Synthesis and Anticorrosive Properties of Novel PVK-ZrO₂ Nano Composite Coatings on Steel-Substrate

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A novel nanocomposite coating containing poly (*N*-vinyl carbazole) (PVK) and zirconia (ZrO₂) nanoparticles was synthesized using chronoamperometry. The effect of ZrO₂ nano particles into the PVK matrix and its mechanical, corrosion protection ability on 316L SS substrates were studied. The incorporation of the nanoparticles was endorsed by attenuated total reflectance infrared spectroscopy (ATR-IR) and EDAX analysis. The spheroidal morphology and core-shell structure were revealed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The thermal studies exhibited the stability of coating. The anticorrosion performance of PVK-ZrO₂ nanocomposite coatings in 3.5 weight (wt.%) NaCl medium was performed with potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS) studies. The corrosion rate of PVK-ZrO₂ nanocomposite coated 316L SS was found to be 0.58 times lower than uncoated 316L SS and a significant decrease in corrosion potential was realized from $-0.211 V_{SCE}$ for uncoated 316L SS to $0.112 V_{SCE}$ for PVK-ZrO₂ nanocomposite coated 316L SS substrates. The results of this study clearly ascertain that the PVK-ZrO₂ nanocomposite has an outstanding potential to protect 316L SS against corrosion in a 3.5 wt.% NaCl environment. [DOI: 10.1380/ejsnt.2018.5]

Keywords: Smart materials for Anticorrosion; Nanocomposite coatings; Poly (vinyl carbazole) (PVK); Nano ZrO₂ particles; 316L SS; Electrochemical impedance spectroscopy (EIS)

I. INTRODUCTION

In the recent past, ever since the first suggestion made by MacDiarmid (1985), Conducting polymers (CP) have been employed in the development of smart corrosion inhibiting coatings because of their good environmental stability and chemical resistance to the metal surface [1]. There are numerous reports on the passivating effect of electro active polymers on steels in various environments. There is substantial evidence that electroactive polymers, such as polyaniline (PANI), polypyrrole (PPy), polythiophene etc and its derivatives can offer protection to steel in certain corrosion environments [2–4]. However, all these polymer coatings have a serious practical issue, that is, permeation of corrosive species such as oxygen, water and ions to some extent. Incorporation of metal oxide nanoparticles into the conducting polymers minimizes the penetration of these corrosive ions and enhances the corrosion resistance. In the past, several oxide nanoparticles such as; alumina (Al₂O₃) [5], manganese dioxide (MnO₂) [6], vanadium pentoxide (V₂O₅) [7], titania (TiO₂) [8], ferric oxide (Fe₂O₃) [9], tungsten oxide (WO₃) [10], zinc oxide (ZnO) [11], silica (SiO₂) [12] and zirconia (ZrO₂) [13] were incorporated into CP matrix and its corrosion protecting ability was explored. For instance, poly (o-toluidine) /ZrO₂ nanocomposite coating was effective to control the corrosion rate of mild steel [14]. The

conducting poly (*N*-vinyl carbazole) (PVK) is one of the promising conducting polymers due to the following reasons: (i) its ability to form robust thin film, (ii) good thermal, electrical, charge carrier transport, mechanical properties and (iii) it shows large variety of applications in electrochromic devices, light-emitting diodes, sensors, secondary batteries, electrostatic discharge protection [15].

Electrochemical polymerization can be carried out to form *N*-vinyl carbazole (NVC) films on various metal substrates. The corrosion protection offered by self-assembled films of carbazole on copper (Cu) in NaCl solution were recently studied [16]. Exploring the literature confirms that the incorporation of various nanoparticles into PVK matrix enhances properties like antimicrobial [17], charge carrier transport [18], super capacitance [19], photoconductivity [20], optical [21], electrical conductance [22], thermal stability [23] and electrochemical [24]. It is evident from the literature that few investigations were carried out in the past to validate the corrosion protection offered by the PVK nano composite films on steels. Among the inorganic oxide nano particles, ZrO₂ is known for its high strength, high fracture toughness, wear resistance, high hardness and chemical resistance [25]. Several research groups have studied the influence of the ZrO₂ nano particles on the corrosion behavior [26, 27]. The influence of ZrO₂ nanoparticles on the surface and electrochemical behavior of polypyrrole nanocomposite coated 316L SS in simulated body fluid was reported [14]. However, quantitative studies on the effect of ZrO₂ nano particles in PVK coatings as poten-

