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SYNTHESIS AND CHARACTERIZATION OF NEODYMIUM BASED POLYMER COMPOSITES AND THEIR APPLICATION IN CORROSIVE ENVIRONMENT

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ABSTRACT

Copper being a noble metal, corrodes significantly in water containing chloride ions. Extensive use of copper as a structural material in cooling systems of nuclear installation, automobiles, power plant, oil refineries, sugar factories etc., has prompted a thorough investigation on the mechanism of copper corrosion in water containing chloride ions. The corrosion is more rapid in seawater. Rare earth oxides like Neodymium oxide are of interest for purposes such as antireflection coatings, gas insulators and protective coatings. In the present work, polyvinyl alcohol / Neodymium oxide (Nd_2O_3) composites were prepared by sol gel method. The composite samples were characterized by using X- ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. Copper corrosion in 3.5% Sodium chloride solution has been studied by electrochemical methods.

Keywords: Polyvinyl alcohol, Neodymium oxide, polymer composite, Characterization, corrosion.

INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment[1]. The literature on the electrochemical behavior of copper in acidic and basic media is quite extensive, since many technological applications require knowledge of these processes. Copper and copper alloys are widely used in practical applications due to their corrosion resistance and antifouling properties. Copper alloys are widely used in marine environments owing to their resistance to corrosion in saline solutions. Although the initial corrosion rate of copper and its alloys may be high, it decreases as protective product layers are formed. The corrosion resistance provided by a layer of reaction product varies according to the alloy and the composition of the electrolytic solution, and the thickness and electrical properties of a passive film. Rare earth oxides are an important class of materials due to their scientific and technical applications in optical devices, catalysts etc [2-6]. Composites, the wonder materials are becoming an essential part of today's 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 [7]. 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 [8]. 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 [9]. 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 [10]. A good amount of work has been reported on the conduction mechanism in polymeric materials. Among lanthanides, Nd_2O_3 has been widely used in photonic applications, luminescence, catalyst or catalyst promoters and protective coatings etc. For the most of these applications the ultra fine (in nanometer scale) neodymium oxides with well-defined particle morphology are the most essential materials. Therefore, preparation and characterization of Nd_2O_3 nanoparticles have attracted much attention in recentyears.[11]. Wet chemistry has been used for a long time for the preparation of oxide powders. Rare earth oxides, with special properties have been used in many fields such as ceramic industry, catalyst, sensors catalyst carrier and photoluminescence. For example, they can be used as catalyst for dehydrogenation, hydrogenation, esterification reactions. They can be reclaimed and cannot corrode the equipment. With the development of nano-technology, ultrafine rare earth oxides are needed in many fields. As we know smaller the particles size, the larger is the specific surface area and the higher chemical activity. If we can obtain nanometer rare earth oxides, their catalytic activity may be improved highly, especially after they are activated. Moreover, thin films of Nd_2O_3 are of interest for many other purposes such as antireflection coatings, gas insulators and protective coatings. Binary system containing nanometer sized particles and glass matrix is important in various fields of technology, including lasers, opto-and microelectronics and optical fibers[12]. Rare earth (RE) doped glasses are an important class of materials due to their many scientific and technological applications in many fields such as miniaturized optical devices, catalysts, photonics, advanced high temperature superconductors/ceramics and integrated optics. They can also be employed effectively as active media for glass lasers It is well known that the local structure around rare earth ion in glasses defines the properties of the laser emission when these materials are used as an active medium for solid-state lasers.[13] The option to use representatives of the rare earth element group (Ce, La, Sm, Y) for the protection of Al, Fe and Zn articles against corrosion in aqueous solutions was studied for the first time by Hinton and coauthors at the beginning of the eighties of the 20th century According to the literature sources, the surface modification of stainless steels in particular, and the other metal alloys using rare-earth elements, leads to improvement of their resistance to corrosion in aqueous media, containing chloride ions, he increased corrosion stability is due to the formation of thin oxide films [14]. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to study the corrosion behavior of cerium oxide nanocoatings in 3.5% NaCl solution. [15]. The electrochemical behaviour was evaluated in aerated 3.5 wt. % NaCl. All coatings tested shifted the corrosion and pitting potentials to more positive values, indicating protection against corrosion.[16] previous studies showed that for magnesium alloys, rare earth (RE) elements have distinguished feature of corrosion resistance enhancement[17]. In the present work, the corrosion resistance behavior of PVNd composites is studied.

