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Epoxidation Modification of Renewable Lignin to Improve the Corrosion Performance of Epoxy Coating

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The epoxidation modification of renewable lignin was achieved by using epichlorohydrin under alkaline condition. Modified lignin (ELG) was characterized by FTIR and used to improve the corrosion performance of epoxy coatings. SEM images showed that ELG was well-dispersed in epoxy coatings, indicating that good compatibility of modified lignin with the epoxy resin. The anticorrosive properties of ELG/epoxy coatings coated on Q235 steel in 3.5% NaCl solution were studied by polarization curves and electrochemical impedance spectroscopy (EIS). Compared with pure epoxy coating, the addition of ELG greatly improved the corrosion protection performance of Q235 steel. Especially, the epoxy coating with 2% ELG achieves high corrosion protection performance.

Keywords: lignin; epoxy resin; anticorrosion; Q235 Steel

1. INTRODUCTION

Nowadays, much attention has been paid to renewable resources due to the gradual depletion of fossil fuels and serious environment pollution [1, 2]. Lignin, a primary constitute (15–35 wt%) of the cell walls of terrestrial plants, is the second most abundant natural polymer on earth after cellulose [3]. The approximately 50 million tons of industrial lignin are generated as a byproduct of pulp and paper industry annually [4]. However, only a small proportion, less than 2%, is employed as value-added product, and the vast majority is burned as fuel or discarded as waste, resulting in a great waste of resources and serious environmental pollution [4]. Therefore, it is significantly important to exploit the value-added applications based on lignin.

Epoxy coatings have high resistance to organic solvent and alkaline solution, strong adhesion to various substrates, which is widely used as anticorrosive coating [5]. However, the corrosion resistance of pure epoxy coating is limited, and it is hence required to add rust-resisting pigment to enhance the corrosion protection performance [6, 7]. Most of rust-resisting pigments frequently used are inorganic compounds, such as iron oxide (Fe_2O_3), powdered aluminium, glass flake, etc. Tambe et al. investigated the influence of Fe_2O_3 content on the mechanical and corrosion protection performance of coatings [8]. However, dispersibility and compatibility of nano Fe_2O_3 particles with the epoxy coating are poor, resulting in the formation of microvoid in the interfaces between Fe_2O_3 particles and epoxy resin matrix [9]. Liu et al. reported that Fe_2O_3 was modified with epoxy resin under high temperature ball milling, which improved the compatibility between Fe_2O_3 particles and epoxy resin, and hence enhanced the corrosion protection property of epoxy coating [10]. Lignin is an inexpensive natural three-dimensional aromatic polymer, which is expected to incorporate into the polymer matrix to fully realize its potential [11]. However, similar to the inorganic pigment, its incompatibility with polymer matrix is poor [3]. Therefore, lignin needs to be modified to improve the compatibility with polymer matrix.

In the present work, the epoxidation modification of renewable lignin was successfully achieved by the reaction of hydroxyl groups of lignin with epichlorohydrin under alkaline conditions. The modified lignin (ELG) was easily incorporated into industrial epoxy coating systems (ELG-EP). The anticorrosive properties of ELG-EP with various ELG contents were evaluated by electrochemical impedance spectroscopy (EIS) and Tafel polarization curves. Furthermore, the influence of ELG on the corrosion protection property was investigated.

2. EXPERIMENTAL

2.1 Materials

High purity lignin (LG) was provided by Shandong Weili Group Co., Ltd. Bisphenol A epoxy resin E44 and curing agent polyamide were purchased from JiangSu Wujiang City Heli Resin Co., Ltd. Epichlorohydrin (ECH), hydrochloric acid (HCl), tetraethyl ammonium bromide (TEAB), pyridine, toluene, sodium hydroxide (NaOH) were purchased from Aladdin Industrial Corporation. All chemicals were used without further purification.

The Q235 steel was sealed with cured epoxy resin and selected for anticorrosion test. The exposed surface was gradually abraded with SiC abrasive paper up to 1500 grit, then rinsed with distilled water, degreased by ultrasonication in acetone and finally dried with nitrogen.

