UNIVERSITI TEKNOLOGI MARA

ELECTRICAL AND BARRIER PROPERTIES OF MODIFIED POLYANILINE COATING FILMS AND ITS EFFECTS ON THE CORROSION PROTECTION OF MILD STEEL

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Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Applied Sciences

May 2017

AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

The study investigated the coating properties of polyaniline (PANI), polyaniline with nano silica (PANI nSi) and polyaniline with 3-amino silane modified nano silica (PANI 3-APS modified nano silica). Investigation were carried out on the effects of nano silica and amino-silane modified nano silica fillers on the structure, morphology and its influence on the electrical and ionic barrier properties of polyaniline. Fourier Transform Infrared (FTIR) showed the successful formation of PANI, PANI nSi and PANI 3-APS modified nano silica. Correlation between concentration of acid and fillers weight ratio with conductivity were studied. The electrical conductivity of all samples was determined using the bulk resistance value obtained from the Nyquist plot in the frequency range of 0.1 Hz to 100 MHz. PANI prepared in 0.1 M oxalic acid shows the highest room temperature electrical conductivity value of, 2.52 x 10^{-6} S cm^{-1}. The highest electrical conductivity of PANI nSi was 2.4 x10^{-4} S cm^{-1} for PANI containing 20%w/w nano silica fillers. For PANI 3-APS modified nano silica, PANI added with 20%w/w of 3-APS modified nano silica fillers exhibit the highest conductivity values which were 4.0 x10^{-6} S cm^{-1}. PANI, PANI nSi and PANI 3-APS modified nano silica with the optimum condition was selected for further characterization. The study also calculated the conductivity of all selected samples in wet condition. The transference numbers determined the conductivity behaviour of all chosen samples in dry and wet conditions. The transference numbers were calculated using Wagner's polarization method. The transference numbers determined in dry condition revealed that all samples behave as electronic conductor, however, when exposed to wet condition they exhibit as mixed conductor (electronic and ionic). PANI nSi shows the highest conductivity in dry and wet condition. The higher conductivity value is due to the ion-transporting abilities in PANI nSi. Addition of fillers had changed the morphology of polyaniline. Results from X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) support these findings. Thermal gravimetric analysis (TGA) reveals that PANI nSi was more stable compared to PANI and PANI 3-APS modified nano silica. Potential differences studies were further conducted to determine the barrier properties of PANI, PANI nSi and PANI 3-APS modified nano silica. PANI nSi shows the highest potential differences values which indicates the high possibility of the film to resist ions. The resistant measurement results also show that PANI nSi has the highest resistant values. pH measurement indicates that acid leached out from PANI, PANI nSi and PANI 3-APS modified nano silica. The determination of dielectric values of PANI, PANI nSi and PANI 3-APS modified nano silica assisted in understanding the properties of the coatings. Dielectric values at mid frequencies show that the addition of nano silica filler had maintained the dielectric values of PANI nSi. Dielectric results suggest that water diffusions and cations movement through the film had caused acid to leave the film. Potentiodynamic polarization experiment of coated and uncoated mild steel was conducted in 0.5 M hydrochloric acid and 0.5 M sulphuric acid solution further revealed that PANI nSi displays the best corrosion protection in both acidic media. The corrosion inhibition efficiency of PANI nSi is 81.6% in 0.5 M H_2SO_4 and 98.8% in 0.5 M HCl.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF RESEARCH

Corrosion occurs on the metal surface when there is a presence of water, oxygen or ions. Corrosion degrades metal by converting them into oxides or other corrosion products. Corrosion causes the reduction of metal mechanical strength which may lead to structure failure or breakdown. The concequences of corrosion often affect the industries involved in chemical processing, oil and gas and wastewater systems. Thus, the corrosion has to be controlled, as the destruction caused by it often involves expensive replacement processes.

Earlier works (Akbarinezhad et al., 2009; Armelin et al., 2008; Bierwagen, 1996; Funke, 1997; Grundmeier et al., 2000; Vogelsang et al., 1999) had proposed that an insulating polymer coating makes good coating for corrosion barrier protection. However, polymeric coatings are not perfect barriers as water, oxygen and ions can diffuse through it. The diffusion process will cause corrosion to occur beneath the organic coating of the metal interface. The electrolyte beneath the polymeric coating also leads to metal dissolution. Both of the processes contribute to the failure of the protective system.

Funke (1997) proposed that the integrity of polymeric coatings will decrease due to the diffusion of ions as well as corrosive agent such as water and oxygen. Arof et al., (1995) also agreed with Funke and revealed that salt disrupts the crystalline nature of polymer even in dry condition and convert them to amorphous. The amorphous nature will produce greater ionic conductivity. Therefore, the high ionic diffusion impedance nature of a protective coating is critical in determining the barrier performance of polymeric coatings used for corrosion protection of metals (Greenfield & Scantleburg, 2000). Incorporation of the polymeric coating with the pre-treatment coating such as polyaniline is supposed to improve the barrier properties of the coatings system. It has been reported that conductive polymers such as polyaniline when in used with a host polymer coating can impede the diffusion of ions from reaching the metal interface (Wang et al., 2007).