

# Evaluation of the interfacial bond properties between carbon phenolic and glass phenolic composites

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The effects of moisture and surface finish on the mechanical and physical properties of the interfacial bond between the carbon/phenolic (C/P) and glass/phenolic (G/P) composite materials are presented in this paper. Four flat panel laminates were fabricated using the C/P and G/P materials. Of the four laminates, one panel was fabricated in which the C/P and G/P materials were cured simultaneously. It was identified as the cocure. The remaining laminates were processed with an initial simultaneous cure of the three C/P billets. Two surface finishes, one on each half, were applied to the top surface. Prior to the application and cure of the G/P material to the machined surface of the three C/P panels, each was subjected to specific environmental conditioning. Types of conditioning included: (a) nominal fabrication environment, (b) a prescribed drying cycle, and (c) a total immersion in water at 71 °C. Physical property tests were performed on specimens removed from the C/P materials of each laminate for determination of the specific gravity, residual volatiles and resin content. Comparison of results with Shuttle Solid Rocket Motor (SRM) nozzle material specifications verified that the materials used in fabricating the laminates met acceptance criteria and were representative of SRM nozzle materials. Mechanical property tests were performed at room temperature on specimens removed from the G/P, the C/P and at the interface between the two materials for each laminate. The double-notched shear strength test was used to determine the ultimate interlaminar shear strength. Results indicate no appreciable difference in the C/P material of the four laminates with the exception of the cocure laminate, where a 20% reduction in the strength was observed. The most significant effect occurred in the bondline specimens. The failure mode was shifted from the C/P material to the interface and the ultimate strength was significantly reduced in the wet material. No appreciable variation was noted between the surface finishes in the wet laminate.

## 1. Introduction

The Space Shuttle's Solid Rocket Motor (SRM) nozzle is constructed from carbon/phenolic (C/P) and glass/phenolic (G/P) composite materials. The C/P is used as the outer or ablative material of the nozzle ring and it is backed by a thin G/P insulator. These composite rings are adhesively bonded to a structural metal housing, forming the nozzle. Anomalies in performance of the ablative material during flight and static testing have stimulated research to examine the effects of moisture, cure cycles and surface finish on the integrity of the interfacial bond between G/P and the C/P rings.

It is well recognized and reported that the high-performance composites absorb moisture from their surrounding environments, especially under warm

and humid conditions [1–6]. In epoxy-based composites, absorbed moisture has been shown to affect the matrix and the interface dominated properties of the composite. Degradation is evident in the interlaminar shear strength and ultimate strength specifically, as well as other mechanical properties [1–11]. In contrast to the fairly large literature base for the epoxy-based composites, the phenolic-based composites, have essentially remained unstudied with respect to the effect of moisture.

The objective of this research was to assess the integrity of the interfacial bond between the C/P and the G/P materials as a function of the moisture/volatile content present in the C/P material prior to the bonding of the G/P material. Another variable, the effect of surface finish applied to the bonding surface

of the C/P prior to the bonding of the G/P material, was also investigated.

## 2. Materials

Materials were obtained from the Wasatch Division of Morton Thiokol Incorporated (MTI) for use in nozzle material development research. MTI purchased the materials in the form of 1.22 m width preimpregnated (prepreg) broadgoods from the Fiberite Corporation. The C/P and G/P materials are designated by Fiberite as MX-4926 and MXB-6001, respectively. The constituent materials of the MX-4926 prepreg were Polycarbon CSA, an eight-harness satin rayon-based carbon fabric, Borden's SC1008 phenolic resin system and Fiberite 1148 carbon black filler. The constituent materials of the MXB-6001 were United Merchant 184 weave S-glass fabric and Borden's SC1008 phenolic resin system.

A series of physical property tests were conducted on the prepreg materials to ensure conformity with MTI materials acceptance specifications, STW5-2651F and STW5-3279A for the G/P and C/P materials, respectively [12, 13]. The critical properties measured to assess the quality of the materials were the resin content, filler content, volatile content, resin flow, sodium content and cloth content.

