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NASA Contractor Report 172568

DEVELOPMENT OF AN IMPACT- AND SOLVENT-RESISTANT THERMOPLASTIC COMPOSITE MATRIX — PHASE III

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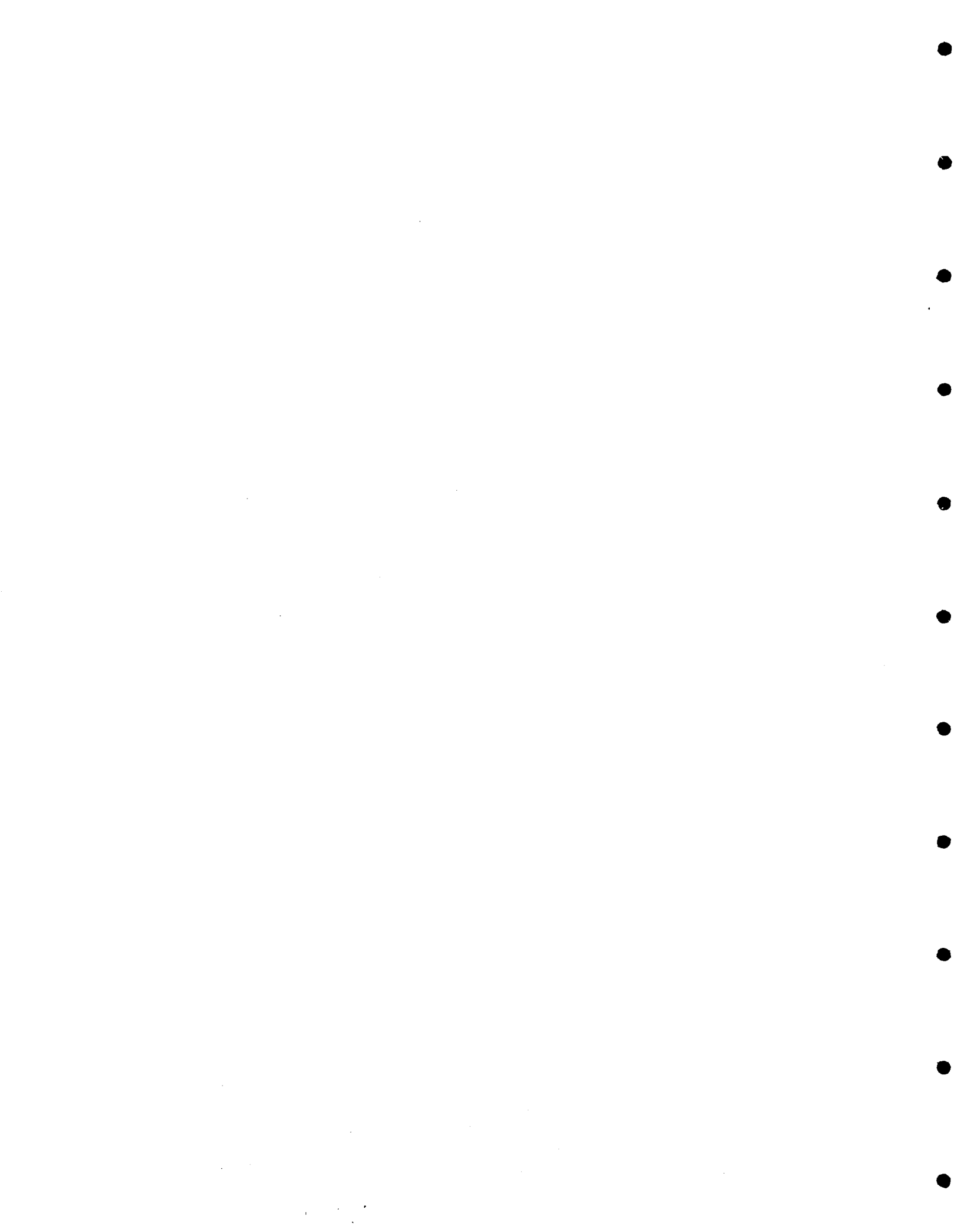C. B. Delano and C. J. Kiskiras
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FOREWORD

This report was prepared by Acurex Corporation for the National Aeronautics and Space Administration, Langley Research Center, under contract NAS1-16808. The work was conducted from September 1983 to January 1985. Use of commercial products or names in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied by the National Aeronautics and Space Administration.

Future aerospace vehicles are being designed for performance requirements that require graphite composites with improved impact resistance. Thermoplastic resins provide composites with improved impact resistance; however, the solvent resistance of most thermoplastics is poor. Program efforts were diverted toward fabrication of high-quality composites from a solvent-resistant thermoplastic polyimide developed during prior efforts.

Mr. Paul Hergenrother was the NASA Technical Monitor. The Materials Development Department was responsible for the work performed on the program. Mr. C. B. Delano was the Program Manager and Mr. C. J. Kiskiras provided technical assistance.

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SUMMARY

This 15-month follow-on program addressed characterization of the polyimide from 3,3',4,4'-benzophenonetetracarboxylic dianhydride with 1,6-hexanediamine and m-phenylenediamine. Methods to produce carbon fiber prepregs which would produce high quality composites received the most attention. The polyimide was selected from the initial 24-month technical effort for its solvent resistance and initial composite properties.

In the first months of the follow-on program low solids content cresol solutions of the polyimide did not provide complete impregnation of the fiber bundles. However, the interply resin was void free. The molecular weight of the polyimide was reduced by the use of monomers and prepolymers to produce 50 plus percent solids impregnating varnishes which gave excellent fiber bundle impregnation. With the fiber bundles filled, the resin content at the prepregs surface was reduced and high pressure molding of such prepregs did not always produce void-free composites. Voids were most evident in the interply regions suggesting need for more resin on the prepreg surface. It was concluded that high fiber volume, thermoplastic prepregs for use by the aerospace community should be perfected, i.e., completely smooth and dense.

It was established that conditions existed for production of smooth and dense prepregs using high pressures (34.5 MPa). A large portion of the effort investigated methods to produce prepregs which would be amenable to use of commercial prepregging equipment. Numerous attempts to produce the prepreg at

atmospheric pressure with varying thermal, squeegeeing, and smoothing schedules invariably led to producing a high melt viscosity in the varnish which after final volatile removal required high pressures for final perfecting of the prepreg. Processing the prepregs under vacuum with heat changes the balance between rate of volatile removal and rate of molecular weight growth and perfected prepregs were produced at lower pressures. Varnish skinning was also eliminated with vacuum treatment.

The need to use the preimidized aliphatic diamine prepolymer in prepregging varnishes was also established to reduce the moisture sensitivity of the prepregs.

The melt viscosity requirements of 100 percent solids neat resins to produce perfected prepregs needs additional study. Uncontrolled molecular weight growth in polymers such as occurs in the condensation polyimides will not be amenable to reproducible low-pressure composite processing. Injection moldable thermoplastics have controlled flow properties.

The selected polyimide neat resin is moldable at 0.69 MPa and temperatures as low as 260°C. However, increasing the molding temperature to 391°C does not decrease its melt viscosity. This phenomenon may be related to the same mechanism which produces the solvent resistance of the resin.

SECTION 1

INTRODUCTION

This report describes a 15-month effort conducted in a follow-on
program to develop improved thermoplastic resins for application in composite
structures for aerospace vehicles. Section 1.1 decribes the advantages
visualized for such a system, Section 1.2 briefly abstracts prior efforts,[1]
and Section 1.3 describes our approach to the follow-on efforts.

1.1   BACKGROUND

The successful development of impact- and solvent-resistant
thermoplastic systems for glass and graphite composites is particularly
attractive from the standpoint of their low-cost, streamline
manufacturability. Hypothetically, thermoplastics only require simple heating
and cooling cycles for component manufacture, whereas thermosets require more
precise, and possibly extended, heating schedules which must be consistent
with the cure chemistry.

Very high modulus (matrix properties) and crosslink density (solvent
resistance) are the excellent features of thermosets, which currently make
them the preferred matrices for graphite composites. Furthermore, since the
B-staged resins are liquids, excellent fiber collimation is achievable in the
prepregs. The impact response of graphite composites to low-speed impact has
been of concern for a number of years. Kevlar, glass, and other fibers are
used with graphite fibers to provide more impact-resistant composites. Such

"hybrids" involve loss of initial mechanical properties (modulus, compressive strength) to provide improved impact properties. Thermoplastics, on the other hand, offer impact resistance not attainable with conventional thermosets.

Aircraft design requires lifetime prediction of their components. Any material which exhibits environmental degradation will compromise the design safety margins for the selected material. Conventional thermosets absorb moisture which lowers their performance, especially at elevated temperatures.

The sensitivity of existing thermoplastics to aircraft fluids and other solvents preempts their serious consideration in aircraft components. This is the basic reason that Acurex proposed insolubility in aircraft solvents as the starting point for the program effort. Exposure to fuel, deicing fluids, and hydraulic fluids are serious concerns.

1.2   PRIOR EFFORTS

With solvent resistance tests conducted on the prior efforts[1] (under stress), the aliphatic-aromatic polyimides showed outstanding promise in view of the state-of-the-art thermoplastic polymers, particularly their resistance to halogenated solvents. While this feature is not unusual for aromatic polyimides, the observed solvent resistance in combination with good moldability of the aliphatic-aromatic polyimides is unique. Polyimides from both pyromellitic (PMDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydrides (BTDA) showed promise. The polyimide from BTDA with 1,6-hexanediamine (HDA) and m-phenylenediamine (m-PDA) was selected as the best candidate for the follow-on effort. It should be noted that this selection was based on a number of factors which are consistent with current requirements of composite resins.

The composite properties which might be obtained from the PMDA-based polyimides are not well known. Molded samples of these resins show the

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unusual ability to support a 450-psi compressive load at temperatures close to their molding temperatures. Differential scanning calorimetric (DSC) measurements suggested that crystalline polymers were obtained, which was confirmed by NASA-Langley personnel with X-ray analysis of the polyimides from PMDA with 1,8-octanediamine and 1,12-dodecanediamine. Both were determined to be highly crystalline. These thermally crystallizable polyimides showed remarkably low weight gains after 24 hr water boil (1,8-octanediamine = 0.2 percent and 1,12-dodecanediamine = 0.0 percent).

1.3   PRESENT EFFORTS

Previous Acurex efforts suggested that low solids content varnishes of polyphenylquinoxaline and polysulfone can be used to prepare carbon fiber prepregs and composites. Although this approach also produces composites from the selected polyimide, fiber bundle impregnation is incomplete and voids are found in the fiber bundles.[1] No voids are observed in the interply resin when the composites are processed at high pressures.

This prompted investigation of higher solids content varnishes at the beginning of the follow-on efforts. This approach which requires that the monomers be unreacted or only partially reacted appears to be successful in completing the inpregnation of the fiber bundles. However, as resin is successfully introduced into the fiber bundles, less interply resin is available for flow in the interply regions to make that region void free.

The basic principle outlined above is seen to be operative throughout this report, and composites with no or low void contents are not easily produced. The need for very smooth completely dense prepregs and/or higher resin flow properties is indicated.

An assumption was made that use of higher temperatures would be beneficial to the melt flow properties of the selected high molecular weight

polyimide based on the behavior of other amorphous thermoplastics. It was visualized that commercial prepreg equipment capable of high temperature processing would be suitable or could be modified to produce high quality thermoplastic prepregs. This may be readily achieved for low fiber volume prepregs particularly with the resin applied in steps. However, high fiber volume thermoplastic prepregs production may require the use of high pressure, particularly with woven fabrics.

Investigation of copolymers from PMDA and BTDA with HDA and 1,8-octanediamine were also planned for this follow-on effort.

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SECTION 2

OBJECTIVE

The overall objective of this program is the development of new thermoplastic laminating resin(s) that can be used with glass or graphite filament reinforcement to provide impact- and solvent-resistant composites for potential use on aerospace vehicles. These composites must have mechanical properties equivalent to state-of-the-art 177°C (350°F) curing epoxy systems. Although several routes can be pursued to improve the impact strength of composites (such as increasing the strain-to-failure capability of the reinforcement) this effort specifically pertains to resin development. Even though the tensile strength and tensile modulus of the reinforcement are considered to be the dominant contributors to impact strength of composites, the matrix also plays an important role by transferring strength and dissipating stress.

Target properties for the polymers are listed below.

• Amenable to impregnation of a reinforcement using conventional equipment

• Long prepreg shelf life at ambient conditions (>6 months)

• Acceptable processibility (maximum curing temperature of 316°C (600°F), maximum curing pressure of 0.69 MPa (100 psi), maximum time at final temperature of 1 hr, insensitive to heatup rate, and no volatile evolution)

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- Thermoformability (thermoform flat-sheet stock to desired configurations at maximum temperature and pressure of 316°C and 0.69 MPa, respectively; ability to undergo thermoforming process twice)

- Acceptable mechanical properties over temperature range of -54° to 93°C (-65° to 200°F) after environmental exposure (humid aging and long-term aging at 93°C)

- Resistant to airplane fluids and solvents (under stress)

- Impact resistance and damage tolerance

SECTION 3

RESULTS AND DISCUSSION

This section has been divided into subsections which deal with different key aspects of the development effort. It was discovered through photomicroscopy at the beginning of this follow-on program that complete fiber bundle impregnation with low solids content, high viscosity resin varnishes would require special attention. The use of very high pressures did not complete the bundle impregnation with the high molecular weight polyimide. The need to complete bundle impregnation prior to attaining the high molecular weight polymer was firmly established. These efforts are described in Section 3.1, Initial Composite Efforts. This discussion sets the stage for the preparation of varnishes which are suitable for achieving fiber bundle impregnation. These efforts are described in Section 3.2, Polymer Synthesis. Characterization of the polymers is described in Section 3.3 and is followed by prepreg preparation in Section 3.4. Composite efforts are described in Section 3.5.

3.1   INITIAL COMPOSITE EFFORTS

Initial efforts focused on methods to obtain void-free 3000 filament count carbon fiber bundles with the polyimide from BTDA with HDA and m-PDA as the resin matrix. Motivation for these efforts was provided by the void contents calculated for composites fabricated from prepreg which had been prepared from a cresol varnish ($\leq$10 percent solids) of the high molecular

weight polyimide. Further discussion of these composites is provided in Section 3.5. Even with high-pressure (34.5 MPa (5000 psi)) processing, void contents in excess of 10 percent were calculated for such composites. Photomicrographs revealed essentially all of the void content to be in the fiber bundles with no voids in the resin encapsulating the fiber bundles. These results were described previously.[1]

The fabric selected for these investigations was a 24 x 23 eight-harness satin weave from Celion 3000. Due to fiber bundle crossovers, distortion by physical methods of the fiber bundles is arrested preventing spreading of the fiber bundles which can occur with unidirectional carbon fiber prepregs. Consequently, the prepregging varnish must penetrate the fiber bundles to wet out the individual filaments. It appeared obvious at the outset that impregnation with 100 percent solids low-viscosity resins (epoxies) would give the sought effect and addition of any quantity of solvent to the resin would be counterproductive, particularly if the resin varnish thickened or solidified with solvent loss. Increasing the solids content of the varnish appeared to be the best approach to maximizing the resin content of the fiber bundles and minimizing the voids created in the fiber bundles upon solvent removal.

Several attempts to employ partial drying cycles in combination with squeegeeing the prepreg prepared from the high molecular weight 13 percent solids cresol solution of the selected polyimide, although successful in reducing the void content of the composites (and fiber bundles), did not lead to total elimination of the fiber bundle voids.

We determined that higher solids content varnishes could be prepared by prepolymerization (and imidization) of the BTDA with the HDA and room temperature addition of a solution of m-PDA. Such varnishes were applied to

the fabric and the final polymerization conducted on the fabric. Both 25 and 50 percent solids content varnishes were applied to the fabric to prepare prepreg and composites for photomicrographic examination of the resin distribution in the fiber bundles. A distinctive improvement in the resin content and distribution in the fiber bundles was evident. However, voids were still observed in the fiber bundles of the 13.8 MPa (2000 psi) processed composites.

Photomicrographs of the composites from 25 and 50 percent solids content varnishes are shown in Figures 1 and 2. Examination of the 400x photomicrographs of the composite shown in Figures 1 and 2 reveals the voids in the fiber bundles. Clearly, the fiber bundles require a higher initial resin content than was obtained from the 50 percent solids varnish single pass, unsqueegeed prepreg. This is also qualitatively confirmed by the large quantity of resin seen in the composites which is outside of the fiber bundles. Calculated void contents of the composites from the 25 and 50 percent solids content varnishes were 3.6 and 2.3 percent, respectively. These void contents are also about one-half of those obtained from our best attempts from the 13 percent solids varnish (see Section 3.5).

