

Continuous Carbonization of Polyacrylonitrile-Based Oxidized Fibers: Aspects on Mechanical Properties and Morphological Structure

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SYNOPSIS

By following the progression of continuous carbonization (300–1250°C) of polyacrylonitrile (PAN)-based oxidized fibers, variations in tensile mechanical properties and morphological structure are reported in detail along the carbonization line. The tensile strength and Young's modulus of the fibers generally increase throughout the carbonization stage. Meanwhile, the fiber diameter displays a significant decrease. The preferred orientation of carbon layer planes is observed to increase remarkably for temperatures over 400°C. In a similar manner, the stacking size increases significantly but reaches saturation around 600°C, a changing point corresponding to that observed for the variation of the Young's modulus. However, beyond about 1200°C, the stacking size again displays a marked increase. Results thus obtained are interpreted in relation to each other. Possible implications are also discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Conversion of polyacrylonitrile (PAN)-based precursors to carbon fibers usually involves the following:

- (a) Low-temperature (200–300°C) thermoxidative stabilization, which forms a ladder structure to withstand subsequent high-temperature treatment.
- (b) High-temperature carbonization ($\leq 1600^\circ\text{C}$) to exclude noncarbon atoms and yield a turbostratic structure.
- (c) An alternative "graphitization" ($> 2000^\circ\text{C}$) to improve the orientation of the basal planes and the stiffness of fibers.

As generally agreed, the mechanical properties of resultant carbon fibers are largely determined by the quality of the precursor used and processing con-

ditions at each stage.^{1–8} During the last three decades, a large quantity of work has been undertaken to understand the fundamental aspects of this complicated process from PAN-based precursors to carbon fibers. The aim of this was to either improve the mechanical properties or decrease the manufacturing cost of carbon fibers. Largely due to the fact that the stabilization process in the carbon fiber manufacture is very time-consuming, and therefore a significant step in determining the cost of final carbon fibers, much of the research work has been devoted to investigate this process.^{1–5,8–15} Unfortunately, relatively little effort has been spent on understanding the carbonization step, especially in the context of a continuous and systematic model.^{6,16–18} Without doubt, our knowledge and understanding of the higher-temperature carbonization of PAN-oxidized fibers is quite limited.

To expand our knowledge of the continuous carbonization processing of PAN-based oxidized fibers, a sequence of work was undertaken in our laboratory by monitoring the morphological structure rearrangements, evolution of mechanical properties, texture variation, as well as the relation of processing variables with final structure and tensile properties of carbon fibers. Preliminary results regarding as-

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pects of morphological and mechanical properties are reported here.

EXPERIMENTAL

Precursor Fiber

A domestically manufactured, wet-spun PAN fiber (a copolymer of acrylonitrile, methacrylate, and itaconic acid) was used as the precursor. Each tow contains 1000 filaments of 1.2 denier.

Continuous Stabilization and Carbonization

Details of the setup for stabilization and carbonization in our laboratory were schematically shown in our earlier report.⁸ The continuous stabilization of PAN precursor constitutes four independent furnaces, with each set to a constant temperature. The temperatures chosen for the four furnaces were 210, 230, 250, and 280°C, respectively. Each furnace was tubed with compressed air with a flow rate of about 4 L/min. A certain amount of stretching was imposed in the stabilization stage. The feeding rate into the stabilization was controlled at 14 m/h. The carbonization of the stabilized fibers was carried out first by passing the fibers continuously through a low-temperature furnace (2 m in length), increasing temperature gradually from 300 to 900°C, and then subjecting them to a very short time of higher-temperature annealing (temperature regime 1200–1250°C) in a second furnace. The two furnaces were separated by a linking quartz tube. The aim of this separation was to facilitate studying the effects of different temperature regions on the final carbon fibers. Argon was purged through both ends of the furnace to maintain an inert atmosphere. Samples for studies were obtained by cutting the fiber bundle at the delivery end and rapidly pulling out at the feed end.

Mechanical Properties

An Instron 1122 testing machine was employed to measure the mechanical properties of fibers on carbonization by a single filament method. A gauge length of 2 cm and a crosshead speed of 5 mm/min were chosen. Each value averaged at least 30 independent records. The diameter of a single filament was measured under an optical microscope.

Density

Densities of various fibers were measured by the density gradient column method. Two columns were used: one comprising *n*-heptane and carbon tetrachloride with a gradient from 1.300 to 1.580 g/cm³, and the other comprising carbon tetrachloride and methyl iodide with a gradient from 1.500 to 1.830 g/cm³.

