Original Article

Cassava starch ternary graft copolymer as a corrosion inhibitor for steel in HCl solution

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\textbf{A R T I C L E  I N F O}

Article history:
Received 9 June 2019
Accepted 16 December 2019
Available online 25 December 2019

Keywords:
Corrosion inhibitor
Hydrochloric acid
Steel
Ternary graft copolymer
Adsorption

\textbf{A B S T R A C T}

Cassava starch ternary graft copolymer of cassava starch-sodium allylsulfonate-acryl amide graft copolymer (CS-SAS-AAAC) was synthesized through cassava starch (CS) chemically modified by grafting two monomers of sodium allylsulfonate (SAS) and acryl amide (AA) simultaneously. The inhibition performance of CS-SAS-AAAC on cold rolled steel (CRS) in 1.0 M HCl solution was experimentally studied by weight loss, electrochemical techniques and surface analysis, and its adsorption was theoretically investigated by both quantum chemical calculation and molecular dynamic (MD) simulation. The results indicate that CS-SAS-AAAC shows an optimum inhibition efficiency as high as 97.2\% at 50 mg L\textsuperscript{-1}, and its inhibitive ability exhibits more stronger than that of CS, SAS or AA. CS-SAS-AAAC behaves as a mixed-type inhibitor through geometric blocking effect. SEM and AFM images clearly reveal that the corrosion of CRS surface is efficiently retarded by CS-SAS-AAAC. Contact angle result suggests that the inhibited CRS surface is of hydrophobic nature. The adsorption active sites of CS-SAS-AAAC are mainly the grafted monomers of SAS and AA.

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\section{1. Introduction}

Adding inhibitors to solution for protecting metals against corrosion is the most practical method, especially for applications for acid pickling of metals, chemical cleaning and oil well acidification [1]. Conventional way is using the synthetic chemicals which cause pollution to the environment not only during synthesis but also when dispose after used. Natural polymers are typically non-toxic, low-cost, available in wide sources, environmentally safe and biodegradable, which is highly desirable as a corrosion inhibitor for metals [2]. Indeed, some natural polymers like pectin [3], Gum Arabic [4,5], chitosan [6], sodium carboxymethyl cellulose [7] and xanthan gum [8] have already been reported to show corrosion inhibition capability of steel in HCl solutions, though the inhibitive efficiency is still not as good as the synthetic corrosion inhibitors [6,7]. Accordingly, chemical modification of natural polymers has been reported as a solution to improving the inhibition efficiency. However, the question how to chemically modify on the natural poly-
mers has been emerged confronting with various chemical modification methods.

Herein, we offer a novel strategy of preparing high performance inhibitor. By graft copolymers like starch graft copolymers, we showed that higher inhibitive performance than the corresponding raw natural polymers. As early as 2011, our work team firstly reported that cassava starch graft copolymer (CSGC) was found to be an effective inhibitor for cold rolled steel (CRS) in HCl solution [9]. In 2014, Roy et al. [10] similarly reported the Guar gum graft copolymer exhibited better inhibitive ability than the raw material of Guar gum. Recently, cationic cassava starch graft copolymer (CCSGC) was found to show higher inhibitive ability than CSGC for CRS in HCl medium [11]. To further improve the inhibitive action, in this paper, the ternary graft copolymer of CS-SAS-AAGC was prepared and examined as corrosion inhibitor for CRS in HCl solution. The adsorption behavior and inhibitive mechanism were deeply discussed according to the combination experimental and theoretical results.

2. Experimental

2.1. Materials and solutions

CRS specimens (0.07% C, 0.3% Mn, 0.022% P, 0.010% S, 0.01% Si, 0.090% Al, and balance Fe) were used for the tested measurements. The aggressive solutions of 1.0 M HCl were prepared by dilution of AR grade 37% HCl with distilled water, and the additive inhibitor concentration range was from 5 to 50 mg L⁻¹. Industrial-grade of CS was purchased from Red River Hong Starch Co. Ltd. in Yunnan province of China, and analytical reagents of AA and SAS were obtained from Shanghai Chemical Reagent Company of China.

2.2. Preparation of CS-SAS-AAGC

CS-SAS-AAGC was prepared according to the procedure reported in our previous paper [12]. In brief, 3 g CS was dissolved in 150 mL H₂O. 0.3 g (NH₄)₂S₂O₈ and 0.35 g NaHSO₃ were added to the CS solution with intensive stirring, followed by adding 6.0 g SAS and 12.0 g AA simultaneously. These mixtures were shifted at 55 °C for about 3.5 h, and cooled down to room temperature. Thereafter, the mixture was participated in absolute C₂H₅OH. The filtrate was then refluxed in acetone for about 24 h to obtain pure CS-SAS-AAGC. The product was finally dried in vacuum at 50 °C for 24 h.

