

Synthesis and Characterization of Tween 80-Modified Hydrophobic Silica Coatings for Corrosion Protection of Steel

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Abstract- In the present study, hydrophobic silica coatings modified with Tween 80 were fabricated on steel substrates using the sol-gel method and evaluated for their structural, surface, thermal, mechanical, and anticorrosion properties. Methyltrimethoxysilane (MTMS) was used as the silica precursor, while Tween 80 was incorporated as a modifying agent. The coatings were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), water contact angle measurements, thermal conductivity measurements, water-jet impact testing, and potentiodynamic polarization. FTIR analysis confirmed the presence of characteristic Si-O-Si, Si-C, C-H, and ester-group vibrations associated with the modified silica network. SEM observations showed the formation of porous, spherical microstructures, with increased porosity and reduced particle size as the Tween 80 concentration increased. The water contact angle increased from $131 \pm 2^\circ$ for the unmodified coating to $148 \pm 2^\circ$ for the 0.3 mM Tween 80-modified coating, with a roll-off angle of approximately 10° . The thermal conductivity decreased from 0.071 to $0.017 \text{ W m}^{-1} \text{ K}^{-1}$ with increasing Tween 80 content. The modified coating also showed good resistance to water-jet impact. Potentiodynamic polarization measurements demonstrated improved corrosion protection, with the corrosion potential shifting from -0.94 V for pristine steel to -0.66 V for the 0.3 mM Tween 80-modified coating and a substantial reduction in corrosion current density. Even after 10 days of immersion in 3.5 wt% NaCl solution, the modified coating retained better corrosion resistance than pristine steel. The results indicate that Tween 80-modified silica coatings provide a promising combination of hydrophobicity, mechanical robustness, low thermal conductivity, and corrosion protection for steel surfaces.

Keywords- Tween 80; hydrophobic silica coating; sol-gel method; corrosion protection; steel; water contact angle; potentiodynamic polarization

I. INTRODUCTION

A wide variety of metals, such as steel, aluminum, copper, and zinc, have been used extensively in industrial

applications and everyday life because of their exceptional mechanical properties and physicochemical characteristics. However, their active chemical properties make them susceptible to corrosion in the environment. Metal surfaces undergo various electrochemical reactions that lead to oxidation. Consequently, corrosion fatigue and stress corrosion cracking may occur in metallic materials, reducing their mechanical properties, degrading electronic and optical properties, shortening the service life of mechanical equipment, and even causing catastrophic failures, resulting in substantial economic losses.

Passivation coatings on metal surfaces are an effective means of protecting metals from corrosion. Chromate-based passive films have been widely used as corrosion inhibitors in the metal industry because of their superior corrosion resistance. However, chromate is highly toxic and poses serious environmental hazards. In addition, increasingly stringent pollution-control regulations and growing environmental awareness have led to the gradual prohibition of chromate-based coatings. Consequently, environmentally friendly passivation films have become increasingly important as alternatives to toxic chromate-containing films. Several studies have investigated the formation of passivation films using metallic compounds [4-6], organic films [7], nanoparticles [8-10], and other composite passivation films [11-12] to replace chromate-containing anticorrosion coatings. Although some of these coatings are impervious to corrosive media such as water, oxygen, and corrosive ions such as Cl^- , corrosion of the metallic substrate cannot be completely prevented once the electrolyte reaches the metal/coating interface [13].

One of the most significant characteristics of a material surface is its wettability, which describes the affinity of the surface for water [14-15]. Surface wettability is generally related to surface energy and surface roughness (surface microstructure) [16-17]. Hydrophobic surfaces, particularly those with high water contact angles, have attracted considerable attention because of their excellent properties, including water repellency, self-cleaning, corrosion resistance, and mechanical robustness [18-19].

Metallic materials have been protected with superhydrophobic films in recent years. One of the main characteristics that distinguishes superhydrophobic films from other surface coatings is their water-repellent ability, which can prevent corrosive media from penetrating the film and inhibit the formation of corrosion cells [20-21]. Micro- and nanostructures on superhydrophobic surfaces can trap a considerable amount of air when exposed to air, greatly reducing the contact area between the surface and water droplets. When a hydrophobic surface is immersed in a corrosive medium, the trapped gas acts as an air film between the solution and the metal surface, thereby enhancing the anticorrosion performance of the superhydrophobic surface. Overall, corrosion of metallic substrates is inhibited by water repellency and the air trapped within the surface structure [19, 22-25]. Owing to these excellent characteristics, superhydrophobic films are promising protective coatings for metals and have been extensively investigated for corrosion protection of steel, aluminum, zinc, copper, and magnesium alloys [26-32].

