PREDICTION OF FINAL PROPERTIES IN CARBON FIBERS USING AS-SPUN DEGREE OF PREFERRED ORIENTATION

T.R. McCormick, A.B. Barnes, W.D. Nothwang, F.M. Dauche, C.C. Fain and D.D. Edie
Center for Advanced Engineering Fibers and Films
Clemson University, Clemson, SC 29634

Introduction

The processing of high thermal conductivity mesophase-based carbon fibers is critical for heat-dissipation applications. These properties are directly related to the degree of preferred orientation of the graphene basal planes with respect to the fiber axis [1,2]. Thus, the development of molecular orientation during fiber formation is essential if the mechanical and transport properties of the graphitized fibers are to be maximized.

In the present work, X-ray diffraction was used to predict the final graphitized properties of carbon fibers by measuring the degree of preferred orientation of the aromatic molecules within the as-spun fibers. It is believed that the as-spun orientation within the fiber should indicate the fiber's potential to develop good final properties. To validate this, fibers were melt spun from three different mesophase pitch-based precursors using various spinning parameters in order to create differences in the degree of preferred orientation between fiber sets.

Experimental

Fiber spinning was accomplished using two different melt-spinning apparati. Two ribbon-shaped fiber groups, designated R1 and R2, were melt-spun from two different precursors using a batch melt-spinning extruder and a continuous melt-spinning extruder respectively. Both sets were formed using flat-entry spinneretes. The round fiber group used in this study, designated Rd, was formed using the batch melt-spinning apparatus. Each group of fibers was produced from a different mesophase pitch-based precursor and contained three different fiber sets.

The degree of preferred orientation in each of the as-spun and graphitized fiber sets was measured using X-ray diffraction. A small unidirectional composite from each fiber set was prepared by submerging a fiber bundle in paraffin wax. Excess wax was removed and fiber alignment was accomplished by hand. After the composite was cooled, it was glued to an aluminum ring. This sample, which has an outside diameter of 2.54 cm and a thickness of 0.8 cm, was then placed into the transmission attachment of a Scintag XDS 2000 diffractometer. The orientation of the graphene basal planes with respect to the fiber axis was quantified for as-spun and graphitized samples by an azimuthal scan of the (0002) diffraction line using CuKα radiation. The prepared unidirectional composite was placed into the transmission attachment of the diffractometer in a horizontal position. A continuous scan over the range of 24° to 28° 2Θ allowed for identification of the (0002) maximum intensity using the background subtraction and profile fitting features of the Diffraction Management System (DMS) software. An azimuthal scan was then performed with the goniometer set at the 2Θ angle of the (0002) maximum, while the sample was rotated in the plane normal to the incident radiation. Intensities were collected during a rotation of 360° in increments of 1° with a hold time of 10 sec/°. The full width half maximum (FWHM) intensity, or Z-value, of the azimuthal scan, was determined using the profile fitting feature of the DMS software. This value represents the relative misalignment of graphene basal planes with respect to the longitudinal axis of the fiber.

Oxidation of the three fiber sets was performed at conditions previously determined to be suitable for each of the three fiber types. All fiber sets were graphitized in a Helium atmosphere from room temperature to 1800°C at 20°C/min, 1800°C to 2400°C at 10°C/min, and held for 15 minutes at 2400°C.

The mechanical properties of each fiber set were determined using the technique described under ASTM D 3379-75 and an Instron Model TM tensile-testing machine. The area measurements for the ribbon shaped fibers were accomplished using optical microscopy. However, the areas of the round fiber set were measured using a laser diffraction technique [3]. For all three fiber sets, fifty single filaments were tested to determine the average modulus and tensile strength.

Electrical resistivities of all fiber sets were determined using a typical four-point probe method similar to that employed by Coleman [4]. For resistivity, approximately 25 single filaments were tested to determine the average electrical resistivity.