2.2 Epoxidation modification of lignin

The epoxidation modification of lignin was typically performed as followed (Scheme 1): 10 g LG was dissolved in 10 wt% NaOH aqueous solution (100 mL). 43.3 g ECH and 0.5 g TEAB were then added into the above-mentioned solution. The reaction was carried out at 80 °C for 3h. After that, the reaction mixture was cooled down to room temperature, and then was filtered and washed with water twice. Finally, the epoxidation modified lignin (ELG) product was dried at 40 °C in vacuum till constant weight. The epoxy value of the obtained ELG was determined by HCl–pyridine method.

2.3 Preparation of ELG/epoxy anticorrosive coatings

The epoxy resin E44 contained ELG powders at various weight ratios (referred as 1 wt%, 2 wt%, 5 wt% and 10 wt%) were mixed with curing agent polyamide and solvent. The weight ratio of E44 and curing agent was 4:1. The mixture was vigorous stirred for 10 min, and then were applied on the Q235 steel electrode surfaces with a bar coater. Coatings were dried at room temperature for 48 h. The dry coating thickness was 90±10 μm measured by Qnicx 4500 apparatus.

2.4 Characterizations

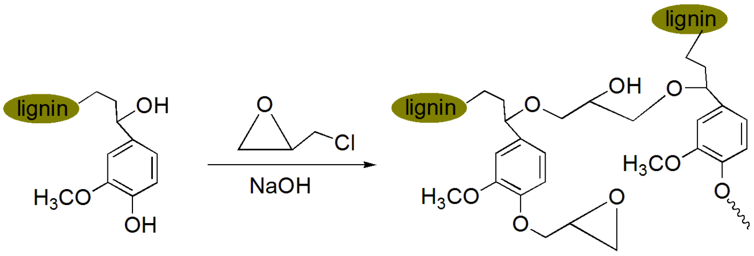
FTIR spectra were obtained on a NICOLET 6700 Thermo spectrometer by collecting 32 scans at a spectral resolution of 4 cm^{-1}. The morphology of the coatings was observed using a FEI Quanta FEG 250 scanning electron microscope (SEM).

Electrochemical corrosion test was performed on a CHI-660E electrochemical workstation. The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were obtained in 3.5 wt% NaCl aqueous solution using classical three-electrode cell system at room temperature. A saturated calomel electrode (SCE) equipped with a Luggin capillary, a platinum plate of 2.5 cm^2 and coating/Q235 steel was used as the reference electrode, counter electrode and working electrode, respectively. Before measurement, the coating/Q235 steel specimen were initially kept at an open circuit potential (OCP) for 0.5 h. For EIS measurement, the test frequency range was 10^5-10^{-2} Hz and the amplitude of the sinusoidal voltage signal was 20 mV. The EIS data were analyzed using ZsimpWin 3.21 software. Polarization curves were performed from -250 mV to +250 mV vs.OCP at a scan rate of 0.5 mV/s.

3. RESULTS AND DISCUSSION

3.1 Preparation and characterization of epoxidation modified lignin (ELG)

Epoxidation modified lignin (ELG) was prepared based on the reaction of hydroxyl groups of lignin with ECH under alkaline condition, as shown in Scheme 1. Figure 1 shows FTIR spectra of LG and the obtained ELG. The sharp absorption peaks at 1600 and 1510 cm^{-1} are assigned to stretching vibrations of the aromatic ring. The peaks at 3440 cm^{-1} and 2930 cm^{-1} belong to stretching vibrations of the –OH and C-H groups of LG, respectively. For ELG, the peak characteristic of –OH groups shifted to 3410 cm^{-1}, and the new peak at 910 and 744 cm^{-1} characteristic of epoxide groups is observed, indicating that the reaction of -OH groups and ECH had occurred [12].



Scheme 1. Synthetic route for epoxidation modified lignin.

