

Influence of Continuous Stabilization on the Physical Properties and Microstructure of PAN-Based Carbon Fibers

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SYNOPSIS

A continuous stabilization and carbonization process was used to prepare polyacrylonitrile (PAN)-based carbon fibers. The stepwise stabilization of PAN fibers was tried at various temperatures. The effect of stepwise stabilization on the physical properties and microstructure of the final carbon fibers is reported in this article. The fixed temperature in stepwise stabilization is kept below the fusion temperature of PAN precursors to avoid overstabilization of the fibers. The optimum stepwise stabilization process not only increases the amount of ladder polymer in stabilized fiber but also improves the physical and mechanical properties of the resultant carbon fibers. The formation of closed pores from open pores in carbon fiber occurs at 1100°C, but the formation of closed pores occurs at 200°C lower for carbon fiber developed from overstabilized fiber. The effect of continuous stepwise stabilization on the properties of resulting stabilized fibers and the variation in physical properties, element composition, and microstructure of carbon fibers during the carbonization process are also reported in this article.

INTRODUCTION

Carbon fibers have been known for nearly a century since Edison first used them as filaments for lamps.¹ Modern carbon fibers were first developed by Shindo² when he pyrolysed polyacrylonitrile (PAN) fiber. Following this discovery by Shindo, the development of commercial carbon fibers was reported by Watt et al.³ Pyrolysis of PAN fibers, the stabilization process, is necessary to obtain high-quality carbon fibers. In this process, a lower temperature treatment (200–300°C) in air (in an oxygen-containing atmosphere) leads to the formation of a ladder polymer. Subsequently, carbonization is carried out at a temperature of up to 800–3000°C in an inert atmosphere. The maximum temperature depends upon the type of carbon fibers ultimately required.^{4–6}

When PAN precursors are heated during the stabilization stage, cyclization occurs and $C\equiv N$ bonds will be converted into $C=N$ bonds, which produce ladder polymers.⁷ During the production process

from PAN fibers, stabilization is still the most time-consuming step. The step of forming ladder polymers is very important, as it influence as the physical properties and the microstructure of the final carbon fibers.⁴

In a laboratory situation, there are two methods for preparing stabilized fibers in a batch process. The fixed-length method requires the PAN fibers to be secured to a rigid frame.⁸ The constant load method attaches a weight to the end of the fiber during the stabilization process.^{9,10} In industrial production, a sequence of ovens or the separated sections of one oven are used to produce commercial carbon fibers.¹¹ Warner and coworkers¹² studied the shrinkage and dynamic behavior of acrylic fibers undergoing continuous stabilization processing. Jain and coworkers^{13,14} studied the effects of continuous stabilization on the formation of consolidated carbon fiber structure from two precursors.

Our previous study¹⁵ presented the results of the modified PAN fibers, which produced high-performance carbon fibers. In another study,¹⁶ we presented a model for the microstructure of the stabilized fibers. We made an additional study of the dynamic mechanical properties of PAN fibers during stabilization.¹⁷ The conventional method of prepa-

ration of stabilized fibers was carried out in these studies. In this article, a continuous stabilization and carbonization process was used to manufacture carbon fibers from PAN precursors. There are two methods for heat treatment during continuous stabilization. Isothermal stabilization was the conventional method for producing stabilized fiber. The second method involved a stepwise increase in stabilization temperature. This method is employed in industry by using an oven with separated sections.

In the present study, the author reports the effect of continuous stabilization on the properties of the resulting stabilized fibers and the final properties of carbon fibers. The progression of carbonization was monitored through measurements of density, elemental composition, mechanical properties, and the stacking height of carbon layer plane (L_c). Before this study, we assumed that if a high temperature stabilization condition has adopted it would decrease the required stabilization time and increase the properties and productivity of carbon fibers more effectively than any conventional process.

EXPERIMENTAL

A special grade of acrylic fiber, Courtelle fiber (Courtaulds Ltd., U.K.), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used in this work. A single tow of Courtelle fiber contains 6000 strands of 1.1 denier monofilament. The precursor was stabilized and carbonized by means of a continuous process, as shown in Figure 1. The stabilization furnace was divided into four zones (one meter with each zone) and set at different temperature regions. In this study, three samples were prepared for stabilization with different temperatures settings, as shown in Table I. Two sets of differential speed rollers—feed rollers and pinch rollers—were

located at the front and rear of the furnace, respectively, as shown in Figure 1. A variable speed of the feed rollers was used to control the speeds of fibers entering zone 1, and a variable speed of the pinch rollers removed fibers from zone 4. In this procedure, the feed rollers and take-up rollers were controlled at the same speed. PAN fibers passed through the furnace in 2.25 h.

