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Enhanced oil recovery performance and time-dependent role of polymeric core-shell nanoemulsion

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KEYWORDS

Enhanced oil recovery; Core-shell nanostructure; Wettability effects; Mobility ratio. Abstract. Nano inverse emulsion polymerization has been used to synthesize high molecular weight polyacrylamide nanoparticles with a hydrophobic nanoscale coating layer with low molecular weight. These core-shell nanoparticles modify the polymer flooding process, which can eliminate almost all problems of classical polymer flooding such as polymer solution high viscosity, polymer absorption and mechanical, thermal and biological degradations of the polymer. The nanostructure was characterized by Dynamic Light Scattering (DLS) particle size analysis, thermal analysis (DSC), and UV-Vis spectroscopy that confirm a core-shell nanostructure for the produced particles with considerable interaction of two polymers with narrow size distribution (90-140 nm). Also, micromodel and solubility experiments show that this method could considerably enhance the performance of classical polymer flooding and reduce polymer usage during the polymer flooding process.

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1. Introduction

There are many limitations within existing polymer flooding technology such as thermal, mechanical, shear, and biological degradation of polymer chains during the Enhanced Oil Recovery (EOR) process [1-4]. Recently, encapsulation and intelligent delivery studies have been considered a sophisticated approach for the protection and controlled release of precious materials in many fields to overcome the above mentioned limitations in polymer flooding with polyacrylamide solutions [5-7].

A novel core-shell nanostructure of polyacrylamide and a hydrophobic polymer (such as polystyrene) is designed and prepared to intellectually control the microscopic and macroscopic sweep efficiency of polymer flooding in oil reservoirs. This nanostructure can release polyacrylamide at the oil-water interface at reservoir temperature (\sim $90^{\circ}\mathrm{C}),$ where water flooding should have maximum viscosity.

2. Materials and method

First, 60 ml of hexane solvent (Merk Chemical Co.) and 0.0035 ml of span 80 surfactant (Sigma-Aldrich Chemie GmbH Co.; $C_{24}H_{44}O_6$) are mixed in a reactor with three entries. After mixing these using a mechanical mixer (3000 max rpm, Griffin & George, GT. Britain) with a speed of around 2000 rpm, the water phase including 5 g hydrophilic monomer of acrylamide (Merk Chemical Co.) and 20 ml of deionized water, is distributed to the previous solution. It should be noted that the distribution process of the water phase is an important parameter affecting the size of core particles. So, the water phase is injected into the mixed organic phase in the reactor via a microinjection. This helps to make the emulsion of polymer nanoparticles. After the water and organic mixing phases, the initiator system (redox), including ferrous

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sulfate and potassium persulfate (Merk Chemical Co.), is injected (5:2 ratio) under temperature condition -15° C, by entering this material into the reactor. The first time period of polymerization is selected such that the reactor remains under the mentioned conditions for 30 minutes and, after that, is immediately moved to very low temperature conditions for 3 or 4 days without mechanical mixing. After this time, nanoparticles of polyacrylamide with high molecular weight (> 10,000,000 Dalton) are produced and it is time to inject the second initiator and monomer of the nanolayer with hydrophobicity properties. Therefore, in the second step of the process, the redox initiator under low temperature conditions $(-15^{\circ}C)$ and styrene monomer are injected for making the nanolayer. It is interesting to point out that the initiator of the second step and the organic monomer must be injected simultaneously, and the initiator on the surface of the polymer nanoparticle causes the making of a chain of polystyrene; this chain is propagated continuously. As one of the goals is to make the smallest organic polymer layer on the particles, the transfer of the chain must be done in specific time and an extra propagation of the polymer nanolayer chain is prevented. In this way, by considering the short time for the second polymerization process (about 30 minutes), a thin layer of polystyrene is made on the nanoparticles of the polyacrylamide and, after this time, the reaction process is terminated. The polystyrene nanolayer is solved in a hexane solvent, so this solvent must be removed from the reactor at the end to prevent a change in particle size distribution and to prevent their tenacity. This separation is done by removing the materials of the reactor and centrifuging at a speed of 5500 rpm for 30 minutes. After that, the material is divided into 3 phases. The bottom phase consists of pure hexane solvent with a dark colour, the middle phase from the mid solid particles is with a white coating and the head phase consists of white fluids which are a mix of hexane and coating particles. The middle phase which is rich in coated nanoparticles is strewn into some water and remains under high speed mixing for 3 minutes. After that, the material is sprayed into a large amount of water at high pressure. After centrifuging and separating the synthesized particles, the goal is to produce the particles in powder form. Water must be removed from the suspension system and the particles become useable as powder in the enhanced oil recovery. This process is done by freeze drying (Millrock Technology Inc.). Finally, the synthesized powders have a coreshell nanostructure whose nanocore of polyacrylamide is 10 million Dalton (molecular weight), and whose size is 80 nanometres. Its shell is a nanolayer of polystyrene with 40,000 Dalton (molecular weight) whose size is 10 nanometres.

