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FINAL REPORT

LARGE DIAMETER GRAPHITE/CARBON COMPOSITE FILAMENT DEVELOPMENT

by

N. E. Quackenbush

Philco-Ford Corporation
Aeronutronic Division
Ford Road
Newport Beach, California 92663

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

July 24, 1970

CONTRACT NAS 3-13204

NASA LEWIS RESEARCH CENTER
Cleveland, Ohio 44135
Project Managers: John P. Merutka
David L. McDanels

NOTICE

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ABSTRACT

The feasibility of making large-diameter composite monofilaments was investigated by pyrolyzing high-modulus graphite fiber/high-char polymer composites. Molding, rolling and wet-die drawing were used to form the monofilaments. The results of this program showed the feasibility of the method. However problems encountered in the impregnation, curing and pyrolysis steps caused nonuniform distribution of the fibers and porosity and cracking within the pyrolyzed carbon matrix. These problems prevented the composite monofilaments from attaining their full potential properties. The full modulus and up to 80% of fiber tensile strength were retained in the best pyrolyzed composites.

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1. SUMMARY

This program was a 12-month effort to establish the feasibility of fabricating large diameter graphite/carbon composite monofilaments. The monofilaments were formed by impregnating graphite fiber bundles with a high-char polymer and then converting the polymer to carbon by pyrolyzation.

The target properties for the finished filament were .002 to .010 inch (5.08×10^{-2} to 25.4×10^{-2} mm) diameter, uniform cross-section, 50×10^6 psi (34.5×10^4 MN/m^2) tensile modulus of elasticity, and 400,000 psi (27.6×10^2 MN/m^2) tensile strength. A circular cross-section was preferred, but a non-round configuration was acceptable if the mechanical properties were satisfactory. Continuous lengths are preferred but not required.

Three methods were developed to form the fiber bundles into composite monofilaments: (1) rolling advanced prepreg between spaced, hard surfaces, (2) drawing through a wet die, and (3) molding. The "wet die" method was the easiest to use and the most adaptable to continuous processing. However problems of fiber fraying using this method caused the molding method to be chosen as the standard for comparison for the various fiber and resin combinations studied in this program.

The results of this program showed the feasibility of the process. However, problems encountered in the impregnation, curing and pyrolysis steps of the process caused non-uniform distribution of the fibers and porosity and cracking within the pyrolyzed carbon matrix. These problems prevented the composite monofilaments from attaining their full potential properties. The fiber modulus was retained through processing, but the fiber tensile strength dropped 20 to 40% in the stronger monofilaments and even more severe strength degradation occurred in the weaker monofilaments.

The best results were obtained using a PAN precursor tow and a furfuryl alcohol binder, formed by the molding process. The pyrolyzed composite monofilament had a nominal diameter of .008 inch (20.3×10^{-2} mm), 76 v/o fiber, tensile strength of 175,000 psi (12.1×10^2 MN/m^2) and a tensile modulus of 54×10^6 psi (37.9×10^4 MN/m^2).

The carbon binder held the graphite fibers together and allowed the combination to act as a composite structure, although the binder did not contribute directly to the tensile properties of the monofilament. To develop the target strengths, it is necessary to use fibers with higher properties, to reduce the strength degradation during processing, or to increase the strength of the carbon matrix binder by post-pyrolysis treatments.

2. INTRODUCTION

Certain types of organic fibers can be converted into high-modulus, high-strength graphite fibers by pyrolysis. The usual form of the finished fibers is either a yarn of several hundred ends or a tow of several thousand ends. The individual fibers are approximately 3×10^{-4} inches (7.6×10^{-3} mm) in diameter and, except for color, are similar to glass fibers in appearance. Tensile strengths are 250,000 to 400,000 psi (17.2×10^2 to 27.6×10^2 MN/m^2) and moduli are 40×10^6 to 80×10^6 psi (27.6×10^4 to 55.2×10^4 MN/m^2).

While the use of graphite fiber reinforcements with plastic matrices has been encouraging, applications to metal composites have been less successful. Penetration of the fiber bundles with the metal binder and the high chemical reactivity between carbon and metals at the processing temperatures are the major difficulties. A larger diameter filament, like the boron filaments, would minimize or eliminate these problems.

The objective of this program was to determine the feasibility of fabricating a large-diameter, high-strength, high-modulus graphite/carbon composite monofilament by the resin conversion method. The composite monofilament was formed by impregnating a bundle of small-diameter graphite fibers with a high-char organic resin, then curing and pyrolyzing the composite monofilament and converting the resin to a carbonaceous binder. The finished filament should be .002 to .010 inches (5.1×10^{-2} to 25.4×10^{-2} mm) in diameter and uniform in cross-section. A round continuous filament is preferred but a non-round shape and a discontinuous length would be acceptable if satisfactory mechanical properties can be obtained. The objectives on mechanical properties are 50×10^6 psi (34.5×10^4 MN/m^2) modulus and 400,000 psi (27.6×10^2 MN/m^2).

Composite monofilaments, reinforced with carbon or graphite fibers have not been produced previously, however graphite fiber reinforced carbon composites have been produced in bulk form. A review of the technology of these composites in bulk form would indicate some of the potential directions to be taken in this investigation.

The manufacturing process for solid bulk graphite uses the technique of forming with an organic binder and pyrolyzing the binder to a carbon. Usually a coke flour is mixed with a coal tar pitch and hot pressed into billets. The billets are converted to graphite by pyrolyzing in an inert atmosphere.(1) As graphite fibers and fabrics became available, higher strength graphite products were made by using the fibrous reinforcements instead of coke flour. The precursor organic binders were the phenolic and furfuryl alcohol type resins instead of coal tar pitch because they impregnated the fibers more easily and were more applicable to fabricating reinformed composites. The composites dropped considerably in tensile strength when carbonized but were still much stronger than bulk graphite. Carbonized graphite cloth laminates were reported to lose 25 to 50% of the tensile strength and gain as much as 80% in tensile modulus, depending on the precursor binder.(2) Since graphite fabric fibers are low modulus, nominally about 6 x 10^6 psi (4.13 x 10^4 MN/m^2), the increased moduli were only about 3 x 10^6 psi (2.07 x 10^4 MN/m^2). Apparently in low modulus reinforced composites, the rigid carbon char can influence composite modulus properties. A unidirectional carbonized composite, reinforced with a 50 x 10^6 psi (34.5 x 10^4 MN/m^2) modulus graphite yarn, had a tensile strength of 70,000 psi (4.82 x 10^2 MN/m^2) and a tensile modulus of 25 x 10^6 (17.2 x 10^4 MN/m^2).(3) Which is about 65% of the tensile strength and 100% of the tensile modulus of an epoxy similarly reinforced. All three examples used additional impregnations and pyrolyzations of a low viscosity furfuryl alcohol binder to build up the density of the carbon matrix. The degradation of tensile strength during carbonization indicates a problem with char binders, but this is early technology. The important indications are the fibers maintained most of their tensile strength and all of their tensile modulus.

As indicated above, the first step involved in forming a carbonized composite is the impregnation of the graphite fibers with resin. Again, the forming of a composite monofilament by impregnating a small bundle of graphite fibers is analogous to the fabrication of large unidirectional composites in bulk form. The small size places severe constraints on the fabrication methods that are normally used. In addition, the ultimate objective of a continuous length places further restrictions on processing.

Large composites using long fiber reinforcement are usually formed by placing impregnated fibers under pressure and heat. The excess resin is forced out during the cure and the finished part can be deflashed, trimmed or machined to maintain the correct dimensions. Whereas, single filaments are too small to be subjected to any size control processing after forming.

The properties of a bulk pyrolyzed composite are usually compared to the properties of the unpyrolyzed resin-fiber composite. In a unidirectional plastic composite reinforced with a high tensile property fiber, the tensile properties of the composite in the direction of the fibers will not exceed the properties of the combined fibers. The tensile properties of the fibers are so much greater than those of the binders that the binder makes no appreciable direct contribution to composite tensile properties. For example, the tensile strength and modulus of an average aromatic amine cured epoxy (DGEBA/MPDA) are 8,000 psi (0.55 x 10^2) and 458,000 psi (31.6 x 10^2 MN/m^2) respectively.(4)

This is about 3% of the strength values and 1% of the modulus values of the graphite fibers. With such a great difference the epoxy will have no significant load when the fibers are at the breaking point.

In unidirectional resin-matrix composites the tensile modulus tends to follow the rule of mixtures. With a 70% fiber volume loading, a 50 x 10^6 psi (34.4 x 10^4 MN/m^2) modulus fiber and only the fiber contributing to modulus; the highest anticipated modulus of a composite filament would be 35 x 10^6 psi (24.8 MN/m^2).

Tensile strength does not follow the rule of mixtures in unidirectional unpyrolyzed resin-matrix composites and is less than the theoretical available strength from the reinforcing fibers. Fiber damage, voids, low interfacial bond or a brittle binder are factors that reduce tensile strength. Also, tensile strength does not correspondingly increase as fiber volume increases. The reinforcing fibers tend to be less effective strengthening agents as the volume increased above 60%. Vendor data on a 50 x 10^6 psi (34.4 x 10^4 MN/m^2) modulus graphite yarn reports a 143,600 psi (9.9 x 10^2 MN/m^2) tensile strength at 60% fiber volume in a unidirectional epoxy composite.(5) The fiber had a 310,000 psi (23.1 x 10^2) tensile which gives approximately 80% of the theoretical fiber strength in the finished composite.

Since the tensile strength of unpyrolyzed resin-matrix composites, reinforced with graphite fibers, show a strength reduction from the predicted properties, it would be expected that similar composites, in the pyrolyzed condition, might also show these strength degradations. Furthermore, carbon chars are weaker than epoxy resin, so that their contribution as matrix material would even be less. The fact that the carbon is weaker may be allowable however, since the function of the matrix in these composite monofilaments will be to hold the fibers together and as long as the shear strength of the char is sufficient to transfer the loads from fiber to fiber, it will allow the composite monofilament to act as a single element.

3. MATERIALS

3.1 Background

The high modulus polyacrylonitrile (PAN) precursor graphite fibers and the high modulus rayon precursor fibers start as different chemical compositions and are processed in completely different manners. Yet, the final structure other than cross sectional shape appears identical. There are important similarities between the two which are probably strong factors in determining structure. Both can be pyrolyzed without melting. Both are highly oriented before pyrolyzation. Both are stretched during processing to increase the orientation of the crystallites. The PAN precursor does not have a specific stretching step like the rayon precursor fibers, but is stretched by shrinking, while constrained, during preoxidation.

The recent suggested structures of both high modulus precursor fibers are a series of long interlocking graphite-like ribbons that are generally aligned with the axial direction of fiber, but may be as much as 25° from a true parallel orientation. There is no evidence of bonding between adjacent ribbons, but the interlocking ribbons do join and form continuous linkages to contribute to the high fiber strength and modulus. The structure is not completely solid. Small needle like pores, 20 to 30 Å wide and greater than 300 Å long, are formed between some of the ribbons and are oriented preferentially along the fiber axis. The pores are completely inaccessible to helium so are well sealed from any surface changes.(6,7,8)

The ribbon structure is still consistent with the earlier concept of highly crystalline carbon polymer fibrils forming within the fibers at the expense of the amorphous carbon phase.(9) The nature of the fibrils and the interlocking to form a high strength structure is explained better by latest ideas. Instead of discrete graphite-like crystals held together by a combination of amorphous carbons and possibly some type chemical bonding between crystals at the edges of the laminae, the ribbons are continuous along the length. Random blending and splitting of the ribbons occurs, but the continuity of the ribbons is maintained. The increase in fiber tensile and modulus after temperature exposures of 4500° to 5400°F (2760-3260°K) and additional stretching at temperature is explained by a straightening of the ribbons.(8) The effect of straightening is to increase alignment with respect to load, reduce the voids and to combine thinner ribbons into thicker ribbons.

Another change in concepts brought out by the recent studies on structure is that the fibers are not graphite nor are they graphitizable.(6,10) The pyrolyzation does form graphite-like layers in parallel groups, but they are not oriented in the crystalline structure of graphite. Heat treatment and stretching increase the order, preferred orientation and crystallite size. However, the order appears limited to c-layer spacing of 3.44 Å, compared to 3.354 Å for graphite.

Five commercially available high-modulus graphite fibers, two rayon precursor and three PAN precursor, were considered as reinforcement for the carbonized composite filaments. They were Thornel-50 (Union Carbide), HMG-50 (Hitco), Fortafil 5Y, (Great Lakes Carbon), Modmor I (Morganite), and Modmor II (Morganite). The description, properties and the designations used to identify the fibers in the rest of the report are listed in Table I.

The fabrication of bulk carbon and graphite products is a form of composite prepared with an organic binder, then converted to a carbonaceous binder by pyrolysis. The organic binders are highly filled with a fine particulate coke, carbon or graphite and molded to shape. Pyrolysis is conducted while the molded products are packed in carbon to support and protect them from oxidation during pyrolysis.

A large number of polymeric materials have been investigated as possible precursor binders for bulk carbonaceous products(11) but only two types are commonly used. Most are made from a coal tar pitch or an acid accelerated furfuryl alcohol with the coal tar pitch as the most common. The porosity and weight loss from the pyrolysis are reduced by reimpregnation with furfuryl alcohol and repyrolyzation. The very low viscosity and high char yield of the 100% furfuryl alcohol liquid make it, possibly, the only reimpregnation system in use.

The long fiber, i.e., fabric, yarn or tow, reinforced carbonaceous composites have been molded with thermosetting resins, like the structural reinforced plastics, rather than the thermoplastic pitches. Phenolics, epoxies and furfuryl alcohol are the principal resins in current practices.(2) Similar to the bulk carbonaceous products, furfuryl alcohol is the reimpregnation material. In some applications the furfuryl alcohol has been modified by other polymers, but it remains the major constituent.

Some coal tar pitches have char yields over 80%. Combinations of these pitches and long carbon fiber reinforcements have not produced the high chars expected. The high char yields of the pitches were measured on mixtures of binder and coke. The initial gaseous decomposition products further decompose to carbon on contact with the hot carbon particles. Carbon fibers do not act like the carbon particles and char yields were between 50 and 60%, not 80+%.

The carbonization of organic polymers is considered a type of polymerization. The carbon to carbon bonds increase during decomposition to form

TABLE I

GRAPHITE FIBER REINFORCEMENTS, VENDOR DATA

Fiber Designation	Precursor Polymer	Form				
		Type	Ends per Strand	Twist		Shape
				(per in)	(per cm)	
R-1-50 (Thornel 50)	Rayon	Continuous Fiber, 2-Ply Yarn	1440	1.5	.59	Crenulated
R-2-50 (HMG-50)	Rayon	Continuous Fiber, 2-Ply Yarn	1440	4	1.6	Crenulated
PS (Fortafil-5Y)	PAN	Discontinuous Fiber, 1-Ply Staple Yarn	700	2	.79	Round
P-I (Modmor I)	PAN	Continuous Fiber, Tow	10,000	0	0	Round
P-II (Modmor II)	PAN	Continuous Fiber, Tow	10,000	0	0	Round

Fiber Designation	Fiber Properties							
	Density (gm/cc)	Diameter		Tensile		Modulus		
		(x 10^{-3} in.)	(x 10^{-2} mm)	(x 10^{3} psi)	(x 10^{2} MN/m^{2})	(x 10^{6} psi)	(x 10^{4} MN/m^{2})
R-1-50	1.63	0.26	0.66	285	19.7	50	34.5
R-2-50	1.8	0.29	0.74	300	20.7	50	34.5
PS	1.9	0.3	0.76	250	17.2	50	34.5
P-I	1.94	0.3	0.76	275	19.0	60	41.4
P-II	1.74	0.3	0.76	400	27.6	40	27.6

high molecular weight carbon polymers. The two major classifications of carbons are graphitic and non-graphitic. Most polymers form non-graphitic carbons. Polymers must go through a fusion state during carbonization to form graphite and the fusion must occur over a temperature range.(12) Materials that fuse at a single temperature, e.g., cellulose triacetate, do not form graphite carbons. Highly cross-linked polymers, such as phenolics, do not form graphite carbons. Other examples of polymer precursors for nongraphitic carbon are cellulose, PAN, furfuryl alcohol and polyvinylidene chloride. Densities, after exposure to temperatures above 4532°F (2773°K), are 1.4 to 1.5 gm/cc. Other than coal tar pitches, graphites can be formed from polyvinyl chloride, polyvinyl acetate or polyacenaphthylene. These polymers fuse during carbonization and form carbons with densities of 1.8 to 2.0 gm/cc, after exposure to temperatures above 4532°F (2773°K). The polyvinyl chloride has been investigated the most detail and it forms a thermoplastic pitch during the initial stages of pyrolyzation (fusion), similar in appearance to the coal tar pitches.

The descriptions of the candidate precursor binders for the program are as follows:

1. Furfuryl alcohol. A low viscosity monomer that polymerizes violently with mineral acids. Small quantities or solutions can be handled with safety if not heated. In most of the work, 5 parts by volume of concentrated phosphoric acid diluted 50% with water was used as the accelerator. The quantities mixed at one time were always less than 20 grams. The amount of material picked up by a single bundle of graphite fibers was so small per unit length no problem on excessive cure rates was encountered.

