

## Study on the Fabrication and Application of Polyimide Fibers

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**Abstract** A series of copolyimide (co-PI) fibers with superior mechanical properties and high thermal stability were fabricated via a wet spinning method from poly(amic acid) solution and followed by coagulation, washing, thermal treatment processes. The effects of the chemical structures of PI, interaction between macromolecules and drawing ratio on the micro-structure and properties of the obtained fibers were investigated. The PI fibers were used to reinforce epoxy resin and excellent interlaminar shear strength (ILSS) of the composites was obtained. The study on the carbonization showed that PI fibers are expected to be good candidates for preparing carbon fibers.

**Keywords:** Polyimide, fibers, composites, carbon

**Introduction:** High-performance polymeric fibers with outstanding mechanical behaviors such as high strength and modulus have undergone significant developments in the past half century for various engineering applications. The driving force of developing these fibers has been of scientific and commercial interests. Aromatic PIs have been well-known as a class of high-performance polymers possessing valuable properties, of which in particular, they exhibit high mechanical properties, outstanding thermal stability, good chemical resistance as well as good electrical and dielectric properties. These combined properties have also made PI fibers as one of the important members in the high-performance polymeric fibers and have many potential applications. Much more attention has been given to prepare PI fibers, some methods have been developed and good results have been obtained.

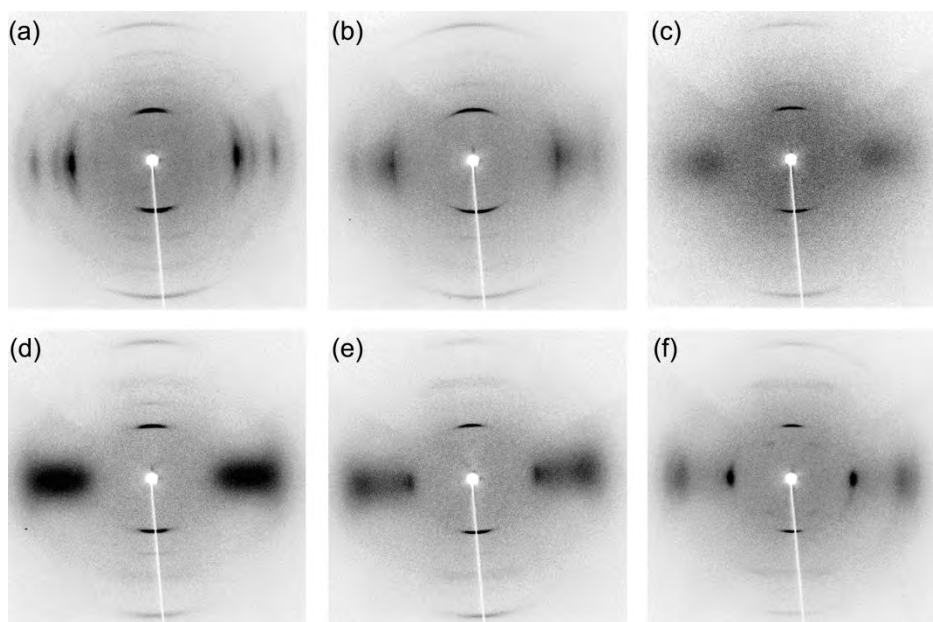
In the present work, PI fibers with high performance and their some applications were investigated and some results were given as follows.

- (1) Co-PI fibers were developed based on a new design of introducing an aromatic heterocyclic diamine monomer, 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone (AAQ) into rigid homopolyimide backbones of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (p-PDA). Effects of the incorporated AAQ moieties on the micro-structure and properties of the prepared fibers were investigated. Fourier transform infrared (FTIR) results indicated that hydrogen bonding is formed between the AAQ and cyclic imide units that effectively strengthens the intermolecular interactions. This has been considered to be the key factor responsible for the significantly enhanced mechanical properties of the co-PI fibers, as shown in table1. Two-dimensional wide angle X-ray diffraction (2D WAXD) (Fig.1) spectra showed that the co-PI fibers are highly oriented with well-ordered 2D structures along both the fiber and transverse directions. The co-PI fibers reached the optimum tensile strength and modulus of 2.8 GPa and 115 GPa, respectively, at

the AAQ/p-PDA molar ratio of 5/5. The fiber also exhibited high thermal stability, with a 5%-weight-loss temperature of 599 °C under N<sub>2</sub> and 564 °C in air.

