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Poly 4-hyroxyaniline Thin Film Coated Stainless Steel 316L by Electro Deposition Technique for Anticorrosion in Saline Water.

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ABSTRACT

Thin films of Poly 4-hyroxyaniline organic Semiconductor polymer were prepared using electro deposition technique through oxidation polymerization by adding (3ml) concentrated HCl and (50) ml of Ammonium per sulfate concentrated (0.03M)to (100)ml of 4-hyroxyaniline (0.04M) at room temperature, The polymer was deposited on Stainless Steel 316L substrate , Structural of the thin films were studied by: Fourier transform infrared (FT-IR) spectroscopy, Field emission scanning electron microscopy(FE-SEM) and Potentiostatic polarization studies for coated and uncoated Stainless Steel 316L by polymer, the results show that the prepared thin films act as a good anticorrosion for Stainless Steel 316L in 3.5% NaCl solution over temperatures range (298-328)K.

Keywords: thin film, steeal 316L, anticorrosion, saline water.

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INTRODUCTION

Conducting polymers (CPs) are becoming an active field of research which has brought a dynamic revolution in the field of chemistry, physics, and engineering in the last several decades.[1] Electrical conductance along the tailorable structure of CPs, followed by optical and electronic properties, has proven their potential application in a large number of organic electronics such as batteries,[2] fuel cells,[3, 4] solar cells,[5] light emitting diodes,[6]supercapacitors,[7], optical displays devices andAnticorrosion [8, 9] The most widely used CPs are polyaniline (PANI),[10]polypyrrole (PPy),[11]and polythiophene.

The conducting polymers and their derivatives are used as sensor since 1980 when, electronic conducting polymer were developed. The interest of these materials has been recognized by the awarding of the Nobel prize in Chemistry in 2000 Generally polyaniline derivatives has been synthesized by chemical oxidative polymerization of aniline compound [12] or by electrochemical method [13]

Most of the studies related to synthesis of polyaniline derivatives use chemical or electrochemical oxidation or reduction that it may switch over the material from fully reduced to fully oxidized form. This work deals with synthesis and characterization of polyaniline thin films by galvonostatic mode of electrochemical deposition method at room temperature. Different preparative parameters, such as deposition potential, concentration of monomer, deposition time and current density were optimized to get uniform and well adherent polyaniline derivatives thin films are a type of conducting polymer which received the most attention due to the discovery of its high electrical conductivity[8] reversible acid-base chemistry in aqueous solution, thermal and environmental stabilities and easiness of synthesis[6]Among all the methods which can be used for the synthesis of polyaniline derivatives such as oxidative synthesis Polyaniline (PANI) has been studied extensively as a special member of the conducting polymer family because of its stability in the presence of air and humidity.

EXPERIMENTAL

Materials and Equipment

Preparation of Specimens : The specimens were cut into cycle shapes with (2.5 cm) diameter and 2.0mm thickness by using wire cut technique. The open side of specimens were Grinded and polished mechanically using grinding wheel machine . a series of grits of increasing fineness, (120,240,320.600, 800, 1200 and 2000) to get a mirror finish. The specimen were degreased with acetone and washed in distilled water , ethanol and stored inside desiccators.

Specimens

Stainless Steel: The specimens **Stainless Steel 316L**, have been used in this investigation. The composition of Stainless Steel 316L determined by atomic absorption which was as in the following Table.

Table (1): Chemical composition of Stainless Steel 316L

Elements	Fe%	C%	Si%	Mn%	P%	S%	Cr%	Ni%	Mo%	Cu%
Wt. %	61.373	0.08	0.311	1.73	0.045	0.030	18.00	14.02	3.03	0.002

Chemicals: All chemicals have been used of the highest purity available. The employed chemical and their companies are listed in Table (2).

Table (2): The molecular weight, purity andsource of Chemicals

Chemicals	M.wt (g.mol^{-1})	Purity (%)	Source
4-Amino phenol C_6H_7NO	109.13	99	BDH
Ammonium persulphate $(NH_4)_2S_2O_8$	228.20	99	BDH
Hydrochloric acidHCl	36.46	98	FLUKA

Preparation ofElectrochemical system

The electrochemical deposition system consists of :

1. power supply: A manually operated potentiostat is a stepwise instrument for measuring potential *E* and current density(*i*)**2**. Voltmeter measuring potential(*V*)**3**. Ammeter measuring density(*i*)**4**. Graphite electrode .a shown in fig(1) and table (3) illustrate the polymer coating condition for stainless steel316L.

