

Article

Multi-Functional Cardanol Triazine Schiff Base Polyimine Additives for Self-Healing and Super-Hydrophobic Epoxy of Steel Coating

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Abstract: The designing of multifunctional materials in system-level efficiency is one of the main targets and a hot topic for the application of novel green or bio-based materials and structures. In this work, the chemical structure of bio-based cardanol that was derived from cashew oil was modified through a reaction with a bishydrazino-s-triazine derivative followed by condensation polymerization or reaction with terephthaldehyde to obtain a Schiff base polymer. The chemical structures of the modified cardanol-bishydrazino-s-triazine-based monomer and the Schiff base polymer were confirmed from FTIR and NMR spectroscopy analyses. The modified cardanol bishydrazino-s-triazine monomer and polymer were added with different weight ratios during the curing of the epoxy/polyamine hardener to improve the thermal, mechanical, and anti-corrosion characteristics of the epoxy coating of a steel substrate. The data elucidated that the presence of a cardanol bishydrazino-s-triazine monomer and polymer improves the thermal, mechanical, adhesion, and anti-corrosion characteristics of epoxy coatings after exposure for more than 1500 h. The presence of a cardanol- bishydrazino-s-triazine polymer more than 3 wt.% during the curing of epoxy networks produces superhydrophobic and self-healing epoxy coatings. The modification of the epoxy coating with the cardanol bishydrazino-s-triazine polymer improves the seawater contact angle by more than 150° and the adhesion strength of the epoxy coating with the steel surface.

Keywords: steel coatings; multifunctional; cardanol; epoxy; self-healing; triazine

1. Introduction

The design and fabrication of multi-functional additives has attracted great attention in both academic and technological research due to their potential applications for adjusting the surface properties of materials and their application for different purposes as protective for active species in dyes, paints, and coatings [1–3]. Additives with multi-functionality have been used instead of other traditional additives to reduce fabrication and design costs. The presence of one multifunctional additive with a lower concentration instead many traditional additives improves the thermal, mechanical, anticorrosive, self-cleaning, antifogging, and self-healing properties of polymer composites and coatings [4–6]. The multi-functional reliable additives used in the coating should not be costly and should exhibit a lower moisture penetration, a high durability, good impact resistance, good substrate adhesion, environmental friendliness, and easy compatibility with organic coatings [7–10]. The smart multifunctional additives have been the target for the production of advanced coatings because they resist different aggressive conditions such as pH, salt, humidity, and marine corrosive conditions that

occur on coating surfaces [7,8]. In this respect, polymeric materials have encouraged innovations as multifunctional additives in paint and coating formulations [11–14]. Nowadays, greener polymers based on natural and bio-resources are widely used as multifunctional, cheaper, and durable additives and coatings [15–18]. Multifunctional epoxy resins, hardeners, and additives are valuable materials for steel coatings to replace conventional, widely used epoxy organic coatings that exhibit lower electrical conductivity, higher crosslinking density, lower toughness and impact resistances due to the presence of micro-cracks [19–21]. One of the drawbacks of epoxy coatings applications is the weak interactions between traditional fillers and epoxy coatings [18,19,22].

The development of bio-based, renewable, multifunctional epoxy resins, hardeners, and additives is a development trend caused by growing environmental issues. Moreover, the linking of renewable multifunctional additives with epoxies facilitates the recycling of epoxy coatings under special conditions and produces environment-friendly epoxies [23]. In this respect, polymers based on renewable resources derived from nonedible oils, fats, starch, and carbohydrates have been investigated due to their easy functionalization with epoxidation or amidation, as well as their excellent biodegradability and weather durability [24–26]. Moreover, the modification of an epoxy coating with a Schiff base containing azomethine or an imine group ($\text{CH}=\text{N}-$) as a corrosion inhibitor or a filler additive [27] for epoxy coatings [28,29] for steel surfaces [30] has been investigated due to its stronger interaction with steel surfaces. The presence of an azomethine group in an epoxy matrix was found to improve adhesion with a steel substrate, and it combined excellent controlled degradability, stability, and antimicrobial properties [27–30]. Cardanol is one of the byproducts of the cashew oil industry that has attracted considerable attention to produce multi-functional epoxies and hardeners due to its cheap price, easily modified chemical structure, and presence of a phenolic benzene ring and hydrophobic alkenyl groups (unsaturated C_{15} - chain) that are used to modify its chemical structure with new functional groups [31–37]. Bio-based cardanol epoxies have been used to improve the anticorrosive performance of steel coatings by the creating higher impedance and electrochemical potential values, but these epoxies cannot act as superior multi-functional coatings. The present work aimed to functionalize the cardanol chemical structure via a reaction with 2,4,6-triazine hydrazide followed by condensation polymerization with terephthalaldehyde to produce Schiff base polyamines as multi-functional additives. The work also aimed to chemically link the modified cardanol Schiff base polymer with the epoxy matrix during the curing of the epoxide ring with the polyamine hardener. It was expected that the chemical linking of the modified cardanol Schiff base polymer with the epoxy networks would improve the mechanical, thermal, self-healing, and anticorrosive properties of epoxy coatings of steel substrates. The investigation of the superhydrophobicity of the cured epoxy coatings in the presence of different weight percentages of cardanol triazine Schiff base polyamines was another goal of the present work.

2. Materials and Methods

2.1. Materials

Cardanol obtained from cashew nut oil was provided by Shanghai Judong Trading. All other chemicals were purchased from Aldrich-Sigma Co., St. Louis, MO, USA, and used as received. Cyanuric chloride (TCT; 98.0%), hydrazine hydrate (80.0%), diisopropylethylamine (DIEA), and terephthalaldehyde (TPA) were used to modify the chemical structure of cardanol. The tetrahydrofuran (THF), hexane, ethyl acetate, butyl acetate, ethanol, toluene, and acetone were used as solvents. The commercial epoxy resin, SigmaGuard™ CSF 650 (90 vol.%), was mixed with butyl acetate as a thinner and its polyamine hardener were purchased from SigmaKalon Group. The epoxy resin was cured with its polyamine hardener at a recommended mixing volume ratio of 4:1 wt.% (epoxy resin: hardener). The steel panel used as substrate was analyzed with energy dispersive X-ray spectroscopy, and it had the following chemical composition (in wt.%): 0.14% C, 0.57% Mn, 0.21% P, 0.15% S, 0.37% Si, 0.06% V, 0.03% Ni, and 0.03% Cr and Fe as balance. The steel panels were washed with xylene,

soap, and water to remove the oil from their surfaces, followed by blasting with a blasting machine to produce rough surfaces (35 μm). The steel panels were washed with acetone and air-dried to remove any rust after blasting to apply the epoxy coatings by the air spray technique.

2.2. Techniques

2.2.1. Preparation of cardanoxo bishydrazino-s-triazine

A solution of TCT (18.4 g, 100 mmol) in THF (100 mL) was added to a mixture of cardanol (29.9 g, 100 mmol) and DIEA (100 mmol) in THF (100 mL) during a period of time of 30 min at 0 °C. The reaction mixture was stirred at the same temperature for 3 h, then filtered from the precipitated salt, washed with THF (20 mL), and kept in the refrigerator 24 h. The reaction progress was identified by thin layer chromatography (TLC) in an ethyl acetate:hexane (1:9) solvent. The solvent was removed under a vacuum, and a reddish-brown liquid was obtained. TLC showed an almost complete reaction and no traces of TCT. The crude liquid was dissolved in ethanol (150 mL), and then hydrazine hydrate (80%, 25 mL) was added to reflux the mixture for 6 h. The solvent was removed under a vacuum, and excess ether was added to obtain a white solid in a yield of 88%. The produced cardanoxo bishydrazino-s-triazine is designated as Card-TH2. Elemental analysis was calculated for $\text{C}_{24}\text{H}_{35}\text{N}_7\text{O}$ (437.59) as: C, 65.88; H, 8.06; and N, 22.41 wt.%. The determined elemental analysis was C, 66.18; H, 8.27; and N, 22.67 wt.%.

