Evaluation of Gr. Fiber/PI PMCs from Hot Melt vs Solution Prepreg

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ABSTRACT

Carbon fiber reinforced high temperature polymer matrix composites (PMC) have been extensively investigated as potential weight reduction replacements of various metallic components in next generation high performance propulsion rocket engines. The initial phase involves development of comprehensive composite material-process-structure-design-property-in-service performance correlations and database, especially for a high stiffness facesheet of various sandwich structures. Overview of the program plan, technical approaches and current multi-team efforts will be presented. During composite fabrication, it was found that the two large volume commercial prepregging methods (hot-melt vs. solution) resulted in considerably different composite cure behavior. Details of the process-induced physical and chemical modifications in the prepregs, their effects on composite processing, and systematic cure cycle optimization studies will be discussed. The combined effects of prepregging method and cure cycle modification on composite properties and isothermal aging performance were also evaluated.

SUBJECT MATTER

- Parent HOTPC Program
  - Technical Program Overview & Strategies
- Prepreg Studies
  - Introduction and Objectives
  - Experimental approaches and Material
  - Characterization/evaluation of resin, prepregs, and composites
  - Controlling Mechanisms
  - Effects on composite properties/performance
- Summary and Conclusion
- Future Study Plan…etc.

PROGRAM SYNOPSIS

Objective:

Evaluate and develop carbon fiber reinforced high temperature polymer matrix composite (PMC) materials and fabrication technology suitable for manifolds, thrust chamber backup supports & attachments or turbo-pump housings in a new generation rocket engine.

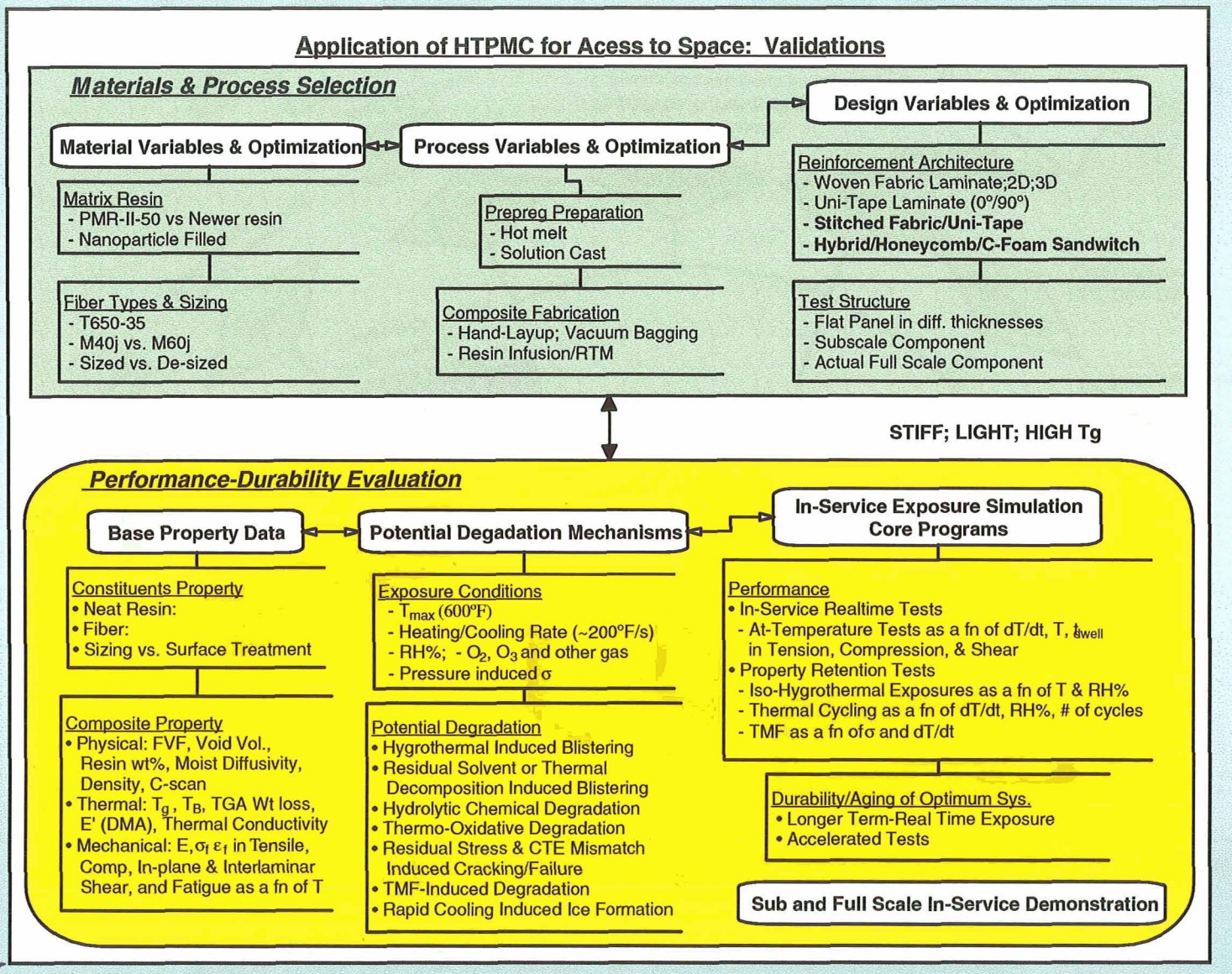
Values:

- Significant weight reduction by replacing metal/ceramic components with PMC
- Increased thrust-to-weight ratio, reduced fuel consumption, thus cost saving
- Utilization of current enabling base technologies in materials, design, process and fabrication areas, i.e., high feasibility!

