Bio-based episulfide composed of cardanol/cardol for anti-corrosion coating applications

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Abstract

Bio-based materials from Cardanol/cardol with episulfide group (CCES) and epoxy group (CCEO) were synthesized and further blended with a commercial bisphenol-A diglycidyl ether type epoxy resin (DGEBA) for anti-corrosion coating application. The curing behavior of CCEO and CCES confirmed that episulfide exhibited a faster curing rate and higher curing conversion than epoxide. Anticorrosion properties of composite system CCEO/CCES and DGEBA were also carried out. Equilibrium water content of CCES-DGEBA blend was much lower than neat DGEBA and CCEO-DGEBA composite system in water absorption test, which met agreement with that CCES-DGEBA blend system revealed better adhesive to the metal compared with DGEBA and CCEO-DGEBA blend in lap sheer strength assessment. Further, CCES-DGEBA blend with 20 wt% of CCES exhibited optimized performance in corrosion resistance as it possessed the higher impedance modulus at low frequencies in EIS bode plots, lowest corrosion current and the highest corrosion voltage in Tafel test.

1. Introduction

Corrosion is one of the most serious problems in industrial world. In order to protect metallic material from corrosion, organic coatings are widely used in anticorrosion field, such as epoxy resins with good adhesion to metal substrates and long-term corrosion resistance [1]. In coating applications, epoxies react with curing agents to form a cross-linked polymeric layer, providing a barrier to prevent metal surface from environmental exposure. However, performances of coatings based on epoxy resin are not always satisfactory, especially its undesired water absorption capacity and poor toughness. Therefore, efforts have been made in order to find proper methods to improve the anticorrosion properties of the coatings. Blend of epoxy resin and proper biomaterial with hydrophobic and flexible group is a practical solution for anticorrosion coatings development, at the same time ensures the environment friendly and sustainable use.

Cardanol and cardol (Scheme 1) are phenol derivatives prepared from cashew nut shell liquid (CNSL), having a substituent of a C15 unsaturated hydrocarbon chain with one to three double bonds. The structure difference between cardanol and cardol is that cardol has two hydroxyls on the meta-positions of benzene while cardanol only has one. Cardanol-based derivatives are thought to be excellent candidates to modify epoxy resins in anti-corrosion use [2–5]. CNSL is an economical, nontoxic, and nonhazardous [6] natural vegetable oil, once showing talent for metal corrosion protection by reducing the corrosion rate by over 90% of carbon steel [7]. The reactive phenolic hydroxyl group of cardonal makes one-step synthesis to cardonal-based epoxy resin with nearly 100% conversion possible. Furthermore, the introduction of a C15 aliphatic chain provides flexibility and hydrophobicity, which can improve the poor toughness and undesired water absorption capacity of epoxy resins.

In recent years, much attention has been paid to explore the mechanical, anti-corrosion properties of cardanol-based epoxy modified conventional epoxy resin systems. Kanehashi et al. [8] synthesized a room temperature curing cardanol-based epoxy coating, which was in rubbery state at room temperature because of the flexible side chains and showed good chemical stability in thermal analysis. Aggarwal et al. [9] prepared epoxy-cardanol resin and investigated its tensile strength, elongation and bonding property with steel, epoxy-cardanol resin exhibited better performance than commercial DGEBA epoxy resin. Kathalewar et al. [10] synthesized a cardanol-based epoxy and blended with DGEBA at various weight percentages for coating application. The properties

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can be opened with less energy\[11,12\]. Further, the S linkage of the one sulfur atom in the ring stays at a higher energy level and thus drophobicity and adhesion to metal surface. Episulfide both polar interaction and water sorption as DGEBA resin did.

such as pencil hardness, impact resistance and chemical resistance of system with 40–60 wt% DGEBA were improved compared to system with neat DGEBA.

Although the modification of cardanol-based epoxy can elevate mechanical and bonding properties of DGEBA resin, the introduction of epoxide group for the cardanol-based epoxy tended to increase both polar interaction and water sorption as DGEBA resin did.

