Synthesis and Characterization of Water-Dispersible Colloidal Polyaniline for Corrosion Inhibition of Mild Steel in Acidic Solution

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Abstract

We report the colloidal nanostructure polyaniline which is extremely water-dispersible and easily synthesized chemically from aniline with commonly used handwash solution (Sunlight^{TM}) as a stabilizing agent. The dispersion colloids of polyaniline exhibit multiple color changes from orange-yellow to dark-green during the progress of polymerization reaction. The as-synthesized polyaniline polyaniline is highly dispersed in aqueous medium for more than 90 days. The UV-vis spectrum of this polyaniline has shown three prominent peaks at 355 nm, 431 nm and 771nm assigned to π-π* transition in the benzenoid ring, second and third peaks are related to doping and polarons respectively. The anti-corrosion studies of water-dispersible polyaniline adsorbed on mild steel exposed to 0.1M HCl solution were performed by potentiodynamic polarization and electrochemical impedance spectroscopy. It has been found that water-dispersible polyaniline is more efficient inhibitor since it showed higher corrosion inhibition efficiency than the monomer, whereas the monomer alone accelerated the rate of corrosion. The maximum corrosion inhibition efficiency of 92.35 % has been evaluated using corrosion current density.

Keywords: Water-dispersible polyaniline, potentiodynamic polarization, Impedance spectroscopy.

Introduction

Polyaniline (PANI) is the conjugated conducting polymer which has been extensively studied for many potential applications; it is generally insoluble in most of the common organic solvents and can be doped with protonation with protonic acid or charge transfer reaction by oxidizing agent. After doping and de-doping with acid-base, polyaniline is a versatile conducting or non-conducting polymer depending upon the chemical reactions [1,2].To enhance the solubility and processabilty of these polymers in organic and inorganic solvents, they have been widely synthesized as co-polymers with different substituent groups[3]. Self-acid doped water soluble polyaniline has been reported by Show-An and Chen et. Al [4]. Generally the introduction of alky and aryl group substituents in the polymer backbone can alter the solubility of the polymer and it becomes more soluble in solvents like N-methyl

pyrrolidone (NMP), tetrahydrofuran (THF) and dimethylformade (DMF) [5,6] etc. Water-soluble conducting polymer can be prepared by introducing the $-SO_3$, and $-COOH$ group to the backbone of polyaniline structure [4,5].The copolymer of poly(aniline-co-anthranilic-acid) is a water-soluble polymer reported by Nguyen and Diaz[7].Water-soluble self-acid doped conducting polymer poly(aniline-co-N-propybenzensulfonic acid-aniline) which has the conductivity up to $4.7x10^{-4}$ S cm^{-1}. Water-soluble Copolymer poly(aniline-co-o-aminobenzenesulfonic acid) has been reported with its highest conductivity of 3.4 S cm^{-1} at room temperature[8]. In this article, we report a water-soluble polyaniline prepared by hand-wash solution without introducing any dopant or any moiety to the structure of PANI and to exploit it as a corrosion inhibitor.

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Experimental

Material

Aniline (Reagent grade) from R&M Chemical Essex, U.K used as received. Potassium Chromate (A.R grade) purchased from (Aldrich, U.K) was used as received. Hydrochloric acid (HCl) (37%) (Aldrich, U.K) was used without further purification. De-ionised water was used throughout the experiment. The handwash solution, Sunlight^{TM} (Unilever, Malaysia) contains mainly citric acid (CA), procured from Tesco, Malaysia.

Synthesis of aqueous colloidal nano polyaniline

Polyaniline aqueous colloids were prepared by chemical oxidation method by dissolving (0.93 mL) aniline in 100 mL of 0.1M HCl solution. In 50mL de-ionised water, hand-wash solution (1 mL) was properly dissolved and added to the above solution. Polymerization was initiated by adding 20 mL of 0.1 M potassium chromate solution (PCS) in the above solution in one portion instead of adding drop wise at 25 ^{o}C and stirred for 30 min on a magnetic stirrer. The colorless solution turns into orange-yellow color and after 30 minutes green color colloidal dispersion appeared; the   reaction was left undisturbed for 24 hrs at room temperature to complete the polymerization. Finally, the dark green color precipitate was collected by filtration using Whatsman filter paper no. 42 and washed thoroughly with distilled

water and subsequently with acetone. The polymer was then dried under vacuum for 24 hrs at room temperature.