A summary of the prepreg acceptance test results may be found elsewhere [14]. All prepreg physical properties met the acceptance criteria stated in MTI specifications. Based on the compliance of all the prepreg physical properties with the specification limits, the materials were accepted for use in the programme.

Carbon/phenolic and glass/phenolic 25.4 cm (fill) by 30 cm (warp) plies were arranged in stacks which when cured yielded an inch (~ 2.54 cm) thick laminate. The C/P and G/P stacks contained 84 and 40 plies, respectively, with the J-type 30 gauge thermocouples placed at the designated plies to monitor temperatures during debulking and subsequent curing.

The C/P and G/P stacks were individually debulked in a tetrahedron press to 86% of their cured density simulating the nominal debulk obtained during the tape wrapping of the materials during the processing of SRM nozzle components.

## 3. Fabrication of glass/phenolic and carbon/phenolic test articles

### 3.1. Lay-up and cure of carbon/phenolic laminates

Three C/P laminates were assembled using the six debulked stacks CP-1 to CP-6 (Fig. 1) as follows: (a) panel A consisted of stacks CP-1 and CP-2, (b) panel B consisted of stacks CP-3 and CP-4, and (c) panel C consisted of stacks CP-5 and CP-6. The three panels were assembled and bagged on a trilateral cure tool. The hydroclave trilateral tool was designed to simultaneously cure three flat panel laminates with cured thickness of 6.28 cm each. The laminates were cured according to the hydroclave cure cycle designed by MTI [15].

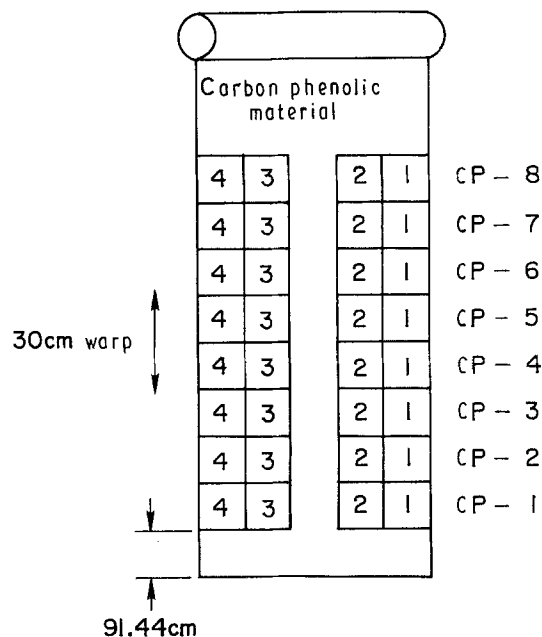


Figure 1 Cutting and stacking plan for carbon/phenolic material (Roll 1B). Procedure: (1) cut 91.44 cm swatches at the beginning and after every 168 plies until 504 plies are cut; (2) cut 504 (25.4 cm by 30 cm (warp) plies of C/P material. Make six stacks (84 plies per stack) by stacking the first four plies, smooth side up, in stack CP-1, the next four in stack CP-2, etc until each stack contains 84 plies.

After the cure, the laminates were nondestructively examined using X-rays to ensure the quality of each. No low-density indications or delaminations were observed in any of the laminates.

### 3.2. Surface preparation

For investigation of the interfacial properties, precise and reproducible duplications of the surface finishes are critical to the creditability and validity of the results. Surface finishes of 0.32 and 0.64  $\mu\text{m}$  were precisely duplicated to match the finishes produced at MTI. The 0.64  $\mu\text{m}$  surface finish (maximum upper limit) is applied by MTI to cured C/P surfaces of SRM nozzle components, prior to over-wrap of the G/P insulator.

### 3.3. Conditioning

The panels were subjected to prescribed environmental conditioning detailed in the following sections.

Panel A (also identified as the as-received panel) was the control. This laminate was fabricated according to nominal processing conditions and environments. In this manner, it represented the typical state of the SRM C/P material prior to the overwrap and curing of the G/P insulator.

