

**THERMAL STABILITY OF SODIUM FORMATE IN POLYMER DRILLING FLUIDS****Wenlong Zheng,<sup>1</sup> Xiaoming Wu,<sup>1</sup> and Yuming Huang<sup>2</sup>**

*The effects of formate salts on the rheological characteristics of water-based solutions were compared for two laboratory research methods, i.e., dynamic rheological analysis at high temperature and high pressure (HTHP) and a static hot-roll aging test. Polymer muds were used for the measurements. HTHP rheology analysis showed that sodium formate retained effectively the dynamic viscosity at HTHP. Hot-roll tests showed that sodium formate had an obvious effect on the rheological characteristics of the polymer fluid at room temperature after preliminary heating. The filtration loss of the polymer fluid with added sodium formate was slightly greater than that of pure polymer fluid although the filtration loss could be controlled by changing the formate concentration. Test results from both methods showed that sodium formate could be used successfully as a polymer drilling fluid stabilizer under HTHP operating conditions.*

**Keywords:** *rheological characteristics, filtration loss, sodium formate, high-temperature high-pressure test, hot-roll test.*

Widely used water-based drilling fluids display remarkable performance, rheological characteristics controllable over broad pressure and temperature ranges, environmental safety, shale inhibition

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capacity, etc. [1]. Careful selection of drilling-fluid additives enables the performance to be controlled over a broad range.

Polymer additives to water-based drilling fluids are used to improve the viscosity, decrease fluid loss into permeable formation, inhibit clay hydration and shale swelling, reduce friction losses through a shear-thinning effect, and for other purposes [2, 3]. On the other hand, polymer additives are susceptible to decomposition at temperatures >150°C, which causes rheological instability in the drilling fluid [4, 5]. The drilling fluid should effectively suspend and carry cuttings during drilling operations [6-8]. Organic salts such as sodium (HCOONa), potassium (HCOOK), and cesium formates (HCOOCs) were studied by several researchers to overcome the thermal instability of the polymers and to assess their ability to stabilize the structure of water-based drilling fluids at HTHP [9, 10].

The rheological properties of starch in HCOONa and HCOOK solutions after hot-roll testing were studied experimentally [11]. The starch thermal stability was shown to increase in aqueous solution at 150°C in the presence of the formate salts. The viscosities of starch solutions with formate-salt additives were studied after thermal aging [12]. The solution viscosity was recovered after heating to 200°C followed by cooling although the viscosity of pure aqueous starch solution decreased after heating to 150°C. Researchers who studied the effects of pollutants on rheological properties concluded that sodium formate was an effective additive for drilling fluid with minimal formation pressure [13]. Formate fluids are typically more soluble and denser and have higher pH values than conventional drilling fluids. They are good inhibitors and, most importantly, highly thermally resistant.

All researchers focused mainly on rheological characteristics and thermal resistance of drilling fluids in hot-roll tests. The effects of formate additives on the dynamic rheological characteristics of polymer fluids under HTHP conditions are poorly studied. Also, the thermal stabilities of formate-salt solutions at various high temperatures were not compared.

The present work investigated the relationship between the shear stress and shear rate of polymer fluids from HTHP test results and the effects of sodium-formate additive on the rheological properties of the polymers at HTHP. Also, apparent viscosities and filtration losses of polymer fluids with sodium formate were compared for HTHP and hot-roll tests. Finally, the influence of sodium-formate thermal stability on the rheological properties of polymer drilling fluids at temperatures up to 220°C was measured.

NaOH, HCOONa, and NaCl (commercial analytical reagents) were used in the work. Three types of thermally resistant polymers, i.e., Driscal-D (synthetic high-molecular-mass polymer specially designed for

