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Electrically conductive PANi multifilaments spun by a wet-spinning process

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Electrically conductive polyaniline (PANi) filaments were successfully spun from a spinning solution prepared from the PANi protonated with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) in dichloroacedic acid (DCA) as a solvent by a wet-spinning process. The conductivity of the fibre is in a range of 145 (±35) Scm^{-1} to 1440 (±300) Scm^{-1}, which depends on the orientation of polymer chains. The fibre has a Young's modulus about 3.2 GPa, and a tensile strength about 0.23 GPa. Thermal analysis by TGA and DSC show that the fibre has five major weight losses at around 100 °C, 165 °C, 215 °C, 315 °C and 465 °C which are associated with the removal of moisture, residual solvent, the decompositions of the AMPSA, and the degradation of the PANi, respectively. The AMPSA in doped PANi performs two-stage thermal decompositions. The conductivity of the fibre was adversely affected by the thermal ageing due to the evaporation of the residual solvent at the temperatures lower than 100 °C and the decompositions of the dopant AMPSA at the temperatures above 100 °C. The temperature dependent conductivity of both aged and unaged fibres is thermally activated at the temperatures between 15 K and 295 K. A negative temperature coefficient was observed in the temperature range of 240 K to 270 K for the unaged fibres. This disappeared when the fibres were thermally aged at 100 °C for 24 hours in vacuum. These results indicate that the residual solvent trapped inside the fibre enhances the electrical conductivity of the fibres, and possibly affects the negative temperature coefficient at the temperatures around 260 K.

1. Introduction

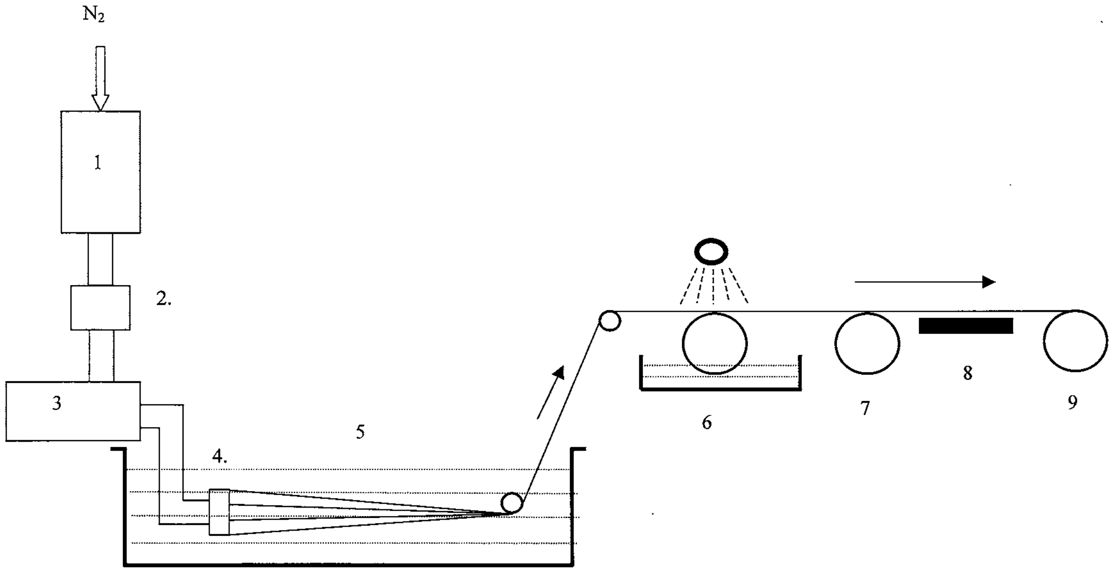
Since the discovery of the solution processibility of PANi [1], many research workers have concentrated their works upon improving the processing techniques and characterising the resulting materials [1–5]. Although PANi fibres can be spun from PANi emeraldine base [6, 7] and its leucoemeraldine base [8] solutions, the conductive fibres are converted (to PANi salt) by using aqueous protonating acids after the processing. The disadvantages of the method are that the resulting material is usually inhomogeneously protonated, and de-doped with relative ease. The mechanical properties of the fibre are also adversely affected upon the protonation. An alternative method to produce conductive PANi fibre is to spin the fibre from protonated PANi solution directly by a wet-spinning process [9, 10], in which the PANi was pre-protonated with sulfonic acid. The PANi fibres obtained from these acidic processing systems exhibit very poor mechanical properties and moderate electrical conductivity.

