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A Cationic Polymeric Alcohol Anti-Sloughing Agent and its Mechanisms

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Abstract

A cationic polymeric alcohol anti-sloughing agent YPVA with well anti-sloughing function and lower side effect of increasing viscosity was developed through modifying the polymeric alcohol (PVA). Degrade PVA firstly, then make the degraded PVA have action groups. It was proved that the modified PVA has ortho-nitrogen radicals by molecular structure analysis through infrared spectrum. Then the anti-sloughing mechanisms of YPVA were investigated deeply through experiments such as rolling and dispersing recovery, zeta potential and particle size distribution measuring, adsorption and pressure transmission. The anti-sloughing mechanisms are mainly as follows: prevent mud shale particles to hydrate and disperse by adsorbing and coating; holdback mud shale particles to hydrate through altering their surface charge and compressing their diffused double layer after adsorbing on them; pressure and block filtrate transfer through forming film and covering on the surface of slits and pores after adsorbing on the surface of rock in the stratum.

Key words: Borehole wall stability; Shale; Cationic polymeric alcohol; Modification; Anti-sloughing mechanisms

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INTRODUCTION

Wellbore instability is a very complex technical problem frequently encountered in the drilling project[1~2]. Over the past years, either focused on rock mechanics analysis, or development of new anti-sloughing agents and drilling fluid systems for shale hydration inhibition, researchers had undertaken extensive research on the wellbore stability problems and made a series of achievement[3~5]. At present, the existing anti-sloughing agents include inorganic salts, polymers, bitumen, lignite and other low molecular weight organic compounds and so on. Among them, asphalt agent for blocking and anti-sloughing is the most effective, but not be able to be applied in the exploratory well for its high fluorescence level[6]. Therefore, domestic and foreign researchers attach great importance to study and develop novel non-fluorescent and efficient anti-sloughing agent. In recent years, PVA class of film-forming anti-sloughing agents have been found to be very effective for wellbore stability without fluorescence problems [7~8]. However, negative effects of PVA, tackifying during the field application, leading to a sharp increase of drilling fluid viscosity, seriously prohibit its promotion and application [9~14]. Therefore, modified polymeric alcohol is developed through degradation and cationic reaction of polymeric alcohol. The evaluating results show its good effect for anti-sloughing and less effect for tackifying. The mechanism for anti-sloughing of the modified PVA is also studied in this article.

1. MATERIALS AND METHODS

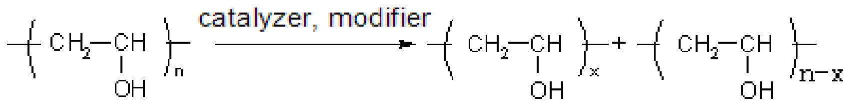
1.1 Materials

Polymeric alcohol (PVA) is industrial product supplied by three-dimension chemical plant in Shanxi province, China. Calcium bentonite is obtained from Weifang Huawei bentonite Co. Ltd, China. Sodium montmorillonite (Na-MMT) was a natural smectic aluminosilicate, obtained from Xiazijie Bentonite Company, China. Polymeric alcohol (SD-301) was supplied by Shandong Shida Chuangxin science & technology Co. Ltd, China. Potassium chloride and soda ash were both purchased from Sinopharm Chemical Reagent Co., Ltd, China. All other experimental materials were used without further purification.

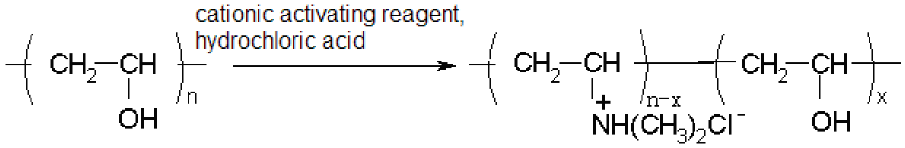
1.2 Preparation of the Modified Polymeric Alcohol

1.2.1 The Principle for Preparation

(1) Principle for degradation reaction of polymeric alcohol



(2) Principle for cationic reaction of polymeric alcohol



1.2.2 Preparation of the Modified Polymeric Alcohol

(1) Degradation of polymeric alcohol

A certain amount of PVA solution was added into a 4_mouths flask of 500mL. The pH was adjusted to be 8.5 and the solution was stirred for 20 minutes in water bath at 75° C. Then, while stirring, a certain amount of catalysts and intensive oxidants was added in. After that, the solution was stirred for 2.5 h at constant temperature to get the product, denoted as JPVA.