**Table 1.** The intrinsic viscosities of the synthesized BPDA/(p-PDA/AAQ) co-PAs with different AAQ/p-PDA molar ratios and the mechanical properties of the corresponding co-PI fibers.

co-PI fibers	AAQ: p-PDA (molar ratio)	[ $\eta$ ] /(dL·g <sup>-1</sup> )	Tensile strength/(GPa)	Modulus /(GPa)	Elongation /(%)
co-PI-0	0	1.78	1.2	64.6	2.1
co-PI-1	1:9	1.72	1.3	67.2	2.3
co-PI-2	3:7	2.05	2.7	104.8	3.1
co-PI-3	5:5	1.83	2.8	115.2	3.1
co-PI-4	7:3	1.63	2.7	113.1	2.7
co-PI-5	9:1	1.99	1.9	104.3	2.0



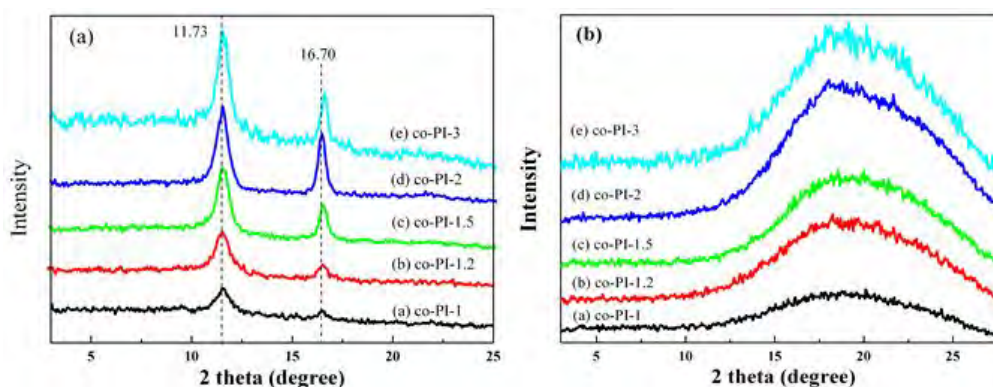
**Fig. 1.** 2D WAXD patterns of (a) co-PI-0, (b) co-PI-1, (c) co-PI-2, (d) co-PI-3, (e) co-PI-4 and (f) co-PI-5

(2) High-performance co-PI fibers were also prepared based on copolymerization of BPDA, p-PDA, 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 4,4'-oxidianiline (ODA) monomers. The fibers were drawn at high temperature (above 400 °C) under tension to different draw ratios (up to 3 times), and the effects of draw ratios on structure and properties of the prepared fibers were investigated. 2D WAXD spectra (Fig.2) showed that the orientation and apparent crystallite size of the co-PI fibers developed with increasing draw ratio. SEM and Atomic force microscopy (AFM) analyses suggested that the heat drawing process roughened the fiber surface due to different deformations of the soft core and tough skin of the co-PI fibers during tension. As shown in Table 2., the co-PI fibers had a

remarkable increase in mechanical properties with elevated draw ratios, which was associated with enhancement of the crystal orientation degree. After extensive drawing, the co-PI fibers reached the optimum tensile strength and modulus of 2.8 GPa and 136 GPa, respectively. The drawn fibers also exhibited a high glass transition temperature.

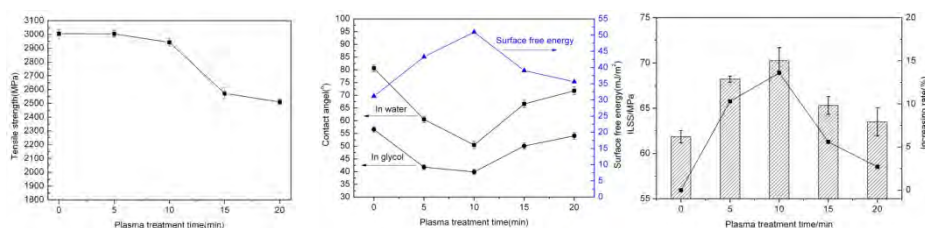
**Table 2.** Mechanical properties of the co-PI fibers with different draw ratios

