ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

Research Progress on Functionalized Polymer Microspheres for Deep Profile Control and Flooding

Jinjin Cheng, Jianmin Shi*, Wenwei Wu, Shasha Zhao, Bingang Chen, Yaoguo Wang

Polymer Research Institute of Sichuan University, Chengdu, Sichuan, 610065, China
**Corresponding author*

Abstract: *Based on a comprehensive review of literatures concerning polymer microspheres for enhanced oil recovery over the past five years, this paper centers on profile control agents composed of acrylamide, providing a detailed overview of the preparation methods of functionalized polymer microspheres. According to the functional characteristics, the research progress of fluorescent polymer microspheres, smart polymer microspheres, and organic-inorganic nanocomposite microspheres is highlighted. Additionally, the characterization parameters and methods of polymer microspheres are summarized. The challenges and issues associated with the application of polymer microspheres in deep profile control and oil displacement technologies are discussed, which holds significant implications for the development of heterogeneous and low-permeability oil reservoirs.*

Keywords: *Polymer microsphere, Profile control agent, Functionalization*

1. Introduction

With the extensive development of oil resources and excessive water flooding procedures, most oilfields have evolved into fractured reservoirs with characteristics of high temperature, high salinity, and high water cut. Different from traditional water plugging and profile control techniques, deep profile control technology has been practiced successfully to enhance oil recovery (EOR) in low-permeability oil reservoirs. The profile control agents, which possess good mobility, can be easily injected through water injection wells, penetrate deep into the oil reservoir and plug the water channels. The fluid flow redirects towards layers with lower permeability and displaces the residual oil. This process expands the sweep volume of injected water, enhances oil displacement efficiency, and ultimately ensures efficient oil recovery[1-3].

For deep profile control and flooding technology, the selection of profile control agents is crucial. In recent years, polymer microspheres, as a widely researched type of novel profile control agents, have been extensively used in the water flooding development of heterogeneous reservoirs. Polymer microspheres have the characteristic of swelling and expanding upon water absorption. Driven by the injected water to migrate through the formation, microspheres gradually expand and self-aggregate, which forms effective blocking in reservoir, causes an in-depth fluid diversion, expands the water swept area, and enhances oil recovery. Additionally, the increased plugging pressure and shear force can induce elastic deformation of the microspheres. Consequently, microspheres can migrate through the pores to the deep formation, forming a characteristic of "migration, plugging, elastic deformation, re-migration, re-plugging" in the profile control and oil displacement process[4]. However, due to the harsh conditions in deep reservoirs, conventional polymer microspheres are prone to dehydration shrinkage and thermal degradation under high-temperature and high-salinity environments[5]. Therefore, current polymer microsphere profile control agents generally use acrylamide (AM) as the basic material, modified by crosslinking with other functional monomers or particles. The functionalized polymeric nano/ microspheres can adapt to different reservoir requirements.

2. The Preparation Methods of Polymer Microspheres

Polymer microspheres can be synthesized with specific size distributions and surface properties by changing the preparation methods and optimizing the preparation conditions. To adapt to the plugging and oil displacement needs of different reservoirs, micron-sized microspheres and nanospheres have been designed and prepared for medium to high and low permeability reservoirs. The preparation methods of

ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

polymer microsphere profile control agents include dispersion polymerization, inverse suspension polymerization, inverse emulsion polymerization, and inverse microemulsion polymerization. Commonly, dispersion polymerization and inverse suspension polymerization are used for synthesizing micron-sized microspheres, while inverse emulsion polymerization and inverse microemulsion polymerization are employed for nanospheres[6].

2.1. Preparation of Micron-Sized Microspheres

The dispersion polymerization method employs organic solvents or water as the disperse medium. Monomers, initiators, and dispersants are dissolved to form a homogeneous system. As the reaction proceeds, monomers polymerize to form microsphere particles suspended in the continuous phase. The polymer microspheres synthesized by this method for enhanced oil recovery have a particle size distribution ranging from 0.1 to 10 μm, and exhibit low apparent viscosity, uniform particle distribution, good injectability, and flowability. Wang et al. [7] dispersed modified SiO_2 with double bonds on the surface in an ethanol/water mixed solvent, then chose AM, block polyether macro monomer (PEP) and SiO_2 as monomers, with ammonium persulfate (APS) as the initiator, polyvinylpyrrolidone (PVP) as the dispersant, and N,N'-methylenebisacrylamide (MBA) as the crosslinker. A core-shell structure and surface-hydrophobic polyacrylamide M-P(AM-PEP) was ultimately synthesized through dispersion polymerization. It was found that the mass ratio of AM to PEP, monomer concentration, crosslinker concentration, and SiO_2 concentration significantly influenced the particle size and stability of microspheres. Microspheres with sizes ranging from micrometer to nanometer scale were obtained under different conditions. After the optimization of synthesis conditions, the prepared microspheres exhibited better swelling behavior, mechanical properties, hydrophobicity, and self-aggregation. Core profile control and flooding experiment demonstrated that the injection of microspheres effectively decreased the water cut and improved the oil recovery.

