CHARACTERIZATION AND DEVELOPMENT OF MATERIALS FOR ADVANCED TEXTILE COMPOSITES

J. Timothy Hartness
Timothy L. Greene
Leo E. Taske
BASF Structural Materials, Inc.
Charlotte, NC

INTRODUCTION

Work ongoing under the NASA Langley - Advanced Composite Technology (ACT) program is discussed. The primary emphasis of the work centers around the development and characterization of graphite fiber that has been impregnated with an epoxy powder. Four epoxies have been characterized in towpreg form as to their weaveability and braidability. Initial mechanical properties have been generated on each resin system. These include unidirectional as well as 8-harness satin cloth. Initial 2D and 3D weaving and braiding trials will be reported on as well as initial efforts to develop towpreg suitable for advanced tow placement.

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EPOXY POWDER CANDIDATES

Epoxy powders thought to be suitable for the BASF powder impregnation process were submitted for evaluation. All of the resins are considered developmental and are proprietary to the resin suppliers. Consideration has been given to acceptable neat resin properties, low moisture pick-up, and processability as well as unreacted glass transition (Tg). A room temperature solid is required that can be ground and delivered in an acceptable particle size. Shown in Table I below are those resin candidates being evaluated along with their neat resin properties.

Table I. Candidate Matrix Resins Physical Properties

	PR-500	RSS-1952	CET-3	High Tg
Tensile Strength (Ksi)	8.3	-	13	-
Modulus (Msi)	507	-	410	-
% Elongation	1.9	-	5	-
Flexural Strength (Ksi)	18.4	16.9	21	19.5
Modulus (Msi)	504	426	450	512
% Elongation	4.2	5.1	7	5.3
Density gm/cc	1.24	1.15	1.27	1.25
Moisture Absorption (%)	1.56	1.2	1.35	1.46
Glass transition cured °C (°F)	205(402)	219(425)	164(326)	243(470)

FUSED EPOXY TOWPREG

Epoxy resin powders are fused on to the unsized graphite fiber using a proprietary technique developed by BASF. The towpreg has been designed with handling and loss of resin the major considerations in a secondary operation. Fused epoxy towpreg examined by SEM after impregnation and then again after weaving into 8-harness satin cloth is shown in Figures 1 and 2. All towpreg must be rewound by most weaving and braiding operations with no significant resin loss or fiber damage. Composite resin contents indicate that no significant resin loss is occurring from initial towpreg manufacture through laminate consolidation.

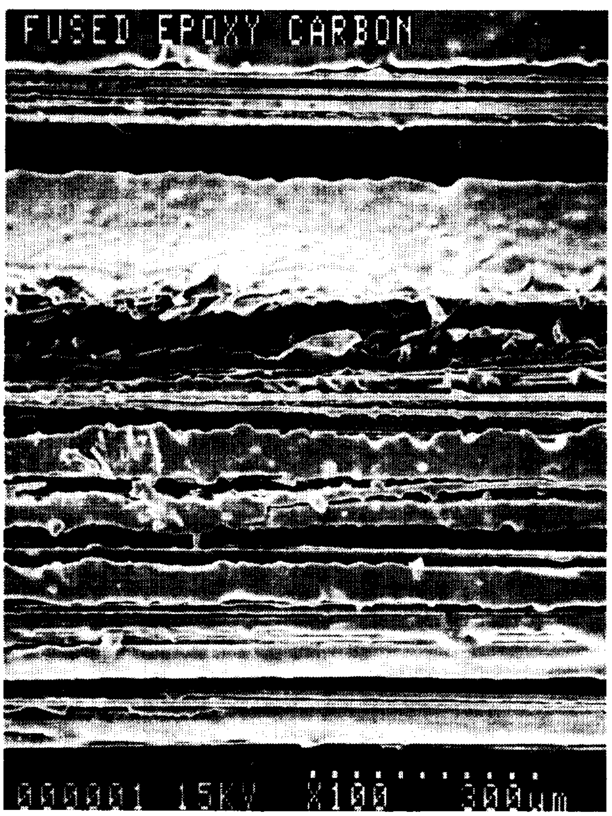

Figure 1. Initial fused epoxy towpreg before weaving.

