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Influence of Precursor Properties on the Thermal Stabilization of Polyacrylonitrile Fibers

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Summary

Thermal stabilization of two kinds of polyacrylonitrile (PAN) fibers was studied by the combination of differential thermal analysis (DTA), thermogravimetric (TG), wide angle X-ray diffraction (WAXD), tension testing, elemental analysis and microscopic examination. The cyclization reaction in fiber P1 occurs at higher temperature with a concentrated heat release, while its incorporation of oxygen is earlier and more rapid than that in fiber P2. Skin-core structure was observed in the as-stabilized fiber of P1, but not in that of P2. During heat treatment, the stress in fiber P1 is about 20MPa higher than that in fiber P2. The results indicate that crystallinity and content of acidic comonomers in PAN fibers are the essential property indices which influence thermal stabilization significantly. Early initiation and sufficient cyclization are important preconditions for obtaining stabilized fibers with uniform microstructure.

Introduction

The manufacture of polyacrylonitrile (PAN)-based carbon fiber usually undergoes three indispensable processes: spinning of precursor fiber, thermal stabilization, and carbonization. It has been popularly accepted that high quality PAN precursor fiber is a significant prerequisite for obtaining carbon fiber with excellent performance [1]. And thermal stabilization is deemed an essential structural transformation process that converts the linear PAN molecular chains to aromatic ladder structure suitable for further carbonization [2, 3]. However, it is not fully clear which property index of PAN fiber has the most influence on the thermal stabilization process. Some researchers have found that “skin-core” structure occur in stabilized fiber due to improper stabilization conditions, such as temperature, time and heating rate [4, 5], but little work has been done to study the effect of precursor properties on the inhomogenous structure. In this study, thermal stabilization of two kinds of PAN fibers was carried out under the same processing conditions. The as-stabilized fibers exhibit differences not only in WAXD patterns, but also in thermal stress, as well as in microstructures. Analyzing these distinctions may provide useful information for fabricating high property PAN precursor fibers that is more favorable for thermal stabilization and for obtaining high strength carbon fibers.

Experimental

Materials

Two kinds of PAN precursor fibers were used in this work. Fiber P1 was wet spun by extruding acrylonitrile/itaconic acid (AN/IA 99/1 wt.%) copolymer solution in dimethylsulfoxide (DMSO) coagulation bath. Fiber P2 was supplied by Asahikasei. Both have 1000 filaments in each single tow. The properties indices were listed in Table 1.

Table 1. Properties of PAN fibers

PAN fibers	Titre (dtex)	Strength (cN/dtex)	Elongation at break (%)	Density (g/cm^3)	Oxygen content (wt.%)	Crystallinity (%)	Crystallite size (nm)
P1	1.05	7.36	9.8	1.177	2.3	63.75	8.5427
P2	1.36	8.15	14.1	1.186	4.2	31.0	10.1265

Thermal stabilization

A self-designed continuous production line, which was reported earlier [6], was used for thermal stabilization. The temperatures in 10 furnace zones piped with flowing and purified hot air were designated in sequence as 195°C, 205°C, 225°C, 235°C, 245°C, 255°C, 265°C, 270°C, 275°C, and 280°C, respectively. The dwell time for the fibers to pass through one furnace zone was about 6min. Proper stretching was imposed on fibers passing through the first four zones by controlling the speed differences. And the fibers passing through the last six zones were kept constant length.

Characterizations

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) was carried out in DTA-40 and TG-40 thermal analyzer (Shimadzu, Japan) at a heating rate of 10°C/min in temperature range from 25 to 500°C in air. The weight of sample fibers was about 3~4mg. The oxygen content in the fibers stabilized at various stages was measured by a Vario EL III elemental analyzer. A DXF-400 Tension Tester was used to measure the tension in fibers on line at five testing points, as shown in previous work [6]. The stress in fibers was calculated using the following formula :

$$\sigma = \frac{F * \rho_v}{\rho_l} \tag{1}$$

where F is the testing tension, σ is the stress, ρ_v and ρ_l are bulk density and linear density of fibers, respectively.

