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Formation of graphite fibre–polypyrrole coatings by aqueous electrochemical polymerization

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The aqueous electrochemically initiated polymerization of pyrrole has been successfully performed on graphite fibres from a solution containing the monomer and toluene-4-sulfonic acid sodium salt. The effects of the initial monomer concentration, supporting electrolyte concentration and applied voltage on the rate of electropolymerization of pyrrole have been investigated in an attempt to ascertain the optimum conditions for the process. The rate of electropolymerization of pyrrole increased with the initial monomer concentration and the applied voltage up to the peak oxidation potential of pyrrole, ~1.5 V, beyond which a significant decrease in the rate occurred. Increasing the concentration of toluene-4-sulfonic acid sodium salt from 0.05 to 0.10 M had little impact on the rate of electropolymerization. However, a sharp increase in the rate occurred when the electrolyte concentration was raised to 0.5 M. The morphology of the electropolymerized pyrrole is highly porous and grainy. The individual single graphite fibre filament is completely covered with polypyrrole after about 30 s of electropolymerization.

(Keywords: pyrrole; aqueous electrochemical polymerization; reaction parameters)

INTRODUCTION

Graphite fibres possess characteristic high strength and high modulus and are used as reinforcements in polymeric composites[1]. The wettability of the fibres by the matrix is one of the most important considerations in composite technology. Adequate bonding between the matrix and the fibre is also necessary for efficient transfer of an applied load from the matrix to the fibres[2]. Various techniques have been used to improve the wettability of fibres by the matrix. They include surface oxidation of the fibres, application of organosilane coupling agents and electropolymerization[3–10]. Subramanian and co-workers pioneered the formation of a polymeric interlayer as a means of improving the interfacial properties of graphite–polymer composites[2,10,11]. Bell and co-workers have also successfully demonstrated the effectiveness of electropolymerized interlayers in the improvement of the shear strength and toughness of electrochemically modified graphite fibre–epoxy resin composites[12–15].

Electrochemical polymerization of pyrrole on graphite fibres has been investigated by Chiu and Lin as a means of improving the interfacial properties of graphite fibre–epoxy resin composites[16]. They postulated that the improved shear strength obtained was due to the high porosity of the polypyrrole-coated graphite fibres. Dujardin *et al.*[17] also reported improved shear strength and elongation for pyrrole-coated graphite fibre–epoxy composites. In the present paper, we report our preliminary investigation of the effect of reaction parameters on the electropolymerization of pyrrole.

EXPERIMENTAL

Materials

Pyrrole monomer (99% pure) was purchased from Aldrich Chemical Company and used as received. Toluene-4-sulfonic acid sodium salt (TSNa) purchased from Fluka Chemika/Biochemika Company was used as the supporting electrolyte. Unsized but surface oxidized T-650 graphite fibres, containing 12 000 filaments per bundle, were supplied by Amoco Performance Products Inc. and used as the working electrode. The graphite fibres were wound on a 6.35 × 6.35 cm H-shaped aluminium frame. The counter-electrodes consisted of two titanium alloy plates, 18.0 × 3.8 × 0.15 cm, supplied by the Machine Shop of the Department of Materials Science and Engineering (University of Cincinnati). An EG&G Princeton applied research potentiostat, model 273A with 270 software program package, was the source of direct current.

Electropolymerization

Electropolymerization was carried out in a 250 ml, three-chamber polypropylene electropolymerization cell[18]. The counter-electrodes were placed in the outer compartments of the cell which contained toluene-4-sulfonic acid sodium salt dissolved in distilled water. A 0.04 μm pore size polypropylene membrane glued to perforated polypropylene sheets separated the middle chamber, containing the graphite fibre working electrode and monomer–electrolyte solution, from the counter-electrode chambers.

