Modification and Application of a Plant Gum as Eco-Friendly Drilling Fluid Additive

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ABSTRACT: *To enhance solubility and the performance of a plant gum (from south peach tree of China, SP gum) as a drilling fluid additive, we explored the potential of Modified SP (MSP) gum by modifying it with epichlorohydrin. The modification conditions, such as the mass ratio of the crosslinking agent, pH and temperature, were optimized and the results show that 56.40 g/100g mass ratio of the crosslinking agent to SP gum with pH=10 at the temperature of 50°C lead to the Modified SP (MSP) gum showed the well performance in the water based drilling fluids. It was discovered that drilling fluids modified with 0.5%wt MSP demonstrated more excellent rheology and lower filtration than that of SP treated drilling fluids, which should be contributed to the good clay inhibition obtained from swelling experiment and high inhibitive to the hydration and swell of the mud supported by mud ball immersing experiments .*

KEY WORDS: *SP gum, Modification, Eco-friendly, Drilling fluid.*

INTRODUCTION

Water-based drilling fluids are more desirable in areas where oil-based fluids may be prohibitive due to cost, logistical or environmental constraints. Among drilling fluid components, the rheology modifier is critically important in ensuring a proper rheological profile which performs specific functions such as suspending weighting agents, hole cleaning, suspending cutting and transporting them up the annulus to the surface, etc. The viscosifiers in water-based drilling fluids are required to give a strong shear-shinning rheology with excellent suspension power [1]. A wide range of polysaccharides can impart the desired viscosity profiles of the fluid in the oil field operation as eco-friendly drilling fluid additive [2,3].

The synthesized polymers with containing stable chains, such as polyacrylamide (PAM) and hydrolyzed polyacrylamide (HPAM), are somewhat un-ecofriendly and quite difficult to degrade after use. In recent years, the development and utilization of green materials, polysaccharides and polyphenols isolated from natural sources, have attracted increasing attention in oil flied operation for their sustainability, biodegradability and biosafety [4,5]. SP gum (from south peach tree of China) is a branched acidic heteropolysaccharide extracted from the secretion of a rosaceae plant and composed of L-arbinose (42.8%), D-galactose (35.7%), D-xylose (14.3%) and D-sedoheptulose (7.2%) [6]. A basically straight chain joined by aldopentose and aldohexose cause SP plant gum having high temperature resistance, shear stability and anti-biodegradation [7].

To enhance the performance of SP gum as a drilling fluid additive in many occasions onshore and offshore platform, great effort has been taken to improve

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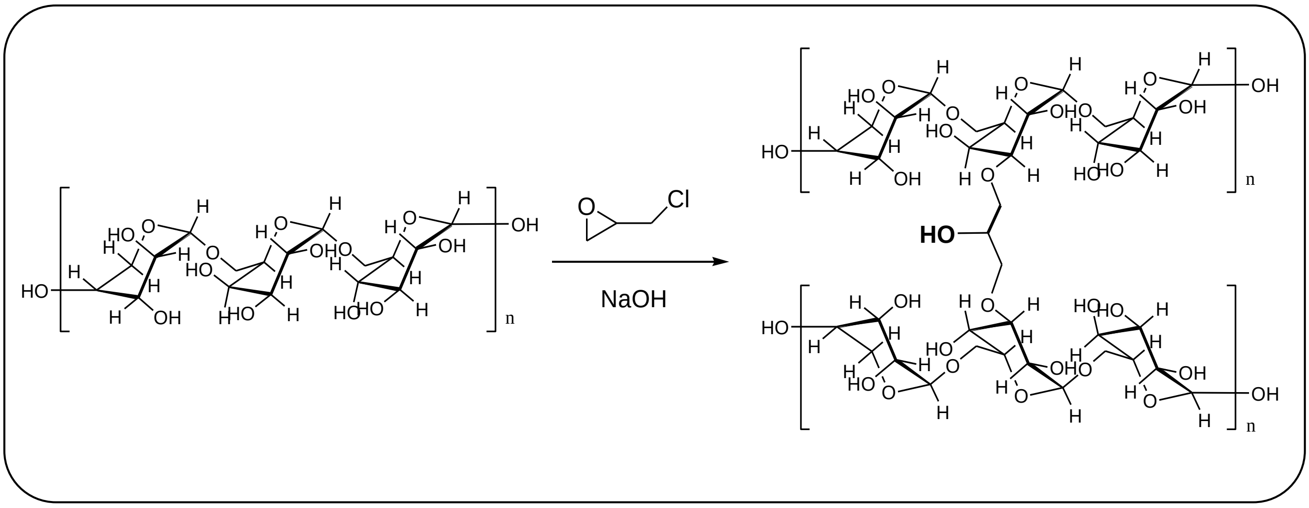