As clearly implied by both photomicrographs, further application of even higher processing pressures will not eliminate the fiber bundles void content for two reasons: first, voids are found inside of filament clusters which would resist further collapse, and, second, the voids appear to have a tubular or cylindrical shape compared to a spherical geometry. Note the long black areas in the 0° fiber bundles in the 100x frames of Figures 1 and 2. Resin flow into such a "structural" hollow cylinder is difficult to imagine compared to simple collapse of a small spherical void.

50x   100x   400x
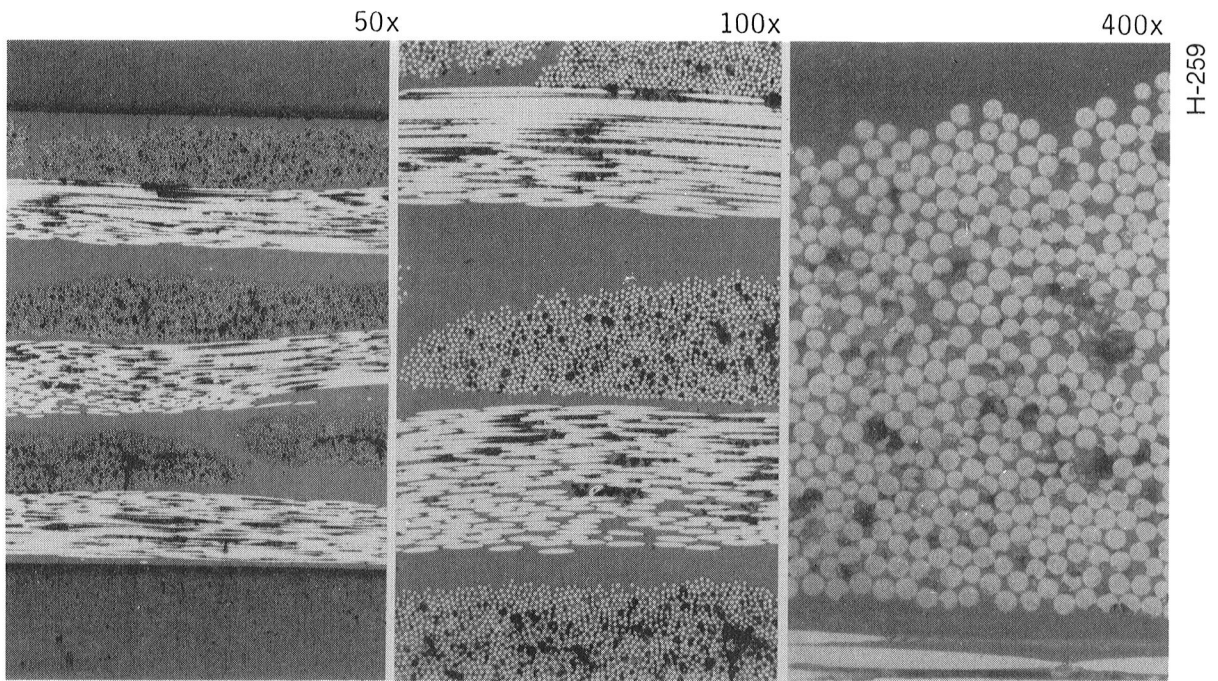
Figure 1.   Composite from 25 percent polyimide varnish

50x   100x   400x
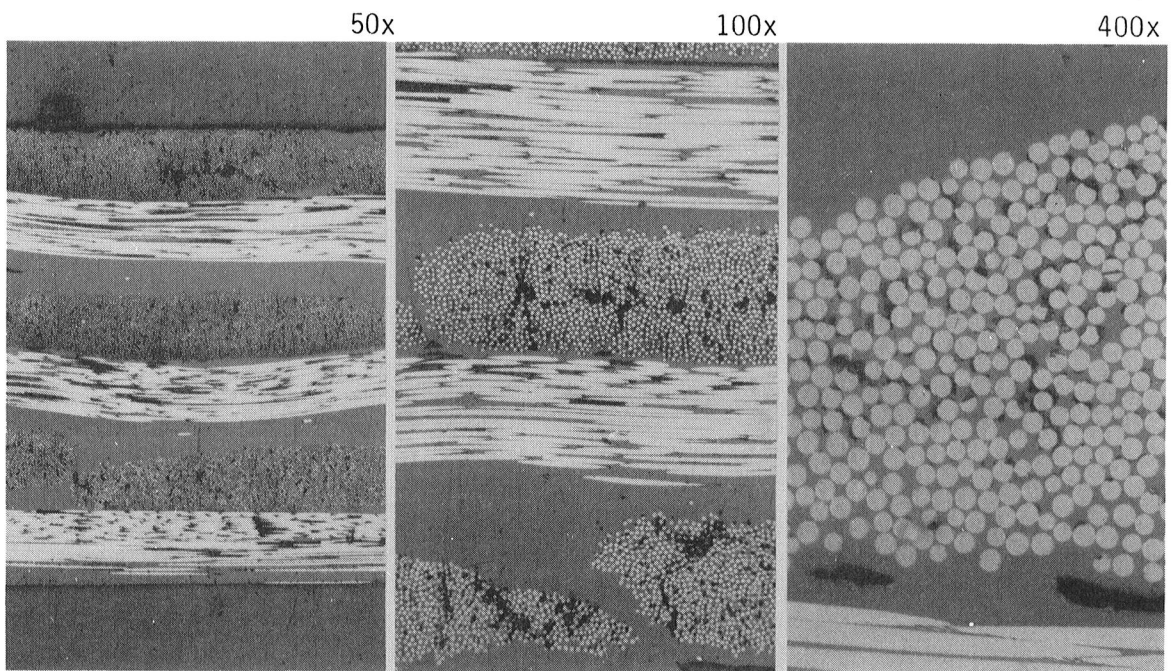
Figure 2.   Composite from 50 percent polyimide varnish

Preparation of prepreg from a PMR-type varnish of the monomers at 50 percent solids lead to a composite in which the fiber bundles were completely free of voids and had sufficient resin to separate the individual carbon filaments in the fiber bundles. Photomicrographs of this composite are provided in Figure 3. This same result was obtained on an eight-harness satin weave carbon fiber composite by Phillips Petroleum with their Ryton resin. Photomicrographs of this composite are provided in Figure 4. The quantity of resin which is outside of the fiber bundles in these two composites is significantly reduced compared to the composites shown in Figures 1 and 2.

The monomer solution was prepared by suspension of the BTDA in methanol at room temperature, followed by addition of the aliphatic amine which led to a clear solution, and finally followed by addition of m-PDA dissolved in sufficient cresol to provide a 50 percent solids solution upon removal of the methanol under high vacuum. Dilution of this varnish to 10 percent solids content and polymerization of the monomers for 1 hr at 180°C gave a new type of end product. The solution was thick, suggesting the presence high molecular weight soluble polymer, but contained a new type of opacity.

Although the excellent fiber bundle impregnation by the PMR approach suggested use of a low viscosity, high solids content varnish to achieve that result, it was not clear that varnish viscosity was the single controlling factor in preparation of well-impregnated fiber bundles. It was clear that at least one approach did exist to impregnate geometrically restricted fiber bundles such as seen in woven fabrics. However, the success of the PMR approach raised more questions such as whether alcohol or solvent addition (other than cresol) is also beneficial in the preparation of quality prepregs from thicker, lower solids content cresol varnishes of higher molecular weight prepolymers.

50x   100x   400x
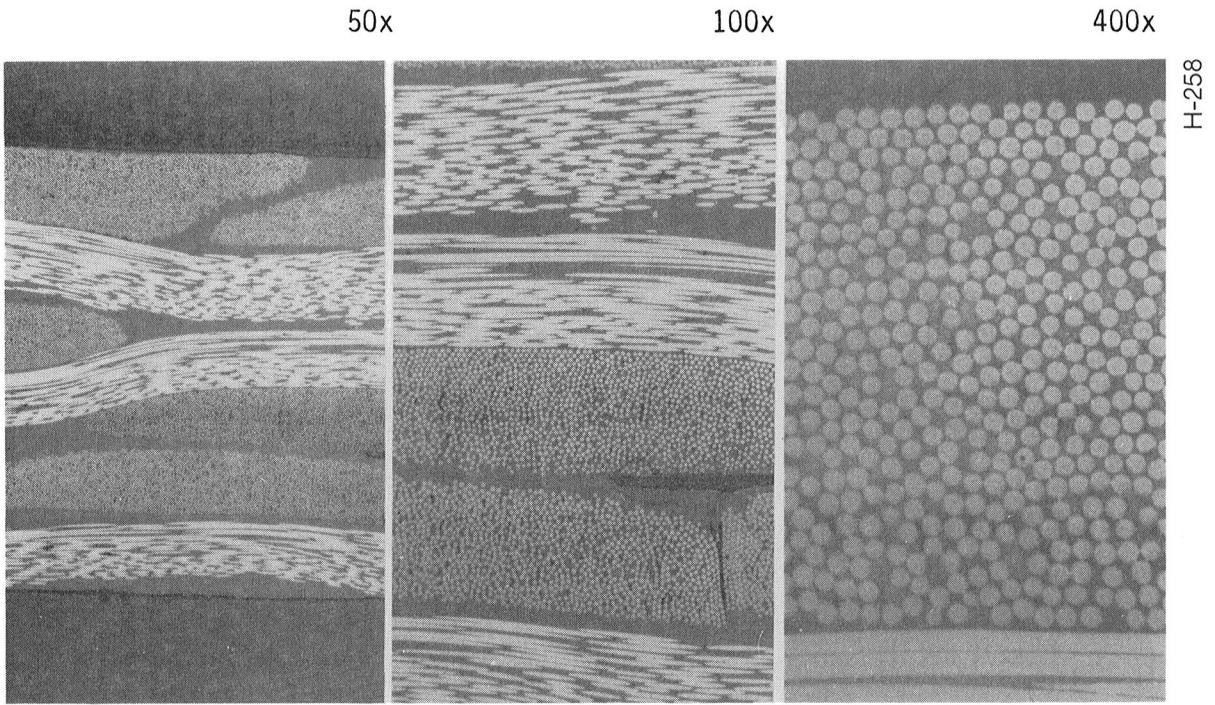
Figure 3. Composite from 50 percent monomer varnish

50x   100x   400x
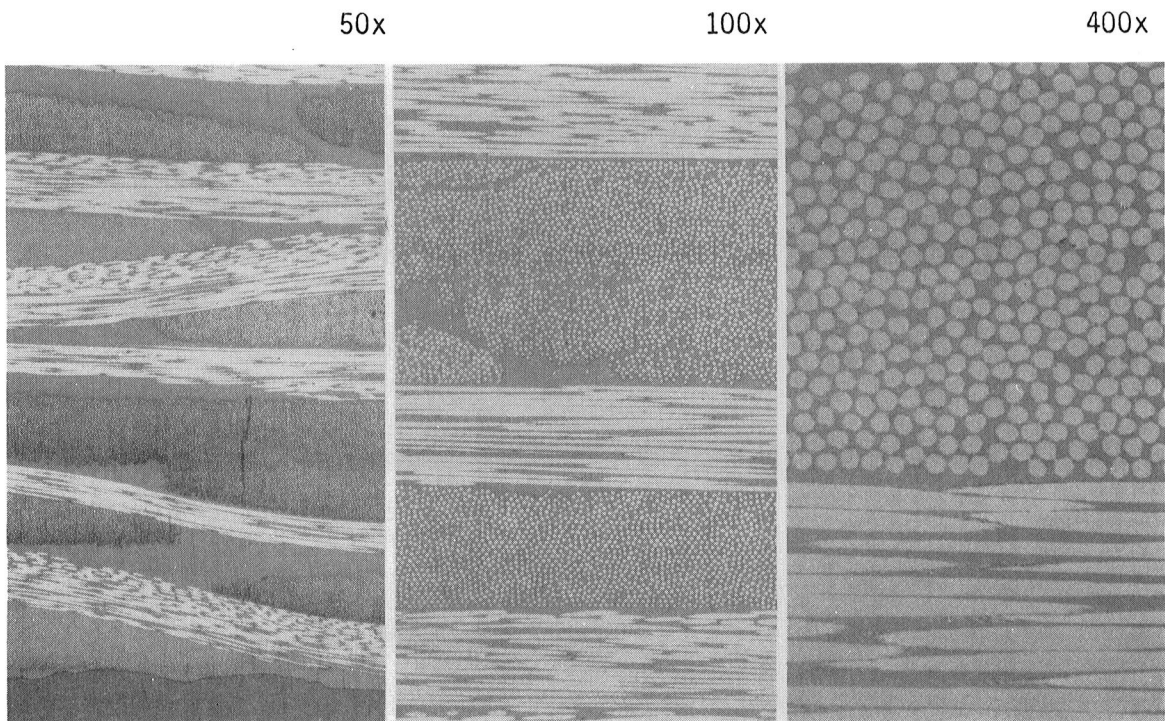
Figure 4. Ryton composite

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3.2 POLYMER SYNTHESIS

Several approaches to preparing the polyimide from BTDA with HDA and m-PDA were investigated. Methods to prepare the cresol soluble high molecular weight polyimide at low solids contents were previously described.[1] Addition of m-PDA to the preimidized BTDA/HDA prepolymer in cresol prior to final polymerization was also found to be successful. Present program effects investigated composites prepared from both types of varnishes as well as alcohol PMR-type condensation of the monomers. The synthetic efforts were driven by the quality of the prepregs and composites obtained.

The methanol PMR approach to aromatic polymides from BTDA is well documented whereas this approach to aliphatic polymides produced a crosslinked product in our hands.[1] Addition of cresol to such varnishes appears to facilitate successful polymerization of the HDA and m-PDA with the dimethylester of BTDA to achieve tough polymers. A key requirement in the attainment of tough polymers (with cresol) appears to be the heating schedule used for the polymerization.

Of the three types of varnishes, only the varnishes from addition of a cresol solution of m-PDA to a cresol solution of the preimidized aliphatic prepolymer and the alcohol PMR can be prepared at greater than 50 percent solids due to the high molecular weight of the fully imidized polyimide.

The polyimide prepared via 180°C condensation in cresol or via the cresol-modified methanol PMR approach differ little with respect to moldability and Tg. The polyimide prepared via the latter method is not soluble in sulfuric acid (swells) suggesting that crosslinking has occurred.

Consequently efforts focused on attempts to prepare a high solids content clear varnish of the partially reacted monomers with no methanol to obtain the noncrosslinked product. These efforts are summarized on the following page.

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- Overnight reaction at room temperature of HDA predissolved in acetone and 50/50 mixtures of acetone/cresol, isopropanol/cresol, and acetone/dimethylformamide with powdered BTDA did not produce clear solutions at 50 percent solids. Clear solutions were obtained with the acetone/dimethylformamide solvent mixture at lower solids concentrations.

- A 25 percent solids concentration of the preimidized form at 180°C HDA/BTDA prepolymer in cresol is successfully diluted to 13 percent solids with toluene and methylene chloride as well as other halogenated solvents. Methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, tetrahydrofuran, and ethyl acetate precipitate the polymer with the same dilution factor.

- Numerous attempts were made to prepare 50 percent solids, clear cresol varnishes of all three monomers diluted with toluene or 1,1,1-trichloroethane. If the initial reaction conditions are carried out below about 60°C, toluene is not compatible with the partially reacted monomer mixtures. If initial reaction is carried out above about 100°C, toluene is compatible with the prepolymers formed. Thus BTDA, HDA, and cresol were reacted together for 1/2 hr at 130°C and the cresol solution of m-PDA was added at 100°C. After the mixture cleared at 120°C, it was cooled to room temperature. Toluene was used to dilute the cresol varnish at room temperature to give the following composition: 48 percent prepolymer, 27 percent cresol, and 24 percent toluene.

- The linear fully imidized polyimide prepared via 180°C condensation in cresol is soluble in a 50/50 mixture of cresol/1,1,1-trichloro-ethane but not a 30/50 mixture of those solvents

Thus low relatively molecular weight, high solids content varnishes containing no methanol can be prepared from the monomers if sufficient condensation has taken place. This is probably related to the quantity of acid-amine salt which has been converted to amic acid and/or imide. The m-PDA requires dissolution in cresol before its addition to cresol solutions of HDA/BTDA prepolymers. All attempts to add the aromatic diamine as a solid to high solids content varnishes of HDA/BTDA prepolymers lead to gel and/or lump formation.

