

Synthesis and Electrochemical Characterisation of Novel Hybrid Copper / Poly (diphenylamine) (PDPA) Nanocomposites

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Abstract: The Poly (diphenylamine) (PDPA) nanoparticles was synthesized by surfactant assisted dilute polymerization method and characterized by UV-Visible, FTIR and Cyclic Voltammetry techniques. The PDPA nanoparticles were then suspended in an acidified copper sulphate electrolytic bath to prepare Cu-PDPA nanocomposites by simple electrodeposition technique. The XRD analysis revealed that the crystallite structure of Cu-PDPA nanocomposites and pure copper coatings was crystalline fcc and the grain size was 32 nm for pure Cu and 27 nm for Cu-PDPA nanocomposites. This decrease in crystallite size of Cu-PDPA nanocomposites shows the inclusion of PDPA nanoparticles was uniformly distributed throughout the copper matrix. The microstructure of the Cu-PDPA nanocomposites was examined by SEM analysis shows cauliflower like crystallites with layer by layer outward growth compared to electrodeposited pure copper coatings. The Electrochemical AC impedance and Tafel polarization studies were performed for electrodeposited copper and Cu-PDPA nanocomposites in 3.5% NaCl solution. It revealed that the Cu-PDPA nanocomposite coatings were found to be more corrosion resistance than electrodeposited pure copper coating.

Keywords: Cu-PDPA Nanocomposites, Poly (diphenylamine) (PDPA) nanoparticles, Electrodeposition, Corrosion resistance.

I. INTRODUCTION

In the recent years, there are numerous research works are concerted on developing metal matrix nanocomposite (MMNC) coatings with particulates, fibers and polymers as second phase reinforcement materials because of their exceptional mechanical, tribological and anti-corrosion properties and their potential engineering applications. Some of the characteristic features of these nanocomposite coatings are improved wear resistance, corrosion resistance, micro hardness and strength compared to pure metals or alloys [1-12]. Particularly, the development of novel metal / polymer nanocomposites has received considerable attention because of its variety of engineering applications. The polyaniline group of conducting polymeric materials has received ample attention because of its simple method of preparation and their electrical, electrochemical and optical properties. Furthermore, the poly (diphenylamine) (PDPA) is

found to be a suitable material for the composite material preparation due to their characteristic properties different from polyaniline (PANI) [13-21].

In the present study, our aim is to prepare a novel hybrid metal / polymer nanocomposite material of Cu-Poly (diphenylamine) (PDPA) nanocomposites by simple and low cost electrodeposition method and the prepared nanocomposites are to be characterized for its mechanical and anticorrosive properties. The electrodeposition technique is an exceptional method for the synthesis of metals, alloys, metal matrix nanocomposites and metal-polymer nanocomposite coatings etc. [1][3][6][9][17]. The advantage of the electrodeposition technique is simple, low temperature technique with industrial applicability.

The objectives of the present work is, (i) To prepare Poly (diphenylamine) polymer by surfactant assisted dilute polymerization method and to characterize the polymer by UV-Visible, FTIR and Cyclic Voltammetry techniques. (ii) To prepare Cu-Poly(diphenylamine) nanocomposites by electrodeposition technique, by suspending the poly (diphenylamine) nanoparticles in the acid copper electrolytic bath and to characterize the Cu-PDPA nanocomposites and pure copper by XRD, SEM, EIS and Tafel polarization techniques to study the structure, microstructure and corrosion resistance properties.

II. EXPERIMENTAL

A. Synthesis of Poly (diphenylamine) (PDPA) Nanoparticles

To the stirring solution of 0.1M diphenylamine monomer in water, 4M sulphuric acid is added to till the complete dissolution of DPA monomer. After the complete dissolution of DPA monomer, 0.005M concentration of surfactant CTAB (cetyltrimethylammonium bromide) is mixed with it and the freshly prepared 0.4M solution of ammonium persulphate is added in drop wise manner to the stirring solution for the duration of 2 hrs. A dark green colored product of poly (diphenylamine) (PDPA) polymer thus obtained is filtered and washed with water and dried [22-25].

