

Tensile Properties of Carbon Fibers from Acrylic Fibers Stabilized under Isothermal Conditions

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Synopsis

A series of carbon fibers were prepared from the acrylic fibers thermally stabilized in air under various temperature–time conditions, and the relation between the extent of stabilization and the tensile properties of carbon fibers was investigated. The density of stabilized fibers was adopted as a measure of the extent of stabilization. The tensile modulus of carbon fibers changed dependently on stabilization temperature. However, the variation of the tensile modulus of carbon fibers with the density of stabilized fibers was small if stabilization temperature was constant. In the relation between the tensile strength of carbon fibers and the density of stabilized fibers, a feature depending on stabilization temperature was not evident, and the tensile strength of carbon fibers showed a maximum in the density range from about 1.34 to 1.39 g/cm³ of stabilized fibers.

INTRODUCTION

The process to produce carbon fibers from acrylic fibers is comprised of two steps; stabilization and carbonization. Acrylic fibers require a low temperature treatment in air prior to carbonization,¹ and this low temperature treatment is referred to as stabilization. During stabilization, acrylic fibers form a partially cyclized structure due to additional polymerization of the nitrile side groups and uptake oxygen from the atmosphere.² The cyclized structure is stable toward heat and can be converted on carbonization to turbostratic carbon with a minimum loss of mass. Stabilization should be carried out under conditions which control the considerable amount of heat evolution which accompanies the cyclization and oxidation reactions, and is a lengthy process.

The processing conditions of stabilization such as temperature–time profile and stretching are thought to affect the properties of resulting carbon fibers. Excepting the patent literature, only a few papers, however, have reported on this problem. Watt and Johnson³ have found that the length change of acrylic fibers during stabilization affects the tensile modulus of carbon fibers. Bahl and Manocha⁴ have reported that the tensile strength of carbon fibers shows maximum at 570 min of an isothermal stabilization at 205°C and that carbon fibers with slow heating rate during stabilization are stronger than those with rapid heating during stabilization.

The variable ranges of the processing factors of stabilization which might be technologically significant are very wide, and various processing factors

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effecting carbonization are expected to influence the mechanical properties of carbon fibers by interacting with a processing history at the stabilization stage. This makes it difficult to deduce the optimum processing conditions.

This study is intended to find an approximate relation between the temperature-time conditions of isothermal stabilization and the mechanical properties of the resulting carbon fibers. For this purpose it is desirable to represent the extent of stabilization by a certain measure, apart from processing conditions. Various measures such as oxygen uptake,^{5,6} moisture absorption,⁷ and X-ray diffraction⁸ have been applied as a measure of the extent of stabilization. In this paper the density of stabilized acrylic fibers is adopted as a measure of the extent of stabilization. The density changes with stabilization have been previously investigated precisely.⁹

EXPERIMENTAL

Material

Acrylonitrile copolymer fibers containing methylacrylate as the major comonomer were used in this study. The acrylic fibers were in the form of continuous filament yarn of 161 tex, comprised of 1000 filaments. The acrylic fibers had the following elemental analysis: C, 67.2; N, 4.9; H, 5.9; O, 2.0 wt %.

Stabilization

The stabilization of the acrylic fibers was carried out by passing a yarn continuously through an air-circulating oven at constant temperatures. The temperature in the oven was controlled with a precision of $\pm 1^\circ\text{C}$. A series of residence time was obtained by changing the running speed of yarn, while the feed and takeup velocities were kept at same values, that is, no extension or contraction was applied to a yarn at stabilization. In order to get a long residence length of yarn in the oven, a yarn was made going and returning many times with the aid of pulleys in the oven. The yarn tension can be assumed approximately uniform over the whole length of yarn from the feed to the takeup side.

