

## Characterization and Development of Organic Coatings for Steel Rebars in Concrete

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### Abstract

Corrosion of the embedded steel reinforcements (rebars) in concrete is the major reason for the deterioration of concrete structures. One of the effective methods of overcoming this serious problem is by applying a barrier coating to the steel rebars. The barrier coating on steel rebars isolates the steel from the immediate environment and also acts as an insulator to prevent the corrosion. Four different coatings have been formulated using resins such as epoxy silicone-polyamide, polyester polyol-aromatic isocyanate, and acrylic polyol-aromatic isocyanate. These formulations consist of either ordinary portland cement (OPC) or fly ash as extender (pozzolanic pigments) and titanium dioxide (TiO<sub>2</sub>) and zinc phosphate as the main pigment. All these coatings have been studied for their barrier protection and other mechanical properties. Evaluation study of these coatings include Electrochemical Impedance Spectroscopy (EIS), chemical resistance tests and mechanical tests such as flexibility, impact resistance, adhesion, hardness and abrasion resistance, etc., as per ASTM standards and the results are discussed elaborately. It has been concluded from this study that the epoxy silicone-polyamide resin based coating formulation shows good mechanical properties in addition to the barrier protection to the steel rebars from the corrosive environments.

**Keywords:** organic coatings, rebars, corrosion, impedance, chemical resistance, fly ash.

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### Introduction

The deterioration of the structural concrete is mainly due to the corrosion of embedded steel reinforcements. Although the concrete is a strong and stone-like material, it contains many capillaries, gel pores and air voids. Therefore, under right conditions of temperature, relative humidity and airflow, it initiates the dissolution by attacking media thereby initiating an accumulation of aggressive species very near to steel reinforcements. When the threshold limit is reached by the progressive accumulation, the corrosion of steel is initiated and continues

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with the formation of corrosion products around the steel reinforcements. As a consequence, pressure will be exerted on the concrete and when this pressure exceeds the tensile strength of the concrete, the structure will start showing the disintegrity and deterioration in the form of cracks in concrete and spalling of concrete by exposing the reinforcements directly to the immediate environment. This problem will be more severe for the structures located in and around coastal and industrially polluted areas, as the density of aggressive species will be high in these locations.

Although there are many methods to control the reinforcement corrosion in concrete, the barrier protection to steel reinforcements is more dependable and effective. The barrier coating on steel rebar isolates the steel from the immediate environment and also it acts as an insulator to prevent the corrosion. However, the efficiency of the barrier coating depends on many factors such as type of resin, intrinsic properties of other ingredients in coating, adhesion of coating to the metal substrate, thickness, other mechanical properties and resistance to chemical aggressive species that are likely to come in contact with the coating. Therefore, designing an effective barrier coating to the steel rebar requires not only a knowledge of corrosion principles, but also of coating formulations as well. By a careful consideration on chemical resistance and mechanical properties, the following formulations based on epoxy silicone-polyamide [1], polyester polyol aromatic isocyanate [2] and acrylic polyol aromatic isocyanate [3] have been selected for rebar coatings.

To evaluate the performance of these coatings, Electrochemical Impedance Spectroscopy (EIS) was adopted in addition to chemical resistance tests and mechanical tests such as flexibility, impact, scratch hardness, vickers hardness, pencil hardness and taber abrasion resistance tests. Experiments have been conducted as per ASTM standards and the results are discussed elaborately for the selection of the best coating suitable for steel rebars to be embedded in concrete.

