Fabrication, characterization and electrochemical performance of PVA/TiO$_2$ polymer composites

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Abstract— Polyvinyl alcohol (PVA)/Titanium dioxide (TiO$_2$) composites were prepared by mixing TiO$_2$ in PVA solution in the proportions of 9:1, 8:2, 7:3, 6:4 5:5 and 4:6 of PVA and TiO$_2$ respectively. The obtained composites were characterized by using XRD and SEM. The pasty solution of the synthesized composites were spin coated over mild steel surface. Polarization and electrochemical impedance studies were performed to study the corrosion behaviour of the synthesized polymer composites in 3.5% NaCl solution. The incorporation of TiO$_2$ in PVA matrix in 4:6 ratio reduced the corrosion current indicating improved corrosion resistance. The electrochemical impedance study showed an increased charge transfer resistance and decreased double layer capacitance at this ratio. PVA/ TiO$_2$ composites could be used as an effective corrosion inhibitor for mild steel in 3.5% NaCl.
Keywords : Corrosion inhibitor; Electrochemical Impedance spectroscopy; Composites, PVA; TiO$_2$

I. INTRODUCTION

Composites, the wonder materials are becoming an essential part of todays materials due to the advantages such as low weight, corrosion resistance, high fatigue strength, and faster assembly. Composite materials having long-term durability for continuous purposes are desirable and cost-effective. There is much interest in the development of inexpensive composite polymers with an appropriate weight, appropriate electric conductivity and/or appropriate impact value for use with practical articles [1]. Polymer composites have steadily gained growing importance during the past decade. Vigorous developments of polymer composite and extensive utilization of polymer materials in technology have led to the polymer composites [2]. The importance of polymers is mainly because polymers are still regarded as a cheap alternative material that is manufactured easily. The intensive use of polymer in broad use has led to the development of materials for specific applications namely composites [3]. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to be processed requiring high temperature. On the other hand, polymers are flexible, can be easily processed at low temperatures and exhibit high dielectric break down field [4]. A good amount of work has been reported on the conduction mechanism in polymeric materials. Water soluble conducting polymer composite, poly(vinyl alcohol-threonine) was chemically synthesized and the corrosion inhibition performance was evaluated [5]. The inhibitive action of synthesized polyvinyl alcohol-sulphanilic acid composite on the corrosion of commercial mild steel in 1M HCl medium has been investigated [6]. The uniform Polyaniline-sodium dodecylsulfate/polyvinyl alcohol composite films were prepared and the anticorrosive nature of films were studied [7]. Polyvinyl alcohol aniline composite was tested for its performance [8] in protecting mild steel against corrosion in 1M HCl. A new corrosion inhibitor namely poly(vinyl alcohol-leucine) composite has been synthesized and its influence on corrosion inhibition of mild steel in 1M HCl has been studied [9].

II. MATERIALS AND METHODS

CHEMICALS AND REAGENTS

PVA and TiO$_2$ were obtained from Alfa Aesar, India and used as such.

Preparation of PVTi composites

A definite quantity of PVA was dissolved in water at 60°C followed by the addition of a known quantity of TiO$_2$ and then it was made into a paste in an agate mortar then it was subjected to heat at 80°C for 30 minutes in a hot air oven and made into a powder. PVTi composites were prepared in the following proportions of PVA and TiO$_2$: PVTi 1 – 9:1,   PVTi 2 – 8:2, PVTi 3 - 7:3, PVTi4 -6:4, , PVTi 5 – 5:5 and PVTi 6 – 4:6.

PXRD

In order to understand the properties of composite material, it is essential to know about the details of its structure. The X-ray diffraction pattern (XRD) technique was used for characterization. The PXRD of PVA, TiO$_2$ and PVTi composites were recorded using Philips X'PERT PRO diffractometer with Cu Kα (λ = 1.54060 Å) incident radiation. The XRD peaks were recorded in the 2θ range of 20°–80°.

SEM

The Scanning electron microscopy produces detailed photographs that provide important information about the surface structure. The morphology of PVA and PVTi composites are recorded using Philips XL30. The samples were gold plated before SEM observation.

COATING OF MILD STEEL SUBSTRATES WITH PVTi COMPOSITES

The mild steel plates of 1 square cm area were polished with emery paper and immersed in 10% dilute sulphuric acid for 30 minutes and then the plates were washed with distilled water and rinsed with acetone. A pasty solution of polymer composites (PVTi) were coated on surface treated mild steel panels using a Apex Spin Coating unit (SCU 2005) and the panels were sintered in a hot air oven for 30 minutes at certain temperatures. Then these plates were used for corrosion studies.

