

Performance evaluation of polyaniline pigmented epoxy coating for corrosion protection of steel in concrete environment

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Abstract

Corrosion protection of mild steel reinforcement offered by a newly developed epoxy based coating system containing inherently conducting polyaniline as one of the pigments has been studied. The synthesis of polyaniline and preparation of epoxy based coating system containing this polyaniline are described here. The corrosion resistant property of epoxy polyaniline system, coated on mild steel was evaluated by various techniques such as electrochemical impedance spectroscopy, potential time studies, cathodic disbondment test, anodic polarization study, salt spray test and chemical resistance test. The corrosion resistance of epoxy polyaniline coating system coated on reinforcement bars embedded in concrete was also studied by an accelerated time to cracking study. The formation of polyaniline was characterized using FTIR, UV, GPC, particle size analyzer and fineness studies. Electrochemical impedance studies reveal that the resistance of the coating decreased initially and then increased due to passivating ability of the polyaniline pigment. Based on the results of different techniques, it is found that epoxy coating with polyaniline pigment is effective in corrosion protection of steel in concrete environment.

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1. Introduction

Durability is the global problem prevailing in the reinforced concrete structures. Normally, the design life of a reinforced concrete structure is about 60 years. In recent days, the instances of failures indicate that failures occur within 10–20 years. Thus, the durability of concrete structures is adversely affected, i.e., the actual trouble free life of structures in aggressive environment is only about one-fifth of the design life. The main reason for lack of durability of concrete structures is corrosion damage to the rebar embedded in concrete. The two most common causes of reinforcement corrosion are (a) localized breakdown of passive film on the steel by chloride ions and (b) general breakdown of passivity by neutralization of the concrete, predominantly by reaction with atmospheric carbon dioxide [1,2].

According to a 1997 report, of the 581,862 bridges in and off the USA federal aid systems, about 101,518 bridges were rated as structurally deficient. The average annual cost, through year 2011, for just maintaining the overall bridge conditions, i.e., the

total number and the distribution of structurally and functionally deficient bridges, was estimated to be US\$ 5.2 billions. The magnitude of this corrosion problem in the construction industry has increased significantly in the last 3 decades and is likely to keep increasing.

Given the importance of the costs associated with the construction industry, it is very much essential to adopt all possible methods to control corrosion in concrete structures. Use of good construction design and procedures, adequate concrete cover depth, corrosion inhibiting admixtures and low permeability concrete alone will not abate the corrosion problem, because concrete has a tendency to crack inordinately. This situation essentially leaves the reinforcing steel itself as the line of defense against corrosion. For this reason, use of a coating system on the reinforcing steel is critical in abating this costly corrosion problem.

Extensive research has been done and many protective coating systems have been developed and tried so far all over the world. Metallic coating like galvanizing, nickel, etc., non-metallic coating like fusion bonded epoxy and cement based coating are some of the examples of the coating systems, which are most widely used with advantages and limitations [3–8]. In recent years, there has been an increasing use of galvanizing

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as a protective method against corrosion of reinforcing steel, particularly in UK and USA. Many researchers evaluated a few non-metallic coatings and suggested that fusion bonded epoxy coating could be considered as a protective coating for reinforcing steel. Cement based coatings are also adopted for corrosion protection of rebars embedded in concrete. However, many adverse reports have been presented by various researchers for these coating systems [9–11].

It is reported that most of the organic coatings have pinholes and accelerated corrosion of steel takes place through pinholes. In order to prevent the corrosion of steel in pinholes, coating system containing conducting polymer such as polyaniline is highly useful. Conducting polymers had been the topic of the large number of investigators during last decades. Their unique properties such as mechanical strength, electrical conductivity, corrosion stability and possibility of both chemical and electrochemical synthesis make them useful in wide area of applications [12,13].

The first documented observations of corrosion protection of steel by polyaniline were reported in 1981 [14]. Since then a number of research papers have been published on the corrosion protection of carbon steel, stainless steel, mild steel, titanium, copper and aluminum with inherently conducting polymers [15–26]. It has been reported that polyaniline containing coating is able to protect steel in acid and neutral environments [27,28]. It has also been shown that the coating containing polyaniline is able to protect the scratches and pin holes in the coating by repassivation of exposed areas [29]. The application of electro polymerized coating and polymer pigmented coating has been recently reviewed [30].

Eventhough a lot of literature is available about the protective ability of polyaniline for different steel, no report is available on the usage of polyaniline containing coating for protection of steel reinforcements in concrete. This paper describes the preparation of polyaniline and its characteristics. In addition, the corrosion performance of the developed coating system based on epoxy containing the inherently conducting polymer ‘polyaniline’ coated on the reinforcement bars has been reported.

