

Research Article

Study on Synthesis of Polyacrylamide Microspheres and its Sealing Characteristics of Drilling Fluid

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Abstract: For the purpose of reducing the invasion depth of solid phase and liquid phase of drilling fluid and improving the quality of drilling mud cake, polyacrylamide microspheres were successfully composed via reversed phase emulsion method. The physical and chemical structures of the samples as well as the grain-size variation were investigated by Transmission Electron Microscopy (TEM) and Laser Particle Size Analysis method (LPSA). The plugging performance of the samples were investigated by core plugging experiment and sand bed filtration experiment. TEM images show that acrylamide has been polymerized, the products consist of a lot of monodisperse microspheres with a size of about 1-6 μm . LPSA images indicate that the particle size of polyacrylamide microspheres vary with time and temperature regularly. The experiment that simulates rock strata with different permeability shows those polyacrylamide microspheres can produce effectively blocked to the core and sand bed and then it establishes the foundation for the next field test.

Keywords: Drilling fluid, microspheres, polyacrylamide, sealing characteristics, synthesis

INTRODUCTION

Due to its special spherical morphology and non-toxic environmental compatibility characteristics, PAM microspheres are widely used in profile control and water shutoff, temporary plugging in well drilling and water treatment (Feng *et al.*, 2008; Jia *et al.*, 2011; Jie *et al.*, 2011; Huang *et al.*, 2011).

PAM microspheres have excellent performance of water shutoff thanks to the expansion deformation of its special 3d mesh structure (Jiang *et al.*, 2011; Qian *et al.*, 2008). Been used as profile control agent to inject into deep strata of different permeability, PAM microspheres adsorb detain in smaller formation pore, make the injection pressure rise rapidly. High pressure in turn push the microspheres deform and move forward to deep formation, injection pressure fall subsequently, thereby it is in a position to divert the fluid flowing in deep formation, improve the volumetric sweep efficiency of injection water, modify the water profile, improve the effect of water injection development, so as to achieve the purpose of enhancing the recovery ratio and increasing oil and decreasing water (Han, 2011). PAM microspheres whose initial size (for nanometer or micrometer) are less than or equal to formation pore diameter, could enter into formation pore smoothly and form a very low permeability temporary plugging layer. Meanwhile PAM microspheres will inflate to several or dozens of

times when sucking water, which is adequate to plug core in complex formation conditions of high temperature and salinity, attain the goal of improving cake quality as well as reducing the invasion depth of drilling fluid solid and liquid, conduce to borehole stabilizing and reservoir protection.

General preparations of polyacrylamide microspheres contain emulsion polymerization, non-soap emulsion polymerization, dispersion polymerization, precipitation polymerization, suspension polymerization, etc., Wang *et al.* (2006). Emulsion polymerization is one of the important methods to prepare monodisperse polymer microspheres which has many advantages, such as high rate of polymerization, huge molecular weight, polymerization reaction heat spread easily, reaction temperature is easy to control, viscosity of polymerization system is very low even at the last period of the reaction, use water as medium, production is safe, little environment pollution, can be used directly as emulsion. Whereas emulsion polymerization application is limited to some extent due to its disadvantage, for instance, reaction rate is high; the degree of production polymerization is difficult to control. Inverse emulsion polymerization is in the leading edge of the emulsion polymerization technology, which has many advantages compared with the solution polymerization. For example, high polymerization rate, production can be dissolved in

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water quickly by means of regulating the PH value or adding emulsifier, application is more convenient than powder type polymer (Han *et al.*, 2010). Accordingly, inverse emulsion polymerization develops rapidly as a supplement to regular emulsion polymerization. In this study, inverse emulsion polymerization was adopted, dispersed the aqueous solution which-dissolved the water-soluble monomer to nonpolar liquids, formed an Water-Oil-in (W/O) emulsion.

EXPERIMENTAL SECTION

Materials: Span-80, acrylamide were purchased from tianjin TaiXing reagent Co., Ltd. (tianjin China); Tween-80 was purchased from zhejiang LongYouXian chemical reagent Co., Ltd. (zhejiang China); N, N'-methylene bis-acrylamide was purchased from shanghai second reagent Co., Ltd. (shanghai China); ammonium persulfate was purchased from shandong Xilong reagent Co., Ltd. (shandong China); acetone was purchased from yantai Laiyang Yuanweii chemical Co., Ltd. (yantai China); ethanol was purchased from tianjin Meining chemical reagent Co., Ltd. (Tianjin China); pure wate was purchased from Kaifeng lankao reagent Co., Ltd.

