Research note

Preparation and Characterization of Polyaniline/CaCO₃ Composite and its Application as Anticorrosive Coating on Iron

A. Olad* and A. Rashidzadeh

Polymer Composite Research Laboratory, Department of Applied Chemistry,
Faculty of Chemistry, University of Tabriz, Tabriz, Iran.

Abstract
Composites of polyaniline with calcium carbonate particles (PANI/CaCO₃) with different CaCO₃ content (0-40 %w/w) were prepared. Two different methods of in situ polymerization and solution mixing were used for PANI/CaCO₃ composite preparation. The composite was characterized using FT-IR, SEM, electrical conductivity measurement and cyclic voltammetry techniques. The incorporation of CaCO₃ particles in polyaniline matrix in both methods of composite preparation was confirmed by FT-IR results. Electrical conductivity measurements showed that the conductivity of the composite decreases by increasing the CaCO₃ loading in polyaniline. Also, the anticorrosive property of the PANI/CaCO₃ composite coating on iron samples was investigated in various corrosive environments. According to the results, the corrosion rate or corrosion current of PANI/CaCO₃ composite coated iron coupons was much lower (96.75%) than polyaniline coated samples. Also, results showed that the corrosion current of composite coated samples varies with the variation of the CaCO₃ content in composite coating, and the optimum CaCO₃ content of composite coating to achieve the best anticorrosive performance on iron is 10 %w/w.

Keywords: *Composite, Conducting polymers, Polyaniline, Calcium carbonate, Corrosion*

Introduction

Since the successful synthesis of conducting polyacetylene in 1977 by Shirakawa et al [1], electrically conducting polymers have generated tremendous interest due to their potential applications in various fields such as rechargeable batteries, electrochromic display devices, separation membranes, sensors and anticorrosive coatings. Conducting polymers are a novel class of synthetic metals that combine the chemical, electrochemical and mechanical properties of polymers with the electronic properties of metals and semiconductors.

Although a variety of conducting polymers have been synthesized and investigated, polyaniline is known as having, probably, the best combination of environmental stability, good conductivity and low cost [2]. As a consequence, polyaniline and its composites have very strong potential on a large scale for the industrial applications mentioned above [3-5]. Polyaniline and its derivatives have been extensively used as anticorrosive coatings on metals [6-10]. However pure coatings of polyaniline and its derivatives

---

∗ Corresponding author: E-mail: a.olad@yahoo.com

suffer from poor mechanical properties and adhesion strength [11,12]. To improve the anticorrosive efficiency, mechanical pro-perties and adhesion strength, polyaniline composites were prepared and applied on various metals for corrosion protection [13-16].

Composite materials nowadays play an increasingly important role due essentially to their lighter weight and better corrosion resistance. These materials usually comprise a polymer matrix in which fibers and/or small filler particles are thoroughly dispersed. For instance, calcite particles constitute one of the most common fillers in composite materials such as plastic and paper. They not only lower the cost but also improve the tensile strength and stiffness of the base resin, leading to composites exhibiting a satisfactory performance improvement. Obviously, the filler must be well dispersed in the matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing [17].

Particle filled polymer composites have become attractive because of their wide applications and low cost. Incorporating inorganic mineral fillers into plastic resin improves various physical properties of the materials such as mechanical strength, modulus and adhesion performance. In general, the mechanical properties of particulate filled polymer composites depend strongly on the size, shape and distribution of filler particles in the polymer matrix and good adhesion at the interface of the polymer matrix and particle surface [18]. Particulate fillers have also been used increasingly to fulfill additional roles, such as enhancing stiffness, decreasing dielectric loss or increasing absorption of infrared radiation.

Calcium carbonate is a common filler that can be obtained in a variety of sizes and surface treatments. Many types of specially precipitated calcium carbonate filler particles have relatively regular shapes [19]. CaCO₃ is one of the fillers used most often and in large quantities to produce polymer composites [20].

The choice of the best method to produce polymer composites may significantly determine the properties of the manufactured composite materials. Known methods to prepare polymer composites, especially polyaniline composites, may be essentially reduced to two methods of in situ polymerization and solution mixing [21]. Each method has its own advantages and limitations. Good homogeneity and low percolation threshold characterize the in situ polymerization of polyaniline in the presence of particulate fillers. On the other hand, solution mixing of polymer and filler particles in a proper solvent sometimes seem to be more technologically desirable from the large scale production view point.