2. Materials adopted

2.1. Materials

Aniline, ammonium per sulphate, sodium chloride, hydrochloric acid of AR grade chemicals were used as received. Technical grade Xylene, Titanium-di-oxide, Silica, Talc, Ammonium Stearate were used without further purification. Technical grade epoxy resin 6071 (Ciba Geigy) and methyl iso butyl ketone (MIBK) solvent were procured and the same were used as such. Triple distilled water was used for preparation of simulated concrete environment. Portland Pozzolana Cement conforming to IS 456–2000 was used in concrete. Local clean river sand conforming to grading zone III of IS 383-1970 was used as graded fine aggregate. Locally available aggregates conforming to graded aggregates of normal size greater than 4.75 mm and less than 10 mm of IS 456-2000 was used as graded coarse aggregates. Ordinary mild steel cylindrical rod with physical property of

UTS 380–420 MPa and yield stress 235–260 MPa was used as reinforcement bar throughout this study.

2.2. Synthesis of polyaniline pigment

Polymer based on conducting aniline has been synthesized by chemical oxidation using standard bench method. Aniline solution was made by adding 20 ml of aniline to 300 ml of hydrochloric acid (1 M) solution. The oxidant solution was prepared by dissolving 11 gms of ammonium peroxydisulfate in 200 ml of 1 M hydrochloric acid solution. Both solutions were precooled to 0 °C in an ice bath. The aniline solution was taken in a beaker and placed in an ice bath on a magnetic stirring plate. The oxidant solution was added within 1 min to the aniline solution while stirring it continuously. The mixture was stirred in the ice bath for about 2 h for ensuring complete polymerization. After this, a dark green precipitate was obtained by filtering the mixture. The precipitate was repeatedly washed with distilled water to remove the excess of acid content and dried at 80 °C in an oven. The emeraldine salt powder of polyaniline was finally obtained by grinding using mortar and pestle and then used as one of the pigments in coating system.

2.3. Preparation of polyaniline containing epoxy system and its application on mild steel specimens

The epoxy resin of epoxy equivalent 480–500 was refluxed with Xylene, MIBK, Cellosolve solvent mixture to get a homogenous binder solution. Anatase titanium-di-oxide, passivating polyaniline pigment, silica, talc were pre-mixed along with aluminium stearate using an attritier for 30 min. These pre-mixed pigments were slowly added to the binder solution and charged in a ball mill. The ball mill was run for 48 h. The coating was then removed from the ball mill and stored in an air tight container (Base). Polyamide hardener with an amine value of 280–320 KOH/g was mixed with Xylene MIBK solvent mixture and stored in an air tight container separately (Hardener). The base and hardener were mixed in a fixed ratio (3:1) and the coating was stirred well for 15 min before application.

The mild steel specimens were coated with this newly developed epoxy polyaniline coating system by brushing. Before application of this coating system, the surface of the specimens was sand blasted to Sa 2 1/2. The coated specimens were then allowed to cure for a period of 7 days at ambient temperature. The thickness of the coating was measured using a coating thickness meter (Elektro Physik) and it was $90 \pm 10 \mu\text{m}$. After curing period, the specimens were subjected to various evaluation techniques.

2.4. Preparation of simulated concrete environment

Simulated concrete test solution was prepared with Portland Pozzolana Cement (PPC). At first 100 g of PPC was transferred to the 250 ml conical flask. Then 100 ml of triple distilled water was added to the cement and thoroughly mixed. The conical flasks containing cement and water mixture were rigidly fixed in

the spring-mounted clamps of the electronic shaker. This shaker was run for 1 h, and then the cement water mixture was filtered through No.1 Whatman filter paper. The pH of the filtered solution was measured using a digital pH meter Model 111E and it was 12.25. This pH value reflects the actual pH value of actual concrete, which normally lies “between 12 and 13”. Hence, this filtered solution was known as simulated concrete environment or cement extract (CE). This cement extract was used through out this study.

3. Experimental

3.1. Characterization of polyaniline pigment

In order to know the formation of polyaniline pigment, various characterization techniques were employed on the synthesized polymer. Fourier Transform Infrared Technique using FTIR Spectrophotometer (Thermo Nicolet, 380) and UV–vis NIR double beam spectrophotometer (Varian Cary 500) were employed for characterization. The molecular weight of the synthesized polymer was found using Gel Permeation Chromatography (GPC). Particle size analysis on the above synthesized polymer was carried out by HORIBALA–910 laser scattering particle size distribution analyzer. The fineness of the pigment was determined using HEGMAN Gauge. The nature of the pigment was found by carrying out the conductivity test using four probe technique.

