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Abstract：   A new method of melt-spun process was developed to prepare PAN precursor fibers using

ionic liquid as the medium of processing. The melt-spun precursor fibers exhibited partially cyclized

structure. For the different structure of melt-spun precursor fibers from solution-spun precursor fibers, it is

necessary to investigate oxidation process of melt-spun precursors. In this paper, the influence of air

circulation on the structure and properties of melt-spun precursor fibers during oxidative process was

investigated by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetry, *etc*. The

results showed that the air circulation almost had no visible effects on the chemical structure of pre-oxidized

fibers. While the crystallinity and the crystal size of pre-oxidized melt-spun fibers increased with the

increase of air circulation. When the air circulation was 6 L/min, pre-oxidized melt-spun fibers had the

maximum density and tensile strength. Meanwhile, the tensile strength of final carbon fiber reached

maximum.

Keyword: Polyacrylonitrile; Pre-oxidized fiber; Oxidative stabilization; Air circulation; Carbon fiber.

1. Introduction

   Carbon fibers have several unique and excellent properties such as low density, very high specific

strength and stiffness, low coefficient of thermal expansion and good fatigue characteristics. They are now

extensively used in resin composite systems and even with metals to yield composite materials of high

specific stiffness, strength, and light weight. These applications range over several diverse fields such as

automotive, sports equipment, aerospace and so on [1]. High performances carbon fibers can be made from

a variety of precursor fibers such as cellulose, pitch, PAN, *etc*. At present, PAN-based carbon fibers occupy

an overwhelming share ($>$90%) of the world total carbon fiber production, mainly because of their relatively well balanced mechanical properties and good handle [2-3]. But high cost of PAN precursor fibers, which accounts for almost 50% of the total cost, limits the potential widespread use of carbon fibers in commercial application in comparison with other structural material like glass fiber and steel. Another high cost for PAN-based carbon fibers production is too low speed of stabilization stage for the cyclization reaction which produces a great heat and can burn out the precursor fibers once the speed is high. Thus, it is necessary to develop a new spinning process or precursor fibers in order to lower the cost of PAN-based carbon fibers. Recently, several research teams have developed some new precursor fibers such as melt-spun PAN precursor fibers, lignin precursor fibers and PAN/lignin precursor fibers. Therein, SGL Carbon (German) attained the biggest achievements because their low cost lignin carbon fibers have been used in the auto industry [4-5].

Solution spinning is used to produce the precursors for commercial PAN-based carbon fibers. Although more costly and more hazardous than melt spinning, solution spinning is necessary because the chains of PAN degrade before they melt [6]. All attempts have failed through melt-spun PAN precursor fibers without an additive. One method of lowering the melting temperature and simultaneously lowering the viscosity of PAN is to form a single phase of melt fusion by a melt additive, such as plasticizer and the PAN copolymer. The plasticizer not only can aid the process, but also hinder the degradation reactions simply by blocking the nitrile groups from reacting with each other. Thus, the melt spinning is realized. Moreover, melt-spun PAN precursor fibers can also avoid the disadvantages of uneven skin-core structure and micropores due to the phase-separation process in the coagulation bath, which can greatly weaken the performance of carbon fibers [7-8].

The manufacture of carbon fibers from PAN-based precursor fibers consists of a low-temperature stabilization followed by a high-temperature carbonization. Although the carbonization conditions have some effects on the properties of final carbon fibers, it is accepted that the initial stabilization step has a more dominant effect on the properties of the product. In this process, precursor fibers are heat-treated at a temperature in the region of 200-300℃, which results in cyclization of the polymer to give rise to a thermally stable structure, often referred to as a ladder polymer [9-10]. The stabilization of PAN precursor fibers is usually conducted in air. The air is a resource of non-pollution and can be easily acquired. During the stabilization stage, it not only can facilitate the cyclization and oxidation reactions, but also take away the waste gas generated by the various reactions, as better mechanical properties and higher carbon yield are thus obtained. Therefore, the air can, to a certain extent, reduce the production cost [5]. Other oxidizing atmospheres such as ozone-enriched air, pure oxygen, sulfur dioxide (SO_2), ammonia/oxygen (NH_3/O_2), bromine/oxygen (Br_2/O_2) and hydrochloric acid/oxygen (HCl/O_2) mixture have been investigated [11]. The

