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INTRODUCTION

The typical process cycle for a carbon-carbon composite begins with an organic matrix impregnated fibrous preform cured according to conventional composite practices (e.g., lay-up, bagging and autoclave cure: hot pressing: etc.). This cured composite is then subjected to a pyrolysis cycle in the absence of oxygen which results in the carbonization of the matrix. Carbonization cycles are carried out to temperatures of 650-800°C for several hours or even days. During these cycles as much as 50% of the matrix mix can be volatilized with simultaneous shrinkage and microcracking. The resultant porous, low density carbonaceous solid is usually densified by additional matrix impregnation and heat treatment steps.

The extreme length of the carbonization process is due to the heating cycle development methodology. The development of the material properties was not understood, so to keep catastrophic defects from occurring, the heating cycle was made very slow. To intelligently control the process the materials process/property relationship must be understood. In this study the relationsip between heating rate and physical development of *thecarbonization of a phenolic preform was investigated.*

EXPERIMENTAL

Eight ply, 30.5cm x 20.3cm (12" x 8") laminates, warp aligned and $[0/45/90-45]_s$[2] of Hercules UHM fiber and a phenolic resin[1] were autoclave cured to 177°C (350°F). The phenolic composites were cured to a void-free("non-porous") microstructure, where porosity was distributed through the fiber tows and resin. the cured resins were weighed and ultrasonically c-scanned with dimensional and density measurements taken.

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The various structured phenolic preforms were then carbonized to 850°C (1562°F) at programmed furnace heating rates of 2, 5, 10, and 50 °C/min. The composites were cut in half; half for testing, half for continued processing. The processing was completed with a graphitization cycle, followed by chemical vapor deposition (CVD), graphitization, then CVD.

Testing of the carbonized and densified composites consisted of weight and dimensional measurements (used to calculate density) and microscopy (fluorescent and bright field) evaluation. These test results showed the influence of the carbonization heating rate, lay-up geometry, and/or phenolic microstructure on the carbon-carbon material development.

## RESULTS AND DISCUSSION

The results from each test were analyzed to determine the effects of the carbonization heating rate, lay-up geometry, and/or phenolic microstructure had on the as carbonized and fully-densified composite microstructure.

When the thickness change from the cured phenolic to the carbonized state was analyzed, it was seen that the only effect was the "non-porous" thicknesses did not decrease as much as the "porous" composite thickness. The fully densified composite thickness any effect from the carbonization heating rate, lay-up geometry, and/or phenolic microstructure. All thickness data are shown in Table 1.

The weight change seen in Table 2, was measured through each process stage. Through the first carbonization cycle the weight change was greatly effected by the different phenolic microstructures, in which the porous phenolic composites lost less weight than the non-porous microstructure. The heating rate and ply construction did not influence the weight change. During densification, the composites carbonized at the different rates showed similar weight increases, however, the weight increase was different for the composites with the different phenolic microstructures and lay-up constructions. The "porous", quasi-isotropic composites gained more weight than the "non-porous", warp-aligned composites.

Density measurements, shown in Table 3, were taken to show the porosity changes during the process. As expected, the density decreased from the cured to the carbonized state, however, there was no density differences seen from the tested composite variables. The results show each composite density increased through the densification cycle to approximately the same final values. The different phenolic microstructures, lay-up geometry, and heating rates did effect the change in density through the various processes.

A microscopy analysis of samples showed the microstructurally "porous" composites contained more porosity than the microstructurally "non-porous" composite, even after the materials had been densified to the final state. The porosity in the "porous" densified samples could be characterized as frequent but larger than the "non-porous" samples. The quasi-isotropic construction seemed to contain less areas of porosity than the warp-aligned construction.

## CONCLUSIONS

With the composite configuration used for these experiments, heating rate did not significantly alter any of the microstructural characteristics. The density, weight change, and thickness were not effected as the composites were carbonized at the faster rates.

The difference in the initial microstructure did provide some differences in the composite microstructure. During the carbonization cycle, the phenolic composites cured to a "non-porous" microstructure, lost more weight yet had less thickness decrease than the "porous" phenolic microstructures. The difference in weight loss was due to the different resin contents and resin distribution in the cured composites. When the composites were densified, the "non-porous" microstructures gained less weight.

