Controllable Preparation, Rheology, and Plugging Property of Micron-Grade Polyacrylamide Microspheres as a Novel Profile Control and Flooding Agent

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ABSTRACT: A series of micron-grade polyacrylamide microspheres were prepared by inverse suspension polymerization of acrylamide (AM) and N,N'-methylene bisacrylamide (MBA) in oil phase, with Span80 and Tween80 as dispersion stabilizers, and ammonium persulfate (APS) as an initiator. The conversion rate and coagulum rate were introduced to optimize the inverse suspension polymerization conditions of micron-grade polyacrylamide microspheres. The swelling property of polyacrylamide microspheres in aqueous solution and the rheology of polyacrylamide microspheres suspension were characterized. The matching factor was introduced to characterize the matching relationship between the particle size of polyacrylamide microspheres and pore-throat size of reservoirs. The optimized synthesis results show that the conversion rate is high, and the coagulum rate is low when the mass ratio of Span80 to Tween80 is 3 : 1. The particle size of the polyacrylamide microspheres is controlled by varying the concentration of dispersion stabilizer. The polyacrylamide microspheres show an obvious swelling property, which depends on the concentration of NaCl and temperature. The polyacrylamide microspheres suspension shows different rheological properties at different temperature and shear rate. When the temperature is low, it behaves as pseudoplastic fluid, dilatant fluid and quasi-newtonian fluid in turn with the increase of shear rate. When the temperature is high, it behaves as dilatant fluid and quasi-newtonian fluid in turn with the increase of shear rate. The micron-grade polyacrylamide microspheres prefer to plug sand pack with optimal matching factor. When the matching factor is 1.35–1.55, the polyacrylamide microspheres can be transported into the deep area of sand pack, and the ultimate plugging rate is more than 85%, which indicates that the matching factor is an effective parameter to evaluate the matching relationship between polyacrylamide microspheres and reservoirs. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1124–1130, 2013

INTRODUCTION

Polyacrylamide plays an important role in many areas, such as water treatment, papermaking, oilfield development, and so on.[1–6] At present, "polyacrylamide nanospheres" is an important profile control agent in high water-cut stage of oilfield development. Owing to their small size, water adsorption selectivity, salt tolerance, high water absorbing capacity, good dispersion in water, and low viscosity in solution, nanospheres can easily be transported into the deep reservoirs, resist water to change the original flow direction and increase the sweep efficiency of reservoirs.[7,8] Usually their size is smaller than the pore throat size of mid-high permeability rocks which are several microns to several tens of microns,[9] the application of polyacrylamide nanospheres in the mid-high permeability reservoirs

faces restriction.[10] A simple way to solve such a problem is to prepare micron-grade polyacrylamide microspheres.

There are some reports on the preparation of polyacrylamide microspheres through inverse suspension polymerization.[11–13] However, the reported researches are focused on the preparation and modification of composite microspheres. In the present article, we prepared micron-grade polyacrylamide microspheres through inverse suspension polymerization of AM and MBA in oil phase, with Span80 and Tween80 as dispersion stabilizers, and ammonium persulfate (APS) as an initiator. The inverse suspension polymerization conditions of preparing acrylic polymer colloid were optimized. The swelling property of polyacrylamide microspheres in aqueous solution and the rheology of polyacrylamide microspheres suspension were studied. The
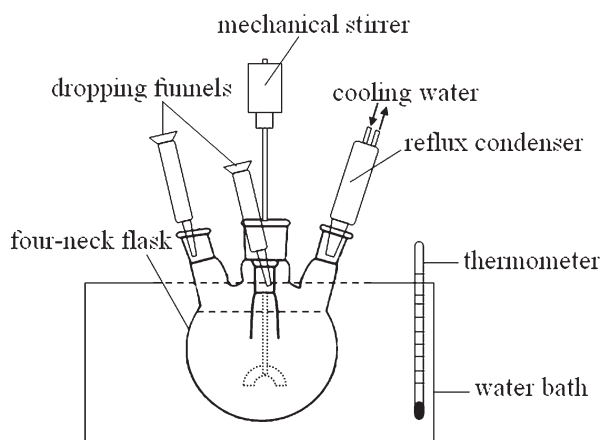
Figure 1. The schematic diagram for inverse suspension polymerization.

matching relationship between the particle size of polyacrylamide microspheres and the pore throat size of reservoirs was characterized.

