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NASA CONTRACTOR REPORT 159196

DEVELOPMENT OF LARC 160/NR150B2 POLYIMIDE GRAPHITE HYBRID COMPOSITES

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PREFACE

This document is the final report of the work accomplished under NASA contract NAS1-15433, "Development of LARC 160/NR150B2 Polyimide Graphite Hybrid Composites" from June 26, 1978 through August 10, 1979.

The project was sponsored by Langley Research Center, National Aeronautics and Space Administration, Langley Air Force Base, Virginia. Robert A. Jewell is Project Monitor.

The work was performed by the staff of SRI's chemistry laboratory. Mr. Milan G. Maximovich was project manager; major contributors to the work were Mr. Orton Bergren and Ms. Susan Lockerby.

SUMMARY

Because graphite-polyimide composite materials exhibit high performance, low weight, and good thermal-oxidative stability, they are promising candidates for space shuttle applications. Materials that are being evaluated all have serious shortcomings. No single material is rated excellent in all important respects: processibility, thermal oxidative stability at 316°C, toughness, and mechanical properties.

The objectives of this project were (1) to develop and optimize a method for co-curing NR150B2[*] and LARC 160 prepregs into hybrid composites and (2) to evaluate and compare the processing characteristics and the properties of the hybrid composites with those of laminates fabricated from the individual component prepregs.

In the course of the work, resin forms were selected and optimized and a new NR150 formulation was investigated. The new formulation greatly facilitated the processing and the performance of this system. Quality control techniques were evaluated and developed, high-quality laminates were fabricated from both individual resin systems, and hybrid laminates were sucessfully co-cured. Optimum hybrid forms were investigated and several novel approaches were explored. An optimum hybrid system was developed that utilizes a LARC curing schedule but shows no degradation of mechanical properties after aging 500 hr in air at 260°C.

POLYMER SELECTION

NR150B2

NR150B2 has proved to be an attractive matrix resin for shuttle-oriented applications. The cured resin exhibits good toughness and outstanding thermal oxidative stability. Workers have reported NR150B2 matrix laminates retaining 80% to 90% of initial 316°C mechanical properties after 3,000 hr of air aging at 316°C (ref. 1). A primary problem with NR150B2, however, has been the development of reliable,

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[*] Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

reproducible processing specifications. The solution of the problem has proved to be neither simple nor straightforward.

The present standard product form of NR150B2, according to Du Pont, is the mix of the tetra acid and the diamine (see fig. 1) at a 45% solids level in a 3:1 mix of ethanol:NMP.

In early 1976, work at SRI showed that this form of NR150B2 is not necessarily the form received by the end user. The diamine and tetra acid were separated; then IR and nuclear magnetic resonance (NMR) studies confirmed the presence of ester groups as opposed to pure tetra acid. Discussions with Du Pont (Private communication from H. H. Gibbs, Du Pont, May 1976.) confirmed that although the tetra acid was used to made up the NR150B2 solution, partial uncontrolled esterification could occur by the time the user received the resin solution.

SRI also discovered another serious problem resulting from the use of ethanol-NMP solvent. Ethanol tended to flash off the surface plies during the cure cycle; this led to low-solvent-content, dense outer plies that retard the escape of NMP which boils at a higher temperature. As a result, residual NMP was trapped in the center of the laminate. The result was blisters and delamination during postcure or, because of plasticization of the matrix, poor mechanical properties at elevated temperatures. Later work on the CASTS program confirmed those problems (ref. 2).

To avoid the series of problems associated with the standard NR150B2 with its mixed NMP-ethanol solvent system, we ordered three batches of NR150B2G from Du Pont. NR150B2G is the designation for the NR150B2 dissolved in pure NMP (approximately 49 wt% resin solids content). Additionally, recent work by Du Pont (P. S. Blatz, "NR150 Polyimide Precursor Adhesive Solution Development." to be published.) for NASA has shown significant processing advantages for NR150B2 from diglyme solutions in adhesive applications. SRI decided to evaluate the diglyme solvent version of NR150B2 in this project along with the pure NMP solvent version.

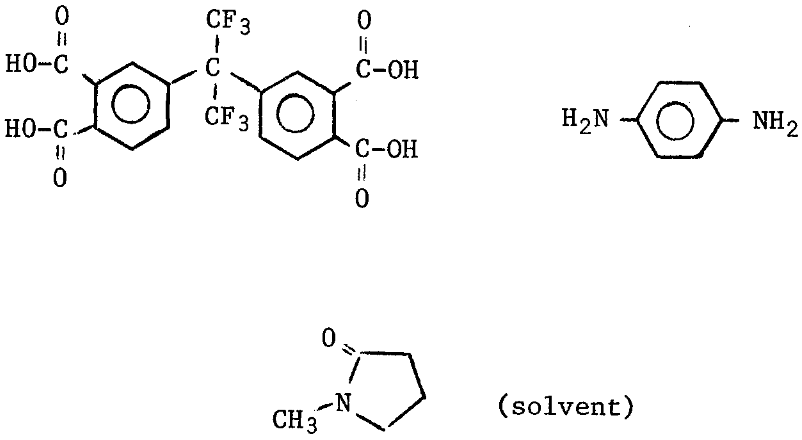


FIGURE 1 NR150B2G SYSTEM COMPONENTS

LARC-160

LARC-160 was developed at Langley Research Center (ref. 3) to overcome processing problems of commercial PI resins and to offer a high performance matrix material with 600°F capability for space shuttle operations. The starting monomers of LARC 160, shown in figure 2, were dissolved in ethanol solution, 66 wt% solids, and were then used to prepare prepreg and subsequent laminates.

In later work at Langley (ref. 4), only a stoichiometric amount of ethanol was used; it resulted in 100%-solids LARC-160. This work was successfully repeated on a pilot scale and the resin was used to prepare solventless prepreg material. The prepreg had good drape and tack and made high-quality laminates.

By using a solvent-free approach, it is possible to avoid all problems associated with solvents of any kind in subsequent fabrication steps. This is highly desirable for both the commercial prepreg supplier and the final fabricator. We therefore selected solvent-free LARC 160, designated LARC 160A3 for use in this project.

Composite Reinforcement

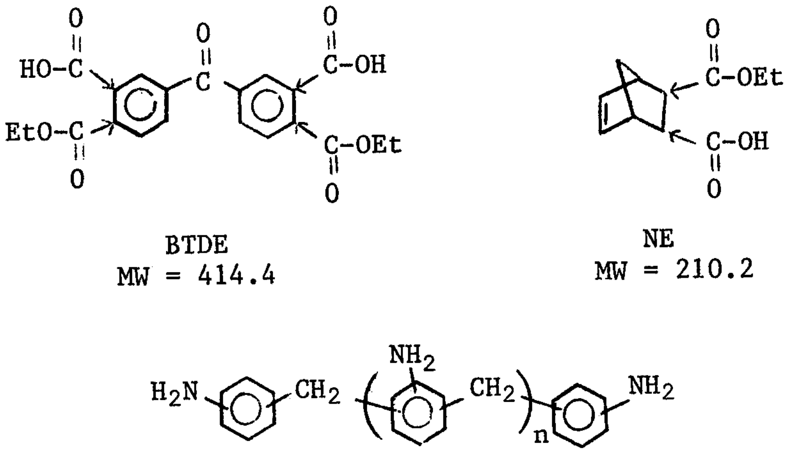
Discussions between SRI and NASA personnel led to the selection of Celion 6000 as the primary reinforcement material. The excellent thermal-oxidative stability, good uniformity, and high mechanical properties of Celion 6000 made it the preferred reinforcement for this work.

CHARACTERIZATION

Our initial approach to resin characterization was to evaluate various characterization techniques as to their efficacy with NR150B2 and LARC 160A3.

Resin Solids Content

A simple determination of cured resin solids was run on the batches of NR150B26S6X, NR150B2G, and LARC 160A3. Three samples of each resin were weighed into tared aluminum cups and placed in an air-circulating oven. LARC 160A3 samples were heated to 149°C and held for 2 hr and then heated to 274°C and held for 2 hr.



BTDE
MW = 414.4

NE
MW = 210.2

n = 0, 1, 2
Jeffamine AP-22
Avg. MW = 234

FIGURE 2 LARC-160 MONOMERS

NR150B2G samples were heated to 149°C and held for 2 hr, heated to 274°C and held for 2 hr, and then heated to 399°C and held for 2 more hr. The results are given in table 1; as shown in the table, reproducibility was good.

IR Fingerprinting

We decided to use IR fingerprinting as a characterization tool. IR fingerprinting of LARC 160A3 was straightforward. A sample of LARC 160 was dissolved in absolute ethanol, a film was cast onto a salt plate, and the ethanol was allowed to evaporate. The resulting IR scan contained a number of distinctive absorption bands and showned only minor amounts of ethanol (fig. 3).

IR fingerprinting for NR150B2G was next pursued. Scans were made of N-methylpyrrolidone (NMP), the NR150B2G solution, and the NR150B2G solution using NMP for a reference. The latter procedure yielded the most informative trace, because of strong interference by NMP in the other trials. The IR scan using this technique was reproducible within this batch of NR105B2G, and excellent correlation was made with the IR scan of NR150B2 produced by General Dynamics, Convair Division (ref. 5) (see fig. 4).

HPLC Studies

We obtained from Du Pont two sets of HPLC conditions for component separation of NR150B2G. The first set of conditions uses a μB C-18 column with a single solvent, acetonitrile. The second set of conditions also uses a μB C-18 column but uses dual solvent gradient elution. One solvent is acetonitrile; the other can be either acidic or basic. If acidic, the solvent interacts with the basic portions of the sample producing fewer ionic species that are preferentially adsorbed onto the column. This allows the acidic components to progress through the column. If a basic solvent is used, it interacts with the acid components, again producing fewer ionic species that are preferentially adsorbed onto the column.

TABLE 1. - CURED RESIN SOLIDS

Sample	Resin Content, wt%		
	NR150B2G52		
	Batch 1	Batch 2	Batch 3
a	49.1	48.9	48.9
b	49.0	48.8	48.9
c	49.0	48.9	48.9
Average	49.0±.1(.2)	48.9±.1(.2)	48.8±.1(.2)
	LARC 160A3		
	Batch 1	Batch 2	Batch 3
a	77.2	77.2	77.3
b	76.8	77.1	77.4
c	77.1	77.2	77.2
Average	77.0±.2(.3)	77.2±,1(.1)	77.3±.1(.1)
	NR150B2S6X52-4		
a	48.3		
b	48.3		
c	48.3		
Average	48.3±0		

