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Dry-jet wet spinning of aromatic polyamic acid fiber using chemical imidization

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Abstract

A solution of about 15% polyamic acid (PAA) prepared from 4,4′-oxydianiline and pyromellitic dianhyride in *N*,*N*-dimethyl acetamide (DMAc) was used for fiber spinning. To obtain a high draw ratio of the PAA fiber during spinning, acetic anhydride or acetic anhydride and pyridine were added to the PAA solution to make it slightly gelled; such gelling contributed to high drawing of the PAA fibers during spinning. Before spinning the properties of the solution after acetic anhydride or acetic anhydride and pyridine were added, and the diffusion property of DMAc into various coagulants were examined. Even though acetic anhydride was only added to the spinning solution, the diffusion rate became slower and the solution viscosity increased, because PAA was converted to the corresponding polyimide (PI). Pyridine affected the rate dramatically. The mechanical properties of the PAA fibers obtained in this system were examined. Solid PI fibers were also obtained by annealing of the PAA fibers. The ultimate stress and initial modulus of the PAA fiber were around 268 MPa and 4.1 GPa, respectively. After the fiber was annealed at 350°C without tension for 30 min under nitrogen, these values increased to around 399 MPa and 5.2 GPa, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dry-jet wet spinning; Polyamic acid fiber; Chemical imidization

1. Introduction

Aromatic polyimides have been extensively investigated for their excellent thermal stability and high mechanical properties, along with their good chemical resistance and electrical properties [1,2]. Because of these outstanding properties, their use in fibers, films, coatings, and composites has been studied for many years. However, these polyimides have the disadvantage of poor solubility, which makes them difficult to process. Additionally, since the glass transition temperature of the polymers is very high and their decomposition occurs before they melt, it is very difficult for them to be thermally processed. These drawbacks have been the driving force behind investigation of polyimide precursor polymers, polyamic acids (PAAs). Generally, polyimides (PIs) are prepared from PAAs. It is well known that the conversion reaction of PAAs into PIs during heating is endothermic, and water can be released during the cyclization reaction [3]. These two characteristic properties contribute significantly to flame retardancy. In addition, PIs produced during heating of PAAs show high thermal stability. PAAs are easy to process due to their good solubility in aprotic solvents such as *N*-methyl pyrrolidone (NMP), *N*,*N*-dimethyl acetamide (DMAc), and *N*,*N*-dimethyl formamide (DMF). PAA films and fibers have attracted considerable attention for their potential use as fire-resistant materials. PAAs also have good ambient temperature mechanical properties similar to PIs [3,4].

The wet and dry spinning methods for production of PAA fibers were introduced in 1965 and 1968, respectively [5,6]. In the wet spinning methods, PAA fiber cannot be fully drawn due to the low diffusion of DMAc into some coagulants, which results in poor mechanical properties of the PAA fiber produced. For example, the ultimate stress and initial modulus of PI fiber made by annealing the PAA fiber spun in the system designed by William E. Dorogy, Jr and Anne K. St. Clair are 206 MPa and 3.5 GPa, respectively, even though the PAA fiber was void-free [7,8]. The reason for these results might be low drawing during spinning.

In general, PAAs can be converted to the corresponding PIs at ambient temperature by treatment with mixtures of aliphatic carboxylic acid anhydrides and tertiary amines [9–12]. Acetic anhydride and pyridine or triethyl amine are normally used. It was reported that partially imidized

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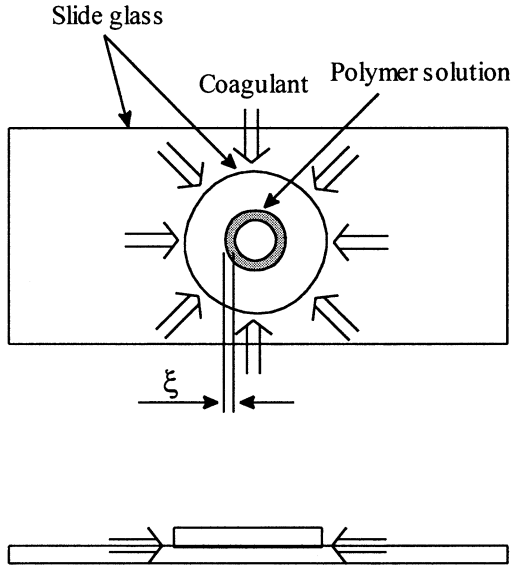