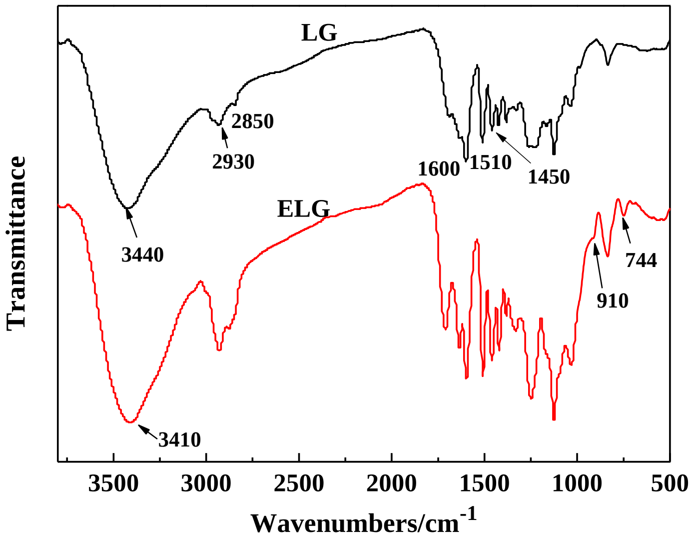


Figure 1. FTIR spectra of LG and ELG.

3.2 Preparation and characterization of ELG/epoxy anticorrosive coatings

The ELG/epoxy coatings (ELG-EP) were obtained by a curing reaction of Bisphenol A epoxy resin E44 contained ELG with low molecular weight polyamide at room temperature.

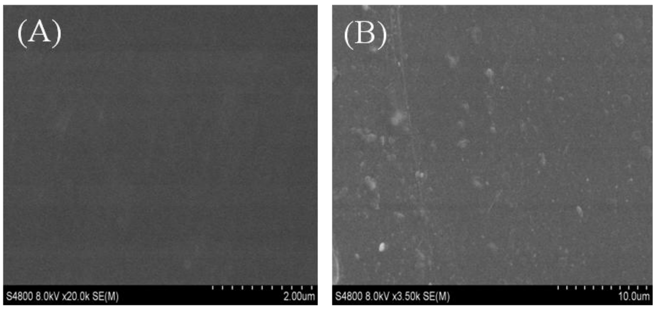


Figure 2. SEM images of fractured surfaces of pure EP (A) and 2% ELG-EP (B) coatings.

In order to study the dispersing state of ELG in epoxy coating, SEM was employed to examine the fracture surfaces of ELG/EP coatings, as shown in Figure 2. The fracture surface of pure epoxy (EP) and 2% ELG-EP coating was relatively smooth and dense. Furthermore, the ELG in epoxy coating was uniformly dispersed, and no aggregates were observed. Similar result has been reported that the modified iron oxide with epoxy resin improved its compatibility and dispersion capability in epoxy coating [10]. However, the content of ELG above 2 wt% resulted in the formation of aggregates.

3.3 Anticorrosive properties of ELG/epoxy coatings

To investigate the corrosion protection performance of the ELG-EP coatings with different contents of ELG, Tafel polarization curves and electrochemical impedance spectroscopy (EIS) were used to study the anticorrosive behaviors of composite coatings. Figure 3 displays the polarization curves of pure EP, 1% ELG-EP and 2% ELG-EP coatings immersed in 3.5 wt% NaCl solution after 2160 h, and their corrosion parameters (corrosion current density (i_{corr}) and corrosion potential (E_{corr})) are listed in Table 1. Compared with pure EP coating, 1% and 2% ELG-EP coating showed more positive E_{corr} and lower i_{corr}, indicating that the ELG-EP coating exhibited better anticorrosive performance than pure EP coating [13, 14].

