



Electrochemical Performance of PMMA/Al₂O₃ Composite Coatings

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Abstract— In this work, a series of composite samples were prepared by sol–gel method using PMMA (Poly methyl methacrylate) and Al₂O₃ (Aluminium dioxide). The as-prepared composites were then characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) patterns and Scanning Electron microscopy (SEM). Electrochemical Impedance Spectroscopy (EIS) and polarization measurements have been used to evaluate the coating performance in 3.5% NaCl. According to the EIS and polarization measurements, the composite coatings showed improved corrosion resistance due to the formation of protective oxide films which act as a barrier to oxygen diffusion to the metal surface.

Keywords: coating, corrosion, PMMA, polymer composite

I. INTRODUCTION

Corrosion of materials is a natural phenomenon that is a cause of concern as it has incurred a total damage of billions of dollars to many industries. Many ways of overcoming the corrosion problem such as inhibitors, anodic protections, cathodic protections and coatings are developed[1]. Mild steel is widely applied in industrial manufacturing, particularly in the automotive and machinery segments, due to its low production costs coupled to excellent mechanical properties and overall integral reliability, however the steel displays a clear tendency to corrode in diverse environmental conditions[2]. Corrosion inhibition of mild steel is a matter of theoretical as well as practical importance [3]. Polymer – ceramic composite based coatings have found ever wider use in various branches of national economy. Coatings are of high economic importance because they provide protection against corrosive and atmospheric attack. Coatings are used to protect substrates against mechanical, chemical, and atmospheric influences. Mild steel is one of the important iron-containing alloys used in many industrial aqueous systems in which water circulates. Various surface techniques have been developed to improve the corrosion resistance of metals. One of the most effective methods is to deposit protective

polymer–ceramic coating on the metal surface[4]. Sol–gel ceramic coatings have been extensively employed for the wear, corrosion and oxidation protection of metals[5]. PMMA, is a transparent polymer possessing properties like light weight, high light transmittance, chemical resistance, colorlessness, resistance to weathering corrosion[6]. Alumina is one of the most widely used engineering ceramic material due to its high elastic modulus, high wear resistance and chemical corrosion resistance, high-temperature stability and the retention of strength at high temperatures [7]. It is an electrical insulator but has a relatively high thermal conductivity. The corrosion characteristic of Al/5%Si/15%SiC composite in 0.5M sodium hydroxide solution using Palm exudate (palm wine) as corrosion inhibitor was investigated by employing gravimetric and potential measurements has been reported [8]. A comparative study of corrosion behavior of Al/Silicon carbide composite with cast iron has also been reported [9]. In the present study, PMMA/ Al₂O₃ composite was investigated for its corrosion inhibition potential by using potentiodynamic measurement and electrochemical impedance spectroscopy.

II. EXPERIMENTAL

Materials

The monomer MMA (Fischer Scientific, India), Al₂O₃ (Fischer Scientific, India), benzoyl peroxide (Fischer Scientific, India), chloroform (Fischer Scientific, India) 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[10].

Preparation of PMAI Composites

A definite quantity of PMMA was dissolved in chloroform followed by the addition of a known quantity of Al₂O₃ 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. PMAI composites were prepared in the following proportions of PMMA and Al₂O₃: PMAI 1 – 9:1, PMAI 2 – 8:2, PMAI 3 – 7:3, PMAI 4 – 6:4, PMAI 5 – 5:5 and PMAI 6 – 4:6.

XRD

The XRD patterns of polymers and polymer composites were recorded using Philips X'Pert pro diffractometer with Cu K α (λ = 1.54060 Å) incident radiation. The XRD peaks were recorded in the 2 θ range of 20°–80°.

FTIR

The FTIR spectrums of polymers and polymer composites were recorded using Shimadzu FTIR spectrophotometer.

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 chemical composition of the mild steel panel was given in Table 1. 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 deionised 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.

