American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)
ISSN (Print) 2313-4410, ISSN (Online) 2313-4402

http://asrjetsjournal.org/

Corrosion Protection of Carbon Steel Oil Pipelines by Unsaturated Polyester/Clay Composite coating

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Abstract

The aim of this paper is to prepare a protective coating on API 5L (carbon steel) alloy which is the widely used materials in oil industry and study its effect on the corrosion behavior of the carbon steel in crude oil environment. Unsaturated polyester (UP) and clay were used to prepare composite consist of 75% of polyester and 25% of clay. The coated specimen was investigated in comparison to uncoated and 100% polyester coated specimens. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were employed on the coated specimens to understand the phases formed on the modified surfaces. The corrosion behavior of the modified surface in comparison with untreated one was investigated by potentiodynamic cyclic polarization in 3.5 M of NaCl and crude oil solution using Solartron made electrochemical interface SI 1287 and Electrochemical Impedance Spectroscopy (EIS) measurements at OCP condition using Solartron make 1255 HF frequency response analyzer (FRA). The results show improvement in the corrosion parameters predicted from the polarization test.

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The EIS measurements for coated specimens after polarization show higher values of total impedance |Z|, polarization resistance (R_p) and low capacitance (C) in comparison with the un-coated carbon steel specimen. This indicates the stability of the surface protected film of these coated specimens and their resistance against dissolution.

Keywords: Corrosion; Carbon steel; Unsaturated Polyester/Clay Composites; electrochemical techniques.

1. Introduction

The surface of a component is usually the most important engineering factor , While it is in use, It is often the surface of a work-piece that is subjected to wear and corrosion .In industrialized countries about 30% of energy generated is ultimately lost through corrosion [1].Corrosion is basically an economic problem. This, the corrosion behavior of any part product is an important consideration in the economic evaluation of any project mode. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to positive value. The environment is called electrolytes since they have their own conductivity for electron transfer [2]. Petroleum product include hydrocarbons are not aggressive to alloy under ambient condition. In spite of this, give rise to the corrosion of tanks, pipes and pumps made of mild steel [3]. In oil, many cases of extensive corrosion have occurred in production tubing, valves and flow lines from the well-head to the processing equipment. The reason for this is that various amounts of water, which can be precipitated as a separate phase in contact with the material surface, and the water contains gases such as CO_2 and H_2S, as well as salts [4] . Protective coatings are unique specialty products which represent the most widely used method of corrosion control. They are used to give long term protection under different corrosive conditions. The function of a protective coating or lining is to separate two highly reactive materials; i.e. to prevent corrosive environment species from contacting the reactive underlying steel structure. This is to say that a coating or a lining acts as a barrier to prevent either chemical compounds or corrosion currents from contacting the substrate [4]. The main coating technique described in this work are polymer-clay composites coating which are attractive as they possess weak thermal and electrical properties and are more resistant to oxidation, corrosion ,erosion and wear than metals in high temperature environments. These coatings are known as (thick coatings) which refers to the property of high hardness in mechanical sense with good corrosion resistance properties. Unsaturated polyester (UP) is one of most commonly used polymer matrix with reinforcing fibers for advanced composites applications due to its low cost, easy handling, rigid, resilient, flexible, corrosion resistant, weather resistant, and flame retardant. Clay has received much attention as reinforcing materials for polymer because of its potentially high aspect ratio and unique intercalation/exfoliation characteristics. The addition of small amount of clay into polymer matrix exhibits unexpected properties including reducing gas permeability, improved solvent resistance, being superior in mechanical properties and thermal stability, and enhanced flame retardant properties [5].