3.2. Electrochemical studies in aqueous environment

3.2.1. Electrochemical impedance spectroscopy (EIS) study

Mild steel panel of size 15 cm × 10 cm × 0.2 cm coated with epoxy polyaniline system was used in this study. A glass tube of 1.2 cm diameter and 3 cm height was fixed on the coated sample using an adhesive (M-seal) and filled with cement extract. Electrochemical impedance spectroscopy measurements were performed on a three electrode corrosion cell, using electrochemical impedance analyzer (Model 6310 EG&G). A platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The experimental setup for this study is given in Fig. 1. The EIS spectrum was collected over a frequency range of 0.01–10,000 Hz using an ac signal of amplitude of 20 mV at the rest potential. The coat-

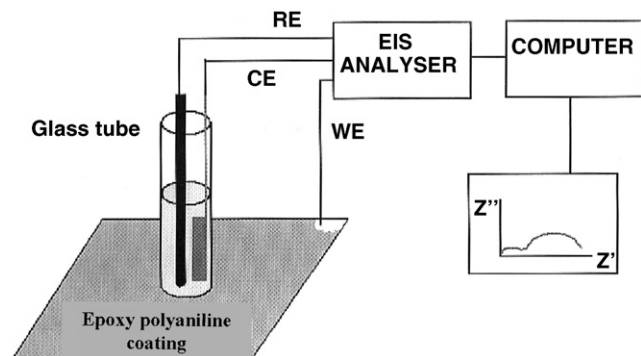


Fig. 1. Configuration of EIS set up.

ing resistance (R_c) and coating capacitance (C_c) were directly obtained from the Bode plots using Z view software. From this value, the corrosion behaviour of epoxy polyaniline system was assessed. This measurement was taken on the coated panels up to 77 days.

3.2.2. Potential–time study

The corrosion resistance of epoxy polyaniline coating was examined by measuring the potential of coated panel exposed in cement extract. Mild steel panel of size 15 cm × 10 cm × 0.2 cm coated with epoxy polyaniline system was used in this study. A surface area of 1 cm² was glued with epoxy adduct as working electrode. A glass tube of 1.2 cm diameter and 3 cm height was fixed on the coated panel for this purpose. Then, this tube was filled with cement extract and a saturated calomel electrode was placed inside the tube. The change in potential of coated panel with time was measured by making electrical contact between saturated calomel electrode and the painted panel through a high impedance voltmeter. Up to 90 days, potential measurements were carried out on coated panels. Similarly, potential measurements were also carried out up to 90 days on uncoated specimens exposed in cement extract.

3.3. Accelerated studies in aqueous environment

3.3.1. Anodic polarization technique

The tolerance to chloride attack was studied on mild steel rebar coated with the developed epoxy polyaniline coating. Mild steel specimen of size 1 cm diameter and 7.5 cm length was coated with this system. Then it was immersed in the cement extract that was premixed with 1000 ppm of chloride, which is the tolerable limit for chloride in concrete. Hence this study was conducted at this chloride level. Five square centimeter area of the coated specimen was exposed in chloride contaminated cement extract and the remaining portions were completely covered with lacquer. Using a current regulator (0–100 mA), the coated rebar was anodically polarized by applying a current density of 290 $\mu\text{A}/\text{cm}^2$ using platinum electrode as auxiliary electrode. The change in potential of coated specimen with time was measured against a saturated calomel reference electrode for 5 min using a high impedance voltmeter. Similarly this study was also carried out on the uncoated specimens exposed in chloride contaminated cement extract.

3.3.2. Salt spray exposure

This study was carried out as per ASTM B117 standard. Mild steel panels of size 7.5 cm × 5 cm × 0.2 cm coated with epoxy polyaniline system were suspended in the salt spray chamber at an angle of 15° to horizontal. 5% salt solution, which approximates the salinity of salt water was prepared and sprayed by atomizer with a nozzle pressure of 10–12 psi. During the test, the chamber was sealed air tight. The temperature and humidity inside the chamber were maintained at 35 ± 2 °C and 97 ± 1%, respectively, throughout the test period of 1000 h. The condition of the coated panels was closely examined periodically for any surface change by visual inspection.

