Old Dominion University Research Foundation

DEPARTMENT OF CIVIL ENGINEERING
COLLEGE OF ENGINEERING & TECHNOLOGY
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA 23529

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POLYMER INFILTRATION STUDIES

By

Joseph M. Marchello, Principal Investigator

Progress Report
For the period March 31, 1991 to September 15, 1991

Prepared for
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Under
Research Grant NAG-1-1067
Robert M. Baucom, Technical Monitor
MD-Polymeric Materials Branch

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P.O. Box 6369
Norfolk, Virginia 23508-0369

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POLYMER INFILTRATION STUDIES

SUMMARY

Significant progress has been made during the reporting period on the preparation of carbon fiber composites using advanced polymer resins. The results are set forth in recent reports and publications, and will be presented in forthcoming national and international meetings.

Current and ongoing research activities reported herein include:

- LaRC Powder Towpreg Process
- Weaving Towpref made from Dry Powder Prepreg
- Composite from Powder Coated Towpreg: Studies with Variable Tow Sizes
- Toughening of PMR Composites by Semi-Interpenetrating Networks

Research during the period ahead will be directed toward several important areas of polymer infiltration into fiber bundles. Preparation of towpreg for textile preform weaving and braiding and for automated tow placement is a major goal, as are the continued development of prepregging technology and the various aspects of composite part fabrication.

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I. Introduction

Polymer infiltration studies during the period have focused on ways of preparing composite materials from advanced polymer resins and carbon fibers. This effort is comprised of an integrated approach to the process of composite part fabrication.

The goal of these investigations is to produce advanced composite materials for automated part fabrication utilizing textile and robotics technology in the manufacture of subsonic and supersonic aircraft. This objective is achieved through research investigations at NASA Langley Research Center and by stimulating technology transfer between contract researchers and the aircraft industry.

The sections of this report cover the July Peer Review presentation on the composites program, status reports on individual projects, current and planned research, and publications and scheduled technical presentations.

II. July 1991 Peer Review

This section summarizes the current and future activities in polymer infiltration and composite materials preparation as presented to the visiting Peer Review Committee on July 24, 1991. The following viewgraph presentations highlight the important features of the project and serve to introduce project status reviews given in subsequent sections of the report.

POWDER IMPREGNATION PROCESS FOR ADVANCED COMPOSITE MATERIALS IN AUTOMATED PART FABRICATION

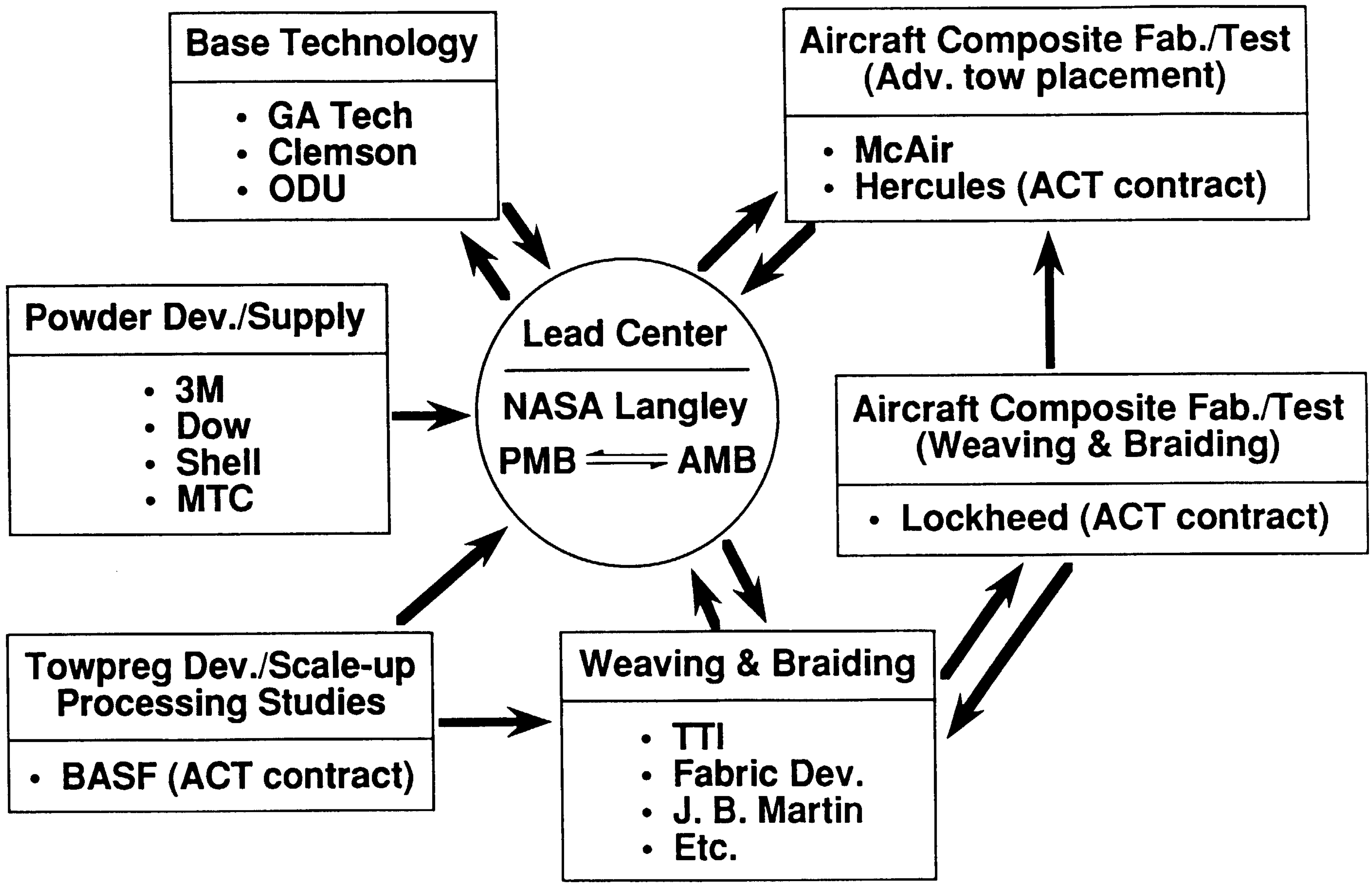
PRODUCT FORMS

- TOWPREG RIBBON FOR ADVANCED TOW PLACEMENT
- WOVEN BROADGOODS
- UNIWEAVE PREPREG TAPE
- 2D/3D WOVEN AND BRAIDED TEXTILE PREFORMS

MATRICES

- SUBSONIC COMMERCIAL A/C: EPOXIES, THERMOPLASTICS
- SUPERSONIC COMMERCIAL A/C: PI, BMI, THERMOPLASTICS

POWDER-COATED PREPREG TECHNOLOGY



ISSUES IN TEXTILE TECHNOLOGY - BROADGOODS, TAPES AND PREFORMS

WEAVING AND BRAIDING PROTOCOL

TOWPREG FLEXIBILITY

POWDER ADHESION

SERVE, TWIST OR SIZE

CONSOLIDATION BULK FACTOR

ISSUES IN ROBOTICS TECHNOLOGY - ADVANCED TOW PLACEMENT

ROBOT HEAD DESIGN

TOWPREG CUSTOM RIBBONIZING

TOW ADD & DROP CAPABILITIES

GAP ELIMINATION & TURNING RADIUS

ON-THE-FLY CONSOLIDATION

CHALLENGES/BARRIERS IN CURRENT TECHNOLOGY

- SOA HOT-MELT, TOUGHENED EPOXY PREPREG AND TOWPREG HAVE SHORT OUT-TIMES, HIGH SCRAP LOSSES AND REQUIRE REFRIGERATION
- SOA TOUGHENED EPOXIES AND THERMOPLASTIC PREPREGS AND TOWPREGS ARE VERY EXPENSIVE ($90-190/LB)
- THERMOPLASTIC MATRICES ARE VERY DIFFICULT TO EITHER HOT MELT OR SOLUTION COAT ONTO CARBON FIBER
- IN SOLUTION IMPREGNATION, SOLVENTS MUST BE HANDLED WITH CARE AND ARE HARD TO REMOVE
- COMMINGLED PROCESS APPEARS TO BE A VERY EXPENSIVE APPROACH
- ENVIRONMENTAL STABILITY OF LOW-COST RTM MATRICES

IMPORTANT FEATURES OF THE POWDER COATING PROCESS

- VERSATILE: THERMOPLASTICS AND THERMOSETS
- OPERATES AT ROOM TEMPERATURE
- NO SOLVENTS INVOLVED
- MANAGEABLE EXPOSURE TO TOXIC MATERIALS
- PREPREG REQUIRES NO SIGNIFICANT REFRIGERATION: REDUCES WASTE/SPOILAGE
- PREPREG CAN BE WOVEN, FILAMENT WOUND, PULTRUDED, THERMOFORMED
- VIABLE ALTERNATIVE TO RTM PROCESSING OF TEXTILE PREFORM COMPOSITES

POWDER-COATED TOWPREG TECHNOLOGY FOR TEXTILE COMPOSITES

OBJECTIVE: Develop powder-coated towpreg technology as a viable alternate to RTM for fabrication of textile composites.

APPROACH:

1. Verify weave capability of powder-coated towpreg by systematically fabricating and evaluating flat composite panels of increasing complexity.

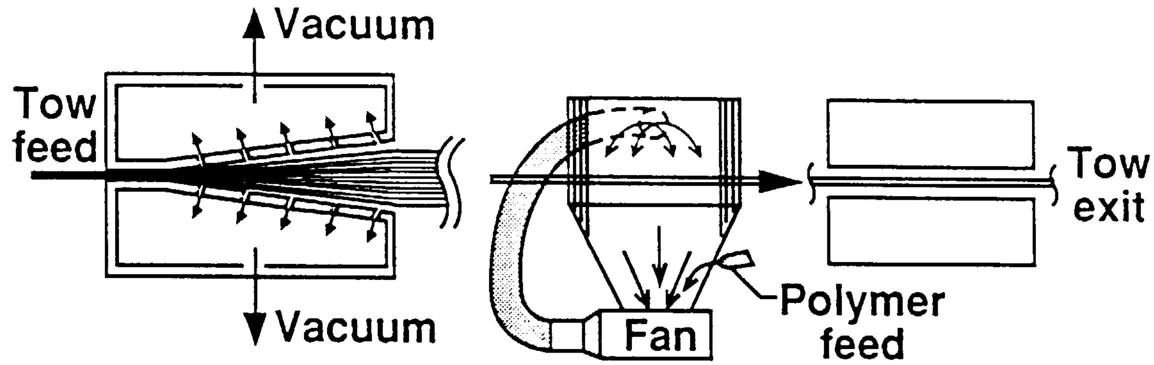
2. Verify braid capability of powder-coated towpreg by fabricating and evaluating braided flat composite panels.

3. Fabricate and evaluate single- and three-stringer panels from powder-coated towpreg.

4. Conduct engineering studies to determine the important physical properties and processing characteristics of powder-coated towpreg.

5. Conduct detailed compaction/consolidation studies to determine the proper fabrication procedures for preforms made from powder-coated towpreg.

DRY POWDER PREPREGGING



Prepreg Processing Modules

Tow spreader chamber

- Adjustable tow spread
- Minimum fiber damage
- Fast line speed

Powder coater

- Recirculating chamber
- Uniform coating
- Precise resin control

Powder fusion

- Convection furnace
- Individual fiber coating

Powder prepregging process analysis

$\phi = \tan^{-1}[f(\Delta P)/F_t]$

ϕ = Fiber angle

F_t = Fiber tension

ΔP = Chamber pressure drop

$P = 195n/U_t$

P = Resin weight fraction

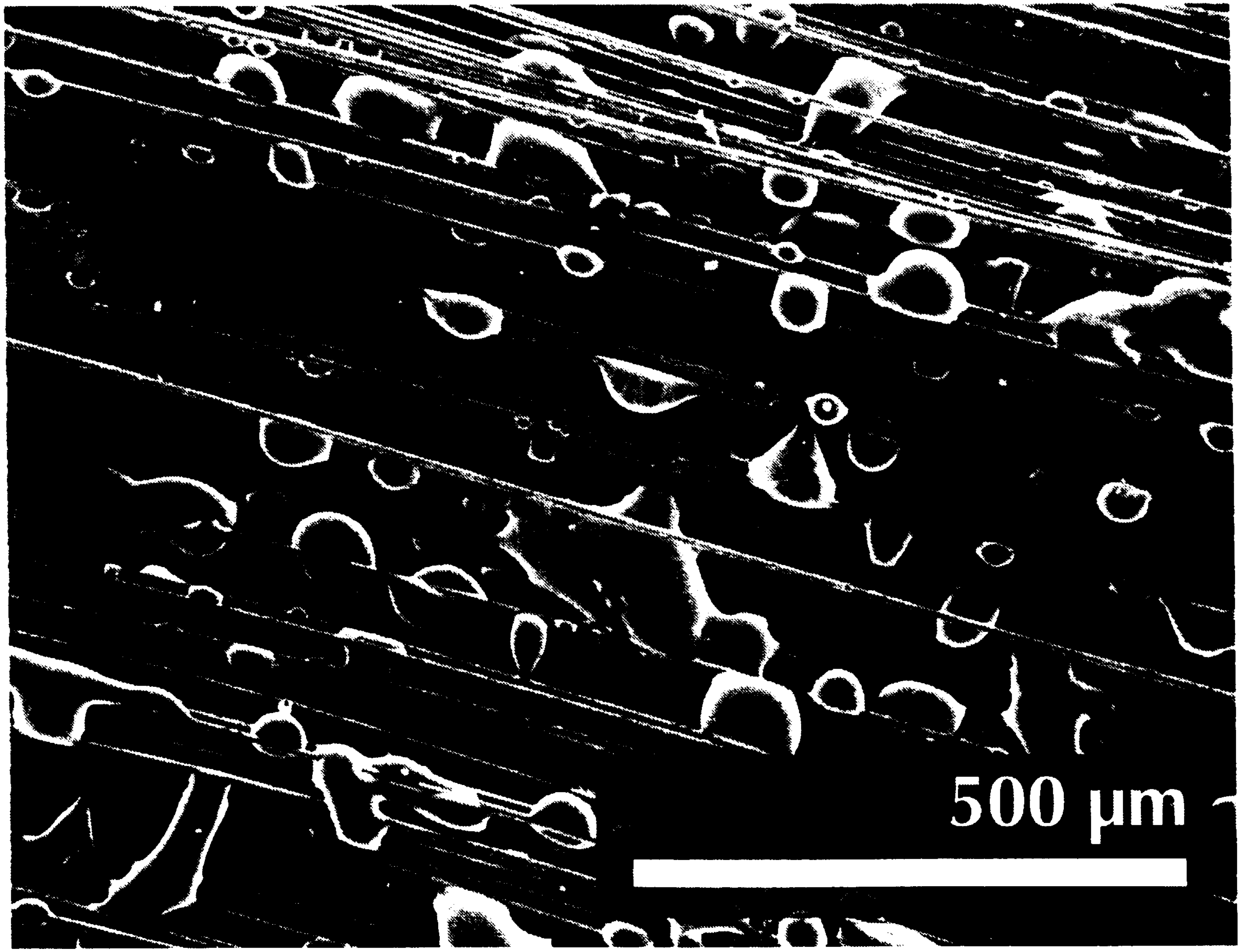
n = Particle cloud density

U_t = Linear tow rate

$T_{oa} = [5 \times 10^{10} + 39 \times 10^{10}/\theta]^{1/4}$

T_{oa} = Ave oven temperature

θ = Fiber heating time


500 µm

DRY POWDER TOWPREG PROCESS

CONCLUSIONS

- Extensively tested at bench scale
- Applicable to thermosets and thermoplastics
- Unidirectional and woven test samples have been of good quality
- Design, theory and operating correlations developed for each process component
- Ready for scale up to commercial level
- Cost estimates are comparable to or less than those of conventional prepreg
- Viable option for producing unidirectional prepreg, woven broadgoods, and woven and braided preforms

OTHER STUDIES

TOW SIZE OPTIMIZATION - COST VERSUS PROPERTIES

PROPERTIES OF TWISTED AND WOVEN TOWS

PREPREGGING POWDER MIXTURES

FUTURE

- CONTINUE EVALUATION OF PROCESSABILITY OF NEW RESINS
- ESTABLISH CONSOLIDATION PROTOCOL FOR POWDER COATED TEXTILE COMPOSITES
- DEMONSTRATE USE OF POWDER COATED TOWPREG IN FABRICATION OF A STRUCTURAL PANEL
- DEMONSTRATE ADVANCED TOW PLACEMENT OF POWDER COATED TOWPREG - THERMOSETS AND THERMOPLASTICS
- CONTINUE HIGH LEVEL OF TECHNOLOGY TRANSFER

III. Weaving Towpreg Made from Dry Powder Prepregging Process

Maylene Hugh August 16, 1991

Introduction

This study investigates the weavability of dry polymer powder coated fibers and the effects of varying yarn bundle sizes on the mechanical properties of the woven cloth. The fibers used are G30-500 (BASF) and AS-4 (Hercules) carbon fibers in tow bundles of 3k, 6k, and 12k filaments. Weaving protocol will be developed for carbon fibers impregnated with a thermoplastic polymer, LaRC-TPI. Once the weaving protocol has been established, a thermosetting polymer, PR-500, will be made into towpreg and then woven.