Table 1

Sample No.	Fluid formula
1	H <sub>2</sub> O+0.5%NaOH+2%Driscal-D
2	H <sub>2</sub> O+0.5%NaOH+2%HE-150
3	H <sub>2</sub> O+0.5%NaOH+2%RHTP-2
4	H <sub>2</sub> O+0.5%NaOH+2%Driscal-D+30%NaCl
5	H <sub>2</sub> O+0.5%NaOH+2%Driscal-D+30% HCOONa
6	H <sub>2</sub> O+0.5%NaOH+2%HE-150+30% NaCl
7	H <sub>2</sub> O+0.5%NaOH+2%HE-150+30% HCOONa
8	H <sub>2</sub> O+0.5%NaOH+2%RHTP-2+30%NaCl
9	H <sub>2</sub> O+0.5%NaOH+2%RHTP-2+30% HCOONa

ultra-high temperature and high salinity applications); HE-150 (suspension of high-viscosity synthetic polymer) (both from Drilling Specialties Company, Chevron Phillips Chemical Company LLC group of companies, USA); and RHTP-2 (copolymer of AM, AMPS, and SSS monomers) (Henan Dragon Oil Additive Co., Ltd., PRC) were used.

Analytical instruments included a GJSS-B12K multi-mixer, ZNN-D6 viscometer, SD-4 API filtration apparatus, XGRL-4A aging oven, Fann 50SL high-temperature rheometer (FANN Instrument Co., USA), and a rotational viscometer for testing drilling fluids at temperatures up to 260°C and pressures up to 1,000 mm Hg (7,000 kPa) in a coaxial cylindrical chamber.

Fluids were prepared by adding polymer (Driscal-D, HE-150, RHTP-2, 8 g) to distilled H<sub>2</sub>O (400 mL) and stirring at 11,000 rpm until the polymer was evenly dispersed. The polymer fluid was treated with sodium chloride or formate to the given ratio of additive mass to fluid volume and stirred for 30 min at room temperature.

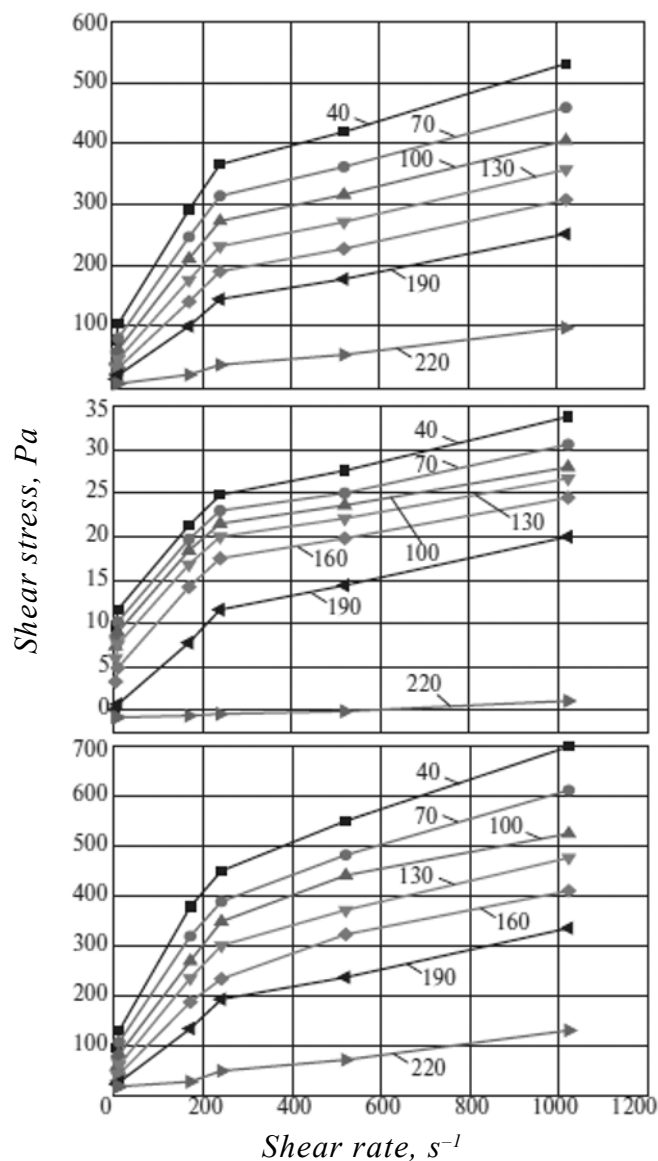


Fig. 1. Shear stress as a function of shear rate for polymer solutions at various temperatures.

Mixtures with various constituent contents were prepared for the experiments to compare the thermal stabilities of formates and chlorides in the polymer fluids. Table 1 presents the mixture constituents.