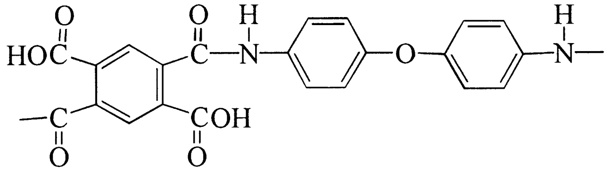
Fig. 1. Measurements of coagulation power.

PAA powder and film were obtained using these agents [9,10]. In our system, to obtain PAA fibers with high mechanical properties for fire-safe materials, acetic anhydride or acetic anhydride/pyridine was introduced into the PAA solution so that it would be slightly gelled before the fiber stream entered the coagulant. In this work, a 20.3% PAA solution in DMAc synthesized from 4,4′-oxydianiline and pyromellitic dianhydride was used. The solution was diluted for PAA fiber spinning. We used a dry-jet wet spinning system to spin a fiber because this method is more effective to draw the fiber during spinning. The spinnability of PAA solutions containing the chemical imidization agent was investigated. The mechanical properties of PAA fibers and the corresponding PI fibers were also examined.

2. Experimental

2.1. Materials

20.3% polyamic acid solution (PAA) in *N*,*N*-dimethyl acetamide (DMAc) was obtained from DuPont. The inherent viscosity of the PAA was 1.10 dl/g. The chemical structure is as follows:



Anhydrous DMAc (99.8%, Aldrich Chem. Co., Inc.) was used as received for diluting the PAA solution. Anhydrous pyridine (99.8%, Aldrich Chem. Co., Inc.) and acetic anhydride (98%, Aldrich Chem. Co., Inc.) were used as received for chemical imidization of the PAA solution.

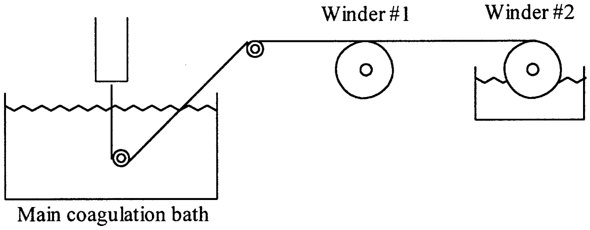


Fig. 2. Fiber spinning equipment.

2.2. Preparation of PAA spinning dope

A solution of PAA (20.3% w/w) in DMAc was diluted to a 15% PAA solution. Around 6 h after 1 equiv. mol of acetic anhydride was added to the PAA solution, the solution was used for a spinning dope. The solution viscosity of the spinning dope was 350–400 poise.

2.3. Measurement of coagulation power (Fig. 1)

PAA solution was dropped onto a glass slide and covered with another slide. A coagulant was then introduced into the capillary between the two slides. The diffusion of the coagulant fronts with time was monitored by a microscope.

2.4. Film preparation

To examine the possibility of spinning of PAA fiber, PAA film was made using various coagulants. PAA spinning dope was poured onto a glass plate and cast with Doctor-knife; the film was then immersed in a coagulant for 30 min. The film was dried in vacuo at 30°C for 24 h.

To monitor the degree of imidization, the PAA film was spin coated from the PAA dope each time after 1 equiv. mol of acetic anhydride was added and immersed into ethanol or ethanol/pyridine (9/1 v/v) mixture for 30 min and then dried under vacuum at 30°C for 24 h.

