

Application of Electrochemically Produced and Oxidized Poly(3,4-ethylenedioxythiophene) as Anticorrosive Additive for Paints: Influence of the Doping Level

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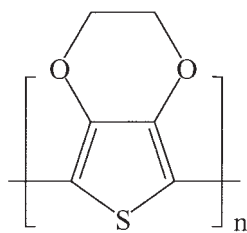
ABSTRACT: This work investigates the resistance against marine corrosion of an epoxy-based coating modified by the addition of electrochemically produced and oxidized poly(3,4-ethylenedioxythiophene) (PEDOT). For this purpose, electrodeposition of PEDOT was performed on steel electrodes by electrochemical polymerization of 3,4-ethylenedioxythiophene. The doping level of the resulting material was increased by chronoamperometry and chronopotentiometry (CP), three different oxidation degrees being achieved. The electrochemical and electrical properties of such three samples, which were used as anticorrosive additives, were examined. Furthermore, the physical properties

of the coating before and after addition of the conducting polymers were characterized using FTIR, thermal analyses, and mechanical properties evaluations. Accelerated corrosion tests indicated that the polymer with the highest amount of positive charge per monomeric unit, which was achieved by CP, enhances considerably the anticorrosive protection imparted by the coating. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1592–1599, 2006

Key words: conducting polymers; coatings; electrochemistry; anticorrosive additive; doping

INTRODUCTION

π -Conjugated polymers have received significant attention throughout the course of the past two decades due to a wide range of promising electronic, electrochemical, and optical applications. Among the many materials that have been developed during this period, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the more successful polythiophene derivatives because of its interesting properties.^{1–9}



PEDOT

PEDOT exhibits not only a high conductivity but also an unusual stability in the oxidized state, being considered as the most stable conducting polymer currently available.^{1–4} Furthermore, the oxidative polymerization of PEDOT monomer using poly(styrenesulfonate) (PSS) as charge-balancing dopant results in the formation of a water soluble polyelectrolyte system PEDOT/PSS with good film forming properties, high conductivity, and excellent stability.^{1,5–8} On the basis of these properties, PEDOT derivatives have been used as antistatic coatings for photographic films, electrode material in inorganic electroluminescent lamps, material for through-hole plating of printed circuit boards, and so on.^{1,4}

A very promising technological application of π -conjugated polymers involves their use as protective coatings on steel, an environmentally friendly approach to corrosion prevention. Since the pioneering studies of DeBerry,^{10,11} who has demonstrated the corrosion inhibition of stainless-steel by polyaniline, there have been significant progresses in the anticorrosion applications of electroactive coatings.^{12–18} Thus, polyaniline coatings are now commercially available as anticorrosive coatings.^{12,13} Furthermore, corrosion retardation have been achieved also by using polypyrrole^{14,15} and, more recently, polythiophene coatings.^{16,17}

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In this work and within a wide project devoted to develop anticorrosive coatings based on polythiophene derivatives, we compare the resistance against marine corrosion of an organic coating before and after being modified by adding PEDOT. The conducting polymer doped with ClO_4^- anions was anodically prepared on steel electrodes. The electrochemical, electrical, and structural properties of the resulting material were determined. Furthermore, to ascertain the influence of the electrochemical doping level on the anticorrosion characteristics of PEDOT, the degree of oxidation of the electrogenerated polymer was modified by chronoamperometry (CA) and chronopotentiometry (CP). The resulting materials, denoted PEDOT-ox, were added to an epoxy-based paint specially indicated for protection in marine environments. Accelerated experiments were carried out in the laboratory to analyze the corrosion performance of the carbon steel pieces coated with this paint after being modified by the addition of a low concentration of PEDOT. The results obtained using conducting polymer with different levels of doping have been compared with those obtained when the paint remains unmodified.

METHODS

Synthesis of PEDOT

3,4-Ethylenedioxythiophene (EDOT) and acetonitrile of analytical reagent grade from Aldrich Chemical were used as monomer and solvent, respectively, without further purification. Anhydrous LiClO_4 from Aldrich, analytical reagent grade, was stored in an oven at 80 °C before its use in the electrochemical trials.

