BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 25, pp. 4761–4765, 1995

0032-3861/95/$10.00+0.00

Film substructure and mechanical properties of electrochemically prepared polypyrrole

M. Gandhi and G. M. Spinks
Department of Materials Engineering, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

and R. P. Burford
Department of Polymer Science, University of New South Wales, Sydney, NSW 2052, Australia

and G. G. Wallace*
Intelligent Polymer Research Laboratory, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia
(Received 6 June 1994; revised 20 February 1995)

The film substructure of electrochemically prepared polypyrrole (PPy) films doped with *p*-toluene sulfonate has been studied using electron and optical microscopy. The solution surface of the films contained characteristic nodular features, which cap underlying cone-shaped structures. The PPy was shown to be optically active, indicating a degree of molecular anisotropy. Examination of fracture surfaces after tensile testing showed that fracture proceeded around the cones, indicating that cone boundaries are points of weakness.

(Keywords: polypyrrole; film substructure; mechanical properties)

INTRODUCTION

In virtually every proposed application for electrically conducting polymers such as polypyrrole (PPy), adequate mechanical properties are required. However, it is well recognized by researchers in this field that the mechanical properties of PPys vary widely, i.e. from being strong and tenacious to being extremely brittle[1]. A number of investigations have been devoted explicitly to the study of the factors that influence the mechanical properties of polypyrrole-based polymers[1–8]. In addition, several other investigators have incidentally reported the mechanical properties[9–15]. To date, however, much of the structure–property relationships still remain to be determined.

This communication reports further observations of the film substructure of electrochemically prepared PPy and explores the relationship between this morphology and mechanical behaviour. Although it is well known that the PPy morphology is highly dependent on the type of counterion[8], only one counterion has been used in this initial study, namely *p*-toluene sulfonate (pTS). This is because it is also known that different counterions produce different molecular conformations in electrochemically prepared PPy[16], which are also likely to affect the mechanical properties. Thus, to isolate the relationship between film morphology and mechanical properties, we have chosen to use only one counterion and to vary the morphology by altering the polymerization conditions. In this paper we report on the effects of using different working electrode materials on PPy morphology and mechanical properties.

* To whom correspondence should be addressed

EXPERIMENTAL

Samples were prepared by electrochemical methods under galvanostatic control. Three different working electrodes were employed: stainless steel (SS), carbon-coated stainless steel and platinum-coated stainless steel. Freshly distilled pyrrole monomer was added to an aqueous solution of the supporting electrolyte, i.e. *p*-toluene sulfonate. Both the monomer and electrolyte concentrations were 0.1 M. The solution was purged with nitrogen gas for 15 min prior to the commencement of polymerization. A current density of 1 mA cm^{-2} was used and polymerization was continued for 30 min for morphological examination and 60 min for mechanical testing. All polymerizations were conducted at ambient temperature (20–24°C).

The surface nodular structure and fracture surfaces of the samples were determined by scanning electron microscopy (SEM) (Leica Stereoscan 440), while the film substructure was investigated by examining the film cross-sections using transmission electron microscopy (TEM) (JEOL 2000FX) and optical microscopy (Nikon Optiphot) techniques. The optical microscopy was conducted on carefully polished (1 μm diamond paste) cross-sections of the films, whilst TEM examination was conducted on ultramicrotomed sections.

The samples were tensile tested to determine their

breaking strength and elongation at break using an Instron 4302 tensile testing machine. Dumb-bell-shaped specimens were cut from the PPy films for this purpose. The gauge length was 50 mm, the width 10 mm and the thickness 20 μm. At least five samples were tested in order to determine the mean and 95% confidence limits.

RESULTS

Polymerization was conducted galvanostatically and the potential of polymerization was found to be constant throughout. Uniform coatings were formed on each substrate. Conductivities were typically of the order of 30–40 S cm^{-1}.

