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Effects of Heat Treatment on Microstructure and Flexural Properties of Unidirectional Carbon–Carbon Composites

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Please note that the vertical axis of Figure 5, page 13, of the above-cited report (Effects of Heat Treatment on Microstructure and Flexural Properties of Unidirectional Carbon-Carbon Composites), is incorrectly labeled. It should read "μm/mm" and not "μm/cm." Please make this correction in your copy of the report.

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Microstructure and mechanical behavior of two unidirectional carbon-carbon (C-C) composite systems have been studied and correlated with their processing schedules. The composites were made with AMOCO T-50 PAN-based carbon fiber and one of two different carbon matrix precursors. The matrices are a state-of-the-art phenol-formaldehyde resin and a polyarylacetylene (PAA) resin obtained from cyclotrimerization of diethynyl benzene. The PAA resins have desirable properties as carbon precursors for C-C composites. The PAA matrix has a high carbon yield of 90% and exhibits less shrinkage during carbonization than the phenolic resin. The cyclotrimerized prepolymer also has good processing characteristics because of the molecular weight increase and reduced enthalpy of polymerization that result from the cyclotrimerization process. Analyses of scanning electron microscope micrographs revealed the appearance of anisotropic structure at heat treatment temperatures greater than or equal to 2400°C. The development of this anisotropic structure appears to progress from an

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initially isotropic texture at 1200 and 1800°C to a graphite-like lamellar anisotropic structure at 2400°C and higher. This anisotropic structure is more pronounced in the PAA-derived matrix. The PAA-derived C-C composites exhibited a change in mode of three-point bend failure at heat treatments of 1800, 2400, and 2800°C. The failure of the 1200°C composites occurred by catastrophic fracture initiating at the tensile face above the loading bar. The other C-C composites failed more gracefully by a combination of accumulated damage due to bearing on the load bar, longitudinal shear, and isolated tensile failures.

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FIGURES

I. INTRODUCTION

While the mechanical properties of carbon-carbon (C-C) composites continue to improve generally with advances in reinforcement and matrix materials, the utilization of fiber strength in these composites is still disappointingly low, being on the order of only 20 to 50% of the rule-of-mixtures prediction (Refs. 1 and 2). In contrast, carbon-fiber-reinforced epoxy composites typically utilize 90 to 95% of the rule-of-mixtures predicted strength. Reasons for the poor translation of reinforcement properties in C-C composites have been discussed by Jortner (Ref. 1), Leong and Zimmer (Ref. 2), and Fitzer and Huttner (Ref. 3). A summary of possible causes for fiber strength degradation in C-C is given by Leong and Zimmer (Ref. 2). From a review of the literature, they conclude that the major factors are:

1. Chemical attack of the fiber by matrix pyrolysis gases.
2. Residual stresses in the fiber, resulting from the thermal expansion between fiber and the matrix.
3. Debonding at the fiber-matrix interface, resulting in isolated filaments and reduced load transfer capability.
4. Matrix cracking, producing stress concentrators within the composite.
5. High heat treatment temperatures, resulting in fiber kinking.
6. Matrix initiated failure, i.e., failure at the failure strain of the matrix.

We are currently investigating the use of polyarylacetylene (PAA) resins as a carbon precursor matrix because their chemical structure suggests the possibility of alleviating some of these problems. Three areas where PAA may demonstrate superiority to state-of-the-art (SOTA) resin systems (e.g., phenol-formaldehyde resin) as a carbon matrix precursor are as follows:

1. The cure of the phenol-formaldehyde resin is a condensation reaction which releases about 17 wt% water. The water released during the curing of the phenolic resin can interfere with the bonding of the matrix to the fiber reinforcement. In contrast, the curing of the PAA matrix is an addition reaction which does not produce any by-products that could interfere with fiber-matrix bonding.

2. The chemical structure of the cured phenolic resin includes 15 wt% oxygen and 7 wt% hydrogen. During the pyrolysis that transforms the phenolic resin to a carbon matrix, the oxygen and hydrogen are lost, and the reinforcing fibers are subjected to high-temperature oxidative gases. The chemical structure of the PAA resin contains 5 wt% hydrogen and no oxygen. During pyrolysis, the fibers are exposed to a more favorable high-temperature reducing environment.

3. The theoretical carbon yield of the phenolic resin system is 78 wt%. The theoretical carbon yield for the PAA matrix is 95 wt%. In practice, these two resins have carbon yields of about 50 and 90%. The higher char yield of the PAA is attractive because it suggests the possibility of high densification efficiency with low composite porosity in a minimal number of cycles.

This report presents some preliminary findings of our investigations with PAA and phenolic resins as carbon matrix precursors for C-C composites.

II. EXPERIMENTAL

A. POLYMER MATRICES

The phenolic resin used in this study is prepared by Borden Company and is designated SC1008. The chemical structures representative of the prepolymer and the cured phenolic resin system are shown in Figure 1.

Polyarylacetylene resins are synthesized from substituted ethynyl benzenes. There are two additional reactions which produce polyarylacetylene resins, namely, cyclotrimerization and linear polymerization (Ref. 4). The chemical structures representative of the monomer and the two polymers are shown in Figure 2.

Our work has been centered around the cyclotrimerized material, as we have found that it can be handled easily in the prepolymer condition, facilitating the fabrication of composites. This prepolymer formulation is based on the work done by Jabloner at Hercules; the Hercules resin is designated HA-43 (Ref. 5). The synthesis of the cyclotrimerized prepolymer is depicted in Figure 3. There are two advantages to the use of the cyclotrimerized prepolymer compared to the linearly polymerized resin:

1. The enthalpy of the cyclotrimerization reaction is a large fraction of the enthalpy produced as PAA is formed. The release of this energy during the cyclotrimerization makes thermal control of the PAA cure easier.

2. The relatively low molecular weight of the prepolymer allows it to be dissolved in low molecular weight solvents for prepregging, making solvent removal easy.

The cyclotrimerization reaction is performed at about 80°C with a nickel catalyst. We have synthesized PAA prepolymer from meta-diethynyl benzene (DEB) and blends of DEB and phenylacetylene (PA). The DEB/PA blends have been cyclotrimerized in ratios of 75:25, 63:37, and 50:50. The characteristics of the blends are basically the same as the DEB-derived PAA, except where noted. The blended prepolymers were made in search of

