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Corrosion Protection of Pure Titanium Implant in Artificial Saliva by Electro-Polymerization of Poly Eugenol

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IN this work, a titanium dental implant was modified by electro-polymerized of 4-allyl-2-methoxyphenol (Eugenol) using direct current lower than 3.5 volt. The modification of titanium dental implant was achieved to improve its corrosion resistant. Fourier transform infrared spectroscopy (FTIR) was employed to confirm the electro-polymerization of Eugenol to Poly Eugenol (PE) on pure titanium. Deposition of PE on titanium was confirmed by X-ray diffraction and was characterized by thermogravimetric analysis (TGA). The surface morphology of polymeric film were examined through scanning electron microscopy (SEM). Coated titanium by (PE) revealed a good corrosion protection efficiency even at temperature ranged (293-323)K in artificial saliva. Where the corrosion current density decrease with increase the temperature. Activation energy and pre-exponential factor (kinetic parameters) were calculated and discussed. Also, thermodynamic values ΔG and ΔH were calculated.

Keywords: PolyEugenol, Titanium, Electro-polymerizaion, Dental implant.

Introduction

In recent years, titanium and Ti based alloys are widely used in the field of bio-medical materials, such as dental restorations, orthopedic prosthetic, dental implant and heart valves [1-4] because of their good biocompatibility and good corrosion resistance properties deriving from the formation of oxide films on surface of metals. It is unimpeachable that the degradation of Ti and its alloys will occur by electrochemical reactions at the interface between surface of titanium alloys and a saliva, inducing in the breakdown of protective titanium oxide passive films, the release of titanium ion and the decrease of the service life of titanium alloys. However, Ti and Ti alloys can generate metal ions which can diffuse and react with the ions present in the human fluid and form complexes and precipitates. These ions can also form hydroxides or oxides with water producing local pH changes that could accelerate the corrosion and adverse reactions [5-7]. Changes in external variables (pH, temperature, O_2) can influence the mode and rate of metal ion release [8].

In recent years, many ways based on surface modification to improving the biocompatibility of Ti-based implants have been suggested [9]. Coating metals with polymer films is a useful strategy that is of great interest for dental applications since it can modify the properties of the metal surface and/or protect it from corrosion. Electrochemical polymerization is an best technique for manufacturing thin passive films on metal surfaces in order to protect them from corrosion, since it enables the synthesis of polymeric films directly onto the metal surface starting from solutions of the relevant monomers [10]. In electrochemical polymerization, the transformation of low molecular weight molecules (monomer) into high molecular weight molecules (polymer) occurs with the assistance of active species such as electrons, ions and radicals [11].

Eugenol (4-allyl-2-methoxyphenol), a methoxyphenol with a short hydrocarbon chain, is the major component (80%–95%) of clove oil [12]. Eugenol has been used as a spice because of its strong odor and as a dental antiseptic. It has been extensively used as a therapeutic agent in dentistry for sedation in patients with toothache, pulpitis, and dental hyperalgesia [13]. Pharmacologic studies have demonstrated that eugenol has local anesthetic [14], bacteriostatic

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and bactericidal, [15] anticandidal, [16] and antifungal [17] properties.

In this paper we describe the construction and performance of an electro-polymerized eugenol film on pure titanium for improvement corrosion resistance, roughness and hardness properties.

The electrosynthesised polyeugenol (PE) coatings were characterized by FTIR, X-ray and scanning electron microscopy (SEM) in order to assess their surface morphologies.

Experimental part

Titanium Preparation

Titanium specimens of 2 ×2 cm^2 area were obtained from grade 2 commercially pure titanium ethanol and finally with acetone then dried by using hair drier. Sheet of 0.5 mm thickness, polished by emery papers 600, 1200 and 2000 mesh grit, then the specimens were cleaned with distilled water, then by acetone.

Before electrochemical polymerization, titanium specimens were treatment by heating (500 ^oC) to formation a barer titanium oxide thin film to increase the current between electrode and eugenol solution.

Artificial Saliva Preparation

Reference electrolyte was used named; modified Fusayama artificial saliva which prepared according to a method that has been described in detail in a previous report [18], which closely resembles natural saliva, its composition are shown in table 1, and pH of this electrolyte was 6.2.

