

# Corrosion Performance of Rosemary-Extract-Doped TEOS:TMSM Sol-Gel Coatings on 304L Stainless Steel

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Pure and rosemary-extract-doped hybrid nanostructure coatings have been generated using sols synthesized via acid catalyzed hydrolysis and condensation of methacryloxypropyltrimethoxysilane (TMSM) and tetraethoxysilane (TEOS) at the molar ratio of 1:1, in combination with rosemary extract. Coatings have been deposited on stainless steel (SS) 304L substrates by spin coating followed by curing at room temperature for 24 h in air and characterized. The morphology, composition and adhesion of hybrid sol-gel coatings have been examined by SEM, EDX and pull-off test, respectively. Addition of high additive concentrations (0.1%) did not disorganize the sol-gel network. Direct pull-off test recorded a mean coating-substrate bonding strength larger than 23.21 MPa for the hybrid sol-gel coating. Corrosion testing of coatings on SS 304L was studied by potentiodynamic polarization measurements and electrochemical impedance spectroscopy after 1 h and 21 days exposure to the physiological saline solution. The corrosion resistances of hybrid rosemary-extract-doped coatings after 1 h and 21 days exposure to the physiological saline solution were higher than that of pure hybrid silica coatings, both of which had thicknesses ranging lower than 100 nm. Also the electrochemical behaviors of doped coating were studied by potentiodynamic polarizations tests in 3.5% NaCl media and the results were shown that this system is applicable in industry.

*Keywords:* corrosion, stainless steel 304L, green inhibitor, rosemary extract, sol-gel coating.

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## INTRODUCTION

The sol-gel process has excellent potential for generating pure inorganic or hybrid organic-inorganic coatings. In case of the latter, where one can incorporate an organic component into an inorganic network, the process opens up a wide range of opportunities for multi-functionalizing and tailoring of a coating. Through modification of the chemical composition of starting materials, the introduction of multi-functionalities such as anti-corrosive and anti-bacterial properties, improved mechanical strength, etc. can be realized in a single layered coating. Usually, sol-gel derived coatings possessing multi-functionalities like anti-corrosion and anti-bacterial properties, when intended for applications on surgical equipment, make use of corrosion inhibitor and anti-bacterial substances dispersed in sols that yield better corrosion resistance and hydrophobic or low surface-free-energy coatings [1–5]. Due to the increasing concerns on the toxicity of some corrosion inhibitors and anti-bacterial substances when used for corrosion resistance and anti-bacterial applications [6, 7], it becomes highly relevant to look for alternate materials that can be dispersed in hybrid sols to generate anticorrosion and antibacterial coatings.

Plant extracts have become important as an environmentally acceptable, readily available and renewable source for a wide range of inhibitors. In general, plant extracts are highly efficient inhibitors

and non-toxicants [8, 9]. Natural organic compounds, rosemary extract is one of them, are biodegradable and do not contain heavy metals or other toxic compounds, besides they are abundant in nature. Rosemary (*Rosmarinus officinalis L.*) is a very important medicinal and aromatic plant belonging to the Lamiaceae family and has been cultivated for a long time. Kliškić [10] determined the corrosion inhibitive extract of rosemary extract on Al-Mg alloy in chloride solution. Ouariachi et al. [11] also reported the inhibitory action of rosemary extract as green corrosion inhibitors on C38 steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Thus rosemary extract is a potential candidate to be used as an inhibitor dopant in the hybrid sol-gel film. Rosemary also has a long list of claims pertaining to its medicinal uses, including antibacterial and antioxidant properties [12, 13]. Luqman et al. [14] have tested anti-bacterial activities of rosemary extract using *Escherichia Coli* (Gram negative) and *E. faecalis* (Gram positive) and found a considerable amount of antibacterial activity by using a low concentration of rosemary extract. Recently, Tovar et al [15] have reported on their investigation of rosemary extract immobilized by polypropylene films for antibacterial applications.

Therefore, in order to generate an eco-friendly, anti-corrosive and anti-bacterial surface that contains a toxic corrosion inhibitor and non-silver antibacterial agent, rosemary extract could be dispersed in a hydrophobic sol-gel matrix derived from hydrolysis and condensation of an alkyl modified

alkoxysilane. Keeping in mind a potential application of such nanostructure coatings for surgical equipment made of stainless steel (such as SS 304 or 316), corrosion resistance of the coating would also be of great concern.

Hence, the objective of the present investigation was to synthesize and characterize rosemary-extract-doped organic-inorganic sol-gel coatings with a deep focus on their corrosion resistance properties as a preliminary investigation prior to their potential use as multifunctional (i.e., anti-bacterial and corrosion resistant) coatings for surgical equipment. Pure and rosemary-extract-doped organic-inorganic hybrid silica coatings on stainless steel (SS) 304L substrates were derived from methacryloxy propyl trimethoxysilane (TMSM) and tetraethoxysilane (TEOS) in combination with rosemary extract and were investigated for their adhesion, thickness, and corrosion resistance in the physiological saline and 3.5% NaCl solutions.

