ELECTROCHEMICAL POLYMERIZATION OF (N-CREATININYL MALEAMIC ACID) COATED LAYER ON STAINLESS STEEL SURFACE AND STUDY ITS ANTI-CORROSION AND BIOLOGICAL ACTIVITY

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ABSTRACT

Electrochemical polymerization of N-Creatininyl maleamic (NCM) acid was carried out on stainless steel plate electrode in a protic medium of monomer aqueous solution using electrochemical oxidation procedure in electrochemical cell. Fourier Transform Infrared FT-IR Spectroscopy has examined the structure of synthesized polymer. The anti-corrosion action of polymer was investigated on stainless steel in 0.2M Hydrochloric acid solution at temperatures range (293-323) K. by electrochemical polarization method. In addition, reinforce the anticorrosion of coating polymer by nanomaterial (TiO$_2$) or (ZnO bulk and nano) by adding these nanomaterials to monomer solution. The results of the experimental study showed that the corrosion current density increases with increasing temperature in the range (293-323) K and the protection efficiency of polymer decrease with temperature increase. Kinetic and thermodynamic of activation parameters Ea, A, ΔH* and ΔS* have been calculated for the corrosion process of S-steel in 0.2M HCl solution in the presence and absence polymeric coating. Furthermore, were studied the effect of the preparing polymer on some strain of bacteria.

Keywords: electro polymerization, N-creatininyl maleamic acid, anti-corrosion, antibacterial.

1. INTRODUCTION

Conducting polymers have a many application for different technical products and processes such as electrochemical displays, sensors, catalysis, redox capacitors, batteries and anti-corrosion (McQuade et al., 2000). Electrodes coated electrically with polymer films have been the most important and widely used in last years. A particularly significant functional of coated polymers in this respect are electronically conducting polymers (Kowalewski 1982). Polymer films of condensed monomer was proposed for corrosion protection of iron (Meneguzzi et al., 2001), mild steel (Meneguzzi et al., 1999), Must be taken into consideration the mobile charge carriers to synthesized polymer electrically conductive. As mentioned before, the electrochemical synthesis refers to the oxidation of the monomer and grafting of the polymer film on the anode. As the oxidation done by applying a positive potential or current, the electrochemical polymerization avoids application of the oxidant, so achieving high purity of the favorite polymer. Some of the characteristic of electro-conducting polymers synthesized electrochemically are dependent on the selection of electrochemical polymerization methods (Gruger et al., 2003).

Stainless steel finds a variety of industrial applications, for mechanical and structural purposes, such as bridges, construction, metal sheets, steam engine parts and automobiles. Different uses are found in most chemical laboratories due to their low cost and availability to manufacture different reaction containers. Because it suffers from severe corrosion during aggression, it must be protected. Acidic medium like HCl have been used in this work. Corrosion commonly occurs on metal surfaces in the presence of oxygen and moisture, including electrochemical reactions. Oxidation occurs at the anodic site and the reduction occurs at the cathode site. In the acidic medium reaction of hydrogen evolution performed (Sethi et al., 2007). Polymeric coatings film is widely used to protect metals against corrosion in atmospheric conditions (Miszczyk et al., 2003). Adhesion is a critical factor in the evaluation of coatings and determines whether the coating is merely a thin sheet of material lying on the substrate or an important and essential component of the used substrate. Three types of adhesive bonds are identified, namely chemical, and polar and mechanical bonds, depending on the characteristics of the substrate and coating. Polymeric coating experts usually say that the preparation of metal surface is the most significant factor in identification the success of any protective coating system. By this, it is meant that surface preparation influences the performance of the coating more than any other factor. Many factors in the preparation of surfaces overcome the safety of paint, involving the residue of grease, rust on the surface, and the grinder scale, which can reduce the adhesion, or mechanical

bonding of the coating to the surface. (Bayliss et al., 2002).

2. MATERIALS AND METHODS

The electrochemical polymerization of NCM onto the S-steel (anode) electrode surface was carried out in a potentiostat using a regulated DC power supply. The electrodes were cleaned and washing by acetone. The solutions employed for polymerization were 0.1g of N-Creatininyl maleamic acid (monomer) (Muna and Osama 2015) in 100ml H_2O with three drops of H_2SO_4 concentration (37%). The polymerization was carried out at 1.1V and at 293K. The polymer film was deposited at the anode surface.

