

Effects of Imidization Temperature on the Structure and Properties of Electrospun Polyimide Nanofibers

Xuejia Li^{1,2}, Xin Wang¹, Qingqing Wang¹, Qufu Wei¹

¹Key Laboratory of Eco-textiles (Jiangnan University), Ministry of Education, Wuxi, Jiangsu CHINA

²College of Textiles and Clothing, Nantong University, Nantong, Jiangsu CHINA

Correspondence to:
Qufu Wei email: qfwei@jiangnan.edu.cn

ABSTRACT

A two-step process for preparing polyimide nanofiber was used in this work, and the nanofibers of precursor polyamic acid (PAA) were prepared by electrospinning. The polyimide nanofibers were obtained through thermal imidization at different thermal imidization temperatures. The influences of different imidization temperatures on morphology, chemical structure, thermal stability, and mechanical properties of the polyimide nanofibers were investigated by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electronic Microscopy (SEM), thermal gravimetric analysis (TGA) and Electromechanical Universal Testing Machine. The experimental results show that the imidization of PAA nanofibers was not complete under 290°C but complete under 350°C. With the rise of imidization temperature from 290°C to 350°C, the polyimide nanofibers became thinner, and the thermal stability of polyimide nanofibers was also improved. The breaking strength and elongation at break of the nanofiber membranes increased at higher imidization temperature.

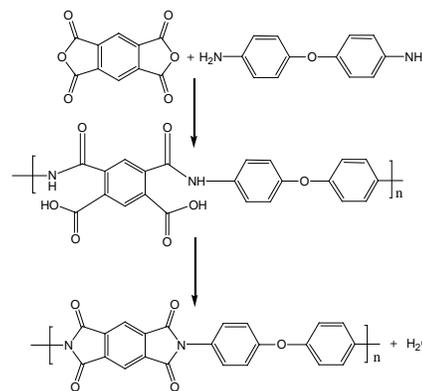
Keywords: polyimide; electrospinning; nanofiber; thermal imidization temperature

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 [1-4]. Continuing research interests are devoted to further improving the performance of polyimides in some specific applications. For example, polyimides can be used as a key component of the gas mask, the constructive material of a membrane which allows the air to go through but precludes the dust or harmful gas in case of a fire, or used in other filtering and separating applications requiring high performance [5-9].

Recently, the electrospinning technique has been demonstrated to be a feasible and low cost way to produce nonwoven fabrics composed of nanofibers with many specific characteristics [10-12]. In this technique, a high voltage is applied on the polymer solution or melt, and the Coulombic repulsive force overcomes the solution surface tension and thus forces the ejection of a liquid jet, which results in the formation of a Taylor cone. The electrified jet of viscoelastic solution then undergoes a stretching process and forms thin fibers on the collector. As the jet travels in air, the solvent evaporates leaving a charged fiber that can be electrically stretched to become very fine fibers. The electrospun fibers can be collected on the receiving screen 10-20 cm apart. One of the major advantages of electrospun nanofibers is that the large surface area-to-volume ratio might provide the materials with even better separation efficiency than the conventional nonwoven fabrics prepared by traditional techniques [13].

Generally, the synthesis of polyimide (PI) takes two steps: the synthesis of polyamic acid (PAA), followed by the imidization process (*Scheme 1*) [14-15].



SCHEME 1. Synthesis of Polyimide in two steps.

In this paper, the precursor PAA solutions were synthesized from pyromellitic dianhydride (PMDA) and 4, 4'-diaminodiphenyl ether (ODA) by copolymerization in polar solvent dimethylformamide (DMF), and the nanofibers of PAA were prepared by electrospinning. The polyimide nanofibers were obtained through thermal imidization. Generally, imidization temperature is selected in the range of 300-350°C, but the influences of imidization temperature on structures and properties of polyimide have not been properly investigated [14-18].

In this work, the influences of different imidization temperatures on fiber diameters, chemical structure, thermostability, and mechanical properties of the polyimide nanofibers were studied and characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electronic Microscopy (SEM), thermal gravimetric analysis (TGA), and mechanical measurement.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) was supplied by Shanghai Resin Institute of China (Shanghai, China). 4, 4'-diaminodiphenylether (ODA) and polar solvent dimethylformamide (DMF) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Synthesis of PI precursor PAA

The preparation of PAA by polymerization was performed by the following processes. Equimolar amounts of PMDA(5.455g, 0.025mol) and ODA(5.032g, 0.025mol) and 42.0g solvent DMF were mixed in a 250mL three-necked flask equipped with a mechanical stirrer, nitrogen inlet and outlet, mechanical intense stirred under the temperature below 10°C for 6h to give a highly sticky polymer solution. In the experiment, PMDA was mixed step by step after ODA was completely dissolved [15].

