

Synthesis of Polyamine Grafted Chitosan Copolymer and Evaluation of Its Corrosion Inhibition Performance

Heping Li*, Hui Li, Yi Liu, and Xiaohua Huang

Key Laboratory of Road Structure and Material of Ministry of Transport, Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, Changsha 410114, P.R. China. *E-mail: lih@csust.edu.cn
(Received December 16, 2014; Accepted March 4, 2015)

ABSTRACT. Two new chitosan derivatives, polyamine grafted chitosan copolymers have been synthesized for corrosion protection of carbon steel in acidic medium. First, methyl acrylate graft chitosan copolymer (CS-MAA) was prepared by the reaction of chitosan (CS) and methyl acrylate (MAA) *via* the Michael addition reaction. Then, CS-MAA was reacted with ethylene diamine (EN) and triethylene tetramine (TN) respectively to synthesize ethylene diamine grafted chitosan copolymer (CS-MAA-EN) and triethylene tetramine grafted chitosan copolymer (CS-MAA-TN), and the structures were characterized by Fourier-transform infrared spectroscopy (FT-IR). At last, the corrosion inhibition activities on Q235 carbon steel were investigated by using gravimetric measurements, metallographic microscope, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The compounds CS-MAA-EN and CS-MAA-TN show an appreciable corrosion inhibition property against corrosion of Q235 carbon steel in 5% HCl solution at 25 °C. It has been observed that CS-MAA-EN shows greater corrosion inhibition efficiency than CS-MAA-TN. The inhibition efficiency of CS-MAA-EN was close to 90% when the mass fraction concentration was 0.2%–0.3%; the inhibition efficiency of CS-MAA-TN was close to 85% when the mass fraction concentration was 0.02%. The present work provided very promising results in the preparation of green corrosion inhibitors.

Key words: Polyamine grafted chitosan copolymer, Synthesis, Electro-chemical study, Corrosion inhibition

INTRODUCTION

Metal corrosion has gradually become a serious problem in our daily life and modern industry fields. In 2000, the loss of corrosion was about 6% of GDP in China. The current methods taken to reduce corrosion including surface coating, electrochemical protection, surface treatment and addition of corrosion inhibitor and some other methods. Adding corrosion inhibitor is an effective way to mitigate metal corrosion,¹ and it has the advantages of low price, processing simply, adaptability widely and so on. It produces a huge preservative efficacy for reducing the loss of equipment resources.^{2–4}

At present, common organic corrosion inhibitors contain amines,⁵ aldehydes,⁶ heterocyclic compounds,⁷ and imidazoline quaternary ammonium salt, etc.^{8,9} O, N, P, S atoms are contained in molecules, and the lone electron pair (such as amino, hydroxyl) in polar groups can be connected with the empty orbital on metal elements (such as the Fe atoms on the empty 3d orbital) to form coordination bonds, so the organic molecules firmly adsorbed on the metal surface and the nonpolar groups formed a protective film to prevent corrosion of metal.¹⁰

In recent years, with the increased awareness of environmental protection, new requirements are put forward for the development and application for corrosion inhibitor. Considering the property and economical goals, the research on environmentally friendly corrosion inhibitor has become the development trend of corrosion inhibitor. Chitosan, as the largest number of natural organic containing nitrogen carbohydrate and the second abundant organic natural resources, is nontoxic, cheap, biodegraded, and thus belonging to a typical “environment friendly” material.^{11,12} Chitosan molecular structure contains a large amount of free –OH and –NH₂ groups.^{13,14} and has good solubility in hydrochloric acid and acetic acid, however in other strong acid like sulphuric acid, solubility is very poor. The film forming nature of chitosan can be used to design the barrier coatings for corrosion resistance of active metals, which exhibit the essential characteristics of good corrosion inhibitor.¹⁵ Chitosan-polypyrrole-SiO₂ composites were synthesized, exhibited significantly high corrosion resistance for mild steel substrate.¹⁶ In this paper, chitosan is used as raw material to synthesize polyamine grafted chitosan derivatives, and its corrosion properties for Q235 steel have been studied.

