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Combined Effect of Processing Parameters on Thermal Stabilization of PAN Fibers

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Summary

Thermal stabilization parameters are the key factors in the production of carbon fibers. The combined effect of stepwise temperature, dwell time and stretching on the properties and structures of PAN fibers was studied by elemental analysis, bulk density determination, tension measurement, FTIR and WAXD. It is indicated that the whole process of thermal stabilization can be roughly divided into four stages by three temperatures of 220°C, 240°C and 270°C, of which the increment rate of oxygen content, as well as the bulk density of fibers, is different, while the dwell time has no obvious effect on them until about 240°C. Stretching plays a great role on the tension in fibers at early stabilization stage, while temperature contributes more at later stage. The stretching is also helpful to suppress the growth of crystallite below 220°C, which has not been reported in published documents.

Introduction

Thermal stabilization (also called preoxidation) is a crucial step in the production of polyacrylonitrile (PAN)-based carbon fibers. It has been known that during heat treatment at 180°C-300°C, precursor fibers undergo various chemical and physical changes, such as intramolecular or intermolecular cyclization, generation of volatile gases, diffusion and incorporation of oxygen, coloration and shrinkage of fibers, which depend strongly upon thermal stabilization parameters, e. g. temperature, heating rate, atmosphere, duration time and stretching ratios [1-3]. Improper processing parameters can lead to excessive weight-loss during subsequent carbonization, and inevitably affect the structure as well as the performance of the resultant carbon fibers [4]. Therefore, much interest has been attracted to optimize the thermal stabilization conditions. Rašković and Marinković [5] studied temperature dependence of processes by heating the 3000-PAN-filament tows in air at a constant rate of 7.5°C/min. Wang et al.[6] evaluated the effect of various processing conditions on the mechanical properties of final carbon fibers. Wu et al. [7] studied the influence of tension on the oxidative stabilization process of PAN fibers by heating the precursor fibers from ambient

temperature up to the investigated temperature at 1°C/min. Błażewicz [8] analyzed the mechanism of stabilization in SO_2 atmosphere.

Nevertheless, most of the previous work was focused on the influence of one single parameter on the properties of carbon fibers, and little was concerning the combined effect of the above-mentioned parameters on thermal stabilization reactions. Besides that, many studies were carried out in laboratory conditions using isothermal heating or one-step heating mode, which have many differences from the stepwise heating used in industrial manufacture. In this study, a series of experiments were conducted on a continuous production line. The combined effect of stepwise temperature, dwell time, and stretching ratios on the properties of oxidized fibers was analyzed in detail, aimed at better understanding the mechanism of thermal stabilization of PAN fibers.

Experimental

Precursor fibers

Acrylonitrile/itaconic acid (99.4/0.6) copolymer fibers fabricated in our laboratory were used as precursor fibers in this study. The fibers were wet-spun in dimethylsulfoxide and had 1000 filaments in each single tow. The average titre of filament is 1.03dtex and the tensile strength is about 7.96cN/dtex.

Thermal stabilization

Thermal stabilization experiments were carried out on a continuous carbon fiber production line as shown in Figure 1. The line is composed of two thermal stabilization furnaces, two carbonization furnaces and eight sets of stretching equipments. Each thermal stabilization furnace has five temperature zones separated from each other. In this study, the temperature of the ten zones were set stepwise in the range of 195°C~280°C. Stretching was applied on PAN fibers by controlling the speed differences between the feed rollers and the take-up rollers, and the duration time in each furnace zone was controlled by the average feeding speed of fibers.
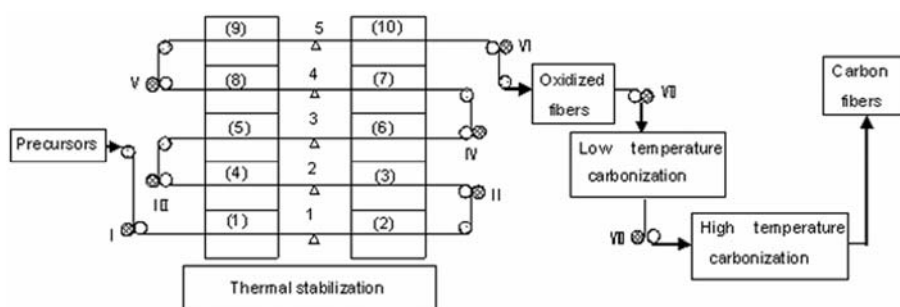

