Asian Journal of Chemistry; Vol. 26, No. 22 (2014), 7716-7720

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17659

Study of Corrosion and Scale Inhibition of Polyepoxysuccinic Acid Derivative

XINHUA LIU[1,2,*], WENJING WANG[3], XINJIA TONG[2], YUNFEI DING[2], XINQIANG ZHAO and HONG SU[2]

[1]School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, P.R. China
[2]Qinggong College, Hebei United University, Tangshan 063000, Hebei, P.R. China
[3]School of Chemical Engineering and Technology, Hebei United University, Tangshan 063000, Hebei, P.R. China

*Corresponding author: Tel: +86 18633168357; E-mail: hualiyiwang@163.com

Received: 24 March 2014; *Accepted*: 27 May 2014; *Published online*: 6 November 2014; AJC-16219

Polyepoxysuccinic acid derivative was synthesized from L-cysteine and polyepoxysuccinic acid a condensation polymer formed by cyclization and polymerization with maleic anhydride. The structure of polyepoxysuccinic acid derivative was characterized by means of FTIR and ^{13}C NMR. The scale inhibition and corrosion inhibition performances of polyepoxysuccinic acid derivative were studied. Scale inhibition and corrosion mechanisms were analyzed by means of SEM. The scale inhibition rate of polyepoxysuccinic acid derivative can reach 98.9 % under Ca^{2+} 400 mg L^{-1}, HCO_3^- 800 mg L^{-1}, polyepoxysuccinic acid derivative 8 mg L^{-1}. Polyepoxysuccinic acid derivative is better than polyepoxysuccinic acid in corrosion inhibition performance and the corrosion inhibition rate can reach 65.14 % at 40 °C in dynamic experiment. SEM showed that the calcium carbonate crystal lattice was distorted completely from calcite to vaterite by using polyepoxysuccinic acid derivative. The surface of the test piece has dense protective adsorption film layer when it was immersed in solution with polyepoxysuccinic acid derivative.

Keywords: Polyepoxysuccinic acid, Modified polyaspartic acid, Corrosion inhibition, Scale inhibition mechanism.

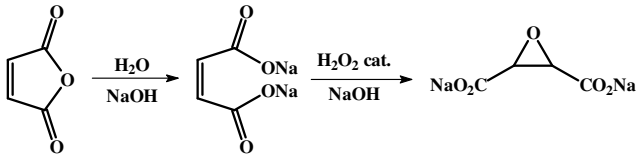
INTRODUCTION

As the World's environmental protection laws and regulations, the idea of a green chemistry and green water treatment agent was deeply rooted in the hearts of people. People hope to design and synthesize a new biodegradable water treatment agent with special structure. The United States developed polyepoxysuccinic acid (PESA) in the early 1990s[1] and Japan and other countries have also studied it and its derivatives[2]. Polyepoxysuccinic acid is a new biodegradable water treatment agent without phosphorus and nitrogen with its scale inhibition, dispersion and become the representative of a new generation of water treatment agent[3-6]. Although the great progress was made to the study of polyepoxysuccinic acid, the scale inhibition performance is still lower than the commonly commercially available phosphorous scale inhibitors in high hardness water quality. In order to achieve good scale inhibition effect, general methods are composed a low phosphorus formula of better scale inhibition performance with other agents or directly increase the amount of it[7-9]. The screening formula is complex and the compound positions with phosphorus damage to the environment. The latter increased the cost and in the case of anti-scaling rate of threshold, even increasing the dosage of it can not increase the rate of scale inhibition. So its application is tremendous limited. In order to improve the performance of polyepoxysuccinic acid, modification to polyepoxysuccinic acid is a available method. Sulfonic acid groups was introduced in molecular structure of polyepoxysuccinic acid by Zhang *et al.*[10]. Scale inhibition mechanism of polyepoxysuccinic acid and scale inhibition mechanism of copolymer of polyepoxysuccinic acid and acrylic acid was studied by Shi *et al.*[11]. It has not been reported that L-cysteine group was introduced in molecular structure of polyepoxysuccinic acid. In addition to the same amino and carboxyl groups as all amino acids, L-cysteine has some special chemical reactions because of sulfydryl, After L-cysteine molecules react with other compounds, the electronic charge distribution of N,O,S atoms containing the lone pair electrons in L-cysteine has changed and caused the change of the corrosion inhibition performance. In consequence, L-cysteine group was introduced in molecular structure of polyepoxysuccinic acid. Polyepoxysuccinic acid derivative with a side chain L-cysteine was synthesized in this paper and the performances of the product were studied. The structure of polyepoxysuccinic acid derivative was characterized by means of FT-IR and ^{13}C NMR. Calcium carbonate crystals in scale samples and corrosive test piece were analyzed by means of SEM.