A Rigaku D/max-rc diffractometer with Ni filtered CuK$_\alpha$ radiation (λ =1.5418Å) was utilized to determine the structural parameters of precursor fibers as well as stabilized fibers. Each sample has a weight around 4mg. The scanning rate is 4°/min with a scanning step of 0.02°. The crystallite size of the laterally order domains (L_c) was estimated by Scherrer equation [7]:

$$L_c = \frac{K\lambda}{B\cos\theta} \tag{2}$$

where λ is the wavelength of CuK_α X-ray, B is the full width at half maximum intensity (FWHM) of the peak around $2\theta = 17°$, and K is a constant 0.89. The aromatization index (AI), described by Uchida et al. [8] was calculated by the following formula:

$$AI = \frac{I_a}{I_a + I_p} \tag{3}$$

where I_a is the diffraction intensity of the aromatic structure around $2\theta=25°$, and I_p is the diffraction intensity of the PAN crystal around $2\theta=17°$. The crystallinity (C) of various fibers is measured by Hinrichen's method [9]:

$$C = \frac{A_c}{A_c + A_a} \tag{4}$$

where A_c is the area under the crystalline diffraction peaks and A_a is the area of amorphous zone.

A tow of as-stabilized fibers was embedded straightly in epoxy resin. The cross-section about 1μm in thickness was cut and examined using a JXA-840 optical microscope with a camera.

Results and Discussion

DTA and TG analysis

DTA and TG curves of PAN precursor fibers P1 and P2 are shown in Figure 1 and 2, respectively. In fiber P1, the initiation temperature of DTA exothermic peak is about 200°C, with a peak maximum at 278.4°C. While in fiber P2, the initiation temperature is about 160°C with a peak maximum at 282.5°C. Thus it can be seen that the cyclization of nitrile in P2 starts at a much lower temperature. Two reasons may be accounted for this. One reason is that P2 have more fractions of acidic comonomers, probably like acrylic acid, methacrylic acid or itaconic acid, which have been reported

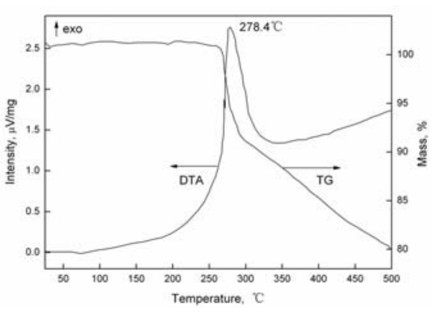

Figure 1. DTA and TG curves of PAN fiber P1

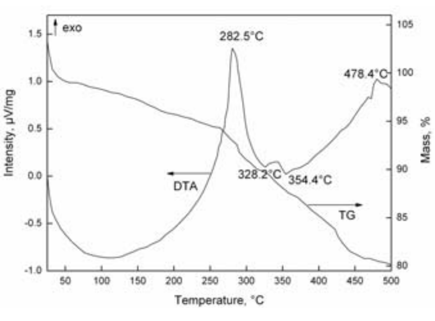

Figure 2. DTA and TG curves of PAN fiber P2

helpful to promote the cyclization reactions in a lot of literature [10-12]. Higher oxygen content in P2 than in P1, as listed in Table 1, can be an evidence for it. Another reason is that P2 has a lower crystallinity. Some researchers have proposed that stabilization reactions occur preferably in the amorphous part of the copolymer because of the less dense structure and more comonomers in it [13-15]. The more amorphous regions in fiber P2 than P1 is likely responsible for the cyclization of nitrile groups at lower temperature. The broader exothermic peak of P2 is a reflection of its lower crystallinity, according to the specificity of exothermic reaction of polyacrylonitrile, reported by Minagawa [16]. As far as the TG curves are concerned, the steep slope in Figure 1 indicates the intense oxidation reactions and dehydrogenation of P1 from 255 to 280°C, while the weight loss of P2 seems more gradually. As a result, the increase of oxygen content is more rapid in P1 than in P2, as shown in Figure 3.