Anodic polymerization of EDOT was studied by cyclic voltammetry (CV), CA, and CP, using a PAR 273A potentiostat–galvanostat connected to a PC and controlled through the PAR M270 program. Electrochemical polymerizations were conducted in a three-electrode two-compartment cell at 25 °C under nitrogen (99.995% pure) atmosphere. The anodic compartment was filled with 40 mL of a 10 mM monomer solution in acetonitrile containing 0.1M LiClO_4 as supporting electrolyte. About 10 mL of electrolyte solution was placed in the cathodic compartment. Steel AISI 316 sheets of 4-cm² area were employed as working electrodes. The counter electrode was a steel sheet of 2-cm² area. To avoid interferences during the electrochemical analyses, the working and counter electrodes were cleaned with acetone before each trial. The reference electrode was Ag/AgCl electrode, containing saturated aqueous KCl solution ($E^0 = 0.222$ V at 25°C), which was connected to the working compartment through a salt bridge with the electrolyte solution.

To change the oxidation degree of the generated polymer, we introduced the material in a new cell, which was filled with the electrolyte solution. The electrochemical doping level was changed by chronoamperometric or chronopotentiometric oxidation. The percentage of ClO_4^- in each collected sample was obtained from reduction of approximately 2 mg of sample with carbon, followed by determination of the amount of chloride ions released by standard ion chromatography. This analysis was performed with a Kontron 600 HPLC liquid chromatograph fitted with a Waters IC-Pak anion column at 30 °C and equipped with a Wescan conductometric detector. The doping level of each collected sample (i.e., the amount of positive charge supported by each monomeric unit) was calculated by stoichiometry using the determined percentage of ClO_4^- .

Electrical conductivities were measured by the sheet resistance method from films synthesized on steel electrodes of 4-cm² area, following a procedure described elsewhere.¹⁹ A Bomem Michelson MB100 FTIR spectrophotometer, with a resolution of 4 cm⁻¹ in the absorbance mode, was employed for the characterization of the polymer films. The samples were placed in an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma).

Coating characterization

The paint used in this work was supplied by HEMPEL S.A. (Barcelona). This is an epoxy resin with two components, the polymer matrix and the crosslinker, used in the shipbuilding industry.

IR characterization of the coating films was carried out using the FTIR spectrophotometer described earlier.

Thermal analyses were carried out using a Perkin-Elmer thermogravimetric analyzer TGA-6 at a heating rate of 10°C/min, from 30 to 600 °C temperature range, under nitrogen atmosphere.

Mechanical properties were evaluated at room temperature with a Zwick Z2.5/TN1S testing machine connected to a personal computer that allows to monitor the experiment. Regular films were prepared by evaporation of the volatile organic solvent of the paint formulation at room temperature. Plate samples with a length of 30 mm, a width of 3 mm, and a thickness of 200–300 μm were cut out from these films and used in stress–strain experiments. The deformation rate was 10 mm/min. Mechanical parameters like Young's modulus, tensile strength, and elongation at break were averaged out at 10 measurements. A micrometer machine Uno-Check-Fe of Neurtek, previously calibrated with a plastic sheet calibration standard of 295

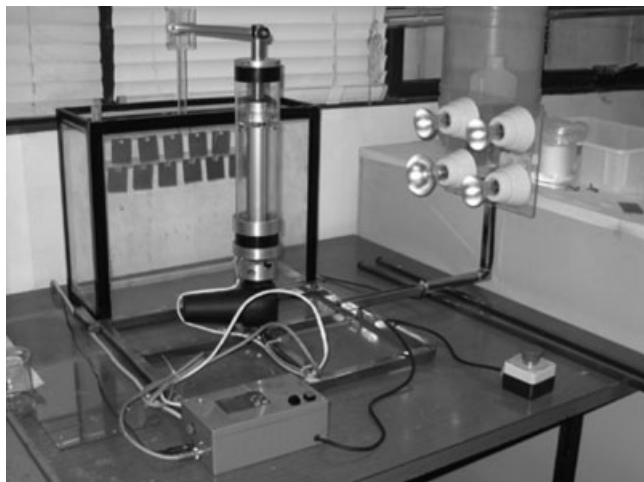


Figure 1 Home-made equipment used for the accelerated corrosion experiments.

μm , was used to obtain the thickness of the samples before the stress-strain experiments.

Modified coatings were prepared by adding grinded PEDOT-ox samples to the paint formulation. After this, homogeneous emulsions were achieved by mechanical stirring of the mixtures. The physical properties of the modified paints were characterized using identical procedures to those described above for the unmodified coating.

