

The Synergistic Rheological Properties of Hydrophobic Associated Polymers by Emulsion Microspheres

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Abstract: Polymer rheology for enhanced oil recovery (EOR) has reached a mature stage, and emulsion microspheres have started a heat wave in profile control. However, there has been no systematic report on the combination of the two and their rheological characteristics. A self-made emulsion microsphere and the hydrophobic association polymer (AP-P4) were mixed to obtain the mixture, and the microstructure of the mixture was obtained by scanning electron microscope (SEM) and optical microscope. At the same time, the rheological characteristics of the mixture were tested at different salinity, shear rate and temperature.

Keywords: Rheological Characteristics; Mixture; Rheological Inertia.

1. Introduction

Polymer microspheres have been widely used [1-3] to treat the strong heterogeneity [4] of the formation to regulate the water injection profile for Enhanced Oil Recovery (EOR) when conventional polymer applications are already mature. In the high water cut stage, polymer flooding or microsphere profile control alone [5-6] did not seem to be very satisfactory, which led researchers to continuously try new ways to conduct tertiary oil recovery.[7-9] However, there has been no systematic report on the combination of polymer microspheres and conventional polymer, such as partially hydrolyzed polyacrylamide (HPAM) [10-11] or hydrophobic association polymer [12-14], or their mixture's rheological characteristics.

In recent years, many researches have been made on the rheological properties of Hydrophobic association polymer and the synthesis of polymer microspheres. Hydrophobic association polymer [15] has been widely used in oil displacement and flooding systems. Bin Chen et al. qualitatively and quantitatively studied the swelling and dissolution process of AP-P4 by means of microscope observation method and colloid weighing method [16]. Thierry et al. studied the effect of nonionic surfactants on rheological properties of hydrophobic associating water-soluble polymers [17]. Wei et al. found that adding hydrophobic association polymer to the emulsion can effectively stabilize the emulsion [18]. Koji et al. successfully prepared the polymer microspheres with pyrrole as the core by sequential anion addition polymerization [19]. Without adding any stabilizer, Qi et al. prepared narrow or monodispersed core-shell polymer microspheres with dense nuclei and thin cross-linked shells with different functional groups such as esters, hydroxyl groups by two-stage distillation and precipitation polymerization. prepared the polymer microspheres [20].

It is worth noting that the current research on synergistic effect of emulsion microsphere and hydrophobic association polymer is still very rare, and the research on the rheological properties of mixtures is more insufficient. According to the current research, hydrophobically associated polymers have

special rheological properties that can effectively produce salt resistance [21-24], and polymer microspheres are also very effective in profile control. But the application of the two is often not synchronous, considering the practical application of simplicity, if they can be synchronous construction, this will greatly reduce the cost of work. And, whether these two types of existing products can effectively act on the formation, good rheological properties are an important consideration. Therefore, it is particularly important to consider the rheological properties of a mixture of microspheres and polymers under synergistic action.

Here, we used prefabricated emulsion microspheres to fully fuse with a hydrophobically associated polymer (AP-P4) to obtain their mixtures. The microstructure of the mixture was proved by scanning electron microscope (SEM) and optical microscope under special conditions. The rheological measurement method was used to study the salt, temperature and shear resistance of the mixture, and a surprising result was obtained: the hydrophobic associative polymer containing emulsion microspheres became actually inert to salt, temperature and shear stress.

2. Experimental Section

2.1. Materials

The emulsion PDS-SiO₂ was prepared in the laboratory in advance. Sodium chloride (NaCl), magnesium chloride (MgCl₂), calcium chloride (CaCl₂) and deionized water were purchased from Chengdu Kelong Chemical Reagents Corporation (Chengdu, China). Hydrophobic association polymer (AP-P4) with a relative molecular weight of about 1.7×10^6 was from Bohai Oilfield. And partially hydrolyzed polyacrylamide (HPAM) with a relative molecular weight of about 1.3×10^7 , industrial products, was from Daqing Refining & Chemical Company.

2.2. Preparation of the Mixed Solution

The measured AP-P4 was dissolved into a solution of 2000 mg/L with deionized water. Prefabricated microsphere emulsions were added to 2000 mg/L polymer solutions for 100mL with different contents (0, 0.5%, 1%, 2%, wt) and fully dissolved for 2 hours (Fig. 1).