EXPERIMENTAL

Materials

Acrylamide (AM, purity above 98.5%), dispersion stabilizer (D, Span80 & Tween80) and ammonium hydroxide (NH$_4$OH, purity above 99.5%) were all purchased from Sinopharm Chemical Reagent (China). N,N'-methylene bisacrylamide (MBA, purity above 98.0%) was obtained from Shanghai Chemical Reagent Company of Sinopharm (China). Ammonium persulfate (APS, purity above 98.0%) was supplied by Shanghai Aijian Degussa Initiator (China). Sodium chloride (NaCl, purity above 99.5%) was obtained from Nanjing Chemical Regent (China). Plant oil was supplied by Qingdao Yihai Food Marketing Company (China). All reagents were used without any further purification. Deionized water was used for the preparation of all aqueous solutions.

Inverse Suspension Polymerization

The inverse suspension polymerization was carried out in a 250 mL four-neck flask. The flask was equipped with mechanical stirrer, reflux condenser, dropping funnels and constant temperature water bath, as shown in Figure 1. A typical recipe for the inverse suspension polymerization is presented in Table I. First, 100.00 g of plant oil and 12.00 g of dispersion stabilizer (m (Sapn80) : m (Tween80) = 3 : 1) were introduced into the four-neck flask. The flask was then placed in the water bath at the constant temperature of 30°C with a stirring rate of 360 rpm. After complete dissolution of the dispersion stabilizer in plant oil, half of the aqueous solution of AM, MBA, and APS (6.65 g of AM, 0.16 g of MBA and 0.33 g of APS were dissolved in 44.00 g deionized water) in the dropping funnel was dripped into the reactor within 15 min. When the water phase was suspended in the oil phase completely, the temperature was increased to 75°C to initiate the polymerization of monomers. Simultaneously, the rest half of aqueous solution of AM, MBA and APS was dripped into the flask with an appropriate dripping rate. NH$_4$OH aqueous solution (20 wt %) was added to adjust the pH to about 7.0. Then, the temperature was kept

75°C for 60 min. Finally, the mixture in the flask was cooled and filtered. Thus, micron-grade polyacrylamide microspheres were obtained.

Characterizations

Fourier transform infrared (FTIR) spectrometric analyzer (Nicolet 5700 FTIR, Massachusetts, USA) was used to analyze the chemical structure of the polyacrylamide microspheres. The particle size of the polyacrylamide microspheres was measured by Rise-2008 laser particle size analyzer (Jinan Runzhi Science and Technology Corporation, China) at 25°C. The sample was dried completely in drying oven at 60°C under constant pressure, and the residual polymer was weighed. The conversion rate was calculated according to the equation: C (%) = (W_1/W_0) ×100%; where C is the conversion rate; W_0 is the weight of the total monomer in the recipe; W_1 is the weight of the residual polymer after drying. The coagulum content was measured by collecting the solid deposited on the reactor wall and stirrer, and the residual of filtered suspension. The coagulum rate is expressed as the weight of coagulum per total weight of monomer added.[14] The variation of particle size was measured to characterize the swelling property of polyacrylamide microspheres in aqueous solution. The viscosity of the polyacrylamide microspheres suspension was measured by LVDV-II+Pro rotational viscometer (Brookfield Corporation, Massachusetts, USA). The temperature was 30°C and the rotate speed was 6 rpm. The rheology of the polyacrylamide microspheres suspension was analyzed through measuring the viscosity variation of the polyacrylamide microspheres suspension at different temperature and shear rate. The matching factor between the particle size of polyacrylamide microspheres and the pore throat size of reservoirs was used to characterize the plugging property of polyacrylamide microspheres in sand pack model. The matching factor was calculated by the equation: $\delta = d_{ave}/(2r)$; where δ is the matching factor; d_{ave} is the average particle size of polyacrylamide microspheres, μm; r is the average radius of pore-throats, μm. The sand pack models were all packed with sand from Block Gudao in Shengli Oilfield, China. The average radius of pore-throats in the sand pack model was calculated according to the Kozeny Equation[15]: $r = (8k/\varphi)^{1/2}$; where k is the permeability of sand pack model, μm^2; φ is the porosity of sand pack model. The residual resistance factor of sand pack was calculated by the equation: $F_{zr} = \Delta P_z/\Delta P_w$; where F_{zr} is the residual resistance factor; ΔP_z is the pressure difference after injecting