EXPERIMENTAL

Materials

LR grade poly Vinyl alcohol obtained from Alfa Aesar, India and *LR* grade of Nd_2O_3 99.9% obtained from SD fine chemicals were used without further purification.

Preparation of specimen

Copper plate (1 x1 x0.1 cm) were polished using abrasive paper of grade 80 -1200 washed with distilled water[18] ,degreased with acetone, cleaned in ultrasonic bath and dried in hot air oven. Then these substrates were used for corrosion studies.

Preparation of PVNd composites

A definite quantity of PVA was dissolved in water at 85°C under stirring for 6 minutes in a 250 ml glass beaker and a known quantity of Neodymium oxide was added to the mixture. Then it was mechanically stirred and was sonicated for 20 minutes using a sonicator (11 L 300H) 36 KHz, Pci sonicator. The polymer composite was obtained in the form of paste.

Then the polymer composite was coated on the surface treated substrate by immersing the substrate into the paste. The substrate with uniformly coated surface was then dried at 120°C in a hot air oven for 10 minutes and made into a powder. PVNd composites were prepared in the following proportions of PVA and Nd_2O_3 : PVNd1 – 10:1, PVNd 2 – 13.33:1, PVNd 3 – 16.66:1, and PVNd4 - 20:1. PVNd5 –23.33:1, PVNd6 – 26.67:1

