

## Polyaniline Based Acrylic Blends for Iron Corrosion Protection

Solange de Souza and Roberto M. Torresi

Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970 São Carlos (SP), Brazil

José E. Pereira da Silva, Susana I. Córdoba de Torresi, and Marcia L. A. Temperini

Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo, Brazil

The use of intrinsically electronic conducting polymers (ICPs) for corrosion protection was reported by Mengoli et al. [1] in 1981 and in 1985 by D. DeBerry [2] using electrodeposited polyaniline (PANI) for steel corrosion protection in strong acid media. After that, researchers have devoted great attention to the corrosion protective character of ICPs and an increasing number of papers have been published about corrosion protection of different metals and alloys [3-8]. The most used form to obtain protective layers was electrochemical polymerization; but these layers are not very effective and after few days the dissolution of the metals is the main process [9]. Other strategy was the use of ICPs forming epoxy or acrylic blends [10]. Both cases present interesting results and it has been postulated that the ICPs stabilizes the potential of the metals in the passive regime by forming a protective layer [10]. Acrylic blends formed by PANI and poly(methyl metacrylate) (PMMA) were prepared and characterized by Heeger and co-workers [11]. This paper describes the protective behavior of this acrylic blend on iron electrode. Raman and FTIR spectroscopies were used to identify the redox behavior of PANI and the formation of the dopant complex passivation layer, in order to clarify and to provide experimental evidence for the mechanism of corrosion protection for metals that can be oxidized by an ICPs layer. It is also shown the reduction of the PANI-PMMA layer during the open circuit experiments in aggressive solutions. The characterization of the insoluble iron-dopant salt is also reported.

Electrochemical experiments were performed in a conventional three electrodes Pyrex<sup>®</sup> cell using Fe rods (Goodfellow, 99.99%,  $\phi=0.5$  cm) as working electrodes, a platinum sheet as counter electrode and all potentials were referred to the saturated calomel electrode (SCE). All experiments were performed at room temperature and all chemical used were A.R degree. Polyaniline (PANI) blends were prepared following the procedure already described in the literature [12]. Electrochemical measurements were made using a FAC 2001 potentiostat/galvanostat. Raman Spectroscopy was used to follow the oxidation changes in the system by the utilization of a Renishaw Raman Imaging Microscope System 3000 with an Olympus metallurgical microscope, a CCD detector and a He-Ne laser ( $\lambda_0 = 632.8$  nm, Spectra Physics mod.127) as the exciting radiation. FTIR spectroscopic measurements were made using a Bomem MB-102 spectrometer.

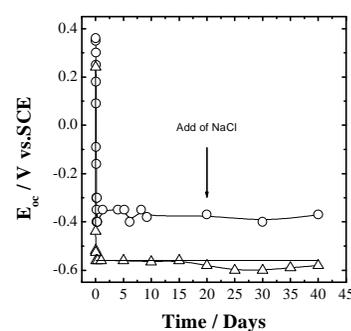
Figure 1 shows the open circuit potential ( $E_{oc}$ ) as a function of time for two different electrodes: Fe/PMMA (open triangles) and Fe/PMMA-20% PANI-CSA (open circles) in  $1.0 \text{ molL}^{-1} \text{ H}_2\text{SO}_4$  solution. The open circuit potential of a naked iron electrode is also shown in the figure for comparison (solid line at  $-0.56\text{V}$ ). The protective character of the conductive coating is clearly shown in the figure by the stabilization of potential at *ca.*

$-0.38\text{V}$  during 30 days, even after the addition of a corrosive  $0.1 \text{ molL}^{-1} \text{ NaCl}$  solution to the electrolytic bath. The relevant role played by the conductive phase (PANI-CSA) in the blend is also demonstrated in the figure by considering the curve obtained with the Fe/PMMA interface that, after few hours in acidic media, the potential evolves to the value corresponding to iron dissolution.

This paper shows the high protective behavior of acrylic blends for iron corrosion, decreasing the current in at least three orders of magnitude for NaCl solutions. Nevertheless, the attained open circuit potential is not so far from the corrosion potential of iron, the presence of PANI in the blend enhances the protective character of the coating. Raman and FTIR spectroscopies clearly show the formation of a camphosulfonate – iron complex as a second protective layer that passivates the electrode.

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**Figure 1** – Open circuit potential as a function of time for (—) naked iron electrode, ( $\Delta$ ) Fe/PMMA electrode, and ( $\circ$ ) Fe/PMMA-PANI-CSA electrode in  $1.0 \text{ molL}^{-1} \text{ H}_2\text{SO}_4$  electrolytic solution. After 20 days,  $0.1 \text{ molL}^{-1} \text{ NaCl}$  solution was added.