Preparation of PAA Nanofibers

A conventional laboratory electrospinning set-up was used. The nanofibers were produced by using the above precursor solution. The polymer solution was electrospun at a positive voltage of 18 kV with a working distance of 20 cm, and the flow rate was set as 0.6 mL/h. The electrospinning process lasted 6h. All the experiments were carried out at room temperature [13].

Preparation of PI Nanofibers

The polyimide nanofibers were obtained through thermal imidization under different thermal imidization temperatures. The series of PI nanofibers obtained at the imidization temperatures of 290, 310, 330 and 350 degrees were denoted as PI-1, PI-2, PI-3 and PI-4, respectively. The imidization of the precursor PAA electrospun nanofibers was performed in a high temperature furnace, in the atmosphere, at a heating rate of 2°C/min and by the following steps: (1) heating up to 80°C and maintained for 1h to remove the residue solvent; (2) heating up to 160°C and maintained for 1h, then up to 250°C and maintained for 1h; (3) finally heating up to 290°C, 310°C, 330°C and 350°C, respectively, and maintained for 0.5h in vacuum to finish the imidization process of the precursor PAA nanofibers [14-15].

Structural Characterizations

A scanning electron microscope (SEM, KYKY-2800B, KYKY Technology Development Ltd.) was used to examine the structures and surface morphology of the precursor nanofibers and polyimide nanofibers. Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded at room temperature using a Bruker EQUINOX-55 spectrometer to investigate the surface chemistry of the electrospun fibers obtained.

Thermal and Mechanical Properties

A NETZSCH TG 209 F1 was employed to analyze the thermal stability of the nanofiber membranes under nitrogen atmosphere at a heating rate of 20°C/min. The mechanical properties were measured using a WDW-100 Electromechanical Universal Testing Machine at a speed of 5mm/min. The samples were prepared in 20 mm width, 100 mm length and about 0.4 mm thickness.

RESULTS AND DISCUSSION

Fibrous Structures

Figure 1 shows the SEM image of PAA nanofibers. The properties of PAA solution depended on the reaction temperature and reaction time as well as the stirring time and the solid content. In the experiment, it was observed that nanofibers with a large number of beads were obtained when PAA solution was prepared by stirring at higher temperature. After a great deal of trial experiments, an appropriate PAA solution was obtained by stirring at the temperature below 10°C for 6h and its solid content was twenty percent .

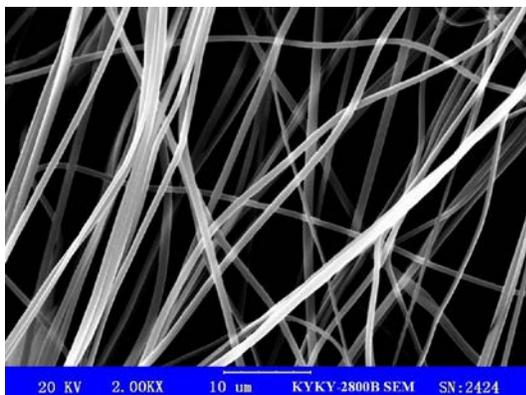


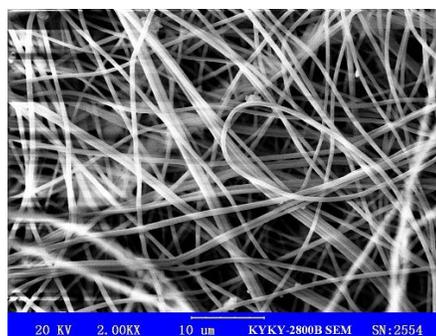
FIGURE 1. SEM image of PAA nanofibers.

As shown in *Figure 1*, continuous nanofibers with smooth surface were obtained in the experiment. The electrospun nanofibers formed a randomly orientated fibrous web. The SEM image revealed that the PAA nanofibers had smooth appearance, uniform thickness and certain intensity. The average diameter and standard deviation of the PAA fibers were about 665 nm and 175 nm, respectively. The number of fibers measured for the diameter distribution was 300.