**Table 1.** Coating formulations (45 PVC).

Sl. No.	System designation	Resin and hardener	Main pigments	Pozzolanic pigment (as an extender)	Solvent used
1.	A	Epoxy silicone/polyamide	TiO <sub>2</sub> Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fly ash	Xylene + MIBK + Butyle cellosolve
2.	B	Epoxy silicone/polyamide	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fly ash	Xylene + MIBK + Butyle cellosolve
3.	C	Polyester polyol/aromatic isocyanate	TiO <sub>2</sub> Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fly ash	Xylene + Butyle acetate
4.	D	Acrylic polyol/aromatic isocyanate	TiO <sub>2</sub> Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Ordinary portland cement (OPC)	Xylene + Butyle acetate

### Experimental

Film formers like epoxy silicone-polyamide, polyester polyol-aromatic isocyanate and acrylic polyol aromatic isocyanate have been selected to formulate four coating systems. Titanium dioxide (TiO<sub>2</sub>) and zinc phosphate [Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] have been used as main pigments. The pozzolanic pigments such as

flyash and ordinary portland cement (OPC) have been used as extenders. The formulation of coatings is shown in Table 1. The pigment volume concentration (PVC) has been kept as 45% for all coatings. This percentage of PVC has been arrived by trial formulations to enhance maximum possible mat finish by reducing the gloss. This will help to increase the bond between the concrete and the coated rebar [4].

Mild steel panels were used for EIS and mechanical tests. For chemical resistance tests, 12 mm diameter and 175 mm length cold-twisted deformed (CTD) bars were used. For EIS studies, adhesion tests, vickers hardness and pencil hardness tests, mild steel panels of size 50 mm x 75 mm were used. For flexibility and impact resistance tests, mild steel strips of size 100 mm x 175 mm were used. For scratch hardness tests 50 mm x 125 mm size mild steel panels were used. For Taber abrasion test 100 mm x 100 mm mild steel panels with central hole were used. All the panels, strips and CTD rods were pretreated with standard pickling solution for the removal of metal oxides and scales formed on the metal surface. After pickling, the metal panels and the rods were washed thoroughly with running water. Formulated coatings were applied with brush so as to have a dry film thickness (dft)  $80 \pm \mu\text{m}$ . Coatings were cured for seven days and the dft was measured with magnetic coating thickness gauge "MIKRO TEST". Values of measured thickness are given in Table 2.

Flexibility is an important property for a coating as the coating should possess sufficient resistance against bending. The flexibility test has been conducted as per ASTM D 522, using conical mandrel and the results are given in Table 2.

When the coated rebars are used in the construction field, they are likely to receive impact loads during its handling and placing. Impact loads normally cause permanent deformations and such deformations may exhibit cracks in the coatings if the coating is of brittle nature. Therefore, it is an absolute requirement to evaluate the response of the coatings against impact loads. Impact resistance of the coatings was measured as per ASTM D 2794 and the results are given in Table 2.

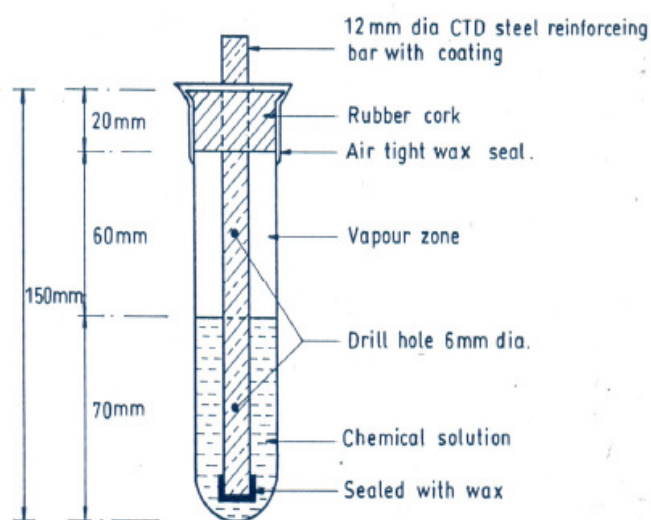
Adhesion of a coating to a metal substrate is an important parameter to be evaluated because the coating and the steel rebar should act as a single unit for force transfer within the structure. The adhesion test was conducted with a "Tensometer". Results of adhesion test for all the four coatings are given in Table 2.

Measurement of film hardness by pencil test is a rapid and inexpensive method, normally adopted for organic coatings with the pencils ranging from softer to harder (6B to 6H). This test has been carried out on all coatings as per ASTM D 3363 standards and the results are given in Table 2.