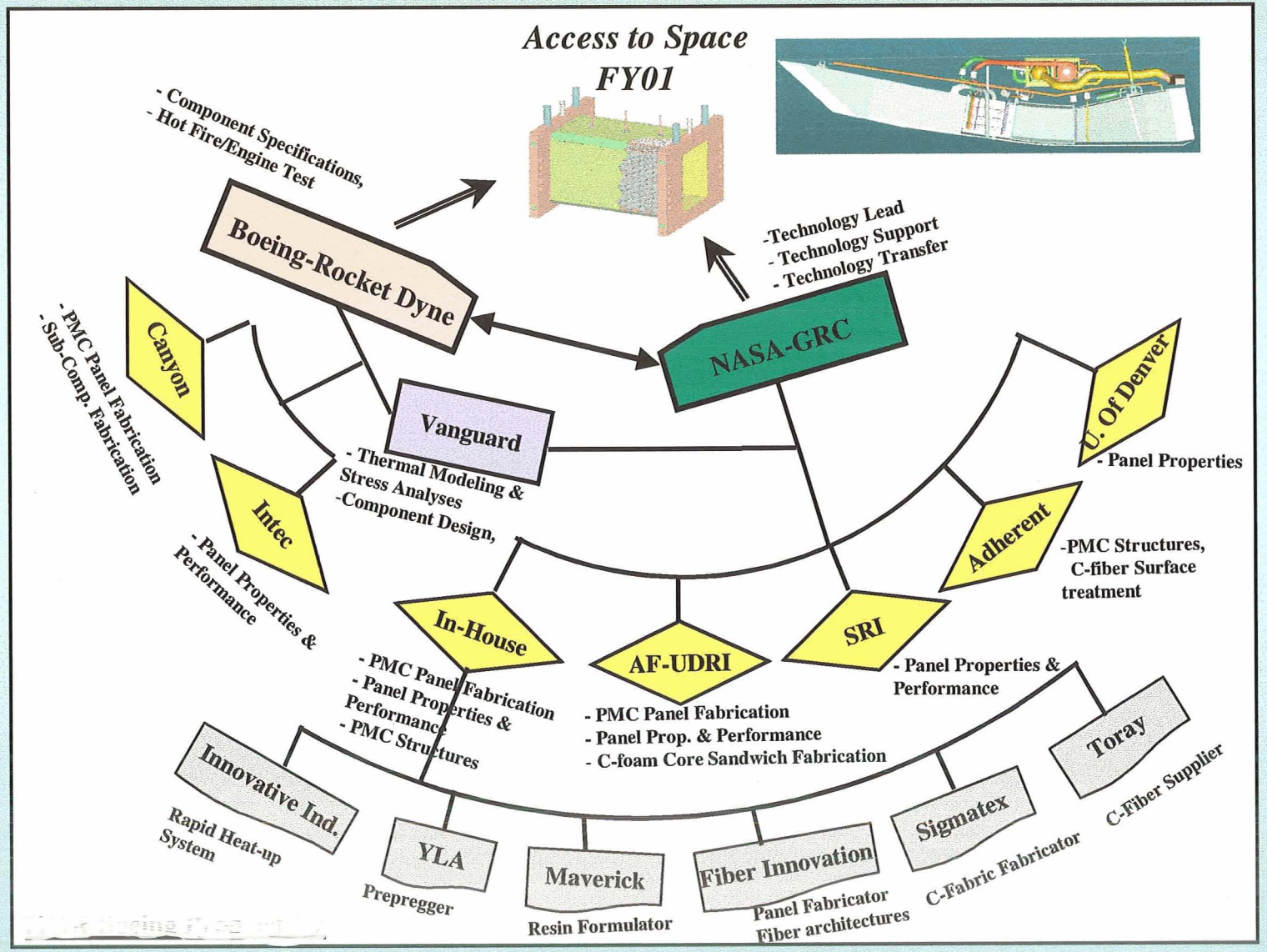
Challenge:

- Needed high thrust-to-weight ratio (>30:1) that must be achieved to make this a viable flight propulsion system. By component weight reductions up to 25-30%,
- Required high stiffness (less than 0.05" deflection in a 12"×12" panel) and high temperature capabilities up to 600°F,
- Required good hygro-thermal stability especially under rapid heat-up exposure up to 200°F/sec

