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Processing Effects on the Mechanical Behavior of Polyarylacetylene-Derived Carbon-Carbon Composites

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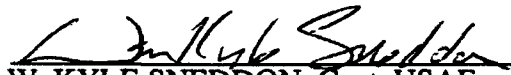
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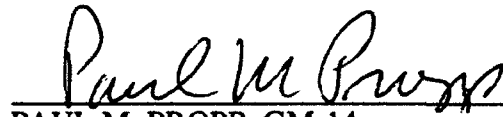
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PREFACE

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I. INTRODUCTION

Carbon-carbon (C/C) composites are attractive materials for structural applications at elevated temperatures. They offer several unique properties, including high specific strength and stiffness, low thermal expansivity, and excellent creep resistance [1].

Carbon-carbon composites can be fabricated by infiltrating a preform through gas-phase chemical vapor deposition (CVD) or liquid infiltration/pyrolysis techniques [2]. In the CVD process, the matrix is introduced to the reinforcement by means of a hydrocarbon gas at high temperature, of the order of 1000°C. To obtain the desired type of carbon microstructure, the infiltrated piece is then heat-treated. In the liquid infiltration/pyrolysis process, the fiber preform is usually vacuum-impregnated with an organic matrix precursor, then the resin-impregnated preform is cured in an autoclave. Pyrolysis (carbonization) of the composite matrix is carried out by heating to temperatures of about 1200°C under controlled atmosphere. The composite is then heat-treated in a separate "graphitization"* step to approximately 2200 to 2750°C.

The process of impregnating the preform and heat-treating it to a desired state is known as a densification cycle. The number of densification cycles required to reach full density depends on the carbon yield of the matrix and the impregnation efficiency of the pitch or resin [4]. A state-of-the-art resin such as phenol-formaldehyde has a char yield of 50–60% by weight. For a resin density of 1.25 g/cm³ and a final carbon density of 1.6 g/cm³ [5], we estimate the volumetric densification yield [6] to be about 40–50%, which necessitates multistep densification cycles to achieve final porosities of 5–10%. Pitches processed at atmospheric pressure have similar char yields, but those processed at pressures from 100 to 1000 atm have yields approaching 85% [7]. However, these pitches are very difficult to work with because of their high viscosity, thermoplastic behavior, and the special requirement for high-pressure equipment.

In all C/C composites, stresses are generated by both the large shrinkage of the matrix during carbonization and the thermal cycling during redensification. Such processing stresses can damage the composite and lead to premature failure. High-char-yield resins, such as the poly-arylacetylenes, have densification efficiencies that are about 50–60% higher than those of phenolic resins or atmospheric-pressure-processed pitch. These translate into lower manufacturing costs as well as greater manufacturing reliability.

*We agree with Fischbach [3] that the use of the term "graphitization" to describe generally this higher heat-treatment-temperature process is to be discouraged since graphitization does not necessarily occur by virtue of the heat treatment alone; it is also a strong function of the precursor material and the heat-treatment time. Nevertheless, given the widespread use of this convention in the industry we will retain it in this publication.

The mechanical properties of C/C composites are governed by the fiber type, matrix precursor, and processing parameters (e.g., temperature and time) that directly affect the fiber-matrix bond. In polymer matrix composites, the strength of the composite depends on the stress-transfer capabilities of the matrix at the fiber-matrix interface: The polymer matrix can strain much more than the carbon fiber, and the strain to failure of the fiber is the controlling factor in failure initiation in the composite. In C/C composites, on the other hand, the carbon matrices have failure strains well below those of the fibers. Upon stressing, the carbon matrix fails first, instead of the fiber initiating failure as in the resin matrix composite. Matrix precursors with high carbonization shrinkage also generate high compressive stresses normal to the interface and promote a strong coupling between fiber and matrix [8]. As a result, cracks which form in the low-strain-to-failure matrix propagate across the fiber-matrix interface to cause immediate, premature failure of the fibers. On the other hand, if the fiber-matrix interface is poorly bonded, interfacial shear and interfacial contraction of fiber and matrix will result in debonding and crack deflection away from its principal direction. Thus, coupling between the fibers and matrix is reduced, and the fibers can meet a higher percentage of their load-bearing capabilities.

In designing C/C composites, the criteria most important in matrix selection are processability, char yield, and microstructure. During pyrolysis, the organic matrix should experience low shrinkage, evolve minimal gases, carbonize with low exotherms, achieve a carbonized state with low energy consumption and speed, and leave a maximum yield of carbon matrix [4]. One class of resin material that promises to meet these requirements is the polyarylacetylenes (PAA).

Polyarylacetylene resin was first synthesized in the late 1950s at the GE Research Laboratory as part of a search for high char yielding polymers. The early formulations underwent severe shrinkage and were highly exothermic during cure [9]. In the 1970s, Hercules patented a process for the production of PAA by techniques that reduce the exotherm and shrinkage. Although the material was easier to process, composites made from the formulations were brittle and had poor structural integrity. In the early 1980s, The Aerospace Corporation's Materials Sciences Laboratory overcame initial problems with PAA through the development of a low-temperature prepolymerization technique and polymer chain modifications [10]. As discussed by Barry et al. [11], the advantages to C/C processing of PAA resins relative to state-of-the-art resins include the following:

1. Curing by addition rather than by condensation reactions, which forms fewer pores and volatile species;
2. Higher char yields on carbonization (85–90%), necessitating fewer redensification cycles;
3. Use of minimal pressures and temperatures, facilitating processing (vacuum-bagging is not essential for all parts); and
4. Lower shrinkage during pyrolysis.

Polyarylacetylene polymers are derived from the polymerization of diethynylbenzene. Typically a prepolymer is first formed by cyclotrimerization of the diethynyl-benzene monomer. Cyclotrimerization is a nickel-catalyzed reaction in which three ethynyl groups are linked to form an aromatic ring (Fig. 1). It liberates much of the exothermic heat of polymerization, enabling controllable, safe curing. Some of the resin shrinkage also is taken up in this prepolymerization step. Several formulations of PAA exist with varying amounts of meta- and para-diethynylbenzenes; phenylacetylene is sometimes included as a chain terminator to reduce cross-link density and improve processability. A detailed discussion of PAA chemistry is given by Katzman [12].

This report describes the effects of processing parameters on the microstructural development, mechanical properties, and failure behavior of PAA-derived unidirectional carbon-carbon composites.

