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### **Composites Part B**



# Self-healing epoxy nanocomposite coatings based on dual-encapsulation of nano-carbon hollow spheres with film-forming resin and curing agent



composites

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#### ABSTRACT

The ability of an active protective organic coating to restore its protection functionality in case of a coating defect is of pivotal importance to ensure durable performance under demanding corrosive conditions. In this paper, a self-healing epoxy system is fabricated by separate encapsulation of epoxy and polyamine in carbon hollow spheres (CHSs) and the autonomous healing performance of the system applied on mild steel is investigated. CHSs were synthesized via a silica templating method using carbonization of polysaccharide shells formed on the surface of silica templates. Consequently, epoxy and polyamine were loaded in separate capsules by dispersion of CHSs into the dilute solutions of epoxy/acetone and polyamine/acetone respectively, under vacuum conditions. The synthesized CHSs were characterized before and after the silica removal using field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The CHSs loaded with the film forming agents were assessed using thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. Furthermore, the protective and self-healing properties of the coatings fabricated were studied using electrochemical impedance spectroscopy (EIS), scanning vibrating electrode technique (SVET) and salt spray testing. The results showed that scribe defects in epoxy coatings with 10 wt % epoxy and polyamine capsules were healed effectively upon efficient release and subsequent recombination of the epoxy and polyamine agents reforming a protective layer at the damaged region.

#### 1. Introduction

Organic coatings are used as an effective and cost-efficient method to protect metallic substrates against corrosion [1–3]. However, the long-term durability and reliability of the polymer coating systems may be at stake when a mechanical damage to the polymer coatings may lead to delamination and under-coating corrosion [1,4,5]. The recent developments in the fabrication of organic coating systems deal with active self-healing polymers and smart coatings attracting substantial attention to the autonomous protection of pores, crazes, scratches and cracks, which can be formed by UV radiation, thermal and mechanical stresses, etc. [1,6,7]. For various polymeric materials such as paints, plastics and coatings, there are different mechanisms of self-healing including the release of healing agents and reversible crosslinking technologies [8,9]. A wide variety of healing agents, such as reactive monomers and film

forming agents, can be loaded into porous structures, hollow fibers and micro/nano capsules [8,10–12]. These containers introduced in a polymer matrix are broken in the case of a mechanical damage. A consequent release of the healing agents from the broken containers via capillary forces in the formed defect can repair the damage [8].

Design and fabrication of self-healing systems containing the micro/ nano capsules to host the healing agents demand interdisciplinary skills and techniques to maximize the corrosion protection efficiency [4,13]. The facile synthesis of the micro/nano capsules and easy and compatible incorporation of them into the polymer matrixes compared to vascular micro/nano hollow nanostructures increases the potential application of the method [14]. Active and healing agents embedded into polymer matrixes have been introduced in a wide variety of polymeric and inorganic containers such as urea-formaldehyde (UF) [15], melamine formaldehyde (MF) [16], polyurethane [17], polyaniline capsules [6,

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Nominal elemental	composition of	of the mild	steel substrates.
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Element	Si	Mn	С	S	Р	Al	Fe
Wt. %	0.34	0.32	0.19	0.05	0.05	0.04	99.01

18], mesoporous CeO<sub>2</sub> [19], TiO<sub>2</sub> [20], SiO<sub>2</sub> nanoparticles [21], montmorillonite [22], halloysite [23–25], zeolite [26] and layered double hydroxide (LDH) nanostructures [3,27,28]. The healing agents are intensively used in liquid form due to the free flow through damaged structures and cracked regions [14]. Different chemicals such as organosilanes [29], natural and synthetic oils [30], o-dichlorobenzene [31], dicyclopentadiene (DCPD) [32] or epoxy resin were encapsulated as healing agents into the containers.

DCPD and epoxy are the most common agents healing damages via polymerization in the presence of appropriate hardeners or catalysts [7, 14]. Epoxy oligomers can be cured with a wide variety of curing agents such as polyamines, polyamides or anhydrides with different chemical structures at ambient conditions without an accelerator [14]. However, for a faster curing, the catalysts can also be encapsulated with the curing agents in a certain concentration to be leached out simultaneously with the epoxy oligomer to accelerate the healing process once a damage occurs. On the other hand, carbon structures are used widely as the container of the film forming agents [33,34]. Among the large family of carbon structures, CHSs possess a broad spectrum of attractive characteristics, namely excellent thermal and mechanical properties, high loading capacity, tunable size and shell structure, controllable shell thickness and porosity and multifunctionality in many fields of application such as nanoreactors, catalysts and drug delivery [35–37].

This work follows up our prior work on the application of CHSs as the host for encapsulation of corrosion inhibitors for corrosion protection of the mild steel surface [38,39]. In the prior publication [12], we doped epoxy and polyamine in separate carbon capsules to investigate the mechanical and long-term corrosion protection properties of the doped

CHSs containing epoxy coatings in the absence of coating defects. The barrier properties of epoxy coatings containing 10 wt % of doped CHSs was shown to remain almost constant for 50 days of immersion in the corrosive solution while the neat epoxy coating and the epoxy coating containing empty CHSs lost their corrosion protection performance during this immersion time. In the present work, CHSs are fabricated and employed as a novel container for encapsulation of epoxy and polyamine as the film-forming agent. The goal is to fabricate self-healing dual-capsule doped epoxy coating on the mild steel substrate able to recover the barrier properties at coating defects. The self-healing ability of the doped CHs containing epoxy coatings applied on mild steel samples was characterized using EIS, SVET, salt spray exposure and FE-SEM.

