

Enhance Plugging Performance of Microgel by Introducing Cationic Group

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Abstract

To enhance plugging performance of microgels, a series of microgels with varied cationic degrees was synthesized by inverse microemulsion polymerization with acrylamide and methylacryloxyethyl trimethyl ammonium chloride as monomers. The properties and performance of cationic microgels were examined by transmission electron microscope, dynamic light scattering analysis, viscosity measurement and plugging test. The results show that cationic microgel exhibits better ability in water adsorption and viscosity enhancement than nonionic microgels. It can efficiently plug formation with permeability lower than $1200 \times 10^{-3} \mu\text{m}^2$ (mD), compared to 800 mD of nonionic microgels. The optimal cationic degree is 10%.

Key words: Cationic microgel; Polyacrylamide; Profile control

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INTRODUCTION

With water-flooding reservoirs matured, serious vertical and lateral heterogeneity gives rise to channeling of injection water along high permeable streaks. This results into water bypass and poor swept volume. Thus facile profile modification treatment is badly needed now than ever before.

Recently considerable attention has been paid to gel technology with varied formulations for different reservoir condition, usually including bulk injection^[1], double fluid cross-linked gel^[2], colloidal dispersion gel^[3], and pre-performed gel^[4]. From these applications and the feedback of field practice, it comes out the state of art of these techniques described as follows. (1) Bulk injection has robust gel chemistry and is highly insensitive to petroleum reservoir environments and interferences, however, great efforts should be devoted to ensure in-depth placement. (2) With double fluid crosslinked gel, crosslinkers like chromium acetate are apt to be adsorbed, dispersed or diluted in advance front. Consequently these adverse behaviors render that the strength of formed gel is questionable. (3) Colloidal dispersion gel treatments are economic and effective due to low polymer concentration and comparable size of polymer coil with pore scale, but its application is restricted by salt effect and fragile temperature resistance. (4) Pre-performed gel, to some extent, wins out from these four gel technique for getting rid of the other three's shortcoming listed above. However, its complex production process including drying, grounding and meshing, multiply the cost of its applicable promotion; furthermore, the mixing of drying gel particle and injection water needs elaborated control of particle swellability.

In the 1997, the industry consortium (BP, Chevron Texaco and Nalco company) developed a novel, time delayed, and highly expanded particle system, named "Bright Water"^[5]. This system composed of microgels with diameter around 0.1-3 μm synthesized by emulsion polymerization. It has been practiced for more than 85 treatments since the first application in Minas Field, Indonesia. Several successful cases have been reported in these years^[6]. According to the profile-control mechanism raised by Chauveteau *et al.*^[7], microgels act by its swellability, viscosification and retention. Introducing cationic group in microgel can improve swellability by

electrostatic repulsion between polymer chains and thus increasing viscosity of microgel solution. However, cationic microgels are seldom reported in profile control.

Based on above analysis, a series of microgels with cationic degree 0-50% (defined by the molar percentage of cationic monomer in total monomer) was synthesized by inverse microemulsion polymerization. The microgel properties including swellability and viscosity were determined. The corresponding performance in plugging test was compared with nonionic polyacrylamide microgels.

1. EXPERIMENTAL

1.1 Materials

Acrylamide (AM) and 78wt% water solution of methylacryloxyethyl trimethyl ammonium chloride (DMC) were used as monomers. Methylene bisacrylamide (MBA) as crosslinker, ammonium persulfate (APS) and sodium sulfite (SDS) as redox initiator, Span80 (Sorbitan monooleate, chemically pure) and Tween60 (Polyoxyethylene (20) sorbitan monostearate, chemically pure) as emulsifier were used without purification. Industrial white oil was chosen as the continuous phase.

1.2 Microgel Synthesis by Inverse Microemulsion Polymerization

The surfactant and oil with predetermined amount were mixed in a three-neck round-bottom flask equipped with stirrer, thermometer and nitrogen inlet. The reactor was placed in the 30 °C water bath. Then the water phase composed of DMC, AM and MBA was added. This mixture was stirred at 300rpm for 10 min to prepare microemulsion. Following 15 min nitrogen purge, the mixture was initiated with 0.01g APS/SDS. After reacting for 1h, a translucent emulsion was obtained for the below use.

