



# Structure evolutions involved in the carbonization of polyimide fibers with different chemical constitution

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## ABSTRACT

Two polyimide (PI) fibers with different chemical structures, pyromellitic dianhydride (PMDA)/4,4'-oxydianiline (ODA) and 3,3',4,4'-biphenyldianhydride (BPDA)/*p*-phenylenediamine (*p*-PDA)/2-(4-aminophenyl)-5-aminobenzimidazole (BIA) fibers, were prepared by wet-spinning process, and followed by carbonization with increasing temperature up to 1600 °C under a high-purity nitrogen atmosphere, resulting in PI-derived carbon fibers. The chemical structure evolutions were traced by Fourier transform infrared radiation spectrometer (FTIR), Elemental analyzer (EA), Thermogravimetry (TG) and the carbonization mechanism was discussed through the molecular simulation and thermo gravimetric-infrared radiation (TG-IR) analysis. The aggregation structure evolutions were characterized by X-ray diffraction (XRD), Raman and scanning electron microscope (SEM) analyses. The graphite structure was formed and gradually became ordered by increasing temperature, finally resulting in carbon fibers with high carbon contents over 95% and high carbon yields over 50 wt%. Moreover, the carbon yields 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.

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## 1. Introduction

Carbon fibers have been widely used for the reinforcement of composite materials due to their high specific strength and modulus [1,2]. It has been reported that carbon fibers can be derived from several precursors like polyarylonitrile (PAN), viscose rayon and pitch [3]. PAN was considered as the most suitable precursor by far for manufacturing high performance fibers due to the combination of tensile and compressive properties as well as the higher carbon yield [4–6]. Moreover, the mesophase pitch-based carbon fibers exhibit high modulus and high thermal conductivities and, gain wide applications as the high thermal conductive and light-weight material [7–9]. The development of carbon fibers from both pitch and PAN is generally subjected to three processes namely stabilization, carbonization and graphitization under controlled conditions [10,11]. This stabilization is necessary to make the materials into thermally stable forms that are able to withstand the extreme temperatures of carbonization without melting or losing molecular orientation. The quality of the resulting carbon fibers depends strongly on the stabilities of their precursors

[12,13]. An insufficient stability may result in an increase in the portion of pores produced during carbonization [14], and however, excessive stabilization leads to a significant weight loss and a low yield of carbon fibers [15]. This oxidative stabilization step is slow and difficult to control. Therefore, some other materials such as cellulose, phenolformaldehyde (PF), and polybenzothiazole (PBO) have been used as precursors to prepare carbon fibers [16]. Newell et al. [17] reported that the polymeric fibers with rigid-rod structures had a high degree of axial orientation and might facilitate the process of carbonization. Furthermore, the large proportion of aromatic carbon in these precursors is more possible to achieve a high carbon yield. In addition, Newell et al. [18] also found that the high-performance fibers like PBO could be converted to an ordered fiber directly without further stabilization.

As a type of high-performance materials, PIs have attracted a great interest in recent years [19–21]. One of the advantages of aromatic PIs as carbon precursors is the wide range of well-defined molecular structure. Many of PIs show simple carbonization behavior by a sharp contrast to pitches composed from various hydrocarbons in different compositions. PIs have other advantages as carbon precursors, many of them giving high carbon yields and the procedures for carbonization and graphitization being simple. The literature demonstrated that the PI materials could be converted into carbon ones through the carbonization and

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graphitization. Bürger et al. [22] investigated the pyrolysis behavior of different commercially available PI films and found that these PI films could be used as the binder precursor for C/C composites. Inagaki et al. [23,24] reported that the highly crystalline turbostratic graphite with low pore and crack content was prepared from PI films. It is investigated that the carbon films could be derived from commercially available PIs such as Kapton<sup>®</sup>, Upilex<sup>®</sup>, and Novax<sup>®</sup> products [25–29]. These carbon films belong to a type of graphite films with a high degree of graphitization, high electrical conductivity, high value of magnetoresistance, and very low anisotropy ratio [30]. Carbonization of PI films proceeded in two steps. In the first step, an abrupt release of oxygen associated with remarkable weight loss and shrinkage occurred over a rather narrow temperature range of 550–650 °C, and in the second, nitrogen and the remaining oxygen were released gradually above 700 °C. In the second carbonization step, a rapid increase of electrical conductivity and growth of carbon layers were observed. The investigation on the graphitization for PI films indicates that there are three factors for getting graphitizing carbon films as follows: (1) The flat and rigid starting molecules; (2) the high degree of preferred orientation of the molecules along the film surface; (3) the less disturbance of the molecular orientation during the departure of non-carbon atoms [31]. According to these open publications, it is possible to prepare carbon fibers from PIs [32]. However, only one commercial product of PI fibers, P84 manufactured by the Austrian Lenzing AG [33], is available a few years ago. Thermal characterization of P84 fiber suggested that such a fiber is a potential candidate as the precursor to obtain carbon fiber [34,35]. Bhat et al. [36] reported that the carbon fiber with a carbon content of 90 wt% was successfully fabricated from P84 PI fiber by heating at 1000 °C in a nitrogen atmosphere. It is also well known that the structures and properties of carbon materials are highly dependent on the chemical natures of the precursors [37]. It has been reported that the degree of crystallinity of the resulting carbon film depends on the structural organization of the initial PI film [38–40]. Moreover, the molecular structure of the PI fiber is versatile with different monomers. However, seldom references could be found regarding the physical and chemical evolutions from PI to carbon fibers during carbonization and the effects of chemical structures of PI fibers on the carbonization behavior.