#### 2. Experimental

#### 2.1. Materials

Tetraethyl orthosilicate (TEOS,  $\geq$  98%), aqueous ammonia (28 wt %), 3-aminopropyltriethoxy silane (APTES,  $\geq$  99%) were purchased from Sigma-Aldrich and ethanol (~99.6%) from Arak Distillation Co. (Iran). Sucrose ( $\geq$ 98%) and sodium chloride ( $\geq$ 99.7%) were purchased from Chem-Lab. Hydrofluoric acid (HF, 40 wt %) and acetone ( $\geq$ 95%) were obtained from Mojallali Co. (Iran). Deionized water (DI) and dual distilled water were used for preparation of all solutions and washing the samples during the experimental steps, respectively. The mild steel substrates (ST12) were obtained from Foolad Mobarake Co. (Iran). The chemical composition of the mild steel substrates is presented in Table 1. Epoxy resin and polyamine were acquired from Kian Resin Co. (Iran). High purity and dehydrated argon gas (99.999%) was purchased from Arkan Gas Co. (Iran). All chemicals were used as received without any further purification.



Fig. 1. Schematic illustration of the synthesis procedure of CHSs.

Composition of the prepared epoxy coatings.

Type of coating	CHS (wt. %)	Ep-DCS (wt. %)	Am-DCS (wt. %)
EP	0	0	0
EP-CHS-2	2	0	0
EP-DCS-2	0	2	1
EP-DCS-5	0	5	2.5
EP-DCS-10	0	10	5

#### 2.2. Synthesis of CHSs

The synthesis of CHSs was performed based on the hard templating approach as discussed in detail in our previous work [38] and illustrated schematically in Fig. 1. First, the monodisperse silica spheres were synthesized by the Stober method to be used as a template [40]. Then, the silica templates underwent a surface modification process using APTES to enhance the adsorption of saccharide molecules on the template surfaces. The modified surfaces were immediately transferred to a Teflon-sealed autoclave containing  $0.5 \text{ mol } l^{-1}$  aqueous sucrose solution to synthesize the silica core/polysaccharide shell structure via the hydrothermal process. The precipitated particles were filtered using a filter paper, washed several times with a mixture of double distilled water and ethanol (1:1 v/v) and fully dried in a vacuum oven for 24 h at 50  $^{\circ}$ C. Subsequently, the silica core/polysaccharide shell structures were calcinated under static conditions in a tubular furnace at 900  $\pm$  10 °C for 3 h under a flowing argon atmosphere. Finally, the silica templates were leached out by exposing the silica core/carbon shell structures in a 10% HF aqueous solution for 24 h. Afterward, the CHSs were filtered and washed with double distilled water and ethanol (1:2 v/v) several times and fully dried in a vacuum oven for 24 h at 50 °C. The same procedure was repeated for surface modification of the synthesized CHSs before loading of the film forming agents to improve the compatibility and dispersibility of the loaded CHSs in the epoxy matrix.

#### 2.3. Encapsulation of film-forming agents

To load epoxy and polyamine film forming agents into the

synthesized CHSs, 2 g of the dried CHSs was added into a 100 ml dilute solution of epoxy resin in acetone (1:3 epoxy:acetone) under stirring (110 rpm) at room temperature. After 24 h of stirring, the suspension was transferred to a 100 ml stainless steel vacuum jar evacuating using an HV vacuum pump (Busch, RH 0030 B, Germany) with an ultimate partial pressure of  $6.7 \times 10^{-4}$  hPa. The slight fizzing of the suspension during the vacuum process indicated that the trapped air through the cores and pores of CHS was removed and replaced with the epoxy solution. The suspension was kept under vacuum for 10 min and followed by a gradual ramp up to the ambient pressure. The process was repeated for 10 times to maximize the loading. Finally, the epoxy loaded CHSs were separated using centrifugation (5000 rpm, 5 min) and washed with a mixture of ethanol and acetone (3:1 v/v) for three times. The same procedure was repeated for the loading of polyamine into the CHSs, whereas the ratio of 1:2 v/v polyamine/acetone solution was used due to the lower viscosity of polyamine hardener as compared to that of epoxy resin. In this work, epoxy- and polyamine-loaded CHSs are denoted as Ep-DCS and Am-DCS, respectively.