Even though continued efforts with the nonmethanol-containing prepregging varnish could have resulted in obtaining the linear polyimide as the composite matrix, demonstration of complete fiber bundle impregnation discussed in Section 3.1 by the cresol-modified methanol varnish suggested that the PMR approach to the resin should be investigated first.

As discussed in the next section, heating varnishes of partially reacted monomers leads to foam due to loss of volatile material. Since part of the foaming tendency can be attributed to loss of methanol from the varnish, glycol was briefly investigated as a substitute for the methanol. A cresol-free, 60 percent solids clear varnish was readily prepared from 8g of BTDA condensed from 4g of glycol at 135°C followed by addition of 4.2g of a glycol solution of the stoichiometric amines at 110°C. The varnish was thick but clear at room temperature. Brief investigations of the polymerization of the glycol solution of the monomers/prereacted monomers led to obtaining opaque semi-tough materials. Addition of cresol to the glycol PMR varnish at 13 and 20 percent by weight lead to opaque, semi-tough and clear, tough polymers respectively after 1 hr treatment at 180°C. Significant improvements in the foaming tendency of the varnish were not obtained. The foaming

tendency was approximately the same as the cresol-modified methanol PMR varnish.

Table 1 provides a log of the varnishes which were prepared and tested for their suitability to prepare the thermoplastic prepreg. The majority of staging and densification investigations were with prepreg prepared from resin batch 78-102 (No. 8). Due to opacity formation in the resin-rich interbundle areas during prepreg staging, varnishes with lower water contents were prepared (Nos. 12 and 13). These varnishes are superior to the varnishes prepared with higher water contents. Much less foaming and no opacity is observed with their staging.

3.3 POLYMER CHARACTERIZATION

3.3.1 Mechanical Properties

Mechanical property testing of the molded (1 hr at 316°C (600°F)) high molecular weight polyimide was carried out. Results obtained on the tensile specimens (ASTM D638-80) and the compression specimens (ASTM D6950-80) are provided in Table 2. All specimens were strain gauged.

The strength and modulus values obtained on the neat resin are good in view of its principal mission as a matrix resin. In view of other thermoplastics, the 25 ksi compressive yield strength at room temperature is excellent. Further, the expected distinction between the resin and thermosets in the compression tests was seen in the failure modes: thermosets usually rupture giving a value designated as the compressive strength in the D695 specification, whereas thermoplastics typically give a yielding failure designated as the compressive yield strength.

The elevated temperature compressive yield strengths (and strains) may be low due to specimen end failures. However, as discussed by Kinlock and Young,[2] observation of a diagonal neck in the elevated temperature tensile

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Table 1a. Varnishes used to prepare prepreg

Table Number	Notebook Reference	Approach	Reaction Size, g	Composition (weight percent)				Comments
				Polymer	Cresol	Alcohol	Imidization Water	
1	78-12	BTDA dissolved in cresol HDA added at RT 1 hr at 180°C Add m-PDA 1 hr at 180°C	248	12.0	88.0	0.0	0.0	I.V. of 1.04 dl/g Composites 78-18A and 18B and 78-28A and 28B
2	78-25	BTDA dissolved in cresol HDA added at RT 1 hr at 180°C Add m-PDA at 80°C	10	25.5	72.2	0.0	2.3	Composite 78-31
3	78-31	Same as previous Vacuum strip	10	43.7	52.4	0.0	3.9	Composite 78-34
4	78-48	HDA dissolved in methanol Solid BTDA added Cresol solution of m-PDA added Vacuum strip	10	51.0	33.7	10.7	4.6	Composite 78-49
5	78-53	Same as 4	124	51.9	32.3	11.1	4.7	Composites 78-55, 78-64, and 78-65
6	78-84	BTDA dissolved in methanol Vacuum strip to honeylike consistency Add cresol solution of HDA and m-PDA Vacuum strip	496	52.3	24.4	18.5	4.7	Composites 68-86 and 78-90, prepreg all treated at 180°C to give foamed product

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Table 1b. Varnishes used to prepare prepreg

Table Number	Notebook Reference	Approach	Reaction size, g	Composition (weight percent)					Comments
				Polymer	Cresol	Alcohol	Glycol	Imidization Water	
7	78-96	50g aliquot of 78-84 Glycol added Vacuum strip	--	49.3	23.1	6.2	17.0	4.5	Prepreg looked promising for low-temperature staging, scaled up
8	78-102	Same as 6 Glycol added Vacuum strip	248	50.1	23.5	4.4	17.3	4.7	1 m^2 prepreg prepared, majority of prepreg investigations conducted with this prepreg
9	78-118	BTDA dissolved in methanol and cresol Methanol solution of HDA added Vacuum strip Cresol solution of mPDA added	248	56.7	29.3	8.9	0	5.1	0.3 m^2 prepreg prepared, does not consolidate like above product, toughest polymer obtained of all batches after 1 hr at 260°C treatment
10	78-119	BTDA dissolved in methanol, cresol, and glycol Cresol solution of HDA added Vacuum strip Cresol solution of mPDA added	248	52.6	26.3	6.9	9.4	4.7	0.3 m^2 prepreg prepared, polymer very brittle after 1 hr at 260°C treatment
11	78-120	Same as 10 but with ethanol and no glycol	248	55.6	30.7	8.7	0	5.0	0.3 m^2 prepreg prepared, turns opaque rapidly with low-temperature staging
12	78-121	BTDA dissolved in ethanol and cresol Ethanol solution of HDA added Vacuum strip 30 min at 180°C, cool to 100°C Cresol solution of mPDA added	124	55.3	42.2-x	x	0	2.5	0.1 m^2 prepreg prepared
13	78-124	HDA dissolved in butanol and cresol BTDA powder added 60 min at 140°C, cool to 100°C Cresol solution of mPDA added	124	63.4	29.7-x	4 + x	0	2.9	0.1 m^2 prepreg prepared

Table 2. Neat resin mechanical properties

	Test Temperature, °C (°F)		
	Ambient	82 (180)	121 (250)
Tensile Properties[a]			
Tensile strength at yield, MPa (psi)	114 (16,500)	89.6 (13,000)	61.4 (9,810)
Elongation at yield (percent)	5.6	4.0[b]	3.4[b]
Modulus, MPa (psi)	3,340 (485,000)	2,550 (370,000)	1,990 (289,000)
Compressive Properties[a]			
Compressive yield strength, MPa (psi)	177 (25,700)	100 (14,500)	89.6 (13,000)
Compressive yield strain (percent)	8.0	4.0	4.7
Modulus, MPa (psi)	3,390 (492,000)	2,590 (376,000)	2,490 (361,000)
Poisson's ratio	0.40, 0.34	0.36, 0.38	0.38, 0.36

[a]Average of two specimens per test
[b]Elongation at break was about 10 percent, however, localized yielding occurred

specimens suggests that shear yielding occurred. Strength and yield strain reductions observed with elevated temperature testing can be in part explained by this mechanism, which is an intrinsic property of the polyimide.

Elimination of the end failures in compression testing may require a larger right cylinder with a smaller slenderness ratio or a different specimen geometry. The slenderness ratio of the right cylinders used for the compression tests was 10.3. Larger cylinders may also increase the precision of the Poisson ratio determination.

3.3.2 Foam Formation

The linear polymer when cast from cresol solution does not skin readily and foam-free films are produced by placing the varnish in a 180°C oven. The foaming in the cresol-modified methanol PMR solution appears to be due to a combination of its strong skinning tendency and loss of its cure volatiles.

Methods to reduce the resin foaming from the resin-rich areas in the PMR varnish prepregs were addressed briefly. After only a few experiments it became obvious that the rapid heatup to 180°C treatment given the prepreg was required to produce a clear, tough resin. Slow heatup reduces the quantity of foam produced whereas rapid heatup increases the quantity. Rapid heatup of the linear polyimide was found to be a requirement in Reference 1 to achieve a cresol soluble polymer. However, premature desolvation of the reactants prior to achieving reaction temperatures also appear to play a role in the need for rapid heatup of the prepreg.

The solvents and surfactants indicated in Table 3 were tested for their ability to modify the foaming behavior of the resin. Varnishes at room temperature were placed directly into a 180°C air-circulating oven.

Cresol and glycol were the only two additives that significantly modified the foaming characteristics of the varnish. Basically the foam's

Table 3. 1 hr at 180°C treatment of PMR varnish

Additive	Quantity Added (%)	Results
None	--	Tough foam
Cresol	13 and 23	Tough film from collapsed bubble
Glycol	13 and 23	Tough film from collapsed bubble
Cyclohexanol	13	Tough single bubble
Dioxane	13 and 23	Tough foam
Xylene	13	Tough foam
2-ethoxyethylether	13	Tough foam
2-pentanol	13	Tough foam
Cyclohexanone	13	Brittle film
Flourad FC-43	4 and 13	Tough foam
BYP-P104	4 and 13	Tough foam
L-534	4 and 13	Tough foam

cell size was increased by those solvents. Although subtle changes in surface tension may be occurring, dilution effects may also be important. Methanol and water can more readily escape the hot varnish at lower viscosities which are produced by the glycol and cresol additions.

3.3.3 TGA Curves

TGA curves for the linear polyimide, the glycol-cresol-modified methanol PMR, and the cresol-modified methanol PMR varnishes after polymerization and treatment for 3 hr at 246°C (vacuum) are given in Figure 5. The 5 to 6 percent at 450°C weight losses seen for the two PMR polymers seems most likely to be volatiles from further condensation. Briefly heating both PMR polymers to 316°C provided weight loss curves which are essentially superimposeable on the weight loss curve of the linear polymer.

3.4 PREPREG PREPARATION

After initial scouting experiments it became clear that the viscosity of the neat, high molecular weight polyimide was not sufficiently reduced at temperatures above Tg to provide for final densification of the prepreg or composites at low pressure, i.e., 0.69 MPa. Thus, 3, 9, and 60-min treatment of 50+ percent solids PMR varnishes at 180°C lead to prepreg which required high pressure processing to give minimum per ply thicknesses in the composite. Further, the PMR resin, unlike the fully imidized high molecular weight polymer produced foam with the rapid heatup to 180°C treatment. These efforts are described in Section 3.4.2.

The next efforts which are described in Section 3.4.3 addressed low-temperature staging of the PMR resin prepreg in combination with smoothing the prepregs with a hot doctor blade prior to final densification with high temperature and pressure treatments. Good quality prepregs were obtained, although resin distribution was not adequate to give uniform thickness
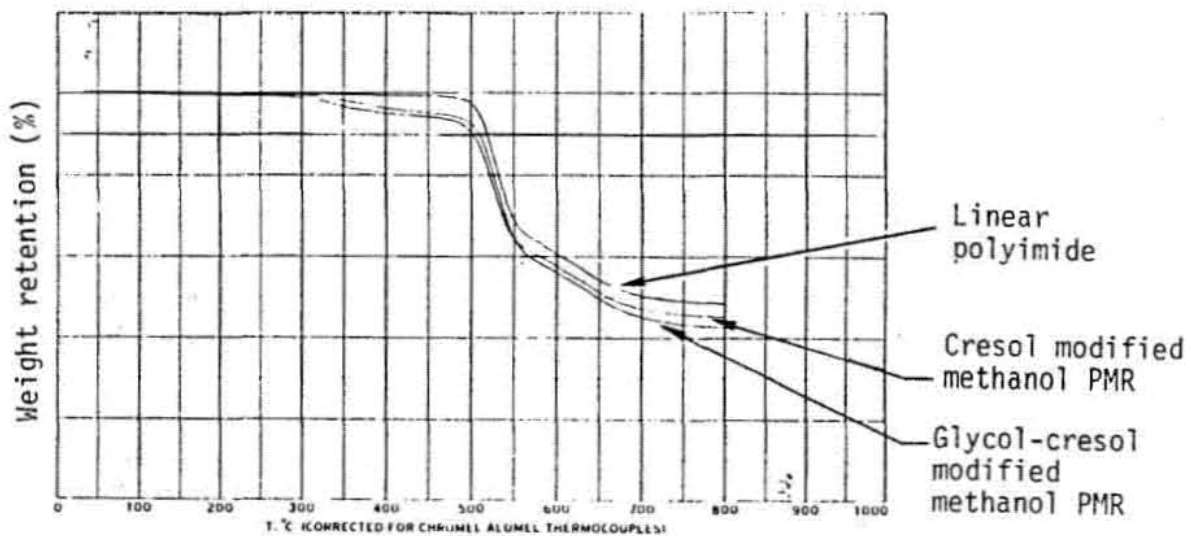
Figure 5. TGA curves of linear and PMR polyimides

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products. Further blade smoothing was incapable of producing completely dense prepreg since the pull force required to move the product under the blade became very high when only moderate pressures were applied to the blades. Powered rollers (i.e., calendaring) were not investigated.

Densification experiments demonstrated the need to address the resin distribution in the prepreg. These efforts are described in Section 3.4.4.

Nearly all of the densification experiments were conducted at 316°C since that upper temperature was specified as a program objective. Higher temperatures were briefly investigated in Section 3.4.5 and the melt viscosity of the selected polyimide was not reduced as expected by using higher molding temperatures. These efforts resulted in lowering our final processing temperatures to 260°C (500°F).

Methods to produce the prepregs at low pressures were then investigated and are described in Section 3.4.6. At this juncture, additional varnishes were prepared and prepregged only to discover that the varnishes were moisture sensitive. Unlike the 78-102 varnish which had been used in investigations up to that point in the program, low temperature staging produced opacity in the prepregs, particularly in the resin-rich areas of the prepregs. The varnish prepared from the preimidized HDA/BTDA prepolymer, which hypothetically contains only half of the imidization water, was found not to produce opacity with low temperature staging.

It was then determined that low pressure processing produces nearly completely dense prepregs if the molecular weight growth of the prepolymers is minimized (minimum heat) and the rate of volatile loss maximized (vacuum).

The required processing steps which have been established thus far for preparation of smooth prepreg with uniform resin distribution from the cresol-modified methanol PMR varnish are outlined below:

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Operation	Comments
1. Hot melt a film of the varnish onto nonporous glass-reinforced Teflon at about 100°C	A second sheet of nonporous glass-reinforced Teflon can also be used on the top of the varnish film to eliminate need for blade cleanup. The film is redoctored as many times as is required to achieve the sought areal weight by adjusting either speed, shims, or temperature.
2. Lay carbon fiber fabric onto Mylar maintaining the fabrics collimation (Kevlar tracers in the fabric are useful for this). Slowly apply varnish film on Teflon to the top of the fabric and hand press the varnish film into the fabric at room temperature.	Bundle impregnation not complete. Fabric size removal is a separate operation.
3. Complete bundle impregnation at elevated temperature (~120°C)	Squeegeeing required and/or bundles in a relaxed state will fill by capillary action with low viscosity varnishes
4. Smooth prepreg to constant thickness, i.e., steel roller with shims on each side of the prepreg. Shim thickness required is calculated in Table 4.	Smoothing at elevated temperatures required for most varnishes. Uniform resin distribution is achieved with careful smoothing.
5. Remove Mylar, replace with sheet of porous glass reinforced Teflon. Turn product over and remove nonporous glass-reinforced Teflon.	The porous glass reinforced Teflon is principally for prepreg handleability. When prepreg is tack free at elevated temperature it is no longer required.
6. Place prepreg horizontally in 100°C air-circulating oven with the porous glass-reinforced Teflon side down	Volatile loss from bottom of prepreg requires use of a shelf with a large open area. Vertical placement of prepreg can destroy uniform resin distribution. Very high temperature staging leads to foam formation and too rapid resin advancement.

Table 4. Relationship between varnish solids content and prepreg thickness[a]

Varnish Solids, Weight (%)	Weight Varnish Pickup On Prepreg (%)	Calculated Prepreg Volume Loss Remaining[b] (%)	Calculated Prepreg Thickness, mm (mils)[b,c]
100	38.0	0.0	0.376 (14.8)
90	40.5	6.3	0.399 (15.7)
80	43.4	13.3	0.432 (17.0)
70	46.7	20.7	0.472 (18.6)
65	48.5	24.6	0.498 (19.6)
60	50.5	28.8	0.526 (20.7)
55	52.7	33.2	0.561 (22.1)
50	55.1	37.8	0.602 (23.7)

[a]Calculated for final fiber volume of 55 percent in prepreg
[b]Assumes that the volatiles have density of 1.0 g/cc, the carbon fiber a density of 1.8 g/cc and the resin a density of 1.36 g/cc
[c]Assumes areal weight of carbon fiber is 0.0372 g/cm^2 and all shrinkage occurs through the prepregs thickness

Operation	Comments
7. Stage prepreg for X hours and smooth in press at 100°C and 100 psi or in vacuum bag at 100°C under full vacuum with cauls. With press smoothing nonporous Teflon is used. With vacuum bag smoothing porous Teflon with 116 E glass bleeder cloth is used.	Staging time prior to smoothing is critical and varnish dependent. Vacuum bag smoothing too soon will lead to resin bleed off. Staging too long leads to inability to smooth prepreg. Smoothing with heated doctor blades can lead to redistributing the resin.
8. Continue oven staging at 100°C until prepreg contains about 10 percent by weight remaining volatiles	0.5 hour at 260°C (500°F) used for volatile content determinations
9. Densify at high temperature (and pressures)	Conditions not established yet

Steps 1 through 7 outlined above appear to be minimum initial steps required to make smooth, completely dense prepregs without vacuum treatment of the prepreg as described in Section 3.4.6.

