NASA Contractor Report 178402

ADVANCED THERMOPLASTIC RESINS - PHASE I

C. L. Hendricks, S. G. Hill, A. Falcone, and N. T. Gerken

BOEING DEFENSE & SPACE GROUP
Aerospace & Electronics Division
Seattle, Washington 98124

Contract NAS1-17432
September 1991

National Aeronautics and
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Langley Research Center
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FOREWORD

This report describes the work accomplished under Contract NAS1-17432, "Advanced Thermoplastic Resins". The contract was sponsored by the National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia 23665-5225.

Dr. Terry L. St. Clair was the NASA Technical Monitor. The Materials and Processes Technology organization of the Boeing Aerospace Company (BAC) was responsible for the work performed under the Contract. Mr. Carl L. Hendricks was Program Manager. Mr. Sylvester G. Hill was Technical Leader, and Mr. Anthony Falcone and Mr. Noel T. Gerken were co-principal investigators. The following personnel provided critical support to the various program activities.

Arlene M.Brown	Composites and Adhesive Group Leader
Oscar N. Davis	Mechanical Testing
James O. Eib	Laminate Fabrication and Material Properties
Frank D. Horan	Laminate and Test Specimen Fabrication
Ronald R. Stephenson	Laminate Physical Properties

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1.0 SUMMARY AND INTRODUCTION

1.1 Summary

This report documents the work performed by Boeing Aerospace for the National Aeronautics and Space Administration, Langley Research Center, under contract NAS1-17432, "Advanced Thermoplastic Resins", Phase I. The original objective of this program was to evaluate three newly developed thermoplastic polyimide resins as composite matrix materials. Five other thermoplastic polyimide resin systems were subsequently added to the program.

The initial resins were evaluated in neat form using dynamic mechanical analysis, and were subsequently used to make unidirectional carbon fiber prepreg tapes for composite laminate evaluation. Some composite processing development was conducted, and laminate physical properties were evaluated. Mechanical testing of the laminates included short-beam shear strength, flexural strength and modulus, and tensile strength and modulus.

The other five resins were innovative formulations of LaRC-TPI (Langley Research Center-Thermoplastic Polyimide) which had various melt flow aid additives. The additives were di(amic acid) in one resin system, and LaRC-TPI itself in a semicrystalline powder form in three of the resin systems. Screening tests of these five systems involved short-beam shear strength and flexural strength and modulus, at both ambient temperature and 450K (350°F), and short-beam shear and flexural testing of crossply laminates. Limited stress/solvent exposure testing was also conducted on three of the composite systems.

Two of the LaRC-TPI resins, the di(amic acid) doped and polyimidesulfone/LaRC-TPI powder resins, were selected for further evaluation on the program. Tensile and compression testing was performed on both of these composite resin systems. In addition, dynamic mechanical analysis (DMA) and compression-after-impact (CAI) testing were performed on the di(amic acid) doped LaRC-TPI composite material. Difficulty in fabricating thick crossply laminates from the

polyimidesulfone material prevented DMA and CAI testing from being conducted on that composite system during this program.

Both the di(amic acid) doped and polyimidesulfone/LaRC-TPI powder resin systems appear to be very promising matrix materials for advanced composite structures. The ambient temperature compressive strength of the di(amic acid) LaRC-TPI of 1090 MPa (158 ksi) (normalized to 57% carbon fiber by volume) compared very well with that reported for DuPont's AVIMID K-III thermoplastic polyimide of 1000 MPa (146 ksi) (Ref. 8). Both LaRC-TPI materials showed good retention of initial compressive strength at 450K (350°F) and at 450K after moisture saturation.

1.2 Introduction

Some current commercially available polymers used as matrices in composite material systems were not originally designed for such applications. As a result many composite systems represent a compromise in matrix and fiber combinations used in various aerospace vehicle structures. Composite structure efficiency can be significantly improved by increasing toughness (resistance to damage) without sacrificing environmental durability. Thermoplastic polyimide resins represent one class of polymers offering the potential for this improvement.

The primary objective of this program was to evaluate several NASA developed, high temperature stable, thermoplastic resins as matrices in carbon fiber reinforced composites. These material systems were evaluated in preliminary screening tests, with some testing at elevated temperatures. Selected material systems were also tested for properties in tension and compression, and to assess the effects of various fluids on the material properties.

The data generated as a result of processing, physical property, and environmental testing were compared to commercially available systems. Candidate systems which exhibit superior properties could be considered for various aerospace vehicle applications.

The program was divided into three tasks. The first two tasks were the "Preliminary Resin Evaluation" and "Preliminary Evaluation of LaRC-TPI Resin Systems", and involved testing of neat resin specimens and screening tests of carbon fiber composites. The third task, "Composite Mechanical Property Evaluation", involved more extensive mechanical testing of composite materials selected from the second task.

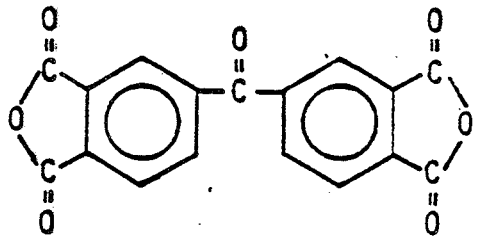
2.0 TECHNICAL DISCUSSION

2.1 Preliminary Resin Evaluation

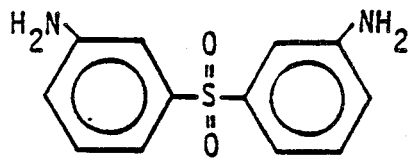
2.1.1 RESIN SYSTEMS

The criteria for selecting composite matrix resins for evaluation on the program were that the resins have a high glass transition temperature, that they have good processability, and that they have good resistance to chlorinated hydrocarbons and water. Three thermoplastic polyimide resin systems were initially selected for evaluation in neat form. The three resins were prepared by M&T Chemicals, Inc., Rahway, New Jersey.

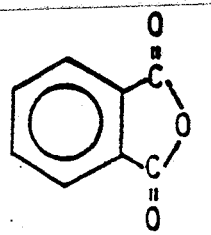
One resin was designated PSI-1111 and was a polyamic acid prepared in diglyme from 3,3', 4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA), 3,3'-diaminodiphenylsulfone (3,3'-DDS), and phthalic anhydride (PA) as shown below.



3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA)



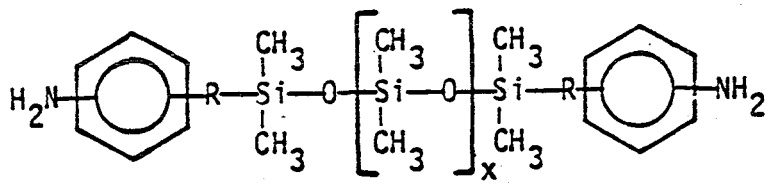
3,3'-diaminodiphenylsulfone (3,3'-DDS)



phthalic anhydride (PA)

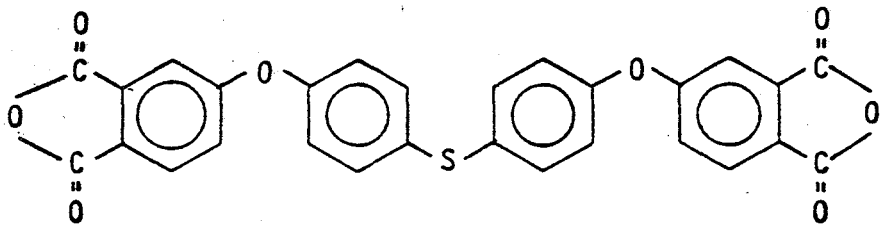
The BTDA and the 3,3'-DDS are reacted in a 1:1 stoichiometry. At the end of the polymerization, 2.0 mole % excess of PA (based on the level of BTDA) was added to the reaction.

The second resin was a polyamic acid prepared in diglyme using BTDA, 3,3'-DDS and siloxane containing aromatic amine groups as shown below.

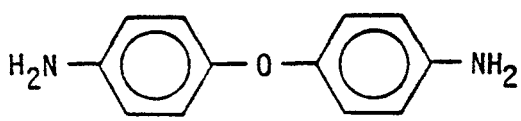


The composition of the polymer was BTDA 50 mole %/3,3'-DDS 47.5 mole %/siloxane diamine 2.5 mole %. The resin was designated M&T 4605-40.

A third resin selected for evaluation was also a polyamic acid, designated M&T 4300 SDA/ODA, and was prepared in diglyme at 24% solids. The key monomers are 4,4'-bis(3,4-dicarboxyphenoxy)diphenysulfide dianhydride (SDA) and 4,4'-oxidianiline (ODA), and are shown below.



4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (SDA)



4,4'-oxidianiline (ODA)

2.1.2 NEAT RESIN PROPERTIES - DYNAMIC MECHANICAL ANALYSIS

The polyamic acid precursor of each polymer was precipitated from the diglyme solution in agitated water. The techniques used are described in NASA Technical Memorandum 84621 (Ref. 1). The resin/diglyme solution, thinned with diglyme to a syrup-like viscosity, was poured into water agitated by a blender. The blender shreds the amic acid as it precipitates. It was then filtered and spread out in a flat pan and dried in an air circulating oven by increasing the temperature 28K (50°F) at thirty minute intervals to 477K (400°F) and holding for thirty minutes. This converted the amic acid to its imide (polymer) form. The polyimide was then ground into a powder suitable for molding. The powder was placed into a matched metal die and cured to produce panels for testing. M&T 4605-40 and PSI-1111 were cured at 613K (650°F) for one hour with 14 MPa (2000 psi) pressure applied at 596K (550°F). M&T 4300 SDA/ODA was cured at 589K (600°F) for one hour with 2000 psi pressure applied at 533K (500°F). The neat resin moldings measured 16.5 cm by 11.4 cm by 1.65 mm (6-1/2 inches by 4-1/2 inches by 0.065 inches) and were uniform and void-free.

Specific gravities were determined for the resins and are listed below.

RESIN	SPECIFIC GRAVITY
M&T 4300	1.34
PSI-1111	1.41
M&T 4605-40	1.36

The neat resin was then evaluated for solvent effects using dynamic mechanical analysis (DMA). The DMA test specimen dimensions and test procedure are listed in Appendix A. DMA was performed on neat resin specimens to determine the glass transition temperature (Tg), the shear storage modulus (G'), the shear loss modulus (G"), temperature/viscosity relationships, and to evaluate resistance to hot water, Skydrol, jet fuel and methylene chloride. For each material, six specimens were fabricated from a single molding and exposed to the conditions listed in the table below.

FLUID	TEMP.	DURATION	PERCENT STRAIN
Control	AMBIENT	None	None
Water	368K (200°F)	24 Hours	None
Skydrol	344K (160°F)	14 Days	0.4
Jet A Fuel	AMBIENT	14 Days	0.4
Methylene Chloride	AMBIENT	14 Days	0.4

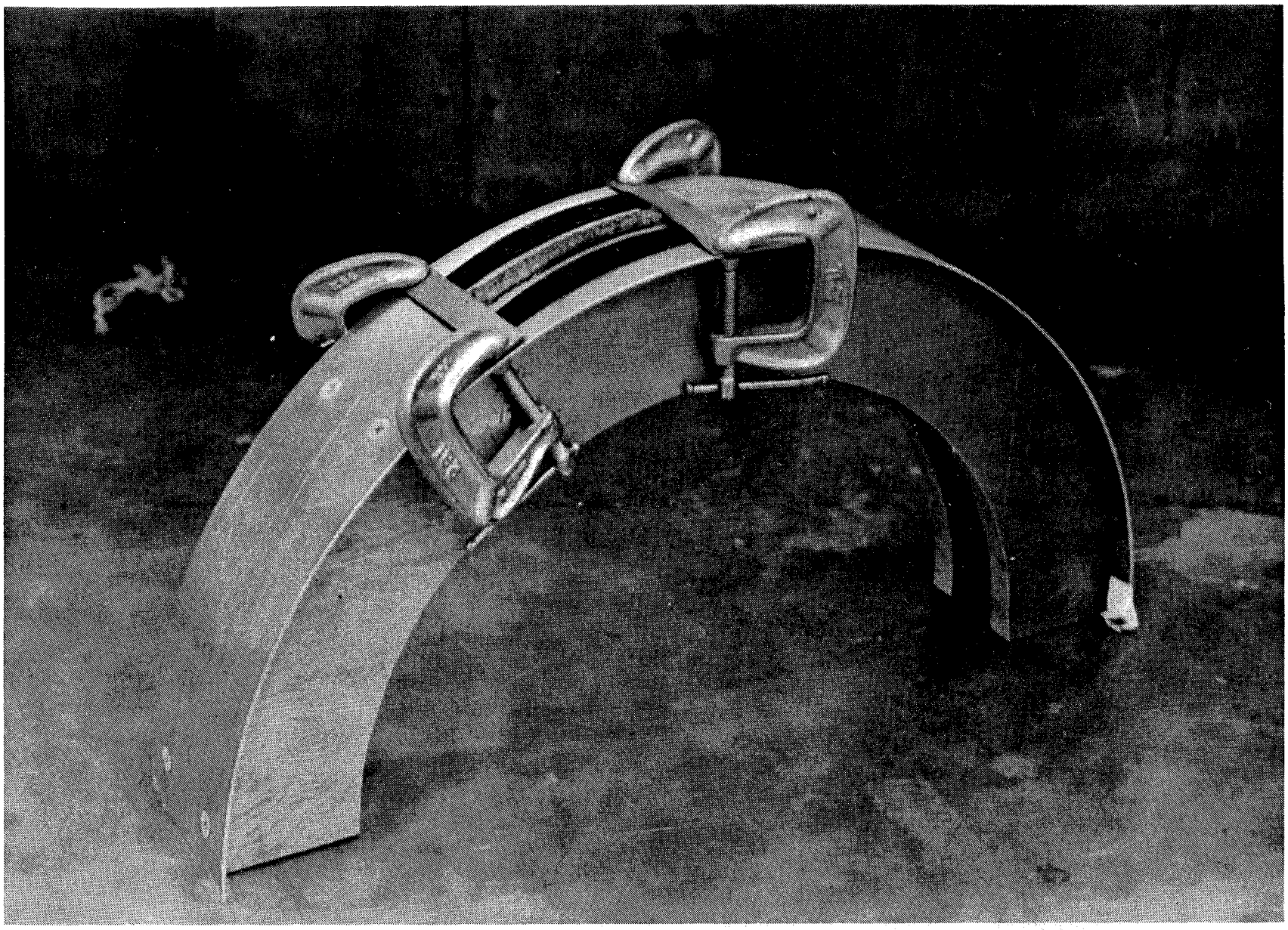
Two specimens served as control specimens. Specimens exposed to Skydrol, jet fuel and methylene chloride were stressed to a 0.4% strain around a 20 cm (8 inch) radius stress jig as shown in Photograph 2.1.2.1. The 0.4% strain level is a Boeing Commercial Airplane (BCA) composite structure design requirement.

Weight gain was determined for the water exposed specimens. The PSI-1111 specimen gained 1.7%. The M&T 4605-40 and M&T 4300 specimens gained 1.4 and 0.86%, respectively.

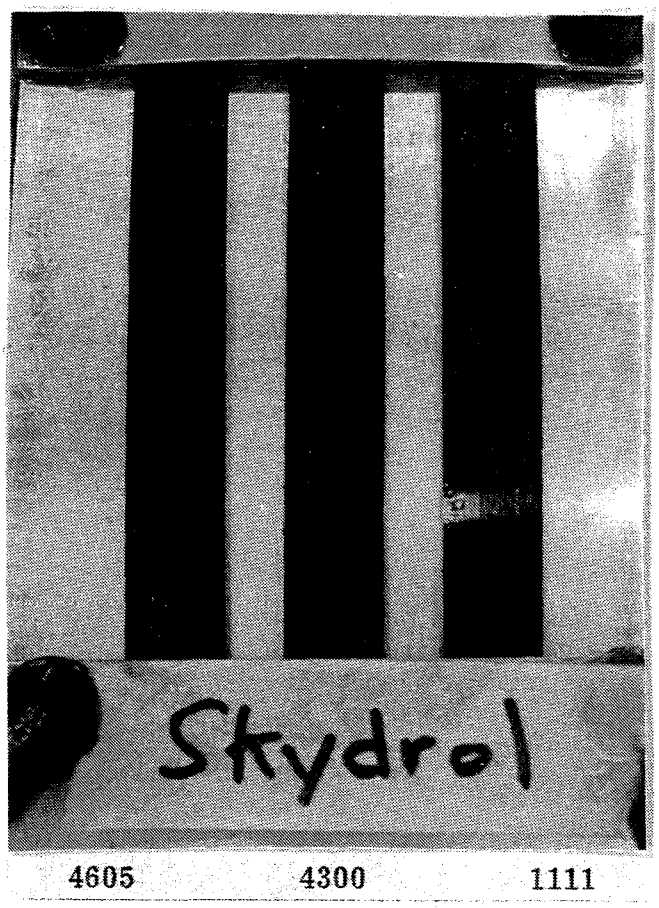
The Skydrol and jet fuel specimens exhibited no visible effects such as solvation, plasticization or micro-cracking (Photographs 2.1.2.2 and 2.1.2.3). The methylene chloride exposed specimens did exhibit visible effects. Slight surface crazing was evident in the PSI-1111 and M&T 4605-40 specimens and severe solvation/plasticization in the M&T 4300 specimen as shown in Photograph 2.1.2.4

A Rheometrics Mechanical Spectrometer was used to perform the dynamic mechanical analysis with the instrument parameters listed in Appendix A. The DMA data provided Tg, viscosity/temperature relationships, G' and G" for the control and the stressed/exposed specimens.

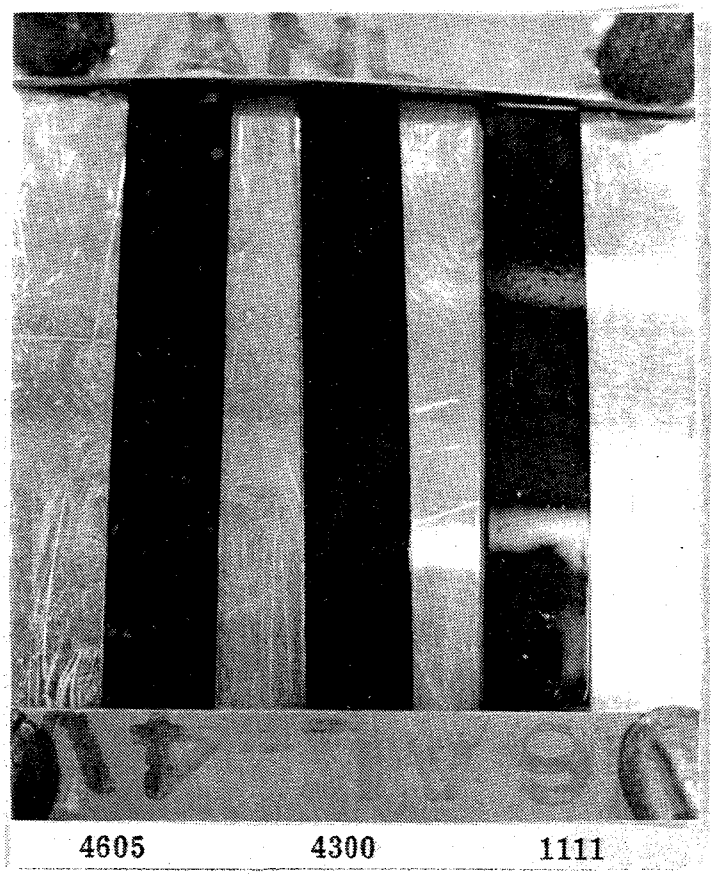
The glass transition temperature (Tg) is defined as the temperature of the maximum shear loss modulus (G"). G" is the inelastic (plastic) component of the total viscoelastic shear modulus. Hence, when G" is at its maximum, the material is at a major transition or softening point which is defined as its Tg.



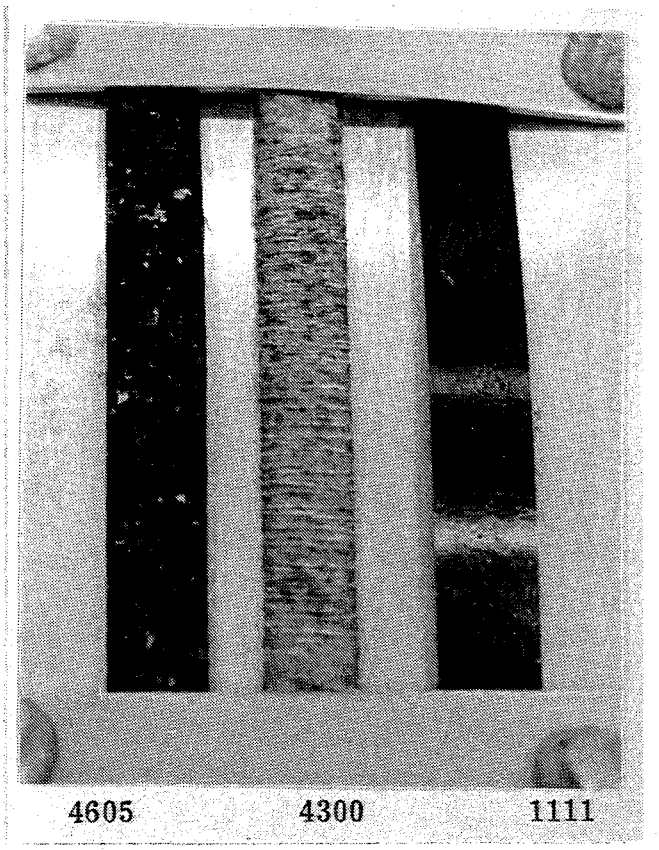
Photograph 2.1.2.1. Twenty-cm Radius Solvent Soak Stress Jig for DMA Specimens



Photograph 2.1.2.2. Stressed DMA Specimens Exposed to Skydrol



Photograph 2.1.2.3. Stressed DMA Specimens Exposed to Jet Fuel



Photograph 2.1.2.4. Stressed DMA Specimens Exposed to Methylene Chloride

The shear elastic modulus (G') is directly proportional to the viscosity. Thus, the DMA data curves also show viscosity/temperature relationships.

Significant DMA data is summarized in Table 2.1.2.1. Tg and G' at two temperatures (293K and 355K) are listed. PSI-1111 had a Tg of 535 K (504°F), M&T 4605-40 about 529K (493°F), and M&T 4300 between 479K and 483K (403°F and 410°F). PSI-1111 also had the highest ambient temperature shear storage modulus (G'), about 2 x 10^{10} dynes/cm^2 (240 ksi). M&T 4605-40 had an ambient temperature G' of about 1.5 x 10^{10} dynes/cm^2 (220 ksi) and M&T 4300 about 1 x 10^{10} dynes/cm^2 (160 ksi). G' values at 355K (180°F) were slightly lower for all three resins and only two (PSI-1111 and M&T 4605-40) met the Boeing Commercial Airplane's minimum requirement for damage tolerant matrix materials of 1.25 x 10^{10} dynes/cm^2 (150 ksi) at 355K (180°F).

Plots of G' and G" for each material and condition are in shown Appendix B. G' curves also showed that M&T 4300 had the lowest viscosity during the melt phase, indicating potentially easier processing. M&T 4605-40 and PSI-1111 G' curves showed a higher viscosity during the melt phase indicating that they may be more difficult to process than the M&T 4300. A discussion of the solvent exposure effects for each resin follows.

The M&T 4300 resin was significantly affected by methylene chloride. Severe solvation/plasticization occurred during exposure as shown in Photograph 2.1.2.4. The G' and G" curves (Figure B.4) were dramatically different from the control specimen curves (Figures B.1 and B.2). G' was much lower at all temperature levels and G" showed no transition point (Tg) indicating severe degradation. M&T 4300 was unaffected by hot water, Skydrol, and jet fuel.

Methylene chloride also had a pronounced effect on M&T 4605-40, although not nearly as extreme as it did on M&T 4300. Tg was lowered about 10K to 519K. G' was slightly less compared to the control specimens. Hot water and jet fuel lowered both Tg and G' slightly. Skydrol had no effect on the resin.

TABLE 2.1.2.1

DYNAMIC MECHANICAL ANALYSIS (DMA) DATA SUMMARY

RESIN/EXPOSURE	Tg(°C)	Shear Storage Modulus, G' 20°C (68°F)		82°C (180°F)	
		$10^9 \frac{dynes}{cm^2}$	(ksi)	$10^9 \frac{dynes}{cm^2}$	(ksi)
M&T 4300					
Control #1	206	11.0	(160)	9.8	(140)
Control #2	210	11.0	(160)	9.9	(140)
Hot Water	207	11.0	(160)	9.7	(140)
Skydrol	207	11.0	(160)	9.8	(140)
Jet Fuel	207	11.0	(160)	9.8	(140)
Methylene Chloride	---	0.3	(4)	0.1	(2)
M&T 4605-40					
Control #1	255	15.0	(220)	13.0	(190)
Control #2	257	15.0	(220)	13.0	(190)
Hot Water	232	14.0	(200)	12.0	(170)
Skydrol	253	15.0	(220)	13.0	(190)
Jet Fuel	248	14.0	(200)	12.0	(170)
Methylene Chloride	246	12.0	(170)	10.0	(150)
PSI-1111					
Control #1	262	20.0	(290)	18.0	(260)
Control #2	262	20.0	(290)	19.0	(280)
Hot Water	257	19.0	(280)	17.0	(250)
Skydrol	265	19.0	(280)	17.0	(250)
Jet Fuel	262	20.0	(290)	18.0	(260)
Methylene Chloride	267	20.0	(290)	18.0	(260)

By comparison the PSI-1111 resin was unaffected by methylene chloride. Tg actually increased slightly to 540K (513°F), and G' was unchanged at ambient temperature and 355K (180°F). Jet fuel had no effect on the PSI-1111 resin. Hot water caused a drop in the Tg of about 5K.

2.1.3 PREPREG FABRICATION

Prepreg (preimpregnated) materials were produced from the three M&T chemical resin systems both in-house and by the Fiberite Corporation. The reinforcement used was unidirectional carbon fiber with widely spaced crossply strands of S-glass fiber, called Unifabric. Composite laminates were fabricated from these prepreg materials for mechanical testing.

Unifabric is made from unidirectional Celion 3K carbon fiber roving with no twist in the warp direction, and has S-glass roving in the fill direction (see photographs 2.1.3.1 through 2.1.3.3). The Unifabric was produced by Textile Products Incorporated. A certification sheet for the Unifabric is reproduced in Table 2.1.3.1.

Prepreg tape was prepared at Boeing using the Unifabric reinforcement with both the M&T 4605-40 and PSI-1111 resins. The resin solutions at 30 wt. % solids were diluted to 15 wt. % solids with diglyme and applied to the Unifabric to obtain a 38 wt. % resin prepreg.

The prepreg tapes received from the Fiberite had resin rich/resin poor areas. In addition, shrinkage occurred during prepregging which caused fiber waviness, and nonuniformity in the prepreg width and fiber density as shown in Photographs 2.1.3.1, 2.1.3.2 and 2.1.3.3. The lack of prepreg uniformity resulted in poor quality composite laminates being produced from this prepreg tape.

The Fiberite prepreg volatile contents and resin contents are listed in Table 2.1.3.2, along with values for percentage resin flow.

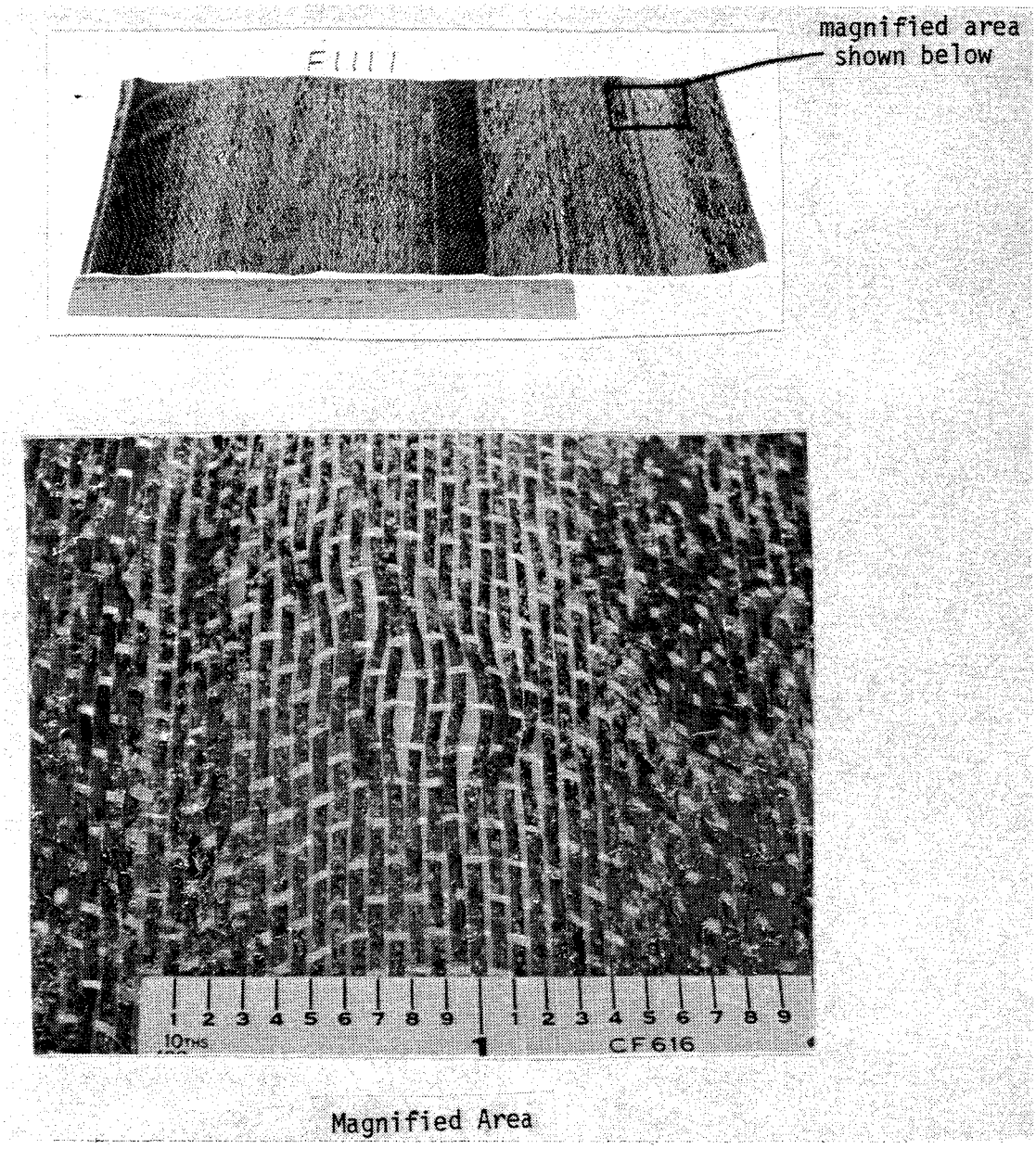
TABLE 2.1.3.1

UNIFABRIC CERTIFICATION SHEET FROM TEXTILE PRODUCTS, INC.
(ANAHEIM, CA)

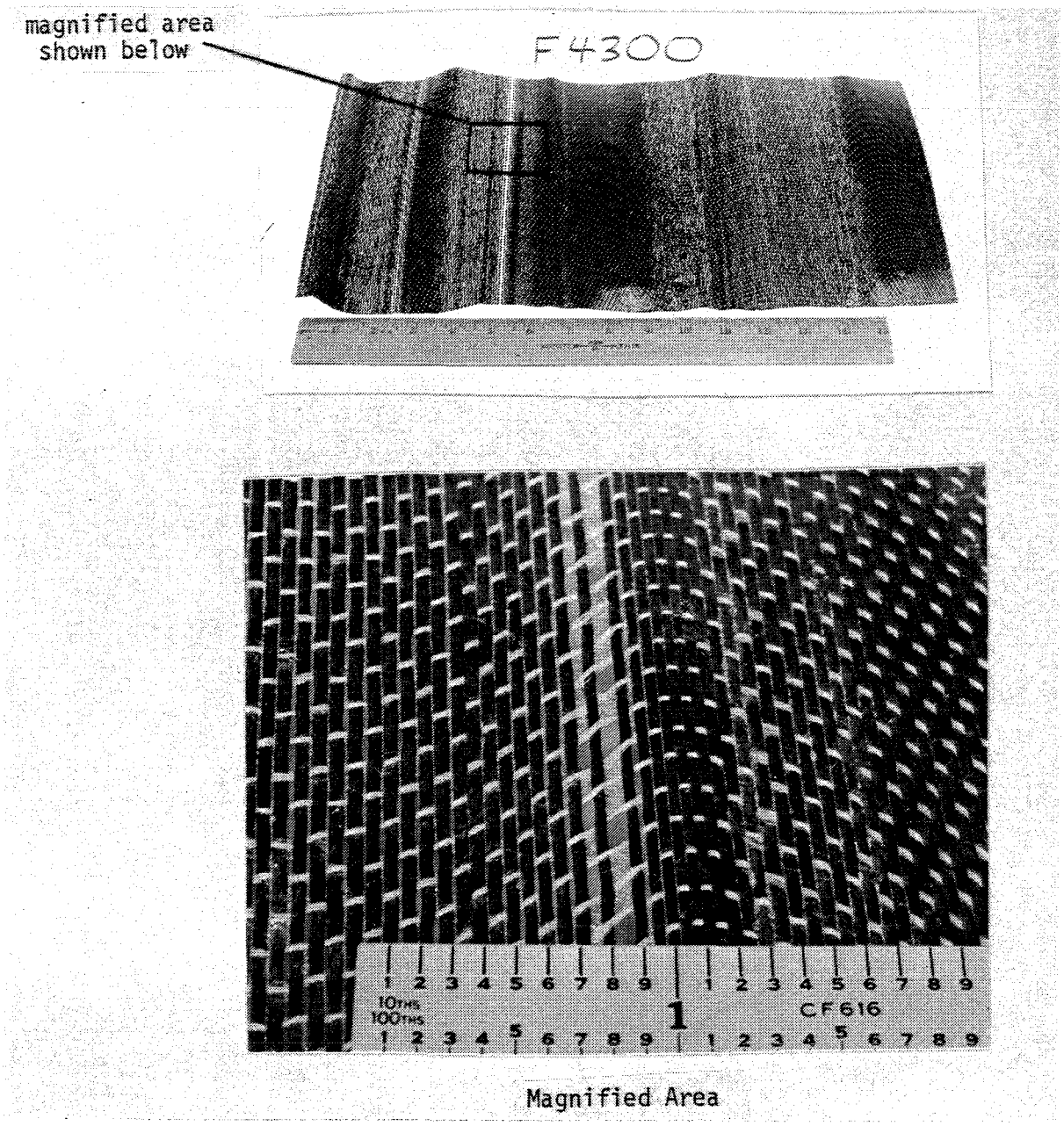
FABRIC CERTIFICATION NO. 83-308

NOVEMBER 4, 1983

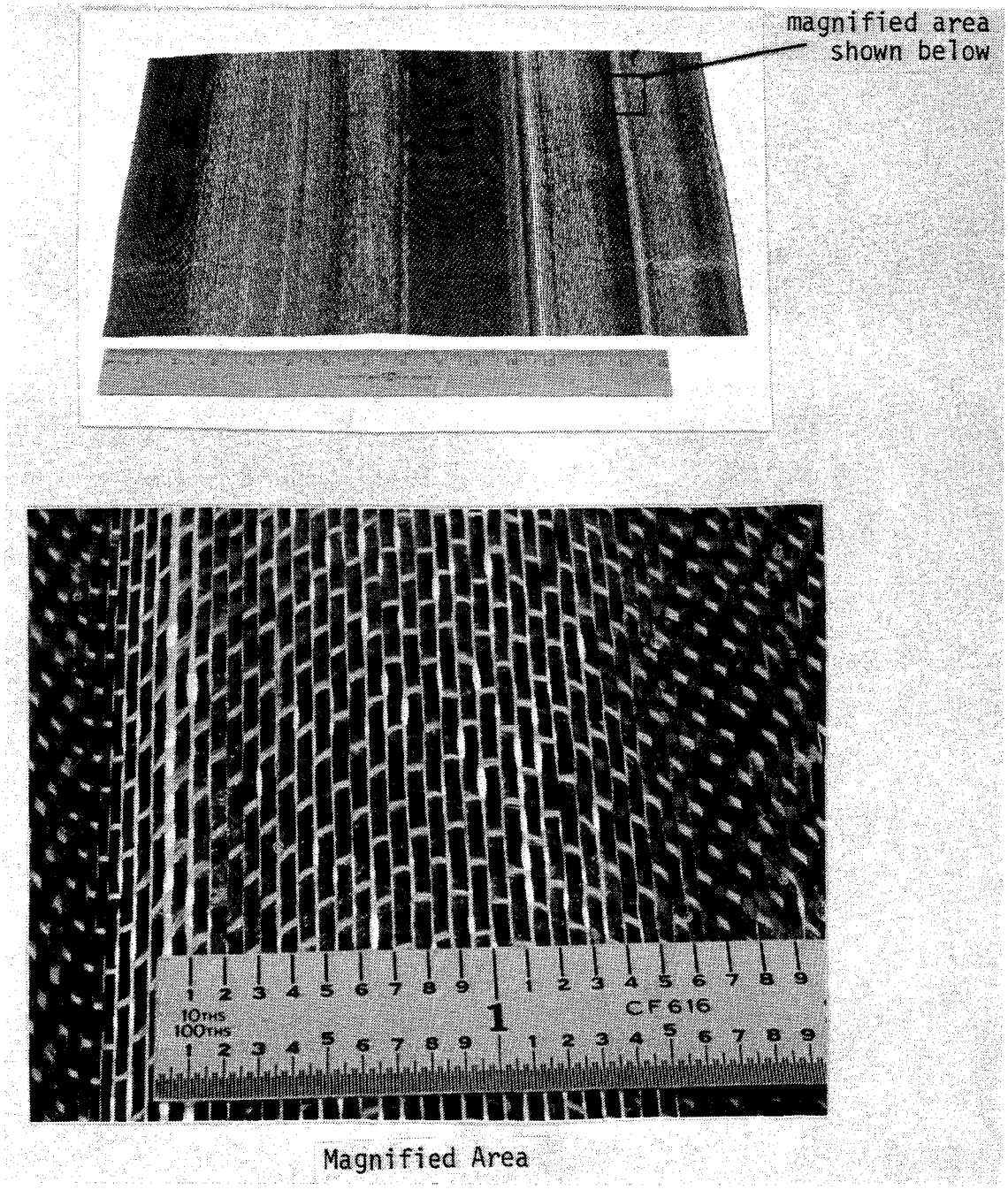
CUSTOMER		Boeing	
ORDER NUMBER		FD 8841	
SPECIFICATION		MS 80002	
FABRIC CONSTRUCTION		Unidirectional	
FINISH DESIGNATION		Epoxy	
YARN	WARP	Celion 3K No Twist	
	FILL	150 1/0 S-Glass	
YARN LOT NUMBER	WARP	HTA-7-2422	
	FILL	--	
LOT NUMBER		643	643
ROLL NUMBER		01	02
QUANTITY (YARDS)		125	125
COUNT	WARP	16	16
	FILL	8	8
ROLL WEIGHT (LBS.)		22.44	22.56
AREAL WEIGHT (G/M^2)		141	142
FABRIC WEIGHT (OZ./SQ. YD.)		4.22	4.23
THICKNESS		0.009	0.009
WIDTH		24"	24"



Photograph 2.1.3.1. F-1111 Prepreg (PSI-1111 Celion 3K Unifabric)



Photograph 2.1.3.2. F-4300 Prepreg (M&T 4300 SDA-ODA/Celion 3K Unifabric)



Photograph 2.1.3.3. F-4605 Prepreg (M&T 4605-40/Celion 3K Unifabric)

TABLE 2.1.3.2

FIBERITE PREPREG PHYSICAL PROPERTIES

PREPREG	RESIN CONTENT 1/ (% WEIGHT)	VOLATILES CONTENT 2/ (% WEIGHT)	PERCENT RESIN FLOW 3/
F 4605	30	14	31
F 1111	33	15	48
F 4300	30	18	32

1/ Resin consists of both the polyamic acid precursor and the polyimide.

2/ Volatiles consists of both solvent and outgassing products.

3/ Percent resin flow is determined as follows:

1. The test laminate, consisting of four 5.1 cm by 5.1 cm plies, is weighed.
2. The laminate is "cured". Typical conditions are 0.69 MPa psi pressure and 620K for 15 minutes.
3. The excess (beyond the original dimensions) resin is trimmed off and the laminate is reweighed.
4. Percent resin flow = $\frac{\text{weight before - weight after}}{\text{weight before}}$

2.1.4 LAMINATE FABRICATION AND EVALUATION

The laminates fabricated from both the prepregs prepared at Boeing and the prepregs made by Fiberite are discussed below. Process equipment tolerances are listed in Appendix D.

Three small laminates, approximately 7.6 cm by 10.2 cm by 2.54 mm thick, were fabricated from each of the two resin prepregs prepared at Boeing. These panels were identified as D, E, and F for the M&T 4605-40 prepreg material and as J, K, and L for the PSI-1111 prepreg material. Each prepreg layup was dried in an oven to a different volatile content to determine which volatile contents would produce good quality laminates. The volatile content of each prepreg layup is listed in Table 2.1.4.1.

The dried prepreg layups were bagged using permeable armalon and Style 120 glass fabric for a bleeder/breather system, and cured at 620K (650°F) and 1.38 MPa (200 psi) autoclave pressure for one hour. Vacuum pressure was applied during heatup and during consolidation at 1.38 MPa. The bleeder/breather material greatly improved the removal of volatiles, compared to some preliminary laminates fabricated without a bleeder/breather system.

The consolidated panels were tested for short-beam shear strength and flexural strength and modulus, and the test results are listed in Table 2.1.4.1. The short-beam shear and flexural test methods used are discussed in Appendix A. The test values were very low for a polymer composite indicating poor fiber wetting, or fiber breakage during impregnation, or that the Unifabric is inadequate as a high strength structural composite reinforcement. The optimal volatile content was determined to be between five and eight wt. % for both systems. (See Table 2.1.4.1).

Several small laminates were prepared from each of the three Unifabric tapes manufactured by Fiberite using the M&T 4605-40, the 4300 SDA/ODA, and the PSI-1111 resins. The Unifabric tapes were designated F4605, F4300, and F1111 according to the resin system used. The laminates were fabricated to establish acceptable processes for cure

TABLE 2.1.4.1

LAMINATE DATA SUMMARY-BOEING PREPREG TAPE

PANEL	RESIN	VOLATILES (% wt.)	SHORT BEAM SHEAR STRENGTH MPa(Ksi)	FLEXURAL STRENGTH MPa (Ksi)	FLEXURAL MODULUS GPa (Msi)	RESIN CONTENT (% wt.)
A	4605-40	2.3	21 (3.1)	320 (46)	70 (9.6)	38
D	4605-40	13.2	35 (5.1)	430 (62)	72 (10.4)	39
E	4605-40	5.3	36 (5.2)	550 (79)	62 (9.0)	30
F	4605-40	3.0	26 (3.7)	310 (45)	68 (9.8)	38
J	PSI-1111	2.5	41 (6.0)	310 (45)	64 (9.3)	36
K	PSI-1111	7.7	41 (6.0)	550 (79)	70 (10.2)	37
L	PSI-1111	12.2	11 (1.6*)	460 (67)	61 (8.9)	37

* values very low due to testing error

cycles. The laminates measured approximately 7.6 cm by 10.2 cm by 2.54 mm thick. The prepreg tapes were dried in an oven at 480K (400°F), 495K (430°F), or 505K (450°F). The laminates were vacuum bagged; permeable Armalon and Style 120 glass were used as a bleeder/breather system. Laminates were cured at 575K to 620K, although lower cure temperatures were evaluated in Boeing IR&D studies. Various cure pressures were also evaluated. Process parameters are listed in Table 2.1.4.2.

Through transmission ultrasonic scans (TTU) were made of each laminate to detect voids and delaminations. Acceptable laminates were tested for short-beam shear strength and flexural strength and modulus. Results are listed in Table 2.1.4.3. Test data were uniformly low compared to conventional graphite/epoxy tape requirements.

A large laminate measuring 15.2 cm by 25.4 cm by 2.54 mm thick was prepared from each prepreg tape. These laminates were designated F4605-A, F4300-A and F1111-A. F1111-A was oven dried in 30K/30 minute steps to 422K (300°F), resulting in a volatile content of 7.4 wt. %. F4300-A was dried to 394K (250°F) yielding 7.9 wt. % volatiles. The laminates were press cured at 616K (650°F) for one hour under full vacuum. Pressure of 1.4 MPa was applied at 150K (300°F), 177K (350°F) and 120K (250°F) to F1111-A, F4300-A, and F4605-A, respectively. The temperature at which the consolidation pressure was applied was chosen as the temperature of lowest viscosity as determined from the DMA experiments on the neat resins.

