Development of Conducting Polymer based Coatings for Electromagnetic Interference (EMI) Shielding and Corrosion Prevention

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Abstract—*Conducting polymers are a new class of polymers, which have potential applications in various fields. The present work was aimed to develop the conducting polymer based coatings for electromagnetic interference (EMI) shielding and corrosion prevention. Polyaniline (PANI) and polypyrrole (PPy) were synthesized using chemical oxidative polymerization method. The synthesized polymers were characterized using SEM and XRD. Coatings were formulated by incorporating PANI/PPy in Polyurethane (PU) matrix at various concentrations. The surface morphology of the coatings was investigated using SEM. The conductivity of the coatings was evaluated using broadband dielectric spectrometer. The EMI shielding was measured by the transmitter setup. The corrosion properties of the coating were evaluated using potentiodynamic polarization and salt spray test. The results showed that 6% PANI and 6% PPy coatings have appreciable EMI shielding and corrosion resistance with moderate mechanical properties*

Keywords: *Conducting Polymer; Electromagnetic Interference; Transmitter setup; Broadband Dielectric Spectrometer; Potentiodynamic polarization*

INTRODUCTION

Conducting polymers have been under extensive research for the past two decades due to their good electrical conductivity, mechanical strength and corrosion resistance. Conducting polymers are composed of conjugated chains containing π delocalized electrons with the polymer backbone of C, H and heteroatom's such as N and S. Their unique π conjugation properties impart electrical conductivity at room temperature. Conducting polymers (CPs) are doped and converted into electrically conductive forms, are called semiconductive polymer [1]. Recently, nanostructured conducting polymer have became a new field of research and development, due to their potential applications in the fields of rechargeable batteries, electro chromic displays, electrochemical sensors, capacitors, and electromagnetic interference (EMI) shielding [2–3]. Electromagnetic interference is one of the unfortunate byproducts, which is the result of the rapid proliferation of electronic devices, also called electromagnetic pollution [4]. EMI manifests itself as a perturbation in the operation of electronic devices [5]. These undesirable EMI signals of interference could cause:

1. Malfunction of the electronic appliances and,
2. Radiative damage of the human body.

Figure 1 shows the pictorial representation of electromagnetic interference on the human body. At present, the most effective means of controlling electromagnetic interference and electrostatic charge dissipation is to use various types of conducting composites having conducting fillers such as metal fibers, metal particulates, carbon black and carbon fiber. However these composite have certain disadvantages like galvanic corrosion phenomenon observed when dissimilar metals are joined and loss of conductivity due to friction [6–8].

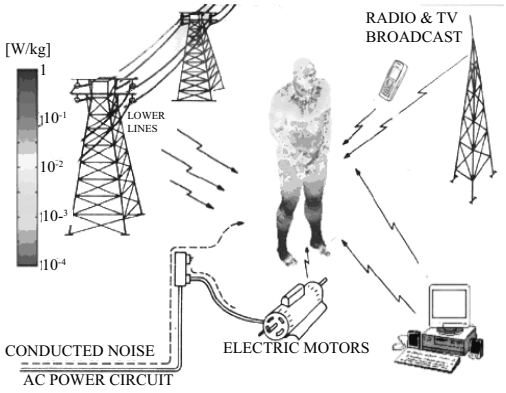


Fig. 1: Pictorial Representation of Electromagnetic Interference [7]

The main objective of the work was to synthesize an electromagnetic interference (EMI) shielding coating using polyaniline (PANI) and polypyrrole (PPy). The blended coating was formulated by incorporating the PANI and PPy in polyurethane (PU) matrix. The corrosion testing was also carried out to evaluate the corrosion resistance performance of the coatings.

EXPERIMENTAL WORK

Materials and Reagents

Aniline and Pyrrole monomers, Sodium persulphate (SPS), procured from Sigma Aldrich, p-toluene sulfonic

acid (PTSA) as dopant bought from Acros Organic, Polyol and diisocyanate, bought from Cipy polyurethane. Additives namely BYK 9076, BYK 530 and BYK 333 were used in the synthesis.

