Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 3, July - September 2017, p. 707 - 717

SYNTHESIS AND CHARACTERIZATION OF POLYANILINE-BASED CONDUCTING POLYMER AND ITS ANTI-CORROSION APPLICATION

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The present study comprises synthesis of nanoparticle sized polyaniline (PANI) (46 to 58 nm) by low cost, environment friendly, reproducible and solvent free method. This polymer was doped with hydrochloric acid (dopant) in different molar ratios and characterized by Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Ultraviolet-visible (UV-Vis) and Fourier-Transform Infrared (FTIR) Spectroscopy. The electrical conductivity of the pelletized PANI was measured. It was found that electrical conductivity of this polymer was increased from 8 to 79 S/cm with 2 M doped PANI. The anti-corrosion properties were analyzed by preparing homogenous dispersion of PANI in flexible epoxy resin. Four blends were prepared by adding 1 % and 1.5 % of 1 M and 2 M doped PANI in epoxy resin. These blends were applied on mild steel by vapor deposition technique and cured at 80 ^{o}C and 150 ^{o}C for 2 h. The coatings were scratched with the help of a knife and tested through salt spray method for 600 h in 3.5 % NaCl solution. The coating with 1.5 % 2 M doped PANI showed excellent anti-corrosion properties.

(Received April 4, 2017; Accepted July 24, 2017)

Keywords: Polyaniline; PANI/ Epoxy blends; Anti-corrosive paints; corrosion testing

1. Introduction

Intrinsically conducting polymers (ICPs) have been extensively studied for the past 30 years due to their numerous potential applications in electrical and electronics fields [1, 2]. At first, these synthetic polymers were considered as insulators. With the development of the idea of doping, this concept has been entirely changed. These conjugated organic polymers could conduct electricity of the order near to that of metals by doping process [3]. The incorporation of these ICPs in epoxy resin results in the enhancement of the electrical properties of the matrix as well as their environmental stability [4]. Recently, a large number of ICPs coated on different substrates have been tested as corrosion inhibitors due to their ability to scavenge the ions that accelerate corrosion process [5]. Thin films of conducting polyaniline (PANI) could be prepared either from any chemical synthetic route or could be directly deposited on the substrate by the electrochemical method [6]. However, flexible PANI/epoxy blends have not been frequently tested in the past as anti-corrosion coatings. Addition of PANI in flexible epoxy resin increases its gel time and fast curing could be achieved [7].

PANI exists in different forms i.e., lecoemeraldine base (LB), pernigraniline (PB) and emeralidine base (EB) which differ in physical and chemical properties [8]. PANI backbone consists of benzoid and quinoid units with the delocalized conjugated structure which is the resonance hybridized having different redox states. Benzoid rings present in the structure are non-conducting in nature. Emerladine salt having pi conjugated system plays an important role in increasing its electrical properties. Protonation of emerlidine could be accomplished by chemical, photochemical or electrochemical methods [9]. Doping of PANI results in the enhancement of its electrical conductivity [10]. The concentration and electronic nature of dopants are the prime

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factors affecting the electrical properties obtained in PANI. Moreover, the anti-corrosion properties of PANI/epoxy blends could be enhanced using different concentrations [11].

Our attempts are focused on the solvent free synthesis of nano sized PANI. The electrical conductivity of the synthesized PANI was increased by the addition of a dopant (hydrochloric acid). In the present study, it was found that the increased dopant concentration resulted in the increase of the conductivity of PANI. Dopant concentration and time were the most important factors that controlled the homogenous dispersion and conductivity of PANI in flexible epoxy resin. This can be accomplished by increasing sonication time. PANI being secondary amine accelerates the curing process. Application of PANI for corrosion resistance purpose was carried out by coating the rectangular plates of mild steel with PANI – blend with different percentages of doped PANI as filler material in the epoxy matrix. We found that PANI in the epoxy resin showed considerable decrease in the corrosion rate (0.34-0.19 g/m^2h) of the coating as compared to neat epoxy (3.25 g/m^2h). It was also revealed that by increasing the concentration of PANI in epoxy matrix and use of highly doped PANI, the corrosion resistance was increased.

