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Effects of Minor Additions of Polypyrrole on the Thermal, Mechanical and Electrochemical Properties of Epoxy-2Pack Coatings

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In this study, polypyrrole (PPy) conductive polymer was incorporated and dispersed in epoxy coating formulations using a sonication process. Mechanical properties of the prepared coating formulations obtained by the addition of 0.16, 0.25, 0.64, and 0.95 wt.% of PPy were evaluated by the conventional mechanical testing following ASTM standards and nanoindentation technique. The anticorrosive properties of the steel coated samples were investigated by exposing to 3.5% NaCl solution for different periods of exposure varied from 1.0 hour to 21 days. The resistance against corrosion was measured by electrochemical impedance spectroscopy (EIS), while the functional group identification was done by FTIR-ATR analysis. The morphology of the surface for the different epoxy coatings was investigated by field emission scanning electron microscopy (FE-SEM). Results revealed that coatings possessed superior anticorrosion properties with increasing percentages of PPy as indicated by EIS data as well as improved the mechanical properties as confirmed by the nanoindentation measurements.

Keywords: protective coatings; polypyrrole; nanoindentation; hardness; corrosion; EIS

1. INTRODUCTION

Organic coatings can be used to improve corrosion resistance of metals by coating substrate with thin, tough, and durable barriers to the substrate. Many factors such as organic material selection according to working conditions, application of these organic materials to metal substrates and the environment in which these coatings are going to employed determines the efficiency of these coatings. Because of some distinctive characteristics of epoxies such as good chemical resistance, excellent adhesion and mechanical properties these coatings are widely used as protective coatings in areas encountering harsh high humid environments [1,2].

The performance of epoxy coatings or organic heavy duty coatings can be enhanced by incorporating proper and suitable corrosion inhibiting pigments for marine and offshore structures applications. The selection of anticorrosion pigments is very crucial. Most effective and excellent corrosion inhibiting pigments are chromates. But they are getting limitations because of their carcinogenic behavior. Therefore, there is continuous approach to replace chromates to achieve an effective and environmentally friendly protective coating. Various inorganic and organic compounds are studied in order to obtain an effective and successful protective coating system [3-8]. The latest development is the incorporation of conductive polymers (CPs) in coating formulations in order to obtain corrosion protection of metals [9,10].

Polypyrrole (PPy) is one of the major alternative material which exhibits high conductivity and good stability [11,12]. PPy has been used in batteries, chemical sensors, ion selective electrodes, and conductive coatings for corrosion protection [13]. It can be used as a suitable alternative material for anticorrosion properties, where the addition of PPy enhances the properties of coatings. As example, GazalaRuhi et al. [14] synthesized PPy/SiO_2 composite by chemical oxidative polymerization; the synthesized material was then loaded to epoxy matrix to manufacture anticorrosive coatings for mild steel. Their work [14] concluded that the addition of prepared composite in coating increased the thermal stability as well as showed high resistance against corrosion in NaCl solutions. Along with all the manufactured coatings with different wt% of composites, coating with 3.0wt% in epoxy matrix shows significant increase in corrosion resistance as compared to 1.0wt%, 2.0wt% and 4.0wt%. Hosseini et al. [15] synthesized PPy-montmorillonite composite epoxy coatings and applied to Al-5000 series alloy using the dipping method. The morphology of epoxy coatings showed some cracks at the surface, while the morphology of composite coating did not show any defects [15]. The electrochemical impedance study of these coatings revealed that epoxy with PPy and montmorillonite showed highest anticorrosion properties as compared to other coatings containing single constituents [15]. Armelin et al. [16] formulated polyaniline (PANI) and PPy containing epoxy paints; the investigators performed immersion test on their paints in 3.5% NaCl solution to explore the coating’s anticorrosion resistance. Their results revealed that paints modified with PANI possess better anticorrosion properties than pure epoxy coatings. It was reported that PANI even in very low concentration was more effective in providing excellent inhibition against corrosion. On the other hand, the modified epoxy with PPy as anticorrosive additive, results showed improved corrosion resistance and the method of adding conducting polymers in matrix resin greatly influence the working efficiency of these polymers [16]. Moreover, the mechanical properties of paints containing conducting polymers were decreased as compared to unmodified coatings and the behavior of those coatings was found to be brittle [16]. Synthesize of PPy by chemical oxidative polymerization from pyrrole monomer was also reported by Abhijit Et al. [17], who then formulated epoxy coatings with various percentages of 1.0 to 5.0 wt% PPy and studied the effect of PPy on the mechanical, chemical and weathering properties for the synthesized conducting polymer. It has been found that modified coatings showed good mechanical and acid resistant properties. The overall results suggested that PPy can be considered as a potential candidate to be used as anticorrosive pigment and as a replacement of toxic chromic pigments [17,18].

The present study aims at fabricating of four epoxy coatings incorporated with low percentages of PPy to be utilized as corrosion defiant coatings in marine application. The anticorrosion performance of these coatings after being immersed in 3.5% NaCl solutions for 1.0 hour, 7.0 days, and 12 days was carried out using EIS method. The effect of adding PPy on the thermal and mechanical properties such as differential scanning calorimetry (DSC), pendulum hardness, scratch resistance, impact strength, and nano-indentation for the synthesized coatings was also reported.

2. EXPERIMENTAL

Coatings were prepared by reacting diglycidyl ether bisphenol-A (DGEBA) epoxy as the matrix resin (Hexion Chemicals, Germany) with polyamidoamine adducts (Aradur®-PA3282) as hardener (Huntsman Advanced Materials). Polypyrrole (PPy) that was employed in this research was purchased from Sigma Aldrich (Catalog number: 530573). Different types of solvents and diluents (xylene, methyl isobutyl ketone (MIBK), and acetone), were purchased from local Saudi Arabian companies to facilitate the homogeneous mixing and compatibility of the formulations.

