Carderock Division Naval Surface Warfare Center

Bethesda, Md. 20084-5000

NSWCCD-TR-65-96/23 September 1996 Survivability, Structures, and Materials Directorate Technical Report

An Evaluation of Low Energy Cure Glass Fabric Prepregs

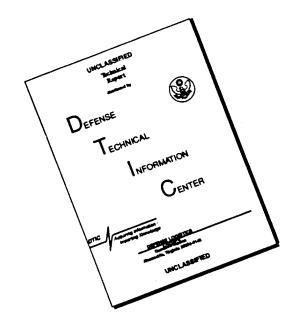
by Thomas Juska Doug Loup Steven Mayes

19961104 003



Approved for public release; distribution unlimited.

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

CONTENTS

page
ABSTRACT
EVALUATION PROCEDURE
RESULTS AND DISCUSSION. 7 WR/LTM21. 8 7781/LTM22. 10 7781/Ampreg 75. 12 Neoxil Prepreg. 14 7781/NB-1101. 16 7781/NB-1107. 18 7781/M10E. 20 7781/RS-1. 22 7781/SP377. 24 1581/E-761E. 26 WR/P-601. 28 7781/P-600. 30 7781/MXB-9420. 32 1583/SP365. 34
ALTERNATIVE CURING METHODS
PROPERTIES OF CARBON FABRIC LAMINATES
IMPACT DAMAGE RESISTANCE
SUMMARY AND CONCLUSIONS
APPENDIX A. THERMAL ANALYSIS

TABLES

		page
1. 2. 3. 4. 5. 6. 7. 8. 9. 11. 12. 13. 14. 15.	Properties of WR/LTM21	11 13 15 17 19 21 23 25 27 29 33 35 37 39
B1.	Properties of the materials evaluated in this study	. 50
	FIGURES	. 9
1. 2. 3. 4. 5.	A micrograph of WR/LTM21 at 30X magnification	11 13 15 17
7. 8. 9.	A micrograph of 7781/M10E at 30X magnification	. 23 . 25
11. 12. 13.	A micrograph of WR/P-601 at 30X magnification	. 29 . 31
14.	A micrograph of 1583/SP365 at 30X magnification	. 35 . 39
17. 18.	Effect of porosity on impact damage area Effect of resin failure strain on impact damage area Effect of post-cure on impact damage area	. 41 . 42
A1.	Modulus-temperature behavior of 7781/NB-1101 as- fabricated, after post-cure, and after water boil Modulus-temperature behavior of 7781/LTM22 as-	
	fabricated and after water boil	
	fabricated after post-cure and after water boil	. 49

ABSTRACT

Low energy cure glass fabric prepregs were evaluated. These materials were formulated to cure at low temperatures, from 140 °F to 220 °F, and under vacuum bag pressure. Several of these material systems are now commercially available and have potential applications in high quality, low cost fabrication of surface ship structures. Most of the prepreg resins are epoxy, but polyester and vinyl ester laminates were included in the evaluation. The test laminates were fabricated with a warps parallel lay-up and tested in tension, compression, flexure, and impact. Limited in-plane shear testing was done, particularly to assess the advantage of a quasi-isotropic vs. warps parallel Thermal analysis was used to stacking sequence. determine as-fabricated, post-cured, and moisture conditioned values of Tq. Single-sided prepreg and notack prepreg were identified as useful material forms for achieving low void content under vacuum bag pressure. The low cure temperature of the prepregs allows vacuum bag fabrication of sandwich panels with a variety of foam cores.

ADMINISTRATIVE INFORMATION

This work described herein was initiated as part of the Ship and Submarine Materials Technology Program sponsored by the Office of Naval Research (ONR 332). The ONR sponsor is Mr. James Kelly and the Carderock Division Technology Manager is Mr. Ivan Caplan (Code 0115). The work was continued to support the Organic Composite Ship Structures Project (RH21S12), Navy Program Elements 0621221N and 062121N sponsored by ONR 334 (J.E. Gagorik). The work was performed by CDNSWC Code 655, supervised by the Section Head, Dr. Roger Crane.

INTRODUCTION

Glass reinforced plastic (GRP) boats are usually fabricated by hand lamination with E-glass fabric and resins which cure at ambient temperature. Due to increasing state and federal restrictions on the emissions of volatile organic compounds (primarily styrene in the case of GRP) alternative fabrication methods are now being developed, such as vacuum assisted resin transfer molding and vacuum bag molding with low energy cure prepregs. In this study we evaluated a number of prepregs for use in ship structures.

Prepreg fabrication is already in limited use in boat building, where the major application appears to be high performance racing sailboats. However, the materials used in these boats are relatively expensive and therefore are not used in typical marine construction. For example, in America's Cup class yachts carbon/epoxy tape is used in the hull, mast, frames, keel, and boom, and the standing rigging is pultruded Kevlar/epoxy (1).

Use of glass fabric prepreg, as a substitute for current materials/fabrication methods, is less common in boat building. There have been some boats built with glass/epoxy prepreg, however, and its use appears to be on the rise in Europe (2). series of 12 meter Fast Carriage Boats (FCB), named the Mersey Class, were built from 1989-1992 for the Royal National Lifeboat Institute (RNLI). The success of the Mersey Class FCB led to two new series of prepreg boats for RNLI, the Trent Class (14m) and the Severn Class (17m). These three classes were built with SP Systems Ampreg 75 glass/epoxy prepreg skins and a crosslinked PVC core in the hulls, decks, bulkheads, and superstructures. Danish Navy has an 18m auxiliary mineclearance vessel (the SAV2) built by Dannyard using Ampreg 75 and crosslinked PVC foam, and the Swedish Navy is building a series of 10m fast attack troop landing craft with the same materials. The Swedish Rescue Authority is building three 16m fast rescue boats with a prepreg/PVC sandwich construction, and the Swedish Customs Authority selected a prototype 14m fast coast guard boat that has glass/epoxy outer skins and carbon/epoxy inner skins. An example of prepreg construction in commercial boatbuilding is the superstructure of the Stena Sealink, a 120 meter fast ferry catamaran, fabricated by Finnyards with SP Systems SE 84 over both balsa and aluminum honeycomb cores. In the U.S. boat building industry we could find only one recent example of glass fabric prepreg construction, a 25' Navy patrol boat built by Eric Goetz Custom Sailboats for the Atlantic Boat Group (3). However, there were several boats built in 1983-1985 by Lazzara Marine with E-glass/epoxy prepreg made by McCann MFG (4).

In addition to these boats, glass fabric prepreg has been used in other marine applications, for example by the U.S. Navy in submarine sonar bow domes and other fairings.

High performance aerospace prepred resins cure at 350 °F or higher. A second class of aerospace/commercial prepreds cure at 250 °F. The high curing temperatures preclude these types of materials from consideration for fabricating large naval structures such as deck houses, masts, hulls, etc.

The prepregs evaluated in this study were as a rule recently developed and can be considered to form a third class of prepreg, characterized by cure temperatures which range from 140 °F to 220 °F. They are called low energy cure prepregs because in addition to the low cure temperature, they have been formulated to consolidate under vacuum bag rather than autoclave pressure.

EVALUATION PROCEDURE

With two exceptions, the materials evaluated were obtained as B-staged prepreg and subsequently cured with vacuum bag pressure at conditions recommended by the manufacturer. Since vacuum bag consolidation can result in relatively high void contents, several of the materials were also cured with 90 psi pressure to assess the effect of void content on mechanical properties.

The lamination schedule oriented all plys with their warp directions parallel, and the mechanical properties were then measured in the warp direction. One of the materials evaluated was tested with a quasi-isotropic layup. The materials were

tested in compression, tension, flexure, and impact. In-plane shear testing was limited to a comparison of the strength and stiffness of a quasi-isotropic laminate to a warps parallel laminate. Fiber and void contents were also measured. Thermal analysis was done to determine the as-fabricated (dry) glass transition temperature (Tg), the Tg after post-cure (maximum dry Tg), and the Tg after a 72 hour water boil. In addition, scanning electron microscopy was used to investigate fabrication quality.

MATERIALS

The prepreg resins tested in this study are mostly rubbermodified, bisphenol A epoxy except where noted, but two
polyesters and one vinyl ester were included. Most of the
epoxies are cured with latent catalysts, particularly
dicyandiamide, but based on the manufacturer's recommended cure
conditions it is clear that other curing agents were used. The
polyesters and vinyl ester were formulated with a high
temperature initiator. It is important to note that polyesters
in prepregs use diallylphthalate (DAP) monomer, as opposed to
styrene. The mechanical properties of the polyester laminates
generally exceeded those of the epoxies, which we believe is due
to the relatively high failure strain of DAP-based polyester.
DAP is unsuitable as the monomer in laminating resins because it
has a high viscosity.

B-Staged Prepreg

B-staged prepreg is the typical material form used in the advanced composites industry. The resin in B-staged prepreg is "advanced", or partially reacted, by the manufacturer to limit resin flow during the lay-up of the part. At elevated temperature the viscosity drops, which facilitates void removal and compaction.

A-Staged Prepreg

The resin in A-staged prepreg is not advanced. A-staged prepregs are rarely used, but are appropriate for low cost manufacturing of large structures: void removal is facilitated by the low viscosity, that is, a vacuum bag is not necessary for compaction, and the time-consuming and variable wet-out step is eliminated.

The two A-staged materials included in the study were Neoxil Prepreg (DSM Italia) and Sunpreg (Sunrez, Inc.). Neoxil Prepreg and Sunpreg are novel material forms which are supplied as wetout fabrics, and will be described in some detail.

Normally A-staged prepreg is made by the fabricator, with an impregnator, and applied to the structure soon after the impregnation. A-staged epoxy prepregs are used to make high performance racing sailboats (3), and A-staged polyester prepregs are used to make large (70'-140') motor yachts (5), and were used in the fabrication of the U.S. Navy MHC 51 Class Coastal Minehunter (6).

Fabrics

Style 7781 fabric (8.9 oz/yd²) was the reinforcement in most of the materials tested, but also evaluated were Style 1581 (8.9 oz/yd²), Style 1583 (16.1 oz/yd²), and two woven rovings (24 and 18 oz/yd²). E-glass roving fabrics, woven or stitch-bonded, are the most suitable reinforcement for marine construction due to their low cost, large ply thickness, and acceptable mechanical properties. Use of yarn-based textile fabrics such as 7781 should (we believe) be limited to applications which require their superior drape or for their ability to achieve closer thickness tolerance. The mechanical properties and impact damage resistance of laminates reinforced with woven roving and woven yarn are comparable (7).

The finish on the textile fabrics was Z6040, with two exceptions discussed later. Z6040 is a glycidyl silane (a molecule with a silane group at one end which bonds to glass, and an epoxy group at the other end which reacts with curing agents in the resin). This is the recommended finish for epoxies, and it is specified for use in sonar domes by the U.S. Navy (HMS 20.04-16 rev. C). Testing at CDNSWC has shown that fiber/matrix adhesion in glass: Z6040/epoxy composites is not significantly degraded by extended water immersion (8).

Prepreg Manufacturers*

We attempted to evaluate a wide variety of low temperature cure prepregs but it must be realized that there are several suitable materials which were not included in this study. The manufacturers of the prepregs tested are given below.

MANUFACTURER Advanced Composites	ADDRESS 5350 S. 129th E. Avenue	PHONE 918-252-3922
Group, Inc.	Tulsa, OK 74134	710 202 0722
Ciba Composites	5115 E. La Palma Ave. Anaheim, CA 92807	714-779-7183
DSM Italia srl	via Silvio Pellico 12 22100 Como-Italy	031-236208
Fibercote Industries, Inc.	172 E. Aurora St. Waterbury, CT 06708	800-755-1344
ICI Fiberite	2055 E. Technology Circle Tempe, AZ 85284	602-730-2000
3M Aerospace	3M Center Bldg. 223-1S St. Paul, MN 55144	612-733-1110
Newport Adhesives and Composites, Inc	•	714-957-1722
SP Systems, Inc.	Love Lane, Isle of Wight England P031 7EU	0983-298453
Sunrez Corp.	1374 Merritt Drive El Cajon, CA 92020	619-442-3353
YLA, Inc.	2970 Bay Vista Court #C Benicia, CA 94510	707-747-2750

^{*} Selection of a material for evaluation does not imply endorsement on the part of the Naval Surface Warfare Center.

