Structure and Microstructure Studies of Epoxy Coating After Natural Exposure Testing

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Summary: In this work, visual evaluation, Scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis and Fourier transform infrared (FTIR) spectroscopy were used to study the degradation of an epoxy coating system applied on mild steel test panels (10cm x 15cm) exposed at two natural exposure test sites. After surface preparation and application of coating, test panels were subjected to natural exposure at industrial and urban test sites located in Karachi, Pakistan. Visual evaluation showed that the major modes of degradation were totally different at two natural exposure test sites. Scanning electron microscopy (SEM) revealed that the testing caused changes in the surface morphology of the epoxy coating systems with natural exposure testing at urban site showing less surface degradation. Good correlation was observed between the SEM and gloss measurements. Energy dispersive X-ray (EDX) analysis indicated the increase in oxygen content and O/C (oxygen/carbon) ratio for exposed coatings as compared to unexposed coating. Increase in O/C ratio showed that the photodegradation of the coatings occurred upon weathering. EDX analysis is in good agreement with the fourier transform infrared (FTIR) spectroscopy results. Both observations indicated a high chemical degradation in the epoxy coating system tested at industrial exposure test site. Photodegradation of the epoxy coating system caused chain scission and as a result loss in intensity of the C-O stretching vibration of aryl ether near 1250cm^{-1} and C=C stretching of aromatic nucleus in the region of 1500-1600cm^{-1} were observed.

Introduction

Corrosion is the deterioration of a metal/material in an aggressive environment [1]. Atmospheric corrosion is one of the most known forms of corrosion [2]. Atmospheric corrosion of steel is an electrochemical process which involves the oxidation of metal at the anode and reduction of oxygen at the cathode as reported by Sangaj, *et al.* [3].

$$Fe \longrightarrow Fe^{2+} + 2e^-$$
$$O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

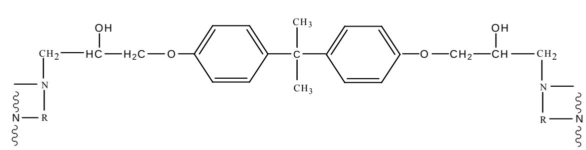
The whole process occurs in the presence of an electrolyte [4]. Products formed at anode and cathode migrate towards one another and precipitate out [3].

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

Further oxidation of ferrous hydroxide results in the formation of hydrated ferric oxide as [3]

$$4Fe(OH)_2 + O_2 \longrightarrow 2Fe_2O_3.\ H_2O + 2\ H_2O$$

M. Natesan, *et al.* [5] stated that internationally the overall cost of corrosion is approximately 4-5% of the gross national product and 20-25% of this cost could be avoided by the use of suitable anticorrosion technology. There are different techniques for controlling corrosion [6] but the most widely used method of protection against atmospheric corrosion is the use of organic coatings [7, 8]. Among different coatings, epoxy coatings have remarkable use in the field of corrosion protection because of their range of properties and versatility [9]. Epoxy coatings contain epoxy resin which involve either in their preparation or cross-linking, the reaction of the epoxide ring (oxirane ring) with amines, carboxylic acids, anhydrides or sulfides [10]. Epoxy resins are polyethers based on condensation reaction between diphenylol propane derivatives and epichlorohydrin [11]. Epoxy resins are of low molecular weight and they only produce useful coatings when they are cross-linked (cured) to form higher molecular weight material. Commonly used curing agents are aliphatic polyamines, polyamine adducts, ketimines and polyamides/amidoamines *etc* [12]. The chemical structure of typical amine-cured epoxy is [9]



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Degradation studies of epoxy coatings have been reported by several authors. J.C. Patterson-Jones proposed the mechanism of the thermal degradation of aromatic amine-cured epoxy resins [13]. V. Bellenger, *et al.* studied the oxidative skeleton breaking in epoxy-amine networks [14]. L. Monney, *et al.* studied the photochemical degradation of an epoxy resin cured with methyltetrahydrophthalic anhydride [15]. V.C. Malshe, *et al.* reported the weathering study of different epoxy paints with various curing agents [9]. D. Kotnarowska studied the influence of ultraviolet radiation and aggressive media on epoxy coating degradation [16]. S. Duval, *et al.* evaluated epoxy coatings in hydrogen sulphide containing sour media [17]. J.T. Zhang, *et al.* reported the influence of curing agent content on the performance of epoxy coatings on mild steels [18]. However, there appears to be little or no work describing the degradation of epoxy coatings by Energy dispersive X-ray (EDX) analysis. Further statistical correlation of the results was also not found. The degradation of a coating differs widely which depends upon temperature, exposure site, time of year, substrate and coating material. The ideal evaluation of the degradation of a coating can only be obtained by its exposure in its intended environment [19]. Epoxy coatings are not known to have long exterior durability. Since these are the most commonly used media for high performance primers, these would eventually be exposed to same elements causing corrosion even if protected by a high performance top coat.

