CHITOSAN-BASED COATING FOR CORROSION PROTECTION OF COPPER

Abstract

Chitosan has attracted a lot of attention in many fields due to its characteristics and potential uses. This polymer is the target of an increasing number of articles and patents each year. Chitosan's application is limited in neutral and basic media due to its weak solubility. In this work, Chitosan/PVP based coatings were investigated for the protection of copper substrates in neutral media. The corrosion resistance of chitosan-based coatings is improved by introducing polyvinyl pyrrolidone (PVP) as binder. Coated and uncoated copper substrates were characterized before and after corrosion treatments by scanning electron microscopy, Fourier transform infrared spectroscopy. Coating on copper substrate was performed by spin coating technique. Potentiodynamic polarization measurements shows that the chitosan/PVP acts as a good inhibitor for corrosion. The investigated inhibitor has shown good inhibition efficiency in 3.5% NaCl solution.

Keywords: Copper; SEM; PVP; NaCl; FT-IR.

Authors

Beena Kumari K. S.
Department of Chemistry
All Saints' College
University of Kerala
Thiruvananthapuram, Kerala, India.
beenagireesh@yahoo.co.uk

Nayana Senan V.
Post Graduate & Research Department of Chemistry
Mahatma Gandhi College
Kesavadasapuram, Trivandrum
Kerala, India.

Lekshmy O.
Post Graduate & Research Department of Chemistry
Mahatma Gandhi College
Kesavadasapuram, Trivandrum
Kerala, India.

I. INTRODUCTION

The exceptional electrical and thermal conductivity properties, corrosion resistance, and mechanical workability, copper and copper alloys are widely used in piping, wiring, and cladding in the electrical, refrigeration, construction, petroleum refining, and transportation industries [1]. However, copper is prone to corrosion in hostile settings, particularly when corrosive species including oxygen, water, chloride, and sulphate ions are present. Sulphate-containing solutions are the most active corrosive species for anodic dissolution of copper. Polymers' durability and affordability as anticorrosive materials have generated a lot of interest. Polymers can effectively adsorb on the surface of metals due to their abundant adsorption sites (functional groups) that exhibit a strong anticorrosion activity. Numerous studies on various dissolution mechanisms have been carried out, and it is generally accepted that Cu(I) and Cu^{+} ions play a major role in copper's dissolution. The use of volatile organic compounds (VOC) or high pigment volume concentrations (PVC) in organic coatings poses environmental hazards [2]. The deacetylated form of chitin, chitosan (CS), has recently drawn increased attention in the field of aqueous and environmentally friendly coatings because chitin is a natural polysaccharide and an important part of the exoskeleton of crustaceans like crabs and prawns. Because of its sustainability, biodegradability, and chemical and pathogen resistance properties, chitosan is an excellent candidate for the creation of protective coatings. There are several alternative deposition processes available to generate thin films of molecule-based compounds on various surfaces. Polymer films are frequently produced using the spin coating process [3]. For the purpose of spreading the fluid using centrifugal force, a second polymer solution is poured on a substrate and is then typically rotated at 1000 to 5000 rpm. Later, the coating will thin as a result of solvent evaporation. This method is applied to the creation of CDs and electrical microchips. The final thickness can be significantly altered by even the smallest modification in the coating spin speed or solution concentration. In this approach, it is possible to manage and link the dynamics of film formation to the ultimate structure of the movie. The "greener" supercapacitor binders polyvinylidene difluoride (PVDF) and polytetrafluoroethylene (PTFE) are being replaced by polyvinylpyrrolidone (PVP). The fact that PVP is non-toxic and soluble in ethanol is one of its main benefits [4]. PVP can also be regarded as one of the top polymers used in the production of micro and ultra-filtration membranes due to its outstanding resistance to corrosion and wear, mechanical characteristics, film-forming qualities, and thermal stability. By delaying the diffusion of corrosive species through the coating and preventing the transfer of charge between nearby anodic and cathodic sites, chitosan coatings serve as a physical barrier and prevent corrosion. The focus of this work is on developing Chitosan/PVP coatings on copper substrate using the spin coating technique because of the significance of polymer-based coating.