Synthesis of PANI-PTSA

Aqueous PANI-PTSA was prepared by mixing monomer aniline with PTSA dissolved in distilled water under stirring at room temperature for 6 h. To prepare aqueous dispersion of PANI-PTSA, oxidant SPS, dissolved in distilled water was added slowly to aniline/PTSA/ water emulsion under stirring at 0- 4^0C for 5 h and then stirs up to 24 h at room temperature, at a molar ratio of SPS to aniline as 1:2. When SPS was added dropwise, the colorless solution of aniline/PTSA, first turned into orange color and after 5 h of stirring, the color turned into green and finally to dark green after 24 h. Dark green color ensures the complete polymerization of aniline as shown in Fig. 2. The dark green colored reaction mixture was filtered and washed with distilled water and methanol several times and dried at 600^0C.

Fig. 2: Dark Green Precipitate of Polyaniline

Synthesis of PPy-PTSA

Aqueous PPy-PTSA was prepared by mixing pyrrole monomers with PTSA dissolved in distilled water under stirring at room temperature for 6 h. To prepare aqueous dispersion of PPy-PTSA, oxidant SPS dissolved in distilled water, was slowly added to pyrrole/PTSA/ water emulsion under stirring at 0- 4^0C for 5 h and then stirred up to 24 h at room temperature. The molar ratio of SPS to pyrrole was 1:2. When SPS was added dropwise, the colorless solution of pyrrole/PTSA first turned into orange color and after 5 h of stirring the color turns into green and finally to dark black color after 24 h. Black color ensures the complete polymerization of pyrrole as shown in Fig. 3. The black color reaction mixture was filtered and washed with distilled water and methanol several times and dried at 600^0C.

Fig. 3: Black Precipitate of Polypyrrole

Paint Formulation

The coatings/films were formulated by the addition of polyol and diisocyanate in 1: 1 ratio with additives such as BYK 333 (wetting agent), BYK 530 (defoaming agent) and BYK 9076 (dispersion agent). Paint formulations were made with different weight percentage (3%, 6%, 9% and 12%) of PANI and PPy.

Preparation of Coatings and Films

The aluminum panels were de-greased and cleaned and then mechanically roughened with emery paper of 400 grit size, cleaned in acetone and dried. The coatings were brush applied on Al substrate so as to achieve uniform thickness. The free films were prepared on silicone release papers with a controlled thickness of 35 to 50 μm. These coatings films were fully cured for 7 days at room temperature, however there touch dry time was 20-25 min and were hard dry in 24 h.

Characterization of Coatings

The surface morphology of coatings was observed using SEM [SEM, Model no. S3400, Hitachi] to understand the PANI/PPy distribution in the polyurethane matrix. The broadband dielectric spectrometer was used to measure the conductivity of the formulated coatings. The electromagnetic interference measurements at 1.8 GHz were carried out using a phase log oscillator of 9 KHz to 3 GHz frequency generator (Rohde & Schwarz FSL-Spectrum Analyzer), using a conical horned antenna and mm wave power receiving set up consisting of pyramidal horned antenna. The setup is shown in Fig. 4. The shielding effectiveness was measured by noting the power with and without the samples by placing them near to the surface of the antenna. Corrosion resistance of the coating was evaluated using potentiodynamic polarization test, using potentiostat (CH Instrument

604C-Electrochemical analyzer). Pencil hardness [ASTM D 3363-92A], scratch resistance [ASTM G171-03], pull-off strength [ASTM D 4541] and impact resistance (BS 3900 E13) were measured to determine the mechanical properties of coatings.

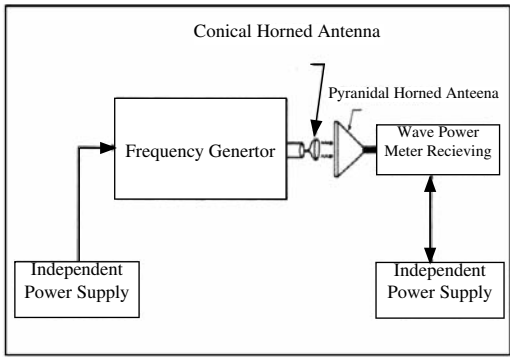


Fig. 4: Transmitter Set Up Used for Measurement of Shielding Effectiveness [6]

Result and Discussion

Characterization of Synthesized Polymer

The polyaniline and polypyrrole were synthesized by chemical oxidative polymerization method. The morphology of the PANI consisted of porous flake-like structure, while PPy existed in clustered or aggregated form, as shown in Fig. 5 and 6 respectively. Figure 7 shows the XRD spectra of PANI particles. The crystalline peaks appear at 20.7° and 25.2°, corresponding to (020) and (200) crystal planes of PANI in its emeraldine salt form, respectively. The diffraction peaks appear at 26.35° and 44.60° as shown in Figure 8, were resulting from the (002) and (101) crystal planes of PPy respectively. The broad amorphous diffraction peak can be ascribed to the scattering of the bare polymer chains from the interplanar spacing.