Powder Prepregging

The powder prepregging process involves three steps: spreading of the tow, deposition of polymer onto the spread tow, and fusion of the polymer onto the fibers. A carbon fiber tow bundle is pneumatically spread to approximately 3 inches in width. The fibers are then impregnated by means of a dry, recirculating, fluidized powder chamber. Radiant heating is used to obtain particle-tow fusion. A thorough description of the system and the design relations developed for it can be found in Reference 1. The current system has been upgraded for prepregging operations at speeds of 30 - 40 ft/min.

Weaving

A weaving protocol is being established for dry LaRC-TPI powder and carbon fiber prepreg. The initial work has been performed on yarns containing 6k filaments. Various aspects, such as yarn shape, flexibility, twist, and damage, are being investigated to determine the weavability of the current state of the towpreg. The set-up of the loom and the weaving of the towpreg is being examined for ways to minimize damage imparted to the woven towpreg.

The first weaving trial involved 6k tow bundles. The towpreg was rewound onto 36 separate spools in order to produce a balanced 3" wide fabric with 12 picks per inch (ppi). Two rewinding machines were used to determine how best to rewind towpreg.

The spools of rewound towpreg were loaded into the loom. Initial weaving efforts revealed problems with loose fiber accumulation in the heddles and comb. Twisting the towpreg at 15 twists/meter has not appeared to have overcome this difficulty. It is planned to investigate hot ribbonizing combined with twisting as a means of reconsolidating the loose fibers into the tow bundle. 3" and 6" wide 8-harness satin cloth will be made for mechanical testing.

Mechanical Test Program

The mechanical tests that are being done for this study will compare unidirectional laminates to [0°/90°] laminates to consolidated panels of 8-harness satin cloth. The effects of tow bundle size within these laminates will be determined by obtaining short beam shear strength and flexural strength and modulus. In addition, the transverse flexural strength will be used to compare tow bundles in unidirectional materials. Compression strengths will be tested in the woven cloths to determine the effects of tow bundle size on the degree of crimp.

Towpreg made from 3k and 6k G30-500, and 12k AS-4 filaments have been frame-wrapped into unidirectional panels to obtain the flexural strength and modulus, the transverse flexural strength and modulus, and the short beam shear strength. The data is shown on Table 1. The 3k and 12k transverse flexural data is forthcoming. Because of the low values obtained for the 6k material, the mechanical tests are being redone.

Reference

[1] R. M. Baucom and J. M. Marchello, *SAMPE Quarterly,* Vol. 21, No. 4, pp. 14-19, July 1990.

Table 1. Mechanical Property vs. Yarn Bundle Size

Mechanical Properties	Yarn Bundle Size 3k, W_{fiber}*	6k, W_f	12k, W_f
Short Beam Shear Strength (ksi)	16.0, 64.0%	9.8, 67.6%	13.7, 68.9%
Flexural Strength (ksi)	226.6, 60.0%	188.8, 62.4%	239.1, 63.8%
Flexural Modulus (Msi)	16.3, 60.0%	15.3, 62.4%	14.6, 63.8%
Transverse Flexural Strength (ksi)	16.8, 60.0%	15.3, 61.9%	22.0, 64.0%

* The fiber weight percentage was determined by acid digestion method.

IV. # Vibrational Resin Content Monitoring

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August 5, 1991

I. Abstract

The frequency spectra of vibrating samples of towpreg coated with thermoplastic polymers were analyzed to determine the resin content of the samples. According to theory, the behavior of the vibrating towpreg should approximate that of a vibrating string with constant mass density, in accordance with the standard string equation. The results of current experiments show that the method, with calibration, is capable of fixing the resin content to within 10% absolute accuracy.

II. Introduction

Thermoplastic composites offer the potential of good toughness and attractive mechanical properties at elevated temperatures. The LaRC Dry Powder Towpreg System utilizes a promising approach to combine thermoplastics with continuous fiber tows. Continuous monitoring of the powder coating operation is essential to ensure a uniform product. The purpose of the resin content monitor is to continuously determine the amount of resin present in a given on-line sample of towpreg. The objective of this project is to construct, calibrate, and demonstrate a resin content monitor using the principle of free vibration.

The principle of free vibration hypothesizes that vibrating towpreg behaves much in the same manner as a vibrating string. Thus, the frequency spectrum of the towpreg was analyzed in response to an induced vibration, and its mass density was determined through use of the standard string equation. From basic physics, we have an equation for the first harmonic vibrational frequency of a given string:

$$f = (1/2L)\,(T/m)^{(1/2)}$$

f = frequency (hz)

L = length (cm)

T = Tension (dyne)

m = mass density (g/cm)

Given a piece of towpreg with known length and under a constant known tension, the mass density can then be calculated based on the frequency response.

III. Materials

A wide variety of polymer coated towpreg samples were obtained from the NASA Langley Prepregging Lab. All of the samples tested were 12K strands, and a variety of polymers (LARC TPI, PEKK) were tested.

IV. Experimental

The towpreg samples were mounted on the experimental vibrational resin content monitor apparatus as is shown in fig. 1. Vibrations in the vertical plane are induced by single manually triggered pulses from an electromagnetic shaker, which is driven by a pulse generator and power amplifier. The towpreg is displaced approximately 2mm by the shaker. The vibrating towpreg then triggers an optical switch (an OPTEK wide gap slotted optical switch model#OPB800W) that utilizes an infrared diode capable of high speed switching. The output signal from the optical switch is sent to an oscilloscope and a frequency spectrum analyzer. The wave form is that of a damped harmonic oscillation. The frequency spectrum decomposition yields a characteristic peak at the frequency of the first harmonic of the vibrating towpreg. (See fig.2)

While the purpose of this project is to validate vibrational monitoring as a means of accurately determining resin content, it is first necessary to accurately fix the resin content of the samples to be studied by the new technique. The prepregging lab weighs 5 ft. lengths of towpreg and then determines the resin content by comparing that weight to a table. In order to validate those results, I independently weighed smaller lengths (approx. 50cm) of the samples for which the prepregging lab had already fixed the resin content. The mass density was then calculated based on this weight and a accurate measurement of the sample length. This mass density was then fitted to a curve of mass density vs. resin content, based on a plot of the table used by the prepregging lab.

The studies of the vibrational resin content monitoring technique had two parts. An initial study focused its attention on demonstrating the theory that the towpreg behaves similar to a vibrating string. There were three basic components to this initial study: the length effect, the mass effect, and the tension effect. The numeric and plotted results of these tests are given in fig. 3.

Further tests concentrated on developing a calibration curve of resin content versus frequency response for a variety of towpreg lengths. These curves were generated from data taken on a series of samples of known resin content, with each curve representing a single towpreg length. Later studies focused on developing static calibration curves at different lengths.

V. Results and Discussion

Static Test Results

The initial experiments focused on supporting the theory that the vibrating towpreg does in fact behave much in the same way as a vibrating string. To accomplish this, three different effects were studied. The first series of tests were intended to prove the linear dependence of the frequency response on the length of the sample. According to the string equation, the frequency is proportional to the inverse of the length of the sample. A plot of data taken over a range of lengths between 16cm and 36cm provided ample evidence that this holds true. The second group of tests looked at samples of towpreg with a range of mass densities; this was accomplished by subdividing a single tow into several pieces. The string equation tells us that the frequency is inversely proportional to the square root of the mass density. For the samples tested, those with the higher mass density consistently responded at a lower frequency, as predicted. The third, and final, series of initial tests studied the dependence of the frequency on the tension applied to the towpreg samples. The frequency response of the towpreg samples was shown to be directly proportional to a root power of the tension, as predicted by theory. It remains to be established that the frequency is proportional to the square root of the Tension, as dictated by the string equation. In each of the three initial tests, the frequency of the vibrating towpreg was shown to vary with the expected parameters, but with slightly different functional dependences. Thus, according to the results obtained, the towpreg follows the general behavior of a string, but does not exactly fit the string equation. This is believed to be due to the stiffness of the polymer coated towpreg.

Once the initial tests proved that the towpreg behaves much like a string, static calibration curves were constructed at several lengths to determine resin content directly from the frequency response. These calibration curves were

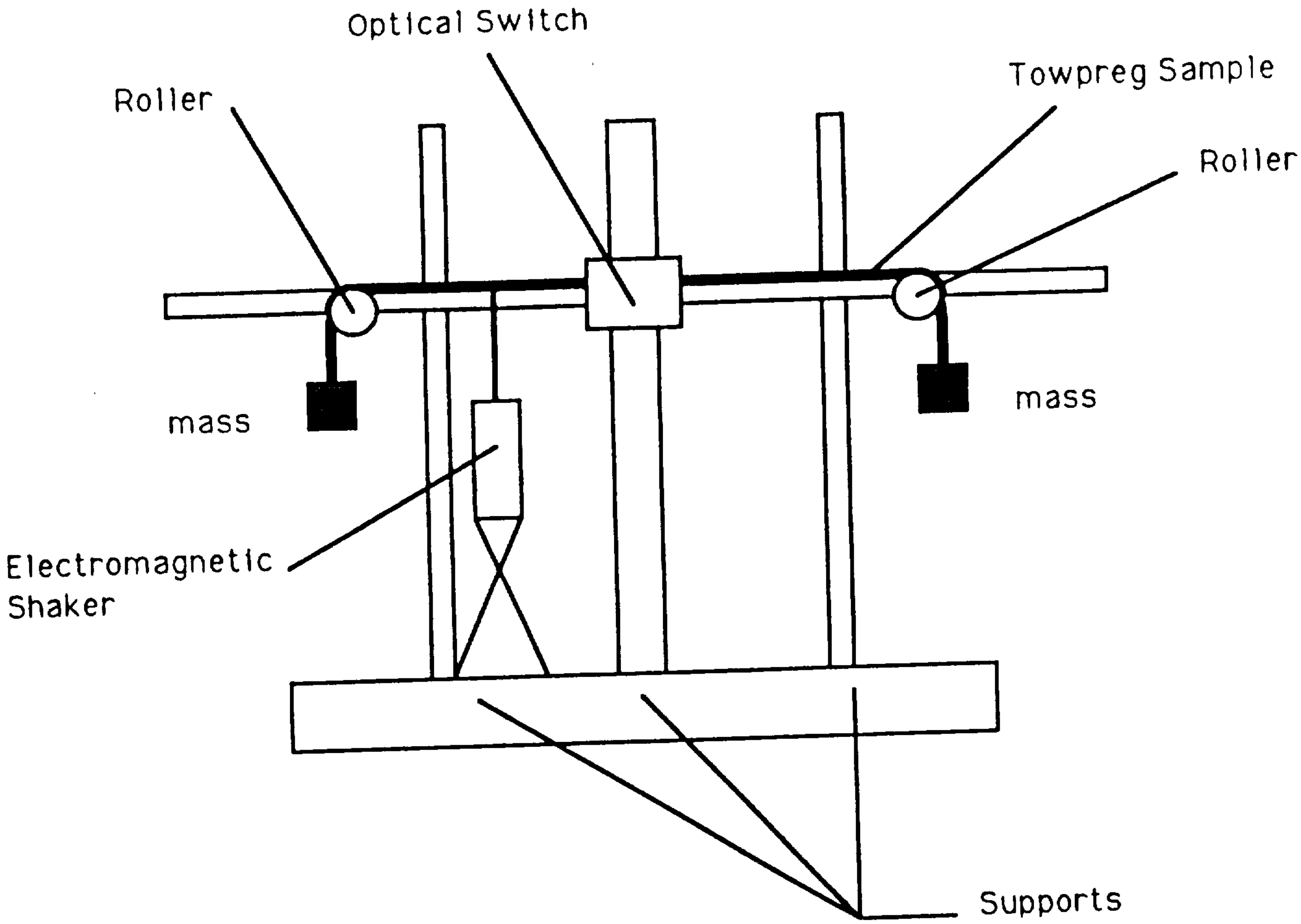
Once the initial tests proved that the towpreg behaves much like a string, static calibration curves were constructed at several lengths to determine resin content directly from the frequency response. These calibration curves were based on testing samples of known resin content; two curves were developed for each length due to the two different methods of fixing known resin content. These two methods of determining resin content lead to different values for the resin content of the same sample of towpreg. A plausible explanation for this difference is that my method uses a shorter sample, which would tend to point out local irregularities in resin content. However, I prefer to use my values for known resin content, because I determine the resin content of each sample that is tested on the vibrational monitor by directly weighing and measuring that sample. The calibration curves were used to predict the resin content, based on vibrational analysis, of several samples of unknown resin content with an error between 2.3% and 14%. These samples were tested using the static calibration curves for lengths of: 20 cm, 30 cm, and 32.5cm. An example of the calibration curves used and the results of the tests on the samples of unknown resin content is in Fig. 4. An alternate form of calibration curve plots mass density versus frequency and then uses another table to convert mass density to resin content, based on the known mass density of a clean piece of tow.

Dynamic Test Results

The dynamic tests of the vibrational resin content monitor were intended to accomplish two goals: First to determine if the apparatus would work under dynamic conditions and second to note modifications that will have to be made to the apparatus in order to obtain acceptable frequency spectra data. The frequency response data obtained (Fig. 5) showed some correlation between frequency and resin content, and the results followed a form similar to the static calibration. The sources of error can be explained by the inherent problems in using this current apparatus for dynamic testing. The main contributors to the scattering of the data are as follows: loose rollers(caused vertical translation of tow which varied with tow speed), poor optical switch alignment (difficult to obtain clear peaks in frequency spectra), speed of tow causes variation in tension under current conditions, and triggering of shaker and capture of waveform difficult to achieve due to lack of an external trigger on apparatus. All of these problems have fairly simple solutions. The loose rollers can be replaced with new ones that are designed to hold the tow stable and guide it to alignment with the optical switch. The optical switch alignment can be improved by carefully designing the new rollers and possibly using a motorized drive to track the switch along with the tow. The speed effect on the tow tension can be reduced by introducing rollers that hold the tow at constant tension at the nodes. Finally, an external trigger can be arranged to capture the damped harmonic waveform at the proper time. These modifications will enable the monitor to be used to create dynamic calibration curves from which a test of unknowns (such as in the static testing) can be completed. This will clearly reveal the potential of the monitor to be used continuously on the running prepregging line.