Synthesis of the polyacrylamide microspheres: In a typical synthesis of the polyacrylamide microspheres,

6.01 g of Span80 and 1.50 g Tween80 were dispersed in 40.16 g white oil in a three-necked flask. Then 36.5 g of acrylamide, 0.02 g of N, N'-methylene bis-acrylamide and 0.01 g of ammonium persulfate were dissolved in 36.5 of distilled water and the system were dispersed in the above oil phase by drop wise adding, with vigorously stirring. After a homogenous solution was obtained, 0.02 g of odium bisulfite solution was added into the system to initiate the polymerization under nitrogen protection and kept stirring for at 35°C until the temperature of the flask fell to the temperature of water bath. After this step, the as-obtained microspheres emulsion were washed with acetone several times cleaned by acetone for twice, then dried in a vacuum at 45°C for 20 h.

Characterization of polyacrylamide microspheres: Transmission Electron Microscope (TEM) and Laser Particle Size Analyzer (LPSA) were adopted to characterize the polyacrylamide microspheres original state and expanding particle size distribution while absorbing water.

RESULTS AND DISCUSSION

TEM of polyacrylamide microspheres: From the Fig. 1, it can be seen that the microspheres have uniform particle size distribution (about 1-6 μm or so) and regular spherical structure.

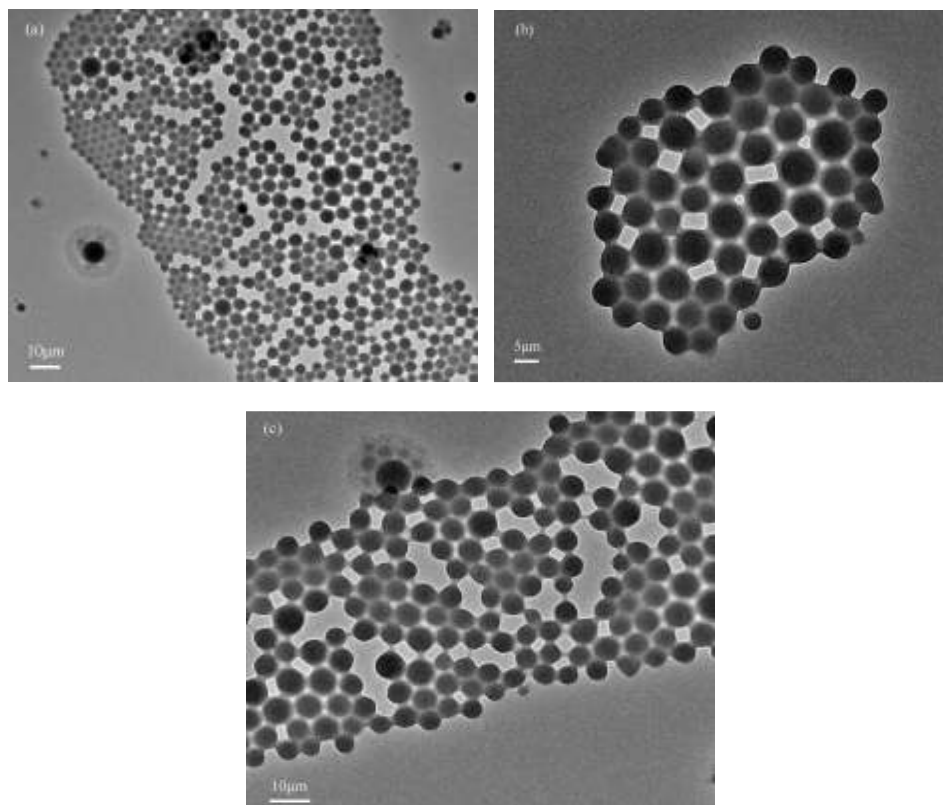


Fig. 1: TEM images of polyacrylamide microspheres

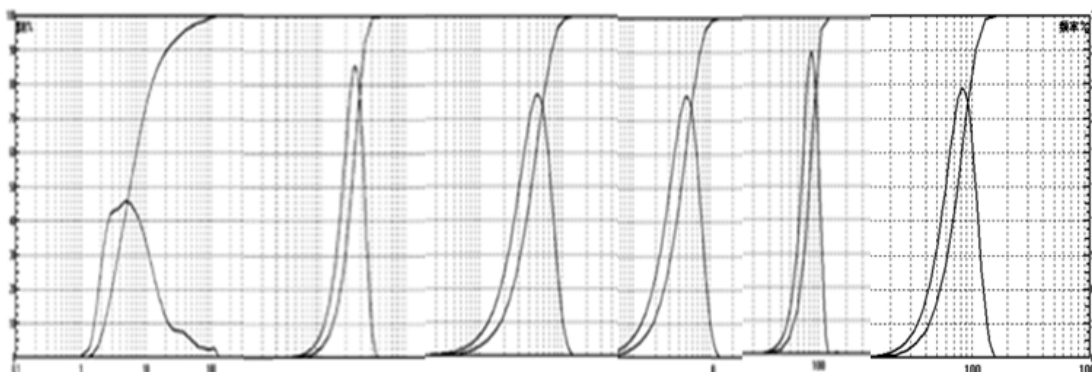


Fig. 2: The particle size distribution of microspheres

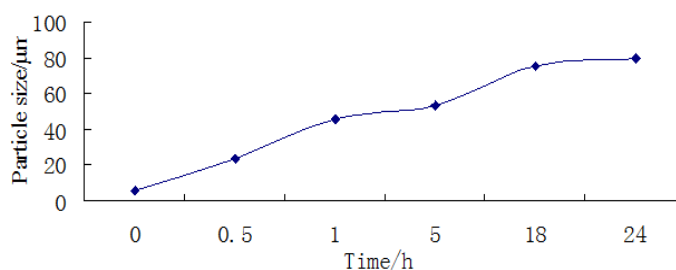


Fig. 3: Median size of microspheres change with time

The expanding properties of microspheres changing with time: The particle size variation of microspheres was measured at the initial time, 0.5, 1, 5, 18 h, respectively later; the expanding discipline of microspheres changing with time can be established.

The median size of microspheres vary with time were exhibited in Fig. 2 and 3.

It was known from Fig. 2 and 3 that the microspheres have excellent inflation performance, whose expansion ratio could be reached more than ten times after swelling 24 h, which indicate that the polyacrylamide microspheres had large specific surface area and strong water swelling property in aqueous solution. If it is applied in the field experiment, the sealing characteristics of drilling fluid would be very significant.

