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EFFECTS OF THERMAL AND MOISTURE CYCLING ON THE INTERNAL STRUCTURE OF STITCHED RTM LAMINATES *

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SUMMARY

Conventional aerospace composites are strong and stiff in the directions parallel to the carbon fibers, but they are prone to delaminations and damage in the through-the-thickness directions. Recent research has shown that substantial improvements in damage tolerance are obtained from textile composites with Z-direction reinforcement provided by stitching, weaving, or braiding. Because of the mismatch in thermal and moisture expansion properties of the various material components, there is a potential for microcracks to develop in the resin matrix. These cracks can form to relieve the mechanical stresses that are generated during curing or in-service temperature cycles.

INTRODUCTION

The NASA Innovative Composite Advanced Primary Structure (ICAPS) program has utilized Z-axis stitching to increase damage tolerance and stabilize and compact dry fiber preforms. These preforms are then impregnated with resin using the resin transfer molding (RTM) technique or autoclave resin film infusion (RFI) (Figure 1).

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* Work done on contract at McDonnell Douglas, NAS1-18580

Microscopic evaluation of panels stitched with fiberglass thread and impregnated with Hercules 3501-6 resin has shown evidence of cracks and voids at the thread/resin interface (Figure 2). Closer inspection reveals two distinct kinds of cracks forming in the resin-rich areas around the thread:

- Resin separation cavities -- These areas appear to form before the epoxy matrix has completely set-up as seen by the smooth fracture surfaces (Figure 3). These voids may be formed due to the resin shrinking away from the surface of the thread during cure.

- Matrix cracks -- These cracks appear to be traditional fracture surfaces created after the resin has hardened. They are most often found at the ends of the separation cavities and propagate into a resin-rich area either inter- or intraply.

This paper describes the work being performed under the NASA Langley Research Center (NASA LaRC) Effect of Environment on Textile Composites program which is investigating the causes, effects, and possible solutions in minimizing microcracking. The research plan designed to address microcracking takes advantage of previous MCAIR, Douglas, NASA LaRC, and DuPont data gathered over the last 10 years. Thermal expansion mismatch and matrix cracks have been observed in conventional prepreg laminates as well as Z-axis stitched parts.

WEIGHT GAIN - HOT/WET ENVIRONMENT

A possible variable in predicting resin cracking is the effect of moisture. If voids and cracks exist around the stitching thread, water could permeate into the laminate and be absorbed into the resin matrix, which could cause fracture propagation during freeze/thaw cycles. A weight gain study (Figure 4) was carried out using 0.325 inch thick wing skin stiffened panels. The control specimens were nonstitched panels with stiffeners secondarily bonded. The stitched specimens were sections from wing element panels fabricated using the resin film infusion method. In each case, the resin system used was Hercules 3501-6 with AS4 fiber.

The specimens were weighed and then placed in a 140°F oven at 95-percent relative humidity. The data show that the stitched panels pick up moisture at twice the rate of the unstitched panels. It is important to note that the 0.54-percent increase in weight is not considered excessive, but the test was only run for 50 days because of an equipment malfunction. This was not enough time for the samples to reach complete saturation, but it is clear that a surface seal coat may be required to protect Z-axis stitched parts in service environments. An unstitched laminate usually reaches moisture equilibrium with a weight increase of approximately 1-percent. This experiment will continue until a saturation level is reached in the stitched specimens.

RESEARCH PLAN DEVELOPMENT

This information collected on in service matrix cracking has been used to define a test program to identify the possible causes of microcracking in stitched laminates. The research will focus on the following key areas:

- Test specimens and fabrication
- Critical environmental parameters/cycle definition
- Resin system selection
- Exterior surface treatments
- Assessment of susceptibility to fuel leaks
- Analytical methods evaluation

The test matrix (Table I) was finalized in a meeting between NASA Langley, McDonnell Aircraft, and Douglas Aircraft. Effort will be distributed between these three principals with Douglas focusing on fabrication, MCAIR on conditioning and testing, and NASA on open hole compression testing and program guidance.

Test Specimens and Fabrication

The test matrix will focus on compression-after-impact (CAI) and open hole compression (OHC) values. These are essentially matrix-dominated properties and should help quantify the effects of microcracks in predicting property knockdowns. The specimens will be 48-ply quasi-isotropic laminates, [45,0,-45,90]6s, per NASA Reference Document 1092.

To fabricate the dry preform panels, the 145 g/m^2 uniwoven dry carbon fabric is cut, laid up, and then sent to Pathe Corporation, New Jersey, to be stitched on a multiple-needle sewing machine (Figure 5). The penetration thread is made up of four strands of 400 denier Kevlar treated with a low melt nylon to aid the stitching process. The stitch density is typical of the 0.20 inch spacing used on the NASA ICAPS program with 40 penetrations per square inch.

The stitched panels will then be impregnated using resin film infusion. This process begins with casting a neat resin plug approximately the size and thickness of the preform. The dry preform is laid on the resin with a perforated caul plate on top. The lay-up is bagged and placed in the autoclave to undergo a step cure cycle where isothermal holds are used to fully impregnate the preform with resin.

Critical Environmental Parameters

Work done under NASA contract by Roberto Cano at LaRC (Ref. 1) showed that compression strength was not substantially affected by cycling between hot/wet and cold environments (Figure 6). The data supports the conclusion that strength knockdowns occur initially during cycling but do not continue to decrease substantially over time.

Earlier studies by Dupont and Douglas indicated that microcracking could be induced in laminates by dry temperature cycling alone. To investigate a potentially more severe environment, it was agreed that specimens would be loaded in bending while temperature and moisture were simultaneously applied.