Two notable suppliers whose materials were unfortunately not included in the evaluation are J.D. Lincoln (714-650-8106) and Bryte Technologies (408-434-9808).

FABRICATION

The laminates made from B-staged prepreg were cured at stable temperatures in an oven. Each material was used to fabricate a laminate consolidated with vacuum bag pressure only. Duplicate laminates were fabricated from many of the prepregs, but were consolidated with autoclave conditions (90 psi). The lay-ups were not debulked. A heat-up rate of 3 °F/minute was used throughout, and the temperature was ramped to the cure temperature without holding at an intermediate temperature. bagging sequence was: peel ply, perforated release film, prepreg lay-up, perforated release film, peel ply, and vacuum bag. Vacuum was transmitted with an edge breather, and a silicone rubber dam surrounded the layup to prevent resin flow out of the The release film was used against the prepreg because the resins are generally high flow and toughened, which were found to penetrate peel ply, making release difficult. A caul plate was not used so that the fabrication would simulate that of a large structure. Also, caul plates can result in an uneven pressure distribution on the lay-up, in the case of vacuum bag molding, due to the presence of surface irregularities (9).

"Cure Temperature"

Epoxy and polyester resins do not have naturally definable cure temperatures. The rate of reaction of a given resin depends on the temperature, and most "cure temperatures" are specified as the temperature at which the resin will cure (essentially) completely in a reasonable period of time. Within limits, lower temperatures and longer times will also completely cure the resin. There is a rule of thumb that for every 18 °F decrease in temperature the cure time is doubled (10).

A further complication in the definition of cure temperature arises over the issue of degree of cure. If the temperature was not high enough and/or the time was insufficient, the resin will not reach full conversion. This is a very common occurrence in the composites industry. In particular, many room temperature curing formulations will not fully cure under ambient conditions.

The DMTA data indicate whether the material analyzed contains an uncured component because post-curing will result in an increase in Tg. (The post-cured value of Tg was determined by rescanning the sample.) The resin Tg continues to increase with degree of cure until the resin has fully reacted, which makes the value of Tg a simple and effective indicator of cure state (11).

Many aerospace applications require performance at elevated temperatures, so the usual practice in that industry is to fully cure the resin. However, a fully cured resin is not essential if elevated temperature performance is not required. Unlike resin Tg, laminate mechanical properties are not proportional to the degree of cure. As will be shown, the manufacturer's recommended cure conditions did not fully cure most of the materials

evaluated in this study, but testing of laminates has shown that post-curing had a negligible effect on mechanical properties. This has also been shown with a "350 °F curing" prepreg, which attained full mechanical properties when cured (for 18 hours) at 300 °F (10).

Use of lower than normal temperatures can allow previously incompatible materials combinations, such as epoxy prepreg with PVC foam core, but this technique should be used with caution. Although full resin cure is unnecessary for most applications, it is also true that a substantially under-cured polymer does not make an acceptable composite matrix resin. A specific minimum value of Tg or degree of cure cannot, however, be recommended at this time.

In addition to as-fabricated and post-cured values of Tg, we have reported transition temperatures after water absorption. The conditioning was done with a 72 hour water boil, which probably saturated the resin. We note that the samples post-cure during the water boil conditioning. Water absorption by undercured resin may result in a greater reduction in Tg than reported here.

FIBER CONTENT AND PERCENT VOIDS

Fiber weight percent and void volume fraction were determined with specific gravity measurements (ASTM D 792) and ignition loss (ASTM D 2584) and the data reduction method specified in ASTM D 2734. Resin density values were provided by the manufacturer. Negative void contents are reported for some of the materials. This is a common occurrence, which we interpret as near zero porosity, caused by the precision of the measurements and variability in resin and glass densities.

MECHANICAL PROPERTY DETERMINATION

Compression testing was done with the ASTM D695 methodology These "dogbone" specimens are end-loaded and side-supported, with nominal dimensions of 3.13" overall length and 0.5" wide in the gage section.

Tensile strength was measured with the ASTM D638 methodology. These are dogbone specimens machined from 6" long, 3/4" wide coupons using a Tensilcut router and a template. The final widths are nominally 1/2". Tensile strains were measured with an extensometer, and Young's moduli determined by linear regression between 1000 and 3000 microstrain.

Flexural strength was measured with the ASTM D790 procedure (three point bending). The sample dimensions were about 5.5" long and 0.5" wide. The span used was 4.5". For a nominal specimen thickness of 0.15", which was typical, the span-to-depth ratio was about 30.

In-plane shear strength and stiffness were determined with ASTM D 4255 (rail shear).

IMPACT TESTING

Impact testing was done with a Dynatup Model 8200 drop tower.

The drop weight was 15.2 lbs., and the impactor was a hemispherical tup with a diameter of 0.5". Impact specimens were 6"x4" panels clamped over a 5"x3" opening. Four spring-loaded clamps secure the specimen over the rectangular hole, two along each of the 6" sides of the panels.

The tests were done at levels of 1000, 2000, 3000, and 4000 in.lbs/in. Impact "level" is the energy in inch-pounds divided by the sample thickness in inches. The data is presented by plotting the area of the damage zone vs. impact level. The damage zone, clearly visible through the translucent panels, was quantified by measuring four diameters (D) through the impact damage zone (at 0°, 90°, and ± 45 ° with respect to the 6" dimension), taking the average of these four numbers (Da) and computing the area $\pi D_a^2/4$.

THERMAL ANALYSIS

Thermal analysis was included in the evaluation to determine the as-fabricated glass transition temperature (Tg), the maximum Tg, and the effect of water absorption on Tg. The value of Tg controls the upper use temperature of the laminate. Samples were tested with dynamic mechanical thermal analysis (DMTA), which also generates qualitative information about the degree of cure. The cure state of the resin is a concern given the low cure temperatures and relative lack of industry experience with the materials in this study.

A Polymer Labs MKII Dynamic Mechanical Thermal Analyzer (DMTA) was used to measure the thermal behavior of the cured prepregs. Samples were tested in the single cantilever beam mode at 10 Hz with a 3 °C/min (5 °F/min) heat rate.

The DMTA determines the "storage modulus" (E') as a function of temperature. E' is essentially Young's modulus. As shown in Appendix A, E' is constant with temperature until the glass transition, during which it decreases abruptly. Since the purpose of the thermal analysis was to determine approximate upper use temperatures of the materials evaluated in this study, Tg was defined as the temperature at which the modulus starts to decrease. This is discussed in more detail in the Appendix. It has been shown that Tg so-defined correlates very well with the heat deflection temperature (ASTM D 648-82) (12).

MICROSCOPY

Scanning electron microscopy was used in conjunction with void content measurements to assess the quality of the fabricated panels. All the micrographs were taken at 30X magnification so void sizes can be compared.

RESULTS AND DISCUSSION

Tabulated values of mechanical and thermal properties follow, together with a discussion of the cure conditions and material characteristics. The study was intended as a survey of available low energy cure prepregs, so the properties reported herein should not be interpreted as design values.

WR/LTM21 (Advanced Composites Group, Inc.)

The Advanced Composites Group, Inc, specializes in epoxy prepregs which cure at just above ambient temperature. The catalyst used in LTM21 causes rapid advancement at low temperatures, and will gel the epoxy if held overnight at 110 °F (13). The low cure temperatures limit the room temperature working life to 1-2 days, but allow the use of conventional, low cost polyester tooling. After the part is demolded, it should be post-cured for about 4 hours at 140 °F to increase mechanical properties and heat deflection temperature (13).

The reinforcement tested was a woven roving material (ACG, Inc. designation GFS002), which is a 24 oz/yd² 2x2 twill with a balanced construction of 10 ends per inch (epi) in both warp and fill. A 12" x 12" panel was made with 6 plys of prepreg, at about 22 mils/ply, with a warps parallel lay-up. It was fabricated under vacuum bag pressure at 140 °F for 8 hours.

The mechanical properties (measured in the warp direction), weight percent fiber and void content, and thermal properties are given in Table 1. The mechanical properties did not indicate unfavorable effects of the low cure temperature. The void content, 0.9%, is very low for vacuum bag molding, with the voids located in the resin rich areas as shown in Figure 1. The weight percent fiber is relatively high, with a correspondingly high Young's modulus.

The thermal properties of LTM21 are notable for the high value of Tg which results from a 140 °F cure temperature, and for their high ultimate Tg after post-cure. The LTM20 series are modifications of tooling prepreg technology, which are designed for high temperature performance. The as-fabricated value of Tg in Table 1 was taken as the temperature at which the modulus shows a slight decrease, about 189 °F (87 °C). In contrast, epoxy laminating resins cured at 140 °F have significantly lower values of Tg (about 150 °F), due mostly to the diluent required for fabric wet-out. The highly reactive resin advanced (postcured) during the measurement, resulting in a maximum Tg of over (The maximum Tg of laminating resins varies from about 300 °F. 150-190 °F). The high post-cured value of Tg, the highest of all the materials in this study, is indicative of multi-functional epoxies. Water boil caused a drop in Tg of about 75 °F. large drop in Tg due to water absorption is also indicative of the presence of TGMDA or novolac epoxy in the formulation, which absorb more water than bisphenol A epoxy formulations.

The large increase in Tg after post-cure indicates that the laminate fabricated at 140 °F had a relatively high degree of "under-cured" resin. The effect of moisture on the unreacted components of the resin may be significant. However, the water boil conditioning may tend to mask the effects of water by advancing the cure. For future studies it may be preferable to assess moisture effects under more realistic temperature conditions.

Table 1. Properties of WR/LTM21.

COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	59.9 2.1
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	76.0 3.1
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	74.8 4.0
TENSILE MODULUS (msi) (MEAN)	4.2
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	77.9 0.3
VOID CONTENT (%) (MEAN) (STD DEV)	0.9 0.2
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED)	189 306
(°F) (AFTER 72 HR BOIL)	225

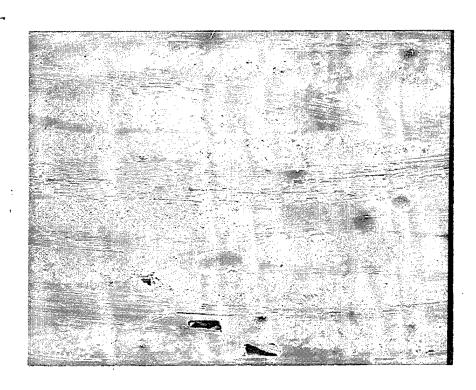


Figure 1. A micrograph of WR/LTM21 at 30X magnification.

7781/LTM22 (Advanced Composites Group, Inc.)

There are several materials in the LTM series, namely, LTM21, LTM22, LTM23, LTM25, and LTM28. The working life increases in the series from 1-2 days for LTM21 to 30 days for LTM28. The minimum cure temperature also increases, from 70 °F for LTM21 to 160 °F for LTM28. LTM22 has a slightly longer working life and higher minimum cure temperature than LTM21, but the cured properties of the two resins are essentially identical (9). The LTM series is also marketed as MARINEPREG, which has been used to make several successful racing sailboats (14).

Two 16-ply panels were fabricated with a warps parallel layup, one using vacuum bag/oven molding and the other with 90 psi. The cure conditions were 140 °F for 8 hours. The properties of these laminates are given in Table 2. The compressive strength was relatively low, and the tensile strength relatively high, which together indicate poor fiber/matrix adhesion (15). In addition, impact testing of 7781/LTM22 resulted in large delaminations on the compressive face (as discussed later) which is further indication of poor bonding (7).

The reason for the poor adhesion was probably the finish used on the fabric, which was Volan. Volan was the first coupling agent developed (in the 1950's) for bonding resin to glass. At that time use of Volan finish was a significant improvement over the greige fabrics they supplanted. Volan is a chromiummethacrylate complex, whose unsaturated (methacrylate) functionality makes this coupling agent more suitable for polyesters and vinyl esters than for epoxies (although Volan finish is marketed as tri-compatible). Good performance with a polyester laminate in a U.S. Navy structure has been reported (16). However, Volan is generally considered to be inferior to silane coupling agents such as Z6040 (for epoxy) or Z6030 (for polyesters and vinyl esters). Another reason use of Volan should be avoided is that the finishing bath is toxic waste due to the chromium content.