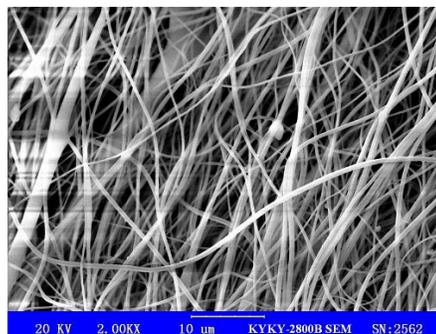
Figure 2 shows the SEM images of PI nanofibers which were obtained under different imidization temperatures and their average diameters and standard deviations are presented in *Table I*.

TABLE I. Effect of imidization temperature on nanofiber diameter distribution.

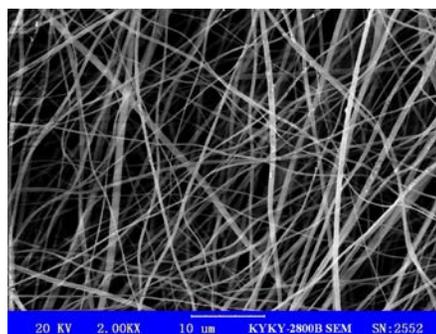
Imidization temperature(°C)	Average diameter (nm)	Standard deviation (nm)
290	587	114
310	426	129
330	305	127
350	217	110



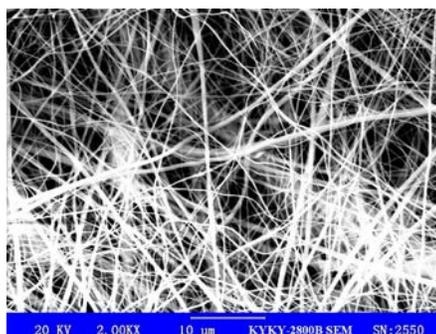
(a)



(b)



(c)



(d)

FIGURE 2. SEM images of PI nanofibers: (a) PI-1; (b) PI-2; (c) PI-3; (d) PI-4.

The nanofibers looked thinner through thermal imidization, as shown in *Figure 2*. When the imidization temperature was 290°C, the average diameter of the nanofibers was about 587 nm. The average diameters of the PI nanofibers decreased with the increasing of imidization temperature. When the imidization temperature increased to 350°C, the average diameter decreased to 217 nm, as revealed in *Table I*. This could be attributed to the further volatilization of vestigial solvent in the PI nanofibers with the increase of processing temperature and the continuous overflow of water molecules during the imidization.

Chemical Characterization

The Fourier Transform Infrared Spectroscopy (FT-IR) of PAA nanofibers is shown in *Figure 3*.

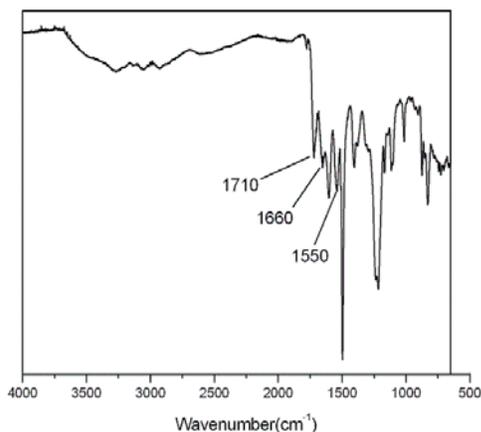


FIGURE 3. FT-IR spectrum of PAA nanofibers.

As shown in *Figure 3*, the absorption peak attributed to N-H(NH₂) and O-H(COOH) bondings appeared in the range from 2900 to 4000 cm⁻¹. The absorption peak at 1710 cm⁻¹ indicated that there was C=O(COOH) bondings. The absorption peak at 1660 cm⁻¹ was the C=O(COOH) vibration in the amide, and the absorption peak at 1550 cm⁻¹ was the C-NH(CONH) vibration in the amide. All the above-mentioned characteristic peaks coincided with pertinent literature, which represented the polyamide acid molecular structure characteristics.

FT-IR spectra of PI nanofibers were employed to study the effects of imidization temperature on the surface chemistry of nanofibers of polyimide, which is illustrated in *Figure 4*.

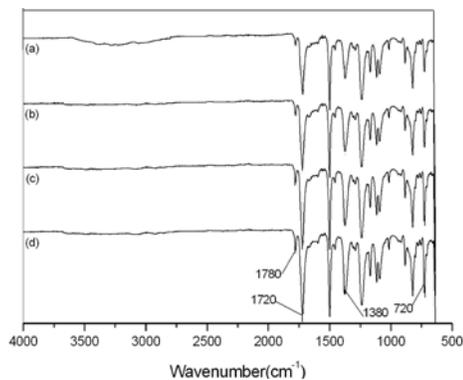


FIGURE 4. FT-IR spectra of PI nanofibers: (a) PI-1; (b) PI-2; (c) PI-3; (d) PI-4.