In this paper, we report that the conductive PANi fibres were prepared from a new acidic processing system in which the AMPSA was used as a protonating acid, and the DCA as a solvent [11, 12]. The experimental results show that the fibre has high conductivity and excellent mechanical properties. It also demonstrates that cold drawing, annealing and the shear stress inside the orifice of the multi-hole spinneret also affect the fibre's mechanical and electrical properties. These will be used as guidelines for producing high performance of electrically conductive PANi fibres.

2. Experimental

2.1. Spinning solution

High molecular PANi (emeraldine base) was synthesised in Durham using our standard method. A detailed description of its synthesis can be found elsewhere [13]. The molecular weight of the polyaniline Mw is $\sim 2 \times 10^5$ Dalton, which was determined by GPC at



1. Dope pot
2. "TF" and "F" series compact inline filters
3. Slack & Parr metering pump
4. Spinning device with spinneret
5. Coagulation bath (Acetone solution)
6. First roller with water spray and washing bath
7. Second roller
8. Heating facility
9. Take-up roller

Figure 1 Wet-spinning process for spinning PANi fibre from the PANi:AMPSA (DCA) system.

column temperature of 80 °C using both polyvinylpyridine and polystyrene standards [14]. AMPSA and DCA were obtained from Aldrich chemicals and used without further purification. PANi and AMPSA were dried in vacuum oven at 40 °C for at least 48 hours before mixture. The doping level 60% (that is a 1:0.6 mole ratio of PANi:AMPSA) and 9%w/w solid concentration were chosen in this study because they are favourable for the high conductivity from the work with the PANi:AMPSA$_{(0.6)}$ (DCA) system and stable solution for spinning fibre. The PANi was well mixed with AMPSA using a mortar and pestle. 16.65 g PANi:AMPSA$_{(0.6)}$ were dissolved in 107.71 ml DCA solvent. The solution was firstly stirred with a glass rod slowly, and then further stirred using an Ultraturrax T25 homogenizer at 9500–25000 rpm for 10 min.

2.2. Wet-spinning process

The spinning rig for wet-spun PANi fibre is shown schematically in Fig. 1. The polymer solution prepared above was poured into a stainless steel dope pot. Nitrogen gas was used to drive the polymer fluid through 3/8" stainless steel tubing, and through two inline filters (*Swagelock*) before the polymer fluid entered into a Slack & Parr metering pump. The nominal micro sizes of the filters were 140 μm and 40 μm, respectively. The polymer solution was then extruded through a single-hole spinneret, 150 μm in diameter (or a 10-hole spinneret, each hole was 75 μm in diameter) directly into an acetone coagulation bath. The first roller speed was 4–5 m/min and the take-up roller speed was 7–10 m/min. The nascent fibre was continuously wound onto the first roller with one wrap and then collected on the take-up roller. The as-spun fibre had been partially drawn (the draw ratio is 1.75 to 2) between the first and the take-up rollers. The fibre could be further drawn (3 × draw ratio) manually at room temperature depending on the residual solvent content in the fibre.

2.3. Thermal ageing

Thermal ageing of the fibres was performed at 50 °C, 100 °C, 150 °C, and 190 °C for various periods of time in a vacuum oven. Equal length of fibres were firstly placed parallel to one another on a paper frame and then mounted on a metal frame by clamping the ends of fibre bundle. The fibre bundle was slightly stretched and the length of the fibre bundle then fixed during the thermal ageing. After thermal ageing, the samples were cooled down in air and conditioned at room temperature for at least 24 hours before testing.