The laminate fabricated with vacuum bag consolidation had a large void content. However, inspection of the micrograph in Figure 3 shows that the voids do not have the appearance of trapped air. They have a peculiar rectangular cross-section which possibly coincide with the yarn. (Voids of this nature occurred in a number of materials included in this study). Currently we have no confirmed explanation for the cause of these distinctive voids. The panel of 7781/LTM 22 cured under 90 psi pressure had no detectable voids and very similar fiber content, and it is interesting to note that the large void content had only a negligible effect on the mechanical properties.

The thermal properties, given in Table 2, are similar to those for LTM 21. The 140 °F cure temperature resulted in a Tg of about 189 °F (87 °C) with a very high maximum Tg near 300 °F. The 72 hour water boil caused a fairly large decrease in Tg. The DMTA scans from which the values of Tg were determined are shown in the Appendix, Figure A2.

Table 2. Properties of 7781/LTM22

	VACUUM BAG	90 PS1
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	48.7 4.8	51.2 5.3
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	63.5 1.9	67.8 1.2
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	69.3	73.6
TENSILE MODULUS (msi) (MEAN)	3.4	3.5
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	65.9 0.5	66.9 0.1
VOID CONTENT (%) (MEAN) (STD DEV)	4.5 1.2	-0.3 0.0
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	189 293 217	

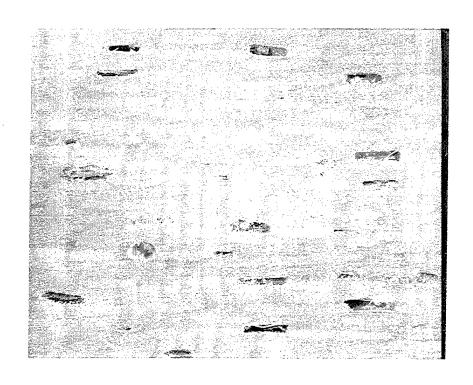


Figure 2. A micrograph of 7781/LTM22 at 30X magnification.

7781/Ampreg 75 (S.P. Systems, LTD.)

S.P. Systems, Inc., makes a large number of composite products for the marine market. Ampreg 75 was formulated for the fabrication of large marine structures (17). It has a long out time (30 days minimum), excellent flow under vacuum bag pressures, and a low cure temperature (180 °F). Ampreg 75 was used for the fabrication of an America's Cup boat (Montedison), a Whitbread Race boat, and a series of 18 rescue craft (RNLI Fast Carriage Boat), among others.

The reinforcement tested was Style 7781 finished with Z6040. Two 16-ply panels were fabricated with a warps parallel lay-up, one using vacuum bag/oven molding and the other with 90 psi. In both cases the temperature was held at 180 °F for 6 hours, as recommended by S.P. Systems (17).

The mechanical properties in the warp direction, weight percent fiber and void content, and thermal properties are given in Table 3. The panel consolidated under vacuum bag pressure had a void content of 4.3 %, although the effect on mechanical properties was small. As seen in Figure 3, some of the voids are roughly rectangular in cross-section as with 7781/LTM22. A possible explanation for the voids is that they are caused by resin flow (into the edge breather), as opposed to air entrapment, due to the small panel size used in this study (2).

From the thermal analysis, Ampreg 75 appeared to attain full cure after 6 hours at 180 °F since there was no change in Tg after post-cure. Water boil reduced the service temperature by about 45 °F.

Table 3. Properties of 7781/Ampreg 75

	VACUUM BAG	90 PSI
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	60.7 3.0	63.8 4.4
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	61.8	66.1 2.4
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	81.6 3.5	90.1 1.2
TENSILE MODULUS (msi) (MEAN)	3.1	3.3
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	65.5 1.0	62.8 0.5
VOID CONTENT (%) (MEAN) (STD DEV)	4.3 0.3	0.2 0.1
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	205 205 158	

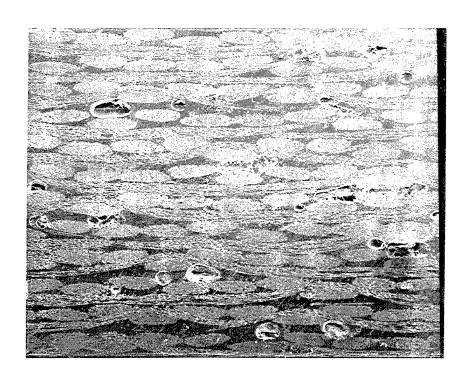


Figure 3. A micrograph of 7781/Ampreg 75 at 30X magnification.

NEOXIL PREPREG (DSM Italia)

Neoxil Prepreg is a new type of epoxy prepreg, developed specifically for boat building (18). It is unique in that a vacuum bag is not required for compaction. The plys are laminated with rollers or squeegees, as in hand lamination with wet resins.

Removal of air without vacuum bag pressure is possible because the unique resin in Neoxil Prepreg is essentially A-staged. The formulation is predominantly epoxy, but contains about 10% polyester. The polyester component is cured subsequent to impregnation of the fabric, but the epoxy component is not advanced. The prepreg is calendered to remove air and to flatten the prepreg, and the cured polyester network preserves this condition. The surface of Neoxil prepreg is flat but the resin has a low viscosity, which together allow removal of air with squeegees. Also, the prepreg (and cured laminate) is transparent, so trapped air is conspicuous.

The curing agent for the epoxy is an anhydride. Exposure of anhydride curing agents to moisture prior to cure may result in an unacceptable degradation in performance, particularly in elevated temperature properties. Water hydrolyzes the anhydride to the acid, which has several unfavorable consequences, the end result of which is a lower crosslink density after cure. Anhydride-cured laminates are very common and water contamination is rare, but precautions against exposure must be followed which are unnecessary for amine or catalytic cure formulations.

The minimum recommended cure temperature is about 180 °F (for 15 hours) but it will cure as low as 150 °F if held for 48 hours (19). The anhydride:accelerator curing agent allows a working life of a few days.

A version of the matrix resin was developed for use as an "interlaminar resin", which facilitates air removal. It can also be used in secondary bonding new prepreg to cured laminate.

DSM Italia reports that Neoxil prepreg can be co-cured with honeycomb cores, and that it adheres well to PVC foam and balsa. It is also compatible with polyester resin and gel coats.

An 8-ply cured laminate, [0/90]₂₅, was procured from DSM Italia. The micrograph in Figure 4 shows a void-free laminate. The reinforcement was a unidirectional woven roving, i.e., a light fill was used to hold the warp ends together. A unidirectional fabric was used for several reasons: no overlaps are required, (butt) joints between adjacent plys within a layer are non-structural, the fibers have no crimp, and there are no discontinuous fibers in any load path (18).

The results of the mechanical and thermal testing are reported in Table 4. The values of compressive and flexural strength were among the highest tested in this study. These high values are probably due to the unidirectional fabric, which has no crimp. The tensile strength was significantly less than the compressive, which is unusual.

Thermal analysis indicated that the resin was not fully cured, since the Tg increased about 20 °F with post cure. The 72 hour water boil reduced the service temperature by about 45 °F below the maximum dry value.

Table 4. Properties of Neoxil Prepreg

COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	68.6 1.7
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	50.1 6.0
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	87.2 2.3
TENSILE MODULUS (msi) (MEAN)	2.8
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	57.0 1.4
VOID CONTENT (%) (MEAN) (STD DEV)	5 0.1
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	198 216 169

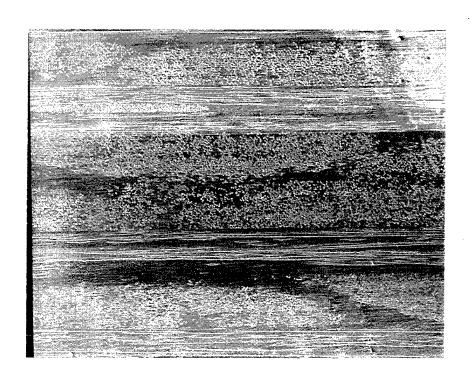


Figure 4. A micrograph of Neoxil Prepreg laminate at 30%.

7781/NB-1101 (Newport Adhesives and Composites, Inc.)

Newport Adhesives and Composites, Inc., specializes in low cost unidirectional carbon tape prepregs for the recreation market, such as golf club shafts, fishing rods, and sailboat masts. Newport Adhesives also supplies glass fabric prepregs for applications such as radomes, and high temperature curing carbon prepregs for aerospace markets (20).

The 7781 fabric tested in this study was made by Burlington

Glass Fabrics and finished with BGF 558 (Z6040).

Newport Adhesives supplies single-sided prepreg as a standard product form. In single-sided prepreg, a film of resin is lightly "tacked" onto one side of the fabric. The advantage of this form, as opposed to fully wet out fabric, is that very low void contents can be attained with vacuum bag pressure, as indicated in Table 5 and the micrograph in Figure 5. The problem of entrapped air common with vacuum bag lamination is vastly reduced because the dry fabric layers provide a path for the air to escape when the vacuum is drawn. Only hot-melt prepregs can be made single-sided. Single-sided prepreg has the disadvantage of bulk, or thickness, of the layup prior to resin flow and subsequent compaction.

The recommended cure temperature for NB-1101 is 235-275 °F. The effect of lower cure temperatures was investigated briefly by curing one 16-ply panel at 180 °F for 5 hours and another at 250 °F for 1 hour. As indicated in Table 5, there was little effect of the lower cure temperature on mechanical properties. The major difference between the laminates was in Tg, which increased about 30 °F upon post-cure. Water boil reduced the Tg by 40 °F below the maximum dry value.

Table 5. Properties of 7781/NB-1101

	180F,5hrs	250F,1hr
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	57.0 5.1	62.3 2.7
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	50.6 1.8	48.3 0.8
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	68.5 1.3	69.6 1.2
TENSILE MODULUS (msi) (MEAN)	2.9	3.0
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	60.3 0.2	60.3 0.2
VOID CONTENT (%) (MEAN) (STD DEV)	0.4 0.0	0.6 0.1
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	203 230 187	230 230 -

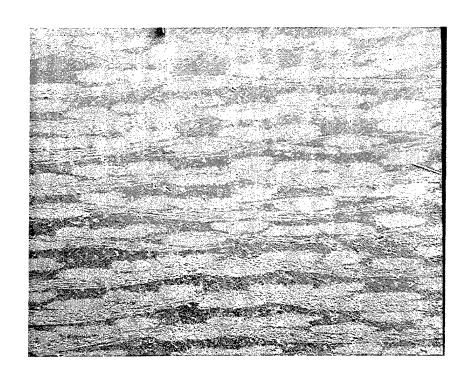


Figure 5. A micrograph of 7781/NB-1101 at 30X magnification.

7781/NB-1107 (Newport Adhesives and Composites, Inc.)

NB-1107 has a longer working life than NB-1101 and contains a fire retardant. Newport Adhesives recommends a maximum out time of 7 days for NB-1101 and 30 days for NB-1107. A sample of 7781/NB-1107 prepreg stored at ambient conditions at CDNSWC retained tack for 30 days.

Two 16-ply panels of 7781/NB-1107 were fabricated by vacuum bag lamination at 205 °F for 5 hours. Single-sided prepreg was used in the fabrication. In one panel the lamination schedule was warps parallel, designated [0]₁₆, and the second panel was quasi-isotropic. In the latter the warp direction was oriented

 $[0/+45/90/-45]_{2s}$

The mechanical properties of the NB-1107 laminates are given in Table 6. The major effect of the quasi-isotropic layup was a substantial increase in the in-plane shear strength and stiffness. It should also be noted that the shear stress-strain curve for the warps parallel laminate was highly non-linear (with failure at 3-5 % strain) while that for the quasi panels was fairly linear up to failure at about 2 % strain. The highly non-linear shear stress/strain behavior is typical of warps parallel lay-ups (7). The values of tensile and compressive strength of the quasi-isotropic laminate were only about 20 % less than those of the warps parallel laminate, and the Young's modulus was about 30 % less.

Use of single-sided prepreg again resulted in very low void contents, as can be seen by inspection of the micrograph of the warps parallel laminate in Figure 6. The quasi-isotropic laminate appeared, by its transparency, to have a similar low void content. No neat resin density was available so the void content could not be quantified.

The thermal analysis of NB-1107 showed that 205 °F for 5 hours did not fully cure the resin, as expected. Post-curing resulted in an increase in Tg of about 25 °F. The decrease in Tg after water boil was relatively large at 70 °F, possibly due to the presence of the fire retardant in NB-1107.