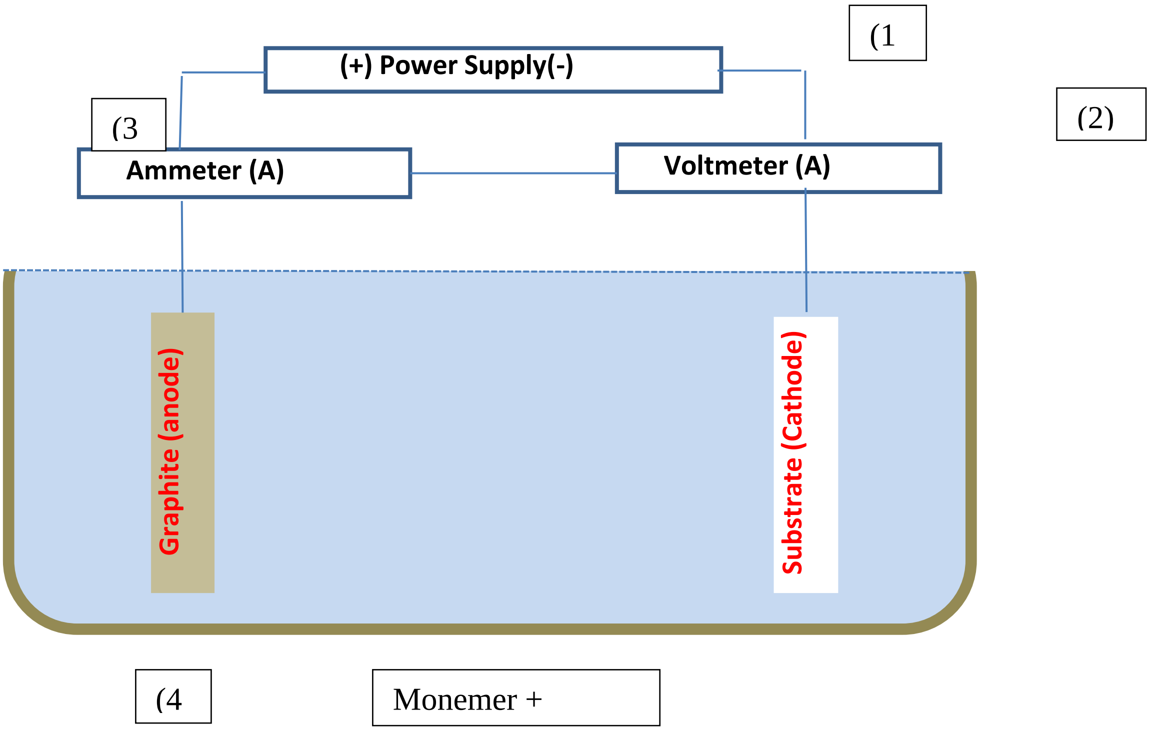

Fig (1): The electrochemical deposition system

The coating conditions for preparing Poly4-hyroxyaniline (P4-HA) are shown in table (2) and the structure of the polymer shown in fig.(20