Figure 1. Schematics of carbon fiber production line with (1)~(10) thermal stabilization furnace zones, (I~VIII) stretching rollers, and (1~5) tension testing sites

Measurement and Characterization

Content of elements for various samples was measured on a Vario EL III elemental analyzer. 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. Fourier transform infrared (FTIR) measurement was conducted by loading samples on KBr disks (0.5 mg sample mixing with 200 mg KBr) on a Bruker Vector 22 spectrometer (America). The sample fibers were gotten from the production line after heat-treated at different temperatures. The tension in fibers was examined using a DXF-400 Tension Tester (made in Germany) at five testing sites, marked with "Δ" in Figure 1. A Rigaku D/max-rc X-ray diffractometer with Ni-filtered CuK$_\alpha$ radiation was used to analyze the structure changes during thermal stabilization. The scanning rate is 4°/min with a scanning step of 0.02°. The crystallite size (L_c) was calculated from the Scherrer formula:

$$L_c = \frac{K\lambda}{B\cos\theta} \tag{1}$$

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

$$AI = \frac{I_a}{I_a + I_p} \tag{2}$$

Where I_a is the peak intensity at around 2θ = 25.5˚, and I_p is the peak intensity at around 2θ = 17˚.

Results and discussion

Combined effect of processing parameters on element contents of stabilized fibers

Figure 2 shows the changes of element contents (wt.%) during the thermal stabilization of PAN precursor fibers. It is clear that between the temperature range of 195°C~230°C, there is no observable change in all of the element, while after 230°C the percent of O increases remarkably along with the gradual decrease of C, H and N. The element content of the fibers stabilized at stepwise temperatures is listed in Table 1. From Table 1, it can be calculated that element contents of O, C, H, N in the as-stabilized fibers gain or lose 270.1%, 6.3%, 33.3%, 10.2% respectively compared to those in precursor fibers, indicating that oxygen intake reaction prevails over the volatile gases decomposition during the low temperature stabilization of PAN fibers [9, 10]. Therefore, it is necessary to investigate the variation of oxygen content in detail.

A series of experiments were carried out under different processing parameters. In each experiment, the same PAN fiber was used as precursor, and the step-wise temperature settings are identical, but the dwell time of fibers in each furnace zone is different. Figure 3 shows the combined effect of temperature and time on the oxygen content of fibers stabilized at various stages. It can be seen that the oxygen content increases with the progress of stabilization, and longer dwell time in each furnace zones contributes to higher oxygen content. It should be noted that the slopes of the curves are different at different temperature stages, indicating that the increment rate of oxygen content is not the same with the rising of temperature. Below about 220°C, the oxygen content reveals no obvious increase, and has no apparent distinction under

different processing time. Between 220°C~240°C, it begins to increase with the rising of temperature. When fibers undergo heat treatment above 240°C, the oxygen content increases evidently, and from this temperature, the dwell time starts to have much influence on it. The longer the dwell time is, the higher the increment rate of oxygen content is. Above 270°C, the higher temperature promotes the diffusion of oxygen, causing it rushing to a very high value within a rather short time. Corresponding to the dwell time of 6min and 8min in each furnace zone, the oxygen content of the as-stabilized fibers is 11.32% and 13.98%, respectively. The former oxygen content is within the optimum range of 8~12% [2,11-13], while the latter is excessive, suggesting that the dwell time of 6min in each furnace zone is more suitable for the present settings of temperature to produce high quality carbon fibers.
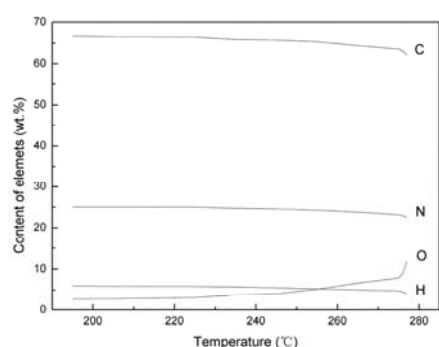