2. Materials and Methods

2.1. Polyester/Clay Composite Preparation

The matrix used in this study was unsaturated polyester UPE (SIR Saudi Arabia). It was viscous liquid, transparent, thermosetting polymer type. The liquid converts to solid coating by adding methyl-ethyl-ketone-peroxide (MEKP) as hardener, which is transparent liquid with 2% for each 100gm of UPE at room temperature. Iraqi white clay (chemical composition in Table 1) was dried using an oven at 80°C for 6 h before being used. The polyester/clay composites, with clay loadings (25 wt%), were prepared by mixing the desired amount of clay with polyester resin using a mechanical stirrer with speed of 800 rpm at 60°C for 2 h. The MEXOPE catalyst was added into the polyester/clay mixture by stoichiometric ratio. The mixture was then mixed using a mechanical stirrer and degassed in a vacuum oven. The implementation of the composite (mixing ratio 75% polyester and 25% clay) was done on carbon steel substrates using paint sprayer device.

Table 1: Chemical composition of Iraqi kaolin clay

SiO2	**Al2O3**	**Fe2O3**	**TiO2**	**MgO**	**Na2O**	**CaO**	**L.O.I**
52.48	31.31	2.094	1.43	0.33	0.28	0.462	10.93

2.2 Sample Preparation

Surface condition of a specimen plays an important role in coating binding and corrosion resistance. Hence, it is necessary to prepare uniform surface and requires careful specimen preparation. Specimen preparation for surface analysis and electrochemical studies involve the following steps; square carbon steel type (API 5L-GR.B PSL1) specimens of 20 mm diameter with thickness of 5 mm were cut out from the as received carbon steel. The specimens were grinded with SiC emery papers with different grits started from 80 grit, and continued by 120, 230, 400, 600, and 800 grit to get flat surface. The specimens then were cleaned with ethanol in order to enable coating detachment after spraying. Spraying was carried out immediately after cleaning.

2.3 Surface Analysis

The modified surfaces were structurally characterized using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The phases present in the as received and coated specimens of carbon steel alloy were determined using XRD. Incorporating Rigaku's patented cross beam optics (CBO) technology X-ray diffractometer using Cu Ka radiation was used for this study. X-ray diffraction patterns were collected for different 2Ɵ values ranging from 10 to 100^o with a 0.05^o step and counting time of 5s per step.

2.4 Electrochemical Studies

Anodic cyclic polarization was conducted on the coated specimens in comparison to the uncoated one in oil simulated solution. Three electrodes standard corrosion cell was used for corrosion measurements. Platinium foil was used as auxiliary counter electrode; saturated calomel electrode (SCE) as reference and the specimens was acted as working electrodes respectively. The samples were polarized from -0.6 V to 1.5 V with scan rate of 0.5 mV/s and then reversed until it was intersected the forward scan. Electrochemical Impedance Spectroscopy (EIS) measurements at OCP condition in 3.5 M of NaCl and Kirkuk crude oil solution (Table 2 chemical composition of Kirkuk crude oil) were carried out at the same setup used for potentiodynamic polarization. A Solartron make 1255 HF frequency response analyzer (FRA) and SI 1287 potentiostat/glvanostat electrochemical interface controlled by commercial software program Zplot, version 3.4d, (C) 1990-2015, Scribner Associated, Inc., . All experiments were done in standard corrosion cell provided with a platinum counter electrode (CE) and Saturated Calomel Electrode (SCE) as reference electrode, whereas the coated carbon steel specimen was acted as working electrode (WE). The resulted curves of the potentiodynamic polarization and the impedance spectroscopy were analyzed using CView 3.4d and ZView3.4d software from which all the corrosion parameters were predicted [6].

Table 2: Kirkuk crude Oil chemical composition

API	Viscosity	H2S	Sulphur	Asphaltene	Wax
33.2	9.30 centi stock @ 80F	360 ppm	2.5 %	2.23%	3.1 %

3. Results and Discussion

3.1 Phase Analysis (XRD)

Figure 1 shows the XRD curves of the polyester [polyethylene terephthalate $(C_{10}H_8O_4)_n$] used in the clay/polyester coating composite and the carbon steel specimen coated with 100% polyester. The diffraction data obtained from Figure 1 were indexed using the ICDD powder diffraction files (PDF) cards 34-0529, 06-0696 for Fe, 26-1079 for Graphite and 27-1905 for polyester. Polymers are weak scatterers and frequently have only a few weak peaks[7].