Table (3) represents the polymer coating conditions

polymer	V(volt)	I(mA)	Ph
Poly4-hyroxyaniline (P4-HA) $(C_6H_5NO)n$	9.6	80	5.6

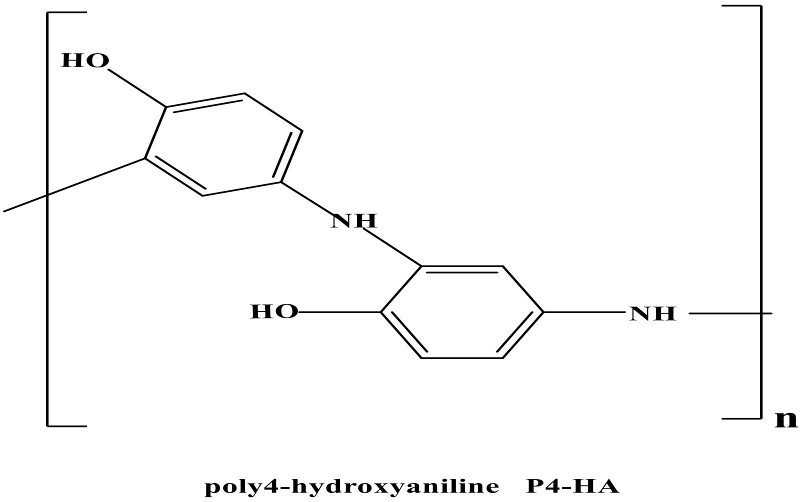

Figure (2) the Poly4-hyroxyaniline structure

Preparation of Corrosion Cell

Corrosion cell made of Pyrex with (1L) capacity consists of two vessels, internal and external. The thermostat was used to control the temperature of seawater which flows through the external vessel at (25, 35, 45 and 55)°C. Figure (3) **s**hows the corrosion cell and three electrodes. placed in the internal vessel.

The three electrodes are:

1-The potential of working electrodes was detected using reference electrodes based on its potential. The potential of a reference electrode is well known and accurate, and it is combined with two tubes; the inner tube contains AgCl, Ag, KCl, and the outer tube (luggin tube) filled with the prepared seawater solution (3.5% NaCl). The reference electrode, a luggin tube placed at the distance 2mm from working electrode.

2. The auxiliary electrode consists of high purity platinum metal; its length is (10 cm).

3. The working electrode is the studying and testing subject which potential and current will be measured; this electrode is formed from 20cm length metallic wire connected to the mounted specimen. The sample inserted in the holder in which the diameter of the exposed surface to the seawater solution is ($1cm^2$).

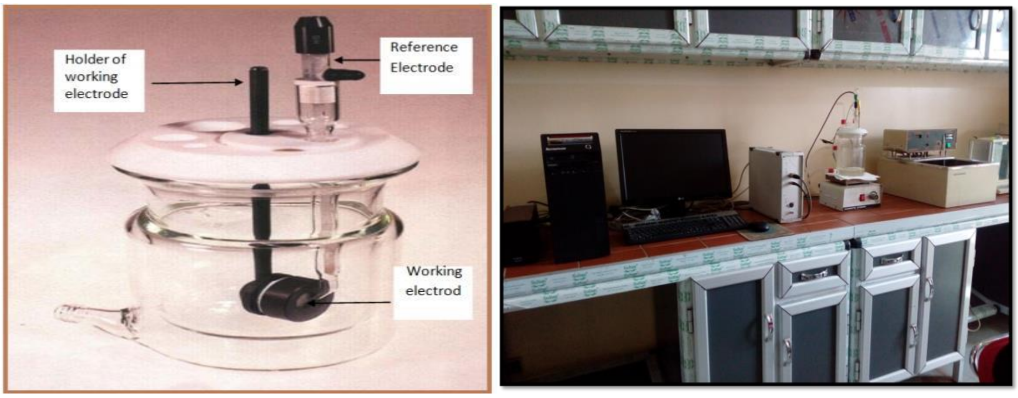

Figure 3: (a) The corrosion cell and the three electrodes.(b)experimental set up

FT-IR Spectrum of Poly4-hyroxyaniline

The PreparedPoly4-hyroxyaniline Polymer was diagnosed by using iPerkin Elmer FT-IR Spectrophotometer model 1720X.i.The absorptions bands are shown in figure (4)andtable (4).