Wide-angle X-ray Diffraction (WAXD)

A Sinku Riko 2037 X-ray diffractometer with Ni-filtered CuK α radiation was used to give the structural parameters of the fibers. The step-scan method was employed to determine the stacking size L_c , which was calculated by the Scherrer formula¹⁹:

$$L_c = \frac{K\lambda}{\beta \cos \theta}$$

in which λ denotes the wavelength and β represents the half-value width at $2\theta = 25.5^\circ$, corresponding to (002) lattice planes. K signifies the Scherrer constant (0.89 was used).

The orientation index in terms of percentage was calculated by the following formula¹⁹:

$$\pi = \frac{180^\circ - H^\circ}{180^\circ}$$

in which H is the half-value width on the azimuthal intensity scans.

Corrections for nonhomogeneous strains and instrumental broadening were not affected in the above calculations. The results thus obtained are mainly for the purpose of providing a basis for comparison.

RESULTS AND DISCUSSION

Progression of Mechanical Properties

Data from Figures 1–4 show the variation of the diameter, tensile strength, Young's modulus, and ultimate elongation of stabilized fibers at the carbonization stage with increasing temperature. It can be seen that the diameter diminishes throughout the carbonization treatment, from the original value of about 9.5 μm dropping to 6.8 μm . This suggests that densification and consolidation occurs during the whole carbonization annealing. In Figure 2, during the initial range of treatment (temperature increas-

ing from 300 to 400°C), a small dip in tensile strength is observed. After that, the tensile strength demonstrates a rapid and continual increase over the remaining temperature region. Meanwhile, the Young's modulus shows an overall increasing trend (Fig. 3). But, clearly, two steps in the increasing rate can be discerned, i.e., from 300°C up to about 600°C, the increase is relatively small and gradual; above that temperature, the improvement is significant and dramatic (Fig. 3). Examining the data in Figure 4, it is found that the elongation registers a general tendency to decrease over the carbonization. However, a changing point around 600°C seems to exist, at which a significant drop in value is observed (Fig. 4). After that, the rate of decrease becomes very gradual.

It has been proposed that during the early stages of carbonization (usually less than 600–700°C) the stabilized fibers undergo further cyclization in the uncyclized portions, forming ladder structure, cross-linking, and some chain-scission reactions, while evolving some small molecules like water, hydrogen, and other volatiles.^{16,17} The carbon basal planes from the aromatized structure in the stabilized fibers begin to form and increase in dimensions.^{16,17} Meanwhile, as these reactions and structure rearrangements occur within the fiber, consolidation and

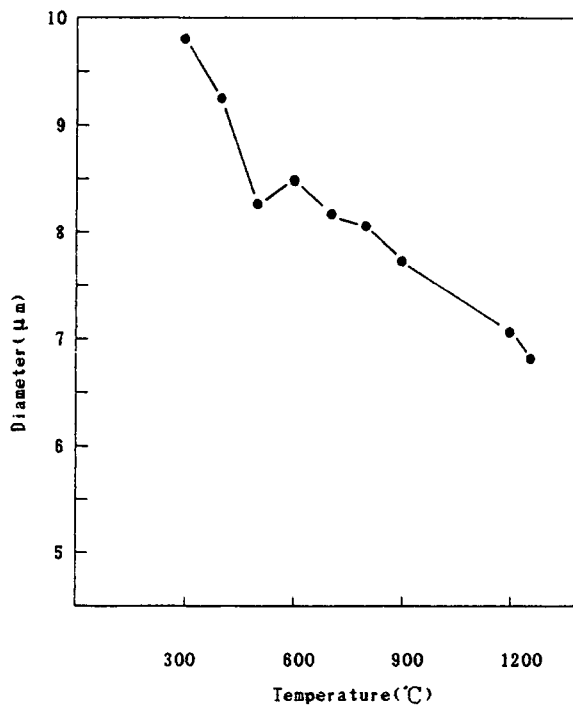


Figure 1 Variation of diameter with carbonization temperature.