2. Epoxy novolac - furfuryl alcohol. A blend of a semi-solid polyglycidyl ether of phenol formaldehyde novolac and furfuryl alcohol. Ratio of 1:4 by weight was blended in most experiments. Boron trifluoride/monoethyleneamine complex at 3 parts per 100 parts of epoxy novolac were used as an accelerator for the epoxy novolac. The furfuryl alcohol was accelerated with the 50% phosphoric acid.

3. PI. A low molecular weight polyimide prepolymer that can be imidized at 325°F (435°K) before final molding and curing. The resin is supplied as 40% solution in demethyl formamide.

4. PQ. A polyphenylene-quinoxaline copolymer. Supplied as a high-viscosity 20% solution in metacresol. Incompatible with all the common solvents except limit quantities of aromatic hydrocarbons.

5. PAN homopolymer. A continuous fiber yarn. Dissolved in hot dimethyl formamide to obtain an impregnating solution.

6. PAN copolymer. A high acrylonitrile/acetate staple yarn dissolved in hot dimethyl formamide to obtain an impregnating solution.

7. Phenolic. A high char phenolic solution in methylethyl ketone solvent.

3.2 Preliminary Materials Evaluation

Char yields were determined on the dried and fully cured candidate precursor binders by charring at 1382°F (973°K). The resin castings were placed on graphite blocks in a tube furnace with a low flow of dry nitrogen. The temperature was increased from room temperature to 1382°F (973°K) in two hours and held at temperature for three hours. Percentage char yields were:

1.	Furfuryl alcohol	55%
2.	Epoxy novolac-furfuryl alcohol	53%
3.	PI	57%
4.	PQ	77%
5.	PAN - homopolymer	48%
6.	PAN - co-polymer	42%
7.	Phenolic	58%

The PQ char had large blisters but thin sections were solid and the char was the most resistant to breaking of all the chars formed. The PI char was not quite as tough as the PQ char and developed a uniform structure with fine surface cracks on the exterior. Both furfuryl alcohol chars were comparable in toughness and slightly more easily broken that the PI char. The epoxy novolac modified resin was free of blisters. The straight furfuryl alcohol char had a dull appearance, in contrast to the glassy appearance of the other chars, and developed some blisters. The PAN chars were the weakest. This was expected because they were not preoxidized, as the fibers are, prior to pyrolyzation. The PAN co-polymer char was porous as well as weak. The phenolic char was badly blistered although it appeared strong.

The initial composite filaments were prepared to determine the general forming characteristics and handling properties of both the fiber bundles and the precursor binders. Horizontal one-ply strands of the graphite fibers were stretched over round bar supports and impregnated with a 1.5% solution of polyvinylidene chloride in methylethyl ketone. The fast drying and high shrinkage of the solution gave a quick check on the forming properties. The P-1-50 was the best of the yarns. A single ply was easy to separate from the yarn and it forms an almost round composite filament .009 - .010 inch (22.9 - 25.4 x 10^{-2}mm) in diameter. The R-2-50 was as good, but the extra twist made it harder to separate. The PS staple yarn didn't compact well and the yarn bundle formed a fuzzy filament .015 inch (38 x 10^{-2}mm) in diameter. Also, the PS yarn had a tendency to retain the curl of the spool, from which it was removed, increasing the susceptibility to breaking.

Using 2 inch (5.08 mm) graphite pulleys with an approximate .010 inch (25.4 x 10^{-2}mm) grove, R-1-50 was horizontally stretched at 150 gram tension. One ply bundles of yarn were impregnated with the candidate binders and pyrolyzed. The impregnated fiber bundles were dried by hot air or passing an electrical current through the bundle. Pyrolyzation was accomplished by passing through a tube furnace under dry nitrogen. The rate through the tube was 3 ft/min (.914 m/min).

All pyrolyzed filaments broke under slight bending with jagged fractures, typical of a composite with poor binder quality. Additional reimpregnations and pyrolyzation of the filaments with the initial binder were tried on each filament but no improvements were noticed. The PI resin was impregnated at 27% solids and slowly dried. The filament appeared sound and approximately round. The PQ resin reduced to 11% solids in toluene, blistered during pyrolyzation, even after a 500°F (533°K) drying. The cured phenolic badly blistered during pyrolyzation and formed an irregular shaped filament. The PAN homopolymer solution at 5% solids formed a skin on the exterior of the fiber bundle with little penetration to the interior fibers. Multiple impregnations prior to pyrolyzation did not increase the fiber penetration.

The furfuryl alcohol in the first series filaments was cured with maleic acid instead of phosphoric acid. Maleic acid cures are much slower than the phosphoric and heating to 250°F (394°K) was needed to obtain cures. At 250°F (394°K) furfuryl alcohol has a vapor pressure equal to 125 mm mercury.(13) The straight furfuryl alcohol had a tendency to blister and both the straight and the epoxy novolac modified furfuryl alcohol lost considerable binder during cure. The small amount of binder material and the relatively large surface area of the filaments made volatilization during cure a much more serious problem than it is in the conventional process associated with the fabrication of larger-mass composite structures. A 20 gram sample of maleic acid accelerated epoxy novolac-furfuryl alcohol lost 70% weight in a cure at 260°F (400°K). The low binder content of furfuryl alcohol, with or without the epoxy novolac, produced round appearing pyrolyzed filaments low in flexural strength like the other binders.

More durable filaments were made, with the maleic acid accelerated epoxy novolac-furfuryl alcohol binder, by using three impregnation and pyrolyzation cycles and a slower stepwise cure before the pyrolyzations. The cures covered a 24 hour period in 5 steps and reached 350°F (450°K). The final filaments would easily take a 4 inch (10.2 cm) radius bend. When they did fail, the break was a sharp fracture. By switching to the phosphoric acid cure for furfuryl alcohol, a comparable quality filament could be obtained with one minute cures at 265°F (403°K). The phosphoric acid would also cure at room temperature in 48 hours. The improved filaments were about .010 inches (25.4×10^{-2}mm) in diameter and uniform in appearance. There was no exterior evidence of blistering but large voids and resin rich areas were seen when the cross sections were examined under a microscope.

4. COMPOSITE FILAMENT FABRICATION

The initial filament fabrication emphasis was placed on methods that could be adapted to continuous processing or to bulk quantities of material. Essentially, the filaments were formed without pressure or a forming mold. While the experiments were actually conducted under static conditions, that is, the fiber bundles were held stationary, the procedures could be, without too much development, scaled up to handle long lengths of filament. Most of the work used a single ply of R-1-50 as the fiber bundle. A single ply of this reinforcement could be uniformly and easily separated in long continuous lengths and one ply formed a composite filament approximately .010 inches (25.4×10^{-2} mm). Some filaments were prepared with fibers from the P-1 tow to evaluate the filament forming qualities of round fiber against the crenulated shape of the rayon precursor fibers. The first filaments with the P-1 fibers appeared to be an improvement but subsequent runs were not as uniform as the filaments reinforced with R-1-50.

The eventual requirement of long continuous lengths was also a restriction on the high char binders that could be used. Consequently, the furfuryl alcohol types of resins are the simplest to use and were the predominant binders for this part of the composite filament development. Some filaments were prepared with the polyquinoxaline resin (PQ). The high char content and tough dense char formation made it an attractive precursor binder, but the poor processing properties prevented uniform consolidation of the fiber bundle.

The effort on forming techniques, that could be used to prepare long continuous lengths of composite filaments, produced filaments worth testing from only one system of the R-1-50 yarn and the furfuryl alcohol type binders. To compare other fibers and binders a technique was worked out that compression molded short lengths of the composite filament. The process was tedious, but uniform small filaments could be molded to shape in the same manner as the larger compression molded articles.

The first pyrolyzation in a graphite/carbon composite typically produces a weak char with numerous small voids. Reimpregnation and recharring are needed to increase char density and strength. Furfuryl alcohol monomer is the usual reimpregnant because it is low enough in viscosity to penetrate the charred structure. Similarly, regardless of the initial resin binder, the low viscosity furfuryl alcohol monomeric binders were used for all reimpregnation.

Progress on the filament forming was checked by photomicrographs of the filament cross sections.

4.1 Filaments Formed Without Pressure

The initial materials evaluation had shown that the processing characteristics of the high char precursor binder were more important to graphite fiber reinforced composite filament formation than char properties and char yield. Starting with one ply of the R-1-50 yarn and furfuryl alcohol activated with phosphoric acid, composite filaments were formed and pyrolyzed by different routes to study the effects of varying process procedures.

Glass tubings were drawn down to .015 inch (38.1 x 10^{-2}mm), .010 inch (25.4 x 10^{-2}mm) and .008 inch (20.3 x 10^{-2} mm) diameter orifices. About 3 meters of an impregnated yarn strand were pulled through each orifice to meter the amount of resin and shape the fiber bundle. Only the .015 inch (38.1 x 10^{-2} mm) orifice permitted the fibers to be pulled through without damage. Both the .010 (2.54 x 10^{-2} mm) inch and .008 inch (20.3 x 10^{-2} mm) collected loose fibers on the upstream side and blocked the orifice opening, causing the prepreg yarn to break. Changing from a shallow to a high taper leading to the reduced tubing cross section did not overcome the tendency to block the smaller orifices. Frequent broken fibers are typical of graphite yarns and tows but it was believed the furfuryl alcohol would act like a heavy size and prevent the fibers from breaking off.

Simple horizontal stretching the yarn strands over grooved graphite rollers at 150 grams tension and impregnating by wicking furfuryl alcohol along the yarn, produced filaments that would easily take a 4-inch (10.2 cm) radius bend after pyrolyzation without breaking. Figure 1 is a R-1-50 reinforced filament prepared in this manner. Three impregnations and pyrolyzation cycles were used. Some blistering was visible on the exterior of the fiber but not shown in the photograph. The large voids indicated an ineffective compaction during cure. Without some means of forcing the fibers together, this should be expected.

The large white spots, seen in the photograph, are pockets filled with the aluminum oxide polishing abrasive. The pockets are most likely voids exposed during polishing. The black spots are believed to be rich areas of pyrolyzed binder. The fiber free grey areas are believed to be voids that filled with resin during the mounting process.

Increasing tension during impregnation and cure increased the peripheral irregularity without reducing voids. Reducing tension during impregnation, to assure complete filling of interstices between fibers and curing under high tension gave almost the same results as high strand tension for the entire procedure.

Increasing twist, prior to impregnation and cure reduced the size of the voids, but the number of voids and peripheral irregularity increased.

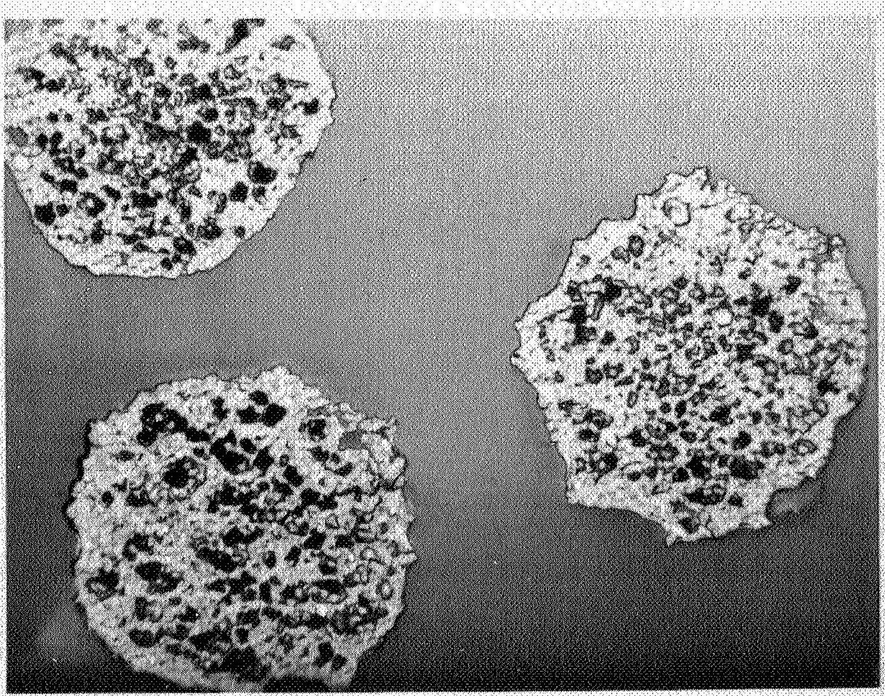


FIGURE 1. PYROLYZED R-1-50/FURFURYL ALCOHOL, 150 gram tension, 200X.

Figure 2 is a R-1-50 reinforced filament made using the same process but with an extra two twists per inch (2.54 cm). The cross sectional area was reduced, the surface was more irregular and the voids were more numerous but dispersed and much smaller. The number of voids indicates compaction should be increased.

A relative uniform periphery was obtained by decreasing the fiber bundle tension from 150 grams to 31 grams during impregnation and cure. As seen in Figure 3, the large voids of Figure 1 were eliminated but deep cracks developed.

The PQ resin was tried as shrink coating over furfuryl alcohol impregnated R-1-50 fibers. The PQ condenses to a tough solid char when the solvent is well removed before pyrolyzation. Instead of compressing the fiber bundle and increasing compaction, the opposite effect took place. The expected shrinkage occurred and breaks in the filament periphery allow the shrinking

FIGURE 2. PYROLYZED R-1-50/FURFURYL ALCOHOL, 150 gram tension, plus 2 twists per inch, 200X.

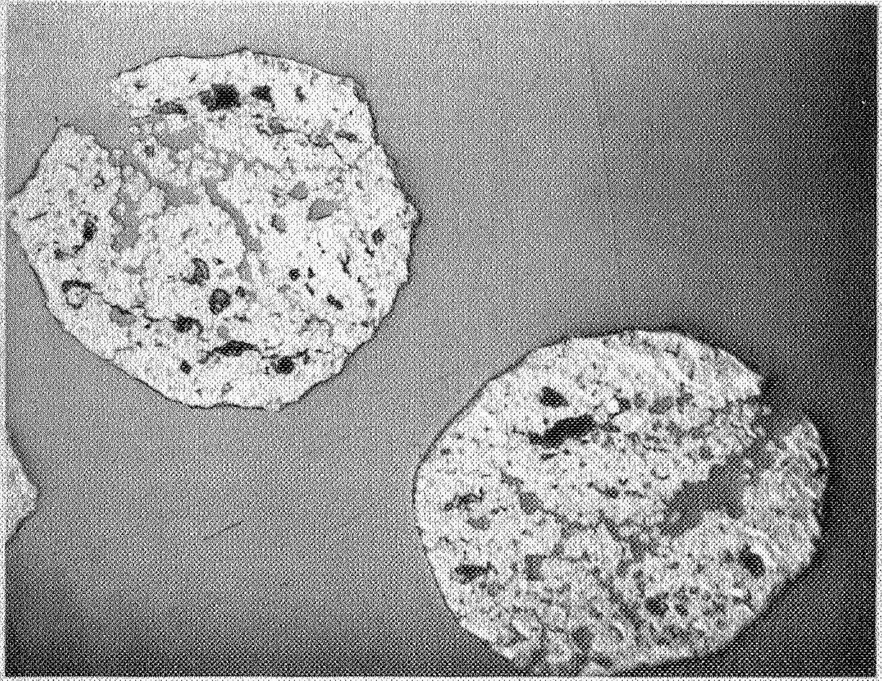


FIGURE 3. PYROLYZED R-1-50/FURFURYL ALCOHOL, 31 gram tension, 200X.

PQ to pull the filament apart. Figure 4 shows the badly damaged filament. It was found that any thick binder overcoating on unpyrolyzed filaments tended to break and open up the fiber bundle during pyrolyzation, but the effect was more pronounced with the PQ resin.

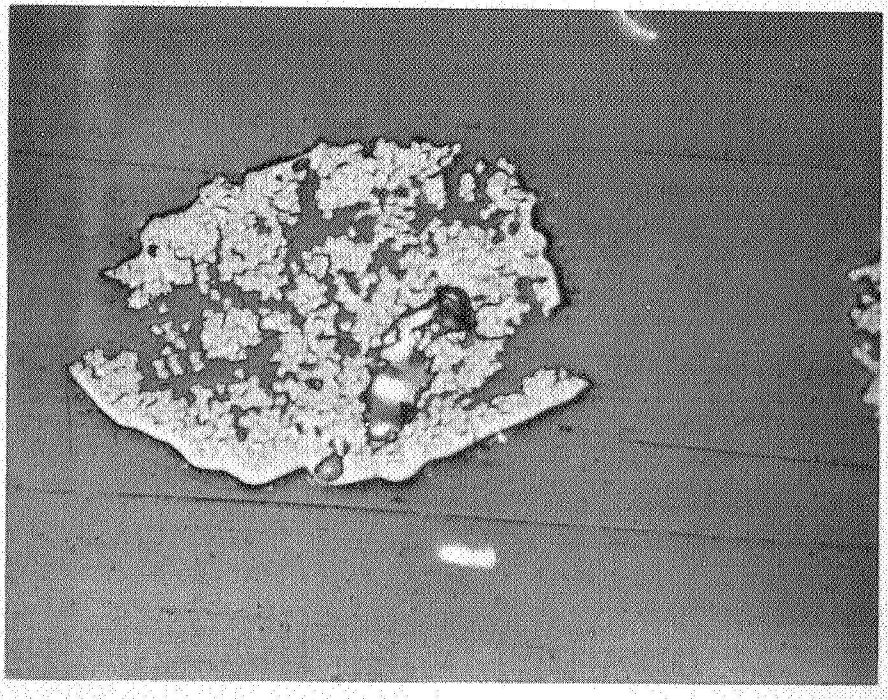


FIGURE 4. PYROLYZED R-1-50/FURFURYL ALCOHOL PQ OVERCOAT, 200X.