Corrosion studies

The metallic substratum used for corrosion experiments consists on steel F-111 with elemental composition $C \leq 0.20\%$, $Mn \leq 1.40\%$, $P \leq 0.045\%$, $S \leq 0.046\%$, and $N \leq 0.014\%$; and density $7.86 \times 10^3 \text{ kg m}^{-3}$. Rectangular steel pieces of $40 \times 50 \times 1 \text{ mm}^3$ with a diameter hole of 4 mm were degreased with acetone and stored in a dried atmosphere until the application of the coating. Samples for the corrosion tests were prepared by immersion of the steel pieces into a bath containing the paint. This procedure yielded samples with a film thickness of around 90–100 μm , which were in agreement with those recommended by the manufacturer ($\sim 100 \mu\text{m}$). Furthermore, painted steel pieces were sealed on the edges and around the hole securing the pieces to minimize local attacks at such positions.

The corrosion study was performed using a home-made equipment developed at our laboratory for the accelerated corrosion tests.²⁰ It consists of a support to put the steel pieces, which is controlled by a programmable device, and a bath containing the corrosive solution (Fig. 1). This device allows program controlled cycles that are formed by the following processes: immersion, wringing, drying, and cooling. The corrosive solution used to mimic the marine environ-

ment contains 3.5% aqueous solution of sodium chloride ($\text{pH} = 6.6$). The operating conditions of one cycle, which takes 60 min, were (a) immersion of the painted steel pieces into the solution (15 min); (b) wringing of the steel pieces (30 min); (c) drying forced with two bulbs 230 V – 100 W (5 min); and (d) cooling at room temperature (10 min). Samples were extracted and analyzed by optical microscopy at 180, 360, 540, and 720 cycles. The coating surfaces were observed using an Olympus BX-5 light polarizing microscope, operating in reflection mode with an Olympus C3030Z digital camera coupled.

RESULTS AND DISCUSSION

Electrochemical polymerization of EDOT

Figure 2 shows the cyclic voltammogram of 10 mM EDOT in acetonitrile with 0.1M LiClO_4 on a steel electrode. Two anodic peaks, O_1 and O_2 , were detected. The anodic peak potential of the first peak, $E_p^a(O_1) = 1.58 \text{ V}$, is higher than that obtained on a Pt electrode using similar experimental conditions ($E_p^a(O_1) = 1.34\text{--}1.45 \text{ V}$).^{21,22} The anodic peak potential of the second peak O_2 overlaps the oxidation of the medium at a potential higher than 3.00 V. A very small reduction shoulder appears in Figure 2 at about 0.19 V since the oxidation of EDOT at 1.80 V is almost irreversible. Onset of polymerization occurred at 1.20 V, this value being very similar to that reported for 50 mM EDOT in acetonitrile with 0.05M Et_4NClO_4 on a Pt electrode (1.25 V).²

On the basis of the results displayed in Figure 2, we decided to generate films of PEDOT by CA under a constant potential of 1.40 V. This condition was expected to ensure the polymerization of the monomer but avoiding the degradative crosslinking reactions that typically take place at higher potentials. This po-

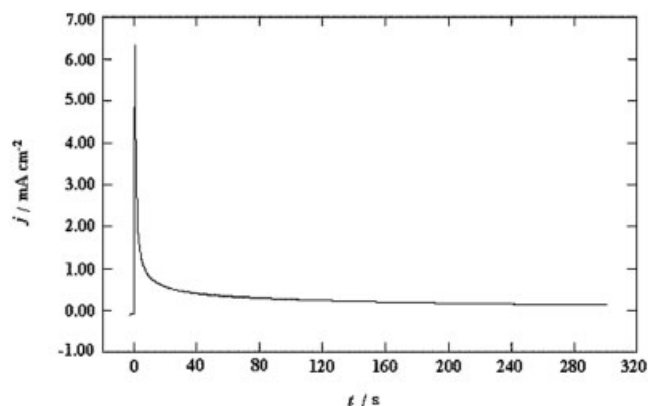


Figure 2 CV for the oxidation of a 10 mM EDOT solution in acetonitrile with 0.1M LiClO_4 on a 4-cm² steel electrode (initial and final potentials: -0.50 V ; reversal potential: 2.00 V ; scan rate: 100 mV s^{-1} ; temperature: 25°C).

