

Effect of Thermal Aging on Electrical Conductivity of the 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid-Doped Polyaniline Fiber

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Received 8 March 2000; accepted 17 May 2000

ABSTRACT: The thermal characteristics of inherently conductive polyaniline (PANi) fiber have been studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Fibers show five major weight losses at $\sim 100^\circ\text{C}$, 165°C , 215°C , 315°C , and 465°C , which are associated with the removal of moisture, residual solvent, decompositions of the sulfonic acid and degradation of PANi fiber, respectively. The 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) that dopes the PANi (in fiber form) performs two-stage decompositions. The conductivity of the drawn fibers aged at 50°C , 100°C , 150°C , and 190°C under vacuum for various periods of time decreases, particularly at temperatures higher than 100°C . The reduction in conductivity of the fiber aged at temperatures lower than 100°C is mainly due to the evaporation of the residual solvent (15–20% in the as-spun fiber). Further decrease in conductivity of the fiber aged at temperatures higher than 100°C is caused by the decomposition of the dopant AMPSA. The temperature-dependent conductivity of the fiber was measured at 15 K (-258.5°C) to 295 K (21.5°C). The conductivity of both aged and un-aged fibers is all temperature activated, however, the conductivity of the un-aged fibers is higher than that of the aged fibers. Although a negative temperature coefficient was observed in the temperature range from 240 K (-24.5°C) to 270 K (-3.5°C) for the un-aged fibers, it was disappeared when the fibers were thermal aged at 100°C for 24 h in vacuum oven. These results indicate that the residual solvent trapped inside the fiber enhanced the electrical conductivity of the fibers and its “metallic” electrical conductivity at temperatures ~ 263 K (-10°C). © 2001 John Wiley & Sons, Inc.† J Appl Polym Sci 79: 2503–2508, 2001

Key words: electrical conductivity; thermal aging; polyaniline; fibers

INTRODUCTION

As a conductive material, polyaniline (PANi) has attracted considerable attention since the discov-

ery of the solution processibility of PANi.¹ Using a wet-spinning technology, the PANi fibers could be spun from its base polymer solutions^{2–4} and doped polymer solution.^{5,6} The PANi fiber spun from its doped polymer solution displays high conductivity, has lightweight and good flexibility, and offers easier ways for postprocessing. These unique properties of the conductive fiber will open many new fields of applications, such as electromagnetic interference shielding composites and conductive textiles. Further investigation of the

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Correspondence to: J. Zhou
Contract grant sponsor: DERA; Contract grant sponsor: EPSRC; Contract grant number: GR/M40387

Journal of Applied Polymer Science, Vol. 79, 2503–2508 (2001)
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effect of the PANi structures and various dopants on the electrical conductivity and mechanical properties of the fiber are under way in our research group.

In this article, we present a procedure for spinning long continuous length of inherently conductive fiber from the solution of PANi doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), using dichloroacetic acid (DCA) as a solvent, i.e., the PANi:AMPSA (DCA) system. The effect of the thermal aging on the conductivity of the fiber was studied. The decomposition of AMPSA in PANi:AMPSA (DCA) fiber was also examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results show that the evaporation of the residual solvent and decompositions of the AMPSA during the thermal aging reduce the electrical conductivity of PANi fiber.