In this work the preparation of polyaniline/ calcium carbonate (PANI/CaCO₃) composite with different CaCO₃ content (0-40% w/w) by two methods of insitu polymerization and solution mixing is well described. The composite was characterized using FT-IR, Scanning Electron Microscopy (SEM), conductivity measurement and cyclic voltammetry techniques. The anticorrosive properties of polyaniline/ CaCO₃ composite coating on iron were investigated using standard corrosion test methods and was compared with anticorrosive properties of pure polyaniline coating. Adhesion strength of the PANI/CaCO₃ composite coating on iron coupons was also investigated to evaluate the effect of CaCO₃ presence on the adhesion strength of polyaniline on iron.

Experimental
Reagents and Materials
Ammonium persulphate (Merck No. 101200), aniline (Merck No.101261), hydrochloric acid (Merck No.100312), 1-methyl-2-pyrrolidone (NMP) (Merck No. 806072), sulphuric acid (Merck No.100713), sodium chloride (Merck No.102406), calcium carbonate (Merck No.102059), acetone (Merck No.100014) and ammonia (Merck No.105426) were all purchased from

Merck chemicals and were used as received. Aniline was distilled prior to use.

Metal sample preparation
Iron coupons with 2×2×0.05 cm dimensions were used in corrosion studies. The chemical composition of the iron samples was analysed (Table 1). In order to remove any existing passive film, the surface of the iron coupons were mechanically polished using 100 and 400 grade emery papers and then rinsed with distilled water and acetone prior to coating with composite or pure polyaniline layer and corrosion experiments.

Table 1. Chemical composition of the iron samples

Element	Percent (%w/w)	Element	Percent (%w/w)
Fe	99.521	Co	0.0131
C	0.0351	S	0.0158
Si	0.0133	Cu	0.0481
P	0.0145	W	0.0022
Mn	0.2408	Al	0.0347
Ni	0.0325	Sn	0.0005
Cr	0.0284	-	-

Synthesis of PANI/CaCO$_3$ composite
PANI/CaCO$_3$ composite was prepared using in situ polymerization and solution mixing methods. In the first method aniline polymerization was carried out in HCl 1.5M acidic media using ammonium persulphate as the oxidant/initiator in the presence of calcium carbonate filler particles. For comparative aims, pure polyaniline was also synthesized exactly according to the above mentioned method without the use of CaCO$_3$ particles. In the solution mixing method the so prepared pure PANI powder in emeraldine base form was dissolved in NMP solvent. Then different amounts of calcium carbonate were added to the solution of polyaniline in NMP. The solution casting method was used to apply a thin layer (100μm) of pure or composited polyaniline coatings on iron coupons. The solvent evaporation was carried out in an oven at 60°C for 2 hours. A FT-IR equipment model Tensor 27 from Bruker was used in the characterization of PANI/CaCO$_3$ composite. SEM micrograph of PANI/ CaCO$_3$(10%w/w) composite was recorded using LEO 440i from UK. Also, a homemade four point probe was used to measure the electrical conductivity of pure and PANI/CaCO$_3$ composite free standing films.

Corrosion tests
Throughout this work, tafel plots were carried out using a conventional three-electrode electrochemical cell with a platinum gauze as a counter electrode and an Ag/AgCl as the reference electrode. The working electrode was the iron sample (coated or uncoated).
The tofel plots were recorded by sweeping the potential of the working electrode around the equilibrium potential (±250mV) at a rate

of 25mV/s. To measure the open circuit potential of the samples, a two-electrode system was used with the sample as working and an Ag/AgCl as reference electrodes.