Table I. A Recipe for Preparing Micron-Grade Polyacrylamide Microspheres

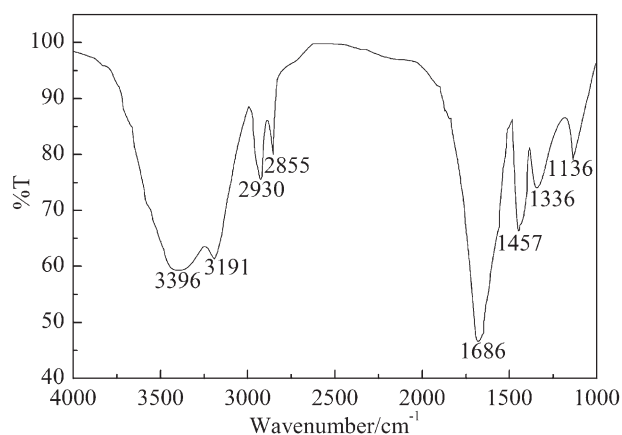| Material	Mass/g
[AM] Acrylamide (monomer)	6.65
[MBA] N,N'-methylene bisacrylamide (crosslinking agent)	0.16
[APS] Ammonium persulfate (initiator)	0.33
[D] m (Span80) : m(Tween80) = 3 : 1(dispersion stabilizer)	12.00
Plant oil (dispersion agent)	100.00
Deionized water	44.00

Figure 2. FTIR spectrum of the polyacrylamide microspheres.

Figure 3. Influence of amount of APS on (a) conversion rate and (b) coagulum rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyacrylamide microspheres, kPa; ΔP_w is the pressure difference in original water injection, kPa. The plugging rate was calculated by the equation: $\eta(\%) = (k_1 - k_2)/k_1 \times 100\%$; where η is the plugging rate; k_1 is the original permeability of sand pack, μm^2; k_2 is the permeability of sand pack after injecting polyacrylamide microspheres, μm^2.

RESULTS AND DISCUSSIONS

FTIR Spectrum of Polyacrylamide Microspheres

Figure 2 is FTIR spectrum of the polyacrylamide microspheres. In Figure 2, 3396 and 3191 cm^{-1} are the characteristic stretching vibration peaks in the amino group; 2930 and 2855 cm^{-1} are the characteristic stretching peaks of C—H (CH$_2$, CH); 1686 cm^{-1} is the stretching vibration absorption peak of C=O in the amide group; 1457 cm^{-1} is the bending vibration absorption peak of C—H (CH$_2$); 1336 cm^{-1} is the characteristic absorption peak of C—N—C; 1136 cm^{-1} is the stretching vibration absorption peak of C—N in the amide group. The stretching vibration of C=C disappears within the range of 1500 and 1680 cm^{-1}. FTIR spectrum shows that AM and MBA are copolymerized to form the polyacrylamide microspheres.

Influence of Concentration of APS on Conversion Rate and Coagulum Rate

Figure 3 shows the influence of the concentration of APS on conversion rate and coagulum rate. In Figure 3, the conversion rate increases gradually with the increase of the concentration of APS. The free radicals are the active centers of polymerization. The generation rate of free radicals is low when the concentration of APS is low. Less is the number of active centers, lower is the reaction rate. Thus, the conversion rate is lower. When the concentration of APS is increased, the generation rate of free radicals is quickened. Thus, the reaction rate is higher, and the conversion rate is raised. Figure 3 also shows that the variation of coagulum rate is not obvious but the coagulum rate increases greatly when the amount of APS is more than 0.33 g. This probably is caused by the fact that the number of free radicals is excessively large and the free radicals cannot take part in the reaction in time, thus aggravating the polymerization reaction when the concentration of APS is excessively high. Therefore, the amount of APS is strictly controlled. In this
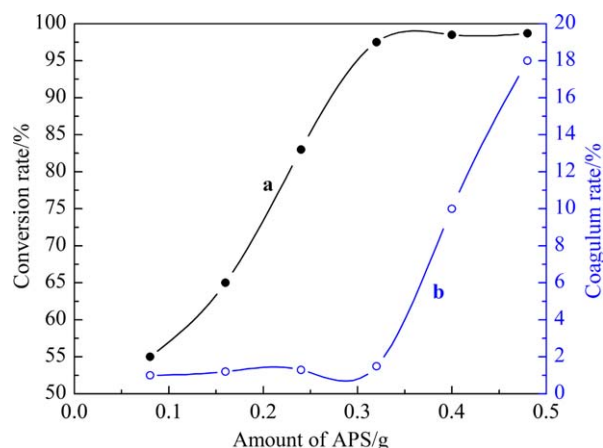
study, the conversion rate is very high and the coagulum rate is very low when the amount of APS is 0.33 g.

