

STUDY ON THE CHANGES OF STRESS AND STRAIN DURING THE PROCESS OF THERMAL STABILIZATION OF MODIFIED PAN PRECURSORS

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Introduction

Carbon fibers offer the highest specific strength and modulus of all reinforcing fibers, which are mainly selected as reinforcements in composite materials. In order to meet expanded use in some high-tech sectors, many novel approaches, such as dry-wet spinning [1], steam drawing [2], increasing the molecular weight of precursors polymer [3], modifying the precursors prior to stabilization [4], etc. have been performed to increase the tensile strength of PAN-based carbon fibers. Studies on the physical, mechanical and thermal characteristics of different polyacrylonitrile (PAN) precursors have led to the basic understanding that these characteristics vary markedly for different precursors and the mechanical properties of the resultant carbon fibers also establish a direct correlation with characteristics of the starting precursor. There are, however, some limitations during spinning, which do not permit to produce a precursor with all the desired characteristics combined together [5]. Therefore, post spinning modifications on PAN have been used as useful methods which have resulted in certain improvements in the properties of resulting carbon fibers. Post spinning modification using KMnO_4 has been studied in detail and it is observed that with KMnO_4 treatment of PAN fibers, carbon fibers displays an improvement of 20-40 % in the tensile strength in comparison to the carbon fibers developed from unmodified fibers because of the plasticizing effect, catalytic effect of KMnO_4 [6].

However, it is not fully to understand the relationship between different modification results and the structure and properties of PAN precursor fibers or carbon fibers, especially, the thermal stress and strain changes of modified fibers during the thermal-oxidation stabilization were not reported within our knowledge. This paper is mainly concentrated on comparative studies on the changes of thermal stress and strain of original and modified PAN precursor fibers with different heat treatment temperature.

Experimental

A special grade of Polyacrylonitrile precursor with AN/MA/IA (92.8/1.2/6 wt.%) was selected, which was supplied from Courtaulds Ltd.(The United of Kingdom). The original, that is unmodified, PAN precursor fibers were named as U samples, the modified PAN precursor fibers using 5 wt.% aqueous KMnO_4 solution were name as K samples, and

the modified PAN precursor fibers using 4 wt.% aqueous SnCl₄ solution were designated as S samples.

The thermal-oxidation stabilization of the original and different modified PAN precursor fibers was carried out in a 3-temperature-zone furnace in air with a flow rate of 1 L/min from 50 to °C 350 °C.

The mechanical properties of the various fibers were determined with a YG001-A tensile testing machine at a crosshead speed of 10 mm/min and 20 mm of testing gauge. In each specimen, 50 filaments were tested and their average value was reported here. Density of various fibers was obtained at 25 °C by the use of density gradient column method. FT-IR measurements were made for the KBr disks (0.5 mg sample with 200 mg KBr) for the specimens by the use of a Nicolet750 Magna—IR. Elemental analysis (EA) was carried out with a Carto Erba Azione 1106 model elemental analyzer. A Rigaku X-ray diffractometer, providing Ni-filtered Cu K_α (λ=0.154178 nm) radiation, was used to record the wide-angle diffraction pattern of the original fibers and their modified counterparts. The step-scan method was selected to measure the stacking size (L_c) using the following equation:

$$L_c = K\lambda / B \cos\theta \quad (1)$$

Where, λ is the wavelength of Cu K_α X-ray; B is the width at half maximum intensity of the peak at $2\theta=17^\circ$ and 25° for PAN precursors and carbon fibers, respectively; and K is the apparatus constant (=0.89). The step-interval was set at 0.02°. The preferred orientation of the precursors (001) and the resultant carbon fibers (002) were determined by an X-ray diffractometer with a special fiber-specimen attachment. The width at half-maximum intensity was used as an index of orientation, which may be used to calculate the parallelism of the crystalline part of structure by the following equation:

$$\pi = \frac{180 - H}{180} \times 100\% \quad (2)$$

Where, π is the orientation index, H is the width at half-maximum intensity.