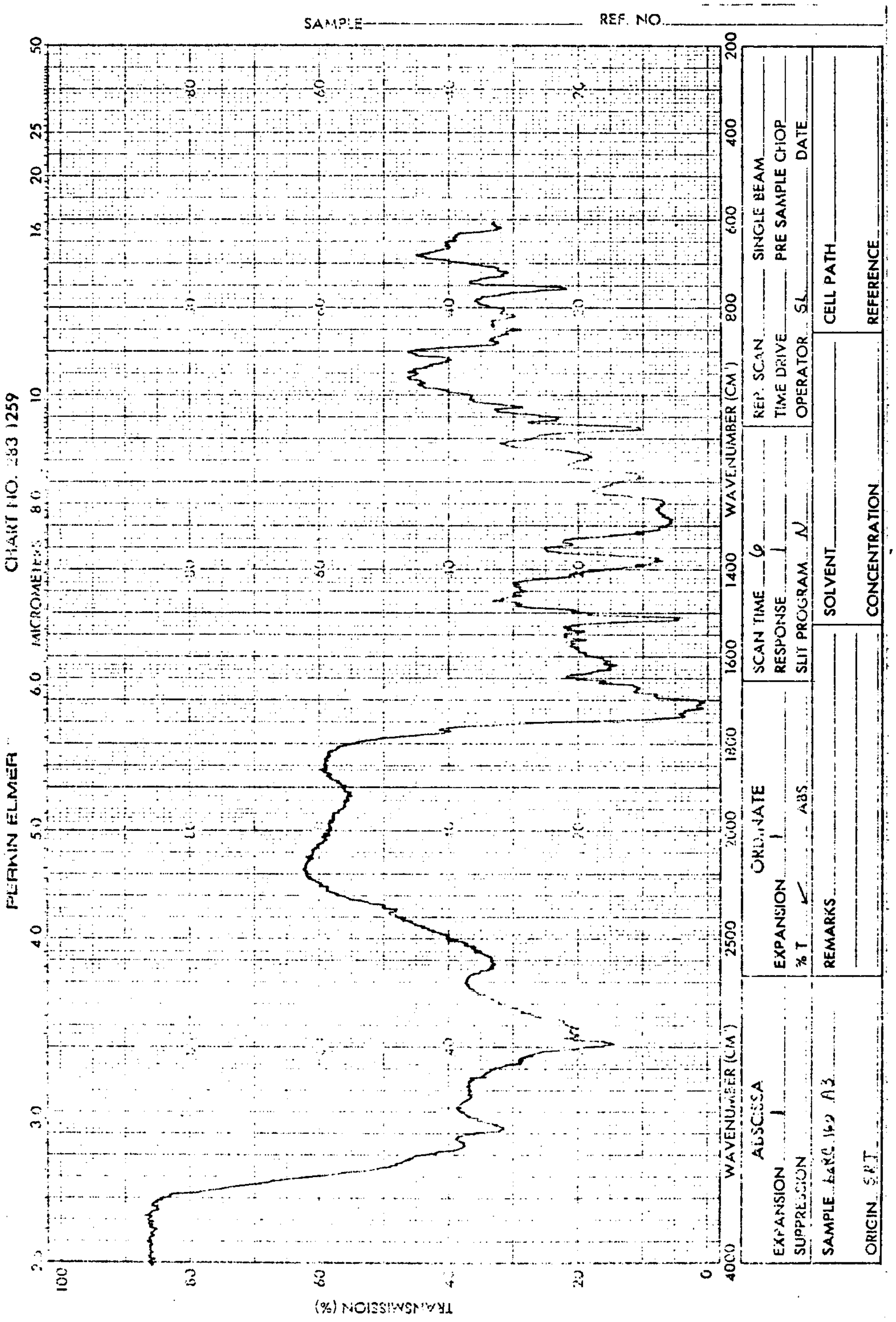
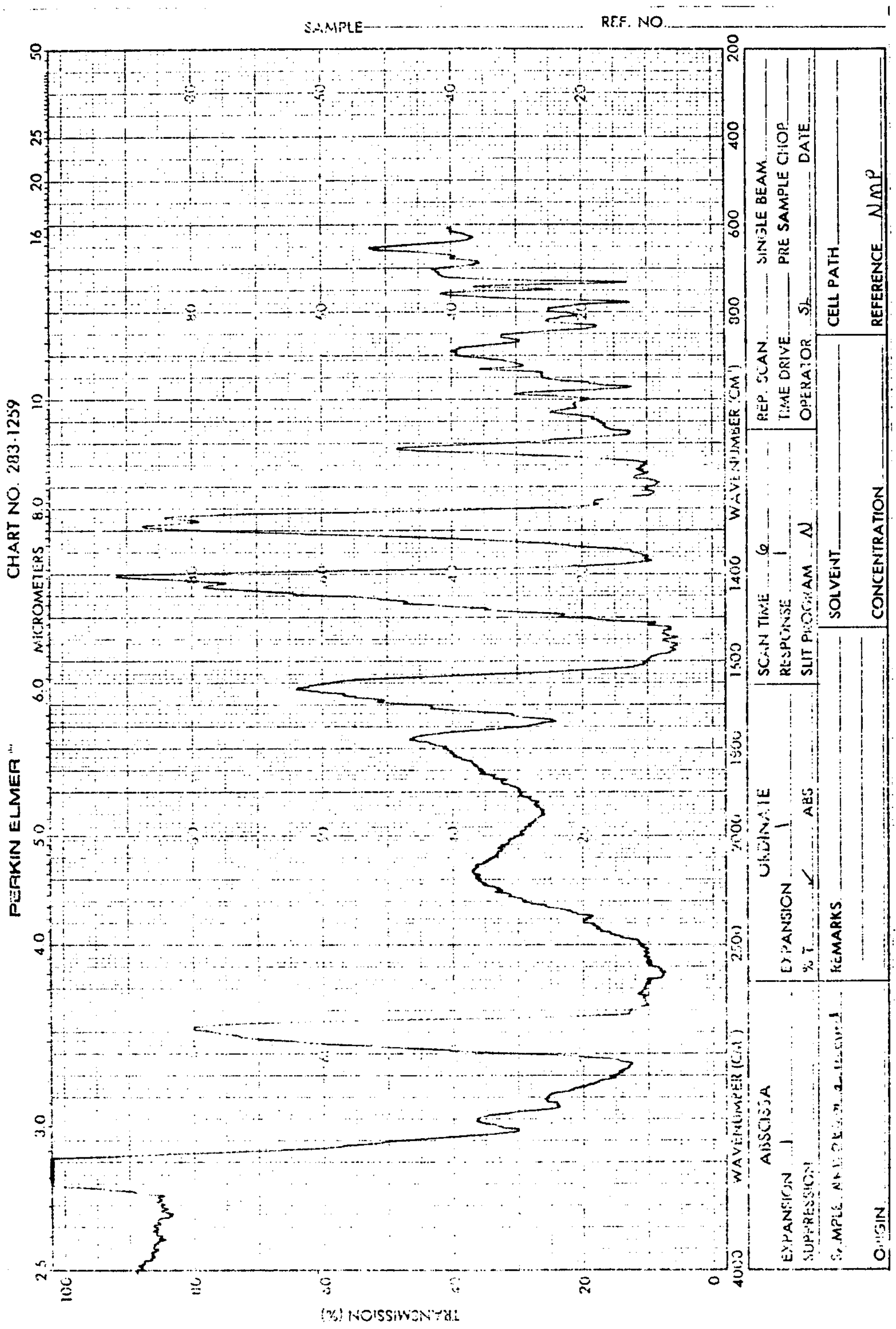


Figure 3 IR SCAN, LARC 160A3



EXPANSION 1
SUPPRESSION
SAMPLE
ORIGIN
EXPANSION 1
% T ✓
ABS
SCAN TIME 6
RESPONSE 1
SLIT PROGRAM N
REP. SCAN
TIME DRIVE
OPERATOR SL
SINGLE BEAM
PRE SAMPLE CHOP
DATE
REFERENCE NMP

Figure 4. IR SCAN, NR150B2G

We separated the components of NR150B2G and verified each by comparing the retention times with those of known solutions.

Solutions for analysis were made by dissolving 36-42 mg of the NR150B2G or NR150B2S6X solution in 10 ml of N-methyl pyrrolidone (NMP). Twenty-five microliters of a pH 7.5 buffer were added just prior to analysis.

We made 25 μl injections onto the 4 mm i.d. x 30 cm μ Bondapak C_{18} column. Elution was at the rate of 1.5 ml/min. The elution program began at 0% acetonitrile-100% water for 10 min. This was followed by a program that began at 100% acetonitrile-0% H_2O, which was accomplished in 15 min.

In addition to the expected components of NR150B2 solutions, a number of peaks occur between 17.5 and 22.5 min. We hypothesized that these are various amide-acid oligomers and that their presence and quantity affect processing.

We tried several solvent combinations during the course of preparing PPDA solutions for HPLC analysis. We observed that the solutions changed from clear white to orange at different rates; a PPDA-acetonitrile solution stored under nitrogen was the slowest to change. An investigation of this phenomenon was beyond the scope of this project; however, we recommend that one be carried out because the phenomenon affects either quality assurance or processing.

Calculations to compare the integrated areas of the major peaks were made; the results are shown in table 2.

The reproducibility of this technique within a batch varied from 1% to 22% and depended both on the batch number and the peak under consideration. The observation was made that within a batch, the later the injection the greater the percentages of the tetra acid and the diamine in NR150B2G. There are a number of differences in the amounts of components between batches.

Table 2. - RESULTS OF HPLC OF THREE BATCHES OF NR1502BG AND ONE BATCH OF NR150B2S6X

Peak	Retention time, min	HPLC column injection number[a]				Average ±5(%)
		1[b]	2[b]	3[b]	4[b]	
NR150B2G52-1						
Tetra acid[c]	1.2	27.0	27.42	28.05	-	27.50±0.52(2)
PPDA[d]	5.9	15.39	15.54	16.22	-	15.72±0.44(3)
A[e]	19.7	17.85	18.94	18.67	-	18.49±0.57(3)
B[e]	20.0	14.40	12.63	9.92	-	12.32±2.26(18)
C[e]	20.6	11.8	12.00	12.11	-	12.00±0.12(1)
NR150B2G52-2						
Tetra acid[c]	1.2	21.35	25.13	25.88	26.28	24.66±2.26(9)
PPDA[d]	5.9	11.74	14.50	15.53	16.25	14.51±1.98(14)
A[e]	19.7	10.24	10.65	10.71	11.20	10.7±0.39(4)
B[e]	20.0	20.98	21.09	18.51	16.95	19.38±2.0(17)
C[e]	20.6	10.24	12.84	12.83	12.49	12.10±1.25(10)
NR150B2G52-3						
Tetra acid[c]	1.2	28.22	28.62	30.45	-	29.10±1.19(4)
PPDA[d]	5.9	16.81	19.41	20.45	-	18.89±1.87(10)
A[e]	19.7	11.72	10.45	11.75	-	11.31±0.74(7)
B[e]	20.0	22.19	15.88	15.23	-	17.77±3.84(22)
C[e]	20.6	7.66	7.70	7.99	-	7.88±0.18(2)
NR150B2S6X52-4						
Tetra acid	11	21.00	24.62	24.46	-	23.36±2.05(9)
PPDA[d]	581	11.54	12.79	11.73	-	12.02±0.67(6)
D[f]	179-285	63.37	57.55	58.92	-	59.95±3.04(5)

[a] All values are percentages of the total integrated areas of the injection.

[b] The number in a series of column injections; for example, injection No. 2 is the second injection in a series of three (or in the case of NR150B2G52-2 a series of four injections).

[c] Tetra acid is 2,2bis(3',4'-dicarboxyphenyl)hexafluoropropane.

[d] PPDA is para phenylene diamine.

[e] Unidentified major peak.

[f] A series of peaks.

Triplicate injections were also made of the single batch of NR150B2S6X. These results are also shown in table 2. Here again reproducibility is not satisfactory.

All three batches of LARC 160A3 were analyzed in the same manner as the NR150B2G samples. Solutions for analysis were made by dissolving 40-60 mg of LARC 160A3 in 10 ml of NMP (N-methyl pyrrolidone) and adding 25 μl of PH 7.5 buffer just before analysis.

The conditions used for separation were the same as those for NR150B2G. We made 25-μl injections onto a 4 mm i.d. x 30 cm μm bondapak-C_{18} column; the UV detector wavelength was set at 254 nm; and the elution rate was 1.5 ml/min. The elution program began with a 10-min hold at 0% acetonitrile-100% water followed by a 15-min gradient elution to the final solvent, 100% acetonitrile-0% water.

Known solutions of all three components of LARC 160A3 were injected onto the column to determine retention times. Three peaks were attributed to ethyl esters of benzophenone tetracarboxylic acid. A series of peaks was identifiable as Jeffamine AP-22. The norbornene acid-ester did not absorb at 254 nm and was not identified. In addition, there was another series of peaks in LARC 160A3 that was not apparent during the analysis of components. The unknown series has a shorter retention time than Jeffamine AP-22. The identity of the components in this series is unknown. The results of triplicate analyses for each batch are shown in table 3.

Reproducibility within a batch of LARC 160A3 was generally better than that for NR150B2 and therefore, batch-to-batch variations were better defined.

Although further HPLC development was beyond the scope of this project, we recommend that several additional steps be taken to develop HPLC into a quantitative technique for the QC of LARC 160 and NR150B2 resins.