Table 1. Incorporation of polypyrrole in optimized epoxy-2pack formulations.

Sample Code	**Resin 1001 wt.%**	**PPy Wt% Doped**	**Xylene**	**MIBK**	**Dispersing Agent**	**Hardener D-3282 wt%**
EC-PPy1	82.91	0.16	20	20	1	16.57
EC-PPy2	82.08	0.25	20	20	1	16.41
EC-PPy3	79.58	0.64	20	20	1	16.15
EC-PPy4	78.33	0.95	20	20	1	15.91

Required amount of epoxy resin was taken in a beaker and mounted on high speed mechanical stirrer. Small quantity of xylene was added to matrix for dilution and in order to facilitate mixing of conducting polymer. After dilution of matrix resin, polypyrrole conducting polymer (PPy) in different percentages was added to matrix and continued to stir at 3000 RPM for 30 minutes to dissipate heat during mixing cooling bath was also used for continuous removal of heat from the matrix. After complete mixing the prepared formulation was left for stabilization. The formulation ingredients and their percentages are mentioned in Table 1. For complete mixing and dispersion, sonication was performed for 60 minutes at 50°C. The hardener was then added to matrix at low speed (600 RPM) to avoid air bubble formation, when mixing completed, prepared formulations were coated on glass panels for mechanical properties and on steel panels for anticorrosion behavior in 3.5% NaCl solutions.

The properties of PPy modified epoxy coatings were evaluated using various characterization techniques. Thermo Scientific FTIR spectrometer (model Nicolet IN10) using universal sampling accessory was used to perform the spectroscopic analysis of prepared coatings. Morphology of coating samples was checked using field Emission scanning electron microscope (FE-SEM) from JEOL (JSM7600F) with an operating voltage of 5kV and working distance of 4.5mm.

The mechanical properties of coatings were evaluated using conventional mechanical testing equipment generally used to measure coating properties such as pendulum hardness (ASTM D 4366), which measures coating hardness with respect to number of oscillations on sample surface from 6^o to 3^o at room temperature using Koenig pendulum tester (sheen instruments Ltd, UK). Scratch resistance (ASTM D-7027) using automatic scratch tester (REF 705, Sheen Instruments Ltd, UK) by applying different loads on coating with the help of scratching probe. Continuous weight is added on the probe until it damages the coating; the weight at which coating gets damaged is recorded as scratch load. Impact resistance is measured using BYK-Gardner impact tester using ASTM D-2794 (Model IG:1120). To measure impact strength a standard weight is dropped on indenter placed at coating surface which creates deformity in coatings. The height of dropping weight is increased gradually until it damages or cracks the coatings, which can be visualized using microscope, the height at which coating damages is recorded as impact failure reading for the coatings in force-inch-pound (f-in-lb).

Glass transition temperature (T_g) of coatings samples were measured using differential scanning calorimetry (DSC) using Q600 from TA instruments. The samples were placed in a pan (approximately 13mg) and placed in heating chamber. Heating was performed on sample from room temperature to 100°C at heating rate of 10^o C/min. The glass transition temperature (T_g) was taken by mid-point calculation of heat capacity changes during heating cycle.

Hardness and modulus of coating samples were evaluated using standard nanoindentation test. The test was performed under closed environment at constant temperature using Nanotest (Micro Materials, UK). Indentations were performed using Berkovich (a three sided pyramidal) indenter. Load controlled program was used to measure hardness and indentations 250mN was applied on all coating samples at loading unloading rate to 10mN/s at maximum load indenter, which was held constant for 60 s and then unloaded again at the same rate. The curves were analyzed using software provided by Micro Materials for analysis using Oliver-Pharr theory [19].

The anticorrosive properties of epoxy/PPy coatings were investigated using electrochemical impedance spectroscopy (EIS) using three electrode cell. The Ag/AgCl was used as reference electrode, stainless steel as counter electrode, and coated steel panels were used as working electrode respectively. Using Autolab Ecochemie PGSTAT 30 EIS, the data was collected. A frequency sweep has been carried out against 5mV sinusoidal wave perturbation at corrosion potential values. The scanned frequency range was from 100kHz to 1mHz.

3. RESULTS AND DISCUSSION

3.1. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

The accumulation of conducting polymer into stoichiometric mixture of epoxy matrix and hardener and its effects on cross linking reaction were studied using ATR-FTIR. Figure 1 shows the spectrum obtained for (a) EC-PPy1, (b) EC-PPy-2, (c) EC-PPy-3, and (d) EC-PPy-4 respectively. In order to achieve this objective prepared formulation were applied on small glass slides and their spectroscopic analysis was carried out after complete curing for 7 days.

We compared the main ATR-FTIR infrared spectroscopy absorption bands for DGEBA and Aradur®-PA3282 components with those of the standard epoxy after the curing process. As can be seen from Figure 1, the more important bands of DGEBA component arise from: hydroxyl groups (3500–3400 cm^{-1}), epoxy methane group (3038 cm^{-1}), C\H vibration (2964, 2927 and 2873 cm^{-1}), aromatic C-C (1606,1507 cm^{-1}), C\H of methylene group (1459cm^{-1}), a doublet of the gem-dimethyl groups from bisphenol A (~1380 cm^{-1}), aromatic ether (1237 cm^{-1}), quaternary carbon with two methyl groups (1182 cm^{-1} and C\H out-of-plane bending from p-substituted benzene (828 cm^{-1}). On the other hand, component B is a polyamide with absorbance characteristics that correspond to the amide and methylene groups: Amide group (3350-3100 cm^{-1}), C\H stretching of alkyl groups (2922 cm^{-1} and 2853 cm^{-1}). Many changes occur in the range of 3500–3200 cm^{-1} since in the cured coating; this broad band corresponds to both O\H and N\H stretching vibrations.