Figure 2. Changes of element contents as a function of stepwise temperature
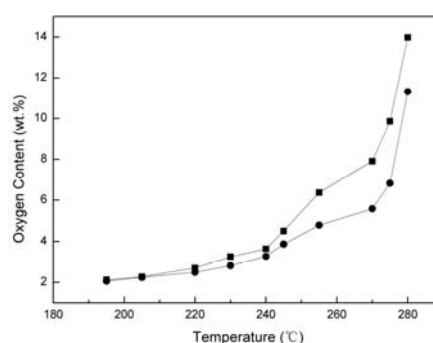

Figure 3. Changes of oxygen content as a function of stepwise temperature and dwell time of 8min (■) and 6min (●) in each furnace zone

Table 1. Element contents of fibers after heat-treated at stepwise temperatures for 6min in each furnace zone

Temperature (°C)	O (%)	C (%)	H (%)	N (%)
25	2.380	66.35	6.193	25.08
195	2.703	66.67	5.978	25.05
205	2.785	66.5	5.92	25.05
220	3.068	66.42	5.844	25.05
230	3.717	65.89	5.735	24.76
240	4.108	65.71	5.541	24.59
245	5.208	65.34	5.295	24.31
255	6.688	64.41	5.039	23.83
265	7.912	63.55	4.829	23.21
270	9.022	63.05	4.488	22.97
275	11.32	62.15	4.130	22.51

Combined effect of processing parameters on bulk density of stabilized fibers

Figure 4 shows the changes of bulk density of fibers stabilized under three conditions. It is obvious that the whole trend of curves in Figure 4 is very similar to that in Figure 3. There are also three turning points at about 220°C, 240°C and 270°C, dividing the thermal stabilization into four different portions with different increment rate. Below

about 220°C, the bulk density has a slight increase because of the rearrangement of chain segments and the initiation of cyclization reactions in amorphous regions [4, 7]. Between 220°C~240°C, the linear polymerization [14] of nitrile takes place, causing the increase of bulk density at a higher rate with the rising of temperature. When the temperature is above 240°C, the bulk density increases rapidly, as a result of intramolecular or intermolecular cyclization as well as mass changes by oxygen incorporation and dehydrogenation. Similar to the change of oxygen content, the bulk density also gets to be influenced greatly by dwell time from 240°C, indicating that oxidative reaction plays a great role in enhancing the bulk density of stabilized fibers especially at higher temperature.

These results can be further confirmed by FTIR analysis. Figure 5 shows the FTIR spectra of PAN precursor fibers and the fibers stabilized at various stages. There appears remarkable decrease in the intensity of nitrile band at 2242cm^{-1} and methylene band at 2940cm^{-1}, 1454cm^{-1}, suggesting the initiation of cyclization at about 205°C. The band at 1600cm^{-1} has not made any significant change until 220°C, but from 235°C it converts to a sharp intense peak because of the formation of –C=C– as a result of dehydrogenation [15], along with the presence and increase of a shoulder-like peak at 1772cm^{-1} (due to cyclic C=O [16]) and the band at 810cm^{-1} (due to C=C–H [17]), indicating the extended conjugation of the cyclized structure and the incorporation of oxygen in cyclized backbone. When the temperature rises to 275°C, the band at 2940cm^{-1}, 2242cm^{-1}, 1454cm^{-1} almost vanishes, giving mainly a broad band extending from 1595cm^{-1} to 1000cm^{-1} because of various modes of vibrations of C=C, C=O, C=N, C–C and their mixed modes [15].
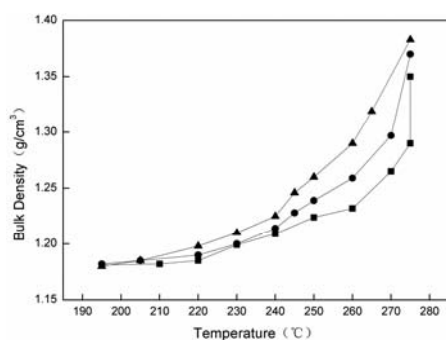