VI. Conclusion

The primary objective of this project was to establish the validity of the hypothesis that towpreg will behave like a classical vibrating string, and verify that vibrational resin content monitoring is possible. Based on the results obtained from tests using the vibrational technique of monitoring resin content, it can be concluded that the initial hypothesis is valid and that it is possible to utilize frequency response analysis as a means of monitoring resin content. The results of the dynamic tests show that modifications will have to be made to the apparatus, but that the vibrational technique will work on a towpreg production line. Despite the fair accuracy of the monitor apparatus at this point, the technique of vibrational analysis is, however, of use to the dry powder prepregging line, in that it is of value to regulate the line even if the absolute accuracy of the monitor is only fair. Currently, the technique is capable of fixing resin content (under static testing) with an absolute error of between 2.3% and 14% (see Fig. 4, column rc pr. -rc / rc). It is worthwhile to note that the deviation between the resin content values calculated by the prepregging lab and my own mass density method are between 6.3% and 13.5% for the same towpreg samples (see Fig. 4, column rc1-rc / rc1). Thus, the vibrational technique is capable of fixing the resin content at least to the same degree of absolute accuracy as the current weighing technique. Thus, vibrational resin content monitoring holds promise for enabling continuous monitoring of the production of towpreg by the dry powder prepregging line.



Vibrational Resin Content Monitor

Fig. 1 Monitor Set-up

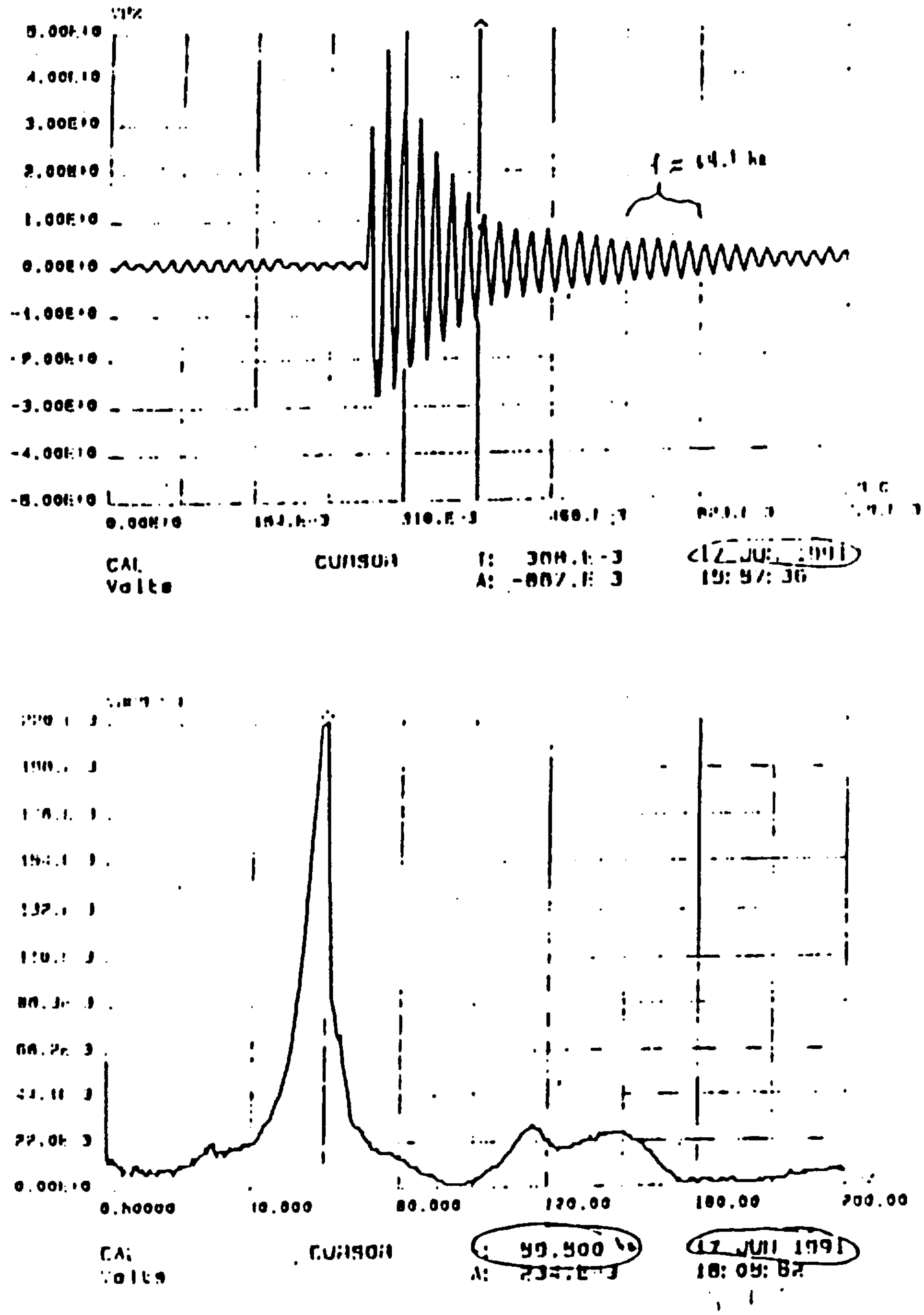
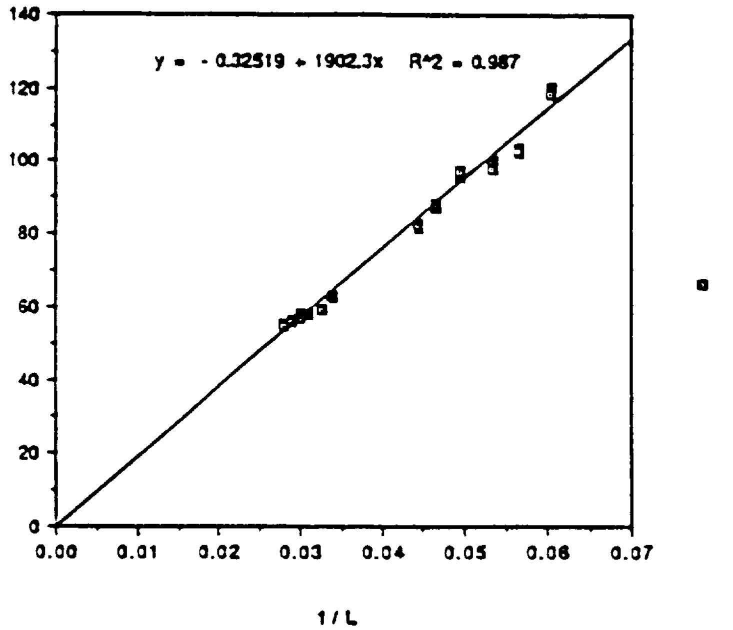


Fig. 2 Waveforms

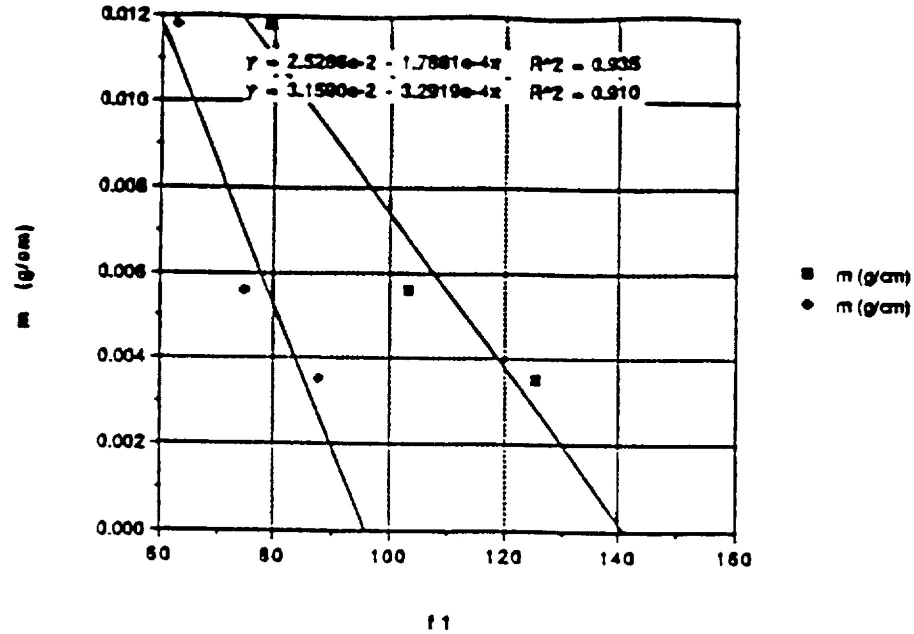
Data from "6/27stiff"



6/27stiff

	L	1/L	f	log(f)	log(L)
1	16.50000	0.06061	120.000	2.079	1.217
2	16.50000	0.06061	120.000	2.079	1.217
3	16.50000	0.06061	119.000	2.076	1.217
4	16.50000	0.06061	120.500	2.081	1.217
5	17.70000	0.05650	103.500	2.015	1.248
6	17.70000	0.05650	103.000	2.013	1.248
7	17.70000	0.05650	102.500	2.011	1.248
8	17.70000	0.05650	103.000	2.013	1.248
9	18.70000	0.05348	99.500	1.998	1.272
10	18.70000	0.05348	99.000	1.996	1.272
11	18.70000	0.05348	100.000	2.000	1.272
12	18.70000	0.05348	98.000	1.991	1.272
13	20.20000	0.04950	96.000	1.982	1.305
14	20.20000	0.04950	97.000	1.987	1.305
15	20.20000	0.04950	97.500	1.989	1.305
16	20.20000	0.04950	97.000	1.987	1.305
17	21.50000	0.04651	87.500	1.942	1.332
18	21.50000	0.04651	88.500	1.947	1.332
19	21.50000	0.04651	88.000	1.944	1.332
20	21.50000	0.04651	88.500	1.947	1.332
21	22.50000	0.04444	82.000	1.914	1.352
22	22.50000	0.04444	82.000	1.914	1.352
23	22.50000	0.04444	81.500	1.911	1.352
24	22.50000	0.04444	83.000	1.919	1.352
25	29.60000	0.03378	63.500	1.803	1.471
26	29.60000	0.03378	63.250	1.801	1.471
27	29.60000	0.03378	62.750	1.798	1.471
28	29.60000	0.03378	62.750	1.798	1.471
29	30.70000	0.03257	59.250	1.773	1.487
30	30.70000	0.03257	59.500	1.775	1.487
31	30.70000	0.03257	59.250	1.773	1.487
32	30.70000	0.03257	59.250	1.773	1.487
33	32.20000	0.03106	58.500	1.767	1.508
34	32.20000	0.03106	58.500	1.767	1.508
35	32.20000	0.03106	58.500	1.767	1.508
36	32.20000	0.03106	58.500	1.767	1.508
37	33.20000	0.03012	58.000	1.763	1.521
38	33.20000	0.03012	57.250	1.758	1.521
39	33.20000	0.03012	57.250	1.758	1.521
40	33.20000	0.03012	57.250	1.758	1.521
41	34.40000	0.02907	56.250	1.750	1.537
42	34.40000	0.02907	56.250	1.750	1.537
43	34.40000	0.02907	56.500	1.752	1.537
44	34.40000	0.02907	56.250	1.750	1.537
45	35.80000	0.02793	55.000	1.740	1.554
46	35.80000	0.02793	55.000	1.740	1.554
47	35.80000	0.02793	55.250	1.742	1.554
48	35.80000	0.02793	55.000	1.740	1.554

Fig. 3a Length Effec

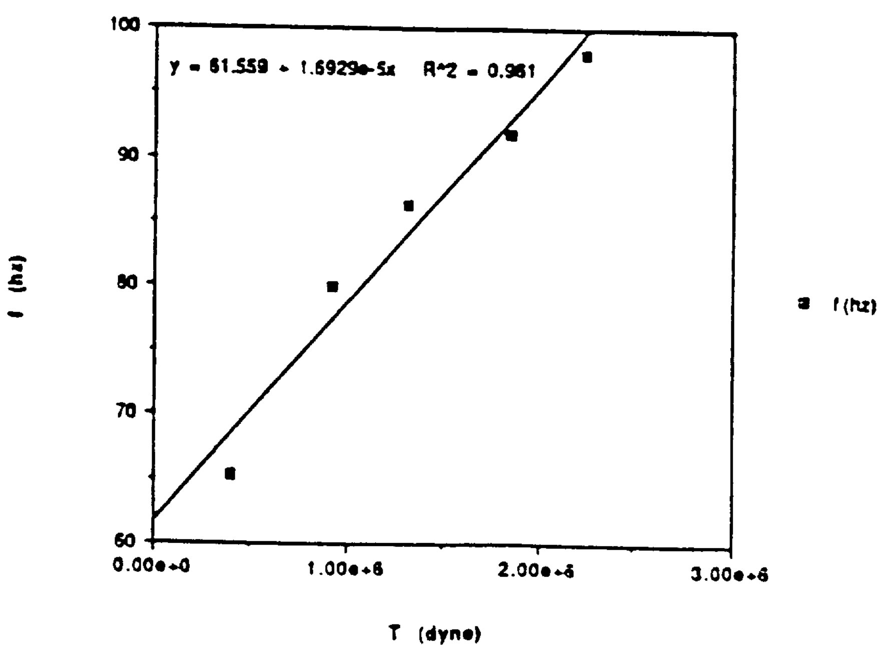


Mass Effect

	L1 (cm)	f1	L2 (cm)	f2	m (g/cm)
1	21.500	125.300	30.300	87.380	0.00354
2		103.125		74.500	0.00558
3		78.800		62.450	0.01180

Fig. 3b Mass Effec

Data from "Tension Effect"



Tension Effect

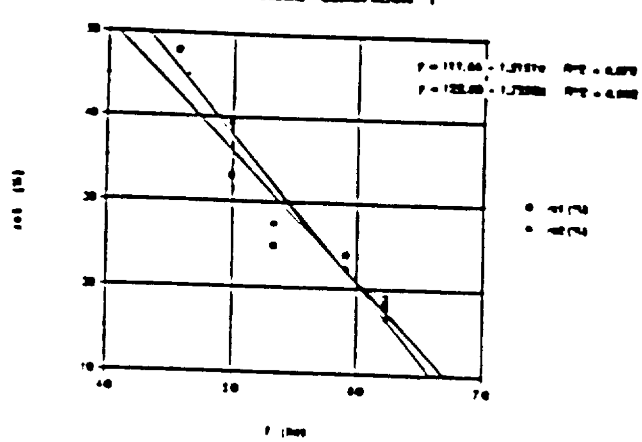
	T (g)	T (dyne)	T^1/2	f (hz)	log(T)	log(f)
1	40.340	395332.000	628.754	65.250	5.597	1.815
2	93.990	921102.000	959.741	79.330	5.964	1.903
3	134.330	1316434.000	1147.360	86.250	6.119	1.936
4	187.980	1842204.000	1357.278	91.375	6.265	1.963
5	228.320	2237536.000	1495.340	98.125	6.350	1.992

Fig. 3c Tension Effec

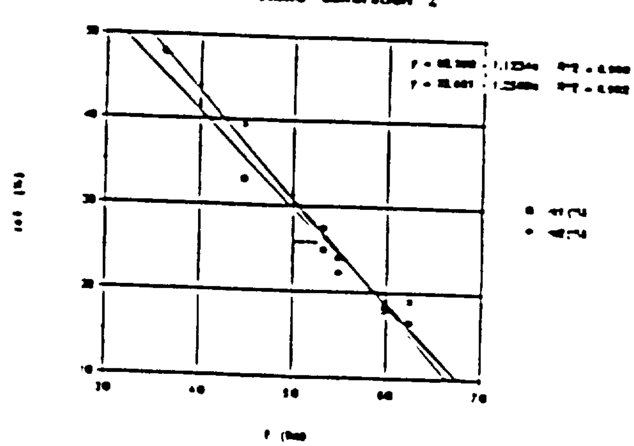
Static Test of Unknowns

	L (cm)	ra1 (%)	ra (%)	m (g/cm)	ra1 pred. (%)	ra pred. (%)	ra pr.-ra/ra	ra1-ra/ra1
1	20.000	19.400	25.400	0.01184	18.540	18.680	-0.260	0.310
2		31.100	26.900	0.01211	23.600	24.000	0.108	-0.135
3		37.800	35.400	0.01368	37.370	38.810	0.096	-0.063
4		39.100	35.800	0.01377	32.480	33.570	-0.062	-0.084
5								
6	30.000	19.400	25.400	0.01184	16.760	18.470	-0.351	0.310
7		31.100	26.900	0.01211	26.200	26.800	-0.004	-0.135
8		37.800	35.400	0.01368	36.300	37.880	0.070	-0.063
9		39.100	35.800	0.01377	40.860	39.030	0.097	-0.084
10								
11	32.500	19.400	25.400	0.01184	19.370	18.790	-0.260	0.310
12		31.100	26.900	0.01211	29.700	30.700	0.140	-0.135
13		37.800	35.400	0.01368	34.830	36.700	0.037	-0.063
14		39.100	35.800	0.01377	33.310	34.950	-0.023	-0.084