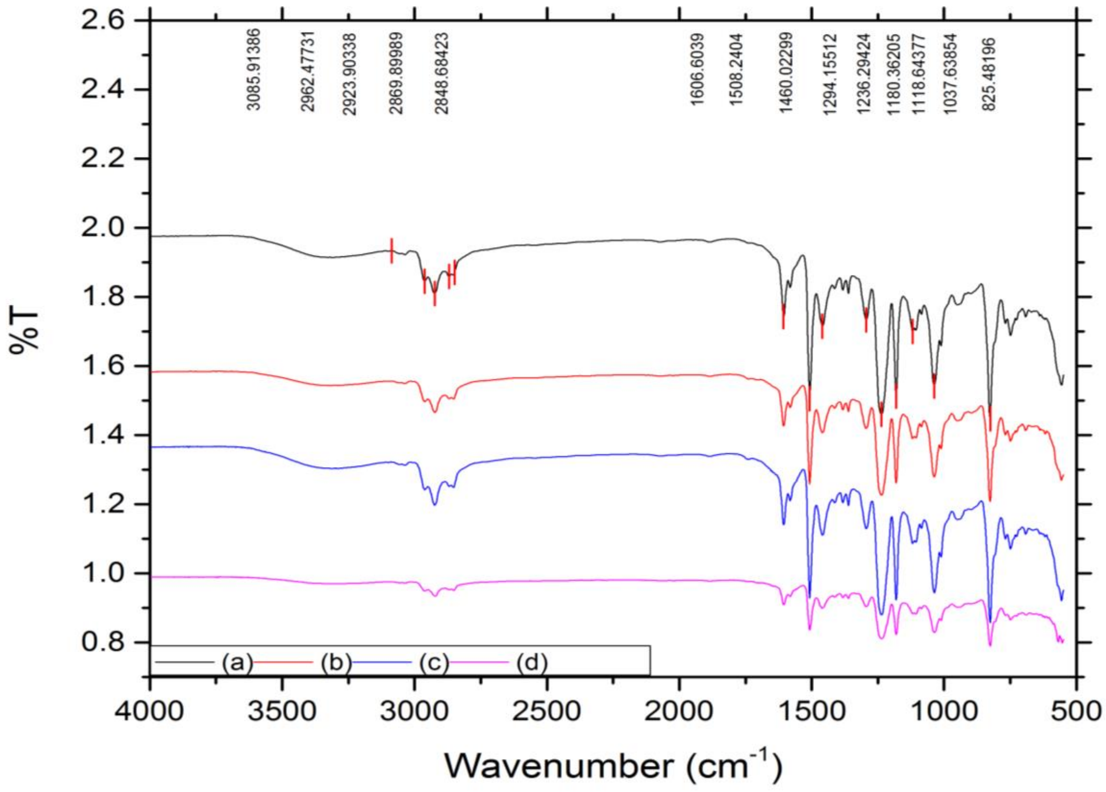

Figure 1. ATR-FTIR spectra of epoxy formulations with various compositions of polypyrrole.

The ATR-FTIR spectrum of the standard of the epoxy allows us to conclude that this cured coating combines the structural units of the oligo (hydroxyl-ether of bisphenol A) and the polyamide curing agent. As expected, the addition of a small concentration of conductive polymer to the coating formulation is not appreciable by ATR-FTIR spectroscopy, which is fully consistent with previous studies [20]. Therefore, the ATR-FTIR spectra of the EC-Ppy1, EC-Ppy2 EC-Ppy3 and EC-Ppy4 have identical spectrum to that of epoxy standard formulation optimized with Aradur®-PA3282 hardener (spectrum is not shown) [7]. The analysis of spectrum obtained after incorporating various types of solvents and additives in polymeric resins is a difficult task because of the bands corresponding to those solvents and additives. Apart from this difficulty, a detailed spectrum analysis of epoxy after complete curing concluded that curing process was complete as there was no absorption as 917 cm-1 which indicates absence of terminal epoxy group. Furthermore, the presence of strong bands in the 1247 cm^{-1} region was identified a Ar-C–O–C–alkyl (ether group) of the thermostable polymer bisphenol-A of the molecule of DGEBA epoxy resin [16].

