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Preparation, Characterization and Anticorrosive Properties of a Novel Pmma/ Zro_2 Composite

KEYWORDS: PMMA, polymer composite, coating, ZrO_2

S. Devikala	P. Kamaraj	M. Arthanareeswari
Department of Chemistry, SRM University, Kattankulathur-603 203, India.	Department of Chemistry, SRM University, Kattankulathur-603 203, India.	Department of Chemistry, SRM University, Kattankulathur-603 203, India.

ABSTRACT *In this study, a series of composite samples were prepared by sol–gel method using PMMA (Polymethylmethacrylate) and ZrO2 (Zirconium dioxide). The as-prepared composites were then characterized by X-ray diffraction (XRD) patterns and Scanning Electron Microscopy (SEM). Electrochemical Impedance Spectroscopy (EIS) and polarization measurements have been done to evaluate the coating performance in 3.5% NaCl. The EIS and polarization measurements showed an improved corrosion resistance of the composite coatings due to the formation of protective oxide films which act as a barrier to oxygen diffusion to the metal surface.*

INTRODUCTION

Corrosion is a natural process that has troubled human beings ever since the use of metals. Hence, efforts to develop more efficient and environmentally compliant methods to prevent corrosion have been ongoing throughout this century. Three approaches commonly are used to reduce the rate of corrosion: cathodic protection, passivation (anodic protection), and barrier coatings[1]. The protection offered by coatings contributes to lifetime of many products such as bridges, pipelines etc. It is often not economical to protect these items without coatings, because corrosive environments such as weather, sea water and corrosive gases would damage them too quickly . PMMA, is a transparent polymer possessing properties like light weight, high light transmittance and chemical resistance[3]. Zirconium dioxide has traditionally received a lot of attention due to its chemical stability, non-toxicity, low cost and other advantages. As a result, it is widely used as a white pigment, gas sensor, anti-reflection coating in many thin-film optical devices, biomaterials and catalyst/additive in catalytic reactions[4]. One of the most effective methods is to deposit protective polymer–ceramic coating on the metal surface[5]. Sol–gel ceramic coatings have been extensively employed for the wear, corrosion and oxidation protection of metals[6]. In recent years, organic/inorganic composite materials have attracted considerable attention in both scientific and industrial circles, because they offer attractive potential for diversification and application of traditional polymeric materials[7]. Corrosion protection of metal matrix composites (MMC) by anodizing or by application of a polymer coating has been evaluated by electrochemical impedance spectroscopy (EIS)[8]. Polymer composite coatings as corrosion inhibitors has been reported[9-11]. In continuation of our quest for developing anti corrosion agent with high effectiveness and efficiency, the present paper aims at the development of PMMA/ ZrO_2 composite to function as an anti corrosion agent has been prepared.

Experimental

Materials

The monomer MMA (Fischer Scientific, India), ZrO_2 (Alfa Aesar), benzoyl peroxide (Fischer Scientific, India), chloroform and petroleum ether (Fischer Scientific, India) were obtained and used as such.

Preparation of PMMA

The purified monomer (MMA) (10ml) was taken in a polymerization tube and 50mg of benzoyl peroxide which acts as a catalyst was added to accelerate polymerization, in the polymerization reaction. The polymerization tube was then kept in a water bath at 60-70 °C with periodical shaking. A hard viscous polymer was obtained after 90 minutes of heat treatment. The polymerized mass was dissolved in chloroform and then transferred into a beaker. The viscous polymer solution was precipitated by the addition of petroleum ether. The precipitated polymer was then filtered and oven dried at 60 °C. The polymer formed was found to be syndiotactic[12].

Preparation of PMZr Composites

A definite quantity of PMMA was dissolved in chloroform followed by the addition of a known quantity of ZrO_2 and then it was made into a paste in an agate mortar and was subjected to heat at 110 °C for 30 minutes in a hot air oven and made into a powder. PMZr composites were prepared in the following proportions of PMMA and ZrO_2: PMZr 1 – 9:1, PMZr 2 – 8:2, PMZr 3 - 7:3, PMZr 4 -6:4, PMZr 5 – 5:5 and PMZr 6 – 4:6.

Characterization techniques

XRD

The XRD patterns of polymers and polymer 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 SEM images of polymers and polymer composites were recorded using Hitachi Scanning Electron Microscope SU1510. The samples were gold plated before SEM observation.

Coating of Mild Steel Substrates with Polymer Composites

Substrate Preparation

Mild steel panels were used in corrosion studies. The mild steel panels were polished with emery paper and immersed in 10% dilute sulphuric acid (pickling) at 70-80 °C for 30 minutes to remove the rust and mill scale. The pickled panels were rinsed thoroughly in de ionized water and then rinsed with acetone to remove the acid residues present on it after pickling. The pickled and rinsed mild steel panels were subjected to coating immediately. A pasty solution of polymer composites 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 110 °C. Then these plates were used for corrosion studies.

Electrochemical Impedance and Polarization studies

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of 1 cm^2 area was used as the working electrode. A platinum electrode and satu-

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rated calomel electrode were used as counter and reference electrode respectively. Prior to each experiment the working electrode surface was polished with emery paper. Biologic Electrochemical analyser (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 -2V to an anodic potential of 2V with respect to corrosion potential at a sweep rate 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.