Table 3. - RESULTS OF HPLC OF LARC 160A3

Peak	Retention time, min	Percentage of total integreated area of HPLC injection				
		1^{a}	2^{a}	3^{a}	4^{a}	Average±5(%)
		LARC 160A3(Batch 1)				
BTDE	1.1	2.22	2.09	2.28		2.28±0.22(10)
BTDE	3.3	5.03	5.06	5.03		5.04±0.02(.3)
BTDE	5.9	21.53	21.39	21.43		21.45±0.07(.3)
A^{b}	17.6-23.3	34.87	34.63	34.86		34.79±0.14(.4)
Jeffamine AP-22	24.3-28.0	35.75	36.01	35.80		35.85±0.14(.4)
Peak within Jeffamine series	24.6	11.09	11.20	11.25		11.18±0.08(.7)
Peak within Jeffamine series	25.8	8.75	8.75	8.79		8.76±0.02(.2)
		LARC 160A3(Batch 2)				
BTDE	1.1	4.29	2.77	4.88		4.65±0.31(7)
BTDE	3.3	3.98	4.28	4.07		4.11±0.15(4)
BTDE	5.9	17.48	16.77	17.71		17.32±0.49(3)
A^{b}	17.6-23.3	29.83	28.45	28.47		28.92±0.79(3)
Jeffamine AP-22	24.3-28.0	43.61	44.48	44.60		44.23±0.54(1)
Peak within Jeffamine series	24.6	20.07	19.90	19.64		19.87±0.22(1)
Peak within Jeffamine series	25.8	5.97	5.98	5.90		5.95±0.04(.7)
		LARC 160A3(Batch 3)				
BTDE	1.1	3.06	3.23	3.12	3.08	3.14±0.08(3) 3.12±0.09(3)^{d}
BTDE	3.3	4.76	4.85	15.05	4.82	7.37±0.12(69) 4.81±0.05(1)^{d}
BTDE	5.9	20.70	21.23	8.10	21.30	17.83±6.45(36) 21.08±0.33(2)^{d}
A^{b}	17.6-23.3	29.56	28.63	28.45	29.18	28.96±0.51(2) 29.12±0.47(2)^{d}
Jeffamine AP-22	24.3-28.0	41.17	41.86	42.65	41.41	41.77±0.65(2) 41.48±0.35(.8)^{d}
Peak within Jeffamine series	24.6	19.13	19.29	20.90	19.75	19.79±0.80(4) 19.39±0.32(2)^{d}
Peak within Jeffamine series	25.8	6.11	6.09	6.08	6.14	6.11±0.03(.5) 6.11±0.03(.5)^{d}

[a] Number in series of column injection; e.g., injection No. 2 is second injection in a series of three or four.

[b] Unidentified series of peaks.

[c] Values are significantly different from those of other injections at 3.3 and 5.9 min.

[d] Excluding injection No. 3

First, the solution to be separated must be stable for the duration of the analysis; second, the relative absorbances of all components should be determined because it is possible to determine molar ratios of quantities; third, all components should be completely identified; and fourth, the reproducibility of multiple injections should be improved.

Separation Using Ion-Exchange Columns

Acid-base titration was used as an analytical tool to determine acid and amine numbers. Difficulties were encountered, however, when titrating solutions, such as NR150B2G and LARC 160A3, that are mixtures of an acid and a base. The exact nature of the interference has not been explored. We began to look at ion-exchange resins as a means for separating acidic and basic components of the NR150B2 and LARC 160 binder solutions.

By using a strong anion exchange, such as Rexyn-RG-1 with the OH^- form, all acidic components would be captured on the column and all basic components would be eluted. The eluent could then be titrated with acid. Also, by using a strong cation exchanger, such as Rexyn RG-50 in the H^+ form, all acidic components would be eluted and could be titrated with base.

We explored this method of separation, using a 1.8 cm x 25 cm column of Rexyn RG-1 (OH). Elutions were run for about 3 hr at a slow (200-300 ml/hr) elution rate.

When a solution of NR150B2 was separated on the column using a 50% H_2O/50% EtOH eluant, a broad purple band was eluted. We attempted to compare an IR of the purple component with one of known PPDA, but we were unable to obtain either IR by casting from solution onto salt plates.

Because of time and budget constraints we will be unable to continue the development of ion exchange into a useful technique. Further work is necessary to investigate techniques for determining which component(s) are eluting, and also to develop methods for determining when essentially quantitative elution of a component has occurred.

Acid and Amine Titrations

The procedure for acid titration was developed by Du Pont. It consists of weighing a sample of resin (±0.001 g) and dissolving it in 50 ml of acetone. A potentiograph with a glass-Calomel combination electrode is used to titrate the sample with 0.1 N tetrabutyl ammonium hydroxide (TBAH) in isopropanol.

Using these conditions, we titrated duplicate samples of each batch of NR150B2G, NR150B2S6X, and LARC 160A3 for their acid content. The results of the titration are given in tables 4 and 5.

Reproducibility was good for LARC 160A3 and for the second equivalence point of NR150B2.

A comparison of the three batches of NR150B2G shows that Batch 52-3 is noticeably different from the others, not only in the acid titration, but also in the amine titration and the HPLC analysis.

Of the three batches of LARC 160A3, Batch 1 is noticeably different from the other two batches in acid titration and the amine titration.

Additional research is necessary to deveolop titration into a truly quantitative tool. The reliability of the technique should be examined with respect to each resin. Calculations of the theoretical acid content should be correlated to the actual acid content, and the presence of other species, such as esters, amine salts, and polyamide acid moieties, should be investigated. This information should then be correlated to processing conditions.

The determination of the amine content was more difficult. Du Pont did not have a satisfactory procedure for determining the amine content of NR150B2G. We therefore made a brief literature search for conditions that would be applicable, and found two possibilities. The first was to make a glacial acetic acid solution of the amine and then titrate with perchloric acid dissolved in acetic acid. The second was to use acetonitrile as the solvent and titrate with HCl. The former was discarded as being too hazardous (ref. 6), and we explored the latter.

Table 4. - ACID TITRATION OF NR150B2G and NR150B2S6X

Equivalence Point	Acid Content, mg/meq[a]			
	NR150B2G52-1	NR150B2G52-2	NR150B2G52-3	NR150B2S6X-4
First point				
Sample a	628	625	607	640
Sample b	642	598	607	633
Average	635	612	607	637
Second point[b]				
Sample a	296	295	288	296
Sample b	295	293	293	297
Average	295.5	294	290.5	296.5

[a] Milligrams of raw resin divided by milliequivalents.

[b] Point reported by Du Pont.

Table 5. - ACID TITRATION OF LARC 160A3

Sample	Acid content, mg/meq[a]		
	Batch 1	Batch 2	Batch 3
a	423	318	334
b	421	318	334
Average	422	318	334

[a] Milligrams of raw resin divided by milliequivalents.

PPDA is soluble in Ac≡N. There was good separation of the equivalence points of the two amine groups. During the titration, a gray-white precipitate began to form almost immediately, and near the second equivalence point the precipitate turned pinkish brown. We presume that the gray-white precipitate is the $^{+}H_3N\text{-}R\text{-}NH_2$ form of PPDA and the pinkish precipitate is the $^{+}H_3N\text{-}R\text{-}NH_3^{+}$ form.

A sample of NR150B2G was placed in Ac≡N, and a gray-white precipitate formed immediately. The solution was stirred until mixing was complete. The slurry was then titrated with 0.1 N HCl in Ac≡N. Additional precipitate of the same color appeared during titration; as the titration continued, the color turned pinkish brown. Two well-defined equivalence points were observed.

Triplicate titrations of NR150B2G using Ac≡N, however, had a variation of 11%. This was attributed to the collection of the gray-white precipitate around the edge of the titrating vessel. When the precipitate was scraped from the vessel walls into solution during a titration, a significant change in potential was noted.

The problem was solved by using tetrahydrofuran (THF) as the solvent for the NR150B2G and 0.1 N HCl in Ac≡N as the titrant. Two samples of NR150 were titrated; again, two well-defined equivalence points were found. Analysis of the points revealed a variation of only 1%. Triplicate samples of all four batches of NR150 were titrated under these conditions. The results are summarized in table 6.

A similar line of investigation was undertaken for LARC 160A3. With the similarities between the two resins (both are monomeric mixtures of acids and amines), one would expect similarities in their behavior during titration. We ascertained that Jeffamine AP-22, like PPDA, is soluble in acetonitrile and produces a precipitate upon titration. LARC 160A3, like NR150B2G, is not completely soluble in acetonitrile. The precipitate of each binder solution bears a strong resemblance to the precipitate that forms during the titration of the respective amines.

Table 6. - AMINE TITRATION OF NR150B2G AND NR150B2S6X

Equivalence Point	Amine Content, g/meq[a]			
	NR150B2G52-1	NR150B2G52-2	NR150B2G52-3	NR150B256X52-4
First point				
Sample a	1256	1237	1177	1353
Sample b	1251	1170	1136	1362
Sample c	1232	1252	1139	1244
Average[b]	1246 ±13(1)	1220 ±44(4)	1151 ±23(2)	1320 ±66(5)
Second point				
Sample a	644	637	611	703
Sample b	637	630	492	701
Sample c	639	641	618	684
Average[b]	640 ±(0.6)	636 ±6(0.9)	607 ±13(2)	696 ±10(1.4)

[a] Grams of raw resin divided by milliequivalents.

[b] Average ±5(%).

The final conditions for titrating amines in LARC 160A3 were essentially the same as those for NR150B2G; the sample is dissolved in THF and titrated with 0.1 N HCl is acetonitrile. The data are summarized in table 7; the reproducibility was similar to that obtained with NR150B2 samples.

Note that again, no direct, definitive correlations could be made between these data and observed processing anomalies.

PROCESS DEVELOPMENT OF CONSTITUENT RESINS

Prepreg Development

Prepregging parameters were readily established for the various batches of resin. Little difficulty was encountered in obtaining high quality prepreg. The level of wet-out and bundle penetration was determined through sectioning and visual and optical inspection. Table 8 summarizes prepregging parameters for the various resin batches.

NR150B2 Processing

We began the process development using the prepreg made from NR150B2G batches 52-1 and 52-2, and staging and cure cycles developed by Milan Maximovich at Whittaker R&D (see below).

After staging NR150B2G 52-1 prepreg 1 hr at 177°C, a simple flow test was conducted. Layup was made (5 cm by 5 cm [0, 90]) and placed in the following bleeder assembly system:

Top caul plate
1 layer Kapton
3 plies 181 glass
2 plies Armalon
Layup
2 plies Armalon
3 plies 181 glass
1 layer Kapton
Base caul plate.

The assembly was then placed in a 399°C press and 21.1 MPa was applied. This was held 15 min, then cooled. Based on resin content, the layup lost 11.2% in volatiles. There was no flow into the Armalon or 181 glass cloth, but fusion of the plies was good.

Table 7. - AMINE TITRATION OF LARC 160A3

Sample	Amine Content, g/meq[a]		
	Batch 1	Batch 2	Batch 3
a	454	342[b]	399
b	467	401	297
c	462	391	400
Average[c]	461 ±7(1.5)	396 ±7(1.8)[d]	399 ±2(0.5)

[a] Grams of raw resin divided by milliequivalents.

[b] Difficult, arbitrary analysis of titration curve.

[c] Average ±5(%).

[d] Average does not include sample whose curve was difficult to analyze.

Table 8. - PREPREGGING PARAMETERS

Resin and batch	Orifice size, mm	Banding rolls	Temperature, °C	Pot Temperature °C	Prepregging speed cm/min
NR150B2G-1	1.6	yes	Ambient	Ambient	152
-2	1.6	yes	38	38	152
-3	1.4	yes	38	38	152
NR150B2S6X	1.6	yes	Ambient	Ambient	152
LARC 160A3-1	1.3	yes	66	52	152
-2	1.3	yes	93	79	152
-3	1.3	yes	79	52	152

Using the same prepreg (staged 1 hr at 177°C), we made a trial $[0°]_{12}$ laminate (2675-19), 5.7cm by 5.7 cm. Table 9 shows the physical properties. The steps in the cure cycle are:

1. Apply full vacuum
2. Heat to 199°C[*] with vacuum only
3. Hold 1 hr
4. Apply 2.07 MPa
5. Heat to 249°C
6. Hold 1 hr
7. Heat to 352°C
8. Release pressure
9. Heat to 399°C under vacuum only
10. Apply 2.07 MPa
11. Heat to 427°C
12. Hold 1 hr
13. Cool slowly

This schedule was used to cure all small NR150B2 laminates discussed below.

