Chemical and electrochemical corrosion studies of *ricinus communis* oil based poly(urethane-ricinoleamide) coatings

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Abstract: In view of the depletion and possible exhaust of fossil fuels in near future, enormous increase in the cost of petroleum products and production of volatile organic compounds (VOC) by synthetic polymers and their application, the proposed article reports the development of sustainable resource based high performance Ricinus communis oil (Castor Oil) [RC] poly(urethane-ricinoleamide) [PUR] corrosion resistant coatings on mild steel. The physico-mechanical properties were investigated using standard methods. The corrosion resistance performance of PUR coatings was evaluated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in acid (3.5 wt% HCl) and alkaline (3.5 wt% NaOH) mediums. The weight loss measurement was also carried out under tap water (Cl- ion 63 mg/l; Conductivity 0.953 mS/A). Salt mist test (5 wt% NaCl) was performed on these coatings. The effect of additional –OH functionality of RC oil on the corrosion resistance performance of PUR coatings was also discussed. These investigations reveal that the PUR coatings provide protection to the mild steel by reducing the corrosion current density by 104 times as compare to bare MS. These coatings also exhibits higher corrosion resistance performance as compared to other reported sustainable resource based coating systems, hence show good potential for their commercial application.

Keywords: barrier; coatings; crosslinking; electrochemistry; renewable resources

1. Introduction

Prevention of metallic corrosion of is one of the most challenging task in materials science; causes enormous economic losses in many applications, including the automobile, aerospace, ship manufacturing industries etc. One of the effective ways to combat corrosion is by the use of organic coating. The functional groups present in organic moieties generally influence the mechanical and corrosion combating ability of organic coatings [1]. The presence of polar functionalities in polymer coating effectively enhances the adhesion at metal-coating interface, which plays a significant role in the corrosion resistance performance of coatings [2]. However, it is important to develop coating systems with new functionalities that prevent cathodic disbonding of coatings, caused by corrosive environment, either via oxygen reduction or other corrosive ions, that lead to the process of delamination, e.g. in case of steel, surface is covered by a thin ferric oxide film, produces through the reduction of Fe$^{3+}$ to Fe$^{2+}$ results in the production of partially soluble oxides in the presence of corrosive environment, responsible for the delamination of the coating [3,4].

Most of the coatings used now a days are petro based, The enormous increase in the cost of petroleum, depletion of fossil fuel and the strict environmental legislation to control the exhaust of green house gases has posed a binding on the frequent use of hydrocarbon based chemicals and monomers that involved the use of organic solvents, which produces volatile organic component (VOC) [5, 6]. Hence, to meet these challenges in the synthesis of polymers and their application in paints and coatings there
is an urgent need to use promising alternative eco-friendly sustainable resource based precursors like lignin, natural rubber, rice husk, vegetable seeds oil etc. for the synthesis of polymer resins to substitute the petrochemical based polymers [7, 8]. Among these sustainable resources, vegetable oils are found to be more useful precursor for the development of anticorrosive polymeric coating materials [1, 8]. The presence of various functionalities and conjugations in the fatty acid chains of vegetable oils help in the introduction of required properties, which induces value added high performance protective properties in polymers such as high gloss, good plasticity and UV resistance properties [9, 10]. Various vegetable seed oils like pongamia, soya, sunflower, linseed, castor (Ricinus communis) etc. have been used in the synthesis of polymeric coatings. Ricinus communis (RC) a non-drying oil contains about 90% ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid), having hydroxyl functionality of 2.7. Mostly it is used without modification as a raw material for the manufacture of polyurethanes [9]. Polyurethane (PU) is an important class of polymers that have found extensive application in paint and coating industries due to their excellent mechanical and good chemical/corrosion resistance performance [11]. These properties of PU can be attributed to the presence of two types of moieties (i) soft aliphatic chain and (ii) hard urethane moiety. The combination of these two moieties induces value added properties in PU. Karak et al have developed castor and sunflower oil based hyper-branched PU which show higher physico-mechanical and chemical resistance properties [12,13]. Petrovic et al has synthesized PU without isocyanate route, by the reaction of aromatic and cycloaliphatic diamines with carbonated soybean oil [14]. Larock et al have developed waterborne PU using different vegetable oil e.g. peanut, corn, soybean, and linseed oil and find out the effect of residual unsaturation present in this on mechanical properties of coatings [15]. Feng and Zhang et al have worked on waterborne polyurethanes derive from vegetable oil by the incorporation of rigid moiety i.e. cyclic aromatic rings into soft polymer hydrocarbon chain networks [16]. However, for commercial applications we need coatings with advanced properties like high mechanical strength, excellent chemical and corrosion resistance, thermal resistance and stability etc. In order to meet these requirement, physical and chemical properties of PU can be modify either just by physical amendment like blending or through the formation of interpenetrating network with other polymers [17] or by judicious modification in composition and structure of two basic building blocks, viz., polyol and diisocyanate of polyurethanes [12, 13]. Introduction of amide linkage in the polyurethane backbone can improve the adhesion as well as alkali resistance properties. Literature survey reveals that no work have been reported on the corrosion resistance performance of the RC oil based poly(urethane-amide) coatings.