3.3.3. Chemical resistance test

This test was carried out as per ASTM A775/A775M-94d standard. Epoxy polyaniline coated mild steel reinforcement bars of length 10 and 1 cm diameter were used in this study. The top and bottom edges were completely protected with lacquer. Three molar calcium chloride, 3 M sodium hydroxide, saturated calcium hydroxide and distilled water were prepared as individual test solutions and they were filled in the separate glass container up to the half of its height. The coated rebars in triplicate were partially immersed in each test solution, so that they were in long term contact with both liquid and vapour phase of the test solution. The glass container was completely sealed and they were kept at ambient temperature. The coated rebars were kept in the above condition for 45 days. Every 24 h, the surface condition of coated rebars was examined for appearance of blisters, disbondment from base metal or any coating defect throughout the test period.

3.3.4. Cathodic disbondment test

The resistance of the coating against chloride permeation was tested as per ASTM A775/A775M-94d standard. Two identical mild steel rebars of 1 cm diameter and 100 cm length were coated with epoxy polyaniline system. After curing period of coating was over, one end of the rebars was soldered with insulated copper electrical wire to serve as electrical contact point. The other end of the rebars was protected with an insulating material to a length of 2.5 cm. The coated rebars were suspended vertically in a transparent non-conductive plastic container of size 15 cm × 15 cm × 90 cm. The container was filled to a height of 80 cm with an aqueous solution of 7% sodium chloride. The coated rebars were suspended vertically so as to have a clearance of 2.5 cm from the bottom, 4 cm from each side and 4 cm in between the rebars. The exposed area of the rebar on which the test was conducted was 240 cm². In this test, one rebar acts as anode and the other rebar acts as cathode. A potential of 2 V was impressed between the epoxy-polyaniline coated rebars for a period of 60 min using a DC regulated power source (Aplab L3220S). The voltage between the coated rods was measured by a high impedance voltmeter. The current was measured for every 5 min intervals using an Avometer. After the test was over, the surface condition of the one rebar, which act as anode was visually examined for any corrosion products of iron. The other rebar, which act as cathode was also visually examined for any coating failure as evidenced by evolution of hydrogen. This test was also carried out on the uncoated rebars.

3.4. Study on concrete specimens

3.4.1. Time to cracking study

Cylindrical concrete specimens of size 5 mm × 15 mm with design strength of 20 MPa were cast for this study. The experimental setup for this study is given in Fig. 2. One centimeter diameter and 15 cm length mild steel rebar coated with epoxy polyaniline system was used as reinforcement bar. One end of the coated rebar was soldered with insulated copper electrical wire to serve as electrical contact point. The other end of the rebar was protected with an insulating material to a length of 2.5 cm.



Fig. 2. Experimental setup for time to cracking study.

This coated rebar was centrally positioned in the concrete during casting and kept in potable water for 7 days at ambient temperature. Afterwards, the reinforced concrete specimen was kept in a glass container. A cylindrical perforated stainless steel auxiliary electrode of size 10 cm diameter and 15 cm height was also kept in the glass container and then it was filled to a height of 15 cm with an aqueous solution of 3.5% sodium chloride. Similarly, this test was also performed on the concrete specimen with uncoated reinforcement bar.

In this test, the embedded reinforcement specimen acted as anode and the external stainless steel cylindrical electrode served as cathode. A constant potential of 6 V was applied between the embedded rebar and stainless steel electrode using a DC power source unit (Aplab L3220S). Then, using an Avometer, variation of current with time was measured every 12 h. During the test period, the reinforced concrete specimens were visually examined for cracking of concrete every 24 h. An increase in current indicates the onset of corrosion and cracking of the concrete is visible there after.

4. Results and discussion

The UV–vis and FTIR spectrum of polyaniline pigment are given in Figs. 3 and 4, respectively. The UV–vis spectrum shows the absorption peak at 336 nm showing the π – π^* transition in the benzenoid ring and 578 nm shows the donor–acceptor interaction of quinonoid ring. The well known cation radicals and localized polaron peaks were observed at 449 and 775 nm.

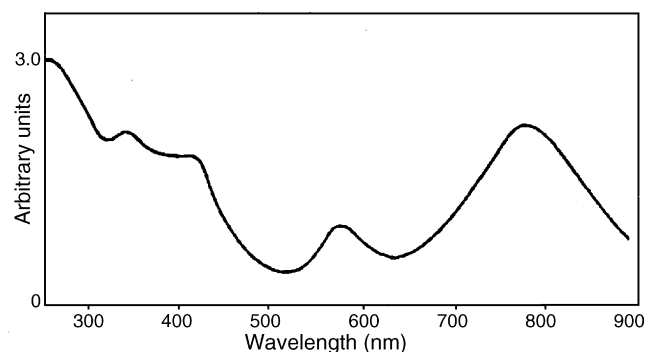


Fig. 3. UV–vis spectrum of polyaniline pigment.