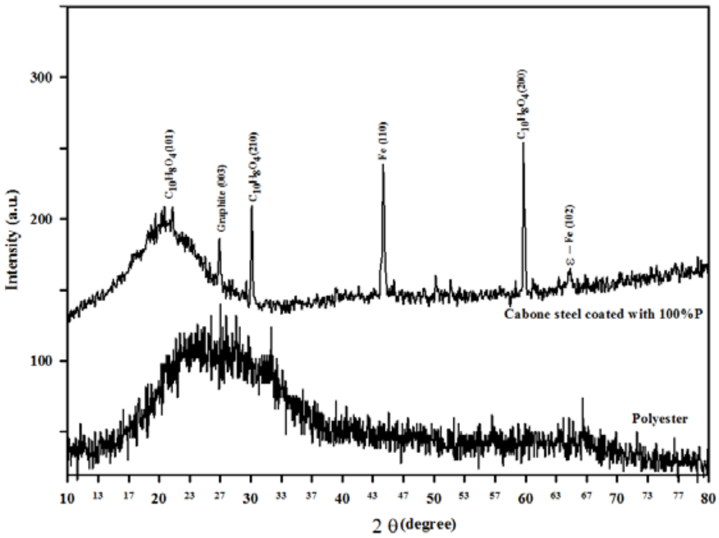


Figure 1: X-Ray diffraction patterns of the 100% polyester coated carbon steel in comparison to the as received polyester.

The XRD patterns of the polyester in Figure 1 show a pattern with very broad features consistent with incoherent scatter from an amorphous solid. This broad diffuse halo are at 2θ = 23.5, which indicates that the material are amorphous in nature whereas the 100% coated specimen shows a pattern semi-crystalline behavior[8]. The crystallite size of the polyester which is varied between (5 to 145 nm) has been calculated by Scherrer equation [9] using FWHM presented in Table 3. The XRD pattern in Figure 2 are showing the diffraction reflections of the carbon steel coated with 25% clay+75% polyester composite comparing with uncoated carbon steel.

Table 3: Full width half maximum FWHM, grain size and miller indices (h k l) of carbon steel coated with 100% polyester.

2θ Degree	FWHM (β)	d (Å)	crystallite size nm	(h k l)		
				Polyester $(C_{10}H_8O_4)_n$	Graphite	Fe
20.452	0.0274	4.256	5.133	101		
26.608	0.0027	3.351	51.893		003	
30.141	0.0020	2.965	69.699	210		
44.508	0.0010	2.036	145.545			110
59.835	0.0012	1.544	127.357	200		
64.860	0.0200	1.437	8.1709			102