The present article thus reports the physico-mechanical and corrosion protective performance of Poly(urethane-ricinoleamide) [PUR] coatings with the aim to (i) develop the eco-friendly coatings with promising corrosion resistance behavior and to (ii) understand the fundamental mechanism of chemical as well as electrochemical corrosion protective performance of these coatings and to (iii) study the effect of the additional –OH functionality of RC oil on the physico-mechanical and corrosion protection performance of PUR coatings further (iv) to compare the physico-mechanical and corrosion protection performance of PUR coatings with those of other vegetable seed oil based reported PU coatings[17-19].

2. Experimental Section

2.1. Materials

RC oil [Mn: 930; hydroxyl value- 160-168; acid value- 2.45], diethyl ether, diethanol amine (DEA), ethyl methyl ketone (EMK) (S.D. fine chemical, Mumbai, India) and toluylene 2,4-diisocyanate (TDI) (Merck India) were of analytical grade, and used as such.

2.2. Synthesis of HERA and PUR

2.2.1. Synthesis of HERA

Synthesis of HERA is reported elsewhere [18], as reported earlier [18], a calculated amount of RC oil (0.1 mol) was added drop wise in DEA (0.32 mol) in which we have added freshly prepared sodium methoxide (0.007 mol) solution (in methanol). The reaction mixture were kept in a three-necked
conical flask (fitted with a thermometer and condenser) over a magnetic stirrer at a temperature of 110 °C. Progress of the reaction was monitored by TLC (Thin Layer Chromatography). When the reaction was complete (3 h), it was then cooled down to room temperature. Purification has been done with the help of a separatory funnel through solvent and non-solvent methods.

2.2.2. Synthesis of PUR
As reported in our earlier publication [18], In-situ synthesis were performed in which pure HERA (1 mol) along with TDI having different amount (0.8, 1 and 1.2 mol) were taken in a minimal amount of EMK (20 ml, for dilution and complete mixing), placed in a three-necked conical flask fitted with the thermometer, dropping funnel, and cooling condenser. Nitrogen gas was continuously propelled through the reaction mixture along with constant stirring at room temperature for about 2h. The progress of the reaction was monitored by TLC (Thin Layer Chromatography) and hydroxyl value was regularly checked after a constant time intervals. When desired hydroxyl value of the product (PUR) was reached reaction was stopped. Rotary vacuum evaporator was used to remove the solvent (EMK) to obtain the PUR which is a light yellow-colored liquid.

2.3. Characterization
2.3.1. Coating preparation on mild steel
The 70 wt% solution of PUR (using different weight percentage of TDI (i.e., PUR-0.8, PUR-1.0 and PUR-1.2, where suffix indicate the no. of moles of TDI) in ethyl methyl ketone, were applied on finely polished and degreased mild steel strip having the following specification: IS: 6240 HR: Iron 98.0%, Carbon 0.16%, Manganese 0.30%, Silicon 0.25%, Sulphur 0.030%, Phosphorous 0.030%, Aluminium 0.02%) by brush technique. Two different dimensions of MS strips were used one of 70 mm x 30 mm x1 mm for physic-mechanical characterization and other is of 25 mm x 25 mm x 1 mm for corrosion resistance test.

2.3.2. Physico-Mechanical Studies
The specular gloss at 60° (gloss meter, model RSPT-20; digital instrument Santa Barbara CA), scratch hardness (BS 3900), and impact resistance (IS: 101 par 5/sec-31988) physico-mechanical tests were performed on PUR coated 70 mm x 30 mm x 1 mm size mild steel strips. The five coated samples were tested and their mean average values were determined using error bars representing standard deviation. Coating thickness was measured with Elcometer instrument (Model 345; Elcometer instrument, Manchester UK).

2.3.3. Corrosion Resistance Measurements
2.3.3.1. Weight Loss Measurement
Corrosion resistance properties of PUR coated MS with reference to uncoated MS were investigated in acid (3.5 wt% HCl), alkali (3.5wt% NaOH) and tap water (Cl ion 63mg/l; Conductivity 0.953 mS/m) using ASTM G31 method. Before application of PUR coating the rough edges and faces of the MS specimen becomes smooth by grounded it to 120-grit finish on polishing unit which is cooled by water and marked for their identification with vibratory tool. After that it was washed with 10% nitric acid for 10 minutes at about 50 °C, Alconox cleaner was then used with soft bristle brush to scrubbed the MS specimen. Further, distilled water, methanol and acetone were used to rinse MS to get finely finished samples, which were then dried. The dried samples were accurately measured for their length, width, and thickness. The test was performed in corrosion flasks by weighing samples before and after the immersion in corrosive media. In order to prevent loss of water through evaporation each flask was equipped with an Allihn condenser. Within the flask fluropolymy filament was used to suspend test samples in such a way that they did not touch either the side wall of the vessel or each other. The total surface area of the test sample per flask was controlled so that the minimum recommended solution volume to surface area ratio (0.2 ml/mm²) was maintained. The flasks were kept in the standing condition without any agitation or exposure to air. The corrosion cells were periodically monitored and weight loss were measured during the immersion time.
The protective behavior of the coatings against the dissolution of MS was evaluated by calculating the corrosion protection rate (CR) for each one of the samples. The calculation was performed using the following expression.

$$CR = \frac{\Delta g}{Atd}$$

Where $\Delta g$ is the change in weight loss of the specimen, $A$ is the area of the specimen, $t$ is the time (year), and $d$ is the density of the specimen. The results were given in milli-inches per year (MPY).