Influence of Mass Ratio of Span80 to Tween80 on Coagulum Rate

In this study, the mass ratio of Span80 to Tween80 is varied when the amount of dispersion stabilizer is constant. Figure 4 shows the influence of the mass ratio of Span80 to Tween80 on coagulum rate. In Figure 4, the coagulum rate decreases first, then increases with the increase of the mass ratio of Span80 to Tween80. The key to preparing inverse suspension is the hydrophilic-lipophilic balance (HLB). When the amount of Tween80 is excessively small, the HLB value will be very low. Thus, the ability of water containing is limited. When the amount of Tween80 is excessively large, the interfacial films of oil–water phase will be hydrophilic excessively. In these two conditions, the monomer droplets in the inverse suspension can coalesce easily and the coagulum rate is higher. In our study, the stability of the inverse suspension polymerization is very high when the mass ratio of Span80 to Tween80 is 3 : 1.
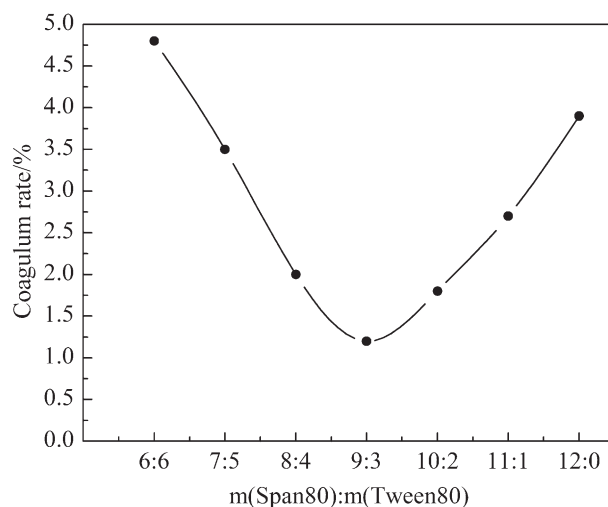

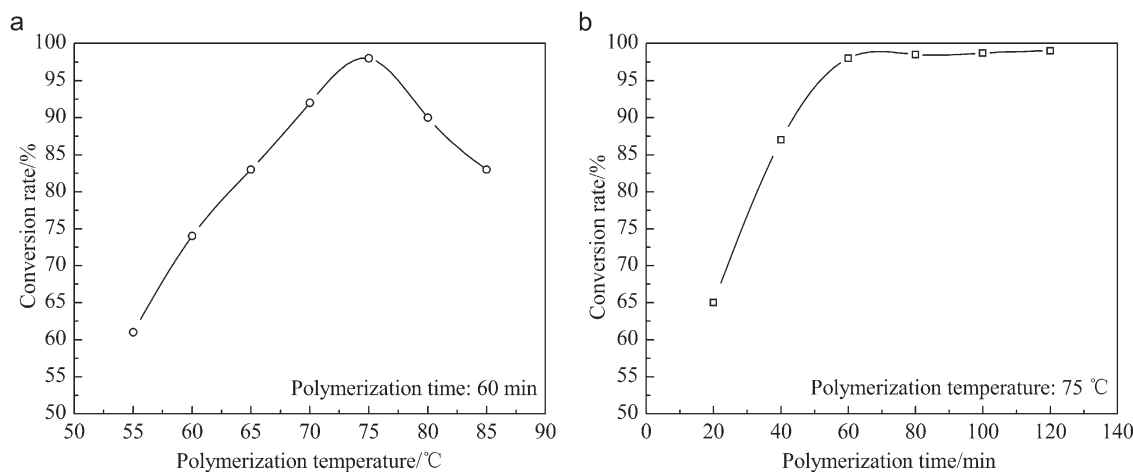**Figure 4.** Influence of mass ratio of Span80 to Tween80 on coagulum rate.

Figure 5. Influence of (a) polymerization temperature and (b) polymerization time on conversion rate.