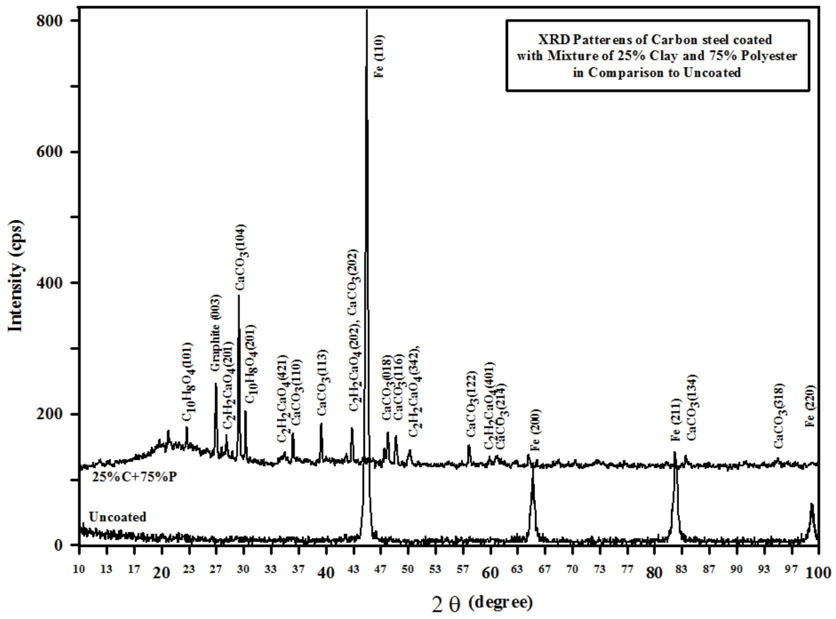


Figure 2: X-Ray diffraction pattern of the 25% clay+75% polyester coated carbon steel with uncoated carbon steel.

The clay/polyester coated layer shows more crystallanity when clay content in the composite mixture was 25%. The diffraction data was predicted and indexed according to the ICCD card no (14-0819, 26-0908, 05-0586, 33-0268,26-1079, 27-1905[10]. The full width half maximum (FWHM), miller indices, and the crystallite size that predicted from the diffraction reflections in Figure 2 are presented in Table 4.

Table 4: Full width half maximum FWHM, grain size and miller indices (h k l) of carbon steel coated with 25% clay+75% polyester**.**

2θ Degree	FWHM (β)	d (Å)	Crystallite size nm	(h k l)			
				$CaCO_3$	$C_2H_2CaO_4$	Graphite	$C_{10}H_8O_4$
20.886	0.0054	4.253	25.666				120
23.089	0.0027	3.852	51.543	012			
26.652	0.00274	3.344	51.898			003	
27.915	0.0020	3.196	69.354		201		
29.434	0.0030	3.034	46.407	104			
30.21	0.0010	2.957	139.54				210
34.891	0.0164	2.571	8.8202		421		
36.012	0.0027	2.493	53.099	110			
39.449	0.0034	2.284	42.906	113			
43.200	0.0027	2.094	54.315	202	130		
47.546	0.0024	1.912	63.031	018			
48.534	0.0041	1.875	36.712	116			
57.444	0.00274	1.604	57.586	122			
60.794	0.016478	1.523	9.755	214			

2- SEM Observation

The surface morphology in Figure 3 show large aggregates and a homogenous distribution of the clay in the polyester matrix. The addition of clay into the UP may led to an increase in the surface toughness. The toughening mechanism in the clay reinforced polymer composites may be attributed to the stress disturbance caused by the clay particles. These clay particles acted as obstacles, causing the crack to take a more tortuous part, manifesting a meandering crack trajectory. Therefore, these clay particles have a better resistance to crack propagation[11]. Moreover, a large number of agglomerates can be observed in SEM micrograph of Figure 2, where such an observation can confirm the reduced mechanical performance at clay loading of 25%. Since the clay is composed of heavier elements (Al, Si and O) than the interlayer and surrounding matrix (C, H and N), they appear darker in bright-field images[12, 14]. The denser and more compact morphology of UP/ clay composite with the increase in clay concentration are responsible for enhancing the conductivity[15].

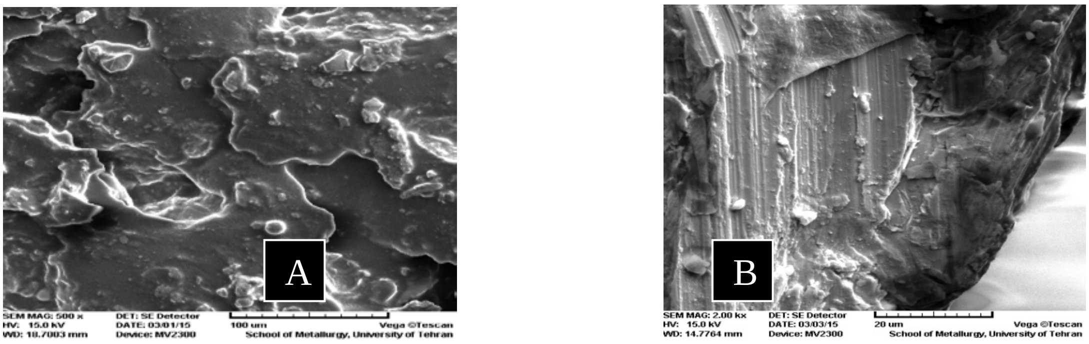


Figure 3: SEM image for Top surface of 25% Clay+75% Polyester:(a) Top view (b) cross section view