The rheological characteristics of H<sub>2</sub>O are independent of pressure because of its relatively small compressibility [14]. The rheological parameters of all water-based drilling fluids were studied at constant pressure and various temperatures.

Rheological characteristics were determined as follows from the HTHP tests. A measured amount of the fluid being studied was placed into an experimental cell. Then, the rheometer was heated over an hour to the

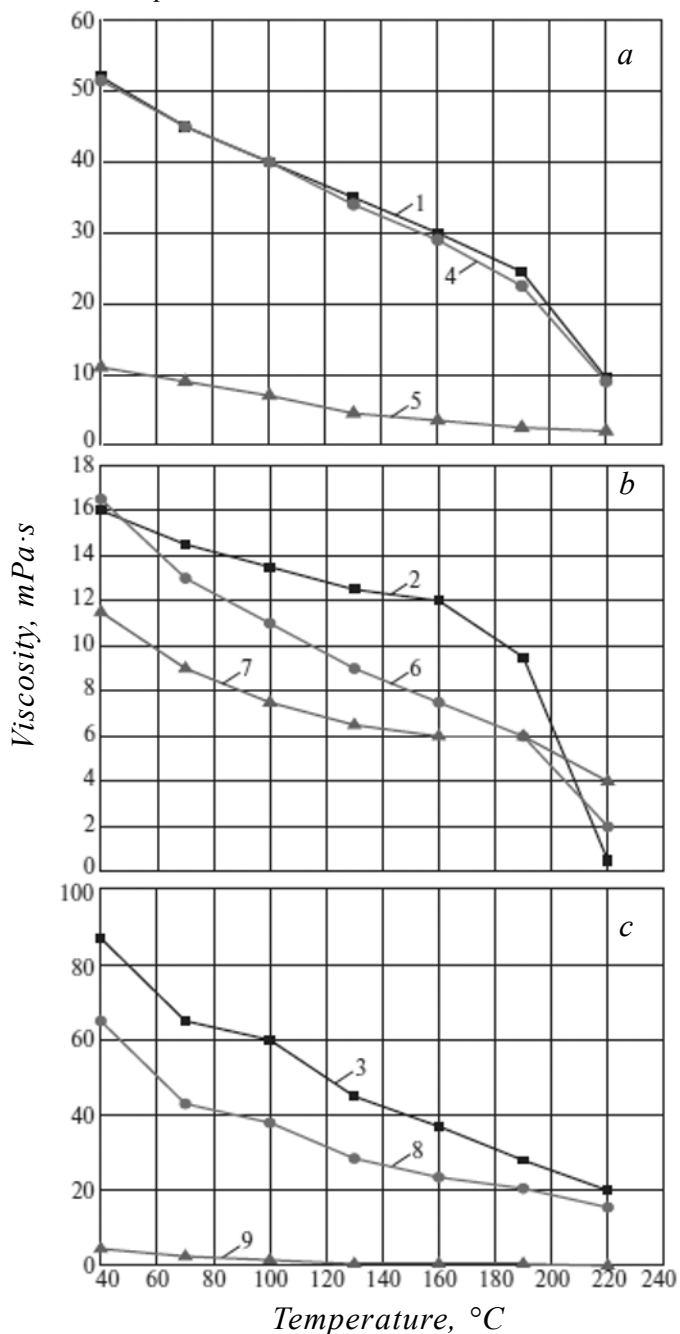


Fig. 2. Temperature dependences of viscosities of polymer solutions (numbers on curves are sample Nos.) containing sodium formate or chloride: Driscal-D (a), HE-150 (b), and RHTP-2 (c).

given experimental temperature. Next, the fluid was stirred for 30 min at a high shear rate ( $1,022 \text{ s}^{-1}$ ). The shear stress and fluid viscosity were measured at various shear rates from 1 to  $511 \text{ s}^{-1}$  (shear rates of 2.5, 5.1, 85, 170, 255, and  $511 \text{ s}^{-1}$  were used for the measurements), various temperatures (40, 70, 100, 130, 160, 190,  $220^\circ\text{C}$ ), and constant pressure (1,000 mm Hg). Measurements were taken for 1 min at each shear rate for each temperature. The shear stress was recorded at 2-s intervals for each shear rate.