3. Results and discussion

Figure 1 shows the Dynamic Light Sattering (DLS) results of polyacrylamide-polystyrene nanoparticles. The average diameter of core-shell particles is in the range of 80 and 140 nm.

Differential Scanning Calorimetry (DSC) analysis was carried out using samples of approximately 5-10 mg placed in closed aluminium crucibles. The analyses were performed under a nitrogen flow of $15 \text{ mL}.\text{min}^{-1}$ at a heating rate of $5^{\circ}\text{C}.\text{min}^{-1}$ from 40 to 250°C temperature. Two scans were obtained for each sample and the data analyses were made using the curve resulting from the second scan. Glass transition temperatures (Tg) of materials were obtained from the first derivative of DSC curves (Figure 2). According to Figure 2, the polymeric nanostructure has two glass transition temperatures in a range of 100-190°C, due to the presence of a polystyrene shell $(103^{\circ}C)$ and a polyacrylamide core $(109.5^{\circ}C)$ in accordance with the sequential degradation process.

UV-Visible spectroscopy was carried out using samples of approximately 3-9 mg placed in closed



Figure 1. Size distribution of core-shell nanoparticles, obtained by DLS method.



Figure 2. Glass temperatures of core-shell nanoparticles, obtained by DSC method.



Figure 3. UV-Vis spectrum of polyacrylamide-polystyrene system.



Figure 4. Scheme of dissolution test.

quartz packs. According to Figure 3, there is an absorbance peak for the core-shell sample at a wavelength of 400 nm, which is similar to pure polystyrene, to verify complete coating of the hydrophilic polymer by hydrophobic polystyrene.

For investigating the behaviour of polyacrylamide release from its nanolayer coating and the effects on the rheological properties of the water phase in underground reservoirs with a wettability variable, a test is planned as the coating particles remain on oil or xylene for a specific period of time. In this period, after sampling, the viscosity of the water phase is measured via a dilute viscometer (Figure 4).

Under these conditions, in contacting the synthesized particles by the organic phase under the temperature close to the underground oil reservoirs (90- 100° C), the hydrophobic coating solves in the oil phase gradually, and the polyacrylamide molecules through the shell have an opportunity to diffuse into the pushing phase (water). This case causes the controlled release of polyacrylamide and the increase of water viscosity to enhance sweep efficiency. The molecular release of polyacrylamide, because of its high molecular weight, requires a long time, and one of the goals of this study is that particles should move towards deep areas of oil reservoirs and remain in special fractures. According to the special components of oil, these materials cause



Figure 5. Viscosity of pure polyacrylamide in water phase vs. time.



Figure 6. Viscosity of core-shell nanoparticles in water phase vs. time.

 Table 1. Comprative results of water, pure polymer, and core-shell flooding processes.

EOR method	$\mathbf{RF}\%$
Water flooding	44.17381
Polymer flooding	61.02884
Core-shell flooding	59.40461

the inflation and dissolution of polystyrene in the oil phase and this causes the release of the inside materials of the shell. As identified in this test, for the time of release, and for the polyacrylamide nanoparticles which are coated in the water phase, the dissolution of pure polyacrylamide with 6 million Dolton (molecular weight) under the temperature 90-100°C takes 6 days (Figure 5), but the total release of the nanoparticles of polyacrylamide from the nanolayer of the polystyrene takes 21 days to dissolve in the water phase under similar conditions (Figure 6).