3.2. Field emission scanning Electron Microscopy (FE-SEM) analysis

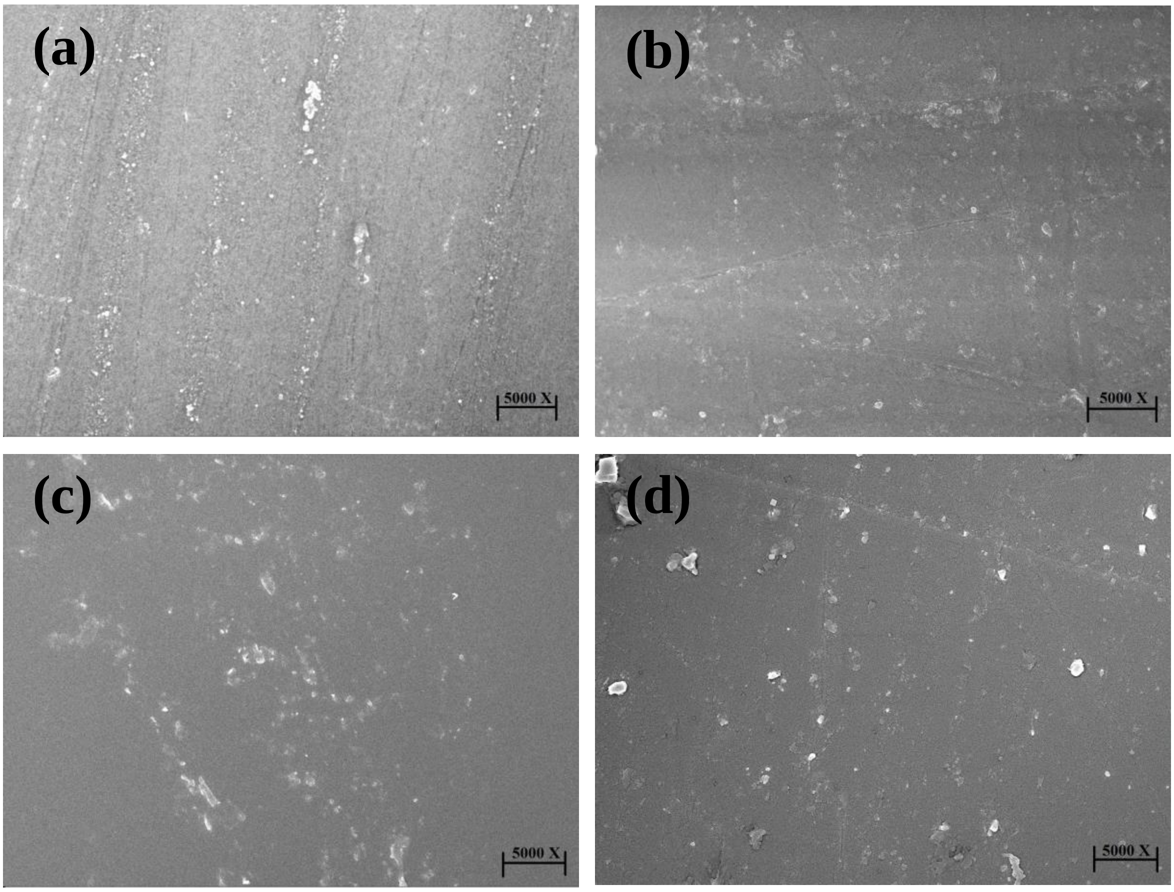

Figure 2. FE-SEM images of polypyrrole incorporated epoxy coatings, (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively.

The morphology and pigment particles distribution on the film surfaces were investigated via field emission scanning microscopy (FE-SEM). The FE-SEM images obtained on the surface of the (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3 and (d) EC-PPy4 are depicted in Figure 2, respectively. It is seen from Figure 2 that a uniform, homogeneous, crack free, continuous close packed structure and highly adherent protective film is formed on the substrates, which leads to the good corrosion resistance of steel coated with the polypyrrole incorporated epoxy coatings.

3.3. Mechanical properties investigation

The results of mechanical properties (pendulum hardness, scratch and impact resistance) after adding polypyrrole (PPy) are reported in Table 2. It can be seen from Table 2 that addition of PPy in epoxy matrix does not significantly change any property of coatings. A slight increase in pendulum hardness is recorded with increasing PPy percentage, whereas scratch and impact properties are slightly reduced, which might be possible because of slight variation in coating thickness at specific test area of the sample. The results described in Table 2 suggest that adding PPy does not significantly increases the mechanical properties [17].

Table 2. Mechanical properties of various PPy incorporated epoxy coatings.

Sample Code	Wt.% PPy	Dry film thickness	Pendulum hardness	Scratch resistance	Impact strength
EC-PPy1	0.16	60-80	131	6	56
EC-PPy2	0.25	60-80	128	6	48
EC-PPy3	0.64	60-80	128	5	48
EC-PPy4	0.95	60-80	138	5	48

3.4. Differential scanning calorimetry (DSC) analysis

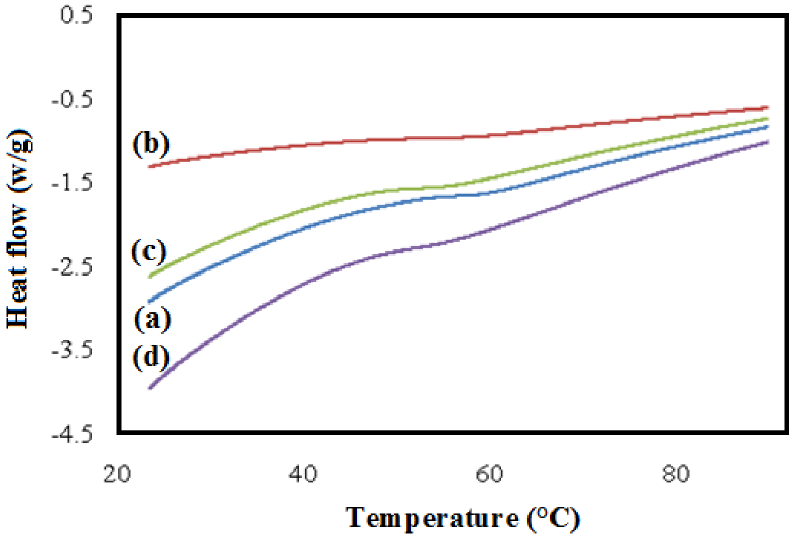

Figure 3. DSC curves of neat and modified epoxy formulation with polypyrrole, (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively.

DSC analysis of epoxy coatings with different percentages of PPy was performed to understand and report the effect of PPy additions on the changes in the thermal properties of the different manufactured epoxy coatings. Figure 3 represents the DSC thermograms of (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3 and (d) EC-PPy4 modified epoxy coatings, respectively. The pattern of DSC thermograms obtained for all the formulations were identical. An approximated glass transition temperature (Tg) value of 58 °C was recorded for all the formulated coatings samples, which is attributed to room temperature curing of diglycidyl ether of bisphenol A (DGEBA). The addition of PPy in the epoxy matrix did not stimulate any changes in Tg of modified coatings and indicates that the addition of PPy to the epoxy matrix does not alter the thermal properties of coatings [20]. The values of Tg for the different fabricated PPy incorporated epoxy coatings are listed in Table 3.