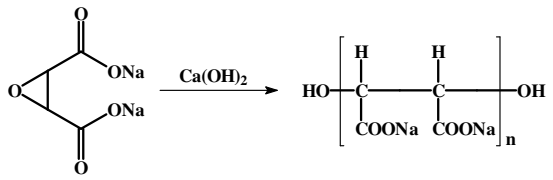
EXPERIMENTAL

L-cysteine, maleic anhydride and sodium hydroxide were analytical pure. Epoxy sodium succinate was synthesized from by cyclizing of maleic anhydride. Polyepoxysuccinic acid was prepared from epoxy sodium succinate by pyrocondensation. Polyepoxysuccinic acid derivative was prepared from polyepoxysuccinic acid and L-cysteine. The structure of the product was characterized by FT-IR and ^{13}C NMR spectra. Calcium carbonate crystals in the scale samples and corrosive test piece were observed with SEM and the scale corrosion mechanism of polyepoxysuccinic acid derivative was studied.

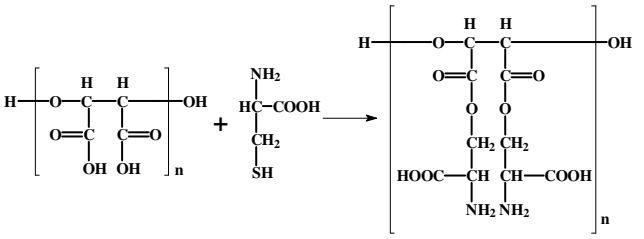
Synthesis of epoxy sodium succinate: Epoxy sodium succinate was synthesized by cyclization of maleic anhydride at 65 ºC, reacted for 4.5 h.



Synthesis of polyepoxysuccinic acid: Polyepoxysuccinic acid was synthesized by pyrocondensation of epoxy sodium succinate at 85 ºC, reacted for 2 h.



Synthesis of polyepoxysuccinic acid derivative: Polyepoxysuccinic acid and L-cysteine are put in three bottles and heated in the methyl silicone oil. The reaction temperature was 95 ºC 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 ºC for 6 h. Finally, the pale yellow of polyepoxysuccinic acid derivative was obtained.



Rate of scale inhibition performance: A certain concentration of Ca^{2+}, HCO_3^- and polyepoxysuccinic acid derivative were injected in deionized water, heated to 80 ºC for 12 h , standing, cooling and taking clear liquid. A few drops of hydrochloric acid was injected, heated and cooled. Mass concentration of Ca^{2+} was determined by EDTA method to assess the scale inhibition performance of scale inhibitors. The rate of scale inhibition is calculated by eqn. 1:

$$\eta = \frac{(C_1 - C_0)}{(C_2 - C_0)} \times 100\ \% \quad (1)$$

where C_1 is mass concentration of Ca^{2+} of heated water sample with polyepoxysuccinic acid derivative, mg L^{-1}; C_0 is mass concentration of Ca^{2+} of water sample without polyepoxysuccinic acid derivative, mg L^{-1}; C_2 is mass concentration of Ca^{2+} of preparing water sample, mg L^{-1}.

Measurement of the rate of corrosion inhibition: The aqueous solution of different concentration of corrosion inhibitor was prepared in a beaker. The polished A_3 II carbon steel slices after weighing is immersed in a solution, put the beaker in a constant temperature bath and keep the temperature at 40 ºC. and rotated at stated velocity for 72 h.The samples were washed rapidly with deionized water. After natural drying, the corrosion samples were wiped off corrosion products, dryed after cleaning with acetone and weighed with analysis of weighing scales.The rate of corrosion is calculated by eqn. 2:

$$b = \frac{8760 \times \Delta m \times 10}{A \cdot \rho \cdot T} \quad (2)$$

where Δm is the poor quality of the corrosion samples (g); A is surface area of the test piece (cm^2); ρ is the density of test piece (g cm^{-3}); T is test time of test piece (h).