Evaluation on the microspheres sealing characteristics: The sealing characteristics are one of the important index to measure the microspheres properties. The pore structure of the core and sand bed is heterogeneous in a certain range, which could be simulated as stratum with different permeability. What is more the migration of microspheres in the strata will be reflected, if the core and sand bed are adopted to determine the depth of microspheres enter into the strata.

Evaluation on core plugging and plugging strength: The microspheres that obtained via compound

emulsifier span-80/Tween-80 were configured to certain volume of microspheres solution in order to carry through the core plugging experiment. The principle to analysis the experiment result is Darcy law and unidirectional seepage field theory.

The core flooding test:

- **Test process and data processed:** Made the core evacuated and saturated before the test. Technology parameters of instrument were as follows:
 - The displacement pressure of test was 3.5 MPa
 - The confining pressure was greater than the liquid flow pressure for 2~2.5 MPa or so
 - The flow of pump was 1 mL/min
 - The displacement time was 4 h
 - The reaction temperature was ambient temperature
 - The volume of drilling fluid was 500 mL

During this process it was need to write down the pressure of the first drop of liquid, the highest pressure and stable pressure. Thanks to the end of the experimental device was bled off, the indication of pressure gage in front of the core was the differential pressure of the flow between both ends of the core. Therefore the plugging rate could be calculated as follows according to Darcy law:

$$R = 1 - \frac{\Delta p_1}{\Delta p_2}$$

Table 1: The core plugging rate table

Core	Length/cm	Gas log permeability/ $10^{-3} \mu\text{m}^2$	Oil flooding stable pressure/MPa	Flow back stable pressure/MPa	Plugging rate
F13	3.97	22.8	0.061	1.78	0.9657
F16	3.99	22.3	0.062	1.91	0.9675
M17	4.03	82.9	0.073	1.11	0.9342
M20	4.05	83.1	0.076	1.27	0.9402
G13	4.12	120.5	0.095	0.99	0.9040
G15	4.15	120.9	0.098	1.19	0.9176
J4	4.36	235.5	0.015	0.36	0.9583
J5	4.39	239.7	0.021	1.35	0.9844

F13, M17, G13, J4 were plugged by 35% microspheres white oil solution; F16, M20, G15, J5 were plugged by 0.3% microspheres aqueous solution