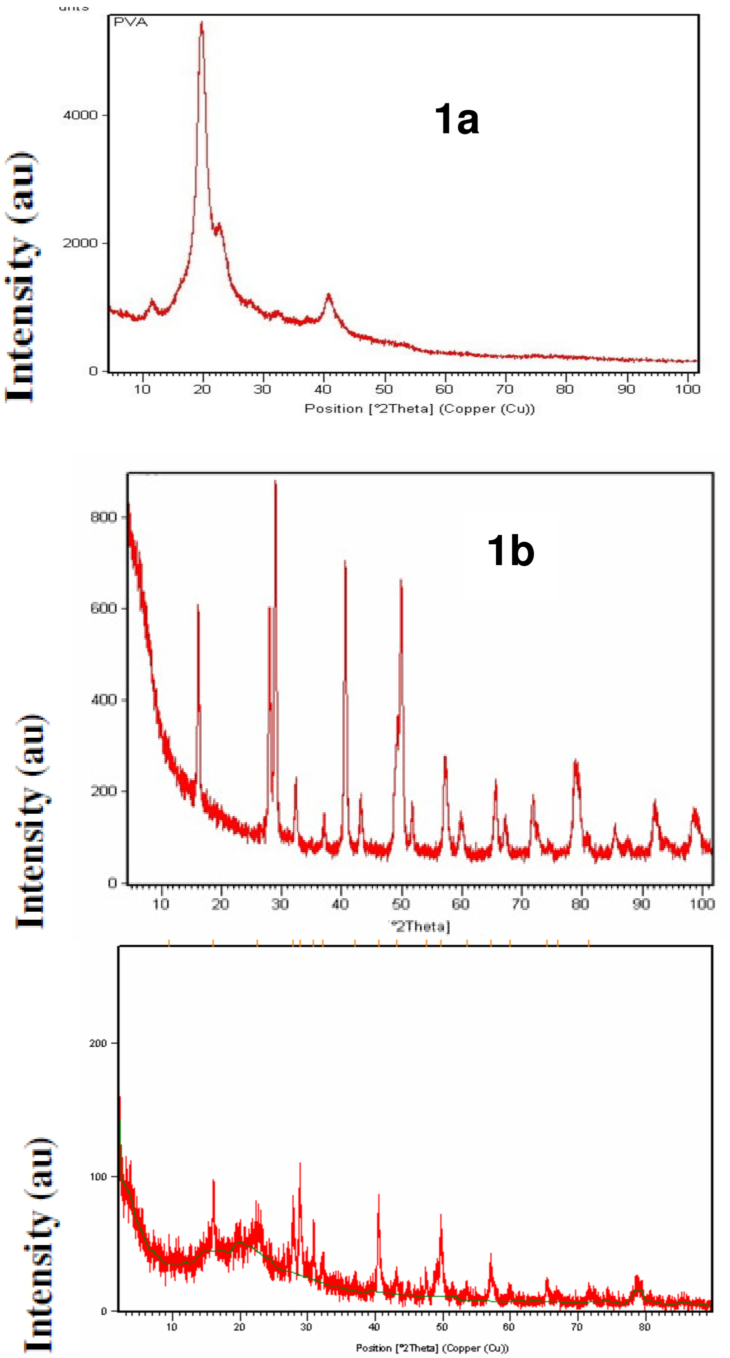


Fig.-1: FTIR Spectra of (a) PVA (b) Nd_2O_3 (c) PVNd1

Characterization Techniques

The X-ray diffraction pattern (XRD) technique was used for characterization. The PXRD of PVA, Nd_2O_3 and PVNd composites were recorded using Philips X'PERT PRO diffractometer with Cu Kα (λ=

1.54060Å) incident radiation. The XRD peaks were recorded in the 2θ range of 20°–80°. The FTIR spectrums of PVA, Nd_2O_3 and PVNd composites were recorded using Shimadzu FTIR spectrophotometer. The Scanning electron microscopy produces detailed photographs that provide important information about the surface structure. The morphology of PVA, Nd_2O_3 and PVNd composites were recorded using Philips XL30. The samples were gold plated before SEM observation.

Electrochemical Characterization

The experiments were performed in a classical three-electrode electrochemical cell. Copper specimen of 1 cm^2 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 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 -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 analyzed using Nyquist plots.

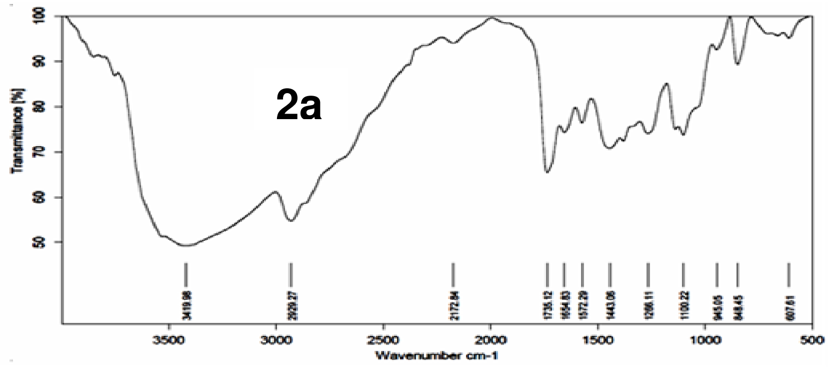
RESULTS AND DISCUSSION

PXRD

The XRD pattern of pure PVA shows a characteristic peak (Fig. 1(a)) for an orthorhombic lattice centered at 2θ values 19.40 and 40.0°, indicating the presence of semi crystalline phase [19]. The average crystallite size is found to be 3.45 nm. XRD of pure Nd2O3 was shown in the figure 1(b). Peaks appear at 2θ: (0 1 1)30.7, 40.4(0 1 2), 49.8(1 1 1) and the relative intensities obtained match with JCPDS Card No: 74-1147. The average crystallite size is found to be 23.87 nm. The average crystallite size of PVNd composites was found to be 13.87nm.The PVNd composite peaks became sharper by increasing the concentration of PVA confirming the formation of crystalline composites. [Fig. (1 (c)]

FTIR

The FTIR spectra for pure PVA and Nd_2O_3 are shown in Fig. (2a) and (2b). A band at 3419 cm-1 is due to the intermolecular hydrogen bonded OH stretching frequency of PVA [20-21]. And the band at 2929 cm^{-1} is due to CH stretching, 1443 cm^{-1} is due to CH-OH bending, 1100 cm^{-1} is due to C-O stretching, 848 cm^{-1} is due to C-C stretching. The following changes in the spectral features have been observed after comparing the spectrum of PVA with that of pure PVA and Nd_2O_3. The intermolecular hydrogen bonded O-H stretching frequency of PVA appears in the range of 3419 cm^{-1} In addition to this, the C-H stretching of CH2 exhibited at 2929 cm^{-1} in pure PVA. The C-H bending of CH_2 in pure PVA exhibited absorption at 1443 cm^{-1}, C - C stretching occurs at 1266 cm^{-1} in pure PVA. All these changes in the FTIR spectra are clear indications for the formation of PVNd composite [Fig. (2(c)]