The resistance of a coating against scratch is determined by this test. The instrument used for this test is an automatic scratch tester which was supplied by Sheen Instruments Ltd., Richmond, Surrey, England. This test has been conducted as specified in British Standards BS 3900 : Part E 32 (scratch) based upon DEF-1053, Method 15. The results of this test on all four coatings are given in Table 2.

Vickers Hardness Test has been conducted on all four organic coatings to have a comparative indentation micro hardness of the coatings. The instrument used for this test was LECO, DM 400 hardness tester USA. This method consists of applying a load to the coated surface by means of vickers diamond pyramid shaped indenter having a face angle or included angle  $136^\circ$ . A number related to the applied load on the surface area of the permanent impression made by a square based pyramidal diamond indenter is calculated as per ASTM E 92-82 standards. This test has been conducted on all four coatings with a load of 10 grams and the results are given in Table 2.

Taber abrasion test is a well known and most widely used method of measuring abrasion or wear resistance of coatings. This test has been carried out as per ASTM D 4060-90. The abrading wheels used are of CS-10 designation. The weight on each wheel was 1 kg. The number of revolutions adopted was 1000 and the vacuum level was kept at 60. The Taber abrasion index was calculated for all coatings and is given in Table 2.



**Figure 1.** Test setup for chemical resistance test.

### ***Chemical resistance test***

Chemical resistance test has been conducted on coated steel reinforcing bars in accordance with ASTM A775/A775 M, section A 1.2 (coating requirements). Steel rods used were of 12 mm diameter CTD rods of length 175 mm. The test set up was fabricated according to the requirements given in ASTM G20 for immersing the coated rods partially (Fig.1). Aqueous solutions of 3.0 M  $\text{CaCl}_2$ , 3.0 M NaOH and a saturated  $\text{Ca}(\text{OH})_2$  and distilled water were used. Damages were made intentionally by drilling radial hole of 6 mm diameter to a depth of 6 mm through the coating one in immersion zone and the other one in vapour zone. Coated rods with and without damages were immersed in chemical solutions as shown in Fig.1 separately as one rod in one set up for all the coatings and monitored regularly for a period of 60 days for developments such as blisters, softening, lose of bond, holidays pinholes and undercutting of coatings. Results are given in Tables 3 to 6.

**Table 2.** Mechanical properties of coating systems.

Sl. No.	System	Average coating thickness (μm)	Flexibility test (ASTM D522)	Impact test (ASTD D2794)	Adhesion Test		Pencil hardness test (6B to 6H) (ASTM D3363)	Scratch hardness test (BS:3900 Part E32) (N)	Vickers hardness test (ASTM E92 ISO 4516: 1930) VHN	Taber abrasion index
					Load at failure (KN)	Stress at failure (N/mm <sup>2</sup> )				
1	A	80 ± 10	Passed (3mm)	Passed	10.899	22.19	Passed	20.60	17.60	112.6
2	B	80 ± 10	Passed (3mm)	Passed	10.910	22.22	Passed	22.07	18.70	93.0
3	C	80 ± 10	Passed (3mm)	Passed	9.147	18.63	Passed	19.62	13.20	103.5
4	D	80 ± 10	Passed (3mm)	Passed	8.973	18.27	Passed	24.52	18.30	104.4

**Table3.** Chemical resistance test of coated rebar in 3 M CaCl<sub>2</sub> solution.

SI No.	Coating	After 30 days		After 45 days		After 60 days	
		Without damage	With damage	Without damage	With damage	Without damage	With damage
1.	A	No changes	Rust formed in the damaged spot. No undercutting blisters	No changes	Rust in the damaged spots. No under-cutting and blisters. No discolouration	No changes	Rust formed in the damaged spot. No under-cutting and blisters. No visible discolouration
2.	B	No changes	-do-	No changes	-do-	No changes	-do-
3.	C	No changes	-do-	No changes	-do-	No changes	-do-
4.	D	Pinhole rust formed. No undercutting. No blisters	-do-	Pinhole rust is formed. No undercutting of coating. No blisters	-do-	Pinhole rust.No under-cutting of coating. No blisters.	-do-

