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Review of Polyarylacetylene Matrices for Thin-Walled Composites

Prepared by

W. T. BARRY, C. A. GAULIN, and R. W. KOBAYASHI
Materials Sciences Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, CA 90245

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Prepared for

SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Base
P. O. Box 92960
Los Angeles, CA 90009-2960

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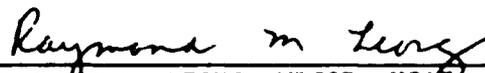
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PAUL PROPP, AF MATERIALS LAB WCO, USAF
MOIE Project Officer
WRDC/WCO OL-AB



RAYMOND M. LEONG, MAJOR, USAF
MOIE Program Manager
AFSTC/WCO OL-AB

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Polyarylacetylenes (PAAs) have been successfully employed over the past fifteen years as matrices in the fabrication of thin wall carbon-carbon composites. Because of the proprietary nature of the early polymer, its exact composition was not known. Recent interest in high performance thermal protection systems prompted a detailed reinvestigation of these materials. A brief review of the chemistry of the PAAs involved is discussed in light of our current experiences. The studies reaffirm our belief that these resins are prime candidates for carbon-carbon matrices and offer advantages in fabricability over currently used resins.						
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PREFACE

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1. INTRODUCTION

This report summarizes work which was initiated about fifteen years ago¹ and updates our work on the utilization of polyarylacetylenes (PAAs) as matrix precursors for thin wall carbon-carbon composites.

A. BACKGROUND

The initial motivation for this study was to develop special carbon composites for ballistic reentry vehicles related to penetration strategies. Basically, all the material systems developed were predicated on the well known capacity of carbon to absorb large quantities of energy before vaporizing. Considerable attention was given to the development of both 2-dimensional and 3-dimensional carbon shells of thin wall construction for potential reentry application. Most of the early processing employed in the fabrication of the articles used either phenolic or furfuryl resins as the initial matrix precursor. The particular application addressed required the development of both special carbon fibers and a technique for placing them in a particular geometry, which required special control over layer thickness, placement, and fiber density. To this end, we restricted the yarn bundles to 1000 filaments and the twist to 1 per inch. (Some twist was necessary in order to maintain yarn integrity.) Details of the construction dictated filament winding as the preferred fabrication technique.

With our filament design concept fixed, our next concern became a suitable matrix resin with which to bind the material system together. Our preference was for a resin which (1) can be wet-wound for ease of filament winding, (2) has a high char yield, (3) cures by addition rather than condensation, and (4) requires minimal pressure and temperature for processing. Fortunately, at this time Jabloner et al.² at the Hercules Experimental Station were developing high temperature molding compounds based on PAAs (see Fig. 1). This was a rather short-lived venture on the part of Hercules, but we succeeded in obtaining several hundred pounds of pre-

polymer before the pilot plant was shut down. This material, known as HA-43, was stored under refrigeration and used in developmental studies over nearly a decade without obvious signs of aging or deterioration.