The cycle (Figure 7) requires 90 minutes to complete and simulates a worst-case environment for the aircraft. Specimens will be examined after 10, 100, and 1,000 cycles, and surface crack density will be compared to service parts to establish cycle-to-flight ratios.

Resin System Selection

Resin system selection for the program was finalized during a NASA, MCAIR and Douglas meeting in Langley, Virginia. The baseline carbon fiber will be Hercules AS4, and the following resin systems were chosen for evaluation:

- Hercules 3501-6
- Hercules 3502
- Dow Chemical CET-3
- 3M PR 500

The resin systems selected present a fairly broad cross section of properties thought to contribute to microcracking. The CET-3 and PR 500 show good improvement over 3501-6 in shrinkage, moisture resistance, and fracture toughness. The Hercules 3502 is excellent in hot/wet properties retention and has the lowest viscosity during the process cycle for good fiber wet-out.

Laminate compression properties developed at NASA Langley confirm predictions from the neat resin data (Table II). Resin modulus is a good indicator of the relative compression strength of a quasi-isotropic specimen. These properties will then be compared after being notched or impacted and subjected to moisture/temperature cycling.

Previous process experience was important to the resin selection criteria. Excellent results were achieved at both NASA and Douglas with the PR 500 (Figure 8). Cross sectional micrographs of a Kevlar-stitched, NASA-processed panel show good fiber wet-out and no evidence of postprocessing microcracks, as seen in Figure 2. A nonstitched Douglas panel 0.50 inch thick also showed good results when using PR 500. Reports from the industry indicate the CET-3 material should have similar processing characteristics, which led to its selection.

Exterior Surface Treatments

The Kevlar panel study performed by DuPont recognized that surface finish preparation and materials could have a marked effect on the onset of microcracking. The most promising candidates were investigated further:

- Calendered Kevlar S-285
- Koroflex® flexible primer from DeSoto Corporation
- Film adhesives cocured to the panel's tool side
- Nonwoven Kevlar mat impregnated with adhesive

This program will focus on the use of Koroflex to minimize surface cracking. This solution makes the most sense from a weight and manufacturing viewpoint, and test results showed no cracking after 3,000 hot/cold cycles.

Assessment of Susceptibility to Fuel Leak

Potential microcracking in wing skin panels creates concerns of possible fuel absorption or leakage through the skins. This program will expand on the work done by C.F. Griffin of Lockheed on fuel containment under the NASA ACEE program (Reference 2).

A MCAIR chamber designed to environmentally cycle test coupons while exposing them to JP5 fuel under pressure will be used to evaluate post impact leakage (Figure 9). The specimens will be coated on the surface opposite the impact with Chemglaze® or polysulfide sealer per production process standards. The coupons will then be impacted to the threshold level of visible damage (~ 35 foot-pounds), C-scanned, and subjected to the pressurized fuel. Fluorescent dye added to the fuel will help detect the degree of penetration into the damaged laminate.

Analytical Methods Evaluation

The analytical methods task will be jointly coordinated among MCAIR, NASA LaRC and Virginia Polytechnic Institute (VPI). The objective of the analytical program is to develop models that will be used to determine stress states in and around a stitch through a composite lamina. Once developed, these models will be used to perform parametric studies with different resin systems, stitching fibers, and/or processing cycles to identify those combinations that minimize microcracking. The modeling effort focus is divided as follows:

- MCAIR - Develop three dimensional models.
- NASA LaRC - Develop two dimensional plane strain models.
- VPI - Develop two dimensional axisymmetric models.

Processing stresses that develop in the matrix pockets around the stitch are of particular interest, since they can be used to predict when microcracks will occur. Preliminary axisymmetric models of a stitch surrounded by concentric annuli of matrix and composite (Figure 10) have been used to predict order of magnitude stresses in a matrix pocket. Through-the-thickness stress distributions, predicted by the 3D models, near the stitch/matrix and matrix/composite interfaces are shown in figure 11 for a -275°F temperature change (Tg to room temperature). Since the tensile and shear strengths of the neat resin are roughly 8-10 ksi, the predicted stresses could easily have caused cracking. In addition, this simple model demonstrates that a complex three dimensional stress state exists in the matrix pocket.

Several more detailed models are being developed for this study, all of which utilize the finite element method to characterize a representative volume element (RVE) of the stitched composite. In these models, the RVE is taken as a single stitch and half of the composite between it and adjacent stitches (Figure 12). The laminates being modeled are always mid-plane symmetric, and only include 0, 90, and ±45 degree plies.

The MCAIR model utilizes three dimensional solid brick elements to explicitly model each ply of the laminate. The mesh for this model is based on the intersections of the matrix pockets in 0, 90, and ±45 degree plies. A generic mesh for a single ply, regardless of orientation, has been developed. This mesh includes all possible matrix pockets, and can be used for any ply by specifying that matrix properties be used for elements in the appropriate pocket, and that lamina properties be used for elements in all other areas. Since the same mesh is used for all plies, a laminate model is built by stacking the required number of ply models (Figure 13). Symmetry conditions are used at the mid-plane of the laminate, and anti-symmetry conditions are used along a plane through the centerline of the stitch to reduce the size of the model to one-fourth of the actual RVE.

The three dimensional model is very powerful, since it will predict three dimensional distributions of all six stress components. One drawback is the considerable amount of modeling time and substantial computing resources required, although the use of a generic ply mesh helps. The two dimensional models at NASA LaRC and VPI will be faster to run and should provide good ballpark correlation especially when using geometric parameters as variables.

