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Effect of surfactant concentration in modifying solution on corrosion properties of the coatings based on vinyltrimethoxysilane (VTMS) and poly(3,4-ethylenedioxythiophene) (PEDOT)



A. Kucharczyk ^a, L. Adamczyk ^{a,*}, K. Miecznikowski ^b

^a Department of Materials Engineering, Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, Al. Armii Krajowej 19, 42-200 Czestochowa, Poland

^b Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, University of Warsaw, ul. Ludwika Pasteura 1, 02-093 Warszawa, Poland

* Corresponding e-mail address: lidia.adamczyk@pcz.pl

ORCID identifier:  <https://orcid.org/0000-0001-6489-972X> (A.K.);

 <https://orcid.org/0000-0003-4811-5387> (L.A.);  <https://orcid.org/0000-0001-7401-5844> (K.M.)

ABSTRACT

Purpose: This paper presents an analysis of the structure and physicochemical properties of coatings based on an organofunctional silane (VTMS), a conductive polymer (PEDOT), and a surfactant (polyoxyethylene glycol monolauryl ether BRIJ).

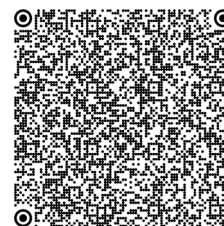
Design/methodology/approach: The coatings were deposited on X20Cr13 stainless steel and glassy carbon specimens using sol-gel immersion. The obtained coatings were characterised in terms of topography, microstructure, roughness, adhesion to the steel substrate, thickness, and corrosion resistance. Corrosion tests were conducted in sulfate environments with pH = 2 without or with the addition of Cl⁻ ions.

Findings: The use of different surfactant concentrations in the modifying solution is intended to improve the deposition efficiency and increase the degree of dispersion of silane and conducting polymer.

Research limitations/implications: The tested coatings were found to slow down the corrosion of the steel substrate, thus effectively protecting it from this phenomenon. The use of a surfactant compound is intended to increase the degree of dispersion of silane and polymer in the modifying solution to improve deposition efficiency.

Practical implications: Test carried out in corrosive media have shown that the coatings proposed in the above work, based on VTMS silane, PEDOT polymer and BRIJ surfactant, significantly increase the corrosion resistance of the tested materials, which confirms their effectiveness and possibility of application in various industries.

Originality/value: The novelty of this paper is the use of silane (VTMS), polymer (PEDOT) and surfactant (BRIJ) as components of the anticorrosion coating.



Keywords: Vinyltrimethoxysilane, Poly(3,4-ethylenedioxythiophene), Polyoxyethylene glycol monolauryl ether, Stainless steel, Sol-gel method

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PROPERTIES

1. Introduction

Corrosion is considered to deteriorate metal as a result of a reaction with the environment and is often difficult to eliminate completely. Corrosion processes are accompanied by a series of reactions that change the composition and properties of both the metal surface and the local environment, such as the formation of oxides, diffusion of metal cations into the coating surface, and local changes in pH and electrochemical potential [1,2]. The study of the corrosion of steel and iron attracts interest among researchers [3,4] due to the economic losses related to electrochemical corrosion. One of the methods to improve the corrosion resistance of metals and their alloys is to deposit protective coatings on their surfaces [1-6].

Compatibility between organic and metal substrates is critical to the stability and corrosion resistance of coatings to atmospheric conditions. The low pH of the environment and the presence of aggressive ions from the halogen group accelerate the deterioration of steel components. An alternative to conventional anti-corrosion coatings is silane coatings, usually deposited using the sol-gel method on metal substrates (steel, aluminium, titanium, etc.) [7-13]. Silane coatings are synthesised using non-toxic and safe precursors (metal alcoholates, salts, or nitrates). Sol-gel coatings are characterized by low processing temperatures and film homogeneity [14-16]. Deposition of thick sol-gel layers (with a thickness of more than 1 μm) and high drying temperatures ($>400^\circ\text{C}$) can lead to the cracking of silane coatings [17,18]. The resulting defects, such as micropores or gaps, provide an easy diffusion path for aggressive ions such as Cl^- , Br^- , and I^- . These sites are a source of corrosion initiation [19-21]. To improve the protective properties of silane coatings, attempts have been made to modify them with conductive polymers and surfactants [22-24].

Conductive polymers (CPs) are a special class of polymeric materials that are characterized by, among other things, good environmental stability and electrical conductivity. They also have good functional properties (mechanical, optical, and electronic) [25,26]. In anti-corrosion coating technology, there is growing interest in

modifying coating composition by adding a conductive polymer at low concentrations (0.2-0.3 wt%) [27-29]. Factors determining the corrosion protection of CPs include doping levels and electrochemical stability [27,30]. The function of conductive polymer-based coatings is to separate the metal surface from the corrosive environment and to act as a barrier to prevent and slow the diffusion of aggressive ions and corrosion products. The use of a conductive polymer as an anticorrosion coating depends largely on adhesion and deposition parameters. CP-based coatings should have very good anodic and barrier properties, be free of any defects, and strongly adhere to the metal surface [31]. To date, polymer-based coatings have been obtained by deposition of polyaniline, polypyrrole, and polythiophene [32-38]. Modifying coatings on metallic substrates based on conductive polymers involves introducing substances that increase adhesion to the steel substrate [39,40]. One of the most durable conducting polymers is poly(3,4-ethylenedioxythiophene) (PEDOT). It belongs to the group of electrochromic polymers, which change colour as a result of the flow of electric current. It conducts electricity at low voltage, but at high voltage, its conductivity decreases, and the polymer behaves like a semiconductor. PEDOT is soluble in organic solvents (e.g., ethanol) [41-48].