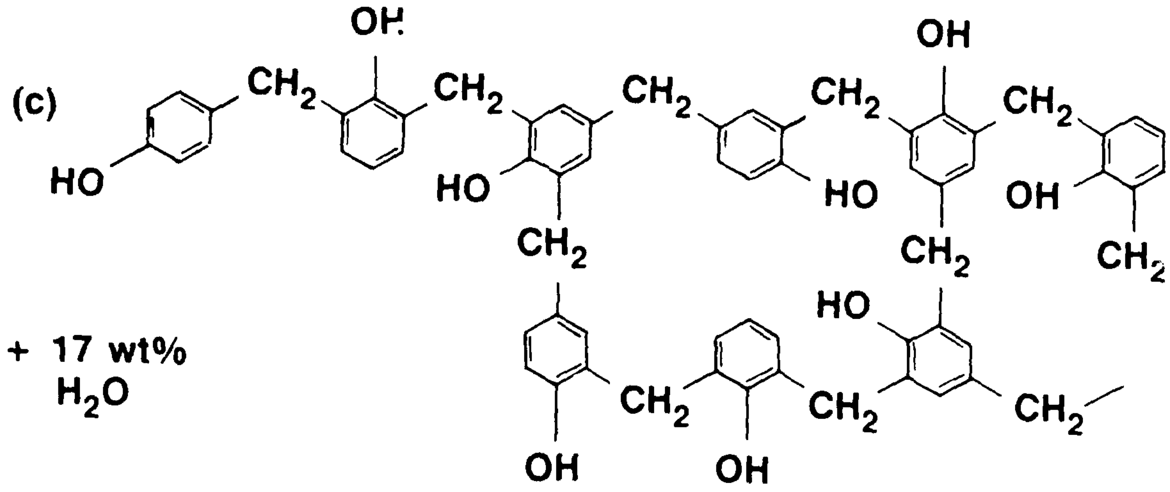


Figure 1. Chemical Structure Representative of Cured Phenolic Resin System

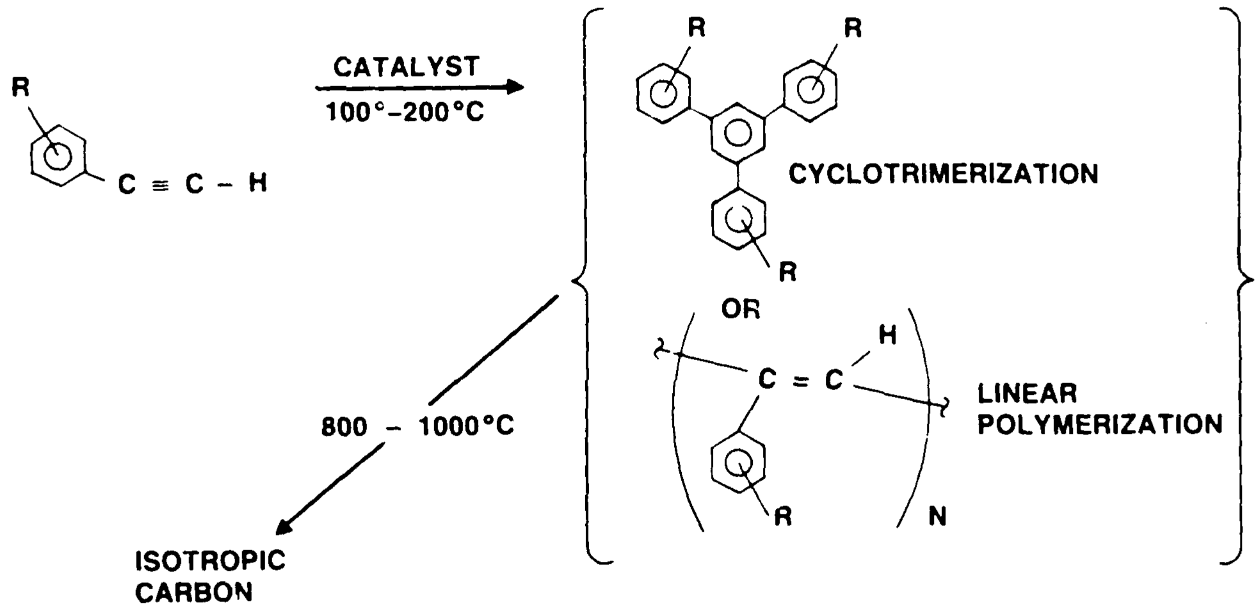


Figure 2. Polyarylacetylenes Synthesized from Substituted Ethynyl Benzene by Cyclotrimerization and Linear Polymerization

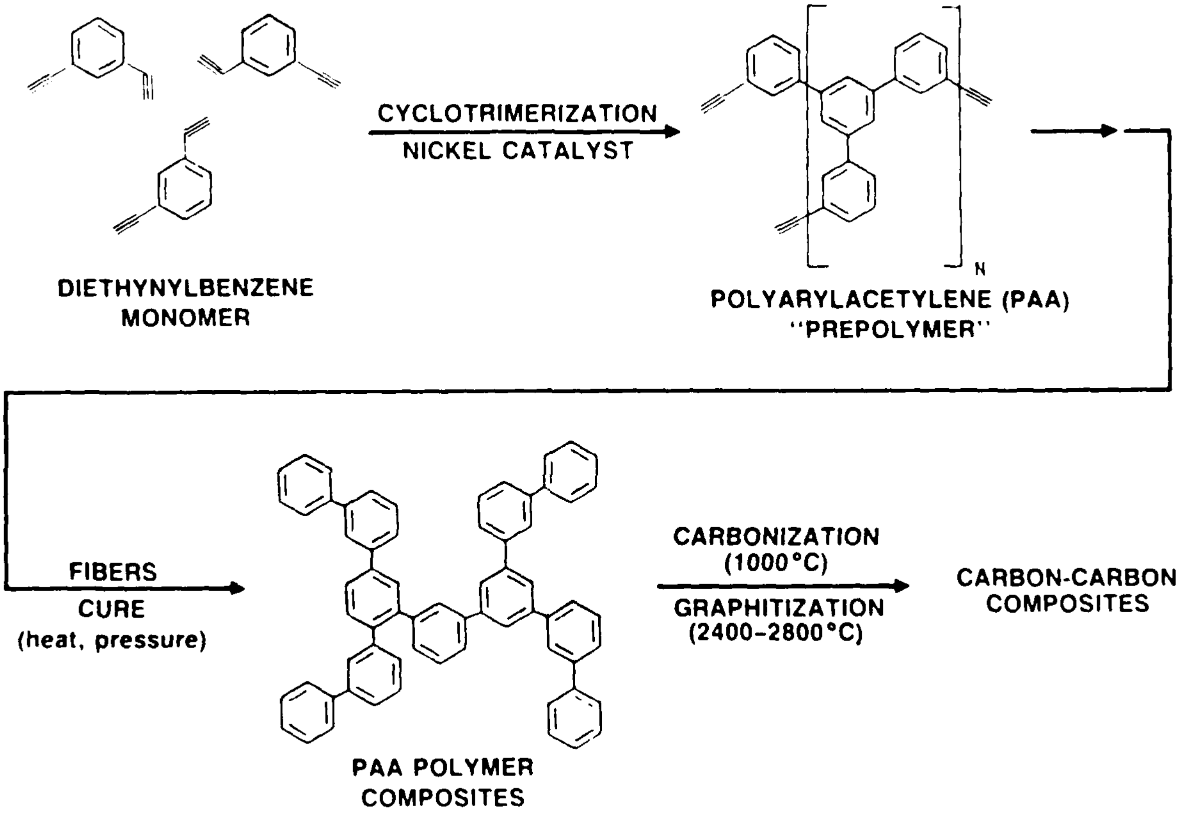


Figure 3. Synthesis of Cyclotrimerized PAA Prepolymer

easier prepreg processing; the use of PA reduces the polymer cross-link density and so improves flow.

Both PAA and phenolic resins were subjected to thermogravimetric analyses; results are shown in Figure 4. The observed carbon yield of DEB is 90%. The blends with PA have slightly lower char yields: 87% for 75:25 and 82% for the 63:37 DEB/PA materials. The observed char yield is close to the theoretical yield of 95%. The onset of mass loss is about 425°C, indicating that the PAA has a high thermal stability. The char yield observed for the phenolic resin is about 50%. This yield is significantly lower than its theoretical carbon yield of 79%. The mass loss from the phenolic resin starts at about 200°C, only about 20°C above the resin cure temperature.