2.2.2. Synthesis of polymeric Schiff base CardT-Schiff base (CardT-TPA)

Card-TH2 (8.8 g, 20 mmol) was mixed with TPA (2.68 g, 20 mmol) in 100 mL of toluene in the presence of 5 drops of acetic acid. The reaction mixture was finally refluxed for 24 h. The yellow precipitate was filtered, washed with ethanol, ether, and then dried at 60 °C for 6 hours (79% yield, 8.5 g). The produced polymeric Schiff base is designated as CardT-TPA.

2.3. Characterization

Nitrogen content was measured by using a Tecator Kjeltex auto analyzer. A Tecator 1007 digester was used for the initial digestion of the samples. The inherent viscosity of CardT-TPA was performed with 0.5% (w/v) solutions in a THF solvent at 25 °C with an Ubbelohde viscometer. The chemical structures of Card-TH2 and CardT-TPA were confirmed by using ^1H NMR (Bruker AC-400 MHz spectrometer) in deuterated dimethylsulfoxide (DMSO) and Fourier transform infrared (FTIR; Perkin Elmer 1430, Norwalk, CT, USA) spectroscopy. The number average and weight average molecular weights (M_w) of CardT-TPA were determined with gel permeation chromatography (GPC; Agilent 1100 series consisting of a refractive index detector and an Agilent PL gel 10 μm column, Agilent Technologies Waldbronn Germany) using THF as a solvent. The glass transition temperature (T_g) of CardT-TPA was evaluated by using differential scanning calorimetry (DSC Q-100 equipment, TA Instruments Q Series™, Toronto, ON, Canada) at temperatures ranging from 5 to 200 °C at a heating rate of 20 °C.min⁻¹ under a nitrogen atmosphere. The morphology of the cured epoxy modified with Card-TH2 and CardT-TPA was investigated by using a scanning electron microscope (SEM JEOL, JSM 5600 LV, Tokyo, Japan). The contact angle measurements of seawater droplets on the surfaces of the coated epoxy that was modified with Card-TH2 and CardT-TPA films were determined by using sessile drop (drop shape analyzer DSA-100) at 25 °C. Thermogravimetric analyses (TGA) of Card-TH2 and CardT-TPA and their blends with epoxy were evaluated (Mettler Toledo, model: GA/DSC1, Basel, Switzerland) under a nitrogen flow rate of 60 mL.min⁻¹ in the temperature range of 25 to 800 °C with a heating rate of 10 °C.min⁻¹. The DSC and TGA analyses were repeated three times to detect the accurate result of thermograms.

The salt spray resistance of the coated steel panels with epoxy coatings and their blends with Card-TH2 and CardT-TPA toward seawater was investigated with a salt spray cabinet (manufactured by CW Specialist Equipment Ltd. model SF/450) at a humidity above 99% and a temperature of 35 °C.

2.4. Application of Coatings of The Steel Substrate

The epoxy resins modified with Card-TH2 and CardT-TPA were mixed in the presence a butyl acetate solvent by using a planetary centrifugal mixer (AR-100). The weight contents of Card-TH2 and CardT-TPA ranged from 0.1 to 5 wt.%, related to the total weights of both the epoxy resin and its polyamine hardener. The epoxy Card-TH2 and CardT-TPA blends were mixed with the recommended polyamine hardener and sprayed on blasted and clean steel panels (roughness 35 μm) with an average dry film thickness of 100 μm . The curing of the sprayed films was carried out at 120 $^{\circ}\text{C}$ for 4 h.

2.5. Mechanical, Chemicals and Salt Spray Resistance of Modified Epoxy Coatings

The adhesion strengths of the cured epoxy with the steel substrate were determined by using a hydraulic pull-off adhesion tester in the range of 0–25 MPa according to American standard for testing materials (ASTM) D-4541. The abrasion resistance of the epoxy films was determined in terms of weight loss using ASTM D-4060 and applied with CS-17 wheels for 5000 cycles. The hardness of the epoxy coating films was measured according to ASTM D-3363 by using Erichsen hardness test pencil, model 318S, with a scratching force in the range from 0.5 to 20 N. The flexibility or bending and impact tests were evaluated by a conical mandrel and an impact tester according to ASTM D-522 and ASTM D-2794, respectively.

2.6. Corrosion Resistance of Modified Epoxy Coatings

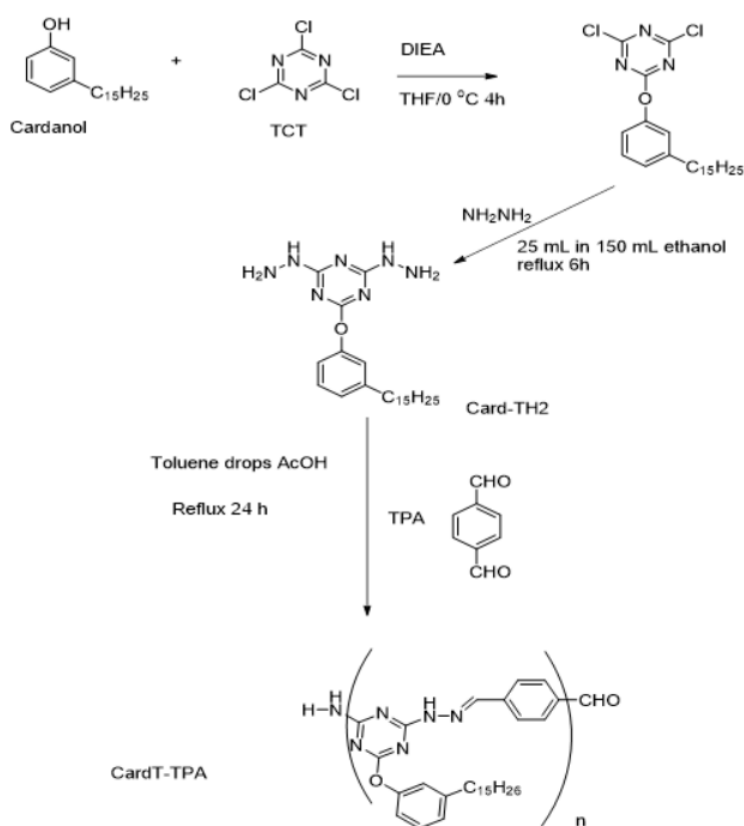
The ASTM B117 international standard procedure was used to evaluate the salt spray or corrosion resistance of the epoxy that was modified with Card-TH2 and CardT-TPA using seawater. The salt fog and the humidity inside the cabinet were maintained as 99% at a temperature of 35 ± 2 $^{\circ}\text{C}$. The coated steel was inspected for corrosion on the scribed area according to ASTM D-1654 based on blistering, rusting, and loss of adhesion.

3. Results and Discussion

Cardanol reacts with TCT in the presence DIEA, as the former is an acid acceptor, controls the reaction of cardanol with TCT and produces cardanoxo 1,2-dichloro-2,4,6-triazine as illustrated in Scheme 1. The remaining cardanoxo 1,2-dichloro-2,4,6-triazine reacted with hydrazine to form Card-TH2 that condensed with TPA to produce a CardT-TPA Schiff base polyimine, as represented in the experimental section and illustrated in Scheme 1. The physicochemical characteristics of the CardT-TPA yellow powder are summarized in Table 1. The solubility of Card-TH2 and CardT-TPA in organic solvents such as DMSO, THF, and butyl acetate confirmed that the prepared materials did not crosslink during the preparation procedure. The agreement of the theoretical and experimental data of nitrogen content elucidated the purity of the produced Schiff base polyimine (CardT-TPA). Moreover, the average molecular weight of CardT-TPA (M_n ; Table 1; determined from GPC using a THF solvent) elucidated that the repeating unit (n) of the polymer was 10 units. The inherent viscosity of CardT-TPA (0.5% w/v solutions in THF) confirmed its excellent solubility in an organic solvent.