Figure 1 shows a scanning electron micrograph of the solution side of the PPy film prepared on the platinum electrode. This surface was typical of all films studied. Distinct nodular protrusions covered the film surface and were similar to those previously reported[17]. Each of the PPy samples showed similar nodule size distributions, indicating that the composition of the electrode surface does not significantly affect the film morphology, at least under the conditions employed in this study. An interesting result was observed when the nature of the film substructure was investigated using TEM. Distinct cone-shaped structures were evident below each of the surface nodules, and were observed in all of the films, regardless of the substrate material used during polymerization (*Figure 2*).

The cone-shaped features were also evident on polished cross-sections when using optical microscopy. Cones of similar size and shape were evident in all of the films (*Figure 3*). However, the nature of the film structure varied within each film. For example, *Figure 4* shows a region of the PPy film formed on the carbon electrode which has a rather featureless region, whereas *Figure 3b* shows a cluster of cones in another region of the same sample.

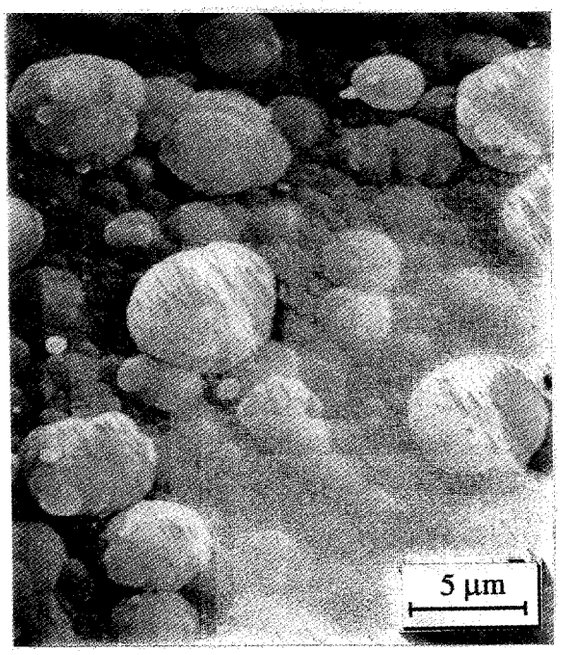

Figure 1 Scanning electron micrograph of the solution surface of electrochemically prepared PPy

