

Stability and mechanical properties of electrochemically prepared conducting polypyrrole films

BIANTING SUN*, J. J. JONES, R. P. BURFORD†, M. SKYLLAS-KAZACOS
*School of Chemical Engineering and Industrial Chemistry, University of New South Wales,
 PO Box 1, Kensington, New South Wales 2033, Australia*

The stability and mechanical properties of polypyrrole *p*-toluene sulphonate films prepared under various preparation conditions were studied and are reported here. Relatively high retention of conductivity and flexibility properties in air at room temperature were found for the films. More stable films were produced from propylene carbonate diluent than from acetonitrile and solvent mixtures. Acid treatment caused conductivity to increase and the mechanical properties to decrease slightly. However, both properties decreased dramatically after exposure of the films to sodium hydroxide solution. The effect of solutions containing different vanadium ions was also observed, the films being stable in V³⁺ and V⁴⁺ acid solutions, but unstable in V⁵⁺ solutions. The thermal stability of polypyrrole films grown at different temperatures and from different solvents was considerably high and fairly constant. Anisotropy in the mechanical properties was also observed for the two directions (along and across) within the same plane of the film. Incorporation of the plasticizer, di-iso-butyl phthalate (DIBP) into the films improved the mechanical properties. A high extendable acrylic-polypyrrole composite film was also prepared, capable of straining over 100%.

1. Introduction

The conducting polymer polypyrrole has received a great deal of attention since the first preparation by Kanazawa and co-workers of the flexible film by electrochemical oxidation [1]. This polymer is characterized by having high conductivity and also good stability, properties useful for commercial applications. It has also been shown that films of polypyrrole can be cycled repeatedly between the oxidized and reduced states, without any evidence of decomposition [2, 3].

Polypyrrole has been found by many investigators to possess fair environmental stability in air, with moderate reduction of conductivity [1, 4, 5]. However, polypyrrole films are sensitive to the presence of Lewis bases in solution, which apparently act as nucleophiles leading to degradation of the electrode properties [6]. The influence of acids, including sulphuric acid, and bases, including sodium hydroxide, and alternative treatment of both acids and bases on conductivity of different polypyrrole salts, including poly (pyrrole phenyl sulphonate) and poly (pyrrole perchlorate) has been reported [7-9]. Results from elemental analysis indicated an ion-exchange process during treatment. Although instability of polypyrrole film under halogen oxidation was reported by Bard *et al.* [10], i.e. under the evolution of bromine and chlorine gases, the influence of other chemicals on stability has been less reported.

Polypyrrole-BF₄ films with various anions are also thermally stable materials. Thermogravimetric scans

show only a slight weight loss, increasing to 10% at 300°C, with markedly larger extents of weight loss above that temperature [11]. Diaz *et al.* observed that polypyrrole doped with perchlorate, tetrafluorate or hexafluorophosphate lost conductivity and decomposed at temperatures higher than 150°C in air. However, they found that toluene sulphonate-containing films did not decompose until 280°C [12].

The mechanical properties of polypyrrole compare quite well with those of polystyrene and polymethylmethacrylate (PMMA). Polypyrrole films have elongations very much smaller than fully saturated linear polymers like polyethylene and polytetrafluoroethylene. Cross-linked aromatic polymers, such as phenol formaldehyde and melamine formaldehyde, are more on polypyrrole *p*-toluene sulphonate decreased with increasing current density and improved dramatically on addition of water to the electrolyte in trace (1%) quantities [14] and a linear decrease of Young's modulus with potential was also observed by Satoh *et al.* [15].

Diaz *et al.* [12] have shown that the nature of the cosolvent and also the anion used in the preparation of the conducting polymer, influences various mechanical properties such as Young's modulus, tensile strength, etc. In a recent study, an initially strong and tough polypyrrole film was found to undergo a reduction in mechanical performance after ageing in air [5].

We have further investigated the stability in air of

* Permanent address: Department of Chemistry, Hebei Teacher's University, Shijiazhuang, China.

‡ Author to whom all correspondence should be addressed.

polypyrrole films prepared at lower temperatures, and from different solvents. The influence of various media, such as acid, base, acid solutions containing vanadium ions and sodium dihydrogen vanadate solutions on the stability of the film conductivity are described. The thermal and mechanical stability of polypyrrole films and polypyrrole composites prepared by addition of plasticizers are also reported here.