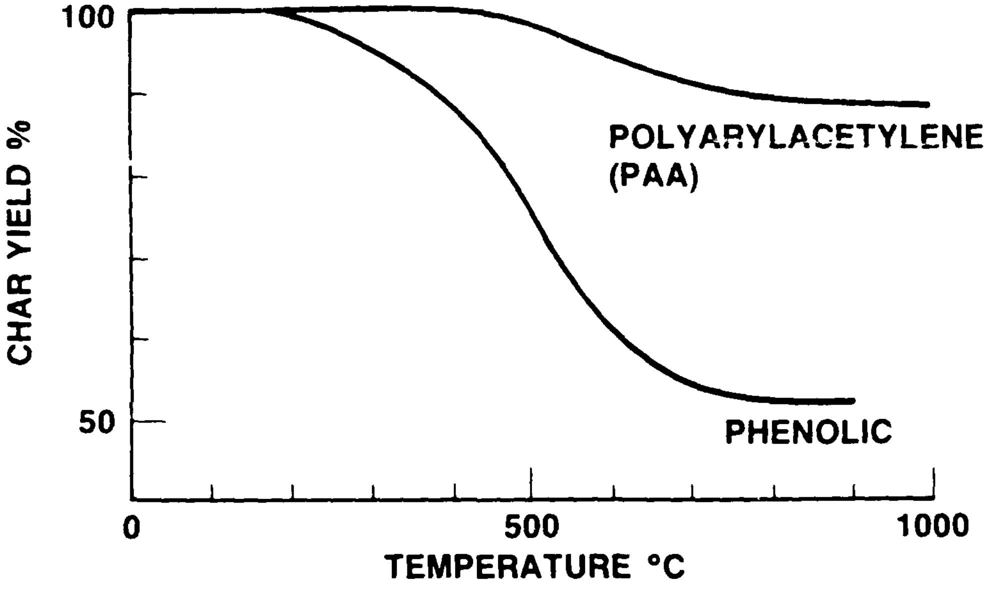
The reduction in mass of these resins during pyrolysis is accompanied by concurrent changes in their volumes. Results of thermomechanical analyses are shown in Figure 5. The overall reduction in volume to 750°C for the phenolic resin is about 2.5 times the change in volume of the PAA polymer. The fact that the phenolic resin loses 5 times the mass but only 2.5 times as much volume indicates that the carbon char left by the phenolic resin at 750°C has a lower density than that of the PAA resin.

Specimens of both PAA and phenolic resins have been heat treated to temperatures of 1200, 1800, 2400, and 2800°C. These specimens were mounted in epoxy and examined first by optical microscopy; they were then etched and examined by scanning electron microscopy (SEM).

B. COMPOSITE FABRICATION

The fabrication of unidirectional composites from the PAA prepolymer and AMOCO T-50 fibers is depicted in Figure 6. The T-50 fiber reinforcement was supplied as a 3000-filament tow. The T-50 fiber has the following properties: density, 1.80 g/cm^3; tensile strength, 412 ksi; Young's modulus, 56.5 Msi; elongation, 0.7%; sizing, 1.10% (UC 309); and no twist. The tow was prepared for prepregging by winding it on a rack, with about a 0.25-in. spacing between each turn. A 25- to 35-wt% solution of

