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Technical Assessment for Quality Control of Resins

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16. Abstract

Survey visits to companies involved in the manufacture and use of graphite-epoxy prepregs were conducted to assess the factors which may contribute to variability in the mechanical properties of graphite-epoxy composites. In particular, the purpose was to assess the contributions of the epoxy resins to variability. Companies visited represented three segments of the composites industry - aircraft manufacturers, prepreg manufacturers and epoxy resin manufacturers. Several important sources of performance variability were identified from among the complete spectrum of potential sources which ranged from raw materials to composite test data interpretation. Principal factors were difficulties which arise from 1) fabrication processing, 2) test sample design and preparation and 3) the test techniques. No direct evidence was obtained that showed the resin did or did not contribute to composite performance variability.

The role of the epoxy resin in all phases of the technology is discussed and recommendations made for utilization of physical and chemical methods for assurance of resin matrix quality and reproducibility. Methods proposed for further study are, in order of priority, liquid chromatography (LC), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

Recommendations were made that a review team should make a thorough assessment of graphite-epoxy testing practices and develop a set of basic principles which would be used to correct the most common errors in testing these composites. In the area of fabrication, it was recommended that further study of fabrication procedures be made and that National Aeronautics and Space Administration accepted guidelines be developed for fabrication methods.

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONT.)

LIST OF FIGURES AND TABLES

LIST OF FIGURES AND TABLES (CONT.)

I. FOREWORD

TECHNICAL ASSESSMENT FOR QUALITY CONTROL OF RESINS

Prepared by Rex B. Gosnell
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for
McDonnell Douglas Astronautics Company

Survey visits to companies involved in the manufacture and use of graphite-epoxy prepregs were conducted to assess the factors which may contribute to variability in the mechanical properties of graphite-epoxy composites. In particular, the purpose was to assess the contributions of the epoxy resins to variability. Companies visited represented three segments of the composites industry - aircraft manufacturers, prepreg manufacturers and epoxy resin manufacturers. Several important sources of performance variability were identified from among the complete spectrum of potential sources which ranged from raw materials to composite test data interpretation. Principal factors were difficulties which arise from 1) fabrication processing, 2) test sample design and preparation and 3) the test techniques. No direct evidence was obtained that showed the resin did or did not contribute to composite performance variability.

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II. INTRODUCTION AND BACKGROUND

In March of 1976, the National Aeronautics and Space Administration Research and Technology Advisory Committee on Materials and Structures made the following recommendations:

1. NASA participate aggressively and become an active partner in the DOD effort which addresses the development of materials specifications and practical qualification and acceptance test methods for resin matrix composites and adhesives.

2. NASA explore the use, effectiveness and relevance of analytical test methods which in combination with end use performance tests could form the basis of materials specifications and practical qualification and assurance test methods.

NASA has initiated a major expansion of composite programs directed toward the advancement of technology for early introduction of composite primary structures into the production of subsonic commercial transports. These programs will focus the application of emerging technologies that will provide the basis for lightweight aircraft designs which will require substantially less fuel than those currently operating. In order to stimulate the use of composites as a viable aircraft structural material, the technologies must be proven readily and reliably applicable to new aircraft in the long term and some derivative aircraft in the near term.

One of the several areas in which expanded activities are planned at the Langley Research Center is a study of the quality control of graphite-epoxy composite materials systems. The overall objective is to develop and improve quality control tests to assure that reliable, reproducible, high-quality, prepreg is available such that it can be fabricated into reliable, reproducible, high-quality composites. The first phase of this activity which is reported in this document, involves an assessment study to define problems and needs associated with state-of-the-art 450°K epoxy systems. The objective of this study was to assess all parameters that were thought to affect the reproducibility of the various properties of graphite-epoxy composites used in commercial aircraft. The study was particularly designed to address the contribution of the epoxy resin to reliability. Synthesis, purity, quality assurance and graphite fiber prepregging processes were examined to determine the adequacy of controls and quality sensitivity to given variables. Factors which bring about deviation in graphite-epoxy composite performance were defined and a set of guidelines to ensure a degree of control over critical variables recommended. Raw material suppliers, formulators and prepreggers, and major users were surveyed. The results of this assessment study and survey will serve as the basis for formulating a sound contractual quality control program that will meet the needs of suppliers, prepreggers, and major users.

With energy efficiency as the principal driver, the building of confidence in the use of graphite-epoxy materials in primary structures requires that a more fundamental understanding of all sources of variability including physical and chemical parameters of these composite materials is established. From this understanding will grow the intelligence to control these factors which indeed have an important effect on reliability and durability.

The integrity or quality of an advanced composite aircraft component is the product of the participation of a number of sources of variability. This spectrum of sources of variability has been generalized under the following categories:

Resin

Fiber

Fiber Surface Treatment or Sizing

Resin Processing (including curative system)

Fiber Impregnation

Prepreg Handling and Storage

Component Design

Tooling

Fabrication Processing

Test Sample Preparation

Testing

III APPROACH

The survey and assessment was carried out by means of visits to companies classified into three categories of involvement in the graphite-epoxy prepreg industry. These classifications included the aircraft manufacturer or user of impregnated goods, the epoxy impregnated graphite fiber or fabric manufacturer or "prepregger", and the suppliers of epoxy resins commonly used in "prepreg" capable of 450°K performance in laminated form. The results of these technical visits and discussions are highlighted in the following sections.

The discussions were directed toward the experiences of the technical personnel involved in the manufacture of graphite-epoxy composites. The primary intent was to gain a more complete understanding of the importance of various sources of variability listed earlier and their effect on the reliability of finished epoxy graphite composite. In each company, a slightly different profile of experience, philosophy, approach and capability was observed.

In the narratives reviewing these visits described in the following sections, all the details of the discussions are not presented. Rather, certain selected highlights are given especially when a unique idea, approach or analysis was identified. These concepts or individual observations are supported where possible with data.

Emphasis was placed on how the epoxy component was affecting processing and final composite performance. Attempts were made to collect any data or observations that would indicate the resin <u>was</u> or <u>was not</u> responsible for variable behavior in prepreg or composite.

With each of the three classifications of companies the flow of the discussion was somewhat different. The intent was to cover the following items:

Commercial Aircraft Manufacturers

Incoming Materials

- Receiving responsibility
- Inspection and materials acceptance specifications
- Types and number of rejections resin, fiber or process related?
- Storage, inventory and distribution
- Methods of supplier selection
- Activity in development of improved QC methods

Processing

- Inventory monitoring (255°K storage time and out time)
- Fabrication sequence and routine
- Modified processes (resin content, gel time, flow)
- History of problems
- Process variables and process control specifications
- Experiences on resin quality assurance
- Recommendations on improved hardware quality assurance
- Composite performance specifications

General

- Attitudes on prepreg variables versus process variables
- Assessment of temperature and humidity requirements
- Philosophy of design allowables and safety margin
- Future acceptance payoff in primary structure
- Attitudes: Cost, customer service, polymer problems, resin component identification
- Testing
- Batch-to-Batch records

Prepreggers

Incoming Materials

- Receiving responsibility
- Inspection and materials acceptance specifications
- Types and frequency of rejections - fiber, resin
- Materials availability
- Storage
- Activity in new QC methods for epoxy raw materials
- Adequacy of viscosity and epoxy equivalent weight; historical data

Processing

- Manufacturing instructions
- In process controls: temperature, viscosity and resin advancement
- Processing method

General

- Analytical equipment capability
- Attitudes on matrix component identification
- Efforts in matrix quality assurance methods
- Experiences in interfacing with fabricators
- Awareness of problems in primary structure
- Testing

Resin Manufacturers

Process Controls

- Reproducibility assessment
- Complexity of product composition
- Manufacturing instructions

General

- Product Specifications
- Batch-to-batch records
- Contaminants: chlorohydrins, sodium, water, etc.
- Development of new analytical methods
- Structural of compositional effects vs neat resin properties
- Plans for new highly functional epoxies
- Attitudes on service to prepreg industry

In the case of commercial aircraft manufacturers, the selection of Boeing Commercial Airplane Company, Lockheed-California Company, and McDonnell Douglas Corporation was made. In addition, General Dynamics, Fort Worth Division, was chosen because of their high useage of graphite-epoxy materials and the commitment of composite materials to the empennage on the F-16. Lockheed Missiles and Space Company was selected because of their activity in chemical characterization of prepreg resins.

A number of prepreggers have a 450°K type epoxy resin for graphite prepreg. Most are based on Ciba-Geigy Corporation's Araldite MY720 which is primarily a highly functional tetraglycidyl derivative of methylene dianiline. Such 450°K epoxy systems are listed:

- Narmco 5208
- Hercules 3501
- Fiberite 934
- Hexcel F-263
- U.S. Polymeric E-759
- Ferro CE-9015
- 3-M SP-286
- Reliable RAC-6350

Manufacturers of the first four were chosen for visits because of their involvement with the commercial airplane builders.

The resin suppliers were selected on the basis of use of their resins in typical graphite epoxy matrix formulations. These included Shell Development Company, Dow Chemical USA, Ciba-Geigy Corporation, and Union Carbide Corporation. Union Carbide Corporation was of interest because of their licensing agreement with Ciba-Geigy Corporation covering Araldite MY720.

IV. COMPANY SURVEY VISITS

A. Commercial Aircraft Manufacturers

1. McDonnell Douglas Aircraft Corporation, Long Beach, CA

A visit was made to McDonnell Douglas Corporation on January 6, 1977 and discussions were held with the following personnel:

Dr. H. C. Schjelderup, Chief Design Engineer, M&P Eng.

R. W. Shannon, Section Chief, Polymeric Materials, M&P Eng.

H. M. Toellner, Lead Engineer, M&P Eng.

Dr. Dave Purdy, Branch Chief, Structural Advanced Technology (Structures Engineering)

Dr. Steve Elliott, Section Chief, Advanced Materials (Structures Engineering)

George Lehman, Section Chief, Composites (Structures Engineering

Prepreg Acceptance

As with other commercial aircraft houses, there has been no formal production utilizing graphite-epoxy prepreg at McDonnell Douglas but nevertheless about 1360 kg of graphite-epoxy prepreg has come into the plant through Material and Processing Engineering who has the responsibility of quality control in development and production programs.

Materials acceptance specifications are operative for three types of material including unidirectional tape, unidirectional woven and bidirectional woven. Values for these prepreg acceptance criteria as typified by those for unidirectional material are shown in Table I.

Table I

COMPARATIVE AIRCRAFT MANUFACTURER'S MATERIAL SPECIFICATIONS

450°K EPOXY GRAPHITE PREPREG UNIDIRECTIONAL

PREPREG PROPERTIES

	Lockheed California Company	Boeing Aircraft Company	McDonnell Douglas Aircraft	General Dynamics Ft. Worth
Spec Date	9/24/76	Preliminary	9/12/75	6/27/75
Volatiles % Max	3	2	3	2
Resin Content %	41±3	42±3	42±2*	40±4
Flow %	15-29	Nominal ±3%	Thickness/ply Control	Thickness/ply Control
Areal Wt. gm/m^2	144±5	None	147-157	None
Gel Time Mins.	Report	Nominal ±5%	16-20*	See Text
Infrared	Report	None	None	None

*Cumulative batch average

McDonnell Douglas uses no chemical specifications per se (except resin content and gel time) but relies on mechanical performance specifications. They have not done any work in the development of new chemical or instrumental techniques for quality assurance.

They have had very little rejection problems with graphite-epoxy prepreg but have been required to make some process changes to handle low gel times and high resin content. Technical rejections based on mechanical performance testing have been resolved in improved test fixtures and techniques in concert with the prepreg supplier. The general feeling at McDonnell Douglas is that the prepreg processes have some flexibility and in production, the specifications might be opened up somewhat.

McDonnell Douglas does not monitor out-time at 297°K but excessive overaging has not been a problem because of rapid useage. After storage of 90 days at 255°K, reverification is required. They found that retests still gave good values after 18 months at 255°K.

They have had some minor difficulty with unflagged wet and dry spots and mislabeling from prepreggers.

Batch-to-Batch Variability

McDonnell Douglas has an interesting historical record of Narmco 5208 batch-to-batch data collected over approximately the last four years. The data shown in Table II was collected on materials sampled on rolls from 30 to 35 production batches. Certain difficulties of the normalization technique are recognized by McDonnell Douglas. Raw test data is shown in

Table II

HISTORICAL BATCH TO BATCH DATA
MECHANICAL PROPERTY COEFFICIENT OF VARIATION *
MCDONNELL DOUGLAS AIRCRAFT

	Number of Prepreg Rolls Sampled	C_v
Normalized Tensile Strength	31	5.37%
Normalized Tensile Mod.	29	6.92%
Normalized Compression Strength	30	7.76%
Normalized Compression Mod.	31	6.37%
Normalized Flexural Strength	126	5.38%
Normalized Flexural Mod.	126	6.18%
Short Beam Shear	126	5.10%

*Normalized on a thickness/ply basis

histogram format in Figures 1, 2, 3, and 4. Gel time on 55 rolls showed a 21.86 minimum mean at 450°K with a coefficient of variation of 6.62 per cent.

Resin content variability is typified in the histogram shown in Figure 5. The data was taken from 59 rolls of 5208 prepreg. The coefficient of variation was 5.64 per cent.

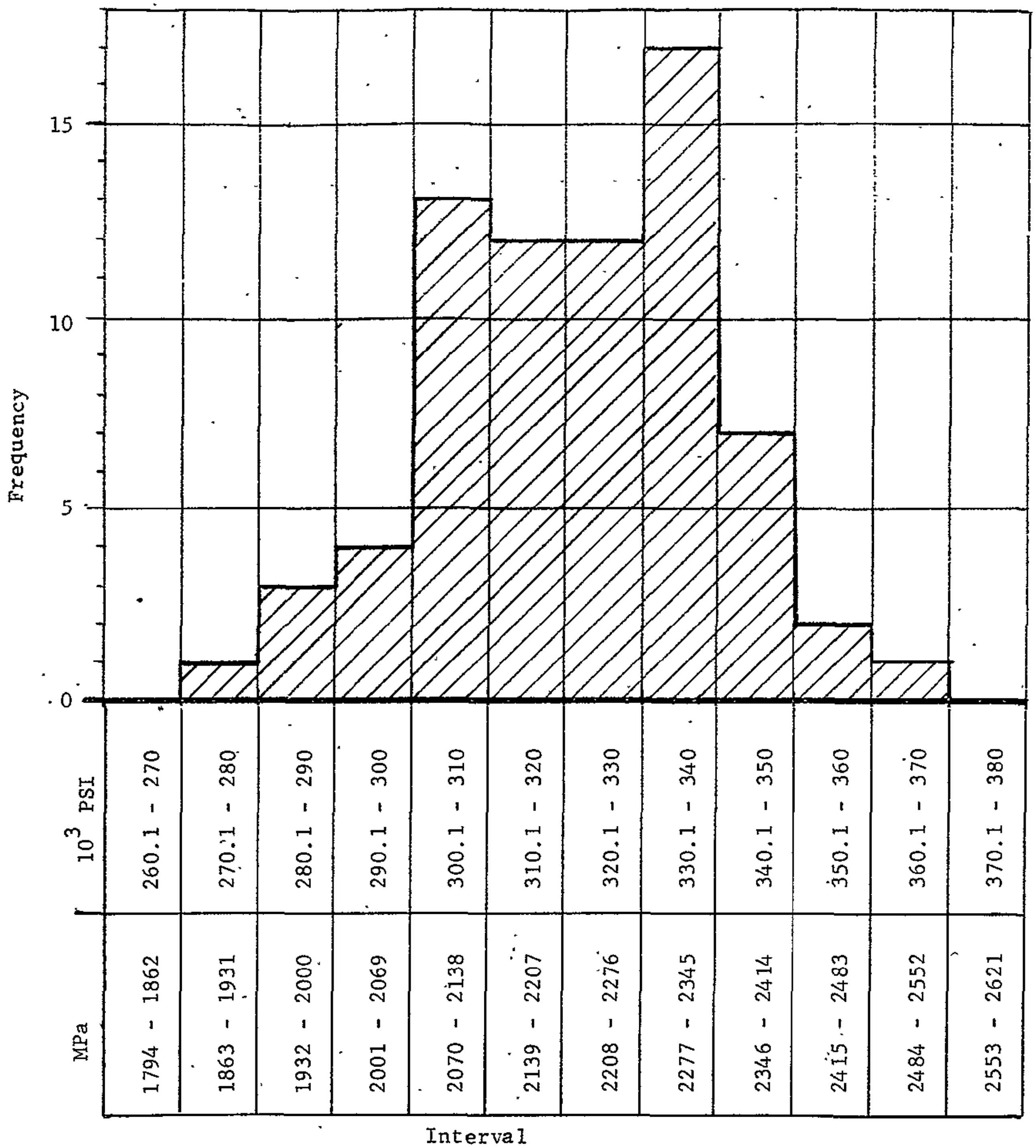
A cumulative average of flexural strength on batch-to-batch testing over the last four years is shown in Figure 6. No conclusions can be made about resin or any other factor. Such data represents a summation of factors such as improvement in fabrication skill as well as testing technique.

Other Factors in Composite Variability

Comparative data for flexural strength using autoclave cures versus elastomer expansion cures on twenty-two rolls of Narmco 5208 have been collected by McDonnell Douglas. While the mean value for elastomer expansion cures was about 4 to 5 per cent higher than autoclave cures, the coefficient of variation was almost identical at 6.25 per cent and 6.51 per cent, respectively.

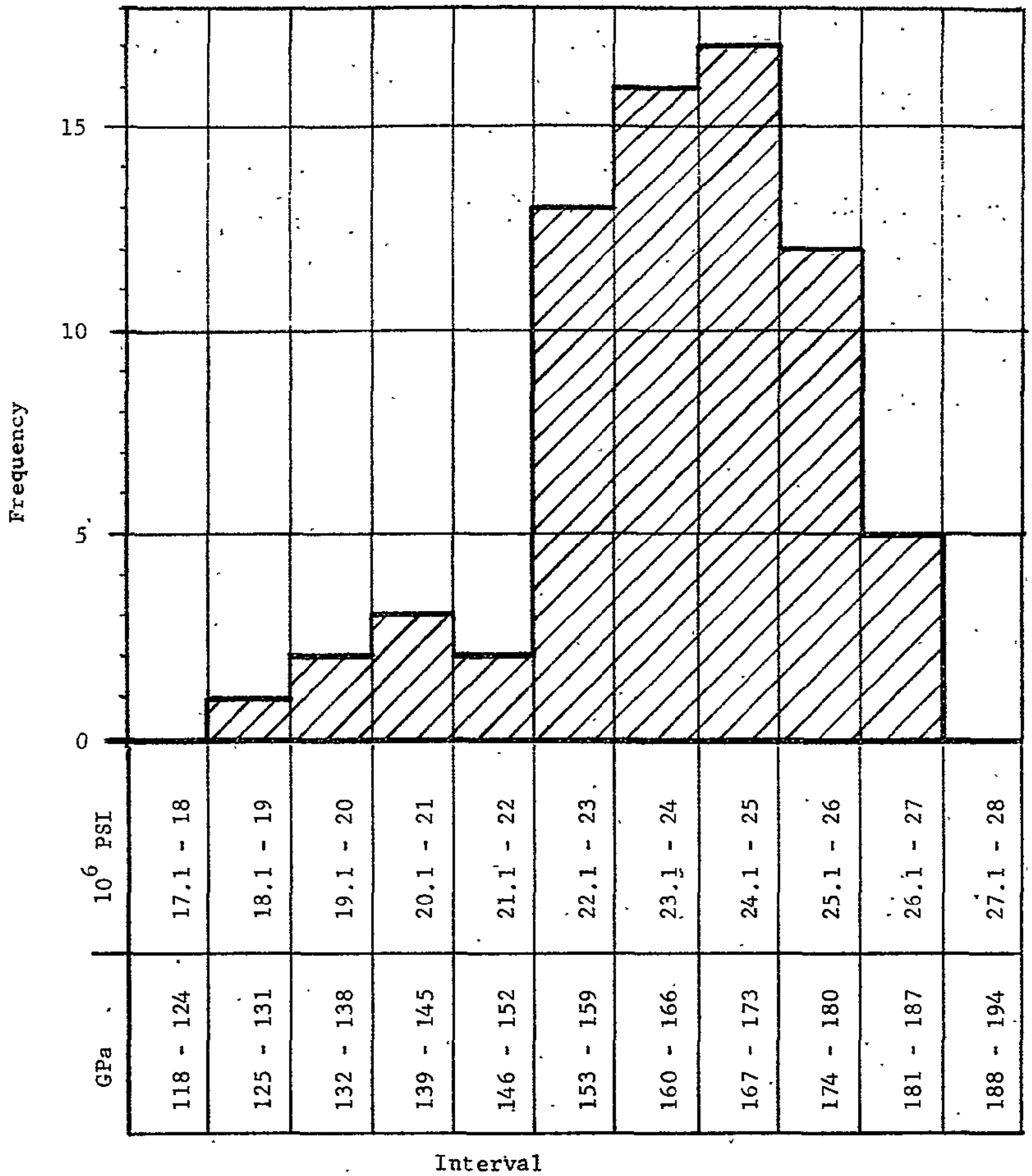
General process specifications are used for both type cures. More detailed specifications for processing each major component such as the DC-10 rudder are also used to ensure processing uniformity. These process specifications are supported with manufacturing instructions for each part.

With regard to the question of the quality of thick laminates, McDonnell Douglas has not made any complicated thick sections. McDonnell Douglas is heavily committed to the stiffened skin