Compared to epoxy resins, episulfide resins show excellent hydrophobicity and adhesion to metal surface. Episulfide containing one sulfur atom in the ring stays at a higher energy level and thus can be opened with less energy\[11,12\]. Further, the S linkage of the opened sulfur ring has significant advantages over epoxy monomers in low water absorption for its low polarity\[11\]. Thiol generated from ring opening forms self-assembled monolayer on metals, which improves the interfacial adhesion with Cu, Ag and other metals\[13–15\]. All these advantages of episulfide make it an alternative solution in corrosion resistance instead of epoxy resins.

However, as far as we know, few researches have systematically studied episulfide based on cardanol/cardol and their modification of epoxy resins; in addition, cardol has two hydroxyl groups on the meta-position, the effect of functionality on the property of CNSL-based epoxy has not been fully understood, let alone cardol type episulfide. Therefore, to further expand the application of the cardanol-based epoxy and reduce the drawbacks of epoxide, mono or multi-function episulfide was introduced into the system in this work. Epoxy resin was synthesized from cardanol (CEO) and from cardanol/cardol mixture (CCEO). Further, episulfide resin was synthesized through episulfide reaction from CEO (CES), so as to CCES from CCEO. These four derivatives were separately mixed with one of the most commercial epoxy DGEBA and cured with polyamide. The study of curing behavior, thermal, water sorption, mechanical and anti-corrosion properties of the system would be helpful for evaluating the different modified effect between epoxy-based and episulfide-based cardanol (cardanol/cardol) resin, and at the same time exploring the influence of functional degree on the blended system\[16–18\].

2. Experimental methods

2.1. Materials

Cardanol with 95% purity, S6036 containing 60% cardanol and 36% cardol, diglycidyl ether of bisphenol A (DGEBA)-type epoxy resin D.E.R. 331, and curing agent polyamide D.E.H.140 were provided by Dow Chemical Co. (China). The epoxy equivalent of D.E.R. 331 is 182–192 g eq\(^{-1}\) and the amine value of D.E.H. 140 is 360–400 mg KOH g\(^{-1}\). Epichlorohydrin, thiourea, sodium hydroxide, magnesium sulfate, and acetone were purchased from Shanghai Chemical Reagent Co. (China) and hydrochloric acid (36.0%–38.0%) was purchased from Taicang Zhitang Chemical Plant (China), respectively.

Synthesis of cardanol/cardol-based epoxy and episulfide (Scheme 2).

Cardanol (0.2mol, 60.4 g), hexadecyl trimethyl ammonium Bromide (0.6 g) as phase transfer catalyst and epichlorohydrin (2 mol, 185 g) were mixed in four-necked round-bottom flask. The reaction was carried out in an inert atmosphere at about 110–120 °C with stirring for 10 h. Then, at 60–65 °C, NaOH (0.21 mol, 16.8 g) aqueous solution (50 wt%) was slowly added over 6 h under vigorous stirring. Another 3 h reaction time was needed after the addition of NaOH solution. The resultant mass suspension was distilled at reduced pressure to evaporate water and unreacted epichlorohide. After filtration off the salt, the organic liquid was washed with warm distilled water (60 °C) for three times and dried with anhydrous MgSO\(_4\). A reddish brown liquid was obtained (yield 92%). The procedure was applied to the epoxidization of S6036 as well. Thus, cardanol-based epoxy resin (CEO) and cardanol/cardol based epoxy resin (CCEO) were obtained.

The synthesis of episulfide-cardanol (CES) and episulfide-cardanol/cardol resin (CCES) was essentially the same and followed the literature procedure\[19\]. After thiourea (0.1 mol, 7.8 g) dissolved in isopropyl alcohol (30 ml) at 20 °C, CEO (0.05 mol, 19.2 g) was added into the system and stirred for 24 h. The resultant was precipitated in distilled water and washed with water for several times, after dried with anhydrous MgSO\(_4\), a reddish brown liquid CES was obtained (yield 89%).

2.2. Preparation of mixtures of CEO, CCEO, CES, and CCES with DGEBA

CEO/CCEO/CES/CCES with 0, 10, 20, 30 wt% was blended with DGEBA resin matrix according to the proportion in Table 1. All the composite systems were further cured with polyamide at 60 °C for 4 h and RT for 24 h. The samples used in this study were composed of constant stoichiometric ratio 1:1.