In contrast, the suspension polymerization method employs organic solvents as the disperse medium. Aqueous monomer solution forms water-phase droplets suspended in the organic continuous phase under the action of dispersants and agitation. Water-phase polymerization is initiated by a water-soluble initiator inside the droplets, forming an oil-in-water emulsion of microspheres. The polymer microspheres synthesized by this method for enhanced oil recovery have a particle size distribution ranging from 0.1 to 1000 μm. This method offers advantages such as mild reaction conditions and minimal side reactions. Tang et al. [8] dispersed modified SiO_2 nanoparticles and Span 60 emulsifier uniformly in aviation kerosene as the oil phase. AM, acrylic acid (AA), surfactant, polyethylene glycol 200, NaOH, NH_4Cl, and MBA crosslinker were dissolved in deionized water as the aqueous phase. Using APS as a water-soluble initiator, polymer/nano-SiO_2 composite microspheres were synthesized by suspension polymerization. As the SiO_2 loading increased to 2.0%, the average particle size of microspheres decreased from 24.6 μm to 13.6 μm, which effectively enhance migration and plugging effects. Sand pack tests showed a maximum plugging rate of 93.64%, indicating that the microsphere-based EOR agent could realize in-depth profile control in reservoirs.

2.2. Preparation of Nanoscale Microspheres

The inverse emulsion polymerization method employs non-polar organic solvents as the disperse medium. Aqueous solution of monomers is uniformly dispersed in the organic continuous phase under high-speed mechanical stirring and the emulsification of surfactants, forming an oil-in-water (W/O) emulsion. Monomers in the emulsion are polymerized by water-soluble or oil-soluble initiators, resulting in the formation of polymer microspheres. The polymer microspheres synthesized by this method for EOR have a particle size distribution ranging from 100 to 1000 nm, and exhibit advantages such as fast polymerization rate, high molecular weight, and uniform size distribution. Mohammadi et al. [9] used Span 80 and Tween 85 as the complex emulsifier system, and cyclohexane as the continuous phase of the inverse emulsion. The monomer solution containing AM and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was slowly dripped into the rapidly stirred organic phase. Polymerization was initiated by APS under a nitrogen atmosphere, resulting in a milk-white inverse W/O emulsion. After centrifugation and lyophilization, P(AM-AMPS) microspheres acceptable long-term stability at elevated temperatures and salinity levels were obtained. The particle sizes of microspheres ranged from approximately 20 to 243 nm. To achieve high molecular weight characteristics, the optimal synthesis condition was obtained using Box-Behnken design combined with response surface methodology.

Inverse microemulsion polymerization is based on the inverse emulsion polymerization method. By adjusting the ratio of water-soluble monomers, water, organic solvents, and surfactants, the water phase

ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

is uniformly dispersed in the organic solvent to form nano-micelles. The polymerization of monomers occurred inside the micelles with the presence of initiators, ultimately resulting in spontaneously formed isotropic, semi-transparent/transparent and thermodynamically stable microemulsion products. The synthesized polymer microspheres have a particle size distribution ranging from 10 to 100 nm, and exhibit advantages such as small particle size, narrow size distribution, fast reaction rate, well dispersibility, and high stability. Ma et al. [10] introduced complex emulsifiers into the plant oil as the oil phase, dissolved a certain proportion of hyperbranched polyacrylamide (HBPAM), AM, AMPS, and MBA crosslinking agent in distilled water as the water phase. Using the APS-sodium bisulfite redox system as the initiator, a new type of polymer microspheres with like “ball in ball” structure was synthesized via inverse microemulsion polymerization. With the increase of HBPAM content, the average particle size of the microspheres increased from 38 nm to 82 nm, and the rheological properties, thickening ability and shear resistance significantly improved. After the injection of microsphere emulsion dispersion, HBPAM released from cross-linked network as a result of being swelled and sheared by pore throat, which improved the viscosity of dispersion, thereby enhanced the plugging rate and oil recovery.

