

Investigating the Accelerated Electrochemical Corrosion Protection Performance of Coal-Tar and Bitumen Enamel Coating for Pipelines

B. Aghabarari¹, S. Pourhashem², B. Moeinifard³

¹ Nanotechnology and Advanced Materials Department, Materials and Energy Research Center, Karaj, Iran

² Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

³ Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

Corresponding author e-mail: b.aghabarari@merc.ac.ir

Abstract

This work attempts to give a general zoom to the nanostructured carbon materials from their appearance, discovery and fabrication, until their applications and impacts in the scientific field. The three main carbon nano-allotropes: fullerenes, carbon nanotubes and graphene, are revised in order to establish a general overview. Finally, some alternatives on the potential growing of these materials are also presented.

Keywords: Coal-Tar Enamel, Bitumen Enamel, Organic Coatings, Electrochemical Corrosion Tests

1. Introduction:

Corrosion of pipelines is an extreme challenge for oil and gas industry. The harsh environment of pipelines application has great effect on selecting the appropriate coatings for them. Different types of coatings are used for corrosion protection of pipelines in industry and meanwhile, coal-tar and bitumen enamel coatings are widely applied for enhancing their service-life [1-3].

Coal tar coating is blend of epoxy resins and coal tar with black color which is extremely used in harsh corrosive environments. Coal tar acts as filler in polymer matrix, providing high moisture resistance, UV resistance, thermal stability, toughness, and good adhesion to metallic substrate. These coatings show excellent resistance against salt water and cathodic disbondment and therefore, they are widely used for protection of off-shore metallic structures, ships submerged hull areas, cooling towers, and ballast tanks [1, 4, and 5].

Bitumen coatings are mainly composed of aliphatic hydrocarbons with good resistance against water and chemicals. They are extensively used as an alternative for coal tar coatings due to lower amounts of carcinogen in bitumen enamel coatings. However, these coatings have shortcomings regarding fume extraction during used and low flexibility at very low temperatures [1, 4].

Therefore, in this research, we have investigated the corrosion protection efficiency of industrially used coal-tar and bitumen coatings for pipe-lines.

2. Experimental:

Industrially used coal-tar and bitumen enamel coatings on mild steel substrates with dimension of 3 × 4 cm² are used for corrosion protection evaluations. The degradation process of coatings is examined in the

synthetic groundwater by electrochemical methods using Potentiostat/Galvanostat (PGSTAT 30). The electrochemical cell consists of the sample, Pt wire, and saturated calomel electrode (SCE) as working, counter, and reference electrode, respectively. The synthetic ground water with pH value of about 7.25 is used as corrosive electrolyte and its chemical composition is presented in Table 1.

Precursor	Amount (mg/mL)
CaCl ₂	133.2
MgSO ₄ ·7H ₂ O	59
NaHCO ₃	208
H ₂ SO ₄	85
HNO ₃	22.2

Table 1. Chemical composition of synthetic ground water.

The potentiodynamic polarization tests are repeated 7 times for accelerating the degradation of coatings. For potentiodynamic polarization tests, open circuit potential (OCP) of system at equilibrium state after immersion is recorded as corrosion potential (E_{corr}). Then, the polarization curve was plotted by sweeping the applied potential from -0.4 to +0.4 V with respect to OCP at scan rate of 1 mV/sec on 1 cm² anode. Corrosion current density (i_{corr}) was determined from Tafel plot by extrapolating the linear portion of the curve to E_{corr} . Tafel constants including anodic (β_a) and cathodic (β_c) slopes were calculated for anodic and cathodic parts of Tafel plot, respectively. The polarization resistance (R_p), corrosion rate (C.R.), the coating porosity (P), and the corrosion protection efficiency (PE) are calculated based on following equations [3, 6]:

$$R_p = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c) i_{corr}} \quad (1)$$

$$CR (mm/year) = \frac{3270 i_{corr} (A/cm^2) \cdot EW}{D (\beta/cm^2)} \quad (2)$$

$$P = \frac{R_p^{substrate}}{R_p^{coat}} \times 10^{-|\Delta E_{corr}/\beta_a^{substrate}|} \quad (3)$$

$$PE\% = 100 \times \left(1 - \frac{R_p^{substrate}}{R_p^{coat}}\right) \quad (4)$$

Then, the corrosion protection performance of coatings is determined by electrochemical impedance

spectroscopy (EIS). The EIS tests were carried out in frequency range of 10^{-2} to 10^5 Hz with AC amplitude of 10 mV at OCP. All electrochemical tests are repeated three times.

3. Results and discussion:

Fig. 1 shows the OCP values of samples during immersion in synthetic groundwater. Accordingly, the coated substrates have more positive OCP values compared to bare one. Meanwhile, the type of coating has great effect on OCP values of samples; the OCP value of the coal-tar enamel coated sample is more noble than bitumen enamel sample.

