Structural Changes during the Thermal Stabilization of Modified and Original Polyacrylonitrile Precursors

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ABSTRACT: A polyacrylonitrile (PAN) precursor fiber of a special grade for preparing carbon fibers was modified by the impregnation of an aqueous $KMnO_4$ solution. The effects of the modification on the lateral and morphology structure, related to the crystalline properties of both the precursors and preoxidized fibers, such as the orientation index, crystal size, and crystallinity index, were measured by wide-angle X-ray diffraction. For both modified and original PAN fibers, a comparative study of the changes of the elemental content during the process of preoxidation, the relations between the thermal stress and heat-treatment temperature, and the effect of the modification on the skin/core structure of a preoxidized fiber were also introduced by the use of elemental analysis, optical microscopy, and so on. The modification of $KMnO_4$ was demonstrated to increase the density, increase the crystallinity index, increase the preferred orientation index, and decrease the crystal size for a modified precursor fiber and for a preoxidized fiber developed from a modified precursor fiber after a different heat-treatment temperature. $KMnO_4$ also showed a catalytic action, accelerating the rate of preoxidation and reducing the time of thermal stabilization; this improved the homogenization of the cross-section structure and led to an improvement in the tensile strength of 15–20% and an improvement in the elongation of 20–30% in the resulting carbon fibers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2047–2053, 2005

Key words: fibers; modification; stabilization

INTRODUCTION

Carbon fibers offer the highest specific strength and modulus of all reinforcing fibers, which are mainly selected as reinforcements in composite materials, such as carbon-fiber-reinforced resins, metals, and cements and carbon/carbon composites. Hence, they are attractive for many applications ranging from sporting goods to aircraft fields. Although carbon fibers can be produced from a variety of precursors, such as polyacrylonitrile (PAN), mesophase pitch, and rayon, for preparing a high-performance carbon fiber, PAN fiber is presently recognized as the most important and promising precursor, especially as the preferred reinforcement for structural composites because of its excellent specific strength and stiffness and its light weight and lower cost. 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 the precursors polymer,[3] and modifying the precursors before stabilization,[4] have been used to increase the tensile strength of PAN-based carbon fibers.

Now, it is popularly accepted that the quality of high-performance carbon fibers depends mainly on the composition and quality of the precursor fibers. However, the physical[5] and/or chemical modification of a PAN precursor is useful for reducing the stabilization time when a PAN fiber is preoxidized and for improving the properties of resultant carbon fibers. Bahl et al.[6] treated PAN fibers with a CuCl aqueous solution to yield good-quality carbon fibers, which showed an improvement in the tensile strength of about 100% and an improvement in Young's modulus of 50%. With the intention of removing surface defects and attenuating the fiber diameter while simultaneously inducing molecular orientation, Chen and Harrison[7] used a postspinning modification in a 30% dimethylformamide solution of PAN fibers to prepare carbon fibers with a 32% increase in the modulus over untreated fibers. The resultant carbon fibers had remarkably uniform, smooth, and flat fracture surfaces without apparent skin/core morphology. Tsehao and coworker[8,9] prepared high-quality carbon fibers with PAN fibers pretreated with $KMnO_4$ or $CoCl_2$ and discussed the reasons that a modified PAN fiber can reduce the stabilization time and improve the mechan-

ical properties of the resulting carbon fiber. A patent describes the processes for the preparation of carbon fiber from a modified PAN fiber with ammonia and/or low-molecular-weight amines. In our previous reports, the effects of $CoSO_4^{10}$ and $NiSO_4^{11}$ on improving the morphology and properties of a PAN precursor, its preoxidized fiber, and the resultant carbon fibers were also introduced.

From all these previous works, some conclusions can be drawn: The postspinning modification of PAN fibers can result in the reduction of the thermal stabilization time, the optimization of the external and inner structure, and the improvement of the mechanical properties. In this article, we concentrate on a comparative study of PAN fibers modified with $KMnO_4$ and original fibers, the changes in the thermal stress and strain, the supermolecular structure, and the relationship between them and the properties of the fibers.

EXPERIMENTAL

A wet-spun precursor with a comonomer (6 wt % methyl acrylate and 1 wt % itaconic acid) was selected for this study. The fibers, containing 3000 filaments with 1.2 dtex for a single one, were thermally stabilized and carbonized on a bench scale in a laboratory system.