Fig. 1: Reaction of SP gum with epichlorohydrin.

the solution of SP gum by modification. The modifying conditions of SP gum and their inhibit properties have also been investigated in detail.

EXPERIMENTAL SECTION

Materials

The sodium montmorillonite (SD-1005) was obtained from Zhejiang Sanding Technology Co., LTD containing SiO_2, 64.07%; Al_2O_3, 19.11%; CaO, 4.48%; MgO, 3.61%; Na_2O, 3.07%; Fe_2O_3, 2.64%; P_2O_5, 1.71%; K_2O, 0.72%. SP gum sample was purchased from Changzhou Shuangjia Chemical Engineering Company, and other chemicals were obtained from Sinopharm Chemical Reagent Beijing Company.

Modification of SP gum

SP gum was modified according to the reaction with epichlorohydrin as shown in Fig. 1. SP gum, NaOH and water were mixed and stirred at certain temperature until a homogeneous gel was formed. Then, epichlorohydrin was added and the mixture was heated at certain temperatures for 6 h. The gel was cooled to room temperature and the pH was adjusted with dilute acetic acid. The solvent was distilled off under reduced pressure, and the residue was dried to give the modified SP gum (named as MSP).

Rheology tests

The performances of gums in the mud were investigated using prepared test mud according to the reported method [8-10]. Water-based mud (Bentonite: Na_2CO_3 : H_2O = 4: 0.2: 100 by weight) were aged for 24 h at room temperature to hydrate the bentonite. The required quantity of plant polysaccharides was added to the base mud under stirring at high speed for 20 min. Then, the rheological property of the treated mud as well as that of the base mud was measured to determine the rheological parameters such as Apparent Viscosity (AV), Plastic Viscosity (PV), Yield Point (YP) and filtration quantity (FL).

Clay linear swelling test

Bentonite (8g) dried at 105°C for 2h was used to make a generic core (10 MPa pressure for 5 min) and the generic core was fixed into a NP-01 type shale swelling apparatus (Qingdao Haitongda special Instruments co., LTD). The thickness changes of the generic core in contact with 100mL tap water or other aqueous solutions for 8 h were recorded. The swelling rate, %SR, was calculated as follows:

$$\%SR = (\Delta H/H_0) \times 100$$

where H_0 is the thickness of the generic core and ΔH is the increase of thickness as time goes on due to hydration swelling. The smaller the %SR is, the stronger the anti-swell ability of the additive.

Mud ball immersing test

Bentonite (10 g) was used to make a mud ball and the mud ball was immersed in 100mL tap water or other aqueous solutions for 36 h. Watch the details of

Table 1: Effect of epichlorohydrin on performance of MSP modified drilling fluid.

Sample	epichlorohydrin g/100g SP	AV/mPa·s	PV/mPa·s	YP/Pa	FL/mL
Base mud	-	3.8	2.0	1.8	27.8
Base mud+0.5% MSP	11.2	7.5	4.9	2.7	14.5
	22.4	7.0	4.2	2.9	16.0
	44.8	9.1	5.2	4.0	14.4
	56.4	9.8	5.6	4.2	13.0
	68.6	9.0	5.1	3.9	14.1

Table 2: Effect of pH on performance of MSP in drilling fluid.