3- Electrochemical Investigations

3.2 Potentiodynamic Cyclic Polarization

Figure 4 shows the polarization curves for the uncoated carbon steel and composite (caly+polyester) coated at different mixing composition in the as received crude oil solution from Karkuk Iraq Oil Company. Table 5 demonstrates the electrochemical parameters predicted from the polarization studies shown in Figure 4. The results that no pitting corrosion occurs for all polyester coated samples. In addition, the samples coated with 100% polyester and 25% clay+75% polyester have more uniform corrosion resistance than control (uncoated) sample.

Table 5: Electrochemical parameters obtained from the potentiodynamic cyclic polarization

Treatment conditions	OCP (V)	I_{corr} (A/cm^2)	E_{corr} (V)	I_{pass} (A/cm^2)	C_R (MPY)
untreated	-0.6797	1.25 x10^{-5}	-0.473	3.73 x10^{-2}	5.289
25%Clay+75%Polyester	-0.4632	1.53 x10^{-7}	-0.253	7.63 x10^{-4}	0.064
100%Polyester	-0.5286	1.28 x10^{-7}	-0.290	2.25 x10^{-6}	0.053

During the cyclic polarization in oil solution, the uncoated specimen shows very stable oxide film over wide range of potential in the cathodic region but with extremely high corrosion potential E_{corr} (-0.473V) and corrosion current I_{corr} (1.25x10^{-5} A/cm^2) comparing to the other coated specimens. The active corrosion does not occur in the potential range from 0.25 V_{SCE} to more than 1 V_{SCE}. For specimens coated with clay and polyester in different mixing ratios are passive over wide range of potential. The passive current density in Figure (4) of the composite coated specimens showed decrease in its values indicating thinner and stable passive film formation at the surface and the lowest value was recorded for specimen coated with 100%polyester comparing to the uncoated one (2.25 x10^{-6} and 3.73x10^{-2} A/cm^2 respectively).

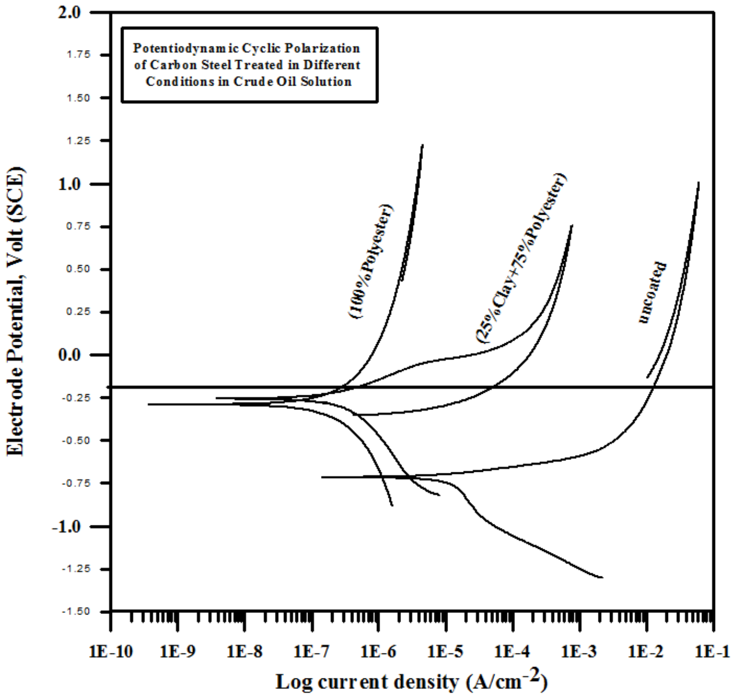


Figure 4: Cyclic polarization for the uncoated and composite (clay + polyester) different mixing ratios carbon steel in crude oil; Sweep rate 1 mV/sec.