**Table 4.** Chemical resistance test of coated rebar in 3 M NaOH solution.

SI No.	Coating	After 30 days		After 45 days		After 60 days	
		Without damage	With damage	Without damage	With damage	Without damage	With damage
1.	A	No changes	No changes	No changes	No changes	No changes	No changes
2.	B	No changes	-do-	Discolouration of immersed zinc started. No rust/pinhole formed.	Discolouration of immersed zinc started. No rust/pinhole formed.	Immersed zinc discoloured. No rust/pinhole formed.	Immersed zinc discoloured. No rust/pinhole formed.
3.	C	No changes	-do-	Coating started dissolving. No rust/pinhole formed.	Coating started dissolving. No rust/pinhole formed.	90% of the coating dissolved. No rust/pinhole formed.	90% of the coating dissolved. No rust/pinhole formed.
4.	D	-do-	-do-	No changes	No changes	No changes	No changes

**Table 5.** Chemical resistance test of coated rebars in saturated Ca(OH)<sub>2</sub> solution.

Coating	After 30 days		After 45 days		After 60 days	
	Without damage	With damage	Without damage	With damage	Without damage	With damage
A	No changes	Rust formed at damaged spot No blisters, Under cutting and discoloration	No changes	Rust formation is in progress. No blisters and discoloration	No changes	Progressive rust formation in the damaged spot. No blisters and discoloration
B	-do-	-do-	-do-	No changes	No changes	No changes
C	Pinholes rust formed	Rust formed in the damaged spot. Blisters farmed in 3% of the area immersed	Pinhole rust is in progress no Blisters	Progressive rusting in the damaged spot. Blisters growth was observed.	progressive pinhole rusting	Progressive rusting in the damaged spot. 6% of the submerged area showing blisters formation.
D	-do-	Rust formed in the damaged spot. Blisters are just started forming in the immersed zone.	Progressive rust formation in the pinholes. Blisters are just started forming in the immersed zone.	Nearly 3% of the area immersed showing blisters formation. Progressive rust formation in the damaged spot.	Progressive rust formation in the damaged spot. Nearly 5% of the immersed area showing blisters.	Nearly 9% of the area immersed showing blisters. Progressive rusting of damaged spot.

**Table 6.** Chemical resistance test of coated rebars in distilled water.

Coating	After 30 days		After 45 days		After 60 days	
	Without damage	With damage	Without damage	With damage	Without damage	With damage
A	Blisters are formed at the interface between solution and vapour phase	Rust formed at the damaged spot. No undercutting No discoloration	Blisters formed at the interface between solution and the vapour phase	Rust formed at damaged spot No blisters No Under cutting No discoloration	Reduced blister growth at the interface. No visible corrosion spot.	Formation of rust at the damaged spot. No pinholes, undercutting and discoloration
B	No changes	Slight rust formation at the damaged spot. No undercutting No discoloration	No Changes	Slight rust formation at the damage spot. No pinhole discoloration	No pinholes, slight discoloration was observed	Slight rust formation at the damaged spot. No Blisters Under cutting Slight discoloration of coating observed.
C	Small blisters formed in the submerged zone	Rust in the damaged spot. Blisters formed in the submerged zone	No corrosion spot observed. Small blisters formed in the immersed zone	Rust in the damaged spot. Growth of blisters were observed in immersed zone	No rust or corrosion spot. 6% of area immersed showing blisters. No discoloration	Rust in the damaged spot. Nearly 8% of the immersed area showing blisters growth
D	Formation of pinhole rust. Few blisters formed in the submerged zone	Rust in the damaged spot. Formation of pinholes	Formation of Pinhole rusts. Blisters in the submerged zone	Formation of rust in damaged spot. Corrosion was observed in the damage at vapour phase. Few more pinholes formed	10% of the submerged area showing blisters. Formation of few more pinhole rusts	Rust formation in the damages spots. 10% of the submerged area showing blisters.