For corrosion measurements, a three-electrode cell involving a working electrode (S-steel plate), reference electrode (saturated calomel electrode) and axillary electrode (platinum electrode) was subjected for the potentiostatic measurements [Advanced potentiostat winking MLab-200(2007) [Bank Elektronik–Intelligent controls GmbH with all accessories] Cell + Three Electrode + working electrode holder (Germany)]. Anodic and cathodic polarization of s. steel was carried out under potentiostatic conditions in 0.2M HCl in the absence as well as in the presence-coated layer at different temperature 293-323K. Also, in presence of 0.05g of ZnO (bulk-nano) and TiO_2 nanomaterial which add to improve the coated layer against corrosion and bacteria.

3. RESULT AND DISCUSSION

3.1. Mechanism of Polymerization: Depending on the published literature, a cationic (Léonard-Stibbe et al., 1994) or a radical mechanism (Mertens et al., 1996) can be suggested to demonstrate electro polymerization reactions and, in particular, the growth of the PCM layers. The first considera tion is the cationic mechanism (Scheme A): Applying the anodic potential to the NCM solution leads to the transfer of one electron from the monomer solution to the working electrode A1. This transport leads to a radical cation formation that absorbs on the surface of the electrode that is represented in A2. Alternatively, if the lifetime of A2 is long enough compared to the average time of the NCM molecule to diffuse toward the electrode, the NCM molecules can be added by a cationic mechanism at the charged ends of oxidized NCM A4. This process by diffusion leads to the formation of a grafted polymer with nanomaterial compounds. Now we include a radical mechanism (Haaf et al., 1985) (Scheme 1B). The radical coordi-

nate of A is B. First, the chemisorbed radical cannot be labeled in B2 as a result of the electrochemical process. However, we face the fact that the radical mechanism is not particularly favored under the current electrochemical conditions. In fact, the radical mechanism continues through the hemolytic fusion of the double bond (Scheme B). However, the dissolution of the C = C bond is highly unlikely given the initial polarization of the bond, which is further improved under the field created by the electric double layer (Raynaud et al., 1990). Moreover, this electric field stimulates the reorientation of the molecule (Geskin et al., 1996). This all makes the radical mechanism unlikely to represent the growth of PCM films under anode electrochemical conditions.

Scheme 1. Proposed Cationic (A) and Radical (B) Mechanisms for the Growth of PCM Films
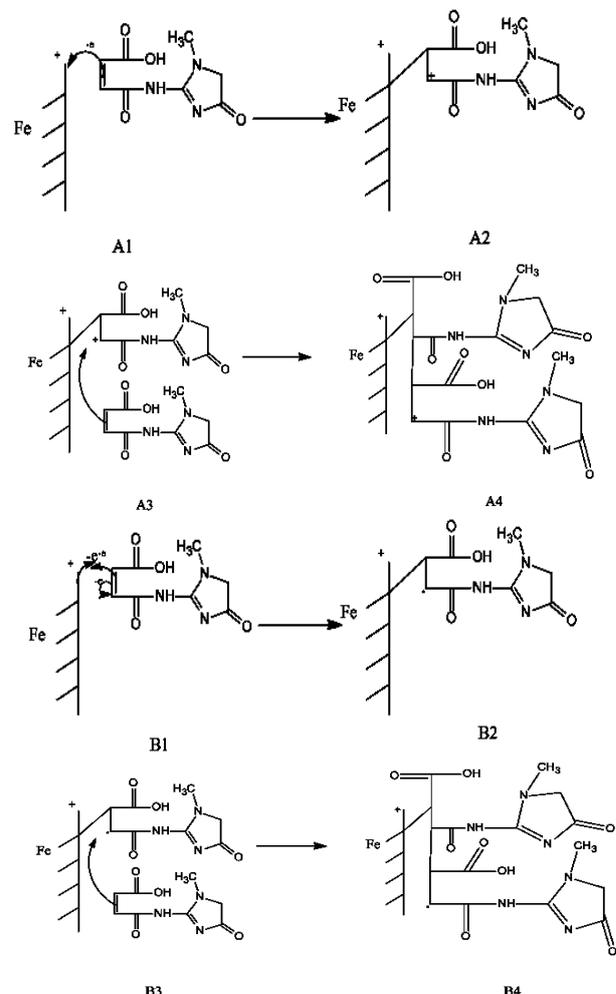
3.2. Structure of PCM: FTIR spectra of PCM coating film prepared from NCM are shown in Fig.2. In this spectrum, the characteristic bands of the NCM Fig.1 double bond C=C 1614 cm^{-1} are disappear and confirm the formation of PCM. The bands are