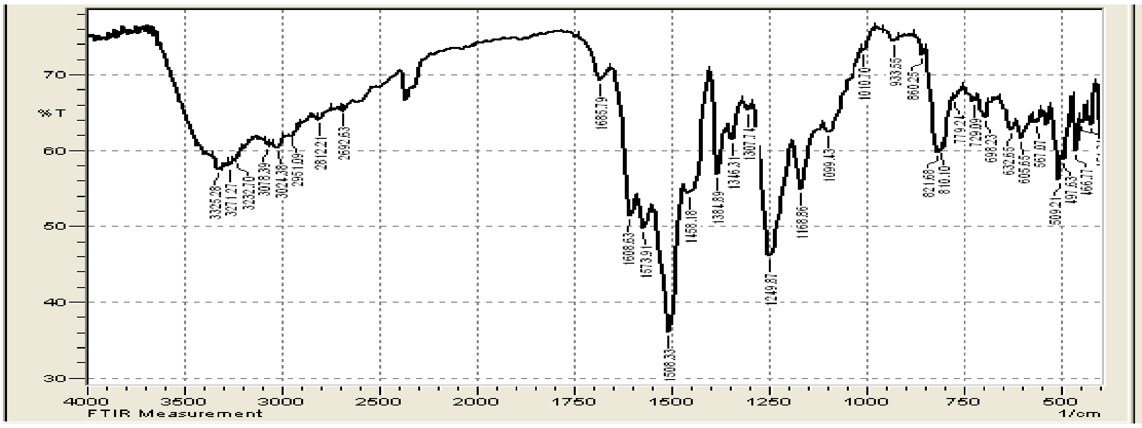

Figure (4) absorption of FT-IR spectrum of Poly 4-hydroxyaniline

Table (4): The absorption bands of Poly4-hyroxyaniline

Vibration groups	Absorption bands(Cm^{-1})
Stretching vibration (O-H)	3323
Stretching vibration band (C-H) aromatic	3078
Stretching vibration (N-H)	2951
Stretching vibration band (C=C) to the benzene ring	1508
Stretching vibration band (C– N)	1384
bending band (C-H) to the benzene ring	1249
Stretching bend N-ph	1168
Stretching band(C-H)to the benzene ring triplet compensation	810
Stretching vibration C-OH	509

RESULTS AND DISCUSSION

1- Potentiostatic polarization studies for uncoated S.S 316L : The potentiostatic polarization curves for uncoated and coated S.S 316L in 3.5%NaCl solution at temperatures range (298-328)K are show in figure(5)&figure (6) andobserved that in table (5)

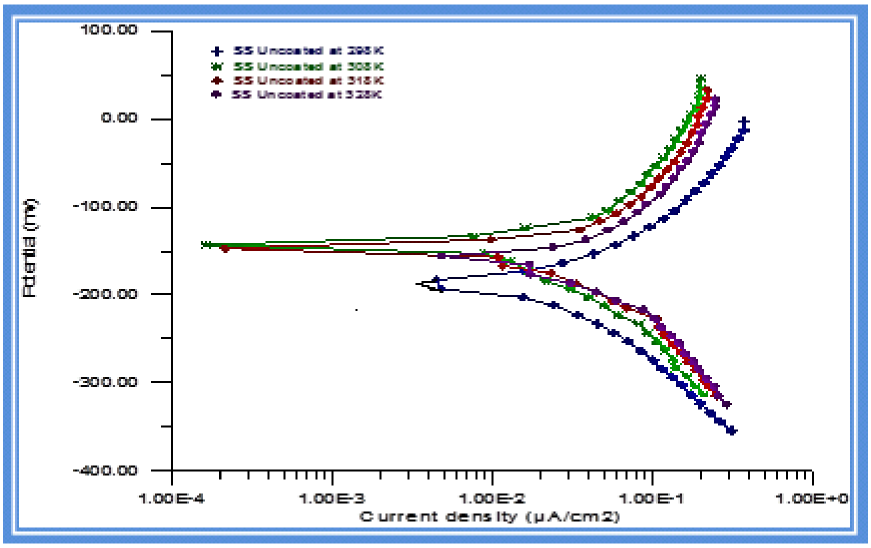

Figure (5): Potentioatatic Polarization curves for uncoated S.S 360L in 3.5% NaCl solution at the temperatures range (298-328) K.

Table (5): Corrosion parameters for the uncoated and coatedS.S alloyin 3.5% NaCl Solution at a Temperature range (298-328) K.