The purpose of this study is to intensively understand the conversion mechanism and structural evolutions from PI fibers into the carbon ones during carbonization, and to discover the effect of chemical structures of PIs on the carbon fibers. The PI fibers with different chemical structures were prepared through wet spinning, followed by high-temperature imidization and drawing [41,42]. Then, the carbon fibers were obtained by increasing temperature to 1600 °C. The Fourier transform infrared radiation spectrometer (FTIR), Elemental analyzer (EA), X-ray diffraction (XRD) and Raman etc. combined with molecular simulation were used to analyze the structure evolutions during carbonization.

## 2. Experimental

### 2.1. Materials

Pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyldianhydride (BPDA) were purchased from Beijing Sinmaya Chemicals Co., Ltd., and sublimated under vacuum before use. 4,4'-Oxydianiline (4,4'-ODA), *p*-phenylenediamine (*p*-PDA), 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) were purchased from Beijing Sinmaya Chemicals Co., Ltd. and recrystallized in ethyl acetate prior to use. Dimethylacetamide (DMAc) was purchased from DuPont Co. and used after distillation.

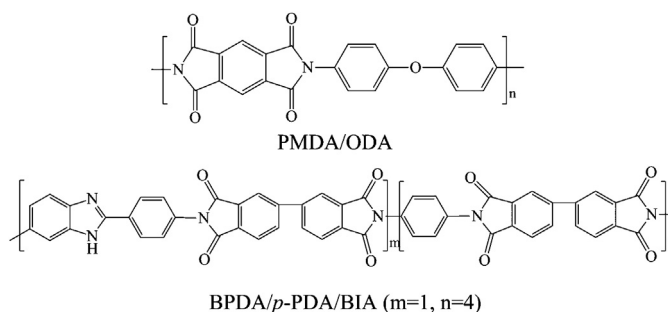


Fig. 1. Chemical structures of the PMDA/ODA and BPDA/*p*-PDA/BIA fibers.

### 2.2. Preparation of polyamic acid (PAA) solutions

Polyamic acid (PAA) precursors with different chemical structures for wet spinning were prepared by copolymerizing the dianhydride and diamine in DMAc solvent. In a typical synthetic process: the PAA solution was synthesized by dissolving the diamine (ODA or mixed *p*-PDA/BIA) in DMAc followed by the addition of equimolar amount of dianhydride (PMDA or BPDA) gradually. The solutions were then stirred at 0 °C for 10 h, forming viscous solutions of PAAs. The viscosities of the resultant polymers were 1.63–2.05 dl/g at a concentration of 15 wt% in DMAc.

### 2.3. Preparation of PI fibers

The PAA solutions for wet spinning were degassed under vacuum at 45 °C to remove the existing air prior to use. First, the PAA fibers were produced by extruding the viscous PAA solutions through the spinneret (1000 holes, 0.07 mm in diameter) using high-pressure nitrogen into the H<sub>2</sub>O coagulation with the concomitant drawing on three sets of spinning rollers with an overall drawing ratio of 2. The PI fibers were then obtained by imidizing the PAA precursors under a drawing ratio of 1.05 continuously through a high-temperature tube oven at 280 °C for 3 min and subsequently, through another high-temperature tube oven at 400 °C for 5 min. The chemical structures of the resulting PMDA/ODA and BPDA/*p*-PDA/BIA fibers are shown in Fig. 1. The PMDA/ODA fiber possesses tensile strength and modulus of 734 MPa and 14.2 GPa, respectively. The BPDA/*p*-PDA/BIA fiber possesses tensile strength and modulus of 3.3 GPa and 130 GPa, respectively.

### 2.4. Carbonization of PI fibers

The prepared PI fibers were fixed on the polished artificial graphite plates and then heated to 500, 600, 800, 1000, 1200, 1400 and 1600 °C in a tubular furnace under high-purity nitrogen atmosphere. For carbonization, all samples were heated at the heating rate of 10 °C/min and held at the final temperature for 1 h.

### 2.5. Characterization

Single fiber tensile testing was performed on an YG001A-1 instrument at an extension rate of 10 mm min<sup>-1</sup>. Changes of chemical structures during carbonization were characterized by Fourier transform infrared radiation spectrometer (FTIR, Nicolet 670, USA), using the samples prepared in a KBr matrix. The outlet of the thermogravimetric (TG 1100 SF, Mettler Toledo) was coupled on-line with an infrared radiation spectrum (IR iS10, Nicolet). The chemical composition variation during carbonization was determined by Elemental analyzer ((EA, Vario EL cube). Thermogravimetric analysis (TGA, TA Q 50) was performed under a nitrogen atmosphere to evaluate the thermal behavior of the polymers and the change in weight. The carbon yields of the fibers were determined

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