Many authors have noted that microcracking was induced in polymeric materials when the material was subjected to extreme thermal gradients. [2, 8, 11, 16]. This damage to the material was irreversible and resulted in degradation of the ultimate interlaminar shear strength and ultimate tensile strength. Such damage can be unintentionally created in materials during conditioning if sufficient precautions are not observed.

In the phenolic-based composites, there are additional concerns relating to potential effects on the

properties by changing the state of cure when these materials are subjected to extreme thermal gradients.

A research programme was initiated at the Southern Research Institute (SRI) [17] to determine an effective and nondamaging drying process for C/P materials, which provided accelerated weight loss without altering the cured state or microcracking in 0.5 in. cube (1.27 cm cube) samples.

Panel B (also identified as the dry panel) was subjected to a modified SRI drying cycle which included corrections for size and shape of the laminates. The drying cycle was designed to yield drying of the bonding surface to a depth of 1.27 cm into the thickness of the laminate. The cycle was as follows: (a) desiccate for 66 days, (b) dry at 38°C and 0.1 torr (1 torr =  $1.333 \times 10^2$  Pa) vacuum for 11 days, (c) dry at 60°C and 0.1 torr vacuum for 6 days, (d) dry at 71°C and 0.1 torr vacuum for 13 days.

Panel C (also identified as the wet panel) was subjected to controlled moisture conditioning. It was originally placed into an environmental chamber maintained at 71°C and 95% relative humidity (r.h.). After 47 days in the chamber, the panel was relocated and submerged in water at 71°C with the machined surface placed upward in a pan. This was done to accelerate the absorption process.

The per cent weight gain versus time data were plotted as shown in Fig. 2. The conditioning resulted in a 0.96% weight gain.

### 3.4. Lay-up and cure of glass/phenolic to carbon/phenolic laminates

Lay-up and cure of the G/P immediately followed the conditioning of the C/P laminates. Prior to the lay-up

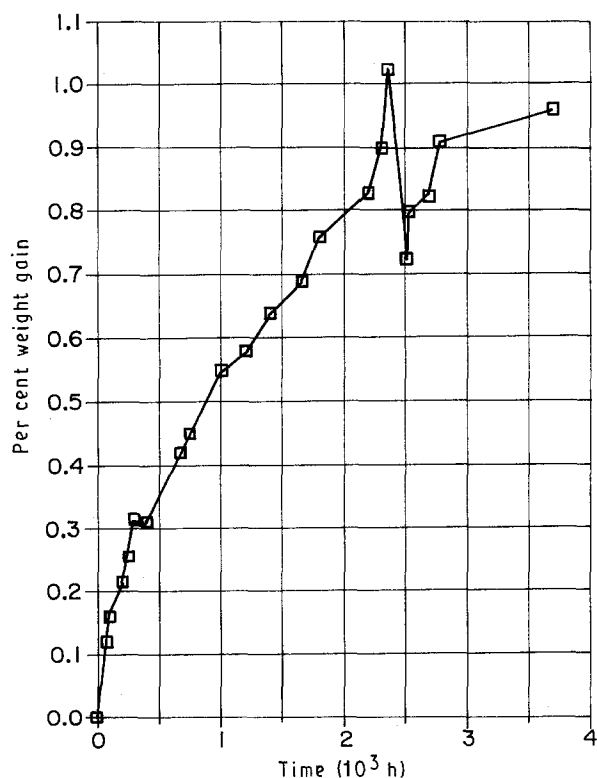


Figure 2 Per cent weight gain for wet panel.