2. Experimental

2.1. Synthesis of PANI

Ammonium persulphate, analytical grade hydrochloric acid (37 %) and aniline were purchased from Sigma Aldrich. The aniline was further purified by distillation. Ammonium persulphate was used as received. A low viscosity epoxy resin LY564 and its hardener Aradur 22962 (cycloaliphatic polyamine) were purchased from Huntsman chemicals.

2.2. Synthesis of PANI

The polymerization of aniline was accomplished by the oxidation of aniline with ammonium persulphate by the chemical oxidation method (Fig. 1) [6]. Solvent free polymerization of PANI was carried out by pouring distilled aniline (23.28 mL) in a pre-cleaned porcelain mortar. Concentrated hydrochloric acid (18.75 mL) was added drop wise in the mortar and the obtained mixture was grinded to get white paste. The grinded ammonium persulphate (57 g) was step wise added to the reaction mixture to initiate the oxidation of aniline and again grinded till dark green coloured PANI particles were obtained. The whole mixture was poured into a beaker and washed with 200 mL acetone, 200 mL ethanol and 600 mL of deionized water to remove the impurities and then the obtained product was dried under vacuum at 60 °C for 12 h.

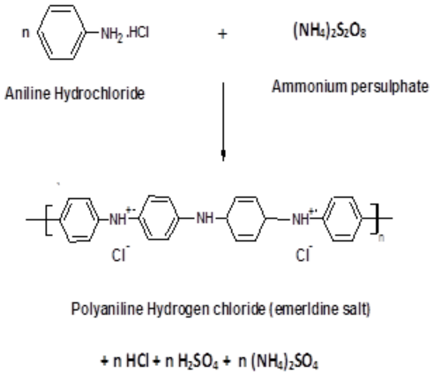

Fig. 1 Synthesis of PANI by chemical oxidation process.

2.3. Doping of PANI

Doping of PANI was carried out by using hydrochloric acid in different molar concentrations (1.0 and 1.5 M). Undopped PANI (0.8 g) was added equally in 1 M and 2 M HCl and sonicated for about 2 h [12]. The resultant mixture was kept for 72 h at room temperature, filtered by using Whatman filter paper and dried at 60 °C for 24 h.

2.4. Dispersion of PANI in Epoxy Resin

Doped PANI was mixed in epoxy resin and sonicated in an ultrasonic bath for 2 h till the homogenous dispersion of PANI in resin was obtained [13]. The mixing ratio of PANI, epoxy (LY 564) and hardener (22962) is tabulated in Table 1.

Table 1. Ratio of PANI /Epoxy resin.

Sample ID	Mass of Epoxy (g)	Mass of Hardener (g)	Mass of doped PANI (g)
1%, 1 Molar Doped PANI/Epoxy	20	5	0.25
1.5%, 1 Molar Doped PANI/Epoxy	20	5	0.375
1%, 2 Molar Doped PANI/Epoxy	20	5	0.25
1.5%, 2 Molar Doped PANI/Epoxy	20	5	0.375

2.5. Preparation of Substrate

ASTM G-1 standard was followed for the preparation of mild steel (MS) substrate for anti-corrosion study of PANI/Epoxy coated samples (ASTM, 2003). Four plates having dimension 6 X 4 inches with 1.5 mm thickness were used. Substrate for PANI composite coating was at first cleaned and polished with the help of fine emery paper. Degreasing process was done by sonicating the plates of mild steel with acetone and then mild steel plates were dried at 60 °C for 1 h before further processing [14].

2.6. Application of Epoxy Resin on Substrate

Weighed amount of hardener was mixed with PANI dispersed epoxy resin and then coated on the plates. The coated plates were then placed in the oven to cure the resin according to following curing cycle (Table 2).

Table 2. Curing cycle of resin.