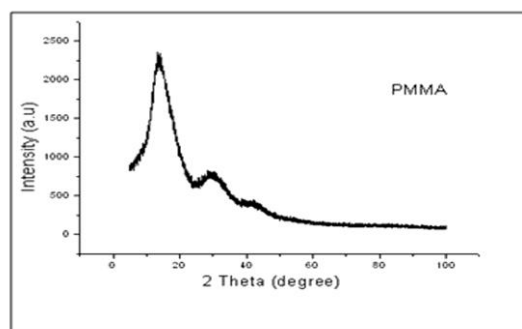
Electrochemical Impedance and Polarization studies

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of 1 cm² area was used as the working electrode. A platinum electrode and saturated 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 10⁵ to 10⁻² Hz was impressed at the OCP and the impedance data were analysed using Nyquist plots.

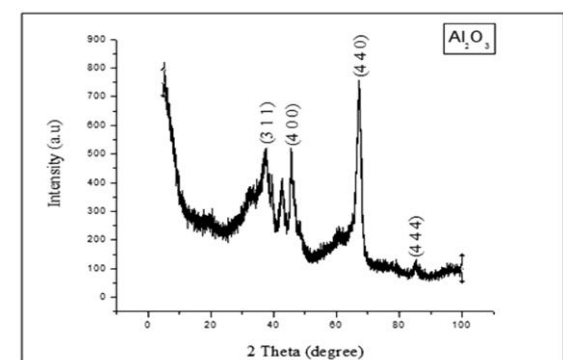
III. RESULTS AND DISCUSSION

XRD

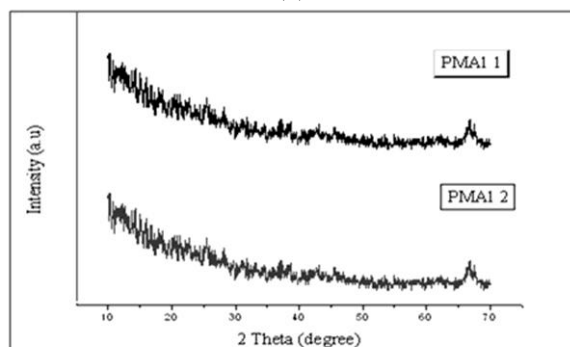
The XRD pattern for PMMA (Fig. 1(a)) show peaks at 2 θ 14.50, 22.49, 29.45 and 41.41° and relative intensities obtained for the polymer match with the JCPDS Card no. 13-0835 file, identifying it as PMMA. The average crystallite size of PMMA is determined using X Pert' High Score plus software and it is found to be 0.1344 μ m. The peak positions (2 θ =37.53 (3 1 1), 39.27 (2 2 2), 45.66(4 0 0), 66.60 (4 4 0) and 84.46° (4 4 4) and relative intensities obtained for Al₂O₃ match with the JCPDS Card no. 50-0741 file, identifying it as Al₂O₃ with γ phase (Fig. 1(b)). The average crystallite size is found to be 0.1654 μ m. The broad diffraction peaks of polymer composites (Fig.1(c–e)) suggest that the Al₂O₃ are very small in size. The crystallite size of polymer composites are decreased which in turn favours higher ionic conduction [11]. From the XRD study, it can be concluded that Al₂O₃ is homogenously dispersed throughout the polymer matrix with maximum uptake of Al₂O₃ [12]. The average crystallite size is calculated using Xpert' High Score plus software and fitted in Scherrer formula and not from the figure and it is found to be 0.1335 μ m.