results indicated that these gases facilitated the cyclization and oxidation reactions to shorten the stabilization time. However, these atmospheres can easily corrupt the equipments and pollute the environment. In the past years, investigations are mainly focused on the stabilization mechanism and reactions in the air atmosphere of solution-spun precursor fibers and pay less attention to influence of the air circulation. Although the structure of melt-spun PAN precursor fibers with partially cyclized structure and less micropores is different from solution-spun precursor fibers, the air can further facilitate the cyclization and oxidation reactions, which is necessary for the pre-oxidization of melt-spun PAN precursor fibers. In this paper, our objective is to study the influence of air circulation on the structure and properties of pre-oxidized fibers coming from melt-spun precursor fibers.

2. Experimental

2.1 Materials

2.1.1 Preparation of precursor fibers

The PAN precursors used in this study was experimentally plasticized melt-spun fibers. The ionic liquid [BMIM]Cl was provided by Shanghai Chengjie Chemical Industry Co., Ltd (Shanghai, China). Dried PAN powder and ionic liquids with a weight ratio of 38:62 were mixed using a high-speed mixer. The mixtures were extruded at $180℃\sim200℃$ using a single screw spinning machine which had a spinneret of 36 holes with a diameter of 0.3 mm and length to diameter (L/D) ratio of 3:1. Then the fibers were collected on a spool at a winding speed of 400m/min. The as-spun fibers were drawn in two steps with a total drawing ratio of 4 in water. The ionic liquids were also removed during the drawing process. The properties of the melt-spun PAN precursor fibers were listed in TableⅠ.

Table   Properties of melt-spun PAN precursor fibers

Linear density (dtex)	Density (g/cm^3)	Crystallinity (%)	Orientation		Tensile strength (GPa)	Extension (%)
			Preferred orientation	Sound velocity orientation		
1.75	1.177	48.29	89.10	93.40	0.71	9.34

2.1.2 Preparation of pre-oxidized fibers

Continuous stabilization was carried out in a tubular furnace with gradient temperature between $180℃$ and $280℃$ that was divided into five zones with individual temperature controller for each zone. The temperature profile inside the furnace was determined with thermocouple probes. In order to minimize the relaxation of molecular orientation during stabilization process, the external tension (0.56cN/dtex) was applied. To keep constant external tension of the precursor fibers, weights were placed on the thread-line and the feed speed was adjusted so as to maintain the weight position. The air provided by air compressor was first preheated to $190℃$ and then fed into the furnace paralleling to the fibers. The air circulation was

adjusted by the flow meter. All samples were stabilized for 1 hour.

2.2 Characterization

2.2.1 FTIR spectroscopy

A Nicolet 8700 (USA) FTIR spectrometer was used to collect infrared spectra of pre-oxidized fibers. KBr discs of pre-oxidized melt-spun fibers were prepared by standard method. A measure of the extent of reaction (EOR) was quantified in terms of a parameter similar to those described already, but based on the relative intensities of vibrational bands associated with the PAN and ladder structures, respectively.

A strong absorption band spectrum of original PAN featured at around 2240 cm^{-1} which was assigned to nitrile C≡N stretching. The fully cyclized ladder polymer yielded a spectrum containing a moderately intense band at around 1600 cm^{-1}, due to a vibration of the conjugated C=C/ C=N bonds[12]. For a partially stabilized sample, the EOR of FTIR conversion index may be defined in terms of the intensities of these peaks as

$$EOR = I_{1600} / (I_{1600} + I_{2240}) \qquad (1)$$

Where I_{1600} is the intensity of the conjugated band at around 1600 cm^{-1}, which is associated with the developed structure, and I_{2240} is the nitrile band at around 2240 cm^{-1} belonging to the PAN molecules [13].