Results and discussion
FT-IR spectra
The PANI/CaCO$_3$ composite prepared by both methods of in situ polymerization and solution mixing methods was characterized using FT-IR technique. Figures 1 and 2 show the FT-IR spectra of PANI/CaCO$_3$(10%w/w) composites prepared respectively by in situ polymerization and solution mixing methods. In these figures characteristic bands corresponding to CaCO$_3$ are seen at 800 and 1100-1500 cm^{-1}. In addition, the vibration bands at 1141, 1306, 1495 and 1583 cm^{-1} in both figures are the characteristic bands for polyaniline. In this spectrum the prominent absorption peaks at 1583 and 1495 cm^{-1} are attributed to the quinoid and phenylene ring deformation respectively. The peaks at 1300-1290 cm^{-1} are assigned to C-N stretching of the secondary amine of PANI backbone. The peaks at 1114 cm^{-1} and 1111 cm^{-1} can be assigned to an in plane bending vibration of C-H which formed during protonation. Therefore, the FT-IR technique confirms the incorporation of CaCO$_3$ particles in the polyaniline matrix using both methods of in situ polymerization and solution mixing for composite preparation.
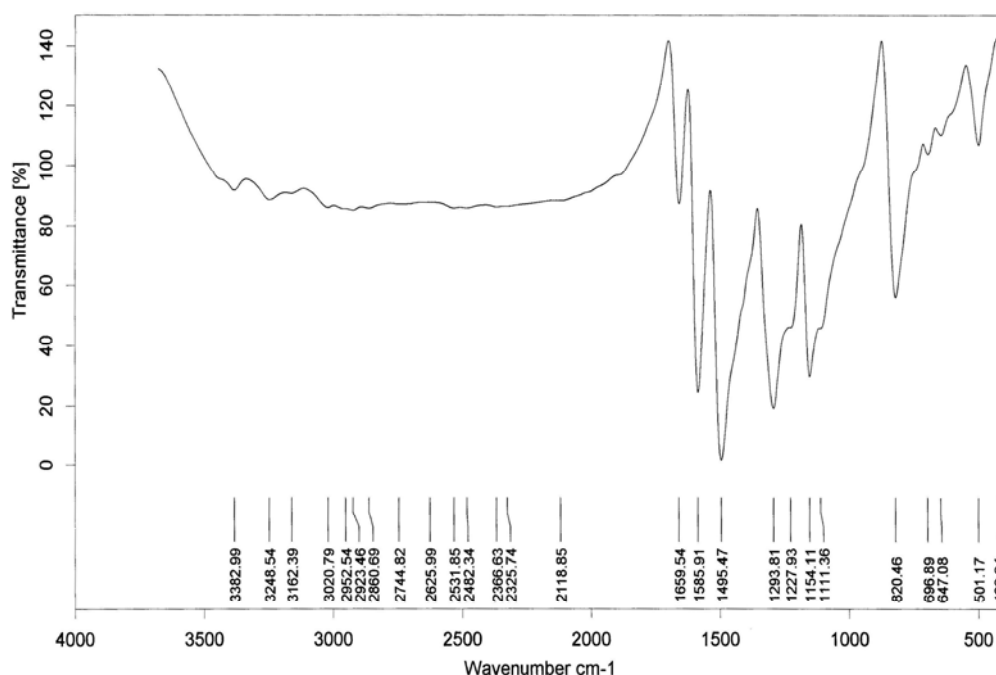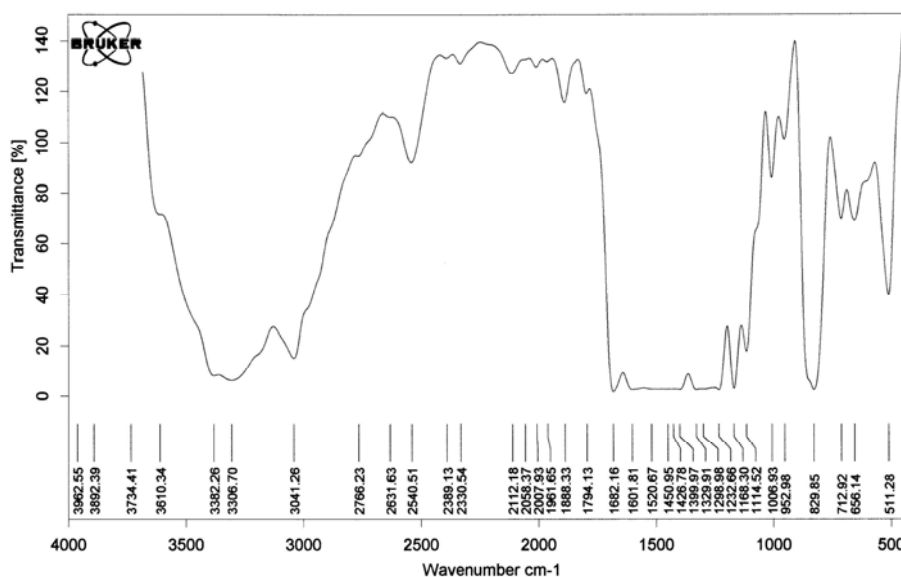