EXPERIMENTAL

Reagents and Instruments

Chitosan (CS, deacetylating degree 95%), methyl acrylate (MAA) and triethylene tetramine (TN) were purchased from Aladdin Chemistry Co., Ltd., China; Methanol, anhydrous ethanol, ethylene diamine (EN) were purchased from Sinopharm Chemical Reagent Co., Ltd, China; hydrochloric acid, acetone and sodium hydroxide were purchased from Taishan Chemical Factory Co., Ltd, China. All reagents were at analytical grade and all solutions were prepared with deionized water.

The Q235 carbon steel specimens (size $\approx 5 \text{ cm} \times 2.5 \text{ cm}$ and 0.2 cm thick) were mechanically grinded with different grit size of SiC papers from 400 to 1200. Further, they were degreased with acetone in an ultrasonic bath to remove the impurities, then rinsed thoroughly with double distilled water and dried in air. Prior to each experiment, the specimens were treated as described and freshly used without further storage.

Infrared (IR) spectra were obtained with an Avatar-360 infrared spectrometer (Nicolet America company); Surface characterizations were recorded with an UMT230i metallographic microscope (Chongqing Aopu Photoelectric Technology Co Ltd); Electrochemical properties were measured with a CHI660C electrochemical workstation (Shanghai Zhenhua Instrument Co., Ltd.).

Synthesis of Polyamine Grafted Chitosan Copolymer

Synthesis of methyl acrylate graft chitosan copolymer (CA-MAA): CS (32 g) and MAA (100 mL) were added to MeOH (150 mL) in an 500 mL round-bottomed flask and stirred in water bath at 67°C for 48 h. The solid product was filtered and washed several times with methyl alcohol. CS-MAA was obtained after dried under vacuum. IR (ν_{max} , cm^{-1} , KBr): 3432 (–OH, –NH₂); 2925, 2868 (–CH); 1736 (–C=O); 898 (glucopyranose ring).

Synthesis of ethylene diamine grafted CS copolymer (CS-MAA-EN): CS-MAA (32g) and EN (30 mL) were added to MeOH (150 mL) in an 500 mL round-bottomed flask and stirred in water bath at 67°C for 24 h. The solid product was filtered and washed several times with methyl alcohol respectively. CS-MAA-EN was obtained after dried under vacuum. IR (ν_{max} , cm^{-1} , KBr): 3431 (–OH, –NH₂); 2921, 2872 (–CH); 1655 (amide, –C=O); 885 (glucopyranose ring).

Synthesis of triethylene tetramine grafted CS copolymer (CS-MAA-TN): 32 g of CS-MAA and TN (30 mL) was added to MeOH (150 mL) in an 500 mL round-bottomed

flask and stirred in water bath at 67°C for 24 h. The solid product was filtered and washed several times with methyl alcohol respectively. CS-MAA-TN was obtained after dried under vacuum. IR (ν_{max} , cm^{-1} , KBr): 3435 (–OH, –NH₂); 2920, 2859 (–CH); 1646 (amide, –C=O); 889 (glucopyranose ring).

Corrosion Inhibition Performance

Gravimetric measurement: For gravimetric measurements, the carbon steel coupons measuring $5 \times 2.5 \times 0.2 \text{ cm}^3$ were used. Inhibitor efficiency was determined by hanging the steel coupon measuring $5 \times 2.5 \times 0.2 \text{ cm}^3$ into a 5% HCl (500 mL) in the absence and presence of the inhibitors (CS, CS-MAA-EN and CS-MAA-TN, 0.1% by weight) at 25°C for 72 h. All subsequent concentrations of inhibitors were expressed in mass fraction concentration unless otherwise stated. At the end, the coupons were cleaned with distilled water, abraded lightly with emery paper, then washed with distilled water, acetone and dried at 110°C .

The corrosion rate was calculated by the following Eq. (1):

$$V_{\text{corr}} = \frac{W_0 - W_1}{At} \times 100 \quad (1)$$

Here, V_{corr} ($\text{mg}/\text{cm}^2 \text{ h}$) is the corrosion rate of metal steel sheets; W_0 (g) is the mass of metal steel sheets before corrosion; W_1 (g) is the mass of metal steel sheets removal from corrosion solutions; A (cm^2) is the surface area of hanging sheet, and t (h) is the immersion time.

The percent inhibition efficiency were calculated according to the following formula (2):

$$\eta = \frac{v_0 - v_1}{v_0} \times 100\% \quad (2)$$

where v_0 is the corrosion rate ($\text{mg}/\text{cm}^2 \cdot \text{h}$) in the absence of inhibitor and v_1 is the corrosion rate ($\text{mg}/\text{cm}^2 \cdot \text{h}$) in the presence of inhibitor.