- HIGH CHAR YIELD — 90 WEIGHT %
- HIGH THERMAL STABILITY — ONSET OF MASS LOSS AT 425°C
- LOW SHRINKAGE



	THEORETICAL YIELD	OBSERVED YIELD
PAA $(C_{10}H_6)_n$	95% CARBON	90% CARBON
PHENOLIC $(C_7H_6O)_n$	79% CARBON	50% CARBON

Figure 4. TMA of Phenolic and PAA Resins

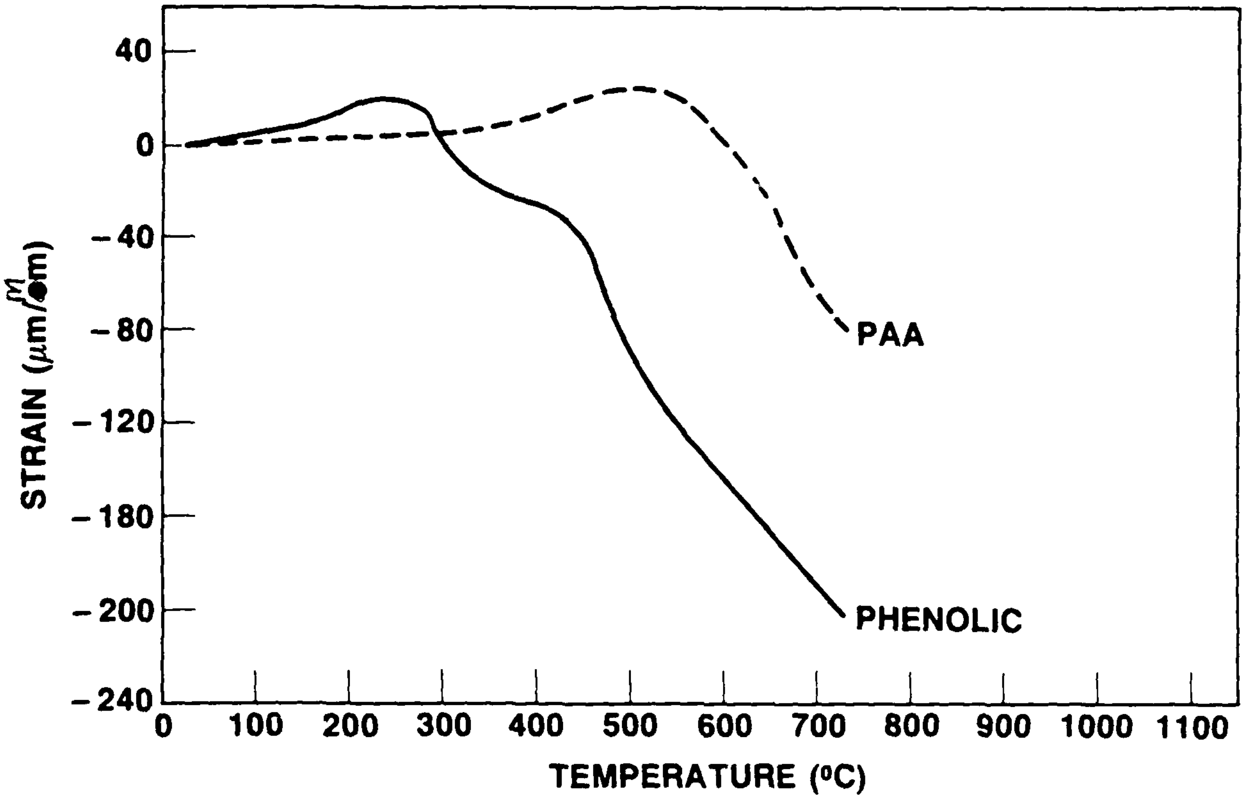


Figure 5. Thermomechanical Analysis of PAA and Phenolic Resins

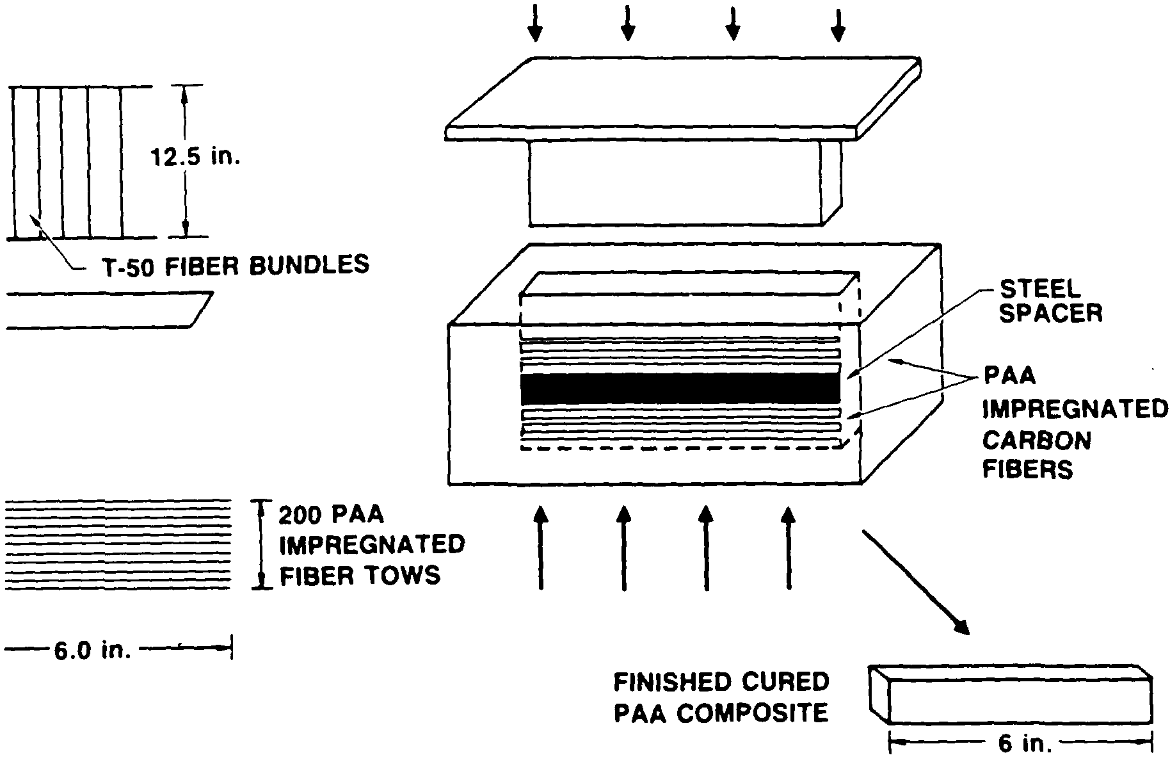


Figure 6. Fabrication of Unidirectional PAA Composites

the cyclotrimerized PAA prepolymer in methyl ethyl ketone (MEK) was applied to the windings by hand with an eye dropper. The rack with prepregged tow was stationed in a hood overnight, where the MEK could evaporate, leaving the prepreg nearly solvent free. The prepregged composites were cut from the rack and trimmed to 6-in. lengths. Cured PAA/T-50 composites were prepared by placing 200 prepregged composites in a steel mold, with careful attention to maintaining parallel stacking of the composites. The cover was placed on the mold, and the whole assembly inserted into a press with its platens preheated to 100°C. The press was closed and pressure applied to generate 600 psi compaction load. The cure schedule is shown in Figure 7: 2 hr at 100°C, 1-hr ramp to 177°C with a 3-hr residence, 1-hr ramp to 177°C with a 3-hr residence, 1-hr ramp to 250°C with a 10-hr residence, followed by a power-off cool-down. The dimensions of the PAA/T-50 composites removed from the mold were 6 x 0.5 x 0.2 in.

Early in the fabrication of these composites, we examined the effect of compaction pressure on the consolidation of the PAA composites. Pressures from 50 to 1100 psi were investigated, with the best composite consolidation occurring between 500 and 1000 psi. The 600-psi compaction pressure results in a unidirectional PAA composite with 50 to 55% fiber volume. In addition, the fibers and matrices were uniformly distributed, with very low porosity.

The fabrication of phenolic resin/T-50 composites proved to be more difficult than expected. The fibers were wound on a rack very similar to that used for the PAA matrix composites. The rack consisted of a ring stand to which was affixed two horizontal parallel bars about 7 in. apart. Metal washers were bonded to the bars at 1-in. spacings to act as fiber retainers. The fibers were wrapped in layers 1 in. in width and two tows thick. The fibers were then drip impregnated with an eye dropper, until approximately 150 windings of the tow had been wound. Care was taken to evenly spread the resin over the fibers with the side of the eye dropper.

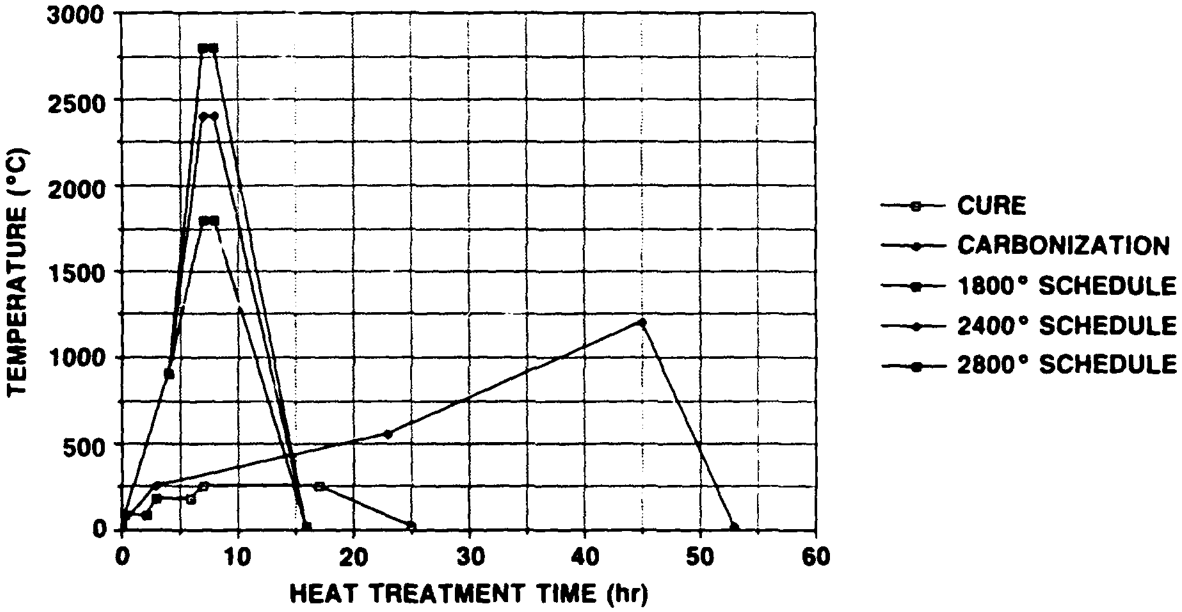


Figure 7. Heat Treatment of PAA/T-50 Composites

The resin used for this study was Borden Chemical SC1008, which is a resol-type phenolic resin (excess formaldehyde, alkaline, no catalyst required). The major difficulty in working with the SC1008 resin is that it is a liquid at room temperature. Therefore, after impregnation, the fibers remain wet for an extended period of time (> 2 weeks). The resin in this fluid state is unacceptable for handling and processing. As a result, the impregnated fiber bundles or "prepregs" must be partially polymerized by a mild heat treatment prior to processing. This practice is commonly referred to as B-staging.

After the desired number of tows was wound and impregnated, the whole rack was then placed in the oven for B-staging. The temperature and duration of heat treatment at about 120°C produced prepregs which were dry and rigid at 25°C and had the proper flow characteristics during cure. After B-staging was completed, the 300-tow prepregs (two tow sections from each winding) were cut from the rack and trimmed to 6-in. lengths.

For processing, a mold was fabricated from aluminum in the shape of a trough with bolted-on end plates. The interior dimensions of the mold were 6 x 1 x 1 in. The top of the mold was a slip fit within the mold container and was drilled through with about twenty-five 0.125-in. holes in three rows along its length. The two prepregs were placed in the mold, and the end plates were then bolted on and the top inserted. The mold was then vacuum bagged and cured in an autoclave under a 40-psia (25-psig) nitrogen blanket using the cure schedule recommended by Monsanto for low-pressure curing. The cure schedule for the phenolic resin was: ramp from room temperature to 100°C in 75 min; hold at 100°C for 60 min; ramp to 121°C in 50 min; hold at 121°C for 60 min; ramp to 171°C in 28 min; hold at 171°C for 120 min; and allow a power-off cool-down.

The phenolic/T-50 composites had fiber volumes of 70 to 75%. The composites were well consolidated with good fiber distribution, but their porosity was on the order of 9%.

The cured PAA and phenolic matrix composites were heat treated to produce C-C composites. The schedule for carbonization was the same for all the composites, taking about 2 days to achieve heat treatment to 1200°C, followed by an overnight power-off cool-down. Various composites were heat treated to 1800, 2400, or 2800°C. Carbonization and heat treatment schedules are shown in Figure 7.