Table 3. DSC analysis of the PPy modified epoxy coating formulations.

Sample	**Tg (°C)**
EC-PPy1	58.3
EC-PPy2	57.4
EC-PPy3	58.6
EC-PPy4	58.4

3.5. Nano-indentation measurements

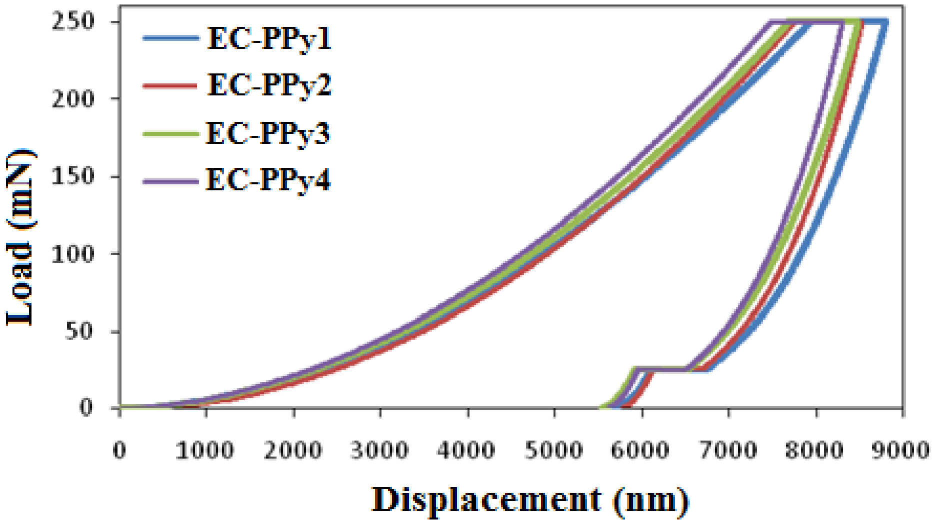

Figure 4. Nano-indentation analysis for polypyrrole incorporated epoxy coatings, (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively.

Nano-indenter has been used to measure the indentation hardness and modulus for coatings. Load control method was used to measure the properties of coatings utilizing Berkovich type indenter by conducting the test in the sequence as loading-holding-unloading. Figure 4 represents the mean load vs. depth curves of coatings incorporated with different PPy percentages, all the sample were loaded until maximum load of 250 mN was reached. The addition of PPy into the epoxy shifted the curves to the lower depth values. The formulation with minimum percentage of PPy (EC-PPy1) recorded the highest depth, both prior and after holding period, while and on the other hand, coating with highest PPy percentage (EC-PPy4) had the lowest recorded depth before and after holding period of 60s. This indicates that the addition of PPy increased the load bearing property of coatings [21]. Where at maximum load, the depth recorded for EC-PPy1 coating was 7946 nm, while the depth recorded for EC-PPy4 coating at maximum load of 250 mN was 7494 nm. The reduction in depth penetration or increased resistance to indentation might be the resultant of induced rigidity by PPy in matrix's complex cross linked structure.

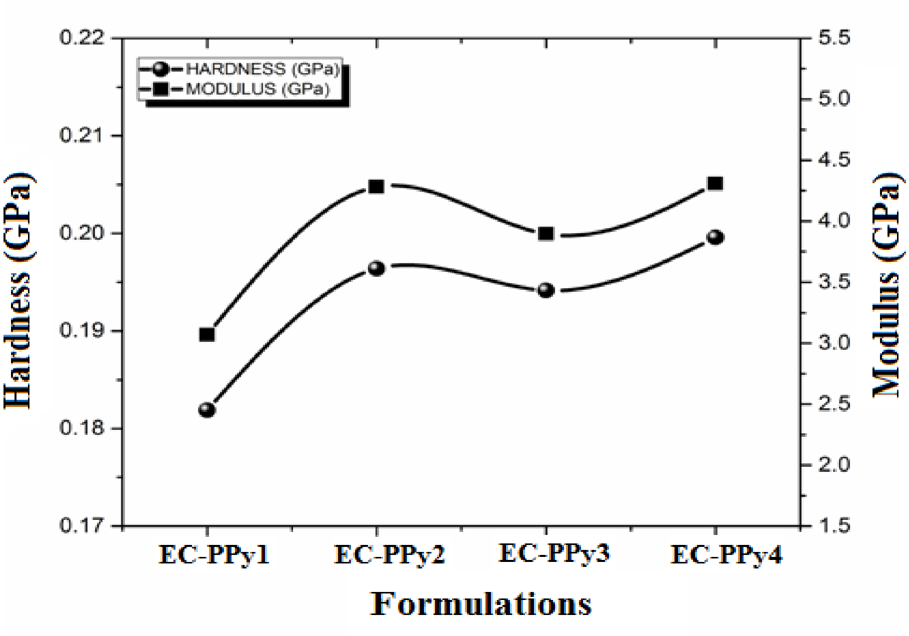

Figure 5. Changes of the hardenss and elastic modulus for the coatings with the increase of PPy content.

The hardness and modulus results were obtained from the load depth curve analysis using software provided by Micro Materials which works on the principle of Oliver and Pharr method [19]. The modulus and hardness results were calculated using the following equations suggested by desired analysis method.

$$H = \frac{F_{max}}{A} \quad (1)$$

$$E_r = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i} \quad (2)$$

$$E = \frac{E_i E_r (1-\upsilon^2)}{E_i - E_r (1-\upsilon_i^2)} \qquad (3)$$

Where H is the hardness, Fmax is the maximum load, A is the projected contact area at maximum load, E is the modulus of sample, υ is the poisson's ratio (0.35 for polymer samples), E_i (1141GPa) is the modulus of diamond indenter, and vi (0.07) is poisson's ratio of diamond indenter [22,23].

