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# Evaluation of the Fluidized Preoxidation for Producing High Behavior PAN Based Carbon Fiber

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## Summary

In order to resolve the present shortcomings of preoxidation such as preoxidation technology taking too much time, lower production and higher energy consumption for producing high performance carbon fiber, a new type of fluidized preoxidation technology and its effect on the oxidated fibers have been studied in detail. The fluidized fibers have been compared with preoxidized fibers made under conventional technology. It has been found that the technology succeed in the excellence of high efficiency of mass transfer, heat transfer and energy saving. The oxygen content of preoxidized fibers fluidized attained to 11.1%, and the density of 1.42g/cm$^3$ of preoxidized fibers fluidized can be attained. It was founded that the fluidization-treated PAN fibers not only provide an increase in the tensile strength by about 17%, in the elongation at break by about 13%, and in the carbon yield by about 3%, but also provide a decrease in the tensile modulus by about 7%, and in the fineness by about 21%, when compared with the untreated PAN carbon fibers.

## Introduction

It is well known that the properties of the final carbon fibers are determined by a combination of the nature of the precursors and the morphological rearrangements that occur in the stabilization and carbonization step [1-5]. Much interest has been attracted to optimize the thermal stabilization conditions. Rašković and Marinković [6] studied temperature dependence of processes by heating the precursors in air and at a constant rate of 7.5°C/min. Błażewicz [7] analyzed the mechanism of stabilization in $SO_2$ atmosphere. Watt and his co-workers [8] realized the process of streaming to restretch PAN precursors to improve the mechanical properties of the resultant fibers. Blakslee et al [9] utilized the neutron irradiation technique to increase the Young's modulus of carbon fibers. Cooped and Mayer [10]filled boron into carbon fibers, while Bahl [11] and Ko [12-16] respectively utilized various solutions such as CuCl, potassium permanganate ($KMnO_4$) to modify PAN fibers so as to promote the mechanical properties of the resultant carbon fibers. Cagliostro [17] had modified precursors with benzoic acid to improve the tensile strength of carbon fibers.

Nevertheless, most of the previous works were focused on the influence of the modified precursors on the properties of carbon fibers, and many studies were carried out in laboratory conditions using such the modifying mode, which have many differences from the stepwise used in industrial manufacture. However, it is not fully clear which behavior index of PAN fiber has the most influence on the thermal stabilization process. In this study, because the fluidized preoxidation technology has the excellence of high efficiency of mass transfer, heat transfer and energy saving in improving production efficiency of carbon fiber and reducing energy consumption, a new type of fluidized preoxidation technology has been used to the stabilization process for the PAN fibers, and a series of experiments were conducted on a continuous production line. Of course, the combined effect of factors on the properties of oxidized fibers was analyzed in detail, with the aim of generating guidelines to improve the quality of the resultant carbon fibers.

## Experimental

### *Precursors and its stabilization and its carbonization*

A free-radical copolymerization of 99.4 wt% acrylonitirle (AN) and 0.6 wt% ammonium itaconate [$IA(NH_4)_2$] was initiated by azodiisobutyronitrile (AIBN) in dimethylsulfoxide (DMSO). The spinning solution consists of 23% copolymer with an average molecular weight of about $1.4\times10^5$. The fibers extruded under pressure through a capillary tube of 0.06mm diameter with each single tow containing 1000 filaments, were passed through three dimethylsulfoxide (DMSO) coagulating baths, the wet-spun filaments were washed and drawn in three steps in a water bath, followed by lubrication with a heat-resistant amine modified silicone oil. The resultant filaments were dried to be compact, further drawn in steam, set, dried, and wound to obtain PAN precursors. The jet stretch was 0.5 and the overall draw ratio was 14.0. The properties of PAN precursors were listed in Table 1.

The structure graph of fluidization oven is shown in Figure 1, the structure graph of fluidization oven test line is shown in Figure 2.

