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Electrochemical synthesis and characterization of polypyrrole/chitosan composite on platinum electrode: Its electrochemical and thermal behaviors

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ABSTRACT

The electrochemical polymerization of conducting polymers is a simple and most convenient method for preparation of a film on the metal surface. The polypyrrole/chitosan composite film has been electrochemically synthesized on platinum electrode by using cyclic voltammetry (CV) technique. The synthesis solution was prepared by dissolving of pyrrole and chitosan in aqueous oxalic acid solution. The characterization of this film was done using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermal analysis (TG–DTA) techniques. The synthesized composite film was different in aspect of morphology when compared to chitosan and polypyrrole. The TG–DTA results revealed that the composite film had better thermal stability with respect to chitosan. The electrochemical measurement has shown that the composite film is very stable and electroactive.

1. Introduction

Conducting polymers can be synthesized chemically or electrochemically (Borole, Kapadi, Mahulikar, & Hundivale, 2006; Chan et al., 1993). The electrochemical polymerization of conducting polymers is a simple, relatively inexpensive and most convenient method for preparation of a film on the metal surface (Umare, Borkar, & Gupta, 2002). There have been in several studies subjecting impending applications of conducting polymers for various purposes; corrosion protection, electro catalysis, energy storage, sensors and microelectronics (Hechavarria, Hu, & Rincon, 2003; Herrasti, Recio, Ocon, & Fatas, 2005; Ivanov, Mokreva, Tsakova, & Terlemezyan, 2003; Jeevananda, Seetharamu, Saravanan, & D'Souza, 2004; Liao & Gu, 2002; Rahman, Abul-Hamaley, & Abul Alem, 2005). There are some important points for consideration in applications of conducting polymer coatings; porosity, adhesion and water permeability. With the purpose of develop better quality coating; numerous studies have been dealing modification of polymer coatings. Copolymerization and composites preparation are the easy and powerful methods of making systematic changes in the polymer properties, and are widely used in the production of commercial polymers (Motheo, Pantoja, & Venancio, 2004; Sazou, 2001).

Chitosan has long been marked as one of the most promising natural polymers. This natural polymer exhibits characteristic properties; such as chemical inertness, high mechanical strength, biodegradability, biocompatibility, high-quality film-forming properties, and low cost (Yavuz, Uygun, & Bhethanabotla, 2008). Chitosan is used wide application area such as separation membranes, food packaging, wastewater treatment, drug delivery systems and biosensor (Kurita, 1998; Mathur & Narang, 1990; Ravi Kumar, 2000; Yavuz et al., 2008). As reported in the literature, the poor electrical conductivity of hydrogels results in a poor response time and high operational voltage limits its applicability in sensor applications. For this reason, composites have been attempted by incorporating a rigid conducting polymer into a flexible matrix (such as chitosan) to combine the good processability of the matrix and electrical conductivity of the conductive polymer (Yavuz et al., 2008). Polypyrrole films generally exhibit better conductivity and are more easily synthesized by electro polymerization, when compared to other conducting polymers (such as; polyaniline derivatives) (Kim, Cho, Liu, Choi, & Joo, 2003; Li et al., 2001). A recent work has been reported on the synthesis of polypyrrole/chitosan composite by using potentiostat at constant voltage (Abdia, Kassima, Mahmud, Yunus, & Talib, 2009). However, there is no reported study on the synthesis of polypyrrole/chitosan composite on the platinum electrode in oxalic acid solution by using cyclic voltammetry. Also, there is no reported study on the spectral characterization, electrochemical behavior and thermal properties of this composite.

In this study, polypyrrole/chitosan composite film has been electrochemically synthesized in aqueous oxalic acid solution on the platinum electrode via cyclic voltammetry method. Oxalic acid solution has been chosen as the electrolyte for the deposition of the composite. Because, this solution medium was provided some

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advantages that conducting polymer films formation on the surfaces of metals. For example; mild steel interacts with the oxalate ions to form a passive layer of iron (II) oxalate prior to the formation of the polymer. This layer is strongly influenced by the electrochemical parameters of deposition (Herrasti et al., 2005; Tuken, Arslan, Yazıcı, & Erbil, 2004).

Characterization of the composite film has been carried out using CV, FT-IR, SEM micrographs and TG–DTA techniques.