Characterization

UV-vis Spectra

The UV-vis spectrum of colloidal dispersible-PANI is shown in Figure 1.Polymer samples were prepared by dissolving appropriate quantities of PANI in 1.0 M HCl aqueous solution and filtered through Watsman filter paper 42. UV-vis spectrum was recorded on JASCO (V-35 Spectrophotometer) at ambient temperature. The spectrum was recorded in the range of 280-1100 nm
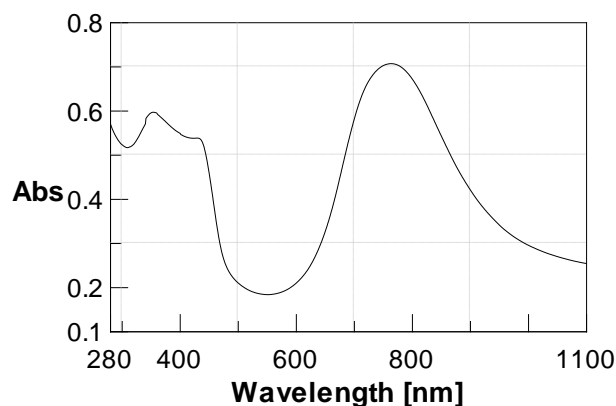

Figure 1- Electronic spectrum of polyaniline prepared by the dispersion polymerization pathway using CA surfactant dissolved in 1.0 M HCl.

IR spectra

The polymer was characterized by recording its IR spectrum with Perkin-Elmer-2000 Fourier transformation infra red spectroscopy (FTIR) using KBr pellet, Figure 2. The scanning resolution of IR was 4 cm^{-1}.
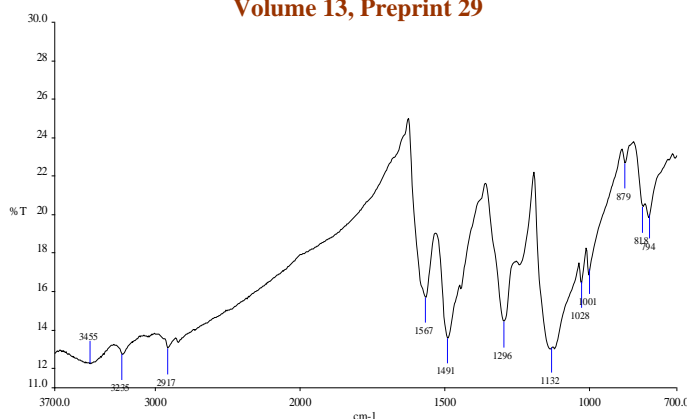
Figure 2- Infrared spectra of polyaniline prepared by the dispersion polymerization pathway using CA as the surfactant

Thermogravimetry analysis (TGA)

The polyaniline was filtered and collected in the form of powder, purified by washing with water and subsequently with acetone until the extract became colorless. Figure-3 showed the thermogravimetry analysis of the PANI at heating rate 20 ^{o}C/min under inert nitrogen atmosphere in the temperature range of 30 to 800 ^{o}C on the platinum pans using Perkin-Elmer Thermogravimetric Analyzer TGA 7.
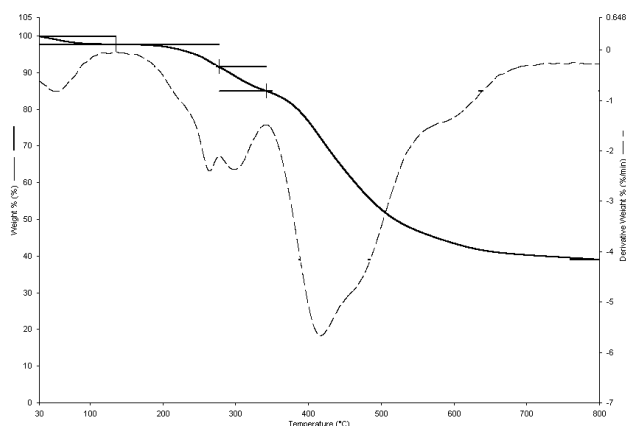