Temperature	**Ramp Time (°C/min)**	**Total Time (min)**	**Stay Time (min)**
80 °C	1	55	120
150 °C	1	70	60

3. Characterization

3.1 UV-Visible Spectroscopy

Doped and undoped PANI samples were analyzed using JASCO V-670 UV-Visible spectrophotometer equipped with NIR assembly. Samples were scanned from 100-1200 nm using methanol as a reference solvent in 1 cm path length quartz cell.

3.2 Elemental Analysis

The elemental analysis of the PANI was carried out by using Thermoelectron Elemental Analyzer Flash EA1112. At first, acetanilide was run as a primary standard after 1-2 blanks to plot the calibration curve. Then PANI powder sample was run for the determination of percentage composition of carbon, hydrogen, nitrogen, sulphur and oxygen.

3.3. FT-IR Spectroscopy

The doped PANI powder and cured PANI/Epoxy blend were characterized with a JASCO 6800 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) attachment. The 16 spectra for each sample type were collected between 4000 cm^{-1} and 500 cm^{-1} at a resolution of 4.0 cm^{-1} using TGS detector.

3.4. Morphological Characterization

Morphological characterization of the prepared samples was carried out by MIRA field emission scanning electron microscope.

3.5. Crystallinity

Bruker X-ray diffractometer was used for XRD characterization using a copper target (Cu Kα) and wavelength (λ) of 0.15418 nm. Data was collected in the range of 2θ = 10 to 60° at a resolution of 0.02° per step with a 1 s integration time per step.

3.6. Electrical Conductivity

Electrical conductivity of the samples was measured at room temperature on pressed pellets by a two-point probe technique. Typically, 0.1 g sample was pelletized at 70 MPa for 3 min using a hydraulic press. The obtained pellet dimensions were 13 mm in diameter and 1mm in thickness. Three pellets were prepared for each sample. Current−voltage (I−V) measurements were carried out with Keithley 4200 SCS semiconductor parameter analyzer. Dual sweep mode was operated within a voltage range of -1 to 1 V with a difference of 0.01 V per measurement. Five physical locations were measured on each pellet side to confirm consistency within each sample: One location at the center of the pellet and four others nearer the edge in the four adjacent quadrants. Each I−V measurement was repeated five times at least for every location for reproducibility confirmation. The values reported are averaged over 25 readings for each sample.

3.5 Thermogravimetric Analysis

Cured epoxy samples were analyzed with Metller Tolledo Thermogravimetric analyzer using 70 μL crucible size at a constant heating rate of 15 ^{o}C/min from 25 ^{o}C to 800 ^{o}C.

3.7 Differential Scanning Calorimetry

Cured epoxy samples were analyzed with Metller Tolledo Thermogravimetric analyzer using 70 μL crucible size at a constant heating rate of 15 ^{o}C/min from 25 ^{o}C to 800 ^{o}C.

4. Results and discussion

4.1. UV-Visible Spectroscopy

UV-Visible spectra of the doped and undoped samples were recorded using JASCO V-670 UV-Visible spectrophotometer in the range of 190-1200 nm using 1cm path length quartz cell. Solutions were prepared by dissolving PANI in doped and undoped state in methanol separately. For complete dissolution of PANI in methanol, the solution was sonicated for 20 min before analysis. Methanol was used as a reference solvent. UV-Visible spectroscopic study of PANI showed two bands in the region of 300-400 nm and in 500-650 nm. These two absorption bands were obtained due to n-π* and π-π* transitions in the PANI structure (Fig. 2a). No remarkable difference was observed in the UV-Vis spectra of PANI except that the peak was shifted from 310 nm to 320 nm. As both spectra were recorded, using methanol as a solvent. So, this small change may be observed due to the presence of the hydrogen ions in the doped PANI (protonation by the dopant) which may cause the shifting of the peak (Fig. 2b)[15].

