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PROGRESS OF POLYMER MICROSPHERES FOR PROFILE CONTROL IN OIL FIELD

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For the past decades, long-term water flooding processes have to water channeling in mature reservoirs, which is a severe problem in oilfields. The development of better plugging ability and cost-effective polymer microspheres is a key aspect for the control of excess water production. Research on polymer microspheres applicable in a heterogeneous reservoir to plug high permeable channels has been growing significantly as revealed by numerous published scientific papers. This review intends to discuss different types of the polymer microspheres and oil displacement efficiency. The related difficulties and future prospects of polymer microspheres are also covered. The review provides a basis to develop polymer microspheres for future applications in oilfields. It will assist the researchers to further develop polymer microspheres to improve the oil recovery from mature reservoirs under economic conditions to meet the requirements of future oilfields.

Key words: polymer microspheres, fluorescent polymer microspheres, elastic polymer microspheres, profile control, oil displacement.

Introduction

The production of non-renewable oil is becoming more difficult as the development time of the field lengthens. As a means to enhance the productivity levels, petroleum field engineers strive to implement specific methods to address this issue. The great number of oil reservoirs around the world have been developed with a use of water injection, which consequently results in destruction of pore structures. Expanded radius of pore throats in the oil reservoirs are a common effect of the incessant application of water flooding [1]. Furthermore, combination of these aspects can cause the structure of “preferential channels”, which settles among flooding and producing wells. By the time the preferential channels become a holder of the redundant water in the system, decreases the capability of water circulation [2–3]. In other circumstances this can lead to the large percentage of water content in the final stages of oil production. The complications of oil reservoir eroding can bring adverse effects on oil recovery ratio, inflate the energy expenditure and, finally, violate the elements of the surroundings [4].

Following stages of chemical flooding, as well, can be diminished in impact, due to the presence of presential channels enclosed by injection wells and production wells. Polymer gels and other profile control techniques can prevent, to some extent, the flood water from inefficient circulation along the preferential channels [5-10]. In order to counter the negative repercussions of the water flooding, the last decades advanced profile control techniques, especially, the polymer gel treatments have been widely practiced [11]. However, when it comes to in-depth breakthroughs of reservoirs and pore throats with greater radii, the influence of treatments mentioned below are limited.

Due to the deeper understanding of reservoirs, the use of chemicals in deep processing of reservoirs has received a lot of attention. The incessant works in production of preformed particle gels (PPG), polymer microspheres, inorganic gel coatings, and other deep liquid flow-diverting agents are promising ways of solving the given problem [12–18].

It is commonly known that polymer microspheres are distinguished by high resistance capabilities to the heat, salt and quality to migrate in the in-depth levels [19]. Nano-sized and micro-sized polymer microspheres are predominantly used in profile control. Concerning oil fields with harsh waterlogging issues, as well as immensely dispersed oil which are remained in deep reservoirs, adopting polymer microspheres are implied to adjust water eroding and enhance the swing efficiency. Today, the technology of deep control of polymer microspheres is being examined worldwide and is successfully applied to obtain an increased oil content and a reduced water content in fields [20–23].

Rather high reservoir compliance abilities and possibility of oil rearrangement in deep reservoirs are considered as main advantages of polymer microsphere and are being thoroughly studied worldwide. Furthermore, many researchers have underlined the importance of relation between polymer microsphere size and reservoir pore channel and how obtaining these data can immensely result in profile control regulations.

Zhao et al. [24] and Dai et al. [25] explained the correspondence between polymer microspheres and rock core pores. They applied the matching factor and figured out, that the optimum shut-off and in-depth fluid diversion effects of polymer microspheres are possible obtained only in particular scope of the matching factor. It is considered, that micron-sized are suitable for high permeability cores, whereas nano-sized polymer microspheres can be applied to cover low-permeability cores [26]. When it comes to the in-depth oil displacement mechanism, polymer microspheres are aimed to encompass in-depth strata and attain in-depth fluid diversion [25–29]. Micron-sized polyacrylamide elastic microspheres may pertain the water flow by throat plugging through the mechanisms of trapping plugging, bundle plugging, and joined plugging [30].

The polymer microspheres, in spite of wide research, characterization, and applications in numerous reservoirs, they possess few limitations under the harsh reservoir conditions. With this aim in mind, the review article aims to elaborate and summarize the current polymer microsphere techniques from innovations to applications and problems associated with them along with their advantages, as well as the limitations for future developments of polymer microspheres for harsh reservoir conditions. Hence, this paper strives to provide thorough material bases for the further investigations of polymer microspheres and more efficient execution in oil development processes.

Polymer microspheres

As stated in the preceding studies, at the moment the majority of developed oil reservoirs are prevailing with induced fractures or high permeability channels, which can be named as thief zones. The preeminent reason of formation of these zones is the continuous water injection. The lack of efficiency of the injected water, which can create the redundant water usage and rapid production drop, can lead to the considerable issues when it comes to the final production stages of the developed oil fields [31–34]. Thus, it has been considered crucial for the oil industry to implement more predictable approaches as “green” water shut-off or coherence control. Gels had been brought in as water plugging agents to solve the occurring issue [35–39]. Applying the gel can lead to blocking off the fractures, as well as regulating direction of the water flow from higher permeable areas to zones with lower permeability.

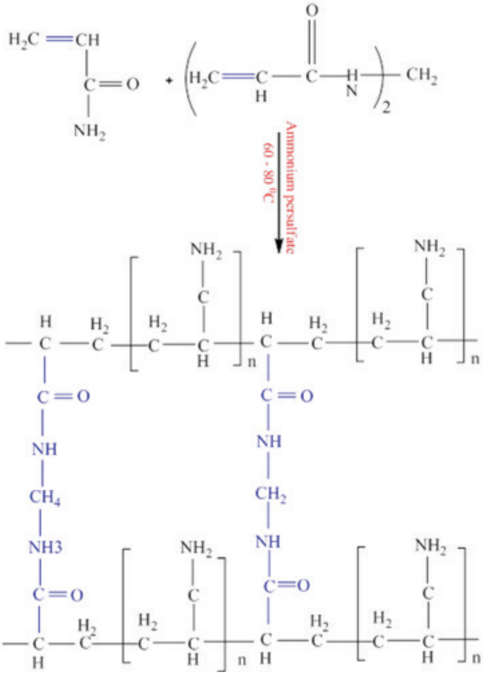

Figure 1. The synthesis reaction of microsphere from AM and MBA [46]

The analyses taken place in Shengli, Dagang and Jidong oilfields have demonstrated that polymer microsphere was a promising conformance control agent in the production of heterogeneous reservoirs, especially the matured reservoirs

[46–47]. Hua and Lin et al. studied the shape, size, rheological properties, plugging properties, profile control mechanism and oil displacement mechanism of the nanoscale polymer microspheres. They addressed the ability of polymer microspheres to decrease water permeability due to the microspheres adsorbed, gathered and linked in the pore throat, which is followed by the adsorbed layers to disintegrate under the pressure, flowing deep inside the reservoir by reason of rather high destructure properties of the microsphere [48]. Yao and Wang et al. mentioned the impact of ionic strength on the movement and confinement of polyacrylamide microspheres in porous media [49]. Yang and Kang et al. Studied the mechanism and in-situencing factors on the former particle size and swelling capacity of polymer microspheres from the synthesis and reservoir condition [50]. Yang and Xie et al. made advancements in the injection parameters of polymer microspheres and polymer composite flooding system. Furthermore, they concluded that the polymer flooding can be significantly enhanced by inclusion of the composites [51].