1.3 Microgel Morphology and Size Characterization

Microgel morphology was observed by transmission electron microscopy (TEM, JEM-2100UHR). Particle size and distribution were measured at 30°C by dynamic light scattering method using Mastersizer 3000 high-speed intelligent particle size analyzer. For each sample, three tests were performed.

1.4 Viscosity Measurement

The viscosity of microgel solution was measured by Brookfield Viscometer LVDVII plus pro with ULA and SC4 spindles at 20 °C.

1.5 Plugging Test

Sand packs were prepared by wet method described by Ding *et al.*^[8] with 120-140 mesh quartz sand in the middle part and 80-100 mesh at both ends to prevent fine sand from leaking. After packing, three procedures were performed, as listed below: (1) inject water to get

the initial pressure P_0 ; (2) inject 0.5wt% microgel solution with slug size 0.5 pore volume (PV) and record maximum pressure P_1 ; (3) inject water continuously and record balance pressure P_2 . The resistance factor (F_r) and the residual resistance factor (F_{rr}) are calculated by P_1/P_0 and P_2/P_0 , respectively. The injection rate is constantly 0.5mL/min.

2. RESULTS AND DISCUSSION

2.1 Microgel Morphology and Size

The morphology of 10%DMC original microgel in inverse emulsion is shown in Figure 1, where the particles are spherical and relatively uniform. The TEM photo of swollen microgels is shown in Figure 2. It can be seen from Figure 2 that the swollen microgels are a kind of particles with a tightly holden core and lightly crosslinked shell.

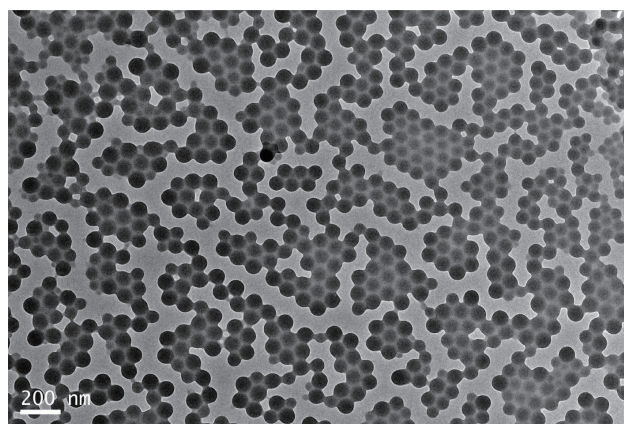


Figure 1
The TEM Photo of 10% DMC Microgel in Inverse Emulsion

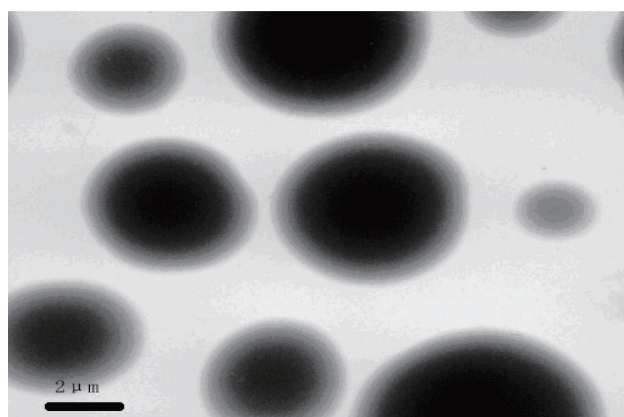


Figure 2
The TEM Photo of 10% DMC Microgel Swollen by Water

The z-average particle sizes of microgels before and after being swollen are shown in Figure 3. In Figure 3, the original microgel size decreases from 100 nm at 0% DMC to 65 nm at 50% DMC. While the swollen microgel size increases from 750 nm up to a maximum 1700 nm at

10% DMC, and then decreases to 700 nm at 50% DMC. The diameter of cationic microgel increases more than 10 times while nonionic microgel increases only 7 times. The maximum swellability about 22 times is achieved at 10% DMC. This size change of swollen microgel can be explained in Flory-Huggins theory, where gel swellability is determined by the balance of three primary forces. They are the elasticity of gel networks, the mixing entropy of polymer chains with the solvent, and a Donnan-type potential due to the osmosis of counterions. As the cationic degree increases, osmotic pressure and mixing entropy favor the swelling. But at the same crosslinker mass fraction (0.02 wt% based on monomer), the increase of crosslinking density with the increasing cationic degree decreases the length and thereof the elasticity of polymer blob in microgel^[9]. The size evolution of swollen microgels results from a balance by these two opposite effects. Similar phenomenon for the P (acrylamide-potassium acrylate) microgels was reported by Kiatkamjornwong^[10].

