

Studies on Corrosion-Resistant Behavior of Siliconized Epoxy Interpenetrating Coatings over Mild Steel Surface by Electrochemical Methods

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Solvent-free siloxane-modified epoxy coatings were developed by the interpenetrating technique using epoxy resin as base (DGEBA, GY 250, Ciba-Geigy) and hydroxyl-terminated polydimethylsiloxane as modifier (commercially known as silicone) with γ -aminopropyltriethoxysilane as cross-linker, dibutyltindilaurate as catalyst, and 25% zinc powder as additive. Hexamethylenediamine (Aldrich) and polyamidoamine (HY 840, Ciba-Geigy) were used as curatives for the siliconized epoxy coatings containing 25% zinc powder. The corrosion-resistant behavior of these coating systems is assessed by electrochemical methods such as electrochemical potential measurements, potentiodynamic polarization, and electrochemical impedance spectroscopic methods. Based on the results obtained from the electrochemical potential measurements for epoxy and siliconized epoxy coating systems, few samples, namely AX₄ and BX₄, have been found to be the best corrosion-resistant coating systems, and they are used for potentiodynamic polarization measurements, electrochemical impedance, and salt-spray tests. The experimental results reveal that the siloxane (10%) modified epoxy coating system (AX₄) with 25% zinc powder cured by hexamethylenediamine offers the maximum corrosion protection to the steel surface rather than the polyamidoamine-cured system (BX₄). The better protective action offered by the coating system (AX₄) is mainly imparted by the reaction of aliphatic amine hydrogens with oxirane groups of the epoxy resin, which gives coating films with a high cross-link density. The observation is further supported by a capacitive behavior in the Nyquist plot and no spreading of visible corrosion product in the salt-spray test.

Keywords corrosion, organic coatings, polymer coatings, potentiometric tests, steel

1. Introduction

The protection of surfaces by organic coatings is the most prominent among the various surface-protection methods due to their performance, commercial feasibility, and ease of application. Furthermore, organic coatings enriched with zinc powder as additive play an important role in the protection of steel surfaces against corrosion.^[1] The use of epoxy coatings for high-performance applications is restricted mainly because of their low impact strength and high rigidity. Numerous investigations have been conducted over many years in an attempt to develop a process and procedure that would allow significant improvements in toughness achieved at minimum expense of mechanical properties.^[2-8] The demand for high-performance polymeric coatings having superior properties such as impact strength, toughness, flexibility, dielectric behavior, high-temperature applications, low coefficient of thermal expansion, and easy processability has led to the development of elastomer-toughened polymeric coatings by the interpenetrating polymer network (IPN) mechanism.^[9-11] The IPNs are novel types of polymer hybrids: they are distinct

polymer networks that cannot be separated physically, and they possess excellent physicochemical properties ideally suitable for high-performance coatings. The IPN coating systems have excellent resistance to weathering, microbial organisms, and ozone.

Under service conditions, organic coatings tend to degrade on aging. The process of degradation of the polymer in a coating is otherwise scientifically known as a process of microseparation with the enlargement of submolecular structures, which leads to poor performance of coating systems. The performance can be improved by the application of IPNs, which avoid the spontaneous phase separation besides having other useful properties.^[2-4] Among the polymeric modifiers for epoxy resins, polydimethylsiloxane, owing to its superior flexibility and thermal stability, is regarded as one of the best materials available to modify epoxy resin.^[12]

In the current study, diglycidyl ethers of bisphenol-A (epoxy resin GY 250, Ciba-Geigy) have been hybridized in the form of an IPN structure with the help of hydroxyl-terminated polydimethylsiloxane, γ -aminopropyltriethoxysilane, dibutyltindilaurate, hexamethylenediamine, polyamidoamine, and zinc powder. The corrosion-resistant behavior of hybrid-siliconized epoxy coating systems is characterized by electrochemical methods.

2. Experimental

2.1 Surface Preparation of Test Specimen

Mild steel specimens (22 gauge), each of an area 37.5 cm² (5 cm × 7.5 cm) with composition C 0.04%, Si 0.01%, Mn

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Table 1 Nomenclature for Coating Systems and Curatives

Curative	Epoxy Coating System (Ciba-GY 250) (X)			
	Siloxane/Epoxy (wt./wt.)	Siloxane/Epoxy (wt./wt.)	Siloxane/Epoxy (wt./wt.)	Siloxane/Epoxy (wt./wt.)
	0/100 (wt./wt.)	0/100 (wt./wt.) with 25% zinc	10/90 (wt./wt.)	10/90 (wt./wt.) with 25% zinc
Hexamethylenediamine (A)	AX ₁	AX ₂	AX ₃	AX ₄
Polyamidoamine (B)	BX ₁	BX ₂	BX ₃	BX ₄