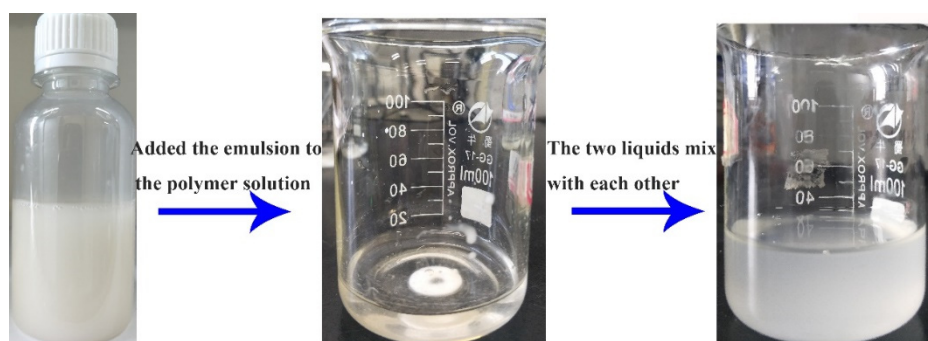


Fig 1. The preparation process of the mixed solution

2.3. Performance Testing of the Mixed Solution

To obtain SEM images of different microspheres, a scanning electron microscope (ZEISS EV0 MA15) was used; the materials to be tested were pre-dried and lightly adhered to a conductive adhesive. The dispersity and distribution of the microspheres in the mixture were tested by using an AMG EVOSFL eyepiece inverted fluorescent digital microscope.

The apparent viscosity of the mixtures under different conditions (such as different concentration of Na^+ , Mg^{2+} and Ca^{2+} , temperature ranged from 20 °C to 120 °C and shear rate for 0-1000 s^{-1}) was tested by a HAAKE MARS III rheometer.

3. Results and Discussion

3.1. Microscope Images of the Mixed Solution

In order to clearly understand the microstructure of the mixture, SEM was used to obtain the microscopic images of the mixture solution after freeze drying, while the microscopic optical image of the mixture liquid was obtained by optical microscope at room temperature. The experimental results are presented in Fig. 2a-b and Fig. 2c, respectively.

Hydrophobic association polymer (AP-P4) has both a hydrophilic main chain and a hydrophobic side group on the molecular chain, and these side groups are associated with each other to form a three-dimensional network structure as shown in Fig. 2a. From Fig. 2d, after the emulsion microspheres mixed with AP-P4, the microspheres entered the polymer chains and attach to them to form some uniformly distributed bump (Fig. 2b). In addition, in the microscopic optical image of the mixture liquid (Fig. 2c), many small and evenly distributed circles of light about 10 micrometers in size, can be easily found. As far as we know, after the polymer is fully dissolved, the water molecules will interact with the polymer chain to make the chain stretch, appearing colorless and transparent aqueous solution. However, due to the microspheres only swell but do not dissolve, these small round spots appeared under the low-power optical microscope. Here, according to the experimental phenomenon in Fig. 2a-c, it can be seen that the microsphere PDS-SiO₂ can attach to the hydrophobic association polymer (AP-P4) to form a "three-dimensional point network structure" (Fig. 2d) without changing the three-dimensional network structure of the polymer.

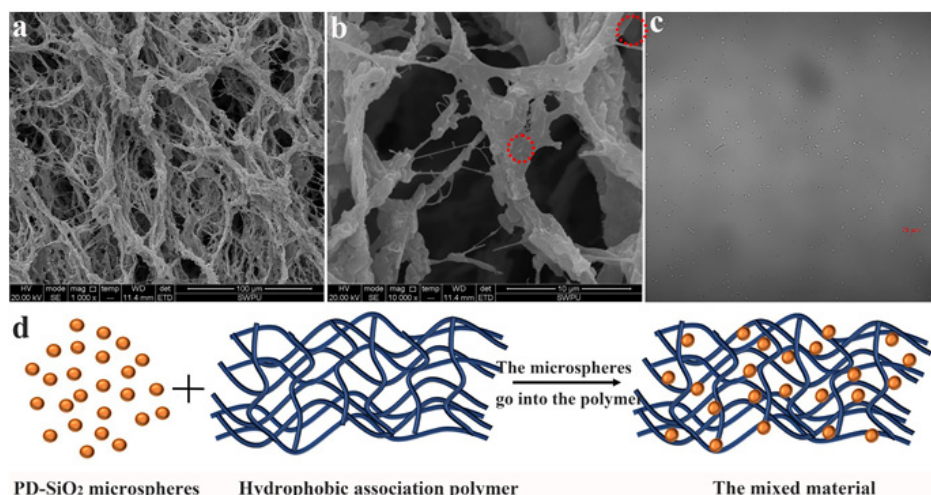


Fig 2. (a-b) The SEM of the mixture solution after freeze drying. (c) The microscopic optical image of the mixture liquid

3.2. Effects of Na^+ , Mg^{2+} and Ca^{2+} on the Viscosity of the Mixed Solution

In practical applications, the polymer will be injected into the formation with high concentration of Na^+ , Mg^{2+} and Ca^{2+} , so the rheological properties of the mixture of Na^+ , Mg^{2+} and Ca^{2+} with different concentrations must be studied in consideration of the actual situation. For comparison, the 2000 mg/L partially hydrolyzed polyacrylamide (HPAM) was used to compare the emulsion mixture at different

concentrations (0, 0.5%, 1%, 2%, wt) with AP-P4 at the same ratio and the following experimental results (Fig. 3a-c and Fig. 3a'-c') were obtained.