2. Experimental

2.1. Materials

Pyrrole (Merck) was distilled under nitrogen atmosphere. Chitosan (Cs) with high molecular weight (75% deacetylated) was also purchased from Aldrich.

2.2. Instrumentation

FT-IR spectra measurements were conducted using a Perkin Elmer RX1 FT-IR spectrometer. Polypyrrole and the composite films were peeled off the surface and their pellets were prepared with KBr. The surface morphology of chitosan and composite were examined by using a JEOL JSM 5500LV scanning electron microscope (SEM) at an accelerating voltage of 10 kV. Thermal behaviors of the samples were performed with DuPont 951 thermal analyzer under air atmosphere from 40 to 600 °C with a heating rate of 10 °C min^{-1}.

2.3. Synthesis of the composite

The synthesis solution of the composite was prepared by dissolving 0.2 g chitosan in 50 ml aqueous solution of 0.3 M oxalic acid 24 h, and by adding 5 mmol pyrrole (as monomer) to the final solution. Electrochemical synthesis of the composite film was carried out by using cyclic voltammetry technique. The electrochemical cell consisted of a standard three electrode system; the counter and working electrode was a platinum sheet (with 2 cm^2 surface area), and Ag/AgCl (sat. with KCl) electrode was used as the reference. The studies were conducted under room conditions by using CHI 606 model electrochemical analyzer under computer control. The potential was scanned from −0.6 to +0.9 V (characterization) and +0.2 to +0.9 V (film growth) at scan rate of 50 mV/s.

3. Results and discussion

3.1. Electrochemical synthesis

The cyclic voltammograms recorded for platinum (Pt) electrode in chitosan solution (a), and pyrrole + chitosan solution (b) are given in Fig. 1. It was shown that the oxygen gas evolution process was found to start at around +0.9 V (Fig. 1a). Also, it should be noted that the hydrogen reduction process was observed beyond −0.3 V (Yalçınkaya, Tüken, Yazıcı, & Erbil, 2008a). As a result, it could not be obtained a chitosan film on the surface.

In Fig. 1b, successive three cycles were given for the solution containing pyrrole + chitosan. The CVs were exhibited extremely different pattern when compared to each other (Fig. 1a and b). The oxidation potential value of pyrrole was also reported to be around +0.70 V (Tuken, Yazıcı, & Erbil, 2007). But, the composite formation process was found to start at around +0.6 V. Besides, it must be noted that the observed current values for composite formation was decreased at the following cycles. This was also related with decreasing conductivity with incorporation of chitosan into the structure. However, the current decrease which observed in this region could not be observed for single pyrrole polymerization (Borole et al., 2006). This could simply be explained with significantly different mechanism of composite formation. The prepared composite film was in oxidized state and its reduction was observed as cathodic wave during the reverse scan, also re-oxidation process was observed at the following forward scan. The surface coverage of the produced homogenous composite film could be regarded as well, since the hydrogen reduction process could not be observed at the first reverse scan. It could be explained that the hydrogen gas evolution which observed beyond −0.3 V (towards negative direction) was inhibited by the formation of composite film on the metal surface.