Figure-3 Thermogravimetric analysis of PANI prepared by dispersion polymerization pathway using surfactant

Electrochemical Studies

The cylindrical electrochemical cell was used with three conventional electrodes cell assembly: counter electrode-platinum wire; reference electrode saturated calomel electrode; working electrode the steel plate(dimension 2.5 cm x 2.5 cm with an exposed area of 1 cm^2, the rest being covered with araldite epoxy). The polishing of working electrode was carried out by different grades of emery papers and subsequently washed and degreased by distilled-water and acetone, respectively. The experiments were

carried out using Potentiostat/Galvanostat/ZRA (Gamry, Reference 600). The potentiodynamic studies were carried out in 0.1M HCl for different concentration water-dispersible polymer as an inhibitor with varying concentrations of CA (1.0x10^{-3} to 4.0x10^{-3}M) at the open circuit potential of the system. The polarization was carried out in the range of -0.3 to 0.3 V from cathodic to the anodic potentials with respect to the corrosion potential at a sweep rate of 1 mV s^{-1}. The Tafel plot of the cathodic to the anodic curves   (-0.3 to +0.3 vs corrosion potential) were extrapolated to obtain the values of corrosion potential (E_{corr}) and corrosion current (I_{corr}). The i_{corr} values were obtained by Tafel plot using Gamry Echem Analyst Software.

To correlate the results of potentiodynamic studies, electrochemical impedance measurements were also carried out at the open circuit potential after exposing the mild steel specimen in experimental solution in the frequency range of 10 KHz to 0.1 Hz. The voltage of 10 mV was applied for sinusoidal wave. The corrosion inhibition efficiency was calculated from the experimentally observed values obtained from the Tafel plot using the equation, $I.E = \frac{icorr - i'corr}{icorr} x100$ where i_{corr} and i'_{corr} are the corrosion currents without and with the addition of the inhibitor, respectively.

Results and discussion

Water-dispersible polyaniline(PANI) nanostructures have been synthesized by conventional chemical oxidative process. The transition from yellow color to dark green color during the progress of reaction occurred which confirmed the three different oxidation stages of Polyaniline [2]. It existed with three oxidation states: leucoemeraldine-emeraldine-pernigraniline [1]. The color that appeared during the polymerization reaction is attributed to its oxidation-reduction stages of these three forms of polyaniline and also indicated the formation of the polymer. The colloidal solution has no precipitate at very low concentration of 10^{-2}M of aniline and surfactant and it was completely homogeneous in the water and remained stable for more than 90 days without any further treatment. The UV-vis spectrum is shown in Figure 1. The polyaniline in its doped form has three characteristic peaks 310-360, 390-450 and 710-840 nm. The absorbance maxima at 310-360 nm is due π-π* electron transition in the benzenoid rings. The second and third absorption peaks are attributed to doping and polaron exciton, respectively. This spectrum of polyaniline is consistent with the water-soluble polyaniline reported by Palniappan and Nivasu[9].

Figure 2 shows the FTIR spectrum of the polymer, the major absorption peaks at 1567 cm^{-1} and 1491 cm^{-1} are attributed to stretching vibration of -C=C- benzenoid and –C=N quinoid ring, respectively. In

the region of 1001–1175 cm^{-1}, aromatic C-H in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appeared at 1132 cm^{-1}, which has been explained as an electronic band or a vibrational band of nitrogen quinine. The C-H out of plane bending mode has been a key to identify the type of substituted benzene. The peak at 819 cm^{-1} is assigned to –C–H$_{(aromatic)}$ out-of-plane bending vibration 1,4 disubstituted aromatic rings. The band at 2917 cm^{-1} is assigned to vibrations associated with the NH^{2+} part in C$_6$H$_4$NH$_2$ +C$_6$H$_4$– groups. The N-H stretching vibrations of –C$_6$H$_4$NHC$_6$H$_4$– groups may be assigned to the broad band at 3222–3455 cm^{-1} [2,10].