F1111-A and F4300-A were tested for compression strength and modulus, tensile strength and modulus, and compressive interlaminar shear strength. A description of the test specimens and test procedures used is given in Appendix A. Results are listed in Table 2.1.4.4 and were uniformly low compared to conventional graphite/epoxy tape requirements. Property translation was again poor, indicating the Unifabric was not a suitable structural composite reinforcement for the candidate resin systems using these fabrication processes.

TABLE 2.1.4.2

LAMINATE PRE-CURE CYCLES AND CURE CYCLES

LAMINATE PRE-CURE CYCLES

DESIGNATION	DESCRIPTION
bb	340K (150°F) to 495K (430°F) in 28K (50°F)/30 min. steps in an air circulating oven
cc	Same as bb except 480K (400°F) final step
dd	Same as bb except 505K (450°F) final step
ee	Same as dd except 2 hours at final step

LAMINATE CURE CYCLES

DESIGNATION	DESCRIPTION
A	Autoclave Cure RT to 450K (350°F) at 1.1 to 1.7K (2-3°F)/min. Dwell 30 min at 450K. Apply 1.4 MPa (200 psi) and raise to 620K (650°F) at 2.2 to 2.8K (4-5°F)/min. Hold at 620K for 1 Hr. Vacuum throughout.
B	Press Cure RT to 480K (400°F) at 5.6K (10°F)/min. max. 480K to 575K (575°F) at 2.2 to 2.8K/min. Hold for 2 hrs at 575K. 3.4 MPa (500 psi) pressure and full vacuum throughout.
C	Same as B except 274K (525°F) cure.
D	Same as C except 6.9 MPa (1,000 psi) throughout.
E	Same as D except 620K (650°F) cure.
F	Same as E except 1.4 MPa (200 psi).
G	Same as F except 590K (600°F) cure.

TABLE 2.1.4.3

LAMINATE DATA SUMMARY - FIBERITE PREPREG TAPES

LAMINATE DESIGNATION	PRE-CURE CYCLE (TABLE 2.1.4.2)	VOLATILES (% WT)	CURE CYCLE (TABLE 2.1.4.2)	TTU 1/	RESIN CONT. (% WT.)	SBS 3/ MPa (Ksi)	FLEX STR MPa (Ksi)	FLEX MOD GPa (Msi)	COMMENTS
F1111-1	none	15	A	--	35	76 (11.0)	--	--	Excessive bleed
F4605-1	none	14	A	--	29	44 (6.4)	--	--	Boardy
F4300-1	none	18	A	--	29	61 (8.8)	--	--	Excessive bleed
F1111-2	bb	2.1	B	6	29	49 (7.1)	529 (76.7)	77.3 (11.2)	
F4300-2	cc	1.3	C	5	37	50 (7.3)	602 (87.2)	83.5 (12.1)	
F4605-2	dd	1.5	B	9	--	--	--	--	Not tested 2/
F4605-3	ee	2.3	D	8	--	--	--	--	Not tested 2/
F4605-4	ee	2.3	E	3	--	68 (9.9)	849 (123.0)	144 (20.9)	
F1111-3	bb	2.1	F	6	--	--	--	--	Not tested 2/
F4300-3	cc	1.3	G	10	--	--	--	--	Not tested 2/
F4605-5	dd	1.5	F	10	--	--	--	--	Not tested 2/

1/ Through transmission ultrasonic (TTU) average print-out, based on a linear scale. Good quality graphite/epoxy laminates scan between 1 and 4. TTU performed at 5 MHz and 5V.

2/ Laminate of poor quality based on TTU data.

3/ Short-Beam Shear Strength

TABLE 2.1.4.4

COMPRESSION AND TENSION TEST RESULTS
FOR LAMINATES F1111-A AND F4300-A

	UNIFABRIC LAMINATE PROPERTIES						CARBON FIBER/ EPOXY COMPOSITE 2/
	F1111-A		F4300-A		F4605-A 1/		
TTU (Ave.)	7		8		11		---
Resin Content (% Wt.)	33.2		43.5		-		33 to 44
Compression Strength MPa (Ksi)	497	(72.1)	409	(59.3)	--		1242 (180)
Compression Modulus GPa (Msi)	87	(12.6)	97	(14.1)	--		131 (19)
Tension Strength MPa (Ksi)	1049	(152)	807	(117)	--		1380 (200)
Tension Modulus GPa (Msi)	102	(14.8)	47	(6.8)	--		131 (19)
Compression Shear MPa (Ksi)	21	(3.1)	20	(2.9)	--		--- ---

1/ Laminate not tested due to poor quality as shown by TTU data.

2/ T-300 Type Carbon Fiber/350°F Cure Epoxy

The mechanical property data indicates that the M&T 4605-40 resin system, using the processes described in this report, is not a suitable structural composite matrix material. F4605 laminates generally contained more voids, and had poorer mechanical properties than the F1111 and F4300 laminates. The only acceptable F4605 laminate was fabricated using 1000 psi pressure, which would preclude autoclave processing.

The M&T 4605-40 was a poor structural composite matrix material because the polymer did not contain an end-cap. Lack of an end-cap allowed the molecular weight (and, hence, the viscosity) to increase rapidly during imidization. Boeing IR&D data indicated that the molecular weight increase occurred between 93K and 478K (200°F and 400°F). Boeing data also showed that the diglyme evaporates in this same temperature range, peaking at about 422K (300°F). The viscosity increased to a point where the volatiles (diglyme and the imidization water by-product) were unable to escape from the laminate, creating porous and void-filled laminates.

In terms of composite mechanical properties and fluid resistance, the PSI-1111 resin appeared to be the best composite matrix resin of the three candidate resins evaluated, and work was continued on this resin The Unifabric reinforcement appeared to have some severe shortcomings as a composite reinforcement. Subsequent composite evaluation was conducted on several thermoplastic polyimide formulations developed at the NASA Langley Research Center, using unidirectional carbon fiber tape as the reinforcement. A discussion of this work follows.

2.2 **Preliminary Evaluation Of LaRC-TPI Resin Systems**

2.2.1 DESCRIPTION OF RESIN SYSTEMS

Since high quality laminates could not be produced from the Unifabric tape prepreg made by Boeing or manufactured by Fiberite, using the processing methods outlined in this report, it was decided to stop work on the Unifabric reinforcement. Other sources of prepreg tape for the resin systems made by M&T Chemicals were investigated by NASA. A supplier able to produce prepreg tape from some LaRC-TPI (Langley Research

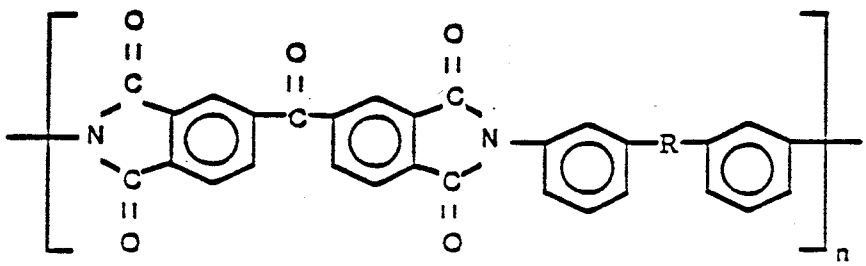
Center - Thermoplastic Polyimide) resin systems that were developed by NASA was located, and arrangements were made to supply Boeing with these prepreg tape materials for evaluation.

Four prepreg tapes with LaRC-TPI resin systems were prepared by Dr. Richard Moulton for evaluation on the contract. A fifth LaRC-TPI prepreg tape was received from Dr. Norman Johnston at NASA Langley. The prepreg tapes were produce with unidirectional carbon fiber reinforcement.

The LaRC-TPI resin systems were all based on solutions of polyamide acid dissolved in diglyme which forms a polyimide on heating, or polyimidesulfone when the amide acid precursor contained sulfone groups. Di (amic acid) (DAA) or semicrystalline LaRC-TPI powder was added to the resin solutions to lower the resin viscosity during processing, aiding in the production of low void laminates. The polyimidesulfone resin was the same as the PSI-1111 resin made by M&T chemicals. The polymerization chemistry of these LaRC-TPI resin systems has been discussed in several papers (Ref. 2,3,4,5).

Work was not continued with the M&T 4605 or M&T 4300 resins because LaRC-TPI appeared to be more processible.

The structural formulas of the LaRC-TPI polyimide and the polyimide-sulfone are shown below.



Polyimide: R = $\diagdown C{=}O \diagup$

Polyimidesulfone: R = SO_2

2.2.2 PREPREG TAPE MATERIALS

The five prepreg tapes received for evaluation were as follows:

SYSTEM	PREPREG RESIN/CARBON FIBER	BATCH NO.	TAPE WIDTH
1	Unimodified LaRC-TPI/Celion 6K	JBMPS-2 Roll 02	15.2 cm
2	Di(amic acid) doped LaRC-TPI/Celioin 6K	BAMFD-1 Roll 02	15.2 cm
3	1:1 slurry of LaRC-TPI: Cryst. LaRC-TPI Powder/Celion 6K	JBMTS-1 R Roll 02	12.7 cm
4	1:1 slurry of Polyimidesulfone: Crystalline LaRC-TPI/T300 3K	JJMPR-1 Roll 03	15.2 cm
5	2:1 slurry of Polyimidesulfone: Crystalline LaRC-TPI/AS-4 12K (unsized)	10986 (30.5 cm long sections)	15.2 cm or 30.5 cm

The prepreg material of system 5 was drumwound prepreg; the other systems were in the form of continuous undirectional tape. The LaRC-TPI materials were made with an aniline endcapped polyamide acid (Ref. 2,3). The semicrystalline LaRC-TPI powder was also endcapped with amine and anhydride endcaps.

The average dry resin content and average volatiles content of each prepreg tape were determined and are listed in the table below. The values listed are averages from three specimens.

PREPREG	VOLATILES (WT%)	DRY RESIN (WT%)
1 Unmodified LaRC-TPI	13.2	31.9
2 DAA Doped LaRC-TPI	21.5	36.2
3 1:1 LaRC-TPI/LaRC-TPI Powder	13.9	31.8
4 1:1 Polyimidesulfone/LaRC-TPI Powder	31.7	54.5
5 2:1 Polyimidesulfone/LaRC-TPI Powder	10.5	37.3

The volatiles content was determined by drying tape specimens at 590K (600°F) for thirty minutes. The dry resin content of the prepreg was determined by acid digestion with sulfuric acid.

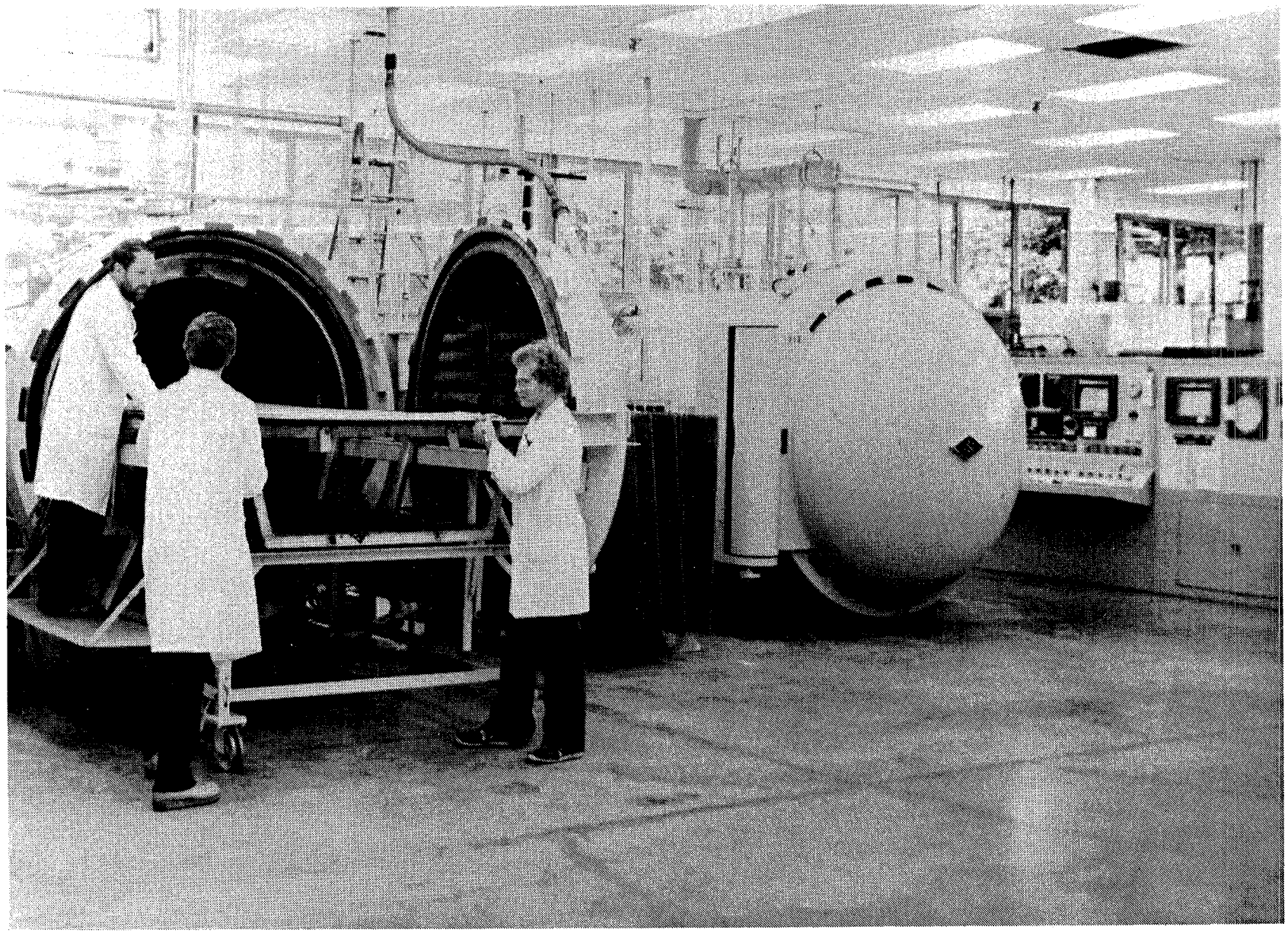
2.2.3 PRELIMINARY SCREENING TESTS OF PREPREG MATERIALS

Laminates were fabricated in both a press with heated platens and in an autoclave, using a consolidation process based on previous Boeing work on LaRC-TPI matrix resins, and on discussions with NASA personnel. Differential scanning calorimetry and thermogravimetric analysis were also performed on the prepreg tape materials and the data used as a guide for processing. The press and autoclaves used are shown in Photographs 2.2.3.1 and 2.2.3.2. The preparation of prepreg layups for consolidation is shown in Photograph 2.2.3.3. Process equipment tolerances are listed in Appendix D.

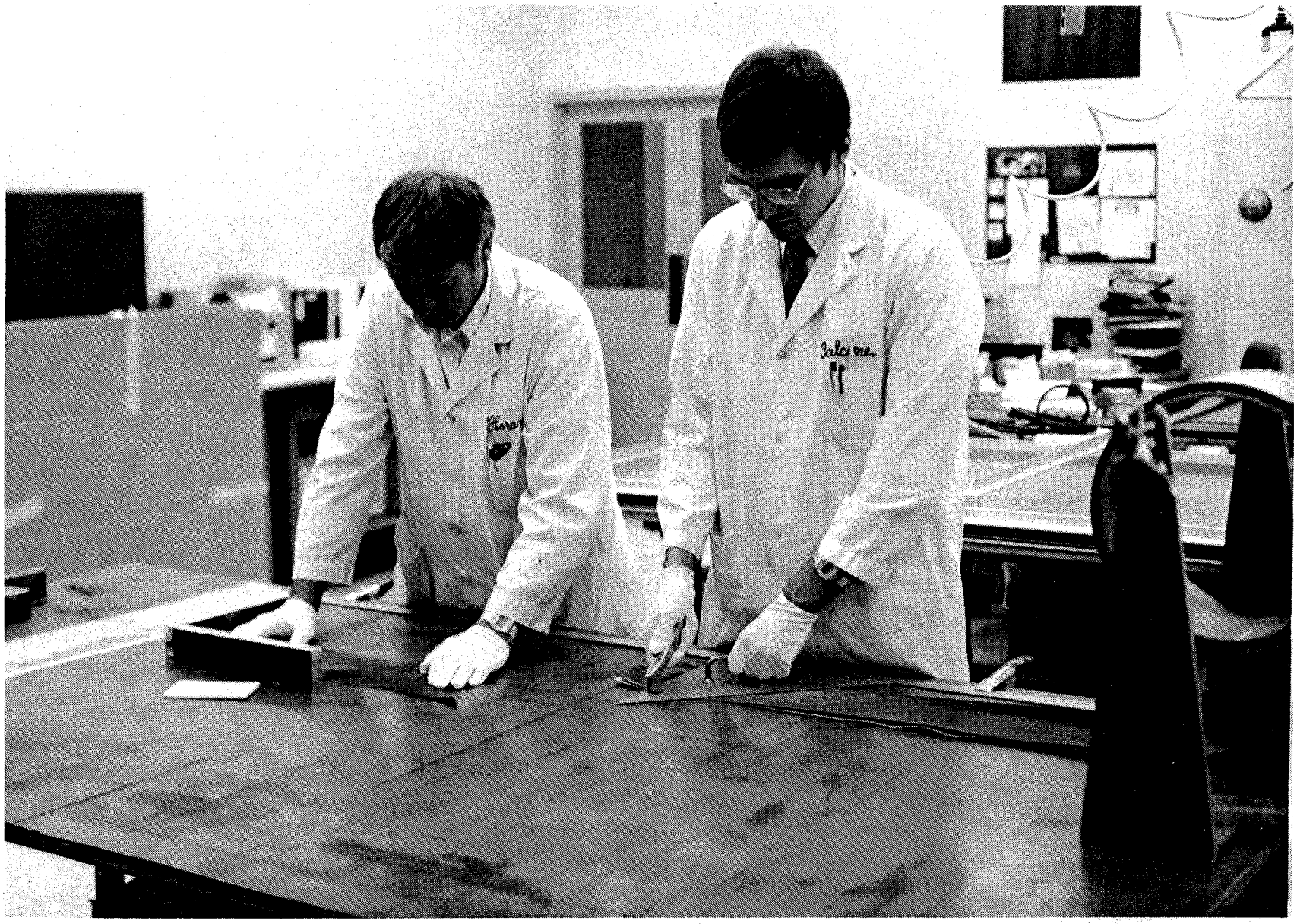
Differential scanning calorimetry (DSC) analysis and thermogravimetric analysis (TGA) were performed on each prepreg tape to obtain information about the transitions that occurred with heating. DSC and TGA analyses were performed using a Perkin-Elmer 7 Series Thermal Analysis System in a nitrogen atmosphere with sapphire as a reference material. DSC and TGA traces for the DAA doped LaRC-TPI prepreg tape are shown in Figures 2.2.3.1 and 2.2.3.2 respectively. Sample weights and heating rates are listed in the figures.

The DSC traces typically displayed a small endotherm around 430K (320°F) and the TGA traces showed a rapid increase in weight loss around 450K (350°F). The endotherm and weight loss occurred because of the loss of condensation reaction byproducts and diglyme solvent from the prepreg. Other than indicating the loss of volatiles the DSC traces were rather featureless and did not show the glass transition or the melting of the semicrystalline LaRC-TPI in those resin systems that contained the powder.

Photograph 2.2.3.1. The PHI (Pasadena Hydraulics, Inc.) Press



Photograph 2.2.3.2. Autoclaves at the Boeing Materials Technology Laboratory in Renton



Photograph 2.2.3.3. Preparation of Layups for Consolidation

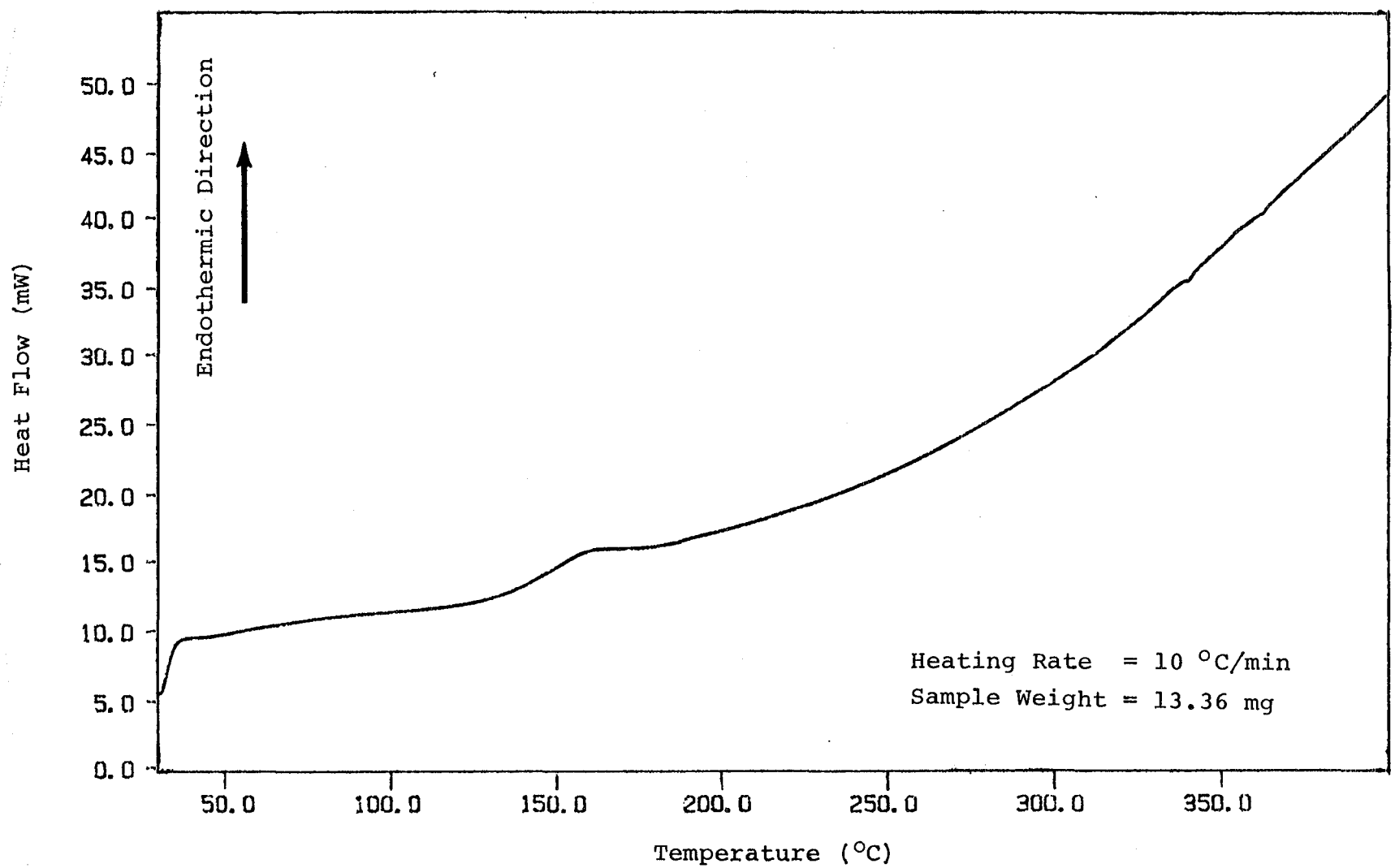


Figure 2.2.3.1. Differential Scanning Calorimetry (DSC) Trace for 2% DAA Doped LaRC-TPI/Celion 6K Prepreg Tape

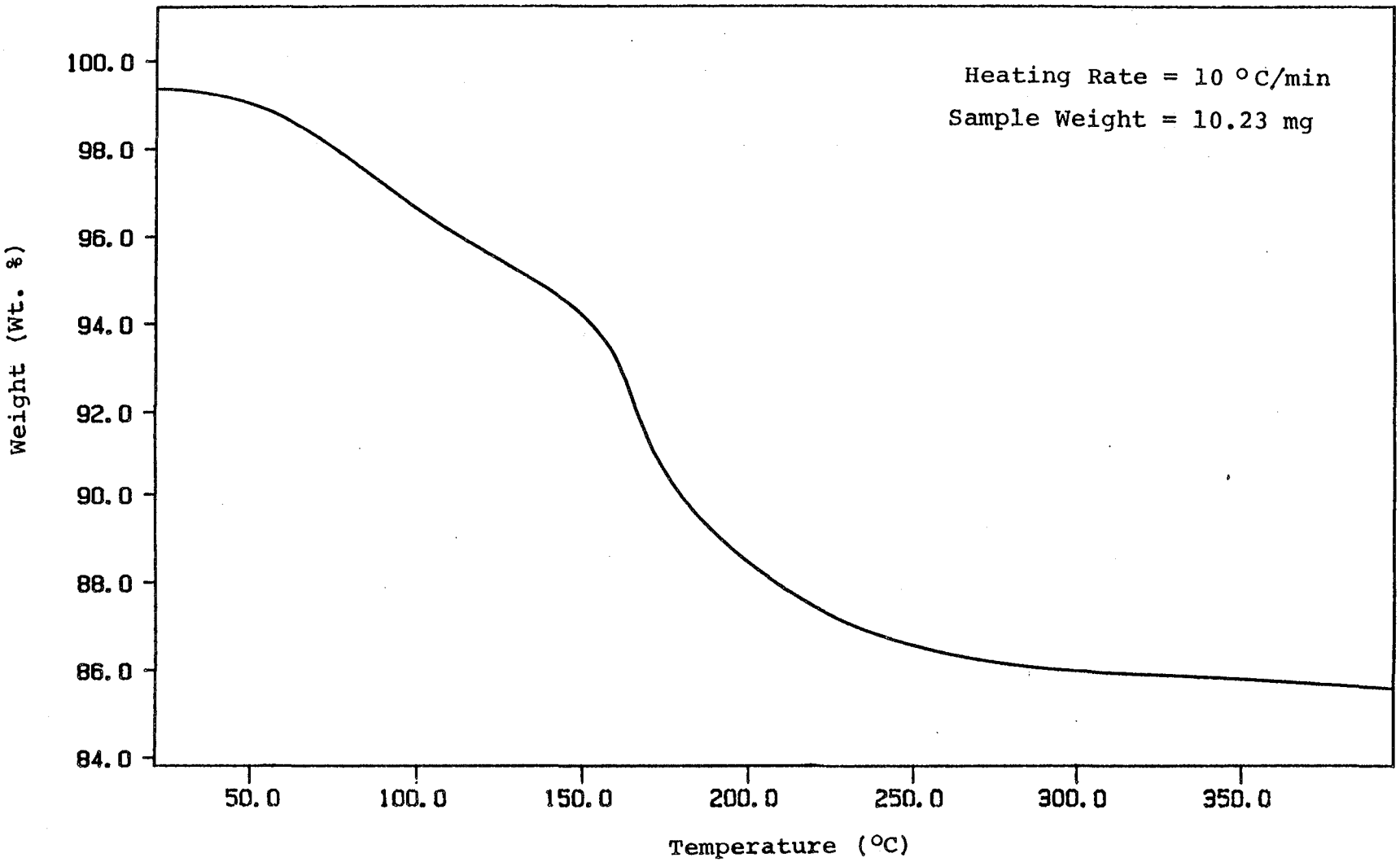


Figure 2.2.3.2. Thermogravimetric Analysis (TGA) Trace for 2% DAA Doped LaRC-TPI/Celion 6K Prepreg Tape

The consolidation process used for the press is summarized below:

1. The layup was heated to 470K (400°F) at 0.6 to 1.1 K/min (1 to 2 °F/min), under a low platen-closing pressure of 0.31 MPa (45 psi).

2. The temperature was held at 470K (400°F) for 30 minutes.

3. A pressure of 2.1 MPa (300 psi) was then applied and the layup was heated to 610K (650°F) at the rate of 2.2 to 3.3K/min. (4 to 6°F/min).

4. The layup was held at 610K (650°F) and 2.1 MPa (300 psi) for 2 hours.

5. The layup was cooled at the rate of 2.2 to 3.3K/min. (4 to 6° F/min.) and the pressure was removed below 420K (300°F).

A similar process was used in the autoclave, however a vacuum was applied during the inital heating to 470K and during the dwell at 470K.

A similar layup assembly was used in both press and autoclave. A diagram of a layup assembly is shown in Figure 2.2.3.3. The part layup was placed between sheets of permeable Armalon fabric and two plies (top and bottom) of Style 120 and Style 181 glass fabric. It was necessary to bake a release agent (Frekote 700) on the permeable Armalon at 450K (350°F) for thirty minutes, to allow easy removal of the Armalon after consolidation. In the press layup the Style 120 and Style 181 bleeder and breather plies were placed above the part layup only, and a layer of permeable Armalon and Kapton film (both with baked-on Frekote 700) were placed beneath the part.

A steel picture frame tool was used in the press consolidation process. A steel vacuum tool was used in the autoclave along with steel or titanium caul plates and edge bars.

A different processing method which involved predrying the prepreg was tried with the DAA (di(amic acid)) doped and polyimidesulfone systems. In this process the plies were cut to size and dried and imidized in a forced

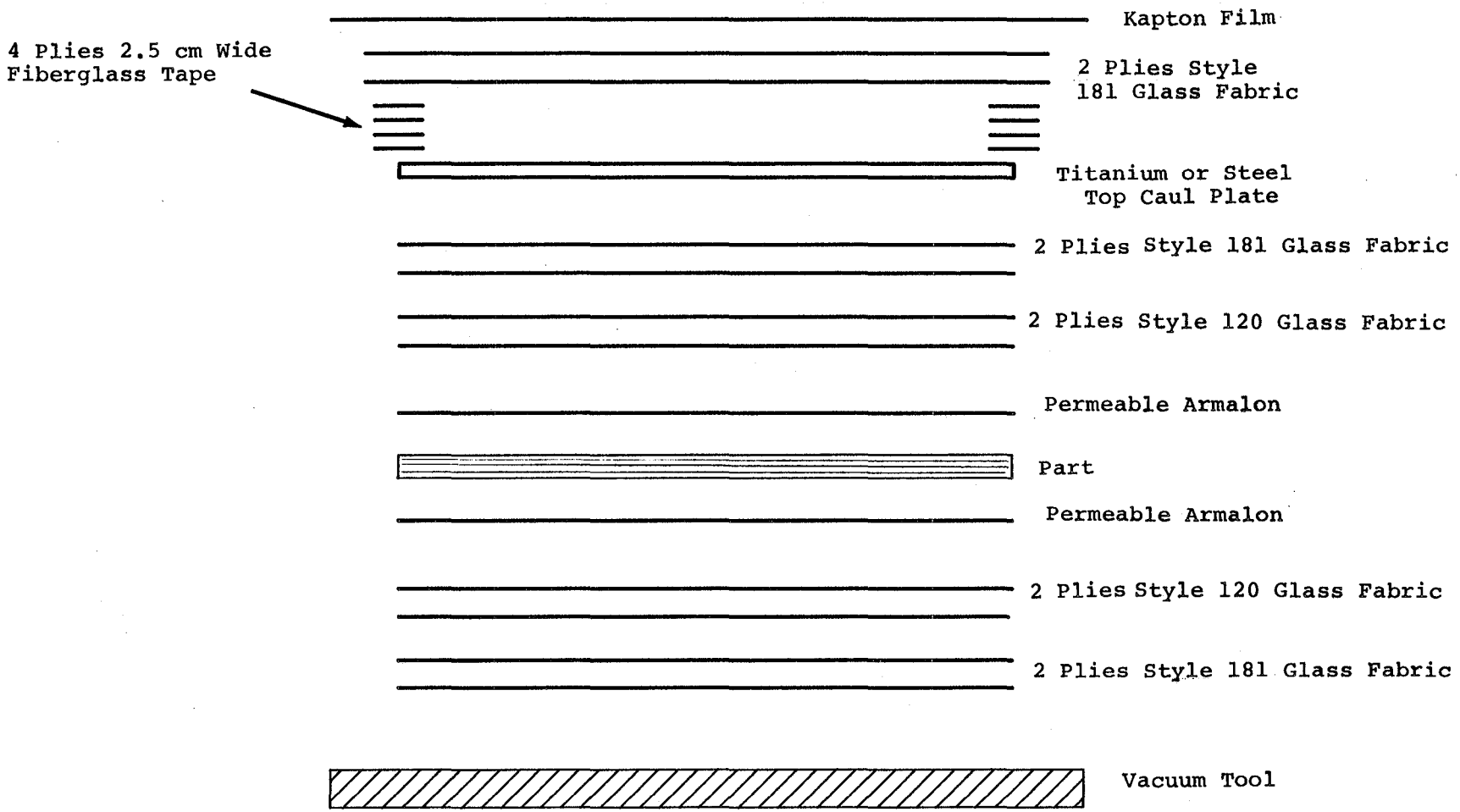


Figure 2.2.3.3. Diagram of a Layup Assembly for LaRC-TPI Processing

air oven between sheets of permeable Armalon, and kept flat by steel plates placed above and underneath the stack of plies. The plies were dried for one hour at 500K (450°F). After the plies had cooled they were assembled in a layup which was placed between Kapton sheets coated with Frekote 700.

The layup was consolidated in a 15.2 cm by 10.2 cm picture frame tool at 615K (650°F) and 2.1 MPa (300 psi) for one hour, and cooled under pressure below 420K (300°F). Practically no fusion of the plies took place, and the plies could be easily peeled from the laminate by hand. This oven-drying process produced laminates unsuitable for mechanical property testing.

Small, 15.2 cm by 10.2 cm, laminates were fabricated to obtain coupons for short-beam shear strength, and flexural strength and modulus determination. The laminate layups were either unidirectional and tested in the zero degree direction, or symmetric (0°/90°) crossply laminates. The laminates were usually 12 plies thick. A symmetric crossply laminate was not made from the LaRC-TPI/LaRC-TPI powder slurry resin system because this material had a low short-beam shear strength and flexural strength and modulus, compared with the other three systems.

The fiber volume fraction, resin content, and void content of each laminate were determined using sulfuric acid digestion of the resin and are listed along with the laminate density in Table 2.2.3.1. A resin specific gravity of 1.30 and a carbon fiber specific gravity of 1.76 were used for the calculation of laminate properties. The fiber volume fraction of the DAA doped LaRC-TPI was rather high compared to the other systems. The void content of the crossply laminates tended to be higher than the void content of the unidirectional laminates. The lower void content of the 2:1 polyimidesulfone/LaRC-TPI laminates may have been due to the higher dwell temperature that was used (505K versus 480K) in processing.

Through-transmission ultrasonic (TTU) scans were also made on each of the 15.2 cm by 10.2 cm laminates and are shown in Figures C1 through C10 in Appendix C. The TTU scans were made at a frequency of 5 MHz and a signal voltage of 6 volts. The higher the number on the scan plot the greater the attenuation of the signal. The double dots indicate almost no

TABLE 2.2.3.1

LaRC-TPI LAMINATE PHYSICAL PROPERTY DATA

		12 PLY UNIDIRECTIONAL				12 PLY, SYMMETRIC (0°/90°)			
	COMPOSITE SYSTEM	RESIN CONTENT, (Vol %)	FIBER CONTENT, (Vol %)	VOID CONTENT, (Vol %)	DENSITY, (g/cm^3)	RESIN CONTENT, (Vol %)	FIBER CONTENT, (Vol %)	VOID CONTENT, (Vol %)	DENSITY, (g/cm^3)
1.	UNMODIFIED LaRC-TPI AND CELION 6K	41.4	57.4	1.2	1.55	34.3	60.5	5.2	1.51
2.	2% DAA Doped LaRC-TPI AND CELION 6K	28.2	69.2	2.6	1.58	30.6	64.3	5.1	1.53
3.	1:1 LaRC-TPI SLURRY AND CELION 6K	40.9	56.3	2.8	1.52	--	--	--	--
4.	1:1 $PISO_2$/LaRC-TPI SLURRY AND T300 3K	46.8	53.2	0.0	1.57	51.6	43.3	5.1	1.43
5.	2:1 $PISO_2$/LaRC-TPI SLURRY AND AS-4 12K	48.7	51.3	0.0	1.61	47.7	52.3	0.0	1.59

* Average of three specimens

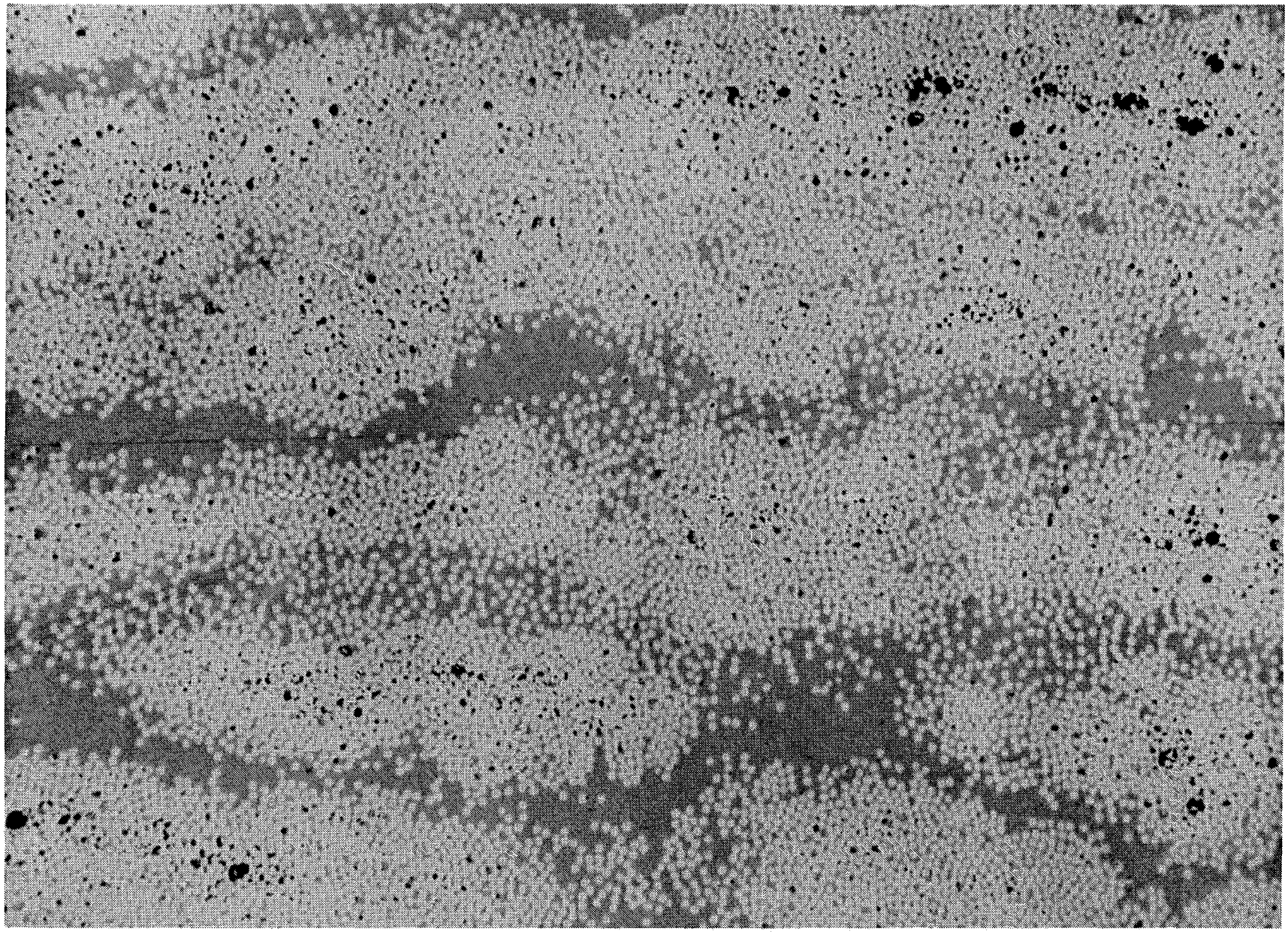
attenuation of the signal. A plot with double dots, ones, and twos indicates that the laminate is of good quality. A number three or higher number indicates the probable presence of voids in the laminate.

The TTU scans indicate that the best quality laminates, both unidirectional and crossply, were obtained from the DAA doped and polyimide-sulfone/LaRC-TPI resin systems. TTU scans are not a conclusive indicator of laminate quality, and must be considered along with laminate void content determinations and with metallographic mounts of laminate cross sections.

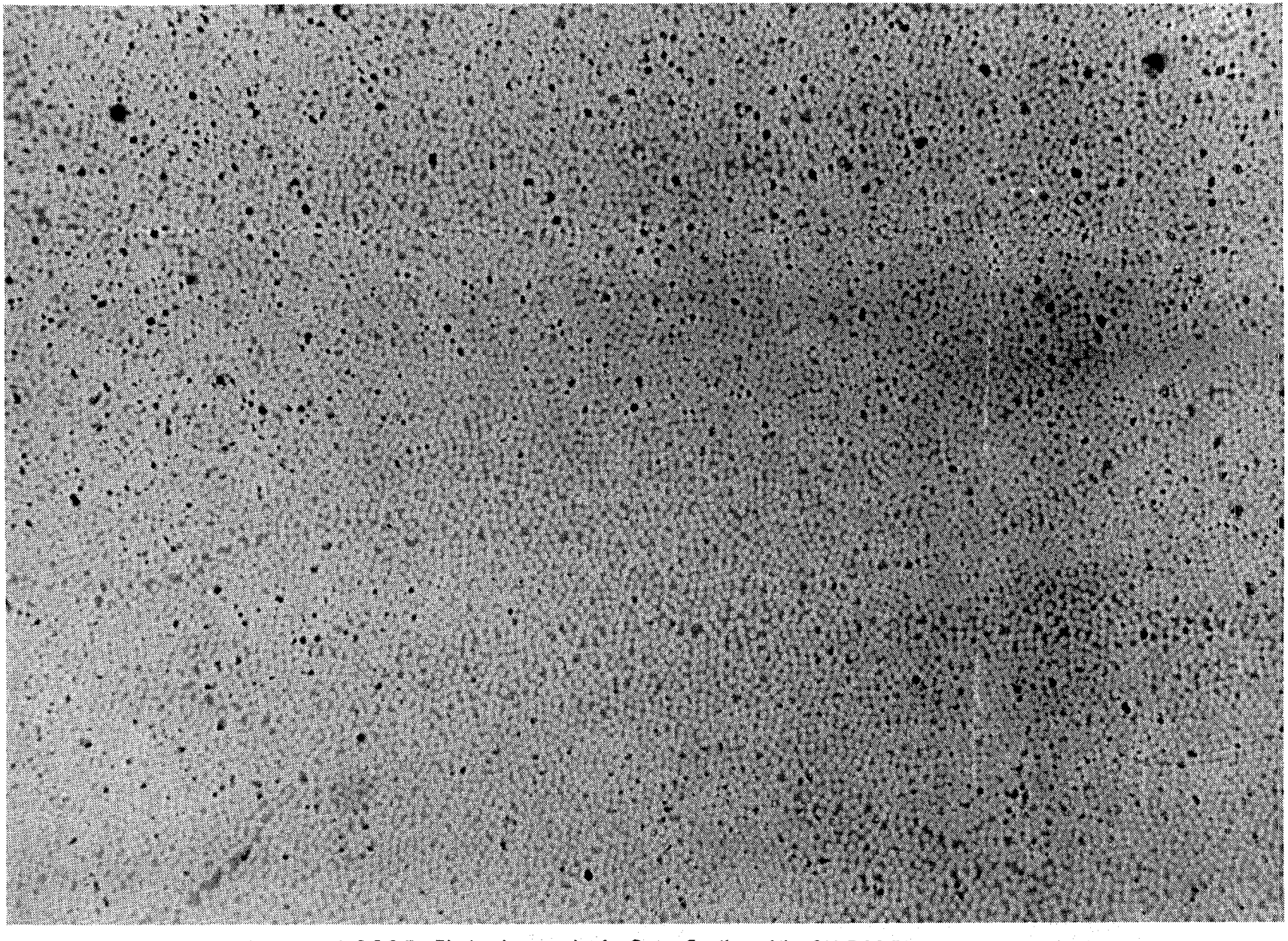
Polished mounts of laminate cross sections were prepared to examine the composite morphology. Photomicrographs of some of these cross sectional mounts are shown in Photographs 2.2.3.4 through 2.2.3.9. All of these cross sections were taken transverse to the fibers in the unidirectional laminates. The most striking difference between the various composite systems is that the unmodified LaRC-TPI resin and the 1:1 LaRC-TPI slurry had stratified layers of fibers and resin, while the other three systems (the DAA doped and the polyimidesulfone) exhibited more uniformly distributed fibers and resin. Apparently the DAA doped and polyimidesulfone had better melt flow characteristics during processing than the unmodified and LaRC-TPI slurry resin systems. As will be discussed later, the DAA doped and polyimidesulfone resin systems also yielded composites with superior mechanical properties.