3.2 Electrochemical Impedance Spectroscopy (EIS)

One of the most successful applications of Electrochemical Impedance Spectroscopy (EIS) has been in the evaluation of the properties of polymer coated metals and their changes during exposure to corrosive environments. EIS is now being used in the evaluation of an ever increasing variety of polymer coatings on metals and alloys. The Nyquist simulated experimental impedance curves with a simple circuit with C_{dl} (double layer capacitance) in parallel with polarization resistance R_p is not a very good overlap. So that, for this reason it is necessary to introduce an equivalent circuit with C_{PE} (the capacitance element of the double layer which is dependent of the frequency because the surface is not homogenous). Most impedance data reported in the literature for polymer coated metals which have been exposed to corrosive media agree with the simple model shown in Figure 5 [2].

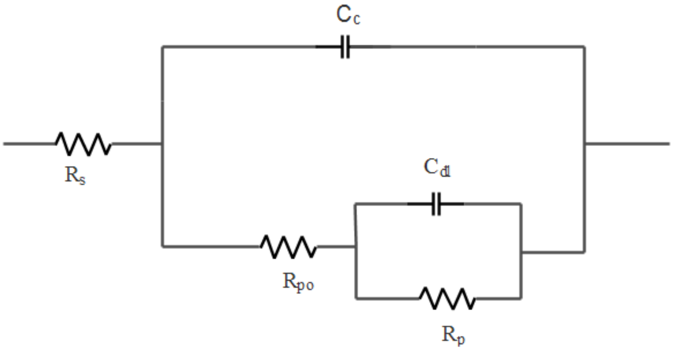


Figure 5: Model for the impedance of a polymer coated metal

The experimental data of electrochemical impedance for carbon steel coated with clay+polyester with different mixing ratios in crude oil solution are presented by the Nyquist plot in Figure 6 and Bode plot in Figure 7. The Nyquist and Bode plots were periodically obtained for both the uncoated and clay/polyester coated carbon steel specimens. They are developed at an AC voltage of 10 mV amplitude with the frequency ranging from 10 Hz to 50 kHz at a constant time of 3 minutes after polarization in crude oil solution (Figures 6&7). The time dependence of the complex plane plots is shown in Figure 6, mostly semicircles are seen for the coated specimens (part of the data has been truncated in order to magnify the region near the origin).

