Preparation of organic polymer flocculant and its application in drilling fluid

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Abstract. A flocculant (DES0-0) was synthesized by epichlorohydrin and diethylamine, followed by adding crosslinking agent such as ethylenediamine, diethylenetriamine and triethylenetriamine to obtain the crosslinked polymer DES0-1, DES0-2, DES0-3. The flocculation effect of DES0-1, DES0-2, DES0-3 and PAM was studied by measuring the volume, transmittance and particle size of the clarified solution after flocculation. The results showed that the flocculation effect of triethylenetetramine crosslinked polymer (DES0-3) and PAM was better. Meanwhile, the flocculation effect was more optimistic in the strong alkali environment.

Key words: Epichlorohydrin; Diethylamine; Flocculant; Crosslinking agent.

1 Introduction

Drilling fluid was often used in modern oil and gas well drilling operations. In drilling operations, drilling fluids provided a series of important functions, such as preventing formation fluids from entering the wellbore, removing drill cuttings, suspending drill cuttings during drilling pauses, and keeping the drill bit cool and clean[1-5]. Due to the rapid development of the petroleum industry, the composition of drilling wastewater had become more and more diversified in recent years. At present, the harmless treatment of drilling fluid waste is only carried out from physical, chemical, biological and other aspects that including coagulation, adsorption, reverse osmosis, chemical oxidation and electrolysis, and biological treatment. It has been widely used in drilling wastewater treatment[6,7]. In conventional operations, drillingfluids were always recirculated by removing useless solid pollutants because they were costly and hazardous if directly discharged to the environment[8-10]. However, due to solid contaminants will increase the viscosity and friction of the drilling fluid, reduce the rate of penetration (ROP), and thereby reduce the performance of the drilling fluid ,the most important task of drilling fluid recycling is to remove the useless solid phase in the return fluid[11]. Flocculation is an effective and economical method to treat water and wastewater[12,13]. Natural and synthetic polymers can make colloidal suspensions unstable and have been found to be widely used as flocculants [14]. Water-soluble synthetic polymers have the disadvantages of non-biodegradability and high cost. Therefore, there is an increasing demand for efficient, inexpensive, and environmentally friendly flocculants for water and wastewater treatment. ndustrial flocculants are sometimes not suitable for oilfields due to their poor water solubility, small molecular weight, low charge density, and high concentration[15]. Polyamines are quaternary ammonium cationic polymers that have been used as flocculants and charge neutralizers in the pulp and mining industries. A number of studies have found that polyamines are effective in a wide pH range are easy to handle and immediately dissolve in aqueous systems[16,17]. Moreover, the cationic polymer neutralizes the charge by compressing the electric double layer, adsorbs and then forms a bridge, and the removal rate is high[18,19]. In this paper, ethylenediamine and epichlorohydrin with two-step polymerize to polyamine (DES0-0), using ethylenediamine, diethylenetriamine and triethylenetetramine as crosslinking agents to synthesize crosslinked polymer DES0-1, DES0-2， DES0-3 mix with PAM. After flocculation， the flocculation was evaluated by measuring in these aspects which and the particle size diameter of the floc and the volume of the supernatant and the light transmittance.

2 Materials and methods

2.1 Materials

Rereagents involved in the experiment, such as epichlorohydrin, diethylamine, ethylenediamine, diethylenetriamine and triethylenetetramine (analytical purity), were purchased from Chengdu Kelong Chemical Reagent Factory. Polyacrylamide (molecular weight is more than or equal to 3 million) were provided by Shanghai Shanpu Chemical Co., Ltd.