The initial furfuryl alcohol impregnant in the Figure 5 filament was advanced to a viscosity of approximately 5,000 centipose (5 N-s/m^2) by allowing phosphoric acid accelerated resin to age 3 days at 75°F (297°K). The higher molecular weight was expected to reduce the volatile loss during cure and thus help hold the fiber bundle together during cure and pyrolyzation. Large cracks still formed although less severe than the previous low tension cure.

FIGURE 5. PYROLYZED R-1-50/ADVANCED FURFURYL ALCOHOL, 31 gram tension, 200X.

The crenulated cross sectional shape of the rayon precursor fibers are possible crack initiation points in the charring resins as the resins are weakened during pyrolysis. To check the effect of round fibers, filaments were prepared from strands of P-1 fibers separated by spreading water wet tows with a rubber roller. Advanced furfuryl alcohol, low tension twisting, high tension and heat cleaning prior to impregnation were evaluated. The first filaments were free of cracks and voids but the initial furfuryl alcohol content was high and the fibers were widely spaced making the filament oversized. Figure 6 is a filament with a reduced initial impregnation of an advanced resin and low forming tension. The filament is still somewhat larger than desired (100 X photograph) but the shape was almost round with only a few large cracks. The filaments in Figure 7 and 8 were formed in the same manner as the filaments in Figure 6 except 1-1/2 and 3 twist per inch (2.54 cm) respectively were added.

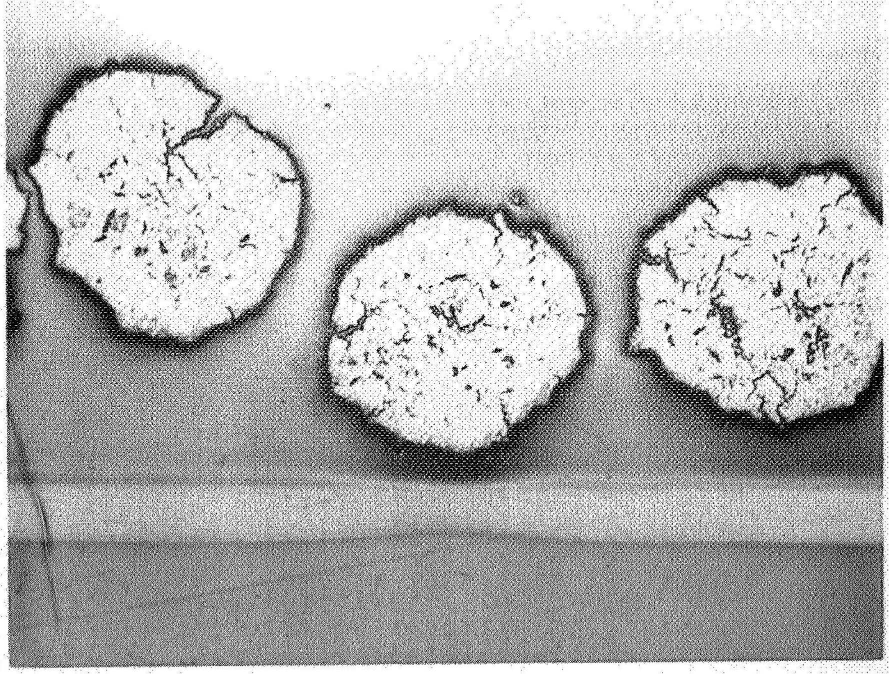


FIGURE 6. PYROLYZED P-I/ADVANCED FURFURYL ALCOHOL, 30 gram tension, 100X.

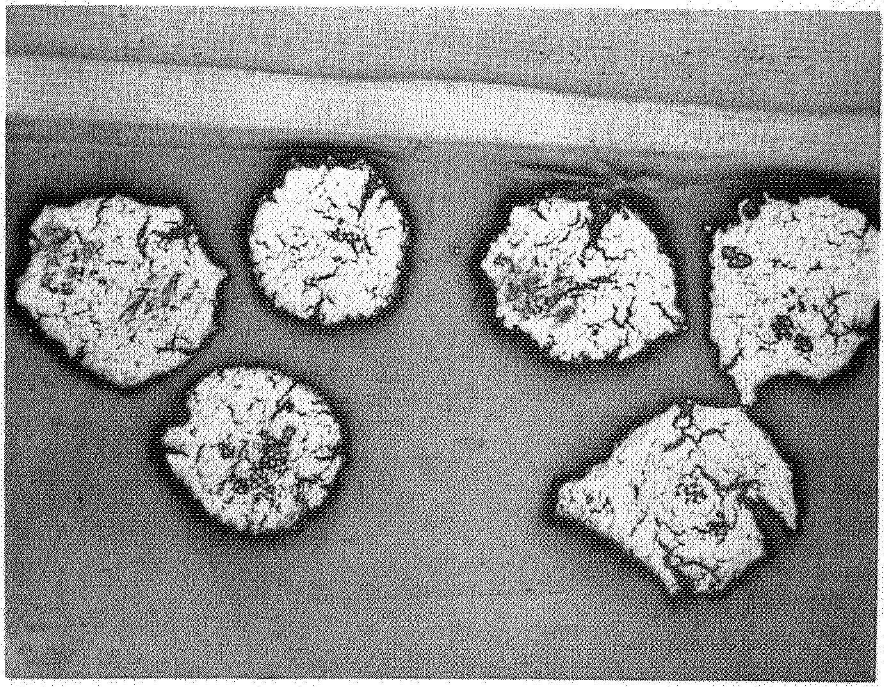


FIGURE 7. PYROLYZED P-I/ADVANCED FURFURYL ALCOHOL, 30 gram tension, 1-1/2 twist/inch, 100X.

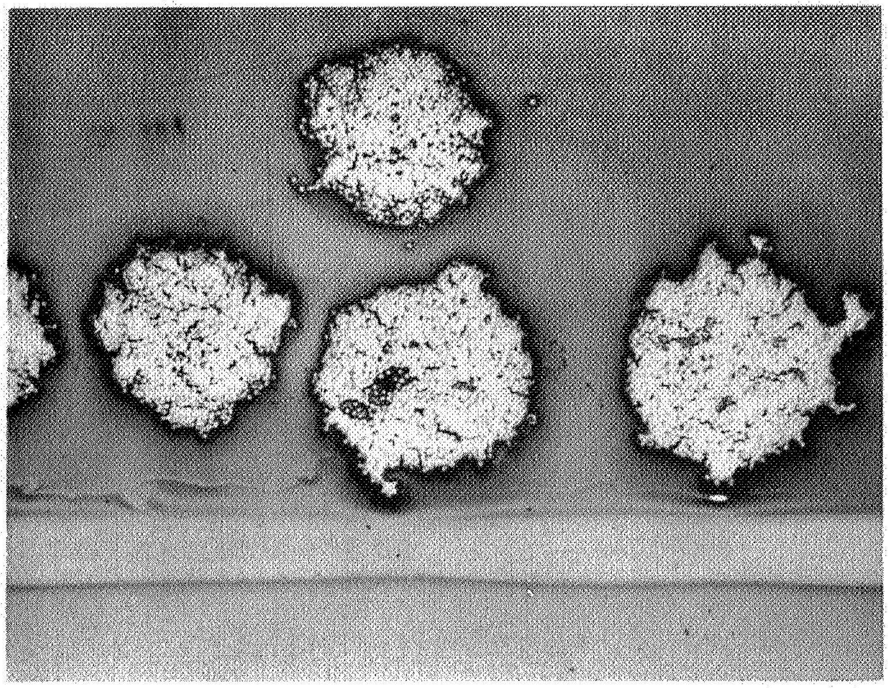


FIGURE 8. PYROLYZED P-I/ADVANCED FURFURYL ALCOHOL,
30 gram tension, 3 twists per inch, 100X.

The twist increased the cross section irregularity and cracking although the higher twist did increase compaction in the inner portion of the filament.

The filaments in Figure 9 were prepared by combining twist and tension to P-1 fiber bundles after impregnation. The procedure produced inconsistent shapes and badly cracked filaments. The twisting forced excess resin to the surface of the filament where it formed small droplets. The high localized shrinkage of the resin droplets, during pyrolyzation, may be the reason the filaments split open so badly.

R-1-50 reinforced filaments formed in the same manner, as the series of filament using P-1 fibers, gave essentially the same results. The R-1-50 were more uniform and much easier to use, and round fibers offered no advantage.

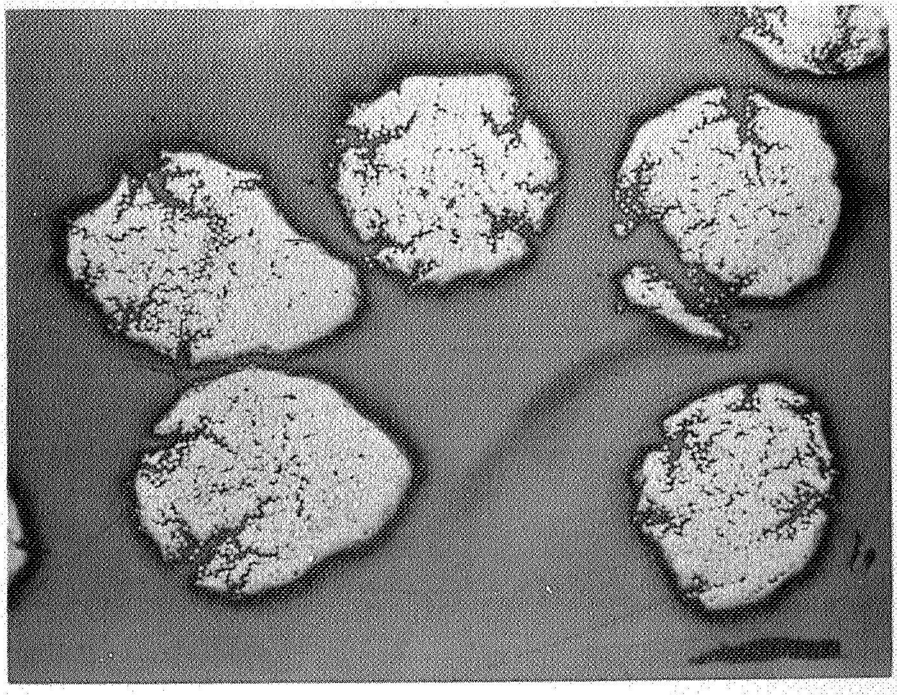


FIGURE 9. PYROLYZED P-I/ADVANCED FURFURYL ALCOHOL. Impregnated before adding 1.5 twists per inch and 150 gram tension, 100X.

In general better filaments were formed by low tension, impregnating the first time with advanced furfuryl alcohol and no extra twisting. Also, twisting had a tendency to form a wavy filament in the longitudinal direction that was not apparent in the cross sectional photographs. The misalignment of fibers along the filament axis was another objection to twist because this could detract from the properties of the filament when used as reinforcement itself. Although no actual flexural measurements were made of the twisted fiber filaments, it was observed flexural strength was always lower than untwisted fiber filaments. When the composite filaments were placed in a bend, the twisted fiber filaments could be bent with less force and they usually broke before reaching a 4 inch (10.2 cm) radius. Whereas, the better untwisted filaments would easily take this degree of bending.

A rectangular cross sectional configuration was attempted since this might be a simple shape to form. R-1-50 fibers were untwisted and flattened with a rubber roller while wet with water.

The flat fiber bundle was then suspended at 30 grams tension, horizontally between two round bars and impregnated with advanced furfuryl alcohol. The cured filaments, Figure 10, return to an almost round configuration with a large center void. Only the filament immediately adjacent to the supporting bars remained flat. It is assumed the surface tension of the binder resin has a tendency to force the fiber bundle in a round shape. This phenomenon would work against any methods set up to form shape other than round.

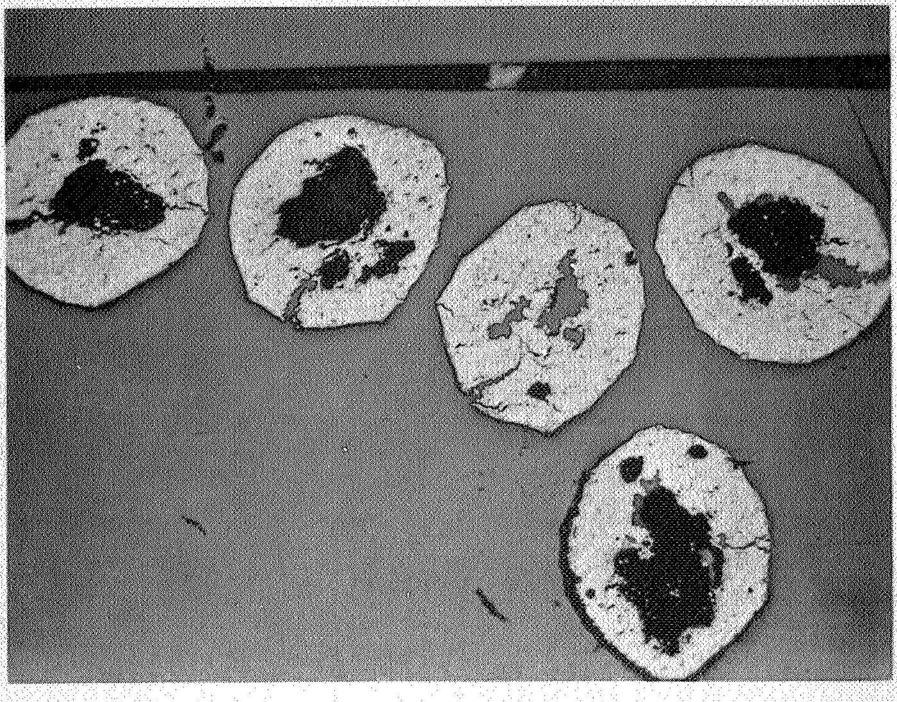


FIGURE 10. CURED R-1-50/ADVANCED FURFURYL ALCOHOL, Preflattened Before Impregnation, 100X.

Mechanical filament forming was attempted by pulling R-1-50 fibers over and under a series of pulleys, with accurately machined progressively smaller semi-circular grooves. Graphite pulleys, 2 inches (5.08 cm) in diameter were arranged according to Figure 11. A water impregnated strand of fiber was drawn through the system under tension. After threading and pulling through an approximate additional 3 feet (0.914 m), the fibers were held statically, dried, carefully impregnated with furfuryl alcohol and cured. The initial water impregnation acts as a weak binder that is easily formed. The shape will remain even after drying if the fibers are not disturbed.