Electrochemical Polymerization of Eugenol

After heating titanium electrode, it was placed in 0.1M NaOH containing 10mM eugenol and it is necessary to use large sheet of titanium as counter electrode, then voltage of (3 V) was applied at room temperature with duration (90 min.), then the electrode washed by distilled water and dry by hair drier.

Characterization and test

Spectroscopic analysis of eugenol and polyeugenol coated formed with fourier transform infrared spectroscopy using KBr pellet technique.

Studying the surface morphologies of PE coating by XRD, AFM and SEM.

The galvanostatic polarization were measured using WENKING M Lab.(Germany). Corrosion cell with three electrodes, (the Calomel electrode was the reference electrode, Titanium dental implant was a working electrode and platinum electrode was an auxiliary electrode. Polarization curves were obtained, for the corrosion of pure titanium before and after treatment. The polarization curve obtained involved the cathodic and anodic regions. Extensive data could be derived from the detailed analysis of each polarization region using extrapolated method to determine both the corrosion current density (i_{corr}) and corrosion potential (E_{corr}). TGA of the obtained coated polymers was performed using a Shimadzu DT-30 thermal analyzer (Shimadzu, Kyoto, Japan). The weight loss was measured from room temperature up to 600°C, at the rate of 10 °C/min to determine the degradation rate of the polymer film.

Results and Discussion

Corrosion test

The polarization curves for the corrosion of pure titanium immersed in artificial saliva before and after electrochemical polymerization by PE at different temperatures were recorded and plotted in figure 1. The polarization curves of blank pure titanium show corrosion potential ranged between (-146.7 to -165.7 mV) and this potential shifted to (-743.2 mV) at 293K after coated by PE, figure (1). Show the corrosion potential shifted to more active with increasing temperature for Ti coated by PE.

Data in the table (2) shows that the corrosion current density, slightly increased with temperature increased for pure Ti but after coated by PE the corrosion current density have not any effect with increasing temperature, this results indicate that the efficiency of PE against corrosion increased at high temperature.

The Protection Efficiency (%P) can be calculated by using the equation [19]:

%P= ((i_corr)b-(i_corr)p)/(i_corr)b x 100……..(2)

TABLE 1. The composition of artificial saliva.

	KCl	NaCl	$CaCl_2.H_2O$	$NaH_2PO_4.2H_2O$	$Na_2S.9H_2O$	urea
g/l	0.4	0.4	0.906	0.69	0.005	1

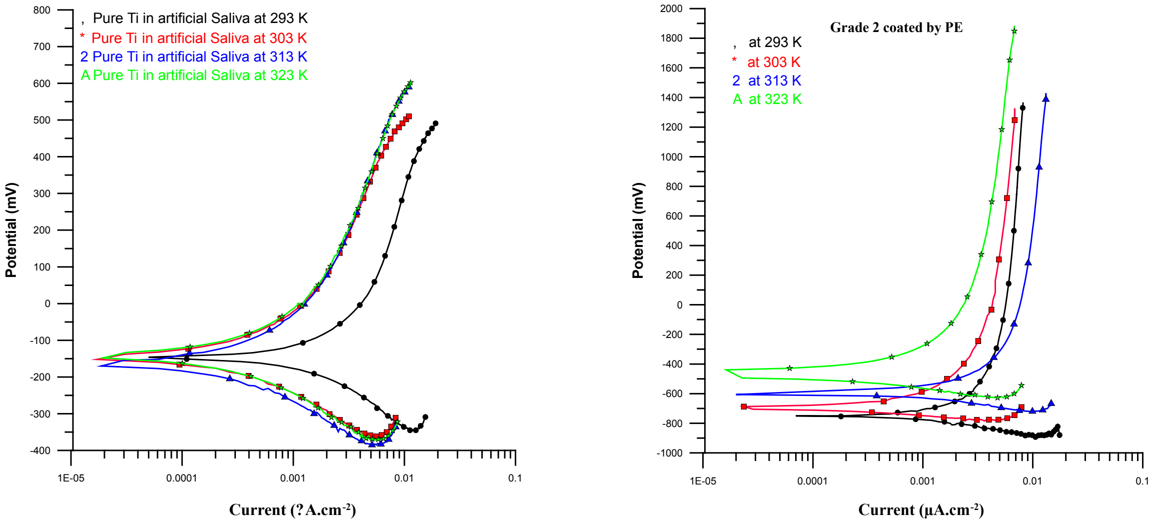


Fig..1. Polarization curves for a) Pure Ti (Blank), b)Ti coated by PE.