***EIS study***

EIS offers a convenient way of evaluating the performance of the organic coating/metal/electrolyte interface. When aggressive ions and water ingress into the coating, they involve themselves in electrochemical reaction (corrosion

process) at coating/metal/electrolyte interfaces. This technique provides both quantitative kinetic and mechanistic information which makes it a very useful tool for developing improved coating system.

In the present study, impedance measurements were carried out using PAR Model 368-1 system with a frequency range from  $10^4$  Hz to 0.1 Hz and the amplitude of the applied signal was 10 mV. The electrochemical cell used for this study consisted of a coated mild steel panel as the working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as the reference electrode in 3% NaCl solution as the electrolyte. Impedance measurements were made and Bode plots were obtained periodically on 0<sup>th</sup>, 1<sup>st</sup>, 7<sup>th</sup>, 15<sup>th</sup> and 30<sup>th</sup> days. For all the four coatings, the solution resistance ( $R_s$ ), charge transfer resistance ( $R_t$ ) and the coating capacitance ( $C_c$ ) were obtained and are given in Table 7.

### **Results and discussion**

Mechanical properties of different coatings are given in Table 2. The flexibility test carried out by conical mandrel on all four coatings exhibited excellent results without any cracks. Similarly, all the four coatings have passed the impact test without any cracks on the coating by direct and indirect impact loads. Adhesion of the coating to the steel plate after pickling is an important property. Although sand blasting can provide still better anchorage of the coating to the substrate, it is avoided for many practical reasons. When sand blasting is done for reinforcements in huge structures like bridges, it is found to pollute the atmosphere. Moreover, it requires heavy machinery, energy and it is a time consuming treatment. To overcome all these problems, pickling was selected, as this treatment is simple and less-time consuming. Results of the adhesion test given in Table 2 bring out the fact that epoxy silicone coatings adhere better with the pickled surface than polyesterpolyol and acrylic polyol resin based urethane coatings. This reveals that the epoxy silicone based formulations have better anchoring property on moderately prepared surfaces [5].

Results of coating hardness tests are given in Table 2. It is seen from the table that all the coatings have passed the pencil hardness test. In, the scratch hardness test, the coating D showed high scratch hardness of 24.52 N as against the minimum hardness of 19.62N for the coating C. Coatings A and B (epoxy silicon coatings) have shown intermediate values. In the penetration hardness test by Vickers hardness test the maximum penetration hardness was obtained for coating B (18.7 VHN) as against the minimum hardness of 13.2 VHN obtained for the coating C. All these hardness test results indicate that the epoxy silicone based formulations form a hard and tough film over the mild steel surface which is found to be better than the formulations of polyurethanes. On comparing the formulations of C and D, the formulation based on acrylic urethane show higher hardness and anchoring property with the substrate than the polyester polyol urethanes [6]. This behaviour is reflected in the adhesion and hardness of these coatings on mild steel substrate.