2.3. Characterization methods

FTIR: Infrared spectroscopy experiments were performed using a Thermo Nicolet 6700 Spectrometer with 4 cm\(^{-1}\) resolution and 32 scans for mid-infrared (MIR) spectroscopy, 128 scans for near-infrared (NIR) spectroscopy.

Thermo Nicolet 6700 Spectrometer equipped with ZnSe crystal and a DTGS detector was used to monitor water diffusion process, the spectra of specimen and filter paper was collected as background. After absorption of 10 ml water, when filter paper was put onto specimen again, data were collected until absorption equilibrium. The experiment was conducted at 25 °C with 4 cm\(^{-1}\) resolution and 64 scans.

NMR: \(^1\)H spectroscopy was recorded on a Bruker 400 MHz NMR spectrometer with CDCl\(_3\) as solvent at room temperature and tetramethylsilane (TMS) as an internal standard.

Epoxide equivalent weight (EEW): The EEW (weight of resin/epoxide equivalent) of epoxy was determined by HCl/acetone titration method. The EEW of CEO and CCEO are 384 and 297 g eq\(^{-1}\), respectively.

DSC: DSC experiments were carried out using Q2000 (TA,
Formulations of all composite system.

<table>
<thead>
<tr>
<th>System</th>
<th>Proportion (wt%)</th>
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<tbody>
<tr>
<td>CEO 10%</td>
<td>10%CEO + 90%DGEBA</td>
<td>CCEO 10%</td>
<td>10%CCEO + 90%DGEBA</td>
</tr>
<tr>
<td>CEO 20%</td>
<td>20%CEO + 80%DGEBA</td>
<td>CES 10%</td>
<td>10%CES + 90%DGEBA</td>
</tr>
<tr>
<td>CEO 30%</td>
<td>30%CEO + 70%DGEBA</td>
<td>CCES 10%</td>
<td>10%CCES + 90%DGEBA</td>
</tr>
<tr>
<td>CCEO 10%</td>
<td>10%CCEO + 90%DGEBA</td>
<td>CESP 10%</td>
<td>10%CESP + 90%DGEBA</td>
</tr>
<tr>
<td>CCEO 20%</td>
<td>20%CCEO + 80%DGEBA</td>
<td>CCES 20%</td>
<td>20%CCES + 80%DGEBA</td>
</tr>
<tr>
<td>CCEO 30%</td>
<td>30%CCEO + 70%DGEBA</td>
<td>CCESP 30%</td>
<td>30%CCESP + 70%DGEBA</td>
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<tr>
<td>70%DGEBA</td>
<td></td>
<td>90%DGEBA</td>
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<tr>
<td>80%DGEBA</td>
<td></td>
<td>10%CES</td>
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<tr>
<td>90%DGEBA</td>
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<td>10%CCES</td>
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<tr>
<td>80%DGEBA</td>
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<tr>
<td>80%DGEBA</td>
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<tr>
<td>90%DGEBA</td>
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<td>10%CCES</td>
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</table>

3. Results and discussion

3.1. Synthesis and characterization of CEO, CCEO, CES, CCES

The change of characteristic peaks of cardanol, S6036 and their four epoxy and episulfide derivatives were characterized by both mid-IR and near-IR measurement, as presented in Fig. 1 and Fig. 2, respectively. In the mid-IR spectra (Fig. 1), the band at 1912 cm⁻¹ is typical of the epoxy group [20], while the intensity of the broad band at 3363 cm⁻¹ assigned to the phenolic hydroxyl group decreased considerably after reaction, indicating the involvement of the group in epoxidation and episulfidation. Further, in the spectra of CES and CCES, a new peak at 619 cm⁻¹ appeared, this asymmetric episulfide ring vibration [21] proved the successful conversion of epoxide to episulfide. In addition, new peaks in near-IR spectra appeared at 4527 and 4488 cm⁻¹, as shown in Fig. 2. The peak at 4527 cm⁻¹ in spectra of CEO and CCEO was assigned to the combination vibrations of epoxy groups, while the peak at 4488 cm⁻¹ in spectra of CES and CCES was linked episulfide groups, respectively. The results agreed with mid-IR measurement and both confirmed that four derivatives were successfully synthesized.