Hot-roll aging was performed as follows. Prepared fluids were rolled at the same temperatures for 16 h in an XGRL-4 roller aging oven. Then, apparent viscosity (AV) was measured on a ZNN-D6 rotary viscometer at 600 rpm ( $q_{600}$  mark on the instrument scale) according to American Petroleum Institute (API) recommended practice:

$$AV = 0.5\theta_{600}$$

Filtration loss was measured on an SD-4 API filtration apparatus at room temperature and 1,000 mm Hg for 30 min. The measured value was reported as the static filter loss of fluid.

Figure 1 shows the dynamic flow behaviors (shear stress vs. shear rate) for the three polymers.

The shear viscosity decreased as the shear rate increased, indicating that all three polymers had good thickening properties. The polymer fluids showed that the decrease of shear stress was greater at high shear rates than at low ones as the temperature increased. Figure 1b shows that the shear stress of HE-150 was close to zero over the whole range of shear rates as the temperature rose to  $220^\circ\text{C}$ . This could indicate that HE-150 polymer chains were extensively decomposed and destroyed at  $220^\circ\text{C}$  and 3.5 MPa. By comparison, Driscal-D and RHTP-2 samples retained some viscosity as the temperature rose to  $220^\circ\text{C}$ .

The amount of HCOONa was 30% based on previous research results. Figure 2 shows the temperature dependences of the viscosities of the polymer fluids with added HCOONa or NaCl.

Figure 2 shows that the viscosities of all three polymer fluids decreased significantly as the temperature increased, which could indicate high-temperature decomposition of the polymers. The viscosity of the Driscal-D fluid with NaCl (Fig. 2a, sample 4) decreased sharply as the temperature increased. Obviously, the electrolyte shielded the polymer chains from degradation. Then, the polymer chains coiled up so that the viscosity of the polymer fluid decreased [15, 16]. An analogous trend was observed for the other two polymer fluids (HE-150 and RHTP-2), i.e., adding NaCl did not improve the flow behavior of the fluids at high temperatures.

Adding HCOONa had noticeable effects on the viscosities of all three polymers. A comparison of Figs. 2a-c led to the conclusion that the viscosities of the polymer fluids with HCOONa were practically constant although low as the temperature increased. This indicated that the temperature had little impact on the viscosities of polymer fluids containing HCOONa. This effect could be explained as follows. HCOONa changes the structure of surrounding water molecules in the fluid, which affects the structure of dissolved high-molecular-mass polymer molecules. The polymer structure becomes more ordered, strong, and stable at high temperatures. The acid radicals ionized by the formate solution are reductants capable of scavenging oxygen from the system. The combination of antioxidant properties and water structural changes enables formates to increase the thermal stability of dissolved polymers.

Hot-roll aging under the same conditions was performed as usual to study the thermal stability (from rheological and filtration behavior) for a deeper understanding of the protection of the polymers by HCOONa. The results were compared with those from HTHP analyses.

All samples were hot rolled at various temperatures for 16 h. Figure 3 shows apparent viscosities (AVs) of polymer fluids with added HCOONa or NaCl.

Figure 3 shows that the AV of all polymer fluids decreased gradually as the temperature increased and then fell sharply at temperatures exceeding 160°C. Obviously, the viscosities of pure polymer fluids are difficult to stabilize at elevated temperatures.