TABLE 2. Corrosion kinetic parameters for pure titanium in artificial saliva at different temperature in the range (293-323)K.

	Temp./K	$-E_{corr}$/ mV	I_{corr}/µA.cm^{-2}	-bc/ mV.dec^{-1}	bc/ mV.dec^{-1}	PE%	Rp/Ω.cm^2
Blank	293	-146.7	1.41	226	336.4	-	41629.96
	303	-151.0	1.50	258.1	423.3	-	46413.99
	313	-165.7	1.60	282.8	455.5	-	47350.11
	323	-147.7	1.65	249	574.8	-	45721.07
Ti coated by PE	293	-743.2	0.702	70.3	204.0	50.21	32339.153
	303	-688.4	0.669	80.9	122.8	55.40	31654.52
	313	-598.9	0.667	99.2	188.2	58.31	42288.74
	323	-555.8	0.602	102.7	171.8	63.52	46361.85

Where $(i_{corr})_b$ and $(i_{corr})_p$ are the corrosion current density (µA.cm^{-2}) pure titanium (Blank) and pure titanium after protection respectively.

The best %P were obtained after coated titanium by P.E which give %P reach to 50% at 293K, table (2) data shows that %P slightly increased with temperature increasing, that indicate i_{corr} for Ti coated by P.E was not effected by temperature while lead to increase in efficiency of polymer on titanium against corrosion [15].

Small polarization near the corrosion potential E_{corr} is conducted to determinate the corrosion resistance on the basis of the following equation, i.e., the Stern–Geary equation:

R_p= *ΔE/Δi=(b_a b_c)/2.303(b_a+b_a)*........ (3)
.1/i_corr

where R_p is the polarization resistance of system, ΔE is the difference between the polarization potential E and the corrosion potential E_{corr}, Δi is the difference between the measured current density i and the corrosion current density i_{corr} , and b_a and b_c are the anodic and cathodic Tafel coefficients, respectively.

Discussion polarization resistance has such as requirements to the measurement of full polarization curves and it is particularly helpful to identifying corrosion trouble and initiates reconditioned action [20, 21].

Kinetic parameters for the corrosion process

Figure (2) shows logarithm of current density plotted against reciprocals temperature for the corrosion of uncoated and coated titanium with P.E, the linearity of the Arrhenius relation for Ti coated by P.E shows opposite to the linearity of Blank Ti, because the polymeric film formed on Ti surface have not effected by temperature, these due to get activation energy equal to (3.622 kJ.mol^{-1}), and decrease in Arrhenius factor indicated decrease in the corrosion sites on Ti surface.

The Thermodynamic Studies

The change in the entropy (ΔS*) for transition state of corrosion process could be derived according to the well–known Arrhenius equation:

$$\log i\_corr/T=\log R/Nh+ \Delta S\ ^*/2.303R-\Delta H\ ^*/2.303RT \quad \ldots\ldots\ (5)$$

Where i_{corr} is the corrosion current density of titanium in artificial saliva derived from tafel plot, h is the Plank's constant, N is the Avogadro number , ΔS^* is the activation entropy and ΔH^* is activation enthalpy. The plot of log i_{corr}/T against 1/T obtained straight lines were obtained with the slope of (-ΔH* / 2.303 R) and an intercept of [(log (R/Nh) + (ΔS*/2.303 R)] from which the values of ΔH^* and ΔS^*, respectively were calculated.

Figure (3) shows the plot of log i_{corr}/T against 1/T, the data in table (3) shows that values of entropy was slightly change after coated the Ti surface by PE.

The free energy change of electrochemical corrosion reaction transition state can by calculated using the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \ \ldots\ldots\ldots.\ (4)$$

Values of ΔG* in different temperature, for Ti coated with polymeric film increased from (70.876 kJ.mol^{-1}) to (84.925 kJ.mol^{-1}) at 293K, the rising in free energy of activation after coated by P.E estimated by (14 kJ.mol^{-1}) for all temperatures.