2.3.3.2. Salt spray test
Salt spray test (ASTM B177-94) of PUR coatings were carried out for a period of 720 h in a salt mist chamber using 5% NaCl solution.

2.3.3.3. Potentiodynamic polarization and Electrochemical impedance spectroscopy (EIS) measurement
Corrosion resistance performance were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques of PUR coated and uncoated MS in 3.5wt% HCl and 3.5 wt% NaOH at room temperature (25 °C) over 240 h using a micro-Metrohm Autolab type III potentiostat with a FRA unit (µ3AVT 70762, Utrecht, Netherlands) potentiostat. In potentiodynamic polarization measurement Tafel plots were obtained using a three-electrode corrosion cell (EG&G Albuquerque, NM, flat cell) containing a counter-electrode (platinum gauze), reference electrode (Ag/AgCl) and a working electrode (coated and uncoated MS test specimen) under different corrosive environment. The test specimen was fitted in corrosion cell with 1 cm² area of the sample exposed to the corrosive medium. The tests were performed in the potential range of $-0.4 \text{ V}$ to $+1.4 \text{ V}$ at a sweep rate of 0.5 mVs⁻¹. Electrochemical Impedance measurements were performed in a frequency range of 100 KHz to 0.1 Hz with an AC amplitude of 20 mV. Nyquist plots were obtained after 0.5 h of immersion equilibration time in corrosive environment up and it is continued up to 240 h. The impedance values were reproducible to ±2–3%. From the impedance plots an appropriate equivalent circuit was proposed (Figure 1)
In the equivalent circuit, $R_s$ is the solution resistance, $R_{pore}$ is the pore resistance, $R_p$ is the polarization resistance and $CPE_{cl}$ and $CPE_{dl}$ are the coating and the double layer capacitance of the PUR respectively. FRA software was used for plotting, graphing and fitting the data. The inhibition efficiency $IE(\%)$ of coating was also determined by using following equation [19].

$$IE\% = \frac{I'_{corr} - I_{corr}}{I_{corr}} \times 100$$

Where $I_{corr}$ and $I'_{corr}$ are the corrosion current densities of coated and uncoated mild steel strips respectively.

3. Results and discussion

3.1. Physico-mechanical properties

The 70% PUR solution in minimal possible solvent was prepared i.e. 30% solvent was used for the preparation of PUR coatings of 102-108 μm thickness using brush technique. The use of such a minimum amount of solvent can be attributed to the low molecular weight of polymer and good functionality of PUR. The use of solvent is very small as compared to those of other reported synthetic polymer coating systems, which involved 50-60% organic solvents [5], which induced more useful effect on the environment by reducing the release of toxic VOC. The curing of PUR coatings involved two stage processes [18, 20, 21]. The first stage involved the evaporation of solvent, a physical process, followed by a chemical reaction between the free –NCO groups of PUR and unreacted –OH of the polymeric chains as well as some other side reactions of –NCO with atmospheric moisture [18, 20, 21]. It was observed (Table I) that with the increase in the loading of TDI, the drying time decreased from PUR-0.8 to PUR-1.2. The drying time of PUR-resins were found to be lower than that of poly(urethane linseed fatty amide) [PULFA] and Poly(urethane Pongamia glabra fatty amide) [PUPGFA] coatings [20, 21]. The PUR coating was found well adhered, stiff and homogenous, along with higher gloss, scratch hardness and impact resistance as compared to those of PULFA and PUPGFA coatings [20, 21]. The PUR coating was found well adhered, stiff and homogenous, along with higher gloss, scratch hardness and impact resistance as compared to those of PULFA and PUPGFA coatings [20, 21]. The gloss and impact strength of PUR coatings were also found higher than that of hyperbranched polyurethane coatings, reported by karak et al [13, 14] and the castor oil based urethane alkyd developed by Sarvari et al. [22]. The high scratch hardness value of PUR coating is due to the presence of aromatic rigid moiety of TDI in the cross-linked structure [23]. The PUR coatings shows the utmost limit of impact resistance (200 lb/inch, limit of the instrument), this can be attributed to the presence of aliphatic fatty acid chain which provide flexibility to the polymer, dispel the impact energy by their segmental motions throughout the cross-linked chains [22, 23]. This is the reason that, they also exhibited the highest limit of the bending test (1/8 diameter of the mandrel) and can be crumpled up to 180° without any breaking, damage or rupture. The presence of additional –OH functionality in case of PUR helped in achieving the optimum cross-linking, which led to the formation of three dimensional cross-linked flexible coatings along with good stiffness and improved
physico-mechanical properties [24]. It was also observed that with the increase in the loading of TDI, the scratch hardness increased from PUR-0.8 to PUR-1.0 and then a decrease is observed in case of PUR-1.2 (Table1). This can be correlated to the fact that with the increased loading of TDI beyond 1.0 mole, an excessive cross linking in the polymeric chain was obtained, that makes the coatings more strained and brittle, resulting in low physic-mechanical properties [24].

