DEVELOP AND DEMONSTRATE MANUFACTURING PROCESSES FOR FABRICATING GRAPHITE FILAMENT REINFORCED POLYIMIDE (Gr/PI) COMPOSITE STRUCTURAL ELEMENTS

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Prepared under Contract NAS1-14784

By

GENERAL DYNAMICS CONVAIR DIVISION
San Diego, California

for

NASA
National Aeronautics and
Space Administration

NASA LANGLEY RESEARCH CENTER
Hampton, Virginia

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V. A. Chase

Prepared by

GENERAL DYNAMICS CONVAIR DIVISION
San Diego, California

FOREWORD

The work reported herein was conducted by General Dynamics Convair Division, San Diego, California, under Contract NAS 1-14784. This is the second quarterly technical report covering contract activities for the period from 8 June 1977 to 8 September 1977. The program is sponsored by the NASA Langley Research Center, Hampton, Virginia. Mr. Edward L. Hoffman of the Manufacturing Technology Section, Materials Division is the NASA Technical Monitor.

At Convair the Program Manager is Mr. Vance A. Chase, material characterization is being conducted by Mr. E. S. Harrison, and fabrication process development is being performed by Mr. J. E. Hilzinger.

J. E. Hilzinger for
V. A. Chase
Program Manager

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SECTION 1
INTRODUCTION

One approach for increasing the efficiency of future reusable space vehicles involves the use of lightweight, elevated temperature resistant structural materials. One of the most promising materials for this application is graphite filament reinforced polyimide matrix composites. NASA's project Composites for Advanced Space Transportation Systems (CASTS) has been established to develop and demonstrate the technology required to achieve Gr/PI structural components with 316C (600F) operational capability.

The primary objective of this program, which is sponsored under the CASTS Project, is the development and demonstration of fabrication processes for graphite composites based on DuPont's NR-150B2 polyimide which are applicable to fabrication of large size structures. The program involves two major tasks and various sub tasks:

TASK I - Process Development

(a) Material development and characterization for Quality Assurance.

(b) Laminate fabrication process development.

(c) Adhesive bonding study.

(d) Stiffened panel development.

(e) Honeycomb panel development.

(f) Chopped fiber molding process development.

(g) NDI development.

(h) Testing for process verification.

(i) Specifications.

TASK II - Demonstration Components

(a) Laminates

(b) Stiffened Panels

(c) Honeycomb Panels

(d) Chopped Fiber Moldings

(e) Structural Component

During the previous reporting period[1] studies were conducted to select a high strength graphite fiber having long term thermo-oxidative stability at 316C (600F). Weight loss measurements were made for graphite fibers and graphite/polyimide composites after thermal aging at 316C (600F) for times up to 1000 hours. Modmor II graphite fiber was selected for use on the contract based on thermal stability at 316C (600F), fiber strength properties, and the willingness of the fiber manufacturer to certify a maximum weight loss of 2% after 500 hours at 316C (600F). A weight loss of 0.76% was measured for the Modmor II fibers after 500-hour exposure times.

Also during the previous period, it was determined that the ethyl alcohol solvent used in the NR-150B2 polyimide solution reacts with the 6F tetra acid to form esters that alter composite processing characteristics. A decision was made to use prepreg based on NR-150B2/N-methylpyrrolidinone (NMP) solution. An initial quantity of prepreg was obtained and fabrication processing studies were initiated.

Physical and chemical material characterization techniques for quality assurance were evaluated for both the resin solution and the prepreg.

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[1] Quarterly Report #1, NAS1-14784.

SECTION 2

PROGRAM ACTIVITIES

2.1 SUMMARY

Fabrication process development was conducted for laminates based on the initial order of Modmor II/NR-150B2-55X (NMP Resin Solution) prepreg. The cure cycle previously developed at Convair for prepreg based on NR-150B2 (ETOH/NMP resin solution) provided excessive flow and resin starvation in the laminate. Studies were conducted into time/temperature hold condition before applying pressure for advancing the resin and reducing resin flow. A cure cycle, involving a two-hour hold at 149C (300F), was developed which gave a minimum resin flow and yielded laminates having a void content < 2%. These laminates (C-9 and C-10) had less than optimum properties due to a low fiber volume and poor quality prepreg. The laminates had flexural strength of 1190 MN/m^2 (170 ksi) and 1141 MN/m^2 (163 ksi) at room temperature. Flexural strength at 316C (600F) for the two laminates was 833 MN/m^2 (119 ksi) and 945 MN/m^2 (135 ksi) for an elevated temperature strength retention of 70 and 83 percent.

Variation of the cure cycle which produced the low void laminates were investigated in an effort to obtain increased resin bleed and a higher fiber volume in the composite. No satisfactory cure cycle which gave resin bleed with low void content was uncovered. This suggests that a net resin (no-bleed) prepreg would be a promising approach for this resin system.

It was determined that the 55% solids resin solution and for the initial batch of prepreg did not have sufficient viscosity to maintain good collimation of the fiber tows. The second prepreg batch, which was much improved, was based on 60% solids resin solution and 30 ±2% resin content. Delays were experienced in receiving the second prepreg batch due to a problem in obtaining the Modmor II fiber. In order to prevent delays on the program, the second batch of prepreg was changed to Celion 3000 fiber.

This material was received near the end of this reporting period. Fiber collimation and handling characteristics of this material were vastly improved over the initial prepreg batch.

The quality assurance task conducted during the reporting period included, ultrasonic C-scan of laminates, infrared scanning study, and chemical characterization of the prepreg resin. Ultrasonic C-scans obtained on laminates C-9 and C-10 were equivalent to high quality graphite/epoxy composites.

2.2 FABRICATION PROCESS DEVELOPMENT

The processing of Modmor II/NR150B2-S5X (100% NMP) graphite/polyimide prepreg began with the autoclave curing of laminate C-4 in accordance with a standard cure schedule previously established for the HMS/NR150B2 (EtOH/NMP solvent) material combination.

Standard NR-150B2 Autoclave Cure Schedule

Initial Cure

(1) With full vacuum heat to 185C (365F) at 1C (1.8F)/minute.

(2) Hold one hour at 185C (365F).

(3) Apply 1400 kN/m^2 (200 psi) while heating to 204C (400F) at 1C (1.8F)/minute.

(4) Hold two hours at 204C (400F).

(5) Cool to 65C (150F) under pressure.

Postcure

(1) Apply full vacuum and heat to 316C (600F) at 1.1C (2F) minute.

(2) Apply 1400 kN/m^2 (200 psi) at 177C (350F).

(3) Hold one hour each at 316, 343, and 371C (600, 650, and 700F).

Extremely high resin flow resulted during the initial cure producing a resin starved laminate having 74.8% fiber volume and approximately 15% void content. Subsequent curing cycles CR-1 through CR-4 added time and/or temperature in an attempt to increase the resin viscosity prior to pressure application and reduce resin flow. Cure schedules studies are summarized in Table I.

TABLE I

CURE SCHEDULE SUMMARY

Cure	Used for Laminate No.	Description
Standard	C-4	See Section 2.2
CR-1	C-6	Standard except hold of 1 hr at 66C (150F) +1 hr at 21C (250F).
CR-2	C-7	Standard + hold of 3 hr at 121C (250F)
CR-3	C-8	Standard + hold of 5 hr at 121C (250F)
CR-4	C-9, C-10	No vacuum until 1 hr at 149C (300F), hold 2nd hr w/vac, raise to 185C (365F) and hold 1 hr, apply 1400 kN/m^2 (200 psi) heat to 204C (400F) and hold 2 hr
CR-4A	C-11	CR-4, except vacuum bag pressure time at 149C (300F) of 1/2 hr
CR-4B	C-13	CR-4, except 1/2 hr w/o vacuum + 1/2 hr with vacuum at 149C (300F)
CR-4C	C-15	CR-4, except total time at 149C (300F) is 1/2 hr w/o vacuum; vacuum applied after 149C (300F) hold during heatup to 185C (365F).
CR-5	C-12	CR-4, except full vacuum and 1400 kN/m^2 (200 psi) applied after 1 hr at 149C (300F), held 2nd hr at 149C (300F)
CR-6	C-16	CR-4, except 1/2 hr w/o vacuum at 149C (300F), vacuum applied after 1 hr at 185C (365F)
CR-7	C-14, C-17 & C-20	CR-4, but with full vacuum from start
CR-8	C-18, C-19 & C-21	CR-4, but with 10-in. vacuum from start
CR-9	C-22(1) C-24	CR-4, but with 5-in. vacuum from start
CR-10	C-23	CR-4, but with 5-in. vacuum from start and only 1 hr at 149C (300F)

(1) Faulty layup

An initial hold temperature of 121C (250F) without pressure was selected to increase resin viscosity sufficiently to obtain controlled resin flow. This hold temperature was based on a resin solution viscosity versus temperature curve which indicated the reaction rate to become significant at approximately 121C (250F). Also, this temperature would not give an excessively high reaction rate and should provide a cure process with wider tolerance on the temperature control, heating rate, etc. Holds at 121C (250F) showed improvement of mechanical properties with increased time, but the time required to obtain the necessary improvements proved excessive (> 5 hr) for a practical cure schedule. As a result, laminate C-9 was prepared with a hold (2 hr.) at 149C (300F). This cure resulted in a substantial reduction in resin flow and gave a laminate with 1.8% void content after the 399C (750F) postcure. Photomicrographs of laminates C-4 through C-9 show progressive increase in quality of the laminates, (Figures 1-5). This is also reflected in Table II which gives the mechanical properties of the laminates. The CR4 cure schedule used for laminate C-9 is summarized below:

Cure Schedule CR-4

(1) Without vacuum heat at 1C (1.8F) min. to 149C (300F) and hold one hour.

(2) Apply full vacuum and hold an additional hour at 149C (300F).

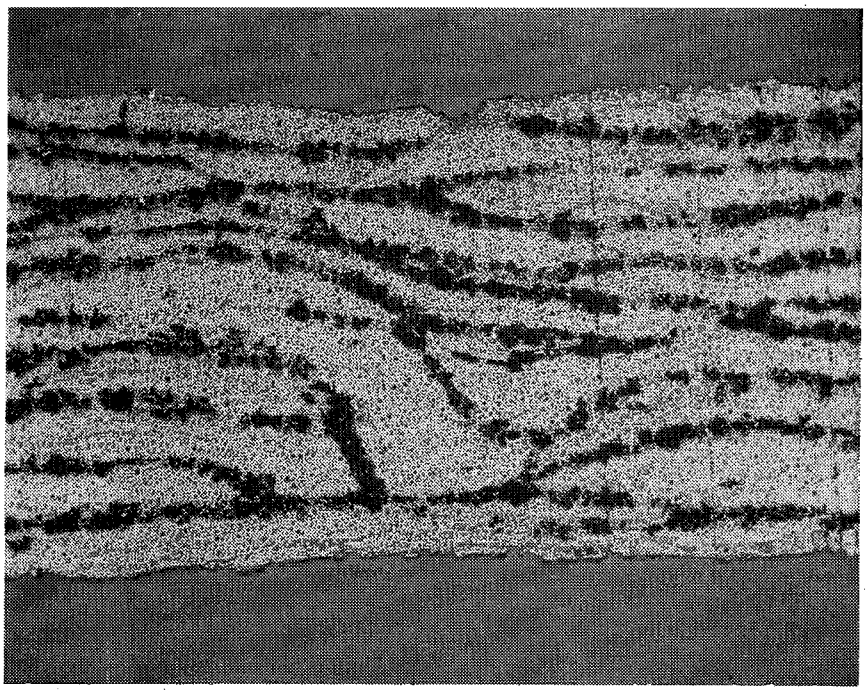
(3) Heat to 185C (365F) at 1C (1.8F) min. and hold one hour.

(4) Apply 1400 kN/m^2 (200 psi) and heat to 204C (400F).

(5) Hold two hours at 204C (400F).

(6) Cool to 65C (150F) under pressure.

While this cure schedule gave a low void laminate, it went too far in advancing the resin and reducing flow as evidence of the low (55%) fiber volume. This is reflected in the less than optimum flexural strength. A further contributing factor to low strength is the poor quality of the prepreg, which due to low resin solution viscosity (55% solids) had tow separation, variations in thickness and resin content (Figure 6).



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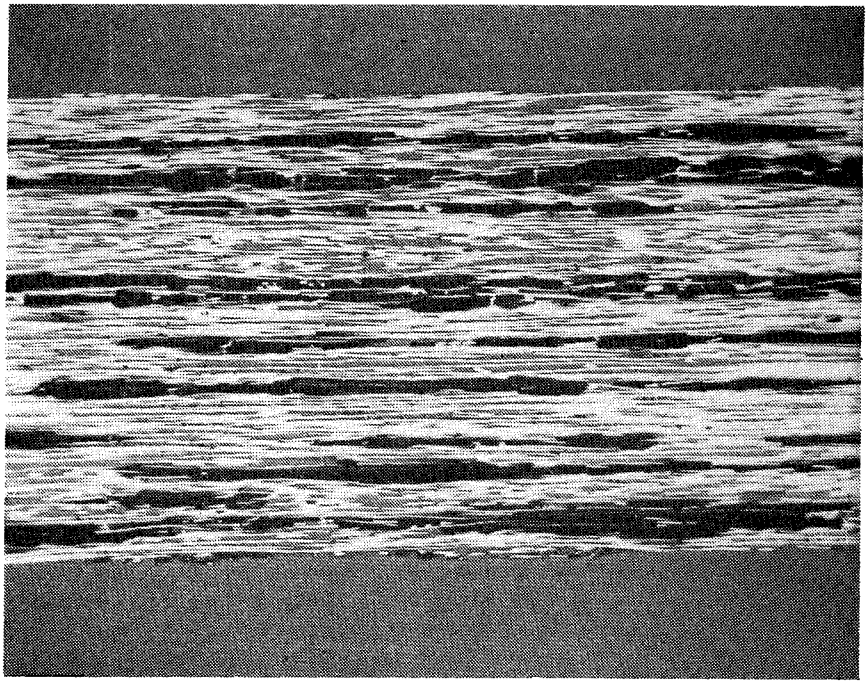
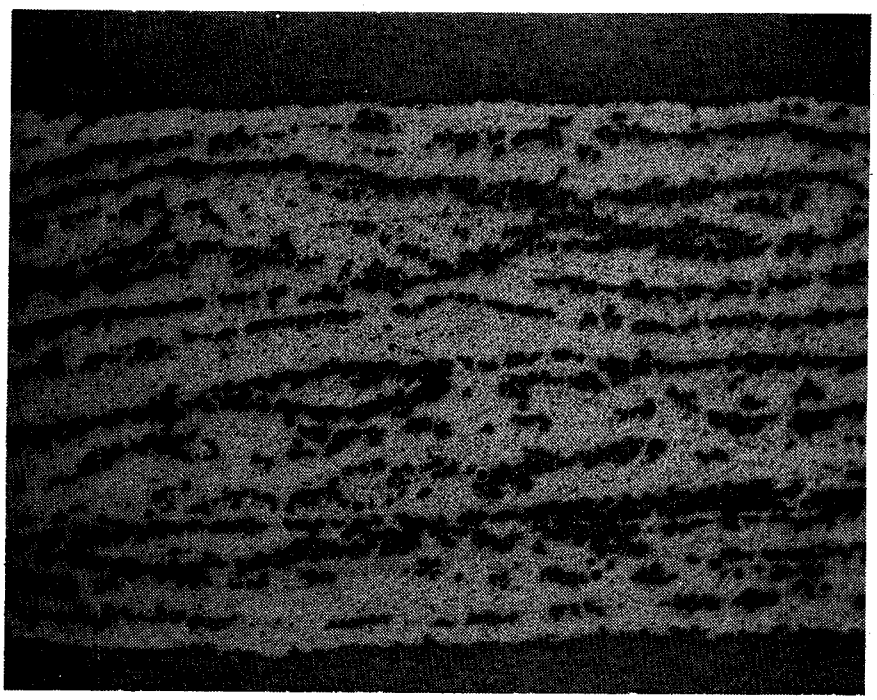