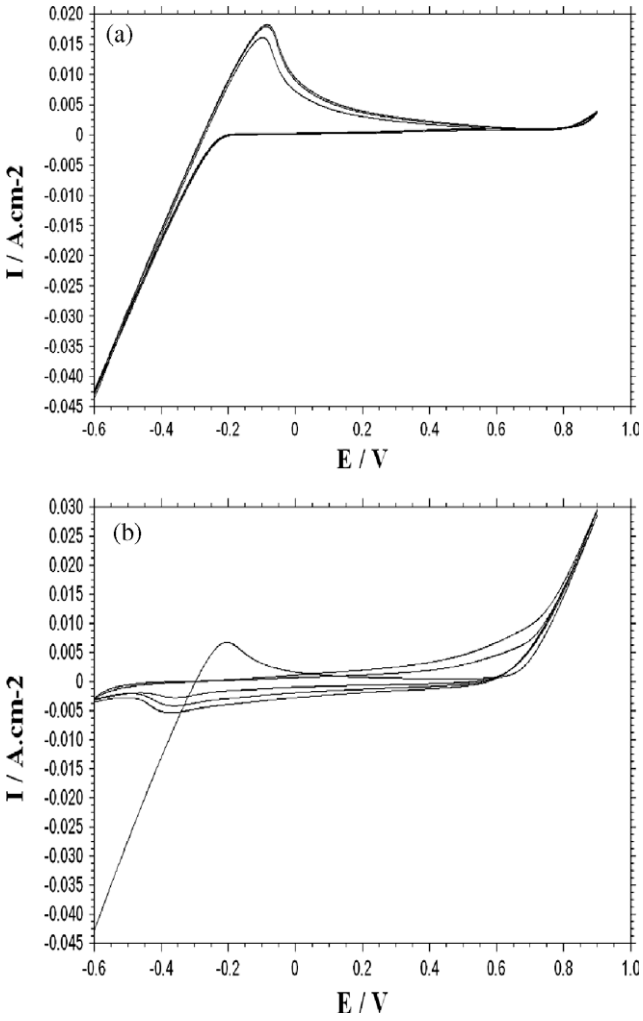

Fig. 1. The voltammograms recorded for Pt electrode in 0.3 M oxalic acid + 0.2 g chitosan (a) and 0.3 M oxalic acid + 0.2 g chitosan + 5 mmol pyrrole (b) scan rate, 50 mV/s (c).

Fig. 2 shows successive voltammogram recorded during the growth of the composite film on the platinum electrode. The potential range applied for the growth was between +0.2 and +0.9 V. The oxidation and reduction peaks (between +0.2 and +0.4 V) of the composite film due to transitions between its oxidation and reduction states are clearly seen in this voltammogram. The synthesis of composite was carried out by 25 cycles.

3.2. Solubility

The solubility of the composite film has been tested in several organic solvents as; DMSO (dimethylsulfoxide), DMF (dimethyl-

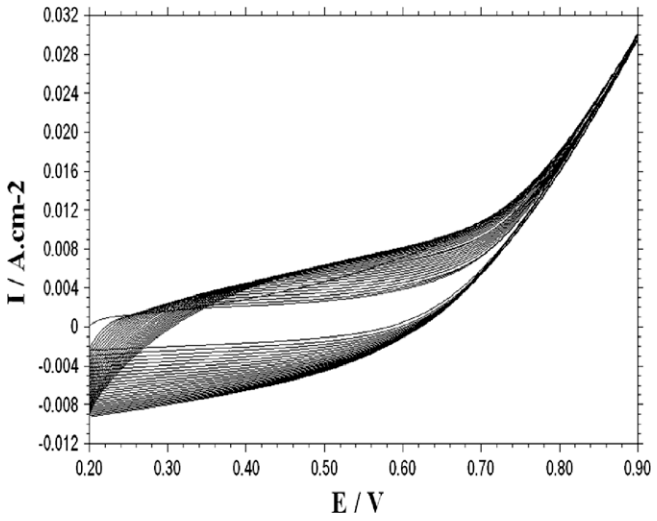

Fig. 2. The voltammogram recorded for during the polypyrrole/chitosan composite film growth on Pt electrode; scan rate, 50 mV/s.

formamide), choloroform, NMP (*N*-methylpyrolidone), THF (tetrahydrofuran) at room temperature. 2 mg sample of composite was tried to dissolve in 2 ml of organic solvent, the mixture was treated in ultrasonic bath for 24 h. The result of the solubility studies has shown that the composite was not soluble in these solvents.

3.3. FT-IR spectra results

FT-IR spectra results of polypyrrole (a), chitosan (b) and the composite (c) are given in Fig. 3. It was reported that in Fig. 3a, the typical –N–H– stretching vibration peak was observed at 3425 cm^{-1}, the peak at around 1600 cm^{-1} assigned to –C=C– stretch of pyrrole ring and the peak at 1033 cm^{-1} is caused by –C–H in-plane deformation of the pyrrole unit (Li et al., 2001). The infrared spectrum of chitosan (Fig. 3b) showed strong peak at 3390 cm^{-1} could be assigned to the axial stretching vibration of O–H superimposed to the N–H stretching band and inter hydrogen bonds of the polysaccharide; C–H stretching at 2879 cm^{-1}; bands due to the Cs-NHAc (acetyl) units (with C=O stretching) at 1655 cm^{-1}, (with N–H bending) at 1579 cm^{-1}, (with C–N stretching coupled with N–H plane deformation) at 1420 cm^{-1} and symmetrical angular deformation of CH_3 at 1376 cm^{-1}; C–N stretching of the amino groups of at 1320 cm^{-1}; C–O–C stretching vibration at 1030 cm^{-1}; and the specific bands of the β (1–4) glycoside bridge at 1154 and 896 cm^{-1} (Mansouri et al., 2004; Tian, Liu, Hu, & Zhao, 2004).