The two dimensional models being developed by NASA LaRC explicitly model the matrix pocket and the cross-sectional shape of the stitch. Since they are two dimensional, much finer meshes can be used, and it is easier to make changes in the geometry. These models will be used to determine the relative effects of different stitch geometries and matrix pockets. The drawback to the NASA LaRC models are that they do not include through-the-thickness shear distributions. The two dimensional axisymmetric models being developed by VPI do include these shears, but can only account for geometric changes in an average sense. For example, the volume of the matrix pocket can be changed, but it must still be an annulus. The VPI model is therefore most appropriate for parametric analyses that consider material property changes.

To support the analyses, photos were taken at several through-the-thickness locations to define thread/resin interfaces (Figures 14, 15, and 16). The displacement of the surrounding carbon fibers due to thread diameter is shown in Figure 17. The triangle shaped resin-rich areas are the principal sites of voids due to shrinkage which can serve as origins of microcracks.

SCHEDULE

The period of performance involves a 12 month effort. The critical path involves the timely receipt of the neat resin systems and panel stitching to be done at Pathe Corporation.

CONCLUSIONS

Douglas and industry experience with resin matrix cracking to date supports the following conclusions:

- Microcracking is not strickly a phenomenon of Z-axis stitched composites.
- Several variables affect the initation and distribution of cracks. Resin systems, stitching threads and process cycles, to name a few, have been shown to affect the microcrack frequency and appearance.

At the conclusion of the task, several key parameters involving microcracking will have been investigated and quantified. This research will focus on answers to the following questions:

- Does microcracking affect long-term strength of stitched composites? Current evidence suggests it does not.
- Can severity of cracking in service be duplicated in the laboratory? DAC and DuPont were successful in a previous program.
- Are these cracks dependent on materials or processes?
- Which neat resin properties are important in eliminating the cracks?
- Will fuel containment be a problem?
- Will surface finish eliminate the observable cracks? Materials currently used in production have eliminated surface cracks in Kevlar/honeycomb panels.
- Can finite-element modeling be used to predict strength knockdowns and identify likely crack sites?

References

1. Cano, Roberto and Furrow, Keith: **Effect of Temperature and Humidity Cycling on Strength of Textile Reinforced Carbon/Epoxy Materials,** Third Advanced Composites Technology (ACT) Industry Review, Long Beach, CA, June 8-11, 1992. NASA CP-3178.

2. Griffin, C.F.: **Composite Wing Fuel Containment and Damage Tolerance - Technology Development,** ACEE Composites Structures Technology Conference, August 13-16, 1984.

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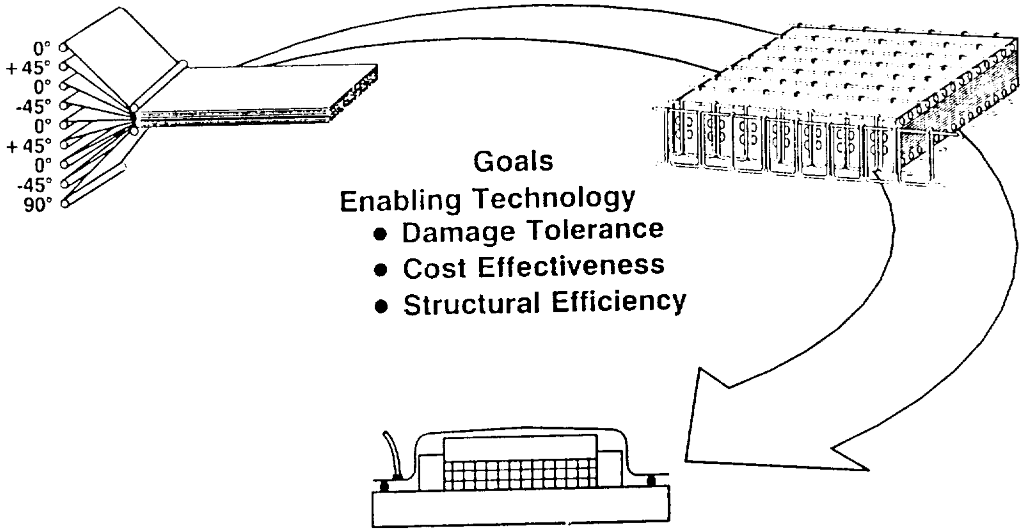
Loken, H.Y.,Dr.: **Review of Water Ingression Into Commercial Transport Aircraft Composites,** Douglas Aircraft Presentation, June 19, 1985.



Goals
Enabling Technology
- Damage Tolerance
- Cost Effectiveness
- Structural Efficiency

Stitching of dry fiber preforms followed by RTM processing holds attractive potential for transport wing structure