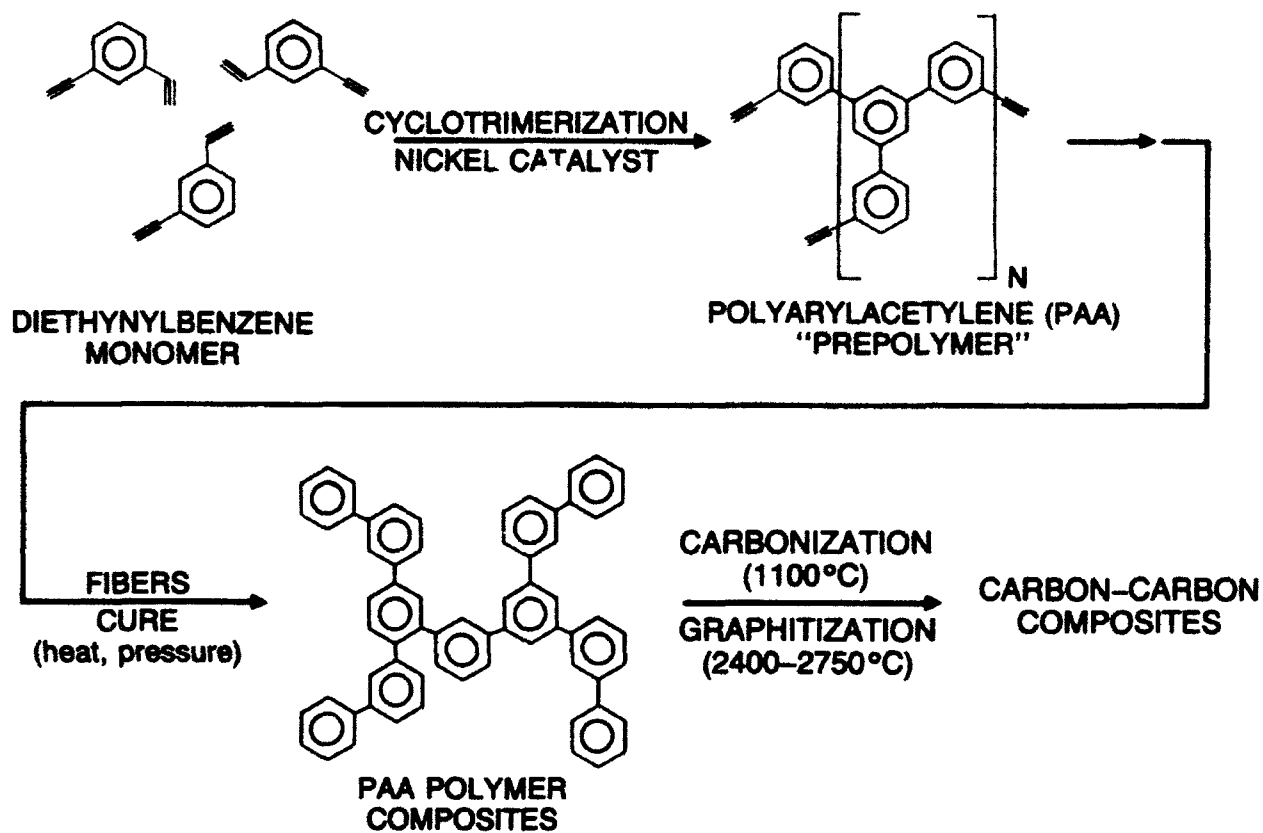


Figure 1. Synthesis of cyclotrimerized PAA prepolymer and subsequent processing steps to produce carbon-carbon composites.

II. EXPERIMENTAL

A. MATERIALS AND PROCESSING

The PAA resin used for the fabrication of all composites in this study was synthesized at The Aerospace Corporation. The phenolic resin, SC1008, purchased from the Borden Corporation, was also used as a matrix precursor for some composites. Amoco T-50 PAN-based carbon fiber, a commercially available fiber supplied as 3000-filament tows, was used in this study. The T-50 fiber has a density of 1.80 g/cm³; tensile strength of 2.758 GPa; Young's modulus of 379 GPa; elongation of 0.7%; sizing; and no twist.

In the process of fabricating unidirectional composites from the PAA prepolymer and T-50 fibers, depicted in Fig. 2, the tow was prepared for prepregging by winding it on a rack, with about a 0.635-cm spacing between turns. A 30 wt.% solution of the cyclotrimerized PAA prepolymer in methyl ethyl ketone (MEK) was applied to the windings by hand with an applicator. The rack with prepregged tows was stationed in a hood overnight for the MEK to evaporate, leaving the prepreg free of solvent. Some of the prepregged composites were cut from the rack and trimmed to 15.24-cm lengths. Cured PAA/T-50 composites were prepared by placing 200 prepregged tows in a steel mold to maintain parallel stacking of the tows. The cover was placed on the mold, and the entire assembly was inserted into a press with its platens preheated to 100°C. The press was closed, and a 4.13-MPa pressure was applied. The cure schedule is shown in Fig. 3. Samples having one of two geometries were prepared from the prepreg. The dimensions of the T-50/PAA composites removed from the mold were 15.24 x 1.27 x 0.51 cm. Other prepreg tows made from phenolic and PAA were cured and carbonized individually to form composite tows approximately 0.063 cm in diameter. Further high-temperature heat treatments of both types of composites were performed in an induction-type graphitization furnace at temperatures up to 1800, 2400, and 2750°C for 1 hr under an argon atmosphere.

To observe the effect of the three heat treatments on fiber tensile properties, the 3000-fiber tows were wrapped about a graphite mandrel and heat-treated in an argon atmosphere at the same temperatures and for the same times as the C/C composites. The mandrel was then removed from the furnace, and the heat-treated carbon fibers were wrapped around aluminum racks and impregnated with the epoxy resin. The epoxy mixture consisted of 100 parts by weight Shell Epon 828, 40 parts Versamid 140, and 8 parts diethylene triamine. After impregnation, the epoxy was cured at 150°C for 4 hr and the composites were further prepared for mechanical testing.

B. MICROSTRUCTURE EVALUATION

The microstructures of the PAA-derived C/C composites were analyzed by scanning electron microscopy (SEM) and optical microscopy. The samples were polished and then