Table 2 Amount of Curatives, Cross-Linking Agent, and Catalyst Used in Siliconized Epoxy Coating Systems (AX and BX)

Siloxane/Epoxy (wt./wt.)	Amount of Curative (g)		Cross-Linking Agent (g)	Catalyst (g)
	AX	BX		
...	Hexamethylenediamine	Polyamidoamine
0/100	15	50
10/90	13.5	45	0.1	0.01

0.17%, P 0.002%, S 0.005%, Cr 0.04%, Mo 0.03%, Ni 1.31%, and Fe 98.393% were used as the substrate material for the current study. The specimens were degreased with acetone and sand-blasted. The test specimens were weighed and placed in a desiccator for conditioning.

2.2 Preparation of Siloxane-Modified Epoxy Coating System

The siloxane-modified epoxy IPN coating system was developed using epoxy resin (DGEBA, GY 250, Ciba-Geigy), referred to as system X. The curatives hexamethylenediamine (Aldrich) and polyamidoamine (HY 840, Ciba-Geigy) are referred to as A and B, respectively. The siloxane component (of molecular weight about 24,000) used in the current work for development of the interpenetrating coating system was derived from octamethylcyclotetrasiloxane (Wacker-Chemie, Germany) through controlled equilibration polymerization reaction. A silane derivative, namely γ -aminopropyltriethoxysilane (Union Carbide, Taft, LA), was used as a cross-linker for hydroxyl-terminated polydimethylsiloxane and epoxy resin along with dibutyltindilaurate as catalyst. The nomenclature of epoxy resin, curatives, and the siloxane content in the IPN coating systems are presented in Table 1.

2.3 Preparation of Siliconized Epoxy Prepolymer Mix

A calculated percentage (wt./wt.) of hydroxyl-terminated polydimethylsiloxane prepolymer, calculated percentage of epoxy resin, and stoichiometric equivalent of γ -aminopropyltriethoxysilane and dibutyltindilaurate catalyst were thoroughly mixed at 90 °C for 20 min with constant stirring. Prior to characterization, the prepolymer mix was subjected to vacuum with the help of a vacuum pump to remove the trapped air inside the blend and also to accelerate the condensation reaction between γ -aminopropyltriethoxysilane and hydroxyl-terminated polydimethylsiloxane by removal of ethanol formed during the degassing process. Based on the stoichiometric equivalent (Table 2), a calculated amount of curatives was sequentially added to the prepolymer blend. The resulting

products were coated over mild steel specimens at 30 °C after the removal of entrapped air, and an ethanol by-product formed during the curing reactions and postcured (mild steel coated specimens after curing at 30 °C were again kept at our oven at 80 °C for complete curing) at 80 °C for 24 h.

2.4 Siloxane Introduction into Epoxy Coating System

To obtain reasonable improvement in impact and hydrophobic behavior of the coating systems without appreciable loss of other characteristics, the tentative requirement of hydroxyl-terminated polydimethylsiloxane component was taken as 10% (wt./wt.). Siliconized epoxy prepolymers of varying siloxane content (i.e., 10%, 20%, and 30%) were prepared and cured with corresponding curing agents. The cured systems were subjected to different tests, namely water absorption, chemical resistance, degree of blistering, degree of rusting, and flexibility. Among the systems developed, the siliconized epoxy systems having 10% siloxane content exhibited superior impact strength and excellent hydrophobicity and flexibility. As the percentage of siloxane increased, the physicochemical properties were found to be decreasing. Hence, 10% siloxane content was taken as an optimum percentage level for the modification of epoxy resin.^[13]

2.5 Application of Coating over Test Specimen

Mild steel specimens after proper surface preparation were coated with epoxy coatings (in the absence and in the presence of 25% zinc powder) and siloxane-modified epoxy coatings (in the absence and in the presence of 25% zinc powder) by brush. Polyamidoamine (HY840, Ciba-Geigy) and hexamethylenediamine (Aldrich) were used as curatives for both epoxy and siliconized epoxy coatings. The coating thickness (dry film thickness) of each specimen in the range of 150-160 μ m was measured using an elcometer. The coated specimens were subjected to immersion in 3% sodium chloride solution for a period of 15, 30, 45, and 60 days at room temperature (27 °C).

2.6 Electrode Preparation

Mild steel specimens (2.5 cm × 2.5 cm) were degreased using trichloroethylene, cleaned, sand blasted, and coated with the coating systems (i.e., A and B, respectively) by brush to a thickness of 150-160 μm and cured for 24 h at room temperature followed by a postcuring for another 24 h in an air oven at 80 °C. In the coated specimen, masking the remaining portion with bee's wax exposed 1 sq. cm area at the center, and these specimens were used for electrochemical measurements.

