



Hydrophobic modification for nanoscale cross-linked polymer microspheres

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ABSTRACT

The properties of nanoparticles, however, are not only dependent on their size and shape, but also are determined by surface modification. As a novel in-depth profile control agent, nanoscale water-soluble cross-linked polyacrylamide microsphere has better compatibility, sealing and oil property. To improve the salt tolerances and shearing resistance, hydrophobic monomer is introduced to inverse microemulsion polymerization, and hydrophobic modified cross-linked polymer nanometer microspheres were obtained. The microscopic morphology, size distribution and plugging effect of the cross-link polymer micro-spheres dispersed system were studied through scanning electron microscopy (SEM), environmental scanning electron microscope (ESEM), fluorescence spectrophotometer, particle size analyzer, microporous membrane filter and the sand-filled pipe. The experimental results show that, the hydrophobic associations come into being in aqueous solution above a certain concentration, and so the particle size logarithmic distribution model of hydro-phobic-modified cross-linked polymer microspheres deviate from double logarithmic distribution model which matches to non-hydrophobic cross-linked polymer microspheres. Hydrophobic modification of cross-linked polymer microspheres have better salt resistance and are able to enter the deep of the sand-filled pipe to form plugging. The disperse system of hydrophobic modified cross-linked polymer microspheres has different matching permeability range from that of non-hydrophobic cross-linked polymer microspheres, and using matching the permeability of core, higher displacement efficiency would be obtained.

Keywords: Nanoscale cross-linked polymer microspheres; Hydrophobic modification; Particle size distribution; Plugging effect

INTRODUCTION

Polymeric nanomaterials with sizes in the range of 1–1000 nm in at least one dimension, have attracted much attention because of their dramatically increased surface area to volume ratio, leading to a variety of unique properties [1]. The nanosized structures afford polymers unique and supreme properties differing from those of the bulk polymer, such as optical, magnetic, thermal, and electrical properties. Polymeric nanomaterials are potentially used in drug delivery, surface coatings, nanoreactors, catalysis and filtration. Many scholars believe that nano materials will be one of the most promising materials in the 21st century, especially the polymer nano materials. In recent years nanometer materials have been widely used for drilling fluid, the profile control, oil displacement and wastewater treatment in the oil and gas fields[2]. Cross-linked polymer microspheres, whose crosslinking degree is controllable, can enter the deep of oil reservoir to carry on the profile, can effectively improve the swept volume of injected water, and can adjust injection profile to reduce heterogeneity, so as to improve oil recovery significantly [3-5]. The size and size distribution, as well as viscoelasticity of microspheres, play a vital role in plugging process [6-7]. The properties of nanoparticles, however, are not only dependent on their size and shape, but are also determined by surface modification [8]. Great breakthrough in the viscoelastic of Hydrophobic modified polypropylene amide has been

obtained [9-13], so we try to introduce hydrophobic chain to cross-linked polymer microspheres, then observe their association in aqueous solution, plugging performance and their resistance to salt in this paper.

EXPERIMENTAL SECTION

2.1 Major materials and equipments

Sodium hydrogen sulfite(NaHSO_3), sodium hydroxide(NaOH), acetic acid(AC), absolute ethyl alcohol, acetone, 2,2'-azobis[2-methylpropionamide] dihydrochloride, and $\text{EDTA}\cdot 2\text{Na}$ are all analytical reagent. White oil (260# solvent oil), Tween-60, Span-80, acrylamide (AM), sodium acrylate (SAA) and 2-Acrylamide-2-methylpropanesulfonic acid (AMPS) are all technical reagent. Crosslinking monomer contains double bonds at both ends, contains intramolecularly long chain alkyl, polyoxyethylene and polyoxypropylene, and hydrophobic monomer is octadecyl fatty alcohol polyoxyethylene ether, they were obtained by laboratory itself.

Environmental scanning electron microscope (ESEM), Quanta-200F, made by American FEI Company. Laser diffraction granulometer, SALD2300, made by Japanese shimadzu Company. Fluorescence spectrophotometer, RF-5301PC, made by Japanese Shimadzu Company. LaB6 Transmission electron microscope (TEM): JEM-2100, made by Japanese JEOL Company.