Continuous carbonization of the stabilized fibers was carried out by passing them through a ceramic reaction tube at temperatures ranging from 400 to 1300°C, increased at 100°C intervals, as shown in Figure 1. The length of the oven was 1 m. The speed of the take-up rollers and the pinch rollers was the same. The passing time of the stabilized fibers was 30 min. An oxygen-free nitrogen atmosphere was passed through both ends of the furnace to maintain an inert atmosphere.

The mechanical properties of the stabilized fibers and the carbon fibers were measured by an Instron 1122 tensile-testing machine at a crosshead speed of 0.5 mm/min and a load cell of 10 g with a testing length of 2 and 2.5 cm for stabilized fibers and carbon fibers, respectively. In each sample, at least 25 filaments were tested, and the average value is reported. The diameters of all fibers were measured under an Olympus BHT microscope with a closed-circuit television camera that magnified the image of the fiber to measure the diameter of the fiber. Thirty fiber diameters were measured in each experiment and the average measurement of these was calculated.

A Rigaku X-ray diffractometer with CuK_α radiation as the source was used to determine the d spacing and the stacking size (L_c , stacking height of layer planes) of carbon fibers and the aromatization index (AI) of stabilized fibers. The Scherrer equation¹⁸ was used to calculate the stacking size from the width of the (002) reflection, B . The width increases as the stacking size (L_c) decreases:

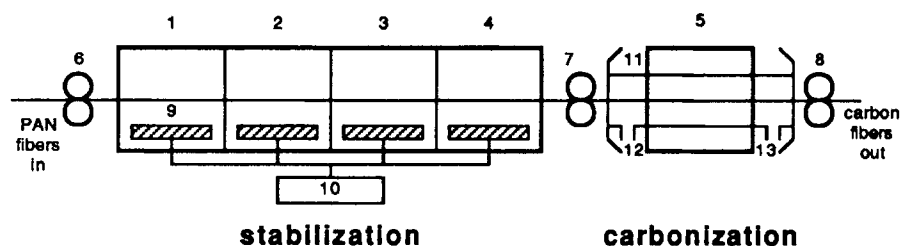


Figure 1 Schematic drawing showing the process of carbon fibers from PAN fibers on continuous stabilization and carbonization: 1, 2, 3, 4, stabilization oven; 5, carbonization furnace; 6, feed rollers; 7, 8, pinch rollers; 9, heating mantle; 10, temperature controller; 11, reaction vessel; 12, 13, nitrogen gas in.

Table I Temperature Conditions of the Stabilization Process

Sample Code	Stabilization Temperature (°C)			
	Zone 1	Zone 2	Zone 3	Zone 4
A	190	230	230	230
B	190	225	275	200
C	190	225	275	300

$$L_c = \frac{k\lambda}{B \cos \Theta},$$

in which $\lambda = 0.154$ nm, k is the apparatus constant (= 1.0), and B is half-value width of the (002) broadened reflection of carbon fibers.

The AI was measured by the following formula¹⁹:

$$AI(\%) = \frac{I_a}{I_a + I_p},$$

in which I_a is the diffraction pattern give by the ladder polymers at $2\Theta = 25^\circ$, and I_p is the diffraction by the PAN crystal at $2\Theta = 17^\circ$.

A Mettler TA 3000 thermal analyzer with a DSC 20 module was used to study the reaction of the PAN precursor. The sample weight was 3.5 mg and the heating rate was $10^\circ\text{C}/\text{min}$, heated to 450°C under an air atmosphere.

Density was measured at 25°C according to the density gradient column method. The density column was prepared with a mixture of *n*-heptane and carbon tetrachloride so that a density gradient of about $1.2\text{--}1.6$ g/cm³ extended from top to bottom. For the measurement of densities from $1.6\text{--}2.0$ g/cm³, a density gradient column prepared with a mixture of carbon tetrachloride and 1,3-dibromopropan was adopted.