2.7 Electrochemical Potential Measurements

The change in electrochemical potential values of the coated specimens immersed in 3% NaCl solution was recorded over a period of 60 days with a time interval of 15 days. The potential values were measured using a high-impedance digital multimeter with a saturated calomel electrode (SCE) with the luggin probe as a reference electrode.

2.8 Potentiodynamic Polarization Measurements (Tafel Extrapolation Method)

Potentiodynamic polarization studies were selectively carried out by the PARC (Princeton Applied Research Corporation, Princeton, NJ) corrosion measurement system for siliconized epoxy coatings AX₄ and BX₄, because these coating systems exhibit better corrosion resistance than other coating systems (AX₁, AX₂, AX₃ and BX₁, BX₂, BX₃). The potential of the electrode was varied by the universal programmer (Model 175, PARC). The potential versus log current plots were made by using the XY recorder (Model RE 0074, PARC). The electrochemical cell used for the current study consists of the prepared coated electrode as the working electrode, a platinum foil as the counterelectrode, a SCE as the reference electrode, and 3% sodium chloride as electrolyte.

2.9 Impedance Measurements

Electrochemical impedance measurements were carried out with the PARC Model 368-1 system over the frequency ranges between 100 mHz and 10 kHz. All the measurements were carried out at the corrosion potential.

The impedance measurements were made for the coating systems AX₄ and BX₄ over mild steel specimens at a higher frequency range (0.1 Hz to 10 kHz) by performing the lock-in experiment followed by a fast Fourier transformed (FFT) experiment, which measures the impedance at a lower frequency range (0.1-4 Hz). In the lock-in experiment, the impedance of the sample was measured by imposing a 10 mV AC voltage (sine wave), measuring the AC current and voltage within the lock-in, then calculating the impedance of the coating at a particular frequency.

For the FFT experiment, the impedance was measured from the Fourier transform of the applied potential and the measured current. The base frequency for the FFT experiment was 0.1 Hz and the upper limit was 4 Hz. Five data cycles were taken and averaged before FFT was taken. The charge transfer resistance and capacitance of the various coating systems studied were obtained from the corresponding Nyquist plots. The resistance values were calculated from the corresponding Nyquist plots,

and the capacitance values were calculated using the equation given below:

$$C_p = 1/2 f_{max} R_p$$

where $\Pi = 3.14$, f_{max} is the frequency in Hz at the maximum point of the semicircle, and R_p is the resistance in ohm · cm².^[14]

