Bulgarian Chemical Communications, Volume 48, Special C (pp. 27-32) 2016

Synthesis and application of conducting polymers and their nanocomposites as a corrosion protection performances

M. Ates*, N. Uludag

Department of Chemistry, Faculty of Arts and Sciences, Namik Kemal University, Degirmenalti Campus, 59030, Tekirdag, Turkey

Received August 25, 2016

Corrosion is explained as metal or alloy changes by chemical or electrochemical process or physical changes because of environmental effects. Corrosion occurs with oxidation and reduction reactions. In this study, Some general informations were given in the introduction section. And then, monomer synthesis, conducting polymers, nanocomposites, copolymers, and applications of corrosion protection performances were examined as a review article in recent papers.

Keywords: Corrosion, nanocomposites, EIS, Ag nanoparticles, copolymer.

INTRODUCTION

We introduce the some formulas, which are used in corrosion science as shown in Table 1. P is the protection efficiency (PE %) [1]. i_0 is the current density of an uncoated film, and i is the current density of the coated film. C_{corr} is the corrosion rate (CR mmy^{-1}) [2]. EW shows equivalent weight (g/eq), A is surface area (cm^2), and d represents density (g/cm^3). Similarly, corrosion rate was also calculated using the following expression

$$R_{corr} = 0.032\times i_{corr}\times M\times n\times d \, , \quad (1)$$

where i_{corr} defines corrosion current density, M is molar mass (g/mol), n represents charge number, and d is density of tested metal (g/mol). Polarization resistance (R_p) was obtained by applying the Stern-Geary formula [3].

$$R_p = (\beta_a+\beta_c)/2.303 \times i_{corr} (\beta_a+\beta_c), \quad (2)$$

where i_{corr} is corrosion current density β_a denotes Tafel slope of the anode and β_c is the Tafel slope of cathode. C_{sp} was obtained from Nyquist plot [4], which was obtained from the slope of a plot of the imaginary component (Z″) of the impedance at low frequency (f), where π=3.14, f=0.01 Hz and Z″ is the imaginary impedance.

Table 1. Some formulas are used in corrosion science.

$P= (i_0-i) / i_0 \times 100$	$C_{corr}= 0.13\times i_{corr}(EW) / A_d$
$R_{corr} = 0.032\times i_{corr}\times M\times n\times d$	$R_p= (\beta_a+\beta_c)/2.303 \times i_{corr} (\beta_a+\beta_c)$
$C_{sp}= -1/ (2\times\pi\times f\times Z'')$	$C_{dl} = 1 / IZI$

* To whom all correspondence should be sent:
E-mail: mates@nku.edu.tr

C_{dl} was obtained from Bode-magnitude plot [5], which gives the extrapolating line to the logZ axis at w=1 (logw=0).

Monomer synthesis for corrosion protection performances

Rodriquez et al [6] have studied cationic polymerization of *N*-vinylcarbazole, initiated by Ph_3C^+ AsF_6 and Ph_3C^+ PF_6 in methylane dichloride at 20 °C and 0 °C. In addition, novel coral-like polyaniline sub-micrometer particles were synthesized by chemical polymerization. The obtained conductivity of PANI can obtain 2.7 Scm^{-1} [7]. 4-methylcarbazole-3-carboxylic acid was synthesized electrochemically on a stainless steel (316L) surface with lithium perchlorate/acetonitrile as the supporting electrolyte [8]. The corrosion performance of poly(4-methylcarbazole-3-carboxylic acid) (PCz) was examined by potentiodynamic polarization curves, open circuit potentials, and electrochemical impedance spectroscopy. The results show that PCz has an effective anodic protection in corrosive test solution. 4-2(Thienyl) benzenamine (TBA) was synthesized by a simple method by Shahhosseini et al [9]. Structure of the synthesized monomer was characterized by IR, ^{1}H-NMR, GC-MS and elemental analysis techniques. The TBA monomer was electrochemically synthesized in acidic aqueous solution by CV method. The corrosion tests in 3.5 wt % NaCl solution was performed by potentiodynamic polarization test and EIS. The results of PTBA were obtained to show enhanced corrosion protection effect on stainless steel electrode compared to PANI and polythiophene. Michel et al [10] have studied to test the controlling the concrete-reinforcement interfacial conditions.