2.5. Fiber spinning

The PAA fiber was spun using the equipment shown in Fig. 2. The spinning was carried out at room temperature. The highly viscous PAA polymer solution was poured into a stainless-steel extrusion cylinder/piston assembly and extruded through a spinneret with a single hole of 100 μm in diameter. The diameter of the cylinder was around 12 mm. About 10 ml of PAA solution was used for the fiber spinning. The rate of piston movement into the extrusion cylinder was controlled by nitrogen pressure and the PAA fiber emerged from the spinneret at around 150 psi. The spinning solution was filtered before it reached the spinneret. The extruded PAA fiber went downward through the air prior to entering a coagulation bath. The air gap was 50 mm. The fiber stream went into the coagulant to a depth of 100 mm and then emerged from the main coagulant bath

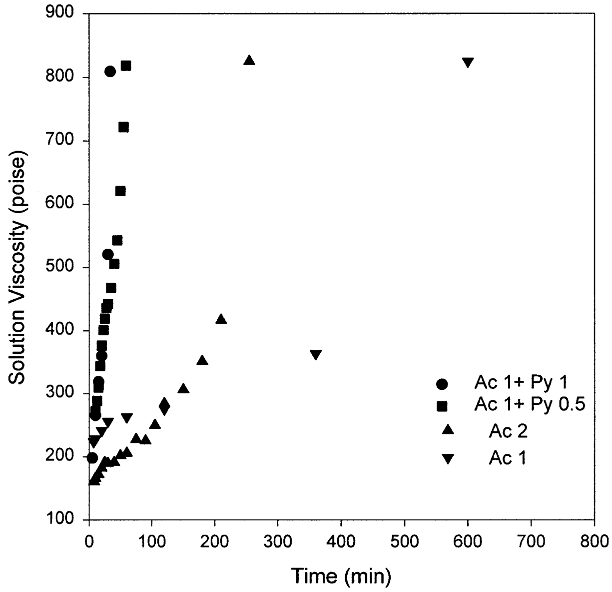


Fig. 3. Variation in solution viscosity of PAA spinning dope after addition of acetic anhydride or acetic anhydride/pyridine.

and was taken up by a winder of about 110 mm in diameter. The resin jet velocity was around 19.0 m/min. The PAA fiber was well formed and could be taken up easily. Two winding rollers were used. The fiber could be drawn by a difference in speed between the two winding rollers. The first and second winder speeds were 17.3 and 34.6 m/min, respectively. While being taken up, the solidifying filament was immersed in a second coagulation bath with the same composition as the main one, to prevent its sticking together, and kept there for 30 min. The coagulant temperature was around 23°C. Then, the fiber was washed with pure water and dried at room temperature.

2.6. Measurements

The PAA solution viscosity was monitored at 23°C by a Brookfield viscometer after the chemical imidization reaction agents were added. Infrared spectra were recorded with a Bio-Rad FTS 175C FT-IR spectrometer to calculate the degree of imidization. The fiber was cut into segments 30 mm long. The samples were tested with a Merlin Instron 5564 at room temperature to determine their mechanical properties. The extension rate was 3 mm/min. The film made by coagulation was cut into 2 × 20 mm strips. The sample films were tested with the same Instron machine with an extension rate of 2 mm/min. Ten fibers or films were taken for each sample for measuring the mechanical properties. To examine the effect of annealing on the mechanical properties of the fiber, it was annealed at 350°C for 30 min without tension under nitrogen. Scanning electron micrographs were obtained on a Jeol 35CF scanning electron microscope. The inherent viscosity of the PAA polymer was determined at 0.5 g/dl in DMAc at 23°C with an Ubbelohde viscometer.

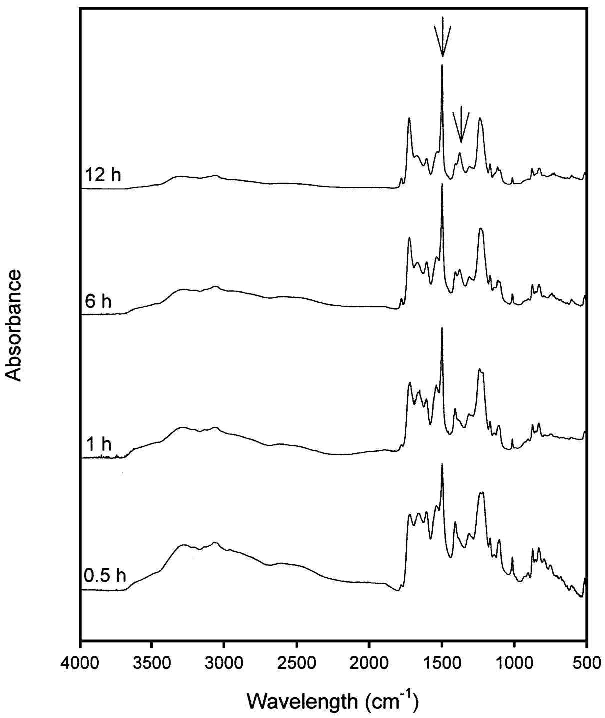


Fig. 4. IR spectra of PAA films obtained after 1 equiv. mol of acetic anhydride was added to the spinning dope.