2. Experimental procedure

2.1. Polypyrrole preparation and conductivity measurements

Films of polypyrrole were prepared by electrodeposition on to titanium substrates. The polymerization solution consisted of propylene carbonate (Sigma Chemical Company), acetonitrile (AJAX Chemicals) or an isovolumic mixture of propylene carbonate and acetonitrile containing 0.75 M pyrrole monomer, 0.25 M tetra ethyl ammonium *p*-toluene sulphonate electrolyte (Alfa Products) and 1% water (vol/vol). Electrodeposition was carried out at constant currents from 0.7 to 3.5 mA cm⁻², with the potential being between 0.7 to 1.10 V versus the saturated calomel electrode (SCE) at room temperature and 0°C, the saturated sodium calomel electrode (SSCE) at -20°C or versus Hg/Hg₂Cl₂/(C₂H₅)₄NCl in propylene carbonate at -40°C.

Square samples of polypyrrole (2 cm × 2 cm) were exposed to the acid, base and acid solutions containing vanadium ions, for various lengths of time, rinsed with distilled water and thoroughly dried. The conductivity was then measured using a four-probe technique [16].

Films of polypyrrole were also prepared from solutions containing 5 wt % of the plasticizer di-2-ethylhexyl phthalate (DEP) (Corflex 400, CSR Chemicals) or di-iso-butyl phthalate (DIBP). The films were removed from the titanium electrode and conductivities then measured. Thermogravimetric analysis and tensile testing were also carried out, as described below.

A composite material was also prepared using the acrylic emulsion polymethyl methacrylate (PMMA). A thin film of PMMA was cast on the surface of the titanium anode by dipping the anode into the PMMA and then drying the film under an infrared lamp. This process was continued a number of times until a substantial film of PMMA was built up on the titanium anode. The anode was then inserted into the polymerization cell and electrodeposition performed as usual.

2.2. Thermal stability analysis

Thermogravimetric analysis (TGA) of the films was performed using a Du Pont Instruments 951 Thermogravimetric Analyser and Series 99 Thermal Analyser. Thermal stability and volatiles content were determined by heating approximately 10 mg sample in the platinum boat. The temperature was raised from 40 to 940°C at 50°C min⁻¹ and a nitrogen atmosphere was employed throughout.

2.3. Tensile tests

Tensile tests of polypyrrole were performed on an Instron 1115 Universal Testing Machine. Parallel-sided strips of polypyrrole approximately 3 to 4 mm wide and 5 cm long were tested. An intergrip distance of 2 cm and a cross-head speed of 5 cm min⁻¹ were employed. Although some samples were epoxy resin bonded to aluminium supports, those could be legitimately tested in normal self-retracting grips. No localized drawing down was observed and fracture was often away from the grip faces.

3. Results and discussion

3.1. Stability of polypyrrole in air

The polypyrrole films grown at -20 and -40°C exhibited good air stability in conductivity with ageing time. Similar results were obtained at room temperature and 0°C [4, 5]. As shown in Fig. 1, the conductivity of a film prepared on a 2 cm × 5 cm substrate at -20°C, within 30 min of removal from the deposition solution was 300 S cm⁻¹. The conductivity along the sample reached a maximum value of 390 S cm⁻¹ by the end of the tenth day and remained relatively high (330 S cm⁻¹) even after three months. The increase in conductivity with storage time during the first few days is due to the decrease in moisture/solvent content of the films on standing, while a slight decrease in conductivity after long storage time is thought to be due to oxygen attack of the conjugated double bond system [4].

The polypyrrole films retain not only high conductivity, but also good flexibility at room temperature, and appear to show negligible chemical change. The only noticeable difference is that the films tend to dry out slightly when exposed to the atmosphere leading to some embrittlement. Again it must be noted that the solvent/moisture present in the films acts as a plasticization agent giving rise to flexibility. It is thought that reimmersion of a dry film in the solvent will restore flexibility.