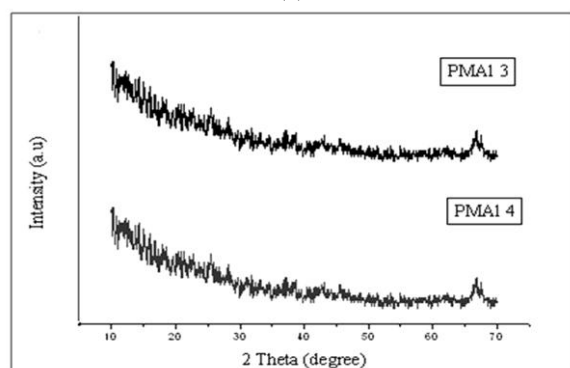
(a)



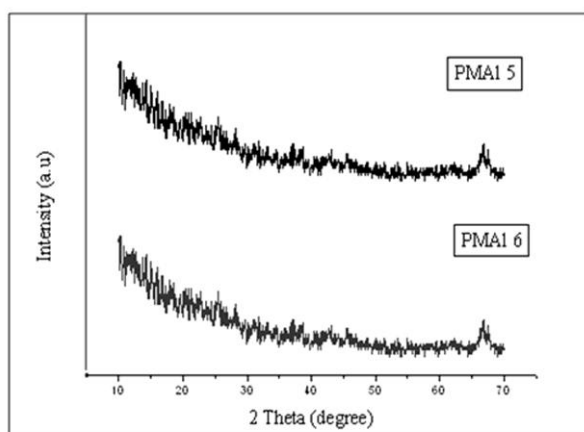
(b)



(c)



(d)

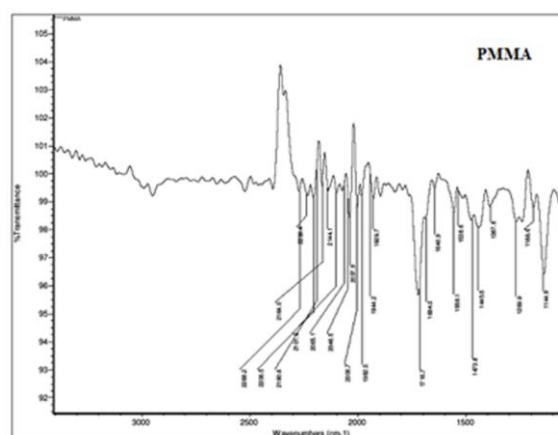


(e)

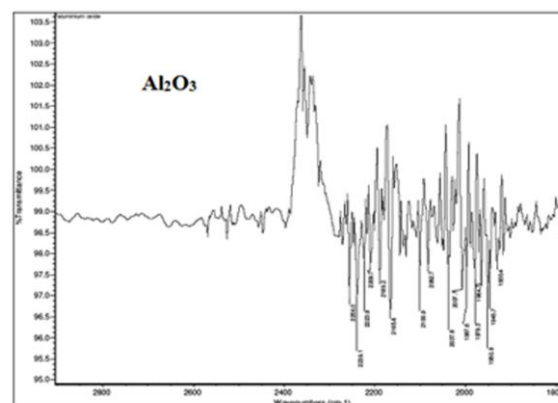
Fig. 1. XRD patterns of (a) PMMA (b) Al_2O_3 (c) PMAI 1 and 2 (d) PMAI 3 and 4 (e) PMAI 5 and 6

FTIR

An absorption band in the range of $1500\text{--}700\text{ cm}^{-1}$ comes from the --C--O stretching vibration ($1270\text{--}990\text{ cm}^{-1}$), --C--H bending vibration ($1450\text{--}1350\text{ cm}^{-1}$), and CH_2 rocking ($810, 750\text{ cm}^{-1}$). The bands at 1387 and 1456 cm^{-1} (Fig.2(a) correspond to symmetrical bending vibration and asymmetrical bending vibration of methyl group respectively. Broader and stronger bands in the region $1300\text{--}1000\text{ cm}^{-1}$ correspond to C--O stretching vibrations, which usually consists of two asymmetric coupled vibrations, i.e. C--C(=O)--O and O--C--C . Peak at 749 cm^{-1} corresponds to out of plane C--H bending [13]. Strong peak appearing in the region 1731 cm^{-1} corresponds to C=O stretching vibrations. A peak at 1716 cm^{-1} is identified as C=O stretching vibrations in the pendant group (--COOCH_3) of PMMA. At approximate 1025 cm^{-1} ether lone pair peak is also present. The bands at $2226, 2208, 2189, 2162, 2078, 2044, 2005, 2037, 1980\text{ cm}^{-1}$ in the composite are characteristic peaks of Al_2O_3 while bands at $1988, 1980, 1983, 1435, 1237$ and 1145 cm^{-1} are characteristic peaks of PMMA. The presence of the absorption band at 1724 , ascribed to the stretching, of the carbonyl group, suggests the existence of PMMA in the composite [14]. The shifts in the pure PMMA and pure Al_2O_3 may be attributed to the interaction between the C=O carbon atoms of PMMA and oxygen atoms of Al_2O_3 (Fig.2(c–e)).