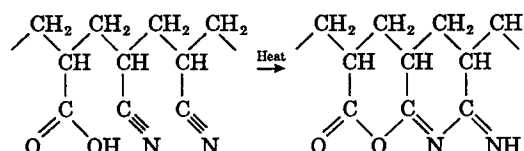
A Perkin-Elmer model 240C Elemental Analyser was used to carry out the elemental analysis. The samples from the carbonization process were analyzed for carbon, hydrogen, and nitrogen. The oxygen content was determined by difference.

RESULTS AND DISCUSSION

Properties of Stabilized Fibers

The degradation of PAN during stabilization is always associated with a large exotherm. Fitzer and Muller²⁰ used DTA measurements to study the kinetics of cyclization and stabilization of PAN being

heat-treated in air and nitrogen, and observed the cyclization to be a first-order reaction. These polymerization reactions may result from the stabilization of PAN fiber in an inert or oxidizing atmosphere, and give rise to a thermally stable cyclized structure often referred to as a ladder polymer. The acid constituent of PAN fibers acts an initiator for ladder polymer by the following mechanism, as shown by Grassie and Hay²¹:



In this study, the temperatures for four zones were on the basis of a DSC study. Figure 2 shows the DSC study for PAN precursor fiber. An exothermic reaction begins at about 180°C . This reaction increases slowly to 225°C , and then rises rapidly until it peaks at 275°C (fusion temperature). This exothermic peak disappears and a second exothermic peak begins at about 300°C . This peak is due to the degradation of stabilized fiber.

The temperature conditions of four zones for all samples are shown in Table I. Samples B and C were prepared to study the effect of stepwise continuous stabilization on the properties of stabilized fibers and resultant carbon fibers. If the oven temperature is set lower than 190°C , the fibers would not have been sufficiently thermally stabilized to center part of the fiber. To prepare sample C, the temperature was set according to Figure 2. The process for sample C is defined as the high-temperature stabilization process because the fourth oven was set at 300°C , a temperature higher than the fusing

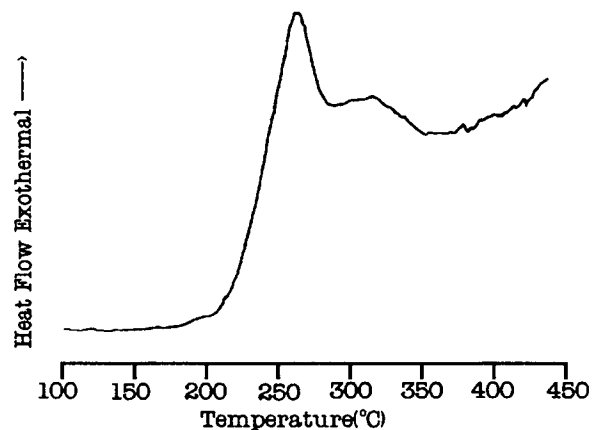


Figure 2 DSC curve of Courttelle fiber (heating rate: $10^\circ\text{C}/\text{min}$, in air).

temperature of the precursor. Sample B, the fourth zone, was set at 200°C to compare with sample C, set at 300°C.

For producing sample A, the four zones were set at 190, 230, 230, and 230°C, respectively. The time of PAN fiber passed through the temperature range of 230°C was about 1 h during the isothermal stabilization.

The properties of stabilized fibers are shown in Table II. In a previous study,¹⁵ we modified the testing method¹⁹ so that the AI value could be used to estimate the amount of ladder polymer instead of being used as an index only. The AI values are 57, 66, and 64% for samples A, B, and C, respectively, indicating that the stepwise stabilization process leads to the formation of a stabilized polymer with a higher ladder content than does isothermal stabilization.

The AI value of sample C is lower than that of sample B. In a previous study,²² we found that the density of stabilized fibers increased with the increase in stabilization temperature. The density values of all samples are shown in Table II. The density and AI values of sample C are lower than these of sample B. This indicates that when the stepwise stabilization is applied above the fusion temperature (275°C), the degradation of stabilized fiber occur. The excess oxygen will be bonded or absorbed in the stabilized fiber.²³ As a result, sample C is richer in oxygen content than samples A and B. Because of a lower AI value, this process also leads to the degradation of ladder polymer and decreases the amount of ladder polymers in sample C. Therefore, sample C has a lower density and AI value. The high-temperature stabilization process has a negative effect on the tensile strength of the final carbon fibers. This will be discussed in the next section.