3.2. Influence of solvents on stability in conductivity

Fig. 2 shows that the stability in the conductivity of the polypyrrole films was affected by different solvents

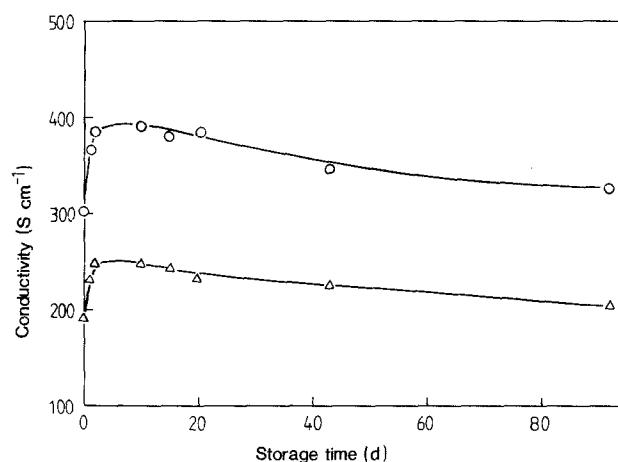


Figure 1 Conductivity of polypyrrole *p*-toluene sulphonate films prepared at -20°C and 0.7 mA cm⁻² against ageing time: (○) along the sample, (Δ) across the sample.

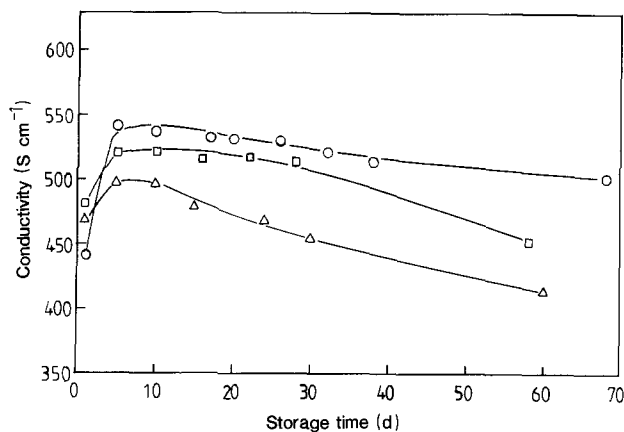


Figure 2 Conductivity of along the sample for the films grown using different solvents: (O) propylene carbonate, (Δ) acetonitrile and (\square) the mixture of propylene carbonate and acetonitrile.

used in the electrodeposition. It can be seen that propylene carbonate produces films of better stability than acetonitrile or mixtures of propylene carbonate and acetonitrile. The conductivity of films produced with propylene carbonate increases dramatically during the first few days and retains the higher value for longer periods. This is thought to be due to differences in properties of propylene carbonate and acetonitrile, such as dielectric constant, viscosity and freezing point. A solvent with high dielectric constant, low viscosity and a low freezing point will play a very important role in the electro-polymerization process, as there appears to be some form of specific solvation which stabilizes the π -segments along the polymer chain. The greater decrease in the propylene carbonate content of the thick films during the first few days is the most likely cause of the greater change in conductivity compared with the thinner films obtained from acetonitrile and mixtures.

3.3. Effect of acid, base and vanadium solutions on conductivity

The influence of acidic and basic media on conductivity and mass changes is shown in Figs 3, 4 and 5. When the polypyrrole film was treated with 1 M NaOH, the conductivity decreased dramatically,

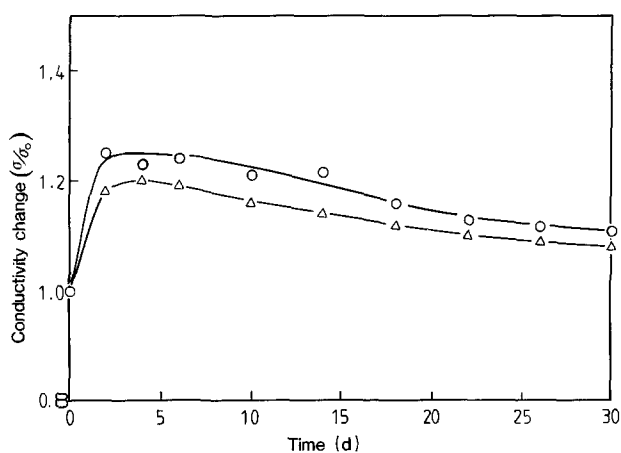


Figure 3 Conductivity changes of polypyrrole *p*-toluene sulphonate films exposed to: (O) 2 M H_2SO_4 and (Δ) 2 M HCl. σ_0 and σ are the initial conductivity and the corresponding quantity after treatments for a time, t , respectively.

