Synthesis and study of polystyrene/montmorillonite nanocomposite emulsion drilling fluid lubricant

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Abstract. Conventional drilling fluid lubricants could effectively improve the lubricity of the system, but the temperature and salt resistance was poor. In this paper, a new type of emulsion drilling fluid lubricant was prepared by mixing a polystyrene/modified montmorillonite (MMT) nanocomposite emulsion with vegetable base oil. The nanocomposite emulsion was prepared by emulsion polymerization of organic MMT, modified with the tributyltetradecylphosphonium chloride and sodium lauryl sulfonate, and styrene. The work revealed effects of the amount of modified MMT and lubricant on the performance of the drilling fluid. It was shown that lubricants have less effect on the rheology and density changes of the drilling fluid. The lubricity, temperature resistance and salt resistance of the drilling fluid were enhanced, while the fluid loss was significantly reduced due to the addition of the lubricant. Our results provide the basic method needed to guide design of the lubricant.

1. Introduction

With the development of oil and gas exploration, drilling of deep and complex reservoirs has been increased, especially for complex structural wells such as large displacement wells, directional wells and ultra-deep wells [1-2]. The contact area between the drill and the casing or the rock of the wellbore increased, which inevitably increased the rotational torque, reduced the drilling speed and accelerated the wear of the drill, and even caused stuck drilling and collapsed wall [3]. Therefore, a certain amount of lubricant was often added to the drilling fluid to improve the lubrication performance of the drilling fluid, reduce the drilling torque, shorten the drilling time and reduce the wear of the drill to ensure safe and efficient drilling [4]. Although drilling fluid lubrication technology has made great progress in recent years, conventional lubricants have problems such as poor temperature resistance, poor compatibility and poor salt resistance [5-6]. Therefore, the development of new high-efficiency, multifunctional drilling fluid lubricants will make up for the shortcomings of traditional lubricants and promote the development of the oil and gas drilling industry.

As a new functional material, polymer/clay nanocomposites have attracted wide attention of the researchers [7-8]. Montmorillonite (MMT), as a model of clay filling materials, could significantly
improve the mechanical, thermal and flame retardant properties of the polymer matrix [9-10]. It has been widely used in coatings, construction industry and petroleum engineering [11-12]. Polystyrene/montmorillonite nanocomposites have been widely used in many fields and reported by many scholars [13-15]. The introduction of polystyrene/montmorillonite nanocomposite emulsion material into the drilling fluid lubrication system not only improved the dispersion stability with the base oil, but also the nanocomposite microspheres could change the friction surface state and repair the worn surface, thereby reducing the friction coefficient and wear [16].

In this paper, organic montmorillonite (P-SLS-MMT) was prepared by intercalation modification with tributyltetradecylphosphonium chloride (TTPC) and sodium lauryl sulfonate (SLS), and polystyrene/modified montmorillonite (PS/P-SLS-MMT) nanocomposite emulsion was prepared by emulsion polymerization of styrene. The drilling fluid lubricant was obtained by mixing the nanocomposite emulsion, vegetable base oil and surfactants. The rheological, fluid loss, lubrication, density change, temperature resistance and salt resistance properties of the lubricant were evaluated to provide a basis for practical applications.

2. Experimental

2.1. Materials
Sodium montmorillonite (MMT) with cationic exchange capacity (CEC) of 100 mmol/100 g was purchased from Huai An Saibei Technology Co. Ltd., China. Analytically pure styrene (St), tributyltetradecylphosphonium chloride (TTPC), sodium lauryl sulfonate (SLS), divinylbenzene (DVB), oleic acid, span-60 and potassium persulfate (KPS) were supplied by Aladdin Industrial Corporation, China. Styrene was washed with NaOH solution, and distilled under reduced pressure before use. Vegetable oil, industrial grade, was used as the base oil.

2.2. Preparation of P-SLS-MMT and PS/P-SLS-MMT nanocomposite emulsion
The modification of MMT with TTPC and SLS was performed according to the method in Yu et al [17]. Polystyrene nanocomposite emulsion with nanofiller of P-SLS-MMT was prepared via emulsion polymerization. A certain amount of P-SLS-MMT and 20.0 mL of St and 2.0 mL of DVB were mixed magnetically at room temperature for 0.5 h. The SLS (0.36 g) was dissolved in 100 mL of distilled water and stirred during 0.5 h under nitrogen atmosphere. Afterwards, the P-SLS-MMT suspension was added into this solution with continuous stirring at 75 °C for 30 min. Finally, the 0.072 g of KPS was added into the mixture for 8 h with stirring. The nanocomposite emulsion prepared with 1.0, 3.0, and 5.0 wt.% (based on the weight of St) P-SLS-MMT loadings was designated PS/P-SLS-MMT-1, PS/P-SLS-MMT-3, and PS/P-SLS-MMT-5, respectively.