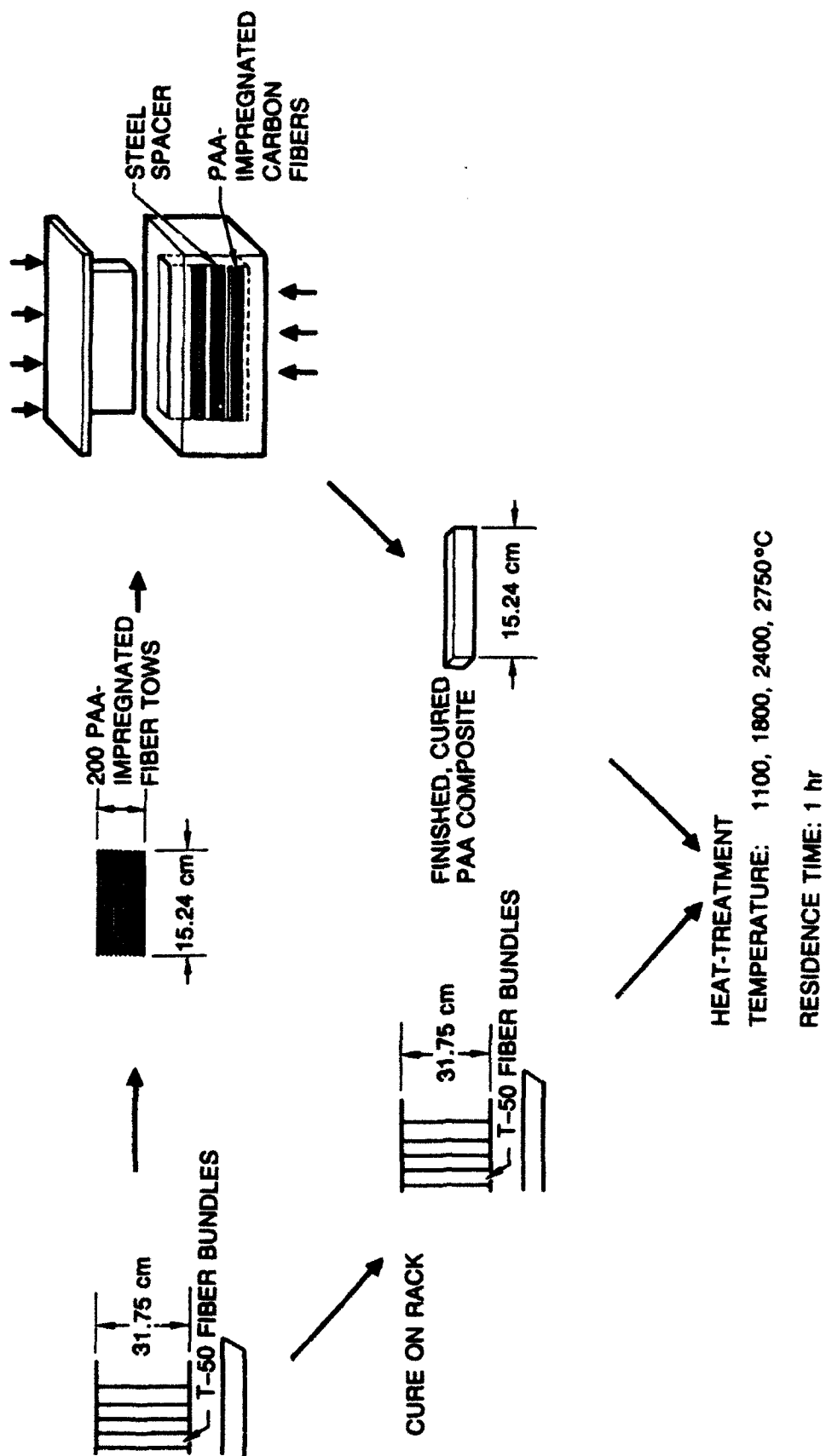


Figure 2. Fabrication process for PAA-derived C/C composites.

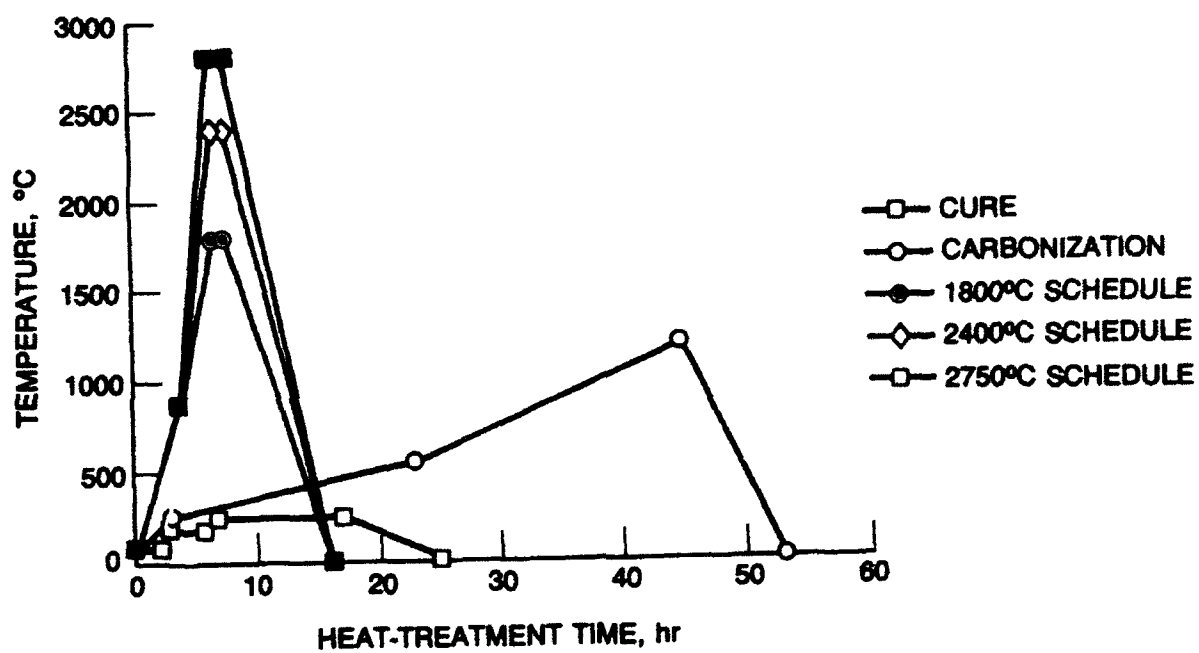


Figure 3. Heat-treatment schedule of PAA/T-50 composites.

xenon-ion-etched. Tensile specimen fracture surfaces were gold-sputtered and examined using an SEM. X-ray diffraction was used to monitor the structural transformation in the C/C composites at various processing temperatures. All specimens were analyzed by copper ($K\alpha$) radiation, using a computer-controlled vertical powder diffractometer equipped with a graphite crystal monochromator and a scintillation detector. The graphite (002) reflection was scanned from 22 to 29 deg at a speed of 2.4 deg/min and operating conditions of 45 kV and 38 mA. The beam was scanned across the primary direction of the fiber axis for all composite samples.

C. MECHANICAL TESTING

Tensile testing was performed on the as-cured T-50/PAA composite strands, the C/C composite strands, and the T-50/epoxy strands. Each end of the 15.2-cm strands was bonded between 5.08-cm cardboard tabs, leaving a 5.08-cm gage length. The samples were loaded to failure in an Instron testing machine at a crosshead speed of 0.13 cm/min. The procedure used in calculating the system compliance is explained in ASTM D 4018-81 Appendix XI, and the procedure for all testing is described in ASTM D-790. Thirty samples were tested at each of the three heat-treatment temperatures.

A three-point-bending test was used to determine the flexural and interlaminar shear strengths. A span of 16.13 cm was used for flexural tests, and the samples were machined to a thickness of 0.13 cm. To prevent shear of the flexural samples, a span/depth ratio of 45:1 was necessary for the unidirectional samples. All interlaminar shear-test samples were machined to a thickness of 1.01 cm and tested with a 5.08-cm span, giving a 5:1 span/depth ratio. Fifteen flexural and 10 interlaminar shear samples were tested for each heat-treatment temperature.

III. RESULTS AND DISCUSSION

A. EFFECT OF PROCESSING ON MICROSTRUCTURE

The effect of heat treatment on the microstructure of PAA-derived C/C composites is exhibited in Figs. 4 through 7. In Figs. 4 and 5, optical micrographs of unidirectional composites heat-treated to 1100 and 1800°C, both composites appear to have good fiber-matrix bonding and relatively low porosity. There is a slightly increased amount of optical activity in the matrix of the 1800°C sample when observed under polarized light. It may be due to enhanced orientation of the matrix with heat treatment.

Upon further heat treatment to 2400°C, a greater amount of optical activity is observed, Fig. 6. Such optical activity is usually located at the fiber-matrix interface and dissipates as it moves outward into the bulk of the carbon. After the 2400°C heat treatment, the composite is essentially a three-phase system consisting of fiber, localized oriented matrix, and an isotropic matrix away from the fiber-matrix interface. The fiber and matrix appear to remain well bonded, and the matrix shows very little observable porosity. Figure 7 shows the cross section of a PAA-derived composite heat-treated to 2750°C. With this heat treatment, the degree of localized orientation has increased and has moved further outward from the interface. Even though there is a sharp increase in the optical activity of the matrix over that of the 2400°C sample, many regions throughout the composite still remain isotropic.

Figure 8 is a plot of real density (by methanol immersion) versus heat treatment for T-50/PAA C/C composite systems. Upon heat treatment to 1100°C, the density of the composite increases as a result of the conversion of a polymer matrix to carbon and an increase in fiber volume fraction from 0.35 to 0.55. Further heat treatment to 1800°C causes a slight decrease in density. Mass analysis shows a very minimal weight loss from 1200 to 1800°C, and, consequently, an increase in volume. The reason for this density decrease is an increase in the closed microporosity of the system as discussed by Kipling et al. [13], who observed the same type of density decreases in a range of nongraphitizable glassy carbons. Further heat treatment to 2400°C shows a large increase in density, which can be correlated with the greater amount of localized optical activity at the fiber-matrix interface. Composites heat-treated to 2750°C show further increases in density to approximately 1.84 g/cm³.