**Table 1.** Properties of PAN precursors

| Fineness (dtex) | Strength (cN/dtex) | Elongation at break (%) | Density (g/cm$^3$) | Oxygen content (wt %) | Crystallinity (%) | Crystallite size (nm) |
|---|---|---|---|---|---|---|
| 1.05 | 7.36 | 11.80 | 1.17 | 2.30 | 61.43 | 8.25 |

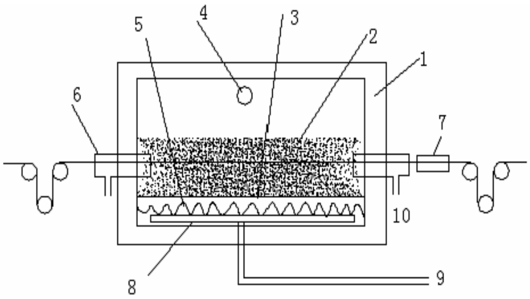


**Figure 1.** The structure graph of fluidization and oxidation oven. 1. furnace body, 2. fluidization particles, 3. plate for arranging the wind, 4. exhaust hole, 5. heating element, 6. sealand cabin, 7. cleaning equipment, 8. arranging-wind supply in advance, 9. air inlet pipe, 10. air-supply port

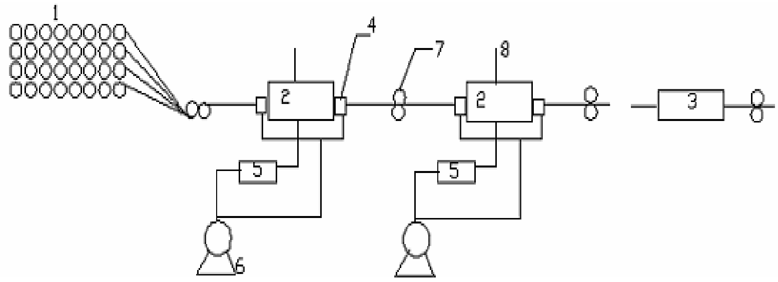


**Figure 2.** The structure graph of fluidization and oxidation oven test line. 1. support for feeding precursors, 2. fluidization and oxidation oven, 3. cleaning equipment, 4. air-tight equipment, 5. hot-blast stove, 6. winding machine, 7. drafting device, 8. heated air circulation apparatus

In this study, the original precursor untreated is designated as P1, the precursor treated with the fluidized particle of active carbon is designated as P2. A self-designed continuous production line, which was reported earlier [2-3], was used for thermal stabilization. Then the fibers were firstly heated in ordinary nitrogen up to about 750°C, and then heated in high—purity nitrogen up to 1400°C to obtain the PAN-based carbon fibers.

### *Measurements and Characterization*

Element analyzer GmbH VarioEL (German) was employed to measure the elements in the PAN precursors and various treated fibers. About 3mg of triturated samples were used. Atomic percentage of carbon, hydrogen and nitrogen were determined by CHN column mode, atomic of percentage oxygen was then determined by difference.

A Rigaku D/MAX-rA X-ray diffractometer (made in Japan) with Ni-filtered CuKα ($\lambda$=0.1541nm) radiation was used to measure the structures of PAN fibers and stabilized fibers at 40Kv and 60mA. The samples were in the disc form prepared by compressing the randomly aligned short fibers. The scanning speed was 6°/ min with the scanning step of 0.02°. The crystallite size ($L_c$) was calculated from the Scherrer formula:

$$L_c = \frac{K\lambda}{B\cos\theta} \qquad (1)$$

Where $\lambda$ is the wavelength of $\mathrm{CuK}_\alpha$ X-ray, $B$ is the full width at half the maximum intensity (FWHM) of the (100) peak at around $2\theta = 17°$, and K is a constant, assigned as 0.89. Aromatization index (AI) was calculated by the following formula:

$$AI = \frac{I_a}{I_a + I_p} \qquad (2)$$

Where $I_a$ is the peak intensity at around $2\theta = 25.5°$, and $I_p$ is the peak intensity at around $2\theta = 17°$.

DSC analysis was carried out using the NETZSCH DSC 404 thermal analyzer (Made in Germany). The samples including the PAN fibers, pre-oxidized fibers and carbon fibers were chopped into short lengths, respectively. The temperature ranges were chosen from 25°C to 1400°C. All measurements were made at a heating rate of 2.5°C/min under ordinary Argon atmosphere with a flow rate of 30cm$^3$/min.

The bulk density of oxidized fibers was determined at 25°C by a density gradient column method in a mixture of n-heptane and carbon tetrachloride with a gradient from 1.00 to 1.60 g/cm$^3$. For the measurement of densities from 1.6 to 2.0 g/cm$^3$, a density gradient column prepared with a mixture of carbon tetrachloride and 1,3-dibromopropane was adopted.