2.2 Preparation of polyamine salt and flocculant

Adding sodium oleate and epichlorohydrin with a molar ratio of 1:1 in a round-bottom flask, 1% potassium iodide was used as a catalyst and ethanol was used as a solvent under refluxing for 2 h to obtain product 1. In another round bottom flask, epichlorohydrin and diethylamine with a molar ratio of 1:1 was added based on ethanol as the solvent, and then transfered product 1 into this flask, continued to reflux for 2 h to evaporate the solvent ethanol to obtain the final product. After dripping, the mixture was heated at 80°C and keept the reaction for 240 min to obtain the polyamine.

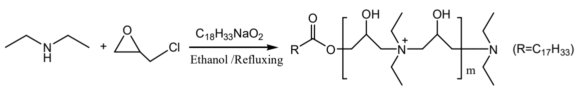

Figure 1 Synthesis mechanism

2.3 Crosslinking reaction

After adding the resulting polyamine salt medicine, a certain proportion of cross-linking agent was added. The reaction was carried out for 5 h kept with 60℃ until there was no pungent odor in the reactant to obtain the DES0-1, DES0-2, DES0-3.

2.4 Synthetic viscosity measurement

The viscosity of the polymer was measured using a 0.8-0.9 mm ubbelohde viscometer. The time of synthetic stream passing through capillary tube was measured at room temperature, followed by the corresponding kinematic viscosity was converted into standard viscosity according to formula.

2.5 Laser particle size determination method

Flocculant was added to the drilling fluid base slurry for flocculation, then transfered an appropriate amount of suspension to measure the particle size and distribution of flocs with laser diffraction particle size analyzer.

2.6 Base slurry configuration

The 4% bentonite was added to a certain amount of water under stirring with certain speed for 2 h, followed by age for 24 h.

2.7 Flocculation performance measurement

After the flocculation by adding flocculant to drilling fluid base slurry, an appropriate amount of suspension was transfered, followed by centrifugation. The volume of the supernatant was measured and the light transmittance was measured with a visible spectrophotometer.

2.8 Characterization of flocculants

A certain amount of synthetic products were analyzed by Fourier infrared spectrometer. The mixture consisting of sample and potassium bromide with a ratio of 1:100 (mass ratio) was put in mold, followed by tablet compressing.

3 Results and discussion

3.1 Optimization of flocculant synthesis conditions

3.1.1 Screening of reactant molar ratio

Table 1 and Figure 2 reflected the viscosity of the synthesized compound under different molar ratios. It suggested that when the molar ratio of epichlorohydrin to diethylamine was 1.5:1, the kinematic viscosity and dynamic viscosity of the compound reach the maximum, implying that the molecular weight of the composite is the largest. The larger the molecular weight, the better the flocculation effect. Therefore, the molar ratio of reactants is 1.5:1.

Table 1 Compound related data in different molar ratios

The molar ratio	Kinematic viscosity m^2/s	Dynamic viscosity /mpa.s
1:1	1.800	2.03
1:2	2.590	2.94
1:1.5	5.025	9.52
1.5:1	12.750	15.58
2:1	10.800	13.50

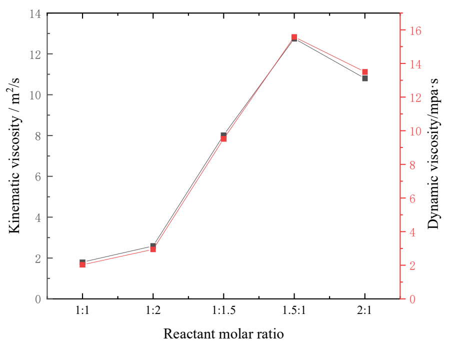

Figure 2 The influence of reactant molar ratio on product viscosity

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3.1.2 Screening of measurement standard for crosslinking agent

Table 2 and Figure 3 showed that the relevant data of the product after crosslinking with a 3% crosslinking agent and a reactant with a molar ratio of 1.5:1. It illustrated that the composition containing triethylenetetramine had the highest viscosity. However, epichlorohydrin and amines were used to synthesize polymers under the condition of a certain amount of crosslinking agent, the greater of the cationicity which the smaller the amine group contained in the crosslinking agent structure. The flocculation had a great relationship with the content of cations, so ethylenediamine was selected as the content determination standard.