Before densification, there was no significant difference between the quasi-isotropic and the warp-aligned composites. After densification, the quasi-isotropic geometry gained more weight and contained less porosity than the warp-aligned composites. Apparently, the fiber weave was spaced to allow the maximum diffusion of the densification gases.

## REFERENCES

W. Phillips, et al., "Carbon-Carbon Composites Technology : Phase I Report", PL-TR-91-3061 (1991) Available NTIS, Springfield VA 22151.

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2 = 2°C/hour carbonization rate
5 = 5°C/hour carbonization rate
10 = 10°C/hour carbonization rate
50 = 50°C/hour carbonization rate
W + Warp Aligned Lay-up
Q = Quasi-Isotropic Lay-up
P = Porous phenolic microstructure
N = Non-porous phenolic microstructure

| Table 1. Thickness Measurements through the Process Stages | | |
|---|---|---|
| Composite ID | 1st Carbed C–C Avg Thickness Change (%) | Densified C–C Avg Thickness Change (%) |
| 2 WN | –5.1 | –0.7 |
| 2 WP | –3.4 | 1.2 |
| 2 QP | –3.6 | 4.5 |
| 2 QN | –5.3 | 2.7 |
| 5 WN | –5.7 | –3.0 |
| 5 WP | –4.2 | 0.8 |
| 5 QP | –3.0 | 1.0 |
| 5 QN | –7.7 | 4.8 |
| 10 WN | –4.2 | –2.9 |
| 10 WP | –3.3 | 0.0 |
| 10 QP | –2.9 | 0.7 |
| 10 QN | –5.5 | 5.8 |
| 50 WN | –3.4 | –2.7 |
| 50 WP | –3.3 | 1.9 |
| 50 QP | –3.6 | 2.4 |
| 50 QN | –6.2 | –1.0 |

| Table 2. Weight Change Data through the Process Changes | | |
|---|---|---|
| Composite ID | 1st Carbed C–C Avg Thickness Change (%) | Densified C–C Avg Thickness Change (%) |
| 2 WN | –26.1 | 15.9 |
| 2 WP | –24.0 | 23.9 |
| 2 QP | –28.5 | 28.4 |
| 2 QN | –27.1 | 24.7 |
| 5 WN | –15.6 | 16.4 |
| 5 WP | –14.1 | 22.4 |
| 5 QP | –17.3 | 27.6 |
| 5 QN | –16.3 | 25.3 |
| 10 WN | –14.8 | 15.4 |
| 10 WP | –15.9 | 20.6 |
| 10 QP | –17.2 | 28.2 |
| 10 QN | –16.5 | 25.4 |
| 50 WN | –15.8 | 21.2 |
| 50 WP | –15.1 | 15.9 |
| 50 QP | –16.9 | 23.1 |
| 50 QN | –17.0 | 28.7 |

Table 3. Density Measurements through the Process Stages

| Composite ID | 1st Carbed C-C | | Densified C-C | |
|---|---|---|---|---|
| | Avg density | Std density | Avg Density | Std density |
| 2 WN | 1.37 | 0.01 | 1.57 | 0.03 |
| 2 WP | 1.34 | 0.03 | 1.57 | 0.02 |
| 2 QP | 1.25 | 0.01 | 1.53 | 0.02 |
| 2 QN | 1.29 | 0.01 | 1.53 | 0.03 |
| 5 WN | 1.37 | 0.02 | 1.56 | 0.03 |
| 5 WP | 1.32 | 0.02 | 1.56 | 0.01 |
| 5 QP | 1.25 | 0.01 | 1.51 | 0.04 |
| 5 QN | 1.30 | 0.01 | 1.51 | 0.06 |
| 10 WN | 1.39 | 0.01 | 1.58 | 0.02 |
| 10 WP | 1.34 | 0.01 | 1.54 | 0.03 |
| 10 QP | 1.25 | 0.02 | 1.51 | 0.03 |
| 10 QN | 1.29 | 0.02 | 1.53 | 0.02 |
| 50 WN | 1.38 | 0.03 | 1.61 | 0.03 |
| 50 WP | 1.30 | 0.01 | 1.56 | 0.01 |
| 50 QP | 1.25 | 0.01 | 1.52 | 0.04 |
| 50 QN | 1.30 | 0.02 | 1.52 | 0.01 |