The vacuum bag assemblies were:

Kapton bag
1 ply 181 glass
Top caul
1 ply 181 glass
Kapton
2 plies 181 glass
2 plies Armalon
Layup double-wrapped in Armalon
2 plies Armalon
2 plies 181 glass
Kapton
Base caul

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[*] All heat-up rates for NR105B2 are $\leqslant$ 5.6°C/min.

Table 9. - PROPERTIES OF NR150B2G3 Laminates

Property	Batch No. - Laminate No.			
	52-1 2675-19	52-2 2676-33	52-3 2675-35	53-3[a] 2675-51
Staging at 177°C, min	60	30	22	24
Surface appearance	Smooth	Smooth	Smooth	Smooth
Resin solids content,%	42.9	49.8	34.0	36.0
Density, g/cm^3	1.59	1.48	1.60	1.57
C-Scan	-	Some mottle	Clear	Dark
Volatiles (based on resin content), %	12.4	15.0	30.4	28.8
Short-beam-shear strength, RT, MPa	87.6	73.5	85.3	87.2
316°C short-beam strength, MPa	51.6	34.1	36.7	38.1
Flexure strength, RT, MPa	-	-	-	1,069
316°C flexure strength, MPa	-	-	-	612

[a] A larger laminate made using the same procedure as that used 2675-35.

Using the second prepreg made from batch 52-1, we laid up and cured a $[0°]_{12}$ trial laminate, 15 by 18 cm. This laminate showed signs of insufficient flow and poor compaction: a dark C-scan and uneven surface finish. We suspected overstaging to be the cause of the problem. No further tests were run on this laminate.

We subsequently monitored resin and volatile content as a function of staging time at 100°C, using the prepreg of NR150B2G52-2/Celion 6000; the results are shown below.

Time, min	15	30	45	60	75
Resin plus volatile content, %	53.2	51.8	51.4	51.2	51.3

This work indicated that most of the loosely bound solvent is released after 30 min at 177°C.

We therefore made a second $[0°]_{12}$ (5.72 by 5.08 cm) trial laminate from prepreg that had been staged 30 min at 177°C. The laminate was then cured.

The resulting laminate (2675-33) had a smooth, even surface, a slightly mottled C-scan, a density of 1.48 g/cm^3, and a resin content of 49.8%. It had an average room temperature short-beam shear strength of 73.5 MPa (see table 9)

We dried additional prepreg made with NR150B2G 52-3/Celion 6000 at 177°C and weighed the samples at 15-min intervals. The results are shown below.

Time, min	15	30	45	60	75
Resin plus volatile content, %	45.0	43.2	43.0	42.5	42.4

We also dried one sample 15 min at 399°C. Based on these data, we determined that 22 min of staging at 177°C should produce a volatile content of 17%, slightly higher than the actual amount of volatiles released by laminate 2675-33 (see Table 9).

The NR150B2G prepreg was dried 22 min and a layup $[0°]_{12}$ layup, 5.1 by 5.7 cm was assembled, vacuum bagged, and cured.

The resulting laminate (2675-35) had a smooth, even surface, C-scanned clear, its resin content was 34.0%, and its density was 1.60 g/cm^3. The average short-beam shear value for this laminate was 85.3 MPa. Table 2 shows the comparison of these results with the other two NR150B2G laminates.

Rather than losing 17% volatiles as indicated by the dried samples of prepreg, this laminate actually lost 30.4%, far more than expected.

A dual probe dielectric scan was also run on a laminate made from the NR150B2G 52-3 prepreg. The laminate was essentially the same as the one above, though no properties were obtained.

A larger panel, laminate 2675-35 (see table 9), was scaled up to 19 by 20 cm. Prepreg was made using NR150B2G 52-3 and NR150 sized Celion 6000 according to the procedure developed in the previous report period. The prepreg was dried 24 min at 177°C to yield the desired volatile content.

From this prepreg, a $[0°]_{10}$, 19 by 20 cm laminate was laid up and cured using the same cure schedule used for laminate 2675-35. The resulting laminate (2675-51) had a good appearance, was 1.9 to 2.0 mm thick, and had a calculated resin content of 28.6%; the volatiles lost during cure were 28.8%, slightly lower than the amount of volatiles lost from the mini-laminate. The panel gave a poor C-scan. The average short-beam shear strengths were 87.2 MPa at room temperature and 38.1 MPa at 316°C. The average flex strengths were 1,069 MPa at room temperature and 612 MPa at 316°C. The results are summarized in table 9.

Because of the poor results obtained with laminates 2675-51, we devised a second cure schedule to improve solvent removal and compaction. Prepreg was made using NR150B2G 52-3 according to the procedures already discussed. It was dried 25 min at 177°C to give the desired volatile content. The $[0°]_{10}$, 21.6 by 19.0 cm layup was cured as follows:

1. Apply full vacuum and 2.1 MPa
2. Heat to 199°C, hold 1 hr
3. Heat to 249°C, hold 1 hr
4. Heat to 399°C, hold 1 hr
5. Heat to 427°C, hold 1 hr*
6. Cool slowly under contact pressure

Using this cure schedule, there was more flow from the ends of the laminate (none into the bleeder). The laminate had a smooth, even appearance and a calculated resin content of 31%; the laminate lost 31% volatiles during cure. The C-scan was poor; approximately one-third of the laminate was light gray and the rest was black. Evaluation of this laminate was discontinued when it cracked during handling.

Various problems continued to manifest themselves as we attempted to scale up the laminate size. Localized blistering and delamination were usually found and we were unsuccessful in fabricating high quality $[0°]_{10}$, 19 by 20 cm laminates from the various NR150B2G batches. Although sound areas of individual laminates gave high properties, flaws were always found.

We tentatively attributed most of our problems to solvent removal. Once a dense, low void surface is found, it becomes very difficult to get additional volatiles out of the center of the laminate. Small laminates facilitate solvent removal and avoid the problem, but larger laminates exhibit localized delamination and voids. If solvent is not removed, plasticization is observed; plasticization results in poor performance at elevated temperatures.

NR150B2S6X Processing

We were aware of the potential problems of NR150B2G at the start of the program, and so had carried along a sample of NR150B2GS6X in our evaluations. This is the designation of NR150B2 solids dissolved in pure diglyme [bis(2-methoxyethyl)ether] solvent.

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*This hold was added because General Dynamics (ref. 3) found that more time at higher temperature improved the mechanical properties.

The diglyme proved far easier to remove during cure than did NMP. We readily fabricated a small laminate that had adequate resin temperature properties but excessive (49%) resin solids content. We scaled up to a 19 by 20 cm laminate, making sure we reduced the resin content.

Prepreg was made using the same conditions as those developed previously except that a 1.4 mm orifice was used instead of the 1.6 mm orifice so as to decrease the resin content.

The prepreg was dried 60 min at 121°C, and a $[0°]_{10}$, 19 by 20 cm layup was made and cured using the standard NR150B2G schedule:

1. Apply full vacuum to be held until cool-down
2. Heat to 199°C under vacuum only, hold 60 min at 199°C
3. Apply 2.07 MPa, heat to 249°C, hold 60 min at 249°C
4. Heat to 352°C, release pressure at 352°C, heat under vacuum only to 399°C
5. Apply 2.07 MPa at 399°C, heat to 427°C, hold 1 hr under pressure and vacuum
6. Release pressure, cool slowly under contact pressure, releasing vacuum below 343°C.

The resulting laminate had a smooth, even surface and a nearly clear C-scan. The resin content was 39.5%, the density was 1.62 g/cm^3, the average room temperature (RT) short-beam shear strength was 91.0 MPa, and the average room temperature flex strength was 1,200 MPa. Elevated-temperature (316°C) short-beam shear and flex strengths were 39.1 MPa and 600 MPa, respectively. A TMA of this laminate indicated expansion beginning at 360°C and a T_g at 385°C. The results are summarized in table 10 and compared with contract goals. A 15.2 by 15.9 cm piece of the laminate was shipped to Langley Research Center.

Because the NR150B2GS6X proved easy to process and reliable, it was chosen for the hybrid application.

LARC 160A3 Processing

We had expected the development and scale-up of LARC 160A3 to proceed with far less difficulty than we found with NR150B2. Unfortunately, this did not prove to be the case.

Table 10. - SUMMARY OF EVALUATION OF NR150B2S6X LAMINATE

Property	Contract goal	Actual
Fiber volume, %	-	55.0
Resin content, %	-	39.5
Specific gravity	-	1.62
Bleed (based on laminate weight), %		0.2
T_g (TMA), °C	340	385
Average short-beam shear strength, RT, MPa	52.2	91.0
Average 316°C short-beam strength, MPa	-	39.1
Average flexure strength (normalized to 60% fiber volume), RT, MPa	1241	1300
Average 316°C flexure strength, MPa	-	660
Calculated void content, %	<4.0	0.4

As with NR150B2, high-quality small laminates (normally 10 cm square) were readily fabricated. Dielectric monitoring was used in all cures. A typical cure schedule for successful small laminates follows:

1. Apply partial vacuum only (5 cm Hg)
2. Heat 2-3°C/min to 163°C
3. Hold 2 hr
4. Heat to 260°C
5. Apply full vacuum and 1.4 MPa
6. Heat to 274°C
7. Hold 1 hr
8. Heat to 316°C
9. Hold 4 hr

The properties of laminate made from LARC 160A3 are summarized in table 11.

We again attempted to scale-up the process but, as was the case with NR150, there were difficulties.

Prepreg was made according to the parameters established earlier. With this prepreg, a $[0°]_{14}$, 19 by 21 cm layup was made and cured using the standard LARC 160 cure schedule.

The resulting laminate had a calculated resin content of 35% and a density of 1.58 g/cm^3. It was 2.3 to 2.7 mm thick and had a lengthwise crack about 8 cm from one edge. The laminate lost 12.9% in volatiles, and there was 21.7% flow. A C-scan indicated that most of the panel was light gray except in the region of the crack, which was dark. The average room temperature short-beam shear strength was 92.9 MPa, and the average flex strength was 1,300 MPa. Average 288°C short-beam shear and flex strength values were 38.5 MPa and 641 MPa, respectively.

To help determine the cause of the crack in the laminate, we mounted, polished, and examined a piece of the laminate under a light microscope. The examination revealed large voids.

We then made a series of three panels of LARC 160A3, each with an adjustment to the processing schedule. Dielectric monitoring was used on all three laminates. The cure cycles and the characterization of the resulting laminates are given in table 12.

Table 11. - PROPERTIES OF LARC 160A3 LAMINATES

Property	Batch No.-Laminate No.			
	1 2675-36	2 2675-41	3 2675-44	1[a] 2675-56
Resin solids content, %	26.6	22.0	24.6	35.0
Density, g/cm^3	1.58	1.55	1.61	1.58
Average short-beam strength, RT, MPa	81.2	75.8	79.3	92.9
Prepreg volatile content, %	0.9	13.76	12.3	12.9
Percent of flow	11.2	25.9	27.1	21.7
Average flexure strength, RT, MPa	-	-	-	1338
Average 288°C short-beam shear strength, MPa	38.3	48.8	42.4	38.5
Average 288°C flexure strength, MPa	-	-	-	641

[a] A larger laminate based on 2675-36

Table 12. - SUMMARY OF THREE PROCESS VARIATIONS OF LARC 160A3

Property	LARC 160A3 laminates			
	2675-68	2675-72	2675-76	2675-79
Lay up	$[0°]_{10}$, 19 x 20 cm	$[0°]_{12}$, 19 x 20 cm	$[0°]_{12}$, 9.5 x 5 cm	$[0°]_{12}$, 19 x 21 cm
Variation on standard LARC 160 curve	Add 30 min at 260°C with full vacuum, 1.4 MPa[a]	Eliminated hold at 274°C	Held 1 hr at 163°C full vacuum, 1.4 MPa, heated to 316°C, held 4 hr	Same as 2675-76
Appearance	Three lengthwise cracks	Several cracks starting	Good	Good
Volatiles, %	14.0	13.0	9.8	12.4
Percent flow	20.3	23.1	29.4	39.5
Resin content, %	31.8	35.5	Calculated: 26.6	33.5
Density, g/cm^3	1.625	1.55	-	1.42 + 1.56
C-scan	Gray	Gray, two dark spots	Light gray	Light gray, one dark spot
Short-beam shear strength, RT, MPa	89.5	94.4	84.8	69.6
Flexure strength, MPa	1,441	1,241	1,372	1,193
288°C short-beam shear strength, MPa	39.4	39.3	35.1	38.5
288°C flexure strength, MPa	903	798	763	641

[a] An attempt to repeat an experimental malfunction at Rockwell International that improved mechanical properties.