2.3. Weight loss measurements

CRS specimens of 2.5 cm × 2.0 cm × 0.06 cm were abraded by a series of emery paper (grade 320-500-800) and then washed with distilled water, degreased with acetone, and finally dried with a cold air stream. Afterwards, they were totally immersed in beakers containing 250 mL HCl tested solutions without and with a series of inhibitor concentration using glass hooks and rods. The experimental temperature was maintained at 20 ± 0.1 °C using a water thermostat. After immersing for 6 h, the CRS sheets were taken out, and were thoroughly scrubbed using brush under running water, and further washed with ethanol to remove corrosion products. In order to get good reproducibility, experiments were carried out in triplicate. The average weight loss (±0.1 mg) of three parallel CRS sheets was obtained, and then inhibition efficiency from weight loss (ηw) values can be calculated according to following equation:

\[ \eta_w = \frac{v_0 - v}{v_0} \times 100\% \]  \hspace{1cm} (1)

where \( v_0 \) and \( v \) are the values of the average weight loss without and with addition of the inhibitor, respectively.

2.4. Electrochemical tests

Electrochemical tests were conducted on a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research) with the three-electrode cell consisting of reference electrode (saturated calomel electrode (SCE) coupled to a fine Luggin capillary, counter electrode (large platinum plate of 2.0 cm × 2.0 cm) and the working electrode (WE) with the exposed surface area of 1.0 cm × 1.0 cm. Before potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements, WE was immersed in 1.0 M HCl solutions for 2 h at Open circuit potential (OCP) to reach a steady state. The polarization curves were obtained in the potential range from -250 to +250 mV versus OCP at a scan rate of 0.5 mV s⁻¹. Inhibition efficiency (ηp) is calculated through the corrosion current density values (\( i_{\text{corr}} \)) [12]:

\[ \eta_p = \frac{i_{\text{corr}(0)} - i_{\text{corr(inh)}}}{i_{\text{corr}(0)}} \times 100\% \]  \hspace{1cm} (2)

where \( i_{\text{corr}(0)} \) and \( i_{\text{corr(inh)}} \) represent corrosion current density values (μA cm⁻²) without and with inhibitor, respectively.

EIS was carried out at a stable OCP level with the employed frequency range from 100 kHz to 10 mHz, and the signal amplitude was 10 mV root mean square. Inhibition efficiency from EIS (ηp) is calculated on the basis of the equation [12]:

\[ \eta_p = \frac{R_{t(inh)}}{R_{t(0)}} \times 100\% \]  \hspace{1cm} (3)

where \( R_{t(0)} \) and \( R_{t(inh)} \) are charge transfer resistance values in the absence and presence of inhibitor, respectively.

2.5. Surface analysis

Scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle measurements were examined by FEI QUANTA 200 scanning electron microscope (America), SPA-400 SPM Unit atomic force microscope (Japan) and OCA20 optical contact angle (Dataphysics company, Germany), respectively.

2.6. Quantum chemical calculations

Quantum chemical calculations based on density function theory (DFT) were performed with DMol³ in Materials Studio 4.0 software from Accelrys Inc. [13], and were done at the GGA/BLYP [14]/DND [15]/COSMO [16] without any symmetry and spin constraints. Through frequency calculations, all
optimized geometric structures of studied molecules are verified that their vibrations have no imaginary frequency. The parameter criteria for the convergence tolerances of energy, maximum force, maximum displacement, SCF convergence criteria and k-point set are $1.0 \times 10^{-3}$ Ha, $2.0 \times 10^{-3}$ HaÅ, $5.0 \times 10^{-3}$ Å, $1.0 \times 10^{-6}$ and $1 \times 1 \times 1$, respectively.

2.7. Molecular dynamics (MD) simulations

MD simulations were performed with Discover program in Materials Studio 4.0 software from Accelrys Inc [13]. Fe (001) plane was firstly cleaved from pure Fe crystal, the surface was then optimized to the energy minimum, and then was enlarged to fabricate an appropriate supercell. After that, a vacuum slab with 1 Å thickness was built above the Fe (001) supercell with 31.53 Å × 31.53 Å × 15.30 Å of total 1331 Fe atoms. Meanwhile, the optimized inhibitor layer without or with 500 H$_2$O molecules were built using the Amorphous cell program. Finally, the adsorption system was built by layer builder to place the inhibitor layer to Fe (001) supercell. All these slabs are separated by a 10 Å vacuum thickness to ensure that the interaction between the periodically repeated slabs along the normal of the surface is small enough. The adsorption system was optimized using COMPASS force field. The MD simulation was performed under 298 K, NVT ensemble, with a time step of 1.0 fs and simulation time of 1000 ps.

3. Results and discussion

3.1. Weight loss measurement

Fig. 1 shows the inhibition efficiency ($\eta$) of CS-SAS-AAGC at different concentrations in the range of 5–50 mg L$^{-1}$ in 1.0 M HCl at 20 °C. $\eta$ increases with increasing CS-SAS-AAGC the additive concentration. For comparison, CS, SAS and AA which are the raw materials of CS-SAS-AAGC were tested at the same condition. As expected also shown in Fig. 1, CS-SAS-AAGC showed more higher $\eta$ than the individual CS, SAS or AA at the equivalent concentration. For CS-SAS-AAGC, the $\eta_{\text{max}}$ was 97.3% at 50 mg L$^{-1}$. The $\eta_{\text{max}}$ for AA, CS and SAS was 57.9%, 34.1% and 25.1%, respectively. These results indicate that both SAS and CS have poor inhibitive ability, and AA has better inhibitive ability than SAS and CS, whereas CS-SAS-AAGC is an effective inhibitor. It is evident that the high inhibitive ability can be attributed to grafting of both SAS and AA onto CS. The addition of N atoms enhances adsorption of the inhibitor on metal surface. Also, the molecule covering area of CS-SAS-AAGC is higher than that of CS, SAS or AA, and likely to efficiently cover more surface area (due to adsorption) of steel.