Data from "static calibration 1"



Data from "static calibration 2"



Data from "static calibration 3"

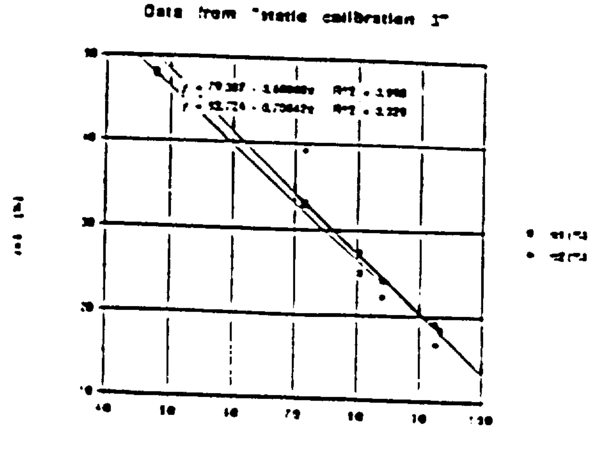


Fig. 4 Calibration Curves

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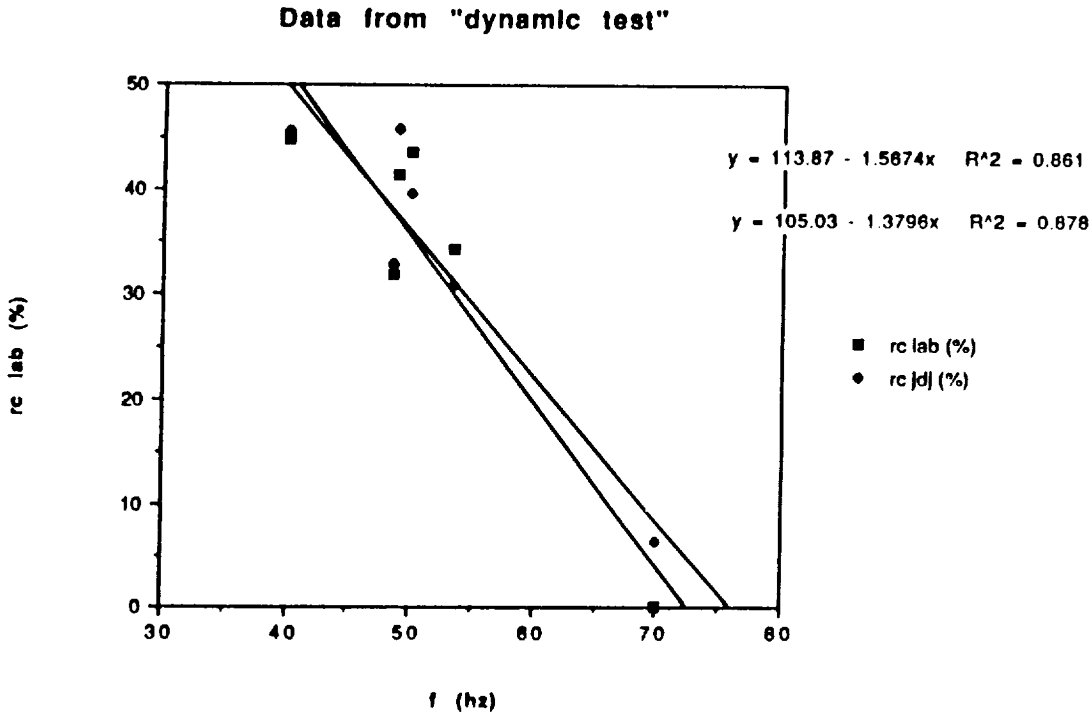


dynamic test

	rc lab (%)	m (g/cm)	rc jdj (%)	f (hz)
1	41.400	0.01605	45.600	49.000
2	43.600	0.01455	39.500	50.000
3	44.800	0.01602	45.700	40.000
4				
5	31.600	0.01319	32.900	48.500
6	34.200	0.01279	30.700	53.500
7				
8	0.000	0.00896	6.500	70.000

Fig. 5 Dynamic Test Results

V. SEMI - IPN TOUGHENING OF PMR - TYPE COMPOSITES

Following safety concerns about MDA, a diamine used in PMR-15, a less toxic alternative designated RP46 has been developed at NASA Langley Research Center (1). This report details the efforts in developing the full potential of RP46 in composite applications across a broad spectrum of application regimes.

A. Development of Prepregs and Composites

The first task undertaken in taking the resin from the test tube to the composite, was to develop high quality prepreg. To this end, RP46 resin solutions of differing concentrations were carefully synthesized and characterized, with respect to various parameters such as density and viscosity. These were prepregged and processed into laminates of different thicknesses and layups. Temperature, pressure and bleed times were optimized to produce laminates with a maximum void content of 1 percent. An insitu high temperature soak cycle was developed to eliminate the long, free standing postcure associated with these systems (Figure 1). Extensive volume fraction measurements of these laminates were undertaken using the chemical digestion method. These results, summarized in Table 1, were used to determine optimum prepregging and consolidation conditions for producing laminates with fiber volume fractions of approximately 60 percent (± 2 percent) and void volumes of less than 1 percent. Similar benchmarking studies on PMR-15 were also conducted, in order to effect a comparison of mechanical properties.

All materials were impregnated using the drum winding technique. Though this apparatus has been described previously (2), a brief description of the process is outlined. An IM - 7 (12K, unsized) fiber tow from a free spinning unwinding creel, passed between two tension bars and onto guide spools (that aligned the fiber) before it entered a sealed resin reservoir. Within the reservoir, the fiber tow passed through the impregnating solution over an assembly of rollers. These served to spread the fibers as it was being impregnated and ensured complete wetout. The tow exited the reservoir through a stainless steel die that squeezed the resin solution through the fiber tow, metered the amount of resin on the fiber and shaped the thickness and width of the impregnated tow. This tow was wound on a 2.5 feet diameter drum backed with a trifluroethylene polymer release film. The entire creel - guide roll - reservoir assembly was maintained on a moving track whose translational speed was adjusted such that the impregnated tow wound on the drum to provide a continous gap-free prepreg. A typical run yielded a 35 square foot sheet of prepreg.

PMR - type resin composites are characterized by low damage tolerance and toughness. While there are several general techniques for toughening of thermosetting resins for composite applications, the present approach relies on toughening by chemical means. In order to be effective, the toughening agent must have a T_g close to the processing (crosslinking) temperatures of both PMR - 15 and RP46, so as to not appreciably lower the use temperatures of the composite systems and yet be co-processible with them to fabricate tough composites. A controlled creation of a tough thermoplastic / PMR semi - IPN at the ply - to - ply interface is therefore likely to provide toughness to the resulting composite without substantial loss of high temperature capability. Matrimid 5218 (Ciba Geigy) is a tough thermoplastic polyimide with a Tg of 315 ° C - 325 ° C, a range compatible with PMR - type composites. It is stable for prolonged periods at the processing temperatures. A DSC scan of the 5218 powder indicated a T_g of about 320 ° C. Further, Matrimid 5218 is physically compatible with the base resins at elevated temperatures, and provides good quality, void-free laminates.

Matrimid 5218 was supplied as fully imidized flakes and was ground to a fine powder using a Retsch Grinder. The particle size distribution is shown in Figure 2. in order to obtain large quantities of controlled, semi - 2 IPN PMR - 15 and RP46 prepreg, several impregnation technologies were evaluated. This resulted in the development of a reproducible, quantitative technique for powder coating prepregs during impregnation, for which a patent disclosure has been filed. In this technique, the 5218 powder was metered onto the wet tow during the impregnation step. This was achieved by mounting a powder filled conical hopper fitted with a central stirrer rod just above the tow as it wound around the drum. An elastomeric nipple was fitted to the hopper at the exit port. The 5218 powder dispensed onto the prepreg was metered by adjusting the annulus between the stirrer rod and the nipple, which could be varied by choosing among several sized nipples. This arrangement is depicted in Figures 3 and 4. In order to effect a suitable comparison with baseline properties of PMR - 15 and RP46 composites, the resin content of the prepregging solution was adjusted to provide a total resin volume content of 40 percent in both the toughened and non - toughened postcured composites. The 5218 powder metered on the prepreg was approximately 12 percent by weight of the total resin content of the B - staged prepreg. The 5218 powder coalesced / reacted during lamination to give a void free resin layer at the ply interfaces. An SEM photomicrograph of the powder coated RP46 prepreg is shown in Figure 5.

The solution wound prepreg was permitted to remain on the drum for several hours to allow most of the methanol to evaporate. The prepreg was then cut into suitable sizes and B - staged in an air oven at 200 ° C for one hour to remove residual solvent and initiate the chemical reaction to the preimidized polymer. The prepreg was then cut and stacked in the desired layup and thickness, backed with XK 22 release agent coated Kapton films and placed in a matched - metal mold. In order to eliminate batch - to - batch variations, pieces of prepreg from several batches were incorporated in each laminate. The mold was placed between the platens of a 50 ton four - post upacting press and subject to the cure cycle prescribed in Figure 1. All panels were scanned ultrasonically so as to ensure defect - free laminates for the mechanical testing. The T_gs of the cured laminates, detected by TMA runs, were as follows :

PMR - 15 : 325 ° C
Toughened PMR - 15 : 290 ° C
RP 46 : 325 ° C
Toughened RP46 : 285 °C.

B. Mechanical Characterization of PMR - type Composites

This section presents the mechanical test results of the baseline PMR - 15 and RP46 composites and the 5218 toughened PMR - type composites. In addition to toughness data, a comprehensive engineering property profile evaluation of all systems was undertaken in order to understand the trade - offs involved with the toughening of PMR - type polyimide resins. The test matrix employed in this study is given in Table 2. Table 2 also provides the laminate layups, sample dimensions and test conditions employed for each of the laminate level property determinations. End - tabbed samples were bonded with 0 / 90 balanced fiberglass laminated end - tabs (G - 10, from Reed Plastics) using Hysol 9309 adhesive. Wherever called for, commercially available room temperature strain gages from Micromeasurements Inc. were employed. All tests were performed in accordance with standardized procedures (ASTM, SACMA).

Figures 6 - 10 depict the mechanical properties of all four systems. The error bars represent one standard deviation from the mean. The flexural strengths of the toughened systems were lower than those of the untoughened systems by 15 - 20 percent. However the flexural strength of the toughened RP46 composite was only marginally lower than that of the PMR - 15 composite, as the RP46 systems showed greater flex strengths than their PMR - 15 counterparts. Flexural modulus like the strength, showed moderate decline with the incorporation of 5218 toughener for both systems. The failure deflection , a measure of toughness in flexure, showed an increase with the addition of toughener. Short Beam Shear strength was also seen to decrease with the incorporation of 5218 toughener.

Unidirectional laminate tensile properties (strength, failure strain and modulus) for all systems were consistent with rule - of - mixtures expectations of IM - 7 fiber based composites. Compression strength declined modestly (~ 5 percent) in toughened systems, while failure strain increased. RP46 based composites showed higher compressive strength values than the PMR - 15 based composites. The compressive modulus was unaffected by toughening. Data scatter in transverse tension data was seen to be high, reflective of internal random flaw dominated behavior. No clear corelations emerged from either strength or ultimate strain data. Modulus values were considerably lower than expected values from similar tests on epoxy / PEEK materials.

Inplane shear strength values were seen to decrease by approximately 15 percent in toughened samples, while modulus values were lower by 10 percent. Compressive properties of quasi - isotropic samples were determined by short block compression tests. Toughening depressed compression strength by 10 - 15 percent, without affecting modulus or ultimate strain values.

Mode I and II fracture toughness values were determined by DCB and ENF specimens respectively . Though the initiation values are influenced by the thickness of the starter flaw, both Mode I and II initiation fracture toughness values increased with the addition of 5218. Likewise, steady state G_c values in both Mode I and II increased in the toughened states. RP46 composites showed higher toughness than PMR - 15 composites in initiation and steady state G_c values in both Mode I and II. Initiation G_c values were higher than steady state G_c values in Mode II , but lower in Mode I. While toughening increased steady state Mode I and Mode II G_c only modestly (20 - 25 percent), the most dramatic improvement was seen in Mode II initiation G_c values

C. Morphological Considerations

Studies were undertaken to determine the morphology of the toughened PMR -15 and RP46 composites. Extensive SEM observations of fractured surfaces in both the toughened composites showed a single phase material. The fracture surfaces were quite tortous, with grooves, holes and matrix lacerations, but even extensive tilt operations in the SEM did not reveal two seperate phases as may be expected from a combination of thermoplastic and thermoset matrices. No evidence of a film or phase was evident at the ply - to - ply interfaces. Fracture surfaces showed evidence of good fiber - resin adhesion. Thermomechanical runs (TMA) on toughened PMR - 15 and RP46 laminates showed only a single transition, reflective of a single phase morphology.

Attempts were made to leach out the thermoplastic 5218 resin in both toughened composites. Composite samples were placed in contact with solvents known to dissolve 5218, such as, methylene chloride, chloroform, dioxane, dimethyl formamide, cyclohexanone, dimethyl acetate and N - methyl pyrolidone, for varying periods of time upto 48 hours. No appreciable weight changes were noted. SEM observations also failed to reveal any leached polymer.

From these observations the morphological picture (of the toughened composites) that emerges is that of a single phase semi - interpenetrating morphology. Given the conditions of laminate fabrication (stacking of PMR - 15 / RP46 prepreg pieces coated with 5218 powder), this leads to several interesting conclusions on the morphology developed in such samples. During the cure cycle, the thermosetting component (PMR - 15 or RP46) continously increases molecular weight by crosslinking, while the thermoplastic component (5218) remains relatively chemically inert. This process of cure in the thermosets is accompanied by a viscosity profile that initially decreases with time (due to the rising temperatures) until a trough is reached, after which the viscosity increases (due to increasing molecular weight weight buildup). The 5218 component however, has been processed to a desired molecular weight distribution prior to incorporation in the prepreg, and hence, initially, has a much higher viscosity than the thermosetting component. It is therefore reasonable to presume that the formation of the single phase semi - IPN morphology is initiated by the flow of the PMR - 15 / RP46 component into the 5218 dominated region at each ply - to - ply interface. Since this is a diffusion phenomenon, the interface region is likely to be marked a concentration gradient, with 5218 and thermoset dominated regions at each end and a varying concentration in between. However, since the miscibility of the two components is excellent over the entire range (in this case 0 - 12 percent), no phase segregation occurs, and a single phase semi - IPN morphology is observed.

From a mechanical standpoint, a key requirement for toughness in a composite, is the suppression of delamination, which is a local or global seperation of adjacent plies in a laminate. Thus it is critical to selectively toughen the ply - to - ply interface where the stresses are quite high. While a purely tough thermoplastic interleaf may toughen the interface, the resulting composite can be vulnerable to attack by solvents. A semi - IPN at the ply - to - ply interface (with a tough thermoplastic), is likely to provide not only improved toughness and solvent resistance, but also better fatigue endurance and creep resistance, due to enhanced chemical crosslinks that hold the polymer chains together. In this manner, by localizing the toughening agent at the most desired location and by providing crosslinked semi - IPN morphologies, toughening of the bulk resin is avoided, considerably alleviating cost, processing and elevated temperature property problems as well as providing potential for enhanced solvent resistance, creep and fatigue properties.