## EXPERIMENTAL

### *Materials*

Tetraethoxysilane (TEOS, Merck, Germany), 3-methacryloxypropyltrimethoxysilane (TMSM, Merck, Germany), Benzoyl peroxide (BPO, Merck, Germany), rosemary extract (Gol Darou, Iran), hydrochloric acid (AR grade) and ethanol were used as starting materials. Coatings were generated on SS 304L substrates of dimensions 12 mm in diameter and 4 mm in thickness with a matt finish surface. The substrates exposed area was mechanically abraded with 220, 400, 800, 1000, 1200, 1500 grades of emery paper and polished by 0.3 micron alumina powder to approach a mirror surface, then degreased, hand washed with distilled water, and rinsed in ethanol.

### *Sol preparation and film deposition*

Hybrid organic-inorganic silica sols were synthesized at room temperature by hydrolysis and polycondensation of ethanol-diluted TEOS in the presence of HCl as a catalyst and TMSM as a co-precursor. First, TMSM (Fluka) was mixed with 2 wt% of BPO. The hybrid sol was prepared by admixing silica precursors. TMSM and TEOS were mixed in the molar ratio of 1:1 in a beaker with 0.01M HCl and methanol (H<sub>2</sub>O/methanol volume ratio was 1:1) at ambient temperature. The resultant solution was stirred at a rate of 240 rpm for 1 h. Hydrolysis and condensation of TMSM and TEOS took place by adding stoichiometric amounts of water to the solution during stirring. Subsequently, the transparent sol solution was completely formed without any phase separation. The hybrid rosemary-extract-doped silica sol was then prepared by addition of

0.012 to 0.05 weight % of rosemary extract to the prepared hybrid SiO<sub>2</sub> sol. Both plain and hybrid rosemary-extract-doped SiO<sub>2</sub> sols were filtered with a 0.4 mm pore size membrane filter and used for coating.

Coatings were generated by the spin coating technique on SS 304L substrates of the doped and undoped hybrid sols. The coatings were air-dried onto the substrates and placed in a furnace to cure at 37°C for 24 h.

### *Characterization*

The coated SS substrates were inspected by both optical and scanning electron microscopes (SEM, VEGA//TESCAN equipped with a field emission gun) for microstructure and presence of defects, if any. Elemental chemical analysis of the coatings was performed by the Energy Dispersive X-ray Spectroscopy (EDX) connected to the SEM. UV-vis reflection spectra were measured using a JASCO, V-570, Rev. 1.00, spectrometer. The effect of the green inhibitor on the adhesion of the coating to the substrate was determined by pull-off tests performed under dry conditions. Samples in dry conditions were sandwiched in an alignment jig between aluminum cylinders with the diameter of 25 mm utilizing an epoxy adhesive (UHU Epoxy Adhesive, Germany). A two-hour curing at 100°C was allowed in the pressure of 30 kPa; the resulting specimens were then subjected to tensile testing in a tensile machine (Model H25KS, Hounsfield, UK) at a cross-head speed of 1 mm·min<sup>-1</sup>. The reported adhesion strength values were averaged over five measurements.

### *Corrosion testing*

Electrochemical measurements were conducted at room temperature in a physiological normal saline solution (0.9 wt% NaCl) using an electrochemical unit (model PARstat 2273). Bare AISI 304L was used as a blank sample. A three-electrode cell was employed using graphite of a convenient area as a counter electrode and a saturated calomel electrode (SCE, Radiometer Copenhagen) as the reference electrode. Potentiodynamic measurements were conducted from the -0.25–0.7 V vs OCP, with a scan rate of 0.001 V·s<sup>-1</sup>. Electrochemical Impedance Spectroscopy analysis (EIS) was performed in a frequency range of 100 kHz to 10 mHz and peak-to-peak a.c. amplitude of 10 mV. This test was performed after 1 h and 21 days of immersion in the electrolyte. Impedance fitting data were analyzed using Zview software. In order to evaluate and compare the corrosion behavior of specimens with and without the inhibitor in industrial applications, they were dynamically polarized in a saline solution containing chloride ions invasive (3.5 wt.% NaCl).

## RESULTS AND DISCUSSION

### *Microstructures of hybrid coatings*

Sols were transparent and colorless before addition of rosemary extract but after the thermal treatment they became slightly transparent, yellow, homogeneous and defect-free. The SEM technique was used in order to examine the structure of the hybrid coatings with various content of rosemary extract. Figure 1 shows SEM micrographs of both doped and undoped hybrid coatings on the SS substrates. The coatings look homogeneous and crack-free, although a secondary phase, as a spots aggregate (smaller than 500nm in diameter), can be observed in the doped thin film. Elemental chemical analysis by EDS was performed on both coatings, showing a different distribution of elements. The EDS analysis displayed in Fig. 1 confirms the presence of carbon in the agglomerates and the incorporation of an inhibitor into the coating.

SEM micrographs of cross-section and plane view of the coated sample are shown in Fig. 2. SEM observations reveal the formation of a defect-free and highly adherent film on the SS substrate, which leads to the improvement of the corrosion resistance of SS 304L. The thickness of the coating is around 83 nm. Figure 2b shows the nanostructure of the coatings, with particles of 23–55 nm.

UV–visible reflectance spectra of doped and undoped hybrid coatings are presented in Fig. 3. The absorbance of the coatings increased with incorporation of rosemary extract in all UV-visible, which is an evidence of the presence of an inhibitor in the coating.