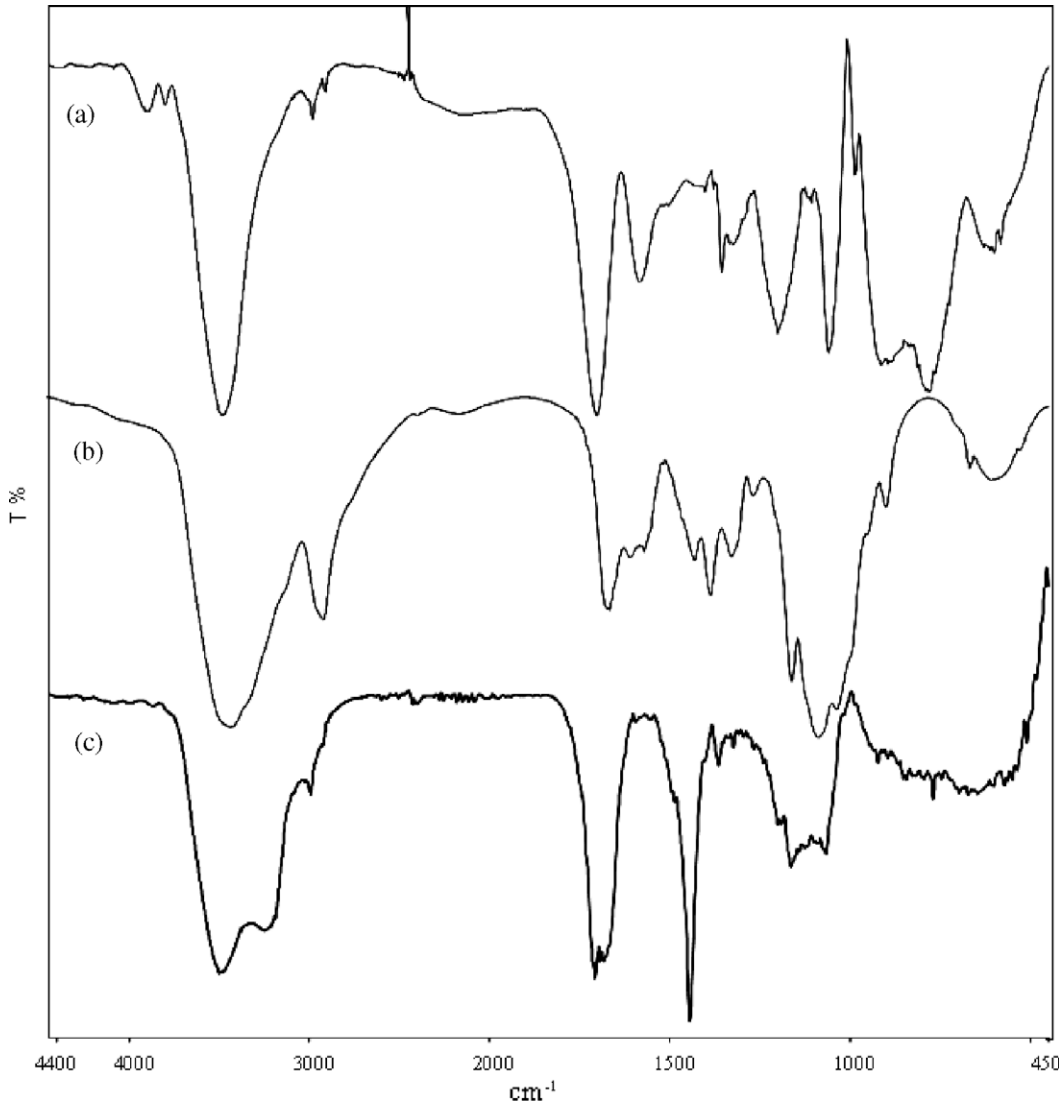

Fig. 3. FT-IR spectra of the polypyrrole (a), chitosan (b), polypyrrole/chitosan composite (c).

