Colloids and Surfaces A 548 (2018) 10–18

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Synthesis and characterization of a β-cyclodextrin modified polyacrylamide and its rheological properties by hybriding with silica nanoparticles

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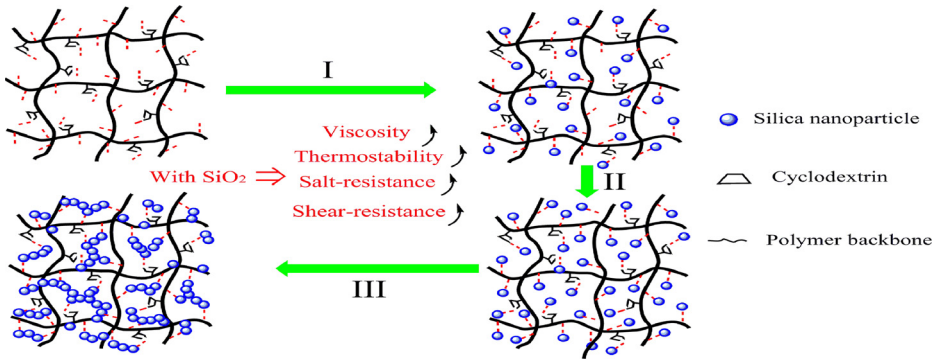
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
β-Cyclodextrin
Copolymer
Silica nanoparticles
Rheology

ABSTRACT

Maleic anhydride modified β-cyclodextrin (MAH-β-CD) was copolymerized with acrylamide (AM) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) to form a copolymer (denoted as AAMC) through redox free-radical polymerization. The copolymer was characterized by FT-IR, ^{1}H NMR and thermal gravimetric analysis. The silica nanoparticles suspension was mixed with AAMC solution, and their rheological properties were investigated under different experimental conditions. Results showed that AAMC/silica hybrid exhibited viscosity enhancement and better salt-resistance, temperature-tolerance and shear-resistance than AAMC. The AAMC/silica hybrid showed an impressive thermal stability at T = 85 °C after 15 days, and the viscosity reached about 2.5 times that of AAMC at 0.8 wt% nanoparticle loading. Dynamic rheology studies indicated that silica nanoparticles acted as physical crosslinkers among polymer molecules so as to enhance the elasticity of the AAMC/silica hybrid. The superior properties of AAMC/silica hybrid indicated that it has the potential to enhanced oil recovery.

1. Introduction

The challenge to enhanced oil recovery (EOR) is a motive force behind the fact that much original oil is left in the formation after primary and secondary recovery processes [1,2]. As is known to all, water-soluble polymer flooding has proved to be an effective method to enhanced oil recovery [3]. Among water-soluble polymers, polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) are widely used in the polymer flooding process of oil fields due to they exhibit an excellent capability of thickening and increase the viscosity of working fliuds, which result in reducing the water/oil mobility ratio, and increasing the sweep volume [4–6]. Nevertheless, new problems

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https://doi.org/10.1016/j.colsurfa.2018.03.039
Received 1 February 2018; Received in revised form 14 March 2018; Accepted 16 March 2018
Available online 17 March 2018

and limitation emerge with the application of the traditional polyacrylamide because of the high-temperature and high-salinity conditions in most oil reservoirs [7]. When the temperature above 60 ℃, the acrylamide group (−CONH) can be easily hydrolyzed [8], leading to a sharp decline of viscosity. Thus, the effect of polymer flooding is seriously affected. Polyacrylamide is sensitive to the presence of inorganic salts. When polyacrylamide is used for high-mineralization reservoirs, hydrolyzed carboxylic groups would interact with different metal cation, divalent cations such as Mg^{2+} and Ca^{2+} in particular, resulting in macromolecular chain curls and the viscosity decreases [9,10]. In addition, polyacrylamide cannot resist high shear rate, and the shear degradation will result in breakage of the polymer backbone [11]. To settle those problems mentioned above, domestic and foreign researchers usually introduce functional groups, hydrophobic monomer, organic/inorganic materials, etc. into PAM [12–14].

Besides, Cyclodextrins (CDs), produced from the bacteria enzymatic degradation of starch, are cyclic oligosaccharides consisting of six to eight glucose units linked by 1,4-α-glucosidic bonds and its shape is similar to torus-shaped ring structure [15–17]. Compared to other cyclodextrins, β-cyclodextrin (β-CD) contains seven glucose units [18]. β-CD contains some relatively high chemical activity hydroxyl groups that are located in the surface of the specific architectural conformation, which provides great advantage and convenience to chemically modified β-CD [19]. The cavity of β-CD is hydrophobic as a glycosidic oxygen bridges, and the shell of β-CD is hydrophilic owing to hydroxyl groups [20,21]. Due to the special structure, β-CD can selectively incorporate suitable hydrophobic molecules to form host/guest inclusion complexes [22]. Meanwhile, some previous researches also indicated that the β-CD modified polymers had been not only widely applied in environment protection, medicine, and food fields but also in the petroleum industry for complex oil reservoirs [23–26]. Many researchers demonstrated that copolymers containg β-CD branched chain structure possessed higher salt tolerance, temperature resistance, and anti-shearing performance than PAM [27], which ensures its potential application for enhancing oil recovery in the complex reservoirs.