The precursor fibers, modified or original, were passed continuously through a furnace for stabilization, which was divided into three zones with a temperature gradient in the range of 220–300°C. The stabilization atmosphere was clean air. The preoxidized fibers were finally heated in oxygen-free nitrogen up to 1350°C to obtain PAN-based carbon fibers.

The density of various fibers was obtained at 25°C with the density gradient column method. The column consisted of a mixture of n-heptane and carbon tetrachloride with a gradient of 1.00–1.60 g/cm³. Elemental analysis was carried out with a Carlo Erba Azione 1106 model elemental analyzer (Milano, Italy). A fiber sample was first washed with acetone, dried *in vacuo* at 105°C, and then analyzed for carbon, hydrogen, and nitrogen. The oxygen content was determined from the difference between these three. In addition, the K and Mn contents were measured with a Hitachi Z-8000 atomic emission spectrometer (Tokyo, Japan). A Rigaku X-ray diffractometer (Tokyo, Japan), providing Ni-filtered Cu Kα radiation (wavelength = 0.154178 nm), was used to record the wide-angle diffraction patterns of the original fibers and their modified counterparts. The step-scan method was selected to measure the stacking size (L_c) with the following equation:

$$L_c = K\lambda / B \cos \theta$$

where λ is the wavelength of the Cu Kα X-ray; B is the width at the half-maximum intensity of the peak at 2θ values of 17 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 the half-maximum intensity was used as an index of orientation, which could be used to calculate the parallelism of the crystalline part of the structure with the following equation:

$$\pi = \frac{180 - H}{180} \times 100\%$$

where π is the orientation index and H is the width at the half-maximum intensity. The crystallinity index of a PAN fiber was measured by a commonly used method, as indicated in refs. 8 and 9.

The titer and mechanical properties of the PAN precursors, preoxidized fibers, and carbon fibers were measured with a YG-001A tensile-testing machine (Changzhou, China) at a crosshead speed of 10 mm/min with a testing length of 20 mm. In each case, at least 25 sample filaments were tested, and an average of 25 filaments was taken for each experiment. The cross section of the fibers was examined in an X5Z-H optical microscope (Shanghai, China) with a camera.

RESULTS AND DISCUSSION

Effect on the lateral structure

A fiber, as one preferred oriental material, its lateral structure including crystallinity and orientation, has a significant effect on the precursors and the resultant carbon fibers. In a review,[12] Chand pointed out that the crystal size, shape, and their distribution in a carbon fiber might depend on the precursor composition, precursor morphology, and some processing conditions. However, it was not always possible to control the processing parameters of a PAN precursor fiber; even the requirements might be contradictory from the spinning and carbonization points of view. Hence, it is interesting to carry out an approach of postspinning modification, which results in appreciable improvements in the performance of the resultant carbon fibers. As shown in Table I, the modification of PAN fibers with $KMnO_4$ as a modifier is very effective for both the PAN precursors and the thermally stabilized fibers. Even though the modification has not greatly changed the diameter of the PAN precursor fiber or preoxidized fiber, the modification plays a very important role in improving the structural order. Table I shows that for a PAN precursor, there is a

TABLE I
Lateral Structure Parameters of the Fibers

Fiber type	Diameter (μm)	Crystallinity index (%)	Crystal size (nm)	Orientation index (%)
PAN precursors				
Original	12.3	59.4	7.31	82.6
Modified	12.2	60.3	7.12	84.7
Preoxidized fibers[a]				
Original	11.5	39.1	3.83	69.3
Modified	11.5	44.1	3.45	74.7

[a] Obtained after heat treatment at 280°C

decrease in the crystal size from 7.31 to 7.12 nm, an increase in the orientation index from 82.6 to 84.7%, and an increase in the crystallinity index from 59.4 to 60.3%; for a thermally stabilized (preoxidized) fiber, there is a decrease in the crystal size from 3.83 to 3.45 nm, an increase in the orientation index from 69.3 to 74.7%, and an increase in the crystallinity index from 39.1 to 44.1%.

