Density-Modulus Relationship in Graphite Fibers Made from Acrylic Yarns

Abstract. *Three types of polyacrylonitrile yarn were converted to graphite fibers. There was a linear relation between density and Young's modulus of the graphite fibers, the ranges observed being 1.58 to 2.18 grams per cubic centimeter and 25 to 112 $\times$ 10^6 pounds per square inch.*

I have found a linear relation between Young's modulus and density for graphite fibers (of acrylic fiber origin) with high tensile strengths and high moduli. The graphite fibers were prepared from three dissimiliar textile fibers; the temperatures of graphitization ranged from 2200° to 2950°C. Moduli based on the averages for single fibers were from 25 million to 112 million pounds per square inch (psi; 1 psi = 70 g/cm^2); fiber densities were from 1.575 to 2.175 g/cm^3.

The acrylic fibers used were: Courtelle tow (Courtaulds Ltd.), a continuous fiber of 1½ denier per filament, containing 6 to 7 percent methyl acrylate comonomer (*1*); an acrylonitrile homopolymer (PAN) yarn of high tenacity, 7.1 g per denier; and Dralon T (Farbenfabriken Bayer A. G.), a moderately oriented yarn prepared with less than 1 percent comonomer. Courtelle filaments have circular cross sections; the other two fibers are mostly dogbone in shape with some trilobar filaments present.

Fiber densities were measured in density gradient columns prepared from *o*-dichlorobenzene and *sym*-tetrabromoethane. Tensile properties of the graphite fibers were determined with an Instron tensile tester. The test method, (*2*) was improved by making compliance corrections which raise the moduli nearer the true values. Most of the tensile strength and modulus values are averages of measurements from at least eight single filaments. The average cross-sectional areas of fibers were obtained from planimetric measurements of 15 filaments in optical photomicrographs.

Values for Young's moduli and for density are plotted in Fig. 1, A–D, with the temperatures of graphitization indicated for each sample. The overall range of moduli seems to depend somewhat on the precursor. For example, of 16 samples of graphite fiber made from Courtelle tow, none had average moduli over 65 million psi. These data (Fig. 1A) had more scatter than the results for graphite fibers from the other precursors, probably because more variations were used in the processing of the Courtelle. However, the increase in density of the fibers is striking as the modulus increases from about 30 to 64 million psi.

Values for samples made from the PAN yarn are given in Fig. 1B. The density increases less with the modulus for the PAN precursor, at least, in the modulus range of 40 to 90 million psi, which I obtained for this group of fibers. (Modulus values for some individual fibers lowered, or in one instance raised, the average enough to be ques-