Stress analysis

When PAN precursor fibers were heat treated, shrinkage may happen because of physical and chemical changes. If fibers were constrained to constant length or restrained by stretching force, stress will occur inside fibers. Many studies have been carried out to determine the effect of processing conditions such as temperature, time and stretching ratio on the shrinkage behavior of PAN fibers, and consensus seems to have been established that the fibers undergo physical shrinkage due to disorientation of molecular chains at the initial stage of thermal stabilization, and chemical shrinkage due to cyclization reactions at higher temperature [17, 18]. However, little is known about how the properties of precursor affect the stress in fibers during heat treatment. In the present work, the changes of stress in P1 and P2 during thermal stabilization are studied and the result is shown in Figure 4. It can be seen that the trend of stress change is almost the same for the two kinds of fibers below 245°C, but has a little difference at higher temperature. However, the stress in P1 maintains about 20MPa higher than that in P2 during the whole process, indicating that there is an intrinsic difference in the properties of precursor fibers, which is retained and keeps affecting the stress in stabilization process. As mentioned above, P1 has a much higher crystallinity and lower elongation at break than P2, indicative of a more rigid structure in it. Under heat treatment, the movement and rearrangement of chain segments is restrained by the micro-crystals which act like crosslink points. Therefore the higher

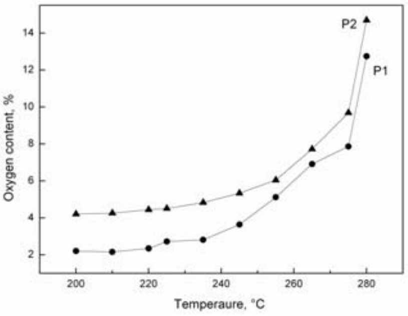

Figure 3. Changes of oxygen content during thermal stabilization of fibers P1 and P2

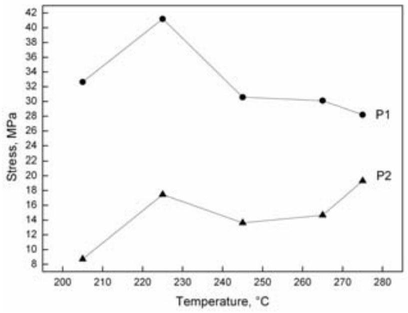

Figure 4. Changes of stress during thermal stabilization of fibers P1 and P2

crystallinity the precursor fiber has, the higher stress in it, especially being stretched at temperature below 230°C. With the temperature increasing, cyclization of nitrile groups takes place, along with the corporation of oxygen and cross-linking reactions. As a result, the stress in P2 increased due to the sufficient aromatization, which will be discussed later, while the stress in P1 shows a declined trend, probably because of the slippage of intermolecular chains caused by over-high stress.

WAXD analysis

In order to determine the structural evolution of the two kinds of fiber during thermal stabilization, WAXD analysis was performed. The diffraction patterns of P1 and P2, as well as their corresponding fibers stabilized after stepwise temperatures, are shown in Figure 5 and Figure 6, respectively. In both figures, the peak around $2\theta=17°$ becomes sharp firstly with their intensity increasing, suggesting an increase in crystallinity and in crystallite size. While above 245°C the peak intensity around $2\theta=17°$ decreases rapidly with rising temperature. It disappears at about 280°C in the stabilized fiber of P1, but at about 265°C in the stabilized fiber of P2. Meanwhile, the center of this peak shifts to a lower degree of about 15°, and a new peak occurs around $2\theta=25°$, indicating the formation of a new structure. Changes of the crystallite size and the crystallinity of the two kinds of fiber during thermal stabilization are shown in Table 2 and Table 3, along with the aromatization index (AI). From these data, it can be seen that the aromatization process of fiber P2 starts earlier than that of fiber P1, as a result, P2 gradually get stabilized with AI value of 57.25%. By contrast, the aromatization of P1 seems more concentrated, and the AI value of its stabilized fibers is 52.73%.