Table 1. Physicochemical characteristics of CardT-TPA.

Characteristics	Units	Value
Melting temperature (T_m)	$^{\circ}\text{C}$	173.6
Glass transition temperature (T_g)	$^{\circ}\text{C}$	68.8
Yield	%	79
Nitrogen content	wt. %	-
Theoretical		16.47
Experimental		16.78
Number average molecular weight M_n	g.mol^{-1}	4594
Inherent viscosity	mL.g^{-1}	0.15



Scheme 1. Synthesis of CardT-TPA (Card-TH2 (cardanoxy bishydrazino-s-triazine) mixed with TPA (terephthalaldehyde)).

3.1. Characterization of Card-TH2 and CardT-TPA

The proposed chemical structures of the Card-TH2 and CardT-TPA (Scheme 1) were confirmed from their FTIR and ^1H NMR spectra represented in Figures 1 and 2a,b, respectively. The etherification of cardanol with TCT was confirmed by the appearance of the C-O stretching group of the phenoxy group at $1096\text{--}1255\text{ cm}^{-1}$. The presence of a band at 803 cm^{-1} (out-of-plane bending of the benzene ring; Figure 1a) elucidated the presence of the *m*-phenoxy group of cardanol [38]. The lowering of the intensity of the phenolic -OH intense band of cardanol at 3315 cm^{-1} (-OH stretching) elucidated its involvement in etherification reaction with Card-TH2 (Figure 1a). The bands at 3640 and 3420 cm^{-1} (NH stretching vibration), 1560 cm^{-1} (NH bending vibration), and 1440 cm^{-1} (C-N stretching vibration) in both Card-TH2 and CardT-TPA spectra (Figure 1a,b) confirmed the incorporation of triazine hydrazide in both chemical structures (Scheme 1) [39]. The appearance of new bands at 1680 and 1620 cm^{-1} (caused to aldehyde and azomethine (C=NH) groups stretching, respectively, of the CardT-TPA) elucidated their chemical structures (Scheme 1 and Figure 1b). The presence of the C-H stretching of the aldehyde group at 2650 cm^{-1} confirmed that the CardT-TPA had an aldehyde end group (Scheme 1). The chemical structures of both Card-TH2 and CardT-TPA were marked and reassigned from ^1H NMR spectra (Figure 2a,b). The azomethine, aldehyde, and NH groups of CardT-TPA were confirmed by the appearance of new peaks at chemical shifts 8.01, 9.85, and 10.56 ppm, respectively. The phenoxy (C-O), azomethine (C=N), and aldehyde end groups (C=O), elucidated from the ^{13}C NMR spectrum of the CardT-TPA polymer, are shown in Figure 3 [40].

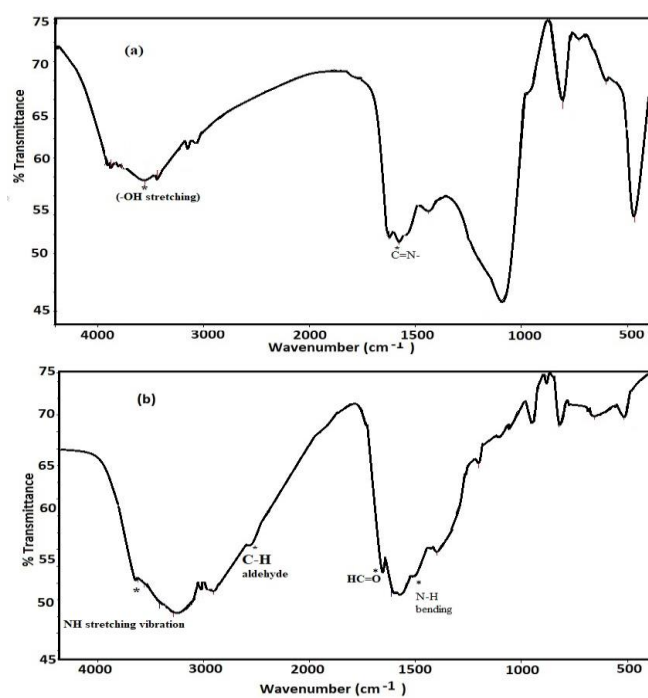


Figure 1. FTIR spectra of (a) Card-TH2 and (b) CardT-TPA.

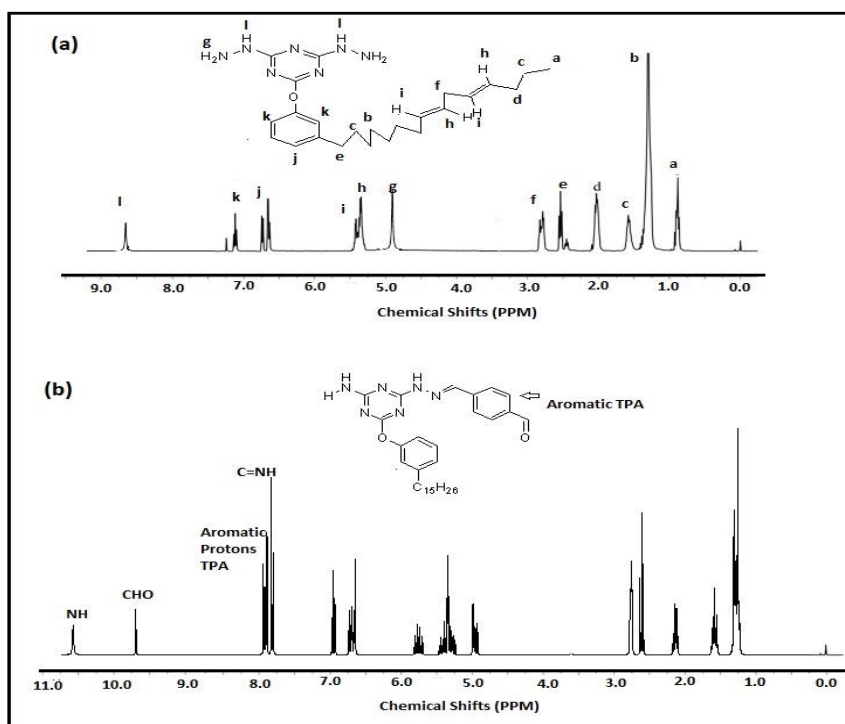


Figure 2. ^1H NMR spectra of (a) Card-TH2 and (b) CardT-TPA.

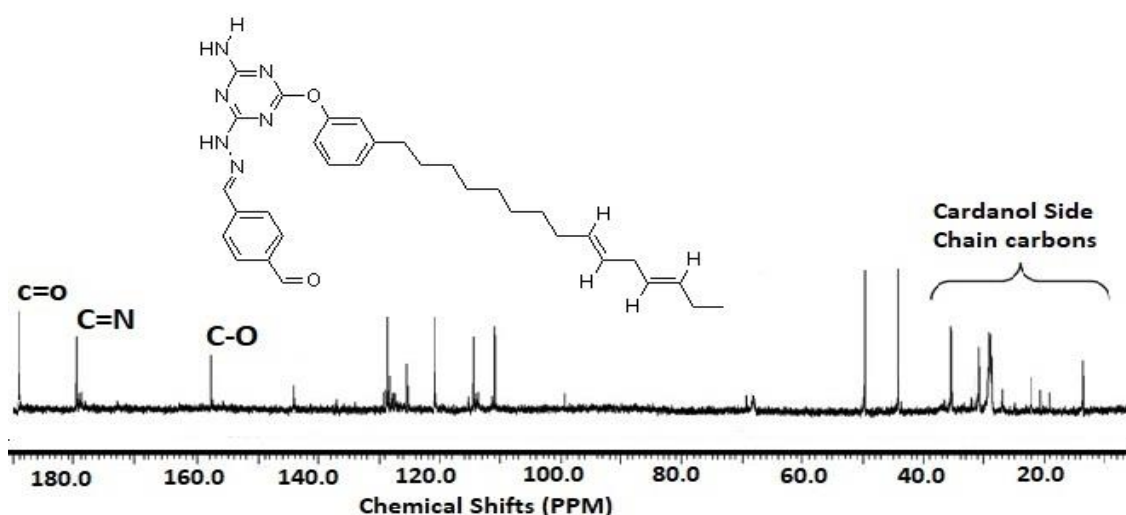


Figure 3. ^{13}C NMR spectrum of Card-TH2.