Table 6. Properties of 7781/NB-1107

[0]₁₆ [0/45/90/45]_{2s}

COMPRESSIVE STRENGTH (MEAN) (Ksi) (STD DEV)	59.2 2.7	48.3 1.0
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	58.3 2.9	48.2 2.7
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	75.2 1.6	57.8 1.3
TENSILE MODULUS (msi) (MEAN)	3.3	2.3
IN-PLANE SHEAR STRENGTH (MEAN) (ksi) (STD DEV)	8.7 0.4	17.1 1.4
IN-PLANE SHEAR MODULUS (MEAN) (msi)	0.33 0.03	0.84 0.07
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	63.3 0.3	63.3 0.2
VOID CONTENT (%) (MEAN) (STD DEV)		
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	216 239 171	

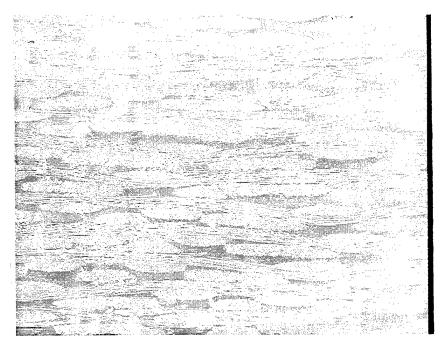


Figure 6. A micrograph of 7781/NB-1107 at 30X magnification.

7781/M10E (Ciba Composites)

Ciba Composites developed Vicotex M10 prepreg several years ago (at their subsidiary in Brochier, France) specifically for marine applications. The concept was to develop a family of prepregs with processing requirements, cost, and mechanical properties intermediate between those of the boatbuilding industry and the aerospace industry (21). The M10 epoxy was formulated to meet these requirements. It has a low viscosity at elevated temperature to facilitate wet-out under vacuum bag pressure, a long (2 month) out time at room temperature so freezer storage should be unnecessary, and it cures at low temperature. M10 was perhaps the first epoxy prepreg formulated to cure as low as 185 °F. The material is now also produced at Ciba Composites in Anaheim under the trade name Vicotex M10E.

As discussed, the "cure" time depends on the temperature. At a cure temperature of 185 °F, Ciba recommends that the material should be held for 12-15 hours (22). The conditions used in this study were 210 °F for 2 hours. The reinforcement used was 7781 finished with Z6040.

Low energy cure prepreg fabrication has been demonstrated by DCAN, who built some relatively large, thick structures. Also, Chantiers Mecaniques de Normandie fabricated a 33 meter catamaran hull (the Geris) with M10 prepreg. It is a cored hull, which was cured in one shot with 9 tons of prepreg on a heated wooden tool (21). In addition, several racing sailboats have been made with M10 prepreg, including two America's Cup boats, the Stars and Stripes (by Eric Goetz Custom Sailboats) and the Ville de Paris.

Ciba Composites has developed a proprietary fabrication approach, called integrated bleeding, which results in a low void content (<2%) as well as reducing fabrication cost. The panels tested in this study were not made with the integrated bleeding system, and consequently the panel had a relatively high void content, as shown in Figure 7.

The mechanical properties of 7781/M10E, recorded in Table 7, are typical for vacuum bag consolidated prepreg (see page 44), in spite of the relatively large void content. The as-fabricated value of incipient Tg is also typical for the low cure temperatures. The post-cured value of Tg, however, is probably lower than the maximum value that M10E can attain. There was evidence on the DMTA plot that the sample of M10E did not reach full conversion during the initial scan. More important is the excellent retention of Tg after the 72 hour boil. This is probably a result of the fact that M10E is not rubber-modified. Use of CTBN rubber increases the failure strain of the resin, but has an adverse effect on both dry and wet Tg.

Table 7. Properties of 7781/M10E

COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	52.1 4.3
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	53.6 2.2
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	77.1 0.9
TENSILE MODULUS (msi) (MEAN)	3.3
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	62.8 0.8
VOID CONTENT (%) (MEAN) (STD DEV)	6.2 0.7
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	217 228 230

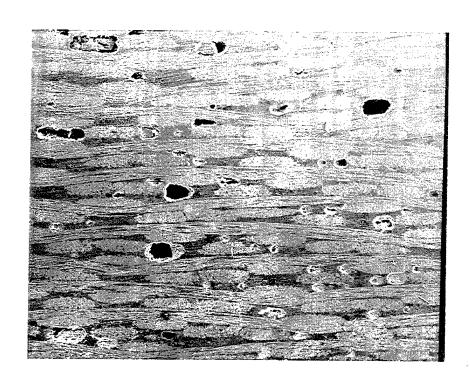


Figure 7. A micrograph of 7781/M10E at 30X magnification.

7781/RS-1 (YLA, Inc.)

YLA, Inc., makes a variety of prepregs and film adhesives for the aerospace market (23). RS-1 is an epoxy prepreg with recommended cure conditions of 200 °F for 1.5 hours. It will remain tacky at room temperature for 4 months. Eric Goetz Custom Sailboats built three America's Cup boats with RS-1 carbon tape prepreg for the America³ Foundation, namely, the DEFIANT, the AMERICA³, and the KWANZA. Goetz also built a 25' patrol boat with glass fabric reinforced RS-1 for the Atlantic Boat Group.

Style 7781 finished with Z6040 was tested in this study. Three 16 ply warps parallel laminates were fabricated with vacuum bag molding. One of the panels was cured at 180 °F for 5 hours. A second was cured at 180 °F for 5 hours and then post-cured at 205 °F for 1.5 hours. The third was processed with an intermediate temperature soak in an attempt to lower the void content. In this panel, the temperature was ramped to 160 °F for 1 hour, followed by 205 °F for 1.5 hours. The properties of these three laminates are given in Table 8.

The thermal analysis indicated that 180 °F for 5 hours did not fully cure the resin, but curing at 205 °F for 1.5 hours does result in full conversion. The maximum Tg appears to be about 221 °F, which the resin attained after being held at 205 °F. Water conditioning reduced the Tg by about 56 °F.

Post-curing did not improve the laminate mechanical These properties were about 10% lower than the properties. average values reported in this study, probably due to the relatively high void contents. Although we have noted that void contents of up to 4-5% had little effect on mechanical properties, the RS-1 laminates had unusually high levels of porosity which probably caused the somewhat lower mechanical properties. As shown in Figure 8, the voids have the rectangular cross-section peculiar to several woven yarn laminates evaluated in this study. As in all such materials, the voids appear to coincide with the yarn, although there are more of them in 7781/RS-1 than usual. The intermediate temperature soak was an attempt to allow resin to flow for a longer period of time prior to the viscosity increase due to curing reactions, but the technique was unsuccessful in this case.

YLA, Inc., can supply single-sided prepreg since they make these materials with a hot-melt process. This form of prepreg would be expected to lower the void content of cured RS-1 laminates as was discussed for the Newport Adhesives 1101 and 1107.

Table 8. Properties of 7781/RS-1

	180F;5hr	180F;5hr 205F;1.5hr	160F;1hr 205F;1.5hr
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	51.9	53.6	55.9
	2.7	0.5	2.7
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	51.8	51.3	55.3
	0.9	1.8	1.6
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	70.8	68.6	71.3
	1.5	1.4	1.9
TENSILE MODULUS (msi) (MEAN)	3.1	3.0	3.0
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	64.7	64.8	63.6
	0.6	0.4	0.9
VOID CONTENT (%) (MEAN) (STD DEV)	8.2	8.8	6.7
	1.6	1.3	1.2
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	200 221 163	221 221	

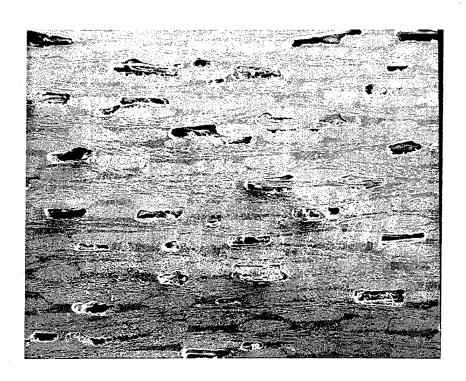


Figure 8. A micrograph of 7781/RS-1 at 30X magnification.

7781/SP377 (3M)

SP377 prepreg was developed for repair of composite substrates. For this reason the resin was formulated to cure below 212 °F to avoid converting water in the damaged laminate to steam. SP377 prepreg has two additional characteristics, both unique to our knowledge, which facilitate the use of the material in repair. One is that the prepreg has no tack. Since the resin will not flow (at ambient temperature) it has a reduced tendency to trap air when a vacuum is drawn on the lay-up, which leads to low void contents. Secondly, SP377 can be stored at room temperature for a relatively long time, up to 1 year if autoclave pressures can be applied (24).

SP377 is available with a variety of reinforcements, including unidirectional carbon and S-2 glass, various E-glass fabrics, and Aramid tape and fabric. The reinforcement tested in this study was Style 7781 finished with Z6040.

Two 16-ply panels were fabricated with a warps parallel layup, one using vacuum bag/oven molding and the other with 90 psi. In both cases the temperature was held at 205 °F for 2 hours, as recommended by 3M (25).

The properties of 7781/SP377 are recorded in Table 9. Although the values of compression strength are typical, the values of tensile strength were relatively low, and as a result the flexural strengths were also below average. In addition, the impact damage areas of the laminates were relatively large, shown in a later section, and the damage occurred on the tensile side of the impact specimens. We are unaware of any resin characteristics which result in a low laminate tensile strength. A possible explanation is that the 7781 fabric was roughly handled, or otherwise damaged, at some point. 3M reported that all laminates tested from this lot of prepreg had a low tensile strength, and the cause is suspected to be a bad lot of 7781.

The low void content in the panel consolidated with a vacuum bag is notable. The technique of using no-tack prepreg to accomplish low porosity appears to be viable. The micrograph of a sample cut from the vacuum bag molded laminate shows the quality indicated by the void content measurement. No-tack prepreg can be used to attain low void contents with tape reinforcement, an advantage this technique has over single-sided prepreg.

The thermal properties of SP377 were very similar to those of Ciba Composites M10E. The values of maximum and wet Tg are about 250 °F and 230 °F, respectively, for both materials. This 20 °F reduction in service temperature after water absorption was the lowest among the materials tested in this study. SP377, like M10E, is not rubber-toughened. As mentioned, rubber modifiers reduce both the dry and wet Tg.

Table 9. Properties of 7781/SP377

	VACUUM BAG	90 PSI
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	56.5 4.3	59.4 3.6
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	41.9 1.8	43.0 4.3
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	59.7 1.3	59.4 3.6
TENSILE MODULUS (msi) (MEAN)	3.1	3.3
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	63.1 0.3	64.4 0.1
VOID CONTENT (%) (MEAN) (STD DEV)	1.8 0.5	0.5 0.1
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	234 252 230	

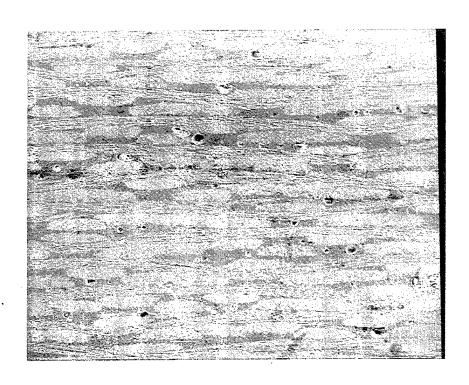


Figure 9. A micrograph of 7781/SP377 at 30X magnification.

1581/E-761E (Fibercote Industries, Inc.)

Fibercote Industries makes a variety of prepregs, including epoxy, polyester, phenolic, cyanate ester, polybutadiene, and silicone resins (26). Many of the products are tailored to meet the requirements of radomes or other electrical applications. E-761E is an epoxy formulated to cure at low temperatures under vacuum bag pressures.

Two 16-ply warps parallel laminates were fabricated, one with vacuum bag molding and the other at 90 psi. The laminates were cured at 180 °F for 5 hours.