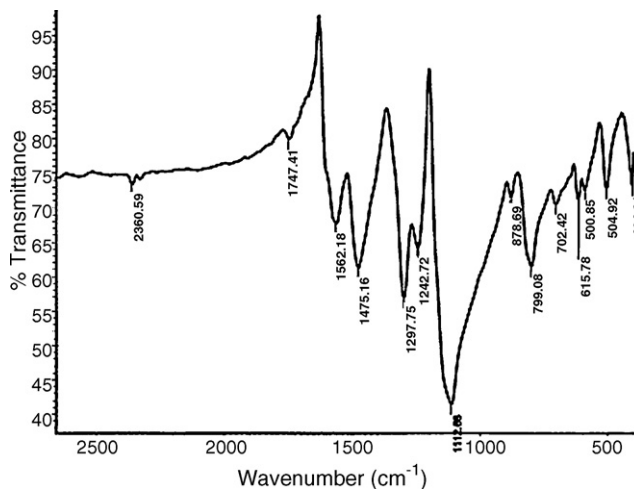


Fig. 4. FTIR spectrum of polyaniline pigment.

From FTIR spectrum, it is found that the major IR absorption bands at 1555 and 1453 cm^{-1} are the characteristic bands due to nitrogen-quinonoid ring structure and peaks for polyaniline are observed at 1632 cm^{-1} , for N–H bending, 1555 and 1494 cm^{-1} for nitrogen benzenoid–quinonoid ring structure, the other IR characteristics are observed at 1126 and 1036 cm^{-1} . Result of Gel Permeation Chromatography reveals that the molecular weight of synthesized polymer was 16,260. HORIBALA–910 laser scattering particle size distribution analyzer give a particle size of 7–10 μm for the synthesized polymer. The fineness of the pigment was found between 8 and 9 using HEGMAN Gauge. Four probe technique reveals that the conductivity of synthesized polymer was 0.02–0.03 S/cm.

The corrosion performance of the epoxy polyaniline coating exposed in cement extract has been found out by impedance measurements for a period of 77 days. The Bode plot recorded for mild steel coated with epoxy polyaniline system is given in Fig. 5. The coating resistance (R_c) and the coating capacitance (C_c) values of the coating obtained by using the equivalent circuit shown in Fig. 6 are given in Table 1. Initially the R_c value of the coating is 13.3 $\text{M}\Omega \text{cm}^2$ and it is decreased to 0.293 $\text{M}\Omega \text{cm}^2$ after 1 day immersion. This reduction in R_c value could be due to penetration of electrolyte through the pinholes present in the coating system. From second day onwards the R_c value of the coating started to increase steadily and reached a value of

Table 1
Impedance parameters of epoxy polyaniline coating on mild steel exposed in cement extract

Time (days)	R_c ($\text{M}\Omega \text{cm}^2$)	C_c (nF cm^{-2})
Initial	13.30	0.508
1	0.239	1.85
2	0.316	1.57
6	0.455	1.98
13	0.574	1.27
27	1.420	0.988
34	1.710	1.05
49	1.830	0.866
77	2.110	0.703

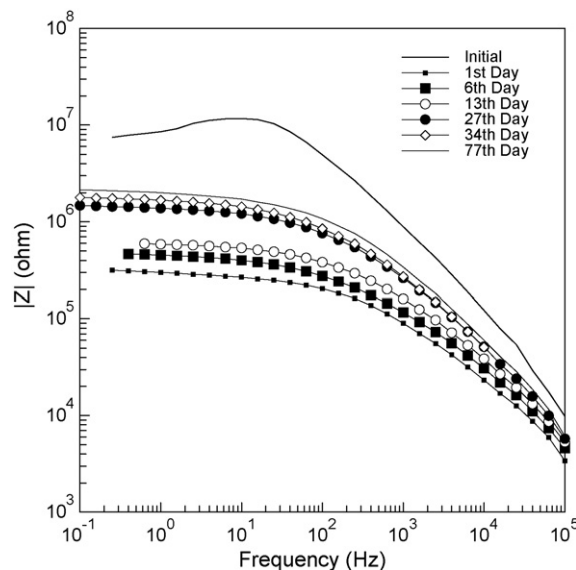


Fig. 5. Bode plot for epoxy polyaniline coated mild steel exposed in cement extract.

2.11 $\text{M}\Omega \text{cm}^2$ at the end of 77 days of exposure. This increase in R_c value with time is due to repassivation of base metal by the polyaniline pigment in the coating system. Similarly the capacitance of the coating is increased from 0.5 to 1.8 nF/cm^2 after 1 day of exposure and reached 0.703 nF/cm^2 after 77 days of exposure. The high R_c and low C_c values of the coating with progress of time indicate the protective nature of epoxy polyaniline coating.