2.2.2 X-ray diffraction (XRD) analysis

A Rigaku X-ray diffractometer (D/Max-2550 PC, Rigaku Co., Japan) providing Ni-filtered CuKα radiation was used to measure the crystalline-related properties of pre-oxidized melt-spun fibers and quantify the extent of conversion from PAN precursor fibers to pre-oxidized fibers during the stabilization process. The step-scan method was used to determine the d spacing and stacking size (Lc, stacking height of layer plane). The step-interval was set at 0.02 degree. The d spacing and Lc were calculated by using equation (2) (the Bragg equation) and (3) (the Scherrer equation), respectively.

$$n\lambda = 2d \sin\theta \qquad (2)$$

$$L(hkl)(in \cdots nm \cdots unit) = K\lambda / B\cos\theta \qquad (3)$$

In which λ = 0.154 nm, K is the apparatus constant (=1.0), and B is the half value width in the radian of the X-ray diffraction intensity (I) vs. 2θ curve. We neglected corrections for instrumental broadening in the calculation. The crystallinity was calculated from the areas of the crystalline diffraction peaks and the amorphous zone using Hinrichen's method [14].

While the extent of conversion from PAN precursor fibers to pre-oxidized fibers was defined an "aromatization index", AI, which was determined by the following equation.

$$AI = I_A / (I_A + I_P) \qquad (4)$$

Where I_A is the intensity of a diffraction peak associated with the aromatized structure at 2θ= 25.5°, and I_P

is the equatorial (100) reflection at 2θ=17° due to virgin PAN precursor fibers [13].

2.2.3 Thermal analysis

Gravimetric thermal analysis was carried out using a Netzsch TG209F1 Iris instrument. The samples were heated in nitrogen at 10℃/min from 50℃ to 900℃.

2.2.4 Elemental analysis

Percentage carbon, hydrogen, nitrogen, and oxygen for various samples were determined with a Elmentar elemental analyzer Vario EL Ⅲ (Germany). Elemental content was converted to the number of carbon, hydrogen, nitrogen, and oxygen atoms per repeat unit and reported as atomic ratios per repeat unit. Since stabilized samples were extremely hygroscopic, care was taken to dry the samples thoroughly before subjecting them to elemental analysis.

2.2.5 Physical properties

Density of pre-oxidized melt-spun fibers was measured by the flotation technique. n-Heptane（0.68 g/cm^3）and 1,2-Dibromoethane (2.17 g/cm^3）were mixed in different proportions to form mixtures in the range of 1.11 g/cm^3 to 1.58 g/cm^3. The diameters of all fibers were measured under an Olympus BHT microscope with a closed circuit television camera. Thirty diameters of pre-oxidized fibers were measured for each sample and the average values were calculated.

Mechanical properties of pre-oxidized fibers which were fixed on a paper tag were performed using a XQ-1 computerized mechanical tester from Donghua University. The test employed a 20mm gauge length and 10mm/min speed. A minimum of 30 tests were carried out for each sample to estimate the average tensile strength.

3. Results and discussion

3.1 FTIR analysis

FTIR is a powerful technique to analyze functional groups of fibers. To elucidate the structure of pre-oxidized melt-spun fibers, it was used to collect the infrared spectra of pre-oxidized fibers. As shown in Figure 1, the FTIR spectra of pre-oxidized melt-spun fibers obtained at different air circulation, we found prominent peaks at 2925cm^{-1}, 2240cm^{-1}, 1583cm^{-1}, 1362cm^{-1}, and 805cm^{-1} [15]. The band around 2925cm^{-1} was related to the asymmetric and/or symmetric stretching modes of C-H group. For the band 2240cm^{-1}, it was attributed to stretching vibrations of the nitrile group. The critical band 1583cm^{-1}, which was red shift of 1600cm^{-1} for the instability of conjugated groups, was assigned to the stretching modes of aromatic rings and/or highly conjugated C=O groups. The bending vibration mode of C-H group occurred at 1362cm^{-1}. The band of C=C－H group usually appeared at 805cm^{-1}[16]. With the increase of air circulation, no major differences in the chemical structure of pre-oxidized melt-spun fibers were detected, indicating that the air circulation had almost no influence on the chemical structure of pre-oxidized fibers