Figure 1. Process Overview

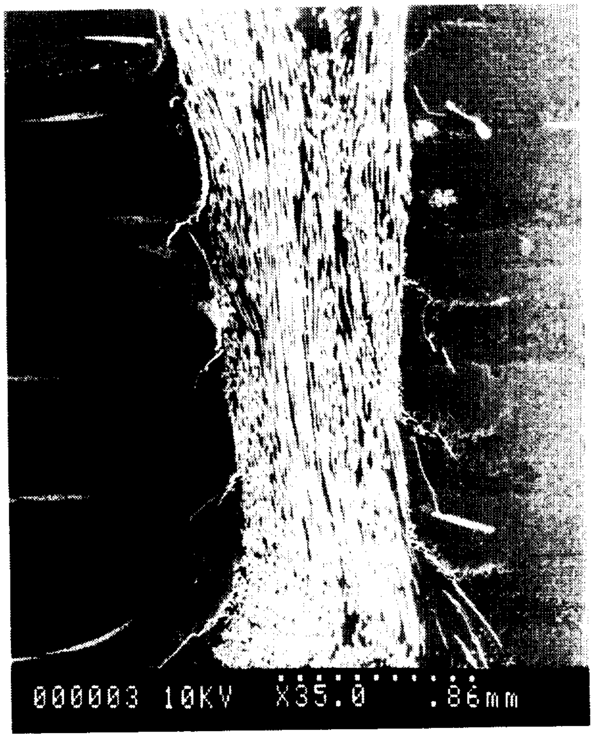


Figure 2. Glass Stitch w/3501-6 Laminate

Figure 3. Resin Cavities at Thread

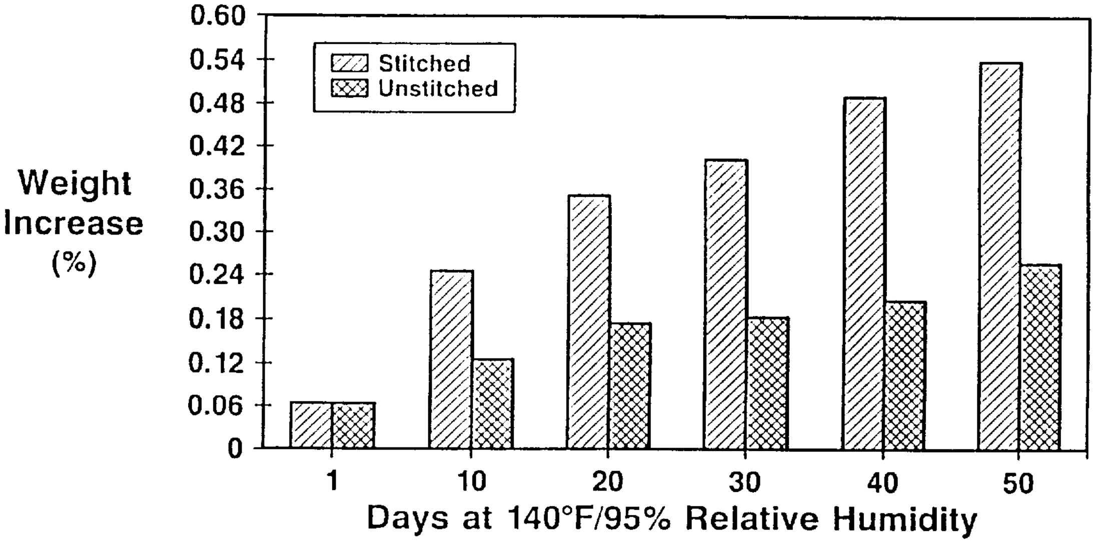


Figure 4. Weight Gain Study

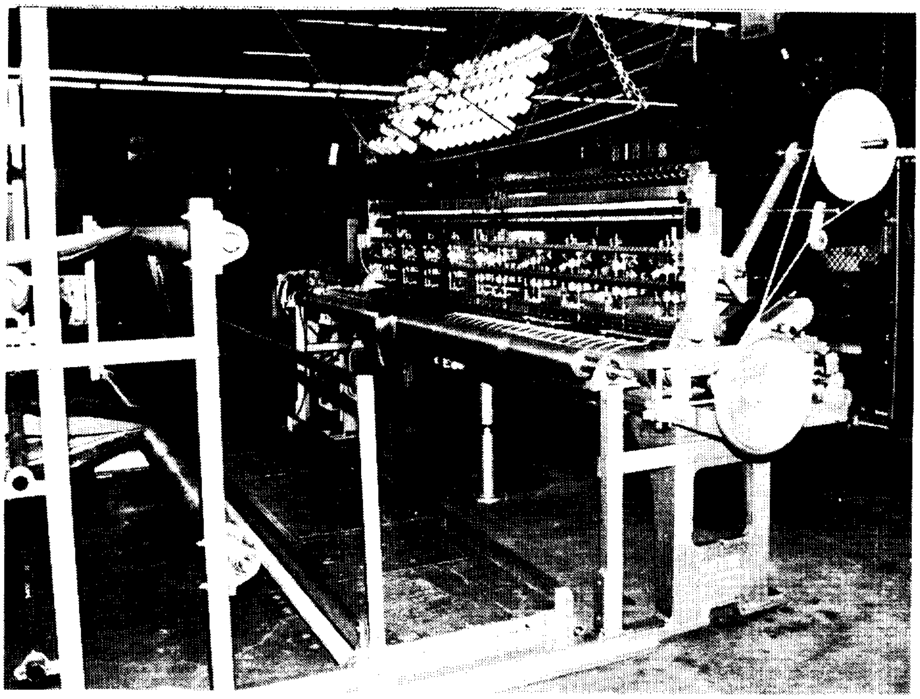
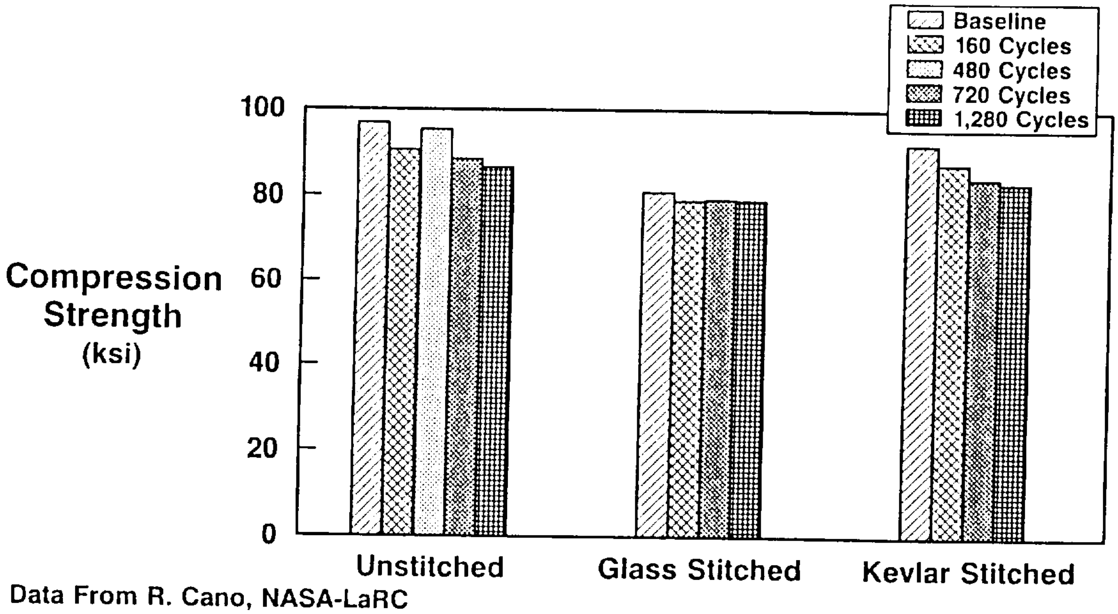