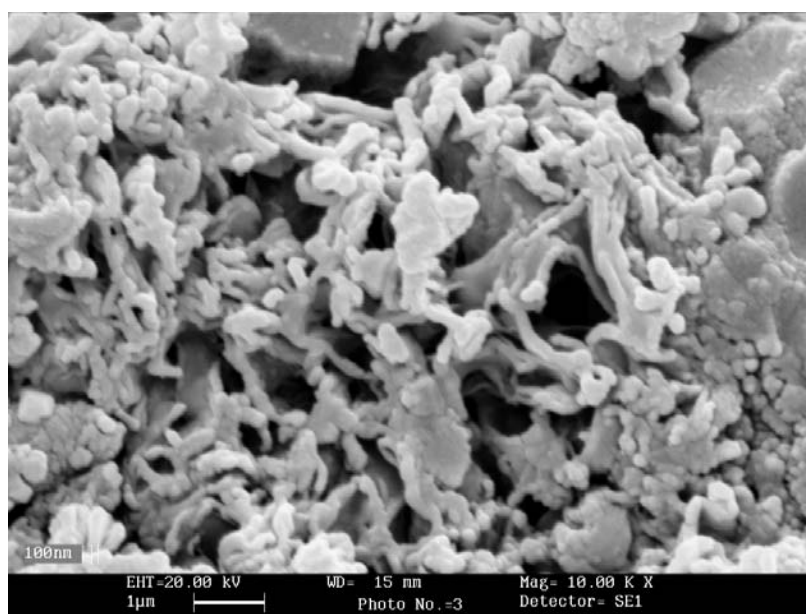**Figure 1.** FTIR spectra of PANI/CaCO$_3$(10%w/w) composite prepared using in situ polymerization method.

Figure 2. FTIR spectra of PANI/CaCO₃(10%w/w) composite prepared using solution mixing method.

SEM micrograph
In order to evaluate the dispersion of CaCO₃ particles in the polyaniline matrix, the scanning electron micrograph was recorded for PANI/CaCO₃ (10%w/w) composite. Figure 3 shows the SEM micrograph of PANI/CaCO₃(10%w/w) composite. According to figure 3, the SEM micrograph confirms the good dispersion of CaCO₃ particles in the polyaniline matrix.

Figure 3. SEM micrograph of PANI/CaCO₃ (10%w/w) composite.

Electrical conductivity

Four point probe technique was used to measure the electrical conductivity of PANI/CaCO$_3$ composite films. The electrical conductivity of PANI/CaCO$_3$ composite, with different CaCO$_3$ content, as free standing film was measured and compared with the electrical conductivity of pure polyaniline film. Free standing films of composite and pure polyaniline with 100μm thickness were prepared by a solution casting method using NMP as solvent. Table 2 shows the electrical conductivity of PANI/CaCO$_3$ composite free standing films with different CaCO$_3$ content in comparison to pure polyaniline (CaCO$_3$ content = 0%w/w). According to the results, the electrical conductivity of composite films, without considering the methods of

preparation, decreases by increasing CaCO$_3$ content in the composite, while the maximum conductivity of 1.275 S/cm was obtained for pure polyaniline. This is due to the nonconductive behavior of CaCO$_3$ particles. Results showed that the electrical conductivity of PANI/CaCO$_3$ composite films prepared by the solution mixing method is higher than composite films prepared by the in situ polymerization method with the same CaCO$_3$ content. This behavior may be due to the higher homogeneity and good dispersion of nonconductive CaCO$_3$ particles in conducting polyaniline matrix in PANI/CaCO$_3$ composite films prepared by the in situ polymerization method.