A tow of oxidized fibers was embedded in epoxy resin and solidified before cutting. Transverse ultrathin sections of 0.7 μm in thickness were cut by a Reichert-Jung ultramicrotome. The ultrathin sections were observed in a JXA-840 optical microscope (OM) with a camera.

The fibers were examined with a scanning electron microscope (SEM), Hitachi Model 8010, at an accelerating potential of 25kV. The specimens were coated with Au to get a better image.

The prepared samples of the thermally stabilized fibers were examined by PHILIPS TECNAI20Π-TWIN high-resolution transmission electron microscopy (made in America) at an accelerating voltage of 200kV.

The fineness was measured by a XD-1 fiber fineness machine, all the fibers were measured by a XQ-1 testing machine (both XD-1 and XQ-1 were made in Donghua University, Shanghai, China) at a crosshead speed of 0.5 mm/min with a testing length of 20 mm and load cell of 15 g, in each case, at least 30 sample filaments were tested, and taken for the average of 30 filaments in each experiment.

## Results and discussion

### *Effect of fluidization on the structure of precursors*

After the precursors were fluidized, some fluidization particles adhered to the surface of the precursors. To avoid the adverse influence on the properties of the resultant carbon fibers, it is necessary to clean the surface of the fibers by supersonic wave. The SEM of the longitudinal surface morphology of fibers is shown in Figure 3. As shown in Figure 3(a), there are lots of fluidization particles on the surface of fiber after the fluidization. Because many smaller active carbon particles in size enter into the plow grooves of the precursors, it needs more energy to drive them out of the grooves of the fibers, the surface of fiber (Figure 3(b)) becomes sleek after the dispose of ultrasonic for more 10 minutes, compared with that of the untreated precursors ((Figure 3(c)).

### *Oxygen element contents and aromatization index (AI) value and density of stabilized fibers analysis*

When PAN fibers are heated in the stabilization process, C≡N bonds will be converted into C=N bonds. Oxygen acts in two opposite ways during stabilization process, on the one hand it initiates the formation of activated centers for cyclization, while on the other hand it retards the reactions by increasing the activation energy. Beside that, oxygen is desirable because it results in the formation of some oxygen-containing groups in the backbone of a ladder polymer. So oxygen intake reaction prevails over the volatile gases decomposition during the low temperature stabilization of PAN fibers, it is necessary to investigate the variation of oxygen content in detail. Figure 4 shows the effect of temperature on the oxygen content of fibers stabilized at various

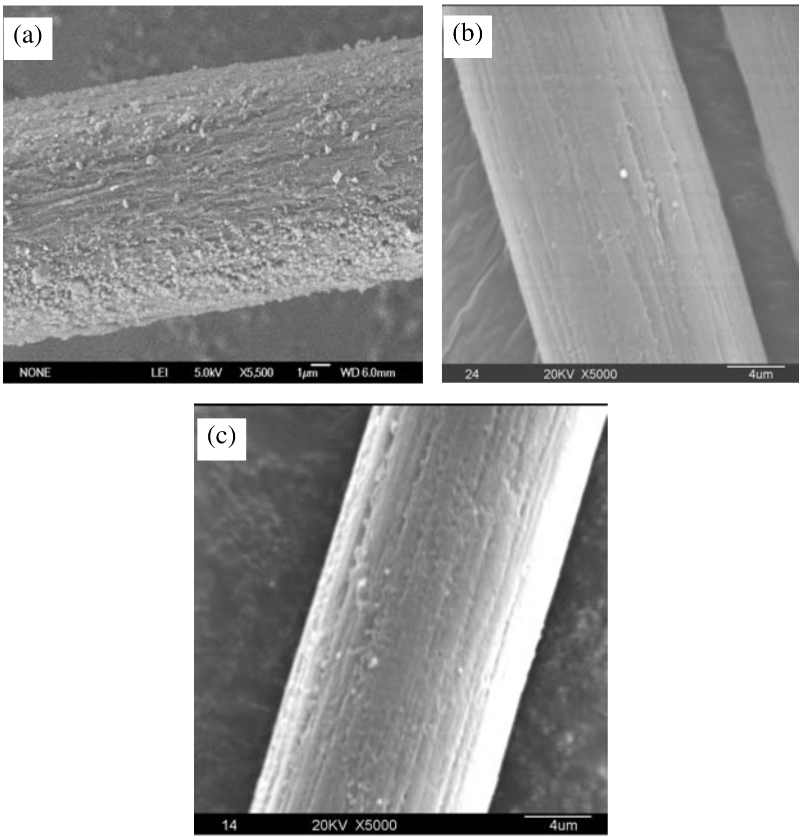


**Figure 3.** SEM of the longitudinal surface morphology of three different fibers. a: P2, the precursor treated with the fluidized particle of active carbon; b: P2, the precursor at the dispose of ultrasonic in 10 minutes after treated with the fluidized particle of active carbon; c: P1, the precursor untreated