B. Preparation of Cu-Polydiphenylamine (PDPA) Nanocomposites

The Cu-PDPA nanocomposite was prepared by suspending the poly (diphenylamine) nanoparticles in an acidified

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copper sulphate bath by DC electrodeposition method.

The bath composition for the electrodeposition of Copper and Cu-PDPA nanocomposites was $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.3M) and H_2SO_4 (1.3M). The concentrations of the poly(diphenylamine) (PDPA) nanoparticles in various baths are 1 g/l, 3 g/l, 5 g/l and 10 g/l. Stirring was applied in each bath during the electrodeposition process to enhance the uniform deposition of PDPA nanoparticles. The Cu-PDPA nanocomposite coatings of $\sim 60 \mu\text{m}$ in thickness were deposited on the copper substrate (cathode) of 4.0 cm^2 surface area. A pure copper bar was used as the anode material for deposition process. The gelatin was used (1.0 g/l) as additive in the electroplating bath solution to get smooth, pore-free and fine grained deposits. The electroplating was carried out by the applied current density of 5.0 A/dm^2 with the pH of ~ 1 at room temperature ($\sim 30^\circ\text{C}$). The electrodeposited pure copper coatings (without PDPA nanoparticles) were also obtained under the same conditions from the acid copper sulphate bath at 30°C [1][3][6][9][17].

III. RESULTS AND DISCUSSIONS

The Poly (diphenylamine) (PDPA) was synthesized by surfactant assisted dilute polymerization method and it was characterized by spectroscopic and cyclic voltammetric techniques.

A. Characterization of Poly (diphenylamine) (PDPA) Polymer

1. UV-Visible Spectral Studies

The UV-Visible absorption spectrum for the synthesized poly (diphenylamine) (PDPA) polymer was taken by Shimadzu UVPC-2401 UV-Visible spectrophotometer is shown in Fig. 1. In the UV-Visible spectrum (Fig. 1), the presence of absorption peak at 337 nm corresponds to the $\pi-\pi^*$ transition in the benzenoid ring.

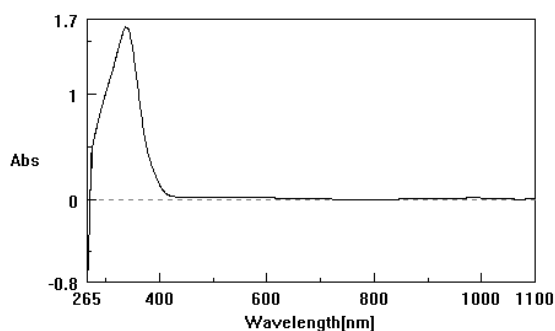


Fig. 1. UV-Visible spectrum for poly(diphenylamine) (PDPA) polymer.

2. FTIR Analysis

The FTIR spectrum of Poly (diphenylamine) was taken with KBr pellets using Perkin Elmer FTIR spectrophotometer (Fig. 2). A small peak at 3385 cm^{-1} indicates the N-H stretching vibration mode. The bands at 1596 cm^{-1} and 1646 cm^{-1} were assigned to N-H bending of 1° amines. The band at 1316 cm^{-1} is due to C-N stretching vibration of aromatic

amine. A small peak observed at 747 cm^{-1} shows the presence of phenyl groups.

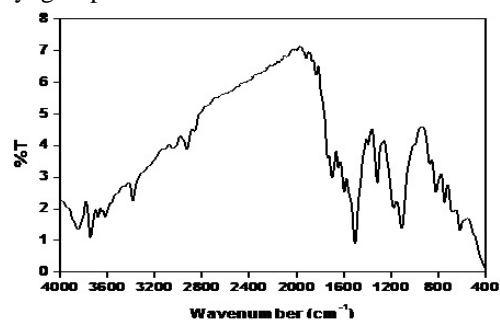


Fig. 2. FTIR Spectrum of Poly (diphenylamine) (PDPA) polymer.