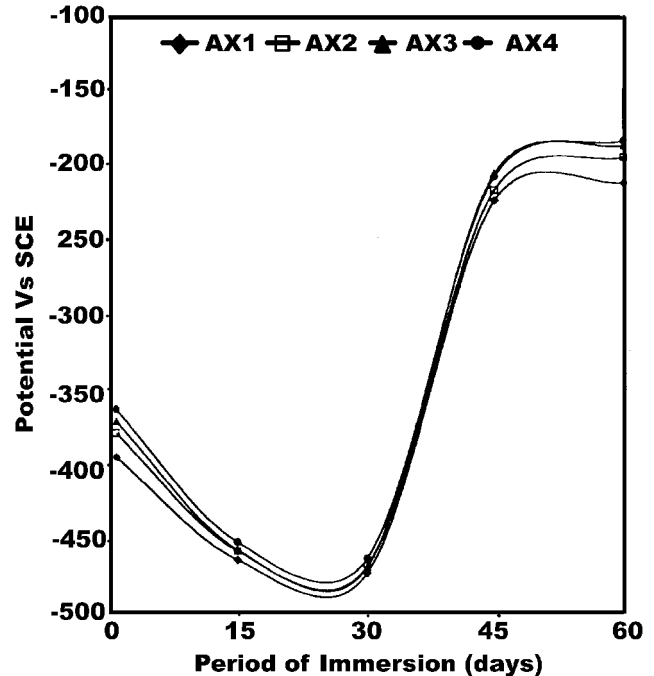


Fig. 1 Electrochemical potential measurements of A-cured systems

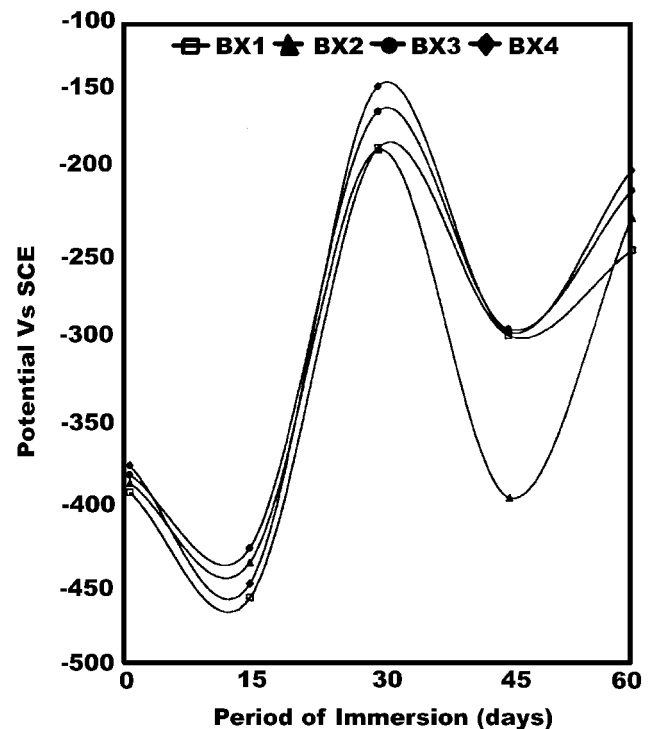


Fig. 2 Electrochemical potential measurements of B-cured systems

2.10 Salt-Spray Test

The salt-spray test was conducted on the coated specimens as per the ASTM B117 standard. For this test, the coated specimens were scratched diagonally and exposed in a continuous salt fog chamber (canning) containing 3% sodium chloride solution at 30 °C. The test had been carried out for a period of 30 days. Three percent sodium chloride solution was sprayed using a compressor with a pressure range of 10–25 psi. The observations on coated panels were taken periodically.

3. Results and Discussion

The electrochemical potential values are presented in Fig. 1 and 2. From the figures it can be observed that the shift in electrode potential values of the coating systems cured with A and B was more negative during the period of the first 15 days. The potential shift toward more negative indicates the initiation of the corrosion mechanism.

In the case of epoxy and siliconized epoxy coating systems (in the presence and in the absence of 25% zinc powder) cured by B, the shift in potential was less negative (Fig. 2) at the end of 15 days of immersion. The shift in potential toward less negative for B-cured systems may be explained due to the accumulation of corrosion products over the working electrode surface, which act as a barrier coating. At the end of 30 days of immersion, the potential shift moved toward more negative (Fig. 2), which may be explained due to the dissipation of corrosion products from the working electrode surface. The potential approaches a steady-state value during the period between 45 and 60 days.

In the case of coating systems cured with A, the potential shift was toward negative (Fig. 1) up to 30 days, after which the shift in potential was toward less negative and reached a steady state during the period between 45 and 60 days. This can be attributed to the reaction of amine hydrogens with epoxy groups, which gives a coating film with less permeability.^[21]

During the period of study, it was observed that the shift in potential for the coating systems studied moves toward less negative (Fig. 1 and 2) irrespective of the curatives employed. This reveals that the permeability of all coatings is very low.

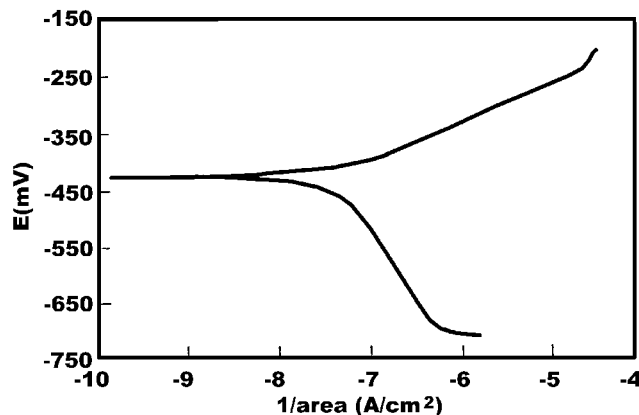


Fig. 3 Polarization measurements of AX₄ coating system after 30 days of immersion

However, among the coating systems studied, the siliconized epoxy coating systems exhibit better corrosion resistance. This may be explained due to low surface tension, large contact angle, and high hydrophobic nature imparted by the inherent molecular structure of the siloxane skeleton.^[12] Further, the addition of zinc powder (25%) into epoxy and siliconized epoxy coatings cured with A and B enhances the corrosion resistance. Among the curatives used, the hexamethylenediamine-cured coating systems, due to their water-repelling nature, exhibit superior corrosion resistance.

The polarization behavior of siliconized epoxy coating systems with the addition of zinc powder (25%) cured by hexamethylenediamine and polyamidoamine over mild steel specimens in 3% sodium chloride solution for different time intervals is presented in Fig. 3 to 6. The polarization values are given in Tables 3 and 4.

