

# Electrical and mechanical properties of polyaniline fibres produced by a one-step wet spinning process<sup>☆</sup>

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Received 17 November 1998; received in revised form 19 January 1999; accepted 20 May 1999

## Abstract

We have recently developed a new acid-solution processing route for the conjugated polymer, polyaniline (PANI) [Adams et al., *J Phys: Condens Matter* 1998;10:8293] that now allows us to demonstrate the wet-spinning of inherently conductive PANi fibres in a one-step process. This is achieved from solutions of PANi protonated with 2-acrylamido-2-methyl-1-propanesulfonic acid in dichloroacetic acid. The fibres were spun into various coagulation solvents, i.e. acetone, butyl acetate and 4-methyl-2-pentanone. ‘As-spun’ fibres have Young’s moduli of 40–60 MPa, ultimate tensile strengths of 20–60 MPa and electrical conductivities of 70–150 S cm<sup>-1</sup>. These fibres may be drawn at room temperature or above to an extension of ~500%, with a concomitant increase in conductivity of up to a maximum of 1950 ± S cm<sup>-1</sup>. It was also shown that the fibres may be drawn at elevated temperatures, then annealed to give fibres with Young’s moduli up to 2 GPa and ultimate tensile strengths up to 97 MPa whilst retaining conductivities of ~600 S cm<sup>-1</sup>. Crown copyright © 1999 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Polyaniline fibres; Dichloroacetic acid; One-step wet spinning process

## 1. Introduction

One of the biggest problems concerning the area of electrically conductive polymers has been the difficulty associated with the processing of materials. Most of them have to be processed in some precursor form, then converted either chemically or otherwise, to the conjugated state which has to be further doped to yield a conductive form. This process can result in the presence of gradients of material properties throughout the product generated by the conversion process. A major advance was made with the discovery by Cao et al. [1] of a processing route for emeraldine salt (ES), the conductive form of polyaniline (PANI). Using functionalised sulfonic acids—camphorsulfonic acid (CSA), in particular—to protonate the polyaniline also rendered the doped polyaniline soluble in many new solvents. Films cast from a 2:1 molar ratio of PANi:CSA in *m*-cresol were found to have conductivities of 400 S cm<sup>-1</sup>. Much interest has been focused on this processing route, including the possibility of stretch aligning films

of the material resulting in increased conductivity in the stretch direction, approaching 1000 S cm<sup>-1</sup> [2].

As processing routes become more advanced, the spinning of fibres becomes a possibility. It is envisaged that electrically conductive fibres may be incorporated into a matrix, either as a chopped fibre-filler or as a structural material, to act as an electromagnetic absorber. Fibres of conductive polyaniline and its derivatives were produced in several different ways; polyblend and block copolymers of PANi and poly(*p*-phenylene-terephthalamide) were spun from concentrated sulphuric acid [3,4]; poly(*o*-toluidine) was spun from sulphuric acid, *m*-cresol and *N*-methyl-2-pyrrolidinone (NMP) [5]; high molecular weight emeraldine base (EB) was spun from NMP [6] and *N,N'*-dimethylpropylene urea (DMPU) [7]; EB was spun from a melt, protonated with dodecylbenzenesulfonic acid (DBSA) [8]; and leucoemeraldine base (LB) was spun, post-oxidised, then doped to give the conductive emeraldine salt (ES) [9].

Of these various routes, the most notable fibres are those produced by post-doping fibres spun from the EB form of polyaniline, yielding conductivities of ~350 S cm<sup>-1</sup>, and the fibres that were spun from the LB form. When drawn to 100% elongation, the LB fibres showed tenacities of ~320 MPa (3.6 gpd (grams per denier)), though this decreases to 170 MPa (1.9 gpd) when protonated. The

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Table 1

A list of various coagulation solvents used in the wet spinning of polyaniline fibres, indicating their solubility parameter, the physical nature of the fibre produced, the ability of the fibres to cold draw, and the electrical conductivity as appropriate

