

Synthesis, Scale and Corrosion Inhibition of Modified Polyaspartic Acid

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Modified polyaspartic acid was prepared from aspartic acid and polysuccinimide that was thermal condensation polymer of aspartic acid. The properties of scale and corrosion inhibition of modified polyaspartic acid were studied. The structure of modified polyaspartic acid was characterized by means of FTIR. Calcium carbonate crystals in scale samples and corrosive test piece were analyzed by means of SEM. The results showed that under Ca^{2+} 400 mg L⁻¹, HCO_3^- 800 mg L⁻¹ and modified polyaspartic acid 6 mg L⁻¹, the scale inhibition rate of modified polyaspartic acid was 100 %. The modified polyaspartic acid possessed good corrosion inhibition performance and the corrosion inhibition rate of modified polyaspartic acid could reach 86.26 %. Modified polyaspartic acid could distort calcium carbonate crystallite and made calcium carbonate crystallite more dispersive. The test piece was immersed in solution with modified polyaspartic acid, the sample had no pits on its surface.

Key Words: Polyaspartic acid, Modified polyaspartic acid, Corrosion inhibition, Scale inhibition mechanism.

INTRODUCTION

Polyaspartic acid is a kind of crude macromolecule polymer which has non-phosphorus and biodegradable environmental friendly scale and corrosion inhibitor. It was the representative of the non-phosphorus biodegradable environmental friendly water treatment chemicals, but its chelating and dispersing performance was still worse than acrylic acid and maleic acid polymers, especially, when applied to water containing high hardness. To improve general scale inhibition of polyaspartic acid had drawn much more attention^{1,2}. The most important method is to introduce groups with the function of scale inhibition to the side chain of polyaspartic acid, such as carboxylic acid group, phosphonic acid group, sulfonic acid group, *etc.*³⁻⁵. The aspartamides obtained by ring opening reaction of polysuccinimide with various amines have been known ever since a long time ago. Hydroxy and sulfonic acid group were introduced in molecular structure of polyaspartic acid by Gao *et al.*⁶. Phosphonic acid group was introduced by Wang *et al.*⁷. Phosphono group was

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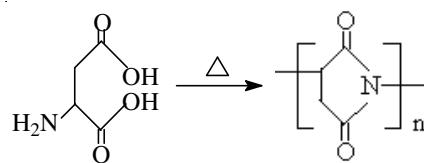
introduced by Liang *et al.*⁸. However, the present inventors observed that the polyaspartamide obtained by ring opening reaction of the polysuccinimide with cysteamine is irritant when they carried out a rabbit eye mucous membrane irritation test to it. Thus, in view of the above-mentioned problem, the present inventors have intensively conducted investigations base on a conception to use a compound, which is safe to organisms and environments, for the ring opening reaction of the polysuccinimide. As a result, it has been found that a polymer supposed to be substantially free from the irritation to organisms and to have high safety to organisms can be obtained by using an α -amino acid, which is one having a good adaptability and an extremely high safety to organisms, for the ring opening reacting of the polysuccinimide. In consequence, aspartic acid group was introduced in molecular structure of polyaspartic acid. Modified polyaspartic acid with a side chain aspartic acid was synthesized in this paper and the performances of the product were studied. The structure of modified polyaspartic acid was characterized by means of FTIR. Calcium carbonate crystals in scale samples and corrosive test piece were analyzed by means of SEM.

EXPERIMENTAL

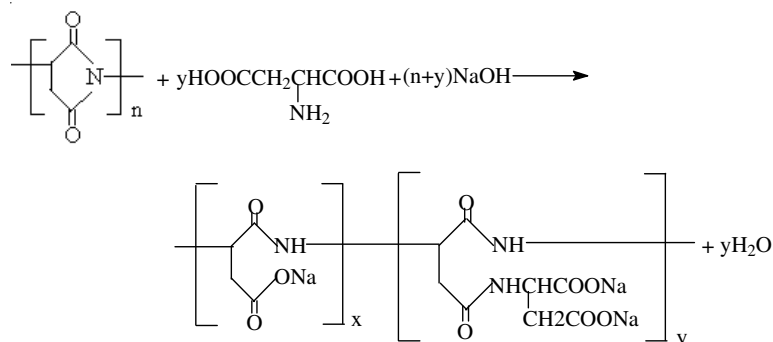
Aspartic acid, polysuccinimide and sodium hydroxide were used as received. Modified polyaspartic acid was prepared from aspartic acid and polysuccinimide that was thermal condensation polymer of aspartic acid. The properties of scale and corrosion inhibition of modified polyaspartic acid were measured. The structure of the modified polyaspartic acid was characterized by means of FTIR. Calcium carbonate crystals in scale samples and corrosive test piece were analyzed by means of SEM.