The data reported in Table 1 indicate that the green inhibitor provided an important increase of the coating–substrate bond strength of plain coatings in comparison to that of the undoped hybrid coatings. Thus the green inhibitor conferred to the coating an adhesive strength exceeding its cohesive strength. The marked increase of the coating adhesion caused by the presence of rosemary extract has not been investigated in detail so far and further studies are needed to elucidate the interfacial reactions involved. To sum up, this can be attributed to a chemical reaction between (+)-catechin, a component of rosemary extract, and iron on the SS surface.

### *Electrochemical results*

#### *Potentiodynamic polarization*

Potentiodynamic polarization measurements carried out on doped/undoped hybrid coatings and their comparison with the bare metal are presented in Fig. 4. The inhibition efficiency ( $IE\%$ ) was calculated using the following equation:  $IE\% = [(I_0 - I)/I_0] \times 100$ , where  $I_0$  and  $I$  are the corrosion

current densities of hybrid coatings without and with different concentrations of the inhibitor, respectively. The electrochemical parameters obtained from polarization measurements such as corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), cathodic Tafel slope ( $\beta_c$ ) and inhibition efficiency ( $IE\%$ ) are given in Table 2. Also the porosity of the coating was calculated using the following equation:

$$F = (R_{p,m}/R_p)10^{-|\Delta E_{corr}|/\beta_a}$$

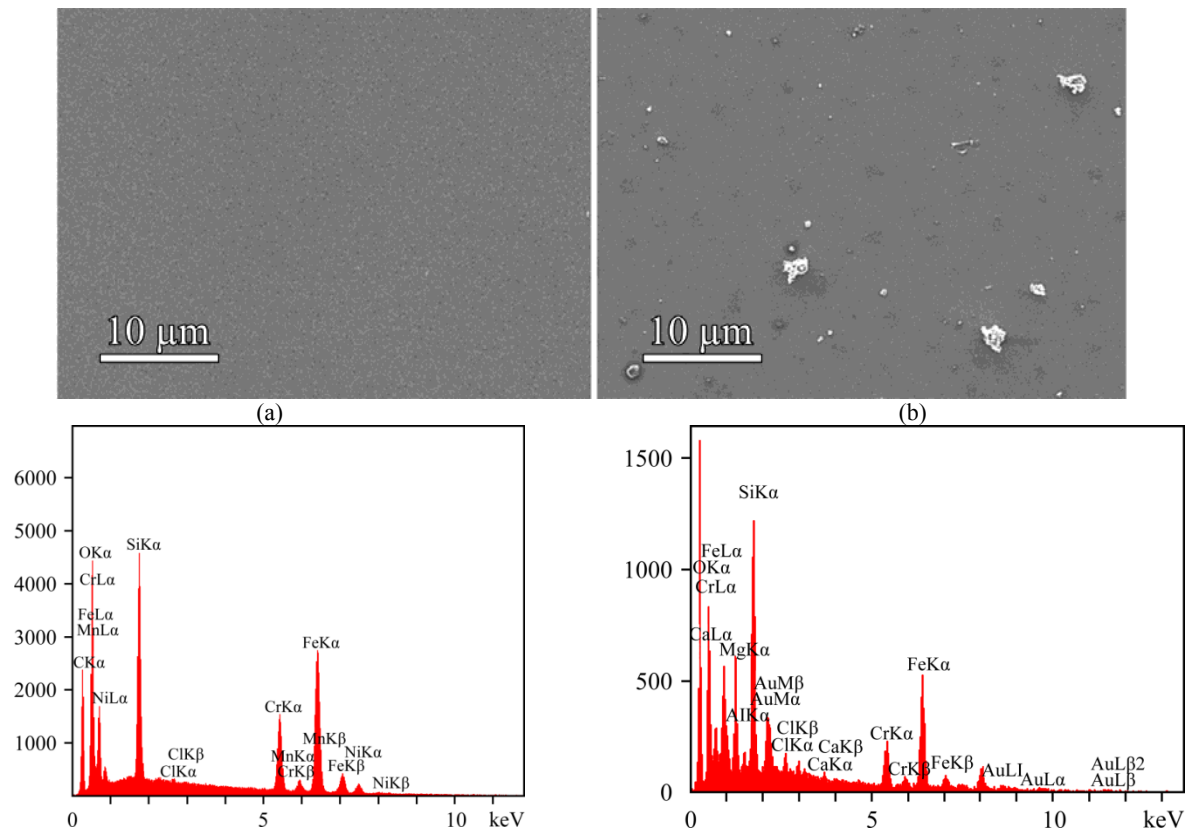
where  $F$  is the total coating porosity,  $R_{p,m}$  the polarization resistance of the bare metal,  $R_p$  the measured polarization resistance,  $\Delta E_{corr}$  the difference between the corrosion potential and  $\beta_a$  the anodic Tafel slope of the bare metal [16].

The data in Table 2 show that the porosity percentage of the coating decreases when increasing the inhibitor concentration.