Normally, polyaniline is a conductive polymer, which confers active protection by exchanging electrons with the metallic substrate. Electrons produced by oxidation of the metal at a corrosion site flow to the surrounding metal surface and are consumed by an oxygen-reduction reaction. If polyaniline coating is present on the metal surface, the electrochemistry during localized corrosion could occur differently. It was postulated that an electronically conductive polymer stabilizes the potential of the metal in the passive regime, maintaining a protective oxide layer on the metal. Oxygen reduction on the polymer coating is thought to replenish the polymer charge consumed by the metal dissolution, thereby stabilizing the potential of the base metal in the passive region and minimizing the rate of metal dissolution.

Fig. 7 illustrates the electrochemistry that occurs at the pinhole if any on the metal/polyaniline coating system. The

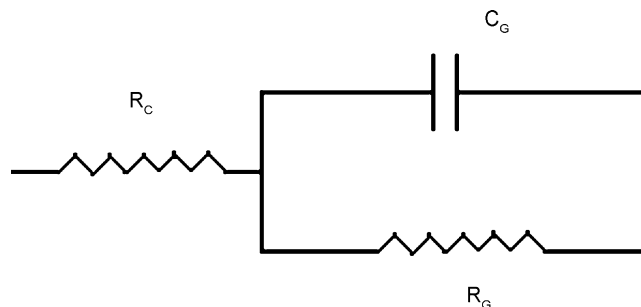


Fig. 6. Equivalent circuit for epoxy polyaniline coating on mild steel.

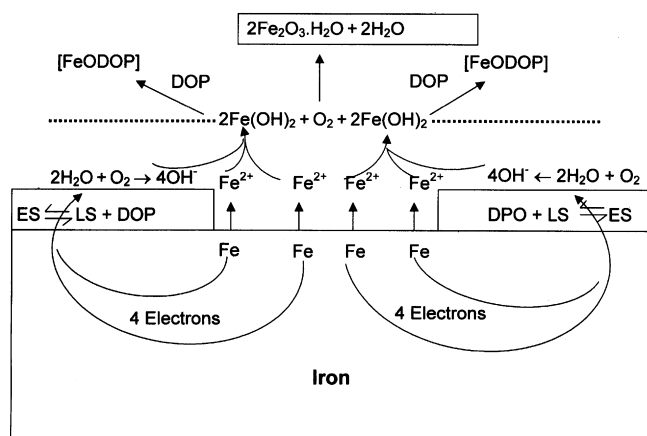


Fig. 7. Schematic diagram of mechanism of passivation occurring on epoxy polyaniline coated mild steel exposed in cement extract.

following redox reactions take place simultaneously both at metal/polymer interface and at polymer/solution interface [31]. At metal/polymer interface, the redox reaction can be expressed as



In this study, polyaniline is an HCl doped emeraldine salt. The oxidized metal ions can be converted into a protective oxide layer, incorporating oxygen diffused into the coating. At the polymer/solution interface, the following redox reaction can compensate for the consumption of an electron in the polyaniline coating.



The open circuit potential (E_{ocp}) of epoxy polyaniline coated and uncoated mild steel was monitored with time in cement extract. The diagram representing E_{ocp} -time variation for coated and uncoated mild steel is given in Fig. 8. In uncoated specimen, the initial potential was -315 mV. With time, the potential move towards cathodic direction and reaches a maximum potential

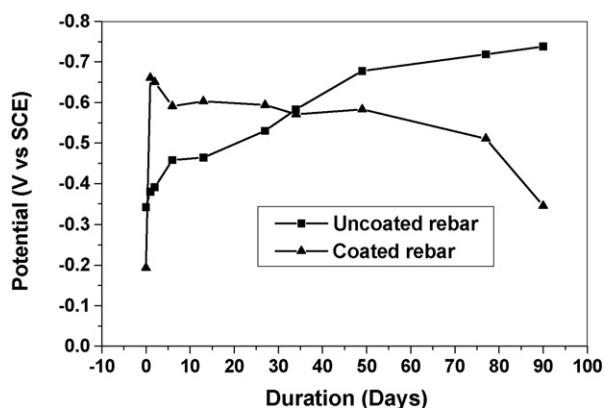


Fig. 8. Potential time behaviour of uncoated and epoxy polyaniline coated mild steel exposed in cement extract.