The infrared spectrum of the composite showed a broad absorption band centered between 3100 and 3450 cm^{-1} due to the overlap of N–H and O–H stretching vibration (Fig. 3c). This band was much broader than the bands which observed in the spectra of chitosan and polypyrrole due to the stretching vibrations of hydrogen bonded (N–H···O, O–H···O and O–H···N). As seen in FT-IR spectrum of composite, the broad doublet band observed at 1600–1660 cm^{-1} range due to the combination of the bands observed at the same range in the spectra of polypyrrole and chitosan. As a result of the characterization techniques; the proposed structure of the composite was given in Fig. 4.

3.4. Morphology

The scanning electron micrographs (SEM) of chitosan (a), polypyrrole (b) and polypyrrole/chitosan composite (c) were given in

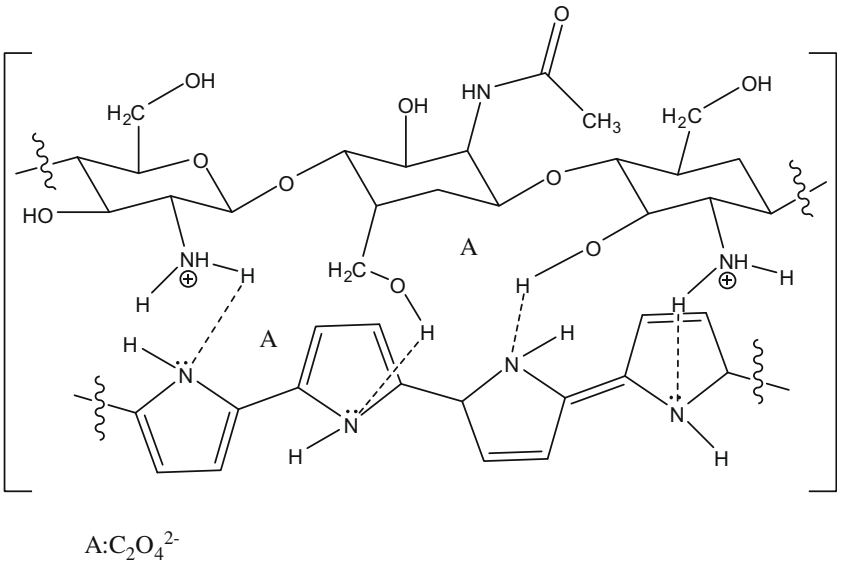

Fig. 4. The structural representation of the composite.