The effect of initial monomer concentration on the rate of electropolymerization was investigated using pyrrole

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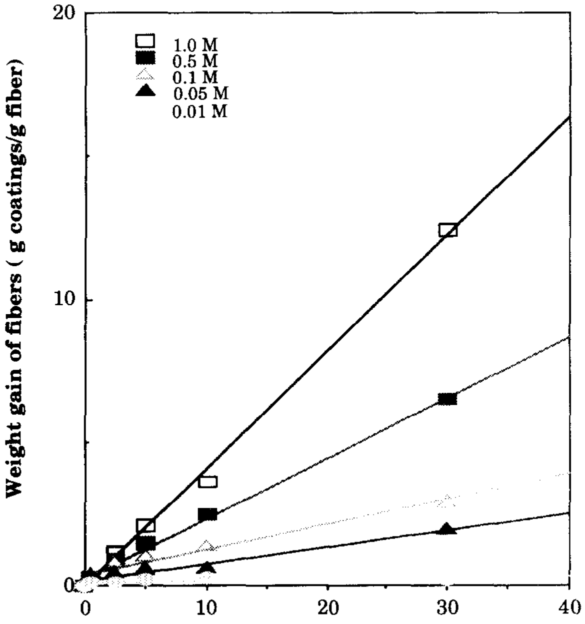


Figure 1 Weight of polypyrrole coatings formed on graphite fibres as a function of initial monomer concentration and electropolymerization time ([TSNa] = 0.125 M, E_{pa} = 2.5 V)

concentrations of 0.01, 0.05, 0.1, 0.5 and 1.0 M. The supporting electrolyte concentration and applied voltage were maintained constant at 0.125 M and +2.5 V, respectively.

Electropolymerization was also performed at four different potentials (E_{pa}), 0.65, 1.0, 1.5 and 2.5 V, in order to determine the effect of the applied voltage. An initial monomer concentration and supporting electrolyte concentration of 0.1 and 0.125 M, respectively, were maintained during these runs. The applied potential range 0.65–2.5 V used in this study was based on previous investigation of aqueous electropolymerization of pyrrole by Satoh *et al.*[19]. They reported highest electrical conductivity for polypyrrole films formed by applying a potential of 0.65 V.

The effect of supporting electrolyte concentration was investigated at four different concentrations, 0.5, 0.25, 0.125 and 0.05 M. The initial monomer concentration of 0.1 M and applied voltage of 2.5 V were maintained during each run. Electropolymerization was carried out for periods of 30, 150, 300, 600 and 1800 s. After electropolymerization, the samples were withdrawn from the cell, rinsed in water and dried at ambient temperature. They were then dried in a vacuum oven for 1 h at 110°C. The weight of the coatings formed on the graphite fibres was measured gravimetrically as the difference between the weight of the uncoated and coated fibres.

Characterization

Functional group analysis of both pyrrole monomer and electropolymerized polypyrrole was performed by Fourier transform infra-red spectroscopy (*FT*i.r.), using a model FTS-40 spectrophotometer (Bio-Rad Corp.). The polypyrrole coatings were extracted (scraped) from graphite fibres containing about 80% by volume of polypyrrole. KBr pellets were made from a 5/100 polypyrrole/KBr powder mixture. Drops of the liquid monomer were spotted on a KBr salt disc until a uniform pyrrole film was deposited on the latter. Both the KBr pellets and monomer-coated KBr salt discs were used in *FT*i.r. spectroscopy.

The morphology of the polypyrrole-coated graphite fibres was examined by scanning electron microscopy (SEM), using a Cambridge Stereoscan S90 equipped with a digital scanner. The samples were shadowed with gold to enhance their conductivity.

Time-of-flight (TOF) (secondary ion mass spectrometry (s.i.m.s.) was performed by a Kratos Prism instrument equipped with a reflection-type mass analyser and a 25 kV liquid metal ion source with a minimum beam size of 500 A.

RESULTS AND DISCUSSION

Effect of reaction conditions

Initial monomer concentration. Figure 1 shows the weight ratio of polypyrrole coatings formed on graphite fibres as a function of time and initial monomer concentration. The weight gain of the fibres varied linearly with the monomer concentration and time. Increasing the initial monomer concentration increases the amount of polypyrrole coating formed on graphite fibres per unit time. *Table 1* shows the rate of electropolymerization of pyrrole (R_p) as a function of the initial monomer concentration ([M]). The rate of electropolymerization increased from 0.102 to 14.65 mg min^{-1} as the initial monomer concentration was increased from 0.01 to 1.0 M. An exponent of 0.99 was obtained from a log–log plot of the rate of polymerization and initial monomer concentration ($R_p \propto [M]^{1.0}$; *Figure 2*) in agreement with the proposed radical-ion mechanism (*Scheme 1*).