Fig. 3a'-c' shows the effects of Na^+ (0-15000 mg/L), Mg^{2+} (0-3000 mg/L) and Ca^{2+} (0-3000 mg/L) at different concentrations on the apparent viscosity of the mixture of AP-P4 (2000 mg/L) and the emulsion (0, 0.5%, 1%, 2%, wt), respectively. As can be seen from the figures, the viscosity of AP-P4 (2000 mg/L) added 0% content of emulsion will first increase and then decrease with the increase of salinity. It is

understandable that, on the one hand, the addition of salt increased the polarity of the solvent, which is conducive to the enhancement of hydrophobic association cooperation, so leading the increase of apparent viscosity. On the other hand, the continuous increased of salt made the anions on the

polymer chain shielded by cations, thus weakening the electrostatic repulsion between ions and resulting in the winding of the polymer chain, which led to the decrease of the apparent viscosity of the solution [24].

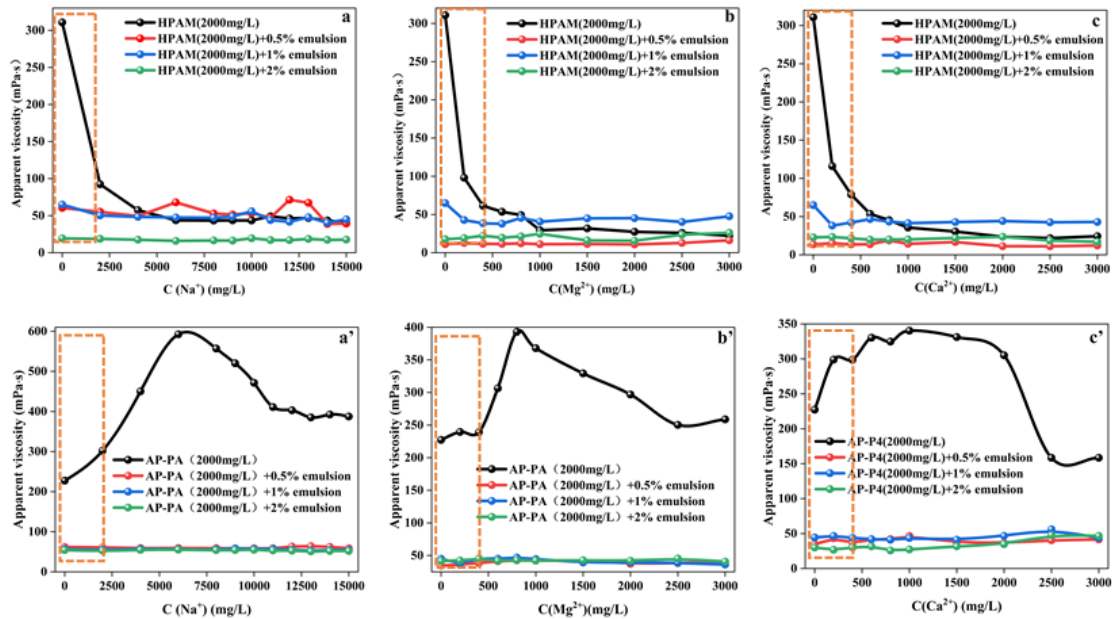


Fig 3. The viscosity of polymer added emulsion (0, 0.5%, 1%, 2%, mol) changed with salinity. (a-c) Partially hydrolyzed polyacrylamide added emulsion. (a'-c') Hydrophobic association polymer (AP-P4) added emulsion

As a supplement, Fig. 4 (a) shows the different schematic diagrams of the above viscosities under low salinity and high salinity. However, when the emulsion was added (whether 0.5%, 1%, or 2%, wt), the trend of the curve changed little rather than first increasing and then decreasing. According to the results in Fig.2, we have already known that when the microsphere emulsion was added, these small-sized microspheres would attach to the polymer molecular chain and uniformly distribute to form a three-dimensional network structure with protrusions. When a clean earthworm is covered in dirt, it becomes much more difficult to move and curl.