Table 2. Electrical conductivity of PANI/CaCO$_3$ composite free standing films with different CaCO$_3$ content, prepared using in situ polymerization and solution mixing methods

| CaCO$_3$ content (%w/w)	Conductivity (S/cm)	
	In situ polymerisation	Solution mixing method
0% (pure polyaniline)	1.275	1.275
10 %	0.1195	0.462
20 %	0.0186	0.405
30 %	0.133	0.358
40 %	0.035	0. 352

Cyclic voltammetry

Cyclic voltammetery studies were carried out to evaluate the electrochemical behavior of PANI/CaCO$_3$ composite. A gold electrode coated with a thin layer of composite was used as working electrode. Various solutions including HCl 0.1M, H$_2$SO$_4$ 0.1M and NaCl 3.5%w/w were used as electrolytes. Figures 4 and 5 typically show the cyclic voltammetry of PANI/CaCO$_3$ composite film with 10%w/w CaCO$_3$, prepared by two different

methods in HCl 0.1M electrolyte at different potential scan rates of 100, 50 and 25 mV/s. Regarding the results, it was found that PANI/CaCO$_3$ composite is electroactive similar to pure polyaniline and represents two pairs of oxidation/reduction peaks in cyclic voltammogram. Also, the results showed that the electrochemical behavior of composite is the completely reversible (Figures 4 and 5).
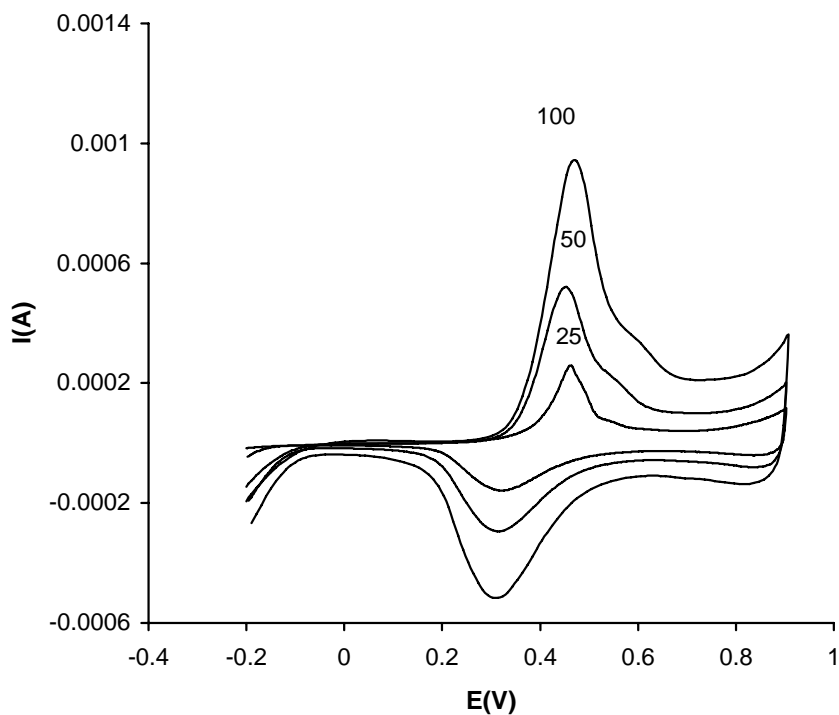
Figure 4. Cyclic voltammetery for PANI/CaCO₃(10%w/w) composite prepared using solution mixing method at different scan rates of 100, 50 and 25 mV/s in HCl 0.1M solution.
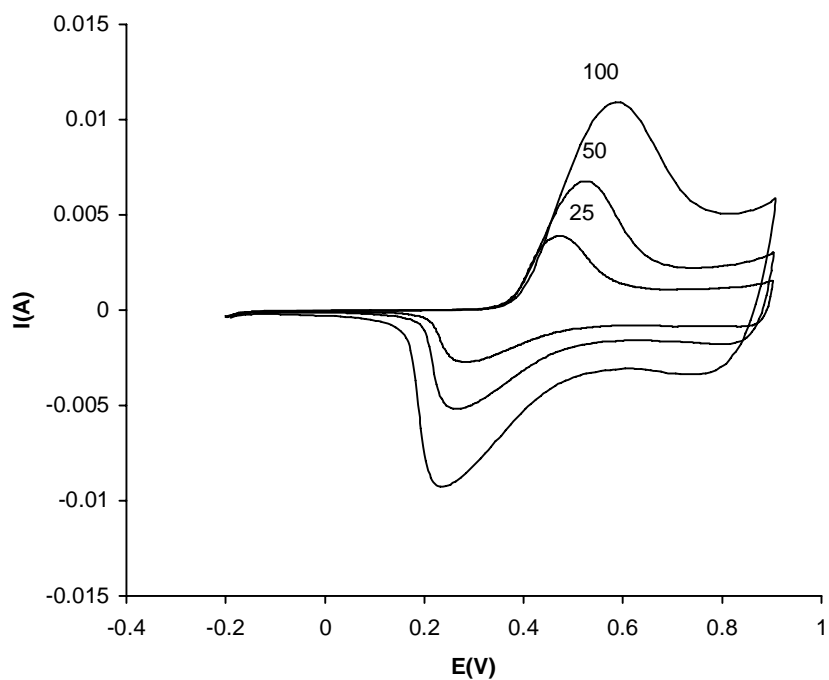