Flexural Strength Raw Data Histogram
72 Rolls Sampled
Narmco 5208/T-300

Figure 1

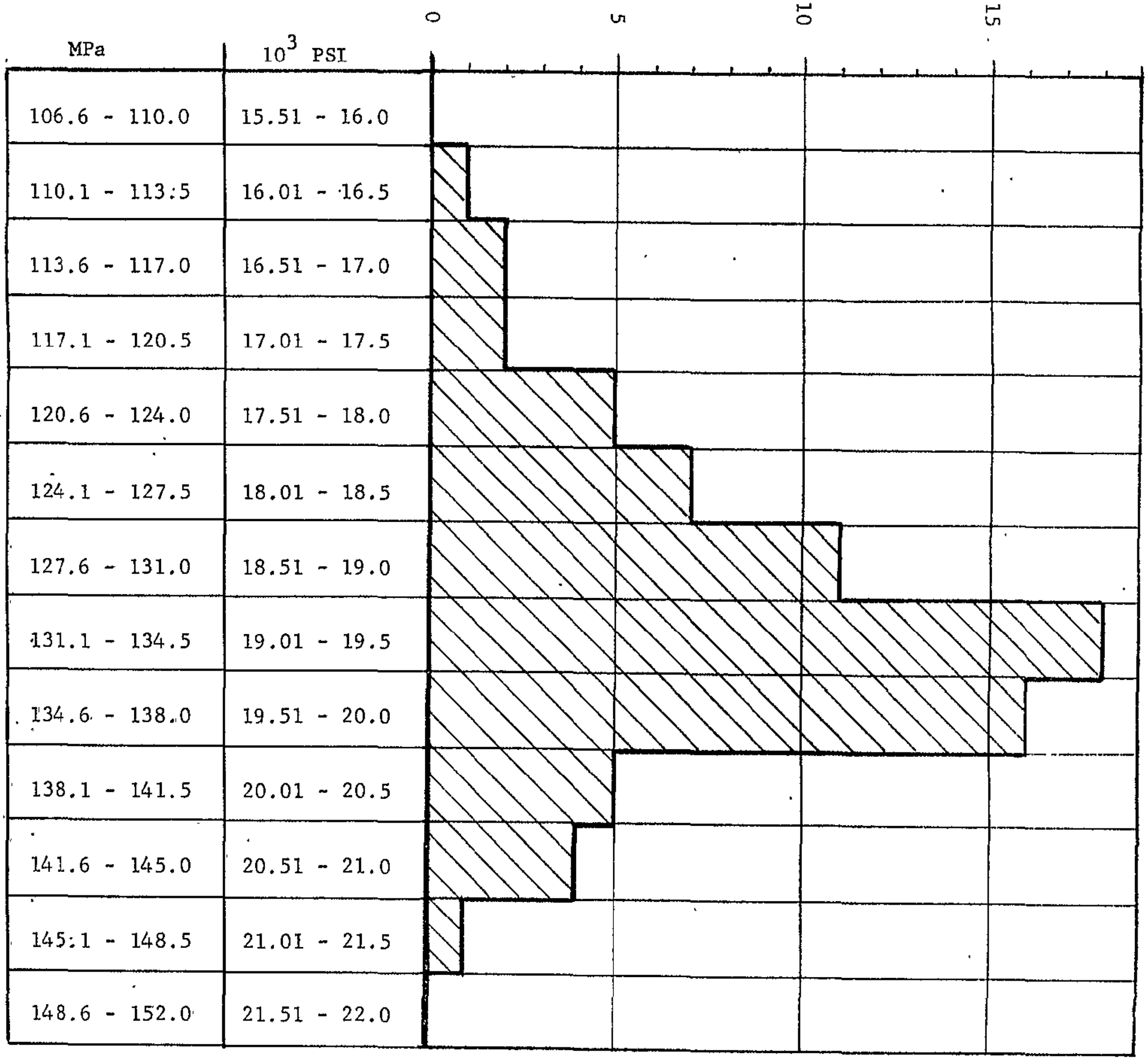


Flexural Modulus Raw Data Histogram

71 Rolls Sampled

Narmco 5208/T-300

Figure 2

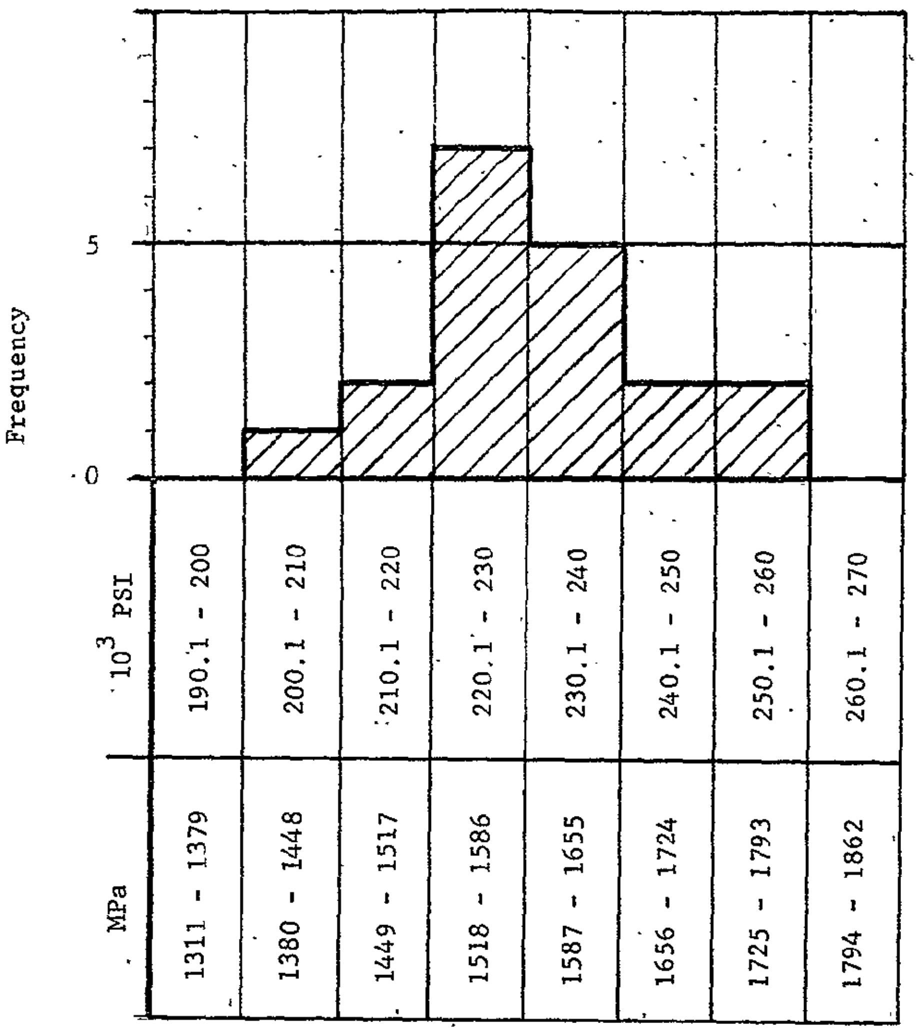


Short Beam Shear Raw Data Histogram

72 Rolls Sampled

Narmco 5206/T-300

Figure 3



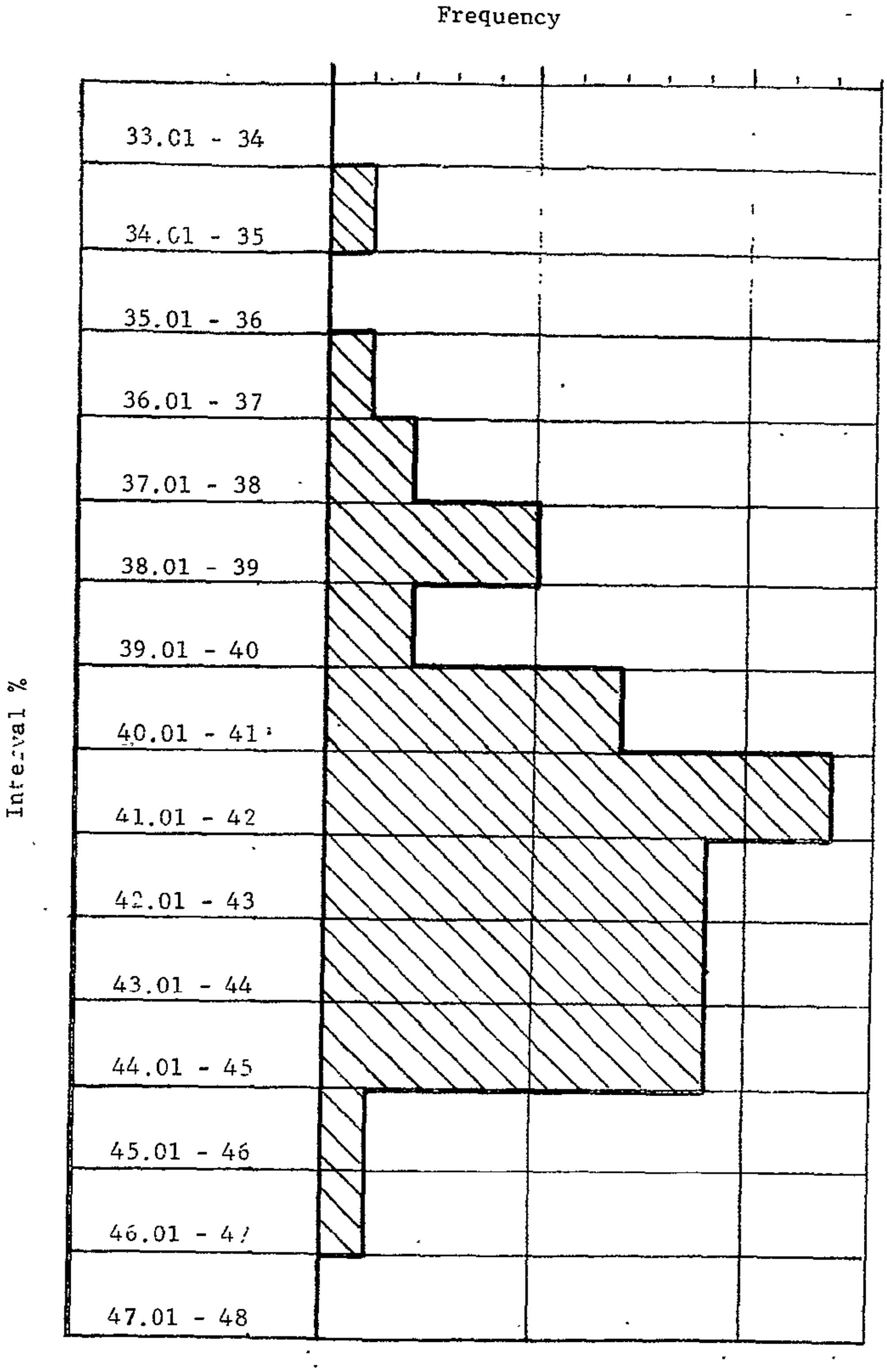
Interval

Sandwich Beam Tension Raw Data Histogram

19 Rolls Sampled

Narmco 5208/T-300

Figure 4



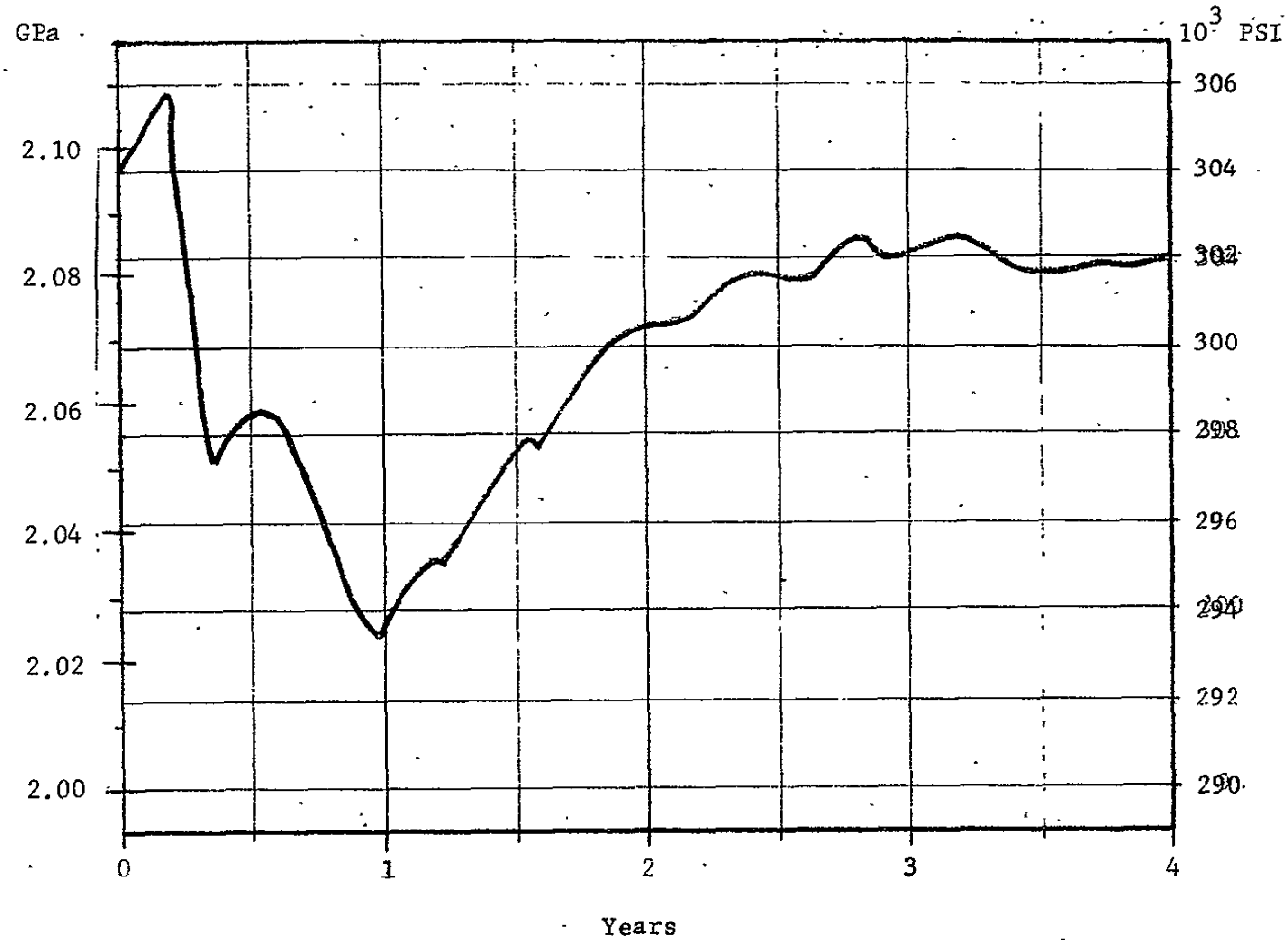
Prepreg Resin Content Raw Data Histogram

59 Rolls Sampled

Narmco 5208/T-300

C_v = 5.64%   Mean = 41.83%

Figure 5



Narmco 5208/T-300

Cumulative Average Roll Sample Tests in Flexural Strength

McDonnell Douglas Aircraft Data

Figure 6

design approach using variably oriented plys. Skins are thin but thicker sections up to 16 plys are encountered on integral stiffeners. Rudder skins are 2 plys 0°, 2 plys +45° and 2 plys -45°. No observations have been made concerning mechanical performance and stacking order.

Reduced variability in hardware will require improved acceptance criteria in final components. McDonnell Douglas believes that damping techniques have potential and have used that approach in the Fokker test on adhesives. No immediate plans are being made for composite damping test development. Presently, for component acceptance they rely upon dimensional measurements, C-scan and cut-off tab testing.

Personnel at McDonnell Douglas thought that temperature and humidity are not serious problems in most hardware on commercial aircraft when 450°K matrices are used. Hot spots would be an exception and primary structure will be conservatively analyzed. They believe that a commercial aircraft is required to meet 355°K requirements.

Other Comments

Because of the large data base on currently used prepreg materials, use will be made of these materials on near-term future aircraft and present aircraft components. For commercial aircraft, McDonnell Douglas would probably have only one qualified source; for military, 3 to 4 sources.

McDonnell Douglas Aircraft has observed perhaps 5 to 6 per cent higher coefficients of variability with glass prepreg than with graphite-epoxy prepreg.

2. Lockheed-California Company, Burbank, CA

Lockheed-California Company was visited on January 7, 1977. Personnel included:

Walter Baumgartner, Research
John Wooley, M&P
Bob Stone, M&P

Prepreg Acceptance

Acceptance criteria for graphite-epoxy prepreg at Lockheed-California Company is shown in Table I. Prepreg is received with a test certification from the suppliers. Lockheed-California Company has not had any serious rejection problems. All suppliers have had minor problems with bad edges, gaps, broken tows, and tensioning problems. Some of these have resulted in roll rejections.

On large parts, such as the L-1011 fin, a requirement exists for the 0° ply to be 25 feet long and free of major defects. For the prepreg, a roadmap is required giving location of unacceptable defects along with flags on the roll showing these locations.

Storage of prepreg has not been a particular problem because usage of graphite-epoxy prepreg has been fairly rapid but Lockheed-California Company does require a retest after 120 days at 255°K storage. Time is recorded also on out-time at 300°K (maximum 10 days). They have had no experience with any materia going over 10 days.

Spars for the L-1011 fin are the responsibility of Lockheed-Georgia and their quality assurance is handled there.

Lockheed-California Co. has used about 450 kg (1000 lbs.) of Narmco 5209 from about 7 to 8 batches and about 225 kg (500 lbs.) of Narmco 5208 from 3 batches. A small amount of Fiberite 934 has been purchased. Batch-to-batch data was not supplied.

Lockheed-California Co. has observed some gel time difficulties in dicyandiamide (dicy) cured systems. This variability was not detectable by infrared. In composite fabrication, solid dicy was apparently filtered out during resin flow and/or debulking. The result was an upset in stoichiometry of the resin system in different areas of the laminate. Similar difficulties with other curing agents in suspension would be monitored by Lockheed-California Co.

Experience with Sources of Variability

Lockheed-California Co. believes that fabrication processing was a significant source of composite variability, but they qualified this conclusion by the statement that little information was available on how changes in the prepreg (chemical or rheological) might impact behavior during fabrication.

Lockheed-California Co. has observed variability arising from their own fabrication shops which are in different locations. Also, specimen preparations and testing are recognized as sources of variability. Scatter is inherent in compression test data, but Lockheed-California Co. still believes that the primary test for composite reproducibility is compression. To resolve these difficulties, they have developed their own compression test which they have named the Ryder test. This procedure is available although a copy was not requested.

Lockheed-California Co. personnel discussed the problem of final part testing. Much emphasis has been placed on prepreg characterization which they believe was well directed. Lockheed-California Co. is also planning a demonstration of composite production readiness by determining the static strength variability and durability of composite structure using loads, temperature and humidity cycles simulating a real-time environment. The substantiation will need to include the variabilities in structure that can realistically be expected from production and quality control technologies.

Control of Finished Hardware Reproducibility

Lockheed-California Co. philosophizes that composites in general exhibit an immense range of potentially critical material and process variables that can have a significant effect upon end-product performance and durability, and failure to measure quality at the end-product stage carries the risk that a critical material or process deficiency escapes detection and control.

The anisotropic nature of composites has impaired the ability to apply chemical and physical test methods to identify and quantify the interactions between raw materials and processes, cured laminate physical-chemical properties, and composite performance. Lockheed-California Co. also cites the potential problems of phase or zone boundary layers reported recently in epoxy resins (1).

The approach to be used by Lockheed-California Co. is to acquire samples of Narmco's 5208 which have been intentionally altered in epoxy/amine equivalence ratio and then eventually relate these to composite mechanical performance supported by chemical and physical characterization of prepreg materials. The mechanical techniques to be used are compression dynamic flexure and statistical creep failure tests. These techniques have been developed by Lockheed-California Co. and make use of some detailed mathematics in the data treatment.

Dynamic mechanical testing has been used for monitoring the cure of 5209 graphite-epoxy laminates as well as determining the dynamic mechanical response of the cured systems. This approach will be applied to the intentionally altered 5208 resin described above as well as to other variables such as fiber surface treatment. Both the dynamic flexure test and statistical creep failure test will be applied to dry and wet samples.

The test apparatus consists of a mechanical driver rod attached to the specimen which is cycled in flexure at 0-50 Hertz. A computer is used in data aquisition, reduction, and readout.

Typical data plots from 5209 studies are shown in Figures 7 and 8. Figure 8 gives test data for the dry laminate made from prepreg containing 2.4 per cent hardener. The material assumes viscoelastic properties at temperatures above 323 - 333°K as indicated by the loss in storage modulus E' (elastic recoverable energy) and an increase in the phase angle and loss modulus E" (unrecoverable plastic energy or heat). Figure 7 gives the test data for a moisture-saturated laminate and indicates that the glass-transition temperature (Tg) is lowered by water plasticization. The storage modulus degrades rapidly above ambient and the transition temperature is lowered to 368°Kas indicated by the peak in the loss modulus curve.

Figure 7 Storage Modulus vs. Temperature - Wet

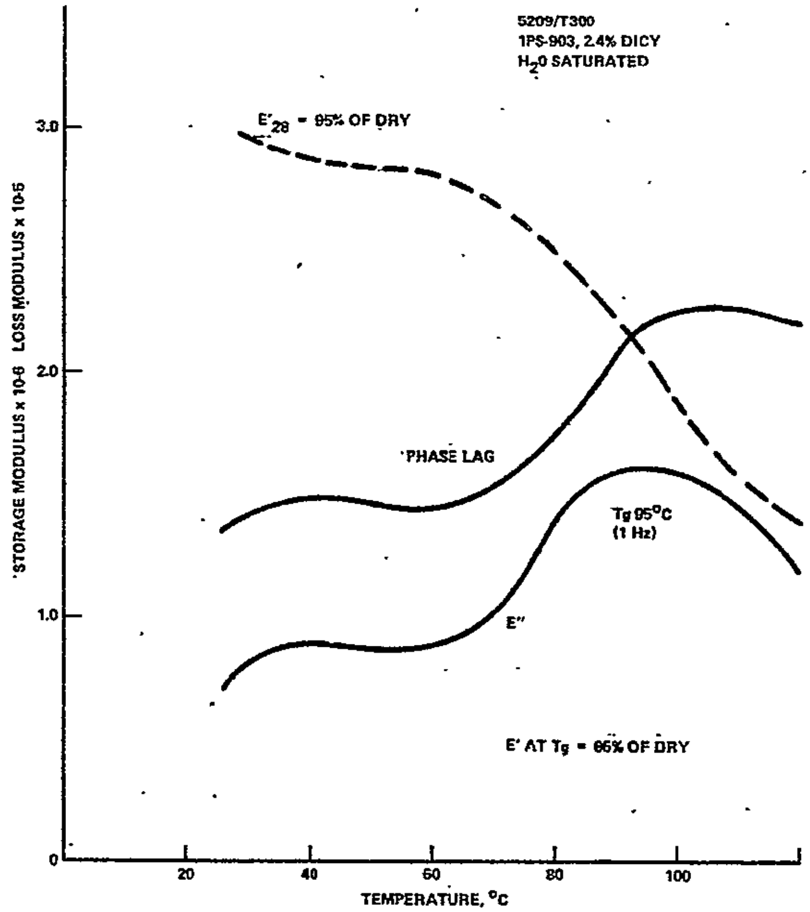
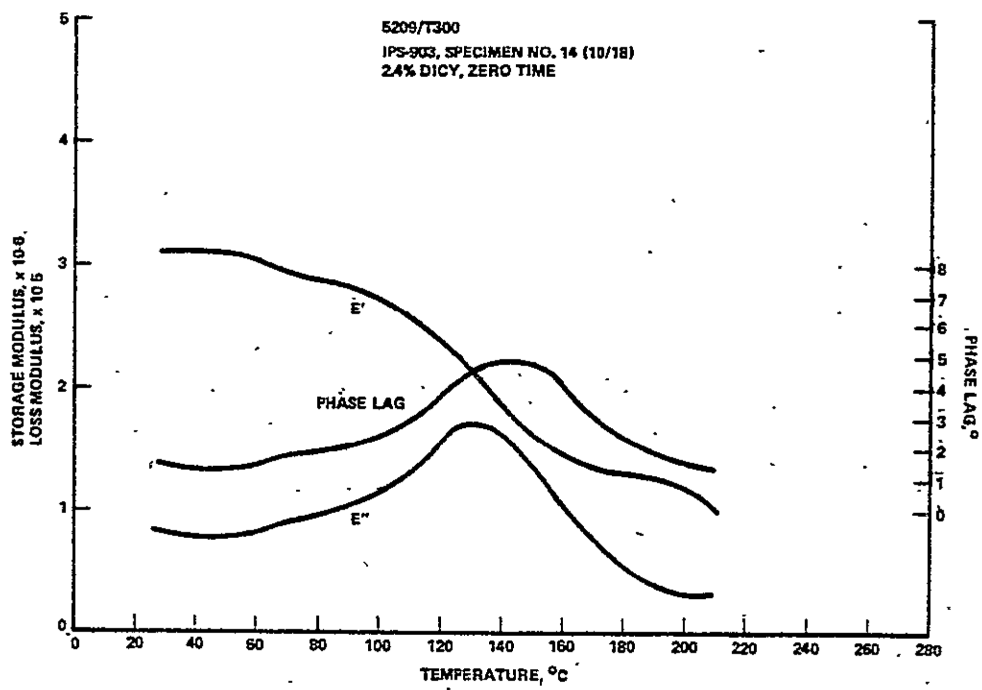


Figure 8 Storage Modulus vs Temperature - Dry



Several conclusions were reached with 5209. An assessment of irreversible composite changes in the dicy cured systems was more evident with finer particle size dicy.

Attitudes on Increased Quality Assurance

The belief was expressed that raw materials would have to be identified specifically by prepreg vendors in order to insure complete chemical characterization for quality assurance. Lockheed-California Co. is aware that costs go up with additional controls, therefore, only meaningful controls should be imposed. Lockheed is a strong proponent of the interaction of chemical, physical, and mechanical characterization of materials in order to attain a thorough assessment of quality and, consequently, reliability.

3. Lockheed Missiles and Space Company, Sunnyvale, CA.

On February 9, 1977 a visit was made to Lockheed Missiles and Space Company and discussions held with:

Clayton May, Staff Scientist
John Fritzen, Research Specialist
Deborah Hadad, Manufacturing Research Engineer

Prepreg Specifications

Lockheed Missiles and Space has had a high usage for graphite-epoxy fabric prepreg. Over 4500 Kg of prepreg, consisting mostly of Fiberite 934 on fabric, have been used. Current activity includes construction of parts for the Trident. Present prepreg specifications call for 40±3 per cent resin with 2 per cent maximum volatiles and 20±4 per cent by weight flow. Gel time is called out in a purchase document specification. Receiving inspection is the responsibility of Operations Services. Table III presents the minimum mechanical properties in cured laminates that the prepreg material must be capable of producing.

Historical batch-to-batch data on Fiberite 934 is available, but it was not supplied. Rejections of prepreg are rare, however material may be designated for specific applications.

Lockheed believes that the prepreg fabric approach reduces operator layup variability. They have no interest in preplied tape layups. Also, they are not pursuing thermoplastic prepreg. They place heavy emphasis on fiber alignment and have observed that misalignment of fiber over 5° results in reduced test values.

Table III

CURED LAMINATE INDIVIDUAL MINIMUM MECHANICAL PROPERTIES*

		Test Temperature	Requirement
Tensile Strength, MPa (10^3 PSI)**	Warp	R.T.	538 (78)
		450°K	510 (74)
	Fill	R.T.	503 (73)
		450°K	462 (67)
Tensile Modulus, GPa (10^6 PSI)		R.T.	64 (9.3)
		450°K	59 (8.5)
Flexural Strength, MPa (10^3 PSI)		R.T.	655 (95)
		450°K	483 (70)
Short Beam Shear Strength, MPa (10^3 PSI)		R.T.	48 (7.0)
		450°K	38 (5.5)
Compression Strength, MPa (10^3 PSI)		R.T.	496 (72)
		450°K	276 (40)
Compression Modulus, GPa (10^6 PSI)		R.T.	60 (8.7)

* Data normalized to 65 per cent fiber volume and a 3000 filament yarn.

** Property and requirements shall apply in wrap and fill direction of laminate except as otherwise specified.

Processing Variables

Variations within a lot of prepreg have been observed which their standard production processing can not handle. Lockheed feels that process control is at the top of the list of requirements to obtain consistent composite performance. Some changes in process recommendations are made as a result of DSC and dielectric behavior studies. In the latter area, Lockheed has made some improvements over dielectric equipment commercially available and have used this technique in developmental work. Their improvement permits the application of higher applied voltages and consequently a higher signal to noise ratio.

Lockheed has looked at other techniques for process monitoring. One such method is the correlation of wetting angle of resins and temperature. Some irregular behavior has been observed with some CTBN modified adhesives.

Chemical Characterization

The manufacturing research laboratory at Lockheed has been quite active in the study of chemical characterization techniques for resin systems of the type used in 450°K curing epoxy graphite prepregs.

It has been shown that mechanical performance tests would not reveal formulation changes which might be introduced intentionally or unintentionally by the prepregger. It was believed that such changes could result in mechanical failure of a fabricated part. Further, the work was based on the belief that physical and chemical characterization of prepreg must be complemented by knowledge of the chemical composition of the formulation.

Initial work dealt with identification of the chemical composition of the various components of the resin used in a commercial epoxy graphite prepreg. The resin system was found to consist of:

Ciba MY 720: 100 parts
Diaminodiphenylsulfone: 32 parts
Boron Trifluroide Complex: 1.5 parts

Confirmation was established by obtaining infrared absorption spectra on a synthesized mixture. This was supported by similar infrared spectra on materials separated by preparative thin layer chromatography. The several methods for identification of the components of the prepreg resin were then assessed for their value and sensitivity in detecting variations in resin composition or staging status.