(a)



(b)

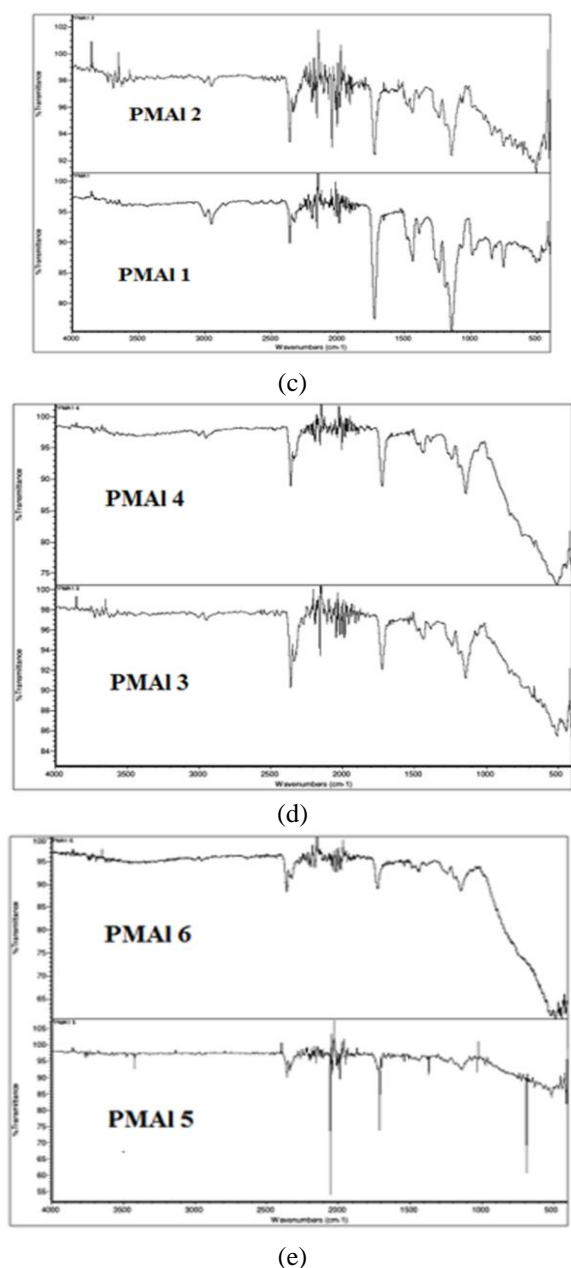
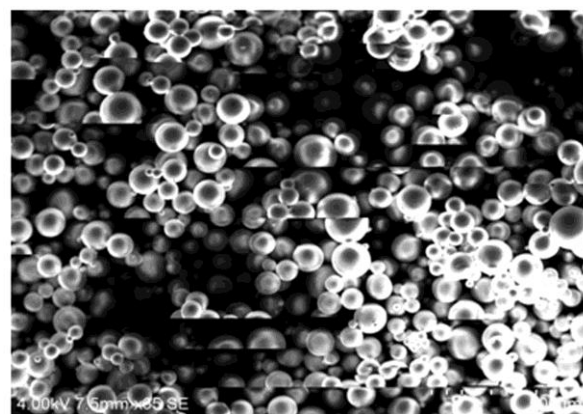