2.4. Thermal analyses

Thermal analysis was carried out using a Perkin-Elmer Thermal Analysis and Universal V2.4 TA Instrument. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) were performed under nitrogen atmosphere from 30 °C to 500 °C. The programmed heating rate was 10 °C/min.

2.5. Conductivity measurement

The resistance of the electrically conductive PANi: AMPSA$_{(0.6)}$ (DCA) fibre at room temperature was measured by a standard four in line contact technique with the Keithley 2400 digital source meter. A current of 1.0 mA was passed between two Pt outer contacts and the potential difference measured between two Pt inner contacts. The distance between the inner contacts was 2 mm and the results obtained were repeatable. The temperature dependent d.c. conductivity was measured over the range of 15 to 295 K under a dynamic vacuum. The sample was first coated with four parallel strips of gold evaporated onto its surface and then placed in the closed-loop helium Cryostat. The four gold strips on the sample were contacted with the four in inline Pt electrode contacts. Same measuring method described above was used to measure the electrical conductivity. The temperature was raised from 10 to 295 K in steps of 5 K, with conductivity measurements made very 10 minutes. The current is applied during each measurement.

2.6. Tensile strength and strain measurements

Load and extension were determined on single filament mounted on paper card using an Instron tensile testing machine. For each sample, ten 2.5-cm filaments were tested at a crosshead extension rate of 2.5 cm/min. The nominal stress is the load divided by initial cross-sectional area that is determined separately for each filament. The strain is the extension divided by the sample length. The Young's modulus quoted here is 2% secant modulus, calculated from the nominal stress at 2% strain.

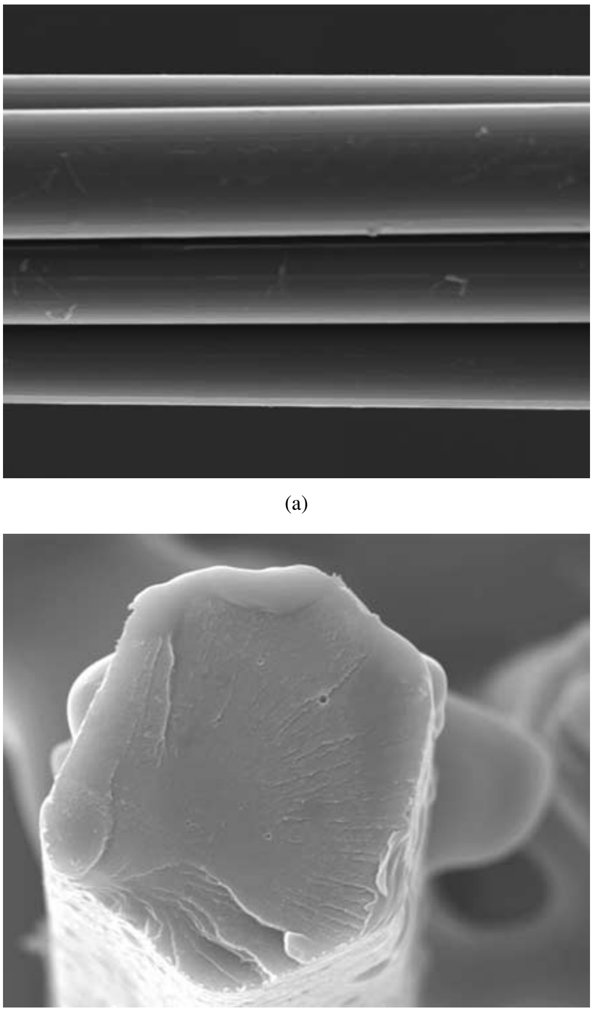
2.7. Scanning electron microscopy (SEM) examination

The structures on the surface and the cross-section of the PANi fibre were examined using SEM. In order to view the microstructure in the cross-section of the fibre, the fibre was firstly fractured in liquid nitrogen to avoid smearing the cross-section of the fibre, then coated with gold. This enables to view a clear microstructure in the fracture area from the SEM micrograph.