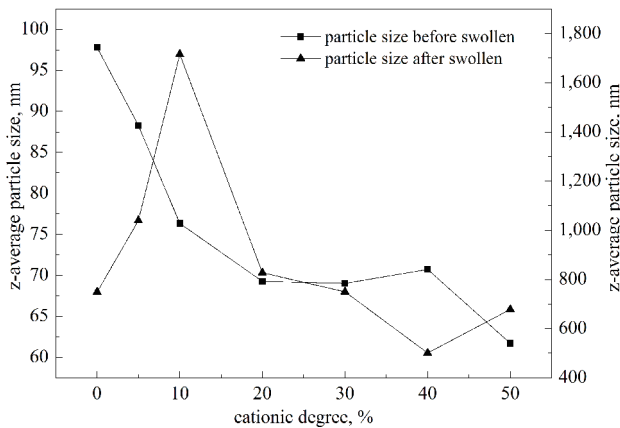


Figure 3
The z-Average Size Evolution of Microgels Before and After Swollen with Cationic Degree

2.2 Viscosity

Here, relative zero shear viscosity (η_{r0}) is used to represent viscosity of microgel solution. To obtain η_{r0} , curves of solution viscosity versus mass concentrations (0.1%-1%) were determined for four type microgels. These microgels are separately 0%, 5%, 10%, 50% cationic degree. These viscosity-shear rate curves are fitted to the Cross model^[11], which is known to provide a good description of the viscosity of colloidal suspension. The calculated η_{r0} versus mass concentration (c) is shown in Figure 4. In Figure 4, η_{r0} increases with the increasing cationic degree of microgels at the same concentration. The η_{r0} of 0% DMC ranges from 1 to 5, while for 50% DMC it ranges from 15 to 290. The viscosity of cationic microgel is ten times that of nonionic microgels at the same concentration. And with c increasing, η_{r0} sharply increases for 50% DMC while only moderately increases for 0% DMC. The increasing viscosity for higher cationic degree is attributed to electroviscous effect^[12].

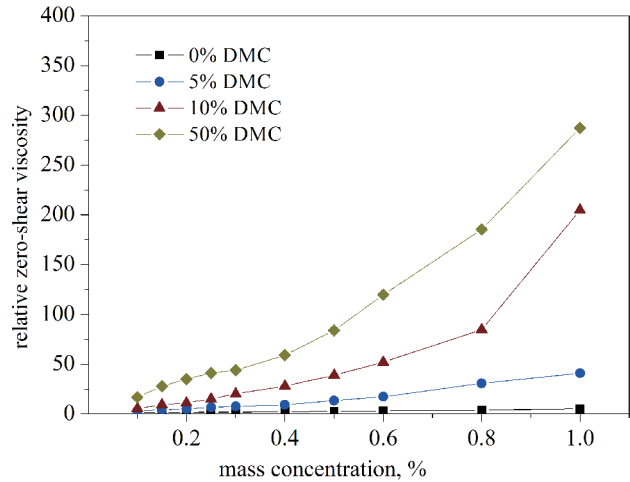


Figure 4
The Relationship of Concentration and Relative Zero-Shear Viscosity for Microgels with Varied Cationic Degrees

2.3 Plugging Test

The above three type microgels, 0% DMC, 10% DMC and 50% DMC were used for plugging test. The F_r and $F_{r\pi}$ for varied permeability tubes in these tests are shown in Figure 5 and Figure 6, respectively.

In Figure 5, The F_r of 0% DMC microgel is much lower than that of 50% DMC at the permeability less than 1000 mD, while beyond this permeability, all of them produce very small F_r . This increase trend in F_r for higher cationic degree agrees with the increasing viscosity.