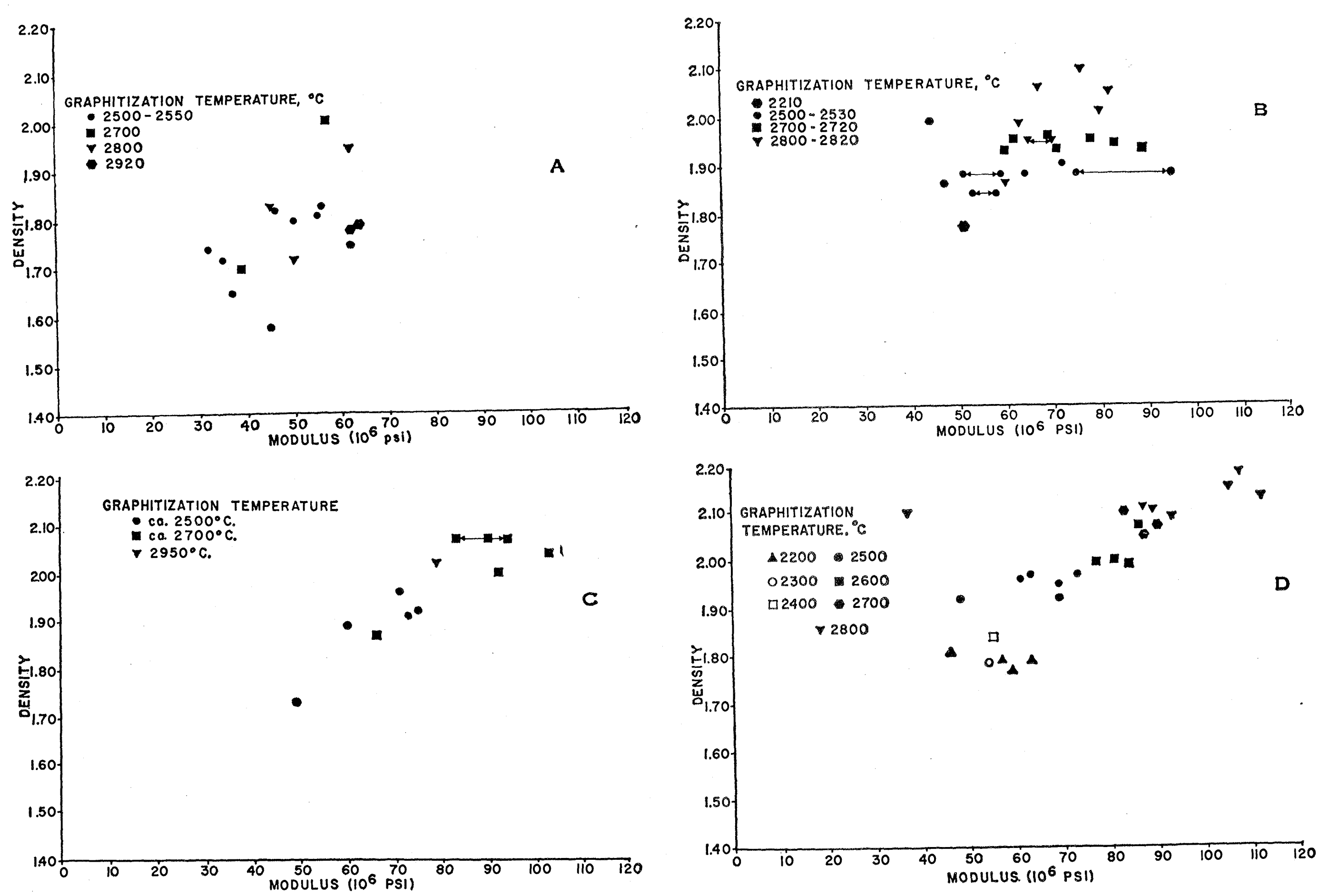

Fig. 1. Density (g/cm^3) and modulus values for graphite fibers from acrylic precursor yarns. (A) Courtelle, (B) PAN, (C and D) Dralon T.