In view of the above, we discussed the degradation modes of the amine-cured epoxy coating at two natural exposure test sites (Industrial and urban) located in Karachi, Pakistan by visual evaluations. Changes in the surface morphology of the coating were studied by Scanning electron microscopy (SEM). Chemical changes in the coating were identified by Fourier transform infrared spectroscopy (FTIR). For the first time, energy dispersive X-ray (EDX) analysis was also used to evaluate the degradation of epoxy coating and results obtained were statistically correlated.

Results and Discussion

Degradation of an epoxy coating at two natural exposure test sites was studied by

- Visual evaluation
- Gloss measurement
- Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis
- Fourier transform infrared (FTIR) spectroscopy

Visual Evaluation

Visual evaluation of the degradation of epoxy coating system was done according to standard ISO 4628 (Part 1) [20]. Assessment of degree of blistering, rusting and cracking was done according to standard ISO 4628 (Part 2, 3, 4) [21-23] from time to time. In these methods, the samples to be evaluated are 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 are 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 methods judge the degree of cracking in terms of quantity, size and depth together with approximate direction.

Table-1 presents the results of visual evaluation of the degradation of epoxy coating systems exposed at two different natural exposure test sites. Natural exposure testing at industrial test site indicated the appearance of blisters and rust after 3 months of exposure. With the passage of time increase in degree of blistering and rusting was observed. After 12 months coating system was removed due to severe corrosion and coating delamination from the scribed region. Coating delamination from the scribed region appeared to be caused by the formation of underlying corrosion products.

In contrast, natural exposure testing at urban test site showed no blister formation or rusting even after 6 months of exposure. Further exposure caused the formation of some blisters and rust on the surface of coating. After 18 months exposure was stopped in order to study the degradation by other methods. In both types of testing cracking was not observed. Blisters formed in industrial environment were more in quantity and large in size. Comparison of the results indicated different modes of degradation of epoxy coating systems in industrial and urban environments. Fig. 2 shows the state of the scribed region of unexposed and exposed epoxy coating systems.

Table-1: Results of visual evaluation of the degradation of Epoxy coating systems exposed at two different natural exposure test sites.

Test sites	Coating's defects after 3 months (May2006-Aug2006)			6 months (May2006-Nov2006)			9 months (May2006-Feb2007)			12 months (May2006-May2007)			15 months (May2006-Aug2007)			18 months (May2006-Nov2007)		
	B	R	Cr	B	R	Cr	B	R	Cr	B	R	Cr	B	R	Cr	B	R	Cr
L_1	$2S_4$	1	0	$2S_4$	2	0	$4S_4$	4	0	$5S_4$	5	0	d	d	d	d	d	d
L_2	0	0	0	0	0	0	$2S_2$	0	0	$2S_2$	1	0	$3S_2$	3	0	$3S_2$	4	0

L_1: Industrial test site and L_2: Urban test site
B: blistering (appearance of various bubbles on the coating's surface)
R: rusting
Cr: Cracking (appearance of cracks on the coating's surface)
0: No detectable paint defect
d: Panels were removed after exposure due to severe corrosion and paint delamination from the scribe region