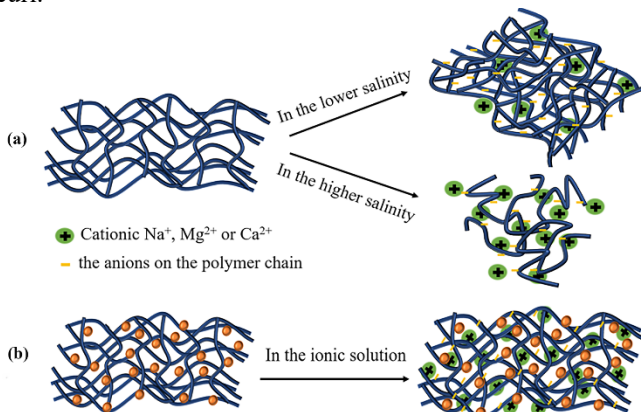


Fig 4. The different schematic diagrams of the AP-P4 and its mixture's viscosities under low salinity and high salinity. (a) AP-P4; (b) Mixture for AP-P4.

Based on this well-known life experience, we seem to understand why the viscosity of the mixed liquids did not change significantly. Or, more specifically, for one thing, the negative charge of the microspheres attached to the polymer chain neutralized part of the positive charge of the solvent, so

that electrostatic repulsion still existed between the negative charges on the original polymer chain. Polymer chains, for another, were burdened by attached microspheres, making it relatively difficult to move or curl (Fig. 4 (b)), and causing the low initial viscosity. To verify the non-uniqueness of this result, the results in Fig. 3a-c were given. Similar to the result of hydrophobic association polymer (AP-P4), the viscosity changes of HPAM without microspheres conformed to the general variation rule, but as long as the microspheres were added, no matter how much, the viscosity of the mixture will be inert to salinity.

3.3. Effects of Shear Rate on the Viscosity of the Mixed Solution

As a reversible physical structure, the network formed by hydrophobic association is characterized by shear dilution with the increase of rotating speed, as shown in Fig. 5a-b (2000 mg/L AP-P4). When shear force was applied to the three-dimensional network structure, the hydrophobic association structure formed by hydrophobic groups was disassembled [25-26], and the faster the rotation speed was, the greater the shear force was. For HPAM, as shear increased, the polymer chains that were originally wound together were unwound, leading the decrease of the hydrodynamic volume and the reduced viscosity (Fig. 5a, 2000 mg/L HPAM). However, the different situations occurred after the addition of polymer microsphere emulsion. At the same rotational speed, the polymer chains attached to the microspheres required greater shear stress to unchain the entangled molecules or to break the structure formed by the interaction of hydrophobic association, which led to the non-obvious characteristics of the shear dilution of the polymer containing emulsion microsphere (PDS-SiO₂).

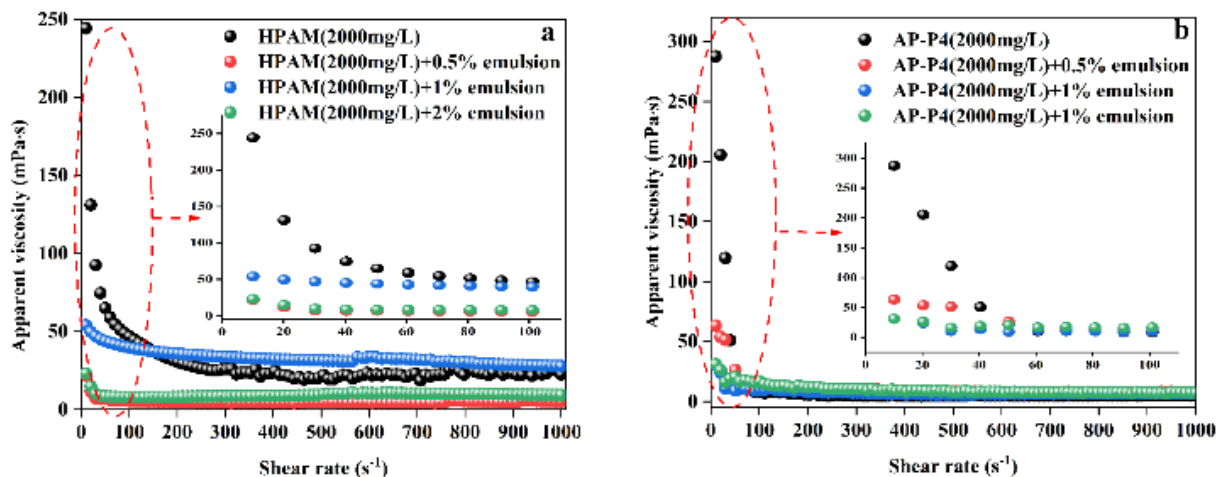


Fig 5. The viscosity of polymer added emulsion (0, 0.5%, 1%, 2%, wt) changed with shear rate. (a) Partially hydrolyzed polyacrylamide (HPAM) added emulsion. (b) Hydrophobic association polymer (AP-P4) added emulsion.