It is observed from the results that as the time of immersion increases, the polarization curves of the hexamethylenediamine-cured system are shifted toward the anodic side, whereas the polarization curves of the polyamidoamine-cured system are shifted toward the cathodic side. The shift of polarization curves toward anodic in the case of the hexamethyl-

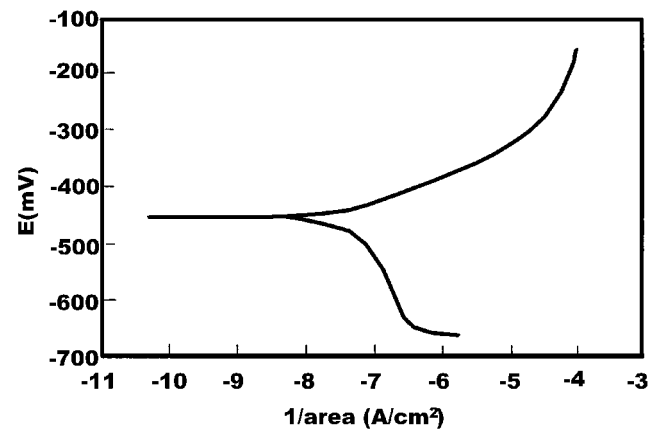


Fig. 4 Polarization measurements of BX₄ coating system after 30 days of immersion

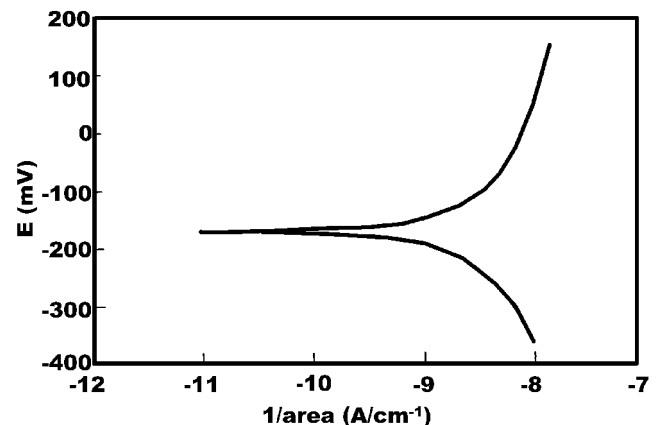


Fig. 5 Polarization measurements of AX₄ coating system after 60 days of immersion

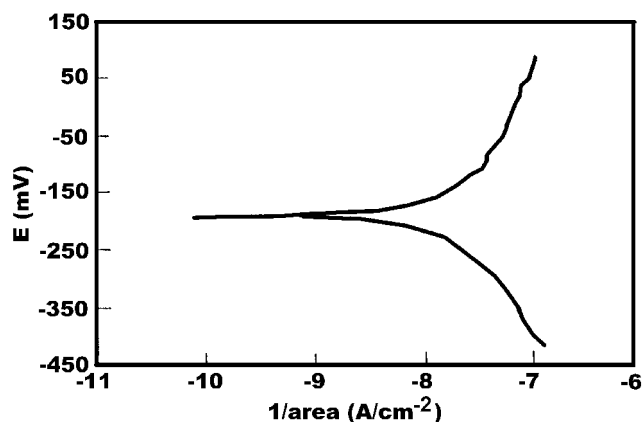


Fig. 6 Polarization measurements of BX₄ coating system after 60 days of immersion

Table 3 Polarization Measurements of Coating Systems After 30 Days

Coating Systems	<i>E</i> (mV)	<i>I</i> _{corrosion} (nA/cm ²)	Corrosion Rate (mpy)
AX ₄	-432.3	32.84	13.96e ⁻³
BX ₄	-456.1	94.2	40.05e ⁻³

Table 4 Polarization Measurements of Coating Systems After 60 Days

Coating Systems	<i>E</i> (mV)	<i>I</i> _{corrosion} (nA/cm ²)	Corrosion Rate (mpy)
AX ₄	-198.2	9.203	3.912e ⁻³
BX ₄	-194.7	47.2	20.07e ⁻³

enediamine coating system indicates that the incorporation of siloxane into the epoxy coatings reduces the transit of reactive species to the substrate (steel specimen) and has an ability to withstand a severe corrosive environment for longer duration. In addition, the incorporation of zinc powder as additive offers protection either by acting as a barrier to corrosive agents (oxygen, water, and ions), by suppressing the cathodic and/or anodic reactions, or by inserting a high electrical resistance between the cathodic and anodic areas of the corrosion reactions.^[15-17]