An advanced concept of an agent for water operation was presented via an increased viscosity of microsphere solutions caused by swelling. In order to reach this objective usual cross-linkers (phenolic, formaldehyde, chromic salt) can be used in polymer gel systems, and also microspheres can be added during the process of injection. Consequently, bulk gels can be formed in the high permeable channels because of cross-linking reactions with carboxyl or amide groups, which usually become available during swelling. This ultimately helps in a further managing of the production water.

Fluorescent polymer microspheres

The quantitative perspective cannot be considered as reliable approach to investigate the plugging behavior and conformance control mechanism. Regarding these reasons, fluorescent polymer microspheres may be able to address the limits of current approaches, consequently, obtain the up-to-date apprehension of polymer microspheres concentration, along with the movements of polymer microspheres inside the reservoir at the time of flooding proceeds. Fluorescent polymer microspheres have a binal objectives, is one being the conformance agent, second acting a role of the oil field tracer. The oil field tracker will be a innovative utilization of fluorescent polymer microspheres in the improvement of oil fields.

Fluorescent polymer microspheres are more commonly seen to get manually dyed through absorption or embedment, consequently leading to the problem of dye outpouring, thus constricting the practical functions of given fluorescent polymer microspheres. To avoid dye outpouring, dyes could be covalently integrated with polymer microsphere by the inverse suspension polymerization [52–53]. Rhodamine B (RhB), which is mostly known for utilizations medical field, environmental protection, textiles, colored glass, and cosmetics, is a traditionally used as a fluorescent dye in current market [54].

Hongbin Yang et al. described the particular kind of fluorescent polymer micro-spheres P(AM-BA-RhB), which performed as a new conformance control agent [55]. The fluorescent polymer microspheres were covalently stained with Allyl Rhodamine B, through inverse suspension polymerization.

Applying the same method of polymerization different fluorescent polymer microsphere, P(AM-BA-AMCO), was prepared by Wan-Li Kang et al. [56–61].

The production of both types of fluorescent polymers uses the same inverse suspension polymerization method, which can be observed in Table 1. The grain shaped outcome of the reaction process projects great absorption capacity, at the same time it was noticed to dry fairly quickly.

In addition, the average particle size of the product can be manipulated by the conditions of the inverse suspension polymerization. Hence, the impact of the preparation conditions such as stirring speed, the concentrations of initiator, dispersant is of utmost importance regarding the average size of the product.

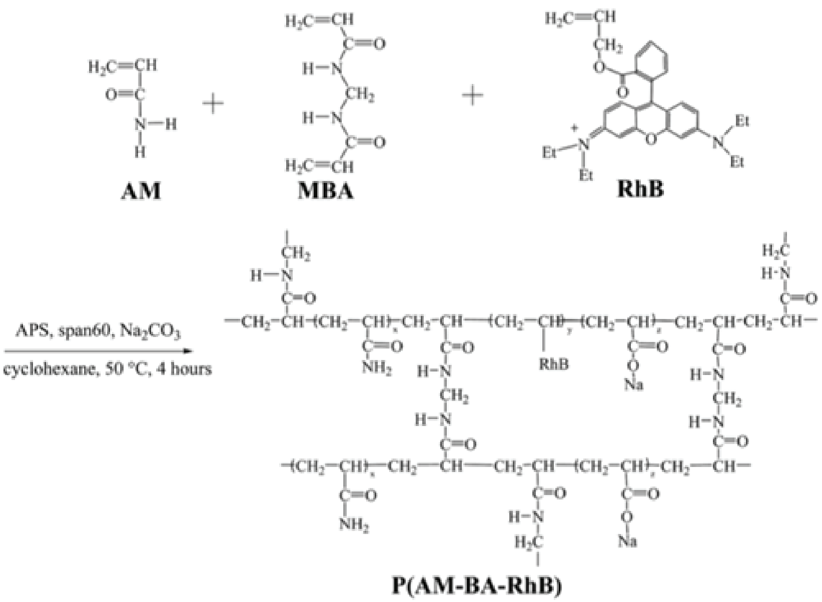

Figure 2. Synthesis route of P(AM-BA-RhB) [64]

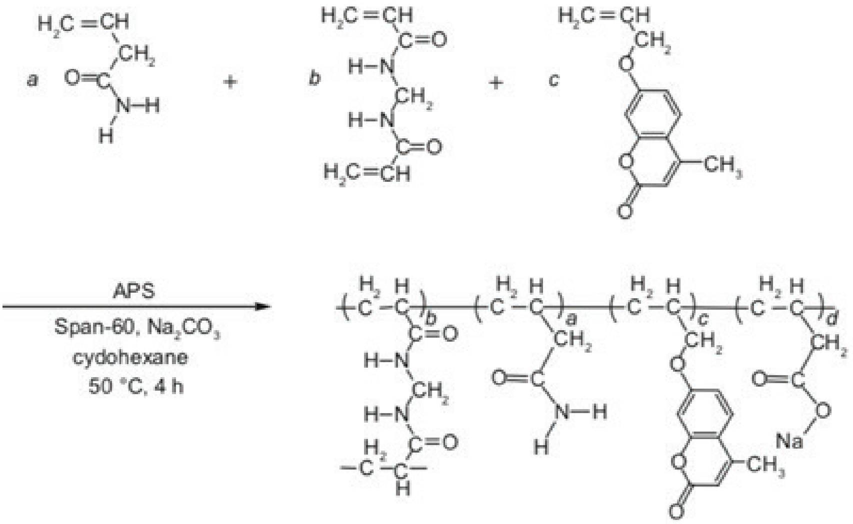

Figure 3. Synthesis route of P(AM-BA-AMCO) [66]

Table 1. Synthesis of fluorescent polymer microspheres P(AM-BA-RhB) and P(AM-BA-AMCO)

Fluorescent polymer	Monomer	Fluorescent monomer	Oil based dispersant	Electro-lyte	Water soluble initiator	Cross linking agent	Synthesis method
P(AM-BA-RhB)	AM	RhB	Span 60	Na_2CO_3	APS	MBA	Inverse suspension
P(AM-BA-AMCO)	AM	AMCO	Span 60	Na_2CO_3	APS	MBA	Inverse suspension

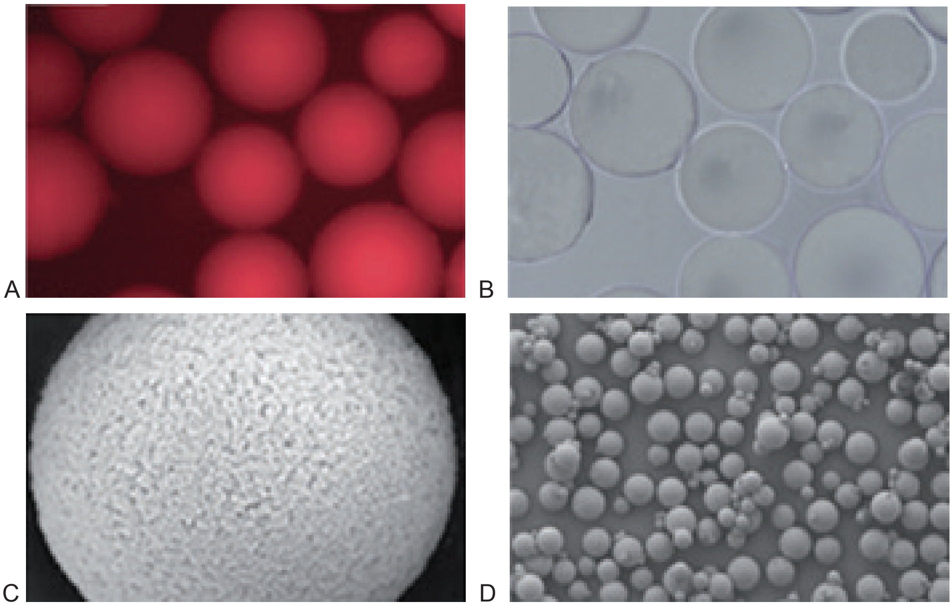

Figure 4. Morphology of fluorescent polymer microspheres P(AM-BA-RhB): (A) the micrograph of swollen microspheres analyzed under the ultraviolet enhancement with an inverse fluorescence microscope; (B) the micrograph of the swollen microspheres under the nature light with an inverse fluorescence microscope; (C) SEM image for microspheres next swelling; (D) SEM image for microspheres before swelling [74]