In the sol-gel method, the raw materials are chemical compounds with high chemical activity. These compounds undergo hydrolysis and condensation to form a stable sol, which subsequently aggregates to form a gel with a three-dimensional network structure. The substrate surface can be coated with molecular- and nanostructured materials after immersion and heat treatment. This method is highly promising for producing nanoparticles with a variety of morphologies and for developing hydrophobic surfaces with corrosion-resistant properties [33-36]. Owing to its environmentally friendly, low-cost, and user-friendly characteristics, the sol-gel method has substantial potential for fabricating superhydrophobic surfaces on metals. Based on electrochemical measurements and surface characterization, many researchers have applied the sol-gel method to improve the corrosion resistance of metals and have achieved effective corrosion protection [37-38].

Superhydrophobic surfaces can usually be achieved in a single step without further modification. The sol-gel process itself can produce a low-energy surface. Using methyltriethoxysilane (MTES), methanol (MeOH), and water under the catalysis of NH_4OH , Venkateswara Rao [39] developed a superhydrophobic surface on copper with a static water contact angle as high as 155° . The copper substrate was coated with a silica network structure. Chemical aging tests showed that the surface remained stable even after treatment with 50% HCl solution and exposure to 95% relative humidity. In the present work, self-cleaning hydrophobic coatings were fabricated on steel using the sol-gel method and evaluated for their potential anticorrosion performance.

II. MATERIALS AND METHODS

2.1 Materials

For the preparation of the scratch-resistant coating, the chemicals used were methyltrimethoxysilane (Sigma-Aldrich Chemie, Germany), methanol (S.D. Fine Chem. Ltd., Mumbai, India), Tween 80 (Thomas Baker, Mumbai, India), and oxalic acid (Loba Chemie, India). Double-distilled water was used in the preparation of the catalyst. All chemicals were used as received, without further purification. Commercially available steel alloy substrates measuring $1.00\text{ cm} \times 4.00\text{ cm}$ were used for coating deposition.

2.2 Fabrication of Hydrophobic Coating

A coating sol was prepared by maintaining the molar ratio of MTMS:MeOH:H₂O at 1:12.04:3.96, respectively, with a variation of 1 to 10 vol% Tween 80 solution and 0.1 M oxalic acid as the catalyst. A 1 to 10 vol% solution of Tween 80 was prepared in methanol. These solutions were added to the sol and deposited at room temperature onto cleaned stainless-steel substrates using a commercial spin coater (Chemat Technology, KW-4A Spin Coater, Northridge, USA) to obtain a thin silica coating. The spin-coating conditions were 2500 rpm for 60 s. The metal substrates were then annealed at 200°C for 4 h for densification of the films and removal of residual solvent. Before coating, the steel substrates were mechanically polished with grade 600 emery paper, degreased with water, and finally cleaned with acetone.

III. CHARACTERIZATION

A Fourier transform infrared spectrometer (FTIR) (Perkin-Elmer Model No. 783, USA) was used to record IR spectra in the range of $4000\text{ to }400\text{ cm}^{-1}$ with a resolution of 1 cm^{-1} . The surface morphology and homogeneity of unmodified and Tween 80-modified coatings were investigated using scanning electron microscopy (SEM) (Model: JEOL-JSM-6360). The water contact angle was measured using a standard goniometer (Ramehart Instrument Co., USA) equipped with a CCD camera. All contact angles were determined using a $10\text{ }\mu\text{L}$ water droplet on the coating surface at room temperature. Potentiodynamic polarization measurements were carried out to evaluate the corrosion resistance of the coatings. All measurements were performed using an electrochemical analyzer (CHI604E, China) in 3.5 wt% NaCl solution at room temperature using a three-electrode system. A self-cleaning test was employed to evaluate the self-cleaning ability of the coatings. The mechanical hardness of the coatings was evaluated using jet-spray and sand-impact tests.