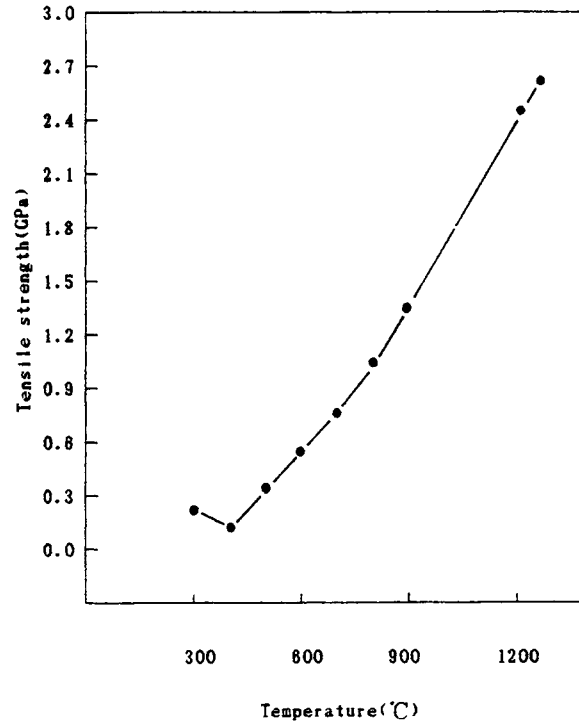


Figure 2 Variation of tensile strength with carbonization temperature.

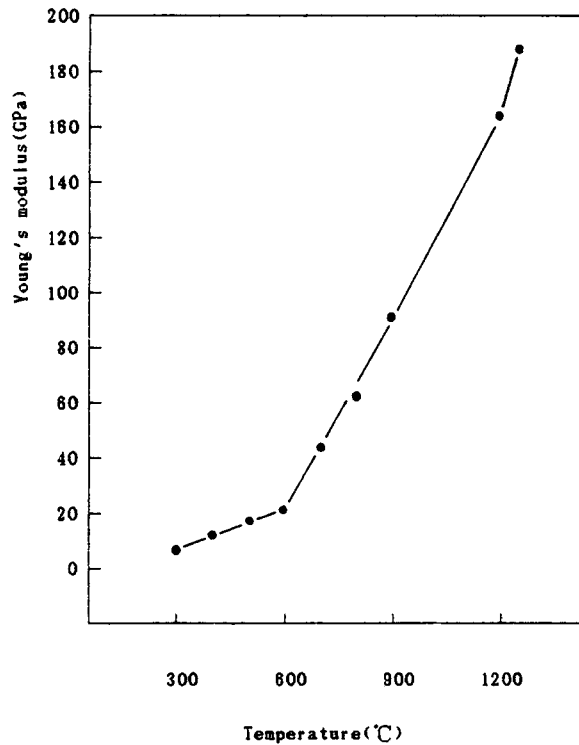


Figure 3 Variation of the Young's modulus with carbonization temperature.

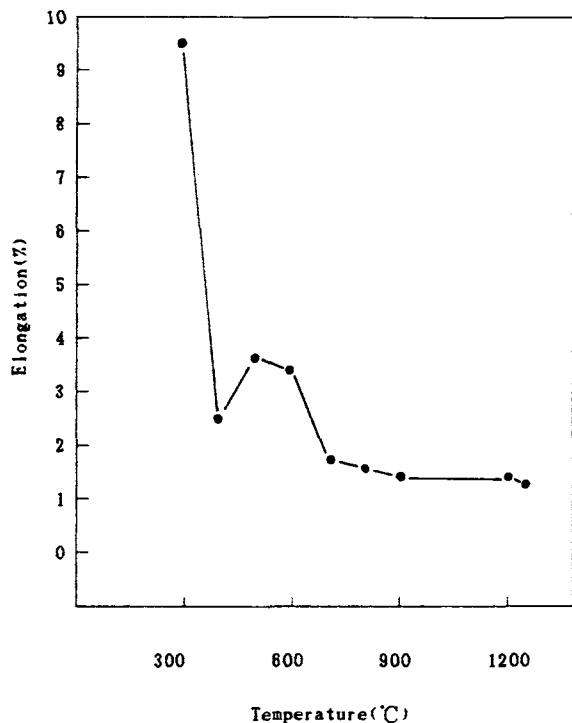


Figure 4 Variation of elongation at break with carbonization temperature.

densification are expected. As a result, the diameter of the fiber decreases, while the tensile properties such as tensile strength and the Young's modulus increase with increase in temperature, and the elongation decays as shown in Figures 1–4. When the temperature is over 600–700°C, condensation reactions between heterocyclic rings, mainly evolving gases like HCN and N₂, are found to be dominant.^{16,17} The carbon basal planes, as a consequence, are much improved in both the orientation and layer plane breadth.^{16,17} Thereby, as these happen, the tensile properties such as strength and modulus are enhanced significantly, as observed in Figures 2 and 3. Besides, due to the carbon layers becoming broader and more aligning, densification ensues, which leads to a decrease in fiber diameter (Fig. 1).