The main tools to investigate the morphology of the P(AM-BA-RhB) polymer microspheres were a fluorescence microscope (Fig. 4A and B), a scanning electron microscope (Fig. 4C and D), as well as an environment scanning electron microscope (Fig. 4). Fig. 4 provides the particle size test, including the three-dimensional joined systems of fluorescent polymer microspheres P(AM-BA-RhB) previous the swelling and subsequently swelling process. According to the illustration given in Fig. 3, the fluorescent polymer microspheres P(AM-BA-RhB) are spherical particles, possess the ability to continuously swell, because of the water absorption for a certain span of time (see Fig. 4D and C) [67–71].

By the time the fluorescent polymer microspheres P(AM-BA-RhB) contact with salted water, due to the applied osmotic pressure the water particles intent to flow directly to the internal systems, by expanding the molecules it is possible to enhance the volume of polymer microspheres. The three-dimensional joined systems can be clearly distinguished in Fig. 4C. The difference of moderate particle sizes of fluorescent polymer microspheres P(AM-BA-RhB) before and after swelling are rather significant. Furthermore, from Fig. 4A and B, it can be detected that the enlarged polymer microspheres P(AM-BA-RhB) acquire quite distinct fluorescent properties. Examined under UV light the polymer microspheres beam red fluorescence, meanwhile under the normal light the polymer microspheres were seen as clear, lucent and transparent [72–74].

The surface topography of P(AM-BA-AMCO) microspheres is given in Fig. 5. The phase-contrast images of Fig. 5A, C were made in daylight conditions. Figure 5B, D was made after ultraviolet enhancement. Additionally, fluorescent microspheres were spherical, with an even exterior, the average diameter was around 200 μm.

In addition, pictures taken from fluorescence microscopy displayed the even distribution of the monomers within the polymer and were able to sustain the fluorescent ability subsequent to the swelling processes. After the latter water flooding test, P(AM-BA-AMCO) microspheres emerged directly from the separated sand pack can be indicated in Figure 5C. examining the formed liquid can be clearly noticed the particles of P(AM-BA-AMCO) microspheres. Nevertheless, these microspheres were able transmit blue fluorescence, despite the fact that the particle shapes and sizes were extruded and distorted. Due to these abilities the P(AM-BA-AMCO) microspheres can be regarded as the promising tracker agents in the oil fields.

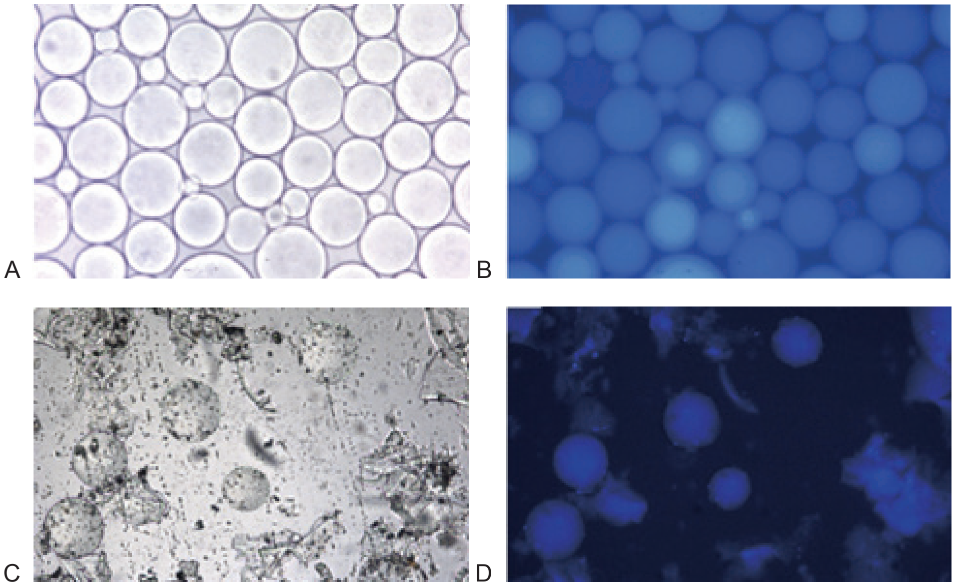

Figure 5. Fluorescence microscope images of P(AM-BA-AMCO) microspheres. (A) Phase-contrast image made under the daylight after swelling for 24 h in brine; (B) Fluorescence micrographs for the (A) made under ultraviolet radiation; (C) Phase-contrast image of microspheres made under the daylight; (D) Fluorescence micrographs for the (C) made under ultraviolet radiation [75]

Thus, fluorescent polymer microspheres have gained wide recognition as a novel conformance-control agent in the recent few years. Due to the high tolerance to the harsh conditions of the pore zones, great elastic properties, the capacity to thoroughly probe sandstone layers. In every flooding experiment with the microspheres in porous media rupture elements were not observed. Consequently, the need to the further research regarding plugging abilities of the microspheres is prevalent for current conformance control technology.

Elastic polymer microspheres

Last ten years, a new conformance control and flooding agent “elastic microspheres” was invited and become more prominent amongst the other agents [76, 77]. Elastic microspheres are spherical shaped with three-dimensional cross- linked system and the design principle is that according to micro-scale feature of reservoir rock’s pore throats, elastic microspheres matching with pore throats were composed; using mechanism of "migration, sealing, elastic deformation and then movement, then blocking" in the reservoir, elastic microspheres are able to plug and transport in high permeability layer continually and enter the deep at last so as to increase swept volume of oil-rich region and enhance oil recovery. Researchers can confirm that elastic microspheres at the harsh conditions of the reservoirs such as high temperature and salinity display rather good impedance properties, stronger intensity of profile control, high resistance coefficient and residual resistance coefficient, lower cost and better applicability and so on. Additionally, it displayed a great impact on profile control and flooding. Yao et al. [78] presented a novel enhanced oil recovery method using pore-scale elastic microspheres after polymer flooding. By using single-tube sand pack models, they studied the resistant coefficient of polymer flooding and elastic microspheres profile control and flooding. Therefore, the outcome of the research indicate that polymer and elastic microspheres have synergistic effect. On the one hand, polymer with higher viscosity can carry elastic microspheres and polymer adsorption can decrease roughness of pore throats which make the movement of elastic microspheres effortless;

besides, elastic microspheres have higher plugging strength so as to prevent polymer from crossing flow straight into the high permeability channel and extend the polymer output time of oil well.