It should be noted that SAS has the lowest inhibition efficiency. The reason could be explained on the basis of its chemical structure. In HCl solution, CRS charges negative owing to the specific adsorption of Cl$^-$. All CS, AA and CS-SAS-AAGC can be protonated by H$^+$, then protonated CS, AA and CS-SAS-AAGC can physical adsorb on negative steel surface through electrostatic attraction, followed by chemical adsorption. On the other hand, SAS is ionized into Na$^+$ and SAS-. There is a strong electrostatic repulsion between the negatively charged steel surface and SAS-. As a result, SAS- hardly physical adsorb onto CRS surface. Thus, SAS exhibits the lowest inhibitive action among these studied compounds.

Table 1 shows a comparison of the $\eta$ of CS-SAS-AAGC with reported natural polymers for steel in HCl solution. Clearly, CS-SAS-AAGC stands out the best inhibition performance among those reported inhibitors. Moreover, CS-SAS-AAGC shows better inhibition than either CSGC or CCGC, which implies that starch grafted with binary vinyl monomers can be deemed as another useful method to prepare the efficient graft copolymer inhibitor.

<table>
<thead>
<tr>
<th>Inhibitor (°C)</th>
<th>$T$</th>
<th>$c$ (HCl)</th>
<th>$c$ (inhibitor)</th>
<th>$\eta$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-SAS-AAGC</td>
<td>20</td>
<td>1.0 M</td>
<td>50 mg L$^{-1}$</td>
<td>97.2</td>
<td>this paper</td>
</tr>
<tr>
<td>pectin</td>
<td>25</td>
<td>1.0 M</td>
<td>2000 mg L$^{-1}$</td>
<td>89.3</td>
<td>[3]</td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>25</td>
<td>1.0 M</td>
<td>4000 mg L$^{-1}$</td>
<td>92</td>
<td>[4]</td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>25</td>
<td>1.0 M</td>
<td>1000 mg L$^{-1}$</td>
<td>95</td>
<td>[5]</td>
</tr>
<tr>
<td>Chitosan</td>
<td>30</td>
<td>0.1 M</td>
<td>4 μM</td>
<td>63</td>
<td>[6]</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>25</td>
<td>1.0 M</td>
<td>0.04%</td>
<td>72</td>
<td>[7]</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>25</td>
<td>15%</td>
<td>500 mg L$^{-1}$</td>
<td>90.8</td>
<td>[8]</td>
</tr>
<tr>
<td>CSGC</td>
<td>20</td>
<td>1.0 M</td>
<td>100 mg L$^{-1}$</td>
<td>85.6</td>
<td>[9]</td>
</tr>
<tr>
<td>CCGC</td>
<td>20</td>
<td>1.0 M</td>
<td>50 mg L$^{-1}$</td>
<td>96.3</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Fig. 1 – Relationship between inhibition efficiency ($\eta$) and inhibitor concentration ($c$) in 1.0 M HCl solution at 20 °C using weight loss method with immersion time of 6 h.
where adsorption coefficients are negligible for the method with immersion time of 6 h.

Fig. 2 – Langmuir adsorption isotherm of inhibitor on CRS surface in 1.0 M HCl solution at 20 °C using weight loss method with immersion time of 6 h.

Table 2 – Parameters of the straight lines of c/θ vs. c and adsorption free energy (ΔG°) in 1.0 M HCl at 20 °C (Weight loss method, immersion time is 6 h).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>r</th>
<th>Slope</th>
<th>K (L mg⁻¹)</th>
<th>ΔG° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAS</td>
<td>0.9952</td>
<td>3.66</td>
<td>0.0428</td>
<td>−25.99</td>
</tr>
<tr>
<td>CS</td>
<td>0.9994</td>
<td>2.63</td>
<td>0.0673</td>
<td>−27.09</td>
</tr>
<tr>
<td>AA</td>
<td>0.9995</td>
<td>1.51</td>
<td>0.0903</td>
<td>−27.81</td>
</tr>
<tr>
<td>CS-SAS-AAGC</td>
<td>0.9999</td>
<td>0.99</td>
<td>0.5058</td>
<td>−32.01</td>
</tr>
</tbody>
</table>

Organic inhibitor generally exhibits inhibitive ability via its adsorption on metal surface, and the adsorption behavior can be elucidated by adsorption isotherm. It is assumed that the adsorption of studied inhibitors on steel surface obeys Langmuir adsorption isotherm [17]:

\[
c = \frac{1}{\theta} \frac{K}{c} + c
\]

where c is the concentration of inhibitor (mg L⁻¹), K the adsorptive equilibrium constant (L mg⁻¹), and θ is the surface coverage with the value of inhibition efficiency (η_{PW}) [17].