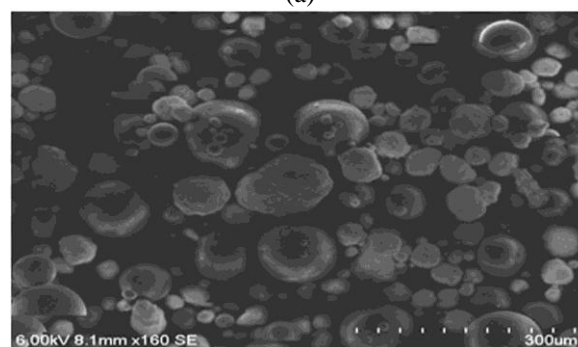
Fig. 2. FTIR spectra of (a) PMMA (b) Al_2O_3 (c) PMMA 1 and 2 (d) PMMA 3 and 4 (e) PMMA 5 and 6

SEM

The SEM image of PMMA, and PMMA 6 is shown in the fig. 3(a) – (b). SEM images reveal the porous nature of polymer composites, which in turn increases conductivity. Incorporation of Al_2O_3 into the PMMA matrix, reduces the crystallinity and alters the original polymer structure and thus the conductivity of polymer composites increases [15]. When the concentration of ceramic oxides are increased, dark spots are observed in the 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 resembles the XRD patterns.



(a)



(b)

Fig. 3 SEM images of (a) PMMA (b) PMMA 6

POTENTIODYNAMIC POLARIZATION STUDIES

The E_{corr} and I_{corr} values of bare mild steel are -706 mV and $35.1 \mu\text{A}/\text{cm}^2$ respectively. The incorporation of Al_2O_3 in PMMA matrix reduced the corrosion currents of PMMA 6 to $0.01 \mu\text{A}/\text{cm}^2$. This indicates that the addition of ceramic oxides in PMMA matrix has improved the corrosion resistance (Fig.4). The reinforcement of ceramic oxides in PMMA composites follows the trend. It is seen that the least corrosion current value i.e. a better corrosion resistance is displayed by sample PMMA 6. The corrosion potential E_{corr} of bare mild steel is -706 mV. The incorporation of Al_2O_3 in PMMA matrix resulted in a positive shift in potential. This also indicates that the addition of ceramic oxides in PMMA matrix has improved the corrosion resistance. An increase in ceramic oxides content in the composites PMMA 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 [16]. The corrosion rate of bare mild is found to be 10.72 mpy whereas for the composites PMMA 1, the corrosion rates are found to be 0.364 mpy (Table 1). This indicates that with increase in the content of ceramic oxides, the corrosion rate decreases. It is significant to note that materials with a corrosion rate less than 1 mpy are generally considered outstanding in relative corrosion rate [17].

Table 1. Corrosion parameters obtained from Polarization studies for bare mild steel and coated PMAI composites

System studied	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mpy)
Bare mild steel	-706	35.1	10.72
PMAI 1	-397	1.19	0.364
PMAI 2	-258	1.04	0.317
PMAI 3	-238	1.02	0.311
PMAI 4	-235	0.64	0.198
PMAI 5	-230	0.31	0.097
PMAI 6	-227	0.01	0.005