The rate of corrosion inhibition is calculated by eqn. 3:

$$W = \frac{b_0 - b}{b_0} \times 100\ \% \quad (3)$$

where b_0 is the rate of corrosion of the test piece without corrosion inhibitor (mm a^{-1}); b is the rate of corrosion of the test piece with corrosion inhibitor (mm a^{-1}).

Preparation of scale sample: The rate of scale inhibition was detected at 80 ºC. The solution was filtered from the conical flask after experiment. The scale cling to bottom and wall of conical flask was dried at the certain temperature, then was brushed away and conserved in the dryer.

FT-IR: The structure of polyepoxysuccinic acid derivative was analyzed in 4000-400 cm^{-1} region with USA PE Spectrum PX-1.

^{13}C NMR: Using deuterium for water (D_2O) as solvent, polyepoxysuccinic acid derivative was dissolved in 5 mm nuclear magnetic test tube, then measured carbon spectrum determination of polyepoxysuccinic acid derivative under 25 ºC.

Structural features of calcium carbonate sample: Using S-250 SEM scanning electron microscope analyze structure of calcium carbonate sample. The calcium carbonate sample was stuck on the sample desk with double-sided adhesive, sprayed gold, then was observed under scanning electron microscope in the condition of 20 kV acceleration voltage.

RESULTS AND DISCUSSION

Fig. 1 showed FT-IR spectra of polyepoxysuccinic acid derivative and polyepoxysuccinic acid. 3430 cm^{-1} peak was the absorption peak of O-H of hydroxide radical and N-H of amino. 1110.24 cm^{-1} peak and 1069.79 cm^{-1} peak were the absorption peak of -COO- of ester base. 1397.64 cm^{-1} peak and 1308.78 cm^{-1} peak were the absorption peak of -COOH of the carboxyl and peak has certain strengthen than poly-

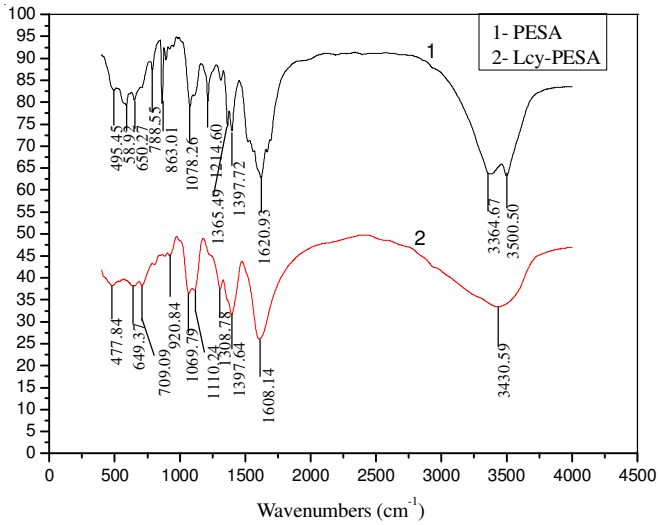


Fig. 1. FT-IR polyepoxysuccinic acid derivative and polyepoxysuccinic acid

epoxysuccinic acid. This absorption peak of polyepoxysuccinic acid derivative was different from polyepoxysuccinic acid. That showed polye-poxysuccinic acid derivative prepared from polyepoxysuccinic acid and L-cysteine.

Fig. 2 showed ^{13}C NMR spectrum of polyepoxysuccinic acid derivative and polyepoxysuccinic acid. Fig. 2(a) showed peak at 170-178 ppm was the absorption peak of carbon of C=O of carboxy group and 72-82 ppm peak was the absorption peak of carbon of -CH- of polyepoxysuccinic acid. Fig. 2(b) showed 171-178 ppm peak was impossible association of carboxy group and ester base because of a certain difference between polyepoxysuccinic acid and its derivative. 53-58 ppm peak was the absorption peak of carbon of C-O-C. 46-47 ppm and 26-39 ppm peak were the absorption peak of carbon of -CH-, CH_2- and -CH-NH_2 from L-cysteine of polyepoxy-succinic acid derivative. That showed polyepoxysuccinic acid derivative prepared from polyepoxysuccinic acid and L-cysteine.

Scale inhibition performance: The test of the rate of static scale inhibition, the scale inhibition performance of polyepoxy-succinic acid derivative and polyepoxysuccinic acid.was detected. The test results are showed in Table-1.