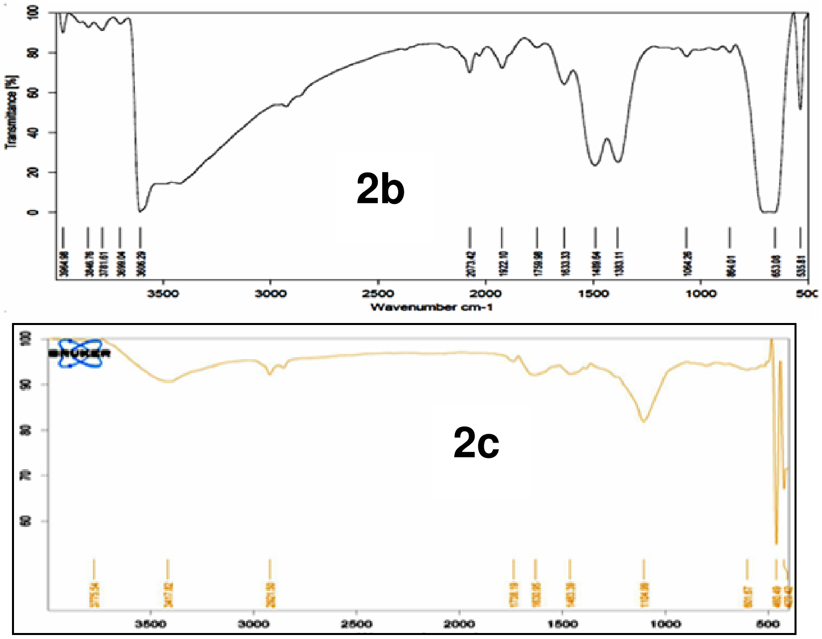


Fig.-2: FTIR Spectrum of (a) PVA (b) Nd_2O_3 (c) PVNd1

SEM

The SEM images of composite PVNd were shown in the figures 3(c). The SEM visualizes the presence of small ratio of secondary phase (Nd_2O_3) which was randomly distributed and get adhered on PVA matrix.