**Table 7.** Values of  $R_t$  and  $C_c$  obtained from EIS.

Coating systems	Days	$R_s$ / /(Ohms)	$R_t$ / /(Ohms)	$C_c$ / /(Farad)
A	0-day	$1.90 \times 10^4$	$9.81 \times 10^5$	$1.05 \times 10^{-6}$
	1-day	$0.40 \times 10^3$	$0.40 \times 10^3$	$3.57 \times 10^{-4}$
	7-day	$8.00 \times 10^4$	$9.20 \times 10^5$	$5.00 \times 10^{-7}$
	15-day	$2.20 \times 10^5$	$1.78 \times 10^6$	$1.42 \times 10^{-7}$
	30-day	$2.20 \times 10^5$	$8.68 \times 10^6$	$2.5 \times 10^{-7}$
B	0-day	$7.00 \times 10^4$	$1.23 \times 10^6$	$1.70 \times 10^{-6}$
	1-day	$4.90 \times 10^4$	$4.51 \times 10^5$	$1.0 \times 10^{-6}$
	7-day	$1.00 \times 10^5$	$4.99 \times 10^7$	$5.00 \times 10^{-9}$
	15-day	$4.00 \times 10^5$	$2.467 \times 10^7$	$3.33 \times 10^{-8}$
	30-day	$2.00 \times 10^5$	$6.80 \times 10^8$	$1.00 \times 10^{-8}$
C	0-day	$0.40 \times 10^3$	$2.96 \times 10^4$	$3.33 \times 10^{-5}$
	1-day	$0.35 \times 10^3$	$0.35 \times 10^3$	$6.25 \times 10^{-4}$
	7-day	$4.00 \times 10^3$	$1.86 \times 10^5$	$3.703 \times 10^{-6}$
	15-day	$4.00 \times 10^5$	$7.60 \times 10^6$	$1.23 \times 10^{-7}$
	30-day	$5.30 \times 10^4$	$6.47 \times 10^7$	$1.50 \times 10^{-6}$
D	0-day	$1.80 \times 10^3$	$1.32 \times 10^4$	$4.44 \times 10^{-5}$
	1-day	$1.0 \times 10^3$	$5.50 \times 10^3$	$8.00 \times 10^{-5}$
	7-day	$1.50 \times 10^4$	$4.85 \times 10^5$	$1.66 \times 10^{-6}$
	15-day	$4.50 \times 10^5$	$3.05 \times 10^6$	$1.66 \times 10^{-7}$
	30-day	$1.75 \times 10^4$	$5.82 \times 10^7$	$8.00 \times 10^{-7}$

Finally the abrasion resistance index was computed for all the coatings with Taber abraser. Among all the coatings, the coating B showed lesser abrasion index of 93 which is considered to be the good abrasion resistance value. The maximum value of 112.6 was obtained for the coating A. Coatings C and D showed intermediate values of 103.5 and 104.4, respectively. Therefore, from all of these mechanical tests on coatings, the coating B shows comparatively good results over rest of the coatings.

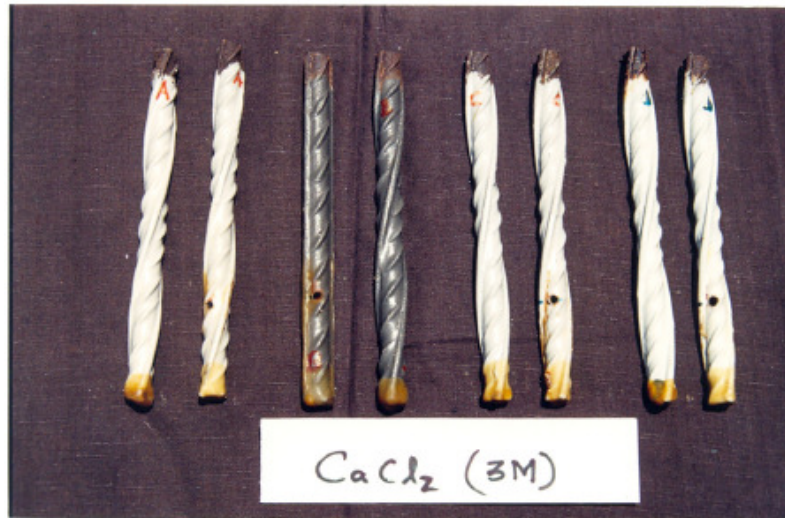
### **Chemical resistance test**

#### **(a) $CaCl_2$ test**

Table 3 and Fig 2 show the results of chemical resistance test carried out on coated rebars immersed partially in 3.0 M  $CaCl_2$  solution with and without damages on coatings for 60 days.

Undamaged coatings such as A, B and C withstood this exposure both in immersed and in vapour zone for a period of 60 days without the formation of any rust, blisters, pinhole, undercutting, etc. The undamaged coating D showed pinhole rust on 30<sup>th</sup> day in the immersed zone. This shows that the film is porous and hence the pinhole rust formation occurs uniformly on the surface. In all the damaged coatings, formation of rust was noticed on the steel surface on 30<sup>th</sup> day. But coatings were intact without any blisters and undercutting till 60<sup>th</sup> day. This result indicates that a passive layer is formed on the surface of the steel which does not allow the corrosive ions to diffuse. This may be due to the formation of a phosphate layer from the zinc phosphate which is present in the formulation.