Sample	pH	AV/mPa·s	PV/mPa·s	YP/Pa	FL/mL
Base mud	-	3.8	2.0	1.8	27.8
Base mud + 0.5% MSP	2	5.3	3.1	2.2	25.3
	4	5.6	3.3	2.3	22.8
	8	9.7	7.2	2.5	14.9
	10	9.8	5.6	4.24	13.0
	12	8.9	5.9	3.12	15.6

the immersed mud balls and check whether there are cracks or dilapidation on the surface.

RESULTS AND DISCUSSION

Reaction conditions optimization

Effect of epichlorohydrin

The effect of epichlorohydrin concentration on the crosslink degree of plant gum was studied by varying the concentration of epichlorohydrin from 11.2 to 56.4 g/100g SP. The results were illustrated in Table 1. It is shown that the AV increases along with the concentration of epichlorohydrin, while the FL decreases if more epichlorohydrin was used at the same conditions, and then the best concentration of the epichlorohydrin was selected at 56.40g/100gSP. The good performance of MSP should be contributed to the more hydrophilic of SP gum after reacted with epichlorohydrin, which caused the fully hydration of SP gum and easier intertwistion each other. As a result, the viscosity of drilling fluid was great enhanced, which can be further intensified due to the extend chains as the result of crosslink between the gum chains to increase the molecular weight of SP gum.

Effect of pH

The effect of pH on the performance of the gum in the drilling fluid was investigated by varying the pH from 2 to 12. The results were presented in Table 2. It can be seen from the result that the *AV*, *PV* and *YP* of drilling fluid in presence of MSP gum were found to increase continuously along with the increasing of the pH value from 2 to 10. Further increasing the pH to 12 caused decrease of drilling fluid rheology. In fact, the reaction of polysaccharide and epichlorohydrin can be efficiently catalyzed by base catalyst, such as NaOH. More OH^- of base catalyst can promote the formation of alcoholate and accelerate the substitution reaction with the chlorine atom of epichlorohydrin, while too much base will lead to a by-reaction of OH^- and epichlorohydrin to produce glycerine. So the pH was selected at 10 in the following experiments.

Effect of temperature

The effect of temperature on performance of MSP was investigated in the temperature range from 30°C to 80 °C, and the result was summarized in Table 3. From the results it can be found that the AV of the MSP modified drilling fluids increased with temperature and reached the highest value at 50°C, further increase of the temperature lead to a decrease of the AV. In addition, the increasing temperature gave great chance to the FL as well, and the best FL value was obtained at 50°C.

Table 3: Effect of the temperature on performance of MSP modified drilling fluid.

Sample	Temperature/°C	AV/mPa·s	PV/mPa·s	YP/Pa	FL/mL
Base mud	30	3.8	2.0	1.8	27.8
Base mud +0.5% MSP	30	6.8	4.5	2.3	19.2
	50	10.5	6.1	4.5	13.1
	70	9.6	6.2	3.5	17.1
	80	8.9	5.9	3.1	15.6

Table 4: Performance parameters in MSP and SP based drilling fluid.

Sample	Concentration/%	AV/mPa·s	PV/mPa·s	YP/Pa	FL/mL
Base mud		3.8	2.0	1.8	27.8
Base mud + SP	0.5	4.5	3.0	1.5	19.4
	1	6.3	4.5	1.8	14.0
Base mud + MSP	0.5	9.8	5.6	4.2	13.0
	1	16.0	9.0	7.2	11.2

It should be contributed to the increased reaction rate of SP and epichlorohydrin at higher temperature. However, the by-reactions, such as the intermolecular polymerization reaction between the epichlorohydrin, can not be avoided if the reaction temperature was excessively high. So the best reaction temperature was selected as 50°C.

Performance of MSP in the water-based drilling fluids

Rheology properties

The rheological behaviors of SP and MSP modified drilling fluids were shown in the Table 4. It was found that the AV in the SP modified drilling fluids was increased from 3.8 mPa·s in base mud to 4.5 mPa·s in presence of 0.5% SP, and reached to 9.8 mPa·s when 0.5% MSP was used. Increasing the amount of additive was in favor of the mud viscosity. 6.3 mPa.s and 16.0 mPa.s were found when the amount of SP and MSP increase to 1.0%. The effect of SP/MSP on the PV of mud was same to AV. Moreover, the fluid-loss decreased slightly from 27.8 mL in base mud to 19.4 mL in SP modified mud and 14.0 mL FL was obtained if MSP was used as additive. From the result it can be concluded that MSP was an efficient drilling fluids additive with good performance to increase the viscosity more than three times and decrease fluid-loss with a percentage of 59.7%.

