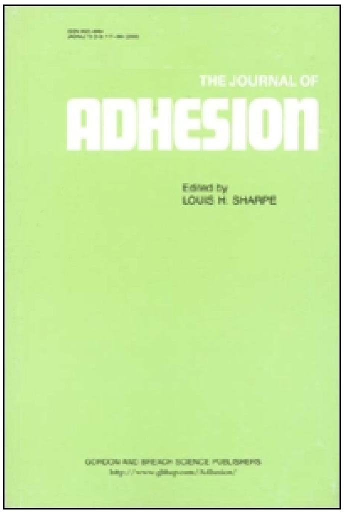


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Carbon fiber-polyaniline composites: Kinetics of electrodeposition of polyaniline onto carbon fibers by cyclic voltammetry

Aydin Aykanat[a]; Jude O. Iroh[a]
[a] Materials Science and Engineering, University of Cincinnati, Cincinnati, OH, USA

To cite this Article Aykanat, Aydin and Iroh, Jude O.(2002) 'Carbon fiber-polyaniline composites: Kinetics of electrodeposition of polyaniline onto carbon fibers by cyclic voltammetry', The Journal of Adhesion, 78: 7, 629 — 643
To link to this Article: DOI: 10.1080/00218460213739
URL: http://dx.doi.org/10.1080/00218460213739

The Journal of Adhesion, 78: 629–643, 2002
Copyright © 2002 Taylor & Francis
0021-8464/02 $12.00 +.00
DOI: 10.1080/00218460290010340

CARBON FIBER-POLYANILINE COMPOSITES: KINETICS OF ELECTRODEPOSITION OF POLYANILINE ONTO CARBON FIBERS BY CYCLIC VOLTAMMETRY

Aydin Aykanat
Jude O. Iroh
Materials Science and Engineering, University of Cincinnati,
Cincinnati, OH, USA

Homogeneous and uniform coatings of polyaniline were successfully deposited on carbon fibers by an aqueous electrodeposition technique using p-toluene sulfonic acid as the electrolyte. Electrochemical deposition of aniline was carried out by cyclic voltammetry in the potential range of $-0.2\,V$ *to* $1.0\,V$ *versus saturated calomel electrode (SCE). The electrochemical deposition parameters such as the number of cycles, scan rate (SR), initial monomer ([M]), and electrolyte concentration ([E]) were systematically varied. The amount of composite coatings on carbon fibers was dependent on the electrochemical deposition parameters. From a weight gain analysis, the rate of the reactions* (R_p) *was calculated. As the aniline concentration was increased up to 0.35 M and electrolyte concentration up to 0.5 M, the deposition rate also increased, whereas an increase in scan rate decreased the deposition rate. Kinetic analysis showed that the rate equation for the p-toluene sulfonic acid system is* $R_p \propto SR^{-1.25} [M]^{0.73} [E]^{0.95}$. *IR spectra also showed an increase in the deposition of polyaniline coatings on carbon fibers with a decrease in the scan rate and an increase in both monomer and electrolyte concentration. The ratio of two oxidation states of polyaniline obtained during electrodeposition, namely emeraldine and pernigraniline, can be varied by changing the electrochemical deposition parameters.*

Keywords: Polyaniline; Electrodeposition; Kinetics; Cyclic voltammetry; Carbon fiber

Received 5 September 2001; in final form 8 March 2002.

This is one of a Collection of papers honoring Hatsuo (Ken) Ishida, the recipient in February 2001 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

We would like to express our sincere thanks to the National Science Foundation for funding this ongoing research.

Address correspondence to Jude O. Iroh, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA. E-mail: jiroh@uceng.uc.edu

INTRODUCTION

In composites the adhesion between the reinforcement and the matrix plays an important role in the transfer of an applied load from the matrix to the fibers and thus ultimately affects the properties of the composites. Diffusion, wetting, chemical bonding, and mechanical interlocking are factors that contribute to the adhesion in composite materials. Poor adhesion between the fibers and the matrix will result in premature failure of the composite [1]. The interfacial and interlaminar strength of composites, particularly carbon fiber-epoxy composites, can be improved by using different surface treatment techniques including oxidative and nonoxidative methods [2]. In general, application of an adherent polymeric interphase increases the surface roughness of carbon fibers and provides stronger mechanical interlocking. It also increases the chemical reactivity of the interfacial region by providing functional groups that form chemical bonding with the matrix [3]. Surface treatment of carbon fibers by an electrochemical polymerization technique provides uniform and homogeneous coatings. By controlling the electrodeposition variables such as applied potential, monomer concentration, electrolyte concentration, and reaction time, the amount and structure of the coating can be easily controlled [4, 6].