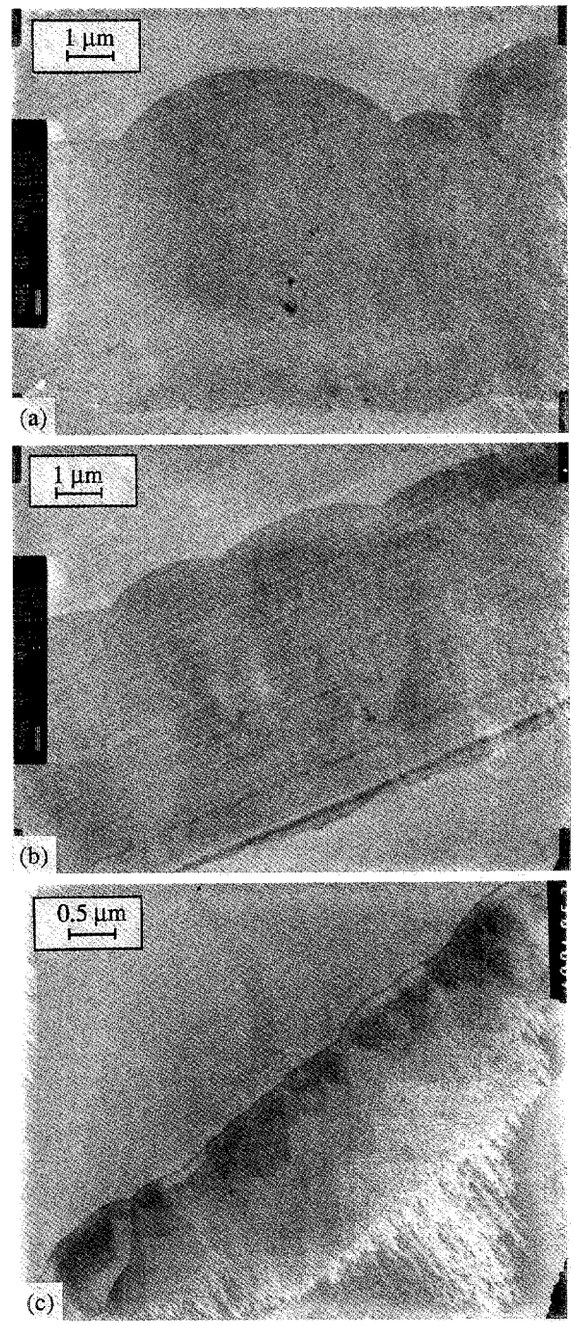

Figure 2 Transmission electron micrographs of ultramicrotomed sections of PPy films: (a) SS electrode; (b) carbon-coated SS electrode; (c) Pt-coated SS electrode. The electrode side of the film is at the bottom in each case, and the nodules can be seen at the opposite (solution) surface; the nodules form the tops of cones

The structural features were enhanced in optical microscopy by using cross-polarized light. The optical activity of the samples was confirmed by rotating the sample and observing the cyclic change in contrast. The optical activity is most likely due to molecular anisotropy, as has been previously reported in X-ray diffraction studies of PPy[17].

Similar results have also been reported by Sutton and Vaughan[18]. These workers also found cone-shaped structures in scanning electron micrographs of acid-etched surfaces of PPy films, although they did not comment on the origin of such features.

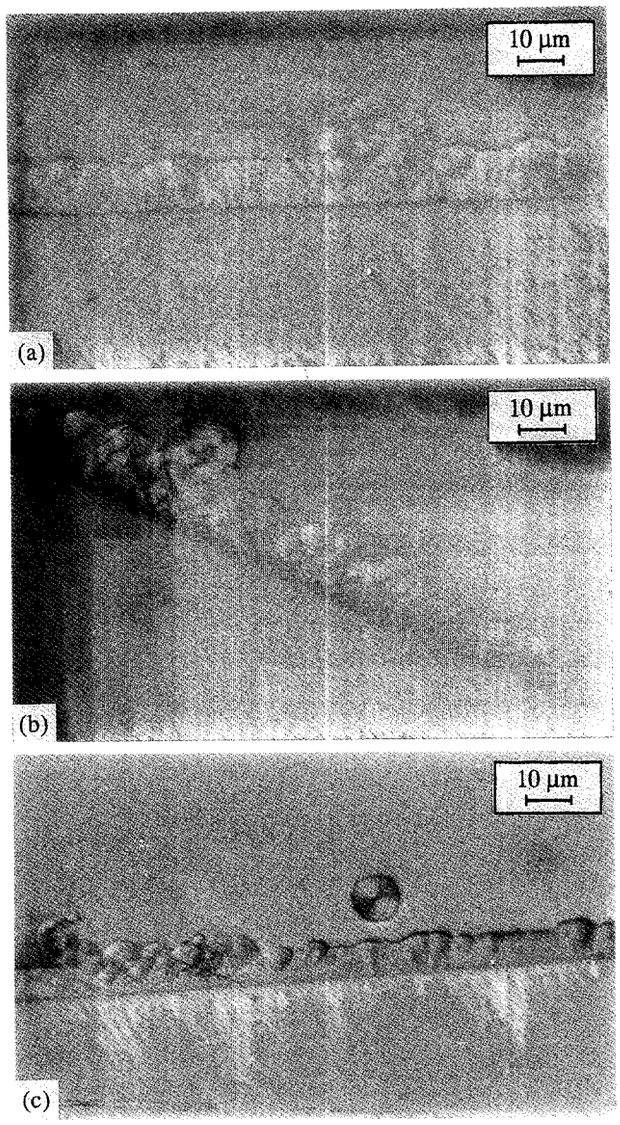

Figure 3 Optical micrographs of polished cross-sections of PPy films: (a) SS electrode; (b) carbon-coated SS electrode; (c) Pt-coated SS electrode