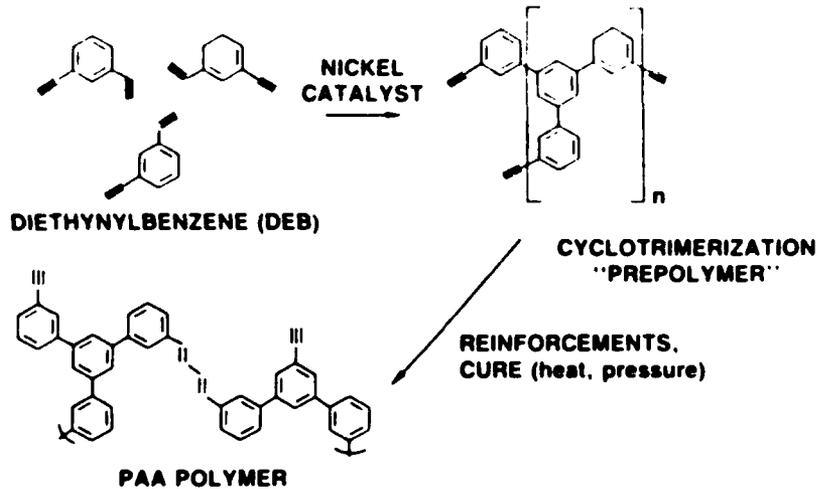


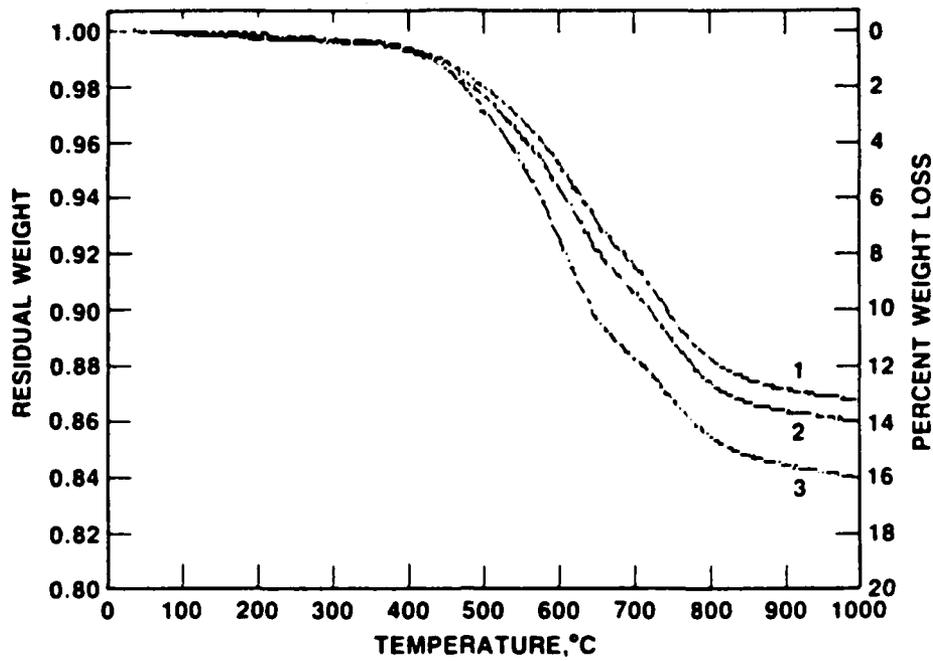
Fig. 1. Synthesis of PAA

Details of the fabrication procedures used in these studies are given in a report submitted to the Defense Nuclear Agency by Haveg Industries.³ Briefly summarized, individual yarns were dip-impregnated in a 33% HA-43 solution in methylethylketone and wound onto a graphite mandrel. Maximum fiber packing (60-70%) and accurate placement was a requirement which necessitated a high winding tension. Because of this, no further debulking on cure was needed and simple vacuum bagging sufficed. Using a solution for ease of application, however, has its penalties, and two to three reimpregnations with HA-43 solution were necessary to bring the composites up to acceptable densities. Carbonization was carried out to 800°C in a female graphite holding fixture to prevent warpage. After final densification, the composites were processed to a maximum temperature of only 1850°C and, as a consequence, virtually no graphitization of the matrix occurred. This temperature limitation was imposed in order to minimize particle growth in the special carbon fibers.

Practically all of the fabrication difficulties encountered in the early phases of this study were attributed to the poor mechanical properties of the fibers. As fiber development proceeded and the quality of the fibers improved, so did the quality of the composites because adequate winding tension could be applied with minimum fiber damage. Correction of these early difficulties resulted in thin wall composites (100-120 mils) which both met the technical requirements and provided adequate mechanical properties. Although the details of the fabrication of these composites are probably not germane to the fabrication of exit cones, this work demonstrated the utility of PAA as a matrix precursor in thin wall carbon-carbon composites.