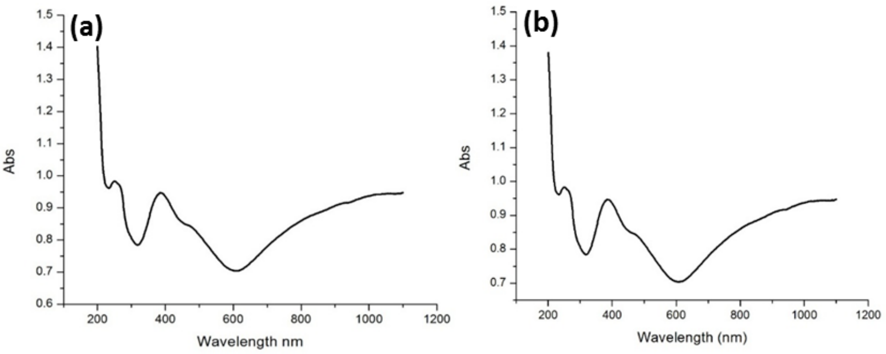

Fig. 2 (a) UV-Visible spectrum of undoped PANI and (b) UV-Visible spectrum of doped PANI.

4.2. Elemental Analysis

Elemental analysis showed the percentage of C, H, N, S and O in the PANI samples [16] in the following ratio as shown in the Table 3.

Elemental analysis shows that synthesis of PANI by chemical oxidation method contain 45.7 % carbon in the chain and 9.3 % nitrogen which is due to the amine groups attached with the polymer structure. The comparatively greater percentage of hydrogen in the structure of PANI confirmed the protonation by the acid.

Table 3. Percentage composition of PANI.

Elements	C	H	N	S	O
%age	45.7	6.6	9.3	14	26

4.3. Direct Current (DC) Conductivity Measurement

The DC conductivity of PANI was determined by two probe DC conductivity meter Kethly 2440. For measuring the conductivity of a sample with resistance in the range of kilo-ohms to mega-ohms, a simple two-probe technique was used [17]. The contacts on the pelletalized PANI were made by using Ag paste. Conductivity was measured by passing current in (mA) through probes of 0.5 micron diameter attached with pelletized polyaniline.

For the measurement of DC conductivity of PANI, at first the PANI powder was pelletized by applying 70 MPa pressure on PANI powder for 3 min. At this pressure, PANI powder appeared in the form of a compressed pellet. Conductivity can be determined through the pellet or across the pellet surface. For that purpose, contacts have been made on the surface of the pellet which allows the charge to be localized at a point during measurement by a two probe DC conductivity meter.

The conductivity of undoped and doped PANI using different molarities of acid at a constant doping time of 72 h is shown in Table 4. The conductivity of these conjugated polymers is dependent on charge carriers to a greater extent (Fig. 3a).

Table 4. DC conductivity of doped and undoped PANI.

Sample ID	Doping time (h)	Conductivity (S/cm)
Un-doped Polyaniline	-	3
Doped polyaniline (1 M)	72	50
Doped polyaniline (2 M)	72	79