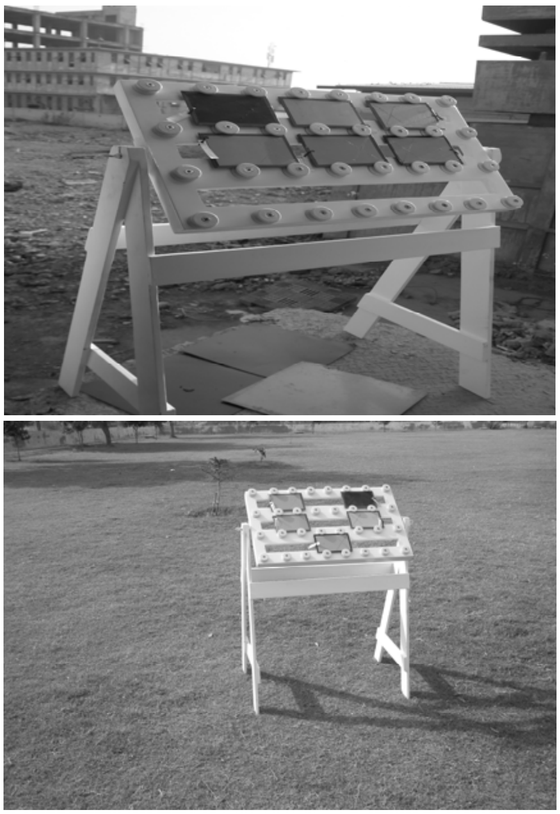


Fig. 1: Mounting of the test panels on exposure racks at natural exposure test sites. a) Industrial site b) Urban site.

Coatings are generally affected by the actions of UV light, air, water and temperature in the natural outdoor environment which causes degradation by building stresses inside the coating systems [24]. In particular, high degradation of the coating's material in an industrial environment is due to the effects of atmospheric pollutants such as oxides of Nitrogen and Sulphur [25].

B.S. Skerry, *et al.* reported the blistering and formation of underlying corrosion products as causes of degradation in their study with title "Corrosion and weathering of paints for atmospheric corrosion control" [24]. Several other authors carried out the studies and revealed blistering, rusting and formation of underlying corrosion products as the degradation causes in various types of coatings [6, 8, 26].

Gloss Measurement

Table-2 presents the results of the gloss measurement of unexposed and exposed coating systems. These results suggested that the natural exposure testing at industrial site caused severe reduction in gloss of the epoxy coating system as compared to natural exposure testing at urban site. F.X. Perrin, *et al.* reported in their study that main reason of gloss reduction is the loss of organic material of the coating [27].

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

Fig. 3 shows the scanning electron micrograph of the surface of unexposed epoxy coating system. The surface of the unexposed epoxy coating system appeared smooth and featureless. B.S. Skerry, *et al.* [24] stated that the smooth and featureless surface of the unexposed coating system is due to the fact that usually a topcoat is formulated as a gloss finish system with a comparatively low pigment volume concentration. Natural exposure testing at industrial site caused substantial changes in the surface morphology of the epoxy coating system, Fig. 4. The surface was badly roughened (Fig. 4a) and large cracks were seen in the micrographs (Fig. 4b). Comparison of these results to the effect of testing at urban test site specified less deterioration of the surface of epoxy coating system, Fig. 5. The reason for the formation of cracks is well elucidated by X.F. Yang, *et al.* [25]. They found that the degradation of the organic part of the coating (resin) produce soluble or gaseous oxidation products which in turn causes loss of adhesion between the pigment and resin and some pigments completely or partially separate out. In this way formation of cracks occurs. B.S. Skerry, *et al.* [24] also stated that the degradation of the organic part of the coating (resin) is responsible for the formation of cracks.

a b c

Fig. 2: State of scribed region of Epoxy coating systems a) unexposed b) after natural exposure testing at industrial site and c) after natural exposure testing at urban site.

Table-2: Comparison of the gloss of unexposed and exposed epoxy coating systems.

Type of testing	Average gloss at 60^0	% gloss retention
Unexposed	58.5	100
Natural exposure testing at industrial site	32.1	54.8
Natural exposure testing at urban site	39.6	67.6

Table-3: Surface composition data of epoxy coating system as determined by EDX.