The NMR analysis was also applied to cardanol, S6036 and their four derivatives, as shown in Fig. 3. The peak at 4.87 ppm (d) corresponds to phenol hydroxyl of cardanol and S6036 disappeared, and five new signals (located at α, β, γ) appeared. For CEO, peaks at 3.95, 4.16 ppm (c) were assigned to CH₂ protons adjacent to aromatic. Two peaks, one located at 2.90 ppm, and the other overlap with peak at 2.80 ppm (α), were corresponded to CH₂ protons of epoxy ring. For CES, peaks at 3.89 and 4.20 ppm (ε) corresponded to CH₂ protons adjacent to aromatic, which was overlap with the peak at 4.16 ppm and 3.35 ppm. Peak at 3.30 ppm corresponded to CH proton (b') of sulfur ring, and, 2.36 and 2.62 ppm (α') overlap with 2.54 ppm corresponded to CH₂ protons of sulfur ring. The results for CCEO and CCES were similar with CEO and CES. The analysis of ¹H NMR spectra, combined with the above results of FTIR measurement, both verified the successful synthesis of CEO, CES, CCEO and CCES.

3.2. Curing study of CEO, CCEO, CES, CCES

The curing behaviors of the four derivatives (CEO, CES, CCEO, CCES) with polyamide were firstly conducted by DSC measurement,
as it significantly affected thermo-mechanical, water sorption, and corrosion resistance properties of the epoxy materials according to our previous studies [22]. The exothermic curves are shown in Fig. 4, the onset temperature, peak temperature and enthalpy are summarized in Table 2.

Compared with epoxy, exothermic onset/peak temperature dropped significantly in episulﬁde, and the order of the four derivatives was CCES < CES ≪ CCEO < CEO, indicating higher curing rate of episulﬁde than epoxy because of higher activity in ring-opening reactions. Besides, episulﬁde showed lower enthalpy as compared to epoxy (enthalpy of CES was nearly 20 kJ/mol lower than CEO). Considering the influence of functional degree, S6036-based derivatives CCEO and CCES showed lower enthalpy and peak temperature when compared with the cardanol-based derivatives CEO and CES. Which suggested that the increase of functional group might link to higher reactivity.

Besides the curing behaviors under variable temperature investigated by DSC, the isothermal curing rate and conversion of the four derivatives was further in situ monitored using FTIR study at 60 °C. The normalized NIR spectra tracking the curing process of CEO are shown in Fig. 5, band at 4530 cm⁻¹ representing the combination vibrations of epoxy groups is used to analyze the curing conversion. According to the calculation method described in our previous paper [23], curing conversions of episulﬁde and epoxy based on change of peak area was calculated and shown in Fig. 6.

Clearly, episulﬁde showed much higher conversion than epoxy group, as ultimate conversions of episulﬁde reached approximately 90%, epoxy got only 60% for the ultimate value. Also, episulﬁde showed much higher curing rate than epoxy group, as the
conversation of CES and CCES was over 70%, but CEO and CCEO was lower than 20% after half an hour reaction time. As to the influence of functional group to curing rate, CCEO has a slightly faster curing rate than CEO, so as to CCES compared to CES. Thus, the result from IR in situ study was accordant with the result from DSC, that episulfide had higher curing rate and conversion than epoxy, and the increase of functional group also benefited to the properties.

### 3.3. Thermal-mechanical properties

Thermal-mechanical properties of DGEBA system blended with CEO, CCEO, CES and CCES with different weight percentage as 0, 10, 20 or 30% were investigated by DMA study. The DMA curves are represented in Figs. 7 and 8, and the glass transition temperature (Tg) value is summarized in Table 3.

![DMA curves](image)

Fig. 6. Curing conversion from IR in situ study for CEO, CCEO, CES, CCES cured with polyamide isothermally at 60 °C.