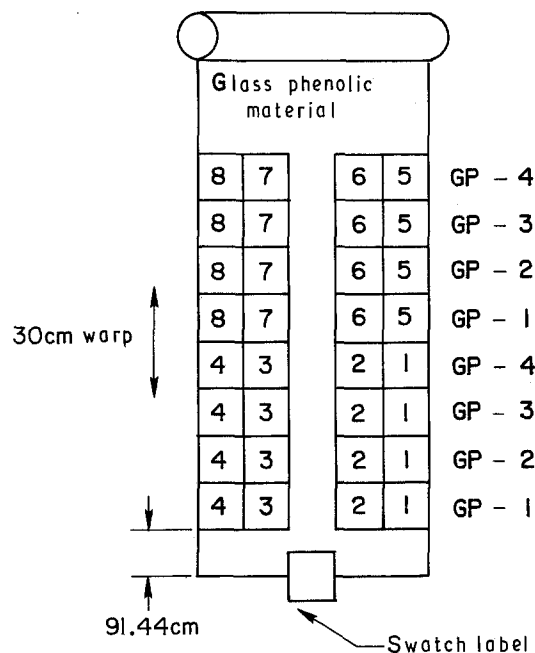


Figure 3 Cutting and stacking plan for glass/phenolic material (Roll 1). Procedure: (1) cut 160 25.4 cm by 30 cm (warp) plies; (2) make four stacks by stacking the first four plies in stack GP-1, the next four in GP-2, etc., until each stack contains 40 plies.

of the G/P debulked stacks, the stacks GP-1 to GP-3 (Fig. 3) were machined to equal the dimensions of their respective C/P laminates. The lay-up and bagging sequences for cure may be found in [14]. The composite laminates were machined and test sections removed.

### 3.5. Lay-up and cure of cocure laminate

A cocure laminate was fabricated using the debulked C/P stacks CP-7 and CP-8 and the debulked G/P stack GP-4. The laminate was assembled and cured according to the autoclave cure cycle presented in [18]. The cured laminate was machined and test sections removed.

## 4. Testing and examination

### 4.1. Physical property tests

A series of physical property tests were conducted on the C/P and G/P materials of each cured laminate to ensure the quality of the materials after curing. The tests were performed according to the procedures contained in the MTI cured material acceptance specification STW5-2845D, which consisted of residual volatile content, specific gravity and resin content [19]. The MTI specifications require that resin content tests be performed using the tested residual volatile specimens. The same test geometry was used for each of the above three tests. The specimen geometry is shown in Fig. 4.

### 4.2. Optical photomicroscopy

Optical photomicroscopy examinations were conducted on specimens taken from the C/P, G/P and at the

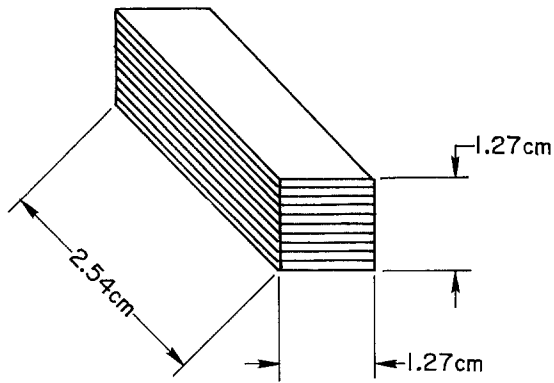


Figure 4 Specimen geometry of specific gravity, residual volatile, and resin content tests.

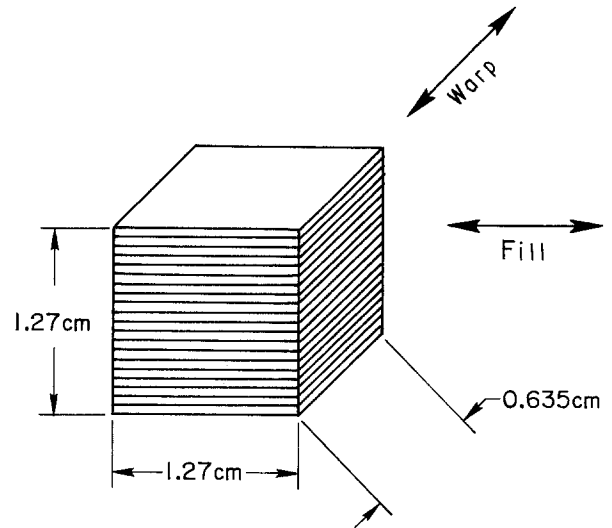


Figure 5 Specimen geometry for photomicroscopy evaluation.

interfaces of each laminate. The objectives were to (a) observe materials for possible microstructural damage, (b) characterize the appearance of the microstructure of the C/P and G/P materials, and (c) characterize the appearance of the different interfaces between the C/P and G/P laminates. A typical final machined specimen is presented in Fig. 5. Prior to the examination, each specimen was mounted in epoxy and then polished. Photomicrographs were taken of each specimen at several magnifications.