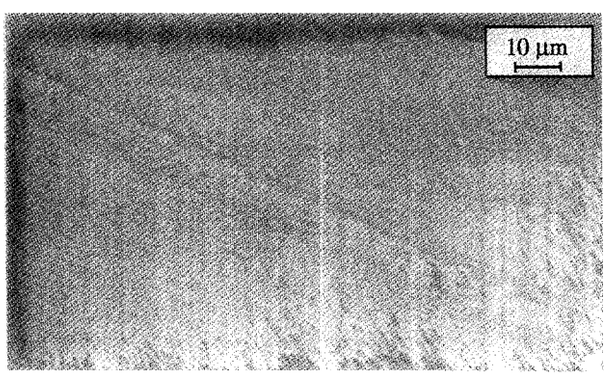

Figure 4 Optical micrograph of a polished cross-section of a PPy film prepared on the carbon electrode

Table 1 Mechanical properties of the PPy films as determined by tensile testing

Polymerization electrode	Breaking strength (MPa)	Young's modulus (GPa)
Stainless steel	63 ± 7	2.4 ± 0.4
Carbon-coated SS	67 ± 6	3.0 ± 0.4
Platinum-coated SS	72 ± 6	3.2 ± 0.2

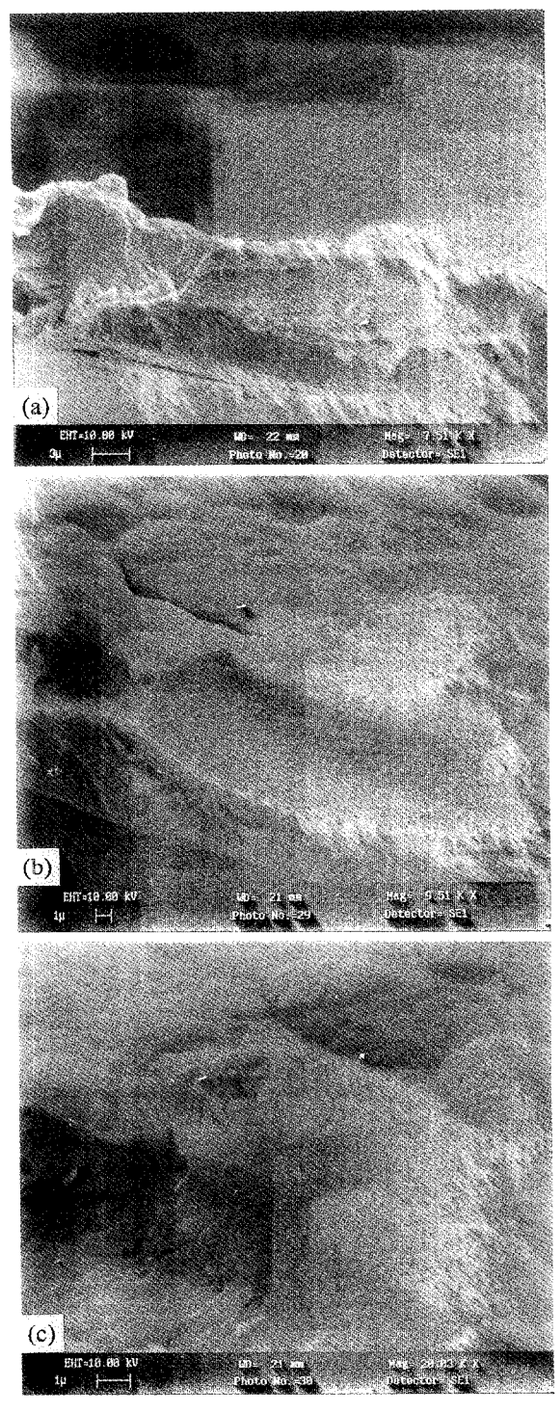

Figure 5 Scanning electron micrographs of the fracture surface of the PPy film prepared on the platinum-coated stainless steel electrode. The fracture path is seen to pass around the cones. Note that (c) is a higher-magnification image of (b)