During the last two decades, conductive polymers have been considered for many industrial applications such as lightweight batteries, electrochemical sensors, gas separating membranes, electrochromic displays, ion exchangers, and corrosion inhibitors.

Among the conducting polymers, polyaniline has attracted considerable attention due to its good chemical and environmental stability, high electrical conductivity, high redox reversibility, and ease of synthesis by chemical and electrochemical techniques [5]. Preliminary research in our laboratory showed that the application of high-temperature, stable, conducting polymer interphases on carbon fibers can be successfully achieved by electrochemical deposition [6–8, 18].

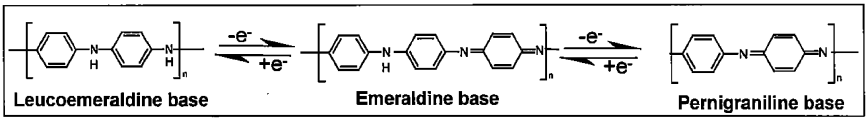
Electrochemical polymerization of aniline has been used extensively because the reaction conditions can be easily controlled and different structures and properties of polyaniline can be obtained. The electrodeposition mechanism of polyaniline is very complex due to the fact that several processes such as the polymerization reaction itself, doping, degradation due to over-oxidation, and adsorption of the electrolyte on the electrode surface take place. Iroh and Rajagopalan studied the effect of electrochemical process variables on the formation of polyaniline coatings on carbon fibers in aqueous toluene sulfonate solution by a constant potential technique [9]. Zinger and Shkolnik synthesized a thick polyaniline coating on carbon fibers by direct oxidation of aniline [10]. Of the electrochemical techniques, cyclic voltammetry (CV) is particularly useful for understanding the basic aspects of polymer growth and the redox mechanism. Jannakoudakis and his coworkers investigated the anodic oxidation of aniline on carbon fiber electrodes by cyclic voltammetry [11−13] and in aqueous methanolic solution at various pH values [11] in order to deposit surface-active groups on carbon fibers.

Polyaniline can exist in three different oxidation states as a result of charge transfer reactions in polymer chains and doping by acid anions. During the oxidation-reduction reaction of the electroactive polymer, the doping agent diffuses either into the polymer or into the solution in order to maintain total charge. The redox reactions of three different forms of polyaniline, namely leucoemeraldine (fully reduced form), emeraldine (intermediate form), and pernigraniline (fully oxidized form), are shown in Scheme 1 [14−15].

In this paper, we report the kinetics of electropolymerization of polyaniline deposition on carbon fibers in p-toluene sulfonic acid aqueous by use of cyclic voltammetry. Electrochemical process parameters such as scan rate, monomer concentration, electrolyte concentration, and reaction time were systematically varied and their effect on the rate of polymerization was investigated. By optimizing the reaction conditions, reactive functional groups were introduced onto the surface of the coating. The SEM pictures of polyaniline coatings on carbon fibers show a dense and rough surface structure [16–18], which will also increase the adhesion of carbon fibers by mechanical interlocking.

EXPERIMENTAL

The electrochemical polymerization of aniline on carbon fibers was carried out in a one-compartment polypropylene cell. The unsized 6K T650/35 carbon fibers used as the working electrode were obtained from AMOCO Performance Products Company. The continuous carbon fiber bundle was wrapped onto an H-shaped polypropylene frame and placed in the center of the cell. A piece of aluminum foil held the fibers securely to the frame. The counter electrodes comprised of stainless



SCHEME 1 Different oxidation states of polyaniline.

steel plates were fitted into the slots and placed on both sides of the working electrode. The working electrode and the counter electrode were used as the anode and cathode, respectively. A saturated calomel electrode (SCE) purchased from Fisher Scientific Company was used as the reference electrode. All the electrodes were connected to an EG&G Potentiostat/Galvanostat Model 273A [9].

In this research work, deionized water was used as solvent for all the reactions. Aniline (99.5% pure) was purchased from Aldrich Chemical Company, and the concentrations of aniline that were used as the monomer were 0.1, 0.25, 0.35, and 0.5 M. For the electropolymerization reactions, p-toluene sulfonic acid was purchased from Aldrich Chemical Company and concentrations of 0.1, 0.25, 0.5, 0.65, and 0.8 M were used in the reactions. For each reaction 100 ml of solution was prepared, and the solution in the electrochemical cell was changed at the end of each reaction. The electrochemical polymerization reaction was performed using cyclic voltammetry between the potential range of -0.2 V to 1.0 V. The reactions were carried out at different scan rates and for different numbers of cycles. Potential versus current curves for the reactions were plotted. The scan rates were 20, 30, 50, and 100 mV/sec, and the numbers of cycles were 1, 2, 3, 4, 5, 10, 15, and 25. At the completion of the reactions, the coated fibers were rinsed with deionized water and dried at room temperature for 24 h. The fibers were then dried in vacuum oven for 1 h at 100°C. The weight of the coated samples was measured with a Denver Instrument Company XE Model 100A until constant weight was obtained.

Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer 1800 FTIR spectrometer. The coated carbon fibers were ground and 1–2 % of the ground carbon fiber was mixed with IR-grade potassium bromide (KBr) powder. Clear and homogeneous pellets were obtained by subsequent pressing of the mixture. The samples were scanned between 4000 to 400 cm^{-1}. The spectra were averaged over 256 scans at a resolution of 8 cm^{-1}. The background spectrum of the uncoated carbon fibers mixed with KBr was subtracted from the acquired spectra.

RESULTS AND DISCUSSION

Electrochemical Deposition of Polyaniline on Carbon Fibers

Polyaniline was deposited on the carbon fibers by cyclic voltammetry using toluene-4-sulfonic acid as the electrolyte.

Figure 1 shows a typical cyclic voltammogram of the electrochemical deposition of 0.1 M aniline on carbon fiber using 0.25 M toluene-4-sulfonic acid as the electrolyte at 20 mV/sec. During the first

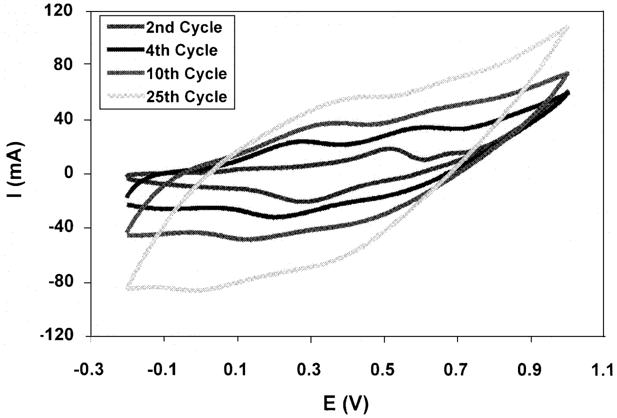


FIGURE 1 Typical cyclic voltammogram of polyaniline coatings on carbon fibers at a scan rate of 20 mV/s.

cycle, the onset of an oxidation wave around 1.0 V versus SCE was observed. This peak is due to the oxidation of aniline, which initiates the electropolymerization reaction. For the second cycle, two redox peaks are seen at 0.2 V and 0.5 V versus SCE. These peaks correspond to the formation of leucoemeraldine and the emeraldine form of polyaniline, respectively. As the number of cycles is increased, the anodic peaks at 0.2 V and 0.5 V versus SCE shift to higher potentials. We believe that this shift is due to both formation of the higher oxidized form of polyaniline and the amount of deposition on the carbon fiber that increases the resistance of the working electrode. The increase in the area between the oxidation and reduction peaks shows the electroactivity of the doped polyaniline coating on the carbon fibers. There is also an increase in the peak currents as we increase the number of cycles. This suggests that the amount of polyaniline coating formed on the carbon fibers increases with increase in the number of cycles.

Effect of Electrochemical Deposition Parameters

In order to study the effect of various electrochemical parameters on the rate of polymerization (R_p) of polyaniline, a systematic investigation of weight gain versus time as a function of the parameters was done. The parameters of importance were

1. Scan rate (v),
2. Concentration of monomer ([M]), and
3. Concentration of electrolyte ([E]).

The weight gain was calculated as follows:

$$\%Weight\ gain = \frac{W_{coated} - W_{uncoated}}{W_{uncoated}} \times 100. \tag{1}$$

The rate of polymerization can be calculated using the weight gain data as follows:

$$R_p = \frac{dM}{dt} = Slope\ of\ weight\ gain\ plot\ versus\ time, \tag{2}$$

where M is the mass of the polymer.

The effect of electrochemical deposition parameters on the rate of polymerization can be represented as

$$R_p \propto \upsilon^a [M]^b [E]^c, \tag{3}$$

where a, b, and c are the order of the reactions.

The reaction orders can be calculated by measuring the slope of the logarithm of rate of polymerization versus logarithm of individual deposition parameters while keeping the other parameters constant. This is shown in Eq. (4):

$$\log R_p = a \log \upsilon + b \log[M] + c \log[E] + \log k, \tag{4}$$

where k is a constant.

