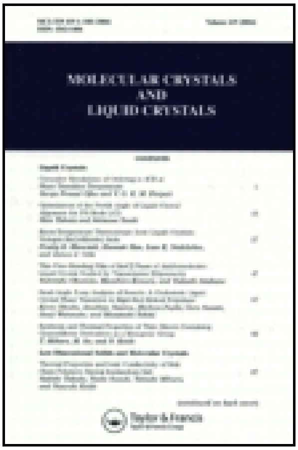

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

PAni-CMC: Preparation, Characterization and Application to Corrosion Protection

S. R. Moraes [a] & A. J. Motheo [a]
[a] Departamento de Físico-Química, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, (SP), Brazil

To cite this article: S. R. Moraes & A. J. Motheo (2006): PAni-CMC: Preparation, Characterization and Application to Corrosion Protection, Molecular Crystals and Liquid Crystals, 448:1, 261/[863]-267/[869]

To link to this article: http://dx.doi.org/10.1080/15421400500403341

Mol. Cryst. Liq. Cryst., Vol. 448, pp. 261/[863]–267/[869], 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500403341

PAni-CMC: Preparation, Characterization and Application to Corrosion Protection

S. R. Moraes
A. J. Motheo
Departamento de Físico-Química, Instituto de Química de São Carlos,
Universidade de São Paulo, São Carlos (SP), Brazil

By using cyclic voltammetry composites of polyaniline and carboxymethylcellulose were synthesized on AISI 304 from a 1M H_3PO_4 aqueous solution containing 0.2M aniline and CMC varying from 0.1 to 1% wt. The characterization was performed by different techniques and it was possible to observe that increasing the CMC content, a more packed structure is promoted, compared to the granular structure of PAni films. The evaluation of the composites to protect the substrate against corrosion showed that in doped and undoped states the composites present effective corrosion protection of AISI-304 and that the composition of the films changes after corrosion tests.

Keywords: carboxymethylcellulose; composite; corrosion; polyaniline

INTRODUCTION

The electrochemical preparation of composites using conducting polymers, in particular polyaniline (PAni), has led to a new class of multicomponent materials and also the development of different techniques to deposit them. The most common preparation methods include solution blending, melt blending and dispersion mixing, each one with their own limitations. There is a large number of polymeric matrixes described in the literature, including polyvinyl chloride [1], polystyrene [2,3] and carboxymethylcellulose (CMC) [4,5]. Composites of conducting polymers with insulating polymers can lead to materials with good mechanical and electrical properties. One of the applications

---

The authors wish to thank CNPq and CAPES, Brazil, for financial support.

Address correspondence to A. J. Motheo, Departamento de Físico-Química, Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, CEP 13560-970, São Carlos (SP) Brazil. E-mail: artur@iqsc.usp.br

of conducting polymers and their composites is the protection against corrosion [6–8] however, it is important to stress that the corrosion protection characteristics of polymeric films depend on many parameters such as, the adhesion on the surface, synthesis conditions and film thickness. One example is that the use of orthophosphoric acid as electrolyte in the electrodeposition of PAni on metallic substrates, due to the interaction of the anion with the metal, promotes the phosphatization of the surface simultaneously with the polymer deposition, making the corrosion protection more effective [9,10]. Herrasti *et al.* [11] used polypyrrole (Ppy) and Ppy/CMC to prevent corrosion of steel using films electrochemically synthesized from aqueous solutions that contained 0.1 M $LiClO_4$, 0.1 M CMC and 0.25 M pyrrole. The results showed that Ppy-CMC is a better than polypyrrole (Ppy) for corrosion protection mainly due to more compact structure of the Ppy-CMC composites. So, in this work the optimized conditions of the electropolymerization of the PAni-CMC composites on stainless steel (AISI-304), from aqueous phosphoric acid solutions, using cyclic voltammetry are presented, together with the evaluation of their degree of corrosion protection.

EXPERIMENTAL

Stainless steel coupons (AISI-304) of 1 cm^2 were used as working electrodes. After mechanical polishing with emery paper (320 to 1200 grades), degreasing in ethanol and drying at 40°C, the electropolymerization of PAni was performed using a potentiostat/galvanostat (EG&G/PARC mod. 273 A). The process consisted of 20 cyclic voltammograms (CV) at 50 $mV\,s^{-1}$ in a one-compartment electrochemical cell containing the electrolyte solution with aniline (0.1 to 0.5 M), 1 M H_3PO_4 and the sodium salt carboxymethylcellulose (NaCMC) (0.1 to 1% wt.). The potential ranges were empirically determined as: i) -0.2 to $+1.4$ V in the first cycle; ii) -0.2 to $+1.2$ V during the following cycles. The counter electrode was a platinum foil (2 cm × 2 cm) and the reference was a commercially obtained saturated calomel electrode (SCE). The corrosion measurements were performed using a potentiostat/galvanostat (EG&G/PARC mod. 273 A). The corrosion studies were performed by measuring the potentiodynamic polarization curves in 3% NaCl aqueous solution at 0.5 $mV\,s^{-1}$ and 25°C. Scanning Electronic Microscopy (SEM) and EDAX were used to visualize the morphology and to determine the composition, respectively. The EDAX analyses were performed in duplicate at two random points on surface of the sample. The composites PAni-CMC were also analyzed by FTIR spectroscopy using a Bomem FTIR MB-102 and KBr pellets.