Figure 1 shows the changes in the orientation index of the PAN fibers during the process of thermal treatment. When the temperature is less than 150°C, the linear PAN macromolecules mainly undergo physical changes. In this period, corresponding to the glass-transition region, the chain units undergo thermal motion, and a trend of relaxation shrinkage in the fibers results. The applied stretching stress, however, constrains to some extent the relaxation shrinkage and promotes the evolution of the molecular structure order along the direction of the applied stress. With the elevation of the temperature from 150 to 230°C, corresponding to the initiating temperature of cyclization for a PAN precursor fiber, if the cyclization index is not high enough to fully constrain the shrinkage or

elongation of fibers arising from the rearrangement and regulation of conformation, there is a higher increase in the orientation index with the result of applied stress in the direction of the fiber axis. Moreover, when the heat-treatment temperature is greater than 230°C (i.e., up to 250°C), the orientation index decreases abruptly because of the deep cyclization and thermal stabilization simultaneously combined with the formation of a ladderlike structure and changes in the molecular configuration. In this period, the fibers strongly decline with great shrinkage and cannot sustain higher stretching.

Figure 1 also shows that the orientation index of the modified fibers is different from that of the original fibers. For example, in the initiation regime, the orientation index increases from 84.7 to 88.5% with a net increase of 4.5% for the modified fibers, whereas the orientation index increases from 83.6 to 86.5% only with a net increase of 3.5% for the unmodified (original) fibers. This is because of the catalytic effect[6,8,9] of $KMnO_4$, which penetrates the inner part of the fibers, reduces the interaction forces among the nitrile groups (i.e., reduces the cohesive forces among the macromolecules), facilitates the improvement of the lateral order, and increases the orientation index with an applied stress. Furthermore, all the fibers display a great decrease in the orientation index beyond 230°C. The modified fibers, however, have a lower reduction and keep a higher orientation index than the unmodified (original) fibers; this may be the reason for the mechanical properties of the resultant carbon fibers improving with chemical modification.
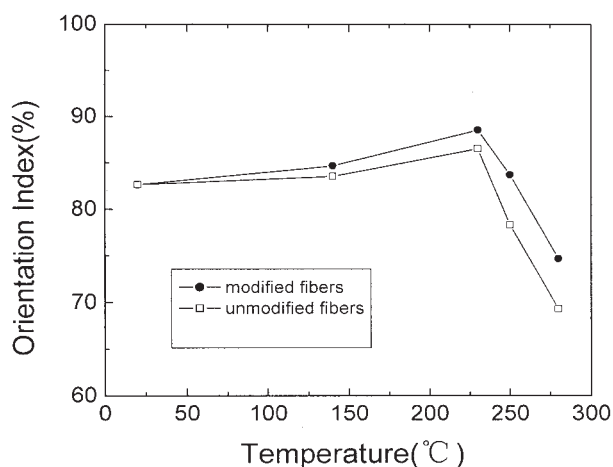
Effect on the thermal stress

Figures 2 and 3 show the changes in the thermal stress for modified and unmodified PAN fibers, respectively, after various temperatures of preoxidation. For both fibers, there are two different stages reflecting the changes in the thermal stress with the increase in the temperature. One is mainly a physical reaction regime below 230°C, and the other is mainly a chemical reaction regime beyond 230°C. In a physical reaction re-
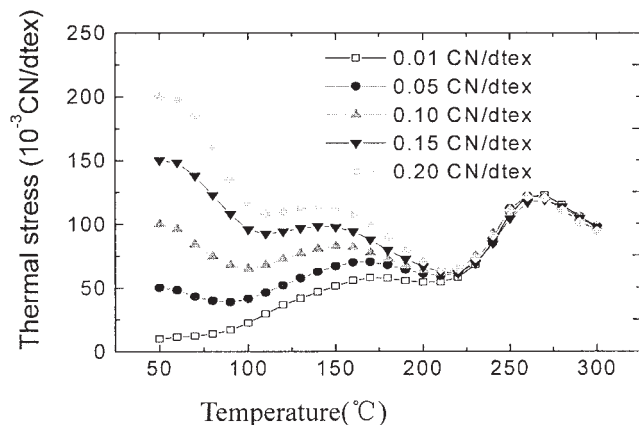

Figure 1 Relationship between the orientation index and heat-treatment temperature for modified fibers and unmodified fibers.

