

# Effect of Electrolytes and Process Parameters on the Electropolymerization of Pyrrole Onto Carbon Fibers

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## SYNOPSIS

The effect of electrolytes such as toluene-4-sulfonic acid sodium salt ( $T_4SNa$ ), dodecylbenzene-sulfonic acid sodium salt ( $DbSNa$ ), alzarin red S monohydrate, and dilute sulfuric acid and reaction parameters, including the monomer concentration, electrolyte concentration, applied voltage, and the reaction time, on the electrochemical polymerization of pyrrole onto carbon fibers was studied. The amount of polypyrrole coatings formed on the carbon fiber surface increased with increased monomer concentration, electrolyte concentration, applied voltage and reaction time, respectively, for each supporting electrolyte. However, the electrolyte concentration and applied voltage were shown to have a greater influence on the amount of polypyrrole coatings formed onto carbon fibers. Scanning electron microscopy micrographs show that the morphology of the coatings were dependent on the nature and concentration of the electrolyte. IR and elemental analysis of the coatings show that the counterion derived from the electrolyte was incorporated into the polypyrrole coatings. The elemental analysis of the coatings show that the ratio of pyrrole units to the counter ion is 2.64/1 for  $T_4SNa$ , 2.79/1 for  $DbSNa$ , and 5.32/1 for sulfuric acid. © 1996 John Wiley & Sons, Inc.

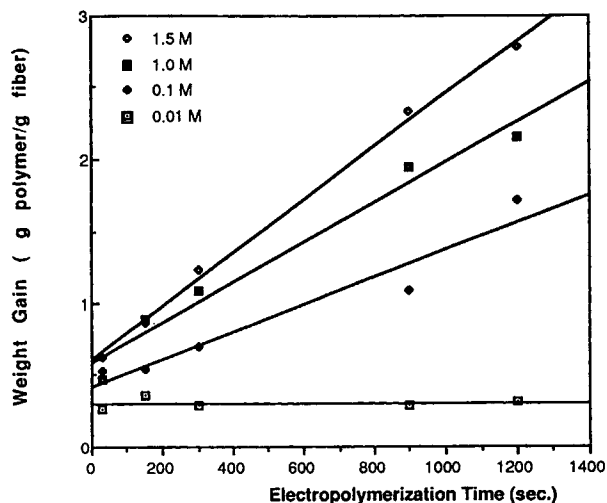
## INTRODUCTION

Fiber-matrix adhesion plays a crucial role in the transfer of an applied stress from the matrix to the fibers and thus ultimately influences the properties of composites.<sup>1,2</sup> In general, both chemical effects and physical effects such as mechanical interlocking and interdiffusion contribute to adhesion.<sup>3,4</sup> By applying a polymeric interphase with controlled properties and morphology, the chemical as well as the physical-mechanical contributions to fiber-matrix adhesion can be optimized. Osaka et al.<sup>5</sup> studied the effect of the counter ions on the electropolymerization and properties of polypyrrole films formed platinum substrate by using reagent grade  $LiClO_4$ ,  $LiPF_6$ ,  $LiBF_4$ , and propylene carbonate as the electrolytes and solvent. They reported a dependency between the counter ion used in the formation of the polypyrrole films and the electrochemical dop-

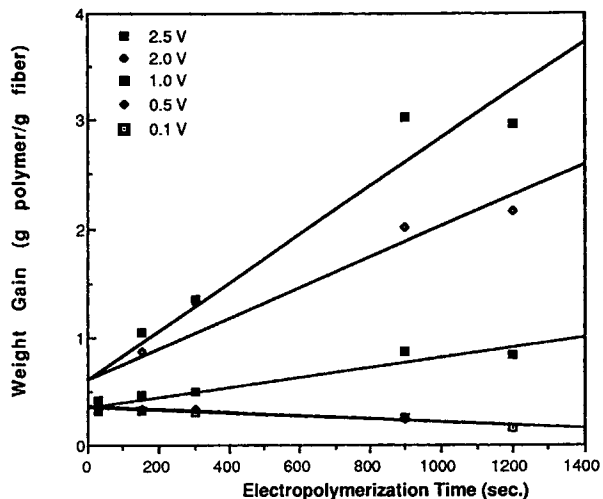
ing-undoping kinetics of electropolymerization of polypyrrole.<sup>5</sup>

A simple morphological model of electrical anisotropy of a conducting polypyrrole based on the arrangement of the polypyrrole chains was proposed by Montemayor et al.<sup>6</sup> They showed that the films grown at lower current densities have a marked chain-oriented morphology and a longer chain length in contrast to the films grown at higher current densities. Mammone and Binder<sup>7</sup> studied the influence of dopant ions on the dielectric and physical properties of electrochemically formed poly-*N*-methylpyrrole using aqueous-supporting electrolytes such as sodium sulphate, sulfuric acid, sodium carbonate, sodium hydrogen phosphate, sodium chloride, hydrochloric acid, and lithium perchlorate. They showed that the morphology and adherence of the polypyrrole films formed on the platinum substrate was dependent on the electrolyte used. Yamaura and coworkers<sup>8</sup> investigated the effect of counter ions on the structure and properties of polypyrrole films formed by anodic oxidation of the monomer in tetraethylammonium salt of  $BF_4^-$ ,  $ClO_4^-$ , and  $PF_6^-$  dissolved in propylene carbonate.

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**Figure 1** Weight gains due to coatings as a function of time for fiber samples coated using different concentrations of pyrrole monomer.  $[T_4SNa] = 0.25M$ ;  $E_{pa} = 1.5 V$ .