Lockheed's preliminary conclusions were:

1. Thin layer chromatography can be used to assure that the chemical ingredients have not been altered,

2. Liquid chromatography offers promise for the determination of the degree of B-stage and component ratios,

3. Differential scanning calorimetry can be used for B-stage determination, rate of chemical reactions and is sensitive to resin-curing agent ratios, and

4. Infrared spectroscopy is a valuable adjunct for the identification of a specific component and in special cases can be used to determine component concentration.

To verify these conclusions, five formulations which might be typical prepreg resins were prepared and then assessed by the analytical techniques.

Using GPC, the ability to quantify certain peaks was demonstrated as shown in Figures 9 and 10 which were obtained on two samples with the curve in Figure 10 obtained on a mixture with double the concentration of Gly Cel A100.

Limitations of GPC were found particularly in its inability to cleanly separate peaks in preparative separations. Also, Lockheed found that DEN 438 was not observed either because of masking or association. See Figure 11, which contains no DEN 438 and is essentially identical to curves such as those shown in Figures 9 and 10 which <u>do</u> contain DEN 438.

Liquid chromatography was found to solve the problem of clean separation of MY 720 and DDS, however Lockheed did not have any success in discriminating other components. See Figure 12, which contains DEN 438 and compare with Figures 13 and 14 for MY 720 and DDS respectively.

Lockheed's conclusion was that no one technique will solve the quality assurance problem. However, by utilizing the well established, analytical methods described, cost and time effective quality assurance programs may be integrated into current procedures resulting in higher reliability finished products.

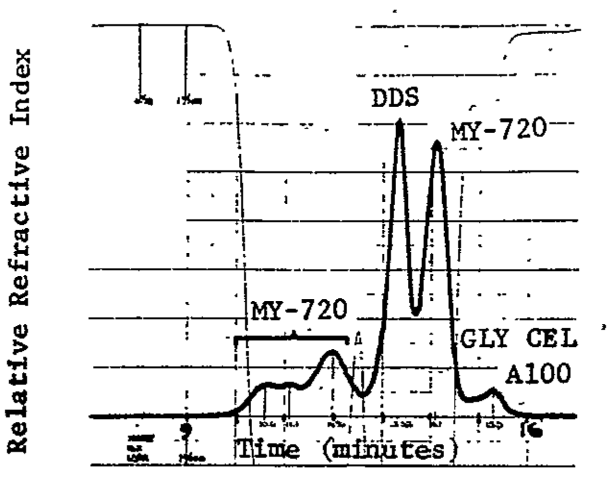


Figure 9 GPC Curve

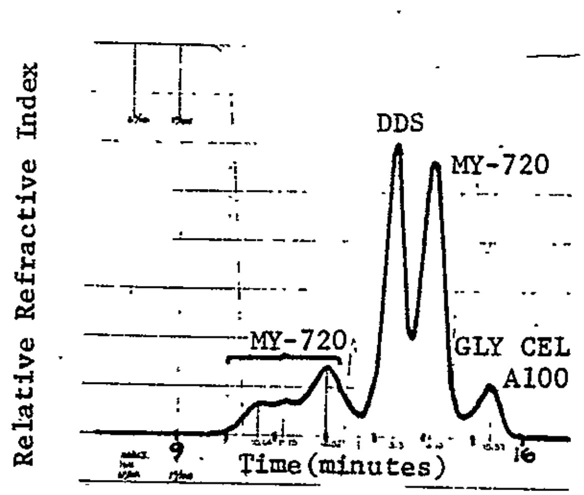


Figure 10 GPC Curve

2X Gly Cel A100

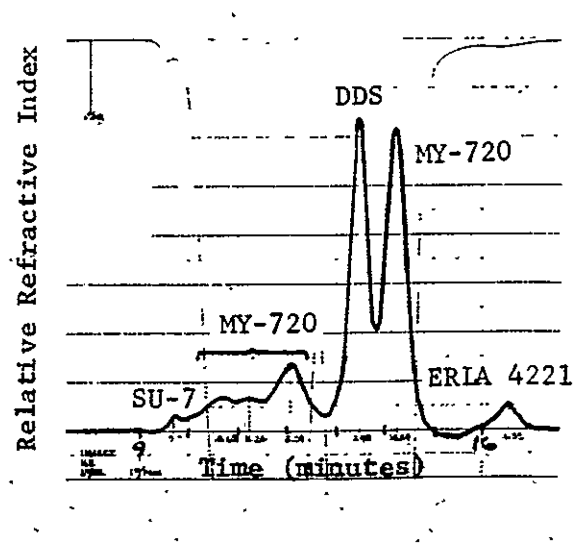
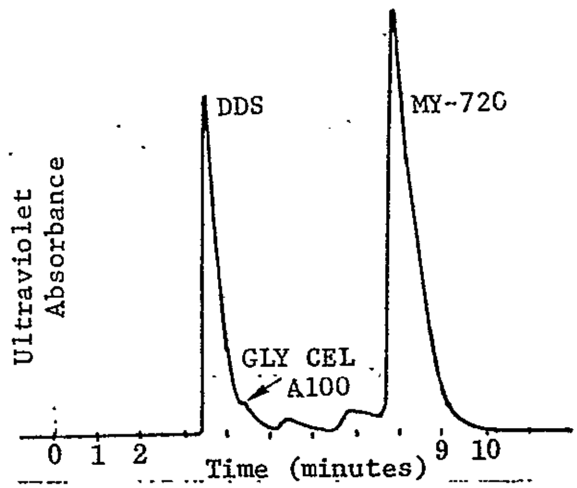
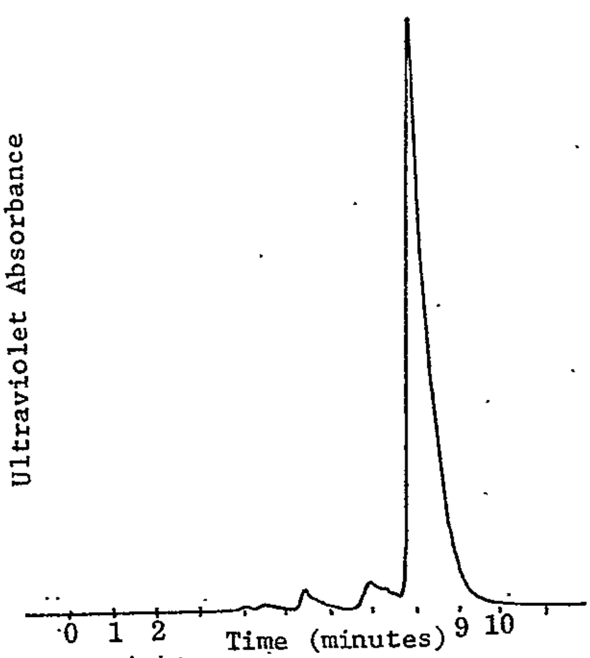


Figure 11 GPC Curve No DEN 438



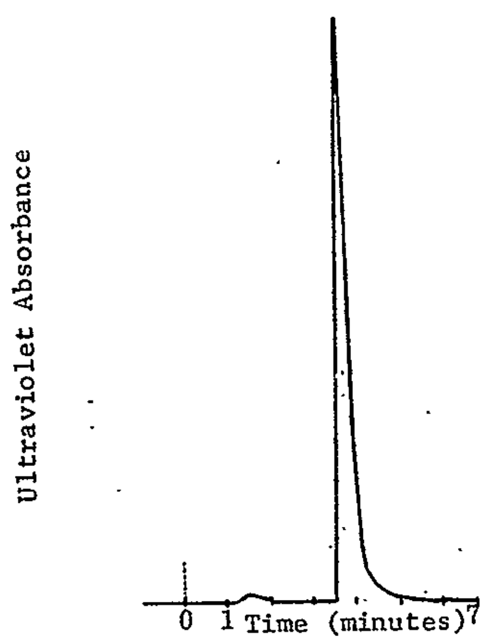
LC: Sample 5
80/10/20/28 MY-720/GLY CEL A-100/
DEN 438/DDS

Figure 12



LC: MY-720

Figure 13



LC: DDS

Figure 14

Additional work at Lockheed is being conducted under AF Contract F33615-76-C-5146 "Exploratory Development for Chemical Quality Assurance and Composition of Epoxy Formulations". Recently, resin matrix formulations were prepared with various alterations in the DDS and BF_3 concentrations intentionally introduced. Laminates were prepared and examined. Preliminary data suggests that Tg is highest at 40 phr of DDS but BF_3 has little if any influence on Tg. In regard to water absorption, higher DDS concentrations tend to pick up slightly more water.

Differential scanning calorimetry (DSC) was conducted on the above resins extracted from Lockheed prepared prepregs. The BF_3 decreases the cure initiation temperature.

Similar samples were submitted to a round robin and results were presented at a meeting in March 1977 on Chemical Characterization held at Rockwell Science Center, Thousand Oaks, CA.

Four materials were prepared by Lockheed M&S for round robin analysis by several companies and government agencies. The samples were prepared with intentional variations in composition.

Base	254-1A	100 pts. MY720, 40 phr. DDS, 2.14 phr. BF_3*
Overstaged	254-1	Same as above with 60 mins. staging at 353°K
High DDS	254-2	100 pts. MY720, 45 phr. DDS, 2.14 phr. BF_3
Low BF_3	254-3	100 pts. MY720, 40 phr. DDS, 1.07 phr. BF_3

*Resicure #2

The first session dealt with DSC techniques on the above samples. The profile of the curves showed a sensitivity to heat up rate. A rate of 5°K/min gave the greatest resolution of three peaks. The highest temperature peak may be due to uncatalyzed addition of DDS to the epoxy. The lowest temperature peak may be the same reaction with BF_3 catalysis and the middle peak may be BF_3 catalyzed homopolymerization or cyclic dimerization. Ciba observes some cyclic dimer in normal manufacture so it is entirely possible that BF_3 might encourage the formation of larger quantities of this material.

The various companies handled the samples differently so results were a little different. The DDS is completely dissolved and when BF_3 is used with this system, the pot life is drastically reduced. Hercules obtains pot life by keeping the DDS in suspension. Although the samples were highly advanced, the analyses were generally quite comparable but obviously more work will be required to really say whether DSC could be used as a viable and meaningful characterization technique.

The requirements for technique standardizations were itemized but not defined:

1. Sample size (10mg tentative)
2. Heating rate (2, 5, 10°K/min. tentatively)
3. Sample handling (storage, etc.)
4. Instrument calibration
5. Sensitivity (for full scale deflection)
6. Purge rate
7. Nomenclature (peak heights, initiation temp. etc.)
8. Baseline

The problems of obtaining DSC on prepreg were recognized but no conclusions on resolution.

The next session's topic was chromatography including GPC and all variants of LC. The LC method appears to have the greatest promise.

An assessment of the GPC studies would indicate that it holds promise but conclusions were drawn on rather small differences in peak heights. DuPont and Waters were not hesitant at all about making such conclusions based on subtle peak height differences. The resolution on GPC is not as good as LC. Mixtures which show 4-6 peaks on GPC will show 25-30 peaks in LC.

4. Boeing Commercial Airplane Co., Renton and Auburn, WA

Boeing was visited on January 4 and 5, 1977 with principal discussions with the following personnel:

Marlin Pollock, Senior Materials Specialist
Carl Hendricks, Specialist Engineer
R. T. Cook, QC, R&D
Duk Kim, QC, R&D
Dan Hoffman, Structures Staff Engineer
M. T. Katsumoto, Supervisor Materials Technology
J. McCarty, Engineering Technology, Mgr.
V. Thompson, Manufacturing
M. Wilhelm, Manufacturing

Quality Control and Design Allowables

Boeing has stated concerns as follows:

- Safe application of the graphite-epoxy material to all primary structural components.

- Production economics that will allow a long production life of the aircraft.

- Long term durability that will insure the consistent return on the investment.

In order to obtain resolution to the above requirements, the questions arise:

1. Can a graphite-epoxy system be produced that has the level of material and property consistencies equivalent to a typical aluminum (2024, 7075, etc.)?

2. What additional controls will be required in matrix or fiber technology to attain the reproducibility required in Item 1?

3. Are the controls achievable based on application of current technology and if so is the cost to achieve these goals reasonable?

Substantial investment in resources will be required to develop the allowables data to support the detail design activities and also to provide the technical information to satisfy stringent FAA certification requirements. Answers to the questions noted will be helpful in formulating Boeing's plans in establishing the level of usage that advanced composites will be committed on primary structure.

Boeing has made a series of company visits to obtain details to help them assess industry enthusiasm and capabilities, and also for industry to understand Boeing's requirement for a "critically controlled" graphite-epoxy system.

Some initially observed attitudes at Boeing on graphite-epoxy design allowables were pessimistic. Boeing cited recent data obtained by McDonnell Douglas, St. Louis in Table IV. See Footnote* The question was posed - why not stay with aluminum? Boeing is, of course, pursuing graphite-epoxy and intends to reduce data scatter.

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*Author's Note: This data can also be interpreted to indicate what happens when all possible sources of variability are permitted full impact on test data. The data variability is obviously quite wide in this testing series. The testing of tension on beam specimens with high ±45° content is especially subject to the effects of edge, notch and discontinuous fibers as well as usual processing variables.

Table IV

TENSILE STRENGTH, MPa (10^3 PSI)

DESIGN ALLOWABLES

	Average	A Value Absolute	A Value Specific	B Value Absolute	B Value Specific	Author Calculated Coefficients of Variation (1)
* Graphite Epoxy						
45°/45°	140 (20.3)	107 (15.5)	1868 (271)	120 (17.4)	2110 (306)	11%
0°/45°/45°	503 (73)	207 (30)	3647 (529)	331 (48)	5778 (838)	26%
0°/45°/45°/90°	414 (60)	239 (34.6)	4185 (607)	310 (45)	5440 (789)	19%
2024 Aluminum	496 (72)	462 (67)	4619 (670)	469 (68)	4688 (680)	3.5%

*McDonnell Douglas St. Louis Data T300/5208

A Values 99% Probability with 95% Confidence Limit

B Values 90% Probability with 95% Confidence Limit

(1) Based on infinite population

Outlook on Composites for Commercial Aircraft

Boeing has made a significant contribution to the establishment of industry confidence in composite materials. Their useage of glass-reinforced resin systems has grown significantly and represents an unmistakable trend in the construction of commercial aircraft. For example, exterior fiberglass useage is reported as follows:

707	20 m^2
727	170 m^2
737	280 m^2
747	930 m^2

A management commitment has been very recently made for significant use of graphite-epoxy composites on the new 7X7 airplane. Expected graphite-epoxy prepreg useage is:

1980	230,000 kg	Pricing expected at $55-66/kg
1985	590,000 kg	
1990	1,270,000 kg	

A fabrication approach has been developed which is a net flow prepreg (edge bleed only) combined with self adhesive properties for the core bond. Boeing uses core sandwich structures with bondable Tedlar film liners on interior surfaces. Graphite skins will be quasi isotropic. Future components will include empennage, control surfaces, flaps and eventually the wing box.

Specifications

Boeing specifications for acceptance and composite performance will be completed later this year. Quality control R&D is involved in the development of such specifications. Tentative acceptance specifications are shown in Table I. Materials have been received through materials engineering for all contract work, R&D activity, and such. About 1860 kg have been purchased. No materials have been rejected except on gross appearance problems. As with other commercial aircraft houses, no production has been conducted except a program involving over one hundred 737 spoilers for NASA Langley. No batch-to-batch data was made available.

A point system is used to monitor out time. No changes or process modifications will be permitted to accommodate materials which are on the fringes of the specification. The feeling is that graphite epoxy prepreg is fairly forgiving but it must not cause any difficulty in specified processing parameters.

Resin Quality Control Methods Development

Boeing has an IRAD program underway this year to carry out a study of resin quality. This study will investigate a diverse group of analytical and instrumental methods including all types of chromatography, infrared, dispersive x-ray, dielectric studies, DSC, elemental analysis, and rheology. Peak separations will be conducted by chromatographic techniques and these peaks will be identified by one or more procedures. Boeing has an impressive array of instrumental capability.

The approach on the IRAD program is to have Narmco prepare several batches with intentionally modified resin/curing agent ratio. Results from these altered batches will be available later this year. Rate of effort is about 1.7 man years. To date, only a couple of regular Narmco 5208 and 5209 batches have been studied chemically to begin collecting batch-to-batch information.

Other mechanical studies are also underway in a 4.5 man year IRAD program. A classical mechanical part of this test program will support the altered batch chemical studies. Boeing is interested in fracture toughness and will conduct other mechanical studies to correlate fracture toughness and interlaminar shear also on this IRAD program.

5. General Dynamics, Fort Worth Division, Fort Worth, TX

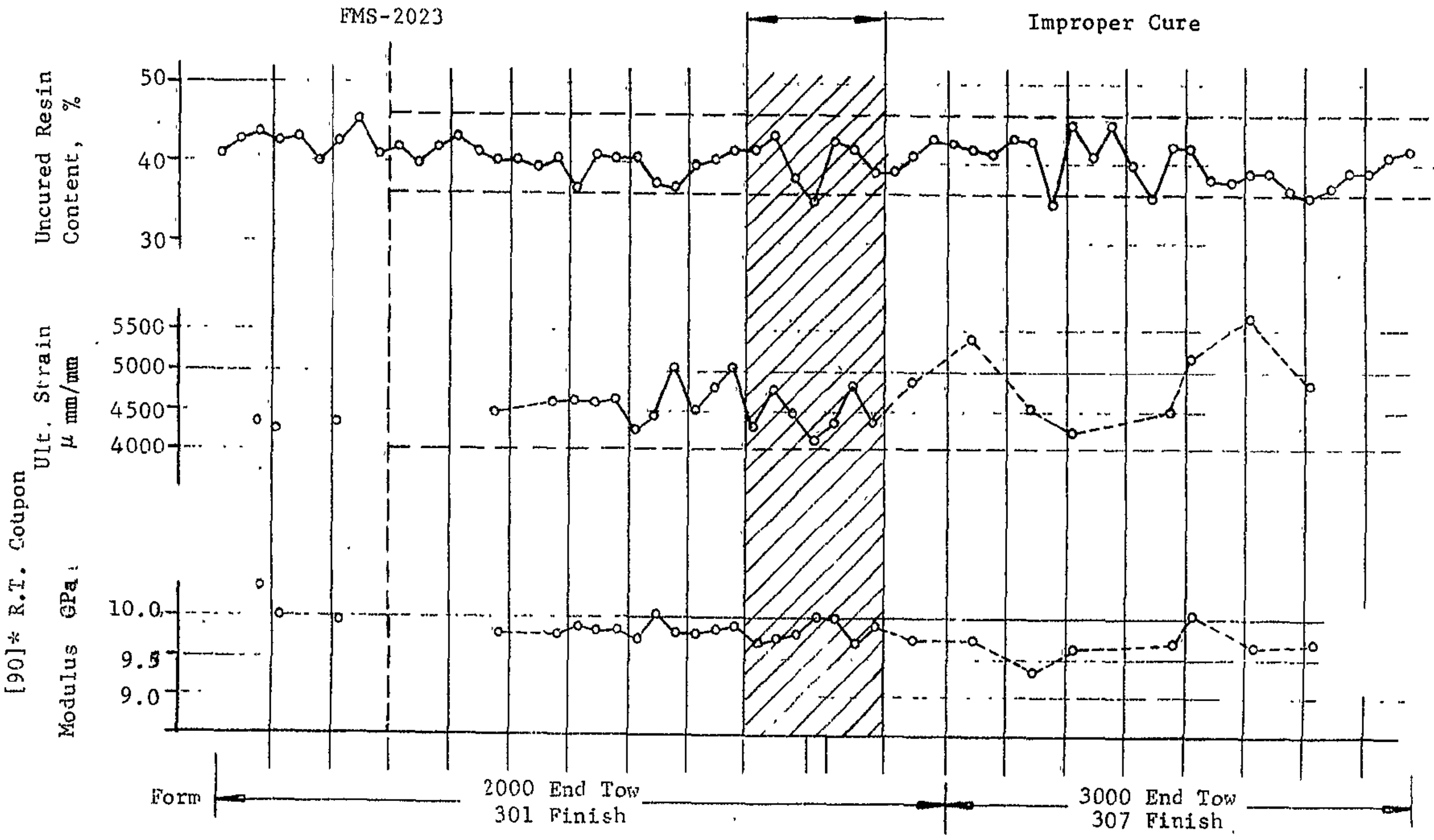
The Forth Worth Division of General Dynamics was visited on February 21, 1977 and discussions were held with:

R. L. Stout, Materials Engineering
W. M. Beatty, Materials Engineering

Prepreg Variability and Design Allowables

A sizeable program was conducted internally at Forth Worth to establish firm design allowables on Narmco 5208/T300 for use on the YF-16 empennage. Acceptance data was statistically analyzed for variance of fiber and resin tension failure modes (2). Tension and compression tests were used to provide design allowables. An early procurement specification (FMS-2023) was a first attempt at reducing mechanical property variation. Callouts were based on three very early batches of Narmco 5208/T300. (Batches 4,5,6). The purpose of the 1973 program at Fort Worth was to assess the quality and performance of an additional 18 batches of prepreg against FMS-2023. Over 950 kg of prepreg purchased through August 1973, demonstrated no significant changes. See Figures 15 and 16.

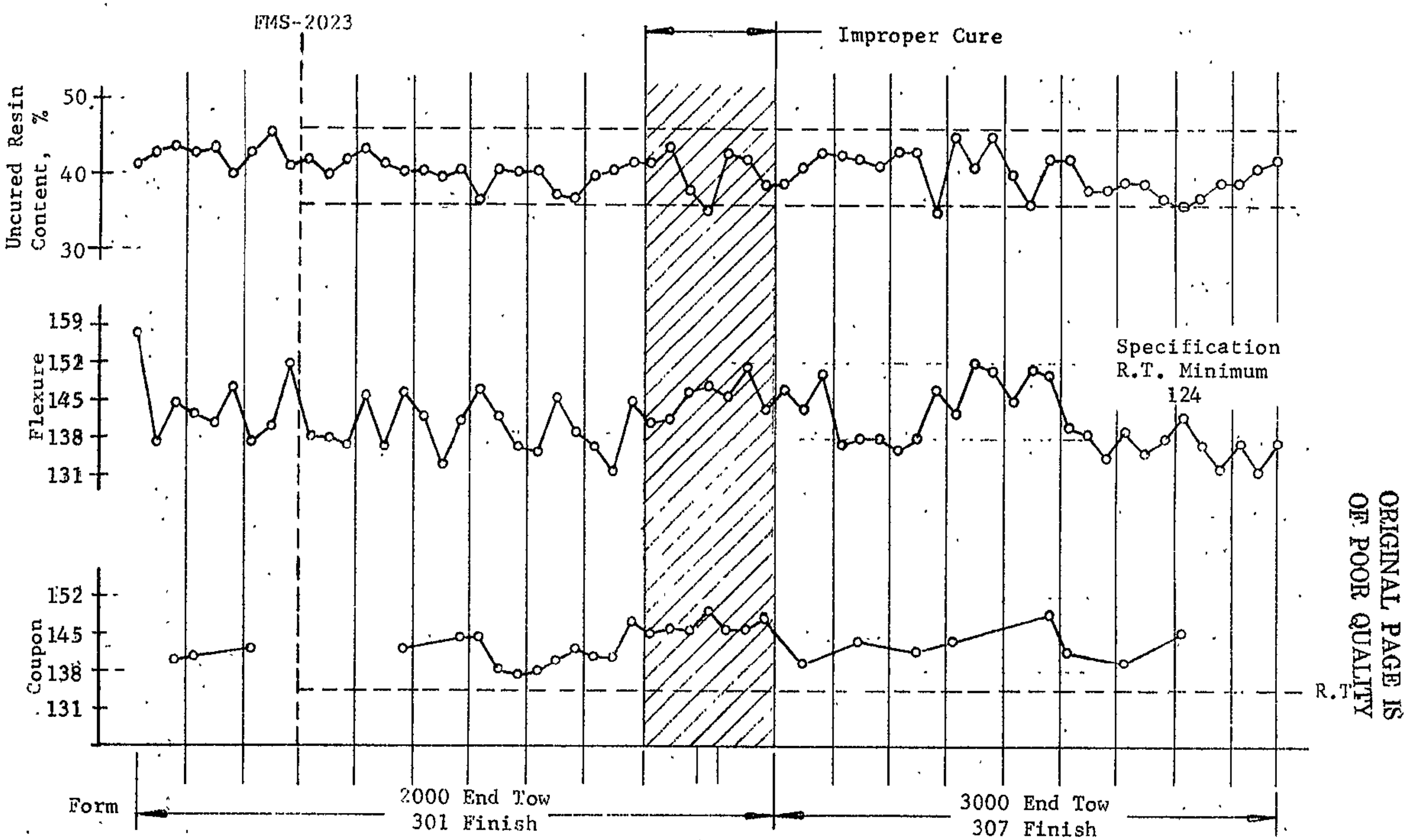
Coefficients of variation were 6 per cent for fiber dominated failures and 13 per cent for resin dominated failures. More recently the coefficient of variation on fiber dominated properties has decreased to about 2 per cent on fiber dominated properties, and to about 8 to 10 per cent on resin-dominated properties (SBS). About 61,000 m of 75 mm wide tape has been purchased to date for the F-15 program with no rejects. Acceptance specifications at General Dynamics may be tightened.