(2) Cationic reaction of polymeric alcohol

200g JPVA Solution was added into a 4_mouths flask of 500mL. The pH was adjusted to be 8.5 and the solution was stirred for 15 minutes in water bath at 65 ° C. Then, while stirring, a certain amount of cationic reagent was added in. After that, the mixture was stirred for 3h at constant temperature and then be cooled to room temperature to add concentrated hydrochloric acid in. Then, the mixture was stirred for 1h to get the liquid products. With mixture of acetone and ethanol by the ration of 2 to 1, the products were precipitated and cleaned three times .Then white solid particles were produced after vacuum drying, which is modified cationic polymeric alcohol.

1.3 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR measurements have been used to characterizing the molecular structure. FT-IR absorption was recorded by a NEXUS FT-IR spectrometer (Thermo Nicolet Corporation), scanning from 4000 to 500 cm^{-1}, with a 4 cm^{-1} resolution in transmission.

1.4 Inhibition test

Shale inhibition performance of cationic polymeric alcohol was evaluated with hot-rolling dispersion test method. The testing procedure of hot-rolling dispersion test can be referred to the methods Blend R described[15].

1.5 Influence on Rheological and Filtration Properties of Slurry

Calcium bentonite is the base mud and its density is 1.028 g/cm^3. The influence of PVA and modified PVA on rheological properties of the base mud has been tested. The rheological properties of the samples in this research were tested with a model ZNN-D6 viscometer. The apparent viscosity, plastic viscosity and yield point were calculated from 600 to 300 rpm readings using the following formulas from API recommended practice of standard procedure for field testing drilling fluids [16].

Apparent viscosity (AV) =$\varphi600/2$ (mPa·s)
Plastic viscosity (PV) =$\varphi600-\varphi300$ (mPa·s)
Yield point (YP) =$(\varphi300-PV)/2$ (N/m^2)

1.6 Test of Adsorption Properties

A stable blue ternary complex can be generated when Polymeric alcohol is mixed with concentrated cobalt thiocyanate and the color depth varied with the concentration of polymeric alcohol. According to Beer-Lambert law[17~18], in a certain range of PVA concentration, the optical density E is proportional to the concentration. Based on this principle, optical density of solution with different concentrations has been determined. Optical density E is proportional to PVA concentration and the correlation coefficient R^2 is 0.9956.

$$E=8\times10^{-5}C-0.0002 \quad (2)$$

Where E is the optical density, dimensionless; C for the PVA concentration, mg/L.

Optical density E of the solution after cationic PVA adsorption on clay particles (room temperature) was tested and according to formula 2, the corresponding cationic PVA concentration can be determined. Then, the adsorption capacity and be calculated with the following formula.

$$\tau=(C_1-C_2)\times V/G \quad (3)$$

Where, τis the adsorption capacity of cationic PVA on the clay particles, mg / g; C1 is cationic PVA solution concentration before the adsorption, mg / L; C2 is the concentration of cationic PVA solution after adsorption, mg / L;V is the volume of solution, L; G is the weight of the clay, g.

1.7 Particle Size Distribution and Zeta Potential Test

With the Zetasizer3000 potential-particle size analyzer of British Malvern company, particle size and zeta potential of dispersed shale particles in water were compared to that in solution of modified PVA to study the influence of PVA on shale particle size distribution. 5.0g shale sample through 100 mesh was added into the stirred cup filled with 300mL distilled water and stirred for 20 minutes. Then, the mixed solution was poured into a 500mL graduated cylinder and kept still for 30 minutes. 10-15mL of the clear liquid in the upper part of the solution was taken and tested.

1.8 Pore Pressure Transmission Test

With SHM (shale hydration machines) device[19], pore pressure transmission was tested. The shale core of an oilfield is with texture uniformity, great hardness and no cracks and therefore suitable for the test. The shale sample used in the test has the size of Φ25.4 × 34.0mm.

The purpose and procedure of the test are as follows:

①Shale samples was saturated with formation water to restore the original formation water content;

②The permeability of the shale can be calculated with the following formula[20~21];

$$k=\frac{ìâVl}{A}\times Äh\ \left[\left(p_m-p_o\right)/\left(p_m-p_{(l,t)}\right)\right]/Ät \quad (4)$$

where k is the shale permeability, μm²; μ is the fluid viscosity, mPa·s; t is the immersing time of shale in drilling fluid, s; β is the fluid static compression ratio, 4.545×10^{-4} MPa^{-1}; V is downstream space volume, cm³; A is sample surface area, cm²; L is sample length, cm; p_m and p_o is the fluid pressure and pore pressure which are 3.10 MPa and 2.41 MPa; p(L, t) is the downstream fluid pressure at a certain time, which is 2.21 MPa.