3. Cyclic Voltammetry Studies

The cyclic voltammogram of poly (diphenylamine) (PDPA) polymer was recorded by using BAS 100W electrochemical analyzer. The cyclic voltammogram of poly (diphenylamine) was recorded by scanning the potential between 0 and +1.3 V at a sweep rate of 100 mV/s using the dip coated electrode in the background electrolyte of $0.1 \text{ M H}_2\text{SO}_4$. Two peaks are found in the anodic side centered on 0.57 V and 0.78 V. The oxidation peaks may be due to the oxidation of the amine moiety present in the polymeric backbone. In addition, a cathodic peak is obtained around 0.46 V representing the subsequent reduction of the oxidized species. The electrochemical response recorded for the synthesized polymer is well in accordance with the literature reports (Fig. 3).

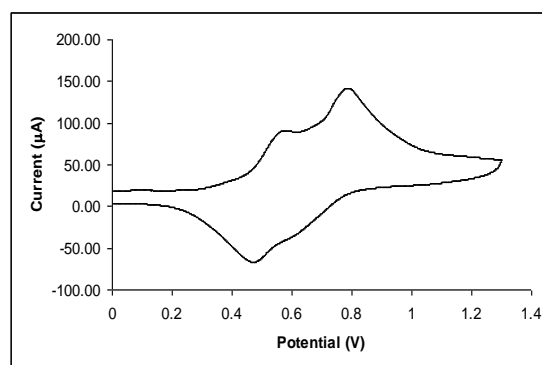


Fig. 3. Cyclic Voltammogram for Poly (diphenylamine) (PDPA) polymer.

B. Characterization of Cu-PDPA Nanocomposites

1. XRD Analysis

The XRD patterns for the electrodeposits of copper and Cu-PDPA nanocomposites are shown in Fig. 4(a & b). By using the Debye-Scherrer formula the average grain size was measured and it was $\sim 32 \text{ nm}$ for Cu and $\sim 27 \text{ nm}$ for Cu-PDPA nanocomposite coatings. Both the samples of pure Cu and Cu-PDPA nanocomposites, shows the structure of crystalline fcc (face-centered cubic) and the preferred orientation of (111) plane, which is matched and confirmed from the JCPDS

reference. This decrease in the average grain size of Cu-PDPA nanocomposites shows the enhanced mechanical and anti-corrosion properties.

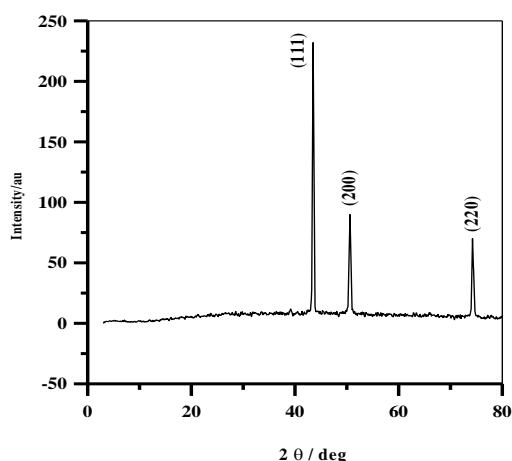


Fig. 4(a).

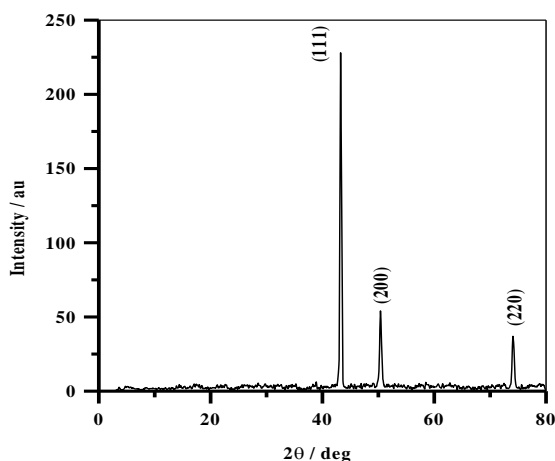


Fig. 4(b).