3.4.1 Coating Methods

Three techniques were employed to coat the carbon fabric with varnish. Low solid content varnishes were solution coated and dried between coats. High solid content varnishes were hot-melt coated directly into the fabric or made into a film of desired areal weight by coating onto Teflon and the film melted into the fabric.

3.4.2 Prepregs From In-Hot 180°C Treatment

Initially prepregs were hung vertically for 1 hr at 180°C in an air-circulating oven and finally treated overnight under high vacuum at 200°C to reduce the volatile content to less than 1 percent. Volatile contents were determined by 30 min treatment at 288°C (550°F) on a small sample cut from the prepreg. Resin foaming occurred from the resin-rich pockets on the prepreg during the first few minutes of the 180°C treatment.

Based on the foam inhibition produced with glycol, glycol was added to an aliquot of the cresol-modified methanol PMR varnish (78-96). 180°C treatment of 1g of this varnish modified the foaming behavior of the varnish and in the prepreg led to a large increase in the cell size of the foam produced.

A 5.2 cm × 5.2 cm (2 inch × 2 inch) × 7 ply graphite composite was fabricated from prepreg from the varnish cited above on sized removed 8-harness satin-weave graphite fabric. Prepreg treatment consisted of 1 hr at 180°C plus 16 hr at 200°C under high vacuum. The composite was molded at 316°C and 34.5 MPa (5000 psi) for 1 hr and gave a per-ply thickness of 0.391 mm (15.4 mils). This thickness corresponds to zero void content composite. It was concluded that polymers from the cresol modified and glycol-cresol modified methanol PMR varnishes were equivalent in moldability. One square meter of 24 × 23 8-harness satin-weave graphite fabric (Celion 3000, sized removed) was impregnated with the 78-102 varnish. Varnish pickup on the prepreg was at 54.2 percent by weight which, after cure, would provide a nominal resin content in the prepreg of 37 percent.

Attempts to advance the polymer and drive off the volatiles were carried out by in-hot treatment of the prepreg. Thus, a swatch of prepreg was inserted into a 180°C air-circulating oven for varying times. Three, 9- and 60-min treatments combined with postflattening efforts led to the per ply thicknesses (single ply) indicated in Table 5. We had originally planned to advance all of the prepreg for 1 hr at 180°C to achieve the high molecular weight resin in the prepreg. However, in view of the single ply thickness of 0.50 mm (19.5 mils) obtained on the 288°C, 34.5 MPa processed prepreg swatch, it became clear that we needed to rethink this approach. This swatch had a final resin content of 39 percent and the thickness calculated for a smooth,

Table 5. Prepreg staging at 180°C versus attainable thickness with pressure

Prepreg Treatment Time at 180°C (min)	Thickness, mm (mils) after 1 min Treatment at:						
	193°C 2.8 MPa	193°C 6.9 MPa	238°C 2.8 MPa	238°C 6.9 MPa	288°C 2.8 MPa	288°C 6.9 MPa	288°C 34.5 MPa
3	0.46 (18)[a]	0.41 (16)[a]	0.38 (15)[a]	0.37 (14.5)[a]	--	--	--
9	0.56 (22)	0.46 (18)	0.53 (21)	0.43 (17)	--	--	--
60	--	--	0.64 (25)	0.58 (23)	0.56 (22)	0.53 (21)	0.50 (19.5)

[a]Some resin lost from the prepreg

zero void content product is 15.3 mils. The 34.5 MPa pressure at 316°C had successfully produced 7-ply composites from 1 hr at 180°C treated prepreg several times with close to zero void contents (calculated).

Inspection of the thick 34.5 MPa, 288°C processed swatch showed the fiber bundles to be full of resin but the interbundle areas to be resin starved. In processing low viscosity epoxy prepregs, one correctly assumes that pressure application can cause resin to be squeezed from the fiber bundles. With high melt viscosity resins however, fiber bundle resin loss appears to be far more difficult. The need for a low melt viscosity in thermoplastic prepregs appeared to be required to produce a smooth, zero void content prepreg. The need for resin flow during composite fabrication would be minimized and high melt index thermoplastic resins could possibly employed.

Consequently, the above considerations led us to postpone attempts to produce prepregs and composites from the high melt viscosity polyimide (1 hr at 180°C treated) and to investigte methods to produce smooth prepregs. With 180°C treatment the glycol-cresol modified methanol PMR varnish thickens rapidly due to both the polymerization rate(s) and the rate of volatile loss. The results presented in Table 5 suggest that prepreg treatment times up to 9 min at 180°C could be used to provide for resin loss from the fiber bundles. Such short processing times are difficult to reproduce without machines and we consequently focused on lower staging temperatures to widen the processing window. Microscopic inspection was used to ensure that the opaque polymer was not produced in the prepreg.

3.4.3 Prepregs Smoothed During Staging

Numerous experiments were carried out toward defining the staging parameters required to produce smooth prepreg from the 78-102 varnish prepreg. The following principles were found to apply to such a product.

- Essentially all of the resin shrinkage occurs through the thickness of the prepreg. This relationship is indicated in Table 4.

- Low viscosity varnishes allow the fiber bundles to relax in the prepreg and increase its thickness. Smooth prepregs produced at low temperatures containing a low-melt viscosity varnish when placed unrestrained into a much hotter environment increase in thickness.

- A low-melt viscosity varnish is required for the resin to be "squeezed" from the fiber bundles to fill interbundle areas to obtain the smooth prepreg

- The volumetric shrinkage of the interbundle varnish is ~50 percent with a 50 percent solids varnish. This leads to insufficient resin in the interbundle areas if the last "smoothing" operation occurred with the majority of the varnish shrinkage yet to occur.

Consequently, the staging and smoothing conditions to produce the smoothest prepreg from the prepreg containing volatiles requires balancing cure shrinkage against melt viscosity. Alternatively a smooth prepreg may be attainable from precure of a resin-deficient prepreg wherein the resin bundles are full and the proper resin content is attained with a second operation.

Smoothing at 316°C

Overnight treatment of the 78-102 prepreg at 110°C reduced its volatile content to about 5 percent (~10 percent in the varnish). Treatment of this prepreg at 316°C for 5 min at 0.69 MPa and 3.45 MPa produced prepregs with

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thicknesses of 0.43 mm (17.0 mils) and 0.42 mm (16.6 mils), respectively. The
zero void content, smooth product would have a calculated thickness of 0.38 mm
(15.1 mils) (36.8 weight percent resin). Specific gravity measurement on the
0.42 mm product suggested a 3 percent void content. The volume percent air
calculated for the 0.42 mm product was 9 percent based on its thickness
discrepancy from the calculated thickness of the smooth product.

Smoothing at 100°C and at 316°C

Prepreg with a calculated volume percent air discrepancy from a smooth
product of 6.5 percent was achieved by a two-stage smoothing operation as
indicated in Table 6. After a 165-min treatment at 100°C the prepreg was
smoothed (resin was pushed into the interbundle areas from the bundles prior
to overnight treatment at 110°C and final smoothing at 316°C).

Inspection of this prepreg showed that there was deficient resin in the
interbundle areas and a smoothing operation after more cure shrinkage would be
beneficial to reducing the calculated volume percent air discrepancy from the
smooth product.

Smoothing Twice at Low Temperature and Once at 316°C

Incorporation of an additional smoothing operation into the staging
cycles prior to smoothing at 316°C led to very smooth prepregs with
thicknesses which were essentially the same as the thickness calculated for
the zero void content product. Processing conditions and characterization
data on three 5.1 cm^2 (2.0 in^2) samples of prepreg are given in Table 7. Foam
formation was not observed in any of the prepreg samples through any of the
processing steps.

Of interest in the data provided in Table 7 is the apparent resistance
of the prepreg to shrink through its thickness with loss of volatiles.
Pressure must be used to densify and smooth the product. Further, the data

Table 6. Physical properties of a twice smoothed PMR prepreg

Staging Conditions	As Made	165 min at 100°C	Press at 100°C	16 hr at 110°C	5 min at 316°C, 6.9 MPa
Calculated resin or varnish content, %	54.2	47.7	47.7	39.6	36.9
Calculated remaining volatile content of prepreg (resin), %	27.5 (50.7)	17.2 (36.0)	17.2 (36.0)	4.3 (10.9)	0.0
Thickness, mm (mils)	--	0.66 (26)	0.49 (19.4)	0.49 (19.1)	0.41 (16.2)

Table 7. Processing and characterization of multiply smoothed prepregs

Sample Number	Thickness, mm (mils)			Calculated Prepreg Volatile Content (%)		
	A	B	C	A	B	C
Processing conditions:						
As made	--	--	--	~28	~28	~28
165 min at 100°C	0.66 (26)	0.66 (26)	0.66 (26)	15.5	15.0	15.0
Press at 100°C and 0.69 MPa[a]	0.47 (18.6)	0.48 (18.8)	0.48 (18.8)	15.5	15.0	15.0
8 hr at 110°C	0.49 (19.2)	0.49 (19.2)	0.49 (19.2)	6.5	7.4	6.5
Press 2 min at 140°C and 0.69 MPa	Not done	Not done	0.48 (18.8)	6.5	7.4	6.5
Press 2 min at 160°C and 0.69 MPa	0.46 (18.0)	Not done	0.46 (18.1)	6.5	7.4	6.5
Press 2 min at 160°C and 3.5 MPa[a]	0.45 (17.7)	0.45 (17.9)	0.45 (17.9)	6.5	7.4	6.5
8 hr at 110°C	0.45 (17.7)	0.45 (17.9)	0.45 (17.9)	5.0	5.5	5.3
Press 2 min at 316°C and 0.69 MPa (Teflon®)	0.43 (16.9)	--	0.44 (17.1)	--	--	0.7
Press 2 min at 316°C and 0.69 MPa (Al)	--	--	--	--	--	--
Press 2 min at 316°C and 6.9 MPa (Al)	0.42 (16.6)	0.43 (16.9)	0.43 (16.8)	0	0	0
Press at 316°C and 34.5 MPa, cool under pressure[a]	0.39 (15.6)	0.39 (15.5)	0.40 (15.7)	0	0	0
Characterization data:						
Calculated thickness of smooth product	0.40 (15.7)	0.40 (15.7)	0.40 (15.7)			
Calculated resin content (%)	40.0	39.9	40.3			
Calculated volume fraction fibers (%)	53.0	52.2	52.7			
Specific gravity, (g/cc)	1.571	1.621	1.609			
Calculated void content (%)	1.3	-0.3	-1.2			

[a]Prepreg smooth

indicate that processing time (creep) as well as temperature is beneficial to obtaining thin products.

The process was successfully scaled up to provide 15.2 cm^2 (6 in^2) pieces of smooth prepreg. However, these pieces did not have uniform thicknesses. Their centers were thicker than their edges and, if used for composites, would lead to composites with similar geometries. Although resin distribution on the prepreg pieces were in part responsible for this result, it is also attributable to slight platen distortion caused by the high-pressure processing in combination with the low-flow properties of the prepreg.

The 34.5 MPa processing pressure requirement to achieve the completely dense product suggests that the best equipment to produce the completely dense smooth prepreg at high pressures may be more akin to a steel mill than equipment used by prepreggers with low viscosity resins.

3.4.4 Prepreg Resin Distribution

As the smooth prepreg product was approached, it became apparent that only very minor differences in resin distribution over the area of the prepreg could lead to only partially smoothed products. Thus with apparently meticulous prepregging procedures only partial smoothing occurs as sketched below:
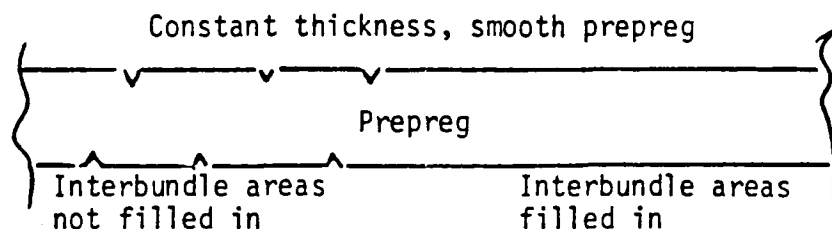
An initially even resin distribution on the prepreg is made uneven by several processes:

- Resin run down on the prepreg by verticle hanging, i.e., in an oven

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- Premature smoothing of the product, i.e., prior to complete impregnation

- Variation in fabric areal weight (in combination with a resin which shrinks)

- Others

To achieve completely dense, smooth, constant thickness prepregs, the resin distribution must be uniform over the entire prepreg area. Prepregs used for composite fabrication which have high flow resins (epoxies) do not have such a requirement.

Smoothing the prepreg prior to its staging at elevated temperature appeared to be the best approach to this problem. Thus the as-prepared prepreg was placed between two parallel shims and rolled smooth (roller pressed down to the shims), as sketched below.
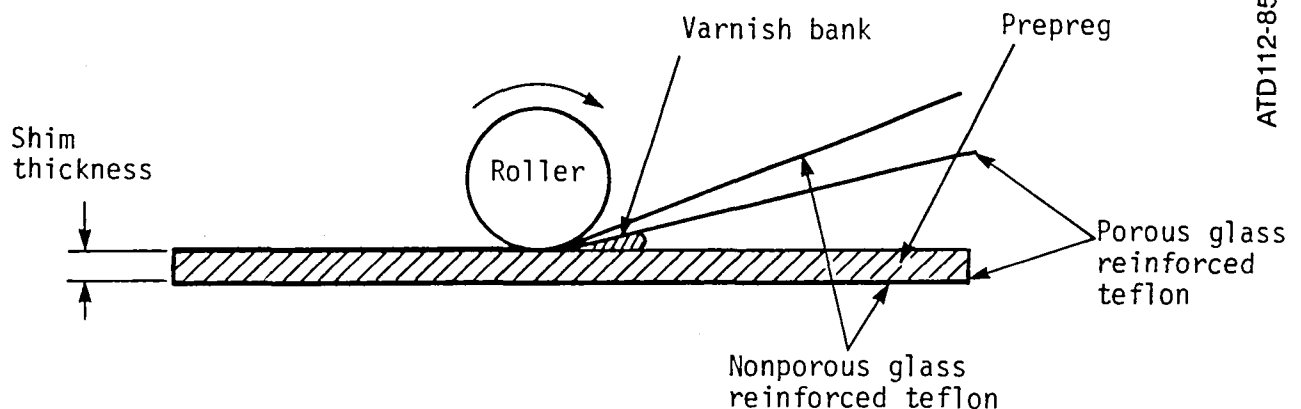
Varnish skinning during low temperature advancement leads to nonuniform viscosity states in the varnish (through the thickness at the prepreg). The varnish in the fiber bundles has a lower viscosity than the resin on the surface of the prepreg. This was seen during press smoothing wherein resin is bled from the edge of the test piece from individual fiber bundles and no through-the-thickness bleed is observed.

Typical staging conditions are indicated in Table 8 for swatches of prepreg initially smoothed to three thicknesses. Item 5 in the table indicates that vacuum bag smoothing occurred on the prepreg and it can be seen that the prepreg volatile loss with this operation is very high compared to the volatile loss which would have been expected for 1 hr treatment at 110°C at atmospheric pressure. Premature vacuum application can lead to a powdery product which does not melt at 260°C from PMR varnishes.

3.4.5 Neat Resin and Prepreg Molding Conditions

Molding condition requirements for the linear, 100 percent solid powdered, high molecular weight BTDA/HDA/m-PDA polyimide and the 16 hr (110°C) treated glycol-cresol modified methanol PMR/graphite fabric prepreg were investigated. As discussed in the next section, increasing prepreg molding temperatures up to 399°C (750°F) did not lead to reduced prepreg thicknesses as expected. Since the prepreg contains about 5+ percent by weight solvent, solvent loss during high temperature smoothing is expected with an increase in the resin's viscosity. Consequently, neat powdered resin was also tested for its flow characteristics up to 399°C. Increased flow with increasing temperature was not observed and the flow properties seem to be slightly reduced with increasing temperature.