Resin Content Vs [90]* Modulus and Ultimate Strain

*Transverse to Fiber Direction

Figure 15



Resin Content VS [0]* Modulus

*In the Fiber Direction

Figure 16

Some fiber abnormality was observed on batch 92. It appeared to have a glassy sheath. The same problem has been observed recently on batch 827.

Processing Variables

General Dynamics recognizes that processing controls are essential in obtaining reliable composites. They have observed some cases of in-batch variability particularly in resin content which has caused problems in processing. Excess resin has been a continuing difficulty and has led General Dynamics to the net resin approach in prepreg requirements.

Heat up rates, flow behavior and void content have been a source of some difficulty in the F-16 horizontal skin (52 plys). Short gel times have been observed to give lower void content.

Lay-up time is a potential source of trouble in part thickness. They allow seven days out time at room temperature on prepreg and two or three times that on the tool.

Skins are layed up with a machine using 75 mm tape. Location of the tape on the perforated paper has been a problem.

Analytical Methods

No chemical fingerprint is used at General Dynamics and they have no instrumental chemical analytical capability except infrared. They have no plans for the development of such methods and rely heavily on mechanical performance tests.

Gel time is not included in the General Dynamics specifications. Rather they use an Arrhenius type plot of the gel times at 394, 408 and 422°K. The reaction rate constant is calculated and used for batch-to-batch reactivity assessment.

Testing Variables

General Dynamics has found that rough edges resulting from sample cutting, contribute to increased data scatter, particularly in notch sensitive tests. They have resolved this problem by using a Micromatic Wafering Saw with a Norton D-220 blade for sample cutting. This sawing method results in a high quality edge surface on the test sample and consequently reduces test data variation.

Another test problem observed has been in short beam shear specimens which do not have parallel top and bottom surfaces.

Recently, an unexplained new observation has been made in flexural specimens failing in compression. Short beam shear specimens are believed to be particularly sensitive to process variables. Void content is a critical parameter in this test.

A test program is currently underway at General Dynamics to correlate humidity effects and cure and post cure.

B. Graphite-Epoxy Prepreggers

1. Fiberite Corporation, Winona, Minnesota

Resin

The visit to Fiberite was made on January 13, 1977.
Discussions were held with:

Clyde Yates, Director Advanced Composites
Dr. Jim Allen, Manager Research and Development
J. W. Fetting, Manager Quality Control

Ciba-Geigy's MY 720is used in Fiberite 934 and 934B prepreg. The material is purchased according to two primary specifications of epoxy equivalent and Brookfield viscosity. Hydrolyzable chloride also is specified at less than 1 per cent. The other values are considered proprietary by Fiberite but the viscosity range was stated to be tight. Fiberite believes that the particular viscosity range batches are selected by the manufacturer to be sold to Fiberite.

In the assessment of resin quality, Fiberite does not have GPC or LC equipment and have not conducted any studies along these lines although they feel that the method has potential. Some caution was noted in acquiring the equipment for a specification requirement because of cost.

Fiberite's confidence level is probably typical of the prepregger's experience. Because of their routine monitoring of prepreg production, they believe that if the starting resin is within specified viscosity and epoxy equivalency values and the process controls are reasonably followed - then it is impossible to produce a graphite prepreg material which is not within the specification.

Fiberite has had no real problems with MY 720 resin except perhaps price. Some delays have been experienced with delivery. Apparently no resin has been rejected and storage has not been a problem.

The role of the resin in graphite-epoxy composites is described by Fiberite in the principal performance areas of importance as 1) temperature service limit, 2) shear strengths and 3) impact strengths.

No chemical analytical work, per se, has been conducted by Fiberite to correlate such compositional variations to composite performance variations.

Processing

The technical responsibility for new product and process development comes under the assignment of Dr. Jim Allen and his staff. All details of process control values and process details are proprietary to Fiberite. Generally, the basic control is defined by data collected at four process points of temperature and time. Other supporting checks include air flow, belt speed, roll openings, temperature settings and resin solution prarmeters.

The resulting product is defined by specifications covering resin content, flow, tack and gel time. Gel time is adjusted by altering curing agent concentration.

Fiberite has made a significant effort in the area of woven graphite prepreg. They have their own weaving capability and offer a variety of weave styles and hybrids. Sizing is a critical source of variability of particular importance in woven goods because of the possibility for fiber damage in the weaving process. Fiberite did not observe any significant increase in data scatter or loss of properties when Union Carbide changed the sizing process on T-300. Type and amount of sizing is not specified by Fiberite in their fiber purchases.

Fiberite's thrust in woven prepreg goods is based on the belief that the stability of fiber position is an important factor in forming around contours or double curvatures. Forty per cent of their graphite prepreg sales are woven goods. Commercial customers (golf shafts, etc.) still use unidirectional prepreg except for 10 per cent using Fiberite's woven goods.

Typical Properties Woven Goods (934 Epoxy)

	MPa (PSI) Warp	Fill
Tensile Str.	662 (96,070)	698 (101,280)
Tensile Mod.	73,773 (10.7×10^6)	77,221 (11.2×10^6)
Flex Str.	929 (134,690)	997 (144,640)
Flex Mod.	73,084 (10.6×10^6)	67,568 (9.8×10^6)
Short Beam Shear	59 (8510)	55 (8030)

Fiber Volume	65% T-300 6,000K
Ply Thickness	.28 mm (.011 inch)
Fabric Description	10 x 10 Warp and Fill in a 5 Harness Satin, 8.5 oz/yd

Cost of highly unidirectional prepreg (97%) is $ 22-33/kg more than unidirectional tape. Higher volume would reduce this differential to a few dollars.

For thermoplastic goods, both woven and unidirectional, Fiberite has taken a solvent approach with polyarylsulfone Only a small amount of such material has been produced.

Fiberite expects the automotive market to utilize woven goods and when this occurs, such prepregs would be a significantly larger percentage of total graphite sales.

Assessment of Other Sources of Variability

Fiberite personnel described experiences which resulted in their conviction that most of the variability problem lies in three important areas.

- Technique in prepreg layup
- Test sample preparation
- Testing methods and techniques

They expressed the opinion that at least part of the scatter or variability problem was related to the experience of metal-testing people and their unmodified extrapolation of isotropic metal testing to anisotropic composites testing. Testing of composites derived from woven goods was stated to be more critical than other forms because of the sensitivity of coupon orientation to warp and fill. Fiberite expressed no concern about small specimens with high edge to volume ratios such as the short beam shear specimen. They prefer a tensile test if only one test is to be used as a specification.

The sandwich beam specimen drew some criticism from Fiberite personnel because of the complexity of its production and the number of innate variables associated with preparation and test.

Attitudes on Composition Revelation and Standardization

Fiberite considers its compositions and processes proprietary. Their position in the market place is maintained by such product and process know-how, particularly the latter. In an agreement with Lockheed M&S, composition is revealed by coded component designations. Although a resident observer has witnessed the process, complete details of the process are not revealed in the agreement.

Fiberite reflected what may be a common concern among pre-preggers, that additional specifications will increase cost both directly and indirectly and that some of those specifications might be imposed and may not be factors leading to improved reliability or durability of the final hardware.

2. Hexcel, Dublin, CA

Resin

Hexcel was visited on January 10, 1977 with the following company personnel present:

Alan Sheppard, District Manager
H. B. Loomis, Manager Special Programs
Sheldon M. Berk, Marketing Director
R. D. Forsberg, Quality Administrator
L. J. Salmela, Quality Administrator
Juan Chorné, Manager Materials Development
Richard J. Moulton, Manager Reinforced Plastics

Hexcel's resin system F-263 uses MY 720 as the principal epoxy component. Acceptance specifications for MY 720 call out viscosity and epoxy equivalent weight. Hexcel has experienced difficulty in viscosity variations although they have had no material rejections. They have been in short supply of MY 720 and have learned to use any resin viscosity they can get. They feel that the epoxy equivalent weight (EEW) is not reliable, and would like to have consistent raw materials so that no changes in processing would be necessary to end up with a reproducible product. This has been accomplished very successfully, particularly with epoxy resins from Shell and Dow.

Variations in viscosity and EEW have not been correlated to any changes in mechanical properties at Hexcel. Likewise, no correlations based on metal ion content, acid number or chlorohydrin content have been conducted. Variations in high temperature performance, they feel are controlled primarily by crosslink density.

Product specifications are built upon in-house composite testing.

Processing

Hexcel has also made a thrust into woven graphite prepreg goods. The processing problems are different than unidirectional tape in many respects, for example tensioning during impregnation.

Woven goods are prepregged using a resin solution in which the epoxy modification has taken place before dissolution. No "B" staging occurs after placing the resin into solution and the solvent is removed at temperatures where advancement is not a problem.

For unidirectional materials, no resin advancement occurs in the hot melt process which is carried out at 318° - 327°K Particle size of DDS or dicy is controlled. A QC drum wind sample is used before the fiber is committed to impregnation. Hexcel offers 300 mm and 710 mm tape and plan to produce 1.22 m tape in a year.

No studies have been made to formally evaluate process variations and any impact on final composite properties with either unidirectional or woven goods. Hexcel is particularly confident that solution coating of woven goods results in a consistent product. Similar experience has been gained with glass fabrics which use the same equipment.

Curing agent levels are fixed values.

Analysis and Testing

Hexcel has no LC or GPC equipment but they have done some cooperative work with Lockheed M&S. No batch-to-batch LC or GPC data has been obtained on prepreg or raw materials. In-house capability relies heavily on standard mechanical tests backed up with environmental exposure methods such as water, temperature, and salt spray. Mechanical testing is conducted on neat resins as well as composite specimens. Some work has been done with acoustical emission.

Technical personnel at Hexcel have noted a number of instances of sources of variability due to testing in the case of customers as well as in-house observations. For example, flexure tests and their sensitivity to up-side and down-side with respect to caul plate (resin rich) surface. They have observed sensitivity in specimen cutting especially with small specimens such as short beam shear.

Hexcel would not like to see an instrumental "fingerprint" specification on prepreg matrix resin - more work needs to be done to come up with meaningful specifications. If that were done, then they would prefer the "fingerprint" approach compared to other alternatives. Hexcel has not done anything along these lines with the exception of the work in cooperation with Lockheed.

Fiber

Hexcel has done some outstanding work on fiber variability. Their studies have been particularly revealing in the sizing level variation in graphite yarn.

The fiber is the determining factor in strength and stiffness of composites. In tape, variations in each tow tend to average because multiple spools are being fed. In fabric the variation may be concentrated in certain areas involving the fill fiber because it is woven in - one at a time, from a single spool.

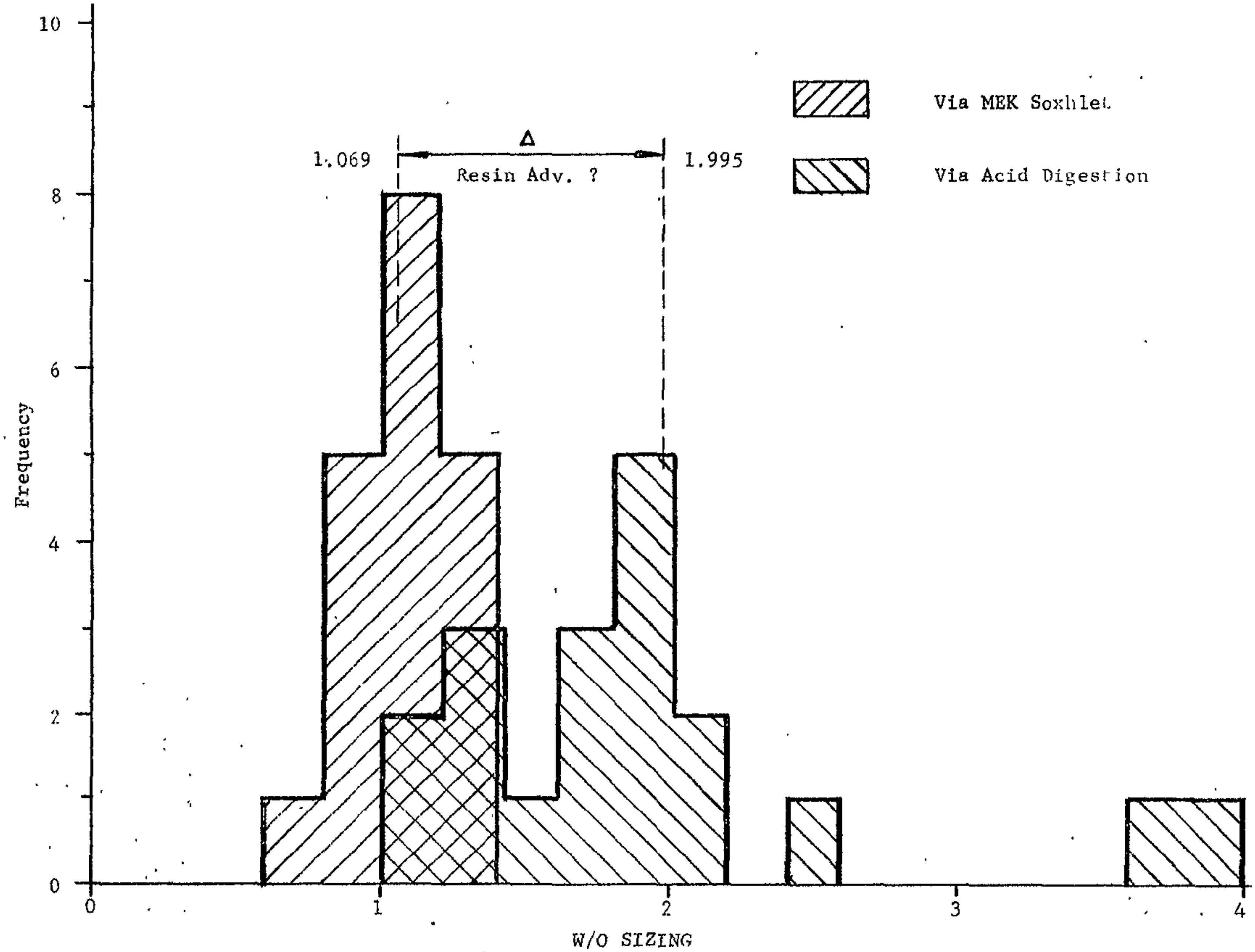
The sizing is important in handleability and fiber protection during the weaving process but is also quite critical in the interface relationship with the matrix resin. The resin used as the sizing material ends up as a significant organic component of the total final matrix system (up to 15 or 20% at high sizing levels).

Hexcel has used two methods for determination of sizing level including:

1) MEK extraction
2) Acid digestion

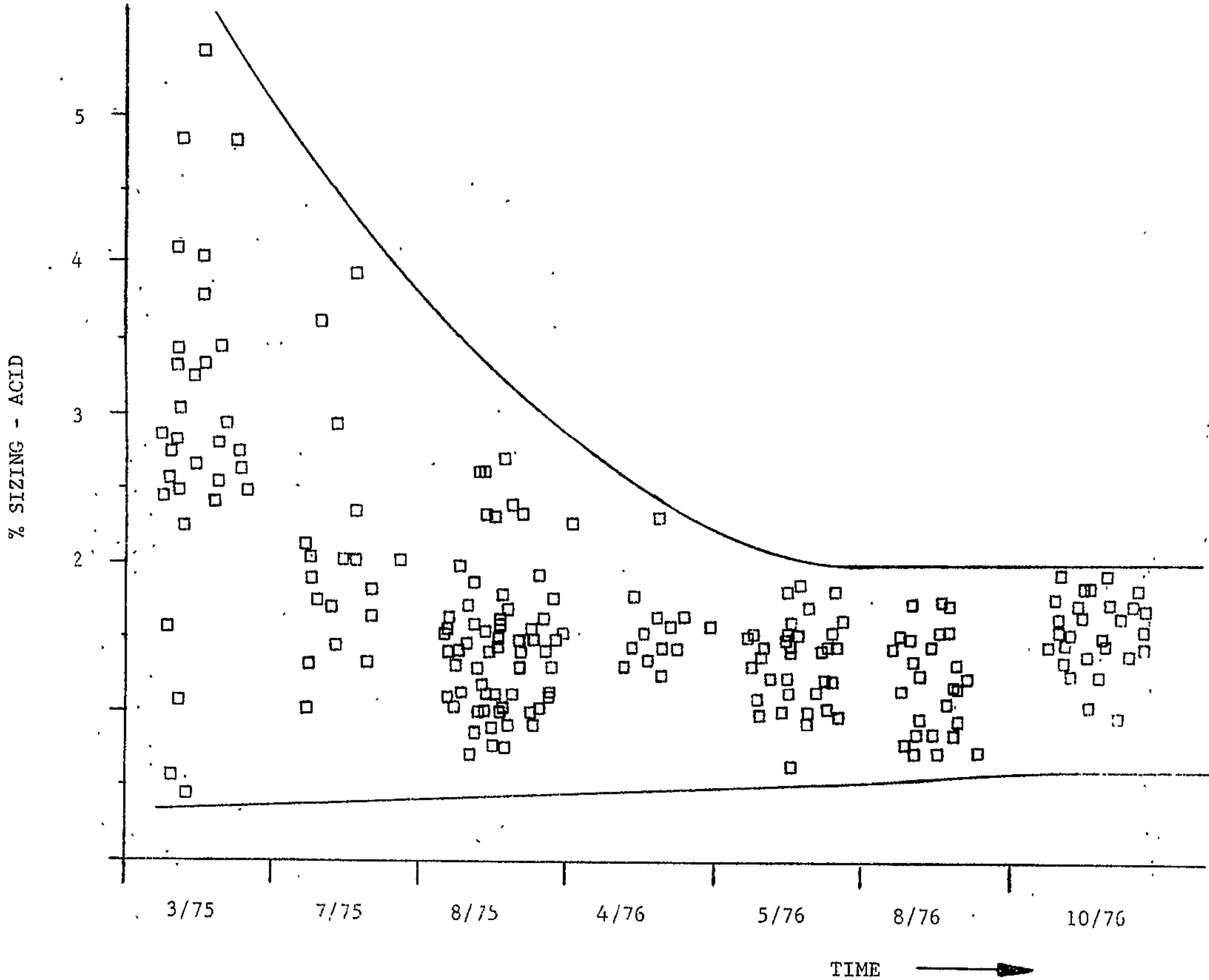
The MEK extraction is carried out by Soxhlet extraction of a yarn sample. Acid digestion is carried out by sulfuric acid and hydrogen peroxide removal of the sizing resin. Both methods are gravimetric.

Typical early T-300 variation is exemplified in Figure 17 which correlates batch frequency against 0.2% step sizing levels. The difference in mean values may be due to resin advancement which results in MEK insolubles. The scatter of sizing level as determined by acid digestion has improved significantly with time as shown in Figure 18. There was poor correlation of the MEK method and the acid digestion method. A new burnout method has correlated more closely to



Sizing Level Histogram

Figure 17



Sizing Level History T-300

Figure 18

the digestion method and may be used for routine acceptance specification.

Attempts to correlate specific gravity with weight per unit length and sizing level (MEK) with weight per unit length were unsuccessful as shown in Figure 19 and 20. Similar unsuccessful correlation was observed in specific gravity and sizing level (acid method) as shown in Figure 21. Multiple points are indicated by numbers.

Hexcel has used a stiffness to sizing level (acid digestion method) ratio as a criteria for fiber acceptance. Actual top and bottom values are proprietary.

The summary of Hexcel experience on fiber variability is shown in Table V. The "start" values are for a few very early batches and "total" values are for all batches. Union Carbide's specifications are on the right and they specify lot averages not single values. Historical fiber sizing level experience is shown in Figure 18.

Hexcel is now carrying out internal work to correlate composite mechanical properties with fiber variations.

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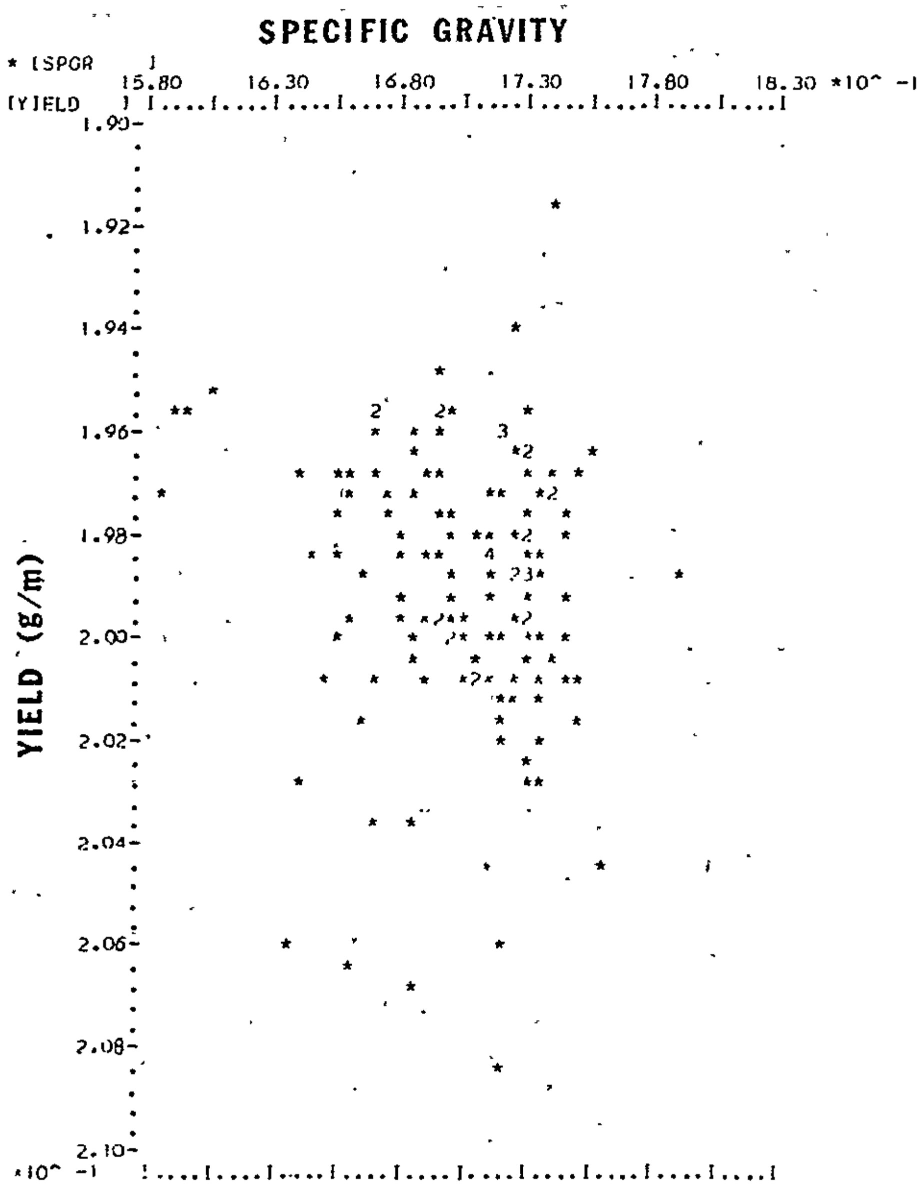
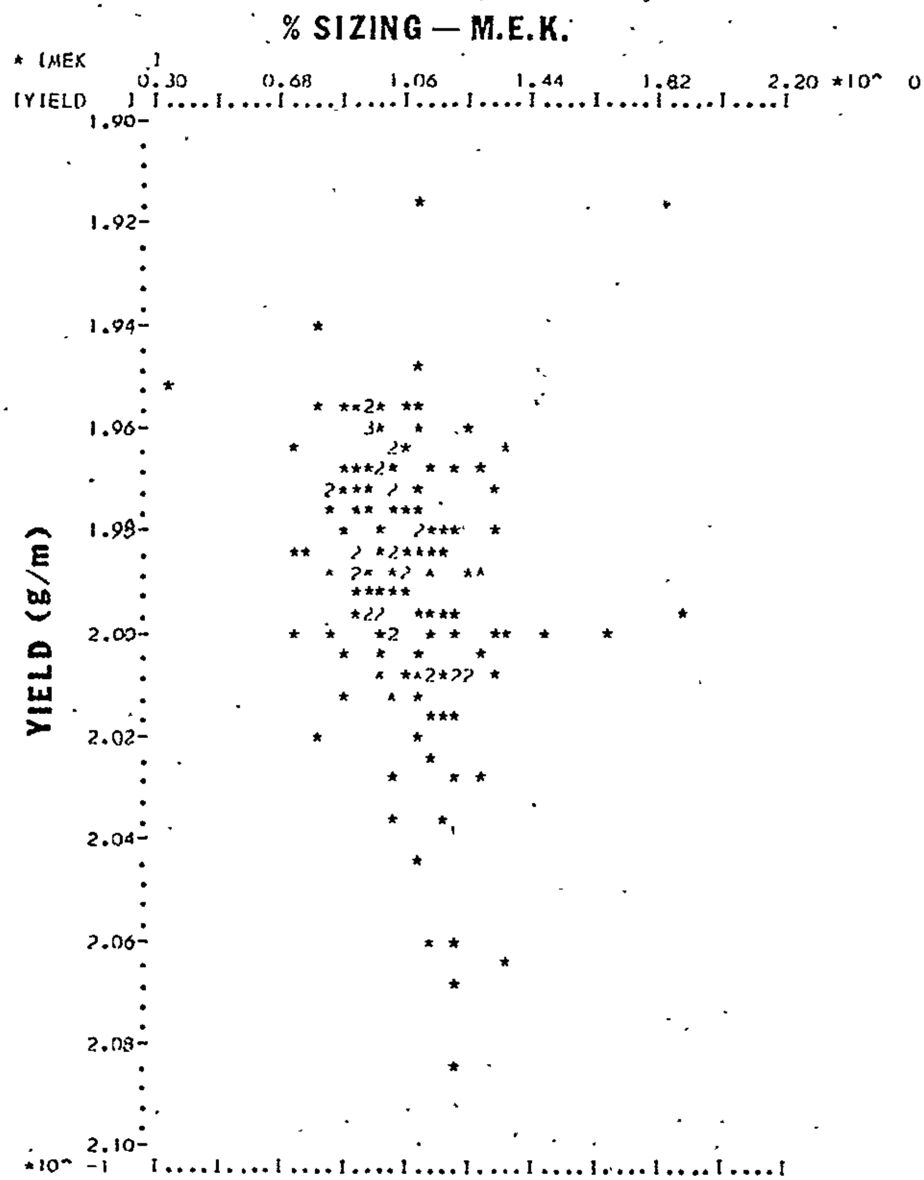