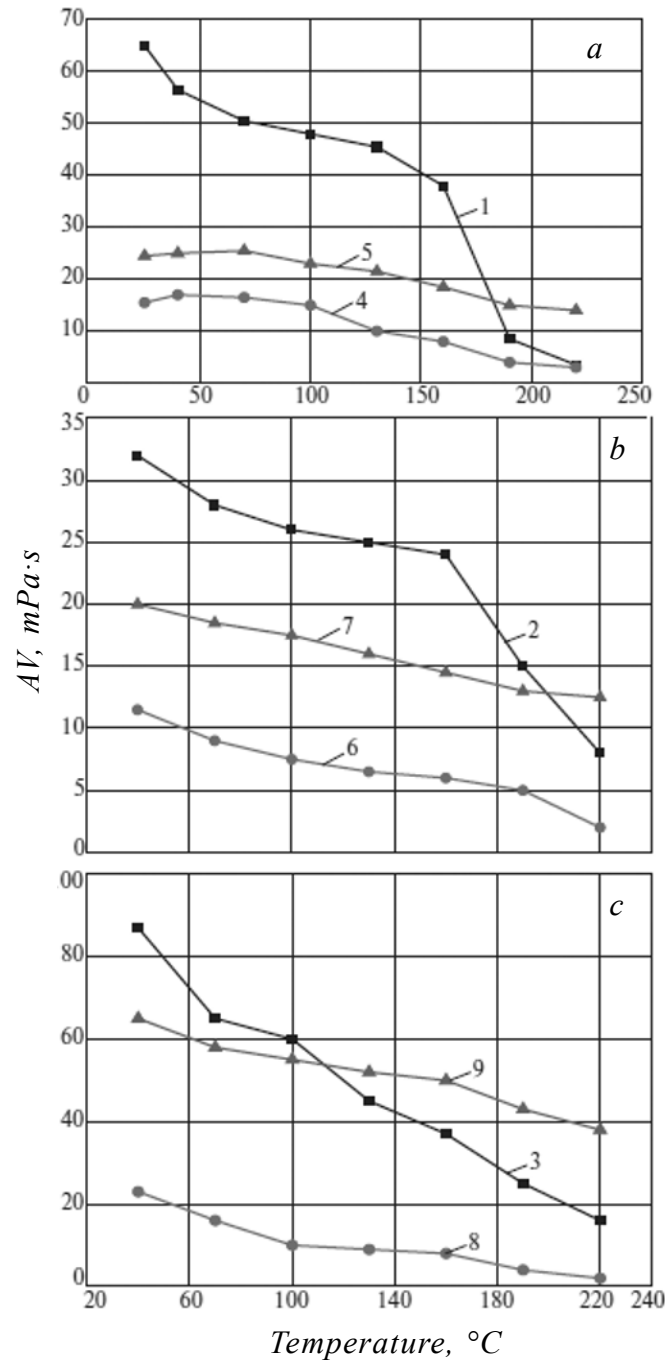


Fig. 3. Temperature dependences of apparent viscosities of polymer solutions (numbers on curves are sample Nos.) containing sodium formate or chloride after hot-roll aging: Driscal-D (a), HE-150 (b), and RHTP-2 (c).

Besides, the AVs of polymer fluids with added HCOONa and NaCl changed similarly. The viscosity decreased gradually with increasing temperature and was less than for pure polymer fluids up to 190°C. Apparently, this was explained by the shielding effect of the charge redistribution caused by the HCOONa or NaCl electrolyte solution.