EXPERIMENTAL

Preparation of PANi: AMPSA (DCA) Fiber Samples

PANi (emeraldine base) was synthesized in Durham using our standard method, described in detail elsewhere.^{7,8} The molecular weight of PANi ($M_w \sim 2 \times 10^5$ Dalton) was determined by gel permeation chromatography (GPC) at column temperature of 80°C, using both polyvinylpyridine and polystyrene standards.⁹ AMPSA and DCA were obtained from Aldrich Chemicals and used without further purification. PANi and AMPSA were dried in a vacuum oven at 40°C for at least 48 h before being mixed. The doping level 60% (i.e., a 1:0.6 mole ratio of PANi:AMPSA) and 9% w/w solid concentration were chosen in this study because they are favorable for the high conductivity from the work with the PANi:AMPSA (DCA) system and stable solution for spinning fiber.^{10,11} The PANi powder was well mixed with AMPSA using a mortar and pestle; 16.65 g PANi:AMPSA was dissolved in 107.71 mL DCA solvent. The solution was first stirred with a glass rod slowly and then further stirred at 9500–25,000 rpm for 10 min, using an Ultraturrax T25 homogenizer. The polymer solution was then poured into a stainless steel dope pot. Nitrogen gas was used to drive the polymer fluid through 3/8-in. stainless steel tubing and through two in-line 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, directly into an acetone coagulation bath. The first roller speed was 4.5 m/min, and the take-up roller speed was 7.5 m/min. The nascent fiber was continuously wound onto the first roller with one wrap and then collected on the take-up roller without further washing. The as-spun fiber had been partially drawn (the draw ratio is 1.67) between the first and the take-up rollers. Fiber could be further drawn ($3 \times$ draw ratio) manually at room temperature depending on the residual solvent content in the fiber.

Thermal Aging

Thermal aging of the fiber was performed at 50°, 100°, 150°, and 190°C for various periods of time in a vacuum oven. Equal lengths of fiber were placed parallel to one another on a paper frame and hold in place by gluing the ends. The glued fiber bundle was then mounted on a metal frame by clamping the glued ends with the paper frame. The paper was then cut away from between the metal frame; the fiber bundle was slightly stretched, and the length of the fiber bundle was then fixed during the thermal aging. After thermal aging, the samples were cooled down in air and conditioned at room temperature for at least 24 h before testing.

Thermal Analyses

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

Conductivity Measurement

The resistance of the electrically conductive PANi:AMPSA (DCA) fiber 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 the two outer Pt contacts and the potential difference measured between the inner two Pt 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 a closed-loop helium cryostat. The four gold strips on the sample

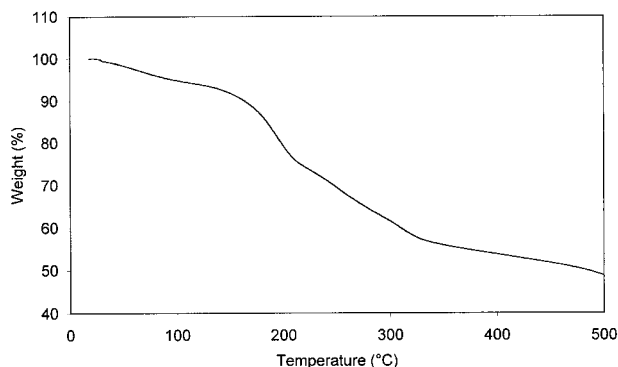


Figure 1 Thermogravimetric analysis (TGA) trace of polyaniline:2-acrylamido-2-methyl-1-propanesulfonic acid (PANi:AMPSA) [dichloroacetic acid (DCA)] fiber.

were contacted with the four in inline electrode contacts. The 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 every 10 min, the current only being applied during each measurement. The conductivity of the fiber was calculated based on the formula $\sigma = IL/VA$, where I is the applied current; V is the potential difference measured between the inner two contacts; L is the sample length, i.e., the distance between the inner two contacts; and A is the cross-sectional area of the fiber.

RESULTS AND DISCUSSION

The as-spun fiber was not further washed, once it came out of the acetone coagulation bath. Hence, there was approximately 15–20% of residual solvent (DCA) left in the fiber as determined by TGA. The fiber was drawn at room temperature to a 3× drawn ratio. The conductivity of the drawn fiber was 515 ± 65 S/cm at room temperature, compared with 145 ± 35 S/cm for the as-spun fiber.