Depending on the unique molecular dimension [28], large surface area [29] and the plentiful hydroxyl on the surface [30], inorganic nano-SiO_2 has been attracting increasing attention in many fields. It is well recognized that introducing nano-SiO_2 into bulk polymers can improve the mechanical, thermal, toughness, electric and rheological properties of polymers [31,32]. To date, the dispersion of silica nanoparticles into pure water-soluble polymer to form a nanocomposite hydrogel have recently attracted considerable attention and achieved significant advancements. Hu et al. showed that prepared HPAM/SiO_2 hybrid showed improved temperature-tolerance and high thermal stability behavior, which showed a promising prospect for HPAM/SiO_2 hybrid for potential application in EOR [8]. Zhu et al. reported that the viscosity of hydrophobically associating polyacrylamide(HAHPAM) was increased by introducing silica nanopartides and the rheological properties was effectively controlled. Moreover, core flooding test show that hybrid has a higher oil recovery factor than HAHPAM solution [33]. Maurya et al. found that when polyacrylamide(PAM) was mixed with silica nanoparticles, salt-tolerance and shear-resistance properties were significantly improved and the oil recovery efficiency was also improved during a polymer flooding process [34]. These water-soluble polymer/silica hybrid exhibits novel and excellent properties because of the strong interactions between these polymer molecules and silica, which are generally attributed to the formation of hydrogen bonds between carbonyl or other groups of polymers and silanol functionalities on the nanoparticle surface. Hence, we think the carbonyl groups of amide, sulfonyl group of AMPS and hydroxyl group of β-CD in AAMC molecule show the possibility to interact with silanol groups at the surface of silica, and the salt tolerance, temperature tolerance, and shear resistance are expected to be improved to some extent. So there should be a wide application prospect in EOR for MMAC/silica hybrids. Nevertheless, there are no reports on such MMAC/silica hybrids in literature.

In this work, β-CD modified polyacrylamide (AAMC) was prepared by redox free-radical polymerization and the structure of the copolymer was determined by Fourier transform infrared (FT-IR) spectroscopy and ^1H NMR, and the thermal stability of AAMC was characterized by thermal gravimetic analysis (TGA). The effect of introducing silica nanoparticles into AAMC aqueous solution was investigated. The solution properties of the AAMC/silica hybrid solution were investigated at different silica loading, shear rates, salt concentration, teamperature and aging times. The steady and dynamic rheological behavior of AAMC/silica hybrid solution was also studied in comparsion with pure AAMC solution. The thickening and rheological properties were enhanced in harsh conditions, which make AAMC/silica hybrid more promising for EOR.

2. Experimental

2.1. Materials

Acrylamide (AM), maleic anhydride (MAH), sodium hydrogen sulfite ($NaHSO_3$), ammonium persulfate ($(NH_4)_2S_2O_8$), and sodium chloride were obtained from Tianjin Guangfu Fine Chemical Research Institute, China. β-Cyclodextrin (β-CD), ammonia (NH_3, 25% aqueous solution), and 2-acrylamido-2-methyl propane sulfonic acid (AMPS), which were purchased from Aladdin Industrial Corporation, China. *N*,*N*-dimethylformamide (DMF), aceton, absolute ethanol, trichloromethane, sodium hydroxide, and tetraethyl orthosilicate were bought from the Beijing beihua Fine Chemicals Co., Ltd. All of them were analytical grade and doubly distilled water was used for all experiment.

2.2. Preparation of SiO_2 nanoparticles

SiO_2 nanoparticles were prepared using StÖber method [35]. The TEOS was added into the mixture of ethanol, ammonia solution and deionized water. And the resulting mixture was stirred at ambient temperature for several hours. Then the particles were centrifuged three time in ethanol and dried in a vacuum oven at 100 ℃ for 12 h.

2.3. Synthesis of β-CD based monomer (MAH-β-CD)

11.36 g of β-CD was placed in a three neck-flask and completely dissolved by the addition of an appropriate amount of DMF. Then slowly added with 9.8 g of MAH. After that, the mixture solution was heated at 80 ℃ for 10 h under the vigorously stirring. After the reation was completed, the solution cooled to room temperature. A white precipitate was obtained after 60 mL of trichloromethane was added and then washed with a large amount of acetone. Finally, dried in a vacuum oven at 80 ℃ [36]. The synthetic process of MAH-β-CD was shown in Fig. 1(a).

2.4. Synthesis of AAMC

29.625 g AM, 7.5 g AMPS, 0.375 g MAH-β-CD were dissolved in 112.5 g deionized water and were added into a 250 mL beaker with continuously stirring for 2 h. The pH value of reaction solution was control to 8–9 with NaOH. Then a certain amount of $(NH_4)_2S_2O_8$ and $NaHSO_3$ (molar ration 1:1, 0.3 wt%) as the initiator were injected into the reaction solution with stirring under nitrogen atmosphere for 0.5 h. After the reaction for 5 h at 50 ℃, a transparent polymeric colloid was obtained and wash with ethyl alcohol several times. Finally, the colloid was cut into pieces and dried in the vacuum oven for 12 h at 60 ℃. The synthetic process of AAMC was shown in Fig. 1(b). We determined the content of C, N, S in the AAMC by elemental analysis, and then calculated the number of functional groups indirectly, as shown in Table 1.