B. CURRENT STATUS

After a brief hiatus, interest in polyarylacetylenes was reawakened with the primary objective not the development of carbon-carbon composites or exit cones, but the development of superior ablative protection systems. Our preference for an organic matrix over a carbon matrix composite was due to its lower thermal conductivity, superior mechanical properties and, finally, ease and cost of fabrication. Because of their known high char yield (Fig. 2), PAAs appeared to be likely candidates for this study. To this end, we decided to reinvestigate the early work of Jabloner,² which had been directed toward molding compounds, and determine the utility of the PAAs in advanced composite systems. It was only after we had established the feasibility of this approach that we again turned our attention to their use in thin wall carbon-carbon composites. Because of the preliminary nature of this study, only a limited amount of data on carbon-carbon composites is available. However, we thought it would be of interest to the community to review the chemistry of PAAs and, in light of our more recent experiences with these materials, comment on those aspects of the chemistry that seem appropriate to the construction of thin wall carbon-carbons.



SAMPLE 1: 100% META RESIN
SAMPLE 2: 75:25 BASE RESIN: PA (PHENYLACETYLENE)
SAMPLE 3: HA-43 NEAT RESIN
HEATING RATE: 4°C/min GAS FLOW RATE: 100 cc/Min

Fig. 2. TGA in Argon of Basic PAA Resins

II. CHEMISTRY

Most of the monomeric diethynyl benzene used in this study was synthesized by the method of Hay⁴ in which commercial divinylbenzene (DVB), consisting of a mixture of meta and para isomers [with meta and para ethylvinyl benzenes (EVB) as a major impurity] are treated with bromine in chloroform solution at 0°C. Most of the 1,4 bis dibromo ethyl benzene (p-BDBEB) compound precipitates out and after filtration leaves a solution of the 1,3-bis 1,2 dibromo ethyl benzene isomer (m-BDBEB), and meta and para ethyl 1,2 dibromo ethyl benzene (p-EDBEB) as impurities. After stripping off the chloroform, the dibromo ethyl (EDBEB) compounds are separated from the m-BDBEB using a thin film evaporator. The residual m-BDBEB is then dehydrohalogenated in tetrahydrofuran (THF) using potassium t-butoxide. After filtering and stripping off the THF and t-butanol by-product, the m-diethynyl benzene (m-DEB) is once distilled and used as is in the preparation of prepolymer.

Although this procedure seems tedious, it is uncomplicated and the yields are high. The commercial DVB (80%) assay that was earlier supplied can, if there is sufficient demand, be obtained up to 95% DVB assay. Meta to para ratios, however, do appear to vary from batch to batch.* If the preference is for meta or para isomer, the assay should be determined before purchasing.

Our choice of the meta isomer was based upon tailoring the polymer for improved mechanical properties and ease of processing. The monomer, a liquid, is also easy to manipulate and purify, whereas the para diethynyl benzene (p-DEB) isomer is a solid at 95°C and requires multiple recrystallizations for purification. We, therefore, made the decision to concentrate on establishing the capabilities of the m-DEB based polymers. Currently a 60/40 meta/para ratio of DEB is being examined.

* Private communication with C. Snoble of Dow Chemical, 1986.

Although a number of potential catalysts for the cyclotrimerization reaction are mentioned in the Jabloner patent, most of our experience has been with the nickel acetylacetonate and triphenyl phosphine complex, which we have found to be a practical system to handle. Prepolymerization was carried out in either toluene or benzene solution--the latter being preferred for large batches since it limits the reaction temperature and prevents a rate which is a runaway exotherm. More recently, the prepolymerization is performed in methyl ethyl ketone (MEK). MEK is preferred since it limits the reaction temperature as does benzene, but is far less toxic. In addition, the reaction time is decreased, presumably due to the polar nature of this solvent. When sufficient reaction has occurred, the solution is cooled to room temperature and the solvent stripped off using a Roto-Vac. Flow characteristics of the prepolymer are then checked using a flat parallel plate rheometer. Flow behavior provides an indication of reproducibility of prepolymerization. Onset of flow below 100°C is desirable for 100% meta-DEB and should decrease incrementally with increased addition of phenylacetylene (PA).