After the thermal imidization, the above-mentioned characteristic peak of polyamide acid gradually disappeared, and at the same time, the new characteristic peak appeared, namely polyimide characteristic peak. The absorption peaks at 1780 cm⁻¹ and 1720 cm⁻¹ indicated that there was asymmetry and symmetric stretching vibration of C=O bondings. The absorption peak at 720 cm⁻¹ was the flexural vibration of C=O bonds and the absorption peak at 1380 cm⁻¹ was the vibration of C-N bondings in PI.

FT-IR spectra of polyimide obtained under different imidization temperatures looked different, so it could be seen that the imidization and the thermal imidization temperature were closely related.

FT-IR spectra of (a), (b), (c) and (d) in *Figure 4* represented PI-1, PI-2, PI-3 and PI-4, respectively. Although the curing temperature was up to 290°C, the FT-IR spectrum indicated that the imidization of PAA was not fully completed. The absorption band at around 2900~3200 cm⁻¹ reveals the existence of N - H and O - H bondings representing the polyamide acid molecular structure characteristics as shown in *Figure 4 (a)*. However, imidization was almost completed at 330 degree. The absorption peak attributed to N - H and O - H bondings did not appear in the range from 2500 and 3500 cm⁻¹ and the absorption peaks about 1780 cm⁻¹, 1720 cm⁻¹, 1380 cm⁻¹ and 720 cm⁻¹ characterizing polyimide groups obviously increased on the FT-IR spectrum of *Figure 4(c)* and *Figure 4(d)*. With the increasing of reaction temperature, the process of imidization continued until the imidization was complete, so the absorption peaks characterizing polyimide groups gradually increased as shown in *Figure 4* [14-16].

Thermal Characterization

Figure 5 showed the weight loss of the PAA and PI nanofibers with temperature at a heating rate of 20 °C /min as measured by TGA in nitrogen atmosphere.

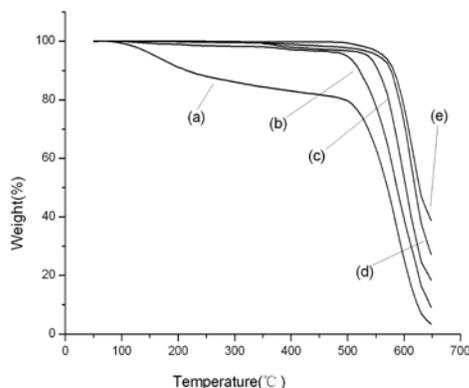


FIGURE 5. TG curves of PI nanofibers: (a) PAA; (b) PI-1; (c) PI-2; (d) PI-3; (e) PI-4.

The five curves in the figure indicate the thermal stability of PAA and PI nanofibers which had a thermal imidization temperature at 290 °C, 310 °C, 330 °C and 350 °C, respectively, and with the imidization time of 0.5 hour under atmosphere conditions. It can be observed from Figure 5 that the temperature, at which weight loss of 5% occurred, was 128 °C, but this temperature increased to 492 °C, 535 °C, 552 °C and 561 °C for PI-1, PI-2, PI-3 and PI-4 respectively, when there was a thermal weight loss of 5%. It was also found that the temperature of thermal weight loss of 5% was raised with the increasing of thermal imidization temperature of PAA. The result implied that imidization temperature had a significant influence on thermal weight loss [17-18].

Mechanical Testing

The mechanical properties of PMDA-ODA PI thin membranes with different imidization temperatures are listed in Table II.

TABLE II. Mean values of the mechanical properties for PMDA-ODA PI nanofiber membranes.

Imidization temperature(°C)	Break strength (MPa)	Elongation at break(%)
290	8.70 ± 0.49	5.85 ± 0.38
310	18.86 ± 0.36	12.06 ± 0.37
330	26.71 ± 0.50	17.40 ± 0.49
350	28.55 ± 0.49	18.12 ± 0.38

The data in Table II indicate that the mechanical properties of the PI nanofiber membranes relied significantly on their imidization temperatures.