#### 2.4. Preparation of self-healing epoxy coatings

The self-healing epoxy coatings were prepared by direct mixing of Ep-DCS in epoxy resin at concentrations of  $\sim 2$ ,  $\sim 5$  and  $\sim 10$  wt %. To ensure the complete reaction between the released epoxy and polyamine from Ep-DCS and Am-DCS in the stoichiometric ratio (2:1 w/w), Am-DCS was added to the polyamine hardener at concentrations of  $\sim 1$ ,  $\sim 2.5$  and  $\sim 5$  wt %, respectively. It is worth mentioning that the ratio of Am-DCS dispersed in the polyamine hardener added to the epoxy resin containing Ep-DCSs was moderately increased to enhance the stoichiometric pairing between epoxy and polyamine capsules. The prepared epoxy coatings containing no CHSs, 2 wt % unloaded CHS and 2, 5 and 10 wt % Ep-DCS were denoted according to Table 2.

Prior to the coating application, ST12 mild steel substrates  $(8 \text{ cm} \times 10 \text{ cm} \times 0.1 \text{ cm})$  were washed with a mixture of dishwashing liquid and doubled distilled water. Subsequently, they were washed with doubled distilled water for complete removal of the detergent, ground by sandpaper grade numbers 400, 600, 1000 and 1200, and



Fig. 2. Schematic illustration of epoxy and polyamine loaded CHSs (a) and self-healing behavior of the epoxy coating containing the loaded CHSs and curing reactions between epoxy and polyamine agents (b).



Fig. 3. FE-SEM images of the synthesized silica templates (a) and CHS (b).

delamination percentages of coatings were calculated by Eq. (1).

Delamination percentage (%) = 
$$\frac{A_d}{A_t} \times 100 \%$$
 (1)

degreased in acetone using a bath ultrasonication for 5 min. Next, the prepared epoxy coatings without and with capsules were mixed with polyamine hardener at a 2:1 wt ratio of epoxy resin to polyamine hardener. The mixture was then applied immediately on the cleaned mild steel samples by a film applicator (Elcometer 3520 Baker) with a wet film thickness of  $60 \pm 2 \,\mu$ m. The coated mild steel samples were placed in the clean room at  $24 \pm 1$  °C and  $30 \pm 2$  RH for 3 h followed by exposure to a vacuum oven at 100 °C for 1 h to ensure complete curing. The dry film thickness of the coatings was  $50 \pm 3 \,\mu$ m measured using a coating thickness gauge, model Elcometer 456. Fig. 2 schematically shows the self-healing steps of coatings in the presence of Ep-DCS and Am-DCS capsules upon a damage. It can be seen that the capsules broken release their contents leading to the healing of the scratched area.

#### 2.5. Characterization techniques

FE-SEM (Mira III-XMU, TESCAN, Czech Republic) was employed to study the morphology and particle size of the synthesized silica templates and CHSs. For the FE-SEM analysis, a drop of ethanol containing dispersed nanoparticles was placed on the surface of an aluminum foil  $(1 \text{ cm} \times 1 \text{ cm})$ . FE-SEM was also used to study the morphology of the scratched region after the healing as well. The morphological evaluations of the silica core/carbon shell structures before and after HF acid treatment were performed using TEM (EM 900, ZEISS, Germany). During the sample preparation for TEM analysis, the CHSs after silica core removal were dispersed in ethanol using a probe sonicator (Adeeco APU500c, Iran) to break possible agglomerates and to obtain a uniform suspension. The loading of epoxy and polyamine into the CHSs was assessed using thermogravimetric analysis (TGA, LINSEIS analyzer (L-801I, Germany) within the temperature range of 25-600 °C and a heating rate of 10 °C min<sup>-1</sup> under argon atmosphere. FTIR was used to investigate the composition of the synthesized CHSs before and after the epoxy and polyamine loading within the wavenumber range of 400–4000  $\text{cm}^{-1}$  using the KBr pellet. The glass transition temperatures  $(T_q)$  of the epoxy coatings without and with the doped CHSs were determined by a differential scanning calorimeter (DSC, Q100, TA, USA) with a thermal ramp from 25 to 80  $^\circ$ C at a heating rate of 10  $^\circ$ C min<sup>-1</sup> under pure nitrogen atmosphere.

Corrosion protection of the epoxy coatings was studied by salt spray testing according to ASTM B117, in which the concentration of NaCl solution, temperature and pH were 5 wt %,  $36 \pm 1$  °C and ~6.5, respectively. In order to perform salt spray tests, the coated mild steel samples were X-scribed using a cutter knife  $(10 \pm 2 \text{ mm} \times 50 \pm 5 \mu\text{m})$  and after preconditioning for 6 h at ambient condition  $(24 \pm 1$  °C and  $30 \pm 2$  RH), they were exposed in the salt spray test for 240 h. The

in which,  $A_d$  and  $A_t$  are the delaminated area and the total area of the coating, respectively. In order to measure the delamination percentage, the delaminated area was cut using a sharp blade and the total area of the delaminated coatings was calculated using ImageJ software.