Figure 5. Cyclic voltammetery for PANI/CaCO₃(10%w/w) composite prepared using in situ polymerization method at different scan rates of 100, 50 and 25 mV/s in HCl 0.1M solution.

Corrosion studies

The electrochemical tafel slope analysis was used to evaluate the anticorrosive performance of PANI/CaCO₃ composite coating on iron samples. The tafel plots for coated and uncoated iron samples were recorded by sweeping the potential from equilibrium potential toward negative and positive potentials against Ag/AgCl reference electrodes in HCl 0.1M, H₂SO₄ 0.1M and NaCl 3.5%w/w electrolytes. The iron coupons were coated with 100μm coatings of pure polyaniline and the PANI/CaCO₃ composite layer by solution casting method using NMP as solvent. Figure 6 typically shows the tafel plots for polyaniline and PANI/CaCO₃ (10%w/w) composite coated iron samples in NaCl 3.5%w/w and HCl 0.1M solutions. It can be seen that the corrosion current of PANI/CaCO₃ composite coated samples is much lower than pure polyaniline coated samples. Therefore, it was found that the incorporation of CaCO₃ particles in polyaniline matrix promotes the anticorrosive efficiency of PANI/CaCO₃ composite coating on iron samples. In order to investigate the effect of CaCO₃ percent in PANI/CaCO₃ composite on the anticorrosive efficiency of composite coatings, the tafel plots for PANI/CaCO₃ composite coated iron samples with different CaCO₃ content of composite coating were recorded in HCl 0.1M solution (Figure 7). Comparison of the corrosion current and corrosion potentials of PANI/CaCO₃ coated iron samples with different CaCO₃ content of composite showed that the anticorrosive properties of PANI/CaCO₃ composite coatings with 10%w/w and 20%w/w CaCO₃ content is much better than composite coatings with 30%w/w and 40%w/w CaCO₃ content. This may be due to the decreasing adhesion strength of composite coating on iron by increasing composite CaCO₃ content.
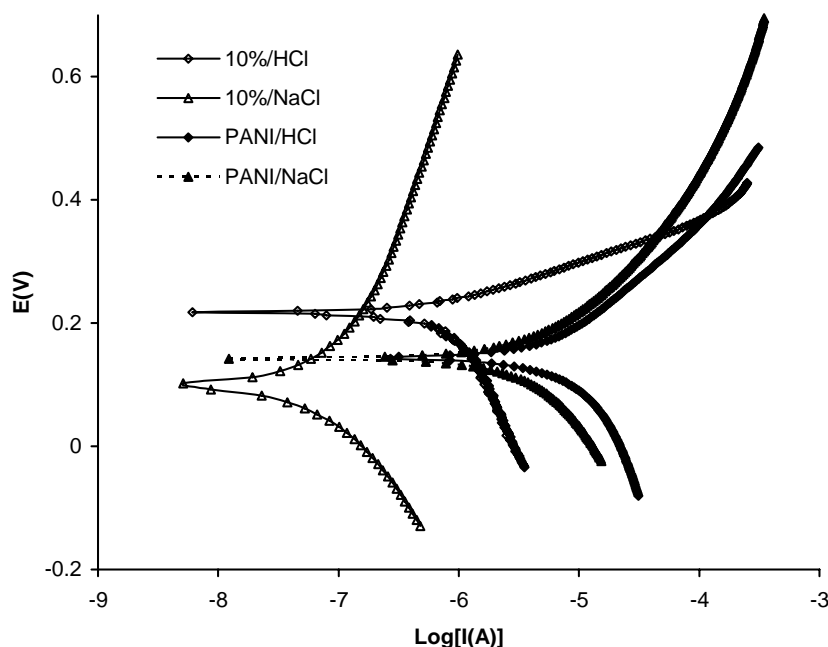
Figure 6. Tafel plots for pure polyaniline and PANI/CaCO₃(10%w/w) composite coated samples in HCl 0.1M and NaCl 3.5%w/w solutions. The composite was prepared by solution mixing method
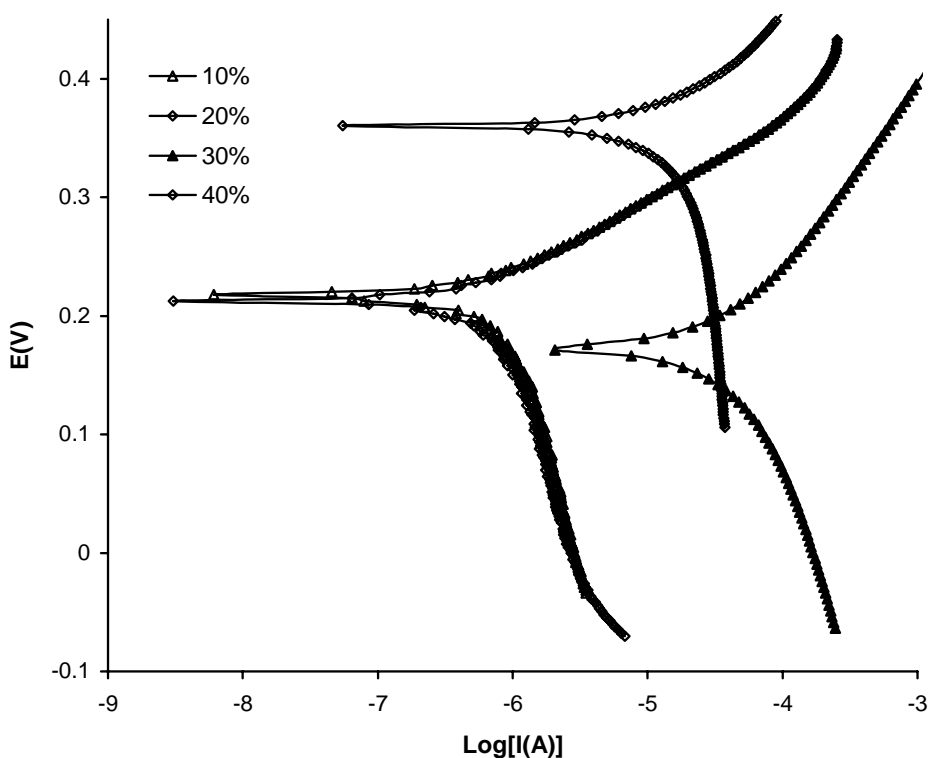
Figure 7. Tafel plots for PANI/CaCO₃ composite coated iron samples with different CaCO₃ content in HCl 0.1M solution. The composite was prepared by solution mixing method