Carbonization

The carbonization of thermally stabilized acrylic fibers was made by passing a stabilized yarn continuously through a carbonization furnace at a constant speed. No extension or contraction was applied to the yarn at carbonization. Nitrogen gas was flowed through the carbonization furnace. The oxygen concentration in the carbonization atmosphere was about 10 ppm. Figure 1 shows the temperature distribution in the carbonization furnace used for this experiment. The maximum furnace temperature was 1250°C and the residence time of yarn at the temperature range from 1200°C to 1250°C was 4 min.

Linear Density

The linear density of stabilized fibers was calculated from a mass of known length. Acrylic fibers exhibit increased moisture absorption with stabili-

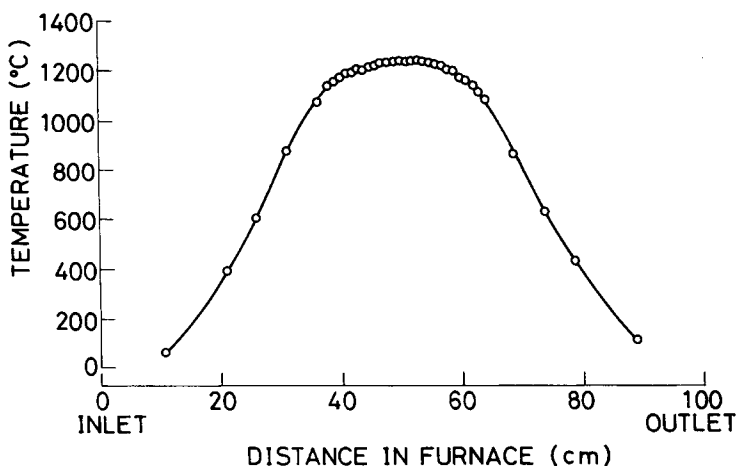


Fig. 1. Temperature distribution in carbonization furnace.

zation. Hence, the mass was determined by weighing a specimen at 110°C after keeping the specimen at the temperature for 3 min.

Density

The density of stabilized fibers was measured in a *n*-heptane-ethylene dibromide density gradient column at 25°C.

The density of carbon fibers was determined at 30°C by the sink-float method using a carbon tetrachloride-ethylene bromide mixture.

X-Ray Diffraction

The X-ray diffraction measurements were made with a Rigaku Denki diffractometer using Ni filtered CuK_α radiation. The X-ray beam was directed to a specimen perpendicularly to its fiber axis. The intensity distribution of the equatorial diffraction arc at the Bragg angle $2\theta = 25.5^\circ$ was measured both for the stabilized and carbonized fibers, and the half width X_h of the intensity distribution at half maximum intensity was determined. From the values of X_h and θ the orientation parameter was calculated according to the description adopted by Farrow and Bagley¹⁰ as follows:

$$\text{orientation parameter} = \frac{90 - \phi}{90}$$

where $\sin \phi = \cos \theta \sin (X_h/2)$.

Tensile Properties

The tensile modulus and strength of carbon fibers were determined on carbon fiber-epoxy matrix composite strands. A diglycidil ether of bisphenol A type epoxy and hardener, 4-methyl hexahydrophthalic anhydride, were used as the matrix. The amount of the hardener was 100 parts by weight for 100 parts of the epoxy resin. The composite strands were cured at 160°C for 4 h. The tensile test was carried out with a Tensilon tensile tester at a

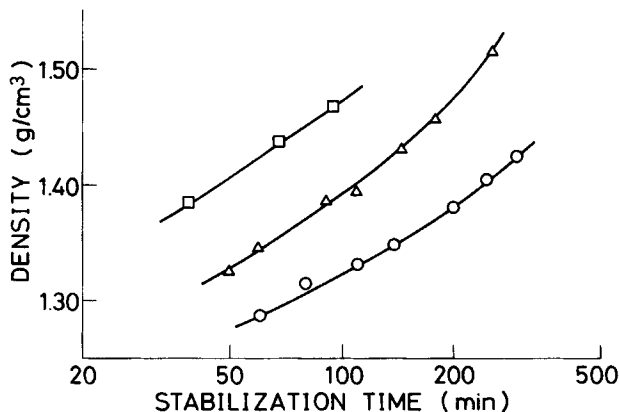


Fig. 2. Variation of density with stabilization time for acrylic fibers. Stabilization temperature (°C): (○) 240; (△) 255; (□) 270.

cross head speed of 0.4 mm/min. The gage length was 10 cm. The tensile modulus and strength per unit area of carbon fibers were found from the load-extension curves. The error in tensile modulus due to machine deflection was negligible. Each value was the average of 10 determinations. The cross-sectional area of the carbon fibers was calculated from their linear density and density.