II. MATERIALS AND METHODS

1. **Preparation of Copper Samples:** The working electrodes were prepared by the pure copper. The copper specimens were mechanically cut into 40 × 20× 2 mm dimensions, embedded in epoxy resin, and only $1cm^2$ was exposed to the electrolyte. The samples were abraded with a range of emery papers (800 to 3000 grade) before all the trials. The copper specimens were cleaned using an ultrasonic cleaner and ethanol and acetone, followed by room-temperature drying. Chitosan (Mol.wt. = 5000), with a 78% deacetylation content, was purchased from Sigma-Aldrich Co. Ltd. All other chemicals

and reagents used were of analytical grade. Sodium Chloride (3.5%) solutions was prepared by dilution of AR NaCl with deionized water.

2. **Coating of Copper Samples with Chitosan/PVP:** The polished copper substrates were dried and tested for corrosion studies. The chitosan and PVP were dissolved separately in ethanol. Each solution was spin-coated onto the copper surface and then dried at room temperature for 24 h. The dried samples were kept in desiccator for corrosion analysis.

3. **Electrochemical Measurements:** The experiment was performed in a typical three-compartment glass cell. The copper substrate, platinum electrode and saturated calomel electrode were used as the working electrode, counter electrode, and reference electrode respectively. The electrochemical tests were carried out at 30 ^{0}C with a CHI6041E electrochemical apparatus. With a scanning rate of 1 mV/S^{-1}, the cathodic and anodic Tafel curves were recorded with respect to the OCP value. All potentials are shown in mV (SCE).

4. **Surface Characterization:** The copper substrates were dipped for three days in 100 mL solution of 3.5% NaCl with and without chitosan/PVP coating. The scanning electron microscope (FEI Nova Nano SEM 450) was used to examine the surface morphologies of these copper specimens. The Perkin Elmer Spectrum 100 FTIR spectrophotometer was used to measure the FT-IR spectra in order to investigate more about how chitosan bonds to the surface of copper. The spectral range was from 4000 to 500 cm^{-1}. For comparison, FT-IR spectrum of the pure chitosan powder was obtained in the KBr pallets.

III. RESULTS AND DISCUSSION

1. FT-IR Spectra of Chitosan

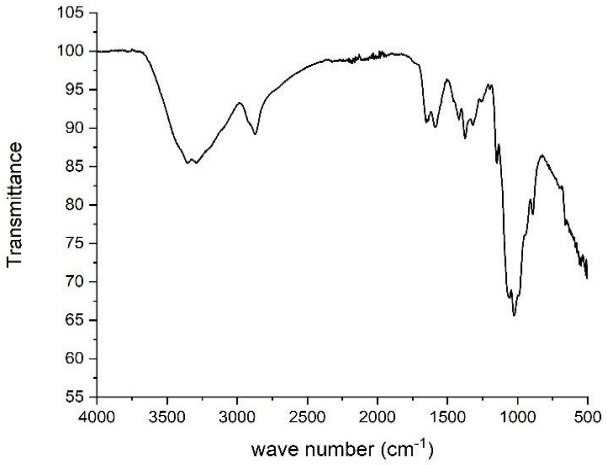

Figure 1: FT-IR Spectra of Chitosan

The N-H stretching of amines band may correspond to two minor overlapped peaks at 3354 and 3296 cm^{-1} in the chitosan spectrum, which has a broad O-H stretching band that emerges above 3500 to 3000 cm^{-1}. At 2868 cm^{-1}, the C-H stretching band may be seen. The symmetric methyl bending vibration was recorded at 1373 cm^{-1}, the N-H

bending vibration at 1575 cm^{-1}, the symmetric and asymmetric stretching vibrations of C-O at 1145 and 1025 cm^{-1}, respectively.

The coated copper surface was characterised by IR spectrum. All the bands were shifted and it confirms the coating on copper surface. The figure 2 shows the vibrational bands of coated copper surface.

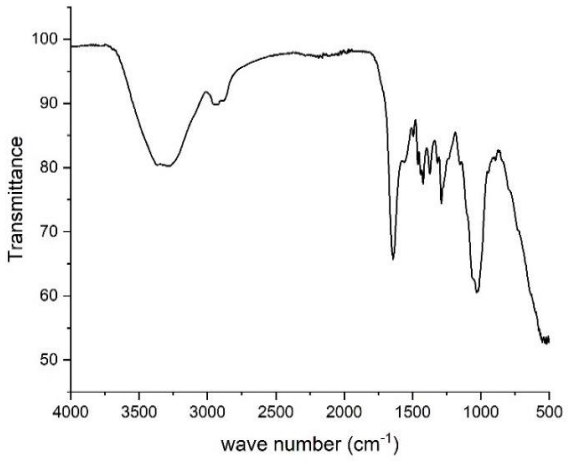

Figure 2: FT-IR Spectra of Coated Chitosan

2. **Potentiodynamic Polarization Study:** Tafel curves of copper electrode in 3.5% NaCl solution in the absence and presence of chitosan/PVP coating are shown in figure 3 which shows that the cathodic and anodic curves were different in the case of with and without coating. The E_{corr}, i_{corr}, η, βc and βa values, were obtained from Tafel curves. These parameters are given in Table 1. It was clear that the value of i_{corr} decreased substantially in the presence of coating [5]. This indicates the protective effect of coating on copper which reduced the anodic dissolution. The corrosion inhibition efficiency attained a maximum of 98%.