The results from the TGA trace of PANi:AMPSA (DCA) as-spun fiber are shown in Figure 1. Five major weight losses of the fiber were observed in the temperature range 20–500°C. The first weight loss, ~5%, occurs between 80°C and 100°C, owing to the loss of moisture. Generally, the wet-spun fiber will contain a certain amount of residual solvent until it is completely dried. The weight loss at a temperature below 200°C is therefore assigned to the loss of the residual solvent (DCA) (bp at 195°C) trapped inside the fiber. The next two stages of weight loss, starting at

215°C and 315°C, are unlikely to be attributable to the structural decomposition of the PANi.^{12–14} Therefore, the weight loss below 315°C could be attributed to the evaporation of AMPSA that may perform two-stage weight loss during thermal aging. The mechanism of the thermal decomposition of AMPSA in its dopant form in PANi has not been fully investigated. It is assumed that the dopant will decompose into small fragments at a temperature of about 195°C, because AMPSA itself will melt and decompose at that temperature.¹⁵ The weight loss at 215°C is likely due to the evaporation of the decomposed small fragments of AMPSA, and possible any excess AMPSA that 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 (Fig. 2). The fifth weight loss at temperature of 465°C is probably caused by the structural decomposition of the PANi itself.

Figure 2 shows the DSC result of the PANi:AMPSA (DCA) fiber. Three endothermic peaks and two exothermic peaks occur within the temperature range 20–500°C. The first and second endothermic peaks at ~90°C and ~195°C are probably attributable to the removal of moisture and residual solvent (DCA), consistent with the TGA results. The endothermic peak at 195°C is also associated with the melting of the AMPSA. The third endothermic peak at ~315°C is perhaps 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.

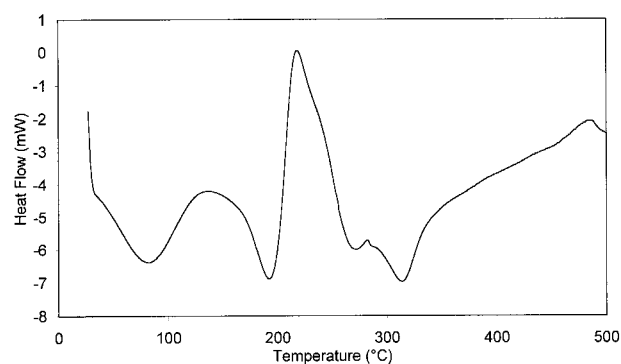


Figure 2 Differential scanning calorimetry (DSC) trace of polyaniline:2-acrylamido-2-methyl-1-propanesulfonic acid (PANi:AMPSA) [dichloroacetic acid (DCA)] fiber.

Table I Effect of Thermal Aging on the Electrical Conductivity of Polyaniline Fiber

Temperature (°C)	Aging Time (h)	Conductivity (S/cm)
50	0	515
	1.0	503
	2.0	498
	4.0	500
	12.0	493
	18.0	492
	24.0	490
100	0.5	495
	1.0	461
	2.0	434
	4.0	283
	12.0	220
	18.0	201
	24.0	175
150	0.5	345
	2.0	34.1
	4.0	11.0
	8.0	0.89
	16.0	0.15
	24.0	0.14
190	0.5	2.59
	2.0	8.59×10^{-3}
	4.0	2.84×10^{-3}
	8.0	1.07×10^{-3}
	16.0	—

Exothermic peaks in DSC have been related to chemical processes, such as recrystallization¹⁶ or crosslinking reactions,^{12,17–20} without decomposition. An exothermic peak at $\sim 215^\circ\text{C}$ is observed in the DSC trace of the PANi fiber. This relatively large exothermic peak, accompanied by a weight loss transition on the TGA trace (Fig.1), indicates that it could be attributed mainly to decomposition of the AMPSA. The assumed procedures involve breaking down the hydrogen bonds between the solvent (DCA) and AMPSA, and decomposition of AMPSA. As the AMPSA decomposes into small fragments in the polymer, then the conductivity of the fiber is expected to decrease, which are discussed later.