RESULTS AND DISCUSSION

Figure 2 shows the relationships between density and stabilization time for the acrylic fibers stabilized at 240°C, 255°C, and 270°C in air for various times. The higher the stabilization temperature is, the shorter the stabilization time required to reach a constant value of density. The density of the acrylic fibers approaches a constant value of about 1.58 g/cm³ at longer stabilization times independently of stabilization temperature.⁹

In Figure 3(A) the linear density is plotted as a function of density for

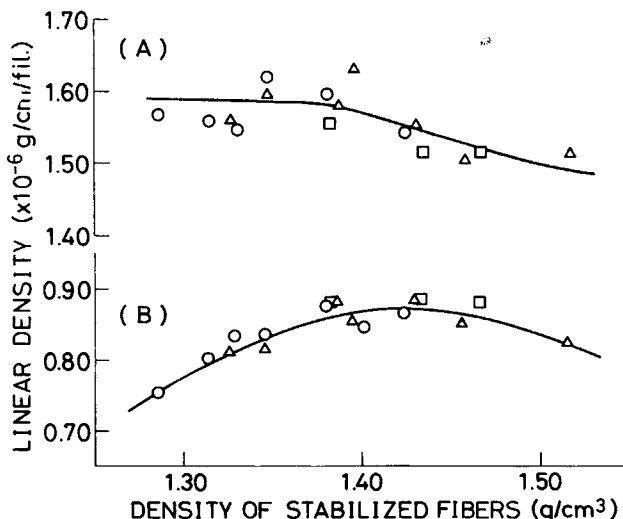


Fig. 3. Plots of the linear density of stabilized fibers (A) and that of carbon fibers (B) against density of stabilized fibers. Stabilization temperature (°C): (○) 240; (△) 255; (□) 270.

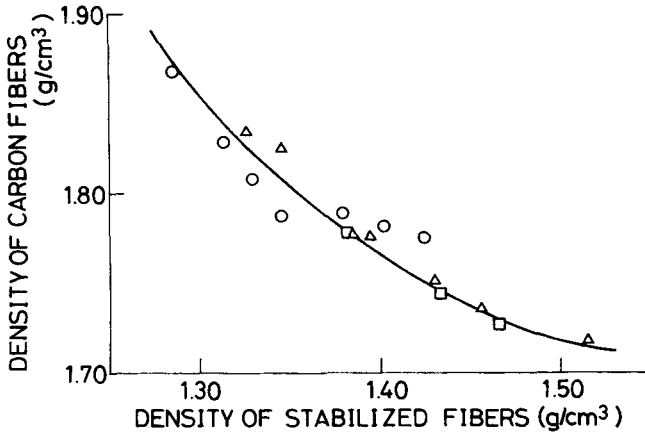


Fig. 4. Plots of the density of carbon fibers against that of stabilized fibers. Stabilization temperature (°C): (○) 240; (△) 255; (□) 270.

the stabilized fibers. The linear density of stabilized fibers tends to decrease at higher densities. That is, the degradative loss in mass during stabilization becomes evident when the acrylic fibers are heat-treated until yielding densities higher than about 1.40 g/cm³. In Figure 3(B) the linear density of carbon fibers is plotted against the density of the stabilized fibers from which the carbon fibers were obtained. The linear density of carbon fibers seems to form a broad maximum over the density range from about 1.39 to 1.49 g/cm³ of stabilized fibers. The stabilized fibers which have densities lower than about 1.38 g/cm³ give carbon fibers of lower linear densities, and exhibit a significant loss in mass during carbonization.