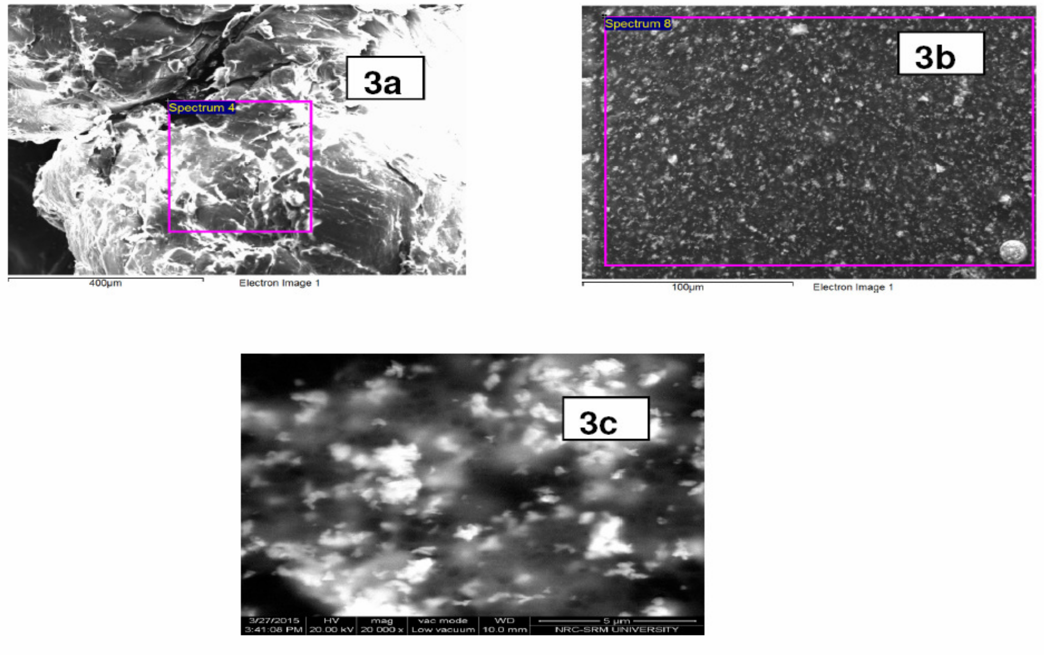


Fig.-3: SEM images of (a) PVA (b) Nd_2O_3 (c) PVNd1

EDAX

Fig.4(c) shows the corresponding EDAX spectra of samples PVNd 1 which indicate the presence of neodymium and oxygen. It is observed that the atomic percentage of neodymium is less than that of Neodymium oxide.

