Synthesis and characterisation of composite partially phosphorylated polyvinyl alcohol–aluminium phosphate as protective coating

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Partially phosphorylated polyvinyl alcohol–aluminium phosphate was synthesised through continuous stirring and condensation at 80°C. The compositions of the resulting phosphorylated polyvinyl alcohol–aluminium phosphate samples were varied, by adjusting the ion ratio and concentration of complex forming additives in the electrolyte solution. The as-synthesised phosphorylated polyvinyl alcohol–aluminium phosphate was then subjected to various chemical, thermal and structural characterisations. Fourier transform infrared studies show the bonding between phosphorylated polyvinyl alcohol and ALPO₄ at phosphate containing group. Differential scanning calorimetric studies show that T_g, T_m and degree of crystallinity increase as ALPO₄ filler was added to the system. Electrochemical impedance spectroscopy analysis shows good promising new inhibitor material for mild steel immersed in NaCl medium.

Keywords: Protective coating, Composite, Phosphate, Interfacial bonding, Thermal stability

Introduction

The developments in new polymer-inorganic composite materials with polyacid promise a wide application. Polyvinyl alcohol (PVA) modified with phosphoric acid (PA) is used as fire retardant materials,¹ electrolyte,² membrane,³ metal chelating,⁴ paper making,⁵ sensor,⁶ synthetic bone,⁷ nanoparticles/nanocomposite⁸ and anticorrosion coating.⁹ Polyvinyl alcohol has been reported as corrosion inhibitor for mild steel in 0.5 M H₂SO₄ with 30% of maximum efficiency.¹⁰ Polymer composite PVA-L-serine-coated mild steel is also reported giving 95% efficiency of 0.6% by weight.¹¹ Phosphorylated polyvinyl alcohol (PPVA) combined with PANI forms a nanoparticle coating, giving two mechanisms of protection: passive layer of Fe₂O₃ and iron-phosphate secondary complex.⁹ Meanwhile, aluminium phosphate (ALPO₄) is used as a new approach in organic coating. ALPO₄ explores an inhibition of corrosion of steel in 0.33 M H₃PO₄ and improves 84% efficiency at 10⁻² M of ALPO₄.¹² The purpose of this study is to enhance the adhesive between coating material (PPVA–ALPO₄) and mild steel. In this work, a polymer composite made of PPVA–ALPO₄ was synthesised and its inhibition effect on the corrosion behaviour of mild steel in 3.5% NaCl was investigated.

Methodology

Partially phosphorylated polyvinyl alcohol was obtained from a mixture of PVA (6.6 g), phosphoric acid (PA) (0.10–0.5 M) and deionised water (25 mL). Meanwhile, the refluxing process was conducted at 80°C with continuous stirring. Composite was prepared by adding ALPO₄ filler (1 and 2 wt-%) to PPVA with continuous stirring for 1 hour and then coated to mild steel (MS) by brush technique. Metals underwent the process of grinding, blasting and etching before coated with coating materials. Coated and uncoated samples were immersed in 3.5% of NaCl for 40 days. The chemical properties were analysed using a Perkin-Elmer System 2000 FTIR scan at 4 cm⁻¹ resolution in the range 4000 to 400 cm⁻¹. The thermal properties were recorded using Mettler Toledo thermogravimetric analysis/SDTA851 from 25 to 1000°C and using Perkin-Elmer DSC-7 at 20–350°C in air with heating rate of 10°C min⁻¹. Degree of crystallinity was calculated from the melting endothermic area, where ΔH is the enthalpy of fusion from DSC thermograms and ΔHₒ is the enthalpy of fusion for 100% crystalline PVA (ΔHₒ = 138.6 J g⁻¹).¹³ Corrosion was measured using electrochemical impedance spectroscopy (EIS) for MS specimens (5 cm x 4 cm x 1 mm) of equal composition. The tri-electrode system of EIS was used with working electrode, reference electrode and counter electrode.
platinum mesh counter-electrode and saturated calomel electrode as the reference electrode.