<table>
<thead>
<tr>
<th>System</th>
<th>Tonset (°C)</th>
<th>Tpeak (°C)</th>
<th>Entalphy (kJ/mol)</th>
<th>System</th>
<th>Tonset (°C)</th>
<th>Tpeak (°C)</th>
<th>Entalphy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEO</td>
<td>98</td>
<td>152</td>
<td>90</td>
<td>CES</td>
<td>69</td>
<td>108</td>
<td>74</td>
</tr>
<tr>
<td>CCEO</td>
<td>87</td>
<td>137</td>
<td>81</td>
<td>CCES</td>
<td>54</td>
<td>90</td>
<td>72</td>
</tr>
</tbody>
</table>

value of the modified system dropped 15–30 °C, as the side aliphatic chain of cardanol/cardol provided flexibility for the cured networks. With the increasing percentage of derivatives, the decrease of Tg increased from 13 °C for CEO 10% system to 32 °C for CEO 30% system. And Tg decreased with the increasing derivatives content in CCEO, CES and CCES system as well.

Whereas episulfide modified system exhibited higher Tg than epoxy modified system, and stayed closely to neat DGEBA. The Tg dropped from neat DGEBA of 89 °C to CCES 10% system of 86 °C, but to CCEO 10% system of 81 °C. With the increase of derivatives content, the decrease of Tg for CCES 30% system was also less than the decrease for CCEO 30% system. As reported by many reports [24,25], Tg was influenced by crosslink density and free volume. The curing conversion of CES and CCES was 90%, higher than 60% of CCEO and CEO, which increased the crosslink density and made up for the gap in Tg decrease.

According to the curing behavior of 4 derivatives, the curing rate and conversion of CCES was higher than CES, and so as to CCEO versus CEO. Comparing the Tg of CCES (CCEO) modified system with CES (CEO) modified system, the value was 86 °C for CCES 10% system but 80 °C in CES 10% system, while 81 °C for CCEO 10% system but 76 °C in CEO 10% system, which mainly resulted by improved crosslink density with the increase of functional group. Therefore, CCES 10% showed highest Tg value in modified systems, as with the less percentage content of flexible side aliphatic chain, while the curing conversation of episulfide modified system was higher than epoxy modified system, and the increase of functional group in CCES system further made improvement of crosslink density.

### 3.4. Adhesive strength with copper

The lap sheer strength of the modified system was tested by single lap joints method, as an indicator reflecting the adhesive performance of coating with copper. Fig. 9 shows the properties of modified systems with different derivatives content. Strength of neat DGEBA was significantly increased when mixed with four derivatives. The maximum peel strength reaching 200% in CCES-20% modified system compared to neat DGEBA. With the proportion increasing from 0% to 20%, the lap shear strength was enhanced in all modified system, and the improvement from 10 wt% to 20 wt% was far more significant than that from 0% to 10%. When the proportion increasing from 20 wt% to 30 wt%, the lap shear strength was improved in CEO, CCEO and CES system, but still...
lower than the 20 wt% CCES system, even though it dropped in 30 wt%.

It is generally accepted that the peel strength is highly dependent on the adhesive strength of the copper-resin interface and the flexibility of matrix resin. As the long side aliphatic chain of these four derivatives offered flexibility of the matrix resin, the peel strength of all modified system was improved. The chemical bonds between the metal and episulfide further enhanced adhesive strength between copper and resin interface. Thus episulfide blended system exhibited better performance than epoxy roughly, the peel strength of CCES 20% and CES 20% was 14.6 MPa and 12.7 MPa separately, while CCEO 20% and CEO 20% was 10.3 MPa and 10.4 MPa. But the influence of functional group (CEO vs. CCEO or CES vs. CCES) in peel strength was not obvious.

3.5. Water sorption

Besides the thermal and mechanical properties, water sorption is also a critical property, which is closely related to the corrosion resistance. Thus gravimetric measurement was further conducted in our study to investigate the equilibrium water content and diffusion coefficient of water sorption at 25 °C, as shown in Fig. 10.