TABLE I
Doping Level (DL, Positive Charges Supported by Each Monomeric Unit) and Conductivity (Ω , in S/cm) of the Overdoped PEDOT Species

PEDOT Species	Sample	DL	Conductivity
Original	Generation by CA at constant potential of 1.40 V	0.54	31
PEDOT-ox1	Oxidation of the films at 1.50 V	0.95	41
PEDOT-ox2	Oxidation of the films at 1.90 V	1.10	20
PEDOT-ox3	CP oxidation of the films at 2.5 mA cm^{-2}	1.25	43

tential provided adherent and uniform films with excellent properties as high conductivity, electrochemical stability, and ability to form electroactive polarons. Elemental analysis of the generated polymer indicated that the monomeric units support 0.54 positive charges balanced with ClO_4^- counterions.

Oxidation of PEDOT: Preparation and electrical properties

To modify the doping level, i.e., the amount of positive charge supported by each monomeric unit, anodic oxidations of the generated films were performed in a two-compartment test cell. Table I summarizes the method used for preparation of the different oxidized films and the measured electrical conductivities.

Films of PEDOT were oxidized by CA at 1.50 V during 300 s, the resulting samples being denoted PEDOT-ox1. As can be seen in Figure 3, which shows a typical chronoamperogram recorded during this process, the current density becomes stabilized at a low value, around 0.125 mA cm^{-2} . Elemental analysis of this species revealed that the polymer contains 41 wt % of ClO_4^- counterions that corresponds to 0.95 positive charges per monomer unit. This value is considerably higher than that found for the films depos-

ited before oxidation. Consequently, the contribution of the quinoid-like structure to the polymer chain is expected to be higher in PEDOT-ox1 than that in the original sample. Furthermore, the electric conductivity measured for the former sample is 10 S cm^{-1} higher than that obtained for the latter one (see Table I).

After the successful results obtained by CA at 1.50 V, the oxidation of PEDOT was tried at 1.60 V. However, the current density of the corresponding chronopotentiograms decayed to zero indicating that no oxidation process occurs at this potential. Next, oxidation by CA was performed at a greater potential, 1.90 V. In this case, chronoamperograms were almost identical to those displayed in Figure 3, which is consistent with a net value of current in the work electrode. The doping degree detected for the resulting material (hereafter denoted PEDOT-ox2) was 1.10 positive charges per monomer unit, this value being higher than that obtained for PEDOT-ox1. In spite of this, the conductivity measured for PEDOT-ox2 was 21 S cm^{-1} smaller than that obtained for PEDOT-ox1 (Table I). This important reduction is consistent with a degradation process by overoxidation of the polymer chains at high potentials.

The limitations showed above for the CA led us to choose the CP as an alternative method for increasing the oxidation degree of PEDOT. This was achieved by fixing the value of the current density to 2.50 mA cm^{-2} during 300 s, the resulting material being denoted PEDOT-ox3. These conditions increase the charge by about 25% with respect to that used in the formation of the films. Figure 4a shows a typical chronopotentiogram obtained during this process. Although the potential of the system stabilized at 1.400 V and, therefore, the generation potential was not surpassed, the elemental analysis revealed 1.25 positive charges per monomer unit. This high doping level should be attributed to an increase quinoid-like structure in the polymer chain. However, as the potential did not surpass the 1.40 V, no degradation of the chain by overoxidation was detected. The high conductivity measured for PEDOT-ox3, 43 S cm^{-1} (Table I), is consistent with the salt structure of this material.

The electroactivity of the three oxidized materials was studied by CV in the potential range from -0.50 to 1.80 V. The control cell was filled with acetonitrile

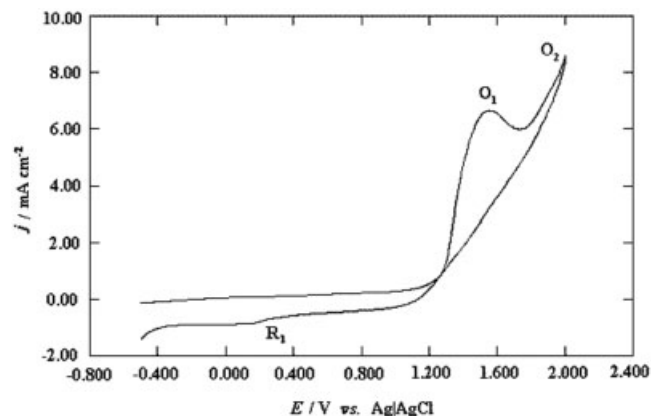


Figure 3 Chronoamperogram obtained for the oxidation of a PEDOT film in acetonitrile with 0.1 M LiClO_4 by applying a constant potential of 1.50 V, at 25°C . The film was generated by CA under a constant potential of 1.400 V on a 4-cm^2 steel electrode.