A physical change of some type (crystallization) seems to be occurring with increasing temperatures to explain these results. Although crosslinking cannot be ruled out, it does not seem likely. This result parallels the result, wherein 1 hr treatment at 316°C (600°F) lead to improved solvent resistance and a slight increase in density.[1]

Table 8. Staging of prepregs processed to a thickness

Table No.	Staging Conditions	Thickness[a] mm (mils)	Weight[b] (g)	Weight Loss[c] (%)	Resin Content[d] (%)	Thickness[a] mm (mils)	Weight[b] (g)	Weight Loss[c] (%)	Resin Content[d] (%)	Thickness[a] mm (mils)	Weight[b] (g)	Weight Loss[c] (%)	Resin Content[d] (%)
1	Initial	0.46 (18)	6.74	--	42.7	0.53 (21)	8.64	--	55.3	0.58 (23)	9.57	--	59.7
2	2 hr at 100°C	--	6.19	8.2	37.6	--	7.65	11.4	49.5	--	8.55	10.7	54.8
3	Plus 2 hr at 110°C	--	5.93	4.2	34.9	--	7.25	5.2	46.7	--	8.03	6.1	51.9
4	Plus 3 hr at 110°C	--	5.84	1.5	33.9	--	7.19	0.8	46.3	--	7.90	1.6	51.1
5	Plus 1 hr at 110°C in vacuum bag[e]	0.39 (15.5)	5.64	3.4	31.6	0.48 (19)	6.80	5.4	43.2	0.50 (19.5)	7.22	8.6	46.5
6	Plus 5 hr at 110°C	0.48 (19)	5.45	3.4	29.2	0.50 (19.5)	6.52	4.1	40.8	0.55 (21.5)	6.86	5.0	43.7
7	0.5 hr at 260°C in vacuum bag[e]	0.39 (15.5)	5.08	6.8	24.0	0.46 (18)	5.93	9.0	34.9	0.47 (18.5)	6.14	10.5	37.1

[a]Prepreg rolled smooth with shims on each side of the product
[b]25.8 cm^2 (4 in^2) swatch
[c]Weight losses indicated are for each step
[d]Assumes areal weight of carbon fabric is 0.0372 g/cm^2
[e]Full vacuum

3.4.6 Prepreg Producibility with Low Pressure Processing 78-102 Varnish

As noted in Table 7, completely dense, smooth samples of prepreg were produced with high pressure processing of the product. Efforts then focused on producing the prepreg at 0.69 MPa (100 psi) processing pressure. These results are presented in Table 9. The graphite fabric prepreg was prepared from the 78-102 varnish.

The most obvious result from this investigation was that increasing temperatures did not lead to thinner prepregs. The thinnest prepregs produced at 0.69 MPa were obtained in the first two instances at 260°C. A direct relationship between final prepreg thickness and the prepregs thickness prior to final processing exists. However, the results presented in Table 9 also suggested that longer processing times at lower temperatures needed to be investigated.

Other PMR Varnishes and Opacity

As the prepreg from the 78-102 varnish neared consumption, additional varnish(s) required preparation. Unlike the 78-102 varnish, these varnishes exhibited a high degree of moisture sensitivity not noted in the glycol-modified 78-102 varnish. The absorbed moisture had two effects on the prepreg. The melt viscosity of the resin was lowered dramatically with the absorbed moisture and the varnish became opaque at 110°C after a few minutes staging at that temperature.

Staging for extended times at 100°C also produced opacity, whereas immediate treatment at 180°C did not produce opacity except in very thick films (foams). The phenomena is related to the thickness of the varnish film being staged. Very thin films of all varnishes gave staged products which are clear whereas thick films usually do not. Once opacity has developed in the

Table 9. Processing and characterization of smoothed prepregs

Table Number	Processing Conditions Prior to Final Treatment	Varnish Code	Results of Final Treatment				
			Conditions	Volatile Loss (%)	Sample Weight (g)	Thickness,mm[a] (mils)	
1	165 min at 100°C	78-102	30 min at 260°C and 0.69 MPa	6.9	1.60	0.44-0.46 (17.5-18)	
2	plus smoothed at 100°C and 0.69 MPa		6 min at 288°C and 0.69 MPa	6.2	1.56	0.48-0.51 (19-20)	
3	plus 16 hr at 110°C		6 min at 316°C and 0.69 MPa	7.8	1.59	0.48-0.51 (19-20)	
4	Thickness = 56 mm (22 mils)		(plus 6 min at 316°C and 6.9 MPa)	--	--	0.41 (16.0)	
5			6 min at 343°C and 0.69 MPa	8.9	1.57	0.48-0.51 (19-20)	
6			6 min at 371°C and 0.69 MPa	9.3	1.56	0.48-0.51 (19-20)	
7			6 min at 399°C and 0.69 MPa	9.7	1.55	0.48-0.51 (19-20) Average resin content = 38%	
8	60 min at 100°C	78-102	6 min at 232°C and 0.69 MPa	5.1	1.54	0.46 (18.0)	
9	plus smoothed at 110°C with blade		30 min at 232°C and 0.69 MPa	5.4	1.55	0.42 (16.5)[b]	
10	plus 70 min at 100°C		30 min at 260°C and 0.69 MPa	6.9	--	0.42 (16.5)[b]	
11	plus smoothed at 110°C with blade		30 min at 260°C in vacuum bag	6.7	1.53	0.43 (17.0)	
12	plus 50 min at 100°C		30 min at 316°C in vacuum bag	7.9	--	0.44 (17.5) Average resin content = 37%	
	plus smoothed at 110°C with blade plus 8 hr at 110°C Thickness = 0.46 mm (18 mils)						
13	60 min at 100°C	78-102	6 min at 232°C and 0.69 MPa	4.4	1.58	0.42 (16.5)	
14	plus smoothed at 110°C with blade		6 min at 260°C and 0.69 MPa	--	--	0.41 (16.0)	
15	plus 70 min at 100°C		30 min at 260°C and 0.69 MPa	4.8	1.50	0.41 (16.0)[b]	
16	plus smoothed at 110°C with blade		6 min at 288°C and 0.69 MPa	4.7	1.49	0.41 (16.0)	
17	plus 50 min at 100°C		30 min at 288°C and 0.69 MPa	5.6	1.49	0.41 (16.0)	
18	plus smoothed at 112°C with blade		6 min at 316°C and 6.9 MPa	6.3	1.55	0.39 (15.5)[c] Average resin content = 36%	
	plus 16 hr at 110°C plus processed with blade at 200°C (product not smooth) Thickness = 0.42 mm (16.5 mils)						

[a]To the nearest 0.5 mil
[b]Prepreg smooth
[c]Prepreg flat but interbundle areas not filled in

varnish, no set of conditions was found to eliminate the opacity including rapid heatup to 260°C. Opaque resin films were not as tough as clear resin films.

Smooth prepregs in which the interbundle areas are filled, develop opacity in these areas. Prepregs with very little resin in the interbundle areas usually did not develop opacity. Initial treatment of the prepregs under vacuum prior to staging at elevated temperature increases the time to opacity. Room temperature storage of the prepreg decreases the time (days) to opacity.

Relevant to contract goals, a two- or three-step prepreg coating operation (vacuum staging and possibly other options) could hold potential for eliminating the opacity. However, preparation of a varnish with less water appeared to be the most worthy of investigation.

Consequently, a 55 percent solids varnish (78-121) was prepared from the fully imidized HDA/BTDA prepolymer via 1 hr reaction at 180°C followed by addition of a cresol solution of the m-PDA at 100°C. This varnish was similar to that used to prepare the composites discussed in Section 3.1 (see Figures 1 and 2). The major difference between the two varnishes is that the one described in Section 3.1 used BTDA whereas this varnish used the half ester of BTDA.

Sixteen-hour advancement of thick resin films at 100° or 140°C did not produce opacity in the resin, probably due to its reduced water content. This varnish contained about 50 percent of the calculated water content of the normal PMR varnishes (see Table 1).

Prepregs From Partially Imidized and Normal PMR Varnishes

Prepreg processing condition and prepreg characteristics after final heat treatments for 0.69 MPa processed prepregs are presented in Tables 10

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Table 10. Processing of PMR prepreg

Table Number	Processing Conditions Prior to Final Heat Treatment	Varnish Code	Results of Final Heat Treatment				Comments
			Conditions	Volatile Loss (%)	Sample weight (g)[a]	Thickness mm (mils)	
1	Rolled to 0.58 mm (23 mils) shims 120 min at 100°C plus 3 hr at 110°C	78-118	Vacuum bag, 200°C, hold 60 min	--	1.77	0.58 (23)	Foamed
2	Thickness = 0.61 mm (24 mils)		Vacuum bag, 260°C, hold 60 min	15.1	1.74	0.58 (23)	Foamed
3			Vacuum bag, 260°C Apply 0.69 MPa when part temperature is 260°C, hold 60 min	10.1	1.59	0.53 (21)	Looks good
4			Same as above, apply 6.9 MPa when part temperature is 260°C, hold 60 min	9.6	1.60	0.53 (21)	Looks good
5			260°C, hold 5 min Apply full vacuum After 5 min, apply 0.69 MPa After 10 min, vent vacuum Hold 16 hr at temperature	16.1	1.62	0.53 (21)	Looks good
6	60 min at 100°C plus smoothed at 100°C with blade plus 70 min at 100°C plus smoothed at 100°C with blade plus 50 min at 100°C plus smoothed at 110°C with blade plus 8 hr at 100°C	78-102	Same as Item 1	--	1.52	0.44 (17.5)	
7	Thickness = 0.46 mm (18 mils)		Same as Item 2	8.2	1.57	0.047 (18.5)	
8			Same as Item 3	7.2	1.54	0.43 (17)	
9			Same as Item 4	7.1	1.57	0.44 (17.5)	Looks good
10			Same as Item 5	8.7	1.58	0.43 (17)	
11	165 min at 100°C plus smoothed at 100°C and 0.69 MPa plus 16 hr at 110°C	78-102	Same as Item 1	--	1.59	0.50 (19.5)	
12	Thickness = 0.56 mm (22 mils)		Same as Item 2	7.3	1.52	0.48 (19)	
13			Same as Item 3	7.7	1.44	0.43 (17)	
14			Same as Item 4	7.4	1.50	0.43 (17)	
15			Same as Item 5	8.9	1.43	0.43 (17)	
16	3 hr at 100°C plus 3 hr at 110°C press smoothed 20 hr at 110°C no longer smooth	78-119	60 min at 260°C, 0.69 MPa	6.7	1.54	0.44 (17.5)	

[a] 24 x 23 8-harness satin weave Celium 3000 fabric with size removed, areal weight 0.038 g/cm², 5.0 cm² sample

and 11. Table 10 indicates results for the normal PMR varnish and Table 11 indicates results for the PMR varnish prepared by preimidization of the HDA/BTDA prepolymer prior to addition of the m-PDA (see Table 1).

The major difference observed between the two types of varnishes during staging was that for equivalent volatile losses, the prepreg containing the preimidized aliphatic prepolymer varnish was much more flexible, indicating that the varnish had a lower Tg. Further staging did not produce opacity in the preimidized HDA/BTDA prepolymer varnish.

Table 12 abstracts the best results obtained on the low-pressure processed prepregs presented in Tables 9, 10, and 11. Comparison of the observed prepreg thicknesses to the calculated thicknesses for the completely dense, smooth product indicates that porosity yet existed in the prepregs, unlike the completely dense prepreg samples obtained from high pressure processing of the prepregs indicated in Table 7.

The last four entries in Table 12 (numbers 6 through 9), although not promising from the standpoint of dense prepreg products, showed interesting properties which appeared to be directly related to the different varnishes used. Prepregs prepared from varnish 78-121 (numbers 6 and 8) did not appear to be as susceptible to densification at high temperature as prepregs prepared from varnish 78-124. Further characterization of these prepregs is described below.

Analysis of Two Preimidized HDA/BTDA Varnish Prepreg Samples

Further characterization of the prepreg swatches mentioned above from preimidized HDA/BTDA prepolymer varnishes which had been processed together in a vacuum bag through 260°C with 0.69 MPa pressure was performed. These samples are indicated in Table 13 as Nos. 1 and 3. Number 3 is seen to be 0.08 mm (3 mils) thinner than No. 1. Additional processing of the same

Table 11. Processing of precondensed aliphatic prepolymer PMR prepreg

Table Number	Processing Conditions Prior to Final Heat Treatment	Varnish Code	Results of Final Heat Treatment				Comments
			Conditions	Volatile Loss (%)	Sample weight (g)[a]	Thickness mm (mils)	
1	4.75 hr at 110°C	78-121	260°C, 2 min bump 2 min bump 2 min, 0.69 MPa	10.7	1.50	0.48 (19)	
2			2 hr at 260°C, 0.69 MPa	7.9	1.63	0.42 (16.5)	
3			1 hr at 260°C, 0.69 MPa	10.0	1.53	0.44 (17.5)	
4			45 min at 210°C, 0.69 MPa	11.3	1.49	0.55 (21.5)	
5	1 hr at 140°C		1 hr at 260°C, 0.69 MPa	•8.9	1.54	0.50 (19.5)	
6	2 hr at 110° C		1 hr at 260°C, 0.69 MPa	20.4	1.52	0.48 (19)	Foamed
7	2 hr at 110°C		Vacuum bag 110° → 210°C	Bled off varnish	1.44	0.37 (14.5)	
8	16 hr at 100°C		45 min at 210°C, 0.69 MPa	7.6	1.71	0.53 (21)	
9	16 hr at 100°C		20 min at 260°C, 0.69 MPa	10.3	1.65	0.48 (19)	
10	4 hr at 100°C		Vacuum bag + 0.69 MPa RT → 260°C, hold 1 hr	Bled off varnish	1.18	0.34 (13.5)	Smooth
11	16 hr at 100°C			--	1.66	0.50 (19.5)	
12	2 hr at 100°C	78-124		Bled off varnish	1.18	0.34 (13.5)	Smooth
13	8 hr at 100°C	78-121		10.8	1.65	0.50 (19.5)	Not smooth
14	8 hr at 100°C	78-124	Processed with above	10.4	1.47	0.42 (16.5)	Almost smooth
15	8 hr at 100°C	78-121	RT → 260°C, hold 1 hr 0.69 MPa	11.7	1.59	0.52 (20.5)	Not smooth
16	8 hr at 100°C	78-124	Processed with above	10.8	1.55	0.44 (17.5)	Almost smooth

[a]24 x 23 8-harness satin weave Celium 3000 fabric with size removed, areal weight 0.038 g/cm^2, 5.0 cm^2 sample

Table 12. Summary of the thinnest 0.69 MPa processed prepregs

Table Number	Varnish Code	Reference	Observed Thickness mm (mils)	Calculated Thickness of Smooth Product mm (mils)	Comments
1	78-102	Table 6, Sample A	0.43 (16.9)	0.39 (15.4)	Not smooth
2	78-102	Table 9, No. 15	0.41 (16.0)	0.37 (14.7)	Smooth
3	78-102	Table 10, No. 10	0.43 (17.0)	0.38 (15.0)	Not smooth
4	78-121	Table 11, No. 2	0.42 (16.5)	0.40 (15.6)	Not smooth
5	78-121	Table 11, No. 7	0.37 (14.5)	0.34 (13.3)	Smooth
6	78-121	Table 11, No. 13	0.50 (19.5)	0.39 (15.5)	Not smooth
7	78-124	Table 11, No. 14	0.42 (16.5)	0.35 (13.8)	Almost smooth
8	78-121	Table 11, No. 15	0.52 (20.5)	0.38 (15.1)	Not smooth
9	78-124	Table 11, No. 16	0.44 (17.5)	0.37 (14.6)	Almost smooth

Table 13. Physical properties of 0.69 and 6.9 MPa processed prepreg

Table Number	Varnish Code	Final Heat Treatment	Properties		Volume Discrepancy from Smooth Product, %[b]	Void Content, %[c]
			Resin Content, %[a]	Thickness, mm (mils)		
1	78-121	60 min at 260°C, 0.69 MPa	40.7	0.49 (19.5)	20	1.9
2	78-121	Above plus 20 min at 260°C, 6.9 MPa	40.4	0.41 (16.0)	2	1.7
3	78-124	Same as 1	36.9	0.42 (16.5)	15	1.9
4	78-124	Same as 2	36.1	0.37 (14.5)	4	2.0

[a]From caustic digestion
[b]Prepregs only measured to nearest 0.01 mm (0.5 mil). This leads to potential error in volume discrepancy of ±3%, i.e., 20 ± 3%.
[c]Void contents from observed specific gravity and calculated specific gravity from digested sample using 1.36 g/cc and 1.788 g/cc for the resin and fiber densities, respectively

swatches was carried out at 6.9 MPa (1000 psi) at 260°C and good densification occurred as indicated in the table as numbers 2 and 4. Specific gravities and resin contents from digested samples were determined.