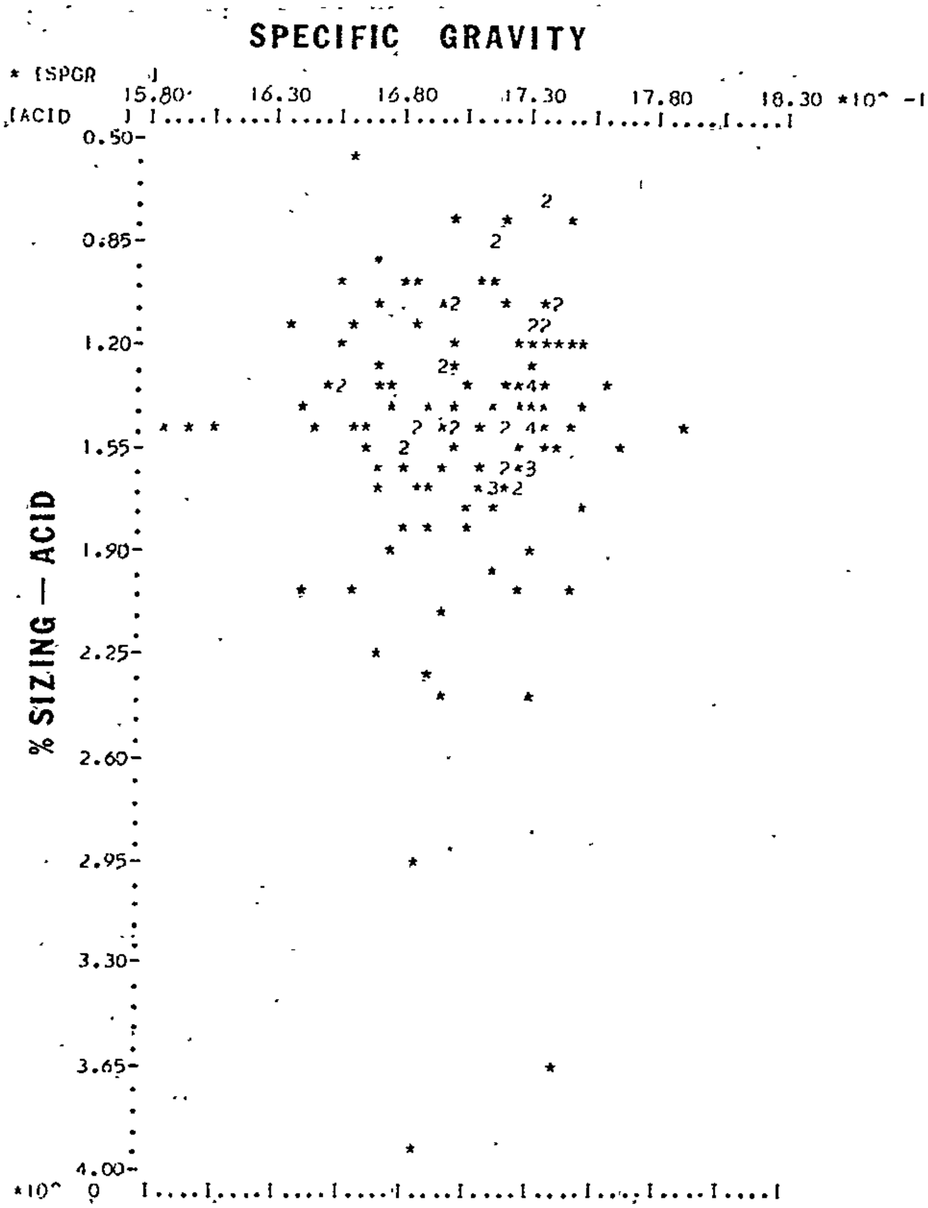
Specific Gravity vs Weight Per Unit Length

Figure 19



Sizing Level vs Weight Per Unit Length

Figure 20



Specific Gravity vs Sizing Level

Figure 21

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Table V Fiber Variability

	HEXCEL QC SUMMARY [11 lots>3500 lbs]			U.C. SPECIFICATION [1lot=1000 lbs]			ACCEPTABLE LIMITS	
VARIABLE	MEAN	STD.DEV	RANGE (3σ)	NOM	STD. DEV	RANGE (3σ)	MIN	MAX
YIELD								
@ START*	.1972	.0029	.1885 – .2059	.1953	.0029	.1866 – .2040	.1850	– .2060
TOTAL	.1989	.0031	.1896 – .2082					
SPECIFIC GR.								
@ START*	1.7363	.0151	1.6910 – 1.7816	1.74'	.0114	1.705 – 1.774	1.70'	– 1.78'
TOTAL	1.7085	.0289	1.6218 – 1.7952					
STRAND BRK. LOAD (lbs.)	64.47	4.65	50.52 – 78.42	–	–	–	–	–
STRAND TENSILE (ksi)	355.85	28.81	269.4 – 442.3	361	19.149	301 – 420	312	–
% SIZING - MEK								
@ START*	2.70	1.15	0 – 6.1					
TOTAL	1.007	.1518	.551 – 1.462	–	–	–	<2.0	–
% SIZING - ACID								
@ START*	(-4 s)							
TOTAL	1.7103	.5720	0 – 3.426	–	–	–	<20	–
"STIFFNESS" (gms)	38.003	9.823	28.534 – 67.47					

3. Hercules Incorporated, Magna, Utah

Resin

The visit to Hercules was made on February 16, 1977 with:

Ken Swertfeger, Mgr. of Materials and Mfg.

John Weidner, Advanced Composites

Dr. Richard Hoffman, Supervisor Applied Resin Systems Development

The Hercules product 3501 utilizes a Ciba-Geigy epoxy resin. Acceptance specifications include epoxy equivalent weight, per cent volatiles, viscosity and workmanship. They have not observed any resin storage stability problems and are presently trying to establish a six month's inventory.

As for difficulties with resin variability, Hercules stated that they would see it in processing behavior before it became evident in mechanical property testing.

Shipping and storage of the final prepreg have not been a problem.

Analytical Methods

In studies of analytical methods for the base resin acceptance, Hercules has looked at thin layer chromatography but determined that it was not quantitative and six batches all looked the same, ten to twelve spots were observed* In GPC, they also found no observable differences and have not done anything in liquid chromatography. They have a Waters instrument but have not observed the detail in their GPC's as shown in Figure 28.

*Author's Note: This conflicts with Lockheed's opinion as discussed on page 32.

It is the belief at Hercules that infrared might be adequate for a viable fingerprint, but probably not alone.

Hercules has found that elemental analysis for sulfur is quite unreliable - in fact they could not get accuracy or reproducability on known 3501 compositions. They feel that this approach, as used by some for characterization, is not valid.

The hardner is specified according to amine equivalent weight, melting point, water content, and workmanship. The catalyst is specified by melting point, solubility, moisture content and workmanship.

Testing Variables

Hercules has observed graphite-epoxy composites performance variability which has as its source the test sample and the test. For example, the resin gradient problem mentioned earlier has been observed. Another problem they observed became evident in a series of round robin tests. Outside testing on tensile coupons failed at 58 per cent of their value obtained in-house. Examination of bonded tabs showed opening near the ends which resulted in premature failure not in the gauge section. The variation was traced to the type of adhesive used in tab bonding. Other testing differences result from span to depth ratios which are not accurate or standardized.

The sandwich beam test includes more fabrication variables including fiber orientation effects and strain gauge location difficulties although the specimen eliminates the Poisson's effect. Hercules has no data regarding experimental scatter with the sandwich beam tests as compared to other test data scatter.

Hercules has observed no significant historical variation in test values through recent years. They have determined a 6 per cent coefficient of variation in unidirectional tensile specimens with half of that variation due to specimen preparation and test. Apparently this was determined by a statistical treatment of test data.

Process Variables and Controls

All production steps on Hercules prepreg products have written process specifications which are then documented with a Manufacturing and Inspection Record on each batch.

Resin Advancement Process

- Step-by-step Q.C. sign-off
- Monitored by viscosity increase
- Control of degree of advancement
- Mechanism of advancement determined by GPC

Completed 3501-5 Resin

- Thermal history rider on each can of resin
- Final viscosity check before use

Prepreg Quality Control Inspection Data

- Time-temperature limits on resin in process
- Resin lot records
- Fiber lot records
- Visual defect inspection and tagging

They feel confident in their reproducibility because two technicians and the Q.C. man must all make an error for the product to be improperly formulated. Batches have been scrapped in the past however, but very rarely at the present time.

Minimal quantities of prepreg have been returned by customers with the most common complaint being tack—too much or too little. Hercules points out that this is the most esthetic of all customer requirements and that his idiosyncracies only determine his desires in temperature vs tack behavior.

Hercules' 3501-5A has been formulated for long tack life. This tack life is related to the character of the staged resin used in the prepregging step but variability due to resin source has not been observed by Hercules.

Fiber effects on the final product have been examined by Hercules. Short beam shear increases but unidirectional tensile goes down as sizing level is increased. Tow tensile strength goes down at both high and low extremes of sizing level. Since Hercules is a fiber manufacturer and a prepreg manufacturer, they have absolute control over all operating parameters - they control the fiber process as well as the prepreg process.

The amount of hardner is controlled in the process specification at a fixed proprietary level (±0.25%). Cure parameters have been studied at Hercules and formulation variations in the 3501 series have been made. Effects are determined by physical testing and supported by T_g information determined by a Perkin Elmer DSC.

The actual value for water pickup equilibrium concentration vs hardner is not critical but more importantly the effect on mechanical properties is the only real measurement of its significance.

Other Factors in Variability

Fabricators have been satisfied with the level of reproducibility on Hercules prepreg.

This prepreg manufacturer, however, believes that a need exists for greater understanding of basic design of the part as well as the tool in some instances. It could be summarized as a need for increased knowledge in using the product to optimize its capabilities. Every part to be fabricated from graphite epoxy requires special consideration in advance to enable successful fabrication.

Other factors in fabrication that cause difficulty include heat up rates, thickness variation and lay up time.

Attitudes on Composition and Process Revelation

Hercules wants to protect the proprietary aspects of their business. They are willing to enter into secrecy agreements but believe they cannot protect beyond about six years. This is sufficient because competitors will know it by then anyway. This applies to composition. Proprietary processing details should remain secret for much longer.

If absolutely necessary, they are not opposed to in factory processing monitoring and have done this already on occasion - with as much legal protection as is possible in non-disclosure agreements. Air frame manufacturers insist on complete material and processing traceability.

Eleven batches of resin will be prepared in support of the materials study under the B-1 program at Grumman. These will consists of compositional variations.

4. Narmco Materials Inc., Costa Mesa, CA

Narmco was visited on March 10, 1977 with the following personnel participating in the discussions:

Virgil Jaenicke, President
Leonard Suffredini, General Manager
Jerry Sauer, Quality Control
Fred Geenan, Technical Service
Dale Black, Technical Service, Manager

Resin

The major and minor epoxy components of Narmco's 5208 are required to fall between upper and lower limits of viscosity and epoxy equivalent weight. Epoxy equivalent weight is determined by a standard wet method. In general, off specification materials are useable in other products. The resin specification values are proprietary. Narmco expressed its commitment to all phases of quality assurance as evidenced by a high number of personnel involved in such activity.

All materials involved in the preparation of prepreg (resin, hardener, fiber) must be supplied with complete vendor certified test results. In-house verification occurs on a random basis. Controls are such that incoming materials are held in the receiving area until Q.C. department releases them to the factory. Cost controls on time, materials, and product yield are felt to be sufficiently accurate that they too can be indicative of any problems in all phases of production including composition.

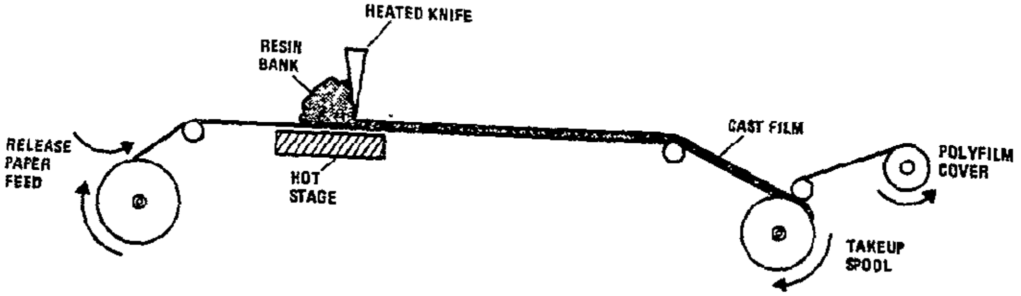
The acceptability of staged resin is well established before committing it to expensive fiber. Narmco stated that they have not conducted tests designed to correlate resin raw material variability and mechanical performance. Narmco believes that resin which does not meet specifications would be first observed in abnormalities in processing behavior.

Process Controls

Operating instructions are formalized documents which describe how to build the product. These instructions are supported with in-process controls on flow, gel point, resin solids and volatiles. Narmco has developed a method for flow which utilizes a known uncatalyzed mixture of a solid and liquid epoxy standards. This standard mixture is used to establish comparative flow behavior during resin preparation in a "flow disc". This is a known quantity of resin subjected to a known force and time. The diameter of the resulting disc has been found to give a reliable reference to end up with prepreg of proper tack, drape, and flow.

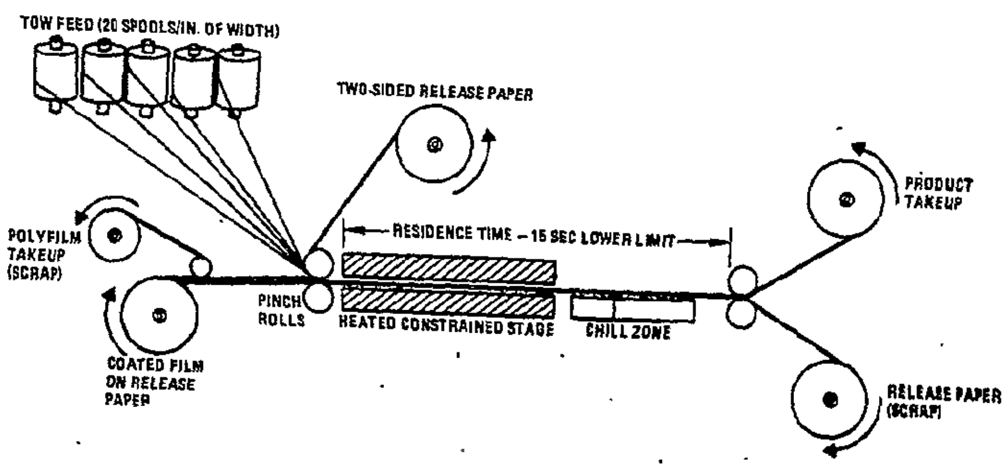
Narmco states that all work in manufacturing is performed in accordance with standard procedures and manufacturing instructions which are prepared by the engineering department. The testing and inspection is specified by QC in accordance with in-house and customer requirements. Unidirectional prepreg is produced on four twelve inch machines.

Elements of a hot melt two step process used by Narmco are shown in Figures 22 and 23. The first step is the preparation of a resin film laid down on a release paper. This roll of material can then be stored under refrigeration until ready for use in the actual prepregging step shown in Figure 23.



Elements of melt-cast film equipment.

Figure 22



Elements of melt transfer process for high-modulus fiber as used by Narmco Materials, Inc.

Figure 23

Processing by either hot melt coating or solvent coating is carried out at time and temperature conditions which do not cause any change in the B-stage status of resin. Provision has been made for temporary line shutdown, but this is normally not required.

Details of check points and process parameters are proprietary to Narmco.

DDS

Beginning with DDS purchases in 1968, Narmco has had no rejections of the curing agent. Their specification calls out a melting point of 445-449°K. No insolubles have been observed.

Fiber

Narmco has observed some sizing level variations in the past on T-300, but recently the reproducibility has been very good. Narmco had data on 20 batches of Celanese Celion fiber with all batches showing sizing levels of 1.0 - 1.1 per cent. Areal weight reproducibility is readily attainable in all fibers at ±5g/meter in 300 mm width prepreg (240 tows).

In work now under study at Narmco and General Dynamics, Ft. Worth, some apparent differences in fiber structure have been observed in T-300. Photomicrographs show what appears to be an anomalous glass structure in the fiber.

In general, the published specifications for fiber are readily met by the suppliers in strength, modulus, density and sizing levels.

Some artifacts have been observed such as carbon chunks and marks on fiber resulting from distilled pitch-like organics ending up on the fiber and subsequently carbonized. These occurrences are rare and easily eliminated.

Product Specifications

Resin content is specified according to customer requirements and may be as low as 39 per cent or as high as 44 per cent. Narmco specifies resin content to ±3 per cent. Resin content is obtained on every roll (20 rolls/batch). Also called out on each batch is fiber areal weight, flow, gel; tack and drape. Mechanical properties are run on every batch and specified according to customer requirements. As a minimum, room temperature and 450°K values are tested and specified for flexure and shear on each batch. Typical specification values for mechanical properties of Narmco Rigidite 5208 on Thornel 300 are listed in Table VI.

Analytical Methods Development

Narmco feels that infrared spectroscopy is of value only as a qualitative tool and is not appropriate for detailed characterization.* Some work has been done on dielectric probe immersion but the success of their "flow disc" method described earlier has made resin advancement tracking fairly reliable.

The most significant recent analytical development work that Narmco has done lies in the area of liquid chromatography. They have a Spectra Physics LC system suitable for gradient elution and set up with a computing integrator. Studies have been conducted on components of 5208 as well as batch-to-batch

*Author's Note: This conflicts with Hercules opinion as expressed on page 67.

Table VI Typical Specification Values

		RT	450°K
0°	Flexural Ultimate Stress MPa (10^3 PSI)	1655 (240)	1379 (200)
0°	Flexural Modulus GPa (10^6 PSI)	131 (19)	124 (18)
0°	Interlaminar Shear Ultimate MPa (10^3 PSI)	97 (14)	83 (12)
0°	Tensile Ultimate Stress MPa (10^3 PSI)	1448 (210)	1241 (180)
0°	Tensile Modulus GPa (10^6 PSI)	128 (18.5)	117 (17)
0°	Compression Ultimate Stress MPa (10^3 PSI)	1448 (210)	1241 (180)
0°	Compression Modulus GPa (10^6 PSI)	124 (18)	117 (17)
90°	Tensile Ultimate Stress MPa (10^3 PSI)	34 (5)	21 (3)
90°	Tensile Strain at Ultimate (μ mm/mm)	4500	5000
90°	Flexural Ultimate Stress MPa (10^3 PSI)	62 (9)	41 (6)
90°	Flexural Modulus GPa (10^6 PSI)	7.6 (1.1)	6.9 (1)

All values normalized at 65 per cent fiber volume information on finished materials. The batch-to-batch data is considered proprietary at the present time although Narmco seems optimistic that the method is amenable to quality control.

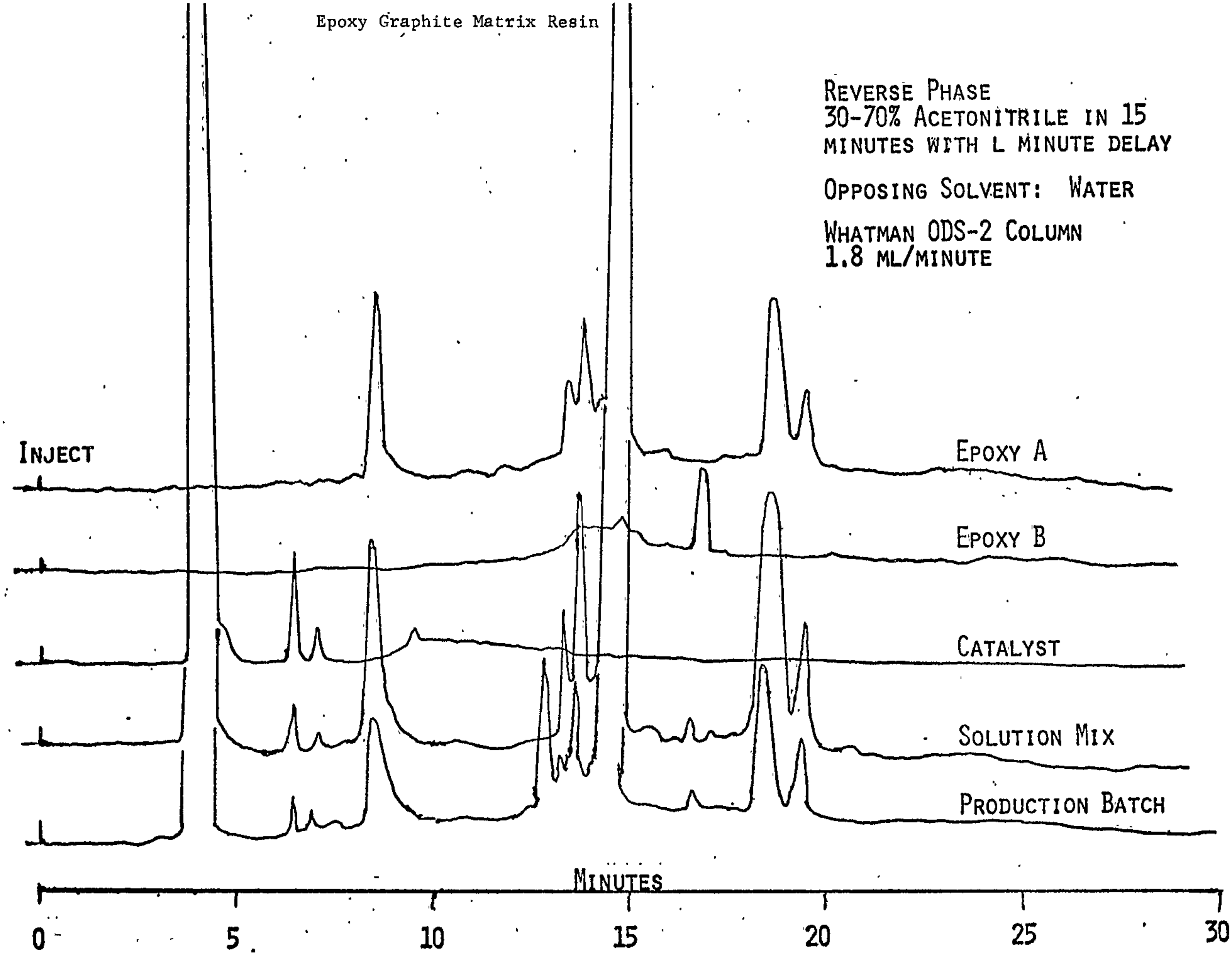
Presently they are concerned about arbitrary limits based on LC which is a highly sensitive technique. Peaks may be detected which are traces and have no significance in the characterization of resin for its reliability or durability. Narmco uses an attenuation setting on the UV detector which reduces background.

Typical results are shown in Figure 24. The two components of 5208 are shown in the curves labeled Epoxy A and Epoxy B while DDS is shown in the next curve. The detection of a reaction product is demonstrated in the solution mix curve and the advanced production batch curve which has been heated in a melt. The appearance of a new peak at about 13 minutes is probably the 1:1 adduct of DDS and the major epoxy component.

The LC will be used to define any peak differences in 9 batches of 5208 resin to be prepared for Rockwell in connection with a chemical characterization program on the resin as used on the B-1 program. Nine three-hundred-pound batches will be prepared with the following abnormalities.

	Curing Agent	Epoxy A	Epoxy B
1.	Nominal Amine Assay	Nominal E.E.W.	Nominal E.E.W.
2.	Low Amine Assay	Low E.E.W.	Low E.E.W.
3.	High Amine Assay	High E.E.W.	High E.E.W.
4.	Nominal Amine Conc.	High Conc.	Low Conc.
5.	Nominal Amine Conc.	Low Conc.	High Conc.
6.	High Amine Conc.	High Conc.	Low Conc.
7.	High Amine Conc.	Low Conc.	High Conc.
8.	Low Amine Conc.	High Conc.	Low Conc.
9.	Low Amine Conc.	Low Conc.	High Conc.

Data from mechanical testing of the above systems (after composite fabrication) and the resin analysis (LC and regular acceptance standards) will be compared.


Epoxy Graphite Matrix Resin
Reverse Phase
30-70% Acetonitrile in 15 minutes with L minute delay
Opposing Solvent: Water
Whatman ODS-2 Column
1.8 mL/minute
Inject
Epoxy A
Epoxy B
Catalyst
Solution Mix
Production Batch
Minutes
0
5
10
15
20
25
30

Other Sources of Variability.

Technical service personnel at Narmco have witnessed and tracked down a large number of various fabricating and testing improprieties. As might be expected, they have high confidence in the reproducibility of the prepreg and are able to demonstrate the nature of various fabricating or testing problems to the customer.