B. SIDE VIEW (50X)

NOTES: 1. STANDARD CURE
2. SP GR, 1.40
3. FIBER VOL %, 70.5
4. VOID %, 14.6

Figure 1. Photomicrograph of Laminate C-4



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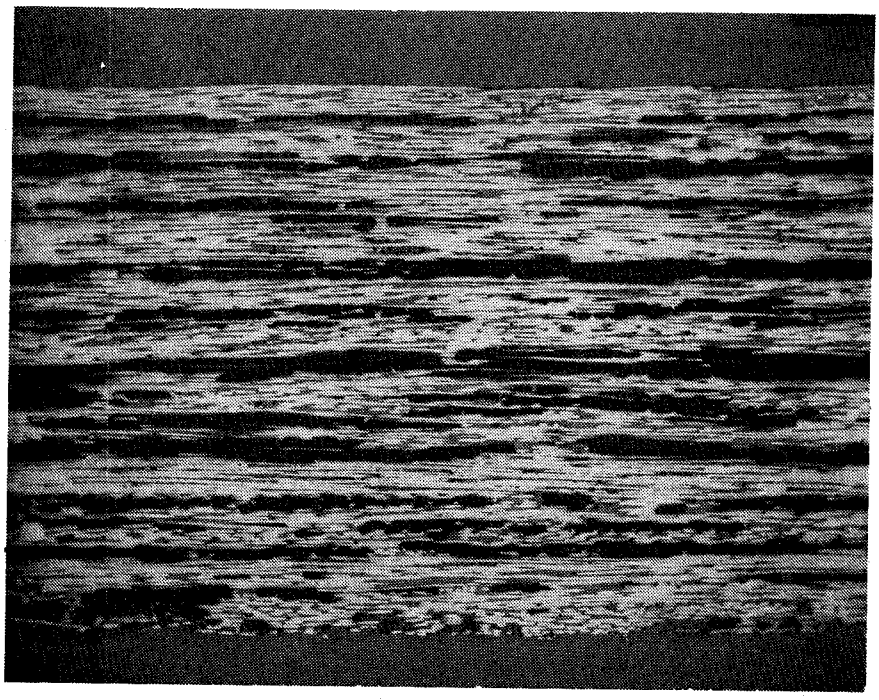
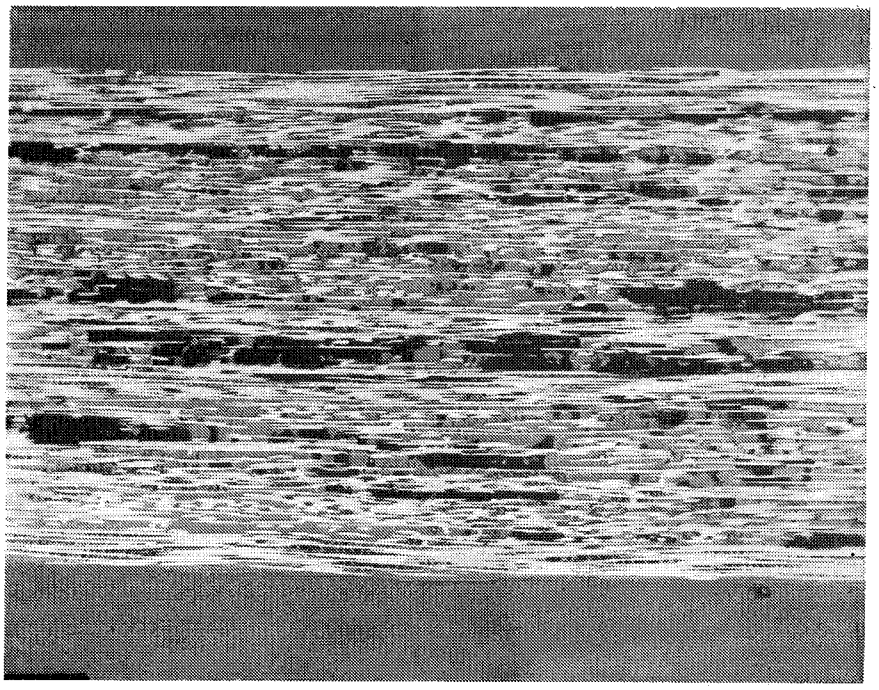


B. SIDE VIEW (50X)

NOTES: 1. STANDARD CURE + HOLD OF 1 HR AT 150F & 1 HR AT 250F
2. SP GR, 1.42
3. FIBER VOL %, 67.3
4. VOID %, 13.4

Figure 2. Photomicrograph of Laminate C-6

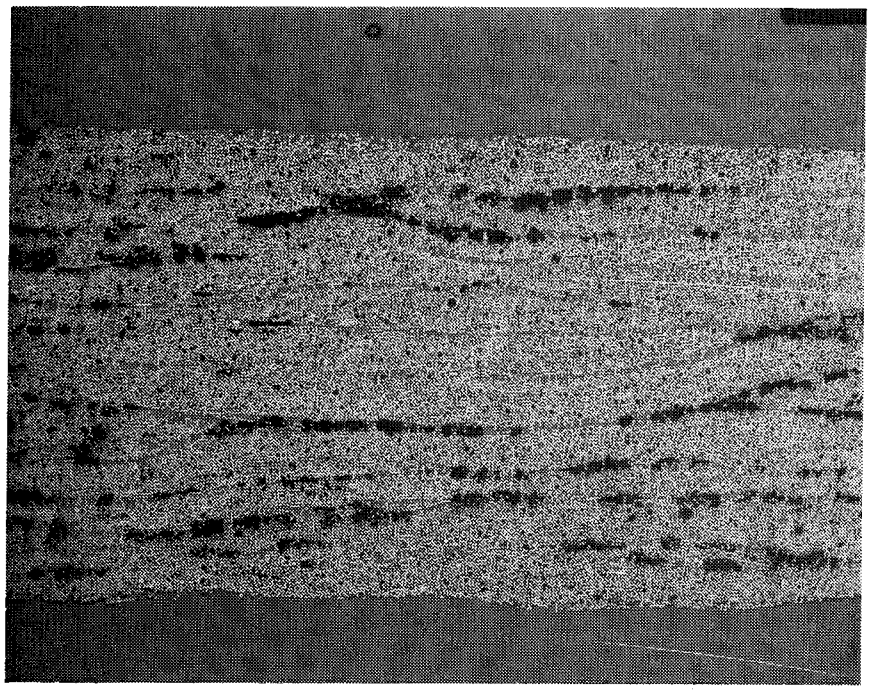
A. END VIEW (50X)



B. SIDE VIEW (50X)

NOTES: 1. STANDARD CURE + HOLD OF 3 HRS AT 250F
2. SP GR, 1.40
3. FIBER VOL %, 63.1
4. VOID %, 13.5

Figure 3. Photomicrograph of Laminate C-7



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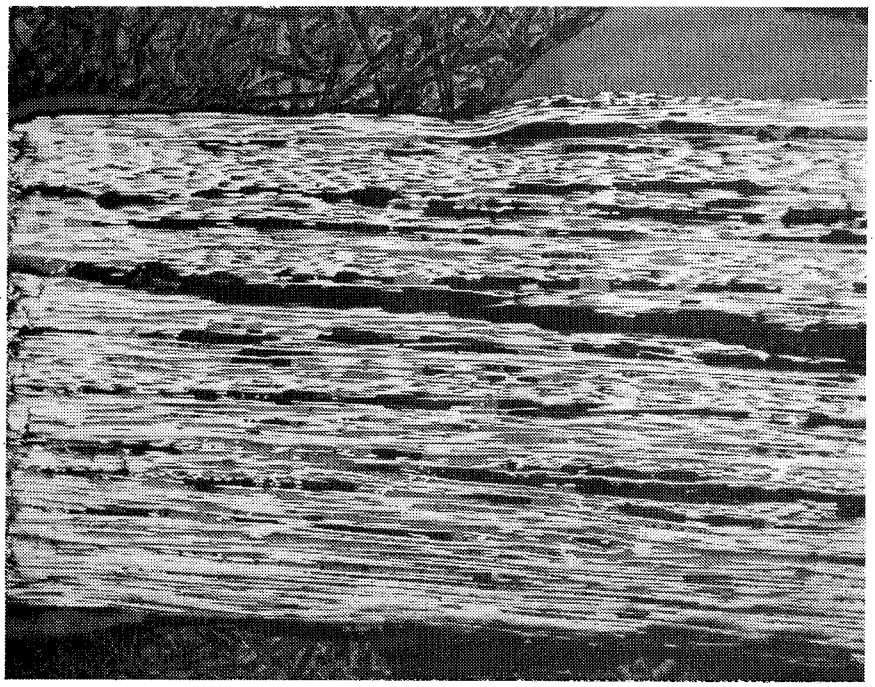
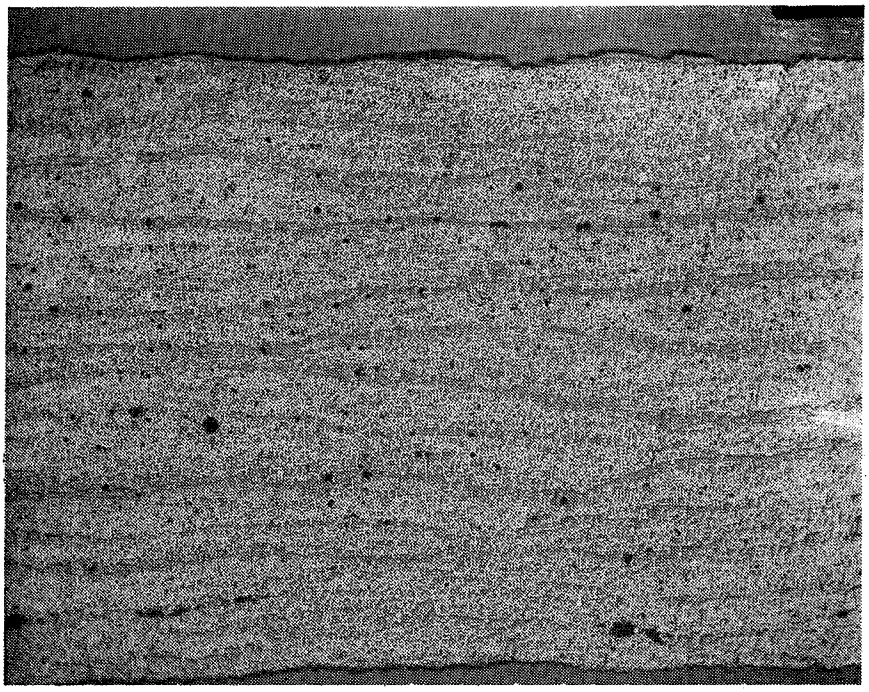


B. SIDE VIEW (50X)

NOTES: 1. STANDARD CURE + HOLD OF 5 HRS AT 250F
2. SP GR, 1.38
3. FIBER VOL %, 63.4
4. VOID %, 14.9

Figure 4. Photomicrograph of Laminate C-8



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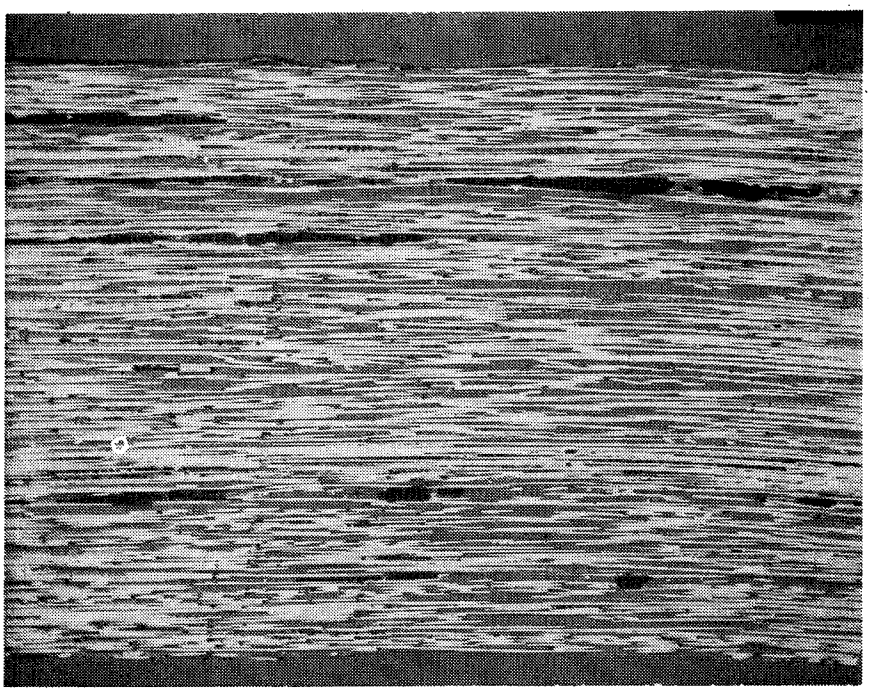


B. SIDE VIEW (50X)

NOTES: 1. STANDARD CURE + 2 HRS AT 300F (CR-4)
2. SP GR, 1.56
3. FIBER VOL %, 55.4
4. VOID %, 1.8

Figure 5. Photomicrograph of Laminate C-9

PROPERTIES FOR MODMOR

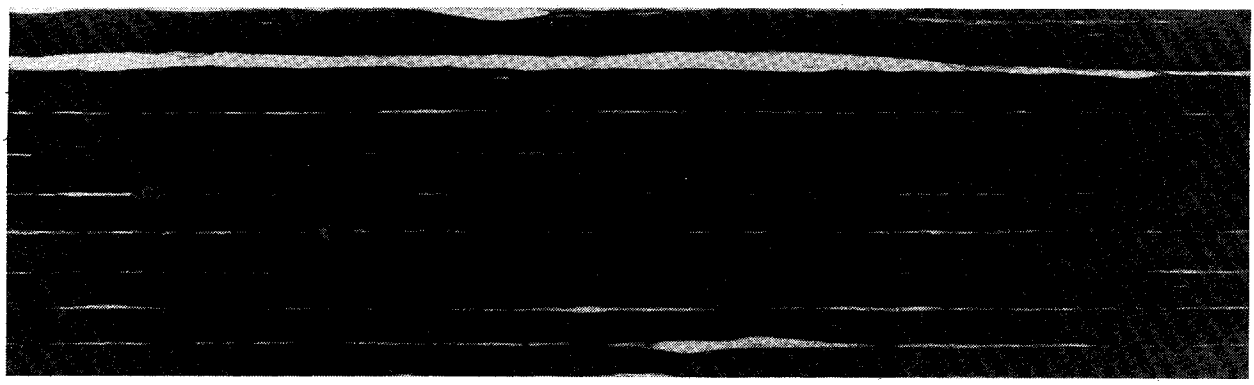
Laminate No.	C-4	C-6	C-7	C-8	C-9	CR-10	CR-11
Cure	STD	CR-1	CR-2	CR-3	CR-4	CR-4	CR-4A
Postcure	STD	STD	STD	STD	STD	STD	STD
Orientation	0°	0°	0°	0°	0°	0°	0°
Flexural Strength MN/m^2 (ksi)							
RT	511(73)	469(67)	700(100)	833(119)	1190(170)	1141(163)	1085(15
232C (450F)	357(51)	413(59)	462(66)	490(70)	966(138)	966(138)	917(131
316C (600F)	245(35)	301(43)	336(48)	406(58)	833(119)	945(135)	875(125
Short Beam Shear Strength MN/m^2 (ksi)							
RT	24.5(3.5)	39.2(5.6)	49(7.0)	40.6(5.8)	69.3(9.9)	82.6(11.8)	62.3(8..
232C (450F)	—	35(5.0)	33.6(4.8)	39.2(5.6)	58.1(8.3)	45.5(6.5)	57.4(8..
316C (600F)	—	22.4(3.2)	27.3(3.9)	23.8(3.4)	45.5(6.5)	41.3(5.9)	43.4(6..
Specific Gravity	1.40	1.42	1.40	1.38	1.56	1.55	1.51
Fiber Content, % Wgt.	74.8	71.9	68.0	68.4	60.7	57.4	61.5
Fiber Volume, %	70.5	67.3	63.1	63.4	55.4	52.0	56.2
Cured Ply Thickness, mm (mil)	0.112(4.4)	0.114(4.5)	0.137(5.4)	0.112(4.4)	0.132(5.2)	0.114(4.5)	0.114(4.
Glass Transition Temp., C	353	359	357	—	360	351	351
Void, %	14.6	13.4	13.5	14.5	1.8	1.7	5.1