#### 4.3. Interlaminar shear strength test

Matrix/interface dominated properties are considered to be among the most critical to SRM nozzles and the critical failure mode for phenolics was determined to be delamination [20]. Observations made in the past after static and flight tests, which support delamination as being the critical failure mode include ply-lift in the virgin C/P material and separation of the insulating (G/P) material from the ablative (C/P) material. The critical properties for prediction of the margin of

safety for delamination at the G/P and C/P interface are interlaminar shear and across-ply tension. In this programme, the property selected for evaluation of surface finish and moisture effects on the interface between the C/P and G/P materials was interlaminar shear strength. A double-notched shear specimen was used for the determination of the ultimate interlaminar shear strength at room (21 °C) for the C/P, G/P and at the interface between these materials.

The basic cutting plans for the specimen removal may be found elsewhere [14]. Specimens were first excised as blanks, then machined to the specified dimensions shown in the schematic presented in Fig. 6. The gauge section was maintained at 1.00 cm (fill) by 0.76 cm (warp) by 1.27 cm (A/P), allowing four plies to be isolated in the gauge section for the C/P specimens and two plies in the gauge section for the G/P specimens. The number of plies isolated in the gauge section was determined by dividing the A/P dimension of

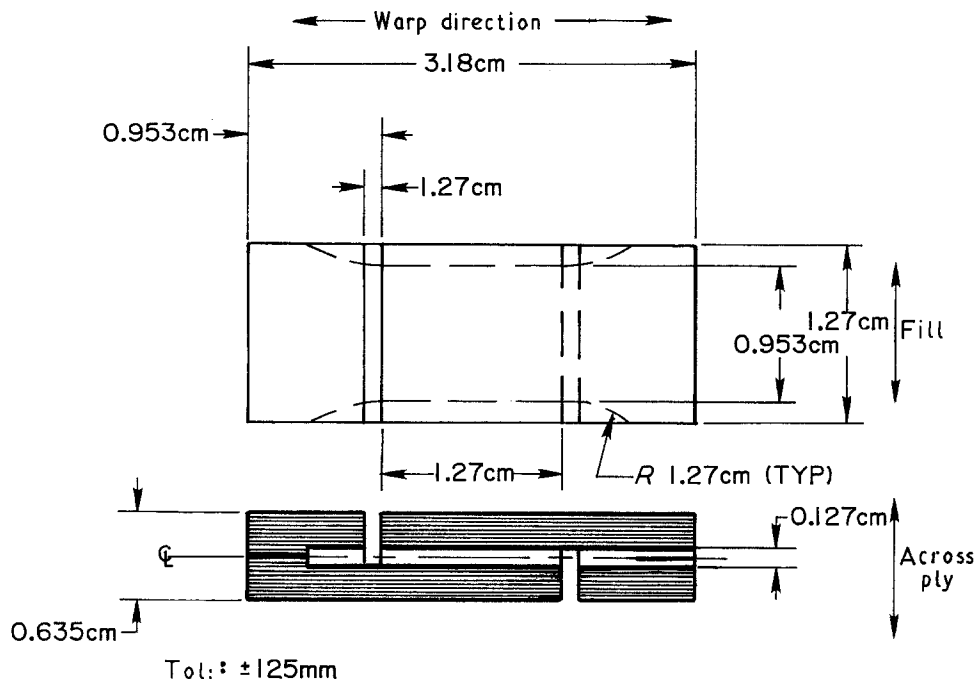


Figure 6 Specimen geometry for DNS test.

the gauge section by the cured ply thickness of each material. For the interface specimens, approximately two plies of C/P and one ply of G/P were isolated in the gauge section with the bondline centered in the gauge section. The specimens were loaded in axial compression to provide pure shear at the gauge section. Each specimen was loaded at a rate of  $4.48 \times 10^3$  N min<sup>-1</sup> [21]. The load versus time plot obtained from the Instron for each specimen was transformed into a stress versus time plot by dividing the load values by the shear (gauge) area. The data obtained from the linear stress versus time plot were used to determine the ultimate interlaminar shear strength.