Polymer and elastic microspheres are observed to show interdependent properties. The polymer can make the movement of elastic microspheres freely; the elastic microspheres can prevent polymer from flowing towards the inside of the high permeability channel and prolong the polymer production time of oil well. Compared to polymer flooding (1000 mg/L) and (2000 mg/L), polymer (1000 mg/L) and elastic microspheres (1000 mg/L) flooding can enhance oil recovery by 5.6 and 4.4%. Polymer and elastic microspheres profile control and flooding can cause positive affect on oil recovery.

Low elastic polymer microspheres

In recent years, the uplift point is a main descriptive value of the manufactured polymer microspheres. The uplift point polymer microspheres perform low deformation and injection capabilities, at the same time shear failure as an reaction to the water distend. Thus, causes limited plugging effect [79]. This concludes the basis to immediate production of polymer microspheres which obtains the rather low emporium, performs reliable deformation ability in the injection process, at the same time able to resist the distortion, so as to meet the requirements of “injection” and “plugging” in the oilfield. Additionally, at present, the swelling ratio of polymer microspheres could be regarded as the major concern.

Herein, based on the previous research about the compatibility of low elastic polymer microsphere (L-EPM) with porous medium by laboratory experiments [80]. The filtration characteristics and formation damage degree of L-EPM conformance control system were emphatically evaluated in the work conducted by Yang H. et al. [81], where the conformance control mechanism of the L-EPM conformance control system was investigated thoroughly the conformance control abilities for oil and water and conformance control impact under heterogeneous conditions. The outcome of the research can drastically change the viewpoint of the usage percentage of L-EPM, the efficient application as the conformance control treatment of L-EPM in fractured and heterogeneous reservoirs.

Low elastic polymer microsphere (L-EPM) is commonly regarded a propitious conformance control agent. The aspects of filtration deplete, core damage, selective conformance control abilities of L-EPM conformance control system were researched in the last few years. The results showed that L-EPM system had less damage to the matrix core and the influence of filtration loss on conformance control treatment could be neglected in indoor experiments. After the reparation of the permeability zone, the increase of the production rate was clearly observed.

Viscoelastic polymer microspheres

Viscoelastic microspheres are unique type of viscoelastic blocking agent, possess distinctive structure compared to polymer gels, the major objective while the production process of the viscoelastic polymers is the pore zone conditions [82, 83]. By implementing viscoelastic microspheres on the production wells, the engineers intend to decrease the negative environmental impact [83]. Compared to the pore throat radius viscoelastic microspheres with larger radius are able to flow through the porous media under pressure change, the result of which is the expulsion reaction is drastically enhanced.

Viscoelastic microspheres are prepared by different particle size based on pore characteristics of the target layer in underground conditions. Viscoelastic microsphere and preformed particle gel are two similar plugging agents. Both of them have the property of swelling and plugging; however, the preparation method, initial size, and appearance are different.

By implementing inverse suspension polymerization to produce the viscoelastic polymer, it can be possible to regulate the size of viscoelastic polymer microspheres regarding the condition of the pore zone which will be subsequently treated. The main advantage working with the viscoelastic polymers is their strength to sustain their form and high resistance to the pressure. Under the pressure viscoelastic polymers were observed to not fracture, however, they are able to transform, which indicates good rheological capabilities.

Disseminated viscoelastic microsphere has the complex structure that is formed by including viscoelastic microspheres and polymer solution. Mostly viscoelastic microsphere aims to enhance the viscoelastic abilities of the system as well as to block the high permeability channel, afterwards the polymer solution can append the viscoelastic microspheres in order to compensate the strength of the disseminated viscoelastic microsphere network. As a result, the water can go into the low permeability area and displace the remaining oil [84]. At the moment, disseminated viscoelastic microsphere flooding operations are widely used in different oil fields in China due to the of the advanced rheological capabilities of the dispersion system, e.g., the shear-thickening abilities. It worth to mention the lack of research performed about the rheological properties of disseminated viscoelastic microsphere structure. Although dilatant fluid has been studied experimentally, few investigations from the perspective of energy have been reported [85]. Recent research related to shear-thickening fluids have enriched the understanding of the fluids' characterization with large amplitude oscillatory shear amplitude measurements methods [86]. Jiang et al. [87] studied the influence of particles on the mechanical performance of the poly(styrene-acrylic acid) based dilatant fluid and displayed an applicable mechanism for the shear thickening behavior. They found that the shear thickening effects were considerably affected by the surface charges and the particles' hardness, in which case they could be controlled by varying the monomer ratio of the precursor and the relative crosslink density.

Recent studies show that cooperation of viscoelastic microsphere with the surface-active agent widely implemented in conformance control technology. The surface-active agents are taken up by viscoelastic microspheres. Therefore, the surface-active agents can alter the prominent characteristics of the viscoelastic microspheres such as deformation properties. The efficiency of oil production can be greatly affected by before mentioned components, which require further investigations to be completed in this area of research.

The profile control that employs viscoelastic microspheres for enhancing oil recovery is a novel technology that has attracted widespread interest. Viscoelastic microspheres are observed to affect plug high-permeability zones, influence the level of the sweep volume of low-permeability zones, which can better improve the effect of development, thus can be represented as a promising conformance control agent.

Polymer nano-composite microspheres

Controlling the water cut and improving the sweep efficiency are crucial for enhanced oil recovery (EOR) in heterogeneous reservoirs. Toward the goals, polymer microspheres gained significant popularity and have been widely applied to profile control and EOR. These kind of elastic spheres with nano and micro scaled size are able to block the high permeability channels via adsorption, accumulation and bridging, and divert the subsequent flow into the upswept areas [88]. However, the commonly observed polymer microspheres display significant disadvantages because they perform scarcely in rough reservoir conditions, such as high temperature, high salinity and high mechanical shearing, losing the profile control ability [89]. These can be regarded as the major objectives of the current petroleum industry to advance the abilities of these microspheres. By including inorganic nanofillers into multifarious polymer matrices on the nanoscale in order to produce the polymeric/inorganic nanocomposites can be seen as the comprehensive way to solve the main drawbacks of polymer materials [90]. These composite materials obtain the ability to perform the capacity such as mechanical, thermal, toughness, electrical and rheological properties, it can be observed that they are extensively applied in the fields of high-performance functional coatings, engineering plastics, catalysis, medicine, biology, and petroleum industry. Regarding different advancements achieved in the field of nanocomposite materials with microspores, the main obstacle remains to be the taking full advantage from both chemical and science aspects. Nanofillers are mainly exploited in composite materials applying nanotubes, layered silicates (e.g., MMT, kaolin), nanometals (e.g., Ni, Co), nano-oxides (e.g., ZnO, ZrO_2), semiconductors (e.g., InSb, CdS), and so on, among which SiO_2 particles, probably the most frequently used inorganic nanomaterials, have been attracting increasing attention in many fields [91]. These particles with unique molecular dimension, high surface activity and specific surface area can behave as structure and morphology directors, introducing high-efficiency energy dissipation mechanism and generating a variety of enhanced capabilities in nanocomposites [92]. Additionally, organic polymer matrices and inorganic nanofillers are observed to show disbalance between each other, then commonly affects in bad performance when preparing the nanocomposites. Because the pristine SiO_2 nanoparticles tend to aggregate on account of their surface energy and the polycondensation of silanols, they cannot disperse uniformly in the polymer matrix, limiting the specific nanometer effect.