Another popular silane coating modifier is BRIJ. This compound belongs to the group of non-ionic surfactants, which are characterized by a strong effect on the surface properties of liquids. Surfactants (e.g. emulsifiers, detergents, wetting agents) are molecules that reduce surface and interfacial tension at the interface between solids, liquids, and gases [49]. The polar groups of these compounds (hydroxide or ether groups) are solvated in an aqueous environment and can easily dissolve in them. Easy modification and good surface properties that are independent of the pH of the environment can be used in various fields of the economy [38]. The addition of a surfactant to a modifying solution containing silane and a conducting polymer reduces interfacial energy, thus limiting gel breaking. Furthermore, surfactants improve the crosslinking of silane and polymer by breaking them into smaller particles [50].

The present study is devoted to the investigations of the preparation and characterization of protective anticorrosion coatings based on a silane (VTMS), a conductive polymer (PEDOT), and a non-ionic surfactant (BRIJ) deposited on X20Cr13 stainless steel. No examinations on the use of the above-mentioned reagents as components of anti-corrosion coatings have been found in the studies published to date. Previous studies have shown the possibility of using vinyltrimethoxysilane-based coatings for corrosion protection on the surface of X20Cr13 stainless steel [11,51]. The obtained coatings are characterized by very good adhesion to the substrate, uniform surface and provide corrosion protection for X20Cr13 steel in a strongly acidic sulfate environment with Cl⁻ ions (pH = 2). Studies using the BRIJ surfactant as a modifying additive for VTMS-based silane coatings have demonstrated its beneficial effect on the corrosion protection of X20Cr13 steel [52]. The use of a surfactant compound is intended to increase the degree of dispersion of silane and polymer in the modifying solution to improve deposition efficiency.

2. Experimental methodology

2.1. Materials

3,4-ethylenedioxythiophene (EDOT, Sigma Aldrich) as the monomer, vinyltrimethoxysilane (99% VTMS, Sigma Aldrich), ethyl alcohol (EtOH, Sigma Aldrich), polyoxyethylene glycol monolauryl ether (BRIJ, Sigma Aldrich), acetic acid (AcOH, Chempur), and deionized water were used as reactants. All reagents had a p.a. purity grade.

2.2. Coatings preparation

To prepare the modifying solution, 4.84 ml of 3.16 mol dm⁻³ vinyltrimethoxysilane (VTMS) was used along with 1.08 ml of EtOH and 0.1 mol dm⁻³ of AcOH. The solution was placed on a magnetic stirrer and stirred for 1 day at 800 to 1,000 rpm. A solution consisting of 0.1 mol dm⁻³ EDOT and BRIJ (dissolved in ethanol) was then added. Three concentrations of surfactant were used in the experiment: 0.01, 0.05, and 0.1 mol dm⁻³. The solution was placed again on a magnetic stirrer for 24h to obtain a gel consistency. After obtaining the gel consistency, the solution was deposited on the electrodes (X20Cr13 steel, glassy carbon) by sol-gel immersion (20 minutes). The coated specimens were placed in a silica gel desiccator until the coatings dried completely (about one day).

The prepared sol-gel was deposited on the electrodes and underwent cyclization to obtain polymer in the gel structures. The cyclization process was carried out by cyclic

voltammetry in a solution of 0.1 mol dm⁻³ H₂SO₄ at a rate of 50 mVs⁻¹ in the potential range from -1.0 to 2.0 V for 1,200 s. The figures show the first cycle of the voltammogram. The experiments were conducted at a room temperature of 24°C in laboratory settings.

Coating synthesis consists of three stages:

- 1) deposition of sol-gel,
- 2) drying for about one day,
- 3) polymerization using cyclic voltammetry (CV).

2.3. Preparation of electrodes

X20Cr13 stainless steel rods with a diameter of 5 mm were placed in polymethyl methacrylate holders and pretreated by polishing on sandpaper with grit of 600, 1000, and 2000. Next, the specimens were cleaned with ethanol and degreased in acetone.

2.4. Characteristics of coatings

Microstructural properties and surface roughness were evaluated using a KEYENCE VHX - 7000 digital microscopes (Keyence, Mechelen, Belgium). The thickness of the coatings was measured using a Testan DT-20 AN 120 157 metres (Anticorr, Gdańsk, Poland) with an integrated probe designed for ferromagnetic and non-ferromagnetic measurements. The chemical composition of the coatings deposited on the steel was evaluated using a JEOL JSM-6610 LV scanning electron microscope with an EDS X-ray microanalyzer (JEOL, Tokyo, Japan). Microscopic maps of the surface were made using an atomic force microscope (ATM) (NanoScope V MultiMode 8 Bruker, Bremen, Germany). The adhesion of the tested coatings was evaluated in a qualitative test using Scotch tape (Scotch™, St. Paul, MI, USA). The characteristics of the coatings were determined using a SHIMADZU IRAffinity - 1S FTIR spectrophotometer with a QATR 10 (QATR-FTIR) attachment (Shimadzu, Japan, Kyoto). Electrochemical measurements were conducted in a three-electrode system using a CHI 706 measuring station (CH Instruments, Austin, Texas, USA). The working electrodes were X20Cr13 steel and glassy carbon without and with a coating, whereas an auxiliary electrode was platinum, and a reference electrode was a saturated calomel electrode (SCE).

3. Results

3.1. Electrochemical analysis on X20Cr13 steel and glassy carbon

Cyclic voltammetry was chosen as the method for polymerization of the polymer contained in the gel

structures. Figure 1 shows the first polymerization cycle of VTMS/PEDOT/BRIJ coatings deposited on X20Cr13 stainless steel and glassy carbon.

The main difference during the coating deposition on X20Cr13 steel compared to glassy carbon is revealed in the first measurement cycle when the steel undergoes successively active dissolution, passivation, and transpassivation. Sakmeche et al. [53] conducted XPS examinations for PEDOT coatings deposited on either pure metal (Fe, Al) or steel substrates. They found that the EDOT electropolymerization process leads to forming of a coating/oxide layer complex. During the first cycle (Fig. 1 A) of the potential sweep from - 0.6 V in the positive direction, a sharp increase in current density is observed for the steel studied, which is associated with active substrate dissolution. The anodic peak reaches a maximum at a potential of approx. - 0.4-0.2 V. Next, with a further increase in potential, the current density decreases, indicating steel passivation (most effective in the range of 0.25-1.0 V). Rao and Singhal [54] demonstrated that in addition to $(\text{Cr,Fe})_2\text{O}_3$,

the oxide layer deposited on stainless steel contains hydroxides (mainly $\text{Cr}(\text{OH})_3$ and CrOOH).