	Temp/ K	Ecorr. / mV	Icorr. / $mA.cm^{-2}$	-bc/ $mv.Dec^{-1}$	ba/ $mv.Dec^{-1}$	W.L/ $g.m^2.d^{-1}$	Rp/ $\Omega.cm^2$	CR/ mpy	PE%
Un coated	298	190.7	17.62	104.6	92.6	4.42	1290.1	8.0171	----
	308	178.5	19.08	87.5	161.3	4.78	1210.8	8.6814	----
	318	146.9	22.56	145.3	98.7	5.65	1131.5	10.264	----
	328	179.5	25.92	74.9	148.9	6.50	834.80	11.793	----
Coated byP4HA	298	32.2	1.71	102.9	121.3	0.429	1413.7	0.778	90.295
	308	17.0	2.53	122.3	108.8	0.635	9881.9	1.151	86.74
	318	14.9	3.32	110.0	113.3	0.832	7299.6	1.510	85.284
	328	12.8	4.52	123.5	126.1	1.13	5993.8	2.056	82.562

Values of corrosion potentials E_{corr}, corrosion current densities i_{corr}, cathodic and anodic Tafel slopes bc and ba, Rppolarization resistancethe determination of the (Rp) by eq. (1),CRcorrosion ratedetermination by eq. (2),W.L Weight loss,P.LPentration loss,PEprotection efficiencydetermination by eq. (3).

$$RP = \left(\frac{B}{icorr}\right) \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$B = \frac{\beta a \beta c}{2.303\ (\beta a + \beta c)}$$

$$CR = 0.13\ \left(\frac{e}{p}\right) icorr \ldots\ldots\ldots(2)$$

e:Chemical equivalent

p:density 0f SS 316L

$$PE\% = \left(1 - \frac{icorr}{i^{\circ}corr}\right) \text{ x } 100 \ \ldots\ldots\ldots\ldots(3)$$

icorr:corrosion current densities with polymer coated

$i^{\circ}corr$:corrosion current densities without coated

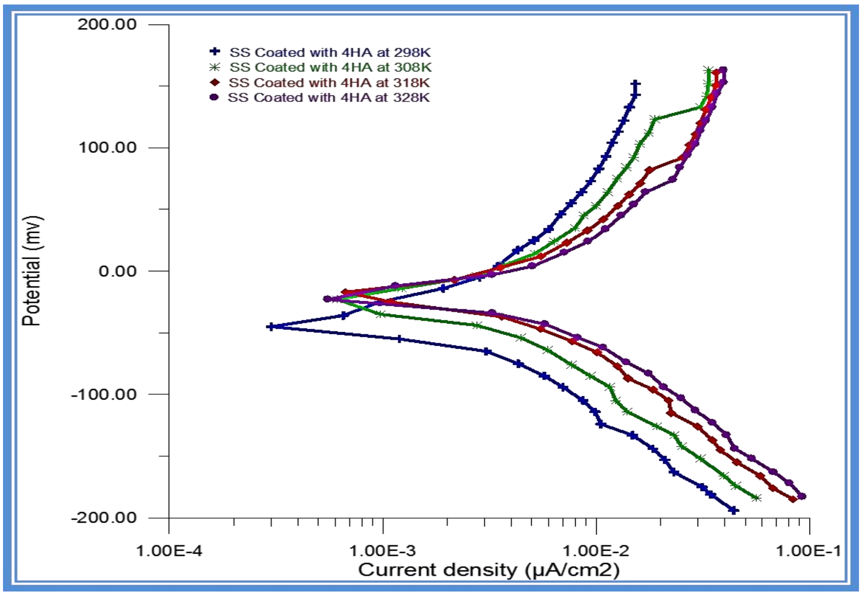

Figure (6): Potentioatatic Polarization curves forcoatedS.S 316L by polymer in 3.5% NaCl solution at the temperatures range (298-328) K

The corrosion current density values increased from 17.62mA.cm^{-2}at 298K to 25.92mA.cm^{-2}at 328Kfor the uncoated S.S316L alloy were obtained by the extrapolation of the linear logarithmic section ofcathodic and anodic Tafel line to the point of intersection show in fig. (5) and observed that in table (5)The values of the polarization resistance (Rp) for all uncoated specimens have been generally decreased when the temperature was increased from (298 to 328) K. The greatest Rp values have been observed at 298K, CR corrosion rate determinationincreasedwhen the temperature was increasedfrom (298 to 328) K, As well asshow in fig. (6)and table (5) .The corrosion current density values increased from 1.71 mA.cm^{-2}at 298K to 4.52 mA.cm^{-2} at 328K for the coated S.S316L alloy