3. Functionalized Polymer Microspheres

3.1. Fluorescent Polymer Microspheres

During the actual enhanced oil recovery process, there is often a significant amount of uncertainty regarding the migration and distribution of microspheres in the reservoir's deep layers. Through accurate monitoring of the actual concentration and particle size changes of microspheres underground, as well as timely adjustments to the flow direction, the effectiveness of microsphere-enhanced oil recovery and water control can be significantly improved. However, conventional methods for detecting the concentration of polymer microspheres currently face challenges such as high operational requirements, limited measurement ranges, and insufficient detection efficiency or accuracy. Therefore, introducing fluorescent substances into the microspheres as tracers and preparing stable fluorescent polymer microspheres offer a promising solution. By utilizing their fluorescence properties, the concentration of microspheres in the extraction fluid can be sensitively quantified. This approach holds the potential to achieve efficient detection and dynamic adjustment of microsphere-enhanced plugging and oil recovery processes, thereby optimizing and improving oil field development strategies. [11]

Yang et al. [12] utilized organic fluorescent dyes as tracers, namely allyl oxyfluorescein, rhodamine B, and acryloyloxy coumarin, to synthesize three kinds of fluorescent polymer microspheres via reverse-phase suspension polymerization with AM monomers followed by MBA crosslinking. Performance testing results showed that the addition of trace hydrophobic fluorescent monomers had minimal impact on the initial particle size and swelling properties of the microspheres. However, the fluorescence and creep performance of the microspheres were closely related to the type and structure of the fluorescent monomers, necessitating consideration of the influence of fluorescent dyes on microsphere structure and oil recovery performance in practical applications.

Lai et al. [13] synthesized carbon quantum dots (CQDs) using citric acid and ethylenediamine as raw materials and introduced them into microspheres as fluorescent substances to produce CQDs@PPG fluorescent polymer microspheres. The performance of these microspheres in plugging and displacement in sand-filled tubes was studied. Results indicated that the fluorescent peak value was unaffected by swelling, salinity, pH, and temperature. The concentration of CQDs@PPG in a different position could be directly obtained through a fluorescence spectrophotometer, which confirmed the significant plugging, elastic deformation, and deep modulation drive after the injection of microspheres. As the injection volume of CQDs@PPG was 0.5 PV, the plugging rate within 1000 mD porous media could reach 90%, and the EOR achieved 25.33% when applied to heterogeneous porous media.

3.2. Intelligent Polymer Microspheres

Intelligent polymer microspheres can sense subtle stimuli or changes in the external environment, such as temperature, pH, magnetic fields, light, electricity, pressure, and ion intensity, and produce corresponding sensitive responses [14]. When used as displacement agents for deep migration, intelligent polymer microspheres can change their physical structure or chemical properties in response to changes in reservoir conditions, thereby achieving intelligent and controllable plugging and displacement, enhancing the performance of displacement agents, and improving oil recovery efficiency.

ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

In addressing low-permeability reservoirs, Zhou et al. [15] prepared temperature-sensitive P(NIPAM-AM) microspheres by reverse-phase microemulsion polymerization of N-isopropylacrylamide (NIPAM) and AM. PNIPAM exhibits hydrophilicity and microsphere swelling at low temperatures, while it becomes more hydrophobic and the microspheres shrink at high temperatures. As the microspheres move from injection water into deeper reservoirs where the external temperature gradually increases, the particle size and hydrophilicity of P(NIPAM-AM) microspheres significantly decrease. This enables the microspheres to migrate to deeper reservoir formation more easily. Furthermore, the particle size and hydrophilicity of the microspheres were reduced, making it easier to reach the oil-water interface, reduce the oil-water interface tension, and enhance the structural disjoining pressure. Consequently, residual oil became easier to peel from the rock. Simulated core plugging evaluation showed that compared to PAM nanoparticles, injecting P(NIPAM-AM) increased the recovery efficiency by up to 7%.