2.2 Experimental methods

2.2.1 The preparation of cross-linked polymer microspheres

Weigh certain mass of AM, AMPS, AC, SAA, sodium hydroxide solution (35wt%), cross-linked monomer (crosslinking ratio is 0.4mol%), ultrapure water, $\text{EDTA}\cdot 2\text{Na}$ (0.1wt%) respectively, and dissolve all the solid under 7°C . After adding some ammonium persulfate, filtrate the solution, and obtain water phase solution.

Weigh certain mass of Span - 80, Tween-60, hydrophobic monomer, respectively. Adding suitable amount of white oil, Emulsifier's content ensure to be 22.5% of total quality. Adjust HLB values through changing dosage of the Span - 80 and Tween 60. Mix the solution uniformly, and obtain the oil phase solution.

Pour the mixed oil phase into the jacketed reactors with a stirring device in a low temperature, and then drop water phase. After stirring for 1 hour under certain mixing speed, determine the electrical conductivity of emulsion. When the electrical conductivity meets the requirements, raise the temperature to designed initiation temperature. After nitrogen flooding for 1 hour, initiate polymerization reaction. Only when initiation is successful, raise the temperature to 55°C for 1 hour, and then raise the temperature to 70°C for 3 hours to make the reaction as completely as possible. After the reaction, when product is cooled, precipitate out of the polymer microspheres with anhydrous ethanol and wash it with acetone for at least three times. Then dry the polymer microspheres in the oven for 12 h, following 48 hour's extraction by n-heptane. Finally, the microspheres are ready for analysis.

2.2.2 Morphological characterization of cross-linked polymer microspheres

By scanning electron microscopy (SEM), transmission electron microscopy (TEM) and environmental scanning electron microscope (ESEM), morphology and size of the cross-link polymer microspheres dispersed system are observed.

2.2.3 Particle size characterization of cross-linked polymer microspheres

Together with laser diffraction particle size analyzer and fluorescence spectrophotometer, the particle size distribution and the hydrophobic association of microspheres in solution will be shown.

2.2.4 Characterization of salt tolerances by microporous membrane filtration

Using low microporous membrane filtration method, microspheres solution is filtrated through microporous membrane under the pressure of 0.1 MPa. When the filtrate reaches 5 mL in the measuring cylinder, a stopwatch will start the time. Then records will be written once every 5 mL outflows, until the total outflows reaches 40 mL.

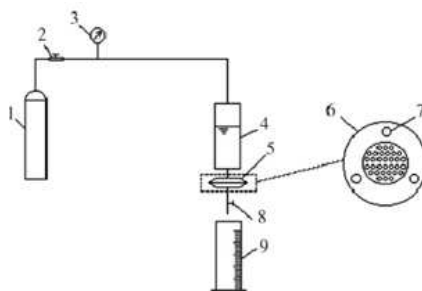


Figure1 Low differential microfiltration membrane device

1. nitrogen gas cylinder 2. reducing valve 3. pressure meter 4. filter flask 5. flange 6. top view from underside of the flange 7. bolt connection 8. valve 9. measuring cylinder

2.2.5 Characterization of plugging effects by sand-filled tube experiments

Cross-linked polymer microspheres dispersed system of 0.04 wt.% is prepared with simulation water of oil field, swelled for 10 days under 60°C. Then the dispersed system will be injected to sand-filled tube at a speed of 0.4 mL/min. When the water permeability of sand-filled tube is suitable, the flow differential pressures along with the sand-filled tube must be recorded.