**Table 1 Physico-mechanical Characterization of PUR coatings on MS**

| Resin code | PUR-0.8 | PUR-1.0 | PUR-1.2 |
|------------|---------|---------|---------|
| Gloss at 45° | 64      | 76      | 80      |
| Scratch hardness (Kg) | 1.2     | 3.0     | 1.7     |
| Impact resistance (150 lb/inch) | 200     | 200     | 200     |
| Bending (1/8 inch) | Pass    | Pass    | Pass    |
| Drying time*(min) | 12      | 10      | 10      |
| Coating Thickness (μm) | 102     | 104     | 108     |

### 3.2. Corrosion Analyses

#### 3.2.1. Weight loss studies

The corrosion resistance performance of PUR in 3.5 wt% HCl, 3.5 wt% NaOH and tap water was explored for a period of 360, 240 and 408 h respectively. The graph between weight loss vs. time is provided in Figure 2. Their corrosion rates for PUR coated and uncoated MS are shown in Table 2. In 3.5 wt% HCl, uncoated MS shows rapid weight loss just after 1 h, however PUR-0.8, PUR-1.0 and PUR-1.2 coatings show no visual deterioration or dissolution up to 196, 288 and 172 h respectively. Similarly the corrosion rate for bare MS was very high (4.582 mgy) as compared to PUR coated MS (Table 2). These results show that PUR coatings provide protection to the MS against acidic corrosion. In 3.5 wt% NaOH and tap water also the corrosion rate for PUR coated MS was very low as compare to bare MS (Table 2). It is evident from the results that the reasonably low weight loss and corrosion rate for PUR coated MS as compared to that of bare MS was observed in all the mediums. The decrease in corrosion rate and weight loss for PUR coatings can be attributed to the fact that the presence of additional –OH functionality in PUR coatings make it more compact owing to the formation of cross linked structure. Furthermore, amide and urethane carbonyl groups of PUR interacted with the iron substrate as they have lone pair of electrons on oxygen/nitrogen atoms, which interacted with the vacant d-orbitals of iron present on the surface. This will lead to increase in the adhesion of coating with the metal substrate, through the formation of compact and well adhered coating that act as a strong barrier, results in the higher corrosion protective performance. It is evident from the graph (Figure 2) and inhibition efficiency calculated from weight loss data (Table 2), that in all the mediums as the loading of TDI increase from 0.8 to 1.0 mole, a decrease in weight loss and corrosion rate and subsequently increase in inhibition efficiency were observed. However, as the loading of TDI increases to 1.2 moles again a decrease in inhibition efficiency and increase in corrosion rate was observed. The low corrosion resistance performance displayed by PUR-0.8 as compared to PUR-1.0 can be correlated to the presence of some pores, developed due to less cross-linking not providing adequate protection, while in PUR-1.2, it might be due to the formation of a highly cross-linked structure, which resulted in a strained structure. It was further observed that the protection offered by PUR coating is slightly higher in acidic medium as compared to alkali. Lower corrosion resistance performance of PUR in alkaline medium can be attributed to the saponification of ester group on longer exposure to the corrosive environment. However, the corrosion resistance performance of PUR in alkaline medium was higher as compared to other reported such systems [13,14, 20, 21]. This can be attributed to the sandwiching of ester groups in between the urethane-amide linkages, which has prohibited the saponification of ester to some extent, furthermore, the presence of urethane and amide functional groups impedes the diffusion of corrosive ions through the formation of compact and well adhered coating that act as a strong barrier [20]. The corrosion
protective performance of the PUR is found significantly superior to those of previously reported PULFA and PUPGFA coatings [20, 21]. In NaOH, PUR-1.0 was found deteriorate after 192 h, while PULFA and PUPGFA coatings were found to deteriorate after 72 h and 144 h respectively [20, 21]. The PUR-1.0 coatings were found to be unaffected in the tap water up to 480 h, while in HCl, only up to 288 h. On the other hand the reported PULFA-1.0 and PUPGFA-1.0 coatings exhibited no change in HCl up to 240 h and 120 h, respectively [20, 21]. Therefore, it can be concluded that the presence of additional –OH functionality in PUR coatings make it more compact owing to the formation of cross linked structure, while in PULFA and PUPGFA, linear chain structure were formed due to the absence of secondary hydroxyl groups [20, 21]; this can be attributed for their poor corrosion resistance performance.

![Graph](image1)

![Graph](image2)
3.2.2. Potentiodynamic polarization (PDP) measurement

The corrosion resistance behavior of uncoated and PUR coated MS strips was assessed by potentiodynamic polarization measurement in 3.5 wt% NaOH and 3.5 wt% HCl solution at different immersion times. The tafel plots obtained in acidic and alkaline environment are shown in Figure 3 and 4 respectively. The values of corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), tafel slopes parameters; beta cathodic ($b_a$) and beta anodic ($b_c$), obtained from these plots are listed in Table 3. Electrochemical corrosion potential ($E_{corr}$) is the potential difference between a metal dipped in a given environment and an appropriate standard reference electrode (Ag/AgCl).