Effect of Scan Rate

Figure 2 shows the plot of percentage weight gain of fibers due to the formation of polyaniline coatings on carbon fibers with respect to time

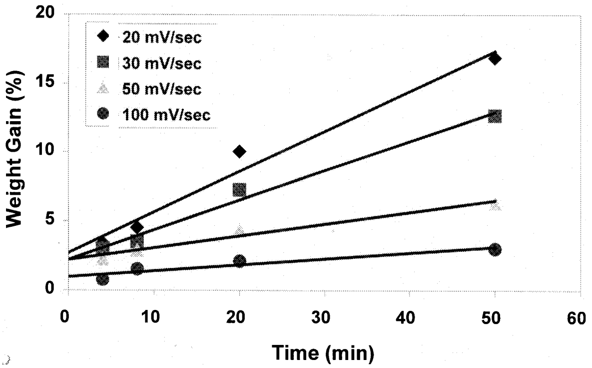


FIGURE 2 Effect of scan rate on the weight gain of polyaniline coating on carbon fibers.

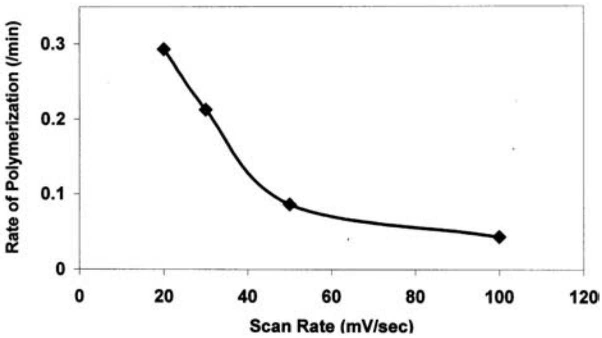


FIGURE 3 Scan rate versus rate of polymerization of polyaniline coating on carbon fibers.

for different scan rates. The figure shows a linear relationship between the weight gain of the carbon fibers and the reaction time due to deposition. After 25 cycles, when the scan rate was 20 mV/s, the weight gain due to deposition was around 18%, whereas it was around 4% at the scan rate of 100 mV/s. This is due to the fact that at high scan rates, for a constant number of cycles, the reaction time is less. By using the slopes of the lines in Figure 2, the rate of polymerization can be calculated.

Figure 3 shows the plot of rate of polymerization with respect to scan rate. Since scan rate is related to the reaction time, as the scan rate decreases reaction time increases and the rate of polymerization increases. An exponential decrease in the rate of reaction can be seen with an increase of scan rate. From the slope of log rate of polymerization against log scan rate (Figure 4) an exponent of -1.25 was obtained: $R_p \propto SR^{-1.25}$.

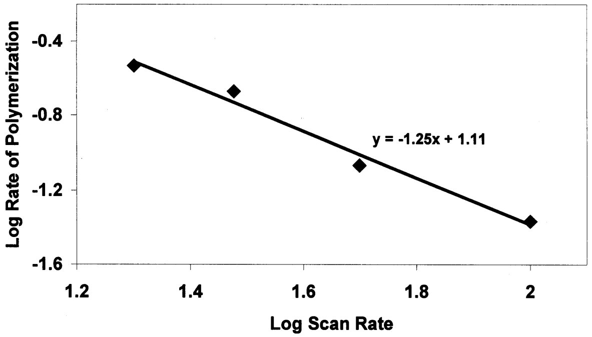


FIGURE 4 Log scan rate versus log rate of polymerization.

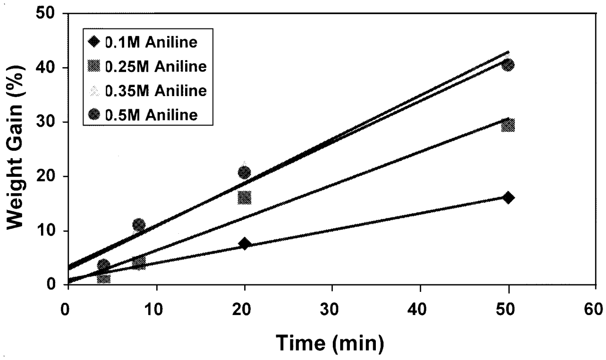


FIGURE 5 Effect of monomer concentration on the weight gain of polyaniline coating on carbon fibers.

Effect of Monomer Concentration

Figure 5 shows the plot of percentage weight gain of fibers due to the formation of polyaniline coatings on carbon fibers with respect to time for different monomer concentrations at the scan rate of 20 mV/s. As the monomer concentration increases, the amount of deposited polymer coating increases linearly. By using the slopes of the lines in Figure 5, the rate of polymerization can be calculated.

