Blended Coatings from Polyaniline (PANI) and Chemically doped Sodium docecyl benzene sulphonate (SDBS)/SiO₂ Nanocomposites: Influence on Corrosion Protection of Mild Steel

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ABSTRACT  
In this work, investigation on corrosion protection performance of chemically synthesized polyaniline (PANI) / SiO₂ nanocomposite coatings has been carried out on Mild Steel (MS). Sodium docecyl benzene sulphonate (SDBS) doped conducting PANI / SiO₂ at different ratios was synthesized by employing in -situ polymerization technique. The developed coatings were characterized using Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA), Transmission electron microscopy (TEM), Contact angle, Atomic force microscopy (AFM) and corrosion analysis. The FTIR analysis indicates the strong interaction between PANI and SiO₂ nanoparticles. The contact angle study reveals the hydophillicity character of the nanocomposite coatings with a water contact angle of 74.9°. Corrosion resistance of uncoated mild steel and the coated sample in 3.5 % NaCl aqueous solution has been evaluated using weight loss methods. Additionally the Electrochemical Impedance Spectroscopy (EIS) studies have been also conducted to evaluate the corrosion protection characteristics of the coatings. PANI containing SiO₂ (PSC III) coating showed excellent resistance after immersion in 3.5 % NaCl solution for 1 month time period.  

Keywords: PANI, Coating, Corrosion, nanocomposite
INTRODUCTION:

Corrosion process which involves gradual destruction of materials exposed to environmental conditions through chemical or electrochemical reactions has been a primary concern globally. Around 3% of the global gross domestic product (GDP) annually is effected by the corrosion process[1-2].Corrosion protection employing polymeric coatings have generated considerable research interests in the recent years. Conducting polymers such as polypyrrole, polythiophene, polyaniline, polyacetylene etc. have been reported to be widely employed as coatings over the metal substrates to these substrates against corrosion [3-4]. Amongst the various conducting polymers, polyaniline (PANI) based systems have been reported to demonstrate improved corrosion protection properties as compared with the other polymers [3].

PANI known for its conducting properties [5] has good stability, high electrical conductivity [6] in addition to energy storage and electrochemical properties. PANI has been employed for multitude of applications like sensors, super capacitors, electrochromic display, fuel cells rechargeable organic batteries, drug delivery as well as in corrosion protection coatings. However, the major impediments of PANI includes limitations in processability predominantly due to its insolubility in majority of common solvents; brittle structure which prevents its wider applicability. These problems can be largely averted by changing the oxidation state of PANI, incorporation of dopants or preparing blends/composites of PANI with other polymers and reinforcing it with nanofillers[7].

Conducting polymer composites of PANI reinforced with nano fillers have been known to show its potentiality for corrosion protection. Encapsulated metal oxide based particles within the shell of PANI have bestowed improved physico-mechanical and chemical properties while retaining the conducting properties with synergism between the matrix polymer and the
inorganic particles [8-9]. Several inorganic/organic particles like SiO$_2$, TiO$_2$, Graphene, Fe$_3$O$_4$, ZnO, ZnMoO$_4$ etc have been reinforced within PANI employing emulsion polymerisation technique to achieve desired attributes [10].

Among various inorganic particles, SiO$_2$ nanoparticles having a porous structure can be suitably modified for its potential application in corrosion protection coatings [11]. Al-Dulaimi A et al have reported single step insitu method of synthesising PANI/SiO$_2$ composite having improved corrosion protection characteristics in corrosive solvents [12]. Similar several reports pertaining to the anti-corrosive paints of PANI/SiO$_2$ have been reported by several workers havebeen reported [13-20].

In the current investigation PANI/SiO$_2$ nanocomposite coatings has been prepared using single step-in-situ-polymerisation technique. Sodium dodecyl benzene sulphonic acid (SDBS)was used as a dopant owing to its improved solubility. An in-depth study on the morphology of the synthesised nanocomposite coatings was carried out employing Fourier Transform Infrared spectroscopy (FTIR), Transmission electron microscopy, X-ray diffraction (XRD) and atomic force microscopy. The corrosion study was investigated through weigh loss method and the electrochemical impedance spectroscopy and contact angle study of the nanocomposite coatings have been reported.