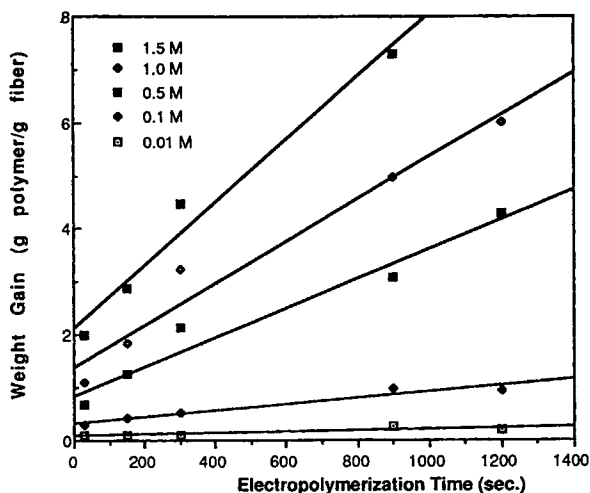
**Figure 3** Weight gain due to coating as a function of time for fiber samples coated with different voltages.  $[pyrrole] = 0.5M$ ;  $[T_4SNa] = 0.25M$ .

It was shown that the electrical conductivity and elongation of the film were dependent on the structure of the counter ions.<sup>8</sup> The films containing smaller counter ions showed higher electrical conductivity but the anisotropy in the conductivity of the stretched films was independent of the size of the counter ion.<sup>8</sup>

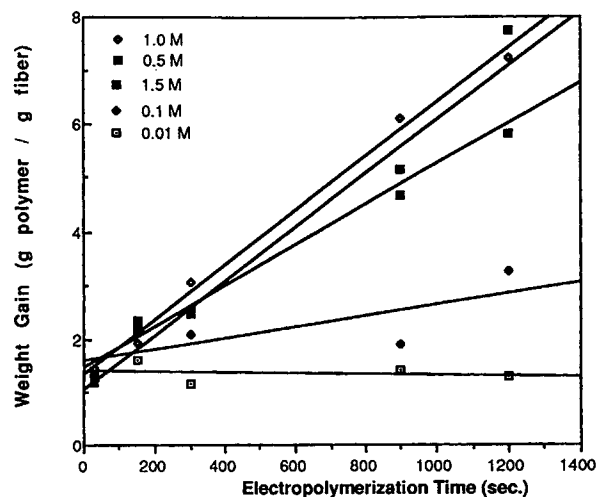
Electrochemical polymerization of polymers onto graphite fibers was performed by several researchers.<sup>9-16</sup> Iroh et al.<sup>9-11</sup> studied the electrochemical copolymerization of styrene and *N*-(3-carboxyphenyl) maleimide onto graphite fibers. Details of the mechanism and the kinetics of the reaction were reported.

They showed that the amount of coatings formed during electropolymerization increased with increased comonomer concentration and current density.<sup>9,10</sup> Electropolymerization of acrylamide was also performed by the same authors in an aqueous solution of acrylamide dissolved in dilute sulfuric acid solution.<sup>12</sup> In addition, Grunden and Iroh<sup>13</sup> successfully formed graphite fiber-polypyrrole coatings by aqueous electrochemical polymerization.

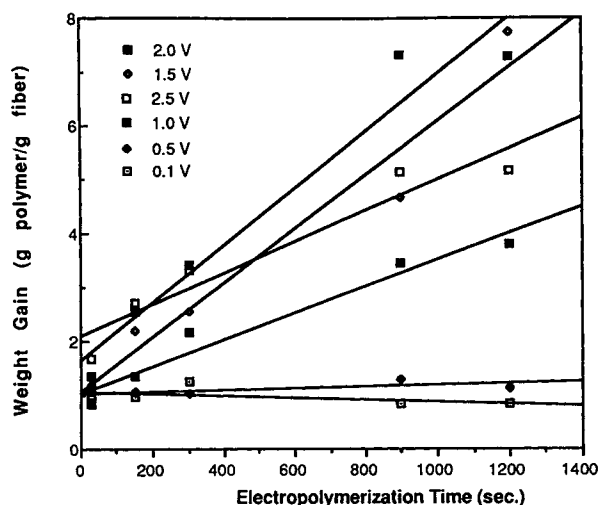
Attempts have been made to electrochemically form polymeric coatings onto fibers with the goal to improve the adhesion between the fibers and the matrix. Iroh et al.<sup>14</sup> electropolymerized poly(styrene-



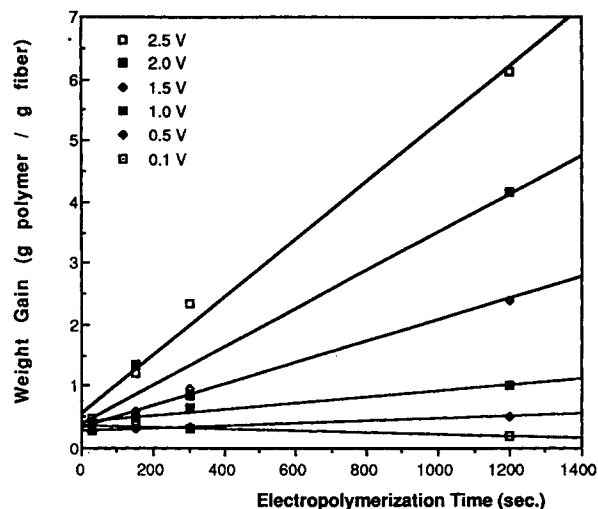
**Figure 2** Weight gain due to coating as a function of time for different concentrations of the supporting electrolyte  $T_4SNa$ .  $[pyrrole] = 0.5M$ ;  $E_{pa} = 1.5 V$ .