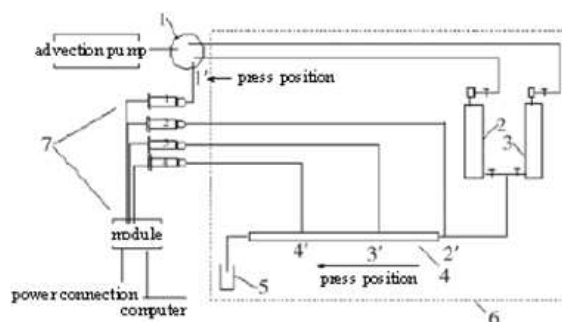


Figure 2 Sand-filled tube model

1. six-way valve; 2. storage tank of microspheres; 3. storage tank of water; 4. sand-filled tube; 5. beaker; 6. thermostat; 7. pressure sensor (measuring range: 200 kPa)

RESULTS AND DISCUSSION

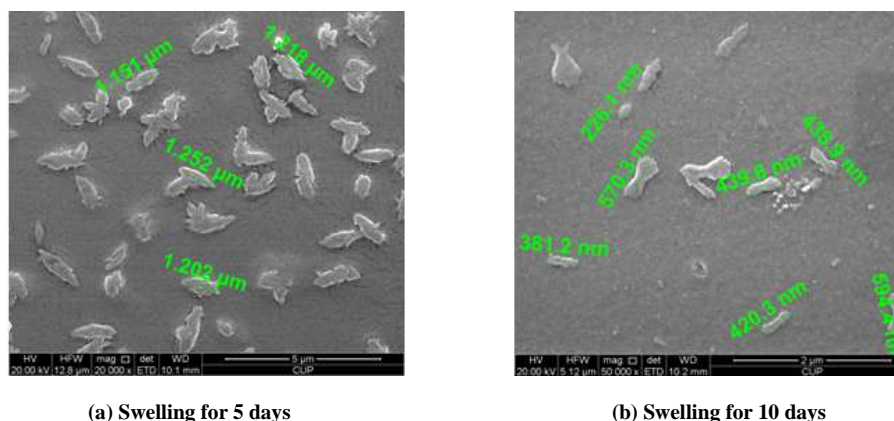
3.1 Morphological characterization of cross-linked polymer microspheres

(1) Characterization by SEM (scanning electron microscope)

The 0.02 wt. % of cross-linked polymer microspheres dispersed system was prepared with deionized water, then was preserved sealed in dark place. After swelling for 5 days 10 days, we observed the morphology of microspheres through SEM. The results were shown in figure 3. When the swelling time is relatively short (5 days), polymer microspheres agglomerate together to form larger spherical blobs, which size were from several microns to even dozen microns; When swelling for 10 days, the agglomerations gradually separated, polymer microsphere size at about 100 nm to 300 nm.

(2) Characterization by TEM

The cross-linked polymer microspheres are easy to reunite, but through TEM, not only can we see the size of aggregation, but also can distinguish the size of the individual particle which size is about 50 nm (figure 4).



(a) Swelling for 5 days

(b) Swelling for 10 days

Figure 3 SEM photos of microspheres

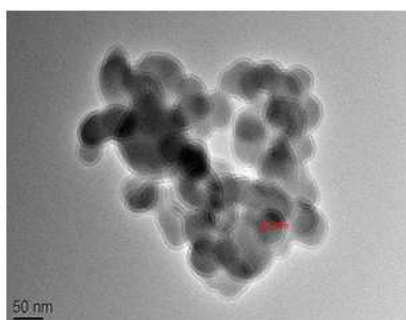


Figure 4 TEM photos of microspheres

(3) Characterization by ESEM

Relative to the SEM and TEM, the biggest advantage of ESEM is we can observe the particle's morphology and size in wet environment. Firstly, take a drop of aqueous solution containing a certain quality of cross-linked polymer microspheres and frozen it to ice, then with ice sublimating in low pressure, cross-linked polymer microspheres wrapped in the ice would emerge in the form of polymer coils, as shown in figure 5.

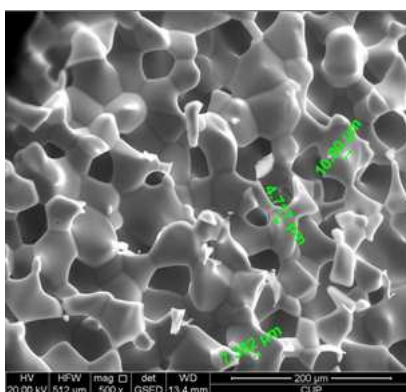


Figure 5 ESEM photos of microspheres

3.2 Particle size characterization of cross-linked polymer microspheres

(1) Characterization of particle size by laser diffraction granulometer

In order to highlight particle size characterization of the hydrophobic associated cross-linked polymer microspheres in the aqueous solution, just not joining the hydrophobic monomer, we obtained non-hydrophobic cross-linked polymer microspheres through polymerization under the same conditions. The comparison of particle size distribution of the both is as shown in figure 6 and figure 7.