Figure 6 shows the plot of rate of polymerization with respect to monomer concentration. From 0.1 M to 0.35 M aniline concentration the rate of polymerization increases. Beyond 0.35 M aniline concentration, aniline is only sparingly soluble in water; therefore, the rate of the reaction does not change significantly. Besides this, a high

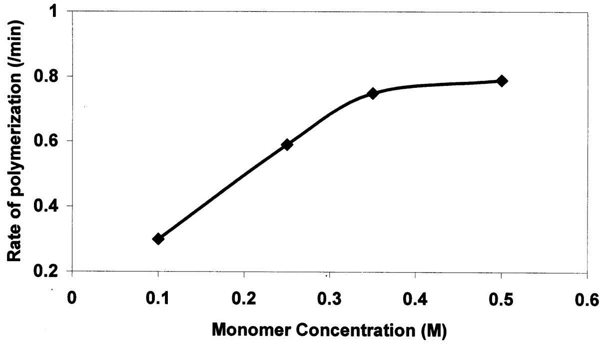


FIGURE 6 Monomer concentration versus rate of polymerization of polyaniline coating on carbon fibers.

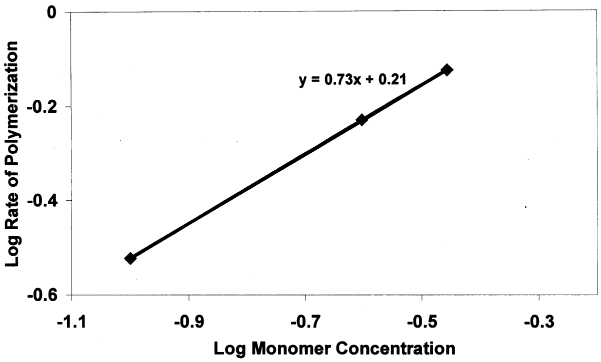


FIGURE 7 Log monomer concentration versus log rate of polymerization.

concentration of aniline also slows down the diffusion of the electrolyte both into the solution and into the polymer that has already been deposited. From the slope of log rate of polymerization versus log scan rate (Figure 7) between 0.1 M and 0.35 M aniline concentrations an exponent of 0.73 was obtained: $R_p \propto [M]^{0.73}$.

Effect of Electrolyte Concentration

Figure 8 shows the plot of percentage weight gain of fibers due to the formation of polyaniline coatings on carbon fibers with respect to time for different p-toluene sulfonic acid concentrations. As the electrolyte concentration increases, the amount of deposited polymer coating increases linearly. By using the slopes of the lines in Figure 9, the rate of polymerization can be calculated.

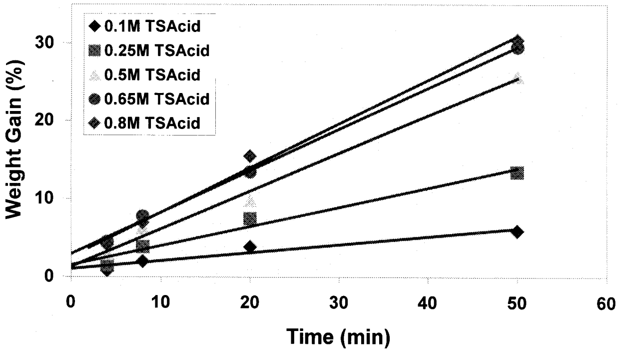


FIGURE 8 Effect of electrolyte concentration on the weight gain of polyaniline coating on carbon fibers.

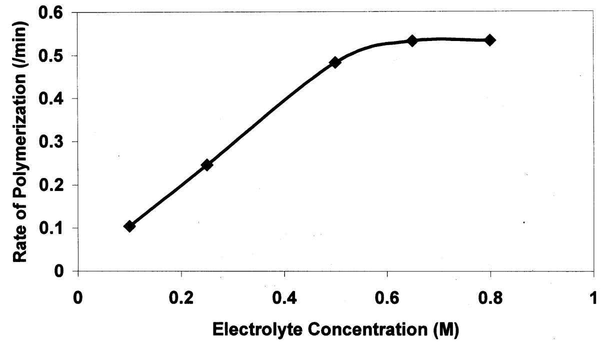


FIGURE 9 Electrolyte concentration versus rate of polymerization of polyaniline coating on carbon fibers.