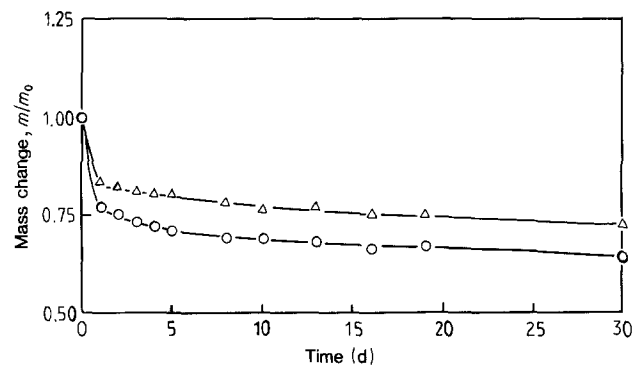


Figure 4 Mass changes of polypyrrole *p*-toluene sulphonate films exposed to: (O) 2 M H_2SO_4 and (Δ) 2 M HCl. m_0 and m are the initial mass and the mass after treatments for a time, t , respectively.

dropping quickly to low values in 15 min (Fig. 5). At longer treatment times the decrease in conductivity levelled off, as previously reported [7-9]. Increasing the sodium hydroxide solution concentration to 2 M accelerates the decrease in conductivity. The effect of acid on conductivity, however, differs somewhat from a previous report [8], where the conductivity first increased with treatment time, reaching a maximum within 30 min and then levelled off to slightly lower than the initial value. In the present study, however, the conductivity of the films increased as a function of treatment time during the first week, and then continued to increase, levelling off after 30 d at a value greater than the initial conductivity of the sample. This is shown in Fig. 3.

The decrease in mass and changes in TGA traces after acid and base treatment shown in Figs 4 and 6 suggest that *p*-toluene sulphonate ions are being replaced by HSO_4^- , SO_4^{2-} , Cl^- , or OH^- . According to Münstedt [5], OH^- covalently bonds with the polypyrrole, leading to a decreased conjugation length and hence lower conductivity. Sulphuric or hydrochloric acid treatments are said [5] to lead to replacement of *p*-toluene sulphonate ions by smaller SO_4^{2-} , HSO_4^- , or Cl^- ions and so an improvement in conductivity. No changes in backbone covalent bonding are supposed to occur, in contrast to the base treatment.

An interesting phenomenon which occurs if the acid and base treatments are alternated is shown in Fig. 5. In the first 120 min the film was treated with 1 M NaOH

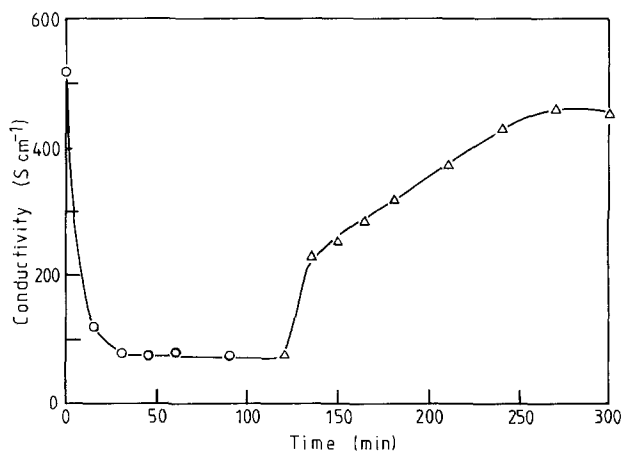


Figure 5 Conductivity of polypyrrole *p*-toluene films by alternating exposures to (O) 1 M NaOH and (Δ) 1 M HCl, respectively.

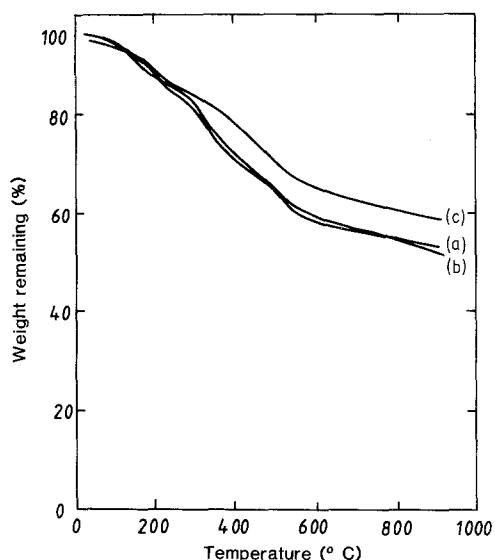


Figure 6 Thermogravimetric analysis weight loss trace for polypyrrole *p*-toluene sulphonate films prepared at 0.7 mA cm^{-2} and (a) -20°C , (b) -40°C and (c) sample (a) treated with acid solution, respectively.

solutions, and as expected conductivity decreased. After 120 min, however, the film was exposed to an acid solution of the same concentration as the base, and the conductivity increased again, reaching a value slightly less than the initial value. The phenomenon observed with alternative acid and bases treatment is similar to that reported by Müstedt *et al.* [7, 8] and Inganäs *et al.* [9]. In the present study, it was also noted that the effect of the base solution is much more dramatic than acid treatment for the same concentration.