Coagulation solvent	Solubility parameter (MPa <sup>1/2</sup> )	Appearance of fibre	Maximum draw ratio (%)	Maximum conductivity as spun/drawn (S cm <sup>-1</sup> )
4-Methyl-2-pentanone	17.2	Smoothly cylindrical	500	150/1700
Butyl acetate	17.4	Smoothly cylindrical	500	110/1200
Diacetone alcohol	18.8	Ribbon	–	–
2,4-Pentanedione	19.5	Ribbon	–	–
Acetone	20.5	Smoothly cylindrical	530	100/1900
Cyclopentanone	21.3	Ribbon	–	–
Water	48.13	Fibre did not skin	–	–
Methyl phenylacetate	–	Ribbon	–	–

Young's modulus of these doped fibres is reported to be 3–4 GPa, with conductivities of  $\sim 140 \text{ S cm}^{-1}$  [9]. The main problem with all these methods, however, is the fact that doping has to be achieved post-spinning. Thus, if the acid can get into the fibre, then it is also possible for it to get out again on storing or while in use. Secondly, only very small acid molecules can be used, and in most cases the fibres are so dense that only doping of the fibre skin is achieved. Thirdly, as we have shown previously [10], the use of functionalised sulphonic acids gives rise to high levels of crystallinity in the PANi, which directly correlates to a metallic electrical conductivity contribution in the material [11]. Therefore, to be able to retain such desirable conductivity properties in fibres, in a simple one-step spinning process, whilst increasing mechanical properties and long term stability of the conductivity, a new spinning methodology was required.

The realisation of this new method stems from our discovery of a new combination of sulfonic acid dopant and solvent for the processing of PANi, namely 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and dichloroacetic acid (DCA) [12]. The conductivity of films of this material is lower than PANi:CSA, though we have found that they have favourable material properties. The films may be stretch aligned more easily than PANi:CSA, and thus higher conductivities are more readily achieved.

## 2. Results and discussion

### 2.1. Fibre spinning methodology

The polyaniline used in these experiments is high molecular weight polyaniline synthesised at  $-25^\circ\text{C}$ ; a detailed description of the synthesis can be found elsewhere [13]. During these investigations, we employed various mole ratios of PANi:AMPSA in the spinning dope. The standard mixture, however, was a 1:0.6 mole ratio, a ratio that we have found favourable from our work with previous doped PANi systems [11]. The PANi and AMPSA powders were

mixed in a mortar and pestle. The powders were then added to DCA and stirred under nitrogen at 20 000 rpm for  $\sim 10$  min using an Ultra-Turrax T25 Homogeniser. The amount of DCA used varied according to the concentration of solution being prepared. The maximum concentration we could achieve was 10% (w/w), before the solution became too viscous to consider spinning. Solutions of 5% (w/w) or less did not form a continuous fibre. The standard solution we used for spinning consisted of 9% solid in solution (w/w).

The dope solution was poured into the stainless steel dope pot of the spinning rig. A nitrogen gas supply was then used to force the solution through an in-line  $140 \mu\text{m}$  filter, and then through a single  $150 \mu\text{m}$  spinneret orifice ( $l/d = 2$ ). The end of the spinneret was just submerged in the coagulation solvent, i.e. there was no air gap. The rate at which the fibre was spun was not controlled. The fibre was spun into the coagulation solvent, then removed after all the fibre was spun. No take-up mechanism was employed. This method will, obviously result in some variation of physical characteristics along the length of the fibre due to varying amounts of time spent in the coagulation bath. However, the amount of fibre spun at any one time was small, and such variations were negligible. Finally, the fibres were allowed to dry in air for  $\sim 24$  h.

### 2.2. Coagulation solvents

A range of coagulation solvents were investigated, the results of which are summarised in Table 1. We found three solvents that resulted in the formation of smoothly cylindrical fibre; acetone, butyl acetate and 4-methyl-2-pentanone (MIBK). Samples of fibres spun into these solvents, specifically acetone, were investigated in more detail. The fibres described as a 'ribbon' appeared to have formed a skin upon entering the coagulant which did not shrink with further extraction of DCA, resulting in the fibre collapsing upon itself. These solvents may well be of interest in the future if dope solutions of higher concentrations are spun, or if non-cylindrical fibres are required.