pH-sensitive microspheres generally contain ionizable functional groups such as -COOH, -SO_3H, -NH_2, etc. When the environmental pH changes, these groups undergo ionization or hydrolysis, resulting in a change in the charge density within the polymer microspheres. The repulsion between charges affects the swelling behavior and apparent viscosity of the microspheres, thereby exhibiting pH responsiveness. By controlling the quantity of ionizable groups, microspheres can adapt to different pH conditions in reservoirs, enhancing the adaptability and applicability of profile control agents. Jamali et al. [16] used AM, SiO_2, and AA containing -COOH to prepare pH-sensitive microspheres via reverse-phase suspension polymerization. When the solution pH increased from 5.5 to 7.3, the carboxyl groups hydrolyzed into carboxylate anions, and the electrostatic repulsion of ions led to a drastic increment of the equilibrium swelling ratio. The sensitivity of microspheres to the reservoir environment was increased and more swelling performance were observed. It was observed that the smart microspheres could improve macroscopic sweep efficiency and oil recovery in micromodel and core-flooding tests.

Magnetic polymer microspheres typically consist of a magnetically responsive metal or metal oxide core, such as Fe, Ni, Co, and their oxides, enclosed by a polymer shell containing active groups. The magnetic core possesses magnetic field-responsive characteristics, make it possible for microspheres to achieve precise directional movement and aggregation within porous media, reduce oil adhesion to rock surfaces, address the low sweep efficiency caused by heterogeneity, and thus improve oil recovery rates. Khalil et al. [17] utilized magnetically responsive Fe_3O_4 as the core and temperature-responsive PNIPAM as the shell to prepare Fe_3O_4@PNIPAM microspheres via reverse-phase microemulsion polymerization. These microspheres exhibited superparamagnetism, allowing rapid recovery and reuse from produced fluid in the presence of a magnetic field. Additionally, the integration of PNIPAM onto Fe_3O_4 nanoparticles induced changes in wettability, reduced interfacial tension, enhanced imbibition, and improved the rate and efficiency of oil recovery. Moreover, the temperature-dependent flow behavior demonstrated by the dehydration of the PNIPAM shell was beneficial in achieving high viscosity and low mobility ratio, further facilitating plugging and oil displacement.

3.3. Organic-Inorganic Nanocomposite Microspheres

Organic-inorganic nanocomposite microspheres refer to microspheres containing both organic and inorganic components, with inorganic nanoparticles either coated on the surface or embedded inside organic polymer matrix. The composites can enhance temperature and salt resistance as well as plugging strength through the utilization of inorganic components, while improve the viscoelastic properties and displacement efficiency of the microspheres by using organic polymers. Types of inorganic nanoparticles in displacement agents include nanocarbon materials, non-metallic nanoparticles, and metal oxide nanoparticles[18, 19].

Nanocarbon materials are composed of carbon as the basic unit and have at least one-dimensional characteristic size smaller than 100 nm in three-dimensional space. These materials have unique advantages such as wide availability of raw materials, strong electrical and thermal conductivity, excellent mechanical properties, and easily tunable surface chemical properties. Ji et al. [20] synthesized microspheres with an average particle size of 955 nm by compounding hydrophilic graphene with AM, AA, and 4-acryloylmorpholine terpolymer. Results showed that compared to polymer microspheres, the composite microspheres exhibited significantly improved viscoelasticity, thermal stability, water retention, and shear resistance. The microspheres maintained excellent deformation recovery and swelling stability even under high pressure and temperature conditions. Additionally, the incorporation of graphene enhanced the nanomechanical properties of the microspheres, imparting them with high dispersibility and fluidity in aqueous media. Consequently, the composite microspheres demonstrated higher migration ability and flow controllability during plugging and displacement processes, leading to increased plugging efficiency to 72.2% and oil recovery rate to 32.81%.

ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

Nano SiO_2 and nano TiO_2 possess similar physicochemical properties in terms of particle size, morphology, specific surface area, temperature resistance, and compressive strength. Nano SiO_2 research is more mature and has entered the stage of commercial production and application, while nano TiO_2 excels in surface activity and adsorption performance, and it exhibits photocatalytic degradation properties. Liu et al. [21] prepared PDS-SiO_2 microspheres using modified nano SiO_2 as the core and coating with copolymers of AM, AMPS, and acryloyloxyethyl trimethyl ammonium chloride without the addition of emulsifiers. These microspheres exhibit excellent swelling properties and elasticity at high temperatures and high salinity. Utilizing the characteristic of increased swelling rate with temperature, the micro-pore size of the microspheres can be designed to enhance the plugging effect. Song et al. [22] used AM, AA, sodium alginate (SA), and TiO_2 to prepare P(AM-AA-SA)@TiO_2 microspheres suitable for the medium-high permeability reservoir environment via the reverse microemulsion polymerization method. Compared with P(AM-AA) microspheres, the modified microspheres showed characteristics of good injectability, high temperature resistance, high salt resistance, slow swelling and slow release. At high temperature and high salinity, the EOR effect was significant, with a plugging rate of up to 95.3% and an increase in oil recovery rate of 12.89%.