The thermal stability of the Card-TH2 and CardT-TPA was evaluated from TGA thermograms, as shown in Figure 4. The initial decomposition temperatures of Card-TH2 and CardT-TH2 were 230 and 310 °C, respectively. The first decomposition steps of Card-TH2 and CardT-TH2 ended at 350 and 420 °C with weight losses 30.5% and 20.1 wt.%, respectively. The decomposition could be seen in the nitrogen decomposition of Card-TH2, which contained more hydrazide groups than CardT-TPA (Scheme 1), followed by the decomposition of the phenoxy group of cardanol. Moreover, the end aldehyde and amine groups of CardT-TPA were also degraded in this step. The second decomposition steps of Card-TH2 and CardT-TPA started from 360 to 500 °C and from 450 to 630 °C, respectively. The weight loss percentages (wt.%) of the second degradation step of Card-TH2 and CardT-TH2 were 42.5 and 35.9 wt.%, respectively. The second degradation step could be seen in the decomposition of the azomethine group ($-\text{CH}=\text{N}-$) and triazine of both Card-TH2 and CardT-TPA. The remaining residues of Card-TH2 and CardT-TPA at 750 °C were 25 and 45 wt.%, respectively. By comparing the thermal stability data of Card-TH2 and CardT-TPA with the same Schiff base polymer prepared without cardanol [41], it was found that the presence of cardanol increased the initial degradation step of CardT-TPA, in addition to the increasing of the remaining residue at 750 °C of more than 30 wt.%. The presence of an unsaturated alkyl chain ($\text{C}_{15}\text{H}_{26}$), a strong electron affinity property, structural symmetry, and the excellent co-planarity of triazine cyclic structure was responsible for the higher thermal stability of CardT-TPA, which contained more repeating units than Card-TH2 [41]. The thermal degradation residues that were left were mainly polycyclic species that are difficult to decompose and carbons; additionally present was the formation of crosslinked cyclic structures that increased for CardT-TPA when compared with Crd-TH2 or other previously reported Schiff base polymers of triazine [41].

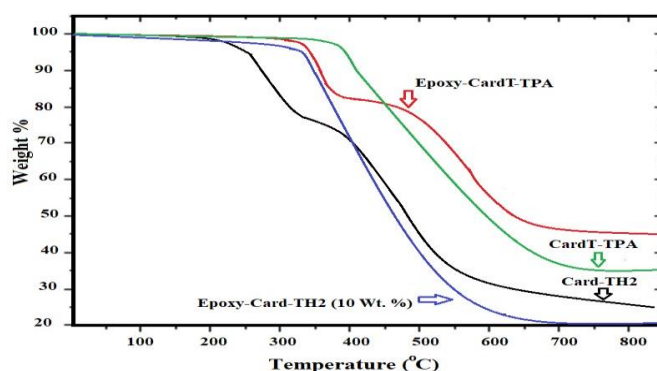
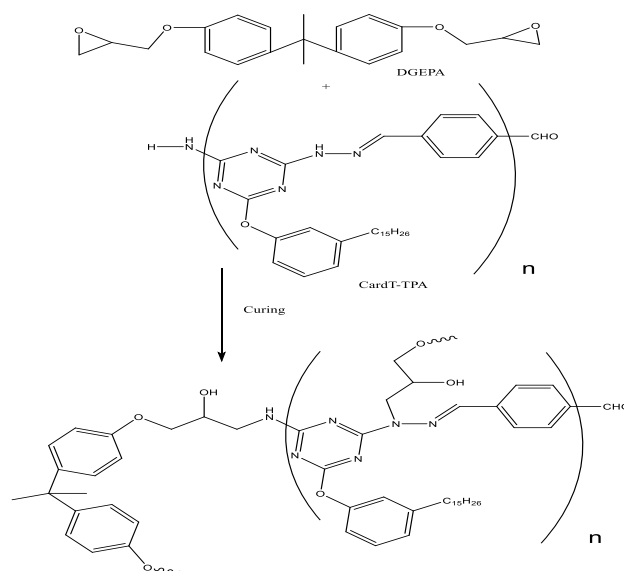


Figure 4. TGA thermograms of Card-TH2 and CardT-TPA.

3.2. Wettability of Epoxy Modified Films

An epoxy resin based on diglycidyl ether bis-phenol A (DGEPA) can be cured with a polyamine to produce epoxy networks with high crosslink densities. Cardanol modified to be applied as an epoxy resin and a polyamine hardener to produce new advanced and greener epoxies [42–44]. Cardanol-based polybenzoxaine was used as capping for amino-modified silica nanoparticles during the blend of epoxy/polyamine coatings with anti-corrosion and superhydrophobic coatings by using simple spray and thermal curing methods [44]. In this respect, different weight percentages (0.1–5 wt.%) of Card-TH2 and CardT-TPA were mixed with a polyamine hardener and an epoxy solvent-based system, as illustrated in the experimental section. The chemical structures of Card-TH2 and CardT-TPA were designed to insert an amine group for linking with epoxy resins during the curing process with polyamine hardener. The curing mechanism of DGEPA with CardT-TPA and the polyamine hardener is represented in Scheme 2. It is proposed that the amine groups of both Card-TH2 and CardT-TPA (Scheme 1) can be cured with either DGEPA or a DGEPA/polyamine system to link with an epoxy matrix. The lower seawater droplet contact angles than steel surfaces of the epoxy coatings modified with Card-TH2 and CardT-TPA and cured on glass (Table 2) confirmed the low adhesion of the epoxy coatings with the glass surface.



Scheme 2. Curing of epoxy/polyamine with CardT-TPA.

Table 2. The contact angle of the seawater droplet measurements of epoxy films adhered with different substrates; the contact angles were measured five times at different locations on the epoxy surfaces to determine the average of the results.

Epoxy Composites	Composite Contents (wt.%)	Water Receding Contact Angles on the Different Substrates (Degree)	
		Steel	Glass
Blank	0	69.3 ± 2.1	59.1 ± 5.0
	0.1	83.1 ± 6.0	75.6 ± 4.2
	1.0	95.6 ± 4.1	92.9 ± 3.1
	3.0	110.3 ± 2.1	104.8 ± 5.1
	5.0	125.3 ± 2.1	112.9 ± 3.2
Epoxy/Card-TH2	0.1	117.3 ± 5.0	110.4 ± 6.0
	1.0	135.3 ± 4.1	132.3 ± 2.1
	3.0	145.3 ± 6.3	140.9 ± 3.2
	5.0	164.3 ± 6.1	159.3 ± 6.1