Figure 5 illustrates the response of hardness and modulus values for EC-PPy1, EC-PPy2, EC-PPy3 and EC-PPy4 modified epoxy coatings. It can be seen that the increase of PPy content in the epoxy matrix increased both the values of hardness and modulus. For lowest percentage of PPy in epoxy, the hardness and modulus values were recorded to be 0.181 and 4.097, respectively while the values of hardness and modulus obtained with the highest percentage of PPy in coating were 0.199 and 4.308, respectively. Thus, the increase of ~ 10% in hardness and approximate 20% increase in modulus were recorded with highest percentage of PPy, EC-PPy4. The obtained values of hardness and elastic modulus of all the coatings formulations are listed in Table 4 from which we can confirm that the increase of PPy content within the epoxy coating increases the values of both the hardness and modulus.

Table 4. Nano-indentation analysis for PPy incorporated epoxy coatings.

Formulation	Hardness (GPa)	Modulus (GPa)
EC-PPy1	0.181	3.608
EC-PPy2	0.196	4.281
EC-PPy3	0.194	3.896
EC-PPy4	0.199	4.308

3.6. Electrochemical impedance spectroscopy (EIS) measurements

The conventional formulation of the optimized DGEBA epoxy coating resin and Aradur®-PA3282 cross linker has been modified by adding a very low concentration of PPy varied from 0.16 wt.% to 0.95 wt.%. In order to report the effect of PPy on the anti-corrosive properties of the newly fabricated EC-PPy epoxy coatings, EIS measurements were carried out on coated steel panels after different exposure periods of time, 1.0 h, 7.0 days, and 21 days.

The EIS technique has been widely employed to understand the kinetic parameters for the corrosion and corrosion inhibition of metal/solution interface [6-8,24-27]. Figure 6 shows the typical Nyquist plots obtained for (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively after exposure to stagnant and freely aerated 3.5% NaCl solutions for 1.0 h. In order to report the effect of prolonging the exposure period of time on the degradation as well as the anti-corrosion properties of our manufactured EC-PPy coatings, similar EIS plots were obtained for the coated steel panels after their immersion in the NaCl solutions for 7.0 days and 21.0 days and the spectra are shown in Figure 7 and Figure 8, respectively. All EIS experimental data were best fitted to an equivalent circuit as shown in Figure 9. The values of the parameters shown on the equivalent circuit were obtained using Power Sine software and listed in Table 5. The parameters of fitting circuit are defined as Rs is a solution resistance, Q1 and Q2 are constant phase elements (CPEs), RP1 and RP2 are polarization resistances.

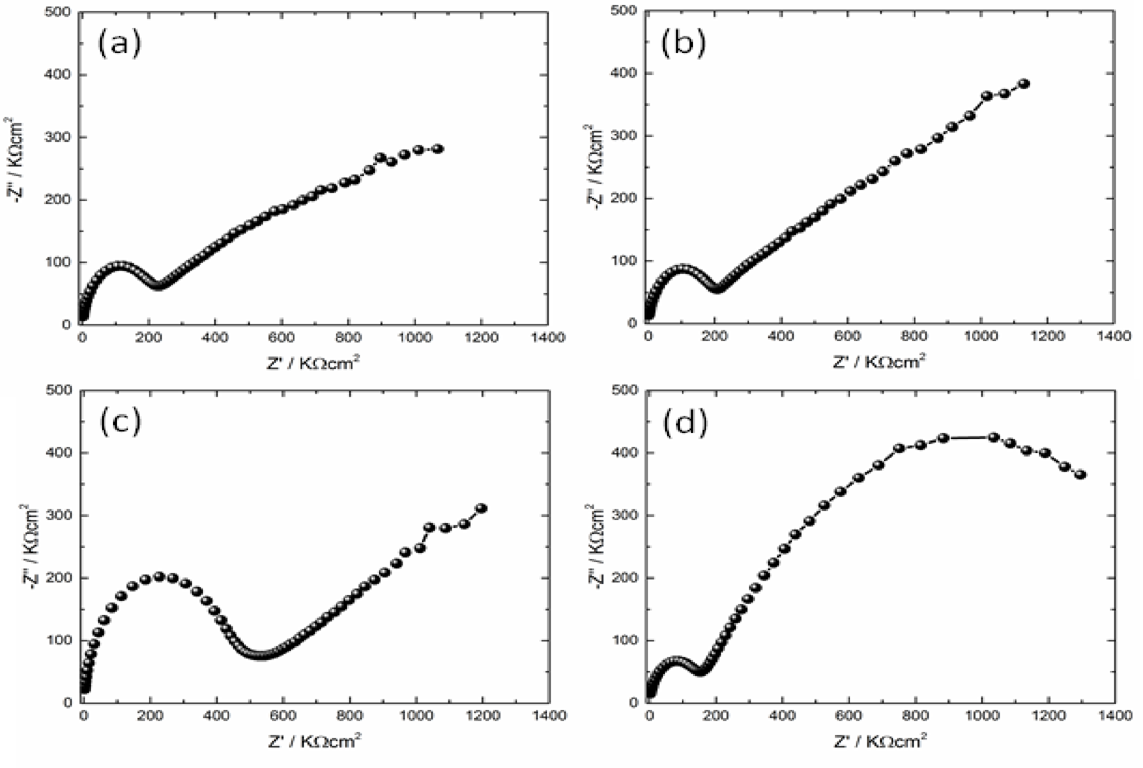

Figure 6. Nyquist plot obtained for (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively after exposure to 3.5% NaCl solutions for 1.0 h.