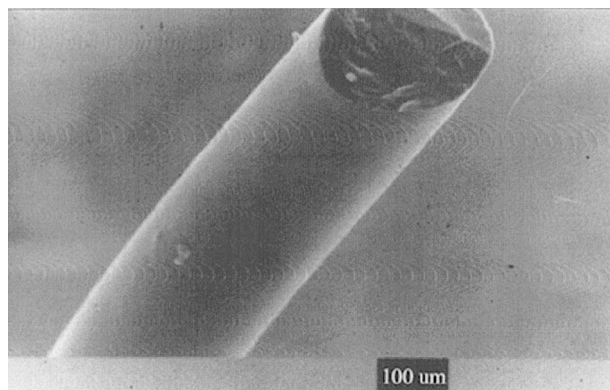


Fig. 1. A SEM image of a cross section of a PANi:AMPSA<sub>0.6</sub> fibre spun into acetone, then fractured under liquid nitrogen.

It should be noted that of the coagulation solvents tried, those that formed fibres have solubility parameters within the range 17.2–21.3 MPa<sup>1/2</sup>, compared to the solubility parameter of 22.5 MPa<sup>1/2</sup> for DCA. However, a coagulation solvent cannot be selected by solubility parameter alone, as the chemical reactivity of the solvent with the constituents of the fibre must be taken into account.

### 2.3. Physical appearance of the fibre

A SEM image of a typical fibre spun into acetone, then cleaved under liquid nitrogen is shown in Fig. 1. It reveals the fibre to have a smoothly cylindrical surface, and to contain no voids at this resolution. Higher resolution SEM and X-ray analysis would be required to determine the presence of any micro-voids that would play an important part in the fibre's mechanical characteristics. Typical as-spun fibres have a diameter of around 220 μm, and densities of ~1.6 g cm<sup>-3</sup>.

### 2.4. Tensile measurements

An Instron tensileometer with a 10 N load cell was used to perform mechanical tests on single fibres. It was discovered that fibres of this new material drawn at room temperature and above. All fibres were found to drawn to ~500% via a necking process; this necking process precluded us from being able to record fibre characteristics as a function of extension. This behaviour was not

previously seen in our stretch orientation studies on PANi-CSA films [2]. The Young's modulus of all the as-spun fibres was between 20 and 40 MPa, and the tensile strength at break (UTS) between 20 and 80 MPa. The Young's modulus and UTS increase slowly on storage of unstretched films. Note that the fibres actually form a stable neck and stretch elongate during such measurements.

Certain fibres that had been spun into acetone were later drawn at elevated temperatures (363 K) and then left under strain for various times. The effect on Young's modulus and UTS are summarised in Table 2. (At least two samples were measured for each value quoted. Only values for samples that broke away from the clamps were used.) After an initial drop, the UTS rises, this trend becomes more evident when the data is normalised with respect to density. The value of Young's modulus shows no definite trend, though the highest value is recorded for the sample that spent the longest time under strain at 363 K, i.e. 2 GPa.

### 2.5. DSC results for fibres of PANi-AMPSA<sub>x</sub>

The DSC results for an unstretched PANi-AMPSA<sub>0.6</sub> fibre, spun into acetone, is shown in Fig. 2. This shows the same feature as the DSC measured in a 60% protonated film [12], except that the magnitude of the observed transition is slightly larger at 0.46 J g<sup>-1</sup> K<sup>-1</sup>, the transition being centred at 260 K. For comparison, a similarly protonated film, between 210 and 283 K, shows an endothermic transition of magnitude ca. 0.30 J g<sup>-1</sup> K<sup>-1</sup>, centred at 240 K. This reflects the increased amount of solvent in the fibre. Above 280 K, the film DSC trace is featureless with a gentle rise, indicative of a plasticised system. This would explain the ability of this material to be drawn at room temperature or higher, unlike PANi-CSA<sub>0.5</sub>, which can only be drawn at 420 K or higher [2]. It is thought that both AMPSA and the solvent could plasticise the fibres (and films), however, a film of PANi-AMPSA<sub>0.3</sub> showed no measurable (DSC) transition and could not be stretched at room temperature, whereas a 100% AMPSA film did have the same endotherm and could be stretched at room temperature. X-ray photoelectron studies on doped films reveal that there is only a residual amount of solvent left in the films (note in the high vacuum of the XPS spectrometer). This indicates that the observed transition is mostly dependent on the amount of