Specific common problems cited include:

- Excessive resin flow due to improper dams and poor tool design
- Poor control on fiber orientation in layup
- Cutting test samples with improper fiber orientation
- General mechanical difficulties in testing
- Altered curing cycles
- Personnel turnover and related lack of experience
- Improper test specimen design such as brittle adhesive for tensile tab bonding
- Using the same adhesive for tab bonding of RT and 450°K tensile tests
- Improper materials selection in sandwich beam test specimen fabrication
- Improper selection of bag films and bag sealants
- Faulty temperature monitoring and thermocouple location

In addition, there are minor occurrences of gross misuse of the materials and run a wide range of sometimes unbelievable SNAFUs which indicates a still existing troublesome level of misunderstanding of the capabilities and limitations of organic polymeric materials in the industry. For example - the use of the release polyethylene film for fabrication and throwing away the adhesive - has been documented.

C. Epoxy Resin Manufacturers

1. <u>Union Carbide Corporation, Chemical and Plastics, Bound Brook, N.J.</u>

Union Carbide Corporation (UCC) was visited on January 20, 1977 with the following personnel involved in the discussion.

Dr. Al S. Burhans

<u>Position in Highly Functional Epoxy Resins</u>

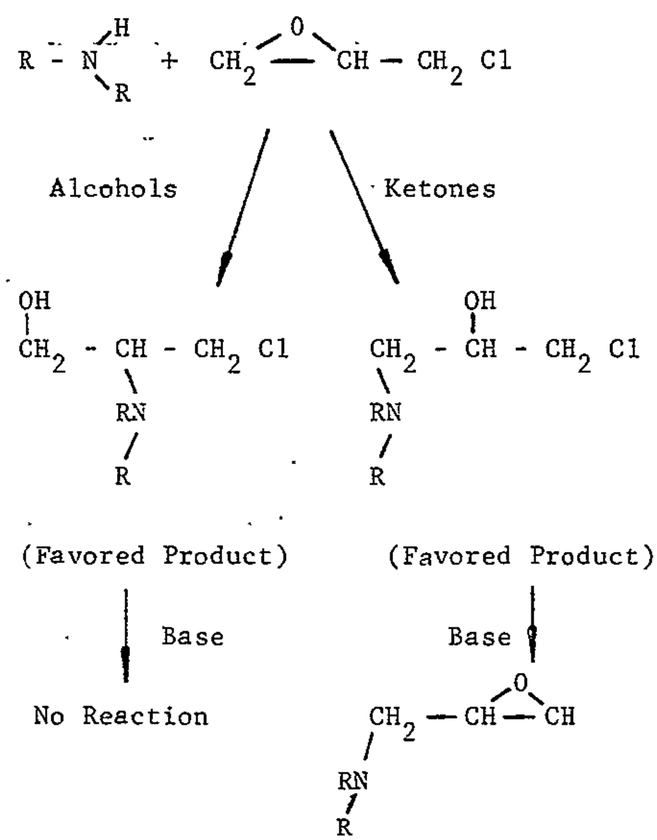
The activity of UCC in highly functional epoxies over the last several years has changed significantly. Ten to fifteen years ago, UCC was active in epichlorohyrin derived types such as the classical bis-phenol A diglycydyl ether and the triglycidyl substituted p-aminophenol (ERL 0500 and the distilled version ERL 0510). The epichlorohydrim derived glycidyl amines as well as others were patented under U.S. Patent 2,951,825 assigned to UCC. Although the patent expires in September of 1977, the patent and related know-how was sold recently to Ciba-Geigy. Covered under that agreement is the highly functional tetraglycidyl derivative of methyene dianiline (now Ciba-Geigy Araldite MY 720). This patent and know-how was sold in an exclusive agreement to Ciba-Geigy Corporation.

UCC is active in peroxidation of olefins to form epoxies in their plant at Institute, West Virginia. Today, UCC has interest only in cycloaliphatic epoxide systems and offers five systems for sale. The epichlorohydrin systems have been deleted from their line.

UCC never produced tetraglycidyl-methylene dianiline and consequently could not make any contribution to the effects of resin composition variables upon the properties of the resulting cured resin.

General Considerations - Epichlorohydrin Derived Epoxies

UCC found that solvent effects could influence the direction of addition of hydroxyl compounds or amines across the epichlorohydrin. Ketones tend to increase secondary hydroxyl containing chlorohydrins and alcohols tend to increase primary hydroxyl formation.



Only the chlorohydrin containing the secondary hydroxyl can be ring closed to the epoxy by treatment with strong base. In specifications for epichlorohydrin derived epoxies, the hydrolyzable chlorine content refers to the unclosed chlorohydrin on the right which has survived the base.

treatment without forming the epoxy. The 1,3-chlorohydrin on the left can not ring close to the epoxy and is unchanged by treatment with base. The hydrolyzable chlorine content does not include chlorine contained in the 1,3-chlorohydrin because of its stability toward base. The factor which may influence the variability of epichlorohydrin derived epoxies is not so much indicated by the hydrolyzable chlorine but more importantly should be defined in terms of free hydroxyl content which has a pronounced effect upon reactivity of the resin. Hydrolyzable chlorine would give inaccurate indication of the amount of primary hydroxyl present as the 1,3-chlorohydrin.

In practice, Mr Burhans stated that the 1,2-chlorohydrin forming process would frequently result in some unclosed chlorohydrin or "hydrolyzable chlorine" and that value would probably be a reasonably true indication of the level of hydroxyl content - but not conclusive.

The formation of varying amount of 1,3-chlorohydrin and its associated undetected hydroxyl content (by hydrolyzable chlorine) could be an important factor in differences in curing rate behavior of such epoxies.

Historical Information

Other comments made by Al Burhans pertained specifically to ERL 0510 and ERL 0500 production and consequently could also be considered informative concerning glycidyl amines.

UCC stopped making ERL 0500 for their sales in July of 1975 but did make some resin for Ciba-Geigy into 1976. Before they stopped sales activity, volume was something less than 45,000 kg/year and the resin was being made in 5700 liter batches and sold for $7.70/kg. Comparative specifications for UCC and Ciba-Geigy are shown on Table VII.

Table VII

Specifications for Triglycidyl - Paraminophenol

	Union Carbide		Ciba-Geigy	
	ERL-0500	ERL-0510	CG-0500	CG-0510
Visc. cps 298°K	1500-5000	550-850	1500-5000	550-850
Sp. Gr.	1.215-1.235	1.206-1.225	-	-
Clarity	Clear	Clear	Sl. Haze	Sl. Haze
Hydrolyzable Cl	0.8 Max.	0.8 Max.	0.5 Max 0.1-0.4 Typ.	0.5 Max 0.15-0.2 Typ.
E.E.W.	105-115	95-107	105-115 107.5-112Typ.	95-106 100-102 Typ.
H_2O%	0.2 Max	0.2 Max	-	-
Free Epichlorohydrin	.05 Max		1.0 Max Vols.	-
Polymer Content* (Not in Specifications)	25-30%	5%		

*A function of storage, thermal history, cooldown time, etc.

UCC assessed the process method for glycidyl amines and determined that a continuous process was feasible but not recommended and that control would be easier to maintain on a batch process.

2. Shell Chemical Company, Houston, Texas

Shell was visited on February 22, 1977, and discussions were held with:

Dr. Ron S. Bauer, Staff Research Chemist

C. V. Wittenwyler, Technical Service Representative

The primary purpose of the visit was to explore the studies made by Shell on an Air Force contract several years ago (3). The synthetic study included the preparation of the tetraglycidyl methylenedianiline. Unfortunately the visit was not successful in resurrecting any additional information other than that found in the report because all personnel involved in the study contract have since relocated, retired or are deceased.

A secondary purpose was to attempt to determine any general information regarding epoxy resin variability and its relation to cured resin performance.

Epoxy Resin Variability

Shell's line of epoxies are all epichlorohydrin derived. Consequently, the chlorohydrin problem is of concern. In particular it is a sensitive area when the curing agent system includes a benzyldimethylamine catalyst which is usually used in a very low concentration (less than 1 phr). The high basicity of the amine serves to split out hydrogen chloride and form the epoxy from 1,2-chlorohydrin - but in the process neutralization of the base occurs and the catalytic effect and the subsequent reactivity of the system is reduced markedly. On other more near stoichiometric amine curves, the effect is unnoticeable according to Shell.

Other than this however, Shell has made no evaluation of compositional variations in batch-to-batch epoxy resins and has not correlated these variations to any mechanical properties such as glass transition temperature.

Generally, the philosophy is that if the resin meets the product specifications of viscosity and epoxide equivalent - then the liquid resin is "good stuff". Shell's customers, according to Dr. Bauer, are high volume users in some more mundane areas and consequently are not very sophisticated or concerned about subtle differences in composition or behavior. It appears that Shell relies to some extent on the community technical base for customer service in these areas.

Shell contributes to this community technical base, in some cases out of European labs (R. B. Weatherhead).

Shell seems to have considerable strength in technology of basic resin structure and its utility in coatings, insulation and industrial applications, but any information along the lines of the effects of subtle resin variations was not located.

The position of the company is one which is basic in phenol, acetone and epichlorohydrin, therefore the epoxy line is based on bisphenol A. The company is not basic in amines and consequently has no plans to produce glycidyl amines.

3. Dow Chemical Company, Freeport, Texas

Dow was visited on February 23, 1977 and participants in the discussion from Dow were:

Dr. Ralph Shelley, Research Chemist
Charles M. Vettors, Research Supervisor

Resin Variables

The facility at Freeport is primarily directed toward technical service and the specific activities of the above individuals were in epoxy resins for laminated composites, printed circuit boards and adhesives. They were aware of the use of Dow's epoxy resins in graphite fiber reinforced composites and have visited many of the prepreggers. Their technical service activity in the laboratory has not been involved with graphite fiber reinforced systems but was nevertheless quite pertinent to such systems.

Their analytical activity has been primarily focused on GPC. Dow has been able to come up with guideline conclusions about the contributions of various peaks in the GPC to glass transition temperature, fiber wetting by resin, adhesion, moisture resistance, dielectric properties and mechanical properties. Unfortunately, these data are considered proprietary and Dow feels that such information is of considerable value to them in being able to provide such technical service to their customers and sell more resin. Revelation of the total technical package is deemed not worth the exposure. Some sophisticated applications requiring detailed information, uses a low poundage of resin.

The interpretation of peaks in terms of molecular weight and number of molecules was treated by a proprietary computer program which gives peak ratios in both weight and number as well as number average molecular weight and weight average molecular weight. Both types of MW shifts have been assessed in terms of their effect on the various properties mentioned above. A total MW_w/MW_n ratio is used as a fingerprint parameter.

These GPC runs and the computer treatment of the data is not run routinely on every batch, but a number of batches have been analyzed and a considerable data base has been established. A batch will be sampled for analysis, for example, if a customer observes a particular difficulty in resin behavior. The molecular weight distribution effects on the properties of epoxy novalacs have been studied. Two typical curves are shown in Figures 25 and 26. Actual peak identification is conducted by isolation and analyses of higher resolution and subjected to mass spectrometric analysis. The left tail is material with increasing degree of polymerization. The computer readout is shown for these GPC curves in Tables VIII and IX respectively. The tabulation includes each peak fraction by weight in a step approach using the elution count as the ultimate reference.

A similar treatment has been given to bisphenol type epoxies. (See Figure 27). One valuable conclusion from such studies has been an evaluation of catalysts effects on the reaction of bisphenol type resins, especially in regard to the ratio of linearity and branching of the polyether segment. Studies of these differences have been carried out and assessed in terms of their effect on mechanical properties.

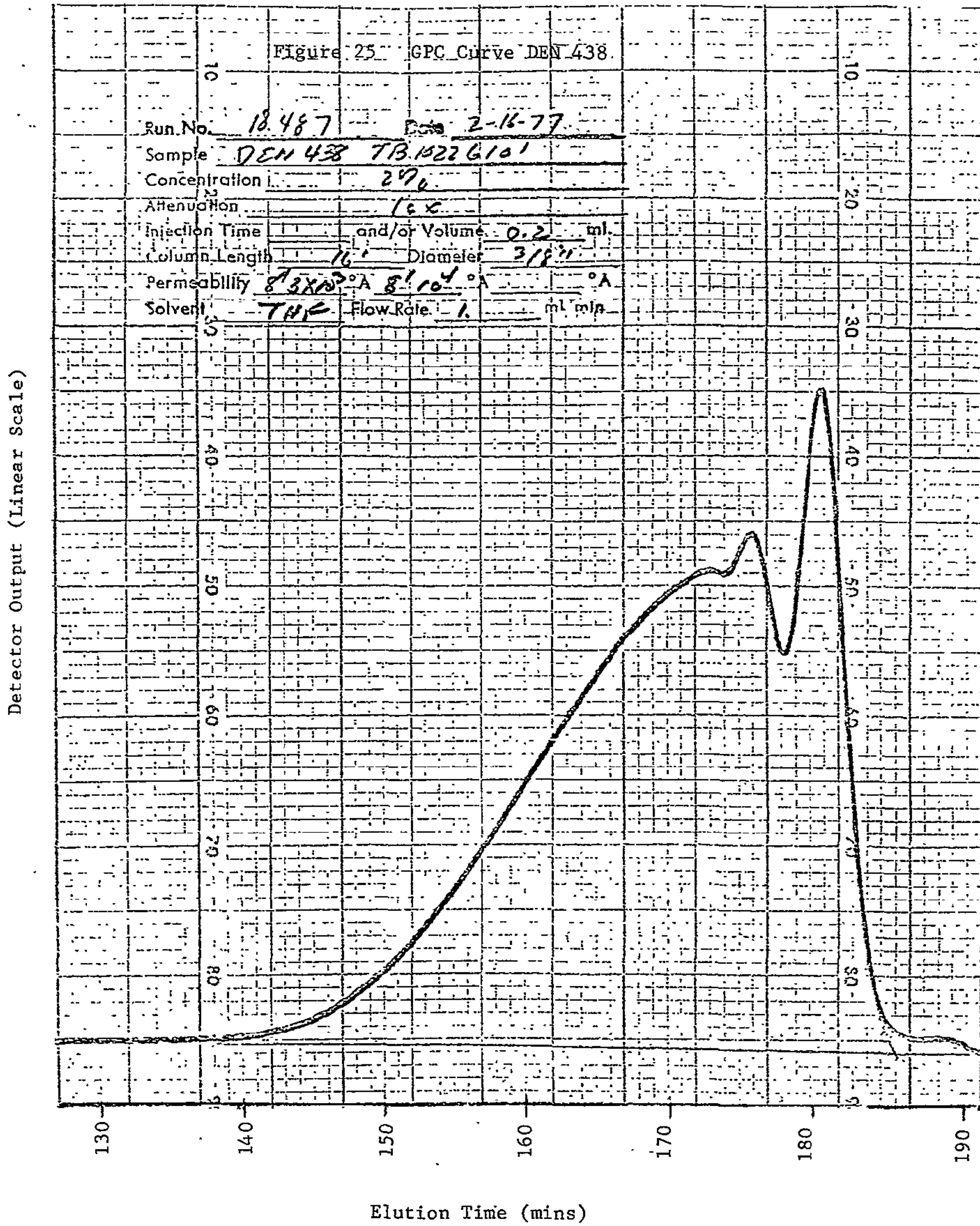
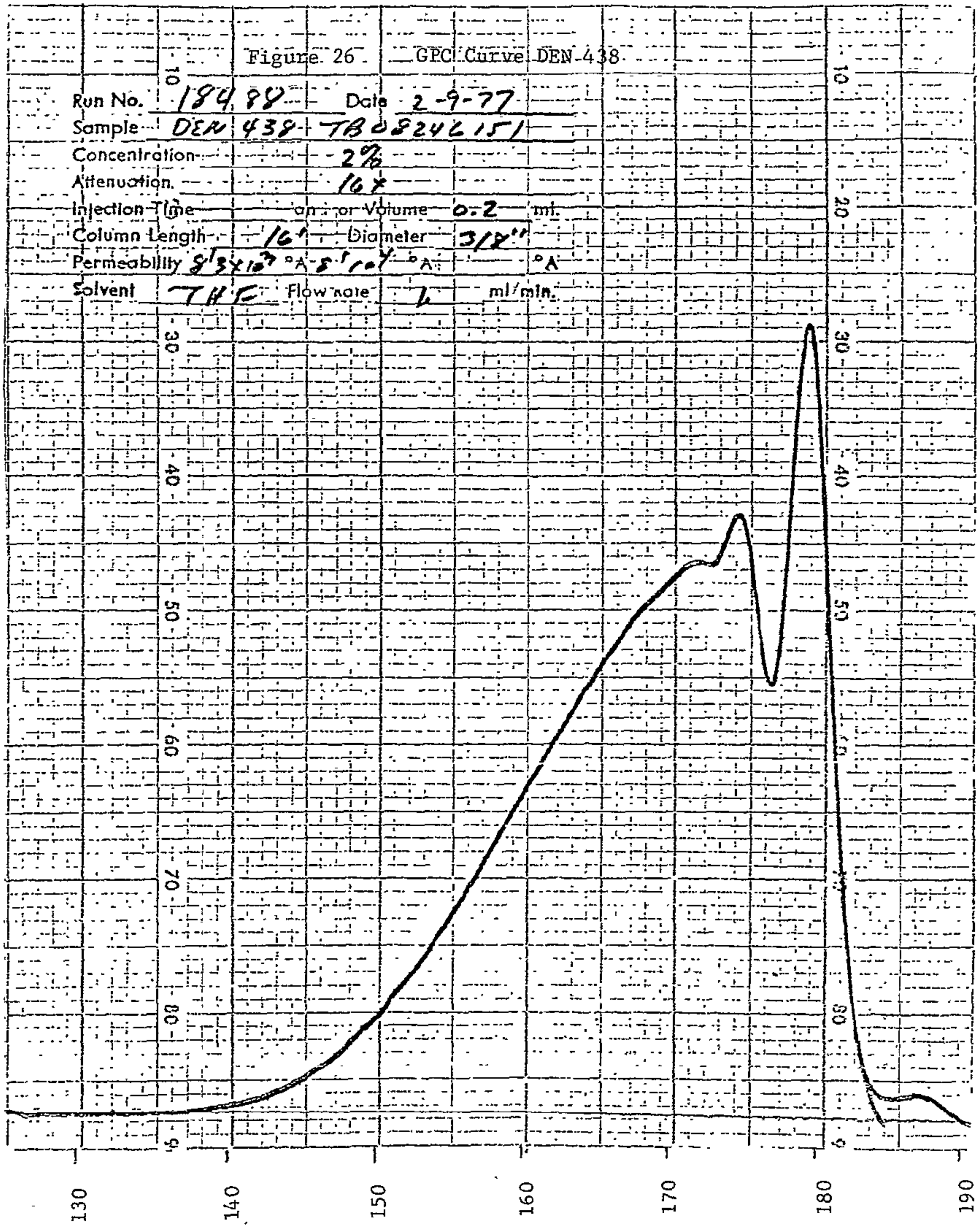


Figure 25 GPC Curve DEN 438
Run No. 18487 Date 2-16-77
Sample DEN 438
Concentration 2%
Attenuation 16x
Injection Time and/or Volume 0.2 ml.
Column Length Diameter
Permeability °A °A °A
Solvent THF Flow Rate 1 ml/min
Detector Output (Linear Scale)
130
140
150
160
170
180
190
Elution Time (mins)



Elution Time (mins)

**** GEL PERMEATION CHROMATOGRAPHY ****

CENTRAL LABORATORY
B-1219
COLUMN: COLDEN6

DATE: #>
TIME: 0748

RUN NO. 18487 DEN 438 1B10226101 SCAN DATE:021677

COUNT	OBS HT	CALC HT	SIG	K	FRAC PCT	CUM PCT	MOL WT.
148.0	17.0	16.7	1.35	7.15	.63	1.38	5900.
150.0	25.1	24.9	1.35	7.32	.64	2.38	4900.
151.0	30.2	30.1	1.35	9.27	.81	3.11	4450.
152.0	35.2	35.1	1.35	10.56	.92	3.98	4000.
153.0	40.3	40.2	1.35	11.54	1.01	4.94	3700.
154.0	46.4	46.6	1.35	12.11	1.06	5.98	3300.
155.0	54.4	54.3	1.35	17.35	1.52	7.27	3000.
156.0	61.5	61.8	1.35	17.94	1.57	8.81	2700.
157.0	68.5	68.7	1.35	20.22	1.77	10.48	2500.
158.0	75.6	75.4	1.35	23.01	2.01	12.38	2250.
159.0	82.6	83.0	1.35	22.17	1.94	14.36	2020.
160.0	91.7	91.5	1.35	28.29	2.48	16.56	1850.
161.0	99.7	99.8	1.35	29.95	2.62	19.11	1700.
162.0	106.8	107.0	1.35	31.61	2.77	21.81	1500.
163.0	113.8	113.7	1.35	33.49	2.93	24.66	1400.
164.0	120.9	121.0	1.35	35.05	3.07	27.66	1280.
165.0	128.9	128.8	1.35	38.29	3.35	30.87	1150.
166.0	136.0	135.9	1.35	41.69	3.65	34.37	1030.
167.0	141.0	141.4	1.35	40.55	3.55	37.97	960.
168.0	146.1	145.7	1.35	44.67	3.91	41.70	880.
169.0	150.1	149.9	1.35	43.82	3.84	45.58	800.
170.0	154.2	154.8	1.35	43.18	3.78	49.39	720.
171.0	158.3	158.6	1.35	50.04	4.38	53.47	636.
172.0	159.3	158.1	1.35	53.08	4.65	57.98	636.
173.0	158.4	159.2	1.35	35.68	3.12	61.87	636.
174.0	165.4	167.6	1.35	41.47	3.63	65.24	474.
175.0	168.5	167.3	1.35	80.29	7.03	70.57	474.
176.0	146.5	146.0	1.35	41.56	3.64	75.91	474.
177.0	131.6	134.5	1.35	11.82	1.04	78.25	375.
178.0	160.6	166.7	1.35	18.09	1.58	79.56	312.
179.0	210.7	209.0	1.35	115.43	10.11	85.40	312.
180.0	194.7	195.1	1.35	86.99	7.62	94.26	312.
181.0	121.8	125.4	1.35	14.82	1.30	98.72	255.
181.0 TO 186.0 MLS					1.28	100.00	TO 162.

WEIGHT AVERAGE MOL. WGT. 1163.

NUMBER AVERAGE MOL. WGT. 622.

VISCOSITY AVG. MOL. WGT. 1037. A = .70

WGT. AVG. / NO. AVG. 1.870

SAMPLE WGT% ACCOUNTED FOR 100.38%

CYCLES THRU THE CURVE FIT LOOP 10

L. B. WILKINSON

Table VIII Computer Printout

ORIGINAL PAGE IS
OF POOR QUALITY

****** GEL PERMEATION CHROMATOGRAPHY ******

CENTRAL LABORATORY
B-1219
COLUMN: COLDEN6

DATE: 0>
TIME: 1125

RUN NO. 18488 DEN438 TB08246151 SCAN DATE:000977

COUNT	OBS HT	CALC HT	SIG	K	FRAC PCT	CUM PCT	MOL WT.
148.0	19.0	18.8	1.35	6.07	.48	1.36	5900.
149.0	23.0	22.7	1.35	7.40	.59	1.89	5400.
150.0	27.0	27.6	1.35	5.08	.40	2.39	4900.
151.0	34.0	33.5	1.35	13.29	1.06	3.12	4450.
152.0	39.0	39.6	1.35	9.10	.72	4.01	4000.
153.0	46.0	45.6	1.35	15.54	1.24	4.99	3700.
154.0	52.0	52.2	1.35	13.45	1.07	6.14	3300.
155.0	60.0	59.9	1.35	17.68	1.41	7.38	3000.
156.0	68.0	67.7	1.35	21.80	1.73	8.95	2700.
157.0	75.0	75.0	1.35	21.06	1.67	10.66	2500.
158.0	83.0	83.0	1.35	23.53	1.87	12.43	2250.
159.0	92.0	91.7	1.35	28.65	2.28	14.50	2020.
160.0	100.0	99.9	1.35	29.55	2.35	16.82	1850.
161.0	108.0	108.1	1.35	30.66	2.44	19.21	1700.
162.0	117.0	116.7	1.35	35.74	2.84	21.85	1500.
163.0	125.0	125.1	1.35	36.87	2.93	24.74	1400.
164.0	133.0	133.1	1.35	39.11	3.11	27.76	1280.
165.0	141.0	140.8	1.35	42.00	3.34	30.99	1150.
166.0	148.0	148.0	1.35	44.07	3.51	34.41	1030.
167.0	154.0	154.2	1.35	45.25	3.60	37.97	960.
168.0	160.0	159.6	1.35	48.51	3.86	41.69	880.
169.0	165.0	164.9	1.35	47.78	3.80	45.52	800.
170.0	170.0	170.7	1.35	48.35	3.85	49.35	720.
171.0	174.0	174.2	1.35	55.67	4.43	53.48	636.
172.0	175.0	173.3	1.35	57.71	4.59	57.99	636.
173.0	175.0	176.7	1.35	35.46	2.82	61.70	636.
174.0	186.0	188.3	1.35	50.88	4.05	65.13	474.
175.0	186.0	184.4	1.35	96.05	7.64	70.98	474.
176.0	154.0	154.3	1.35	34.77	2.77	76.18	474.
177.0	137.0	143.5	1.35	6.52	.52	77.82	375.
178.0	184.0	190.6	1.35	21.86	1.74	78.95	312.
179.0	247.0	245.1	1.35	143.51	11.42	85.53	312.
180.0	224.0	224.6	1.35	98.79	7.86	95.16	312.
181.0	131.0	136.8	1.35	10.47	.83	99.51	255.
181.0 TO 185.0 MLS					.49	100.00	TO 175.

WEIGHT AVERAGE MOL. WGT. 1165.