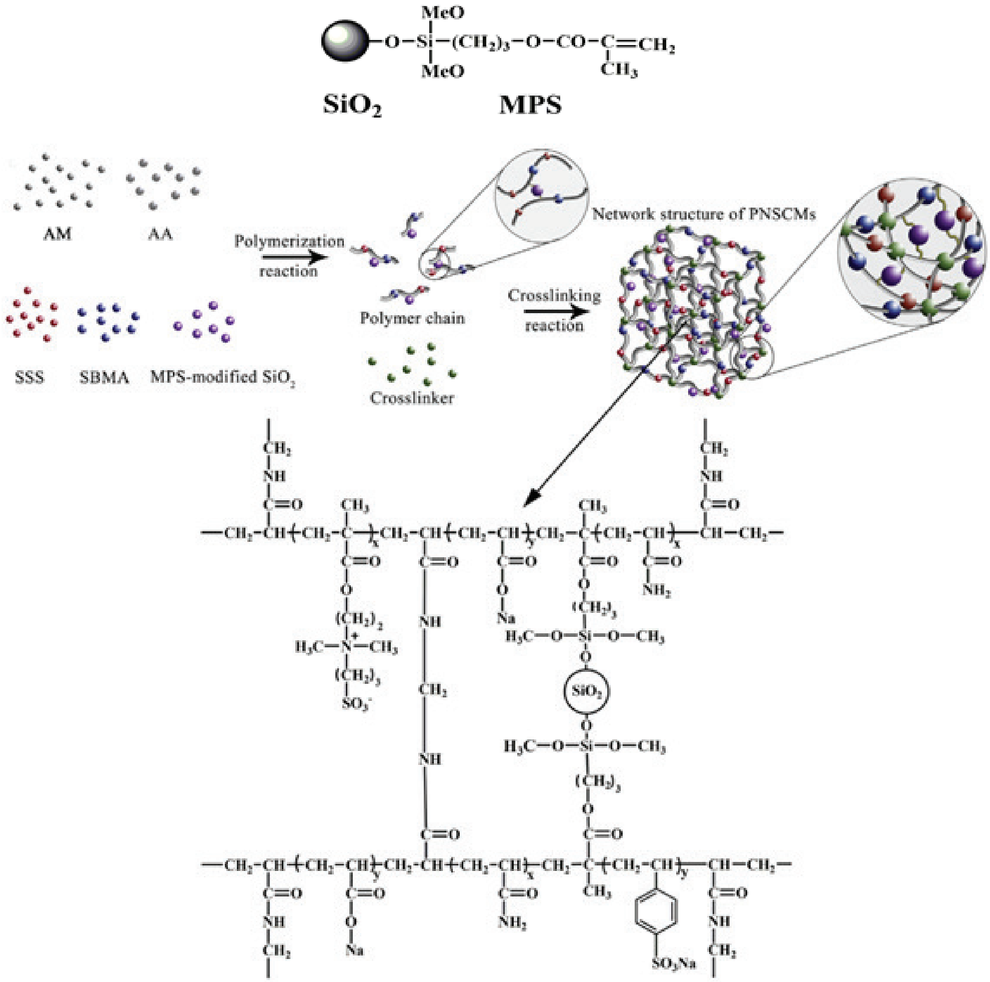

Figure 6. Structural formulas and synthesis processes of (A) MPS-modified SiO_2 and (B) PNSCMs [95]

Thus, it is imperative to conduct surface modification to better improve the performance of silica particles, which can not only effectively enhance silica particles' dispersibility, but also combine them with other materials by chemical interaction simultaneously. Chemical methods involve modification either by grafting polymers or modifiers. The silane coupling agent 3- methacryloxypropyltrimethoxysilane (MPS) is one of the most conventionally operated modifiers, which has hydrolyzable and organo- functional ends [93,94]. The hydrolysable methoxy groups react with the silanols on the SiO_2 surface, while the alkyl chains containing CC double bonds react with the polymer chains. Hence, these functionalized SiO_2 nanoparticles would exhibit outstanding compatibility with the organic phase and can be efficiently trapped. Therefore, Tang et al. [95] proposed the polymer/nano-SiO_2 composite microspheres (PNSCMs) using MPS-modified SiO_2 as reinforcing material to obtain ideal conformance control agent. The nanofiller MPS-modified SiO_2 was prepared by surface modification of the pristine SiO_2, and its structural formula is shown in Fig. 6A, which contains polymerizable reactive groups, and exhibits good dispersion ability and certain oil-water amphiphilicity. PNSCMs were made through inverse suspension polymerization. 2.4 g of emulsifier span 60 and different weight fractions of MPS-modified SiO_2 nanoparticles (0, 0.5, 1.0, 2.0 wt %, compared to the water phase) were dispersed in 80 mL of aviation kerosene as the oil phase. AM, AA, SSS, SBMA, MBA, NaOH, NH4Cl, and PEG-200 were diffused in deionized water as the aqueous phase.

The advanced capabilities of the given agent are appropriate swelling capacity, tolerance to harsh conditions including high temperature, salinity and shear, excellent elastic deformation capacity and dispersion stability, and can migrate into and plug the high-permeability formation, however, they need further research and field applications to manifest their success.

Polymer microspheres oil displacement

The difference between oil recovery and enhanced oil recovery after profile control and injecting of polymer microspheres are mainly determined on the utilization degree of the remaining oil in the low-permeability layer. The given data above implies that microspheres with a different particle sizes are more efficient when it comes to enhancing the oil recovery from reservoirs under certain reservoir conditions, rather than microspheres with the same particle size. In the point of water injection, the high-permeability layer had the minimum retention threshold pressure, the maximum retention pressure differential (the gap within the injection pressure and retention threshold pressure), the major fluid absorption capability as well as deviation rate [90–95]. Correspondingly, the low-permeability layer had the highest retention threshold pressure and the lowest deviation rate. At the point of chemical flooding, the polymer microspheres are injected, took time to settle, and shut off the high-permeability layer, decreased the flow cross-section of pores; and immediately boosted the flow resistance. Due to the actions taken by polymers, the medium and low-permeability layers are constrained to absorb the fluid. Later, at the point of water injecting, with the extraction of polymer microspheres, the diversion level of high-permeability layer increased again, meanwhile the diversion of medium and low-permeability layers plummeted drastically [96–98]. The correlation between the water cut of each layer and the pore volume (PV) injected in the experiment were detected. The high-permeability layer water cut degree was close to maximum in the final steps of water flooding, but next the insertion of microspheres, the water cut dropped to a certain degree, while the oil recovery extended to the point. That can imply an inclusion to profile control, the polymer microspheres can also, to the certain point, activate the remnant oil and diminish the oil saturation. Fig.7 illustrates the movement of polymer microspheres in core pores. In the quite big pore spaces, the large the fluid in the center flowed faster, and the fluid closer to the edge flowed more slowly, so the fluid imposed a small force on the remnant oil on the of the rock pore [99, 100,102]. The polymer microspheres in a insignificant pore throat changed their shape and size, and the injected water moved onward gradually (Figure 7A).