Element	Binding Energy	Unexposed	Natural exposure testing at Industrial site	Natural exposure testing at urban site
	kev	mass%	mass%	mass%
C	0.277	53.23	38.28	45.99
O	0.525	25.57	36.71	30.7
Al	1.486	1.16	1.52	0.89
Si	1.739	14.74	15.38	15.81
Cl	2.621	0.27	0.24	0.23
Ca	3.69	0.22	0.3	–
Ti	4.508	3.7	5.71	4.68
Fe	6.398	1.11	1.86	1.71
Total		100	100	100

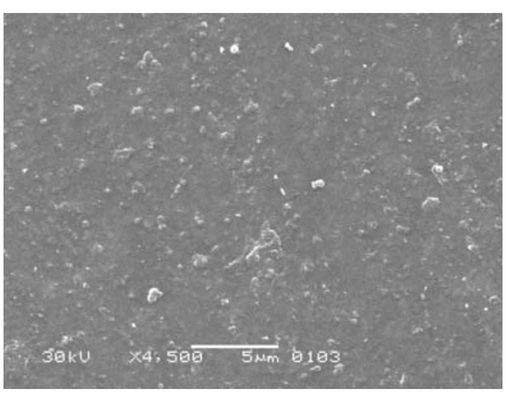
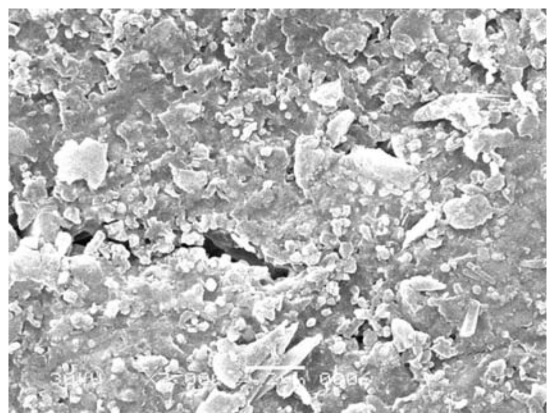


Fig. 3: SEM micrograph showing the surface morphology of unexposed epoxy coating system



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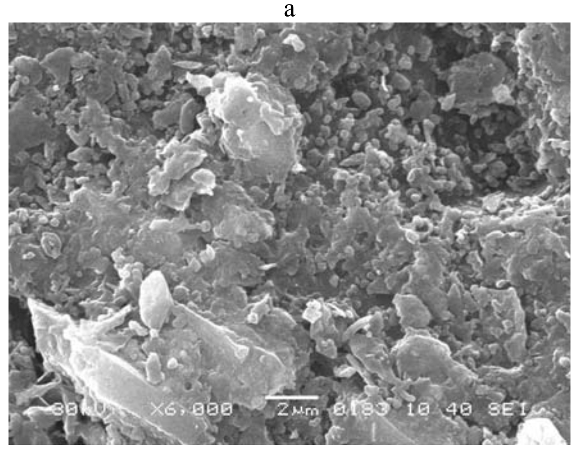

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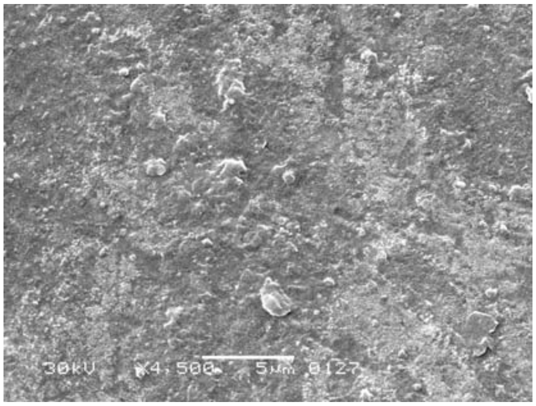
Fig. 4: SEM micrographs showing the surface morphology of the epoxy coating system after natural exposure testing at industrial site



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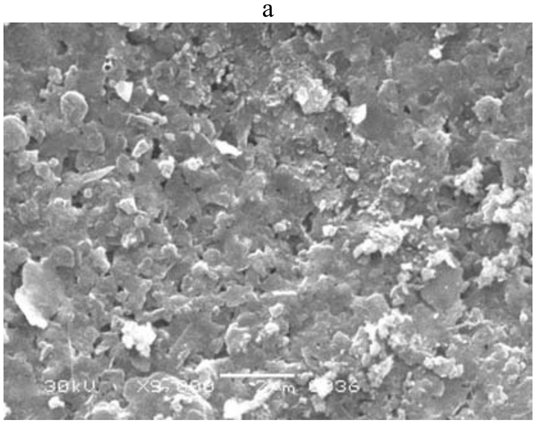

b

Fig. 5: SEM micrographs showing the surface morphology of the epoxy coating system after natural exposure testing at urban site.