The shift of polarization curves toward the cathodic side in the case of the polyamidoamine-cured coating system may be explained due to the moisture-absorbing nature of the curative, which permits the permeation of the corrosive species to the metal substrate in addition to its polar amide linkage. At the end of 60 days, the polarization measurements reveal that the corrosion potential and open circuit potential of the two systems behave in a similar manner. The corrosion current of coatings AX₄ and BX₄ ranges from 47.2 to 9.203 nA/sq. cm, which shows that the systems AX₄ and BX₄ exhibit good resistance to corrosion under the experimental conditions. However, the hexamethylenediamine-cured siliconized epoxy coat-

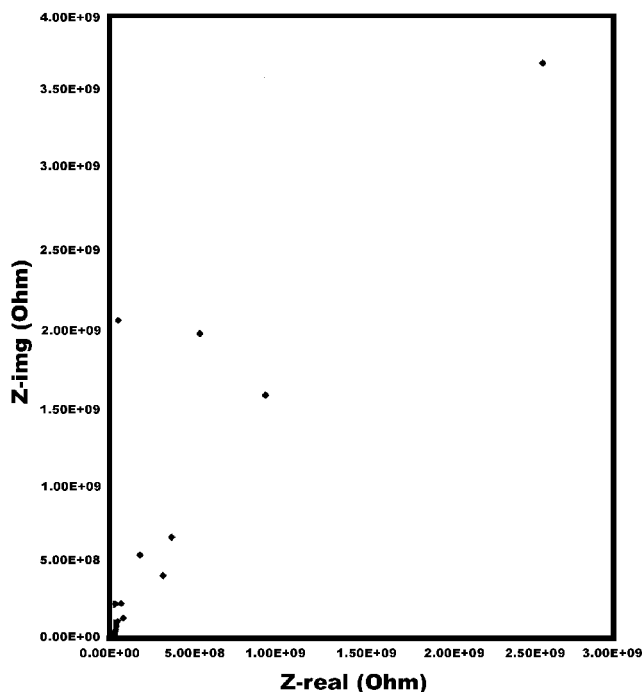


Fig. 7 Nyquist plot of AX₄ coating system

ing system with zinc powder (25%) having very low corrosion current (9.203 nA/sq. cm) has higher corrosion resistance than the polyamidoamine-cured system (BX₄). The electrochemical potential data also tend to support this observation.

The Nyquist plots obtained for the siliconized epoxy coating systems AX₄ and BX₄ studied after 24 h of immersion in 3% sodium chloride solution at their respective open circuit potential are illustrated in Fig. 7 and 8, respectively. It can be seen that, with the exception of coating system AX₄, the other coating system BX₄ exhibits an incomplete semicircle in the high-frequency region, followed by a low-frequency diffusion tail commonly called a Warburg diffusion tail.^[18] The formation of an incomplete semicircle suggests that the sodium chloride solution has started permeating through the coating in the case of coating system BX₄. In contrast to this observation, a linear portion in the high-frequency region is noticed in the case of coating system AX₄, indicating the existence of a capacitive behavior. The formation of a low-frequency diffusion tail in coating system BX₄ confirms that the corrosion process is a diffusion-controlled reaction. The formation of a linear portion in the high-frequency region in coating system AX₄ shows that the coating is limiting the corrosion of the steel specimen by a diffusion barrier type mechanism. The capacitance (*C*_c) and resistance (*R*_p) calculated for the coating systems AX₄ and BX₄ are presented in Table 5. The open circuit potential (o.c.p) of the coating systems AX₄ and BX₄ are also included in the same table for comparison. The resistance and the capacitance values of all the coating systems (AX₄ and BX₄) are in the range of 10⁹ ohm · cm² and 10⁻¹⁰ F, respectively. The capacitance values associated with the high-frequency semicircle are much lower than typical double-layer capacitance values and therefore cannot be due to corrosion reactions at the substrate/coating interface. These values are, however, comparable to the

