International Journal of Engineering & Technology, 7 (3.6) (2018) 315-321

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Study Of Corrosion Protection Effect of Low Cost Bio Extract-Polymer Coating Material for Mild Steel in Acidic and Marine Environments-a Cost Effective Approach

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Abstract

The present study was carried out to analyze the performance of an anti-corrosion coating obtained from Carica Papaya extract and PMMA polymer applied on mild steel. This combination was characterized by using FTIR, XRD, Zeta potential measurements and thermogravimetric methods and the presence of major constituents in papaya extract was identified with the functional groups and hetero atoms which able to forms a passive film on the metal surface and protects mild steel from corrosion. These results were verified by visual observation and gravimetric method and then confirmed by electrochemical studies such as Tafel and AC impedance studies. Cyclic voltammetry result study showed that papaya extract confers electroactive property to the polymer. Zeta potential and contact angle measurements of this extract and coating material reinforce protection against corrosion due to high potential& more interfacial tension of the metal surface and hydrophobic nature of film, which repulse the water drops on metal surface, thus giving more adherent, non-porous film.

Keywords: *Carica papaya, PMMA, mild steel, inhibition efficiency.*

1. Introduction

Mild steel is a material which we come across in our day to day life. Corrosion of this metal, as a result of chemical or electrochemical reaction with its environment, disrupts the useful properties of the material. [1] Therefore it is necessary to reduce or control rate of corrosion of mild steel. Corrosion prevention technology has many options at its disposal for the successful corrosion mitigation of engineering materials. One of the very important methods of minimizing corrosion today is the use of corrosion inhibitors. The basic action of inhibitor is attributed to an increase in over voltage of the hydrogen ion discharge due to the cathodic reaction of the corrosion process or an increase in ohmic resistance of an inhibitor film at the metal - electrolyte interface or due to adsorption on the metal surface. [2] Coating the metal surface with polymer provides high corrosion resistance and durable thin film without changing their thickness. [3] Present scenario uses natural plant extract as pickling inhibitors to reduce metal dissolution and polymer material as coating material to control atmospheric corrosion because of its formation of adherent thin films on metal surface [4].In this present study, a new step was taken to prepare new corrosion resistant bio-polymer material with durability, outstanding mechanical and physical properties and high grain boundary volume fraction using PMMA (poly methyl methacrylate) and carica papaya (C.P) fruit skin (from waste) to protect mild steel from corrosion. C.P extract is a natural product of plant origin which is easily available and low in cost. During the literature review, it was noticed that the major constituents present in C.P fruits are sterols, teriterpenes, carbohydrates, glycosides, alkaloids, sapponin, pectin and tannins. [5,6] The fatty acids, myristic, palmitic, steric, oleic, linoleic, lauric, 4-methyl acetophenone, benzyl isothiocyanate, phenyl acetonitrole and myristoleic acids were detected in leaves, flowers and fruits . [7] Phytochemical analysis result showed that there are many constituents with hetero atoms are present which are able to protect metals from corrosion. So, a new corrosion protection coating material for mild steel tried with mixture of PMMA-C.P fruit skin extract (P.C.P). It was expected to provide high adherent film with high inhibition efficiency due to combined effect of PMMA and major constituents present in C.P (synergetic effect). [8]

2. Experimental

2.1. Materials and Methods

Mild steel (MS) specimens were cut into pieces having area 5cm x 1cm which had a percent nominal composition as measured by vacuum emission spectrometer DV-4, (PRICOL, Coimbatore, Tamil Nadu, India) of C -0.06, Mn- 0.4, Si- 0.05, P- 0.03, S- 0.0277, Cr- 0.022, Mo - 0.014 and Ni- 0.0117. The specimen were polished to obtain a smooth surface using different grade emery papers (No. 1/0 to 4/0) and were degreased with CLARKS solution (50g of stannous chloride + 20g of antimony trioxide in 1000mL of conc. HCl), followed by washing with tap water

followed by distilled water, dried and stored in a dissector for further study.

PMMA (99%), Trichloroethylene (95%) and ethanol ACS grade was purchased from Sigma-Aldrich and were employed as purchase without any further purification. Different concentrations of polymer solution (1%, 2%, 5%, 10%, 15%) was prepared by mixing with the trichloroethylene, stirred using a magnetic stirrer for a duration of 3 hrs and further sonicated for 30 min at 40^0C to obtain an uniform solution using an ultra Sonicator instrument. This polymer coating on MS was done by dip coating method and exposed in 1% HCl/ 3.5% NaCl solution for 3hrs, 6hrs and 12hrs. Initially visual observation method used to identify the optimum concentration and confirmed by gravimetric technique. It was identified that 10% concentrations provide maximum inhibition efficiency (I.E) in both methods and mediums. So, for further studies 10%PMMA solution was used.