within the range of air circulation in this paper.
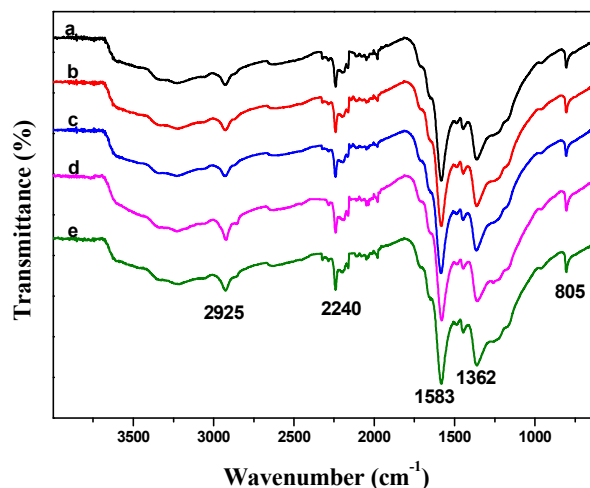
Figure 1 FTIR spectra of pre-oxidized melt-spun fibers obtained at different air circulation

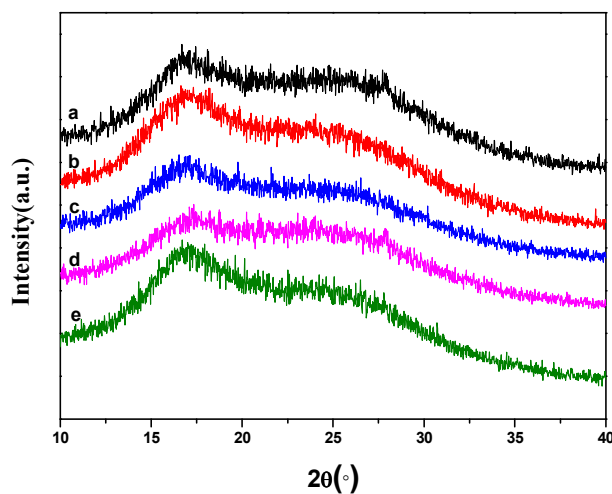(a) 2L/min; (b) 4L/min; (c) 6L/min; (d) 8L/min; (e) 10L/min

The parameter EOR was a useful comparative measure for the extent of cyclization reaction during the stabilization stage of PAN precursor fibers. The values of EOR varied from 0 for no reaction to 1 for complete reaction of the nitrile group. Values of EOR for pre-oxidized melt-spun fibers were shown as a function of the air circulation in Figure 2. It was showed that the air circulation had some effects on the EOR of pre-oxidized melt-spun fibers. When the air circulation was 6 L/min, the EOR reached the maximum value.
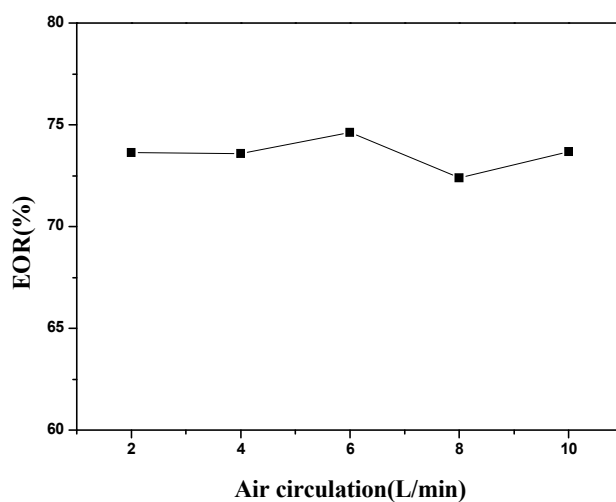
Figure 2 Effects of air circulation on the EOR of pre-oxidized melt-spun fibers

