

# Studies on the Evaluation of the Performance of two Types of Polyurethane Coatings on Steel Rebars for the Prevention of Corrosion in Concrete Structures

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## Abstract

The performance of two resin combinations, such as acrylic polyol – aromatic isocyanate and polyester polyol – aromatic isocyanate as durable and effective rebar coatings for steel in concrete has been examined by studying their mechanical properties and by using accelerated tests such as salt spray test and electrochemical impedance spectroscopy. It is found that polyester polyol-aromatic isocyanate combination performs better than acrylic polyol-aromatic isocyanate combination. Incorporation of fly ash in the coating is found to influence the performance of the coating.

**Keywords:** concrete corrosion, surface coatings, rebar, electrochemical impedance spectrum analysis.

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## Introduction

It is generally accepted that an embedded steel rebar in concrete is immune to corrosion by highly alkaline environment provided by the surrounding concrete. However, the passive steel bar begins to corrode, when the concrete is subjected to carbonation and/or by chloride attack. Various methods are prevalent to combat the corrosion of steel rebar in concrete. The methods include the variation of concrete formulations, cathodic protection, addition of inhibitive admixtures, utilization of protective coating or galvanized rebars and so on. Amongst the long term measures, the most reliable and widely used method for the protection of concrete reinforcing bars against corrosion are the coatings based on a variety of resins such as epoxy, epoxy coal tar, alkyd, alkyd-esters,

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acrylic and polyurethane, etc. These resins can be coated on rebars either in the term of a solvent based coating or as a powder coating. The protection by coating is generally based on the principle of creating an inert and impermeable barrier layer between the metal substrate and the corroding environment. Lin and Ding have examined the utility of amino-terminated, polyurea, polyurethane modified epoxy as rebar coatings [1]. Wang et al. have reported the use of acrylic latex for reinforcement coatings [2]. Al-Hashim et al. [3] have studied the protective properties of solvent based acrylic coating by electrochemical impedance spectroscopic method. Shreekant Patil and Shenoy have examined the use of polyurethane coatings for the corrosion protection of reinforced rebars in concrete structures [4]. It has been reported that the reaction of polyisocyanate with polyols has a great impact on the properties of the finished coating [5]. It is observed that the interaction of polyols with polyisocyanate gives greater cross-linking density, and increases the rigidity, hardness, toughness, abrasion resistance and chemical resistance. So in the present study the possibility of using a combination of polyisocyanate with acrylic polyol or polyester polyol as durable and effective rebar coatings has been examined by studying the mechanical properties of these combinations and using accelerated tests. Results are reported.

## **Experimental**

### ***Materials***

Cold rolled mild steel panels were used for this study. Resins used such as acrylic polyol (G.P.BOND 141), polyester polyol (TACO POL – 6-1) and aromatic isocyanate (TACO BOND P-1-175) were procured from M/s.Grand Polycoat, Vadodara, Gujarat. Ordinary Portland cement conforming to IS: 811243 (Dalmia Brand) and fly ash procured from Neyveli Lignite Corporation, Neyveli, Tamilnadu, were used as extender pigments. Titanium dioxide and zinc phosphate were used as main pigments in different solvent based coating formulations. Composition of eight different coating formulations prepared and used in this study is given in Table 1.

### ***Methods***

#### ***Preparation of coated mild steel panels for different studies***

Mild steel panels of different sizes were used for different studies. For tests such as salt spray, adhesion and hardness, panels of size 50 mm x 75 mm were used. For flexibility, panels of size 100 mm x 150 mm were used. For abrasion resistance, panels of 100 mm x 100 mm size were used. After pickling and degreasing of the panels, the formulated coatings were applied using a brush in two coats so as to have a uniform film thickness. All the coated panels were allowed to cure for a duration of seven days in the laboratory environment.