Results and Discussion

The thermal stress change in a fixed-length stabilization process

Figure 1 shows the changes of thermal stress of original and modified PAN precursor fibers with different heat treatment temperature in a fixed-length stabilization process. It has been shown that some easily discernible regimes can be seen. In the first regime, when the heat treatment temperature is up to T_g , the macromolecules are inclined to shrink with the result of thermal motion of chains owing to their conformational changes. When the temperature is up to 150–210 °C, the macromolecules undergo enough stretching because of a great deal of chain motion resulting in slippage among the PAN macromolecules. Hence, the thermal stress of original PAN fibers starts to lower. Contrarily, those modified K or S fibers all the same display various increase trends, the modified K fibers show higher thermal stress than do of S fibers. This is because of much inclusion of oxygen for modified K fibers during their modification process, the

oxygen content of modified K fibers have increased by 71 % compared to original ones, as a result of active reaction site, much included oxygen makes the cyclization and oxidation start earlier at ca. 175 °C, other than 210 °C for original fibers.

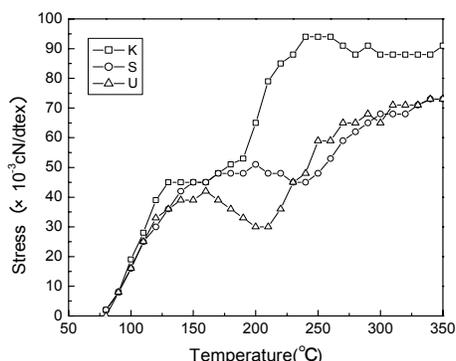


Figure 1. The thermal stress of various fibers in a fixed-length stabilization process

Figure 2 is the FT-IR spectra of U, K, S fibers and their stabilized fibers. The vibrations characteristic of PAN structure are those of CN nitrile groups at ca. 2243-2241 cm^{-1} , the strong band at 1732 cm^{-1} is attributed to the C=O stretching due to the presence of ester or acid. The most prominent structural changes are the decrease in the intensities of C≡N band and the decrease of those for aliphatic C—H ones once the precursor fibers are heated to an adequate elevated temperature, especially for modified K and S fibers.

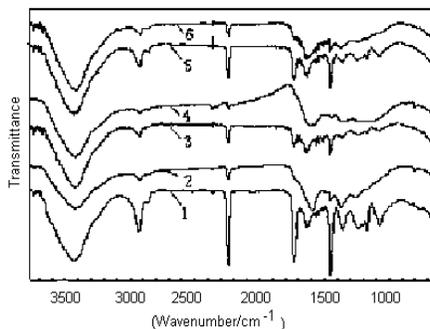


Figure 2. The FT-IR spectra of 1.U,3.K,5.S and their stabilized fibers of 2.U,4.K,6.S after 250 °C

The strain change in a fixed-preload stabilization process

Figure 3 shows the strain changes of U and modified K fibers in a various fixed-preload stabilization process. Both U and K fibers display shrinkage when a preload is 20 CN/dtex, and K fibers have higher shrinkage than original U fibers, which is in agreement with higher thermal stress for K fibers in a fixed-length stabilization process when they undergo constraint heat treatment. When the preload is up to 150 CN/dtex, both U and K fibers display elongation trends, the higher the preload is, the much elongation the fibers do. But, the K fibers always display lower elongation, especially in a higher temperature region. Because the K fibers have been modified for a 5 % stretch, resulting in differences in element composition, later order, crystal size and orientation index from the original U fibers, as has been listed in Table 1. The catalytic effect of KMnO_4 causes lower initiating cyclization temperature and much ladder structure, which results in lower tensile strength, as shown in Table 2.