General procedure

Synthesis of polysuccinimide: Polysuccinimide was synthesized by pyrocondensation of L-aspartic acid monomer under the condition of temperature 240 °C, reacted for 4 h.



Synthesis of modified polyaspartic acid: Water was added into polysuccinimide to form a suspension. Aspartic acid was dissolved in 10 % NaOH solution, which was slowly dropped into the suspension. The reaction temperature was below 25 °C and pH was kept at 8-9 for 24 h. The product was acidified with dilute HCl and then filtrated. The filtrate was washed with pure ethanol several times. The obtained product was dried under vacuum at 80 °C for 6 h. Finally, the red-brown powder of modified polyaspartic acid was obtained.



Measurement of the rate of static scale inhibition: EDTA titration, water sample is confecting water (containing calcium carbonate 400 mg L⁻¹). Heating 500 mL confecting water with an amount of modified polyaspartic acid to 80 °C for 10 h. Using EDTA titration detected the content of calcium carbonate in the cooling and filtrating water. The rate of scale inhibition is calculated by formula (1).

$$\text{Rate of scale inhibition} = \frac{\rho_2 - \rho_0}{\rho_1 - \rho_0} \times 100 \% \quad (1)$$

where ρ_2 is mass concentration of Ca²⁺ of heated water sample with modified polyaspartic acid, mg L⁻¹; ρ_0 is mass concentration of Ca²⁺ of water sample without modified polyaspartic acid, mg L⁻¹; ρ_1 is mass concentration of Ca²⁺ of preparing water sample, mg L⁻¹.

Measurement of the rate of corrosion inhibition: The corrosion inhibition performance of modified polyaspartic acid was estimated by rotating hanging piece corrosion test. The main steps as follows: A 1600 mL solution with water treatment chemical is prepared in a beaker and the content of water treatment chemical is 100 mg L⁻¹. Put the beaker in a constant temperature bath and keep the temperature at 40 °C. Then hang test piece in solution and rotate at stated velocity. The test piece is taken out from solution after 72 h, then dipped in the solution of hydrochloric acid pickling for 3-5 min, washed with water, dipped in pure ethanol for 3 min, blot up with filter paper and dried in dryer for 4 h. The rate of corrosion of water treatment chemical is calculated by formula (2).

$$X = \frac{8760 \times (W_0 - W) \times 10}{A \times D \times T} \quad (2)$$

where W is the mass of the corrosive test piece, g; W₀ is the initial mass of the test piece, g; A is surface area of the test piece, cm²; D is the density of test piece, g cm⁻³; T is test time of test piece, h.

The rate of corrosion inhibition of water treatment chemical is calculated by formula (3).

$$\text{Rate of corrosion inhibition} = \frac{X_0 - X_1}{X_0} \times 100 \quad (3)$$

where X_0 is the rate of corrosion of the test piece without water treatment chemical, mm a^{-1} ; X_1 is the rate of corrosion of the test piece with water treatment chemical, mm a^{-1} .

Preparation of scale sample: The rate of static scale inhibition of sample was measured at 80°C . The solution was poured from the beaker at the end of experiment. The scale cling to bottom and wall of beaker was dried at the room temperature, then was brushed away and conserved in the dryer.

Detection method

Characterization of modified polyaspartic acid: Using USA Perkin-Elmer Spectrum 100 FT-IR analyze the structure of modified polyaspartic acid in $4000\text{--}500\text{ cm}^{-1}$ region.

Characterization of scale sample: Using China KYKY-2800B SEM scanning electron microscope analyze structure of scale sample. The scale sample was evenly pasted on the sample desk and then was observed by using scan electron microscope under the condition of acceleration voltage 20 kV and amplified factor $500\text{--}3000$.

RESULTS AND DISCUSSION

Fig. 1 showed FT-IR spectrum of modified polyaspartic acid and polyaspartic acid. 1716 cm^{-1} peak was the absorption peak of C=O of carboxy group. This absorption peak of modified polyaspartic acid was stronger than polyaspartic acid. 3392 cm^{-1} peak was absorption peak of N-H of amide. This absorption peak of modified polyaspartic acid take place displacement compared with polyaspartic acid. That showed modified polyaspartic acid prepared from polyaspartic acid and polysuccinimide.