Microcracking can sometimes be a problem with high temperature composite resin systems such as PMR-15 polyimide. The microcracks are intralaminar cracks that result from high thermal strains produced by large temperature changes during the final stages of processing. Intralaminar cracks form perpendicular to the plane of the plies because ply shrinkage in the transverse direction (to the fibers) is constrained by the adjacent 90 degree plies. A cross section of such a crossply laminate taken at a 45 degree angle will show cracks in all plies. The cracks run through the ply thicknesses, perpendicular to the plane of the laminate plies.

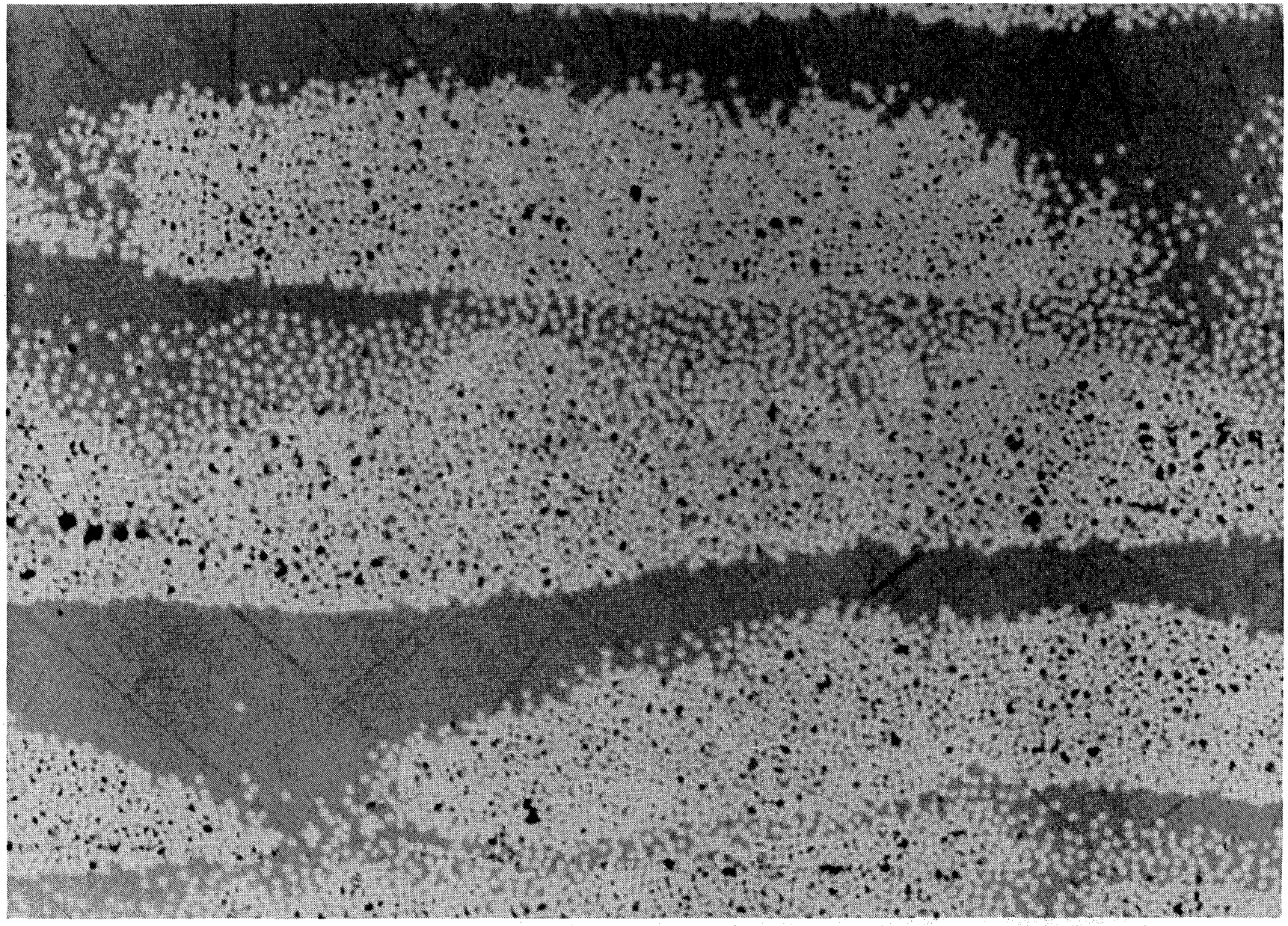
Metallographic mounts were prepared of laminate cross sections taken at 45 degrees of symmetric ($0^{o}/90^{o}$) crossply laminates fabricated from the



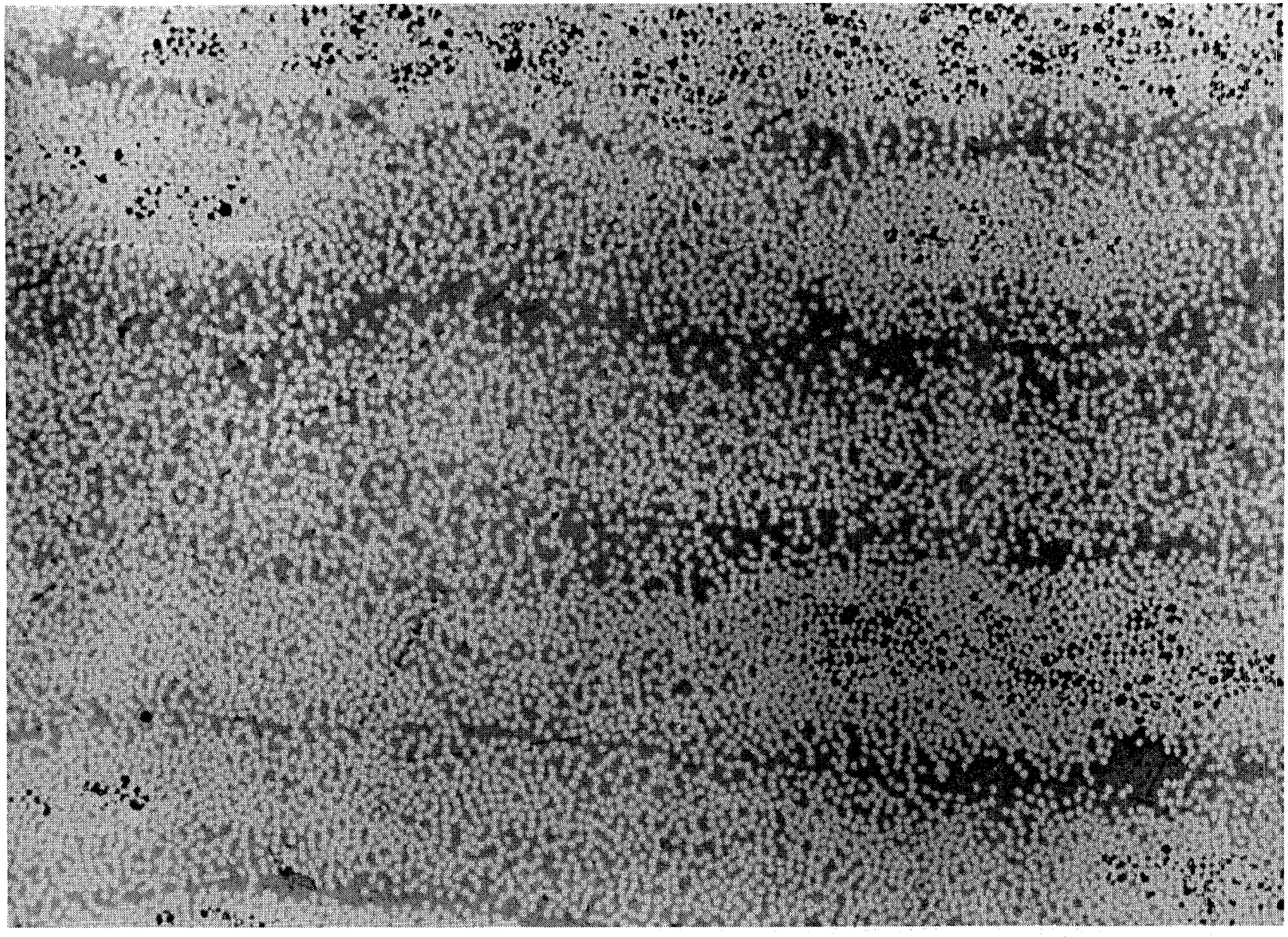
Photograph 2.2.3.4. Photomicrograph of a Cross-Section of the Unmodified LaRC-TPI Unidirectional Laminate



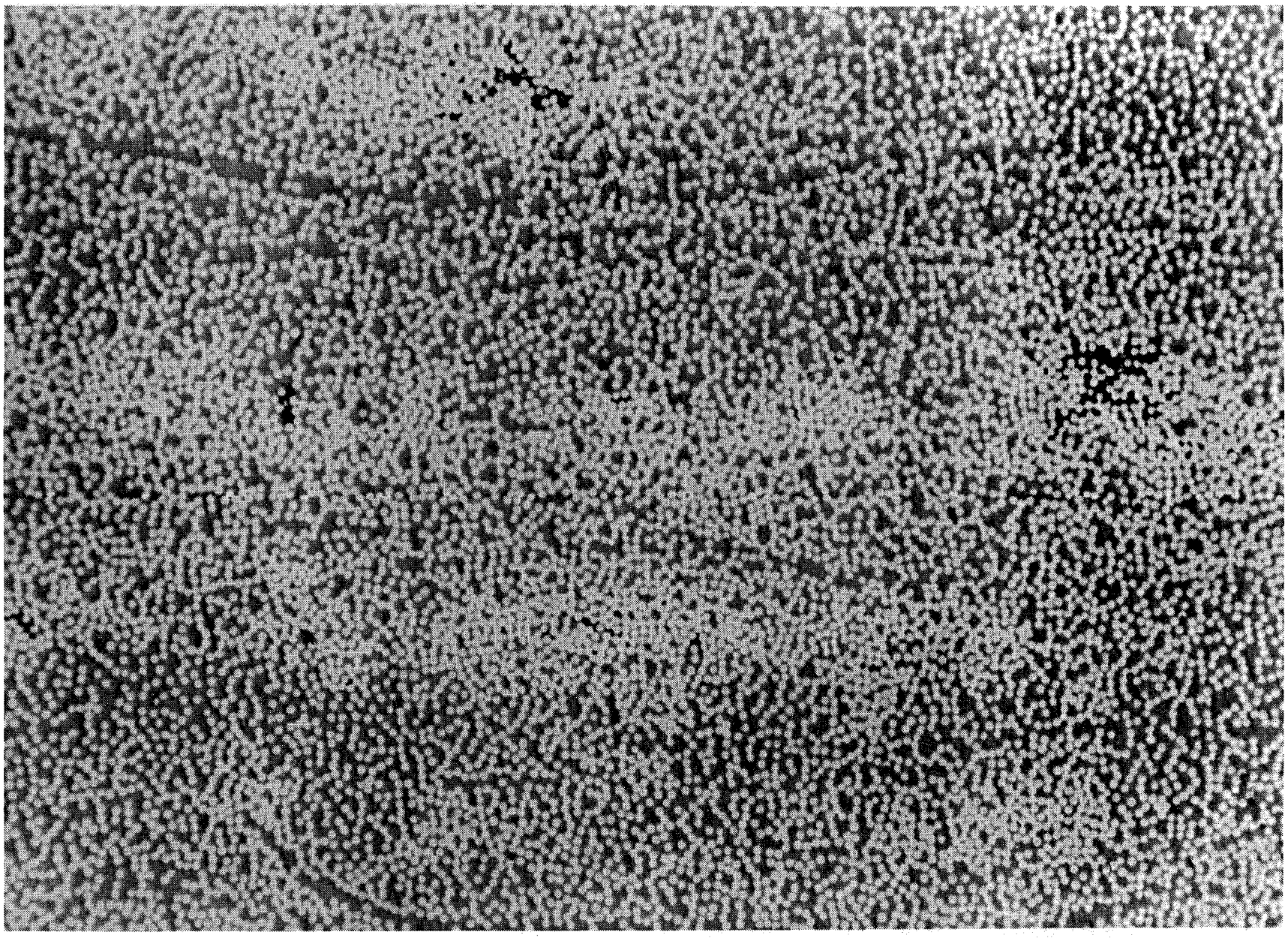
Photograph 2.2.3.5. Photomicrograph of a Cross-Section of the 2% DAA Doped LaRC-TPI Unidirectional Laminate



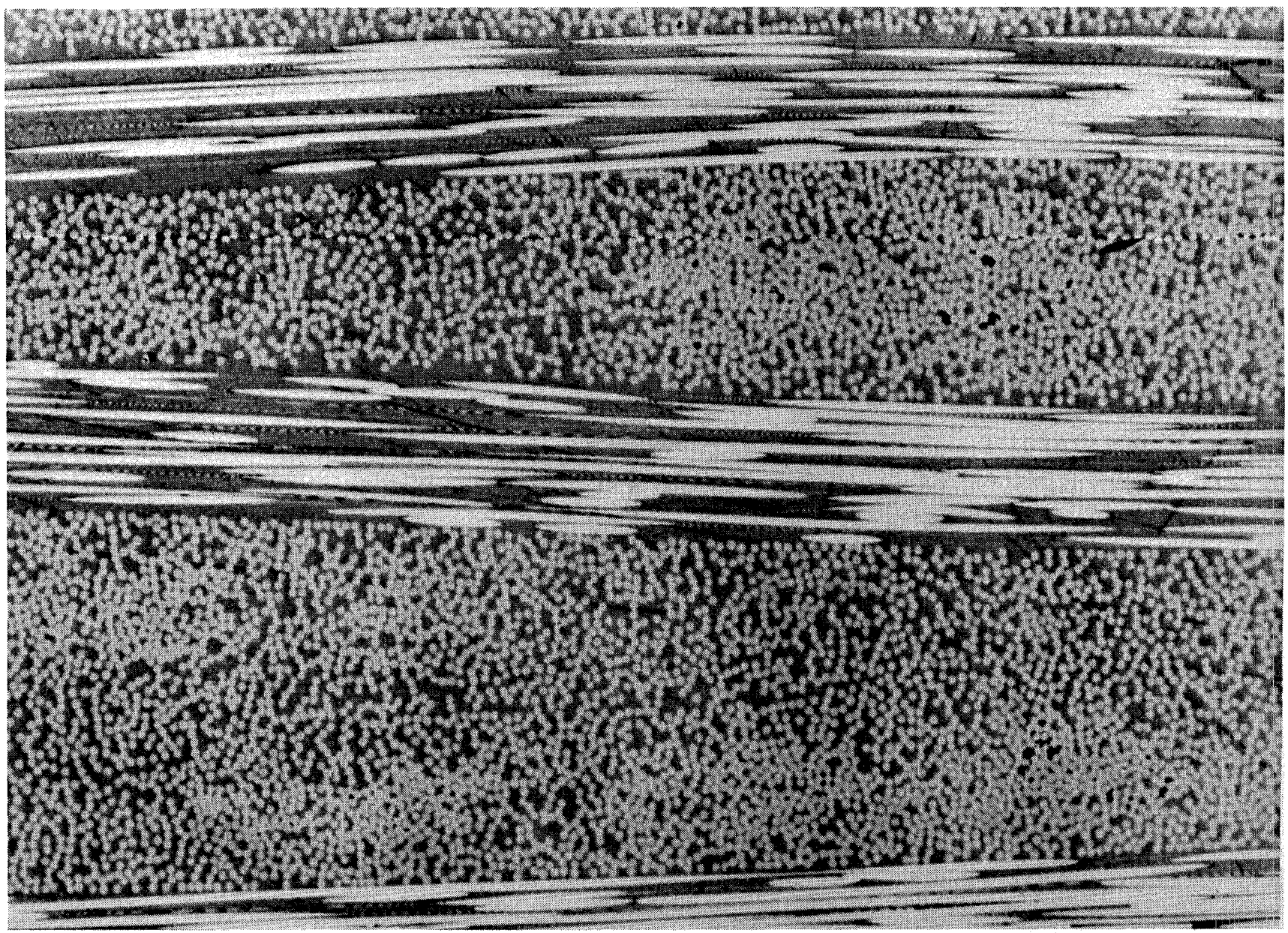
Photograph 2.2.3.6. Photomicragraph of a Cross-Section of the 1:1 LaRC-TPI Slurry Unidirectional Laminate



Photograph 2.2.3.7. Photomicrograph of a Cross-Section of the 1:1 Polyimidesulfone/ LaRC-TPI Slurry Unidirectional Laminate



Photograph 2.2.3.8. Photomicrograph of a Cross-Section of the 2:1 Polyimidesulfone/ LaRC-TPI Unidirectional Laminate



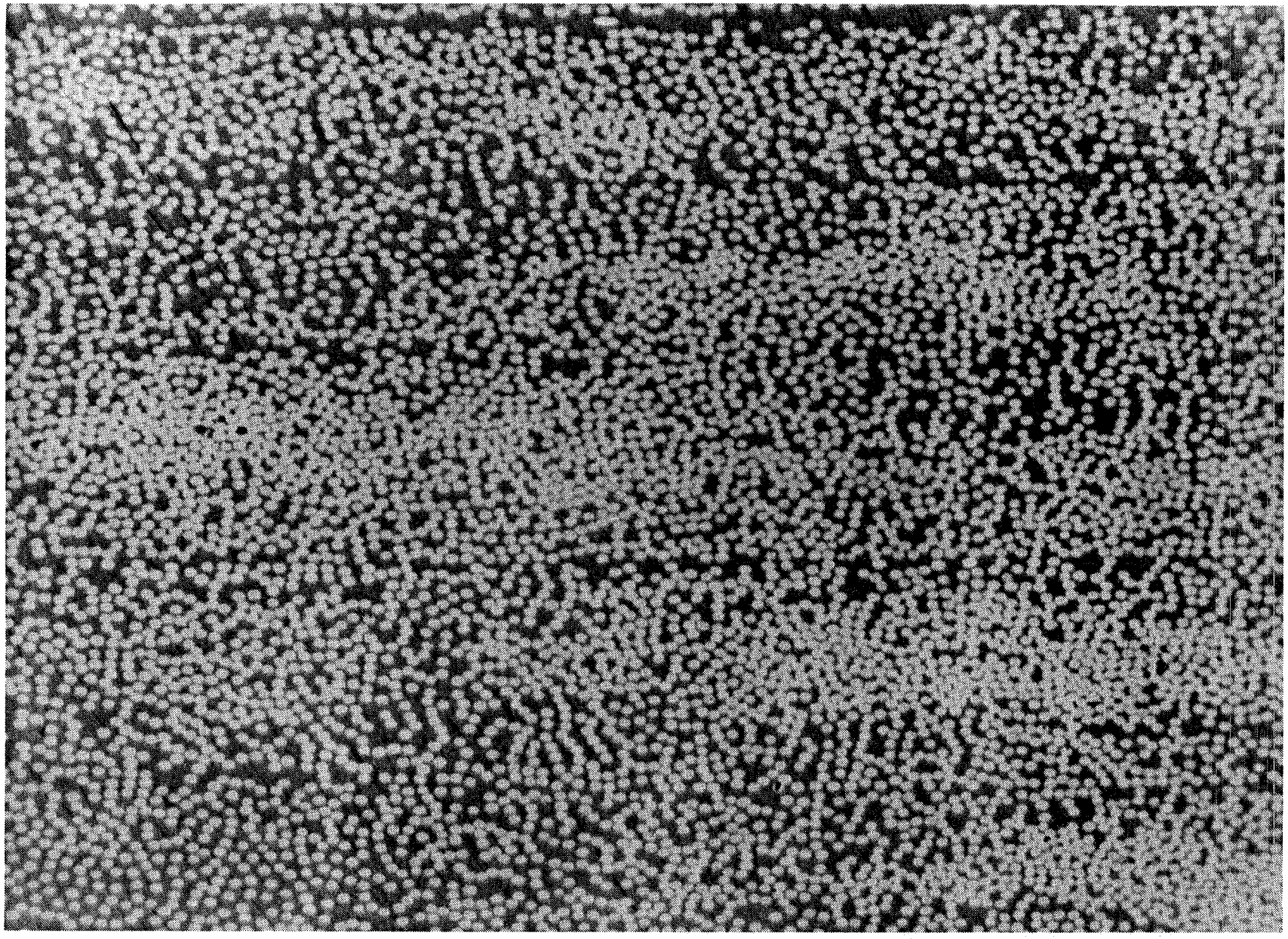
Photograph 2.2.3.9. Photomicrograph of a Cross-Section of the 2:1 Polyimidesulfone/ LaRC-TPI Crossply Laminate

DAA doped and polyimidesulfone/LaRC-TPI resin systems. A photomicrograph of the cross section of the 2:1 polyimidesulfone/LaRC-TPI laminate is shown in Photograph 2.2.3.10. No intralaminar cracks were observed in this cross section, or in a similar section of the crossply laminate fabricated from the 2% DAA doped LaRC-TPI. Microcracking did not appear to occur in these LaRC-TPI laminates as fabricated.

The average short-beam shear strengths of the five LaRC-TPI composite systems are listed in Table 2.2.3.2, for both unidirectional and crossply laminates. Average flexural strengths and moduli are listed in Table 2.2.3.3, and the values are normalized to a fiber volume fraction of 55% in Table 2.2.3.4. The unidirectional laminates were tested at both ambient temperature and 450K (350°F). Three to five specimens were tested for each property at each test temperature. The short-beam shear strengths are also plotted in the bar graph of Figure 2.2.3.4. The flexural strengths and flexural moduli were also normalized to a fiber volume fraction of 55% and plotted in the bar graph of Figure 2.2.3.5. Comparing the mechanical property values in Tables 2.2.3.2 and 2.2.3.4, and in Figures 2.2.3.4 and 2.2.3.5 shows that the best composite resin systems appear to be the DAA doped and the polyimidesulfone/LaRC-TPI.

The short-beam shear and flexural properties of the DAA doped and polyimidesulfone/LaRC-TPI resin systems compare very favorably with other thermoplastic composite matrix materials such as polysulfone, polyethersulfone, and DuPont's thermoplastic polyimide AVIMID® K-III. Typical short-beam shear strengths for these graphite reinforced composites range from 64 to 99 MPa at ambient temperature, and from 43 to 58 MPa at 450K (Ref. 6, 7, and 8). DuPont reports a room temperature short-beam shear strength of 99 MPa for AVIMID® K-III (IM-6 carbon fiber, 56 volume %). The short-beam shear strengths for the DAA doped and polyimidesulfone LaRC-TPI systems (unidirectional laminates) in Table 2.2.3.2 range from 77 to 115 MPa at ambient temperature, and were about 60 MPa at 450K.

Comparing flexural strength and moduli of these composite systems, the flexural strength at ambient temperature of thermoplastic composites ranges from about 1,070 to 1,482 MPa and the flexural modulus ranges



Photograph 2.2.3.10. Photomicrograph of a Cross-Section of the 2:1 Polyimidesulfone/ LaRC-TPI Crossply Laminate, Taken at an Angle of 45 deg

TABLE 2.2.3.2

AVERAGE SHORT-BEAM SHEAR STRENGTHS OF 5 LaRC-TPI COMPOSITE SYSTEMS*
(ASTM D2344)

Unidirectional Laminates	AMBIENT TEMP. MPa	(Ksi)	450K(350°F) MPa	(Ksi)
Systems				
(1) Unmodified LaRC-TPI and Celion 6K	73.1	(10.6)	45.4	(6.58)
(2) 2% DAA Doped LaRC-TPI and Celion 6K	91.0	(13.2)	60.0	(8.74)
(3) 1:1 LaRC-TPI Slurry and Celion 6K	44.3	(6.42)	34.3	(4.97)
(4) 1:1 $PISO_2$/LaRC-TPI Slurry and T300 3K	77.2	(11.2)	59.6	(8.67)
(5) 2:1 $PISO_2$/LaRC-TPI and AS-4 12K	115	(16.7)	59.8	(8.67)
Symmetric (0°/90°) Crossply Laminates				
Systems				
(1) Unmodified LaRC-TPI and Celion 6K	16.1	(2.33)	--	--
(2) 2% DAA Doped LaRC-TPI and Celion 6K	59.3	(8.60)	--	--
(3) 1:1 LaRC-TPI Slurry and Celionn 6K	--	--	--	--
(4) 1:1 $PISO_2$/LaRC-TPI Slurry and T300 3K	39.8	(5.77)	--	--
(5) 2:1 $PISO_2$/LaRC-TPI Slurry and AS-4 12K	83.4	(12.1)	--	--

* Average of three to five specimens

Table 2.2.3.3. **Average Flexural Strength and Modulus of Five LaRC-TPI Composite Systems (ASTM D790)***

Unidirectional Laminates	AMBIENT TEMPERATURE				450K (350°F)			
	STRENGTH		MODULUS		STRENGTH		MODULUS	
	MPa	(Ksi)	GPa	(Msi)	MPa	(Ksi)	GPa	(Msi)
Systems								
(1) Unmodified LaRC-TPI and Celion 6K	1 820	(264)	141	(20.4)	1 120	(163)	106	(15.4)
(2) 2% DAA Doped LaRC-TPI and Celion 6K	1,480	(214)	132	(19.2)	1,230	(178)	130	(18.8)
(3) 1:1 LaRC-TPI Slurry and Celion 6K	828	(120)	100	(14.5)	511	(74.1)	101	(14.7)
(4) 1:1 $PISO_2$/LaRC-TPI Slurry and T300 3K	1,140	(165)	91.0	(13.2)	903	(131)	86.2	(12.5)
(5) 2:1 $PISO_2$/LaRC-TPI Slurry and AS-4 12K	1,460	(211)	101	(14.6)	986	(143)	97.2	(14.1)
Symmetric (0°/90°) Crossply Laminates								
Systems								
(1) Unmodified LaRC-TPI and Celion 6K	203	(29.5)	37.4	(5.42)	--	--	--	--
(2) 2% DAA Doped LaRC-TPI and Celion 6K	828	(120)	42.1	(6.10)	--	--	--	--
(3) 1:1 LaRC-TPI Slurry and Celion 6K	--	--	--	--	--	--	--	--
(4) 1:1 $PISO_2$/LaRC-TPI Slurry and T300 3K	511	(74.1)	32.0	(4.64)	--	--	--	--
(5) 2:1 $PISO_2$/LaRC-TPI Slurry and AS-4 12K	1,080	(157)	67.9	(9.85)	--	--	--	--

* Average of three to five specimens

Table 2.2.3.4. **Average Flexural Strength and Modulus of Five LaRC-TPI Composite Systems (ASTM D790), Normalized to a Carbon Fiber Volume Fraction of 55%**

UNIDIRECTIONAL LAMINATES	AMBIENT TEMPERATURE				450K (350°F)			
	STRENGTH		MODULUS		STRENGTH		MODULUS	
	MPa	(Ksi)	GPa	(Msi)	MPa	(Ksi)	GPa	(Msi)
Systems								
(1) Unmodified LaRC-TPI and Celion 6K	1,740	(253)	135	(19.5)	1,070	(156)	102	(14.8)
(2) 2% DAA Doped LaRC-TPI and Celion 6K	1,180	(170)	105	(15.3)	978	(141)	103	(14.9)
(3) 1:1 LaRC-TPI Slurry and Celion 6K	809	(117)	97.7	(14.2)	499	(72.4)	98.7	(14.4)
(4) 1:1 $PISO_2$/LaRC-TPI Slurry and T300 3K	1,180	(171)	94.1	(13.6)	934	(135)	89.1	(12.9)
(5) 2:1 $PISO_2$/LaRC-TPI Slurry and AS-4 12K	1,570	(226)	108	(15.7)	1,060	(153)	104	(15.1)
Symmetric (0°/90°) Crossply Laminates								
Systems								
(1) Unmodified LaRC-TPI and Celion 6K	185	(26.8)	34.0	(4.93)	--	--	--	--
(2) 2% DAA Doped LaRC-TPI and Celion 6K	753	(109)	38.3	(5.55)	--	--	--	--
(3) 1:1 LaRC-TPI Slurry and Celion 6K	--	--	--	--	--	--	--	--
(4) 1:1 $PISO_2$/LaRC-TPI Slurry and T300 3K	649	(94.1)	40.6	(5.89)	--	--	--	--
(5) 2:1 $PISO_2$/LaRC-TPI Slurry and AS-4 12K	1,140	(165)	71.4	(10.4)	--	--	--	--

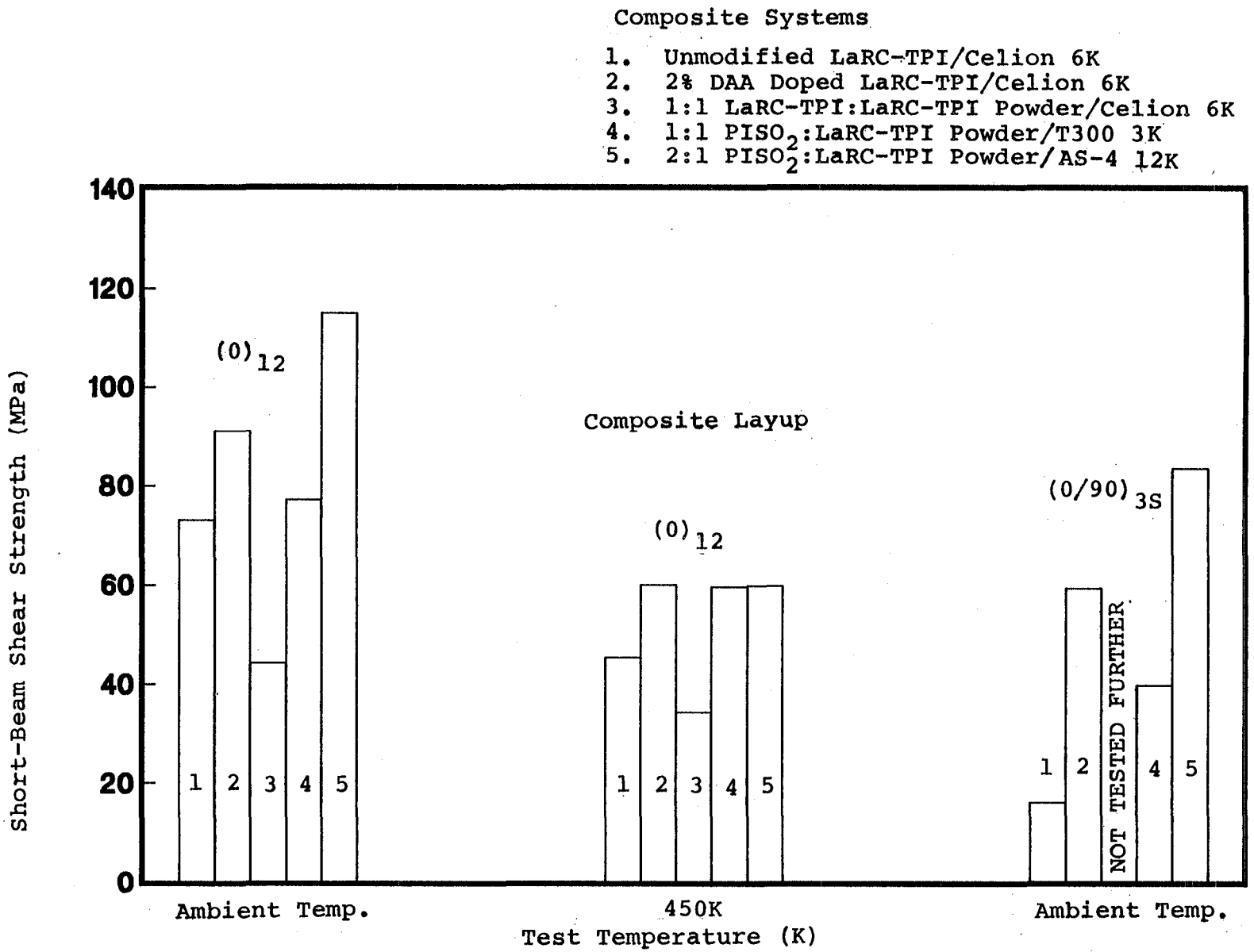


Figure 2.2.3.4 Average Short-Beam Shear Strengths of Five LaRC-TPI Composite Systems

Composite Systems

1. Unmodified LaRC-TPI/Celion 6K
2. 2% DAA Doped LaRc-TPI/Celion 6K
3. 1:1 LaRC-TPI:LaRC-TPI Powder/Celion 6K
4. 1:1 $PISO_2$:LaRC-TPI Powder/T300 3K
5. 2:1 $PISO_2$:LaRC-TPI Powder/AS-4 12K

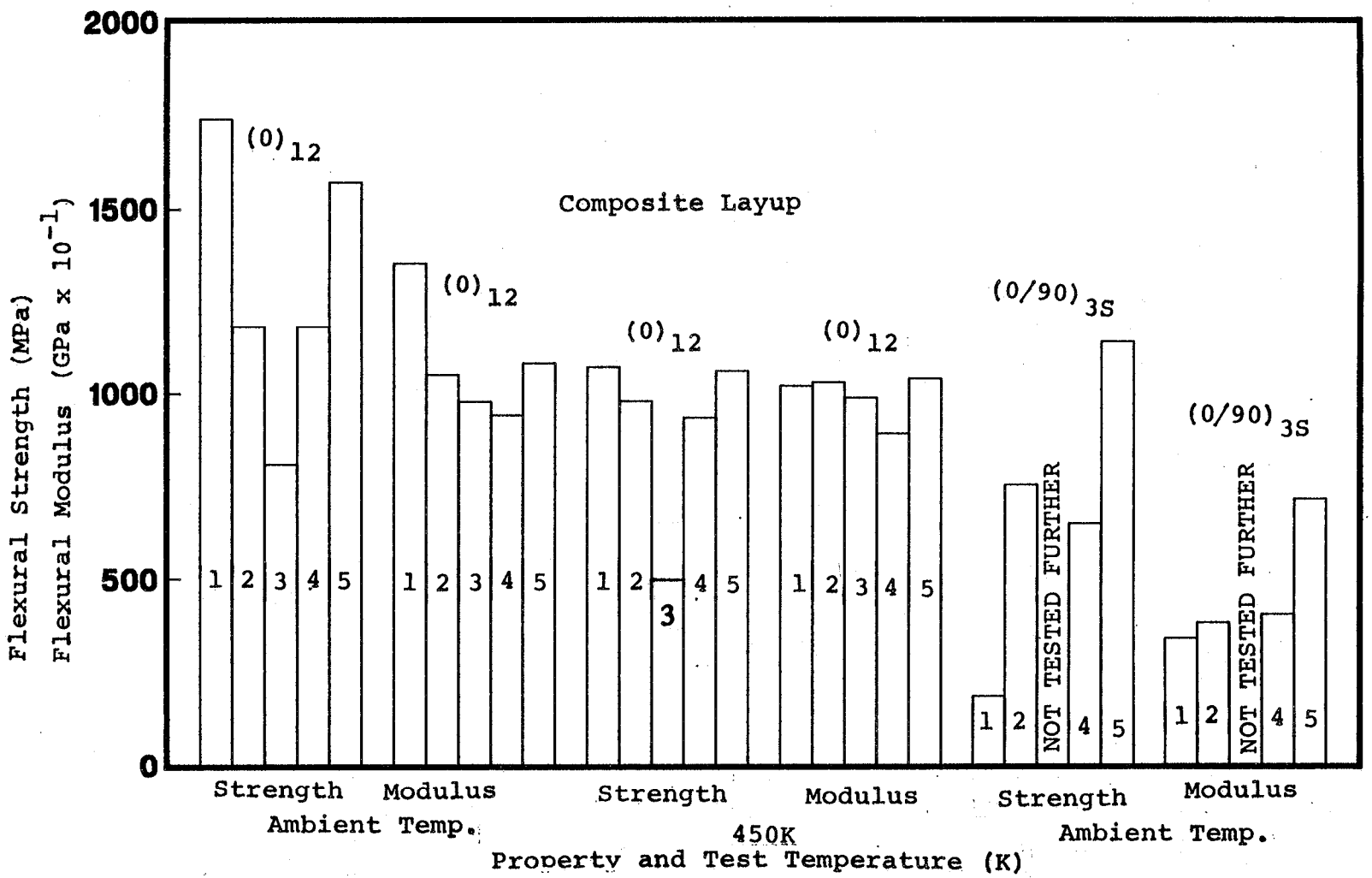


Figure 2.2.3.5 Flexural Strength and Modulus of Five LaRC-TPI Composite Systems Normalized to Fifty-Five Volume Percent Carbon Fiber Reinforcement

from 123 to 193 GPa (Ref. 6, 7, and 8). DuPont reports values of 1,482 MPa and 116 GPa for the flexural strength and modulus respectively of AVIMID® K-III at ambient temperature. In Table 2.2.3.4 the flexural strengths of the DAA doped and the polyimidesulfone LaRC-TPI systems range from 1,180 to 1,570 MPa and the flexural moduli from 94 to 108 GPa.

At 450K the flexural strength of some typical thermoplastic composites ranges from 710 to 1,089 MPa and the flexural modulus ranges from 138 to 163 GPa (Ref. 6, 7, and 8). The flexural strength of AVIMID® K-III composites at 450K was 1,089 MPa, and the flexural modulus was 141 GPa. For the DAA doped and polyimidesulfone LaRC-TPI systems in Table 2.2.3.4 the flexural strength was 934 to 1,060 MPa, and the flexural modulus was 90 to 104 GPa at 450K.

Based on the superior mechanical properties of the DAA doped and polyimidesulfone LaRC-TPI composite resin systems, these resins were selected by Boeing with the concurrence of the NASA technical monitor for further evaluation in the program. Additional mechanical tests were performed on laminates made from new batches of the two wt. % DAA doped LaRC-TPI and from the 2:1 polyimidesulfone/LaRC-TPI slurry. The results of tension, compression, compression-after-impact, and dynamic mechanical analysis on these composite systems are reported in the next section.

2.3 Composite Mechanical Property Evaluation

2.3.1 PREPREG TAPE MATERIALS

Composite laminates were fabricated from the two LaRC-TPI resin prepreg systems selected for evaluation in the final phase of the program. The resins selected were the di (amic acid) (DAA) doped LaRC-TPI and the 2:1 polyimidesulfone/semicrystalline LaRC-TPI powder slurry. Tensile tests, compression tests, and dynamic mechanical analysis were performed on one or both of the LaRC-TPI composite systems.

The prepreg materials were prepared by Dr. Richard Moulton of AM Technology Inc. The prepregs were in the form of 15.2 cm (6 inch) wide unidirectional tapes, with sized Celion 6K carbon fiber as the reinforcement.

The resin content and volatiles content of each roll of prepreg tape are listed below.

Prepreg System	Roll No.	Batch No.	Volatiles (wt %)	Resin (wt%)
2% DAA Doped LaRC-TPI	02	DT-347	15.3	47.8
	03	DT-347	17.6	37.9
2:1 $PISO_2$/LaRC-TPI	02	DT-348	14.8	41.5
	03	DT-348	11.8	52.8

Each value was obtained from the average of three specimens. The volatiles content was determined by drying the specimens at 590K (600°F) for thirty minutes.

2.3.2 Laminate Fabrication

All of the LaRC-TPI laminates that were tested were fabricated at Boeing with the exception of one 15.2 cm by 15.2 cm by 40 ply laminate produced at NASA-Langley, which was used for compression-after-impact testing.

Laminates were consolidated in an autoclave using the following process:

1. The layup was heated at the approximate rate of 4.4K/min (8°F/min) to 520K (475°F) under vacuum and a low autoclave pressure of 0.1 MPa (15 psi).
2. The layup was held at 520K for 30 minutes.

3. The layup was heated to 620K (660°F) at the rate of 4.4K/min. A consolidation pressure of 2.1 MPa (300 psi) was applied at 560K (550°F) and the vacuum removed.
4. The layup was held at 620 K and 2.1 MPa for one hour.
5. The laminate was cooled at the approximate rate of 4.4K/min. under 2.1 MPa until the temperature dropped below 422K (300°F).

A diagram of the layup assembly used in laminate fabrication is shown in Figure 2.2.3.3. The prepreg layups were placed between two layers of permeable Armalon that had Frekote 700 release agent baked on at 450K (350°F) for 30 minutes. Two layers of Style 120 glass fabric followed by two layers of Style 181 glass fabric were placed adjacent to the Armalon, above and below the layup. The layup assembly was constructed on a vacuum tool and steel or titanium caul plates were placed on the top ply of Style 181 glass cloth over the prepreg layups. Four layers of one inch wide fiberglass tape were placed along the edges of the caul plates, and the entire layup assembly was covered by two layers of Style 181 glass cloth with Kapton film on top.

The laminate produced by NASA-Langley was a 40 ply quasi-isotropic laminate and was fabricated by drying the prepreg material prior to layup and consolidation in a press. The resin system was a 1:1 slurry of $PISO_2$ and LaRC-TPI powder to which 2.5 wt. % DAA was added, and the fiber reinforcement was unsized Hercules AS-4 12K carbon fiber. The prepreg was predried in air for one hour at 530K (500°F). The 40 ply layup was heated at 530K for five hours, 550K for two hours, 620K for one hour, and cooled to ambient temperature. A consolidation pressure of 2.1 MPa was applied from the time the laminate reached a temperature of 530K until it was cooled below 420K.

Through transmission ultrasonic (TTU) scans of the six laminates that were fabricated and mechanically tested are shown in Appendix C (Figures C.11 to C.15). A frequency of 5 MHz and a signal voltage of 6 volts were used to make these scans. Low numbers on the TTU scans indicate little attenuation of the signal; the double dots on the scan pattern indicate almost no attenuation of the signal. The TTU scans indicate that these are good, dense laminates.

The physical properties of the six laminates are listed in Table 2.3.2.1. All the laminates had low void contents. According to some sources in the ACDP (Advanced Composite Development Program) Group at Boeing the recommended fiber volume fraction for tough composite laminates is around 55 volume %, so these fiber volume fractions are in an acceptable range.

A good crossply laminate could not be produced from the 2:1 polyimidesulfone ($PISO_2$)/LaRC-TPI material using the processing procedure listed previously due to the exceptionally high inherent viscosity (0.69 versus the usual 0.5 dl/g at 298K) of the resin polyimidesulfone-diglyme solution. A crossply laminate ($\pm$45 degrees, 16 plies) was needed for dynamic mechanical analysis coupons. No further attempts to fabricate crossply laminates and thick laminates from this system were made; NASA is having this resin system reformulated using an endcap additive to limit the polymer molecular weight and thereby reduce the inherent viscosity.

Thick 20 ply (15.2 cm by 22.9 cm) and 32 ply (35.6 cm by 20.3 cm) laminates could not be produced from the other resin system, the 2% DAA doped LaRC-TPI, using the above processing procedure. Three changes were made in the processing procedure for the thicker laminates. The dwell time at 520K (475°F) was increased from 30 minutes to one hour, the heating rate between 520K and 620K (660°F) was reduced from 4.4 to 2.8K/min (8 to 5°F/min), and the consolidation time at 620K was extended from one hour to one hour and 40 minutes. It was hoped that the longer dwell time and slower heating rate would permit sufficient solvent and condensation reaction byproducts to be removed from the thicker laminates. The 20 ply and 32 ply laminates were to be used for compressive interlaminar shear and compression-after-impact test coupons.

A 20 ply and 18 ply laminate were made from the 2% DAA doped LaRC-TPI prepreg material as well as a 32 ply quasi-isotropic laminate using the modified processing cycle. Thicker, 3.05 mm steel caul plates were used

TABLE 2.3.2.1

LAMINATE PHYSICAL PROPERTIES*
DAA DOPED AND POLYIMIDESULFONE LaRC-TPI LAMINATES

LAMINATES	DRY RESIN CONTENT (% VOLUME)	FIBER CONTENT (% VOLUME)	VOID CONTENT (% VOLUME)	DENSITY (g/cm^3)
2% DAA Doped LaRC-TPI #S2B2L4(0)8 (Tension) Batch DT-347, Roll 03	47.2	52.8	1	1.56
2% DAA Doped LaRC-TPI #SSB2L1(0)10 (Tension) Batch DT-347, Roll 03	47.0	53.0	1	1.53
2% DAA Doped LaRC-TPI #S2B2L3(±45)4S (Compression) Batch DT-347, Roll 02	47.9	51.1	1	1.52
**2% DAA Doped 1:1 $PISO_2$/LaRC-TPI AS-4 12K #GD-717A	41.4	53.2	1	1.60
2:1 PISO2/LaRC-TPI #S5B2L1(0)8 Batch DT-348, Roll 03	49.0	51.0	1	1.56
2:1 PISO2/LaRC-TPI #S5B2L4(0)10 Batch DT-348, Roll 03	43.2	56.8	1	1.58

* Averages of three specimens per laminate. Based on a resin specific gravity of 1.30 and a carbon fiber specific gravity of 1.76.