Results and discussion

Figure 1 shows the thermogravimetric analysis diagrams for all samples. Phosphorylated polyvinyl alcohol–aluminium phosphate samples have more weight residue compared to PPVA and PVA because of more cross-linking productions of diphasphate, triphosphate and reaction with ALPO₄. This results in more char formation, which remains unoxidised in the waste. Degradation process occurred after PVA was modified with PA and added with filler, and water evaporation started at 100°C.¹⁴ Meanwhile, the elimination of water and volatiles product, formation of di-phosphate and tri-phosphate,¹⁶ breaking of PPVA complex occurred in the temperature range of 120–190°C,¹⁷ which involve 35% of total weight loss. The spontaneous degradation of PPVA, PVA breakage backbone and degradation continued¹⁴ at 190–460°C. PVA starts to decompose at 460–700°C,¹⁸ and the residue oxidation occurred at 700–950°C.¹⁸ The char formation occurred at the final stage and leaves a residue remain unoxidised at temperature higher than 950°C.¹⁸

Figure 2 shows the DSC results for all samples. T_m of PVA decreases as PA added.² However, an increasing trend in T_g and T_m was observed for PPVA–ALPO₄ composite samples. Meanwhile, in samples F3C2, there is no trace of T_g recorded. T_g is shifted from 83 to 87°C since the Al³⁺ groups are substantially branched out with the PPVA molecules. Increase in T_g shows there are more crystalline phase in the composite. The composite PPVA–ALPO₄ becomes more crystalline compared to PPVA complexes.

Figure 3 shows the FTIR spectra of all samples. The characteristic peaks of PVA (F0) are OH, C–H, C=O, CH₂ and C–O–H.¹⁹ Meanwhile, the new characteristic peaks of PPVA are POH, P=O, C–O–P, overlapping of P–OH and vHPO₄²⁻, vHPO₄²⁻ and O–P–O. The missing of acetate group peak C=O, broadening of OH and reduce in intensity of C–H group proved the interaction of PV A and PA.¹⁹,²⁰ All phosphate groups in PPVA have reduced intensity of OH, and C–H peak proved interaction of PPVA and ALPO₄. Interaction at PO–H bands (2355–2328 cm⁻¹), C–O–P bands (1230, 1196,
1166 cm$^{-1}$), overlapping of C–O–P and P–O (930–970 cm$^{-1}$) and O–P–O bands (603, 565 cm$^{-1}$) showed phosphate bonding reacted with aluminium content.$^{21}$ Peak for O–P–O bonding shows a decrease in intensity and more broaden as more ALPO$_4$ is added.

Figure 4 shows the value of coating resistances and capacitances calculated from Nyquist plot for coated and uncoated mild steel with PVA, PPVA and PPVA–ALPO$_4$. Coating of mild steel with PPVA–ALPO$_4$ was untreated and treated at 40°C. Coating resistance of untreated mild steel increases as coated with PVA. PVA is a well-known coating material that can provide protection surface on mild steel.$^{11}$ Meanwhile, coating resistance of coated mild steel with PPVA is exposing mild steel with free moving ions that lead to less coating resistance. However, introducing ALPO$_4$ limited the activity of free ion, prevented leach out phenomenon in PPVA electrolyte and provided more stable phosphate ion that can bind on the mild steel surface. Heat treatments produced better interaction between PPVA–ALPO$_4$ and mild steel. As a result, coating resistance increased to $5 \times 10^5$ Ω. Figure 4 shows an increase of coating resistance with decrease of coating capacitance. This proved that the corrosion decreased. The calculated corrosion inhibitor efficiency (IE) for sample MS4 is 99.85% higher compared to 30%$^{10}$ and 95%$^{11}$ using PVA and composite PVA–l-serine, respectively.

**Conclusion**

Polyvinyl alcohol that reacted with phosphoric acid is successfully synthesised and consists of both covalent bonding and hydrogen bonding. Amount of phosphoric acid and water content influence bonding in the phosphorylated polyvinyl alcohol complexes. Excessive phosphoric acid will lead to more hydrogen bonding form, more plasticisation effect and later on lead to
dehydration. The plasticisation effect of phosphorylated polyvinyl alcohol complexes are contributed not only from acid but also from water. The processing time and temperature also influence the behaviour of complexes to behave as hydrophilic or hydrophobic. Introduction of aluminium phosphate promise better composite coating properties. From thermal and structural studies, it can be concluded that phosphorylated polyvinyl alcohol and aluminium phosphate are having interaction. Studies on composite of phosphorylated polyvinyl alcohol–aluminium phosphate as coating material on mild steel proved to be good inhibitor for mild steel after treating at 40°C.

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