Figure 5. Pathe Multi-Needle Machine



Data From R. Cano, NASA-LaRC

Figure 6. NASA Compression Data

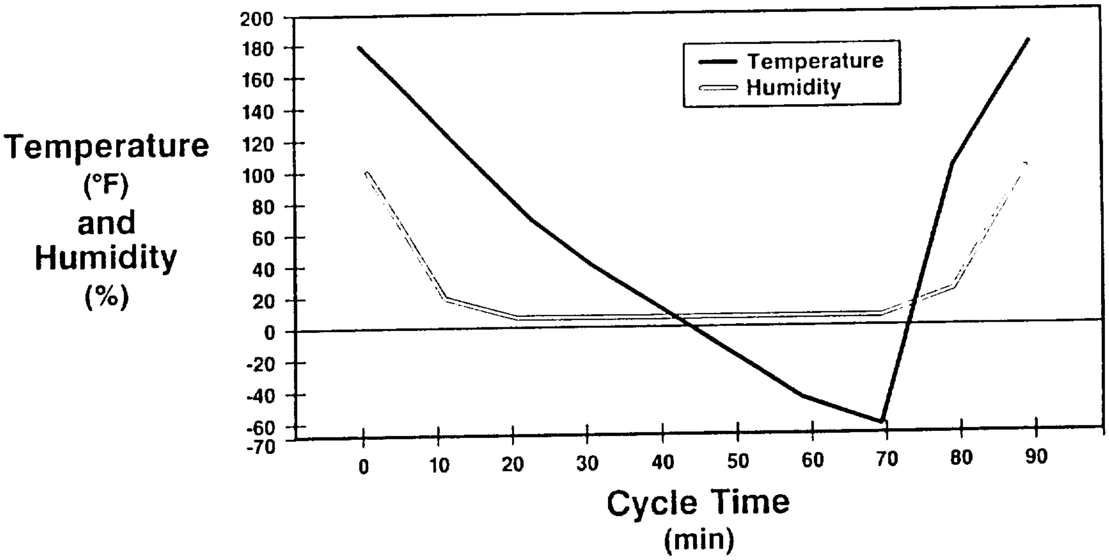


Figure 7. Enviromental Cycle

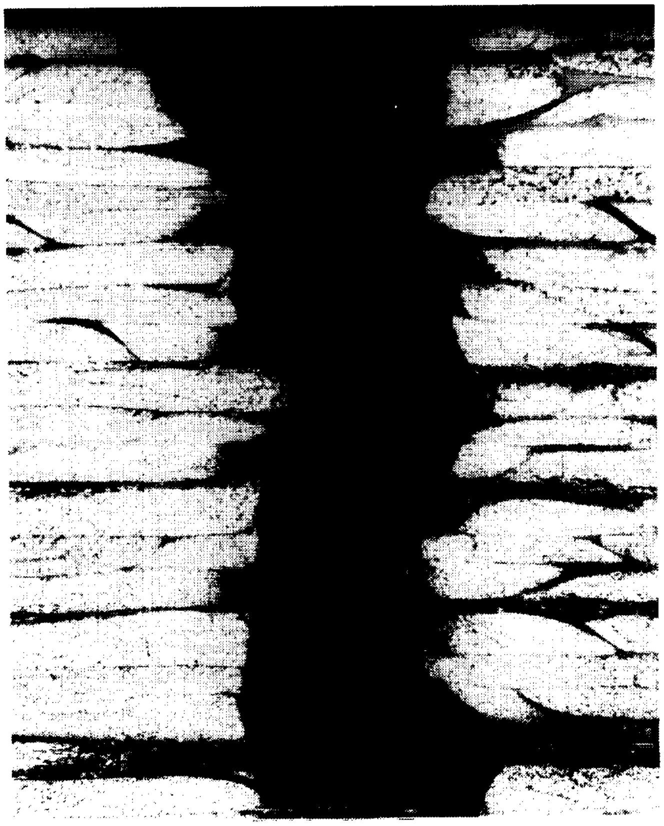


Figure 8. PR 500 w/Kevlar Stitch

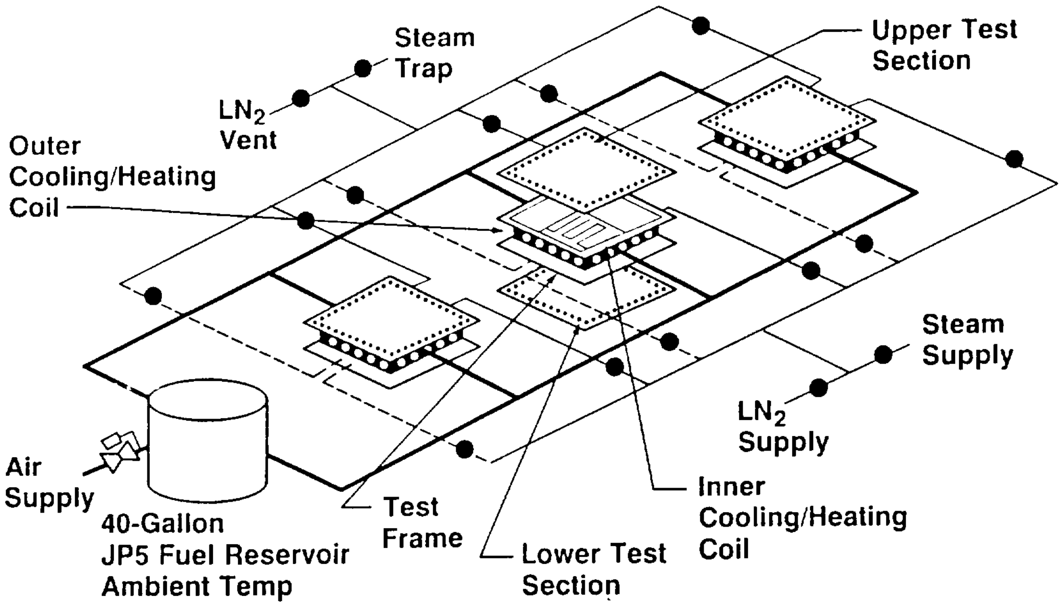
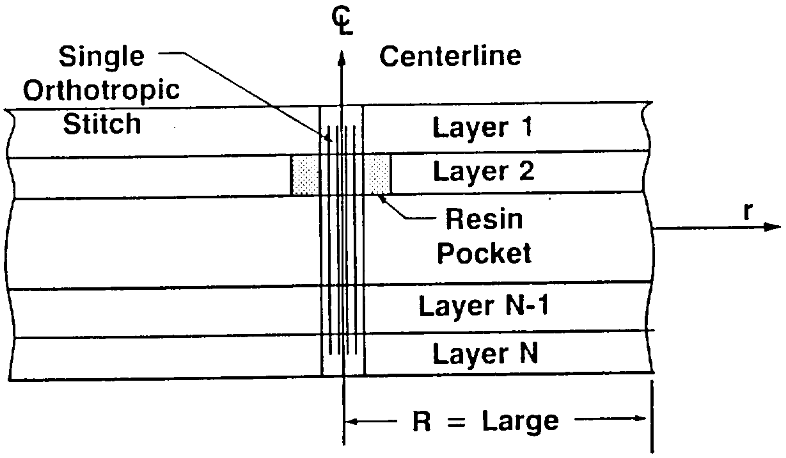