TABLE-1
SCALE INHIBITION RATE IN THE ABSENCE AND PRESENCE OF POLYEPXYSUCCINIC ACID AND POLYEPOXYSUCCINIC ACID DERIVATIVE

Chemical	Dosage (mg L^{-1})	Scale inhibition rate (%)
PESA	8	72.9
LCY-PESA	8	98.9

Table-1 showed that polyepoxysuccinic acid derivative is better than polyepoxysuccinic acid, under Ca^{2+} 400 mg L^{-1}, HCO_3^- 800 mg L^{-1} and polyepoxysuccinic acid derivative composite 8 mg L^{-1}, the scale inhibition rate of polyepoxy-succinic acid derivative can reach 98.9 %.

According to the test of the rate of corrosion inhibition the corrosion inhibition performance of polyepoxysuccinic acid derivative and polyepoxysuccinic acid was detected. (Table-2).

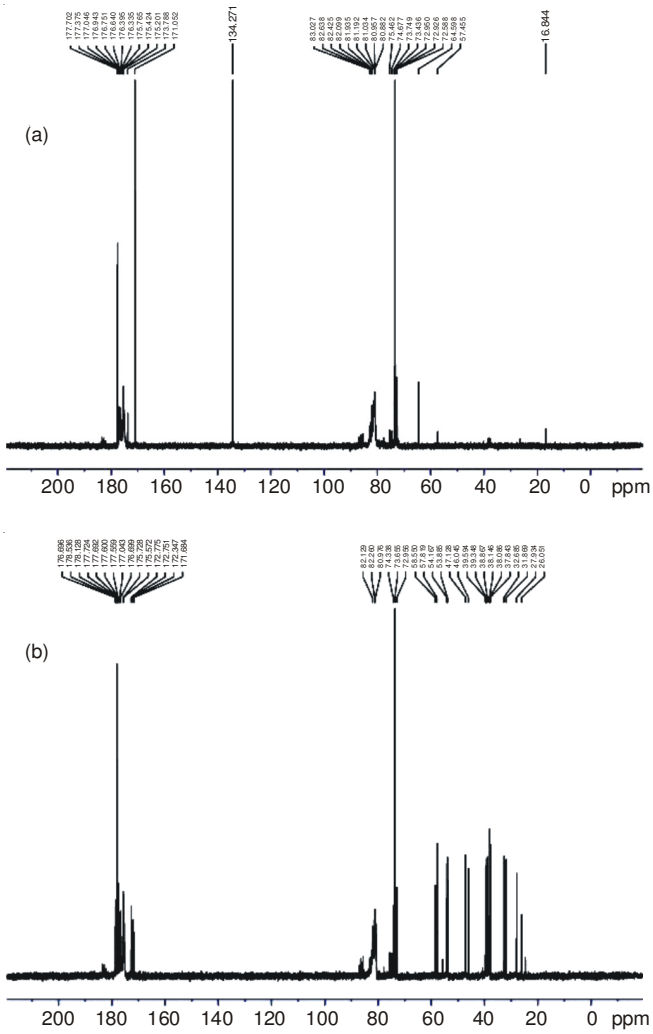


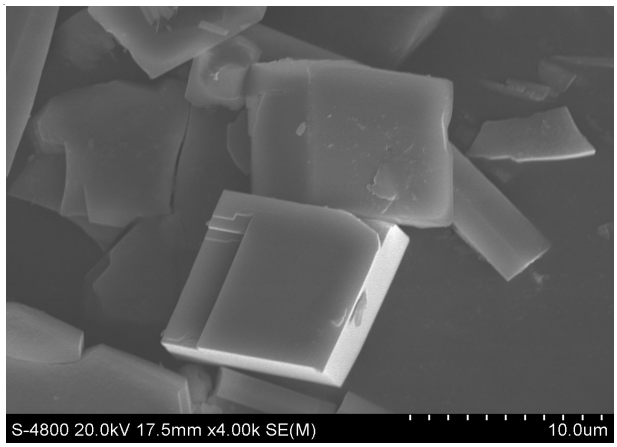
Fig. 2. ^{13}C NMR spectrum of (a) PESA and (b) PESA-LCY

TABLE-2
CORROSION INHIBITION RATE IN THE ABSENCE AND PRESENCE OF POLYEPOXYSUCCINIC ACID AND POLYEPOXYSUCCINIC ACID DERIVATIVE