** Laminate fabricated by NASA-Langley.

DMA–Dynamic mechanical analysis

CAI– Compression-after-impact

for the 18 ply and 32 ply laminates to avoid the extremely uneven thickness that resulted in the 20 ply laminate, possibly due to uneven resin content across the tape width. All three of these laminates had very high void contents according to the TTU scans, and very uneven thicknesses (variation of about 0.25 mm to 0.5 mm from points about 25 mm apart).

A small (15.2 cm by 10.2 cm) unidirectional laminate that was 20 plies thick was fabricated in a press using a vacuum-bagged picture frame tool to determine a suitable processing cycle based on the processing technique used successfully to produce thin laminates. A slower initial heating rate of 0.6 to 1.1K/min was tried to permit thorough removal of volatiles without causing a substantial increase in resin viscosity prior to consolidation. Good quality thick laminates could not be produced from the DAA doped LaRC-TPI by this modified process, however.

The 32 ply quasi-isotropic laminate was also post consolidated at a much higher pressure in a press with heated platens, in an effort to obtain a good quality panel from the DAA doped LaRC-TPI material for compression-after-impact testing. The laminate was wrapped with Kapton film coated with Frekote 700 release agent. The wrapped laminate was placed in a picture frame tool and held at 620K for 45 minutes, reconsolidated at 6.9 MPa (1000 psi) and 620K for one hour, and cooled to 420K under pressure. A TTU scan of this laminate showed that the laminate still had many voids present around the periphery of the panel. Compression-after-impact coupons could not be obtained from this panel.

2.3.3 MECHANICAL PROPERTIES

Tensile test coupons were fabricated from eight ply laminates prepared from both LaRC-TPI prepreg systems. A dimensioned drawing of the tensile test specimen is shown in Appendix A along with the tensile testing procedure and calculations. The tabs bonded to the coupon were made from a glass fabric reinforced epoxy material. The epoxy adhesive used to bond the tabs was cured at 450K (350°F) since some of the specimens were to be tested at 450K. However, the tabs came off of the specimens during machining. The poor bond strength probably resulted from differences in

thermal contraction of the tab and coupon material. Carbon fiber tabs could not be used because the testing machine grips cannot penetrate the tab surface to hold the specimens without slipping during testing.

Another difficulty with the tab bonding is that thermoplastics are generally more difficult to bond with adhesives than thermoset materials because of their inherently lower surface energies.

The tabs were rebonded to some of the tensile test coupons using a low temperature cure epoxy adhesive to minimize the thermal contraction problem. These specimens were tested at ambient temperature only.

The average tensile strength, normalized to a 60% fiber volume fraction, of the DAA doped LaRC-TPI laminate was 1,760 MPa (255 Ksi) and of the 2:1 polyimidesulfone ($PISO_2$)/LaRC-TPI was 1,430 MPa (207 Ksi). The average normalized tensile modulus of each material was 126 GPa (18.2 Msi) and 121 GPa (17.5 Msi) respectively (complete tensile test data are listed in Appendix B, Table B.13). These ambient temperature tensile strength and modulus values compare very well with not only thermoplastic but also thermoset composite materials. Typical graphite/epoxy and graphite/polyimide composite tensile strengths and moduli are around 1360 to 1500 MPa and 130 to 180 GPa respectively (Ref. 6). Typical tensile strengths for graphite reinforced thermoplastic composites range from 1310 MPa to 1660 MPa although poly(etheretherketone) has an average tensile strength of 2310 MPa (Ref. 8). The tensile modulus of typical graphite/thermoplastic composites is around 140 GPa (Ref. 8).

Compression test coupons were fabricated from ten ply laminates from both prepreg resin systems. Both compression ultimate strength and compression modulus specimens were fabricated according to the specifications listed in Appendix A. A graphite-epoxy (450K cure) laminate was used for the tab material along with a 450K cure epoxy adhesive. Again the adhesive bonds were marginal. Several of the tabs had some disbond after machining. The best specimens were selected for testing and tested at ambient temperature, 450K, and at 450K after water saturation (332 hours in water at 345K (160°F)).

The hot/wet compression specimens were coated with a masking elastomeric material (Adcoat CHEM MILL MASK #AC 854) so that only the gauge section between the tabs was exposed. This coating reduced the diffusion of water into the adhesive bonds during the exposure period. The untabbed compression modulus specimens were not coated with CHEM MILL MASK. The compression specimens were placed in a 500 ml beaker filled with distilled water which was covered with a large watch glass and placed in a 345K (160°F) steam chest.

The testing procedure for the compression specimens was based on ASTM D695, "Standard Test Method for Compressive Properties of Rigid Plastics", which has been modified by The Boeing Company for testing continuous fiber reinforced composite laminates. The compression testing procedure and calculations are outlined in Appendix A. A crosshead speed of 1.3 mm/min (0.05 in/min) was used in testing. A load-deflection curve was recorded for all compressive strength and modulus specimens. The compressive modulus specimens were loaded to about 6,000 microstrain to obtain a load deflection curve.

The 450K-dry test specimens were heat soaked in the environmental chamber for ten minutes prior to testing. The CHEM MILL MASK elastomer coating was peeled from the hot/wet specimens and the specimens were heat soaked in the chamber for two minutes prior to testing, to insure that the specimens did not dry out completely.

The average compressive strengths and moduli, normalized to a constant fiber volume fraction of 60%, of the two LaRC-TPI materials are summarized in Table 2.3.3.1. The room temperature compressive strengths of the 2% DAA doped specimens were better and had less variation than those of the 2:1 $PISO_2$/LaRC-TPI material, in part because a better tab adhesive bond was obtained with the former. The coefficient of variance reported here is the standard deviation divided by the mean. The 2% DAA doped material also had better properties at 450K (350°F). Interestingly, the 2:1 $PISO_2$/LaRC-TPI material had a higher compressive strength under hot/wet conditions than the 2% DAA doped material.

TABLE 2.3.3.1

AVERAGE COMPRESSIVE STRENGTH AND MODULUS (MODIFIED ASTM D695) 1/.
NORMALIZED TO A FIBER VOLUME FRACTION OF 60 PERCENT
2% DAA DOPED AND POLYIMIDESULFONE/LaRC-TPI LAMINATES

	AMBIENT TEMPERATURE		450K (350°F) 3/		450K/WET 4/	
COMPOSITE	STRENGTH MPa (Ksi)	MODULUS GPa (Msi)	STRENGTH MPa (Ksi)	MODULUS GPa (Msi)	STRENGTH MPa (Ksi)	MODULUS GPa (Msi)
2% DAA Doped LaRC-TPI/Celion 6K	1,140 (166)	104 (15.2)	728 (106)	100 (14.5)	384 (55.6)	113 (16.4)
Std. Dev.	122 (17.7)	--	26.4 (3.83)	--	86.7 (12.6)	--
Cov. 2/	0.11	--	0.04	--	0.23	--
2:1 $PISO_2$/LaRC-TPI/ Celion GK	911 (132)	103 (14.9)	546 (79.1)	89.4 (13.0)	431 (62.4)	110 (16.0)
Std. Dev.	256 (37.1)	--	125 (18.1)	--	65.0 (9.42)	--
Cov. 2/	0.28	--	0.23	--	0.15	--

1/ Average of 5 specimens for strength and 3 to 4 specimens for modulus.

2/ Coefficient of variance (standard deviation divided by the mean).

3/ 10 minute thermal exposure time at 450K prior to testing.

4/ 332 hours in water at 345K followed by a two minute thermal exposure time at 450K prior to testing.

The 2% DAA doped LaRC-TPI material exhibited better retention of ambient temperature compressive strength at 450K than the polyimidesulfone/LaRC-TPI, however the $PISO_2$ material had a higher retention of compressive strength under hot/wet conditions. The DAA doped LaRC-TPI retained 63% of its ambient temperature strength at 450K and 33% at 450K/water saturated. The $PISO_2$/LaRC-TPI retained 60% of its ambient temperature strength at 450K and 47% at 450K/water saturated. The percentage weight gain of the compressive modulus specimens is listed in Table 2.3.3.2 and averaged 1.06% for the DAA doped LaRC-TPI and 0.98% for the $PISO_2$/LaRC-TPI.

The compressive moduli in Table 2.3.3.1 decreased by a small amount at 450K from room temperature values. The compressive modulus increased 13 to 23% over the 450K test values after exposure to water at 340K for two weeks. The LaRC-TPI resins may have experienced some postcuring during the elevated temperature moisture exposure. The compressive properties listed in Table 2.3.3.1 were not normalized to a constant fiber volume fraction.

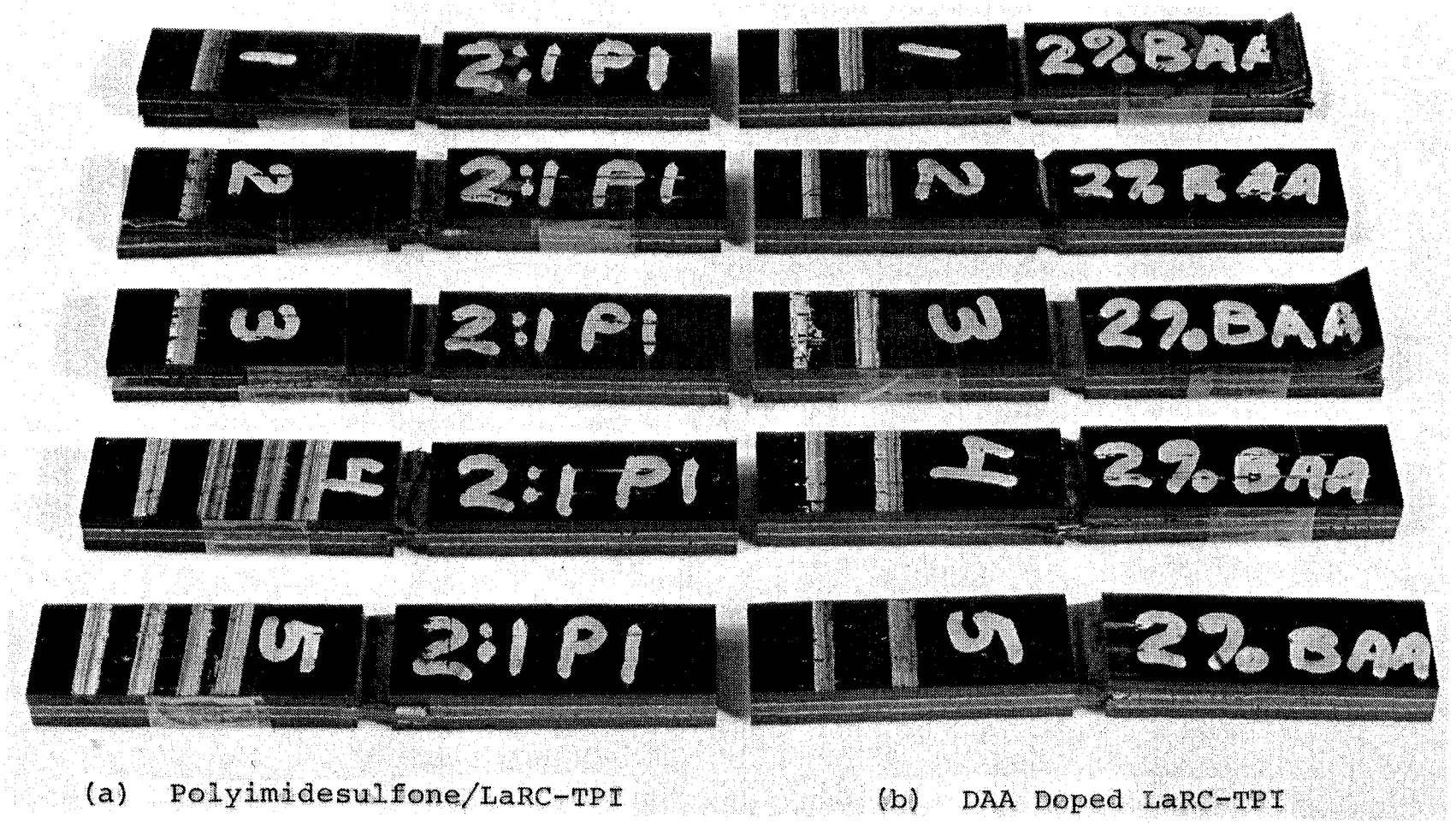
Ultimate compressive failure occurred either in the gauge section or at one end of the compressive strength specimens. The tested specimens are shown in Photographs 2.3.3.1, 2.3.3.2, and 2.3.3.3. Failure tended to occur within the gauge section in the room temperature test specimens, while failure tended to occur at the ends of the specimens tested at 450K. Good quality adhesive bonds between the tabs and the coupon are critical for this compression test. Failure of the adhesive bond first will usually result in failure of the coupon at the unsupported end (end brooming). At elevated temperature the tabs tended to come loose resulting in an end-failure of the specimen. Some of the moisture-saturated specimens tested at 450K failed in the gauge section, however.

The compressive strength and modulus of the 2% DAA doped LaRC-TPI composite compare well with those of DuPont's AVIMID® K-III thermoplastic polyimide which has an average compressive strength of about 993 to 1007 MPa (144 to 146 Ksi) and compressive modulus of 103 to

TABLE 2.3.3.2

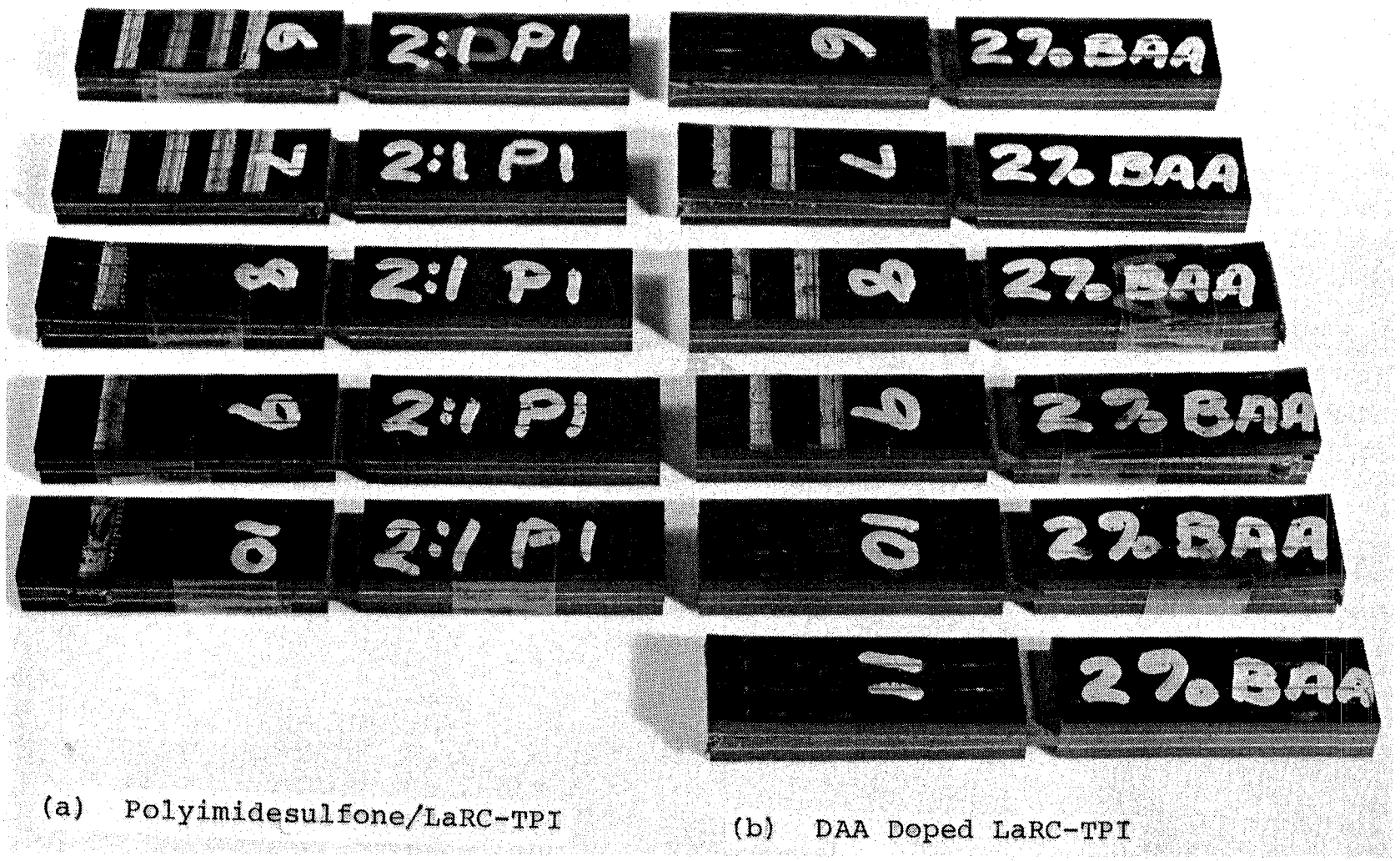
PERCENTAGE WEIGHT GAIN OF COMPRESSIVE MODULUS SPECIMENS AFTER 332 HOUR SOAK IN WATER AT 345K (160°F)

SPECIMEN	SPECIMEN WEIGHT (gm)	WEIGHT AFTER EXPOSURE (gm)	% WT. GAIN
2% BAA Doped LaRC-TPI			
1	2.5544	2.5814	1.06
2	2.4738	2.5049	1.26
3	2.4323	2.4592	1.11
4	2.5280	2.5483	0.80
		AVERAGE	1.06
2:1 $PISO_2$/LaRC-TPI			
1	2.4594	2.4843	1.01
2	2.322	2.3435	0.93
3	2.5030	2.5296	1.06
4	2.3233	2.3450	0.93
		AVERAGE	0.98

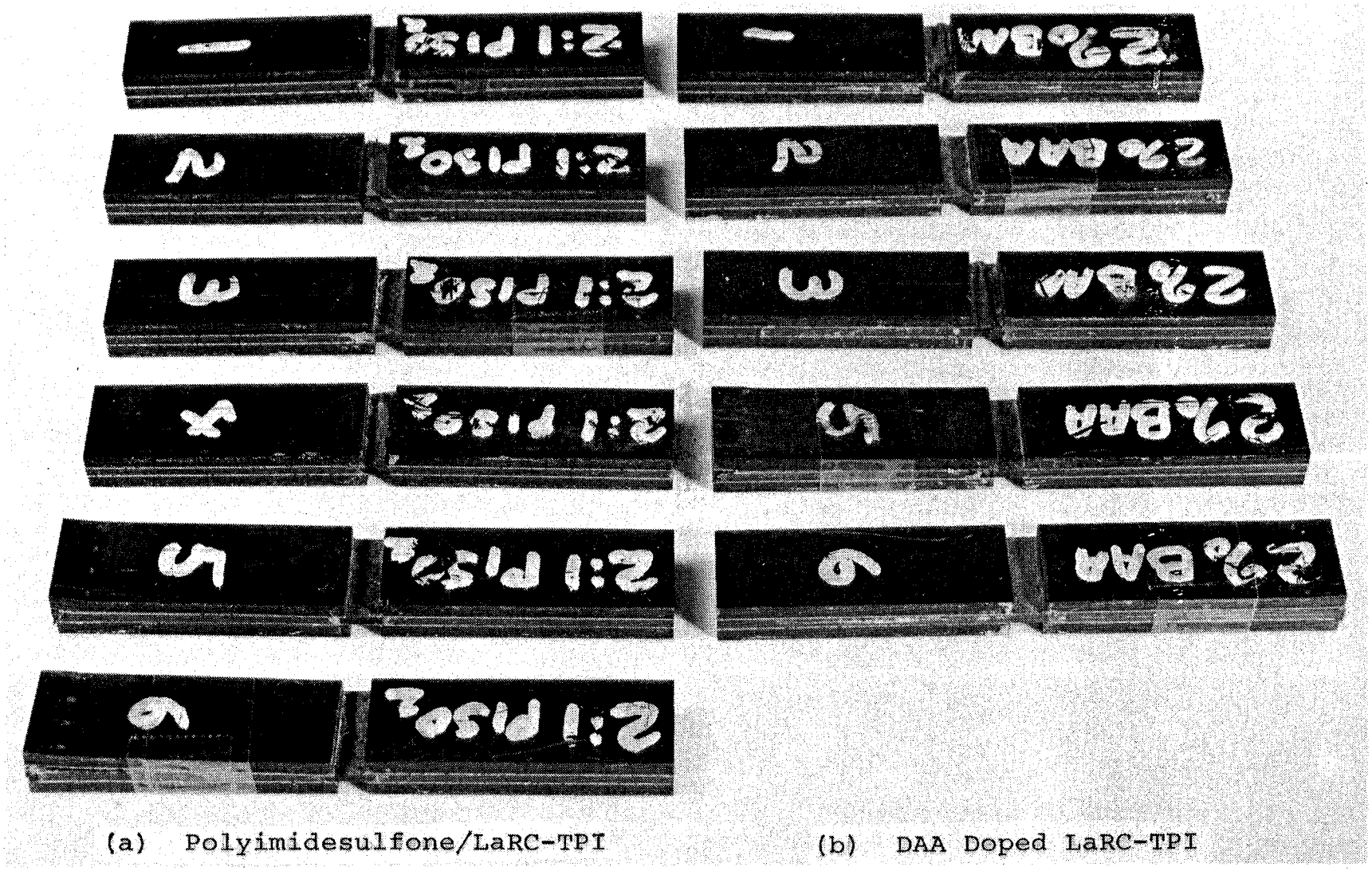


(a) Polyimidesulfone/LaRC-TPI (b) DAA Doped LaRC-TPI

Photograph 2.3.3.1. Photograph of the Ambient-Temperature Compression Strength Test Specimens – DAA Doped and Polyimidesulfone/LaRC-TPI



Photograph 2.3.3.2. Photograph of the 450K Compression Strength Test Specimens— DAA Doped and Polyimidesulfone/LaRC-TPI



Photograph 2.3.3.3. Photograph of the 450K/Moisture-Saturated Compression Strength Test Specimens – DAA Doped and Polyimidesulfone/LaRC-TPI

110 GPa (15 to 16 msi) (Ref. 7). The AVIMID® K-III compressive strength and modulus values were for AS-4 and IM-6 carbon fiber composites with fiber volume fractions of about 57%, tested using the IITRI (Illinois Institute of Technology Research Institute) compression test method. The 2:1 $PISO_2$/LaRC-TPI was more difficult to bond to, however improved tab adhesive bonds would probably yield higher values than reported here.

The compressive strength of the 2% DAA doped LaRC-TPI material at 450K of 643 MPa is slightly higher than that reported for graphite-polysulfone composites (Ref. 6) of 621 MPa at 450K. The compressive strength of the 2:1 $PISO_2$/LaRC-TPI specimens at 450K was lower (517 MPa) in part because of the poorer adhesive bonds between the tabs and coupons.

Compression-after-impact (CAI) testing was performed on one LaRC-TPI composite system, using the panel fabricated by NASA Langley. The CAI test procedure is listed in Appendix A. The test specimen was impacted at a level of 6.65 J/mm (1500 in-lb/in). The compressive strength of the impacted specimen was 308 MPa (44.7 Ksi) which compares well with DuPont's AVIMID® K-III resin composite laminates which had a compressive strength of about 282 MPa (40.9 Ksi) at the same level of impact energy (Ref. 7) and same fiber volume fracture of 60%. The modulus of the impacted specimen was 37.7 GPa (5.46 Msi) with a strain-to-failure of 0.85%. The percent strain reported for K-III was 0.65% (Ref. 7).

Dynamic mechanical analysis (DMA) was performed on the 2% DAA doped LaRC-TPI composite material with specimens from a 16 ply laminate (15.2 cm by 15.2 cm) with a symmetric ± 45 degree layup. A good quality ± 45 degree crossply laminate could not be produced from the batch of the 2:1 $PISO_2$/LaRC-TPI material, as discussed earlier. The DMA coupon dimensions and DMA test procedure are listed in Appendix A. The DMA traces provide information on the glass transition temperature (Tg), the relationship between viscosity and temperature, and the shear storage modulus (G') and shear loss modulus (G") as functions of temperature. Neat resin LaRC-TPI specimens were not available for DMA.

DMA traces were run on specimens exposed to five aircraft fluids and on an unexposed control specimen. The five fluids were water, methylene chloride, Skydrol hydraulic fluid, jet fuel, and deicing fluid (ethylene glycol). All of the exposed specimens were stressed at a level of 0.4% strain during the 350 hour fluid exposure, except for the specimen exposed to water. The specimen exposed to water was placed in water at 368K for 24 hours prior to testing.

The DMA traces for the 2% DAA doped LaRC-TPI coupons are shown in Appendix B (Figures B.19 to B.24). The glass transition temperature is defined as the temperature at which G" is a maximum, which is at 511K (238 C) in the G" versus temperature trace of the unexposed specimen. This is the same Tg that was determined by other investigators (Ref. 3). G' is directly proportional to the resin viscosity, and the G' trace in Figure 2.3.3.1 indicates that a rapid dropoff in resin viscosity occurs at about 513K (240°C). The loss tangent (tan delta) is the tangent of the loss angle between the complex shear stress and complex shear strain and is equal to the ratio of G" to G'. The loss tangent was a maximum at 525K (252°C).

For comparison, DuPont reports a Tg for AVIMID® K-III of 523K (250°C) which was determined by thermomechanical analysis (Ref. 7).

The results of DMA for each exposed specimen were as follows. The coupon exposed to water at 368K had many delaminations near the center which formed when the water froze during the low temperature DMA testing. Surprisingly, there was no drop in the storage modulus of the delaminated specimen but G' actually increased. This increase in G' agrees with the increase in the compressive modulus observed in the hot/wet compression test specimens. There may be a post curing process taking place in the 2% DAA doped LaRC-TPI specimens exposed to hot water.

The glass transition temperature remained about the same in the water-exposed specimen (508K) and the jet fuel-exposed specimen (512K). The specimen exposed to methylene chloride showed a large drop in the glass transition temperature to 446K (173°C), while the specimens exposed to hydraulic fluid and deicing fluid had increased glass transitions of 523K and 522K, respectively. Methylene chloride did not cause any surface cracking

or other changes in the appearance of the specimens. The drop of G' in the low temperature region of the jet fuel exposed specimen was due to some difficulties in adjusting the equipment and has no significance.

Conclusions that can be drawn from this work are that the tensile and compressive properties of 2% DAA doped LaRC-TPI composites compare well with DuPont's AVIMID® K-III polyimide composites and other high performance thermoplastic composites. The 2% DAA doped LaRC-TPI material had better tensile and compressive properties than the polyimidesulfone/LaRC-TPI material. However, the polyimidesufone/LaRC-TPI material showed better retention of compressive strength under hot/wet conditions than the 2% DAA doped LaRC-TPI. A Tg of 511K was determined by DMA for the 2% DAA doped LaRC-TPI composite system. Of the five fluids used in DMA testing of the 2% DAA doped LaRC-TPI, methylene chloride produced the most severe effect, lowering Tg by 65K. Exposure to hot water (345K) may cause a post curing of the LaRC-TPI polymer which could account for the higher compressive modulus compared to the modulus of the unexposed specimens.

3.0 CONCLUSIONS AND RECOMMENDATIONS

3.1 CONCLUSIONS

- Methylene chloride caused microcracking of the PSI-1111 and M&T 4605-40 resins, and severe solvation and plasticization of the M&T 4300 resin.

- M&T 4300 was unaffected by hot water, Skydrol, and jet fuel.

- Hot water and jet fuel lowered both Tg and the shear storage modulus of the M&T 4605-40 resin. Skydrol had no effect on the resin.

- The Tg and shear storage modulus of the M&T PSI-1111 resin were not affected by methylene chloride, jet fuel, or hot water.

- Of the three M&T resins evaluated the M&T 4300 had the lowest melt viscosity, indicating potentially easier processing.

- Good quality prepreg materials and composite laminates could not be produced from the Unifabric reinforcement using the M&T matrix resins and the processing techniques discussed in this report.

- The M&T 4605-40 resin would need an endcap to prevent a rapid increase in the polymer molecular weight and polymer viscosity during imidization.

- The PSI-1111 resin appeared to be the best composite matrix material of those evaluated in the initial phase of this contract based on its mechanical properties and fluid resistance.

- Of the five LaRC-TPI composite resin systems evaluated in the preliminary screening tests the di(amic acid) doped and polyimidesulfone/LaRC-TPI powder resin systems had the best mechanical properties.

- The mechanical properties of the best LaRC-TPI resin systems were comparable to those of other high performance thermoplastic matrix resins and other thermoplastic polyimides.

- Adhesive bonding of tabs to compression test specimens was more difficult with the polyimidesulfone/LaRC-TPI material, than with the DAA doped LaRC-TPI.

- The polyimidesulfone/LaRC-TPI material showed better retention of compressive strength under hot/wet test conditions (450K) than the di(amic acid) doped LaRC-TPI, about 47% versus 33%.

- The compression strength after an impact of 6.65 J/mm (1500 in lb/in) of the DAA doped polyimidesulfone/LaRC-TPI laminate was comparable to that of AVIMID® K-III polyimide carbon fiber composite, and the strain at failure was 0.2% higher.

- Of the five fluids used for exposure of the dynamic mechanical specimens methylene chloride produced the most severe effect, lowering the glass transition temperature (Tg) by 65K; hydraulic fluid and deicing fluid increased Tg by about 10K, while water and jet fuel had little effect on Tg.

3.2 RECOMMENDATIONS

- Further evaluation of the di(amic acid) doped LaRC-TPI and the polyimidesulfone/LaRC-TPI composite matrix materials should be conducted. Additional composite testing could include compression and tensile testing after thermal aging and after fluid exposure, fatigue/toughness testing, and creep tests.

- Further processing studies are needed to make good quality thick (32 ply) LaRC-TPI composite laminates. This might involve investigation of other LaRC-TPI resin formulations in addition to those evaluated in this work.

- Further work on methods of producing high quality LaRC-TPI resin prepregs is needed since a combination of solvent and melt-based prepregging is involved.

4.0 REFERENCES

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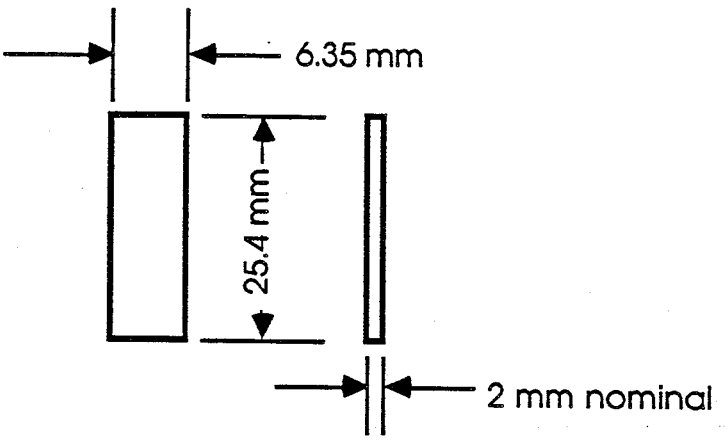
APPENDIX A

MECHANICAL TEST SPECIMENS AND TEST METHODS

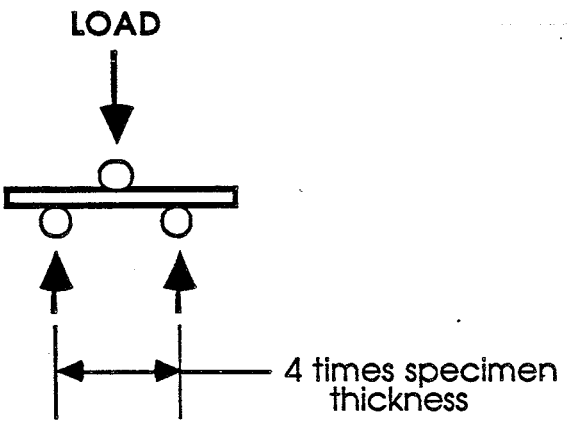
INTERLAMINAR SHORT-BEAM SHEAR STRENGTH

Based on ASTM D2344 and Boeing Company Testing Procedures

1. Specimen Geometry



2. Specimen Loading



3. Testing Procedure - Per ASTM D2344

1) Test machine crosshead speed: 1.3 mm (0.05 in.)/min

2) Record load to break specimen.

4. Calculations

Calculate the apparent shear strength from the formula:

$$S = \frac{0.75\,P}{wt}$$

where:

S = shear strength, N/m^2 (or psi),

P = load at break, N or (lb_f),

w = width of specimen, m (or in.) and

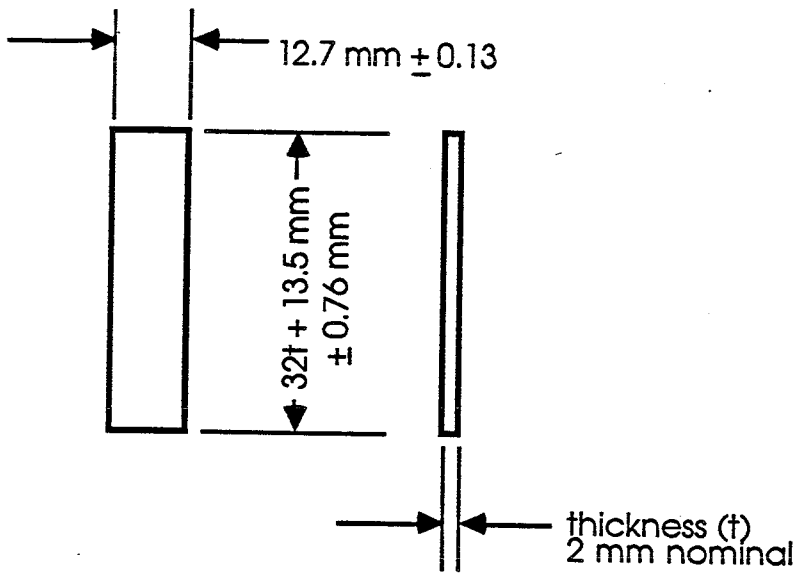
t = thickness of specimen, m (or in.).

Calculate the arithmetic mean and standard deviation of the values of shear strength obtained.

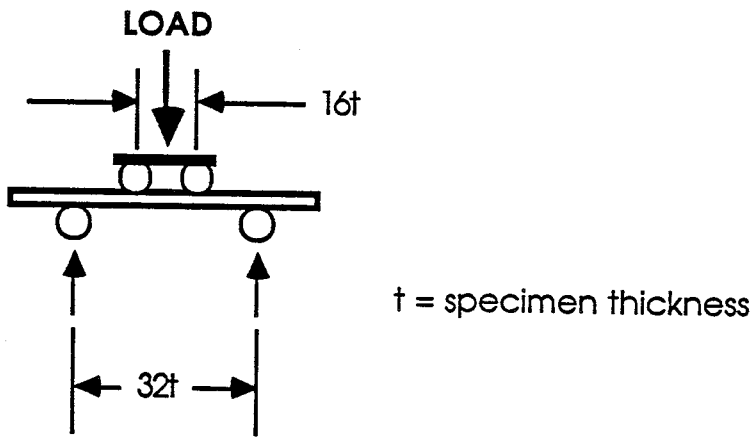
FLEXURAL STRENGTH AND MODULUS

Based on ASTM D790 and Boeing Company Testing Procedures

1. Specimen Geometry



2. Specimen Loading



Support span equals 32 times the specimen thickness (t).

Load span equals one half of the support span.

FLEXURAL STRENGTH AND MODULUS

Based on ASTM D790 and Boeing Company Testing Procedures

(CONTINUED)

3. Testing Procedure - Per ASTM D2344

   1) Test machine crosshead speed: 1.3 mm (0.05 in.)/min

   2) Record load at specimen failure.

4. Calculations

Calculate the flexural strength from the formula:

$$S_f = \frac{3PL}{4\,wt^2}\left(1 - \frac{10.91\,(Dt)}{L^2}\right)$$

where:

S = flexural strength, N/m^2 (or psi),

P = load at break, N or (lb_f),

w = width of specimen, m (or in.)

t = thickness of specimen, m (or in.).

L = length of the support span, m (or in.) and

D = maximum deflection of the center of the beam, m (or in.)

Calculate the flexural modulus from the formula:

$$E_B = \frac{0.17L^3m}{wt^3}$$

where:

E_B = tangent flexural modulus of elasticity in bending, N/m^2 (psi),

m = slope of the tangent to the initial straight-line portion of the load-deflection curve, N/m (lb_f/in.) of deflection,

w = width of specimen, m (or in.),

t = thickness of specimen, m (or in.) and

L = length of the support span, m (or in.).

FLEXURAL STRENGTH AND MODULUS
Based on ASTM D790 and Boeing Company Testing Procedures
(CONTINUED)

Calculate the arithmetic mean and standard deviation of the values of the flexural strength and modulus obtained.

TENSILE STRENGTH AND MODULUS
Based on ASTM D3039 and Boeing Company Testing Procedures

1. Specimen Geometry
   See Figure A.1

2. Specimen Loading
   Specimen inserted into the test machine grips to the tab taper edge.

3. Testing Procedure - Per ASTM D3039
   1) Test machine crosshead speed: 1.3 mm (0.05 in.)/min
   2) Measure strain with an extensometer or a strain gauge.
   3) Record load at specimen failure.

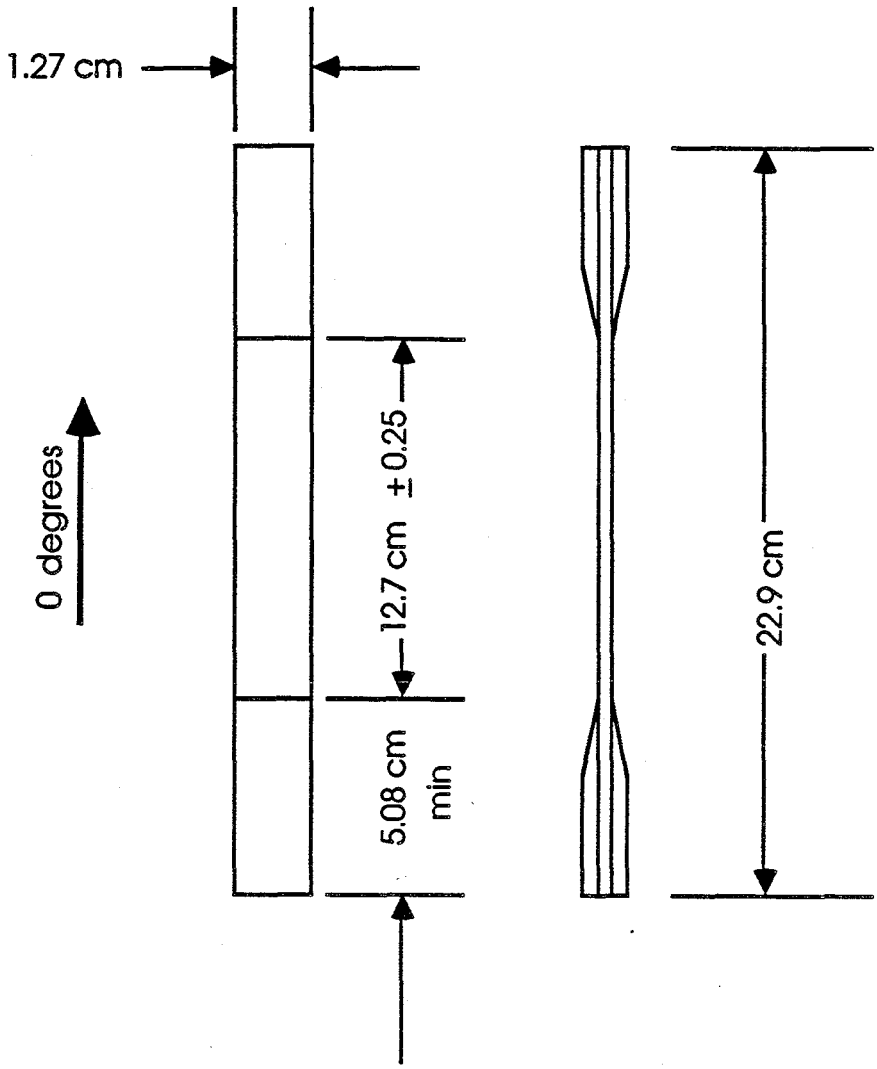
4. Calculations
   Calculate the tensile strength from the formula:

$$S_u = \frac{P}{wt}$$

where:

S_u = ultimate tensile strength, N/m^2 (or psi),
P = tensile load at break, N or (lb_f),

w = width of specimen, m (or in.) and
t = thickness of specimen, m (or in.).



GENERAL NOTES:

1. For grade 145 prepreg and a 0 degree orientation, use 8 plies.
2. Tab material to be glass fiber/epoxy. Tabs bonded to coupons with epoxy adhesive.
3. Tab taper to be 3 to 5 degrees.
4. Sand blast coupon area under tabs or hand sand with 100 grit paper in 0 degree direction. Solvent wipe sanded surfaces prior to bonding. Tabs to be fabricated with peel ply at bonding surfaces
5. Edges of opposing bonded tabs shall match within 0.508 mm.
6. Edges shall be machined and tested parallel to the fiber direction. Edges flat and parallel within 0.127 mm.

Figure A.1
TENSILE TEST SPECIMEN

TENSILE STRENGTH AND MODULUS

Based on ASTM D3039 and Boeing Company Testing Procedures

(CONTINUED)

Calculate the tensile modulus of elasticity from the formula:

$$E_t = \frac{lm}{wt}$$

where:

E = tensile modulus of elasticity, N/m^2 (psi),

l = gauge length of the extensometer, m (or in.),

m = slope of the plot of load as a function of deformation within the linear portion of the curve,

w = width of specimen, m (or in.), and

t = thickness of specimen, m (or in.).

Calculate the arithmetic mean and standard deviation of the values of the tensile strength and modulus obtained.

COMPRESSIVE STRENGTH AND MODULUS

Based on ASTM D695 and Boeing Company Testing Procedures

1. Specimen Geometry

   See Figure A.2.

2. Specimen Loading

   ASTM D695 compression fixture used to test both strength and modulus specimens.

3. Testing Procedure

   1) Test machine crosshead speed: 1.3 mm (0.05 in.)/min
   2) Record load deflection curve for all specimens.
   3) Record load at strength specimen failure.
   4) Measure strain with an extensometer on untabbed modulus specimens.
   5) Load modulus specimen to a minimum strain value of 0.0030 mm/mm.

4. Calculations

   Calculate the ultimate compressive strength from the formula:

$$S_u = \frac{P}{wt}$$

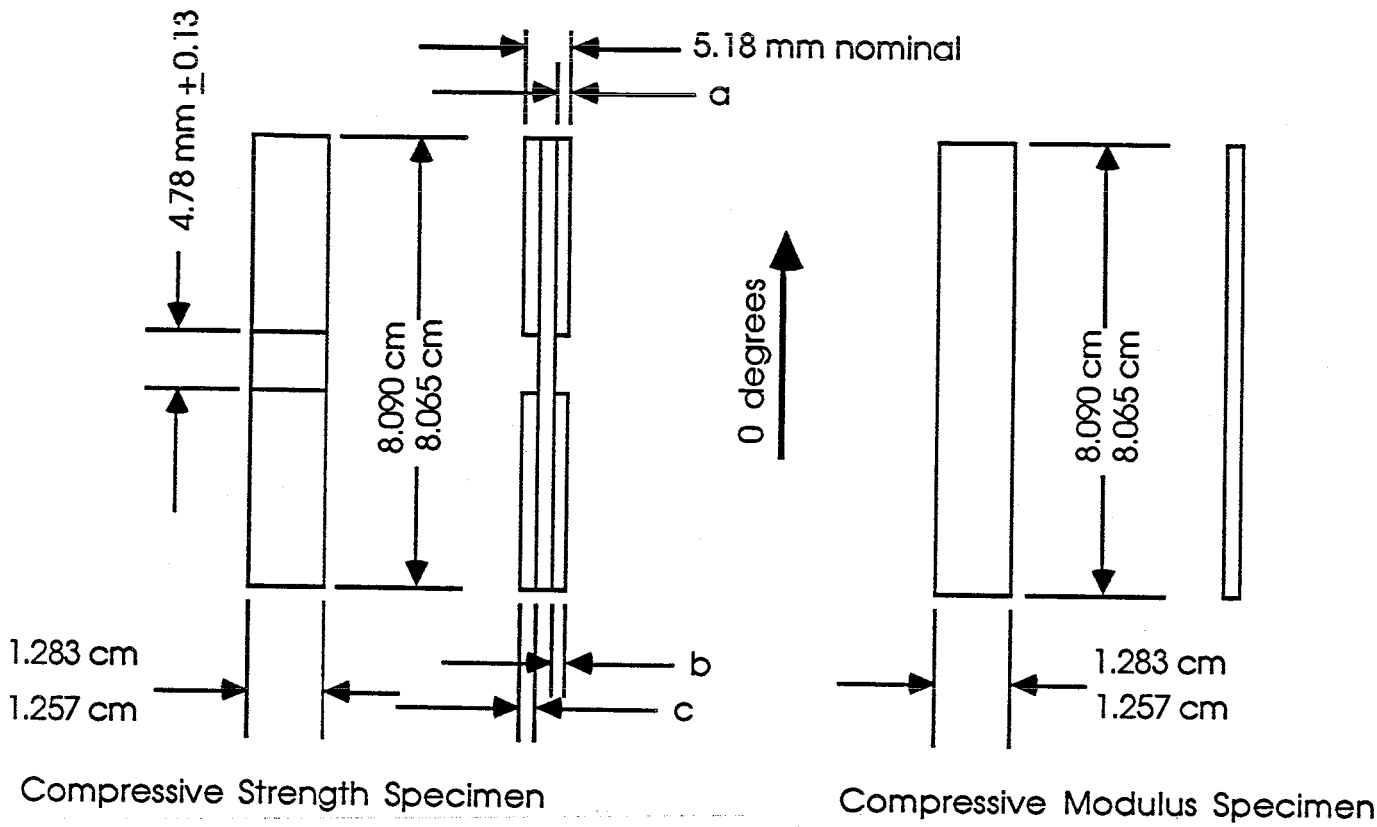
   where:

   S_u= ultimate tensile strength, N/m^2 (or psi),

   P = tensile load at break, N or (lb_f),

   w = width of specimen, m (or in.)

   t = thickness of specimen, m (or in.).