NUMBER AVERAGE MOL. WGT. 624.

VISCOSITY AVG. MOL. WGT. 1039. A = .70

WGT. AVG. / NO. AVG. 1.868

SAMPLE WGT% ACCOUNTED FOR 100.55%

CYCLES THRU THE CURVE FIT LOOP 10

L. B. WILKINSON

Table IX Computer Printout

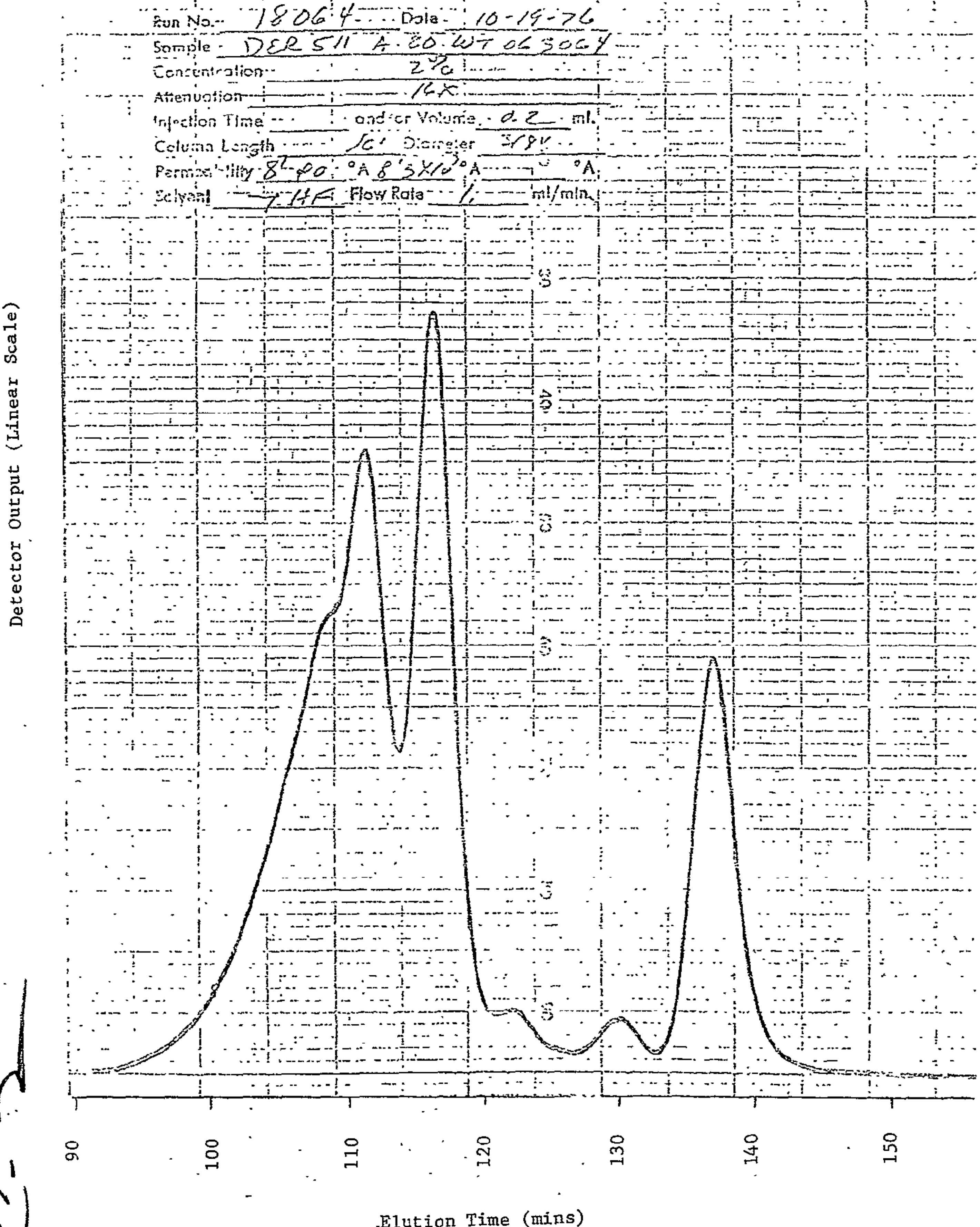


Figure 27 GPC Curve DER 511

To date, the GPC analysis has been used pretty much for internal comsumption and no limits of variation of peak heights or peak height ratios have been included in product specifications. The ratio of MW_w/MW_n has not been used as a product specification. Higher molecular weight resins result in a greater variation in MW_w/MW_n.

With the knowledge that Dow has gained with the GPC analysis on epoxy novalacs and bisphenol A types, they feel confident that these finding could be extrapolated to glycidylamines and they would be able to predict how peak changes could affect properties such as moisture resistance.

Dow's technical rationale follows an approach that tighter crosslink density results in less water impenetration. Also that shorter distances between epoxies result in tighter cures. Some anomalies in cure have been observed, including the evolution of NH_3 when amine systems were cured in contact with copper. No acrolein formation has been observed.

The preparation of an epoxy resin might be compared to "baking a cake". Dow has used the analogy of "landing an airplane". Instrument readings and sightings are taken along the reaction sequence to guide the final product into the range of acceptable specifications when everything comes to a halt. These product specifications include, primarily, viscosity and epoxide equivalent weight. Color and density are supporting values. With solid resins the softening point is also called out.

In-process parameters which are monitored include heat up rate. The GPC analysis described above has been used to detect distributional differences in batches prepared in summer and winter.

Dow expressed the feeling that the mode of epichlorohydrin addition was fairly reproducible and that more important variations include the time and temperature parameters. In-process checks may also include epoxy equivalent weight or phenolic OH.

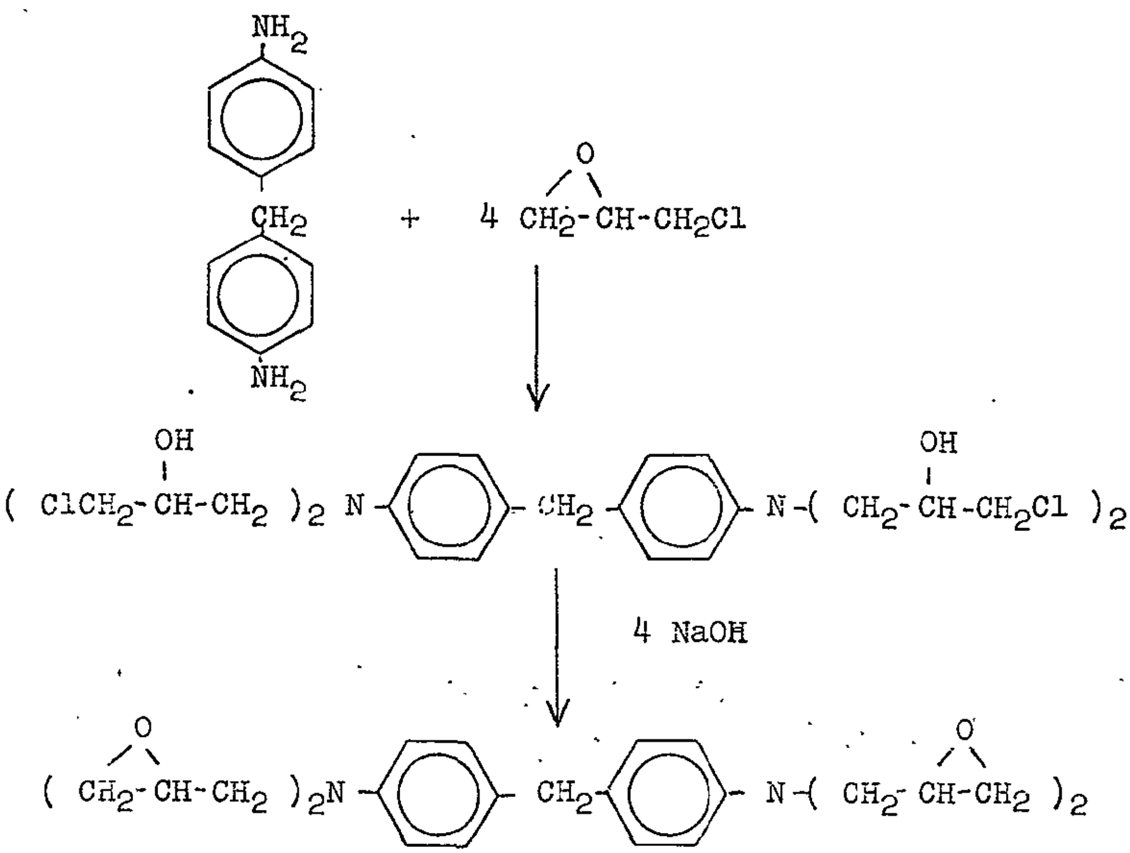
New Resins

In the past, Dow has looked at glycidyl amines, but at the present time they have no plans to produce such epoxies. They have recently introduced the triglycidylether of trimethylolmethane.

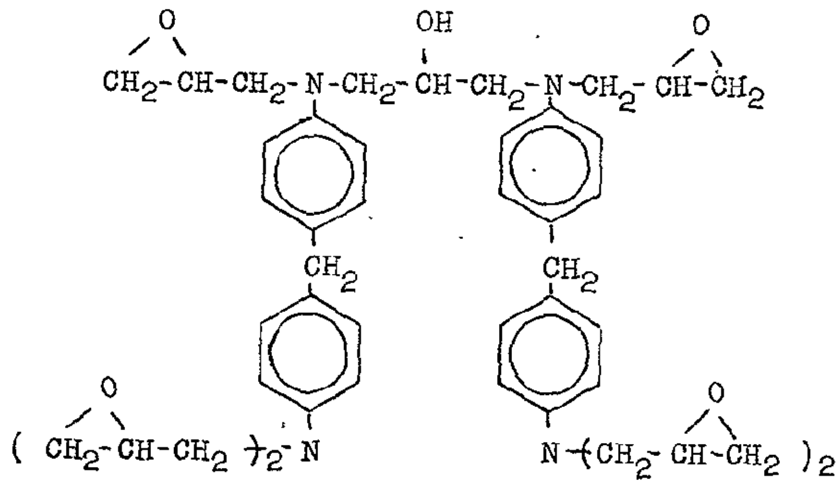
4. Ciba-Geigy Corporation, Ardsley, N.Y.

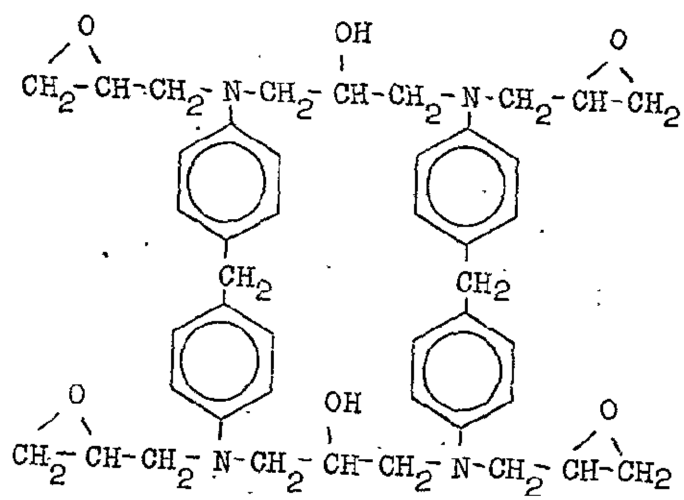
A general presentation of the purpose of the visit was made to about ten personnel from Ciba-Geigy on January 21, 1977. More specific discussions were concentrated in a meeting with Gordon Buchi, Manager, Electrical and Structural Applications - in the Resins Department.

As might be expected much of the discussion dealt primarily with Araldite MY 720, the principal ingredient in a number of 450°K carbon fiber prepregs. The reaction sequence can be written in an idealized form as follows:

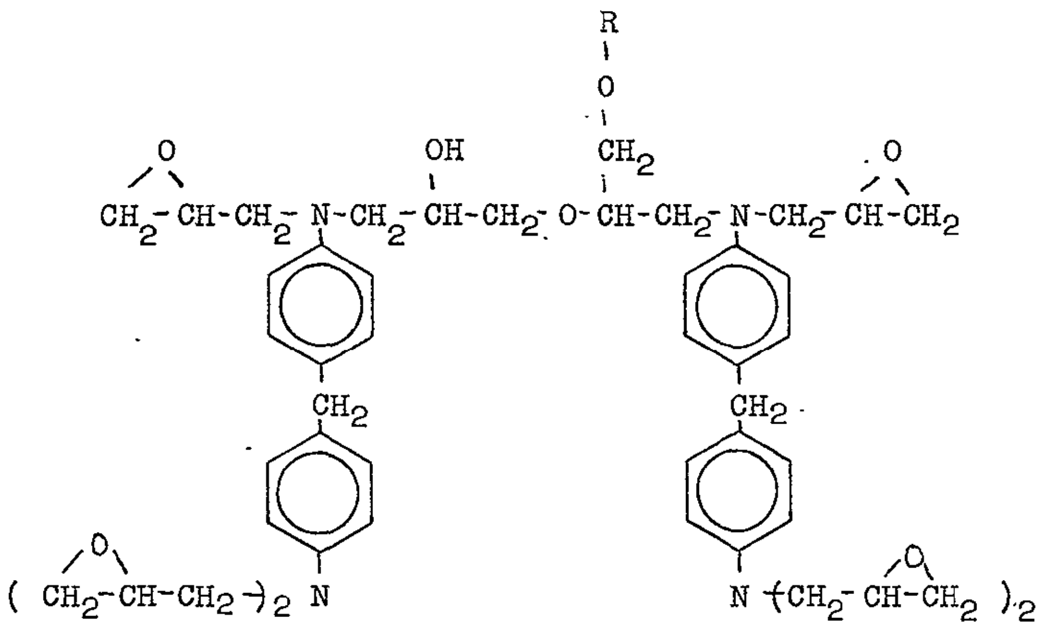


DIMERS

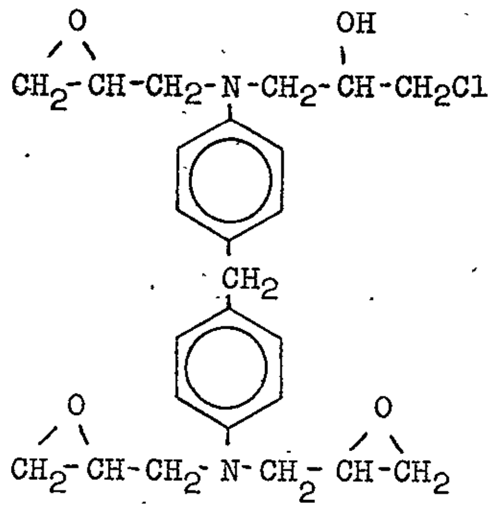


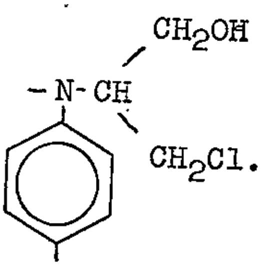


TRIMER AND HOMOPOLYMERS

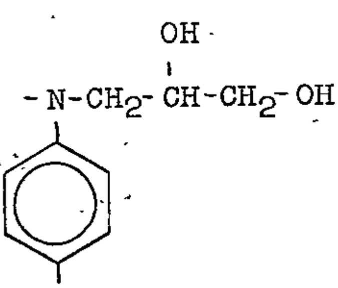


CHLOROHYDRINS:





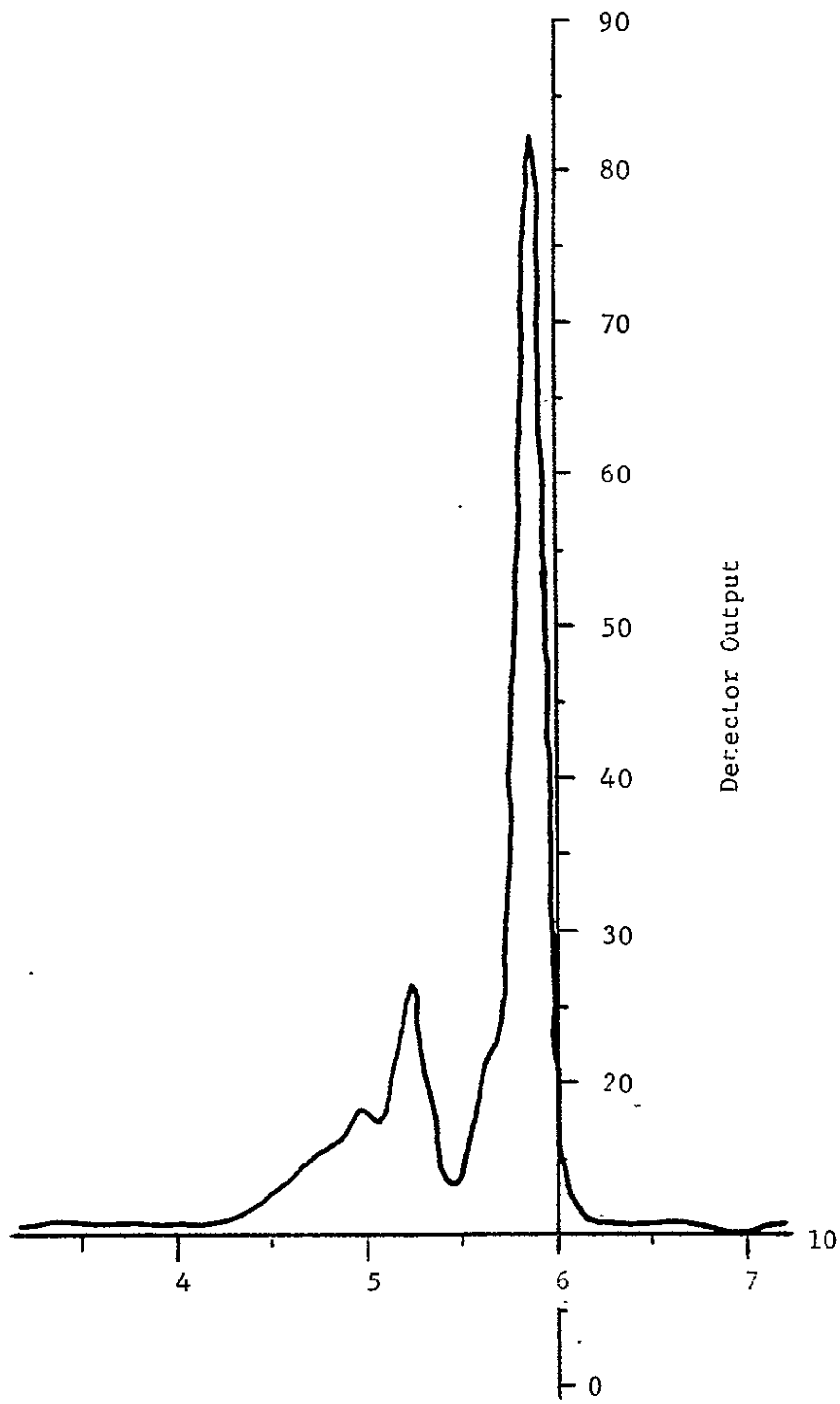
GLYCOLS:



The theoretical equivalent weight per epoxy group is 105, in practice however, the typical equivalent weight per epoxy runs around 125. This indicates that the idealized structure of tetraglycidyl-methylene dianiline is not the only product and the GPC shows that indeed higher molecular weight oligomers and other products are also formed in the reaction. Gel permeation chromatography data is not obtained on a routine basis and in fact the GPC curve shown in Figure 28 was the only data made available. No liquid chormatographs have been obtained on MY 720 at Ciba-Geigy. A previous presentation at an Air Force meeting (October, 1976) showed only a typical type LC curve which was not actually obtained on MY 720.

In the GPC shown in Figure 28, the shoulder on the left side of the principal peak is believed to be chlorohydrin and the next peak, to the left is dimer and the trimer is the last peak with higher oligomers and homopolymers appearing as a shoulder on this peak. The other components may be represented by the chemical structures on the preceding pages.

Ciba-Geigy's feeling is that the product specifications shown in Table X along with the controls and process procedure serve to define the product and that it is a "fashioned" product which will be consistent. The position of Ciba-Geigy is that if they were asked to improve the quality of the resin they would ask, "What constitutes improved quality?". In their opinion, decreasing oligomer content would result in a product giving more brittle properties.



ARALDITE MY 720

Figure 28 GPC Curve

MY 720 SPECIFICATION

PROPERTY	C.G.T.M.	SPECIFIED VALUES	TYPICAL VALUES
EPOXY VALUE EQ/100G	200	0.75 - 0.85	0.79 - 0.82
E.E.W.		117 - 133	122 -127
VISCOSITY CPS. 50°C	116	25,000 MAX.	10 - 15,000
HYDROLYSABLECHLORINE %	195	0.53 MAX.	0.15 - 0.50
IONIC CHLORIDES PPM.	148	< 300	7 - 12
ACETONE INSOL. PPM	199	< 500	10 - 100
VOLATILES		< 1%	< 2%

Table X

No data has been released from neat castings in an effort to assess resin variables at Ciba-Geigy. Some early work was done in the UK with anhydrides. Apparently, nothing has been done with diaminodiphenylsulfone cured castings. Eporal (DDS) is made in Europe. Specifications are shown in Table XI.

Process Variables

The reaction ratio of epichlorohydrin to amine affects the viscosity and molecular weight of the resulting product. The reaction is run in a proprietary solvent and the removal of this solvent also affects the formation of higher oligomers in the heated stripping step. Reduced epichlorohydrin ratios and extended heating both increase the viscosity.

The raw material, methylene dianiline, fulfills the specification shown in Table XII. Epichlorohydrin is not recycled. There was no indication that Ciba-Geigy has experienced any problem from contaminants in epichlorohydrin which is purchased outside. Its specifications were not disclosed except that GC is used. As stated above, the amount of epichlorohydrin fed to the reaction vessel influences the final viscosity. Depending on the use and the customer - MY 720 is sold at different viscosities. Typically, values of 10,000 - 15,000 cps at 323°K are obtained (spec. max. is 25,000 cps), material with a viscosity as low as 5000 cps might be sold.

Some typical production records are shown in Table XIII. Batch size is 2500 kg Production was estimated to be about 45,000 kg /year with expectations of a 400-500 per cent increase in 4-5 years.

EPORAL SPECIFICATION

PROPERTY	SPECIFICATIONS	TYPICAL VALUES
APPEARANCE	PINK-BEIGE POWDER	-
MELTING POINT °C	170 - 180	175 - 177
WATER CONTENT %	1% MAX.	0.15 - 0.25
ASSAY %	98% MIN.	98.8 - 99.8
PARTICLE SIZE MM	0.6 AVERAGE	-

Table XI

MDA SPECIFICATION

PROPERTY	ALLIED T.M.	SPECIFIED VALUE	TYPICAL VALUE
COLOR APHA			
5% SOLN. IN ACETONE		250 MAX.	30 - 100
ASSAY %	224	99 MIN.	99.5 - 99.8
MELTING POINT °C	107	90 MIN.	90 - 91

Table XII

MY 720 BATCH TO BATCH DATA 2500Kg/batch

Batch No	Year	Visc. 323°K cps	Epoxy Value EQ/100g	EEW	%Cl. Hyd*	
12	1976	9,000-10,000	.82	122	.21	
11	1976	9,000-10,000	.83	120	.19	
10	1976	9,000-10,000	.83	120	.21	
9	1976	10,000-15,000	.84	119	.16	
8	1976	10,000-15,000	.85	118	.19	
7	1976	20,000-25,000	.77	130	.22	Some may have been produced in Europe
6	1975	20,000-25,000	.80	125	.15	
5	1975	20,000-25,000	.79	127	.20	
4	1975	10,000-15,000	.82	122	--	
3	1974	10,000-15,000	.80	125	--	
2	1974	15,000-20,000	.80	125	--	Produced in Europe
1	1974	10,000-15,000	.84	119	--	

*Ref. Page 81

Table XIII

Ciba-Geigy stated that under production conditions, there is no known way of economically producing pure tetraglycidyl-methylene dianiline. Further, they stated, there is no evidence that the "pure" product would offer any advantages.