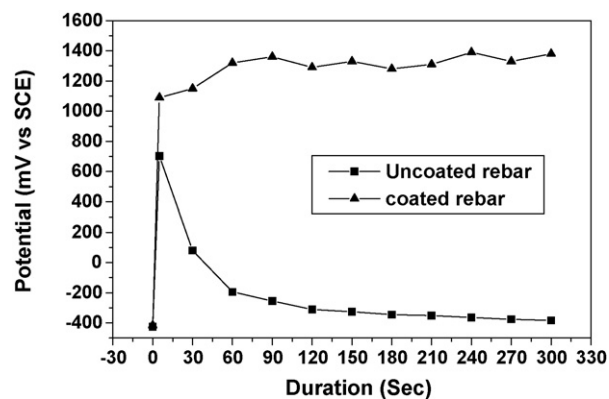


Fig. 9. Anodic polarization behaviour of uncoated and epoxy polyaniline coated rebar exposed in cement extract with 1000 ppm of chloride.

value of -720 mV after 90 days. Throughout the test period, the potential of uncoated specimen increases with time. Whereas on epoxy polyaniline coated specimen, the initial E_{ocp} value was measured to be -193 mV versus SCE. In the beginning the potential value is shifted towards active direction and reached a very high potential of -661 mV at the end of 24 h. This increase in potential value indicates the diffusion of electrolyte through the pinholes in the coating. With time, the potential has shifted towards noble direction and reached a higher value of -354 mV after 90 days. The higher value even after 90 days of immersion in cement extract is an indication of higher protective ability of the coating. The higher potential value is due to the formation of passive film on steel substrate by polyaniline pigment.

The variation of potential of uncoated and epoxy polyaniline coated rebar exposed in chloride containing cement extract during anodic polarization test is shown in Fig. 9. In the case of uncoated specimen exposed in chloride containing cement extract, the open circuit potential of mild steel rebar was -0.424 V. After impressing current, the potential rises to $+0.703$ V. Hereafter, the potential value was drastically reduced within a short period of 30 s and moved towards cathodic direction. At the end of the test period, a potential value of -0.384 V was obtained. It can also be seen from the figure that the initial potential of coated rebar was -0.416 V. Once the current was applied, the potential of rebar was shifted towards the anodic direction and immediately reaches 1.09 V, which is higher than the oxygen evolution potential. In this rebar, a high positive potential value in the order of around $+1.30$ V was maintained throughout the test period. If any breakdown occurs on the coating due to the conjoint action of added chloride and applied current, sudden fall in the potential value will be observed as in the case of uncoated specimen. But no such instance occurred in this system. This indicates the passive state of the coated rebar even under accelerated condition. The visual observations on the rebar specimens revealed that no rust spot or failure of coating system was observed on the epoxy polyaniline coated rebar immersed in chloride containing cement extract. This indicates the impermeable property of the newly developed epoxy polyaniline coating system.

The results of various evaluation techniques such as cathodic disbondment test, chemical resistance test and salt spray test are

Table 2
Results of cathodic disbondment, chemical resistance and salt spray, studies

Evaluation technique	Environment studied	Duration	Findings	
			Uncoated specimens	Coated specimens
Cathodic disbondment test	7% NaCl	60 min	Severe rusting was observed on anode rebar Hydrogen evolution occurred on cathode rebar Increase in current throughout test period	No rust formations on anode rebar No hydrogen evolutions on cathode rebar Current is 0.0 A throughout test period
Chemical resistance test	3 M CaCl ₂ , 3 M NaOH, Sat. Ca(OH) ₂ , distilled water	45 days	No blisters, chocking, coating peel off and formation of rust on the exposed coated rebars	
Salt spray exposure	5% NaCl	1000 h	No rust formation on coated specimens	

presented in Table 2. From the experimental results of cathodic disbondment test, it can be seen that the uncoated rebar shows severe corrosion on anode rebar and evolution of hydrogen occurs on the cathode rebar. The current also increased with time. The result of epoxy polyaniline coated rebar shows zero current throughout the test period indicating its resistive ability against the penetration of chloride ions. The visual observation also reveals that there is no hydrogen evolution on the cathode rebar surface. No rust products were found on the anode rebar surface (Fig. 10). These results clearly indicate the perfect protective nature of the epoxy polyaniline coating even in the presence of 7% chloride. The results of chemical resistance test reveals that there are no symptoms of any blisters, chocking, coating peel off and formation of rust spots on the epoxy polyaniline coated rebars, which indicates the better corrosion resistance in alkaline environmental conditions. It can be seen from the table that there is no formation of rust spot on the epoxy polyaniline coated panels even after 1000 h of exposure in salt spray test. This indicates the high corrosion resistant property of epoxy polyaniline coating in saline environment.