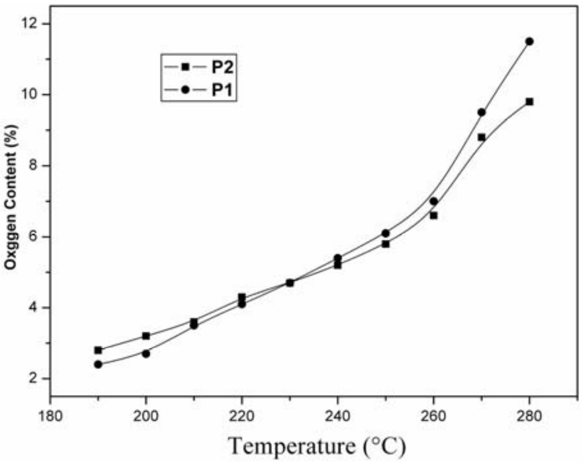


**Figure 4.** Changes of oxygen content as a function of stepwise temperature

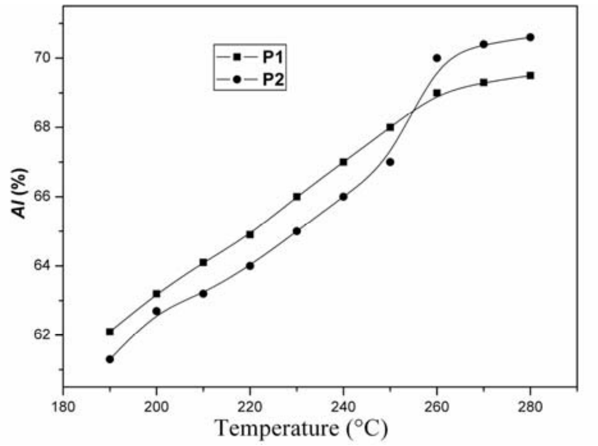


**Figure 5.** *AI* values of PAN fibers as a function of stabilization temperature

stages. It can be seen that the oxygen content increases with the progress of stabilization. Above 260°C, the same trend for two fibers is that the higher temperature promotes the diffusion of oxygen, which causing it to reach a very high value within a rather short time. Above 270°C, the oxygen content of P2 was 9.8%, which is less than that of P1 fiber with 11.8%, and all indicate that the formation of the ladder polymers is slow and steady. This action can minimize the chances of the precursor during excessive rupture and chain scission of the precursor during stabilization process.

It was found that the aromatization index (*AI*) value increases as the temperature increases, AI value should be a criterion for checking the stabilization process and as a method to estimate the amount of the ladder polymer. Figure 5 presents plots of the aromatization index versus the temperature. As shown in figure 5, the *AI* values of two stabilized fibers increase when the temperature is raised. Before the 260°C, the amount of ladder polymer increases rapidly, whereas above 260°C it increases slowly with the temperature increasing. At one time, before 260°C the *AI* value of the stabilized fiber developed from P2 is lower than that of the stabilized fiber developed from the original precursor. But above 260°C the *AI* value of the former is higher than that of the latter.

Density, as an intrinsic behavior, reflects the substantial compactness in the examination of some hyper-molecular structure and texture structure, and higher compactness matches well with larger density value for the same materials. Figure 6 shows the variation of density with the temperature increasing. The density of the stabilized fibers increases as the temperature is raised. In the early stage of about under 260°C, the density of both fibers increases rapidly, and above 260°C it increases less rapidly with the temperature is increasing, whereas the density of the fibers developed from P2 is higher than that of the fibers developed from P1. This is because that the transformation of ladder polymers from AN units initiated in the disordered phase, and then proceeds in the boundary of the ordered phase. When the treatment temperature is high enough to collapse the intermolecular and intramolecular dipolar interactions among the nitrile groups in the ordered phase, the ladder polymers are formed in the ordered phase.