ELECTROCHEMICAL MEASUREMENTS

POLARIZATION AND IMPEDANCE STUDIES

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of 1 cm2 area was used as the working electrode. A platinum electrode and saturated calomel electrode were used as counter electrode and reference electrode respectively. The saturated calomel electrode was connected via Luggin capillary, the tip of which was held very close to the surface of the working electrode to minimize the IR drop. Open circuit potential (OCP) measurements were recorded for 30 minutes, the time necessary to reach quasi stationary state for open circuit potential, followed by polarization measurements at a scan rate of 1mV/s for Tafel plots. Prior to each experiment the working electrode surface was polished with emery paper. Biologic Electrochemical analyzer (model SP 300) with EC Lab software was used for data acquisition and analysis. For polarization and impedance studies the period of immersion maintained was 30 min. Polarization technique was carried out from a cathodic potential of -250mV to an anodic potential of +250mV with respect to OCP at a scan rate of 1 mV/s. In EIS technique a small amplitude ac signal of 10 mV and a frequency spectrum from 10^5 to 10^{-2} Hz was impressed at the OCP and the impedance data were analysed using Nyquist plots.

III. RESULTS AND DISCUSSION

PXRD

The XRD pattern of pure PVA shows a characteristic peak for an orthorhombic lattice centered at 19.40 and 40.0°, indicating the presence of semicrystalline phase [10]. The average grain size is found to be 0.1486µm. The peak positions (2 = 25.30 (1 0 1), 38.57 (1 1 2), 48.04 (2 0 0), 53.88 (1 0 5), 62.68 (2 0 4), 70.29 (2 2 0), 75.05 (2 1 5) and 83.16° (3 1 2) and relative intensitites obtained for TiO_2 match with the JCPDS Card no. 78-2486 file, identifying it as TiO_2 with anatase phase. The average crystallite size is found to be 0.1858µm. The weakening and broadening of the XRD peaks may be attributed to the decrease of the sample crystallite size with increase in TiO_2 content. The introduction of TiO_2 can suppress the crystallite size and the suppression is more remarkable with the introduction of higher TiO_2 content. The intensity of the XRD peaks decreased with increasing TiO_2 concentration, indicating a reduction in crystallinity of the host polymer. The polymer composite samples with different TiO_2 contents contain anatase and tetragonal phases of TiO_2. However, the peaks are broader and reduced in intensity as TiO_2 content increases. In addition, the locations of peaks are shifted toward smaller angle. The effect of TiO_2 content on crystallite size has also been evaluated from XRD data. The crystallite sizes of polymer composites with different TiO_2 concentration have been calculated from Scherrer equation. The average crystallite size is found to be 0.1399 µm.

SEM

The SEM images of PVA and PVTi 6 shows the presence of beads proved that ceramic oxides are scattered inside the PVA matrix. Incorporation of TiO_2 into the PVA matrix, reduces the crystallinity and alters the original polymer structure and thus the conductivity of polymer composites increases.

ELECTROCHEMICAL IMPEDANCE STUDIES

The I_{corr} of bare mild steel is 35.1 µA/cm^2 . The incorporation of TiO_2 into PVA matrix reduced the corrosion currents of PVTi 6 to 1.1 µA/cm^2 respectively. This indicates that the addition of ceramic oxides in PVA matrix has improved the corrosion resistance. The corrosion potential E_{corr} of bare mild steel is -706 mV. The incorporation of TiO_2 into PVA matrix resulted in a positive shift in potential (Fig. 1). An increase in ceramic oxides content in the composites PVTi 6 resulted in a significant shift to more positive value indicating its better corrosion resistance behaviour compared to all the other 5 composite samples. Thus, it's understood that the addition of ceramic oxides upto 10-60wt% favours the corrosion resistance [11]. The corrosion rate of bare mild is found to be 10.72 mpy, whereas for the composites of PVTi 1 and PVTi 6 are found to be 2.89 and 0.33, mpy(Table 1). This indicates that with increase in the content of ceramic oxides, the corrosion rate decreases.
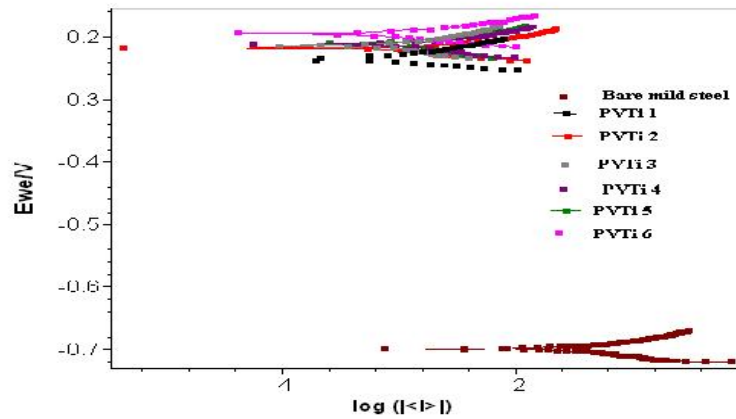
Figure 1 Tafel plots for bare mild steel and PVTi composites