The peeled off skin of C.P fruit was taken as bio-extract for present study. It dried in the shadow and50g of dry powder mixed with 500 mL ethanol, stirred for three hours in a closed glass vial and kept overnight. Next day the filtrate volume was made upto 500 mL using the same ethanol solution. A trial was made on choosing the optimum concentration of the C.P extract by mixing different concentration (1 %to15%) with10% PMMA solution, where this combination was stirred using same magnetic stirrer for a duration of 3 hrs and sonicated for 30 mins and immediately coated on MS by dip coating, air dried in dust free atmosphere for 24 hrs. Then the coated specimen was then exposed to the electrolyte solution of 3.5%NaCl and 1% HCl. The concentration of 10% C.P+10% PMMA(P.C.P) dip coated specimen showed an adherent film without any peel off even after 12hrsand hence same combination of 10% PCP was chosen for the further studies.

2.2. Characterization

2.2.1. XRD

X ray powder diffraction (XRD) pattern was recorded for the coated specimen using Rigaku Model Ultima IV instrument with Cu K alpha radiation (Philips, Eindhoven, Netherlands). The spectrum was plotted between intensity and 2θ values. For both XRD and FTIR methods, the spectrum were recorded for 10% P.C.P film coated on MS sample after immersion of 6hrs in 1% HCl solution, then removed, washed well, dried and the surface was carefully scratched off. For C.P extract, the spectrum was recorded for the dry powder after evaporation of the solvent.

2.2.2. FTIR

The FTIR spectra were recorded by using FTIR spectrophotometer (Shimadzu, Japan) from the range of 4000-500 cm^{-1} as KBr pellets. The scratched thin film was then mixed with KBr and made into pellets and the FTIR spectrum was recorded between percentage transmission and wave number.

2.2.3. Zeta Potential and Particle Size Distribution

Zeta potential is an electrochemical aspect of a particle's surface, and information about a particle's dispersibility, aggregability, and adhesion ability obtained from this measurement. If zeta potential takes a cross value of around zero, the repulsive force between particles becomes weak and the particles eventually aggregates. So,Zeta potential of C.P extract and P.C.P combination was measured using Zeta Potential analyzer (Zetasizer Ver. 6.32, USA)at room temperature in the count rate of 15.6 kcps in the measurement position of 4.65mm for the duration of 1/2hr. The particle suspension was diluted with deionized water and the potential measured.

2.2.4.Gravimetric Method

The coated and uncoated (blank) MS specimens were weighed and three specimen were immersed in 100mL of this electrolyte solution (1% HCl/3.5% NaCl) for a constant time of 3hrs, 6hrs and 12hrs to carry out the experiments in triplicates at 25^0C; were taken out and washed thoroughly with tap water followed by rinsed with distilled water, dried and reweighed. The difference in weight gives weight loss for varying concentration (1%,2%,5%,10% & 15%) and inhibition efficiency (I. E.) was calculated using the equation:

$$I.E = \frac{W_0 - W}{W_0} * 100 \quad (1)$$

Where, W_o& W -weight loss without & with coating.

2.2.5.Potentiodynamic Polarization Methods

Polarization studies of Tafel plot, AC Impedance studies and cyclic voltammetry were carried out using CH 660 electrochemical work station. A three electrode assembly of MS as working electrode, saturated calomel electrode (SCE) as reference and platinum as auxiliary electrode was used.10 mL of 1% HCl /3.5% NaCl was taken in a 10 mL beaker, then a polished electrode (mild steel with diameter 0.2 cm x 0.2 cm) was introduced and allowed to attain a constant potential for 15 mins. The counter electrode is placed at +0.5 V cathodic to its open circuit potential (OCP).

2.2.5.1.Tafel Plot

Tafel plot performed on sample by polarizing about 3V anodically with the potential scan rate of 0.2V/s. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), and inhibition efficiency (I.E) was calculated.

2.2.5.2. Impedance Spectrophotometry

Impedance measurements were carried out with the same instrument that was used for Tafel method and the cell set up similarly. At each corrosion potential, an AC sine wave of 0.005 V amplitude is applied to the electrode with the frequency of 10000 Hz to 0.1Hz and it was super imposed at it OCP. In this method the charge transfer resistance (R_{ct}) is obtained at various frequency from the plots of Z' (real parts) vs Z'' (imaginary part) from Nyquist plots. The value ($R_p + R_s$) corresponds to the points where the plot cuts Z- axis at low frequency and solution resistant (R_s) corresponds to the point where the half wave semicircle cuts the Z-axis at high frequency and the difference gives the polarization resistant (R_p) values.