GENERAL NOTES:

1. Dimension b must equal dimension c to within 0.254 mm and the difference between dimension a and c must be less than 0.064 mm.
2. Support tabs shall be fabricated from a composite material having a matrix and fiber reinforcement with mechanical properties comparable to the material being tested. Support tabs shall have the same layup as the test panel.
3. Tabs shall be made of 12 plies of Grade 145 prepreg, or equivalent thickness when using other grades.
4. Prepare the specimen and tabs prior to bonding by hand sanding the bonding areas with 150 grit sandpaper or by sandblasting. Solvent wipe sanded surfaces prior to bonding.
5. Edges shall be machined and tested parallel to the fiber direction. Edges shall be flat and parallel within 0.127 mm. Ends of specimen shall be flat within 0.025 mm.

Figure A.2
COMPRESSIVE STRENGTH AND MODULUS SPECIMENS

Figure A.2

COMPRESSIVE STRENGTH AND MODULUS SPECIMENS

COMPRESSIVE STRENGTH AND MODULUS

Based on ASTM D695 and Boeing Company Testing Procedures

(CONTINUED)

Calculate the compressive modulus of elasticity from the formula:

$$E_t = \frac{lm}{wt}$$

where:

E_t = tangent compressive modulus of elasticity, N/m t (psi),

l = gauge length of the compressometer, m (or in.),

m = slope of the plot of load as a function of deformation within the linear portion of the curve,

w = width of specimen, m (or in.), and

t = thickness of specimen, m (or in.).

Calculate the arithmetic mean and standard deviation of the values of the compressive strength and modulus obtained.

COMPRESSION-AFTER-IMPACT

Based on Boeing Company Test Methods

1. Specimen Geometry
   See Figure A.3

2. Specimen Loading
   See Figures A.4 and A.5

3. Testing Procedure - Per Boeing Company Test Method

   1) Impact performed on impacter with a hemispherical tip indenter with a diameter of 15.7 mm (0.62 in.).

   2) The impact support fixture for the specimen shall be as shown in Figure A4.

   3) The compression test machine shall be a universal test machine equipped with parallel base plate and loading head or equivalent.

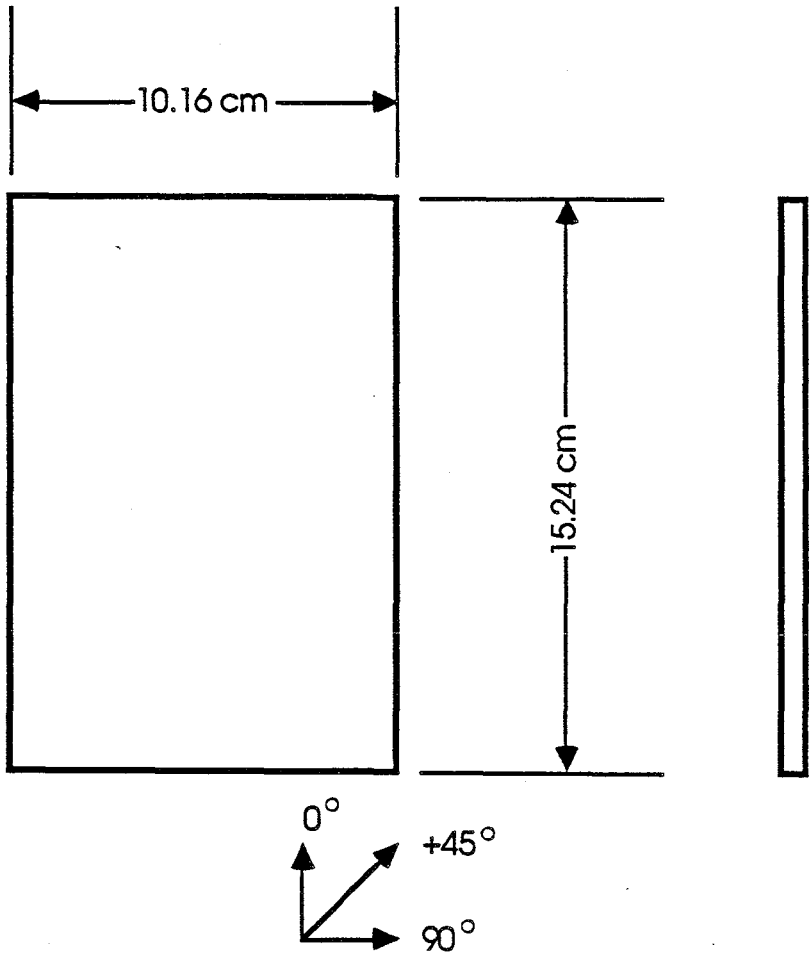
   4) The test support fixture shall be as shown in Figure A5.

   5) Measure specimen length, width, and thickness to the nearest 0.025 mm (0.001 in.) prior to impact.

   6) To perform the impact, place the specimen in the support fixture of Figure A5.2. The impactor shall weigh 4.5 to 6.8 Kg (10 to 15 lbs) and be dropped from an appropriate height to achieve the required impact energy. The impactor shall strike the panel once.

   7) The speed of testing shall be 1.3 mm (0.05 in.)/min. +/-0.25 mm.

   8) Record the ultimate load, N or (lb_f).



GENERAL NOTES:

1. Layup for grade 145: (+45/0/-46/90)4s, 32 plies.
2. Unless otherwise specified, dimensional tolerances are ±0.254 mm.
3. Ends of specimen must be parallel within 0.0127 mm.
4. Surfaces and edges of specimen must be perpendicular within 0.0254 mm.
5. Edges of specimen must have a 32 RHR finish in accordance with ANSI B46.1

Figure A.3

COMPRESSION IMPACT COUPON

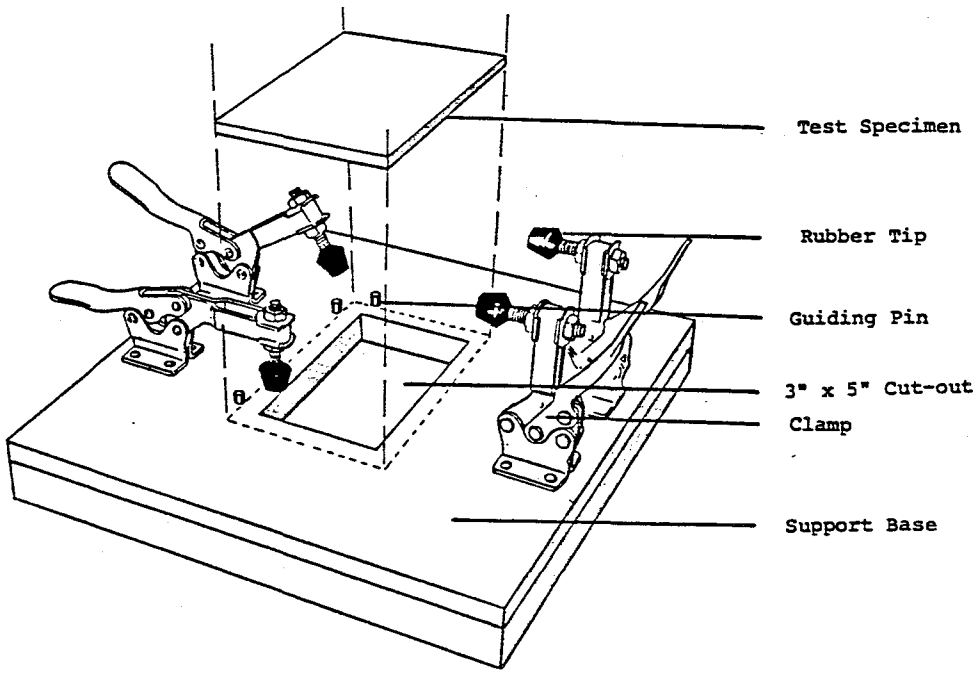


Figure A.4

COMPRESSION-AFTER-IMPACT SPECIMEN IMPACT FIXTURE

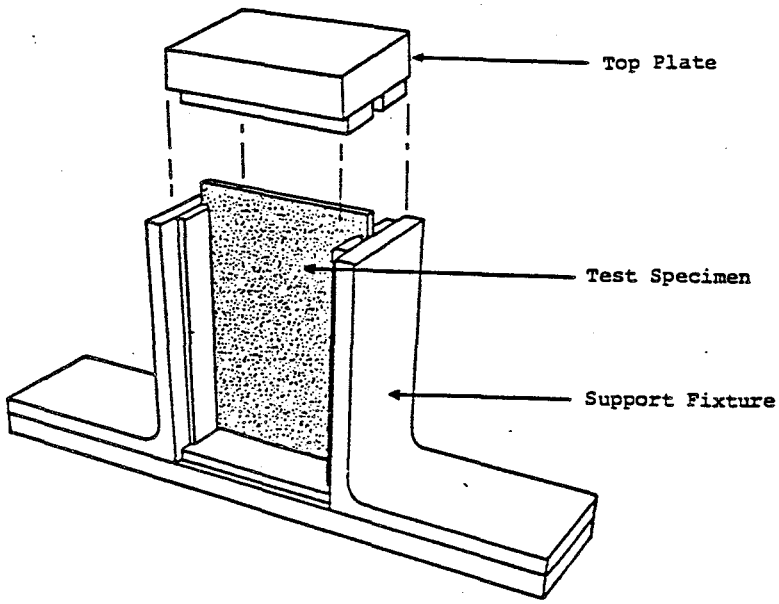


Figure A.5

COMPRESSION-AFTER-IMPACT TEST FIXTURE

4. Calculations

Calculate the ultimate compressive strength from the formula:

$$S_C = \frac{P}{wt}$$

where:

S_C= compression strength after impact, N/m^2 (or psi),

P = load at break, N or (lb_f),

w = width of specimen, m (or in.)

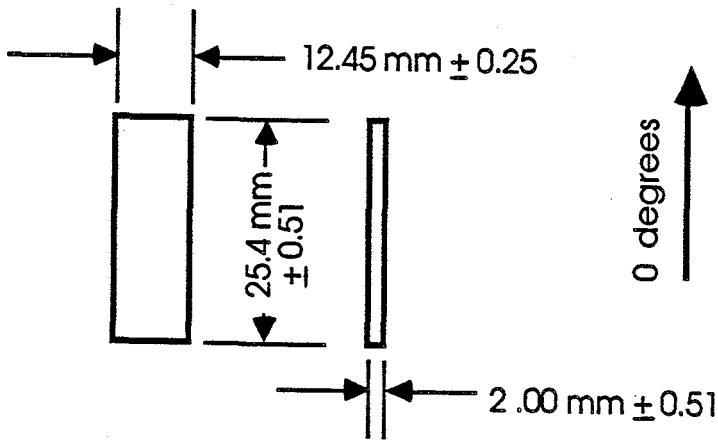
t = thickness of specimen, m (or in.).

Calculate the arithmetic mean and standard deviation of the values of compression strength after impact obtained, if a sufficient number of specimens have been tested.

DYNAMIC MECHANICAL ANALYSIS

Based on Boeing Company Testing Procedures

1. Specimen Geometry



Layup: ± 45

2. Specimen Loading: torsion.

3. Testing Parameters

Test coupons stressed to a 0.4% strain level during fluid exposure.

Mode:	Temperature Sweep
	5K per step
	1 minute at each step
Percent Strain:	0.05%
Frequency:	10 rad/sec
Temperature Range:	180K to 570K (-90 C to 300 C)

4. Data Recorded

1) Shear Storage modulus (G') at all temperatures.

2) Shear loss modulus (G") at all temperatures.

APPENDIX B

MECHANICAL TEST DATA FOR INDIVIDUAL SPECIMENS

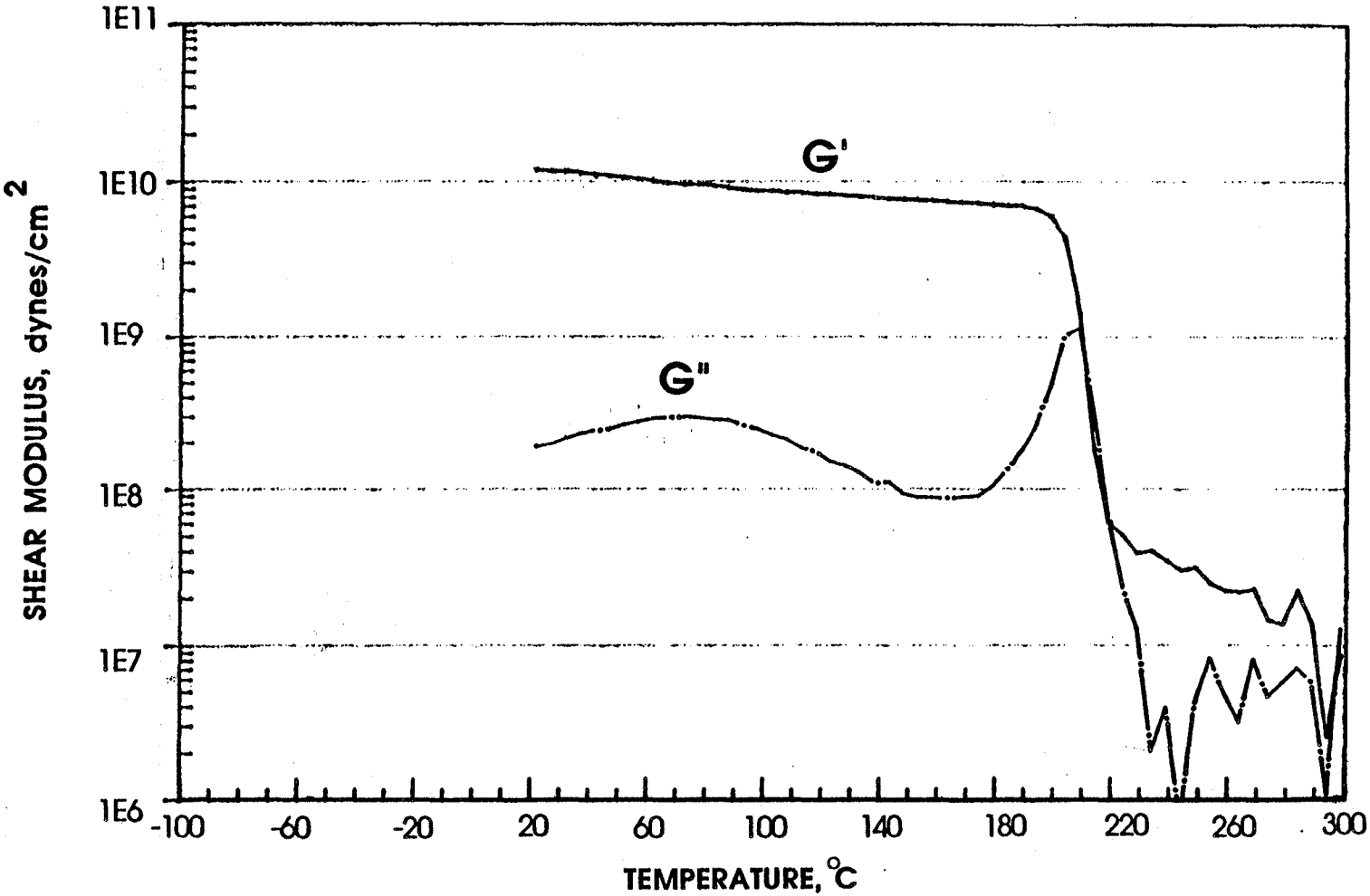


Figure B.1 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4300, Control Run No. 1, Unexposed Specimen

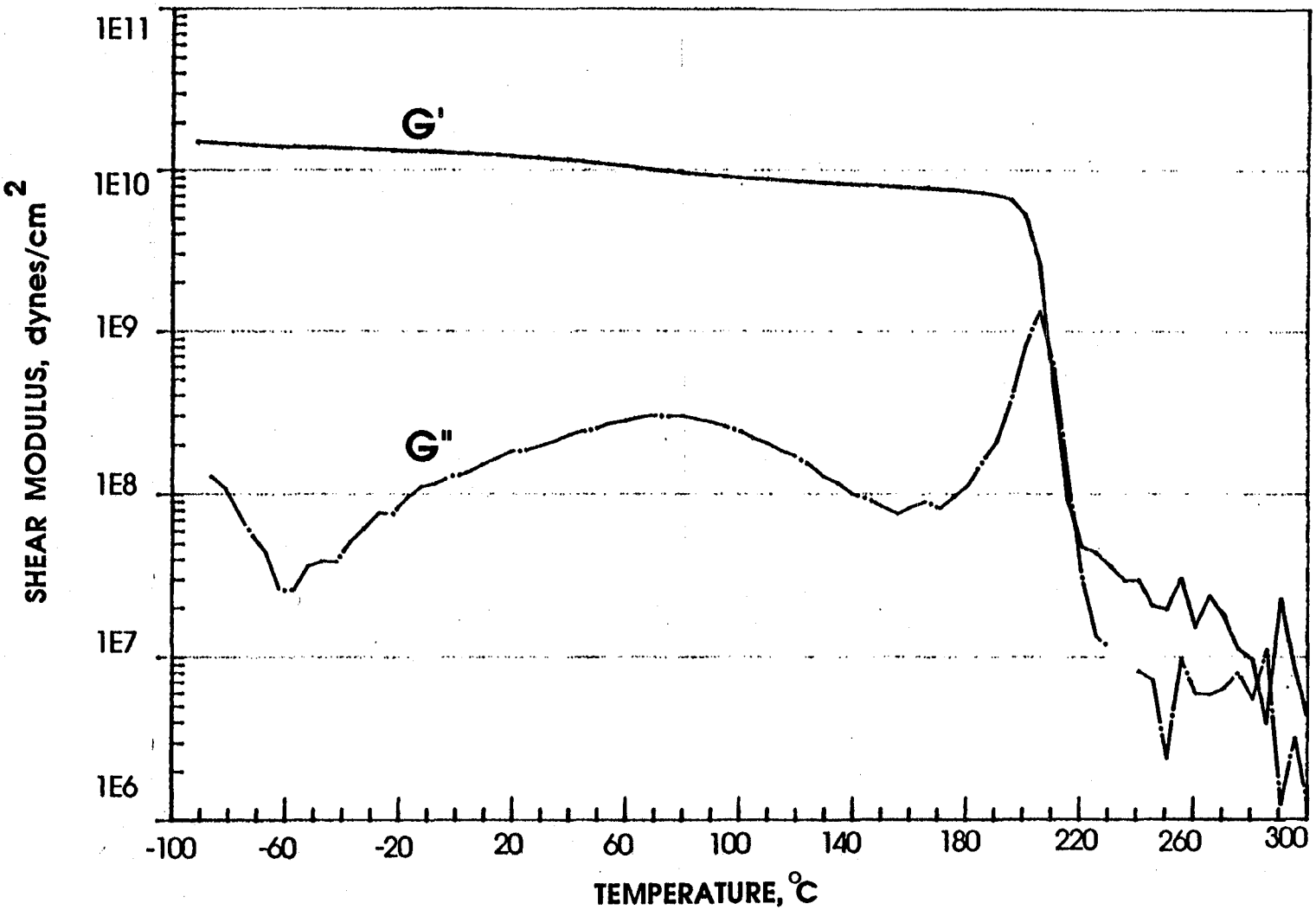


Figure B.2 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4300, Control Run No. 2, Unexposed Specimen

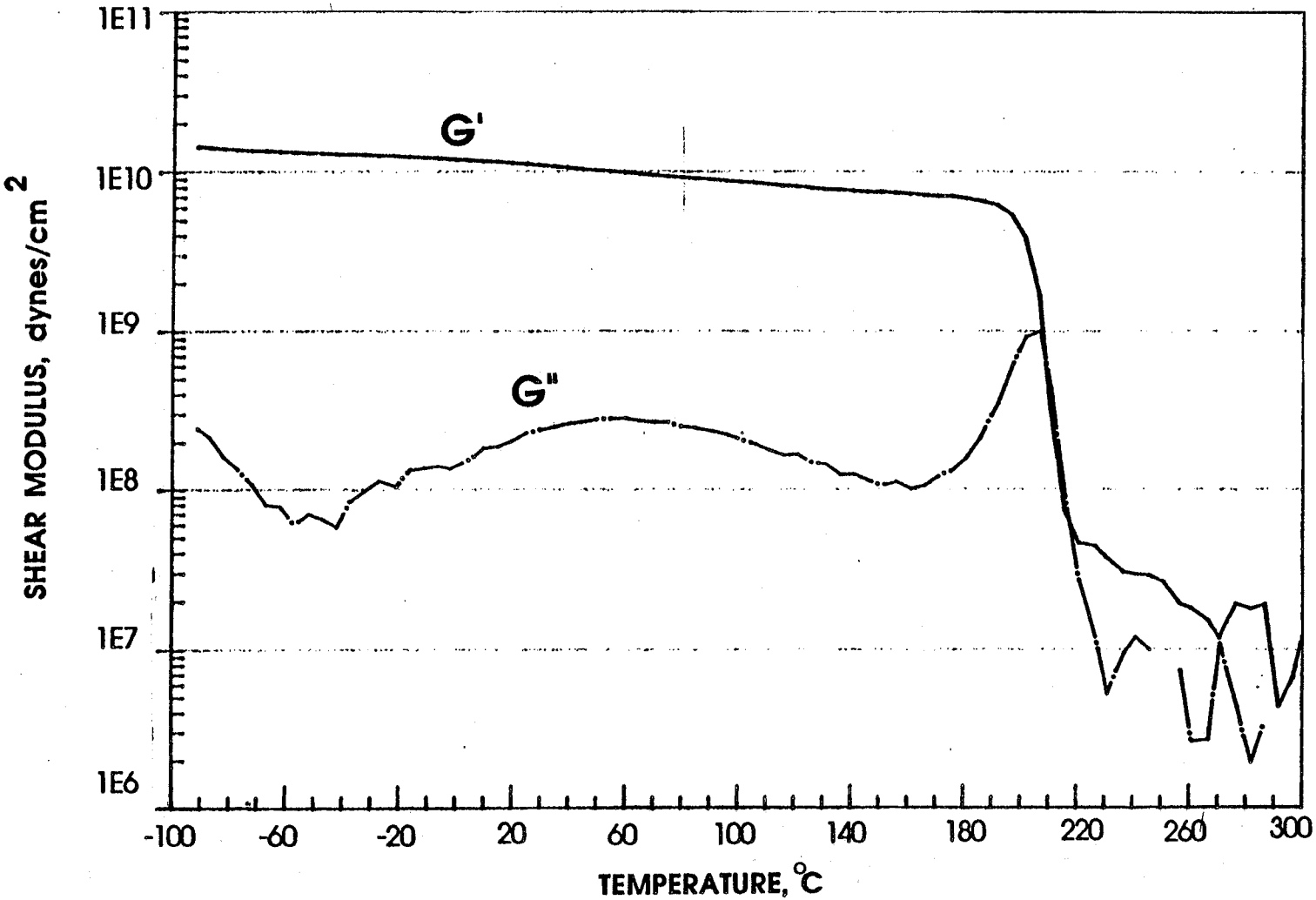


Figure B.3 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4300, Hot/Wet Exposure

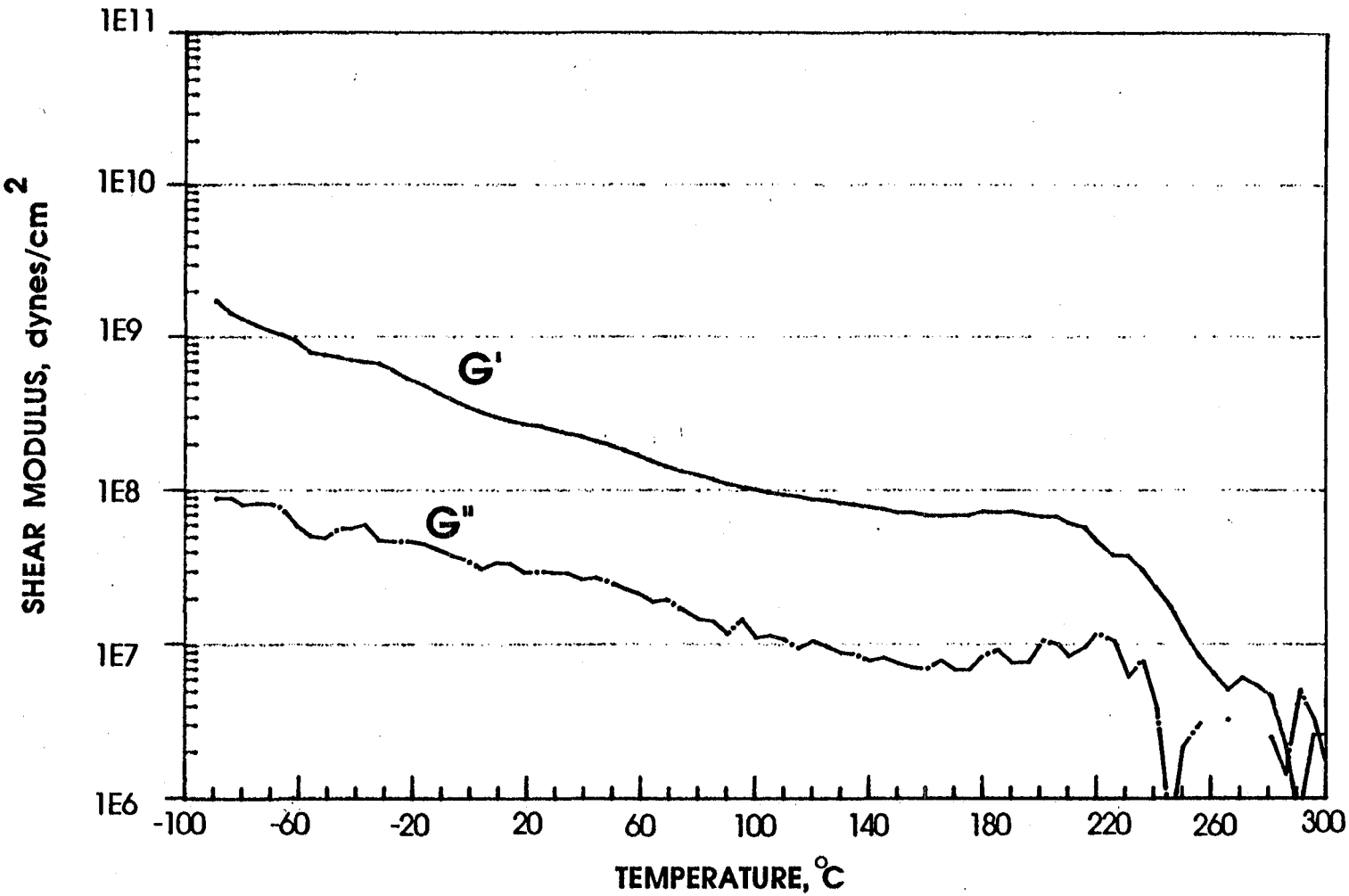


Figure B.4 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4300, Specimen Exposed to Methylene Chloride

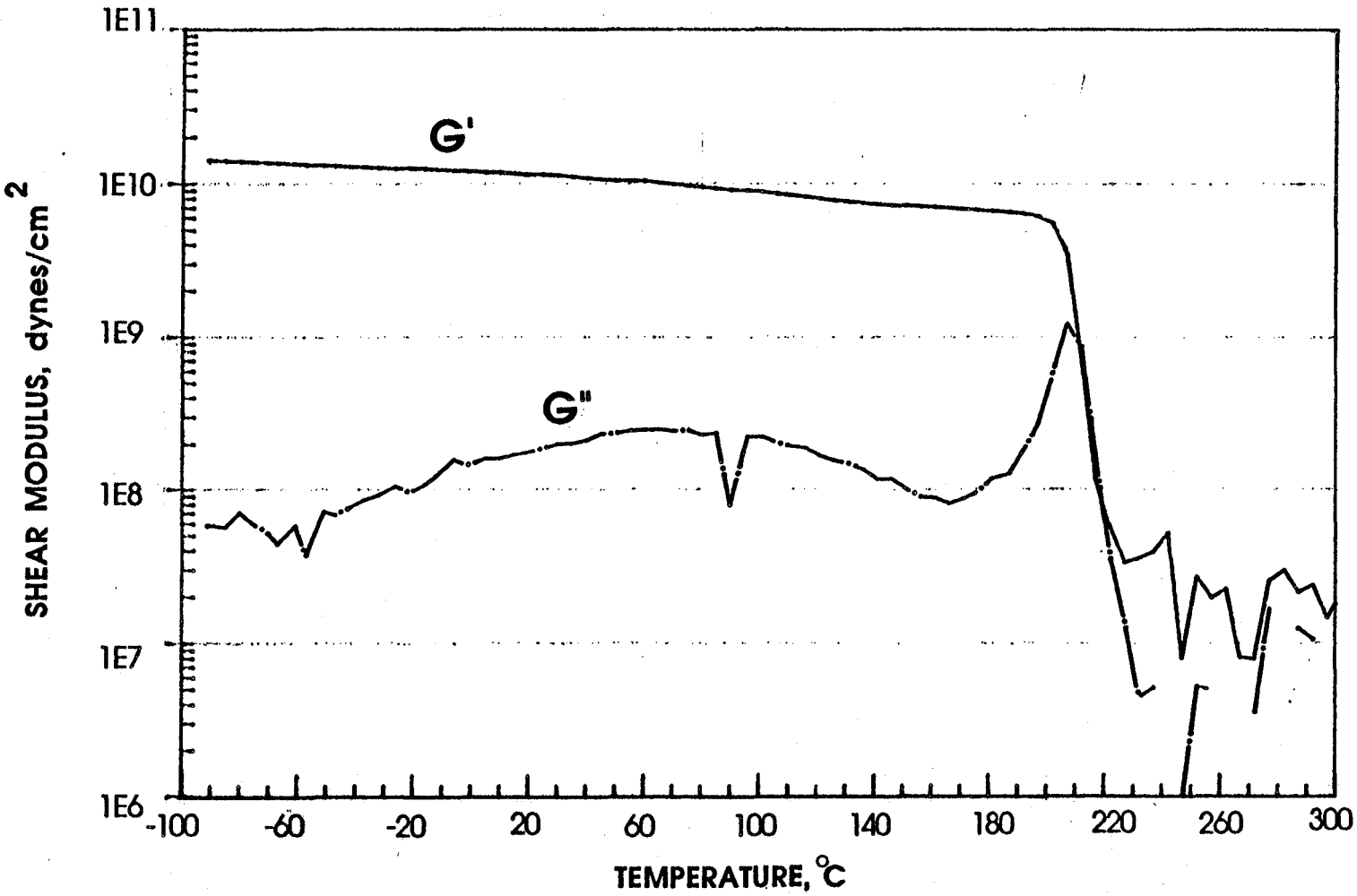


Figure B.5 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4300, Specimen Exposed to Skydrol

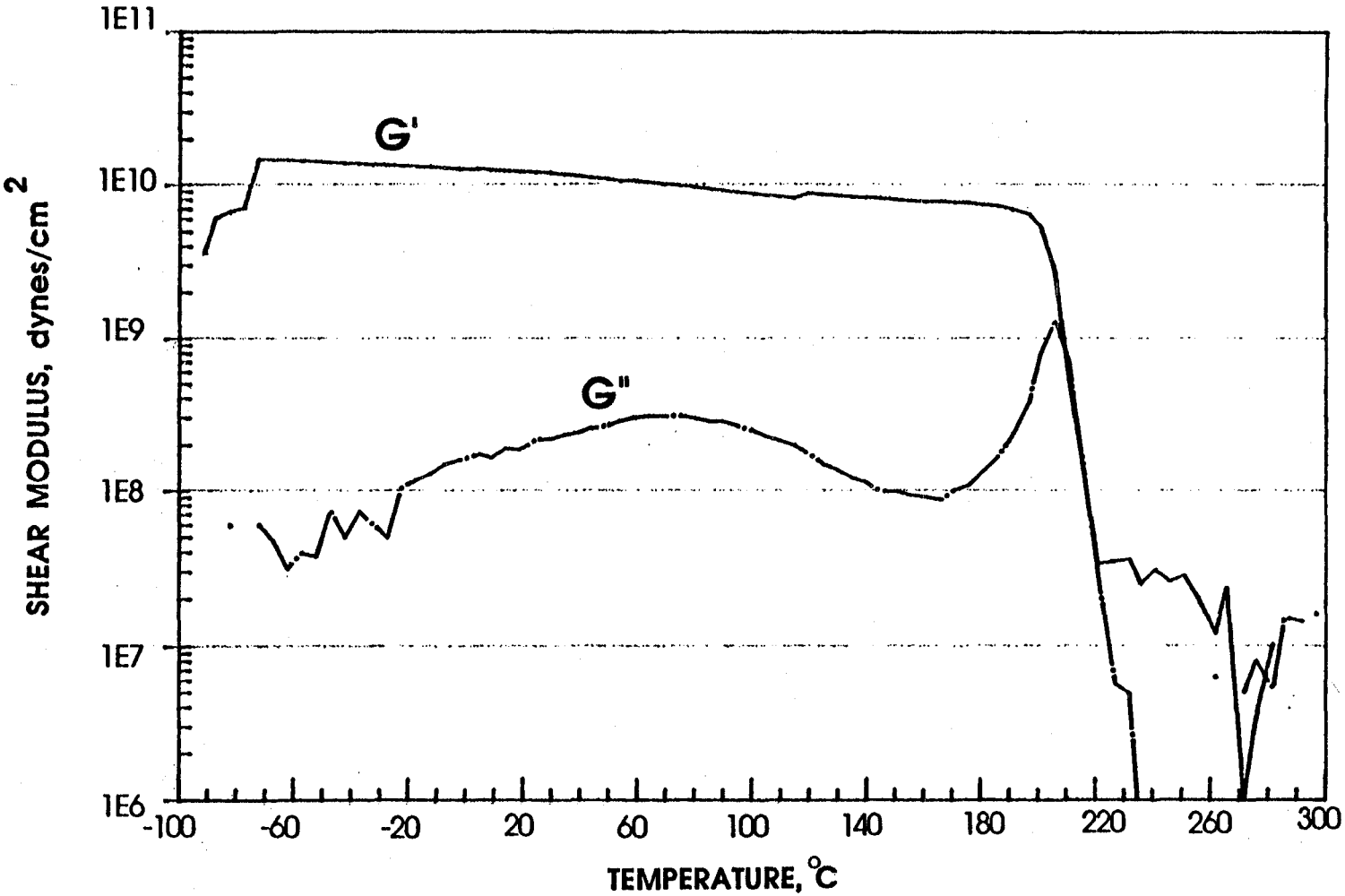


Figure B.6 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4300, Specimen Exposed to Jet Fuel

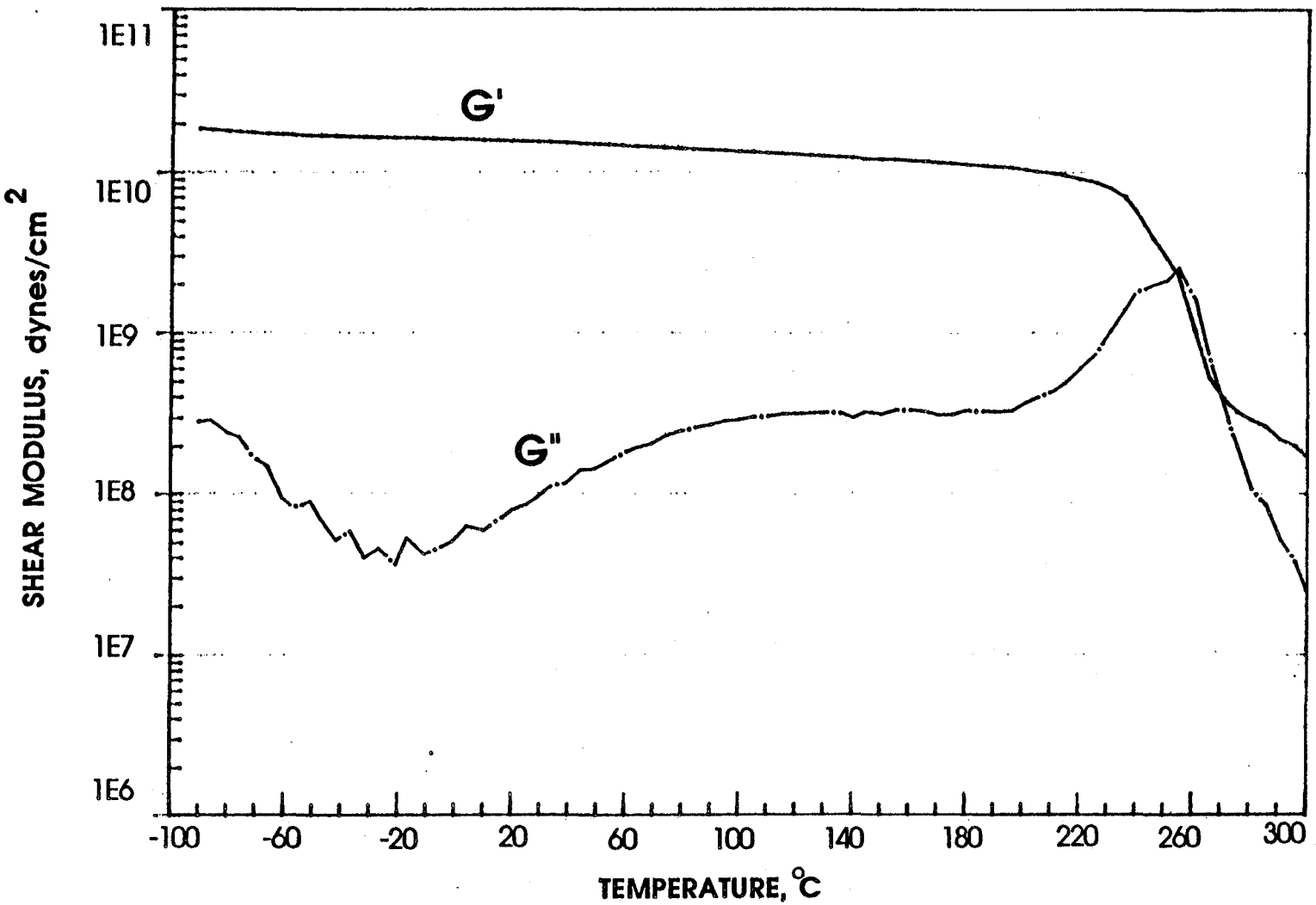


Figure B.7 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4605, Control Run No. 1, Unexposed Specimen

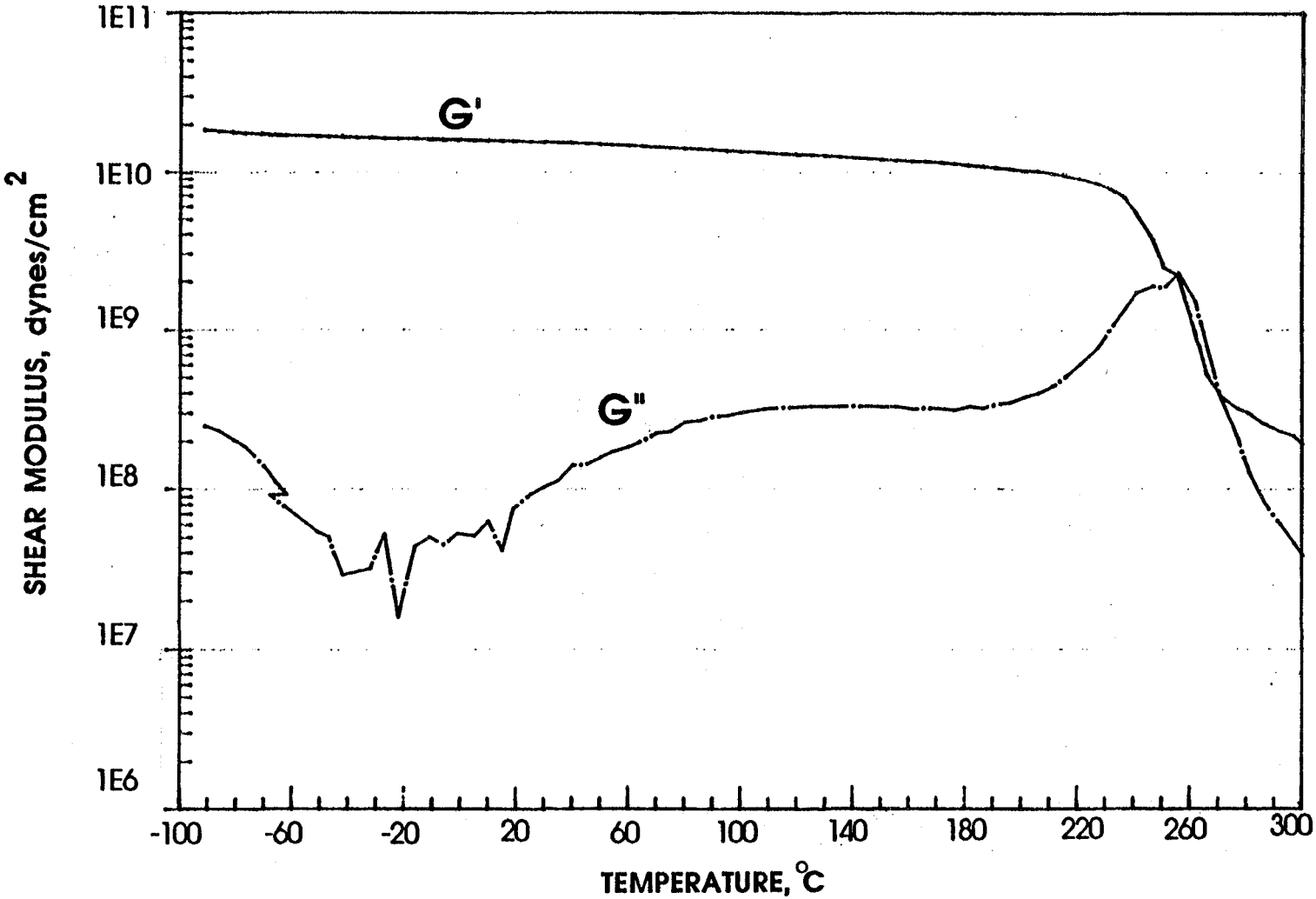


Figure B.8 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4605, Control Run No. 2, Unexposed Specimen

