

Atmospheric Corrosion Resistance of Epoxy Duplex Coated Electrogalvanized Steel Exposed in Marine, Industrial and Urban Sites at Pakistan

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Summary: An epoxy based duplex coating system (Electrogalvanized Mild Steel/Etch Primer/Epoxy-Polyamide Primer/ Epoxy-Amine Topcoat System) embedded with iron oxide, zinc chromate and titanium dioxide pigments was studied to ascertain its corrosion resistant synergistic performance at various anthropogenic sites of Karachi coastal city while salt spray test was also executed for reference. Coating performance was ascertained by visual morphological inspection, gloss measurements, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray (EDX) analysis and by Fourier Transform Infrared (FTIR) Spectroscopy. SEM & EDX results corroborated high degradation of epoxy coating at marine site experiment as substantial increment in oxygen/carbon ratio and high concentration of Ti at coating surface due to ex-corporation of pigments were noticed. Worst performance of epoxy coating at marine test site as compared to salt spray testing may be due to the salt-laden winds of Karachi coastal city and corrosive constituents incorporated in atmospheres from industrial and automobiles exhaust. General diminution trend in gloss value, depletion of morphological features witnessed through SEM micrographs, curtailment of aryl ether and aromatic nuclei signals in FTIR spectrum, and emergence of new peaks in the 1620-1800 cm⁻¹ region correspond to formation of new oxidation products; concluded that an insignificant protection offered by the epoxy coating due to its outdoor aging which led to ex-capsulation of pigments under moist conditions. Appraisal of these results have furnished an average coating performance correlation of 547.5 hpy (hours of salt spray test equivalence per year exposure test) at marine test site and 528 hpy at industrial test site in terms of blistering while equivalence mean in terms of rusting were found 680 hpy and 567 hpy at marine and industrial test sites respectively.

Key words: Epoxy coatings, Corrosion and Galvanized steel.

Introduction

Employment of various corrosion mitigation techniques like protective coatings, galvanizing, anodizing, sacrificial anode and impressed current cathodic protection are in vogue to preserve engineering structures and metallic installations. Generally choices for techniques are determined by their synergistic performance, nature of corrosive environment and severity of service conditions [1-3].

Epoxy coatings have remarkable use in the field of corrosion protection because of their range of properties and versatility [4]. Epoxy coatings exhibit good corrosion resistance and outstanding adhesion to numerous different substrates. This is due to oxirane ring moiety in epoxy monomers, most of which transformed into alcoholic functional group by oxirane ring opening during polymerization (Fig. 1). During curing, these functional groups form three dimensional cross-linking network of ether linkages which convert cured film into thermosetting, mechanically strong and flexible texture thus offer good barrier attributes. Moreover, these cross linkages become polarized owing to presence of electronegative oxygen thus furnish good adhesion to

polar and metallic surfaces. However, being organic framework, epoxy coatings are prone to degradation subject to meteorological conditions particularly sun light exposure and humidity level. Therefore cumulative performance of epoxy based coating systems mainly depends upon service conditions and other corrosion control procedures applied in parallel [5, 6]. In recent years, many researchers have modified epoxy coatings to explore its improved performance. M. Golabadi *et al.*, have found significant corrosion and cathodic disbondment resistance of epoxy coating after zinc phosphate conversion pretreatment [7]. Zhengqing Yang *et al.*, substantially improved anti-corrosion and self-cleaning property by introducing superhydrophobicity in epoxy coating via fluorographene modification [8]. Saheli Bera *et al.*, formulated epoxy-silane hybrid coating for enhanced corrosion protection & adhesion on galvanized steel [9]. It is pertinent to highlight that in current communication, performance attributes of epoxy based coating system applied on electrogalvanized mild steel were first time reported in different anthropogenic (marine-industrial-urban) conditions of Karachi city.

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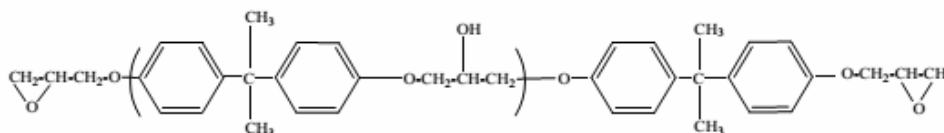


Fig. 1: Molecular structure of a typical epoxy polymer.

Experimental

Test Materials and Specimen Preparation

Electrogalvanized mild steel (EGMS) test coupons of dimensions $101.6 \times 152.4 \times 1.4$ mm were machined from EGMS sheet acquired from Hino Pak Motors Limited (Body Operation Plant). Each test coupon comprised 1.2 mm thick mild steel layer of composition 99.05% Fe, 0.25% C and 0.7% Mn while 0.2 mm thick zinc layer was electroplated on its surface. These coupons were first sand blasted and washed with solvent according to protocol SSPC-SP1 to remove grease and oils [10]. Then etch primer was mounted on each coupon. An epoxy-polyamide primer embedded with Iron Oxide & Zinc Chromate pigments and an epoxy-amine topcoat loaded with Titanium Dioxide & Iron Oxide pigments were applied with an air-operated spray in compliance with the manufacturer's recommendations. This was followed by the drying of coated panels in air. The average dry film thickness of coating system (Primer + top coat) was measured with the help of Elcometer 456 digital coating thickness gauge and it was found to be 200 μm . Surface of each dried and cured coated panel was scribed with an X of size 3×3 inch, reaching the EGMS base in order to test coating resistance to the under film corrosion. Backsides and edges of specimens were secured with tape to prevent premature coating failure. One set of prepared coated panels was kept as control.