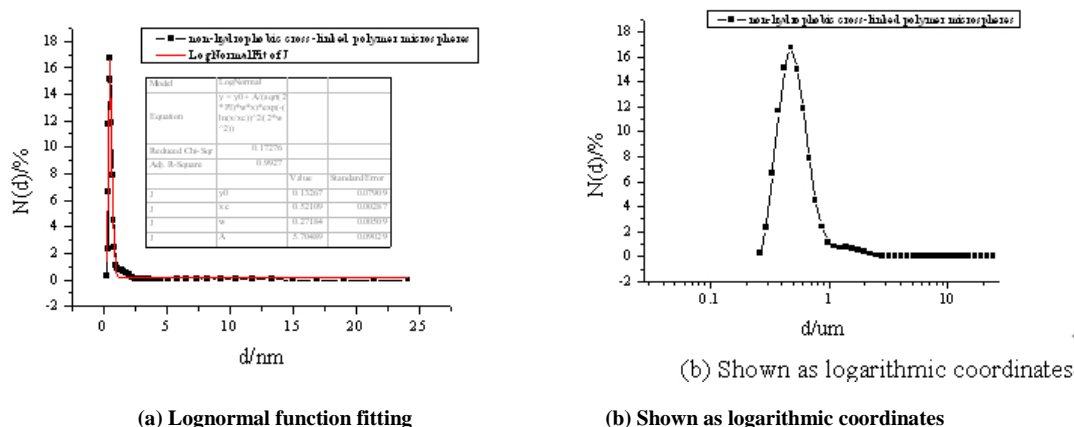


Figure 6 Particle size distribution of non-hydrophobic cross-linked polymer microspheres after swelling 5 days

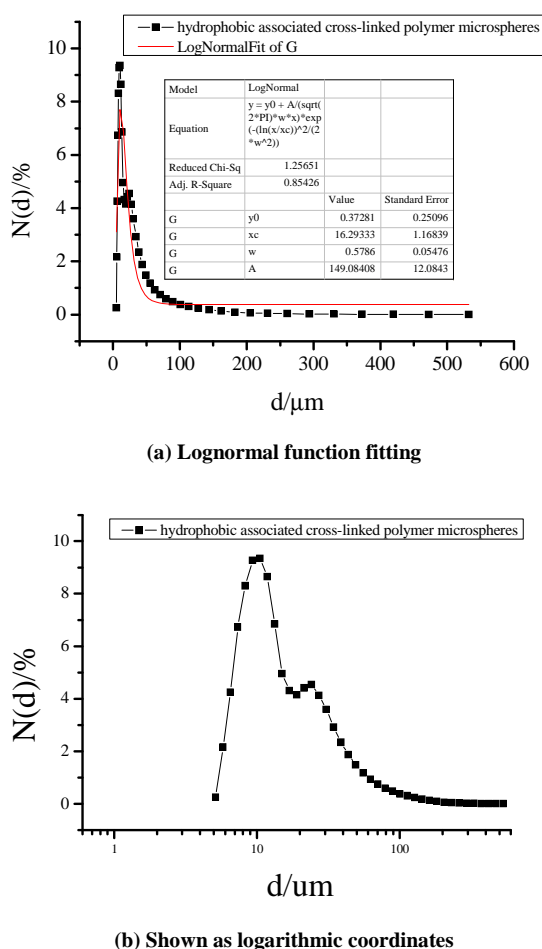


Figure 7 Particle size distribution hydrophobic cross-linked polymer microspheres after swelling 5 days

From figure 6 and figure 7, we can see the differences between the two types of cross-linked polymer microspheres. The particle size distribution of the hydrophobic associating type cross-linked polymer microspheres is bimodal, rather than unimodal distribution of the non-hydrophobic cross-linked polymer microspheres. After fitting the both the particle size distribution by lognormal function, the fitting correlation coefficients and average particle sizes of the two are not same, for the non-hydrophobic cross-linked polymer microspheres, $R^2 = 0.9927$, the average particle size $x_c = 0.52 \text{ um}$ and for the hydrophobic cross-linked polymer microspheres, $R^2 = 0.8543$, the average particle size $x_c = 16.29 \text{ um}$. All those show that due to the hydrophobic association, hydrophobic cross-link polymer microspheres cooperate into larger aggregate particles, and the distribution deviates from the logarithmic normal distribution more than that of non-hydrophobic cross-linked polymer microspheres.