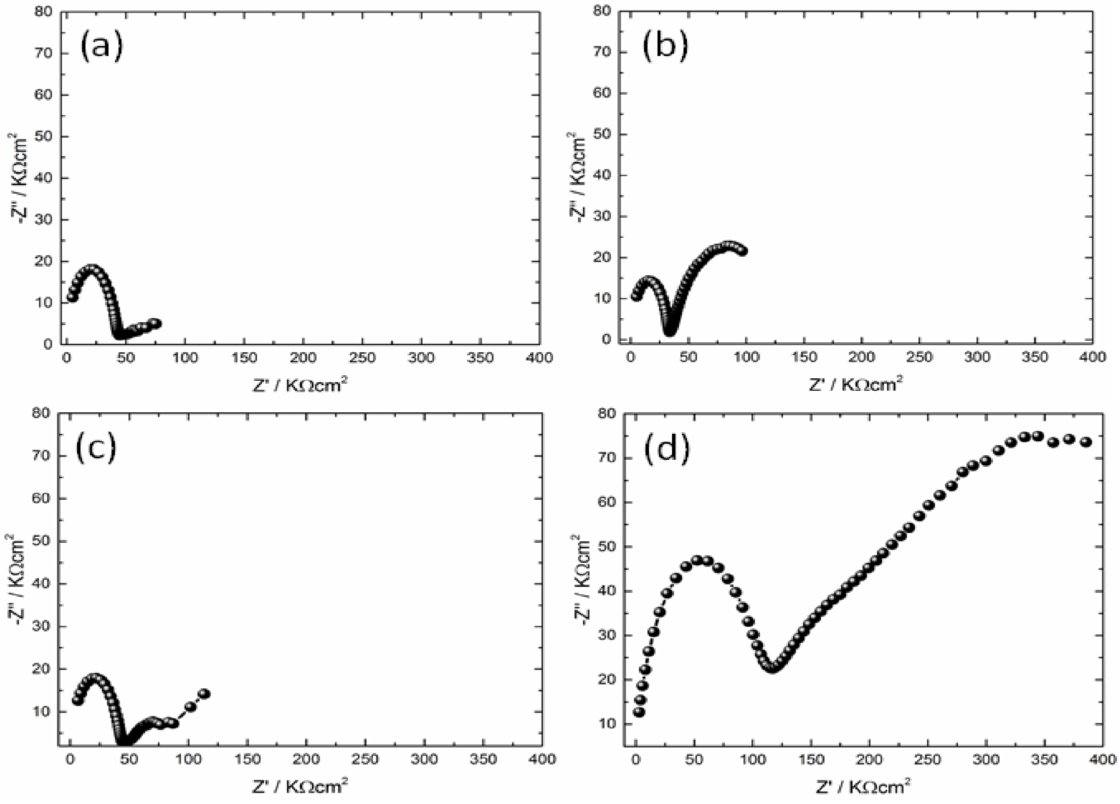

Figure 7. Nyquist plot obtained for (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively after exposure to 3.5% NaCl solutions for 7 days.

It is clearly seen from Figure 6, Figure 7, and Figure 8 that all Nyquist spectra show a semicircle followed by a segment, which indicates that applying the incorporated PPy epoxy provides great protection against the corrosion of steel in the chloride test solutions. The increase of PPy percentage as shown in Figure 6 increases the diameter of the semicircle and length of the segment, which means that PPy greatly increases the corrosion resistance. Where, the largest diameter and segment was recorded for 0.95% PPy (Figure 6, curve d).