RESULTS AND DISCUSSION

It is possible to observe from Figures 1(a) and 1(b) that the cyclic voltammograms of stainless steel in a solution of 1.0 M H_3PO_4 contained CMC exhibit the oxidation peaks characteristic of PAni. In first cycle (Fig. 1(a)) can be observed one peak around 1.2 V attributed to oxidation of both monomer and CMC molecule in medium. The CV profiles change completely up to 20th cycle as exemplified in Figure 1(b). The comparison between the PAni-CMC and PAni profiles indicates that they are similar to PAni electrodeposited on platinum in acidic media. This is an interesting point because it indicates that there is the possibility of the electron transfer occurring between the metallic alloy, polyaniline and the polyelectrolyte (CMC), mediated by a thin oxide film.

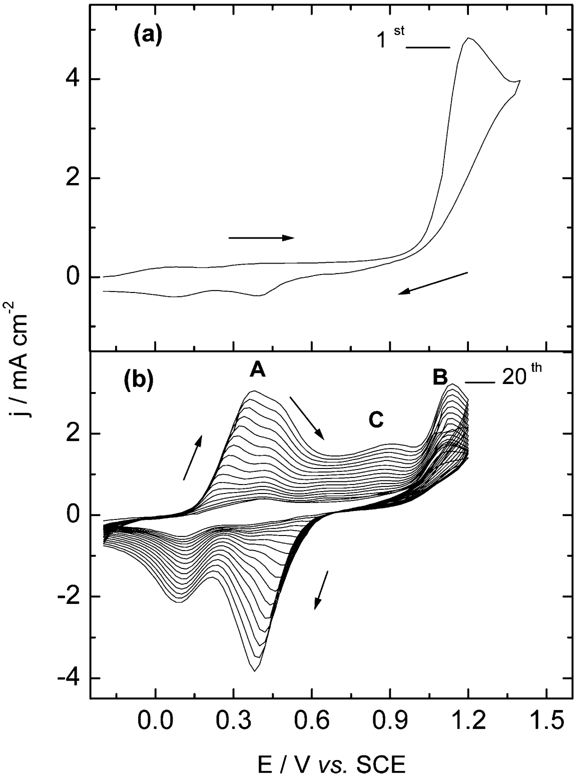

FIGURE 1 Growth voltammograms of PAni-CMC obtained from 1.0 M H_3PO_4 solution containing 0.2 mol L^{-1} aniline and 0.1% CMC. v = 50 mV s^{-1}. (a) first cycle and (b) up to 20th cycle.

The infrared spectra of CMC and PAni-CMC composite containing 0.1 and 1% wt in its doped and undoped states is presented in Figure 2. The main vibrational modes that characterize the presence of CMC are given by the peaks at around 2855 and 2926 cm^{-1} (C–H stretching) and by the peaks at around 1774 cm^{-1}, which correspond to C=O in the CMC structure [12]. Some peaks related to CMC and PAni overlap, which makes it difficult to isolate the effect of CMC in the blend.

Due to the overlaps, the spectrum of PAni-CMC electrodeposited on steel is very similar to PAni itself. The main vibrational modes of PAni are: at 3200–3400 cm^{-1} (N–H stretch of aromatic amine); 1570 and 1483 cm^{-1} (nitrogen quinone (Q) and benzoid ring (B)); at 1301 cm^{-1} (C–N stretch of secondary aromatic amine); at 810 cm^{-1} (out of-plane bending of aromatic C–H). The lack of CMC C=O bonds could be due to interaction with the Fe of the steel substrate. The peak attributed to the N–H stretching vibration in PAni appears at around 3579 cm^{-1}.