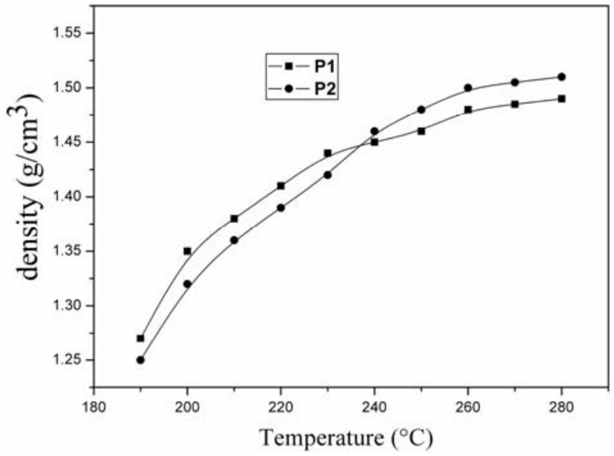


**Figure 6.** *Density* of PAN fibers as a function of stabilization temperature

*Tensile strength of stabilized fibers analysis*

The tensile strength of stabilized fibers as a function of stabilization temperature is shown in Figure 7. As shown in figure 7, the tensile strength of stabilized fibers decreases rapidly at the beginning and then decreases gradually with the temperature increasing. When PAN fiber is heated in the stabilization process, the cohesive energy between the relative chains will drop rapidly, which results in the decrease in strength of the stabilized fiber, and the extent of the decrease in strength will be independent on the percentage conversion of C≡N bonds being converted into C=N bonds. Tensile strength is bigger for the fiber developed from P2 than that of the fiber developed from P1 above 210°C.

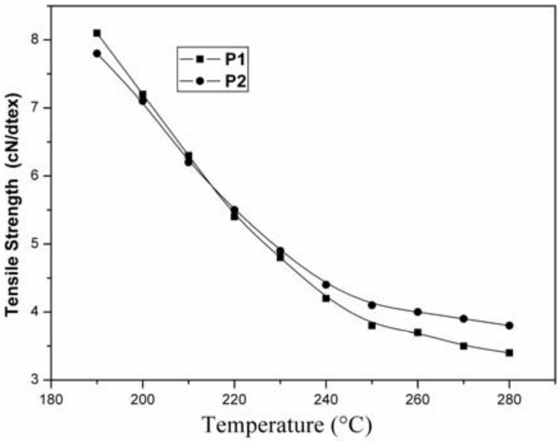


**Figure 7.** Tensile strength of PAN fibers as a function of stabilization temperature

*Morphology of fiber in stabilization*

Transverse ultrathin sections cut from samples P1 and P2 after the process of stabilization were observed by optical microscope as shown in Figure 8. It can be seen that, the diameter of the fiber becomes smaller with the increase of heating temperature due to the shrinkage along radial direction induced by intermolecular cross-linking reaction. Above 260°C, skin-core morphologies of the fiber can be observed. The higher temperature promotes the diffusion of oxygen, which causes to reach a very high value within a rather short time, and the more oxygen atoms concentrate in the skin of the fiber, thereby the skin-core boundary is distinct. However, it can be clearly seen that it is more denser for P2 stabilized fibers fluidized, whereas P1 fibers have some voids which result in a decreased density, meanwhile, oxygen is bonded to the molecular backbone in various groups, and dehydrogenation turns the cyclized structure into an aromatized structure and crosslinking between molecular chains, which result in an increase in the size of the ladder structure. In that case, no skin-core structure is visible in the cross-section of the stabilized fibers, so these could be identified as fully stabilized fibers. Carbon fibers developed from fully stabilized fibers have better mechanical properties than those developed from partially stabilized fibers. The rate of skin to core is 84/100 for P2 fibers, higher than that of 65/100 for P1 fibers.

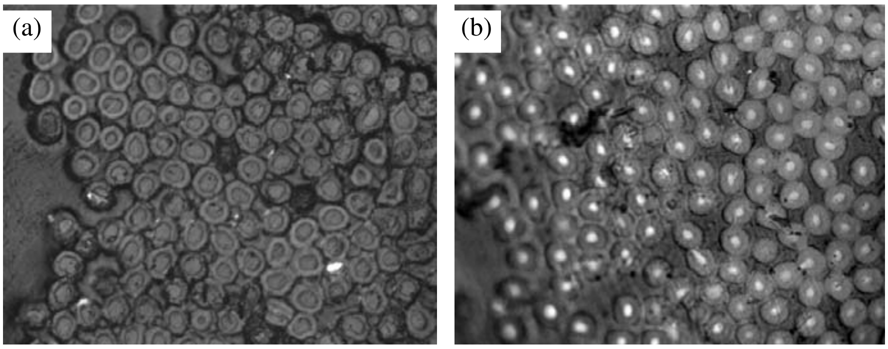


**Figure 8.** Cross-section morphology of (a): the stabilized fibers untreated; (b): the stabilized fibers developed from the fluidized precursors (×400)

