



Polyaniline nanotubes: Facile synthesis, electrochemical, quantum chemical characteristics and corrosion inhibition efficiency



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ABSTRACT

This work represents the preparation of polyaniline in its free and self-doped forms. The polymers were formed as nanotubes using template free self-curling preparation. Chemical oxidation polymerization of aniline and 4-aminobenzene sulphonic acid individually as monomers was carried out without adding acids or templates. The electron microscope image of the polymer reveals the nano-tubular structure with inner diameter of 20–30 nm and outer diameter of 80–100 nm. Quantum chemical calculations of the repeating units were calculated to correlate the chemical structure to the mechanism of inhibition. The corrosion inhibition behavior of the polymers in 1 M HCl has been evaluated using Tafel's extrapolation method and electrochemical impedance spectroscopy (EIS). Self-doped polyaniline showed the greater inhibition efficiency compared with un-doped polyaniline. Results of electrochemical impedance and Tafel's polarization measurements consistently showed that both compounds can be effectively used as corrosion inhibitors.

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1. Introduction

Polyaniline (PANI) is one of the highly promising polymers due to its low cost, ease of preparation, good thermal and electrical properties, environmental stabilities, and versatile applications [1]. It possesses exceptional structural properties due to the inception of nitrogen heteroatom between the phenyl rings along the polymer backbone. Polyaniline can be synthesized for specific applications like rechargeable batteries, biosensors, corrosion protection materials, organic electronic materials. Additionally, polyaniline (PANI) possesses a large amount of amine and imine functional groups, which can interact with metal ions [2]. Moreover, nano-scale materials with large specific surface areas are expected to have higher efficient coverage of metal surfaces than the regular scale ones. Polymeric nanotubes are an alternative material to better-explored traditional materials, showing advantages such as easy synthetic access and good uniformity and dispersion, predefined unexpected physical and electrical properties depending on their chemical composition and fiber, tubular or needle-like morphology. They are therefore promising candidates for some targeted applications.

Acids are widely used in industries such as pickling, cleaning, descaling *etc.* Because of their aggressiveness, inhibitors are applied to reduce the rate of unexpected metal dissolution [3,4]. Organic compounds rich in hetero atoms such as nitrogen, the unsaturated bonds, and the plane conjugated systems including all kinds of

aromatic cycles have been reported as effective inhibitors [5,6]. In the past few years, conducting polymers have been recognized as excellent corrosion inhibitors for metals in corrosive environment [7,8]. Polyaniline (PANI) has been considered as a hot topic of intensive research due to its unique characteristics [6–12]. In the present work, a facile synthesis method and a comparison between the inhibitive behavior of polyaniline nanotubes and self-doped poly aminobenzene sulphonic acid nanotubes are reported to study the inhibition performance of new synthesized polymer on steel in 1 M HCl solution using, electrochemical techniques. Correlations were attempted to correlate the theoretical parameters and the electronic properties of the studied molecules and their effect on the inhibition efficiency.

2. Experimental

2.1. Materials

Aniline (Merck) was purified by vacuum distillation before polymerization. All other reagents are of analytical grade and were used without further purification. The aggressive solution, 1 M HCl, was prepared by dilution of analytical grade, 37% HCl with distilled water. All solutions were prepared using distilled water.

2.2. Chemical oxidation polymerization of aniline and amino-benzene sulphonic acid

Polyaniline powder was synthesized through oxidation polymerization. Briefly, 5.0 g (0.054 mol) freshly distilled aniline (or amino

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benzene sulphonic acid) was mixed with 80 ml deionized water. The mixture was stirred for 10 min before cooling below 5 °C for 60 min. 0.054 mol potassium persulphate dissolved in deionized water was added to the monomer solution under low temperature vigorous stirring. After addition of the oxidant, the mixture was further stirred for a period of 60 min and left unstirred overnight at low temperature (0–5 °C). The precipitated polymer (dark powder) was filtered and extensively washed with deionized water until the washing liquid was colorless. In case of self-doped polyaniline, the product was water soluble and was precipitated in acetone, filtered, washed several times with acetone and finally dried at 50–60 °C in a vacuum oven, powdered in a mortar and stored until use. Polyaniline will be referred to as PANI while polyaminobenzene sulphonic acid will be referred to as self-doped PANI.

2.3. Characterization of the prepared polymers

FT-IR spectra were recorded on a Nicolet Is-10 FT-IR Thermo Fisher Scientific spectrometer. The samples were characterized by powder X-ray diffraction (XRD) using a Philips X'Pertpro Pan-analytical instrument. Data was taken for the 2θ range of 10–100° with a step of 0.02°. High Resolution Transmission Electron Microscopy (HR-TEM) imaging was performed using a Jeol-JEM Japan 2100 operating at 200 kV, the sample for TEM was prepared by sonication for sample in ethyl alcohol and depositing onto a copper coated carbon grid and then let the solvent to evaporate.