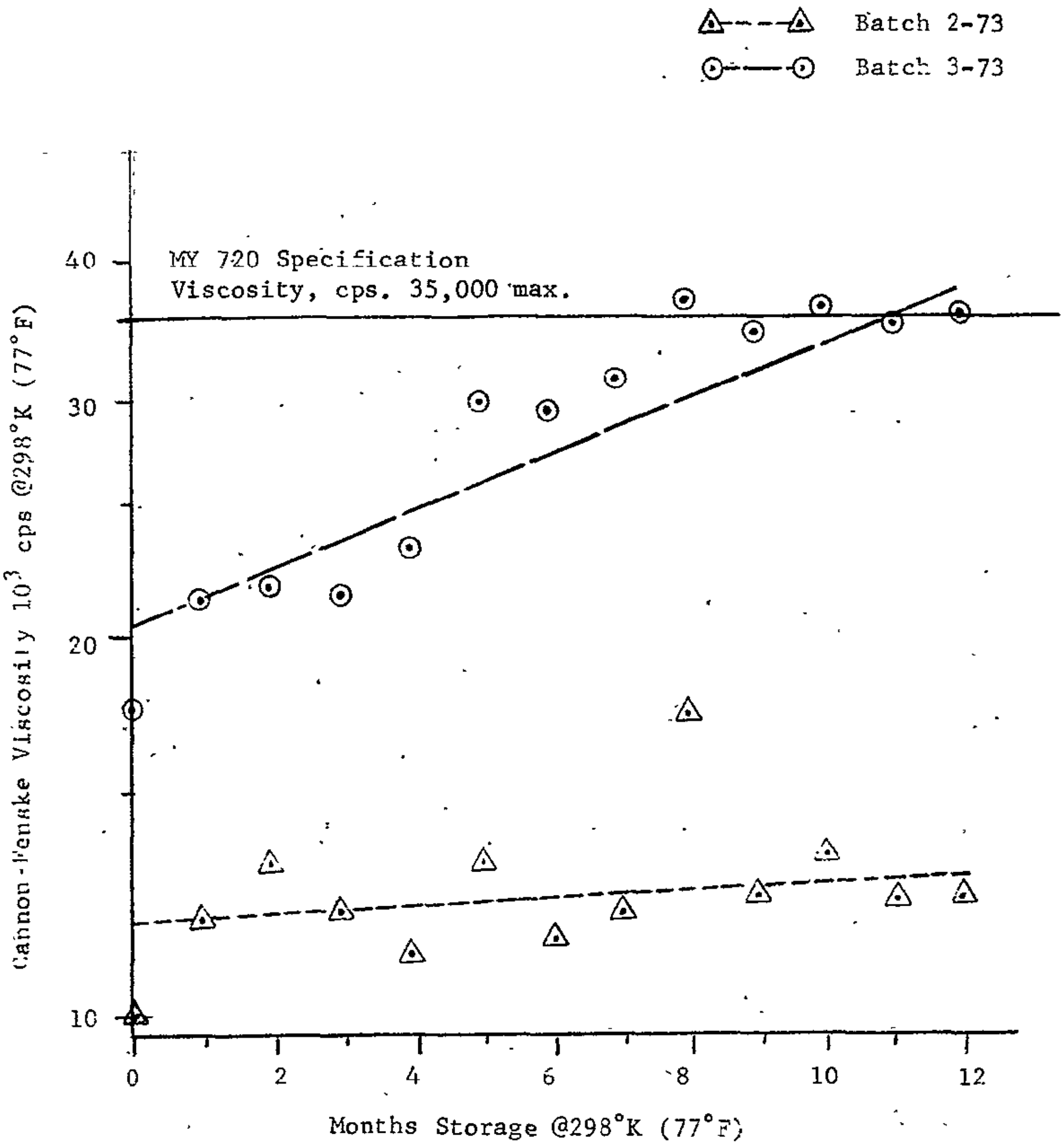
A significant factor in the cost of the presently produced MY 720 is the safety problem. Because of the inherent hazard in the hot pot full of highly reactive resin, only skilled professionals are currently used to make the production batches.

Ciba-Geigy stated that the LC curves that might be obtained on MY 720 would be sensitive to minor components which would be expected to vary in a series of normal batches. Such variation would cause unjustified concern about the composition and performance of the resin. Ciba-Geigy feels that all the important data that might be reflected in an LC is satisfied by the specifications. They agree that earlier production batches especially those prepared in Europe, may have had variability, but they seem confident that the resin produced now is consistent.

In their laboratories, no data has been obtained on assessment of differences in reactivity or viscosity versus temperature of the MY 720/Eporal system. The effect of storage at 298°K and 323°K are shown in Figures 29 and 30.

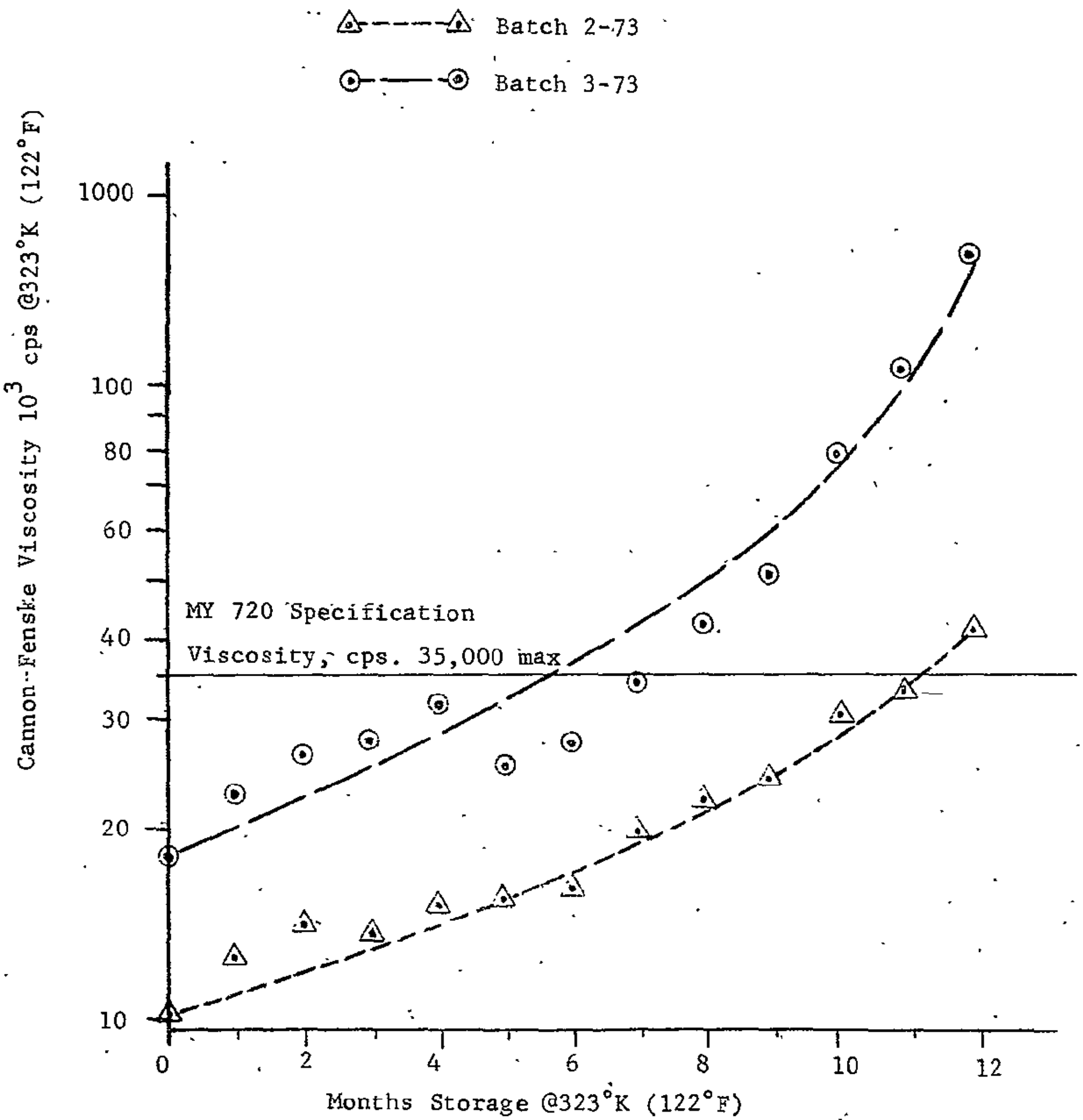
Future Plans

Ciba-Geigy has made a commitment to be a significant supplier in the speciality epoxy resin business. Their plans for new highly functional epoxies are proprietary. The sales of MY 720 to the graphite prepreggers is not as large as other users, but they expect that aerospace use will increase significantly in the next 5-8 years.



Viscosity vs. Storage at 298°K (77°F) for MY 720

Figure 29



Viscosity vs. Storage @323°K (122°F) for MY 720

Figure 30

V. DISCUSSION

The following is a constructive assessment of observed deficiencies in certain critical phases of graphite-epoxy composites preparation. Of particular concern are the variabilities arising in fabrication and testing. In resin reproducibility, a rationale is presented which leads to analytical monitoring techniques which will provide tools useful by all segments of the industry.

A. Fabrication Processing and Design

In all the technical surveys described earlier, it was the unanimous opinion that fabrication processing is a most significant source of composite variability.

An educational effort will improve the skill of the fabricator in reducing variability arising from this source. The need for comprehensive understanding of the behavior of these polymeric systems seems to be self-evident, yet a number of problems persist where it is obvious that the behavior and limitations of polymeric systems are not completely understood. It will suffice here to merely list the difficulties observed by prepreggers and fabricators:

- o Inappropriately altered cure schedules
- o Slow heat up rates
- o Poor heat uniformity through the part
- o Faulty monitoring of temperature
- o Poor layup practices (time, fiber orientation, debulking, dams, etc.)
- o Poor part design and materials selection
- o Inadequate tooling
- o Inexperienced personnel combined with poor supervision

B. Testing

The basic mechanical performance and/or quality of polymer, fiber, prepreg or composite is primarily determined by mechanical testing. Although nondestructive testing is used for quality control purposes, such as visual, various acoustic techniques, dynamic mechanical x-ray, etc., for actual mechanical properties, destructive testing is still required.

Because the data generated by testing are to be the basis for material selection, material acceptance (and rejection) and design, it is essential that test results represent the true performance of the material. Unfortunately, discussions during the survey visits identified many problems in the testing of composite materials which often clouded or hid the true performance of the composite material.

The problems in testing produce three distinct quantitative discrepancies: values that may be too high, values that may be too low, and a variability in the values which results in severe penalties in design minimum values.

The observed sources of problems in testing are caused through many test deficiencies. Among these sources of problems are:

- Test Methods
  - Test fixture design
  - Test specimen design

- Test Specimen Quality
  - Material variability
  - Fabrication variability

- Test Instrumentation

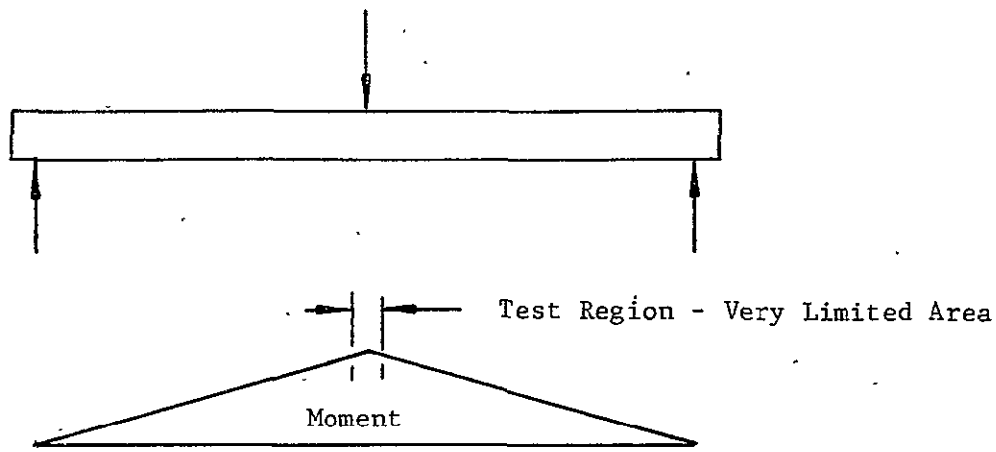
- Test Data Reduction

  Inappropriate interpretation and presentation of data
  Insufficient descriptive data

Although an attempt has been underway for many years to standardize test methods, only limited success has been achieved. One of the problems is that often cost is more of a driving force than is the quality of the test method. Another problem is that the wide range of properties exhibited by metals, polymers, and composites makes one test method impractical for all materials.

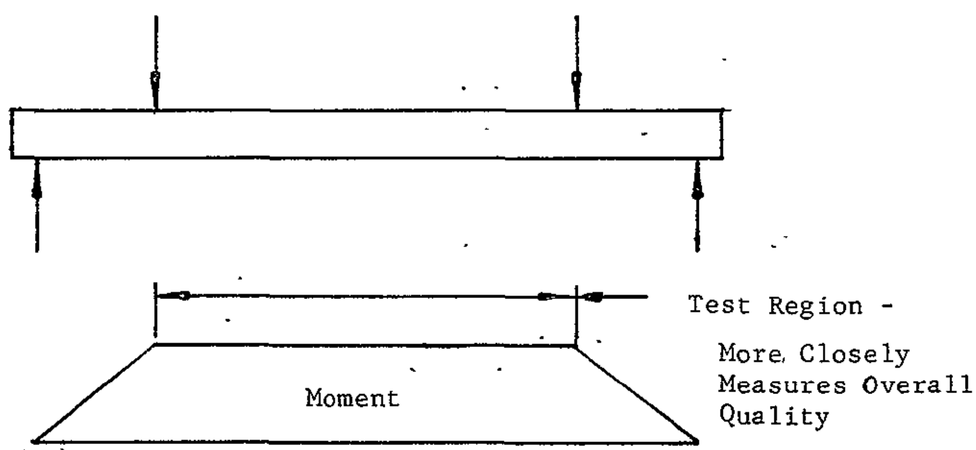
Test fixture design is of course integrally associated with the test specimen configuration. In isotropic materials a certain test fixture may provide a reasonable test result. The same fixture when applied to composite materials may not. For example, the rail shear test provided in-plane shear stress allowables for isotropic material but results in nearly a 50 per cent error (high side) in in-plane shear ultimate for a unidirectional composite. This is due to damping of fibers by the test fixture.

Thus a fixture may contribute to errors and/or variability in a test specimen when in fact no variability may exist. Conversely, a specimen loaded in flexure by means of the three-point loading relies on only one concentrated area for failure. Thus the overall quality of the specimen is not necessarily represented by those test results. However, utilizing the same specimen, in a four-point loading fixture results in a much broader area of the specimen being subjected to the maximum stress. Thus the test method tends to measure the minimum strength of the overall test specimen. This is shown schematically on Figures 31 and 32.



Three Point Loading Test Method

Figure 31



Four Point Loading Test Method

Figure 32

A given test method will determine both test fixture and test specimen. However, often variations in test specimen dimensions are possible for a given test method. A good example is the short-beam shear specimen. Although the test method is fixed, variations in the ratio of span length to specimen thickness may give different test results even though the composite laminate does not vary in quality or properties. Thus, reported data may vary excessively without justification.

The comments on short beam shear may also apply to flex beam specimens but to a lesser degree. The influence of interlaminar shear stiffness on flexural modulus has been neglected by all but a few investigators, for example.

On of the major contributions to test data scatter is of course the quality of the test specimens. Some believe that test results are the basic indication of laminate quality, and in fact that such an indication which data is to be obtained. If so, then the test results must eliminate all other variables. If, for example, quality of the laminating process is to be determined by test, then other non-contributory variations in the composite should be filtered out. That is possible if a normalization technique is applied to the following variables (not all independent):

- fiber strength
- resin properties
- volume fraction fiber/resin
- fiber distribution
- ply thickness
- fiber orientation and/or misalignment

If the quality of the fiber is the subject of the test, then another set of variables should be segregated. Only characteristics sensitive to fiber properties should be analyzed. Care in laminate fabrication, fiber volume fraction, fiber orientation, etc. then become extremely important.

Another source for data scatter is the use of various methods of collecting data. The data by strain gage, extensometer, dial gage, head travel, etc. can be significantly different. The instrumentation can be categorized either as collecting data on a point basis or over an area. The area data represents more average data in the case of stiffness, and minimum data in the case of strength. Point data, however, are isolated data points randomly distributed over the statistically normal curve for the parameters being tested.

The analysis and reporting of data is the last opportunity to carefully define (properly) the test fixture, specimen, instrumentation, and the data itself. If the variables of the test are properly reported and either normalized or a least well defined, the scatter of test data should be significantly reduced.

Complete reporting is costly, of course. It is expensive to obtain the required knowledge and to report it accurately. However, if the reduction in scatter of test data, reliability in design properties, accuracy in quality determinations, and maximum utilization of the advantage of composites are to be achieved, the cost for the additional data is essential.

Several comments were made by those technical people visited, that the ASTM was notoriously slow in defining test procedures in a timely manner.

C. Fiber and Surface Treatment or Sizing

The importance of the reinforcing fiber in composite reproducibility has been recognized. Several investigators have observed its role, especially in early test data variability in fiber-controlled properties. More recently, the quality of fiber as well as the control of surface treatment has improved considerably.

Perhaps the most vexing problem still remaining that some believe is not answered, is the role of surface treatment in moisture resistance and durability. There is the belief that water problems are a surface phenomenon and fiber treatment is an incompletely explored fertile area.

The fiber producers appear to be most sensitive to process control and uniformity in their product. The control parameters designated in Table XIV by Celanese seem to be adequate for the production of reliable and durable parts for commercial aircraft.

D. Resin

There have been a number of opinions expressed that for use in commercial aircraft, fiber reinforced resins should be specified in a manner similar to metal,i.e., exact chemical identity should be cited. Unfortunately, a number of mistakes have already been made in trying to apply to fiber-reinforced resins, measurement and evaluation methods used previously on metals. As mentioned earlier, a number of testing samples and techniques are suitable for isotropic materials but are definitely inappropriate for application to anisotropic systems.

Also, the fact needs to be stressed with process engineers and fabrication technicians that these thermosetting resins are "alive"

CARBON FIBER

PROCESS CONTROL/UNIFORMITY

PROCESS ELEMENT	CONTROL PARAMETER
PRECURSOR FEED	COMPOSITION DENIER PHYSICAL QUALITY PHYSICAL PROPERTIES
PREOXIDATION	TEMPERATURE (MULTIPOINT, CONTINUOUS) TENSION (ROLL SPEED)
CARBONIZATION / GRAPHITIZATION	TEMPERATURE - PROFILE AND PEAK TEMPERATURE (MULTIPOINT, CONTINUOUS) TENSION (ROLL SPEED) FURNACE PRESSURE INERT GAS FLOW OXYGEN CONCENTRATION RESISTIVITY
SURFACE TREATMENT	MEDIA CONCENTRATION TEMPERATURE VOLTAGE
SIZING	RESIN CONCENTRATION SIZE LEVEL

Table XIV

and that the way these materials are handled determines their molecular structure. Process controls are the key to resin performance reproducibility. Metals too, are sensitive to processing but usually not to the same degree as thermosetting resins.

In epoxy resin manufacture, for example, it has been pointed out by several resin producers that the resin is a "fashioned" product and is more aptly described by the process that makes it than by its exact chemical composition. In the manufacture of epoxy resins like Ciba-Geigy's MY 720, a number of molecular species are known to be present in the product. If the pure compound were prepared, the cost would be excessive and it probably would not be suitable for matrix resin, at least not without some attempt to run up the molecular weight. The principal species in production resin is accompanied by a number of important molecules of higher molecular weight. These higher molecular weight species are formed during the thermal exposures that the production process requires. This is evidenced in the typical GPC curve shown in Figure 28. When the reaction mixture is exposed to longer times at elevated temperatures, it is known that the result is a shift in the molecular weight profile of the finished product. There is observed a decrease in the amount of the principal component, in this case, the tetraglycidyl methylenedianiline, and an increase in the concentration of dimer, trimer and higher oligomers within the main sequence to high polymer. Within certain limits, this shift is not a problem, however, because the prepregger merely continues this reaction sequence in his formulative preparation of the polymer, tailoring it for suitable behavior in impregnation and final flow, tack, and drape. If the requirements, which are usually determined by viscosity (supported by epoxy equivalent weight), some shift in the raw materials molecular composition is inconsequential. In fact, the final cure is an extension of these types of reactions, facilitated by a curing agent or catalyst.

This shift in molecular weight profile is the most significant variable in epoxy resins. It should be monitored at the prepreg stage, because the prepregger continues this shift in molecular weight profile or chemical composition Refinement in methods suitable for monitoring molecular composition in prepreg is required.

Furthermore, the polymerization process is not finished by the prepregger The fabricator continues the polymerization to the ultimate in the final part. The determination of the exact molecular composition at that point is a monumental task of staggering complexity. Consequently, other means, usually mechanical, are utilized to describe the nature of the resulting cured resin and fibrous reinforcement.

There are other components in this type of epoxy resin which are not in the main sequence to high polymer. Some, such as the chlorohydrin, alter the main sequence. These hydroxyl - containing species participate in nucleophilic attack on epoxy groups, and a modified sequence continues with more epoxies reacting. These chlorohydrins are of two types, the 1,3 and 1,2 chlorohydrins. The latter type is detectable by its hydrolyzable chlorine atom. Its quantity is a part of the supplier's specification. The ratio of these types of chlorohydrins is probably very reproducible as defined by the epoxy resin manufacturing process, but it is not known. This ratio could be assessed by obtaining total chlorine as well as hydrolyzable chlorine, but the chlorine is not the important factor; the hydroxyl group is what may alter the polymer sequence. High hydrolyzable chlorine and the associated high hydroxyl content, results in an early increase in the viscosity vs time at temperature curve.

Other materials present in epoxy resins include sodium, water, solvent, and perhaps traces of epichlorohydrin. Their concentrations are low and their role in the alteration of resin behavior is not known but it is expected to be insignificant.

In all discussions with technical personnel, no evidence was collected that would indicate that the resin variants were or were not responsible for changes in mechanical performance.

Gel permeation chromatography has been mentioned as a tool for characterization of prepreg matrix resins. It is somewhat lacking in resolution although some have had more success than others. The analysis itself does not take long, but definition of a procedure is time-consuming. The success that Dow has had indicates considerable potential. In prepreg characterization, it would be a fairly simple procedure to extract the resin with a suitable solvent and run the analysis although one must also be aware of the sizing.

Liquid chromatography represents a fairly new technique for this type of analysis. Gradient elution has demonstrated remarkable resolution capability. In particular it has the power to show more clearly the early changes in molecular weight profile which occur in staging and storage of epoxy graphite prepreg. The peak for the apparent 1:1 amine/epoxy adduct begins to grow and other lower-weight materials show corresponding decreases. Epoxy resin suppliers are somewhat dismayed about the possible use of such a sensitive technique as a method for composition specification. However, realistic interpretation of such data will have to be a part of an educational process. Undoubtedly some peaks may be more important than others, but a truncated curve may still be useful. Alternately, attenuated readout could be used.

Differential scanning calorimetry offers a different vantage point and therefore is also attractive. An enthalpy assay is possible with some temperature peaking characteristics. Some difficulty has been observed in accurate enthalpy determinations at low heat-up rates. A possible solution is to have an early very rapid heat-up rate to the initiation temperature and then use a 5 °K/min rate or time base for an enthalpy assay. Some differences in equipment sensitivity from different manufacturers has been observed. Other problems may involve sample prepration. The DSC technique may be used in support of other techniques.

Other resin characterization techniques have been mentioned in the review of technical visits. Some are very interesting and may have potential but further work on feasibility is needed. These methods include the kinetic treatment of gel time and the wetting angle versus temperature.

E. Prepreg Processing

The analytical methods discussed above seem to be viable techniques for the monitoring of prepreg processing. All in all, it seems evident that by using processing controls and manufacturing instructions on each step, the prepreggers are doing a most creditable job in controlling the process. It appears that they have long recognized that such controls are the way to make money and be able to sell the same product week in and week out, not to discount their awareness for the need of reproducibility from the user's standpoint.

The use of a compositional profile analysis along with process controls and regular specifications on prepreg would represent a screening sequence which utilizes the present analytical know-how to the best advantage. It would provide a control on prepreg that would ensure that processing was uniform and that the produce would behave reproducibly.

Specifications on uncured prepreg have resulted in the high level of reproducibility cited by the fabricators. These specification have gone a long way in defining the behavior (See Table I). Supporting these specifications with a compositional assay and a thermodynamic analysis would make it most difficult for a deviant batch to slip through to an aircraft part.

VI. SUMMARY AND RECOMMENDATIONS

A. Resin

As a result of the survey described in this report the following recommendations are offered to fulfill the primary objective of this study.

These recommendations present methods for characterization which will provide meaningful criteria for quality assurance and reproducible performance from epoxy graphite prepreg. For reasons explained in the test, these methods are applicable not only for the resin in the prepreg but for all assessment of compositional variation in the staging history of the polymer, from raw resin to aged prepreg.

The suitability of liquid chromatography to quality control prepreg is quite evident. The technique requires equipment which is moderate in cost ($12-20K), and once technique is developed, the analysis can be run in a fairly short time. Therefore the recommendation is made that this powerful analytical tool be exploited for this application.

The recommendation is also made that a similar study be conducted using GPC. Because of the similarity of equipment and technique, the approach would be much the same as the LC study.

In addition, the recommendation is made that DSC is investigated as a complementary tool for use in conjunction with LC or GPC. The capability for the method has not been demonstrated for this type of activity. Some of the problems are discussed the the text. Included in the program should be the demonstration of sufficient sensitivity to be of diagnostic value when combined with information from LC or GPC.

More specific recommendations were presented to NASA Langley as a program concept for development of these analytical techniques for characterization of resin in prepreg.

B. Testing

The National Aeronautics and Space Administration should support a review team of three or four qualified composite test and design engineers to make a more thorough assessment of graphite composite testing practices and develop a set of 5 to 10 basic principles which would be used to correct the most common errors in testing graphite-epoxy fiber composites. Such principles would be a significant step toward standardization and improved relevance of test data at least in the commercial aircraft industry. The study should also make an attempt to quantify the role or potential role of various sources of variability in their contribution to test data scatter.

In addition, NASA should consider support of a program to investigate the dynamic mechanical properties of graphite composites. This program should take advantage of the unique nature of dynamic mechanical tests which assess the overall integral performance of a composite specimen. The advantages of this approach are that it is 1) insensitive to local imperfections and 2) not controlled largely by one compositional element.

C. Fabrication

The problem of fabrication as a source of variability is a difficult one because of its broad range of factors. Perhaps as the industry matures, most of these factors will be identified more clearly and avoided. NASA could help in several ways. It could sponsor further study to elucidate the best approach, perhaps through symposia, workshops or a joint prepregger - fabricator committee with a charter to define guidelines for fabrication procedures. Such guidelines could become a contribution to the AFML Advanced Composite Design Guide; some believe that the Design Guide does not give sufficient attention to the polymerization aspects of prepreg useage and that the emphasis is primarily manipulative in its description.

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