The straight fitted lines of c/θ vs. c for SAS, CS, AA and CS-SAS-AAGC are shown in Fig. 2, and their linear regression parameters are given in Table 2. All linear correlation coefficients (r) are almost equal to 1, which indicates that the adsorption of these studied inhibitors on steel surface follows Langmuir adsorption isotherm. It should be noted that the slopes for SAS, AA and CS are deviated from 1, while that for the graft polymer of CS-SAS-AAGC is almost equal to 1. This result implies that interaction force among adsorbed inhibitor molecules of CS, SAS or AA is relative stronger, while is almost negligible for CS-SAS-AAGC [18]. Larger K means that stronger adsorption ability for a given inhibitor, and generally leads to better inhibitive performance. K values of these inhibitors follow the order: CS-SAS-AAGC > AA > CS > SAS, which agrees well with the order of inhibition efficiency, and suggests that the product of CS-SAS-AAGC exhibits more stronger adsorptive ability than the raw materials of CS, SAS or AA.

Fig. 3 shows potentiodynamic polarization curves of the CRS electrode corrosion in 1.0 M HCl solution without and with CS-SAS-AAGC at 20 °C. Comparing with the curves for un inhibited HCl solution, both cathodic and anodic curves for CRS in inhibited solution containing CS-SAS-AAGC shift to lower current densities, and their polarization over-potentials are more strengthened significantly. As a result, the corrosion of CRS is efficiently retarded by CS-SAS-AAGC, and the inhibitive action is enhanced with the increase of inhibitor concentration.

The extrapolation of Tafel linear cathodic and anodic regions is an ordinary method to get electrochemical corrosion parameters. For the strong polarization region, cathodic and anodic Tafel lines are difficult to obtain owing to significant change in the surface state of electrodes. For the reason, in order to obtain electrochemical parameters of corrosion processes by fitting the weak polarization region of −50 to −10 mV (vs. E_{corr}) and 10−50 mV (vs. E_{corr}) [22]. However, this weak region could suffer from their sensitivity to mea-
suring errors owing to using only a few data points [23]. By considering these points, optimum fitted Tafel lines in weak polarization region should be wider with more experimental data. Accordingly, the corrosion parameters including corrosion current densities (\(I_{\text{corr}}\)), corrosion potential (\(E_{\text{corr}}\)), the cathodic Tafel slope (\(b_c\)), and anodic Tafel slope (\(b_a\)) were calculated by fitting the weak polarization curves of Tafel polarization in the optimum region of −200 to −10 mV (vs. \(E_{\text{corr}}\)) and 10−100 mV (vs. \(E_{\text{corr}}\)). Table 3 lists polarization curves parameters including corrosion potential (\(E_{\text{corr}}\)), current densities (\(I_{\text{corr}}\)), cathodic Tafel slope (\(b_c\)) and anodic Tafel slope (\(b_a\)), which are obtained by fitting optimum both cathodic and anodic Tafel linear regions, and then the inhibition efficiency (\(\eta_p\)) can be calculated from \(I_{\text{corr}}\). In the presence of CS-SAS-AAGC, \(I_{\text{corr}}\) decreases remarkably comparing with uninhibited HCl blank solution. \(\eta_p\) increases with an increase of the CS-SAS-AAGC concentration, and the maximum \(\eta_p\) of 50 mg L\(^{-1}\) CS-SAS-AAGC reaches the satisfying value of 96.5%, which indicates that the graft polymer of CS-SAS-AAGC can almost completely retard the corrosion of CRS in 1.0 M HCl solution.

Along with the increase of CS-SAS-AAGC concentration, \(E_{\text{corr}}\) shifts to the positive value with the increase in CS-SAS-AAGC concentration, but the maximum shift of \(E_{\text{corr}}\) value (27 mV) is much less than 85 mV, so CS-SAS-AAGC acts as a mixed-type inhibitor [24,25]. Tafel slope of \(b_c\) almost remains stable, while changes to some extent for \(b_a\), which implies that the adsorption of CS-SAS-AAGC does not change the cathodic hydrogen permission mechanism, while mainly change the anodic corrosion mechanism.

### Table 3 – Potentiodynamic polarization curves parameters for the corrosion of CRS in 1.0 M HCl solutions containing different concentrations of CS-SAS-AAGC at 20 °C.