In the case of both electrodes (Fig.1 B-D), once the potential exceeded ca. 1.0 V, oxidation of the EDOT monomer [53] occurred (a sharp increase in current density), leading to the formation of a coating. A further increase in current density for the stainless steel substrate ($E > +1.1$ V) (Fig. 1 A) is due to its transpassivation and subsequent release of oxygen on its surface. During the return sweep, a negative current peak appears at ca. 0.2 V- to 0.1 V, which may be related to the reduction of the polymer layer deposited on the electrode and/or (in the case of a steel substrate) the reduction of oxidation products of the steel [53].

Figs. 1 B-D show voltammetric curves recorded on glassy carbon and X20Cr13 stainless steel coated with VTMS/PEDOT/BRIJ with BRIJ concentration in the potential range from -1.0 V to 2.0 V. The literature reports [28] describing PEDOT show that in non-aqueous solutions, the oxidation and reduction peaks are in the potential range from -0.2 V to 0.9 V. Voltammetric curves for glassy carbon

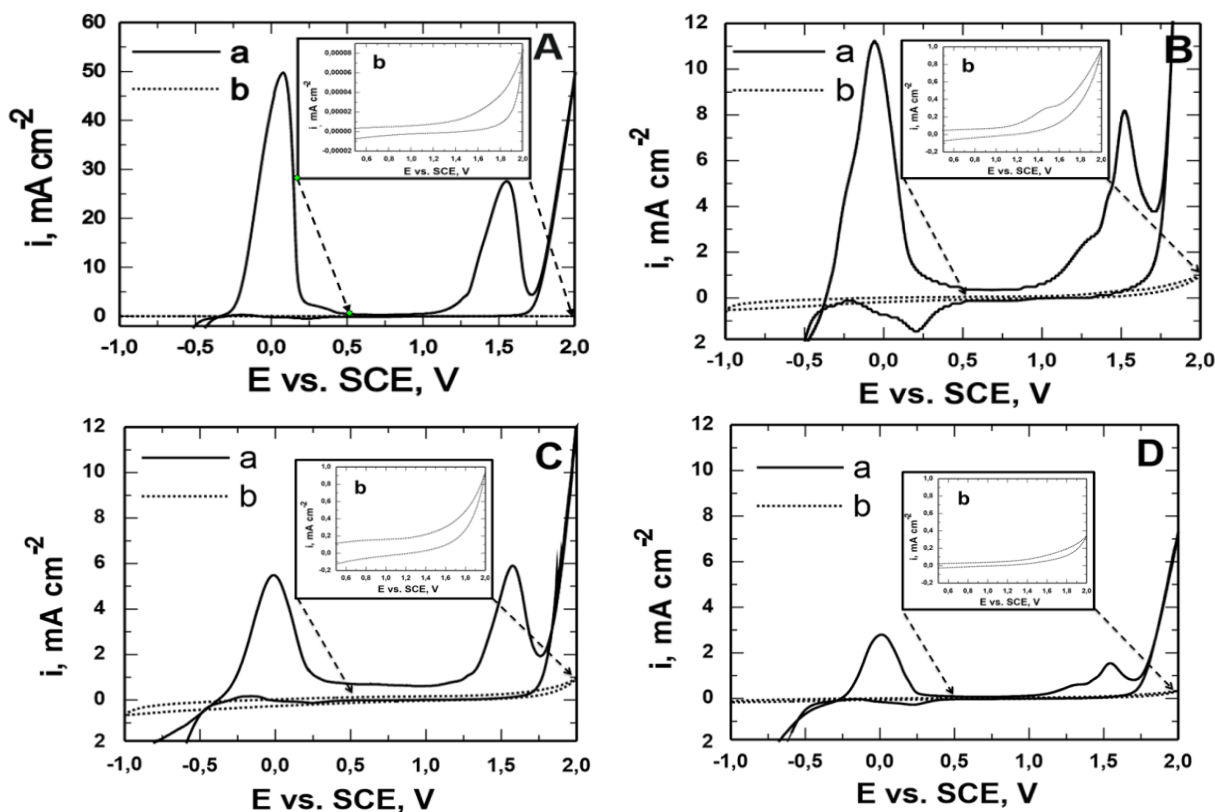


Fig. 1. The first cycle of the voltammetric response from the polymerization process for X20Cr13 stainless steel (a) and glassy carbon (b) without coating (A) and with VTMS/PEDOT/BRIJ coatings with BRIJ concentration: 0.01 (B), 0.05 (C) and 0.1 (D) mol dm^{-3} . Electrolyte: 0.1 mol dm^{-3} H_2SO_4 . Polarization speed 50 mVs^{-1} . Insert: b – voltammetric response for glassy carbon, range 0.6-2.0 V

show very good symmetry, with the charges of the cathodic part equal to those of the anodic part, indicating the reversibility of the oxidation and reduction reactions in the potential range from -1.0 V to 2.0 V. However, as discussed above, in the case of X20Cr13 stainless steel, differences in the voltammetric responses recorded for the tested coatings are evident.

3.2. Microstructural observations

The topography of the resulting coatings was evaluated using a digital microscope. Figure 2 shows the morphology of the tested coatings deposited on the surface of X20Cr13 stainless steel. The photos show all three coatings and the substrate with polishing marks. The coatings evenly cover the surface of the specimen, forming a compact, tight, and uniform structure with no structural voids.