Figure 4. Changes of bulk density as a function of stepwise temperature and dwell time of 6min (■), 8min (●) and 12min (▲)
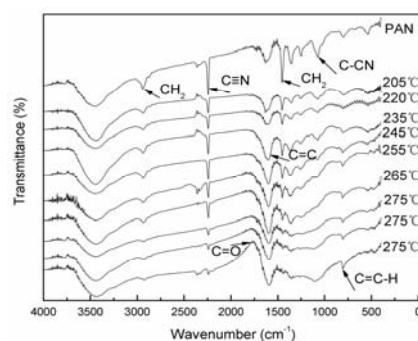
Figure 5. FTIR spectra of PAN fibers and the fibers stabilized at various stages

The results presented so far indicated that the reaction mechanism and the rate of thermal stabilization of PAN fibers depend strongly on the combined effect of dwell time and stepwise temperature. As for the two parameters, stepwise temperature seems very important to the whole thermal stabilization process, while dwell time have obvious effect only at higher temperature. Although cyclization reaction initiates at low-temperature (<220°C), it mainly produces molecular rearrangements in amorphous region, contributing to slight increase in the bulk density, even though longer dwelling time was applied. Between 220°C~240°C, linear polymerization of nitrile takes place extensively while the incorporation of oxygen is little, and dwell

time also has no much effect on it. Above 240°C, extended cyclization of nitrile, conjugation of cyclized structure, incorporation of oxygen and dehydrogenation reactions propagate not only in amorphous region but also in crystalline region due to the enough energy supplied by higher temperature, causing the uprush of oxygen content and bulk density especially over 270°C. These results are consistent with the findings of Rašković and Marinković[5] and can also be testified by the following experiments in this paper.

Combined effect of processing parameters on tension in stabilized fibers

As PAN fibers are heated in air, shrinkage or stretch will occur in fibers because of the disorientation of molecular chains or the propagation of chemical reactions. In order to control this, stretching is often applied to improve the properties of resultant carbon fibers [7, 19-21].Warner et al. [18] proposed that when the glass transition temperature was exceeded, the fiber tension increased due to entropic recovery. And at a later time as stabilization reactions began, the tension increased because of chemical reactions occurring in the fibers. In the present experiment, PAN fibers were allowed to relax during heat-treatment from 180°C to 270°C. The length changes and shrinkage ratio of fibers are shown in Figure 6. It is found that the shrinkage behavior of fibers undergoes four stages, which is a rapid shrinkage stage below 195°C, a decay stage between 195°C to 220°C, then another intense shrinkage stage between 220°C~240°C, and at last a retention stage above 250°C. Accordingly, the free shrinkage of fibers during heat-treatment can be also considered as evidence that there is different reaction mechanism in different temperature range during thermal stabilization of PAN fibers.
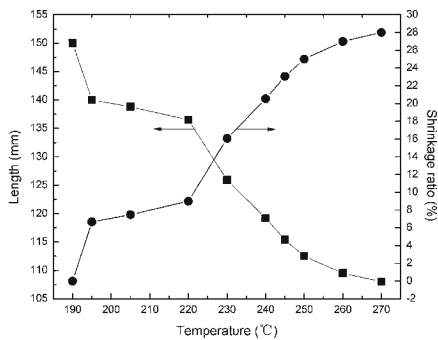