IV. RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The organic modification and hydrophobicity of the silica coatings were confirmed by Fourier transform infrared (FTIR) spectroscopic studies.

The coated material was removed from the metal substrate, and the powder was heated at 100 °C for one hour to remove residual moisture. The coating powder was then milled with potassium bromide (KBr) to form a very fine powder. This powder was compressed into a thin pellet for FTIR analysis in transmission mode because KBr is transparent in the IR region.

Fig. 1 FTIR spectra of unmodified silica coatings (a) and Tween 80-modified silica coatings (b)

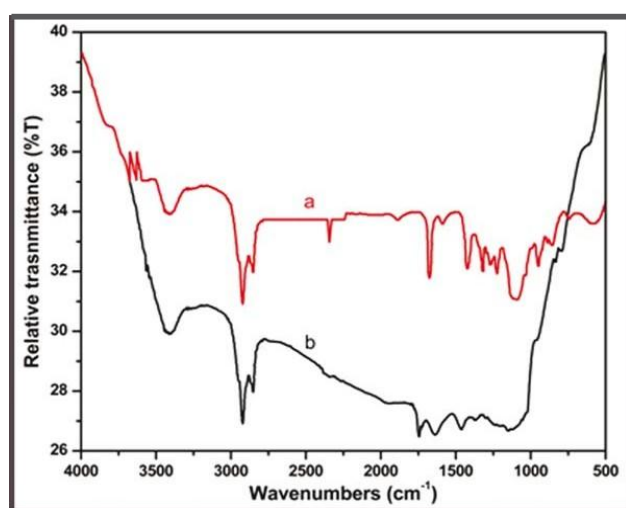


Fig. 1(a) and (b) show the FTIR spectra of the silica coatings prepared without polymer, using only the MTMS precursor, and with Tween 80, respectively. Several characteristic peaks were observed in the range of 4000 to 500 cm^{-1} , indicating the presence of methyl groups in the silica coating. The absorption peak near 1080 cm^{-1} , characteristic of the Si-O-Si bond, was present in all coating spectra [40-41]. C-H stretching and bending modes were observed at 2950 and 1400 cm^{-1} in samples (a) and (b). Si-C bonds were observed at 765 and 1265 cm^{-1} in both samples [42-43]. The new vibration near 1740 cm^{-1} is related to an ester group in Tween 80 (spectrum b). The ester group in Tween 80 is expected to show a vibration near 1735 cm^{-1} [44-45], but the observed band was shifted to 1740 cm^{-1} , probably due to the presence of Si-C groups. The FTIR spectra suggest that Tween 80 is strongly associated with the silica network. The broad absorption band at 3400 cm^{-1} corresponds to polar -OH bonds and residual Si-OH groups.

4.2 Scanning Electron Microscopy (SEM)

The SEM micrographs of pure SiO₂ and SiO₂ modified with different concentrations of Tween 80 are shown

in Fig. 2. The SEM images show that the microstructural arrangement is nonhomogeneous, with grains and voids. Hierarchical porous spherical microstructures with diameters of around 1-2 μm were formed in the modified coatings. The unmodified silica coatings prepared with MTMS as the precursor had closely packed (denser), well-grown grains with random orientations compared with the Tween 80-modified samples. The silica particles in the Tween 80-modified coatings were approximately 1 μm in size, spherical in shape, and formed a relatively well-oriented network with ordered branching. MTMS as a precursor might reduce the pore volume because of the smaller grains. This causes individual grains to come closer together, increasing the effective area of grain-to-grain contact and resulting in greater densification or lower porosity. It was observed that when the effective concentration of the dopant becomes greater than the solid-solution limit, the energy associated with grain-boundary movement increases [46]. The Tween 80-modified silica coating showed that, as the Tween 80 concentration increased from 0.1 mM to 0.3 mM, the particle size decreased and the porosity of the coatings increased. The SEM micrographs of the Tween 80-modified silica coatings revealed strong bonding among the silica particles. This bonding may increase the toughness of the coating and could be responsible for its resistance to surface scratches, such as those evaluated by the pencil-scratch test.