2.2.5.3. Cyclic Voltammetry

The electrochemical stability of the PMMA and P.C.P coating was evaluated by using cyclic voltammetry (CV) measurements. The counter electrode is placed between +0.3 V and -0.1V to its open circuit potential (OCP). The CV plot was performed on the sample with the potential scan rate of 0.05 V/s with 2 sweep segments. From the study, parameters such as potential (E_{corr}), current (I_{corr}) and I.E were calculated for the blank and coated samples in 1% HCl and 3.5% NaCl.

2.2.6.Thermogravimetric Analysis

TGA and DTA analysis was carried out in N_2 atmosphere with a TGA instrument V4 SA-TGA2050 model using thermal advantage software for the data treatment. The heating temperature was in the range between 30- 800^0Cat the heating rate of 20^0C/min.

2.3. Surface Analysis

FESEM and EDX studies were done to analyze surface morphology of metal specimen using the ZEISS SIGMA instrument, Japan.

2.3.1. FESEM

FESEM (Field Emission Scanning Electron Microscope) with high resolution instrument was used to study the surface morphologies of the coated specimen after exposure for 6Hrs in 10% C.P, and 10% P.C.P in 1% HCl medium. The acceleration voltage between cathode and anode is commonly in the order of magnitude of 0.5 to 30 kV and the apparatus required an extreme vacuum (10^{-6} Pa) in the column of the microscope.

2.3.2. EDX

Energy dispersive X- ray Spectroscopy (EDX) was used to identify the elemental composition of a cubic micron of sample. This technique works under a sensitivity of 0.1 % for elements heavier than C. It represents the concentrations using a peak with its axis ranging from 0-16 keV. MS specimen used for this study was exposed in 1% HCl in the presence of 10 % C.P, and 10 % P.C.P for the period of 6Hrs.

2.3.3. Contact Angle

The contact angle (C.A) photographs for the coated MS specimen after exposed with (10 % C.P ,10% P.C.P) in 1% HCl was recorded using the instrument HO-IAD-CAM 01 and photograph could provide the surface tension of the metal .The wettability of the MS surface was identified by Drop shape analyzer. The shape of the drop was analyzed by measuring the contact angle between water drop and coated metal surface and surface energy was calculated by using the interfacial tension (IFT) values.The IFT values used to measure the strength of contact between solid-liquid phases.

3. Results and discussion

3.1.Characterization

3.1.1. XRD

Figure 1 (a) shows the XRD diffraction for mild steel exposed 6hrs in 10%C.P after exposing in 1% HCl solution, the high intense peaks at 2θ of 34.30^0, 47.475^0, 56.508^0, 62.766^0 indexed to (110), (103), (200), (112) planes, and the average crystalline particle size measured from full width at half maximum (FWHM) and Debye-Sherrer formula according to the following equation:

$D = (0.89\lambda) / (B \cos\theta)$ (2)

Where, 0.89-shape factor, θ- Bragg angle, λ- X-ray wave length, B- line broadening at half the maximum intensity (FWHM) in radians. The mean size of the particle was calculated as around 49.7nm.

Figure 1b shows the XRD diffraction for mild steel exposed 6hrs in 10 % P.C.P having the peaks at 2θ values of 32.68^0,36.54^0,82.28^0, 34.39^0,6.23^0 corresponds to (100),(102),(200), (002), and (101) plan with the average crystalline size of the particle was analyzed to be 38.45nm. Both films are polycrystalline as well as amorphous in nature[9].The broad band is related to amorphous structure of polymer as expected. As the consequence, the stirring and sonication P.C.P mixture used for synthesis the coating material did not causes any alteration of the crystallographic structure of C.P extract.

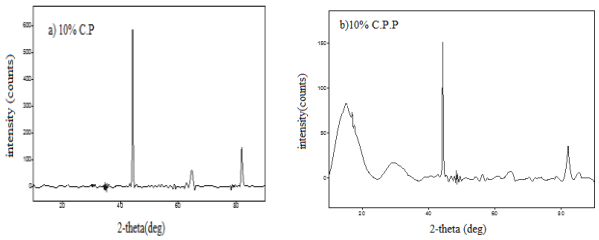

Figure 1: XRD spectra ofMS coated specimen in 1% HCl (a) 10% C.P, (b) 10 % P.C.P at 25^0C

3.1.2. FTIR

FTIR spectrum recorded for the10% C.P and 10% P.C.P coated sample after treated with 1% HClat room temperature for the period of 6hrs is shown inFigure2(a&b). Transmission bands at 1635.64 and 3400 cm^{-1} are attributed to, C=C stretching and O-H stretching and/ N-H stretching vibrations respectively. The bands at 599.86, 555.50 cm^{-1} are due to C- Cl group. Weak bands around 2100 and 1200 cm^{-1} is due to N=C=S stretching vibration (isothiocyanate) and C-O stretching vibration (alkyl-aryl ether groups). The results conforms the presence of functional groups with hetero atoms, aromatic ring, oxygen which mainly bonded with metal and protect it from corrosion. [10]FTIR spectrum was compared with phytochemical studies result, which confirms the presence of major constituents with same functional groups such as C=O, O-H, N-H, and aromatic ring [11,12].