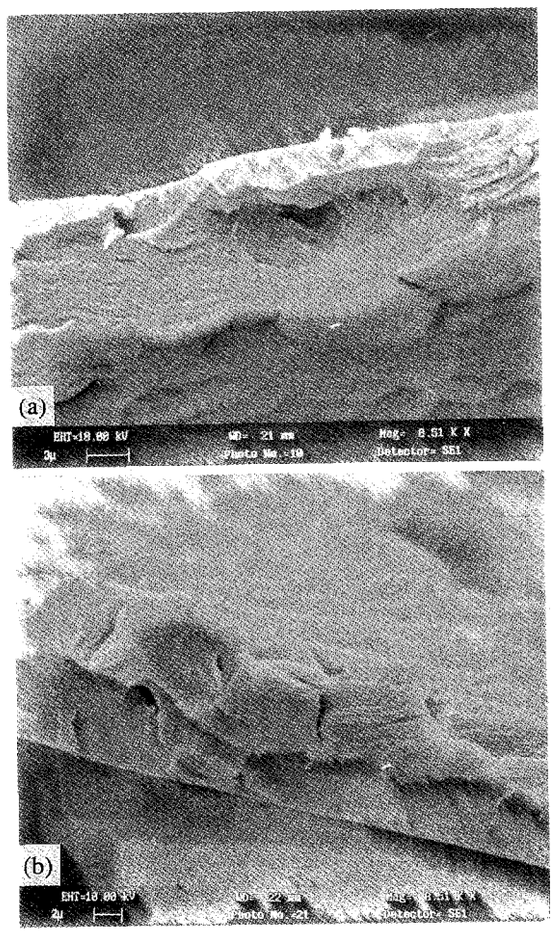

Figure 6 Scanning electron micrographs of the fracture surface of the PPy film prepared on the platinum-coated stainless steel electrode. Microcracks adjacent to the main crack path are evident in each case

The breaking strengths and Young's moduli of the films are given in *Table 1*. No significant differences in the breaking strength were observed, while the PPy film prepared on the stainless steel electrode showed a slightly lower average modulus.

Examination of the fracture surfaces from the tensile test samples clearly shows that the crack path follows the nodule boundaries, at least along the solution side of the film (*Figures 5* and *6*). *Figure 5* shows hollows and undulations on the fracture surface resulting from the crack proceeding around the cones. *Figure 6* highlights microcracks at cone boundaries adjacent to the main crack path.

DISCUSSION

The observation of cone structures within the PPy films in this and previous work[18] indicates that electrochemically prepared PPy films do not deposit on the electrode homogeneously. Differences in terms of composition and/or molecular orientation occur throughout the film. Since observation of the cone substructure was enhanced using cross-polarized light, the latter phenomenon is more likely.

Similar features have been reported in other electrochemical plating systems. Studies of the morphology of electrodeposited metals[19,20] show that in some cases cone-shaped grains are observed in the cross-section. This growth mode is found to occur when the grains grow preferentially in the direction of the electric field, i.e. perpendicular to the electrode surface. The result is elongated grains, which can fan outwards as the crystal grows so that the grain boundaries reveal cone-shaped structures. In these circumstances the surface of the metal was rough and nodular in texture, as has been reported above for PPy.

The similarity in structure between electrodeposited metals and electropolymerized PPy suggests a similar deposition mechanism may occur in both cases. Metal plating has been described as involving heterogeneous crystal nucleation on the electrode surface and preferential growth of the crystals in the direction of the electric field[19,20]. Some evidence is also available from the literature to support the idea of heterogeneous nucleation of PPy on the electrode surface[21]. Christensen *et al.*[21] have observed 'micro-islands' of deposited PPy in the very early stages of deposition by scanning tunnelling microscopy, which may represent the nuclei of the cones.