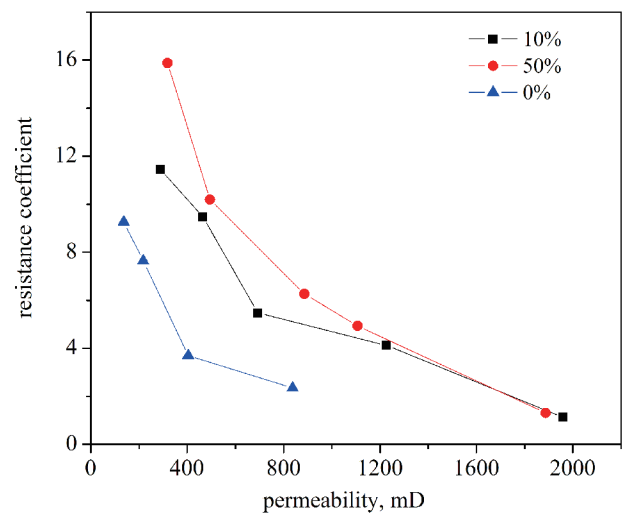


Figure 5
The Resistance Factor of Microgel with Different Cationic Degrees, 0%, 10% and 50%, at Varied Permeability

In Figure 6, similar results of $F_{r\pi}$ are obtained when comparing nonionic microgels with cationic one. The obvious difference is the close $F_{r\pi}$ between 10% DMC and 50% DMC microgel at tested permeability range. Further, the $F_{r\pi}$ of 10% DMC microgel is a bit larger than that of 50% DMC microgel at low permeability. The reason for

these F_{rr} changes is that 10% DMC microgel has larger size and lower zeta potential. So its shell layer is more lightly crosslinked and apt to intertwine each other to form cluster. This cluster effect increases the retention of particle when passing through pore throats. For 50% DMC microgel, it has higher zeta potential and more preferable to forming adsorption on sand surface by electrostatic attraction. The effect of cluster retention is stronger than that of electrostatic adsorption at low permeability.

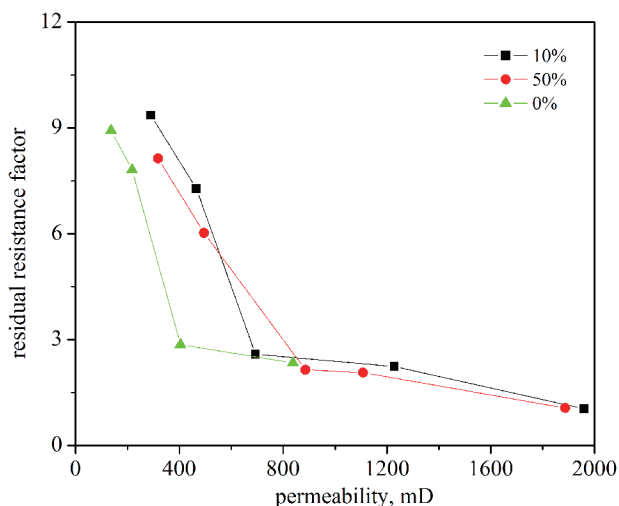


Figure 6
The Residual Resistance Factor of Microgels with Different Cationic Degrees, 0%, 10% and 50%, at Varied Permeability

If plugging rate of 50% ($F_{rr}=2$) is taken as the criterion for selecting microgels, the nonionic microgels are limited for use at formation permeability lower than 800 mD. The cationic microgels extend this limitation to 1200 mD. And 10% DMC microgel is the best fit for use because of its lower cost than 50% DMC microgel.

CONCLUSION

Microgels with different cationic degrees are synthesized by inverse microemulsion polymerization with AM and DMC as monomers. These microgels have a size range 50-100 nm in inverse emulsion and expand to 700 nm to 1700 nm after swollen by water. The maximum swellability is achieved at 10% DMC. The viscosity of cationic microgels is about ten times of nonionic microgels at the same concentration. In plugging test, the cationic microgels extend the permeability limitation for effective use to 1200 mD from 800 mD of nonionic microgels. 10% DMC microgel is the best fit for use because of its low cost.

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