Figure 2. Towpreg after weaving showing good wet-out.

TOWPREG HANDLING STUDY

A test was developed by Atlantic Research Corporation (ARC) to evaluate the handleability of the fused epoxy towpreg. A test was designed to simulate the rubbing or friction behavior that occurs during the braiding operation. One tow is held stationary under tension loads equivalent to the actual braid conditions while another tow is repeatedly passed over it and back similar to a bow passing over violin strings. Acid digestion of the resin was performed by BASF to determine resin loss. The results are shown in Table II below. Results indicate that no significant resin loss should be anticipated due to braiding. It is thought that the 80 rub abrasion condition is a worst case condition.

Table II. Tow Preg Assessment Matrix Digestion Results

SAMPLE	NO.	RESIN CONTENT (WT.%)	MATRIX LOSS (WT.%)
Virgin Tow Preg (RSS-1952/AS-4	1	35.9	
	2	35.4	
	3	36.3	
	Avg.	35.9	----
Bobbin Wound Only	1	35.5	
	2	35.1	
	3	36.1	
	Avg.	35.6	0.3
40 Rub Abrasion	1	36.2	
	2	35.2	
	Avg.	35.7	0.2
80 Rub Abrasion (Worst Case Level)	1	34.3	
	2	33.9	
	Avg.	34.1	1.8

INITIAL UNIDIRECTIONAL PROPERTIES

Each candidate material was initially characterized using an unsized Hercules AS-4 (6K) fiber. Fiber bundles were impregnated with a resin content of 35 ± 2% by weight. The higher resin content was chosen with cloth in mind in which a higher resin content is normally chosen to more easily wetout the more complex fiber architecture. Shown in Table III are the initial unidirectional properties generated.

Table III. Unidirectional Mechanical Properties

	PR-500/AS-4	RSS-1952/AS-4	CET-3/AS-4	High Tg/AS-4
3 Pt. Flexural Strength (Ksi)				
RT - Dry	233	234	206	250
180°F - Dry	248	207	-	-
180°F - Wet*	175	187	-	-
3 Pt. Flexural Modulus (Msi)				
RT - Dry	15.8	15.9	19.1	17.1
180°F - Dry	16.0	16.3	-	-
180°F - Wet	17.1	16.7	-	-
4 Pt. Shear Strength (Ksi) (16:1)	12.8	10.1	-	10.2
90° - 3 Pt. Flexural Strength (Ksi)	-	7	-	-
Fiber Volume %	56.4	52.0	61.9	60.3
Void Content %	<1	<1	<1	<1
Equilibrium Moisture Gain % *	0.65	0.55	-	-

*Underwater @ 160°F

FRACTURE TOUGHNESS

Fracture toughness using double cantilever beam (DCB) and end-notch flexure (ENF) was determined for the PR-500 and RSS-1952 matrix resins combined with AS-4 unsized fiber. After tow impregnation, the unidirectional composites were manufactured by winding over a removeable frame after being placed in a graphite molding tool. Teflon film was inserted at the mid-plane as a crack starter. Piano hinges were bonded on the DCB specimens. The DCB specimens were .5" x 8" x .125" while the ENF were 1" x 8" x .125". The DCB data was reduced using ASTM compliance with the ENF data being reduced by Beam Theory. Both systems fall into the brittle resin family which was not surprising. Shown in Table IV is the generated data. Evaluation of the other two resins is ongoing.