Electrochemical measurements: The Tafel polarization curves studies were carried out in a 500 mL of 5% HCl solution in the absence and presence of various concentrations of inhibitors at 25°C . The experiments were started only after a stable open circuit potential (OCP) was achieved usually within the exposure time of 30 min. The electrochemical cell, assembled in a 750 mL round-bottomed flask, consisted of a saturated calomel electrode (SCE) as a reference electrode, carbon steel working electrode, and the graphite counter electrode (5 mm diameter). The SCE electrode was connected to the cell using a Luggin-Haber capillary salt bridge, the tip of which was separated from the surface of the working electrode by a distance of 2 mm. An electrometer was used

to connect all three electrodes to a Potentiostat (Model 283). A rate of 5 mV/min was used to scan a range of ± 200 mV with respect to open circuit potential.¹⁷ The percent inhibition efficiency (η) of tafel polarization curves was calculated Eq. (3).

$$\eta = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100\% \quad (3)$$

Here, I'_{corr} is the corrosion current density of HCl aqueous solution containing various amount of inhibitor, and I_{corr} is that of HCl solution without inhibitor.

Electrochemical impedance spectroscopic measurements (EIS) were carried out using AC signals of 5 mV amplitude for the frequency spectrum from 100 kHz to 0.01 Hz. The Nyquist representations of the impedance data were analysed with Zsimpwin software. The electrode was kept for half an hour in the test solution before starting the impedance measurements. The charge transfer resistance (R_{ct}), was obtained from the diameter of the semicircle of the Nyquist plot. The inhibition efficiency of the inhibitor was estimated from R_{ct} values in presence and in absence of the inhibitor by using Eq. (4).

$$\eta = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100\% \quad (4)$$

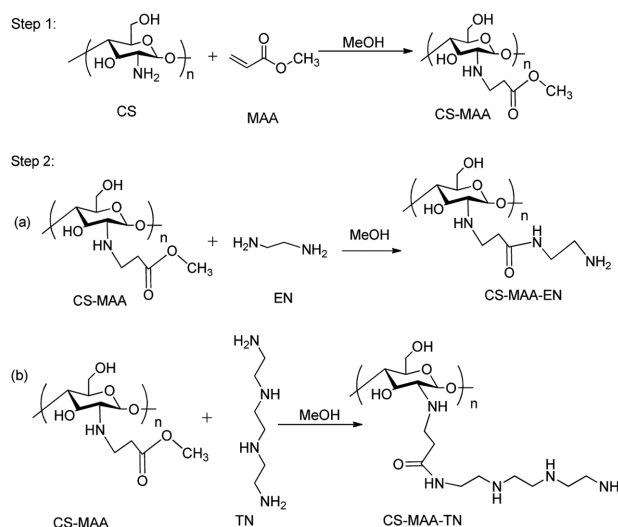
where, R'_{ct} and R_{ct} are the charge transfer resistance values without and with the addition of inhibitor.

RESULTS AND DISCUSSION

The Synthesis of Polyamine Grafted Chitosan Copolymer

The polyamine grafted chitosan copolymers were synthesized, and the synthetic route is shown in *Scheme 1*.

The structures of CS-MAA, CS-MAA-EN and CS-MAA-TN were characterized by IR. The data of IR were listed in the experimental section. CS-MAA had the broad absorption band at 3432 cm^{-1} is due to O-H and N-H stretching vibration; the absorption peak at 2925 and 2868 cm^{-1} are due to C-H stretching; the most obvious change, the IR spectra of CS-MAA compared with the CS, is the strong absorption peak at 1736 cm^{-1} , it was caused by C=O stretching vibration of ester groups. Compared with CS-MAA, the IR of CS-MAA-EN display a new peak at 1655 cm^{-1} , which is due to C=O stretching vibration of amide; and the IR of CS-MAA-TN, the peak of 1646 cm^{-1} is C=O stretching vibration of amide, which indicates amidation between CS-MAA and amine. More information of the absorption peak of $-\text{COOCH}_3$ only has a very weak absorption in the CS-MAA-EN and CS-



Scheme 1. Synthetic route of polyamine grafted chitosan copolymer.