(2) Characterization of hydrophobic association by fluorescence spectrophotometer

Fluorescence spectrophotometer is the most powerful tool to study of intermolecular hydrophobic association. In the fluorescence spectra of pyrene molecular used as probe, the intensity ratio of first one and the third peak, I_1 / I_3 , is sensitive to the polarity variation of environment in which pyrene molecules are. As the value of I_1 / I_3 decreases, polarity environment of pyrene also decreases. Prepare the following aqueous solution, which contain the mass of the polymer microspheres are 0.01%, 0.01%, 0.05%, 0.15%, 0.20%, 0.25% respectively. Among them, the concentration of pyrene is 5×10^{-6} mol/L. With the increase of the polymer microspheres' concentration, the value of I_1 / I_3 gradually decreases (as shown in figure 8), that shows hydrophobic microzone is gradually formed in the solution. After the mass fraction is more than 0.15%, the values of I_1 / I_3 level off, the result shows uniform hydrophobic microzones have formed in the solution. In addition, when the mass fraction is over 0.3%, the value of I_1 / I_3 quickly drops, as indicates that large hydrophobic micro zones are damaged, but net structure forms in the solution.

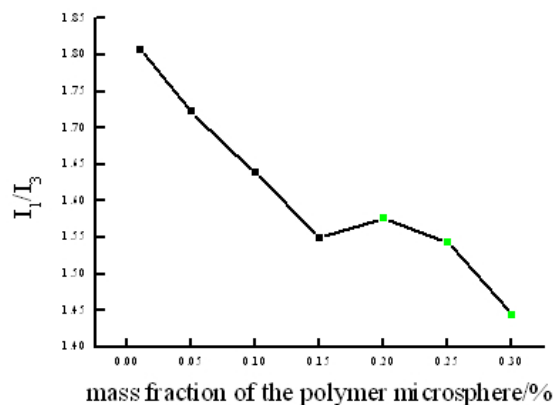
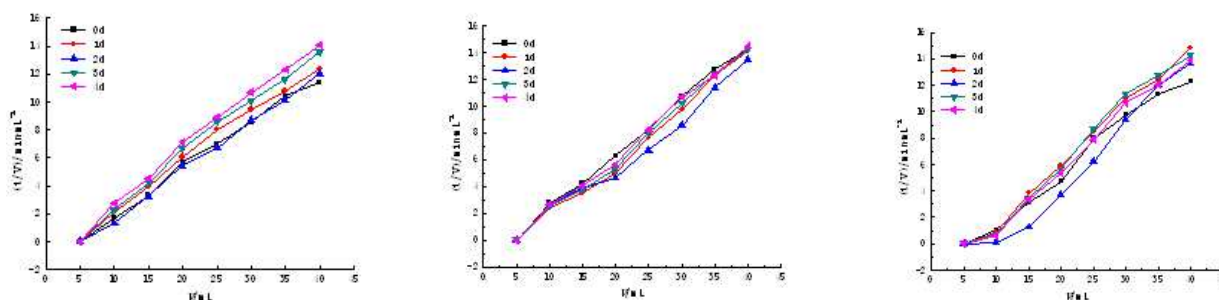


Figure 8 I_1 / I_3 values of pyrene changing with the mass fraction of hydrophobic microspheres

3.3 Characterization of salt tolerances by microporous membrane filtration

With deionized water, 0.8% NaCl and 1.5% NaCl aqueous solution, respectively, 0.02 wt.% of cross-linked polymer microspheres solution were prepared and kept in the dark for 3 days. Then every 24 h experiments of microporous membrane filtration were carried out to evaluate plugging effect. Figure 9 shows the relationship between time-consuming of filtration unit volume and filtration volume of different salinity dispersions. Filtration unit volume time-consuming and filtration volume meet good linear relationship. In very short time, plugging process on the surface of the microsphere in the film-hole turned to the surface filtering process. With the increase of NaCl's concentration, there were not obvious variation in the plugging effects, which illustrated the cross-linked polymer microspheres have good salt resistance.