D. Conclusions

A manufacturing science outline for the scale up of composites with experimental resin systems has been developed. Careful control of the resin solids content in prepregging solutions, (monitored by solution viscosity), can lead to laminates with controlled volume fractions of resin and fiber. An effective, alternate cure cycle has been devised for PMR - type composites. Based on the results of this methodology, approximately 50 laminates (of different thicknesses and layups) were manufactured with V_f = 60 percent (±2 percent) and a void content of ~ 1 percent, for a comprehensive study of the engineering properties of such systems.

The inherent flexibility of the ether link in 3,4' ODA apparently imparts better flow characteristics and moderately higher toughness to RP46 composites as compared to PMR - 15 composites. This increased toughness is obtained at no sacrifice in engineering strengths and stiffnesses. These factors combined with the lower health risks associated with 3,4' ODA provide an attractive combination of properties for high temperature aerospace and aeroengine applications, including replacement of the PMR - 15 market.

A methodology for selectively toughening ply - to - ply interfaces in PMR - type composites using gradated semi - IPN morphology has been outlined. PMR - 15 and RP46 composites toughened by 5218, show enhanced toughness with small attendant dropoffs in engineering strength and stiffness. Such toughened systems can be processed into thick, multiangle composites with ease.

REFERENCES

1. R. H. Pater, "The 316 ° C and 371 ° C Composite Properties of an Improved PMR Polyimide : LaRC RP46", 36th International SAMPE Symposium, April 15 - 18, 1991, San Diego, CA.

2. M. L. Wilson and C. E. Stanfield, "Apparatus for Impregnation of Weak Fibers", NASA Technical Briefs, May 1989, pp 84 - 85.

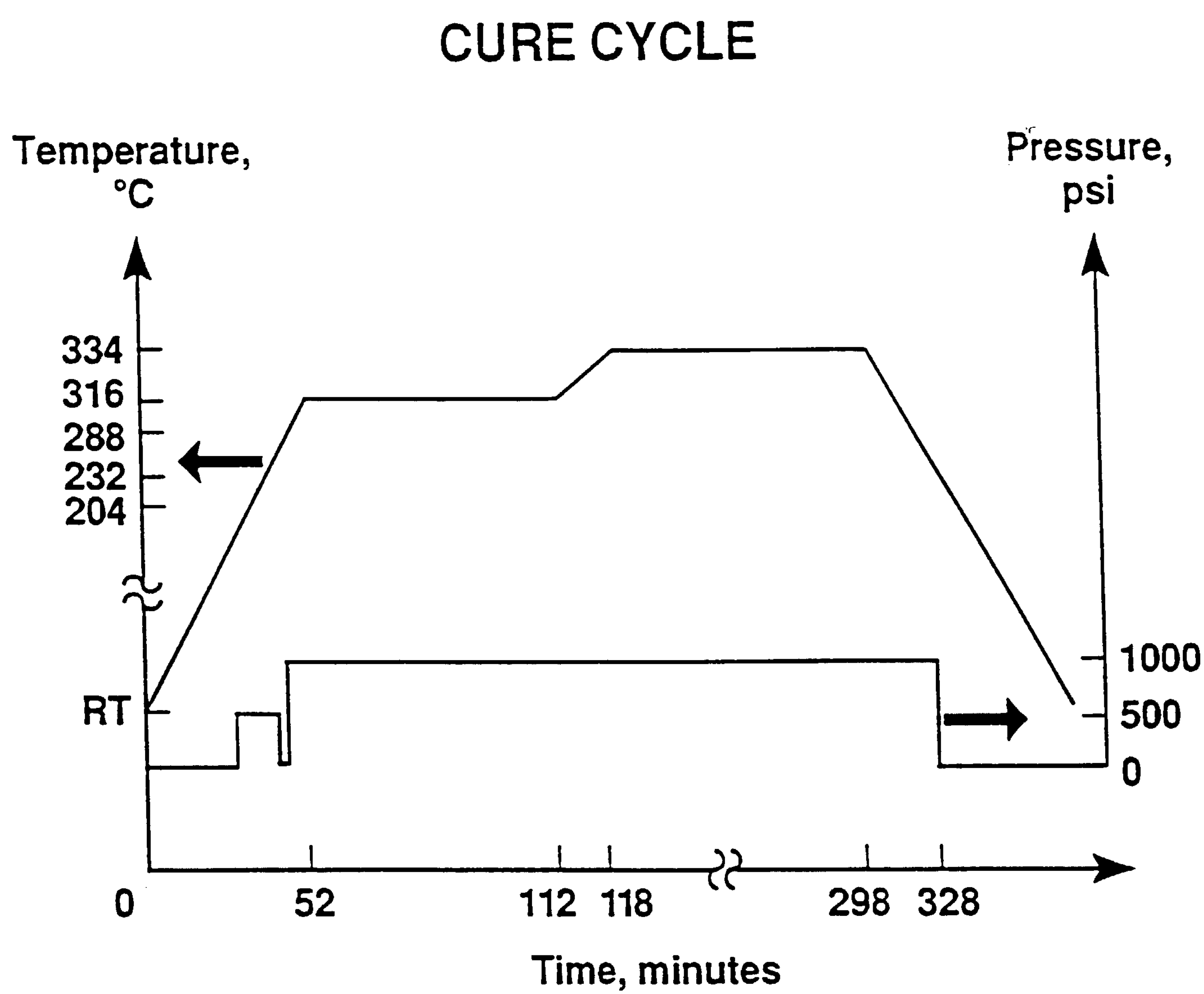
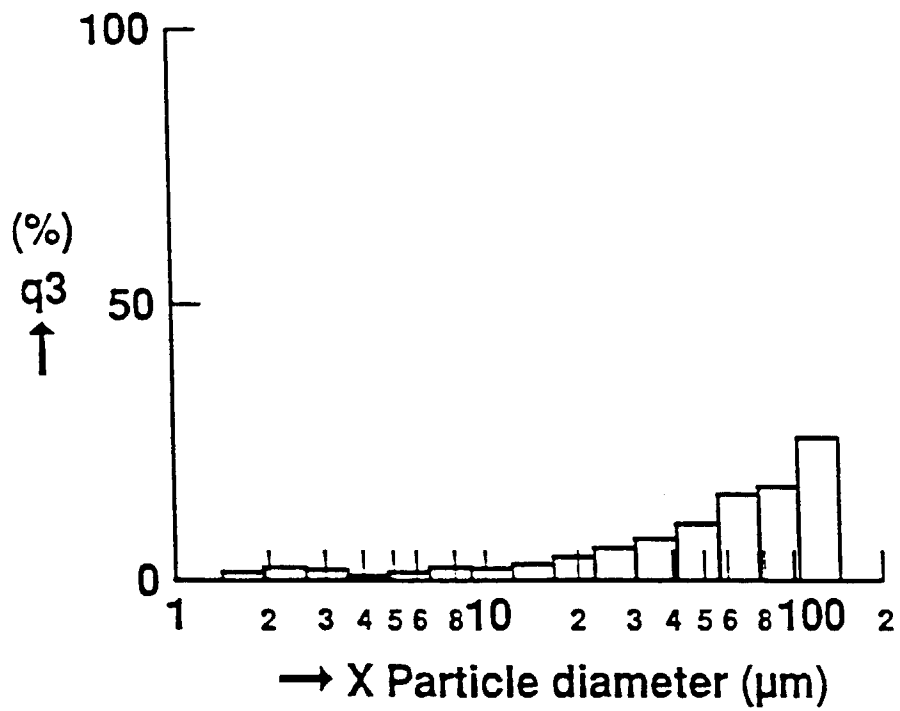

CURE CYCLE
Temperature, °C
334
316
288
232
204
RT
Pressure, psi
1000
500
0
0
52
112
118
298
328
Time, minutes

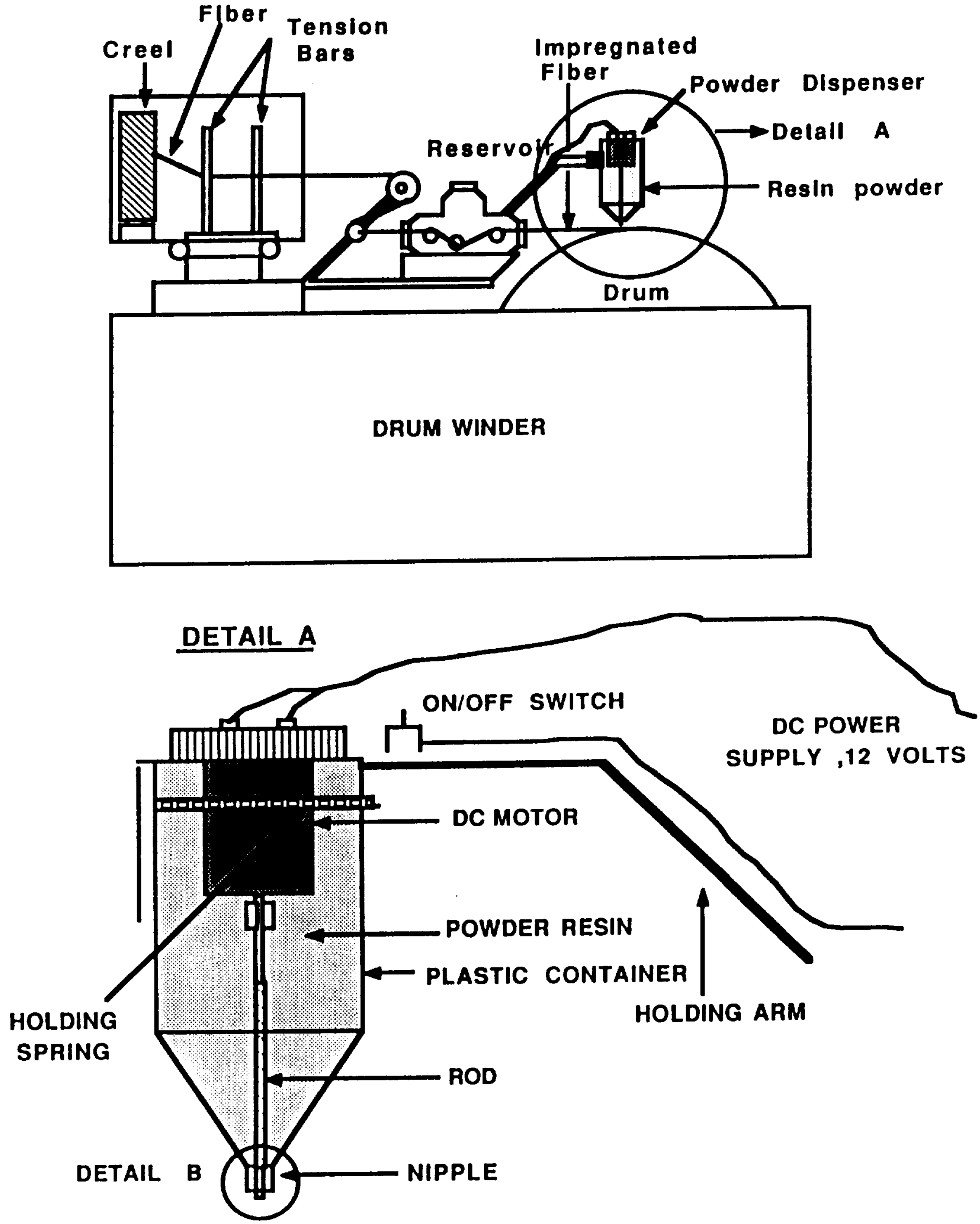
FIGURE 1

PARTICLE SIZE DISTRIBUTION DATA FOR MATRIMID 5218 POWDER



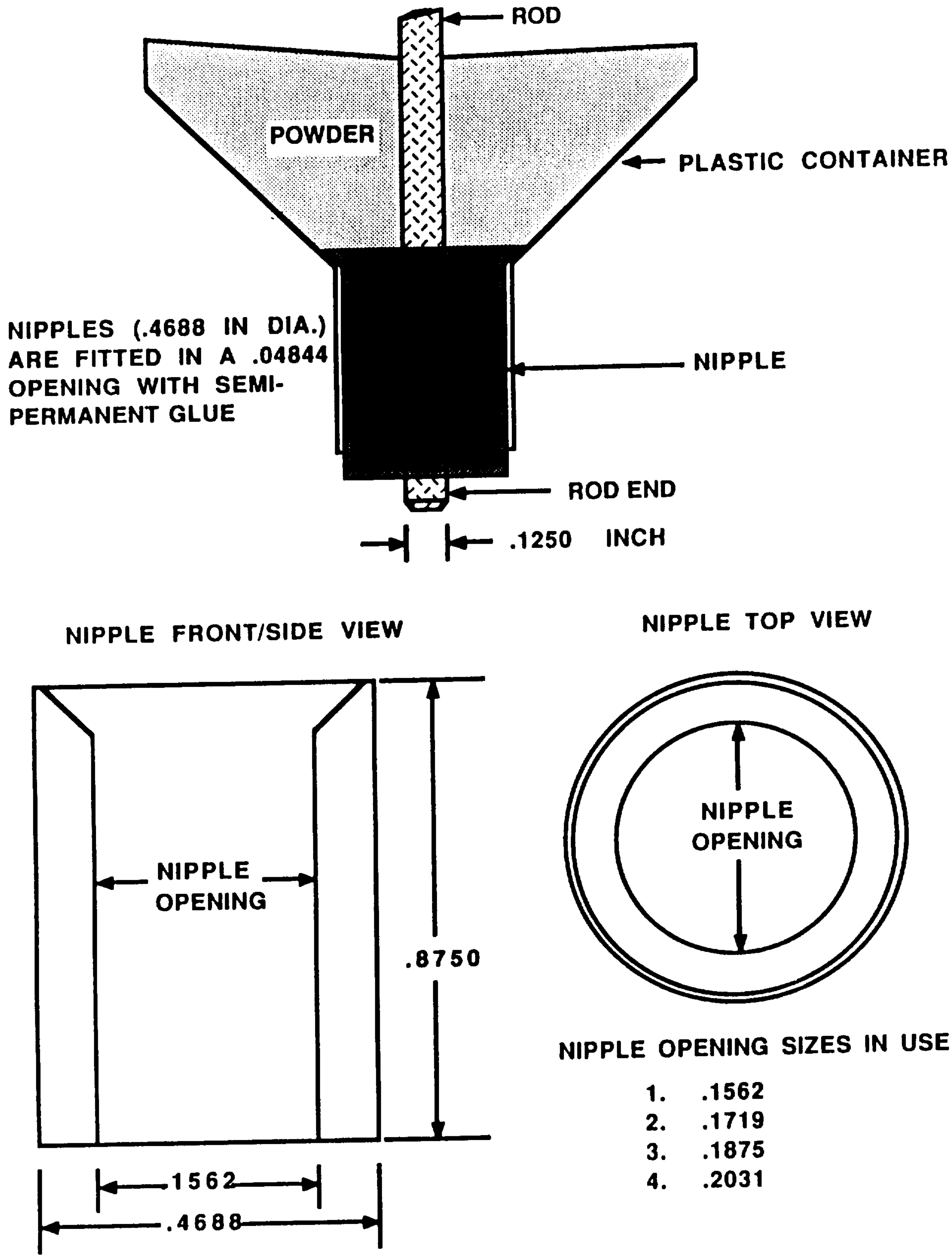
	Diameter X: (μm)	Dif. q3: (%)	Cum. Q3: (%)
1	150.0 - 110.0	96.2	100.0
2	110.0 - 80.0	17.0	73.8
3	80.0 - 59.0	15.4	56.8
4	59.9 - 43.0	10.2	41.4
5	43.0 - 31.0	7.2	31.2
6	31.0 - 23.0	5.6	24.0
7	23.0 - 17.0	4.2	18.4
8	17.0 - 12.0	2.6	14.2
9	12.0 - 9.0	2.1	11.6
10	9.0 - 6.6	2.2	9.5
11	6.6 - 4.8	1.2	7.3
12	4.8 - 3.5	0.9	6.1
13	3.5 - 2.6	1.5	5.1
14	2.6 - 1.9	1.9	3.6
15	1.9 - 1.4	1.4	1.7
16	1.4 - 1.0	0.2	0.3
17	1.0 -		0