Fig. 6 shows the comparison of the EDX spectra of the unexposed and exposed epoxy coating systems and Table-3 presents the surface composition data of epoxy coating systems as determined by EDX analysis. EDX analysis showed the presence of C, O, Al, Si, Cl, Ca, Ti, and Fe in the unexposed coating. In order to find the correlation between the unexposed and exposed coating systems, Principle of component analysis (PCA is a method of statistics) was applied on the data obtained from EDX analysis, Fig. 7. Graph shows that no correlation was observed for carbon, oxygen, silicon and titanium and the major chemical change occurred in the mass% of C and O.

Fig. 8 shows the comparison of O/C (oxygen/carbon) ratio as determined by EDX analysis for unexposed and exposed epoxy coating systems. This indicated the raise in O/C ratio of the exposed coatings as compared to unexposed coating. Particularly, O/C ratio after natural exposure testing at industrial site is higher than that of the O/C ratio obtained after natural exposure testing at urban site. This was due to the high degradation of coating material in industrial environment. X.F. yang, *et al.* [28] suggested that the increase in O/C ratio is due to the reaction of environmental oxygen with the coating which results in oxidation of coating. Several photo-oxidation products form as a result of oxidation of coating [29].

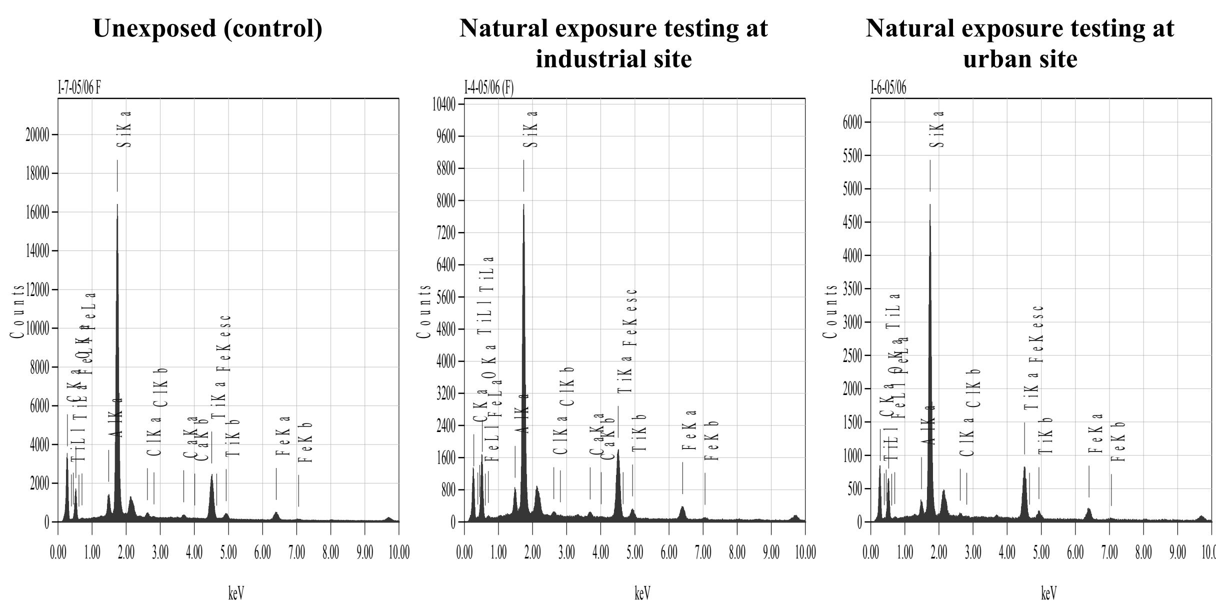

Fig. 6: Comparison of the EDX spectra of the epoxy coating systems a) unexposed b) after natural exposure testing at industrial site and c) after natural exposure testing at urban site.