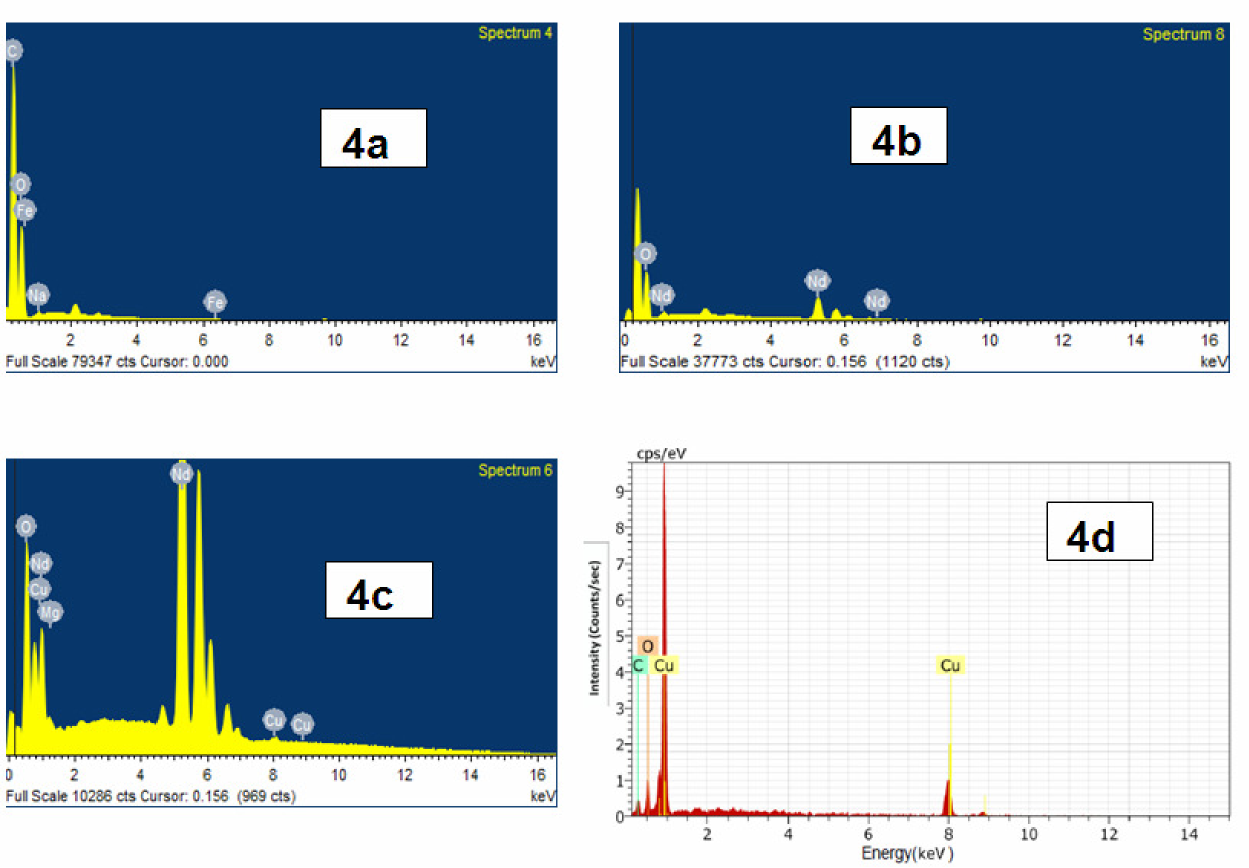


Fig.-4: EDAX images of (a) PVA (b) Nd_2O_3 (c) PVNd1 (d) bare Copper

Potentiodynamic Polarization Studies

The electrochemical polarization behaviour of blank and PVNd composites were studied in 3.5% NaCl solution. The decrease in the I_{corr} and E_{corr} values is due to the decrease in the chloride ion attack on the copper surface due to the barrier of composites[22]. The polarization parameters are given in the Table-1. E_{corr} values get slightly shifted in the positive direction with increase in the concentration of polymer is due to the decrease in the rate of anodic reaction. The decrease in E_{corr}, I_{corr} and corrosion rate are mainly due to the decrease in the chloride attack on the copper surface, which causes decrease in Cu dissolution by the adsorption of composites. Figure-5 represent Tafel curves obtained with PVNd composites in 3.5%NaCl.With increase in concentration of PVA, resulted in decrease of cathodic current density (I_{corr} ($\mu A/cm^2$).

Table-1: Polarization parameters obtained from Tafel plot

System studied	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)
Blank	-230	14.00	3.24
PVNd 1	-237	9.5	2.89
PV Nd 2	-226	8.1	2.47
PV Nd 3	-219	6.8	2.07
PV Nd 4	-216	5.1	1.55
PV Nd 5	-211	3.5	1.06
PV Nd 6	-200	1.1	0.33

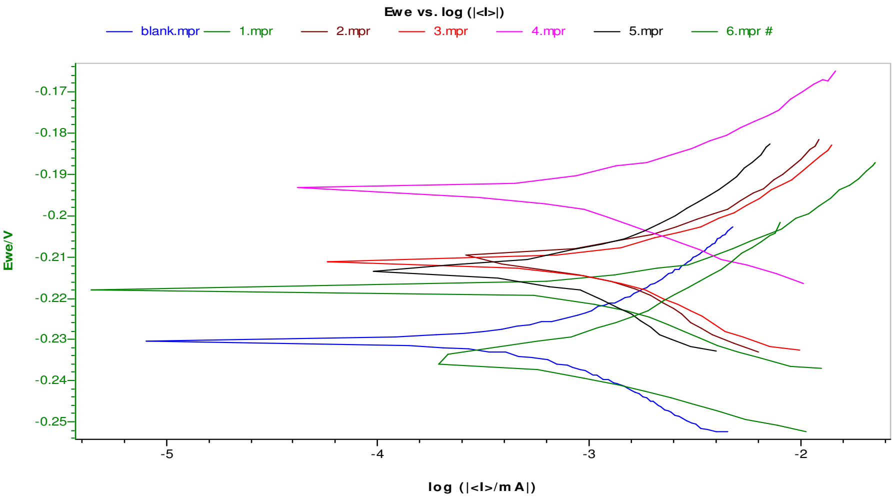


Fig.-5: Tafel plots for bare substrate and PVNd composites coated substrate

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a powerful tool in the investigation of corrosion and adsorption phenomena[23.] In order to have an electrochemical parameters on the inter surface metal /solution, electrochemical impedance measurements were carried out in 3.5 % NaCl after 30 minutes of immersion (Fig.6). Nyquist plots for blank and PVNd composites were shown in the figure 6.It is observed that there is a increase in the diameter of capacitive loop, with the increased concentration of PVA, which indicate that the corrosion resistance of copper increases gradually[24]. And it also indicates that PVNd composites can protect copper electrode from being corroded. The decrease in corrosion current (I_{corr}.) and rate of corrosion values are mainly due to the decrease in the chloride ions attack on the copper surface, which causes the decrease in Cu dissolution by absorption of the inhibitor molecules. Table 2 shows that the value of R_{ct} increase with increase in PVA concentration in case of composites when compared with the blank. It reveals that the addition of polymer depress the charge transfer process, and decrease the rate of corrosion of copper [24]. The recorded impedance values increase with increase in PVA concentration indicating that the electrode surface gets more protection. Compared with the blank, the C_{dl} values tend to decrease significantly which indicates that the charge transfer process of the corrosion reaction in 3.5% NaCl is prevented effectively by forming the adsorption film on the surface of copper.