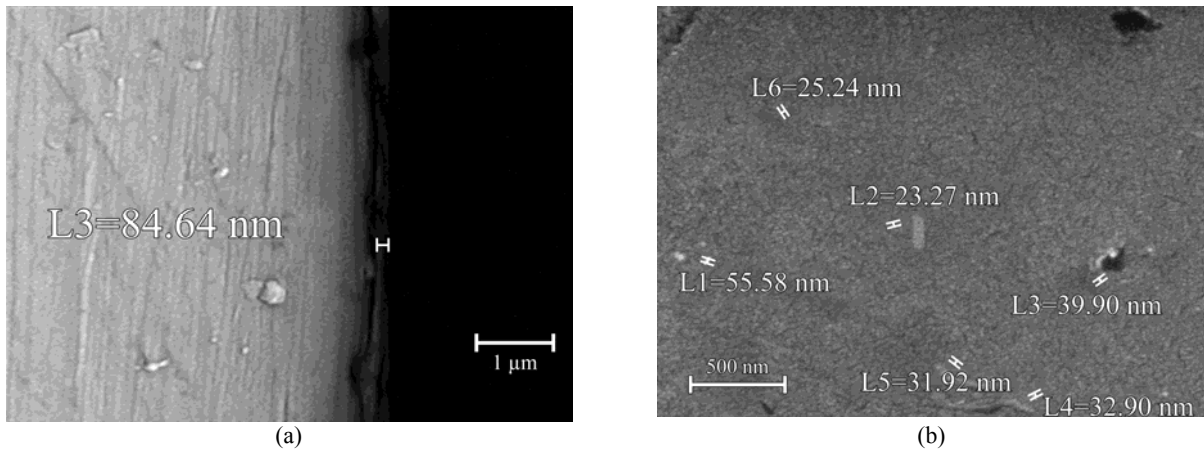
Clearly, in comparison with the corrosion potential ( $E_{corr}$ ) of the bare steel substrate (-279 mV),  $E_{corr}$  of the coated steel increased when used with hybrid coatings. Additionally,  $E_{corr}$  was further enhanced by adding an inhibitor (Rosemary extract) to the hybrid coating, reaching (-2 mV) for the coating containing 0.05% inhibitor. This increase represents a nobler electrode potential being achieved by applying the hybrid rosemary-doped coatings.

Corrosion current density is commonly utilized as an important parameter to evaluate the kinetics of corrosion reactions. The corrosion rate is normally proportional to the corrosion current density measured through polarization. In the given study it was found out that the bare steel substrate dissolved far more quickly than any coated system. By examining the current density at the same polarized potentials, a significant reduction of the dissolution current due to applying a hybrid coating can be observed. Moreover, the reduction in corrosion current densities became more significant when doping hybrid coatings with rosemary extract and it was proportional to the inhibitor concentration in the applied coatings. In addition, the coating with 0.05% inhibitor demonstrated a pseudo-passive behavior with the lowest corrosion current density. This is the lowest corrosion rate of the coated systems, and is interpreted as shielding protection of a substrate by a barrier coating. It was also noticed that the inhibition efficiency increases with increasing the concentration of the inhibitor content in the coating. The highest inhibition efficiency was obtained for a coating with 0.05% rosemary extract. It has to be mentioned that the difference in the inhibition efficiency obtained by adding 0.05% and 0.1% of rosemary extract was not large, which can be set as a threshold amount for the added inhibitor.

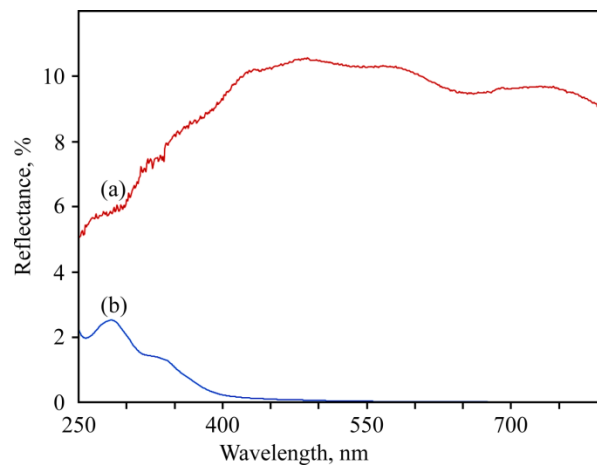
Figure 5 shows SEM micrographs for the bare metal, hybrid coatings undoped and doped with



**Fig. 1.** SEM images of: (a) undoped hybrid thin film, and (b) hybrid thin film doped with 0.05% rosemary extract. EDX patterns shown as SEM images below.



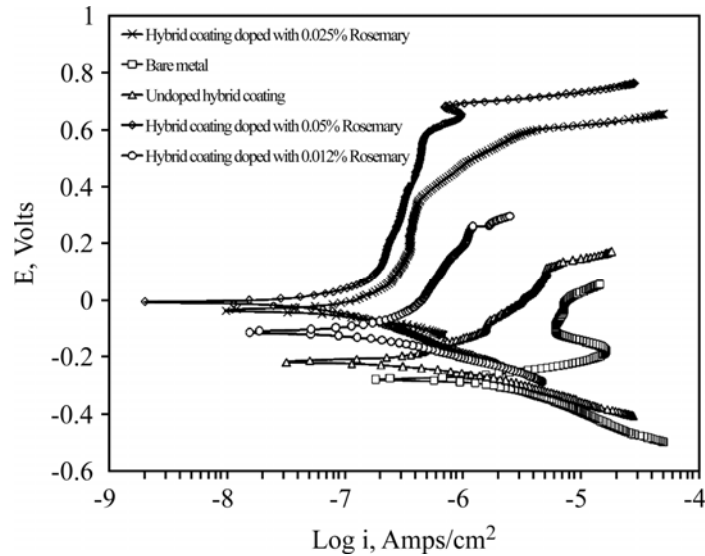
**Fig. 2.** SEM micrographs for stainless steel 304L coated with hybrid thin film: (a) cross-sectional view, (b) plane view.