3. Results and discussion

The physical appearance of the fibres was shown in Fig. 2. The electron micrographs show a smooth regular nature to the surface of the PANi fibre (multifilament bundle). The cross section of a single filament from the bundle shows very low microvoid content. This solid structure acts as the foundation for the high mechanical properties of the fibre. A semi-hexagonal shape indicates that the solidification of the fibre during the wet-spinning process is not instantaneous. It implies that certain amount of residual solvent was presented in the as-spun fibre.

The as-spun single fibre had conductivity of 145 ± 35 Scm^{-1}. The Young's modulus of the as-spun fibre was found to be between 0.3 and 1.1 GPa. The ultimate tensile strength (UTS) was between 25 and 52 MPa. Upon cold drawing to an extension of $300 \pm 50\%$ of its initial length, the conductivity of the fibre increased dramatically, with final values of 515 ± 65 Scm^{-1}. The Young's modulus and the tensile strength of the drawn fibre were increased to 3.2 GPa and 0.23 GPa, respectively. By using a smaller, multi-hole spinneret, multi-filaments can be spun. The conductivity of the single fibre can reach up to 1440 ± 300 Scm^{-1}. The Young's modulus and the tensile strength of the fibre were in the same magnitude values as the drawn fibre observed above, as shown in Table I. The experimental results show that the conductivity and mechanical properties of the fibre


(a)

(b)

Figure 2 SEM micrographs of a) smooth regular surface of PANi multifilament's bundle (×1300); b) cross-section of a single filament from the bundle, showing very low micro-void content and semi-hexagonal shape.

TABLE I Electrical conductivity and the stress and strain of the PANi fibres prepared from PANi:AMPSA$_{(0.6)}$ (DCA) system

Sample	Fibre diameter (um)	Conductivity (S/cm)	Strain at breaking (%)	UTS (MPa)
SB15-699A[a]	80	145	29.1	52
SB15-699AD[b]	45	515	19.8	226
SB27-1299[c]	30	1200	98.8	208
SB29-0100[d]	30	1440	41.2	231

Note: a). As-spun fibre.
b). Cool drawn the as-spun fibres manually at room temperature.
c). As-spun multifilament.
d). As-spun multifilament, applied heat treatment during the wet-spinning process.

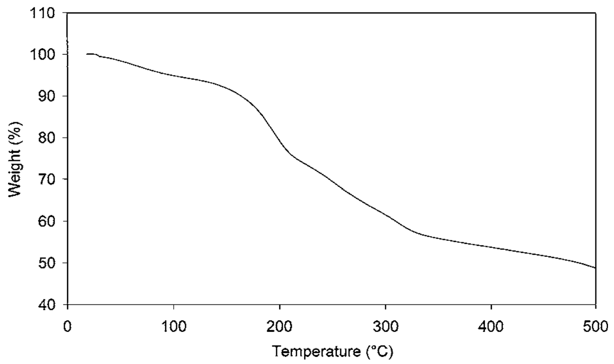


Figure 3 TAG trace of PANi:AMPSA (DCA) fibre.

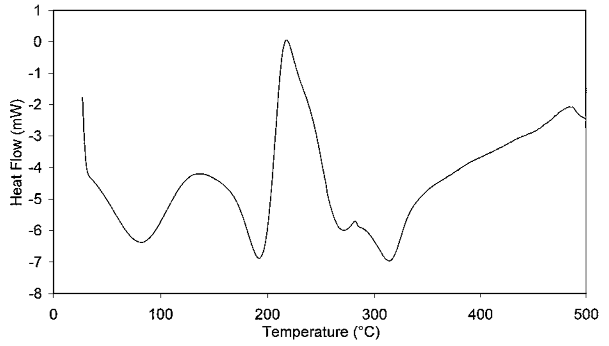


Figure 4 DSC trace of PANi:AMPSA (DCA) fibre.

are significantly improved by drawing and using small, multi-hole spinneret. This implies that the improvement in the orientation of polymer chains by increasing the shear stress in the small orifice of the spinneret and further drawing would be preferred to the electrical conductivity and mechanical properties of the fibre.

