HOLLOW CARBON FIBERS

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Introduction

Ultra-lightweight materials are enabling for a number of applications including space-based and transportation. Heretofore, innovative designs using existing materials has been the approach to produce lighter-weight components. Graphite fiber, because of its lightweight and high strength, reinforced composites has been a material of frequent choice to produce lightweight systems. Hollow graphite fibers with the same strength at the same fiber size would be lighter than standard solid graphite fibers and thus would save weight with a potential of up to 50%. They key to achieving large weight savings with graphite fiber composites is to demonstrate a reliable process for producing hollow fibers with high strength.

Experimental

Pitch was selected as the precursor to produce hollow graphite fibers. Both petroleum and coal tar pitch was investigated as precursors. Two approaches were investigated to produce hollow graphite fibers. In one variation, a known readily spinnable fiber composition of Nylon or Polystyrene, which had a low char yield, was spun as a core to a pitch fiber. The easily spinnable and strong core fiber would make the pitch much stronger in the green stage and when pyrolized/carbonized, the inner core fiber would shrink because of the low char yield and leave a hollow core inside the high char yield pitch sheath. The other spinning variation was to insert a fine needle in the spinerette head, which would leave a hollow core as the pitch quickly cools after it exits the spinerette head.

The pitch precursors were prepared by dissolving in boiling 1-methyl-2-pyrrolidinone (NMP) and filtering to remove any insolubles followed by boiling off the NMP. The pitches were heated with stirring under various protocols to provide softening points ranging from 135 to 232°C. Both isotropic and mesophase pitches were utilized.

Results and Discussions

It was possible to produce hollow fibers with both spinning techniques. The dual spinning approach was more sensitive to spinning conditions as the softening point of the pitch needed to be within no more than 15-20°C of the polymer-core material. Also, during pyrolysis/carbonization, the temperature rise needed to be very slow to prevent the gases generated by core material from rupturing the carbon sheath. Expansion of the core before shrinkage from the pyrolysis could also crack the outer carbon sheath. For these reasons, more emphasis was placed on the second spinning method of using a needle in the spinerette head. It was possible to spin hollow fibers from all the pitches, however, the higher the softening point of the pitch, the easier it was to produce a hollow fiber.

After spinning a pitch fiber, it must be stabilized by oxidation to prevent fusion during subsequent pyrolysis/carbonization. It was found oxidation must be performed at a slow rate of no more than about 1°C/minute and preferably slower to prevent the thin fiber walls from distorting or cracking. After stabilization it was also necessary to heat at a slow rate to maintain the integrity of the fiber wall.

The savings in weight at 25% and 50% for a hollow carbon fiber is shown in Figures 1 and 2 with respect to fiber ID, OD and wall thickness. Obviously the thinner the wall and the larger the diameter the greater the weight savings. However, for practical components the OD should not exceed about 50μ and preferably for compositing a smaller diameter in the 15-20μ size range is most desirable. The weight savings relative to commercial PAN based fiber at 7.5μ is shown in Table I.

The investigations to produce hollow graphite fibers showed that a wall thickness less than about 2μ was not practical under the conditions investigated. Thus, a wall thickness in the 3μ+ range is desired, which, when coupled with the desired weight savings from Figures 1 and 2, and Table I, defines the OD of fiber required.

It was possible to produce hollow fibers as shown in Figures 3 and 4. The strength of the hollow fibers from various batches varied from as low as 0.86GPa to as high as 4.2 GPa. The typical strength was in the 2.7-3.7 GPa range, which is similar to commercial PAN fibers and generally higher than commercial pitch based fibers. Sufficient hollow fibers were produced to fabricate a carbon-carbon composite. A duplicate composite was made using a commercial pitch fiber, P30X. The hollow fiber composite had a density of 1.15 g/cc and the P30X composite had a density of 1.68 g/cc. The strength of the hollow fiber composite was 149MPa and the P30X was 160 MPa. The strengths were within about 7% but the hollow fiber composite was 46% lighter. In the case of space based materials applications, this is a significant advantage as well as in transportation. For optical support systems, the isotropic property in the fiber is quite desirable to avoid differential expansion in different planes.

Conclusions

Hollow graphite fibers offer the potential of significant weight savings. It was demonstrated hollow fibers could be produced with good strengths that was translated to provide good composite strengths with a 46% weight savings in comparable tests using solid graphite fibers.