Table IV. Fracture Toughness of Unidirectional Composites

	PR-500/G30-500	RSS-1952/AS-4
Mode I (DCB)		
Avg G_{1C} (in lbs/in^2)	1.19	1.16
Std. Dev.	0.12	0.34
	(12 data points)	(48 data points)
Mode II (ENF)		
Avg G_{2C} (in lbs/in^2)	5.64	3.53
Std. Dev.	1.05	0.36
	(23 data points)	(16 data points)

THERMAL ANALYSIS

Composite samples fabricated from PR-500/AS-4 and RSS-1952/AS-4 were analyzed to determine a dry and wet glass transition (Tg) temperature. Analytical techniques consisting of Differential Scanning Calometry (DSC), Thermal Mechanical Analysis (TMA), and Dynamic Mechanical Analysis (DMA) were compared. Wet glass transition was established using the DMA with a heating rate of 50°C/minute in both the dry and wet condition. The temperature was selected to simulate the time/temperature profile of a specimen being tested hot/wet in a flexural or shear test. Shown in Table V are the results. The change in Tg after moisture aging was 16°C and 20.6°C for the PR-500 and RSS-1952 respectively.

Table V. Thermal Analysis DMA

Heat Rate °C/Min	PR-500/AS-4 Tg °C (G'Onset)/Tan Δ Peak	RSS-1952/AS-4 Tg °C (G'Onset/Tan Δ Peak
2 (dry)	195/219	207/226
10 (dry)	211/228	221/233
50 (dry)	231/247	241/250
50 (wet)	215/230	220/230

(3 specimens/data point)

		PR-500/AS-4 (Tg)°C	RSS-1952/AS-4 (Tg)°C
DSC	2 (dry)	192	207
DSC	10 (dry)	197	211
TMA	2 (dry)	174	163
TMA	10 (dry)	-	173

2D WEAVING

Initial weaving studies were conducted using Hercules AS-4 (6K) unsized fiber. This choice was based on a compromise between fiber coverage and cost as well as the decision to use a 6K fiber in some of the 3D weaving and braiding. A rule of mixture analysis indicates a similar property translation as compared to a 3K fiber selection. In the 6K selection, a 10 x 10 construction is used versus a 20 x 20 or 24 x 24 picks per inch. Hot/wet properties seem to be lower than expected with a percent of RT-dry being 49% and 69% for the PR-500 and RSS-1952 respectively. Percent translation with the unidirectional composite was 75% and 80% respectively. The difference may be explained in terms of edge effect where twice as many edges are exposed to moisture and the moisture profile and diffusion rates vary versus the unidirectional condition. Further study will be conducted on this issue.

Shown in Table VI are 8-harness satin cloth properties generated to date.

Table VI. Mechanical Properties 8-Harness Satin Cloth

	PR-500/AS-4	RSS-1952/AS-4
3 Pt. Flexural Strength/Modulus		
RT - Dry (Ksi/Msi)	107/7.3	99/7.5
180°F - Dry	103/7.3	90/7.5
180°F - Wet	53/6.7	68/7.4
325°D - Dry	71/7.2	-
325°F - Wet	36/6.3	-
4 Pt. Shear Strength (16:1)		
RT - Dry (Ksi)	6.0	5.6
180°F - Dry (Ksi)	3.0	-
Fiber Volume %	56	52
Void Content %	<1	<1

TENSILE & COMPRESSION MECHANICAL PROPERTIES 8-HARNESS SATIN CLOTH

Tensile and compression properties were generated for 8-harness satin cloth using 6K towpreg. A quasi-isotropic layup consisting of 20 plies with a shorthand nomenclature of $[45, 0]5_s$ was used. This resulted in a panel thickness of approximately 0.25". Panels C-scanned clear and were cut according to NASA specifications (1" x 9" x 1/4" Tensile, 1.5" x 1.75" x 1/4" Compression). Five specimens were tested per data point. Data is shown in Figure 3. Tensile specimens were tested without tabs in hydraulic grips. The effect of the 6K crimp needs to be considered when examining this data. The 180°F wet property is surprisingly low as compared to unidirectional properties.