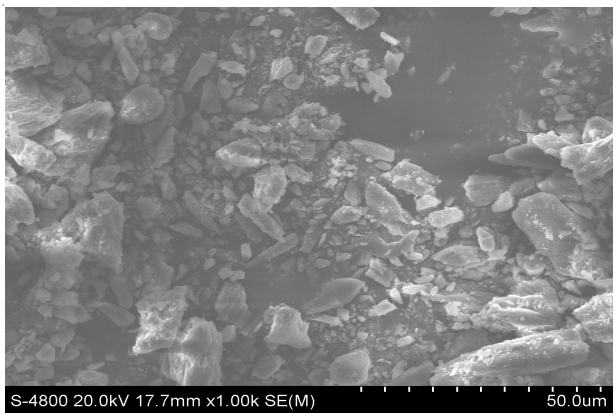
Chemical	Dosage (mg L^{-1})	Corrosion rate (mm a^{-1})	Corrosion inhibition rate (%)
Blank	0	0.3615	-
PESA	120	0.1530	57.68
LCY-PESA	120	0.1260	65.14

It was found that polyepoxysuccinic acid derivative is better than polyepoxysuccinic acid in corrosion inhibition performance and the corrosion inhibition rate can reach 65.14 %, while the corrosion inhibition rate of polyepoxysuccinic acid is 57.68 % in dynamic experiment under the temperature of 40 ºC. Polyepoxysuccinic acid derivative has improved on the corrosion inhibition. Its application performance was extended.

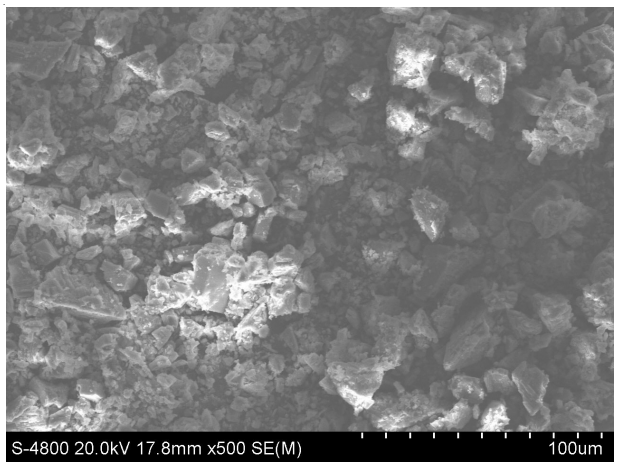
Results of SEM: Fig. 3(a) showed the most of the calcium carbonate crystals were calcite without LCY-PESA in the solution. Fig. 3(b) showed the calcium carbonate crystal lattice was distorted completely after 1 mg L^{-1} polyepoxysuccinic acid derivative was added in the configurating water, which was vaterite, the calcium carbonate crystal grain obviously less than the calcium carbonate crystal grain of the configu-



(a) SEM photograph of calcium carbonate sample from blank solution



(b) SEM photograph of calcium carbonate sample from the solution with 1 mg L^{-1} polyepoxysuccinic acid derivative



(c) SEM photograph of calcium carbonate sample from the solution with 2 mg L^{-1} polyepoxysuccinic acid derivative

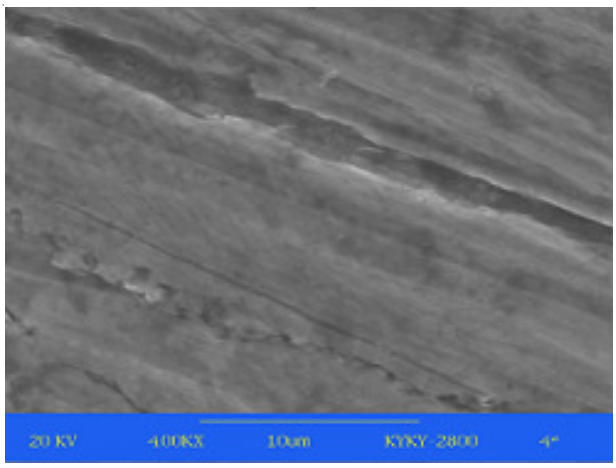
Fig. 3. SEM photograph of $CaCO_3$ sample from the solution with modified polyaspartic acid

rating water. Fig. 3(c) showed the calcium carbonate crystal lattice was distorted completely when the dosage of polyepoxysuccinic acid derivative was 2 mg L^{-1} and then crystal were finer.