Acknowledgements

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Table I. Fiber relationships to weight savings relative to commercially available 7.5μ PAN graphite fibers

Fiber Diameter of Commercial Fiber μ	ID of Fiber to Achieve 25% Net Savings	Wall Thickness at 25% wt. Savings in μ	ID of Fiber to Achieve 50% Net Savings	Wall Thickness at 50 Wt. Savings μ
7.5	3.14	2.18	5.03	1.24
12	4.37	3.82	7.79	2.11
OD of Hollow Fiber				
15	5.47	4.77	9.74	2.63
20	7.29	3.63	12.99	3.5

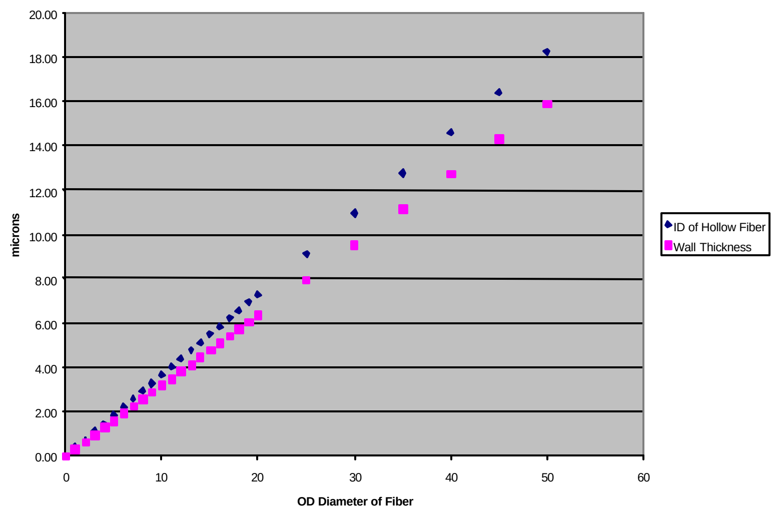

Figure 1. 25% wt% savings over similar diameter C fiber.

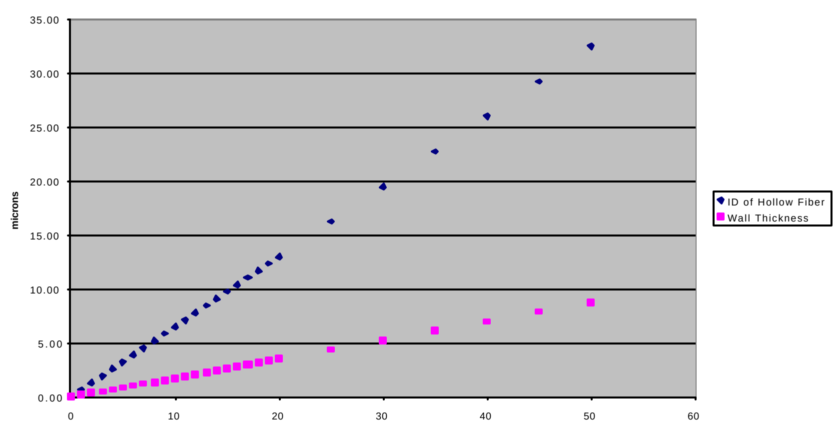

Figure 2. 50 wt% savings diameter C fiber.

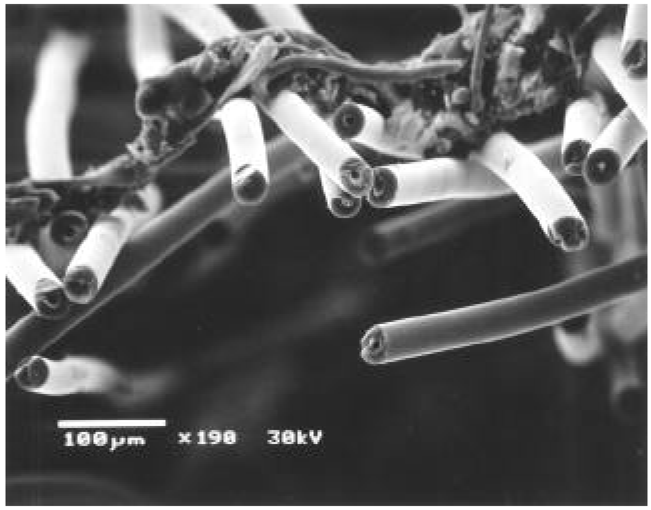

Figure 3. Hollow carbon fibers.

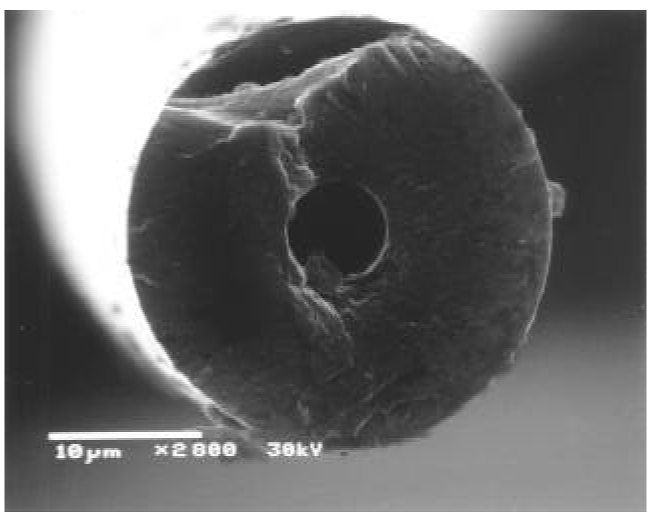

Figure 4. Hollow carbon fiber.