Equilibrium water content was influenced by both free volume and polarity [26]. The equilibrium water contents calculated in Table 4 showed the trends as follows. Firstly, with the same
proportion, all the CES modified systems had lower equilibrium water contents than CEO modified systems, as the lower polarity and higher crosslink density of epoxidized. And so as to the trend between CCES and CCEO modified system. Secondly, in each modified system, the equilibrium water content increased via proportion of derivatives increasing (1.45 for CCES 10% and 1.86 for CCES 30%), which comes from the improved free volume. Thirdly, it is hard to tell apart the trend of modified system with different proportion, for example CES-10% and CES-30%. As one of the influence factor free volume of CCES-30% was higher than CES-10%, while the other influence factor polarity of CCES-30% was lower than CES-30% and CES-10%.

The diffusion coefficient is another important index affecting the properties of epoxy materials. It is generally accepted that the behavior in initial water sorption process of epoxy conforms to Fickian diffusion:

\[
\frac{M_t}{M_\infty} = 4 \left( \frac{D}{d} \right) \frac{t}{\pi^{1/2}}
\]

where \(D\) is the diffusion coefficient, \(d\) is the thickness of the specimen, \(M_t\) is water sorption at time \(t\), and \(M_\infty\) is the equilibrium value of the diffusing water at infinite time.

Diffusion coefficients could be calculated from initial slope of sorption curves, and the data are calculated in Table 4. Different from equilibrium water content, polarity had little effect on diffusion coefficient mainly. Therefore, the systems modified with CES and CCES showed not only lower equilibrium water contents, but also lower diffusion coefficients than CEO and CCEO. And when the functional group increased from CES to CCES, diffusion coefficients was lower as well, as the increase of sulfur atom declined the polarity.

In order to have a better understanding of water absorption in the epoxy and epoxidized system, the dynamic diffusion process of water molecules in CCEO and CCES was tracked by ATR-IR measurement until equilibrium. As illustrated in Fig. 11, the peak at 3700-3000 cm\(^{-1}\) of hydroxyl stretching vibration increased with the diffusion of water molecules. Based on the water diffusion process in ATR-IR spectra, 2D correlation spectra were formed to discuss the micro mechanism of diffusion process, shown in Fig. 12. In this paper, 2D correlation analysis is based on Noda’s theory \[27\]:

\[ \begin{align*}
(1) & \text{if } \Phi(r_1, r_2) > 0, \Psi(r_1, r_2) > 0, \text{ that means band } r_1 \text{ varying prior to band } r_2; \\
(2) & \text{if } \Phi(r_1, r_2) < 0, \Psi(r_1, r_2) < 0, \text{ that means band } r_1 \text{ varying after band } r_2; \\
(3) & \text{if } \Phi(r_1, r_2) > 0, \Psi(r_1, r_2) < 0, \text{ that means band } r_1 \text{ varying after band } r_2; \\
(4) & \text{if } \Phi(r_1, r_2) < 0, \Psi(r_1, r_2) > 0, \text{ that means band } r_1 \text{ varying prior to band } r_2.
\end{align*} \]

The absorption of hydroxyl has been divided into 3 regions: free water molecular without hydrogen bond (S\(_0\)), water molecular with one hydrogen bond (S\(_1\)) and water molecular with two hydrogen bond (S\(_2\)). In the analysis of water diffusion in polar polymer system, many researchers obtained 4 absorption peaks (located around 3600, 3500, 3400 and 3200 cm\(^{-1}\)) based on peak fitting. Musto et al. carried out series of work \[28-31\], and assigned S\(_2\) into S\(_{2L}\) (loosely bonded S\(_2\)) and S\(_{2T}\) (tightly bonded S\(_2\)). Based on the analysis of Musto et al. and 2D spectra in our actual study, OH stretching peak at 3600 cm\(^{-1}\) was assigned to S\(_0\), 3520 cm\(^{-1}\) to S\(_1\), 3350 cm\(^{-1}\) to S\(_{2L}\) and 3200 cm\(^{-1}\) to S\(_{2T}\). As shown in Table 5.