**Figure 4** Weight gain of fibers due to coatings as a function of time for fiber samples coated using different pyrrole concentrations.  $[T_4SNa] = 1.0M$ ;  $E_{pa} = 1.5 V$ .



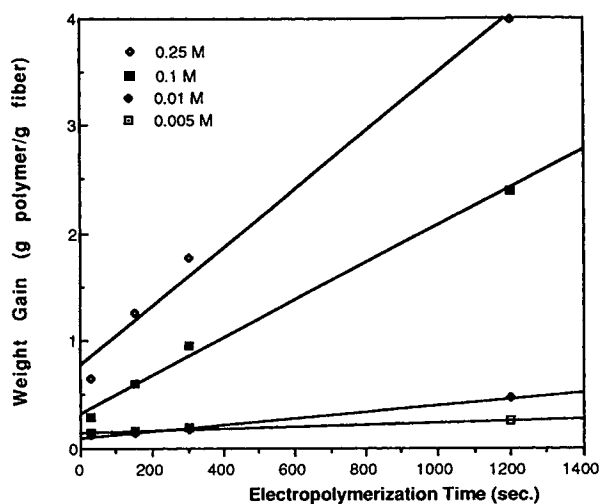
**Figure 5** Weight gain due to coatings as a function of time for fiber samples coated using different applied voltages. [pyrrole] = 0.5M; [T<sub>4</sub>SNa] = 1.0M.



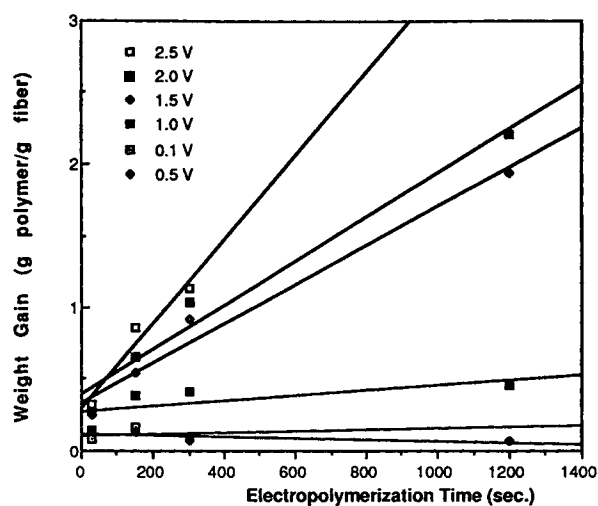
**Figure 7** Weight gain due to coatings as a function of time for fiber samples coated using different applied voltages. [pyrrole] = 0.5M; [DbSNa] = 0.1M.

*co-N*-[(3-carboxyphenyl)maleimide)] matrix, of about 3.0- $\mu$ m-thick coatings, onto graphite fiber pre-forms and mechanically tested the resulting composites. They reported very high impact strengths,  $\sim 226$  kJ/m<sup>2</sup> for the composites. Chiu and Lin<sup>15</sup> formed polypyrrole coatings onto carbon fibers by continuous electropolymerization and subsequently impregnated the polypyrrole modified graphite fibers with an epoxy matrix. They reported that the interlaminar shear strength (ILSS), of the polypyrrole modified graphite fibers-epoxy resin composites was increased by more than 15%. They noted that the increase in the ILSS was dependent on the doping

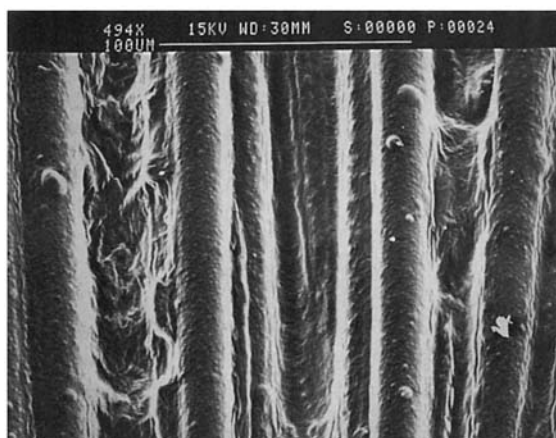
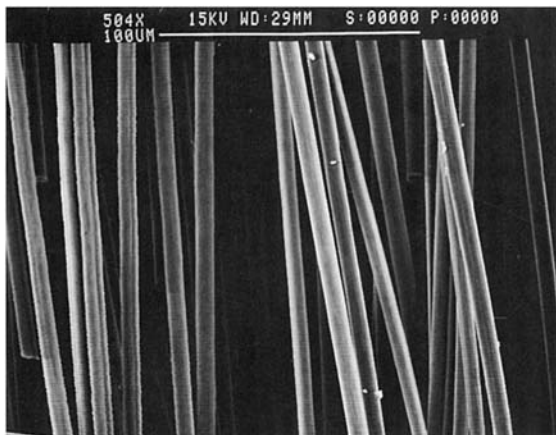
species used during electrochemical polymerization and the concomitant surface morphology of the polypyrrole coatings. Other studies involving the effect of electrodeposition of polymers onto graphite on the impact strength and interfacial shear strength of graphite fiber-epoxy resin composites was performed by Subramanian et al.<sup>16</sup> They applied a variety of copolymer coatings onto graphite fibers and subsequently impregnated the modified graphite fibers with epoxy resin matrix. They reported a significant improvement in the mechanical and interfacial properties of the electrochemically modified graphite fiber-epoxy resin composites.