Figure 6. Length changes and shrinkage ratio of fibers as a function of temperature
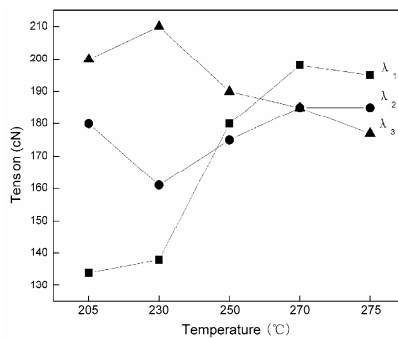

Figure 7. Tension changes in fibers as a function of stretching ratio and temperature

Figure 7 shows the tension in fibers stabilized at various stages under different stretching ratios, which is tabulated in Table 2. It can be seen that temperature and stretching have combined effect on the tension of fibers during thermal stabilization. At the stretching ratio of λ_1, that the fibers are kept constant length, the tension in fibers is relatively low at low temperature stage, but it rises rapidly with the increase of temperature. It is clear that the change of tension in curve λ_1 can be nicely explained by the evolution of shrinkage ratio in Figure 6, which has the same variation trend. At the stretching ratio of λ_2 and λ_3, the tension in fibers is rather high at low

temperature stage because fibers are stretched by large stretching ratio. While with the increase of temperature, the two curves show more obvious decline trend compared with the curve of λ_1. The decline of tension is properly due to two reasons: on the one hand stress may be partly released at high temperature through the volatilization of light molecular weight gases; on the other hand, the diameter of fibers will decrease because of stretching and compact structure. It should be noted that outer stretching contribute greatly on the tension in fibers at early stabilization period, while temperature has more influence on the tension in fibers at later stabilization period. The former is mainly due to the constraint of physical shrinkage, and the latter is mostly attributed to chemical shrinkage caused by cyclization reactions.

Table 2. Stretching ratios during thermal stabilization

Curve legend	Stretching ratio at 205°C	Stretching ratio at 230°C	Stretching ratio at 250°C	Stretching ratio at 270°C	Stretching ratio at 275°C
λ_1	0	0	0	0	0
λ_2	2.0	0	0	0	0
λ_3	3.4	2.6	0	0	0

Combined effect of parameters on crystallite size of stabilized fibers

WAXD has usually been used to study the structure changes during thermal stabilization by many researchers. Some indicated that the intensity at about $2\theta=17°$ and $2\theta=29.5°$ reduced gradually with the progress of stabilization reactions, which resulted in the decrease of crystallinity, crystallite size and chain orientation of fibers [22]. Some proposed that the crystallite size first increased at the beginning of stabilization, and then decreased at higher temperature [23, 24]. In this study, it is found that the changes of crystallite size depend not only on temperature, but also on stretching applied on fibers. Two experiments were carried out using the same precursor fibers and stepwise temperature settings. In the one experiment, the fibers was stretched by 2.5% and 5.7% between 195°C to 230°C, while in the other experiment, no stretching was applied on the fibers. The WAXD results of fiber samples stabilized at various stages in two experiments are shown in Figure 8 and Figure 9.
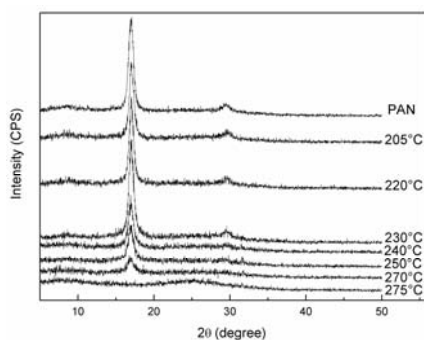