III. RESULTS

A. PHYSICAL PROPERTIES

The change in volume due to heat treatment of the composites was measured geometrically. The dimensions of each composite were recorded prior to and after heat treatment; the results for PAA/T-50 and phenolic/T-50 composites are shown in Figure 8. In all cases, the shrinkage was confined to the cross section transverse to the fiber orientation. The shrinkage of the PAA/T-50 composites increased with increasing heat treatment temperature. The behavior of the phenolic/T-50 composite was similar to that of the PAA/T-50 during carbonization to 1200°C, both undergoing a shrinkage of about 7%. The higher temperature heat treatments caused the PAA/T-50 composites to continue to consolidate to the extent of 27% at 2800°C. The phenolic/T-50 composites appeared to stop shrinking after the initial carbonization.

The densities of the composites were determined by the weight and dimension method (bulk density), and by both helium pycnometry and mercury porosimetry (real density). The results of the helium pycnometry and mercury porosity measurements are comparable. Porosities were calculated from the real and bulk densities. The results for the PAA/T-50 composites are shown in Figure 9. The cured composite had a porosity of about 1%. Heat treatment to 1200°C caused the porosity to increase to 6%. Heat treatment to 1800°C resulted in no further increase in the porosity of the composite. Heat treatment to 2400°C caused the porosity to increase to 15%. The highest heat treatment of 2800°C resulted in a porosity of 19% for the PAA/T-50 composites.

The results of the measured real and bulk densities for the phenolic/T-50 composites are shown in Figure 10. The porosity of the cured composite is 6%. Carbonization of the composite to 1200°C caused the porosity to increase to 13%. Heat treatments to 1800, 2400, and 2800°C resulted in porosities of 13, 15, and 27%, respectively.