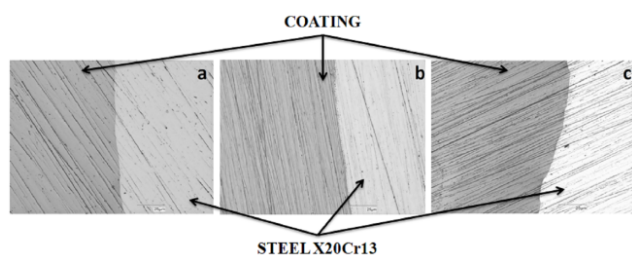


Fig. 2. Topography of VTMS/PEDOT/BRIJ coatings with BRIJ concentration: 0.01 (a), 0.05 (b) and 0.1 (c) mol dm⁻³. KEYENCE VHX - 7000 microscope (magn. 1000)

3.3. Thickness of the coatings

One of the key parameters affecting the corrosion resistance of steel components is the thickness of protective coatings. In this study, this parameter was analyzed using two methods. Profiles were examined (Fig. 3) to evaluate the thickness of the coatings. The mean thickness of VTMS/PEDOT/BRIJ coatings for individual BRIJ concentrations (measured at two sites on the specimen) was: 0.01 mol dm⁻³: 26.66 μm (a); 0.05 mol dm⁻³: 24.97 μm (b); 0.1 mol dm⁻³: 21.89 μm (c). The recorded thickness was measured using a KEYENCE digital microscope.

Table 1.

Coating thickness measurement results using DT – 20 AN 120 157 meter

	Coating thickness VTMS/PEDOT/BRIJ, μm		
	concentration of BRIJ 0.01 mol dm ⁻³	concentration of BRIJ 0.05 mol dm ⁻³	concentration of BRIJ 0.1 mol dm ⁻³
Average	30.22	25.93	23.08

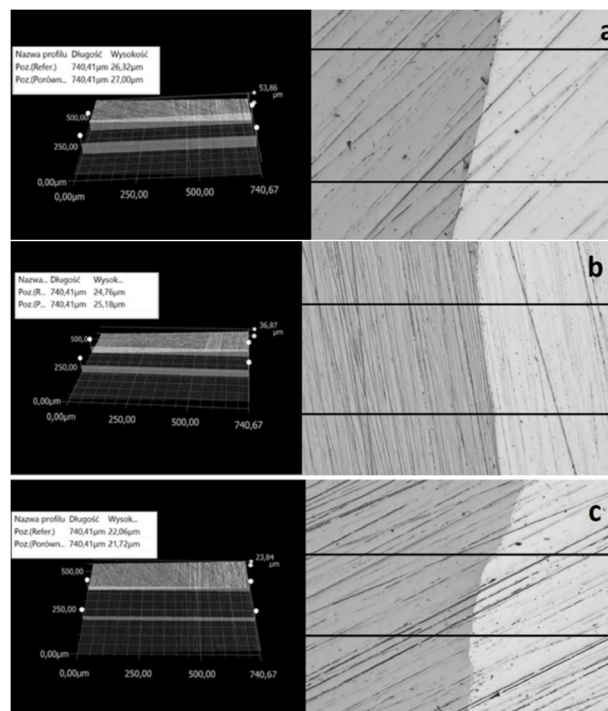


Fig. 3. Surface profile of VTMS/PEDOT/BRIJ coatings with variable BRIJ concentration: 0.01 (a), 0.05 (b), 0.1 (c) mol dm⁻³

To compare coating thickness, in addition to the method described above, thickness measurements were performed using a Testan meter. A series of 10 measurements (at different sites on the specimen) was performed. Table 1 shows the average thickness for the individual VTMS/PEDOT/BRIJ coatings. The results are consistent with the thickness evaluated using a digital microscope.

Based on measurements with two instruments (digital microscope and thickness gauge), the mean coating thickness was:

- VTMS/PEDOT/BRIJ with BRIJ concentration of 0.01 mol dm⁻³: 28.44 μm,
- VTMS/PEDOT/BRIJ with BRIJ concentration of 0.05 mol dm⁻³: 25.45 μm,
- VTMS/PEDOT/BRIJ with BRIJ concentration of 0.1 mol dm⁻³: 22.49 μm.

The differences in coating thickness between the methods were small, confirming the suitability of the methods used to measure coating thickness. Based on the thickness measurements, it can be concluded that as the content of BRIJ in the coating increases, the surface and interfacial tension decreases, resulting in a thinner coating.

3.4. Surface roughness of the coatings

Surface roughness measurements of VTMS/PEDOT/BRIJ coatings deposited on X20Cr13 stainless steel performed using a KEYENCE digital microscope are shown in Table 2. Test results varied depending on the concentration of BRIJ used in the modifying solution. The content of BRIJ added in the VTMS/PEDOT/BRIJ coating contributes significantly to the dispersion of silane and polymer particles, thus affecting the coating roughness. As the concentration of BRIJ in the modifying solution increases, the value of the R_a parameter for the tested VTMS/PEDOT/BRIJ coatings decreases.

Table 2.
Roughness of VTMS/PEDOT/BRIJ coatings deposited on X20Cr13 steel

Coating VTMS/PEDOT/BRIJ	R_a , μm
concentration of BRIJ $0,01 \text{ mol dm}^{-3}$	8.05
concentration of BRIJ $0,05 \text{ mol dm}^{-3}$	7.47
concentration of BRIJ $0,1 \text{ mol dm}^{-3}$	5.29

3.5. Chemical composition of the VTMS/PEDOT/BRIJ coating

The chemical composition of the coatings was determined using a scanning electron microscope equipped with an EDS X-ray chemical analyzer. Based on the chemical analysis, the silicon content for each coating was (wt%) 32.44% for VTMS/PEDOT/BRIJ with 0.01 mol dm^{-3} BRIJ, 29.52% for VTMS/PEDOT/BRIJ with 0.05 mol dm^{-3} BRIJ, and 27.62% for VTMS/PEDOT/BRIJ with 0.1 mol dm^{-3} BRIJ. The remainder of the chemical composition consisted of C and O (wt%).