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tial material for corrosion protection are scanty. Hence, it becomes important to investigate the following objectives (i) to electropolymerise PVK coatings on 316L SS using chronoamperometric technique, (ii) to synthesize PVK-ZrO₂ nano composite coatings by incorporating the ZrO₂ nano particles into the PVK matrix using chronoamperometric technique (iii) to examine the surface, thermal and mechanical characteristics of the nanocomposite coatings and (iv) to examine the protection ability of PVK and PVK-ZrO₂ nano composite coatings in 3.5 wt. % NaCl medium. The results of this work were compared with our earlier work to elucidate the properties of the PVK-ZrO₂ nanocomposite coatings and the effect of varying weight ratio of ZrO₂ nanoparticles [5].

II. EXPERIMENTAL SECTIONS

A. Chemicals

Analytical grade *N*-vinyl carbazole (VC) monomer, acetonitrile (ACN), LiClO₄ and all other chemicals used in this study were purchased from Sigma Aldrich. ZrO₂ nano particles were synthesized using the procedure reported elsewhere [27].

B. Equipment and Techniques

1. Deposition of coating and electrochemical characterization

All the electropolymerization processes and electrochemical corrosion experiments were carried out with electrochemical workstation CHI 760D in a standard cell equipped with 316L SS as working electrode, platinum (counter electrode) and standard calomel electrode (SCE) as reference electrodes. Prior to the deposition of the coating, 316L SS substrates with dimensions 12 × 15 × 2 mm were abraded up to 600 # using silicon carbide (SiC) emery sheets and ultrasonicated in acetone for about 15 min. to remove the impurities. It was further rinsed with water and air dried. The 316L SS samples were passivated in 50 % nitric acid for about 10 minutes and used for electrochemical polymerization. Electro polymerization of vinyl carbazole (VK) on the working electrode (316L SS) was performed with the chronoamperometric technique by applying a constant potential of 1.2 V_{SCE} for 1000 s in ACN with 0.1 M LiClO₄ as supporting electrolyte [5]. All the potentials were measured with respect to SCE electrode. For the incorporation of ZrO₂ nanoparticles into the PVK matrix, 1, 2 and 3 wt.% of ZrO₂ nano particles with respect to monomer (*N*-vinyl carbazole) concentration was dispersed in the acetonitrile solution containing monomer and LiClO₄ by ultrasonication method and electropolymerization was carried out to prepare the PVK-ZrO₂ nanocomposite coatings, the coating solution was magnetic stirred gently for adequate dispersion of ZrO₂ nanoparticles into the PVK matrix during the electropolymerization. Coated 316L SS substrates were removed from the solution and rinsed with acetonitrile, to remove unreacted monomer molecules and

dried in air. The PVK nanocomposite (1, 2 and 3 wt.%) coated substrates were labeled as PVKZ-1, PVKZ-2 and PVKZ-3 respectively.

Potentiodynamic polarization curves were recorded over the potential range of -0.5 to 1.0 V_{SCE} at a constant sweep rate of 1 mV/s. The values of corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic (β_a) and cathodic (β_c) Tafel slopes were extracted from polarization plots and reported in Table 2. The ASTM-G (102-89) was used to calculate the corrosion rate (CR) from the polarization parameters using the following equation [13].

$$\text{CR} = K1 \times i_{\text{corr}}/D \times \text{EW}. \quad (1)$$

Where, $K1 = 3.27 \times 10^{-3}$ mm g/ μA yr, CR is the corrosion rate (mm/y), i_{corr} is the corrosion current density ($\mu\text{A cm}^{-2}$), EW is the equivalent weight of the substrate and D is the density (g cm⁻³) of the substrate.