An electrochemical workstation (CorrTest, CS350, China) was used for EIS measurements for the coated samples with an artificial scratch applied by a cutter knife ( $10 \pm 1 \text{ mm} \times 50 \pm 5 \mu \text{m}$ ) in a three-electrode cell including saturated calomel electrode (SCE, 3 M KCl, reference electrode), platinum plate (counter electrode) and mild steel coated samples (working electrode). EIS measurements were conducted at open circuit potential (OCP) with a  $\pm 10 \text{ mV}$  perturbation and a frequency range of 10 kHz to 10 mHz after 24 h immersion in 3.5 wt % NaCl solution (pH =  $\sim$ 6.5). Before immersion of the coated mild steel samples in the corrosive solution for EIS measurements, all samples were scratched and then preconditioned at  $24 \pm 1$  °C and  $30 \pm 2$  RH for 1, 3 and 6 h to ensure the complete reactions of epoxy and polyamine released from the carbon capsules. In this case, the working electrode exposed to the electrolyte was the coating with the defect area. The total surface area of the exposed region was of  $4 \text{ cm}^2$  and the effective electrode (i.e. the coating defect) area was 0.5 mm<sup>2</sup>.

SVET technique (Applicable-Electronics, USA) was employed to evaluate the initial steps of the corrosion and self-healing processes of the epoxy coatings at the artificial defects in 0.3 wt % NaCl solution. Before the measurements, artificial defects with dimensions of 1 mm  $\times$  25  $\mu m$  were formed on the coatings using a scalpel. The preconditioning time for the scratched coatings before immersion in the corrosive solution for SVET measurements was 6 h at 24  $\pm$  1 °C.

The measurements were performed on areas with dimensions of 1 mm  $\times$  3 mm (11  $\times$  11 points for each map) every 1 h during 24 h while the mean acquisition time per scan was 15 min. The vibrating tip was a thin platinum needle, with an electrodeposited black platinum sphere on the tip (approximately 20  $\mu m$  in diameter). Calibration of the tip was performed before the experiments for the 0.3 wt % NaCl solution. All measurements were carried out with the SVET tip located at 100  $\mu m$  above the sample surface. The SVET data was analyzed using Quikgrid software.

For the salt spray test, the edges and back of the samples were sealed with a hot melt beeswax-colophony mixture. For EIS measurements and SVET measurements, the exposed areas were square with dimensions of 2.5 cm  $\times$  2.5 cm and 3 mm  $\times$  3 mm, respectively. Triplicates were prepared for each EIS, SVET and salt spray measurements.



Fig. 4. TEM images of the carbon spheres before (a) and after (b) the silica core removal using 10% HF acid solution.

#### 3. Results and discussion

#### 3.1. Characterization of synthesized CHSs

By FE-SEM, surface morphology and diameter of the prepared silica templates and CHSs were evaluated. Fig. 3 shows FE-SEM images of the pristine silica templates and CHSs. Fig. 3a shows that the synthesized silica templates are monodisperse in the spherical form with relatively smooth surfaces and an average diameter of  $\sim 210 \pm 40$  nm. Fig. 3b shows smooth spherical shapes of the CHSs synthesized with an average diameter of  $200 \pm 35$  nm. A comparison of Fig. 3a-b shows that the diameter of CHSs is smaller than those of silica templates due to the hard core removal [41,42]. The shell dimensions remain relatively constant after the core removal due to the formation of the graphene-based carbon structure with relatively high mechanical strength [12,38]. Thus, the morphology of the carbon capsules is hardly subjected to any change after the template removal. In addition, the small particles shown in the background of Fig. 3b, are related to the surface morphology and heterogeneities of the aluminum foil. CHSs, like other types of nanoparticles, have a tendency to form agglomerates. As shown in Fig. 3b, the number of particles in the aggregates is typically less than five. This might be due to the elimination of aggregates during the carbonization and silica extraction processes. These claims are also shown in our previous publication [12]. As reported, dispersion and distribution of doped CHSs in the epoxy matrix are uniform due to the low content of agglomerations in the synthesized CHSs and the amino-functionalization of carbon shells making them more compatible with the epoxy chains.

The structures of CHSs before and after the template removal are further investigated by TEM as presented in Fig. 4. It can be seen that the morphology of the carbon capsules alters entirely by the acid treatment. In fact, after calcination of polysaccharide shells, considerable pores and voids are created in the carbon shell presumably due to thermal degradation and release of oxygen-containing groups [38,43]. The formed pores and voids are expected to offer easy access for the HF aqueous solution to penetrate through and extract the silica templates. Although both TEM images show a spherical morphology for CHSs before and after acid treatment, Fig. 4b demonstrates a textural structure for CHSs after the acid treatment. Therefore, the porous shell and core structures of CHSs after the template removal provide an excellent free volume to encapsulate the film forming materials. Some of CHSs were broken during the sonication process due to the resulting mechanical stresses. As reported in the literature [44], the healing efficiency of the coatings decreases upon mechanical failure of the capsules' shells. For



Fig. 5. FTIR spectra of the neat epoxy and polyamine, CHS and epoxy and polyamine encapsulated CHSs.

FTIR characteristic absorption peaks of CHS and epoxy (Ep-DCS) and polyamine (Am-DCS) encapsulated CHS.