3.6. AFM analysis

The surface morphology of VTMS/PEDOT/BRIJ coatings deposited on the surface of X20Cr13 steel is shown in Figure 4. The recorded values of the R_a parameter for individual coatings are smaller than those obtained with the digital microscope due to the different areas of analysis ($1 \mu\text{m} \times 1 \mu\text{m}$). The obtained values of the R_a parameter

showed that the VTMS/PEDOT/BRIJ coating with a BRIJ concentration of 0.1 mol dm^{-3} had the lowest roughness compared to the other coatings. This means that the addition of BRIJ affects the surface roughness of the coating: the higher the BRIJ content, the more dispersed the silane and polymer particles, as confirmed by publications [55,56].

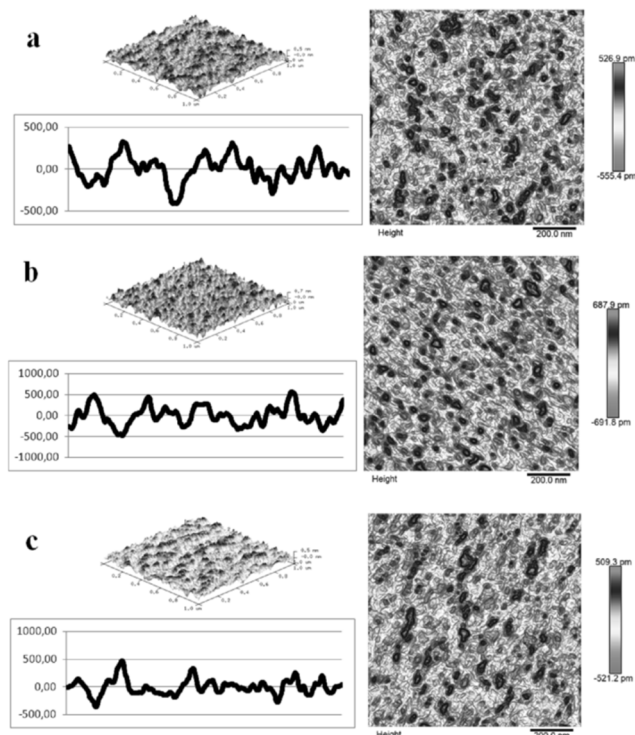


Fig. 4. AFM images of the surfaces of coatings applied to X20Cr13 steel. VTMS/PEDOT/BRIJ coating with BRIJ concentration: 0.01 (a), 0.05 (b) and 0.1 (c) mol dm^{-3}

3.7. Adhesion to substrate

Immediately after the deposition of the VTMS/PEDOT/BRIJ coatings, their adhesion to the X20Cr13 stainless steel was tested using Scotch™ tape. The coatings were characterized by good adhesion to steel substrates.

3.8. Analysis of coating composition

Characterization of coatings based on vinyltrimethoxysilane (VTMS), poly(3,4-ethylenedioxythiophene) (PEDOT) and polyoxyethylene glycol monolauryl ether (BRIJ) deposited on X20Cr13 steel was determined using a Fourier transform infrared spectrophotometer with attenuated total reflectance (QATR - FTIR). A detailed description with drawings of the

absorbance peaks for VTMS and PEDOT coatings was presented in publications [11,30].

VTMS/PEDOT/BRIJ coating spectrum cannot be considered a simple combination of PEDOT and VTMS spectra. The characteristic bands of VTMS/PEDOT/BRIJ coatings have higher absorbance and wavelength shifts compared to PEDOT and VTMS spectra.

Characteristic absorbance peaks observed for VTMS/PEDOT/BRIJ coatings (Fig. 5) in the 2000-500 cm^{-1} range are:
 1276 cm^{-1} : asymmetric stretching and bending vibrations of the C-H bond belonging to the -Si-(OCH₃) group;
 1.604 cm^{-1} and 1.409 cm^{-1} : stretching vibrations of the C=C bond in the CH₂=CH- group;
 1.006 cm^{-1} , 889 cm^{-1} , and 753 cm^{-1} : vibrations of the Si-O-C bond;
 a broad band from 1.150 cm^{-1} - 1000 cm^{-1} corresponds to asymmetric stretching vibrations of Si-O-Si bonds;
 a peak at 686 cm^{-1} corresponds to the Si-C bond;
 967 cm^{-1} : asymmetric bending vibrations of the Si-OH bond.

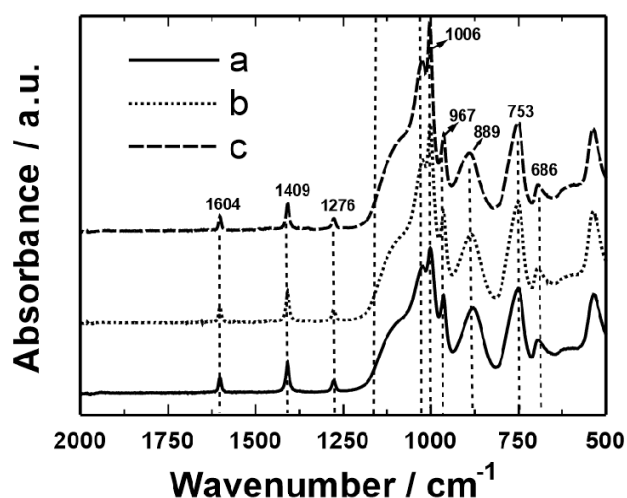


Fig. 5. FTIR spectra for VTMS/PEDOT/BRIJ coatings with BRIJ concentration: 0.01 (a), 0.05 (b), 0.1 (c) mol dm^{-3}

3.9. Corrosion testing

In order to evaluate the kinetic tendency for general or pitting corrosion, open circuit potential (OCP) measurements were carried out for X20Cr13 steel without and with VTMS/PEDOT/BRIJ coating at varying BRIJ concentration of: 0.01 (b), 0.05 (c), and 0.1 (d) mol dm^{-3} .

Figures 6 A and B show the measurements of the open circuit potential (OCP). Immediately after immersion in corrosive solutions, uncoated steel shows a potential of

about -0.4 V. With longer exposure times, the corrosion potential for steel is -0.5 V. For X20Cr13 steel coated with VTMS/PEDOT/BRIJ, the potential is, depending on the BRIJ concentration:

- 0.01 mol dm^{-3} : approx. 0.2 V,
- 0.05 mol dm^{-3} : approx. 0.45 V,
- 0.1 mol dm^{-3} : approx. 0.1 V.