Fig. 2 shows the potentiodynamic polarization curves of samples. The results derived from polarization curves are presented in Table 2. The results derived from potentiodynamic polarization tests show that coal-tar coated sample has more positive E_{corr} , lower i_{corr} , lower porosity, higher polarization resistance (R_p) and higher corrosion protection efficiency (PE); revealing enhanced corrosion protection capability

of coal-tar enamel coating compared to bitumen enamel coated sample. Indeed, the corrosion rate for bare substrate, bitumen enamel coating, and coal-tar enamel coating is 0.07502, 0.00904, and 0.00159 mm/year, respectively. The calculated coating porosity for bitumen enamel coating and coal-tar enamel coating is 1.81% and 0.05%, respectively; therefore, the higher corrosion resistance of coal-tar epoxy coatings can be attributed to the lower amount of porosity and defects in its structure, compared to bitumen enamel coating.

Moreover, the EIS results including Bode and Nyquist plots are presented in Fig. 3 and Fig. 4, respectively. The Bode plots indicate that the Z modulus for coatings at low frequency of 0.01 Hz ($|Z|_{0.01\text{Hz}}$) is significantly more than bare sample. The $|Z|_{0.01\text{Hz}}$ value for coal-tar enamel sample and bitumen enamel sample is 24.5×10^4 and 5.1×10^4 Ohm.cm², respectively. The higher Z modulus of coal-tar sample confirms that the coal-tar enamel coating is more appropriate for achieving enhanced corrosion protection for pipelines due to their higher corrosion resistance.

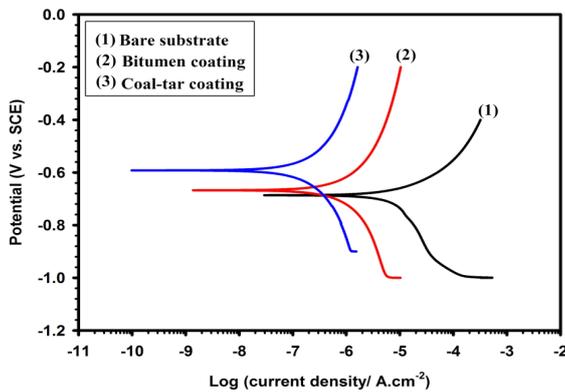


Figure 1. The variation of OCP for bare substrate, bitumen enamel and coal-tar enamel coating.

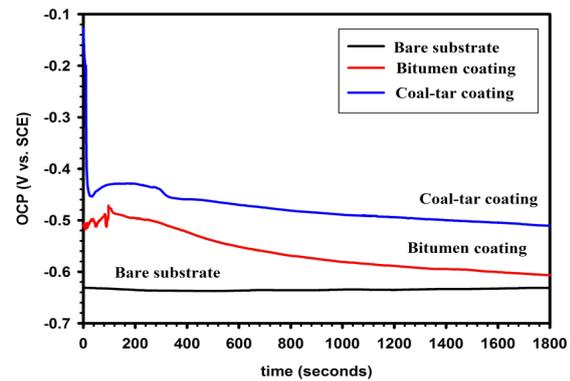


Figure 2. The potentiodynamic polarization curves for bare substrate, bitumen enamel and coal-tar coating.

Sample	E_{corr} (V/SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (V/dec)	β_c (V/dec)	C.R. (mm/year)	R_p ($\text{k}\Omega.\text{cm}^2$)	PE (%)	P (%)
Bare substrate	-0.691	6.4	0.102	0.237	0.07502	4.81	-	-
Bitumen coating	-0.675	0.778	0.264	0.260	0.00904	73.16	95.42	1.81
Coal-tar coating	-0.599	0.136	0.256	0.171	0.00159	326.18	98.98	0.05

Table 2. The electrochemical parameters derived from polarization curves.

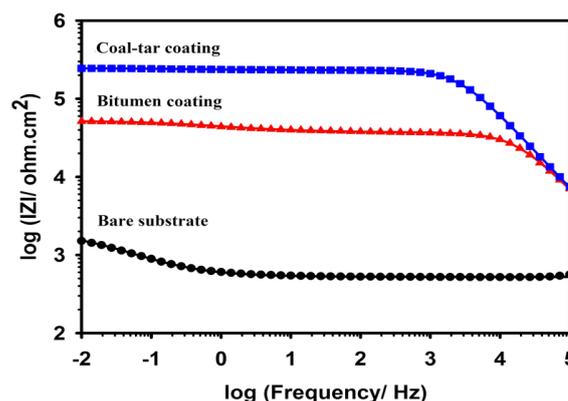


Figure 3. The Bode plots for bare substrate, bitumen enamel and coal-tar enamel coating.