3. Results and discussion

A solution of PAA (20.3% w/w) in DMAc was obtained from DuPont. The PAA was prepared from 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA), which is well known as the precursor of the polyimide Kapton®. The solution was diluted to a 15% PAA solution because the solution viscosity of the 20.3% PAA solution was too high to spin fiber in our system. The 15% PAA solution was used for a spinning dope after acetic anhydride was added. PAAs can be converted to the corresponding PIs by treatment with mixtures of aliphatic carboxylic acid dianhydrides and tertiary amines. Acetic anhydride and pyridine or triethyl amine are normally used. This work includes such treatment of PAA spinning dope before spinning of PAA fiber, to ensure high drawing during spinning. After the chemical imidization reaction agents were added to the spinning dope, the solution viscosity increased with time, as the PAA was converted to the corresponding PI. The increase in solution viscosity depended on the amounts of the chemical imidization reaction agents. Fig. 3 shows the variation in solution viscosity of PAA spinning dopes after acetic anhydride or acetic anhydride/pyridine were added. The abbreviations Ac 1 and Py 1 mean that 1 equiv. mol of acetic anhydride and 1 equiv. mol of pyridine, respectively,

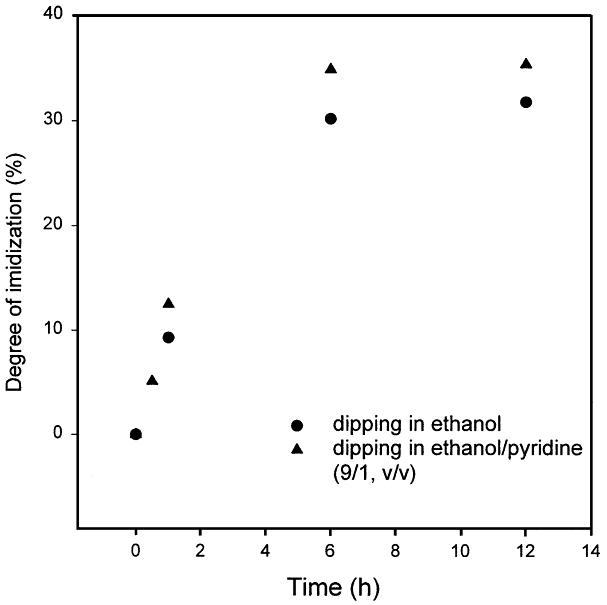


Fig. 5. Degree of imidization of PAA films obtained after 1 equiv. mol of acetic anhydride was added to the spinning dope.