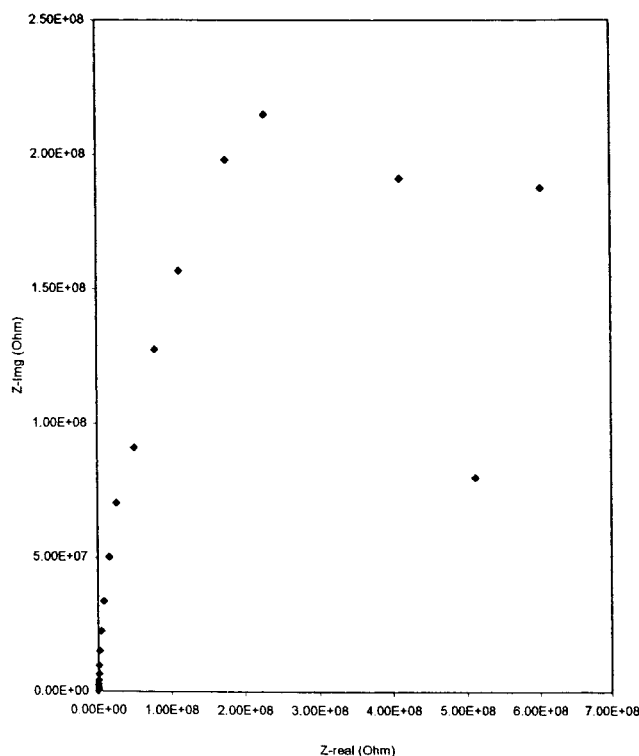


Fig. 8 Nyquist plot of BX₄ coating system

Table 5 EIS Data for Different Coating Systems Studied

Coating Systems	<i>E</i> (mV)	Paint Film Resistance (<i>R_p</i>) (ohm · cm ²) × 10 ⁹	Paint Film Capacitance (<i>C_p</i>) (F/cm ²) × 10 ⁻¹⁰
AX ₄	-363	10.0	0.63
BX ₄	-377	0.6	2.65

values reported elsewhere for conventional polymeric coatings.^[19] On this basis, the high-frequency semicircle in the Nyquist plot (Fig. 8) can be attributed to the siliconized epoxy coating. The high values of resistance of the order of 10⁹ ohm · cm², compared to that of conventional coatings, which are normally in the range of 10⁶ ohm · cm²^[19,20], confirm that there was no contact between the electrolyte and metal substrate and suggest that the coating systems studied exhibit better corrosion resistance to steel surfaces over conventional coatings.

The Bode plots of coating systems AX₄ and BX₄ are presented in Fig. 9 and 10. From these plots it can be seen that there are two linear segments in each plot: one linear segment is parallel to the frequency axis in the low-frequency region followed by the other segment with a slope close to the value of -1 in the high-frequency region. This value represents the coefficient of impedance over the frequency ranges between the threshold frequency and 10 kHz for coating systems AX₄ and BX₄. The threshold frequency is the frequency at which the value of impedance of the coating system changes with the applied frequency. The threshold frequency varies according to the nature of the coating systems. The Bode plot of coating systems AX₄ and BX₄ can be explained with the help of thresh-

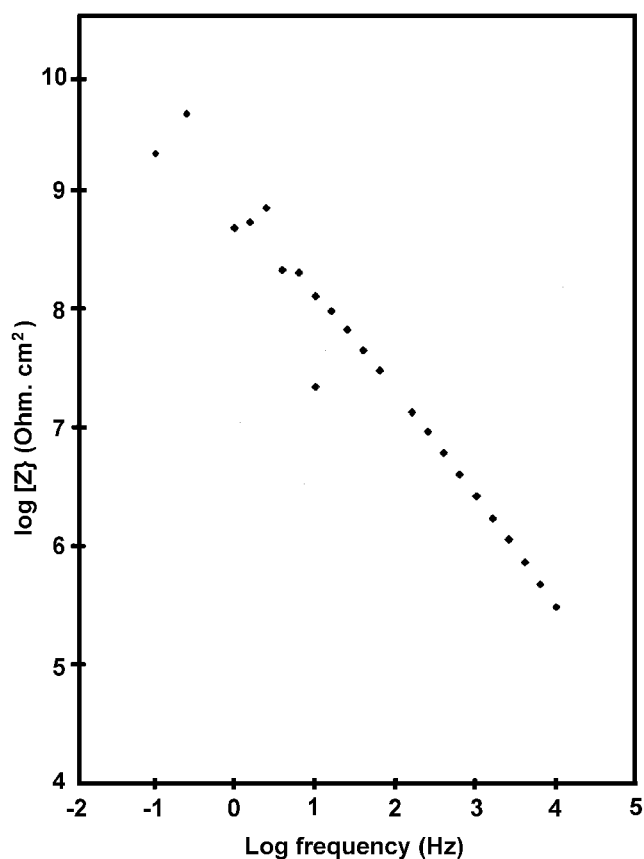


Fig. 9 Bode plot of AX₄ coating system

old frequency limits and the variation of logarithmic values of impedance with frequency. Between the coating systems of the current study, system AX₄ possesses the lowest limit of the threshold frequency (0.063 Hz), and system BX₄ exhibits the highest threshold frequency (2.0 Hz).