**Figure 6** Weight gain due to coatings as a function of time for samples coated using different concentrations of DbSNa. [pyrrole] = 0.5M; Epa = 1.5 V.



**Figure 8** Weight gain due to coatings as a function of time for fiber samples coated using different applied voltages. [pyrrole] = 0.5M; [sulfuric acid] = 0.1M.



**Figure 9** SEM micrographs of uncoated carbon fibers (top) and carbon fibers modified with polypyrrole coatings with smooth morphology (bottom).

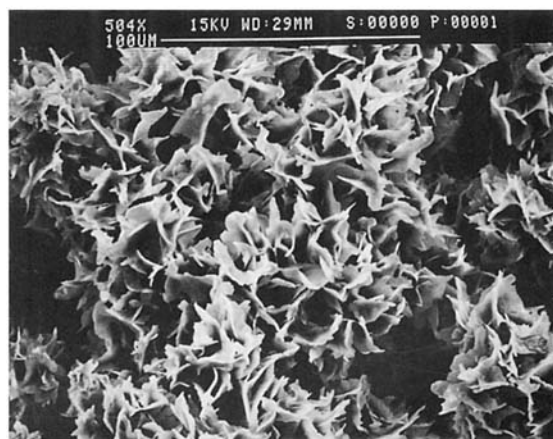
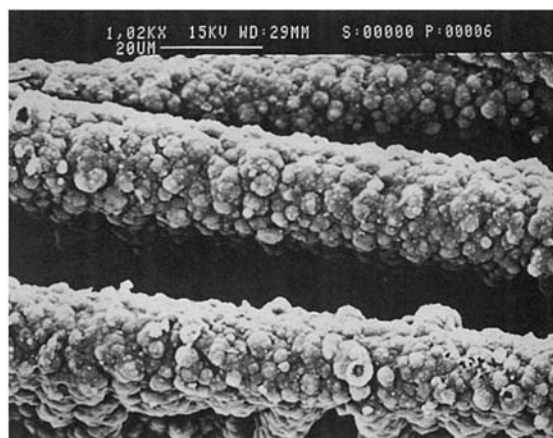
In this paper, we report the effect of electrolytes and process parameters, such as the monomer concentration, electrolyte concentration, applied voltage, and the reaction time, on the electrochemical polymerization of pyrrole and morphology of polypyrrole coatings formed onto carbon fibers.

## EXPERIMENTAL

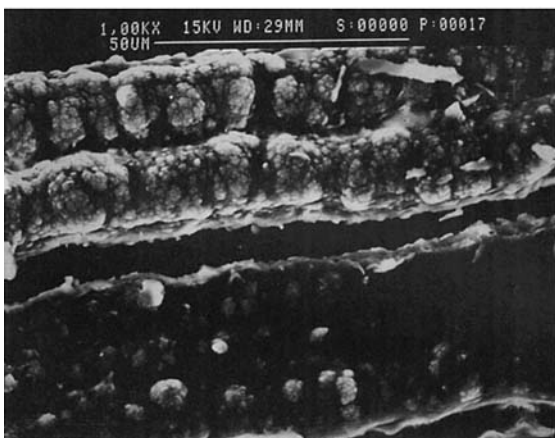
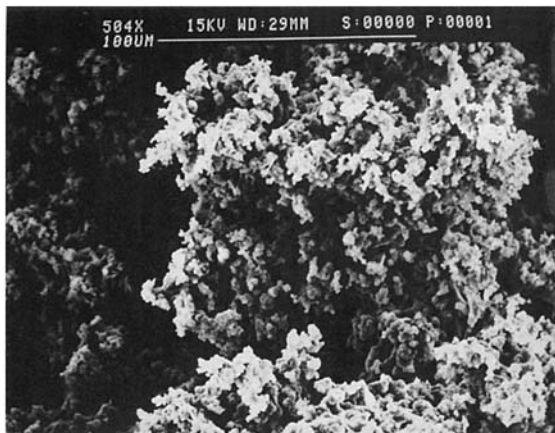
### Electrochemical Polymerization

The electrochemical polymerization of pyrrole was carried out in a three-compartment polypropylene cell. The middle compartment contained the monomer, carbon fiber (working electrode), and a saturated calomel electrode and was separated from the two-side counter electrode compartments by a  $0.04\mu$

pore-sized polypropylene membrane. The counter electrodes comprised of two titanium alloy plates  $20 \times 65 \times 1$  mm fitted into slots in the side compartments. A 40-mm-long bundle of Thornel T650/35 carbon fibers purchased from Amoco Performance Products Inc. was used as the working electrode. The fiber bundle was wrapped around a rectangular polypropylene frame and placed in the center compartment. A piece of aluminum foil held the fibers securely to the frame, leaving about 4 cm of taut aligned fibers available for coating. Leads were connected from the aluminum foil on top of the frame and from the counter electrodes to an EG&G Potentiostat/Galvanostat Model 273A. The center compartment contained 150 mL of an aqueous solution with the desired concentrations of pyrrole and the supporting electrolyte. Each side compartment



**Figure 10** SEM micrographs of carbon fibers modified with polypyrrole coatings with microspheroidal (top) and leafoidal (bottom) morphologies.