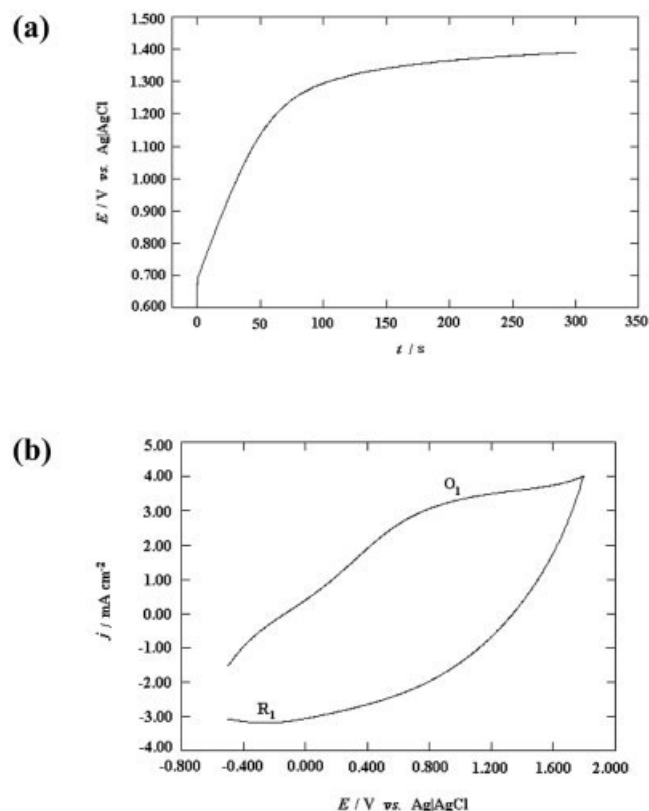


Figure 4 (a) Chronopotentiogram recorded for the oxidation of a PEDOT film in acetonitrile with 0.1M LiClO₄ by applying a constant anodic current density of 2.50 mA cm⁻², at 25°C. (b) Control voltammogram for the oxidation of PEDOT-ox3 at 25°C (initial and final potentials: -0.50 V; reversal potential: 1.80 V). In both cases the film was generated by CA under a constant potential of 1.40 V on a 4-cm² steel electrode.

containing 0.1M LiClO₄. In the control voltammograms of PEDOT-ox1 and PEDOT-ox2, no oxidation and reduction peaks were detected. A poorly defined oxidation peak O₁', with peak potential E_p^o(O₁') = 1.08 V, was detected for PEDOT-ox3 [Fig. 4(b)], while a broad reduction peak R₁', with E_p^c(R₁') = -0.26 V, was found in the cathodic scanning. This material shows notable electrochemical stability as evidenced the fact that the redox properties are almost unaltered after 10 consecutive oxidation–reduction cycles. However, PEDOT-ox1 and PEDOT-ox2 showed a considerably lower chemical stability.

Coating characterization

The characteristic groups of the paint employed in this work are reflected by the IR spectrum, which is displayed in Figure 5(a). The wave numbers of the main IR absorption bands are summarized in Table II. The epoxy resins contain one or more terminal epoxy groups at their molecules, which are identified by the principal absorption band at 917 cm⁻¹. The interpre-