The coated Ti by P.E gave the high change in enthalpy, this means that this case need more energy to corrosion occur and these results show good agreement with the result of protection efficiency.

FTIR

To get more information about the structure of the PE formed on titanium plate and to identify functional groups present in it, reflectance FT-IR spectra were recorded for the monomer and polymer formed on a titanium plate by electrochemical polymerization, which is shown on Fig. 4.

Bands at 3465 and 3436 cm^{-1}, respectively, are assigned to the hydroxyl stretch groups in phenol, and the band at 1539 cm^{-1} possibly indicate for C=O stretch of carboxylic acid sodium salts of the electro-polymerization in alkaline solution. The band at 1639 cm^{-1} may be assigned to the C=O stretch of carbonate groups included in the polymeric film on titanium plate, and tasks of prevalent bands are summarized in Table 4.

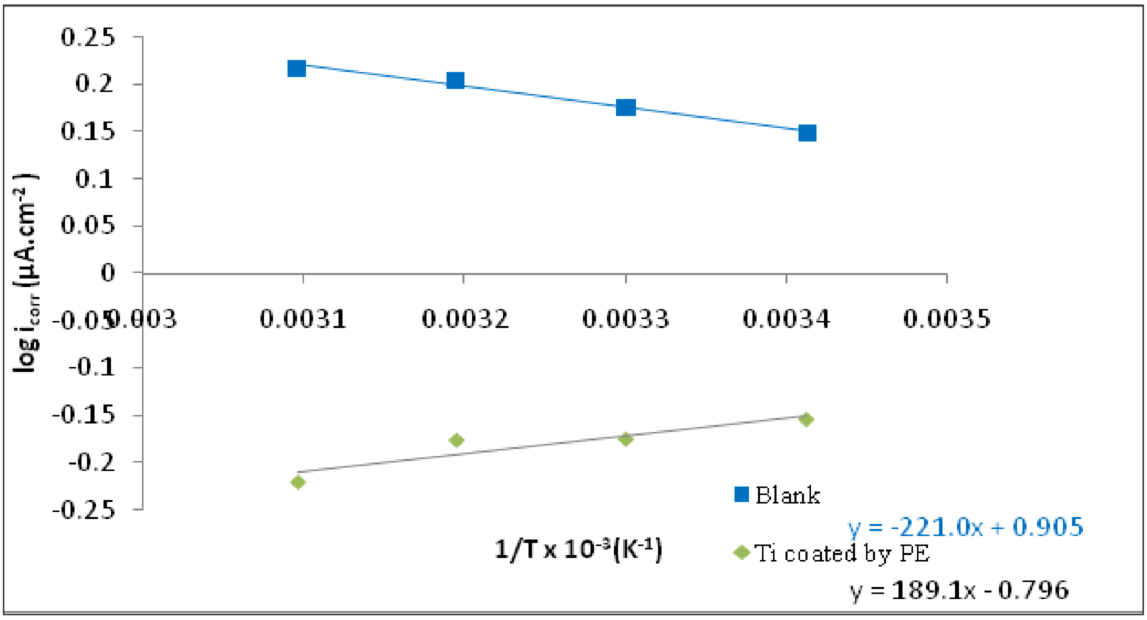


Fig..2. Arrhenius Plot of logi$_{corr}$ Versus 1/T for the corrosion of titanium in artificial saliva solution.