TABLE II

MODMOR II/NR-150B2-S5X GRAPHITE/POLYIMIDE COMPOSITES (12 PLY)

CR-11	CR-12	CR-13	CR-14	C-15	C-16	C-17	C-18	C-19	C
CR-4A	CR-5	CR-4B	CR-7	CR-4C	CR-6	CR-7	CR-8	CR-8	C
STD	STD	STD	STD	STD	STD	STD	STD	STD	S
0°	0°	0°	0°	0°	0°	0°	0°	0°	0
1085(155)	1316(188)	994(142)	(50)	1057(151)	147(21)	350(50)	1162(166)	1113(159)	2
917(131)	896(128)	763(109)	—	665(95)	147(21)	—	—	—	
875(125)	784(112)	602(86)	(38)	595(85)	119(17)	259(37)	588(84)	665(95)	1
62.3(8.9)	63(9.0)	49.7(7.1)	(3.3)	59.5(8.5)	16.8(2.4)	25(3.6)	50(7.1)	51(7.3)	1
57.4(8.2)	46.2(6.6)	41.3(5.9)	—	40.6(5.8)	15.4(2.2)	—	—	—	
43.4(6.2)	32.9(4.7)	31.5(4.5)	(2.9)	31.5(4.5)	16.8(2.4)	21(3.0)	16(4.5)	17(4.8)	5
1.51	1.45	1.55	1.35	1.56	1.41	1.39	1.43	1.48	
61.5	70.7	60.9	75.4	61.3	69.0	73.9	69.3	69.8	7
56.2	66.0	55.6	71.1	56.1	64.0	69.5	64.5	65.1	6
0.114(4.5)	0.104(4.1)	0.117(4.6)	0.122(4.8)	0.117(4.6)	0.124(4.9)	0.124(4.9)	0.114(4.5)	0.124(4.9)	0
351	359	352	355	356	356	337	355	360	
5.1	10.7	2.7	17.5	2.1	13.0	15.1	14.3	8.8	1

C-18	C-19	C-20	C-21	C-22	C-23	C-24
CR-8	CR-8	CR-7	CR-8	CR-9	CR-10	CR-9
STD	STD	STD	STD	STD	STD	STD
0°	0°	0/90°	0/90°	0°	0°	0°
1162(166)	1113(159)	238(34)	427(61)	602(86)	490(70)	714(102)
—	—	—	—	—	—	—
588(84)	665(95)	154(22)	252(36)	350(50)	378(54)	392(56)
50(7.1)	51(7.3)	13(1.9)	31(4.5)	38(5.5)	30(5.4)	41(5.9)
—	—	—	—	—	—	—
16(4.5)	17(4.8)	5(1.3)	11(3.1)	28(4.0)	25(3.6)	27(3.9)
1.43	1.48	1.44	1.40	1.32	1.38	1.34
69.3	69.8	73.6	68.6	68.3	69.1	65.0
64.5	65.1	69.2	63.8	63.4	64.3	59.9
0.114(4.5)	0.124(4.9)	0.124(4.9)	0.124(4.9)	0.135(5.3)	0.132(5.2)	0.132(5.2)
355	360	—	354	360	360	360
14.3	8.8	11.7	13.1	18.3	14.4	16.3



II/NR150B
LOT 6B-74

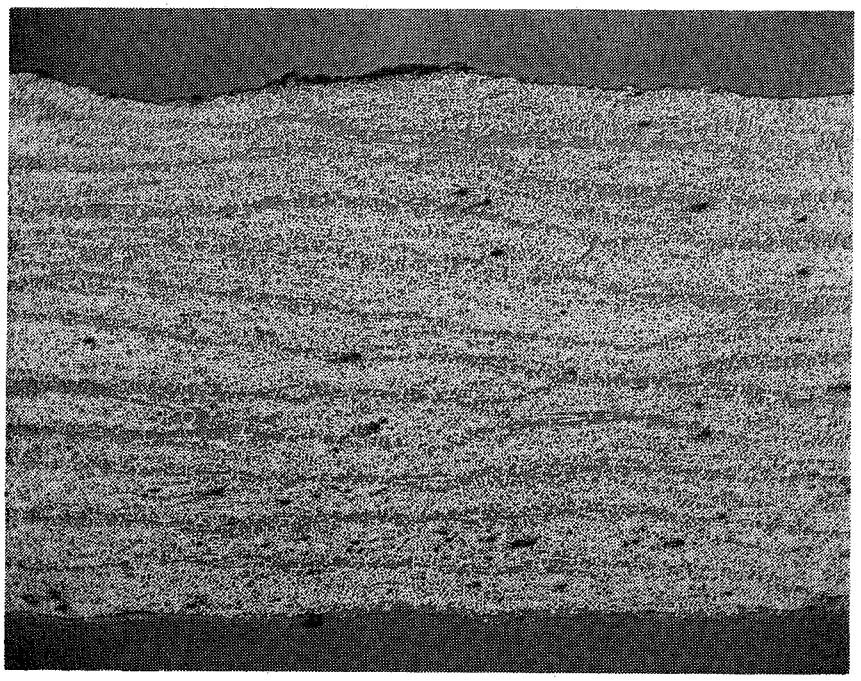
Figure 6. Initial Batch of Three-Inch Modmor II/NR150B2-55X Prepreg Based on 55% Polymer Solution

Laminate C-10 was prepared using the same CR-4 cure cycle and for laminate C-9 in order to evaluate the reproducibility of the process. Laminate C-10 had a void content of 1.7% indicating that the process is reproducible. Photomicrographs of laminate C-10 are shown in Figures 7 and 8.

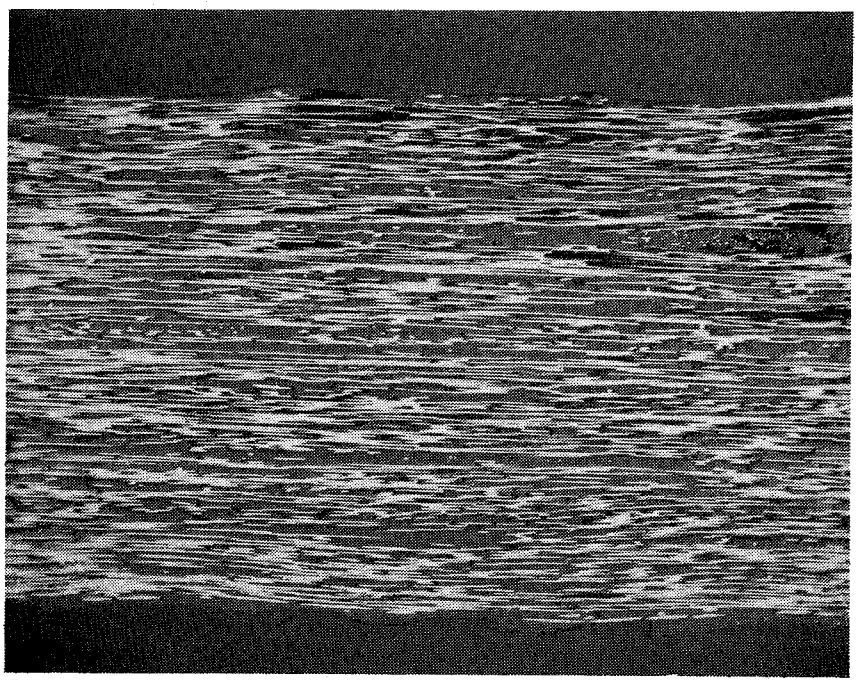
While laminates C-9 and C-10 were very satisfactory in terms of void content, little resin flow was experienced, resulting in a higher than desirable resin content (55 and 52% fiber volume). Laminates C-11 and others prepared during this period involved attempts to obtain increased resin flow and higher fiber volume.

Laminates C-11, C-13, and C-15 (Figures 9, 11 and 12) involved successive modifications of the CR-4 cure schedule by reduction of hold time at 149C (300F) in one-half hour increments. For laminate C-11 the hold time at 149C (300F) without vacuum bag pressure was reduced to one-half hour (cure CR-4A) from the one hour used in the CR-4 cure. Mechanical properties were comparable to laminate C-10.

Laminate C-13 was prepared using cure cycle CR-4B which involved a one-half hold at 149C (300F) without vacuum pressure followed by an additional one-half hour at 149C (300F) with vacuum bag pressure. This cure cycle gave a void content of 2.7%, but gave no improvement as far as increasing the fiber volume. Mechanical properties were somewhat lower than what was obtained on the previous laminates.



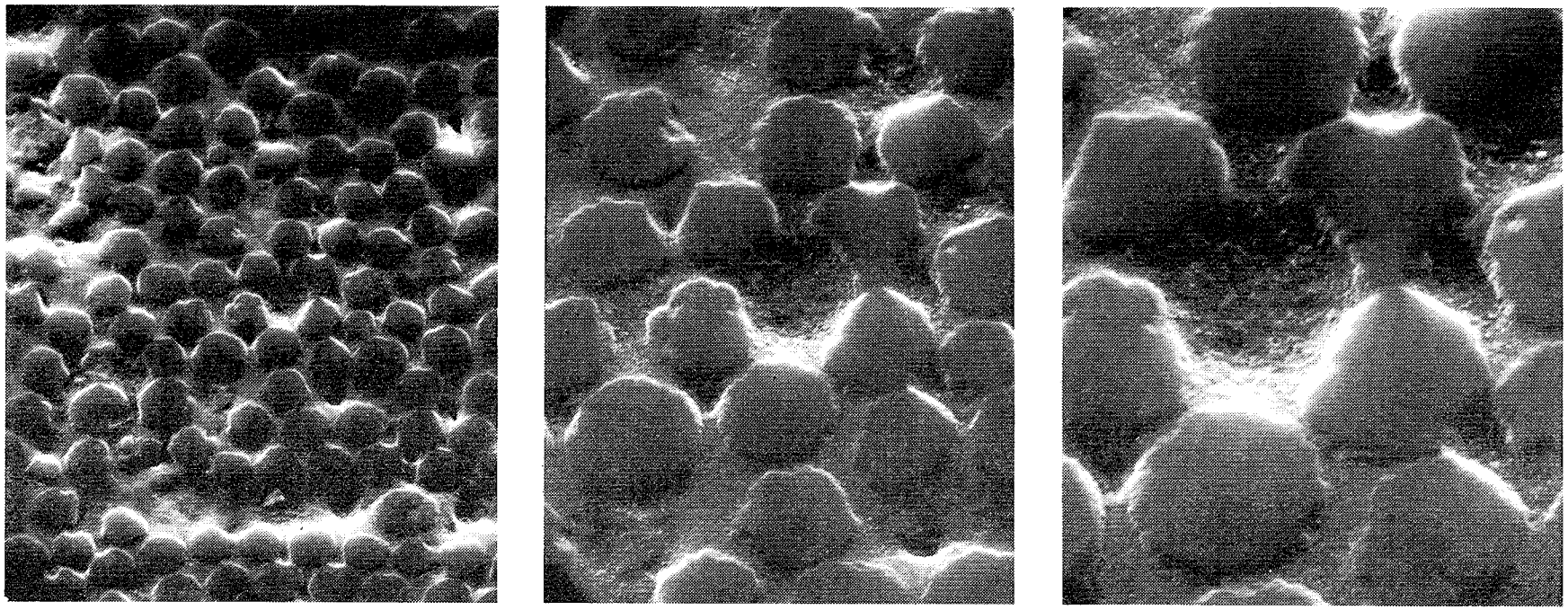
A. END VIEW



B. SIDE VIEW

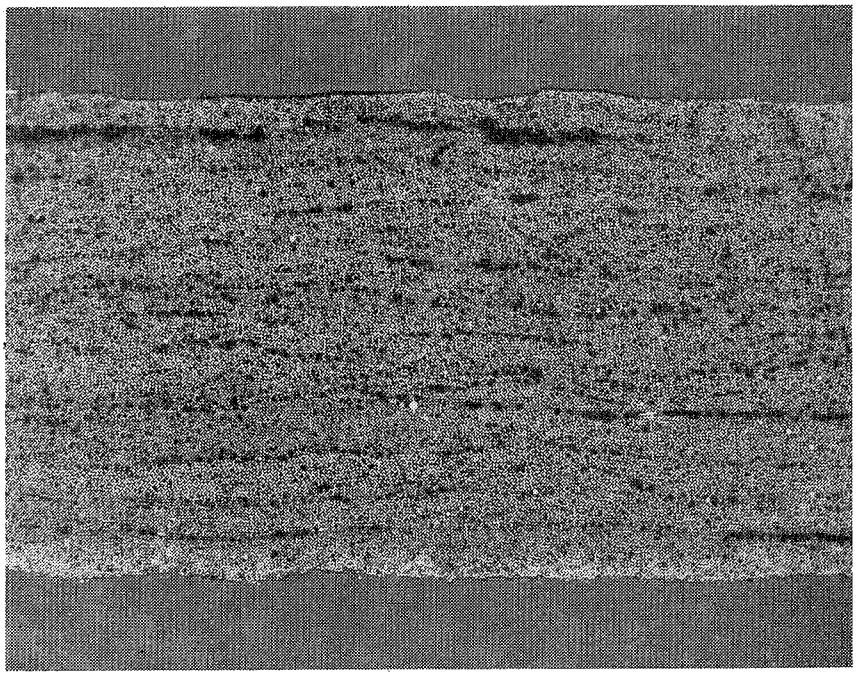
NOTES: 1. CR-4 CURE (Same as Laminate C-9)
2. SP GR, 1.55
3. FIBER VOL %, 52.1
4. VOID %, 1.7