2.3. Preparation of vegetable oil-PS/P-SLS-MMT lubricant and the base drilling fluid
The drilling fluid lubricants were prepared by using vegetable base oil, 22.2 wt.% of PS/P-SLS-MMT emulsion, and 11.0 wt.% of span-60 and 28.8 wt.% of oleic acid. The mixture was vigorously stirred for 1 hour at room temperature to obtain the lubricant. The base drilling fluid was prepared by adding 0.8 g of Na₂CO₃ and 20.0 g of MMT into 400 mL of distilled water with stirring for 1 h and then sealed for 24 h.

2.4. Characterization
The rheological properties of the drilling fluid were evaluated using a ZNN-D6 six speed viscometer. The fluid loss performance of the drilling fluid was tested by a SD3 medium pressure filter. A TM-3 liquid densitometer was used to study the density of the drilling fluid. The lubrication performance test was carried out in an EP-2A extreme pressure lubrication instrument. A GW300 high temperature roller furnace was used to test the high temperature resistance of drilling fluids.
3. Results and discussion

3.1. The rheological property
A series of lubricants with different PS/P-SLS-MMT nanocomposite emulsion were added into base drilling fluid to study the rheological behavior, and the results were shown in Table 1.

As shown in Table 1, the apparent viscosity and plastic viscosity of drilling fluid decreased slightly with the increase of lubricant addition, while the values of yield point and gel strength increased slightly, indicating that the lubricant possessed a slight effect on the rheological properties of drilling fluid. The fluid compatibility and performance stability were observed in the lubricants with the drilling fluid. The decrease in the drilling fluid viscosity was due to the fact that the addition of the lubricant enhanced the negative charge of the suspended clay particles, and the strength of the internal structure of the drilling fluid was weakened. Meanwhile, compared with PS emulsion, lubricants added with PS/P-SLS-MMT nanocomposite emulsions had a relatively smaller effect on the rheological properties of the drilling fluid. This result indicated the nanocomposite emulsion lubricants possessed better compatibility with the base drilling fluid.

### Table 1. Drilling fluid rheological properties of different PS/P-SLS-MMT lubricant contents

| System               | use level (wt.%) | Apparent viscosity /mPa*s | Plastic viscosity /mPa*s | Yield point /Pa | Gel Strength /Pa/Pa |
|----------------------|------------------|---------------------------|--------------------------|----------------|---------------------|
| PS                   | 0                | 8.2                       | 5.6                      | 2.03           | 2.0/8.0             |
|                      | 0.2              | 7.9                       | 5.4                      | 2.14           | 2.7/8.2             |
|                      | 0.5              | 7.7                       | 5.3                      | 2.32           | 3.0/8.4             |
|                      | 0.8              | 7.6                       | 5.4                      | 2.34           | 3.4/9.5             |
|                      | 1.0              | 7.4                       | 5.6                      | 2.46           | 4.0/10.0            |
|                      | 1.2              | 7.1                       | 5.9                      | 2.42           | 3.8/9.0             |
| PS/P-SLS-MMT-1       | 0                | 8.2                       | 5.6                      | 2.03           | 2.0/8.0             |
|                      | 0.2              | 7.8                       | 5.2                      | 2.08           | 3.0/8.5             |
|                      | 0.5              | 7.6                       | 5.2                      | 2.12           | 3.0/8.5             |
|                      | 0.8              | 7.5                       | 5.3                      | 2.20           | 3.5/8.0             |
|                      | 1.0              | 7.4                       | 5.3                      | 2.23           | 3.7/9.0             |
|                      | 1.2              | 7.4                       | 5.1                      | 2.32           | 4.2/9.0             |
| PS/P-SLS-MMT-3       | 0                | 8.2                       | 5.6                      | 2.03           | 2.0/8.0             |
|                      | 0.2              | 7.6                       | 5.4                      | 2.06           | 2.0/8.0             |
|                      | 0.5              | 7.5                       | 5.3                      | 2.14           | 2.5/8.5             |
|                      | 0.8              | 7.3                       | 5.1                      | 2.23           | 2.5/8.8             |
|                      | 1.0              | 7.2                       | 5.2                      | 2.33           | 3.0/8.5             |
|                      | 1.2              | 7.0                       | 5.0                      | 2.49           | 3.0/9.0             |
|                      | 0                | 8.2                       | 5.6                      | 2.03           | 2.0/8.0             |
| PS/P-SLS-MMT-5       | 0.2              | 7.6                       | 5.4                      | 2.07           | 2.5/8.0             |
|                      | 0.5              | 7.5                       | 5.3                      | 2.13           | 2.6/8.5             |
|                      | 0.8              | 7.5                       | 5.1                      | 2.22           | 3.0/8.5             |
|                      | 1.0              | 7.4                       | 5.1                      | 2.46           | 3.5/9.0             |
|                      | 1.2              | 7.1                       | 5.0                      | 2.53           | 3.5/9.5             |