**Figure 11** SEM micrographs of carbon fibers modified with polypyrrole coatings with porous (top) and capsular (bottom) morphologies.

contained 100 mL of an aqueous solution of the electrolyte. Four types of electrolytes were used, namely toluene-4-sulfonic acid sodium salt ( $T_4SNa$ ) and dodecylbenzene-sulfonic acid sodium salt ( $DbSNa$ ), purchased from Fluka Chemical Inc., and sulfuric acid ( $H_2SO_4$ ) and Alizarin Red S monohydrate, purchased from Aldrich Chemicals Inc. The monomer concentration and electrolyte concentration were incrementally varied between 0.01 and 1.5M, respectively. The applied voltage varied from 0.1 to 2.5 V. Electropolymerization was carried out with each set of parameters for reaction times of 30, 150, 300, 900, and 1200 s, respectively.

#### Analysis of the Electropolymerized Coatings

The amount of polypyrrole formed during electropolymerization was determined gravimetrically. El-

emental analysis of the polypyrrole coatings was performed by Galbraith Laboratories, Inc. The coatings were scraped off an aluminum substrate and sent for analysis. The morphology of the coated fibers was examined by scanning electron microscopy (SEM). SEM samples were coated under identical conditions except for one parameter. Finally, IR spectroscopic analysis was performed on the coatings by means of the potassium bromide (KBr) pellets.

## RESULTS AND DISCUSSION

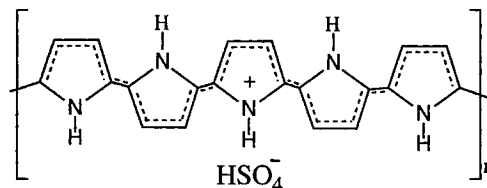
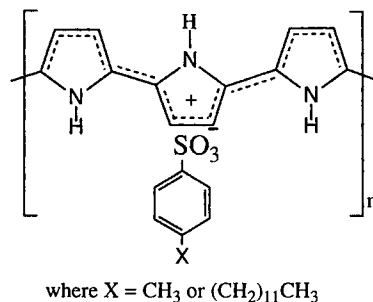
### Effect of Parameters

The amount of polypyrrole coatings formed on the carbon fibers increased with increased pyrrole concentration, electrolyte concentration, applied voltage, and electropolymerization time. Generally, no significant amount of polypyrrole coatings was formed onto the carbon fibers at very low monomer concentration of  $\sim 0.01M$ , low electrolyte concentration  $\sim 0.01$ – $0.05M$ , and low applied voltage of  $\sim 0.1$ – $0.5$  V after about 1200 s of continuous electropolymerization. In fact, increased electropolymerization times did not result in increased amount of coatings formed onto carbon fibers (bottom curve, Figs. 1–8).

Figures 1–3, show the effect of reaction parameter such as monomer concentration (Fig. 1), electrolyte concentration (Fig. 2), and applied voltage (Fig. 3) on the weight gain of fibers due to electropolymerization of pyrrole. As shown in Figure 2, varying the electrolyte concentration from 0.1 to 1.0M (900% increase) resulted in an increase in the weight gain from 0.8 to 6.0 g ( $\sim 650\%$  increase), corresponding to an electrolyte concentration increase-to-weight gain increase ratio of 4/3. The monomer concentration, applied voltage, and reaction time were maintained constant at 0.5M, 1.5 V, and 1200 s, respectively. The effect of monomer concentration and applied voltage on the weight gain of fibers are shown in Figures 1 and 3, respectively. Increasing the monomer concentration from 0.1 to 1.0M (900% increase) resulted in a weight gain increase from 1.0 to 2.0 g (100% increase) (Fig. 1), corresponding to a monomer concentration increase-to-weight gain increase ratio of 9/1. Note that the electrolyte concentration used to obtain the data presented in Figure 1 is 0.25M. At a higher electrolyte concentration  $\sim 1.0M$ , the same range of monomer concentration, 0.1–1.0M, resulted in  $\sim 600\%$  (0.9–6.0 g) increase in the weight gain, which corresponds to a monomer

concentration increase-to-weight gain increase ratio of 3/2. However, note that a 300% increase in the electrolyte concentration caused  $\sim 600\%$  in the weight gain of fibers, corresponding to an electrolyte concentration increase-to-weight gain increase ratio of 1/2.

Further comparison of the effect of monomer concentration and applied voltage on the weight gain of the fibers due to formation of polypyrrole can be made by reviewing Figures 1 and 4 and 3 and 5, respectively. The weight gain of fibers increased with increased monomer concentration (Figs. 1 and 4). Increasing the concentration of the electrolyte  $T_4SNa$  from 0.25 to 1.0M (300% increase) resulted in an increase in the weight gain from about 200% (2.0 g polymer/g fiber) to 790% (7.9 g polymer/g fiber), corresponding to about 300% increase in weight gain, corresponding to an electrolyte concentration increase-to-weight gain increase ratio of 1/1, for electropolymerization performed by using 1.0M pyrrole and applied voltage of 1.5 V for 1200 s. Figures 3 and 5 show the effect of applied voltage and electrolyte concentration on the weight gain of fibers for electropolymerization performed by using 0.5M of pyrrole and  $T_4SNa$  as the electrolyte. Increasing the electrolyte concentration from 0.25 to 1.0M (300% increase) resulted in an increase in the weight gain from 0.9 to 3.6 g ( $\sim 300\%$  increase), which corresponds to an electrolyte concentration increase-to-weight gain increase ratio of 1/1, for the electropolymerization performed by using an applied voltage of 1.0 V and pyrrole concentration of 0.5M. Increasing the applied voltage from 1.0 to 2.0 V (100% increase) resulted in a weight gain increase from 0.8 to 3.2 g ( $\sim 300\%$  increase), corresponding



**Scheme I.** Representation of doped polypyrrole formed onto graphite fibers by aqueous electrochemical polymerization.

to an applied voltage increase : weight gain increase of 1 : 3 and 3.1–7.4 g ( $\sim 140\%$  increase), which corresponds to an applied voltage increase : weight gain increase of 5 : 7, for electrolyte concentration of 0.25 and 1.0M, respectively (Fig. 4).