(a) Prepared with deionized water

(b) Prepared with 0.8% NaCl aqueous solution

(c) Prepared with 1.5% NaCl aqueous solution

Figure 9 Microporous membrane filtration of microsphere dispersions in decentralized system

3.4 Characterization of plugging effects by sand-filled tube experiments

The mass fraction of 0.04% cross-linked polymer microspheres dispersed system prepared with 0.8% NaCl solution were swelled for 10 days under 60°C , and then injected into the sand-filled tube. Figure 10 shown the pressures of different positions along with sand-filled tube changed with the injection volume of microsphere dispersion system, among them, the P1 was pressure differential for top 20 cm of sand-filled tube, the P2 for middle 20 cm, and the P3 for last 20 cm.

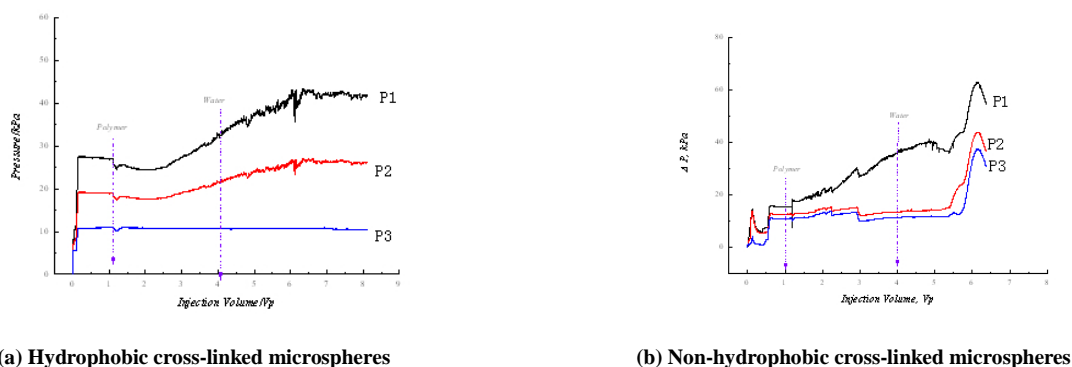


Figure 10 Flow pressure differential curves of cross-linked polymer microsphere dispersions

Table 1 plugging experimental parameters of sand-filled tube

Disperse system	Concentration of microspheres/(mg/kg)	permeability of sand-filled tube / $10^{-3} \mu\text{m}^2$	Plugging position	resistance coefficient	residual resistance factor
non-hydrophobic cross-linked microspheres	400	1023.68	middle	5.375	4.375
hydrophobic cross-linked microspheres	400	1063.57	back	9.60	6.40

Figure 10 and Table 1 show that hydrophobic cross-linked microspheres can enter more deeply than non-hydrophobic cross-linked microspheres, and has higher resistance coefficient and residual resistance factor, so hydrophobic cross-linked microspheres have perfect plugging performance.

CONCLUSION

- (1) Cross-linked polymer microspheres can be well dispersed in aqueous solution and the polymer microsphere's size are able to achieve 100-300 nm after swelling for 10 days.
- (2) The hydrophobic cross-linked polymer microspheres can associate in the disperse system, so particle size distribution deviates more from the logarithmic normal distribution, which is different from the non-hydrophobic cross-linked polymer microspheres.
- (3) Microporous membrane filtration experiments show the plugging capability of hydrophobic cross-linked polymer microspheres does not decrease with increasing salinity, so the microspheres have stronger salt resistance.
- (4) Microspheres with different properties and morphologies have different matched permeability for the sand-filled tube, hydrophobic modified cross-linked polymer microspheres have larger scope of matched permeability and also can enter into the deep of sand-filled tube.

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