Table 2 Data related to the composition with different crosslinking agents

Type of crosslinking agent	Kinematic viscositym^2/s	Dynamic viscosity /mpa·s
Ethylenediamine	10.76	13.00
Diethylenetriamine	12.26	15.23
Triethylenetetramine	14.63	19.74

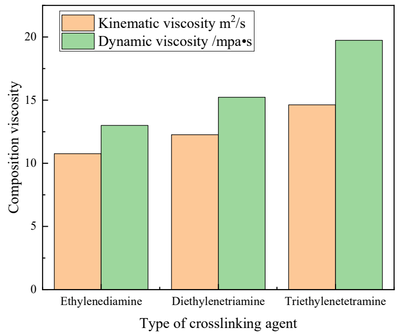


Figure 3 The effect of crosslinking agent on polymer viscosity

3.1.3 Determination of the dosage of crosslinker

Dethylamine crosslinking with reactants which the molar ratio was 1.5:1 were seleced to explore the influence of the content of the cross-linking agent on the viscosity of the synthetic products. A blank which added a certain amount of distilled wate was set during the measurement, and then set five different dosages of 0%, 1%, 2%, 3%, 4% to determine the optimum dosage of crosslinking agent. It can be seen intuitively from Table 3 and Figure 4 that the viscosity of the composition containing 4% of the crosslinking agent was relatively large, and the viscosity of the 3% and 4% organic polymer composition was not very different. Comparing with the cationicity,due to it was found that 3% of the polymer had a higher cationicity, a polymer with a content of 3% was selected.

Table 3 Data related to the composition with different content of cross-linking agent

Crosslinking agent content	Kinematic viscositym^2/s	Dynamic viscosity /mpa.s
0%	6.30	7.70
1%	7.01	8.47
2%	8.36	9.78
3%	10.99	13.23
4%	12.64	15.29

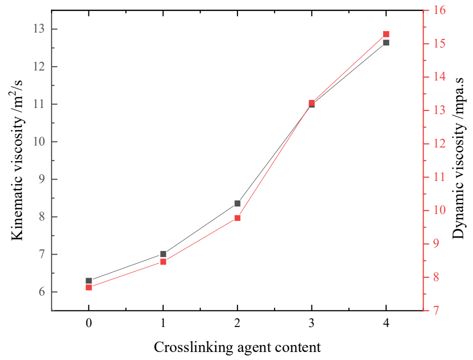


Figure 4 The influence of crosslinking agent content on polymer viscosity

3.2 Evaluation of flocculation effect of flocculant and PAM

The mixture which had different concentrations of flocculant and 70ppm PAM was added to the drilling fluid base slurry. The flocculation effect on the drilling fluid base slurry was investigated by analyzing the volume and permeability of the centrifugal liquid and the particle size diameter of the flocs. The experimental results were followed.

Table 4 DES0-0 and PAM compound flocculation effect

DES0-0	0	0.10 %	0.15 %	0.20 %	0.25 %	0.30 %
Volume of supernatant/ mL	152. 0	152.0	150.0	153.0	157.0	157.0
Transmittanc e /%	99.5	79.4	90.0	96.4	99.0	100.0
Particle size diameter /μm	503. 1	144.6	148.2	150.5	152.5	281.0

Table 5 DES0-1 and PAM compound flocculation effect

DES0-1	0	0.4%	0. 5%	0.6%	0.7%
Volume of supernatant/mL	151.8	130.2	128	140	139.8
Transmittance /%	98.8	81.8	85.3	91.6	98.1
Particle size diameter /μm	463.5	151.3	153.2	154.6	189.7