Sampl	e	CHS	Epoxy	Ep-DCS	Polyamine	Am-DCS	Ref.
NO.	Functionality	Wavenumber (cm <sup>-1</sup> )	Wavenumber ( $cm^{-1}$ )	Wavenumber ( $cm^{-1}$ )	Wavenumber ( $cm^{-1}$ )	Wavenumber (cm <sup>-1</sup> )	
1	O–H stretching	3481	3479	3485	3460	3475	[46,47]
2	O–H bending	1376	1363	1388	1371	1384	[45,48]
3	C-H stretching of oxirane rings	-	3074	3078	-	-	[49]
4	C–H bending of oxirane rings	-	764, 1080	772, 1086	-	-	[49]
5	C–H asymmetric stretching	2967	2976	2974	2963	2961	[49]
6	Si-O-Si asymmetric vibration	1035	-	1036	-	1040	[45,50]
7	Si–O–C asymmetric vibration	1148	-	1143	-	-	[45,48]
8	-NH <sub>2</sub> and N–H stretching	3266	-	-	3318	3312	[45,51]
9	-NH <sub>2</sub> and N–H bending	757, 1569	-	-	747, 1608	745, 1596	[45,51]
10	C–N stretching	1465	-	-	1477	1460	[45,51]
11	C=C stretching of aromatic rings	-	1614	1615	-	-	[45,49]
12	C=O stretching of carboxyl groups	1655	-	-	-	1672	[45]
13	C–C stretching of aromatic rings	1553	1516	1515	1733	1735	[45,49]
14	C–O–C stretching of oxirane groups	-	842	839	-	-	[45,49]
15	C–O stretching of oxirane groups	-	920	924	-	-	[49]



Fig. 6. TGA (a) and DTG (b) thermograms of the pure epoxy and polyamine, CHS and epoxy and polyamine encapsulated CHSs.

the preparation of coating samples, instead of sonication which results in relatively high mechanical stresses on the carbon shells, a controllable mechanical mixer was used to limit the applied stresses on the carbon shells and to avoid mechanical fracturing of the carbon shells during the mixing process.

#### 3.2. Characterization of epoxy and polyamine loaded CHSs

Encapsulation of epoxy and polyamine in CHSs was assessed using FTIR. FTIR spectra of the neat epoxy and polyamine, and CHSs before and after loading of epoxy and polyamine are presented in Fig. 5 and the main FTIR absorption bands are tabulated in Table 3. The wide peak at 3400 - 3500 cm<sup>-1</sup> is attributed to the stretching vibration of O–H bond of the physically adsorbed water onto the capsule surfaces, oxidized carbon shells and unreacted silanol groups of APTES used as the surface modifier. The peaks at ~1035 cm<sup>-1</sup> of the CHS are assigned to the asymmetric bending vibration of the Si–O–Si network indicating a successful grafting of APTES onto the CHS surfaces. The peak at ~1663 cm<sup>-1</sup> is related to C=O bond originating from the presence of carboxyl groups on the surface of CHSs [45]. Moreover, the peaks at ~3266 cm<sup>-1</sup>, ~1465 cm<sup>-1</sup>, and (~757 and ~1486 cm<sup>-1</sup>) are assigned to -NH<sub>2</sub>, C–N, and N–H respectively, indicating successful silanization of CHSs.

As illustrated in Fig. 5, FTIR spectra of the neat epoxy and Ep-DCS are analogous and the main characteristic peaks of epoxy chains are clearly visible with some negligible shifting for Ep-DCS originating from the presence of carbon capsules. The peaks of C=C ( $\sim$ 1615 cm<sup>-1</sup>), C-C ( $\sim$ 1515 cm<sup>-1</sup>), C-O-C ( $\sim$ 839 cm<sup>-1</sup>) and C-O ( $\sim$ 924 cm<sup>-1</sup>) observed for

the neat epoxy and Ep-DCS indicate the presence of epoxy resin in CHSs implying successful incorporation of the epoxy resin in the capsules. In addition, some characteristic peaks of CHSs in the Ep-DCS spectrum such as N–H (726 cm<sup>-1</sup>), Si–O–Si (1043 cm<sup>-1</sup>) and Si–O–C (1143 cm<sup>-1</sup>) overlap with those of epoxy chains.

The main peaks at 3312, 745, 1596 and 1460 cm<sup>-1</sup> can be assigned to  $-NH_2$ , N–H, and C–N bonds of the olyamine chains, respectively. The same peaks appeared in the spectrum of Am-DCS originating from polyamine, thereby confirming encapsulation of polyamine in CHSs. As seen in the spectrum of Am-DCS, some characteristic peaks of CHSs overlap with those of epoxy chains. The peak at 1671 cm<sup>-1</sup> in the spectrum of Am-DCS is assigned to the carboxyl groups of carbon shells. Therefore, it can be inferred that APTES is successfully grafted onto the CHS surfaces and epoxy and polyamine are loaded into CHSs.

The thermal properties and weight fraction of the dopants in Ep-DCS and Am-DCS were investigated by TGA analyses. TGA and derivative TG (DTG) of the pure epoxy and polyamine, CHS, Ep-DCS, and Am-DCS are presented in Fig. 6. Three considerable weight loss steps are observed for CHS at 25–180 °C (~10%), 180–250 °C (~30%) and 250–600 °C (~8%) temperature regions related to evaporation of the physically adsorbed water, thermal decomposition of organic segments of APTES grafted onto the CHS surfaces and changes of the shells carbon scaffold structures, respectively.