Table 2  
Various characteristics of fibres held under strain at 363 K for varying lengths of time

Time (h)	UTS (MPa) (±3%)	Young's modulus (GPa) (±10%)	Density (g cm <sup>-3</sup> ) (±5%)	Specific tensile strength (dN tex <sup>-1</sup> ) (±8%)	Conductivity (S cm <sup>-1</sup> ) (±50)
0	83	1.4	1.6	0.51	990
2	68	1.5	1.7	0.39	630
16	73	1.2	1.6	0.45	640
64	97	2.0	1.5	0.63	590

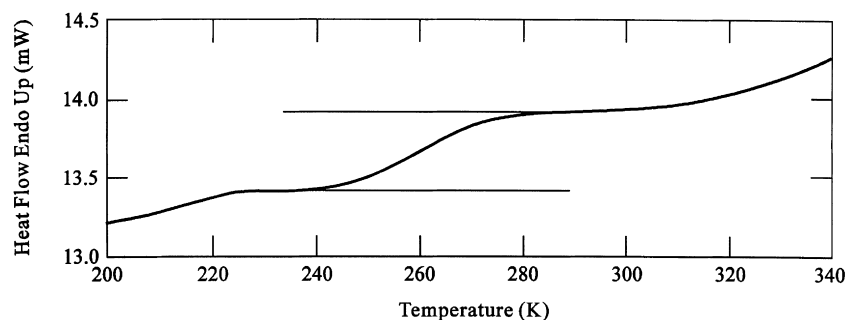


Fig. 2. DSC endotherm for a 60% protonated polyaniline fibre.

AMPSA in the film, which suggests that the counter ions become mobile above this transition temperature. As the AMPSA counter ions are hydrogen bonded to the PANi backbone we can view them as essentially ‘side chains’ to the PANi backbone. This melting of the side chains will, thus, allow motion of the PANi backbone as well, as is the case for *N*-alkyl substituted PANi [14].

### 2.6. Electrical conductivity of PANi-AMPSA fibre

The conductivity of the fibres was measured using a potential-probe method. A current is passed between two outer contacts, and the resultant potential drop is measured between two inner contacts (spacing 3 mm). Knowing the dimensions of the fibre, the current flowing and the measured potential drop, the conductivity of the sample may be calculated. All values for the as-spun fibres were found to lie within the range 70–130 S cm<sup>-1</sup>. On drawing at

363 K, the conductivity was seen to increase to a maximum of 1950 ± 180 S cm<sup>-1</sup>. This was the maximum value attained along a short section of fibre (3 mm), and should be considered as an upper limit at this time. Simple two-probe conductivity measurements over 100 mm of fibre resulted in conductivity values of ~1000 S cm<sup>-1</sup>, which we believe represents the present reproducible bulk conductivity for these fibres.

The conductivity of fibres that had been drawn and held under a tension of 0.8 N at elevated temperatures is included in Table 2. The conductivity is seen to drop by ~40% to ~600 S cm<sup>-1</sup> after the first hour, and then remains constant within experimental error. This drop may be attributed to the initial loss of solvent and absorbed atmospheric water from the fibre, causing a decrease in the degree of acid dissociation. The electrical conductivity of three fibres spun into acetone was measured as a function of temperature; one as-spun, one cold drawn and one drawn at 363 K. The results are shown in Fig. 3. The form of the conductivity data is the same as for films of the same material, a detailed discussion of which may be found in Ref. [11].

The unstretched fibre has a higher ‘turnover’ temperature than that of a film. The value of the turnover temperature was previously attributed to the degree of crystallinity of the material [10], and hence this would imply that fibres have a smaller crystalline fraction than films. This is consistent with the method of production of the fibres in which the DCA is removed rapidly by the coagulation solvent, whereas during the production of a film the DCA is allowed to evaporate slowly, thereby allowing crystallites to form.