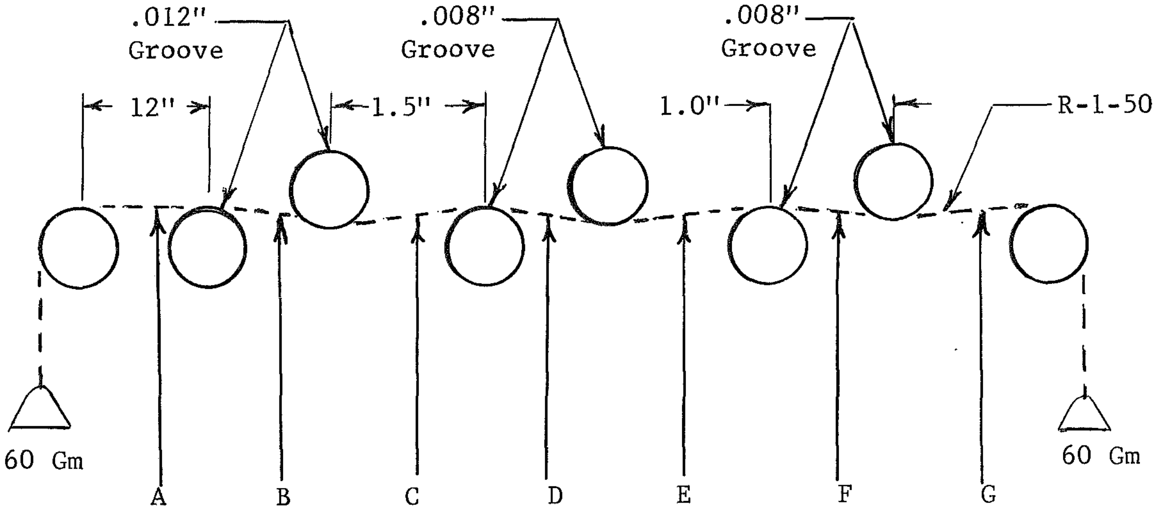


FIGURE 11. FILAMENT FORMING WITH 2-INCH GROOVED PULLEYS

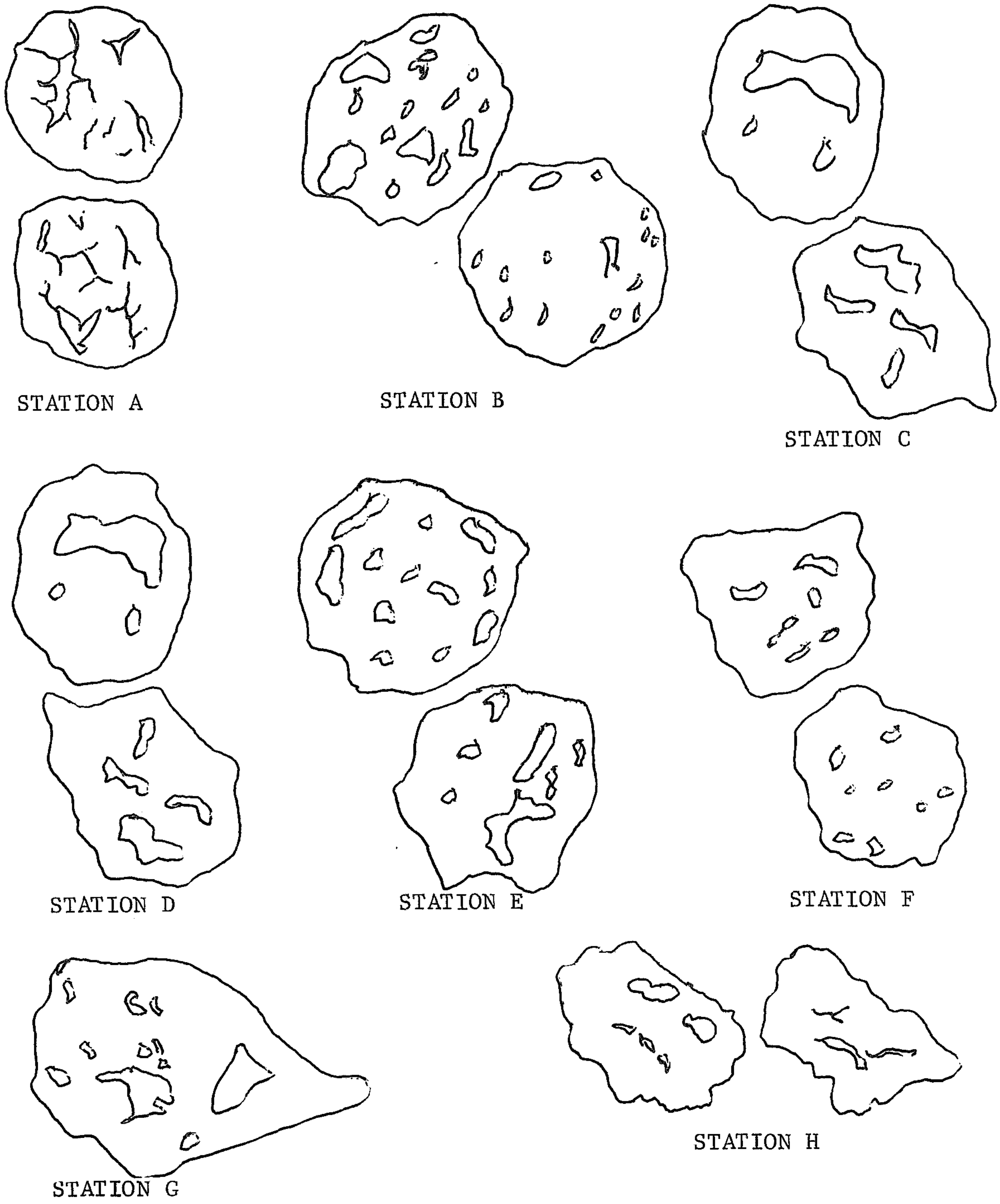
Samples were taken at the station points indicated by the arrows. Sketches of the samples, Figure 12, show the smaller grooves form the most irregular shape even though a well compacted filament is the size of the smallest groove used. An oversize groove is the best forming shape to use.

Formed filaments have been pyrolyzed from room temperature to 1318^{o}F (1023^{o}K), a time as short as 2 minutes and as long as 6 hours. Initial cracking in furfuryl alcohol binder filaments starts between 688 and 778^{o}F (673^{o} and 723^{o}K) and becomes progressively more pronounced as the temperature rises to 1318^{o}F (1023^{o}K). The short cycles are desirable for a continuous process, but obviously, will contribute to cracking. The longer cycles have reduced cracking, but the improvement is minor for cycles longer than 2 hours.

Other ideas that did not improve filament uniformity were the addition of graphite powder to reduce binder shrinkage, curing under 18 inches (45.8 cm) of mercury to apply an isostatic pressure during cure and pyrolyzing under 2 inches (5.08 cm) of a low melting bismuth alloy to apply isostatic pressure during pyrolyzation. The graphite was added to fiber as water dispersion or as a dispersion in furfuryl alcohol. The graphite additions caused a breakup in the filaments rather than a more compact structure. The cure under mercury had slightly better shape than a cure in air but not enough to adopt as processing step. The pyrolyzation in the bismuth alloy was conducted at 915^{o}F (798^{o}K) and the degree of cracking was the same as a comparable sample exposed to 915^{o}F (798^{o}K) in nitrogen.

Furfuryl alcohol modified with an epoxy novolac, as the initial impregnating resin, and a low tension during cure formed a filament with low cracking and fairly uniform shape. The epoxy would be expected to increase surface tension. Higher surface tension should pull the fiber bundle together and help form a more rounded shape. Figure 13 shows the finished filament.

The composite filaments, formed with the higher surface tension epoxy novolac modified furfuryl alcohol, were improved in uniformity and slightly reduced in size by drawing the impregnated fibers through a small circular die. Glass tubing was bent at a right angle and drawn down to an .008 inch (20.3 x 10^{-4} mm) orifice. The tube was filled with about 3 inches (7.62 cm) of resin. R-1-50 fibers drawn down vertically into the large end, through the resin and horizontally out the orifice at 15 grams tension, formed uniform circular cross sections with only a few small cracks. The diameter of the filaments, Figure 14, was about .008 inches (20.3 x 10^{-4} mm) over .001 inch (2.54 x 10^{-4} mm) smaller than the free-formed filaments. Keeping the fiber bundles completely immersed in the resin on the upstream side is the major difference between the successful die forming and the unsuccessful earlier attempt. The die forming, a simple procedure, was considered a practical way to form long lengths of a well-compacted uniform filament.



STATION A

STATION B

STATION C

STATION D

STATION E

STATION F

STATION G

STATION H

FIGURE 12. FILAMENTS FORMED ON GRAPHITE PULLEYS, 100X

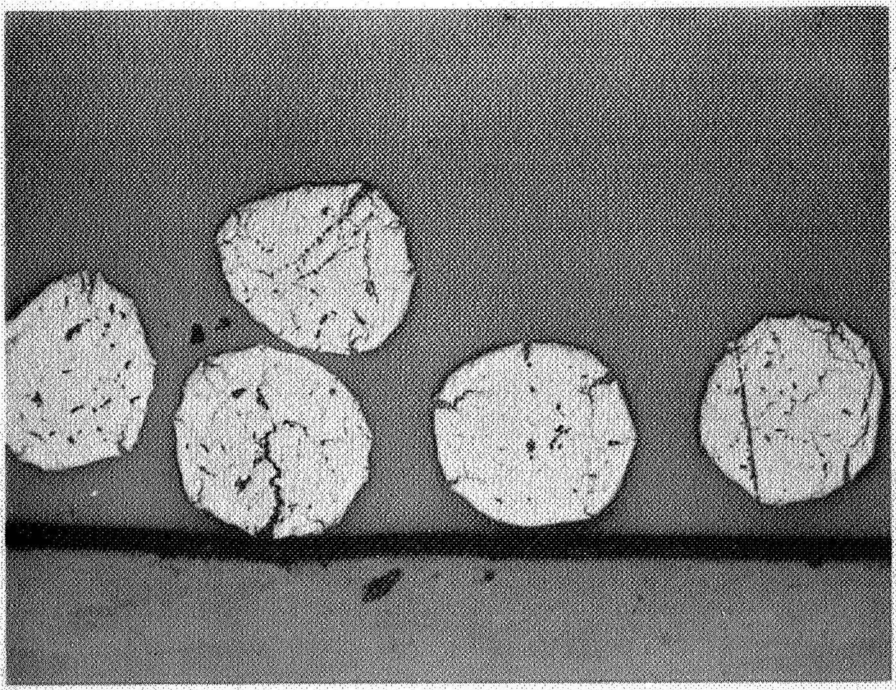


FIGURE 13. PYROLYZED R-1-50/EPOXY NOVOLAC-FURFURYL ALCOHOL, 15 gram tension, 100X.

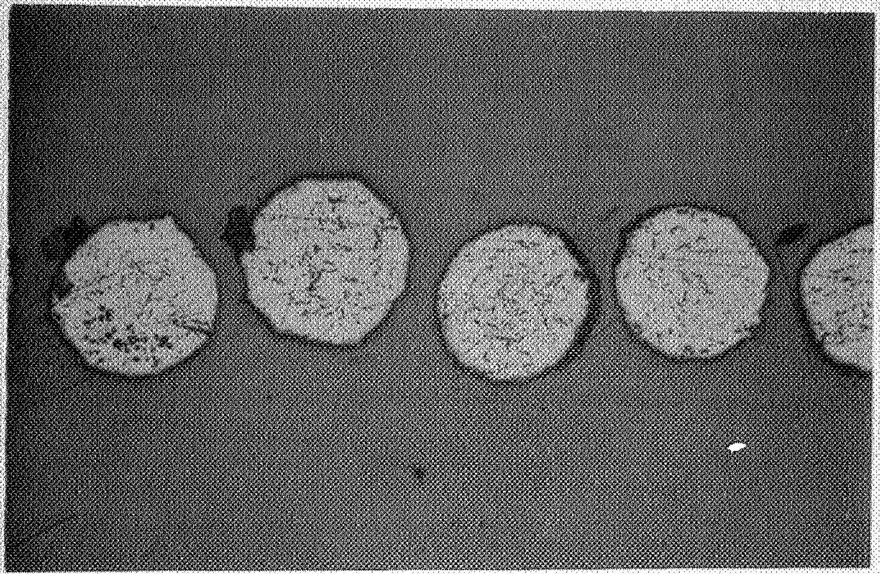


FIGURE 14. PYROLYZED R-1-50/EPOXY NOVOLAC-FURFURYL ALCOHOL, Die formed, 100X.

Mechanical rolling impregnated fibers in a direction normal to the filament axis also formed uniform, round, small filaments. A viscosity increase in the binder was necessary to hold the filament shape after rolling. This in turn required a lubricant because the binder became tacky and would adhere to the surfaces used for rolling. The filaments in Figure 15 were impregnated with a furfuryl alcohol advanced to about 40,000 centipoise (40 N-s/m^2) and cut with solvent to a suitable impregnating viscosity. After the solvent had dried, the fiber bundle was rolled twice between two glass surfaces separated by .008 inch (20.3 x 10^{-2} mm) wires and lubricated with mineral spirits. The glass surfaces were 1 inch (2.54 cm) wide and the filaments moved continuously between the glass as it was rolled. The mineral spirits prevented sticking and evaporated after rolling with no residue. The pyrolyzed filaments were the same size and as well shaped as the die formed filaments. While more difficult to use than the die method, rolling is a second practical procedure for fabricating long lengths of composite filaments.

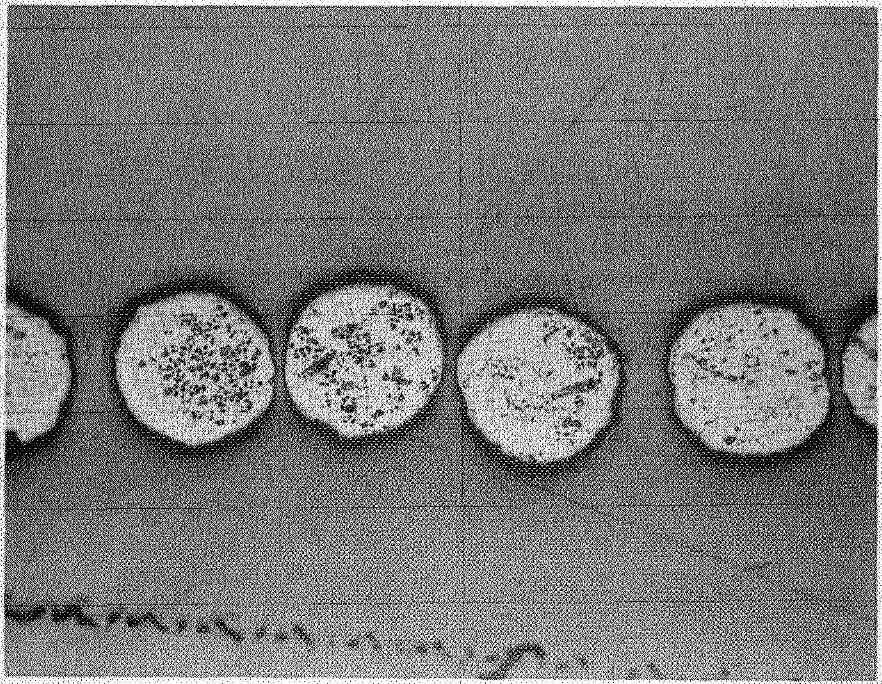
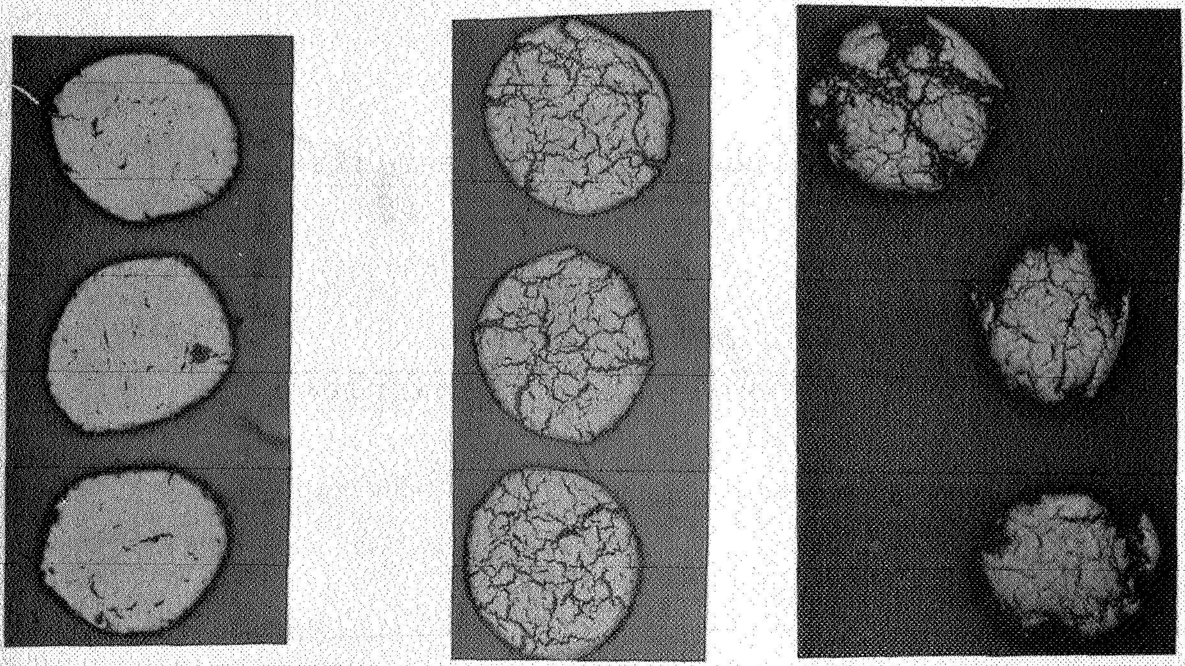


FIGURE 15. PYROLYZED R-1-50/HIGHLY ADVANCED FURFURYL ALCOHOL, Mechanically Rolled, 100X.

A limited attempt was made to change the amorphous carbon binder to a more crystalline carbon by heating to a graphitization temperature under tension. Free-formed filaments prepared from R-1-50/epoxy novolac-furfuryl alcohol were heated as electrical resistance elements to 4300°F (2643°K). Prior to heating the filaments had been pyrolyzed to 1292°F (923°K) and were free from large cracks and voids. Heating times varied from 5 seconds to 8 minutes. Tension varied from 30 to 2700 grams. Time from room temperature to 4300°F (2663°K) was short, 30 to 60 seconds. All filaments became badly cracked from the heating and cracking increased with increasing tension. The filaments tensioned at 2000 grams and 2700 grams broke in 25 seconds and 5 seconds respectively. Figure 16 shows the change after the high temperature exposure. Time limitations prevented an evaluation of slower heating, reimpregnation and recharring or graphite seeding of the amorphous binder.



A. 1228°F
Pyrolyzation only

B. 4300°F, 30 gr. tension
8 min. at temperature

C. 4300°F, 2000 gr. tension,
25 sec. at temp.

FIGURE 16. PYROLYZED R-1-50/EPOXY NOVOLAC-FURFURYL ALCOHOL, Heated to 4300°F, 100X.

4.2 Pressure Molding Filaments

The rolling and die forming produced composite filaments worth testing, but the results cover only one type of fiber reinforcement and one type of resin binder. A method was developed that would apply pressure, during heat cure, to a prepreg strand in a narrow molding channel. The finished filaments were short discontinuous lengths but long enough to test comparative tensile properties.

A soft metal wire was placed over the molding channel and coined with a hydraulic platten press. The deformed metal compressed the fiber bundle to the shape of the channel. Nickle and stainless wires were too hard and did not coin well. Silver, copper and aluminum coined satisfactorily with dead soft aluminum giving the best results because it required the lowest force to deform.