TGA and DTG thermograms of the pure epoxy and polyamine indicate that the main weight loss of epoxy and polyamine occurs at 200–340 °C (~84%) and 100–220 °C (~69%) temperature ranges. During the polymerization of epoxy and polyamine, some solvent molecules, unreacted monomers, and the small epoxy and polyamine chains



Fig. 7. DSC curves of cured neat and CHSs doped epoxy coatings.

 $T_{\rm g}$  values obtained from DSC curves of cured neat and CHSs doped epoxy coatings.

Coating	EP	EP-CHS-2	EP-DCS-2	EP-DCS-5	EP-DCS-10
$T_{g}$ (°C)	$46\pm1$	$44\pm1$	$42\pm1$	$36\pm2$	$39\pm2$

with low molecular weights also remain in the form of dimer, trimer, and so on in the produced products. Thus, the main drop-offs in TGA curves at the mentioned temperature ranges are related to the evaporation of such small molecules as reported also in the literature [7]. The subsequent stages of weight loss of the pure epoxy and polyamine occurred at the temperature range of 300-380 °C is  $\sim$ 7.5% and  $\sim$ 16%, attributed to the thermal fracture of epoxy and polyamine chains and decomposition of the carbon scaffold of their chains [52,53].

Moreover, the overall weight loss behaviors of Ep-DCS and Am-DCS are the same as the pure epoxy and polyamine due to the high thermal stability of the carbon shell compared to that of the epoxy and polyamine agents. The lower initial weight loss temperatures of Ep-DCS and Am-DCS compared to the pure epoxy and polyamine is due to evaporation of the trapped solvent molecules from the doped carbon capsules and the higher specific surface area of the carbon capsules, which accelerates the evaporation rate and thermal decomposition of the loaded materials [54]. As shown in the TGA thermogram of Am-DCS, a continuous weight loss of about 67% at around 190 °C is observed which is due to the evaporation of solvent molecules at the initial temperature to about 100 °C and unreacted monomers and small volatile chains of amines at the temperature range of 100–190 °C, respectively. The

second main weight loss stage of approximately an extra 21% for Am-DCS related to the thermal decomposition of polyamine chains and remaining carbon scaffolds was observed at 220–360 °C. Furthermore, the lower values of the remaining weight of Ep-DCS and Am-DCS as compared to CHS indicates that the content of epoxy and polyamine loaded in CHSs are ~39 and ~44%, respectively based on the weight of Ep-DCS and Am-DCS capsules.

As we reported in our earlier work [38], the mean pore size of the carbon shells is about 3.4 nm. Thus, the agents with lower molecular sizes pass through these pores and reach the interior space of CHSs. The higher extent of loading for Am-DCS in comparison with Ep-DCS can be attributed to the lower molecular weight ( $\geq$ 1170 and  $\leq$ 250 g mol<sup>-1</sup> for epoxy and polyamine, respectively) and the shorter chains of polyamine compared to epoxy resin facilitating the diffusion of polyamine into the carbon shells.

#### 3.3. Thermal analysis of the epoxy coatings

Fig. 7 shows the DSC curves of the cured epoxy coatings. The inflection points ( $T_g$ ) of the DSC curves listed in Table 4 indicate a transition from glassy to a rubbery state. It can be seen that  $T_g$  is between 35 and 55 °C for all coatings, while EP coating has the highest  $T_g$  value. In fact, incorporation of CHSs in the epoxy matrix leads to a reduction of  $T_g$  due to a decrease of the chemical reactions between epoxy and polyamine due to the formed steric hindrance between the epoxy and polyamine groups in presence of CHSs.

An interaction between the solid particles and polymer chains develops a restricted segmental region around the solid particles based on Eisenberg's model [55] resulting in an increase of  $T_g$ . Therefore, the CHSs loading restricts the segmental motion of the epoxy chain around CHSs explaining the higher  $T_g$  value of EP-DCS-10 compared to that of EP-DCS-5. The decrease of  $T_g$  and the crosslinking process lead to a reduction of the adhesion strength between the coatings and mild steel substrates, which in turn changes in the failure mechanism of the coating. In fact,  $T_g$  and crosslinking density of the coating govern the failure morphology upon the stress applied [47,56].

#### 3.4. Evaluation of self-healing performance of epoxy coatings

The effects of incorporation of 2, 5 and 10 wt % of doped CHSs on self-healing and corrosion protection properties of the epoxy coatings are studied using salt spray, EIS and SVET tests. The macroscopic self-healing performance of the epoxy coatings without and with Ep-DCS and Am-DCS applied on the mild steel substrates was studied by salt



Fig. 8. The appearance of the coated mild steel samples after 240 h exposure to salt spray.

The delamination percentages of the self-healing epoxy coatings after 240 h exposure to salt spray. Mean values are calculated from triplicate samples with standard deviations  $(\pm)$ .

spray testing. The appearance of the coatings after 240 h exposure is depicted in Fig. 8. The delamination percentages of the epoxy coatings from the mild steel substrates, calculated by Eq. (1) after 240 h exposure to the 5 wt % of NaCl salt spray, are tabulated in Table 5. It can be seen that EP and EP–CHS–2 samples have the largest rust and delamination areas as compared to the other coated samples containing doped CHSs indicating their limited coating protection performance. Also, the accumulation of corrosion products is obvious at the scribes and under the coating around the scribes. This suggests that the electrolyte



Fig. 9. Nyquist ((a), (c) and (e)) and Bode ((b), (d) and (f)) plots of the coated samples with artificial defects preconditioned for different times after 24 h immersion in 3.5 wt % NaCl solution.