Figure 9. Fuel Leak Test Set-Up



VPI modeling focuses on an analytical tool that provides short computational times and qualitative assessment of cracking

Figure 10. VPI Model, 2D

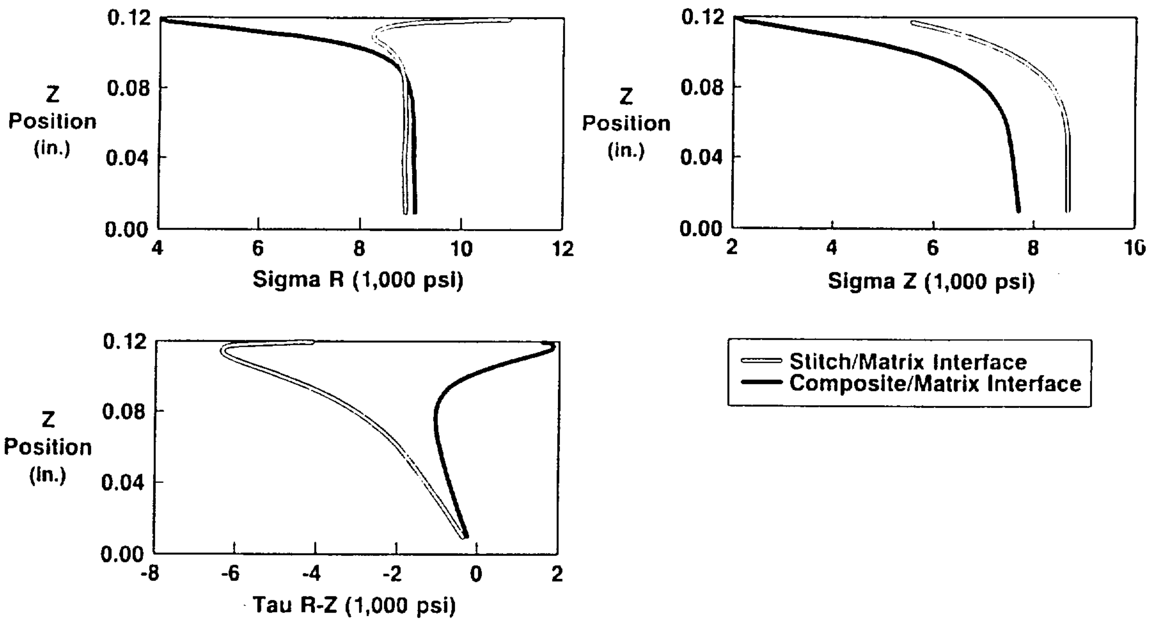
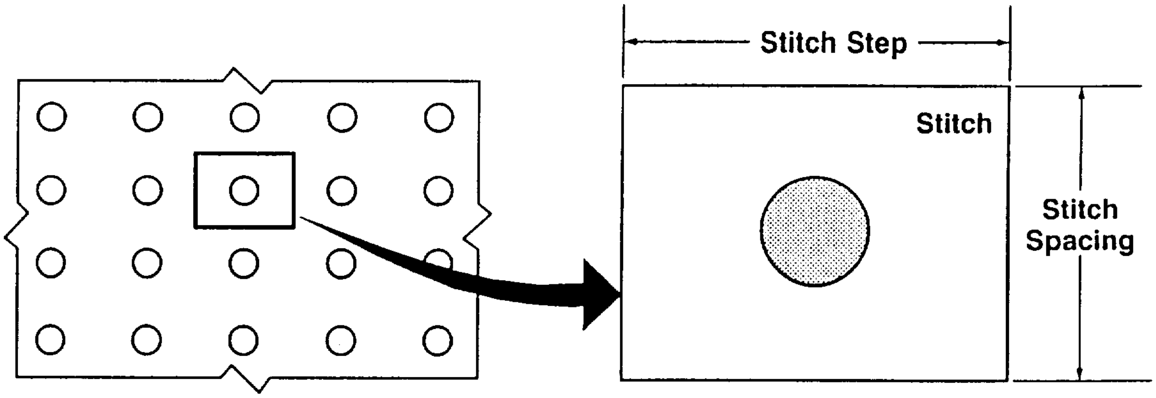
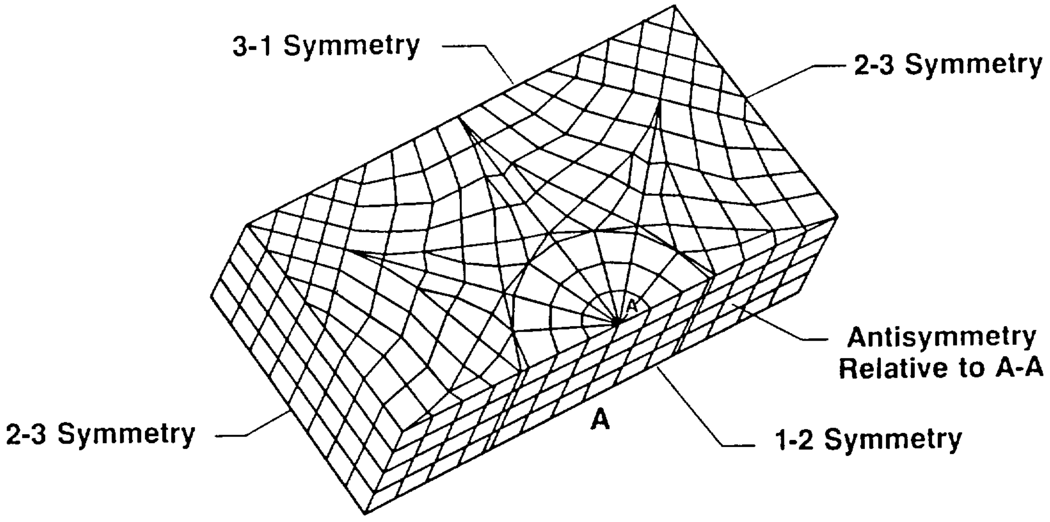