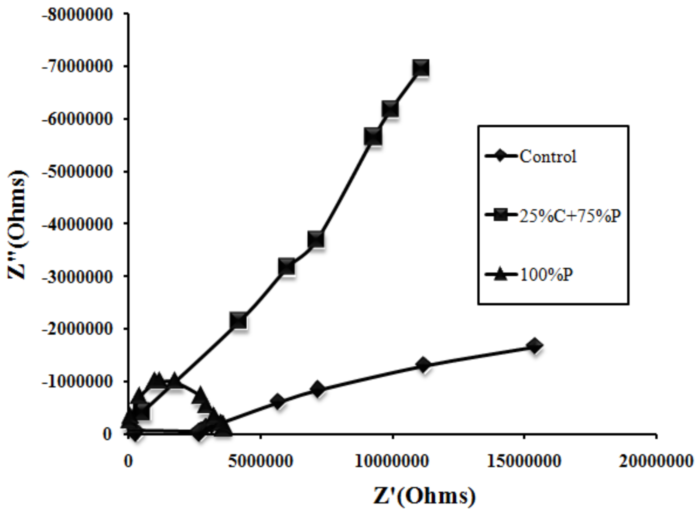
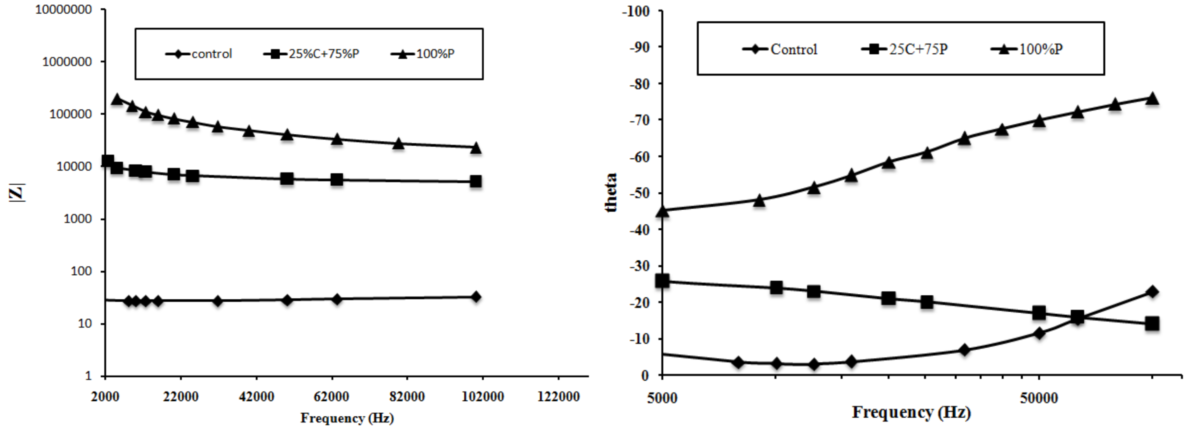


Figure 6: Nyquist plots of the control (uncoated) and clay/polyester coated carbon steel in crude oil



(a) (b)

Figure 7: Bode plots of control (uncoated) and clay/polyester carbon steel in crude oil (a) Impedance (b) Phase angle.

The circular behavior of the clay/polyester coated specimens indicates the pure capacitive characteristic. Such behavior was confirmed by Alsamuraee et. al. [16], they observed that for two systems coating protection at different immersion times pu/pvc coating continues closed to pure capacitor for most of the frequency range covered in the measurements. The two systems coatings applied on carbon steel provide very effective protection against corrosion. Pu/pvc coating appeared good stability in corrosion environment. The total impedance |Z|, polarization resistance (R_p) and the capacitance (C) values which were obtained from the above EIS plots recorded for all specimens after polarization are given in Table 6. Higher values of |Z|, polarization resistance (R_p) and low capacitance (C) were obtained for the specimens 25%clay+75%polyester and 100%polyester in comparison with the un-coated specimen [17]. This indicates the stability of the surface protected film of these two specimens and their resistance against dissolution.

Table 6: Impedance parameters of uncoated (control) and Clay/polyester coated carbon steel after immersion in crude oil solution

Treatment conditions	Rs	CPE-T (f)	CPE-P(f)	Rp(Ω)	|Z|	C (f)
control	27.36	1.3379E-4	0.7919	633.4	260.24	1.2594E-4
25%C+75%P	3496	1.7609E-6	0.41482	3.33E5	7.18×10^4	1.7609E-6
100%Polyester	-6701	1.611E-9	0.74737	1254	3.37×10^5	1.611E-9

4. Conclusions

XRD pattern collected for the specimen coated with clay/polyester composite consist of mixing ratios of clay and polyester show an semi-crystalline and dense feature (partially crystalline and partially amorphous. The electrochemical investigations show that the active corrosion does not occur in the potential range from 0.25 V_{SCE} to more than 1 V_{SCE} for specimens coated with clay and polyester in different mixing ratios and it was passive over wide range of potential. EIS plots recorded for all specimens after polarization show higher values of impedance |Z|, polarization resistance (R_p) and low capacitance (C) especially for the specimens 100% polyester in comparison with the un-coated specimen. This indicates the stability of the surface protected film of coated specimens and their resistance against dissolution.

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