Accelerated (Salt Spray) Testing (SST)

Accelerated testing was performed as per ASTM B-117 norms. Salt spray chamber was used to provide high humidity (95-98 %) and continuous salt spray (5 % wt. NaCl) at 35 °C. Duly coated test coupons were affixed and orientated at 45° to the normal on plastic racks [11].

Natural Exposure Testing (NET)

NET was performed at three different anthropogenic test sites (marine-industrial-urban) located in Karachi, Pakistan. NET was carried out according to ISO standard 8565 [12]. One set of prepared coated panels was placed at the marine exposure test site in Karachi, Pakistan. This test site was located at Hawke's bay of Arabian Sea coast ($24^{\circ} 51' 02.63''$ N, $66^{\circ} 53' 08.26''$ E). Second set of

coated panels was exposed at the industrial S.I.T.E area of Karachi, Pakistan ($24^{\circ} 54' 12.08''$ N, $67^{\circ} 00' 34.21''$ E). Third set was positioned for natural exposure at the urban test site (University of Karachi) in Karachi, Pakistan ($24^{\circ} 56' 40.37''$ N, $67^{\circ} 00' 34.21''$ E). At the test sites, the test specimens (coated panels) were mounted on exposure rack, facing 45° southward.

Assessment of the Performance of Coatings

Performance of coating is rationally related with number of paint defects. Visual assessment of the morphological conditions of subject coating system was performed according to ISO norms 4628-1(Part 1) [13]. Assessment of degree of blistering, rusting and cracking was done by time to time according to standard ISO 4628 (Part 2, 3, 4) [13] while the degree of filiform corrosion was assessed by ISO 4628 (Part 10) [13] at the end of exposure. In these methods, the samples to be evaluated were compared to a set of standard photographs showing various degrees of each type of failure. For the assessment of blistering, the pictures in the ISO standard represent blister densities from 2 to 5, with 5 being the highest density. Blister size is also numbered from 2 to 5, with 5 indicating the largest blister. Results were reported as blister density followed by blister size. The scale used by ISO in assigning the degree of rusting ranges from Ri0 to Ri5, with Ri5 indicating the highest degree of rusting. The ISO method judge the degree of cracking in terms of quantity, size and depth together with approximate direction. Scribes were also engraved on epoxy cured EGMS test coupons to appraise coating performance when coating defects may be appeared due to mechanical impact (Fig. 2). Visual assessment results were tabulated in Table-1 & 2.

Gloss Measurement

Gloss of control and tested coupons were measured by Horiba IG-330 Gloss meter according to the ISO 2813 standard [14]. The samples were cleaned and 60° gloss was measured. Each sample was rotated about 45° after each measurement. A total of 10 readings were made on each sample at each measurement. Data reported were the average of the readings.

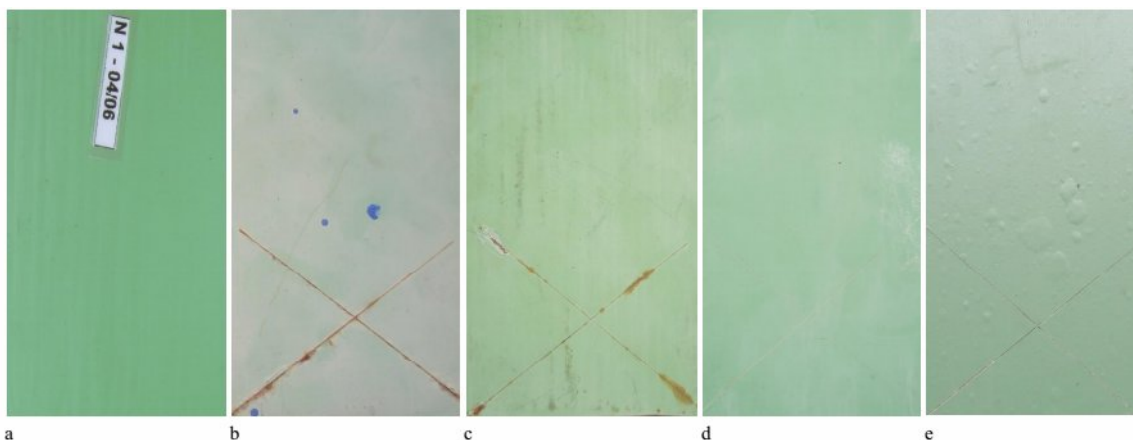


Fig. 2: State of scribed region of epoxy coating systems over electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after salt spray testing.

Table-1: Results of visual examination of the anticorrosive performance of epoxy duplex coating system applied on electrogalvanized mild steel and exposed at different anthropogenic test sites.

Test sites	Coatings defects after																	
	12 months			18 months			25 months			27 months			29 months			30 months		
	(May2006-May2007)			(May2006-Nov2007)			(May2006-Jun2008)			(May2006-Aug2008)			(May2006-Oct2008)			(May2006-Nov2008)		
	B	R	Cr	B	R	Cr	B	R	Cr	B	R	Cr	B	R	Cr	B	R	Cr
L ₁	0	0	0	2S ₃	2	0	3S ₃	4	0	4S ₃	5	0	d	d	d	d	d	d
L ₂	0	0	0	2S ₂	1	0	2S ₂	1	0	3S ₂	2	0	4S ₂	3	0	d	d	d
L ₃	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	d	d	d

L₁: Marine test site; L₂: Industrial test site and L₃: Urban test site

B: blistering; R: rusting; Cr: Cracking

0: No detectable paint defect

d: Panels were removed after exposure

Table-2: Visual examination results of salt spray testing of epoxy duplex coating system applied on electrogalvanized mild steel.