Temperature resistance

Since the temperature resistance is very important factor to keep good performance of drilling fluid in deep well, the rheology of MSP based drilling fluids were tested by rolling heated for 16h at different temperature from 30°C to 160°C. From the result summarized in Fig. 2 it can be found that the AV and PV of MSP modified drilling fluid increased slightly with the temperature at the range from 30°C to 80°C, and the FL decreased with rising temperature. The reason for the good performance of MSP based drilling fluid at the high temperature of 80°C should be contributed to the good solubility and well molecule flexibility of SP gum after modifiying. When the temperature reached to as high as 80°C~120°C, the rheology and fluid loss properties of MSP based drilling fluid changed significantly due to the degradation of the MSP gum under high temperature.

Clay inhibition

The clay inhibition of drilling fluid is an important factor to the stable of wall of well. The shale expansion tests of MSP based drilling fluid were investigated on NP-01 shale expansion instrument, and for comparison the performance of tap water has also been added and summarized Fig. 3. It was shown that there was no significant different swelling rate between SP gum solution and water indicating the weak inhibition of SP gum.

Table 5: The absorption rate and description of the mud ball in different time.

Immersing fluid	Absorption rate /%					
	10 h	24 h	36 h	48 h	60 h	72 h
Tap water	91.8	129.6	133.7	Dilapidation		
1%SP	88.7	120.6	145.5	Dilapidation		
1%MSP	30.1	46.8	56.8	65.7	72.6	79.7

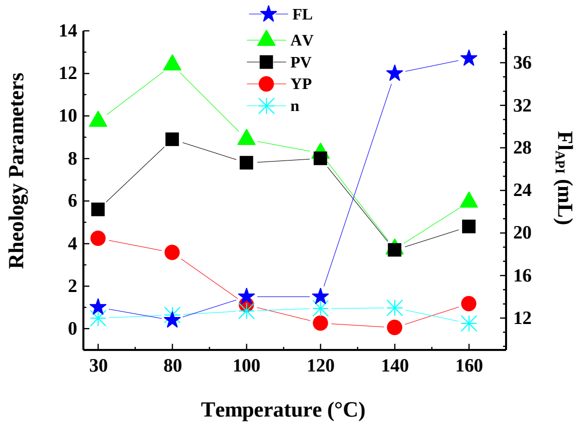

Fig. 2: Effect of temperature on reheology property of MSP modified drilling fluids.

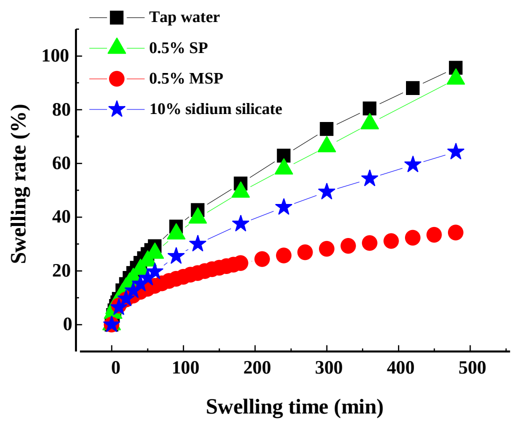

Fig. 3: The swelling rate of the clay in different solutions.

However, the swelling rate in 8h was only 34.2% in presence of 0.5%wt MSP gum solution, which was obviously lower than that of SP gum and even more effective than that of 10%wt sodium silicate solution. From the results it can be confirmed that MSP gum has significantly strong clay inhibition in the water-based drilling fluids.