The thermal analysis results from the TGA and DSC traces of the as-spun fibre are shown in Figs 3 and 4, respectively. In Fig. 3, five major weight losses of the fibre were observed in the temperature range of 20 °C to 500 °C. The first weight loss, ~5%, occurs between 80 °C and 100 °C due to the loss of moisture. The weight loss at the temperatures below 200 °C is therefore assigned to the loss of the residual solvent (DCA) (bp. at 195 °C) trapped inside the fibre. The next two stages of weight loss, starting at 215 °C and 315 °C, are unlikely to be due to the structural decomposition of the PANi [15–17]. Therefore, the weight loss below 315 °C could be attributed to the evaporation of AMPSA that may perform two-stage weight loss during thermal ageing. The mechanism of the thermal decomposition of AMPSA in its dopant form in PANi has not been fully investigated. However, it is likely that the dopant will decompose into small fragments at the temperatures about 195 °C, because AMPSA itself will melt and decompose at that temperature [18]. The weight loss at 215 °C is likely due to the evaporation of the decomposed small fragments of AMPSA, and possible any excess AMPSA which does not protonate (or bond to) the imine nitrogen groups on the PANi chains. The later weight loss at 315 °C is ascribed to the loss of the decomposed AMPSA counter-ions that were bonded to the imine nitrogen groups on the polymer chains. These results are consistent with the thermal transitions observed from the DSC trace (see Fig. 4). The fifth weight loss at temperature of 465 °C is likely due to the structural decomposition of the PANi itself.

In Fig. 4, three endothermic peaks and two exothermic peaks occur in the temperature range of 20 °C to 500 °C. The first and second endothermic peaks at ~90 °C and ~195 °C are most likely due to the removal of moisture and residual solvent (DCA), which were consistent with the TGA results. The third endothermic peak at ~315 °C is possible due to the weight loss of the decomposed fragments of AMPSA counter-ions that were bonded to the imine nitrogen groups on the PANi chains.

Exothermic peaks in DSC have been related to chemical processes, such as recrystallization [19] or cross-linking reactions [15, 20–23], without decomposition. An exothermic peak at ~215 °C is observed in the DSC trace of the PANi fibre. This relative large exothermic peak, accompany with a weight loss transition on the TGA trace (see Fig. 1), indicates that it could be attributed mainly to decompose the AMPSA. The assumed procedures involve breaking down the hydrogen bonds between the solvent (DCA) and the AMPSA, and the decomposition of the AMPSA. As the AMPSA decomposes into small fragments in the polymer, then the conductivity of the fibre is expected to decrease, which will be discussed later.

A second small exothermic peak also appears at ~285 °C with no transition of weight loss occurring in the TGA trace at this temperature. This small exothermic peak could be due to cross-linking and/or the glass transition of the PANi. The feasibility of cross-linking induced during the thermal ageing at that temperature will not be further discussed in this paper. The glass transition temperature of PANi at ~250 °C has been reported, using MDSC technology, by other researchers [16]. This implies that the small exothermic at 285 °C is more likely associated with the glass transition of the PANi. The higher glass transition temperature of the PANi:AMPSA$_{(0.6)}$ (DCA) fibre could be assigned to the higher molecular weight of the PANi and the fact that the PANi is in the doped form.

Evaluation of the effect of thermal ageing on the conductivity of the PANi:AMPSA$_{(0.6)}$ (DCA) drawn fibre was performed at 50 °C and 100 °C, 150 °C and 190 °C for various periods of time in an oven under vacuum. Table II shows the results of the electrical conductivity and tensile stress and strain of the drawn fibres measured at room temperature after the thermal ageing. Fig. 5 shows that the effect of the thermal ageing on the electrical conductivity of the fibre.

When the fibre was aged in vacuum oven at 50 °C, as shown in Fig. 5, the conductivity is not significantly affected during the ageing time of 24 hours. The conductivity only changed ~5% from 515 S/cm to 490 S/cm. It was believed that this small change in fibre's conductivity was likely due to the loss of moisture and residual solvent trapped inside the fibre [15].