Coating defects	Time duration in hours			
	720	850	930	1100
Blistering	0	2S ₄	2S ₄	3S ₄
Rusting	0	1	1	1

0 = No detectable paint defect

Assessment of Degree of Corrosion around the Scribe

Test panels were washed with fresh tap water and air dried. Coatings were removed with the help of paint remover to expose the scribed region. After the removal of coatings, test panels were again washed with fresh tap water and then dried in air. This was followed by the application of varnish on the test panels (ISO4628-8) [13]. Degree of corrosion around the scribe was visually ascertained.

Energy Dispersive X-ray (EDX) Analysis and Scanning Electron Microscopy (SEM)

Energy Dispersive X-ray analysis was carried out with an X-ray machine (JEOL 6380B) by employing Cu-K radiation. Small slices of coatings were cut from test coupons and EDX spectra were obtained by direct radiation on the specimen surface.

Scanning electron microscopy (SEM) was also used to study the surface characteristics of control (unexposed) and exposed coating systems. Small sections of the coatings were coated with gold up to 300Å using a gold coater (JEOL JFC 1500). Finally the SEM micrograph was taken by using a scanning electron microscope (JEOL 6380A), operated at 10⁻⁷ Torr vacuum and 30 kV.

Fourier Transform Infrared (FTIR) Spectroscopy

Chemical changes in the epoxy duplex coating exposed in natural outdoor and accelerated environments were investigated by Fourier transform infrared spectroscopy (FTIR). Infrared spectra were also taken for unexposed (control) coating systems. The whole coating systems including topcoat and primer were scraped from both the unexposed and exposed test panels and KBr discs were made. For

exposed panels, it was ensured that the corrosion products were not included in the material used for testing. The spectra were obtained using a Shimadzu 8900 Fourier transform infrared spectrophotometer running with Omnic software, in the 4000-400 cm^{-1} range. The spectrophotometer was operated in transmission mode. Spectra were recorded at a resolution of 2 cm^{-1} and 20 scans.

Statistical Analysis

Principal component analysis (PCA) was applied on the data obtained from EDX analysis in order to study correlation between accelerated and natural exposure testing. The data was processed by using the software Statistica (Version 10). The results were presented on a bi-dimensional plot and the significant loadings were marked when $\geq |0.7|$.

Results and Discussion

Electrogalvanized mild steel (EGMS) test coupons (4" \times 6" \times 1.4 mm dimensions) painted by epoxy-polyamide Primer and epoxy-amine Topcoat System were subjected to atmospheric exposure of marine site (L_1), industrial site (L_2) and urban site (L_3), and also to salt spray testing. Coating performance was evaluated by visual inspection, gloss measurement, degree of corrosion around the scribe, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) analysis and by Fourier Transform Infrared (FTIR) spectroscopy. Principal component analysis (PCA) was also carried out for the data obtained from EDX analysis in order to study correlation between accelerated and natural exposure testing.

Visual Inspection

During visual inspection for coating degradation in the scribed region, coated panels were periodically rated for blistering, rusting and cracking according to ISO 4628 (Part 2, 3, 4) [13]. Degrees of filiform corrosion were assessed after the complete deterioration of coatings according to standard ISO 4628 (Part 10) [13]. Pre and post exposure test conditions of test panels were snapped in photographs to determine the deterioration experienced by coatings. Scribed region was focused

in the photographs because significant changes may be observed in this region.

Natural exposure testing (NET) at marine site (L_1) indicated no signs of degradation even after 12 months of exposure. However few blisters of small size and rust were noticed after 18 months of exposure. Subsequently gradual increase in degradation signs were observed while no cracking was witnessed. Further exposure was stopped after 27 months (Table-1). Blistering and rusting were commenced about 18 months of NET at industrial site (L_2). With the passage of exposure time period; gradual increase in degree of blistering and rusting were experienced while cracking and filiform corrosion were not detected during exposure time period. Exposure test was wound up after 29 months of study. NET at urban site (L_3) exhibited good performance of coating even after 29 months of exposure. During this time span any blistering, rusting and cracking were not detected. Further study was ceased after 29 months of exposure experiment.

Main results of salt spray testing of the subject epoxy duplex coating system were summarized in Table-2. There was no sign of degradation detected even after 720 hours of exposure. Some blisters and rust formation appeared at about 850 hours of experiment. Blisters of large size were observed all over the surface. Further exposure experiment was terminated after 1100 hours.

Aforementioned results categorically demonstrated awesome performance of subject epoxy coating system at urban test site (L_3) as no single coating defect was detected during exposure experiment. On the other hand any cracks or filiform corrosion around the scribe was not witnessed in epoxy duplex coating system even after 29 months of exposure at all above test sites. Comparison of these results have furnished an average correlation in terms of blistering up to 547.5 hpy (hours of salt spray test equivalence per year exposure test) at L_1 and 528 hpy at L_2 while equivalence mean in terms of rusting were found 680 hpy and 567 hpy at L_1 and L_2 respectively (Table-3).

Table-3: Correlation of epoxy duplex coating system performance at various natural exposure test sites and salt spray testing in terms of required time period for defects to be appeared.