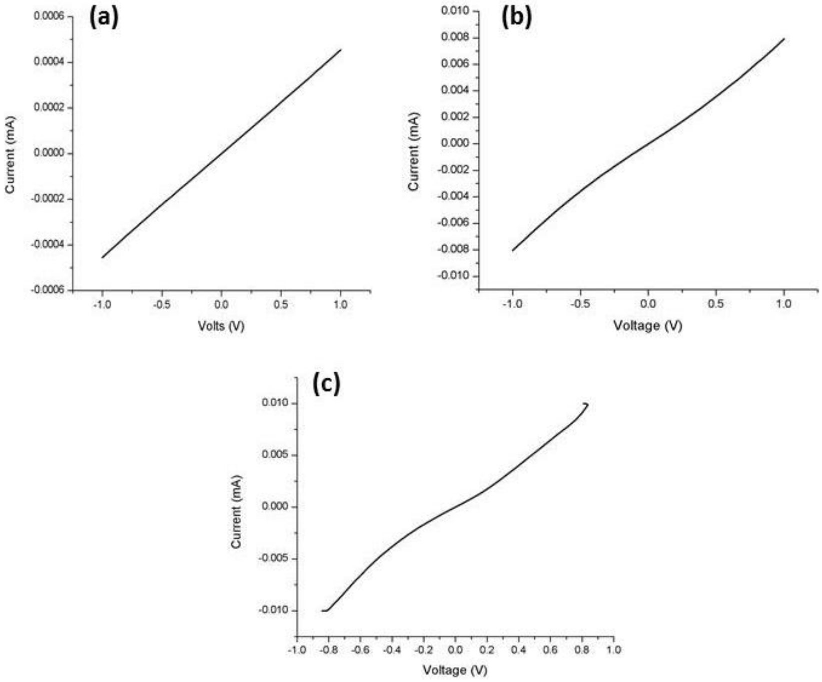

Fig. 3 (a) DC conductivity plot of undoped PANI, (b) DC conductivity plot of 1M doped PANI and (c) DC conductivity plot of 2 M Doped PANI.

The extent of doping increases protonation in the PANI backbone. It was found that the conductivity of the sample was increased by increasing the molarity of the dopant. 1 M doped PANI for the period of 72 h shows the conductivity of 50 S/cm (Fig 3b). However, when this concentration was increased from 1 to 2 M then abrupt increase (79 S/cm) in the conductivity was observed (Fig. 3c). This change may be attributed to the increasing number of the charge carriers present in the PANI backbone.

4.4. Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR analysis of HCl doped PANI/Epoxy blend showed peaks at 2961 cm^{-1}, 2875 cm^{-1} and 2352 cm^{-1} in the region from 3500 to 2000 cm^{-1} which are due to C-H stretching (2961) and C≡N stretching (2352). In going through the region 1800 to 1100 cm^{-1}, peaks of aromatic rings appeared due to C-C and C-N stretching and C-H in plane bending at 1506 cm^{-1}, 1028 cm^{-1} and 1177cm^{-1}, respectively (Fig. 4) [18].

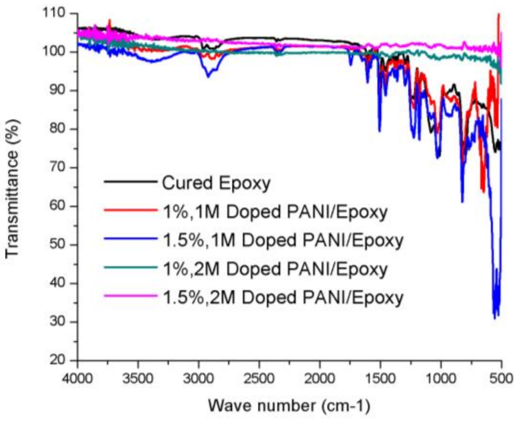

Fig. 4. Comparison of FT-IR spectra of different PANI samples.

The peaks appeared at 1505 and 1608 cm^{-1} were due to C═C stretching of quinonoid (N═Q═N) and benzenoid (N═B═N) rings [19]. Moreover, C−N bending vibrations were observed around 1255 cm^{-1} for aromatic amines. As doping of hydrochloric acid protonated PANI backbone, the characteristic band of (C−N+•) appeared at 1255 cm^{-1} due to stretching vibrations in the polaron structure. The benzoid and quinonoid rings stretching confirmed the synthesis of PANI.

4.5. X-Ray Diffraction (XRD)

The XRD analysis of powder PANI was done on BRUKER X-Ray Diffrectrometer. XRD spectra reveal that the peak of undoped PANI was at 26 (2θ) while in case of doped PANI it was shifted to 27 (2θ) (Fig. 5a) [20]. The major difference in the XRD pattern was not observed because no appreciable change in the structure of PANI was observed except that charge carriers were added in the PANI chains (Fig. 5b).