In Figure 2b,bands at 3450, 1635.64 cm^{-1} is due to N-H stretching and C=C stretching (aromatic). Sharp peaks at 597.93 and 555.50 may be due to the presence of C-H bending and C-Cl group present in the coating material. The FTIR band at 406.98cm^{-1} is shifted towards higher wavenumber 449.41 $cm^{-1}$for the C.P after mixing with PMMA. A very weak band at 1350, 1250 cm^{-1} and 2100 cm^{-1} is due to the presence of C-O stretching, CΞN (nitrile group), N=C=S (isothiocyanate)groups.555 cm^{-1}band is observed same position for both C.P and P.C.P. A band at 3400 cm^{-1}vibration is the main component accompanied by the N-H stretching and same contributes of backbone and side-chain vibrations. In general, the spectra of both samples are very similar to each other, which indicate the structure of C.P is not more affected by electrolysis and mixing with polymer, stirring and sonication processes and exposing in HCl solution.

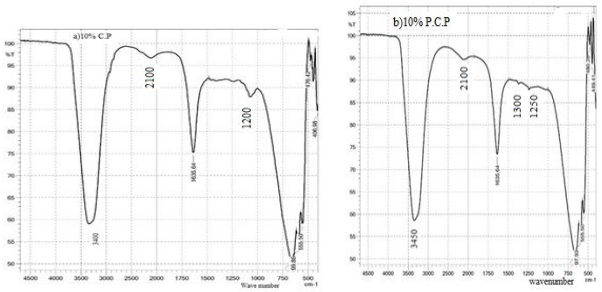

Figure 2: FTIR spectra for coated specimen after exposed 6hrs in(a) 10% C.P and b) 10% P.C.P at 25^0C

3.1.3. Zeta potential and particle size distribution

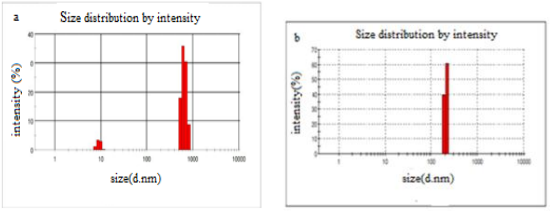

Figure 3: Zeta potential spectra for (a) 10% C.P and b) 10% P.C.P at 25^0C

The stability and dispersibility of carica papaya constituent molecules in C.P extract and P.C.P combination were estimated using zeta potential measurement and presented in Figure 3a & b. The surface potential of C.P extracts are -7.4, and -92.6eV, average particle dispersion size is 650 d.nm and for P.C.P particle size is 208.4 d.nm and its zeta potential is -199.1eV. This increase in negative charge and smaller size of the particle distribution in P.C.P. than C.P is due to the high negative surface, which reflects the high stability and aggregation of the particle on metal surface because of repulsion force between adjacent molecules[13]. It is a physicochemical aspect corresponding to the phenomenon of C.P. and P.C.P coating adhesion. Our data showed a shift ofthe potential from a zero point for C.P and P.C.P, however, the absolute shift values for both were in a similar range and the shift range did not depart far from the zero point for C.P, but increased levels of P.C.P. which, indicate the higher levels of oxidization, and alterations in band that may be due to aggregation, adhesion, and permeability[14].

3.1.4.Gravimetric Method

The I.E calculated by using weight loss method of mild steel in 1% HCl and 3.5% NaCl medium at room temperature with different exposure time are tabulated in table 1.