Prepolymers have been prepared from pure m-DEB, copolymers of m-DEB with phenyl acetylene (PA), and m-DEB blended with several processing aids (Fig. 3) which have the effect of both plasticizing and reducing the cross-link density of the system. Rheometer data for a number of these compositions are shown in Fig. 4. From this it is evident that the pure meta isomer requires substantial pressures for processing, whereas compositions with processing aids are vacuum bag moldable at 80° - 90°C. A further major processing consideration is an exotherm. Differential thermal analysis (DTA) (Fig. 5) shows that the exotherm begins at about 110°C and for this reason we have been extremely careful to densify below this temperature and to maintain a long dwell time before increasing temperatures through the exotherm zone. For thin wall composites this may not be necessary and more processing studies are needed in this area. Processing aids with terminal phenyl groups such as diphenyl butadiyne and II are quite stable compounds and are not incorporated into the polymer structure until

cure temperatures of about 200°C are reached, at which a second lesser exotherm can be expected. Just how and whether they are incorporated is highly uncertain and requires further study since they do appear to be viable processing aids.

An alternate processing aid is the addition of monomer. The monomer acts as a plasticizer to the prepolymer in the processing. The monomer is presumably cyclotrimerized into the polymer during cure due to residual catalyst. Addition of monomer needs to be balanced between the required plasticization and the increase in the exotherm resulting from the cyclotrimerization reaction. Typically, 10% of the monomer is added.