The polymer microspheres emerge from the tight pore throat, than followed by immediate penetration occurred in the bigger pore throat at a specific displacing force, by thus the microspheres and fluids moved at an drastically growing speed in the large pore formations. Furthermore, the fluid streamline in the bigger pore spaces moves from the center to the perimeters of the pore throats. As the result, the remnant oil on the exteriority of the rock pore had gotten hit by the flowing fluid at the high speed, so the remnant oil was extracted from the surface of the rock pore and carried along with the fluid (Figure 7B). At the time when the polymer microspheres arrived at the small and tight pore throats, the fluid flow speed had been noticed to significantly drop, the fluid in the initial large pore formations leak out of disorder, and some of the fluid acted on the remnant oil at the linking point of the large and small core pores, so some remnant oil had been removed and carried along with sequent fluid (Figure 7C). In the majority of times the polymer microspheres enforced the remnant oil through the couple of mentioned actions to enhance the oil recovery from reservoirs. However, it is crucial to mention the limitations of the EOR.

In addition, the EOR mechanism is based on the polymer microspheres to regulate the fluid entry profiles of heterogeneous reservoirs, at the same time to increase the injected water-swept volume. The polymer microspheres possess great advantage at activating the remnant oil through brief shut-off → breakthrough → temporary shut-off [88, 103–107].

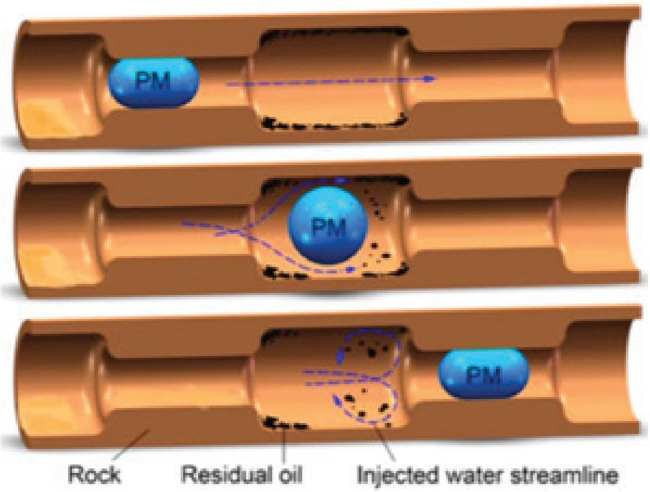

Figure 7. Migration of polymer microspheres in the core pore: polymer microspheres (A) temporarily shut off a narrow and small pore; (B) break through the small pore and enter a big pore; (C) temporarily shut-off a small pore [102]

Conclusions

In this paper, we summarized thoroughly the different types of polymer microspheres from the initial stage to current situation. Various polymer microspheres systems are described in detail, such as fluorescent polymer microspheres, nano-composite polymer microspheres, elastic and viscoelastic polymer microspheres, for better understand the current polymer microsphere technology. The problems which are now faced in these microspheres are discussed and solutions are proposed to overcome respective shortcomings.

Nano-composites has been successfully entered into the design of polymer microspheres, can behave as structure and morphology directors, introducing high-efficiency energy dissipation mechanism and generating a variety of enhanced capabilities in nano-composites. The use of nanoparticles turned out to be successful in many kinds of reservoirs, especially in ultra- deep carbonate reservoirs. Their applications have also shown excellent results in the production of medium to heavy oils.

It can be noted that polymer microspheres have been widely investigated in the last decades, however, they must still be optimized for example to introduce new technologies like the addition of nanoparticles. Systematic work is still required for producing more residual oil by using improved environmentally friendly methods. The area of profile control is still under strong consideration to further enhance the efficiency of oil recovery under harsh conditions.

The particles of polymer microspheres can change their shape and size depending on the specific pore zones, and are able to pass through pores throats with ease, thus can enter the in-depth structure and plug the high permeability channels. It can be concluded that polymer microspheres can be utilized as a highly promising profile control agent, additionally, fluorescent polymer microspheres can act as an oil field tracker.

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References

1. Alhuraishawy A.K., Bai B., Imqam A., Wei M., Fuel, 2018, 214, 332–350.
2. Sharifpour E., Riazi M., Ayatollahi S., Ind. Eng. Chem. Res., 2015, 54, 11136–11146.
3. Jia H., Pu W., Zhao J., Jin F., Ind. Eng. Chem. Res., 2010, 49, 9638–9654.
4. Zhao G., Dai C., Zhao M., You Q., J. Appl. Polym. Sci., 2014, 131, 39946.
5. Zhao G., Dai C., You Q., Zhao M., Zhao J., J. Sol-Gel Sci. Technol., 2013, 65, 393–398.
6. Dai C., Zhao G., You Q., Zhao M., J. Appl. Polym. Sci., 2014, 131, 40154.
7. Dai C., Zhao G., You Q., Zhao M., J. Appl. Polym. Sci., 2014, 131, 39462.
8. Pu J., Zhou J., Chen Y., Bai B., Energy Fuels, 2017, 31, 13600–13609.
9. Yang H., Kang W., Yu Y., Lu Y., Li Z., Wang M., Liu T., J. Appl. Polym. Sci., 2015, 132, 42278.
10. Yang H., Kang W., Jian Z., Bin Z., Colloids Surf., 2015, 487, 240–246.
11. Yao C., Lei G., Hou J., Xu X., Wang D., Steenhuis T.S., Ind. Eng. Chem. Res., 2015, 54, 10924–10934.
12. Yang H., Kang W., Wu H., Yu Y., Zhu Z., Wang P., Zhang X., Sarsenbekuly B., RSC Adv., 2017, 7, 8117–8129.
13. Seright R.S., SPE Prod. Facil., 1997, 12, 49–62.
14. Lin M., Zhang G., Hua Z., Zhao Q., Sun F., Colloids Surf., 2015, 477, 49–54.
15. Yang H., Kang W., Yin X., Tang X., Song S., Lashari Z. A., Bai B., Sarsenbekuly B., Powder Technol., 2017, 313, 188–199.
16. Wan T., Huang R., Zhao Q., Xiong L., Luo L., Tan X., Cai G., J. Appl. Polym. Sci., 2013, 130, 697–701.
17. Liu C., Liao X., Chang M., Zhang Y., Mu C., Li T., Qin R., Fu R., Bie X., Zheng J., SPE 158293 presented at SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 8–10 October 2012.
18. Yao C., Lei G., Li L., Gao X., Energy Fuels, 2012, 26, 5092– 5101.
19. Suleimanov B.A., Ismailov F.S., Veliyev E.F., J. Pet. Sci. Eng., 2011, 78, 421–447.
20. Saghafi H.R., J. Pet. Sci. Eng., 2018, 166, 977–999.
21. Niu L., Lu X., Xiong C., Tang X., Wu X., Jia X., Zhang S., Pet. Explor. Dev., 2013, 40, 698–789.
22. Yang H., Kang W., Yu Y., Yin X., Wang P., Zhang X., Powder Technol., 2017, 315, 478–485.
23. Ma Q., Zhang Z., Miao J., Guan Y., Xiao M., Guan Y., Chemistry & Bioengineering, 2010, 27, 80–81.
24. Zhao S., Pu W., Wei B., Xu X., Fuel, 2019, 235, 234–259.
25. Dai C., Liu Y., Zou C., You Q., Yang S., Zhao M., Zhao G., Wu Y., Sun Y., Fuel, 2017, 207, 111–127.
26. Nanthakumar A., Pon R. T., Mazumder A., Yu S., Watson A., Bioconjugate Chem., 2000, 11, 284–288.
27. Bosma G., Pathmamanoharan C., Hoog E. H., Kegel W. K., Blaaderen A., Lekkerkerker H. N., J. Colloid Interface Sci., 2002, 245, 291–300.
28. Jardine R. S., Bartlett P., Colloids Surf., A, 2002, 211, 117– 132.
29. Baggiani C., Anfossi L., Baravalle P., Giovannoli C., Giraudi G., Barolo C., Viscardi G., J. Sep. Sci., 2009, 32, 3298–3300.
30. Bao X., Shi J., Nie X., Zhou B., Wang X., Zhang L., Liao H., Pang T., Bioorg. Med. Chem., 2014, 22, 4827–4835.
31. Kang J., Yan J., Liu J., Qiu H., Yin X., Yang X., Wang E., Talanta, 2005, 66, 1015–1024.
32. Wang C. C., Masil A., Fernandez N., Talanta, 2008, 75, 125–140.
33. Liu Q.H., Liu J., Guo J.C., Yan X.L., Wang D.H., Chen L., Yan F.Y., Chen L.G., J. Mater. Chem., 2009, 19, 2018.
34. Yang W.B., Xia M., Li A., Yang L., Zhang Q., React. Funct. Polym., 2007, 67, 608–616.
35. Mart´ınez V. M., Arbeloa F. L., Prieto J. B., Arbeloa I. L., J. Phys. Chem., B, 2005, 109, 7441–7446.
36. Hua Z., Lin M., Guo J., Xu F., Li Z., Li M., J. Pet. Sci. Eng., 2013, 105, 71–75.