Table 6 DES0-2 and PAM compound flocculation effect

DES0-2	0	0.4%	0. 5%	0.6%	0.7%
Volume of supernatant/mL	151.8	145	157	148	151
Transmittance /%	98.8	94.2	94.3	96.7	95.9
Particle size diameter /μm	463.5	147.5	151.7	158.5	169.7

Table 7 DES0-3 and PAM compound flocculation effect

DES0-3	0	0.10%	0.2%	0.25%	0.30%
Volume of supernatant/mL	153	126.1	137.2	145.1	146.5
Transmittance /%	98.5	90.8	90.9	95.1	98.9
Particle size diameter /μm	489.1	147.5	150.6	153.8	156.5

With the continuous increase of the mass fraction of flocculant was added into the drilling fluid, the high molecular chain will have the effect of net capture and adsorption bridging on the bentonite. Meanwhile, due to the rich positive charge contained on it will neutralize the negative charge on the end face of the bentonite, which will have the effect of pulling and sinking the solid suspension and the transmittance and the particle size diameter of flocs are also increasing. The DES0-3 had a better effect with PAM.

3.3 Flocculation effect of flocculant in different pH environment

The pH value of the drilling fluid base slurry was adjusted by hydrochloric acid and sodium hydroxide. The experimental results of the flocculation effect on the drilling fluid base slurry at different pH were investigated by analyzing the volume and permeability of the centrifuged liquid and the particle size diameter of the flocs. The experimental results were followed.

Table 8 Flocculation effect of DES0-0 under different pH conditions

pH	4	5	6	7	8
Volume of supernatant/mL	173.0	177.0	175.0	160.0	160.0
Transmittance /%	99.4	100.0	99.5	99.0	99.0
Particle size diameter /μm	114.4	125.3	112.6	106.1	183.2

Table 9 Flocculation effect of DES0-1 under different pH conditions

pH	4	6	7	9	11
Volume of supernatant/mL	145.1	146.1	134.2	134.0	143.0
Transmittance /%	97.4	99.9	86.9	94.1	91.8
Particle size diameter /μm	103.2	182.2	141.3	146.1	133.2

Table 10 Flocculation effect of DES0-1 under different pH conditions

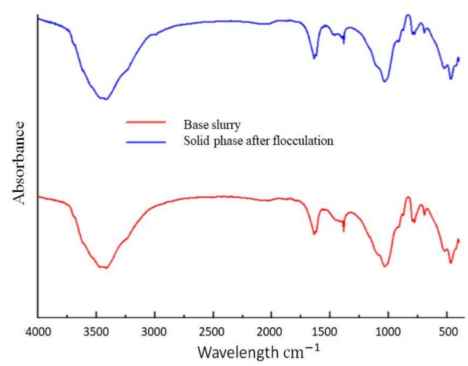
pH	4	6	7	9	11
Volume of supernatant/mL	170.0	171.1	172.5	160.3	168.6
Transmittance /%	98.8	99.9	99.9	88.8	95.1
Particle size diameter /μm	153.3	196.4	191.3	156.3	163.2

Table 11 Flocculation effect of DES0-1 under different pH conditions

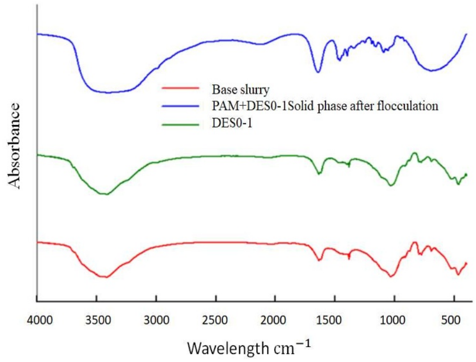
pH	4	6	7	9	11
Volume of supernatant/mL	155.1	152.0	152.2	151.1	159.5
Transmittance /%	87.2	96.8	97.5	93.6	97.5
Particle size diameter /μm	110.3	92.5	93.1	112.5	176.4