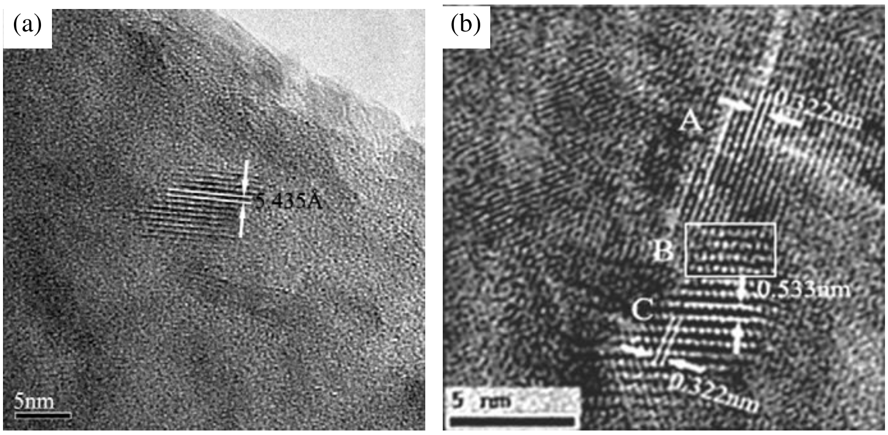


**Figure 9.** Lattice-fringe image of the cross-section of (a) the stabilized PAN fibers developed from the original P1; (b) the stabilized PAN fibers developed from the P2, zone A is the transformed part, zone C is the transforming part, and zone B within the rectangular frame is the transition part

The lattice-fringe image shown in Figure 9 indicates that the structure is made up of the amorphous phase and the ordered phase, and distinct interfaces are visible between the crystals and the matrix. There is more amorphous phase of the stabilized fibers developed from the original P1 than that of from P2. The interplanar spacing for the stabilized fibers developed from P2 is 0.533nm, smaller than 0.5435nm for that developed from the P1, which suggests initiating the structural transformation need small amount of energy. This is the other reason that there are more carbon planes for the stabilized fibers developed from the P2, which results in the better mechanical properties of the resultant carbon fibers.

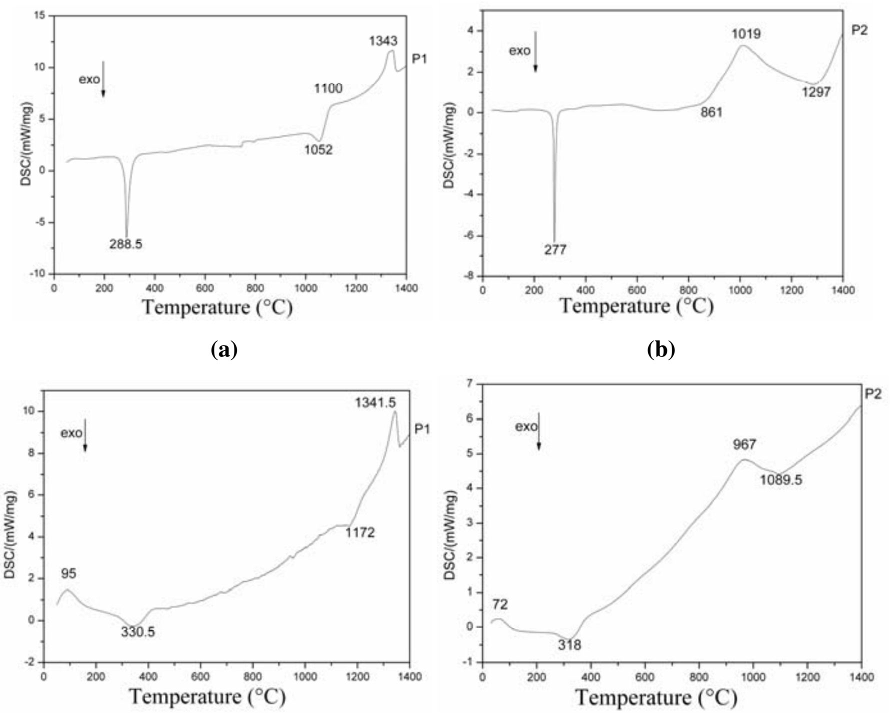
### *DSC analysis of the precursors and the stabilized fibers*