Progression of Morphological Structure

Figure 5 shows the variation of density vs. carbonization temperature. Density increases very quickly in relation to an increase in temperature when carbonization temperature remains below 900°C. This increase corresponds to the diameter decrease, which is the result of consolidation and densification occurring within the fiber. However, when temperature

rises over 900°C, a drop in density is observed (Fig. 5). A similar observation has been reported by Gibson,²⁰ by Abhiraman et al.,⁶ and by Ko.¹⁴ This drop has been attributed to the conversion of open pores, which were supposed to be accessible to density measurement solvents, to closed pores.^{6,20} If this assumption is true, it suggests that consolidation occurs around the pores during the high-temperature stage of carbonization.

Figures 6 and 7 show the variation of stacking size and orientation of the carbon basal planes during carbonization. A common feature in both plots is that, in the initial temperature region (300–400°C), both values appear quite low and steady, i.e., no obvious incremental change is observed. When temperature is over 400°C, significant increases in stacking height and orientation are displayed (Figs. 6 and 7). However, in Figure 6, a change point around 600°C can be seen, above which the stacking size becomes relatively constant until 1200°C. The orientation, however, displays a steady increase after 400°C (Fig. 7).

Comparing the data on the Young's modulus changes in Figure 3, it can be observed that when the temperature is below 600°C, although the stacking size and orientation improve significantly, the

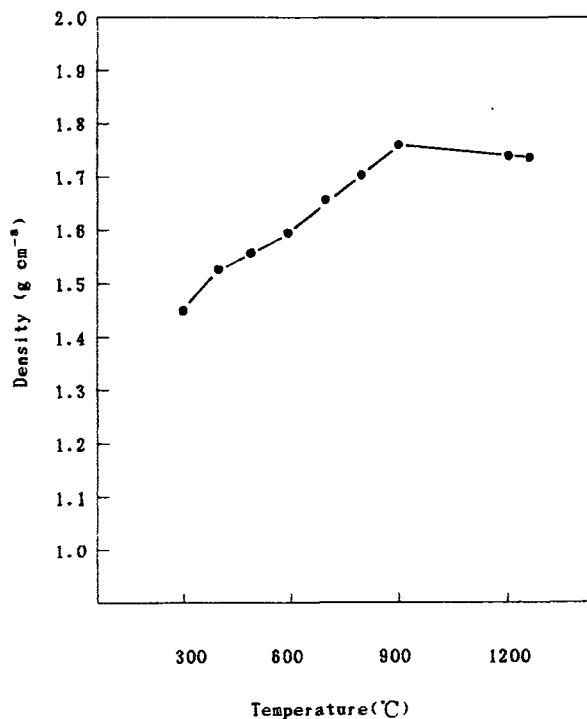


Figure 5 Variation of density with carbonization temperature.

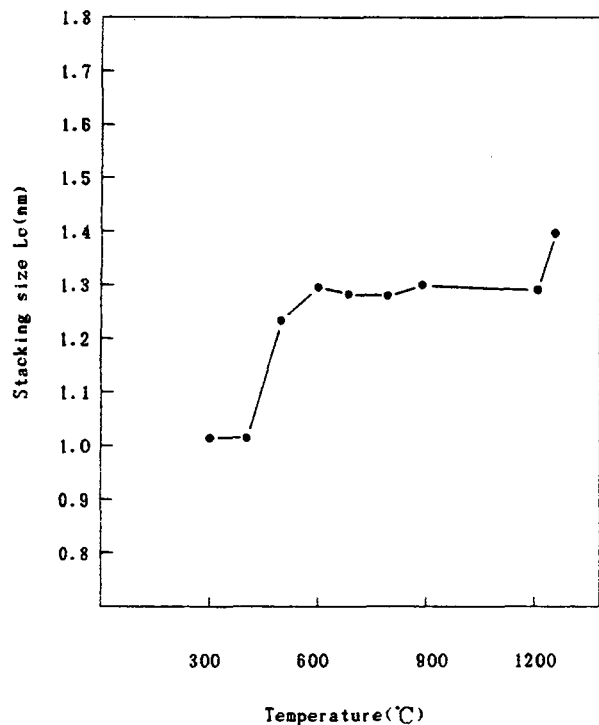


Figure 6 Variation of stacking size with carbonization temperature.