Figure 4 shows the relationships between the density of carbon fibers and that of stabilized fibers. The density of carbon fibers decreases with increasing density of the stabilized fibers.

In Figure 5 the tensile modulus of carbon fibers is represented as a function of the density of stabilized fibers. The variation of the tensile modulus of carbon fibers with the density of stabilized fibers is small if stabilization temperature is constant. The tensile modulus of carbon fibers, however, changes with stabilization temperature. That is, the carbon fibers

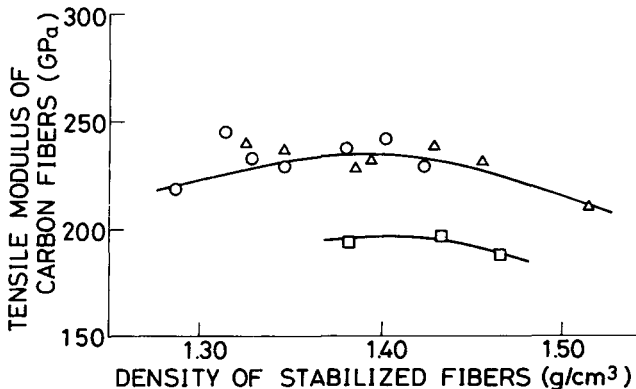


Fig. 5. Plots of tensile modulus of carbon fibers against density of stabilized fibers. Stabilization temperature (°C): (○) 240; (△) 255; (□) 270.

TABLE I
Stabilization Conditions and Orientation Parameter

Stabilization conditions	Stabilized fibers		Carbon fibers	
	Density (g/cm ³)	Orientation	Orientation	Tensile modulus (GPa)
240°C for 300 min	1.423	0.73	0.79	230
255°C for 145 min	1.429	0.73	0.79	240
270°C for 68 min	1.433	0.69	0.78	197

which were prepared from acrylic fibers stabilized at 270°C are lower in tensile modulus than those prepared from acrylic fibers stabilized at temperatures below about 255°C.

The values of the orientation parameter for stabilized fibers and those of resulting carbon fibers are shown in Table I, where the stabilized fibers were prepared under three different temperature–time conditions giving similar densities after stabilization. The tensile modulus of carbon fibers is thought to reflect more or less the orientation of carbon networks, although a significant difference is not found among the values of the crystalline orientation of the carbon fibers in Table I. On the other hand, the orientation after the stabilization stage is lower for the fibers stabilized at 270°C than for the fibers stabilized at temperatures below 270°C. This implies that the cyclized structure of higher orientation, which is formed during stabilization, favors the growth of oriented carbon networks.

In Figures 6(A), (B), and (C) the tensile strength of carbon fibers is represented as a function of stabilization time at 240°C, 255°C, and 270°C, respectively. As is seen in Figure 6(A), the tensile strength of the carbon fibers from the acrylic fibers stabilized at 240°C is maximized at 150 min of stabilization time.

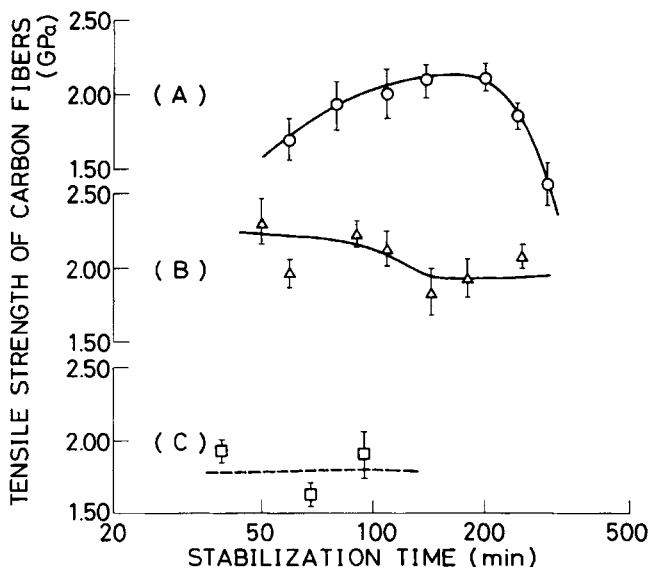


Fig. 6. Variation of tensile strength of carbon fibers with stabilization time. Stabilization temperature (°C): (A) 240; (B) 255; (C) 270.