2- Kinetic and Thermodynamic Studies : Thermodynamic parameters play an important protection mechanism.From Eq. (4) the values of the slopes of these straight lines permit the calculation of the similar Arrhenius activation energy (Ea) [7].

$$\text{Log}I_{corr} = (-Ea/2.303RT) + \text{Log } A \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where R is the gas constant ($R \approx 8.314\ J\ K^{-1}\ mol^{-1}$), and determine the Arrhenius factor from intercept. Moreover, transition state Eq. (5) were used.

$$\text{Log}(I_{corr}/T) = \text{Log}\ (R/\ Nh) + \Delta S^{*}/2.303R - \Delta H^{*}/2.303R \ldots\ldots.(5)$$

Where Icorr is corrosion current density, T is temperature in K, h is the planks constant (6.626×10^{-34} J.s), N is the Avogadrs number ($6.023 \times 10^{23}\ mol^{-1}$), ΔH^{*} is the enthalpy of activation and ΔS^{*} is the entropy of activation. Straight line were obtained from the plots of log Iorr/T vs. 1/T, with the slope of ($-\Delta H^*/2.303R$) and an intercept of [log (R/Nh) +($\Delta S^*/2.303R$)] from which the values of ΔH^* and ΔS^*, respectively were obtained. ΔH^*, ΔS^*,Ea and A values for S.S 316L alloy before & after polymer coated were illustrated in table(6)

The protection efficiency (PE) was obtained from equation (3) at temperature range (298-328)K, as show in table (6).

Table (6): The thermodynamic parameter at different temperatures for Uncoated S.S 316Land coated with polymer thin film in 3.5 % NaCL solution.

	Temp/ K	1/T/ K^{-1}	$i_{corr.}$/ $\mu A.cm^{-2}$	Log $i_{corr.}$	Log ($i_{corr.}$/T)	ΔG*/ $KJ.mol^{-1}$	ΔH*/ $KJ.mol^{-1}$	ΔS*/ $J.mol^{-1}$	Ea/ $KJ.mol^{-1}$	A/ Molecules. $cm^{-2}.s^{-1}$
Uncoated	298	0.0033	17.62	1.246	-1.228	65.92	8.137	-193.909	10.722	7.883E+26
	308	0.0032	19.08	1.280	-1.207	67.86				
	318	0.0031	22.56	1.353	-1.149	64.61				
	328	0.0030	25.92	1.413	-1.102	69.80				
Coated	298	0.0033	1.71	0.232	-2.241	71.60	23.34	-161.949	3.67	25.92E+26
	308	0.0032	2.53	0.403	-2.085	73.22				
	318	0.0031	3.32	0.521	-1.981	74.84				
	328	0.0030	4.52	0.655	-1.860	76.46				

When a metal undergoes corrosion there is a change in Gibbs free energy, ΔG, of the system, which is equal to the work, associated with the corrosion reaction.

The results may be summarized in the following :

a- In general, values of ΔG were positive suggesting the existence of thermodynamic feasibility for the corrosion for Uncoated S.S 316L and coated with polymer thin film in 3.5 % NaCL solution. ,the positive values of ΔG that mean, these reaction are occurring unspontaneous.
b- The values of ΔG are increased with increasing temperature for specimens polymer coated more than polymer uncoated.
c- Values of (ΔS) were positive or negative depending on the positive or negative dependencies of (ΔG) values on temperatures The positive values of ΔS show an increase random at solid /solution interface during the adsorption process.

3-Morphological Study of coated S.S 316L by polymer : FESEM is a technique which uses electromagnetic lenses and an electronic beam to illuminate samples under vacuum [10, 11]. A scanning electron microscope scans a focused electron beam over a surface of a sample to create an image. The electron interaction with the atoms of the surface, producing various signals that can be used to obtain information about the surface topography and composition. The Surface morphology and thickness of the electrodepostion technique for S.S 316L coated by polymer was studied usingthis technique (from a Hitachi S4160).More uniform grains may lead to more protection results, the surface morphologies and the cross-section were analyzed by a Zeiss Supra 55VP PGT/HKL.system, which offers an ultra-high resolution at a relatively low voltage. The imageand cross section view ofpolymer thin film shown in Fig. (7&8) respectively.