**Table 1.** Composition of different coating formulations (for 100 mL).

No.	Coating system	Composition
1	A <sub>1</sub>	Resin : acrylic polyol-aromatic isocyanate Pigment : anatase TiO <sub>2</sub> , zinc phosphate ordinary Portland cement
2	A <sub>2</sub>	Resin : acrylic polyol-aromatic isocyanate Pigment : anatase TiO <sub>2</sub> , zinc phosphate, fly ash
3	A <sub>3</sub>	Resin : acrylic polyol-aromatic isocyanate Pigment : zinc phosphate, ordinary Portland cement
4	A <sub>4</sub>	Resin : acrylic polyol-aromatic isocyanate Pigment : zinc phosphate and fly ash
5	B <sub>1</sub>	Resin : polyester polyol-aromatic isocyanate Pigment : anatase TiO <sub>2</sub> , zinc phosphate ordinary Portland cement
6	B <sub>2</sub>	Resin : polyester polyol-aromatic isocyanate Pigment : anatase TiO <sub>2</sub> , zinc phosphate, fly ash
7	B <sub>3</sub>	Resin : polyester polyol-aromatic isocyanate Pigment : zinc phosphate and ordinary Portland cement
8	B <sub>4</sub>	Resin : polyester polyol-aromatic isocyanate Pigment : zinc phosphate and fly ash

*Gel permeation chromatography*

Resins used in this study were analysed for their molecular weight and their dispersity index using gel permeation chromatography system supplied by M/s. Shimadzu Corporation, Tokyo, Japan, Model No. (190-E 001). Results are given in Table 2.

**Table 2.** Results of gel permeation chromatography measurements on different resins.

Resin	Weight average molecular weight (M <sub>w</sub> )	Z-average molecular weight (M <sub>z</sub> )	Dispersity index
Acrylic polyol	18,443	42,329	2.2945
Polyester polyol	4664	8521	1.8259
Polyurethane	1319	3325	2.5208

*Measurement of mechanical properties*

Dry film thickness (dft) for all the coatings was measured using Elkometer. Flexibility of all the coatings was measured using conical mandrel tester as per ASTM D522 standard. Hardness of all coatings was measured with both pencil test as per ASTM standard D 3363 and also by automatic scratch tester supplied by M/s. Sheen Instruments Ltd., Surrey, London, as per British Standards BS: 3900 part E32 (Scratch) based on DEF-1053, Method 15. Impact test on all coated panels were carried out as per ASTM D2794 standard. Results of all these measurements are given in Table 3.

**Table 3.** Results of measurements of different mechanical properties of different coatings.

Coating	Adhesion test		Flexibility test (ASTM D 522)	Impact test ASTM D2794
	Load at failure (kN)	Stress at failure (N/mm <sup>2</sup> )		
A1	8.793	17.27	P	P
A2	8.772	17.86	P	P
A3	8.614	17.54	P	P
A4	8.919	18.16	P	P
B1	9.992	18.31	P	P
B2	9.147	18.63	P	P
B3	8.961	18.25	P	P
B4	9.102	18.93	P	P

*Salt spray (fog) test*

Salt spray test was conducted as per ASTM D 117 standard using 5% NaCl solution. The coated panels of size 50 mm x 75 mm with and without diagonal scribes were used for this experiment. Panels were kept suspended for duration of 1000 hours. Afterwards these panels were washed using clear running water for subsequent evaluation as per ASTM D1654 and ASTM D714 standards. This test was conducted on all coatings and the results are reported in Table 4.

**Table 4.** Evaluation of coated specimens after salt spray test.

	Rating of failure (ASTM D 1654)				Degree of blistering (ASTM D714)
	At scribe		At unscribe		
	Rating No.	Creepage (mm)	Rating No.	Percentage of area corroded	
A1	7	2.0	7	10	Few small clusters Blister size No.8
A2	9	0.5	8	6	Few small clusters Blister size No.6
A3	7	2.0	6	40	Few small clusters Blister size No.5
A4	9	0.5	8	1	Few small clusters Blister size No.6
B1	7	4.0	6	8	Few small clusters Blister size No.8
B2	9	2.0	8	2	Few small clusters Blister size No.6
B3	7	3.0	6	4	Few small clusters Blister size No.8
B4	9	0.5	9	0.5	Few small clusters Blister size No.6

*Electrochemical impedance spectroscopy (EIS)*

Impedance measurements were carried out using PAR Model 368.1 system with frequency range from 10<sup>9</sup> Hz to 0.1 Hz and applied signal of amplitude 50 mV. Electrochemical cell used for the study consisted of a coated mild steel panel as

the working electrode, a platinum foil as the counter electrode, a saturated calomel electrode as the reference electrode, and 3% NaCl solution as the electrolyte. Impedance measurements were carried out at different duration ranging from 1 hour to 30 days. Values of charge transfer resistance ( $R_t$ ) and coating capacitance were obtained for all the coatings and results are reported in Table 5 and 6.

All the coatings were screened by above tests for choosing coatings with best performance.