were added to the 15% PAA solution in DMAc. The tertiary amine plays several important roles in the conversion, which proceeds by nucleophilic substitution. It converts a carboxylic acid to a better nucleophile and also the aliphatic dianhydride to a salt form, which is more susceptible to nucleophilic attack. PAAs can be converted very slowly to the corresponding PIs without pyridine because DMAc can act as a tertiary amine. In a similar manner, all aprotic solvents, such as NMP and DMF, can act like DMAc. Addition of more acetic anhydride increases the rate of conversion. By 10 min after acetic anhydride was added, the solution viscosity of the PAA solution was lower than that of pure 15% PAA solution, around 220 poise. Pyridine affected the rate especially dramatically. All tertiary amines, such as triethyl amine, 3-picoline, 2,6-lutidine, imidizole, and isoquinoline act like pyridine. A dope solution viscosity of 350–400 poise was good enough for spinning in our system. Because the solution viscosity of the spinning dope can attain this value within 30 min after pyridine and acetic anhydride are introduced to the solution and the viscosity can change very quickly during spinning, we added only 1 equiv. mol of acetic anhydride to the solution and used the solution as a spinning dope, 6 h after the addition. Since spinning is completed within 30 min in our system, the viscosity of the spinning dope does not change significantly during spinning. Fig. 4 shows infrared spectroscopy of PAA films after 1 equiv. mol of acetic anhydride was added to the PAA spinning dope. The film was spin coated from the PAA dope each time after 1 equiv. mol of acetic anhydride was added and immersed into ethanol for 30 min and then dried under vacuum at 30°C for 24 h. The film thickness was about 5 μm. To monitor the cyclization steps, the imide band near 1380 cm^{-1} was used because this peak shows very little effect from anisotropy, when it is normalized to the 1500 cm^{-1} aromatic band [13]. As shown in Fig. 4, the intensity of the peak near 1380 cm^{-1} increased with storage time after 1 equiv. mol of acetic anhydride was added to the solution, meaning that the imidization reaction proceeded. In the case of the chemical imidization process, the isoimide form as well as the imide form can be formed [14]. However, the conversion to the isoimide form was negligible because the characteristic IR band, about 915 cm^{-1}, was very small. This isoimide form immediately rearranges to the imide form during thermal imidization. Also, a change in the imide absorption band near 1780 cm^{-1}, which is most widely used, could be observed. According to this result, the degree of imidization was calculated based on the ratio of the peak intensity between 1380 and 1500 cm^{-1} for PAA film annealed at 350°C for 30 min under nitrogen. As shown in Fig. 5, the degree of imidization increased to around 30% with the storage time after acetic anhydride was added to the PAA spinning dope. Even though the film was immersed into ethanol containing 10% pyridine for 30 min before drying, the degree of imidization increased by 3–5%, because the diffusion rate of acetic anhydride was not low enough to allow the acetic anhydride to react with pyridine in the PAA fiber. Therefore, the fiber spun in this system is slightly imidized, which means it is an amic acid–imide copolymer in a strict sense.

Before spinning of the PAA fiber, the diffusion rate of DMAc into water was investigated. The specific growth rate of the solid layer forming on the surface of PAA solution treated with water was measured (Fig. 1). The thickness of the solidified layer is proportional to the square root of time according to the following equation [15]:

$$\Xi = 1/4 \lim_{t \to 0} (\mathrm{d}\xi^2/\mathrm{d}t)$$

where Ξ is the initial boundary growth rate, ξ, the thickness of solidified layer, and t, the time.

It is well known that the experimental values of Ξ are reproducible and reflect the effects of spinning dope, coagulation bath composition, temperature, etc. Ξ does not depend explicitly on the radius of the sample and spinning velocity, but only on the rate of mass transfer and phase separation. The diffusion rates of DMAc in the PAA spining dope into water are shown in Fig. 6. The diffusion rate of DMAc in PAA solution could be measured only by water in this system because it was too low to measure when other solvents such as ethanol and isopropanol were used. The transfer rate of DMAc out of PAA solution decreased with storage time after acetic anhydride was added to the PAA solution, meaning that the PAA solution was solidified with time after acetic anhydride was added, due to imidization. The value of PAA solution, 6 h after 1 equiv. mol of acetic anhydride was added, was too low to measure. The boundary growth rate does not represent the real diffusivity of solvent into coagulant, but it can be considered as a

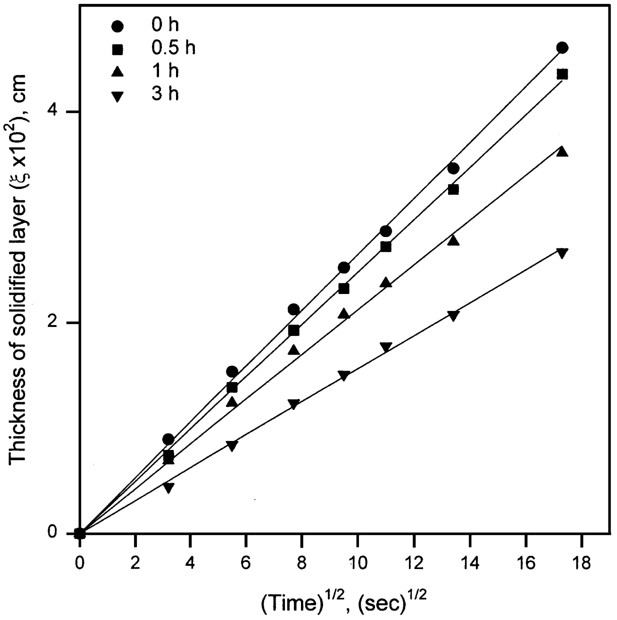


Fig. 6. Variation in diffusion rate of DMAc in PAA solution into water after addition of 1 equiv. mol of acetic anhydride.

