The Mechanical Properties of Carbon Fibers Grown by the Pyrolysis of Natural Gas

W. E. Yetter, C. P. Beetz, Jr.
and G. W. Budd
General Motors Research Laboratories
Warren, Michigan 48090-9055

Introduction

In this paper we examine the mechanical and structural properties of carbon fibers produced by the pyrolysis of natural gas. The method of fiber growth involves flowing natural gas through a type 304 stainless steel tube held at elevated temperatures (900-1200°C).[1,2] Filamentary forms of carbon produced from carbon-containing gases at elevated temperatures have been known for some time. Baker[3] reviews the literature on submicron diameter fibers, or "vermicules," produced during the high temperature disproportionation of CO or hydrocarbon gases. The fibers of more interest to us here, however, are straight fibers of macroscopic length with diameters of at least several micrometers -- i.e. fibers of potential utility for such applications as composite reinforcement. Previous reports of macroscopic fibers produced by "Chemical Vapor Deposition" (CVD) during the pyrolysis of carbonaceous gases date back to P. and L. Schutzenberger[4] (1890), and to C. and H. Pelabon[5] (1903). More recently, macroscopic fibers have been grown by Gibson, et al.,[6] Bourdeau and Papalegis,[7] Weisbeck[8] Hillert and Lange,[9] Katsuki, et al.,[10] Onum and Koyama,[11] and Koyama, et al.[12] Weisbeck, Hillert and Lange, and Koyama, et al. all report a similar fiber structure: concentric layers (like the annular layers of a tree) of turbostratic carbon with a high degree of alignment of the graphitic basal planes along the fiber axis. No mechanical properties have been described for any of the above CVD fibers, however, with the exception of the fibers grown by Bordeau and Papalegis[7] and by Koyama, Endo, and co-workers.[12,13]

Our aim in this paper will be to describe the mechanical properties of carbon fibers produced by pryolysis of natural gas and to suggest the microstructural sources of these properties. Variations between batches of fibers indicate that fiber properties are to some extent a function of the exact growth conditions. Therefore, we will present data for three different, although typical, growth batches.

Experimental Procedure

The fibers tested were from growth batches labeled here as 201, 205 and H7C (79, 60 and 38 fibers, respectively). Single fibers were mounted on gage tabs with crystal bond 509. Fiber diameters were determined from photographs taken through an optical microscope at 1100X. Load vs time curves were recorded using an Instron apparatus (model TM-SML) under control of a DEC PDP-11/03 computer. All tensile data was corrected for Instron compliance using 10 μ diameter tungsten wires for calibration. In order to preserve fibers fractured in testing, a technique adopted from that of Jones[14] et al. was used. The fibers were strained to failure at a rate of 0.125 mm/min for batches 201 and 205 and 0.05 mm/min for H7C. Fiber fracture surfaces were examined in a scanning electron microscope.

Tensile Strength and Strength-Limiting Defects

The as prepared fibers fail in a brittle fashion. Figure 1 shows a typical pair of matching fracture surfaces, the cup-and-cone failure is quite common and sometimes becomes quite exaggerated, due to the tendency of the fracture front to follow the easy-shear directions of the graphitic basal planes.

Average tensile strength values for batches 201, 205 and H7C are given in Table 1. Each tensile strength distributions is quite wide: the standard deviations are 57%, 51%, and 55% for batches 201, 205, and H7C, respectively. A wide spread in strengths is, of course, expected for a brittle material which contains defects with a range of types and sizes. To determine the nature of these defects we have examined the fracture surfaces of one of the tested fiber batches, H7C, in the scanning electron microscope.

Roughly 90% of the H7C fibers tested were

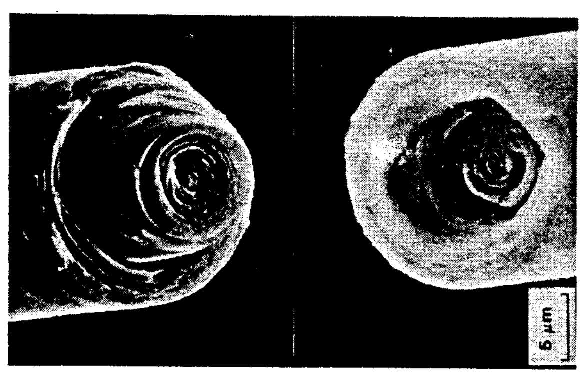

Figure 1. The opposing fracture surfaces of a PYROGRAF fiber broken in tension. Note the layered structure and the "cup-and-cone" nature of the fracture; also note that the two pieces key into each other.

Table 1. Summary of Tensile Test Results.