3.2. The fluid loss performance
The effect of API filtration of different PS/P-SLS-MMT nanocomposite lubricants in the base drilling fluid was investigated, and the results were shown in Fig. 1.
In Figure 1, the fluid loss of the drilling fluid was significantly reduced when 0.2 wt.\% of the lubricant was added, and then the amount of fluid loss decreased slightly with the addition of the lubricant. When the amount of lubricant exceeded 0.8 wt.\%, however, the amount of fluid loss increased. The fluid loss of the vegetable oil-PS/P-SLS-MMT lubricant was significantly reduced compared to the vegetable oil-PS sample. This result indicated that the better fluid loss performance was obtained in nanocomposite lubricant. Meanwhile, the best fluid loss performance was observed in the lubricant prepared by PS/P-SLS-MMT-3, which indicated that the 3.0 wt.\% addition of modified MMT was the optimum addition.

3.3. The density change
A series of vegetable oil-PS/P-SLS-MMT nanocomposite emulsion lubricants were added to the base drilling fluid to investigate the density changes. The results were shown in Table 2.

| System                  | 0   | 0.2 wt.\% | 0.5 wt.\% | 0.8 wt.\% | 1.0 wt.\% | 1.2 wt.\% |
|-------------------------|-----|-----------|-----------|-----------|-----------|-----------|
| PS                      | 1.030 | 1.031   | 1.028     | 1.020     | 1.015     | 1.016     |
| PS/P-SLS-MMT-1          | 1.030 | 1.030   | 1.028     | 1.024     | 1.019     | 1.018     |
| PS/P-SLS-MMT-3          | 1.030 | 1.031   | 1.029     | 1.023     | 1.020     | 1.020     |
| PS/P-SLS-MMT-5          | 1.030 | 1.031   | 10.30     | 10.24     | 1.017     | 1.019     |

As shown in Table 2, the drilling fluid density decreased slightly with the increase of the amount of lubricant, but the reduction was not large. When the amount of lubricant addition was 1.0 wt.\%, the drilling fluid density was reduced by 0.015, 0.011, 0.010 and 0.013 g/cm\(^3\) for the PS, PS/P-SLS-MMT-1, PS/P-SLS-MMT-3 and PS/P-SLS-MMT-5 lubricant samples, respectively. The density variation was lower than the ±0.08 g/cm\(^3\) of the standard. The results revealed that the prepared emulsion lubricants had the higher emulsion stability, lower foaming performance and lower influence on drilling fluid density. Furthermore, the effect of nanocomposite emulsion lubricants on density was slightly lower than that of PS sample, especially for PS/P-SLS-MMT-3 lubricant.

3.4. The lubrication property
An EP-2A lubrication instrument was used to evaluate the lubrication property of lubricants prepared with different amounts of P-SLS-MMT, and the results were summarized in Figure 2.

As shown in Figure 2, with the amount of lubricant increased, the lubrication coefficient reduction rate (R) obviously increased, and then gradually reached to a flat plateau. When the amount of lubricant
added was 1.0 wt.%, the R value increased to 80.4-86.4%, indicating that the lubrication performance of the drilling fluid was significantly improved. Moreover, this result suggested that the 1.0 wt.% was optimum dosage. All the R values of the PS/P-SLS-MMT nanoconposite lubricants were higher than PS sample, indicating that the lubrication performance of the PS emulsion was enhanced due to the introduction of the modified MMT layers. In addition, when the amount of nanocomposite lubricant added was less than 0.8%, the R values of the lubricants were not much different from each other. However, when the amount of the lubricant exceeded 0.8%, the highest R values were observed in PS/P-SLS-MMT-3 sample. This result was due to the fact that the nanocomposite microspheres with the smaller particle size were more easily adsorbed and filled into the friction surface to form a high-strength lubricating protective film, and the microspheres also could change the sliding friction state into rolling friction to effectively reduce the friction coefficient [18].