Coining a round wire over a narrow opening projects a convex surface like the cross-section sketched in Figure 17-A. The rounded surface forces the fiber bundles, in an inconsistent pattern, up along the sides of the molding channel and produces an irregular filament shape. Wire, preflatten before coining like the sketch in Figure 17-B, projects a flat surface into the opening which will form a uniform shape. The force used to coin the aluminum was 3,000 to 5,000 pounds per lineal inch (5260 to 8740 N/cm). This load is higher than necessary to deform the aluminum but is needed, with mechanical stops to keep the deformation consistent along the length.

a. Round

b. Flattened

FIGURE 17. SHAPE CHANGE OF COINED ALUMINUM WIRES

The first molded filaments were formed in a 3-in. long (7.62 cm) "V" groove, .012 inches (30.3×10^{-3} cm) deep, cut in the surface of a flat ground steel plate. The cured filaments were triangular in cross section and fairly uniform along the length. For longer filaments, more uniform shape was desired and a thread grinding wheel was used to cut the groove. A 9-inch (22.8 cm) steel plate was used as the base. The grooves were uniform along the length, but the cross-sections were rounded at the bottom instead of the sharp "V" cut in the 3-inch (7.62 cm) plate. The change in shape produced a ribbon-like molding about .015 inch (28.1×10^{-3} cm) wide and .005 inch (12.7×10^{-3} cm) thick. The filaments were uniform and the tensile properties were equal to or better than the 3-inch (7.62 cm) moldings. Since the objective of the molding process was a method to form composite filaments from more than one fiber and one binder, the flat shape serves the purpose as well as the triangular shape.

The 9-inch (22.8 cm) plate had 12 grooves but slight inconsistencies in groove depth and the high force used to coin the aluminum wire made it impractical to mold more than two filaments at a time. The steps used were as follows:

1. Clean the grooves and coat with release agent.
2. Flatten straight, .065 inch (16.5×10^{-3} cm), aluminum wire between steel plates shimmed to .040.
3. Place a preweighed amount of fiber with a known amount of impregnating resin in molding grooves.
4. Cover the filled grooves with the flattened aluminum wire.
5. Cover the wires with steel top plate shimmed to 32 mils.
6. Place the assembly in a heated platten press and apply 100,000 pounds load and hold until cured.
7. Remove the assembly, cool and strip the molded filaments.

The fiber and resin combinations prepared were:

1. R-1-50/furfuryl alcohol
2. R-1-50/P-13N (polyimide)
3. R-1-50/NAV-P-10 (polyquinoxaline)

4. P-I/furfuryl alcohol

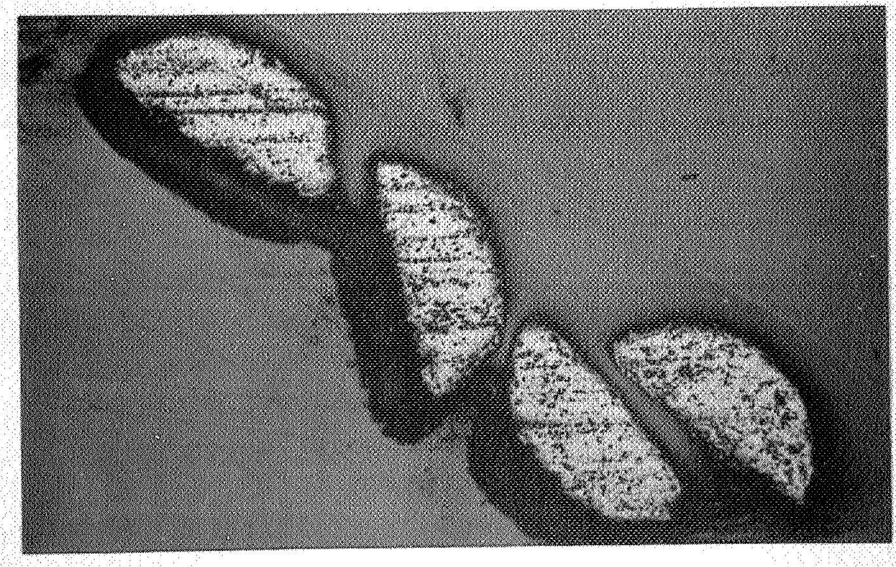
5. P-II/furfuryl alcohol

Impregnating a uniform prepreg bundle for molding from R-1-50 yarn is easily done. A single strand is uniform in weight, 0.013 grams per foot (30.5 cm) on the spool used for composite filaments, and the resin pickup is reasonably uniform if the application method is consistent. Separating an equal volume of fiber from a 10,000 fiber tow of P-I or P-II is more difficult. The tow has low twist, but the individual fibers are frequently tumbled along the length of the tow. That is, they vary in their relative position along the length. A small bundle may be in the middle of the tow at one point and at the outer edge at another, or the bundle may split into two or more smaller bundles. Previously, the tows had been separated by wetting with water, untwisting and spread by rolling with rubber rollers. This was considered too severe for a careful evaluation of retained tensile properties in composite filaments. In this work, water wet tows were separated into bundles 3 to 4 times greater than needed. Then the fibers were dried and carefully stripped off until the desired weight was reached. The process was tedious and the loss was high. The P-II (high strength) tows were noticeably harder to separate than P-I tows because the fibers were more firmly interlocked.

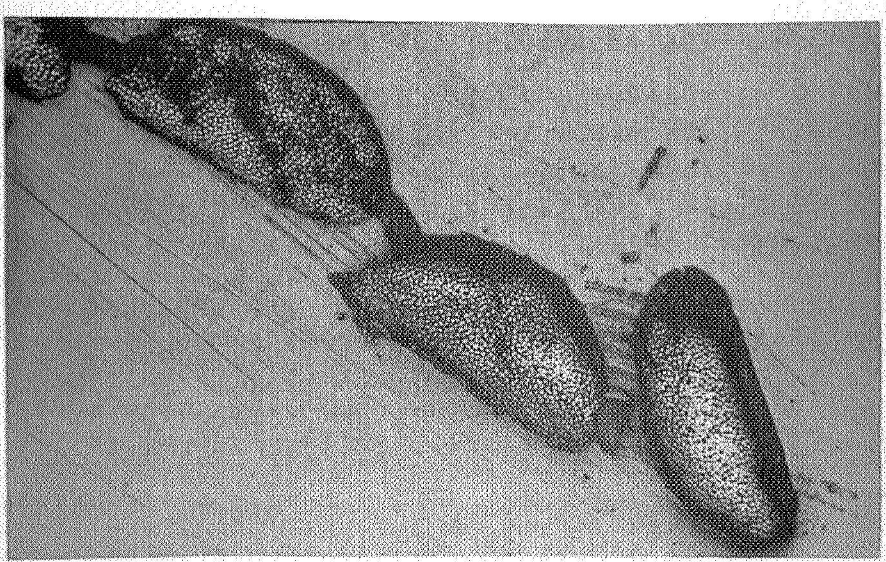
A check was made on the uniformity of a carefully separated P-II fiber bundle. A 30 inch (73.3 cm) length with an average weight of 0.0125 grams per foot (30.5 cm) was cut into 3 inch (7.3 cm) lengths. The weight of each length converted back to grams per foot in order was:

No.	Wt. (gm/ft or 30.5 cm)
1	0.0116
2	0.0102
3	0.0124
4	0.0152
5	0.0156
6	0.0138
7	0.0128
8	0.0120
9	0.0116
10	0.0112

The wide spread in weights means tensile and modulus calculations on the 9 inch molded filaments are probably not too accurate. P-I and P-II fiber bundles were originally weighed as 3 foot (91.4 cm) pieces before impregnation and molding.



A. MOLDED ONLY, 100X

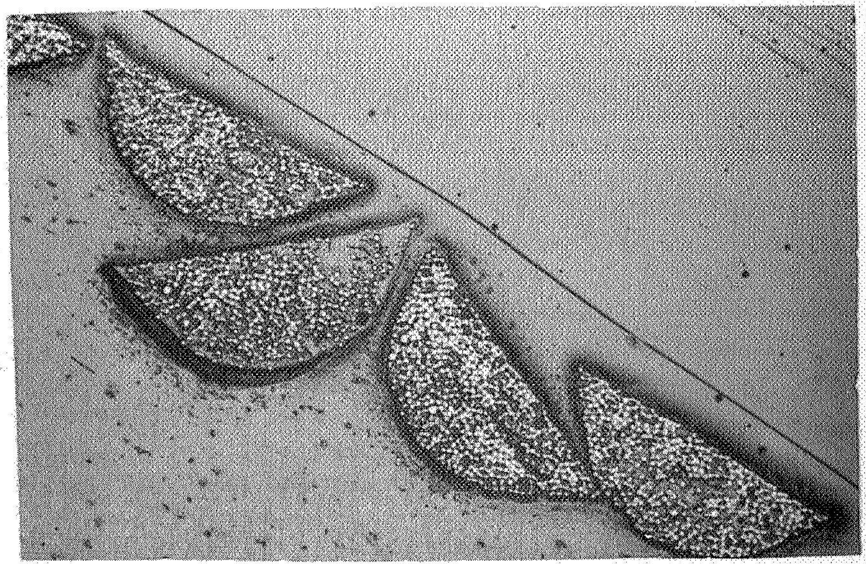


B. MOLDED AND PYROLYZED, 100X.

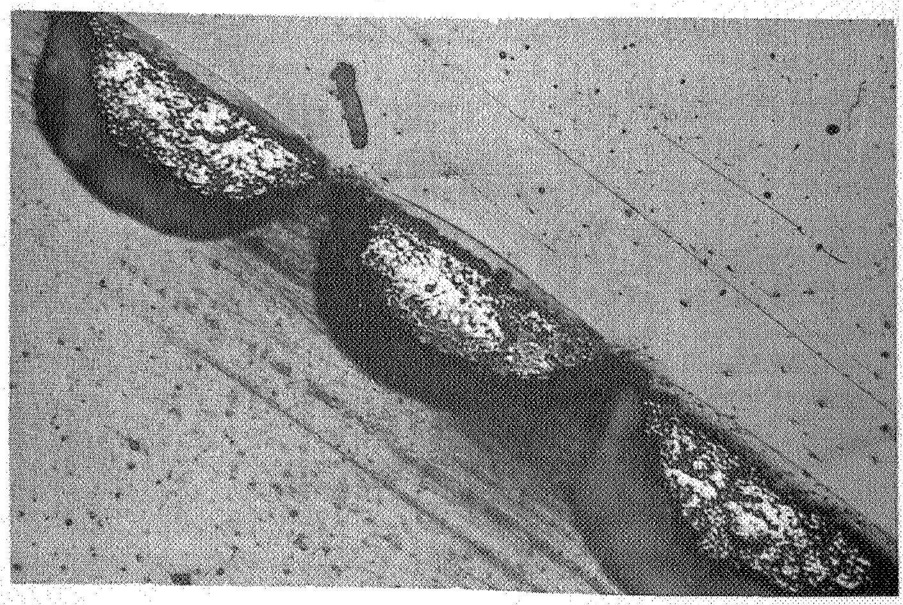
FIGURE 18. MOLDED R-1-50/PI

The PQ resin was difficult to impregnate uniformly on a single strand of yarn. The high solution viscosity and low solids produced small beads at intervals along the length. In larger composites with a large number of yarn strands these slight inconsistencies can be tolerated. However, in a single strand, the beads of PQ resin, flowing only with high pressure, tends to break the fibers at that point during molding. Most of the filaments molded with PQ resin as a binder broke into several pieces during demolding. In addition to the breakage the binder content was very low. The P-I resin also requires high pressures to mold, and the formed filaments were lower in strength than expected. However, no problems were encountered on filament breakage because the impregnation was more uniform. The low strengths of the filaments formed with both P-I and PQ resins indicater binders, that flow only under high pressure, tend to break up the fibers in a small single bundle molding.

Figure 18, R-1-50/P-I, and Figure 19, P-I/highly advanced furfuryl alcohol, are examples of the molded filaments. The voids around the filaments are caused by poor quality of the casting and are not the results of a fiber property. The filament shape is quite uniform, considering the method of fabrication. The flat surface of each filament was the area in contact with the deformed metal wire. It confirms that the projected surface of the metal uniformly compresses the fiber bundles.



A. MOLDED ONLY, 100X



B. MOLDED AND PYROLYZED, 100X

FIGURE 19. MOLDED P-I/HIGHLY ADVANCED FURFURYL ALCOHOL.

5. TESTING

5.1 Test Procedure

Several of the more durable early pyrolyzed R-1-50 composite filaments were tested for flexural modulus in a three point loading. Values varied from 48 x 10^6 psi (33.1 x 10^4 MN/m^2) to 14 x 10^6 psi (9.7 x 10^4 MN/m^2). Much of the variation can be attributed to variations in measuring the diameter and in assuming a round shape; flexural modulus varies inversely to the 4th powers of the diameter. The smaller diameter filaments had the higher flexural modulus. The average for all tests was 27.8 x 10^6 psi (19.2 x 10^4 MN/m^2), about the same value as a larger epoxy composite reinforced with a 55 volume percent R-1-50 type fiber. Although the average flexural modulus was realistic, the test was not sufficiently accurate for filaments with irregular cross sections. A few additional flexure determinations were made with some of the later better-rounded filaments, but the test was dropped in favor of tensile modulus.

Strand testing is a common way to evaluate the tensile properties of carbon yarns. While under light tension, the yarns are impregnated with a room temperature curing epoxy resin. The cured strands are then tested by pulling in a tensile machine with rubber covered clamps to prevent cracking. The carbon chars lack the toughness of the epoxy resin and even the rubber facings damaged the pyrolyzed filaments.

To avoid clamping damage, the filaments were mounted between tabs at each end. The first tabs were .020 inch (50.8 x 10^{-3} cm) aluminum, 1/2 inch (1.27 cm) wide bonded together with an epoxy cement. Because the mass of aluminum tabs was so much greater than that of the filaments, it was difficult to handle the specimens without breaking the filaments.

The next tensile tests were made on 3-inch (7.62 cm) composite filaments sandwiched between a layer of No. 69 medium weight, cold pressed illustration board and a layer of data processing card. The pieces of illustration board were 1-1/2 inches (3.81 cm) wide and 5 inches (12.7 cm) long with a 1 inch hold (2.54 cm) cut from the center. The filaments were cradled across the cutout at the center line. The portion in contact with the paper board were bonded in place with adhesive and a cover from a data processing card. After mounting in the test machine, the sides of the one-inch cutout were burned through with a hot wire.

Examination of mounting tabs after testing indicated the test machine clamps may have damaged the bonded portion of some of the filaments and caused low test values. A sandwiching between two layers of the illustration board was then used to avoid clamp damage. The two layers of board gave fairly consistent results but problems did occur when the adhesive wicked away from the filaments and left a starved bond line. Also, attempts to determine modulus by precutting one side of the cutout hole and mounting an extensometer on the cut side gave low results. The illustration board apparently stretched under the load and the effective gage length of the filament was greater than one inch. Combinations of illustration board and metal tabs, increased amounts of adhesive and metal sandwich mounts lead to the configuration shown in Figure 20.

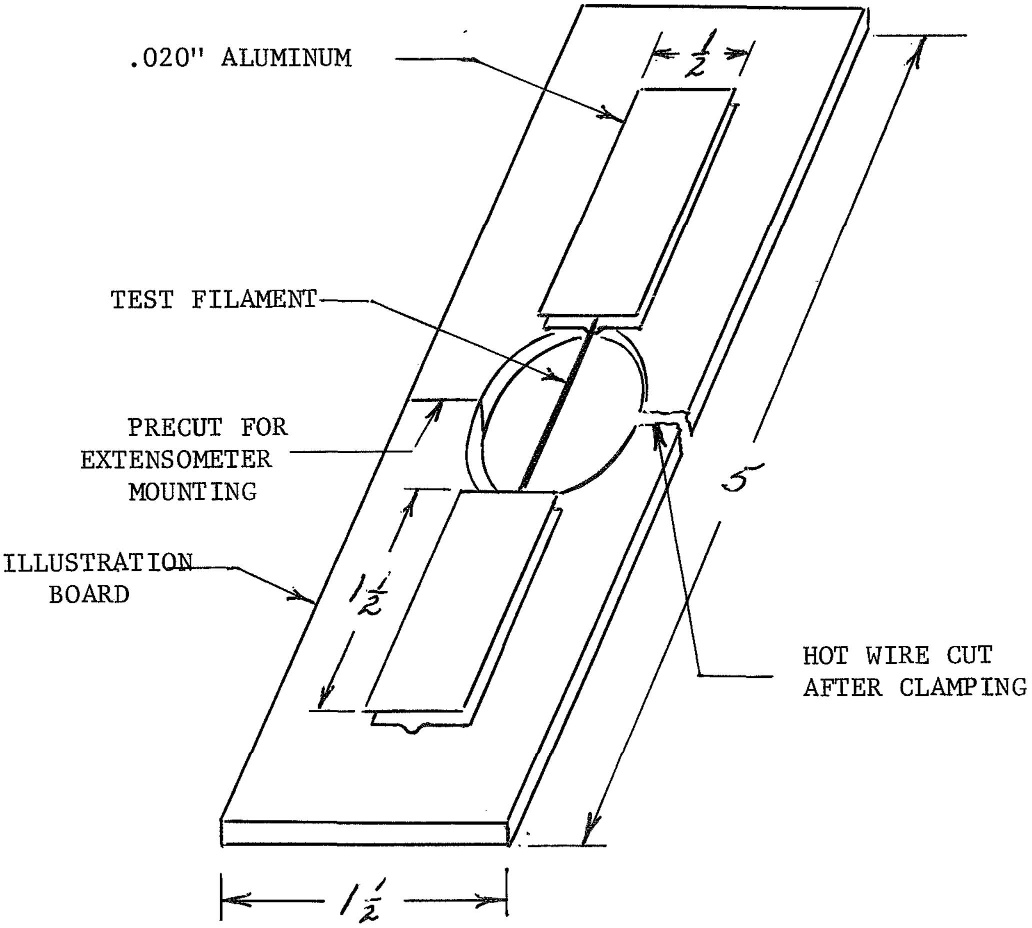


FIGURE 20. TENSILE TEST MOUNTING

Eastman 910 was used as the bonding cement. A 1 inch (2.54 cm) extensometer was mounted on the left side to determine the approximate modulus. The aluminum tabs are rigid enough to keep most of the filament strain in the gage length. The groove in the bottom tab keeps the adhesive around the filament and prevents test machine clamp pressure directly against the filament.