For the fibre thermally aged at 100 °C under vacuum, its conductivity was found to decrease from 515 S/cm to 430 S/cm (16.5%) in the first 2 hours and then gradually decreased from 430 S/cm to 175 S/cm in the next 22 hours. It is possible that the initial change in the

TABLE II Effect of thermal ageing on the electrical conductivity and the mechanical properties of the drawn fibres[a]

Temperature (°C)	Ageing time (hour)	Conductivity (S/cm)	Strain (%)	UTS (MPa)
50	0	515	19.76	226
	1.0	503	18.40	237
	2.0	498	16.32	245
	4.0	500	15.52	247
	12.0	493	15.04	256
	18.0	492	14.72	238
	24.0	490	14.32	201
100	0.5	495	15.25	269
	1.0	461	11.00	279
	2.0	434	11.0	307
	4.0	283	10.37	317
	12.0	220	10.24	327
	18.0	201	6.83	318
	24.0	175	5.17	280
150	0.5	345	12.08	298
	2.0	34.1	7.56	357
	4.0	11.0	6.24	395
	8.0	0.89	5.52	390
	16.0	0.15	4.80	347
	24.0	0.14	4.56	326
190	0.5	2.59	6.52	428
	2.0	8.59×10^{-3}	5.76	380
	4.0	2.84×10^{-3}	5.60	380
	8.0	1.07×10^{-3}	4.80	367
	16.0	-	4.00	272

Note: a). The as-spun fibre was drawn at room temperature manually, the draw ratio was about 3.

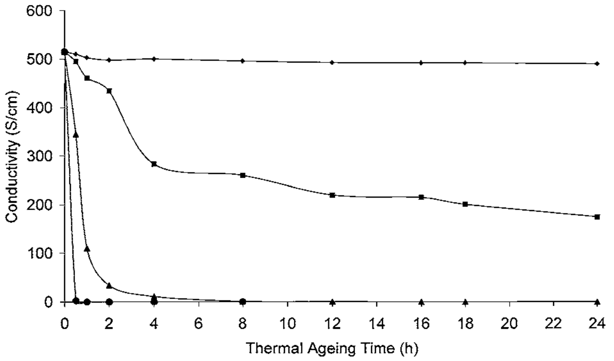


Figure 5 Effect of thermal ageing time on the conductivity of the drawn fibres thermally aged in vacuum oven at: ◆ 50 °C; ■ 100 °C; ▲ 150 °C and ● 190 °C.

fibre's conductivity is mainly due to gradually loss of moisture and residual solvent trapped inside the fibre. Then the conductivity decreases due to further release the residual solvent that was hydrogen bound to the AMPSA by thermal ageing.

When the fibre was aged at the temperature of 150 °C, its conductivity decreased swiftly in the very earlier period of ageing time (from 515 S/cm to 11 S/cm in the first 8 hours). Then the conductivity of the fibre gradually levelled out at a very low conductivity (0.15 S/cm). During that thermal ageing time, the residual solvent (DCA) was lost completely and the AMPSA started to decompose. The fibre was still conductive albeit with low conductivity for the next 16 hours. This result suggests that some decomposed small AMPSA fragments were still bound to imine nitrogen groups in the polymer chain (continuing to protonate the PANi). The result also consistent with the assumption of the two-stage weight loss of the AMPSA.

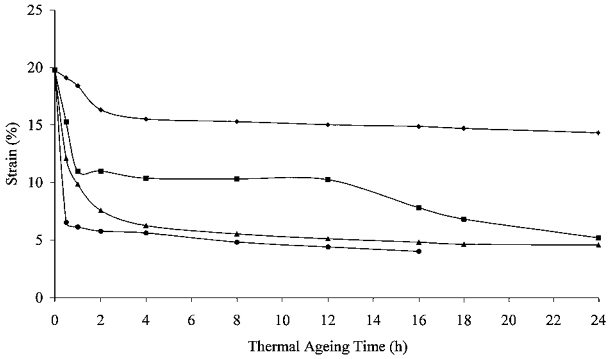


Figure 6 Effect of thermal ageing time on the strain of the drawn fibres thermally aged in vacuum oven at: ◆ 50 °C; ■ 100 °C; ▲ 150 °C and ● 190 °C.