3.2 XRD analysis

PAN is often considered to be a "laterally ordered" polymer, with no c-axis order; this structure is based on the absence of meridional or off-axis XRD reflection. It is generally believed that PAN forms relatively stiff, rod-like molecules due to the intra-molecular dipole repulsions of its nitriles. The diffraction profiles of pre-oxidized melt-spun fibers were given in Figure 3. As evident in Figure 3, we found a broad weak reflection peak at around 2θ=17° corresponding to the (100) plane of the pseudo-hexagonal cell or the (200) plane of the orthorhombic cell [17-18], which appeared in all pre-oxidized fibers. The intensity of this peak increased with air circulation increasing. A new peak started to appear at about 2θ=25.5° corresponding to the (002) plane of the pre-graphitic structure (the ladder polymer) with the increase of the air circulation [19], which was used to measure the extent of stabilization and usually called the aromatization index. The results clearly demonstrated that the crystalline morphology of melt-spun PAN precursor fibers was largely maintained during this stage, although considerable aromatization of crystal lamellae occurred.

Figure 3 XRD patterns of pre-oxidized melt-spun fibers obtained at different air circulation

(a) 2L/min; (b) 4L/min; (c) 6L/min; (d) 8L/min; (e) 10L/min

AI values of pre-oxidized melt-spun fibers based on equation (4) were listed in Table Ⅱ, as well as the crystallinity and lateral crystal size determined from the breadth of the (100) reflection. As shown in Table Ⅱ, it was evident that the crystal size and crystallinity increased with air circulation increasing. The possible reason was that the increase of air circulation gave rise to the formation of skin-core structure of pre-oxidized melt-spun fibers which made the reactions insufficient, leading to the considerable crystalline morphology of melt-spun PAN precursors remained [20]. But the air circulation had little effects on the d_{100} spacing, because the cyclization reaction mainly occurred in the amorphous structure and then gradually transited to the crystal structure in the stabilization stage. We also found that AI values of pre-oxidized melt-spun fibers obtained at different air circulation were around 45%. It was widely accepted that its value

between 45% and 60% was suitable for the resulting carbon fibers [21], therefore, pre-oxidized melt-spun

fibers obtained in present work will be enabled to undergo the subsequent carbonization process.

Table II XRD diffraction data of pre-oxidized melt-spun fibers

Air circulation (L/min)	d_{100} (Å)	Crystal size (nm)	Crystallinity (%)	AI (%)
2	5.3047	1.465	23.83	45.74
4	5.1153	1.527	30.21	44.70
6	5.2108	1.570	32.09	45.32
8	5.1286	1.649	38.13	47.68
10	5.1994	2.091	40.23	43.60

3.3 Thermal analysis

To assess the effects of air circulation on the thermal property of pre-oxidized melt-spun fibers, TGA

was performed in nitrogen at 10℃/min. As shown in Figure 4, the carbon yield of pre-oxidized fibers at 900

℃ was influenced by air circulation. Higher carbon yield was achieved when the air circulation was 6

L/min, once it exceeded 6 L/min, the carbon yield obviously decreased. The possible reason was that the air

circulation had some effects on the cyclization and oxidization reactions especially in crystal region during

the stabilization process.
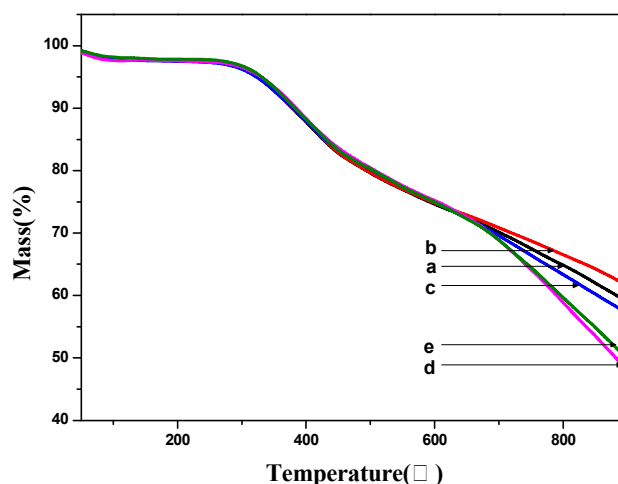
Figure 4 TGA curves of pre-oxidized melt-spun fibers