2.4. Quantum chemical calculations

The molecular parameters were carried out based on MINDO3 semi-empirical method ever used for organic inhibitors calculation [13] at an Unrestricted HartreeFock (UHF) level which are implemented in Hyperchem 8.0. The molecule 2D sketch was obtained by ISIS Draw 2.1.4.

2.5. Electrochemical techniques

Carbon steel working electrode of the following chemical composition was used as the metal to be protected: 0.07% C, 0.24% Si, 1.35% Mn, 0.017% P, 0.005% S, 0.16% Cr, 0.18% Ni, 0.12% Mo, 0.01% Cu and the remainder is Fe. A pre-treatment was carried out prior to each experiment, in which specimen surface was mechanically ground with 400, 600, 800 and 1000 emery paper, washed with acetone and bi-distilled water then dried and put into the cell [14]. The electrochemical measurements were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4) under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. All potentials given in this study were referred to this reference electrode. After measuring the E_{ocp} , the electrochemical measurements were performed. The polarization curves were obtained in the potential range from –800 to –300 mV (SCE) with a 2 mV/s scan rate.

The corrosion inhibition efficiency (η_p) was calculated using the following equation [15,16]:

$$\eta_p = \left(\frac{i_{corr} - i_{corr}^0}{i_{corr}} \right) \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr} are the corrosion current density values with and without inhibitor, respectively, which determined by extrapolation of the cathodic and anodic Tafel lines to the respective free corrosion potential.

2.6. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were carried out as described elsewhere [17]. A small alternating voltage perturbation (5 mV) was imposed on the cell over the frequency range of 100 kHz to 30 mHz at open circuit potential.

2.6.1. The inhibition efficiency (η_1)

The corrosion inhibition efficiency (η_1) was calculated from the values of R_{ct} using the following equation [18,19]:

$$\eta_1 = \left(\frac{R_{ct}^0 - R_{ct}}{R_{ct}^0} \times 100 \right) \quad (2)$$

where R_{ct}^0 and R_{ct} are the charge transfer resistance values in the presence and absence of the inhibitor, respectively.

2.6.2. The double layer capacitance (C_{dl})

The double layer capacitance (C_{dl}) was calculated from the following equations [20,21]:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (3)$$

where, f_{max} is the frequency at maximum imaginary component of the impedance. The Helmholtz model equation [22]:

$$\delta_{org} = \frac{\epsilon \epsilon_0 A}{C_{dl}} \quad (4)$$

where ϵ is the dielectric constant of the medium, ϵ_0 is the vacuum permittivity, A is the electrode surface area, and δ_{org} is the thickness of the protective layer.

3. Results and discussion

3.1. Self-curling, chemical oxidation polymerization of PANI and self-doped PANI

Among different methods of Polyaniline synthesise, the chemical oxidation is the widely used most prominent one. The chemical oxidation polymerization is practically viable due to feasibility of synthesis mechanism and low cost production.

Powder nanotubes of PANI and self-doped PANI were prepared successfully using oxidation polymerization method which demonstrated that it is not essential for successful polymerization to have no substitution in the p-position to the amino group. Thiemann and Brett [23] found the same results when they studied the oxidation polymerization of both 2-amino benzene sulphonic acid and 4-amino benzene sulphonic acid. Fig. 1 shows the FT-IR spectrum of the prepared materials.

PANI and self-doped PANI nanotubes have similar basic backbone structural peaks [24].

The FT-IR of the backbone structures of PANI and self-doped PANI nanotubes are basically similar [24]. The main typical bands are assigned as follow; the bands at 829 and 1145 cm^{-1} are due to the aromatic C–H in-plane bending and the out-of-plane deformation of C–H in the disubstituted benzene ring. The C–H out-of-plane bending vibrations band from a para-substitution pattern at 829 cm^{-1} and the N Q N absorption peak at 1145 cm^{-1} (with Q representing the quinoid ring) indicate the head-to-tail coupling of aniline monomers [25]. The main chain characteristic bands at 1507 and 1588 cm^{-1} was attributed to the C=N and C=C stretching modes for the quinoid and benzenoid rings, respectively. Bands at 1300 and 690 cm^{-1} can be assigned to C–N stretching of the secondary aromatic amine and aromatic C–H out-of plane bending vibrations, respectively. The broad bands in the range of 3000–3500 cm^{-1} correspond to secondary amine stretching (N–H) vibrations [26]. For self-doped PANI nanotubes, beside the characteristic peaks, the bands at

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