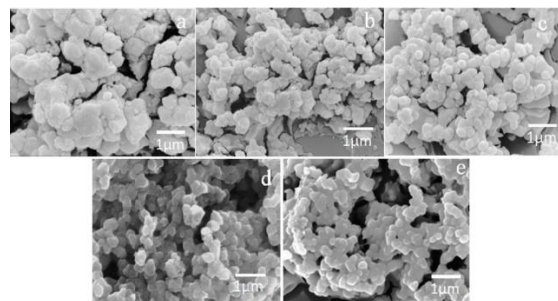


Fig. 2 SEM micrographs of unmodified (a), 2% Tween 80-modified (b), 4% Tween 80-modified (c), 6% Tween 80-modified (d), and 8% Tween 80-modified (e) SiO₂ coatings

4.3 Thermal Conductivity (K)

The thermal conductivity was measured using a C-T meter (Teleph Company, France; accuracy: 10–3 W–1 m–1 K–1) with a ring-probe arrangement. The probe measures the thermal conductivity (K) by sandwiching the ring probe between the coating powder obtained from the substrates. The rise in the temperature of the sample (ΔT) due to the supplied heating power (0.09 W) is given by

$$\Delta T = \left(\frac{RL^2}{L} \right) \left(\frac{1}{4\pi k} \right) [\ln(t) + C^{te}] \quad (1)$$

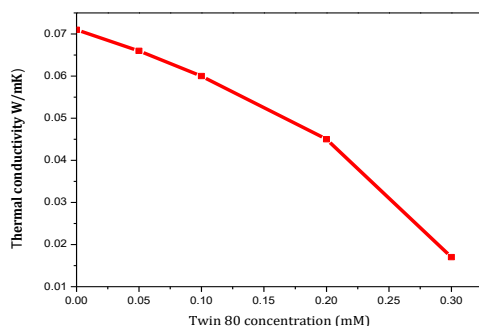


Fig. 3 Variation in thermal conductivity of silica coatings modified with Tween 80

The thermal conductivity of the coating depends on the density of the silica network. Thermal conduction in silica coatings occurs through solid conduction and radiative transmission mechanisms. The decrease in thermal conductivity of the silica coatings prepared with Tween 80 is shown in Fig. 3.

As the concentration of Tween 80 increased, the thermal conductivity decreased from 0.071 to 0.017 W m⁻¹ K⁻¹ for 0% Tween 80 to 0.3 mM Tween 80, respectively. The decrease in thermal conductivity may be due to the reduction in the density of the coating. It was observed that, with increasing Tween 80 content, the samples exhibited lower thermal conductivity. The specific heat of the silica coating was found to increase from 146 to 103 kJ m⁻³ K⁻¹ with increasing Tween 80 content. Hence, the greater the porosity, the lower the thermally conducting solid content in the network [47]. The decrease in thermal conductivity with increasing organic content can be explained by the lower thermal conductivity of organic compounds. These low-thermal-conductivity materials have potential applications in thermal insulation systems [47].

4.4 Contact Angle Measurement

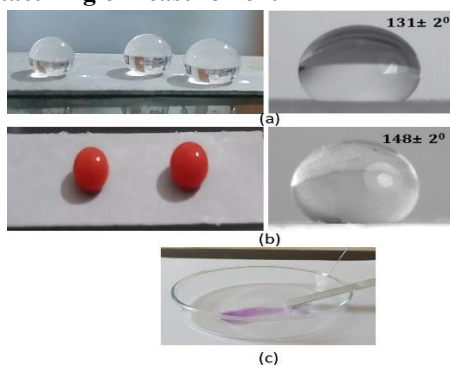


Fig. 4 Water contact angle images and photographs of water droplets on unmodified (a) and 0.3 mM Tween 80-modified coatings, and the water-spray jet test (c)

The hydrophobic behavior of the silica coating was quantified by placing a 10 μ L water droplet on the coating

surface using a contact angle meter. The small mass of the water droplet minimizes gravitational effects during measurement of the water contact angle.