**Fig. 10.**  $|Z|_{0.01 \text{ Hz}}$  impedance modulus values of the scratched epoxy coatings at different preconditioning times.

containing chloride ions reaches the metal-coating interface at the scribes. Cathodic activity under the coating leads to a local increase of pH and subsequent cathodic delamination due to weakening of the bonds between the coating and metal substrate [57,58]. In fact, the epoxy coating containing empty CHSs provides empty sites for storage of the electrolyte passing through the coating and expanding active cathodic regions. On the other hand, the addition of Ep-DCS and Am-DCS into the epoxy coatings enhances the self-healing properties and corrosion protection of the coatings. The lower amount of corrosion products and delamination of EP-DCS-2 coating is attributed to the self-healing properties of this sample towards scratches and physical barrier properties of doped CHSs dispersed in the epoxy matrix decreasing the diffusion of corrosive electrolyte through the intact area of the coating. The dual-capsule epoxy coatings reveal the best corrosion protective and healing ability, where no blister, corrosion spots, rust or considerable delamination is detected after 240 h exposure to the salt spray. The healing properties of epoxy coatings containing Ep-DCSs and Am-DCSs are correlated to the chemical reactions of the released epoxy and polyamine groups in the scratched regions restricting the accessibility of aggressive species to the metal-coating interface.

EIS analysis was used to evaluate the self-healing and corrosion protective abilities of the coatings with an artificial defect at different preconditioning times. Fig. 9 displays Nyquist and Bode plots of the coated mild steel samples, preconditioned for 1, 3 and 6 h after scratching, immersed for 24 h in the 3.5 wt % NaCl solution. It can be seen that EP and EP-CHS-2 scratched samples show the lowest impedance modulus values at low frequencies. Additionally, these values and the diameter of semicircles in Nyquist plots are almost constant as the preconditioning time elapses. In the case of the coatings containing doped CHSs, the impedance values at low frequencies showed an ascending trend and reached a maximum impedance value for the 10 wt % doped CHSs sample after 6 h preconditioning time. The epoxy coating and composite coatings with no encapsulated film forming agents do not exhibit any active corrosion protection resulting in unhindered corrosion in the coating defects. The ascending trend of the semi-circle diameter for the epoxy coatings containing various contents of Ep-DCS and Am-DCS implies that the release of the film forming agents, due to the fracture of the carbon capsules at the scratched regions, leads to the formation of a protective barrier layer.

The impedance modulus at the frequency of 0.01 Hz ( $|Z|_{0.01 \text{ Hz}}$ ) can be related to the charge transfer reactions (polarization resistance) at the metal-electrolyte interface [59]. These values for the scratched epoxy coatings immersed for 24 h in the 3.5 wt % NaCl solution after various preconditioning periods are summarized in Fig. 10. It can be seen that |  $Z|_{0.01 \text{ Hz}}$  values for EP and EP-DCS-2 are as low as  $9 \pm 1 \text{ k}\Omega \text{ cm}^2$  at different preconditioning times due to the lack of the capsules and healing agent in CHSs, while an increase of the Ep-DCS and Am-DCS contents in the epoxy results in higher  $|Z|_{0.01 \text{ Hz}}$  values in Bode plots. This is due to the release of more healing agents to the scratched regions and the formation of a more uniform and compact barrier layer. Moreover, the artificial defects show increased healing as a function of preconditioning time due to the release of more film-forming agents and completion of the chemical reactions in the scratch and show the highest  $|Z|_{0.01 \text{ Hz}}$  value, 91 k $\Omega$  cm<sup>2</sup>, for EP-DCS-10 after 6 h preconditioning time. Therefore, it can be inferred that the epoxy coatings with the doped CHSs demonstrate self-healing behaviors, while the protection efficiency is improved with preconditioning time due to release and prolonged curing of the released healing agents at the scratch prior to exposure to the corrosive environment.

The self-healing characterization and localized corrosion activity of the prepared coatings at the artificial defects were investigated using SVET mapping of the local cathodic and anodic current densities. The current density maps of the prepared coatings with artificial defects after 2, 12 and 24 h exposure to 0.3 wt % NaCl solution the corrosive solution and the corresponding optical images of the scanned area after 24 h exposure are shown in Fig. 11 and Fig. 12, respectively. Figs. 11 and 12 indicates that EP coating shows the typical corrosion behavior at the scratch. Both cathodic and anodic regions are observed in the scratched area of the EP coated sample after 2 h immersion with an expanding and increasing intensity with immersion time. For EP coating, no improved corrosion resistance is observed at the defect due to the absence of any healing agent. Therefore, the scratch remains unprotected during the measurements.