Influence of Polymerization Temperature and Time on Conversion Rate

Figure 5 shows the influence of polymerization temperature and time on conversion rate. In Figure 5, the conversion rate increases first, then decreases with the increase of polymerization temperature. When the polymerization temperature is low, the initiation rate is low too. Thus, the reaction cannot proceed completely and the conversion rate is lower. When the polymerization temperature is increased, the initiation rate is quickened. Thus, the reaction rate is higher, and the conversion rate is raised. However, the transfer rate of chains is also quickened when the polymerization temperature is excessively high. Under the influence of chain termination, the conversion rate is lower. Besides, the adsorption and description balance of dispersion stabilizer on interfacial films is weakened when the polymerization temperature is excessively high. Thus, the reaction becomes unstable, and the conversion rate is lower. Figure 5 also shows that the conversion rate obtains the maximum value when the reaction time is about 60 min. When the reaction time is prolonged further, the variation of the conversion rate is not
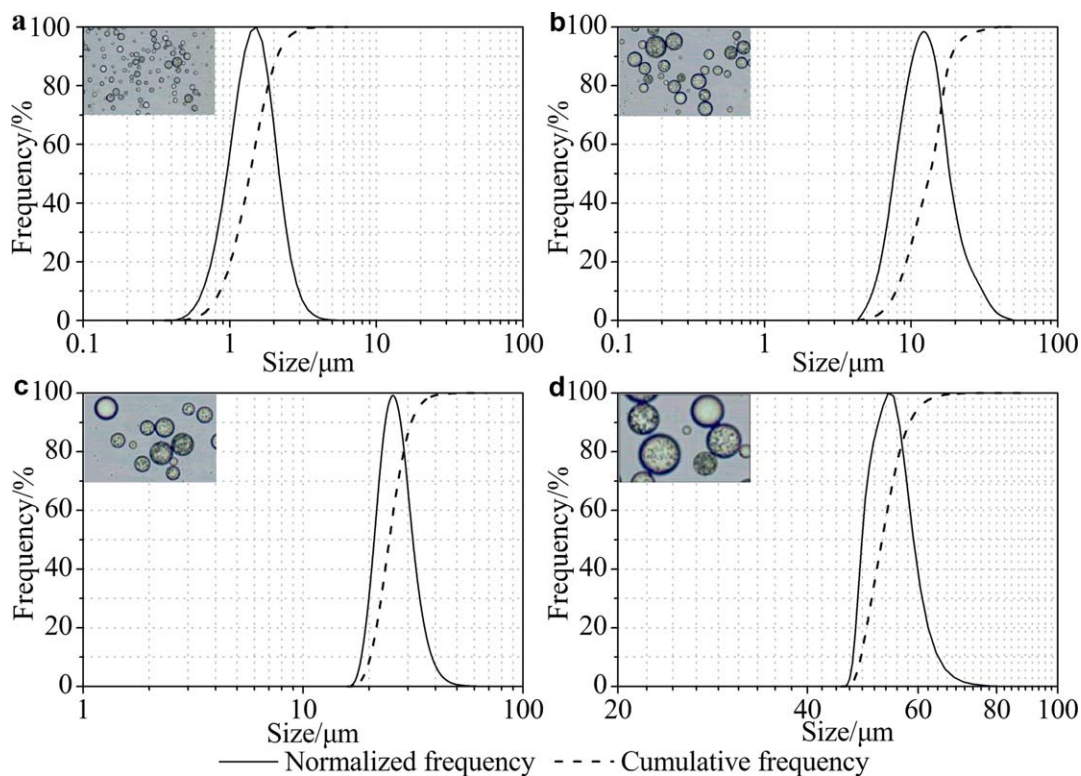