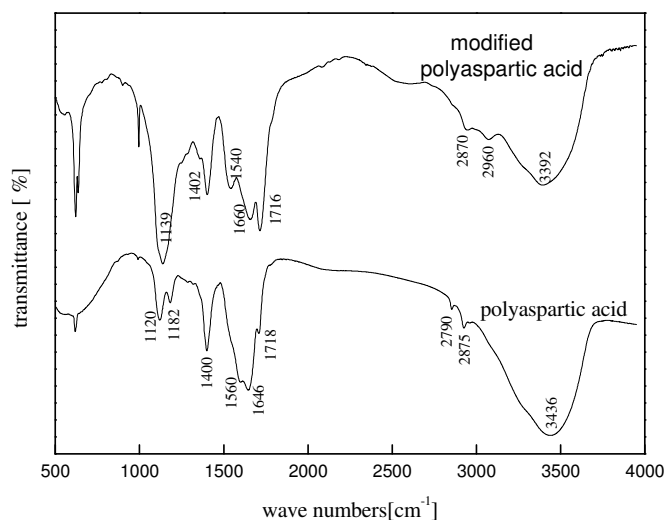


Fig. 1. FT-IR spectrum of modified polyaspartic acid and polyaspartic acid

Scale inhibition performance: The measurement of the rate of static scale inhibition, the scale inhibition performance of modified polyaspartic acid was evaluated. The results are showed in Table-1.

TABLE-1
RELATION BETWEEN DOSAGE OF PASP-ASP AND SCALE INHIBITION RATE

Dosage (mg L ⁻¹)	2	3	4	5	6
Scale inhibition rate (%)	88.1	91.35	98.67	99.22	100

PASP-ASP = Modified polyaspartic acid

Table-1 showed that modified polyaspartic acid is a better scale inhibitor, under Ca²⁺ 400 mg L⁻¹, HCO₃⁻ 800 mg L⁻¹ and modified polyaspartic acid composite 6 mg L⁻¹, the scale inhibition rate of modified polyaspartic acid can reach 100 %.

Corrosion inhibition performance: According to the method of measurement of the rate of corrosion inhibition, the corrosion inhibition performance of modified polyaspartic acid was evaluated (Table-2).

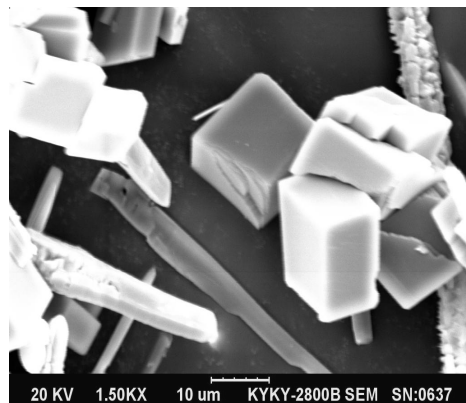
TABLE-2
RESULTS OF ROTATION SPECIMEN METHOD

Chemical	Lost mass of test piece/g	Corrosion rate/mm a ⁻¹	Corrosion inhibition rate/%
Blank	0.03406	0.18853	–
PASP	0.01724	0.09543	49.38
PASP-ASP	0.00468	0.02591	86.26

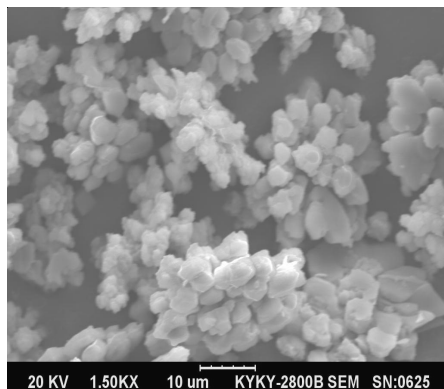
PASP = Polyaspartic acid; ASP = Aspartic acid.

It was found that modified polyaspartic acid possessed good corrosion inhibition performance and the corrosion inhibition rate can reach 86.26 %. The corrosion inhibition rate of modified polyaspartic acid increased 36 % than polyaspartic acid in dynamic experiment.

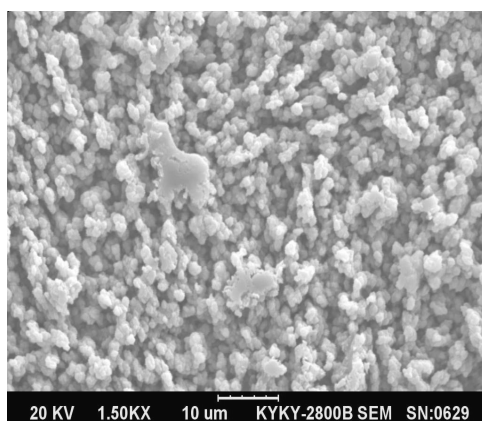
Results of SEM: Fig. 2(a) showed the most of the CaCO₃ crystals were calcite in the scale samples from blank solution. Fig. 2(b) showed CaCO₃ crystal lattice was distorted completely after 1.4 mg L⁻¹ modified polyaspartic acid was added in water, which was vaterite, CaCO₃ crystal grain obviously less than CaCO₃ crystal grain of blank solution. Fig. 2(c) showed CaCO₃ crystal lattice were distorted completely when the dosage of modified polyaspartic acid was 2.8 mg L⁻¹ and then crystal were more finer. The results of SEM showed that almost all calcite and aragonite could be transformed into vaterite by using modified polyaspartic acid. The reason is modified polyaspartic acid not only formed steady complex with Ca²⁺ in water to decrease concentration of Ca²⁺ in aqueous solution and decreased probability of forming CaCO₃ deposition, but also make action with Ca²⁺ of formed CaCO₃ crystal lattice to make surface of crystal lattice formed a double layer and brought static exclusion among crystal lattice to block collision among them and formation of bigger crystal and block collision between heat transfer surface of metal and formation of scale.