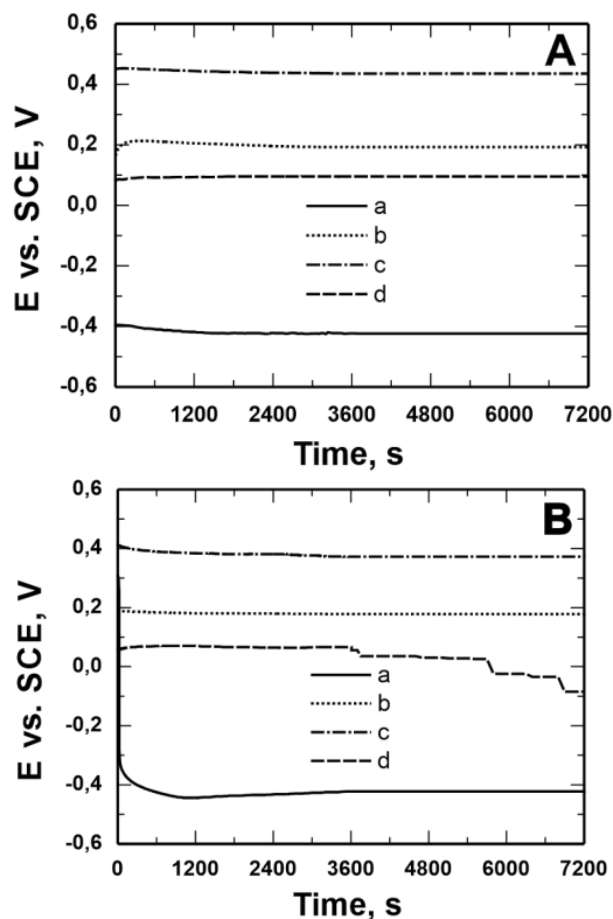


Fig. 6. Measurement of the OCP open potential from the exposure time in the solution: 0.5 mol dm^{-3} Na₂SO₄ pH = 2 (A) and 0.5 mol dm^{-3} Na₂SO₄ + 0.5 mol dm^{-3} NaCl pH = 2 (B) for X20Cr13 steel uncoated (a) and covered with VTMS/PEDOT/BRIJ coatings with BRIJ concentration: 0.01 mol dm^{-3} (b), 0.05 mol dm^{-3} (c), 0.1 mol dm^{-3} (d)

The dependence of the open circuit potential of uncoated and coated steel on the time of immersion in a corrosive solution containing chloride ions is shown in Figure 6B. Uncoated X20Cr13 steel undergoes active dissolution after about 50 hours of immersion in a corrosive solution, as described in the paper [11]. In contrast, steel coated with

VTMS/PEDOT/BRIJ coatings shows potential in the passive range after immersion in a corrosive solution. The potential of steel coated with VTMS/PEDOT/BRIJ for individual BRIJ concentrations is:

0.01 mol dm⁻³: decreases from 0.2 V to ca. 0.17 V after 2 h;

0.05 mol dm⁻³: decreases from 0.4 V to ca. 0.38 V after 2 h;

0.1 mol dm⁻³: initially increases from 0.06 V to 0.08 V for 1h, then decreases, reaching -0.1 V.

Figure 7 shows microscopic observations made after measuring OCP in a sulfate solution with the addition of Cl⁻ ions. The VTMS/PEDOT/BRIJ coating with a BRIJ concentration of 0.1 mol dm⁻³ shows local corrosion effects (pitting), indicating ineffective corrosion protection (Fig. 8c).

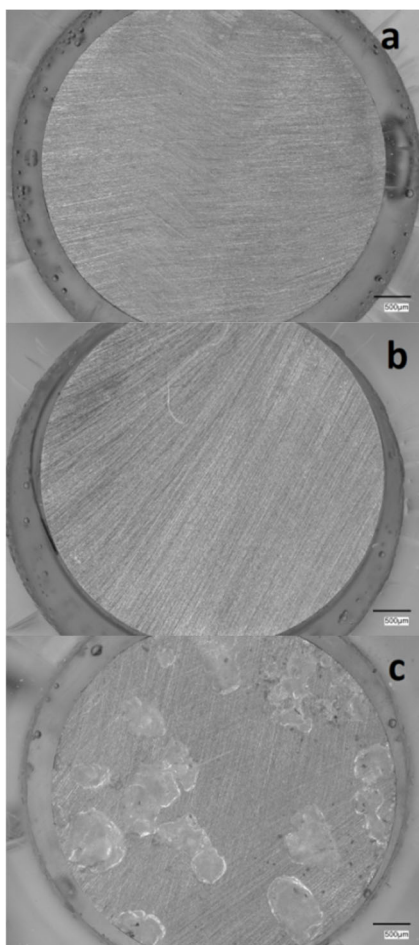


Fig. 7. Pictures of VTMS/PEDOT/BRIJ coatings after OCP tests in a solution of 0.5 mol dm⁻³ Na₂SO₄ + 0.5 mol dm⁻³ NaCl pH = 2. BRIJ concentration: 0.01 (a), 0.05 (b) and 0.1 (c) mol dm⁻³. KEYENCE VHX-7000 digital microscope, magn. 50