Polypyrrole films were found to be very stable in acid solution containing vanadium ions. As can be seen in Fig. 7, the conductivity of the polypyrrole increases within the first few days, similar to the results of acid treatment, and then levels off. The increase obtained with V^{4+} acid treatment was more pronounced than with the V^{3+} acid solution. However, when a polypyrrole film was immersed in $2 \text{ M V}^{5+}/2 \text{ M H}_2\text{SO}_4$ solution, it dissolved within a few days. After an exposure of the film to pH7 sodium dihydrogen vanadate solution, the conductivity increased slightly during the first few days, and then decreased

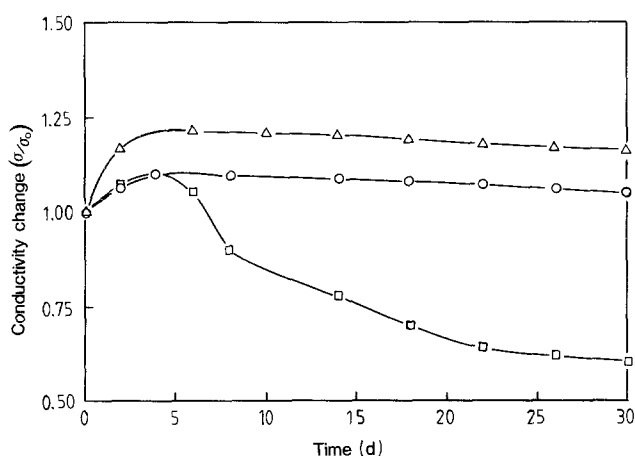


Figure 7 Conductivity changes of polypyrrole *p*-toluene sulphonate films exposed to: (O) $2 \text{ M V}^{3+}/2 \text{ M H}_2\text{SO}_4$, (Δ) $2 \text{ M VF}^{4+}/2 \text{ M H}_2\text{SO}_4$ and (\square) $2 \text{ M NaH}_2\text{VO}_4$, respectively.

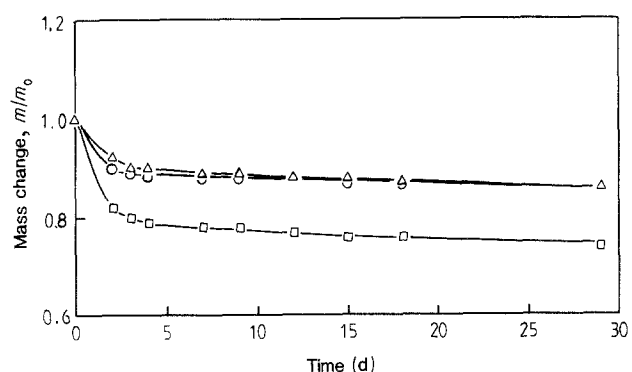


Figure 8 Mass changes of polypyrrole *p*-toluene films exposed to: (O) $2 \text{ M V}^{3+}/2 \text{ M H}_2\text{SO}_4$, (Δ) $2 \text{ M V}^{4+}/2 \text{ M H}_2\text{SO}_4$ and (\square) $2 \text{ M NaH}_2\text{VO}_4$, respectively.

gradually. This behaviour is also thought to be due to ion exchange, as for the acid solution. The mass loss of polypyrrole films in different vanadium ion solutions is also presented in Fig. 8, and shows that when the films are exposed to acidic vanadium solutions, the *p*-toluene sulphonate ions are replaced by sulphate or hydrogen sulphate anion, so that same mass change is observed. Different oxidation states of vanadium gave slightly different results with conductivity, the V^{4+} giving higher conductivity than the V^{3+} acid solution. When the film was exposed to the stronger oxidizing agent V^{5+} , however, it rapidly dissolved. The mass loss and atomic adsorption spectroscopic analysis for the polypyrrole film immersed in sodium dihydrogen vanadate further support an ion exchange between the dihydrogen vanadate *p*-toluene sulphonate ions.

