Single-Step Processing of Pitch-Based Carbon-Carbon Composites

*T. Ferguson, C. Lin, D. D. Edie, and A. A. Ogale**
Department of Chemical Engineering, and
Center for Advanced Engineering Fibers and Films
Clemson University, Clemson, SC 29634-0909

S. Manocha and L. M. Manocha
Sardar Patel University
Vallabh Vidyanagar, Gujrat 388120

Abstract

The single-step processing of carbon-carbon composites is a route to lowering the cost of such materials [1]. The present study investigated co-processing of pitch-based fibers and resin-based matrices into carbon-carbon composites. Ribbon-shaped pitch fibers were used as reinforcement and compression molded using phenol-formaldehyde and polyfurfuryl alcohol as matrix precursors. After stabilization, the samples were carbonized at temperatures ranging from 1100°C to 3000°C in a single step. The density of the composites ranged from 1.2 to 1.7 g/cm^3. The single-step composites displayed an average strength of about 14 MPa and an average flexural modulus of 9.4 GPa. Microscopic studies reveal that the matrix does not develop any preferred orientation in the vicinity of the fibers. There is also not much evidence of fiber-matrix bonding in composites with graphitized fibers.

Experimental

Two types of composites were prepared: Type I consisted of discontinuous ribbon-shaped pitch-fibers / phenol-formaldehyde matrix, whereas Type II consisted of unidirectional ribbon-shaped pitch-fibers / polyfurfuryl alcohol matrix. Type I composites were prepared as rectangular plaques nominally 103 cm x 10 cm x 3 mm, whereas Type II composites were nominally 50 mm x 8 mm x 2 mm. In Type I composites, as-spun pitch fibers were used. In Type II composites, both as-spun and graphitized fibers were used.

Type I composites were stabilized in a forced-air convection oven at 180°C for 24 hrs and at 250°C for about 48 hrs. These composites were carbonized in a Lindberg furnace 7 °C/min up to 160 °C, 1 °C/min up to 280 °C, 1 °C/min up to 500 °C, and 3 °C/min up to 1100 °C. Type II composites were stabilized at 180°C for 10 hrs and carbonized to 1000°C @ 20°C / hr. A few of these samples were further heat treated to 3000°C under Argon. The microstructure of the composites was studied using polarized optical microscopy (OM) and scanning electron microscopy (SEM).

Results and Discussion

Type I single-step composites that were composed of 50 wt. % ribbon-shaped fibers were found to have a flexural strength of 14.0 ± 6 MPa, a flexural modulus of 9.4 ± 0.1 GPa, and a density of 1.20 ± 0.08 g/cm^3. The "composites" consisting of 100 wt. % pitch fibers had similar flexural properties, but a much greater density of 1.71 ± 0.02 g/cm^3.

As illustrated in Fig. 1a, OM analysis of the samples revealed that the 50 wt. % composites contained about 33% void and had only a few deformed carbon fibers that survived the carbonization cycle. The 100 wt. % composite, however, had only 15.2 % void and contained clearly discernable ribbon shaped carbon fibers with cross-sectional dimensions of ≈ 10 μm X 50 μm after the carbonization cycle; see Fig. 1b. The 75 wt. % pitch fiber sample had some loss of fibers after carbonization, but retained many more 10 μm X 50 μm ribbon shaped fibers than did the 50 wt.% composites.

For Type II composites, Fig. 2 displays SEM micrographs of carbonized composites made with as-spun pitch fibers and graphitized pitch based fibers. For as-spun fibers, the matrix is found to be well adhered to the fibers. For composites made with graphitized fibers, the matrix is found to have shrunk away from the fibers. In the carbonized composites, the fibers were observed to be pulled out of the matrix. The same phenomenon was observed for graphitized samples. The matrix close to the fibers does not show any optical activity. Therefore, even after heat treatment to 3000°C, the matrix in such composites is not highly graphitic. This is contrary to the observations made in composites with PANOX fibers as reinforcement [2].

Conclusions

Ribbon shaped pitch fibers can be co-carbonized with matrix resins to obtain carbon-carbon composites in a single step. However, as the fraction of phenol-formaldehyde resin in a composite becomes greater, the single-step stabilization process becomes more difficult because of oxygen-diffusion limitation. For polyfurfuryl resin composites, the matrix appears to be well-adhered to the fibers after carbonization. However, orientation in the matrix in the vicinity of the fibers is not significant.

Acknowledgment

This research is based upon work partially funded by the National Science Foundation under Grant No. INT-9602141.

References

1. W. K. Kowbel, V. Chellappa, J. C. Withers, and P. O. Ransone, "Application of Net-Shape Molded Carbon-Carbon Composites in IC Engines", J. Advanced Materials, 27(4), 2-7, 1996.

2. L. M. Manocha, H. Bhatt, and S. M. Manocha, "Development of Carbon-Carbon Composites by Co-Carbonization of Phenolic Resin and Oxidized PAN Fibers," Carbon, 34 (7), 841-849, 1996.

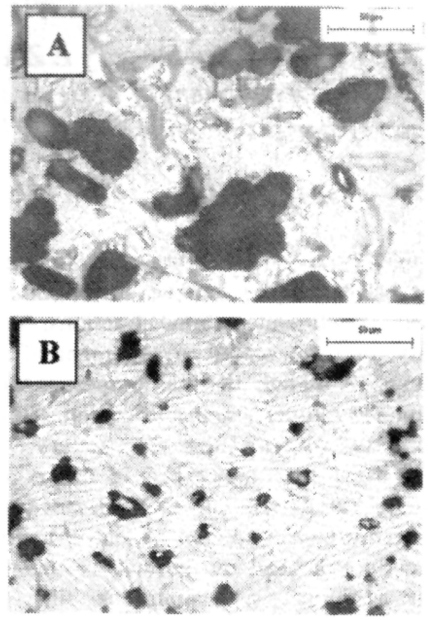

Fig. 1: Optical micrographs of carbon-carbon composites consisting of ribbon-shaped pitch based carbon fibers and phenol-formaldehyde based matrix. a: 50 wt% fibers; b:100 wt% fibers.

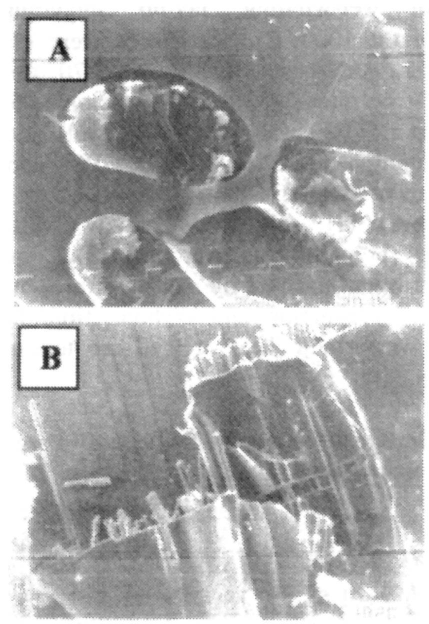

Fig. 2: SEM micrographs of carbon-carbon composites consisting of ribbon-shaped pitch based carbon fibers and polyfurfuryl alcohol based matrix.