Figure 9 shows the plot of rate of polymerization with respect to electrolyte concentration. From 0.1 M to 0.5 M p-toluene sulfonic acid concentration the rate of polymerization increases. From 0.5 to 0.8 M electrolyte concentration the rate of the reaction does not change significantly. Actually, this result is in accordance with the results obtained from the effect of monomer concentration. Since the optimal concentration of the electrolyte is 0.5 M, the rate of the reaction is highest at this concentration. As the concentration of the electrolyte increases the thickness of the coating will also increase, and that makes the diffusion of the electrolyte more difficult. Therefore, the rate of the reaction does not change after a certain concentration of the electrolyte. From the slope of log rate of polymerization versus log scan rate (Figure 10) between 0.1 M and 0.5 M p-toluene sulfonic acid concentration an exponent of 0.95 was obtained: $R_p \propto [E]^{0.95}$.

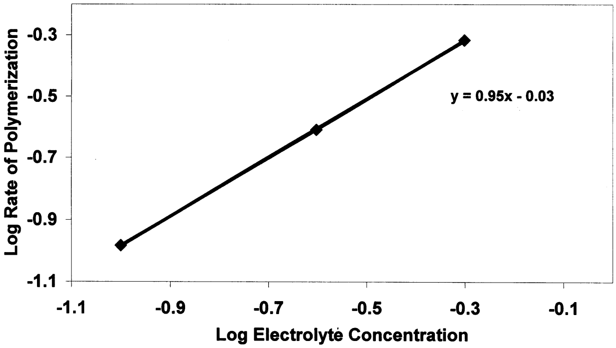


FIGURE 10 Log electrolyte concentration versus log rate of polymerization.

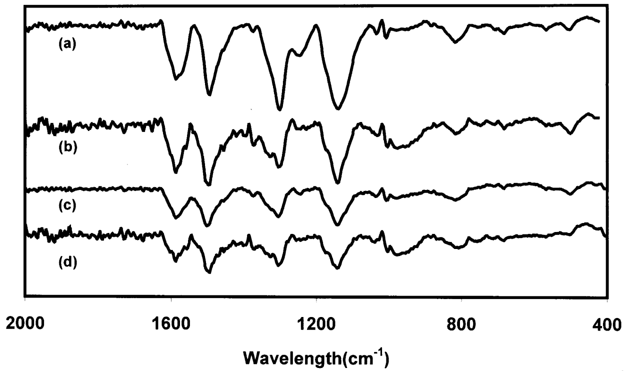


FIGURE 11 Infrared spectra of polyaniline coatings as a function of scan rate, (a) 20 mV/s, (b) 30 mV/s, (c) 50 mV/s, and (d) 100 mV/s.

Infrared Spectra of Carbon Fibers with Deposited Polyaniline

Effect of Scan Rate

Figure 11 shows the comparison of the infrared spectra of polyaniline coatings on carbon fibers as a function of scan rate. The characteristic polyaniline peaks occur at 1600, 1500, 1300, and 830 cm^{-1}. These peaks are due to C=N stretch, C–N stretch, N–H deformation, and p-substituted benzene ring, respectively. In addition to this, we see peaks due to toluene sulfonate (dopant) at 1180, 1030, and 1010 cm^{-1}. As the scan rate increases, the intensity of the 1300 and 1180 cm^{-1} peaks decreases. This shows the decrease in the deposition and amount of dopant. This result agrees with both the cyclic voltammograms and weight gain data.

After deconvolution of the 1600 and 1500 cm^{-1} peaks and calculation of the peak areas, we observed that an increase in scan rate increases the 1600 to 1500 ratio (Figure 12). This result suggests that at high scan rates the polyaniline coating on carbon fibers have more quinoid structure (pernigraniline base) than benzenoid structure (emeraldine base). Although the reaction time is short at high scan rates, with the application of higher voltage per unit time, higher oxidation states of polyaniline were obtained.

Effect of Monomer Concentration

Figure 13 shows the comparison of the infrared spectra of polyaniline coatings on carbon fibers as a function of monomer concentration after 25 cycles. As the concentration of the monomer increases, the intensity of the characteristic polyaniline peaks at 1600,

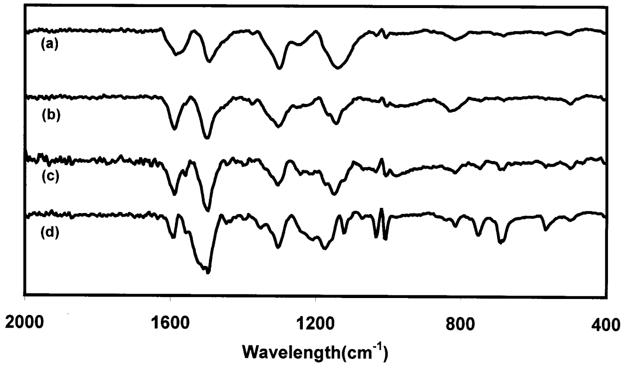


FIGURE 12 Ratio of the 1600 and 1500 cm^{-1} peaks as a function of scan rate.