measure of diffusivity. The parameter Ξ provides a fairly accurate measure of the solidification rate. 0.5, 1, and 3 h after 1 equiv. mol of acetic anhydride was added, the initial boundary growth rates Ξ of the PAA solution coagulated in water were 1.55×10^{-6}, 1.10×10^{-6}, and 0.61×10^{-6} cm²/s, respectively. The value of pure PAA solution was 1.74×10^{-6} cm²/s. The magnitude of Ξ depends on the rate of mass transfer and phase and structural transitions in the polymer–solvent–non-solvent system in exactly the same way as does the solidification rate in the real wet-spinning process [15].

Aromatic PAA fiber was produced using the equipment shown in Fig. 2. About 6 h after 1 equiv. mol of acetic anhydride was added to the PAA solution, the highly viscous PAA polymer solution was poured into a stainless-steel extrusion cylinder/piston assembly. The rate of piston movement into the extrusion cylinder was controlled by nitrogen pressure, and the PAA fiber emerged at around 150 psi. Two winders with different speed were used, and the fiber was drawn by the difference in speed between the two winders.

When pure 15% PAA solution was used as a spinning dope, the fiber emerged at around 150 psi and the resin extrusion rate was 45.3 m/min which was over two times greater than that of 15% PAA solution containing 1 equiv. - mol of acetic anhydride at essentially the same pressure. This might be due to low solution viscosity, around 220 poise. This fiber stream was not so fully coagulated in ethanol that it could not be taken up at winder #1. This might be due to low diffusion of DMAc into ethanol. In the ethanol/water (5/5 v/v) coagulation bath, the fiber could be taken up at winder #1 and drawn at winder #2, but the speed ratio between the two winders could not be over 1.25. The diameter of the PAA fiber taken up at winder #2 was around 60 μm. The ultimate stress, initial modulus, and elongation of the PAA fiber were 63.8 MPa, 2.2 GPa, and 13%, respectively. As a result, water was needed to obtain PAA fiber at winder #1, but the faster diffusion of DMAc into the ethanol/water mixture made the fiber weak. Also, the draw ratio between the winders was limited due to the faster diffusion rate. Pure 15% PAA film was made and put into two different coagulants, ethanol and ethanol/water (5/5 v/v), for 30 min and dried at 30°C for 24 h under vacuum. The PAA film made in ethanol was transparent, but that made in ethanol/water mixture was not. The ultimate stress and initial modulus of the pure PAA films made in ethanol and the ethanol/water mixture were 99.3 MPa and 3.8 GPa and 52.7 MPa and 1.8 GPa, respectively. The ultimate stress and initial modulus of the PAA film made in pure ethanol were two times greater than those of the PAA film made in the ethanol/water mixture. It might be concluded that water in the coagulation bath largely affects the mechanical properties of the PAA fiber. The diffusion rate