In synchronous 2D correlation spectra, 3350 cm\(^{-1}\) as the center for the circle, there is a very strong correlation peaks, indicating that hydroxyl vibration changed obviously with time. In asynchronous spectra of CCES, \(\Psi(3350,3600) < 0, \Psi(3350,3520) < 0\) and \(\Psi(3350,3200) > 0\) indicated that the diffusion speed of S\(_{2L}\) was faster than S\(_0\), S\(_1\) and S\(_{2T}\). Also in asynchronous spectra of CCEO, \(\Psi(3350,3600) < 0, \Psi(3350,3520) < 0\) and \(\Psi(3350,3200) > 0\) demonstrated that S\(_{2T}\) was the fastest in water diffusion compared to S\(_0\), S\(_1\) and S\(_{2T}\) (see Table 6).

3.6. Corrosion resistance

It was accepted that mechanical property and water absorption behavior are the critical properties, which are closely related to the corrosion resistance. With the derivatives content increasing from 10 wt% to 30 wt%, the equilibrium water content increased in all modified system because of increasing free volume by side aliphatic chain, while peel strength showed little improvement at 10 wt% and marked rise at 20 wt%, but in CCES modified system dropped at 30 wt%. Take the performance balance into account, CCES/CE 20 wt% and CCEO/CEO 20 wt% with relatively high peel strength and acceptable water absorption was chosen for further corrosion resistance test and comparison. The XPS spectra and SEM with EDS
mapping of the four modified systems were shown in Fig. 13 and Fig. 14. The full spectrum of CES-20% and CCES-20% modified system in Fig. 13 revealed peaks with binding energies of 163.9 eV, which corresponded to S 2p3. While the EDS results at 2.3–2.4 KeV further confirmed the S element in CES-20% and CCES-20% modified system.

Tafel polarization measurement was applied to investigate the corrosion rate and resistance of system[32]. Tafel curve is shown in Fig. 15, using the logarithmic current density (Log A/cm²) as a function of voltage (E). The Tafel curve can be divided into 3 zones. The curve at low potential (|U| < 120 mV) is attributed to the polarization zone, the curve at middle potential (with a sharp slope) is attributed to the Tafel zone, and the curve at high potential (horizontal part) is attributed to the diffusion zone. Extrapolation of the curves in Tafel regions to the point of intersection provides both the corrosion potential (Ecorr) and the corrosion current (Icorr).

Theoretically, the lower corrosion current and the higher corrosion voltage of the sharp slope is, the stronger corrosion resistance and slower corrosion rate of the coating will be. As the corrosion rate (CR) could be calculated from corrosion current Icorr values by following equation:

$$CR = I_{corr} 	imes K \times EW / \rho A$$

where the K is the corrosion rate constant, EW is the equivalent weight, $\rho$ is the material density and A is the sample area for MS plate. Thus, Icorr could be used to judge the corrosion rate qualitatively (see Table 7).

The data including corrosion potential, corrosion current and
resistance of 20% modified system and neat DGEBA were calculated in Table 8. The results showed that the corrosion voltage of CCEO/CEO 20% was lower but the corrosion current was higher than DGEBA. While the corrosion voltage of CCES/CES 20% was higher, the corrosion current was lower than DGEBA. Thus, the resistance of CCES/CES-20% was higher than the resistance of DGEBA and CCEO/CEO 20%. Considering the influence of functional group, the CCEO 20% had higher resistance than CEO 20%, and so as to the CCES 20% compared to CES 20%, which mainly resulted by the increased crosslink density. Among all the modified systems, CCES 20%
modified system showed the lowest corrosion current and the highest corrosion voltage in corrosion resistance. And the anticorrosion resistance of CCES-20% system \((1.85 \times 10^8 \Omega)\) increased by 14\% than neat DGEBA, which was in good agreement with EIS results.

Electrochemical impedance spectroscopy (EIS) was also carried out to investigate the impedance modulus of epoxy-coated steel sheets in 3.5\% NaCl solution. Bode plots obtained from the impedance measurement was shown in Fig. 16. It provided information about impedance at low (0.1–1 Hz) and high frequency (0.1–1 MHz) \((Z)\) during water uptake of coating, which represented coating resistance and capacitance respectively. In the previous works, the high impedance modulus at low frequencies and occurrence of one time constant indicated effective barrier protection of a painted metal \([33–35]\). In this article, value \(\log |Z|\) was also used as a function of exposure time to evaluate the corrosion resistance performance of the coatings.