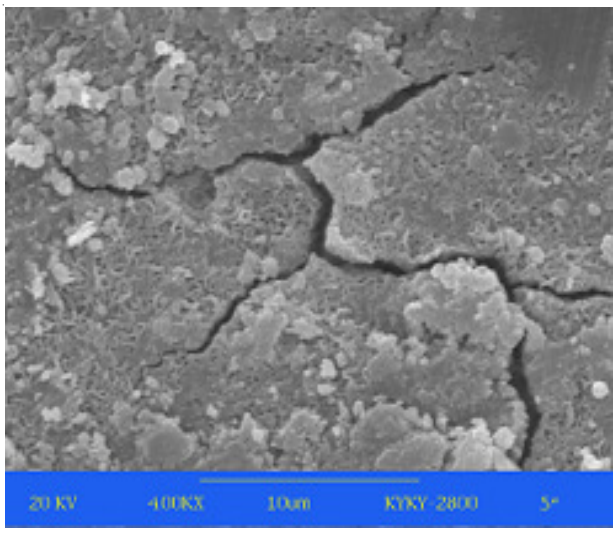
This further illustrated that the scale inhibition rate was improved due to the presence of calcium carbonate by calcite crystal shape and structure into the ball aragonite structure.

Polyepoxysuccinic acid derivative not only can form stable complex compound and Ca^{2+} in aqueous solution, reduce the Ca^{2+} concentration in the aqueous solution, reduce the possibility of forming such as $CaCO_3$ precipitation, but also make action with Ca^{2+} of formed $CaCO_3$ crystal lattice, result to physical adsorption and chemical adsorption. The electric double layer was formed on the surface of micro crystal and there are electrostatic repulsion between micro crystal, hampering the collision between them and the formation of large crystals, also hindering collisions and the formation of scale between micro crystals and the heat transfer surface of metal[12].

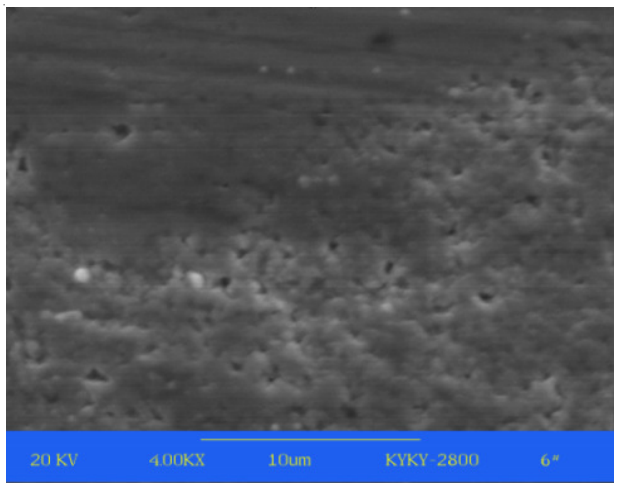
Surface analysis of corrosive test piece: Fig. 4(a) showed that there is only some the mechanical scratches before the test piece was immersed in solution. Fig. 4(b) showed the surface has a large number of corrosion products if the test piece of carbon steel was immersed in blank water. Fig. 4(c) showed that there is a relatively dense protective adsorption film layer on surface of the test piece when the test piece of carbon steel was immersed in solution with polyepoxysuccinic acid. While Fig. 4(d) showed the surface of the test piece is very dense protective adsorption film layer if it was immersed in solution with polyepoxysuccinic acid derivative. This is the reason why the corrosion inhibition rate of polyepoxysuccinic acid derivative was higher than polyepoxysuccinic acid.



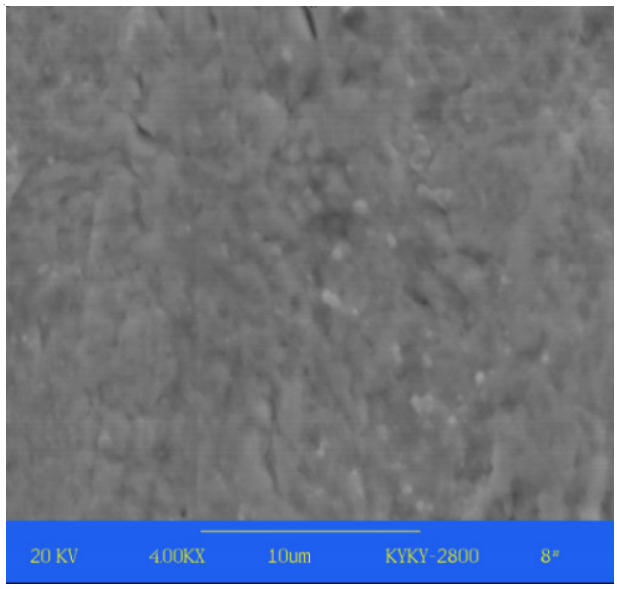
(a) SEM image of glazed carbon steel surface