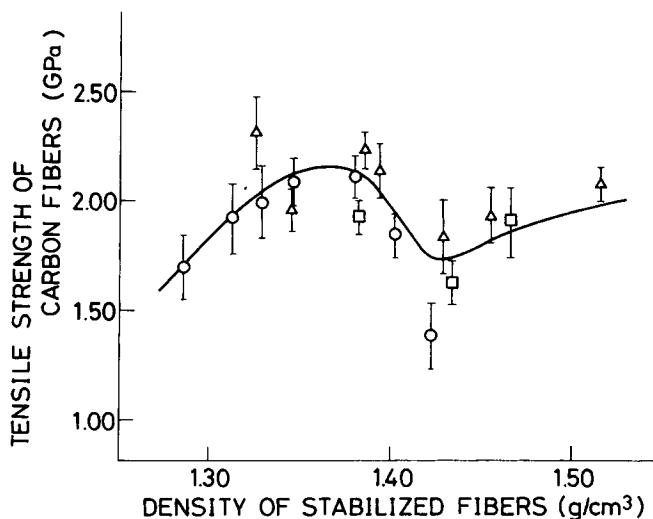


Fig. 7. Plots of tensile strength of carbon fibers against density of stabilized fibers. Stabilization temperature (°C): (○) 240; (△) 255; (□) 270.

The tensile strengths of carbon fibers in Figures 6(A), (B), and (C) are replotted in Figure 7 as a function of the density of stabilized fibers. It appears that the optimum density of stabilized fibers for producing carbon fibers higher in tensile strength lies in the range from about 1.34 to 1.39 g/cm³. The oxygen content of the stabilized fibers having densities in this range is about 5–9 wt %.⁹

From the view point of processing acrylic fibers to carbon fibers in a short time, a density required for stabilized acrylic fibers is desirable to be low. Moreover, as is depicted in Figure 4, the density of carbon fibers decreases with increasing density at the stabilization stage. This suggests that the extent of microvoid formation in carbon fibers increases with increasing density of the stabilized fibers. A microvoid can be a defect that decreases strength. In conclusion, it appears that the acrylic fibers require a stabilization giving densities in the range of about 1.34–1.39 g/cm³. Excess stabilization yielding densities higher than 1.39 g/cm³ appears to introduce excessive microvoids into the carbon fibers, resulting in reduced strength.

References

1. A. Shindo, *Rept. Gov. Ind. Res. Inst., Osaka, No. 317*, (1961).
2. P. J. Goodhew, A. J. Clark, and J. E. Bailey, *Mater. Sci. Eng.*, **17**, 3 (1975).
3. W. Watt and W. Johnson, *Appl. Polym. Symposia*, **9**, 215 (1969).
4. O. P. Bahl and L. M. Manocha, *Carbon*, **12**, 417 (1974).
5. U. S. Pat. 3,539,295 (1970).
6. R. M. Gill, *Carbon Fibres in Composite Materials*, The Plastics Institute, London, 1972, p. 50.
7. Jpn. Pat. Application, 51-25487 (1976).
8. Jpn. Pat. Application, 50-29532 (1975).
9. A. Takaku, S. Terui, F. Taga, N. Okui, and J. Shimizu, *Sen-i Gakkaishi*, **38**, T-398 (1982).
10. G. Farrow and J. Bagley, *Text. Res. J.*, **32**, 587 (1962).

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