The high-temperature DSC curves obtained upon heating the P1 or P2 precursors, and the fibers from original P1 or P2 precursors after preoxidation investigated in argon with a heating rate of 2.5°C /min and with a flow rate of $30cm^3/min$ are given in Figure 10. It can be seen that there are quiet a few differences between the plots of P1 and P2 precursors. In the range of 25-400°C, the peak value of 288.5°C for P1 precursor is higher than that of 277°C for P2 ones, this is because that the cyclization of PAN fibers during stabilization is always associated with a large exothermic, and the other possible reason is that the fluidization can reduce the required time for stabilization; in the range of 400-1400°C, P1 precursors have a stronger exothermic at 1052°C compared with those of P2 ones at 861°C and at 1297°C, but have a strong endothermic peak at 1343°C which may be an important factor to facilitate dealing with the carbonization process, compared with that of P2 ones at 1019°C. One of possible reason is that this endothermic reaction can alleviate the breakage of a filament due mainly to denitrogenation during the final carbonization process.

In Figure 10 (c) or (d), in the range of about 70-100°C, there is a endothermic peak of P1 stabilized fibers at 95°C compared with that of P2 stabilized fiber at 72°C. This is because when the precursors is heated in air, more functional groups form as a result of the incorporation of oxygen and penetration from the surface to inner part of the fibers with the temperature increasing, and improve the hygroscopicity of stabilized fibers, which results in the release of the water. The stabilized fibers still have an exothermic peak in the range of 200-400°C with a peak for P1 at 330.5°C and for P2 at 318°C, which indicates that the interlinking molecular cyclization of stabilized fibers is not fully accomplished, also this conclusion can be attained by the cross-section morphology of the stabilized fibers after the stabilization was over at 280°C. Moreover, the stabilized fibers after the fluidization treatment start to react at a slow temperature. Hence, a precarbonization process is required to further perform enough intermolecular cyclization, at one time, the precarbonization fibers do not show the same exothermic reactions as that of the corresponding stabilized fibers from identical original PAN precursors.

### *Evaluation of mechanical properties of carbon fibers*

The mechanical properties of carbon fibers developed from treated and untreated are shown in table 2. It is noted that the fluidization-treated PAN fibers provide an increase in the tensile strength by about 17%, in the elongation at break by about 13%, in the carbon yield by about 3%, but also provide a decrease in the tensile modulus by about 7%, in the fineness by about 21%, when compared with the untreated PAN carbon fibers.



**(a)** **(b)**

**(c)** **(d)**

**Figure 10.** The DSC curves in argon of (a) P1 precursors; (b) P2 precursors; (c) Preoxidized fibers developed from P1 after 280°C; (d) Preoxidized fibers developed from P2 after 280°C

**Table 2.** The mechanical properties of carbon fibers developed from treated and untreated

| Sample code | Tensile strength (MPa) | Tensile modulus (MPa) | Fineness (dtex) | Elongation at break (%) | Carbon yield (%) |
|---|---|---|---|---|---|
| P1 | 3.36 | 242 | 1.10 | 1.34 | 94 |
| P2 | 3.92 | 225 | 0.87 | 1.52 | 97 |

## Conclusions

The effect of fluidization of PAN precursors on the properties of the resultant PAN fibers and on the mechanical properties of the based carbon fibers has been investigated, and the main conclusions and advantages can be drawn as follows:

The fluidization could minimize the chances of the precursor during excessive rupture and chain scission of the precursor during stabilization by the characterization of oxygen element.

The stabilized fibers developed from the treated precursors have a higher AI value, a higher density, the higher oxygen content, and the higher tensile strength than those of the stabilized fibers untreated. Judged from the cross-section morphology of the stabilized fibers after stabilized at 280°C, the rate of skin to core of the former is bigger than that of the latter.

It is certain that carrying out the further the fluidization with the precursors is essential in order to obtain high performance carbon fibers, because it can promote the increase of the tensile strength, the increase of elongation at break, the increase of carbon yield, and optimize morphology with as few voids flaws as possible.

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