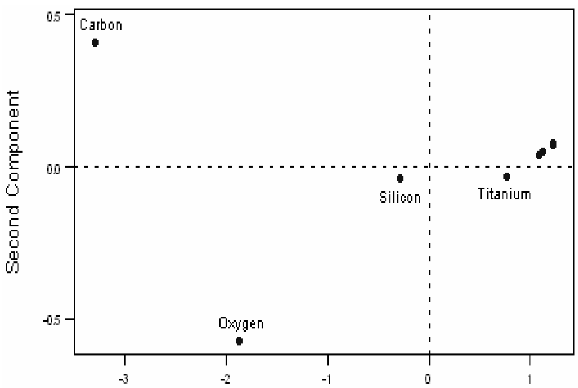

Fig. 7: Graph after the application of PCA on the data obtained from EDX analysis.

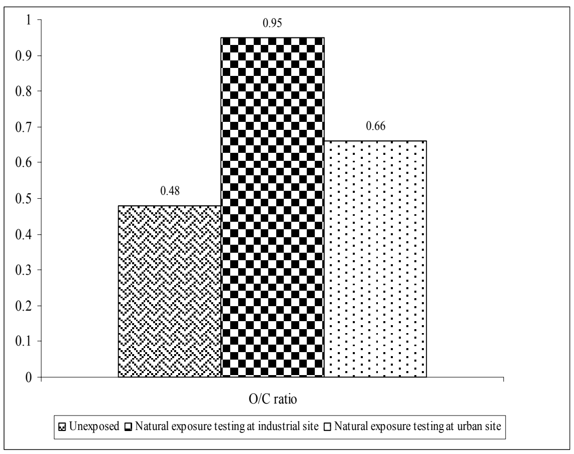

Fig. 8: Comparison of O/C (oxygen/carbon) ratio as determined by EDX analysis for epoxy coating systems.

Correlation Between Gloss Measurement and SEM Results

Good correlation was observed between gloss measurement and SEM results. Natural exposure testing at industrial site indicated high degradation of the surface of epoxy coating as compared to testing at urban site (Fig. 4 and 5). This surface roughening explained the decrease in gloss for the epoxy coating system exposed at industrial test site (Table-2). This was consistent with the finding of F.X. Perrin, et al [27]. They related the loss of gloss with the increase of the surface roughening for the coating systems.

Fourier Transform Infrared (FTIR) Spectroscopy

The IR spectrum of unexposed epoxy coating system (Mild steel/Epoxy-polyamide primer/ Epoxy-amine topcoat system), (Fig. 9. [a]) showed a band due to O-H stretching near 3420cm^{-1}. The band located around 3036cm^{-1} was due to aromatic C-H stretching. Aliphatic C-H stretching was observed in the region of 2800-2962cm^{-1}. The bands in the region of 1500-1600cm^{-1} were due to C=C stretching of aromatic nucleus (benzene ring). C-O stretching vibration of aryl ether was observed near 1246cm^{-1} and the band near1038cm^{-1} was due to aliphatic C-O stretching. The band at 829cm^{-1} was due to the 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 500-575cm^{-1} [30, 31].

Natural exposure testing at industrial site showed decrease in the peak intensities of C-O stretching vibration of aryl ether near 1250cm^{-1} and C=C stretching of aromatic nucleus in the region of 1500-1600cm^{-1}, (Fig. 9. [b]). It was an indication that chain scission and mass loss in the coating have taken place. The spectrum also showed the formation of new chemical species having peaks in the region of 1620-1800cm^{-1}. Due to the formation of oxidation products, two prominent bands at 1658cm^{-1} and 1725cm^{-1} were observed, which could be attributed to C=O stretching of ketone and C=O stretching of amide respectively. The carbonyl band at 1725cm^{-1} has been attributed to the formation of ketone products by Bellinger [14] or to aldehyde formation by Petterson- Jones [13]. In either case the products are formed by the release of water molecules by dehydration of the hydroxyl groups.

Natural exposure testing at urban site revealed changes in the similar regions ,however, the changes were less severe as compared to natural exposure testing at industrial site, (Fig. 9. [c]). In this case, less decrease in the peak intensities of the C-O stretching vibration of aryl ether near 1250cm^{-1} and C=C stretching of aromatic nucleus in the region of 1500-1600cm^{-1} were observed. This was an indication of less chemical degradation of the epoxy coating system due to natural exposure testing at urban site.

