Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 29 Oct 2010

To cite this article: Alvaro Meneguzzi, Minh Chau Pham & Carlos Arthur Ferreira (2002): Electrosynthesis of a Double Layered Intrinsically Conducting Polymer Composite on Iron Substrates, Molecular Crystals and Liquid Crystals, 374:1, 583-588

To link to this article: http://dx.doi.org/10.1080/10587250210464

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 583-588

1058-725X/02 $12.00 + .00

Electrosynthesis of a Double Layered Intrinsically Conducting Polymer Composite on Iron Substrates

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To increase the corrosion resistance of an iron substrate, conducting polymers were electrochemically synthesised from a solution containing 1,5-diaminonaphthalene and aniline. MIRFTIRS, AFM and electrochemical characterisation indicated the formation of a two layers composite polymer. The first layer, of poly(1,5-diaminonaphthalene) was compact, homogeneous, thin and adherent to the substrate and the top layer, of polyaniline, was thick and fibrous.

Keywords Conducting Polymers; Composite; Polyaniline; Poly(1,5-diaminonaphthalene).

INTRODUCTION

The use of Intrinsically Conducting Polymers (ICP) for the protection of metals, was demonstrated for the first time in 1985 by De Berry [1]. He electrosynthesized polyaniline (PAni) on to SS 430 stainless steel to increase its corrosion protection and has found that the protection mechanism is an anodic passivation. MacDiarmid *et al* [2], obtained the same protection of SS 430 stainless steel using a film of chemically synthesised PAni and considered the mechanism of protection as an anodic passivation.

In a previous work [3], during electropolymerization of a new ICP, poly(1,5-diaminonaphthalene) (PDAN-1,5) in acidic aqueous medium on mild steel, was obtained a compact, homogeneous, low conductivity, very adherent to the surface but very thin film (approximately 0.1 μm). Conversely, it is well know that polyaniline films can be easily growth on inert electrodes, and they are conducting, thick, heterogeneous, but porous and poorly adherent to the substrate. In this work, a copolymerization of DAN-1,5 and aniline was tried, aiming to obtain a material presenting a mixture of the two polymers properties.

EXPERIMENTAL

1,5-Diaminonaphthalene was of 97% purity from Aldrich. Aniline was previously distilled under N_2. The electrochemical studies were carried out in a three-electrode cell. Two different shapes were used for the working electrode, rods or plates made of 99,99% iron from Goodfellow. The reference electrode was a saturated calomel electrode. For *in situ* multiple intern reflection Fourier transform infrared spectroscopy (MIRFTIRS) was utilised a ZnSe crystal coated with an alternate Pt strip by sputtering.

RESULTS AND DISCUSSION

To obtain a film with protective property and the desired characteristics such as homogeneity, compactness, adherence, high conductivity and good thickness, PDAN 1.5 and PAni were electrosynthesised on to iron substrate from acid solution.

Comparing the voltammograms obtained from PDAN – 1.5 and PAni synthesised individually with the voltammogram from the system containing both monomers, the later is the sum of the two former showing redox system located in typical values for both polymers analysed individually [7] suggesting the formation of a composite instead of a copolymer.

In the first stage of the synthesis and in presence of both monomers, the voltamogram showed very similar to the voltamogram obtained when only one monomer, DAN-1.5, was present. This result confirms the formation of a composite layered film. It also was observed that the interface polymer–metal is predominantly PDAN-1.5 and the second layer is formed mainly by PAni.

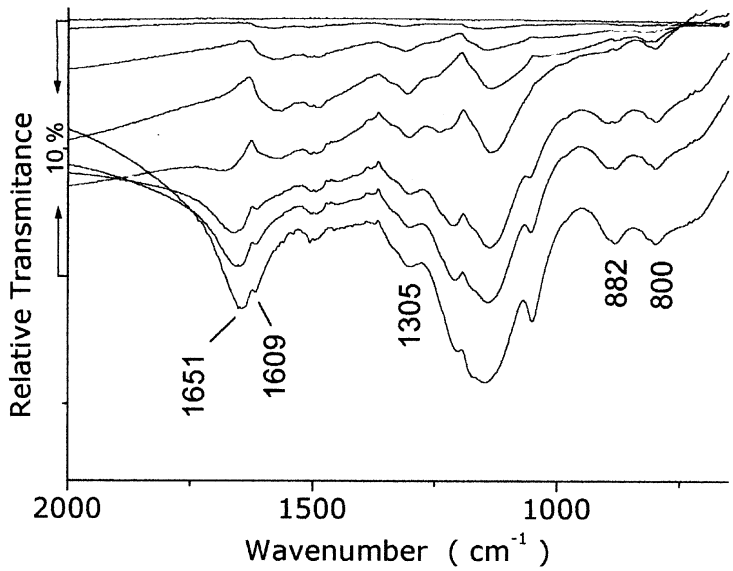

FIGURE 1 *In situ* MIRFTIRS spectra recorded during polymer film growth by CV (between 0 and 0.9V) in 2 M H_2SO_4 + 10^{-3} M 1,5-DAN + 5.10^{-2} M aniline. Each spectrum was obtained before a potential cycle.