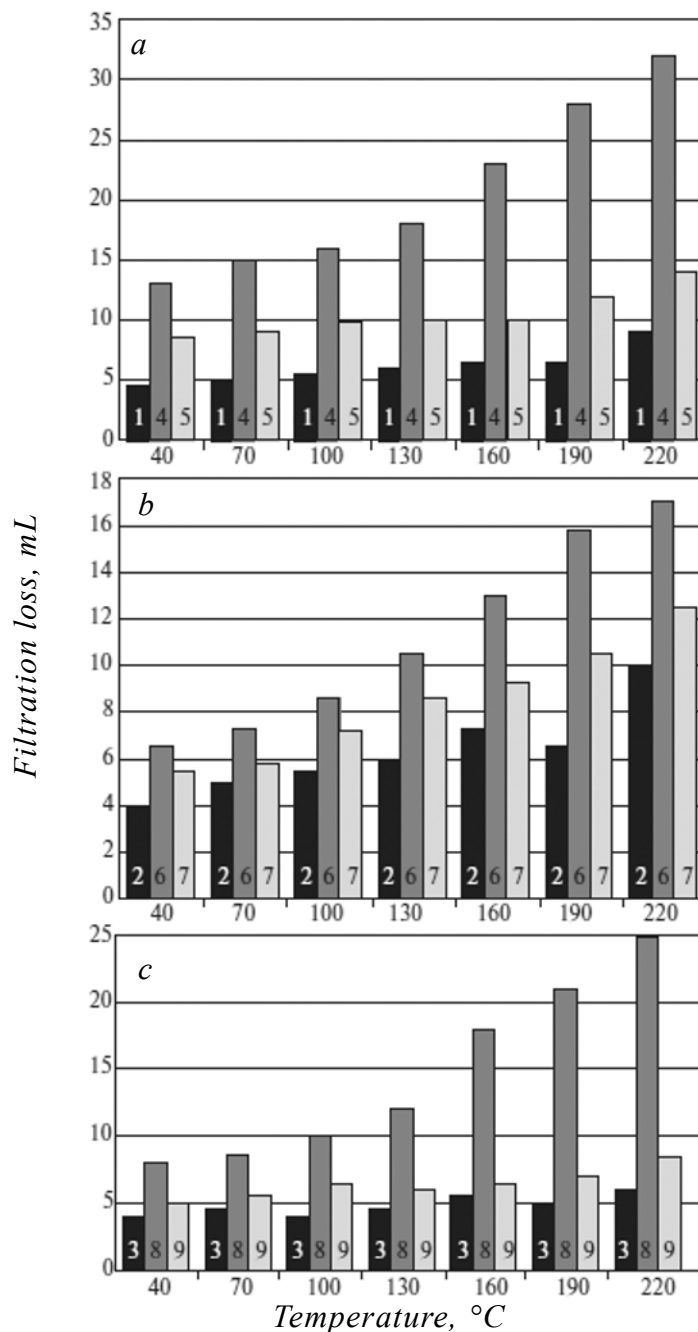


Fig. 4. Filtration losses of polymer solutions (numbers on bars are sample Nos.) containing sodium formate or chloride after hot-roll aging at various temperatures: Driscal-D (a), HE-150 (b), and RHTP-2 (c).

It can be seen that the AVs of polymer fluids with added HCOONa (from hot-roll tests) were even higher than those of fluids with added NaCl, i.e., HCOONa fluids were capable of retaining the viscosity. The AVs of polymer fluids with HCOONa were greater than those of pure polymer fluids at temperatures up to 220°C, in contrast with HTHP rheology analyses. This was particularly prominent for RHTP-2 fluids, i.e., HCOONa exhibited high-temperature protection of polymer fluids.

Filter losses of fluids with added HCOONa and NaCl were studied to confirm the effects of HCOONa on the thermal stability of the polymer fluids. Figure 4 shows filter losses of fluids after hot-roll aging at the given temperatures for 16 h.

Figure 4 shows that the filter losses of the polymer fluids at elevated temperatures increased if HCOONa and NaCl were added. This was evidently caused by coiling of polymer chains in the presence of the electrolyte. The filter losses for polymer fluids with added NaCl were twice those with added HCOONa. The additives caused slight increases of filter losses for the polymer fluids. However, the filter losses remained in the acceptable range for drilling fluids. It could be concluded that added HCOONa did not significantly change the filter losses of the polymer fluids and could be used successfully as a high-temperature thermal stabilizer of polymer drilling fluids.

The viscosities of the polymer fluids at elevated temperatures were reduced for the following two reasons:

1. Physical, i.e., rising temperature increased the thermal motion of polymer hydrophobic groups and weakened the influence of hydrophobic association. It caused molecular chains to contract and separated entangled molecular chains from each other, thereby decreasing the viscosity. The physical changes were reversible.

2. Chemical, i.e., the polymer component had a critical temperature above which the molecular chains broke at weaker bonds and reactive groups, which led to irreversible viscosity reductions.

Many researchers reported that HCOONa can act as a thermal stabilizer in thermal aging tests. Thermal stability was analyzed using thermal aging by heating polymer drilling fluids with HCOONa additives to a given temperature for 16 h in a roller oven and then cooling to ambient temperature. Rheological behavior was measured at room temperature and normal pressure. Viscosities measured in this manner turned out to be greater for HCOONa. Viscosities measured at room temperature after thermal aging were mostly recovered because the physical processes responsible for the viscosity changes were reversible.

The viscosity measured by thermal aging is useful for representing the mud performance at the wellhead but does not portray the performance of the drilling fluid at HTHP in the deep well. The dynamic viscosity measured from HTHP tests was much lower because the viscosity dropped due to both physical and chemical changes.

Thus, viscosity changes of polymer drilling fluids with added HCOONa were characterized from different viewpoints by combining the two methods.

Hence, the experimental results showed that HCOONa was a good thermal stabilizer and could be used as a stabilizer for deep-well polymer drilling fluids.

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