37. Bai B., Zhou J., Yin M., Pet. Explor. Dev., 2015, 42, 527–533.
38. Sang Q., Li Y., Yu L., Li Z., Dong M., Fuel, 2014, 136, 285–316.
39. Tongwa P., Bai B., J. Pet. Sci. Eng., 2014, 124, 37–49.
40. Guan S., Fan H., Duan J., Song C., J. Daqing Pet. Inst., 2007, 31, 108–112.
41. Imqam A., Bai B., Fuel, 2015, 148, 168–179.
42. Li J., Niu L., Lu X., J. Pet. Sci. Eng., 2019, 178, 1075–1193.
43. Xie K., Lu X., Pan H., Han D., Hu G., Zhang J., Zhang B., Cao B., SPE Prod. Oper., 2018, 33, 482–606.
44. Raffa P., Broekhuis A., Picchioni A. F., J. Appl. Polym. Sci., 2016, 113.
45. Goudarzi A., Zhang H., Varavei A., Taksaudom P., Hu Y., Delshad M., Bai B., Sepehrnoori K., Fuel, 2015, 140, 511–513.
46. Durán-Valencia C., Bai B., Reyes H., Fajardo-López R., Barragán-Aroche F., López-Ramírez S., Polym. J., 2014, 46, 280–294.
47. Almohsin A., Bai B., Imqam A.H., Wei M., Kang W., Delshad M., Sepehrnoori K., presented at SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 12–16 April 2014.
48. Hua Z., Lin M., Dong Z., Li M., Zhang G., Yang J., J. Colloid Interface Sci., 2014, 424, 67–74.
49. Yao C., Wang D., Wang J., Hou J., Lei G., Steenhuis T. S., Ind. Eng. Chem. Res., 2017, 56, 8157–8165.
50. Yang H., Kang W., Liu S., Bai B., Zhao J., Zhang B., J. Dispersion Sci. Technol., 2015, 36, 1678–1685.
51. Yang J., Xie X., Zhang J., Zheng X., Wei Z., Pet. Explor. Dev., 2014, 41, 795–797.
52. Lashari Z.A., Yang H., Zhu Z., Tang X., Cao C., Iqbal M.W., Kang W., J. Mol. Liq., 2018, 263, 88–128.
53. Abdulbaki M., Huh C., Sepehrnoori K., Delshad M., Varavei A., J. Pet. Sci. Eng., 2014, 122, 689–755.
54. Al-Ibadi A., Civan F., SPE Prod. Oper., 2013, 28, 378–412.
55. Yang H., Hu L., Chen C., Gao Y., Tang X., Yin X., Kang W., RSC Adv., 2018, 8, 10478-10480.
56. Kang W., Hu L., Zhang X., Yang R., Fan H., J. Geng, Pet. Sci., 2015, 12, 483-487
57. Irvine R., Davidson J., Baker M., Devlin R., Park H., presented at SPE Asia Pacific Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia, 11–13 August 2015.
58. Yang H., Hu L., Chen C., Gao Y., Tang X., Yin X., Kang W., RSC Adv., 2018, 8, 10480–10487.
59. Zhu D., Hou J., Chen Y., Zhao S., Bai B., Energy Fuels, 2018, 32, 3452–3781.
60. Li M., J. Huaqiao Univ., 2007, 28, 109–110.
61. Li J., Liu Y., Na Z., Zeng Z., Jiang H., Dispers J., Sci. Technol., 2014, 35, 111–145.
62. Zhou Y., Jiang H., Wang C., Li B., J. Dispers. Sci. Technol., 2014, 35, 1011–1013.
63. Yang H., Hu L., Chen C., Gao Y., Tang X., Yin X., Kang W., RSC Adv., 2018, 8, 10478-10485.
64. Lin M., Zhang G., Hua Z., Zhao Q., Sun F., Colloids Surf. A Physicochem. Eng., 2015, 477, 35–44.
65. Kang W., Hu L., Zhang X., Yang R., Fan H., Geng J., Pet. Sci., 2015, 12, 485-490
66. Yan L., Peng C., Ye Z., Chem. Res. Appl., 2012, 24, 996-1001.
67. Yu Z., Li Y., Sha O., Su Z., Zhou W., J. Appl. Polym. Sci. 2016, 131.
68. Xie K., Cao B. X., Lu W., Jiang Y., Zhang Q., Li K., Song J., Wang W., Liu J., Pet. Sci. Eng., 2019, 177, 534–565.
69. Xie K., Cao W., Lu X., Song K., Liu Y., Zhang Y., Liu J., Wang J., Na W., J. Dispers. Sci. Technol., 2019, 1–10.
70. Xie K., Lu X., Li Q., Jiang W., Yu Q., SPE J., 2016, 21, 001–007.
71. Li J., Niu L., Lu X., Energy Sci. Eng., 2019, 7, 2022–2038.
72. Pye D.J., J. Pet. Technol., 1964, 16, 908–913.
73. Al Adasani A., Bai B., J. Pet. Sci. Eng., 2011, 79, 10–23.
74. Al-Mjeni R., Arora A., Cherukupalli S., Wunnik P.K., Edwards J.N.M.V., Felber J., Gurpinar B.J., Hirasaki O., Miller G.J., Jackson C.A., Oilfield Rev., 2010, 22, 18–34.