The current measured during the time to cracking study on concrete specimens embedded with uncoated specimen is shown in Fig. 11a (inserted figure). From the figure, it can be seen that the magnitude of current increased with time. The time taken for cracking of concrete was 4 days, where a maximum current flow of 52 mA was noticed. Thereafter fall in current was

observed. The current measured during time to cracking study on concrete specimens embedded with coated rebar is shown in Fig. 11. From the figure, it can be seen that the current flow is minimum up to 30 days of exposure. Increase in current indicates the coating failures on rebar due to chloride attack and decrease in the current value indicates the repassivation at corroded spots due to the presence of polyaniline. After 30 days, the current increased steadily and reaches a maximum value of 8.4 mA at

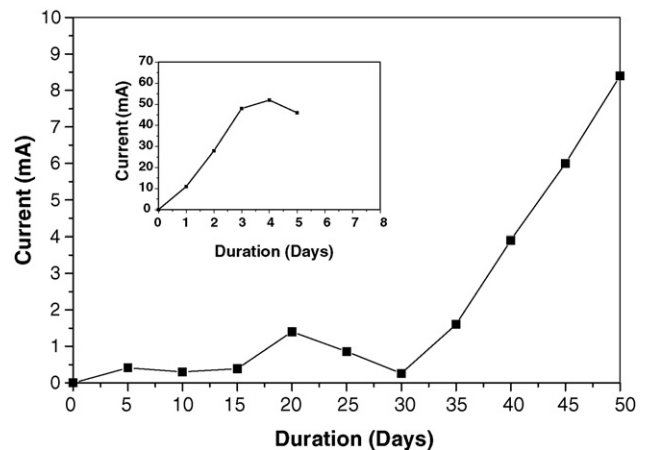


Fig. 11. Corrosion current measured at different time intervals during time to cracking study.



Fig. 10. Surface condition of rebar after cathodic disbondment test.

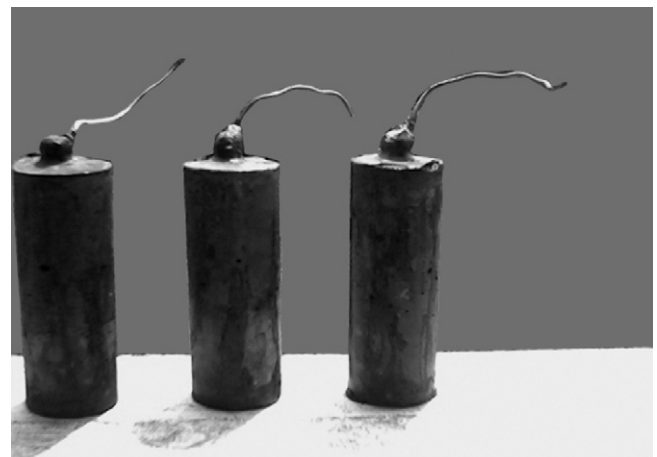


Fig. 12. Surface condition of concrete specimens after time to cracking study.

the end of 50 days. On 45th day rust products oozed out from the concrete and cracking of concrete was observed on 50th day (Fig. 12). Later the concrete specimen was broken open and the epoxy polyaniline coated rebar was visually examined. This observation reveals that the rust products appeared only at selected portions of the epoxy polyaniline coated rebar.

5. Conclusions

Corrosion protection of mild steel rebar by epoxy polyaniline coating system was studied. The performance evaluation studies were conducted under both aqueous and actual concrete environments. The coating system has shown appreciable corrosion protection properties at $90 \pm 10 \mu\text{m}$ thickness. Polyaniline was used as one of the pigments in the epoxy base system. Eventhough there is some reduction in R_c value initially due to penetration of electrolyte through the pinholes, increase in R_c value with progress of time was found. This is due to repassivation of base metal by the presence of polyaniline in the coating. This result was clearly indicated by the electrochemical impedance study. The potential time study has also reflected the above finding. Accelerated corrosion studies such as anodic polarization, cathodic disbondment test and salt spray test have clearly indicated the excellent corrosion resistant and impermeable property of epoxy polyaniline coating against chloride attack. In addition to the above properties, better alkali resistance property of the coating was also evidently showed by the chemical resistance study. Time to cracking study discloses that the newly developed coating is able to withstand more than 30 days for initiation of crack in concrete even in presence of 3.5% NaCl. The above results have obviously indicated appreciable corrosion resistant property of epoxy polyaniline coating system even under accelerated conditions.

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