The protection efficiency (PE) of the PVK-ZrO₂ coatings was determined using the following equation [13]

$$\text{PE}\% = [R'_{\text{pol}(\text{coated})} - R_{\text{pol}(\text{uncoated})}/R'_{\text{pol}(\text{coated})}] \times 100\%.$$

The coating porosity is one of the important parameters, which strongly influences the corrosion protection behavior of the coatings. By determining the coating porosity one can estimate the overall corrosion resistance of the coated substrate [28]. The porosity of PVK-ZrO₂ nanocomposite coating on 316L SS substrates was determined from potentiodynamic polarization resistance measurements using the following relation [13]

$$P = R_{\text{ps}}/R_{\text{pc}} \times 10^{-(|\Delta E_{\text{corr}}|/\beta_a)}$$

where, P is the total porosity, R_{ps} is the polarization resistance of the 316L SS, R_{pc} is the measured polarization resistance of polymer coated 316L SS, ΔE_{corr} is the difference between corrosion potentials and β_a is the anodic Tafel slope for uncoated 316L SS substrate.

Electrochemical impedance spectroscopy measurements were carried out in 3.5 wt.% NaCl solution at room temperature ($25 \pm 2^\circ\text{C}$) using an electrochemical system, Frequency Response Analyzer (FRA). The test specimens were allowed to attain equilibrium in NaCl solution under open circuit potential (OCP) for 45 minutes prior to the electrochemical tests. EIS spectrum of PVKZ-1, PVKZ-2 and PVKZ-3 were carried out with the amplitude 10 mV in the frequency range between 100 kHz–0.01 Hz. Using Zsimpwin software and non-linear least-square fitting procedure, the charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and coating resistance (R_c) values were determined by fitting the experimental results to equivalent circuits (EC).

2. Surface characterization

Attenuated total reflectance infrared (ATR-IR) spectroscopy analysis (Perkin Elmer Spectrum Two Spectrometer via reflection mode) was employed in the spectral range of 400–4000 cm⁻¹ to characterize the electro polymerized PVK-ZrO₂ coated substrates. Surface morphologies of PVK-ZrO₂ coated substrates were investigated with scanning electron microscope (SEM) (Hitachi model

S3400), was generally operated at 15 keV accelerating voltage and secondary electron imaging mode. Energy dispersive X-ray (EDAX) analysis was used to find out the presence and distribution of elements in the PVK-ZrO₂ nanocomposite coatings, transmission electron microscopy (TEM) was performed using a JEOL-200FX at an accelerating voltage of 200 kV. The samples were dispersed in *N*-methyl pyrrolidone (NMP) and copper grids were then prepared by dipping them into the NMP solution.

3. Hardness test

Vickers micro hardness measurements were performed on PVK-ZrO₂ coated surfaces at a load of 0.5 kgf with a dwell time of 10 s using the MATSUZAWA model MMT-X series micro hardness tester. The Vickers hardness (HV) value is the quotient obtained by dividing the indentation force by the square mm area of indentation observed in the microscope. For each substrate, at least 10 measurements were made at various sites and an average value is reported.

4. Adhesion test

The scotch tape test was performed on PVK-ZrO₂ nanocomposite coated 316L SS substrates to evaluate the adhesion strength in accordance with ASTM D 3359. The typical procedure for the scotch tape test was given as follows. A lattice pattern with six cuts in each direction is made, with a separation of 1.0 mm and 25 grids were generated. At room temperature adhesive tape was placed on the grids. The scotch tape was then removed after 1 min with a firm, steady pulling action. The adhesion strength of the coatings was estimated by inspecting the grid area using the illuminated magnifier and counting the number of squares peeled off compared to the total number of squares. Each test result was repeated at least three times. Adhesion tests were performed before and after the polarization studies for comparison.

5. Thermal Characterization

The thermal stability of the PVK-ZrO₂ nanocomposite was investigated, using a SDTQ-600 WATERS at a heating rate of 5 °C min⁻¹ under nitrogen (N₂) atmosphere (flow rate 50 ml/min).

III. RESULTS AND DISCUSSION

A. Electrochemical polymerization of PVK and PVK-ZrO₂ nanocomposite

Chronoamperometry is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current from faradic processes occurring at the electrode was monitored as a function of time [29]. Electropolymerization of PVK-ZrO₂ nano composite was

FIG. 1. Chronoamperogram for PVKZ-1, PVKZ-2 and PVKZ-3 substrates.

carried out using a chronoamperometric technique by applying a constant potential of 1.2 V_{SCE} for 1000 s. Figure 1 compares the current-time (*I*-*t*) responses recorded during the growth of the coating in ACN and LiClO₄ as supporting electrolyte, with nano ZrO₂ particles. The observed changes in the trends of current explain the nucleation, degradation and polymerization processes involved. In general increase in current suggests the nucleation processes and decrease in current is correlated to the degradation process. The steady-state current indicates the competition between the polymerization and the degradation processes [30, 31]. The nature of the current change varied significantly as the ZrO₂ nano particles were introduced into the coating electrolyte. Thus, compared to the PVK [5], the current density decreased for all the composites. The decrease in current density is attributed to the influence of nano ZrO₂ particles and its varying wt.% and henceforth the polymer growth and morphology.