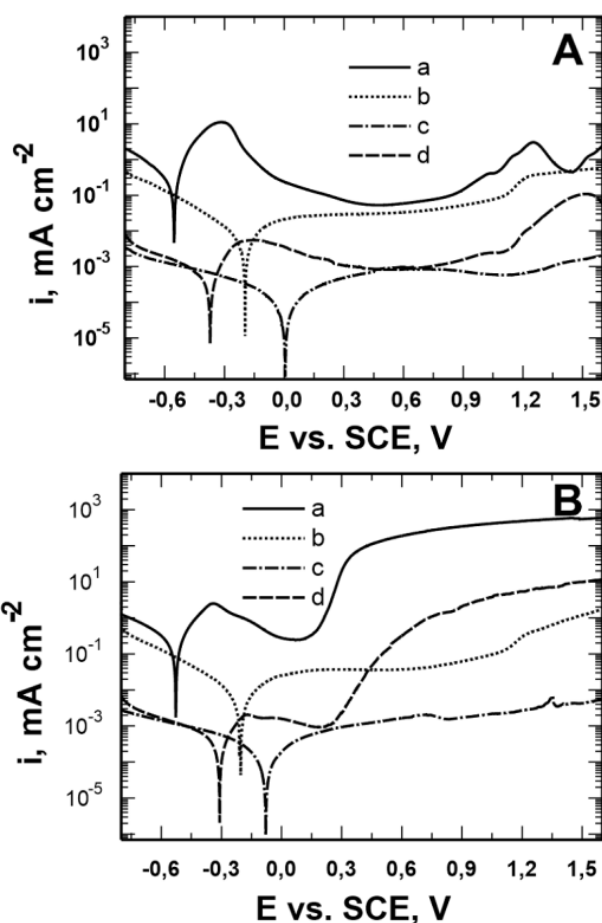


Fig. 8. Potentiodynamic polarization curves recorded in the solution: 0.5 mol dm⁻³ Na₂SO₄ pH = 2 (A) and 0.5 mol dm⁻³ Na₂SO₄ + 0.5 mol dm⁻³ NaCl pH = 2 (B) for X20Cr13 steel uncoated (a) and covered with VTMS/PEDOT/BRIJ coatings with BRIJ concentration in the solution: 0.01 (b), 0.05 (c) and 0.1 (d) mol dm⁻³. Polarization speed 10 mVs⁻¹, solutions in contact with air

In order to determine the greatest effect of BRIJ concentration on the corrosion properties of the VTMS/PEDOT/BRIJ coatings on X20Cr13 steel, their ability to inhibit general and pitting corrosion was evaluated using potentiodynamic curves. The experiment was conducted in two corrosion solutions: 0.5 mol dm⁻³ Na₂SO₄ pH = 2 – general corrosion (Fig. 8A) and 0.5 mol dm⁻³ Na₂SO₄ + 0.5 mol dm⁻³ NaCl pH = 2 – pitting corrosion (Fig. 8B). Potential range was -0.8 to 1.6 V for uncoated and coated X20Cr13 steel, respectively. As shown in Fig. 4, the VTMS/PEDOT/BRIJ coatings obtained in the study inhibit cathodic and anodic processes. There was a shift in the corrosion potential of the steel of about 0.5 V compared to

the uncoated steel (the VTMS/PEDOT/BRIJ coating with a BRIJ concentration of 0.05 mol dm^{-3}). Anodic current densities for VTMS/PEDOT/BRIJ-coated steel in the passive range are 1 to 3 times lower than for uncoated steel.

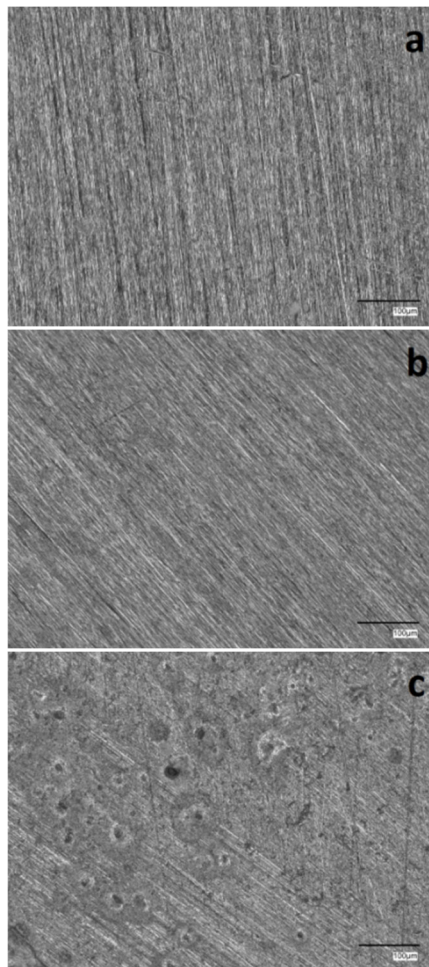


Fig. 9. Pictures of VTMS/PEDOT/BRIJ coatings after potentiodynamic tests in a corrosion solution of $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.5 \text{ mol dm}^{-3} \text{ NaCl}$ pH = 2. BRIJ concentration: 0.01 (a), 0.05 (b) and 0.1 (c) mol dm^{-3} . KEYENCE VHX-7000 digital microscope, magn. 400

To evaluate the ability of the obtained coatings to inhibit pitting corrosion, potentiodynamic curves were obtained for a solution of $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.5 \text{ mol dm}^{-3} \text{ NaCl}$ pH = 2 (Fig. 8B). The corrosion potential of X20Cr13 steel for all coatings is shifted by about 0.1-0.5 V toward positive values compared to the corrosion potential recorded for uncoated steel ($E_{\text{corr}} = -0.527 \text{ V}$). Lower cathodic and anodic current density values were observed for coated compared to uncoated steel. The polarization curves show that the pitting

nucleation potential (E_{pit}) is 0.12 V for uncoated steel and 0.28 V for VTMS/PEDOT/BRIJ-coated steel with a BRIJ concentration of 0.1 mol dm^{-3} , respectively. As shown in Figure 8B, when VTMS/PEDOT/BRIJ coatings with BRIJ concentrations of 0.01 and 0.05 mol dm^{-3} were used to protect the steel, no breakthrough potential of the passive layer (pitting nucleation potential) was observed. The silane coating with a conductive polymer and a non-ionic surfactant effectively inhibits the access of aggressive anions to the steel substrate, thereby protecting the substrate from pitting corrosion (BRIJ concentration of 0.01 and 0.05 mol dm^{-3}). Microscopic observations made after the measurement showed no local corrosion effects under the VTMS/PEDOT/BRIJ coating for BRIJ concentrations of 0.01 and 0.05 mol dm^{-3} (Figs. 9 a and b). The coating with a BRIJ concentration of 0.1 mol dm^{-3} shows local pitting corrosion sites (Fig. 9c). The high content of BRIJ in the coating leads to the greater dispersion of silane and conductive polymer particles, resulting in a thinner coating.