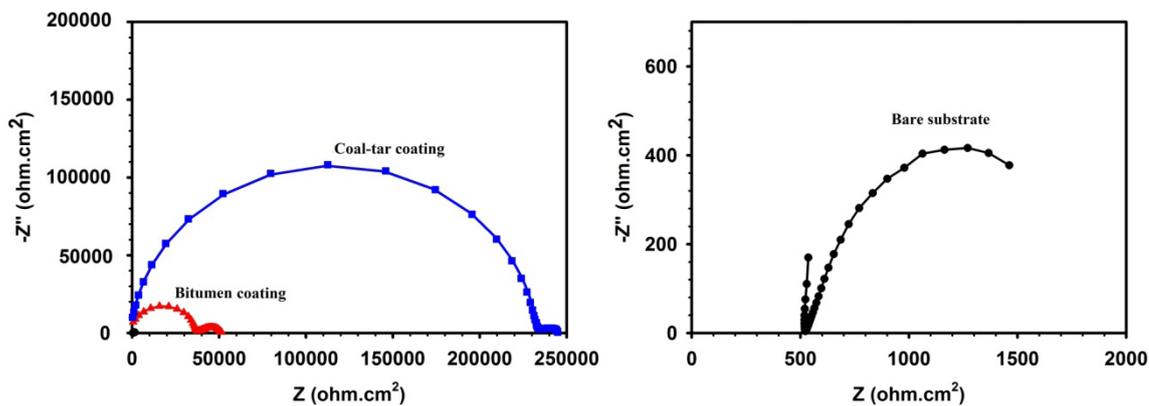


Figure 4. The Nyquist plots for bare substrate, bitumen enamel and coal-tar enamel coating.

Further, the results of EIS are fitted by electrical equivalent circuit (Fig. 5) by using NOVA software. The proposed equivalent circuit consists of solution resistance (R_s), coating constant phase element (Q_{coat}), pore resistance (R_{pore}), double layer constant phase element (Q_{dl}), and charge transfer resistance (R_{CT}). The calculated parameters are mentioned in Table 3. The results show that the coating resistance and charge transfer resistance for coal-tar enamel coating is significantly more than bitumen enamel coating; revealing that the defects of coal-tar coatings are less than bitumen enamel coating. The enhanced

corrosion protection capability of this sample can be attributed to the pore structure and chemical composition of coal-tar enamel coating.

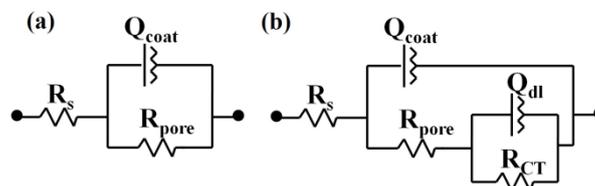


Figure 5. Electrical equivalent circuit used for fitting EIS results; (a) bare substrate, (b) coated substrate.

Sample	CPE _{coat}		R _{pore} (Ω cm ²)	CPE _{dl}		R _{ct} (Ω cm ²)
	Y ₀ (Ω ⁻¹ cm ⁻² s ⁿ)	n		Y ₀ (Ω ⁻¹ cm ⁻² s ⁿ)	n	
Bare substrate	-	-	-	2.52 × 10 ⁻³	0.634	1.3 × 10 ³
Bitumen coating	5.89 × 10 ⁻¹⁰	0.923	38.7 × 10 ³	2.79 × 10 ⁻⁵	0.528	15.5 × 10 ³
Coal-tar coating	4.40 × 10 ⁻¹⁰	0.947	234 × 10 ³	5.04 × 10 ⁻⁵	0.532	15.8 × 10 ³

Table 3. Calculated electrochemical parameters via electrical equivalent circuit.

Accordingly, coal-tar coatings have higher corrosion protection capability than bitumen enamel coatings. The improved corrosion resistance of coal-tar sample is due to lower amount of defects and pores in its structure. The compact structure of coal-tar can decrease the uptake of water and corrosive agents. Besides, coal-tar has is inherently hydrophobic and has higher adhesion strength to metallic substrate [5].

4. Conclusion:

In this research, the corrosion protection performance of coal-tar coating and bitumen enamel coating is investigated. The corrosion resistance of samples is considered by electrochemical methods. The results clearly indicate that coal-tar coated sample has higher corrosion protection efficiency than bitumen enamel coating.

Reference

[1] L. Niu, Y.F. Cheng, "Development of innovative coating technology for pipeline operation crossing the permafrost

terrain", *Const. Build. Mater.* 22 (2008) 417-422.

[2] S.M. Cambier, G.S. Frankel, "Coating and interface degradation of coated steel, Part 2: Accelerated laboratory tests", *Electrochim. Acta.* 136 (2014) 442-449.

[3] S.H. Lee, W.K. Oh, J.G. Kim, "Acceleration and quantitative evaluation of degradation for corrosion protective coatings on buried pipeline: Part II. Application to the evaluation of polyethylene and coal-tar enamel coatings", *Prog. Org. Coat.* 76 (2013) 784-789.

[4] S. Papavinasam, M. Attard, and R.W. Revie, "Evaluation of external pipeline coatings for corrosion protection-A review", *Corr. Rev.* 26 (2008) 373-438.

[5] S.D. Jagtap, S.P. Tambe, R.N. Choudhari, B.P. Mallik, "Mechanical and anticorrosive properties of nontoxic coal-tar epoxy alternative coating", *Prog. Org. Coat.* 77 (2014) 395-402.

[6] S.H. Lee, W.K. Oh, J.G. Kim, "Acceleration and quantitative evaluation of degradation for corrosion protective coatings on buried pipeline: Part I. Development of electrochemical test methods", *Prog. Org. Coat.* 76 (2013) 778-783.