Dopant Anion Effects in the Inhibition by Polyaniline of Corrosion-Driven Organic Coating Delamination on Iron

H.N. McMurray, G. Williams and Andreas Gabriel
Materials Research Centre, School of Engineering,
University of Wales Swansea, Singleton Park
Swansea, SA2 8PP, U.K.

In recent years the ability of polyaniline (PAni), to protect carbon steel from corrosion in severe marine (chloride rich) environments has attracted significant attention.[1] However, the mechanisms involved are still incompletely understood, as are the requirements for effective coating formulation.[1] Here we have sought to compare PAni emeraldine base (PAni-EB) with the PAni-phenylphosphonate (PAni-PP) and PAni-paratoluenesulphonate (PAni-PTS) emeraldine salts as inhibitors of corrosion-driven coating delamination (cathodic disbondment) on pure iron. In so doing, we have used a scanning Kelvinprobe (SKP) to follow delamination kinetics and to determine the effect of PAni on substrate potentials.[2] We have also used depth-profiling secondary ion mass spectrometry (SIMS) to follow the growth of PAni-induced oxide films at the coating-iron interface.

PAni-EB was obtained from Aldrich and used as supplied. PAni-PTS and PAni-PP were prepared from PAni-EB by reaction with an excess of the conjugate acid followed by washing and drying in air. Polyvinylbutyral (PVB) coatings containing a PAni volume fraction (ϕ) of between zero and 0.3 were solution-cast onto 99.999% pure iron to give a dry film-thickness of 30μm. Oxide growth studies and coating delamination studies were all carried out at 20°C and a relative humidity of 93-95%. SIMS depth profiles were obtained after coatings were mechanically striped (peeled) from the substrate surface and calibrated by periodically measuring the sputtered crater depth (D) using AFM. Oxide layer thickness was estimated as D_{50}, ie the depth over which the O^{2-} ion current fell to half its initial value. In delamination studies a corrosion cell was established by placing a 0.86 mol dm^{-3} NaCl (aq) solution onto a penetrative coating defect and progress of the delamination front followed using SKP.[2]

For PVB/PAni-EB coatings, potentials (E_{intact}) measured over the intact coating remained constant at ca 0.2 V vs. SHE as ϕ was increased from zero to 0.3. For all ϕ the interfacial oxide film thickness was found to be time-independent, with D_{50} = ca 50nm. Coating delamination kinetics were parabolic, ie delamination distance increased with the square root of time in a fashion consistent with under-film cation migration being the rate determining step. Furthermore, the parabolic rate constant was found to be independent of ϕ at ca 0.5 mm min$^{-1/2}$. It would therefore appear that PAni-EB is effectively inert and does not exert any influence on the kinetics or mechanism of coating disbondment

For PVB/PAni-PP and PVB/PAni-PTS coatings E_{intact} increased with ϕ, reaching a maximum of ca 0.55V (in the case of PAni-PTS) when ϕ = 0.25 - 0.3. Furthermore, E_{intact} was found to be reversibly dependent on atmospheric pO_2, suggesting that PAni re-oxidation (by O_2) is responsible for maintaining the PAni potential. In the case of PAni-PTS D_{50} values increased linearly with time, as seen in curve (i) of fig 1. Conversely, for

PAni-PP D_{50} values became constant at ca 150nm after 20 hours, as seen in curve (ii) of fig 1. It would therefore appear that the iron surface is not passive, or only weakly so, in contact with PVB/PAni-PTS but strongly passive in contact with PVB/PAni-PP. Progressively increasing ϕ was found to decrease rates of coating delamination, although red rust was still observed in the defect region and defect E_{corr} values fell to -0.4V. Fig. 2 shows defect-delamination distance vs time plots for various values of ϕ PAni-PP. The ϕ = 0 curve is parabolic but curves become linear and decrease in slope as ϕ increases. Delamination was found to cease when $\phi \geq 0.25$. Similar results were obtained using PAni-PTS, except that delamination rates remained non-zero even when ϕ = 0.25. These findings are consistent with cathodic O_2 reduction rates at the iron-coating interface being suppressed through PAni-mediated increases in E_{intact}. However, the nature of the interfacial oxide film (as influenced by the dopant anion) also appears to exert a significant influence at higher ϕ.
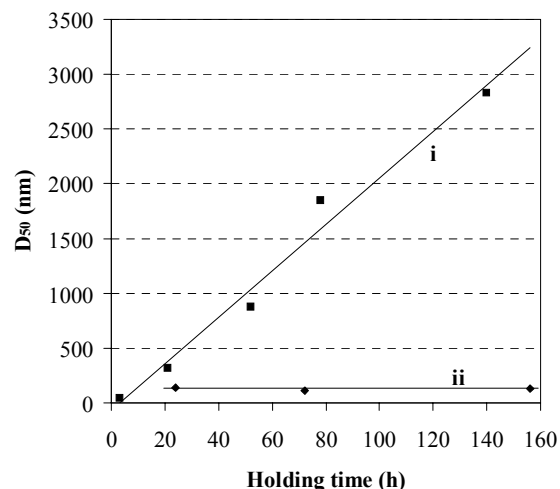

Figure 1: Oxide film thickness (D_{50}) vs. holding time for PVB/PAni-ES (ϕ_{pa} = 0.3) coated iron held at 20°C and 93% rh. Curve (i) PAni-PTS and curve (ii) PAni-PP
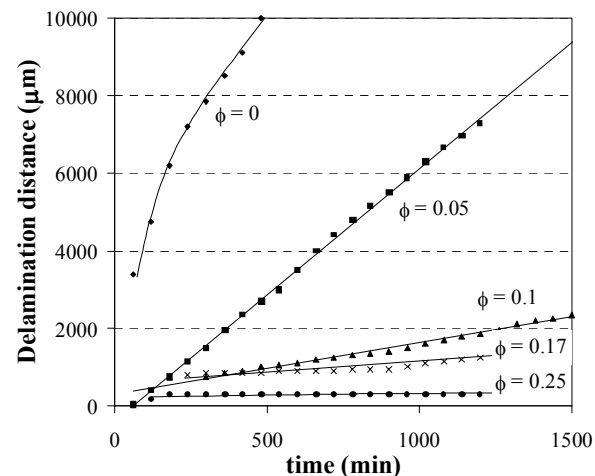

Figure 2: Plots of delamination distance vs. time for PVB/PAni-PP on iron.

References

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