Supporting electrolyte concentration. The dependence of electropolymerization of pyrrole on the electrolyte concentration and electropolymerization time is shown on *Figure 3*. *Figure 4* also shows the dependence of the rate of polymerization on the electrolyte concentration. Initially the supporting electrolyte concentration did not seem to have any significant impact on the rate of electropolymerization of pyrrole. Note that a fivefold increase in the concentration of toluene-4-sulfonic acid sodium salt (0.05–0.25 M) resulted in no increase in the rate of polymerization (2.23–2.29 mg min^{-1}). Increasing the electrolyte concentration to 0.5 M, however, resulted in a sharp increase in rate to about 3.307 mg min^{-1}. We believe that, as the electrolyte concentration was increased to 0.5 M, the electrolyte began to react and incorporate itself into the growing macroradical ion (*Scheme 1*).

Table 1 Dependence of rate of electropolymerization of pyrrole on the initial monomer concentration

Pyrrole concentration, [M] (mol l^{-1})	Polymerization rate R_p (mg min^{-1})
0.01	0.102
0.05	1.942
0.10	3.008
0.50	7.356
1.00	14.650

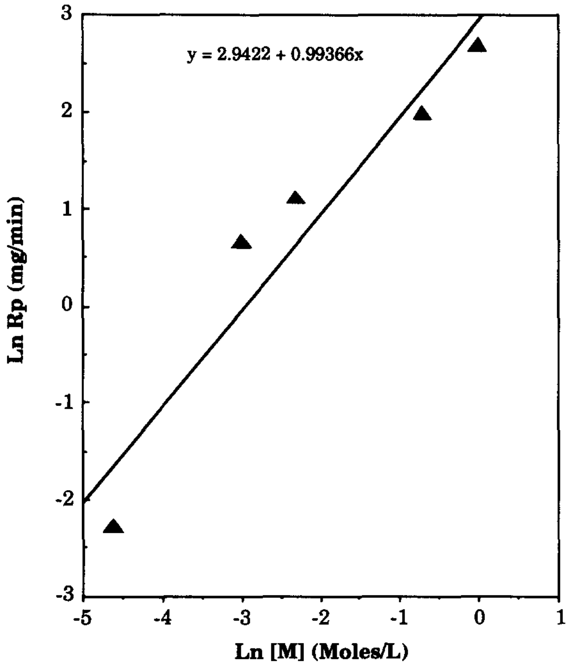
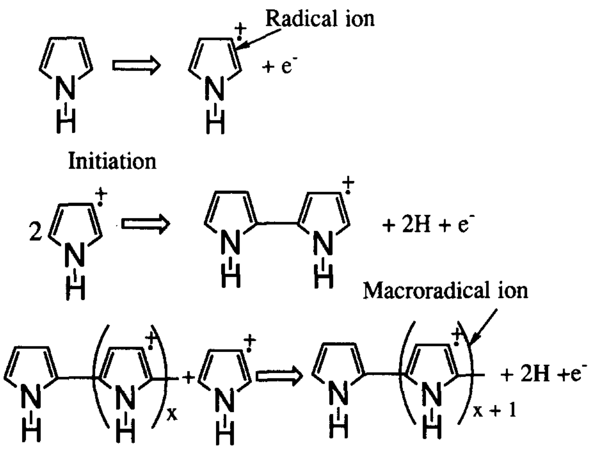


Figure 2 Determination of the initial monomer concentration exponent



Scheme 1 Electrochemical polymerization of pyrrole[20]

Applied voltage. *Figure 5* shows the weight gain of fibres due to formation of polypyrrole coatings as a function of polymerization time and applied voltage. The weight fraction of polypyrrole coatings increased as the applied voltage was raised from 0.65 to 1.50 V. Further increase in the applied voltage beyond 1.5 V resulted in a decrease in the weight fraction of coatings. This result is in agreement with the proposed direct initiation mechanism. The rate of electron transfer and chain growth by coupling is highest[20] about the peak oxidation potential of pyrrole, ~1.2 V. The rate of electropolymerization of pyrrole is maximum at 1.5 V (*Figure 6*).