1500, 1300, and 830 cm^{-1} increases. At 0.5 M aniline concentration, the dopant peaks due to the electrolyte becoming more clear and sharp (Figure 13). Figure 14 shows the ratio of quinoid groups to benzenoid groups with respect to monomer concentration. At 0.1 M aniline concentration the amount of the quinoid groups is 1.3 times that of the benzenoid groups. But as the concentration of the monomer increases, the amount of quinoid groups decreases. As the concentration of aniline is increased to 0.5 M, the ratio drops to 0.7. This result shows that at high aniline concentration, polyaniline coatings on carbon fibers have more benzenoid structure (emeraldine base) than quinoid structure (pernigraniline base). As the thickness of the coatings increases with the increase in the monomer concentration, the diffu-

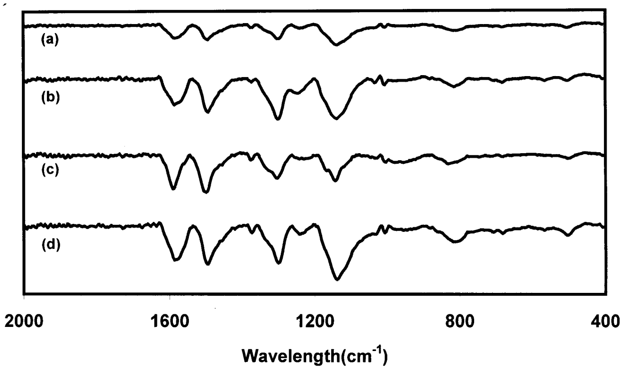


FIGURE 13 Infrared spectra of polyaniline coatings as a function of monomer concentration, (a) 0.1 M, (b) 0.25 M, (c) 0.35 M, and (d) 0.5 M.

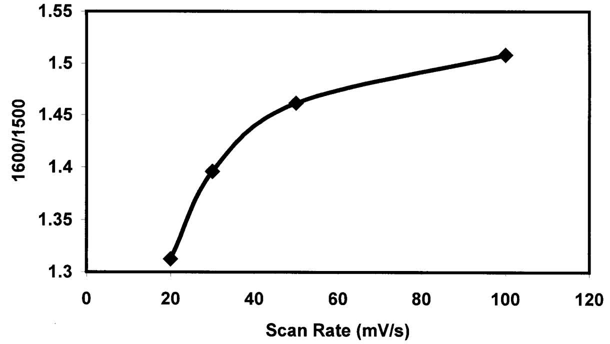


FIGURE 14 Ratio of the 1600 and 1500 cm^{-1} peaks as a function of monomer concentration.

sion-controlled mechanism of polyaniline deposition causes a decrease in the amount of the fully-oxidized form of polyaniline.

Effect of Electrolyte Concentration

Figure 15 shows the IR spectra of polyaniline coatings on carbon fibers with respect to electrolyte concentration after 25 cycles. Figure 16 shows a linear decrease in the 1600/1500 peak ratio. At 0.1 M electrolyte concentration the amount of quinoid groups is almost 1.5 times that of benzenoid groups. But, as the concentration of the electrolyte increases, the amount of quinoid groups decreases linearly. At 0.65 M electrolyte concentration, the ratio dropped to 0.8 M. This result can also be explained by a diffusion-controlled mechanism.

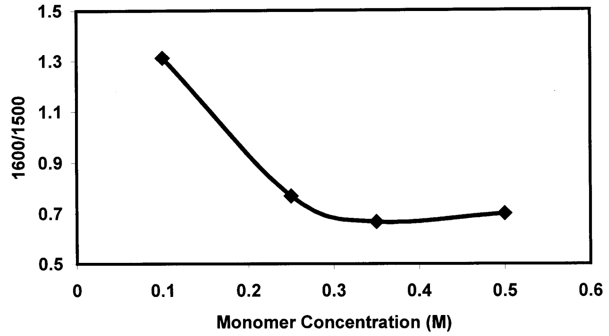


FIGURE 15 Infrared spectra of polyaniline coatings as a function of electrolyte concentration, (a) 0.1 M, (b) 0.25 M, (c) 0.5 M, and (d) 0.65 M.