2. RESULTS AND DISCUSSION

2.1 Analysis of YPVA Molecular Structure

As is shown in Figure 1, 2906.59 cm^{-1} and 1341.59 cm^{-1} are for the CH absorption peak; 2934.06 cm^{-1} absorption peak for -CH of -CH_2; 3280.21 cm^{-1} is for the OH stretching vibration absorption peak; 1234.59 cm^{-1} and 647.52cm^{-1}, are for OH bending vibration absorption peak in plane and out of the plane respectively; 1141.32 cm^{-1} are for the CO stretching vibration absorption peak. Comparing Figure 1 and Figure 2, it is known that each peak absorption intensity in Figure 2 is lower than that of Figure 1. Absorption bands of the constituent groups of polymeric alcohol are in the shift range, indicating that the polymeric alcohol degradation is only due to molecular strand breaks. Comparing Figure 3 and Figure 1, it is known that in Figure 3, in addition to the absorption peak in the range of the shift of polymeric alcohol groups, there are also the following characteristic absorption peaks: 3000 cm^{-1}, 1171.50cm^{-1}, 1465.04cm^{-1} and 1374.51 cm^{-1} ,which are characteristic absorption peaks for double dimethy l; 3428.57cm^{-1} for absorption peak of N-H; 1133.09cm^{-1}, 1083.71 cm^{-1} for absorption peak of the C-N; 1629.64cm^{-1} and 1561.06 cm^{-1} for absorption peak of N-H of –NH^+. It is indicated that positive nitrogen side groups are introduced into the YPVA by cationic reaction.

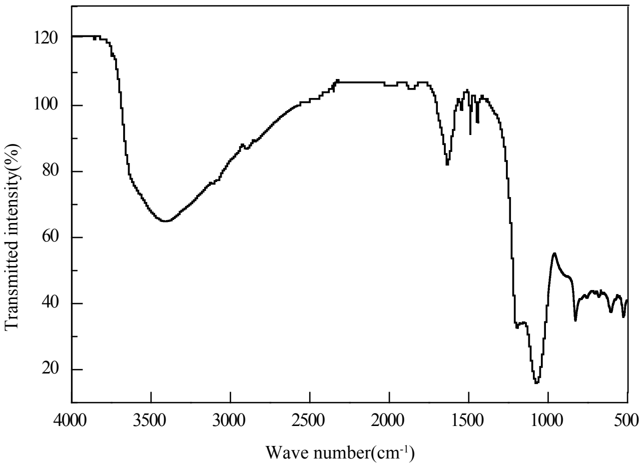


Figure 1
Infrared Spectra of the PVA

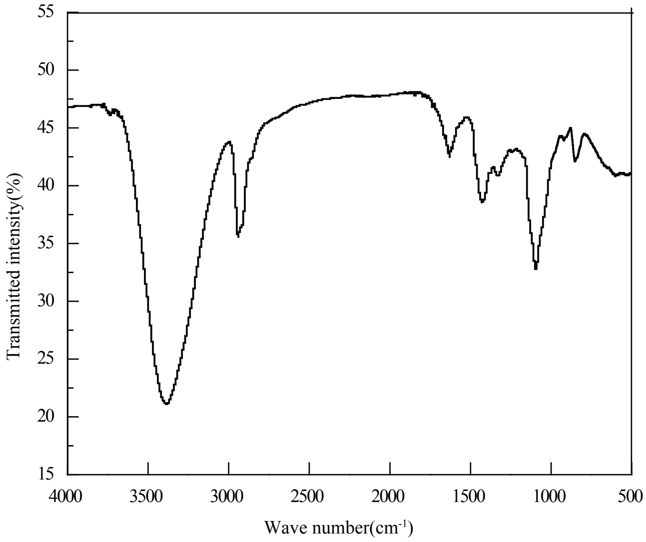


Figure 2
IR Spectra of JPVA (Product after Degradation of PVA)