Further the coatings adhere well on the metal surface and hence there are no blisters formed on the surface.



**Figure 2.** Photograph of coated rebars immersed in 3 M  $\text{CaCl}_2$  solution for a duration of 60 days.

(b) *NaOH test*

Table 4 and Fig 3 show the results of chemical resistance test carried out on coated rebars immersed partially in 3.0 M NaOH solution, with and without damages on coatings, for 60 days.



**Figure 3.** Photograph of coated rebars immersed in 3 M NaOH solution for a duration of 60 days.

Due to high alkalinity of the solution, there was no corrosion or rust spot on any of the rods (damaged and undamaged rods) until a period of 60 days. But the coating C (polyester polyol coating) dissolved in the solution upto about 90% during this period. This is due to alkali hydrolysis of polyester resin with NaOH [7]. The coating B started showing a change of colour from dark gray to dull gray from 45<sup>th</sup> day in the immersed zone. This may be due to the reaction of loosely

adhered zinc phosphate with the caustic soda to form zinc oxide at the initial stage. Therefore there is no possibility of the formation of this zinc oxide because zinc oxide plugs the micro pores on the surface. No blisters, rust, undercutting of coating were noticed. This shows that the coating is intact on the surface.

(c) Ca(OH)<sub>2</sub> test

Table 5 and Fig 4 show the results of coated steel rods with and without damages immersed partially in a saturated solution of Ca(OH)<sub>2</sub> for a period of 60 days.



**Figure 4.** Photograph of coated rebars immersed in 3 M Ca(OH)<sub>2</sub> solution for a duration of 60 days.

Undamaged coatings such as A and B showed good results with no blisters, pinholes, rust spots and under cutting of coatings. However undamaged coatings such as C and D showed pinhole rust but no blisters and under cutting till 30<sup>th</sup> day of immersion. Damaged coatings such as C and D started showing blisters and rust after 30 days and were in progress further. This result indicates that the polyurethane coatings are affected by the Ca(OH)<sub>2</sub> electrolyte due to depolymerisation of resin component. Once the depolymerisation occurs, the passive layer formed by the zinc phosphate is also affected by the calcium hydroxide. This may be due to the formation of calcium phosphate which is a soluble salt. This is the mechanism for the formation of blisters and followed by rust spots on the coated rods after 45 days. On the other hand, the coating based on epoxy silicone performs well in the calcium hydroxide solution because of its resistance towards neutral and alkaline environments [1].

(d) Test in distilled water

Table 6 and Fig 5 show the results of coated steel rods with and without damages immersed partially in distilled water for a period of 60 days

Table 6 also shows the result of chemical immersion test carried out using coated bars with and without damages on coatings and partially immersed in distilled water for a duration of 60 days.



**Figure 5.** Photograph of coated rebars immersed in distilled water for a duration of 60 days.

Undamaged area of coating A should show the formation of blisters at the interface between the distilled water and vapour phase after 30 days of partial immersion in distilled water. This blisters formation continued till 60 days. The damaged coating A showing rust formation at damaged spots after 30 days and were in progress until 60 days. The undamaged coating B did not show any blister or pinhole formation until 45 days and at the end of 60 days few pinholes where formed. The damaged coating B started showing rust formation at damages after 30 days of immersion and was in progress thereafter. At the end of 60 days of immersion, a slight discoloration of coating was observed. The undamaged coating C (polyester polyol coating) started developing small blisters after 30 days in the submerged zone. The formation of blisters were in progress until 60 days and 6% of the immersed area showed blisters. However, no rust or corrosion spot was identified over the coated surface. The damaged coating C had started showing rust in the damaged spot and blisters at the immersed zone after a duration of 30 days. This was in progress until 60 days and at the end of 60 days exposure, 8% of the submerged area showed blisters. Undamaged coating D started showing blisters formation from 30 days of immersion along with few pinholes. At the end of 60 days of immersion, 10% of the submerged area was affected by the blisters and the formation of few more pinholes. The damaged coating D started showing rust in damages and a few pinholes after 30 days. Slight delamination of coating near the damage was observed along with the rust at the interface between distilled water and the vapour phase after 45 days. In the immersion zone, 10% of the area was affected by blisters after 60 days of immersion. It was agreed [8] that the coating in the deionized water will show more blisters in the immersed zone than in the fresh or salt water. This is because the coating normally absorbs 0.1 to 0.3% of water by weight of coating upon exposure to water or electrolyte [9-11] and dissolves some quantity of inhibitive pigment of the coating and became filled with water. Further the blisters will absorb water and swell. Blisters thus formed on coating are known as neutral blisters [12]. The number of blisters and the area covered by the