relatively broad mainly because the polymer has a broad chain length distribution.
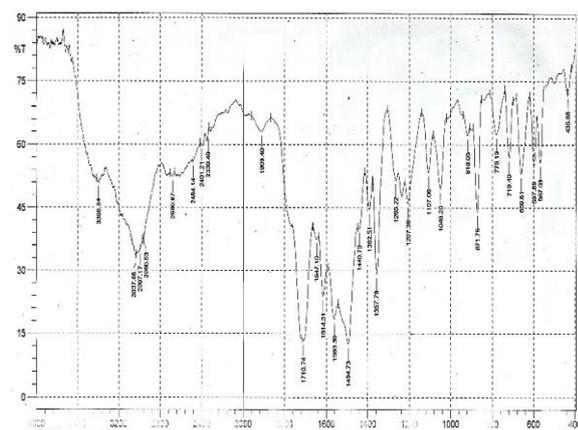
Fig. 1. FTIR spectra of NCM
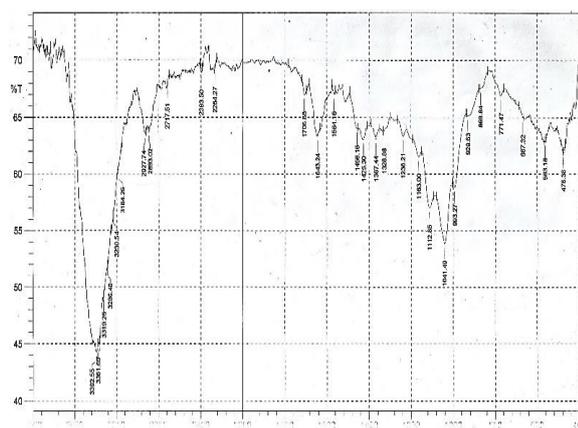
Fig. 2: FTIR spectra of PCM

The band appeared at 1710 cm^{-1} that confirmed the presence of C=O carboxyl groups, the absorption of imide group was appeared at 1643 cm^{-1}, the absorption bonds of N-H and O-H carboxylic group make overlap and appeared at 2700-3300 cm^{-1} (Silverstein et al., 1963; Shirner *et al., 1980)*

3.3. Potentiostatic polarization measurements

The effect of polymeric coating film on the anodic and cathodic polarization curves of S-steel in 0.2M HCl solution at different temperature 293-323K was studied. The effect of adding different nanomaterial compound [TiO$_2$ and ZnO (bulk, nano)] is represented in figure 3 for PCM. The corrosion current density (I$_{corr}$) was calculated by the extrapolation of anodic and cathodic Tafel lines. Table (1) represents the effect of polymer coating with and without nanomaterial on the corrosion parameters of S-steel electrode. These parameters are anodic Tafel slope (ba), cathodic Tafel slope (bc), corrosion potential (E$_{corr}$), corrosion current density (I$_{corr}$), protection efficiency (P%), weight and penetration loss. Protection efficiency was calculated by using equation (1) (Abdel et al., 1983).

$$P\% = \left(1 - \frac{I_{corr}\ coated}{I^{\circ}_{corr}\ uncoated}\right) 100 \qquad (1)$$
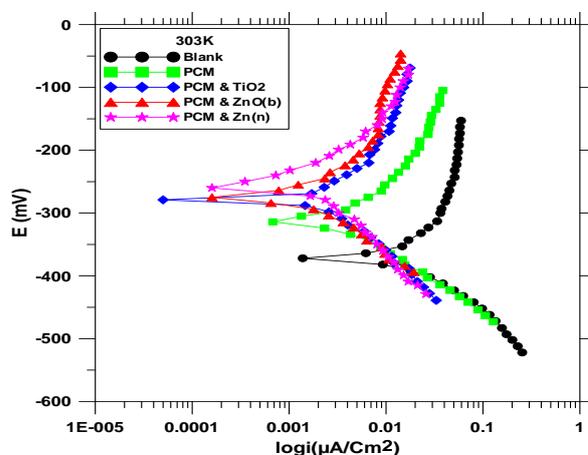
Fig. 3: Polarization plots of S-steel coated with polymer and nanomaterial in 0.2M HCl at 303K.