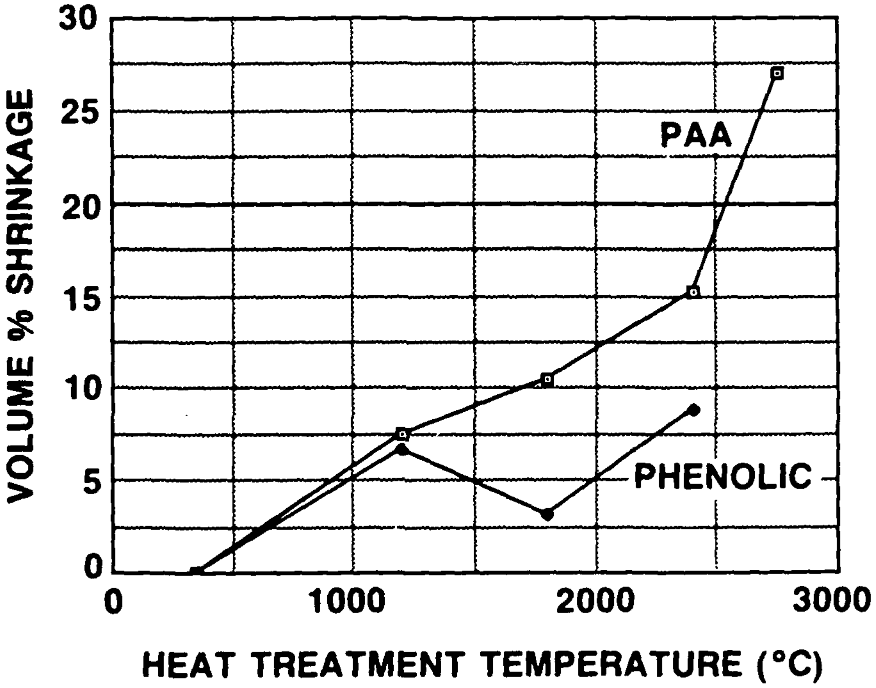


Figure 8. Composite Shrinkage Due To Heat Treatment

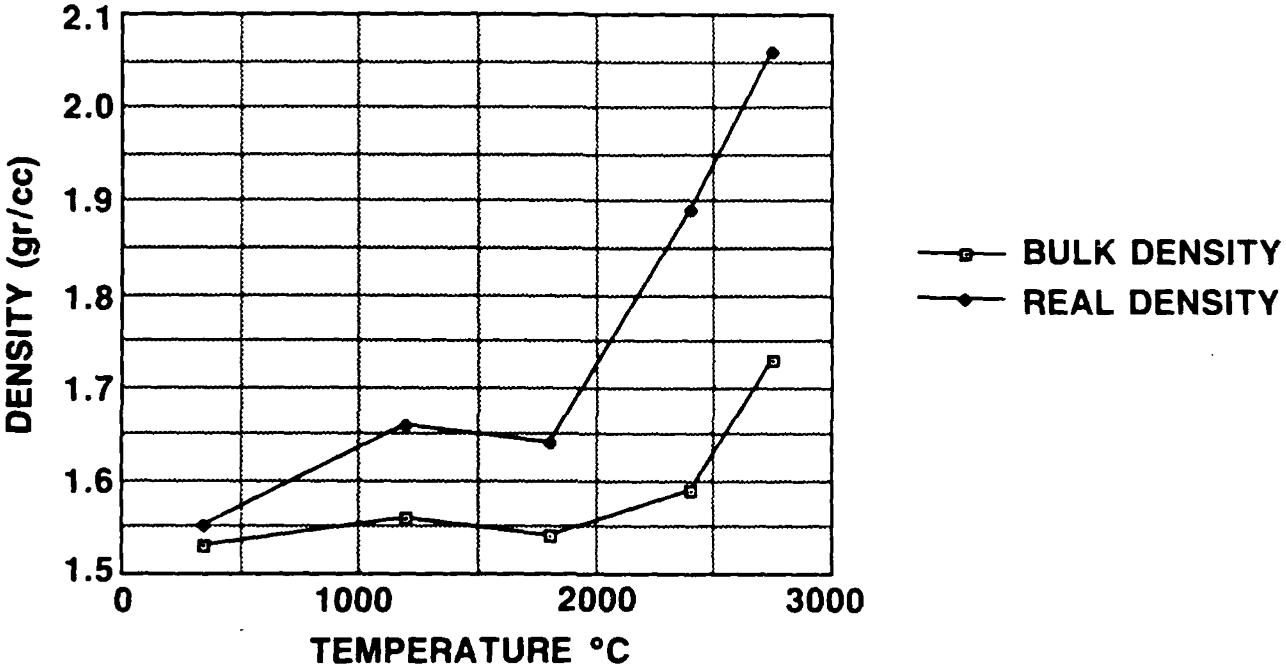


Figure 9. Real and Bulk Densities of PAA/T-50 Composites After Heat Treatment

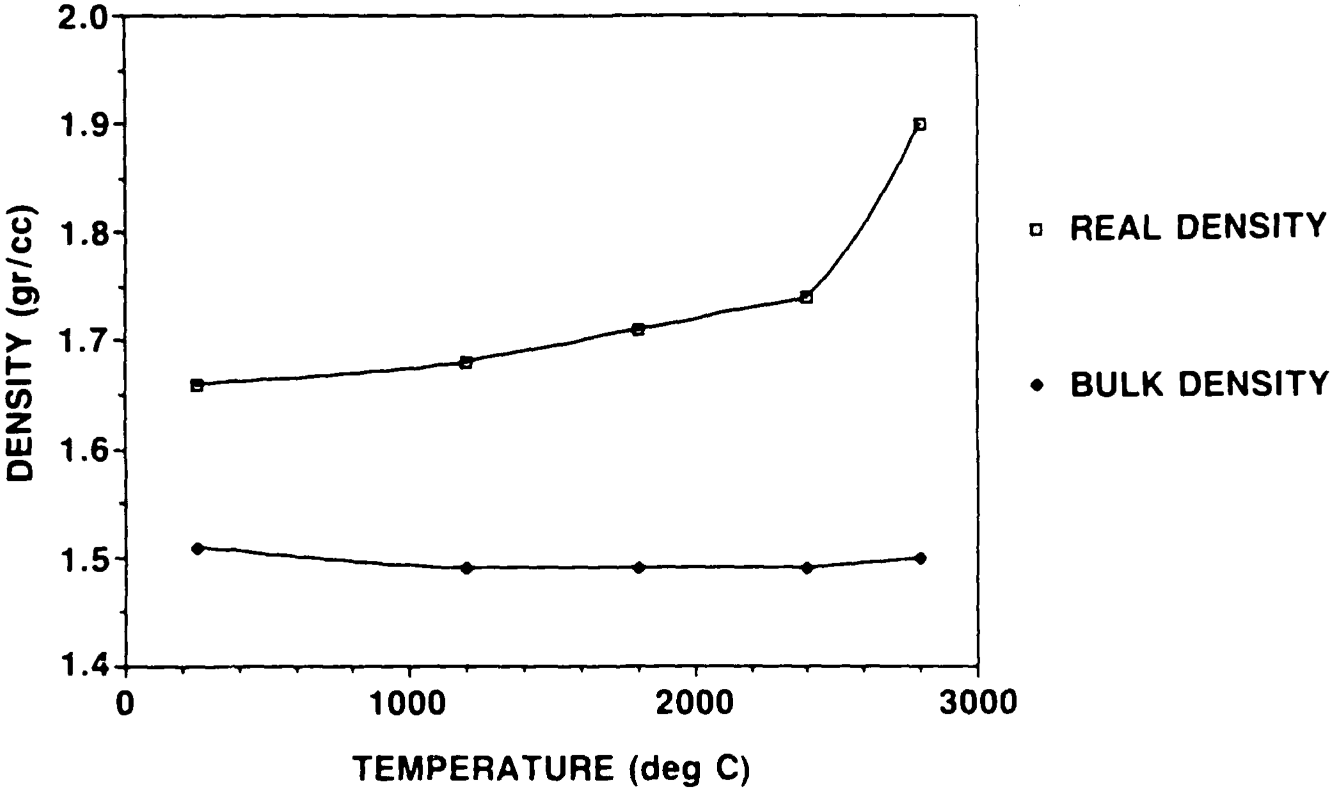


Figure 10. Real and Bulk Densities vs Heat Treatment Temperature for Phenolic/T-50 Composites

B. MICROSTRUCTURE

The unidirectional C-C composites were mounted in epoxy and polished prior to being etched in a xenon ion etching apparatus. The unidirectional composites were heat treated to examine the microstructures of each of the carbon matrices The processing of unidirectional composites from the PAA and phenolic precursors resulted in composites with differing fiber distribution. Fiber volumes were determined from 200 and 500X magnification micrographs. The volume of fibers is determined by counting the number of fibers in the area of the micrograph and multiplying by their average cross section. The fiber volume is the area of the fibers divided by the area of the micrograph. The composites derived from the PAA resin had fiber volumes of 50 to 55% in the as-cured condition. The phenolic resin composites were fabricated with a 70 to 75% fiber volume.

The microstructures of the unidirectional composites revealed that there were striking differences due to fabrication and processing of the PAA and phenolic prepolymers. The cured composites exhibited good infiltration with small or no matrix pockets between the fiber tows. The void volume of the cured composites was on the order of 1% for the PAA matrix and 9% for the phenolic matrix composites. The remnants of the poorer impregnation of the phenolic resin are found in each of the heat-treated samples. The carbon matrix formed by PAA prepolymer has pockets of matrix located between the fiber tows which appear to be remnants of the processing of the unidirectional composites. These matrix pockets have cracks, with widths of 10 to 50 μm and extending for several hundred micrometers after carbonization. There is some evidence of voids resulting from small areas of poor impregnation of the fibers.

The descriptions of the microstructure which follow are from PAA and phenolic-derived C-C composites at the same heat treatment in areas of good infiltration, not bordering on matrix pockets. The PAA prepolymer exhibited the most uniform fiber distribution.

1. COMPOSITES HEAT TREATED TO 1200°C

The unidirectional composites derived from the PAA and phenolic-derived carbon matrix are shown in 200X SEM micrographs in Figure 11. The PAA and phenolic-derived carbon matrices are isotropic. The PAA composite has well-distributed matrix with very little matrix cracking and 6% porosity. The phenolic-based C-C composite exhibits very poor matrix distribution and 13% porosity. The regions of higher porosity tend to occur when the fiber volume is lower. Examination of these matrices in the SEM at 150 to 2500X magnification reveal that they are completely isotropic with no evidence of graphitic structure.

2. COMPOSITES HEAT TREATED TO 1800°C

Composites heat treated to 1800°C are shown in 500X SEM micrographs in Figure 12. The PAA and phenolic-derived carbon matrices are isotropic. The unidirectional C-C composite formed from PAA has a slightly higher fiber volume than the 1200°C composite. The matrix is well distributed throughout the composite, and the fibers are uniformly distributed within the matrix. Heat treatment of the PAA-derived composite to 1800°C does not cause the porosity to increase above that found in specimens heat treated to 1200°C.

For the phenolic-derived C-C composite, where matrix is present, the fibers are very densely packed and appear to be well bonded to the matrix. The porosities measured at 1200 and 1800°C heat treatments are the same: 13%.

Examination of matrices derived from both PAA and phenolic precursors at 500 to 5000X magnification reveal that they are completely isotropic with no evidence of graphitic structure.

3. COMPOSITES HEAT TREATED TO 2400°C

Composites heat treated to 2400°C are shown in 500X SEM micrographs in Figure 13. The PAA-derived C-C composite has continued to shrink, increasing the fiber volume. The matrix is still well dispersed throughout

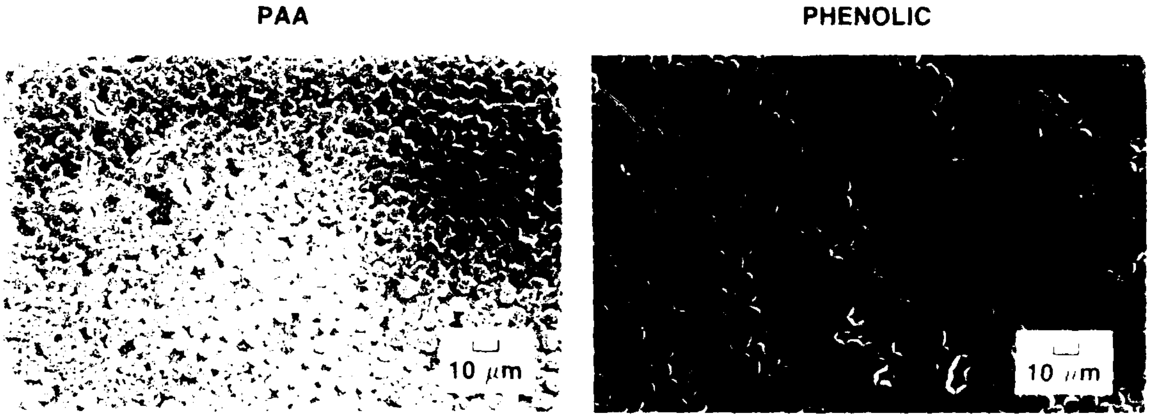
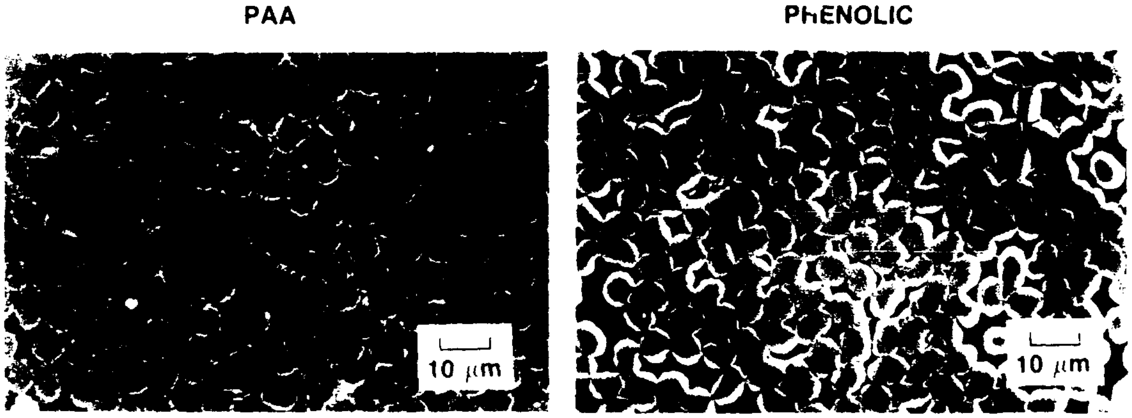