Results and Discussion

Three different precursors were spun into round and ribbon-shaped fibers in order to test the reliability of as-spun degree of preferred orientation as an indication of final properties. For simplification, these fiber groups are referred to as Rd, R1 and R2, with each group consisting of three different fiber sets. It is believed that the degree of preferred orientation in the as-spun fibers should be indicative of the degree of preferred orientation in the graphitized fibers as well as the fibers potential to develop other desired properties, such as high modulus and high thermal conductivity. The basis for this hypothesis lies in the belief that factors which typically lead to large crystallite size and low $d_{(0002)}$ spacing also contribute to alignment of the basal planes. Past work has shown that, the ability of the fiber to develop a highly oriented structure during graphitization is limited by the fiber orientation in the as-spun state. Figure 1 shows the correlation between as-spun and graphitized degree of preferred orientation for the three fiber groups. The fiber group Rd exhibits the best degree of preferred orientation in both the as-spun and graphitized states. Similarly, R1 proved to be better than R2. Similar trends should exist for other fiber properties such as modulus and electrical resistivity. In fact, the ranking of the fiber groups predicted in Figure 1 is also present for both modulus and electrical resistivity. Figures 2 and 3 show that in fact, there exists such a correlation for modulus and electrical resistivity, respectively.

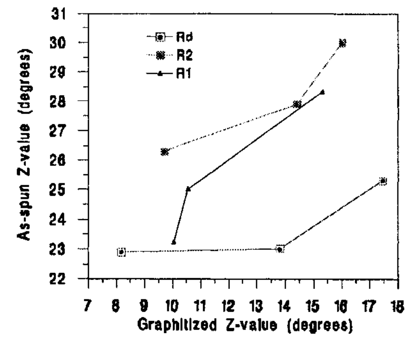

Figure 1. As-spun vs. Graphitized Z-value for R1, R2 and Rd.

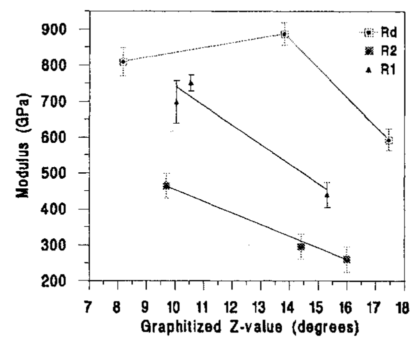

Figure 2. Modulus vs. Graphitzed Z-value for R1, R2 and Rd (Based on 95% confidence interval).

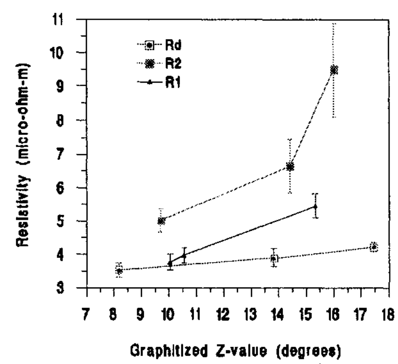

Figure 3. Electrical resistivity vs. Graphitized Z-value for R1, R2 and Rd (Based on 95% confidence interval).

Conclusions

Although it is true that many factors effect the final properties of carbon fibers, the degree of preferred orientation is critical. It is indicative of a fiber's ability to develop high modulus and low electrical resistivity. The reproducibility of the correlation between the degree of preferred orientation and properties such as modulus and electrical resistivity also holds true for fibers spun from different precursors under various spinning conditions. Therefore, it can be concluded that as-spun degree of preferred orientation provides an efficient, cost effective method for estimating a fibers ability to develop improved mechanical and transport properties.

Acknowledgments

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References

1. Ruland, W., *Appl. Poly. Symp.*, 1969, 9, 293.
2. Rand, B., in *Handbook of Composites, Strong Fibers*, Vol 1, ed. W. Walt and B. V. Perov, Elsevier, New York, 1985, p. 495.
3. Tzeng, S.S. and Diefendorf, R.J., in *Proceedings of 21st Biennial Conference on Carbon*, Buffalo, NY., 1993. pp.12-13.
4. Coleman, L. B., *Rev. Sci. Instrum*, 1975, 46(8), 1125.