Thermogravimeric Analysis

TGA analysis of the as-synthesized polymer showed three major weight loss steps in the Figure 3.The first weight loss step occurred in the temperature range of 30 to 100 ^{o}C due to evaporation of moisture content present in the polymer. The second weight loss appeared at 200 to 300 ^{o}C due to the decomposition of oligomers present. The final weight loss step observed in the temperature range from 300 to 800 ^{o}C due to the structural decomposition in the C-C bonds of the conjugated polymer. The thermal stability of the as-synthesized polymer was consistent with the HCl-doped polyaniline reported in the earlier results [11,12].

Potentiodynamic Studies

Figure 4 shows the potentiodynamic polarization curves for mild steel in 0.1 M HCl with the addition of different concentrations of handwash solutions (CA) to ANI. The corrosion kinetics parameters such as b$_a$, b$_c$ and E$_{corr}$ were obtained by potentiodynamic polarization studies. These parameters which are obtained from the Tafel Plot at different concentrations of handwash solution are given in Table I.
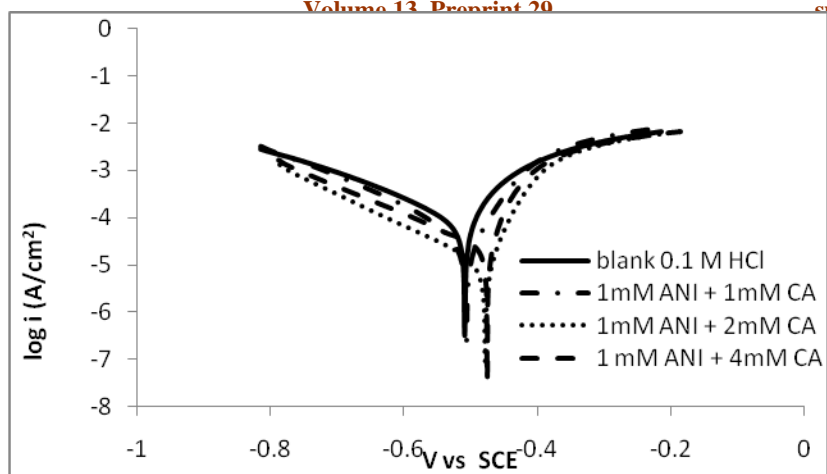
Figure 4-Potentiodynamic polarization behavior of mild Steel in 0.1M HCl with the addition of different concentrations of surfactant (CA) to ANI.

Table I

Corrosion kinetics parameters derived from the potentiodynamic curves of mild steel in 0.1 M HCl with different concentrations CA to aniline (1×10^{-3} M).

	I_{corr}	E_{corr}	b_a	b_c	$Rate_{corr}$	%I.E
	$\mu A\ cm^{-2}$	mV vs SCE	mV dec^{-1}	mV dec^{-1}		
Blank	587.5	-512.9	143	264.7	85.4	
CA-inhibitor ($\times 10^{-3}$ M)						
1.0	245.2	-508.8	95.9	192.2	35.66	58.26
2.0	44.94	-481.7	50.2	158.7	06.53	92.35
3.0	253.9	-498.0	76.8	184.9	36.80	56.78
4.0	114.2	-477.6	61.7	198.1	16.61	80.56

It has been found that with the addition of surfactant concentration to the test solution, the value of Tafel constants, b_a and b_c, are decreased but the extent of decrease to b_a is greater than b_c. It has been observed from the data in Table I that there a decrease in corrosion current (I_{corr}) value with increasing the surfactant concentrations. The lowest I_{corr} value was obtained at $2x10^{-3}$M concentration of CA. Thus, the addition of handwash solution together with aniline acted as an inhibitor, and shifted the E_{corr} values to towards more positive direction with respect to the E_{corr} recorded for carbon steel electrode without an inhibitor. This indicated that the polymer adsorbed on the carbon steel electrode behaved predominantly as an anodic inhibitor. The displacement in the corrosion potential has confirmed the protection of the metal surface by water-dispersible nanostructure polyaniline. These results are comparable with the i_{corr} value obtained for polyaniline depostion on carbon steel studied by Srikanth *et al* [13].