A second small exothermic peak also appears at $\sim 285^\circ\text{C}$ with no transition of weight loss occurring in the TGA trace at this temperature. This small exothermic peak could be due to crosslinking and/or the glass transition of the PANi. The feasibility of crosslinking induced during the thermal aging at that temperature will not be further discussed in this article. The glass transition temperature of PANi emeraldine base at

$\sim 250^\circ\text{C}$ has been reported by other researchers, using MDSC technology.¹³ This implies that the small exotherm at 285°C is most likely associated with the glass transition of PANi. The higher glass transition temperature of PANi:AMPSA (DCA) fiber 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 conductivity of the PANi:AMPSA (DCA) drawn fiber at different temperatures was performed at 50°C , 100°C , 150°C , and 190°C for various periods of time in an oven under vacuum. Table I and Figure 3 show the results of the effect of the thermal aging time on the electrical conductivity measured at room temperature. When the fiber was aged in a vacuum oven at 50°C , the conductivity was not significantly affected during the aging time of 24 h. The conductivity only changed $\sim 5\%$ from 515 S/cm to 490 S/cm. This small change in the fiber conductivity is most likely attributable to the loss of moisture at that temperature.

For the fiber thermally aged at 100°C under vacuum, conductivity was found to decrease from 515 S/cm to 430 S/cm (16.5%) during the first 2 h and then to decrease gradually from 430 S/cm to 175 S/cm during the next 22 h. It is possible that the initial change in the fiber's conductivity is mainly due to gradual loss of moisture and residual solvent trapped inside the fiber. The conductivity then decreases because of further release of the residual solvent that was hydrogen bound to the AMPSA by thermal aging.

When the fiber was aged at a temperature of 150°C , its conductivity decreased swiftly in the very earlier period of aging (from 515 S/cm to 11 S/cm in the first 8 h). Then the conductivity of the fiber gradually leveled out to a very low conduc-

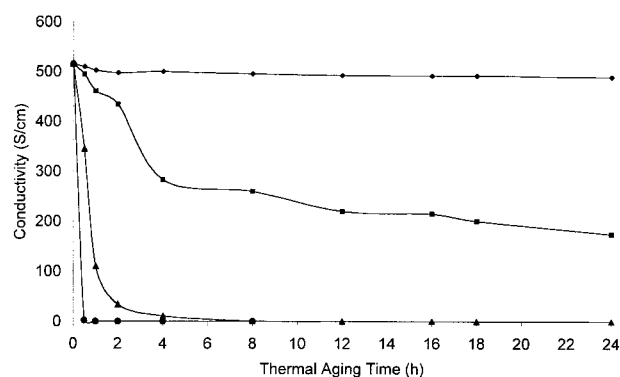


Figure 3 Relationship between the conductivity of the fiber and time of thermal aging in vacuum oven at: \blacklozenge , 50°C ; \blacksquare , 100°C ; \blacktriangle , 150°C ; \bullet , 190°C .

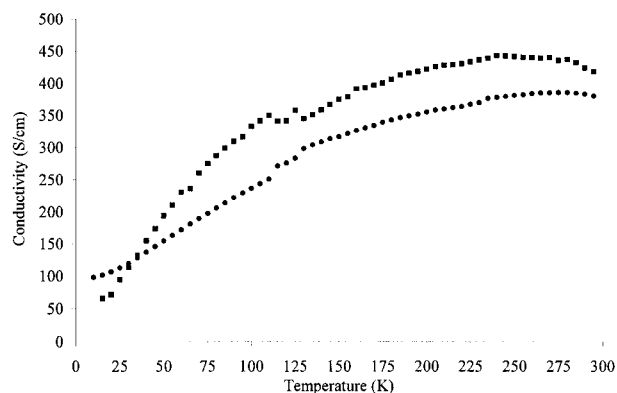


Figure 4 Conductivity of the drawn ($3\times$ drawn ratio) fibers. ■, un-aged fiber; ●, fiber aged at 100°C for 24 h in oven under vacuum.

tivity (0.15 S/cm). During that thermal aging time, the residual solvent (DCA) was lost completely and the AMPSA began to decompose. The fiber was still conductive, albeit with low conductivity for the next 16 h. 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). This result is also consistent with the assumption of the two-stage weight loss of the AMPSA.