Properties of Carbon Fibers

During the carbonization stage, the noncarbon elements are removed as volatiles, such as: H₂O, HCN,

NH₃, N₂, CO, CO₂, and so on, to give carbon fibers with a yield of about 50% of the mass of the original PAN fiber.^{8,22} Watt and coworkers^{8,22} studied the volatile products evolved during low-temperature carbonization (below 1000°C) and tried to deduce the chemical processes that were occurring. In this work, we were concerned with the effect of stepwise stabilization on the physical properties of carbon fibers.

Figure 3 shows the variation in densities of stabilized fibers during the continuous carbonization process. Density increases very rapidly below 1100°C for samples A and B, and below 900°C for sample C. This led to the finding that the crosslinking of ladder polymer as well as the lengthening and broadening of carbon basal planes led to the re-packing of the structure in carbon fibers. But the density increase was followed by a sharp drop after these temperatures. A similar phenomenon has been found by several authors.^{14,24} One reason for this drop in apparent density may be the conversion to closed pores from open pores. Due to the closure of the fiber surface, the penetration of solvents from the fiber surface into the inside structure become inaccessible. This results in a decrease in the measured density, suggesting that a rearrangement of the structure occurs around the open pores at these temperatures. But, this finding needs to be confirmed with a small-angle X-ray diffractometer and a mercury porosimeter to measure the pore size and surface area of the fibers.

In sample C, the formation of closed pores occurs 200°C lower than in samples A and B. Above this temperature (900°C), the density of sample C decreases with increasing carbonization temperature, indicating that overstabilization introduces a large amount of closed pores in fiber. This could limit the tensile strength of the final carbon fibers.

Figures 4 and 5 give the results of the nitrogen and the carbon content analysis during the continuous carbonization stage. During carbonization, the carbon content increases and the nitrogen, hydrogen, and oxygen contents decrease. Watt and coworkers⁸ found that the temperature range from 500–1000°C involved an intermolecular reaction, evolving HCN and N₂ and leading to the lengthening and broadening of carbon basal planes from ladder polymer. They also found when heat treatment of carbon fibers continued above 1000°C the remaining nitrogen was eliminated through continued lengthening and broadening of the microfibrils.

Below 1000°C, sample C had a greater nitrogen content and a lower carbon content than sample A and B. Above this carbonization temperature, sam-

Table II Properties of Stabilized Fibers

Sample Code	Density (g/cm ³)	AI (%) ^a	Oxygen Content (%)
A	1.407	57	20.3
B	1.463	66	22.7
C	1.458	64	23.8

^a AI was tested by wide-angle X-ray diffraction.¹⁵

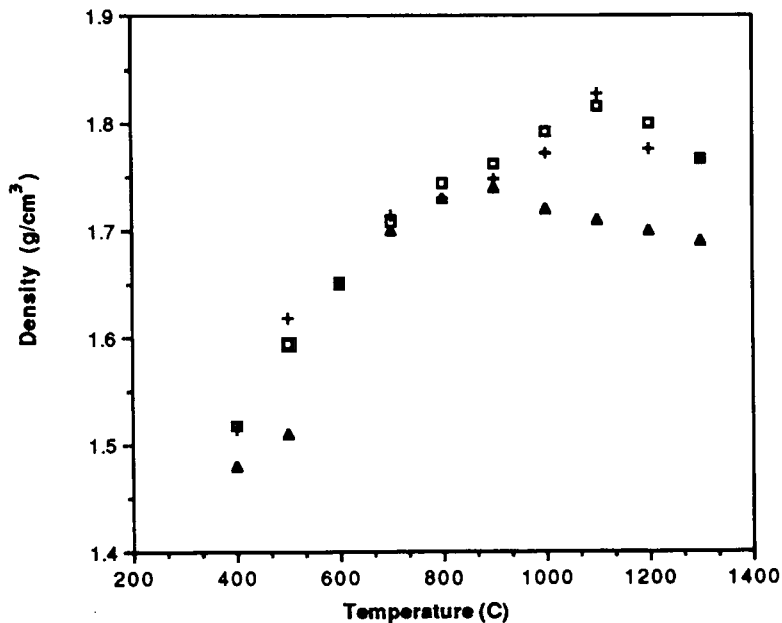


Figure 3 Density of carbon fibers as a function of carbonization temperature: (□), sample A; (+), sample B; (Δ), sample C.