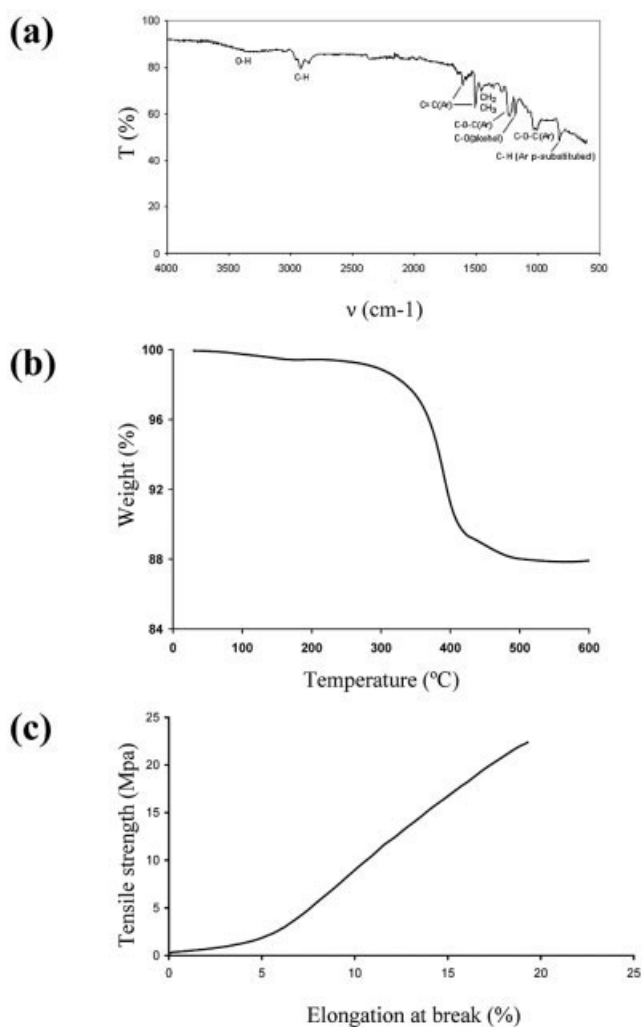


Figure 5 (a) IR absorption spectra, (b) thermogravimetric curve at scan rate of 10°C/min, and (c) tensile stress–strain curve at deformation rate of 10 mm/min for the coating studied in this work.

tation of the spectrum allows us to check that the coating is completely cured. Thus, the absorption of the terminal epoxy group at 917 cm⁻¹ disappears. The strong bands in the 3570–3200 cm⁻¹ region were assigned to the O–H stretching. Furthermore, the bands

TABLE II
Absorption Bands in the IR Spectra of the Epoxy Resin Used in This Work

ν (cm ⁻¹)	Absorption band
3570–3200	O–H (stretching)
2962	C–H aromatic
2850, 2870, 2924	C–H aliphatic
1458, 1450	CH ₂
1380	CH ₃
1604, 1508	C=C (aromatic ring)
1232, 1028	C–O–C(Ar)
1180	C–OH (hydroxy)

TABLE III
Mechanical Properties of Commercial Polymers and Experimental Parameters for the Coating Studied in This Work

Material	Young's modulus E (MPa)	Tensile strength σ_{\max} (MPa)	Elongation at break ϵ_b (%)
Epoxy coating	920	22	2
HDPE	1070–1090 ^a	22–31	10–1200
PP	1170–1720 ^a	31–41	100–600

^aFrom Ref. 24, converted to SI units.

around 1028–1232 cm^{-1} were identified as C—O—C(Ar) (ether group) of bisphenol A, a thermally stable polymer typically found in epoxy resins and extensively characterized in previous work.²³ Furthermore, the presence of aromatic groups has been detected through characteristic absorption bands at around 1510 and 1600 cm^{-1} .

Thermogravimetric analysis is a useful tool to establish the thermal stability of the material used as coating. In this case, the thermogravimetric curve [Fig. 5(b)] was very similar to those recently reported for other two-components epoxy resins.¹⁷ Thus, the thermal stability of the coating was evidenced by the high temperature required for decomposition, this degradation process starting at about 350°C. Furthermore, the percentage of inorganic components identified in the coating was greater than 80%.

The mechanical properties of drying coatings are particularly important for paints used in marine environments since they have to protect the steel surface from the corrosion attack. The tensile stress–strain curve obtained at a deformation rate of 10 mm/min is displayed in Figure 5(c) and Table III compares the mechanical properties determined for the epoxy resin with those provided for high-density polyethylene (HDPE) and polypropylene (PP),²⁴ two important commercial thermoplastics. As can be seen, the tensile stress–strain behavior is comparable to that provided by HDPE but poorer than that of PP. However, the low value of elongation at break reflects that the elastomeric character of the epoxy resin is remarkably poor, which is due to the high percentage of inorganic components contained by this coating.