It is apparent that the processing for LARC 160A3 would require additional development beyond the scope of the project. We therefore, decided to continue the project by evaluating LARC 160 as the other matrix resin.

LARC 160 Process Development

A batch of LARC 160 was synthesized (ref. 3) and prepregged onto NR150-sized Celion 6000. Prepregging parameters were similar to those used for LARC 160A3, Batch 1. The only difference was that the pot temperature for LARC 160 was 66°C instead of 52°C. The LARC 160 prepreg had more drape and tack than the LARC 160A3 prepreg.

A preliminary, $[0°]_{12}$, 4 by 8 cm layup was made from the LARC 160 prepreg and cured according to the standard LARC 160 cure schedule. The resulting laminate (2675-83) exhibited excessive flow during cure. Its calculated resin content was only 15%. It had a density of 1.51 g/cm^3 and an average short-beam shear strength of 57.6 MPa (see table 13).

We then fabricated a second LARC 160 laminate (2675-85). To reduce the flow, we first dried the prepreg 20 min at 60°C; this procedure also reduced the drape and tack of the prepreg. This $[0°]_{12}$, 4 by 8 cm laminate was laid up and cured according to the standard LARC cure schedule. The resulting laminate had a resin content of 21%, a density of 1.59 g/cm^3, an average short-beam shear strength of 96.5 MPa, and an average flex strength of 1,476 MPa (see table 13).

A third LARC 160 laminate was fabricated using the same conditions as for laminate 2675-85. The prepreg was dried 20 min, laid up with a $[0°]_{12}$, 19 by 20 cm laminate, and cured using the standard LARC 160 cure schedule. This laminate had a resin content of 24.4%, a density of 1.61 g/cm^3, a T_g of 340°C, and a nearly clear C-scan. It had an average ambient short-beam shear strength of 104.5 MPa and an average ambient flexure strength of 1,482 MPa. Testing at 316°C gave an average short-beam shear strength of 50.5 MPa and an average flex strength of 938 MPa (see table 13).

Table 13. - DATA SUMMARY OF LARC 160 LAMINATES

Property	LARC 160 laminate		
	2675-83	2675-85[a]	2675-87[a]
Layup	$[0°]_{12}$, 4 x 8 cm	$[0°]_{12}$, 4 x 8 cm	$[0°]_{12}$, 19 x 20 cm
Volatiles	18	12.5	12.7
Bleed	22	22.5	-
Density, g/cm^3	1.51	1.59	1.61
Resin content, %	15[b]	21	24.4
T_g, °C	-	-	340
C-scan	Nearly clear	Nearly clear[c]	Nearly clear
Short-beam shear strength, RT, MPa	57.6	96.5	104.5
316°C short-beam shear strength, MPa	-	-	50.5
Flexure strength, RT, MPa	-	1476	1482
316°C flexure strength, MPa	-	-	938

[a] Prepreg dried 20 min at 60°C before curing.

[b] Calculated resin content.

[c] Optical examination of a polished sample indicated that the laminate contained scattered small voids.

Since LARC 160 proved readily processable, we selected it as the other resin form for hybrid development. Table 14 summarizes LARC 160 properties and compares them with contract goals.

HYBRID COMPOSITE DEVELOPMENT

Clad Hybrid

An initial 4 by 10 cm, $[0°]_{12}$ hybrid laminate was fabricated. It had six-ply core of LARC 160 clad with three plies of NR150B2S6X on each side. The LARC 160 prepreg was dried 20 min at 60°C and the NR150B2S6X prepreg was dried 60 min at 121°C. The six LARC 160 plies were laid up, wrapped in Armalon, and vacuum-bagged as follows:

Kapton bag
1 ply 181 glass
Top caul
2 plies 181 glass
Armalon
Armalon-wrapped layup and shims
Armalon
2 plies 181 glass
Base caul

Full vacuum was applied to the assembly; however, shims were used to prevent the application of pressure to the LARC 160 layup. The assembly was heated to 163°C (2°C-3°C/min), held 2 hr, and cooled. The LARC 160 core exhibited no bleed and had a calculated resin content of 48%.

Three NR150B2S6X skins were then applied to each side of the LARC 160 core. The hybrid layup was wrapped in Armalon, vacuum-bagged* and cured as follows:

1. Apply full vacuum
2. Heat to 200°C (5°C/min)
3. Hold 1 hr

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*The same vacuum bag assembly was used as the LARC 160 core, except that the shims were removed.

Table 14. - LARC 160 LAMINATE PROPERTIES

Property	Contract goal	Actual
Resin content, %	-	24.4
Specific gravity, %	-	1.61
T_g (TMA), °C	340	345
Average ambient short-beam shear strength, RT, MPa	82.7	104.5
Average 316°C short-beam shear strength, MPa	-	50.5
Average ambient flexural strength, RT, MPa	1,379	1,500
Average 316°C flexural strength, MPa	-	940
Calculated void content, %	<2	<2

4. Apply 2.1 MPa
5. Heat to 260°C
6. Hold 1 hr
7. Heat to 399°C
8. Hold 2 hr
9. Cool slowly under vacuum and pressure.

As the assembly approached 399°C, the vacuum bag began to leak, and the cure was discontinued. The resulting laminate appeared well-compacted. The outer plies of NR150B2S6X did not bleed, but a small amount of LARC 160 flowed from the ends of the laminate. Because of the incomplete cure and the high resin content in the LARC 160 core, evaluation of this laminate was discontinued.

A second 19 by 21 cm, $[0°]_{12}$ hybrid was fabricated using processing similar to that used for the initial hybrid laminate. The LARC 160 prepreg was dried 20 min at 60°C and the NR150B2S6x prepreg was dried 1 hr at 121°C. The $[0°]_6$ LARC 160 core was cured, as before, for 2 hr at 163°C. The thickness of the shims, however, was reduced to induce bleeding, 3.1% in this case. This left the core with a 47% resin content.

Three NR150B2S6X skins were applied to each side of the core. The layup was vacuum-bagged and cured according to the procedure used for the initial hybrid laminate. The resulting laminate appeared well compacted; it had a resin content of 44%, a T_g of 340°C, and a density of 1.52 g/cm^3.

A C-scan of this laminate was dark. Microscopic examination of a polished cross selection revealed very few visible defects at the LARC NR150 interface (fig. 5). There were large cracks throughout the LARC 160 core as well as a few small scattered voids (fig. 6). Average short-beam shear values were 76.9 MPa and 44.0 MPa at room temperature and 316°C, respectively. The flexure strength was 1,160 MPa at room temperature and 620 MPa at 316°C (see table 15). The flexures specimens failed in shear in the LARC 160 core.

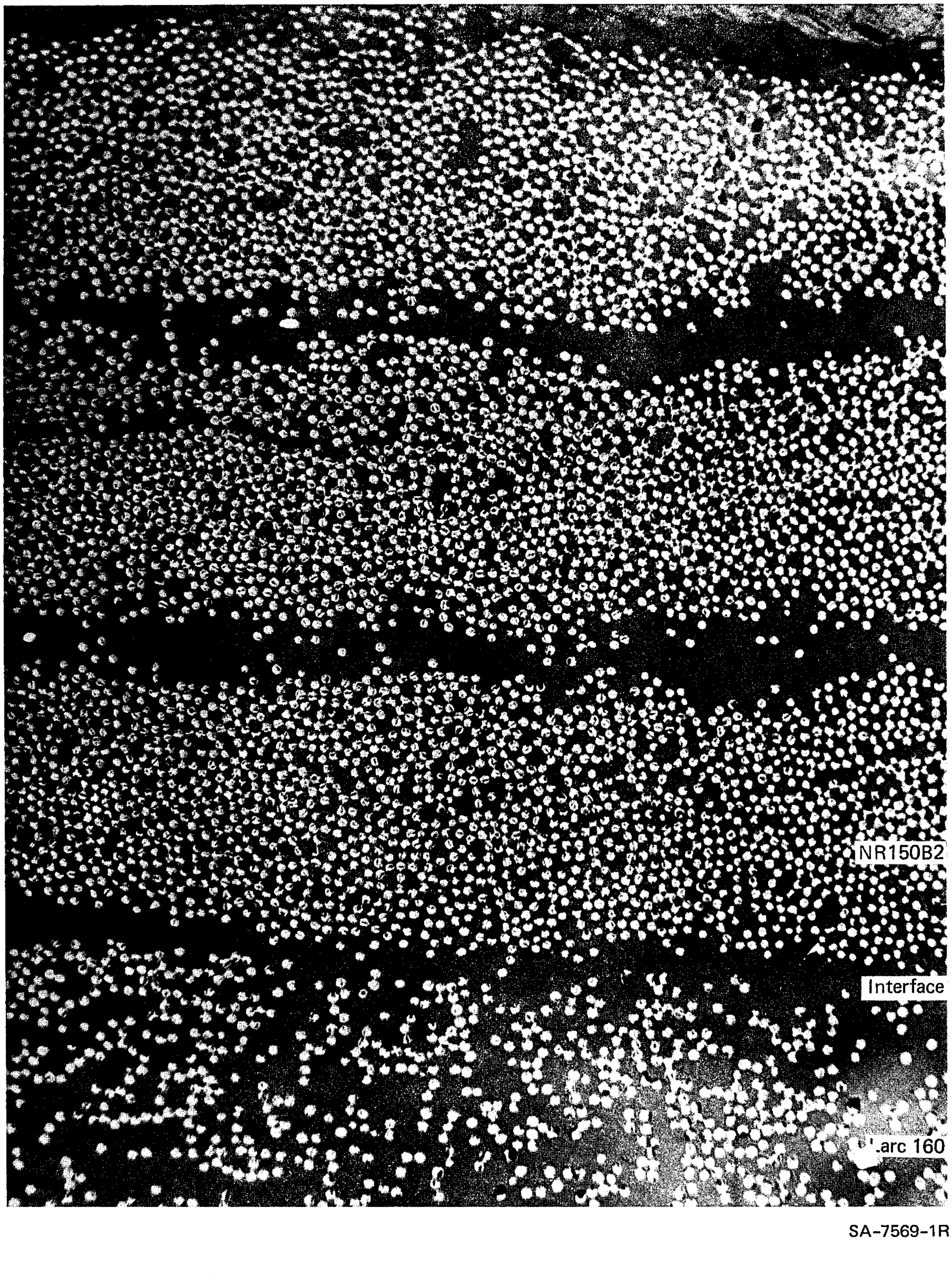

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Figure 5. – LARC-NR150 interface

(Note the high resin content in the LARC ply (bottom) and the continuous interface.)

SA-7569-2

Figure 6. – Cracks in LARC 160 resin rich core.