FIGURE 2



POWDER DISPENSER ASSEMBLY

FIGURE 3



NIPPLE OPENING SIZES IN USE ARE

1. .1562
2. .1719
3. .1875
4. .2031

POWDER DISPENSER DETAILS

FIGURE 4

SEM PHOTOMICROGRAPH OF RP46-5218/IM-7 PREPREG

FIGURE 5

STRENGTH

Rate = 0.05 in./min (1.27 mm/min)

IM-7 Fiber

$V_f = 0.6$

Room Temperature Dry

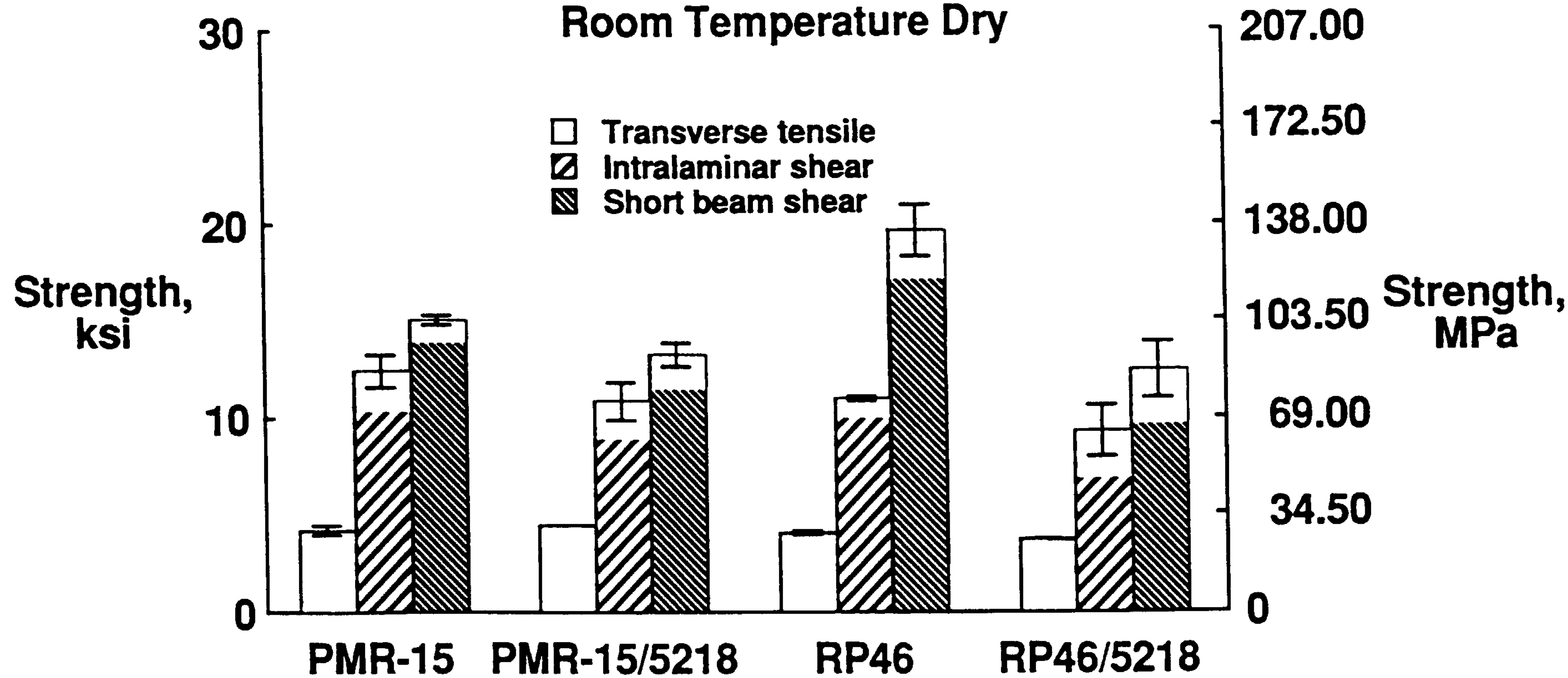


FIGURE 6

STRENGTH

Rate = 0.05 in./min (1.27 mm/min)

IM-7 Fiber

$V_f = 0.6$

Room Temperature Dry

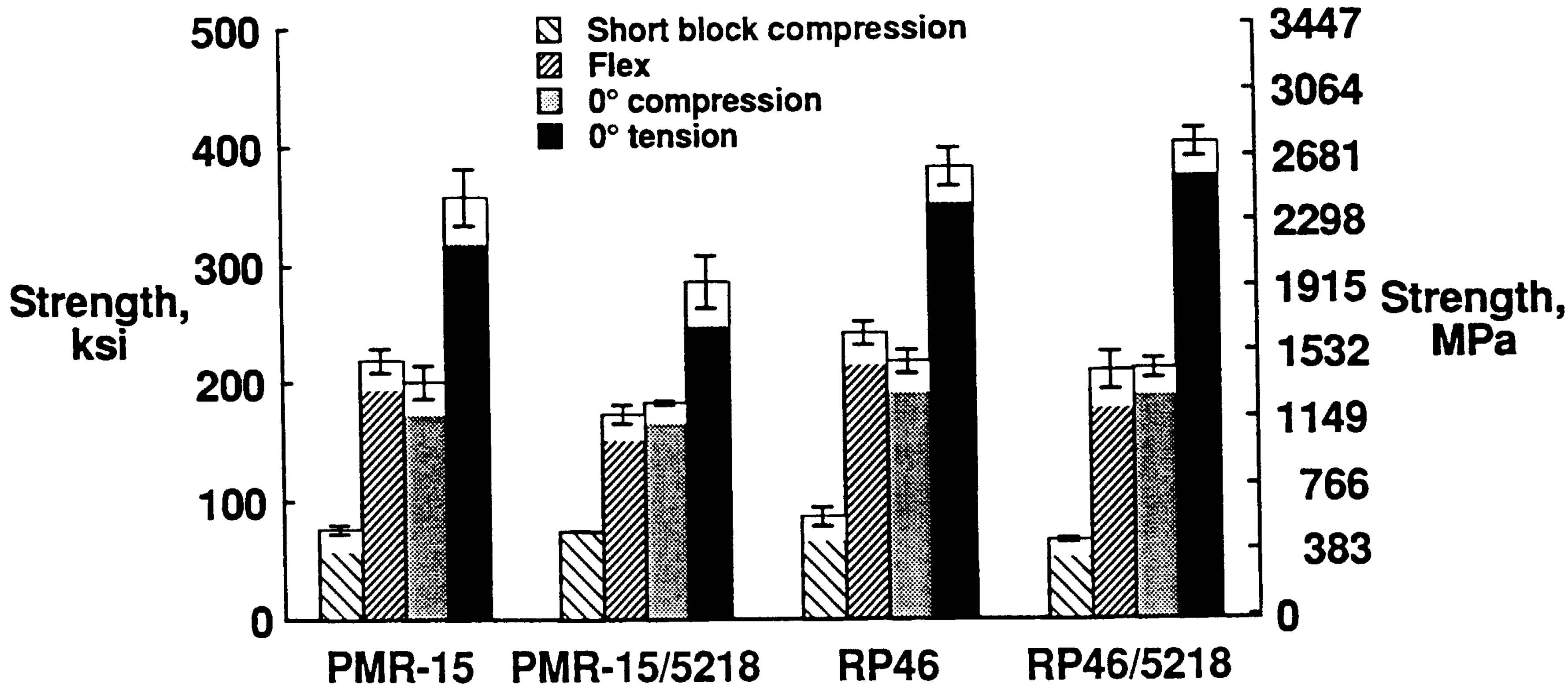


FIGURE 7

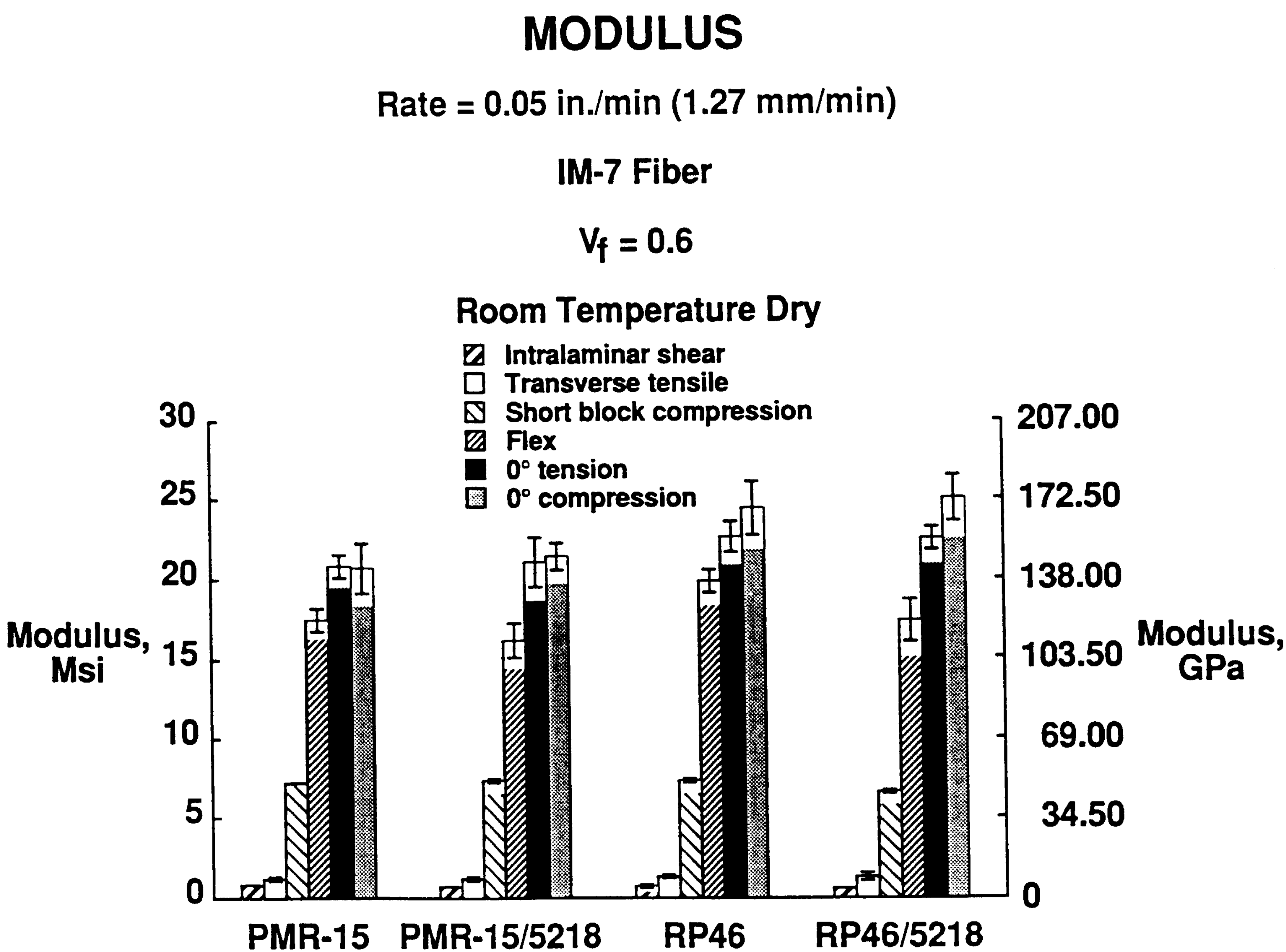

MODULUS
Rate = 0.05 in./min (1.27 mm/min)
IM-7 Fiber
$V_f = 0.6$
Room Temperature Dry
Intralaminar shear
Transverse tensile
Short block compression
Flex
0° tension
0° compression
Modulus, Msi
30
25
20
15
10
5
0
Modulus, GPa
207.00
172.50
138.00
103.50
69.00
34.50
0
PMR-15
PMR-15/5218
RP46
RP46/5218

FIGURE 8

FAILURE STRAIN/DEFLECTION

Rate = 0.05 in./min (1.27 mm/min)

IM-7 Fiber

$V_f = 0.6$

Room Temperature Dry

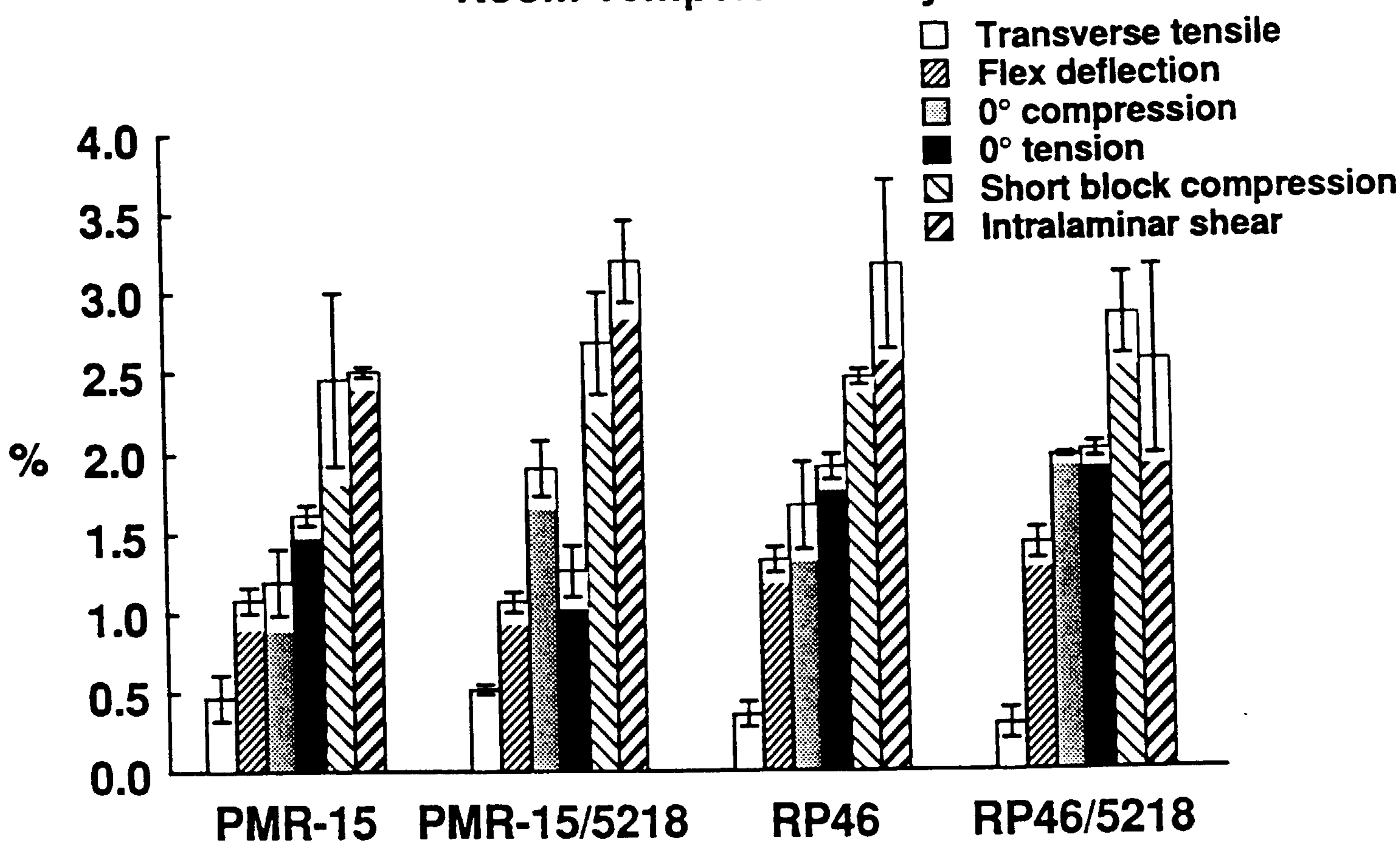


FIGURE 9

INTERLAMINAR FRACTURE TOUGHNESS

Rate = 0.05 in./min (1.27 mm/min)