ple C had a lower nitrogen content and a higher carbon content than other samples. This indicated that the formation of carbon basal planes is slower below 1000°C for sample C than it is for samples A and B. Sample C had a lower carbon content below 1000°C, indicating that overstabilization breaks down the molecular structure of ladder polymers and

promotes the evolution of CH₄ and H₂ from this breakdown.

Above 1000°C, the nitrogen content of sample C is lower than that of samples A and B, as shown in Figure 4. The carbon content of this sample is higher than other samples (as shown in Figure 5), indicating that the condensation reaction between car-

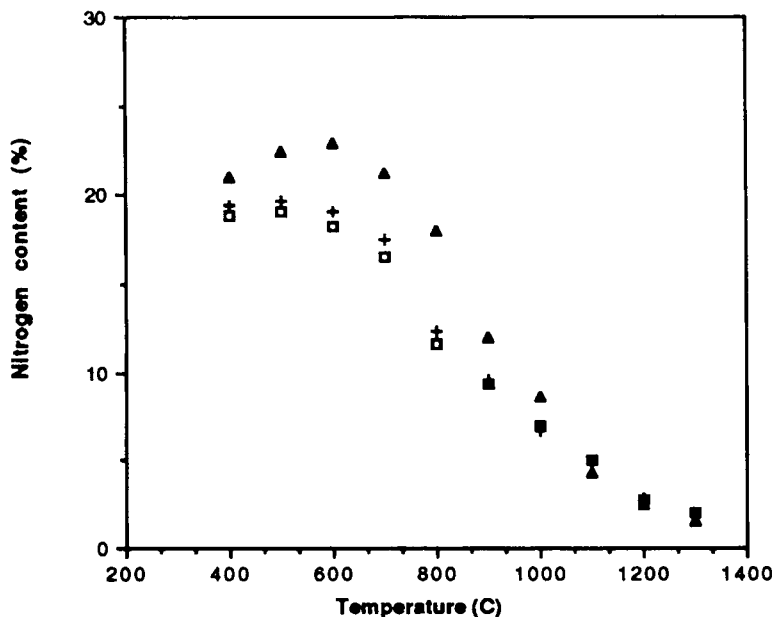


Figure 4 Nitrogen content of carbon fibers as a function of carbonization temperature: (□), sample A; (+), sample B; (Δ), sample C.

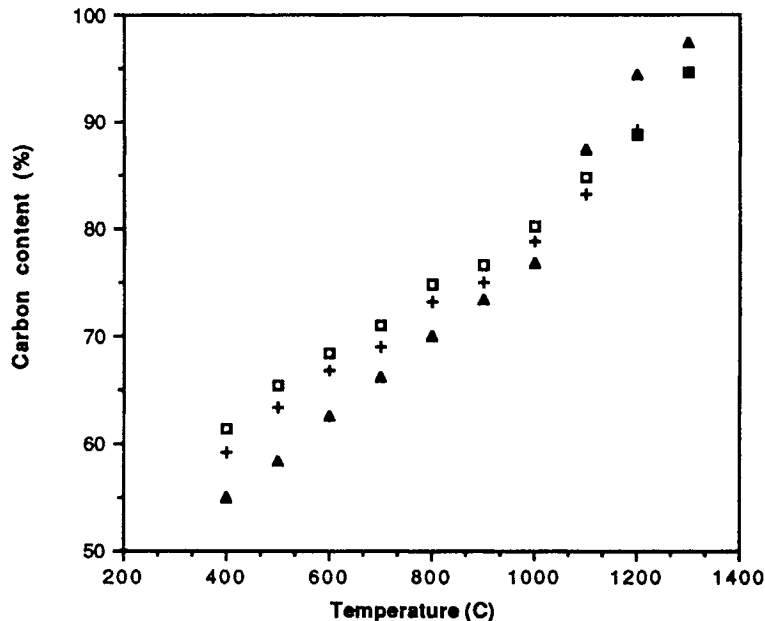


Figure 5 Carbon content of carbon fibers as a function of carbonization temperature: (□), sample A; (+), sample B; (△), sample C.

bon basal planes in sample C were greater than in samples A and B. This meant that the most of the carbon basal planes were formed above 1000°C for sample C. These reactions led to a random orientation and introduced defects in the carbon fibers, resulting in a negative effect on the mechanical properties of the final carbon fibers.