Figure 7. Photomicrograph of Laminate C-10 at 50X

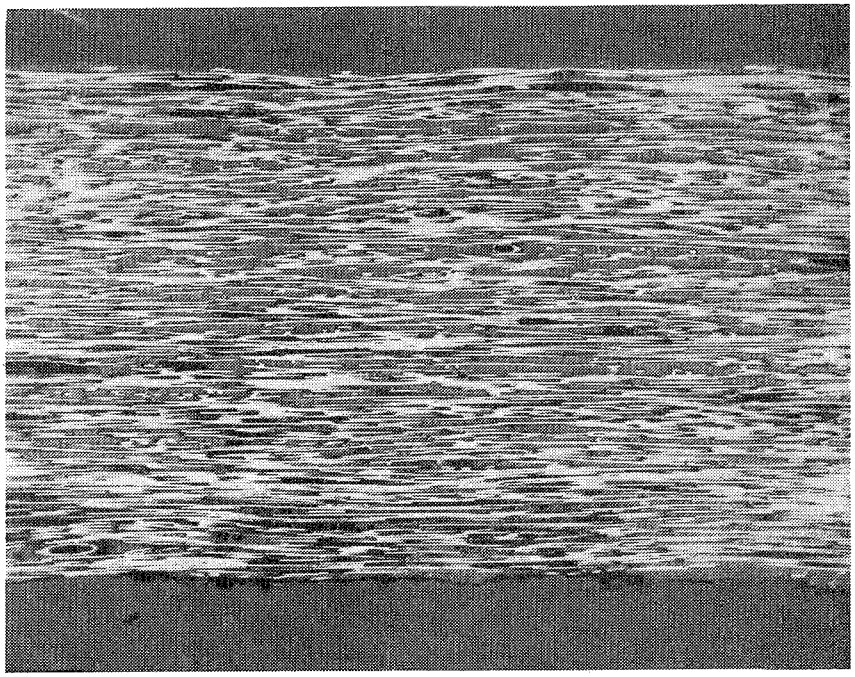


100X 2400X 4000X

Figure 8. SEM of Laminate C-10



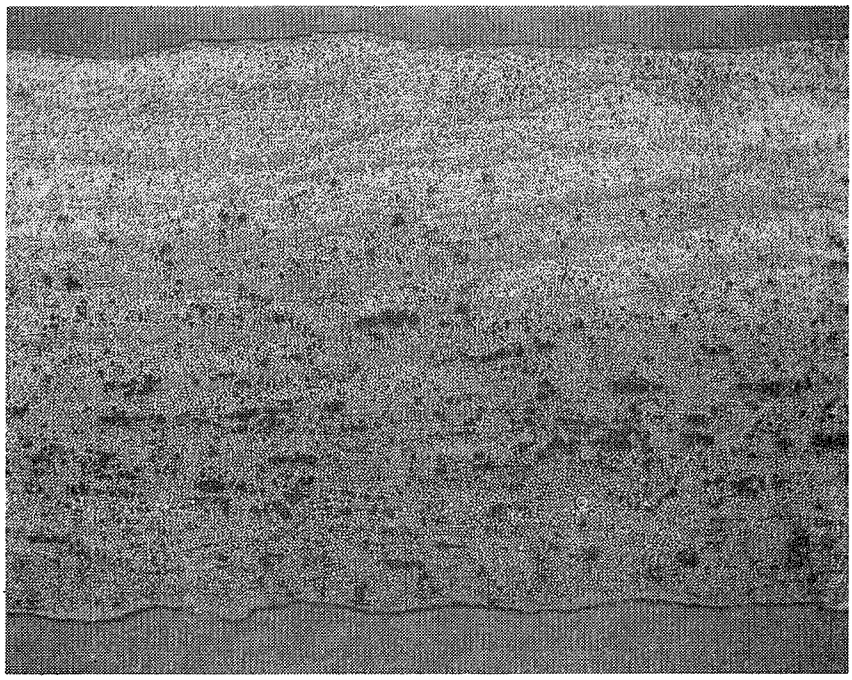
A. END VIEW



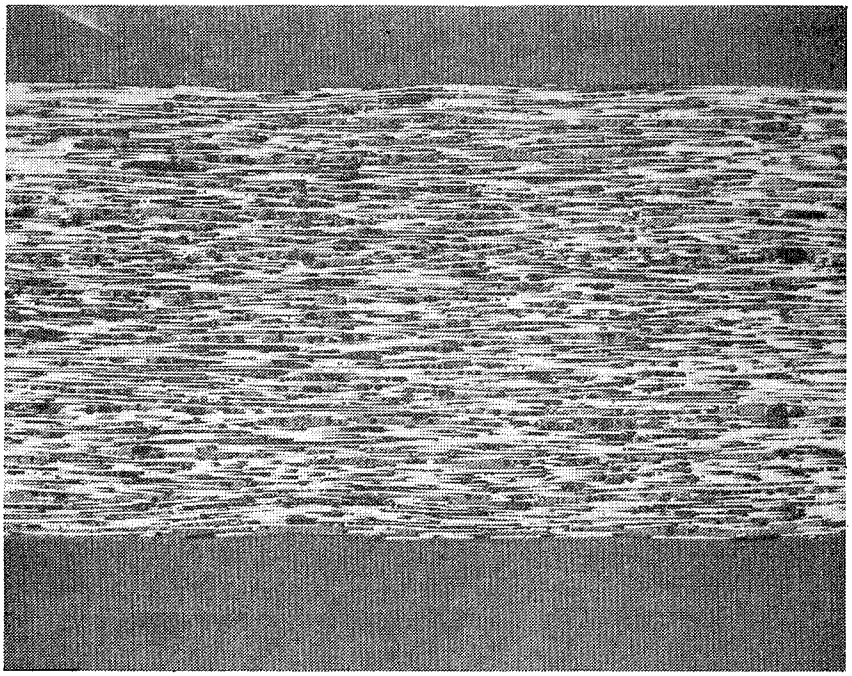
B. SIDE VIEW

NOTES: 1. CR-4A CURE
2. SP GR, 1.51
3. FIBER VOL %, 56.2
4. VOID %, 5.1

Figure 9. Photomicrograph of Laminate C-11 at 50X



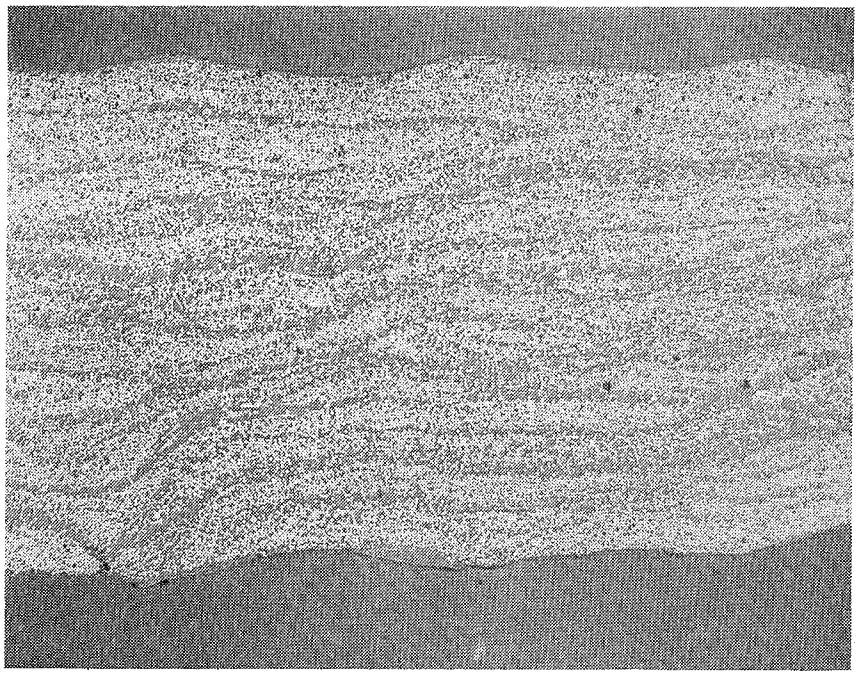
A. END VIEW



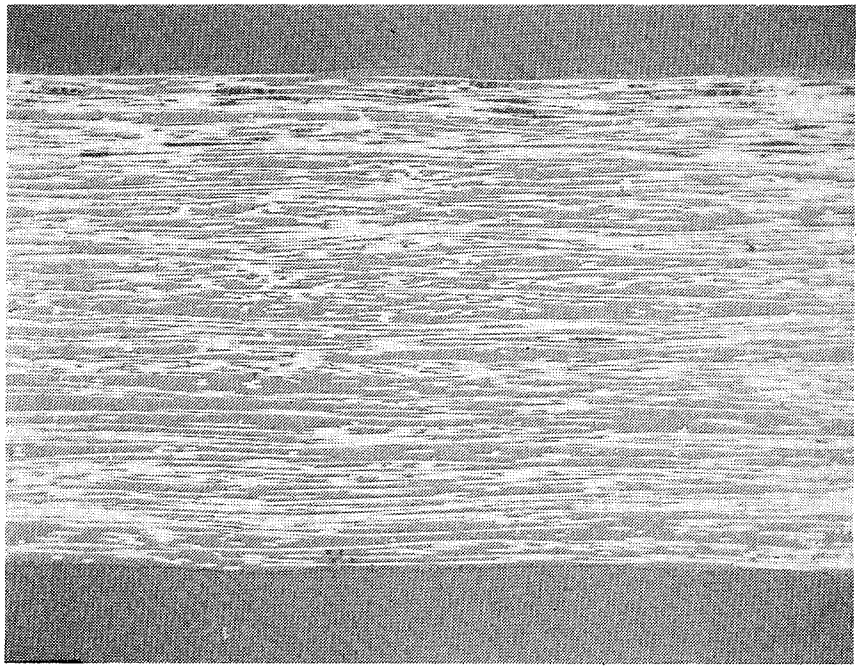
B. SIDE VIEW

NOTES: 1. CR-5 CURE
2. SP GR, 1.45
3. FIBER VOL, 66.0
4. VOID %, 10.7

Figure 10. Photomicrograph of Laminate C-12 at 50X



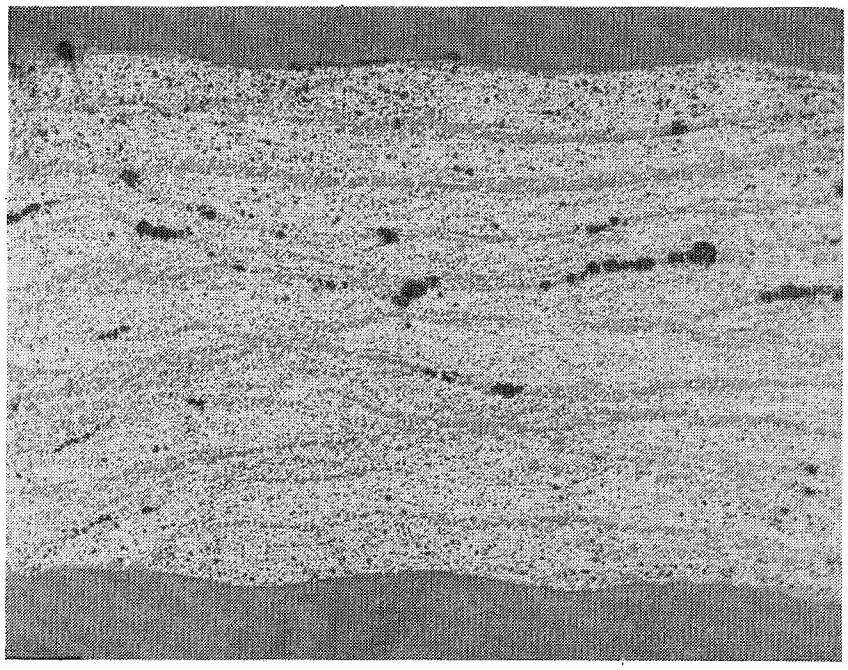
A. END VIEW



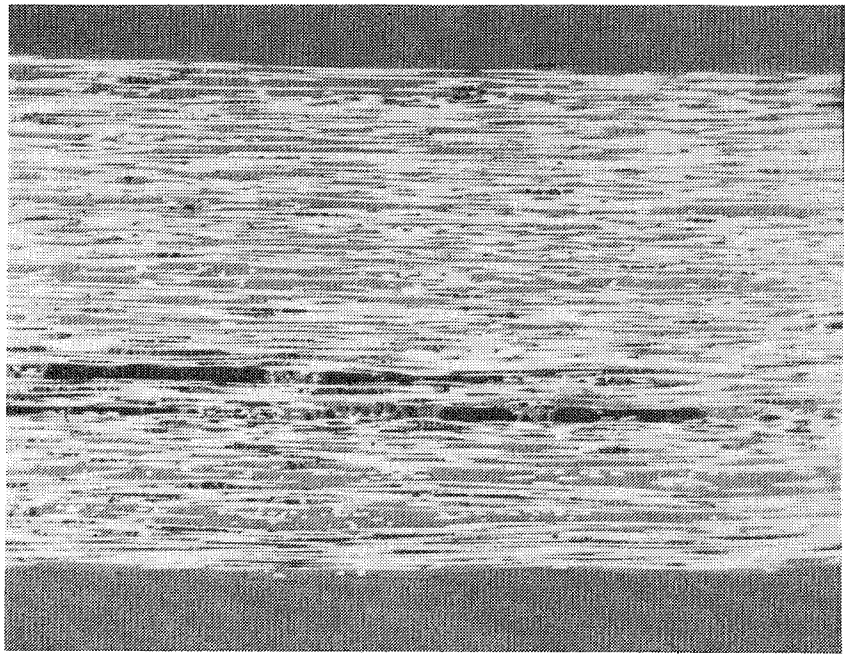
B. SIDE VIEW

NOTES:
1. CR-4B CURE
2. SP GR, 1.55
3. FIBER VOL %, 55.6
4. VOID %, 2.7

Figure 11. Photomicrograph of Laminate C-13 at 50X



A. END VIEW



B. SIDE VIEW

NOTES: 1. CR-4C CURE
2. SP GR, 1.56
3. FIBER VOL % 56.1
4. VOID %, 2.1

Figure 12. Photomicrograph of Laminate C-15 at 50X

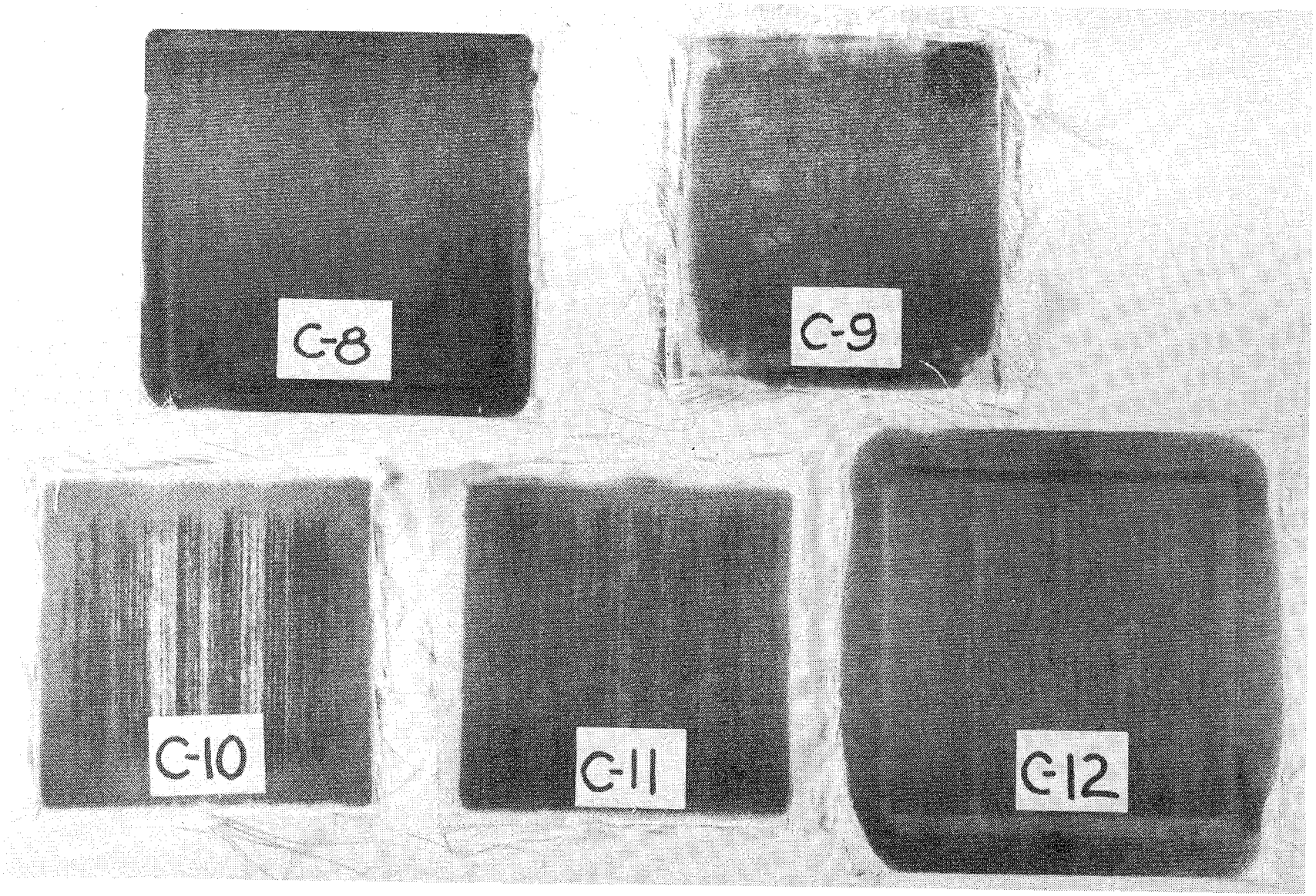


Figure 13. Glass Fabric Bleeder for Laminates C-8 through C-12 Shows Effect of Process Variations on Resin Flow

Laminate C-15 was prepared using cure cycle CR-4C which consisted of a one-half hour hold at 149C (300F) without vacuum pressure followed by applying vacuum bag pressure and raising directly to 185C (365F). On this laminate, a void content of 2.1% was measured with the fiber volume being substantially unchanged from the previous laminates. However, photomicrographs (Figure 12) of a specimen from this laminate did not confirm the calculated low void content indicating that the laminate was not uniform or a non-representative sample was used for the photomicrograph. Mechanical properties were similar to previous laminates except there appeared to be a tendency for a lesser retention of strength at 316C (600F).