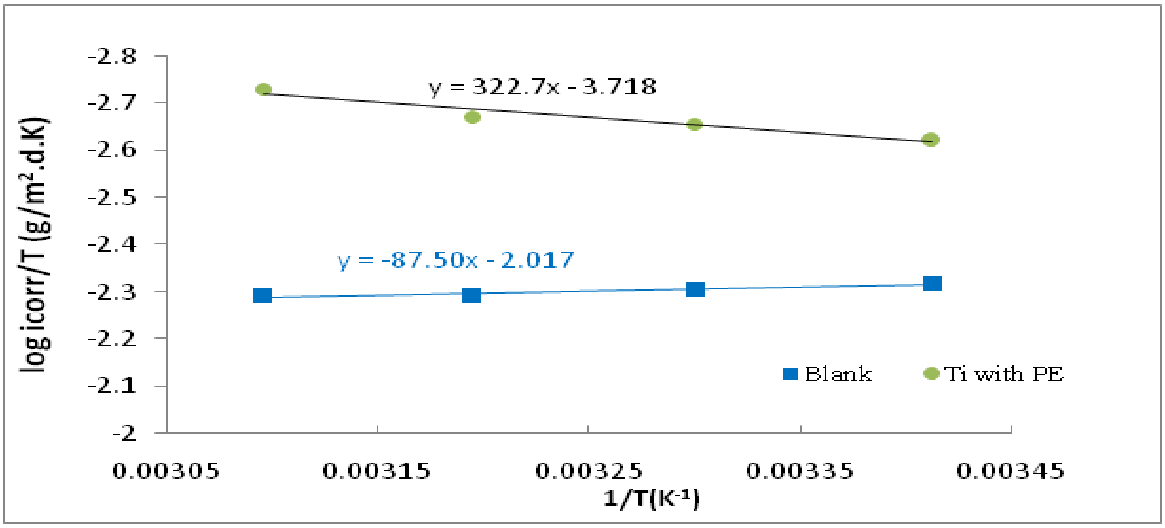


Fig..3. Plot of logi$_{corr}$/T Vs 1/T for titanium in artificial saliva.

TABLE 3. Kinetic and thermodynamic parameters for pure titanium in artificial saliva at different temperature in the range (293-323)K.

	ΔG^* /kJ.mol^{-1}				ΔH^*/ kJ.mol^{-1}	ΔS^*/ kJ.mol^{-1} .K^{-1}	Ea/kJ.mol^{-1}	A x10^{24} Molecules.cm^{-2} .S^{-1}
	293	303	313	323				
Blank	70.876	73.238	75.599	77.962	1.676	-0.23618	4.232	4.84
Ti coated by PE	84.925	87.613	90.300	92.988	6.179	-0.26876	3.622	0.096

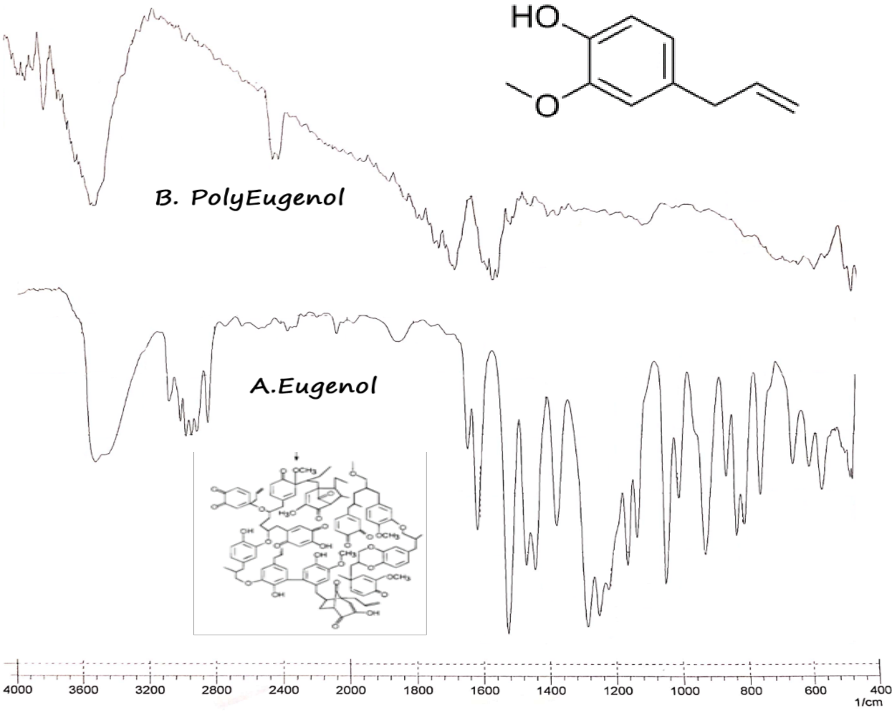


Fig..4. FTIR spectra of a) Eugenol, b) Hypothesized PolyEugenol.