The monomer concentration and electropolymerization time were maintained constant at 0.5M and 900 s, respectively. Figures 6 and 7 show the effect of applied voltage and electrolyte concentration on the weight gain of fibers for the electropolymerization performed by using 0.5M pyrrole and  $DbSNa$  as the electrolyte. The weight gain of fibers

**Table I** Elemental Composition from Microanalysis for Coatings Formed with  $T_4SNa$  (2-4oa),  $DbSNa$  (6-4oa), and  $H_2SO_4$  (10-xtr)

Sample	Elements	Results (wt %)	Pyrrole/Electrolyte (mole ratio)
2-4oa	Carbon	57.68	2.64/1
	Hydrogen	4.35	
	Nitrogen	10.33	
	Oxygen	16.38	
	Sulfur	8.96	
6-4oa	Carbon	66.35	2.79/1
	Hydrogen	6.94	
	Nitrogen	7.79	
	Sulfur	6.40	
10-xtr	Carbon	48.91	5.32/1
	Hydrogen	3.95	
	Nitrogen	14.28	
	Sulfur	6.14	

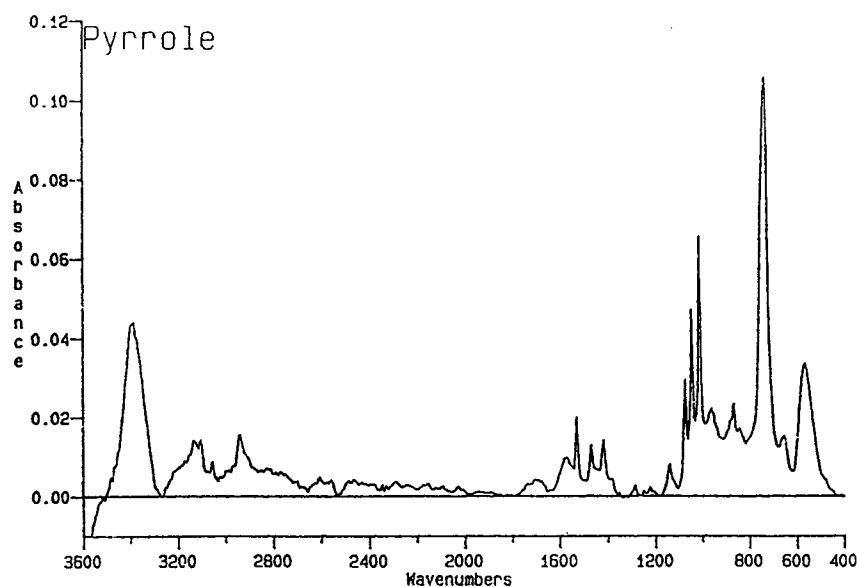


Figure 12 IR spectrum of pyrrole.

increased with increased electrolyte concentration (Fig. 6) and increased applied voltage (Fig. 7). Increasing the [DbSNa] from 0.01 to 0.1M (900% increase) increased the polypyrrole yield from 0.4 to 2.5 g (~ 500% increase) for electropolymerization of pyrrole carried out by using 0.5M pyrrole and an applied voltage of 1.5 V at an electropolymerization time of 1200 s (Fig. 6). Increasing the voltage from 1.0 to 2.0 V (100% increase) increased the coating yield from 0.25 to 1.0 g (~ 300% increase), corresponding to an applied voltage increase-to-weight gain increase of 1/3 (Fig. 7). Note that the monomer concentration, electrolyte concentration, and reaction time were maintained constant at 0.5M, 0.1M, and 1200 s, respectively. The ratio of the applied voltage increase-to-weight gain increase increases at lower applied voltage. For instance, a 10-fold increase in the applied voltage from 0.1 to 1.0 V resulted in only a 300% (0.25–1.0 g of coatings) increase in the weight gain (Fig. 7). The effect of the applied voltage on the electropolymerization of 0.5M pyrrole carried out by using sulfuric acid as the electrolyte is shown in Figure 8. The weight gain of the fibers increased with increased applied voltage and increased reaction time (Fig. 8).

### Coatings Morphology

The SEM micrographs (Figs. 9–11) show that polypyrrole coating morphologies varied with electropolymerization parameters. Figure 9 (top) shows uncoated fibers (control). Figure 9 (bottom) shows a relatively smooth coating, whereas Figures 10 and

11 show rougher and more textured coatings. Figure 10 shows a polypyrrole coatings with microspheroidal (top) and leafoidal (bottom) morphologies, whereas Figure 11 shows more of a porous (top) and capsular morphologies. Figure 11 (top) is a representative of coating with a surface of pores and granular structure. The more intricate coatings surfaces may result in a mechanical interlocking effect desired for improved adhesion between the fiber and the matrix in advanced composites.