The glass fabric tested was Style 1581 finished with Volan. Style 1581 is similar to Style 7781. Both are 8.9 oz/yd², 9 mil thick fabrics with a 57x54 8HS construction. The only difference is that 7781 is woven with an ECDE 75-1/0 yarn and 1581 has an ECG 150 1/2 yarn. As discussed earlier, Volan is not recommended for epoxies, and in general we feel that silane coupling agents are currently the best materials for fiber/matrix adhesion. However, this resin appears to be an exception. Fibercote personnel, who use silane finishes for many of their resins and are aware of the poor performance of Volan with epoxies, nonetheless recommended Volan with E-761E (27). We do not know if Fibercote's recommendation was based on experience, or if the resin formulation has chemical functionality compatible with the methacrylate group in Volan.

As can be seen in Table 10, the mechanical property data did not indicate the effects of poor adhesion, namely, a high tensile strength and low values of compression and flexural strength. To the contrary, the laminate had good as-fabricated properties typical of those seen with other prepregs using silane finished 7781 fabrics. The possible effect of water on the mechanical performance was not addressed in this screening evaluation.

The void content of the laminate fabricated by vacuum bag molding was relatively low at about 3%. As can be seen in Figure 10, the voids do not have the characteristic rectangular cross-section which have been observed in several laminates. The properties of the panel cured with 90 psi were only marginally better than the panel with 3% voids.

Thermal analysis showed that E-761E was not fully cured after 5 hours at 180 °F since post-curing increased the Tg about 18 °F. Water boil resulted in a decrease in Tg of about 54 °F.

Table 10. Properties of 1581/E-761E

	VACUUM BAG	90 PSI
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	63.1 2.6	66.0 1.2
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	55.3 2.1	58.3 3.0
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	75.9 0.7	78.6 3.2
TENSILE MODULUS (msi) (MEAN)	3.4	3.5
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	62.4 0.6	62.6 1.1
VOID CONTENT (%) (MEAN) (STD DEV)	2.8 0.4	0.1 0.2
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	217 235 181	

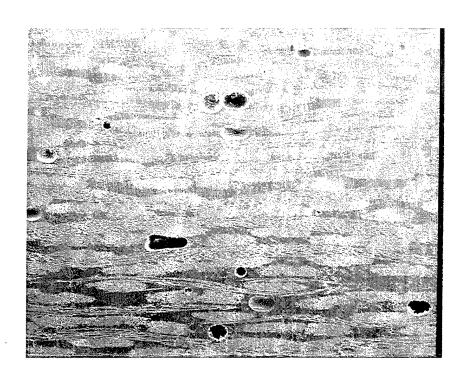


Figure 10. A micrograph of 7781/E-761E at 30X magnification.

WR/P-601 (Fibercote Industries, Inc.)

P-601 is a low cost, flame retardant polyester with a recommended cure temperature of 250 °F (28). The monomer in P-601, as with most polyester prepregs, is diallylphthalate (DAP) as opposed to styrene used in laminating resins. DAP has a high viscosity and low volatility, both of which are required for prepregs. An additional benefit of DAP-based polyesters is that the DAP imparts a high value of failure strain to the resin (29). A study of the effect of resin on laminate mechanical properties and impact damage resistance showed that the properties are controlled by the resin failure strain (30). Laminate strength increased with resin failure strain up to a value of about 4%. An ultimate elongation of 4% is evidently required to obtain the maximum potential from the glass reinforcement. The poor properties of typical polyester laminates, compared with those of vinyl esters and epoxies, can be attributed to their low elongations at failure, which are normally 1-2%. The properties of the polyester laminates evaluated in this study however, were equivalent or superior to those of epoxy laminates.

The reinforcement tested was an 18 oz/yd² woven roving. Two 8-ply warps parallel laminates were cured for 3 hours at 220 °F, one by vacuum bag molding and the other with 90 psi pressure. The properties of the laminates are given in Table 11.

As can be seen by comparing the mechanical properties in Table 11 with those in Tables 1-10, the polyester performs as well as an epoxy.

The major drawback with polyesters is the service temperature. It is clear that the 220 °F, 3 hour, cure conditions did not fully cure P-601 since the as-fabricated value of about 163 °F was almost 30 °F less than the post-cured value. The water conditioning reduced the ultimate Tg by about 35 °F. Although we did not do mechanical testing on water conditioned laminates in this evaluation, the thermal data suggests a maximum use temperature for P-601 of about 150 °F.

The vacuum bag molded laminate had a relatively low void content at about 2%. However, the effect on compressive strength was significant for this low level. Inspection of figure 11 shows that the voids were larger than those shown in the micrographs of woven yarn fabrics. It is possible that void size has a greater effect on laminate properties than void content.

Table 11. Properties of WR/P-601

	VACUUM BAG	90 PSI
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	64.3 5.2	70.2 8.8
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	61.3 4.0	64.1 3.9
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	87.5 3.0	90.6 5.2
TENSILE MODULUS (msi) (MEAN)	3.3	3.4
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	57.0 0.9	60.3 1.7
VOID CONTENT (%) (MEAN) (STD DEV)	2.3 0.2	0.0 0.1
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	163 190 156	



Figure 11. A micrograph of WR/P-601 at 30X magnification.

7781/P-600 (Fibercote Industries, Inc.)

P-600 is a low cost DAP-based polyester prepreg resin formulated to have a 220 °F cure temperature (26). It is not flame retardant. Fibercote Industries describes the resin as a general purpose polyester, which implies that the formulation uses phthalic anhydride as the unsaturated acid. These are also called orthophthalic polyesters, and are not recommended for service requiring continuous exposure to water because they will blister.

The 7781 fabric evaluated was finished with I550. I550 is a tricompatible finish, meaning it bonds to polyesters, vinyl esters, and epoxies. It is described as a mixture of Volan (for polyesters and vinyl esters) with an epoxy compatible silane (31). The mechanical properties and impact damage areas did not indicate poor adhesion.

Two 16 ply warps parallel laminates were cured for 2 hours at 190 °F, one by vacuum bag molding and the other with 90 psi pressure. The properties of these laminates are given in Table 12.

The porosity of the vacuum bag molded laminate was about 5%, which again was manifested as voids with a rectangular cross-section which appeared to be associated with the yarns. A comparison of the mechanical properties between the two laminates indicates that voids had a relatively large effect on the values of strength.

The thermal characterization of P-600 showed an as-fabricated Tg of 129 °F, fairly typical for an ortho polyester. Post-curing increased the Tg about 27 °F. Water absorption reduced the maximum Tg by only about 11 °F. As shown in the Appendix, Figure A3, the glass transition for polyesters is more gradual than the transition for epoxies, which makes assignment of the Tg value less precise.

Table 12. Properties of 7781/P-600

	VACUUM BAG	90 PSI
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	43.0 6.3	50.6 5.9
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	54.5 3.2	58.7 2.8
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	66.7 1.2	78.7 3.1
TENSILE MODULUS (msi) (MEAN)	2.9	3.1
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	62.6 0.4	64.7 0.6
VOID CONTENT (%) (MEAN) (STD DEV)	5.2 0.4	0.2 0.0
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	129 156 145	

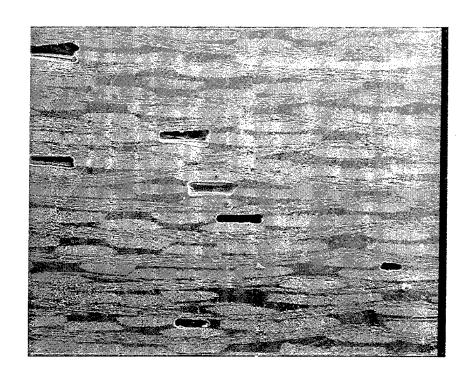


Figure 12. A micrograph of 7781/P-600 at 30X magnification.

7781/MXB-9420 (ICI Fiberite)

9420 is a vinyl ester prepreg resin recently developed by ICI Fiberite. As with the two polyester prepregs tested in this study, the unsaturated oligomers were dissolved in diallylphthalate monomer. The recommended cure conditions are 275 °F for 1 hour (32). The 7781 fabric tested was finished with Volan.

Two 16 ply warps parallel laminates were fabricated, one at 220 °F for five hours under vacuum bag oven cure conditions, and the second at the same temperature and time but under 90 psi pressure. Testing of the autoclave-cured laminate was limited to measurement of flexural strength. An evaluation of the effect of post-cure was also limited to flexural strength.

The properties of 7781/MXB-9420 are given in table 13. The relatively high tensile strength and low compressive strength indicate that the fiber/matrix bond strength was somewhat lower than normal. Use of a vinyl silane in place of Volan is recommended. Neither post-curing the vacuum consolidated laminate or curing in an autoclave improved the flexural strength. Although the recommended cure temperature was 275 °F, the laminate appeared to have fully cured at 220 °F since the Tg did not increase upon post-cure.

The void content of the MXB-9420 laminate was relatively low. The micrograph in figure 13 shows a porosity very similar to that of 1581/E-761E shown in figure 10, page 27, characterized by voids which do not have the distinctive rectangular cross-section commonly observed in this study.

Table 13. Properties of 7781/MXB-9420

	220F;5hrs vacbag	220;5hrs 275F;1hr	220F;5hrs 90 psi
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	50.4 2.9		
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	61.1		
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	67.3 1.8	66.3 1.2	69.4 1.6
TENSILE MODULUS (msi) (MEAN)	2.9		
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	60.9 1.5		
VOID CONTENT (%) (MEAN) (STD DEV)	2.6 0.1		
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (POST CURED) (°F) (AFTER 72 HR BOIL)	219 219		

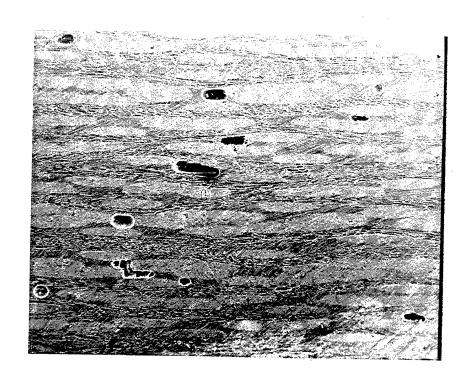


Figure 13. A micrograph of 7781/MXB-9420 at 30X magnification.

1583/SP365 (3M)

1583/SP365 is one of 4 prepregs qualified to Hitco Materials Specification 20-04.16 rev. C for use in U.S. Navy sonar bow domes. The others are Fiberite 1583/7780, American Cyanamid 1583/5920, and U.S. Polymeric 1583/E719. Since the sonar domes are large, thick structures cured in an autoclave there are specifications on prepreg working life and handling characteristics. In addition, the requirement on Mode I fracture toughness is restrictive, where an incipient value of 14 in.lbs/in² is specified. This high value of fracture toughness is achieved by extensive rubber-modification.

1583/SP365 is not a low energy cure prepreg. It was included in this study as a baseline material, a representative of the class of laminates which have been used successfully in naval applications. Two 16 ply warps parallel laminates were fabricated at 300 °F for 4 hours, one using vacuum bag molding and the other cured under 90 psi pressure. The mechanical and thermal properties of these two laminates are given in Table 14.

The high level of rubber modification does not lend itself to vacuum bag consolidation. As shown in Table 14 and Figure 14, the laminate cured without autoclave pressure had about 13 % voids. This high void content clearly had a significant effect on mechanical properties. The resin Tg was relatively low at 212 °F, also due to the level of rubber, and the Tg was reduced by about 35 °F after water absorption.

Table 14. Properties of 1583/SP365

		VACUUM BAG	90 PSI
COMPRESSIVE STRENG (ksi)	TH (MEAN) (STD DEV)	37.5 2.0	59.2
TENSILE STRENGTH (ksi)	(MEAN) (STD DEV)	35.3 1.2	47.3
FLEXURAL STRENGTH (ksi)	(MEAN) (STD DEV)	48.9 1.9	71.4 2.1
WEIGHT PERCENT FIB	ER (MEAN) (STD DEV)	68.5 1.4	69.5 0.6
VOID CONTENT (%)	(MEAN) (STD DEV)	12.9 0.3	0.1 0.1
(EMPERATURE FABRICATED) POST CURED) 72 HR BOIL)	212 212 176	

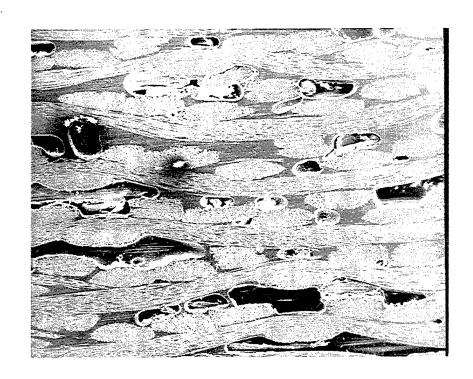


Figure 14. A micrograph of 1583/SP365 at 30X magnification.