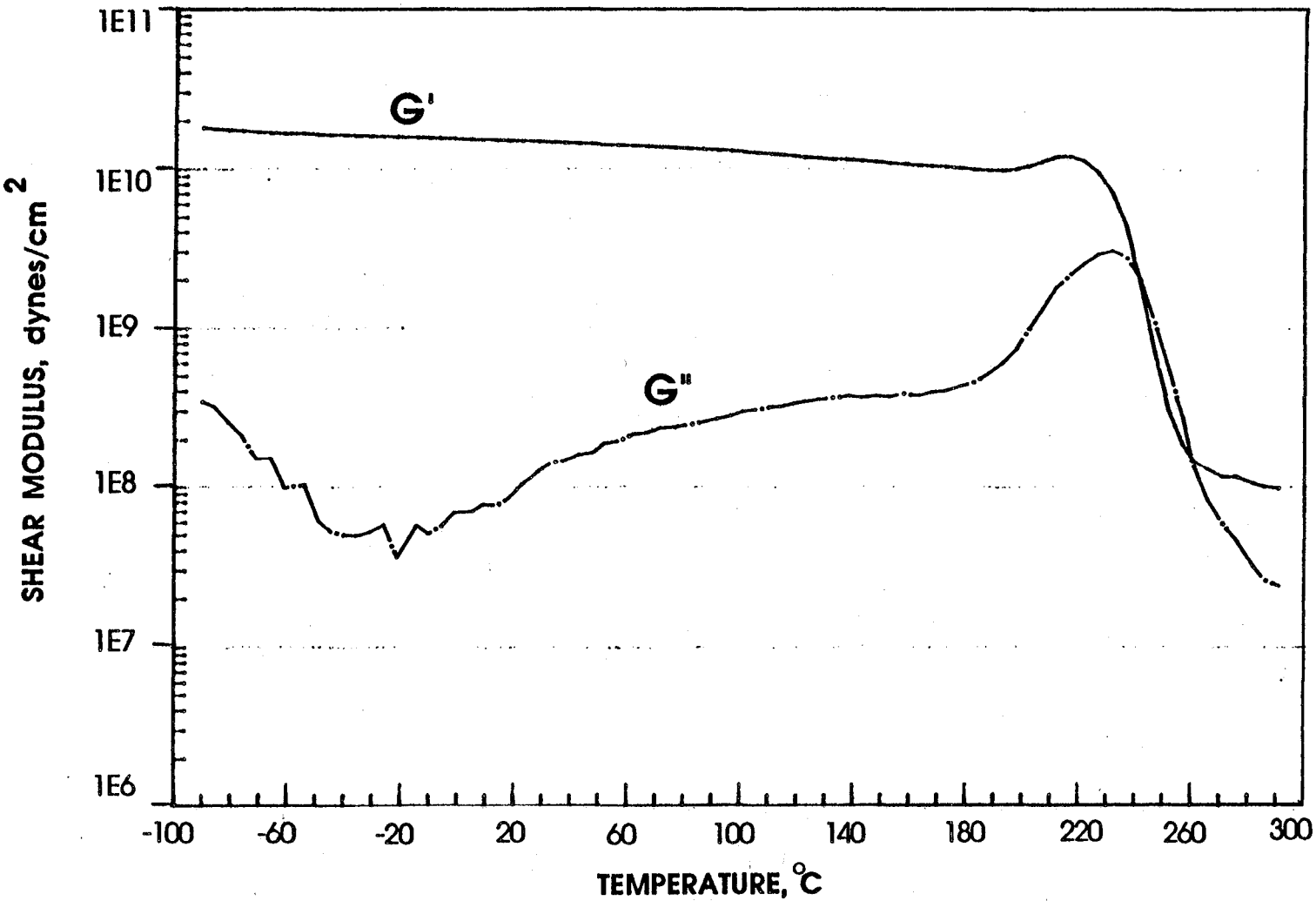


Figure B.9 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4605, Hot/Wet Exposure

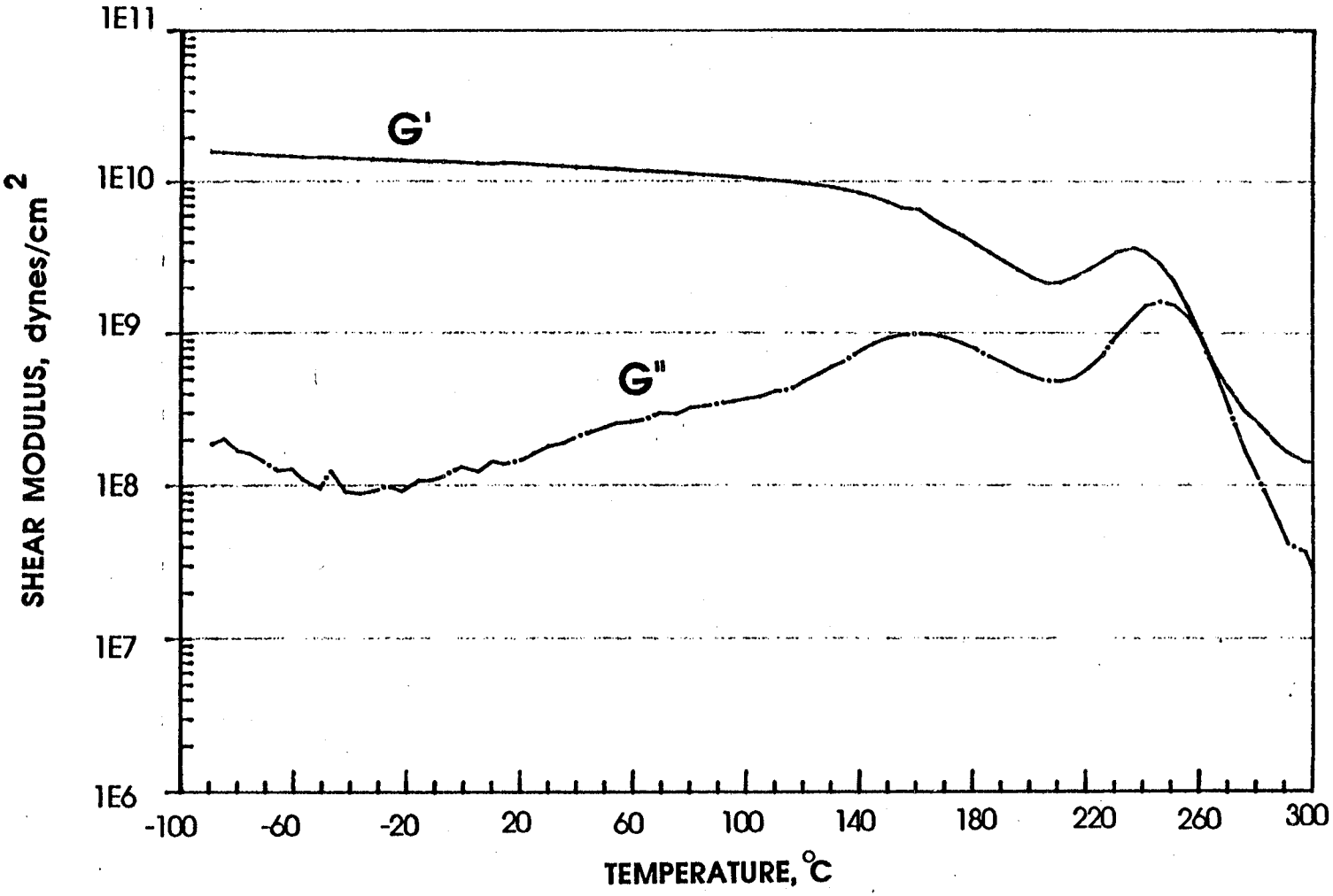


Figure B.10 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4605, Specimen Exposed to Methylene Chloride

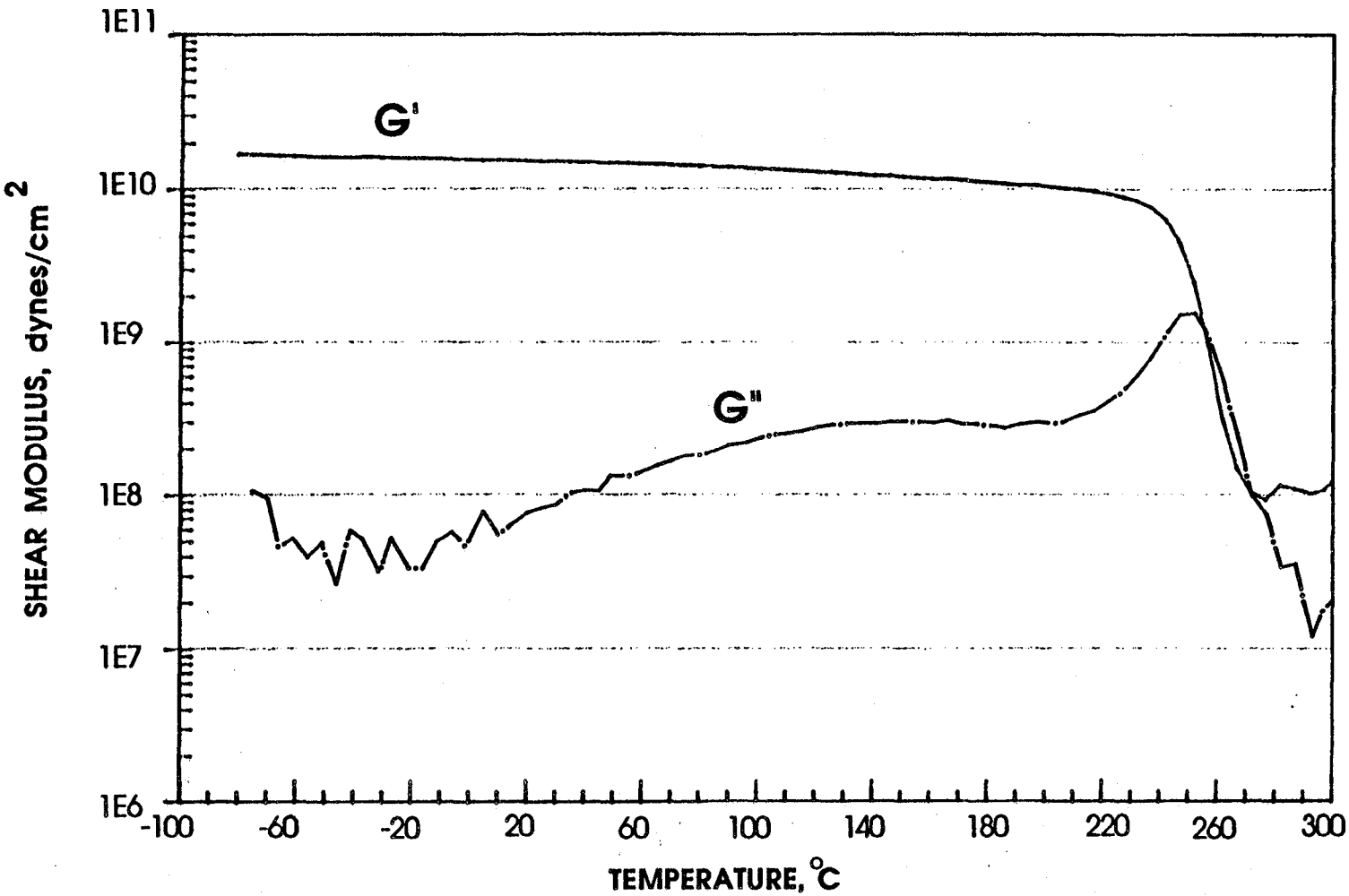


Figure B.11 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4605, Specimen Exposed to Skydrol

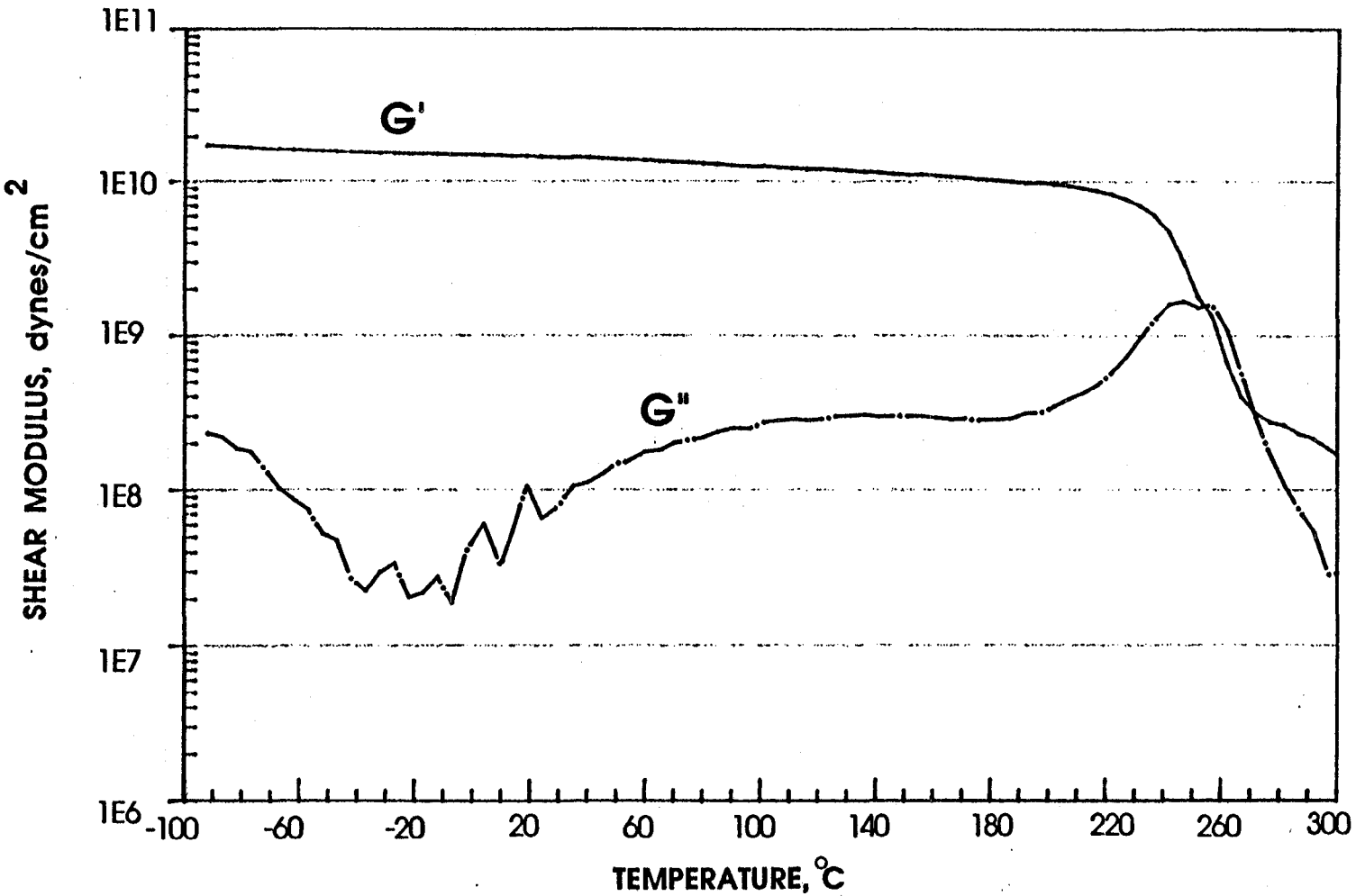


Figure B.12 Dynamic Mechanical Analysis Traces for NASA Polyimide MT-4605, Specimen Exposed to Jet Fuel

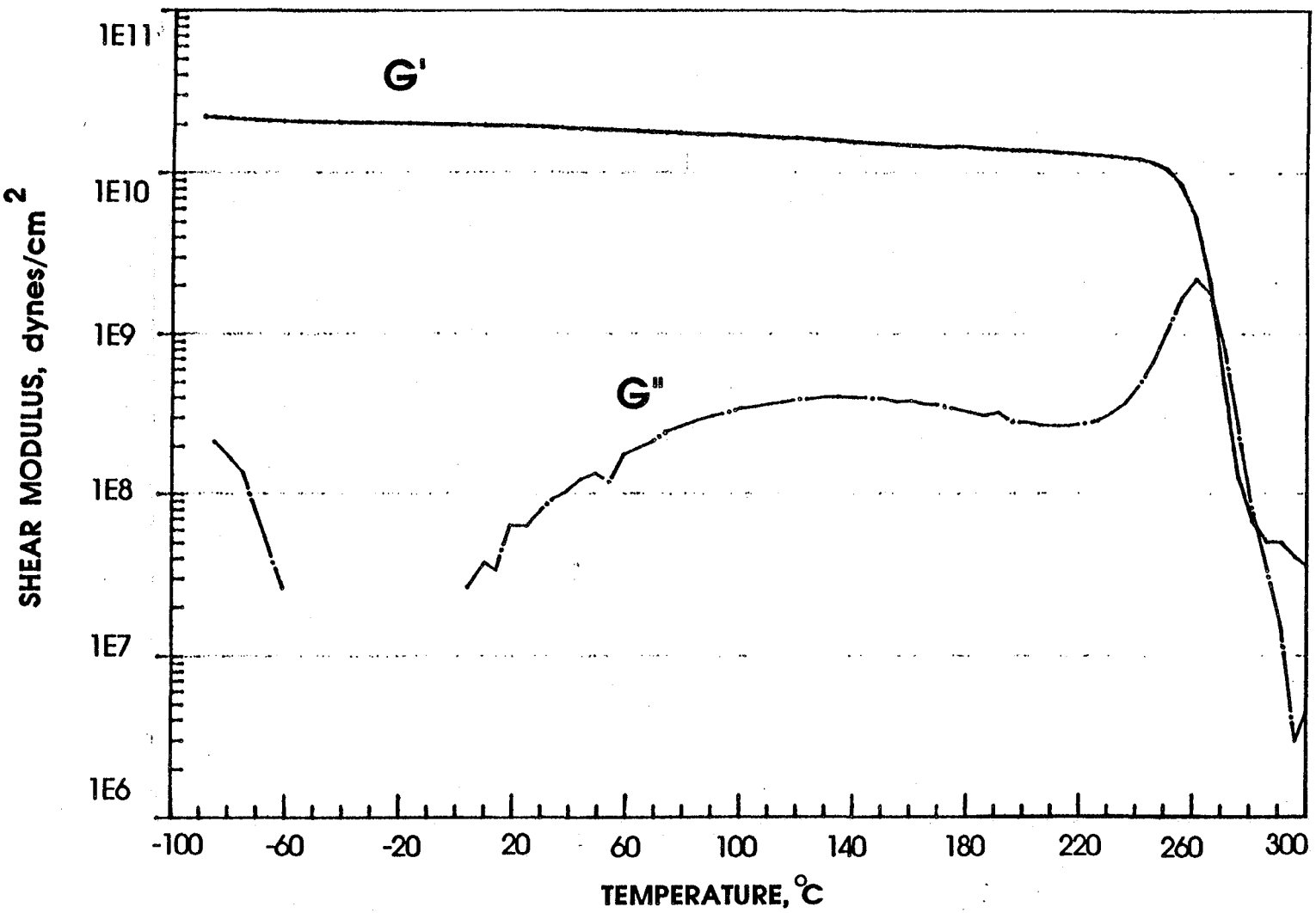


Figure B.13 Dynamic Mechanical Analysis Traces for NASA Polyimide PS-1111, Control Run No. 1, Unexposed Specimen

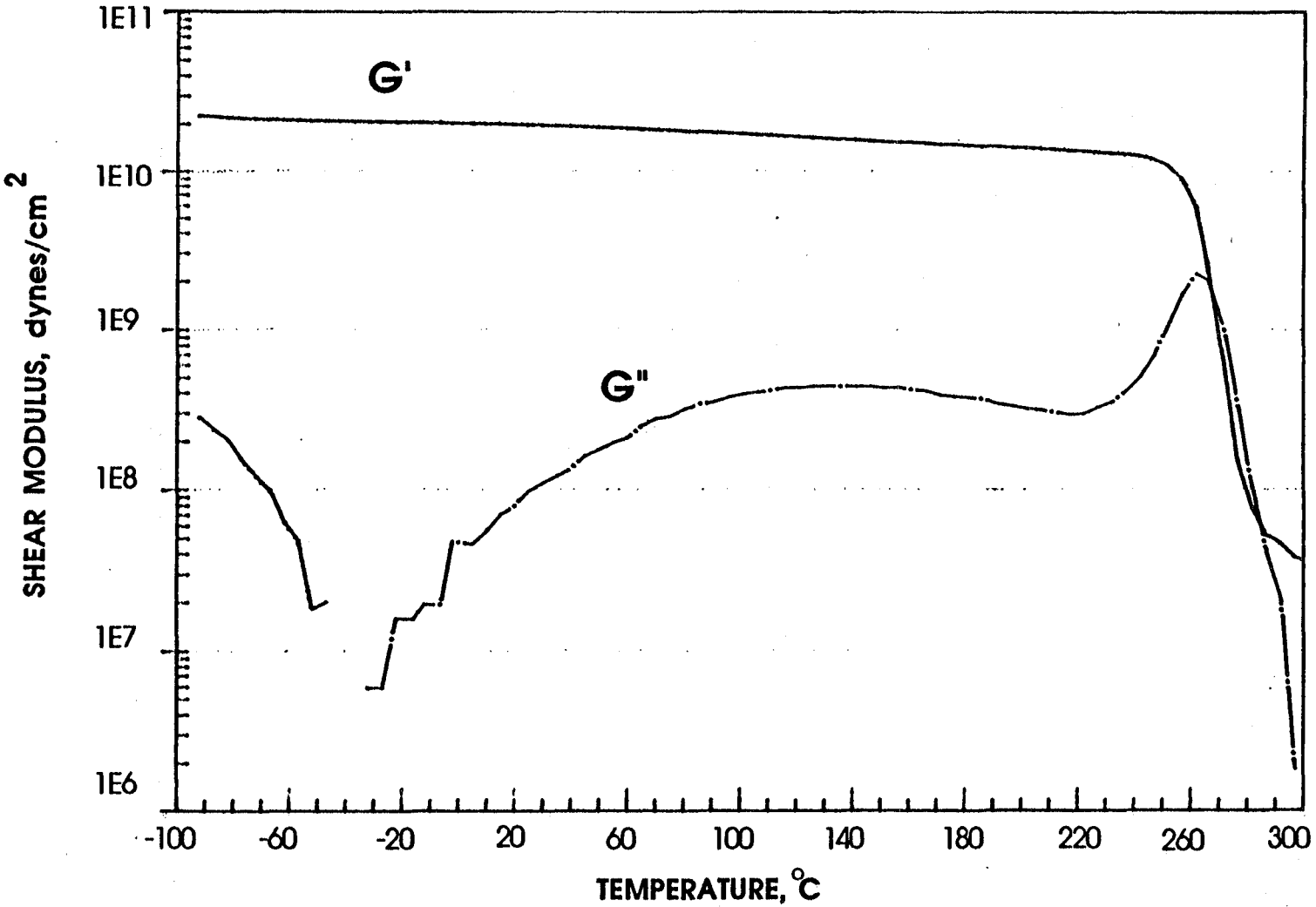


Figure B.14 Dynamic Mechanical Analysis Traces for NASA Polyimide PS-1111, Control Run No. 2, Unexposed Specimen

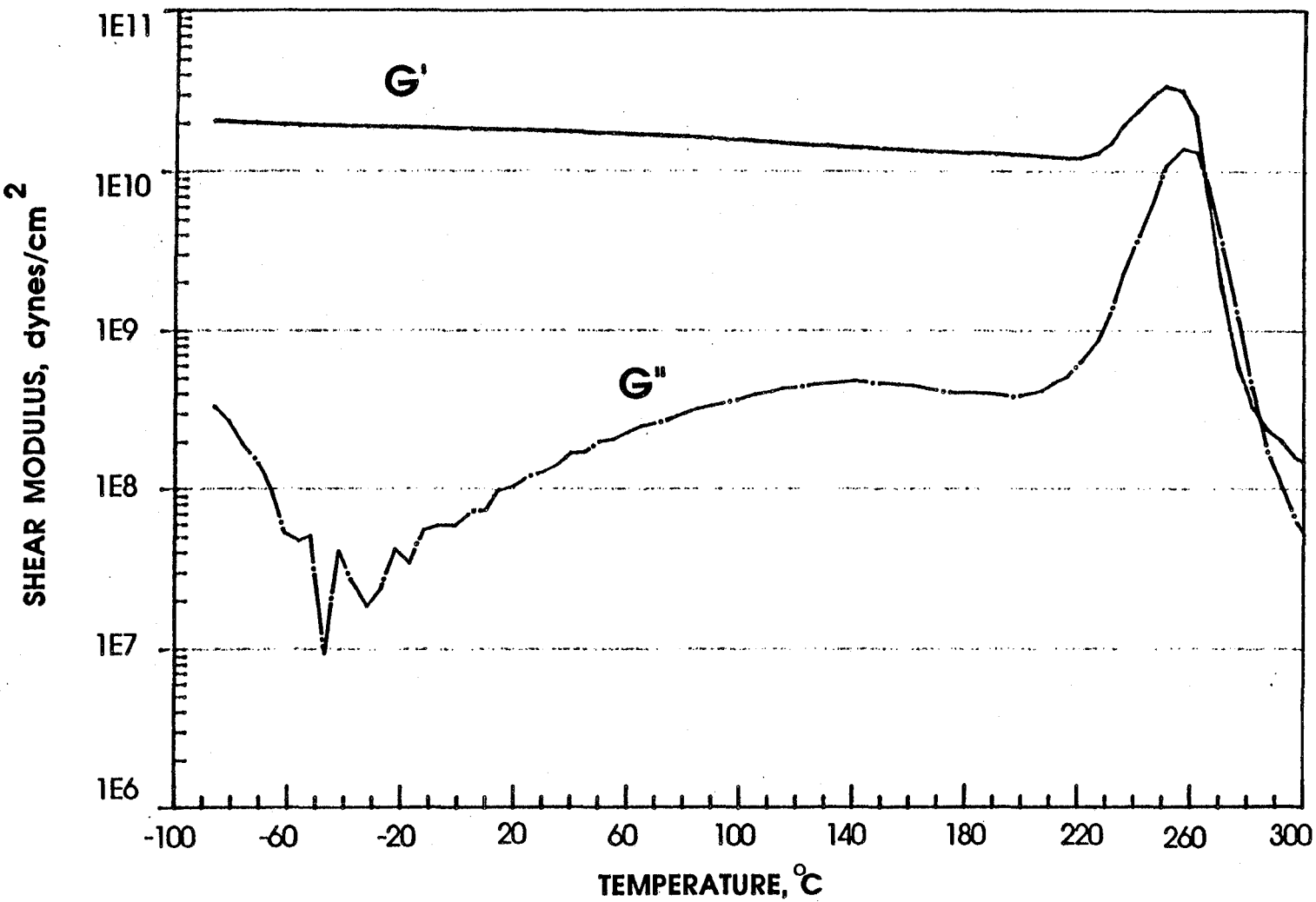


Figure B.15 Dynamic Mechanical Analysis Traces for NASA Polyimide PS-1111, ot/Wet Exposure

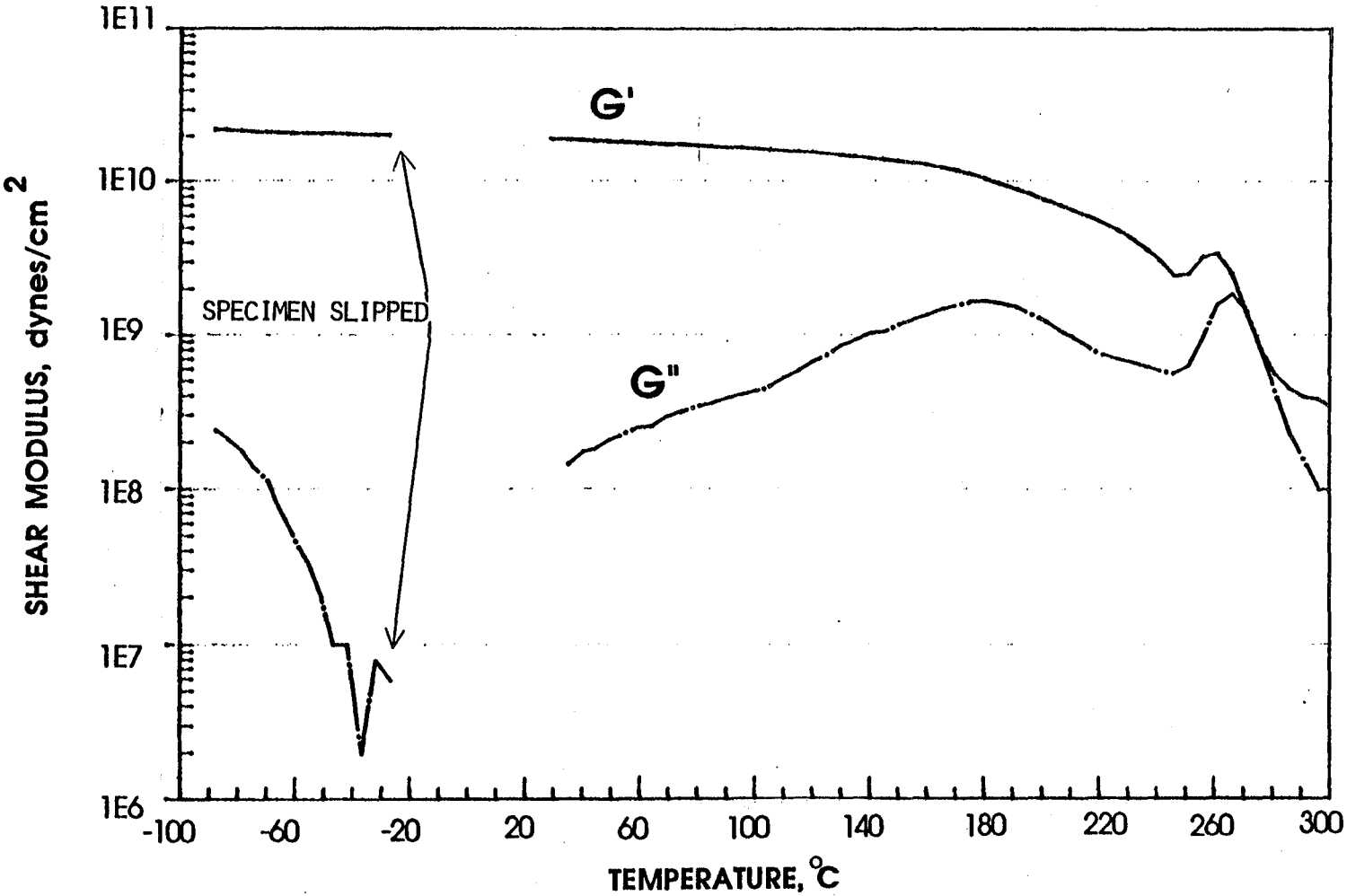


Figure B.16 Dynamic Mechanical Analysis Traces for NASA Polyimide PS-1111, Specimen Exposed to Methylene Chloride

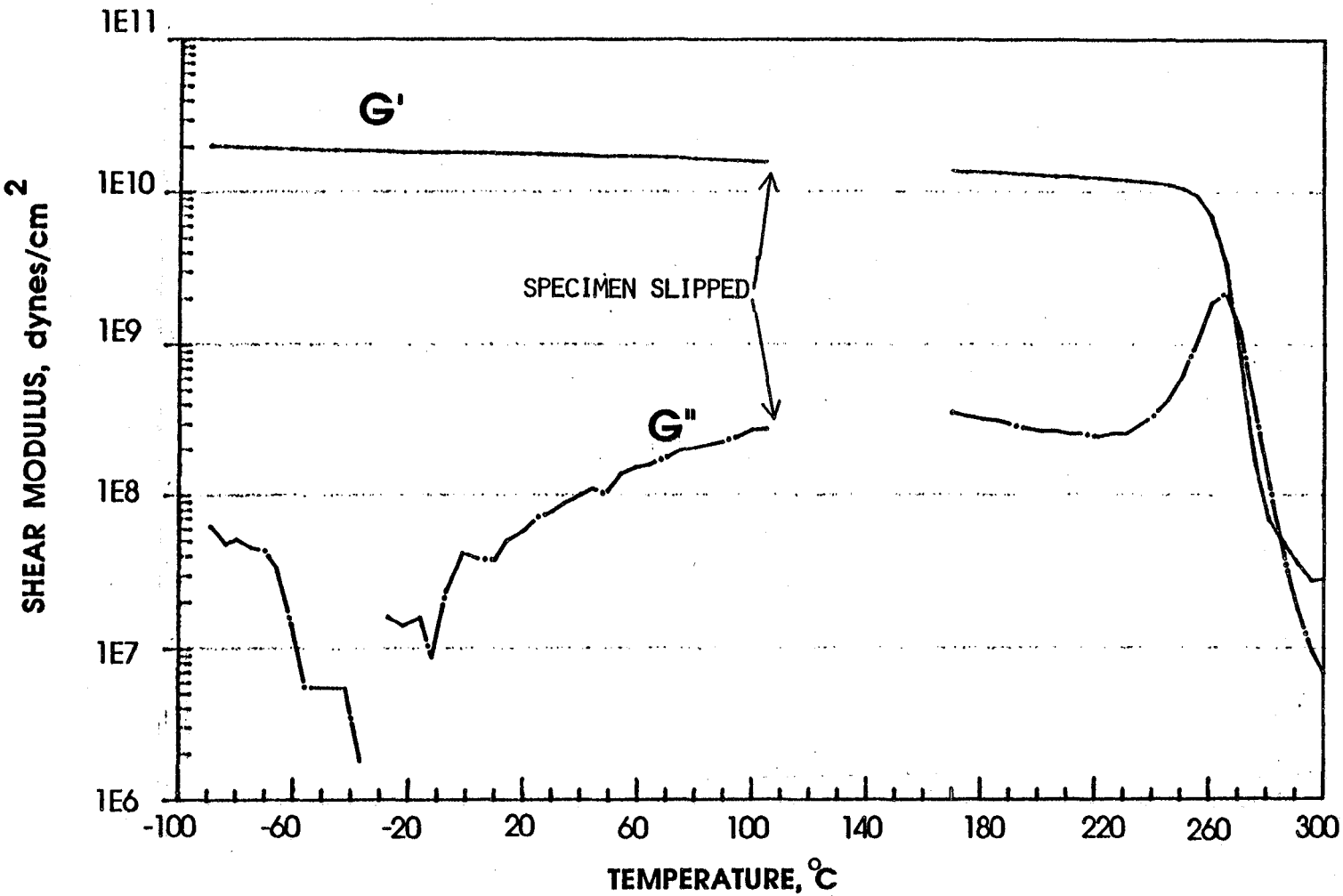


Figure B.17 Dynamic Mechanical Analysis Traces for NASA Polyimide PS-1111, Specimen Exposed to Skydrol

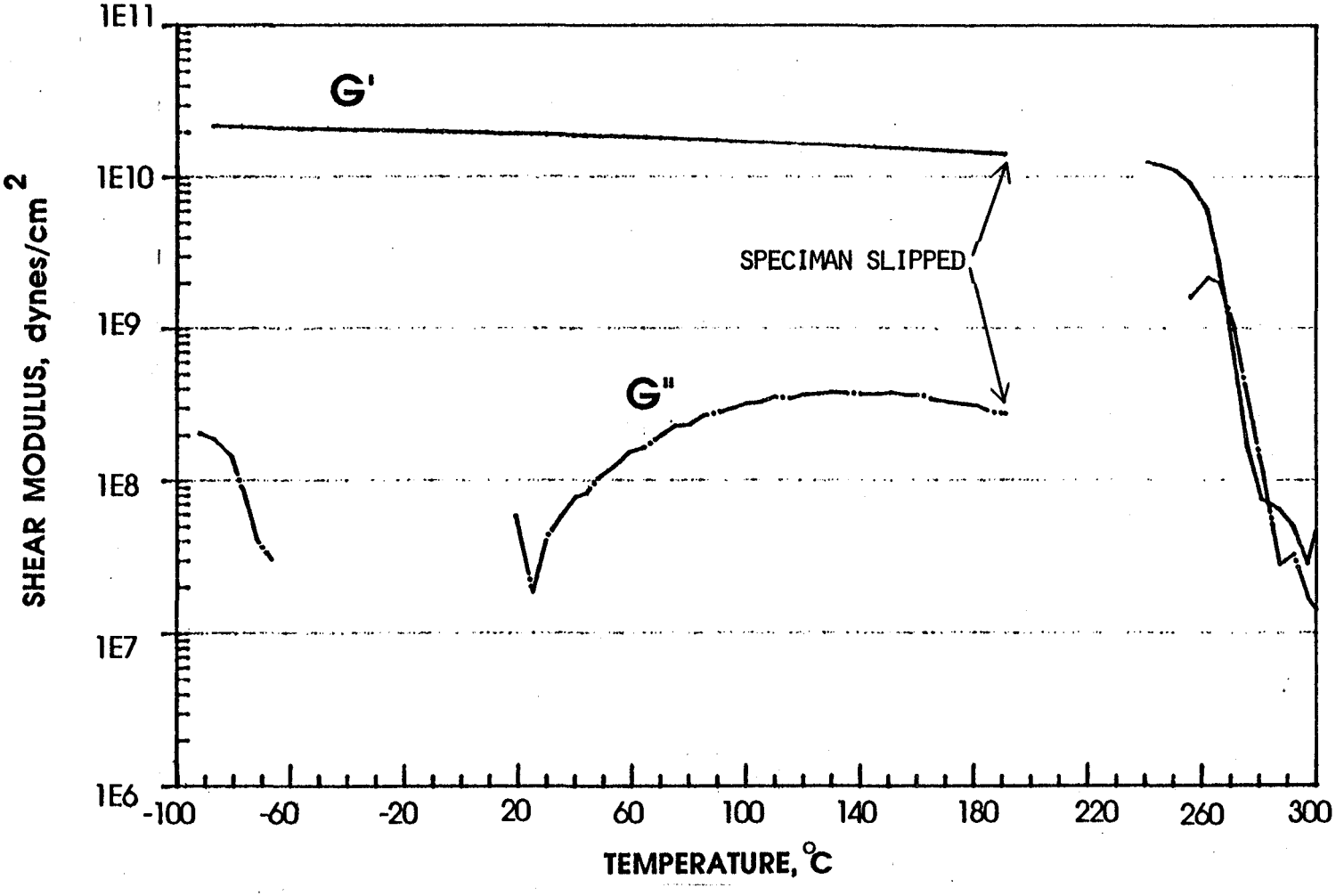


Figure B.18 Dynamic Mechanical Analysis Traces for NASA Polyimide PS-1111, Specimen Exposed to Jet Fuel

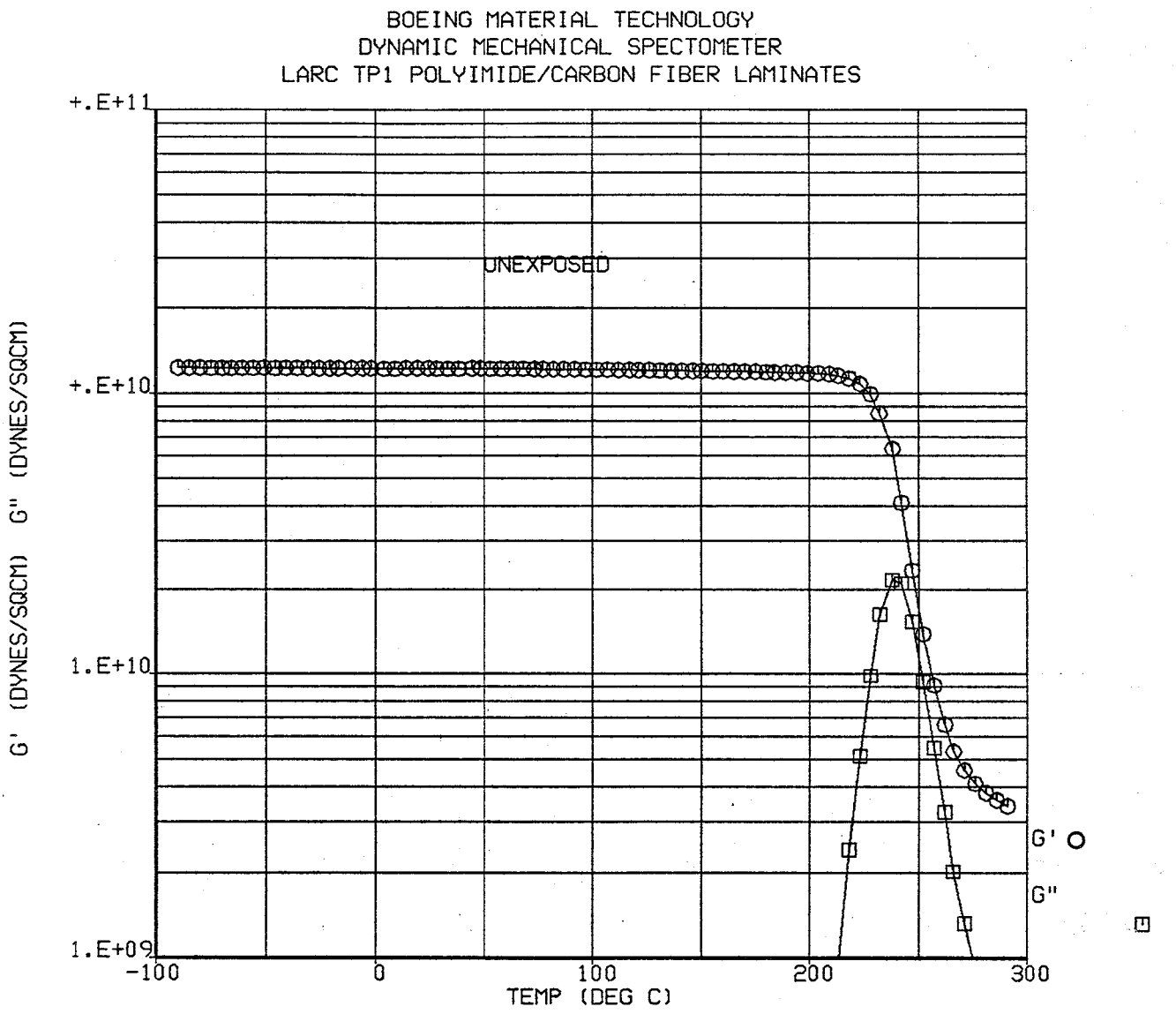


Figure B.19 Dynamic Mechanical Analysis Traces for an Unexposed 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Composite Coupon

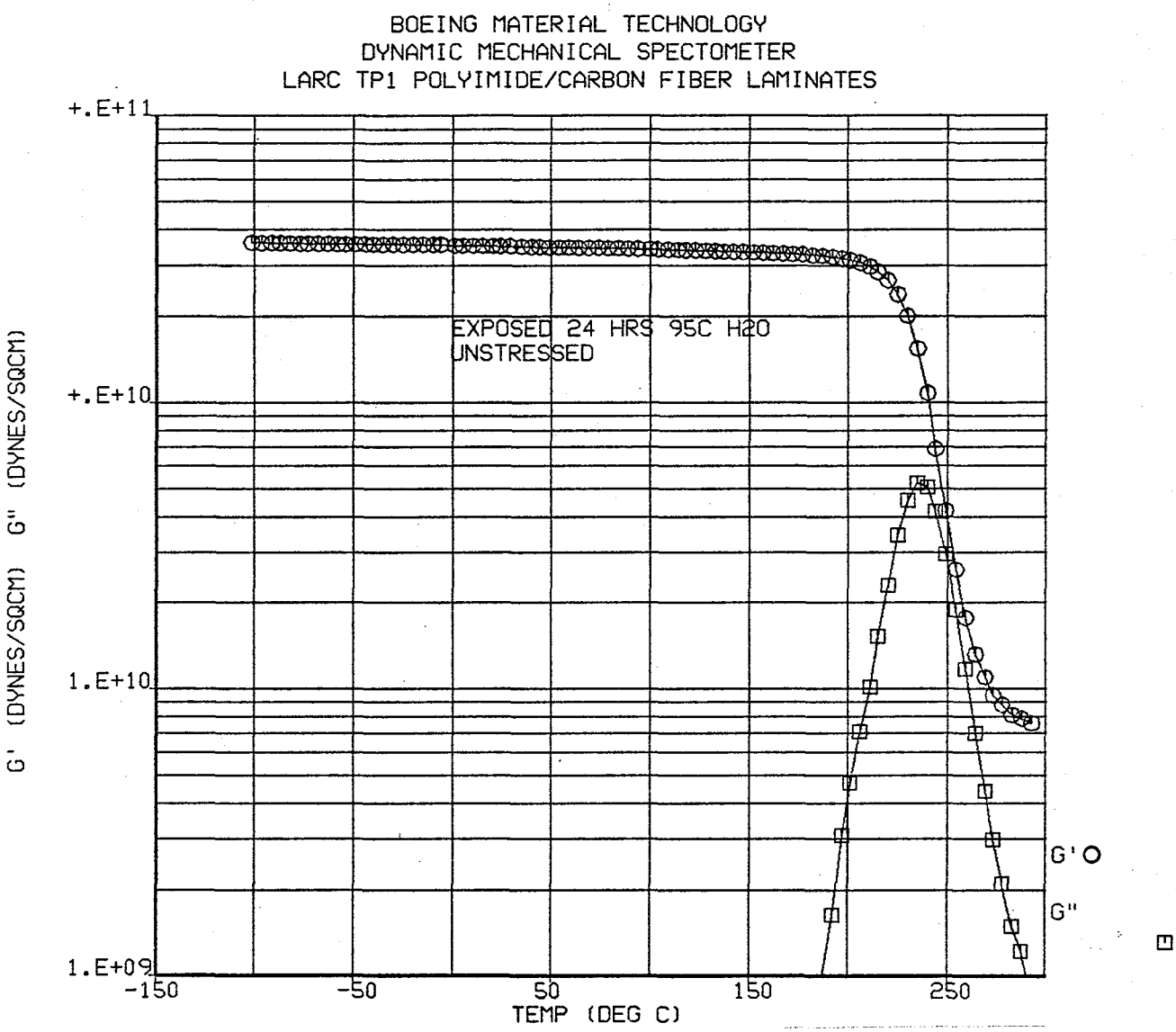


Figure B.20 Dynamic Mechanical Analysis Traces for a 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Composite Coupon Exposed to Water at 368K for 24 Hours

