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Corrosion Science 47 (2005) 811–822
CORROSION SCIENCE
www.elsevier.com/locate/corsci

Polyaniline acrylic coatings for corrosion inhibition: the role played by counter-ions

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Available online 13 August 2004

Abstract

The interest in providing new corrosion protection systems for different metals and metal alloys is related to restrictions to the use of chromium (VI) compounds owing to their environmental problems. This work presents the electrochemical behavior of a polymeric blend formed by camphorsulphonate or phenylphosphonate-doped polyaniline (PANI) and poly-(methyl methacrylate) used for iron corrosion protection in sulphuric acid solutions with or without chloride ions. Results indicate that these blends act by a two-step protection mechanism. First, a redox reaction between Fe and PANI takes place leading to PANI reduction and concomitant anion release. Then, iron cations form a passivating complex with the PANI doping anion (camphorsulphonate or phenylphosphonate) that simultaneously acts as a second physical barrier to avoid penetration of aggressive ions. So, considering these processes, it is possible to conclude that PANI is an anion reservoir, which can release anions in a smart way when damage is produced on the surface of the coating.

Keywords: Active corrosion protection; Polyaniline; Acrylic blends; Iron

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doi:10.1016/j.corsci.2004.07.014

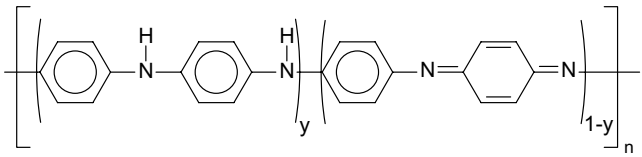
1. Introduction

Several papers have been published about corrosion protection by using conducting polymers on different metals and alloys: aluminum and aluminum alloys [1–5], mild steel [6–11], stainless steel [12,13], iron [14–18], copper [19], and other metals [20,21]. The use of intrinsically conducting polymers (ICPs) in epoxy or acrylic blends [22–24] to give smart coatings is also a new strategy for corrosion protection [25–28]. Kinlen et al. [25,28] have provided direct information about the redox processes occurring in the polymeric layer by the scanning reference electrode technique (SRET), and Souza et al. [29] have obtained information not only about the redox processes between the conducting polymer and iron, but also about the formation of a second protective layer at the polymer/metal interface involving the participation of the dopant-anion of the polymer.

This paper describes the protective behavior of polyaniline (PANI) acrylic blends on iron electrodes aiming to demonstrate the actual role played by the anion in the corrosion mechanism. Two dopants (camphorsulphonate and phenylphosphonate anions) with different passivating characters were investigated. As phosphonate salts are widely used for corrosion protection in aqueous systems [25], phenylphosphonate anion seems a good candidate to compare with camphorsulphonate anions, which were already described [29]. Raman spectroscopy, open circuit potential and cyclic voltammetry measurements were used to identify the redox behavior of PANI and the formation of the dopant complex passivating layer which produces a very significant inhibition of the corrosion rate. These techniques were also combined in order to clarify and to provide experimental evidence for the corrosion mechanism.

2. Experimental

PANI (Scheme 1) blends were prepared following the procedure already described in the literature [30,31]. PANI was obtained by oxidative polymerization of distilled aniline (Aldrich) in 1.0 $mol l^{-1}$ HCl aqueous solution using ammonium peroxydisulphate (Merck) as oxidant. The powder obtained was filtered and washed with purified water (UHQ Elga System) and dedoped in a 1.0 $mol l^{-1}$ NH_4OH solution. After the dedoping procedure, PANI powder was filtered and dried at room temperature in a vacuum oven. The material was doped again by placing it in an aqueous 1.0 $mol l^{-1}$ camphorsulphonic acid (HCSA) (Aldrich) (Scheme 2) or in a solution prepared by



Scheme 1. Polyaniline.