2. Experimental

2.1 Material

Aniline procured from M/s NICE chemicals Pvt. Ltd, Kochi, Kerala, India and distilled prior to its use and stored at 10$^0$C. SDBS (Sodium Dodecyl Benzene Sulphonate), 1-methyl-2-pyrrolidone (NMP), and APS (ammonium persulphate), were purchased from M/s HimediaIndia. Nanosilica (175–225 m$^2$/g[BET]) with 90% purity was purchased from M/s Sigma Aldrich USA. Epoxy clear with amine hardener (Finehard 486) was procured from
M/s Fine finish organics Pvt ltd, Mumbai, India. Xylene, Sodium chloride (NaCl), 1-butanol and double distilled water were used for solution preparation. Stainless steel coupons for corrosion studies were purchased locally from Bhubaneswar, Odisha.

2.2 Synthesis of PANI/ SiO$_2$ Nanocomposite Coatings

PANI/ SiO$_2$ nanocomposite coatings were prepared using chemical oxidative using ammonium persulphate (APS) as the initiator in 1(M) HCl solution. In a four necked round bottom flask, 100 ml solution comprising of 0.2 M Aniline and 0.04 M SDBS was taken to which 0.1 g of nano-SiO$_2$ was added. Subsequently, 0.2 M APS was added drop wise and the reaction was carried out under nitrogen atmosphere for 3h at 50$^\circ$ C in an ultrasonic bath to ensure complete the polymerization process. Nano-SiO$_2$:Aniline weight ratio was maintained at 0.10:1(PANI/SiO2-I). Then, the reaction mixture was kept at equilibrium state for 4 h and the final product obtained was filtered, washed with double distilled water till colorless filtrate was obtained and then dried at 60$^\circ$ C for 24 h in air oven. The aforesaid process was repeated to synthesize nanocomposites at variable weight ratios of Nano-SiO$_2$:Aniline - 0.15:1(PANI/SiO2-II) and 0.20:1(PANI/SiO2-III) respectively.

2.3 Preparation of PANI/ SiO$_2$ composites coating on mild steel

Mild steel panels were coated at variable loadings of PANI/SiO2(PSC) and neat PANI formulated with epoxy resin to evaluate the corrosion resistance properties of the coatings. Prior to coating the surface of the mild steel panels were subjected to gritting using emery paper followed by washing and cleaning with trichloroethylene and acetone to remove contamination if any on the surface. 6g of solid epoxy resin was dissolved in 4 ml xylene solution to which 1% PANI/SiO$_2$ solution was added and ultrasonicated for 2 hrs. Then 1g hardener was added and the mixture was further sonicated for 1 hr to obtain the coating formulation. Xylene– butanol mixture at a ratio of 9:3 was added to maintain the viscosity of
coating. Finally the coating formulation was coated onto mild steel substrate of 1 cm² using drop coating method and was dried at 600 °C for 4 h. A coating thickness of 110± 10 µm was maintained in all the formulations.

2.4 Characterization of the PANI and its nanocomposite coatings

After the successful growth of polymer nanocomposite coatings, the microstructural and electrochemical corrosion properties were investigated using various characterization tools. The structural information of polymer nanocomposites coatings was performed using Fourier transform infrared (FTIR) spectroscopy (Thermo Scientific, Nicolet 6700, USA) in the attenuated total reflectance mode from 400-4000 cm⁻¹. The X-ray diffraction pattern of the polymer nanocomposite coatings were examined using Shimadzu X-ray diffractometer with a measuring angle from 5 to 80° and the scan rate was maintained 5°/min. The surface morphology of the polymer nanocomposites was characterized by Transmission electron microscopy (TEM, 1400 JEOL Japan). Samples of ~2 mg was dispersed in 5 ml of ethanol and sonicated for 5 mins to disperse uniformly. A drop dispersed solution was then placed on a copper grid and kept in the oven for complete dry or evaporate the sample. The surface topography and roughness of the coatings were examined using Atomic Force Microscopy (AFM, XE-100). The measurements were performed in non-contact mode at room temperature. The wetting properties of the coated surface was acquired by contact angle measurement (Phoenix SEO Pvt. Ltd, Korea). The thermal stability of the samples was examined by Thermogravimetric analysis (TGA) (M/s TA instruments, USA) at a heating rate of 10°C/min in the temperature range from 30 to 700 °C under nitrogen atmosphere.