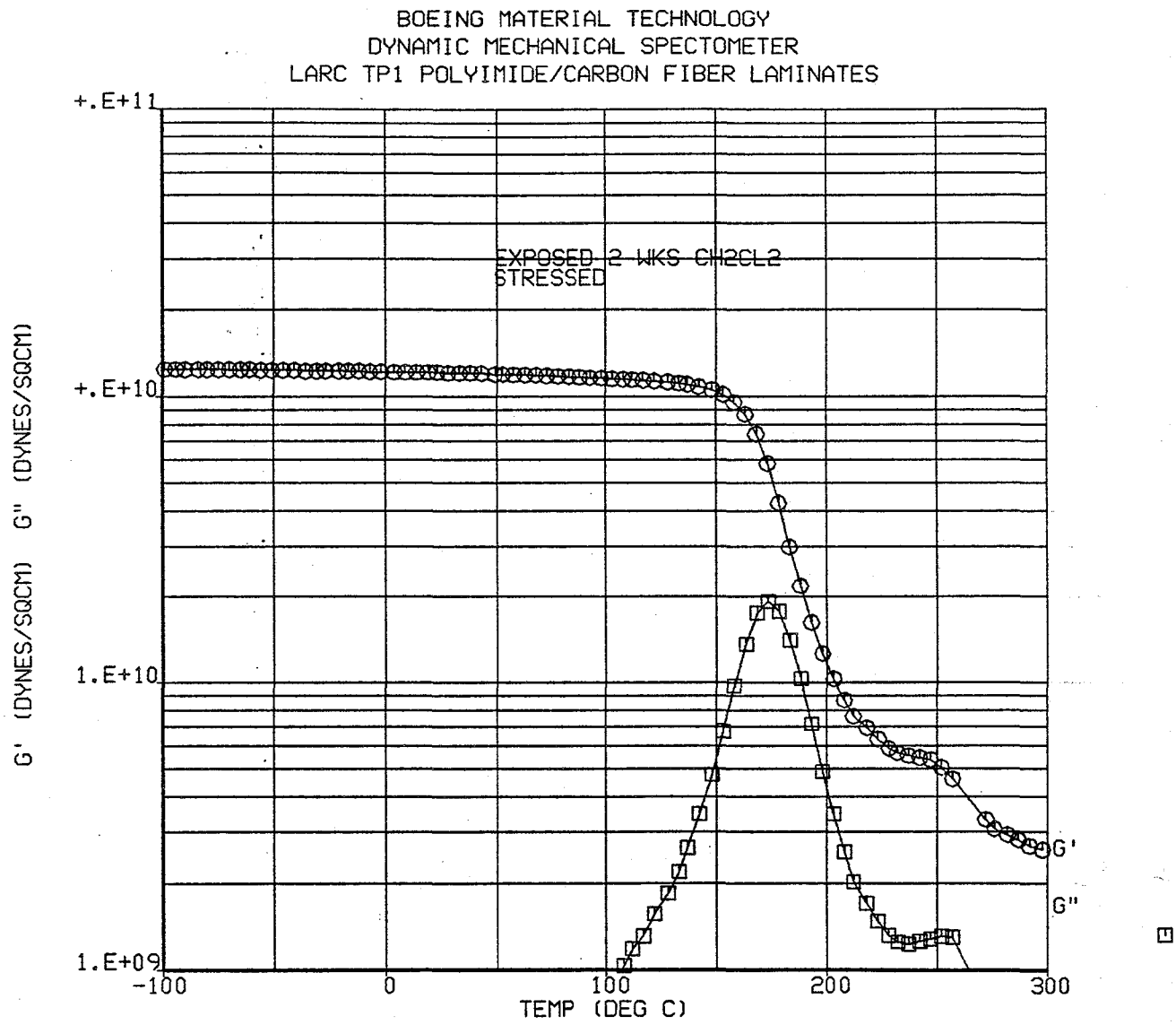


Figure B.21 Dynamic Mechanical Analysis Traces for a 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Composite Coupon Exposed to Methylene Chloride at Ambient Temperature for 350 Hours

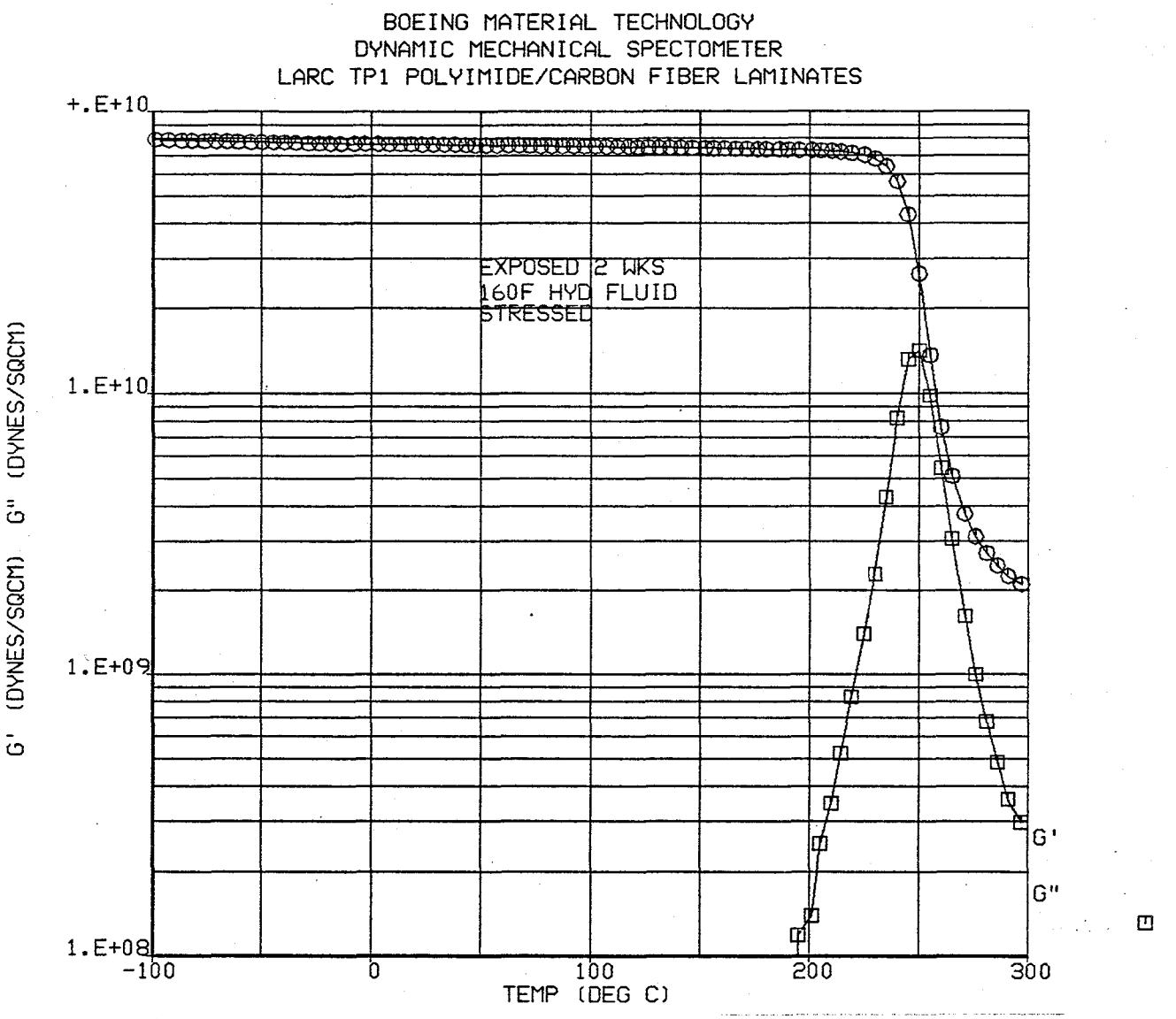


Figure B.22 Dynamic Mechanical Analysis Traces for a 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Composite Coupon Exposed to Skydrol Hydraulic Fluid at 344K for 350 Hours

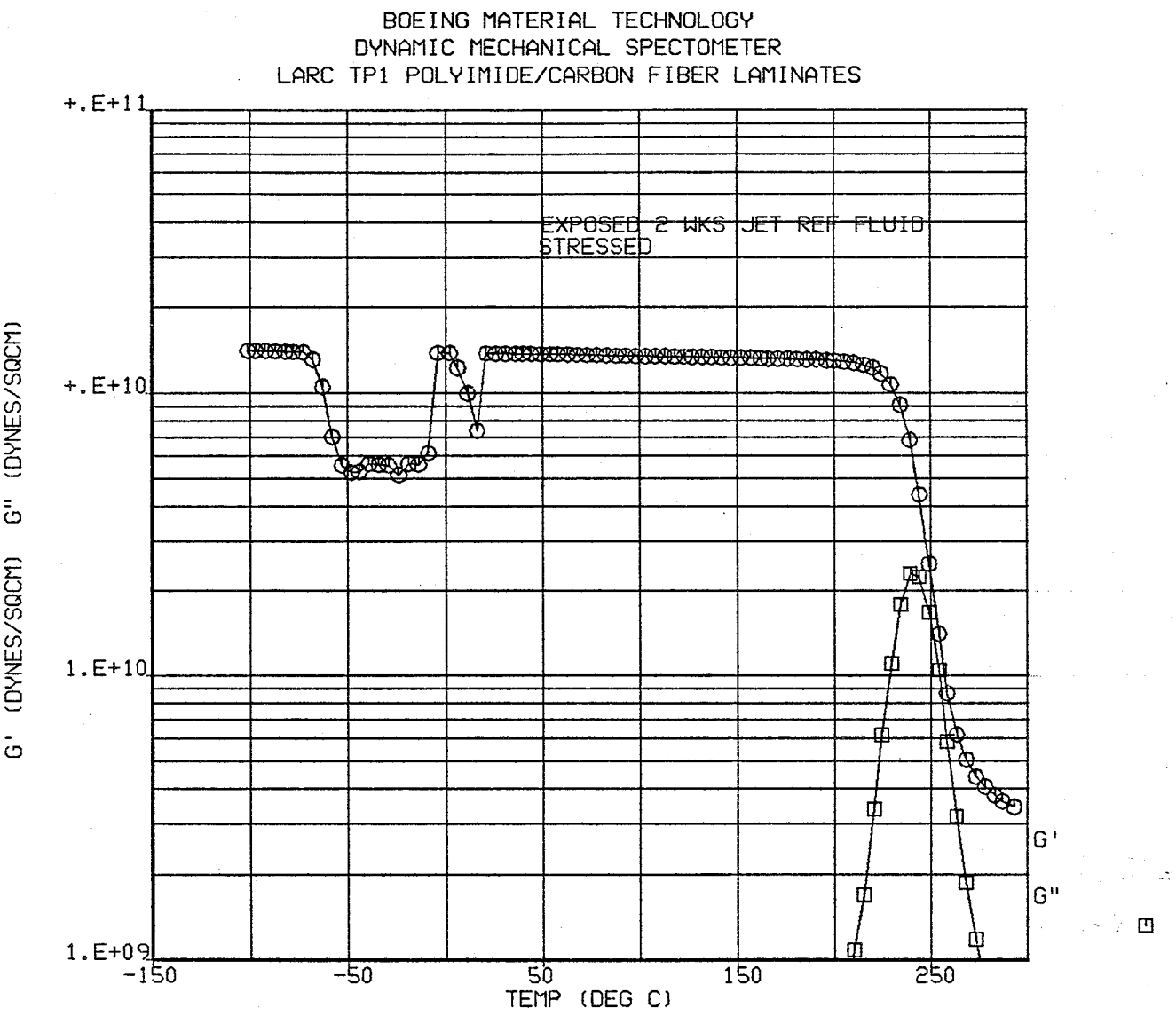


Figure B.23 Dynamic Mechanical Analysis Traces for a 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Composite Coupon Exposed to Jet Fuel at Ambient Temperature for 350 Hours

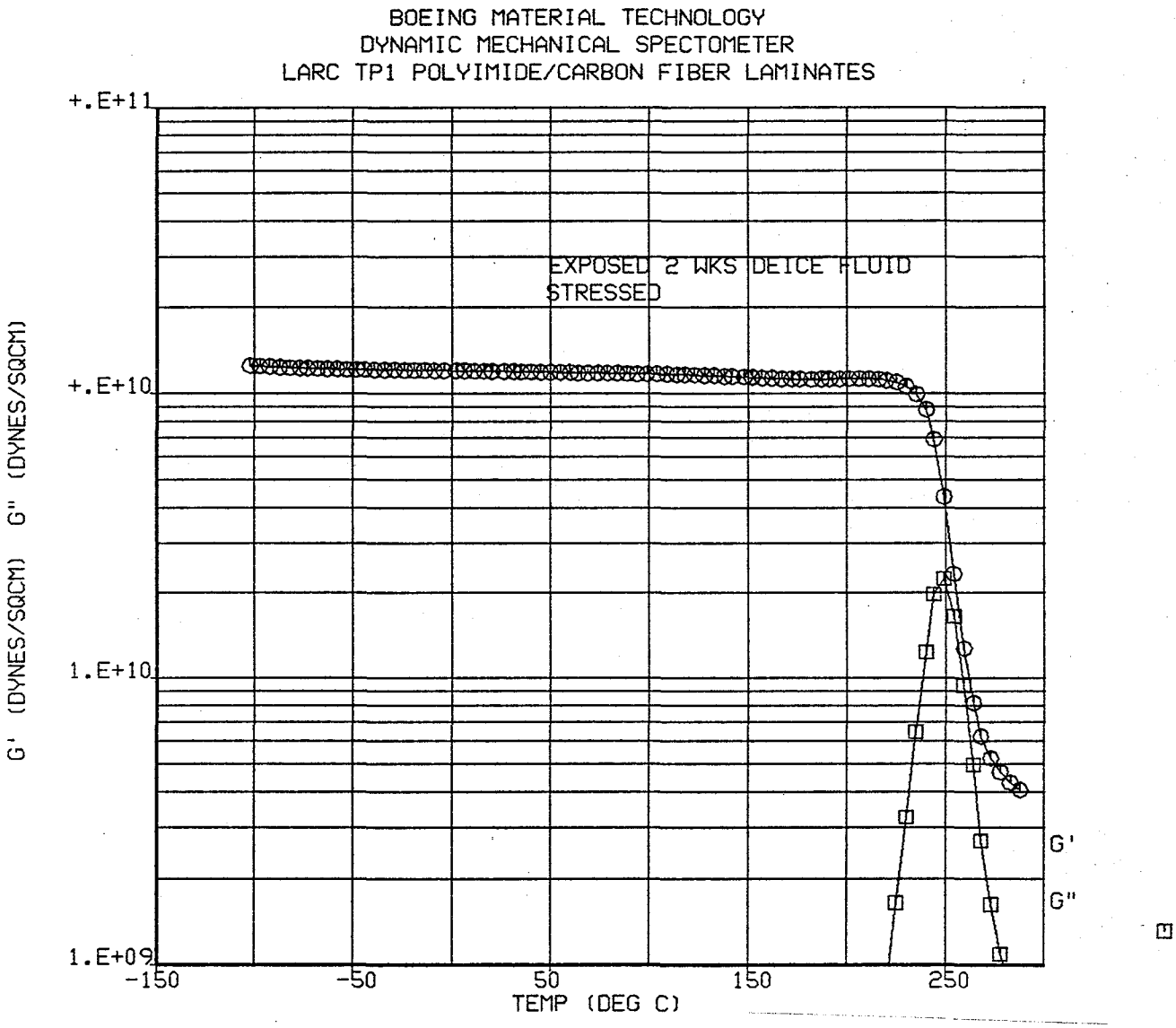


Figure B.24 Dynamic Mechanical Analysis Traces for a 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Composite Coupon Exposed to Deicing Fluid at Ambient Temperature for 350 Hours

TABLE B.1

LAMINATE DATA - BOEING PREPREG TAPE

Panel	Resin	Short Beam Shear Str., MPa (ksi)	Flexural Strength MPa (ksi)	Flexural Modulus GPa (msi)
A	4605-40	N/A	306 (44.4)	68 (9.8)
			450 (65.2)	66 (9.5)
			273 (39.6)	67 (9.7)
			281 (40.7)	65 (9.4)
			292 (42.3)	65 (9.4)
D	4605-40	39 (5.6)	422 (61.2)	72 (10.4)
		34 (4.9)	436 (63.3)	75 (10.8)
		33 (4.8)	433 (62.8)	69 (10.0)
		35 (5.0)	448 (64.9)	72 (10.4)
E	4605-40	36 (5.2)	511 (74.0)	58 (8.4)
		34 (4.9)	579 (83.9)	66 (9.6)
		36 (5.2)		
		39 (5.6)		
F	4605-40	25 (3.6)	322 (46.7)	76 (11.0)
		27 (3.9)	299 (43.3)	59 (8.6)
		12 (1.7*)	305 (44.2)	67 (9.7)
		11 (1.6*)		
J	PSI-1111	41 (5.9)	428 (62.1)	55 (8.0)
		43 (6.2)	386 (55.9)	73 (10.6)
		12 (1.8*)		
		16 (2.3*)		
K	PSI-1111	43 (6.2)	542 (78.4)	86 (12.4)
		41 (5.9)	553 (80.2)	64 (9.3)
		9 (1.3)*	549 (79.5)	62 (9.0)
		12 (1.8)*		
L	PSI-1111	10 (1.4)*	428 (62.0)	57 (8.3)
		10 (1.4)*	482 (69.9)	63 (9.1)
		11 (1.6)*	469 (67.9)	63 (9.2)
		14 (2.1)*		

* Low values due to testing error. Not included in Table 2.1.4.1 Averages

TABLE B.2

LAMINATE DATA - FIBERITE PREPREG TAPES

Laminate	Short Beam Shear Str., MPA (ksi)	Flexural Strength MPa(ksi)	Flexural Modulus GPa (msi)
F1111-1	76 (11.0)	----- Not Tested -----	
	76 (11.0)		
	74 (10.7)		
	77 (11.1)		
F4605-1	42 (6.1)	----- Not Tested -----	
	45 (6.5)		
	44 (6.4)		
	46 (6.7)		
F4300-1	59 (8.6)		
	62 (9.0)		
	58 (8.4)		
	63 (9.1)		
F1111-2	50 (7.2)	489 (70.8)	78 (11.3)
	48 (7.0)	570 (82.6)	76 (11.0)
	50 (7.2)		
F4300-2	51 (7.4)	636 (92.2)	84 (12.2)
	50 (7.3)	622 (90.1)	84 (12.2)
	50 (7.2)	549 (79.6)	82 (11.9)
F4605-2		----- Not Tested -----	
F4605-3		----- Not Tested -----	
F4605-4	66 (9.5)	863 (125)	161 (23.4)
	68 (9.9)	800 (116)	153 (22.2)
	70 (10.2)	883 (128)	117 (17.0)
F1111-3		----- Not Tested -----	
F4300-3		----- Not Tested -----	
F4605-5		----- Not Tested -----	

TABLE B.3

SHORT-BEAM SHEAR STRENGTH: UNMODIFIED LaRC-TPI AND CELION 6K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMP. MPa (Ksi)		450K(350°F) MPa (Ksi)
Specimen		Specimen	
1	75.2 (10.9)	1	43.2 (6.26)
2	73.8 (10.7)	2	46.3 (6.72)
3	68.7 (9.96)	3	45.8 (6.64)
4	75.2 (10.9)	4	45.6 (6.61)
5	73.1 (10.6)	5	46.0 (6.67)
Average	73.1 (10.6)		45.4 (6.58)
Std. Dev.	2.67 (0.387)		1.26 (0.183)
Coeff. of Var.	0.04 (0.04)		0.03 (0.03)
Symmetric (0°/90°) Crossply Laminate			
Specimen			
1	16.1 (2.33)		
2	14.3 (2.08)		
3	18.1 (2.63)		
4	15.5 (2.24)		
5	16.4 (2.38)		
Average	16.1 (2.33)		
Std. Dev.	1.38 (0.200)		
Coeff. of Var.	0.09 (0.09)		

TABLE B.4

SHORT-BEAM SHEAR STRENGTH: 2% DAA DOPED LaRC-TPI AND CELION 6K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMP. MPa (Ksi)		450K(350°F) MPa (Ksi)
Specimen		Specimen	
1	95.9 (13.9)	6	62.6 (9.07)
2	99.3 (14.4)	7	62.5 (9.06)
3	76.6 (11.1)	8	62.5 (9.06)
4	82.8 (12.0)	9	58.6 (8.50)
5	101 (14.6)	10	55.3 (8.02)
Average	91.0 (13.2)		60.3 (8.74)
Std. Dev.	10.8 (1.56)		3.26 (0.472)
Coeff. of Var.	0.12 (0.12)		0.05 (0.05)
Symmetric (0°/90°) Crossply Laminate			
Specimen			
1	61.1 (8.86)		
2	57.6 (8.35)		
3	64.8 (9.40)		
4	53.0 (7.68)		
5	60.2 (8.73)		
Average	59.3 (8.60)		
Std. Dev.	4.41 (0.639)		
Coeff. of Var.	0.07 (0.07)		

TABLE B.5

SHORT-BEAM SHEAR STRENGTH: 1:1 LaRC-TPI SLURRY AND CELION 3K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMP. MPa (Ksi)		450K(350°F) MPa (Ksi)
Specimen		Specimen	
1	6.50	6	4.91
2	5.81	7	4.57
3	6.56	8	5.09
4	6.56	9	4.93
5	6.67	10	5.37
Average	6.42		4.97
STD. DEV.	0.346		0.291
Coeff. of Var.	0.05		0.06

Symmetric (0°/90°) crossply laminate was not fabricated due to low SBS and Flex. Strength of unidirectional laminate.

TABLE B.6

SHORT-BEAM SHEAR STRENGTH: 1:1 $PISO_2$/LaRC-TPI SLURRY AND T300 6K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMP. MPa (Ksi)		450K(350°F) MPa (Ksi)
Specimen		Specimen	
1	74.5 (10.8)	6	59.6 (8.64)
2	82.8 (12.0)	7	59.0 (8.55)
3	71.0 (10.3)	8	60.2 (8.73)
4	75.9 (11.0)	9	58.2 (8.44)
5	82.1 (11.9)	10	61.0 (8.85)
Average	77.2 (11.2)		59.6 (8.64)
Std. Dev.	5.04 (0.731)		1.09 (0.158)
Coeff. of Var.	0.07 (0.07)		0.02 (0.02)
Symmetric (0°/90°) Crossply Laminate			
Specimen			
1	41.9 (6.08)		
2	37.0 (5.36)		
3	40.3 (5.85)		
4	41.0 (5.94)		
5	38.6 (5.60)		
Average	39.8 (5.77)		
Std. Dev.	1.98 (0.287)		
Coeff. of Var.	0.05 (0.05)		

TABLE B.7

SHORT-BEAM SHEAR STRENGTH: 2:1 P1SO$_2$/LaRC-TPI SLURRY AND AS-4 12K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMP. MPa (Ksi)		450K(350°F) MPa (Ksi)
Specimen		Specimen	
1	112 (16.2)	6	59.4 (8.61)
2	117 (16.9)	7	59.3 (8.60)
3	112 (16.3)	8	58.3 (8.45)
4	121 (17.5)	9	58.2 (8.44)
5	116 (16.8)	10	63.9 (9.26)
Average	115 (16.7)		59.8 (8.67)
Std. Dev.	3.60 (0.522)		2.33 (0.338)
Coeff. of Var.	0.03 (0.03)		0.04 (0.04)
Symmetric (0°/90°) Crossply Laminate			
Specimen			
1	89.7 (13.0)		
2	91.0 (13.2)		
3	75.9 (11.0)		
4	77.9 (11.3)		
5	82.1 (11.9)		
Average	83.4 (12.1)		
Std. Dev.	6.81 (0.988)		
Coeff. of Var.	0.08 (0.08)		

Table B.8. Flexural Strength and Modulus: Unmodified LaRC-TPI and Celion 6K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMPERATURE					450K (350°F)			
	STRENGTH		MODULUS			STRENGTH		MODULUS	
	MPa	(Ksi)	GPa	(Msi)		MPa	(Ksi)	GPa	(Msi)
Specimen					Specimen				
1	1,870	(271)	142	(20.6)	4	1,030	(150)	118	(17.1)
2	1,830	(266)	139	(20.1)	5	1,100	(160)	91.7	(13.3)
3	1,750	(254)	141	(20.5)	6	1,230	(179)	108	(15.7)
Average	1,820	(264)	141	(20.4)		1,120	(163)	106	(15.4)
Symmetric (0°/90°) Crossply Laminate									
Specimen									
1	230	(33.4)	35.5	(5.14)					
2	203	(29.5)	39.6	(5.74)					
3	210	(30.5)	34.2	(4.96)					
4	193	(28.0)	38.0	(5.51)					
5	180	(26.1)	39.7	(5.76)					
Average	203	(29.5)	37.4	(5.42)					
Std. Dev.	18.9	(2.74)	2.46	(0.357)					
Coeff. of Var.	0.09	(0.09)	0.07	(0.07)					

Table B.9. Flexural Strength and Modulus: 2% DAA Doped LaRC-TPI and Celion 6K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMPERATURE					450K (350°F)			
	STRENGTH		MODULUS			STRENGTH		MODULUS	
	MPa	(Ksi)	GPa	(Msi)		MPa	(Ksi)	GPa	(Msi)
Specimen					Specimen				
1	1,460	(212)	132	(19.1)	4	1,140	(165)	134	(19.5)
2	1,540	(224)	137	(19.9)	5	1,230	(179)	123	(17.8)
3	1,420	(206)	129	(18.7)	6	1,300	(189)	132	(19.1)
Average	1,480	(214)	133	(19.3)		1,230	(178)	130	(18.8)
Symmetric (0°/90°) Crossply Laminate									
Specimen									
1	821	(199)	40.6	(5.88)					
2	903	(131)	42.8	(6.21)					
3	676	(98.0)	41.2	(5.97)					
4	897	(130)	42.8	(6.21)					
Average	828	(120)	41.9	(6.07)					

TABLE B.10

FLEXURAL STRENGTH AND MODULUS: 1:1 LaRC-TPI SLURRY AND CELION 6K

UNIDIRECTIONAL LAMINATES	AMBIENT TEMPERATURE STRENGTH MPa	(Ksi)	AMBIENT TEMPERATURE MODULUS GPa	(Msi)		450K (350°F) STRENGTH MPa	(Ksi)	450K (350°F) MODULUS GPa	(Msi)
Specimen					Specimen				
1	766	(111)	104	(15.1)	4	441	(63.9)	97.2	(14.1)
2	800	(116)	101	(14.6)	5	417	(60.4)	108	(15.6)
3	903	(131)	95.2	(13.8)	6	677	(98.1)	100	(14.5)
Average	828	(120)	100	(14.5)	Average	511	(74.1)	101	(14.7)

Symmetric (0°/90°) crossply laminate was not fabricated due to the low short-beam shear and flexure strength of the unidirectional laminate.

TABLE B.11

FLEXURAL STRENGTH AND MODULUS: 1:1 $PISO_2$/LaRC-TPI SLURRY AND T300 3K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMPERATURE STRENGTH MPa	(Ksi)	MODULUS GPa	(Msi)	450K (350°F)	STRENGTH MPa	(Ksi)	MODULUS GPa	(Msi)
Specimen					Specimen				
1	1,150	(167)	86.9	(12.6)	4	92.4	(134)	90.0	(12.9)
2	1,000	(145)	93.1	(13.5)	5	88.3	(128)	83.5	(12.1)
3	1,255	(182)	93.1	(13.5)	6	91.0	(132)	85.5	(12.4)
Average	1,140	(165)	91.0	(13.2)		90.3	(131)	86.2	(12.5)
Symmetric (0°/90°) Crossply Laminate									
Specimen									
1	501	(72.7)	32.4	(4.70)					
2	520	(75.4)	30.5	(4.42)					
3	530	(76.9)	30.2	(4.38)					
4	501	(72.7)	34.5	(5.00)					
5	501	(72.7)	32.4	(4.70)					
Average	511	(74.1)	32.0	(4.64)					
Std. Dev.	13.5	(1.95)	1.72	(0.250)					
Coeff. of Var.	0.03	(0.03)	0.05	(0.05)					

TABLE B.12

FLEXURAL STRENGTH AND MODULUS: 2:1 $PISO_2$/LaRC-TPI SLURRY AND AS-4 12K

UNIDIRECTIONAL LAMINATE	AMBIENT TEMPERATURE STRENGTH MPa	(Ksi)	MODULUS GPa	(Msi)	450K (350°F)	STRENGTH MPa	(Ksi)	MODULUS GPa	(Msi)
Specimen					Specimen				
1	1,440	(290)	99.3	(14.4)	4	910	(132)	94.5	(13.7)
2	1.430	(208)	100	(14.5)	5	986	(143)	93.8	(13.6)
3	1,490	(216)	103	(15.0)	6	1,070	(155)	103	(14.9)
Average	1,460	(211)	101	(14.6)		986	(143)	97.2	(14.1)
Symmetric (0°/90°) Crossply Laminate									
Specimen									
1	1,110	(161)	69.0	(10.0)					
2	1,090	(158)	67.9	(9.85)					
3	1,062	(154)	68.9	(9.99)					
4	1,080	(157)	66.6	(9.66)					
5	1,060	(153)	67.3	(9.76)					
Average	1,080	(157)	67.9	(9.85)					
Std. Dev.	22.1	(3.21)	1.01	(0.147)					
Coeff. of Var.	0.02	(0.02)	0.01	(0.01)					

TABLE B.13

TENSILE STRENGTH AND MODULUS AT AMBIENT TEMPERATURE
(NOT NORMALIZED TO A CONSTANT FIBER VOLUME)

2% DAA DOPED LaRC-TPI AND CELION 6K; LAMINATE S2B2L4(0)8				
Specimen	Tensile Strength MPa	(Ksi)	Tensile Modulus GPa	(Msi)
1	1,620	(235)	113	(16.4)
2	1,410	(205)	110	(15.9)
3	1,530	(222)	114	(16.5)
4	1,620	(235)	110	(16.0)
5	1,400*	(203)*	109	(15.7)
6	1,290*	(187)*	108	(15.7)
Average	1,540	(224)	111	(16.0)
Std. Dev.	--		2.38	(0.345)
Coeff. of Var.	--		0.02	(0.02)

* Not ultimate failure - specimen slipped. Omitted from average.

2:1 P1SO$_2$/LaRC-TPI AND CELION 6K; LAMINATE S5B2L1(0)8				
Specimen	Tensile Strength MPa	(Ksi)	Tensile Modulus GPa	(Msi)
1	1,180	(171)	106	(15.3)
2	1,230	(179)	105	(15.2)
3	1,210	(176)	95	(13.8)
4	1,230	(179)	104	(15.1)
5	1,320**	(191)**	101	(14.7)
6	1,200	(174)	107	(15.5)
Average	1,210	(176)	103	(14.9)
Std. Dev.	23.6	(3.42)	4.28	(0.62)
Coeff. of Var.	0.02	(0.02)	0.04	(0.04)

** Omitted from average.

TABLE B.14

COMPRESSIVE STRENGTH AND MODULUS - 2% DAA

DOPED LaRC-TPI/CELION 6K

(NOT NORMALIZED TO A CONSTANT FIBER VOLUME FRACTION)

LAMINATE S2B2L1(0)10

AMBIENT TEMPERATURE				450K (350°F)			
SPECIMEN	STRENGTH MPa (ksi)	SPECIMEN	MODULUS GPa(msi)	SPECIMEN	STRENGTH MPa (ksi	SPECIMEN	MODULUS GPa (msi)
1	1,150 (167)	2	95.2 (13.8)	6	674 (97.7)	6	91.7 (13.3)
2	876 (127)	3	91.7 (13.3)	7	661 (95.9)	7	83.5 (12.1)
3	945 (137)	4	89.7 (13.0)	8	636 (92.2)	8	89.7 (13.0)
4	1,070 (155)			*9	451 (65.4)		
5	1,030 (149)			10	628 (91.0)		
Average	1,010 (147)		92.2 (13.4)	11	619 (89.7)		
				Average	643 (93.3)		88.3 (12.8)

345K WATER SOAK/TESTED 450K			
SPECIMEN	STRENGTH MPa (ksi)	SPECIMEN	MODULUS GPa(msi)
1	297 (43.0)	1	103 (14.9)
2	448 (65.0)	2	104 (15.1)
3	337 (48.8)	3	92.4 (13.4)
** 4	--- ----	4	101 (14.6)
5	368 (53.4)		
6	245 (35.5)		
Average	339 (49.1)		100 (14.5)

* Omitted from calculation of average. ** Not tested due to tab disbond.

TABLE B.15

COMPRESSIVE STRENGTH AND MODULUS - 2:1 PISO_2/LaRC-TPI//CELION 6K
(NOT NORMALIZED TO A CONSTANT FIBER VOLUME FRACTION)
LAMINATE S5B2L4(0)10

AMBIENT TEMPERATURE				450K (350°F)			
SPECIMEN	STRENGTH MPa (ksi)	SPECIMEN	MODULUS GPa(msi)	SPECIMEN	STRENGTH MPa (ksi	SPECIMEN	MODULUS GPa (msi)
1	1,120 (163)	1	93.8 (13.6)	6	407 (59.0)	6	81.4 (11.8)
2	1,100 (159)	2	104 (15.1)	7	401 (58.2)	7	86.2 (12.5)
3	822 (119)	3	93.8 (13.6)	8	586 (85.0)	8	86.2 (12.5)
4	631 (91.5)	4		9	677 (98.1)		
5	626 (90.8)			10	512 (74.2)		
Average	862 (125)		97.2 (14.1)	Average	517 (74.9)		84.6 (12.3)
345K WATER SOAK/TESTED 450K							
SPECIMEN	STRENGTH	SPECIMEN	STRENGTH				
1	401 (58.1)	1	106 (15.4)				
2	463 (67.1)	2	104 (15.1)				
3	354 (51.3)	3	106 (15.3)				
4	479 (69.4)	4	99 (14.4)				
Average	408 (59.1)	Average	104 (15.1)				

APPENDIX C

THROUGH-TRANSMISSION ULTRASONIC SCANS OF THE TEST LAMINATES

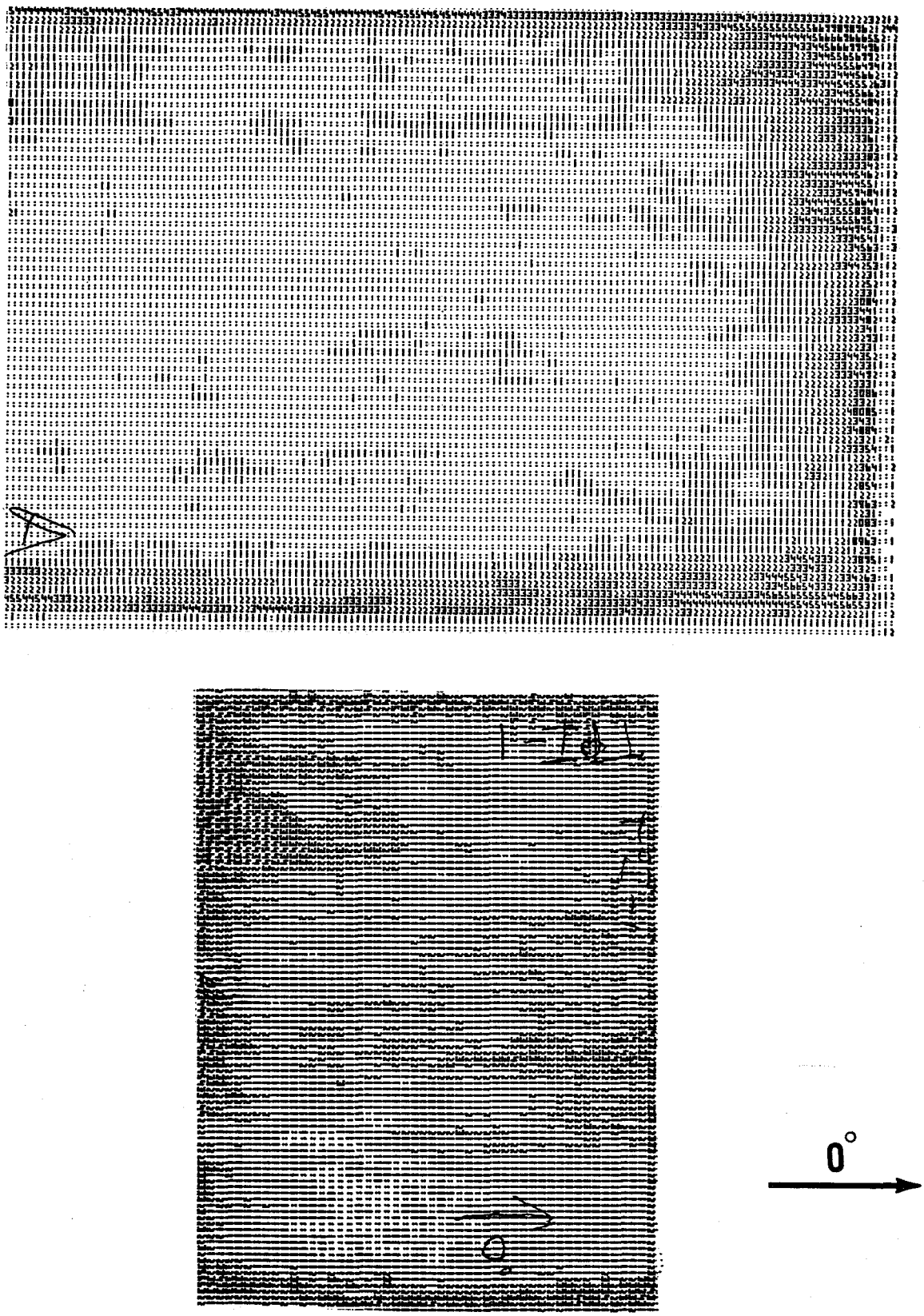


Figure C.1 Through-Transmission Ultrasonic Scan of Laminate S1B1L1(0)12, Unmodified LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

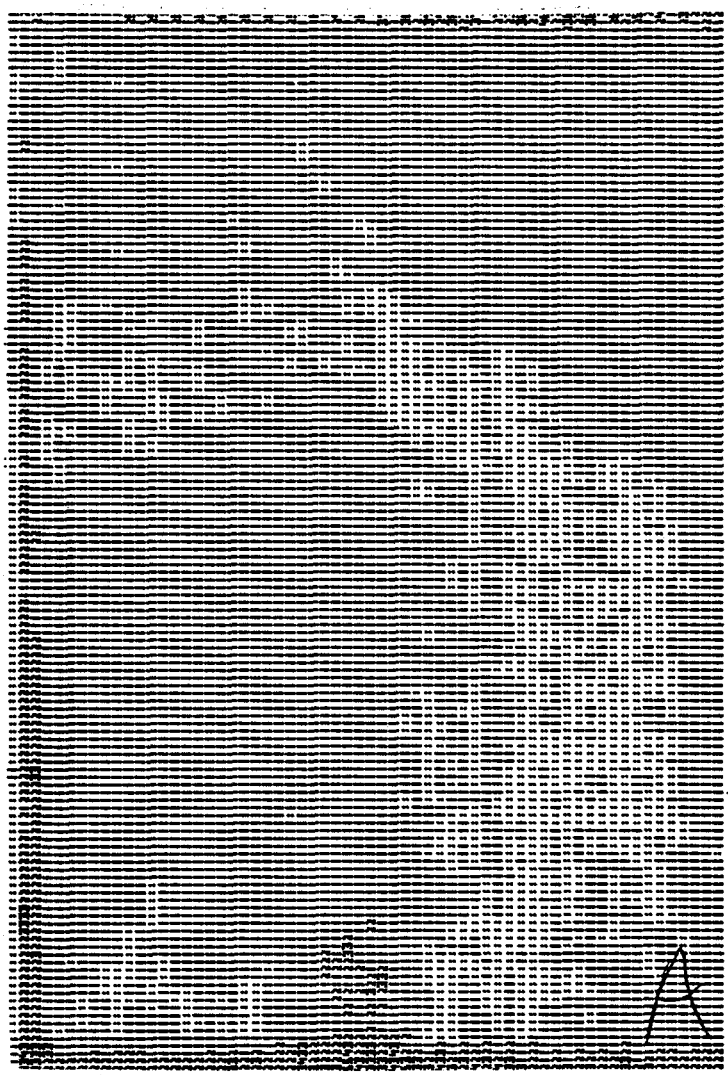


Figure C.2 Through-Transmission Ultrasonic Scan of Laminate S2B1L1(0)12, 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

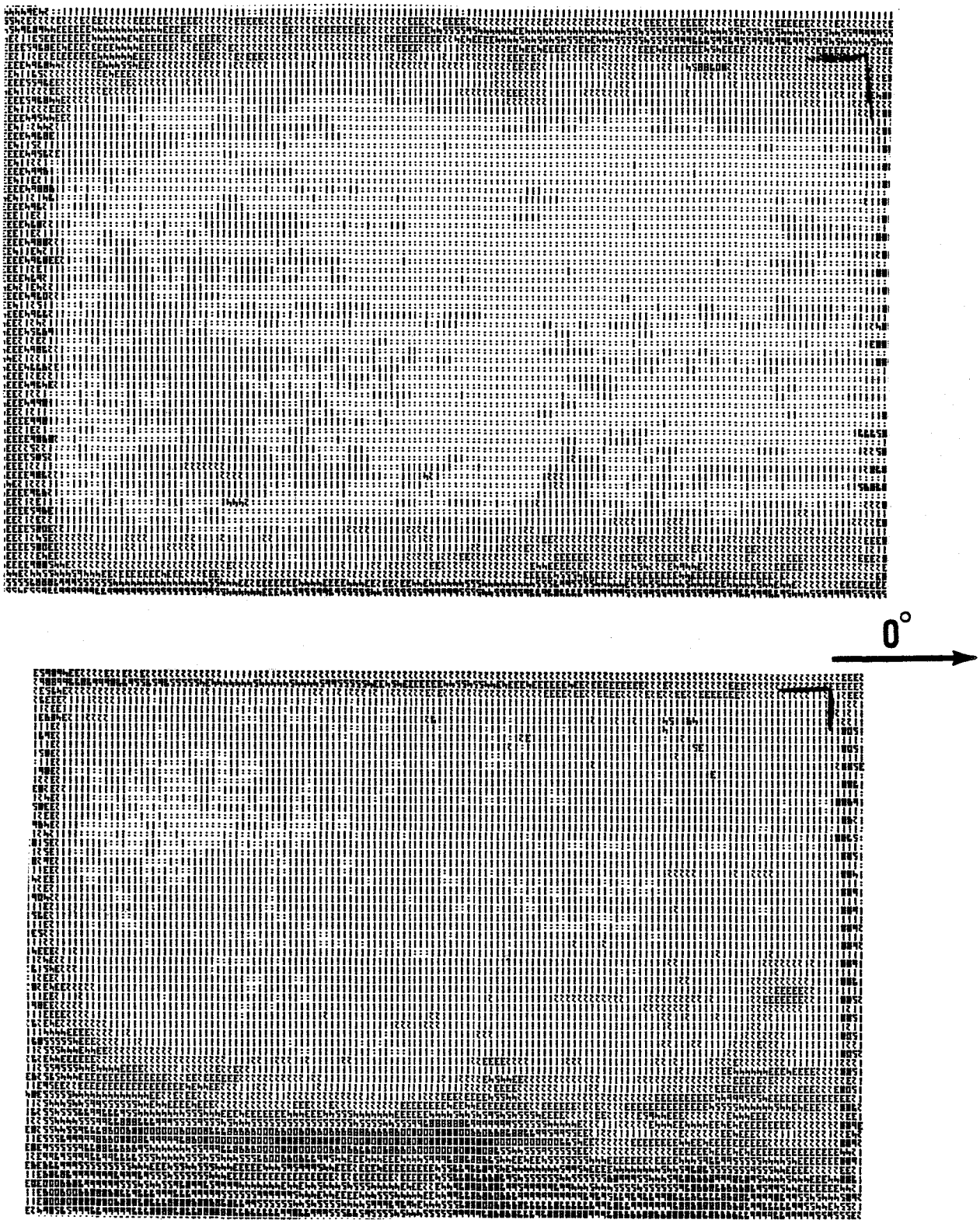


Figure C.3 Through-Transmission Ultrasonic Scan of Laminate S3B1L1(0)12, 1:1 LaRC-TPI Powder Slurry and Celion 6K Carbon Fiber Reinforcement