Correlation Between EDX Analysis and Infrared Results

EDX analysis illustrated high O/C ratio obtained for epoxy coating system exposed at industrial test site which correspond to increase photo-degradation of coating (Fig. 8). Fourier transform infrared spectroscopy also revealed high oxidation of coating's material and formation of oxidation products for the epoxy coating system exposed at industrial test site (Fig. 9b).

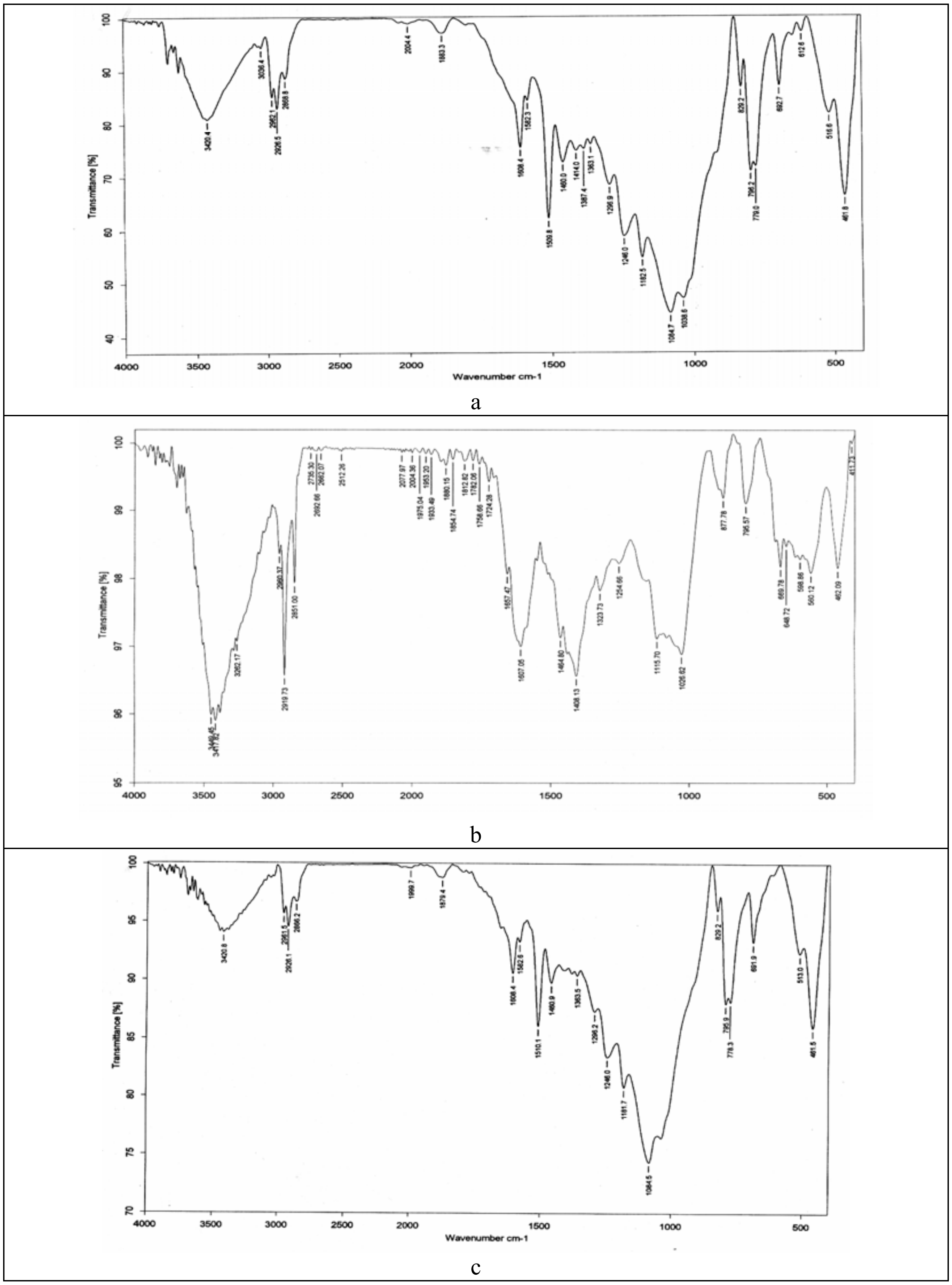

Fig. 9 Infrared spectra of Epoxy coating systems a) unexposed b) after natural exposure testing at industrial site and c) after natural exposure testing at urban site.