Co-PI fibers	Draw ratio	Tensile strength	Fixed-length modulus	Elongation
		(MPa)	(GPa)	(%)
co-PI-1	1	481.29	28.85	1.945
co-PI-1.2	1.2	1883.53	91.04	2.32
co-PI-1.5	1.5	2618.21	106.85	2.85
co-PI-2	2	2697.24	134.49	2.415
co-PI-3	3	2794.76	136.36	2.375



**Fig. 2.** Set of WAXD fiber patterns scanning along the (a) meridian and (b) equator directions

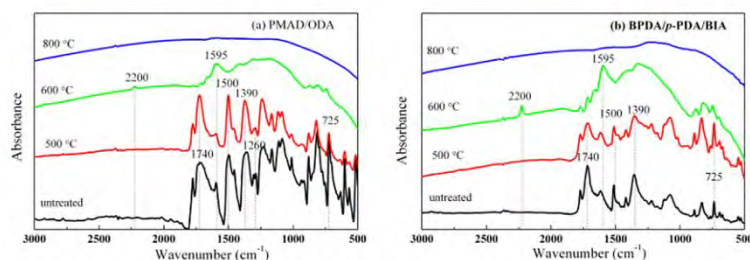
- (3) PI fiber-reinforced epoxy composites were prepared and oxygen plasma was used to enhance the surface behavior of PI fibers. The effects of different plasma treatment time on the mechanical properties, the surface properties of PI fibers and the interfacial adhesion of PI fiber/epoxy composites were investigated. Some results are shown in Fig. 3. The surface chemical composition, surface morphologies, and surface free energy of the fibers were characterized by X-ray photoelectron spectroscopy, scanning electron microscopy, and dynamic contact angle analysis, respectively. The results suggest that some oxygen containing groups were introduced onto the PI fiber surfaces, the surface roughness of fibers was enhanced, the surface free energy of the fibers and the interfacial adhesion of composites were improved by the oxygen plasma treatment. The interlaminar shear strength (ILSS) of the composites increased to 70 MPa when the fibers were treated for 10 min, which shows good interfacial adhesion properties.



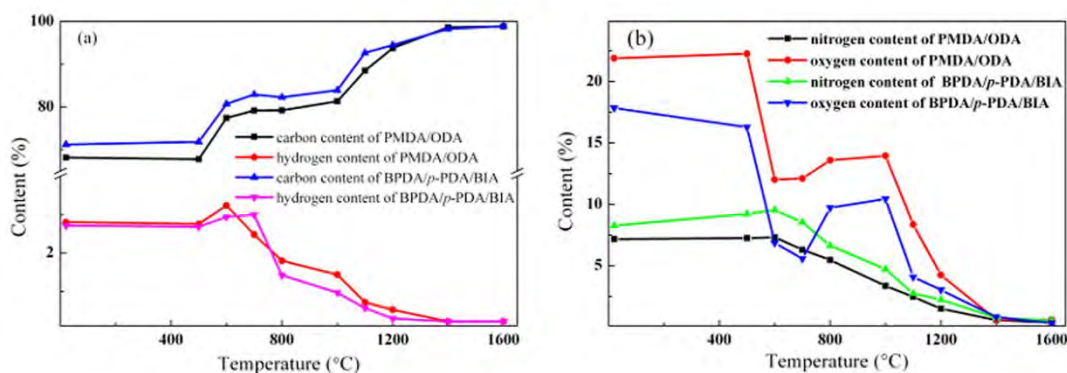
(a) (b) (c)

**Fig. 3.** The effects of plasma treatment time on (a) the tensile strength of PI fibers, (b) the contact angle and the surface free energy of PI fibers, and (c) the interlaminar shear strength (ILSS) of PI/epoxy