Inorganic nanoparticles can also be designed with composite structures. Cao et al. [23] coated SiO_2 and TiO_2 shells separately onto nano Fe_3O_4, and then encapsulated them with polyacrylamide to prepare hybrid composite polymer microspheres Fe_3O_4@SiO_2@PAM and Fe_3O_4@TiO_2@PAM with monodispersed multilayer core-shell structures. The results showed that the oil displacement agent with silica shell exhibited better temperature and salt resistance, while the TiO_2 shell-based microspheres possessed better acid resistance.

4. Characterization of Polymer Microspheres

The composition and structure of different polymer microsphere displacement agents vary significantly, but their performance characterization is generally similar, mainly including morphology and size, swelling properties, rheological properties, temperature and salt resistance, and plugging and displacement performance.

Microspheres with smaller initial particle size and more uniform dispersion are easier to inject into the formation and migrate to the deeper pore throats. Under the pushing of succeeding water, the swelling ratio of microspheres continuously increases until it reaches equilibrium, matching with pores of different permeabilities to achieve effective plugging and displacement. Therefore, before determining their oil displacement effect, the morphology, particle size distribution, and swelling ratio of the obtained microspheres under different times, temperatures, and salinities are often analyzed. Morphological observations provide information about the shape, particle size, and aggregation structure of microspheres. Common methods for morphological characterization include optical microscopy, scanning electron microscopy, environmental scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. Average particle size and particle size distribution are mainly characterized using dynamic light scattering, which measures the particle size range at each frequency to obtain the particle size distribution. Microspheres with narrow particle size distribution and uniform size are more consistent, making them more conducive to injection and plugging and displacement in the later stages. The swelling ratio reflects the swelling capacity of microspheres and their matching degree with pores. It can be divided into volume swelling, mass swelling, and average particle size swelling. High salinity and low temperature can lead to a decrease in the swelling ratio of polymer microspheres, resulting in a decrease in plugging and displacement performance[24].

To prevent problems such as flocculation, fragmentation, and degradation of polymer microspheres due to high temperature and high salinity after entering deep formations, testing of the microspheres' rheological properties and temperature and salt resistance is essential. Rheological properties are typically analyzed using a rheometer. By measuring the apparent viscosity of microsphere solutions at different shear rates, the microspheres' shear resistance can be determined. Additionally, measuring the changes in storage modulus and loss modulus of microspheres at different frequencies and temperatures reveals their viscoelastic properties. Good shear resistance and viscoelasticity are important criteria for determining whether microspheres can penetrate deeper into formations, reflecting their strong ability for deep migration, plugging capacity and oil displacement efficiency[25]. Temperature and salt resistance involve placing microspheres in simulated high-temperature, high-salinity formation water and observing changes in morphology, particle size, and swelling ratio. This ensures that microspheres can maintain a stable structure during actual field applications. Studies have shown that introducing monomers with rigid structures (such as N-vinyl pyrrolidone), sulfonic acid groups with strong hydration ability, and forming complexes with metal ions and carboxyl groups can improve the temperature and salt resistance of microspheres[26].

ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

The commonly used evaluation methods for the plugging and displacement performance of polymer microspheres are sand-packed tube experiments and core flooding experiments. Sand-packed tube experiments simulate the plugging and migration behavior of polymer microspheres downhole. The plugging performance is judged based on pressure changes during the injection process and the plugging capacity[27]. Core flooding experiments, akin to scaled-down versions of sand-packed tube experiments, involve the use of actual or artificial rock cores to measure the amount of oil displaced by microspheres under certain conditions. This helps determine the oil displacement efficiency of the microspheres[28]. Based on the results of plugging and displacement experiments, the oil displacement mechanism of polymer microspheres can be analyzed. Parameters such as interfacial tension, structural separation pressure, wettability, emulsification, and sweep efficiency are also subjected to relevant testing and analysis[29,30].