TABLE 1 Corrosion parameters obtained from Polarization studies of bare mild steel and coated PVTi composites

System studied	E_{corr} (mV)	I_{corr} (µA/cm^2)	Corrosion rate (mpy)
Bare mild steel	-706	35.1	10.72
PVTi 1	-237	9.5	2.89
PVTi 2	-226	8.1	2.47
PVTi 3	-219	6.8	2.07
PVTi 4	-216	5.1	1.55
PVTi 5	-211	3.5	1.06
PVTi 6	-200	1.1	0.33

The small high frequency semicircle, which is observed in the Nyquist plot of bare mild steel in 3.5% NaCl is attributed to the single time constant of charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}). The emergence of second semi circle is observed in the Nyquist plots of polymer composites (Fig. 2), indicating that the charge transfer resistance becomes dominant in the corrosion process due to the presence of protective polymer composite on mild steel surface and the corresponding equivalent circuit models is given in the figures 3 and 4. Studies reported in literature [12] showed that the diffusion process is controlled by diffusion of dissolve oxygen from the bulk solution to the electrode surface and the Warburg impedance, which is observed in the low frequency regions, is ascribed to diffusion of oxygen to the mild steel surface. The high frequency capacitive loop is so small that it is almost shielded by a straight line in the low frequency region. The measured impedance parameters such as charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are shown in the table 2. The R_{ct} values increased as the concentration of ceramic oxide is increased, whereas C_{dl} values decreased. This is because the water molecules in the electrical double layer are replaced to a very large extent by the composites having a very low dielectric constant [13]. This suggests that the polymer composites function by adsorption at the metal solution interface [14].

TABLE 2 Electrochemical parameters obtained from Impedance studies for bare mild steel and coated PVTi composites

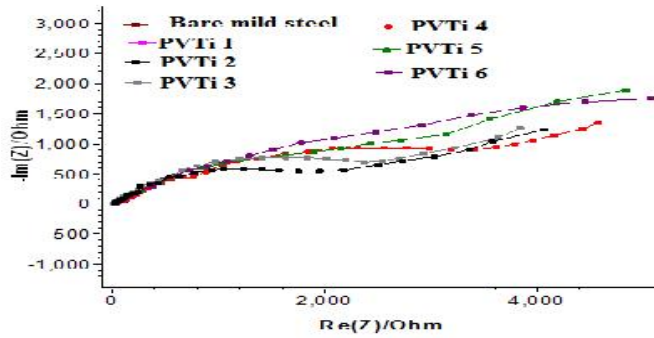| System studied	R_{ct} (Ohm cm^2)	C_{dl} (µF)
Bare mild steel	23.4	2.583×10^{-2}
PVTi 1	1732	3.750×10^{-3}
PVTi 2	2512	1.216×10^{-3}
PVTi 3	2615	0.944×10^{-3}
PVTi 4	3695	0.841×10^{-3}
PVTi 5	3871	0.545×10^{-3}
PVTi 6	35484	0.112×10^{-3}

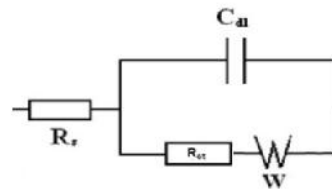Figure 2 Nyquist plots for bare mild steel and PVTi composites

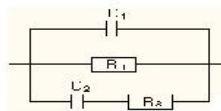Figure 3 Equivalent circuit model for bare mild steel

Figure 4 Equivalent circuit model for PVA composites

IV. CONCLUSION

A series of composite samples were prepared by sol–gel method using PVA/ TiO2 and were characterizsed using XRD and SEM. From the XRD studies, it can be concluded that the increase in oxide concentration in all the composites shall decrease the crystallinity of the polymer considerably. Electrochemical Impedance Spectroscopy (EIS) and polarization measurements have been used to evaluate the coating performance in 3.5% NaCl. EIS and polarization measurements showed the improved corrosion resistance of composite coatings due to the formation of protective oxide films which act as a barrier to oxygen diffusion to the metal surface. From the results, it can be concluded that PVA composites will have potential application as corrosion resistant coatings.

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