Resistance against corrosion of the paint containing conducting polymer

In this section we describe the influence of the doping level in the anticorrosion performance of the paint modified by a low concentration of PEDOT (0.2%, w/w). Results obtained with the modified coating are compared with those provided using the unmodified formulation.

PEDOT-ox1, PEDOT-ox2, and PEDOT-ox3 samples were added to the paint formulation using the procedure described in the Methods section. As well as the mechanical properties must be controlled for the quality performance of the dried paint, adherence to the substratum, and film thickness is very relevant to the surface protection. Both excellent adherence and a good thickness were achieved for all the paints. Basically, the compositions with and without oxidized PEDOT form smooth films, with a regular surface free of crevices or blister after drying time, as observed from optical micrographs. Mechanical properties and FTIR absorption spectra of the modified paint were almost identical to that of the original paint (Fig. 5, and Tables II and III), indicating that no alteration is produced by the addition of conducting polymer when a very small concentration is used.

Figure 6 compares the photographs of steel pieces painted with and without conducting polymer. The texture, adherence, and regular surface of the initial samples were similar to that observed without con-

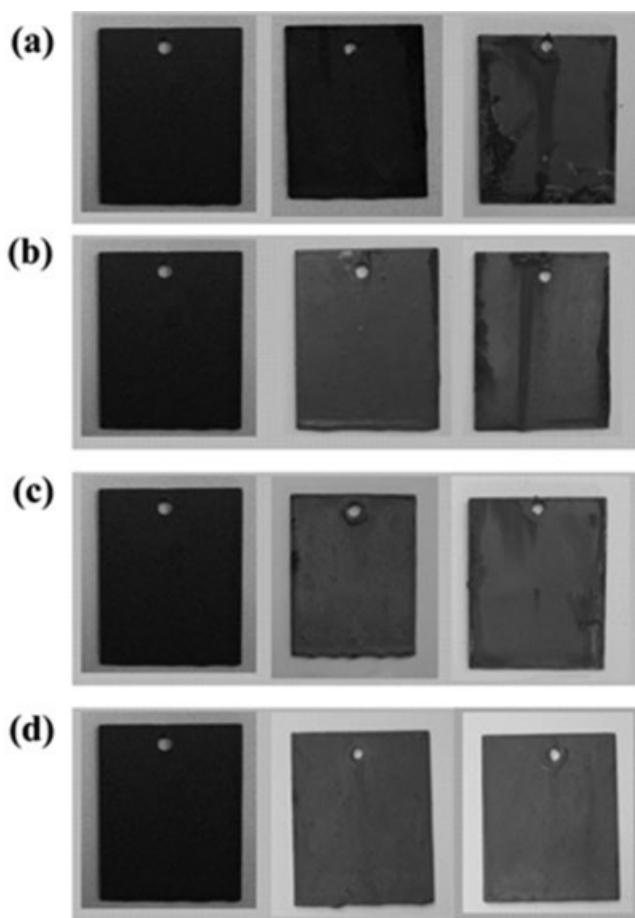


Figure 6 Photographs of the painted rectangular test pieces: (a) sample without conducting polymer; (b) sample with PEDOT-ox1; (c) sample with PEDOT-ox2; and (d) sample with PEDOT-ox3. From left to right: initial samples, samples after 360 cycles and samples after 720 cycles.

ducting polymer. Extractions of samples after 180 and 360 cycles in NaCl solution indicated that the protection imparted by PEDOT-ox3 is slightly better than that offered by PEDOT-ox1 and PEDOT-ox2. However, in all cases the corrosion is scarce and located at the border zones. After 540 cycles, the film without conducting polymer shows important signals of degradation as is evidenced by the apparition of several crevices resulting in an accentuated corrosion process of the steel piece. On the other hand, the pieces protected by films with PEDOT-ox1 and PEDOT-ox2 were considerably affected by corrosion after 540 cycles, while no significant signals of degradation were detected for PEDOT-ox3. Finally, the protection imparted by PEDOT-ox3 follows without apparent alteration after 720 cycles.