<table>
<thead>
<tr>
<th>(c) (mg L(^{-1}))</th>
<th>(E_{\text{corr}}) (mV vs. SCE)</th>
<th>(I_{\text{corr}}) (μA cm(^{-2}))</th>
<th>−(b_c) (mV dec(^{-1}))</th>
<th>(b_a) (mV dec(^{-1}))</th>
<th>(\eta_p) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−459</td>
<td>203.0</td>
<td>123</td>
<td>55</td>
<td>−</td>
</tr>
<tr>
<td>5</td>
<td>−446</td>
<td>43.5</td>
<td>121</td>
<td>82</td>
<td>78.8</td>
</tr>
<tr>
<td>20</td>
<td>−436</td>
<td>8.9</td>
<td>101</td>
<td>69</td>
<td>95.6</td>
</tr>
<tr>
<td>50</td>
<td>−432</td>
<td>7.2</td>
<td>121</td>
<td>82</td>
<td>96.5</td>
</tr>
</tbody>
</table>

3.3. **Electrochemical impedance spectroscopy (EIS)**

Nyquist diagrams of CRS electrode in 1.0 M HCl solutions at 20 °C without and with 5, 20, 50 mg L\(^{-1}\) CS-SAS-AAGC are shown in Fig. 4. Each Nyquist spectra appears an individual capacitive loop, indicating that the corrosion of CRS in 1.0 M HCl solution is mainly controlled by charge transfer at electrode/solution interface [26,27]. As compared with that for blank solution, it should be noted that the general shape for all inhibited concentrations remains unchanged, which suggests that the addition of CS-SAS-AAGC does not alter the corrosion mechanism [28,29]. Clearly, the diameter of capacitive loop is enlarged significantly when CS-SAS-AAGC was added to 1.0 M HCl, which confirms that the corrosion of CRS is drastically retarded. It should be noted that these capacitive loops are depressed semicircles, not the perfect semicircles, which could be attributed to the frequency dispersion as a result of the geometrical factors like roughness and inhomogeneous of electrode surface [30].

It should be noted the steel surface may adsorb intermediates like (FeH\(^+\))\(_{\text{ads}}\), (FeCl\(^-\))\(_{\text{ads}}\) and inhibitor molecules, but no inductive arc appears in the Nyquist diagram associated with these adsorbed species. In general, an inductive arc is related to the unstable state of electrode surface that is caused by adsorbed intermediates. These adsorbed intermediates does not lead to instability state of CRS electrode, and so there is only one depressed capacitive loop in the present inhibition system.

EIS results are fitted by the typical Randles equivalent circuit of \(R_s(Q_s)\) that has been plotted several times in our earlier published papers [9,11,12,17]. \(R_s\) and \(R_t\) are the solution resistance and charge transfer resistance, respectively. \(Q\) is composed of the double capacitance (\(C_d\)) and the depression coefficient (\(\alpha\)) with the following relationship [31,32]:

\[
C_d = CPE \times (2\pi f_{\text{max}})^{\alpha - 1}
\]

where \(f_{\text{max}}\) represents the frequency at which imaginary impedance is maximal in Nyquist plot. All EIS parameters of \(R_s, R_t, Q, f_{\text{max}}, \alpha\), chi-squared (\(\chi^2\)), \(C_d\) and \(\alpha\) are summarized in Table 4. The low \(\chi^2\) values in Table 4 verifies that the fitted data has good reliability using Randles equivalent circuit. It should be noted that \(\chi^2\) is relative higher in the presence of 50 mg L\(^{-1}\) CS-SAS-AAGC. In general, the fitted error will become larger for more complex system. Thus, this result could be attributed to more complex adsorption process on electrode/solution interface after adding higher inhibitor dosage to acid media. \(R_s\) values are as low as 3.1–3.5 Ω cm\(^2\), and so the solution resistance can be negligible. There is frequency dispersion on electrode/solution interface owing to \(\alpha < 1\). Also, the addition of CS-SAS-AAGC slightly change the value of \(\alpha\) which suggests that the depressed nature of electrode/solution interface
almost remains unchanged after adding CS-SAS-AAGC to the HCl solution. \( R_t \) increases remarkably for the inhibited solution, which means that the corrosion of CRS is efficiently retarded by CS-SAS-AAGC. The corresponding \( \eta_r \) can reach a higher value of 78.9% even at a little concentration of 5 mg L\(^{-1}\), and is higher than 93% at 50 mg L\(^{-1}\). Therefore, CS-SAS-AAGC exhibits the efficient inhibitor for corrosion of CRS in 1.0 M HCl solution. In contrast, the decrease of both \( Q \) and \( C_{dl} \) in the presence of CS-SAS-AAGC can be related to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [33,34]. Values of \( \eta_w \), \( \eta_t \), \( \eta_r \) from three experimental methods are good agreement in between.

### 3.4. Surface analysis

SEM, AFM and contact angle images of CRS surface are summarized in Fig. 5. CRS sample before immersion appeared smooth and some abrading scratches on the whole surface (Figs. 5a and b), and its water contact angle was in the range of 71.4–72.3° (Fig. 5c), so water was easy to spread on the whole CRS surface. When CRS surface was totally immersed in 1.0 M HCl solution for 6 h, the surface was severely damaged and turned rather rough (Figs. 5d and e), and its contact angle is dropped to as low as 43.1–45.3° given in Fig. 5(f), which can be related to the rather rougher corroded CRS surface. With the addition of 50 mg L\(^{-1}\) CS-SAS-AAGC, as Figs. 5(g) and (h) show, the corrosion degree of CRS surface was retarded to more extent, and appeared relative more compact and uniform. In Fig. 5(i), the contact angle of the inhibited CRS surface was obtuse angle of 102.7–103.8°, and so it turned into the hydrophobic nature, which can efficiently shield CRS surface from corrosion attack by acid water solution.