In situ FTIR spectra (Figure 1) obtained by multiple internal reflection (MIRFTIRS) according to the technique developed by Pham *et al* [6], where IR radiation is incident on the internal layer of the film formed on a modified prism, are similar to PDAN-1, 5 spectra [7,8,9]. On the other hand, *ex situ* external reflection FTIR spectra corresponds to PAni spectra [8,9]

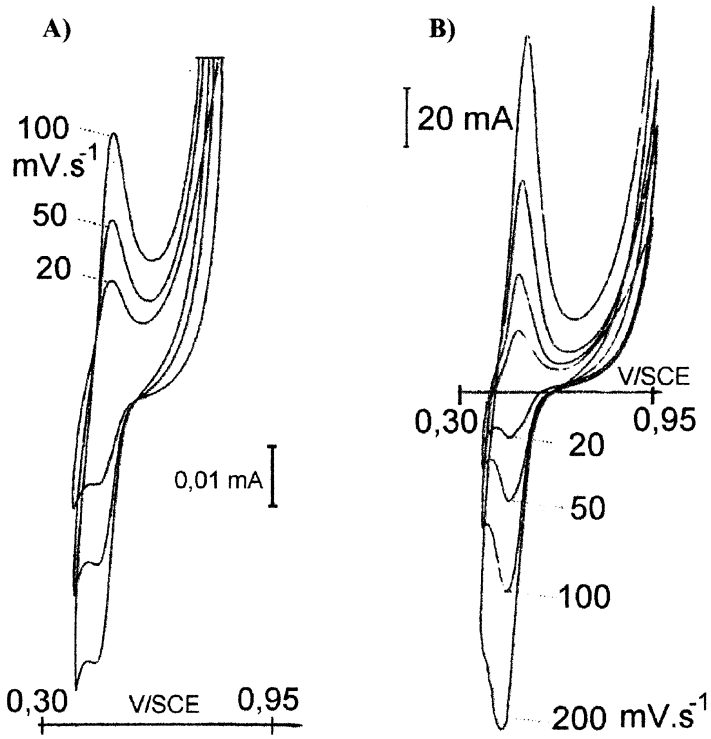

FIGURE 2 CV response of an A) PDAN-1,5; B) PDAN-1,5/PAni for 10 minutes synthesis of films-coated Fe electrodes at different scan rates in 2M H_2SO_4.

Electrochemical behaviour of PDAN-1,5/PAni composite after 10 minutes of cycling in H_2SO_4 2M (Figure 2 A) is easily related to a PDAN-1,5 cycled in the same medium (Figure 2 B).

SEM image of PDAN-1,5/PAni obtained after 15 minutes of synthesis on Fe electrodes (Figure 3A) displayed a morphology similar to PDAN-1,5 alone and the beginning of a fibrous composite formation on the first layer. After 60 minutes, the film morphology is similar to PAni obtained in this medium (Figure 3B).

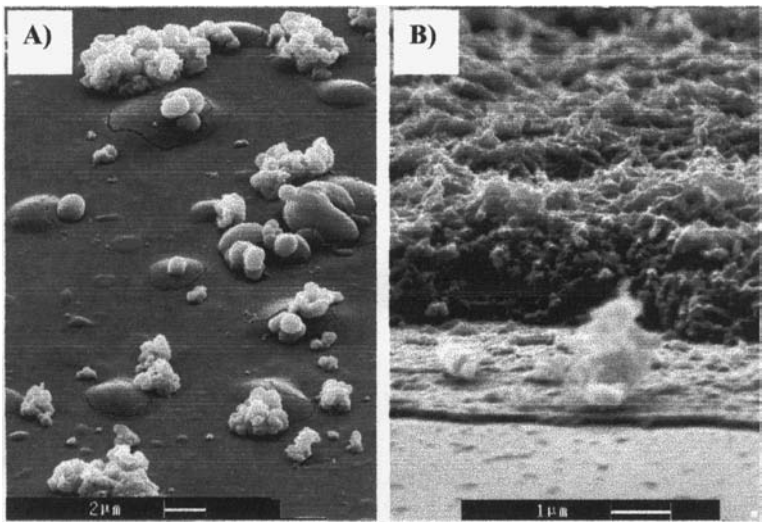

FIGURE 3 SEM image of electrochemically formed PDAN-1,5/PAni composite in 2 M H_2SO_4 a) short formation time, b) long formation time.

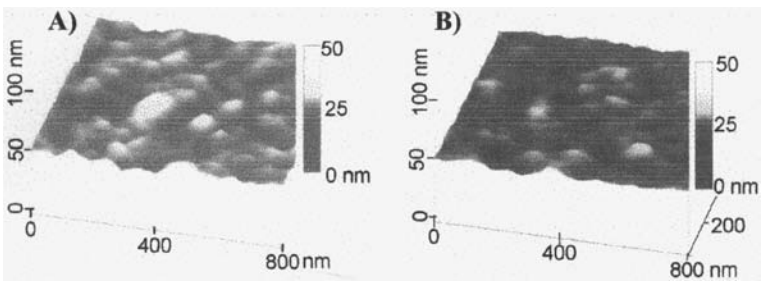

FIGURE 4 AFM image of an electrochemically formed composite PDAN-1,5/PAni in 2 M H_2SO_4. A) initial time, B) longer time.

In a similar way, AFM images of a PDAN-1,5 (Figure 4A) film and PDAN-1,5/PAni composite film (Figure 4A) synthesised on Fe electrode after 10 minutes of cycling show a very similar morphology.

CONCLUSION

These results confirm that the electrosynthesis of a film on Fe electrodes from a solution containing 10^{-3} M DAN-1,5 + 5.10^{-2} M aniline in a 2M H_2SO_4 medium leads to the formation of a multilayered composite film whose first layer is PDAN-1,5 and the second layer is PAni. This configuration is in opposition to the expectation of obtaining a copolymer under the conditions of this work.

ACKNOWLEDGEMENT

Authors are grateful to CAPES-COFECUB international program (184/96).

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