Fig. 4. XRD Patterns of electrodeposits (a) Pure Cu, (b) Cu-PDPA (5 g/l) nanocomposite.

2. Corrosion Resistance Measurements

2.1. Electrochemical AC Impedance Spectroscopy (EIS) Analysis

The anti-corrosion property of the Cu-PDPA nanocomposites and pure copper electrodeposits were tested in electrochemical impedance spectroscopy (EIS) and Tafel polarization techniques using a three electrode cell setup. The electrodeposited samples of 1.0 cm² area was used as the working electrode, the saturated calomel electrode (SCE) was used as reference electrode and the platinum wire is used as auxiliary electrode. These three electrodes are immersed in 3.5% NaCl solution to record the Nyquist plot. From the Nyquist plots (Fig. 5(a&b)), the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) values are measured and are presented in the Table 1. The charge transfer resistance (R_{ct}) values for Cu-PDPA nanocomposite coating was increased with increasing PDPA nanoparticle content in the Cu-PDPA nanocomposites and the double layer capacitance (C_{dl}) values was decreased compared to

electrodeposited pure copper coatings (Table 1). It revealed that Cu-PDPA nanocomposite coatings were more corrosion resistance than the electrodeposited pure copper in 3.5% NaCl solution (Fig. 5(a&b)).

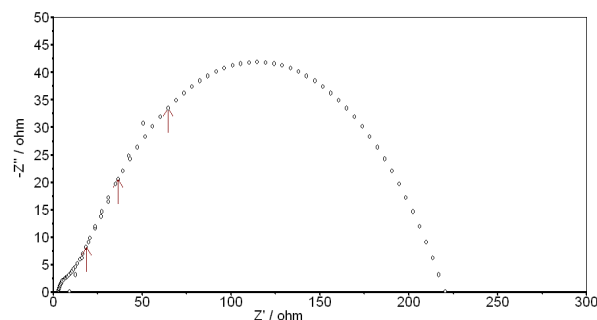


Fig. 5(a)

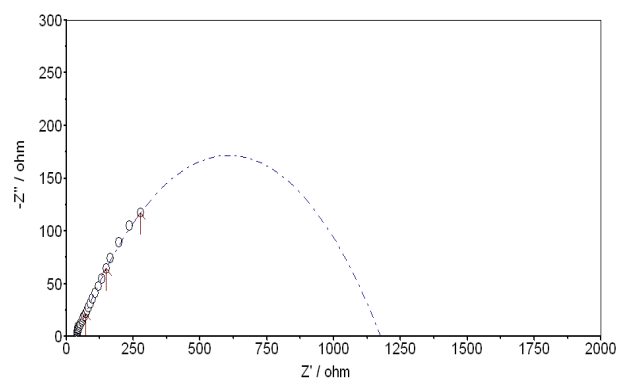


Fig. 5(b)

Fig. 5(a&b). Nyquist plots for the electrodeposits (a) Copper (b) Cu-PDPA (10 g/l) Nanocomposite.

Table 1. Impedance parameters derived from the Nyquist plots for the electrodeposits of Copper and Cu-PDPA nanocomposites.

Electrodeposits	PDPA content in gpl	R_{ct} (Ω/cm^2)	C_{dl} ($\mu F/cm^2$)
Copper	0	220	53.07
Cu-PDPA nanocomposite	1	540	31.22
Cu-PDPA nanocomposite	3	650	26.53
Cu-PDPA nanocomposite	5	950	22.74
Cu-PDPA nanocomposite	10	1200	12.24

2.2. Tafel Polarization Studies

The corrosion potential (E_{corr}), the corrosion current (i_{corr}), tafel slopes b_a & b_c and the corrosion rate for the electrodeposited pure copper and Cu-PDPA nanocomposites were measured from the Tafel polarization curves (Fig. 6) and the results are presented in Table 2.

The corrosion current (i_{corr}) was decreased for all the Cu-PDPA nanocomposite coatings compared to electrodeposited pure copper. The corrosion rate was decreased gradually for all the Cu-PDPA nanocomposites compared to electrodeposited pure copper.