4.6. Thermal Studies (TGA/DSC)

4.6.1. Thermogravimetric Analysis

The thermal analysis of PANI/Epoxy blends was also carried out to observe the thermal behavior of these materials (Fig. 6a). The analysis was carried out at 15 °C min^{-1} in inert atmosphere. The comparison of degradation of neat cured epoxy and PANI/Epoxy blend is shown in the Table 5.

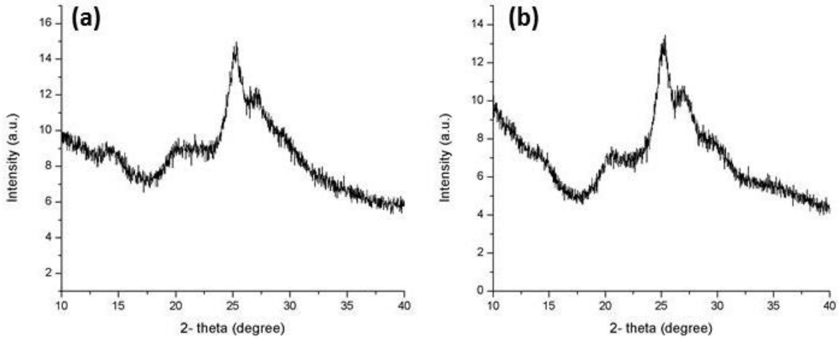

Fig. 5. XRD of: (a) undoped PANI and (b) doped PANI.

Table 5. Degradation temperature of epoxy and PANI/epoxy blends.

Sample ID	Degradation Temperature (°C)
Neat Cured Epoxy	351
1%, 1Molar Doped PANI/Epoxy	351
1.5%, 1Molar Doped PANI /Epoxy	347
1%, 2Molar Doped PANI/Epoxy	349
1.5%, 2Molar Doped PANI/Epoxy	351

From TGA data, it was found that epoxy resin started degradation near the temperature range of 351°C and a phase change was observed in the polymer matrix. The behavior of 1 M doped PANI with loaded concentration of 1% started degradation at 351 °C. This behavior was same for the 2 M doped PANI with 1.5 % loading concentration. However, a remarkable difference was observed in case of 1.5 % loaded concentration with 1M doped PANI. As there was no cross-linkage between PANI chains which could cause an enhancement in the degradation temperature and the doped PANI acted as filler in the epoxy matrix.

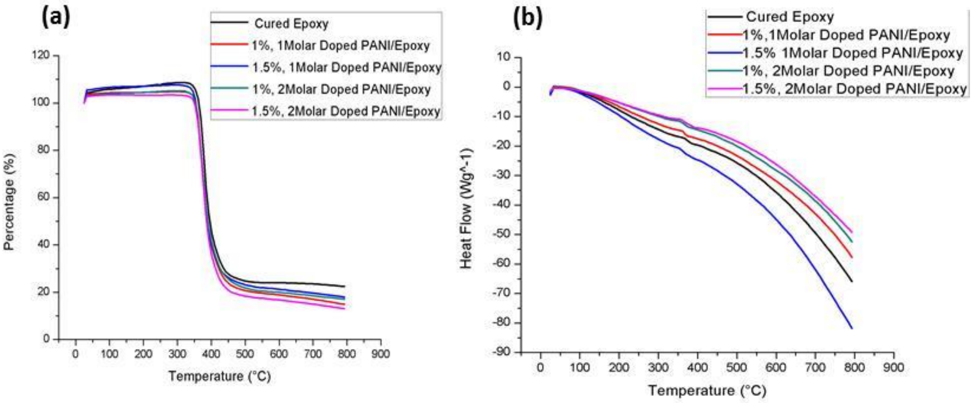

Fig. 6 (a) Combined TGA curves of PANI samples and (b) DSC curves of PANI/Epoxy blends.