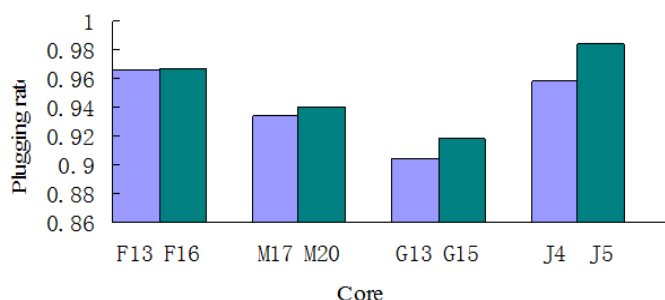


Fig. 4: The core plugging rate table

where,

R = Plugging rate

Δp_1 = The pressure between both ends of the core before plugging

Δp_2 = The pressure between both ends of the core after plugging

- **Plugging rate test:** The calculated plugging rate is exhibited in Table 1.

The corresponding plugging rate of different core is exhibited in Fig. 4.

It could be seen from the Table 1 that the plugging rate of the microspheres aqueous solution is higher than the microspheres white oil solution with regard to the similar permeability core, which provided further evidence for the theory that the microspheres could expand and produce elastic deformation to block formation pore and fracture effectively. The microspheres produced more effective plugging to the higher permeability core. Owing to the pore of the higher permeability core was much bigger, the depth of microspheres entrance was even huger, in addition, the entrance microspheres quantities were larger and the stabilized flow back pressure was higher as well, in consequence the plugging rate of the higher permeability core is bigger than that of the lower permeability core.

- **Variation of filtrate volumes:** Figure 4 showed that the low permeability cores have compact structure and low porosity; therefore the sealing characteristics of microspheres white oil solution is

correspond to microspheres aqueous solution. In addition, it could be seen from the Fig. 5 that along with the improvement of the core permeability, the filtrate volumes increased too and the sealing characteristics of microspheres aqueous solution was better than microspheres white oil solution as well. Therefore, there are an appropriate degree range of microspheres aqueous solution, within that context, the ideal sealing characteristics of drilling fluid can be reached.

Evaluation on plugging strength: Made the core evacuated and saturated before the test. Technology parameters of instrument are as follows:

- The displacement pressure of test was 3.5 MPa
- The confining pressure was greater than liquid flow pressure for 2~2.5 MPa or so
- The pressure of pump is 15 MPa
- The displacement time was 4 h
- The reaction temperature was ambient temperature
- The volume of drilling fluid was 500 mL

The Fig. 6 showed that the microspheres could achieve anticipate plugging strength to the low permeability core, kept the setting pressure 15 Mpa for 30 min. Nevertheless, the microspheres could not achieve anticipate plugging strength to the medium high and high permeability core, what is more, the highest plugging pressure decrease with the increase of core permeability.