Coating Defects	Blistering			Rusting				
	2S _x	3S _x	4S _x	1	2	3	4	5
L ₁ (months)	18	25	27	15	18	21	25	27
L ₂ (months)	18	27	29	18	27	29	-	-
L ₃ (months)	NA	NA	NA	NA	NA	NA	NA	NA
SST (hrs)	850	1100	NA	850	NA	NA	NA	NA
Correl. SST/L ₁ (hpy)	567	528	-	680	-	-	-	-
Correl. SST/L ₂ (hpy)	567	489	-	567	-	-	-	-

L₁: Marine test site, L₂: Industrial test site, L₃: Urban test site, SST: Salt Spray Test
NA: Not achieved that defect level, hpy: hours of SST equivalence per year of Natural exposure test

Gloss Measurement

Any topographical degradation in coating surface may also be emulated in its gloss value therefore condition of coating could be rationally examined by monitoring gloss value of surface. Comparison of the gloss value of epoxy duplex coating systems measured under different exposure conditions were depicted in Fig. 3. It was noticed after natural exposure testing that maximum reduction in gloss was recorded for the epoxy duplex coating system exposed at marine test site (L_1) while minimum decrement in gloss was measured at urban test site (L_3). Comparison of the gloss measurements after salt spray and natural exposure testing revealed that the former induced less reduction in gloss of the coating system.

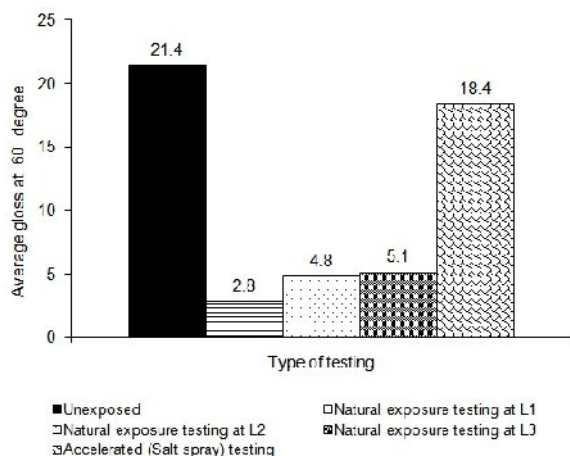


Fig. 3: Comparison of the gloss value of epoxy duplex coating systems subject to natural exposure testing at marine test site (L_1), industrial test site (L_2), urban test site (L_3) and salt spray testing.

Literature showed that the reduction in gloss of epoxy coating after accelerated and natural exposure testing was noticed by several researchers. B. del Amo, *et al.* studied the performance of epoxy paint containing zinc molybdenum phosphate corrosion inhibitors [15]. They ascertained the performance of epoxy paint through visual examination as per ASTM norms by electrochemical and accelerated tests including salt spray test. V. C. Malshe, *et al.* reported the weathering characteristics of epoxy paints with different curing agents [4]. They had determined yellowness, weight loss and gloss reduction by carrying out salt spray as well as natural exposure testing. E. Almeida, *et al.* reported the performance of epoxy paint on different substrates after various salt spray and natural exposure tests by carrying out visual examination according to ISO 4628 norms [16]. X. Gu, *et al.* reported the changes

in gloss and surface topography of epoxy coating after natural exposure testing [17]. S. Dutta, *et al.* had compared the gloss loss of epoxy and epoxy modified paints by different accelerated tests [18]. All abovementioned research work have studied diminution in gloss value of epoxy coating upon weathering and linked up this with loss of cross linking among organic materials of the coating.

It was apparent from the results obtained in this study that the natural exposure testing at marine, industrial and urban test sites caused high degradation of the coating systems tested as compared to salt spray testing. It was assumed that modes of degradation may be similar on account of key factor of 'salt spray' playing role both in natural weathering in form of mist of salt spray emerging in the atmosphere of Karachi coastal city and also in salt spray test [4]. However, it was found completely different in salt spray and natural exposure testing. That was most likely due to the presence of several corrosive constituents of marine and industrial environment, emerging from the mist of salt spray in the atmosphere and due to industry and automobiles pollution which caused high degradation of the binder and loss of cross linking hence small organic units formed and eliminated from the polymer matrix while on other hand these factors were absent in the mist of salt spray test. V. C. Malshe, *et al.* had specified that the aromatic moiety and secondary hydroxyl groups may play a vital role in the degradation of epoxy resin which ultimately caused reduction in gloss of the coating system. This was confirmed by the fact that methyl substitution on aromatic part causes faster and increased chalking of the epoxy paint. The secondary hydroxyl group was the next contributing factor to the degradation of epoxy paints after the aromatic moiety as evidenced by the remarkable control of chalking on silylation of the hydroxyl groups [4].

Scanning Electron Microscopy (SEM) Analysis

Customarily, a coating film protects underlying metal substrate by cordoning off its contact with environmental corrodants. However, prolong weathering caused polymeric degradation of coatings vide photo-oxidation processes which reduces barrier function of coating by producing cracks in surface morphology. Physical and chemical degradation of an epoxy coating as a result of weathering is greatly influenced by its surface morphology and bulk microstructure [19]. In subject study, SEM was also employed to record topographic micrographs of test panels after their exposure to various natural environments and salt spray test (Fig. 4).