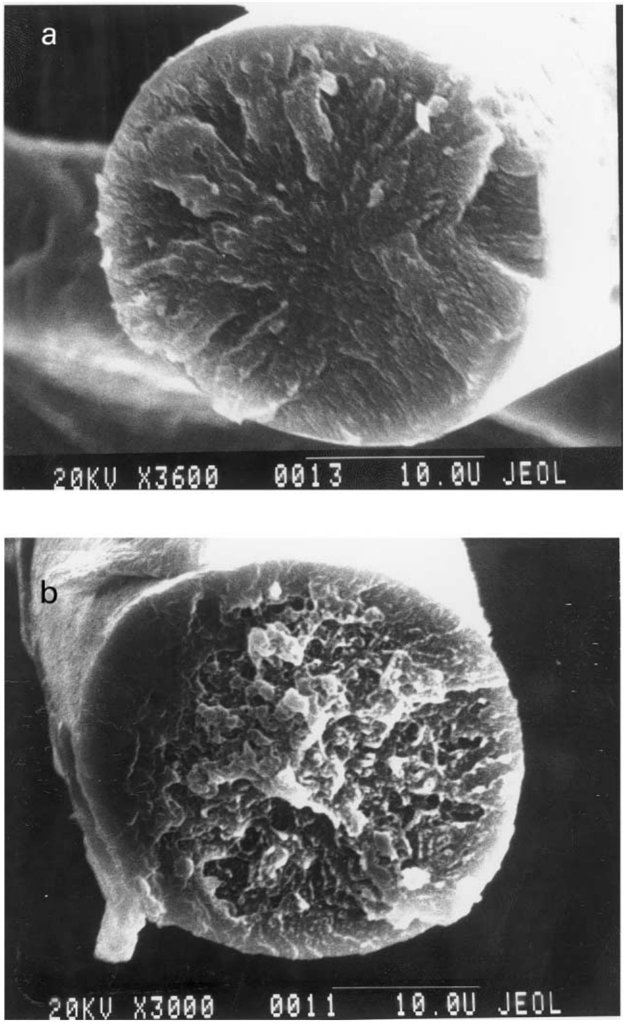


Fig. 7. Cross-section of fractured PAA fibers spun in ethanol (a) and ethanol/water/pyridine (4.5/4.5/1.0, v/v/v) (b).

Table 1
Mechanical properties of PAA fiber spun in ethanol (spinning condition: resin viscosity 355 poise at 23°C; resin temperature 23°C; resin jet velocity 19.0 m/min; air gap 5 cm; coagulation bath ethanol; coagulation bath temperature 23°C; first winder speed 17.3 m/min; second winder speed 34.6 m/min)

	Winder #1 annealed[a]		Winder #2 annealed	
	Before	After	Before	After
Diameter of fiber (μm)	48.2 (5.5%)[b]	45.2 (6.6%)	21.4 (3.2%)	19.1 (3.7%)
Ultimate stress (MPa)	118 (6.5%)	242 (17.0%)	268 (6.2%)	399 (16.6%)
Initial modulus (GPa)	3.0 (12.9%)	3.3 (18.7%)	4.1 (15.4%)	5.2 (7.1%)
Elongation (%)	20.9 (28.7%)	13.3 (28.8%)	16.0 (20.1%)	11.1 (18.0%)

[a] Annealed at 350°C without tension for 30 min under nitrogen.

[b] Coefficient of variation in parentheses.

of DMAc into water is faster than into ethanol, to affect the fiber morphology. Additionally, water is known to degrade the PAA due to hydrolysis [16]. Therefore, water cannot be used as a coagulant to obtain PAA fiber with high mechanical properties. Since pure PAA fiber could not be taken up in ethanol due to low diffusion of DMAc in this system, the PAA had to be slightly solidified before the fiber stream went into the ethanol coagulant. Otherwise, the PAA fiber stream would have to be in ethanol for a long time to be taken up. When chemical imidization reaction agents were introduced to PAA solution, the solution viscosity increased and solidified slightly with time due to chemical imidization. Even though the diffusion rate of DMAc in slightly solidified PAA solution into ethanol was lower than that of pure PAA solution, the PAA fiber could be taken up in ethanol at winder #1 and fully drawn at winder #2.