FT*i.r. spectroscopy*

The *FT*i.r. spectra for pyrrole and the electropolymerized polypyrrole are shown on *Figure 7*. The two spectra are similar except that the characteristic absorption peaks are significantly broadened in the *FT*i.r. spectrum for polypyrrole. Also, the strong absorption peak occurring at 1295 cm^{-1} due to the sulfonic group is absent in the pyrrole spectrum. A broad peak absorption attributed to the –NH– group is observed at 3100–3700 cm^{-1} for the polymer. The –NH– peak absorption for the monomer is very strong and sharp and occurs at 3400 cm^{-1}.

Coating morphology

Figures 8a and *8b* show scanning electron micrographs of polypyrrole formed on graphite fibres at an applied

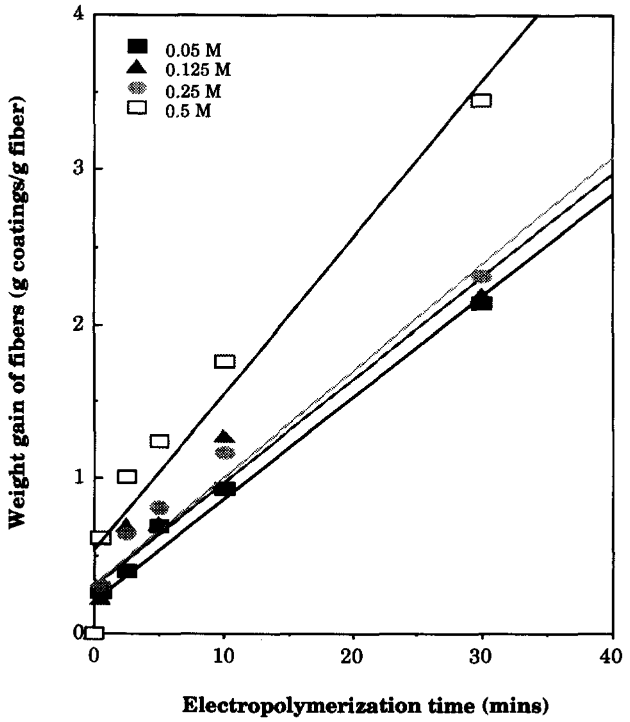


Figure 3 Weight of polypyrrole coatings formed on graphite fibres as a function of electrolyte concentration and electropolymerization time (E_{pa} = 2.5 V, [M] = 0.1 M)

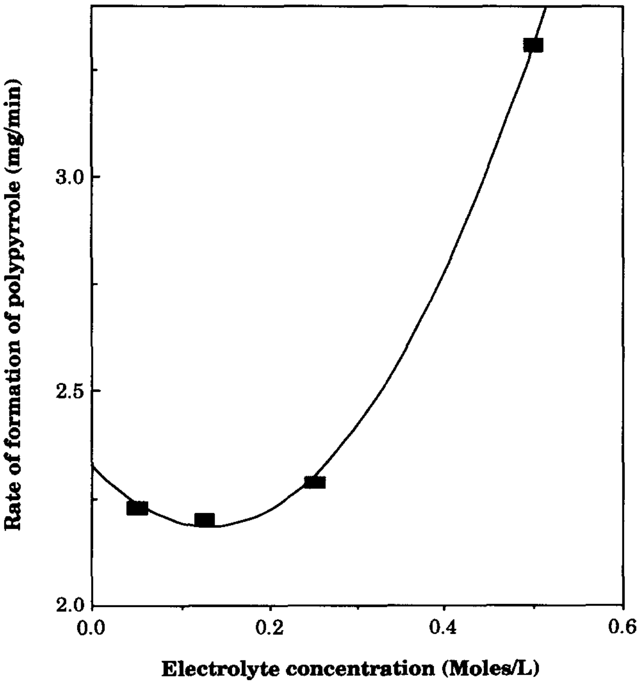


Figure 4 Dependence of rate of electropolymerization of pyrrole on electrolyte concentration ([M] = 0.1 M, E_{pa} = 2.5 V)