Experimental

Materials Preparation

The substrate was a 1.2mm thick with a size of 4"x 6" mild steel which was provided by Hino Pak Motors Limited (Body Operation Plant). The coating used in this study was commercially available epoxy-polyamide primer/ epoxy-amine topcoat coating system. Prior to application of the coating, the mild steel surface was degreased with suitable solvent [32] followed by pretreatment with 5% $Zn_3(PO_4)_2$ + 15%

H_3PO_4 solution . After surface preparation substrate was coated with the corresponding coating system according to the manufacturer's recommendations. This was followed by the drying of coated panels in air. Then the dry film thickness measurements were performed using Elcometer 456 digital coating thickness gauge (ASTM D1186) [33] and average dry film thickness was calculated. Table-4 presents the main characteristics of epoxy coating system tested along with average dry film thickness. In order to test resistance to the under film corrosion, the bottom of each dried and cured coated panel was scribed with an X. One set of coated panel was kept as control.

Exposure Method

Natural exposure test was performed at two exposure test sites in Karachi, Pakistan (industrial and urban) according to ISO 8565 norm [34] by mounting the coated panels on exposure racks. Table-5 present the characteristics of natural exposure test sites.

Assessment of the Degradation of Coating

Visual evaluation of the degradation of the coating in the scribed region on coated panels was done according to ISO 4628 norm [20]. Following assessment tests were performed from time to time: blistering [21], rusting [22] and cracking [23].

Photographs of the unexposed (control) and exposed test panels were taken for the comparison of the changes experienced by coating.

Gloss Measurement

Horiba IG-331 Gloss checker was used for the gloss measurement of unexposed (control) and exposed panels (ISO 2813) [35]. For this purpose, the samples were cleaned and 60^0 gloss was measured. The data presented are the average of three measurements.

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

In order to study the changes in the surface characteristics, small sections of the unexposed (control) and exposed coating systems were coated with gold up to $300A^0$ using a gold coater (JEOL JFC 1500). For imaging and EDX analysis, scanning electron microscope (JEOL 6380A), equipped with an X-ray detector for energy dispersive X-ray analysis (EDX) was operated at 10^{-7} Torr vacuum and a 30 kV voltage.

Fourier Transform Infrared Spectroscopy (FTIR)

Chemical changes in the coatings exposed at two natural exposure test sites were studied by Fourier transform infrared spectroscopy (FTIR). Infrared spectrum was also taken for unexposed (control) coating system. Coatings 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 $2cm^{-1}$ and 20 scans.

Conclusions

Coating industries are interested in the production of coatings with good service life. They usually evaluate the coatings in short time by accelerated test methods because natural exposure testing usually takes a long time but it provides ideal evaluation.

In this work a combination of different methods and measurements were used to evaluate the degradation of epoxy coating systems exposed at two natural exposure test sites (industrial and urban) located in Karachi, Pakistan. The coating's degradation was determined by visual evaluation, gloss measurement followed by both SEM/EDX analysis and FTIR spectroscopy.

Table-4: Main composition of epoxy coating system tested.

Primer		Topcoat		Generic Type	Total Average
Resin or binder type	Pigments	Resin or binder type	Pigments		DFT* (µm)
Epoxy-Polyamide	Iron oxide, Zinc phosphate and others	Epoxy-Amine	Titanium dioxide, Iron oxide and others	Epoxy	198

* = Dry film thickness; µm = micrometers; 1 µm÷25.4 =1 mil

Table-5: Characteristics of natural exposure test sites.

Type of test site	Latitude	Longitude	Elevation [m]
Industrial	$24^0$54′ 12.08″ N	$67^0$00′34.21″ E	19.51
Urban	$24^0$56′ 40.37″ N	$67^0$00′34.21″ E	45.72

It was apparent from the results of visual evaluation in Table-1 that major modes of degradation were completely different at two natural exposure test sites. Good correlation was observed between gloss measurement and SEM results. The evidences provided by gloss measurement and SEM were not enough to describe the level of degradation of coating. Hence the data obtained by EDX analysis is of prime importance for the coating's manufacturer for the improvement of coating's performance as well as for the development of new coatings. Authentication of the soundness of EDX analysis was also established by correlating with the FTIR studies.

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