Figure 2 Relationship between the temperature and thermal stress of unmodified fibers under different preloads.

gime, the preload strongly influences the shape of the changing thermal stress. At the start, thermal stress relaxation attributed to inhibited shrinkage occurs under macroscopic restraints, that is, if a higher preload is applied. The higher the preload is, the greater the thermal stress relaxation is. The thermal stress increases as the thermal-treatment temperature increases. However, at 110–150°C, corresponding to the glass-transition temperature of a PAN fiber, both fibers display an increase in the thermal stress due to the maximum changes of entropy. Because the chains start to undergo a thermal motion, partial stretching of the macromolecules results. When the temperature is 150–230°C, the molecules undergo enough stretching because of a great deal of chain motion resulting in slippage among the PAN macromolecules. Hence, the thermal stress of the fibers is lowered. At the end, in a chemical reaction regime, when the temperature is elevated beyond 230°C, the thermal stress increases
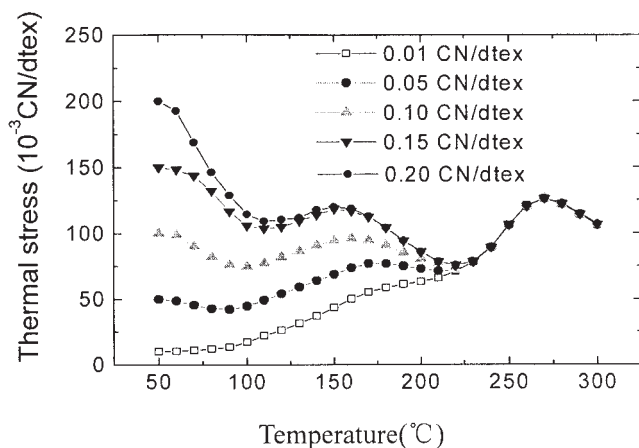

Figure 3 Relationship between the temperature and thermal stress of modified fibers under different preloads.
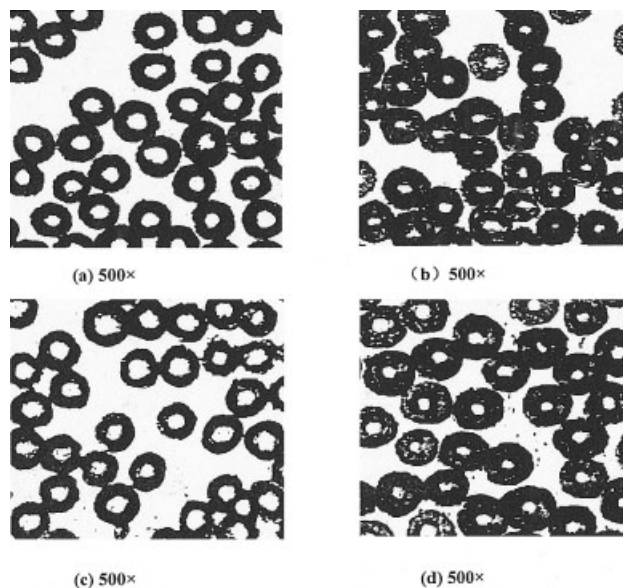

Figure 4 Skin/core morphology of preoxidized fibers developed from modified fibers at (a) 250 and (b) 300°C and of unmodified fibers at (c) 250 and (d) 300°C.

first and then reaches a maximum, following a decrease. The thermal stress mainly results from thermal stabilization and has no apparent differences between the modified and unmodified fibers; it is mainly determined from the conformation size of a backbone molecule.

The modified precursors need less preload to reach the same thermal stress than the unmodified fibers do during the thermal stabilization stage. The temperature at the thermal stress transition peak is lower for modified fibers than that for unmodified fibers in the region of chemical reaction, and this indicates that modified fibers can be fully preoxidized at a lower temperature, demonstrating the catalytic action of $KMnO_4$, which accelerates the rate of preoxidation, reduces the time of thermal stabilization, and initiates the cyclization at a lower temperature. To understand this mechanism, the reason is further interpreted in the next section.

Effect on the skin/core structure and elemental composition

In the thermal stabilization process, a skin/core morphology is formed and developed, which is controlled by the thermal-treatment temperature, reaction time, atmosphere, and other conditions, such as the chemical composition of the fiber. Figure 4 shows the skin/core morphology of preoxidized fibers after different heat-treatment temperatures. The black skin is the far preoxidized part, whereas the core is the not fully preoxidized part because the penetration of oxygen