Figure 11. PAA and Phenolic Derived C-C Composites Heat Treated to 1200°C


PAA

PHENOLIC

Figure 12. PAA and Phenolic Derived C-C Composites Heat Treated to 1800°C

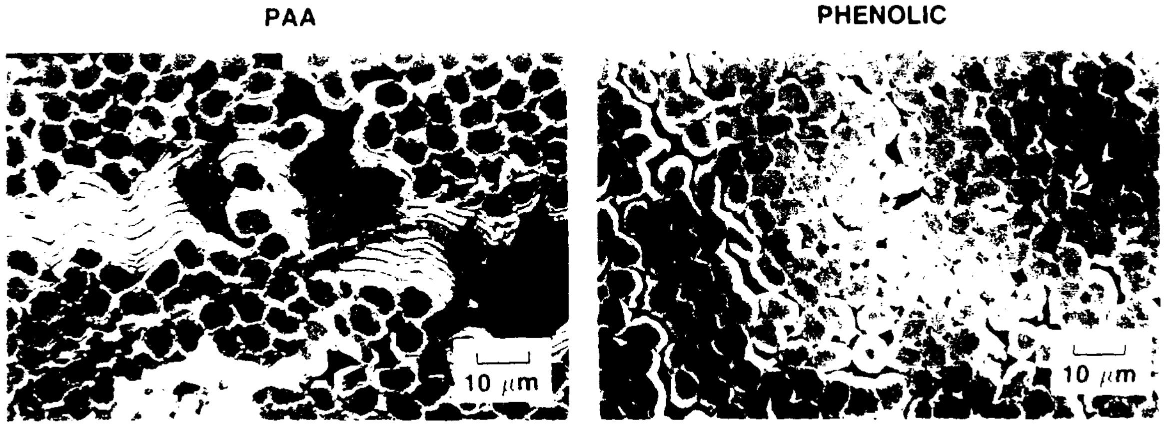


Figure 13. Development of Anisotropic Orientation in PAA and Phenolic C-C Composites Heat Treated to 2400°C

the composite and is well bonded to the fibers. The void volume has increased to 15%. The matrix has developed significant anisotropic orientation during the heat treatment to 2400°C. The xenon etching reveals the density gradient in the carbon matrix, which is indicative of the developing lamellar structure. The layered structure is well developed around the filaments and appears to have been initiated at the fiber matrix interface and to be progressing radially away from the filament surface.

The phenolic-derived composites' void volume has increased to 15%. These composites also show some development of anisotropic orientation, though it is much less extensive than in the PAA-derived C-C composites. The matrix has continued to shrink, and at 2400°C the fibers are generally in contact with each other in the matrix-rich areas. This results in the development of a crack network in the matrix-rich areas which was not observed at the lower heat treatment temperatures.

4. COMPOSITES HEAT TREATED TO 2725°C

Composites heat treated to 2725°C are shown in 1000X SEM micrographs in Figure 14. The PAA-derived C-C composite continued to shrink with increasing heat treatment, and the porosity increased to 19%. In addition, the lamellar structure of the matrix is very extensive and of a finer structure than for the matrix heat treated to 2400°C. The matrix appears to be well bonded to the filaments.

The unidirectional C-C composite derived from the phenolic resin has undergone only a slight amount of shrinkage compared with the lower heat treatment temperatures of 1800 and 2400°C, but there is a large increase in the porosity to 27%. The development of anisotropic orientation in the matrix has increased compared to the 2400°C matrix, but is still significantly less extensive than in the PAA-derived carbon at this temperature.

C. THREE-POINT BEND

Specimens of the PAA-derived C-C composites were prepared for mechanical testing in a three-point bend apparatus. The specimens were cut

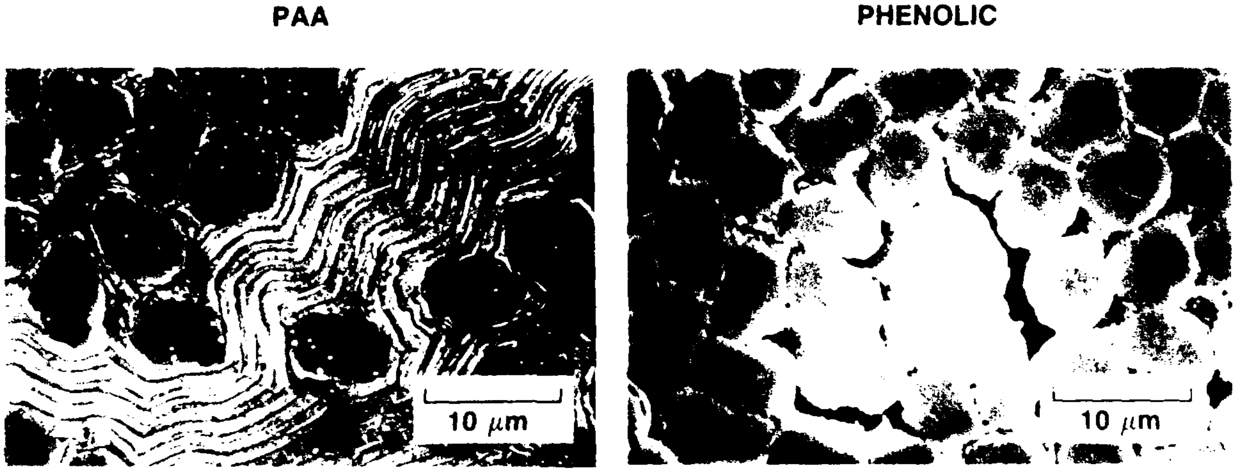


Figure 14. Anistropic Orientation of PAA and Phenolic C-C Composites Heat Treated to 2725°C

from the C-C composite to dimensions of approximately 0.060 x 0.200 x 2.200 in. The specimens had one of the 0.060- x 2.200-in. sides polished for optical examination during the testing. Samples have been tested from composites which have been heat treated to 1200, 1800, 2400, and 2800°C. Typical load deflection curves for the 1200, 1800, 2400, and 2800°C specimens are shown in Figure 15. The four 1200°C composites all failed in a catastrophic manner. The composites heat treated to 1800, 2400, and 2800°C all exhibited a much more progressive failure.

Photomicrographs representative of these composites during the testing are shown in Figure 16. In all of the photomicrographs, the center loading bar is located in the bottom center of each picture. The pictures are of the untested composite (top), the composite just after the first significant reduction in load (middle), and the composite at the end of the test (bottom). The composites heat treated to 1200°C all exhibited a fracture initiating at the tensile surface and propagating down through about 70% of the composite cross section directly above the load bar. All of the other composites, regardless of heat treatment temperature, exhibited longitudinal shear and bearing failure modes in addition to small domains where tensile failures were observed.