3.4. Thermal stability of polypyrrole films

The results obtained for various thermal analyses were similar in many respects to earlier reports [6, 7, 10]. An interesting feature of all these traces was that even after the material was subjected to a temperature of 900°C only a moderate weight loss occurred in all samples, showing temperature stability.

Fig. 6 shows the results of thermogravimetric analyses for polypyrrole films produced under three conditions. Thermal stability varied only slightly with preparation temperature. Thus the weight loss of a sample prepared at -40°C was only slightly less than that of sample made at -20°C . After acid treatment, however, a significant difference in the weight loss is observed, as shown by comparing Figs 8a and c. The

TABLE I Tensile properties of polypyrrole toluene sulphonate prepared at -20 and -40°C

Sample*	Sample condition	σ_b (MPa)	E_b (%)	E (GPa)
1	grown at -40°C (after 5 mon)	48	12.4	1.4
2	grown at -20°C (after 3 mon)	40	31	0.9
3	grown at -20°C (after 5 mon)	31	4.8	1.4
4	same sample as no. 3 (acid treated for 24 h)	29	3.4	0.43
5	same sample as no. 3 (base treated for 24 h)	-	-	-

* All samples tested in along direction.

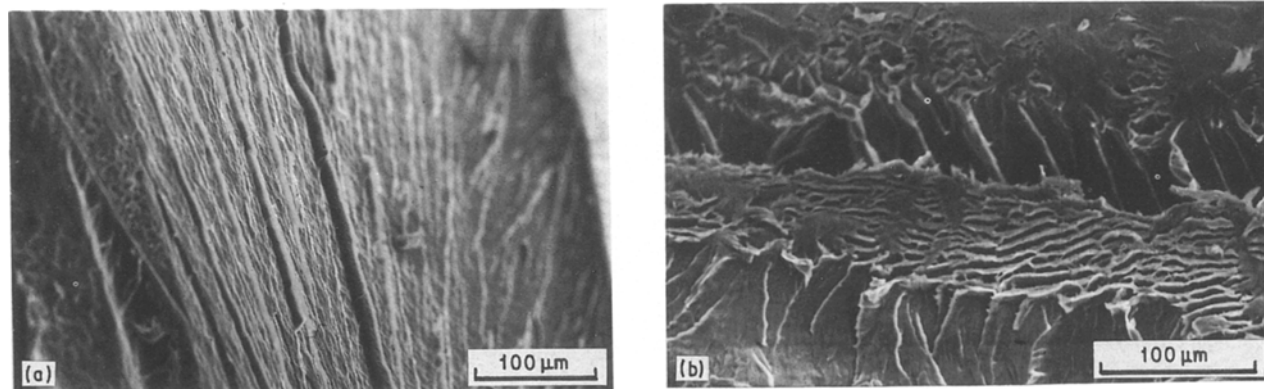


Figure 9 SEMs of polypyrrole *p*-toluene sulphonate films showing possible structural orientation: (a) along the sample, (b) across the sample.

original material shows a 21% and 44% weight loss at 360 and 900° C, respectively, while the sample treated with acid solution only gives 15% and 38% under the same thermal conditions. This suggests that as a result of the acid treatment, ion exchange occurs with replacement of the large *p*-toluene sulphonate ions with smaller chloride ions, so that the weight loss of a film treated with acid solutions is less than that of the original sample. Thermal properties of films produced from different solvents show no obvious difference.

3.5. Mechanical properties of polypyrrole

Table I summarizes the mechanical properties of polypyrrole samples prepared at different temperatures and treated by acid and base solutions. It was found that the tensile strength of polypyrrole increased with decreasing electrodeposition temperature. This is again explained by the higher conjugation in the polymer backbone and ordering of polypyrrole chains. There may also be a change in molecular weight but this has not been quantified. Ductility for films produced under the same conditions declined with ageing time, as a result of loss of moisture and solvent which had acted as plasticizers [5]. The influence of acid and base on the mechanical properties is also illustrated in Table I. After exposure to sulphuric acid solution, the polypyrrole films shrank, became hard, somewhat brittle and weaker. Sodium hydroxide treatment also caused severe embrittlement of the films, which were too fragile to test.