5. Conclusion and Outlook

Due to the expansion of oilfield development scale, the extension of water flooding, and the exacerbation of heterogeneous formations, the application of polymer microspheres has shown significant effects on improving water flooding efficiency and oil recovery, especially in low-permeability oil fields. The widespread application of polymer microsphere profile control agents will remain a major trend in the future. Recently, researchers have incorporated different monomers and composites to develop new functionalized polymer microspheres through various preparation methods. According to reservoir characteristics, the performance of polymer microspheres has been optimized by adjusting reactant ratios and preparation conditions. Nonetheless, there are still some urgent issues that need to be addressed and improved in the current study.

(1) The profile control agents currently utilized are primarily polyacrylamide-based microspheres, which have exhibited promising results in laboratory experiments and numerical simulations. However, there is a scarcity of data regarding their performance in actual reservoirs. Efforts should be made to reduce production costs, improve actual oil recovery effects, and diversify the materials and functions of polymer microspheres.

(2) Residual oil is present in harsh reservoir environments characterized by high temperatures and salinity levels. Additionally, current oil fields exhibit diverse geological conditions. Therefore, further optimization and design should be summarized to achieve control over the size, structure, and surface properties of polymer microspheres, thereby enhancing their adaptability and stability in complex geological conditions.

(3) There is a need for systematic research on the mechanisms of polymer microspheres in EOR. Comprehensive analysis of the synergistic effects of multiple mechanisms is required to achieve unity among structure, performance, and mechanism. Additional verification is needed in areas such as the microstructure and surface properties of polymer microspheres, the properties of porous media, and the interactions between fluids and porous media.

(4) By integrating advanced simulation and testing techniques, it is important to analyze the structural properties of different functionalized microspheres, predict their behavior and effects in reservoirs, and establish systematic, rational, standardized, and effective performance evaluation indicators.

References

[1] Shagymgereyeva S, Sarsenbekuly B, Kang W L, et al. Advances of polymer microspheres and its applications for enhanced oil recovery. Colloids and Surfaces B: Biointerfaces, 2024, 233: 113622
[2] Zhang X, Deng J N, Yang K, et al. High-strength and self-degradable sodium alginate/ polyacrylamide preformed particle gels for conformance control to enhance oil recovery. Petroleum Science, 2022, 19(6): 3149-3158.
[3] Chen X, Li Y Q, Liu Z Y, et al. Investigation on matching relationship and plugging mechanism of self-adaptive micro-gel (SMG) as a profile control and oil displacement agent. Powder Technology, 2020, 364: 774-784.
[4] Shi X D, Yue X A. Migration and plugging mechanisms of self-aggregated microspheres as a novel profile control. Journal of Petroleum Science & Engineering, 2020, 184: 106458.
[5] Gao K, Liu J Y, Li X, et al. Lignin nanoparticles as highly efficient, recyclable emulsifiers for enhanced oil recovery. ACS Sustainable Chemistry & Engineering, 2022, 10(29): 9334-9344.
[6] Kawaguchi H. Functional polymer microspheres. Progress in Polymer Science, 2000, 25(8): 1171-1210.
[7] Wang Q H, Chen B, Wang X J, et al. Preparation and profile control evaluation of core-shell structure and surface-hydrophobic modified polyacrylamide microsphere. Journal of Applied Polymer