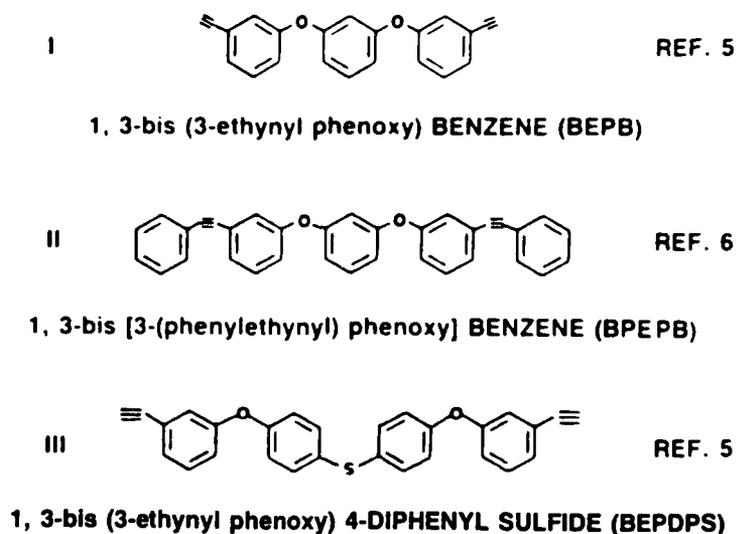


Fig. 3. Processing Aids Under Investigation

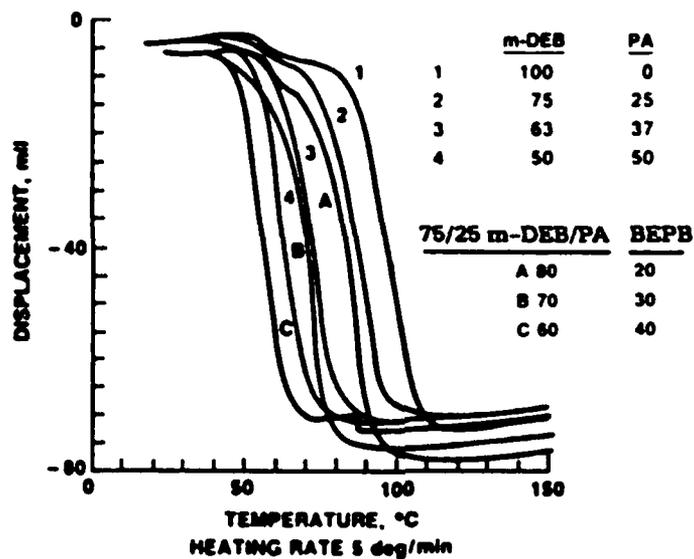


Fig. 4. Melt-Viscogram

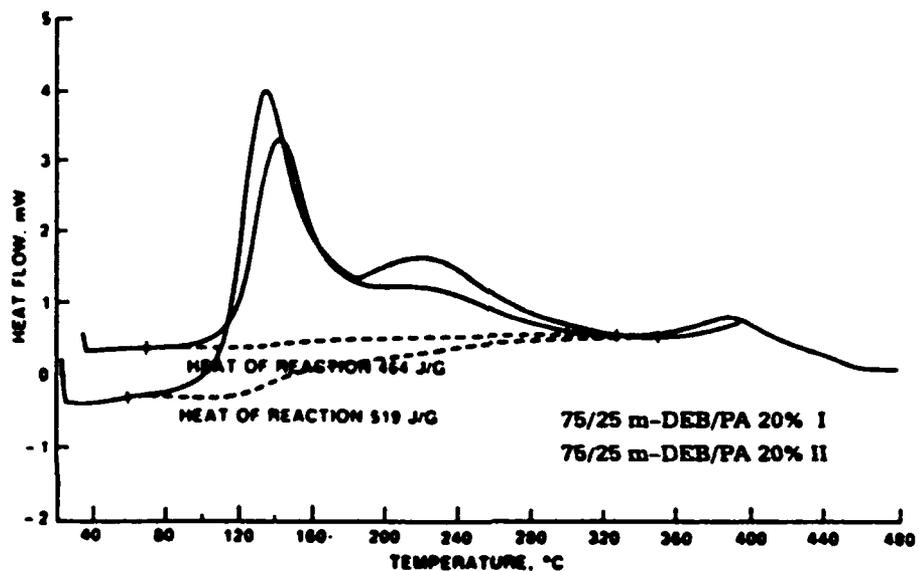
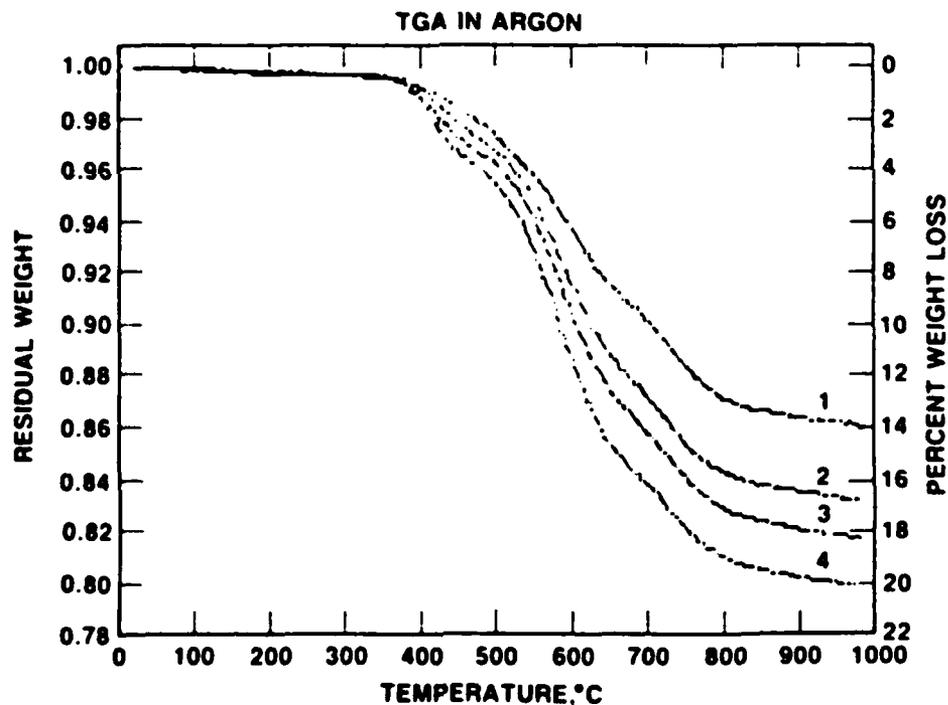