2.4.1 Electrochemical Impedance studies (EIS):

The electrochemical characteristics of as-prepared epoxy and PS coatings were tested using an electrochemical workstation in 3.5% NaCl solution. The exposed area of the coating
is 1 cm². The EIS and Tafel are measured in a three-electrode system. The coated substrate was a working electrode, saturated calomel electrode (SCE) was taken as reference electrode and platinum as a counter electrode. The following equations was used to evaluate the protection efficiency of the coating.

\[ P(\%) = \frac{R_{ct} - R_{ct}^*}{R_{ct}} \times 100 \]  

(1)

\[ P(\%) = \frac{i_{corr} - i_{corr}^*}{i_{corr}^*} \times 100 \]  

(2)

Where, P(%) is the protection efficiency, \( R_{ct} \) and \( R_{ct}^* \) is the charge transfer resistance of coated and uncoated substrate, \( i_{corr} \) and \( i_{corr}^* \) is the corrosion current density coated and uncoated substrate.

### 2.4.2 Weight loss method

To further evaluate corrosion properties of as-prepared PANI/SiO2 coated mild steel was extensively studied by weight loss method. The bare and PANI/SiO2 coated mild steel with a dimension of 2cm×3cm were immersed in 1.0 mol L⁻¹ NaCl medium for 30 days. Before and after immersion, the bare and coated mild steel were weighed in the electronic balance. After 30 days, the test specimens were removed from the solution and washed exhaustively with distilled water, followed by acetone and dried in air. The changes in the coated substrate were visually inspected after 30 days of immersion. Moreover, the changes in weight were calculated according to the weight loss (g cm⁻² h⁻¹) formula as follows

\[ W_L = \frac{W_1 - W_2}{at} \]  

(3)

The corrosion rate (CR) of the PS coated mild steel substrate was estimated by weight loss method using the following equation.

\[ CR(\text{mmyear}^{-1}) = \frac{(W_1 - W_2) \times 87.6}{atd} \]  

(4)
Where, $W_1$ is the initial weight (before immersion) of the sample (mg), $W_2$ final weight (after immersion) of the sample (mg), $a$ is the surface area of the sample (cm$^2$), $t$ is the end time of immersion (h) and $d$ is the density of bare mild steel substrate (7.85 g cm$^{-3}$).

3. Results & Discussion

3.1 FTIR analysis

Fig 1. Represents the FTIR spectra of PANI Neat and PANI/SiO$_2$ nanocomposites, respectively. The peak corresponding to 1575 and 1483 cm$^{-1}$ represented the stretching vibration of C=N and C=C in all the samples. The bands at 1292 cm$^{-1}$ and 1245 cm$^{-1}$ confirmed the C–N stretching mode of the benzenoid ring. The peak at 1118–1112 cm$^{-1}$ assigned to C–H mode in plane bending vibration during protonation [21]. The FTIR spectrum corresponding to the presence of SiO$_2$ was observed at 1061 cm$^{-1}$ and 807 cm$^{-1}$ attributed to the stretching and bending vibrations of Si–O–Si, respectively. The C–N stretching vibration in protonic acid doped PANI from PANI-SDBS, where SO$_3^-$ group of SDBS is bounded with the nitrogen atom of PANI was observed at 1302 cm$^{-1}$. Further in the case of PSC there was shift of peaks to higher wavenumbers at 1565 cm$^{-1}$, 1483 cm$^{-1}$, 1292 cm$^{-1}$ and 1245 cm$^{-1}$ respectively as compared with neat PANI due to the dispersion of silica nanoparticles in the matrix. Similarly, the bending vibration of Si–O–Si peak at 1056 cm$^{-1}$ was found to be shifted to lower wavenumbers. The behaviours indicated interaction between PANI and SiO$_2$ nanoparticles.
3.2 XRD analysis

The XRD pattern of PANI and PANI/SiO$_2$ is represented in Fig 2. The peak related to PANI was observed at $2\theta = 20$ and $25^\circ$, indicating (020) (200) semi-crystalline planes as reported by Chin et al. [22]. However, with the incorporation of SDBS, the intensity of the d200 peak reduced in presence of dopant. Further as observed from the x-ray diffractograms of PANI/SiO$_2$ nanocomposite it is observed that a relatively intense peak at $2\theta = 20$ was observed which revealed higher crystalline nature of PANI in presence of the dopant and SiO$_2$.