Partial explanation for the thickness difference between the prepregs made from the two varnishes lies with their resin contents.* Calculated final thicknesses for the completely dense products calculated from the digested samples were 0.399 mm (15.7 mils) (78-121) and 0.356 mm (14.0 mils) (78-124).

The prepreg from 78-121 reduced 0.120 mm (4.0 mils) in thickness and the prepreg from 78-124 reduced 0.051 mm (2.0 mils), suggesting that a difference in flow properties also existed during the original processing. The difference between the volume discrepancies from the smooth products and their calculated void contents suggests that essentially all of both prepregs' porosity was open to the water used for the specific gravity measurement.

Consequently, it was concluded that part of the explanation for the thickness difference between the two prepregs lay with the differing resin contents of the samples. However, it seemed that at least one other principle was also operative and was not discernable from the Table 13 data. We expected that differences in the melt viscosities of the two varnishes could be found.

Varnish Flow Indices

The results described above prompted indexing the relative melt viscosities of the two varnish batches as well as two others (78-118 and 120) not prepared from the preimidized HDA/BTDA prepolymer. The influence that 10 weight percent cresol, glycol, and butanol had on the melt viscosities of

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*Previously calculated resin contents have been calculated from the nominal areal weight of the fabric and differ from the resin contents obtained by digestion.

the varnishes was also investigated. Weighed varnish samples were pressed with 23 Kg force to give a disk of the varnish. The area of the disk was calculated and divided by its weight to index its flow in unit area per unit weight (cm^2/g).

The methodology to index the relative flows of the varnishes was as follows: Preweighed varnish samples were pressed at room temperatures and dimensioned. The resulting disks were then staged at 100°C on nonporous Teflon (Teflon sheets used for pressing were removed). The staged disks were powdered, weighed, and pressed at 100°C to give relative flows at 100°C. From the initial solid contents of the varnishes in combination with the weight loss data due to the staging step, a new solids content could be calculated for the varnish which was being tested. The disks, after press-out at 100°C, were staged for another 1.5 hr at 100°C, weighed and pressed again at 100°C. All pressing times were for 3 min.

Table 14 provides the results of the relative flows of the four varnishes and the varnishes with the three diluents. The table indicates both the calculated flow index and the solids contents of the varnishes calculated from the original solids contents of the varnish from the weight losses incurred through the staging operations.

Observations from the flow index screening tests given in Table 14 are tabulated below:

- Dilution of the four varnishes by cresol, glycol, and butanol leads to a lower solids content and higher flow index at room temperature. Flow is approximately related to the diluents' molecular weight. Cresol is less effective than the lower molecular weight diluents, glycol and butanol.

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Table 14. Flow indices of four varnishes with diluents[a]

Table Number	Varnish Condition	Press-Out Conditions	Varnish Codes	Modifier			
				Control	10% Cresol	10% Glycol	10% Butanol
1	As prepared	23 Kg force, RT, 3 min	78-118	25 (57)	32 (52)	46 (52)	37 (52)
2	As prepared	23 Kg force, RT, 3 min	78-120	23 (56)	26 (51)	41 (51)	44 (51)
3	As prepared	23 Kg force, RT, 3 min	78-121	29 (55)	38 (50)	46 (50)	46 (50)
4	As prepared	23 Kg force, RT, 3 min	78-124	12 (63)	21 (58)	32 (58)	34 (58)
5	Staged 1.5 hr at 100°C	23 Kg force, 100°C, 3 min	78-118	45 (62)	57 (57)	110 (61)	52 (62)
6	Staged 1.5 hr at 100°C	23 Kg force, 100°C, 3 min	78-120	74 (59)	92 (57)	109 (59)	84 (63)
7	Staged 1.5 hr at 100°C	23 Kg force, 100°C, 3 min	78-121	65 (65)	59 (64)	49 (67)	50 (74)
8	Staged 1.5 hr at 100°C	23 Kg force, 100°C, 3 min	78-124	113 (67)	109 (64)	48 (69)	46 (71)
9	Staged 3.0 hr at 100°C	23 Kg force, 100°C, 3 min	78-118	32 (79)	32 (71)	29 (75)	32 (73)
10	Staged 3.0 hr at 100°C	23 Kg force, 100°C, 3 min	78-120	28 (76)	34 (75)	36 (74)	35 (72)
11	Staged 3.0 hr at 100°C	23 Kg force, 100°C, 3 min	78-121	<10 (77)[b]	<10 (74)[b]	16 (75)	12 (77)
12	Staged 3.0 hr at 100°C	23 Kg force, 100°C, 3 min	78-124	19 (77)	15 (76)	21 (77)	19 (80)

[a]The table shows two numbers for each composition. The first number is flow index in cm^2/g and the second number is estimated solids content of the sample in percent and is shown in parentheses.
[b]Disk not formed due to low flow

- Solids contents of the varnishes are approximately related to their flow indices at room temperature

- After staging at 100°C, the solids contents of the varnishes increases due to the volatiles lost. The 78-121 and -124 varnishes appear to lose volatiles more readily than the 78-118 and -120 varnishes in the beginning (1.5-hr samples) and then more slowly later (3.0-hr samples).

- Glycol appears to be an excellent plasticizer for the 78-118 and -120 varnishes in the beginning (1.5-hr samples) but this plasticization action is lost with continued staging (3-hr samples). This type of plasticization benefit is not observed for the 78-121 and -124 varnishes.

- After 1.5 hours staging, the normal PMR varnishes (78-118 and -120) continue to show the same relative relationships, i.e., samples with plasticizers have higher flow indices than their unplasticized controls. The preimidized HDA/BTDA prepolymer varnishes (78-121 and -124) show a reordering of flow indices. The control specimen has the highest flow index, followed by the cresol plasticized specimens and then by the glycol- and butanol-diluted specimens. Explanation for this is not readily apparent. The disks' exposed areas for volatile loss, which is directly proportional to the room temperature flow indices, show an inverse relationship to the 100°C flow indices after the 1.5-hr staging.

- Another factor, however, seems to also be important in two varnishes from the preimidized HDA/BTDA prepolymer (78-121 and -124). The quantity of cresol initially used in the preparation of the varnish appears to be important.

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The polymer-to-cresol weight ratio in 78-121 is 1.3 to 1, whereas in 78-124 it is 2.1 to 1 (see Table 1). All flow indices of staged polymers containing a greater quantity of cresol are less than the polymers containing less cresol. Compare table item numbers 7 and 8 and 11 and 12 of Table 14. Such cresol catalysis also suggests an explanation for the cresol-diluted 78-121 and -124 samples having reduced flow indices from their controls in the 1.5- and 3.0-hour samples.

The 16 disks were then staged for an additional 5 hr at 100°C to give a total of 8 hr at 100°C. At this point, the varnish samples foamed for the first time; however, the four glycol-modified samples foam very little compared to the other 12 samples. With the 78-118 and -120 varnishes, seven of the eight samples turned opaque. The butanol-modified 78-120 samples remained clear. All of the 78-121 and -124 samples remained clear.

The disks were then pressed at 200°C for 3 min. Volatile loss resulted in obtaining foamed samples and rendered the flow indices meaningless. The solids contents of the varnishes at this point were about 85 percent. Pressing the powdered polymers from the 200°C treated disks at 260°C for 3 min led to a surprising result. The eight samples 78-118 and -120 varnish samples fused well but did not flow, whereas the eight samples from the 78-121 and -124 varnishes, in addition to fusion, exhibited some thermoplastic flow.

Analysis and Comparison of Flow Properties of Prepregs From Normal PMR and Preimidized HDA/BTDA PMR Varnishes

Based on the suggestion that cresol was a catalyst in the preimidized HDA/BTDA varnish, prepreg samples of the two varnishes were staged under vacuum and flow characteristics of the "reduced" cresol content prepregs investigated. Specifically sought from this investigation was verification of the concept that the varnish which had the lowest molecular weight at a very

high solids content would give the highest flow characteristics and, as a consequence, the densest prepregs at low pressure. Included in this study were prepreg swatches from the normal PMR varnish in the as-prepared state, as well as one sample from the normal PMR varnish which had been staged for 16 hours at 100°C in an air-circulating oven.

It had been previously established that premature desolvation of normal PMR varnishes led to powdered samples, and some minimum staging in the presence of solvent was required to maintain polymer clarity. The 16-hr-staged at 100°C sample from the normal PMR varnish was also included in the study for this reason. The expected result was obtained during the study: both prepreg samples from the preimidized HDA/BTDA varnish and the prepreg samples from the staged normal PMR varnishes remain clear throughout the investigation, whereas prepreg samples from the unstaged as-prepared normal PMR varnish turned opaque.

The results of this study which are described below appears to validate the concept that the best varnish for low-pressure processing must have some minimum flow characteristics at a high solids content or densification will be difficult if not impossible at low pressures.

The results are presented in Table 15. The prepreg processing conditions are cumulative. Samples 6 through 10 had received conditions specified for samples 1 through 5; and so on. Solids contents estimated for the varnishes were back-calculated from the finally digested samples and their individual weights after each processing condition. Resin contents were obtained similarly. Prepreg thicknesses are recorded only to the nearest 0.013 mm (0.5 mil). The hypothetical prepreg thicknesses were calculated for the smooth products and assumed a fiber density of 1.788 g/cc, a resin density of 1.36 g/cc, and that the volatiles have a density of 1.0 g/cc.

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Table 15. Physical properties of prepreg processed under vacuum and 2.69 MPa (100 psi)

Table Number	Prepreg Condition	Varnish Code	Calculated Solids Content of Varnish (%)	Properties			
				Resin Content (%)	Thickness mm (mils)	Thickness of Smooth Product mm (mils)	Volume Discrepancy from Smooth Product (%)
1	16 hr at 100°C	78-102	81	39.1	0.495 (19.5)	--	--
2	60 min high vacuum	78-118	78	43.0	0.559 (22)	--	--
3	120°C, smoothed	78-120	68	39.9	0.470 (18.5)	--	--
4	at 100°C in press	78-121	67	45.4	0.508 (20)	--	--
5		78-124	72	49.4	0.521 (20.5)	--	--
6	Vacuum bag + 0.69 MPa, 100°C,	78-102	81	38.9	0.483 (19)	--	--
7	20 min	78-118	78	43.0	0.559 (22)	--	--
8		78-120	68	39.9	0.495 (19.5)	--	--
9		78-121	70	44.4	0.533 (21)	--	--
10		78-124	75	48.5	0.559 (22)	--	--
11	Vacuum bag + 0.69 MPa, 120°C	78-102	82	38.8	0.483 (19)	--	--
12	20 min	78-118	78	43.0	0.533 (21)	--	--
13		78-120	70	39.1	0.495 (19.5)	--	--
14		78-121	78	41.6	0.483 (19)	--	--
15		78-124	77	47.9	0.533 (21)	--	--

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Table 15. Physical properties of prepreg processed under vacuum and
2.69 MPa (100 psi) (continued)

Table Number	Prepreg Condition	Varnish Code	Calculated Solids Content of Varnish (%)	Properties			
				Resin Content (%)	Thickness mm (mils)	Thickness of Smooth Product mm (mils)	Volume Discrepancy from Smooth Product (%)
16	Vacuum bag + 0.69 MPa, 140°C 20 min	78-102	83	38.5	0.483 (19)	399 (15.7)	18
17		78-118	84	41.2	0.533 (21)	404 (15.9)	19
18		78-120	79	36.2	0.467 (19)	373 (14.7)	18
19		78-121	83	40.1	0.483 (19)	389 (15.3)	19
20		78-124	82	46.4	0.533 (21.5)	373 (17.4)	21
21	Vacuum bag + 0.69 MPa, 160°C 20 min	78-102	85	37.8	0.470 (18.5)	394 (15.5)	16
22		78-118	86	40.5	0.533 (20)	396 (15.6)	19
23		78-120	84	34.9	0.470 (18)	363 (14.3)	21
24		78-121	86	39.3	0.445 (18)	381 (15.0)	17
25		78-124	84	45.8	0.495 (20)	434 (17.1)	15
26	Vacuum bag + 0.69 MPa, 180°C 20 min	78-102	88	37.2	0.457 (18)	386 (15.2)	16
27		78-118	92	39.4	0.483 (19)	384 (15.1)	21
28		78-120	89	33.6	0.432 (17)	351 (13.8)	19
29		78-121	89	38.5	0.432 (17.5)	373 (14.7)	16
30		78-124	88	44.5	0.470 (18.5)	419 (16.5)	11

Table 15. Physical properties of prepreg processed under vacuum and 2.69 MPa (100 psi) (continued)

Table Number	Prepreg Condition	Varnish Code	Calculated Solids Content of Varnish (%)	Properties			
				Resin Content (%)	Thickness mm (mils)	Thickness of Smooth Product mm (mils)	Volume Discrepancy from Smooth Product (%)
31	Vacuum bag + 0.69 MPa, 200°C 20 min	78-102	91	36.4	0.445 (17.5)	378 (14.9)	15
32		78-118	92	39.0	0.457 (18.0)	378 (14.9)	17
33		78-120	95	32.2	0.419 (16.5)	340 (13.4)	19
34		78-121	90	38.1	0.419 (17.0)	371 (14.6)	14
35		78-124	92	43.5	0.445 (17.5)	406 (16.0)	9
36	Vacuum bag 0.69 MPa, 220°C 20 min	78-102	93	35.9	0.445 (17.5)	373 (14.7)	17
37		78-118	94	38.4	0.445 (17.5)	373 (14.7)	16
38		78-120	94	32.4	0.406 (16.0)	340 (13.4)	16
39		78-121	93	37.3	0.406 (16.5)	363 (14.3)	14
40		78-124	93	43.1	0.445 (17.5)	404 (15.9)	9
41	Vacuum bag 0.69 MPa, 240°C 20 min	78-102	95	35.3	0.445 (17.5)	368 (14.5)	17
42		78-118	97	37.8	0.432 (17.0)	335 (13.2)	22
43		78-120	97	31.8	0.394 (15.5)	335 (13.2)	15
44		78-121	96	36.6	0.394 (15.5)	356 (14.0)	10
45		78-124	96	42.3	0.419 (16.5)	394 (15.5)	6

Table 15. Physical properties of prepreg processed under vacuum and 2.69 MPa (100 psi) (continued)

Table Number	Prepreg Condition	Varnish Code	Calculated Solids Content of Varnish (%)	Properties			
				Resin Content (%)	Thickness mm (mils)	Thickness of Smooth Product mm (mils)	Volume Discrepancy from Smooth Product (%)
46	Vacuum bag 0.69 MPa, 260°C 20 min	78-102	97.1	34.8	0.432 (17.0)	366 (14.4)	15
47		78-118	99.3	37.2	0.432 (17.0)	363 (14.3)	16
48		78-120	99.1	31.3	0.394 (15.5)	334 (13.1)	15
49		78-121	98.9	36.0	0.394 (15.5)	351 (13.8)	11
50		78-124	98.9	41.7	0.419 (16.5)	389 (15.3)	7
51	Vacuum bag 0.69 MPa, 266°C 20 min	78-102	98.0	34.8	0.432 (17.0)	363 (14.3)	16
52		78-118	99.5	37.2	0.419 (16.5)	363 (14.3)	13
53		78-120	99.3	31.2	0.381 (15.0)	333 (13.1)	13
54		78-121	99.6	35.8	0.381 (15.0)	348 (13.7)	9
55		78-124	99.6	41.5	0.406 (16.0)	386 (15.2)	5
56	Vacuum bag 6.9 MPa, 260°C 20 min	78-102	100.0	34.2	0.419 (16.5)	0.358 (14.1)	15
57		78-118	100.0	37.0	0.406 (16.0+)	0.361 (14.2)	11
58		78-120	100.0	31.1	0.381 (15.0)	0.330 (13.0)	13
59		78-121	100.0	35.7	0.381 (15.0-)	0.348 (13.7)	9
60		78-124	100.0	41.4	0.406 (16.0-)	0.386 (15.2)	5

Table 15. Physical properties of prepreg processed under vacuum and
2.69 MPa (100 psi) (concluded)

NOTES: • Numbers 1 through 50 were processed with 1-ply TX 1040 and 1-ply 116E glass on each side of the prepreg
       • Numbers 51 through 55 were processed with 1-ply TX 1040 each side
       • Numbers 56 through 60 were processed against bare metal
       • All swatches were a nominal 25.8 cm^2 (2 in x 2 in)
       • Void contents calculated for the final products from specific gravity measurements were:

                78-102 3.3%
                78-118 3.5%
                78-120 4.9%
                78-121 2.1%
                78-124 1.7%

       • Very slight bleed occurred on all swatches tested at 120° and 140°C except for the prepreg from the 78-102 varnish
       • The polymers after 140°C treatment were semitough and no longer bled off
       • All prepreg swatches were smooth after all of the processing steps except for the swatch from the 78-102 varnish, which was not smoothed by any of the processing steps

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The volume percent discrepancy between the observed thickness and the smooth product is indicated and probably has close to only a ±3 percent precision due to reporting the prepreg thickness to only 0.013 mm (0.5 mil), surface roughness due to the porous Teflon and 116E glass bleeder, and the density assumptions mentioned above. The accuracy of the volume percent discrepancy calculation would be increased significantly if small samples were cut from the centers of the processed samples to eliminate edge effects (edges typically have higher voids). The decision to digest the entire sample was made to obtain accurate resin contents for the processed samples. Future processing studies of this type, however, should include data from a sample cut from the center of the processed sample, as well as data from the entire sample. In the present study, we expected that thickness reductions of the samples with processing conditions would give us the information we sought. It is now clear that far more information can be obtained from the small samples with more attention to experimental design.