![Fig. 2 Lubrication effect of PS/P-SLS-MMT in base drilling fluid](image)

### 3.5. Temperature resistance
A certain amount of base drilling fluid was mixed with 1.0 wt.% of the lubricant, and then the drilling fluid was treated at 120, 150, 180 and 200 °C for 16 h to study the temperature resistance performance. The experimental results were shown in Table 3.

| System          | 25°C | 120 °C | 150 °C | 180 °C | 200 °C |
|-----------------|------|--------|--------|--------|--------|
| PS              | 80.4 | 81.2   | 80.9   | 76.7   | 72.5   |
| PS/P-SLS-MMT-1  | 83.3 | 84.5   | 83.9   | 81.4   | 76.7   |
| PS/P-SLS-MMT-3  | 86.4 | 87.2   | 87.6   | 84.2   | 79.3   |
| PS/P-SLS-MMT-5  | 84.9 | 85.6   | 86.2   | 82.3   | 78.6   |

It could be seen from Table 3 that as the temperature increased, the R values of the drilling fluid gradually decreased, but the overall variation was relatively small, indicating that the high temperature lubrication stability was obtained in the prepared lubricants. However, it was interesting to observed
that the R values slightly increased after the treatment of the lower temperatures (<150 °C). This result revealed that the high temperature conditions would favor the uniform dispersion of the polymer microsphere emulsion in the drilling fluid, thereby improving the lubrication performance of the system. However, when the aging temperature was too high, the decrease of the lubrication performance was observed due to the thermal decomposition of the surfactant and the polymer microspheres in the lubricants. On the other hand, the agglomeration between the microspheres in the higher temperature could reduce the adsorption performance, and thus the lubricating effect was decreased. The R values of the nanocomposite emulsion lubricants were higher than the PS sample, indicating that the high temperature lubricity of the PS microsphere was improved with the introduction of P-SLS-MMT layers. Furthermore, after 180 °C aging, the R values of the nanocomposite lubricants could still be higher than 80.0%, indicating that the nanocomposite lubricants could be used in the 180 °C to effectively reduce the friction coefficient.

3.6. Salt resistance
The 1.0 wt.% of the lubricant was added to the base drilling fluid with different NaCl contents, and the lubrication performance was tested after homogenization. The experimental results were shown in Figure 3.

![Fig. 3 Effect of NaCl content on lubrication performance of drilling fluid](image)

As shown in Figure 3, the R values of the drilling fluid gradually decreased with the increasing of the salt content of the system. When the NaCl content was 50×103 mg/L, the R values of PS, PS/P-SLS-1, PS/P-SLS-3 and PS/P-SLS-5 emulsion lubricants were 75.0%, 77.6%, 81.2% and 78.5%, respectively. This result indicated that the introduction of P-SLS-MMT layers in PS matrix could effectively enhance the salt resistance of the lubricant. Furthermore, the R values of the vegetable oil-PS/P-SLS-MMT-3 lubricant were the highest, indicating that the best salt resistance was obtained in this sample and it could be used in high salt content drilling fluids.

4. Conclusion
The PS/P-SLS-MMT nanocomposite emulsion was prepared via the emulsion polymerization of styrene with the P-SLS-MMT as nanofiller. The drilling fluid lubricants were successfully synthesized by mixing the vegetable oil, surfactants and nanocomposite emulsion. The effect of the type and amount of lubricant on the performance of the base drilling fluid was investigated. Compared with the PS emulsion lubricant, the higher R values and greater temperature resistance and salt resistance were obtained in the PS/P-SLS-MMT nanocomposite emulsion samples. The great compatibility and density stability were
observed in the base drilling fluid with the lubricants. The overall performance of vegetable oil-PS/P-SLS-MMT-3 lubricant was the better than vegetable oil-PS/P-SLS-MMT-1 and vegetable oil-PS/P-SLS-MMT-5 samples. When the amount of PS/P-SLS-MMT-3 lubricant added was 1.0 wt.%, the API fluid loss of the drilling fluid was reduced from 31.0 mL to 17.1 mL, the R value at room temperature was 85.4%, the temperature resistance was 180 °C, and the R value could reach 81.2% in the drilling fluid with 50×10^3 mg/L NaCl content. The prepared lubricant was suitable for high temperature and high salt content to reduce the friction in the drilling engineering.

