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Synthesis of polyaspartic acid–melamine grafted copolymer and evaluation of its scale inhibition performance and dispersion capacity for ferric oxide

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ABSTRACT

Polyaspartic acid–melamine grafted copolymer (denoted as PASPM) was synthesized by using polysuccinimide and melamine as the starting materials. Resultant grafted copolymer was characterized by means of Fourier transform infrared spectrometry (FTIR) and NMR. The scale inhibition behavior of PASPM copolymer against $CaCO_3$ and $Ca_3(PO_4)_2$ scales was evaluated using static scale inhibition method, and its dispersion capacity for ferric oxide and ability to retard deposition of $CaCO_3$ were also examined. It was found that PASPM was able to efficiently inhibit deposition of $CaCO_3$ and had good dispersion ability for Fe_2O_3. The maximum inhibition efficiency, as high as 98.97%, was reached at an inhibitor concentration of 10 mg/L. The best dispersion efficiency for Fe_2O_3 was reached when 34 mg/L of PASPM was introduced into the tested solution, corresponding to 39.1% of light transmittance of the solution.

1. Introduction

In recent years, the consumption and pollution of industrial water increases significantly with the rapid development of modern industry, which intensifies shortage of fresh water resource [1]. To alleviate the pressure on water resources shortage, it is imperative to apply water-treatment agents to process industrial water for the purpose of slowing down large area corrosion and saving water [2–4]. Early in 1950s, P. Shakkthivel et al. initially studied water-treatment agents [5,6]. Since then, inorganic scale-corrosion inhibitor, polyphosphate salt scale-corrosion inhibitor, green natural polymer water-treatment agents and soon have been successfully developed [7]. However, currently used water-treatment agents usually possess unsatisfactory overall performance and cause secondary pollution, which restricts their application in industry [8]. As a result, intense attention is being paid to environmentally acceptable "green" chemicals as scale-inhibitors and for water treatment as well [9–11].

Currently available "green" water treatment agents mainly include poly-aspartic acid (PASP), polyepoxysuccinic acid, polyalkyl-epoxysuccinic acid, and natural polymers [12]. Of those "green" water treatment agents, PASP possessing nontoxicity and good biodegradability is attracting more and more attention as a representative scale inhibitor [13]. In the meantime, PASP molecule contains carboxylic group with good chelating ability and dispersability, making it feasible to absorb or combine with metal ions such as Ca^{2+}, Mg^{2+}, thereby preventing $CaCO_3$ deposition[14]. Therefore, PASP is of particular interest as a "green" chemical water treatment agent and a potential replacement of phosphoric acid series[15]. Nevertheless, polyaspartic acid has poor inhibition performance for $Ca_3(PO_4)_2$ scale and poor dispersion capacity for ferric oxide, which seriously limits its use [16]. To overcome those shortcomings and improve the service performance of polyaspartic acid, numerous efforts have been made to introduce hydrophobic group, carboxylic group, sulfonic group and phosphonyl to the side chain of PASP, which, thanks to the ring-opening reaction of polyaspartic acid by amine-group catalysis, is feasible [17].

In the present research, we intend to introduce amino group to the side chain of PASP by way of graft copolymerization and investigate the scale-inhibition performance and dispersion capacity of resultant grafted copolymer. This, hopefully, is to contribute to overcome the corrosion and scale problems as well as precipitation of ferric oxide in open re-circulating cooling systems associated with traditional water treatment agents [18]. Thus polyaspartic acid–melamine grafted copolymer was synthesized by using polysuccinimide and melamine as the starting materials. The molecular Weight was about 10,000. The anti-scale behavior of as-synthesized PASPM copolymer against $CaCO_3$ scale in artificial cooling water was investigated by conducting static scale inhibition test, and its effect on the formation of $CaCO_3$ calcium was investigated by means of scanning electronic microscopy and Fourier transform infrared spectrometry. Besides, the transmittance of the supernatant of the copolymer solution was measured to evaluate its dispersion ability for ferric oxide (Scheme 1).

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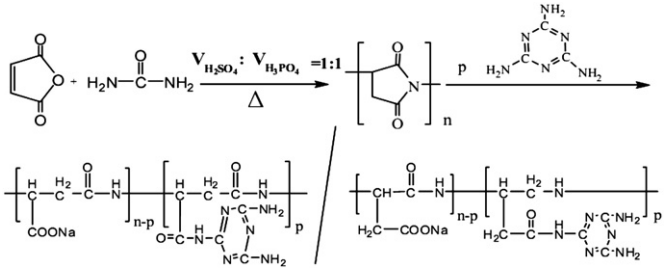

Scheme 1. Synthesis routes to polyaspartic acid–melamine graft copolymers.

2. Experimental section

2.1. Instruments and agents

Instruments used in the present research include DF-101S thermostatic magnetic stirrer, 722 grating spectrophotometer, FA1004A electronic balance, DHT thermostatic electric jacket equipped with a stirrer, AUATAR-360 Fourier transform infrared spectrometer (FTIR), AVANCE 400 nuclear magnetic resonance, Ubbelohde viscosity meter, D-971 blender equipped with a stepless speed regulator, and JSM 5600LV scanning electron microscope (SEM). The chemicals used include analytical grade maleic anhydride, melamine, urea, ethanol, acetone, calcium chloride, sulfuric acid, phosphoric acid, hydrochloric acid and sodium tetraborate.