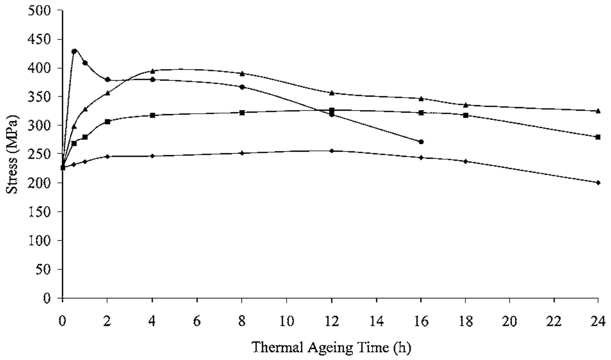


Figure 7 Effect of thermal ageing time on the stress of the drawn fibres thermally aged in vacuum oven at: ◆ 50 °C; ■ 100 °C; ▲ 150 °C and ● 190 °C.

At the thermal ageing temperature of 190 °C, the conductivity of the fibre decreases dramatically in the first 8 hours ageing time. After that time, the fibre was no longer conductive. This clearly indicates that the thermal ageing at this higher temperature completely decomposed all the AMPSA dopant and destroyed the small fragments that were bound to the imine nitrogen groups in the polyaniline chains in 8 hours ageing time.

Figs 6 and 7 show that the effect of the thermal ageing on the strain and stress of the fibres, respectively. The reduction in strain is depended on the level of temperatures and the ageing time, as shown in Fig. 6. With the increasing of the temperature, the strain can be reduced from 19.76% to 4.0%. These results were assigned to be the loss of the residual solvent and dopant, which were acted as plasticizers. The stress of the fibres was also depended on the level of temperatures and the ageing time, as shown in Fig. 7. With the increasing of the temperature, the stress was generally increased from 226 MPa up to 428 MPa (2.14 gpd up to 4.05 gpd). At the temperatures of 50 °C and 100 °C, the stress increased slightly at very short period of thermal ageing time. After that time, the stress was level out and then gradually decreased at longer period of the time. These results were mainly associated with the densification of fibre by the loss of the residual solvent during the thermal ageing time. Further loss of the residual solvent could form some flaws or defects in the fibre caused by inhomogeniously densification. At the temperatures of 150 °C and 190 °C, the stress increased to the maximum value at very shorter period of time and then decreased with the increasing of the ageing time. The increases in the stress were associated to the thermally induced cross-linking and densification of the fibres. Afterwards the decreases in the stress of the fibre were ascribed to the decomposition of the dopant, as the result shown by thermal analysis. These results show that the dopant presented in the fibre not only was for the conductivity, but also for the mechanical properties of the fibre.

The temperature-dependent d.c. conductivity of the PANi:AMPSA$_{(0.6)}$ (DCA) fibres are shown in Figs 8 and 9. Table III summaries the typical peak positions and their accompanying conductivity values. From each sample, the conductivity is thermally activated, but the drawn fibres have much higher conductivity than that of the as-spun fibres. This significant increase in the conductivity is associated with the orientation of polymer chains in the drawn fibres. A negative temperature coefficient was observed at the temperature range of 240 K (as-spun fibre) to 270 K (drawn fibre). Similar results of this transition behaviour had been reported in the cases of the PANi:AMPSA (DCA) stretched film and drawn fibre, and had been ascribed to a "metallic" conducting component [24, 25].

When the fibre was aged at 100 °C for 24 hours in vacuum oven, the negative temperature coefficient was disappeared. The conductivity of the aged fibres also decreased. These results indicate that the loss of the conductivity and the vanishing of the negative temperature coefficient in the thermal aged fibre are due to the loss of the residual solvent. The other possibilities will be further investigated on whether the thermal ageing at 100 °C under vacuum for 24 hours would induce cross-linking or other possible chemical changes in the PANi, which may affect the negative temperature coefficient.