IM-7 Fiber

$V_f = 0.6$

Room Temperature Dry

$(0)_{24}$ with 0.0005 in. (0.0127 mm)

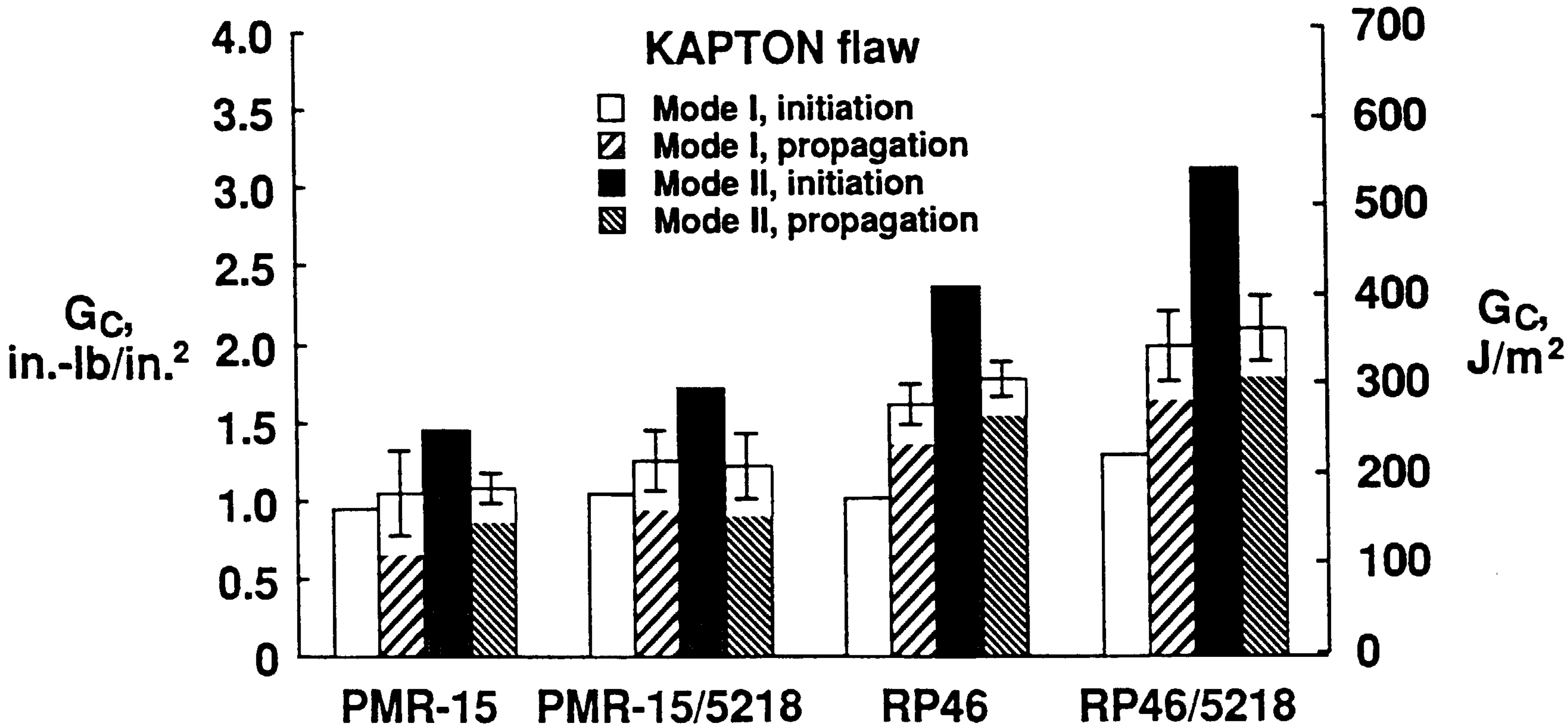


FIGURE 10

RP46 PROCESS STANDARDIZATION DETAILS

SOLIDS CONTENT (*1), %	SOLUTION VISCOSITY (*1 *2), CPS	SOLUTION DENSITY (*1), G/CC	B-STAGED PER PLY THICKNESS (*3), IN	CURED LAMINATE Vf (*4), %	POSTCURED LAMINATE Vf (*5), %	POSTCURED PER PLY THICKNESS (*5), IN
34.0	4.1	0.880	0.014	60.1	62.5	0.0061
38.7	4.5	0.893	0.017	58.3	60.2	0.0067
41.6	6.7	0.937	0.020	57.0	58.1	0.0071

*1 in Methanol
*2 Brookfield viscosity at 25 ° C
*3 1 hour at 200 ° C
*4 Standard Processing Cycle
*5 Modified Processing Cycle

TABLE 1

TEST MATRIX

Test Conditions: RTD, $v_f = 0.6$ Rate = 0.05 in./min

#	Laminate	Loading	Size			Quantity
			Length, in.	Width, in.	Thickness, in.	
1.	$(0)_n$	0° flexure	3.0	0.5	0.08	10
2.	$(0)_n$	Short beam shear	0.75	0.25	0.125	10
3.	$(0)_8$	Longitudinal tension	6.0	0.5	0.048	5
4.	$(0)_{16}$	Longitudinal compression (IITRI)	6.0	1.0	0.10	5
5.	$(90)_{16}$	Transverse tension	6.0	1.0	0.10	5
6.	$(\pm 45)_{2s}$	Intralaminar shear (tensile)	6.0	0.75	0.05	5
7.	$(-45/0/45/90)_{4s}$	Short block compression	1.75	1.5	0.20	3
8.	$(0)_{24}$ with 0.0005 in. KAPTON insert at midplane	DCB	6.0	1.0	0.16	2
9.	$(0)_{24}$ with 0.0005 in. KAPTON insert at midplane	ENF	6.0	1.0	0.16	2
10.	$(-45/0/45/90)_{4s}$	CAI (Boeing)	6.0	4.0	0.20	2

TABLE 2

VI. Current and Planned Research

Research during the coming year will be directed toward several important areas of polymer infiltration into fiber bundles. These efforts include:

- a study to establish the parameters for weaving carbon fibers impregnated with dry polymer powder. Previous weaving studies have dealt with towpreg flexibility and adhesion of powder particles. During the coming year, the optimal weaving protocol will be established and bulk factor and mechanical properties obtained.

- an investigation of towpreg ribbon customization for advanced tow placement. These activities will be directed toward preparation of powdered tow for robotic towpreg ribbon placement during aircraft part fabrication.

- assembly and operation of a second powder prepreg line to expand the research effort and provide the capability for preparing composite test samples from small quantities of new research resins and advanced materials.

- assist in the installation, testing, and operation of a six-inch prepreg machine being purchased by NASA. The machine is under construction and will be delivered in January 1992. This new experimental machine will be invaluable in research on new ways of conducting polymer infiltration of fiber bundles.

The following table itemizes current project activities of the composite group. The major emphasis is on powder impregnation, frame winding of towpreg, consolidation, and quality control.

WORKLOAD
COMPOSITE GROUP
8 / 1 / 9 1

POWDER LINE
HUGH TPI 3K 5000FT
HUGH TPI 6K 5000FT
MARCHELLO RIBBONIZING
MARCHELLO HARMONICS
MARCHELLO MIXED POWDERS
MARCHELLO GLASS/NYLON FIBER POWDER IMPREGNATION
KRISHNA IMIDIZED RP46 2000FT
KRISHNA BISMALEIMIDE 2000 FT

POWDER FRAME WINDING
HUGH LARC TPI 3/6/12K FIBERS

SOLUTION FRAME WINDING
KRISHNA RP46 3-3*6
MARCHELLO CPI

FIBER TWISTING
HUGH 5000 FT LARCTPI 12K

DRUM WINDING

PRESS WORK
HUGH 12K COMPRESSION
HUGH 12K TWISTED FLEX/SBS/TRANS. FLEX
HUGH 3/6/12K UNI/BIDERECTION FLEX/SBS/TRANS. FLEX

AUTOCLAVE
CHECKOUT

NEAT RESIN WORK
J. SMITH

LAP SHEARS
J. SMITH 9 SETS
JENSON 3 SETS
CROAL 13 SETS

SPECIAL PROJECTS:

3 POINT SHEAR HOLDER
MIA SCIOCHI

CREEP MACHINE
KRISHNA

U.V. SYSTEM
CONNELL

EQUIPMENT UTILIZATION
SMITH

STRINGER PANEL
BAUCOM

B. S. TUBE
BAUCOM

QUENCHING
NELSON

METAL DEPOSITION BOX
MARCHELLO

POWDER LINE QUALITY CONTOL
GAMMA GAUGE/OSCILLATION TECHNIQUE – Marchello / Hugh

BULK FACTOR STUDIES
WOVEN FIBER STUDY/PRESS EXPANSION – Hugh / Baucom

VII. Publications and Presentations

A recent publication and abstracts of papers to be presented are:

Joseph M. Marchello and Robert M. Baucom, "LaRC Powder Towpreg Process," Transactions of the 36th International Symposium, pp 68-80, San Diego, CA, April 15-18, 1991.

Maylene K. Hugh, Joseph M. Marchello, Janice Maiden, and Norman J. Johnston, "Weaving Towpreg Made from Dry Powder Prepregging," to be presented at the Fiber-Tex Conference, North Carolina State University, October 15-17, 1991.

Maylene K. Hugh, Joseph M. Marchello, Robert M. Baucom and Norman J. Johnston, "Composites from Powder Coated Towpreg: Studies with Variable Tow Sizes," to be presented at the 37th International SAMPE Symposium, Anaheim, CA, March 9-12, 1992.

N. J. Johnston, K. Srinivasan, and R. K. Pater, "Toughening of PMR Composites by Semi-Interpenetrating Networks," presentation to be determined, 1992.

36th International SAMPE Symposium
April 15-18, 1991

LaRC DRY POWDER TOWPREG PROCESS

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and
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ABSTRACT

The dry powder towpreg process overcomes many of the difficulties associated with melt, solution and slurry prepregging of advanced composite materials. In the process, fluidized powder is deposited on spread tow bundles and melted on the fibers by radiant heating to adhere the polymer to the fiber. Bench scale design and operating data have been correlated for use in process scale up to commercial operation.

Powdered towpreg has been woven and molded into preform material of good quality. Cost estimates suggest that processing costs are comparable to those of conventional hot melt prepreg. In the future, from a part fabrication point of view, powder coated prepreg tape, woven broad goods and woven and braided preforms may be considered as options to similar materials made by other methods.

1. INTRODUCTION

Several years ago the NASA Langley Research Center (LaRC) began investigating ways to powder coat carbon fibers (1). The concerns that gave rise to this research were the high melt viscosities of thermoplastics, which made them difficult to prepreg, and the toxicity and handling problems associated with the use of organic solvents.

Experiments at LaRC and elsewhere have confirmed many of the expectations for powder prepregging (2,3,4,5). Some of the important features of the powder coating process are:

- Versatile: Thermoplastics and thermosets
- Operates at room temperature
- Involves no solvents
- Has manageable exposure to toxic materials
- Requires no significant refrigeration: reduces waste/spoilage
- Can be woven, pultruded and thermoformed
- Offers a viable alternative to RTM processing of textile preform composites

As part of the NASA Advanced Composite Technology Program, BASF is producing both thermoplastic and thermoset towpreg in quantities of about 50 pounds per month. It is being made by the powder-slurry process using a single tow system (4). The towpreg yarn is fabricated into broadgoods and preforms for testing. It also has been pultruded into uniform width ribbon for advanced tow placement. The availability of these quantities of powder-based composite materials for testing will provide the basis for wider choices of advanced materials in the future.

The dry powder process under development at LaRC overcomes many of the difficulties associated with other prepreg methods (5). In the process fluidized powder is deposited on spread tow bundles and fused to the fibers by radiant heating. This paper reports the results of experiments that have provided test materials and design and scale up information needed for process development and cost analysis.

2. EXPERIMENTAL

The experimental system was composed in sequence of the tow feed spool with tow tension brake; the fluidization chamber with powder feeder; the electric oven, the quality control monitor; the take-up spool with tow speed control, Figure 1. Unsized Hercules AS-4 carbon fibers in 3K and 12K tows were used with six matrix polymer powders, Table 1.

2.1 DESIGN RELATIONS

The experimental equipment and operating procedures have been described in detail in previous reports (2,3). The bench scale dry towpreg system was operated over a wide range of conditions to confirm design theory and operating correlations for each component and thereby provide the basis for scale up to produce commercial quantities of towpreg.

2.1.1 Tow Spreader The tow bundle enters the spreader at the throat of a flat expansion section, air enters at the tow outlet and is drawn through holes in the sidewalls of the expansion section into a vacuum manifold. The angle of fiber spread in the pneumatic tow spreader is the result of the force balance between the tow tension applied by the brake and the air drag on the tow fibers due to flow toward the spreader walls. Tow spread is controlled and maintained by adjusting the tension and vacuum pressure.

2.1.2 Powder Deposition In the powder deposition chamber, the expanded fiber tow behaves like a fibrous filter. Particle collection is by momentum impaction due to van der Waals forces, Brownian diffusion and in some cases electrostatic force. Fiber filter theory (2) provides the design relationship for the level of powder deposition on the tow as it passes through the chamber. Towpreg resin level is a function of residence time, gas velocity, and tow spread. The appropriateness of the design correlation for the powder deposition rate was demonstrated for powders over a wide range of operating conditions during experiments at LaRC (2,3).

2.1.3 Powder Recirculation The fluidized bed unit is comprised of two different particle fluidization systems - upflow and downflow. In the external return tube gas flows up through the fluidized powder and conveys it to the top of the fluidized deposition chamber. The powder and gas flow into the chamber, pass through and around the spread tow with some powder being deposited on it, and flow down to the fan inlet at the bottom. The fan accelerates the particles and gas into the external tube to complete the flow cycle.

The sum of the pressure losses for each step in the cycle represents the flow resistance that must be counteracted by the fan motor. Consideration of the magnitudes of the various terms indicates that flow friction in the return tube and support of the suspended column of solid particles makes up over 90% of the pressure drop or work required of the fan (3).

2.1.4 Cloud Density The fan horsepower, system total pressure losses, and powder material balance may be used to calculate the cloud density achievable for a specific design at a given set of operating conditions (2). The cloud density is an important factor in establishing the rate of powder deposition on the tow.

The stalling condition of the recirculation system is reached when the air flow in the tube equals the maximum carrying velocity at which point powder accumulates in the vertical tube stopping the fan. Operation just below the air flow stalling point provides the maximum particle cloud density.

2.1.5 Powder-Tow Fusion Towpreg flexibility and powder-fiber fusion are important for weaving and molding applications. These properties of the towpreg depend upon the temperature of the oven and the time that the powder laden tow takes to travel through the oven. Flexural rigidity data were obtained for towpreg having a range of resin content and fused at several different oven temperatures and residences times. The standardized cantilever test, ASTM D1388-64, for fabrics, was used to determine the flexural rigidity of towpreg samples (7).

2.1.6 Quality Control For the single tow powder slurry process, resin levels have been successfully maintained within a range of ± 2% over extended periods of continuous operation (4). This has been accomplished, operating at constant tow speed, by adjusting the powder slurry application rate at the start to achieve the desired tow resin content, and maintaining it constant during the run. For these runs the oven temperature was set at the level which had been predetermined to give good powder-tow fusion and acceptable towpreg flexibility.