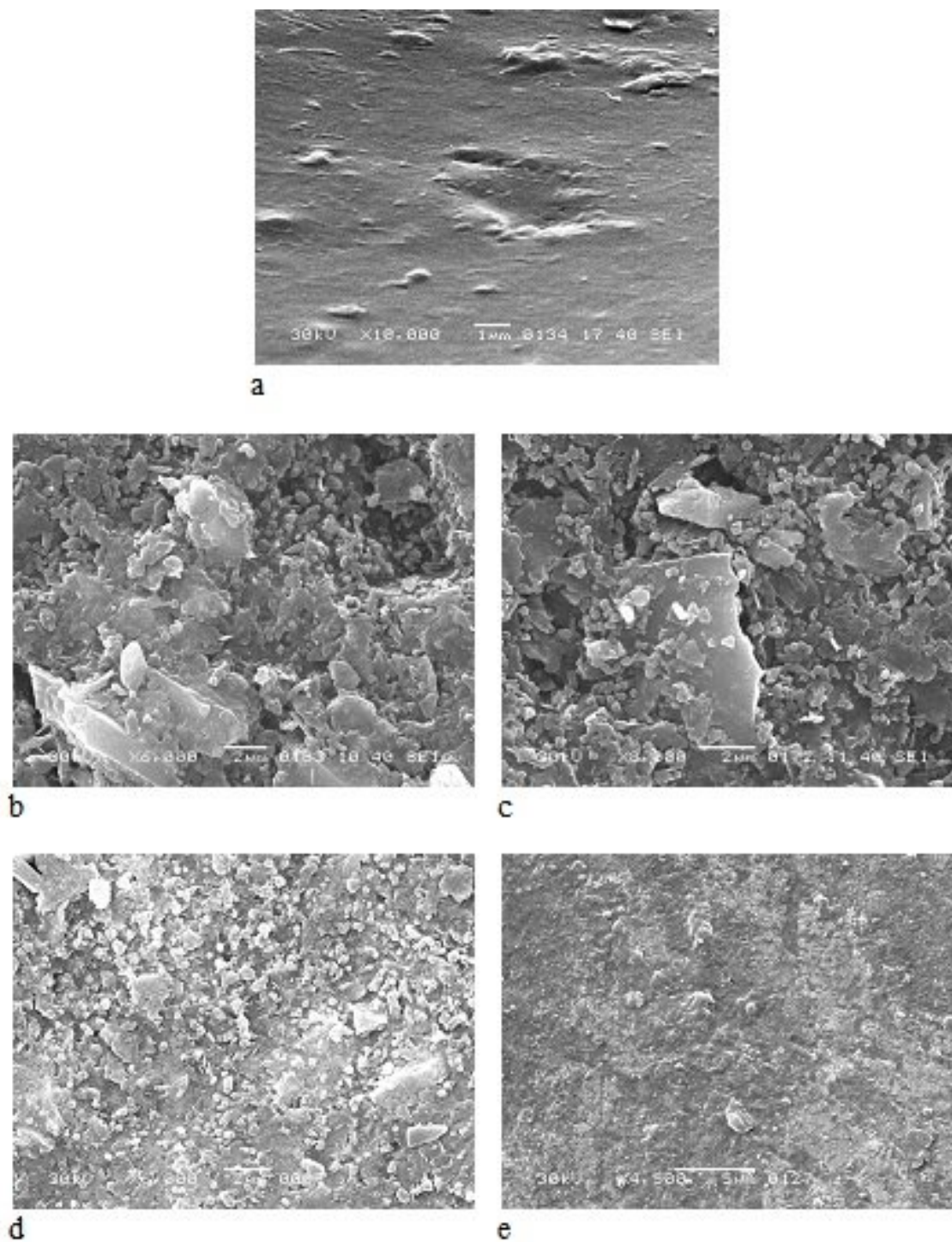


Fig. 4: Scanning electron micrographs of the surface of epoxy duplex coating systems applied on electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after salt spray testing.

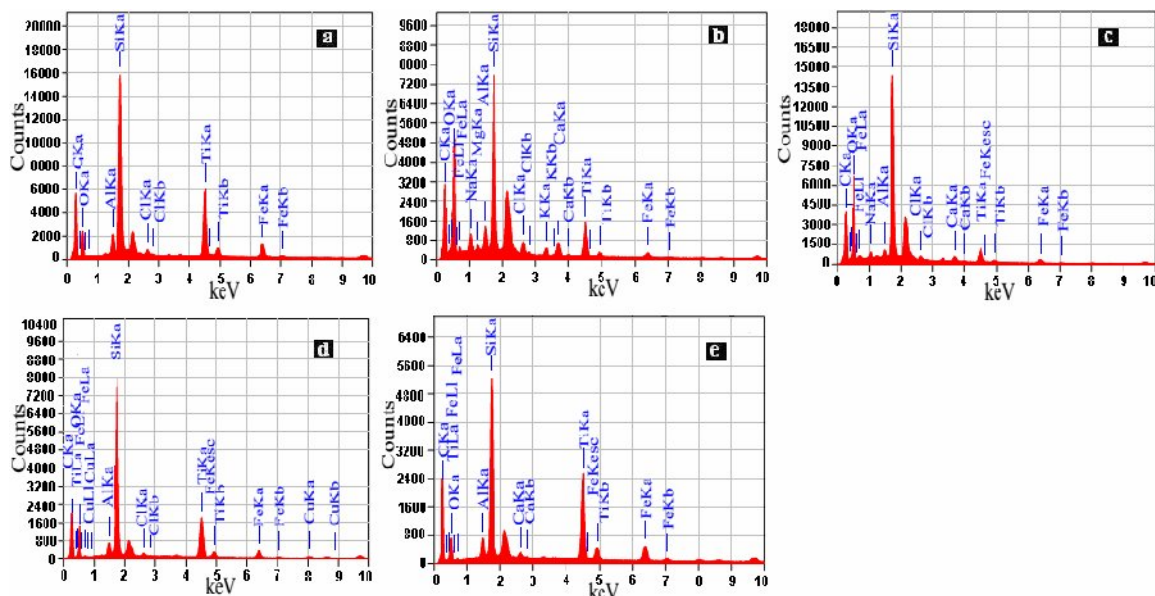


Fig. 5: EDX spectra of the surface of epoxy duplex coating systems applied on electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after salt spray testing.