## 5. Results and discussion

### 5.1. Physical property tests

A summary of the physical property test results is presented in Table I. Based on the compliance of all the physical property tests results with the specification requirements, the C/P and G/P materials of the four laminates were accepted as representative nozzle materials.

### 5.2. Photomicroscopy

Examination of the photomicroscopy specimens at a magnification of 1000 revealed no evidence of microstructural damage such as microcracks, voids or delaminations in any of the materials. The shape of the fibres and presence of fillers in the matrix materials were used in characterizing the appearance of the materials. The C/P fibres exhibited the typical non-uniform crenulated cross-sections, while the G/P fibres exhibited uniform circular cross-sections. The matrix material of the C/P material revealed the presence of the carbon-black filler; no fillers were present in the G/P matrix material. The carbon-black filler appears in the photomicrograph as the light spots in the matrix material.

The different C/P to G/P interfaces were also characterized based upon their appearances. Three different interfaces were observed: (a) 0.32  $\mu$ m, (b) 0.64  $\mu$ m, and (c) the cocure interface. Surface finish is defined as

the mean distance between peak and valley, measured in microinches (tens of nanometres). Observed from the examination was that the distance from peak to valley for the 0.32  $\mu$ m surface finish was half that of the 0.64  $\mu$ m interface. The appearance of the cocure interface was unmachined with evidence of the carbon-black filler migration across the interface. The migration was attributed to the cocuring of both the G/P and C/P materials.

### 5.3. Interlaminar shear strength

The results of the interlaminar shear strength tests are summarized and presented in Table II for the four laminates. Analysis of the data yielded the following results.

(a) There were no appreciable differences in ultimate strength observed for the G/P material among the four laminates.

(b) There was no significant difference in the ultimate strength of the C/P material of the three laminates which received the hydroclave cure. There was, however, a 20% reduction in ultimate strength in the C/P material of the cocure laminate. The reduction in the C/P material of the cocure when compared with the strengths of the three other laminates was attributed to the difference in the pressures of the autoclave and hydroclave cure cycles. The cocure laminate was cured using the autoclave cure cycle where the maximum gauge pressure obtained was  $1.655 \times 10^6$  Pa, while the hydroclave cured laminates experienced maximum gauge pressure of  $7.24 \times 10^6$  Pa.

(c) The results from the evaluation of the interfacial bond strength showed for the cocure, dry and as-received laminates, that the ultimate strength of the interface was at least as high as that of the C/P material of each laminate, because failure occurred in the C/P material of the gauge section. The most significant effect occurred in the interface specimens of the wet laminate, where the failure mode was shifted from the C/P (observed for the as-received, dry and cocure interface specimens) to the interface and the ultimate strength was significantly reduced. The effect of moisture at the interface is believed to have masked any

TABLE I Summary of the physical property test results

Panel	Status <sup>a</sup>	Material	Residual volatiles (%)	Resin content (%)	Specific gravity
As-received	*	C/P	2.9	30.9	1.5
	†	C/P	2.6	30.8	1.5
	†	G/P	1.1	22.2	2.1
Dry	*	C/P	2.9	31.1	1.5
	†	C/P	2.7	30.7	1.5
	†	G/P	1.1	22.1	2.1
Wet	*	C/P	2.9	31.1	1.5
	†	C/P	2.8	29.5	1.5
	†	G/P	1.1	22.6	2.1
Cocure	†	C/P	2.8	32.4	1.5
		G/P	1.2	23.6	2.1

\* Proceeding CP cure and prior to conditioning.

† Proceeding the GP cure.