At a thermal aging temperature of 190°C , the conductivity of the fiber decreases dramatically during the first 8 h aging time. After that time, the fiber was no longer conductive. This clearly indicates that thermal aging 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 PANi chains in an aging time of 8 h.

The temperature-dependent D.C. conductivities of PANi:AMPSA (DCA) fibers are shown in Figures 4 and 5. In Table II, typical peak positions and their accompany conductivity values are presented. For each sample, the conductivity is thermally activated, but the drawn fibers have much higher conductivity than that of the as-spun fibers. This significant increase in the con-

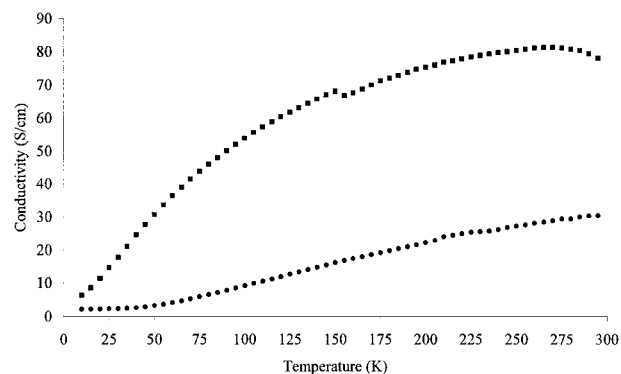


Figure 5 Conductivity of the as-spun fibers. ■, un-aged fiber; ●, fiber aged at 100°C for 24 h in oven under vacuum.

ductivity is associated with the orientation of polymer chains in the drawn fibers. A negative temperature coefficient was observed at the temperature of 240 K (drawn fiber) to 270 K (as-spun fiber). Similar results to this transition behavior had been reported in the cases of PANi:AMPSA (DCA) in the stretched film and drawn fiber and have been ascribed to a “metallic” conducting component.^{21,22}

When the fiber was aged at 100°C for 24 h in vacuum oven, this negative temperature coefficient disappears. The conductivity of the aged fibers also decreases. These results indicate that the loss of the conductivity and the vanishing of the negative temperature coefficient in the thermal aged fiber are due to loss of the residual solvent. Other possibilities will be further investigated: whether the thermal aging at 100°C under vacuum for 24 h would induce crosslinking or other possible chemical changes in the PANi, which may affect the negative temperature coefficient.

CONCLUSIONS

This article presents the effect of thermal aging on the conductivity of PANi:AMPSA (DCA) fiber.

Table II Conductivity of Polyaniline Fiber

Sample	Peak Conductivity σ (S/cm)	Temperature of Peak σ (K)	Conductivity $\sigma_{295\text{ K}}$ (S/cm)
As-spun fiber	81	270	78
Thermal aged as-spun fiber	30	295	30
Drawn fiber	442	240	417
Thermal aged drawn fiber	385	280	379

Thermal aging of the fiber performed at 50°C, 100°C, 150°C, and 190°C for various periods of time in vacuum oven result in a decrease in conductivity, particularly at temperatures higher than 100°C. The reduction in conductivity is ascribed to the removal of residual solvent. Further reduction in conductivity of the fiber aged at higher temperatures is caused by the decomposition of the AMPSA. Complete loss of the conductivity of the aged fiber does not take place until the loss of decomposed fragments of the AMPSA counter-ions, which remain bound to the imine nitrogen groups in the polymer chain. The residual solvent trapped in the fiber is thus favorable to the electrical conductivity of the fiber. The release of the residual solvent also reduces the conductivity and influences the “metallic” conductivity observed in those fibers.

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