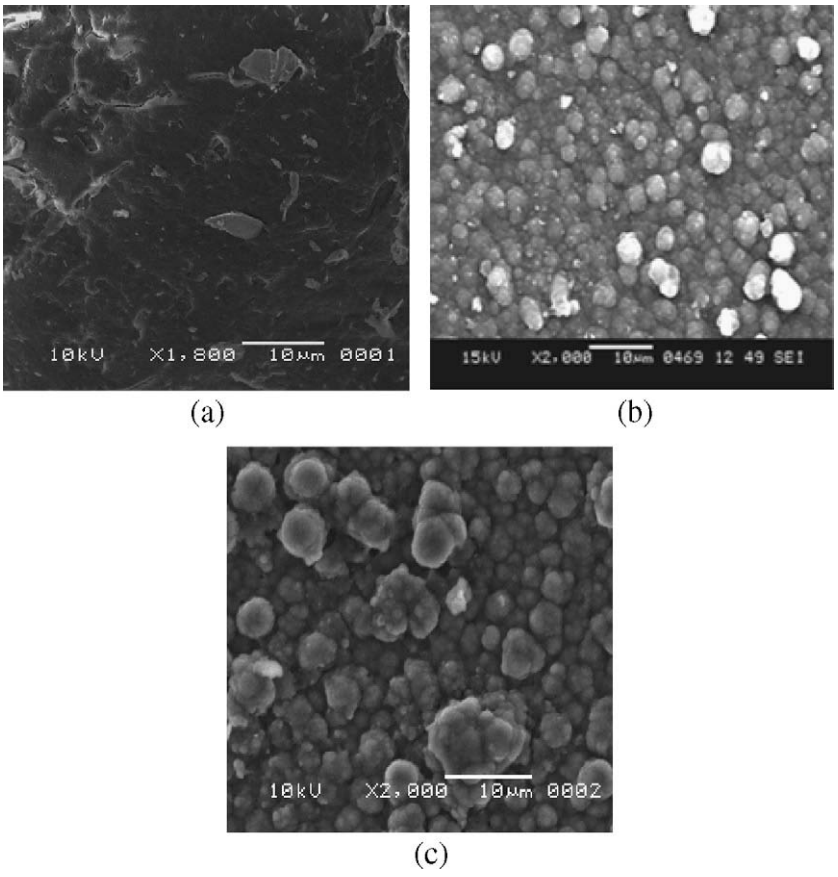

Fig. 5. The SEM micrographs of chitosan (a), polypyrrole (b) and polypyrrole/chitosan composite (c).

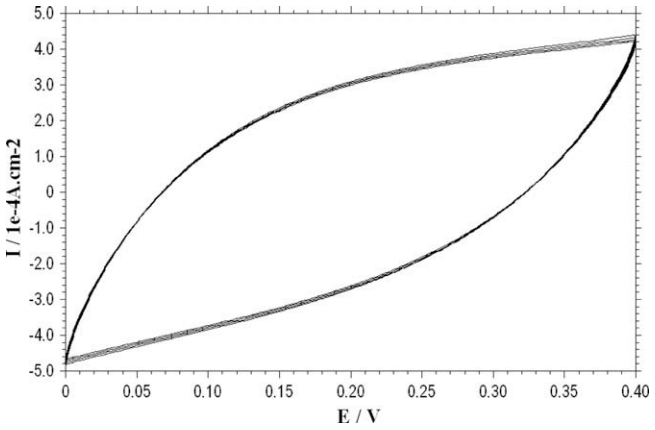

Fig. 6. Successive CVs recorded for polypyrrole/chitosan composite coated sample on the Pt electrode in 3.5% NaCl.

Fig. 5. Polypyrrole film has given the well known cauliflower-like spherical particles (Yalçınkaya, Tüken, Yazıcı, & Erbil, 2008b). However, chitosan has a smooth surface (Demetgül & Serin, 2008). The SEM micrographs were indicating to significant differences among morphologies of single polypyrrole, chitosan and the composite. Therefore, this differences can be attributed to the formation of the composite.

3.5. Electrochemical behavior

The successive cycles which are given in Fig. 6 were recorded in 3.5% NaCl solution. They have given to get the information about the stability and electroactivity of the composite film obtained on Pt electrode. The oxidation of the composite film was observed in the forward scan and the reduction was realized at the reverse scan (redox behavior) (Lyons, 1994). The current density values involved during these successive cycles were informative in aspect of composite film's electroactivity and degradability (Yalçınkaya et al., 2008b). It must be noted that the current values were highly stable, that the composite film did not undergo any degradation and regularly changed between its redox states. It could be resulted that the composite film was also very stable and extremely electroactive.

3.6. Thermal stability

The thermal stability and the degradation behavior of polypyrrole/chitosan composite were studied by TG–DTA under air atmosphere. The TG–DTA curves of polypyrrole/chitosan composite were given in Fig. 7. It is well known that chitosan have two mass loss stages as water elimination and the decomposition (not shown). These stages are observed at 40–100 °C range and 280–400 °C range, respectively (Demetgül & Serin, 2008).

At the TG–DTA curve of the composite, the weight loss was observed at 40–140 °C assigned to the water elimination as two stages with endothermic process. The first stage of the thermal degradation was observed at 150–200 °C range which attributed to removal of dopant molecules (oxalate ion) from the polymer structure. Besides, the minimum weight loss was occurred at 300–370 °C range assigned to the decomposition of chitosan chains which not contributed to the composite. On the other hand, the maximum weight loss was observed at 380–440 °C range which attributed to the degradation and interchain crosslink of the composite as an exothermic process (Sharma, Saxena, Annapoorni, & Malhotra, 2001).