Figure 11. 3D Model Analysis Results



A representative volume element (RVE) for stitched laminates will be utilized by each of the investigators

Figure 12. Representative Volume Element



MCAIR modeling encompasses through-the-thickness effects, utilized to ensure the accuracy of the previous models

Figure 13. MCAIR 3D Model

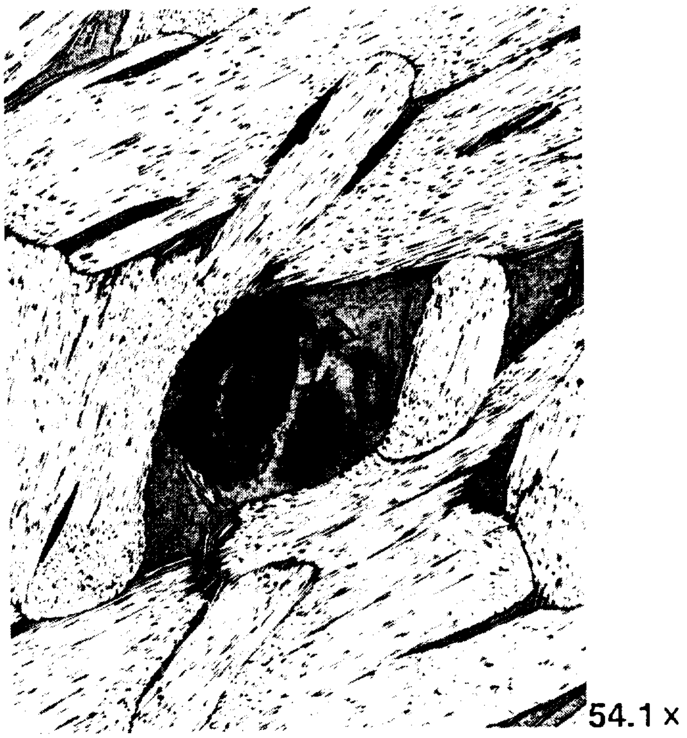


Figure 14. Ply of 48, PR 500

Figure 15. Ply 8 of 48, PR 500

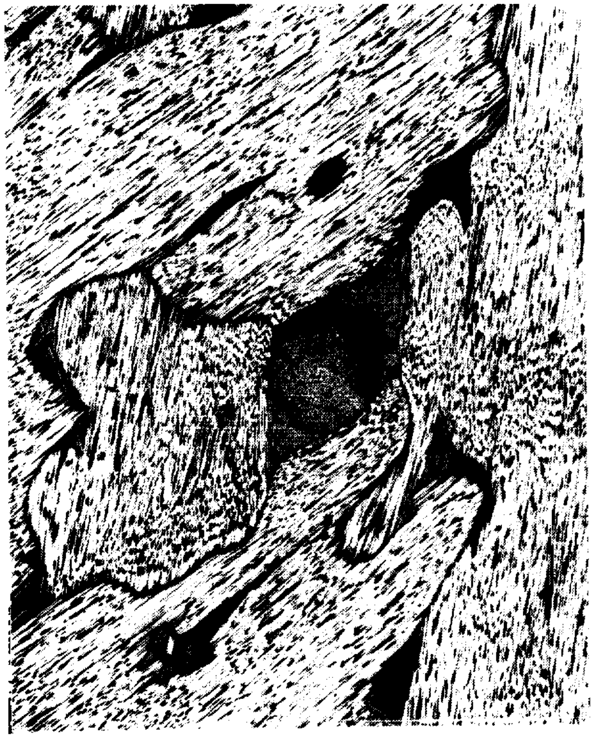


Figure 16. Ply 24 of 48, PR 500

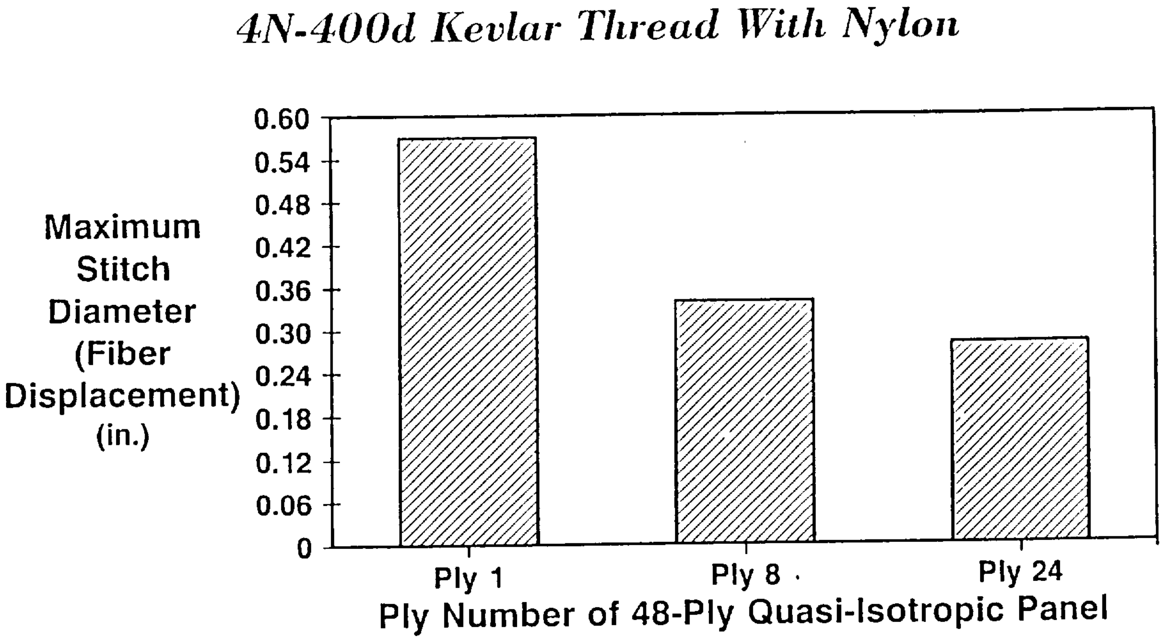


Figure 17. Fiber Displacement Around Stitch

Table I. Microcracking Test Matrix

Environment	Material	Surface Finish	Test	No. of Cycles				Total
				0	10	100	1,000	
Simultaneously Applied Thermal and Moisture Cycles (90-min Duration) Specimens Loaded in Bending	AS4/3501-6 Uniweave	Unfinished	OHC	3	3	3	3	12
			CAI	3	3	3	3	12
			Microphotography	3	3	3	3	12
		Primed and Painted	Visual Inspection	3	3	3	3	12
		Sealant	Impact and Leak Proof Test	2		2		4
	AS4/3501-6 Kevlar Stitched RTM	Unfinished	OHC	3	3	3	3	12
			CAI	3	3	3	3	12
			Microphotography	3	3	3	3	12