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This study focuses on the relation between macroscopic damage at the concrete-steel interface and corrosion initiation of reinforcement embedded in plain and fibre reinforced concrete.

Conducting polymers for corrosion protection performances

PANI are mostly used in corrosion protection of metals. Mostly, electropolymerization method was used to polymerize of the monomer due to its economical process [11]. It is necessary to passivate the metal before the electropolymerization method [12]. PANI has a large amount of amine and imine functional groups, which can interact with metal ions [13]. Grubac et al [14] have studied the reactive surface of Mg alloy which was coated with the nontoxic biocompatible polypyrrole film synthesized by electrochemical oxidation from an aqueous salicylate solution. The chemical polymerization of polyaniline (PANI) on cellulose fiber is used for various applications [15]. PANI by itself has poor mechanical properties but, by incorporation of micro or nanoparticles, its physical properties can be improved. The cellulose / PANI composite combines the properties of cellulose and conducting polymer of PANI, having application in corrosion protection of metals [16, 17]. Polyaniline (PANI), Polypyrrole (PPy) nanofilms, PANI/TiO_2 and PPy/TiO_2 nanocomposites were synthesized electrochemically on Al1050 electrode [18]. Perrin et al [19] have synthesized PANI dispersions consisting of 270 to 380 nm sized particles which were obtained by oxidation with ammonium peroxydisulfate (APS) in n-dodecylphosphonic acid (DPA) micellar solutions.

Bilal et al [20] have reported a sophisticated emulsion polymerization route for the synthesis of PANI. They work with two dopants i.e., dodecylbenzenesulfonic acid (DBSA) and sulfuric acid (H_2SO_4). Potentiodynamic measurements show that coatings of PANI can supply extra ordinary resistance to the steel surfaces particularly against the harsh corrosive environment of the oceans. In literature, a novel polyurea containing oligoaniline pendants (PU-p-OA) was synthesized by one step reaction way [21]. The inhibition effect of the electroactive PU-p-OA coatings on the cold rolled steel (CRS) in 5 wt % sodium chloride solution was examined by Tafel plot analysis and EIS method. Düdükcü et al have prepared poly(5-nitroindole)(P5NI) on 316L stainless steel (SS) [22]. P5NI coating against SS corrosion was studied in 3.5% NaCl solution by EIS, anodic polarization and the open circuit potential time (E_{ocp}-t) diagrams. Billaud and co-worker [23] and Xu et al [24] studied the tests of polymerization of 5-nitroindole and showed that poly(5-nitroindole) films have easily electrodeposited by direct anodic oxidation of 5NI when certain conditions were applied. Polyaniline doped a phosphomolybdic acid was synthesized on stainless steel (SS304) by electropolymerization method [25]. The corrosion resistance of the coating was used in 1 M H_2SO_4 solution by electrochemical methods.

Recently, the inorganic materials added to the PPy coatings improved the mechanical and barrier properties of the coatings as corrosion inhibitor hosts [26-28]. Lei et al [29] have studied the polypyrrole films which were deposited on copper from “green” inhibitor of phytic acid solution for corrosion protection of copper. As a result, PPy coating prepared in the phytic acid solution at pH 4 show the most protective property against copper solution. Corrosion protection behaviour of poly(*N*-methylpyrrole) coated steel was examined in 0.5 M HCl solution by potentiodynamic polarization and EIS methods [30]. The results indicate that the P(NMPy)-DS coating supply effective protection for the stainless steel against to corrosion because of the fact that the large negatively charged dodecyl sulphate dopant in the polymer structure electrostatically repels corrosive chloride ions and delays their access to metal surface. A novel electroactive hyperbranched poly(aryl-ether keton) with oligoaniline segments has been synthesized by K_2CO_3-mediated nucleophilic aromatic polycondensation [31].

In literature, polycarbazole, polycarbazole/ nanoclay and polycarbazole/Zn nanoparticles were chemically and electrochemically synthesized on a stainless steel (SS304) electrode [32]. The modified films was performed on SS304 by open circuit potential monitoring, potentiodynamic polarization and electrochemical impedance spectroscopic measurements to test the corrosion protection efficiency against 3.5 % NaCl solution. The highest protection efficiency (PE= 99.81%) was found for chemically synthesized PCz films. In literature, carbazole and *N*-vinylcarbazole were electrochemically polymerized in copper electrode and corrosion ability was studied in 0.5 M NaCl solution [33]. Strong adherent electro-active polymer films of poly(*N*-vinylcarbazole) (PVCz) and its nanocomposites with P(VCz)/nanoclay and P(VCz)/Zn nanoparticle have been electrodeposited on stainless steel (SS304) by chronoamperometric method using 0.3 M oxalic acid/butanol solution [34]. Conducting polymers have been extensively studied as protection for corrosion of metals in recent years. Previous research on the corrosion protective properties of some conducting polymers is listed in Table 2.