2.2. Preparation of polyaspartic acid–melamine grafted copolymer

9.8 g of maleic anhydride and a proper amount of water were added to a three-neck flask and heated at 60 °C, generating a colorless transparent liquid [19]. Into the colorless transparent liquid was added 4.2 g of urea at an increased temperature of 80 °C, followed by 1 h reaction. At the end of the reaction, the mixed solution was concentrated and heated to 200 °C, followed by addition of 0.82 ml of mixed acids (H_2SO_4 : H_3PO_4 = 1 : 1) and dehydration for 3 h. Resultant dehydrated solution was cooled to room temperature, washed with deionized water, filtrated with an air pump, and dried, generating orange solid polysuccinimide [20–22]. A proper amount of as-dried polysuccinimide and water were mixed and heated at 70 °C under stirring, generating a suspension [23]. The suspension was batch added 0.1575 g of melamine in 1 h , then separated by centrifugal settling, washed with deionized water at 70 °C for three times, and dried, generating orange solid powder. The sediment was hydrolyzed with 10% sodium hydroxide solution. Into resultant alkaline hydrolyzed solution was added aqueous solution of HCl to reach a pH value of 7.0, generating orange transparent liquid, PASPM solution [24].

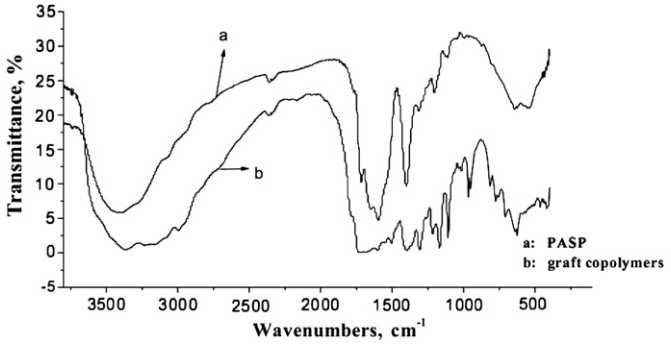

Fig. 1. IR spectra of PASP and PASPM.

2.3. Evaluation of scale-inhibition performance and ability to disperse ferric oxide

2.3.1. Inhibition performance of PASPM copolymer against $CaCO_3$ scale

Static scale inhibition tests were conducted according to China National Standard method (GB/T 16632–1996) to evaluate the scale inhibition efficiency of synthesized PASPM copolymer against $CaCO_3$ scale [25]. Briefly, in a volumetric flask (capacity 1 L) was prepared an aqueous solution containing 250 mg/L Ca^{2+} and 250 mg/L HCO_3^-. Resultant solution was uniformly mixed with a known amount of PASPM copolymer as the scale inhibitor and allowed to react in a water bath at 80 °C for 6 h. At the end of the reaction, resultant mixed solution was collected and cooled to room temperature. The concentration of Ca^{2+} in the solution was measured using titration of ethylene diamine tetracetic acid (EDTA). The scale inhibition efficiency of the PASPM copolymer against $CaCO_3$ scale was calculated as:

$$\eta_{CaCO_3} = \frac{V_1 - V_0}{V_2 - V_0} \times 100\% \quad (1)$$

where V_o (ml) is the volume of EDTA consumed by a certain amount of calcium cation in the absence of scale inhibitor in to-be-tested solution (control test); V_1 is the volume of EDTA consumed by a certain amount of calcium cation in the presence of scale inhibitor in to-be-tested solution; and V_2 is the volume of EDTA consumed by all calcium cations in to-be-tested solution.

2.3.2. Inhibition performance of PASPM copolymer against $Ca_3(PO_4)_2$ scale

A solution containing 250 mg/L Ca^{2+} and 10 mg/L PO_4^{3-} was prepared in a volumetric flask (capacity 1 L) in the same manner described in Section 2.4. The pH value of resultant solution was adjusted to 9.0 with borax. Then the solution was evenly mixed with a known amount of scale inhibitor and allowed to react in a water bath at 80 °C for 10 h. At the end of the reaction, the mixed solution was cooled to room temperature and centrifugally separated. The content of PO_4^{3-} in the supernatant was measured with a 722-spectrophotometer (710 nm, 1 cm cuvette; in relation to distilled water) [26]. The inhibition efficiency of the scale inhibitor against $Ca_3(PO_4)_2$ scale was calculated as:

$$\eta_{Ca_3PO_{42}} = \frac{\rho_1 - \rho_0}{\rho_2 - \rho_0} \times 100\% \quad (2)$$

where ρ_0 is the concentration (mass fraction) of PO_4^{3-} in the absence of scale inhibitor in to-be-tested solution; ρ_1 is the concentration of PO_4^{3-} in the presence of scale inhibitor in to-be-tested solution; and ρ_2 is the concentration of all PO_4^{3-} in to-be-tested solution.

2.3.3. Ability of PASPM copolymer to disperse ferric oxide

A solution containing 150 mg/L Ca^{2+} and 10 mg/L Fe^{2+} was prepared. The pH value of the solution was adjusted to 9.0 with borax. Then the solution was evenly mixed with a known amount of PASPM copolymer. Resultant mixed solution was stirred for 15 min and heated at 50 °C for 5 h before being cooled to room temperature and centrifugally separated. The transmittance of the supernatant was measured with a 722-spectrophotometer (710 nm, 1 cm cuvette; in relation to distilled water) [27]; and it was supposed that a smaller light transmittance referred to a better dispersion ability of the copolymer [28].

2.3.4. Corrosion inhibition efficiency of PASPM copolymer

Weight loss of rotating hung steel slices was measured to evaluate the corrosion inhibition efficiency of PASPM copolymer, which was conducted at a temperature of 45 °C, rotating speed of 80 rpm, and a pre-coating time of 72 h [29]. Briefly, carbon steel slices with a surface area of 28.00 cm^2, consisting of 0.17%~0.23% C, 0.17%~0.37% Si, 0.35%~0.65% Mn, ≤0.25% Cr, ≤0.3% Ni, ≤0.25% Cu, and balance Fe, were