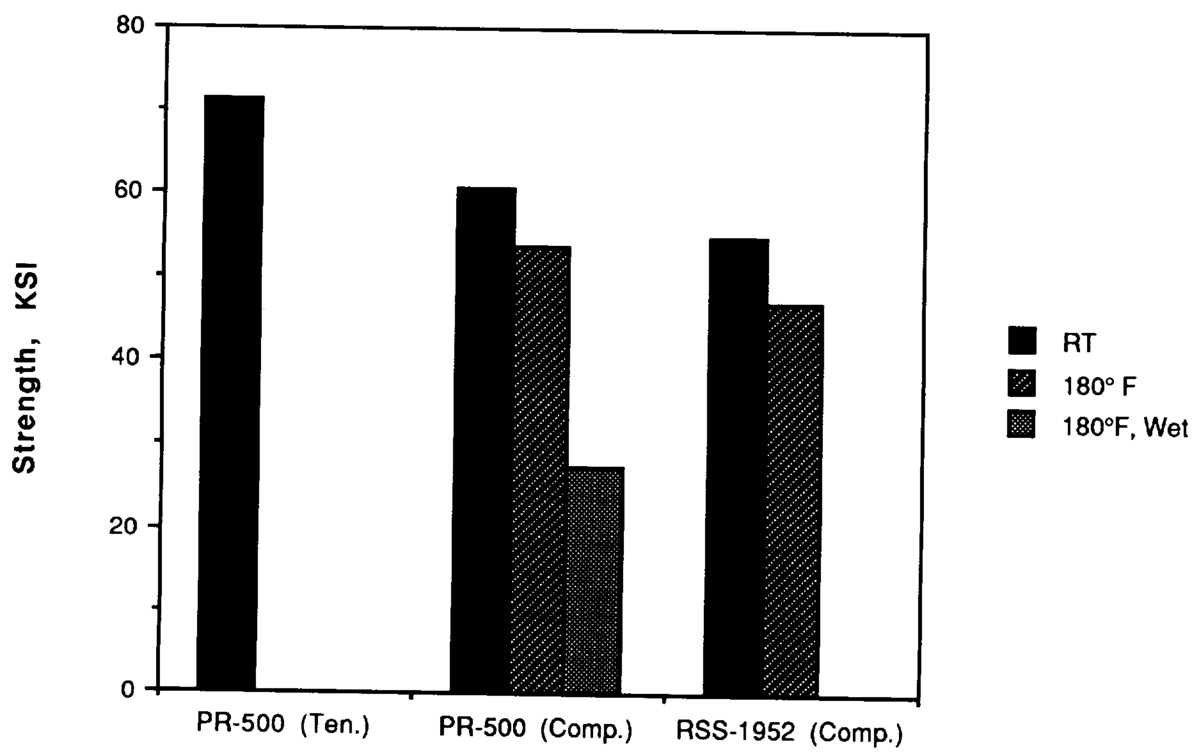

Figure 3. Tensile and short block compression properties on 8-harness satin cloth quasi-isotropic lay-up.

ADVANCED TEXTILE PREFORM EVALUATIONS

A study was initiated for evaluating the use of powder epoxy towpreg in more advanced and rigorous textile processes such as braiding and 3-D weaving. The following areas were seen as key issues for each preforming method:

- Tow Handling Characteristics
- Powder Loss Potential
- Preform Consolidation Process Development

3-D woven preforms produced by Textile Technologies, Inc. and braided preforms produced by Fiber Innovations were used for this initial evaluation work.

3-D WOVEN PREFORM CONSTRUCTION

A three inch width multilayer 3-D construction was chosen for preliminary feasibility evaluations. The particular architecture chosen utilized both 3K and 6K powder epoxy towpreg with a nominal 39% (by weight) resin content. Shell RSS-1952 powder epoxy was the resin used. Preform construction was as follows: (See Figure 4).