Conclusion

The preparation of PANI/CaCO₃ composite by two methods of in situ polymerization and solution mixing was successfully done. The electrical conductivity measurements showed that the PANI/CaCO₃ composite films are conductive with conductivities lower than pure polyaniline film prepared in a similar method. The electrical conductivity was decreased by increasing the CaCO₃ content of the composite. The reversible electroactive behavior for PANI/CaCO₃ composite was confirmed by cyclic voltammetry techniques. Results of the corrosion studies showed that the anticorrosive property of PANI/CaCO₃ composite coating on iron samples is better than pure polyaniline. It was found that the PANI/CaCO₃ composite coating with the 10%w/w CaCO₃ content has the best anticorrosive properties on iron samples.

Acknowledgement

References

1. Shirakawa, H., Lois, E. J., Macdiarmid, A. G., Chiang, C.K. and Heeger, A. J., "Synthesis of electrically conducting organic polymers: halogen derivatives of poly(acetylene), (CH)ˣ, " *J. Chem. Soc., Chem. Commun.,* 16, 578 (1977).
2. Pud, A., Ogurtsov, N., Korzhenko, A. and Shapoval, G.," Some aspects of preparation methods and properties of polyaniline blends and composites with organic poltmers , " *Prog. Polym.* Sci., 28, 1701 (2003).
3. Gemeay, A. H., El-Sharkawy, R. G., Mansour, I. A. and Zaki, A. B., "Preparation and characterization of polyaniline/ manganese dioxide composites and their catalytic activity," *Journal of Colloid and Interface Science*, 308, 385 (2007).
4. Majid, K., Awasthi, S., Singla, M. L., "Low

temperature sensing capability of polyaniline and Mn_3O_4 composite as NTC material," *Sensors and Actuators A,* 135, 113 (2007).