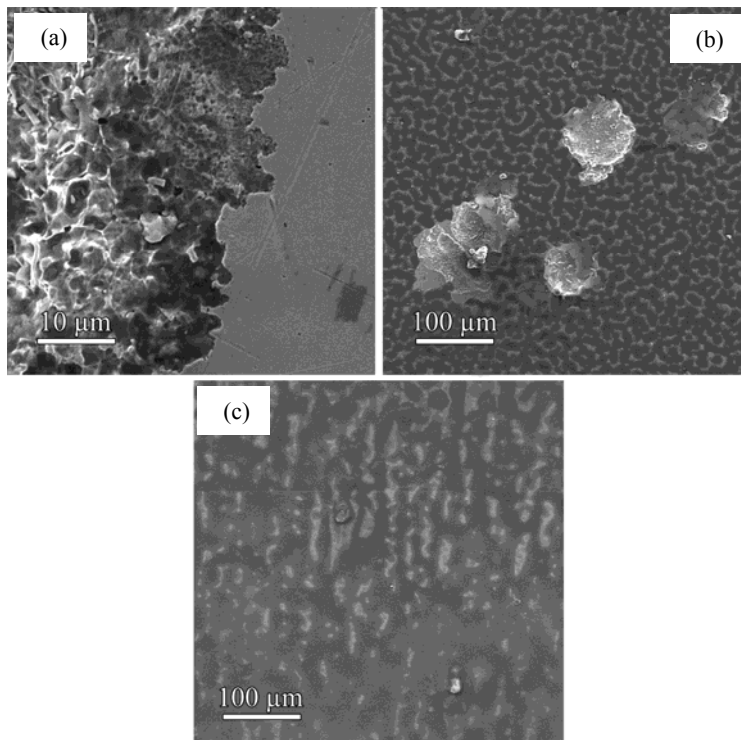
**Fig. 3.** UV-vis reflectance spectra of: (a) undoped hybrid thin film, and (b) hybrid thin film doped with 0.05% rosemary extract.

**Table 1.** Pull-off adhesion test under dry conditions

Sample	Bond Strength (MPa)	Detached area
No inhibitor	22.44 ± 1.1	0
0.05% Rosemary extract	24.03 ± 1.1	0

**Fig. 4.** Potentiodynamic polarization curves for hybrid thin films in physiological normal saline solution with various rosemary extract content and their comparison with those of bare metal.**Table 2.** Kinetic parameters and calculated porosity of undoped and doped hybrid sol-gel thin films and their comparison with bare metal in physiological normal saline solution

Sample	$\beta_a$ (mV/dec)	$E_{corr}$ (mV/SCE)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$IE$ (%)	Porosity (%)
Bare Metal	148	-279.3	2.74	—	—
No inhibitor	138	-216.9	0.33	88.1%	1.19
0.012% Rosemary extract	125	-113.2	0.26	90.7%	0.93
0.025% Rosemary extract	113	-37.8	0.12	95.5 %	0.45
0.05% Rosemary extract	97	-2.0	0.05	98.2%	0.18

**Fig. 5.** SEM images of: (a) the bare metal, (b) undoped hybrid thin film and (c) hybrid thin film doped with 0.05% rosemary extract after potentiodynamic tests in physiological normal saline solution.



0.05% rosemary extract after potentiodynamic polarization in the physiological saline solution. If compared, SEM micrographs of doped and undoped hybrid coatings at the same magnification reveal the following: doped films have a smooth surface and no cracks.

After electrochemical tests on a doped hybrid coating, no localized corrosion was detected, but on both bare metal and undoped hybrid coatings a localized corrosion was observed in forms of small cracks and pits of different sizes. According to Figs. 5a and 5b, the regions surrounding some of the localized corrosion were damaged: this may indicate a preferential localized attack. This localized attack can lead to delamination and lifting of the coating from the metal surface. Moreover, localized corrosion is known as the most dangerous type of corrosion for metallic orthopedic implants, since it is eventuated to permeate noxious component from metal structure to body environment that occasionally lead to death. Therefore an inhibitor utilized in the micro-structure of the coatings can increase the corrosion resistance to this form of corrosion.

#### *Electrochemical impedance spectroscopy (EIS)*

EIS measurements are particularly useful in long time tests because they do not perturb the system dramatically, and it is possible to monitor a gradual change of the coating-metal system over time.

The typical Nyquist, Bode and Phase angle plots of hybrid coatings both undoped and doped with 0.05% rosemary extract and their comparison with the bare metal after immersion of 1 h and 21 days are shown in Figs. 6a,b and c, respectively.