4.6.2. Differential Scanning Calorimetry

Differential canning calorimetry was done under nitrogen atmosphere at heating rate of 15 $^{\circ}$C/min. DSC curves of neat epoxy reveals the energy changes as a function of temperature (Fig. 6b). The glass transition temperature of the neat cured epoxy was found to be 369 ^{o}C (Table 6). With the addition of different concentration of doped PANI in the epoxy resin matrix, the glass transition temperature showed variation. The T_g values of 1.5 % loaded concentration doped with 1M dopant showed a difference of 10 ^{o}C while 1 % loaded concentration of the same molarity showed a difference of 6 ^{o}C.

Table 6. Glass transition temperature (T_g) of PANI/Epoxy blends.

Sample ID	T_g (^{o}C)	Difference (^{o}C)
Neat Cured Epoxy	369	Reference 369
1 %, 1Molar Doped PANI/Epoxy	363	6
1.5 %, 1Molar Doped PANI /Epoxy	359	10
1 %, 2Molar Doped PANI/Epoxy	358	11
1.5 %, 2Molar Doped PANI/Epoxy	359	9

The decrease in the glass transition temperature shows that there was no cross linkage between the epoxy matrix and PANI chains. The highly doped nano particle sized PANI in the epoxy resin caused a decrease in the glass transition temperature which suggests that the doped PANI nanoparticles cause flexibility in the resin [21].

The amine groups present in between the two benzene rings were protonated. The protons were donated by hydrochloric acid. As no free sites were available, so the possibility of the cross linkage with the epoxy resin was not possible and PANI acted as a filler in epoxy matrix.

This behavior was not observed in the previous studies. Lower doped PANI resulted in the cross linkage with the epoxy chains which caused an increase in the glass transition temperature. However, this behavior was contrary to this due to the absence of active sites [6].

4.7. Field Emission Scanning Electron Microscopy

Field Emission Scanning Electron Microscopy (FESEM) was used to study the morphology, particle size and diameter of PANI nanoparticles and PANI/Epoxy blend. The samples were analyzed by MIRA 3-XM Field Emission Scanning Electron Micrograph (TESCAN).

To prepare samples for FESEM analysis, at first samples were sonicated in ethanol for 20 min [22]. Solvent dispersed PANI powder was allowed to vaporize on a glass substrate at 80 $^{\circ}$C on heating plate in order to get uniform layer of PANI on the glass substrate. The micrograph reveals that the average particle size of PANI was in the range of 49.70 to 56.83 nm (Fig. 7). However, some cluster of PANI could be seen along with the PANI particles. This suggests that chemical oxidation method is advantageous to control the particle size of the PANI particles. Moreover, the homogenous dispersion of PANI in ethanol resulted in the breakdown of the PANI chains and homogeneity was observed on the substrate surface.

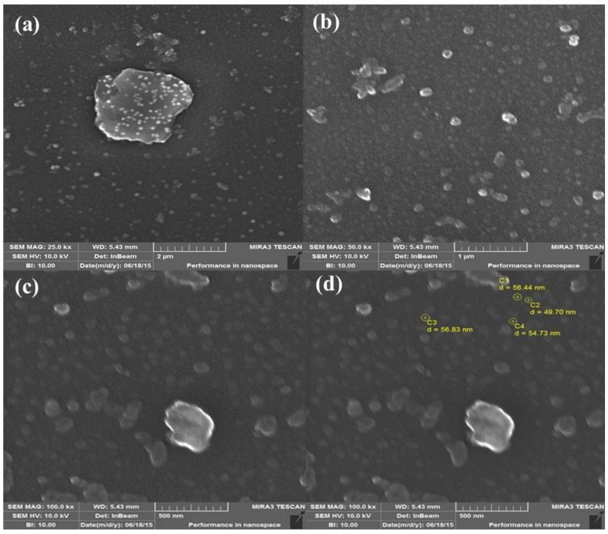

Fig. 7 SEM photographs of PANI samples.

4.8. Anti-Corrosion Studies

According to standard ASTM B117 coatings containing PANI pigments exposed in salt fog cabinet. The cross has been marked on the surface of coating and placed in the salt fog humidity cabinet for exposure up to 600 h. The micrographs/photographs of the samples were taken after cleaning the samples with ethanol followed by drying process [23].