Table 1. The different inhibitors for the inhibition of corrosion of Q235 carbon steel exposed in 5% HCl at 25 °C for 72 h

Solutions	V_{corr} (mg/cm ² ·h)	η (%)
5% HCl	0.962	—
0.1% CS+5% HCl	0.179	81.4
0.1% CS-MAA-EN+5% HCl	0.093	90.34
0.1% CS-MAA-TN+5% HCl	0.207	78.48

MAA-TN. The change could conclude that ester groups of CS-MAA had been amidated by EN and TN. It could be proved that the synthesis was successfully.

Weight Loss Measurement

In a constant temperature bath, usually a set of experiments including three blanks were carried out simultaneously. Triplicate determinations were made for each experiment. The average $\eta\%$ reported in *Table 1*. The standard deviation of the experiment is about 0.4–3.4%.

Table 1 shows that when the inhibitor concentration is 0.1%, the best property of inhibiting corrosion is CS-MAA-EN, the corrosion rate is $0.093\text{ mg}/(\text{cm}^2\cdot\text{h})$, and the inhibition efficiency is 90.34%; and followed by CS with its corrosion rate is $0.179\text{ mg}/(\text{cm}^2\cdot\text{h})$, inhibition efficiency is 81.4%; and then is CS-MAA-TN, with the corrosion rate is $0.207\text{ mg}/(\text{cm}^2\cdot\text{h})$, and inhibition efficiency is 78.48%.

The corrosion resistance of CS-MAA-EN is superior to that of CS, because CS-MAA-EN has more active $-\text{NH}_2$ groups. The lone electron pair of $-\text{NH}_2$ went through the 3d empty orbital of Fe, and then coordination reaction took place, and formed a layer of compact protective film on the surface of Q235. Thus the metal materials and corrosion

medium were separated, preventing further corrosion of the metal materials.

Comparing to CS, CS-MAA-TN exhibits lower anticorrosive efficacy. The reasons may be that as number of $-NH_2$ active group increases in molecules, the adsorption-desorption balance of inhibitor and metal material is destroyed. The corrosion products of Q235 steel will break off from the surface of the metal under the action of gravity, and the corrosion inhibitor can't readsorption timely that exacerbating the corrosion of metal base part.¹⁴ On the other hand, may be the branch chains of CS-MAA-TN are too long, and the adsorption sites are not uniform, these factors are the disadvantages to form the tight protection film, which resulting in the decrease of inhibition efficiency.

Surface Characterizations

The morphology of the hanging pieces before and after corrosion was determined by metallographic microscope, as shown in Fig. 1.

Fig. 1 showed that Q235 carbon steel specimen had a serious corrosion in 5% HCl solution, smooth or bright metal surface can hardly be found on the specimen. When adding mass fraction concentration of 0.1% CS, CS-MAA-EN and CS-MAA-TN inhibitors into 5% HCl solution system, the corrosion area on the surface is significantly reduced in each group of Q235 carbon steel, in which the corrosion area of

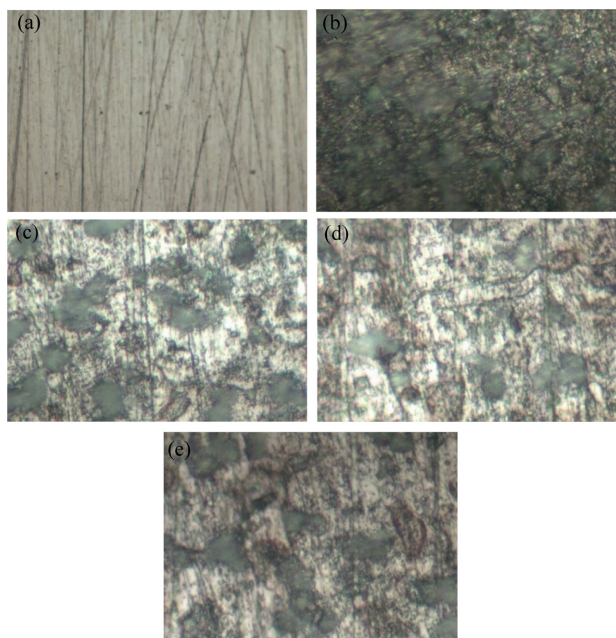


Figure 1. Metallographic microscope images of Q235 carbon steels immersion in different corrosive medium for 72h (enlargement 800 times; a, before corrosion; b, 5% HCl; c, 0.1% CS + 5% HCl; d, 0.1% CS-MAA-EN + 5% HCl; e, 0.1% CS-MAA-TN + 5% HCl).