Figure 6. Average particle size of polyacrylamide microspheres (a: d_{ave} = 1.52 μm, m(D) = 15.00 g; b: d_{ave} = 12.05 μm, m(D) = 12.00 g; c: d_{ave} = 27.44 μm, m(D) = 8.00 g; d: d_{ave} = 53.72 μm, m(D) = 4.00 g). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
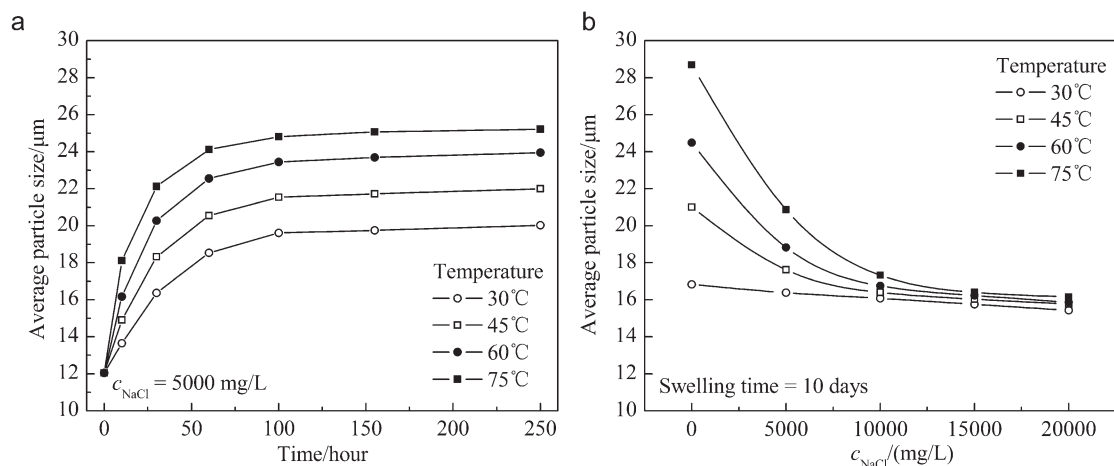
Figure 7. Influence of (a) time and temperature and (b) temperature and salinity on particle size of polyacrylamide microspheres in aqueous solution.

obvious. In this study, the conversion rate is up to 98.0 % when the reaction temperature and time is 75°C and 60 min, respectively.

Influence of Amount of Dispersion Stabilizer on Particle Size of Polyacrylamide Microspheres

In this study, the amount of dispersion stabilizer is varied when the mass ratio of Span80 to Tween80 is 3 : 1. The influence of the amount of dispersion stabilizer on the particle size of polyacrylamide microspheres is given in Figure 6. Figure 6 shows that the particle size of polyacrylamide microspheres decreases with the increase of the amount of dispersion stabilizer. The result reveals that the particle size of polyacrylamide microspheres can be controlled by varying the amount of dispersion stabilizer. Figure 6 also shows that the polyacrylamide microspheres are regular spherical particles and the particle size distributions are narrow.

Swelling Property of Polyacrylamide Microspheres in Aqueous Solution

The polyacrylamide microspheres can swell through absorbing water. In this study, the original particle size of polyacrylamide microspheres is 12.05 μm. The variation of the average particle

size of polyacrylamide microspheres in aqueous solution is given in Figure 7. Figure 7(a) shows that the average particle size increases rapidly in the first 3 days and obtains the maximum value when the time is about 10 days. Figure 7(b) shows that the average particle size decreases with the increase of concentration of NaCl and increases with the increase of temperature. When the concentration of NaCl is larger than 10,000 mg/L, the variation of average particle size is not obvious. In fact, polyacrylamide microspheres are crosslinked particles with three-dimensional network structure and many free hydrophilic groups ($-CONH_2$) inside. Polar water molecules can combine with these groups easily, and cause microspheres to swell. However, inorganic ions can compress the hydration layer and reduce the hydration degree. Thus, the particle size is smaller when the concentration of NaCl is higher. The particle size of polyacrylamide microspheres varies with the concentration of NaCl. High temperature will lead to the polymer network outward expansion, and the water absorption will increase too. The result shows that polyacrylamide microspheres have better swelling property. This property can increase their transport and plugging capacity in deep formation of reservoirs.
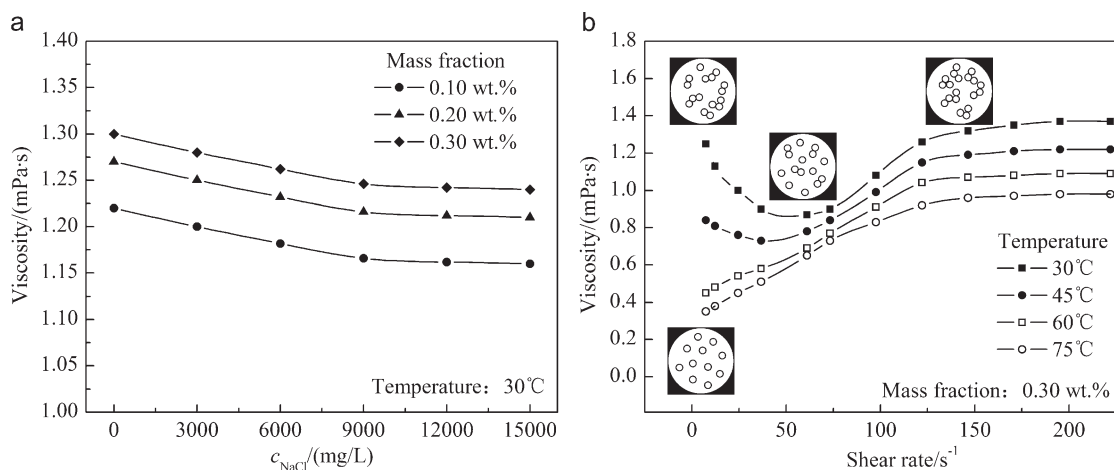