The anti-corrosion micrographs were recorded after 600 h exposure of PANI plates in the 3.5% NaCl environment (Fig. 8). These micrographs show that MS plates coated with neat epoxy get rusted after 600 h and blisters started to appear on the cross mark surface. Corrosion was penetrated form the bare surface to the inner surface which chip off the coating. More area beneath the coating was affected due to the penetration of rust.

PANI/Epoxy blend loaded with 1.5 % and 1% concentrations also showed the penetration of corrosion near the cross mark surface but this penetration was too less as compared to neat epoxy coated MS plate. However, 2 M HCl doped PANI with 1% and 1.5% loaded concentrations showed less corrosion. This corrosion resistance property was attributed to the scavenging effect of the PANI [6].

2M HCl doped PANI with 1% and 1.5% loaded concentrations were found to be the optimized concentration which make the epoxy resin more corrosion resistant. The scavenging effect is due to the higher doping which renders the penetration of rust under the surface of coating due to the presence of protons in the PANI structure.

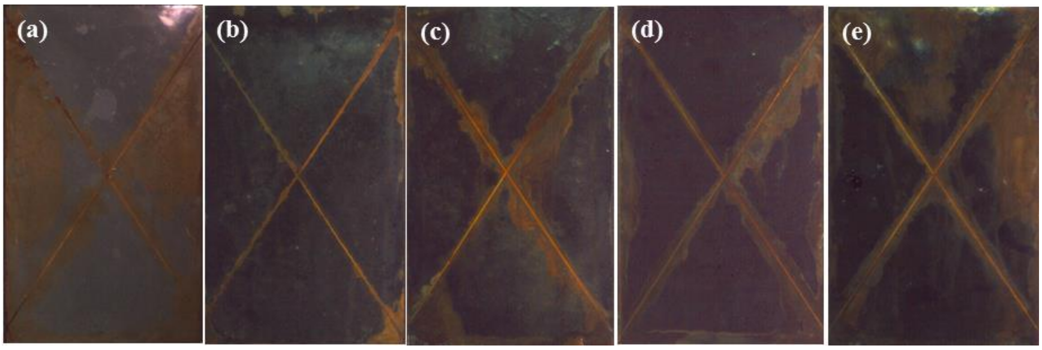

Fig 8. Anticorrosion study on MS plates: (a) Neat Epoxy coated, (b) 1% 2 M doped PANI /epoxy blend, 1%, (c) 1 M Doped PANI/Epoxy blend, (d) 1.5%, 2 M Doped PANI/Epoxy blend, 1.5% and (e) 1 M Doped PANI/Epoxy blend.

Table 7. Corrosion rate of PANI/Epoxy coated steel plates samples.

Sample ID	**Corrosion Rate(g/m^{2}h)**
Neat Cured Epoxy Coated Plate	3.25
1%, 1M Epoxy/ PANI Blend	0.34
1.5%, 1M Epoxy/ PANI Blend	0.4
1%, 2M Epoxy/ PANI Blend	0.2
1.5%, 2M Epoxy/ PANI Blend	0.19

5. Conclusions

The successful enhancement of DC conductivity of PANI was achieved by varying the concentration of HCl which acted as electron donating species. With the variation in the doping concentration of HCl, DC conductivity was increased from 50 – 79 S/cm which was 3 S/cm in case of undoped PANI. Application of PANI for corrosion resistance purpose was carried out by coating the rectangular plates of mild steel with PANI – blend with different percentages of doped PANI as filler material in the epoxy matrix.

We found that PANI in the epoxy resin showed considerable decrease in the corrosion rate (0.34-0.19 g/m^{2}h) of the coating as compared to neat epoxy (3.25 g/m^{2}h). It was also revealed that by increasing the concentration of PANI in epoxy matrix and use of highly doped PANI, the corrosion resistance was increased. Moreover, the T_g of epoxy resin was decreased with the increase in the filling as well as doping concentration of PANI in epoxy matrix.

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