Düdükcü et al [40] have studied the use of electrochemically synthesized polyindole (PIN) film, which was investigated for protective coating on 304 stainless steel. Corrosion tests demonstrated that PIN coating had important barrier effect to SS for significant immersion times in aggressive medium.

Thiophene, 3-hexylthiophene and its nanocomposites with TiO_2 were electropolymerized on Al1050 electrode by chronoamperometric technique [41]. Tüken et al [42] have electropolymerized poly(thiophene) on nickel coated mild steel (MS) electrode, in $LiClO_4$ containing acetonitrile medium (ACN-$LiClO_4$). The nickel coating showed like a physical barrier and supplied some protection to MS against corrosion. The corrosion behaviour of PPy/PTh film coated copper was tested in 3.5% NaCl solution [43]. EIS, anodic polarization curves and open circuit potential-time (E_{OCP}-t) diagrams were examined. The PPy/PTh coating provides important protection against copper corrosion for considerable immersion times. Silva et al [44] have studied the effect of thermal annealing of poly(3-octylthiophene) (P3OT) coatings on the corrosion inhibition of stainless steel in an NaCl solution.

Nanocomposites for corrosion protection performances

Poly(vinylacetate) (PVAc) coating over carbon steel was prepared by addition of emulsion nanoparticles in different concentrations (1%, 2% and 1.5%) in PVAc [45]. 2% of PANI/TiO_2 nanocomposite in PVAc has the best corrosion protection in HCl. The growth of conducting polymers in the interlayer region of the clays has shown to dramatically improve the properties of conducting polymers [46]. Polypyrrole / Ni organic-inorganic hybrid materials were synthesized by electrochemically on carbon steel (AISI 1018) by combining potentiostatic and potentiodynamic methods [47]. Ashassi-Sorkhabi et al [48] have studied the effect of co-incorporation of a kind of nanomaterials and organic additives in a polymer matrix coating on corrosion performance of St-12 steel. Sonoelectrochemically the PPy, PPy-chitosan, PPy/MWCNTs and PPy/MWCNTs/chitosan films were studied on the base alloy.

The results show that PPy/MWCNTs/chitosan nanocomposite coating shows better corrosion protection than others. Valença et al [49] have synthesized polypyrrole/Zn nanoparticles hybrid nanocomposites and used them as additives in an epoxy paint to protect SAE 1020 carbon steel from corrosion.

Alhummade et al [50] have investigated the polyetherimide-graphene composites (PEI/G) which is used in corrosion inhibition coatings on copper substrates. In literature, a soluble terpolymer of aniline, 2-pyridylamine (PA) and 2,3-xylidine (XY), poly(AN-co-PA-co-XY) and its nanocomposite with ZnO nanoparticles were chemically synthesized by oxidative polymerization method with ammonium persulfate as an oxidant [51]. Polyaniline (PANI) and its nanocomposites containing TiO_2, Ag and Zn nanoparticles were electrocoated on an Al1050 electrode by cyclic voltammetry [52].

Table 2. Corrosion properties of some conducting polymer films obtained from literature.

Polymer	Measurement Technique	Solution	Results
PPy	Impedance spectroscopy	H_2SO_4	PPy doesn't provide anodic protection of mild steel electrode. After short immersion time, PPy has in contact with H_2SO_4 become undoped [35, 36].
PANI	Tafel extrapolation	H_2SO_4	Corrosion of copper electrode occurs for synthesis from aniline in presence of H_2SO_4 or from aniline sulphate without using H_2SO_4 in the reaction medium [37].
PPy	Potentiodynamic method	H_2SO_4	The corrosion resistance of the substrates was reduced after longer immersion times [38].
PTh	EIS and anodic polarization curves	$LiClO_4$/ACN	PTh top coat was improved the barrier efficiency and anodic polarization curves [39].