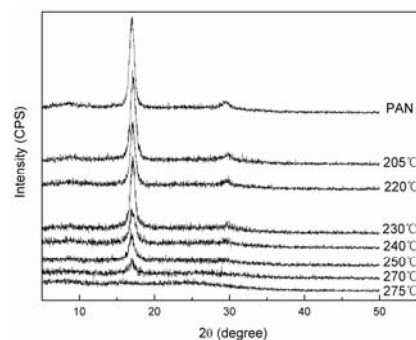**Figure 8**. WAXD patterns of fibers at various stages stabilized without stretching

Figure 9. WAXD patterns of fibers at various stages stabilized under 2.5% and 5.7% stretching

From the two figures, it can be seen that the variation trend of the peak intensity at $2\theta \approx 17°$ are observably different between non-stretched fibers and stretched fibers from room temperature to 220°C. But from 240°C to 275°C both figures show similar weaken trend in the intensity at $2\theta \approx 17°$ and $2\theta \approx 29.5°$. This suggests that stretching have much effect on fiber structure at low temperature but have little effect at high temperature during the thermal stabilization of PAN fibers.

The detailed data including peak intensity, FWHM and crystallite size, calculated from Figure 8 and Figure 9 by Origin software, are tabulated respectively in Table 3 and Table 4. It indicates that if there is no stretching on fibers, the crystallite size increases with the rising of temperature at low temperature. Otherwise, if fibers are stretched, the crystallite size keeps nearly unchanged until the temperature rises to 240°C. Therefore it can be speculated that stretching is helpful to suppress the growth of crystallite, which will bring uniform structure in the stabilized fibers and improve the tensile strength of the resultant carbon fibers.

The aromatic index (AI) of as-stabilized fibers under two conditions was also calculated. As for the fibers treated with stretching and without stretching, AI is 62.7% and 64.9%, respectively, indicating that stretching has little influence on the stabilization degree of PAN fibers.

Table 3. XRD data of fibers at various stages calculated from Figure 8

Temperature (°C)	Intensity at $2\theta \approx 17°$(CPS)	Planar spacing (Å)	FWHM (°)	Crystallite size (nm)
25	2398.8345	5.22	0.7812	10.176
205	1960.6171	5.21	0.6888	11.541
220	2200.6312	5.21	0.6604	12.038
230	2491.1273	5.22	0.7556	10.521
240	1241.6718	5.24	0.7612	10.443
250	911.1162	5.21	0.8853	8.980
270	374.0195	5.25	0.9849	8.070

Table 4. XRD data of fibers at various stages calculated from Figure 9

Temperature (°C)	Intensity at $2\theta \approx 17°$(CPS)	Planar spacing (Å)	FWHM (°)	Crystallite size (nm)
25	2406.8173	5.22	0.7837	10.143
205	2202.9292	5.18	0.8204	9.691
220	1686.4665	5.19	0.7648	10.386
230	1842.2629	5.18	0.7439	10.688
240	689.3733	5.21	0.8907	8.925
250	902.7953	5.23	1.0393	7.648
270	381.6965	5.23	1.0643	7.469

Conclusions

Temperature, dwell time and stretching are the essential processing parameters during thermal stabilization of PAN fibers. Among the three parameters, temperature is the most important one that decides the changes of structure and properties, while stretching and dwell time have much effect at lower temperature and higher

temperature respectively. Through analyzing the changes of element contents, bulk density, tension and crystallite of stabilized fibers, conclusions were drawn as follows:
(1) The increment rate of oxygen content, as well as bulk density of fibers, is different at four stages which are divided by 220°C, 240°C and 270°C during thermal stabilization process. Different dwell time have distinct effect only above 240°C.
(2) The tension in fibers at early stage depends strongly on stretching due to physical shrinkage, while it mainly depends on temperature at later stage due to chemical shrinkage.
(3) Stretching is helpful to suppress the growth of crystallite, so it may be utilized as a feasible method to obtain uniform structure of carbon fibers.

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