TABLE II
Some Structural Parameters and Properties of PAN Precursors, Preoxidized Fibers, and Carbon Fibers

| | Precursors | | Preoxidized fibers | | | | | | Carbon fibers | |
| | | | Unmodified | | | Modified | | | | |
	Unmodified	Modified	250°C	270°C	300°C	250°C	270°C	300°C	Unmodified	Modified
Density (g/cm³)	1.1971	1.2128	1.2788	1.3657	1.4489	1.3043	1.3891	1.4737	1.789	1.802
Skin/core ratio (%)	—	—	74.8	81.2	84.4	77.5	83.4	86.6	—	—
Tensile strength (GPa)	0.66	0.58	0.36	0.32	0.30	0.34	0.31	0.28	3.75	4.33
Young's modulus (GPa)	6.53	5.69	4.01	3.37	3.58	2.89	2.77	2.52	203.8	182.7
Elongation (%)	14.6	12.8	11.3	10.5	9.3	10.7	9.8	7.9	1.84	2.37

from the outer skin to the inner core needs some time. As soon as the dense skin is formed, the penetration rate of oxygen is lowered. Because this increases the barrier of oxygen to further diffusion across the layer, this will result in longer times for full stabilization of the fibers and a steeper oxygen gradient, which can negatively affect the structure and properties of the resultant carbon fibers. Although this drawback can be overcome to some degree by an increase in the preoxidation time, it is not adequate for reducing the cost of production, and the skin/core phenomena cannot be fully eliminated. Furthermore, the overpreoxidized skin will cause more defects in the resultant carbon fibers. The modification of PAN precursor fibers with $KMnO_4$ as a modifier improves the skin/core ratio during the thermal-treatment process, as shown in Table II, facilitating the development of homogeneity in comparison with that from unmodified fibers. This is because $KMnO_4$ can promote the cyclization and preoxidation. The decomposition of $KMnO_4$ helps the release of oxygen, as indicated in the following equation:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

Because the modified fibers have higher density, the release of oxygen in the inner part of the fibers will add more active reaction sites, and this results in fast

preoxidation and consolidation in the core part of the fibers.

The impregnation with a $KMnO_4$ aqueous solution causes changes in the elemental composition in the modified fibers in comparison with the unmodified fibers, as shown in Table III. In water, the dissociation of $KMnO_4$ provides K^+ and MnO_4^-, which can diffuse into the fibers. The interaction between K^+ and a fiber is mainly in the nature of physical absorbance, whereas the interaction between MnO_4^- and a fiber can be demonstrated as follows:
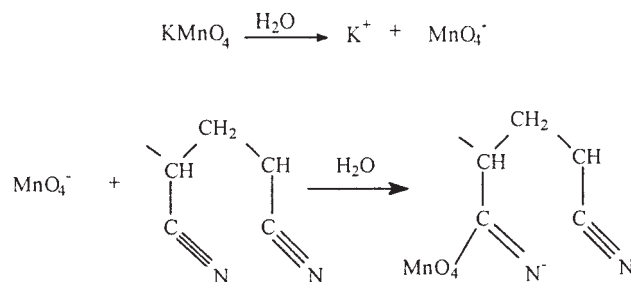
Hence, MnO_4^- has a strong tendency to attack the molecule of a PAN fiber. Because MnO_4^- has a higher density electron cloud, whereas the N atom of a nitrile group in a PAN macromolecule has higher electronegativity, electrophilicity of the C atom attached to the N atom in a nitrile group results. The manganese

TABLE III
Elemental Compositions of the PAN Precursor and Preoxidized Fibers

Fiber type	C (%)	H (%)	N (%)	O (%)	Mn (%)	K (%)	C/N/H/O
Precursor							
Unmodified	66.21	5.76	24.18	3.68	0.0008	0.009	3.00/0.94/3.11/0.13
Modified	64.63	5.58	23.51	6.15	0.336	0.208	3.00/0.94/3.09/0.19
Preoxidized fibers[a]							
Unmodified	63.75	4.18	22.52	8.40	—	—	3.00/0.91/2.34/0.30
Modified	62.98	4.60	22.33	8.62	—	—	3.00/0.91/2.61/0.31

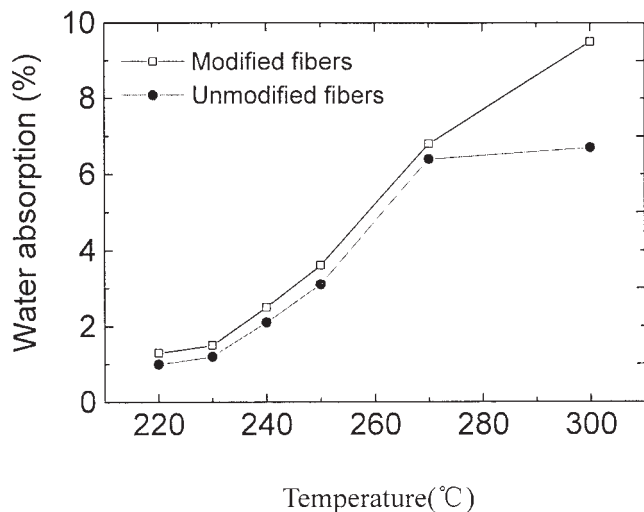[a] Obtained after heat treatment at 280°C