TABLE II Tensile properties of polypyrrole toluene sulphonate prepared at 25° C using different solvents at 0.7 mA cm⁻²

Sample	Sample condition	σ_b (MPa)	E_b (%)	E (GPa)
1	using propylene carbonate solvent (after 1 mon – along direction)	59	20.7	2.1
2	same sample as no. 1 (across direction)	33.5	11.7	1.1
3	using acetonitrile solvent (after 1 mon – along direction)	2.0	1.9	2.2
4	using mixtures P.C. solvent (after 1 mon – along direction)	55	11.1	2.2

The influence of solvent on mechanical properties is shown in Table II. The film produced from propylene carbonate solution gave the higher breaking strain. The film obtained from acetonitrile possessed poor mechanical properties.

It was also noted that polypyrrole *p*-toluene sulphonate films prepared from propylene carbonate were not only anisotropic in conductivity [4, 5], but also in their mechanical properties as shown in Table II. Thus, the tensile strength of the film measured “along” the sample was also higher than “across” the sample. Scanning electron micrographs for the two directions are shown in Fig. 9 and illustrate a difference in the structural order in two directions.

The addition of the plasticizers into the electropolymerization solution significantly improved mechanical properties and in particular, increased the yield strain. The DIBP plasticizer was seen to improve the mechanical properties to a greater extent than the DEP (Table III).

Although examination of the tensile samples suggests only brittle failure, with composite films ductile fracture was observed, as shown in Fig. 10. This is noteworthy as in all previous fractures of polypyrrole films, brittle fracture predominated.

The electro-oxidation of pyrrole using an elastic acrylic-coated titanium electrode gave rise to a black composite film which was flexible and self supporting. Although these films could be stretched over 100% and return to their original film structure, on release, as shown in Fig. 11, the conductivity values obtained for this sample were quite low. Such improvements in

TABLE III Tensile properties of polypyrrole and additive (DEP and DIBP) at 25° C and 0.8 V (versus SCE)

Cosolvent	σ_b (MPa)	E_b (%)	E (GPa)
Acetonitrile	27.5	23.5	4.30
+ 5% DIBP			
Propylene carbonate	21.0	20.5	3.4
+ 5% DIBP			
Propylene carbonate	14.0	4.70	0.85
+ 5% DEP			
Acetonitrile	10.0	7.64	1.7
Propylene carbonate	21.0	8.82	1.7

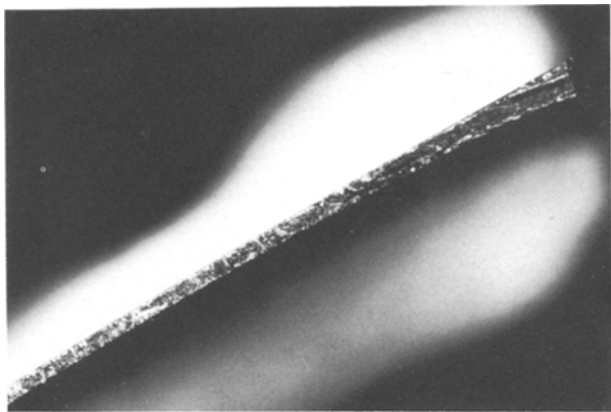


Figure 10 Polypyrrole *p*-toluene films produced ductile fracture (right-hand side) and brittle fracture (left-hand side) after the tensile tests.

the mechanical properties of the conducting film would be significant in applications where high flexibility is important such as for antistatic rubber belting.

4. Conclusions

Our polypyrrole *p*-toluene sulphonate films show relatively high stability in air at room temperature not only with regard to conductivity, but also in their flexibility. Propylene carbonate was found to be a better solvent than acetonitrile or mixtures of propylene carbonate and acetonitrile, and resultant polypyrrole *p*-toluene sulphonate films had more stable conductivity and tensile strength. The thermal stability and mechanical properties of the polypyrrole films increased with decreasing preparation temperature. Anisotropy was observed in tensile strength as well as in conductivity.

The conductivity increased and mechanical properties decreased slightly for films treated by acid solution. However, both of the properties fell off dramatically after the films were exposed to sodium hydroxide solution. Alternate treatment of acid and base solutions caused an alternative change in the conductivity of film. The influence of acidic V^{3+} and V^{4+} solutions on the conductivity of the polypyrrole films was observed to be similar to that of acid solution alone. However, films dissolved quickly in acidic V^{5+} solution as a

result of polypyrrole oxidation by the highly oxidizing V^{5+} ion. When polypyrrole film was exposed to the neutral sodium dihydrogen vanadate solution, both conductivity and mass decreased gradually. It was also noted that mechanical properties were improved by incorporating the plasticizer, DIBP, into the polypyrrole film during polymerization. Over 100% elongation was obtained on stretching a composite film of acrylic-polypyrrole.