3.4. Effects of Temperature on the Viscosity of the Mixed Solution

In general, an increase in temperature will result in a significant decrease in the viscosity of the polymer solution. Here, the viscosity changes of aqueous solution of HPAM and AP-P4 with no emulsion was measured with the increase of temperature (Fig. 6a-b). Obviously, the viscosity of both polymer aqueous solutions was decreasing as the temperature increased, which is consistent with theoretical studies. For AP-P4, the two main reasons are understandable: 1. The polymer structure changed with the increased of temperature, resulting in the weakening of the hydrophobic function of the hydrophobic groups. Additionally, the accelerated Brownian motion [27-28] resulted in the destruction of the three-dimensional network structure. 2. The increased of water dissociation degree led to the decrease of polarity, which was

not conducive to hydrophobic association. Then there were similar situations of the two mixtures. After adding the microsphere emulsion, the viscosity of the mixture immediately dropped to a lower value at 20 °C, then hardly changing even if the temperature continued to rise. As mentioned earlier, the slowed motion of the polymer chains attached to the microspheres weakened hydrophobic association was the cause of the low initial viscosity. Furthermore, this attachment will hinder Brownian motion and reduce the damage degree of the physical three-dimensional network structure, delaying the decrease of viscosity (Fig. 6b). While, for HPAM, although no need to consider hydrophobic association, but similarly, this viscosity change will be affected by the slow molecular movement of the attached molecular chain (Fig. 6a). In other words, the viscosity of the mixture into which the microspheres are added became inert to the temperature.

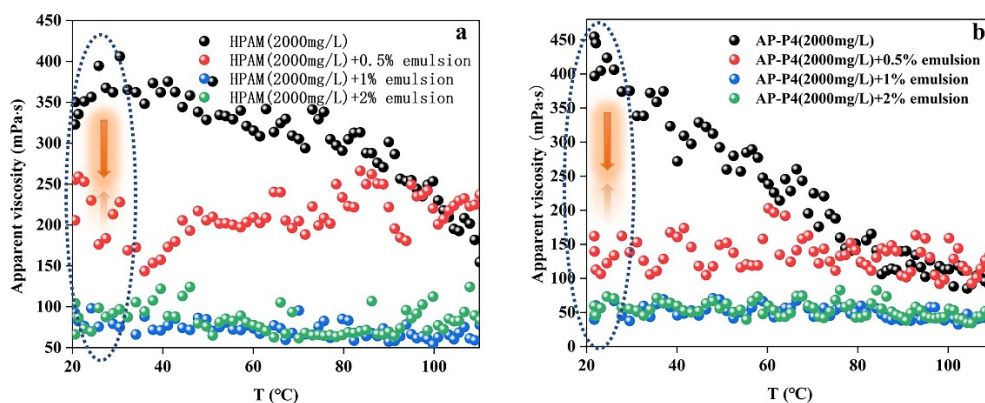


Fig 6. The viscosity of polymer added emulsion (0, 0.5%, 1%, 2%, wt) changed with temperature. (a) Partially hydrolyzed polyacrylamide (HPAM) added emulsion. (b) Hydrophobic association polymer (AP-P4) added emulsion

4. Conclusion

The rheological properties of the mixture were studied by mixing the microsphere-containing emulsion (PDS-SiO₂) with the hydrophobic association polymer (AP-P4) commonly used in oil field. The results showed that adding the microsphere-containing emulsion could change the rheological trend of AP-P4. According to the images obtained by SEM and optical microscope, the microspheres who did not dissolve when the mixture is in an aqueous solution were

uniformly attached to the polymer chain. In the experiment of the influence of Na⁺, Mg²⁺ and Ca²⁺ ions on the viscosity of the mixture, it can be concluded that the mixture can become inert to the salinity, and the viscosity will hardly change with the increase of the salinity. The shear test also showed that the addition of microspheres had a great influence on the shear dilution of the polymer, namely the mixture would maintain a trend of basic invariability at a lower initial viscosity under the increasing shear action. Coincidentally, the similar law that the viscosity of the mixture was inert to temperature has

been shown in temperature resistance experiments. This unprecedented phenomenon also provides a lot of potential for the study of rheological properties of polymers.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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