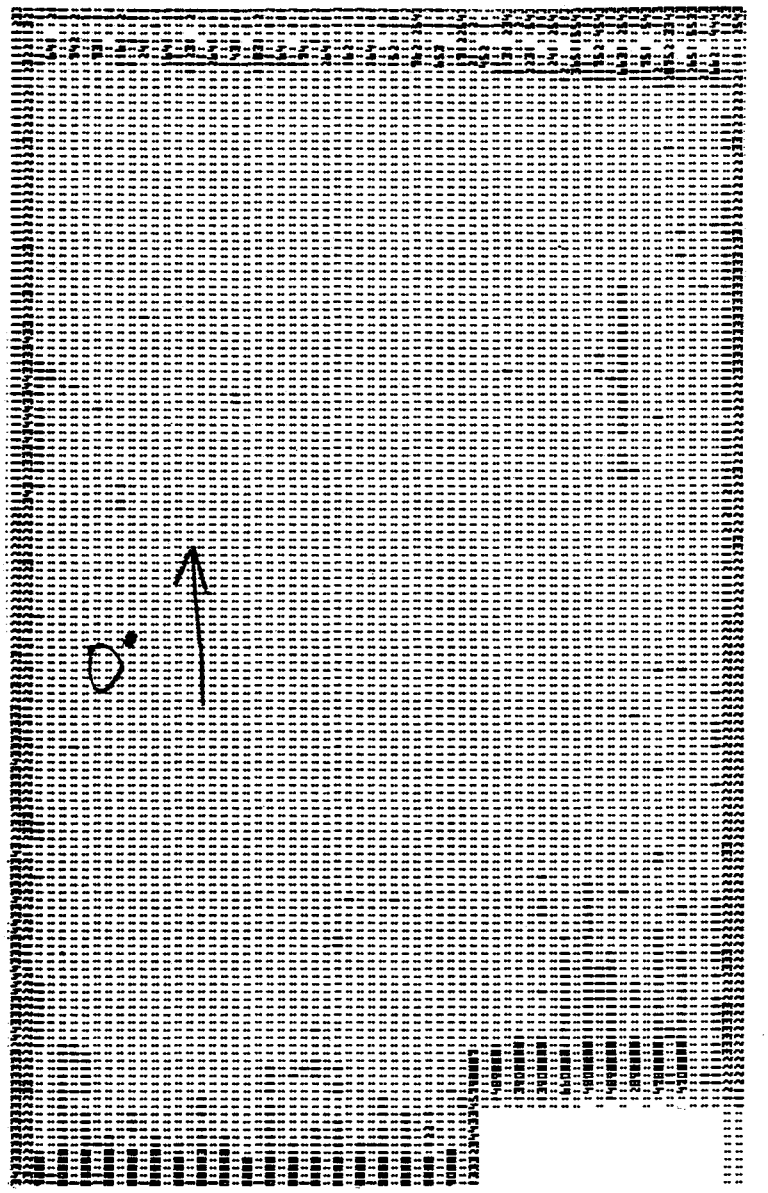


Figure C.4 Through-Transmission Ultrasonic Scan of Laminate S4B1L1(0)12, 1:1 PISO2/LaRC-TPI Powder Slurry and T300 3K Carbon Fiber Reinforcement

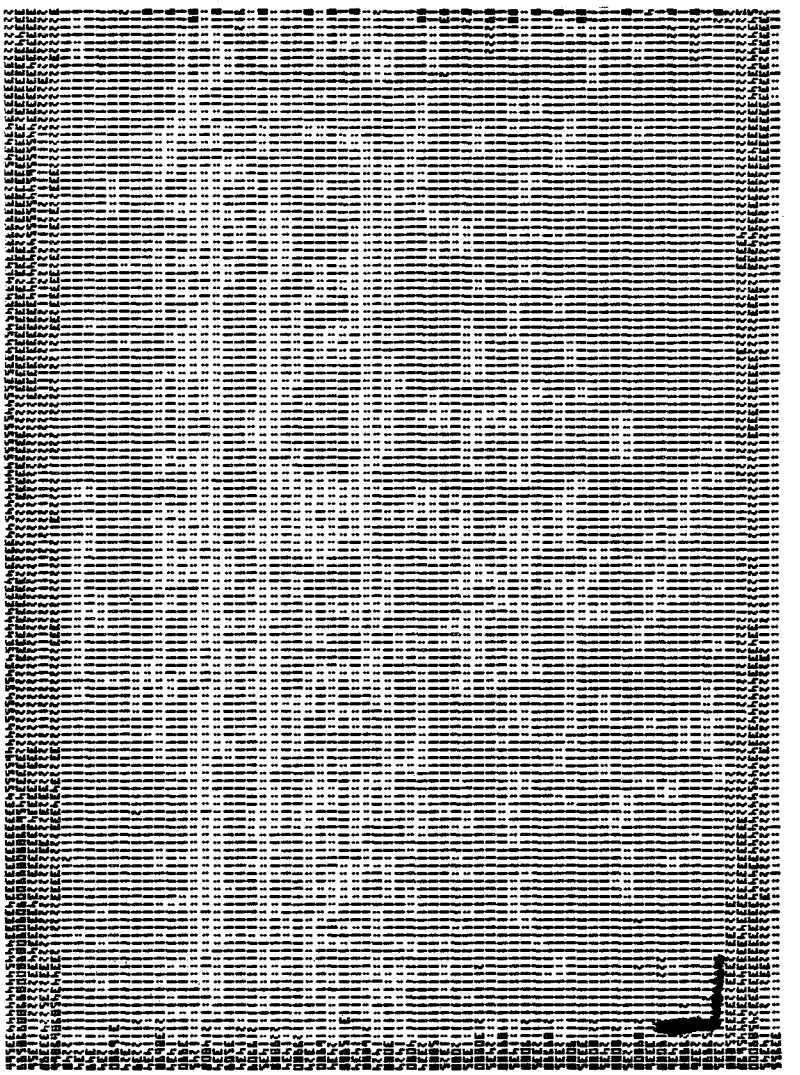


Figure C.5 Through-Transmission Ultrasonic Scan of Laminate S5B1L1(0)12, 2:1 P1SO2/LaRC-TPI Powder Slurry and AS-4 12K Carbon Fiber Reinforcement

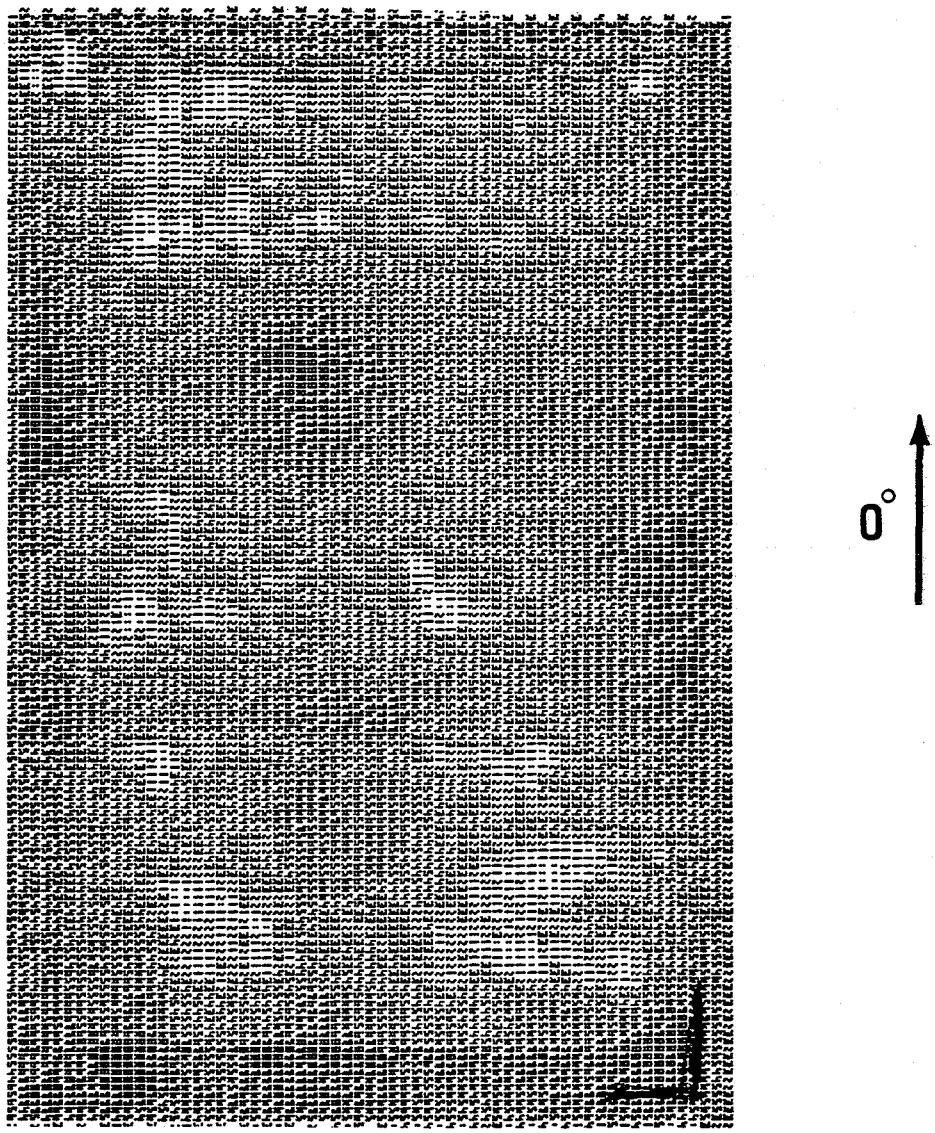


Figure C.6 Through-Transmission Ultrasonic Scan of Laminate S1B1L2(0/90)3s Unmodified LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

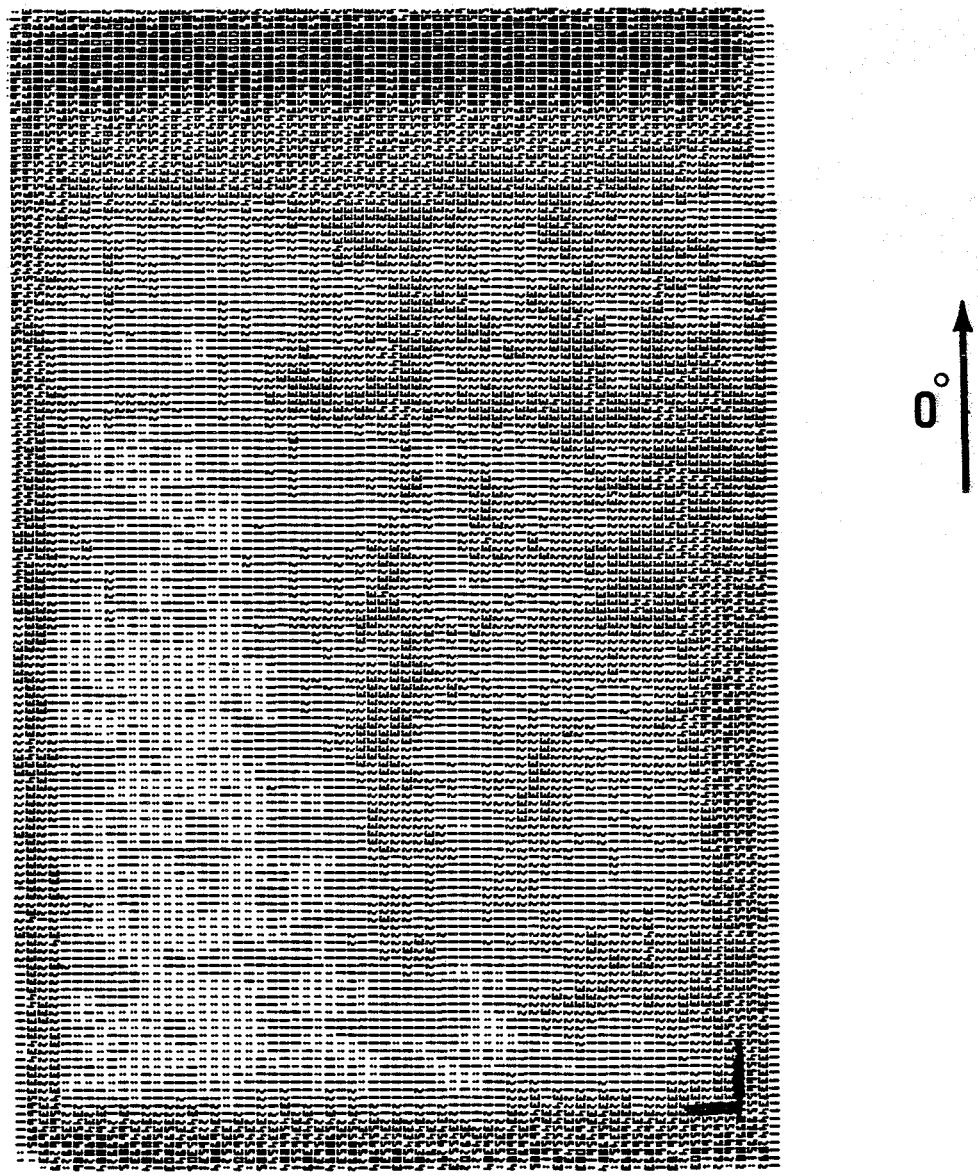


Figure C.7 Through-Transmission Ultrasonic Scan of Laminate S2B1L2(0/90)3s
2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

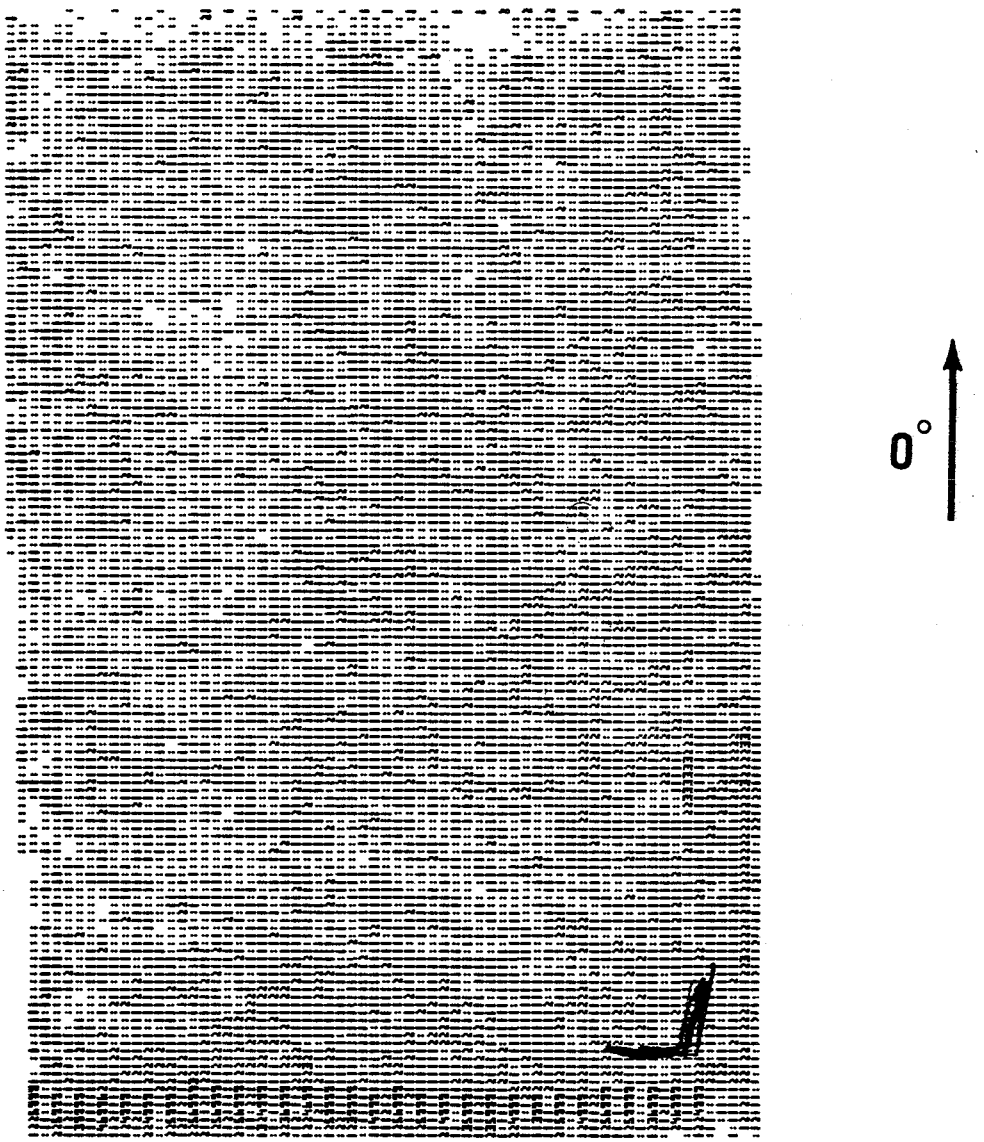


Figure C.8 Through-Transmission Ultrasonic Scan of Laminate S4B1L2(0/90)3s 1:1 P1SO2/LaRC-TPI Powder Slurry and T300 3K Carbon Fiber Reinforcement

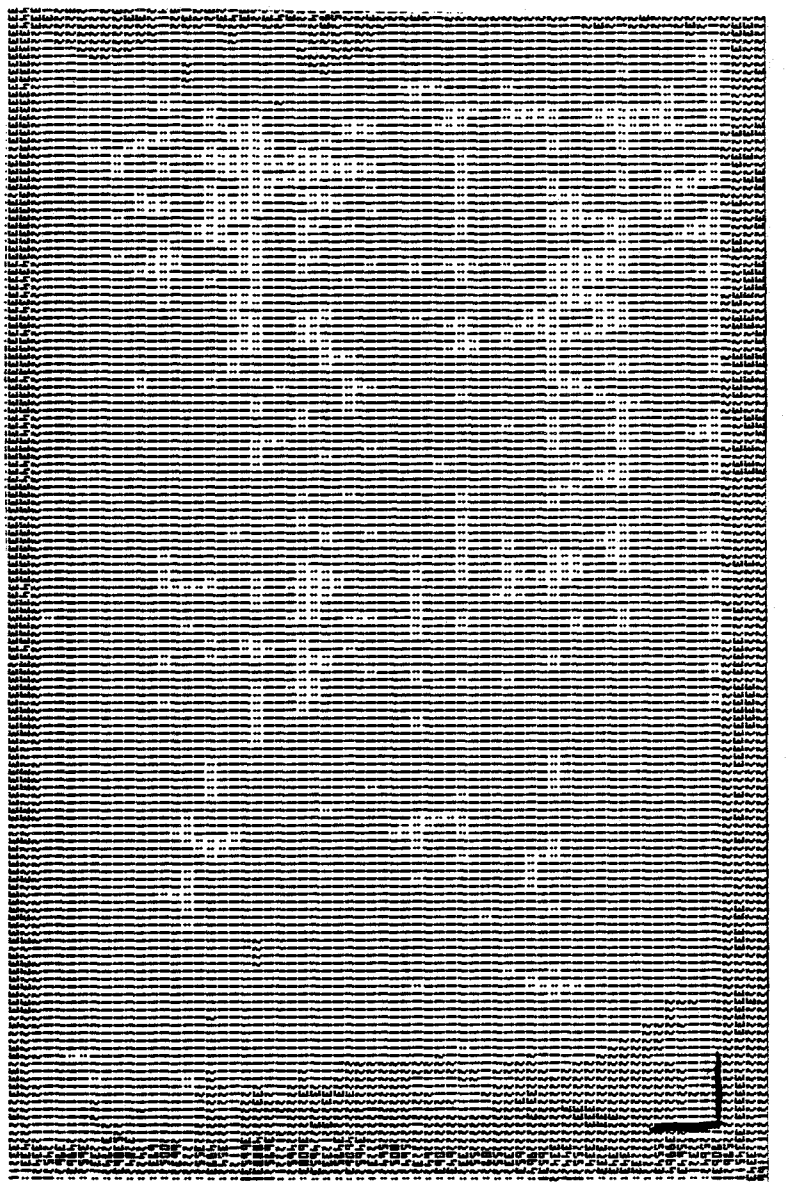


Figure C.9 Through-Transmission Ultrasonic Scan of Laminate S5B1L2(0/90)3s 2:1 PISO2/LaRC-TPI Powder Slurry and AS-4 12K Carbon Fiber Reinforcement

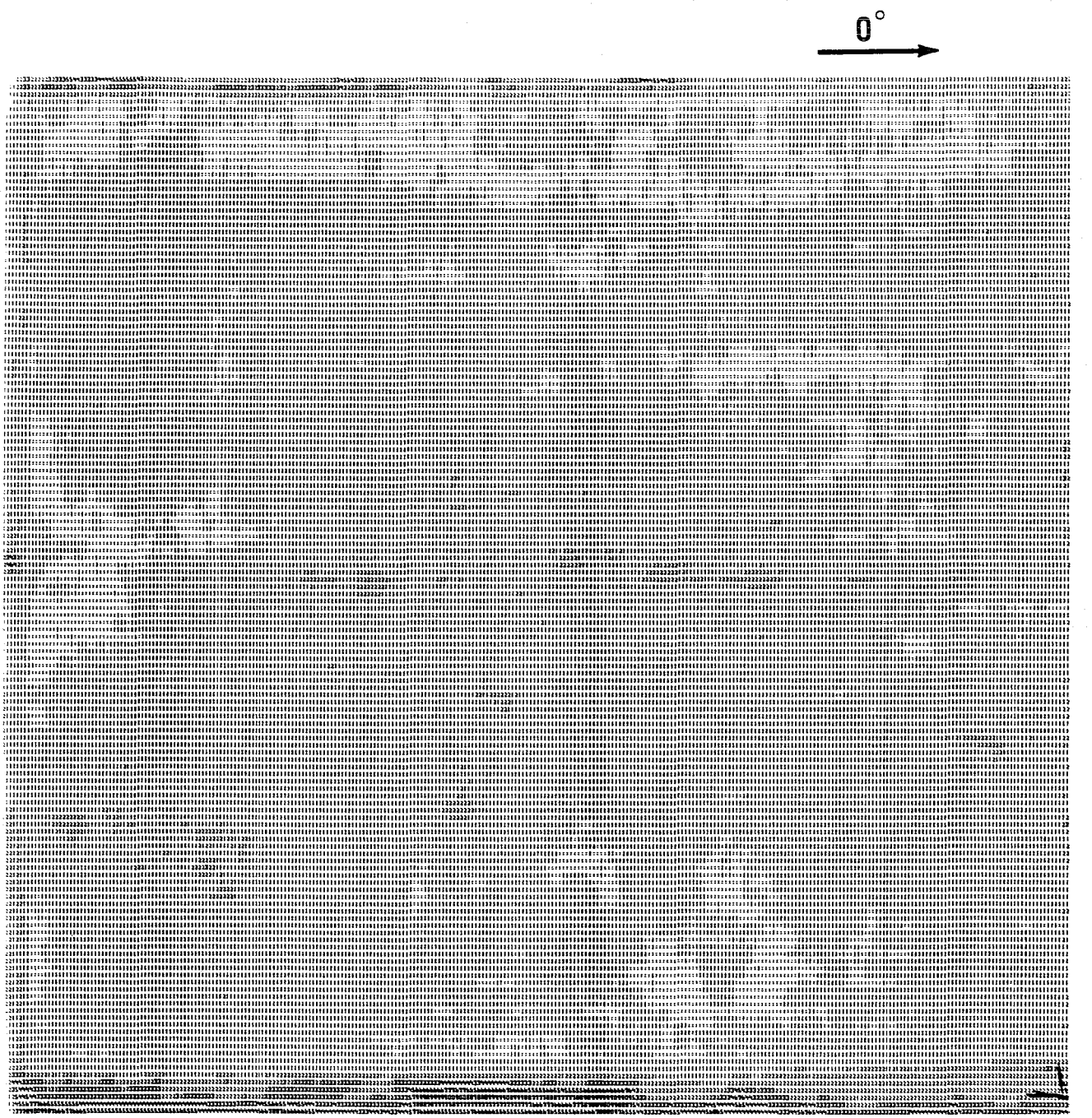


Figure C.10. Through-Transmission Ultrasonic Scan of Laminate S2B2L4, (0)8, 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

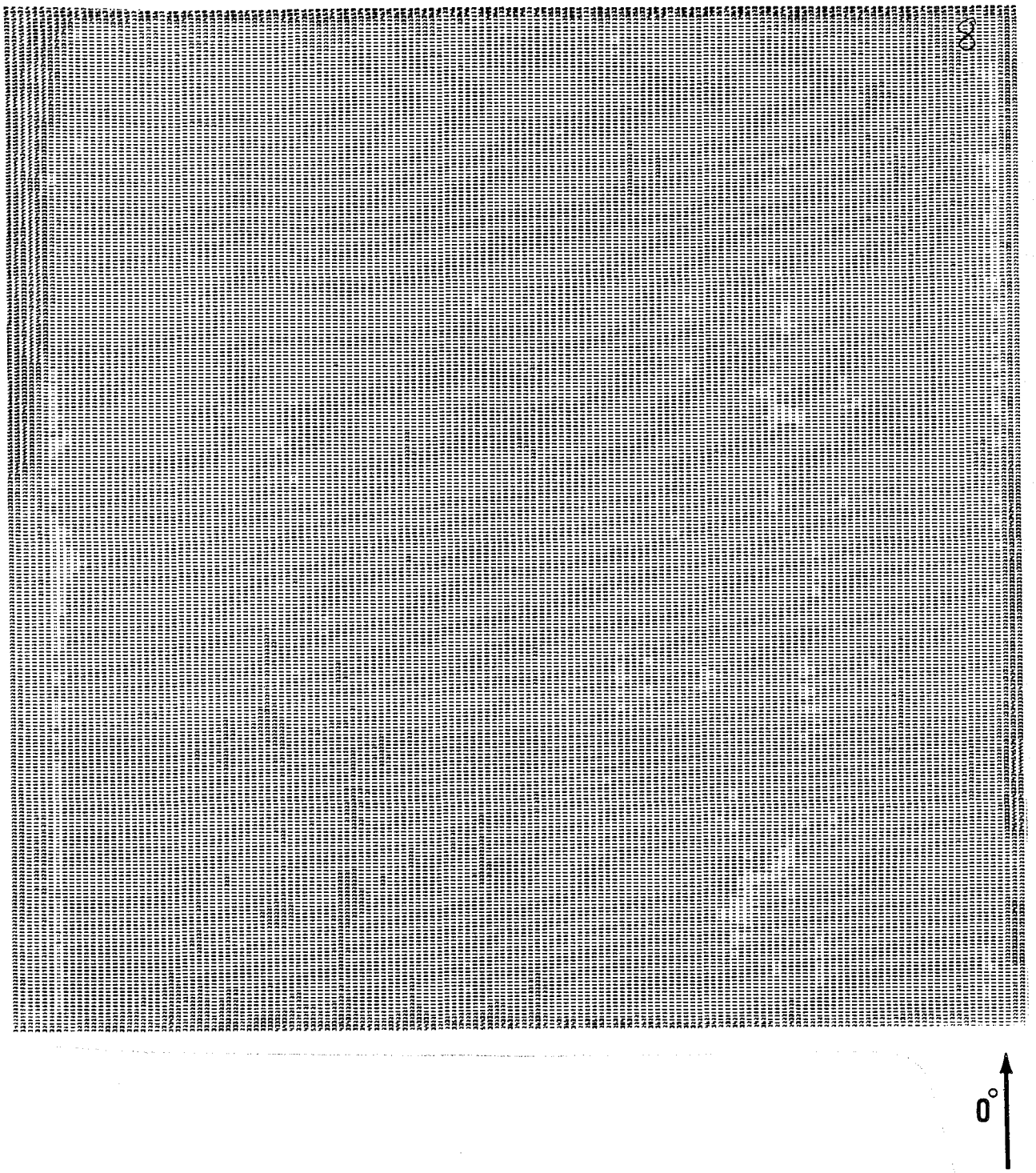


Figure C.11. Through-Transmission Ultrasonic Scan of Laminate S5B2L1, (0)8, 2:1 PIS02/LaRC-TPI Powder Slurry and Celion 6K Carbon Fiber Reinforcement

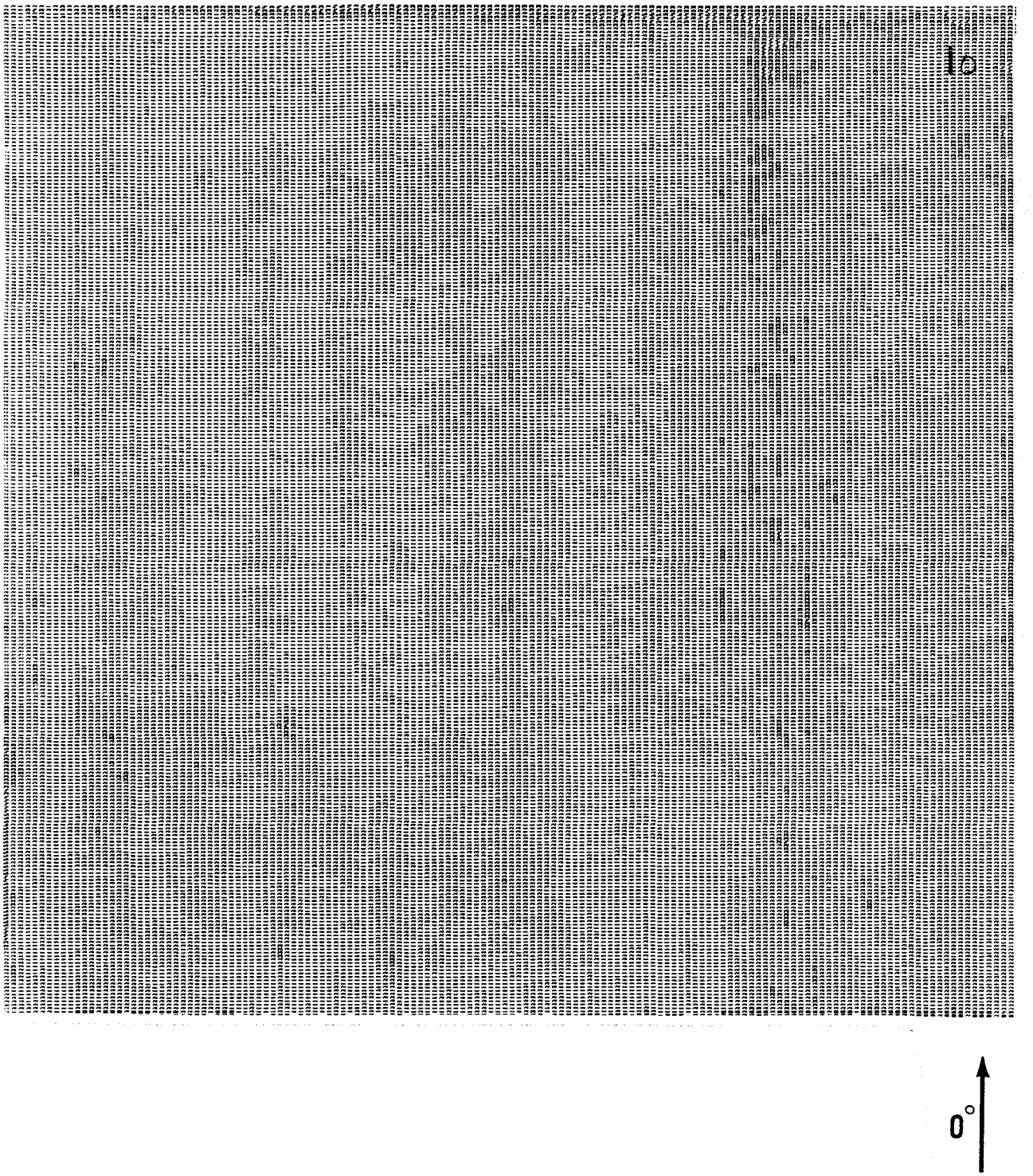


Figure C.12. Through-Transmission Ultrasonic Scan of Laminate S2B2L1, (0)10, 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

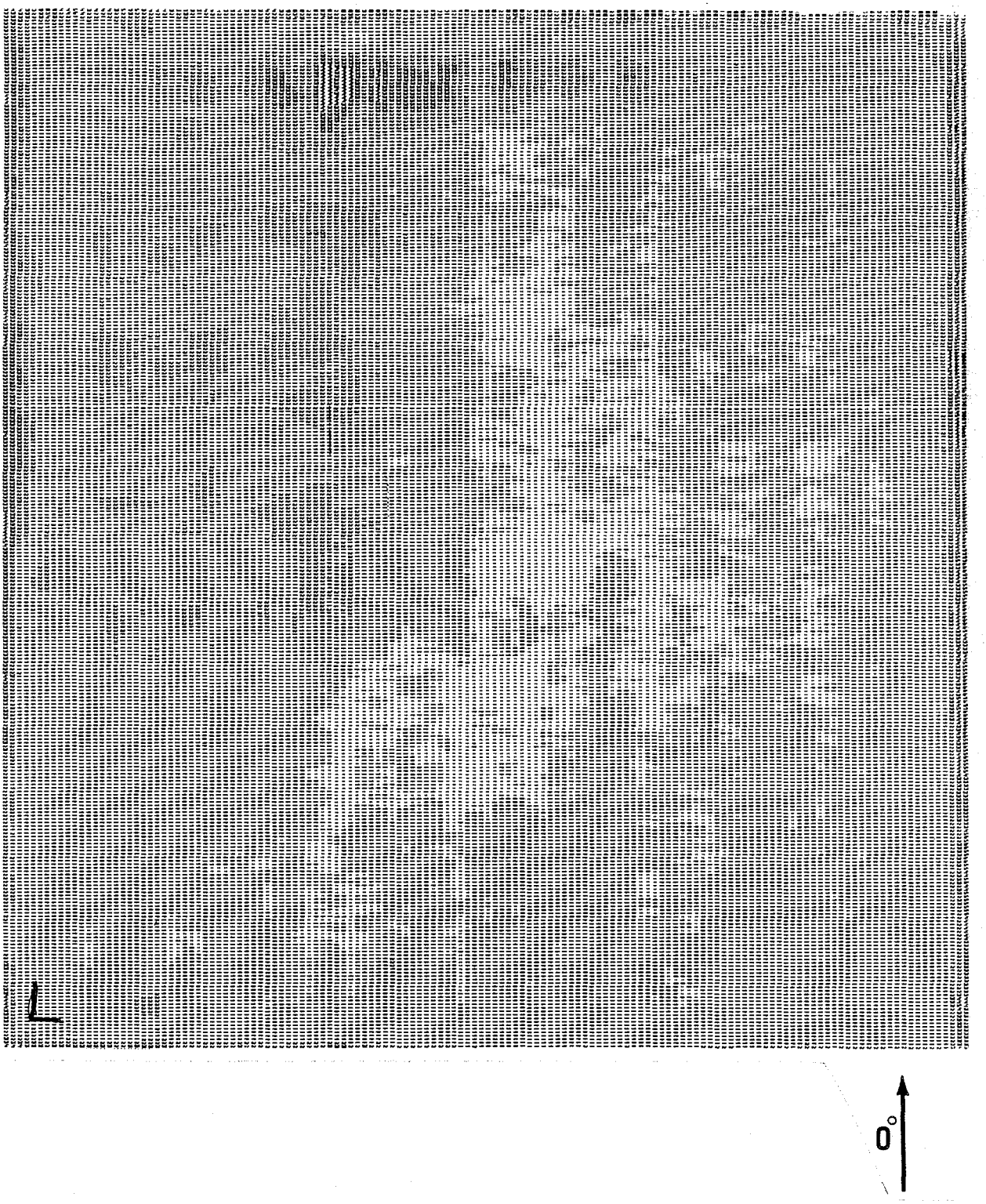


Figure C.13. Through-Transmission Ultrasonic Scan of Laminate S5B2L4, (0)10, 2:1 PIS02/LaRC-TPI Powder Slurry and Celion 6K Carbon Fiber Reinforcement

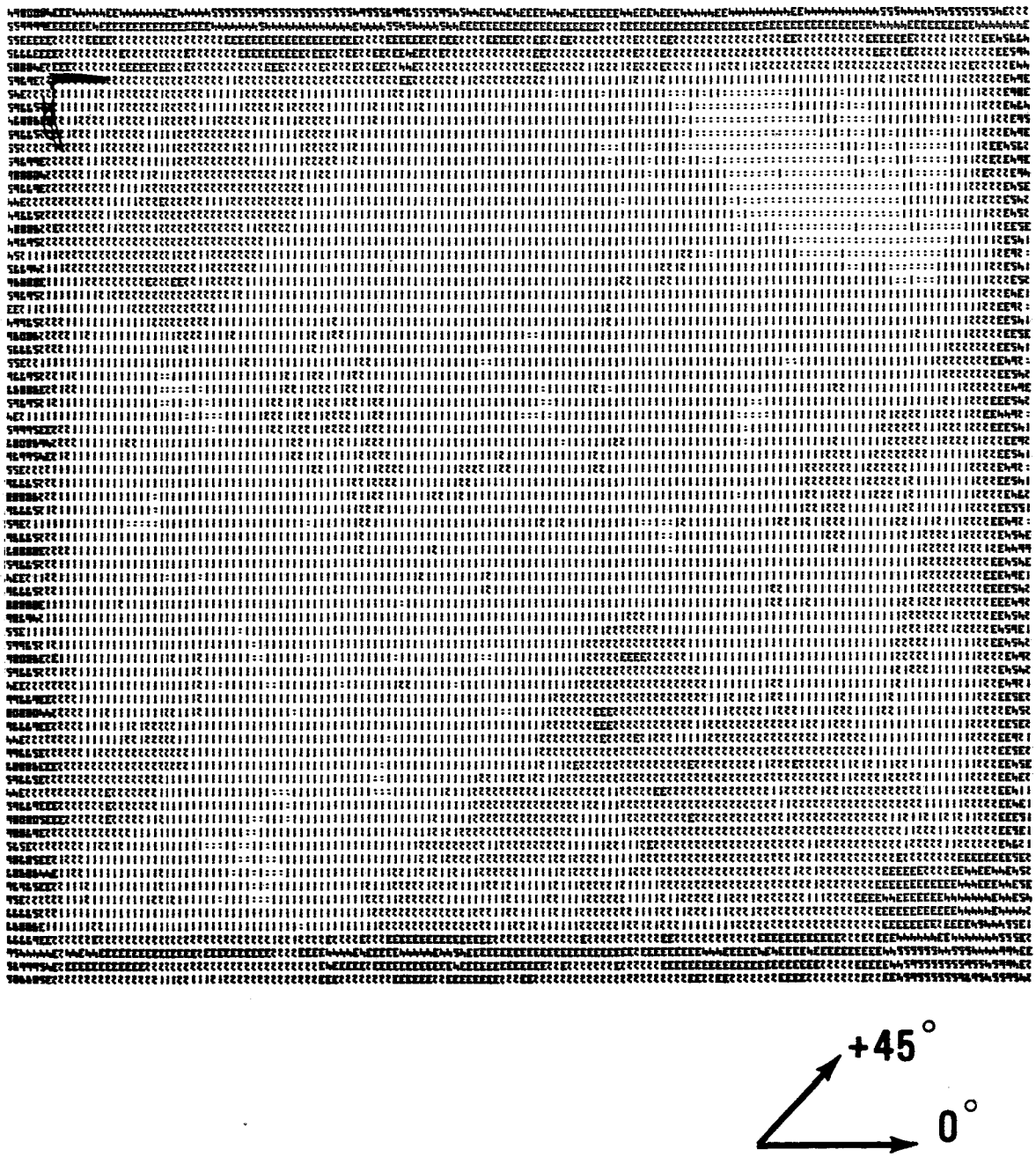


Figure C.14 Through-Transmission Ultrasonic Scan of Laminate S2B2L3(+45)45, 2% DAA Doped LaRC-TPI and Celion 6K Carbon Fiber Reinforcement

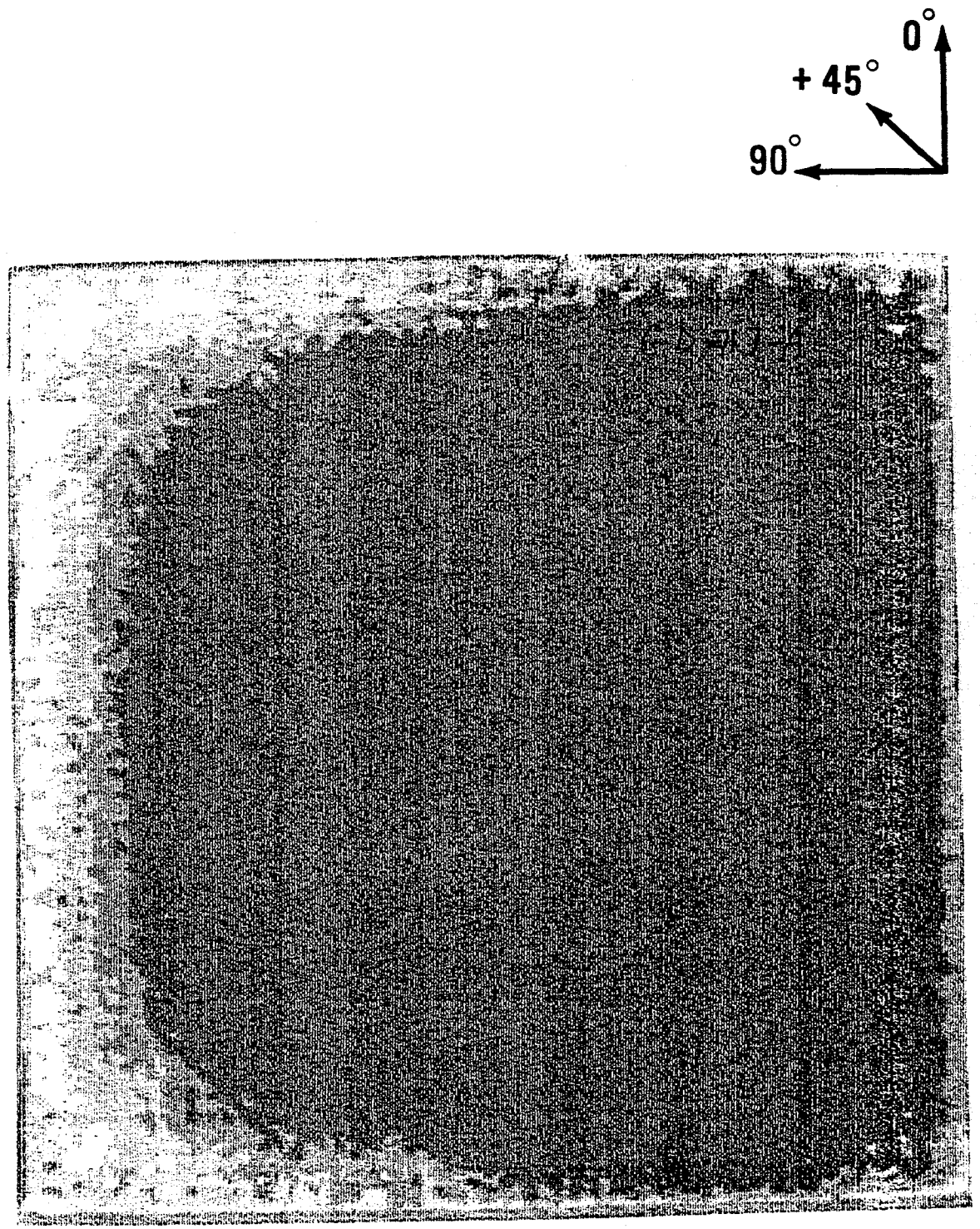


Figure C.15 Through-Transmission Ultrasonic Scan of Laminate 60-717 A, 2% DAA Doped, 1:1 PISO2/LaRC-TPI Powder Slurry and AS-4 12K Carbon Fiber Reinforcement. Laminate fabricated by NASA Langley.

APPENDIX D

PROCESS EQUIPMENT TOLERANCES

Heated Platen Press:

Temperature:	± 6
Pressure:	± 1% of Range (26,700 N, 133,000 N, or 267,000 N) and ± 3% of Actual Reading

Example

2.1 MPa (300 psi) consolidation pressure
15.2 cm by 10.2 cm laminate
133,000 N range
Accuracy: ± 0.15 MPa

Time:	± 5 minutes

Autoclave:

Temperature:	± 6 (air) ± 2K (part)
Pressure:	± 0.035 MPa
Time:	± 10 seconds (computer controller)

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Final Report

16. Abstract

Eight thermoplastic polyimide resin systems were evaluated as composite matrix materials. Two resins were selected for more extensive mechanical testing and both were versions of LaRc-TPI (Langley Research Center - Thermoplastic Polyimide). One resin was made with LaRC-TPI and contained 2 weight percent of a di(amic acid) dopant as a melt flow aid. The second system was a 1:1 slurry of semicrystalline LaRC-TPI powder in a polyimidesulfone resin diglyme solution. The LaRC-TPI powder melts during processing and increases the melt flow of the resin. Testing included dynamic mechanical analysis, tension and compression testing, and compression-after-impact testing. The test results demonstrated that the LaRC-TPI resins have very good properties compared to other thermoplastics, and that they are promising matrix materials for advanced composite structures.

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