It was expected that the presence of hydrophobic phenyl and a side alkyl group ($C_{15}H_{26}$) of cardanol would enhance the hydrophobicity of the cured epoxy coatings. The superhydrophobicity of the epoxy organic coating was evaluated from the wetting characteristic that measured the static contact angle of seawater droplet measurements on the epoxy coatings modified with Card-TH2 and CardT-TPA cured on steel and glass surfaces, as summarized in Table 2 and Figure 5a–c. The data of the contact angles (Table 2 and Figure 5a–c) elucidate that the presence of the different weight contents of Card-TH2 and CardT-TPA, ranging from 0.1 to 5 wt.%, changed the seawater contact angle from the hydrophilic coating of the epoxy blank at 69.3° to the hydrophobic contact angles ($95\text{--}150^\circ$) and superhydrophobic contact angles ($150^\circ\text{--}180^\circ$) of the coating. It was previously reported that [44,45] the modified cardanol polymers were used as cappings for different nanomaterials to produce superhydrophobic surfaces when mixed with epoxy coatings due to their ability to form rough surfaces. In this respect, the SEM images of the cured epoxy in the presence Card-TH2 and CardT-TPA are represented in Figures 6 and 7a–c, respectively. The morphology of the epoxy modified with Card-TH2 (Figure 6a–c) was changed from a smooth surface (epoxy blank) to flat with slight wrinkles (Card-TH2 wt.% ranged from 0.1 to 5 wt.%; Figure 6a–c), thus confirming that the epoxy coating modified with Card-TH2 had a dense crosslinked network. The hydrophobicity of the epoxy coatings could be seen in the presence of long alkyl chains in cardanol ($C_{15}H_{26}$) that imparted hydrophobicity to the epoxy/Card-TH2. The SEM images of the epoxy modified with CardT-TPA (Figure 7a–c) were uniformly distributed with lots of micro rough structures. Hence, the rough concave–convex structures were formed from the presence of dangling chains of the CardT-TPA polymer that linked from one of its ends to the cured epoxy/polyamine hardener. The rough concave–convex structures and the presence of a low surface energy material of the cardanol-based polyimine were responsible for the superhydrophobicity of the epoxy modified with CardT-TPA (5 wt.%; Figure 7c) [44–46].

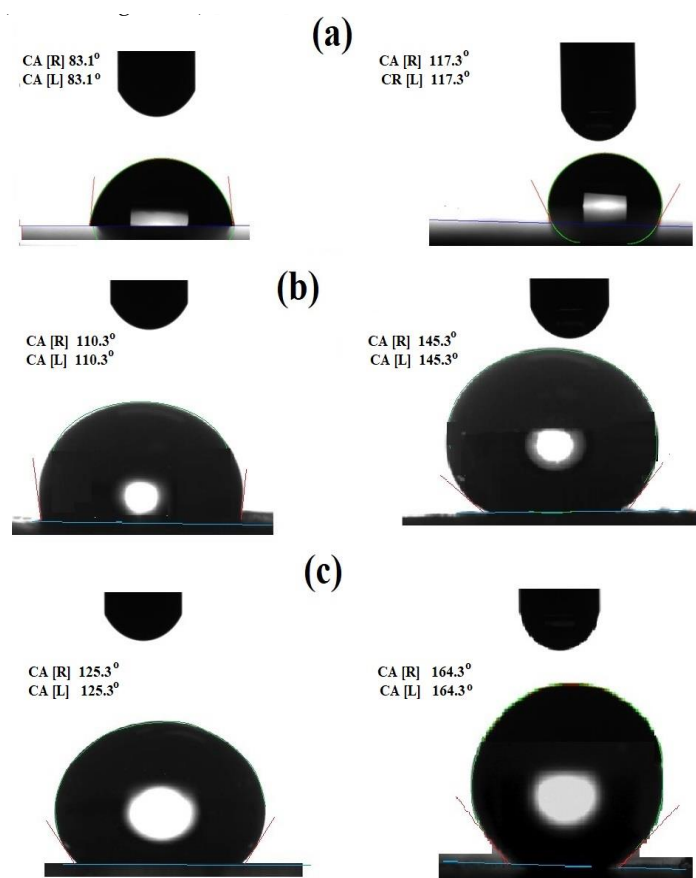


Figure 5. Seawater droplet contact angle on the epoxy modified with Card-TH2 (left) and CardT-TPA coatings (right) with different weight percentages of (a) 0.1, (b) 3, and (c) 5 wt.% on the steel surface.

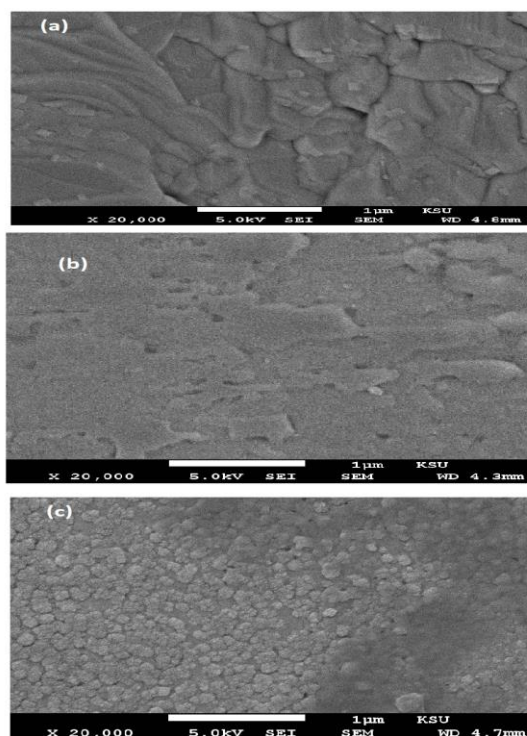


Figure 6. SEM photos of the modified epoxy films in the presence Card-TH2" (a) 0.1, (b) 3, and (c) 5 wt.%.

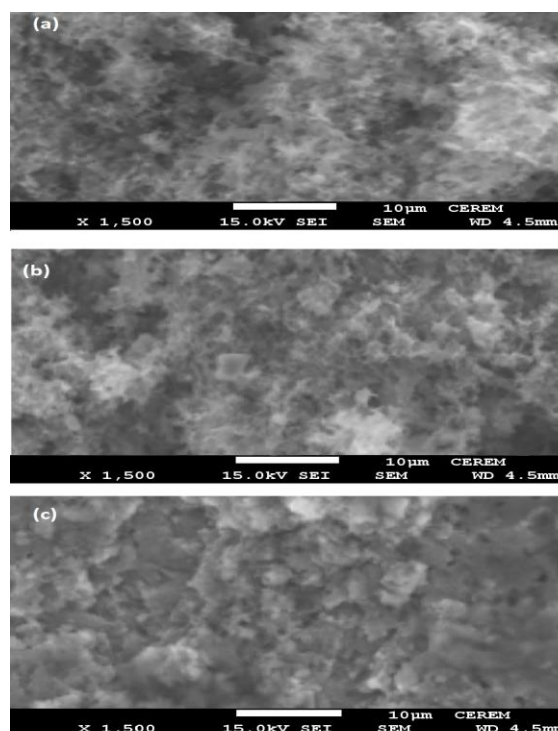


Figure 7. SEM photos of the modified epoxy films in the presence CardT-TPA: (a) 0.1, (b) 3, and (c) 5 wt.%.

It was necessary to determine the chemical structures of the cured DGEPA/polyamine in the presence Card-TH2 and CardT-TPA to investigate the incorporation of the cardanoxy triazine group in the polymer network. In this respect, the FTIR spectra of DGEPA/polyamine in the presence

Card-TH2 and CardT-TPA (10 wt.%) are shown in Figure 8a,b, respectively. The presence of a C=N-stretching vibration at 1620 cm^{-1} in the spectrum of DGEPA/polyamine in the presence Card-TH2 (Figure 8a) elucidated the curing of the hydrazide group in the epoxy network. The appearance of C-H aldehyde, C=O, and C=N-stretching vibrations at 2657 , 1680 , and 1620 cm^{-1} , respectively—caused by aldehyde and azomethine—confirmed the insertion of CardT-TPA into the epoxy network (Figure 8b and Scheme 2).