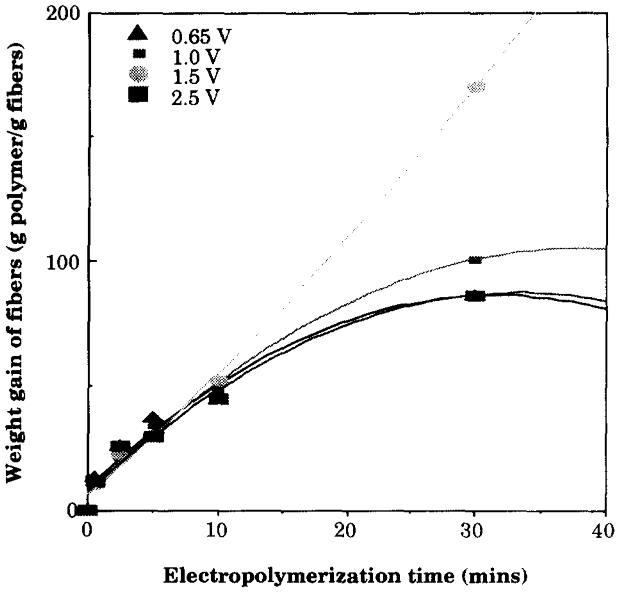


Figure 5 Weight of polypyrrole coatings formed on graphite fibres as a function of applied voltage and electropolymerization time ([TSNa] = 0.125 M, [M] = 0.1 M)

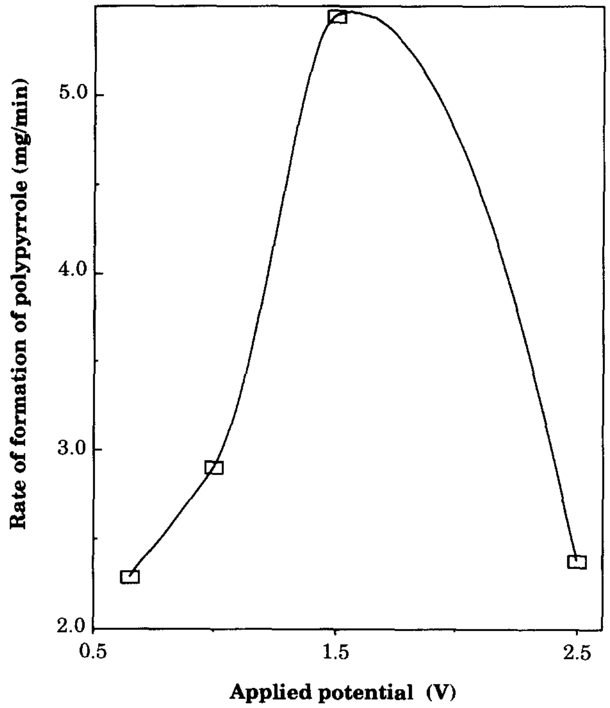


Figure 6 Dependence of rate of electropolymerization of pyrrole on applied potential ([M] = 0.1 M, [TSNa] = 0.125 M)

voltage of 2.5 V. The coatings are porous and grainy. It is believed that the porosity and grain size of the electropolymerized polypyrrole are dependent on the supporting electrolyte used[16].

TOF-s.i.m.s.

Figures 9a and *9b* show negative s.i.m.s. spectra for electropolymerized polypyrrole. The hydrocarbon and hydrogen peaks are clearly shown. The peak occurring at $m/z = 18$ represents the NH_4^+ group. The peaks at $m/z = 42$, 56 and 80 are due to groups containing nitrogen. The peaks at m/z values of 64 and 65 may be due to the polypyrrole repeat unit. The peak at $m/z = 26$ may be due to the CN group in pyrrole. Peaks for $C_8H_7SO_3$ and $C_8H_7SO_4$ occur at $m/z = 183$ and 199, confirming the incorporation of toluene sulfonate in the coatings.

These findings, in agreement with previous results[16], suggest the structure for the polypyrrole formed on the graphite fibre surface illustrated in *Scheme 2*.

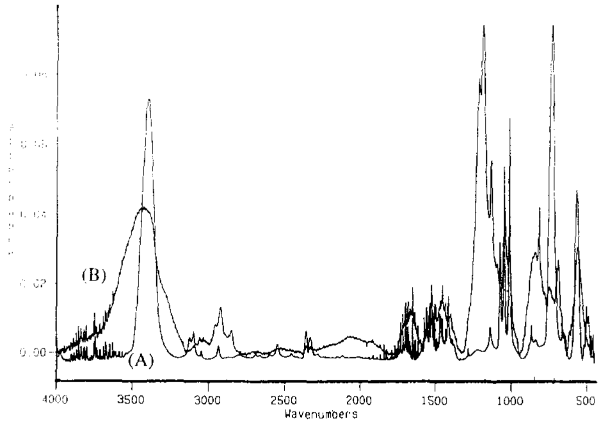


Figure 7 *FT*i.r. spectra for (A) pyrrole and (B) polypyrrole formed by electrochemical polymerization