The Nyquist plots of uncoated steel at the immersion time of 1 h and 21 days are shown as a depressed semicircle, while the plot of the steel coated in the presence of the inhibitor at the same soaking time of 1 h and 21 days is pictured as a depressed semicircle but with a long tail in the low frequency region. The tail is inclined at the angle of  $45^\circ$  to the real axes, at a very low frequency. This behavior indicates that the diffusion process of ions takes place on the coated specimen after the addition of rosemary-extract inhibitor. The Bode plots for the hybrid coated steel (both doped and undoped) show a higher charge transfer resistance than the plain steel in the test solution. Nevertheless, these values tend to decrease after 21 days of immersion indicating the decrease in the charge transfer resistant of both coated systems with and without inhibitor. This behavior is due to the solution diffusivity to the coating and its water uptake. However, phase angle plots of uninhibited or inhibited hybrid coated steel were different after 21 days, thus indicating a different corrosion behavior of both systems; more precise information on the behavior of the studied system

can be obtained from phase angle diagrams. The hybrid coated steel shows the formation of a new phase angle at low frequencies after 21 days of immersion, which tells about coating delamination taking place at the coating/steel interface due to the water uptake. This was not observed on the doped sample, where a shift towards a lower frequency was noticed, indicating that the major protection effect is due to the inhibitor added to the coating. The presence of an inhibitor increases the impedance and changes other aspects of the behavior. These results support the data of polarization measurements that an inhibitor improves the protection behavior of the coating.

For the interpretation of the electrochemical behavior of a system from EIS spectra, an appropriate physical model of the electrochemical reactions occurring on the electrodes is necessary. The electrochemical response to impedance tests for the coated materials under consideration was best simulated with the equivalent circuit depicted in Fig. 7. This widely accepted scheme has been deduced to represent the electrochemical behavior of a metal covered with an unsealed porous film [17, 18]. The equivalent circuit consists of the following: a solution resistance  $R_s$  of the test electrolyte, a capacitance  $C_{dl}$  and polarization resistance  $R_p$  of the coatings, and a capacitance  $C_{coat}$  and  $R_{coat}$  for the remainder of the coating layer regarded as intact (non-defective).

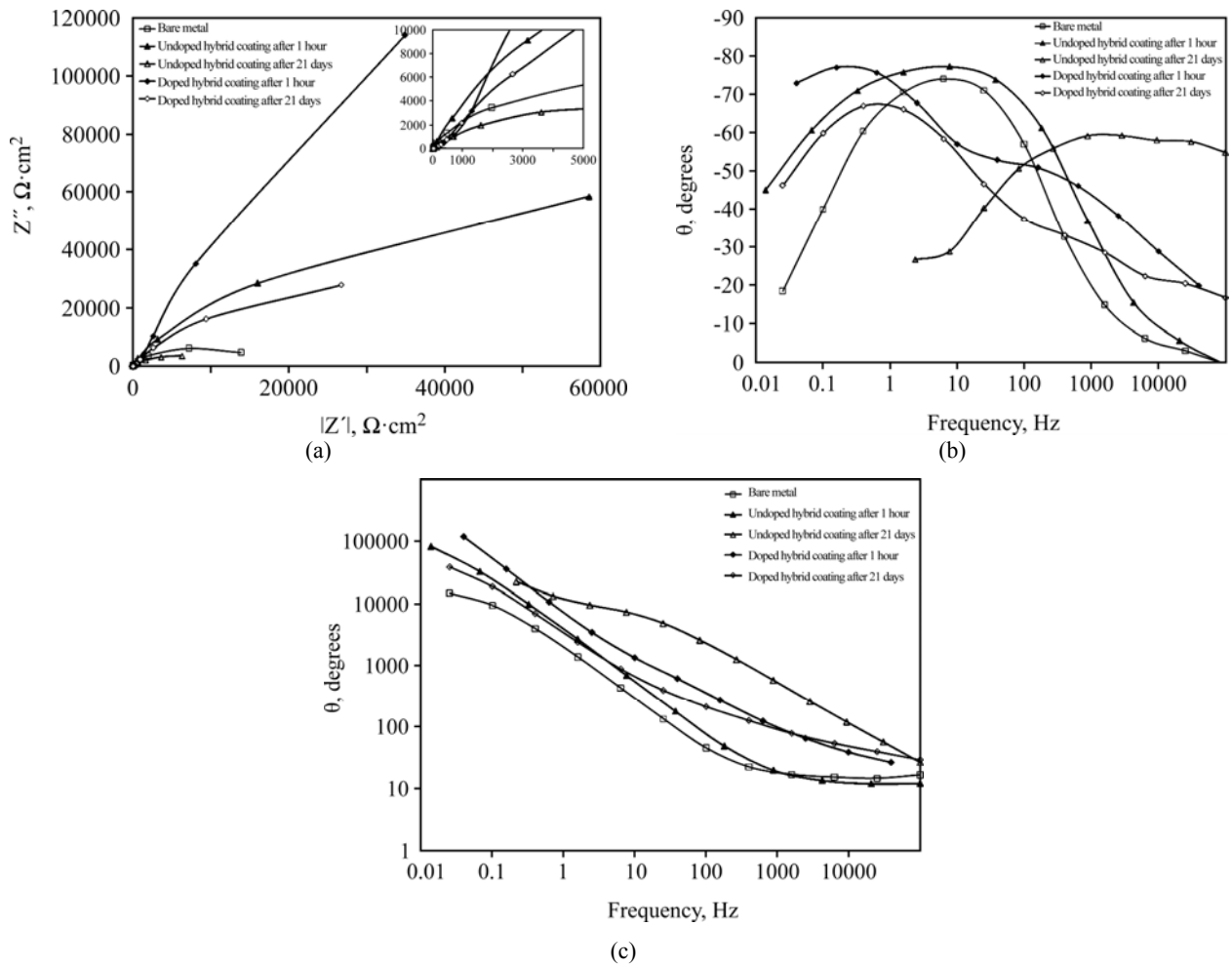
The inhibition efficiency of hybrid coatings both undoped and doped with the optimum rosemary extract content and of the bare metal after 1h and 21 days of immersion in the physiological saline solution, respectively, was evaluated by  $R_p$  and  $C_{dl}$  values of the impedance. Values are given in Tables 3 and 4, respectively.