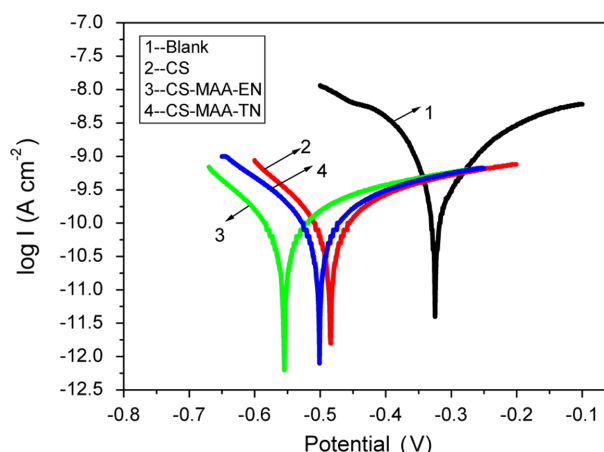


Figure 2. Tafel polarization curves at 25 °C for Q235 carbon steel in 5% HCl containing 0.1% mass fraction of CS, CS-MAA-EN and CS-MAA-TN.

the coupon in the solution adding CS-MAA-EN is the smallest, and followed by solution adding CS and CS-MAA-TN. This result is basically consistent with the weight loss experiment, which further shows polyamine grafted chitosan inhibitor can be adsorbed on the surface of Q235 carbon steel material, forming a compact protective film to prevent the rapid corrosion in acid medium.

Tafel Polarization Measurement

The tafel polarization curve for the inhibition in 5% HCl solution are shown in Fig. 2.

In Fig. 2, it can clearly be seen that the corrosion potential shifted negatively obviously in solutions adding inhibitor. Corrosion potential of CS-MAA-EN relative blank system negative shift value is 230 mV, indicating its strongest inhibitory effect on the cathodic reaction.

The analytical parameters of Fig. 2 are outlined in Table 2; E_{corr} is the corrosion potential, I_{corr} is the self-corrosion current density.

It can be seen from Table 2, the corrosion current density of the solution system adding corrosion inhibitors are decreasing, showing that the three kinds of corrosion inhibitor all had inhibitory effect on Q235 carbon steel. The current density of CS-MAA-EN was minimum, and CS-MAA-EN formed

Table 2. Results of Tafel plots in solutions containing 0.1% mass fraction of the inhibitor in 5% HCl at 25 °C

	Blank ^a	CS	CS-MAA-EN	CS-MAA-TN
E_{corr}/V	-0.325	-0.484	-0.555	-0.501
$I_{corr}/A \cdot cm^2 (\times 10^{11})$	70.1	11.2	9.325	13.51
η (%)	—	84.04	86.71	80.75

^aThe blank was 5% HCl solution.