Polarization resistance ($R_p$) was obtained from Stern-Geary Equation [25]:

$$ R = 2.303 \frac{b_a b_c}{b_a + b_c} \left( \frac{1}{i_{corr}} \right) $$

Where $i_{corr}$ is the polarization resistance, $b_a$ and $b_c$ are tafel slope parameters. They are calculated using
following equations:

\[
b_a = \frac{RT}{\alpha n F}
\]

\[
b_c = \frac{RT}{(1-\alpha)nF}
\]

Where \( R \) is the universal gas constant \( T \) is the given Temperature, \( \alpha \) is the charge transfer coefficient and \( n \) is the number of electrons

The Tafel curves in both the media shows that the corrosion potential for PUR coated MS shifts towards more positive potentials than that of uncoated MS (Table 3). The corrosion current density (\( i_{corr} \)) of uncoated MS was found 4.25 \( \times \) 10^{-5} and 1.67 \( \times \) 10^{-4} in 3.5 wt% HCl and 3.5 wt % NaOH respectively which were very high as compared to PUR coating (Table 3). Furthermore, Table 3 demonstrates an increase in the polarization resistance value of PUR in comparison to bare MS. The positive shift in \( E_{corr} \), \( R_p \) and decrease in \( i_{corr} \) confirms that the PUR coated MS depressed the anodic current of the corrosion reaction and offered resistance to MS against corrosion [25]. It was also evident from the Table 3 that, as the loading of TDI increases from 0.8 to 1.0 mole an increase in \( E_{corr} \), \( R_p \) and decrease in \( i_{corr} \) were observed, this indicates that the corrosion protective performance increases with increased loading of TDI. However, as the loading of TDI increases further i.e. 1.2 moles in PUR-1.2, a decrease in \( E_{corr} \), \( R_p \) and increase in \( i_{corr} \) value were observed. This observation have suggested that the corrosion protective efficiency of PUR coating increases with the increase in loading of TDI up to certain level i.e. 1.0 mole. The -OH functionality and the urethane linkages jointly lead to the formation of compact dense and well adhered coatings, which hindered the migration of the corrosive ions, thereby, providing sufficient protection to the mild steel. Furthermore, amide and urethane carbonyl groups of PUR interacted with the iron substrate as they have lone pair of electrons on oxygen/nitrogen atoms, which interacted with the vacant \( d \)-orbitals of iron present on the surface. This will lead to increase in the adhesion of coating with the metal substrate [26, 27]. More amide carbonyl groups were introduced in coatings, with the increased loading of TDI, which increased the adhesion between coating and metal substrate, leading to the improved corrosion protective efficiency of the coating. However, if the amount of TDI increased further (up to 1.2 moles) a decrease in \( E_{corr} \) and increase in \( I_{corr} \) occurred, showing that the corrosion resistance performance of the coating decreased due to the excessive cross linking caused by higher amount of TDI, which makes the coating brittle. This observation was also supported by the values of inhibition efficiency (\( IE \)) which was found maximum (94.02% and 90.1% in acid and alkaline medium respectively after 24 h) for PUR-1.0. It was further observed that with time, the \( E_{corr} \), \( R_p \) value of PUR coated MS decreases while that of \( i_{corr} \) increases, these trends have suggested that the corrosion resistant performance of the coating decreases with time. However, even after 240 h the PUR-1.0 coatings shows inhibition efficiency of 66% and 52% in acid and alkaline medium respectively. These results have shown that PUR coatings still provide protection to the MS against corrosion even after 240 h. PDP results also exhibited that the coatings show better corrosion resistance performance under acidic medium as compared to alkaline medium, the rigid moiety (aromatic ring of TDI) is protonated and getting adsorbed at the cathodic sites of MS, reducing the rate of cathodic reaction [25]. It can be concluded from the above discussion that the PUR-1.0 coatings were exhibiting best corrosion resistance performance in both the corrosive medium among all three compositions that may be due to optimum cross linking. The corrosion resistant performance of PUR coatings were also found higher than that of other vegetable oil based PU. Yeganeh et al [CO PU PY] has developed poly(urethane-co-pyrrole)s derived from castor oil, found \( E_{corr} \) and \( I_{corr} \) value in the range of -0.1 to +0.3 V and \( 10^{-5} \) to \( 10^{-7} \) A/cm² respectively, which are lower than that of PUR coatings. Heidarian et al had worked on corrosion resistance performance of castor oil based polyurethane/organically modified montmorillonite (OMMT) clay nanocomposite coatings, and find out \( R_p \) value 4.01 \( \times \) 10^7 \( 10^3 \) Ω for 5%NaCl which is almost similar to PUR coatings i.e. 6.89 \( \times \) 10^7 \( 10^3 \) Ω for PUR-1.0 in 3.5 wt% HCl solution. The corrosion resistance performance of PUR is also comparable to that of commercial PU systems. A.S. Khanna et al [Polyester PU] had developed poly (ester–urethane–urea) performed corrosion resistant performance
in 3.5%NaCl, find out the $R_p$ value $8.24 \times 10^7 \Omega$, which is comparable to that of PUR ($6.89 \times 10^7 \Omega cm^2$). However no work had been reported on the electrochemical corrosion resistant performance of vegetable oil based PU in NaOH and HCl to best of our knowledge.

### Table 3.
Table 3. Electrochemical parameters obtained from polarization curves of PUR coated and uncoated MS in 3.5 wt% HCl and 3.5 wt% NaOH for different intervals of time. The value in the parenthesis denotes the no. of hours after which measurements were taken.