Figure 5 Water absorption of preoxidized fibers developed from unmodified and modified precursors at different temperatures.

metal ion was also found to catalyze the formation of graphitic and turbostratic carbons during the carbonization and graphitization stages in experiments conducted by Tsehao K. et al.[8] They also found that, because of the presence of an uncompleted d-electron shell, manganese forms strong chemical bonds with the π-benzene complex of carbon, and this results in a mixed sandwich compound. The structural model of this sandwich compound was put forward by Ko et al.[8] The modification of PAN fibers with KMnO$_4$ also increases the oxygen content in a PAN fiber, as shown in Table III. The carbon and hydrogen contents in a modified PAN fiber have no significant differences in comparison with those in an unmodified PAN precursor fiber, whereas the oxygen content is 6.15% in a modified PAN fiber and is higher than 3.68% in an unmodified fiber, with an increase of 67%. The oxygen, as an active site, will promote the cyclization and preoxidation rate, and this is in agreement with the fact that the concentrated oxygen in a modified PAN precursor fiber can result in a higher skin/core ratio during the process of thermal stabilization, demonstrating the improvement in the homogeneous structure in the inner and outer parts of preoxidized fibers. As a result, the higher oxygen content in a modified PAN precursor fiber also results in much more oxygen-containing functional groups, such as —C=O and HO—C=O, as shown in an X-ray photoelectron spectroscopy study (not presented here), which will increase the water absorption in a PAN fiber, especially after its preoxidation stage. Figure 5 shows the relationship between the water absorption and the preoxidation temperature. The preoxidized fibers developed from modified precursors display higher wa-

ter absorption than those developed from unmodified original PAN fibers. When the heat-treatment temperature reaches 270–300°C, the water absorption of the preoxidized fibers developed from unmodified fibers increases gradually, and this indicates a maximum content of functional groups, whereas the water absorption of the preoxidized fibers developed from modified fibers still displays a higher increase. This may be the reason that a modified fiber can be fully preoxidized because of the presence of higher oxygen content. The preoxidation of a PAN fiber converts C≡N bonds into C=N groups, a ladder polymer is formed, and the cohesive energy between the relative chains drops appreciably; this accounts for the decrease in the tensile strength of the preoxidized fibers. The conversion percentage of C≡N groups to C=N groups depends on the extent of preoxidation or thermal stabilization. Hence, the preoxidized fibers developed from modified precursors display lower tensile strength than the unmodified fibers after different temperatures, even for a modified precursor fiber because of the presence of a significant number of C=N groups arising from the attack of KMnO$_4$. Therefore, the preoxidized fibers developed from modified precursors have more ladder polymers, a higher oxygen content, and a higher density (see Table II) than those from unmodified fibers; it may be reasonable to assume that the strength of the resultant carbon fibers developed from modified fibers is greater than that developed from unmodified fibers. In fact, as shown in Table II, the carbon fibers developed from modified PAN fibers show an improvement in the tensile strength of 15–20% and an improvement in the elongation of 20–30% but a decrease in Young's modulus of about 10%.

CONCLUSIONS

The modification of PAN precursors with potassium manganate as a modifier improves the desirable properties and structures of fibers, varying from precursor fibers to preoxidized fibers, even resultant carbon fibers. The modification of KMnO$_4$ can increase the density, increase the crystallinity index, increase the preferred orientation index, and decrease the crystal size for a modified precursor fiber and a preoxidized fiber developed from a modified precursor fiber after different thermal-treatment temperatures. A modified PAN precursor fiber can be fully preoxidized at a lower temperature, showing a catalytic effect of KMnO$_4$, which accelerates the rate of preoxidation and reduces the time of thermal stabilization. The modification also increases the oxygen content in a PAN precursor fiber, resulting in an increase in the skin/core ratio for preoxidized fibers developed from modified precursors and further improving the uni-

formity of the cross-section structure. Carbon fibers developed from modified PAN precursors display an improvement in the tensile strength of 15–20% and an improvement in the elongation in 20–30% but a decrease in Young's modulus of about 10%.

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