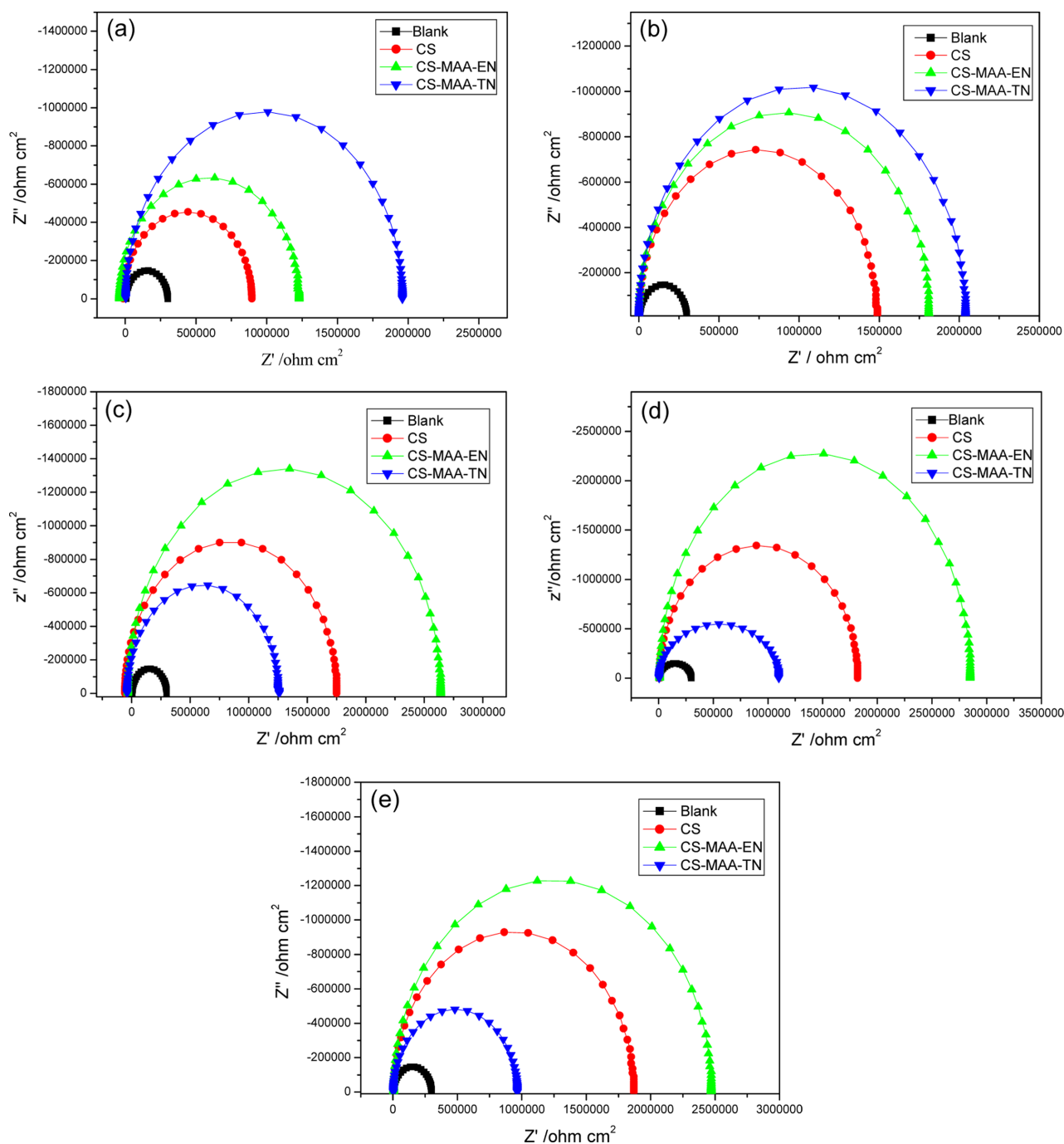


Figure 3. The Nyquist plot of Q235 carbon steel in 5% HCl in absence and presence of various mass fraction concentrations of corrosion inhibitors: (a) 0.02%, (b) 0.05%, (c) 0.1%, (d) 0.2%, and (e) 0.3%.

the most dense sustained-release film on the electrode surface, its corrosion rate is of the maximum, illustrating that among the three inhibitors of mass fraction concentration of 0.1%, the corrosion effect of CS-MAA-EN was the best. The data of Tafel polarization corrosion rate is accorded with the results of weight loss methods.

Electrochemical Impedance Spectroscopy

The Nyquist plots for the Q235 carbon steel working electrode in 5% HCl aqueous solutions containing various amounts of inhibitors are shown in Fig. 3. The main electrochemical parameters and inhibition rate obtained from Fig. 3 is shown in Table 3.

Table 3. The EIS electrochemical parameters and inhibition rate of inhibitor at different mass fraction concentration

Inhibitors	Concentration (%)	$R_{ct} (\times 10^4 \Omega \text{ cm}^2)$	η (%)
CS	0.02	90.8	62.26
	0.05	149.2	80.2
	0.1	181.1	83.43
	0.2	182.3	83.79
	0.3	187.3	84.22
CS-MAA-EN	0.02	130.1	77.45
	0.05	182.5	83.79
	0.1	267.1	88.95
	0.2	285.4	89.65
	0.3	247.3	88.06
CS-MAA-TN	0.02	196.2	84.8
	0.05	204.3	84.54
	0.1	130.2	77.31
	0.2	110.1	73.18
	0.3	96.6	69.46