Table 15. - DATA SUMMARY OF EARLY LARC 160/NR150B2S6X HYBRID LAMINATES

Property	LARC 160/NR150B2S6X Laminate	
	2675-90	2675-93
Layup	$[0°]_{12}$, 19 x 21 cm	$[0°]_{12}$, 19 x 21 cm
Density, g/cm^3	1.52	1.59
Resin content, %	43.7	31.5
T_g, °C	340	354
C-scan	Dark	Dark
Short-beam shear strength, RT, MPa	76.9	78.5
Short-beam shear strength, 316°C, MPa	44	43.3
Flexure strength, RT, MPa	1,158	1,620
Flexure strength, 316°C, MPa	620	820

A third hybrid laminate $[0°]_{12}$, 19 by 21 cm, was fabricated with a reduced resin content in the LARC 160 core. The LARC 160 and NR150B2S6X prepreg were dried as for the other hybrid laminates and eight plies of LARC 160 prepreg were laid up. The layup was wrapped in Armalon and vacuum-bagged as follows:

1. Kapton bag
2. 1 ply 181 glass
3. Top caul
4. Kapton
5. 1 ply 181 glass
6. 1 ply Armalon
7. Armalon wrapped layup
8. 1 ply Armalon
9. 1 ply 181 glass
10. Kapton
11. Base caul

In this third laminate, the amount of bleeder was reduced and the shims were removed. The core was compacted as before:

1. Apply full vacuum (=0.1 MPa)
2. Heat to 163°C (2°C/min)
3. Hold 2 hr
4. Cool

The resin content of the core was reduced to 25%. The core was then clad with two plies of NR150B2S6X prepreg on each side, and the hybrid was cured using the same schedule as used for the first two hybrid laminates.

The resulting laminate had a resin content of 31.5%, a density of 1.59 g/cm^3, a T_g of 354°C, and a dark C-scan. Examination of a polished cross section revealed the presence of a few cracks in the LARC 160 core. The short-beam shear strength of this laminate was 78.5 MPa at room temperature and 43.3 MPa at 316°C. The flexure strength was 1,500 MPa at room temperature and 820 MPa at 316°C.

A fourth hybrid composite, $[0°]_{12}$, 12 by 21 cm, was fabricated. The six-ply, LARC 160 core was laid up, vacuum bagged, and cured by the following procedure:

1. Apply full vacuum (∿0.1 MPa)
2. Heat to 163°C (2°C/min)
3. Hold 2 hr
4. Cool

This cycle resulted in a imidized LARC 160 composite blank with a resin content of 24%.

The blank was then clad with three plies of NR150B2S6X prepreg on each side. The layup was vacuum bagged as follows:

Kapton bag
1 ply 181 glass
Top caul
2 plies 181 glass
1 ply Armalon
Layup
1 ply Armalon
2 plies 181 glass
Base caul

The laminate was then cured according to the same schedule used for the previous three hybrids. On reaching 399°C, the vacuum bag began to leak, which reduced the vacuum about 20% for the remainder of the cure.

The resulting laminate appeared well consolidated and had a resin content of 34% and a density of 1.62 g/cm^3. The C-scan and the optical microscopy of a cross section showed evidence of a few scattered voids in the NR150 skins (fig. 7). The cracks in the LARC 160 core that we observed in the previous three hybrids were not observed in this panel. The average short-beam shear strength of this laminate at room temperature was 84.1 MPa and the average flexural strength was 1,370 MPa.

Two additional $[0°]_{12}$, 19 by 21 cm hybrid laminates were fabricated under the same conditions as those used on the fourth hybrid laminate. Precautions were taken to ensure full vacuum throughout the cure.

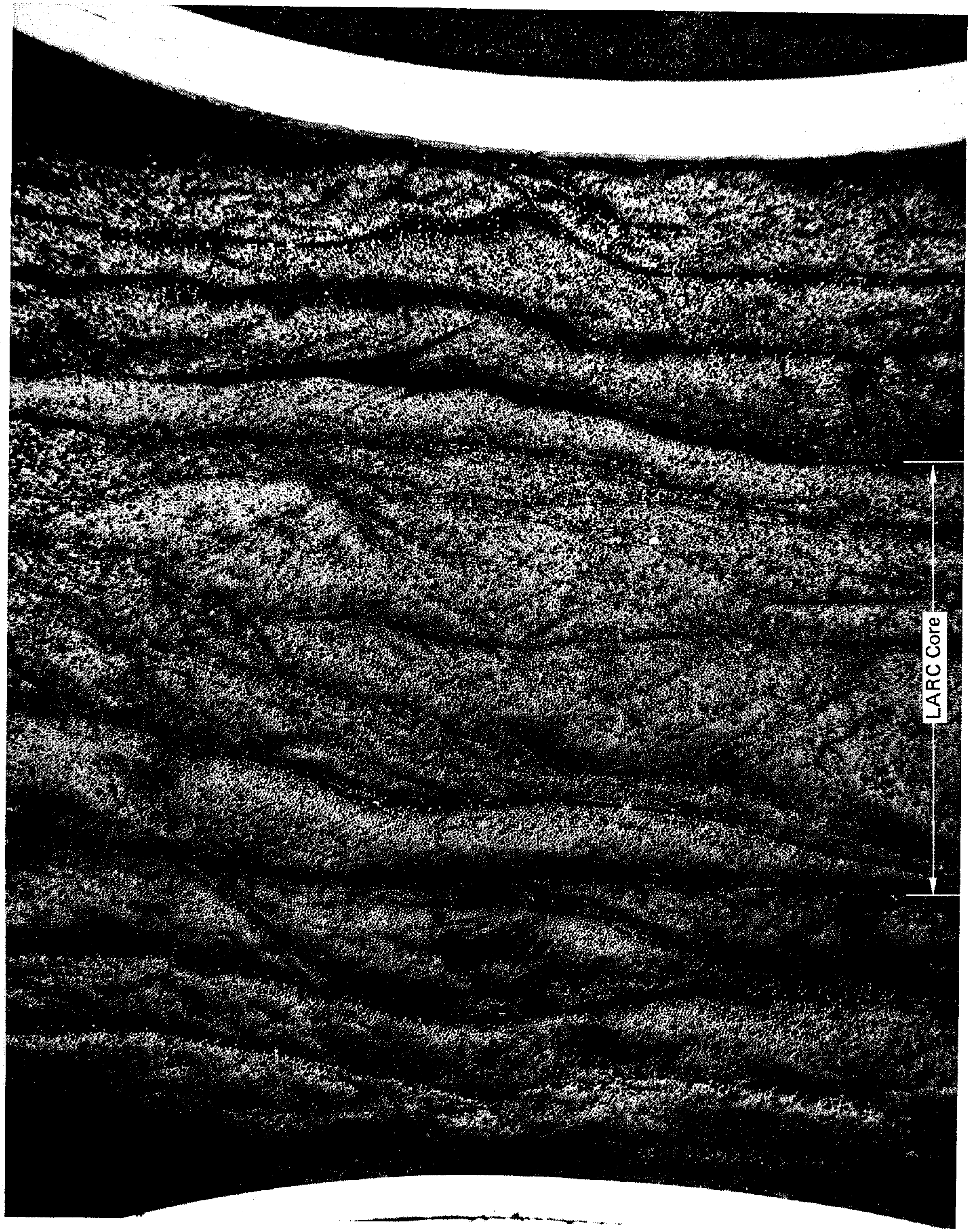

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Figure 7. – Fourth hybrid laminate.
(Note scattered voids in the skin and absence of cracks in the LARC core.)

The fifth hybrid composite had a resin content of 35%, a density of 1.61 g/cm^3, an average room temperature short-beam shear strength of 72.2 MPa, and an average room temperature flexural strength of 1,100 MPa.

The sixth hybrid composite had a resin content of 36%, a density of 1.60 g/cm^3, an average room temperature short-beam shear strength of 82.7 MPa, and an average room temperature flexural strength of 1,550 MPa.

The optical microscopy of polished sections and C-scans of these laminates were similar to each other and to that of the fourth hybrid composite.

A 15 by 15 cm section of the sixth hybrid composite was delivered to Langley Research Center. The fourth and fifth laminates were machined into additional short-beam shear and flexure specimens for thermal-oxidative aging. They were aged at 316°C in air for 0, 125, 250, and 500 hr. Specimens lost 0.45% of their weight after 125 hr at 316°C, 0.57% after 250 hr, and 1.05% after 500 hr.

Broken specimens of aged and unaged samples were viewed with a scanning electron microscope (SEM). There were areas on either side of the specimens where very few broken fibers protruded from the matrix resin. In between these two areas were found numerous fibers with little or no resin adhering to their surface. The boundary between the different areas was abrupt. There was no visible difference between aged and unaged samples. Figures 8 and 9 show these specimens.

The aged specimens were then tested at room temperature and 316°C. The results are given in table 16.

Interleaved Hybrid

Additional prepreg was made from both LARC 160 and NR150B2S6X. The LARC 160 prepreg was dried 20 min at 60°C and the NR150 prepreg for 1 hr at 121°C.

SA-7569-4

Figure 8. – SEM of failed specimen, 100X.
(Note the area of clean fibers in the lower picture.)

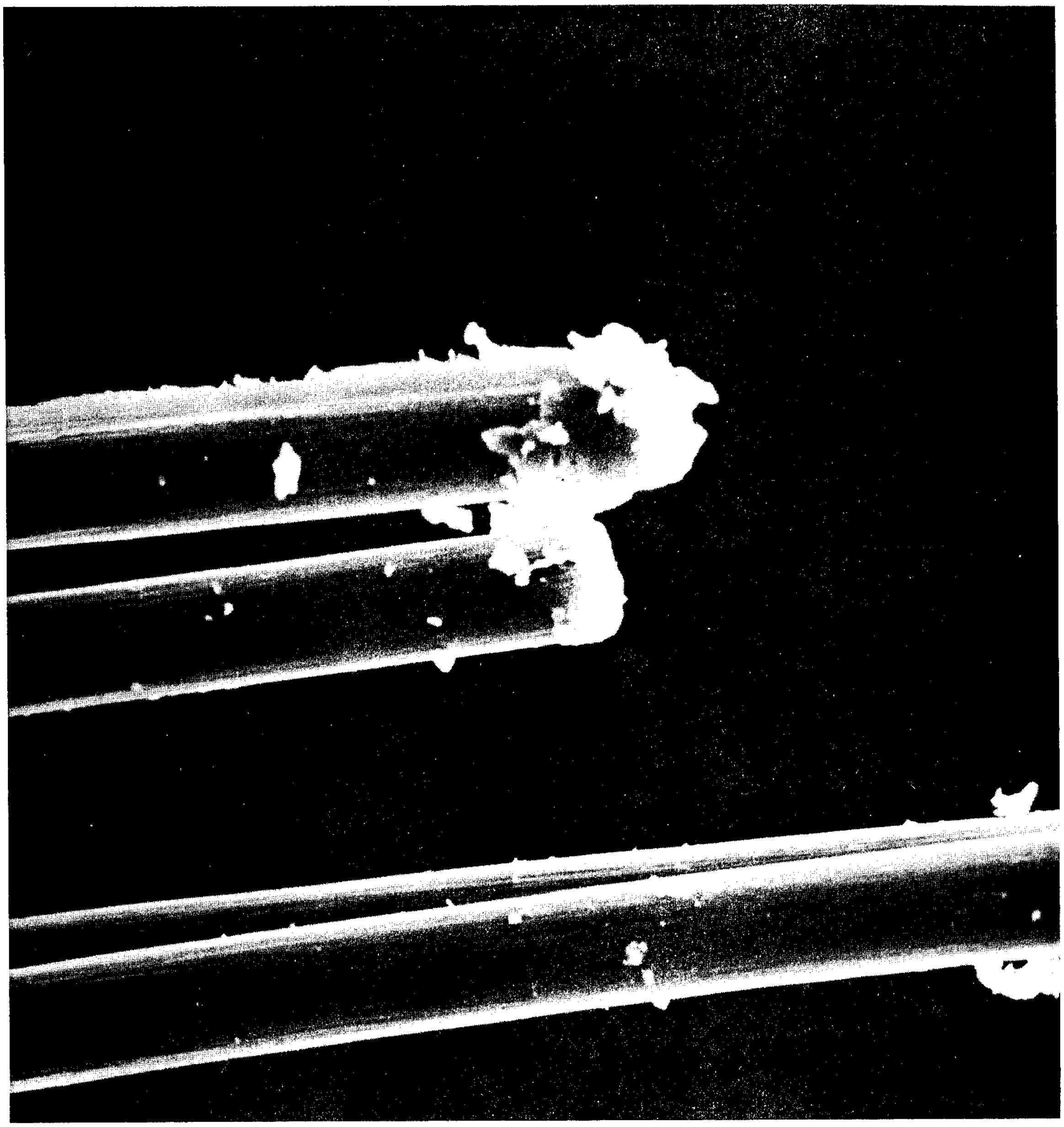

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Figure 9. – SEM of resin-poor fibers area, 1000X. (Very little resin adheres to the fiber.)