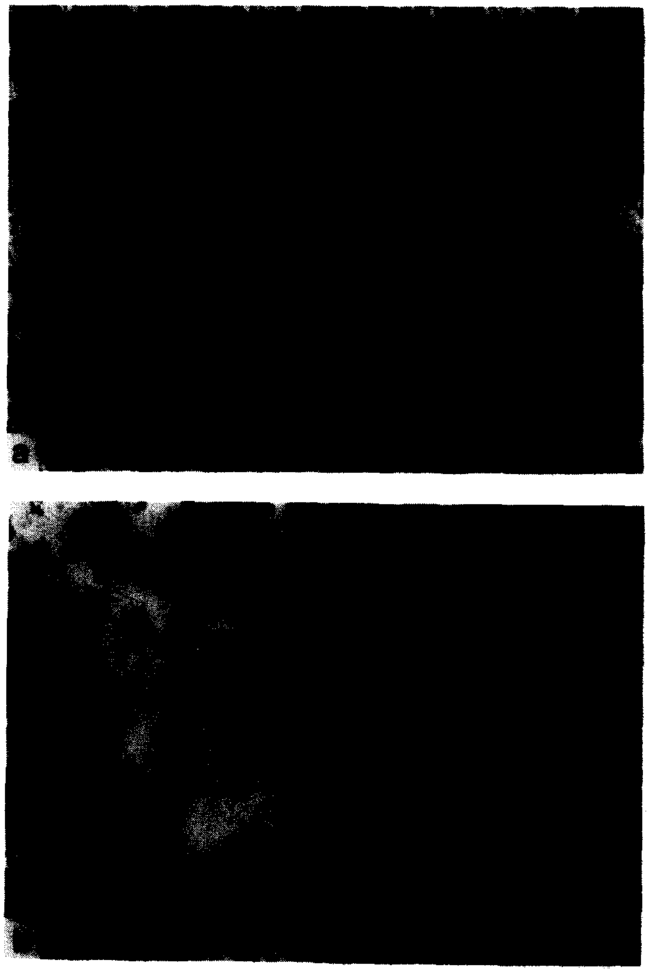


Figure 8 SEM micrographs of polypyrrole coated on graphite fibres by electrochemical polymerization: (a) 145 × ; (b) 74 000 ×

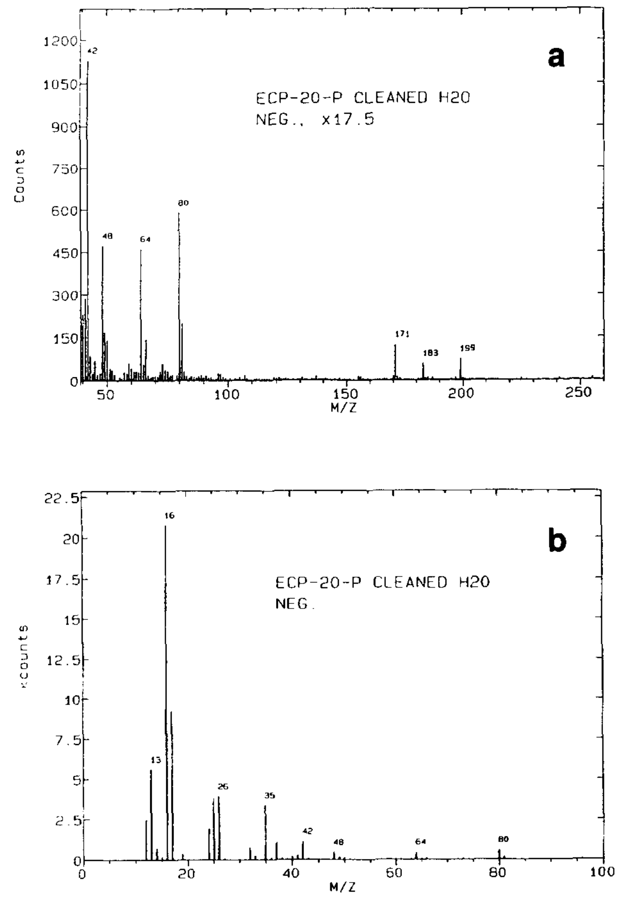
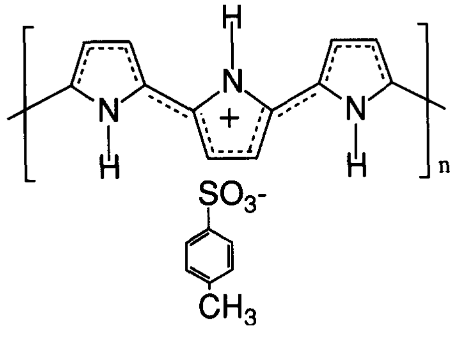