It indicates that the Cu-PDPA nanocomposites were more corrosion resistance than the electrodeposited pure copper in 3.5% NaCl solution (Table 2).

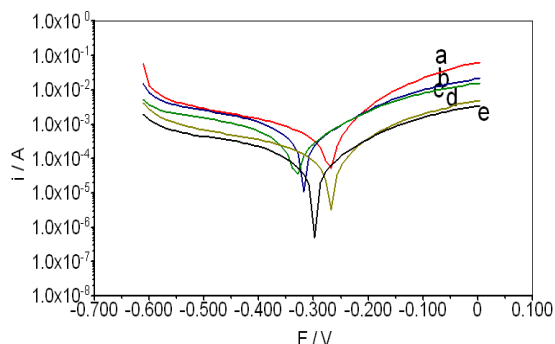


Fig. 6. Tafel plots for the electrodeposits (a) Copper, (b) Cu-PDPA (1 g/l), (c) Cu-PDPA (3 g/l), (d) Cu-PDPA (5 g/l), (e) Cu-PDPA (10 g/l) nanocomposites.

Table 2. Tafel parameters for the electrodeposits of Copper and Cu-PDPA nanocomposites.

Electrodeposits	PDPA content in gpl	E_{corr} (V) vs SCE	i_{corr} ($\mu A/cm^2$)	Corrosion rate / mm year ⁻¹
Pure Cu	0	-0.269	101.6	1.178
Cu-PDPA nanocomposite	1	-0.332	88.79	1.029
Cu-PDPA nanocomposite	3	-0.318	20.14	0.2335
Cu-PDPA nanocomposite	5	-0.285	7.45	0.0863
Cu-PDPA nanocomposite	10	-0.270	2.22	0.0257

3. Scanning Electron Microscopy (SEM) Analysis

The microstructure of the Cu-PDPA nanocomposites and copper electrodeposits was examined by SEM analysis is shown in Fig. 7(a & b).

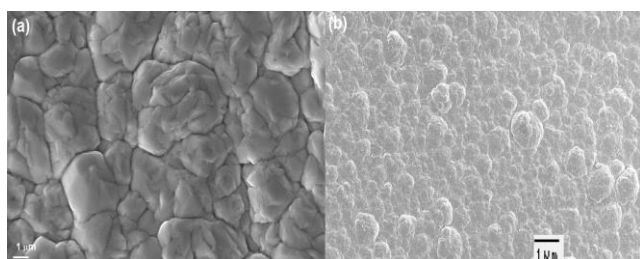


Fig. 7. SEM images of electrodeposits (a) Pure Cu, (b) Cu-PDPA nanocomposites.

The Pure copper (Fig. 7(a)) shows smooth surface with uniform copper crystallites compared to Cu-PDPA nanocomposites (Fig. 7(b)). The Cu-PDPA nanocomposite

shows uniform distribution of poly (diphenylamine) (PDPA) nanoparticles with cauliflower like crystallites with layer by layer outward growth on the copper matrix (Fig. 7(b)).

IV. CONCLUSIONS

- The Poly (diphenylamine) (PDPA) nanoparticles was synthesized by surfactant assisted dilute polymerization method and it is used for the preparation of Cu-PDPA nanocomposite coatings by simple and low temperature electrodeposition technique.
- The crystallite structure and the average grain size of the electrodeposits of copper and Cu-PDPA nanocomposites were measured by XRD analysis. The average grain size calculated by using Scherrer equation was ~32 nm for copper and ~27 nm for Cu-PDPA nanocomposites and the structure was crystalline fcc for both the electrodeposits of pure Cu and Cu-PDPA nanocomposites.
- From the SEM analysis, the surface morphology of the Cu-PDPA nanocomposite coatings showed cauliflower like crystallites with layer by layer outward growth compared to pure copper coatings.
- The Electrochemical impedance spectroscopy (EIS) and Tafel polarization studies confirmed that the Cu-PDPA nanocomposites found to be more corrosion resistance than the electrodeposited copper coatings in 3.5 % NaCl solutions.

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