$$C_{dl} = 1/(R_p 2\pi F_{max})$$

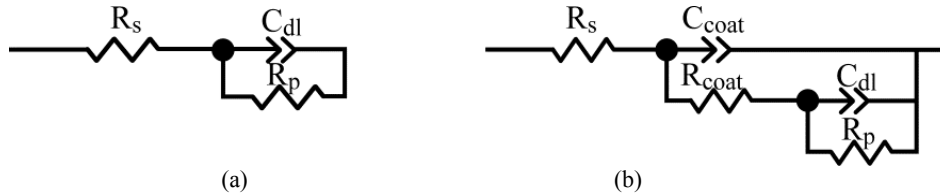
where  $C_{dl}$  and  $R_p$  and  $F_{max}$  are double layer capacity, polarization resistance and frequency maximum, respectively.

$$\%IE = (R_2 - R_1)/R_2 \times 100.$$

Data presented in Tables 3 and 4 showed that the values of  $R_p$  increase when an inhibitor is added to the coating, while those of  $C_{dl}$  tend to decrease. A large  $R_p$  is associated with a slower corroding system [19]. Furthermore, a better protection provided by an inhibitor is associated with a decrease in  $C_{dl}$  [19]. The decrease in  $C_{dl}$ , which results from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [20]. It follows from the data in Tables 3 and 4 that  $C_{dl}$  is decreased upon adding an inhibitor to the coating. These results suggest that rosemary extract enhances the corrosion protection of the applied coating on steel. Inhibition efficiencies obtained from the Tafel



**Fig. 6.** Nyquist, Bode and Phase angle plots of undoped and hybrid thin films doped with 0.05% rosemary extract after soaking in physiological normal saline solution for 1h and 21 days and their comparison with bare metal.



**Fig. 7.** Equivalent circuits for: (a) undoped hybrid and (b) hybrid thin film doped with 0.05% rosemary extract.

**Table 3.** Impedance parameter of undoped and hybrid sol-gel thin film doped with 0.05% rosemary extract and their comparison with bare metal in physiological normal saline solution after 1h soaking

Sample	$R_p$ ( $k\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )	% IE
Bare metal	11.35	118	—
No inhibitor	53.2	50.81	—
0.05% Rosemary extract	398	4.19	86.6%

**Table 4.** Impedance parameter of undoped and hybrid sol-gel thin film doped with 0.05% rosemary extract and their comparison with bare metal in physiological normal saline solution after 21 days soaking

Sample	$R_p$ ( $k\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )	% IE
Bare metal	11.35	118	—
No inhibitor	11	1.7	—
0.05% Rosemary extract	82.661	0.73	84%

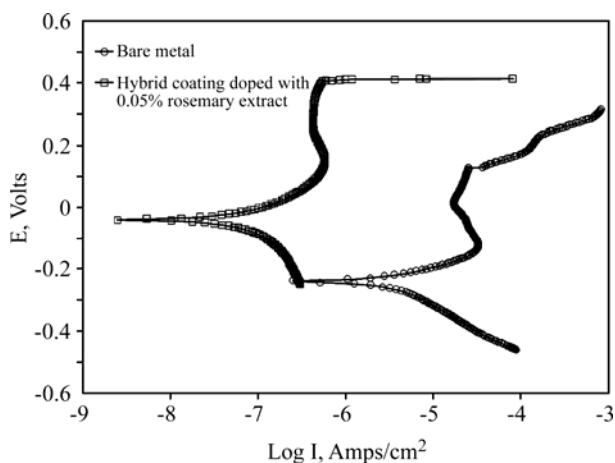
**Table 5.** Kinetic parameters of hybrid coating doped with 0.05% rosemary extract in 3.5 wt.%NaCl at  $37 \pm 1^\circ\text{C}$

Sample	$-E_{corr}$ (mV/SCE)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$-\beta_a$ (mV/dec)	$-\beta_c$ (mV/dec)	mpy	%IE
Bare metal	$0.243 \pm 0.016$	$4.38 \pm 0.73$	$136 \pm 5.3$	$198.2 \pm 4.9$	2.027	—
Doped coating	$0.041 \pm 0.001$	$0.096 \pm 0.008$	$101 \pm 4.7$	$159 \pm 3.7$	0.044	97.6

extrapolation and impedance methods are in good agreement.

#### Intensive test

Figure 8 shows the potentiodynamic polarization curves for the bare metal and coated samples in the presence of rosemary inhibitor in 3.5% NaCl solution. Electrochemical parameters of these curves are given in Table 5. According to the Table, coating systems containing inhibitors reduced the corrosion current density from  $4.38 \mu\text{A}/\text{cm}^2$  (corresponds to the bare metal) to  $0.096 \mu\text{A}/\text{cm}^2$  (for rosemary inhibitor). Also, by integrating a set of inhibitors and coatings, the corrosion potential transferred to more noble values, so the inhibitor can improved the corrosion resistance of a substrate in 3.5% NaCl solution. According to the intensity of this test, it can be concluded that rosemary inhibitor contributes to effective protection against corrosion, in saline solution containing chloride ions invasive, for 304L stainless steel.