Figure 9 S.i.m.s. spectra for polypyrrole coated on graphite fibres by electrochemical polymerization



Scheme 2 Representation of polypyrrole formed on graphite fibres from an aqueous solution of pyrrole using toluene-4-sulfonic acid sodium salt as the electrolyte

CONCLUSIONS

The electrochemical polymerization of pyrrole on graphite fibres is dependent on the initial monomer concentration, applied voltage and electrolyte concentration. The rate of formation of polypyrrole is highest near the peak oxidation potential of pyrrole. The effect of electrolyte concentration was minimal below 0.25 M. However, a sharp rise in the rate of polymerization occurred when the electrolyte concentration was raised to 0.5 M. Both *FT*i.r. spectroscopy and s.i.m.s. confirm the presence of SO_3^- in the electropolymerized film. SEM shows that the polypyrrole coatings are porous and grainy. The graphite fibres are properly covered with polypyrrole film after about 30 s of electropolymerization as shown by the SEM micrographs.

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REFERENCES

1 Agarwal, B. D. and Broutman, L. J. 'Analysis and Performance of Fiber Composites', 2nd edn, John Wiley and Sons, Inc., New York, 1990
2 Subramanian, R. V. *Pure Appl. Chem.* 1990, **52**, 1929
3 Tanaka, F. A., Hashimoto, K. and Kobayashi, M. *Polym. Prepr.* 1990, **20**, 853
4 Brennan, J. J., Jermyn, T. E. and Boonstra, B. *J. Appl. Polym. Sci.* 1964, **8**, 2687
5 Kardos, J. L., Cheng, F. S. and Tolbert, T. L. *Polym. Eng. Sci.* 1973, **13**, 455
6 Delollis, N. J. *SAMPE J.* 1979, **15**, 10
7 Hull, D. 'An Introduction to Composite Materials', 3rd edn, Cambridge University Press, Cambridge, 1981, pp. 36–58
8 Kelly, A. *Compos. Mater.* 1974, **6**, 174
9 Scola, D. A. *Compos. Mater.* 1974, **6**, 217
10 Subramanian, R. V. and Jakubowski, J. J. *Polym. Eng. Sci.* 1978, **18**, 590
11 Subramanian, R. V. and Jakubowski, J. J. *Org. Coat. Plast. Chem.* 1979, **40**, 688
12 Chang, J., Bell, J. P. and Shkolnik, J. *J. Appl. Polym. Sci.* 1987, **34**, 2105
13 Bell, J. P. and Rhee, H. W. SPE/ANTEC'88, Transactions, 1988, p. 1590
14 Bell, J. P., Chang, J. and Rhee, H. W. *Polym. Compos.* 1987, **8**, 46
15 Iroh, J. O., Bell, J. P. and Scola, D. A. SPE APC/RETEC Conference on Advanced Polymeric Composites for Structural Applications, Loss Angeles, CA, 14–17 November 1988
16 Chiu, H. T. and Lin, J. S. *J. Mater. Sci.* 1992, **27**, 319
17 Dujardin, S., Lazzaroni, R., Rigo, L., Riga, J. and Verbist, J. J. *J. Mater. Sci.* 1986, **21**, 4342
18 Iroh, J. O., Bell, J. P. and Scola, D. A. *J. Appl. Polym. Sci.* 1993, **47**, 93
19 Satoh, M., Kaneto, K. and Yoshino, K. *Synth. Metals* 1986, **14**, 289
20 Diaz, A. F. and Kanazawa, K. K. in 'Extended Linear Chain Compounds' (Ed. J. S. Miller), Plenum, New York, 1982, p. 417