### 3.5. Quantum chemical calculations

CS is composed of about 17% amylose and 83% amylpectin [35,36], and it reacts with vinyl monomer through a chain reaction mechanism consisting of chain initialization, chain growth and chain termination steps [37]. Since CS consists of a large number of glucose units, one glucose molecule was chosen as the simple model in our recent studies [12,38]. In this paper, amylose disaccharide (ALDS) and amylpectin disaccharide (APDS) are further chosen to be the calculation models, and their molecular structures are presented in Figs. 6(a) and (b), respectively. For the vinyl monomers, only one SAS and one AA molecule are studied in order to simplify the theoretical calculations. In water solution, SAS was ionized into Na\(^+\) and SAS\(^-\). The VMs of SAS and AA were simultaneously added into the reaction system. Thus, SAS- or AA could simultaneously react with ALDS or APDS to respectively form four molecules of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA or APDS-AA-SAS, and their corresponding molecules are shown in Figs. 6(c–f).

The optimized molecular structures of ALDS, APDS, ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS at the level of GGA/BLYP/DND/COSMO are shown in Fig. 7. The glucose in two disaccharide molecules of ALPS and APDS is the chair conformation, and this conformation remains unchanged in ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS. Comparing with raw molecules of ALPS and APDS, it is evident that products of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS becomes more larger and has more polar N, S and O atoms.

The dipole moment (\( \mu \)) can be used to determine the physical adsorption ability of an inhibitor molecule on metal surface, and higher \( \mu \) results in better inhibition performance [39]. In Table 5, \( \mu \) values of grafting polymers of APDS-AA-SAS, APDS-SAS-AA, ALDS-AA-SAS and ALDS-SAS-AA are more higher than raw molecules of ALDS and APDS, which indicates that the improved inhibition force of grafting polymer could be attributed to stronger physical adsorption than raw material.

Besides physisorption, the chemisorption can also be considered, and it is usually can be elucidated by molecular orbitals. Among various molecular orbitals, two frontier orbits of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the most reactive orbitals. Both HOMO and LUMO electron densities of ALDS, APDS, ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS were also shown in Fig. 7. For either ALDS or APDS, HOMO is well located on the pyran ring of one glucose molecule, while LUMO is focused on another glucose molecule. With respect to four graft compounds of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS, HOMO is mainly located on the substituted group of SAS\(^-\), while LUMO is focused on another substituted group of AA. On the other hand, either ALDS or APDS is absent for both HOMO and LUMO. In a word, the active adsorption sites of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA or APDS-AA-SAS are the grafted monomers of SAS and AA. SAS- group in donate electrons to the empty d-orbitals of Fe atom to form coordinate bond, while AA can accept electrons from Fe atom to form back-donating bond.

Values of the energy of HOMO (\( E_{\text{HOMO}} \)) and that of (\( E_{\text{LUMO}} \)) were calculated and listed in Table 5. Energy gap (\( \Delta E \)), absolute electronegativity (\( \beta \)), global hardness (\( \gamma \)) and global softness (\( \varsigma \)) are calculated from following relationships [40]:

\[
\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}
\]

\[
\beta = -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}})
\]
According to the principle of hard acid-base theory, the parameter $\beta$ is related to the chemical potential. Higher $\beta$ value corresponds to better inhibitive performance. According to Eq. (10), $\gamma$ is equal to $\Delta E/2$. The lower $\gamma$ value implies more polarizability and higher inhibitive action. The parameter $s$ is reciprocal to $\gamma$, thus higher $s$ value is related to more efficiency. The parameter $\Delta N$ exhibits inhibition performance resulted from electrons donation. If $\Delta N < 3.6$, the chemisorption and inhibition efficiency increase with increasing in electron donating ability to metal surface [44].

Experimental results from weight loss, polarization curves and EIS confirm that CS-SAS-AAGC significantly improves the inhibition performance comparing with raw material of CS. As can be seen from Table 5, comparing with the chosen raw compounds of ALDS and APDS, either polymer of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA or APDS-AA-SAS has higher values of $E_{\text{HOMO}}$, $\beta$ and $\Delta N$, and lower values of $E_{\text{LUMO}}$, $\Delta E$ and $\gamma$. Thus, there is a good correlation between inhibition efficiency and the quantum chemical parameters of $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, $\Delta E$, $\beta$, $\gamma$, $s$ and $\Delta N$. Among four chosen polymers of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS, APDS-AA-SAS has the highest $E_{\text{HOMO}}$, $\beta$ and $\Delta N$, and the lowest $E_{\text{LUMO}}$, $\Delta E$ and $\gamma$.
\[ \Delta E \] and \( \gamma \). It can be deduced that APDS-AA-SAS stands out the strongest adsorptive ability.

### 3.6. Molecular dynamics (MD) simulations

MD simulations is a powerful tool to theoretically study the adsorption orientation of inhibitor on metal surface and obtain the calculated adsorption energy value [45]. To further theoretically study the adsorption behavior and inhibitive mechanism of CS-SAS-AAGC, the adsorption modes of four grafted molecular forms of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA or APDS-AA-SAS on Fe (001) surface were studied by MD simulations.