When the results of polypyrrole/chitosan composite compared with the results of the chitosan in terms of the thermal behaviors; there are many important differences can be observed might be due to the interaction between polypyrrole and chitosan.

As a result, when the thermal behaviors of the composites were given in the literature (Yavuz et al., 2008) examined, it can be easily stated that the polypyrrole/chitosan composite exhibited a better final degradation temperature than chitosan.

4. Conclusions

Polypyrrole/chitosan composite film has been successfully synthesized on the platinum electrode, from aqueous oxalic acid solution by cyclic voltammetry technique. Characterization of the composite film was performed by FT-IR, cyclic voltammetry, SEM micrographs and thermal analysis (TG–DTA). The SEM has shown that the composite film was homogenously covering the metal surface, without any crack or significant defect. Also, the TG–DTA measurements have proved that the composite film had better thermal stability when compared to chitosan. The results of the electrochemical behavior studies have shown that the composite film is very stable and extremely electroactive. The higher stability

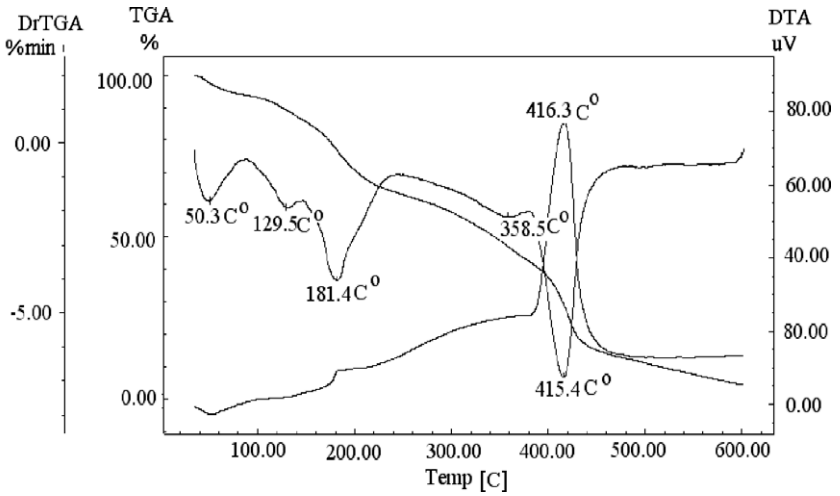

Fig. 7. TG/DTG/DTA/curves for pyrrole/chitosan composite.

of synthesized composite film is promising for the applications (electrocatalysis, biosensor, anticorrosive coating etc.).

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References

Abdia, M. M., Kassima, A. B., Mahmud, H. N. M. E., Yunus, W. M. M., & Talib, Z. A. (2009). Electrical and shielding properties of conductive polymer composite matrix with chitosan. *Solid State Science and Technology, 17*(1), 12–21.

Borole, D. D., Kapadi, U. R., Mahulikar, P. P., & Hundivale, D. G. (2006). Electrochemical synthesis and characterization of conducting copolymer: Poly(*o*-aniline-co-toluidine). *Materials Letters, 60*, 2447–2452.

Chan, H. S. O., Ng, S. C., Sim, W. S., Seow, S. H., Tan, K. L., & Tan, B. T. G. (1993). Synthesis and characterization of conducting poly(*o*-aminobenzyl alcohol) and its copolymers with aniline. *Macromolecules, 26*, 144–150.

Demetgül, C., & Serin, S. (2008). Synthesis and characterization of a new vic-dioxime derivative of chitosan and its transition metal complexes. *Carbohydrate Polymers, 72*, 506–512.

Hechavarria, L., Hu, H., & Rincon, M. E. (2003). Polyaniline-poly(2-acrylamido-2-methyl-1-propanosulfonicacid) composite thin films: Structure and properties. *Thin Solid Films, 441*, 56–62.

Herrasti, P., Recio, F. J., Ocon, P., & Fatas, E. (2005). Effect of the polymer layers and bilayers on the corrosion behaviour of mild steel: Comparison with polymers containing Zn microparticles. *Progress in Organic Coating, 54*, 285–291.

Ivanov, S., Mokreva, P., Tsakova, V., & Terlemezyan, L. (2003). Electrochemical and surface structural characterization of chemically and electrochemically synthesized polyaniline coating. *Thin Solid Films, 441*, 44–49.