In anticipation of the need for closer resin level control and for the more complex needs of scaled up multi-tow units, an instrument for on-line continuous detection of the towpreg resin content was developed in conjunction with Analytical Services and Materials, Inc. of Hampton, VA. Towpreg is composed of electrically conducting carbon fibers and dielectric polymer resin. The resin level monitor measures the electric capacitance of the towpreg, which is a function of its resin content.

Once the system design has been selected, the operating variables are used to achieve towpreg quality control during production. The process outputs to be maintained, within certain setpoints, by the control system are towpreg resin content, powder fusion, and flexibility. During continuous operation, regulatory control over output variances is accomplished by adjusting the tow speed, powder feed rate, and oven temperature.

3. COST ESTIMATION

A preliminary estimate of the cost to make towpreg by the dry powder process was made based on the cost of the bench scale equipment. There are no multi-tow dry powder units upon which to base cost projections for commercial operation. Assuming that the process can be scaled up to the 25 tow level in 5-tow units, projections of the cost of such a system were made and are presented in Table 2.

Process engineers have found that for many types of equipment the scale up cost to larger sizes correlates with the ratio of the capacity increase to the sixth tenths power (7). That is, if the cost of a given unit at one capacity is known, the cost of a similar unit with X times the capacity is approximately X 0.6 times the cost of the initial unit. The single-tow system cost $30,000 which when multiplied by the 0.6 power of 25 gives a cost of $207,000 for a 25-tow system. This is comparable to the projected cost of $187,500 in Table 2 made by examining each item of equipment and operating step.

A somewhat similar economic analysis has been made for prepreg tape made using electrostatic fluidized bed coating. In that case the payout period was projected to be less than 2,400 hours, or about one year for a one-shift per day operation (6). Here the processing cost using fluidized bed powder impregnation is estimated to be $9.30 per pound of 3K towpreg. This figure does not include the cost of fiber and powdered resin, and is based on scale up production from a single-tow to a 25-tow system (8).

There are opportunities for reducing powder impregnation costs. For example, to make 3, 6, or 12K towpreg requires nothing more than a tow slot size adjustment. Assuming the 25-tow system operates at 25 cm/sec tow speed, the running time for 1.0 kg (2.2 lb) spools of fiber would be: 5.2 hours for 3K tow; 2.13 hours for 6K tow; and, 1.07 hours for 12K tow. Allowing for loading and unloading between runs, it is assumed that for 3K tow one run would be made per 8-hour shift. For 6K there would be two runs, and four runs for 12K tow. If the run time per year is 1,000 hours, regardless of tow size, the estimated annual production cost of $173,250 gives towpreg costs of $9.30 for 3K, $4.65 for 6K and $2.33 for 12K.

The impact of tow and resin costs are reflected in Figure 2. The powder impregnation process alone costs approximately $9.30 per pound of towpreg. Grinding solid resin to powder costs about $3.00 per pound. The cost of towpreg is the cost of the resin and tow plus the cost of milling the resin into powder and impregnating the fiber tow.

Towpreg may be stitched into uniweave tape/sheet or woven and braided into broadgoods and preforms. The cost to weave towpreg yarn in an 8 harness satin, 40 inches wide, is approximately $10.00 per pound. These estimates suggest that the costs incurred in producing powder coated towpreg should be comparable to, and perhaps even less than, those incurred for producing conventional hot melt prepreg.

4. RESULTS AND DISCUSSION

Extensive testing of the bench scale dry towpreg system over a range of conditions has confirmed design theory and operating correlations for each component and provides the basis for scale up to produce commercial quantities of towpreg. The unit operated reliably with the various powders, using both 3K and 12K tows, for periods as long as eight hours, at tow speeds as high as 50 cm/sec (2).

Test specimens of both unidirectional fiber towpreg and woven towpreg were prepared and molded for testing, Table 3. The short beam shear strength, flexure strength and flexure modulus of the unidirectional and woven composite samples fabricated from polyimide and epoxy powder matrix composites are comparable to the same properties obtained from laminates made from conventional prepreg systems with similar fiber/matrix combinations. Weaving experiments indicate that the towpreg used as fill material must have a flexural rigidity below 10,000 mg-cm so that it bends and follows the shuttle action without breaking. Towpreg used as beam material must have a flexural rigidity below 100,000 mg-cm so that it does not break during heddle and comb action, and it must bind together the fibers so that they do not come loose, resulting in material thinning and comb clogging. This last condition requires using resin fusion to bind the unidirectional tow fibers in the beam material (2,3). Towpreg yarn abrasion during weaving also may be minimized by adding twist to the yarn during rewinding, putting sizing on the yarn, or serving the yarn by wrapping it with thread.

5. CONCLUDING REMARKS

Significant progress has been made on the development of the LaRC dry powder towpreg system. Polymer powders can be deposited on a moving carbon fiber tow in a recirculating fluidized bed and then fused to the tow using radiant heating. The flexibility of the resulting towpreg may be controlled by adjusting the temperature and time of the oven fusion process such that weavable towpreg can be obtained. Unidirectional and woven test samples, using both thermoplastic and thermoset powder towpreg have been of good quality.

Design information and operating data correlations have been developed for scale up to commercial operation. Cost estimates suggest that processing cost are comparable to those of conventional hot melt prepreg. In the future, from a part fabrication point of view, powder coated prepreg tape, woven broad goods and woven and braided preforms may be considered as options to similar materials made by other methods.

6. ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Mr. John Snoha in constructing and operating the fluidized bed system. They also greatly appreciate the advice and suggestions of Dr. Terry St. Clair and Dr. Norman Johnston.

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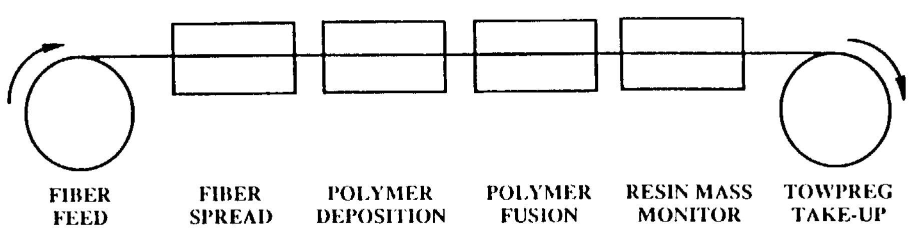

- STABLE, ADJUSTABLE TOW SPREAD.
- UNIFORM POLYMER APPLICATION/DISTRIBUTION.
- EXCELLENT POLYMER MELT FUSION TO CARBON FILAMENTS.
- CONTINUOUS RESIN MASS FRACTION MONITOR/CONTROL.

FIGURE 1. DRY POWDER PREPREGGING

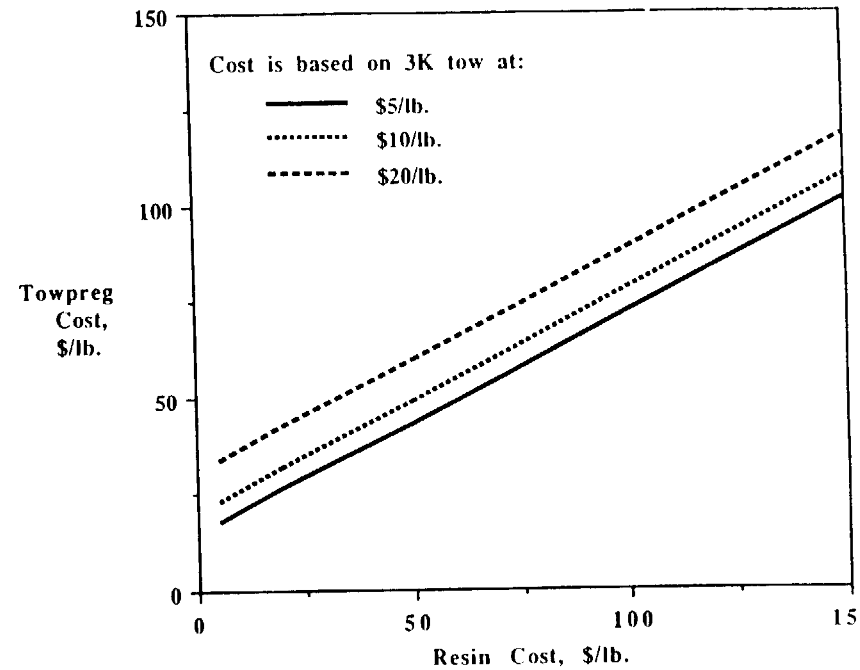

FIGURE 2. TOWPREG COST ESTIMATION

TABLE 1. POWDER PREPREG PRECURSOR DATA*

Polymer Description	Particle Size, μ	Supply Source
LARC-TPI 2000	7.0	Mitsui Toatsu Chemical, Inc.
LARC-TPI 1500	19.0	Mitsui Toatsu Chemical, Inc.
PEEK 150	17.0	ICI Fiberite
PMR-15 PI	1.5	Dexter-Hysol Aerospace
PR500 Epoxy	19.0	3M Company
Fluorene Epoxy	3.0 (12.0)**	3M Company

*All prepreg utilized unsized Hercules AS-4 graphite fibers in 3K and 12K tows

**The fluorene epoxy was supplied in two different particle sizes

TABLE 2. TOWPREG COST ESTIMATION

Equipment	Laboratory Single-tow Unit (Dollars)	Projected Twenty-five tow Unit (Dollars)
Feed Spool Creel and Tension Brakes	1,500	7,500
Pneumatic Spreaders and Vacuum Systems	2,000	10,000
Powder Screw Feeders	6,000	30,000
Powder Deposition Chambers and Recirculation Fans	2,000	10,000
Electric Ovens	1,500	7,500
Resin Level Sensors and Controllers	5,000	25,000
Takeup Spools and Speed Controls	6,000	60,000
Subtotal	24,000	150,000
Installation @ 25% of equipment cost	6,000	37,500
Total Cost	30,000	187,500

*No multi-tow information is available. The above estimate assumes that the 25 tow system is made up of 5 deposition chambers, each handling 5 tows, complete with pneumatic tow spreader and feeder. There are 5 resin level sensors, one for each chamber. The creel, ovens, and takeup system may be single units or multiple units.

Powder Coating Costs

Direct Costs**	Dollars/Year
Equipment (3 year life)	62,500
Space (1,000 sq ft @ 10 $/yr sq ft)	10,000
Utilities (20,000 KWH/yr @ 4.15/KWH)	3,000
Personnel (1 FTE + benefits)	40,000
Subtotal	115,500
Indirect Costs @ 50%	57,750
Total Annual Cost	173,250

Tow Size	Towpreg, lb/yr	Coating Cost, $/lb
3K	18,600	9.30
6K	37,200	4.65
12K	74,400	2.33

**Equipment life is taken to be 3 years using linear depreciation and no scrap value. With storage and handling access the system would occupy 1,000 sq ft. The majority utility required is electricity for the motors and ovens estimated at 20,000 KWH/yr. 1,000 Hours per year of coating run time.

TABLE 3. MECHANICAL PROPERTIES OF DRY POWDER COATED COMPOSITES

Composite-AS-4 Carbon Fiber-	Short Beam Shear strength ksi (MPa)	Flexure Strength ksi (MPa)	Flexure Modulus msi (GPa)
12K Unidirectional LARC-TPI 2000*	12.3 ± 1.3 (848 ± 8.9)	323 ± 14.1 (2227 ± 97)	19.4 (134)
3K 0/90 4-Harness woven, LARC-TPI 1500**, Specimen:			
0° Beam	134 ± 3.5 (924 ± 24)		8.1 (56)
0° Fill	83 ± 4.0 (572 ± 28)		5.7 (39)
3K Unidirectional PR 500***	14.5 ± 0.4 (100 ± 2.8)	206 ± 11.1 (1419 ± 76)	16.4 (113)
3K Unidirectional fluorene-based epoxy****	11.8 ± 0.6 (81.3 ± 4.1)	240 ± 15.8 (1654 ± 109)	15.4 (106)

	molding conditions	resin content
*	1 hr/660°F/800 psi	33.5 wt %
**	1 hr/700°F/300 psi	29 wt %
***	4 hr/350°F/85 psi	32.5 wt %
****	4 hr/350°F/85 psi	35 wt %

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CHEMISTRY AND PROPERTI
ACETYLENE TERMINATE

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ABSTRAC

As part of a NASA program to develop new h
structural materials, the chemistry and proper
materials and their cured resins are under inv
work is to develop materials that are readily p
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high as 177°C. An acetylene terminated asp
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the form of neat resin moldings, adhesive spe
specimens and laminates gave good mechar
high as 177°C. In addition, preliminary lamin
from a blend of a new N-methyl substituted A

KEY WORDS: Resins; Thermosets/Acetyle
Characterization/Evaluation

WEAVING TOWPREG MADE FROM DRY POWDER PREPREGGING PROCESS

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Janice Maiden, Textile Technologies, Inc.
Norman J. Johnston, NASA Langley

A study was conducted to establish the parameters for weaving 3k, 6k, and 12k carbon fiber impregnated with LaRC-TPI dry powder. The resulting eight-harness satin broad goods were fabricated into test specimens to determine mechanical properties.

Previous studies for weaving the dry powdered tows dealt with tow flexibility and adhesion of powder particles to carbon fiber. Manipulation of the thermal treatment step in the prepregging process enabled successful control over these two variables. Abrasion and fiber damage during weaving were unresolved matters. In this investigation, tow bundle twisting was used to reduce the separation of filaments, tow-to-tow abrasion, and fiber loss.

Optimal weaving protocol was established and bulk factor and mechanical property data were obtained for the consolidated woven material. Utilization of appropriate textile techniques for composites processing is an important factor for automating the production of quality composite parts from powdered towpreg.

Composites From Powder Coated Towpreg: Studies With Variable Tow Sizes

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Abstract

Part fabrication from composite materials usually costs less when larger fiber tow bundles are used. On the other hand, mechanical properties generally are lower for composites made using larger size tows. This situation gives rise to a choice between costs and properties in determining the best fiber tow bundle size to employ in preparing prepreg materials for part fabrication.

To address this issue, unidirectional, bidirectional, and eight harness satin composite specimens were fabricated from powder-coated 3k, 6k, and 12k carbon fiber reinforced LaRC-TPI towpreg. Short beam shear strengths and longitudinal and transverse flexure properties were obtained. Knowledge of the variation of properties with tow size may serve as a guide in material selection for part fabrication.

TOUGHENING OF PMR COMPOSITES BY SEMI - INTERPENETRATING NETWORKS

N. J. JOHNSTON, K. SRINIVASAN AND R. H. PATER

ABSTRACT

Polymer composites are increasingly being required to operate for prolonged durations at high temperatures. In the past, the material of choice for most elevated temperature applications was PMR - 15, even though it suffered from two major drawbacks : brittleness and component toxicity. Recently, there have been increased efforts devoted to synthesizing and characterizing new, non - toxic polymers capable of withstanding high temperatures for long periods. Several such organic polymers have been investigated. One such potential PMR - 15 replacement is LaRC RP46. Further, to improve the damage tolerance of PMR - type resin systems, an attempt has been made to develop a semi - Interpenetrating Network (semi - IPN) at ply interfaces by utilizing a tough thermoplastic resin. Matrimid 5218 (Ciba Geigy) is a tough thermoplastic polyimide with a Tg of 315 ° C - 325 ° C, a range compatible with PMR - type composites. A controlled creation of a 5218 / PMR semi - IPN at the ply - to - ply interface is therefore likely to provide toughness to the resulting composite without substantial loss of high temperature capability.

PMR - 15 and RP46 prepregs were drum wound using IM - 7 fibers. Prepregging and processing conditions were optimized to yield good quality laminates with fiber volume fractions of 60 percent (± 2 percent). Samples were fabricated and tested to determine comprehensive engineering properties of both systems. These included 0° Flexure, Short Beam Shear, Transverse Flexure and Tension, 0° Tension and Compression, Intralaminar Shear, Short Block Compression, Mode I and II Fracture Toughness and Compression After Impact properties. Semi - 2 - IPN toughened PMR - 15 and RP46 laminates were also fabricated and tested for the same properties.