For these simulated adsorption modes, it takes about 100 ps to become the relative stable state, and almost remains unchangeable from 300 to 1000 ps. The equilibrium adsorption configurations of ALDS, APDS, ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS on Fe (001) planes are shown in Fig. 8. Clearly, all molecules are likely to adsorb Fe (001) surface with flat orientation, while can cover larger metal surface comparing with vertical or non-planner orientation. For ALDS and APDS, the flat adsorption orientation is caused by the simultaneous interactions with one glucose as well as another glucose. For the graft polymers of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS, the adsorption active sites are SAS and AA. When SAS and AA strongly interact with steel surface, the molecular skeleton of two glucoses acts as a barrier between metal surface and aggressive acid solution, which then exhibits good inhibitive action.

The important parameter of adsorption energy (\( \Delta E_{\text{ads}} \)) of inhibitor molecule on Fe (001) plane can be calculated by the following equation [46]:

\[
\Delta E_{\text{ads}} = E_{\text{total}} - (E_{\text{inh}} + E_{\text{surf}})
\]

### Table 5 – Quantum chemical parameters for inhibitor molecules at GGA/BLYP/DND/ COSMO level.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( M ) (Debye)</th>
<th>( E_{\text{HOMO}} ) (eV)</th>
<th>( E_{\text{LUMO}} ) (eV)</th>
<th>( \Delta E ) (eV)</th>
<th>( \rho ) (eV)</th>
<th>( \gamma ) (eV)</th>
<th>( s ) (eV(^{-1}))</th>
<th>( \Delta N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALDS</td>
<td>8.7841</td>
<td>5.947</td>
<td>0.297</td>
<td>6.244</td>
<td>2.825</td>
<td>3.122</td>
<td>0.320</td>
<td>0.669</td>
</tr>
<tr>
<td>APDS</td>
<td>6.8048</td>
<td>6.008</td>
<td>0.034</td>
<td>6.042</td>
<td>2.987</td>
<td>3.021</td>
<td>0.331</td>
<td>0.664</td>
</tr>
<tr>
<td>ALDS-SAS-AA</td>
<td>25.5993</td>
<td>5.280</td>
<td>0.571</td>
<td>4.709</td>
<td>2.926</td>
<td>2.040</td>
<td>0.490</td>
<td>0.865</td>
</tr>
<tr>
<td>ALDS-AA-SAS</td>
<td>34.9197</td>
<td>5.440</td>
<td>0.663</td>
<td>4.777</td>
<td>3.052</td>
<td>2.388</td>
<td>0.419</td>
<td>0.826</td>
</tr>
<tr>
<td>APDS-SAS-AA</td>
<td>50.7614</td>
<td>5.689</td>
<td>0.595</td>
<td>5.094</td>
<td>3.142</td>
<td>2.547</td>
<td>0.393</td>
<td>0.757</td>
</tr>
<tr>
<td>APDS-AA-SAS</td>
<td>60.8065</td>
<td>5.367</td>
<td>2.417</td>
<td>2.950</td>
<td>3.892</td>
<td>1.475</td>
<td>0.678</td>
<td>1.054</td>
</tr>
</tbody>
</table>
where $E_{\text{inh}}$ and $E_{\text{surf}}$ are the energies of individual inhibitor molecule and Fe (001) plane, respectively. $E_{\text{total}}$ is the total energy of Fe (0011) plane with the adsorbed inhibitor molecule.

For the CS simulation models, $\Delta E_{\text{ads}}$ values of ALDS and APDS are $-626.3$ and $-554.9$ kJ mol$^{-1}$, respectively. With respect to the graft polymer models, $\Delta E_{\text{ads}}$ values of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS are $-987.4$, $-960.0$, $-962.3$ and $-1072.9$ kJ mol$^{-1}$, respectively. More negative $\Delta E_{\text{ads}}$ generally means more stronger interaction force of inhibitor molecule with metal surface. Thus, all four graft polymer molecules of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA and APDS-AA-SAS exhibit stronger adsorptive ability than the raw chemical compounds of ALDS and APDS.

In summary, the improved inhibition ability of CS-SAS-AAGC can be well theoretically confirmed by MD simulations. Further comparison reveals that APDS-AA-SAS has the most negative value of $\Delta E_{\text{ads}}$ among four graft polymer molecules, which implies that APDS-AA-SAS is of the strongest adsorptive ability and the best inhibitive performance. This result agrees well with the above quantum chemical calculations.