It can be seen from table 8,9,10,11 that the flocculation effect of the DES0-1, DES0-2 and PAM is the best when pH is 6, while the flocculation effect of the products synthesized with DES0-3 and PAM is the best when pH is 11. This is because the crosslinked products of diethylamine and triethylenetetramine as crosslinking agents can dissociate more cations which enhance the electrostatic attraction under alkaline conditions, so that the adsorption performance is improved, and the flocculation effect is also improved. However, due to the total negative charge of the bentonite particles itself is small, the total negative charge of the base slurry itself is small cause to the adsorption capacity for cations is small. When the pH was too high, the cations dissociated from the flocculant will appear to be excessive. On the contrary, the particles will be repelled due to the positive charge, which is not conducive to agglomeration.

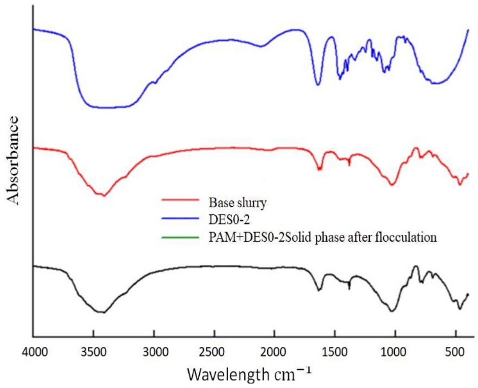
3.3.1 Infrared analysis



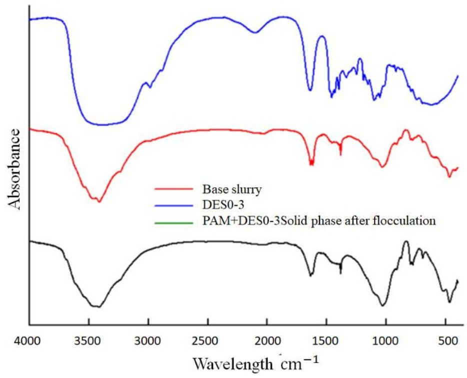
(a) DES0-0



(b) DES0-1



(c) DES0-2



(d) DES0-3

Figure 5 FTIR spectra of polymer

It can be concluded from the above infrared spectra that the special peak shape of the ternary epoxy in the molecular structure of epichlorohydrin had disappeared. 978cm^{-1} was the characteristic absorption peak in the molecular structure of quaternary ammonium salt. A series of sharp peaks from 2800cm^{-1} to 3050cm^{-1} were the stretching vibration peaks of methyl CH_3 - and methylene CH_2 -, which indicates that cationic quaternary ammonium salt had been formed. The absorption peak of water molecular structure appeared at about 3300 cm^{-1}. Compared with the infrared characteristic peaks of the base slurry and flocculant, the main characteristic absorption peaks of the base slurry and flocculant were shown in the infrared spectrum of the solid phase after flocculation and indicating that the flocculant had been adsorbed on the base slurry and played the role of adsorption flocculation.

4 Conclusions

In this paper, a series of crosslinked polymer such as DES0-1, DES0-2, DES0-3, was synthesized via adding ethylenediamine, diethylenetriamine and triethylenetriamine to a flocculant (DES0-0) obtained by epichlorohydrin and diethylamine, followed by flocculation evaluation. The results suggested that the relative molecular mass of triethylenetetramine (DES0-3) was higher than ethylenediamine (DES0-1) and diethylenetriamine (DES0-2). The polymer chain had a great effect on the net capture, adsorption and bridging of bentonite, and a pull-sinking effect on suspended solids. Meanwhile, it was found that the cross-linked product of triethylenetetramine as a cross-linking agent will not dissociate too many cations. The excess cations would cause the particles to be positively charged and charge repulsion, which is not conducive to agglomeration. Therefore, the triethylenetetramine cross-linked polymer can achieve better results when it is compounded with PAM under alkaline conditions.

Acknowledgments

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