Fig. 5. Differential Thermal Analysis (DTA)

Composite fabrication was carried out using conventional procedures. The prepolymer was redissolved in MEK and used to dip-impregnate fabric sheets. After vacuum bagging, they were then either press molded or cured in a high temperature autoclave in a nitrogen atmosphere. Pressures varied from 400 psi for the pure m-DEB prepolymer, to atmospheric pressure for those with processing aids. Postcuring has been carried out at 250°C, based on the DTA data, but the upper limit for optimum properties has not been established. Figure 6 shows the effect of the processing aids on char yield. The influence of the oxygen in these molecules is evident, but the yields are still very high, which implies that char yield can be traded off for ease of fabrication of complex structures with a minimum weight loss penalty.



SAMPLE 1: 75:25 BASE RESIN
SAMPLE 2: 20% BEPB/75:25 NEAT RESIN
SAMPLE 3: 30% BEPB/75:25 NEAT RESIN
SAMPLE 4: 40% BEPB/75:25 NEAT RESIN

Fig. 6. Effect of Processing Aid on Char Yield

Preliminary carbonization studies have been started on the 75/25 meta-diethynyl benzene copolymer for the purpose of determining residual mechanical properties after exposure to moderate ablation conditions. It was not our intention to redensify these composites, therefore the data is indicative of only the first step in the carbonization cycle carried out at 1200°C (see Tables 1 and 2). Each mechanical datum represents an average of three tests. Resin content, fiber volume, and postcured porosity were all calculated based on material balance and final density. Carbonized porosity and density were determined by mercury porosimetry. The choice of T-300 reinforcement for the PAA composites was determined by structural requirements. FM 5064, a commercial carbon phenolic widely used as a carbon-carbon precursor, is shown for comparison of carbonization efficiency. We used flexural strength as the primary criterion for strength retention since this is a matrix dominated property. From this limited data it appears that the PAA composites retain substantial strength after a single carbonization. The use of particulate fillers in this system is also probably unnecessary and merely complicates processing and quality control.

An area of interest to carbon-carbon (C-C) applications is that of graphitization of the resin. Although our earlier studies using HA-43 did not require us to graphitize and our current applications do not either, we

Table 1. Physical Properties of As-Cured and Carbonized Composites

COMPOSITE	BEFORE CARBONIZATION (post-cured)				CARBONIZED		
	RESIN (+ filler) CONTENT wt (vol) %	FIBER CONTENT (vol) %	DENSITY (g/cc)	POROSITY (%)	CHAR YIELD (%)	DENSITY (g/cc)	POROSITY (%)
T 300/PAA	29 (40)	60	1.55	3.9	95.6	1.62	8.0
T 300/PAA/P-33 10%	30 (40)	60	1.55	2.6	95.6	1.65	9.1
CARBON/PHENOLIC (FM 5064)	TBD	TBD	1.46	5.5	84.6	1.55	18.7

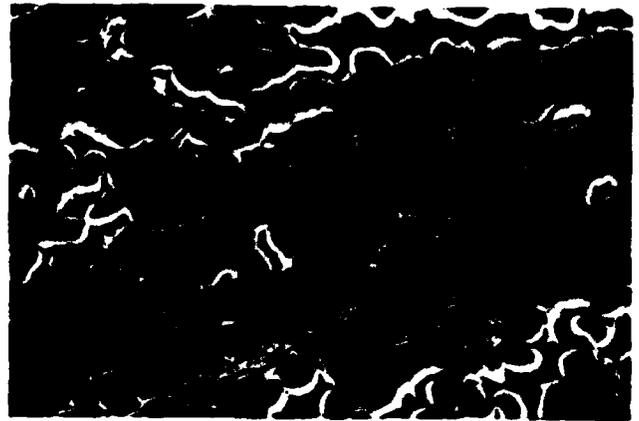
Table 2. Mechanical Properties of As-Cured and Carbonized Composites