Laminate C-12 was prepared using cure cycle CR-5 which consisted of a 1 hour hold at 149C (300F) without pressure followed by applying both vacuum and 1400 kN/m^2 (200 psi) autoclave pressure, holding for a second hour at 149C (300F) and then continuing the standard cure. This process resulted in high resin flow and a 66% fiber volume. However, a void content of 10.7% was calculated for the laminate. Examination of the photomicrograph of the laminate cross section (Figure 10) show the voids to be concentrated in two thirds of the laminate thickness with the remaining one third being very low in porosity. Surprisingly, this laminate gave the highest flexural strength measured to date 1316 MN/m^2 (188 ksi). Figure 13 illustrates the difference in rim flow for five of the cure cycles evaluation.

Laminate C-16 was prepared using cure cycle CR-6 which involved a half-hour hold at 149C (300F) with no pressure after which the laminate was increased to 185C (365F) for a one-hour hold at which time both vacuum and autoclave pressure was applied. High void content (13%) and high fiber volume (64%) were obtained on this laminate. Mechanical properties were practically non-existing with a flex strength at RT 147 MN/m^2 (21 ksi). This laminate was inadvertently heated at a rate of 1.4C/min (2.6F/min) on the increase to 185C (365F) rather than the normal 1C/min (1.8F/min).

Laminates C-14, C-17, and C-20 were prepared at the same time to study the effect of flow for a cross ply panel (C-20) and the possibility of controlling flow by different bleeder combinations on C-14 and C-17. These laminates were cured using the CR-4

cure schedule, but with vacuum bag pressure being applied at the start of the curing operation. Examination of the bleeders for these laminates showed excessive resin flow and specific gravity measurements (Table II) are indicative of high void content.

Laminates C-18, C-19, and C-21 were cured at the same time in a manner similar to the previous three with vacuum pressure being reduced to ten inches of mercury to give approximately 35 kN/m^2 (5 psi). Laminate C-19 used a neat bleeder system, that is, the bleeder was the same area as the laminate layup. Laminate C-21 had a cross ply orientation. Specific gravity measurements on these three laminates indicate some improvement in void content. Also, the neat bleeder approach appears to offer promise in that the highest specific gravity for the three laminates was obtained for that laminate.

Laminates C-22 and C-23 were cured using cure cycle Cr-9 and CR-10 and was an attempt to study the effect of slight vacuum bag pressure during the 149C (300F) hold. Laminate C-22 was held at 149C (300F) for two hours with 127 mm (5 inches) of mercury which produced $\sim$ 35 kN/m^2 (5 psi) pressure. Laminate C-22 was held at the same temperature pressure condition except for a time duration of only one hour. Unfortunately, excessive bleeder material was mistakenly laid up with these laminates causing excessive resin bleed which results in high porosity and high fiber content. Due to this error, the results were not meaningful to the fabrication process study.

The studies conducted to date have demonstrated that NR150B2/graphite composites may be fabricated (CR-4 cure cycle) having void content less than 2% (Laminates C-9 and C-10). However, it appears that the obtaining proper conditions of time, temperature, and pressure to achieve a low void content while obtaining a high fiber volume through resin bleeding is difficult to achieve. The laminate fabrication studies were conducted since laminates C-9 and C-10 also indicate that if satisfactory processing conditions could be defined, the allowable tolerances would be very narrow. These results suggest that the "no bleed" approach where the prepreg is obtained with a net

resin content is a promising approach to this problem. The low void laminates cured by the C-4 cure cycle have showed little or no resin bleed out.

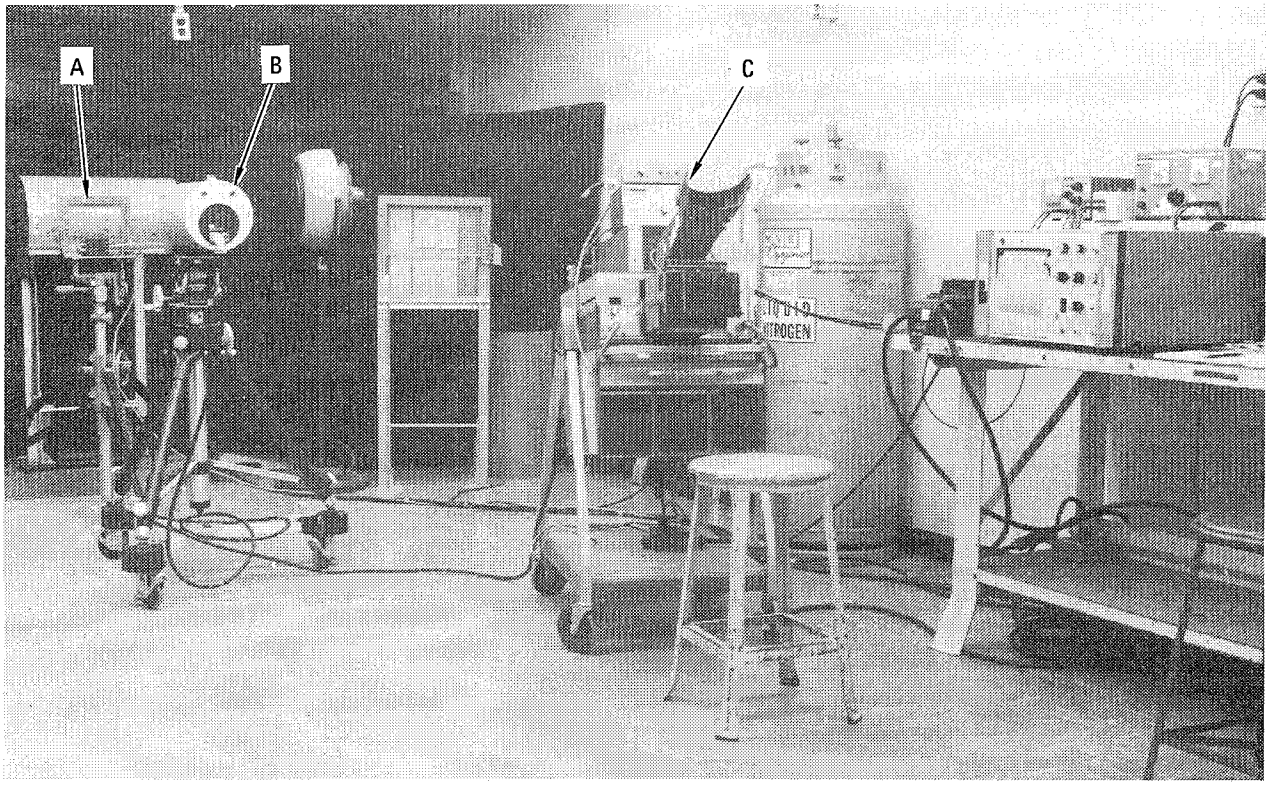
Near the end of this reporting period a five-pound quantity of prepreg based on Celion 3000 fiber and 60% solids resin solution with a net resin content (no bleed approach) was received. The Celion material was employed because of delays in obtaining Modmor II fiber and the necessity to maintain the fabrication process development effort. This material was a vast improvement in terms of uniformity and fiber collimation, with good tack and drape. The Celion prepreg was used to evaluate the possibility of performing the 149C (300F) advancement setp in an oven rather than the autoclave. Laminates C-28, C-29, and C-30 were vacuum bagged without bleeder and advanced in an oven at 149C (300F) for 1, 2, and 3 hours respectively. After removal from the oven, they were rebagged with bleeder and subjected to the standard C-4 autoclave cure without the 149C (300F) hold. The laminates exhibited no bleed during cure and visually appear to be of good quality. As of this time, no further results are available for these laminates.

Laminate C-31 involved an evaluation of the possibility of performing the 149C (300F) advancement step in an oven unrestrained (no vacuum bag). However, excessive distortion of the layup was experienced. This distortion along with the extreme boardness of the layup after advancement made it impractical to cure laminate C-31.

2.3 NON-DESTRUCTIVE EVALUATION (NDE) STUDY

An evaluation was conducted to determine the feasibility of using an infrared scanner for NDE of NR-150B2/graphite composites. The system used for this evaluation was based on an AGA 680-S infrared scanner, which employs a liquid nitrogen-cooled detector of indium autimonide (INSB). The system characteristics include a temperature resolution of 0.2C (0.3F) at 30C (86F), a raster frame rate of 16 frames per second, a line scan frequency of 1600 per second, with 210 lines (interlaced) per frame, and a resolving capability of 140 elements per line. The IR lens had a 15-degree field of view. The ultimate resolution at a lens-to-subject range of 46 cm (18 inches) is better than 0.812 mm (0.032 inch). The system operates on the principle

that defect areas will have a different thermal conductivity which will be indicated on the IR scan pattern. The primary advantage of this approach over ultrasonic C-scan is the speed with which the test can be conducted. The test set-up is shown in Figure 14. Figure 15 illustrates the display/control arrangement.



A. CURVED PANEL TEST SPECIMEN

B. IR CAMERA

C. DISPLAY/CONTROL

Figure 14. I.R. Scanner Arrangement

The test sequence used for this program involved heating the back surface of the panel while observing the changes in the infra-red-detected heat-level and dispersion on the front surface. When an indication was detected on the cathode ray tube (CRT), a scope-photo was taken of the infrared display pattern. This method was sufficient for all but the thinnest section of the test panel. Here, the time was too brief (much less than two seconds). An auto-triggered scope camera would have been appropriate for the thin section, but was not available. For all thicker sections, the time was two seconds or greater, and manual triggering was adequate.

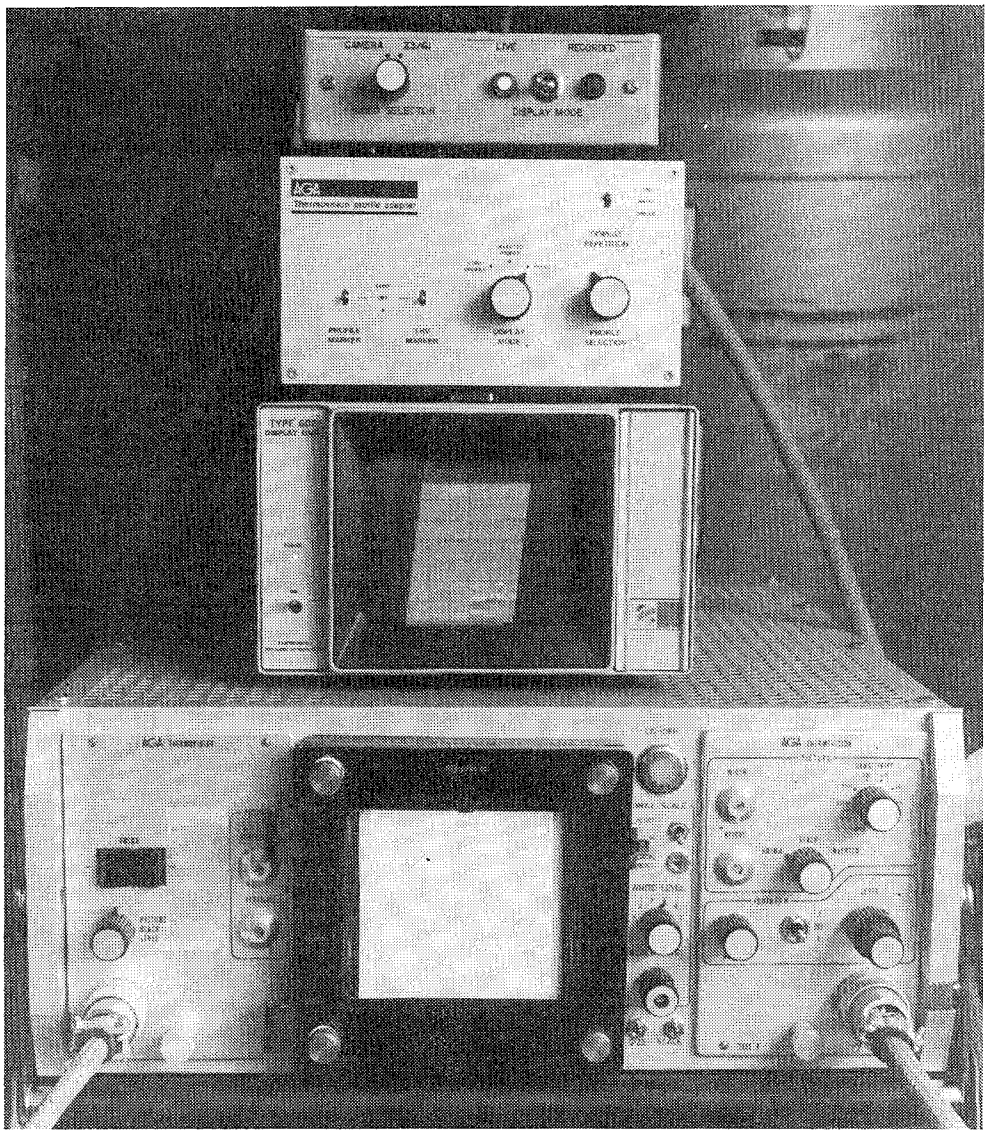


Figure 15. I.R. Scan Display/Control

Heating to the panel was supplied by one or two (selective) 2700 Watt quartz lamps. Heating level was controlled by a variable transformer. The technique involved turning up the voltage to a predetermined level and time, then promptly turning it off.

The evaluation was conducted on test panel No. C-5 which was fabricated in a stepped fashion to give thicknesses of 40 plies, 24 plies, 12 plies, and 6 plies. The panel measured 61 × 30 cm (24 × 12 inches), with each section being six inches long. The properties for the laminate are given in Table III. Due to the relatively high thermal conductivity of the solid laminate, each section of the panel had to be heated and observed individually.

TABLE III

PROPERTIES FOR MULTIPLY STEPPED, NDI LAMINATE

No. Plies	Specific Gravity	Fiber Weight %	T_g, °C	Void %
6	1.54	65.2	359	5.9
12	1.52	63.9	356	7.3
24	1.54	63.7	360	5.9
40	1.57	61.6	360	3.7

NOTES:

(1) Cured by standard cure cycle.

(2) 30 cm (12 in.) × 61 cm (24 in.) × 15 cm (6 in.) steps.

(3) HMS/NR150B2 (EtOH/NMP solvent).

Except for the 6 ply section, heat was applied for three seconds at a heater-to-panel spacing of 18-21 cm (7 - 8 1/2 inches). Heater power was varied by using 130 Volts peak for the 40-ply and 24-ply sections, 100 Volts peak for the 12-ply sections and 80 Volts peak for the 6-ply section. Lower peak voltages were ineffective, as were greater spacings. The maximum peak voltage available was not fully adequate for the 40-ply section.