- 6K tow for both warp and fill, with a 14 x 14 tows/inch construction
- 3K tow for "Z" direction fiber, 7 tows/inch construction
- Nominal (cured) thickness calculated at .040"

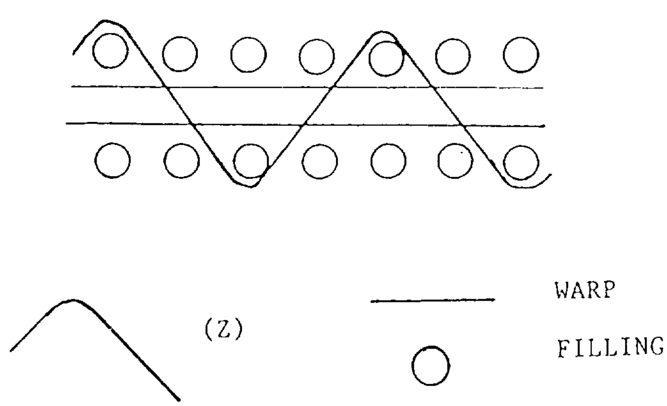

Figure 4. Multilayer 3-D preform fiber architecture.

BRAIDED PREFORM CONSTRUCTION

Powder epoxy tow was evaluated in both biaxial and triaxial braid constructions to determine suitability for use in a braiding process. The tow was braided on a 1" diameter mandrel, with the resulting braided sleeving slit open and laid flat for consolidation. Initial preform specifics were as follows:

- 24 carrier machine, 1" diameter mandrel
- 24 ends at +/- 68° used for biaxial sleeving
- 24 ends at +/- 68° plus 12 ends at 0° used for triaxial sleeving
- 6K towpreg, 39% (weight) resin content used for both constructions

Shown below in Figure 5 is a picture of a braided epoxy preform prior to cure.

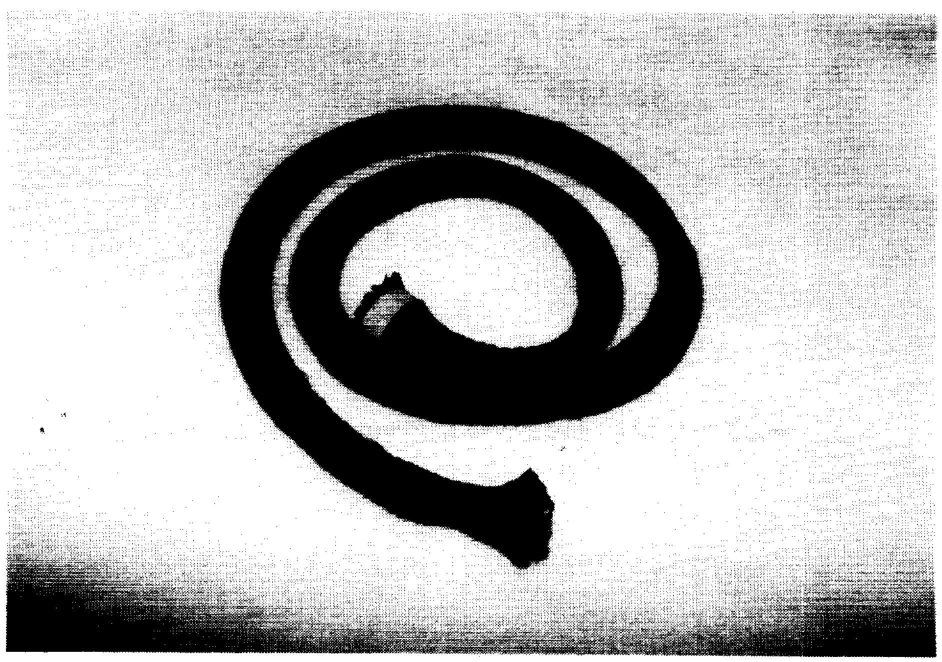

Figure 5. Braided powder epoxy preform prior to cure.

PREFORMING RESULTS

Handling characteristics of the powder epoxy tow were evaluated through the use of the braiding and 3-D weaving processes. Issues such as powder loss and fiber damage as a result of "working" of the towpreg in the process as well as basic feasibility concerns were addressed.