Application of 6.9 MPa at 260°C to the 0.69-MPa-processed samples did not result in observing significant thickness reductions on any of the samples. This must be attributed either to the high molecular weight of the matrix resin or attainment of their nearly complete densification prior to application of the 6.9 MPa. This is in sharp contrast to the results indicated in Table 13. The two sets of samples are compared in Table 16. The results presented in Table 16 appear to vindicate the concept that "minimum" cresol is beneficial to retarding the rate of molecular weight growth of the polymer and increasing its melt processability, since the prepregs for the Table 13 products were initially staged for 8 hr at 100°C in an air-circulating oven and the Table 15 products were initially staged for 1 hr at 120°C under high vacuum.

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Table 16. Thickness comparison of prepreg samples

	Varnish Code	Table 13 Processed		Table 15 Processed		Varnish Code	Table 13 Processed		Table 15 Processed	
		0.69 MPa	6.9 MPa	0.69 MPa	6.9 MPa		0.69 MPa	6.9 MPa	0.69 MPa	6.9 MPa
Observed prepreg thickness, mm (mils)	78-121	0.49 (19.5)	0.37 (16.0)	0.38 (15.0)	0.38 (15.0)	78-124	0.42 (16.5)	0.37 (14.5)	0.41 (16.0)	0.41 (16.0)
Resin content, %		40.7	40.4	35.8	35.7		36.9	36.1	41.5	41.4
Void content from specific gravities on digested samples, %		1.9	1.7	2.3	2.1		1.9	2.0	1.8	1.7

3.5   COMPOSITES

A log of the composites fabricated from the varnishes described in Table 1 is provided in Table 17. Processing the composites at 316°C and 0.69 MPa regardless of varnish used does not lead to obtaining void-free composites. Processing at 316°C and 34.5 MPa leads to 14.6 percent void content in the composite from varnish from the linear polymer (no. 3) and 1.3 percent void content from the PMR varnish (no. 15).

Void contents of composites from the linear polymer varnish can be reduced by squeegeeing the prepreg as indicated by composites 4, 5, 6, and 7; however, bundle impregnation was not complete as indicated by photomicroscopy. Composites 8 and 9 from the preimidized HDA/BTDA prepolymer varnish showed the same deficiency and their photomicrographs are noted in Figures 1 and 2. These two composites were prepared early on the program prior to the extensive prepreg investigation and these varnishes contained no alcohol.

Complete bundle impregnation is achieved with the PMR varnish in composite no. 10 (Figure 3) and is essentially complete in composite no. 11 shown in Figure 6. Photomicrographs of composites from dilution of this varnish to 10 and 25 percent solids content are shown in Figures 7 and 8. The 10 percent solids varnish required 15 coats to obtain the sought resin weight percent on the prepreg. Calculated void contents of these 2000 psi processed composites were 3.8 and 2 percent respectively, and even though some void content can be seen within the individual fiber bundles, the majority of the voids are found in the interply resin.

Comparison of the void and fiber distribution and quantity of interply resin in the two composites from the 10 and 25 percent solids PMR varnishes to those obtained from the linear polymer varnish, show that the PMR varnish composites are superior to all of the composites obtained from the 100 percent

Table 17. Polyimide Celion 3000 composites processed at 316°C

Number	Notebook Reference	Varnish Solids Content (percent)	Prepreg Volatiles[a] (percent)	Number of Plies	Processing Pressure (MPa (psi))	Time at Temperature (hours)	Final Resin Content (percent by weight)	Final Ply Thickness (mils)	Void Content[b]
1	78-15A	13	2.7	6	0.69 (100)	1	34.0	19.4	27.1
2	78-15B	13	2.7	6	6.9 (1000)	1	36.2	17.9	16.6
3	78-16	13	2.7	6	34.5 (5000)	1	35.8	17.3	14.6
4	78-18A	13	<1	5	13.8 (2000)	1	34.2	15.0	2.7[c]
5	78-18B	13	<1	5	13.8 (2000)	1	33.6	15.2	7.9
6	78-28A	13	<1[d]	3	13.8 (2000)	1	37.8	16.7	7.5
7	78-28B	13	<1[e]	3	13.8 (2000)	1	35.8	15.6	5.3
8	78-31	25	<1	3	13.8 (2000)	1	36.0	15.4	3.6
9	78-34	47.6	<1	3	13.8 (2000)	1	36.6	15.4	2.3
10	78-49	51.0 (PMR)	<1	3	13.8 (2000)	1	36.0	15.0	1.1
11	78-55	51.9 (PMR)	<1	7	13.8 (2000)	1	37.2	15.9	4.1
12	78-64	25 (PMR)	<1	3	13.8 (2000)	1	36.0	15.4	2.0
13	78-65	10 (PMR)	<1	3	13.8 (2000)	1	37.1	15.8	3.8
14	78-86	52.3 (PMR)	<1	7	0.69 (100)	1	37.0	20.0	24.0
15	78-90	52.3 (PMR)	<1	7	34.5 (5000)	1	37.0	15.4	1.3

[a]Weight loss with 0.5-hr treatment at 288°C (550°F)
[b]Calculated from discrepancy between calculated mils/ply and observed mils/ply
[c]Composite laid up with fabric weave nested, i.e., 0, 90, 0, 90, etc.
[d]Fabric pretreated with 5 percent solution of polymer and dried
[e]Fabric pretreated with 2 percent solution of polymer and dried
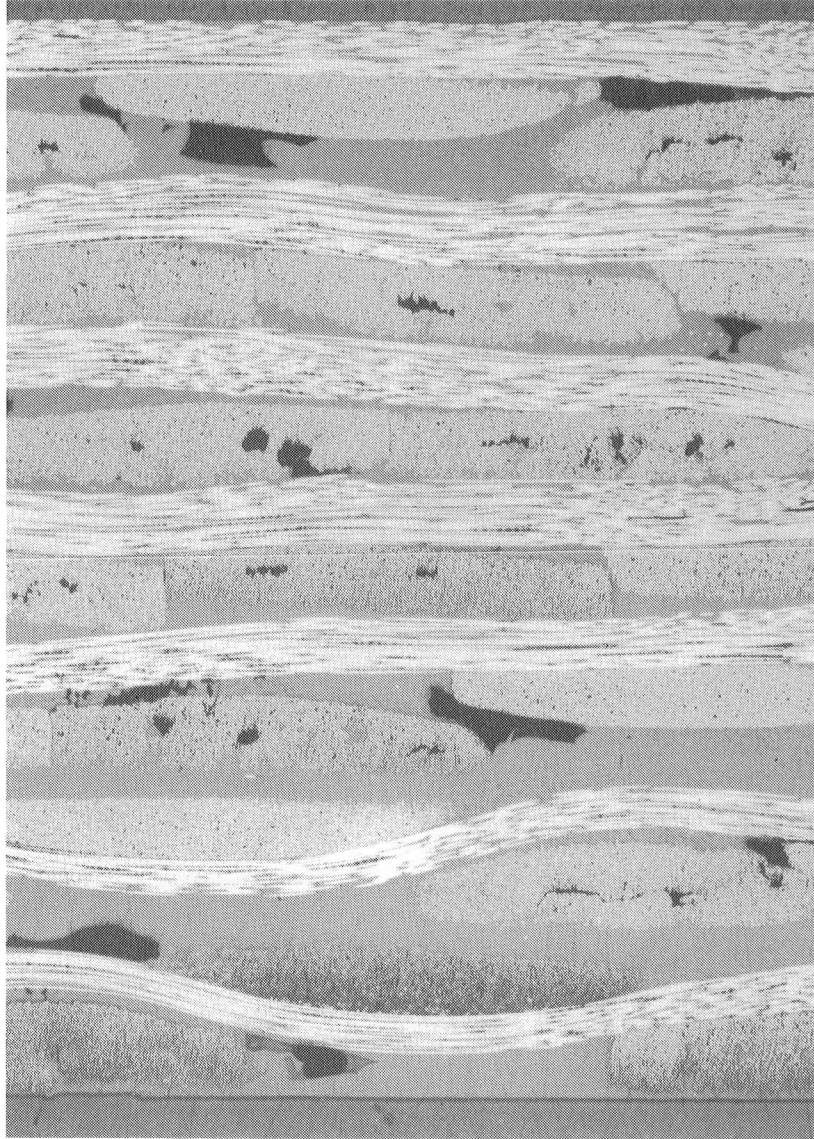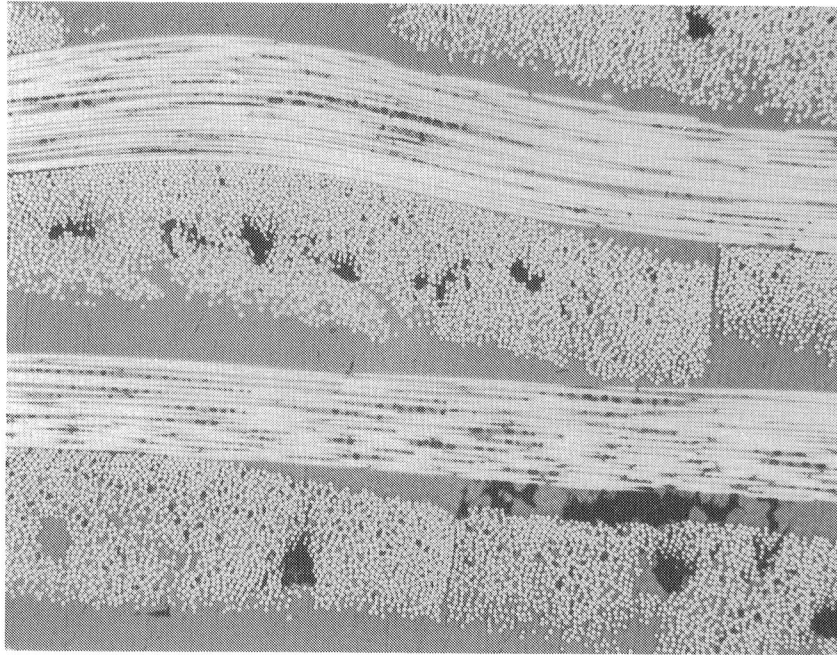
61

50x

H-574

Figure 6. Composite from 50 percent PMR varnish
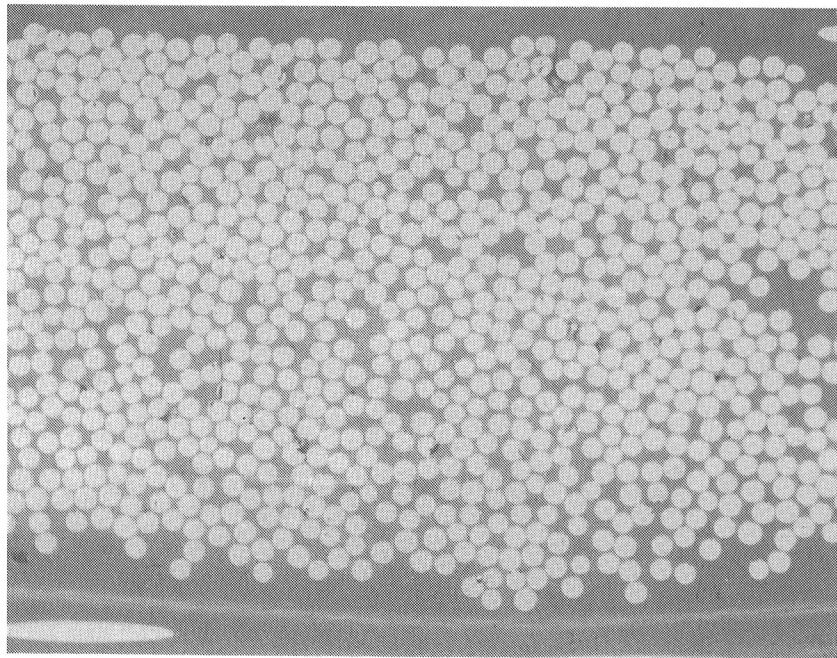
100x

H-573

400x

Figure 6. Composite from 50 percent PMR varnish (concluded)