Table 1: Concentration as a Function of Time of Immersion and Inhibition Efficiency of Coated MS in 1% HCl&3.5% NaCl at Room Temperature

Coated material Conc. (%)	Inhibition Efficiency (%)											
	PMMA						PMMA- CaricaPapaya					
	1% HCl			3.5% NaCl			1% HCl			3.5% NaCl		
	3hrs	6hrs	12hrs	3hrs	6hrs	12hrs	3hrs	6hrs	12hrs	3hrs	6hrs	12hrs
1	85.63	80.94	71.84	87.75	86.65	84.67	89.90	85.45	84.45	89.90	88.65	85.42
2	91.01	85.75	85.68	89.90	89.25	88.54	92.45	86.76	88.97	92.56	89.92	88.67
5	94.29	91.15	86.28	92.28	90.45	90.25	98.65	92.06	90.25	91.67	89.95	91.45
10	98.30	91.76	89.08	97.45	95.72	92.67	99.56	99.56	98.45	99.67	98.67	96.87
15	92.20	90.45	88.56	93.67	94.45	90.45	94.76	92.45	93.25	98.56	93.67	92.56

Almost 100% protection was provided by 10% P.C.P coating than PMMA for the period of 3hrs exposure. The period of immersion of 3 hrs, 6hrs and 12 hrs only slightly vary the I.E values and maximum efficiency was obtained even after exposing 12hrs of 10 % P.C.P. So, this concentration of 10% was chosen as the optimum concentration having maximum corrosion protection in 1% HCl and 3.5% NaCl medium. From Figure 4(a & b), the P.C.P coated mild steel, specimen surface was observed to have the same brightness even after 24hrs exposing without any pick of corrosion products or peel off of film in both sever corrosive medium. But 10% PMMA coated specimen showed slight bulging of film and small pits observed in 1% HCl and removal coated film by batch wise in 3.5% NaCl solution. These results are evidence of the high protective nature of the C.P.C film compared to PMMA for long duration in acidic as well as marine environment due to synergistic effect of many chemical constituents present in C.P extract [7]. These C.P chemical constituent helps the polymer adhere on metal surface for a long duration without peeling off or dissolution in strong corrosive medium.

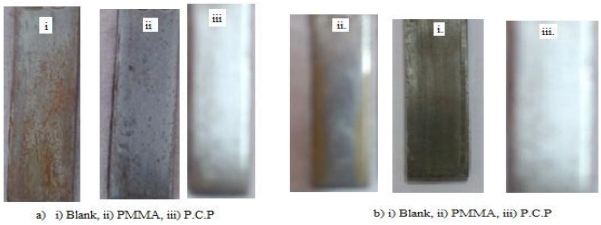

Figure 4: (a & b): Photographs of MS specimens after exposing for 24hrs at 25^0C in a) 1% HCl and b) 3.5% NaCl solution

3.1.5. Potentio Dynamic Polarization Studies

Polarization studies had been carried out for PMMA andP.C.Pat room temperature for 10 % & 15% in 1% HCl and 3.5% NaCl environments. Results obtained by Tafel, impedance & C.V studies are presented in tables 2 -4 and Figure 5-10(a&b) respectively. From Tafel polarization studies, the corrosion parameters such as I_{corr}, E_{corr} were deduced and I.Ewas calculated. From table 2, it can be noted that I_{corr} values for P.C.P coated specimens is very low than that for blank. The maximum protection efficiency of 96% and 98% noted in 1% HCl and 3.5% NaCl respectively. E_{corr} values increased for coated specimen over blank. When 10% C.P extract is mixed with PMMA, the corrosion resistant values increases and corrosion potential values increases. From Figure 4, it can be concluded that mixing of C.P extract with PMMA to the acidic as well as saline medium changes the shape of the anodic and cathodic curves which may be because of the good adsorption of the C.P molecules on MS surface. A slight shift of E_{corr} values to the cathodic side was observed, more for the coated system than blank, inferring that cathodic polarization is more predominant than anodic. These observations clearly indicated that the C.P mixed PMMA coating act as mixed type inhibition in both medium. In addition, the displacement in the E_{corr} values is less than 0.85V which further supports the mixed nature of tested coating materials. [15]. The Tafel lines in Figure 5-6(a&b) are almost parallel to the blank plot on cathodic side with regular variation, which indicates that the mechanism of cathodic reaction maintain the same after mixing C.P extract with PMMA.

Table 2: Potentiodynamic Polarization Data of PMMA, and P.C.P Coated on MS in 3.5% NaCl and 1 M HCl at 25^0C

Medium	Conc.	(-)E_{corr}(V)	I_{corr}(A)	I.E(%)
1% HCl	Blank	0.7645	$2.23*10^{-4}$	-
	10% PMMA	0.4536	$8.12*10^{-6}$	96
	15% PMMA	0.5464	$2.55*10^{-5}$	89
	10% P.C.P	0.4536	$8.22*10^{-6}$	96
	15% P.C.P	0.5443	$2.43*10^{-4}$	90
3.5% NaCl	Blank	0.8325	$2.44*10^{-4}$	-
	10% PMMA	0.7732	$7.18*10^{-6}$	97
	15% PMMA	0.5989	$1.82*10^{-5}$	93
	10% P.C.P	0.3707	$4.83*10^{-4}$	98
	15% P.C.P	0.5464	$2.41*10^{-3}$	89