ISSN 2616-5880 Vol. 5, Issue 2: 11-17, DOI: 10.25236/AJMC.2024.050203

Science, 2022, 139(45): e53110.
[8] Tang X C, Kang W L, Zhou B B, et al. Characteristics of composite microspheres for in-depth profile control in oilfields and the effects of polymerizable silica nanoparticles. Powder Technology, 2020, 359: 205-215.
[9] Mohammadi M S, Sahraei E, Bayati B. Synthesis optimization and characterization of high molecular weight polymeric nanoparticles as EOR agent for harsh condition reservoirs. Journal of Polymer Research, 2020, 27(2): 41.
[10] Ma X, Zhou Y H, Yi P, et al. Design, preparation and properties of new polyacrylamide based composite nano-microspheres with like "ball in ball" structure. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022, 654: 130037.
[11] Yang H B, Hu L L, Chen C, et al. Synthesis and plugging behavior of fluorescent polymer microspheres as a kind of conformance control agent in reservoirs. RSC Advances, 2018, 8(19): 1478-1488.
[12] Yang H B, Hu L L, Chen C, et al. Influence mechanism of fluorescent monomer on the performance of polymer microspheres. Journal of Molecular Liquids, 2020, 308: 113081.
[13] Lai N J, Wang D D, Wang J Q, et al. Stability, treatment, and enhance oil recovery ability of fluorescent preformed gel CQDS@PPG, and its migration status study. Chemistry and Technology of Fuels and Oils, 2023, 58(6): 1053-1066.
[14] Su M R, Ruan L, Dong X Y, et al. Current state of knowledge on intelligent-response biological and other macromolecular hydrogels in biomedical engineering: A review. International Journal of Biological Macromolecules, 2023, 227: 472-492.
[15] Zhou Y H, Luo Z, Xu M, et al. Preparation and properties of temperature-sensitive P(NIPAM-AM) nano-microspheres in enhanced oil recovery. Energy & Fuels, 2023, 37(1): 204-213.
[16] Jamali A, Moghbeli M R, Ameli F, et al. Synthesis and characterization of pH-sensitive poly (acrylamide-co-methylenebisacrylamide-co-acrylic acid) hydrogel microspheres containing silica nanoparticles: Application in enhanced oil recovery processes. Journal of Applied Polymer Science, 2020, 137(12): 48491.
[17] Khalil M, Fahmi A, Nizardo N M, et al. Thermosensitive core-shell Fe3O4@poly(N-isopropylacrylamide) nanogels for enhanced oil recovery. Langmuir, 2021, 37(29): 8855-8865.
[18] Asl F O, Zargar G, Manshad A K, et al. Experimental investigation and simulation for hybrid of nanocomposite and surfactant as EOR process in carbonate oil reservoirs. Fuel (Guildford), 2022, 319: 123591.
[19] Sircar A, Rayavarapu K, Bist N, et al. Applications of nanoparticles in enhanced oil recovery. Petroleum Research, 2022, 7(1): 77-90.
[20] Ji J Q, Zhao J Q, Ke Y C. In situ fabrication of graphene-scaffold poly(acrylamide-acrylic acid-4-acryloylmorpholine) microspheres as a novel plugging agent for profile control. Journal of Materials Science, 2020, 55(29): 14137-14152.
[21] Liu L, Gou S H, Fang S W, et al. Organic-inorganic microspheres of temperature-controlled size for profile control. Journal of Molecular Liquids, 2020, 317: 113993.
[22] Song Z Z, Hu J H, Liu P, et al. Synthesis and performance evaluation of alginate-coated temperature-sensitive polymer gel microspheres. Gels, 2023, 9(6).
[23] Cao M J, Cai Q, Guo G F, et al. The synthesis and water-swelling performances of magnetic composite microspheres with multi-shell structures via a combination method. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2020, 602: 125114.
[24] Liu J C, Almakimi A, Wei M Z, et al. A comprehensive review of experimental evaluation methods and results of polymer micro/nanogels for enhanced oil recovery and reduced water production. Fuel (Guildford), 2022, 324: 124664.
[25] Yang H B, Shao S, Zhu T Y, et al. Shear resistance performance of low elastic polymer microspheres used for conformance control treatment. Journal of Industrial and Engineering Chemistry, 2019, 79: 295-306.
[26] Wang H Y, Lin M Q, Dong Z X, et al. Study on the association behavior of synthesized hydrophobically associating polymer microspheres. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2020, 598: 124829.
[27] Wang S, Tang Z L, Qu J, et al. Research on the mechanisms of polyacrylamide nanospheres with different size distributions in enhanced oil recovery. RSC Advances, 2021, 11(1): 5763-5772.
[28] Li J B, Niu L W, Wu W X, et al. The reservoir adaptability and oil displacement mechanism of polymer microspheres. Polymers, 2020, 12(4): 885.
[29] Geng J M, Shi X D, Han P, et al. Experimental study on charged nanogels for interfacial tension reduction and emulsion stabilization at various salinities and oil types. Energy & Fuels, 2020, 34(12): 15894-15904.
[30] Liang T, Hou J R, Qu M, et al. High-viscosity α-starch nanogel particles to enhance oil recovery. RSC Advances, 2020, 1(14): 8275-8285.