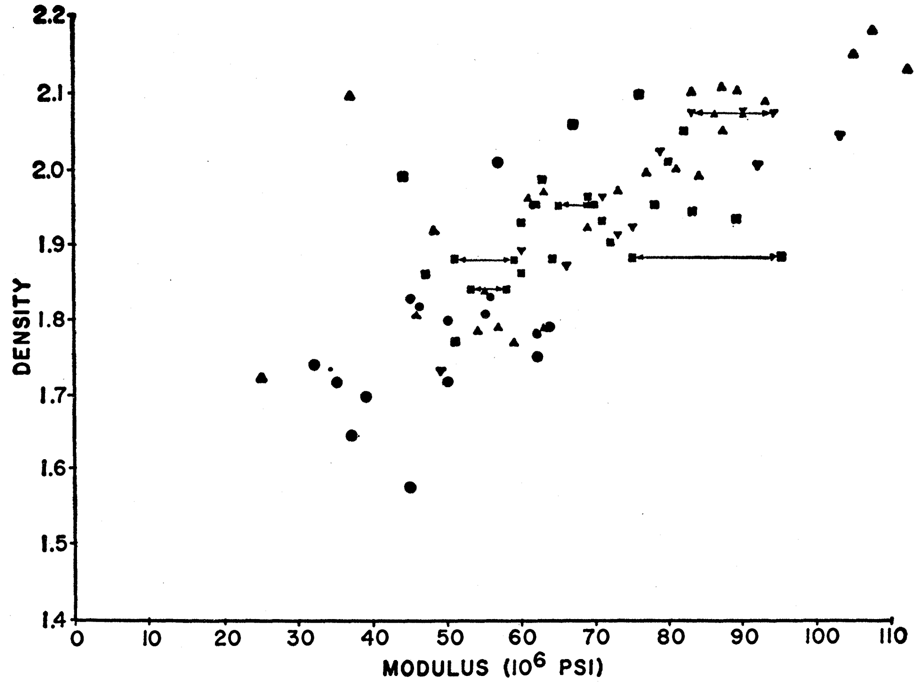

Fig. 2. Density (g/cm³) and modulus values for graphite fiber samples from all of the acrylic precursors: (●) Courtelle, (■) PAN, (▲ and ▼) Dralon T.

tionable; in these instances, both averages were plotted, and the values were connected by arrows.)

Two different sets of processing conditions were used in the first treatment stage for Dralon T; the graphite fibers from Dralon T were divided into two corresponding groups. The data for these fibers are shown in Fig. 1, C and D. The values in Fig. 1C can be represented by either a linear relation or by a curve for which the slope decreases slightly with increases in temperature. The same sort of slope could be drawn for the data in Fig. 1D, with the inflection more clearly defined above 90 million psi.

Data for all the samples are plotted in Fig. 2 and show that all of the series fit the same general linear relation between density and modulus. Several other variables were under investigation in these experiments and may account for the considerable scatter in much of the data.

Certain parameters can influence density or modulus, or both, at a specific graphitization temperature (*3*). However, the data in Fig. 2 show a relation between the two properties which holds in spite of these precursor and processing variations.

Data for the tensile strengths of these fibers is much more scattered. Least-squares lines were plotted by computer for the changes in fiber density as tensile strength was increased. These showed a slight decrease for Courtelle-precursor samples, an even slighter increase for PAN-derived fiber, and no density change for the fibers from Dralon T.

The data on the density and modulus properties for the acrylic-derived fibers should be compared with those for graphite fibers prepared from other precursors. Although other polymers have been used in precursor yarns, rayon and polyacrylonitrile give the graphite fibers with the highest moduli (*4*). Some investigators have reported on density-modulus relations in rayon-derived fibers. Gibson and Langlois (*5*) showed that the apparent density increased directly with the Young's modulus between 20 and 50 million psi. Bacon and Schalamon (*6*) found a similar increase; they stated that the behavior had not yet been well characterized but gave values of 1.35 and 1.95 g/cm³ for fibers with 10 and 100 million psi moduli, respectively. A linear interpolation between the two values was considered an adequate representation of the available data. The density-modulus line for these graphite fibers would be substantially lower than the trend shown in Fig. 2 for fibers from acrylic polymers.

A higher modulus at equivalent density cannot be assumed to be due to a higher degree of graphitization in the rayon-derived fibers. Rayon precursors form graphite fibers with long, needle-like micropores parallel to the fiber axis. These pores, described by Perret and Ruland (*7*), represent as much as 30 percent of the fiber volume; they are inaccessible to helium and account for the low density. On the basis of comparative x-ray diffraction patterns and interlayer spacings, the acrylic-derived fibers are actually more graphitic (*8*).

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References and Notes

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Horseshoe Crab Lactate Dehydrogenases: Evidence for Dimeric Structure

Abstract. D-*Lactate dehydrogenase of* Limulus polyphemus *occurs in six molecular forms, not in five as does the* L-*lactate dehydrogenase of vertebrates. The electrophoretic pattern of bands in an apparent genetic variant is incompatible with a model of tetrameric molecular structure, and suggests, rather, that the three more anodally migrating isozymes are dimer molecules, the polypeptide subunits of which are encoded by two genetic loci and are not involved in the formation of the lower triad of isozymes.*

Long and Kaplan (*1*) reported that the lactate dehydrogenase (LDH) of the horseshoe crab *Limulus polyphemus* differs from the LDH of vertebrates in being specific for D-lactate rather than for L-lactate, in having a molecular weight of 65,000 as opposed to 140,000 to 150,000, and in occurring in six