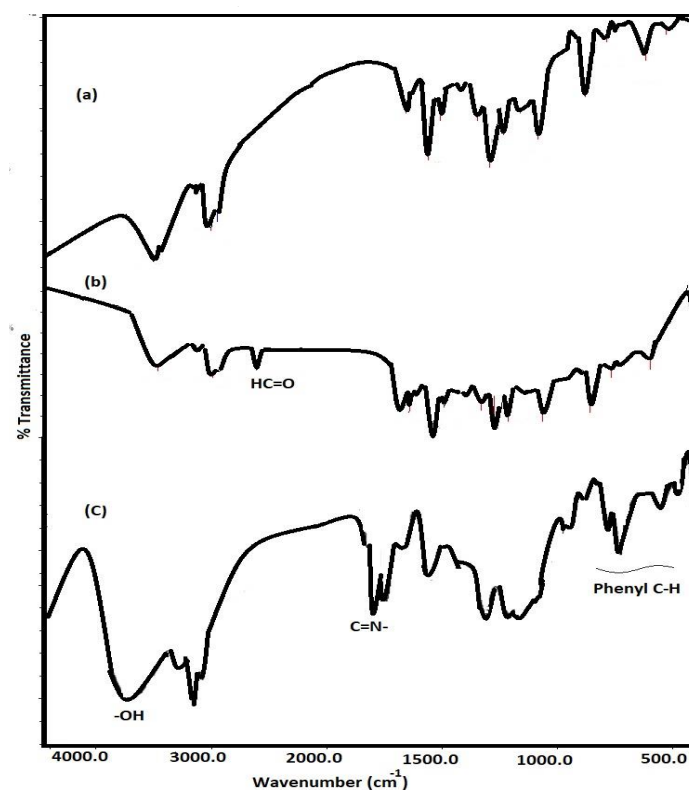


Figure 8. FTIR spectra of cured epoxy in the presence (a) Card-TH2 (10 wt%), (b) CardT-TPA (10 wt%), and (c) CardT-TPA (10 wt%) after scratching and exposure to salt spray fog.

3.3. Mechanical Properties of The Cured Epoxy Coatings

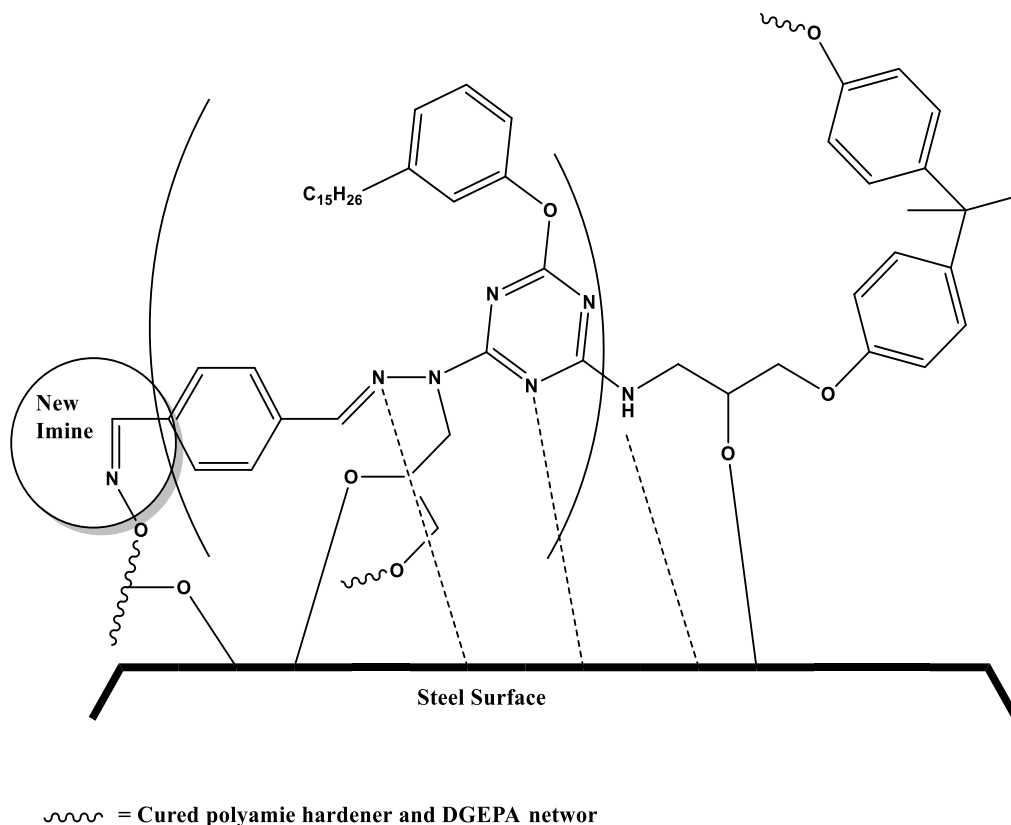
Some of the drawbacks of superhydrophobic materials is their lower adhesion with metallic substrates and their poor mechanical properties. Regarding this, the epoxy resin was modified with Card-TH2 and CardT-TPA during curing with the polyamine hardener, and the resin was then applied as an organic coating on steel substrate surfaces, as reported in the experimental section. The adhesion strength was determined by using a pull-off hydrolytic tester, and the mechanical properties of the coatings (impact resistance, pencil hardness, bending resistance, and abrasion resistance) were measured and are summarized in Table 3. The adhesion data of the cured epoxy/polyamine hardener in the absence (blank) and presence of both Card-TH2 and CardT-TPA confirmed the increasing of the adhesion strength with the increasing amounts of Card-TH2 and CardT-TPA from 0.1 to 5 wt.%. It was noticed that the epoxy/polyamine system that was cured with CardT-TPA and that had a weight content of more than 1.0 wt.% showed superior adhesion with the steel surface. This meant that the cardanol oriented its hydrophobic phenoxy substituted with long alkyl ($\text{C}_{15}\text{H}_{26}$) to the exterior surface of the coating without interaction or contact with the steel substrate during the curing of the epoxy/polyamine matrix. The curing mechanism of CardT-TPA with epoxy resin is represented in Scheme 3. The increasing of the hydroxyl group contents that were produced from the curing of the epoxy oxirane with the hydrazide amine end group and the hydrazide amine group bonded with the azomethine group increased the adhesion of the epoxy with the steel surface. Moreover, the presence

of the hydroxyl and azomethine groups facilitated the chelation of the bonded CardT-TPA with the steel surface more than Card-TH2, which did not contain the azomethine group. By comparing the mechanical properties of the present system with the cured epoxy coatings based on modified cardanol as epoxy or polyamine hardener [23,33,41,47], it was found that the compatibility and chemical curing of Card-TH2 and CardT-TPA increased the mechanical strength of the cured epoxy resin. The higher impact resistance and lower weight loss of the cured epoxy films in the presence CardT-TPA (5 wt.%; Table 3) elucidated that the cured epoxy absorbed more impact energy more than other systems. The chemical curing of Card-TH2 and CardT-TPA with an epoxy matrix enhanced their dispersion and reduced any agglomerates that initiated catastrophic failure [47]. The presence of the flat with slight wrinkles morphology of the epoxy that was modified with Card-TH2 (Figure 6a–c) reduced the mechanical properties of the epoxy coatings than that modified with CardT-TPA, which showed a uniform distribution with lots of micro rough structures and rough concave–convex structures (Figure 7a–c). The convex structures and the presence of the low surface energy material of the cardanol-based polyimine were responsible for the superior impact, hardness, and abrasion resistance (Table 3). The presence of Card-TH2 and CardT-TPA in the epoxy coatings increased the flexibility of the cured epoxy resins to pass the bending test, although this presence also increased the network crosslink density with their chemical curing with epoxy/polyamine networks.

Table 3. Mechanical tests of the cured epoxy resins modified with different weight percentages of Card-TH2 and CardT-TPA; the tests were repeated five times to determine the average of the results.