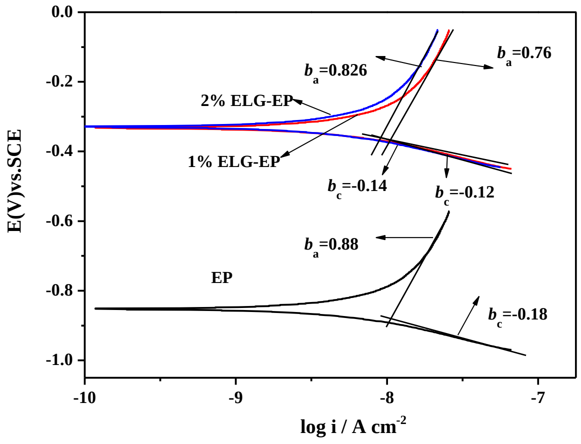


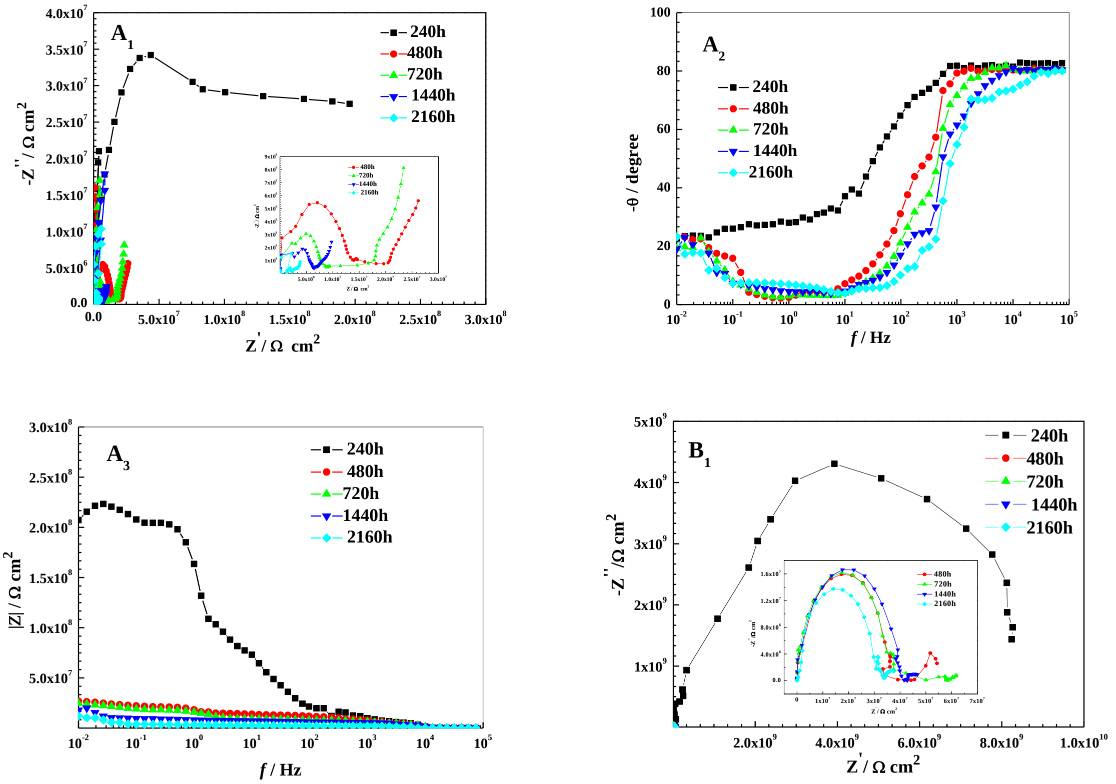
Figure 3. Tafel polarization curves of pure EP, 1% ELG-EP and 2% ELG-EP coatings/Q235 steel immersed in 3.5 wt% NaCl solution after 2160 h.

Table 1. Corrosion parameters of different coatings in 3.5 wt% NaCl solution under 2160 h immersion time.

Coatings	E_{corr} (V vs SCE)	i_{corr} (10^{-8}A cm^{-2})	b_a (V/dec)	b_c (V/dec)
EP	-0.873	1.064	0.88	-0.18
1% ELG-EP	-0.366	0.726	0.76	-0.14
2% ELG-EP	-0.344	0.709	0.82	-0.12