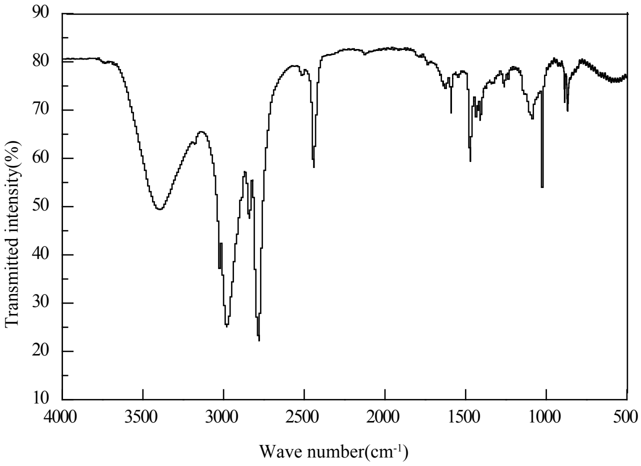


Figure 3
IR Spectra of YPVA (Product after Cationic Reaction of JPVA)

2.2 Performance Evaluation of Modified PVA

3.2.1 Shale Hydration Inhibition Performance Evaluation

It is shown in Figure 4 that the recovery rate of 2% PVA solution is greater than that of 2.0% polyols, 5.0% KCl and 2.0% JPVA solution. The recovery rate of 2% YPVA is 55.84%, greater than that of the other solutions, indicating its excellent inhibition performance of shale dispersion. Therefore, it can be concluded that cationic reaction of PVA can greatly improve its shale dispertion inhibition performance.

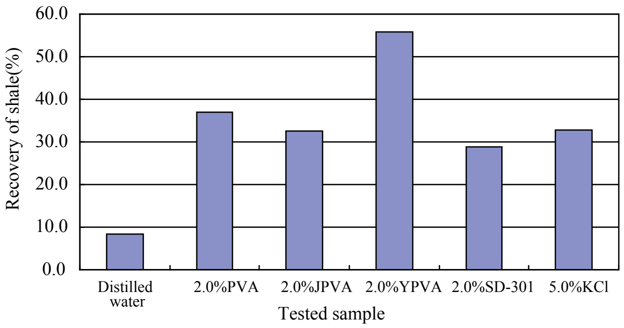


Figure 4
Results of Shale Inhibition Evaluation Test

2.2.2 Influence on the Rheological and Filtration Properties of Base Mud

It can be known from table 1 that influence of modified PVA on apparent viscosity, plastic viscosity and yield point of base mud were significantly lower than that before modification, indicating that tackifying negative effect can be significantly reduced by modification. After polymeric alcohol was added in, water loss of the mud was more than that of base mud. The reason was that PVA adsorbed on the surface of the clay particles to change the particle size distribution so that the cake became loose.

Table 1
Influence of PVA and Modified PVA on the Rheological and Filtration Properties of Base Mud

Formulation	AV mPa.s	PV mPa.s	YP Pa	APIFL mL
Base mud	10	7	3	29.0
base mud+3%PVA	17.5	11	6.5	34.0
Base mud+3%JPVA	8	5	3	25.4
Base mud+3%YPVA	9	5	4	35

Note: Base mud is composed of water of 400mL and Na_2CO_3 of 1.0 gram and Ca-montmorillonite

2.3 Anti-sloughing Mechanism of Modified Polymeric Alcohol

2.3.1 Adsorption Properties on Sodium Bentonite

As is shown in figure 5, as the concentration increased,the adsorption amount of both the polymeric alcohol and modified polymeric alcohol on sodium bentonite increased and adsorption isotherms complied with Langmuir adsorption law. The adsorption capacity of cationic YPVA is larger than that of PVA and JPVA and the adsorption capacity of JPVA is the minimum. The reason is that besides hydrogen bonding, electrostatic forces are another mechanism for cationic YPVA adsorption and the adsorption capacity is enhanced. According to the relationship between the shale recovery and the adsorption capacity (Figure 6), the larger adsorption capacity, the better inhibition of shale dispersion.