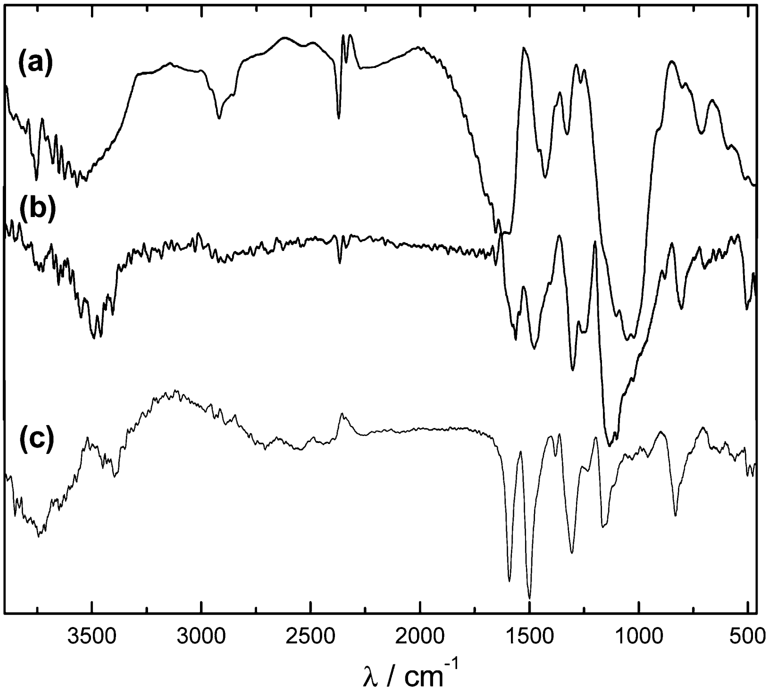

FIGURE 2 Infrared spectra of (a) commercial CMC and polymer electropolymerized on AISI-304 from 1 M H_3PO_4 solution containing 0.2 M aniline and 1% CMC. (b) doped and (c) undoped state.

However, for PAni-CMC, this peak appears at lower wave numbers (around 3400 cm^{-1}) due to significant H-bonding between PAni and the CMC [13].

The potentiodynamic curves for uncoated stainless steel and stainless steel coated with PAni-CMC in 3% NaCl aqueous solution are shown in Figure 3. As reported before [6,9,11], the corrosion potential presents a displacement to more positive values when PAni-CMC covers the steel surface. For all the PAni-CMC-coated samples used, significant decreasing of the corrosion current and a displacement in the pitting potential (between 144 to 240 mV) were observed when compared to uncoated samples. When the composite was undoped (Fig. 3 (b)) the potential shifts still remained. However, higher corrosion potential, closer to that of PAni, were observed for PAni-CMC 0.1 and 1% wt CMC. It is important to observe from Figure 3(b) that undoped PAni-CMC composites present inhibitor properties, depending on the CMC content perhaps, due to the morphological and electrical changes in the films [5].

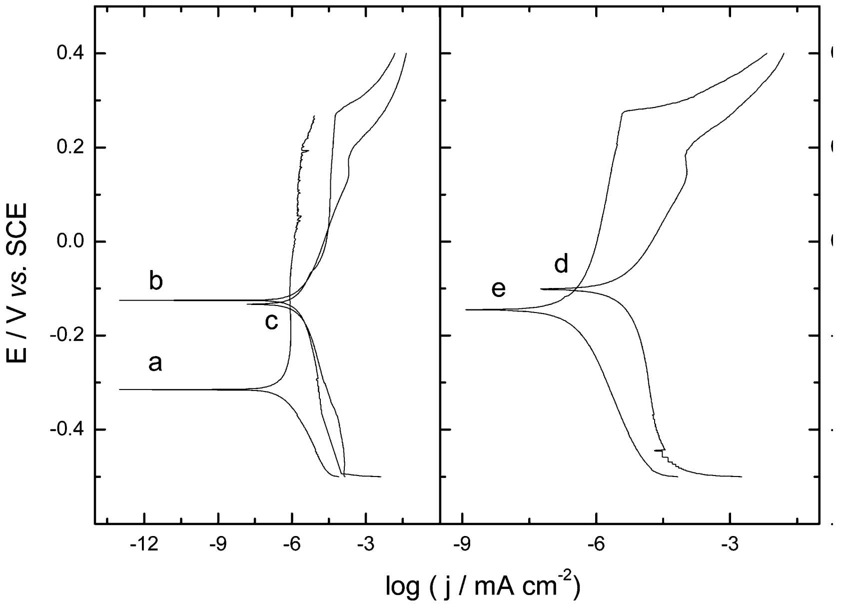

FIGURE 3 Potentiodynamic curves recorded in 3% NaCl aqueous solution. (a) AISI-304 uncoated and recovered with (b) doped PAni-CMC 0.1%; (c) Undoped PAni-CMC 0.1%; (d) doped PAni-CMC 1%; (e) Undoped PAni-CMC 1%.

In Figure 4, it can be observed that the morphology of the composite films is dependent on the CMC content – i.e., on increasing the CMC content the films seems to become more compact. The analysis performed indicates that CMC may act as a cross-linking agent.

Thus, CMC molecules can influence the growth mechanism of PAni-CMC and lead to a more packed structure with very few pores. On the other hand, it seems that a material depletion occurs during the corrosion assays, which decreases when the CMC content increases. These results are expected when considering the less porous structure of the CMC-containing deposits, which thus present better mechanical characteristics.