5. Mirmohseni, A., and Oladegaragoze, A.," Detection and determination of Cr^{VI} in solution using poltaniline modified quartz crystal electrode," J. Appl. Sci., 85, 2772 (2002).

6. Gonzalez-Rodriguez, J. G., Lucio-Garcia, M. A., Nicho, M. E., Cruz-Silva, R., Casales, M. and Valenzuela, E., "Improvement on the corrosion protection of conductive polymers in pemfc environment by adhesives," *Journal of power Sources* 186, 184 (2007).

7. Jeyaprabha, C., Sathiyanarayanan, S. and Venkatachari, G., "Effect of cerium ions on corrosion inhibition of PANI for iron in 0.5 M H_2SO_4," Applied Surface Science, 253, 432 (2006).

8. Zhong, L., Zhu, H., Hu, J., Xiao, S. and Gan, F., "A passivation mechanism of doped polyaninle on 410 stainless steel in deaerated H_2SO_4 solution," *Electrochimica Acta*, 51, 5494(2006).

9. Chang, K. C., Jang, G. W., Peng, C. W., Lin, C. Y., Shieh, J. C., Yeh, J. M., Yang, J. C. and Li, W.T., "Comparatively electrochemical studies at different operational temperatures for the effect of nanoclay platelets on the anticorrosion efficiency of DBSA-doped polyaniline/Na^+-MMT clay nanocomposite coatings," *Electrochimica Acta*, 52, 5191(2007).

10. Mirmohseni, A., and Oladegaragoze, A.," Anti-corrosive properties of polyaniline coating on iron, " *Synth. Met.*, 114, 105 (2000).

11. Dispenza, C., Lo Presti, C., Belfiore, C., Spadaro, G., and Piazza, S., "Electrically conductive hydrogel composites made of polyaniline nanoparticles and poly(N-vinyl-2-pyrrolidone),"*Polym.,* 47, 961 (2006).

12. Abu, Y. M. and Aoki, K., "Corrosion protection by polyaniline-coated latex microspheres," *J. Elec. Chem.,*583, 133 (2005).

13. Hu, Z. A., Shang, X. L., Yang, Y. Y., Kong, C. and Wu, H. Y., "The electrochemical synthesis of polyaniline/polysulfone composite films and electrocatalytic activity for ascorbic acid oxidation," *Electrochimica Acta*, 51, 3351(2006).

14. Pan, W., Yang, S. L., Li, G. and Jiang, J. M., "Electrical and structural analysis of conductive polyaniline/polyacrylonitrile composites," *European Polymer Journal*, 41, 2127(2005).

15. Pud, A., Ogurtsov, N., Korzhenko, A. and Shapoval, G., "Some aspects of preparation methods and properties of polyaniline blends and composites with organic polymers," *Prog. Polym. Sci.,* 28, 1701 (2003).

16. Samui, A. B., Patankar, A. S., Rangarajan, J. and Deb, P.C., "Study of polyaniline containing paint for corrosion prevention," *Prog. Org. Coat.,* 47, 1 (2003).

17. Shui, M., "Polymer surface modification and characterization of particulate calcium carbonate fillers," *Appl. Surf. Sci*., 220, 359 (2003).

18. Suryasarathi, B., Mahanwar, P.A., "Effect of Particle Size of Filler on Properties of Nylon-6," *J. Miner. Mater. Charac. Eng.*, 3, 23 (2004).

19. Zhu, H., Zhong, L., Xiao, S., and Gan, F. "Accelerating effect and mechanism of passivation of polyaniline on ferrous metals," *Elect. Act.*, 49, 5161 (2004).

20. Silva, A. L. N., Rocha, M. C. G., Moraes, M. A. R., Valente, C. A. R., and Coutinho, F. M. B., "Mechanical and rheological properties of composites based on polyolefin and mineral additives," *Polym. Test.* 21, 57 (2002).

21. Osman, M. A., Atallah, A., and Suter, U. W., "Influence of excessive filler coating on the tensile properties of LDPE–calcium carbonate composites," *Polym.* 45, 1177 (2004).