Table 16. - MECHANICAL PROPERTIES OF NR150-CLAD LARC 160 HYBRID LAMINATES (3-6-3) AFTER AGING

Thermal-oxidative aging at 316°C, hr	Mechanical Property							
	Short-beam Shear Strength[a]				Flexural strength[a]			
	RT, MPa	Retention, %	316°C, MPa	Retention, %	RT, Mpa	Retention, %	316°C, MPa	Retention, %
0	80.7	100	37.2	100	1317	100	671	100
125	76.3	95	46	124	1510	115	876	131
250	76.3	95	47.2	127	1538	117	889	132
500	60.3	75	45.8	123	1462	111	883	132

[a] Results shown are averages of five specimens taken from laminates 4, 5, and 6.

Six 19 by 21 cm plies of LARC 160 prepreg were imidized using the following schedule (Cycle 1):

1. Apply full vacuum and contact pressure
2. Heat to 163°C (2°C/min)
3. Hold 2 hr
4. Cool

This schedule produced six separate plies with resin contents of 24% to 26%.

The LARC 160 plies were interleaved with six plies of staged NR150B2S6X to produce a layup in the following configuration:

$$[\text{NR150, LARC 160, NR150, LARC 160 NRL50, LARC 160}]_s$$

The laminate was then vacuum-bagged and cured according to the schedule used for prior hybrids.

The resulting laminate had a resin content of 32 wt%, a density of 1.53 g/cm^3, an average room temperature short-beam shear strength of 66.2 MPa, and an average room temperature flex strength of 1,248 MPa. The plies appeared to fail sequentially; the laminate did not fail as a unit in testing.

A C-scan of this laminate showed half of the laminate to be completely dark and the other half to be mottled. A microscopic examination of the polished section showed numerous voids in the center NR150 layers; these voids are probably responsible for the C-scan results.

Nor further exploration was made into this type of hybrid.

NR150-Coated LARC 160 Hybrid

Additional LARC 160 prepreg was made and dried 20 min at 60°C. A $[0°]_{12}$, 19 by 21 cm, LARC 160 layup was made and imidized according to the following cycle (Cycle 1):

1. Apply full vacuum (0.1 MPa)
2. Heat to 163°C (2°C/min)
3. Hold 2 hr
4. Cool

This produced a LARC 160 core with 26% resin.

The LARC core was then painted with NR150B2S6X solution until both sides were completely coated, and the hybrid was dried 1 hr at 121°C.

The laminates were then vacuum-bagged and cured according to the following schedule (Cycle 2):

1. Apply full vacuum
2. Heat to 199°C (2-3°C/min)
3. Hold 1 hr
4. Apply 2.07 MPa
5. Heat to 260°C (2-3°C/min)
6. HOld 1 hr
7. Heat to 316°C (2-3°C/min)
8. Hold 4 hr
9. Cool slowly under vacuum and pressure

Short-beam shear and flex specimens were machined from this laminate for testing at room and elevated temperature. The remainder of the laminate was aged for 250 hr at 316°C in air, which resulted in a weight loss of 1.2%. Test specimens were again machined from the laminate. The remainder of the laminate was aged an additional 250 hr (total 500 hr) at 316°C. After 500 hr, the laminate had lost a total of 2.0% of its weight. Test specimens were machined from the remainder of the laminate. Short-beam shear and flexural strengths are given in table 17.

The resulting laminate had a resin content of 31 wt%, a density of 1.60 g/cm^3, and a uniform light-grey C-scan. Microscopic examination of a polished cross section showed only a few scattered voids. The interface of the two resins was discernible at magnifications of 200 and 500 (see figs. 10, 11).

Table 17. - MECHANICAL PROPERTIES OF NR150-COATED LARC 160 LAMINATE AFTER AGING

Thermal-oxidative aging at 316°C, hr	Mechanical Property							
	Short-beam shear strength				Flexural strength			
	RT, MPa	Retention, %	316°C, MPa	Retention, %	RT, MPa	Retention, %	316°C, MPa	Retention, %
0	98.9	100	40	100	1277	100	745	100
250	100	101	45.5	136	1482	116	1020	137
500	82.7	84	52.7	132	1524	119	1014	136

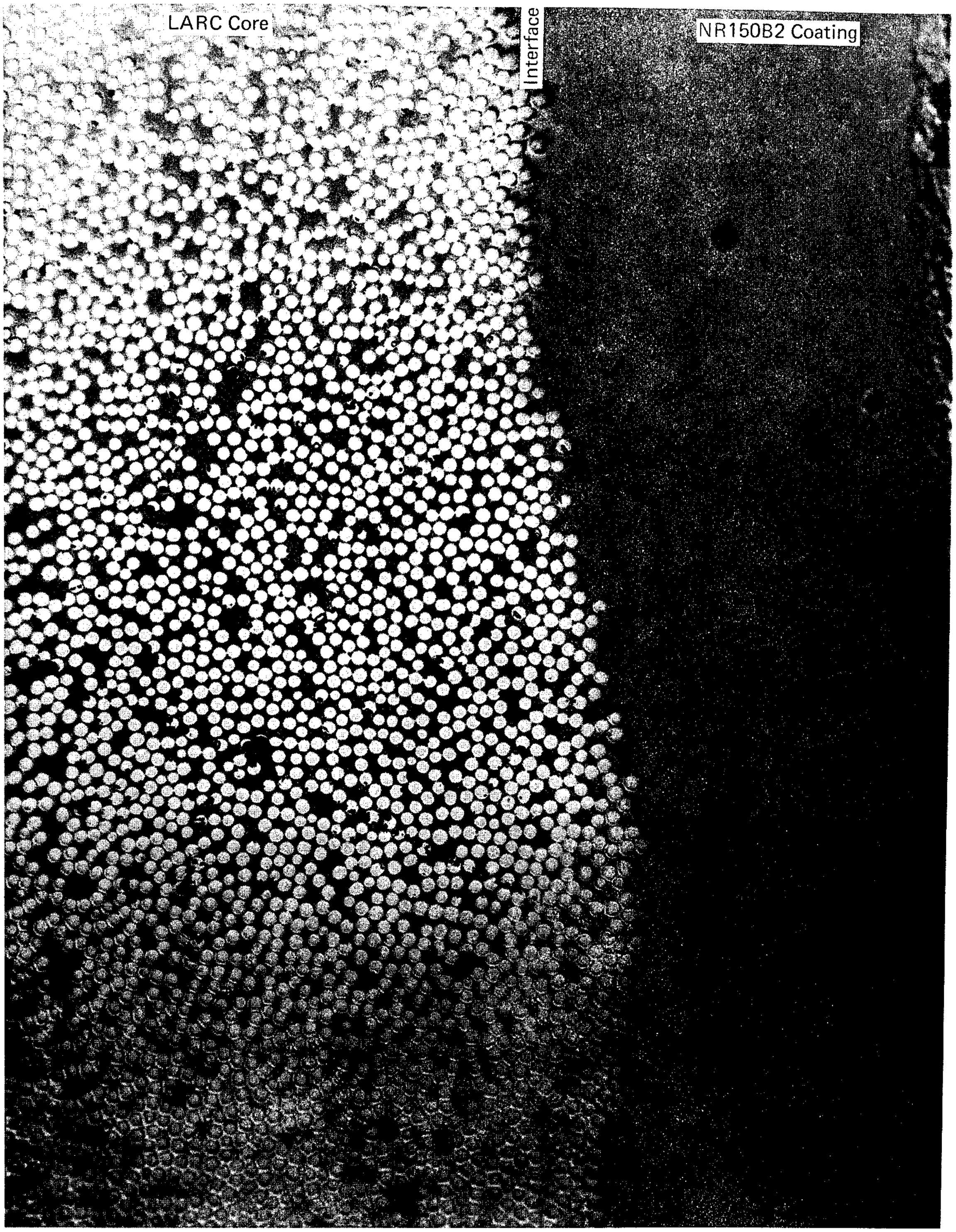

Figure 10. — Interface, 200X.

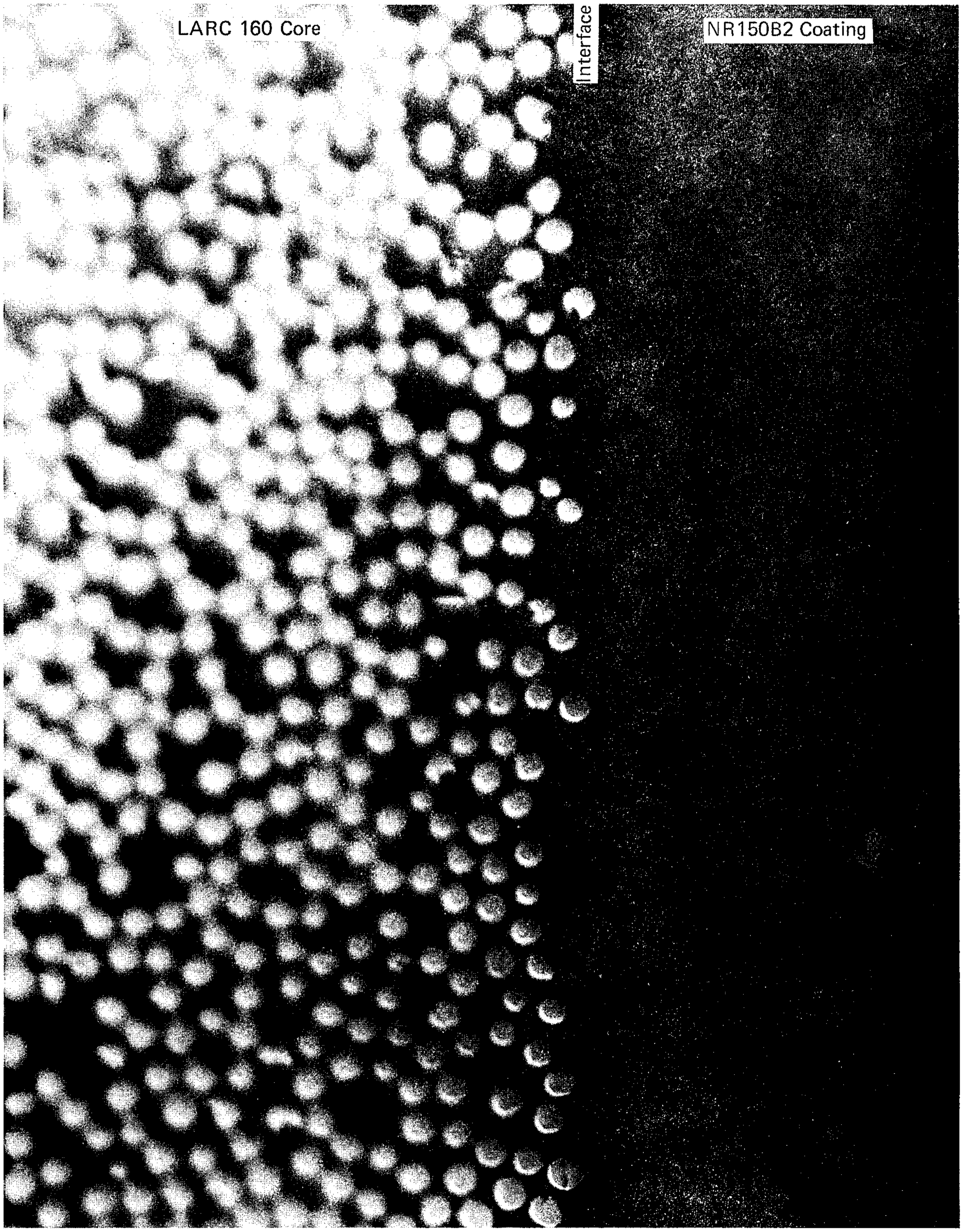

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Figure 11. – Interface, 500X.