The change observed in two peaks corresponding to phosphorus and chloride before and after the corrosion assays (from the EDAX spectra (Fig. 4)) are represented as a function of the CMC content. The film composition presents changes and a significant reduction in the P content is observed after the corrosion assays. The dependence of the P content on the CMC content after the corrosion assays is different to that before. It is interesting to note the PAni film presents the highest reduction of P content (≈97%). On the other hand, for the PAni-CMC composites the P content varies from 97 to 63% with increasing CMC content, with the lowest value observed for 0.3% of CMC.

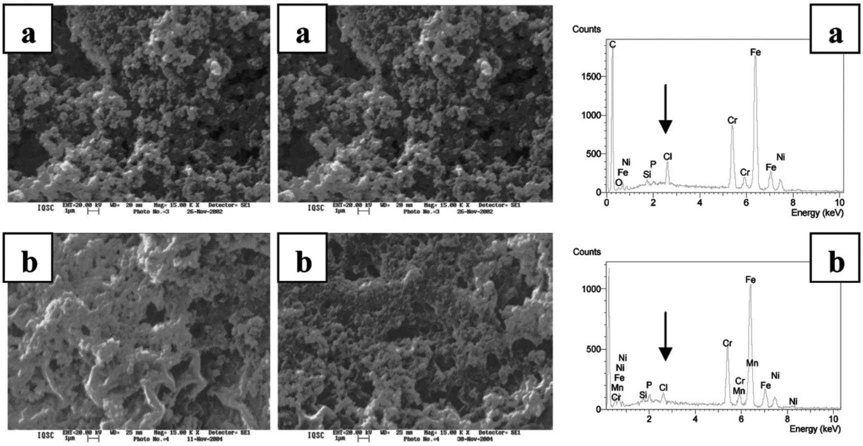

FIGURE 4 SEM micrographies of AISI-304 recovered with PAni and PAni-CMC composites, before and after corrosion analysis. In right-hand side, EDAX spectra of the samples after corrosion tests. Polymer (a) PAni and (b) PAni-CMC 0.3%.

The PAni film presents the highest Cl content (≈5.2%) however, for PAni-CMC the Cl content varies between 4.3 and 2.9%. The chloride content increases with increasing CMC concentration in the PAni-CMC composite and a maximum content is observed at a CMC concentration of around 0.6%. For a CMC concentration higher than 0.6% the Cl content decreases.

CONCLUSION

It is possible to electropolymerize PAni in presence of different CMC content by cyclic voltammetry from aqueous H_3PO_4 solutions on stainless steel. The presence of CMC in the composite influences the structure of PAni. The CMC interacts with PAni throughout –H bonding and it alters the morphology of the PAni-CMC composite, which becomes less porous and more packed with increasing CMC concentration. All PAni-CMC composite films presented corrosion inhibiting properties. The composition analysis confirmed that the composition of PAni-CMC is different to PAni both before and after corrosion.

REFERENCES

[1] Roichman, Y., Titelman, G. I., Silverstein, M. S., Siegmann, A., & Narkis, N. (1998). *Synth. Met.*, *98*, 201.

[2] Jousseaume, V., Bonnet, A., Morsli, M., & Cattin, L. (1999). *Eur. Phys. J. AP*, *6*, 7.

[3] Banerjee, P. (1998). *Eur. Polym. J.*, *34*, 841.

[4] Otero, T. F., Herrasti, P., Ocon, P., & Alves, C. R. (1998). *Electrochemi. Acta.*, *43*, 1089.

[5] Otero, T. F. & Vazquez, M. V. (1995). *J. Electroanal. Chemi.*, *397*, 171.

[6] Mirmohseni, A. & Oladegaragoze, A. (2000). *Synth. Met.*, *114*, 105.

[7] Su, W. & Iroh, J. O. (1997). *Electrochim. Acta.*, *17*, 2685.

[8] Moraes, S. R., Huerta-Vilca, D., & Motheo, A. J. (2002). *Mol. Cryst. Liq. Cryst.*, *374*, 391.

[9] Moraes, S. R., Huerta-Vilca, D., & Motheo, A. J. (2003). *Prog. Org. Coat.*, *48*, 28.

[10] Kraljic, M., Mandic, Z., & Duic, Lj. (2003). *Corros. Sci.*, *45*, 181.

[11] Herrasti, P. & Ocón, P. (2001). *Appl. Surf. Sci.*, *172*, 276.

[12] Aspinall, G. O. (Ed.) (1982). *Spectroscpic Methods. The Polysaccharides*; Academic Press: New York, Vol. 1.

[13] Armes, S. P. & Aldissi, M. (1990). *Polymer.*, *31*, 569.