TABLE II Summary of interlaminar shear test results

Panel	Glass/phenolic (MPa)	Carbon/phenolic (MPa)	Interface 0.32 $\mu\text{m}$ surface finish	Interface 0.64 $\mu\text{m}$ surface finish
Cocure	25.17 (5.71) <sup>a</sup>	20.60 (2.93)	23.26 CP <sup>b</sup> (3.71)	
As-received	25.17 (2.58)	25.32 (3.49)	26.46 CP <sup>c</sup> (3.49)	26.48 CP <sup>c</sup> (2.38)
Dry	29.14 (5.89)	26.13 (4.96)	25.75 CP <sup>c</sup> (3.38)	25.69 CP <sup>c</sup> (6.79)
Wet	26.42 (3.01)	27.63 (12.22)	12.71 BL <sup>d</sup> (4.44)	14.10 BL <sup>d</sup> (7.00)

<sup>a</sup> Coefficient of variation given within parentheses.

<sup>b</sup> Surface finish not applicable.

<sup>c</sup> Failed in carbon/phenolic.

<sup>d</sup> Bondline failure.

potential variations in surface finish, and to have caused the shift in failure mode.

(d) There was no appreciable difference between the 0.32 and 0.64  $\mu\text{m}$  surface finishes for the wet laminate. It was found that the individual specimen results for the 0.32 and 0.64  $\mu\text{m}$  surface finish were within the bounds of the 95% confidence interval of the 0.64  $\mu\text{m}$  surface finish results. The results obtained from the test showed that there was no significant difference in the ultimate strengths of the two populations.

The test results (mean value) for the C/P material of the as-received laminate were compared against the mean values of the existing MX-4926 C/P material databases [20, 22] to assess the reliability of the results obtained in the programme. The mean value for the ultimate strength obtained from the existing databases with curing and test parameters identical to those of this programme was approximately  $25.86 \times 10^6$  Pa. Comparison of the database results with the results of

this programme, clearly indicate that the results are in agreement with those of previous programmes.

#### 5.4. SEM examination

The double-notched shear specimens were visually examined after testing to determine the mode of failure. Of the specimens tested, only two distinguished modes were observed. These were across laminar and interlaminar failure.

Examination of the fracture surfaces by the conventional technique of optical microscopy rendered accurate observations impractical and therefore the scanning electron microscopy was required. Scanning electron microscopy (SEM) examination was performed using a Cambridge 250 MK2 scanning electron microscope. The fractured surfaces were etched with gold prior to their examination.

Interlaminar failure (presented in Fig. 7) was characterized by a fracture surface exhibiting one or more of the following features: (a) large areas of exposed denuded fibres, (b) thin cracks between the fibres and matrix, and (c) clear imprints in the matrix where fibres were removed. This type of failure was characteristic of the interface specimens of the wet laminate and the glass phenolic material of all laminates.

Across-laminar failure (presented in Fig. 8) was characterized by a fracture surface exhibiting similar features of interlaminar failure with the addition of some extensive fibre breakage across individual plies of material. This type of failure was common to all

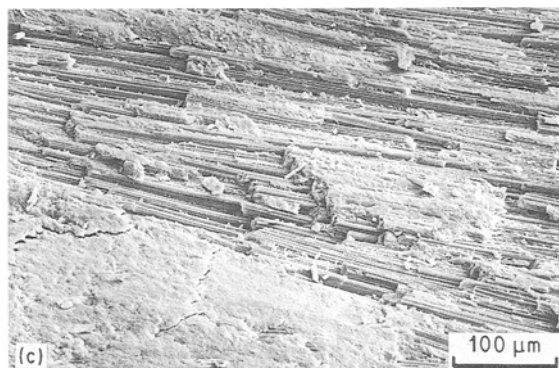
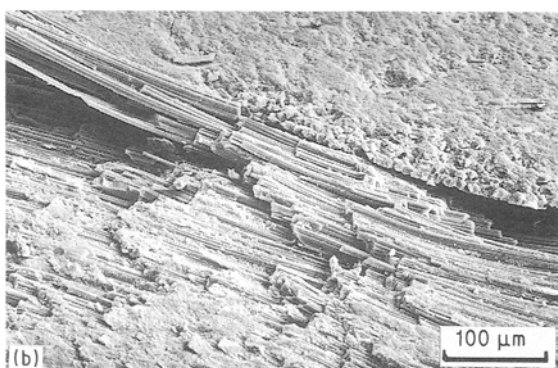
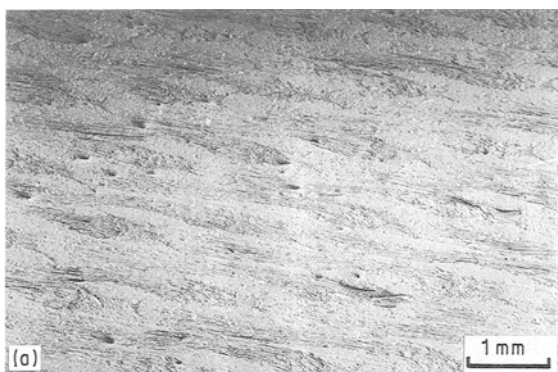