As is well known, EIS is a powerful tool to evaluate the anticorrosive properties of organic coatings [15-17]. Figure 4 depicts the Nyquist and Bode plots of pure EP, 1% ELG-EP, and 2% ELG-EP coatings immersed in 3.5 wt% NaCl solution under different times (240–2160 h). In the early stage of immersion, the phase angle of pure EP coating was closed to 80° at the range of 10^3–10^5 Hz and 23° at frequency of 10^{-2} Hz, and gradually decreased in the whole frequency range (Figure 4A_2). After 720 h immersion, the phase angle decreased rapidly and approached 19° at frequency of 10^{-2} Hz, and then remained unchanged during the subsequent immersion. For the 1% ELG-EP coating, the phase angle was about 80° in the 10^1–10^5 Hz range (Figure 4B_2). After 720 h immersion, the phase angle was closed to 80° at the range of 10^2–10^5 Hz and approached 2° at frequency of 10^{-2} Hz, and then kept unchanged in the latter stage immersion. For the 2% ELG-EP coating, the phase angle was about 90° in the 10^0–10^5 Hz range and approached 70° at frequency of 10^{-2} Hz (Figure 4C_2). After 720 h immersion, the phase angle was above 80° at the range of 10^1–10^5 Hz and approached 26° at frequency of 10^{-2} Hz, and then kept at this level. However, the phase angle of 2% ELG-EP coating was higher than that of pure EP and 1% ELG-EP over the whole frequency range in the same immersion time. But the content of ELG above 2 wt% resulted in the formation of aggregates, and hence the corrosion rate increased [18].

The impedance modulus at 10^{-2} Hz ($|Z|_{0.01\text{Hz}}$) represents the ability of the coating to impede the flow of current between anodic and cathodic areas, which is inversely proportional to corrosion rate [13, 19]. The $|Z|_{0.01\text{Hz}}$ of pure EP coating in the initial 240 h immersion were 2.26×10^8 Ω cm^2. After 480 h immersion, this $Z|_{0.01\text{Hz}}$ dropped gradually and maintained at 4.5×10^7 Ω cm^2 (Figure 4A_3).