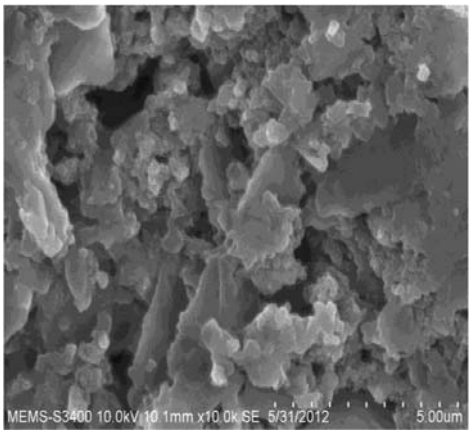


Fig. 5: SEM Micrographs of PANI Particles

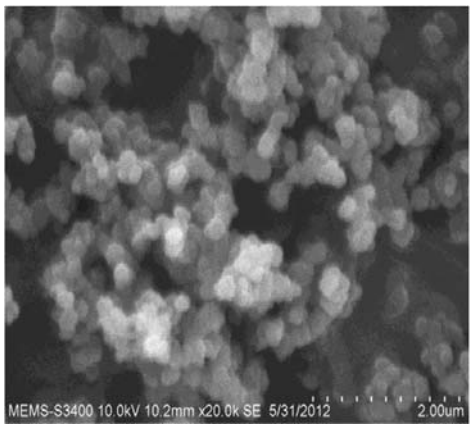


Fig. 6: SEM Micrographs of PPy Particles

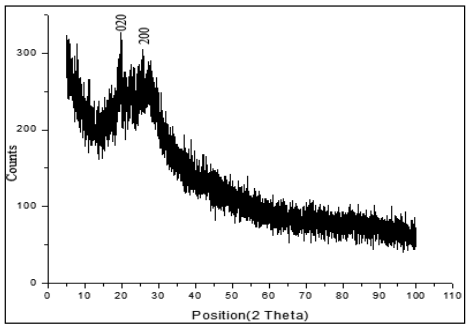


Fig. 7: XRD Spectra of PANI Particles

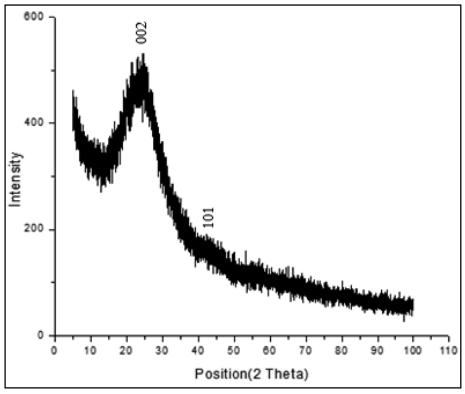


Fig. 8: XRD Spectra of PPy Particles

Characterization of Coatings

SEM Analysis

The surface morphology of coatings was analyzed using SEM to understand the distribution of PANI/PPy particles in the polyurethane matrix. Figure 9 shows the micrographs of PU-PANI and PU-PPy composite, where the distribution of PANI and PPy particles is found to be homogenous and uniform. However, a few lumps are

found to exist in matrix polymer, which may be due to the difference in polarity between PU and PPy/ PANI (PANI/ PPy being highly polar and PU being non-polar in nature).

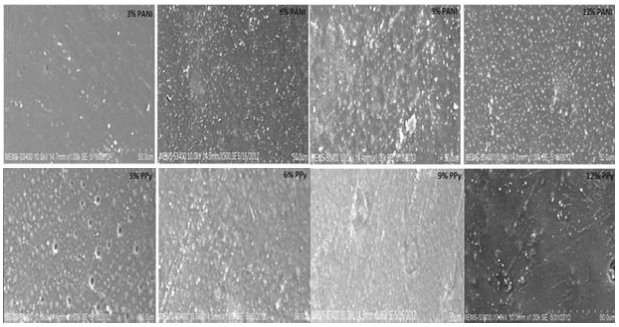


Fig. 9: SEM Micrographs of PU-PANI and PU-PPy Coatings

Conductivity Measurement

The conductivity of coatings was found to increase on increasing the frequency. Fig. 10 shows that at any particular frequency, with the increase in filler (PANI/PPy) concentration, conductivity increases. The increase of conductivity with loading may be due to the increased charge carriers concentration and easier formation of conducting network through better inter-particle contact among PANI/PPy particles, dispersed in the polyurethane matrix (Fig. 11).