75. Manrique E.J., Thomas C.P., Ravikiran R., Izadi Kamouei M., Lantz M., Romero J.L., Alvarado V., presented at SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 24–28 April 2010.
76. Zhao H. Z., Wu Z.L., Zheng X.Y., Lin M.Q., Li M.Y., Fine Chem., 2015, 62–64.
77. Pu W., Zhao S., Wang S., Wei B., Yuan C., Li Y., Colloids Surf. A Physicochem. Eng. Asp., 2018, 540, 235–265.
78. Yao C., Lei G., Cheng M., R. J. of Appl. Sci., 2013, 3634–3637.
79. Okubo M., Iwasaki Y., Yamamoto Y., Colloid Polym. Sci., 1992, 270, 733–737.
80. Yang H., Kang W., Yin X., Tang X., Song S., Lashari Z. A., Powder Technol., 2017, 313, 191–200.
81. Yang H., Zhou B., Zhu T., Wang P., Zhang X., Wang T., Galkine S. V., J. Pet. Sci. Eng., 2021, 196, 107708.
82. Thomas A., Gaillard N., Favero C., Oil Gas Sci. Technol. Rev. d’IFP Energ. Nouv., 2012, 67, 889–901.
83. Gaillard N., B.; Giovannetti T., Leblanc, A., Thomas O., Braun C., presented at SPE Latin American and Caribbean Petroleum Engineering Conference, Quito, Ecuador, 18–20 November 2015; Society of Petroleum Engineers: Richardson, TX, USA, 2015.
84. Seright R.S., Wavrik K.E., Zhang G., AlSofi A.M., SPE Reserv. Eval. Eng., 2020, 1–15.
85. Jouenne S., J. Pet. Sci. Eng., 2020, 195, 107545.
86. Jensen T., Kadhum M., Kozlowicz B., Sumner E., Malsam J., Muhammed F., Ravikiran R., presented at SPE Improved Oil Recovery Conference, Tulsa, OK, USA, 14–18 April 2018; Society of Petroleum Engineers: Richardson, TX, USA, 2018.
87. Yang H., Kang W., Yu Y., Lu Y., Li Z., Wang M., Liu T., 2015, J. Appl. Polym. Sci., 132(30), .42278
88. Li J., Niu L., Wu W., Sun M., Polymers, 2020, 12, 885-893.
89. Prasad D., Ernst B., Incera G., Leonhardt B., Reimann S., Mahler E., Zarfl M., presented at IOR 2017—19th European Symposium on Improved Oil Recovery, Stavanger, Norway, 24–27 April 2017.
90. Fournier R., Tiehi J.E., Zaitoun A., presented at SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 26–28 March 2018; Society of Petroleum Engineers: Kuala Lumpur, Malaysia, 2013.
91. Bakhshi M., Ozeiri M., Sharif A., Aalaie J., Korean J. Chem. Eng., 2017, 34, 900–911.
92. Viñarta S.C., Delgado O.D., Figueroa L.I., Fariña J.I., Carbohydr. Polym., 2013, 94, 493–502.
93. Schmid J., Meyer V., Sieber V., Appl. Microbiol. Biotechnol., 2011, 91, 922–937.
94. Liang K., Han P., Chen Q., Su X., Feng Y., ACS Omega, 2019, 4, 10610–10618.
95. Tang X., Kang W., Zhou B., Gao Y., Cao C., Guo S., Yang H., Powder Tech., 2019, 205-215.
96. Kim D., Krishnamoorti R., Ind. Eng. Chem. Res., 2015, 54, 3532–3787.
97. Pu W., Zhao S., Wang S., Wei B., Yuan C., Li Y., Colloids Surf. A Physicochem. Eng. Asp., 2018, 540, 235–265.
98. Zaitoun A., Kohler N., presented at SPE International Symposium on Oilfield Chemistry, San Antonio, TX, USA, 4–6 February 1987; Society of Petroleum Engineers: Richardson, TX, USA, 1987.
99. Dubois M., Gilles K., Hamilton J., Rebers P., Smith F., Anal. Chem., 1956, 28, 350–356.
100. Song H., Mohanty K.K., presented at SPE Improved Oil Recovery Conference, Tulsa, OK, USA, 31 August–4 September 2020; Society of Petroleum Engineers: Richardson, TX, USA, 2020.
101. Graveling G.J., Ragnarsdottir K.V., Allen G.C., Eastman J., Brady P.V., Balsley S.D., Skuse D.R., Geochim. Cosmochim. Acta, 1997, 61, 3514–3523.
102. Samoshina Y., Diaz A., Becker Y., Nylander T., Lindman B., Colloids Surf. A Physicochem. Eng. Asp., 2003, 231, 195–205.
103. Al-Hajri S., Mahmood S.M., Akbari S., Abdulelah H., Yekeen N., Saraih N., J. Pet. Sci. Eng. 2020, 189, 106864.

104. Tian Q., Wang L., Tang Y., Liu C., Ma C., Wang T., presented at SPE International Oilfield Nanotechnology Conference and Exhibition, Noordwijk, The Netherlands, 12–14 June 2012.

105. Yao C., Lei G., Cathles L.M., Steenhuis T.S., Environ. Sci. Technol., 2014, 48, 5449–5565.

106. Zaitoun A., Makakou P., Blin N., Al-Maamari R.S., Al-Hashmi A.A.R., Abdel-Goad M., SPE J., 2012, 17, 325–329.

ПРОГРЕСС ПОЛИМЕРНЫХ МИКРОСФЕР ДЛЯ РЕГУЛИРОВАНИЯ ПРОФИЛЯ НА НЕФТЯНЫХ МЕСТОРОЖДЕНИЯХ

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В течение последних десятилетий процессы длительного заводнения приводили к обводнению зрелых коллекторов, что является серьезной проблемой на нефтяных месторождениях. Разработка лучшей закупоривающей способности и экономически эффективных полимерных микросфер является ключевым аспектом для контроля избыточного производства воды. Исследования полимерных микросфер, применимых в гетерогенном резервуаре для закупорки высокопроницаемых каналов, значительно расширяются, о чем свидетельствуют многочисленные опубликованные научные статьи. В данном обзоре обсуждаются различные типы полимерных микросфер и эффективность вытеснения нефти. Также рассматриваются связанные с этим трудности и будущие перспективы полимерных микросфер. Данный обзор обеспечивает основу для разработки полимерных микросфер для будущего применения на нефтяных месторождениях и поможет исследователям в дальнейшей разработке полимерных микросфер для повышения нефтеотдачи зрелых коллекторов, которые будут соответствовать требованиям будущих нефтяных месторождений.

Ключевые слова: полимерные микросферы, флуоресцентные полимерные микросферы, эластичные полимерные микросферы, контроль профиля, вытеснение нефти.

МҰНАЙ КЕН ОРНЫНДАҒЫ ПРОФИЛЬДІ БАҚЫЛАУ ҮШІН ПОЛИМЕРЛІК МИКРОСФЕРАЛАРДЫҢ ПРОГРЕССІ

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Соңғы онжылдықтың ішінде ұзақ су айдау процестері жетілген коллекторлардың сулануына әкелді, бұл мұнай кен орындарындағы күрделі мәселе болып табылады. Жақсы тығындау қабілеті бар және үнемді қолданылатын полимерлі микросфераларды дамыту, артық су өндірісін бақылаудың маңызды аспектісі болып табылады. Жоғары өткізгіш арналарды бітеу үшін гетерогенді резервуарда қолданылатын полимерлі микросфераларды зерттеу айтарлықтай кеңеюде, бұған көптеген жарияланған ғылыми мақалалар дәлел бола алады. Бұл шолуда полимерлі микросфералардың түрлері және олардың мұнай ығыстыру тиімділігі талқыланды. Полимерлі микросфералардың осыған байланысты қиындықтары мен болашақ перспективалары да қарастырылады. Берілген шолу болашақта мұнай кен орындарында қолдану мақсатымен көзделген полимерлі микросфераларды дамытуға негіз береді. Бұл зерттеушілерге болашақ мұнай кен орындарының талаптарын *қанағаттандырарлық экономикалық жағдайда жетілген коллекторлардан мұнай өндіруді арттыру үшін полимерлі микросфераларды одан әрі дамытуға көмектеседі.*

Негізгі сөздер: полимерлі микросфералар, флуоресцентті полимерлі микросфералар, серпімді полимерлі микросфералар, профильді бақылау, мұнайды ығыстыру.

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