Young's modulus does not show the same trend, but increases to a small extent. In the temperature range between 600 and 1200°C, although the stacking size saturates around a certain value, the orientation keeps increasing quite rapidly and the Young's modulus increases very significantly. These data suggest that the carbon basal planes begin their formation at about 400°C and acquire significant increases in stacking height and orientation before 600°C.

During this range of carbonization treatment (< 600°C), as discussed above, significant chemical reactions, such as cross-linking, chain scission, as well as other reactions, occur within the material.^{16,17} As a result of these reactions, remarkable structural rearrangements ensue. The tensile properties of fibers, especially the modulus, are primarily determined by the characteristics of the structure including the orientation order, degree of graphitic order, and the size of crystallites as well. The observed slower rate of increase in the modulus (Fig. 3) during this range is mainly undermined by the lower degree of graphitic order.

In the following carbonization region from 600 to about 1200°C, condensation reactions between heterocyclic rings, which lead to broader layer planes,

were found to be dominant.^{16,17} In this region, though the stacking height of carbon structures levels off (Fig. 6), the orientation of carbon basal planes still keeps significantly increasing (Fig. 7). In addition to this, due to higher-temperature annealing, the degree of graphitic order can be expected to improve. Therefore, as a result of improvements in orientation and graphitic order, the tensile properties, especially the Young's modulus, demonstrate a higher rate of increase (Fig. 3). When carbonization temperature goes over 1200°C, both the stacking size and the orientation improve markedly (Fig. 6 and 7), suggesting that packing and better alignments of crystallites are simultaneously taking place. This further enhances the tensile properties of fibers as shown in Figures 2 and 3.

CONCLUSION

A number of results have been obtained through the studies on continuous carbonization of PAN-oxidized fibers by following the progression in mechanical properties and morphological structure:

1. The tensile strength and Young's modulus of the stabilized PAN-based fibers generally in-

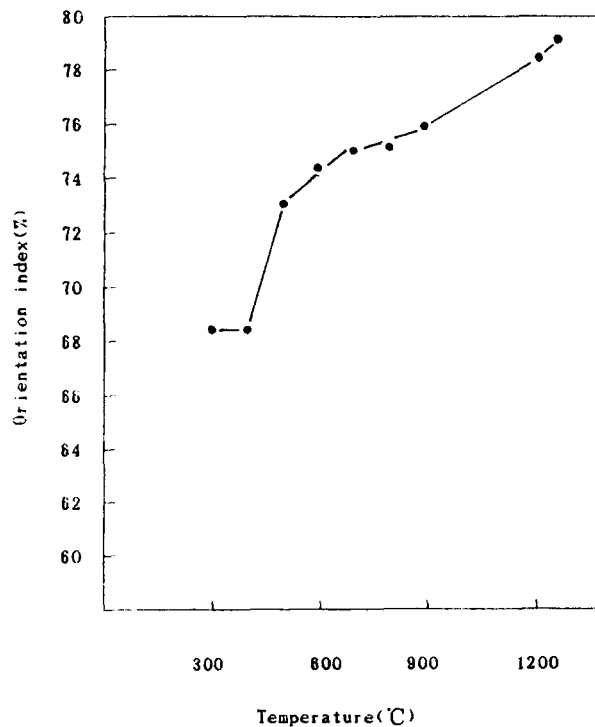


Figure 7 Variation of orientation index with carbonization temperature.

crease throughout the carbonization stage. The ultimate elongation shows an overall decreasing trend. Meanwhile, the fiber diameter displays a significant decrease during carbonization.

2. A change point at about 600°C is observed, before which the extent of increase in Young's modulus is gradual, but after which the rate of increase becomes sharply steeper over the remaining carbonization. This critical temperature is also found in the variation of break elongation and stacking size.
3. The density of fibers rises in the early stage of carbonization but reaches a relative maximum around 900°C, beyond which it decreases to a lower steady value. This apparent density decrease was attributed to open pores converting to closed pores.²⁰
4. The preferred orientation of carbon layer sheets increases significantly for carbonization temperatures over 400°C. In a similar manner, the stacking size of the sheets also increases remarkably but reaches a plateau around 600°C, beyond which it saturates at a steady value until about 1200°C. Thereafter, the stacking size once again demonstrates a high rate of increase in the higher-temperature region.

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