TABLE 4. Assignments of prevalent bands shown in Fig. 4.

Monomer Eugenol		**Poly Eugenol**	
Frequency (cm^{-1})	**Interpretation**	**Frequency (cm^{-1})**	**Interpretation**
3515, 3446	O-H stretch for phenol	3465 , 3436	O-H stretch of carboxylic acid and phenols possibly also of water included in the polymer
3076	Asymmetric =CH_2	2941, 2889	characteristic of sp^3 C-H stretching modes.
2938	Symmetric CH_3	2360, 2325	Asymmetric stretch of CO_2 included in the film
1637	C=C stretching of the aromatic moiety.	1639	assigned to the C=O stretch of carbonate groups in the polymeric film on titanium plate
		1539	possibly indicate for C=O stretch of carboxylic acid sodium salts of the electro-polymerization in alkaline solution
		1170 , 1122, 1060	C-O stretch of dialkyl, diaryl and alkyl-aryl ethers and=or carboxylic acid and phenols

TG/DSC analysis

TG /DSC curves for P.E thin film formed on titanium show weight loss at four regions and as shown in Figure 5. The first one occurs in the region between 20 and 75 °C which is assigned to the loss of weight of about 5% due to absorbed water. The second stage recorded a mass change of 10% at 186 °C, and is the loss of water of lattice accompanied by a small endothermic at peak 299 °C. The gradually loss of mass from 300 to 600 °C is due to the liberation of nitrates and carbonates from precursors. The total mass loss is approximately 42%.

Morphology

Scanning Electron Microscopy (SEM)

Examination of the electro-polymerized PE films deposited on pure Ti by Scanning Electron Microscopy (SEM) is shown in Fig.6. As seen in the photograph the PE thin film was accumulation on titanium surface. After magnification from 2000X to 10000X shaped structure of PE is evenly distributed hexagonal Nano-structures that tend to aggregate in characteristic cluster forms with intervening porosity. The average partials size of PE deposited on pure Ti about (32 nm). Fig.6d show the cross-section SEM for the thin film of PE and enable measurements of thickness of poly thin film reach to (445 nm).

X-Ray Diffraction

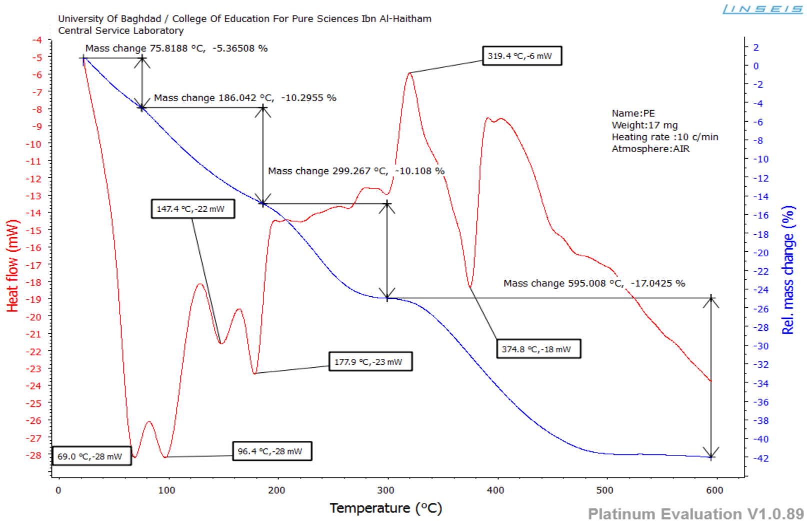
The X-ray diffraction features of the blank Ti and PE formed on titanium plate by electro-polymerization method are displayed in Fig. 7, The XRD pattern for the Ti Coated by PE is shown in Fig. 7(b), and the peak positions are slightly shifted to lower 2-theta (2θ) values compared to that uncoated Ti and The two high-intensity peaks in fig.7b located at 2θ are (25.1° and 25.3°) of polymeric film of eugenol on titanium plate.