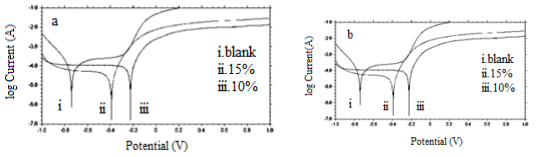

Figure 5: Tafel plot for PMMA coated MS in (a) 1% HCl and (b) 3.5% NaCl solution at 25^0C

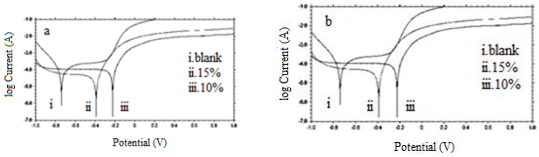

Figure 6: Tafel plot for P.C.P coated MS in (a) 1% HCland(b) 3.5% NaCl solution at 25^0C

Table 3: Impedance Parameters of the PMMA and P.C.P Coated MS in 3.5% NaCl and 1% HCl at 25^0C

Medium	Conc.	R_{Ct}(Ohm cm^2)	C_{dl}(Ohm cm^{-2})	I.E(%)
	Blank	10.21	0.0085	-

3.5% NaCl	10% PMMA	98.24	$2.02*10^{-9}$	99
	15% PMMA	112.76	$5.43*10^{-6}$	85
	10% P.C.P	43.56	$3.11*10^{-9}$	98
	15% P.C.P	123.4	$2.56*10^{-6}$	91
1% HCl	Blank	8.314	0.0036	-
	10% PMMA	86.63	$2.04*10^{-9}$	97
	15% PMMA	103.6	$2.82*10^{-6}$	92
	10 % P.C.P	32.82	$6.26*10^{-9}$	98
	15% P.C.P	166.1	$1.30*10^{-6}$	89

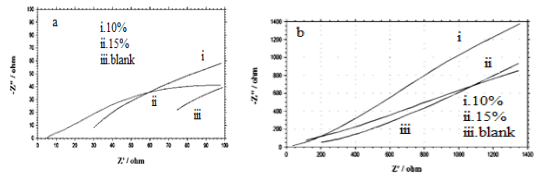

Figure 7: Impedance plot for MS in PMMA in (a) 1% HCland (b) 3.5% NaCl solution at 25^0C

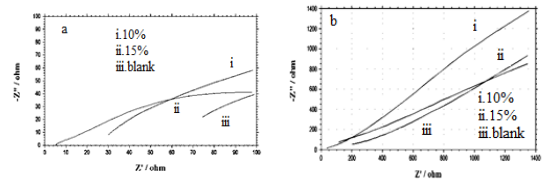

Figure 8: Impedance plot for MS in P.C.P in (a) 1% HCland (b) 3.5% NaCl solution at 25^0C

3.1.6. Impedance Studies

The electrochemical impedance analysis was performed in 1% HCl and 3.5% NaCl for coated and uncoated specimens at room temperature. Figure 7-8(a & b) shows the Nyquist plot of PMMA and PCP coated MS specimen as a function of applied potential from high to low frequency. These impedance curves shows that the semicircle formation takes place for coated specimens than blank in both medium, that infers that the presence of coating on MS in contact with electrolyte undergo a rapid oxidation initially and that provide a layer of passive film at the interface of metal-polymer[16]. This is consistent with Tafel& CV results for which mostly explain the ohmic behavior nature of coated film for MS [17]-[18]. Figure 7-8b shows the semicircle with interfacial polarization in presence of 3.5% NaCl medium. When comparing these figures, it is evident that both the coatings provides better corrosion resistance in MS in both medium but P.C.P coating provide for long duration.

Table 4:C.V Parameters of the Coated MS in 3.5% NaCl and 1% HCl at 25^0C

Medium	Conc.	(-) E_{corr}(V)	I_{corr}(A)	I.E(%)
1% HCl	Blank	0.0048	$2.98*10^{-3}$	-
	10% PMMA	0.0013	$3.46*10^{-4}$	88
	15% PMMA	0.0085	$1.75*10^{-2}$	65
	10% P.C.P	0.0013	$3.16*10^{-4}$	89
	15% P.C.P	0.0085	$1.35*10^{-2}$	65
3.5% NaCl	Blank	0.0054	$2.58*10^{-3}$	-
	10% PMMA	0.0019	$2.59*10^{-4}$	90
	15% PMMA	0.0076	$1.34*10^{-2}$	62
	10% P.C.P	0.0019	$2.19*10^{-4}$	92
	15% P.C.P	0.0076	$1.44*10^{-2}$	66