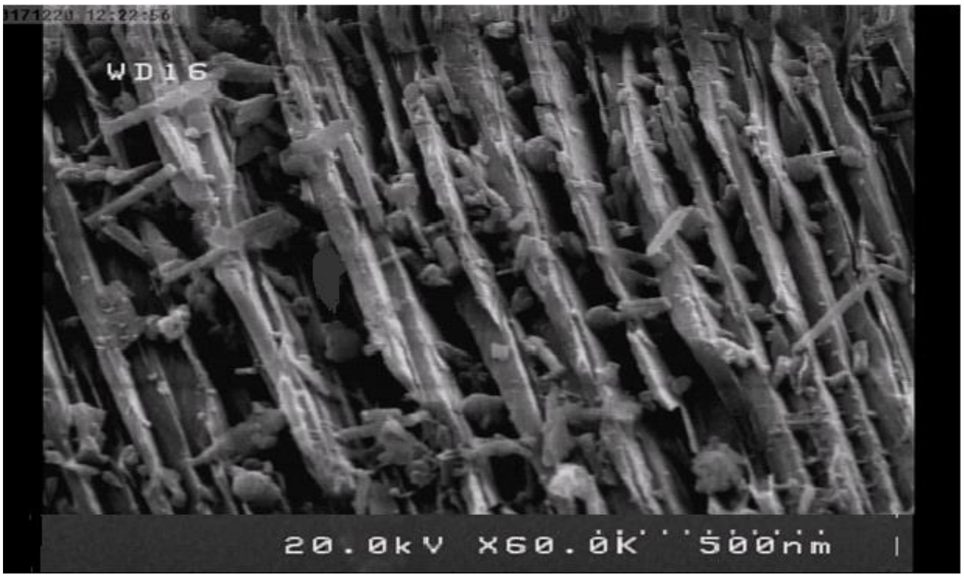

Figure (7): FESEM image of Poly 4-hydroxyaniline film

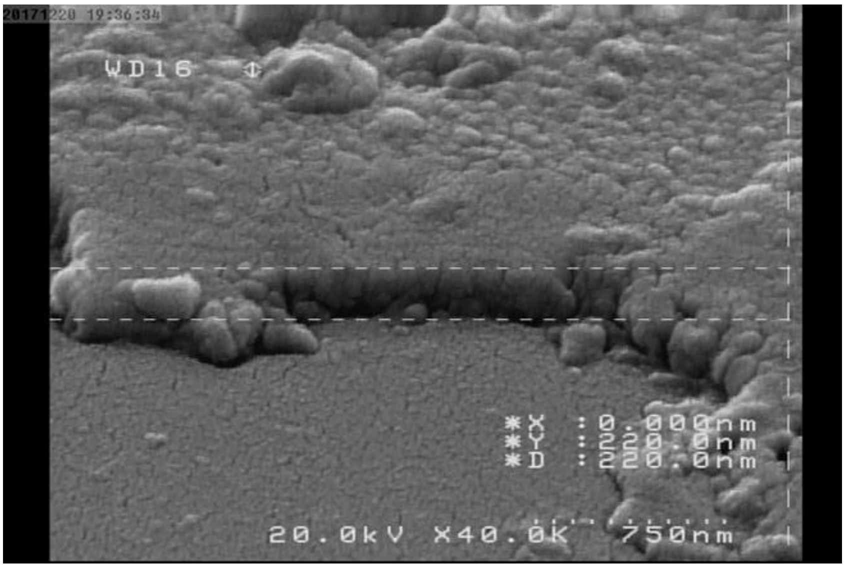

Figure (8): FESEM images of Poly 4-hydroxyaniline film Cross-Sectional view of film Coating indicating a thickness of 220 nm

CONCLUSIONS

Different techniques have been used to analyze Thepolymer thin films the structural ,optical and anticorrosion properties for thispolymer thin films were investigated .

The results show that the nanoPoly 4-hydroxyaniline thin filmsof a thickness of 220nm acts as good protection for the corrosion of S.S 316L in 3.5% NaCl solution, The coated S.S 316L by polymer reduced corrosion rate compared to uncoated alloy, their values obtained from Polarization method and electrochemical impedance, and the standard data obtained are in good agreement.

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