The wetting parameters of a coated surface are usually evaluated by measuring the water contact angle (WCA), which is governed by both surface microstructure and surface free energy. The shapes of water droplets on the unmodified and 0.3 mM Tween 80-modified coatings are shown in Fig. 4(a) and (b), respectively. For the unmodified sample, a WCA of $131 \pm 2^\circ$ was observed. Despite this sufficiently high WCA, the water droplet remained adhered to the coating surface. This may be because of the non-uniform surface structure, where the water droplets could become pinned and remain stationary without sliding. In contrast, the Tween 80-modified sample exhibited a more uniform rough surface morphology and a WCA of $148 \pm 2^\circ$, with a roll-off angle of nearly 10° . The grains were arranged on the substrate, forming sufficient surface roughness, and the air layer became firmly trapped within the rough protrusions. As a result, the water droplet partially rested on the air layer, with a smaller fraction of the liquid in direct contact with the solid surface. This significantly reduced the liquid-solid contact area, corresponding to the Cassie-Baxter wetting state, and resulted in a high WCA and low sliding angle.

4.5 Mechanical Robustness of Coatings: Water-Jet Impact Test

Dynamic impacts can affect or destroy surface morphology, resulting in a decline in superhydrophobicity. Water-jet impact tests were performed to assess the sensitivity of the coating to dynamic impacts.

It is vital that superhydrophobic coatings possess a high degree of mechanical stability for practical applications. The impact of water droplets on the surface during the rainy season can alter the micro- and nanoscale surface morphology of the coating, leading to a decline in superhydrophobicity. A water-jet test was therefore used to evaluate the structural strength of the superhydrophobic coating. A water jet was generated using a 20 mL syringe and sprayed onto the superhydrophobic coating from a height of 3-4 cm above the surface. The velocity of the jet was maintained at approximately 8-9 m/s. Upon impact with the 0.3 mM Tween 80-modified silica coating, the water jet was rapidly repelled without spreading. Fig. 4(c) shows a photograph of the water jet impacting the 0.3 mM Tween 80-modified silica coating.

4.6 Potentiodynamic Polarization Curve

The anticorrosion behavior of various samples, namely pristine steel, unmodified coatings, and Tween 80-modified coatings, was evaluated by electrochemical measurements. The potentiodynamic polarization (PDPC) method was used to assess the protective ability of the

coatings. Fig. 5 shows the potentiodynamic polarization curves for the different samples.

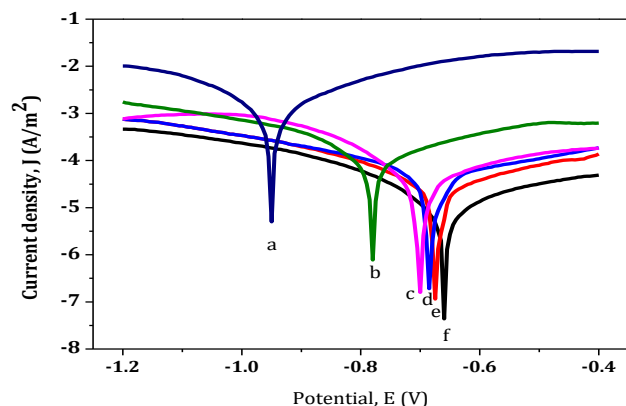


Fig. 5 Potentiodynamic polarization curve (Tafel plot) for pristine steel (a), unmodified sample (b), 0.05 mM Tween 80-modified sample (c), 0.1 mM Tween 80-modified sample (d), 0.2 mM Tween 80-modified sample (e), and 0.3 mM Tween 80-modified sample (f)

All samples were examined using a three-electrode system at room temperature after being submerged in 3.5 wt% NaCl aqueous solution for 48 hours. A coating sample, a saturated calomel electrode, and a platinum electrode were used as the working, reference, and auxiliary electrodes, respectively. The polarization measurements were carried out at a scanning rate of 5 mV/s over a potential range of -1.2 to -0.4 V.

Table 1 shows the results of the potentiodynamic polarization measurements, including the corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic and cathodic Tafel constants (β_a and β_c), and inhibition efficiency ($E_p\%$). The equation used to calculate the inhibition efficiency was

$$E_p\% = \frac{I_{corr(0)} - I_{corr}}{I_{corr(0)}} \times 100 \quad (1)$$

where $I_{corr(0)}$ is the corrosion current density in the absence of the inhibitor (Tween 80), and I_{corr} is the corrosion current density in the presence of the inhibitor (Tween 80). Potentiodynamic measurements show that, as the concentration of Tween 80 increases, the corrosion potential shifts toward more positive values.