The 15% PAA solution was used as a spinning dope 6 h after 1 equiv. mol of acetic anhydride was introduced into the solution and spun in ethanol. Fig. 7(a) shows SEM photos of fractured ends of PAA fibers spun in ethanol. The fiber was void-free; voids would affect the mechanical properties of the PAA fiber. The diameter of the fibers at winders #1 and #2 was about 48 and 21 μm, respectively. The fiber was very uniform. The fiber evenness was shown by the coefficient of variation, which is determined by dividing the standard deviation by the arithmetic mean and multiplying by 100, with its units being %. This diameter was dependent on various conditions, such as resin jet velocity, winder speed, etc. The diameter was slightly decreased after annealing. The mechanical properties of the PAA fiber spun in ethanol was shown in Table 1. The ultimate stress, initial modulus, and elongation of the fiber taken up at winders #1 and #2 with ethanol as a coagulant were 118 MPa, 3.0 Gpa, and 20.9% and 268 MPa, 4.1 GPa, and 16.0%, respectively. After the fiber was annealed at 350°C for 30 min without tension under nitrogen, the ultimate stress and initial modulus increased to 242 MPa and 3.3 GPa and 399 MPa and 5.2 GPa, respectively, because PAA was almost converted to the corresponding PI. Elongation decreased to 13.3 and 11.1%, respectively. Even though the ethanol/water/pyridine (4.5/4.5/1.0 v/v/v) mixture was used as a coagulant, the mechanical properties of the fiber were equal to those of PAA spun in ethanol (Table 2). The ultimate stress, initial modulus, and elongation of the fiber taken up at winder #1 and #2 with ethanol/water as a coagulant were 103 MPa, 3.1 GPa, and 46.5% and 262 MPa, 4.7 GPa, and 14.3%, respectively. After the fiber was annealed at 350°C for 30 min without tension under nitrogen, the ultlmate stress and initial modulus increased and elongation decreased. 10% Pyridine was added to the coagulant to get a slightly higher degree of imidization. Therefore, water could not affect the mechanical properties of the PAA fiber in our system. Fig. 7(b) shows SEM photos of fractured ends of PAA fibers spun in ethanol/water/pyridine. The fiber was

Table 2
Mechanical properties of PAA fiber spun in ethanol/water/pyridine (spinning condition: resin viscosity 363 poise at 23°C; resin temperature 23°C; resin jet velocity 18.7 m/min; air gap 5 cm; coagulation bath ethanol/water/pyridine (4.5/4.5/1 v/v/v); coagulation bath temperature 23°C; first winder speed 17.3 m/min; second winder speed 34.6 m/min)

	Winder #1 annealed[a]		Winder #2 annealed	
	Before	After	Before	After
Diameter of fiber (μm)	45.9 (12.6%)[b]	43.9 (8.5%)	21.0 (1.5%)	18.9 (1.3%)
Ultimate stress (MPa)	103 (15.7%)	261 (17.8%)	262 (19.8%)	363 (15.6%)
Initial modulus (GPa)	3.10 (8.7%)	3.26 (9.5%)	4.66 (8.0%)	5.7 (4.2%)
Elongation (%)	46.5 (28.6%)	19.8 (15.9%)	14.3 (36.4%)	8.0 (16.3%)

[a] Annealed at 350°C without tension for 30 min under nitrogen.

[b] Coefficient of variation in parentheses.

also void-free. In these cases, the solution viscosity and resin jet velocity of the spinning dope were around 360 poise and about 19.0 m/min and the speed ratio between two winders was 2. The PAA fibers spun in the new system described here have excellent mechanical properties, as do the corresponding PI fibers.

4. Conclusions

To spin PAA fiber with high mechanical properties, 15% PAA spining dope was treated with 1 equiv. mol of acetic anhydride before spinning. The diffusion rate of DMAc into ethanol was too low to allow the PAA fiber to be taken up in our system when 15% PAA pure solution was used as a spinning dope. In this case, water has to be added to the ethanol to take up the fiber, but this affected the mechanical properties of the fiber. Adding acetic anhydride to the 15% PAA solution made the diffusion rate of DMAc in the PAA solution into ethanol lower than that of DMAc in pure 15% PAA solution because of chemical imidization. However, the PAA fiber could be taken up and drawn in ethanol during spinning due to slight solidification of the PAA solution. In our system, the mechanical properties of the fiber did not decrease with addition of water. The degree of imidization of the fiber was around 30% and it slightly increased in an ethanol coagulation bath containing 10% pyridine. Actually, this fiber is a polyamic acid–imide copolymer. The fiber was very uniform within 3% of coefficient of variation, and void-free. The ultimate stress and initial modulus of the PAA fiber were around 268 MPa and 4.1 GPa. These values increased to around 399 MPa and 5.2 GPa after the fiber was annealed at 350°C because the PAA fiber was almost converted to the corresponding PI fiber. These values might be significantly increased when the PAA fiber was drawn during annealing. The PAA fibers spun in the new system and their PI fibers had excellent mechanical properties.

Acknowledgements

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