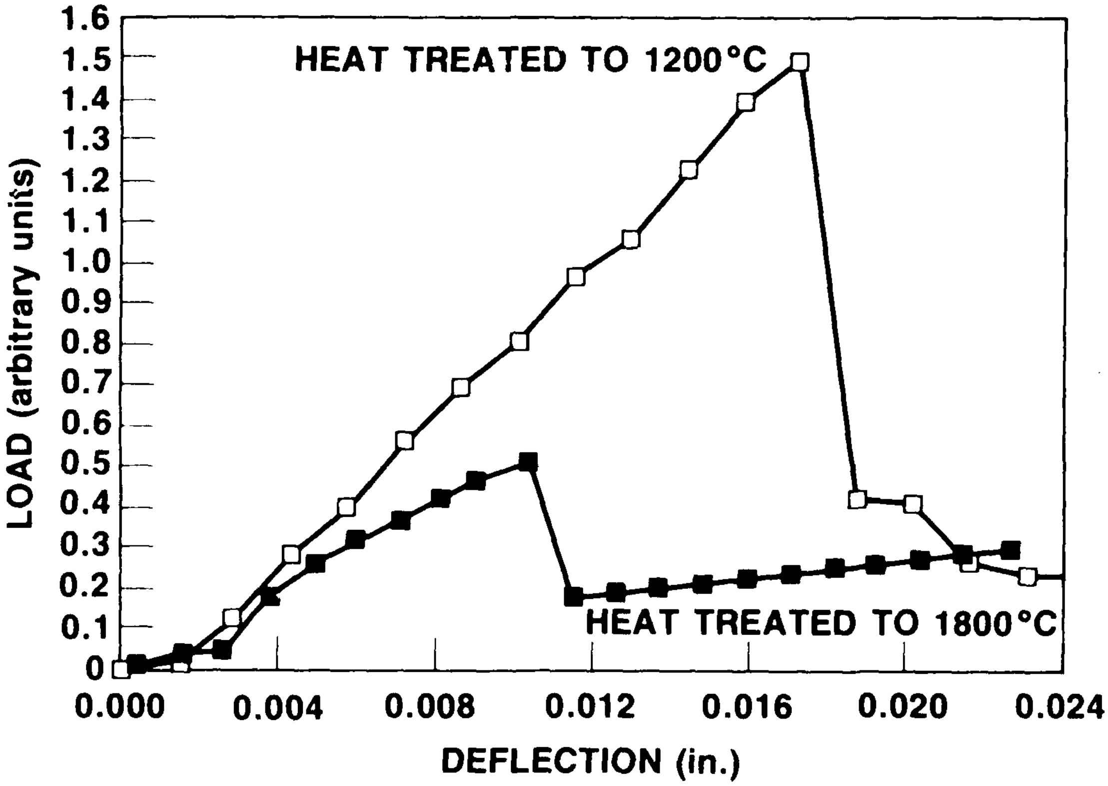


Figure 15. Stress vs Deflection, Three-Point Bend

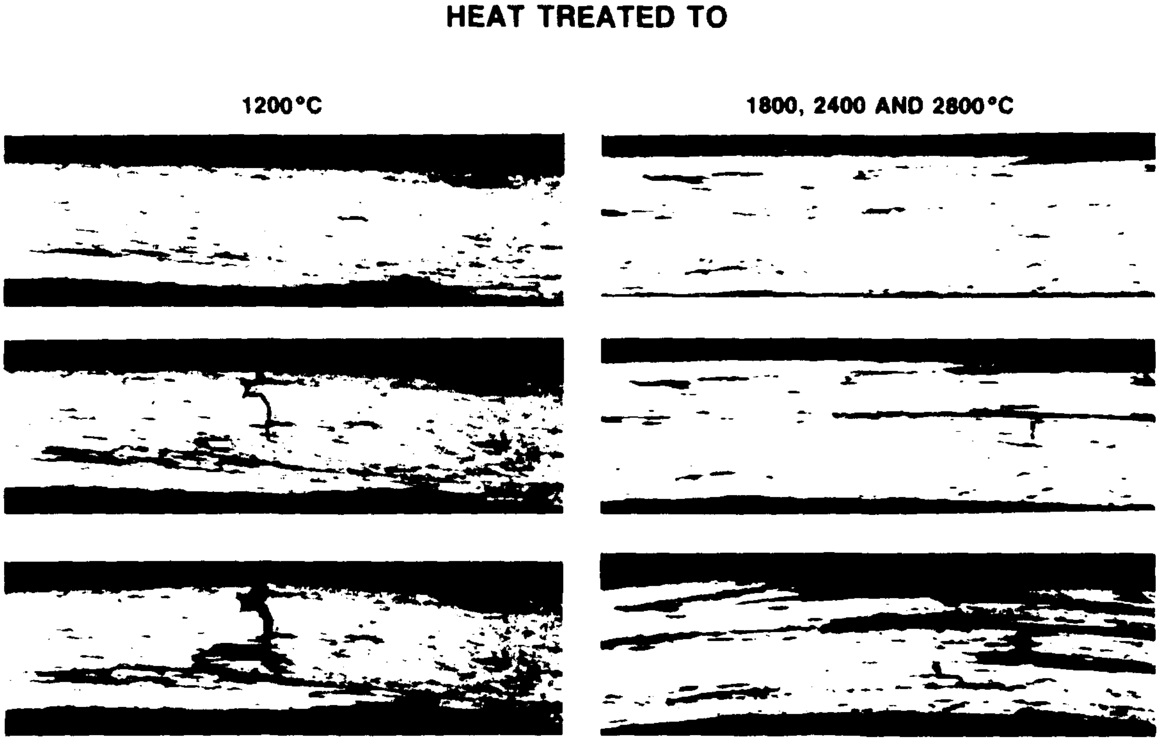


Figure 16. Three-Point Bend Failure Mode for PAA/T-50 C-C Unidirectional Composites

IV. CONCLUSIONS

Polyarylacetylenes have desirable properties as carbon precursors for use in C-C composites. The PAA matrix has a high carbon yield of 90%, far exceeding the 50% yield of current phenolic resins. In addition, the PAA-derived carbon matrix exhibits less shrinkage during carbonization than the phenolic resin.

The cyclotrimerized prepolymer has good processing characteristics due to its molecular weight increase and reduced enthalpy of polymerization, compared to the meta-diethynyl benzene monomers. The cured PAA composite typically has a porosity of 1%, which increases to 6% at 1200°C and 19% at 2800°C. The cured phenolic composite typically has a porosity of 6%, which increases to 13% at 1200°C and 27% at 2800°C.

SEMs of ion-etched cross sections of unidirectional C-C composites reveal the effects of heat treatment on matrix microstructure. Analyses of these micrographs indicated that there is a perceptible appearance of anisotropic structure at heat treatment temperatures greater than or equal to 2400°C. The development of this anisotropic structure appears to progress from an isotropic texture at 1200 and 1800°C to a graphite-like lamellar anisotropic structure at 2400°C and higher heat treatment temperatures. This layered anisotropic structure becomes more pronounced in the PAA-derived matrix.

The PAA-derived C-C composites exhibited a change in mode of three-point bend failure at heat treatments of 1800, 2400, and 2800°C. The failure of the 1200°C composites occurred by catastrophic fracture initiating at the tensile face above the loading bar. The other C-C composites failed by accumulated damage due to bearing on the load bar, longitudinal shear, and isolated tensile failures.

The C-C composites fabricated from the PAA prepolymer have interesting properties. The relative ease of fabrication and continuum of microstructure generated by heat treatment make them a good candidate for the study of structure property relationships in C-C composites.

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LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security projects, specializing in advanced military space systems. Providing research support, the corporation's Laboratory Operations conducts experimental and theoretical investigations that focus on the application of scientific and technical advances to such systems. Vital to the success of these investigations is the technical staff's wide-ranging expertise and its ability to stay current with new developments. This expertise is enhanced by a research program aimed at dealing with the many problems associated with rapidly evolving space systems. Contributing their capabilities to the research effort are these individual laboratories:

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