LARC 160 Clad with NR150 Supported on Glass Surfacing Veil

Unidirectional Celion-reinforced LARC 160 prepreg was made and dried 20 min at 60°C. Glass surfacing veil (random E-glass fiber mat) was impregnated with NR150B2G and dried 24 min at 177°C.

A 19 by 21 cm, $[0°]_{12}$, LARC layup was made and imidized using cycle 1, as described earlier. A ply of the NR150/glass prepreg was applied to each side of the layup and cured according to Cycle 2, as described earlier.

The resulting laminate had a resin content of 43.2%, a density of 1.56 g/cm^3, and a uniform, clear C-scan. The clear C-scan was confirmed by a microscopic examination of a polished cross section. The laminate was void-free and well consolidated. The LARC-NR150B2G interface was barely discernible at magnifications of 200 and 500 (figs. 12, 13).

A portion of the laminate was machined into short-beam shear and flex specimens. The balance was aged 250 hr at 316°C and then additional test specimens were machined from it. Specimens were tested at room and elevated temperature. The results are shown in table 18.

Two final coated panels were fabricated, evaluated, and sent to Langley Research Center. LARC 160 prepreg was prepared and dried 20 min at 60°C. Two laminates, a $[0°]_{15}$ and a $[0°, \pm 60°]_{2s}$ laminate, each 19 by 19 cm, were laid up, imidized with cure Cycle 1 and cured by Cycle 2.

The panels were C-scanned. Short-beam shear and flex specimens were machined from the laminates; the remaining 15 by 15 cm sections from each laminate were labeled and sent to Langley Research Center. Flex and short-beam shear tests were run at room temperature. Specific gravity and resin content determinations were also made; they are summarized in table 19.

Both laminates were uniformly grey (darker at higher sensitivities) on the C-scan, except that 3020-44 had one small black spot in the central area.

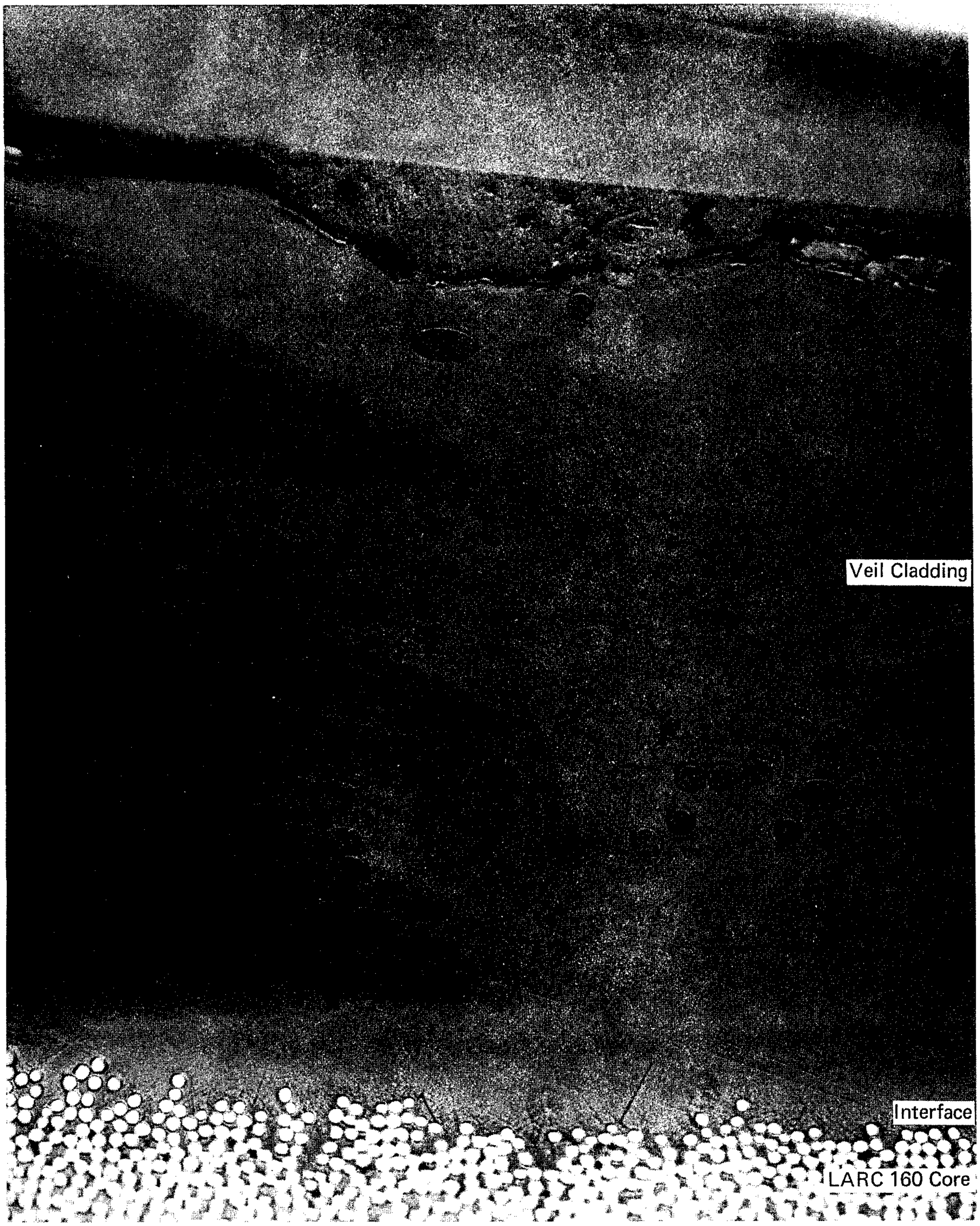

Figure 12. – Veil-clad interface, 200X.

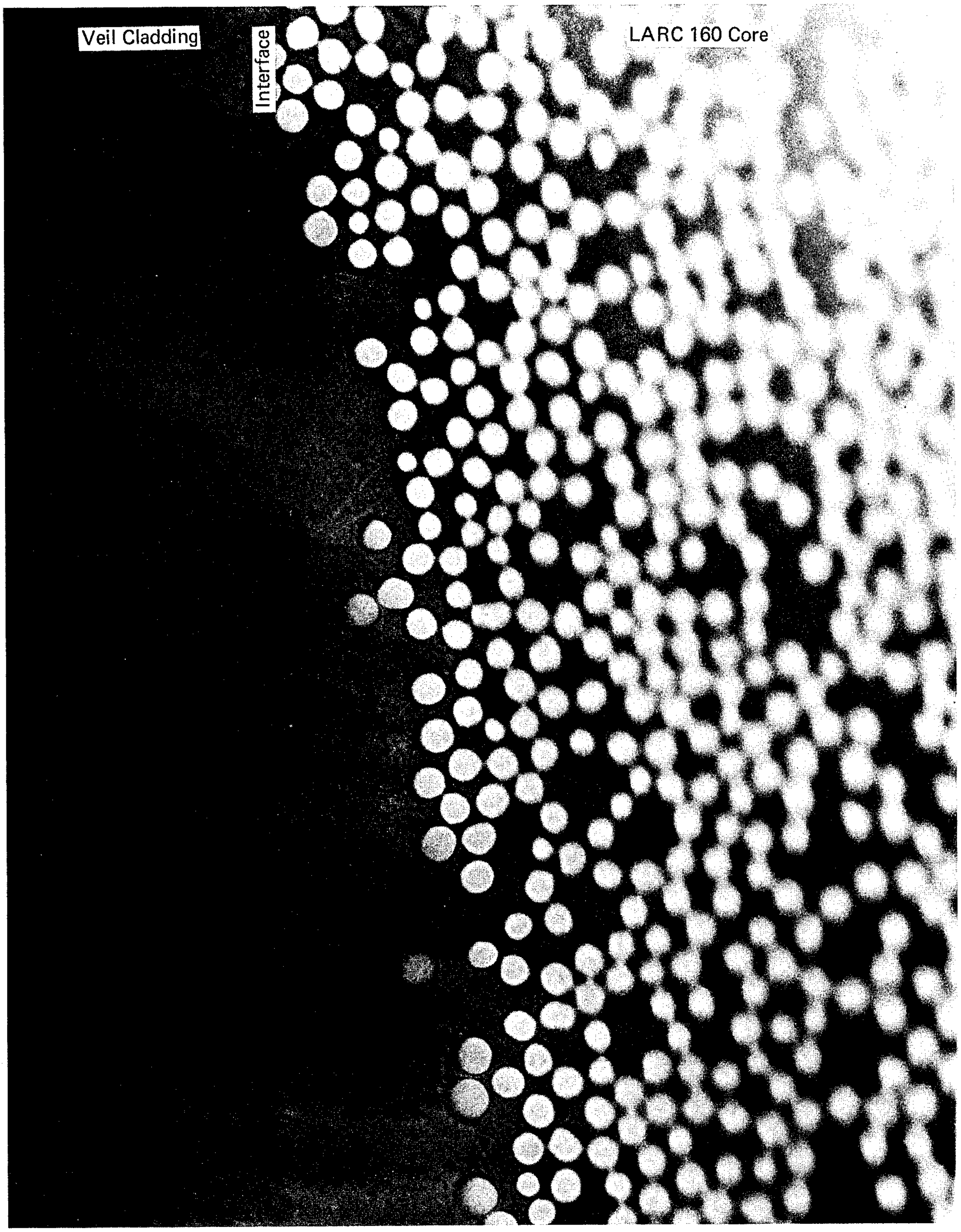

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Figure 13. — Veil-clad interface, 500X.

Table 18.- MECHANICAL PROPERTIES OF AN NR150B2G/ RANDOM-GLASS-MAT CLAD LARC 160 HYBRID LAMINATE AFTER AGING

Thermal-oxidative aging at 316°C, hr	Mechanical Property							
	Short-beam shear strength				Flexural strength			
	RT, MPa	Retention, %	316°C, MPa	Retention, %	RT, MPa	Retention, %	316°C, MPa	Retention, %
0	93.1	100	33	100	845	100	580	100
250	87.6	94	43.1	131	1069	127	834	144

Table 19. - SUMMARY OF NR150B2S6X-COATED LARC 160 LAMINATES

Property	Laminate number	
	3020-44	3020-48
Layup	$[0°, \pm 60°]_{2s}$	$[0°]_{15}$
Resin content, %	32	38
Specific gravity	1.60	1.57
Short-beam shear strength,[a] RT, MPa	42.7	97.0
Flexural strength[b], RT, MPa	855	1,470

[a] Average of five specimens.

[b] Average of four specimens.

CONCLUSIONS AND RECOMMENDATIONS

[Several important results were obtained and conclusions reached during the course of this work.

~~Lon substitute~~ An ~~improved~~ modified NR150B2

~~1.~~ ~~NR150B2GS6X~~ was clearly the best form of NR150B2 for the fabrication of both single resin and hybrid resin panels. The highest T_g values and elevated temperature mechanical properties reported to date with NR150B2 were achieved] during the course of this work.

2. LARC 160 proved superior to LARC 160A3 in scale-up work. More process development work is needed for the A3 version.

3. Quality control techniques need improvement. State-of-the-art procedures do not correlate well with observed processing characteristics and are inadequate for satisfactory material or process control. Some potentially promising QC techniques require more development.

4. The hybrid matrix concept was shown to be feasible. NR150B2 and LARC 160 resins are compatible; NR150B2 surface plies provides good oxidative protection for LARC 160 core areas.

5. Co-cure schedules were successfully developed for the hybrid system, and high-quality hybrid laminates were readily fabricated.

6. A simple protective coat of NR150B2 painted on the surface of an imidized LARC 160 core can be cured by a standard LARC 160 cure schedule and provides excellent protection for 500 hr at 316°C. This simple system and moderate cure schedule meets all performance goals and requirements of this project and may be used to significantly improve the air aging characteristics of LARC 160 laminates.]

author modified

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