Sample	Weight Contents (wt.%)	Impact Test (Joule)	Hardness (Newton)	Pull of Test (MP)	Abrasion Resistance mg/kg Weight for 5000 Cycles Weight loss (mg)
Blank	0	5 ± 0.8	8 ± 0.5	5 ± 0.5	85 ± 2
	0.1	8 ± 0.8	10 ± 1.5	8 ± 0.3	45 ± 4
Epoxy/Card-TH2	1.0	11 ± 1.2	12 ± 2.1	12 ± 0.8	40 ± 3
	3.0	13 ± 1.4	14 ± 1.8	10 ± 0.9	45 ± 2
	5.0	15 ± 2.3	16 ± 2.3	13 ± 1.3	49 ± 3
	0.1	15 ± 2.2	15 ± 1.7	12 ± 1.5	10 ± 2
Epoxy/CardT-TPA	1.0	20 ± 3.1	18 ± 2.4	16 ± 2.3	8 ± 2
	3.0	25 ± 2.6	20 ± 2.5	20 ± 2.4	4 ± 0.5
	5.0	30 ± 2.8	23 ± 1.3	25 ± 3.0	2 ± 0.7

The thermal stability of the cured epoxy resin in the presence 5 wt.% Card-TH2 and CardT-TPA was estimated from TGA, as represented in their thermograms in Figure 4. The disappearance of minor weight loss <5 wt.% at low temperatures (50–120 °C), caused by the moisture and lower mass impurity of the cardanol epoxy [37,44], elucidated the hydrophobicity of the cured epoxy due to the presence of Card-TH2 and CardT-TPA. The presence of Card-TH2 and CardT-TPA increased the initial degradation temperatures of the epoxy to be 350 and 380 °C, respectively. The weight loss rate of the epoxy modified with Card-TH2 in the degradation step was more than that modified with CardT-TPA, not only because of the longer aliphatic chain (C15 and C4) of cardanol but also because of the flexibility and lower crosslink density of the epoxy with the Card-TH2 dispersed phase [37]. The carbonization of the epoxy modified with Card-TH2 and CardT-TPA occurred at 550 and 650 °C, respectively. The remaining residues of the cured epoxy in the presence Card-TH2 and CardT-TPA at 800 °C were 15.64% and 35.12%, respectively. Therefore, the incorporation of CardT-TPA in the epoxy network further enhanced the thermal stability of the epoxy coatings due to the formation of dangling chains of CardT-TPA with the epoxy matrix. The higher thermal stability of the epoxy resin modified with CardT-TPA may have been caused by the more rigid aromatic backbone of the CardT-TPA polymer compared to that modified with Card-TH2.



Scheme 3. Adhesion of the cured epoxy/polyamine in the presence CardT-TPA.

3.4. Salt Spray resistance and mechanism of self-healing

The good mechanical and adhesion characteristics of the cured epoxy/polyamine hardener in the presence Card-TH2 and CardT-TPA (Table 3) confirmed their mechanical coating performance. Accordingly, it was necessary to investigate the anticorrosion performance of the coatings in aggressive salt conditions by using seawater in the salt spray cabinet. The photos of the cured epoxy in the absence and presence different weights percentages after exposure to different times interval ranged from 500 to 2000 h are summarized in Figure 9a–c. The salt spray resistance data of the steel panels coated with epoxy (blank) and modified epoxy coatings are summarized in Table 4. The salt spray resistance of the unmodified epoxy (Figure 9a and Table 4) showed a lower resistivity to salt and seawater humidity at 500 h with blisters, rusts formation, and adhesion failure that occurred after 600 h of exposure time. The adhesion failure was caused by the presence of micro-holes and cracks in the surface of the epoxy that occurred during the curing of the epoxy resin. The presence of Card-TH2 and CardT-TPA at a low weight content (0.1 wt.%) improved the salt spray resistances of the epoxy composites up to 750 h without adhesion failure, although micro-cracks did form (Figure 9b,c). The increasing of the Card-TH2 and CardT-TPA contents at 1 wt.% increased the salt spray resistance of the cured epoxy films from 750 to 1500 h without crack and adhesion failure, as shown in Figure 9b–c and Table 4. These data were correlated with the mechanical and adhesion data (Table 3; Scheme 3) to confirm that the higher salt spray resistance was caused by the strong adhesion of epoxy coatings modified with CardT-TPA. Moreover, it was found that the increasing of the Card-TH2 and CardT-TPA contents up to 3 wt.% increases the salt spray resistance of the epoxy coatings up to 1750 h, thus showing that the good compatibility of Card-TH2 and CardT-TPA contents with epoxy facilitated the interaction of the hydroxyl groups of the epoxy network and the chelation of the triazine hydrazide groups with steel during the curing of the epoxy [48]. The chelation of the triazine hydrazide group with the steel surfaces reduced the porosity of the epoxy films and prevented the diffusion of Cl^- ions into the epoxy of the steel surfaces, in addition to reducing the hydrophobicity and superhydrophobicity of the

epoxy composites. The salt spray resistance of the cured epoxy films in the presence CardT-TPA was increased more than that cured in the presence Card-TH2 due to the self-healing affinity of CardT-TPA in the salt environment.