B. ATR-IR spectroscopy studies

Attenuated total reflection (ATR) infrared spectra of the PVK-ZrO₂ nano composite is shown in Fig. 2. It is compared with the IR data of our previous finding with respect to the synthesis of PVK [5] (see also Table S1 and Fig. S1 in Supplementary materials). PVK-ZrO₂ composite IR spectrum is almost identical to that of the PVK with similar peaks with a slight shift in the stretching bands, which indicates that some interaction exists between PVK and nano-ZrO₂. The main characteristic peaks of the PVK backbone are assigned as follows: 1222, 1450 and 1478 cm⁻¹ are attributed to C-C stretching of the vinyl carbazole and vinylidene groups respectively [32, 33]. The characteristic absorption band corresponding to ring vibration of NVC moiety was found to be 1448 cm⁻¹ [33, 34]. The peaks at 1635 and 3044 cm⁻¹ are attributed to aromatic stretching of rings present in carbazole [33]. The existence of absorption band at 745 and 1157 cm⁻¹ has been interpreted as originating from plane bending vibration of the -C=C of vinylidene

FIG. 2. Attenuated total reflectance Infra-red (ATR-FTIR) spectrum of PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates.

group [33, 34]. In addition, the band around 510 cm^{-1} is assigned to the Zr–O–Zr stretching mode while the one in the 800 cm^{-1} region is related to the Zr–O bending vibration [35]. This confirms the incorporation of ZrO_2 into the PVK matrix resulting in formation of PVK– ZrO_2 nano composites.

C. Coating morphology

Surface morphology and elemental composition of PVK– ZrO_2 coated 316L SS substrates were studied using SEM and EDAX analysis and are shown in Fig. 3 (note that the SEM Micrograph of PVK is shown in Fig. S2 in Supplementary materials). The SEM micrographs revealed a significant variation in coating morphology with the incorporation of ZrO_2 nano particles. The morphology of the PVK– ZrO_2 coated 316L SS shows a uniform globular type spheroidal morphology all over the surface. The chemical composition of the PVK– ZrO_2 coated 316L SS as examined by EDAX analysis shows the presence of zirconium thereby indicating the incorporation of ZrO_2 particles into the polymer matrix. Further insight into the microstructure of the PVK– ZrO_2 coatings can be seen from TEM images, which are shown in Fig. 4. In the TEM image of PVK– ZrO_2 coating, the lighter portion showed the polymer whereas, the dark portion indicated the ZrO_2 nanoparticles. TEM images further confirmed the core shell like morphology.

D. Adhesion strength

The durability and longevity of coatings are largely dependent upon their adhesion to the substrate since this determines the ease of removal and plays a significant role in determining the protecting nature of the coatings [36–38]. Standard tape adhesion test (ASTM D 3359) was carried to examine the adhesion strength between the interface of PVK– ZrO_2 coatings and the 316L SS substrates and

FIG. 3. SEM micrographs and EDAX analysis of PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates.

FIG. 4. TEM micrograph of PVK– ZrO_2 nanocomposite.

the values of the adhesion remaining (AR%) are shown in Fig. 5. All the coatings exhibited 4B (0–5%) which implies good adhesive strength of the PVK– ZrO_2 coating towards 316L SS surface. This increased adhesion strength from 2B (15–35%) to 4B could be attributed to the intercalation of the ZrO_2 nano particles with the polymer matrix of the coating. The increased adhesion strength depends on two factors: (i) mechanical interlocking (ii) chemical bonding. The ZrO_2 nano particles enhanced the adhesion strength by means of mechanical interlocking [39].

FIG. 5. Adhesion strength of the PVK, PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates.

FIG. 6. Vickers's microhardness values of the PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates.