COMPOSITE	BEFORE CARBONIZATION (post-cured)				CARBONIZED	
	TENSILE STRENGTH (PSI)	TENSILE MODULUS (MSI)	FLEXURAL STRENGTH (PSI)	FLEXURAL MODULUS (MSI)	FLEXURAL STRENGTH (PSI)	FLEXURAL MODULUS (MSI)
T 300/PAA	70,580	8.69	53,760	8.26	21,110	8.47
T 300/PAA/P-33 10%	70,830	7.69	33,120	7.15	23,380	6.56
CARBON/PHENOLIC (FM 5064)	19,060	1.51	25,220	1.96	9,900	1.68

conducted a preliminary study of graphitization to 2400°C of two composites - one with pure meta isomer, the other with a 75/25 blend. Based on limited micrographic evidence, we concluded that more extensive ordering and crystal growth appeared to have occurred in the 75/25 specimen. We reasoned that the reduction in crosslink density in the 75/25 copolymer was responsible for greater ease in rearrangement of the carbon skeletal structure to the crystalline form. However, since that initial study, Binegar, et al.⁷ have examined many more specimens, including those from 63/37 m-DEB/PA resin blend. Their scanning electron micrographs of the three resin systems, heat treated to 2700°C, are shown in Fig. 7. These specimens were xenon-ion-etched to enhance their microstructural features. It is clear that the formation of graphitic structure, as evidenced by regions of lamellar microstructure, is comparable in all three specimens, and that the variations in crosslink density over their range of compositions had no major influence on the graphitization process. It should be noted that resins, in contrast to petroleum and coal-tar pitches, show only limited graphitization in the interstices of C-C composites. In bulk, they show no measurable graphitization. It remains to be determined if the graphitizability of the PAA resins differs from that of phenolic and other state-of-the-art resins.

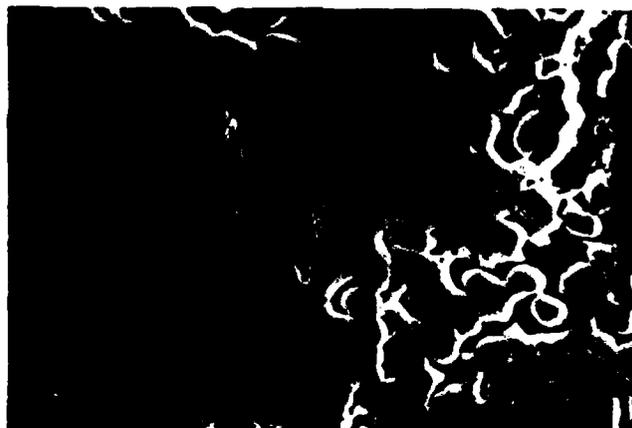


(a)



(b)

10 μm



(c)

Fig. 7. Scanning Electron Micrographs (1000x) of Carbon-Carbon Composites: (a) 100% Meta, (b) 63:37 Blend, and (c) 75:25 Blend. (Ref. 7).

III. CONCLUSIONS

Our study of PAAs resulted in the following conclusions:

1. The very high char yields of PAA resins appear to lend themselves to the fabrication of thin wall carbon-carbon composites. In the past, composites were produced successfully with HA-43 resin using a solution wet-winding procedure.
2. Conventional processing techniques, prepregging, vacuum bagging, press, and autoclave molding, have been demonstrated. Further refinements in processing and curing will be necessary when larger quantities of monomer become available.
3. Vacuum bag or low pressure molding of large or complicated shapes is achievable using processing aids such as BEPB with only a small reduction in char yield.
4. There is no difference in graphitizability of various copolymers of meta-diethynyl benzene with phenylacetylene.

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LABORATORY OPERATIONS

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