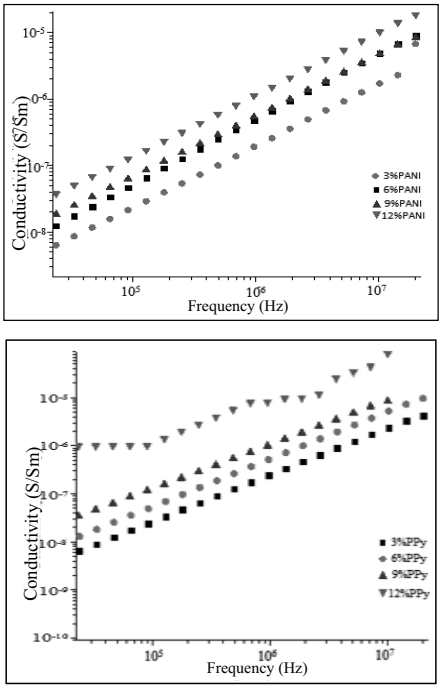


Fig. 10: Variation of AC Conductivity with Frequency (a) PANI and (b) PPy

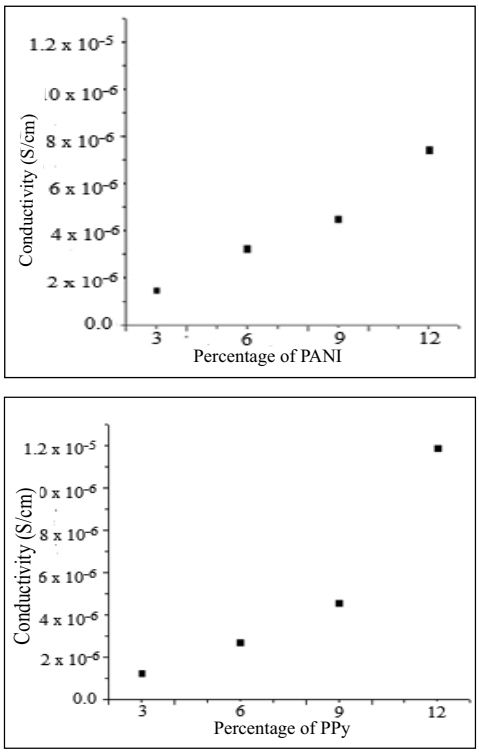


Fig. 11: Variation of Conductivity with Percentage of (a) PANI and (b) PPy

EMI Shielding

According to the electromagnetic wave shielding mechanism of a material, the incident electromagnetic wave in the shielding material is split into four parts: a reflected wave, an absorbed wave, an internal reflected wave, and a transmitted wave. The splitting of electromagnetic waves was shown in Fig. 12.

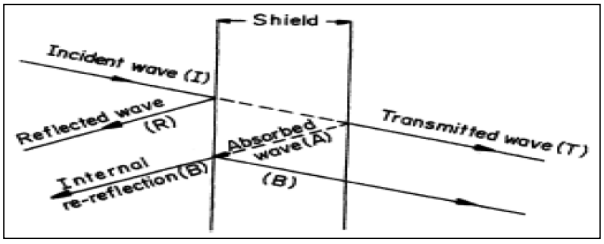


Fig. 12: Splitting of Electromagnetic Wave on Passing through a Shield [6, 7]

Shielding efficiency (SE) can be defined as a measure of the reduction or attenuation in the electromagnetic field strength caused by the insertion of a shield between the source and that point. It is expressed in decibel (dB).This value is actually the ratio of the field strength without the shield to the field strength with the shield and is given mathematically as follows:

$dB = 20 \log E_i / E_o$ (Electric Field)

$dB = 20 \log H_i / H_o$ (Magnetic Field)

In terms of power it is expressed by the following expression

$SE=10 \log P_i / P_o$

Where,

E_i, H_i, P_i is electric field, magnetic field and power of incoming wave respectively.