X-ray scans showing the (002) diffraction peak of T-50/PAA-derived C/C composites are shown in Fig. 9. Samples heat-treated to 1100 and 1800°C exhibit a symmetric peak at $2\theta = 26$ deg. This symmetric peak indicates that there is little or no variation in the crystallinity between the fibers and the matrix, and the d-spacings for the 1100 and 1800°C heat treatments are 3.43 and 3.41 Å, respectively. Upon further heat treatment to 2400°C, an asymmetric curve is formed and shifts to the higher angle side. This asymmetric curve is believed to be due to a convolution of two peaks, one having parameters indicating a graphitic structure and the other having parameters indicating a turbostratic carbon. Since the crystallinity



Figure 4. Scanning electron micrograph (SEM) of T-50/PAA-derived C/C composite heat-treated to 1100°C.

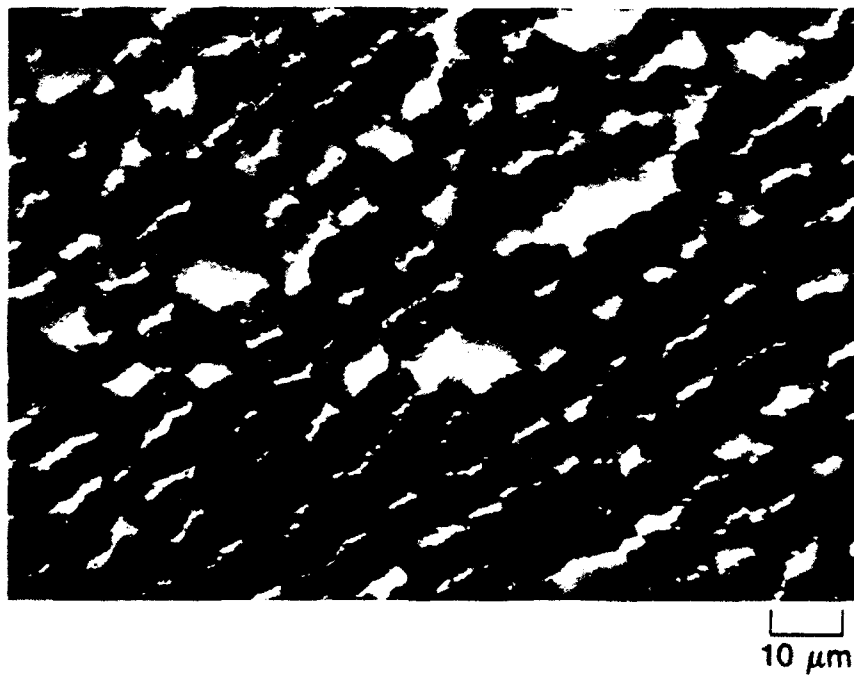


Figure 5. SEM of T-50/PAA-derived C/C composite heat-treated to 1800°C.



10 μm

Figure 6. SEM of T-50/PAA-derived C/C composite heat-treated to 2400°C.



10 μm

Figure 7. SEM of T-50/PAA-derived C/C composite heat-treated to 2750°C.

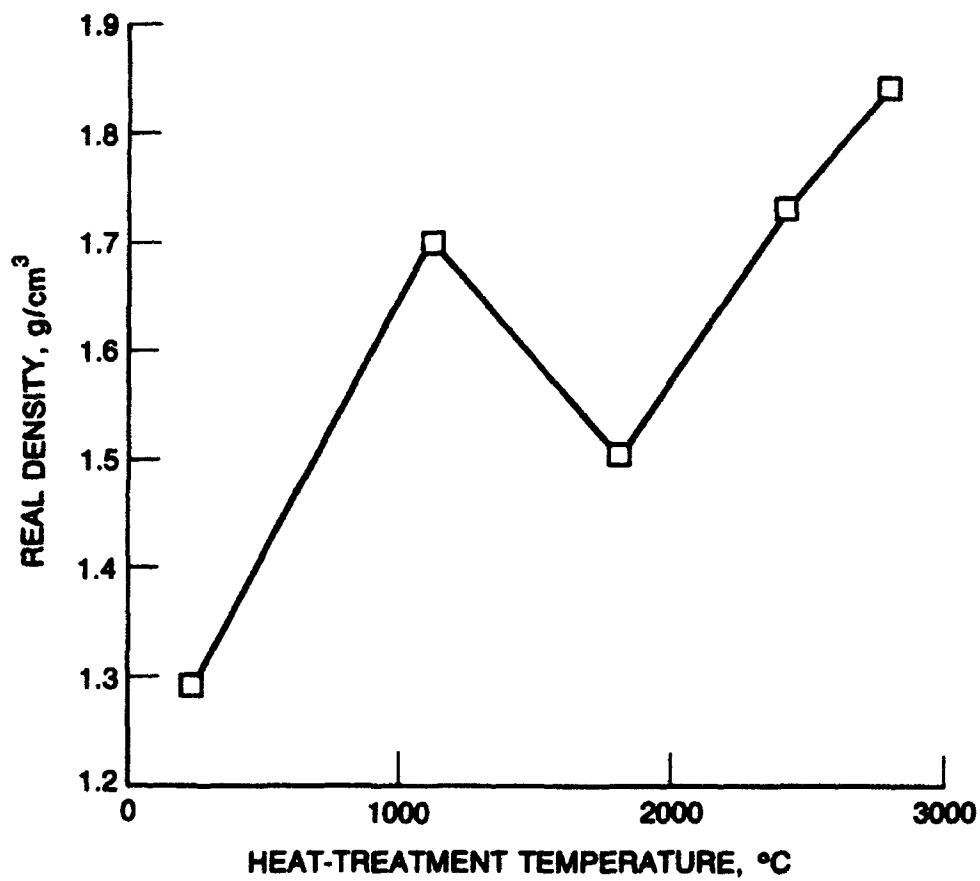


Figure 8. Real density versus heat-treatment temperature (HTT) for PAA/T-50-derived C/C tow composites.