Fig. 7 – Optimized molecular structures and frontier molecule orbital density distributions using density function theory (DFT) method at theoretical level of GGA/BLYP/DND/COSMO: (a–c) ALDS; (d–f) APDS; (g–i) ALDS-SAS-AA; (j–l) ALDS-AA-SAS; (m–o) APDS-SAS-AA; (p–r) APDS-AA-SAS.
3.7. Inhibition mechanism

The overall electrochemical corrosion of CRS in HCl solution can be divided into cathodic hydrogen evolution (2H⁺ + 2e⁻ → H₂) and anodic steel dissolution (Fe → Fe²⁺ + 2e⁻). The cathodic reaction mechanism contains the following steps [47]:

\[
\text{Fe} + \text{H}^+ \leftrightarrow (\text{FeH}^+)_{\text{ads}} \quad (13)
\]

\[
(\text{FeH}^+)_{\text{ads}} + \text{e}^- \leftrightarrow (\text{FeH})_{\text{ads}} \quad (14)
\]

\[
(\text{FeH})_{\text{ads}} + \text{H}^+ + \text{e}^- \leftrightarrow \text{Fe} + \text{H}_2 \uparrow \quad (15)
\]

Since the anions of Cl⁻ could be specifically adsorbed on CRS surface, and the anodic reaction is gone through the following steps [47]:

\[
\text{Fe} + \text{Cl}^- \leftrightarrow (\text{FeCl}^-)_{\text{ads}} \quad (16)
\]

\[
(\text{FeCl}^-)_{\text{ads}} + \text{Cl}^- \rightarrow (\text{FeCl})_{\text{ads}} + \text{e}^- \quad (17)
\]
\[
\text{FeCl}_2 \rightarrow \text{Fe}^{2+} + \text{Cl}^{-}
\]

(19)

The corrosion rate of CRS in HCl is controlled by both cathodic and anodic reactions. When CS-SAS-AAGC is added to HCl media, the corrosion rate of CRS decreases remarkably. The inhibitive performance can be explained on the basis of CS-SAS-AAGC structure. Since CS-SAS-AAGC contains numerous N and O atoms, it can be protonated by \( \text{H}_2\text{O}^+ \) in the acid solution as following:

\[
\text{CS-SAS-AAGC} + x\text{H}_2\text{O}^+ \rightarrow \text{CS-SAS-AAGC}^{x^+} + \text{H}_2\text{O}
\]

(20)

Accordingly, both CS-SAS-AAGC and CS-SAS-AAGC\(^{x^+}\) should be considered for the adsorption molecules, and their adsorption modes are presumed as follows:

(i) SAS is ionized to \( \text{Na}^+ \) and \( \text{SAS}^- \) in aqueous water solution. Accordingly, CS-SAS-AAGC may be negatively charged, and then it can electrostatically interact with the adsorption species of \( \text{Fe}^{3+} \)\(_\text{ads} \) that is important intermediate of initial cathodic reaction (13). As a result, the subsequent reactions (14) and (15) are efficiently retarded.

(ii) Owing to specific adsorption, \( \text{Cl}^- \) can strongly adsorb on CRS surface to form the negative charged intermediate \( \text{FeCl}^+ \)\(_\text{ads} \). Through electrostatic attraction force in between, the protonated CS-SAS-AAGC\(^{x^+}\) can interact with \( \text{FeCl}^+ \)\(_\text{ads} \) in initial anodic reaction (16). Consequently, the subsequent successive reactions (17)–(19) of \( \text{FeCl}^+ \)\(_\text{ads} \) to \( \text{FeCl}^2+ \) and \( \text{Fe}^{2+} \) can be weakened to more extent.

(iii) Besides physical adsorption, the chemical adsorption would be essentially occurred. Either CS-SAS-AAGC or CS-SAS-AAGC\(^{x^+}\) can donate electrons of O and N atoms to the vacant d-orbitals of Fe atom to form coordinate bond, while accept electrons from steel surface to form back-donating bond.

(iv) Owing to the coordination ability of polar functional groups of –OH and N–H\(_2\), CS-SAS-AAGC as well as CS-SAS-AAGC\(^{x^+}\) can react with freshly generated \( \text{Fe}^{2+} \) on steel/solution interface to form some coordination compounds, which adsorb on steel surface to produce a protective shielding isolation film that keeps steel surface from corrosion by HCl.

4. Conclusions

1) CS-SAS-AAGC acts as an efficient inhibitor for the corrosion of CRS in 1.0 M HCl, and the maximum \( \eta \) is 97.2% at 50 mg L\(^{-1} \) and 20 °C. The inhibitive performance of CS-SAS-AAGC is higher than that of CS, SAS or AA.

2) CS-SAS-AAGC functions as a mixed-type inhibitor through geometric blocking effect. Nyquist appears a depressed capacitive loop with one time constant, and the impedance enhances with the increase of additive inhibitor concentration.

3) SEM and AFM images revealed that the CRS surface was efficiently inhibited by CS-SAS-AAGC, and the film formed on CRS surface in inhibited system is of hydrophobic nature.

4) The active adsorption sites of ALDS-SAS-AA, ALDS-AA-SAS, APDS-SAS-AA or APDS-AA-SAS are the grafted monomers of SAS and AA. Quantum chemical calculations and MD clearly indicates that grafting polymers exhibits stronger adsorption ability than raw molecules of ALDS and APDS.

**Conflict of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgements**

Funding support from the National Natural Science Foundation of China (51561027) and Training Programs of Young and Middle Aged Academic and Technological Leaders in Yunnan Province (2015HB049,2017HB030) are acknowledged.

**Appendix A. Supplementary data**

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.12.050.

**References**