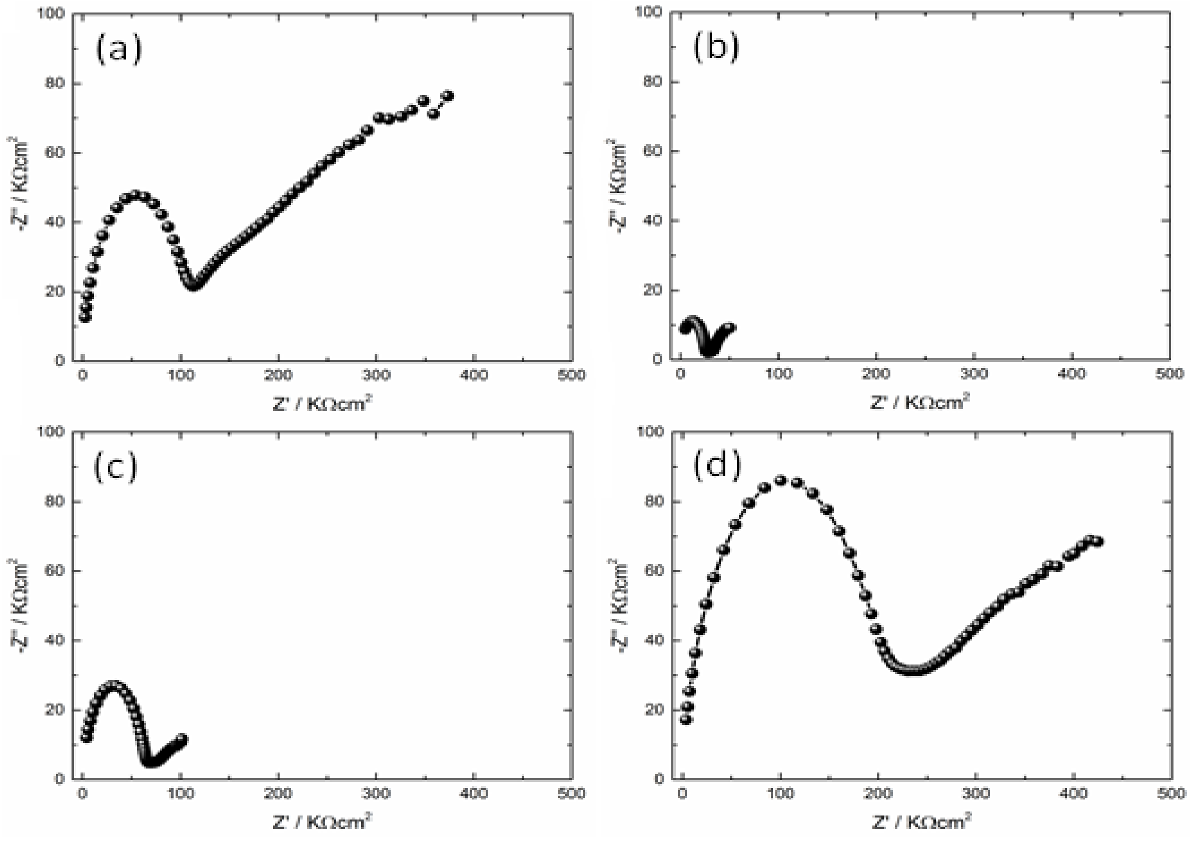

Figure 8. Nyquist plot obtained for (a) EC-PPy1, (b) EC-PPy2, (c) EC-PPy3, and (d) EC-PPy4, respectively after exposure to 3.5% NaCl solution for 21 days.

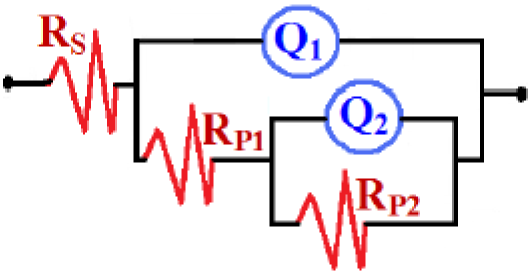

Figure 9. Equivalent circuit model used for fitting the Nyquist plots shown in Fig. 6, Fig. 7, and Fig. 8.

Prolonging the immersion time to 7.0 days, Figure 7, decreased the corrosion resistance of the PPy incorporated coatings as indicated by decreasing the diameter of the recorded semicircle for all PPy coatings containing additives. Further increased in the exposure time to 21 days, Figure 8, provided further decreases in the corrosion resistance compared to the spectra shown in Figure 6 for the coated steel panels immersed for only 1.0 h before measurements. This was confirmed by the impedance parameters listed in Table 5, where the increase of PPy increased the values of Rs, Rp1 and Rp2. On the other hand, the increase of immersion time was found to considerably decrease all resistances, Rs, Rp1 and Rp2. In all cases, the best protection against corrosion was noticed for the incorporated epoxy coating, which contain the highest used PPy concentration, 0.95 wt.%. Liu et al

[28] in their study concluded that the degradation of coatings takes place because of the presence of chloride ions, which diffuse to coating-metal interphase through pin hole or flaws in coatings and attack the metal itself causing its corrosion. The increase in resistances is an indication that protective layer is formed at metal/coating interface that is protecting metal from further corrosion [29]. similar results were also reported by Xing et al. [30], where resistance values after 15 days on exposure in 3.5% NaCl solution were increased.

Table 5. EIS parameters obtained by fitting the Nyquist plots for the different PPy incorporated epoxy coatings immersed in 3.5% NaCl solutions for 1.0 h, 7 days and 21 days respectively.

Sample	**Parameters**						
	R_S / Ω cm^2	**Q_1**		**R_{P1} / kΩcm^2**	**Q_2**		**R_{P2} / kΩcm^2**
		Y_{Q1}/ µFcm^{-2}	**n_1**		**Y_{Q2}/ µFcm^{-2}**	**n_2**	
EC-PPy1 (1h)	309	2.21	0.93	168	1.51	0.35	1830
EC-PPy2 (1h)	138	2.08	0.94	152	1.67	0.34	2780
EC-PPy3 (1h)	733	1.29	0.94	384	2.34	0.24	2600
EC-PPy4 (1h)	193	3.58	0.90	141	596	0.60	1620
EC-PPy1 (7d)	86.3	2.97	0.91	40.5	34.1	0.29	37.3
EC-PPy2 (7d)	881	3.63	0.89	33.9	28.1	0.55	97.9
EC-PPy3 (7d)	446	2.73	0.91	40.5	28.5	0.32	58.2
EC-PPy4 (7d)	105	2.50	0.93	89.5	4.16	0.31	578
EC-PPy1 (21d)	124	1.94	0.95	86.2	4.33	0.30	594
EC-PPy2 (21d)	448	4.04	0.89	25.1	73.6	0.23	394
EC-PPy3 (21d)	203	3.35	0.90	57.3	32.4	0.18	371
EC-PPy4 (21d)	627	2.82	0.90	173	4.96	0.24	814

4. CONCLUSIONS

PPy in different percentages varied from 0.16 wt.% to 0.95 wt.% was successfully incorporated in epoxy matrix. The thermal and mechanical properties of the manufactured coatings were investigated. Also, the corrosion behavior after 1.0 h, 7.0 days, and 21 days in 3.5% NaCl solutions were reported. Results indicated that the incorporation of PPy did not produce any changes in thermal properties of coatings and the coating possessed same T_g irrespective of addition percentage of PPy. On the other hand, it greatly enhanced the mechanical properties. Where, the nanoindentation results indicated that increasing percentage of PPy increased both hardness and modulus of coatings. When compared with the lowest percentage of PPy (0.16 wt.%), an increase of ~10% in hardness and increase of circa 20% in modulus were recorded. Moreover, the addition of PPy produced great effects on the anti-corrosion properties of coatings. This was expressed via EIS data, where the increase of

PPy highly increased the corrosion resistance of the coatings. Increasing the exposure time to 7.0 days and further to 21 days slightly decreased the corrosion resistance of coatings due to its degradation. The comparison of all the results indicates that coatings prepared with highest percentage of PPy (0.95 wt%) possess better mechanical and electrochemical properties. Hence PPy containing coatings can possess better properties and can be considered as suitable alternative of hazardous materials.

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