The current density map of EP-CHS-2 coating shows the cathodic activity at the scratch increasing significantly with immersion time. The absence of anodic activities in this SVET map can be due to the occurrence of anodic reactions at the buried metal-coating interface which are masked for the SVET probe. This observation was supported by the salt spray test where EP-CHS-2 coating showed a higher delamination percentage. For the EP-CHS-2 coating, incorporation of the empty carbon capsules results in many reservoirs for the corrosive electrolyte leading to significant water preservation in the coating and delamination. Thus, the formation of OH<sup>-</sup> ions due to oxygen reduction underneath the coating results in an increase in the local pH at the metalcoating interface [57,58]. The current density map of EP-DCS-2 coating shows no corrosion activity after 12h immersion indicating the release and reaction of epoxy and polyamine agents from Ep-DCS and Am-DCS at the scratch region, partially healing the scratch. While after 24 h of immersion, corrosion activity can be seen which is related to the diffusion of the corrosive electrolyte through the formed thin protective layer in the scratch. The relatively low current density obtained for the epoxy coating with 2 wt % epoxy doped CHSs as compared to the EP and EP-CHS-2 coatings indicates the consequent partial healing of the defect.

The current density maps and optical images of EP-DCS-5 and EP-DCS-10 coatings depict no corrosion activities at the scratch during the experiment. All the currents below  $5 \,\mu\text{A} \, \text{cm}^{-2}$  can be considered at the background noise/current level (Fig. 11). It proves that incorporation of a larger amount of Ep-DCS and Am-DCS in the epoxy matrix improves the self-healing and corrosion protection performance of the epoxy coating. It can be inferred that the release of epoxy and polyamine from the CHSs forms a cured epoxy/polyamine layer after 6 h of preconditioning at the scratched region blocking the penetration of the corrosive electrolyte. SVET observations are in good agreement with the salt spray and EIS measurements. It is worth mentioning that the black color of the optical image of EP-DCS-10 stems from the high concentration of black CHSs in the epoxy matrix.

The morphology of the scratched regions after healing was evaluated using FE-SEM. The micrographs of the containing Ep-DCS and Am-DCS epoxy coated samples preconditioned for 6 h are shown in Fig. 13. The clean scratches on EP and EP–CHS–2 coatings showed no healing effect. That is why the most extensive amount of corrosion products at the scratches was observed after salt spray testing for these coatings due to the lack of active protection. It can be seen from Fig. 13 that the scratch



Fig. 11. Current density maps of the coatings after 6 h preconditioning time at the artificial defects after 2, 12 and 24 h of exposure to 0.3 wt% NaCl solution. Scale unit:  $\mu$ A cm<sup>-2</sup>. Scanned area:  $\sim$ 1 mm  $\times \sim$ 3 mm.

morphology of the epoxy matrix is altered in the presence of doped CHSs. One reason can be attributed to the release and reaction of encapsulated film forming agents from the broken carbon capsules in the scratches increasing the roughness and covering the scratches effectively. As shown in Fig. 13, the applied scratch on EP-DCS-10 coating was fully healed. The dual-capsule containing coatings showed considerable self-healing and corrosion protective abilities which are in good

agreement with the obtained results from salt spray, EIS and SVET analyses.

As shown in Fig. 2, after the release of epoxy and polyamine agents from the broken carbon capsules, amino hydrogens (NH) react with the epoxide groups of the epoxy chains resulting in the reaction of NHs and oxygen of epoxides groups via nucleophilic substitution ring-opening reactions of the oxirane rings [60]. A new protective layer is formed



Fig. 12. The optical images of the defect area of different coatings after 24 h exposure to 0.3 wt % NaCl solution.



Fig. 13. FE-SEM images of the scratched epoxy coatings 6 h after preconditioning for 6 h.

due to the reaction between the released epoxy and polyamine. Crosslinking density and physicochemical characterization of the curing epoxy/polyamine mixture increases with the reaction time [60]. Therefore, the coatings with the longer preconditioning times showed enhanced self-healing and protective performance. The doped carbon capsules could also contribute in the barriers properties of the epoxy coatings and consequently their overall corrosion protection.

#### 4. Conclusions

This work presents the self-healing and protective properties of epoxy coatings with CHSs encapsulated with epoxy and polyamine as film-forming agents. CHSs were synthesized via silica templating method using polymerization and carbonization of polysaccharide shells. CHSs are synthesized successfully in a spherical form with an average particle size of  $\sim$  240 nm. After characterization of the synthesized CHSs, the film forming agents were loaded successfully to CHSs and incorporated into an epoxy coating matrix. The film-forming agents were loaded in CHSs by exposing to epoxy and polyamine/acetone solutions under the vacuum condition. The loading content of epoxy and polyamine for epoxy and polyamine doped carbon capsules were determined to be  $\sim$ 39 and  $\sim$ 44%, respectively. Self-healing and enhanced corrosion protection properties were detected for epoxy and polyamine doped carbon capsules incorporated in epoxy coatings due to the reactions between the released epoxy and polyamine agents in the scratched regions. Enhanced healing was detected during salt spray, EIS and SVET analyses, with increased amounts of epoxy and polyamine doped carbon capsule content and preconditioning time.

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