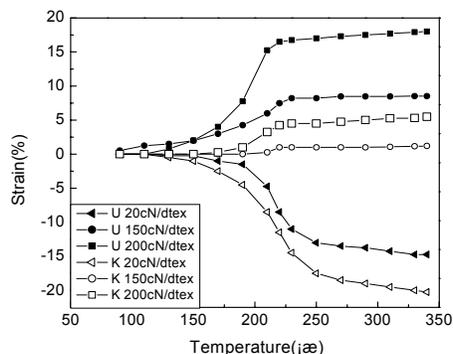


Figure 3. The strain of U and K fibers in different preload vs. temperature

Table 1. The lateral structure index of modified and unmodified fibers

Fiber type	Orientation Index (%)	Crystal Size (nm)
U	82.6	7.31
K	84.7	7.12
Stabilized fibers from U	69.3	3.83
Stabilized fibers from K	74.7	3.45

Table 2. The properties of sample U, K, S and their stabilized fibers after different temperature

Fiber		Diameter (μm)	Density (g/cm^3)	Tensile strength (Gpa)
U	Ambient temp.	12.5	1.1971	0.66
	250 □	11.0	1.2788	0.36
	270 □	10.8	1.3657	0.32
	300 □	10.4	1.4489	0.30
K	Ambient temp.	12.7	1.2128	0.58
	250 □	11.2	1.3343	0.34
	270 □	10.8	1.3891	0.31
	300 □	10.7	1.4737	0.28
S	Ambient temp.	12.9	1.2032	0.62
	250 □	11.5	1.3126	0.35
	270 □	11.3	1.3740	0.31
	300 □	11.1	1.4659	0.30

Effect of preload on the changes of thermal stress

Both U and K fibers undergo thermal stress relaxation when a higher preload ($\geq 100 \times 10^3$ cN/dtex) is imposed at the temperature no more than 90°C , as illustrated in Figure 4 and Figure 5. Modified K fibers undergo higher thermal stress relaxation as compared to original U fibers. When upon heating to 90 - 160°C , thermal stress is increased owing to the physical chains mobility, the original U fibers show faster increase in thermal stress. When the temperature is beyond 130°C , the changes of thermal stress are mainly resulted from chemical reaction, such cyclization and oxidation, the sizes of new formed ladder molecules mainly determined the changes of thermal stress. As a result, the thermal stress is almost independent on the imposed preload when the heat treat temperature is up to 225°C . In the same thermal stress, modified K fibers need lower

preload as compared to original U fibers at identical thermal-oxidation stabilization conditions.

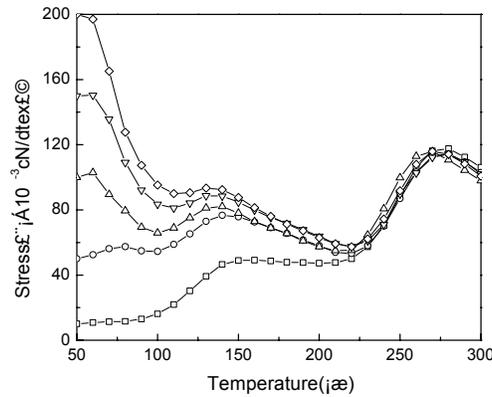


Figure 4. The thermal stress of U fibers in different preload vs. temperature

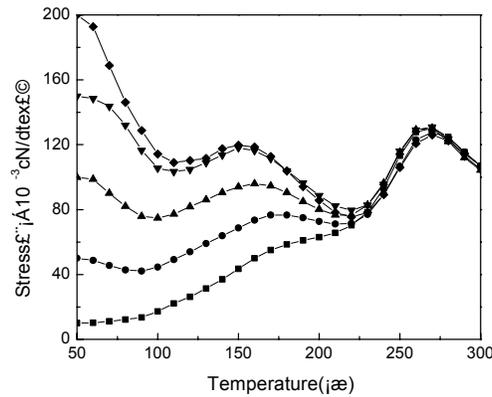


Figure 5. The thermal stress of K fibers in different preload vs. temperature

Conclusions

Compared to the original U fibers, the modified K fibers have increased by 71 % in oxygen content, which makes the chemical-reaction-induced changes of thermal stress start earlier by 20 °C. The modified K fibers display easy shrinkage and difficult stretch, which can be imposed larger preload. In the same thermal stress, modified K fibers need lower preload as compared to original U fibers at identical thermal-oxidation stabilization conditions. The change inflexions of thermal stress and strain take place at similar temperature regions, which means that they can be used as an indication of chemical and physical changes of PAN precursor fibers upon heat treatment.

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