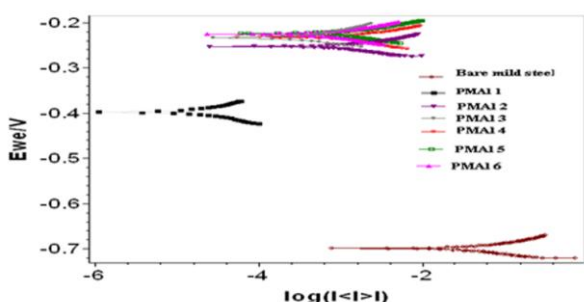


Fig. 4 Tafel plots of PMAI composites

ELECTROCHEMICAL IMPEDANCE STUDIES

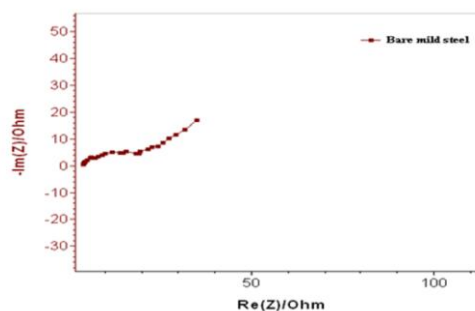
PMMA Composites

The Nyquist plot of bare mild steel is shown in the fig. 5(a). The equivalent circuit used to model corrosion of bare mild steel in 3.5% NaCl, is shown in the fig. 5(b). The model can be used to estimate the charge transfer resistance from the impedance data. Where R_s is the solution resistance, R_{ct} the charge transfer resistance, C_{dl} is the double layer capacitance and W is the Warburg impedance. The Warburg element can be used to simulate a semi-infinite linear diffusion that is unrestricted diffusion. To account for the corrosion behaviour of composite coatings in 3.5% NaCl fig.6(a) at their respective open circuit potentials, an equivalent electrical circuit model for bare mild steel is given in figure 3.56 has been utilized to simulate the metal/solution interface and to analyze the Nyquist plot. The equivalent circuit for PMAI composites is shown in the fig.6(b). 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 [18-21]. Increase in diameter of capacitive loop, indicating the continuous formation of polymer composites containing passive film on the sample surface [22]. 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

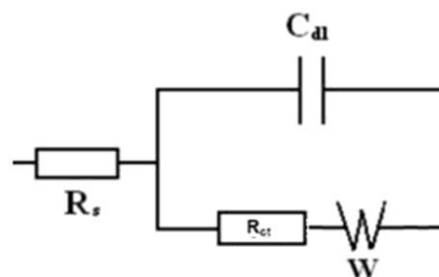
[23-26]. The decrease in C_{dl} is due to increase in thickness of the electric double layer (Table 2). The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface [27,28]. This suggests that when polymer composite adsorbed on the metal surface, it influences 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.

Table 2. Electrochemical parameters obtained from Impedance studies for bare mild steel and coated PMAI composites

System studied	R_{ct} (Ohm cm^2)	C_{dl} (μF)
Bare mild steel	23.4	2.583×10^{-2}
PMAI 1	1682	2.266×10^{-3}
PMAI 2	3699	1.541×10^{-3}
PMAI 3	5298	1.210×10^{-3}
PMAI 4	6753	0.944×10^{-3}
PMAI 5	7706	0.760×10^{-3}
PMAI 6	42215	0.501×10^{-3}

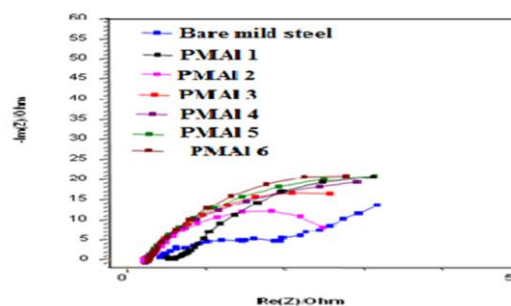


(a)

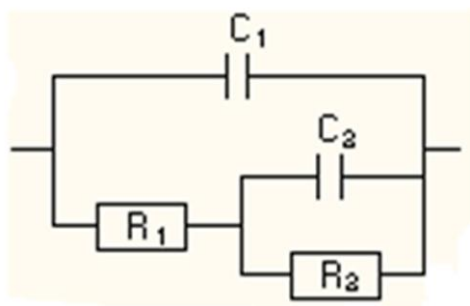


(b)

Fig. 5. (a) Nyquist plot of bare mild steel (b) equivalent circuit model for bare mild steel



(a)



(b)

6 (a) Nyquist plot of PMAl composites (b) equivalent circuit model for PMAl composites

IV. CONCLUSIONS

A series of composite samples were prepared by sol-gel method using PMMA and Al_2O_3 and were characterized using XRD, FTIR 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. According to the EIS and polarization measurements, the composite coatings showed improved corrosion resistance 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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