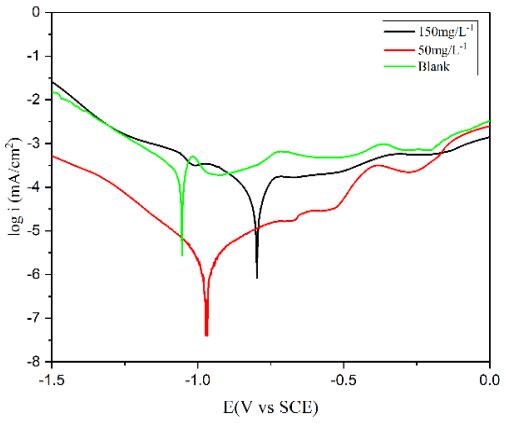

Figure 3: Tafel Plot of Coated and Uncoated Copper Surfaces at 30 ^{0}C in 3.5% Nacl Media

Table 1: Electrochemical Parameters from Polarization Study in 3.5% Nacl Solution with and without Coating

C (mg/L^{-1})	$-E_{corr}$ (mV)	i_{corr} (mA/cm^2)	β_a (mv/dec^{-1})	β_c (mV/dec^{-1})	Ŋ%
0	1046	0.182	239	212	-
50	1054	0.102	286	183	43
150	972	0.002	281	195	98

3. **SEM Analysis:** The surface study of copper after 3 days of immersion was analysed by scanning electron microscopy. The SEM micrographs of copper surface after 3 days of immersion in 3.5% NaCl in the absence and presence of chitosan/PVP coating are shown in figure 4. The figure 4 (a) is the polished copper sample before immersion, found smooth and showed some abrading scratches. Figure 4 (b) represents the damaged copper surface due to the corrosion after the 3 days immersion in 3.5% NaCl solution. SEM images of copper surface after 3 days of immersion in neutral solution with 150mg chitosan/PVP complex is shown in figure 4 (c). Figure 4 (c) shows the formation of protective coating in the surface. The cracking and pitting of copper surface reduced to a considerable extent in the presence of coating. From this it can be confirmed that the chitosan/PVP coating has better ability to act as an inhibitor for corrosion in 3.5% NaCl.

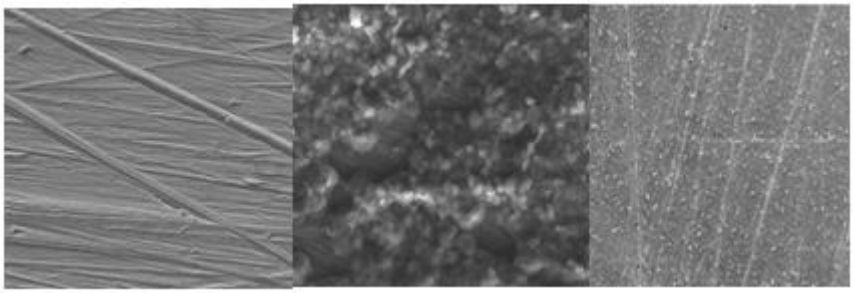

Figure 4: SEM Micrographs of (A) Polished Copper, (B) After Immersion without Coating (C) Coated with 150 Mg Chitosan/PVP in 3.5% Nacl

IV. CONCLUSION

Chitosan-based coatings with PVP effectively inhibit corrosion of copper substrates in 3.5% NaCl solution for 3 days making them promising for sustainable, long-lasting, and safe protection. The incorporation of PVP improves quality, anticorrosion properties, and removability, enhancing the coating's synergistic effect with corrosion inhibitors. The developed chitosan coatings with PVP are successful in the suppression of corrosion, according to the results of the image analysis used to quantify protective efficiency. All these revelations make chitosan-based coatings extremely promising for their use in the safe, long-lasting protection of copper in neutral media.

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