3.10. Polarization resistance

Table 3 shows the values of potential and density of corrosion current and polarization resistance for X20Cr13 steel uncoated (a) and coated with VTMS/PEDOT/BRIJ coatings with BRIJ concentration: 0.01 (b), 0.05 (c) or 0.1 (d) mol dm^{-3} . The values of polarization resistance (Fig. 10) for X20Cr13 steel without (a) and with VTMS/PEDOT/BRIJ coating (b-d) reveal that the anticorrosion effect of the coatings is evident for two corrosion environments (A and B). The coating with a BRIJ concentration of 0.1 mol dm^{-3} provides the weakest corrosion protection. In a sulfate solution with Cl^- ions (pH = 2) (Fig. 10B), the VTMS/PEDOT/BRIJ coating with a BRIJ concentration of 0.1 mol dm^{-3} protects X20Cr13 steel from corrosion to a lesser extent compared to other coatings. The addition of BRIJ at concentrations of 0.01 and 0.05 mol dm^{-3} has an effect on the corrosion resistance of the steel and delays the penetration of the solution into the steel substrate, thus extending its resistance to pitting corrosion.

4. Conclusions

The VTMS/PEDOT/BRIJ coatings obtained using the sol-gel method are tight and adhere well to the X20Cr13 stainless steel substrate. The present study demonstrated that the corrosion and structural properties of the VTMS/PEDOT/BRIJ coatings are significantly affected by the amount of surfactant added. As the BRIJ content in the

Table 3.

Values of potential and corrosion current density as well as polarization resistance for individual coatings

	potential corrosive E , V		current density corrosive i , mA cm ⁻²		polarization resistance $t_g\alpha$, Ω * cm ²	
	general corrosion	pitting corrosion	general corrosion	pitting corrosion	general corrosion	pitting corrosion
a	-0.558	-0.532	0.018	0.007	103.44	170.48
b	-0.196	-0.204	0.102	0.10035	9281.38	9080.29
c	+0.005	-0.079	0.001439	0.002391	708358.93	709048.75
d	-0.372	-0.309	0.013555	0.1218	81554.22	104173.93

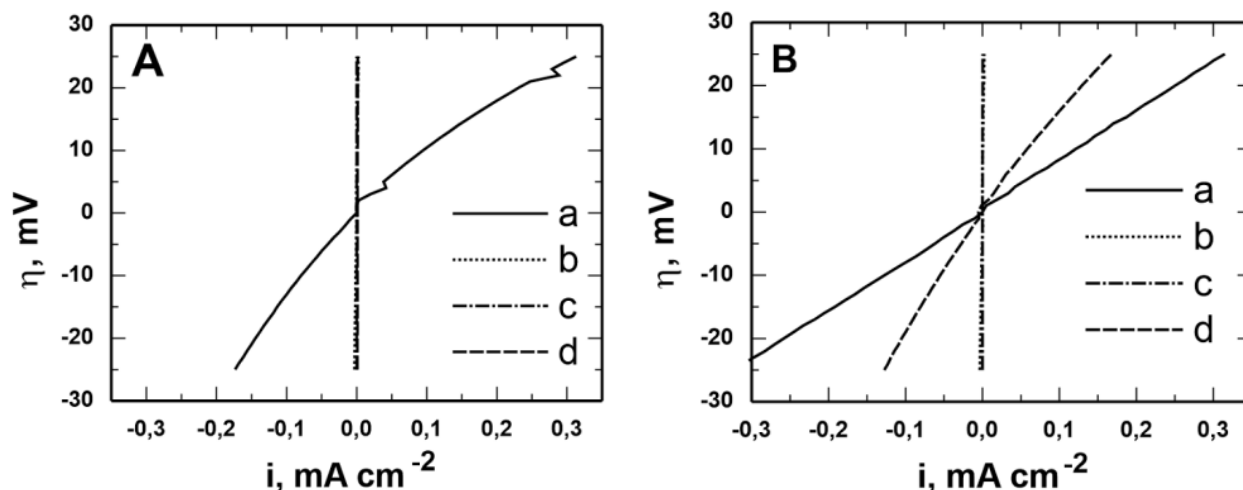


Fig. 10. Changes in external current due to polarization of X20Cr13 steel without (a) and with VTMS/PEDOT/BRIJ coating with BRIJ concentration: 0.01 (b), 0.05 (c), 0.1 (d) mol dm⁻³ in the range of $E_{kor} \pm 25$ mV, in solutions acidified to pH = 2: 0.5 mol dm⁻³ Na₂SO₄ (A) and 0.5 mol dm⁻³ Na₂SO₄ + 0.5 mol dm⁻³ NaCl (B)

modifying solution increases, the thickness and surface roughness of the tested coatings decrease, and the silane and polymer particles are more dispersed. VTMS/PEDOT/BRIJ coatings provide steel with good protection against acidified (pH = 2) sulfate solutions and, in the presence of chloride ions, inhibit the development of pitting and extend the steel resistance time. VTMS/PEDOT/BRIJ coatings deposited on X20Cr13 steel show an anodic protection effect by shifting the potential towards positive values by about 0.5 V and provide barrier protection by reducing current densities in the passive range by 3 times compared to uncoated steel (VTMS/PEDOT/BRIJ coating with a PEDOT concentration of 0.05 mol dm⁻³).

The polarization resistance potentials determined from the recorded curves confirm the improved corrosion properties. The best properties were found for coatings with BRIJ concentrations of 0.01 and 0.05 mol dm⁻³. The analysis of physicochemical properties showed that the VTMS/PEDOT/BRIJ coatings could be successfully used to protect steel against corrosion due to the significant

improvement in the anti-corrosion properties of X20Cr13 steel.

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