**UNIVERSITI TEKNOLOGI MARA**

# ELECTROCHEMICAL SYNTHESIZED OF SINGLE AND BILAYER COMPOSITE COATINGS OF POLYPYRROLE, POLYANILINE AND POLY(M-AMINOPHENOL) FOR CORROSION PROTECTION OF MILD STEEL

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Thesis submitted in fulfilment
of the requirements for the degree of
**Doctor of Philosophy**
**(Science)**

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# 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

In the present study, three single electro-oxidized coatings namely polypyrrole (PPy), polyaniline (PANI), poly(m-aminophenol) (PMAP) and two combined coatings of PPy/PMAP and PANI/PMAP were electrochemically synthesized by cyclic voltammetry on mild steel surface from its single monomer. The aim of this research is to investigate the effects of barrier protection provided by these coatings on mild steel substrates within the scope of its electrochemical impedance towards further oxidation of the base mild steel substrates. The developed coatings were characterized by Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM) and X-Ray Photoelectron Spectroscopy (XPS). The barrier resistance ability of these coatings towards corrosion of mild steel was determined in 0.5 M aqueous sodium chloride solution at various immersion times by the electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. All barrier properties were interpreted through impedance measurement using Nyquist, bode and phase angle plots. Equivalent electrical circuit models derived from the plots were employed to describe the coating barrier behaviour and performance. Oxidation peaks of PMAP, PPy and PANI coatings were observed at potential +1.0 V (Ag/AgCl), +0.67 V (Ag/AgCl) and +0.35 V (Ag/AgCl) respectively. While the oxidation peaks of combined PPy/PMAP and PANI/PMAP coatings were observed at potential regions of +0.8 V and +0.9 V respectively. In FTIR and XPS analyses, the presence of peak around 1082 $cm^{-1}$ and the binding energy for C (1s) recorded at 533.75 eV ascribed to C–O–C etheric linkage supported the formation of electro polymerized PMAP coating on mild steel surface. The formation of PPy coating on mild steel surface was verified by the presence of C–C bonds of the pyrrolic nuclei at 887 $cm^{-1}$ in FTIR analysis. XPS analysis further confirmed the presence of the C–C stretching at 284.81 eV which can be assigned to carbon atoms of the C–C bonds of a pyrrolic nuclei. The electro-oxidation of aniline is confirmed by detection of FTIR absorption peaks at 1565 $cm^{-1}$ and 1426 $cm^{-1}$ which ascribed to the emeraldine form of PANI, specifically to the absorption of the quinoid ring and benzenoid ring. These peaks were further confirmed by the detection of main carbon component (peak C 1s) due to aromatic carbon at 284.88 eV in XPS analysis. The most significant indications on polymerization of PPy/PMAP and PANI/PMAP coatings was the existence of C–O–C etheric bond that established by XPS and FTIR analyses. The presence of these C–O–C etheric bond in FTIR, was demonstrated by broad absorption band at 1092 $cm^{-1}$ for PPy/PMAP and at 1072 $cm^{-1}$ for PANI/PMAP. In XPS, the appearance of this bond was detected from deconvolution peak of O1s observed at 533.85 eV for PPy/PMAP film and 533.92 eV for PANI/PMAP film. EIS measurement revealed that, the combined PPy/PMAP as well as PANI/PMAP coatings shows an excellent barrier ability than single PPy, PANI and PMAP coatings during 24 h of immersion. PPy and PANI electrodeposited as first layer on mild steel surface provide barrier property by inducing the growth of oxide layer at coating/metal interface, hence impedes the penetrations of chloride ions towards metal surface. Meanwhile PMAP coating protects the mild steel through cathodic inhibition where the rate of cathodic reactions was reduced. The potentiodynamic polarization measurement results suggested that, both PPy/PMAP and PANI/PMAP combined coatings give better corrosion inhibition efficiency compared to single coatings. The corrosion inhibition efficiency of PPy/PMAP coating is 89.1% and PANI/PMAP is 88%.

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