TABLE III Temperature-dependent d.c. conductivity of the PANi fibre

Sample	Peak conductivity σ (S/cm)	Temperature of peak σ (K)	Conductivity σ_{295K} (S/cm)
As-spun fibre	81	270	78
Thermal aged as-spun fibre	30	295	30
Drawn fibre	442	240	417
Thermal aged drawn fibre	385	280	379

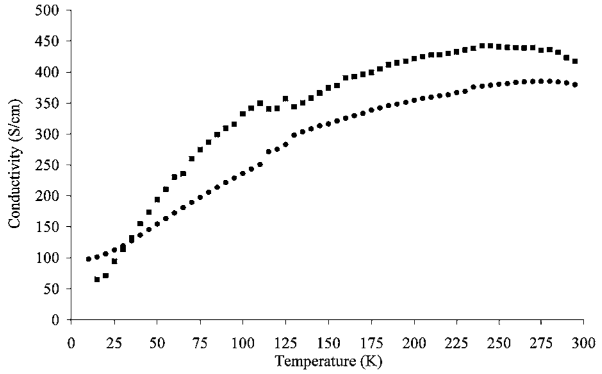


Figure 8 Conductivity of the drawn (3 × drawn ratio) fibres: ■ Un-aged fibre; ● fibre aged at 100 °C for 24 hours in oven under vacuum.

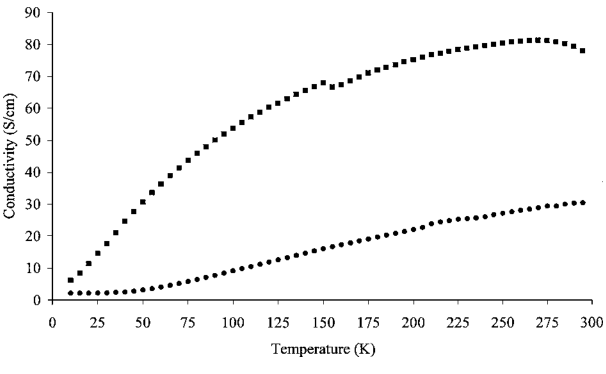


Figure 9 Conductivity of the as-spun fibres: ■ Un-aged fibre; ● fibre aged at 100 °C for 24 hours in oven under vacuum.

4. Conclusions

PANi filaments were successfully spun from a spinning solution prepared from the PANi protonated with the AMPSA in the DCA by a wet-spinning process, in which the acetone was used as a coagulant. Improvement in the orientation of polymer chains enhances the electrical conductivity of the fibre. At the same time, it also increases the mechanical properties. The conductivity and tensile strength of the fibre with improvement in the orientation of polymer chain could reach up to 10 and 5 times, respectively, higher than the fibres with less improvement in the orientation of the polymer chain. The experimental results demonstrate that the electrical conductivity and mechanical properties of the PANi fibres prepared from PANi:AMPSA$_{(0.6)}$ (DCA) system can be possibly further improved after increasing the orientation of polymer chain by post-drawing processes.

Thermal ageing of the fibre performed at 50 °C, 100 °C, 150 °C and 190 °C for various periods of time in vacuum result in a decrease in the conductivity, particularly at temperatures higher than 100 °C. The reduction in the conductivity is ascribed to the removal of residual solvent. Further reduction in the conductivity of the fibre aged at higher temperatures is caused by the decomposition of the AMPSA.

The residual solvent trapped in the fibre is favourable to the electrical conductivity of the fibre, but affects its mechanical properties. The release of the residual solvent also reduces the conductivity and influences the "metallic" conductivity observed in those fibres. The mechanical properties of the fibre can be improved by the thermal ageing process. This can be used to control the balance between the conductivity and mechanical properties of the fibres. By further inducing orientation of the polymer chain and heating treatment during the wet-spinning process, it is likely to produce high conductive and high performance fibres for the particular applications.

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