Bode plots of CCES/CES 20\% showed higher impedance modulus at low frequency than that of CCEO/CEO 20\% and neat DGEBA coating, which indicated the improvement in anticorrosion properties of DGEBA-coated sheet iron. As CES/CCES modified system showed lower polarity, higher crosslink density and stronger chemical bonds between copper and resin interface than CCEO/CEO modified system. Further, the CCES 20\% coated one showed higher impedance modulus at low frequency than CES 20\% and other specimens. As the corrosion resistance property is influenced by both strengths of metal-coating interface and water absorption. Confirmed by the test results above, the peel strength of CCES 20\% were stronger than CES 20\%; while in water sorption measurement, the equilibrium water content of the CCES 20\% system was much lower than CES 20\% because of higher crosslink density by increased functional group. Therefore, the coating of CCES-20\% modified system was more effective than others in providing the corrosion protection of steel in NaCl solution. However, the impedance modulus of CCEO-20\% modified system at low frequency was lower than DGEBA, resulting by the higher equilibrium water content.

Compared the anti-corrosion ability of 20\% modification system in our study, Selvaraj et al. prepared cyclotriphosphazene (ATCP) reinforced caprolactam (Cpl) based cyanate ester (CE) composites into coating application, the \(\log |Z|\) of CCEO-20\% modified system at 0.1 Hz was about 7 in our study, higher than 6.3 of film ATCP(15\%)/CE-Cpl \([36]\). Hu et al. investigated the effect of functional carbon nanotubes (CNTs) and graphene oxide (GO) on the anti-corrosion performance of epoxy coating, the corrosion potential and were almost equal while corrosion current of CCES-20\% was lower than GO&CNT/EP composites \([37]\). However, the corrosion protection performance of an epoxy coating through wet transfer of amino functionalized graphene oxide in Ramezanzadeh et al.’s work, was better than CCES-20\% in our system \([38]\). Thus, the anti-corrosion properties of CCES-20\% in our system maybe better than the coating of polymer film, but still less well than some epoxy composite with like GO and FTiO\(_2\). Furthermore, the decrease of glass transition temperature was from 25 °C to 10 °C at 20\% modified system in our study, while the water sorption drops from 2.01 to 1.76 for CCES 20\%, the coating application of CCES-20\% modified system might be more suitable at normal temperature, but not at high temperature.

4. Conclusion

Cardanol/cardol with a reactive phenolic group and aliphatic double bond, derived from cashew nut shell liquid, has been used in this article to synthesize epoxy and episcufide-type bio-based materials. The prepared resin was then used as partial replacement to DGEBA epoxy resin for coating application.

For the modified system, both the storage modulus and \(T_g\) decreased from neat DGEBA. As the flexible chain may decrease the
crosslinking density and increase free volume. However, Tg of CCES modified system was higher than CCEO modified system and was very close to neat DGEBA, as its higher curing conversion of about 90% enhanced the crosslink density. With the functional group increasing, the crosslink density increased from CEO to CCEO, and CES to CCES.

The equilibrium water contents of CCES (CES) modified system were lower than neat DGEBA as well as CCEO (CEO) modified system in our study. Polarity and free volume influenced the water sorption corporately, the long side aliphatic chain of these four derivatives lowered down polarity at the same time increased free volume. However, benefited from lower polarity of S atom and limited increase in free volume from high curing conversion, episulfide performed better in low water absorption. With the functional group increasing, the crosslink density increased from CES to CCES, which contributed to decline the free volume and equilibrium water content.

System modified by 20% CCES derivative showed better performance in water absorption and peel strength test, and further anti-corrosion measurement by EIS, and Tafel experiment. As the corrosion resistance property is influenced by both strength of metal-coating interface and water sorption, much stronger peel strength and much lower equilibrium water content of CCES-20% system made it more effective than others in providing the anti-corrosion property.

Thus, CCES with optimal 20% weight proportions could be the competitive candidate to enhance the anti-corrosion property of DGEBA as a sustainable and environment friendly materials.

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References