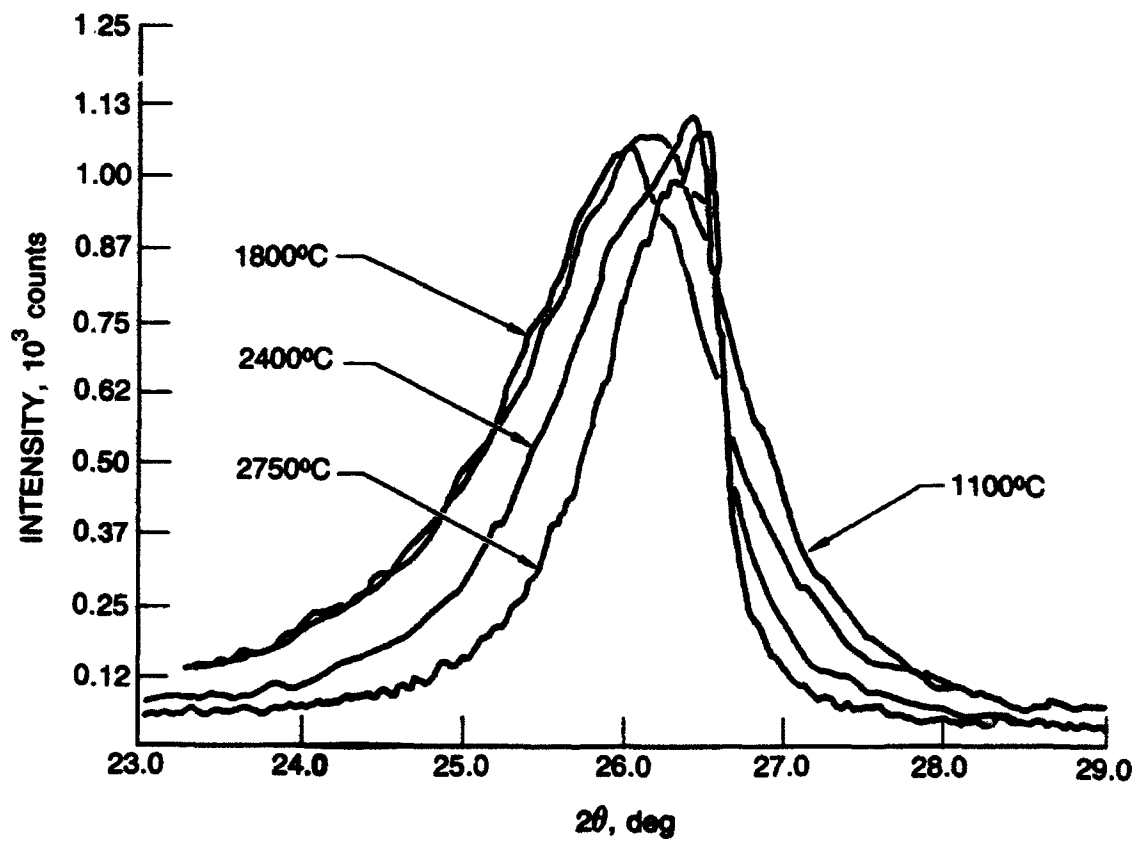


Figure 9. (002) diffraction peaks of T-50/PAA unidirectional C/C composites heat-treated to 1100, 1800, 2400, and 2750°C.

of fibers does not change up to heat-treatment temperatures of 2400°C, we believe that this curve is due to localized graphitization of the matrix in the composite corresponding to a d-spacing of 3.375 Å. Further heat treatment to 2750°C shifts the peak slightly to the right, indicating a more graphitic system with a maximum d-spacing of 3.37 Å.

B. EFFECT OF PROCESSING ON MECHANICAL PROPERTIES

As shown in Fig. 10, the tensile strength of epoxy-impregnated T-50 fiber bundles in the as-cured state is 2.413 GPa, which agrees well with the manufacturer's data. Heat treatment of the fiber at temperatures below 2750°C did not significantly degrade fiber strength. An average strength loss of approximately 896 MPa was observed from this heat-treatment temperature. The elastic modulus showed a 5.0% increase after heat treatments at 2750°C.

In the plot of the tensile strength of C/C tows as a function of heat-treatment temperature, Fig. 11, each point is an average of 30 data points. The scatter of the data points at each temperature was at most +8.0%. Since the strain to failure of PAA resins is greater than that of T-50 carbon fibers, the tensile strength of the as-cured composites was approximately equal to the fiber strength. The fracture surface of a cured (to 250°C) T-50/PAA composite is shown in Fig. 12. Fiber pullout in the range of 30 to 100 μm is evident. Many carbon filaments show matrix residue on their surfaces. In addition to individual filament pullout, large clumps or plates of matrix also protrude from the initial fracture plane. The matrix microstructure is quite amorphous and does not reveal any preferred orientation. Small hairline cracks are observed to travel throughout the matrix interconnecting the filaments.

Upon further heat treatment to 1100°C, the composites exhibit a significant reduction in strength. In the SEM of the fracture surface of a PAA-derived composite after heat treatment at 1100°C, Fig. 13, a brittle fracture without fiber pullout is observed across the fracture surface, and the matrix exhibits no orientation effects. The surface of the bundle shows large matrix cracks perpendicular to the fiber orientation, similar to that of well-bonded ceramic matrix composites. Thus, the drop in strength may be due to the conversion of the polymer matrix to a low-strain-to-failure carbon matrix that is fairly well bonded. For a strong interfacial bond, the crack that forms in the lower-strain-to-failure matrix propagates across the fiber-matrix interface to cause immediate fiber failure. Therefore, failure is brittle and the strength of the composite is governed by the low strain to failure of the matrix.

Upon further heat treatment to 1800 and 2400°C, the tensile strength increases to 1.041 and 1.448 GPa, respectively. Figure 14 shows the fracture surface of a PAA-derived composite heat-treated to 1800°C. Increased fiber pullout is observed over the planar-type brittle fracture of the carbonized composites. Although some individual filament pullout is apparent, there are still areas of fracture with little or no pullout. Upon closer examination, a mixture of matrix orientation is observed. Some interfilament areas reveal increased ordering, whereas other areas are more glassy. Samples heat-treated at 2400°C (Fig. 15) show an increase in the number and extent of fiber pullout lengths over that of the 1800°C samples. Greater orientation can also be seen in the matrix fracture surface. The development of an onionlike sheath

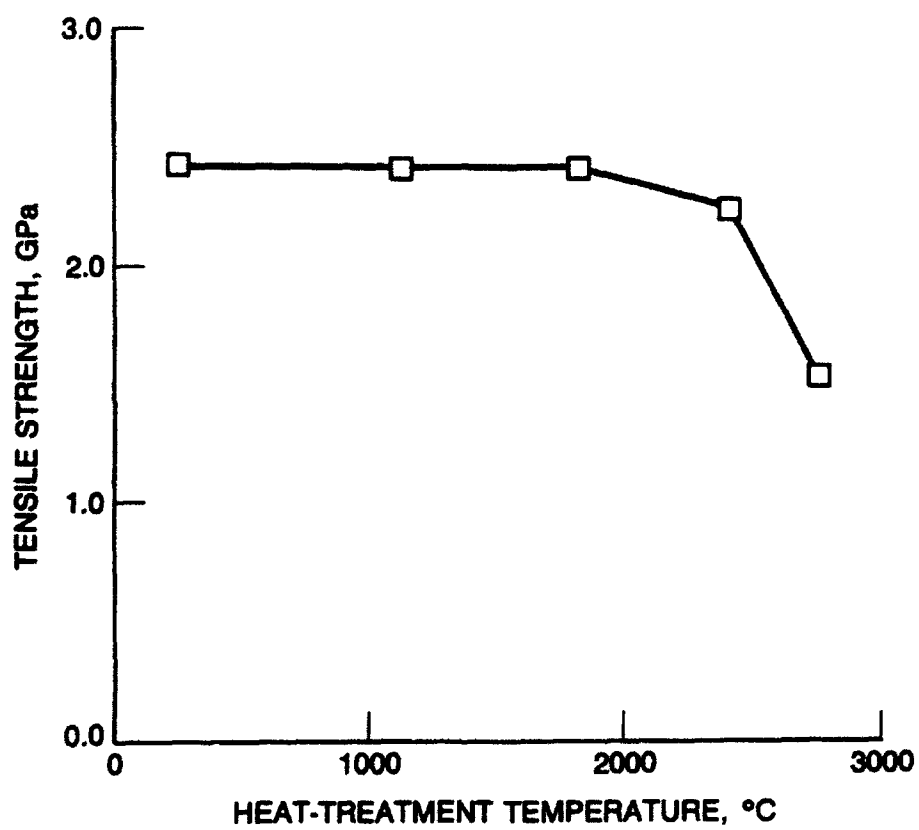


Figure 10. Effect of HTT on fiber tensile strength, as determined from epoxy-impregnated-strand test.