(a) 2L/min; (b) 4L/min; (c) 6L/min; (d) 8L/min; (e) 10L/min

3.4 Elemental analysis

During thermo-oxidative stabilization of PAN precursor fibers, the linear chain structure was transformed into amorphous structure. The physical and chemical transformations brought about the changes of elemental composition. For optimizing oxidative stabilization conditions of PAN precursor fibers, various measurements had been suggested. One which was more popular was the measurement of oxygen content. A pre-oxidized fiber was considered suitably stabilized when its oxygen content was in the range of 8 to 12% [20]. An oxygen content of more than 12% resulted in the deterioration of pre-oxidized fibers quality which gave low-quality carbon fibers, whereas less than 8% oxygen content resulted in low carbon yield due to excessive weight loss during carbonization.

The effect of air circulation on the oxygen content of pre-oxidized melt-spun fibers was given in Table III. With the increase of air circulation, the difference of oxygen content was very little. The possible reason was that, during stabilization stage, the oxygen acted in two opposite ways: on one hand, it initiated the cyclization reaction by forming activated centers, and on the other hand, it inhibited the reaction by increasing the activation energy. The air circulation was lacking at the initial stage of the stabilization, the oxygen as activated center to initiate reaction was the main effect. While, with the increase of air circulation, more activated centers promoted oxidation reaction resulting in the increase of the activation energy, the second effect to inhibit reaction gradually became more important.

Table III   Element analysis of pre-oxidized melt-spun fibers

| Air circulation (L/min)	Element content（%）				Molecular formula
	C	H	N	O	
2	62.78	4.90	23.34	8.98	$C_{5.23}H_{4.90}N_{1.67}O_{0.56}$
4	63.12	4.95	23.50	8.43	$C_{5.26}H_{4.95}N_{1.68}O_{0.53}$
6	63.03	4.90	23.26	8.81	$C_{5.25}H_{4.90}N_{1.66}O_{0.55}$
8	62.59	4.84	23.16	9.41	$C_{5.22}H_{4.84}N_{1.65}O_{0.59}$
10	64.12	4.87	23.88	7.13	$C_{5.34}H_{4.87}N_{1.71}O_{0.45}$

3.5 Physical properties

Since the stabilization of PAN precursor fibers was usually carried out in air, there were many

complicated reactions occurring during this process. The cyclization reaction with the formation of a six-membered ring structure has been accepted as the main reaction. Dehydrogenation and oxidization reactions occurred at the same time. Due to these reactions, the process of stabilization involved considerable heat and mass transfer which resulted in the most noticeable change of density in the fiber. Thus, the density has been employed in the industry as an indicator of the extent of stabilization.

The density of pre-oxidized melt-spun fibers as a function of air circulation was plotted in Figure 5. Owing to the incorporation of oxygen into pre-oxidized fibers structure and the relatively small amount of vaporizing gases leaving the structure, an increase in density was anticipated in pre-oxidized fibers compared with melt-spun precursor fibers. With the increase of air circulation, the density of pre-oxidized melt-spun fibers had the maximum at 6 L/min. Excessive air circulation might result in the insufficient cyclization and oxidation in the crystal structure. Nowadays, it was observed that the density of carbon fibers decreased with increase in the density of pre-oxidized fibers [22], because more microvoids in carbon fibers formed with increasing density of pre-oxidized fibers, leading to the decrease in the tensile strength of carbon fibers. It was also noted that, to produce carbon fibers of high tensile strength, the density of pre-oxidized fibers lied in the range of 1.34-1.39 g/cm^3 [23].