Electrochemical corrosion behavior curves are among the most effective and commonly accepted methods for characterizing the corrosion resistance of samples. The Tafel plot in Fig. 5 and the corresponding results in Table 1 show that the corrosion potential, E_{corr} , shifted toward more positive values, from -0.94 V for pristine steel to -0.66 V for the 0.3 mM Tween 80-modified SiO₂ sample. It was also found that the corrosion current density, j_{corr} , decreased by approximately two orders of magnitude for the 0.3 mM Tween 80-modified SiO₂ coating compared with pristine steel,

demonstrating the ability of the hydrophobic surface to reduce corrosion.

Sample	Pristine Steel	Unmodified	0.05 mM Tween 80 modified	0.1 mM Tween 80 modified	0.2 mM Tween 80 modified	0.3 mM Tween 80 modified
E_{corr} (V)	0.94	0.77	0.70	0.68	0.67	0.67
j_{corr} (A/m ²)	$.2 \times 10^{-4}$	$.4 \times 10^{-5}$	$.51 \times 10^{-5}$	$.41 \times 10^{-5}$	$.03 \times 10^{-5}$	$.4 \times 10^{-5}$
β_a (V)	.20	.22	.14	.29	.25	.21
β_c (V)	.24	.31	.31	.44	.36	.43
$E_p\%$	-	8	4	3	4	8

Table 1 Parameters obtained from PDPC for various samples

Moreover, metal corrosion is strongly influenced by aggressive anions present in the medium, such as Cl^- [48]. Consequently, based on the unique interfacial wetting regime, an important function of the superhydrophobic surface is to significantly reduce the area exposed to Cl^- [49]. The hierarchical micro/nanostructures can trap numerous air pockets between the liquid and solid, thereby drastically reducing the contact area of Cl^- with the substrate (schematic diagram shown in Fig. 6). We conducted a straightforward experiment using an untreated substrate and a superhydrophobic sample submerged at an angle in water to demonstrate the stability of the air layer (see Fig. 6). A distinct difference was observed between the untreated substrate and the superhydrophobic sample. Capillary forces caused the water surface to adhere to the untreated substrate to some extent, whereas water did not reach the surface of the superhydrophobic sample [50].

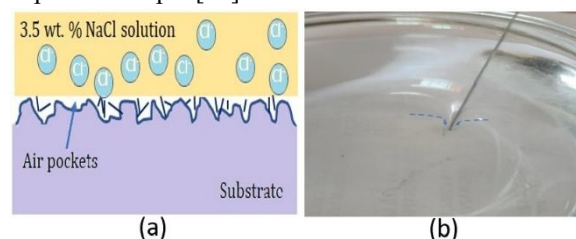


Fig. 6 Schematic diagram of the air layer trapped by hierarchical micro/nanoscale roughness, preventing the transport of Cl^- (a), and experiment demonstrating the existence of a stable air layer on the hydrophobic coating

We also investigated the corrosion behavior of the hydrophobic coatings after longer immersion times in a

corrosive solution. For this purpose, a hydrophobic SiO₂ coating modified with 0.3 mM Tween 80 was immersed in 3.5% NaCl solution for different periods, and potentiodynamic polarization measurements were carried out for each coating. Fig. 7 shows the potentiodynamic polarization curves for the hydrophobic SiO₂ coating modified with 0.3 mM Tween 80 after different immersion periods in 3.5% NaCl solution.

After immersion for 10 days, the anticorrosion performance decreased to some extent but still exceeded that of pristine steel. Moreover, the wetted regions of the superhydrophobic surface, which are vulnerable to corrosion because of the formation of cracks, are key factors contributing to the decrease in corrosion resistance [51]. However, even after immersion in 3.5 wt% NaCl solution for 10 days, the superhydrophobic sample retained significantly better resistance to Cl⁻-induced corrosion than pristine steel. This demonstrates that the three-dimensional microporous superhydrophobic coating has good durability and can help prevent corrosion of the metal substrate.