XRD

The XRD pattern for PMMA show peaks at 2θ 14.50, 22.49, 29.45 and 41.41° and relative intensities obtained for the polymer match with the JCPDS Card no. 13-0835 file, identifying it as PMMA. The average crystallite size of PMMA is determined using XPert' High Score plus software and it is found to be 0.1344 µm. The peak positions (2θ = 30.26 (0 1 1), 34.81 (0 1 1), 34.81 (0 0 2), 43.13 (0 1 2), 50.70 (0 2 0), 60.20 (1 2 1) and 74.53° (2 2 0) and relative intensities obtained for ZrO_2 match with the JCPDS Card no. 50-1089 file, identifying it as ZrO_2 with tetragonal phase . The average crystallite size is found to be 0.1756 µm. From XRD of composites, we can say that the crystallinity of the polymer has been considerably decreased upon the addition of ZrO_2. The average crystallite size is found to be 0.1413 µm.

SEM

Incorporation of ZrO_2 into the PMMA matrix, reduces the crystallinity. When the concentration of ceramic oxides are increased, dark spots are observed in the SEM images which resulted in the amorphization of the composites and the area of dark spots increases as the concentration of oxide is increased. It shows the crystallinity of the composites, which decreases as the concentration of oxide increases and it matches with the results of the XRD patterns.

POTENTIODYNAMIC POLARIZATION STUDIES

The E_{corr} and I_{corr} values of bare mild steel are -706 mV and 35.1 µA/cm^2 respectively (Table 1). The incorporation of ZrO_2 into PMMA matrix reduced the corrosion currents of PMZr 6 to 3.2 µA /cm^2 respectively. This indicates that the addition of ceramic oxides in PMMA matrix has improved the corrosion resistance. The reinforcement of ceramic oxides in PMMA composites follows the trend (Figure 1). It is seen that the least corrosion current value i.e. a better corrosion resistance is displayed by sample PMZr 6. The corrosion potential E_{corr} of bare mild steel is -706 mV. An increase in ceramic oxides content in the composites (PMZr 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 is understood that the addition of ceramic oxides upto (10-60%) favours the corrosion resistance[13].

Table 1. Corrosion parameters obtained from Polarization and impedance studies for bare mild steel and PMZr composite coated mild steel

System studied	E_{corr} (mV)	I_{corr} (µA/ cm^2)	Corrosion rate (mpy)	R_{ct} (Ohm cm^2)	C_{dl} (µF/ cm^2)
Bare mild steel	-706	35.1	10.72	23.4	2.583×10^{-2}
PMZr 1	-693	28.6	8.74	1395	1.698×10^{-3}
PMZr 2	-677	22.1	6.74	1741	1.054×10^{-3}
PMZr 3	-674	18.8	5.75	2332	0.614×10^{-3}
PMZr 4	-669	10.4	3.19	2614	0.319×10^{-3}
PMZr 5	-667	6.5	1.98	2865	0.286×10^{-3}
PMZr 6	-664	3.2	0.97	3515	0.205×10^{-3}

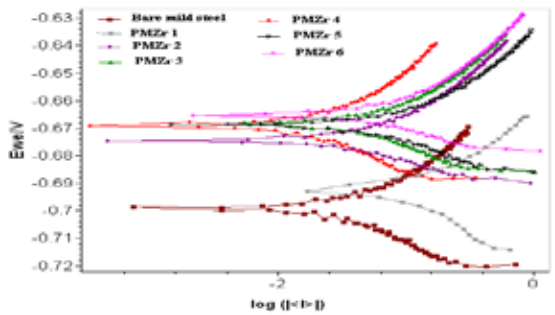

Fig.1 Tafel plots of bare mild steel and PMZr coated mild steel

ELECTROCHEMICAL IMPEDANCE STUDIES

From the Nyquist plots (Figure 2), the diameter of the capacitance loop increased with increasing concentration of ceramic oxides. This is due to the the contact area between substrate and electrolyte is reduced and caused the change of the capacitance loop resulting in the lower corrosion rate[14-17]. Increase in diameter of capacitive loop, indicating the continous formation of polymer composites containing passive film on the sample surface[18].

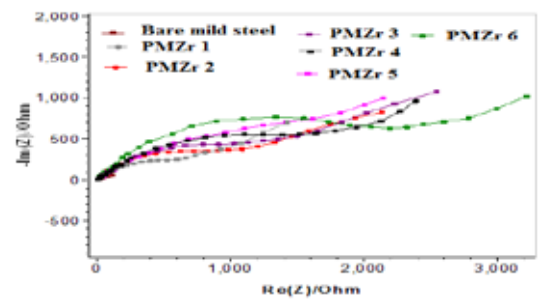

Fig.2 Nyquist plots of bare mild steel and PMZr coated mild steel

The value of C_{dl} decreases with the increase in oxide concentration indicating that polymer composite function by adsorption at the metal/solution interface, leading to protective film on the mild steel surface, and decreasing the extent of dissolution reaction[19-20] (Table 1). Results obtained from the impedance measurements show that R_{ct} values increase and C_{dl} values decrease. The decrease in C_{dl} is due to increase in thickness of the electric double layer. The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface. This suggests that when polymer composite adsorbed on the metal surface, it influences the double layer. This causes decrease in the electrical capacity and it may be attributed to the formation of a protective layer on the metal surface.

CONCLUSIONS

A series of composite samples were prepared by sol–gel method using PMMA/ ZrO_2 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 PMMA composites will have potential application as corrosion resistant coatings.

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