Figure 7 (a-c) Scanning electron micrographs of fracture surfaces depicting interlaminar failure.

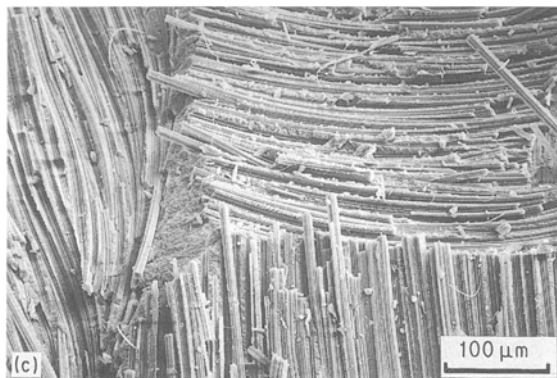
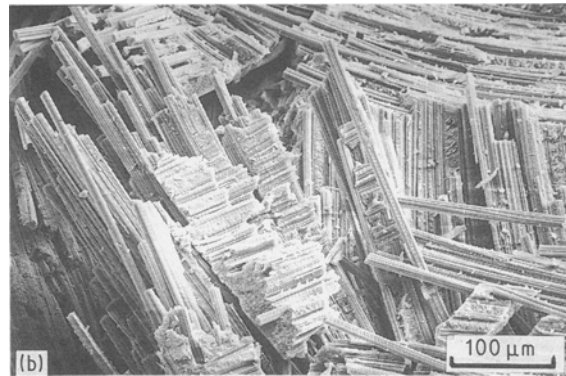
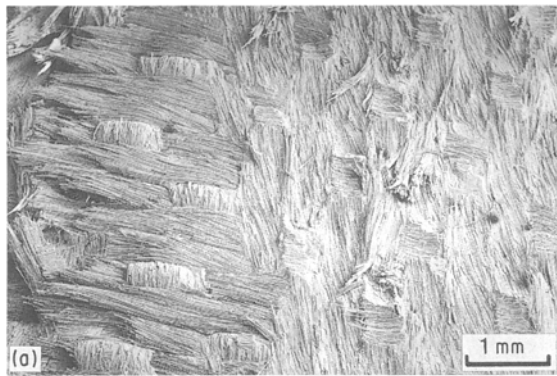


Figure 8 (a-c) Scanning electron micrographs of fracture surfaces depicting cross-laminar failure.

carbon phenolic material and the bondline specimens of the dry, as-received and the cocure laminates. From analysis of fracture surfaces of failed DNS C/P specimens by SRI, it was found that the predominate mode of failure was interlaminar although the presence of across-laminar failure was observed [21].

## 6. Conclusions

The following conclusions were based upon the test results presented in the previous section.

1. Moisture substantially degrades the integrity of the interfacial bond between C/P and G/P materials.

2. The apparent effect of autoclave curing of the C/P material reduces the ultimate interlaminar shear strength of the C/P material by nearly 20% compared to the hydroclave curing of the C/P material.

3. The variation in applied surface finishes had no appreciable effect on the ultimate interlaminar shear strength of the interface in the wet laminate. The variation in the applied surface finishes on the remaining three laminates was not conclusively determined due to the failure having occurred in the C/P material of the gauge section for the interface specimens.

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