In SEM micrographs, surface of the unexposed epoxy duplex coating system was appeared in good health (Fig 4a) while NET at marine site (L_1) has exhibited roughened coating's surface and the underlying pigment matrix was also visible in the micrograph (Fig 4b). SEM Micrographs of NET at industrial site (L_2) illustrated damaged surface as a result pigments were eroded on the surface (Fig 4c) while NET at urban site (L_3) indicated irregular degradation of the coating surface characteristics (Fig 4d). Similarly salt spray test showed slight damages in the coating's surface (Fig 4e).

SEM technique was opted by several scientists to investigate the effects of degradation on epoxy coating. D. Kotnarowska used SEM to study the deterioration of epoxy coating as a result of action of sulphuric acid aqueous solution [20]. V.D. Ramos carried out the investigation of fractured surfaces of the epoxy coatings by SEM [21]. A. B. Cherian, *et al.* employed SEM to study the fractured behavior of modified epoxy networks [22]. M. I. Giannotti, *et al.* measured the changes in morphology of thermoplastic modified epoxy resin with the help of SEM [23]. M. Morcillo, *et al.* also used SEM in order to study the galvanic protection of zinc epoxy polyamide base zinc rich paint [24]. M. C. Deya, *et al.* studied the anticorrosive performance of epoxy paints by incorporating different pigments in the paint [25]. They used SEM in order to study the protective layer formed under the paints. Literature also showed that S. Dutta, *et al.* used SEM to study the surface morphology of epoxy modified

polyurethane paint and standard epoxy paint [18]. R. Naderi, *et al.* studied the performance of epoxy coating after incorporating zinc aluminum phosphate as an anticorrosive pigment in it [26]. They used SEM to study the steel surface under the disbonded coating. J. M. Sanchez Amaya, *et al.* used SEM in order to study the effect of chemical degradation on high solids epoxy coating [27]. N. Fredj, *et al.* carried out the investigation of epoxy coating by SEM [28]. G. Blustein, *et al.* used SEM to study the protective layer formed beneath the epoxy coating [29].

Comparison of these SEM images with gloss measurements have revealed that natural exposure testing (particularly at marine and industrial test sites) had induced high degradation on the surfaces of epoxy duplex coating systems as compared to salt spray testing. This surface roughening explained the high decrease in gloss for all the naturally weathered coating systems. This was also consistent with the finding of F. X. Perrin, *et al* [30], who related the loss of gloss with the increase of the surface roughening for the coating systems.

Energy Dispersive X-ray (EDX) Analysis

Energy Dispersive X-ray (EDX) technique is a useful tool to analyze the elemental composition of weathering products deposited at coating surface by direct radiation on the aged surface of test panels. Fig 5 depicted the energy dispersive X-ray (EDX) spectra of epoxy duplex coating system surface after NET at different test sites as well as after salt spray testing.

EDX analysis performed for the unexposed epoxy duplex coating system have indicated the presence of C, O, Al, Si, Cl, Ti, and Fe elements in peripheral layer (Fig 5a). NET at marine site (L_1) corroborated the occurrence of C, O, Na, Mg, Al, Si, Cl, K, Ca, Ti, and Fe (Fig 5b) whereas NET at industrial site (L_2) showed the presence of C, O, Na, Al, Si, Cl, Ca, Ti, and Fe with different % abundance (Fig 5c). Natural exposure testing at urban site (L_3) illustrated the presence of C, O, Al, Si, Cl, Ti, Fe and Cu (Fig 5d) while C, O, Al, Si, Cl, Ti and Fe were found after salt spray testing (Fig 5e). Moreover, Ti was surprisingly found high in EDX results of coated panels exposed to marine environment (L_1). This may be due to high degradation in the surface characteristics of coating during natural exposure testing at marine test site. All this resulted, in ex-corporation of Ti pigments which is also evident from high erosion of pigments on the surface in SEM image of marine exposed coated panel. In literature C. Ocampo *et al.* compared the resistance of modified and unmodified epoxy coatings against marine corrosion with the help of SEM-EDX [31]. They found that initial regular surface of the epoxy coating was changed to a rough superficial structure after testing. They related the roughening to the appearance of oxides in the polymeric matrix because the EDX analysis revealed an increase in iron and oxygen contents. Results obtained in this study were also consistent with their findings.

Generally extent of degradation is ascertained by surface roughness which appeared at smooth surface of an unexposed coating after salt spray and natural exposure testing. However, an increase in oxygen content and as a result increase in O/C ratio is also used as a tool for determining extent of photodegradation in an epoxy coating due to weathering. Fig. 6 demonstrated the comparison of oxygen/carbon (O/C) ratios in unexposed and exposed epoxy duplex coating systems. Maximum O/C ratio was found after NET of epoxy duplex coating system at marine test site (L_1) followed by at industrial test site (L_2) and at urban test site (L_3) respectively. Comparison of O/C ratios obtained after salt spray testing with that obtained after NET at marine (L_1), industrial (L_2) and urban (L_3) test sites revealed that O/C ratios were higher in latter cases.

Principal Component Analysis

Principal component analysis of the epoxy duplex coating systems applied on electrogalvanized mild steel explained a variance of 99.66 % when 2 components were considered. The variance of the first component was explained by the negative and non-significant loadings of the unexposed, NET at

L_1 , NET at L_2 , NET at L_3 and SST which were not correlated each other. The variance of the second component was explained by the negative and non-significant loadings of the NET at L_1 and NET at L_2 , whereas the positive contributions were mainly due to unexposed, SST and NET at L_3 . However, these contributions were also not significant. These results of PCA analysis has depicted that although all NET stations were located in the territory of Karachi (an industrial metropolitan coastal city) and conditions were not pure marine, industrial or urban rather were intermixed but at particular station one condition was more prevailing and detrimental than other one. Thus non-significant variance co-relationship was established between coating aging results in the terms of defects frequency and intensity. Therefore, these finding were justifying that selection of test station and their classifications were rational.