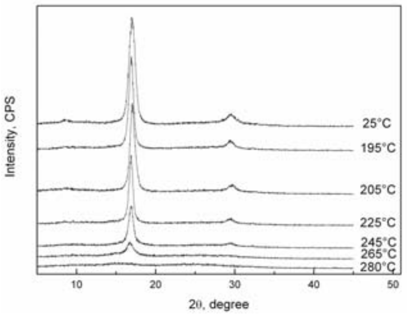

Figure 5. WAXD of PAN fiber P1 and the stabilized fibers at different stages

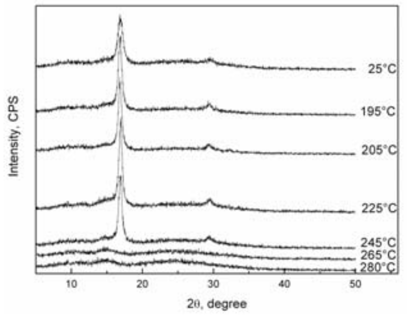

Figure 6. WAXD of PAN fiber P2 and the stabilized fibers at different stages

Microstructure analysis

Based on the analysis stated above, it is known that the cyclization reactions of fiber P2 initiate at very low temperature and proceed rather gradually. By contrast, the cyclization of P1 is late and very intense, mainly because of its high crystallinity and low content of carboxylic acid comonomers. When temperature is above 260°C, the destruction of crystal regions breaks out, leading the molecular chains to an unstable state with high energy. This may supply conditions for the incorporation of oxygen, so the oxygen content of P1 increases rapidly with rising temperature. Once the netlike structure cross-linked by oxygen has been established, the cyclization reactions are restrained. As a result, the AI value of P1 is lower than that of P2. With the oxygen taking in, skin-core structure formed in stabilized fiber of P1, as shown in Figure 7. The dark colored skin is fully stabilized with abundance of oxygen, while the cream colored core is insufficiently cyclized which may not stand high temperature and melt at the late stage of thermal stabilization. However, owing to the sufficient and appropriate cyclization at early stage, the stabilized fiber of P2 has relatively uniform microstructure, as shown in Figure 8.

Table 2. WAXD data related to P1 and the stabilized fibers at different stages

Temperature (°C)	Crystallite size (nm)	Crystallinity (%)	AI (%)
25	8.5427	63.75	\
195	12.1405	58.58	\
205	11.4853	64.90	\
225	13.9142	52.65	\
245	11.0616	45.51	\
265	8.4665	32.77	14.30
280	4.9224	\	52.73

Table 3. WAXD data related to P2 and the stabilized fibers at different stages

Temperature (°C)	Crystallite size (nm)	Crystallinity (%)	AI (%)
25	10.1265	31.0	\
195	13.1500	44.4	\
205	14.4690	49.3	\
225	14.8705	34.7	\
245	14.5025	31.3	6.52
265	6.7989	\	40.47
280	3.5401	\	57.25

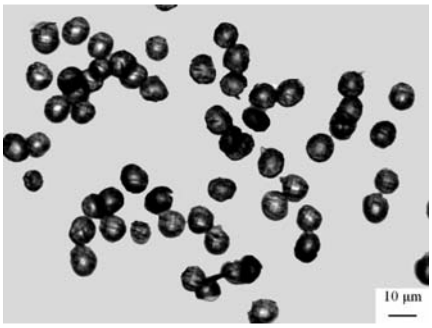

Figure 7. Optical microstructure of the as-stabilized fiber of P1

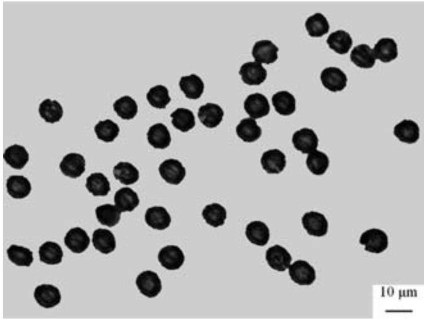

Figure 8. Optical microstructure of the as-stabilized fiber of P2

Conclusions

(1) Crystallinity of PAN fibers is an essential property index that influences thermal stabilization significantly. Excessively high crystallinity leads to high stress in fibers and therefore is unfavorable to cyclization.
(2) High content of acid commoners and relatively low crystallinity can initiate the cyclization of nitrile at lower temperature and make the cyclization milder.
(3) Early initiation and sufficient cyclization is an important precondition for obtaining stabilized fibers with uniform microstructure.

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