The time required for obtaining the IR patterns after the thermal pulse varied with laminate thickness. About 30 seconds was required for the 40-ply (too long, too low heat level), about seven seconds for the 24-ply, about three seconds for the 12-ply, and approximately 1+ seconds for the 6-ply section. Noting the rough doubling of time required for the 6-12-24 ply sequence would lead one to project a nominal time around 12 - 13 seconds with 170 Volts peak applied to the heaters for the 40-ply section. Other data indicate this to be a reasonable projection.

The length of time during which the IR pattern could be observed was very short; being on the order of one tenth of the time required for the indication to appear after

first heat application. For the thinner sections, this necessitated a relatively long exposure (1 second) of the scope camera to assure capture of the IR pattern. Failure to secure a satisfactory exposure by this method determined the need for an auto-triggering scope camera mentioned previously. Review of the Polaroid scope photo of the C-5 test panel reveals an indication of an anomaly in the 12-ply section near the edge of the 24-ply section. This is shown most clearly where an isotherm technique was applied. Three sections of the panel are represented in Figure 16, a portion of the 40-ply section on the left, the 24-ply in the center, and a portion of the 12-ply on the right. In the 12-ply portion, below center, a dark squarish area is surrounded by white speckels. The white speckels represent the areas of high isotherm level, the dark area is revealed as one at a lower surface temperature, indicating a localized condition of reduced conductivity. Analysis of system and infrared camera data

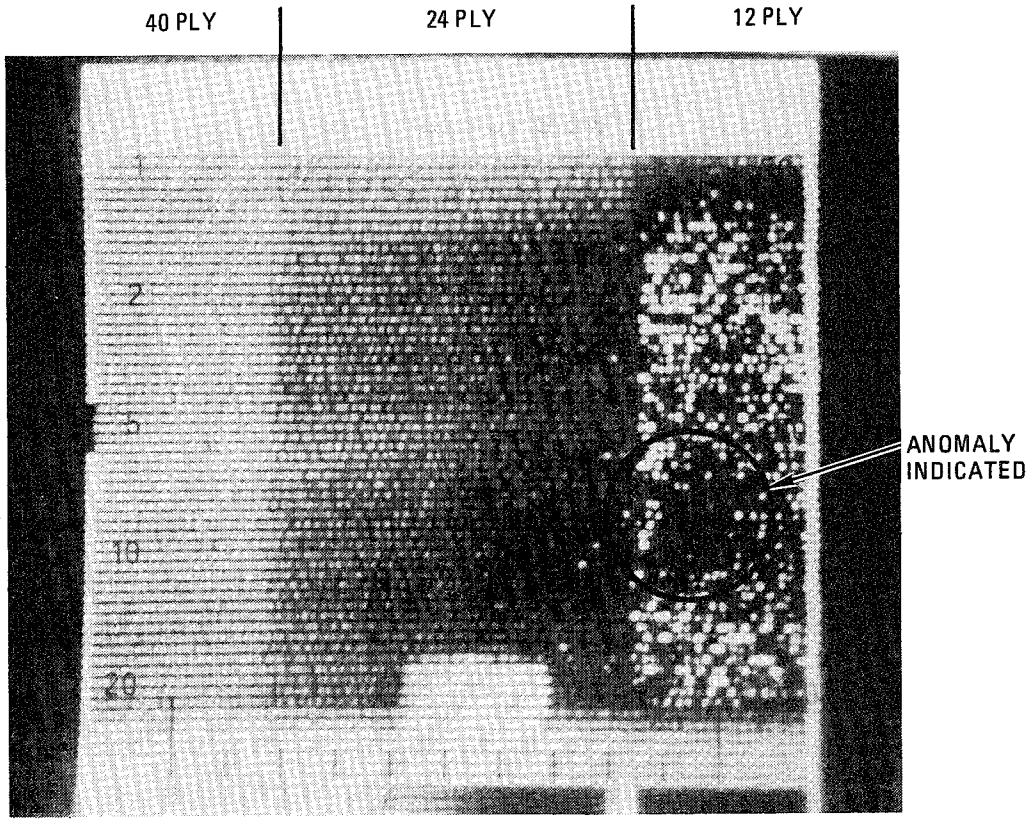


Figure 16. Thermogram for Variable Thickness GR/PI Panel.

reveals the surface temperature difference between the dark area and the surrounding speckel area to be within 3C. For the large part the test panel was indicated to be uniform by the IR-scan.

The multi-thickness panel was next ultrasonic C-scanned to determine if there was a correlation to the IR thermogram. C-scans were conducted at 2.25 MHz and at two gain settings for each thickness of the panel (Figures 17-20). The standard procedure for the C-scan evaluation is to scan the panel at reduced gain levels until high contrast is obtained between the dark (low porosity) and white (high porosity) areas. In terms of low porosity of the laminate (for a given laminate thickness) the lower the gain setting at which a dark scan can be obtained, the higher the quality.

The stripped laminate did not give good C-scans; however, this was not unexpected since the laminate was based on the mixed solvent resin system and also contained a fair degree of porosity. Interestingly, the anomaly indicated on the 12-ply laminate by IR scan (Figure 16) was not apparent on the ultrasonic C-scan (Figure 18). The conclusion resulting from the IR study is that the IR scan is not particularly suitable for identifying areas of typical porosity in a highly thermal conductive graphite laminate. The IR scan offers a rapid and effective means of NDT for locating delaminations on solid laminates and debonds in a honeycomb sandwich.

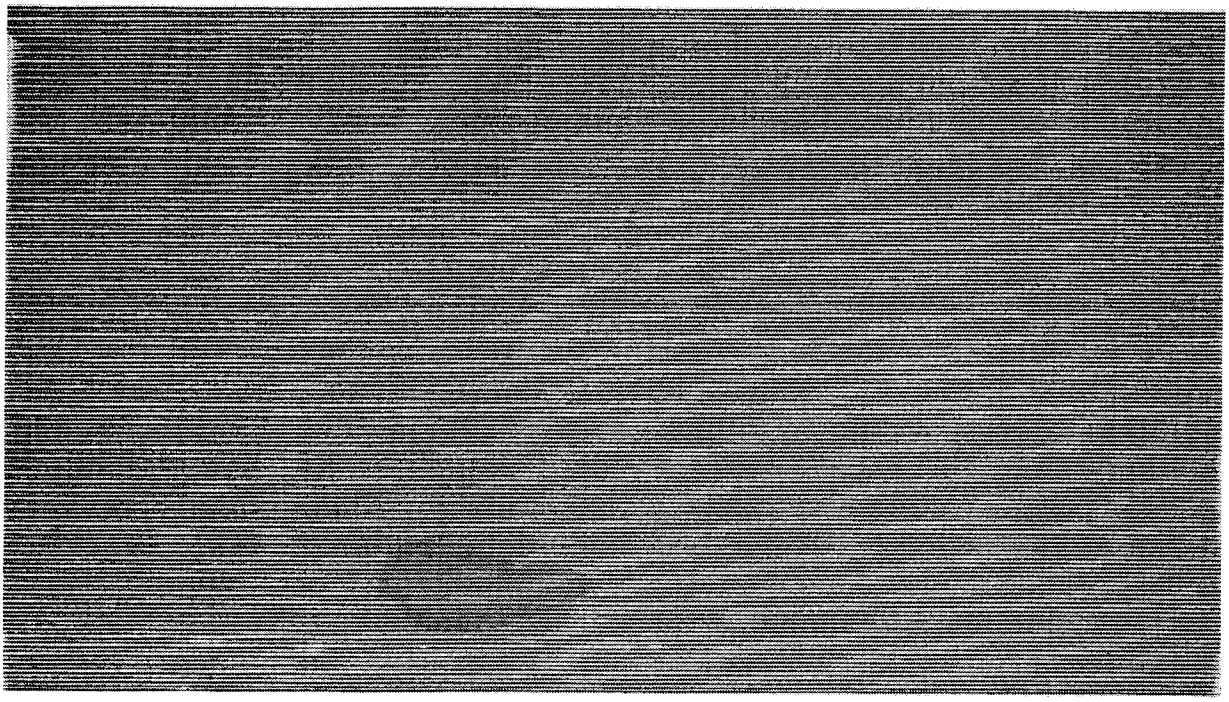
A C-scan is not normally performed on the laminate where physical properties such as low density or high porosity indicate a low quality laminate. However, three of the laminates fabricated during the processing study were ultrasonic C-scanned to obtain comparative data (Figure 21). Laminate C-10, based on cure cycle CR-4 which has resulted in void content $< 2\%$, was included in this series of laminates and gave excellent C-scans at low gain settings and were typical of those obtained for graphite/epoxy composites.

2.4 MATERIAL CHARACTERIZATION

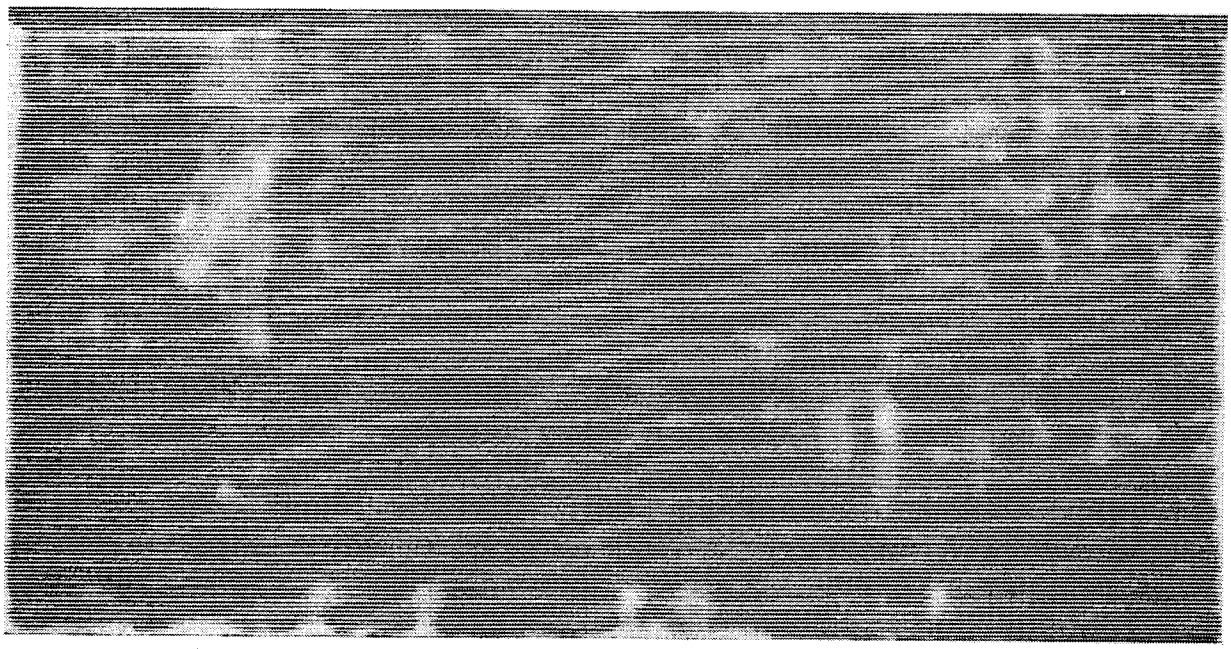
Table IV and V present available data for the resin, fiber, and prepreg for the initial Modmor II lot of prepreg and the recently received Celion 3000 prepreg. Additional characterization is being conducted for the Celion material.

2.5 CONTRACT STATUS BRIEFING

A program status briefing was presented to NASA/LaRC personnel by the Convair Program Manager on 26 July 1977.

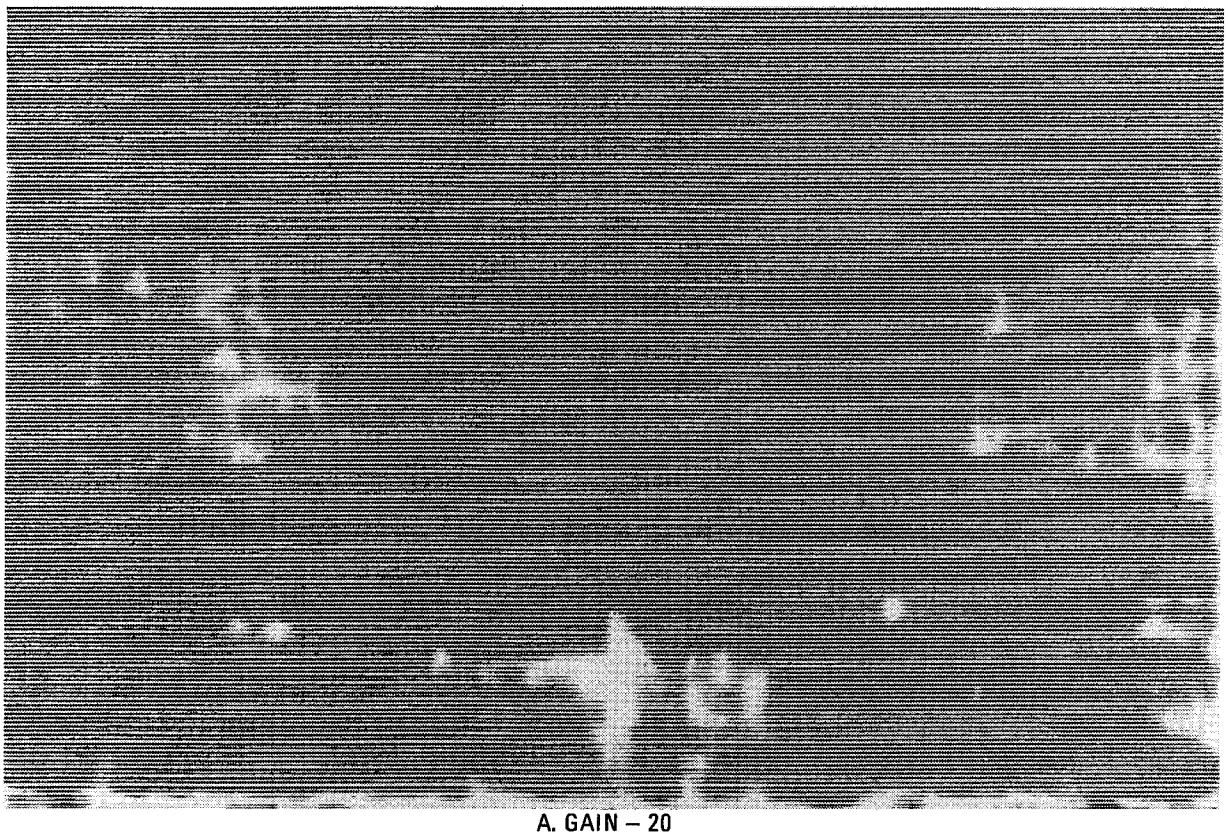


A. GAIN – 6.0

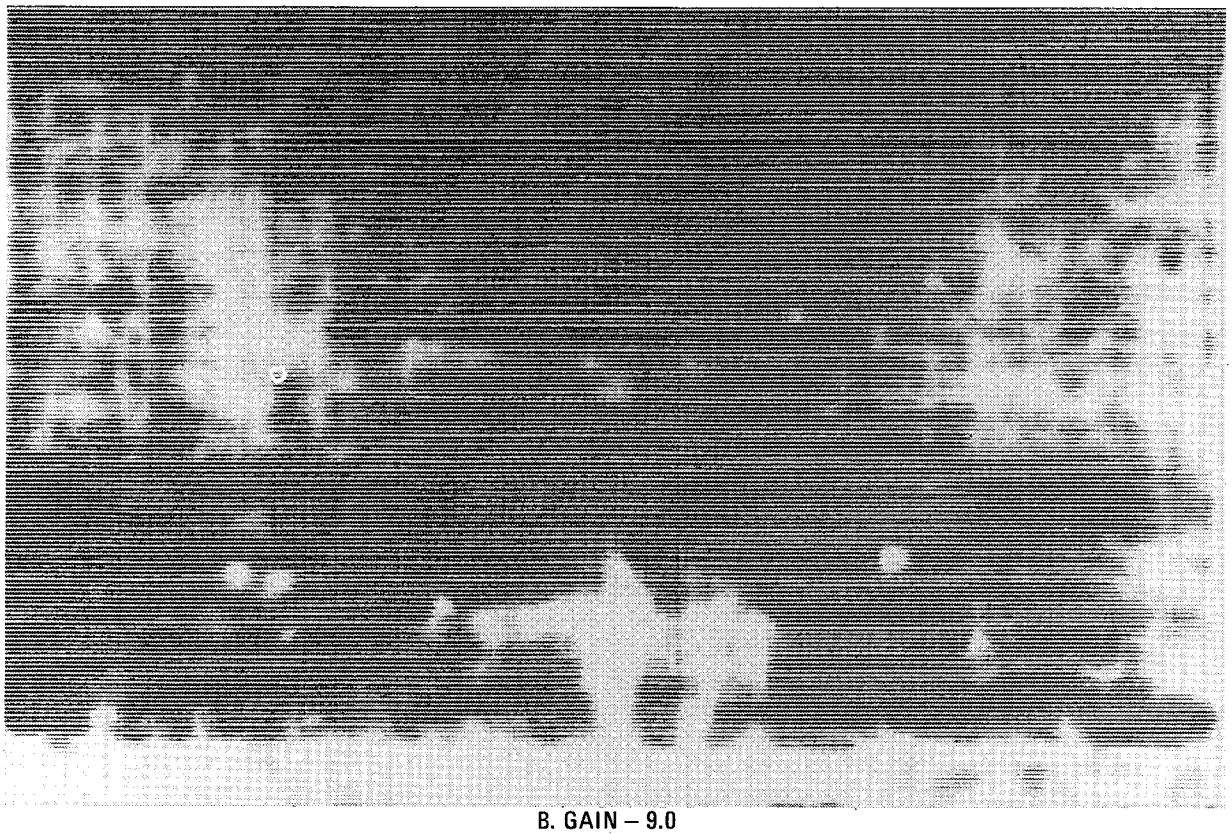


B. GAIN – 2.0

Figure 17. Ultrasonic C-Scan for 6-Ply Laminate Section (2.25 MHz)