(b) SEM image of corrosive test piece from blank water



(c) SEM image of corrosive test piece from the solution with polyepoxysuccinic acid



(d) SEM image of corrosive test piece from the solution with polyepoxysuccinic acid derivative

Fig. 4. SEM image of corrosive test piece from the solution with water treatment chemical

The corrosion inhibition of organic inhibitor molecules form the effective isolation film through the solid adsorption on the surface of the material. So the metal surface is separated from the reactant particles in the medium through corrosion inhibitor molecules space steric hindrance. The strength of the corrosion inhibitor molecules on the metal surface adsorption is not only related to metal surface state and medium conditions, but also associated with molecular structure of corrosion inhibitor. Polyepoxysuccinic acid derivative not only contains carboxyl, hydroxyl, *etc*. polar or non-polar groups as polyepoxysuccinic acid, but also contains amide group, sulfydryl, *etc*. when the metal has empty *d*-orbitals, a lone electron pair of O, N, S atoms of these groupsformed coordinate bonds with empty *d*-orbitals. So the corrosion inhibition rate of polyepoxysuccinic acid derivative is higher than polyepoxysuccinic acid through learning more chemical adsorption.

Conclusion

Polyepoxysuccinic acid derivative was synthesized from L-cysteine and polyepoxysuccinic acid which a condensation polymer through cyclization and polymerization with maleic anhydride. The scale inhibition rate of polyepoxysuccinic acid derivative can reach 98.9 % under Ca^{2+} 400 mg L^{-1}, HCO_3^- 800 mg L^{-1}, polyepoxysuccinic acid derivative 8 mg L^{-1}. Polyepoxysuccinic acid derivative is better than polyepoxysuccinic acid in corrosion inhibition performance and the corrosion inhibition rate can reach 65.14 % under the temperature of 40 ºC in dynamic experiment. The test results of SEM showed that the calcium carbonate crystal lattice was distorted completely from calcite to vaterite by using polyepoxysuccinic acid derivative. The surface of the test piece has dense protective adsorption film layer when it was immersed in solution with polyepoxysuccinic acid derivative.

ACKNOWLEDGEMENTS

This work was supported by the Science Foundation of Hebei Province, P.R. China (06213027).

REFERENCES

1. Betz Laboratories, Inc., US Patent 5062962, (1991).
2. I.T. Kenichi and T.G. Naoko, JP Patent 2001081184 (2007).
3. B.R. Zhang and F.T. Li, *Ind. Water Treat*., **2**, 22 (2002).
4. Y.X. Yu and J.J. Li, *J. Environ. Eng*., **2**, 85 (2005).
5. G. Wei, Y.N. Xu and R.C. Xiong, *J. Beijing Univ. Chem. Tech*., **50**, 59 (2001).
6. W. Lei, F.Y. Wang, M.Z. Xia and F.H. Wang, *J. Chem. Ind. Eng*., **32**, 2207 (2006).
7. D.F. Zidoves and P.M. Prabhu, US Patent 5562830 (1996).
8. H.M. Qin and H.S. Li, *Petrochem. Ind. Technol*., **52**, 52 (2003).
9. Q.H. Tao, Y.Z. Zhao, L.H. Guan, W.L. Liu and M.H. Liu, *Sci. Technol. Chem. Ind*., **52**, 52 (2008).
10. J.M. Zhang and D. Jin, *Ind. Water Treat*., **36**, 38 (2006).
11. W.Y. Shi, Z.M. Lv, F.Y. Wang and Y.T. Zhu, *Chin. J. Chem*., **651**, 651 (2011).
12. Y.H. Gao, Y.J. Wang, Z.F. Liu and H.H. Li, *Asian J. Chem*., **22**, 1495 (2010).