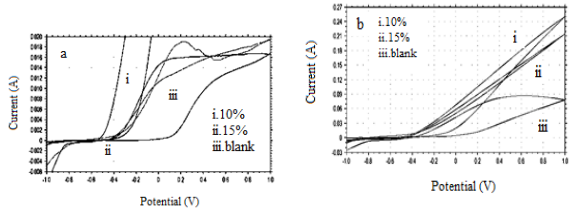

Figure 9: Cyclic voltammogram for PMMA coated MS in (a) 1% HCl and (b) 3.5% NaCl in solution at 25^0C

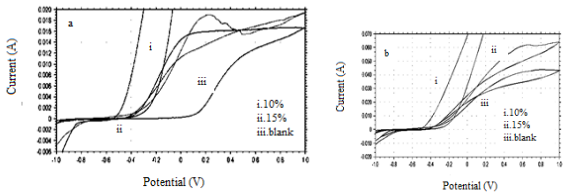

Figure10: Cyclic voltammogram for P.C.P coated MS in (a) 1% HCl and (b) 3.5% NaCl solution at 25^0C

3.1.7. Cyclic Voltammetry Studies

Figure 9 -10 (a & b) shows CV curves of 10% PMMA and 10% P.C.P coated MS specimens in 1% HCl and 3.5% NaCl solutions at room temperature respectively. Figure 9 a (iii) shows the displacement of the oxidative – reductive peaks at -0.73V and +1.24V in 1% HCl. Further the CV curves of 10 & 15% PMMA coated MS in same solution depicted in figure 9 a (i-ii) at -0.5V and +1.34V indicating quasi-reversible system in HCl solution [19]. The PMMA coated MS specimen is reductively- doped in contact with MS in HCl solution at -1.14V. This result indicates that the PMMA coated MS in contact with HCl can be cathodically more polarized. (Fig. 9b) shows the CV curve of PMMA coated MS in contact with 3.5% NaCl solution, predict the peak values between -0.12 and +1.0V for blank and -0.14 - +1.3V for coated specimens. Comparison of these responses of PMMA coated MS in HCl shows larger surface area and larger potential than in NaCl which describes the better reversibility and less ohmic resistance of system in acidic medium than in marine environment [20]. Figure 10(a &b) provide the CV curves for P.C.P coated MS in contact with 1% HCl and 3.5% NaCl solutions with same trend but with more reversibility due to the formation of formation of oxide barrier film on metal. CV in acidic solution shows more ohmic resistance than in NaCl in MS. This is inturn can influence the degree to which a passivating metal may form oxide film and reform (healing) this layer when damage or scratches takes place on its surface [21]. Based on the above discussion, it has estimated that the existence of redox peaks simply illustrate that the coating is active in both medium has observed.

3.1.8. Thermogravimetric Analysis

Thermal stability of the prepared P.C.P was characterized by TGA and DTA and the results are shown in Figure 11 It is shown that the no weight loss rate around 90-100^0C indicate that no moisture present in the sample. The first weight loss peak starting at 163.64^0C is may be due to melting of PMMA. But PMMA started melt at a slightly less temperature than pure PMMA (m.pt of PMMA is 171^0C).The percentage weight loss occurred is only 0.5589%/^{0}C. This may be attributed due to melting and degradation of different morphological components forming the highly complex structure of PMMA. The second step typical melting endotherm with a peak at 394.62^0C, corresponding to the weight loss of 0.8307%/^{0}Cmay be due to the rupture of hydrogen bond of CH_3/ CH_2 groups in PMMA and its ordered region may undergo a solid-liquid phase change [22]. Above 400^0C temperature there is no remarkable amount of degradation represents that the polymer backbone is not degraded. When the temperature reached 800^0C the weight loss of the sample was constant and the residue was 16.1%. So, the P.C.P. coating showed better thermal stability than PMMA.

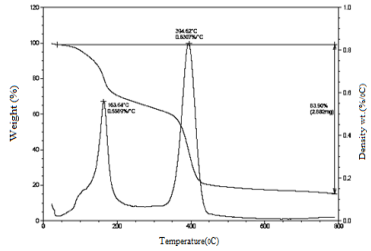

Figure 11: TGA-DTA curve of 10% P.C.P

3.2.Surface Analysis

3.2.1. FESEM

FESEM micrograph of MS specimen exposed in 1% HCl in the presence of 10% C.P, and 10% P.C.P on MS for the period of 6hrsat 25^{0}C was carried out in the magnification of 5000X and presented in Figure 12(a& b).It is seen that the P.C.P coated specimen after exposing in severe corrosive acidic medium features an amorphous and spherical shape with a rough texture. There is no scratch, bulging or peel –off takes place in coated film and non -porous, adherent film observed even after 6hrs exposure with 1% HCl.