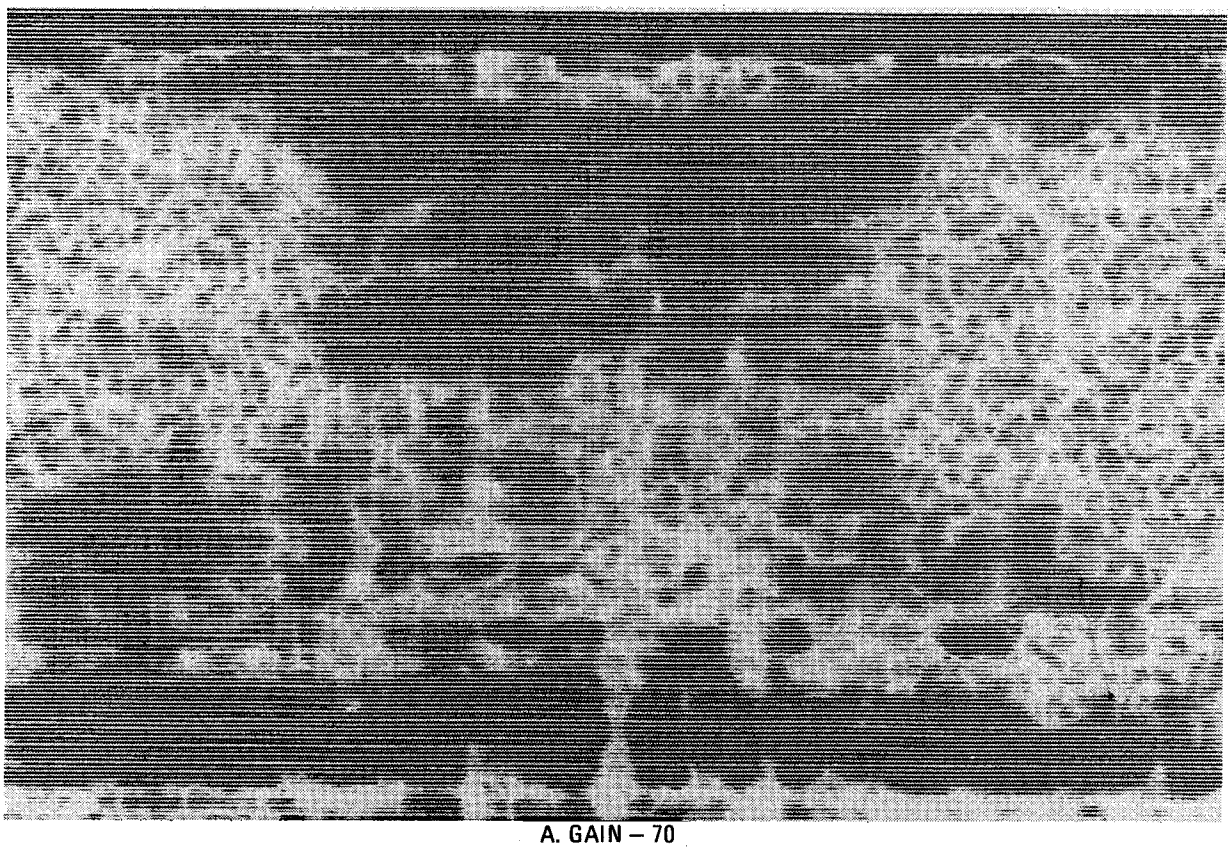


A. GAIN – 20

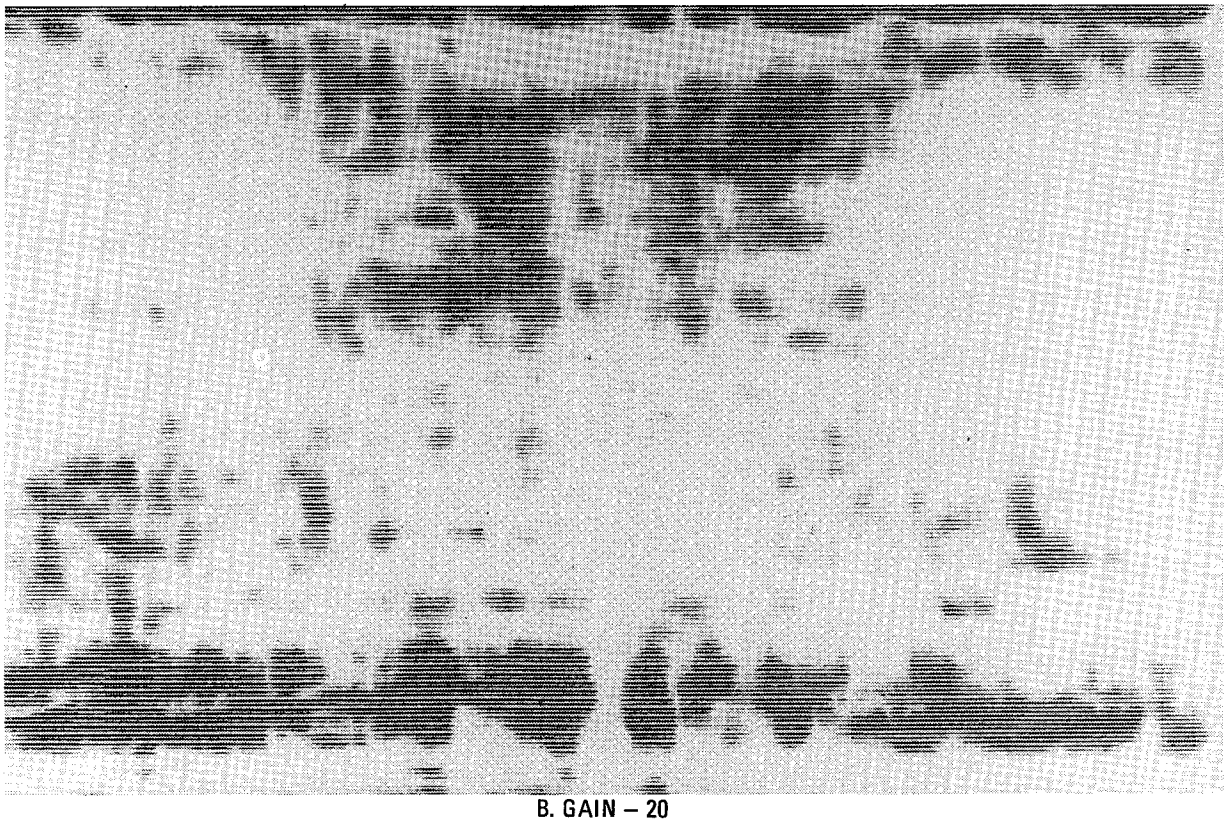


B. GAIN – 9.0

Figure 18. Ultrasonic C-Scan for 12-Ply Laminate Section (2.25 MHz)

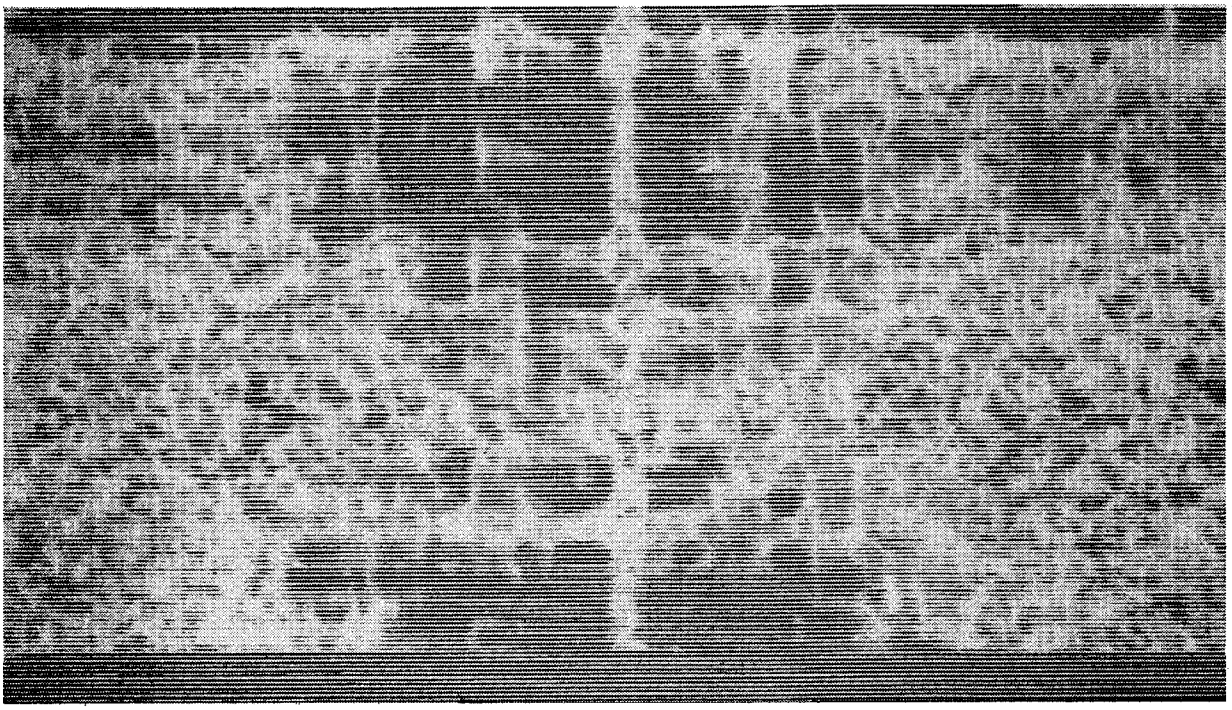


A. GAIN – 70

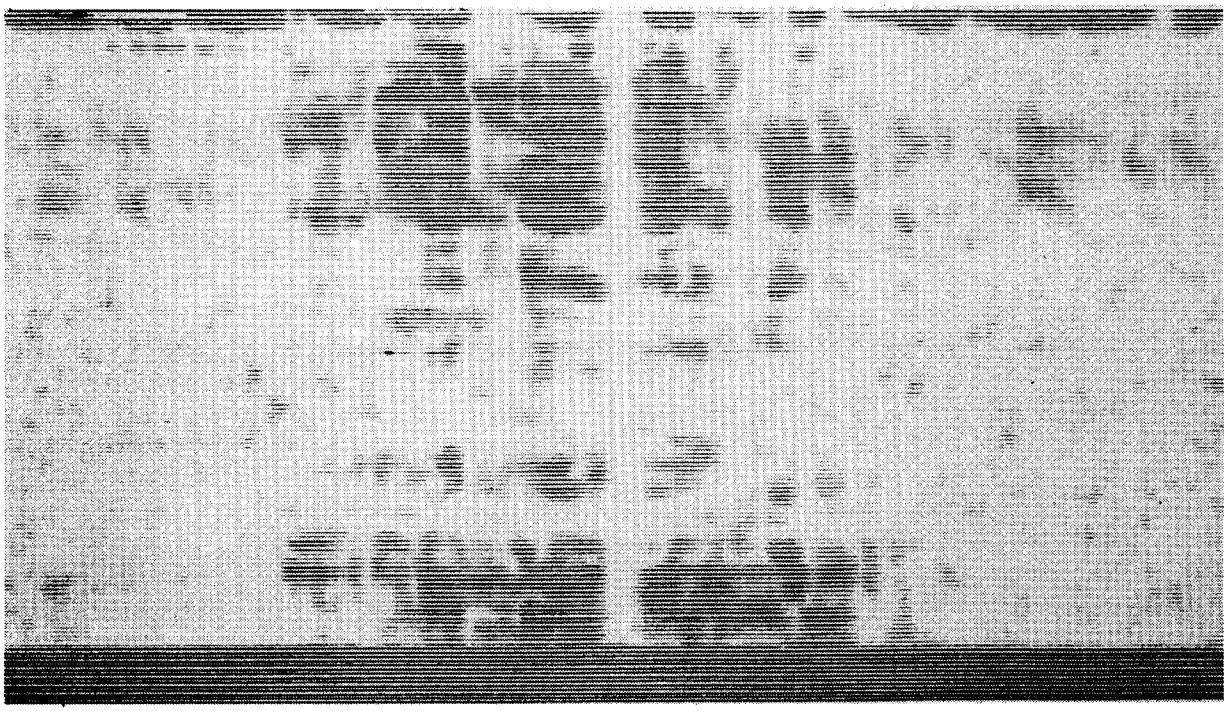


B. GAIN – 20

Figure 19. Ultrasonic C-Scan for 24-Ply Laminate Section (2.25 MHz)



A. GAIN – 70



B. GAIN – 20

Figure 20. Ultrasonic C-Scan for 40-Ply Laminate Section (2.25 MHz)