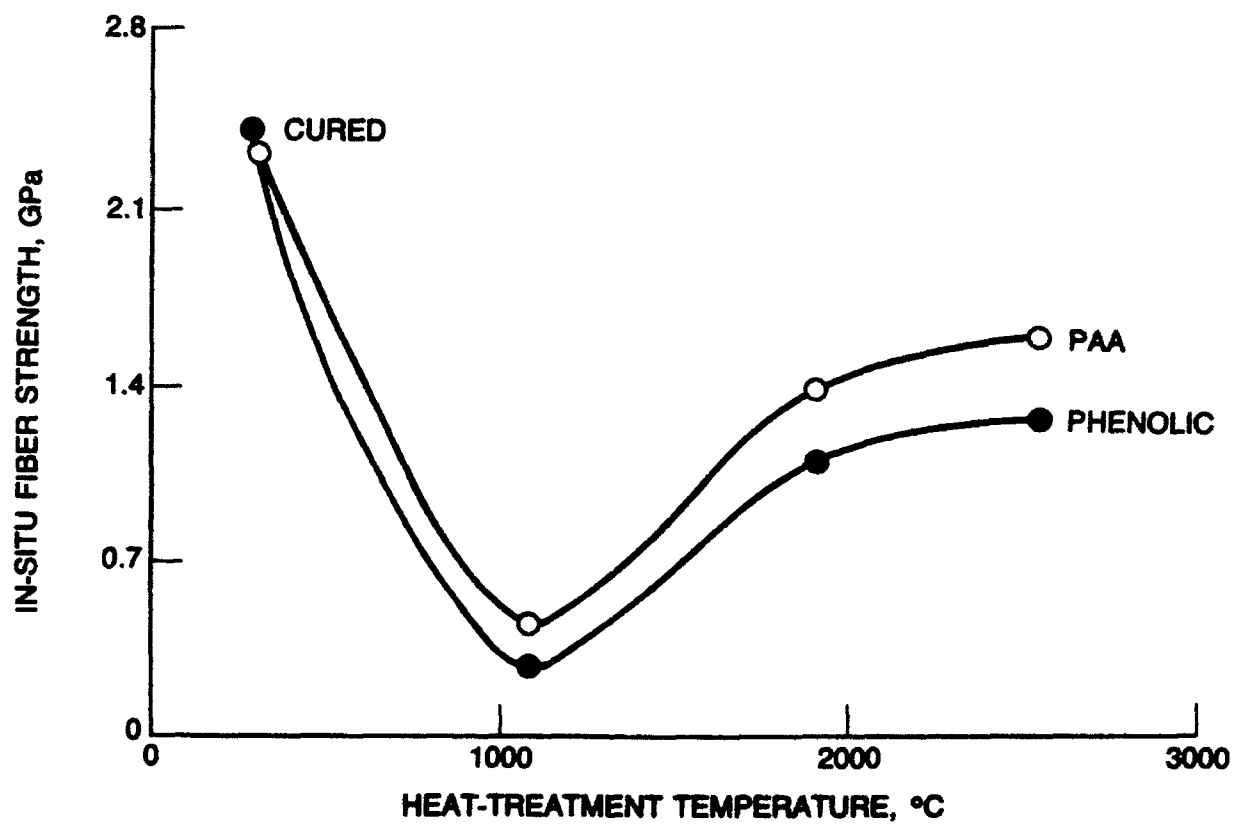


Figure 11. Effect of processing HTT on room-temperature tensile strength of T-50/PAA and T-50/phenolic composites.

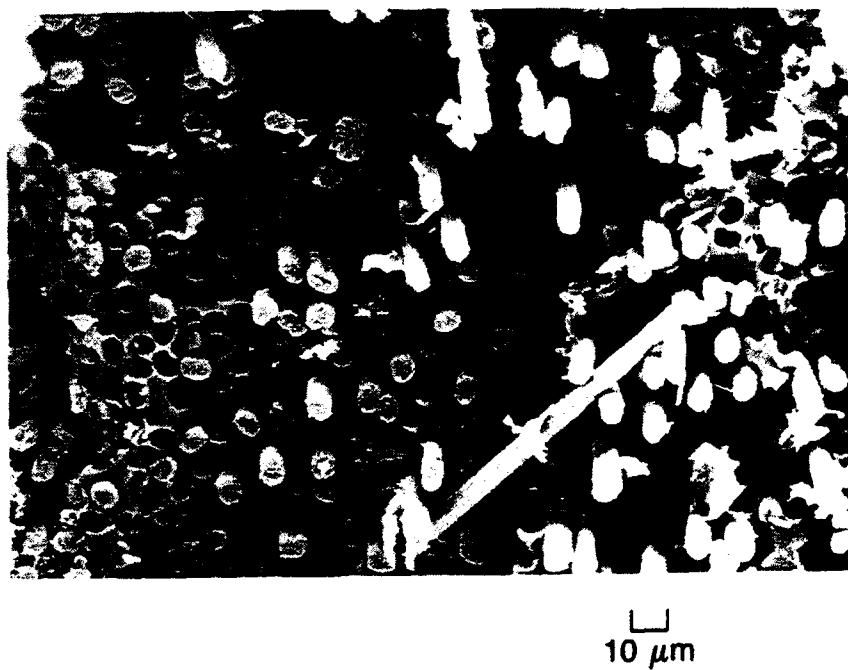


Figure 12. SEM of fracture surface of PAA/T-50 fiber composite cured at 250°C.

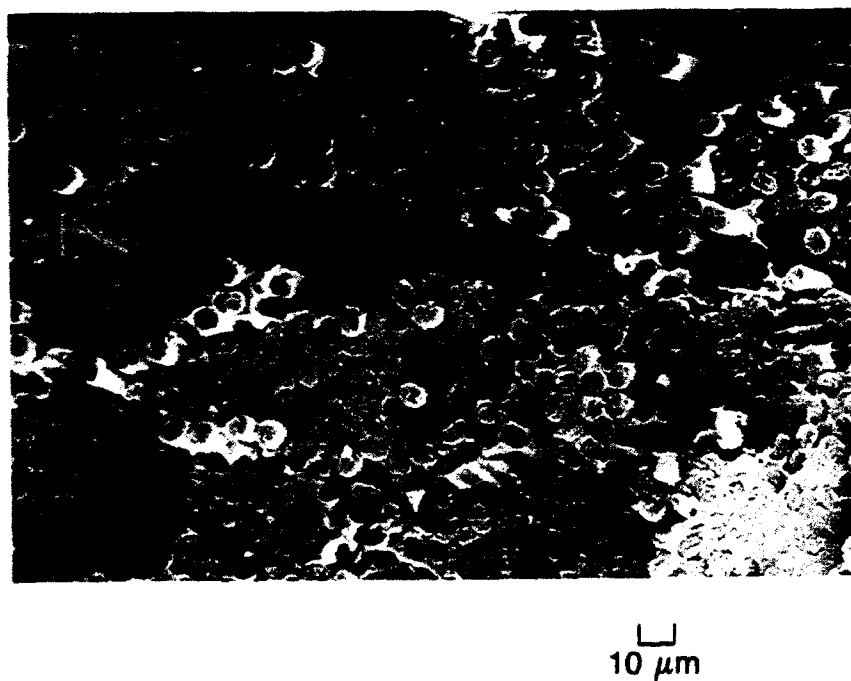
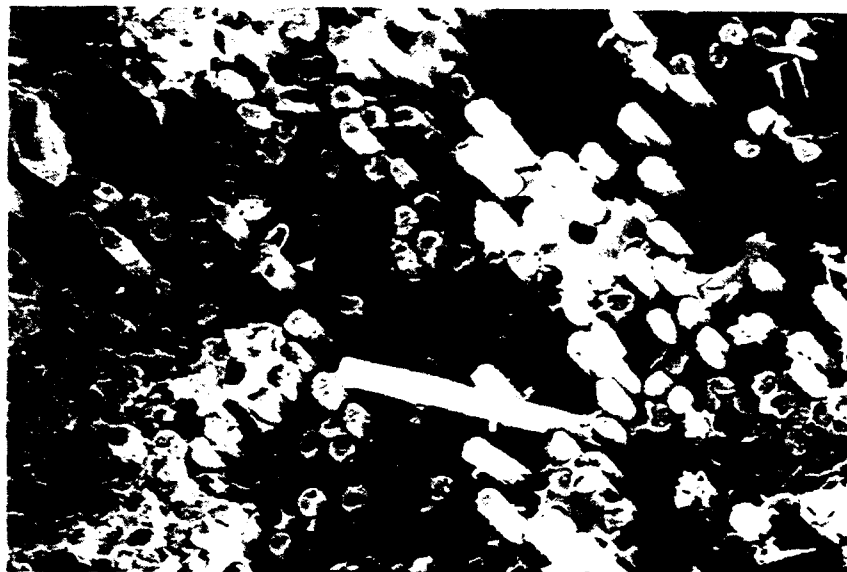