ALTERNATIVE CURING METHODS

<u>UV-Cure</u> (Sunrez, Inc.)

UV-cured A-staged prepreg was evaluated. A-staged prepreg is an uncommon material form due to the short working life of conventional materials, which requires that the fabricator make the prepreg. UV-initiated resins have a long working life as long as the prepreg is shielded from UV light, which allows the fabricator to purchase the material from a supplier. As mentioned, the advantage of A-staged prepreg is that void removal is facilitated by the low viscosity, so a vacuum bag is not necessary for compaction.

Sunpreg is a UV-initiated prepreg made by Sunrez, Inc. Two cured panels were received from Sunrez, which were fabricated by contact molding of UV-initiated prepreg and cured under a mercury vapor lamp. Panel PP001 was composed of 6 plys of ATI 32 stitch-bonded fabric and a UV-initiated version of Derakane 441-400. Panel PP002 had 12 plys of ATI 32 fabric. The panel was tested in the warp direction and the properties are shown in Table 15. The properties are high for a contact molded laminate and reflect the high fiber content. It is clear that the degree of cure achieved with UV initiators was somewhat low in panel PP001 based on the increase in Tg upon post-cure. The initial low value of Tg is not a characteristic of UV initiated resins; we have measured an as-fabricated value of 190 °F, which is a typical Tg for peroxide initiated vinyl ester.

Table 15. Properties of UV-cured prepreg laminates.

	PP001	PP002
COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	45.8	50.7
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	46.2	42.6
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	50.4	51.1
TENSILE MODULUS (msi) (MEAN)	2.9	3.0
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	58.7	61.8
VOID CONTENT (%) (MEAN) (STD DEV)	1.7	1.2
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (°F) (POST CURED)	154 277	

Conductive Cure (ILC Dover, Inc.)

An initial evaluation was made of a new technique for curing prepreg laminates using embedded resistive elements. The nature of the resistive elements and the power density used are currently proprietary to ILC Dover. The approach appears to have significant potential for reducing the cost of structures fabricated with heat cured prepregs, particularly the low temperature curing materials evaluated in this study.

ILC Dover studied various resistive element spacings and power level per resistive element required to achieve a fairly uniform température distribution within the laminate. A 16 ply laminate of warps parallel 1581/E-761E (Fibercote Industries, see page 26) was then cured using these parameters, with the goal of 180 °F minimum temperature for 5 hours. The properties of the laminate are given in Table 16. The properties in the table are comparable to those measured on conventional heat cured laminates. The initial Tg in particular indicates that a sufficiently high internal temperature was attained.

Table 16. Properties of in-situ conductive cured laminates.

COMPRESSIVE STRENGTH (MEAN) (ksi) (STD DEV)	49.9 4.2
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	48.9 1.4
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	63.1 2.0
TENSILE MODULUS (msi) (MEAN)	2.7
WEIGHT PERCENT FIBER (MEAN) (STD DEV)	62.5 0.7
VOID CONTENT (%) (MEAN) (STD DEV)	5.2 0.2
GLASS TRANSITION TEMPERATURE (AS-FABRICATED) (°F) (POST CURED)	214 270

PROPERTIES OF CARBON FABRIC LAMINATES

Laminates composed of carbon reinforcement with low temperature curing epoxies have found applications in sporting goods markets, Formula One chassis and other race car components, and in high performance racing sailboat hulls and masts.

The material tested in this study was a carbon fabric reinforced epoxy (M10E). In a recent study it was found that carbon reinforced epoxies have significantly better mechanical properties than carbon reinforced vinyl esters, evidently caused by poor fiber/matrix adhesion in the latter (7,8). A second advantage to epoxy resins is their relatively low cure shrinkage. The high cure shrinkage of vinyl ester can cause delaminations, particularly in thick laminates in regions of high curvature (33).

CGG130/M10E (Ciba Composites)

The CGG130 fabric was woven by Ciba Composites. It is a 29 oz/yd² 2X2 basket weave with Celion 12K tow at 11 epi both warp and fill. The fabric was prepregged with M10E by Ciba Composites with about 35 wt% resin. A 5-ply, warps parallel laminate was fabricated by vacuum bag molding at 210 °F for 2 hours.

The mechanical properties in the warp direction are recorded in Table 17. The values of tensile strength and modulus are comparable to those measured on carbon fabric/epoxy laminates fabricated by VARTM (7). However, the value of compressive strength was relatively low compared with the VARTM laminates (which failed at about 60 ksi in compression). The compression strength was measured using a second test method, with the same results. All failures were in the gage, so the measured strength values do not appear to be an anomaly of the test method.

We believe that the 44-45 ksi in Table 17 does not represent the potential of carbon fabric laminates in general. For example, 3M reports a compressive strength of 62.5 ksi for carbon fabric reinforced SP377 (25). The most likely explanation for the low values in Table 17 is that the waviness, or crimp, of the tows in the weave have a strong effect on the compressive strength of carbon fabric laminates. In a earlier study, a strong correlation was noted between the crimp of glass rovings (amplitude of distortion) and laminate compressive strength (7). CGG130 is a relatively heavy fabric at 29 oz/yd2, with a cured ply thickness of about 0.028". The extensive waviness of the tows in CGG130 can be seen by inspection of Figure 15. fabric used in the 3M study was only 0.007"/ply, which indicates lighter tows and therefore less crimp. On the basis of the data and the trend observed with glass fabric, we recommend light fabrics or warp uniaxial materials for maximum performance in compression.

The fabrication quality is shown in Figure 15. The porosity is relatively low at about 2.6%, and the voids are smaller and more numerous than those observed in the glass fabric laminates evaluated in this study.

Table 17. Properties of CGG130/M10E

COMPRESSIVE STRENGTH ¹ (MEAN) (ksi) (STD DEV)	44.2 1.6
COMPRESSIVE STRENGTH ² (MEAN) (ksi) (STD DEV)	44.7 5.2
TENSILE STRENGTH (MEAN) (ksi) (STD DEV)	93.5 2.2
FLEXURAL STRENGTH (MEAN) (ksi) (STD DEV)	85.8 4.9
TENSILE MODULUS (msi) (MEAN)	9.2
WEIGHT PERCENT FIBER (MEAN) (STD DEV) VOLUME PERCENT FIBER (MEAN) (STD DEV)	65.9 1.0 55.7 1.2
VOID CONTENT (%) (MEAN) (STD DEV)	2.6 0.2

- ASTM D 695 (end-loaded dogbone)
 End/shear loaded test coupons

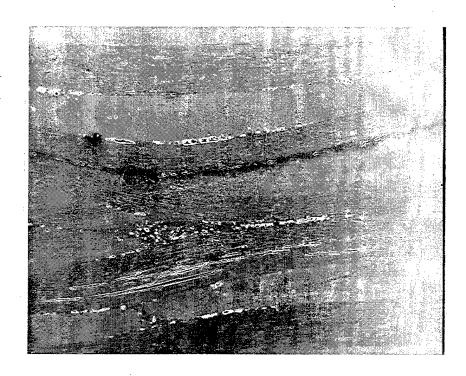


Figure 15. A micrograph of CGG130/M10E at 30X magnification.

IMPACT DAMAGE RESISTANCE

Most of the laminates were impacted at levels of 1000, 2000, 3000, and 4000 in.lbs/in. With the 0.5" diameter tup used in the study, all of the panels were penetrated at 4000 in.lbs/in. A comparison of relative impact damage resistance between the materials is best done at levels which do not penetrate the laminate. In Figure 16 are shown the impact damage areas of the vacuum bag molded laminates after impact at 3000 in.lbs/in.

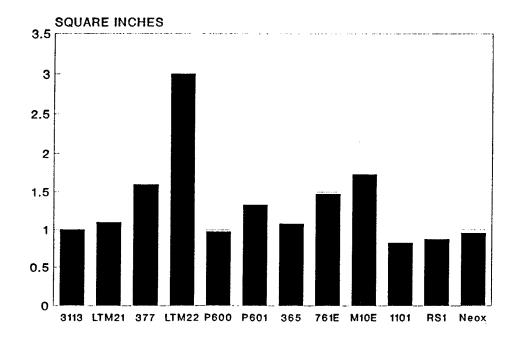


Figure 16. Impact damage area after 3000 in.lbs/in impact.

Effect of Fiber/Matrix Adhesion

As can be seen in Figure 16, there is only one prepreg which has significantly higher damage area than the rest. This is the 7781(Volan)/LTM22 laminate, which evidently has poor fiber/matrix adhesion. The material had low compression strength, and the impact damage indicated above was on the compression side of the impacted plates. In conjunction with the static mechanical properties, the impact data indicates that use of Volan with epoxies should in general be avoided. However, it was also shown that poor adhesion between epoxy resins and Volan-finished fabrics is not inevitable. The static mechanical properties of 1581(Volan)/E-761E evaluated in this study gave no indication of poor adhesion. And although the impact damage area of this material was relatively large, the damage occurred on the tensile side of the plate.

Effect of Porosity

We evaluated the effect of voids on impact damage resistance by comparing damage areas of vacuum bag molded laminates with panels consolidated at 90 psi. In Figure 17 is shown the damage areas at 3000 in.lbs/in impact level. As can be seen in the Figure, void content has a negligible effect on damage area. In the case of the 7781/SP377 laminate, which had relatively poor impact damage resistance (and tensile strength) evidently due to a bad lot of glass fabric, autoclave curing substantially increased the damage area. In both 7781/SP377 panels impact damage occurred on the tensile side of the plates.

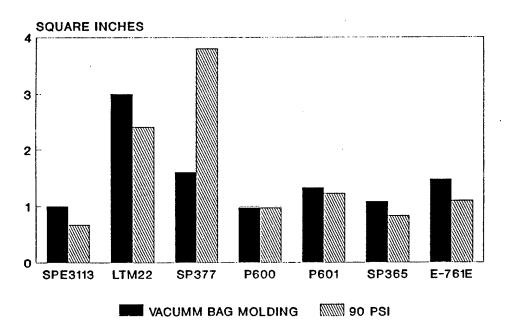


Figure 17. Effect of porosity on impact damage area.

Effect of Resin Failure Strain

We have shown in a previous study that the impact damage area of glass fabric laminates, for a given impact level, is controlled by resin failure strain up to about 4-5% (30). Use of resins whose failure strain exceeds 4-5% did not improve impact resistance. The data (from reference 30) are given in Figure 18, measured on panels made by VARTM with various polyester, vinyl ester, and epoxy resins, and impacted at 1000 in.lbs/in.

In this study, the values of failure strain of the prepreg resins were not available. However, the data appears to be consistent with the earlier study in that the impact damage area of 1583/SP365 shown in Figure 16 is not significantly different from that of the average laminate. The very high toughness SP365 offered no advantage in resistance to impact (but would, we believe, be superior to the average laminate in resistance to damage growth).

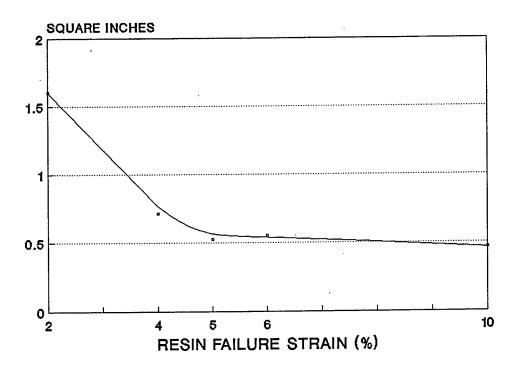


Figure 18. Effect of resin failure strain on impact damage area.

Effect of Post-Curing

The effect of post-cure was investigated for two of the materials, and as shown in Figure 19, it was found that fully cured laminates had slightly higher impact damage areas. The data in Figure 19 are damage areas at 3000 in.lbs/in impact level.

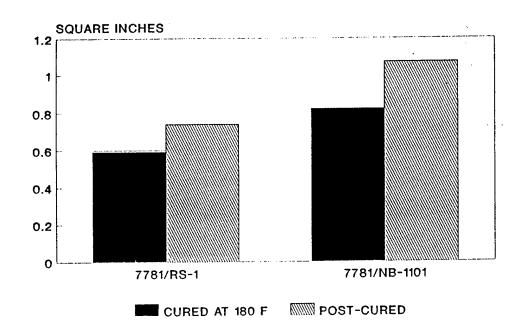


Figure 19. Effect of post-cure on impact damage area.