As shown in Table II, when the imidization temperature was 290 °C, the breaking strength and elongation of the PI nanofiber membranes were about 8.7 MPa and 5.85%, respectively. The breaking strength and elongation of the PI nanofiber membranes increased with the increasing of imidization temperature. When the imidization temperature increased to 350 °C, the breaking strength and elongation of the PI nanofiber membranes were up to about 28.55 MPa and 18.12%, respectively. This can be attributed to the increase of cyclization degree of PI nanofibers with the increase of processing temperature during the imidization.

Additionally, when the temperature was raised from 290 °C to 330 °C, the influence of imidization temperature on the mechanical properties of the PI nanofiber membranes was very significant, and became smaller with temperature rising from 330 °C to 350 °C. This indicates that imidization of PI nanofibers was almost completed at 330 degree, and this result was accorded with the analysis of FT-IR of PI nanofibers.

Obviously, thermal imidization at a high temperature had a positive influence on the break strength and elongation of the PI nanofiber membranes, but the influence of imidization temperature varied in different temperature ranges.

CONCLUSION

The PI precursor was synthesized from PAMD and ODA using mechanically intense stirring under a temperature below 10 °C for 5-6h. PAA nanofibers were successfully prepared by electrospinning. A series of PI nanofibers were obtained through thermal imidization of different thermal imidization temperature. The results show that the imidization of nanofibers was not complete under 290 °C but complete under 350 °C as revealed in the FT-IR spectra; and with the rise of imidization temperature, the polyimide nanofibers became finer, and the thermal stability of polyimide nanofibers was improved. The breaking strength and elongation at break of the nanofiber membranes increased with the increasing of thermal imidization temperature.

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REFERENCES

- [1] Landry, D. J. T.; Coltrain, B. K.; Wesson, J. A. *Polymer* 1992, 33, 1496.
- [2] Saito, J.; Miyatake, K.; Watanabe, M. *Macromolecules* 2008, 41, 2415.
- [3] Katz, M.; Theis, R. J. *Ieee Electrical Insulation Magazine* 1997, 13, 24.
- [4] Xuyen, NT.; Ra, E. J.; Geng, HZ.; Kim, KK.; An, KH.; Lee, YH. *J Phys Chem B* 2007, 111, 11350.
- [5] Mensitieri, G.; Lavorgna, M.; Larobina, D.; Scherillo, G.; Ragosta, G.; Musto, P. *Macromolecules* 2008, 41, 4850.
- [6] Musto, P.; Ragosta, G.; Mensitieri, G.; Lavorgna, M. *Macromolecules* 2007, 40, 9614.
- [7] Moriguchi, I.; Teraoka, Y.; Kagawa, S.; Fendler, JH. *Chem Mater* 1999, 11, 1603.
- [8] Daigo, Muraoka; Lei, Zhang; Yoshiaki, Suzuki; Hiroyoshi, Kawakami. *J MEMBRANE SCI* 2011, 375, 75.
- [9] Hiroyoshi, Kawakami; Kanako, Nakajima; Hideyuki, Shimizu; Shoji, Nagaoka. *J Membrane Sci* 2003, 212, 195.
- [10] Reneker, DH; Chun, I. *Nanotechnology* 1996, 7, 216.
- [11] Xin, Y.; Huang, ZH.; Li, WW.; Jiang, ZJ.; Tong, YB.; Wang, C. *Eur Polym J* 2008, 44, 1040.
- [12] Fong, H.; Chun, I.; Reneker, DH. *Polymer* 1999, 40, 4585.
- [13] Ding, B.; Yu, J. Y. *Electrospinning and Nanofibers*; Chinese Textile & Apparel Press: Beijing, 2011.
- [14] Ding, M. X. *Polyimide*; Chinese Science Press: Beijing, 2012.
- [15] Si Cheng, Dezhi Shen, Xinsheng Zhu, Xingguang Tian, Ddongying Zhou, Li-Juan Fan. *European Polymer J* 2009, 45, 2767.
- [16] Cheng, S.; Li, X. F.; Xie, S. B.; Chen, Y.; Fan, L. J. *J of Colloid and Interface Science*, 2011, 356, 92.

[17] Soo, Jin. Park; Hee, Jin Sohn *J of Colloid and Interface Science* 2009, 332, 246.

[18] Qing, H. Zh; Mian, Dai. *European Polymer J* 2004, 40, 2487.

AUTHORS' ADDRESSES

Xueja Li

Xin Wang

Qingqing Wang

Qufu Wei

Key Laboratory of Eco-textiles

Jiangnan University

Ministry of Education

Wuxi, Jiangsu 214122

CHINA