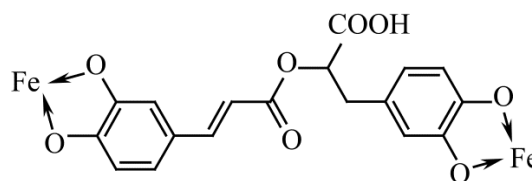


**Fig. 8.** Potentiodynamic polarization curves for: bare metal, and hybrid coating doped with 0.05% rosemary extract in 3.5 wt.% NaCl.

#### Inhibition mechanism

The rosemary contains some tannic acid and the main chemical composition of rosemary extract is rosmarinic acid – a phenolic compound [21], which contains polyphenolic compounds readily form the complex with di- and trivalent metal ions [22, 23]. The inhibitor action of this compound could be explained by the formation of complexes in the form of chelate with iron ions in the solution. The  $\text{Fe}^{3+}$  ion is coordinated with the phenolic groups in the terminal side in each molecule taking phase as shown Fig. 9. The adsorbed layer acts as a barrier between the metal surface and aggressive solution leading to a decrease in the corrosion rate.

The presence of more than one active centre in the chemical composition of rosmarinic acid forces rosemary extract to be horizontally oriented at the metal surface, which increases the surface coverage and consequently raises the inhibition efficiency.



**Fig. 9.** Chemical structure of the complex formed.

As confirmed by electrochemical results, this component, interfering in anodic reactions, helps to decrease the reaction rate, thus decreasing  $\beta_a$  in polarization curves and increasing corrosion resistance. The sol-gel thin film resistance of inhibitor-doped hybrid coatings is by more than one order of magnitude higher than the pore resistance of undoped hybrid coatings at the beginning of immersion in physiological saline solution. During corrosion tests new defects appeared in all of the coatings leading to the formation of conductive pathways and decreasing pore resistance of coatings. However, even after a long immersion, the pore resistance of an inhibitor-containing film is sufficiently high confirming superior stability and barrier properties.

A higher corrosion protection in the case of inhibitor-doped coatings is most probably related to blocking of pores and defects by insoluble complex of rosmarinic acid with iron.

#### CONCLUSIONS

In order to improve corrosion protection for a long term, a green corrosion inhibitor (rosemary extract) has been incorporated into a sol-gel matrix. SEM and EDX analyses have been used to investigate the morphology and composition of the doped sol-gel coatings. EIS measurements have been carried out to simulate the sol-gel film/SS 304L interface and to follow the corrosion process in the physiological saline solution. According to the obtained results, smooth and crack-free coatings – hybrid organic–inorganic thin films preloaded with a green corrosion inhibitor were synthesized. Thus formed coatings provide a weaker barrier protection than that with the incorporation of rosemary extract, when the inhibition efficiency can be over 98%. The inhibition mechanism of rosemary extract is an anodic-type inhibition. The hybrid coating doped with 0.05% rosemary extract produced the maximum inhibition effect. This additive could be a prospective candidate for the development of new environmentally friendly pretreatments. In addition, doped hybrid coatings on SS 304L have been considered as suitable coatings for industrial applications.

#### ACKNOWLEDGMENTS

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#### Реферат

Чистые и легированные экстрактом розмарина гибридные наноразмерные пленки были изготовлены с применением золь, синтезированного гидролизом и тетраэтоксисилана в молярном соотношении 1:1, с добавлением экстракта розмарина. Пленки осадились на подложку из нержавеющей стали марки 304L методом центрифугирования и выдерживались при комнатной температуре в течение 24 часов, с последующим определением характеристик коррозии. Структура, состав и прочность сцепления (адгезии) гибридных пленок, полученных методом золь-гель, с поверхностью сплава анализировались с помощью сканирующей электронной микроскопии (SEM), рентгеноструктурного анализа на основе метода энергетической дисперсии (EDX) и проверки на прочность покрытий, соответственно. Добавление высококонцентрированной примеси (0,1%) не нарушило состояние процесса золь-гель. При анализе характеристик коррозии покрытий на подложке из нержавеющей стали марки 304L использовались потенциодинамические поляризационные измерения и электрохимическая импедансная спектроскопия через 1 час и через 21 день после воздействия физиологического (солевого) раствора. Сопротивление коррозии гибридных пленок, легированных экстрактом розмарина, через 1 час и через 21 день после воздействия физиологического (солевого) раствора было выше, чем у чистых и гибридных покрытий из двуокиси кремния; в обоих случаях толщина покрытия была меньше 100 нанометров. Кроме того, электрохимические свойства легированных покрытий анализировались с помощью потенциодинамических поляризационных измерений в 3,5% NaCl среде. Полученные результаты свидетельствуют, что исследованная система может найти промышленное применение.

*Ключевые слова:* коррозия; нержавеющая сталь марки 304L; ингибитор коррозии на основе растительного сырья; экстракт розмарина; пленки, полученные методом золь-гель.