a.c Impedence measurements

In Figure 5, electrochemical Impedance studies for the different concentrations of CA are shown as Nyquist plots. Impedance measurement provided various parameters such as charge-transfer resistance (R_{ct}), and double layer capacitance (C_{dl}). The R_{ct} values were calculated from the difference in impedance at lower and higher frequency as reported by Haruyama *et al.* [14].
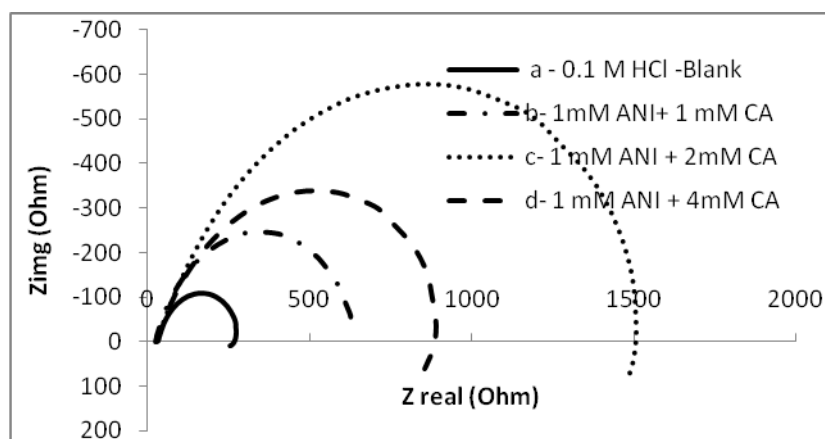

Figure 5- Nyquist behavior mild steel in 0.1M HCl with the addition of different concentration of surfactant (CA) to ANI

The Randles circuit was used as an equivalent circuit where R_s is the solution resistance, C_{dl} is the double layer capacitance, and R_{ct} is the charge transfer resistance using Gamry EChem Analyst Software. The C_{dl} interfacial double layer capacitance is calculated using the equation, $C_{dl} = 1/2\pi f_{max} x 1/R_{ct}$, the surface coverage (θ) derived from C_{dl} values are represented in Table II.

Table II

Electrochemical Impedance data calculated from Nyquist plot for corrosion inhibition of mild steel in 0.1M HCl with different concentrations of CA to Aniline (1×10^{-3} M).

	R_{ct}	C_{dl}	C_f	R_p	R_s	Surface Coverage
	Ω cm^2	μF cm^{-2}	μF cm^{-2}	Ω cm^2	Ω cm^2	θ
Blank	61.86	10.44	250.0	73.32	11.46	----
CA-Inhibitor ($\times 10^{-3}$ M)						
1.0	159.63	5.760	173.0	168.1	8.47	0.44827
2.0	281.8	7.699	73.6	392.8	11.00	0.99262
3.0	169.64	5.709	164.4	142.2	4.66	0.45316
4.0	222.14	5.548	129.2	234.8	11.66	0.46858

The charge-transfer resistance in the Nyquist plot increased from 61.86 to 281.8 Ωcm^2 with corresponding decrease in C_{dl} values from 10.44 to 5.548 μF cm^{-2} after varying the concentration of surfactant solution to aniline in the electrochemical cell. Thus, the better adsorption of inhibitor occurred as result of decrease in double layer capacitance values of aniline to CA at the molar ratio of $(1:2) \times 10^{-3}$ M in 0.1 M HCl. The diameter of semicircle in the Nyquist plots increased with the addition of different concentration of surfactant solution and the similar shape of semicircles predicted the inhibition of corrosion followed the same mechanism for mild steel in 0.1 M HCl. The centre of the semi circle below the x-axis, signifies the existence of micro roughness at the surface of metal during the corrosion process [51-19]. Single semi circle predicted the occurrence of single charge-transfer in the process and the addition of aniline has no effect on corrosion inhibition at all concentrations.

Conclusion

Highly water-dispersible colloidal polyaniline nanostructures were prepared by commonly used hand-wash solution via dispersion polymerization approach. The colloidal solution of PANI in aqueous acidic medium was stable for more than three months without treating with any electrostatic stabilizer. The potentiodynamic studies showed that the as-synthesized polymer predominantly behaved as an anodic inhibitor and it showed highest impedance at 2×10^{-3}M concentration of handwash solution with aniline

for mild steel in 0.1M HCl. The Impedance spectroscopy data (surface coverage) clearly indicated the dispersible polyaniline moleclues adsorbed on mild steel surface and behaved as corrosion inhibitor in acidic medium.

Acknowledgement

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