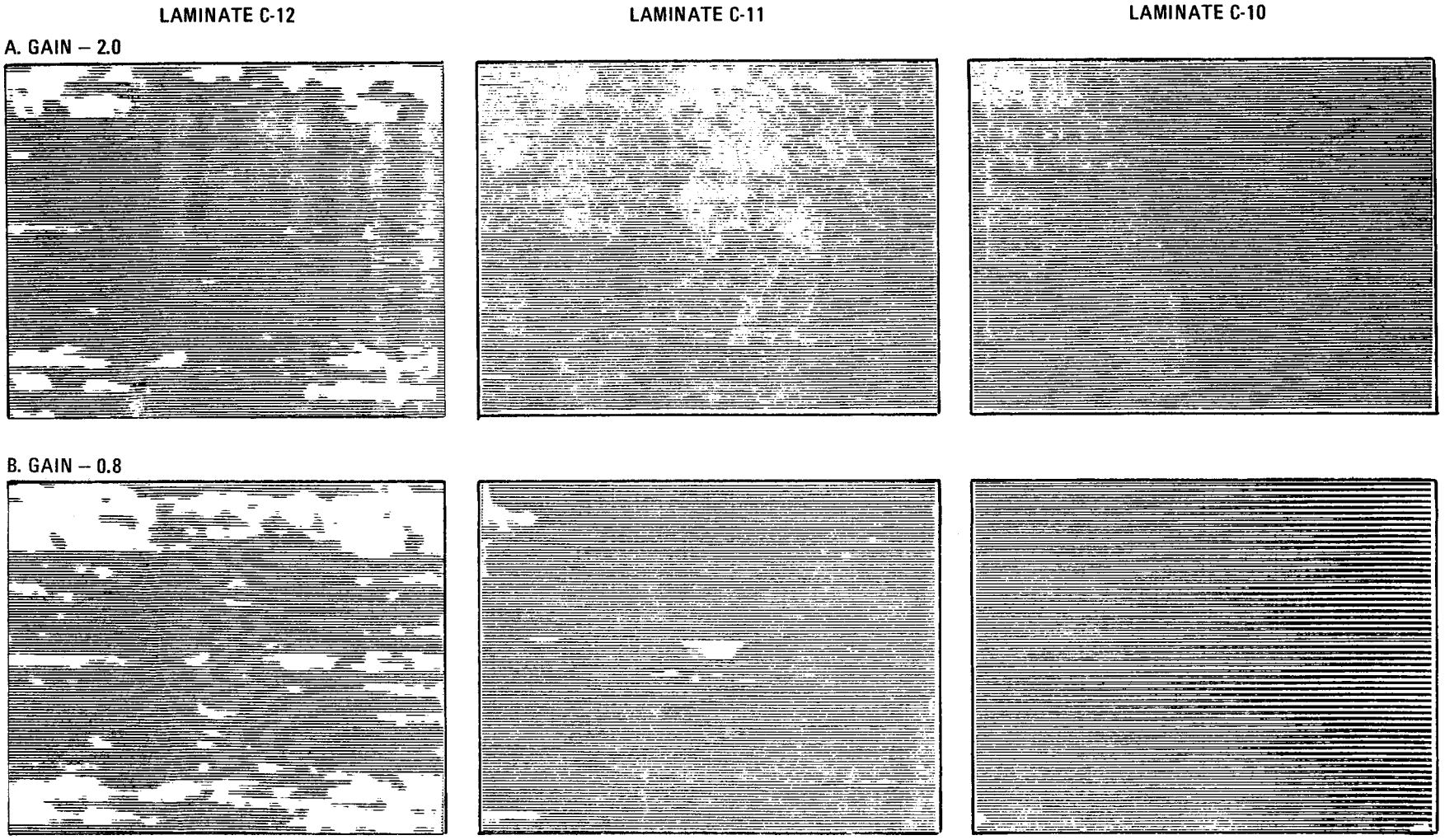


Figure 21. C-Scan for 12-Ply Modmor II/NR-150B2 Graphite/Polyimide Laminates (5 MHz) (Sheet 1)

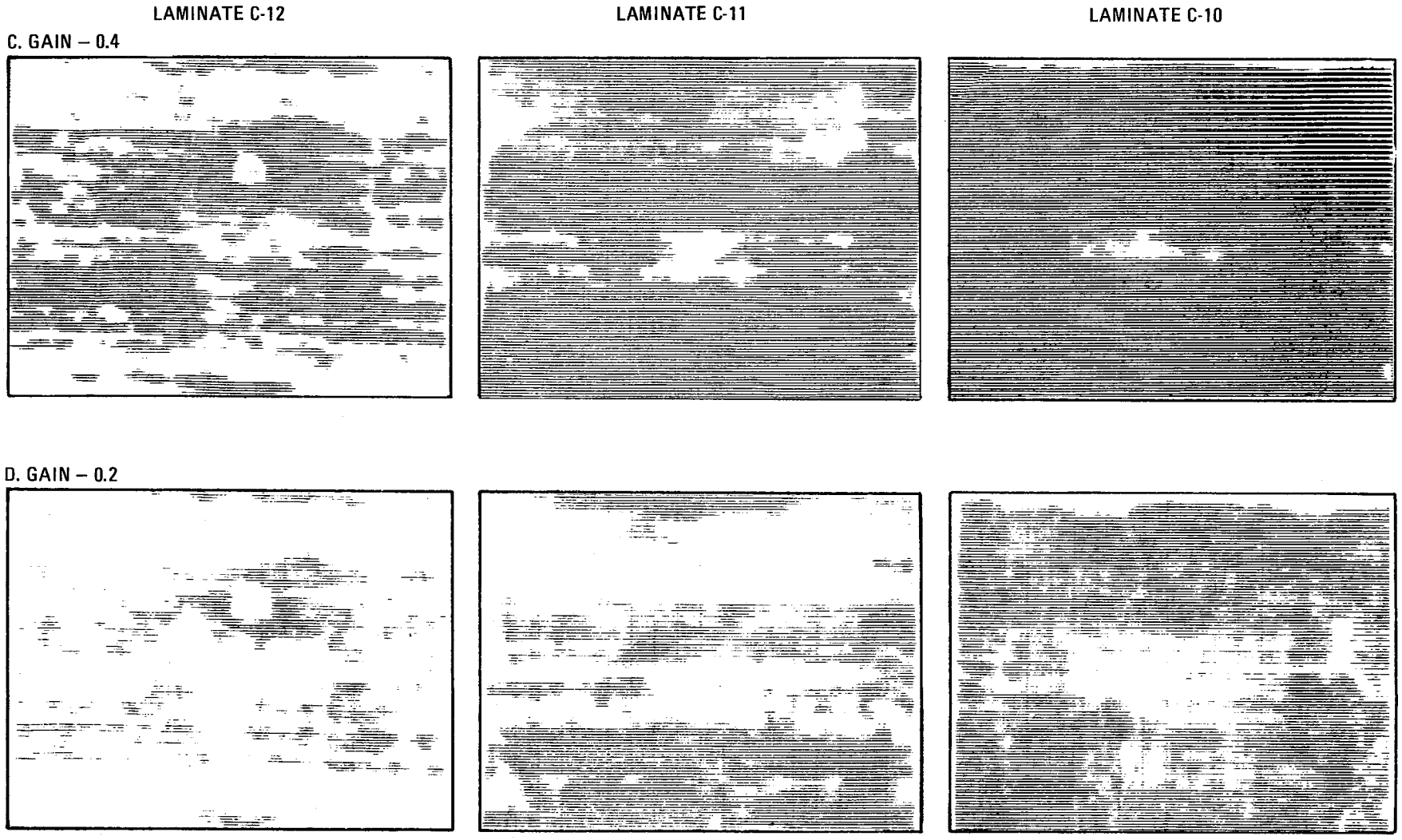


Figure 21. C-Scan for 12-Ply Modmor II/NR-150B2 Graphite/Polyimide Laminates (5 MHz) (Sheet 2)

TABLE IV

PREPREG FIBER AND RESIN DATA

Prepreg Lot No.	6B-74	6D-26[1]
Fiber Type	Modmor II	Celion 3000
Fiber Lot No.	188	HT-7-6X11
Tensile Strength, Mn/m^2 (Ksi)	2534(362)	2856(408)
Tensile Modulus, GN/m^2 (Msi)	301(43)	235(33.6)
Density, gm/cc	ND	1.76
Resin Lot No.	E-14224-34	E14224-76
% Resin Solids	56.3	60.1
Resin Lot No.	—	E1422A-78
% Resin Solids	—	60.7
Solvent Type	NMP	NMP
Gel Time @ 177C (350F) Min.	5.6	—
Viscosity, Cps		
Resin Lot No. E14224	6800[2]	
Resin Lot No. E14224-76		3500[3]
Resin Lot No. E14224-78		4600[3]

[1] Prepared from a blend of two resin lots.

[2] At 75C (167F).

[3] At 95C (203C).

TABLE V

PREPREG PROPERTY DATA

Fiber Type	Modmor II	Celian 3000	Celian 3000
Prepreg Lot No.	6B-74	6D-26	6D-26
Solvent(s)	NMP	NMP	NMP
DuPont Resin Solids (%)	56.3	60.4	60.4
Roll No.	2	1	2
Mfg. Date	5/20/77	8/23/77	8/23/77
Delivery Date	5/26/77	9/1/77	9/1/77
% Resin			
Fiberite	44.6	28.1	27.4
Convair	36.9	32.5	34.0
% Flow			
Fiberite	ND	25.2	25.8
Convair	22.0	22.1	22.4
% Volatiles			
Fiberite	20.2	16.1	16.7
Convair	16.6	12.2	12.1
% Fiber			
Fiberite	35.2(1)	55.8(1)	55.9(1)
Convair	46.5	55.3	53.1
Roll Weight, Kg (lb)	2.13(4.7)	2.49(5.5)	2.49(5.5)
Width, Cm (In.)	7.62(3.0)	7.62(7.62)	7.62(7.62)
Drape	OK	OK	OK
Tack	OK	OK	OK
Gel Time (Min)			
Fiberite @ 204C (400F)	ND	1.5	1.3
Convair @ 204C (400F)	0.6	1.0	—
Fiberite @ 177C (350F)	5.1	4.4	3.5
Convair @ 177C (350F)	2.5	3.0	
Fiberite @ 149C (300F)	ND	11.4	11.0
Convair @ 149C (300F)	7.5	4.2	—
			—
Process Gel, C (F)	140.6(285)	171(340)	171(340)
Areal Weight gm/FT^2	21.44	22.58	25.83

(1)Calculated

SECTION 3

FUTURE ACTIVITIES

(1) Optimize the "No resin bleed" fabrication process and demonstrate reproducibility and applicability to larger size laminates.

(2) Initiate chopped fiber molding study based on Dyglyme solvent for the NR -150B2.

(3) Initiate adhesive bonding and honeycomb panel development tasks.

(4) Continue NDT study with emphasis on ultrasonic C-scan.

(5) Conduct non-autoclave postcure study.

(6) Continue material characterization in order to generate data base for specifications.

SECTION 4

SCHEDULE

The only change in the schedule is the initiation of the chopped fiber molding study earlier than had been previously planned.

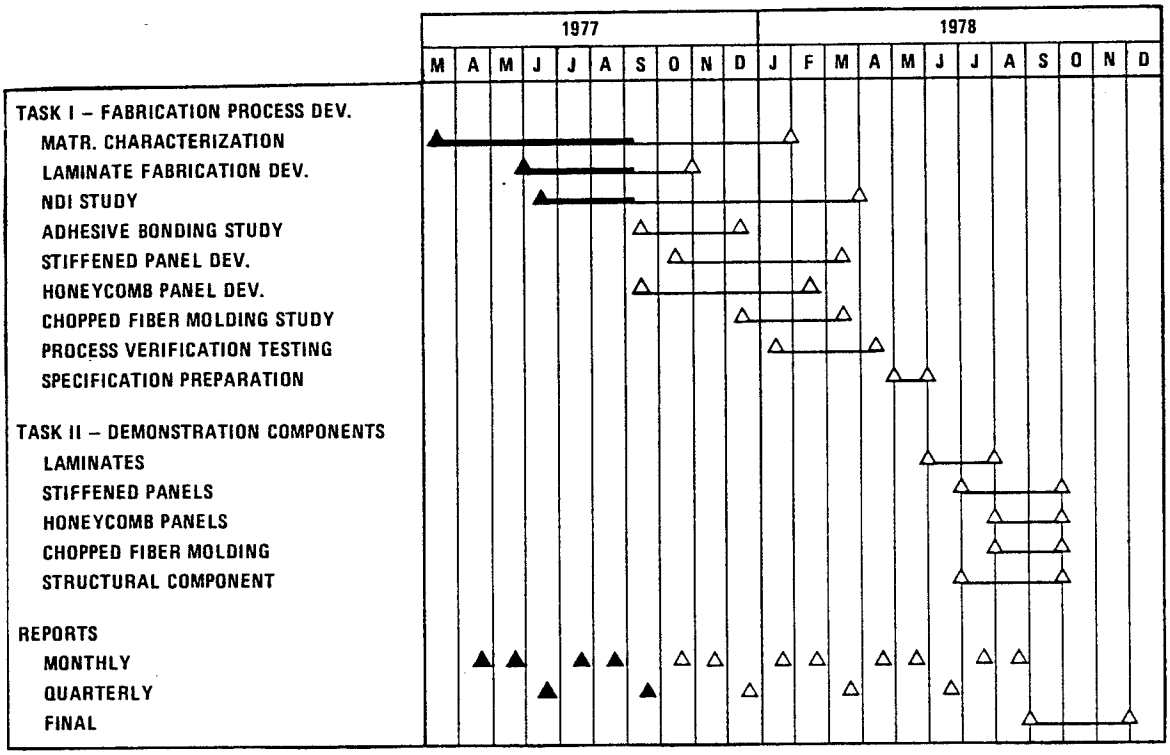


Figure 22. Program Schedule

SECTION 5

PROGRAM COST

As shown in Figure 23, actual expenditures are running below the projected expenditure curve. As new tasks are initiated during the next reporting period, the expenditure rate will increase.

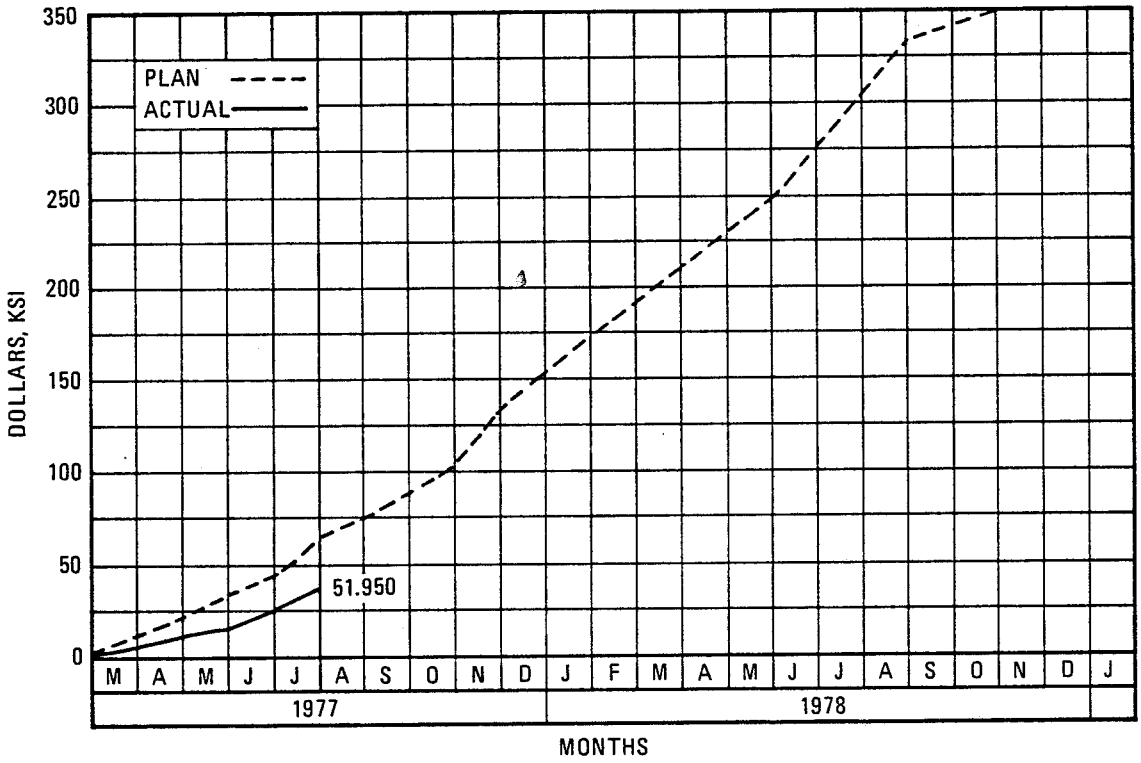


Figure 23. Cost Curves