Copolymers for corrosion protection performances

Govindaraju et al [53] have studied the corrosion performance of zinc modified poly(aniline-co-pyrrole) coatings in 1 M HCl solution, using potentiodynamic polarization and EIS techniques. The interfacial co-polymerization of aniline and m-aminobenzene sulfonic asit in the presence of Cloisite 30B was performed in Sc-CO_2/water to produce the SPANI-clay nanocomposites [54]. Ozyilmaz et al [55] have studied zinc-iron-cobalt (ZnFeCo) particles which were electrochemically deposited on carbon steel (CS) electrode applying current of 3 mA with chronoamperometric technique. They have studied poly(aniline-co-o-anisidine), poly(aniline-co-pyrrole), poly(aniline-co-*N*-methylpyrrole) and poly(o-anisidine-co-pyrrole) copolymer coatings in 3.5% NaCl solution which was investigated by using AC impedance spectroscopy (EIS) technique, anodic polarization and the E_{OCP}-time curves. As a result, copolymer films showed important physical barrier on ZnFeCo plated carbon steel, in longer exposure time. In addition, poly(aniline-co-o-bromoaniline) copolymer has been synthesized using chemical oxidation method in HCl medium [56]. The electrical conductivity of the copolymers is found in the range of 10^{-5} Scm^{-1}. These organic semiconductor materials are used in optoelectronic devices that will replace the conventional inorganic semiconductors. Raotole et al [57] have studied poly(aniline-co-anisidine) (PAOA) coatings, which were used as corrosion protection on mild steel. The results of the potentiodynamic polarization measurements indicated that the PAOA coatings had more effective corrosion protection to mild steel than the respective homopolymers. Gopi et al [58] have studied the electrochemical synthesis of poly(indole-co-thiophene) copolymer on low-nickel stainless steel (LN-SS) with CV method in acetonitrile medium containing lithiumpercholarate. As a result, a 1:1 ratio of indole to thiophene obtained the most stable and corrosion protective copolymer coating. Gopi et al [59] have studied the methacrylate based copolymers which have been synthesized by free radical solution polymerization technique from different mole ratios of *N*-vinylcarbazole and glycidyl methacrylate.

Apptication of corrosion protection performances

There are many metals, such as iron and its alloys which widely used in corrosion resistance in various neutral and aggressive environments [60, 61]. Polycarbazoles have been used in many areas, such as electroluminescent devices, sensors, redox catalysts, and electrochromic displays [62-64]. Lei et al [65] have studied the effect of benzotriazole addition on polypyrrole film formation on copper and its corrosion protection. In 400 h of immersion, copper dissolution was protected with 80% inhibition efficiency relative to that of bare copper. Aravindan et al [66] found that after 300 h of immersion period, the Cu-PPy coating prepared from a solution containg 1:4 water to methanol volume ratio showed a better corrosion protection to SS than coatings prepared from other compositions.

Magnesium and its alloys are used in the applications, such as aerospace and automotive industry because of their excellent properties, such as high damping capacitiy, castability, weldability and recyclability [67]. The big problem is to have their high corrosion susceptibility [68, 69]. Electrochemically synthesized PPy coating on AZ31 magnesium alloy in a solution containing sodium salicylate and monomer of pyrrole through CV technique. Ma et al [70] have investigated the mechanism for localised corrosion in AA 2029-T83 alloy during immersion in 3.5 % NaCl solution. A model is suggested to explain the development of the localised corrosion in the alloy by taking into account heterogeneous plastic deformation during cold working and preferential precipitation of T1 phase at crystallographic defects within deformed grains. Polymer alloys show excellent coating properties. Palraj et al [71] have studied the corrosion resistant interpenetrating polymer networks (IPNs) were synthesized from immiscible resins (epoxy, silicone and thiophene).

CONCLUDING REMARKS

In this review article, new synthesis of monomers, polymers, nanocomposites and copolymers have used for corrosion protection on potential usefulness of other cheap metals or alloys in various medium. New monomer synthesis and new conducting polymer or nanocomposites or copolymer synthesis are important effect for corrosion synthesis are important effect for corrosion protection. Therefore, we analyze which material affect to this process.

Acknowledgments: *Authors acknowledges to Namik Kemal University for financial support at 2^{nd} AIOC ICNTC 2016 Conference in Zagreb, Croatia.*

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