In carbon fibers the crystallites are arranged around the longitudinal axis of the fiber with the layer planes. The layer planes are found by a set of turbostratic stacks of aromatic layers approximately parallel to the fiber axis. The Scherrer equation¹⁸ is used to calculate the values of L_c (stacking height of layer planes) from the width of the 002 reflection of carbon fibers. The variation in L_c during the carbonization stage is shown in Table III. Because of the lengthening and broadening of carbon-based planes during carbonization, the L_c values increased with the increase in temperature. Because of the degradation of the ladder polymer for sample C dur-

ing stabilization, most of the carbon basal planes were formed at a higher carbonization range (above 1000°C). Therefore, the L_c value of sample C was lower than for samples A and B. Because of the optimum stepwise stabilization for sample B, the resultant carbon fiber had a higher stacking height (L_c) in carbon layer planes, which improved the mechanical properties.

The results of the effect of stepwise stabilization on the modulus of carbon fibers during the carbonization stage are plotted in Figure 6. Due to the formation of the carbon basal planes, the modulus for all samples increased rapidly above 500°C. Because sample B was prepared by an optimum stabilization, this fiber has a higher modulus than samples A and B. Although sample C was prepared by the high-temperature stabilization process, the modulus of the resultant carbon fibers showed no evidence of variation during the carbonization stage.

The progression of the changes of tensile strength

Table III Variation in Stacking Height of Carbon Layer Planes (L_c) during the Carbonization Stage

Sample Code	Stacking Height of Layer Planes, L_c (nm)				
	800°C	900°C	1000°C	1100°C	1300°C
A	0.76	1.28	1.17	1.32	1.56
B	1.48	1.54	1.54	1.67	1.72
C	0.94	1.17	1.04	1.23	1.45

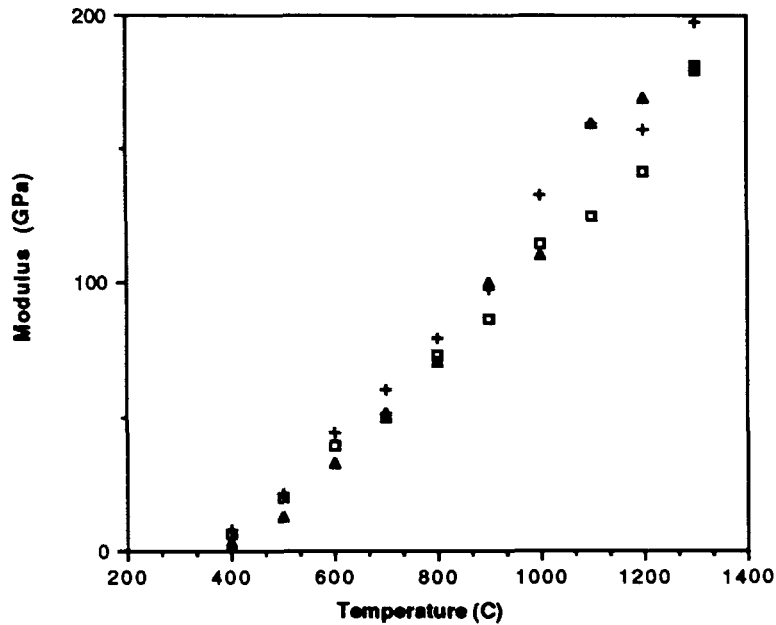


Figure 6 Modulus of carbon fibers as a function of carbonization temperature: (□), sample A; (+), sample B; (△), sample C.

of carbon fibers are plotted as a function of carbonization temperature in Figure 7. The tensile strength of sample C was worse than that of samples A and B. Because sample C was prepared by the high-temperature stabilization process, some of the ladder polymers were broken down. This reaction limited the formation of the length and stacking height (L_c)

of carbon basal planes during the carbonization process. The high-temperature stabilization process also promoted the overabsorption of oxygen in stabilized fibers. The oxygen may form excessive $-C=O$ bonds on the backbone of ladder polymers in sample C. During carbonization, most of the oxygen of $-C=O$ groups escapes as water vapour; as