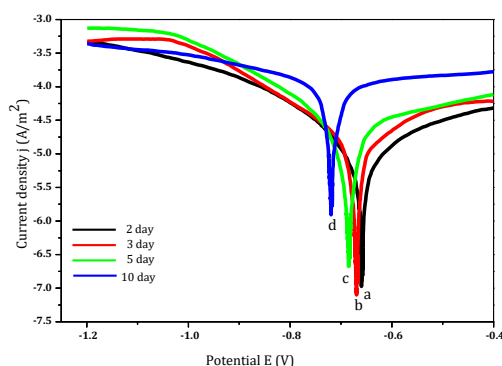


Fig. 7 Potentiodynamic polarization curve (Tafel plot) for 0.3 mM Tween 80-modified silica coatings at various immersion times

Another factor that affects the corrosion of metals is temperature. Temperature significantly influences the rate of electrochemical corrosion. Therefore, polarization measurements at temperatures between 303 and 333 K with 0.3 mM Tween 80 were used to examine the effect of temperature on the effectiveness of Tween 80 as a corrosion inhibitor (Figure 7). Table 2 presents the calculated inhibition efficiency, Ep%, under the investigated conditions.

ample	days'	days'	days'	0 days'
corr (V)	0.66	0.67	0.68	0.72
corr (A/m ²)	.4 × 10 ⁻⁵	.6 × 10 ⁻⁵	.66 × 10 ⁻⁵	.02 × 10 ⁻⁴
a (V)	.21	.22	.23	.58

c (V)	.43	.34	.59	.26
p %	8	6	7	5

Table 2 Parameters obtained from PDPC for 0.3 mM Tween 80-modified silica coatings for various immersion times

The data demonstrate that the inhibition efficiency decreases as the temperature rises from 303 to 333 K. This may be explained by the desorption of Tween 80 molecules from the metal surface at higher temperatures, exposing a larger surface area of the metal to the corrosive medium [52].

Mechanism of Inhibition

A study was conducted on the mechanism of corrosion inhibition of steel in 3.5 wt% NaCl by Tween 80, a nonionic surfactant. Potentiodynamic polarization measurements were used to determine the percentage inhibition efficiency for pitting corrosion at a scan rate of 5 mV/s. The Tween 80 compounds showed varying inhibition efficiencies depending on their concentration. Adsorption of the corrosion inhibitor at the metal/solution interface appears to be the mechanism by which corrosion is inhibited. The adsorption characteristics of an inhibitor can explain its interaction with the metal surface during corrosion inhibition.

Several factors influence inhibition efficiency, including the number of active adsorption sites in the molecule and their charge density, molecular size, mode of adsorption, temperature, and the number of metallic complexes formed. One or more of these mechanisms can retard the cathodic or anodic reactions by adsorption on the metal surface.

- Formation of a physical barrier between the metal and the corrosive medium.
- Reduction of the metal reaction by altering the nature of the metal surface.
- Alteration of the interfacial structure between the metal and the solution.

Adsorption of Tween 80 onto the steel surface is responsible for its inhibitory effect. The adsorbed layer keeps the aggressive solution away from the metal surface, resulting in a decrease in the corrosion rate. Such adsorption is facilitated by the chemical properties of polysorbate compounds and the presence of functional groups, such as carbonyl groups, in their structures. Through their functional groups, surfactant molecules adhere to the metal surface, while their hydrocarbon chains are oriented toward the solution. The hydrophobic nature of these hydrocarbon chains prevents aggressive aqueous anions from reaching the metal surface and thereby inhibits corrosion [53].

CONCLUSION

There is a need to prevent corrosion of metal surfaces induced by water and humidity. The Tween 80-modified scratch-resistant silica coatings exhibited hydrophobic behavior and therefore show potential for anticorrosion applications. Tween 80 promoted strong bonding between the silica particles, resulting in the formation of a solid silica network resistant to scratches produced by the hardest pencil. As the Tween 80 content increased, the thermal conductivity decreased from 0.071 to 0.017 W m⁻¹ K⁻¹ for the samples containing 0% to 0.3 mM Tween 80, respectively. The presence of ester groups associated with Tween 80 was confirmed by FTIR analysis. The porosity of the silica network enhanced the hydrophobicity of the silica coatings. Hence, these scratch-resistant, hydrophobic silica coatings on metal surfaces have potential for use as protective barriers against corrosion.

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