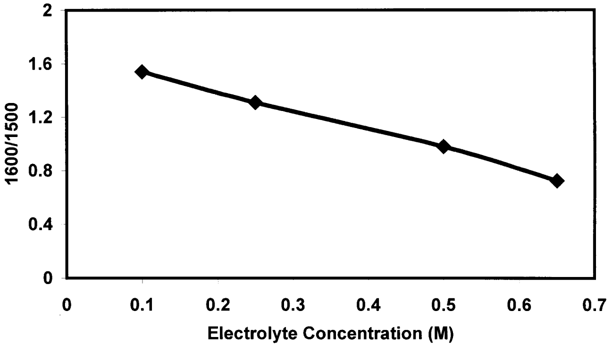


FIGURE 16 Ratio of the 1600 and 1500 cm^{-1} peaks as a function of electrolyte concentration.

CONCLUSIONS

The effect of reaction parameters on the electrodeposition of polyaniline coatings on carbon fibers in aqueous p-toluene sulfonic acid solution was studied. The rate of formation of polyaniline coatings decreases with increase in scan rate. High monomer concentrations ($\geq$0.35 M), did not affect the rate of the reaction significantly. Below 0.35 M monomer concentration, the rate of reaction increases with increasing monomer concentration. Similarly, high electrolyte concentrations ($\geq$0.5 M) did not affect the rate of the reaction significantly. Below 0.5 M monomer concentration, the rate of reaction increases with increasing monomer concentration. The rate equation of the reaction is

$$R_p \propto SR^{-1.25}[M]^{0.73}[E]^{0.95}.$$

Since the deposition of polyaniline onto carbon fibers was initiated by an electrochemical oxidation reaction, the effect of scan rate on the rate of reaction is larger than the effect of electrolyte and monomer concentration. The diffusion-controlled mechanism of the reaction explains the importance of the electrolyte concentration. The higher value of the power of electrolyte concentration compared with that of monomer concentration indicates that the electrolyte not only serves as the dopant but also plays an active role in the electropolymerization of aniline.

The effect of electrochemical deposition parameters on the oxidation state of polyaniline coatings shows that at high scan rates and low electrolyte and monomer concentrations the amount of quinoid groups exceeds that of benzenoid groups, whereas at lower scan rates and high electrolyte and monomer concentrations benzenoid groups are favored. So, as a result, we will obtain a polyaniline structure that has more secondary amine groups than tertiary amine groups. The reactive secondary amine groups on the surface of carbon fibers can improve the adhesion and interfacial strength of the fibers in a polymeric composite.

REFERENCES

[1] Agarwal, B. D. and Broutman, L. J., *Analysis and Performance of Fiber Composites* (John Wiley, New York, 1990).

[2] Drzal, L. T., Rich, M. J., Koenig, M. F., and Lloyd, P. F., *J. Adhesion* **16**, 133 (1983).

[3] Wu, S., *Polymer Interface and Adhesion* (Marcel Dekker, New York, 1982).

[4] Iroh, J. O. and Wood, G. A., *Composites*, *Part B* **29B**, 181 (1998).

[5] Pei, Q. and Bi, X., *J. Appl. Polm. Sci.* **38**, 1819 (1989).

[6] Iroh, J. O. and Wood, G. A., *Polym Eng. & Sci.* **36**, 2389 (1997).

[7] Iroh, J. O. and Williams, C., *Synth. Met.* **99**, 1 (1999).

[8] Iroh, J. O. and Wood, G. A., *Eur. Polym. J.* **33**, 107 (1997).

[9] Iroh, J. O. and Rajagopalan, R., *J. Appl. Polym. Sci.* **76**, 1503 (2000).

[10] Zinger, B. and Shkolnik, S., *Polymer* **30**, 628 (1989).

[11] Jannakoudakis, A. D., Jannakoudakis, P. D., Pagalos, N., and Theodoridou, E., *Electrochim Acta* **38**, 1559 (1993).

[12] Jannakoudakis, A. D., Jannakoudakis, P. D., Theodoridou, E., and Besenhard, J. O., *J. Appl. Electrochem.* **20**, 619 (1990).

[13] Jannakoudakis, P. D. and Pagalos, N., *Synth. Met.* **68**, 17 (1994).

[14] Epstein, A. J., Huang, W. S., and MacDiarmid, A. G., *Synth. Met.* **18**, 303 (1987).

[15] Huang, W. S., Humphrey, B. D., and MacDiarmid, A. G., *J. Chem. Soc. Faraday Trans.* **82**, 2385 (1986).

[16] Iroh, J. O. and Rajagopalan, R., *Surf. Eng.* **16**, 481 (2000).

[17] Cui, C. Q., Ong, L. H., Tan, T. C., and Lee, J. Y., *Electrochim. Acta* **38**, 1935 (1993).

[18] Aykanat, A. and Iroh, J. O., *Composite Interfaces* (in press).