SUMMARY AND CONCLUSIONS

Materials Evaluated

Thirteen low energy heat-cured glass fabric prepregs were evaluated, listed below. Cure conditions vary, but range from 140 °F for 8 hours to 220 °F for 5 hours.

<u>RESIN</u>	<u>MANUFACTURER</u>	<u>CHEMISTRY</u>
LTM21, LTM22	Advanced Composites Group, Inc.	epoxy
RS-1	YLA, Inc.	ероху
Ampreg 75	SP Systems, Inc.	epoxy
E-761E	Fibercote Industries, Inc.	epoxy
P-600, P-601	Fibercote Industries, Inc.	polyester
MXB-9420	ICI Fiberite	vinyl ester
SP377	3M	ероху
M10E	Ciba Composites	epoxy
NB1101,NB1107	Newport Adhesives and Composites	ероху
Neoxil Prepreg	DSM Italia	ероху

Control of Void Content

The laminates were fabricated by vacuum bag molding, except for Neoxil prepreg, which is consolidated by rollers or squeegees as in hand lay-up. There are three methods which can be used to fabricate laminates by vacuum bag molding which result in low (< 2%) void contents. One is to use single-sided prepreg, where the resin film is lightly tacked onto the fabric during the prepregging operation. In this material form, the dry fabric serves as a conduit for the air to escape when a vacuum is drawn. This is the most effective method for achieving low void contents, but it is limited to fabric prepregs made by the hot melt process. The second is a technique developed by 3M in which the resin has no tack; since the resin does not flow at room temperature, it has less of a tendency to trap air. We have found that this method is effective, and it can be used with tape prepregs in addition to fabric. A third method is called integrated bleeding, a proprietary processing technique developed by Ciba Composites, which was not evaluated in this study.

Measured Void Content

Vacuum bag molding with fully wet out, tacky prepreg (the most common form) resulted in void contents of 3%-8% with woven yarn fabric. Single-sided prepreg usually resulted in laminates with <1% voids. The no-tack prepreg laminate we tested had about 2% voids.

Most of the prepregs evaluated were reinforced with a woven yarn fabric, most commonly Style 7781. The voids which resulted from low pressure molding with woven yarn did not have the roughly spherical shape of trapped air. Instead the voids were rectangular in cross-section, and appeared to be associated with the yarns. Two woven roving prepregs were evaluated, and although both were fully wet-out and tacky, the vacuum bag consolidated laminates had low void contents.

Mechanical Properties

The average value of the mechanical properties (t the standard deviation) of the thirteen heat-cured, vacuum bag molded, warps parallel glass fabric laminates are given below:

Tensile Strength	56.6	<u>+</u>	7.1	ksi
Compressive Strength	56.9	±	8.3	ksi
Flexural Strength	74.0	±	8.1	ksi
Tensile Modulus	3.2	±	0.4	msi

Six of the materials were also consolidated with 90 psi to investigate the effect of voids on properties. Unexpectedly, it was found that the mechanical properties were almost independent of void content in most cases.

Degree of Cure

The low cure temperatures used in this study generally did not result in full conversion. This was determined by noting that the glass transition temperature of the as-fabricated material increased after a post-cure. Measurement of the degree of cure would have been useful, but it was outside the scope of this survey, and in addition requires the procurement of a totally unreacted resin or prepreg sample. In some of the materials, we tested the laminates after a post-cure and found that the properties were not significantly different from the as-fabricated values (with the exception of resin Tg).

Impact Damage Resistance

Impact damage areas were measured after low velocity impacts at various impact levels. Except for two material systems, the specimens developed the relatively small, contained damage zones characteristic of glass fabric laminates. In one of these cases, poor fiber/matrix adhesion resulted in a large damage area on the compression side of the plates, and in the other a bad lot of glass fabric resulted in a large damage area on the tensile side. Void content did not significantly affect impact resistance.

Service Temperature

An indication of maximum service temperature was determined by measuring Tg by DMTA, with Tg defined as the temperature at which Young's modulus starts to decrease. The values of resin Tg were measured as-fabricated, after post-cure, and after a 72 hour water boil. As-fabricated values of Tg for the epoxy laminates ranged from 190-230 °F. Post cured values were slightly higher, with one material attaining a Tg above 300 °F. Water absorption reduced the value of Tg by 40-50 °F in most cases. The resins which were rubber-modified had lower dry values of Tg and sustained larger reductions after water immersion. The polyester laminates had lower initial values of Tg (125-165 °F), which were reduced about 30 °F after water absorption.

REFERENCES

- 1. Kramers, S.D., "Engineering for the America's Cup", <u>Proc. of</u> the 1993 <u>SAMPE</u> <u>International</u> <u>Conf.</u>, Philadelphia, PA, 25-28 Oct 1993.
- 2. Cripps, D., S.P. Systems, LTD, personal communication.
- 3. Goetz, E., Eric Goetz Custom Sailboats, personal communication.
- 4. Jones, D.E., Sigma Labs, personal communication.
- 5. Rick and Randy Rust, Westport Shipyard, Inc., personal communication.
- 6. Hepburn, R.D., Magliulo, G., and Wright, T., "The U.S. Navy's New Coastal Minehunter (MHC): Design, Material, and Construction Facilities", Naval Engineers Journal, May 1991.
- 7. Juska, T., Mayes, J.S., and Seemann, W., "Mechanical Properties and Impact Damage Resistance of Composites Fabricated by Low Cost, Vacuum Assisted Resin Transfer Molding", SSM-64-93/04, August 1993.
- 8. Juska, T., "Effect of Water Immersion on Fiber/Matrix Adhesion", SME-92/38, January 1993.
- 9. Ridgard, C., The Advanced Composites Group, Inc., personal communication.
- 10. Boll, D.J., "Curing of 3501-6 Composite Systems", Hercules Advanced Materials Group, Technical Service Bulletin.
- 11. Wisanrakkit, G., and Gillham, J.K., "The Glass Transition Temperature for Monitoring the Isothermal Cure of an Amine-Cured Epoxy System", ONR Contract N00014-84-K-0021, Technical Report No. 16, February 1989.
- 12. P. Puckett, Reaction Molding & Composites Applications Development Lab, Dow Chemical Co., unpublished data.
- 13. Advanced Composites Group, Inc. Product Literature PDS/2017, Issue Draft, 8 July 1991.
- 14. Advanced Composites Group, Inc., "CENTOMIGLIA 92. First and Second for Marinepreg", Product Literature SM1019.
- 15. Megerdigian, C., Robinson, R., and Lehmann, S., <u>Proc. of the</u>
 33rd <u>International SAMPE Symposium</u>, March 7-10, 1988, 571-582.
- 16. Fried, N., and Graner, W.R., "Durability of Reinforced Plastic Structural Materials in Marine Service", <u>Marine Technology</u>, Volume 3, 1966, page 321.

- 17. S.P. Systems, LTD. Product Literature on Ampreg 75, REV-AMPREG75-790-1.
- 18. P. Wilkinson, A. Montorfano, and E. Pfletschinger, "A New Prepreg for Open Mould Production of Large High Performance Pieces, Especially Large Boats and Ships", DSM Italia.
- 19. Neoxil Prepreg Technical Information, DSM Italia.
- 20. Newport Adhesives and Composites, Inc., Product List.
- 21. Berthod, C. Ciba Composites. Presentation at NSWC Carderock Division, November 1993.
- 22. Ciba Composites, M10E Product Data.
- 23. Patz, G. YLA Inc., personal communication.
- 24. Sundsrud, J., 3M ITSD/Aerospace Systems Laboratory, personal communication.
- 25. 3M Aerospace Materials Dept., SP 377 Low Energy Cure Composite Prepreg Family Product Data, 78-6900-1289-9.
- 26. Fibercote Industries, Inc., Resin Matrix Selector, 1992.
- 27. Pieczko, D., Fibercote Industries, Inc., personal communication.
- 28. Fibercote Industries, Inc., P-601 Product Data.
- 29. Bjorksten, J., Tovey, H., Harker, B, and Henning, J., "Polyesters and Their Applications", Reinhold Publishing Corp., 1956, page 168.
- 30. Juska, T., Mayes, J.S., and Russell, M.J., "Evaluation of Marine Construction Materials and Fabrication Methods", <u>Proc. of MACM 5</u>, Composites Education Assoc. Inc., April 1994.
- 31. Lubin, G., <u>Handbook of Fiberglass and Advanced Plastics</u> Composites, Van Nostrand Reinhold, 1969, page 869.
- 32. Harmon, W. ICI Fiberite, personal communication.
- 33. Seemann, W., Seemann Composites, Inc., personal communication.

ACKNOWLEDGMENTS

The authors would like to thank Mr. Thomas Mixon, Ms. Bonnie Wells, and Mr. Timothy Dapp of CDNSWC, Carderock Division. Mr. Mixon fabricated all of the laminates evaluated in this study (except the Neoxil Prepreg panel) and prepared the samples for testing. Ms. Wells did the fiber and void content determinations, as well as the mechanical property testing and data reduction. Mr. Dapp did the thermal analysis.

Appendix A. Thermal Analysis

The values of Tg reported in this study were determined by DMTA with a method we intended to be meaningful and reproducible. Tg is a transition during which amorphous polymers soften, but they do so gradually, over a temperature range of about 50 °C. The glass transition can be detected with several analysis methods, and assigning a single value of temperature to characterize the transition can be done in a variety of ways. As a result, reported values of Tg for the same material can vary significantly.

The stiffness of most polymer matrix composites is fairly constant with temperature until the glass transition, during which it decreases abruptly. The modulus-temperature scans of NB-1101 as-fabricated, after post-cure, and after a 72 hour boil are given in Figure A1. The Tg was defined in this study as the onset of the modulus drop, determined by extrapolating the two linear portions of the log E' vs. temperature curve, as shown.

The thermal properties of NB-1101 typify the behavior of most of the epoxy laminates: the Tg increased about 30 °F after post-cure and decreased about 40 °F due to water absorption.

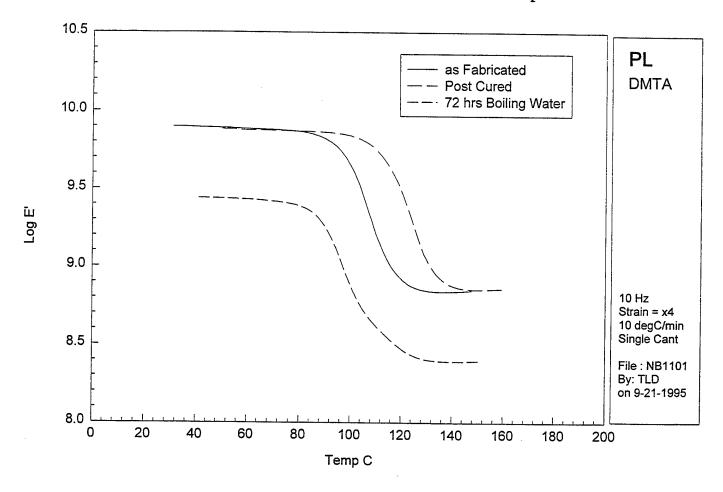


Figure A1. Modulus-temperature behavior of 7781/NB1101 asfabricated, after post-cure, and after water boil.

LTM21 and LTM22 have low cure temperatures and high post-cured values of Tg. The modulus-temperature curve for LTM22 is shown in Figure A2. At about 189 °F (87 °C) the modulus decreases slightly, then recovers, and the material appears to be serviceable up to about 293 °F (145 °C). The fast-reacting resin evidently post-cured during the scan. Therefore, we reported the as-fabricated value as 189 °F and the post-cured value as 293 °F. When we re-scanned the sample to obtain the post-cured Tg, as was done with the other resins, it was found that the Tg was only about 275 °F, probably due to degradation during the first scan. As can be seen, water absorption results in a large drop in Tg. The behavior of LTM 21 was essentially identical to that of LTM22.