Table 1. Corrosion data of S-steel in 0.2M HCl with and without coating

Coating	T\K	-E$_{corr}$ mV	I$_{corr}$ µA/cm²	-b$_c$ mV/Dec	b$_a$ mV/Dec	P%	Weight loss g/m².d	Penetration loss[mm/y]
Blank 0.2M HCl	293	364.1	16.00	109.1	179.5	-	4.01	0.178
	303	368.4	22.45	131.8	349.8	-	5.63	0.250
	313	369.0	25.35	141.1	274.0	-	6.35	0.283
	323	371.1	27.15	123.0	242.4	-	6.81	0.303
PCM	293	314.5	2.29	64.4	74.7	87.93	0.575	0.0256
	303	314.5	3.87	108.8	149.2	82.76	0.971	0.0432
	313	316	4.9	99.3	130	80.67	1.230	0.0547
	323	320.6	6.41	135.3	288.5	76.39	1.610	0.0715
PCM & TiO$_2$	293	264.2	1.25	111.9	93.1	92.18	0.34	0.0140
	303	277.4	2.35	132.0	148.6	89.53	0.59	0.0263
	313	288.3	3.18	119.7	165.5	87.45	0.798	0.0355
	323	316.6	4.00	95.9	146.6	85.26	1	0.0447
PCM & ZnO$_b$	293	275.8	0.99049	82.2	97.6	93.8	0.248	0.0110
	303	276.2	1.59	104.9	135.4	92.91	0.398	0.0177
	313	290.8	2.40	138.0	147.4	90.53	0.602	0.0268
	323	320.5	3.18	147.2	291.7	88.28	0.797	0.0355
PCM & ZnO$_n$	293	249.1	0.68411	105.0	74.4	95.72	0.171	0.00763
	303	251.1	1.15	107.0	107.9	94.87	0.289	0.0128
	313	263.9	1.60	104.7	98.3	93.68	0.400	0.0178
	323	276.1	2.71	128.1	173.9	90.01	6.790	0.0302

When the polymer film crafted with nanomaterial coated on the S-steel the corrosion potential shifted to the noble side. This indicates that a film formed on anodic sites of the metal surface (Anthony and Susai 2012).

3.4. Kinetic and thermodynamic of activation parameters:

The effect of temperature on the corrosion rate of S-steel in free acid in the presence of different coating of polymer was studied in the temperature range of (293–323) K using potentiostatic measurements. In examining the effect of temperature on the corrosion process in the presence of the polymer, the Arrhenius equation below eq. (2 and 3) was used in fig.4 (Umorena et al., 2009):

$$C.R = A \exp(-E_a/RT) \qquad (2)$$
$$\log C.R = \log A - E_a/2.303RT \qquad (3)$$

The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were obtained from (Fig. 5) from the transition state eq. (4 and 5):

$$C.R = RT/Nh \exp^{(\Delta S^*/R)}\exp^{(-\Delta H^*/RT)} \qquad (4)$$
$$\log(C.R/T) = \log R/Nh + \Delta S^*/2.303R - \Delta H^*/2.303RT \qquad (5)$$