On contrary, Chei et al. [22], had reported in their work that SiO$_2$ has no influence on the crystallinity of PANI. Hence, it can be concluded that addition of SiO$_2$ has considerable effect on PANI and that might due to the absorption of PANI on SiO$_2$ surface in presence of SDBS [23].
3.3 TEM Studies

Fig. 3 shows the TEM image of PANI/SiO$_2$ composites. From the figure, it is clear that the SiO$_2$ nanoparticles are uniformly distributed in the PANI matrix. This uniform distribution of SiO$_2$ in the composite may be due to the incorporation of SDBS that acts as dispersant and might be held responsible for the control of homogeneity in the composite. The agglomerated structure of PSC also found due to interparticle interaction of SiO$_2$. Further, a portion of the micrograph has been found to be dark indicating the thickness of the sample was too high for TEM imaging due to mass contrast phenomena.
3.4 AFM studies

The surface morphology of PANI neat and PSC thin films were characterized by Atomic Force Microscopy technique. Figures 4 (a) and (b) shows the 3D Atomic Force Microscopic images of PANI neat and PSC respectively. As observed from the AFM micrographs the SiO2 nanoparticles were dispersed uniformly within the PANI matrix. Also it may be noted that the nanocompositesample displayed increasing root-mean-square (RMS) surface roughness value of 16.06 nm as compared with neat PANI which had an RMS value of 5.87.
Fig 4. 3D Atomic Force Microscopic images of (a) PANI neat and (b) PANI/SiO2-III

3.5 Contact angle

This wettability characteristics of the coated surfaces was tested using contact angle measurements. The data of water contact angle measurements showed that the surface paint had shown fig 5. The hydrophilic nature because the contact angle is less than 90 degree. The measurements revealed that the surface contact angle of PANI Neat and PANI/SiO2–III nanocomposite was found to be 64° and 73°, respectively as shown in Fig.5. This shows an improvement of the PANI/SiO2 in the wettability characteristics as compared to the neat counterpart. Therefore the results indicate that the incorporation of SiO2 reduces the hydrophilicity.

Fig 5. Contact angle of (A) PANI Neat, (B) PANI/SiO2 composite
3.6 TGA Studies

TGA thermograms of PANI Neat, and PANI/ SiO$_2$–III nanocomposites are depicted in Fig. 6. As observed from the thermograms PANI Neat displayed (Fig.6) a three decomposition. The initial decomposition observed at 240$^\circ$C with a corresponding weight loss of about 3–10 % may be attributed to the loss of residual water trapped in the PANI matrix and other volatiles. The decomposition in the second stage at 310 to 450 $^\circ$C involves the loss of dopant SDBS as well as the initial degradation of the backbone matrix polymer. The third stage decomposition observed beyond 570$^\circ$C indicated the degradation of both SDBVS and PANI. SiO$_2$ nanoparticles have thermal stability up to 800$^\circ$C. Thus, incorporation of SiO$_2$ within the PANI matrix improved the thermal stability which is predominantly due to the barrier layer formed by the nanoparticles that prevent outflow of the decomposition of products [24].

![TGA Curves of (a) PANI Neat, (b) PANI/SiO$_2$ composite](image)
3.7 Corrosion studies (weight loss method)

Table 1. Weight loss parameter during the immersion test in 3.5% NaCl for 30 days

| Sample name      | Initial weight (mg) | Weight after immersion 3.5%NaCl for 30 days | Weight loss (mg) | Weight loss (%) | Corrosion rate (mm/year) |
|------------------|---------------------|---------------------------------------------|------------------|-----------------|-------------------------|
| Blank Mild Steel | 4283.1              | 3669.76                                     | 613.34           | 14.32           | 1.59                    |
| Epoxy (Blank)    | 4783.6              | 4227.26                                     | 556.34           | 11.63           | 1.44                    |
| PANI neat         | 4967.5              | 496.58                                      | 470.92           | 9.48            | 1.21                    |
| PANI/SiO2 I       | 4872.8              | 4456.66                                     | 416.14           | 8.54            | 1.08                    |
| PANI/SiO2 II      | 4678.3              | 4373.28                                     | 305.02           | 6.52            | 0.79                    |
| PANI/SiO2 III     | 4769.1              | 4531.60                                     | 237.50           | 4.98            | 0.61                    |

The corrosion rates (CR) in mm/year of blank mild steel, epoxy blank, PANI Neat and PANI/SiO2 is represented in Table 1. As observed from the table the weight loss % in blank mild steel was 14.32% which reduced to 11.63% after coating with epoxy. Further in case of PANI coated samples the weight loss was 9.38% in 3.5% NaCL after 30 days time period.
However, the PANI/SiO2 coated panels showed improved performance in which the weight loss was 4.98%. Comparing the CR rates, it is evident from the test results reported in Table 1, after 30 days of immersion of the blank mild steel, the CR value was 1.59/year which reduced drastically to 0.61 mm/year approximately to the tune of 160% thus revealing the efficacy of the coated nanocomposite panels [21].