The three methods of flooding, provided in the experimental glass micromodel, are compared in Table 1 to show the effects of the used agent in the enhanced



Figure 7. Oil recovery factor vs. pore volume injected in experimental micromodel during core-shell flooding.

oil recovery process. According to the mechanism for testing the percentage of oil recovery by the intelligent flooding process, it is found that, for core-shell polymer flooding, just in the volume of progress deployed by the polymer, active polymer is used, and the percentage of oil recovery is relatively similar to the flooding process of pure polymer (Figure 7). On the other hand, in the flooding process with a new synthesized core-shell nanostructure, just 30% of the active polymer is used compared to that of classic polymer flooding.

4. Conclusions

In this research, through simultaneous inverse emulsion processes of polyacrylamide dilute solution and styrene, nanoparticles of polyacrylamide-polystyrene as coreshell multicomponent nanostructures were successfully synthesized. The results reveal that polyacrylamide and polystyrene size ranges are 80-140 nm and 10-20 nm, respectively. They have the potential to block fractures in oil reservoirs to enhanced immobile oil recovery. Dissolution and micromodel polymer flooding experiments reveal that the time and sweep efficiency of polyacrylamide increase and energy consumption during the flooding process diminishes dramatically using the novel core-shell nanoparticles. Micromodel flooding experiments show that using a core-shell structure can reduce usage of polymer by one-third of the initial value for obtaining the same recovery factor in classical polymer flooding.

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Biographies

Yousef Tamsilian is a PhD degree student of Chemical Engineering in the Institute of Nanoscience and Nanotechnology at Sharif University of Technology, Tehran, Iran. His MS and PhD degree theses were regarding the experimental and modeling study of the rheological behavior of polymeric core-shell nanostructures and smart nanofluids during chemical EOR processes. He has more than nine years of academic experience in the university, and 5 years of professional industrial experience in the petroleum and chemical industries. He has published more than 30 papers in international and national journals and conferences, and three books on the subjects of CFD, thermodynamics, and molecular dynamics. He has also registered two US patents and two Iranian patents with EOR principles. He has a very strong background in the field of nano-structured materials, enhanced oil recovery using polymer flooding, polymerization engineering, modeling of polymer and chemical processes by the CFD method (OpenFOAM Software) and hydrate formation and dissociation in underground porous media. His current research interests lie in the application of colloidal and interfacial phenomena to oil recovery, with applications in chemical EOR processes for smart polymer flooding and surfactant-polymer flooding. His early research work focused on the physico-chemical interactions between surfactants, interfaces and polymer nanoparticles within multi-phase porous media, and their applications in enhanced oil recovery and well stimulation. Later, his work focused on the nanodynamic behavior of multi-component mobility ratios, wettability alteration, and IFT reduction in oil recovery processes. From this background, his current research interests have evolved into two principal themes: 1-Continuum and molecular dynamic modeling and simulation of core-shell nanostructure behavior, and 2-Experimental studies of smart polymer nanoparticles in porous media.

Ahmad Ramazani S.A. graduated from the Chemical Engineering Department of Laval University, Canada, in 1999, and is currently Professor in the Department of Chemical and Petroleum Engineering at Sharif University of Technology (SUT), Tehran, Iran. His PhD thesis was regarding the modeling of the rheological behavior of short fiber filled viscoelastic fluids. He has published more than 300 papers in international and national journals and conferences and has supervised more than 100 master and PhD degree theses. He has also published three books on Heat Transfer, Rheology, and Numerical Mathematics and authored several chapters of different books. His research work is in interdisciplinary subjects mostly relating to experimental and theoretical investigation of polymer relating processes and polymer properties, and the flow of polymeric and non-Newtonian fluids in different engineering fields, including biomedical and petroleum engineering related media. From 2002-2003, he served as head of the biomedical group and from 2003-2008 as head of the polymer engineering group at SUT. He was also executive chair of the 8th International Seminar on Polymer Science and Technology held in 2007 and member of the organizing and scientific groups of several seminars and conferences. He acts as editorial guest of the Macromolecular Symposia Journal Volume, 274, published by Wiley-VCH and currently serves on the editorial board of several international journals. He was invited professor at the Ecole Polytechnique de Montreal in Canada in summer 2009 where he presented some of his research work for the second time as invited professor in CREPEC. He is also chairman and organizer of the ICHEC14, which was held at SUT in 2012.