E_o, H_o, P_o is electric field, magnetic field and power of outgoing wave respectively [7, 9].

Increase in SE with increase in concentration was mainly due to the incorporation of conducting and polar fillers (PANI/PPy) having higher conductivity, permittivity and hence there is appreciable increase in reflection and absorbing efficiency compared to that of non-conducting and nonpolar polymer (Figure 13 and Table 1).

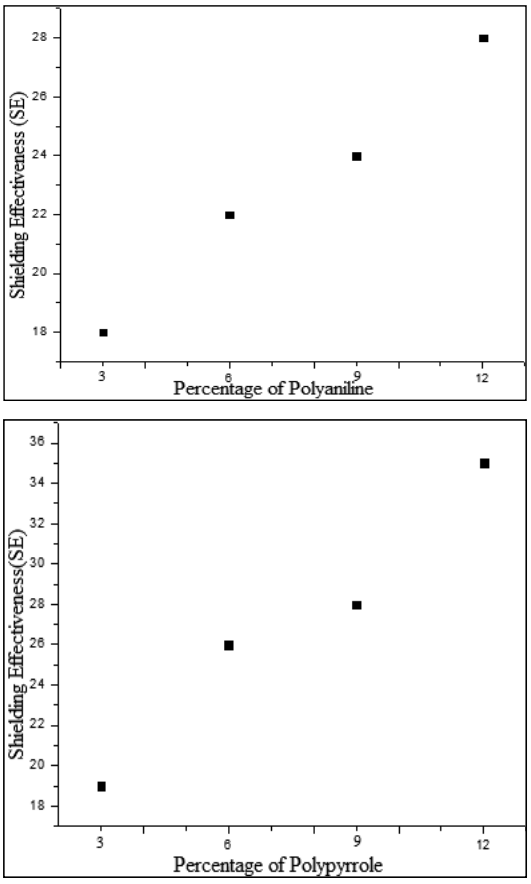


Fig. 13: Variation of Shielding Efficiency with Percentage of (a) PANI and (b) PPy

Table 1: Values of the Shielding Efficiency at 1.8 GHz Frequency

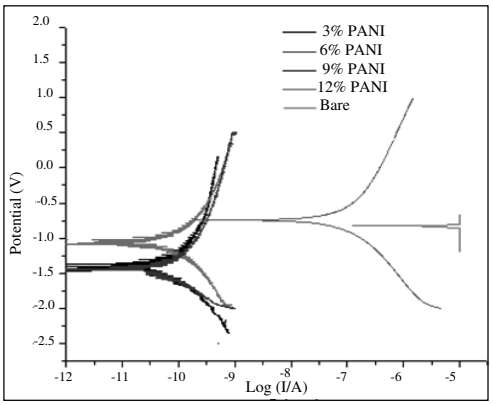
Coating	Thickness (μm)	Shielding Efficiency (%)
3% PANI	35	18
6% PANI	43	22
9% PANI	52	24
12% PANI	45	28
3% PPy	42	19
6% PPy	48	26
9% PPy	53	28
12% PPy	35	35

Potentiodynamic Polarization Studies

The corrosion resistance of coatings was measured using potentiodynamic polarization technique in 3.5 wt% NaCl solution at room temperature. The polarization plots are shown in Figure 14. The values of the corrosion potential (E_{corr}), corrosion current densities (I_{corr}) and corrosion rate (CR), obtained from these curves, are given in Table 2. It was found that the PANI/PPy coated substrate has less corrosion rate than the bare substrate. The results show that these polymers have excellent corrosion resistance. Incorporation of 6 % PANI/PPy gives good corrosion resistance and further increasing the percentage, reduces the corrosion resistance which is indicated by the increase in corrosion rate. It shows that 6% PANI/PPy gives the best corrosion resistance. The increase in corrosion rate at higher concentration might be due to the agglomeration of PANI/PPy particles which restricted the further addition of PANI/PPy for better corrosion prevention.