50x 100x 400x
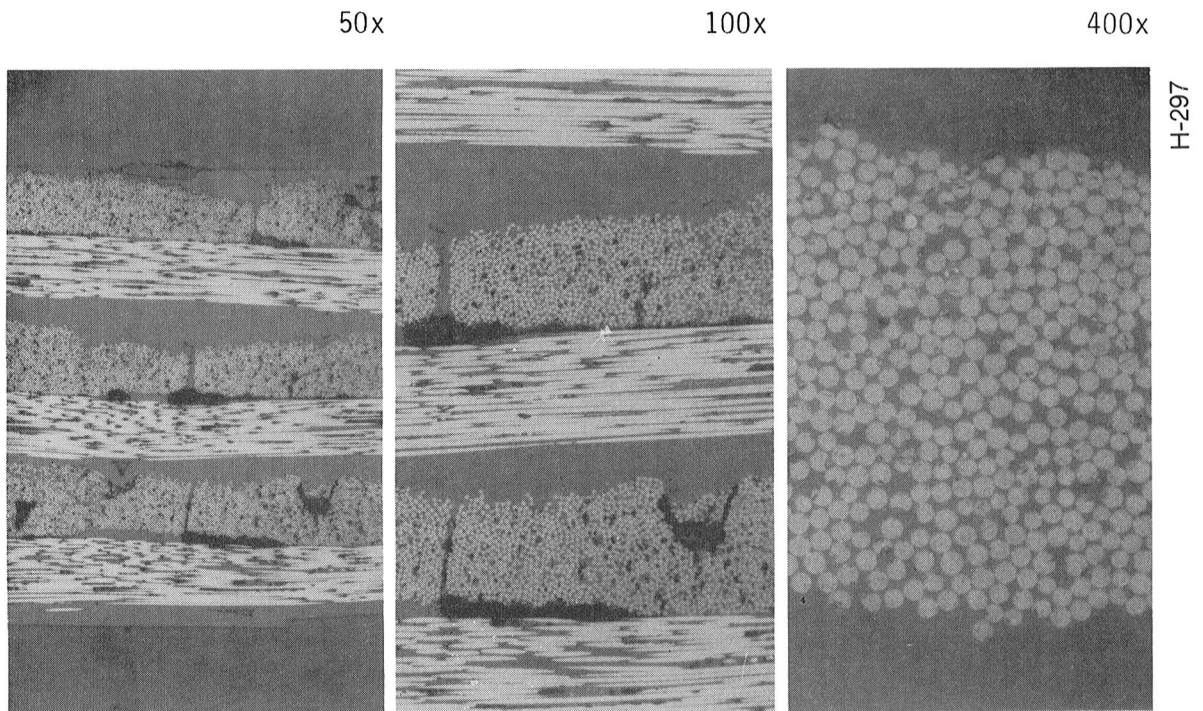
H-297

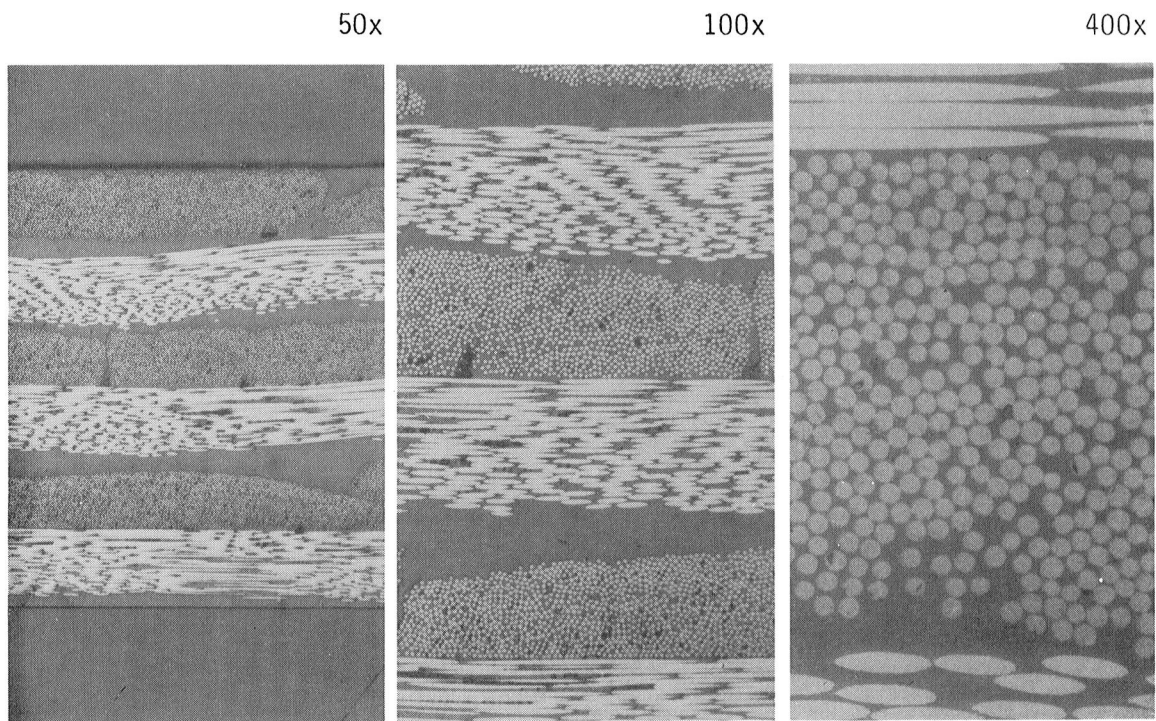Figure 7. Composite from 10 percent PMR varnish

50x 100x 400x

Figure 8. Composite from 25 percent PMR varnish

cresol varnishes including the 50 percent solids varnish shown in Figure 2. The 10 and 25 percent solids PMR varnish composites, however, were not superior to the 50 percent solids PMR varnish where separation of individual carbon filaments within the fiber bundles was achieved. The 25 percent solids PMR varnish composite shows some filament separation suggesting that a solids content of 35 to 40 percent could provide quality composites.

The void contents of composites 10 and 11 were 1.1 and 4.1, respectively (see Figures 3 and 5). Both composites show good bundle impregnation. However, differences in prepreg moldability or varnishes provided a large difference in void contents. The relatively few large voids observed in the composites strongly suggests that insufficient interply resin is present in combination with nonuniform molding pressures from the unsmoothed prepreg to complete the densification. Use of lower fiber volumes or smooth prepreg would be needed to eliminate this type of void. Higher resin flow properties in the prepreg would also be beneficial as discussed below.

Composite no. 14 (Table 17) was prepared via vacuum bag plus 0.69 MPa (100 psi) treatment at 316°C for 1 hr, good ply knitting occurred but the per ply thickness was 0.51 mm (20 mils). The calculated per-ply thickness for the 37 percent by weight resin composite at zero void content is 0.386 mm (15.2 mils). Postprocessing sections of the composite at 316°C (600°F) for 30 min at 6.9 MPa (1000 psi) and 34.5 MPa (5000 psi) produced per-ply thicknesses of 0.445 mm (17.5 mils) and 0.422 mm (16.6 mils). The later thickness represents a void content of about 10 percent. Fabrication of composite no. 15 from a fresh piece of the same prepreg at 316°C and 34.5 MPa (5000 psi) produced a per-ply thickness of 0.391 mm (15.4 mils) which represents a void content of less than 2 percent. Apparently, treatment

of the polymer at 316°C for 1 hr reduces its flow properties as evidenced by the difference in the two void contents. The surface foam on the prepreg was collapsed by the composite molding conditions, but could still be seen under the microscope in resin-rich areas (between the fiber bundles). Both the linear- and cresol-modified PMR resins are molded at 316°C and 0.68 MPa (100 psi) into clear resin buttons.

Mechanical strengths of composite no. 11 were carried out and were previously reported.[1] They are included in Table 18 for the readers convenience. The room temperature strengths of this composite are comparable to strengths obtained from epoxy resins. The room temperature failure mode of the flexural specimens was on the tensile side of the specimens. The elevated temperature strengths, although perhaps adequate if good property retention can be retained after exposure to solvents and/or the environment, showed only a 50 percent retention of the RT flexural strength and a 70 percent retention of the RT shear strength at 121°C (250°F). Comparable dry strength retention for 177°C (350°F) performing 5208-type resin matrices are 80 percent or

Table 18. Composite properties of PMR polyimide

Flexural Strength, MPa (ksi)/Modulus GPa (msi)		
Test Temperature, °C (°F)		
Ambient	82/(180)	121 (250)
751 (109)/ --	551 (80)/49(7.1)	427 (62)/46 (6.7)
696 (101)/ --	503 (73)/47(6.8)	372 (54)/47 (6.8)
Short Beam Shear Strength MPa (ksi)		
76 (11.0)	59 (8.6)	56 (8.1)
81 (11.8)	47 (6.8)	37 (5.3)

greater at 121°C (250°F). All of the elevated temperature flexural specimens failed on the compression side of the specimens in an unusual fashion. The warp fiber bundles near the load nose were "pushed" out of the specimen's top surface.

Several possible explanations for this type of flexural failure exist, however, the neat resin's loss in compressive yield strength and strain at elevated temperature is suspect (assuming that the previously cited end failures on the neat resin compression specimens was not the principal cause of the lower compression yield values).

It should be noted that none of the shear specimens showed the familiar midplane cleavage associated with shear failure of brittle resin systems. All of the shear specimens failed by yielding, including the specimens tested at room temperature.

3.6   OTHER POLYMER COMPOSITIONS

Copolymers of equimolar BTDA and PMDA with two aliphatic diamines were prepared by condensation in cresol and the hardness and solvent resistance properties of the molded polymers were investigated. For comparative purposes samples of other polymers were molded and included in the study.

Barcol hardness values for the as-molded polymers at room temperature and 140°C are indicated in Table 19, as well as hardness values after heat treating the polymer samples overnight at 140°C. Overnight heat treatment increased the hardness of all of the specimens tested at room temperature but was of little benefit to the hardness at 140°C except for the BTDA/MDA polymer.

Of note is the regular relationship between the weight percent aliphatic structure and the hardness of the polymer after annealing at 140°C. This relationship is sketched in Figure 9. The numbers indicated in the

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Table 19. Barcol hardness of molded polymer samples

Number	Polymer Composition[a]	As Molded		Heat Treated 24 hr at 140°C	
		RT Test	140°C Test	RT Test	140°C Test
1	BTDA with MDA	32	25	40	32
2	BTDA with BDA	30	17	36	19
3	BTDA with HDA	18	0	21	0
4	BTDA with ODA	10	0	15	0
5	BTDA with DDA	0	0	6	0
6	BTDA with HDA and m-PDA	32	18	38	18
7	BTDA with ODA and m-PDA	27	13	38	13
8	BTDA and PMDA with HDA	0	0	15	0
9	BTDA and PMDA with ODA	0	0	17	0

[a]BTDA = Benzophenonetetracarboxylic dianhydride
PMDA = Pyromellitic dianhydride
 MDA = 4,4'-methylenedianiline
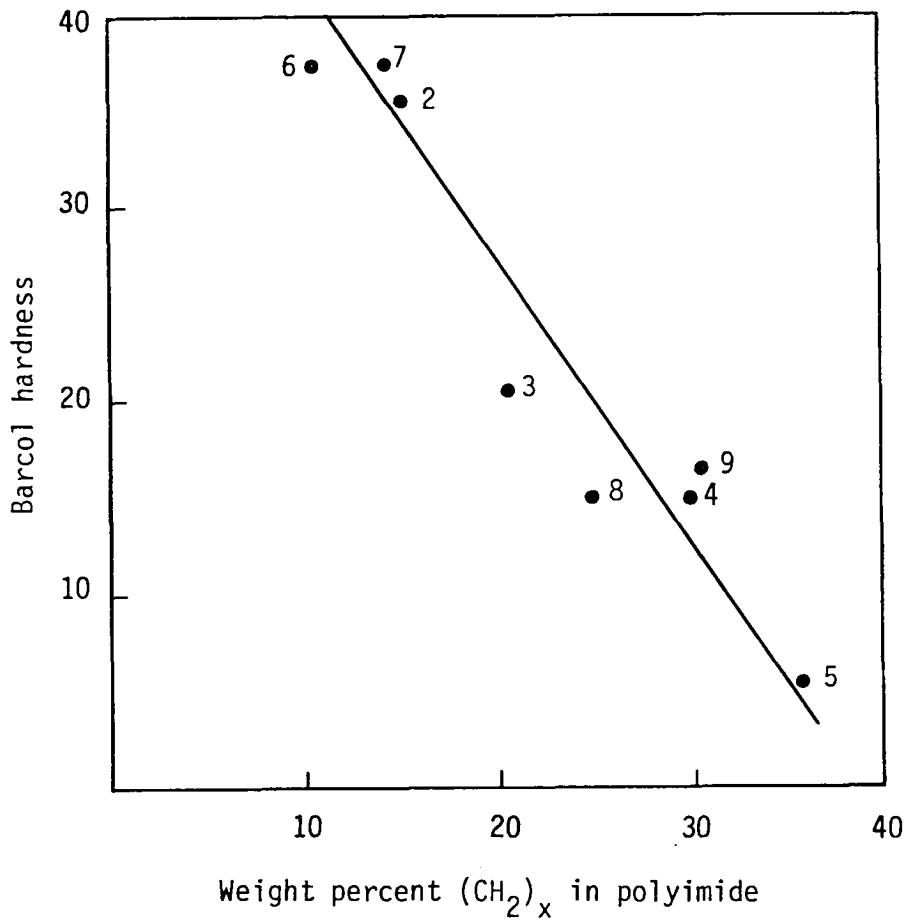 BDA = 1,4-butanediamine
 HDA = 1,6-hexanediamine
 ODA = 1,8-octanediamine
 DDA = 1,12-dodecanediamine

Figure 9. Relationship between hardness and percent aliphatic structure in polyimide

figure are from Table 19. This relationship suggests that the aliphatic portion of the polyimide should not exceed 15 weight percent for the polymer to have good compressive properties at room temperature.

The solvent resistance of seven of the nine polymers tested for hardness is indicated in Table 20. Both of the subject copolymers (No. 6 and 7) have inferior solvent resistance to the selected polyimide (No. 4).

Table 20. Solvent screening of molded polymer samples[a]

Number	Polymer Compositions[b]	Acetone			Chloroform			TCP[c]		
		1 Day	7 Days	50 Days	1 Day	7 Days	50 Days	1 Day	7 Days	50 Days
1	BTDA with MDA	0	0	0	0	1	1	0	0	0
2	BTDA with BDA	0	0	0	9	24	86	0	0	0
3	BTDA with HDA	0	1	3	58	63	44	0	0	0
4	BTDA with HDA and m-PDA	0	0	1	1	3	4	0	0	0
5	BTDA with ODA and m-PDA	0	0	0	1	2	4	0	0	0
6	BTDA and PMDA with HDA	0	1	2	199	187	208	1	0	0
7	BTDA and PMDA with ODA	0	1	4	150	208	211	1	0	0

[a]Percent weight gain
[b]BTDA = Benzophenonetetracarboxylic dianhydride
 PMDA = Pyromellitic dianhydride
  MDA = 4,4'-methylenedianiline
  BDA = 1,4-butanediamine
  HDA = 1,6-hexanediamine
[c]Tricresylphosphate

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 THE NEAT RESIN

- The surfuric acid solubility of the BTDA/HDA/m-PDA polyimide is sensitive to its method of preparation. Reaction of the BTDA with alcohol and subsequent reaction of the two amines with the ester-acid form of the BTDA leads to the PMR polyimide which is insoluble in surfuric acid. Preimidization of the aliphatic amine with the BTDA prior to addition of the aromatic amine leads to sulfuric acid soluble polymers.

- Cresol is required with the PMR approach to achieve tough polymers

- Both linear and PMR polyimides are compression moldable at temperatures as low as 260°C and 0.69 MPa. Increasing the molding temperature to 399°C does not reduce the melt flow properties of either the linear or PMR polymer.

4.2 COMPOSITES

- Fiber bundle impregnation by the resin, if not complete in the prepreg, is not completed by high pressure processing of the composite (up to 34.5 MPa).

- At fiber volumes of interest (i.e., 55+ percent) and with good fiber bundle impregnation, the prepregs surface may contain insufficient resin to produce void-free composites.

- Demonstration of successful compression molding of the neat resin does not indicate that a zero void composite can be prepared. The melt index of the resin no doubt plays a role in composite fabrication. However, more important is that the prepreg used in the composite is perfected, i.e., fully dense, uniform thickness and contains no volatiles.

- Shear testing of composites from the BTDA/HDA/m-PDA polyimide does not produce brittle failures and 5208-like properties were obtained at room temperature

4.3 PREPREGS

It should be noted that conclusions listed below do not apply to injection moldable thermoplastics but rather to condensation polymers where high molecular weight is achieved without regard to the melt viscosity of the neat polymer, i.e., condensation polyimides.

- Preparation of prepregs from high molecular weight, low solids content polyimide cresol varnishes does not produce complete fiber bundle impregnation. Even though the varnish may have originally impregnated the fiber bundles, the requirement to remove 80 plus percent of the varnish volume produces porosity in the fiber bundles.

- Increasing the solids content of the varnish which also requires use of monomers and or prepolymers can give good fiber bundle impregnation. The 50 plus percent solids PMR polyimide varnish is

very successful in this regard. Commercial prepregging equipment can be used to prepare prepregs from such varnishes.

- Removal of volatiles from the prepregs produces effects which may require use of high pressures to overcome. For instance the through-the-thickness shrinkage is not uniform due to the presence of fiber bundles and if the product is smoothed prior to final volatile removal it will not remain smooth with removal of more volatiles.

- High pressure processing of the program prepregs was successful in producing completely dense prepregs (34.5 MPa). Scale-up of such processing pressures to produce perfected prepreg however, is probably not within reach of available prepregging equipment.

- Preimidization of the HDA/BTDA prepolymer before addition of the m-PDA is required to reduce the moisture sensitivity of the prepregs produced. Moisture absorption changed the flow properties of the varnish and further lead to opacity in the resin rich areas of the prepreg with thermal staging.

4.4   OTHER POLYIMIDES

- Copolymers of equimolar quantities of PMDA and BTDA with HDA or 1,8-octanediamine did not produce the excellent solvent resistance exhibited by the homopolymers of PMDA with those diamines.

- The use of 1,4-butanediamine and 4,4-methylenedianiline as monomers or comonomers with other diamines with BTDA may be useful for maintaining good solvent resistance while increasing the elevated temperature compression properties of this class of thermoplastics.

- The flexible rigid segment approach to solvent resistant, low molding temperature thermoplastics is excellent. Shear yielding[2] of this polymer type will probably require further tailoring of the segments to achieve 5208-like properties at elevated temperature.

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15. Supplementary Notes

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16. Abstract

The polyimide from BTDA with 1,6-hexanediamine and m-phenylenediamine was selected from a prior study for the present study. Methods to prepare prepreg which would provide low-void composites at low molding pressures from the thermoplastic polyimide were studied. Cresol solutions of the polyimide were applied to a balanced weave carbon fabric and the cresol removed prior to composite molding. Low-void composites were prepared from smoothed prepregs at high pressures (34.5 MPa) and temperatures as low as 260°C. Lower molding pressures lead to higher void composites. Need for a lower melt viscosity in the neat resin is suggested as a requirement to achieve low-void composites at low pressures. Some mechanical properties are included.

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