The cone-shaped features were also observed on the fracture surfaces of the PPy films, since the crack was found to pass around the cones. This indicates that the cone boundaries are points of weakness that facilitate crack growth. These defects are likely to dominate the fracture of the films and their presence is likely to induce brittle fracture at low stress. The three films studied in this present work showed similar breaking strengths, which may be due to the similar nodular/cone morphology observed in each. Substantial differences in the morphology may produce more significant differences in breaking stress.

CONCLUSIONS

This study has involved an investigation of the film substructure of electrochemically prepared PPy and its relationship to mechanical properties. Distinct cone structures were observed in film cross-sections, which were capped by the nodules on the film surface. Neighbouring cones are presumed to differ in terms of molecular orientation, and are believed to form as a result of an heterogeneous deposition mechanism similar to that observed in some metal-plating operations.

The cone structures were observed to determine the fracture behaviour of the films, since fracture followed the cone boundaries. No differences in breaking strength of the films examined in this investigation were observed, but this was assumed to be due to similarities in morphology.

REFERENCES

1 Cvetko, B. F., Brungs, M. P., Burford, R. P. and Skyllas-Kazacos, M. *J. Appl. Electrochem.* 1987, **17**, 1198
2 Sun, B., Jones, J. J., Burford, R. P. and Skyllas-Kazacos, M. *J. Mater. Sci.* 1989, **24**, 4024
3 Buckley, L. J., Roylance, D. K. and Wnek, G. E. *J. Polym. Sci. Polym. Phys. Edn* 1987, **25**, 2179
4 Wynne, K. J. and Street, G. B. *Macromolecules* 1985, **18**, 2361
5 Diaz, A. F. and Lacroix, J. C. *Nouv. J. Chem.* 1988, **12**, 171
6 Gandhi, M. R., Burford, R. P., Spinks, G. M. and Wallace, G. G. Proceedings of 3rd Pacific Polymer Conference, Gold Coast, December 1993

7 Gandhi, M. R., Burford, R. P., Spinks, G. M. and Wallace, G. G. Proceedings of Interfaces II Conference Ballarat, Australia, November 1993
8 Gandhi, M. R., Murray, P., Spinks, G. M. and Wallace, G. G. *Synth. Met.* (in press)
9 Young, R. J. Proceedings of Electrical, Optical and Acoustic Properties of Polymers Conference, Sydney, Australia, September, 1985
10 Ogasawara, M., Funahashi, K., Demura, T., Hagiwara, T. and Iwata, K. *Synth. Met.* 1986, **14**, 61
11 Hagiwara, T., Hirasaka, M., Sato, K. and Yamaura, M. *Synth. Met.* 1990, **36**, 241
12 Bloor, D., Hercliffe, R. D., Galiotis, C. G. and Young, R. J. in 'Electronic Properties of Polymers and Related Compounds' (Eds H. Kuzmany, M. Mehring and S. Roth), Springer, Berlin, 1985, p. 179
13 Moss, B. K., Burford, R. P. and Skyllas-Kazacos, M. *Mater. Forum* 1989, **13**, 37
14 Wettermark, U. G., Worrell, G. A. and Chen, C. S. *Polym. Mater. Sci. Eng.* 1990, **64**, 267
15 Qian, R. and Qiu, J. *Polym. J.* 1987, **19**, 157
16 Mitchell, G. R., Davis, F. J. and Legge, C. H. *Synth. Met.* 1988, **26**, 247
17 Nannini, A. and Serra, G. *J. Mol. Electron.* 1990, **6**, 81
18 Sutton, S. J. and Vaughan, A. S. *J. Mater. Sci.* 1993, **28**, 4962
19 Raub, E. and Muller, K. 'Fundamentals of Metal Deposition', Elsevier, Amsterdam, 1967, p. 124
20 Winand, R. in 'Application of Polarization Measurements in the Control of Metal Deposition' (Ed. I. H. Warren), Elsevier, Amsterdam, 1984, p. 47
21 Christensen, L., Hendrickson, W. A., Yang, R. and Evans, D. F. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1989, **30**, 100