#### *Field exposure studies*

Coated rebar specimens which show good performance were exposed to outdoor weathering at Mandapam, a coastal site located at Bay of Bengal, India, for 12 months. Bars straight as well as bent were tied by hard plastic wires and suspended from an exposure stand. Periodic observations were made.

## **Results and discussion**

### ***Gel permeation studies***

Results of gel permeation chromatographic studies given in Table 2 show that all the resins have high molecular weight, and values of dispersity index for all these resins are more than unity. This observation indicates that all the three resins are slightly branched polymers having higher viscosity and lower elastic modulus.

**Table 5.** Values of charge transfer resistance ( $R_t$ ) and coating capacitance ( $C_C$ ) obtained from electrochemical impedance spectra for acrylic polyol + aromatic isocyanate coatings.

Coating	Duration	Charge transfer Resistance $R_t$ (ohm)	Coating capacitance $C_C$ (Farads)
A1	1 hr	$1.91 \times 10^7$	$6.36 \times 10^{-9}$
	1 day	$7.43 \times 10^4$	$7.43 \times 10^{-9}$
	7 days	$2.43 \times 10^5$	$8.17 \times 10^{-8}$
	15 days	$4.94 \times 10^5$	$1.24 \times 10^{-8}$
	30 days	$2.11 \times 10^3$	$1.33 \times 10^{-4}$
A2	1 hr	$1.1 \times 10^9$	$4.44 \times 10^{-11}$
	1 day	$2.6 \times 10^5$	$1.63 \times 10^{-9}$
	7 days	$1.18 \times 10^6$	$5.13 \times 10^{-9}$
	15 days	$8.61 \times 10^6$	$8.41 \times 10^{-9}$
	30 days	$1.93 \times 10^6$	$3.12 \times 10^{-9}$
A3	1 hr	$7.69 \times 10^8$	$5.86 \times 10^{-10}$
	1 day	$6.11 \times 10^5$	$2.16 \times 10^{-9}$
	7 days	$2.23 \times 10^6$	$8.33 \times 10^{-9}$
	15 days	$4.26 \times 10^6$	$2.24 \times 10^{-9}$
	30 days	$0.31 \times 10^4$	$1.03 \times 10^{-6}$
A4	1 hr	$1.21 \times 10^9$	$5.23 \times 10^{-11}$
	1 day	$9.96 \times 10^5$	$1.81 \times 10^{-8}$
	7 days	$6.42 \times 10^6$	$7.46 \times 10^{-9}$
	15 days	$0.01 \times 10^6$	$8.14 \times 10^{-9}$
	30 days	$2.12 \times 10^6$	$1.66 \times 10^{-9}$

**Table 6.** Values of charge transfer resistance ( $R_t$ ) and coating capacitance ( $C_c$ ) obtained from electrochemical impedance spectra for polyester polyol + aromatic isocyanate coatings.

Coating	Duration	Charge transfer Resistance $R_t$ (ohm)	Coating capacitance $C_c$ (Farads)
B1	1 hr	$2.84 \times 10^8$	$4.44 \times 10^{-10}$
	1 day	$2.43 \times 10^6$	$3.21 \times 10^{-9}$
	7 days	$4.91 \times 10^7$	$6.46 \times 10^{-10}$
	15 days	$3.14 \times 10^6$	$4.73 \times 10^{-9}$
	30 days	$2.13 \times 10^5$	$9.43 \times 10^{-9}$
B2	1 hr	$2.96 \times 10^8$	$3.33 \times 10^{-10}$
	1 day	$6.12 \times 10^7$	$1.23 \times 10^{-10}$
	7 days	$1.11 \times 10^6$	$8.12 \times 10^{-9}$
	15 days	$7.68 \times 10^7$	$1.41 \times 10^{-10}$
	30 days	$6.47 \times 10^6$	$6.13 \times 10^{-9}$
B3	1 hr	$6.14 \times 10^8$	$1.07 \times 10^{-10}$
	1 day	$4.13 \times 10^6$	$3.24 \times 10^{-9}$
	7 days	$9.11 \times 10^7$	$1.67 \times 10^{-10}$
	15 days	$1.43 \times 10^7$	$4.37 \times 10^{-10}$
	30 days	$7.12 \times 10^5$	$2.19 \times 10^{-8}$
B4	1 hr	$7.14 \times 10^9$	$4.33 \times 10^{-11}$
	1 day	$6.14 \times 10^6$	$1.67 \times 10^{-9}$
	7 days	$4.14 \times 10^7$	$5.37 \times 10^{-10}$
	15 days	$6.14 \times 10^7$	$4.32 \times 10^{-10}$
	30 days	$3.84 \times 10^6$	$7.16 \times 10^{-9}$