Mud ball immersing test

In order to confirm the inhibition to clay of MSP mud ball immersing test were carried out by immersing the mud ball into water, 1wt%SP solution and 1wt%MSP solution respectively, and the results were shown in the Table 5 and Fig. 4. The test showed that high water absorption rate, 133.7% and 145.5%, were found on the mud balls immersed in water and SP solution at 36h respectively, which lead to the mud ball completely collapse after 48h. However, the water absorption rate of mud ball in MSP solution increase with time slightly and only 56.8% absorption rate was found at the same time. Fig. 4 shows the status of the mud balls after immersed in different solution for 36 hours. The surface of the mud ball immersing in MSP is very smooth while obviously fracture can be found on the surface of mud ball immersed in both water solution and SP solution indicating poor inhibition to hydration expansion. The reason for the good inhibition to swelling of MSP may be lie on the increased water-solubility and the longer chain of MSP which improved the inter-linkages between the silanol groups of the clay and the hydroxyl groups of MSP gum and formed a hydrated film on the surface of mud ball. As a result, the water penetration into the mud ball was greatly blocked and the deep hydration of mud was inhibited.

CONCLUSIONS

The modification conditions of SP gum were carried out to improve its solubility in water based drilling fluid. Both the modifiying condition and the performance of MSP based drilling fluid were investigated. From the result it was found that the optimal modifiying conditions were as follows: the mass ratio of the crosslinking agent 56.40g/100g SP gum with pH 10 at the temperature of 50°C. The rheological and fluid loss properties

Water SP solution MSP solution

Fig. 4: The status of mud balls immersed in different fluids for 36 h.

of the MSP were improved effectively with higher viscosity and lower filtration than that of SP gum. Swelling experiment shows that the clay inhibition of MSP is even superior to sodium silicate. Mud ball immersing experiments showed that MSP is high inhibitive to the hydration and swell of the mud.

Acknowledgments

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REFERENCES

[1] Caenn R., Chillingar, George V., Drilling Fluids: State of the Art, *Journal of Petroleum Science and Engineering*, **14**: 22l-230 (1996).

[2] Crini G., Recent Developments in Polysaccharide-Based Materials used as Adsorbents in Wastewater Treatment, *Progress in Polymeric Science*, **30**: 38-70 (2005).

[3] Zhang J., Zhang L., Chen G., Yang N.W., Guo Gang, Cheng S., Research of Polysaccharides-Hydrolyzed Polyacrylonitrile Unthickened Drilling Fluid System, *Natural Gas and Oil*, **32**(4): 62-64 (2014).

[4] Chen G., Zhang J., Yang N.W., Ma Y.F., The Evaluation of Sodium Hydroxymethyl Lignosulfonate as an Ecofriendly Drilling Fluid Additive, *Petroleum Science and Technology*, **32**: 1816-1623 (2014).

[5] Zhang J., Chen G., Yang N.W., Wang Y.G., Preparation of Nitration-Oxidation Lignosulfonate as an Ecofriendly Drilling Fluid Additive, *Petroleum Science and Technology*, **32**: 1661-1668 (2014).

[6] Feng W., Zhang J., Feng W., Qi X., Laboratory Research on the Grafting Modification of PG Tree Gum, *Oil Drilling & Production Technology*, **27**(4): 29-32 (2005).

[7] Zhang J., Chen G., Silanization of Guar Gum to Improve the Temperature Resistance, *Heterocyclic Letters*, **1** (4): 329-333 (2011).

[8] Zhang J., Chen G., Yang N., Wang Y., Preparation and Evaluation of Sodium Hydroxymethyl Lignosulfonate as Eco-Friendly Drilling Fluid Additive, *Advanced Materials Research*, **415-417**: 629-632 (2012).

[9] Chen G., Zhang J., Zhang L., Yang N.W., Preparation and Drilling Fluids Properties Screening of Polysaccharide-Lignin, *Oilfield Chemistry*, **28**(1): 5-8 (2011).

[10] Chen G., Yang N., Tang Y., Zhang L., Zhang J., Synthesis on Drilling Fluid Agent Lignosulfonate Mannich Alkali, *Drilling Fluid & Completion Fluid*, **27**(4), 13-15 (2010).