References

1. K. K. KANAZAWA, A. F. DIAZ, R. H. GEISS, W. D. GILL, J. F. KWAK, A. J. LOGAN, J. F. RABOLT and G. B. STREET, *J. Chem. Soc. Chem. Commun.* (1979) 854.
2. A. F. DIAZ and J. I. CASTILLO, *ibid.* (1980) 397.
3. A. F. DIAZ, J. I. CASTILLO, J. A. LOGAN and W. Y. LEE, *J. Electroanal. Chem.* **129** (1981) 115.
4. B. F. CVETKO, M. P. BRUNGS, R. P. BURFORD and M. SKYLLAS-KAZACOS, *J. Appl. Electrochem.* **17** (1987) 1198.
5. *Idem*, *J. Mater. Sci.* **23** (1988) 2102.
6. A. F. DIAZ, J. M. VASQUEZ VALLEJO and A. M. DURAN, *IBM J. Res. Develop.* **25** (1981) 42.
7. H. MÜNSTEDT, *Polymer* **27** (1986) 899.
8. H. MÜNSTEDT, H. NAARMANN and G. KÖHLER, *Molec. Cryst. Liq. Cryst.* **118** (1985) 129.
9. O. INGANÄS, R. ERLANDSSON, C. NYLANDER and I. LUNSDTRÖM, *J. Phys. Chem. Solids* **45** (1984) 427.
10. R. A. BULL, F.-R. FAN and A. J. BARD, *J. Electrochem. Soc.* **130** (1983) 1636.
11. A. F. DIAZ and K. K. KANAZAWA, in "Extended Linear Chain Compounds", edited by J. S. Miller, Vol. 3 (Plenum, New York, 1983) p. 417.
12. M. SALMON, A. F. DIAZ, A. J. LOGAN, M. KRONBI and J. BARGON, *Molec. Cryst. Liq. Cryst.* **83** (1982) 265.
13. A. F. DIAZ and B. HALL, *IBM J. Res. Develop.* **27** (1983) 342.
14. D. BLOOR, R. D. HERCLIFFE, C. G. GALIOTIS and R. J. YOUNG, in "Electronic Properties of Polymer and Related Compounds", edited by H. Kuzmany, M. Mehring and S. Roth, Springer Series in Solid State Sciences, No. 63 (Springer, Berlin, 1985) 179.
15. M. SATOH, K. KANETO and K. YOSHINO, *Synth. Met.* **14** (1986) 286.
16. A. R. BLYTHE, *Polym. Test.* **4** (1984) 195.

Received 15 August 1988

and accepted 11 January 1989

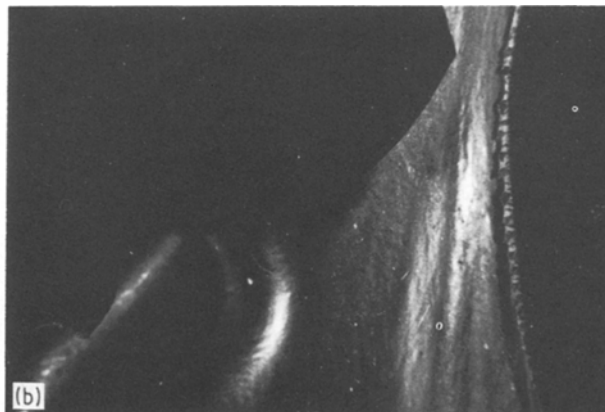
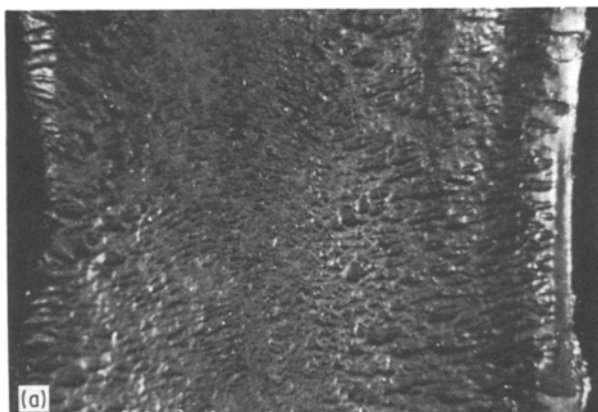


Figure 11 (a) Highly elastic acrylic-polypyrrole composite stretched up to 114% elongation and (b) returned to the original film structure.