Jeevananda, T., Seetharamu, S., Saravanan, S., & D'Souza, L. (2004). Synthesis and characterization of poly(aniline-co-acrylonitrile) using organic benzoyl peroxide by inverted emulsion method. *Synthetic Metals, 140*, 247–260.

Kim, J. W., Cho, C. H., Liu, F., Choi, H. J., & Joo, J. (2003). Physical characteristics of aniline/pyrrole copolymer. *Synthetic Metals, 135–136*, 17–18.

Kurita, K. (1998). Chemistry and application of chitin and chitosan. *Polymer Degradation and Stability, 59*(2), 117–120.

Li, X., Huang, M., Wang, L., Zhu, M., Menner, A., & Springer, J. (2001). Synthesis and characterization of pyrrole and *m*-toluidine copolymers. *Synthetic Metals, 123*, 435–441.

Lyons, M. E. G. (Ed.). (1994). *Electroactive polymer electrochemistry*. New York: Plenum Press [Part 1].

Liao, C., & Gu, M. (2002). Electroless deposition of polyaniline film via autocatalytic polymerization of aniline. *Thin Solid Films, 408*, 37–42.

Mansouri, S., Lavigne, P., Corsi, K., Benderdour, M., Beaumont, E., & Fernandes, J. C. (2004). Chitosan–DNA nanoparticles as non-viral vectors in gene therapy: Strategies to improve transfection efficacy. *European Journal of Pharmaceutics and Biopharmaceutics, 57*, 1–8.

Mathur, N. K., & Narang, C. K. (1990). Chitin and chitosan, versatile polysaccharides from marine animals (PROD). *Journal of Chemical Education, 67*(11), 938.

Motheo, A. J., Pantoja, M. F., & Venancio, E. C. (2004). Effect of monomer ratio in the electrochemical synthesis of poly(aniline-co-*o*-methoxyaniline). *Solid State Ionics, 171*(1–2), 91–98.

Rahman, S. U., Abul-Hamaley, M. A., & Abul Alem, B. J. (2005). Electrochemically synthesized polypyrrole films as primer for protective coating on carbon steel. *Surface and Coatings Technology, 200*, 2948–2954.

Ravi Kumar, M. N. V. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers, 46*, 1–27.

Sazou, D. (2001). Electrodeposition of ring-substituted polyanilines on Fe surfaces from aqueous oxalic acid solutions and corrosion protection of Fe. *Synthetic Metals, 118*, 133–147.

Sharma, A. L., Saxena, V., Annapoorni, S., & Malhotra, B. D. (2001). Synthesis and characterization of a copolymer: Poly(aniline-co-fluoroaniline). *Journal of Applied Polymer Science, 81*, 1460–1466.

Tian, F., Liu, Y., Hu, K., & Zhao, B. (2004). Study of the depolymerization behavior of chitosan by hydrogen peroxide. *Carbohydrate Polymers, 57*, 31–37.

Tuken, T., Arslan, G., Yazıcı, B., & Erbil, M. (2004). The corrosion protection of mild steel by polypyrrole/polyphenol multilayer coating. *Corrosion Science, 46*, 2743–2754.

Tuken, T., Yazıcı, B., & Erbil, M. (2007). Polypyrrole modified nickel coating on mild steel. *Materials Design, 28*, 208–216.

Umare, S. S., Borkar, A. D., & Gupta, M. C. (2002). Influence of copolymer composition on the transport properties of conducting copolymers: Poly(aniline-co-*o*-anisidine). *Material Science, 25*, 235–239.

Yalçınkaya, S., Tüken, T., Yazıcı, B., & Erbil, E. (2008a). Electrochemical synthesis and corrosion performance of poly(pyrrole-co-*o*-anisidine). *Progress in Organic Coatings, 62*, 236–244.

Yalçınkaya, S., Tüken, T., Yazıcı, B., & Erbil, E. (2008b). Electrochemical synthesis and characterization of poly(pyrrole-co-*o*-toluidine). *Progress in Organic Coatings, 63*, 424–433.

Yavuz, A. G., Uygun, A., & Bhethanabotla, V. R. (2008). Substituted polyaniline/chitosan composites: Synthesis and characterization. *Carbohydrate Polymers, 75*, 448–453.