### Coating Composition

The data from the elemental analysis performed on coatings are shown on Table I. Samples 2-40a, 6-40a, and 10-xtr were coated using the electrolytes T<sub>4</sub>SNa, DbSNa, and sulfuric acid, respectively. Note that the elements listed for each sample were the only elements that were tested for in the analysis. For example, sample 2-40a was the only sample of the three tested for oxygen, and none of the samples were tested for sodium. The presence of sulfur in each sample suggests that electrolyte is indeed incorporated into the coatings. Table I also lists the ratios of pyrrole units to electrolyte units. This ratio is obtained by considering the fact that there is one nitrogen atom per pyrrole ring and one sulfur atom per electrolyte unit. The value of this ratio is similar for the sample using T<sub>4</sub>SNa and the sample using DbSNa as supporting electrolytes, close to 3 pyrrole/1 electrolyte unit, despite the fact that the concentration of the latter was only  $\frac{1}{4}$  that of the T<sub>4</sub>SNa (Scheme I). The polypyrrole coatings formed by us-

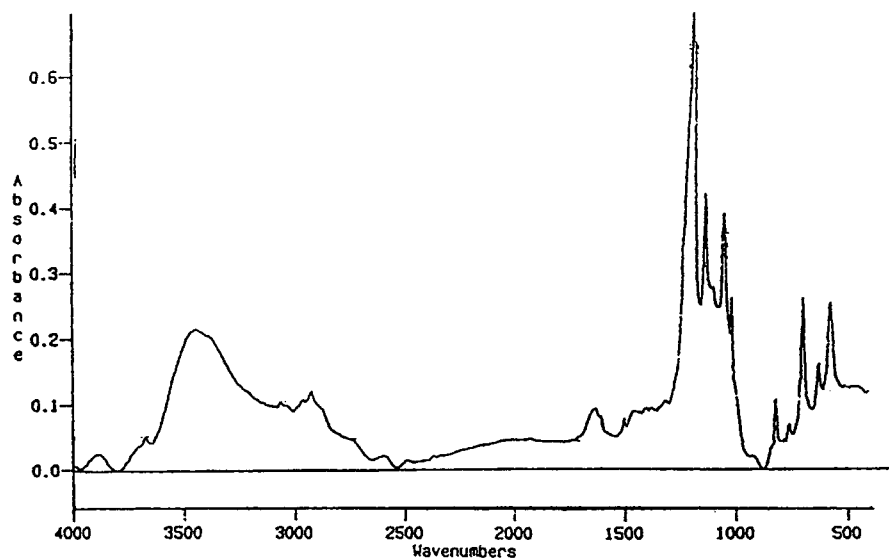


Figure 13 IR spectrum of  $T_4SNa$ .

ing sulfuric acid as the electrolyte have a monomer unit to electrolyte unit ratio nearly double that of the other samples (Scheme I).

Figure 12 shows an IR spectrum of pyrrole. All major peaks characteristic of a spectrum of pyrrole are present. The ring C—H stretch bands appear near  $3125\text{ cm}^{-1}$ .<sup>11</sup> The C=C ring stretches occur in the region of  $1665\text{--}1430\text{ cm}^{-1}$  and are shown in Figure 12.<sup>11</sup> The three distinct peaks between  $1015$  and  $1080\text{ cm}^{-1}$  as well as the large peak near  $735\text{ cm}^{-1}$  are all due to C—H vibrations.<sup>8</sup> Finally, the N—H stretch band results in a strong peak absorption between  $3450$  and  $3225\text{ cm}^{-1}$ .<sup>11</sup>

The IR spectra of the electrolytes  $T_4SNa$ ,  $DbSNa$ , and Alizarin Red S monohydrate are presented in Figures 13–15, respectively. The sulfonic acid salts usually show four peaks near  $1230$ ,  $1190$ ,  $1130$ , and  $1040\text{ cm}^{-1}$ , which correspond to the three S—O groups and one S-phenyl vibration.<sup>17</sup> Bands appear near these regions in the electrolyte spectra. All three spectra also show a broad peak near  $3400\text{ cm}^{-1}$ , which might be a result of water in the sample. In addition, each spectra show a band near  $2900\text{ cm}^{-1}$  due to the methylene group — $CH_2$ —.<sup>18</sup> The  $DbSNa$  has a well-defined split peak vibration near  $2900\text{ cm}^{-1}$ , indicating the presence of an alkyl group.

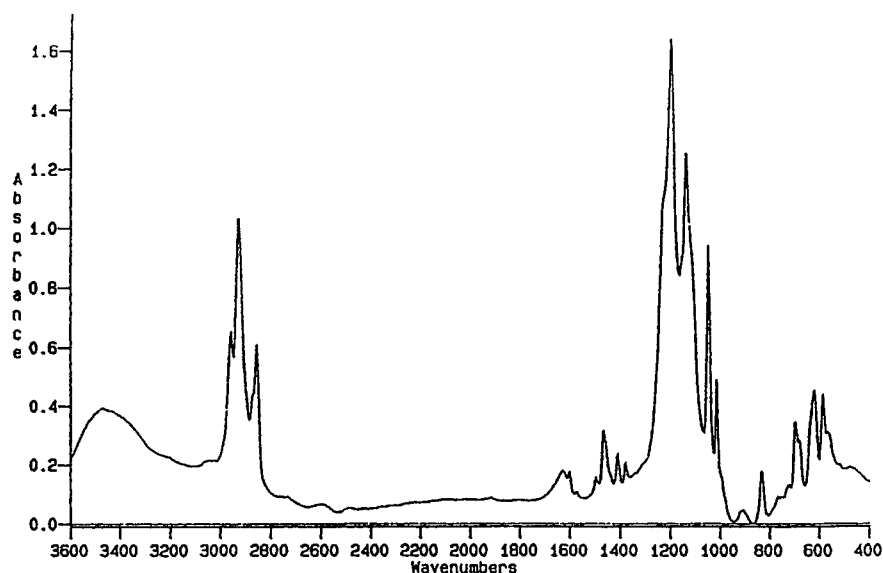


Figure 14 IR spectrum of  $DbSNa$ .



