, Data curation. **Jin-Sheng Sun:** Supervision, Resources, Methodology. **Hui-Cui Sun:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Ren Wang:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Jian-Long Wang:** Project administration, Methodology, Formal analysis. **Bo Liao:** Resources, Methodology, Conceptualization. **Ding-Shun She:** Investigation, Formal analysis. **Hai Yang:** Investigation, Formal analysis.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petsci.2026.03.042>.

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