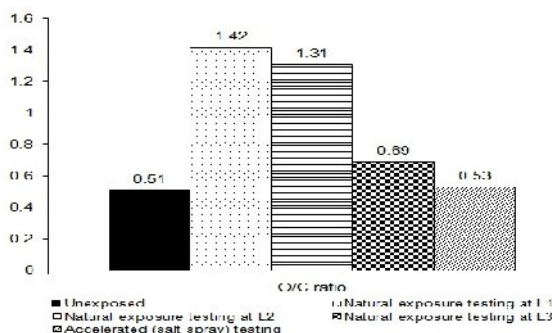


Fig. 6: Comparison of O/C ratios in epoxy duplex coating systems subject to natural exposure testing at marine test site (L_1), industrial test site (L_2), urban test site (L_3) and salt spray testing.

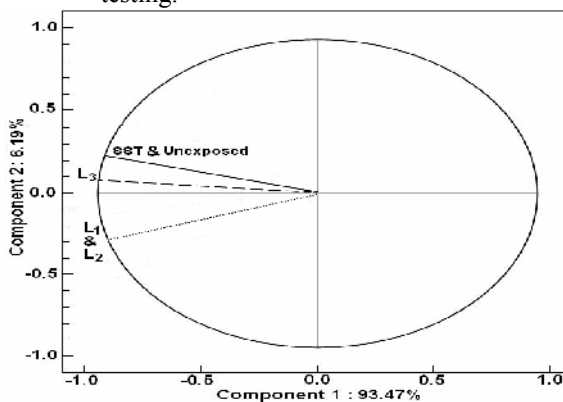


Fig. 7: Loading plots of principal component analysis reported the results of elaborations carried out with EDX data sets obtained for epoxy duplex coating systems (In the axis title of each component the explained variance is reported. NET (Natural exposure testing), L_1 (Marine test site), L_2 (Industrial test site), L_3 (Urban test site), SST (Salt spray testing).

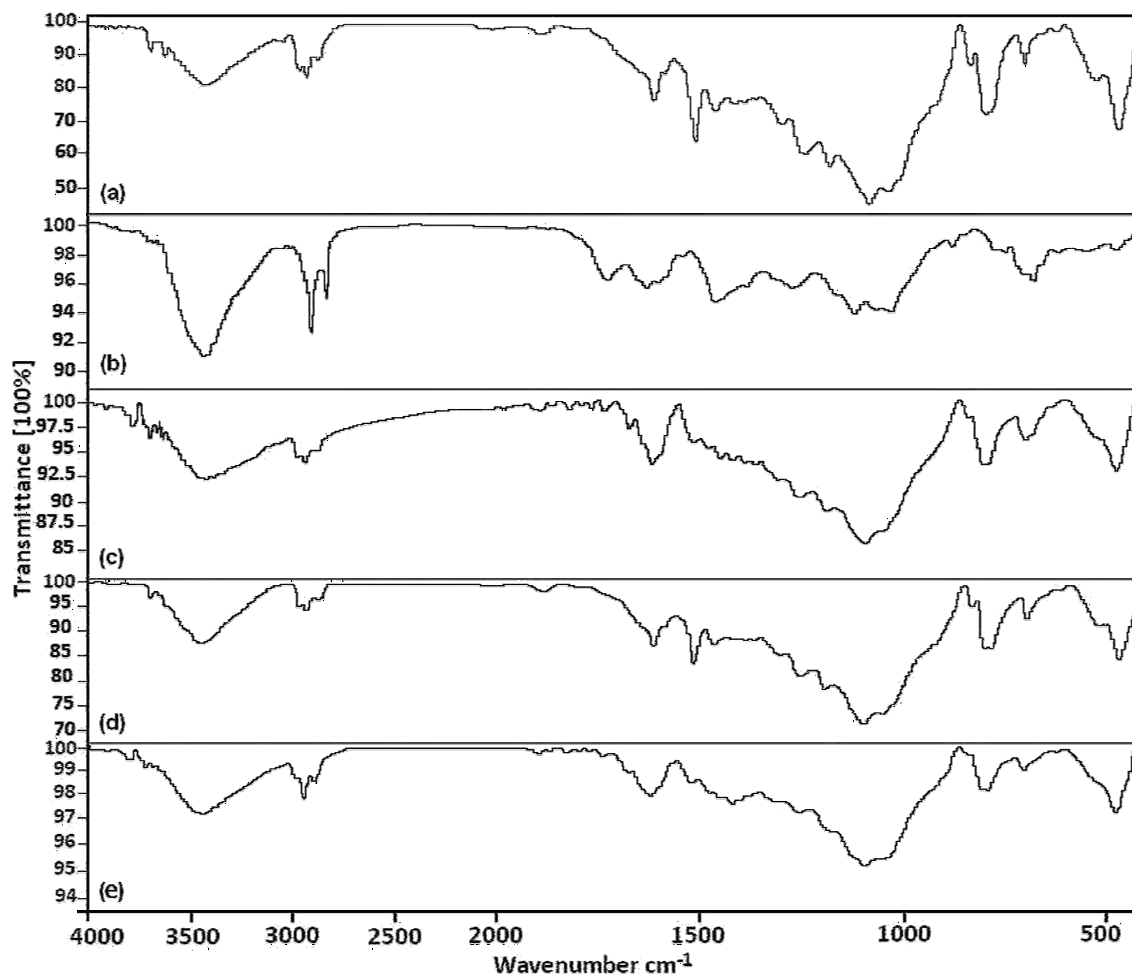


Fig. 8: Infra red spectra comparator of epoxy duplex coating systems applied on electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after salt spray testing.