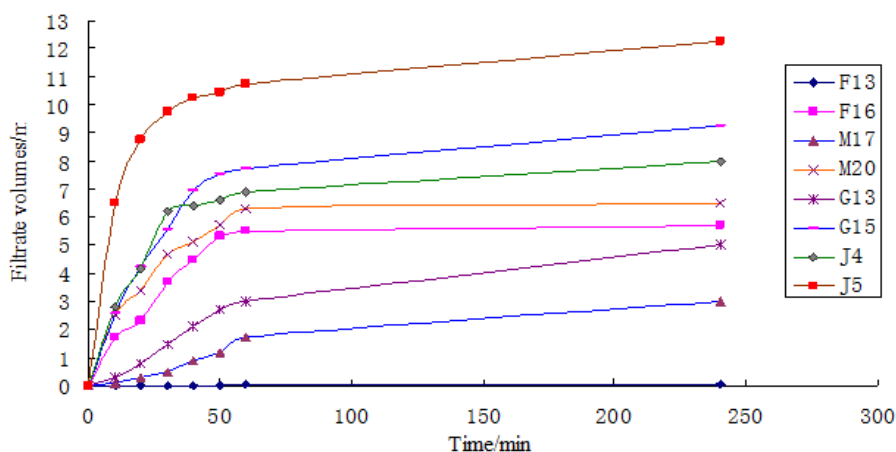


Fig. 5: The filtrate quantity vary with time

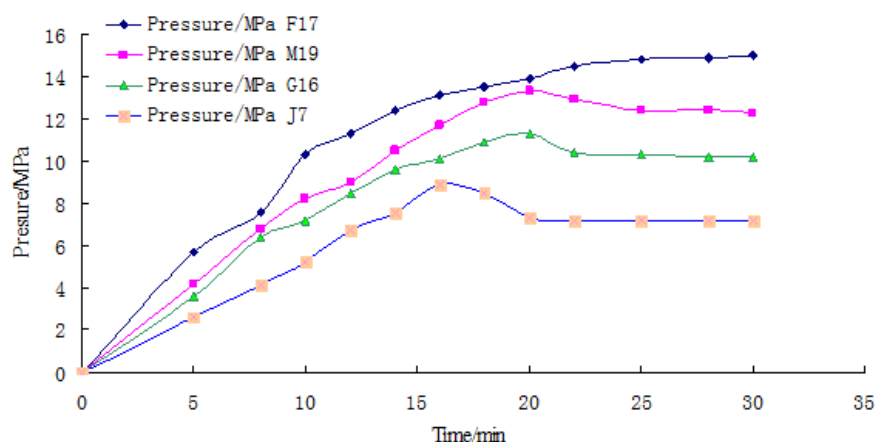


Fig. 6: The core plugging pressure vary with time

Evaluation on resistance to pressure: The microspheres that obtained via compound emulsifier span-80/Tween-80 were configured to 0.3% (wt) of microspheres aqueous solution in order to carry through core plugging experiment. Placed the aqueous solution in FA-BX type portable drilling fluid filtration to determine the plugging performance of microspheres vary with time:

- **Experimental facility and data processing:** The experiment required size of quartz sand was poured into drilling liquid cup. Technology parameters of instrument were as follows:
 - The mass fraction of 0.3% polyacrylamide microspheres aqueous solution was 250 cm³.
 - The pump pressure was 1 MPa.
 - The relief valve pressure was 0.69 MPa.
 - Scheduled filtration time was 30 min.
- **Test result:** The cake gained from drilling fluid filtration was shown in Fig. 7.



Fig. 7: The filter cake of confined time testing

continuous accumulating of microspheres during the filtration process, with a thick of 0.4 cm or so. The layer bellow was filtrate permeability layer, with a thick of 1 cm or so. Microspheres accumulated gradually along with the continuous filtration, made the plugging layer more and more compact. Meanwhile, the filtrate volume became less and less in the same period of time. Thus it could be seen that the microspheres can achieve the expected sealing characteristics of drilling fluid to the sand bed.

It could be seen from Fig. 7 that there were two layers of the cake; the layer above was formed by

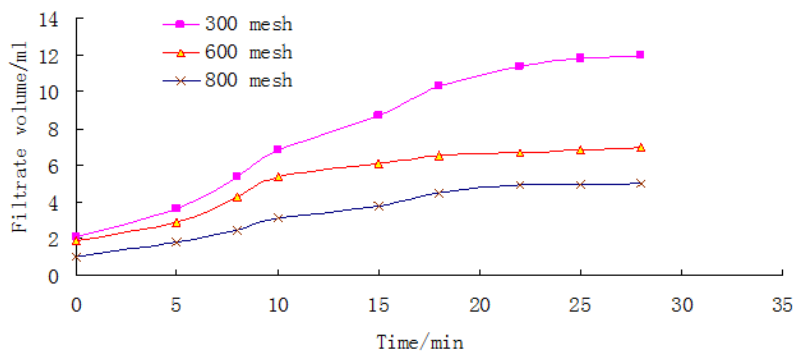


Fig. 8: The filtrate volume changes with time

The variation of filtrate volume is exhibited in Fig. 8. Filtration rate was high in the beginning, then slow down along with filtration process kept on. Filtrate cumulative volume decreased with mesh of quartz sand improved. It can be established that the microspheres formed a plugging layer in the sand bed during the filtration. What is more, in pace with mesh of quartz sand improved, the porosity and permeability reduced, the plugging strength of the microspheres got even better.

CONCLUSION

Polyacrylamide microspheres were successfully fabricated by emulsion polymerization method with the monomer content of 25% (wt). TEM analysis showed that the monodisperse microspheres had uniform size distribution and regular spherical structure, whose particle was 1-6 μm .

The microspheres had high specific surface area, which put up strong expansion property in aqueous solution. The expansion ratio could reach more than ten times after swelling 24 h.

There was an appropriate concentration range of microspheres aqueous solution, within which, the sealing characteristics of drilling fluid of the microspheres could attain the best. With the increase of core permeability, the highest plugging pressure decreased. The microspheres could achieve anticipate plugging strength to the low permeability core, while with regard to the higher permeability core, the sealing characteristics of the microspheres was not so perfect.

With the trend of exploration and development turn into depth, for the sake of improving the applicability of the product, meeting the rigorous formation condition, the future research direction is to introduce temperature tolerant and salt resistant groups or make the acrylamide copolymerized with other monomers.

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