Figure 8. Solution viscosity and rheology of polyacrylamide microspheres.

Table II. The Rheological Properties of Polyacrylamide Microspheres Solution

Temperature (°C)	Fluid type			Non-newtonian index (n)		
	0–60 s^{-1}	60–120 s^{-1}	>120 s^{-1}	0–60 s^{-1}	60–120 s^{-1}	>120 s^{-1}
30	Pseudoplastic fluid	Dilatant fluid	Quasi-newtonian fluid	0.9953	1.0027	1.0004
45				0.9979	1.0028	1.0003
60	Dilatant fluid			1.0037	1.0029	1.0002
75				1.0056	1.0024	1.0001

Viscosity and Rheology of Polyacrylamide Microspheres Suspension

The sample of polyacrylamide microspheres with average particle size of 12.05 μm was used in this study. The viscosity of polyacrylamide microspheres suspension is given in Figure 8. Figure 8(a) shows that the viscosity decreases first, then is almost constant with the increase of the concentration of NaCl. This is caused by the compression effect of inorganic salt on hydration layer. When the concentration of NaCl is higher, the hydration layer becomes thinner gradually. Thus, the swelling degree decreases and the viscosity are lower. When the concentration of NaCl is more than 9000 mg/L, the compression effect is limited, and the variation of viscosity is not obvious. Figure 8(b) and Table II show that the polyacrylamide microspheres suspension presents different rheological properties at different temperature and shear rate. This can be explained by the following fact. There are some aggregates of microspheres in suspension when the temperature is lower. At a lower shear rate (0–60 s^{-1}), the aggregates can be destroyed easily. Thus, the viscosity decreases with the increase of shear rate and the suspension behaves as pseudoplastic fluid. At a higher shear rate (60–120 s^{-1}), the microspheres will coalesce to form aggregates again. Thus, the viscosity increases with the increase of shear rate and the suspension behaves as dilatant fluid. However, there is a balance between destroying and forming aggregates. When the shear rate is more than 120 s^{-1}, the variation of viscosity is not obvious and the suspension behaves as quasi-newtonian fluid. When the temperature is higher, the microspheres can highly disperse in aqueous solution. Thus, the viscosity is lower. At a lower shear rate (0–60 s^{-1}), the microspheres will coalesce to form aggregates. The viscosity decreases with the increase of shear rate and the suspension behaves as dilatant fluid.

Plugging Property of Polyacrylamide Microspheres in Sand Pack Model

In this study, the polyacrylamide microspheres was hydrated in NaCl solution of 3000 mg/L for 10 days and the average particle size was 19 μm. A series of sand pack models ($\varphi = 2.8$ cm, $L = 35.0$ cm) with different pore throat size were used, and the matching factor between the particle size of polyacrylamide microspheres and the pore throat size of sand pack was 0.80–2.00. First, the brine water with salinity of 3000 mg/L was injected for 0.5 PV. Then, the polyacrylamide microspheres suspension (0.20 wt %) was injected for 2.5 PV. At last, only brine water was injected for 1.0 PV. Meanwhile, the injection pressure

was measured. The injection rate was 1 mL/min. The experimental temperature was 30°C.