| Sample | Medium   | $R_p(\Omega)$ | $b_a$ (V/dec$^{-1}$) | $b_c$ (V dec$^{-1}$) | $E_{corr}(V)$ | $I_{corr}$ (A cm$^{-2}$) | Corrosion rate (mpy) | (IE%) |
|--------|----------|---------------|----------------------|----------------------|---------------|--------------------------|----------------------|-------|
| MS     | 3.5% HCl | $7.03 \times 10^2$ | 0.064                | 0.096                | -1.067        | $4.25 \times 10^{-5}$     | 1.48x10$^{-1}$       | -     |
| PUR-0.8 (24 h) | 3.5% HCl | $1.45 \times 10^5$ | 2.183                | 0.579                | -0.535        | $5.74 \times 10^{-7}$     | 6.68x10$^{-3}$       | 91.17 |
| PUR-0.8 (240 h) | 3.5% HCl | $8.67 \times 10^3$ | 1.518                | 0.678                | -0.864        | $3.19 \times 10^{-5}$     | 1.03x10$^{-1}$       | 52.14 |
| PUR-1.0 (24 h) | 3.5% HCl | $6.89 \times 10^7$ | 0.312                | 0.514                | -0.435        | $6.71 \times 10^{-8}$     | 7.71x10$^{-4}$       | 94.41 |
| PUR-1.0 (240 h) | 3.5% HCl | $2.13 \times 10^4$ | 0.278                | 0.776                | -0.788        | $4.22 \times 10^{-6}$     | 5.47x10$^{-3}$       | 66.02 |
| PUR-1.2 (24 h) | 3.5% HCl | $8.12 \times 10^4$ | 2.188                | 0.589                | -0.612        | $5.23 \times 10^{-7}$     | 1.20x10$^{-2}$       | 82.41 |
| PUR-1.2 (240 h) | 3.5% HCl | $2.78 \times 10^3$ | 1.917                | 0.459                | -0.911        | $3.68 \times 10^{-3}$     | 1.34x10$^{-1}$       | 48.02 |
| MS     | 3.5%NaOH | $1.12 \times 10^2$ | 0.049                | 0.160                | -1.081        | $1.67 \times 10^{-4}$     | 6.94x10$^{-1}$       | -     |
| PUR-0.8 (24 h) | 3.5%NaOH | $3.67 \times 10^4$ | 0.163                | 0.197                | -0.610        | $1.53 \times 10^{-6}$     | 4.59x10$^{-3}$       | 85.02 |
| PUR-0.8 (240 h) | 3.5%NaOH | $8.34 \times 10^2$ | 0.483                | 0.230                | -0.977        | $8.98 \times 10^{-5}$     | 5.76x10$^{-1}$       | 50.67 |
| PUR-1.0 (0.5 h) | 3.5%NaOH | $7.61 \times 10^5$ | 1.253                | 0.313                | -0.591        | $3.93 \times 10^{-7}$     | 1.75x10$^{-3}$       | 90.10 |
| PUR-1.0 (240 h) | 3.5%NaOH | $6.78 \times 10^3$ | 1.109                | 0.453                | -0.809        | $8.28 \times 10^{-6}$     | 8.95x10$^{-2}$       | 52.08 |
| PUR-1.2 (0.5 h) | 3.5%NaOH | $2.23 \times 10^4$ | 0.535                | 0.327                | -0.733        | $3.54 \times 10^{-6}$     | 4.12x10$^{-2}$       | 78.88 |
| PUR-1.2 (240 h) | 3.5%NaOH | $5.89 \times 10^2$ | 0.678                | 0.227                | -1.016        | $9.33 \times 10^{-3}$     | 8.12x10$^{-1}$       | 45.56 |
Figure 3 Tafel plots of uncoated and different compositions of PUR coated MS after (a) 24 and (b) 240 h of exposure to 3.5 wt% HCl.
Figure 4 Tafel plots of uncoated and different compositions of PUR coated MS after (a) 24 and (b) 240 h of exposure to 3.5 wt% NaOH.

3.2.4. EIS measurement of PUR coating
Electrochemical impedance spectra of PUR coated and uncoated MS in the form of Nyquist plots were recorded in aqueous 3.5 wt% NaOH and 3.5 wt% HCl after 24 and 240 h of immersion are shown in
Figures 5 and 6. Based on the impedance plots two different equivalent circuits were proposed (Figure 1 a-b). (i) When the shape of nyquist plot revealed the formation of typical one semicircle contained only one time constant (Figure 1 a), where $R_s$ is the solution resistance, $R_{pore}$ is the pore resistance, and $C_d$ represents the coating capacitance. A semicircle with higher diameter indicates the low corrosion rate of the PUR coatings. (ii) When the shape of the nyquist plots is such that it contain two semi circles, a smaller one at high frequency range followed by a larger one at lower frequencies (Figure 1 b). Then it contains two time constants, where $R_s$ is the solution resistance, $R_{pore}$ is the pore resistance offered by coating, $R_{ct}$ is charge transfer resistance, $CPE_c$ represents the capacitance of coating and $CPE_{dl}$ is double layer capacitance. This circuit represents the degradation of the coating. The impedance plot of uncoated MS in the both mediums (Figure 5, 6) can be fitted with the circuit depicted in Figure 1 b, contains two semicircles, a smaller one in the high frequency range followed by a broad one at lower frequencies. The first semicircle is correlated to the development of the corrosion product film and the second one to processes occurring beneath the corrosion product film [29]. Thus, the Nyquist plot of uncoated MS is a characteristic of a coating system undergoing dissolution and disintegration with the formation of a corrosion product at the surface [29].