The conductivity of the stretched fibre is higher than that of any stretched film we have measured, though this is probably because we have not succeeded in drawing a film to 500% extension. This high conductivity of a drawn fibre may be attributed to alignment of polymer chains in the amorphous regions of the material induced upon stretching. The conductivity ‘turnover’ temperature is lower than that of an unstretched film by 20 K, i.e. 215 K. Stretching the fibre at 363 K has the same effect, but the absolute conductivity is higher—possibly a sign that annealing has occurred.

The values of  $\sigma_{15\text{ K}}/\sigma_{300\text{ K}}$  are lower than for the films, which again indicates that the fibres are probably less

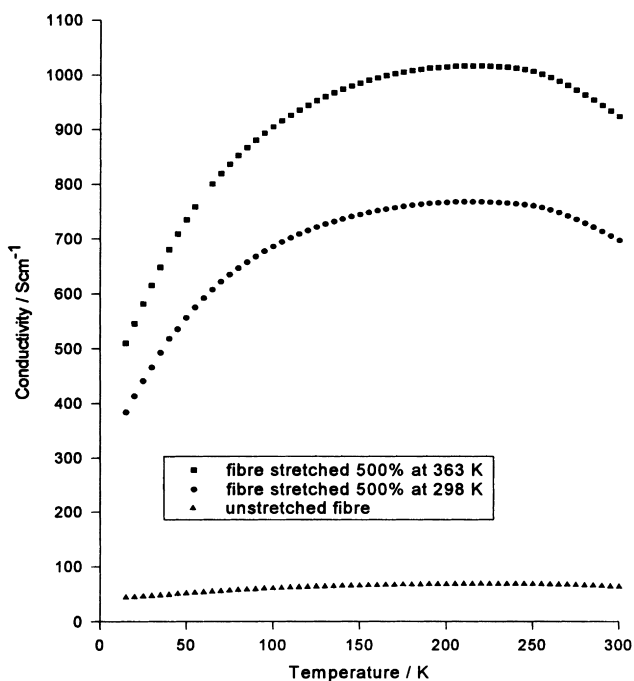


Fig. 3. Temperature-dependent electrical conductivity for PANi-AMPSA films, stretched, unstretched and annealed.

crystalline. Note that the second conductivity transition at  $\sim 250$  K is also preserved, as is the case with the films. This second transition was attributed to an increase in motion of the AMPSA anions when heated above this temperature, from the DSC measurements of the material which shows an endotherm of magnitude  $0.46 \text{ J g}^{-1} \text{ K}^{-1}$ , centred at 260 K. The AMPSA anions can be considered to behave as ‘side chains’ on the PANi backbone, thus the AMPSA can affect the PANi interchain molecular dynamics, and hence affect the electrical transport properties of the bulk polymer.

### 3. Summary

Inherently conductive polyaniline fibres were wet spun from a solution of emeraldine base protonated with 2-acrylamido-2-methyl-1-propanesulfonic acid in DCA (solvent). Various coagulation solvents were used, resulting in three preferred solvents; acetone, butyl acetate, and 4-methyl-2-pentanone. Fibres spun into acetone can be drawn both at room temperature and at 363 K. It was found that drawing the fibres at room temperature yields high conductivities ( $\sim 1000 \text{ S cm}^{-1}$  for the bulk material,  $1950 \pm 180 \text{ S cm}^{-1}$  maximum). Drawing fibres at 363 K and leaving under strain gave superior mechanical properties, UTS 97 MPa, Young’s modulus 2 GPa, whilst retaining enhanced conductivity, i.e.  $650 \text{ S cm}^{-1}$ . The electrical conductivity of the fibres has the same dependence upon temperature as films of the same material, indicating a small ‘metallic’ contribution to the overall electrical transport.

### Acknowledgements

We thank DERA and BICC for both financial and technical support, British Crown Copyright 1999/DERA. Published with the permission of the Controller of Her Britannic Majesty’s Stationery Office.

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