The plugging property of polyacrylamide microspheres with different matching factor is given in Figure 9. Figure 9 shows that the residual resistance factor and plugging rate increase first, then decrease with the increase of matching factor. They obtain the ideal value when the matching factor is 1.35–1.55. When the matching factor is a better value (1.40), the injection pressure presents a characteristic of wave-type variation [Figure 10(a)]. The polyacrylamide microspheres can still transport into the deep area of sand pack constantly. The residual resistance factor and plugging rate are high. When the matching factor is small (0.80), that is, the average pore throat size of sand pack is larger, the polyacrylamide microspheres can be injected easily and transport in sand pack smoothly. The injection pressure is very low in the whole injection process [Figure 10(b)]. Thus, the residual resistance factor and plugging rate are low. When the matching factor is excessively large (2.00), polyacrylamide microspheres cannot be injected in sand pack smoothly. Many polyacrylamide microspheres gather at the injection end of sand pack and in the injection pipeline. And the injection pressure increases rapidly [Figure 10(c)]. Only some smaller polyacrylamide microspheres can be injected in the sand pack. Thus, the residual resistance factor and plugging rate are very low. The results suggest that the matching factor has an obvious effect on plugging property of polyacrylamide microspheres. The results also confirm that the plugging strength of polyacrylamide
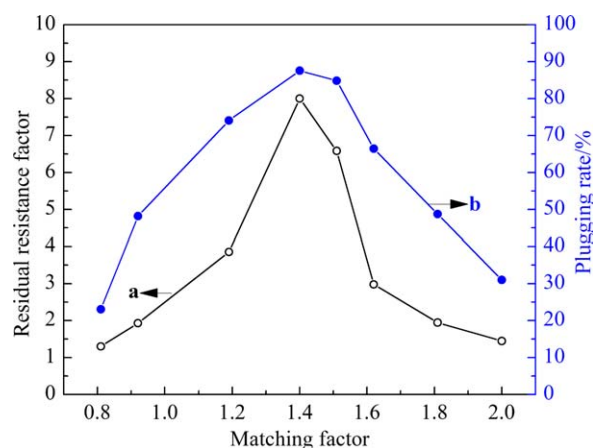

Figure 9. Plugging property of polyacrylamide microspheres with different matching factor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
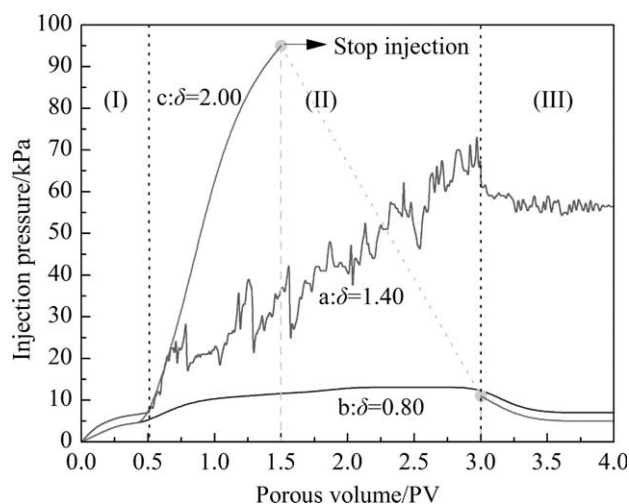
Figure 10. Change curves of injection pressure at conditions of different matching factors (δ) (I: the primary water injection; II: the injection of polyacrylamide microspheres solution (0.30 wt %); III: the succeeding water injection).

microspheres after absorbing in NaCl solution is high. In this study, the ideal matching factor is 1.35–1.55 and the plugging rate is more than 85%.

CONCLUSIONS

A series of micron-grade polyacrylamide microspheres were prepared controllably by inverse suspension polymerization of acrylamide (AM) and N,N'-methylene bisacrylamide (MBA) in oil phase, with Span80 and Tween80 as dispersion stabilizers, and ammonium persulfate (APS) as an initiator. The study shows that the elastic microspheres have good and rapid swelling property. The average particle size increases rapidly in the first 3 days and almost constant after 10 days. This result indicates that the polyacrylamide microspheres have rapid plugging characteristic and good resistance of lost circulation. The viscosity of polyacrylamide microspheres suspension is low and the polyacrylamide microspheres suspension shows different rheological properties (pseudoplastic fluid, dilatant fluid or quasi-newtonian fluid) at different temperature and shear rate.

The plugging experiments show that the polyacrylamide microspheres have strong ability of selective plugging on sand pack. With an ideal matching factor, the polyacrylamide microspheres can still transport into the deep area of sand pack constantly and the ultimate plugging rate is more than 85%. For the micron-grade polyacrylamide microspheres, the ideal matching

factor is 1.35–1.55. These results confirm that the matching factor is an effective parameter to evaluate the matching relationship between polyacrylamide microspheres and reservoirs. These results also confirm that the plugging strength of polyacrylamide microspheres after absorbing in NaCl solution is high.

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