The impedance plots of the PUR in 3.5 wt% NaOH coated MS (Figure 5 a) are modeled by using the equivalent circuit shown in Figure 1a in early time of immersion i.e. up to 120 h. The high value of $R_{pore}$ and low value of $CPE_c$ for PUR coated MS as compare to uncoated MS shows that PUR coating protects the MS against corrosion. The capacitance ($CPE_c$) is of a measure of water uptake by a coating. In the case of MS, the $CPE_c$ values just after 24 h indicated that the water uptake was very high (Table 4), causing rapid deterioration. However, for PUR coated MS, the $CPE_c$ value is very low (Table 4) during the initial immersion time (24 h) and it did not show any significant increase with time. The high value of $R_{pore}$ and low value of $CPE_c$ for PUR coated MS can be correlated to the fact that, urethane and amide linkages interacts with the MS substrate along with the secondary –OH group of Ricinus communis oil, which make a cross linked structure with TDI, that prevent the entry of corrosive ions and decreases the surface wettability of the coating (as discussed in PDP section). The observation further showed that a decrease in $R_{pore}$ and an increase in $CPE_c$ value for the PUR coating with increase in exposure time were observed (Table 4). This can be correlated to the fact that with prolonged exposure to the corrosive environment water uptake increases due to penetration or diffusion of corrosive ions, which in turn results in a higher $CPE_c$ value. After 120 h of immersion the coating was start to degrade and the impedance plot obtained can be fitted with the equivalent circuit shown in Figure 1b. The low frequency semicircle may be associated with the charge transfer of the corrosion reaction of the metallic substrate. However, the $R_{ct}$ value of PUR coatings were found remarkably higher than that of uncoated. The double layer capacitance ($CPE_{dl}$) is related with the area of the metal substrate exposed to the corrosive medium i.e. the delaminated area. This occurs due to the penetration or diffusion of corrosive ions through the coating to the coating-metal interface [30]. As the corrosive ions penetrates inside the coating, corrosion products formed at the coating-metal interface reduces the area of the double layer capacitor, this results to an increase in the $CPE_{dl}$ value. A high value of $CPE_{dl}$ indicated that coating is undergoing dissolution [30]. The corrosion products absorb more electrolyte having corrosive ions through the film, leading to further increase in the dielectric constant of the coating, which has been found to deteriorate for longer immersion time [30]. The $CPE_{dl}$ value of the bare MS was found to be quite high, even after 24 h exposure to the corrosive environment. On comparing the $CPE_{dl}$ values for PUR coatings (0.8, 1.0 and 1.2 moles of TDI), it may be said $CPE_{dl}$ values slowly increased over a longer exposure of 240 h (Table 4). This confirmed that these PUR coatings have a stable coating-metal interface [30].

It was further observed that the $R_{pore}$ and $R_{ct}$ value of PUR coated MS were found increases with the increase loading of TDI and the maximum value were obtained for PUR-1.0 (1.0 mole loading of TDI), this suggested that the optimum content of TDI inhibit the charge transfer reaction at the coating-metal interface. For PUR-1.2 (1.2 mole loading of TDI) excessive cross-linking make the coating brittle and undergoes dissolution, allow the corrosive ions to enter the coating-metal interface, which lowers the $R_{pore}$ and $R_{ct}$ value and make the $C_d$ value very high.

In 3.5 wt% HCl also, PUR coatings exhibiting the same trend as that in alkaline medium. Initially (up to 144 h) the nyquist plot obtained for PUR coated MS (Figure 6a) can be fitted with the circuit shown
in Figure 1a, while after 144 h (Figure 6a), it can be fitted with the circuit shown in Figure 1b. This suggested that coating start degraded after 144 h. However, the value of $R_{pore}$ and $R_{ct}$ were found higher while $CPE_{i}$ and $CPE_{dl}$ were found lower for PUR coated MS as compared to that of bare MS. These results exhibited that in acidic medium also the PUR provide protection to the MS. However, the extent of protection offered by PUR coating in acidic medium is higher than that of alkaline medium as exhibited by the weight loss and potentiodynamic polarization measurements. EIS study also reveals that the corrosion protection offered by PUR coating is higher than other vegetable oil based PU. Yeganeh et al had developed poly(urethane-co-pyrrole)s derived from castor oil and find out the corrosion resistant performance under 3.5% NaCl, observed the $R_{ct}$ in value in the range of $7.0 \times 10^{4}$ Ω which is much lower than PUR ($9.28 \times 10^{6}$ and $7.18 \times 10^{7}$ Ω in alkaline and acidic medium respectively). Further corrosion resistant performance of PUR is comparable to that of commercial PU. Khanna et al had reported Poly(ester-urethane) and observed $R_{ct}$ value $8.24 \times 10^{6}$ Ω, which is comparable to that of PUR-1.0 I both acidic and alkaline mediums [28].
Figure 5 Nyquist plot of PUR coated and uncoated MS after 24 h exposure to (a) 3.5 wt % HCl and (b) 3.5 wt% NaOH
Figure 6 Nyquist plot of PUR coated and uncoated MS after 240 h exposure to (a) 3.5 wt % HCl and (b) 3.5 wt% NaOH
Table 4. EIS measurement of Mild steel (MS) and PUR coated MS in 3.5%NaOH, and 3.5%HCl solution.