Where C.R is the corrosion rate, T the absolute temperature, R the gas constant, h the Plank's constant, A the pre-exponential factor and N is Avogadro's number, ΔS^* the entropy of activation and ΔH^* the enthalpy of activation, E_a^* the activation energy for corrosion process. The calculated kinetic and thermodynamic values are given in Table 2.
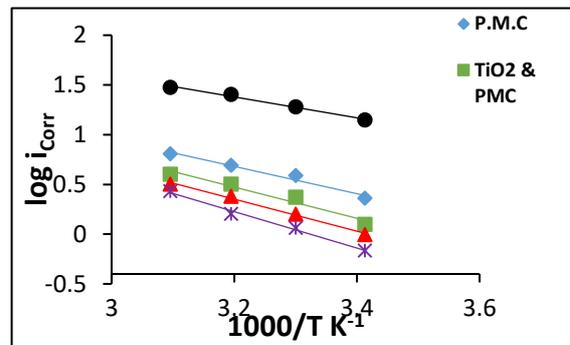
Fig. 4: Arrhenius Plot of log C.R versus 1/T for S-steel in 0.2M HCl in the absence and presence coating
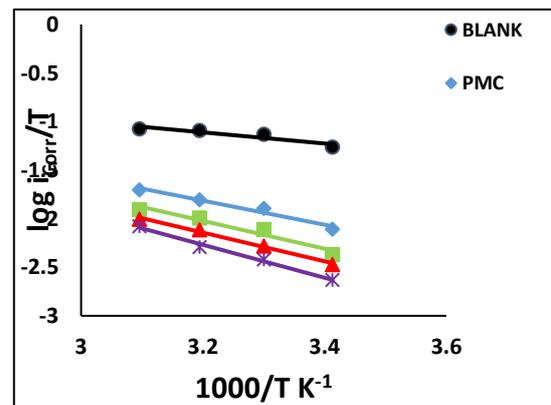
Fig. 5: Arrhenius plots of log C.R/T vs. 1/T for S-steel in 0.2M HCl in the absence and presence coating.

Table 2: Activation parameters Ea, ΔH* and ΔS* for the coated and non-coated S-steel dissolution in 0.2M HCl.

Coating	R^2	E_a kJ.mol^{-1}	A/Molecule. Cm^{-2}.S^{-1}	R^2	ΔH^* KJ. K^{-1}. mol^{-1}	$-\Delta S^*$ J.K^{-1}. mol^{-1}
HCl Blank	0.899	13.565	4.482×10^3	0.852	11.013	183.600
PMC	0.971	26.267	1.17841×10^5	0.957	23.715	156.415
PMC & TiO$_2$	0.955	30.024	3.09670×10^5	0.946	27.468	148.392
PMC & ZnO$_b$	0.993	30.851	3.22329×10^5	0.991	28.301	148.042
PMC & ZnO$_n$	0.991	35.066	1.221518×10^6	0.99	32.515	136.961

The increase in the activation energy in the presence of coating indicates the higher inhibition efficiency of the coating. The increase in Ea in case of the protected S-steel with the addition of different coating indicates that the energy barrier for the corrosion reaction increases. The increase in Ea of the corrosion process could be attributed to the coating molecules onto the metal surface which decreases the interaction between the corrosive medium and the metal surface (Migahed et al., 2008; Abd El-Rehim etal., 2001). The increase in the activation enthalpy (ΔH*) in positive sign in presence of the coatings reflects the endothermic nature of the steel dissolution process and lead to increases the height of the energy barrier of the corrosion reaction and that mean the dissolution of steel became more difficulty. The values of the entropy change of activation (ΔS*) in the presence of the investigated coatings are large and negative. Such variation reflects the formation of an ordered stable film of coating on the S-steel surface (Abdallah et al., 2002; Noor et al., 2008).

3.5. Antimicrobial study

Polymer coatings are miscellaneous use in most diverse applications and sectors. Polymers coating

give a bastion of functionalities for their underlying hosts. In the field of biological activity, such characteristics involve wear-resistance, improved mechanical strength, corrosion protection, enhanced biocompatibility, electrical conductivity and tailored surface chemistry. The results of antimicrobial activity of polymer and polymer with nanomaterial are listed in table 3. The result refers that the polymer and polymer with nanomaterial com-0pounds possess strong activity against *Staphylococcus aureus* and *Escherichia coli*.

Table 3: Antimicrobial activity of the tested polymer and polymer with nanomaterial

compound	*Staph. Aure*	*E. Coli*
PCM	14	15
PCM & TiO_2	16	18
PCM & $ZnO_{(B)}$	22	21
PCM & $ZnO_{(n)}$	24	26

Solvent: DMSO; [C]: 800µg/ml.

4. Conclusion

Electro polymerization protective coatings of PCM on S-steel surfaces can Improvement their corrosion resistance in 0.2MHCl corrosive medium. Also, can enhanced polymer coating against corrosion with nanomaterial (TiO_2, ZnO (bulk-nano)). Next to the resistance to corrosion, polymer coating can also provide antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* bacteria. With additional studies of electroplating technology and their related characterization techniques, electroplating coatings will have broader and more practical applications.

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