CONCLUSION

Polyvinyl alcohol (PVA) / Nd_2O_3 composites were prepared by sol gel method. The polymer composites were characterized using PXRD; FTIR and SEM. Copper corrosion in 3.5% NaCl solution has been studied by electrochemical methods (Impedance Spectroscopy and Polarization Curves). From the results, it reveals that the corrosion rate decreases with increase in the concentration of PVA. Tafel plots showed decrease in the corrosion current density Icorr for the composites when compared to the blank. The charge transfer resistance of the composites was higher than that of the blank, which indicates the presence of composite film blocks the electron transfer from the copper surface to the solution and accordingly protect the surface from corrosion.

Table-2: Impedance parameters of blank and PVNd composites

System studied	R_{ct} (Ohm cm^2)	C_{dl} (μF)
Blank	984	$2.583\text{x}10^{-2}$
PVNd 1	1732	$3.750\text{x}10^{-3}$

PVNd 2	2512	1.216x10^{-3}
PVNd 3	2615	0.944x10^{-3}
PVNd 4	3695	0.841x10^{-3}
PVNd 5	3871	0.545x10^{-3}
PVNd 6	35484	0.112x10^{-3}

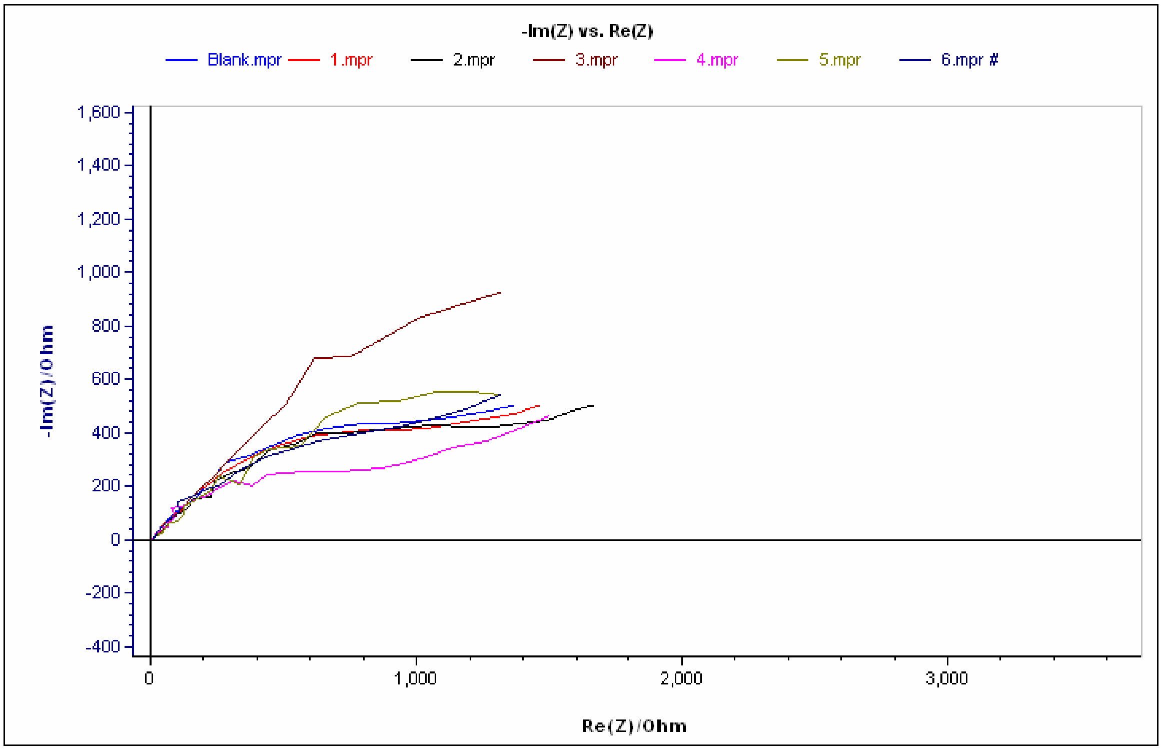


Fig.-6: Nyquist plots of blank and PVNd composites

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