Figure 13. SEM of fracture surface of PAA/T-50 fiber composite heat-treated to 1100°C.



10 μm

Figure 14. SEM of fracture surface of PAA/T-50 fiber composite heat-treated to 1800°C.



10 μm

Figure 15. SEM of fracture surface of PAA/T-50 fiber composite heat-treated to 2400°C.

in the matrix around the fibers is observed. The increased pullout lengths may indicate that a weaker coupling exists between the fiber and matrix in the composites heat-treated to 2400°C.

There are two phenomena by which the strength of these composites may increase. A weak fiber-matrix interface in a brittle composite enables the fiber strength to dominate the overall composite strength rather than allowing the matrix to cause premature composite failure. There may also be a mechanism by which the oriented matrix may prevent oncoming cracks from propagating through to the fibers, so that the fibers strain to a greater degree and fail at higher strengths.

Returning to Fig. 11, the second curve, strength versus processing heat-treatment temperature for T-50/phenolic C/C composites, follows the same trend as for the T-50/PAA C/C composites. The strength utilizations are somewhat lower in these phenolic two-configuration composites than those of the PAA composites. We expect that larger phenolic-derived composites would show a greater variance in strength, owing to the more numerous matrix cracks and porosity associated with larger volatile diffusion paths.

The flexural and interlaminar shear strengths of PAA-derived C/C composites are shown in Table 1. The flexural strengths increase with heat-treatment temperature from 1100 to 2400°C, similar to the tensile data. At 2750°C there is a drop in strength, which is attributed to degradation of the carbon fiber with heat treatment, as shown above in Fig. 10. For comparison, Fig. 16 shows the flexural test samples heat-treated to 1100°C and those that were heat-treated to higher temperatures. The 1100°C sample has a crack that initiated on the surface and traveled across the composite, forcing brittle failure. The samples heat-treated to 2400°C show a less catastrophic type of failure. Crack deflections enable the fibers to carry most of the load without the danger of brittle fracture.

Table 1. Flexural and Interlaminar Shear Strengths of T-50/PAA-Derived Composites

Heat-Treatment Temperature, °C	Strength	
	Flexural, MPa	Shear, MPa
1100	500	8.3
1800	690	4.1
2400	800	4.1
2750	690	3.8

This deflection phenomenon can be better understood by analyzing the fiber-matrix interface. Figures 17 and 18 show typical T-50/PAA longitudinal interfaces for heat-treatment temperatures of 1100 and 2750°C, respectively. The interface of the sample heat-treated to 1100°C (Fig. 17) appears to exhibit good bonding and no observable differences in structure between the fiber and matrix. Since both constituents are relatively the same, one can easily

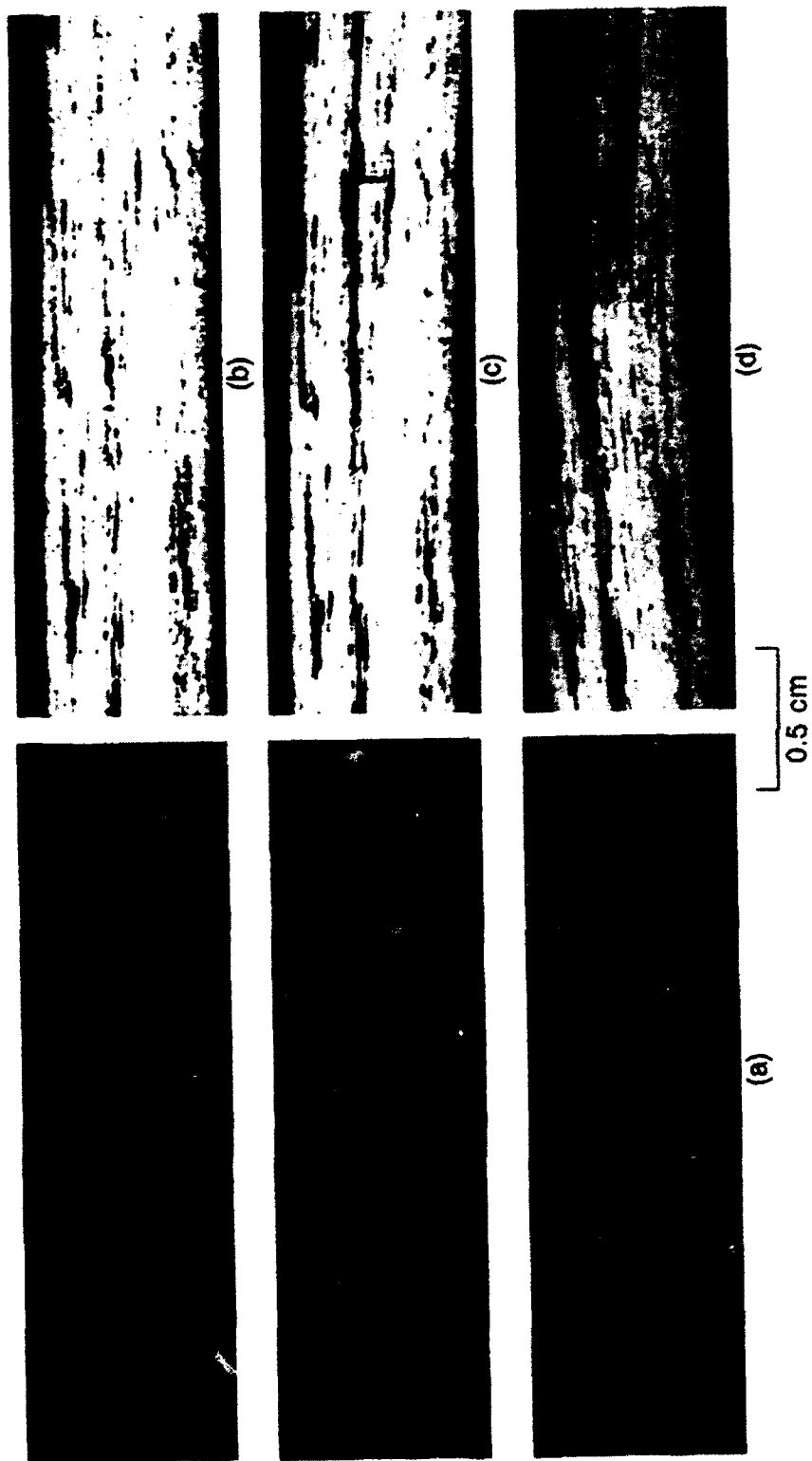


Figure 16. Three-point-bend failure mode for PAA/T-50 unidirectional C/C composites heat-treated to (a) 1200°C (3 times during test); (b) 1800°C, (c) 2400°C, and (d) 2750°C.