E. Microhardness test

Vickers Microhardness (Hv) of PVK- ZrO_2 coatings on 316L SS substrates is compared with the microhardness values of 316L SS and PVK are shown in Fig. 6. The hardness values for PVK and PVK- ZrO_2 coatings on 316L SS are in the range of (2452–7355 MPa) a prerequisite for corrosion protection applications [13]. The Hv value for the PVK- ZrO_2 coatings on 316L SS coating is higher than that of the PVK and attributed to the incorporation of ZrO_2 nano particles. The physical interaction between PVK and ZrO_2 nano particles in the coating attributes for the improvement in microhardness [39].

FIG. 7. Open circuit potential values of PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates in 3.5 wt. NaCl solution for 45 min.

F. Electrochemical corrosion studies

1. Open circuit potential measurement

Potential-time curves are generally used to understand the efficiency of the conducting polymer during corrosion tests as the kinetics of reduction reactions of O_2 and H_2O depends on the E_{ocp} value of the bare metal. When a metal is coated with a highly doped conducting polymer and as long as the conducting polymer remains in its conductive state, the E_{ocp} value of the conducting polymer/metal system is always above that of the bare metal electrode. When the conducting polymer is reduced, the potential value drops to a lower value [40]. Figure 7 shows E_{ocp} measured for PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates in 3.5% NaCl for about 45 min.

The positive shift of the E_{ocp} basically shows the passive state of the underlying metal because of the good corrosion protection ability of the surface film. The E_{ocp} value of PVK- ZrO_2 nanocomposite coated SS shows a similar behavior to that of PoPd/ ZnO nanocomposite coated SS which suggests that this coating polymer maintains its oxidative state and provides corrosion protection to the metal [41]. In addition; this shows that O_2 reduction reaction (cathodic reaction) takes place at the polymer surface. In other words, this confirms the displacement of the electrochemical interface (e.g., from metal-electrolyte interface to polymer electrolyte interface) [42]. Hosseini *et al.* found that polypyrrole/ ZnO nanocomposite coating offered excellent barrier property with constant E_{ocp} value [43]. The constant value of the open circuit potential of PVK- ZrO_2 nanocomposite under the given experimental conditions shows the enhanced anticorrosion performance of ZrO_2 nano particles in PVK matrix acting as a barrier for the ingress of the Cl^- ions, thereby limiting the diffusion of the corrosive species towards the underlying steel substrate. But when the loading is increased to 3 wt.%, a negative shift is observed which infers the maximum loading limit is only 2 wt.%. The decrease of potential towards the negative direction is due to the

FIG. 8. Potentiodynamic polarization curves of PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates in 3.5% NaCl solution.

FIG. 9. Percentage porosity for PVK, PVKZ-1, PVKZ-2 and PVKZ-3 coated 316 L SS substrates.

rapid diffusion of chloride ions through the coating.

2. Potentiodynamic polarization studies

TABLE I. Equivalent circuit parameters of uncoated, PVK and PVKZ-1, PVKZ-2 and PVKZ-3 nanocomposite coated 316L SS substrates.

	316L SS	PVK	PVKZ-1	PVKZ-2	PVKZ-3
E_{corr} (V)	-0.211	0.062	0.209	0.112	-0.027
β_a (1/V)	4.89	4.609	6.039	4.948	4.657
β_b (1/V)	5.739	2.567	4.395	4.486	5.417
i_{corr} ($\mu\text{A cm}^{-2}$)	2.452	0.4457	0.149	0.0553	0.097
R_p (kOhm cm^2)	17.27	135.94	279.1	833	443
PE (%)	—	87	94	98	96
CR (mmY^{-1})	25.88	4.7	1.6	0.58	1.1

TABLE II. Equivalent circuit parameters of uncoated, PVK and PVKZ-1, PVKZ-2 and PVKZ-3 nanocomposite coated 316L SS substrates.