**Measurements of mechanical properties of coatings**

All the coatings possess an average dry film thickness of  $95 \pm 5 \mu\text{m}$ . Table 3 shows the results of different tests carried out for measuring adhesive strength, flexibility and impact strength of different coatings. Acrylic polyol+aromatic isocyanate coatings show values of adhesive strength varying from  $17.27 \text{ N/mm}^2$  to  $18.16 \text{ N/mm}^2$ . Coating A4 shows maximum adhesive strength  $18.16 \text{ N/mm}^2$  followed by the coating A2 which shows an adhesive strength of  $17.86 \text{ N/mm}^2$ . In the case of polyester polyol + aromatic isocyanate coatings values of adhesive strength vary from  $18.25 \text{ N/mm}^2$  to  $18.93 \text{ N/mm}^2$ . Coating B4 shows a value of  $18.63 \text{ N/mm}^2$ . It is also found that polyester polyol + aromatic isocyanate coatings give better adhesive strength than acrylic polyol+ aromatic isocyanate coatings. In acrylic formulations, the molecular weight is high and hence the adhesion can be due to Vanderwals forces. In the case of polyester polyol more polar groups are available compared to acrylic polyol and hence have the adhesion for polyester polyol based coatings [6]. The presence of zinc phosphate in these coatings provides improved drying and enhances the adhesion of the coating to the steel substrate [7]. The performance of these coatings can be rated as

$$B4 > B2 > A4 > A1$$

Results of conical mandrel test for measuring the flexibility of all coatings show that all coatings possess good flexibility. Polyurethane exhibits good flexibility

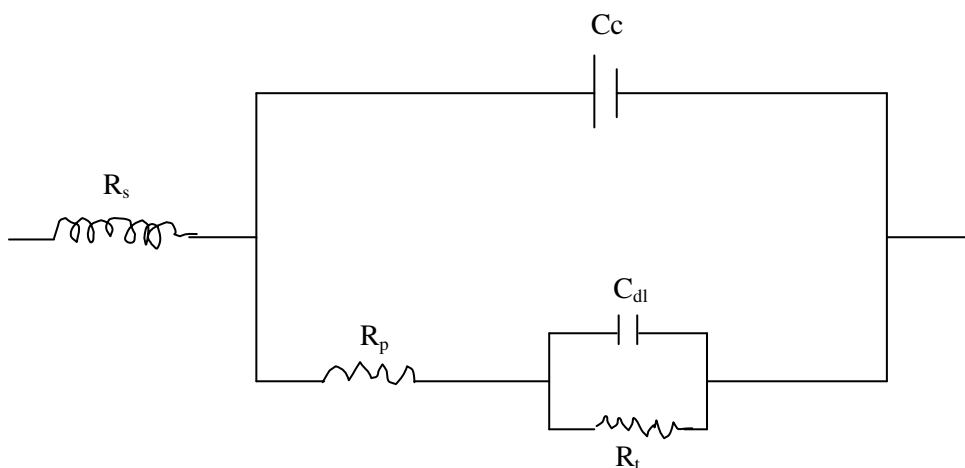
owing to cross linking by isocyanate groups with respective polyol resins. Linear and difunctional chains give more flexibility to the flow [8]. All coatings are found to possess good impact resistance.

### **Salt spray test**

Results of salt spray (fog) test are given in Table 4. It can be seen from the table that coatings based on polyester polyol- aromatic isocyanate combination perform better than those based on acrylic polyol- aromatic isocyanate combination. These coatings show better creepage resistance at scribes as the rating varies from 7 to 9. In unscribed panels percentage of area corroded varies from 0 to 5% for coating B4 to B2. Both coatings B2 and B3 show density formed clusters of blister size No.8. But coatings B2 and B4 show less density formed cluster of blister size No. 6. So both these coatings show better corrosion resistance.

Coatings based on acrylic polyol aromatic isocyanate combination show inferior performance than those based on polyester polyol- aromatic isocyanate combination. Both coatings show better creepage resistance at scribes with rating of 9. In unscribed panels, percentage of area corroded is considerably more and it varies from 1 to 40%. Percentages of area corroded are more both in coatings A1 and A3 and they show density packed clusters of blister size No.8. Coatings A2 and A4 show less dense cluster formation with blister size No.6.