(a) SEM photograph of CaCO₃ sample from blank solution



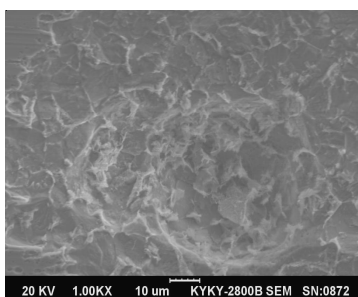
(b) SEM photograph of CaCO₃ sample from the solution with 1.4 mg L⁻¹ modified polyaspartic acid



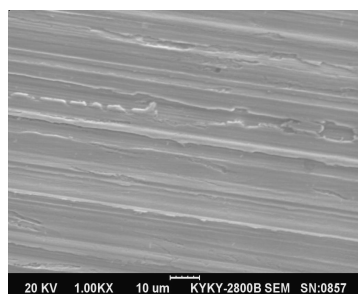
(c) SEM photograph of CaCO₃ sample from the solution with 2.8 mg L⁻¹ modified polyaspartic acid

Fig. 2. SEM photograph of CaCO₃ sample from the solution with modified polyaspartic acid

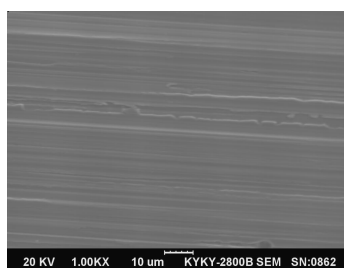
Surface analysis of corrosive test piece: If the test piece was immersed in blank solution, its surface was covered with pits of different sizes after experiment Fig. 3(a), which showed that serious local corrosion occurred. The patterns of the sample immersed in polyaspartic acid and modified polyaspartic acid are showed in Figs. 3(b-c). When immersed in solution with polyaspartic acid, the surface was covered with little pits. While in solution with modified polyaspartic acid, the sample surface has no pits. This indicated that the corrosion inhibition rate of modified polyaspartic acid was higher than polyaspartic acid.



(a) SEM photograph of corrosive test piece from blank solution



(b) SEM photograph of corrosive test piece from the solution with polyaspartic acid



(c) SEM photograph of corrosive test piece from the solution with modified polyaspartic acid

Fig. 3. SEM photograph of corrosive test piece from the solution with water treatment chemical

Thus polyaspartic acid and modified polyaspartic acid could be adsorbed on the metal surface as the metal take place chemical reaction synchronously. Since, the adsorption heat was higher and formed complex compound was more steadier. Therefore, a compact protective membrane of chemical adsorption was formed on the surface of test piece. This could prevent from corrosion effectively. In addition, non-polar group containing -R was directional arranged on the surface of metal and hydrophobe membrane was formed, which prevent the transfer of charge or matter that was relevant to corrosive reaction after polar group *i.e.*, amino and carboxyl are adsorbed on the surface of metal. Thus, corrosion contaminant was supplanted and partitioned with surface of metal by corrosion inhibitor molecule, which slowed corrosion rate of metal⁹, so the corrosion inhibition rate of modified polyaspartic acid is higher than polyaspartic acid.

Conclusion

Modified polyaspartic acid was prepared from aspartic acid and polysuccinimide which is a thermal condensation polymer of aspartic acid. It has a better scale inhibitor, under Ca^{2+} 400 mg L⁻¹, HCO_3^- 800 mg L⁻¹ and modified polyaspartic acid 6 mg L⁻¹, the scale inhibition rate of modified polyaspartic acid can reach 100 %. It possessed better corrosion inhibition performance and the corrosion inhibition rate can reach 86.26 %. The corrosion inhibition rate of modified polyaspartic acid can increase by 36 % than polyaspartic acid in dynamic experiment. Measuring results of SEM showed that almost all calcite and aragonite can be transformed into vaterite by using modified polyaspartic acid. Measured by SEM, the test piece was immersed in solution with modified polyaspartic acid has no pits on its surface.

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