Table 3 indicates that mass fraction concentration of corrosion inhibitor has a great influence on the inhibition effect. When the mass fraction concentration lower than 0.05%, the inhibition efficiency of CS-MAA-TN is the best, which is attribute to the more amine groups in CS-MAA-TN. The corrosion inhibition efficiency of CS increased with mass fraction concentration increasing; The inhibition efficiency of CS-MAA-EN increased with the increasing of mass fraction concentration, however when the concentration was up to 0.3%, the inhibition efficiency of CS-MAA-EN decreased. The inhibition efficiency was close to 90% when the mass fraction concentration was 0.2%–0.3%; The inhibition efficiency of CS-MAA-TN decreased with the increasing of mass fraction concentration, which is due to the branch chains were longer, the excess inhibitor destroyed the balance of adsorption-desorption equilibrium system.

CONCLUSIONS

CS-MAA-EN and CS-MAA-TN have been synthesized, and the anticorrosive performance of Q235 carbon steel materials in acid medium were evaluated by weight loss method, surface characterization, the Tafel polarization curves and AC impedance. CS-MAA-EN showed the highest anticorrosive performance when CS, CS-MAA-EN and CS-MAA-TN mass fraction concentration was 0.1%, the corrosion rate is 0.093 mg/(cm²·h) and corrosion inhibition efficiency is 90.34%. The corrosion inhibition performance of multiple amino grafted chitosan copolymer enhanced with the increased of the amino groups number. However, when the amino groups number increased to a certain extent, the inhibition

performance could be decreased at higher concentrations, that is because the excess inhibitor destroyed the balance of adsorption-desorption equilibrium system. Therefore, the appropriate mass fraction concentration of corrosion inhibitor has a great influence on corrosion inhibition efficiency. So the best inhibition efficiency of CM-MAA-EN was close to 90% when the mass fraction concentration was 0.2%–0.3%; the best inhibition efficiency of CS-MAA-TN was close to 85% when the mass fraction concentration was 0.02%.

Acknowledgments. This work was supported by the Open Fund of Key Laboratory of Road Structure and Material of Ministry of Transport (No. kfj130202), the Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation (No. 2014CL09), Changsha University of Science & Technology, P. R. China.

REFERENCES

- Zhang, Y. X. *Corrosion and Protection*, **2011**, 32, 494.
- Gupta, S. R.; Mourya, P.; Singh, M. M.; Singh, V. P. *Journal of Organometallic Chemistry*, **2014**, 767, 136.
- Obot, I. B.; Sandy, A. U. *Journal of Materials and Environmental Science*, **2011**, 2, 61.
- Madhankumar, A.; Rajendran, N. *Synthetic Metals*, **2012**, 162, 176.
- Raja, P. B.; Sethuraman, M. G. *Materials Letters*, **2008**, 62, 113.
- Mazumder, M.; Al-Muallem, H.; Faiz, M.; Ali, S. *Corrosion Science*, **2014**, 87, 187.
- Devara, Y.; Kesavan, M. G.; Nagarajan, S. *Chemical Science Review and Letters*, **2012**, 16, 1.
- David, E.; Arthur, A. J.; Paul, O.A.; Crystal, A. *International Journal of Industrial Chemistry*, **2013**, 4, 2.
- Sadeghi-Kiakhani, M.; Arami, M.; Gharanjig, K. *Journal of Environmental Chemical Engineering*, **2013**, 15, 406.
- Torres, V. V.; Rayol, V. A.; Magalhães, M. *Corrosion Science*, **2014**, 79, 108.
- Cheng, S.; Chen, S.; Liu, T. *Materials Letters*, **2007**, 61, 3276.
- Carneiro, J.; Tedim, J.; Fernandes, S. C. M. *Surface and Coatings Technology*, **2013**, 226, 51.
- Mahmoud, N.; Haddad, E. *International Journal of Biological Macromolecules*, **2013**, 55, 142.
- Ahmed, A. A.; Benaissa, R.; Jean, S. *Applied Clay Science*, **2012**, 65–66, 173.
- Fekry, A. M.; Mohamed, R. R. *Electrochimica Acta*, **2010**, 55, 1933.
- Ruhi, G.; Modi, O. P.; Dhawan, S. K. *Synthetic Metals*, **2015**, 200, 24.
- Yoo, S. H.; Kim, Y. W.; Chung, K.; Baik, S. Y.; Kim, J. S. *Corrosion Science*, **2012**, 59, 42.