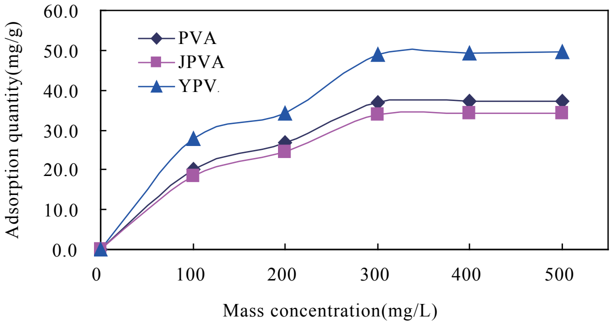


Figure 5
Adsorption Isotherm Line of PVA and Modified PVA on Sodium Bentonite (25oC)

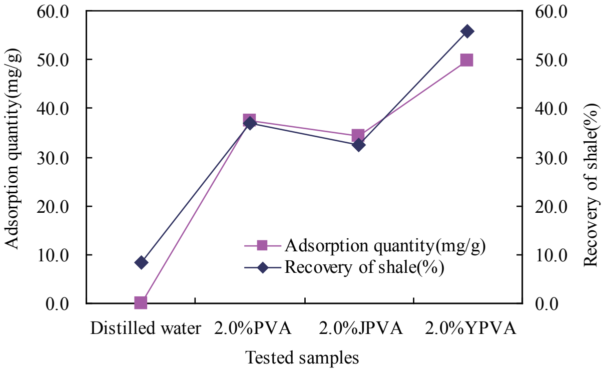


Figure 6
Relationship Between Shale Recovery and Adsorption Quantity of PVA and Modified PVA

2.3.2 Influence on the Particle Size Distribution of Dispersed Shale Solution

As is shown in figure 7, polymeric alcohol and modified polymeric alcohol can increase shale dispersion particle size through absorbing on the surface of the shale particles. With the concentration increasing, particle size increases gradually and then becomes stable. It can be concluded that the, the larger shale dispersion particle size, the better inhibition of shale dispersion (figure 8). The reason is that as the concentration gradually increases, adsorption quantity of modified polymeric alcohol on the particle surface increased. When the concentration increases to a certain extent, the continued adsorption of PVA molecules on the particle surface is hindered due to electrostatic repulsion, inhibiting the aggregation of particles in the medium.

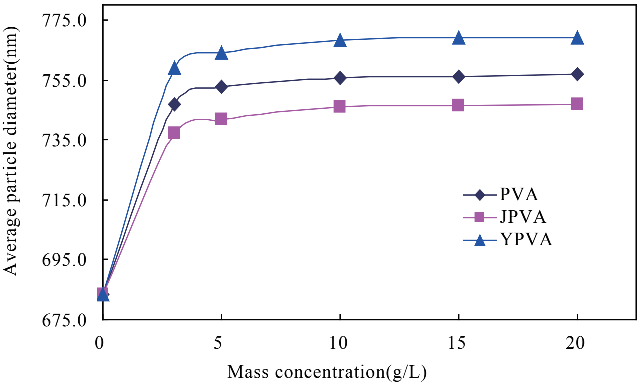


Figure 7
Influence of PVA and Modified PVA on the Shale Particle Size

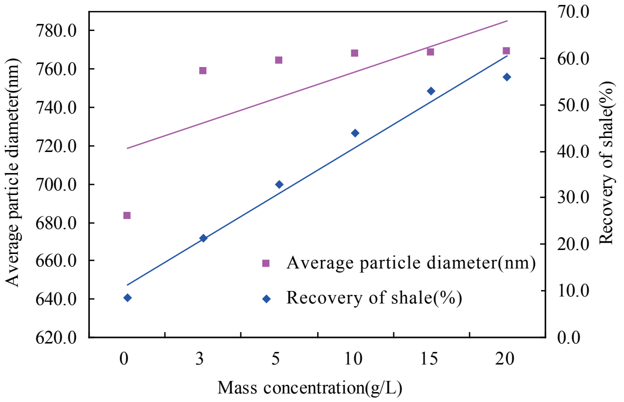


Figure 8
Relationship Between Shale Recovery of PVA and Modified PVA and the Average Shale Particle Size in Their Solutions

2.3.3 Influence on the Zeta Potential of Dispersed Shale Particles

As is shown in figure 9, adsorption of PVA can increase negative charge of dispersed shale particles and adsorption of JPVA will further increase the negative charge of the shale particles. However, YPVA can significantly reduce the negative charge of the shale particles, beneficial for the inhibition of shale particles hydration. It can be seen from Figure 10, as the YPVA concentration increased, the recovery rate of the shale cuttings increased. The reason is that YPVA adsorbed on the surface of shale particles so that shale particles was capsuled up and negative charge of shale particle surface was neutralized by positive charge of polymeric alcohol so that the ionization degree of surface hydroxyl groups was reduced.