The heavy illustration board is a good base for mounting the filaments. It is stiff enough to support the filament, even after cutting out the gage length hole and one side by the hole and is heavy enough to attach an extensometer. It does have one drawback, dimensional stability. Large humidity change or heating (e.g., curing a mounting adhesive) will cause the board to warp, which can influence test results.

Density on the filaments reported was determined by the "sink or float" method. Dibromethane with a density of 2.48 gm/cc and isopropyl alcohol with a density of 0.73 gm/cc were used as the fluid combination.

Moisture pickup on the "as received" fibers and finished filaments was measured after heating the materials for 3 hours at 302°F (423°K). The dried samples were exposed to an ambient laboratory condition of approximately 72°F (295°F) and 50% R.H. and to 72°F and 100% R.H. for a period of 18 hours.

5.2 TEST RESULTS

Table II is a summary description of all the composite filaments tested with the thin aluminum tabs attached to the illustration board (Figure 20). Regardless of the initial binder, all pyrolyzed filaments were reimpregnated with furfuryl alcohol, activated with phosphoric acid, and repyrolyzed. In addition to the pyrolyzed filaments, fiber bundles impregnated and cured with a resilient epoxy, furfuryl alcohol, PQ, PI, and unpyrolyzed molded filaments were tested. No attempt was made to control the amount of epoxy applied to the fibers. The combination of low fiber volume and resilience was expected to give a filament with a tensile breaking load near the ultimate value for the fibers. The other fiber/binder combinations, in the molded and unmolded state, were tested to determine the changes in tensile properties with the different processing steps.

The fiber volume and filament cross-section area of the pyrolyzed filaments in Table II are calculated from the initial fiber weight and the added binder weight. The effect of voids and cracks was ignored. So the actual fiber volume would always be less and the actual cross-section area would be greater than the reported values. Clear, well polished photomicrographs would be needed for each filament tested to determine accurately the fiber loading and filament size. Generally a high fiber volume does indicate porosity. Voids would be expected to become much more frequent as the fiber volume becomes greater than 70% of the combined fiber and binder volume.

Table III is a summary of tensile properties of all the composite filaments in Table II. Tensile values are averages of more extensive data presented in the Appendix; values were normalized from Table A and calculated from Table B of the Appendix. The normalized properties were based on the

TABLE II

SUMMARY OF TENSILE TESTS WITH ALUMINUM TAB MOUNTING
Filament Description

Series	Fiber	Initial Resin	Fabrication Process	Condition	Fiber Vol. (%)	Material Cross Section Area (x 10^{-5} in.^{2})	(x 10^{-4}cm^2)
A	R-1-50 (Thornel 50)	Hi-adv	Roll Between Glass	Pyrolyzed	72	4.78	3.09
B	R-1-50	FA-Epoxy Nov.	Wet Die	Pyrolyzed	66	5.23	3.37
C	R-1-50	Epoxy	Free Standing Cure	Cured Only	--	----	----
D	R-1-50	Hi-adv. FA	Free Standing Cure	Cured Only	--	----	----
E	R-1-50	Hi-adv FA	Mold	Cured Only	--	----	----
F	R-1-50	Hi-adv FA	Mold	Pyrolyzed	59	5.90	3.80
G	R-1-50	Hi-adv FA	Mold	Pyrolyzed	70	4.97	3.20
H	P-1 (Modmor I)	Epoxy	Free Standing Cure	Cure Only	--	----	----
J	P-1	Hi-adv FA	Free Standing Cure	Cure Only	--	----	----
K	P-1	Hi-adv FA	Mold	Cure Only	--	----	----

TABLE II (Continued)

Series	Fiber	Initial Resin	Fabrication Process	Condition	Fiber Vol. (%)	Material Cross Section Area	
						(x 10^{-5}in.^{2})	(x 10^{-4}cm^2)
L	P-1	Hi-adv FA	Mold	Pyrolyzed	62	6.41	4.41
M	P-1	Hi-adv FA	Mold	Pyrolyzed	73	4.66	3.21
N	P-II (Modmor II)	Epoxy	Free Standing Cure	Cure Only	--	----	----
O	P-II	Hi-adv FA	Free Standing Cure	Cure Only	--	----	----
P	P-II	Hi-adv FA	Mold	Cure Only	--	----	----
R	P-II	Hi-adv FA	Hold	Pyrolyzed	75	4.65	3.20
S	R-1-50	Polyimide	Free Standing Cure	Cure Only	--	----	----
T	R-1-50	Polyimide	Mold	Cure Only	--	----	----
U	R-1-50	Polyimide	Mold	Pyrolyzed	63	5.61	3.86
V	R-1-50	Poly-quinxaline	Free Standing Cure	Cure Only	--	----	----
W	R-1-50	Poly-quinxaline	Mold	Cure Only	--	----	----
X	R-1-50	Poly-quinxaline	Mold	Pyrolyzed	67	5.17	3.56

TABLE III

SUMMARY OF TENSILE TEST WITH ALUMINUM TAB MOUNTING

Filament Tensile Properties

Series	Normalized Tensile Strength		Normalized Modulus		Reinforcing Efficiency (%)	Calculated Tensile Strength		Calculated Modulus	
	(x10^{3}psi	(x10^{2}MN/m^{2})	(x10^{6}psi)	(x10^{4}MN/m^{2})		(x10^{3}psi)	(x102MN/m^{2})	(x10^{6}psi)	(x10^{4}MN/m^{2}
A	157	10.8	46	31.7	55	115	7.9	33	22.8
B	171	11.8	52	35.8	60	115	7.9	35	24.1
C	278	19.2	52	35.8	98	---	---	---	----
D	257	17.7	50	34.5	91	---	---	---	----
E	253	17.4	55	37.9	89	---	---	---	----
F	194	13.4	57	39.3	68	116	8.0	32	22.1
G	157	10.8	50	34.5	55	112	7.7	35	24.1
H	274	18.9	48	33.1	97	---	---	--	----
J	295	20.4	48	33.1	107	---	---	--	----
K	287	19.8	50	34.5	104	---	---	--	----
L	235	16.2	56	38.6	86	146	10.1	62	42.7
M	197	13.6	48	33.1	72	149	10.3	35	24.1
N	468	32.3	38	26.2	117	---	----	--	----
O	346	23.8	33	22.7	60	---	----	--	----
P	256	17.7	35	24.1	64	---	----	--	----
R	64	4.4	35	24.1	16	52	3.6	27	18.6
S	265	18.3	50	34.5	93	---	----	--	----
T	120	8.3	57	39.3	42	---	----	--	----
U	101	7.0	49	33.8	37	63	4.3	31	21.4
V	227	15.7	46	31.7	80	---	----	--	----
W	55	3.8	--	----	20	---	----	--	----
X	90	62	48	33.1	68	62	4.3	33	22.7

combined cross-section of the reinforcing fibers. The fiber area was determined from the density, as reported by the vendor, and the weight per unit length. The calculated properties were based on the combined cross-section of the binder and the fiber. The binder cross-section was determined by the increased weight per unit length over the raw fiber and the density of the binder. The complete test data and representative calculations are given in the appendix.

The normalized comparison is desirable because it gives a direct indication of the retained fiber properties in the finished filament. The binder is required to hold the fiber bundles together and to transfer load from fiber to fiber, when the filament is under stress, but the binder tensile properties are only a small fraction of the fiber tensile properties. It is assumed the binder does not directly contribute to filament tensile strength and tensile modulus; and, therefore, the properties of the bundle come only from the fiber. As an example, a R-1-50/epoxy (Series C) filament gave an average breaking load of 9.8 pounds (43.5N). These fibers should be free from mechanical damage since they were free formed and subject only to the wicking of the epoxy resin. Converting to the normalized values for the strength and the elastic portion of stress-strain plot, the average tensile strength was 278,000 psi (19.2 x 10^2MN/m^2) and tensile modulus was 52 x 10^6 psi (35.8 x 10^4 MN/m^2). The vendor listed fiber tensile properties are strength 285,000 psi (19.6 x 10^2 MN/m^2) and modulus 50 x 10^6 psi (34.5 x 10^4 MN/m^2).

The reinforcing efficiency listed in Table II is the normalized tensile strength divided by the vendor reported fiber tensile strength. In cases when the fiber is stronger than the nominal vendor data or the determination of fiber weight in the filament may be in error, the reinforcing efficiency can exceed 100%.

The tensile modulus determinations were considered only approximate values because measurements were not made directly on the filaments. The values obtained, when normalized, generally compare well with the vendor reported fiber modulus. The unusually high or low values are probably test inconsistencies related to mounting the extensometer. Fiber tensile modulus was maintained in all processing including pyrolyzation.

Normalized tensile strength or breaking load consistently dropped with additional processing. Changing from a "free standing cure" with the tough epoxy resin to the more brittle furfuryl alcohol, the highest breaking loads of R-I-50 fibers dropped from over 10 pounds (44.5 N) to less than 9.5 pounds (42.3 N) (Series C and D).

Molding and pyrolyzing the R-I-50/furfuryl alcohol combination further dropped the breaking loads to 7.5 pounds (33.3 N) (Series F) or less. The same trend is shown in the other binder or fiber combinations. Except for the P-II fibers, the drop in strength is probably the result of some mechanical damage to the fiber and to a reduction in the quality of the binder, not from a change in the original properties of the fibers.

The accuracy of the tests on the PAN precursor fiber reinforced composite filaments is somewhat questionable because, as previously pointed out, it was difficult to obtain uniform strands. Still the tests did show some unusual results. The high strength of the P-II fibers was retained in the cured epoxy impregnated strand (Series N). The loss of 80 to 90% of the strength in the molded and pyrolyzed furfuryl alcohol impregnated strands (Series R) was unexpected. A recheck on the P-II fibers was made by testing pyrolyzed "free standing cures" of furfuryl alcohol and the fiber. The breaking loads were again low, between 1 and 2 pounds (4.5 to 9.0 N). The results are not reported in the tabular charts because the thin aluminum tabs were not used to mount the filaments.

PAN polymers exposed to only low temperature pyrolyzation, like the P-II fibers, are reported to exhibit a high chemical catalytic activity.(14) This activity may be responsible for the large loss of tensile strength during pyrolyzation. Regardless of the reasons for low tensile strengths, the P-II fibers appear to be unsatisfactory as reinforcements for carbonized composites.

The molded high modulus PAN precursor fibers, P-I, had the best retention of tensile strength after pyrolyzation. The comparative test averages on Series L and M were normalized strengths of 235,000 (16.2×10^2 MN/m^2) and 197,000 (13.6×10^2 MN/m^2) respectively. The strengths calculated on the void-free cross-section were 146,000 psi (10.1×10^2 MN/m^2) and 149,000 psi (10.3×10^2 MN/m^2) respectively. These are well above any other pyrolyzed filaments tested with aluminum tab mountings. The fiber volumes on the L series were not well controlled, and the spread was quite wide. However, two of the filaments were about 70% fiber volume and they exhibited good retention of tensile properties. The calculated strength based on a void-free cross-section was 175,000 psi (12.1×10^2 MN/m^2) and 163,000 psi (11.2×10^2 MN/m^2). Series M was an attempt to repeat the filaments at the higher fiber volume. The breaking loads in the M series were relatively high, but the increased volume dropped the filament strength to less than 80% of the available fiber strength.

The loss in strength of the molded PI (Series T) and PQ (Series W) binder filaments is believed to be caused by the high pressure needed to produce compaction. The resins have high resistance to flow at the molding temperatures, and the molding process badly damages the fibers. The moderate increase in strength from the molded to the pyrolyzed filaments (Series T to Series U and Series W to Series X) is probably the result of reimpregnation with furfuryl alcohol before the second pyrolyzation. The low flow of the initial impregnant would be expected to form a poor bond to the fibers during molding, and the additional furfuryl alcohol would help improve the fiber/binder bonds.

A considerable variation was found in the test results which is typical of most new high modulus composite materials. The filaments are brittle and easily damaged. Delicate handling is required at all times. Even then, most of the filaments broke at the tab edge rather than in the gage length. This indicates possible damage from excessive flexing at the attachment point or misalignment of the filament during test. A test that does not break in the gage length should record a somewhat lower load than the actual strength of the filaments.

Bonding to the rigid aluminum tabs in Figure 20 mounting appears to be more critical than bonding directly to the illustration board. This difference is noticed as the composite filament binder becomes more brittle. For example, the pyrolyzed composite filaments formed by drawing R-I-50 fibers through a wet die (Series B) were tested by mounting without the aluminum tabs. Covers cut from a data processing card were bonded over the filaments, mounted directly on illustration board, with double-back tape to prevent damage from the test clamps. The average breaking load on these specimens was 7.1 pounds (31.6 N) versus 6.0 pounds (26.7 N) on the same run of filaments tested with the aluminum tabs.

Another aspect of tensile strength variation is the fiber volume in the finished composite filament. A high fiber volume with a fixed amount of fiber will produce a smaller filament size but not necessarily a higher tensile strength. A molded and pyrolyzed R-I-50/furfuryl alcohol filament had approximately 60% fiber volume in the finished composite filaments. A repeat was made at 70% fiber volume for evaluation by NASA Lewis. The average breaking load for the two runs, using the grooved aluminum tab mounting, was 6.8 and 5.5 pounds (30.2 and 25.4 N), respectively. Unidirectional graphite fiber/epoxy composites may show some loss of reinforcing efficiency above 60% fiber volume, but the drop is less than the drop found in molded carbonized composite filaments.

The best pyrolyzed filament produced by a method other than molding was the R-I-50 fibers drawn through an 0.008 inch (20.3×10^{-3} cm) glass die filled with furfuryl alcohol modified with an epoxy novolac (Figure 14). Properties of the filament were:

Shape: Round
Diameter: 0.008 inch (20.3×10^{-3} cm)
Weight: 0.0524 gm/m
Bulk Density: 1.53 gm/cc
Flexural Modulus: 32.90^6 psi (22.7×10^4 MN/m^2)
Tensile Modulus: 34.3×10^6 psi (23.6×10^4 MN/m^2)
Breaking Load: 6.6 to 7.8 pounds (29.3 - 34.7 N)
Tensile Strength: 141,000 psi (9.7×10^2 MN/m^2)
Tensile Strength Range: 133,000 - 155,000 psi (9.2-10.7×10^2 MN/m^2)
Calculated Fiber Volume: 69%

The next best pyrolyzed filament produced by other than molding was the R-I-50 fibers impregnated with a highly advanced furfuryl alcohol binder and rolled between glass surfaces (Figure 15). The properties were:

Shape: Round
Diameter: 0.008 inch (20.3 x 10^{-3} cm)
Weight: 0.0484 gm/m
Bulk Density: 1.50 gm/cc
Flexural Modulus: 34 x 10^6 psi (23.4 x 10^4 MN/m^2)
Tensile Modulus: 32.3 x 10^6 psi (22.4 x 10^4 MN/m^2)
Breaking Load: 6.1 to 7.0 lb (27.1 - 31.1 N
Tensile Strength: 132,000 psi (9.1 x 10^2 MN/m^2)
Tensile Strength Range: 120,000 - 139,000 psi (8.3-9.6 x 10^4 MN/m^2)
Calculated Fiber Volume: 69%

The tensile strength of the two previously mentioned filaments were determined on samples mounted directly to illustration board and covered with tabs cut from a data processing card. Also, the die formed filament was protected with a layer of double back tape between the filament and the tab. These differences do give a higher breaking load than the mounting with aluminum tabs. These are the same filaments reported as Series B and Series A, respectively, in the comparative testing with aluminum tab mountings. The tensile strengths here are based on the cross section area of the photomicrographs. The direct mounting of the filament to the illustration board was not used for the comparative evaluation because it lacked sufficient rigidity to determine modulus with an extensometer. The modulus reported here was taken from the Series B and A data.

The pyrolyzed die formed filament, with the 7.8 lb (34.7 N) breaking load, gave a tensile strength of 155,000 psi (10.7 x 10^2 MN/m^2) based on the actual 0.008 inch (20.3 x 10^{-3} cm) filament diameter. This is considerably better than the 70,000 psi (4.82 x 10^2 MN/m^2) tensile strength on the larger unidirectional graphite fiber reinforced carbon composites reported in the literature.(3) Also the strengths compare well with the 143,000 psi reported on a high-quality, unidirectional 50 x 10^6 psi (34.4 x 10^4 MN/m^2) modulus, 60% loaded, graphite yarn, reinforced epoxy composite.(5) This indicates the reinforcing qualities of the graphite filaments in a pyrolyzed binder are similar to the "state of the art" reinforcement in other binders.