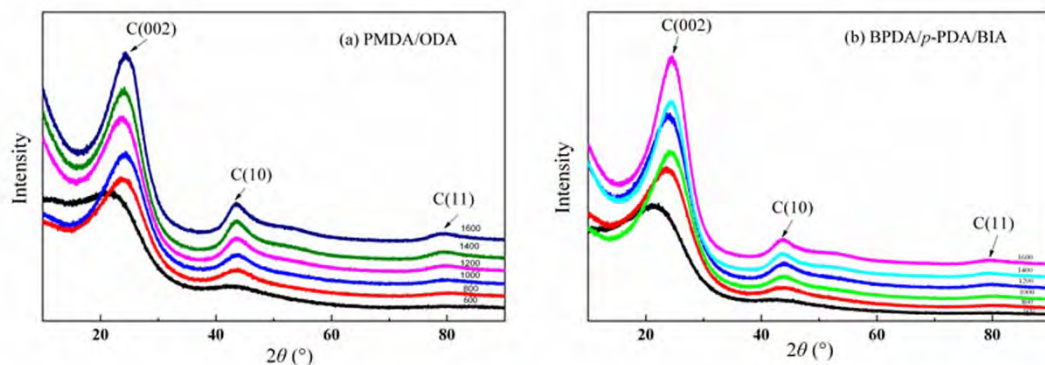
(4) PI-derived carbon fibers were obtained by carbonization with increasing temperature up to 1600 °C under a high-purity nitrogen atmosphere from two PI fibers with different chemical structures, pyromellitic dianhydride (PMDA)/ ODA and BPDA/ *p*-PDA/ BIA. The carbonization mechanism was discussed according to the molecular simulation and thermo gravimetric-infrared radiation (TG-IR) analysis. The physical and chemical variations from PI to carbon fibers during carbonization were traced by FTIR, Elemental analyzer (EA), TG, XRD and Raman analysis, as shown in Fig.4, Fig.5, Fig.6 and Fig.7 respectively. The graphite structure was formed and gradually became ordered by increasing temperature. The degree of graphitization increased and a smooth surface of yield carbon fibers were obtained during carbonization. Moreover, the carbon yield and graphitization degrees strongly depended on the chemical structures of PI fibers. The carbon fiber derived from BPDA/*p*-PDA/BIA demonstrated higher carbon yields, more ordered and more well-defined graphite structures than that derived from PMDA/ODA due to the higher carbon content and lower oxygen content in the molecular structure of BPDA/*p*-PDA/BIA. The results indicate that the PI fiber is a good candidate for the manufacture of carbon fiber.



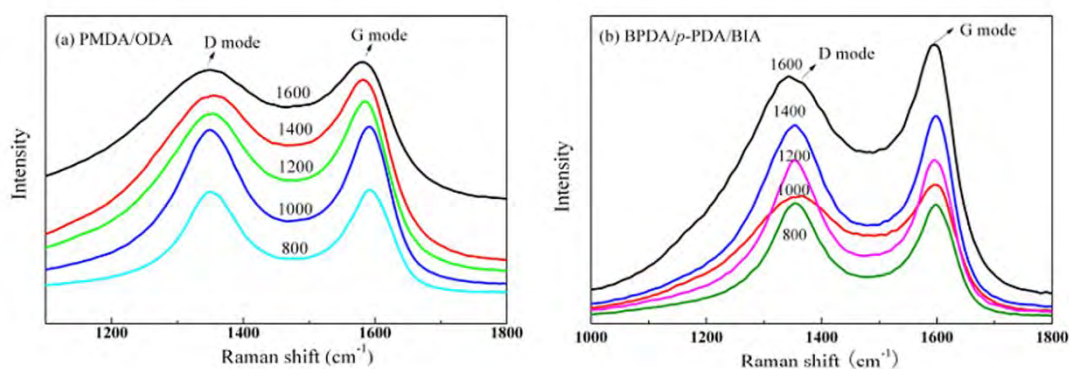
**Fig. 4.** FTIR spectra of fibers derived from PMDA/ODA (a) and BPDA/*p*-PDA/BIA (b) at various temperatures



**Fig. 5.** Changes of atomic contents of fibers derived from PMDA/ODA (a) and BPDA/*p*-PDA/BIA (b) with carbonization temperature



**Fig. 6.** X-ray diffraction curves of the carbon fibers derived from PMDA/ODA (a) and BPDA/*p*-PDA/BIA (b) with temperature



**Fig. 7.** The Raman curves of the PMDA/ODA (a) and BPDA/*p*-PDA/BIA (b)–derived carbon fibers with different carbonization temperatures

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