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References
[1] D. Kania, R. Yunus, R Omar, et al. A review of biolubricants in drilling fluids: Recent research, performance, and applications[J]. J. Petrol. Sci. Eng., 2015, 135: 177-184.
[2] L. Yu, Y. Zhang, F. Wang, et al. Wellbore stability estimation model of horizontal well in clean-featured coal seam[J]. SPE 2014, 167767.
[3] P. He. The development of the new type of vegetable oil drilling fluid lubricant[J]. Ind. Eng. Tec., 2015, 5: 196-198.
[4] W. Zhang, Y. Du, F. Kong. Preparation and performance evaluation of an emulsion drilling fluid lubricant[J]. Oil Gas Che. Ind, 2016, 45(4): 73-76.
[5] W. Wang, Z. Qiu, H. Zhong, et al. Preparation and properties of novel nano lubricant SD-NR for drilling fluid[J]. Fault block oil and gas field, 2016, 23(1): 113-116.
[6] P. Mousavi, D. Wang, C.S. Grant, et al. Measuring thermal degradation of a polyol ester lubricant in liquid phase[J]. Ind. Eng. Che. Res, 2005, 44(15):5455-5464.
[7] A.M. Alans, W.Z. Alkayali, M.H. Al-qunaibit, T.F. Qahtan, T.A. Saleh, Synthesis of Exfoliated Polystyrene/Anionic Clay MgAl-Layered double hydroxide: Structural and thermal properties[J]. RSC Adv., 2015, 5(87): 71441.
[8] L. Zhu, J. Guo, P. Liu, Effects of length and organic modification of attapulgite nanorods on attapulgite/polystyrene nanocomposite via in-situ radical bulk polymerization[J]. Appl. Cla. Sci., 2016, 119: 87-95.
[9] O. Yılmaz, C.N. Cheaburu, D. Durracchio, G. Gulumser, C. Vasile, Preparation of stable acrylate/montmorillonite nanocomposite latex via in situ batch emulsion polymerization: Effect of clay types[J]. Appl. Cla. Sci., 2010, 49: 288-297.
[10] K.J. Shah, A.D. Shukla, D.O. Shah, T. Imae, Effect of organic modifiers on dispersion of organoclay in polymer nanocomposites to improve mechanical properties[J]. Polymer, 2016, 97: 525-532.
[11] O. Yılmaz, C.N. Cheaburu, G. Gülümser, C. Vasile, On the stability and properties of the polyacrylate/Na-MMT nanocomposite obtained by seeded emulsion polymerization[J]. Eur. Polym. J., 2012, 48: 1683-1695.
[12] D. Zhou, Z. Zhang, J. Tang, F. Wang, L. Liao, Applied properties of oil-based drilling fluids with montmorillonites modified by cationic and anionic surfactants[J]. Appl. Cla. Sci., 2016, 121-122: 1-8.
[13] L.M.C. Dykes, J.M. Torkelson, W.R. Burghardt, Shear-Induced Orientation in Well-Exfoliated Polystyrene/Clay Nanocomposites[J]. Macromolecules, 2012, 45: 1622-1630.
[14] R. Ianchis, M.C. Coroea, D. Donescu, I.D. Rosca, L.O. Cinteza, L.C. Nistor, E. Vasile, A. Marin, S. Preda, Advanced functionalization of organoclay nanoparticles by silylation and their polystyrene nanocomposites obtained by miniemulsion polymerization[J]. J. Nanopart. Res., 2012, 14 (11): 1-12.
[15] C. Benbayer, S. Saidi-Besbes, E.T. Givenchy, S. Amigoni, F. Guittard, A. Derdour, Synergistic effect of organoclay fillers based on fluorinated surfmers for preparation of polystyrene nanocomposites[J]. J. Appl. Polym. Sci., 2015, 132 (33): 42347.

[16] J. Jin, Research progress in lubricants for drilling fluids[J]. Appl. Che. Ind., 2017, 46(4): 770-774.

[17] C. Yu, Y. Ke, X. Hu, Y. Zhao, Q. Deng, S. Lu, Effect of Bifunctional Montmorillonite on the Thermal and Tribological Properties of Polystyrene/Montmorillonite Nanocomposites[J]. Polymers, 2019, 11: 834.

[18] Z. Wang, Y. Ma, B. Liu, Understanding and prospect of plastic ball lubricants used in drilling fluids[J]. Inner Mongolia Petrochemical, 2013, 2: 30-32.