Some of the pyrolyzed molded P-I/highly advanced furfuryl alcohol filaments (Series L and M) had a combination of high fiber volume and relatively high breaking load. These filaments probably equal or exceed the tensile strength of the 155,000 psi (10.7 x 10^2 MN/m^2) die formed filament, tested without the aluminum tabs. The highest tensile strength on a calculated 76% void free cross-section and 8.9 pound (39.6 N) breaking load was 175,000 psi (12.1 x 10^2 MN/m^2). However, without photomicrographs of each filament, an accurate comparison cannot be made.

Table IV is a comparison of tensile strength of the best pyrolyzed filaments tested with the aluminum tab mountings. These are single tests based on breaking load and void-free calculated cross-sectional area. Many factors can reduce tensile strength test values of composite, but high tensile values are rarely erroneous. They generally indicate what can be obtained under the best processing and testing methods.

Absorbed moisture on structural reinforcements can be detrimental to composites that require processing temperatures above the boiling point of water. Dried fiber and pyrolyzed filaments were exposed to the air at 50% and 100% R.H.

The weight measurements, Table V, show some moisture pickup, particularly on the molded filaments. The "as received" fibers absorbed little or no moisture. No significant differences were observed between the 50% and 100% R.H. exposures.

The samples were only 2 to 3 inches (5.08 to 7.62 cm) long because the amount of pyrolyzed filaments was limited. Weights were between 2 and 15 mg, and the largest weight changes were only a few tenths of a milligram. So, testing accuracy was low, but an appreciable weight increase was picked up on the molded filaments. The higher weight pickup indicates a greater surface area exposed to the atmosphere. Greater surface area would be the result of filament cracking or high porosity.

TABLE IV

PYROLYZED FILAMENT TENSILE STRENGTH

Filament	Forming Method	Cross Section Area		Breaking Load		Fiber Volume	Tensile Strength	
		(x 10^{-5} in^2)	(x 10^{-4} cm^2)	(lb)	(N)		(x 10^3 psi)	(x 10^2 MN/m^2)
R-I-50/Highly Advanced Furfuryl Alcohol (Series A, No. 3)	Rolled	4.78	3.09	6.0	26.7	72	126	8.7
R-I-50/Epoxy Novolac-Furfuryl Alcohol (Series B, No. 1)	Wet Die	5.23	3.37	6.1	27.1	66	117	8.1
R-I-50/Highly Advanced Furfuryl Alcohol (Series F, No. 4)	Molded	5.84	3.77	7.5	33.3	60	129	8.9
P-I/Highly Advanced Furfuryl Alcohol (Series L, No. 1)	Molded	5.08	3.28	8.9	39.6	76	175	12.1

TABLE V

DRY FIBER AND PYROLYZED FILAMENT MOISTURE PICKUP AT 75°F (297°K)

Material	18 Hours 50% RH (% Wt. Increase)	18 Hours 100% RH (% Wt. Increase)
R-I-50	<1	<1
P-I	<1	<1
P-II	<1	<1
R-I-50/Highly Advanced Furfuryl Alcohol (Rolled)	2-3	2-3
R-I-50/Epoxy Novolac-Furfuryl Alcohol (Die Formed)	2	2-3
R-I-50/Highly Advanced Furfuryl Alcohol (Molded)	6	6
P-I/Furfuryl Alcohol (30 Grams Horizontal Tension)	1	1
P-II/Highly Advanced Furfuryl Alcohol (Molded)	---	12

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The feasibility of the resin-impregnation and pyrolysis method for making large diameter carbon-base composite filaments was shown. Three methods were used to fabricate the filaments, i.e., rolling or wet die or molding. The wet die method of forming produced a pyrolyzed composite filament with a 155,000 psi (10.7 x 10^2 MN/m^2) tensile strength. The P-I fibers formed a molded pyrolyzed filament with a 175,000 psi (12.1 x 10^2 MN/m^2) tensile strength based on a void-free cross-section which would be somewhat higher than actual strength. Both tensile values compare favorably to the reported value for a unidirectional graphite/epoxy composite and is greatly superior to the reported values for graphite/carbon composite.

Problems were encountered in the impregnation, curing, and pyrolysis steps of the process, causing non-uniform distribution of the fibers and porosity and cracking within the pyrolyzed carbon matrix. This prevented the composite filaments from attaining the full potential properties.

1. Tensile modulus of the fibers was retained through the pyrolyzation process.
2. Tensile strength dropped consistently with each processing step. The better pyrolyzed filaments retained 80 to 60% of the available fiber strength.
3. The molding method of forming was satisfactory for furfuryl alcohol type binders but badly degrades single fiber bundles of PI and PQ resins.
4. The P-II fibers appear unsuitable as a reinforcement for carbon composites. The large drop in strength after pyrolyzation cannot be explained but may be related to the high chemical reactivity of PAN precursor carbons pyrolyzed below a graphitization temperature.
5. The P-I fibers show the highest retention of fiber strength after pyrolyzation.

6.2 Recommendations

The fibers used in this program were not expected to produce composite filaments with the target requirements of 400,000 psi (27.6 x 10^2 MN/m^2) tensile strength and 50 x 10^6 psi (34.5 x 10^4 MN/m^2) tensile modulus. By changing to a 75 x 10^6 psi (51.7 x 10^4 MN/m^2) or higher modulus fiber, the modulus goal can be met at 70% fiber volume. The strength cannot be, obtained unless the fibers are increased in strength and/or the binder tensile properties are converted to a load carrying part of the composite.

The recommendations for future work on carbon composite filaments are:

1. Optimize the "wet die" forming process for maximum strength or other methods to eliminate porosity and cracking and obtain a uniform fiber distribution.
2. Optimize the P-I reinforced filaments for maximum strength.
3. Evaluate the fibers with moduli 75 x 10^6 psi (51.7 x 10^4 MN/m^2) or greater as reinforcements.
4. Convert the carbon binder to a more crystalline type polymer by modifying the precursor furfuryl alcohol binder with:
    a. A small amount of colloidal graphite.
    b. A coal tar or polyvinyl chloride pitch.
    c. A non-accelerated cure using heat only (forms a pitch-like material) and heating to a graphitizing temperature.
5. Evaluate stretching the pyrolyzed filaments with the more crystalline binders at a graphitizing temperature to increase tensile strength of both the fibers and the binder.

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APPENDIX

TABLE A

FILAMENT TENSILE TEST WITH ALUMINUM TAB MOUNTING

Normalized Tensile Properties

<u>SERIES A</u>   Material: R-1-50/Highly Advanced Furfuryl Alcohol   Forming: Roll Between Glass
Condition: Pyrolyzed

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (Lbs)	Breaking Load (N)	Normalized Tensile Strength (x 10^3 psi)	Normalized Tensile Strength (x 10^2 MN/m^2)	Normalized Modulus (x 10^6 psi)	Normalized Modulus (x 10^4 MN/m^2)	Reinforcing Efficiency (%)
1	0.0365	---	0.0484	5.2	23.1	149	10.3	45	31.0	52
2	0.0365	---	0.0484	5.1	22.7	146	10.1	45	31.0	51
3	0.0365	---	0.0484	6.0	26.7	171	11.8	47	32.4	60
4	0.0365	---	0.0484	5.3	23.5	151	10.4	--	----	53
5	0.0365	---	0.0484	5.9	26.2	168	11.6	45	31.0	59
SERIES B	Material: R-1-50/Furfuryl Alcohol Epoxy Novolac						Forming: Wet Die Condition: Pyrolyzed			
1	0.0365	---	0.0524	6.1	27.1	174	12.0	43	29.6	61
2	0.0365	---	0.0524	5.9	26.2	168	11.6	57	39.3	59
3	0.0365	---	0.0524	6.1	27.1	174	12.0	54	37.2	61
4	0.0365	---	0.0524	5.9	26.2	168	11.6	54	37.2	59

TABLE A (Continued)

SERIES C Material: R-1-50/Epoxy

Forming: Free Standing Cure
Conditions: Cured Only

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load		Normalized Tensile Strength		Normalized Modulus		Reinforcing Efficiency (%)
				(lbs)	(N)	(x 10^3 psi)	(x 10^2 MN/m^2)	(x 10^6 psi)	(x 10^4 MN/m^2)	
1	0.0365	---	---	10.2	45.3	290	20.0	51	35.1	102
2	0.0365	---	---	10.4	46.2	296	20.4	53	36.5	104
3	0.0365	---	---	8.7	38.7	247	17.0	51	35.1	87
SERIES D	Material: R-1-50/Highly Advanced Furfuryl Alcohol							Forming: Free Standing Cure Condition: Cured Only		
1	0.0365	0.0542	---	9.4	41.7	267	18.4	55	37.9	94
2	0.0365	0.0542	---	8.4	37.3	239	16.5	48	33.1	84
3	0.0365	0.0542	---	9.1	40.4	259	17.9	--		91
4	0.0365	0.0542	---	9.3	41.3	264	18.2	45	31.0	93
SERIES E	Material: R-1-50/Highly Advanced Furfuryl Alcohol							Forming: Mold Condition: Cured Only		
1	0.0365	0.0594	---	8.9	39.6	253	17.4	48	33.1	89
2	0.0365	0.0633	---	9.4	41.7	267	18.4	71	49.0	94
3	0.0365	0.0607	---	9.2	40.8	261	18.0	50	34.5	92
4	0.0365	0.0581	---	8.1	36.0	230	15.7	51	35.1	81

TABLE A (Continued)

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lbs)	Breaking Load (N)	Normalized Tensile Strength (x 10^3psi)	Normalized Tensile Strength (x 10^2MN/m^2)	Normalized Modulus (x 10^6psi)	Normalized Modulus (x 10^4MN/m^2)	Reinforcing Efficiency (%)
SERIES F	Material: R-1-50/Highly Advanced Furfuryl alcohol					Forming: Mold Condition: Pyrolyzed				
1	0.0365	0.0594	0.0581	6.9	30.5	195	13.4	51	35.2	69
3	0.0365	0.0606	0.0594	6.1	27.1	173	11.9	51	35.2	61
4	0.0365	0.0606	0.0581	7.5	33.3	215	14.8	61	42.0	75
5	0.0365	0.0581	0.0559	6.9	30.5	195	13.4	49	33.8	69
6	0.0365	0.0581	0.0508	6.4	28.4	181	12.5	54	37.2	63
7	0.0365	0.0632	0.0632	7.0	31.1	199	13.7	54	37.2	70
8	0.0365	0.0632	0.0645	7.1	31.6	202	13.9	66	45.5	71
SERIES G	Material: R-1-50/Highly Advanced Furfuryl Alcohol (Repeat of Series F at Higher Fiber Volume)					Forming: Mold Condition: Pyrolyzed				
1	0.0365	0.0491	0.0503	5.2	23.1	148	10.2	51	35.2	52
2	0.0365	0.0500	0.0503	6.5	28.9	185	12.8	53	36.5	65
3	0.0365	0.0497	0.0507	4.8	21.3	136	9.4	46	31.7	48
4	0.0365	0.0462	0.0474	5.7	25.3	162	11.2	51	35.2	57
5	0.0365	0.0529	0.0507	6.0	26.7	170	11.7	50	34.5	60
6	0.0365	0.0500	0.0500	6.0	26.7	170	11.7	51	35.2	60
7	0.0365	0.0516	0.0513	5.7	25.3	162	11.2	50	34.5	57
8	0.0365	0.0516	0.0510	4.8	21.3	136	9.4	48	33.1	48
10	0.0365	0.0491	0.0494	5.7	25.3	162	11.2	51	35.2	57
12	0.0365	0.0494	0.0497	4.8	21.3	136	9.4	51	35.2	48

TABLE A (Continued)

SERIES H Material: P-I/Epoxy

Forming: Free Standing Cure
Condition: Cured Only

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lbs)	Breaking Load (N)	Normalized Tensile Strength $(\times 10^3 psi)$	Normalized Tensile Strength $(\times 10^2 MN/m^2)$	Normalized Modulus $(\times 10^6 psi)$	Normalized Modulus $(\times 10^4 MN/m^2)$	Reinforcing Efficiency (%)
1	0.0433	---	---	7.2	32.0	206	14.6	42	28.9	72
2	0.0433	---	---	12.1	53.8	344	23.7	60	41.4	121
3	0.0433	---	---	10.3	45.8	294	20.3	39	26.9	106
4	0.0433	---	---	8.8	39.1	252	17.4	52	35.9	88

SERIES J Material: R-1/Highly Advanced Furfuryl Alcohol

Forming: Free Standing Cure
Condition: Cure Only

1	0.0422	0.0562	---	9.1	40.4	264	18.2	52	35.8	96
2	0.0422	0.0562	---	9.0	40.0	261	18.0	43	29.6	92
3	0.0441	0.0610	---	12	53.2	335	23.1	51	35.1	122
4	0.0441	0.0610	---	9.2	40.8	257	17.7	42	28.9	94
5	0.0432	0.0628	---	12.5	55.5	357	24.6	54	37.2	130

SERIES K Material: R-1/Highly Advanced Furfuryl Alcohol

Forming: Mold
Condition: Cure Only

1	0.0428	0.532	---	10.6	47.0	306	21.1	51	35.1	111
2	0.0435	0.541	---	10.1	44.8	286	19.7	45	31.0	104
3	0.0435	0.541	---	11.4	50.6	324	22.3	50	34.5	118
4	0.0438	0.522	---	9.3	41.3	262	18.1	60	41.3	95
5	0.0413	0.490	---	8.9	39.6	260	17.9	45	31.0	95
6	0.0413	0.490	---	9.6	42.6	281	19.3	48	33.1	102

TABLE A (Continued)

<u>SERIES L</u>

Material: R-I/Highly Advanced Furfuryl Alcohol

Forming: Mold
Condition: Pyrolyzed

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lbs)	Breaking Load (N)	Normalized Tensile Strength (x 10^3psi)	Normalized Tensile Strength (x 10^2MN/m^2)	Normalized Modulus (x 10^6psi)	Normalized Modulus (x 10^4MN/m^2	Reinforcing Efficiency (%)
1	0.0485	0.0623	0.0595	8.9	39.6	227	15.7	71	49.0	83
2	0.0485	0.0623	0.0595	8.3	36.9	212	14.6	51	35.1	77
3	0.0455	0.0904	0.0685	9.2	40.8	250	17.2	65	44.8	91
4	0.0497	0.0930	0.0853	9.5	42.2	236	15.9	--	----	84
5	0.0497	0.0938	0.0879	10.3	45.8	256	17.6	50	34.5	95

<u>SERIES M</u>

Material: R-I/Highly Advanced Furfuryl Alcohol (Repeat of Series L at Higher Fiber Volume)

Forming: Mold
Condition: Pyrolyzed

1	0.0436	0.0588	0.0582	5.5	24.4	156	10.8	44	30.3	57
2	0.0436	0.0588	0.0582	7.7	34.2	218	15.0	55	37.9	79
3	0.0430	0.0533	0.0520	7.4	32.9	213	14.7	55	31.0	78
4	0.0430	0.0533	0.0520	6.7	29.8	193	13.3	46	31.7	70
5	0.0436	0.0575	0.0520	7.3	32.4	207	14.3	--	----	75

TABLE A (Continued)

SERIES N — Material: P-II/Epoxy — Forming: Free Standing Cure — Condition: Cure Only

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lbs)	Breaking Load (N)	Normalized Tensile Strength (x 10^3 psi)	Normalized Tensile Strength (x 10^2 MN/m^2)	Normalized Modulus (x 10^6 psi)	Normalized Modulus (x 10^4 MN/m^2)	Reinforcing Efficiency (%)
1	0.0391	---	---	15.8	70.3	445	30.7	34	23.4	111
2	0.0391	---	---	18.4	81.8	520	35.8	41	28.2	130
3	o.0391	---	---	15	66.7	424	29.3	--	----	106
4	0.0391	---	---	18.2	80.9	514	35.4	41	28.2	129
5	0.0391	---	---	15.6	69.4	440	30.3	37	25.5	110
SERIES O	Material: P-II/Highly Advanced Furfuryl Alcohol						Forming: Free Standing Cure Condition: Cure Only			
1	0.0397	0.0510	---	11.2	49.8	312	21.5	28	19.3	78
2	0.397	0.0604	---	7.9	35.1	217	14.9	31	21.4	54
3	0.0378	0.0588	---	14.7	65.4	430	29.6	32	22.1	108
4	0.0397	0.0630	---	12.5	55.6	366	25.2	35	24.1	92
5	0.0397	0.0710	---	13.8	61.4	403	27.8	38	26.2	101
SERIES P	Material: P-II/Highly Advanced Furfuryl Alcohol						Forming: Mold Condition: Cured Only			
1	0.04.0	0.0552	---	9.6	42.7	269	18.5	43	29.6	67
2	0.0397	0.0568	---	13.2	58.7	365	25.2	43	29.6	91
3	0.0410	0.0578	---	7.8	34.7	211	14.5	27	18.6	53
5	0.0378	0.0410	---	8.2	36.4	240	16.5	35	24.1	60
6	0.0378	0.0410	---	6.6	29.3	193	13.3	29	20.0	48