Further, it is also observed that the siliconized epoxy coating system AX₄ cured with hexamethylenediamine offers maximum resistance toward the corrosion of steel specimens under the experimental conditions. This can be attributed to the low permeability of coating system AX₄ when compared to coating system BX₄, and the Nyquist plot supports this observation. The permeable nature of coating system BX₄ influences the occurrence of semicircle in the Nyquist plot. However, the extent of the permeation of electrolytes and their corrosion-resistant behavior varies according to the nature of coatings and their bonding characteristics.^[21]

The permeability of the coatings involved in the current study differs mainly due to the curatives used. Primary aliphatic amine hydrogens are more reactive than secondary amine hydrogens (probably because of steric hindrance effects), conversely, aromatic amines are very slow to react unless modified and they are cured at high temperatures. However, primary amines provide well-cured coatings at room temperature. The reactions of amine-cured epoxy coatings are based on the oxirane ring opening with active amine hydrogens. In addition, the molecular structure of the curing agent's backbone and the nature of the amine hydrogen greatly influ-

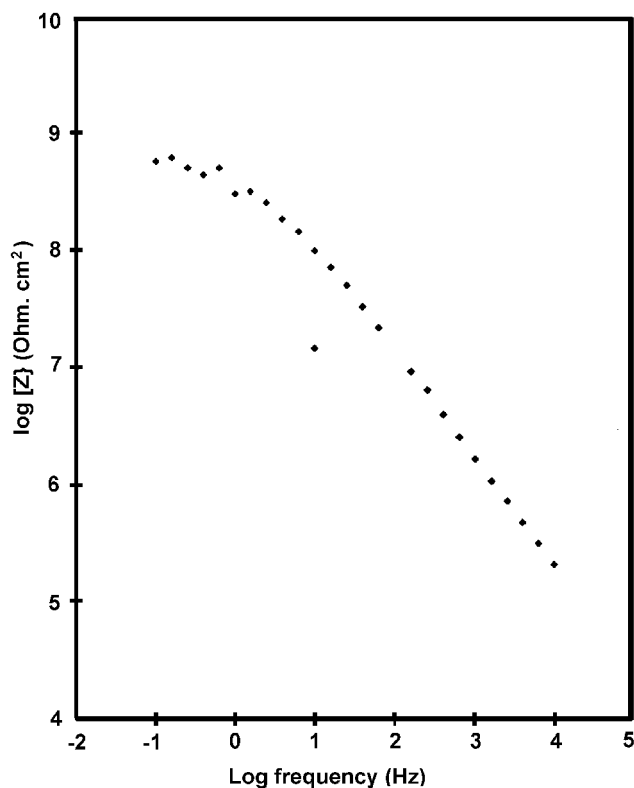


Fig. 10 Bode plot of BX₄ coating system

ence the reaction rates and physicochemical properties of the final network structure of the coating systems. The excellent corrosion-resistant property offered by coating system AX₄ (cured by hexamethylenediamine) may be explained as due to the reaction of aliphatic amine hydrogens with the oxirane group, which gives coating films with high cross-link density and, therefore, imparts better resistance to chemicals, solvents, electrolytes, and inorganic acids under varying environmental conditions.^[21] In addition, the good adhesion and film-forming ability of the hexamethylenediamine curative enhances the water-resistant characteristics of the coating, thereby limiting the corrosion process. As a result, a capacitive behavior in the Nyquist plot is observed for the coating system AX₄. The 720 h salt-spray test also supports the result obtained from electrochemical studies. At the end of the salt-spray test, no visible corrosion products were identified on the surface of the unscratched area. Corrosion products were seen mainly on the scratched area. Further, the spreading of corrosion underneath the paint film is limited in both coating systems studied. However, the extent is low in the case of coating system AX₄ compared with coating system BX₄.

4. Conclusions

Siliconized epoxy coatings containing 25% zinc powder with two different curatives were prepared. The electrochemical behavior of these coating formulations over mild steel specimens in 3% NaCl solution was investigated using elec-

trochemical methods, and the results were compared with those of salt-spray tests. From the results, it is observed that the siloxane (10%) modified epoxy coating (AX₄) with 25% zinc powder cured by hexamethylenediamine offers the maximum corrosion protection, rather than the BX₄ coating system. The higher protective action toward corrosion offered by the AX₄ coating system is mainly imparted by the reaction of aliphatic amine hydrogens with oxirane groups of the epoxy resin, which gives coating films with high cross-link density. The observation is further supported by a capacitive behavior in the Nyquist plot and no spreading of visible corrosion products in the salt-spray test. It is concluded that the hexamethylenediamine-cured siloxane (10%) modified epoxy coatings can be used as a protective coating for steel surfaces under marine environments.

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