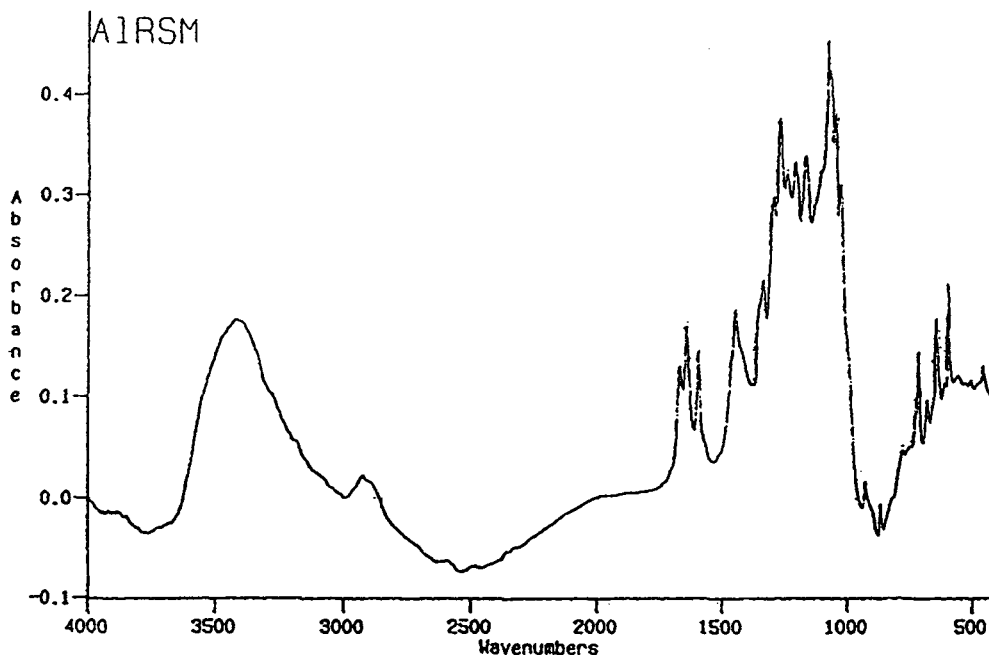


Figure 15 IR spectrum of Alizarin Red S monohydrate.

These peaks are most likely due to the alkyl group attached to the benzene ring (see Fig. 14). As for other similarities, each of the three spectra shows peaks at  $800\text{--}500\text{ cm}^{-1}$ , some of which are due to various ring vibrations.<sup>18</sup> Finally, there is a small peak near  $815\text{ cm}^{-1}$ , indicating two adjacent hydrogens on the benzene ring.<sup>17</sup>

Figure 16 shows a comparison of spectra for pyrrole and an electropolymerized polypyrrole coating,

6-2e. The spectrum for the electropolymerized coating is representative of the spectra for the coatings. The spectrum for DbSNa by itself is shown in Figure 14. One of the most noticeable features of the 6-2e spectrum in Figure 16 is the large peak region located between  $1100$  and  $1000\text{ cm}^{-1}$ . It is evident that this region consists of not only the peaks from the C—H in the pyrrole structure but also the S—O peaks from the DbSNa. Spectra showing comparisons be-

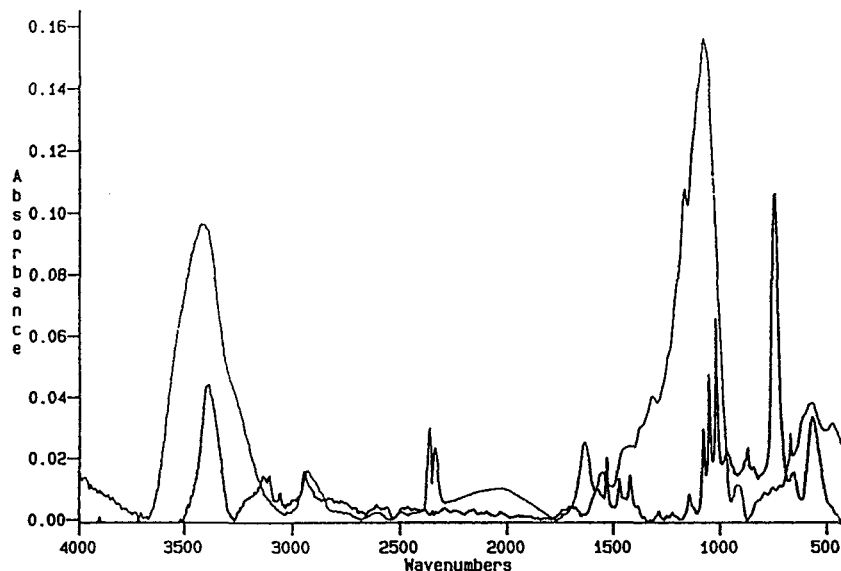


Figure 16 IR spectrum comparing pyrrole to sample 6-2e, coated using DbSNa as the supporting electrolyte.

tween pyrrole and the other supporting electrolytes give similar results. The IR spectroscopic analysis therefore confirms the previous findings that showed that the counter ions derived from the electrolyte was indeed embedded in the coatings.

## CONCLUSION

Polypyrrole has been electrochemically formed onto carbon fiber bundles. The amount of coating formed appears to depend most on the concentration of the supporting electrolyte. Several distinct morphologies of the coatings arise from different process parameters. Elemental analysis and IR spectroscopy all confirm that at least part of the electrolyte is incorporated into the coating.

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