The crystallite size of the sample was calculated from full width at half maximum (FWHM) of the peaks using Debye–Scherrer's approximation (Eq. 1)

$$d= k\lambda/\beta\cos\theta\ldots\ldots$$

Where d is the crystallite size, k is the wavelength of CuKa radiation (k = 1.542A°), β is FWHM for the diffraction peak under consideration (in radians), θ is the diffraction angle, and k is the broadening constant (k=0.9).

The crystallite size has been detected for pure titanium and was the average size equal to (227.5 nm), where the crystalline size for PE peak ((25.1° and 25.3°) was equal to (18.99 nm) while the average partials size of PE deposited on pure Ti in SEM was about (32 nm).



Fig,.5. TG/DSC curves for poly eugenol coated on Ti.

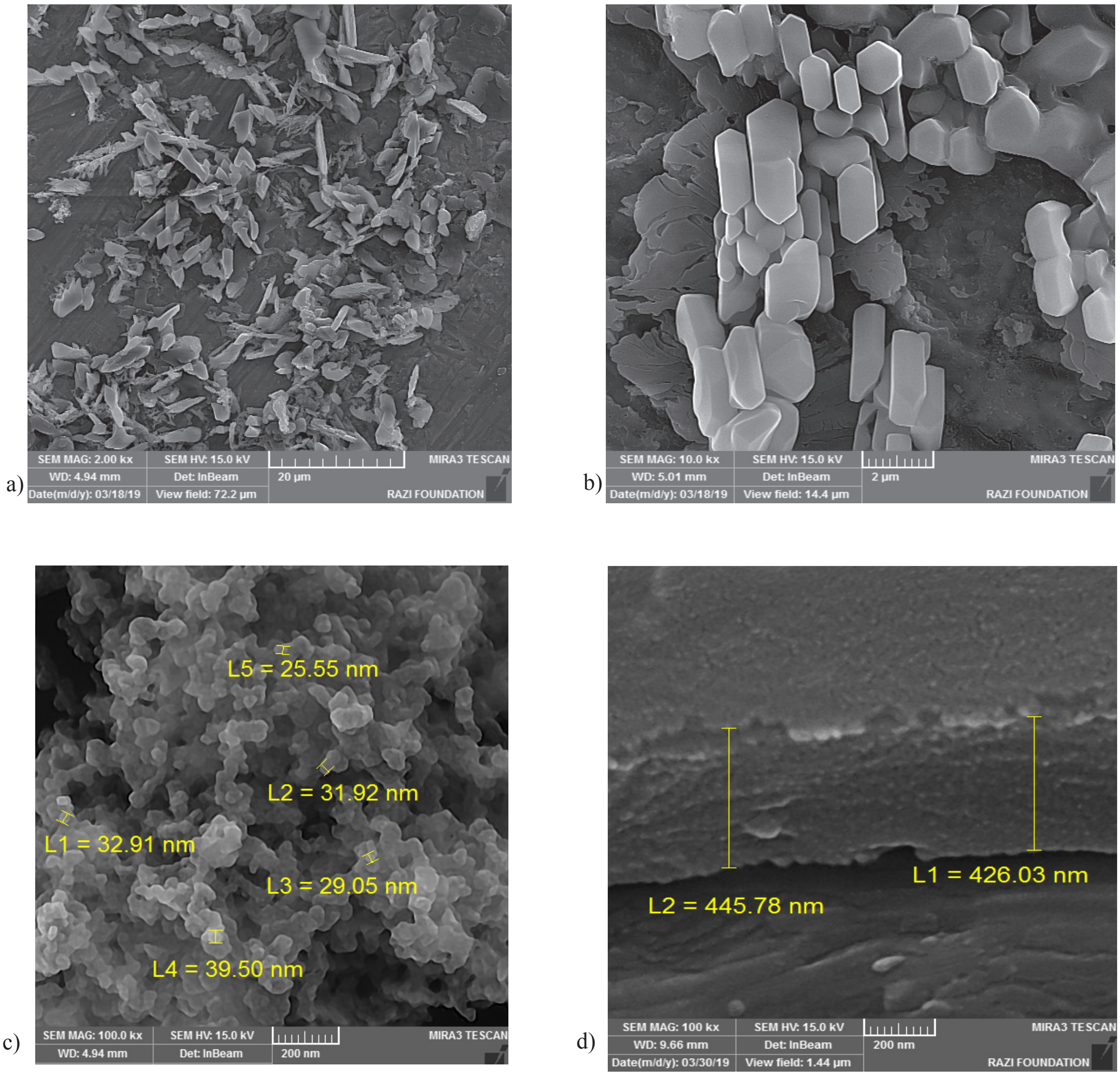


Fig. 6. Scanning electron micrographs of PE films deposited on Ti.