It was well known that, during thermo-oxidative stabilization of PAN precursor fibers, many physical and chemical transformations occurred, affecting the mechanical properties of pre-oxidized fibers. The tensile strength of pre-oxidized fibers was an indication of the degree of reactions. In other words, the decrease in tensile strength of pre-oxidized fibers was due to the loss of inter-chain cohesive energy as a result of intra- and inter-molecular reactions [14]. The single filament tensile strength of pre-oxidized melt-spun fibers was plotted in Figure 5. The results showed that the tensile strength of pre-oxidized melt-spun fibers began to decrease when the air circulation exceeded 6 L/min, indicating that a suitable air circulation during the stabilization stage was very beneficial to improve the tensile strength of pre-oxidized fibers.
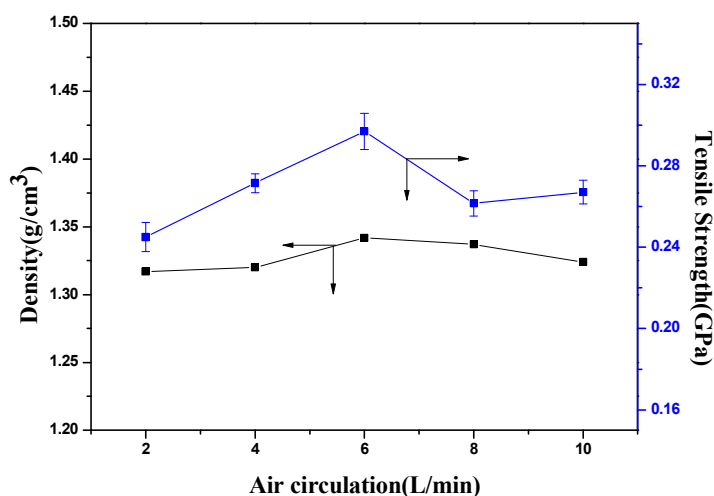
Figure 5 Effects of air circulation on the density and tensile strength of pre-oxidized melt-spun fibers

In order to further confirm the optimal air circulation, static carbonization was performed without external tension. The tensile strength of resulting carbon fibers was given in Figure 6. It was showed that the tensile strength reached the maximal value when the air circulation was 6 L/min. Thus, the air circulation of 6 L/min was reasonable during the stabilization stage.
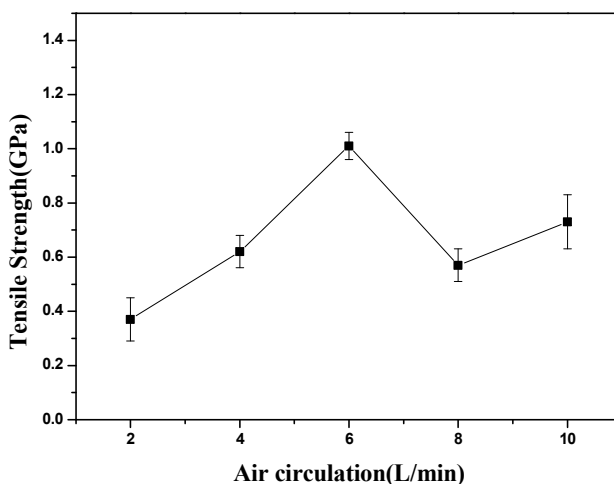
Figure 6 Effects of air circulation on the tensile strength of resulting carbon fiber

4. Conclusions

The purpose of this paper was to investigate the influence of air circulation on the structure and properties of pre-oxidized fibers coming from melt-spun PAN precursors. FTIR revealed that the air circulation almost had no effects on the chemical structure of pre-oxidized melt-spun fibers. However, the crystallinity and crystal size of pre-oxidized fiber gradually increased with air circulation increasing. When

the air circulation exceeded 6 L/min, the carbon yield at 900℃ decreased significantly. The tensile strength of pre-oxidized fibers and the resulting carbon fibers reached the maximum values when the air circulation was 6 L/min. It is therefore believed that the air circulation of 6 L/min was reasonable for the stabilization of melt-spun PAN precursors.

Acknowledgements

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