Batch #	E_I(GPa)	E_F(GPa)	σ_F(GPa)	Diameter (μm)	No. of fibers	Gauge Length (cm)	Strain to-Fail (%)
#201	176	203	0.98	25.3	79	1.27	0.48
#205	143	155	0.91	10.2	60	1.27	0.58
H7C	151	159	0.69	19.7	38	1.27	0.44

recovered intact for SEM inspection. Fracture surface pairs were seen to match for 70% of the recovered specimens. The most common defect was an "intersection," observed at 44% of the failure sites. An intersection is presumably formed when two fibers cross and adhere during thickening, so that subsequently deposited layers surround both. A second type of defect, which we call a "glassy blob," accounts for 9% of the failures. They are thought to form from collisions with large, tarry, viscous hydrocarbon globules floating in the growth furnace. "Surface nodules" account for 6% of the fractures in this particular batch. They appear to be carbon growth catalyzed by the action of larger Fe, or Fe-rich, particles which are generated from the walls of the growth tube by metal dusting corrosion[1] and adhere to the fiber during thickening.

The fourth type of observed defect is the inclusion, a foreign particle incorporated during thickening. Inclusions were found at 6% of the fracture sites. The remainder (35%) of the fracture surfaces in batch H7C contained no visible defects. In these cases the defects probably were either too small to be detected by SEM fractography or were of such a nature as to escape detection (for example, preexisting cracks).

The effects of these types of defects on the tensile strength is summarized in Fig. 2, in which the contributions from each type of defect are stacked to form the total strength distribution. It is clear that the strongest fibers are those that contain "undetectable" defects. The average

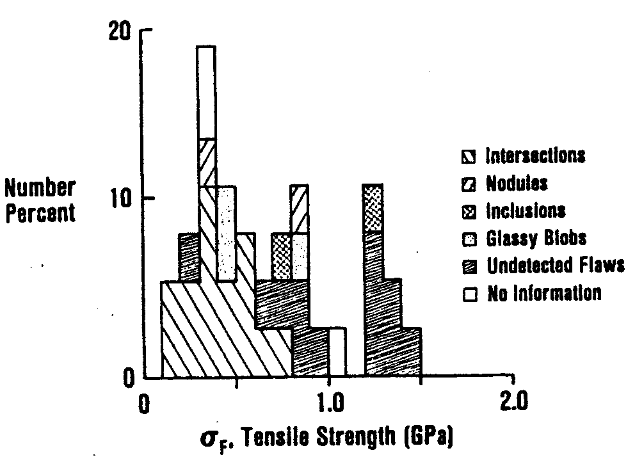

Figure 2. The number frequency vs. tensile strength distribution for H7C, broken down according to the type of failure-causing defect; the number percents in each category are stacked to form the total distribution.

strength of this category is 1.0 GPa. Intersections, on the other hand, are the most severe defect and fibers containing them are clustered at the weak end of the distribution. Fibers containing glassy blobs, surface nodules, or inclusions lie in the middle range.

Acknowledgments

The authors would like to thank G. G. Tibbetts and M. G. Devour for providing the fibers used in these experiments, W. H. Lange for several of our micrographs, R. M. Murie for the use of his scanning electron microscope, J. L. Johnson for assisting with our x-ray diffraction experiment, and G. W. Smith, J. R. Bradley and G. G. Tibbetts for helpful discussions.

References

1. G. G. Tibbetts, Appl. Phys. Lett. 42, 66 (1983).
2. G. G. Tibbetts, "Carbon Fibers Produced by Pyrolysis of Natural Gas in Stainless Steel Tubes," 16th Biennial Carbon Conference, San Diego, CA, 18-22 July 1983.
3. R. T. K. Baker and P. S. Harris, Chemistry and Physics of Carbon, P. L. Walker and P. A. Thrower, eds., (Dekker, New York, 1978), Vol. 14, p. 83.
4. P. and L. Schutzenberger, C. R. Acad. Sci. 111, 774 (1890).
5. C. and H. Pelabon, C. R. Acad. Sci. 137, 706 (1903).
6. J. Gibson, H. L. Riley, and J. Taylor, Nature 154, 544 (1944).
7. R. G. Bourdeau and F. E. Papalegis, U.S. Patent No. 3,378,345, 16 April 1968.
8. R. Weisbeck, Carbon 9, 525 (1971).
9. M. Hillert and N. Lange, Z. Krist, 111, 24 (1958).
10. H. Katsuki, K. Matsunaga, M. Egashira, and S. Kawasumi, Carbon 19, 148 (1981).
11. Y. Onuma and T. Koyama, Oyo Butsuri 32, 857 (1963).
12. T. Koyama, M. Endo, and Y. Onuma, Japanese J. of Appl. Phys. 11, 445 (1972).
13. T. Koyama, M. Endo, and H. Yoshihiro, Japanese J. of Appl. Phys. 13, 1933 (1974).
14. J. B. Jones, J. B. Barr, and R. E. Smith, J. Mat. Sci. 15, 2455 (1980).