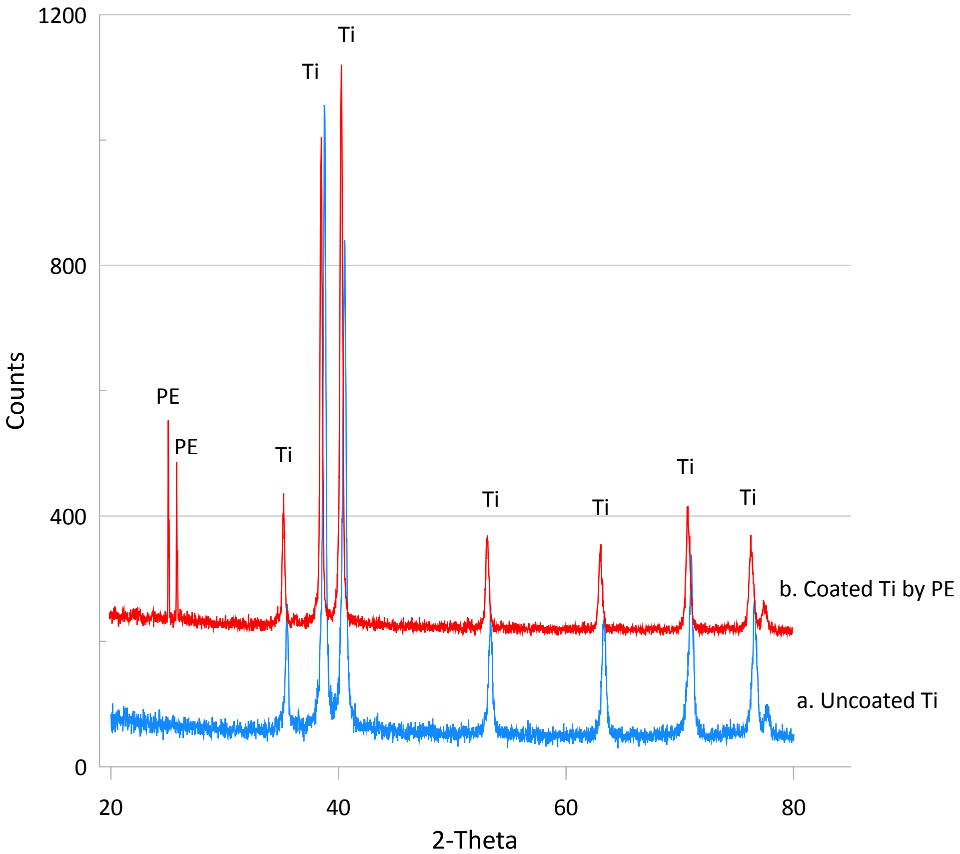


Fig..7. XRD patterns for (a) Uncoated Ti, (b) Coated Ti by PE.

Conclusion

In conclusion, the electro-synthesized P.E coating, provided a better barrier film on Titanium dental implant. Coated pure Ti by P.E due to shifted the corrosion potential to more active potential, and reduce the current density to 50% at 293K, and it's have not any effect with increasing temperature. The protection efficiency of P.E against corrosion reach to 63% at 323K.

The apparent activation energy of pure Ti coated by P.E is 3.622 kJ/mol while these decrease in activation energy result decrease in the activation sites and indicated by Arrhenius factor and this decrease in Arrhenius factor due to decrease in corrosion rate . The free energy change of electrochemical corrosion reaction transition state increased after protection by P.E film.

The average partials size of PE deposited on pure Ti in SEM was about (32 nm), while from XRD data was (18 nm). These results qualify our work to be applied in the field of dental applications.

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