blisters are controlled by the ionic mobility of the electrolyte through the coating films [13]. The formation of blisters at the interface between water and vapour phase can be due to the fact that the vapour density at the interface is more. Therefore the formation of more blisters and thereby more corrosion occurs.

### ***EIS study***

The application of EIS to a polymer coated metal has resulted in a new insight concerning the interaction of the coated metal system with corrosive environments and it provides useful information related to the degradation process of coatings. EIS analysis of impedance data is carried out over a wide range of frequencies using Nyquist complex plane plots or Bode plots in order to determine the individual components of an equivalent electrical circuit model that represents the coated metal/solution interface. The quantitative components that can be measured from the impedance spectra are  $R_s$ ,  $R_t$ ,  $C_c$  and  $C_{dl}$  over the period of immersion. Values of  $R_s$ ,  $R_t$  and  $C_c$  obtained from Bode plots for all four coatings for a period of 30-days are given in Table 6.

The value of  $R_t$  decreases from the initial (0-day) value to the first day value for all the four coatings. This can be ascribed to the uptake of electrolyte by the coating through the capillaries and micropores present in the coatings. This initial uptake of electrolyte is indicative of an increased corroding area rather than an increasing corrosion rate [1]. During the same interval of time, a sharp increase in coating capacitance is observed for all the coatings. This observation is quite in agreement with that made by Brasher and Nurse [2]. According to them, the sharp increase in  $C_c$  is due to the re-orientation in the mode of distribution of water within the coating film. It is observed that the  $R_t$  values of the coatings increase from the 1<sup>st</sup> day values on 7<sup>th</sup> and 15<sup>th</sup> days and attain a steady-state (saturation) value after 15<sup>th</sup> day. This could be seen from the  $R_t$  values of 30<sup>th</sup> day. A quite opposite trend was noticed in  $C_c$  values on the corresponding time interval.

The increase in  $R_t$  values from the first day is attributed to the formation of passive layer between the coating and the substrate. Water penetrates through the coating during the first 24 hours, combines with the micronised zinc phosphate which is present in the coating as an integral part and results in the formation of phosphate passive layer over the mild steel substrate [14]. This passive layer protects the substrate from aggressive ions. Also, zinc ions combine with the excess water to form zinc oxide, which plugs the capillaries and the pores present in the coatings. This might be the reason for the increase in  $R_t$  values from first day till 15<sup>th</sup> day and thereafter on 30<sup>th</sup> day a stabilised value has been obtained. These stabilised values are also on the protective side. Coatings A and B have  $R_t$  values greater than  $10^6$  ohm even after 30 days of duration of this study. According to Skerry and Eden's study [15], coatings having the  $R_t$  value of  $10^6$  ohm continue to protect the mild steel substrate from corrosive ions. Although coatings A and B have  $R_t$  values more than  $10^6$  ohm, the coating B has shown much better  $R_t$  value than the coating A.

## Conclusion

It can be concluded from this study that the selected coating systems have good mechanical properties for protecting the reinforcing rods in concrete. But the chemical resistance behaviour of these formulations clearly indicates that the coatings based on epoxy silicone/polyamide only protect the rebars from the alkaline environment. Further the electrochemical impedance study reveals that of the four systems, the coating B is superior to the other systems. So this coating system is selected as a good formulation for rebars in concrete.

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