	316L SS	PVK	PVK-1	PVK-2	PVK-3
CPE_{po} ($\mu\text{S. s}^n$) cm^{-1}	—	—	—	9.1	16.4
n_{po}	—	—	—	0.85	0.83
R_{po} (kOhm cm^2)	—	—	—	1.1	0.548
CPE_c ($\mu\text{S. s}^n$) cm^{-2}	—	62	23	4.7	10.9
n_c	—	0.79	0.88	0.92	0.85
R_c (kOhm cm^2)	—	0.04	23	70	20
CPE_{dl} ($\mu\text{S. s}^n$) cm^{-2}	26.9	73	15.4	5.2	21.9
n_{dl}	0.84	0.86	0.89	0.91	0.88
R_{ct} (kOhm cm^2)	123	150	270	650	250

Potentiodynamic polarization curves obtained for all the samples in 3.5% NaCl solution are shown in Fig. 8. The plots were drawn to derive the values of different electrochemical parameters like corrosion potential (E_{corr}), corrosion current (i_{corr}), Tafel constants (β_a and β_c), polarization resistance (R_p), protection efficiency (PE) and

corrosion rate (CR) by extrapolating the anodic and cathodic curve using Tafel extrapolation method (Table I). From the results it is seen that the uncoated 316L SS exhibited corrosion potential (E_{corr}) of about -0.211 V [5]. The corrosion potential (E_{corr}) of PVK-ZrO₂ coated substrates shifts towards the positive direction indicates the protection offered by PVK-ZrO₂ coatings. It was also observed that the PVK-ZrO₂ coated 316L SS exhibited lower corrosion current density ($i_{\text{corr}} = (0.149 - 0.097) \mu\text{A cm}^{-2}$) compared to bare 316L SS ($i_{\text{corr}} = 2.45 \mu\text{A cm}^{-2}$) indicates that the PVK-ZrO₂ coatings reduce the metal dissolution. The R_p values for PVK coated SS shows a higher value than the uncoated 316L SS. Incorporation of ZrO₂ nano particles further increases R_p thereby indicating the high protection offered by PVK-ZrO₂. The corrosion rate of PVK-ZrO₂ coatings decreased with the increased protection efficiency of 98%. These results confirm that the PVK-ZrO₂ coating on 316 L SS act as a highly protective layer, which is attributed to the presence of ZrO₂ nanoparticles in polymer matrix based on the corrosion protection mechanism put forth by several researchers [44–46]. But when 3 wt.% ZrO₂ nano particles are added R_p drastically decreases, which confirms the loading limit of the nano particles in the PVK matrix. This shows that the decrease in the barrier property of the coating as the diffusion of electrolyte takes place through the coating. Increase in corrosion current and decrease in protection efficiency corroborates with a decrease in R_p value for PVKZ-3 coatings. Similar results were obtained by Chen *et al.*, in which they found that the insertion of ZnO nanoparticles improved the corrosion properties of polypyrrole [47]. The coating porosity is one of the important parameters, which strongly governs the anticorrosive behavior of the coatings [48, 49]. Therefore, measurement of the coating porosity was determined in order to estimate the overall corrosion resistance of the coated substrate and results are plotted and given in the Fig. 9. The coating porosity decreased with the addition of nano ZrO₂ particles and when the load was increased to 3 wt.% the porosity increased showing the overload of nanoparticles. From the above results it can be con-

FIG. 10. Bode (a) and Nyquist (b) plots for PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates.

cluded that both electrochemical protection and barrier effects cause the corrosion protection of the PVK-ZrO₂ nanocomposite coatings.

3. Electrochemical impedance spectroscopy

Generally, corrosion resistance of the system can be inferred from the total impedance values measured in the low frequency region [50]. In the Bode resistance plot PVKZ-2 coated substrate exhibited higher impedance values in the low frequency region when compared to PVKZ-1 and PVKZ-3. It is inferred that PVKZ-3 shows less capacitive behavior in the middle frequency region and the phase angle value decreased in the low frequency region. This linear portion observed in the low frequency region indicates that the dissolution of the metal ions or natural metal oxides into the solution. However, the steel coated with PVKZ-2, shows an increase in maximal phase angle value with broad time constant suggested that the enhancement of resistive behavior of the protective layer due to the coating on the surface of 316L SS [51, 52]. Further, the specimen coated with PVKZ-2 showed an impedance modulus few order of magnitude higher than the PVKZ-1 (Fig. 10). Thus obtained spectra were fitted using the circuit shown in Fig. 11 consisting of electrolyte resistance (R_s), pore resistance (R_{po}) relating to the diffusion of the electrolyte through the coatings via pore which can affect

FIG. 11. Equivalent circuits obtained from PVKZ-1, PVKZ-2 and PVKZ-3 coatings on 316L SS substrates.