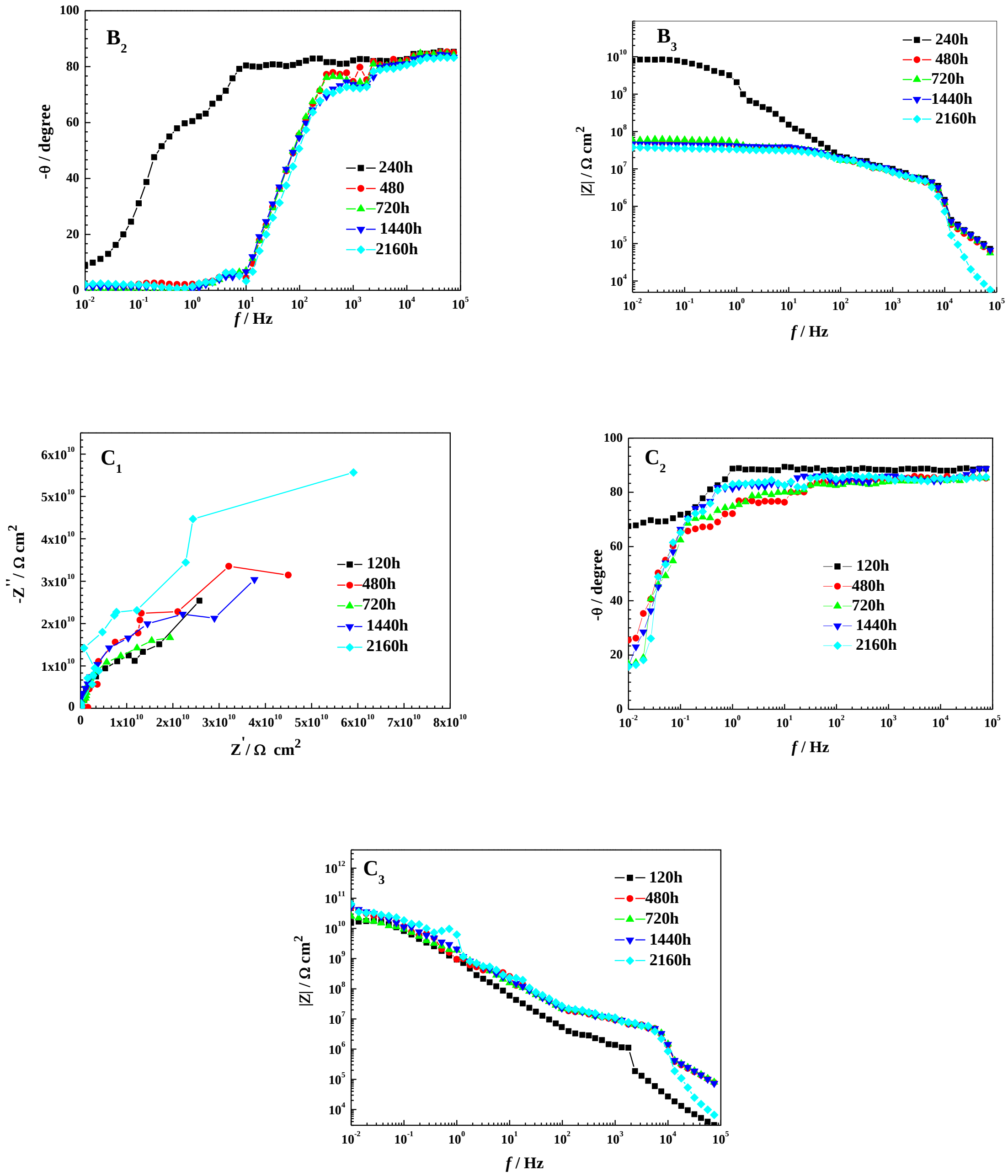


Figure 4. Nyquist and Bode plots of pure EP (A_1–A_3), 1% ELG-EP (B_1–B_3), and 2% ELG-EP (C_1–C_3) coatings immersed in 3.5 wt% NaCl solution under different times.

For the 1% ELG-EP coating, the $Z|_{0.01\mathrm{Hz}}$ decreased gradually from 1.0×10^{10} Ω cm^2 to 8.5×10^{8} Ω cm^2 and then remained stable (Figure 4B_3). For the 2% ELG-EP coating, the $Z|_{0.01\mathrm{Hz}}$ increased from 1.1×10^{10} Ω cm^2 to 6.5×10^{10} Ω cm^2 during 480 h immersion, and then remained at this level (Figure 4C_3). Compared with pure EP coating, the $Z|_{0.01\mathrm{Hz}}$ values of 1% ELG-EP and 2% ELG-EP coatings were much higher in the same immersion time. These results demonstrated that the addition of ELG improved the anticorrosion performance of the epoxy coating, and the epoxy coating containing 2 wt% ELG showed better corrosion protection performance.

For quantitative estimate the evolution of the anticorrosion properties of the composite coatings, EIS data were fitted with equivalent circuits for stage I and II, as shown in Figure 5. R_s, R_c and R_{ct} represent the solution resistance, coating resistance and charge-transfer resistance, respectively. Q_c and Q_{dl} represent the coating capacitance and double-layer capacitance, respectively [20]. In the early stage of immersion, Nyquist plots of pure EP coatings showed pure capacitance loop, and the equivalent circuit R(QR) (Figure 5A) was chosen for the fitting procedure. The pure EP coating showed two capacitance loops with immersion time increased, and the equivalent circuit R(Q(R(QR)) (Figure 5B) was chosen for the fitting procedure [10]. However, for 1% ELG-EP and 2% ELG-EP coatings, their Nyquist plots displayed pure capacitance loop during 2160 h of immersion, and the equivalent circuit R(QR) was selected (Figure 5A) for the fitting procedure.