Fourier Transform Infrared (FTIR) Spectroscopy

IR spectrum of unexposed epoxy duplex coating system showed a band due to O-H stretching near 3420 cm^{-1} (Fig. 8a). Band present near 3036 cm^{-1} was due to aromatic C-H stretching. Aliphatic C-H stretching was noted in the region of $2800\text{--}2962\text{ cm}^{-1}$. Bands in the region of $1500\text{--}1600\text{ cm}^{-1}$ were due to C=C stretching of aromatic nucleus (benzene ring). C-O stretching vibration of aryl ether was observed near 1246 cm^{-1} and the band near 1038 cm^{-1} was due to aliphatic C-O stretching. Band at 829 cm^{-1} was due to out of plane bending vibration of the two adjacent hydrogens on the para disubstituted aromatic rings. C-O-C bending vibration was observed in the region of $500\text{--}575\text{ cm}^{-1}$ [32-33].

FTIR spectra obtained for epoxy duplex coating systems after natural exposure testing at marine, industrial and urban test sites as well as after

salt spray testing showed changes in the similar regions independent of type of testing (Fig.8b, c, d, e). Following changes occurred on weathering:

- i. Decrease in the peak intensities of C-O stretching vibration of aryl ether near 1250 cm^{-1} and C=C stretching of aromatic nucleus in the region of $1500\text{--}1600\text{ cm}^{-1}$. This was an indication that chain scission and mass loss in the coating have taken place.
- ii. Appearance of new peaks in the $1620\text{--}1800\text{ cm}^{-1}$ region which showed the formation of oxidation products. Due to formation of oxidation products, two prominent bands at 1658 cm^{-1} and 1725 cm^{-1} were observed, which could be attributed to C=O stretching of amide and C=O stretching of ketone respectively.

The carbonyl band at 1728 cm^{-1} has been attributed to the formation of ketone products by Bellinger [34] or to aldehyde formation by J.C.

Petterson- Jones [35]. In either case the products are formed by the release of water molecules by dehydration of the hydroxyl groups.

Photodegradation of epoxy coatings has extensively studied by the researchers. A. Rivaton, *et al.* studied the photoageing of diglycidyl ether of bisphenol A without curing agent. The study included the identification of photoproducts and mechanism of formation of photoproducts [36]. Bellinger and Verdu reported the effects of curing agents on photodegradation of epoxy resins [34]. L. Monney, *et al.* studied the DGEBA-MTHPA (Diglycidyl ether of bisphenol A-methyl tetrahydrophthalic anhydride) system and identified the molecular changes and also confirmed the photochemical mechanism proposed by other researchers [37]. J. C. Petterson Jones reported the thermal degradation of glycidyl ether type epoxide resins after curing with aromatic amine [35]. Influence of different curing agents on the thermal and photochemical ageing of epoxy resin was reported by F. Delor-Jestin, *et al.* [38]. D. Kotnarowska reported the influence of aggressive media and ultraviolet radiation on the degradation of epoxy coating [39]. C. Ocampo, *et al.* used FTIR spectroscopy to compare the anticorrosive performance of unmodified and modified epoxy paints against marine corrosion [31]. Y. Malajati, *et al.* recently reported the influence of water on the photodegradation of epoxy resins in aggressive media [40]. They concluded that water affects the degradation of the main photoproducts as well as increase the photooxidation rate. X. Gu, *et al.* studied the photodegradation of the epoxy coating after outdoor exposure [41, 42]. They concluded that chain scission and mass loss in the coating have taken place. In addition to this, formation of new chemical species was also observed by them. FTIR results obtained in this study were in good agreement with the conclusions of V. Bellinger, *et al.*, J. C. Petterson-Jones and X. Gu, *et al.* [34, 35, 41, 42].

Conclusions

This study substantiated that diminution trend in gloss values, EDX analysis, FTIR spectroscopy and SEM micrographs, all revealed high degradation in the surface characteristics of epoxy duplex coating systems during natural exposure testing (particularly at marine and industrial test sites) as compared to salt spray testing. This was more likely due to the presence of several corrosive pollutants in coastal environment, emerging from windblown spray droplets, marine fog and industrial & automobiles exhaust which caused high degradation of the binder and loss of cross linking hence small organic units formed and eliminated

from the polymer matrix on the other hand these environmental detrimental factors were absent in salt spray test. High values of O/C ratios obtained after natural exposure testing as compared to salt spray ageing is just because of the photo oxidative degradation of the binder in the former case and not in the latter case as it does not include an exposition to UV radiation. FTIR results revealed decrement in the peak intensities of C-O stretching vibration of aryl ether near 1250 cm^{-1} and C=C stretching of aromatic nucleus in the region of $1500\text{-}1600\text{ cm}^{-1}$ which was an indication of loss of cross linking due to chain scission in coating. Detrimental oxidation was also evident from emergence of new peaks in the $1620\text{-}1800\text{ cm}^{-1}$ region which correspond to formation of oxidation products.

Comparison of the results of subject study for epoxy duplex coating systems applied on EGMS with our previous published study on mild steel (MS) revealed better corrosion mitigation performance by subject coating formulation with EGMS [43]. Natural exposure testing also showed that the blistering and rusting were severe in the coating systems applied on MS as compared to that applied on EGMS. However, cracks or filiform corrosion around the scribe were not witnessed in epoxy coating system both with MS and EGMS substrate at all test sites.

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Declaration of interest

Authors declare that they have no conflict of interest.

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