Table 2: Values of Corrosion Parameters

Substrate	After 15 Days Immersion			
	Icorr (A cm^{-2})	Corrosion Rate (mpy)	Rp (Ω cm^{-2})	PE (%)
Bare	$1.752X\ 10^{-5}$	$4.654X10^{-1}$	$3.643X10^{3}$	--
3% PAni	$5.943X10^{-11}$	$8.118X10^{-6}$	$4.92X10^{8}$	99
6% PAni	$1.501X10^{-11}$	$4.653X10^{-6}$	$8.07X10^{8}$	99
9% PAni	$1.003X10^{-10}$	$1.369X10^{-5}$	$5.268X10^{8}$	99
12% PAni	$2.439X10^{-8}$	$3.332X10^{-3}$	$1.773X10^{6}$	99
3% PPy	$4.349X10^{-11}$	$5.941X10^{-6}$	$9.99X10^{8}$	99
6% PPy	$1.502X10^{-11}$	$1.510X10^{-7}$	$4.98X10^{9}$	99
9% PPy	$1.227X10^{-10}$	$4.684X10^{-7}$	$4.046X10^{8}$	99
12% PPy	$1.105X10^{-7}$	$1.677X10^{-5}$	$3.435X10^{8}$	99



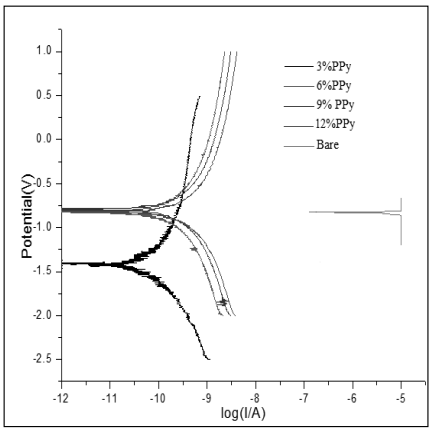


Fig. 14: Polarisation Plot of (a) PU-PANI and (b) PU-PPy Coatings

Mechanical Tests of Coating

It was found from the pencil hardness value that hardness of coating dropped from 3H to 1H. The reason may be the intersolubility of PU and PANI/PPy, decreasing with increase in the content of PANI/PPy because of the polarity difference between PU and PPy/PANI. Scratch resistance test confirmed no effect of PANI and PPy concentration on scratch resistance and all the coatings passed. In pull off adhesion, there was also no effect of concentration of PANI and PPy in the coating. Impact resistance result revealed that there was no disbonding or visible cracking of the coatings. It shows that the coatings are resilient and can withstand rapid deformation and stresses during fabrication. It was found from the cross hatch results that the coatings have excellent adhesion on the substrate and was graded 5B.

General Discussion

When a metal is coated by a conducting polymer films, the electrochemical interface moves from metal solution to polymer solution interface. As long as polymer is in its conductive state it derives that the electrical potential drops at the metal polymer interface and thus the driving force for metal oxidation disappears. The underlying metal is no longer in contact with the aggressive environment. The reduction of O_2 can take place at the polymer surface is also of great importance because this implies that the OH^- species, responsible for disbondment and delamination, has no effect on the adherence of the polymer. A barrier effect is also another feature needed for good protection against corrosion. A strong barrier effect will indeed slow down O_2 and water diffusion through the coating and consequently reduce corrosion at the interface.

Conclusion

The coating systems were formulated by incorporating the PANI and PPy at various concentration (3%, 6%, 9%, 12%) in polyurethane matrix. Formulated coatings were applied on Al panel and coating films were prepared on silicone release paper. The coating films were subjected for the EMI shielding measurement whereas the coated panels were studied for the corrosion behavior and mechanical behavior of coatings. The main results of the work carried out are summarized as follows:

1. The conductivity of coatings increases almost linearly with the increase in the frequency. The conductivity of the coatings increases with increasing the percentage of PPy and PANI. Coating with 12 % PPy and of thickness 35 μm showed the maximum conductivity of 8 x 10^{-5} S/cm.
2. The shielding effectiveness (SE) is a function of concentration of PANI and PPy and varies from 18 to 35 % with the variation of the percentage of PANI and PPy from 3 % to12 %
3. The corrosion resistnce of PANI/PPy coated substrate was better than the bare metal. 6 % PANI and 6 % PPy showed the minimum corrosion rates of 4.653 x 10^{-6} mpy and 1.510 x 10^{-7} mpy respectively. Further on addition of PPy or PANI increased the corrosion rate which may be due to agglomeration of the particles at higher loading.
4. The formulated coating also showed excellent mechanical properties.

The present study showed the potential application of PANI and PPy coatings as novel EMI shielding materials. All coatings were found to have satisfactory EMI, SE and corrosion resistance and good mechanical properties.

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