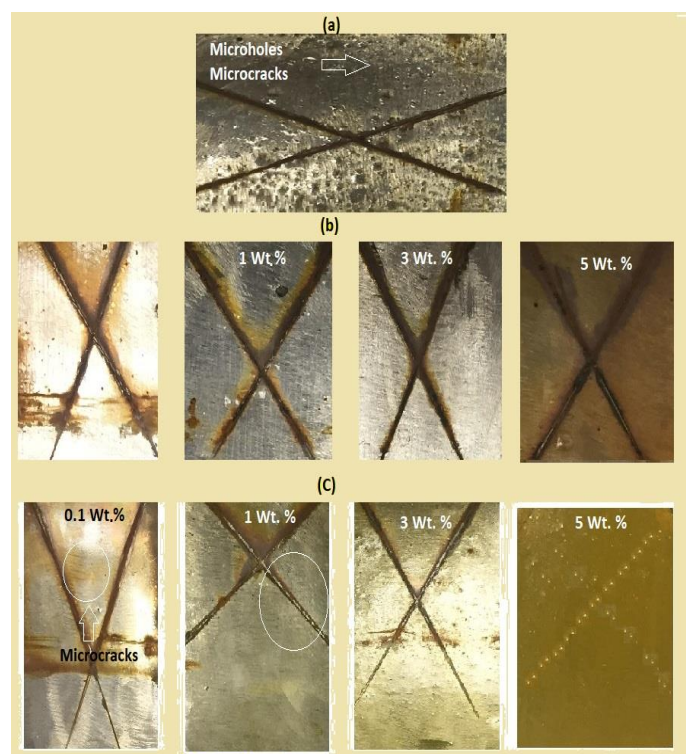


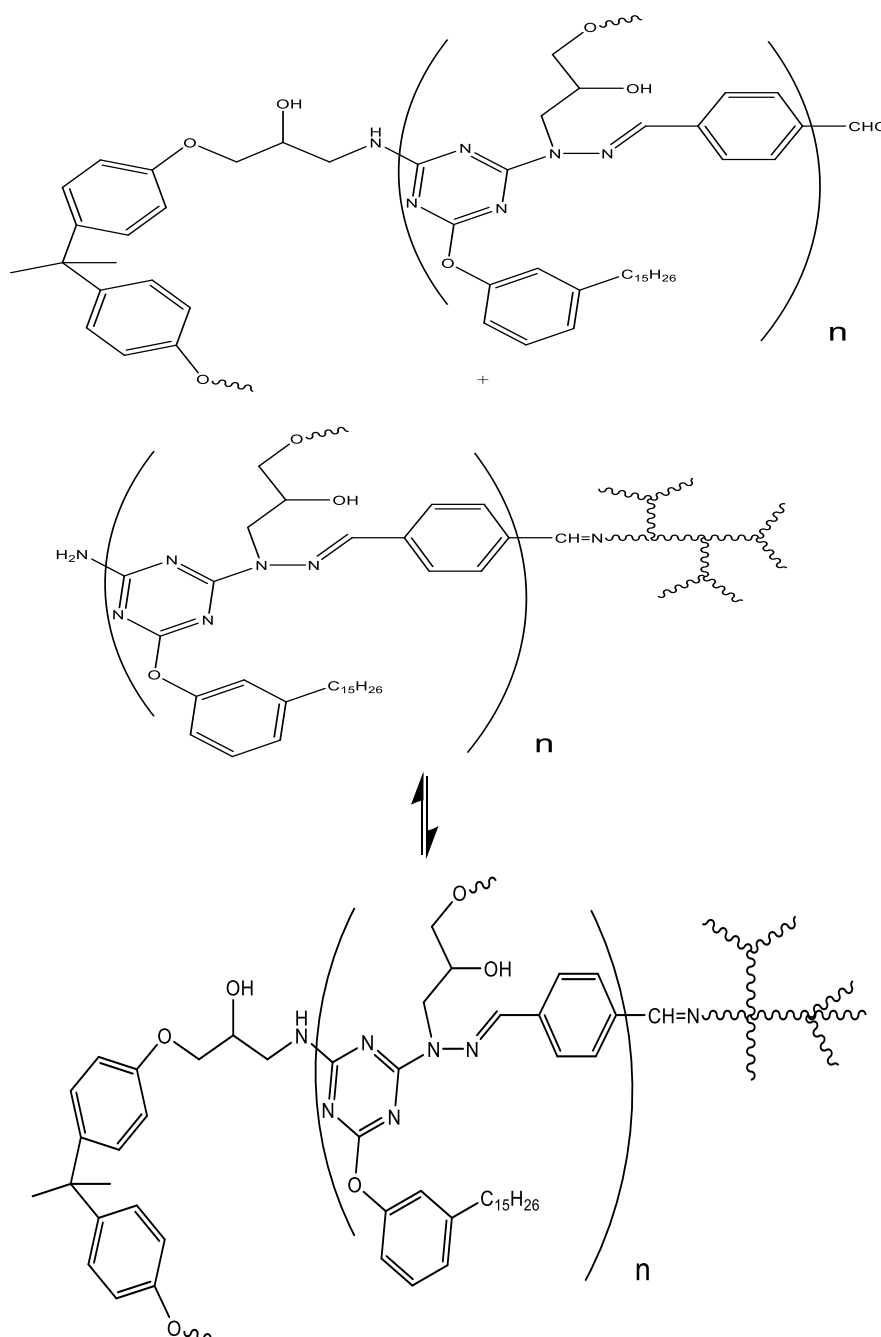
Figure 9. Salt spray resistance of the cured epoxy coatings at different exposure times: (a) epoxy blank after 500 h, (b) epoxy modified with Card-TH2 after 750 h, and (c) epoxy modified with CardT-TPA after period ranged from 1500 to 2000 hrs.

Table 4. Salt spray resistance of the epoxy resins modified with different weight percentages of Card-TH2 and CardT-TPA.

Epoxy Composites	Weight Contents (wt.%)	Exposure Time (hours)	Disbonded Area %	Rating Number (ASTM D1654)
Blank	0	500	20	5
	0.1	1000	5	7
	1.0	1500	1	9
	3.0	2000	0.01	10
	5.0	2000	0.0	10
Epoxy/Card-TH2	0.1	750	5	7
	1.0	1000	3	8
	3.0	1000	4	8
	5.0	1500	6	7

The effect of CardT-TPA in the self-healing of damaged surfaces was observed even at 1 wt.% with the formation of a white thin film at the X-cut, which acted as an anticorrosive bonding layer and blocked the holes and cracks to cause self-healing [49]. The cured epoxy network in the presence CardT-TPA (5 wt.%) showed self-healing characteristics, and the proposed mechanism of self-healing is illustrated in Scheme 4. The presence of an imine group in the chemical structure of the CardT-TPA, amine, and aldehyde end groups facilitated its exchange reaction that included hydrolysis, imine metathesis, and transamination. It was previously reported that the presence of a small amount of primary amine accelerated the imine metathesis [50]. Scheme 4 illustrates the formation of a highly

crosslinked epoxy network through the imine metathesis reactions of the cured CardT-TPA, either with epoxy resin or the polyamine hardener during the curing process. The FTIR spectrum of the cured epoxy network in the presence CardT-TPA (5 wt.%) at the self-healing zone (Figure 9c) showed the disappearance of the aldehyde group of CardT-TPA (the disappearance of C-H aldehyde bending at 2670 cm^{-1}) and the increasing of the concentration of the phenyl group content that appeared with new CH out-of-plane bending region from 650 to 950 cm^{-1} . These data confirmed the proposed metathesis mechanism (Scheme 4).



Scheme 4. Metathesis reaction of epoxy/polyamine CardT-TPA and epoxy/CardT-TPA.

The DSC thermograms of the cured epoxy network in the presence both the polyamine hardener and CardT-TPA in the first and second scans are shown in Figure 10a,b. The exothermic peak with the heat of cure 145.8 J.g^{-1} in the first scan, which was caused by the exothermic curing of the epoxy resin

with the hardener and CardT-TPA, disappeared in the second stage; a new peak appeared at 95 °C, and this was seen in the T_g of the complete curing of the crosslinked epoxy network. This change elucidated the metathesis reaction of the imine epoxy [51].

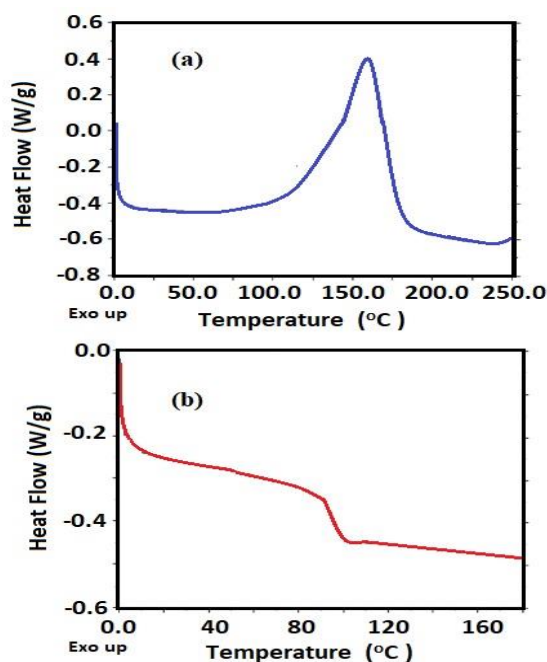


Figure 10. DSC thermograms of epoxy/polyamine in the presence CardT-TPA (10 wt.%): (a) first run and (b) second run under an N₂ atmosphere at a heating rate 10 °C minute^{−1}.

4. Conclusions

New bio-based derivatives were produced from cardanol after etherification with bishydrazino-s-triazine followed by condensation with TPA to produce a multifunctional polymer (CardT-TPA). The medium T_g value of CardT-TPA at 68.8 °C elucidated the flexibility of the Schiff base polymer due to presence of cardanol functional groups. The polymer showed a higher thermal stability when mixed during the curing of the epoxy/polyamine system. The excellent adhesion, mechanical properties, thermal characteristics, and superhydrophobicity of the epoxy films modified with CardT-TPA were caused by its chemical crosslinking and chelation with the epoxy matrix and steel surfaces, respectively. The higher salt spray resistance at more than 2000 h, self-healing, and self-cleaning of the epoxy/polyamine modified with CardT-TPA were confirmed by the metathesis reaction of the cured epoxy/polyamine CardT-TPA and epoxy/CardT-TPA to elucidate the multi-functionality of the prepared polymer.

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