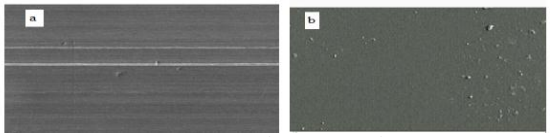

Figure 12: FESEM analysis result for sample after exposed 6hrs in 1% HCl solution at 25^{0}C (a)MS fresh specimen, (b) 10% P.C.P coated.

3.2.2. EDX

The EDX results obtained for10% P.C.P coated MS surface after treatment with 1% HClfor 6hrs at 25^{0}C are shown in Figure 13(a&b). It is seen that elements of C, O, N, S&Cl are identified, where the elements Cl and Fe are from 1% HCl acid medium and MS. The percentage composition of C, N, O and S is comparable to the major constituents present in C.P with phytochemical studies of sterols, teriterpenes, carbohydrates, glycosides, alkaloids[5, 6]. This result is found to be in concordant with the FTIR analysis.

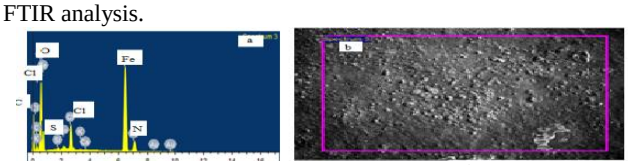

Figure 13: EDX spectra and elemental composition for 10%P.C.P coated sample exposed 6hrs in 1% HCl solution at 25^{0}C

3.2.3.Contact Angle

Contact angle was measured between demineralized water and 10 % C.P and 10% P.C.P coated specimens using Sessile drop method and represented in Figure 14(a & b).These photographs showed that the good wetting property of adsorbed C.P molecules and bad wetting of P.C.P coated MS sample surface. Water drop immediately spread on 10% C.P coated MS surface, and the water particle completely merged and the surface being hydrophilic in nature and the contact angle values measured was 8.5 – 9.4 ^{o}, while the specimen being dip coated with P.C.P partially merged and being hydrophobic in nature and its contact angle value is 74.2 to 74.5^o. Interfacial tension (IFT) value of papaya extract coated MS is 0.0948 and0.099 mN/m Figure14a and P.C.P coated is2.67and 2.70 mN/ m Figure 14b. This shows, for P.C.P coated surface has higher the interfacial tension value, more energy required to merge water drops on the metal surface due toits hydrophobicity[23- 24] and it has more repulsive force than C.P coated surface. So, P.C.P is able to provide better water resistant than C.P extracts.

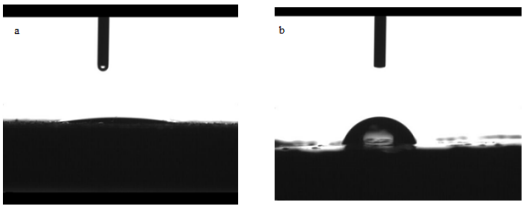

Figure 14: Contact angle for MS coated with (a) 10% C.P extract, and (b) 10 % P.C.P

4. Conclusion

From the present study, we conclude that the P.C. P, as a coating material, is able to provide excellent corrosion protection for MS in severe corrosive medium such as acidic as well as marine environment. The effect of concentration shows that the I.E increases with increasing concentration upto 10% there after there will be decrease due to peel off, pit formation or bulging of the coated film. The results arrived from potentiodynamic polarization results indicate that the natural product and polymer combination act as mixed type inhibition of corrosion with cathodic polarization predominant and high IE values due to the adsorption of chemical constituents on metal surface and also the adherent nature of thepolymerthat is the combined effect of (synergistic effect). The characterization and surface analysis by XRD, FTIR, SEM, XRD and Zeta potential proves the presence of major chemical constituents present in the coated film and adsorbed and offer more corrosion protection on MS surface. Contact angle and Zeta potential studies proves the coated P.C.P film is hydrophobic nature with high IFT values that repulse the water molecule on MS surface there by provide highly protective, impermeable and durable coating film. Finally the C.P extract is prepared from naturally occurring waste product. It can be believed as eco-friendly, non-toxic and low cost material that can be used coating for metals. Thus this combination of P.C.P has found more advantageous in corrosion protection than toxic and more costly organic / inorganic chemical coating.

Acknowledgment

We are grateful to Amrita Vishwa Vidyapeetam, Coimbatore, Tamil Nadu, India for help to carryout this work. The author would like to thank Prof.T. Ramachandran for giving their valuable suggestion for this research and bio-sensor lab staffs and Chemistry Department lab staffs.

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