- 3-D multilayer fabric and biaxial/triaxial braids were sucessfully produced
- Minimal fiber damage and powder loss (< 1%) noted
- High friction noted in braiding process due to powder fused to filament surfaces
- Bulk factor of unconsolidated preforms can be as much as 2.5 x cured thickness

CONSOLIDATION PROCESS DEVELOPMENT (3-D FABRIC)

A cure cycle developed in previous work for manufacture of void-free 8-harness powder epoxy laminates was used for initial 3-D multilayer preform cure evaluations. Resulting 3-D laminates had unacceptable void content. A major difference in cured laminate quality as a result of the more complex fiber architecture was shown.

- Standard 8-harness cure cycle unsuccessful with 3-D material
- Voids consistently located at intersection of "Z" direction tows and fill-direction tows
- Buckling of "Z" direction tows noted due to initial bulk factor and resulting compaction during cycle

Shown below in Figure 6 is a cross-section of a 3-D multilayer preform cured with a "standard" powder epoxy cure cycle.

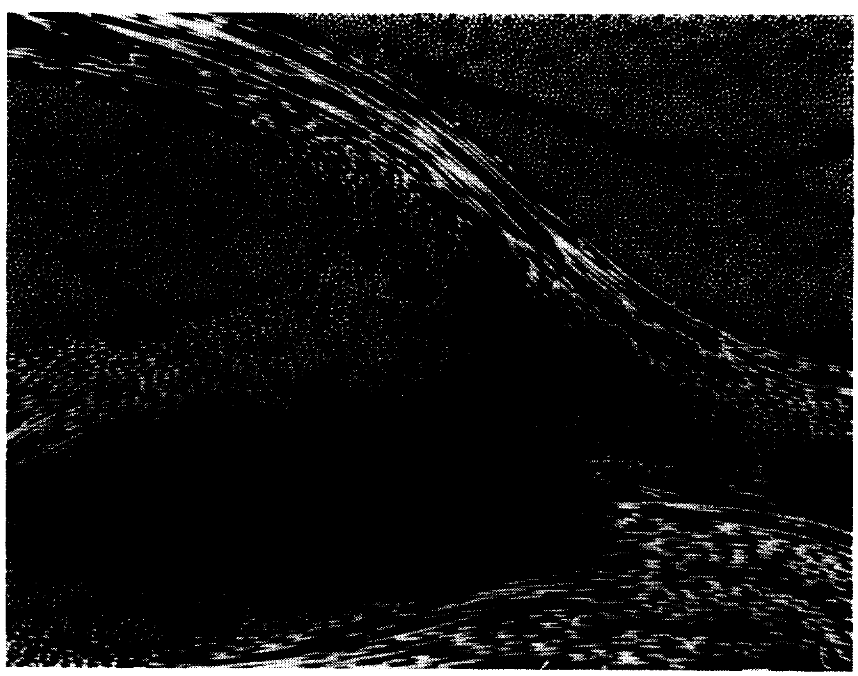

Figure 6. Initial 3-D multilayer preform cross section showing voids at "Z" fiber and fill fiber intersections.

CONSOLIDATION PROCESS DEVELOPMENT (CONTINUED)

Several processing trials were run to develop parameters for producing void-free 3-D laminates. Higher pressure and the addition of narrow (1") 120-style fiberglass cloth strips on two sides of a laminate to act as a breather/bleeder for removal of air from the preform were found to be necessary for good autoclave consolidation. Although the optimized process produced void-free panels in an autoclave, panels cured in a platen press under identical processing conditions (with the exception of vacuum) still had poor surface wet-out and areas of large voids. Apparently evacuation of air from the preform prior to resin flow is necessary for void-free consolidation with this particular fiber architecture, although this was unnecessary with 8-harness fabric. Work to understand the processing/preform architecture relationship continues.

- Autoclave processing/bagging procedures optimized for high quality 3-D laminates preform consolidation (pressure increased to 150 psi, breather strips added)
- Successful process not achieved to date in platen press
- Apparent requirement for evacuation of air from preform prior to resin flow for this architecture

Shown in Figure 7 is a 3-D panel cross-section using an optimized autoclave cycle.