The excellent results provided by PEDOT-ox3 are consistent with its doping level, which is higher than those of PEDOT-ox1 and PEDOT-ox2 (Table I). Furthermore, it should be remarked that the electroactivity of PEDOT-ox3 is very high. This is reflected in Figure 7, which compares the cyclic voltammograms of PEDOT before and after oxidation by CP. Interestingly, PEDOT-ox3 presents a significant ability to store charge. Figure 8 compares the cyclic voltammograms of PEDOT-ox1, PEDOT-ox2, and PEDOT-ox3. As can be seen, the notable electroactivity of the latter is considerably higher than those showed by PEDOT-ox1 and PEDOT-ox2.

CONCLUSIONS

In this work and within a wide project devoted to develop anticorrosive coatings based on polythio-

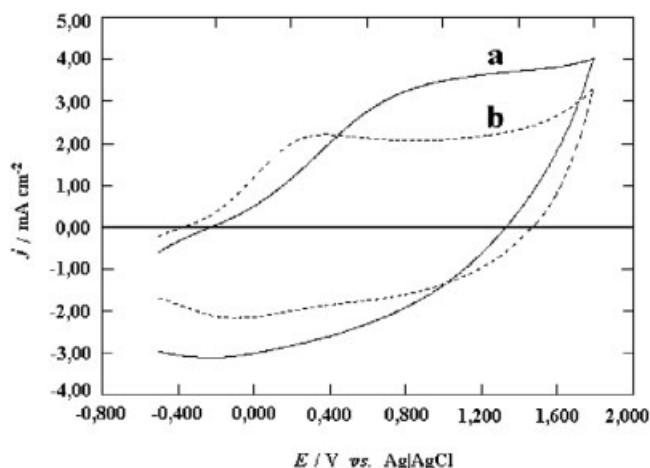


Figure 7 Cyclic voltammograms of the original sample of PEDOT (a), which was generated by CA under a constant potential of 1.40 V, and the same sample oxidized by CP (b) with a constant anodic current density of 2.50 mA cm^{-2} (initial and final potentials: -0.50 V ; reversal potential: 1.60 V ; temperature: 25°C).

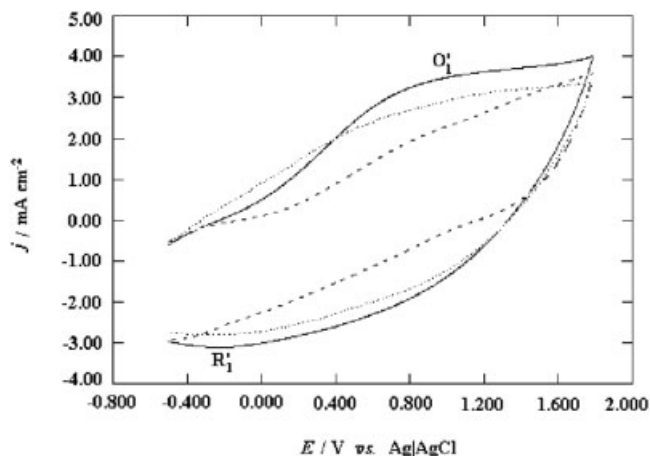


Figure 8 Cyclic voltammograms of the oxidized samples of PEDOT: PEDOT-ox1 (solid line), PEDOT-ox2 (dashed line), and PEDOT-ox3 (dotted line) (initial and final potentials: -0.50 V ; reversal potential: 1.60 V ; temperature: 25°C).

phene derivatives, PEDOT films have been generated on steel electrodes by CA. The oxidation degree of the resulting polymer has been altered using CA and CP. Samples with three different doping levels have been obtained, their electrical and electrochemical properties being characterized.

The properties of a commercial epoxy-based paint used in marine environment have been characterized by FTIR, thermal analyses, and mechanical properties evaluations. These properties remain almost unaltered upon the addition of a small amount of conducting polymer (0.2%, w/w).

Accelerated corrosion tests using NaCl solution indicated that the PEDOT oxidized by CP, PEDOT-ox3, improved the resistance against corrosion of the paint. This electroactive polymer was obtained by fixing the value of the current density to 2.5 mA cm^{-2} . The positive charge supported by each monomer unit of PEDOT-ox3 is considerably higher than that of the polymer initially generated by CA indicating that the doping level of the films obtained under a constant potential of 1.40 V can be increased considerably. Furthermore, the electrical conductivity and electroactivity of PEDOT-ox3 were also significantly higher than those of the samples oxidized by CA. These excellent properties are probably responsible of the success of PEDOT-ox3 as anticorrosive additive of epoxy-based paints.

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