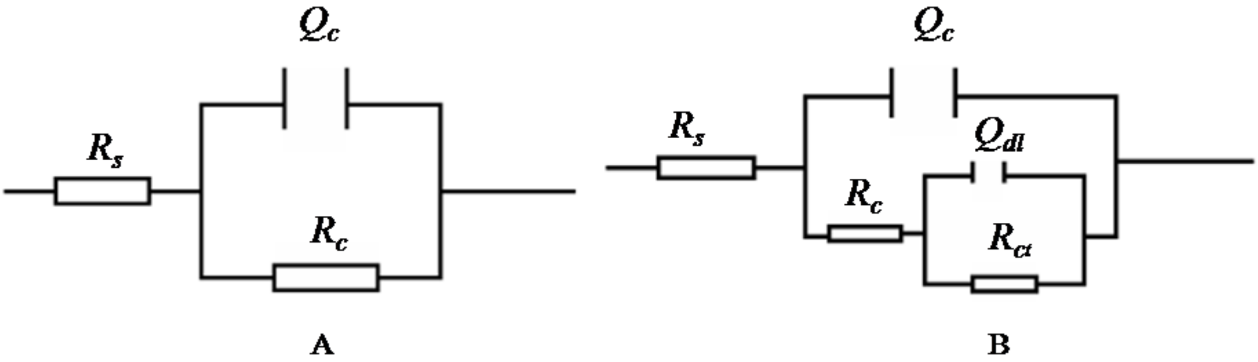


Figure 5. Equivalent circuits used to fit the EIS data.

Figure 6 shows R_c and R_{ct} of different ELG-EP coatings as a function of immersion times. Generally, a higher R_c implies a smaller number of H_2O, O_2 and Cl^- molecules penetrated into the coatings [21]. The R_c of pure EP and 1% ELG-EP coatings decreased from the initial value of 1.0×10^8 Ω cm^2 and 1.0×10^{10} Ω cm^2 to a steady value of 1.1×10^7 Ω cm^2 and 6.0×10^7 Ω cm^2 after 480 h immersion, respectively. However, for the 2% ELG-EP coating, its R_c value remained at about 2.5×10^{10} Ω cm^2 during 2160 h of immersion. R_{ct} is a parameter of the resistance to electron transfer across a metal surface and is inversely proportional to the corrosion rate [22]. The R_{ct} of pure EP coating fluctuated and stabilized at about 3×10^7 Ω cm^2 during 2160 h of immersion. The R_{ct} of 1% ELG-EP and 2% ELG-EP coatings did not emerge during 2160 h immersion, indicating that the addition of ELG improved the corrosion protection performance of the epoxy coating. The above results further demonstrate that 2% ELG-EP coatings showed better anticorrosive effect based on Q235 carbon steel. According to some reports, the remarkably improved corrosion protection property of ELG-EP coatings could be ascribed to the dispersibility, compatibility and interface bonding of modified lignin (ELG) with the epoxy resin were improved, reducing the diffusion channel of water and the interface defect between ELG and the resin [10, 23].

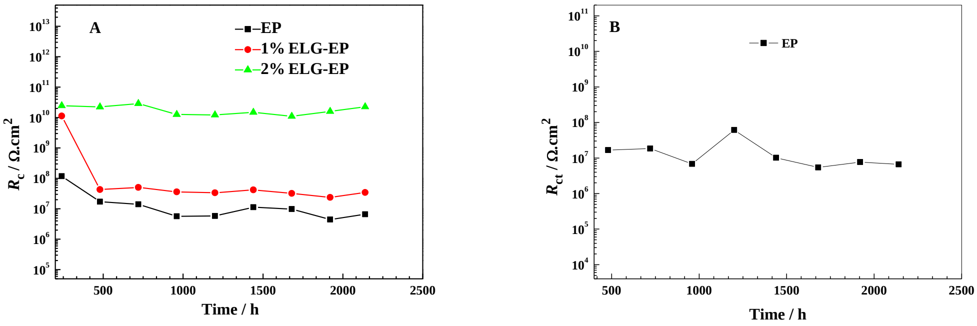


Figure 6. Changes of R_c (A) and R_{ct} (B) curves as a function of immersion times.

4. CONCLUSIONS

Epoxidation modified lignin (ELG) was prepared by the reaction of hydroxyl groups of lignin with ECH under alkaline condition. The ELG was easily incorporated into epoxy systems by mixing epoxy resin with ELG, followed by crosslinking with polyamide curing agent. The epoxy coatings containing 2.0% ELG showed better anticorrosive effect than pure EP coating, on the basis of Tafel polarization curves and EIS. The remarkably enhanced anticorrosive property could be ascribed to the compatibility and interface bonding of ELG with the epoxy resin were improved, reducing the diffusion channel of water and the interface defect between ELG and the resin.

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