Ester containing coating system such as polyester polyol have relatively higher resistance to oxygen transmission compared to their resistance to water transmission [10]. Thus the polyester polyol based coatings performed wet over the acrylic polyol based formulation.



**Figure 1.** Schematic diagrams of the equivalent circuit for coated samples.

### **Electrochemical impedance spectroscopic studies**

An equivalent circuit model for a coated metal/electrolyte system has been used to analyse the electrochemical impedance spectra (EIS) obtained for all coating

systems in 3% NaCl solutions. The circuit, as shown in Fig.1, consists of solution resistance ( $R_s$ ), charge transfer resistance ( $R_t$ ), coating capacitance ( $C_c$ ) and double layer capacitance ( $C_{dl}$ ) elements by fitting the EIS data to the circuit. EIS analysis of the impedance data is carried out over a wide range of frequencies using Bode plots for different duration ranging from 1 hour to 30 days. Values of  $R_t$  and  $C_c$  evaluated from Bode plots for different duration for all coatings are given in Tables 5 and 6. It can be seen that  $R_t$  values for all coatings decrease suddenly from the initial value at 1 hour up to a duration of 24 hours. Therefore they increase and attains almost a steady value after duration of 15 days. Then decreasing of  $R_t$  values for all coatings are evident from 30<sup>th</sup> day. This observation can be explained as follows. The initial decrease in  $R_t$  values can be ascribed to the uptake of the electrolyte through the micropores and capillaries in the coating. Increase in  $R_t$  value after the first day can be ascribed to the formation of passive layer at the interface between the metal substrate and the coating. Water permeated through the coating reacts with the phosphate present in the coating and forms passive phosphate layer on the steel substrate [11,12]. This passive layer protects the metal substrate from aggressive ions. It can be seen from these tests that only four coatings such as A2, A4, B2 and B4 show  $R_t$  values more than  $10^6$  ohms  $cm^2$ . It has been proved that only coatings which show  $R_t$  value of  $10^6$  ohm  $cm^2$  and more can be rated as protective to mild steel substrate from aggressive ions [13]. In this regard the extend of protection by these coatings can be rated as

$$B4 > B2 > A4 > A2$$

It can be seen from the above study that only coatings which contain fly ash as one of the ingredients in the formulation can offer good protection to the steel rebar in concrete. It has been reported earlier that incorporation of fly ash in concrete brings down the porosity of concrete, also increases its electrical resistivity and brings down the diffusion elements such as oxygen and chloride through the concrete [14, - 17]. A similar reason can be attributed to the improved performance of coating such as B2, B4, A1 and A2.

### ***Field exposure studies***

Steel bars of 12 mm diameter and coated with above coating formulations were bent to 90° and exposed at the coastal yard by trying them to the exposure stand to hang freely with adequate spacing between them. While bending, all the coatings showed minute cracks and elongation of the coating at the bend. These bend up rods were exposed for a period of 18 months. Acrylic polyol based polyurethane coatings (A2) showed high corrosion, followed by polyester polyol based coating (B2). It is found that these coatings contain  $TiO_2$  as one of the ingredients (coatings A2 and B2). This can be ascribed to photochemical and photocatalytic degradation. While  $TiO_2$  is an exceptionally good UV absorber, it is also photocatalytic in nature. It can actually accelerate the degradation of organic species, including coatings binders that show a contact with pigments in the presence of water and oxygen [18]. Rods coated with formulations A4 and B4 show better performance even after exposure for 18 months. All the above



studies clearly bring out the fact that mild steel panels coated with formulations A4 and B4 show good performance as surface coatings for protecting the steel rebar in concrete.

### Conclusion

Systematic studies on the performance of acrylic polyol- aromatic isocyanate and polyester polyol – aromatic isocyanate combinations as surface coatings for steel rebars in concrete, by studying their mechanical properties and by accelerated tests, bring out the following main conclusions:

1. polyester polyol- aromatic isocyanate coating perform better than acrylic polyol- aromatic isocyanate coatings;
2. incorporation of flyash in the coating formulation influences the performance of the coating considerably;
3. the presence of TiO<sub>2</sub> in the coating has an adverse effect on the coating performance when exposed in coastal yard.

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