TABLE A (Continued)

SERIES R — Material: P-II/Highly Advanced Furfuryl Alcohol — Forming: Mold — Condition: Pyrolyzed

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lbs)	Breaking Load (N)	Normalized Tensile Strength (x 10^3 psi)	Normalized Tensile Strength (x 10^2 MN/m^2)	Normalized Modulus (x 10^6 psi)	Normalized Modulus (x 10^4 MN/m^2)	Reinforcing Efficiency (%)
1	0.0397	0.0430	0.0526	2.7	12.0	75	5.2	33	22.7	19
2	0.0397	0.0430	0.0526	1.9	8.5	53	3.7	36	24.8	13
3	0.0397	0.0468	---	1.6	7.1	45	3.1	33	22.7	11
4	0.0378	0.0403	0.0452	2.6	11.6	76	5.2	35	24.1	19
5	0.0378	0.0446	0.0452	2.5	11.1	73	5.0	38	26.2	18
6	0.0410	0.0536	0.0530	2.3	10.4	62	4.3	34	23.4	16
SERIES S	Material: R-1-50/PI							Forming: Free Standing Cure Condition: Cured Only		
1	0.0365	0.0516	---	9.9	44.0	282	19.4	48	33.1	99
2	0.0365	0.0530	---	9.8	43.5	280	19.3	54	37.2	98
3	0.0365	0.0530	---	9.8	43.5	280	19.3	45	31.0	98
4	0.0365	0.0530	---	9.0	40.0	255	17.6	51	35.1	90
5	0.0365	0.0543	---	7.9	35.1	226	15.6	--	--	79
SERIES T	Material: R-1-50/PI							Forming: Mold Condition: Cured Only		
1	0.0365	0.0540	---	3.2	14.2	91	6.3	46	31.7	32
2	0.0365	0.0575	---	5.2	23.1	149	10.3	48	37.1	52
3	0.0365	0.0556	---	3.7	16.4	106	7.3	43	29.6	37
4	0.0365	0.0581	---	4.5	20.0	128	8.8	54	37.2	45
5	0.0365	0.0540	---	4.4	19.6	126	8.7	46	31.7	44

TABLE A (Continued)

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lbs)		Normalized Tensile Strength (x 10^3 psi)		Normalized Modulus (x 10^6 psi)		Reinforcing Efficiency (%)
				(lbs)	(N)	(x 10^3 psi)	(x 10^2 MN/m^2)	(x 10^6 psi)	(x 10^4 MN/m^2)	
SERIES U	Material: R-1-50/PI							Forming: Mold Condition: Pyrotyzed		
1	0.0365	0.0552	0.0568	2.6	11.6	74	5.1	44	30.3	26
2	0.0365	0.0552	0.0591	1.1	4.9	31	2.1	40	37.6	11
3	0.0365	0.0572	0.0526	3.8	16.9	108	7.4	51	35.1	38
4	0.0365	0.0575	0.0516	4.9	21.8	140	9.7	51	35.1	49
5	0.0365	0.0581	0.0575	5.4	24.0	154	10.6	57	39.3	54
SERIES V	Material: R-1-50/PQ							Forming: FreeStanding Cure Condition: Cured Only		
1	0.0365	0.0459	---	7.6	33.8	217	15.0	47	32.4	76
2	0.0365	0.0459	---	8.8	39.1	251	17.3	43	29.6	88
3	0.0365	0.0455	---	7.4	32.9	211	14.5	--	---	74
4	0.0365	0.0455	---	8.0	35.5	228	15.7	47	32.4	80
SERIES W	Material: R-1-50/PQ							Forming: Mold Condition: Cured Only		
1	0.0365	0.0472	---	1.6	7.1	45	3.1	--	---	16
2	0.0365	0.0472	---	0.1	0.4	--	--	--	---	--
3	0.0365	0.0455	---	2.4	10.7	68	4.7	--	---	25
4	0.0365	0.0482	---	1.8	8.0	51	3.5	--	---	19

TABLE A (Continued)

SERIES X   Material: R-1-50/PQ   Forming: Mold
Condition: Pyrolyzed

Test No.	Fiber Wt (gm/m)	Formed Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load		Normalized Tensile Strength		Normalized Modulus		Reinforcing Efficiency (%)
				(lbs)	(N)	(x 10^3 psi)	(x 10^2 MN/m^2)	(x 10^6 psi)	(x 10^4 MN/m^2)	
1	0.0365	0.0516	0.0526	3.4	15.1	97	6.7	45	31.0	34
2	0.0365	0.0516	0.0526	3.0	13.3	85	5.9	48	33.1	30
3	0.0365	0.0487	0.0543	2.4	10.7	68	4.7	--	----	24
4	0.0365	0.0491	0.0475	3.3	14.7	94	6.5	51	35.1	33
5	0.0365	0.0481	0.0536	3.8	16.9	108	7.4	46	31.7	38

TABLE B

PYROLYZED FILAMENT TEST WITH ALUMINUM TAB MOUNTING
Void Free Calculated Tensile Properties

SERIES A Material: R-1-50/Highly Advanced Furfuryl Alcohol Forming: Roll Between Glass

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load		Fiber Vol (%)	Material Cross Section Area		Calculated Tensile Strength		Calculated Modulus	
			(lb)	(N)		($x10^{-5}in^2$)	($x10^{-4}cm^2$)	($x10^3psi$)	($x10^2MN/m^2$)	($x10^6psi$)	($x10^4MN/m^2$)
1	0.0365	0.0484	5.2	23.1	72	4.78	3.09	109	7.5	32	22.0
2	0.0365	0.0484	5.1	22.7	72	4.78	3.09	107	7.4	32	22.0
3	0.0365	0.0484	6.0	26.7	72	4.78	3.09	126	8.7	34	23.4
4	0.0365	0.0484	5.3	23.5	72	4.78	3.09	111	7.7	--	----
5	0.0365	0.0484	5.9	26.2	72	4.78	3.09	123	8.5	32	22.0

SERIES B Material: R-1-50/Furfuryl Alcohol Epoxy Novolac Forming: Wet Die

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load		Fiber Vol (%)	Material Cross Section Area		Calculated Tensile Strength		Calculated Modulus	
			(lb)	(N)		($x10^{-5}in^2$)	($x10^{-4}cm^2$)	($x10^3psi$)	($x10^2MN/m^2$)	($x10^6psi$)	($x10^4MN/m^2$)
1	0.0365	0.0524	6.1	27.1	66	5.23	3.37	117	8.1	28	19.3
2	0.0365	0.0524	5.9	26.2	66	5.23	3.37	113	7.8	38	26.2
3	0.0365	0.0524	6.1	27.1	66	5.23	3.37	117	8.1	36	24.8
4	0.0365	0.0524	5.9	26.2	66	5.23	3.37	113	7.8	36	24.8

SERIES F Material: R-1-50/Highly Advanced Furfuryl Alcohol Forming: Mold

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load		Fiber Vol (%)	Material Cross Section Area		Calculated Tensile Strength		Calculated Modulus	
			(lb)	(N)		($x10^{-5}in^2$)	($x10^{-4}cm^2$)	($x10^3psi$)	($x10^2MN/m^2$)	($x10^6psi$)	($x10^4MN/m^2$)
1	0.0365	0.0581	6.9	30.5	60	5.84	3.77	118	8.1	30	20.7
3	0.0365	0.0594	6.1	27.1	58	5.97	3.85	102	7.0	30	20.7
4	0.0365	0.0581	7.5	33.3	60	5.84	3.77	129	8.9	36	24.8
5	0.0365	0.0559	6.9	30.5	62	5.62	3.62	123	8.5	30	20.7
6	0.0365	0.0508	6.4	28.4	69	5.05	3.25	127	8.8	37	25.3
7	0.0365	0.0603	7.0	31.1	54	6.42	4.14	109	7.5	29	20.0
8	0.0365	0.0645	7.1	31.6	53	6.57	4.23	108	7.5	35	24.1

TABLE B (Continued)

SERIES G

Material: R-1-50/Highly Advanced
Furfuryl Alcohol
(Repeat of Series F at Higher Fiber Volume)

Forming: Mold

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lb)	Breaking Load (N)	Fiber Vol (%)	Material Cross Section Area ($x10^{-5} in^2$)	Material Cross Section Area ($x10^{-4} cm^2$)	Calculated Tensile Strength ($x10^3$ psi)	Calculated Tensile Strength ($x10^2 MN/m^2$)	Calculated Modulus ($x10^6$ psi)	Calculated Modulus ($x10^4 MN/m^2$)
1	0.0365	0.0503	5.3	23.1	70	4.99	3.22	104	7.2	36	24.8
2	0.0365	0.0503	6.5	28.9	70	4.99	3.22	130	9.0	37	25.3
3	0.0365	0.0507	4.8	21.3	69	5.05	3.25	95	6.6	32	22.1
4	0.0365	0.0474	5.7	25.3	75	4.64	3.01	123	8.5	38	26.2
5	0.0365	0.0507	6.0	26.7	69	5.05	3.25	119	8.2	34	23.4
6	0.0365	0.0500	6.0	26.7	70	4.96	3.20	123	8.5	36	24.8
7	0.0365	0.0513	5.7	25.3	68	5.10	3.29	112	7.7	34	23.4
8	0.0365	0.0510	4.8	21.3	69	5.07	3.27	95	6.6	33	22.7
10	0.0365	0.0494	5.7	25.3	71	4.90	3.16	116	8.0	36	24.8
12	0.0365	0.0497	4.8	21.3	71	4.87	3.14	99	6.8	36	24.8

SERIES L

Material: P-1/High Advanced
Furfuryl Alcohol

Forming: Mold

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lb)	Breaking Load (N)	Fiber Vol (%)	Material Cross Section Area ($x10^{-5} in^2$)	Material Cross Section Area ($x10^{-4} cm^2$)	Calculated Tensile Strength ($x10^3$ psi)	Calculated Tensile Strength ($x10^2 MN/m^2$)	Calculated Modulus ($x10^6$ psi)	Calculated Modulus ($x10^4 MN/m^2$)
1	0.0485	0.0595	8.9	39.6	76	5.08	3.28	175	12.1	54	37.9
2	0.0485	0.0595	8.3	36.9	76	5.08	3.28	163	11.2	38	26.2
3	0.0455	0.0685	9.2	40.8	59	6.17	3.98	149	10.3	38	26.2
4	0.0455	0.0672	8.5	37.8	61	6.03	3.89	141	9.7	--	----
5	0.0497	0.0853	9.5	42.2	50	7.90	5.09	120	8.3	31	21.4
6	0.0497	0.0879	10.3	45.8	49	8.18	5.27	126	8.7	28	19.3

SERIES M

Material: P-1/Highly Advanced
Furfuryl Alcohol
(Repeat of Series L at Higher Fiber Volume)

Forming: Mold

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lb)	Breaking Load (N)	Fiber Vol (%)	Material Cross Section Area ($x10^{-5} in^2$)	Material Cross Section Area ($x10^{-4} cm^2$)	Calculated Tensile Strength ($x10^3$ psi)	Calculated Tensile Strength ($x10^2 MN/m^2$)	Calculated Modulus ($x10^6$ psi)	Calculated Modulus ($x10^4 MN/m^2$)
1	0.0436	0.0582	5.5	24.4	68	5.08	3.28	108	7.5	30	20.7
2	0.0436	0.0583	7.7	34.2	68	5.08	3.28	152	10.5	38	26.2
3	0.0430	0.0520	7.4	32.9	78	4.43	2.86	167	11.5	45	31.0
4	0.0430	0.0520	6.7	29.8	78	4.43	2.86	151	10.4	35	24.1
5	0.0437	0.0520	7.3	32.4	79	4.40	2.84	166	11.5	--	----

TABLE B (Continued)

<u>SERIES R</u> Material: P-II/Highly Advanced Furfuryl Alcohol Forming: Mold

Test No.	Fiber Wt (gm/m)	Pyrol Wt (gm/m)	Breaking Load (lb)	Breaking Load (N)	Fiber Vol (%)	Material Cross Section Area ($x10^{-5} in^2$)	Material Cross Section Area ($x10^{-4} cm^2$)	Calculated Tensile Strength ($x10^3$ psi)	Calculated Tensile Strength ($x10^2 MN/m^2$)	Calculated Modulus ($x10^6$ psi	Calculated Modulus ($x10^4 MN/m^2$)
1	0.0397	0.0526	2.7	12.0	71	4.96	3.20	54	3.7	24	16.5
2	0.0397	0.0526	1.9	8.5	71	4.96	3.20	38	2.6	26	17.9
4	0.0378	0.0452	2.6	11.6	80	4.18	2.70	62	4.3	28	19.3
5	0.0378	0.0452	2.5	11.1	80	4.18	2.70	60	4.1	31	21.4
6	0.0410	0.0530	2.3	10.4	74	4.96	3.20	46	3.2	25	17.2
<u>SERIES U</u>	Material: R-1-50/PI								Forming: Mold		
1	0.0365	0.0568	2.6	11.6	60	5.75	3.71	39	2.7	27	18.6
2	0.0365	0.0591	1.1	4.9	58	6.02	3.88	18	1.2	23	15.9
3	0.0365	0.0526	3.8	16.9	66	5.29	3.41	72	5.0	34	23.4
4	0.0365	0.0516	4.9	21.8	70	5.18	3.34	95	6.6	36	24.8
5	0.0365	0.0575	5.4	24.0	60	5.83	3.76	93	6.4	34	23.4
<u>SERIES X</u>	Material: R-1-50/PQ								Forming: Mold		
1	0.0365	0.0526	3.4	15.1	67	5.22	3.36	65	4.5	30	20.7
2	0.0365	0.0526	3.0	13.3	67	5.22	3.36	57	3.9	32	22.0
3	0.0365	0.0543	2.4	10.7	64	5.40	3.48	64	4.4	--	----
4	0.0365	0.0475	3.3	14.7	75	4.67	3.01	71	4.9	38	26.2
5	0.0365	0.0536	3.8	16.9	65	5.32	3.43	71	4.9	30	20.7

SAMPLE CALCULATIONS

The tensile strength modulus and reinforcing efficiency calculations were based on the fiber and carbon binder densities. Fiber densities were obtained from vendor data and binder densities from the "sink or float" determinations in blends of isopropyl alcohol and dibromomethane.

The densities used for the fibers were

R-I-50 (Thornel 50)	1.63 gm/cm^3
P-I (Modmor Type I)	1.74 gm/cm^3
P-II (Modmor Type II)	1.94 gm/cm^3

The densities used for carbon binders were

Furfuryl alcohol precursor	1.41
P-I (polyimide) precursor	1.38
PQ (polyquinoxaline) precursor	1.44

The small changes in densities of the P-I and PQ precursor carbon from the reimpregnation with furfuryl alcohol were ignored. Also, the void content was not measured.

Using Series A, Test No. 1 as an example, the calculations were as follows:

1. Fiber Cross Sectional Area (A_f) = Fiber Wt. x $\frac{1}{\text{Fiber Density}}$

$$A_f = .0365 \text{ gm/m} \times \frac{1}{1.63 \text{ gm/cm}^3} \times \frac{1}{100 \text{ cm/gm}} = 2.24 \times 10^{-4} \text{ cm}^2$$

$$A_f = 2.24 \times 10^{-4} \text{ cm}^2 \times \frac{1}{6.45 \text{ cm}^2/\text{in}^2} = 3.47 \times 10^{-5} \text{ in}^2$$

2. Binder Cross Sectional Area (A_b) = (Filament wt) - (Fiber wt) x $\frac{1}{\text{Binder Density}}$

$$A_b = (.0484 - .0365) \text{ gm/m} \times \frac{1}{1.41 \text{ gm/cm}^3} \times \frac{1}{1.00 \text{ cm/gm}} = .845 \times 10^{-4} \text{ cm}^2$$

$$A_b = .845 \times 10^{-4} \text{ cm}^2 \times \frac{1}{6.45 \text{ cm}^2/\text{in}^2} = 1.31 \times 10^{-5} \text{ in}^2$$

3. Filament Cross Section (A_F) = $A_f + A_b$

$$A_F = (2.24 + 8.45) \times 10^{-4}\ \text{cm}^2 = 3.09 \times 10^{-4}\ \text{cm}^2$$

$$A_F = 3.47 \times 1.31 = 4.78 \times 10^{-5}\ \text{in}^2$$

4. Normalized Tensile Strength = Breaking Load x $\frac{1}{A_f}$

$$\text{Normalized Tensile Strength} = 5.2\ \text{lbs} \times \frac{1}{3.47 \times 10^{-5}\ \text{in}^2}$$

$$\text{Normalize Tensile Strength} = 149 \times 10^3\ \text{psi}$$

5. Reinforcing Efficiency = Normalized Tensile Strength x $\frac{1}{\text{Vendor Tensile Strength}}$

$$\text{Reinforcing Efficiency} = \left(\frac{149}{285}\right) \times 10^3\ \text{psi} \times 100$$

$$\text{Reinforcing Efficiency} = 52\%$$

6. Calculated Tensile Strength = Breaking Load x $\frac{1}{A_F}$

$$\text{Calculated Tensile Strength} = 5.2\ \text{lbs} \times \frac{1}{4.78} \times 10^{-5}\ \text{in}^2$$

$$\text{Calculated Tensile Strength} = 109 \times 10^3\ \text{psi}$$