the barrier properties of the coatings, coating resistance (R_c), charge transfer resistance (R_{ct}), pore capacitance (CPE_{po}), coating capacitance (CPE_c), and double layer capacitance (CPE_{dl}). Constant phase element (CPE) is used instead of “C” to distinguish the deviation from the ideal capacitive behavior (note that the EC curves fitting plots of uncoated PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates are given in Fig. S3 in Supplementary materials). R_{ct} values for PVKZ-1 and PVKZ-2 are higher when compared to 316L SS which quantifies the charge transfer resistance offered by the coatings. Very low capacitance (CPE_c) value combined with high resistance value (R_c) for PVKZ-2 indicates enhanced corrosion resistance offered by the coating. However, the R_c decreases and CPE_c increases for PVKZ-3 showing the slight decrease in corrosion resistance with the overloading of ZrO₂ nanoparticles. The coatings being the protective passive layer offer effective barrier properties against the penetration of corrosive ions on metal. The decrease in CPE_{dl} values for PVKZ-1 and PVKZ-2 is attributed to the effect of the nano particles offered in the polymer matrix by controlling the diffusion of corrosive ions at the interface. But the increase in CPE_{dl} values for PVKZ-3 shows the overloading and the commencement of delamination.

G. Thermal characterization

Figure 12 represents the typical TGA and DTA curves with traces of weight loss as a function of temperature under Nitrogen atmosphere. The first and the second weight loss corresponding to 89.06°C and 105–127°C is related to the removal of impurities. The thermal tran-

FIG. 12. TGA and DTA scan for PVK-ZrO₂ nanocomposite.

sition (127–143°C) corresponds to the 3.3% weight loss of low molecular weight oligomers or side products. The transition observed between 266 and 332°C with a weight loss of 15.78%, which can be attributed to the degradation of the backbone units of the PVK and a complete weight loss was not observed even up to 800°C showing 38.16% remains. The effect of ZrO₂ nanoparticles into the PVK matrix is inferred with the restriction to degrade the polymer chain. A comparison of DTA scans in the thermo grams revealed the manifestation of smaller exothermic peaks at 92.25°C, 134.4°C and a sharp peak at 306°C for PVK- ZrO₂ nano composite.

IV. CONCLUSIONS

1. The PVK-ZrO₂ nanocomposite coatings were prepared onto 316L SS using chronoamperometric technique. The mechanical and corrosion performance of the composite coatings were greatly influenced with the varying amounts of ZrO₂ nanoparticles.
2. The incorporation of ZrO₂ nanoparticles was confirmed with the ATR-IR studies and EDAX analysis. The surface characterization revealed the morphological features of PVK-ZrO₂ nano composite coatings.

3. Vickers's microhardness tests confirmed the beneficial role played by ZrO₂ nanoparticles in the PVK matrix by showing enhancement in microhardness.
4. The OCP measurements illustrate the effect of ZrO₂ nanoparticles in the PVK matrix. The corrosion resistance increased with the incorporation ZrO₂ nanoparticles up to 2 wt.% in PVK matrix. Further addition of ZrO₂ nanoparticles showed decrease in corrosion resistance.
5. EIS studies exhibited enhanced charge transfer resistance for the PVK-ZrO₂ nanocomposite coating and coating with 2 wt.% ZrO₂ revealed improved coating resistance. The potentiodynamic polarization results revealed the protecting efficiency of PVK-ZrO₂ nanocomposite coatings in 3.5 wt.% NaCl solution. The protecting efficiency was higher for 2 wt.% ZrO₂ loaded PVK coatings.
6. This investigation indicates PVK-ZrO₂ nanocomposite coatings provide better corrosion protection than the PVK and it can be considered a potential coating material to protect 316L SS against corrosion in aqueous 3.5 wt.% NaCl.

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APPENDIX

Characteristic ATR-IR band assignment for the vibrational bands of PVK coatings, ATR-IR spectra of VK and PVK coated 316 L SS substrates, SEM micrographs of PVK, and EC curves fitting plots of uncoated PVKZ-1, PVKZ-2 and PVKZ-3 coated 316L SS substrates are available in Supplementary materials (https://www.jstage.jst.go.jp/article/ejsnt/16/0/16_5/_article/supplement).

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