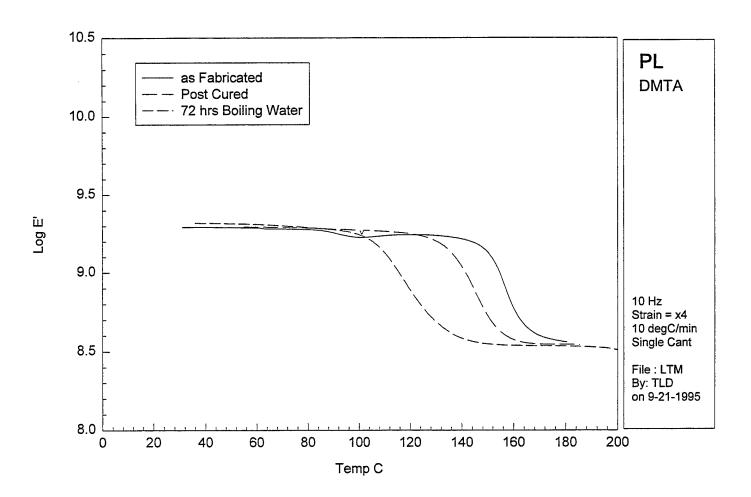


Figure A2. Modulus-temperature behavior of 7781/LTM22 asfabricated and after water boil.

The DMTA scans of a polyester laminate, 7781/P-600, are shown in Figure A3. Both P-600 and P-601 had thermal properties characterized by broad transitions and low values of Tg. In addition, water absorption had little effect on Tg. It is possible that the post-cured value may be lower than the maximum Tg of the polyesters due to degradation during first run.

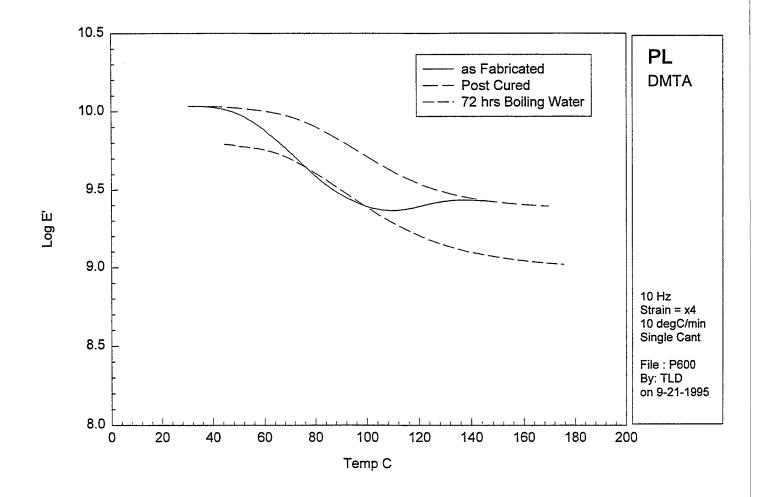


Figure A3. Modulus-temperature behavior of 7781/P-600 asfabricated, after post-cure, and after water boil.

Appendix B. Property Summary.

In table B1 we have assembled the average values of the properties measured in this study. Included in the table are compressive strength, $\sigma_{\rm C}$, tensile strength, $\sigma_{\rm t}$, flexural strength, $\sigma_{\rm b}$, Young's modulus in tension, E_t, glass transition temperatures both dry and after 72 hour boil (Tgd and TgW), wt% fiber, void content (vd%), and cure conditions of the prepregs evaluated. The strength values are in ksi, the moduli in msi, and the glass transition temperatures are °F.

Table B1. Properties of the materials evaluated in this study.

	$\sigma_{\mathtt{C}}$	σt	$\sigma_{ t b}$	Et	Tg ^d	Тg ^W	wt%	vd%	Cure conditions
WR/LTM21	59.9	76.0	74.8	4.2	189	225	77.9	0.9	140F,8hrs,vacbag
7781/LTM22 7781/LTM22	48.7 51.2	63.5 67.8	69.3 73.6	3.4 3.5	189 -	217 -	65.9 66.9	4.5 0	140F,8hrs,vacbag " ,90 psi
7781/Ampreg 7781/Ampreg	60.7 63.8	61.8 66.1	81.6 90.1	3.1 3.3	205 -	158 -	65.5 62.8	4.3 0	180F,6hrs,vacbag " ",90 psi
Neoxil	68.6	50.1	87.2	2.8	198	169	57.0	0	Unknown
7781/1101 7781/1101	57.0 62.3	50.6 48.3	68.5 69.6	2.9 3.0	203 230	187 -	60.3 60.3	0.4	
7781/1107-w 7781/1107-q	59.2 48.3	58.3 48.2	75.2 57.8	3.2	216	171 -	63.3 63.3	-	205,5hrs,vacbag " "[0/45/90/45] _{2s}
7781/M10E	52.1	53.6	77.1	3.3	217	230	62.8	0.7	210F,2hrs,vacbag
7781/RS-1 7781/RS-1	51.9 53.6	51.8 51.3			200 221	163 -	64.7 63.6	8.6 6.7	
7781/SP377 7781/SP377	56.5 59.4	41.9 43.0	59.7 59.4	1		230	63.1 64.4	1.8	205F,2hrs,vacbag " ,90 psi
1581/E761E 1581/E761E	63.1 66.0	55.3 58.3		1		181 -	62.4 62.6		180F,5hrs,vacbag " ",90 psi
WR/P601 WR/P601	64.3	61.3	1	1	i .	156 -	57.0 60.3	2.3	220F,3hrs,vacbag " ,90 psi
7781/P600 7781/P600	43.0 50.6	54.5 58.7	66.7 78.7	2.9	I	145 -	62.6 64.7	5.3	190F,2hrs,vacbag " ",90 psi
7781/9420	50.4	61.1	67.3	2.9	219		60.9	2.6	220F,5hrs,vacbag
1583/SP365 1583/SP365	37.5 59.2	35.3 47.3	ì	 -	212	176 -	68.5 69.5	13 0	300F,4hrs,vacbag " ",90 psi
Carbon/M10E	44.2	93.5	85.6	9.2		-	65.9	2.6	210F,2hrs,vacbag

INITIAL DISTRIBUTION

Copies

CENTER DISTRIBUTION

4 DTIC	Copies	Code	Name
F OND	1	601	Morton
5 ONR	1		Beach
1 332 (Kelly)	<u> </u>	65	
1 332 (Fishman)	1	65X	Benson
1 332 (Sloter)	1	655	Critchfield
1 334 (Gagorik)	1	6551	Phyillaier
1 334 (Rajapakse)	5	6551	Mayes
, , ,	1	6551	Garala
10 NAVSEA	1	6551	Nguyen
1 05P13 (Kadala)	1	6551	Bartlett
1 05P13 (Kurzweil)	1	6551	Potter
1 03P (Packard)	5	6552	Loup
1 03R1 (Camponeschi)	1	6552	Gipple
1 03P2 (Will)	1	6552	Hoyns
1 PM0450 (Brown)	1	6552	Telegadas
1 PMS30041 (Sheedlo)	1	6553	Crane
1 PMS30041 (McGrath)	20	6553	Juska
1 PMS3003 (Hollingsworth)	1	6553	Coffin
1 00C20 (Huss)	1	6553	Williams

- 2 NAVAIR
 - 1 5304 C2 (Moore)
 - 1 5304 C2 (Thompson)
- 1 NRL
 - 1 6383 (Gause)
- 1 Carderock Division, NSWC
 Combatant Craft Detachment
 1 231 (Russell)
- 1 Dahlgren Division, NSWC
 Coastal Systems Station
 1 2310 (Wyman)
- 1 NUWC (Newport, R.I.)
 1 8215 (Tucker)
- 1 NAWC
 - 1 6064 (Cochran)

H. Benson Dexter
NASA Langley Research Center
Mechanics of Materials Branch
2 West Reid Street, MS 188E
Hampton, VA 23681

Mr. Bill Seemann Seemann Composites, Inc. P.O. Box 3449 Gulfport, MS 39505

Mr. George Leon General Dynamics Electric Boat Division Department 452 Groton, Connecticut 06340

Mr. Longin Greszczuk McDonnell Space Systems Company 5301 Bolsa Avenue Huntington Beach, CA 92647

Dr. Don Adams
Mechanical Engineering Dept.
Univ. of Wyoming
Laramie, WY 82071

Dr. Travis Bogetti
Mechanics and Structures Branch
U.S. BRL
Aberdeen, MD 21005-5066

Dr. Jack Gillespie Center for Composite Materials Composites Manufacturing Lab. University of Delaware Newark, DE 19716

Dr. Mac Puckett
Dow Chemical Company
Reaction Molding & Composites
Applications Development Lab
Building B-2009
Freeport, Texas 77541

Mr. Eric Hartwig Cirrus Design 4515 Taylor Avenue Deluth, Minnesota 55811

Dr. Don Hunston Polmer Composites Group NIST Bldg. 224, Rm. A209 Gaithersburg, MD 20899 Mr. Tony Falcone Boeing Aerospace Company P.O. Box 3999, MS 73-09 Seattle, WA 98124-2499

Mr. Brian Eccles Intermarine USA P.O. Box 3045 Savannah, GA 31402-3045

Dr. Jamil Hamdallah CASDE Corporation 1901 N.Beauregard St. Suite 400 Arlington, VA 22311

Mr. Eric Greene Structural Composites, Inc. 18 Cushing Avenue Annapolis, MD 21403

Dr. Ronnal Reichard Structural Composites, Inc. 7705 Technology Drive W. Melbourne, FL 32904

Dr. George Thomas United Defense LP 1107 Coleman Ave. Box 367 San Jose, CA 95103

Mr. George Tunis Hardcore Composites 19 Lukens Drive New Castle, DE 19720

Mr. Paul Biermann Johns Hopkins University Applied Physics Laboratory Johns Hopkins Road Laurel, MD 20707

Mr. Robert Schofield Naval Architect N 1742 Shore Drive Marinette, WI 54143

Mr. Mark Livesay Sunrez Corporation 374 Merritt Drive El Cajon, CA 92020

Mr. Will Warren Ingalls Shipbuilding P.O. Box 149 Pascagoula, MS 39568-0149 Skip McDougall
Hitco Technologies
415 Pier T Avenue
(Terminal Island)
Long Beach, CA 90802

Dr. Craig Cartwright 6061 B.F. Goodrich Blvd Blount Island Jacksonville, FL 32226

Mr. Bruce Pfund Bruce Pfund Special Projects RR#3, Box 419-C Shore Road #7 Windover Turn Westerly, R.I. 02891

Mr. Eric Goetz Eric Goetz Custom Sailboats 15 Broad Common Road Bristol, R.I. 02809

Mr. Everett Pearson TPI, Inc. P.O. Box 328 Warron, R.I. 02885

Mr. Steve Crane U.S. Marine P.O. Box 9029 Everett WA 98206

Dr. Juan Cruz NASA Langley Research Center Aircraft Structures Branch 8 West Taylor Street, MS 190 Hampton, VA 23681

Mr. Paul Lazarus Professional Boatbuilder Magazine RR1, Box 683 Wiscasset, ME 04578

Mr. Robert Scott Gibbs & Cox, Inc. 1235 Jefferson Davis Highway Crystal Gateway 1, Suite 700 Arlington, VA 22202

Jeff Hendrix
BDM Federal, Inc.
4001 North Fairfax Drive
Suite 750
Arlington, VA 22203

Bill Gregory Engineering Technology Center Century Building, Suite 1250 2341 Jefferson Davis Highway Arlington, VA 22202

David Shepard U.S. Coast Guard, G-ENE-5 707 E. Ordnance Road Baltimore, MD 21226

William Harmon ICI Fiberite 2055 East Technology Circle Tempe, AZ 85284

Dr. Jerry Sunsrude 3M 3M Center Bldg. 201-1W-28 St. Paul, MN 55144-1000

Dr. David Jones Sigma Labs 6281 39th St. N., Suite C Pinellas Park, FL 34665

Dr. John Fish Lockheed 1011 Lockheed Way Palmdale, CA 93599-2540

Cedric Berthod Ciba Composites Division 5115 East La Palma Ave. Anahein, CA 92807-9000

Gary Patz YLA, Inc. 2970 Bay Vista Court Benicia, CA 94510

Laura Grasso Fibercote Industries, Inc 172 East Aurora St. Waterbury, CT 06708-2024

Dr. Gerry Flanagan Material Sciences Corporation 500 Office Center Dr, Suite 250 Fort Washington, PA 19034

Chris Ridgard Advanced Composites Group, Inc. 11220 East 112th Street North Owasso, OK 74055