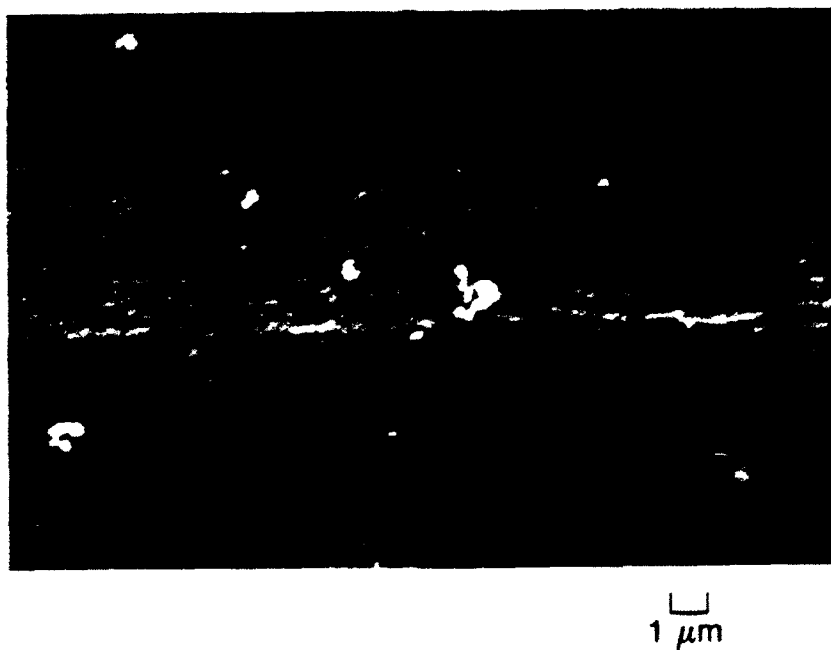


Figure 17. SEM of longitudinal fiber-matrix interface of PAA/T-50 composite heat-treated to 1100°C.

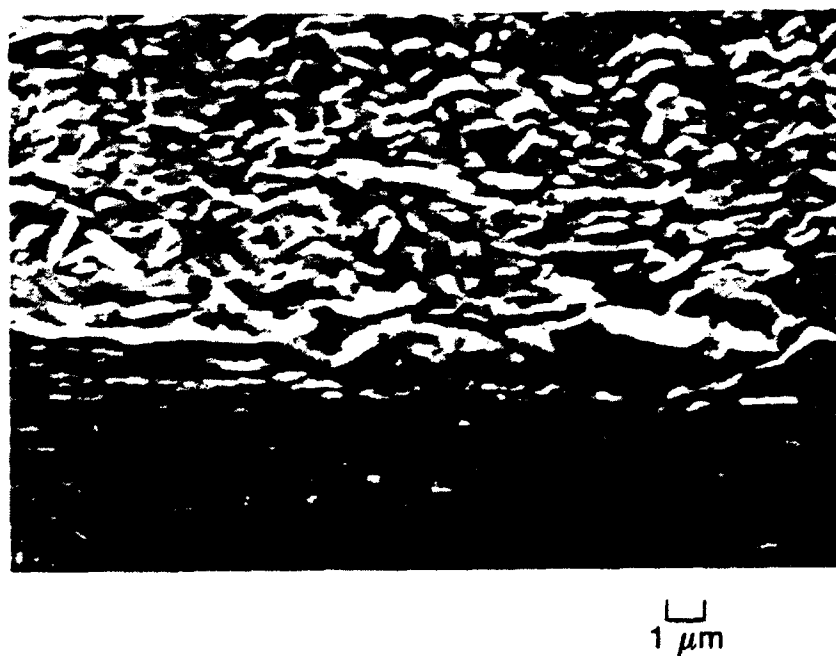


Figure 18. SEM of longitudinal fiber-matrix interface of PAA/T-50 composite heat-treated to 2750°C, showing well-oriented sheath parallel to the fiber direction.

understand how a matrix-initiated crack can propagate through the interface and cause the composite to behave as a monolith. The sample heat-treated to 2750°C (Fig. 18) has a very well-oriented sheath parallel to the fiber direction, usually 2 to 5 μm from the fiber-matrix interface. This sheath is not only more oriented but also has some microporosity in its scale-like structure.

Two mechanisms that may be responsible for the greater strengths encountered in higher-temperature heat-treated C/C composites are apparent in the SEM micrograph of Fig. 19. The micrograph is of a tensile specimen that was strained but was not taken to absolute failure. As expected, cracks propagate perpendicular to the applied load direction. Rather than propagating through the fiber, the crack tips are blunted or deflected before reaching the fiber. On one side of the fiber, crack deflection occurs along the fiber-matrix interface; on the other side, the crack tip is blunted within the well-ordered sheath. These two mechanisms enable the fiber to undergo considerably greater strain before composite failure.

From Table 1 we see that the interlaminar shear strengths of PAA-derived C/C composites are highest at 1100°C, then decrease to an approximately constant value at heat-treatment temperatures of 1800°C and above. These results are consistent with the larger pullout lengths of the higher heat-treatment-temperature specimen and indicate a general weakening of the fiber-matrix bond with heat-treatment temperature.



Figure 19. Longitudinal fiber-matrix interface of PAA/T-50 composite heat-treated to 2750°C, showing two strength-enhancing mechanisms: crack deflection along fiber-matrix interface (top) and blunting of crack tip within well-ordered sheath (bottom).

IV. CONCLUSION

The above results demonstrate that heat treatment of PAA-derived C/C composites leads to a variety of matrix microstructures, ranging from isotropic to some enhanced localized graphitization at the fiber-matrix interface. Such range of microstructures affects the mechanical properties, particularly the fracture modes. For example, after 1100°C heat treatment, flexural and tensile tests reveal a brittle mode of failure resulting in low utilization of reinforcement strength. Heat treatment at higher temperatures promotes several possible mechanisms that effectively increase the strength of these composites. Such increases may be due to increases in the strain to failure of the matrix material, a weakening of the fiber-matrix interface bond, and/or the deflection and blunting of matrix-initiated crack tips. The oriented sheaths formed at high temperature at the fiber-matrix interface are believed to have a major influence on the mechanical properties.

The localized orientation effects that occur in thermosetting-derived C/C composites are very distinct from those of ceramic-matrix composites. The interface controls the mechanical properties; therefore, the bulk of the matrix need not be oriented throughout the composite. As discussed elsewhere [14], the reason for localized graphitization may be the large compressive and tensile stresses that develop at the fiber-matrix interface during carbonization of the resin system. During carbonization, as the fiber expands transversely with temperature, the resin shrinks onto the fiber from the volumetric contraction that occurs during the conversion of polymer to carbon. Such shrinkage causes large interfacial stresses that may preferentially align matrix material. Upon further heat treatment to typical graphitizing temperatures, the once-nongraphitizable carbon transforms locally to a graphitic structure.

Using PAA as a carbon matrix precursor has several advantages over using currently available systems. The high char yield leads to fewer redensifications and therefore fewer processing cycles. PAA-derived composites can be carbonized relatively quickly with less danger of the large pyrolysis shrinkage that can lead to formation of matrix cracks and debonding, as observed typically in phenolic-derived systems.

PAA-derived composites appear very promising for applications that are currently being supplied by phenolic resins. Further studies are in progress to gain a better understanding of this promising materials system.

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