		Primed and Painted	Visual Inspection	3	3	3	3	12
		Sealant	Impact and Leak Proof Test	2		2		4
	AS4/3502 Kevlar Stitched RTM	Unfinished	OHC	3	3	3	3	12
			CAI	3	3	3	3	12
			Microphotography	3	3	3	3	12
		Primed and Painted	Visual Inspection	3	3	3	3	12
		Sealant	Impact and Leak Proof Test	2		2		4
	AS4/CET-3 Kevlar Stitched RTM	Unfinished	OHC	3	3	3	3	12
			CAI	3	3	3	3	12
			Microphotography	3	3	3	3	12
		Primed and Painted	Visual Inspection	3	3	3	3	12
		Sealant	Impact and Leak Proof Test	2		2		4
	AS4/PR500 Kevlar Stitched RTM	Unfinished	OHC	3	3	3	3	12
			CAI	3	3	3	3	12
			Microphotography	3	3	3	3	12
		Primed and Painted	Visual Inspection	3	3	3	3	12
		Sealant	Impact and Leak Proof Test	2		2		4

Note: OHC - to Be Tested by NASA

Table II. Selected Resin Properties

Vendor-Supplied Data

Properties	Hercules 3501-6	Hercules 3502	Dow Chemical CET-3	3M PR 500
Shrinkage (%)*	~ 1.6	~ 1.6	~ 0.75	~ 0.80
Moisture (% Increase) (2 Wks at 200°F)	2.3	2.4	1.6	1.5
Fracture Toughness G1c (J/m^2)	150	120	245	653
Tensile Modulus (ksi)	643	526	425	528
Elongation (%)	1.7	0.9	5.5	1.8

* Highly Dependant on Cure Cycle