| Resin    | Medium    | $R_{\text{pore}}$(ohm) | $C_\varepsilon$(Farad) | $R_\alpha$(ohm) | $C_{\text{dl}}$(Farad) |
|----------|-----------|------------------------|------------------------|----------------|------------------------|
| MS       | 3.5%NaOH  | $3.01 \times 10^4$     | $3.63 \times 10^{-4}$  | $4.50 \times 10^4$ | $2.31 \times 10^{-4}$  |
| PUR0.8 (24h) | 3.5%NaOH  | $1.77 \times 10^5$     | $3.17 \times 10^{-7}$  | -              | -                      |
| PUR0.8 (240 h) | 3.5%NaOH | $5.31 \times 10^4$     | $1.03 \times 10^{-4}$  | $3.40 \times 10^3$ | $2.18 \times 10^{-4}$  |
| PUR1.0 (24 h) | 3.5%NaOH  | $9.28 \times 10^6$     | $9.95 \times 10^{-9}$  | -              | -                      |
| PUR1.0 (240 h) | 3.5%NaOH  | $6.67 \times 10^4$     | $2.98 \times 10^{-6}$  | $1.29 \times 10^4$ | $8.72 \times 10^{-6}$  |
| PUR1.2 (24 h) | 3.5%NaOH  | $4.38 \times 10^5$     | $5.17 \times 10^{-8}$  | -              | -                      |
| PUR1.2 (240 h) | 3.5%NaOH  | $9.45 \times 10^2$     | $6.44 \times 10^{-4}$  | $2.93 \times 10^3$ | $6.56 \times 10^{-4}$  |
| MS       | 3.5%HCl   | $3.13 \times 10^1$     | $7.31 \times 10^{-5}$  | $6.10 \times 10^1$ | $3.41 \times 10^{-4}$  |
| PUR0.8 (24h) | 3.5%HCl   | $2.06 \times 10^6$     | $2.83 \times 10^{-8}$  | -              | -                      |
| PUR0.8 (240 h) | 3.5%HCl  | $9.39 \times 10^3$     | $6.79 \times 10^{-5}$  | $2.17 \times 10^4$ | $7.23 \times 10^{-5}$  |
| PUR1.0 (24 h) | 3.5%HCl   | $7.18 \times 10^7$     | $7.05 \times 10^{-8}$  | -              | -                      |
| PUR1.0 (240 h) | 3.5%HCl | $1.34 \times 10^4$     | $2.98 \times 10^{-6}$  | $8.77 \times 10^5$ | $3.05 \times 10^{-5}$  |
| PUR1.2 (24 h) | 3.5%HCl   | $1.83 \times 10^4$     | $7.91 \times 10^{-8}$  | -              | -                      |
| PUR1.2 (240 h) | 3.5%HCl | $4.25 \times 10^5$     | $9.46 \times 10^{-5}$  | $1.23 \times 10^4$ | $4.91 \times 10^{-4}$  |

3.2.5. Salt spray test
Salt spray test (SST) on PUR coated MS was performed for a duration of 480 h in 5.0 wt% aqueous NaCl solution. The uncoated MS was tested as a control. Initially (up to 48 h), the coated and uncoated both MS specimens have shown glossy and shiny surface. However, after 48 h glossy shiny appearance of uncoated MS was lost, furthermore after 96 h of this test, the whole surface of uncoated MS was covered with dark gray patches, showing significant corrosion damage. However, the PUR-0.8, PUR-1.0 and PUR-1.2 coated MS specimen showed loss in gloss only after 168, 216 and 144 h respectively, although the coating remains intact and no sign of deterioration was observed. The decrease in gloss for PUR with time can be ascribed to the fact that NaCl crystals was deposited at the surface of coatings, which causes the breaking of the bond PUR coating with the metal substrate leading to the roughness and deterioration of the surface. It was further observed that no damage was observed on the coating surface up to 360, 432 and 336 h for PUR0.8, PUR1.0 and PUR1.2 respectively. After that coating starts deteriorating due to the deposition of excessive salt on the surface of the coating, results in the decrease in the adhesion of coating with MS substrate. From the above discussion it can be concluded that PUR coating provide protection to MS in saline media up to 384 h.

3.3. Mechanism of corrosion protection
The mechanism of corrosion protection of PUR coatings can be explained on the basis of the formation of compact, well adhered, uniform, homogenous and impermeable barrier film at the interface of metal substrate and the corrosive media, which impedes the permeation of electrolytic/corrosive ions through coating to metal surface. The secondary -OH functionality and the urethane-amide linkages jointly (formation of hydrogen bond) lead to the formation of compact dense and well adhered coating at the metal surface which prohibited the migration of the corrosive ions, thereby, providing protection to the metal substrate. The amide and urethane carbonyl groups of PUR interacted with the iron substrate which leads to increases the adhesion of coating with the metal...
substrate. As the amount of TDI increases, more amide carbonyl group will be introduced which increases the adhesion between coating and metal substrate leading to improve the corrosion protective performance of the coating. In case of PUR-1.2 coatings, more –OH group will utilize in the formation of urethane linkage causing excessive cross-linking. This high crosslinking induces brittleness in the coating material which significantly reduces the adherence of the coating to the metal substrate leading to poor corrosion protective performance.

4. Conclusion

The ambient cured eco-friendly PUR anticorrosive coatings have shown superior acid resistance and fairly good alkali resistance properties than those of other reported vegetable seed oil based polymeric coatings. Among all the compositions, PUR-1.0 coatings showed excellent chemical/corrosion resistance performance. The potentiodynamic polarization, EIS and weight loss methods of corrosion studies reveal the excellent corrosion resistance performance of PUR coatings in various corrosive media. The PUR coatings have a promising potential for its commercial application as anticorrosive coatings.

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