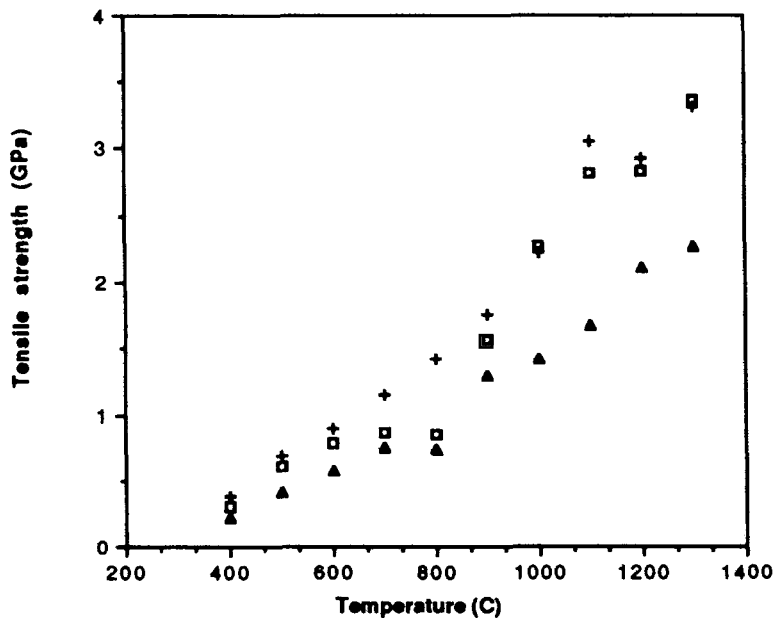


Figure 7 Tensile strength of carbon fibers as a function of carbonization temperature: (□), sample A; (+), sample B; (△), sample C.

Table IV Properties of the Resultant Carbon Fibers (Carbonized at 1300°C)

Developed from	Modulus (GPa)	Strength (GPa)	Density (g/cm ³)	<i>L</i> _c (nm)
A	182	3.36	1.766	1.56
B	198	3.31	1.766	1.72
C	180	2.27	1.690	1.45

a result, crosslinking between adjacent chains take place.²⁵ But some oxygen evolves as CO or CO₂, which leaves defects in the fibers and decreases the tensile strength of the resultant carbon fibers.²³ For these reasons, sample C shows a much lower tensile strength than samples A and B during the whole carbonization process.

The properties of the final carbon fibers are shown in Table IV. The high-temperature stabilization process for sample C led to a poor tensile strength, a lower density, and a lower stacking height in final carbon fibers. The optimum stepwise stabilization for sample B led to a better properties than did the other samples.

It is very interesting to note that sample B was stabilized at 190–225–275–200°C and sample C was stabilized at 190–225–275–300°C during the stabilization process. The only difference was the fourth fixing temperature in oven. In this study, we found that the high-temperature stabilization process could break the molecular chains of the ladder polymer and could have a very negative effect on the tensile strength of the final carbon fibers. In this work, all samples were carbonized at 1300°C. Sample B was prepared by a optimum stabilization process. Therefore, sample B had better mechanical properties and a uniform structure (a higher *L*_c value). We believe that the mechanical properties of sample C will continue to increase when the fiber is carbonized at a higher temperature.

CONCLUSIONS

This study used a continuous stabilization and carbonization process and a stepwise temperature method in the stabilization stage to prepare carbon fibers. We found that the stepwise temperature should not be set higher than the fusion temperature of PAN precursor to avoid over-heat-treatment of the fibers.

The high-temperature stabilization process led to the breakdown of ladder polymers and to an over-

absorption of oxygen in stabilized fibers. These reactions led to a worsening of mechanical properties and defects in the microstructure of the final carbon fibers. On the other hand, the carbon fibers developed by optimum stepwise stabilization have a better tensile strength, a higher modulus, a greater density, and higher stacking height of carbon layer planes.

The formation of closed pores from open pores in carbon fibers occurred at 1100°C during the carbonization stage. This temperature was 200°C lower for the carbon fiber developed by the high-temperature stabilization process.

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