**Electrochemical studies of PS/MS Coatings**

The corrosion properties of as-prepared coatings were analyzed by EIS and Tafel techniques in 3.5% NaCl solution. The Tafel curves acquired for the mild steel, epoxy coating and PANI-SiO$_2$ epoxy coating were shown in Fig 7. The corrosion potential and current density of the blank and coated substrates were obtained from the Tafel curves by the intersection of the extrapolation of anodic and cathodic curves. The calculated electrochemical parameters were given in the Table 2. It is observed that the PS/MS coatings showed improved corrosion resistance compared to the epoxy coatings and bare substrate by decreasing the corrosion current density ($I_{corr}$) and the shift toward the positive side in corrosion potential ($E_{corr}$). Moreover, the PS/MS coatings revealed higher protecting efficiency of 90% compared to other coatings and substrates.
Figure. 7 Electrochemical properties of mild steel, epoxy and PS coatings.

The charge transfers resistance and capacitance of the blank and as-prepared coatings were tested by electrochemical impedance spectroscopy. The bode profiles of the mild steel, epoxy coating and PANI-SiO$_2$ epoxy coatings were displayed in Fig 8. From the curve, it is observed that the increase in charge transfer resistance and decrease in capacitance indicates the better corrosion resistance property of as-prepared PS/MS coatings over epoxy and bare substrate. Moreover, from the periodic evolution, the PS coatings provide better corrosion-resistant performance than epoxy coating. However, a decrease in performance when increasing the immersion time it might be due to the slightly porous nature of the coating induces the corrosion phenomena. The results demonstrate that the PS coating itself has a barrier and redox property, which improves corrosion protection performance.
Figure 8. Bode plots of mild steel, epoxy and PS coatings.

Table 2: Protection performance of PS and Epoxy coatings on steel in 3.5% NaCl

| Samples    | EIS          | Tafel          |
|------------|--------------|----------------|
|            | $R_{ct}$ (Ω cm$^2$) | $C_{dl}$ (μF/cm$^2$) | Protection Efficiency (%) | $I_{corr}$ (μA/cm$^2$) | $E_{corr}$ (mV vs SCE) | Protection Efficiency (%) |
| Blank      | 4.9          | 32             | --                         | 564                  | -588                       | --                         |
| Epoxy 0 hr | 547          | 22             | 99                         | 92                   | -447                       | 83                         |
| Epoxy 1 hr | 141          | 11             | 96                         | 80                   | -482                       | 85                         |
| Epoxy 3 hr | 91           | 18             | 94                         | 82                   | -505                       | 85                         |
| PS 0 hr    | 1262         | 707            | 99                         | 54                   | -253                       | 90                         |
| PS 1 hr    | 1191         | 161            | 99                         | 93                   | -364                       | 82                         |
| PS 3 hr    | 470          | 369            | 98                         | 78                   | -395                       | 86                         |
4. CONCLUSION

PANI / SiO$_2$ nanocomposites have been successfully prepared by situ solution polymerization in aqueous solution containing SDBS as a dopant with different weight ratios of SiO$_2$/aniline. The synthesis and curing of the composites were confirmed by spectral studies. Contact angle analysis indicate the increase in contact angle value due to the incorporation of SiO$_2$. TGA results revealed that inclusion of SiO$_2$ nanoparticles improves the thermal stability of composite to a smaller extent due to the interaction of SiO$_2$ particles and PANI matrix. TEM images of nanocomposites showed the polymer growth on the surface of SiO$_2$ particles. AFM studies indicate the surface roughness value can be increasing by incorporation SiO$_2$ nanocomposites. Corrosion study shows that PANI and PANI/SiO$_2$ nanocomposites coating show good corrosion resistance property on mild steel in 3.5 % NaCl aqueous solution. The results also revealed that corrosion protection property depends on SiO$_2$ content in composite coating and better corrosion resistance is observed for the formulation containing 0.20SiO$_2$ (PSCIII).

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