Figure 7. Cross-section 3-D woven panel cured using optimized autoclave process.

MANUFACTURING PROCESS DEVELOPMENT

Development and evaluation of part-manufacturing methods using the powder epoxy towpreg materials are underway. Due to the high bulk factor inherent in this material form, debulking methods were initially addressed. Through a series of analytical and emperical experiments, a vacuum debulking process has been established for the three materials currently under evaluation (PR-500, RSS-1952, CET-3). Vacuum debulking has been performed primarily by means of a silicone rubber diaphragm bonded to a picture frame, with the diaphragm allowed to elongate and deform around a male debulking mold after heating to the required temperature range. Work to date suggests multiple debulking cycles may be performed before the resin advances to a point that flow is inhibited during final cure.

- Debulk at 200°F under vacuum
- Multiple debulk cycles

Shown in Figure 8 is an integrally stiffened preform after vacuum debulking, prior to cure.

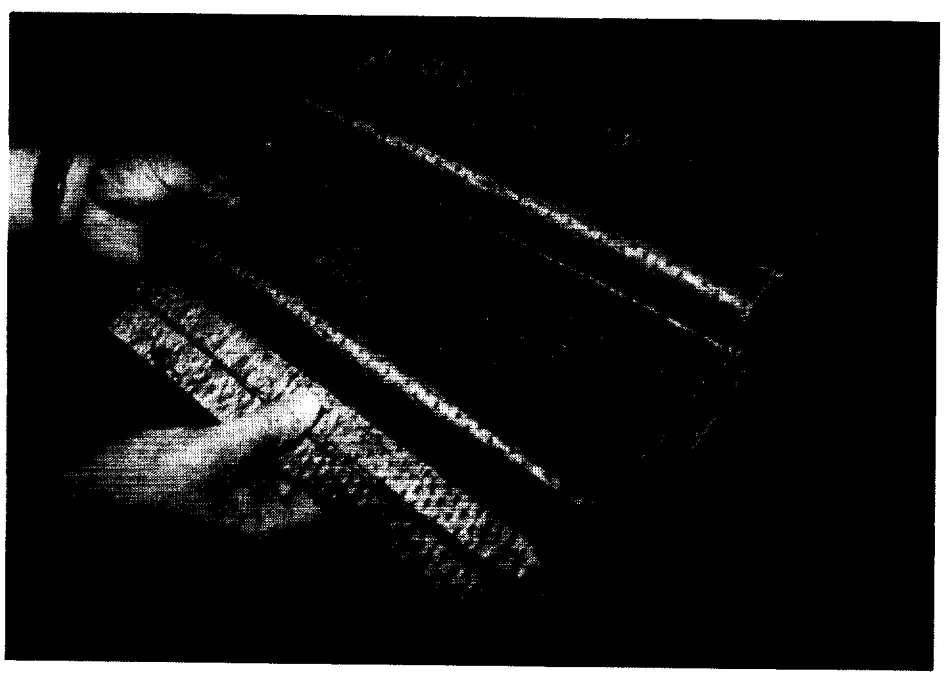

Figure 8. Vacuum debulked preform prior to cure.

DEMONSTRATION PARTS

Press and autoclave part fabrication evaluations are also underway using established processing techniques as well as relatively new approaches including diaphragm forming and stamping. Shown below in Figure 9 are typical epoxy powder parts produced using textile approaches.

Figure 9. Typical parts fabricated using powder epoxy materials.

STATUS

- A viable process has been developed to manufacture a towpreg suitable for textile composites.
- Ongoing evaluation of initial candidate epoxy powders for composites.
- Ongoing effort to demonstrate manufacturing technology using woven, braided, and stitched powder preforms.
- Initial work started to develop a suitable product for advanced tow placement and filament winding.

FUTURE PLANS

- Ongoing project to increase towpreg production 3x over present process.