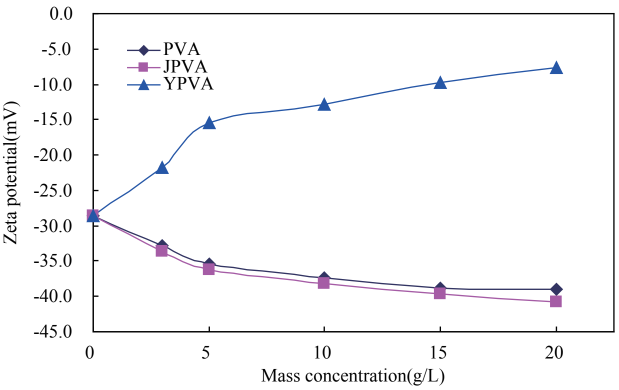


Figure 9
Influence of PVA and YPVA on the Electric Potential of the Dispersed Shale Particles

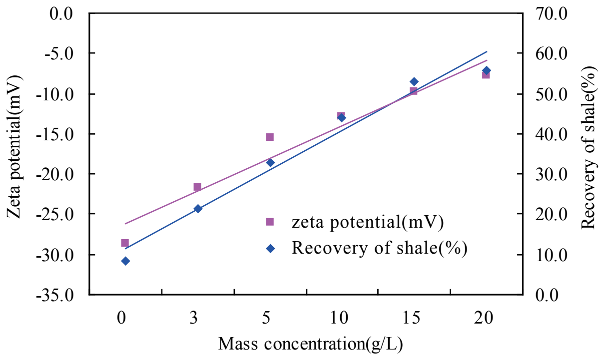


Figure 10
Relationship Between Shale Recovery Rate of YPVA snd the Electric Potential of Dispersed Shale Particles

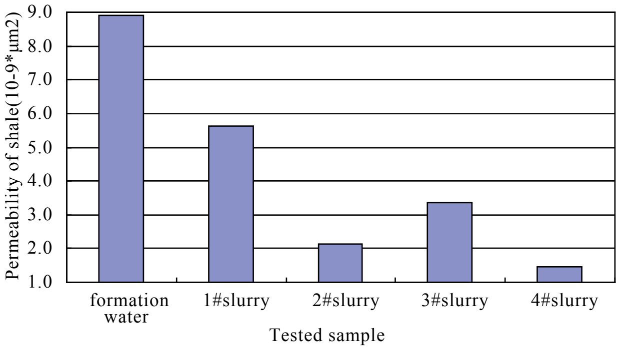


Figure 11
Effect of YPVA on Reducing Pore Pressure Transmission in Shale

2.3.4 Pore pressure (PT) Transmission Test

Formulation 1: 1.031g/cm^3 calcium bentonite base mud + 0.2% polymer coated agent PM-8052 + 0.5% low viscosity cellulose LV-CMC + 3% sulfonated phenolic resin SD-101;

Formulation 2: Formulation 1+ 2% polyol SD-301;

Formulation 3: Formulation 1+2% organic MMH SDPC;

Formulation 4: Formulation 1+2% YPVA;

Permeability of shale samples for solution of formation water, Formulation 1, Formulation 2, Formulation 3, Formulation4are8.9×10^{-9},5.62×10^{-9},2.14×10^{-9},3.37×10^{-9}, $1.46\times10^{-9}\mu m^2$, respectively. Shale permeability was reduced by 2.8 times adding YPVA into the Formulation 1, indicating its good performance to reduce pore pressure transmission. The mechanism is that film can be formed on surface of the shale to block the cracks and pores.

CONCLUSION

The infrared spectrum showed that the cationic reaction introduced positive nitrogen side groups into the modified polymeric alcohol. With adsorption, shale hot rolling dispersion and particle size distribution test, zeta potential analysis, it can be concluded that as the YPVA concentration increased, adsorption amount on Na-montorollinite increased, negative charge of dispersed shale particles was reduced, shale particle size increased and shale recovery rate increases, indicating inhibition property of shale dispersion was enhanced. The pore pressure transmission test results indicate the modified polymeric alcohol has the effect to form film to reduce pore pressure transmission.

NOMENCLATURE

API	American Petroleum Institute
AV	Apparent viscosity
FT-IR	Fourier transform infrared spectroscopy
Na-MMT	Sodium montmorillonite
PV	Plastic viscosity
YP	Yield point

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