OVERALL PLAN



CURRENT ACTIVITIES



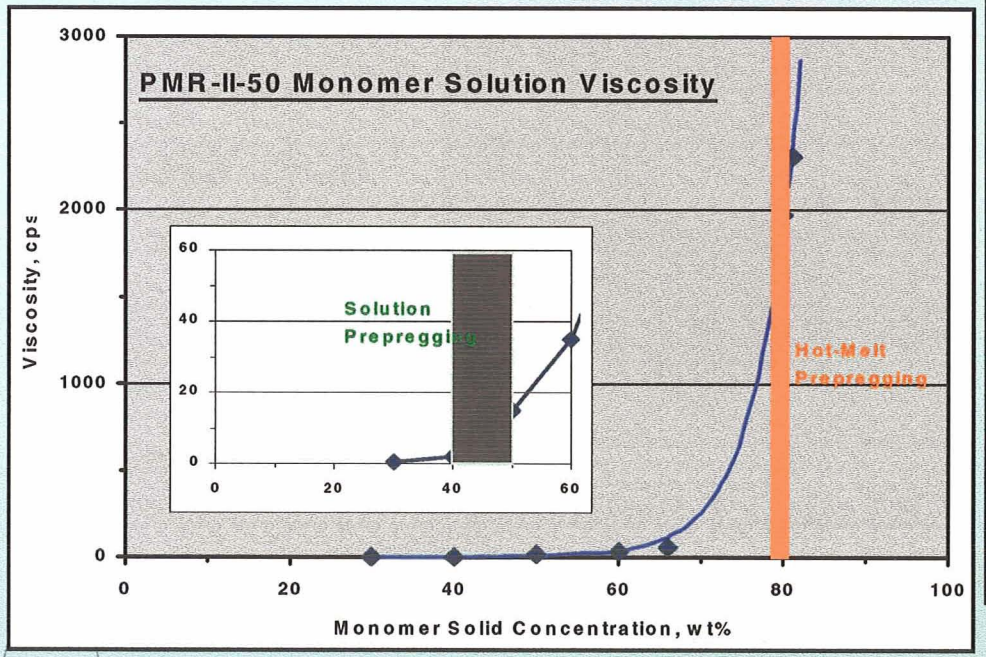
PREPREG STUDY: BACKGROUND

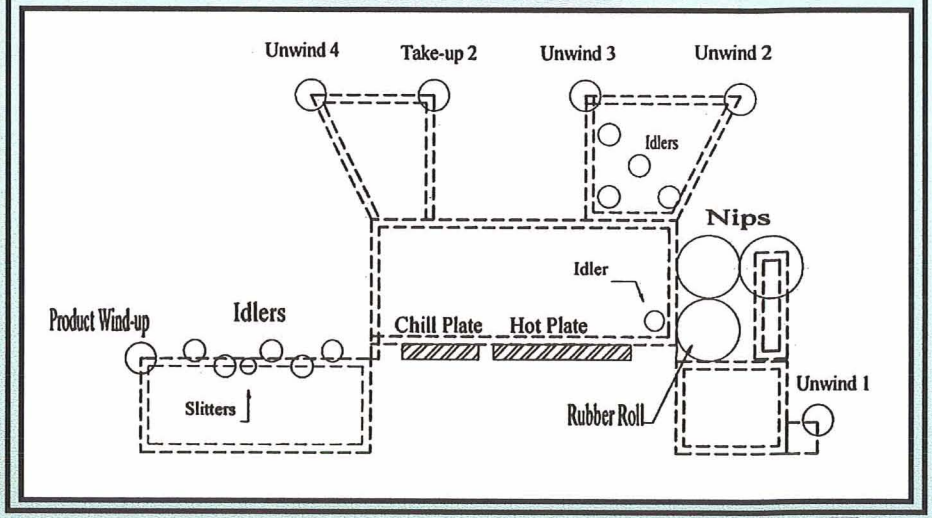
Solution Prepregging

- Conventional, available from lab scale to large production,
- Easier process control

Hot-Melt Prepregging

- Environmentally friendlier,
- Less residual solvent,
- More uniform resin distribution



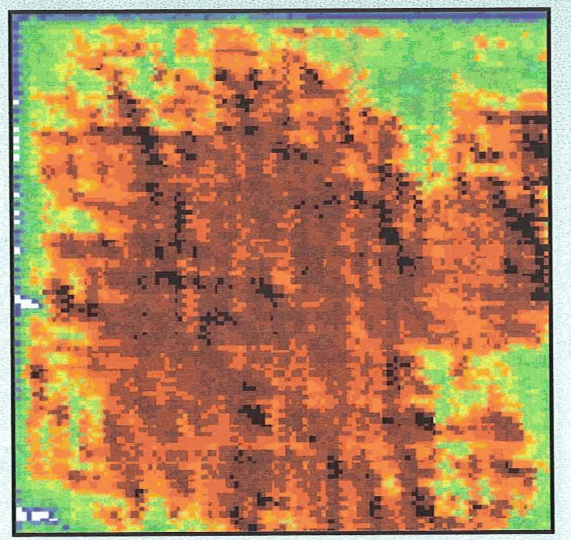


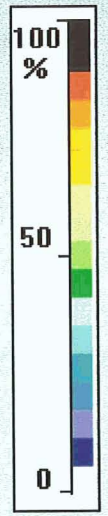
CHALLENGE

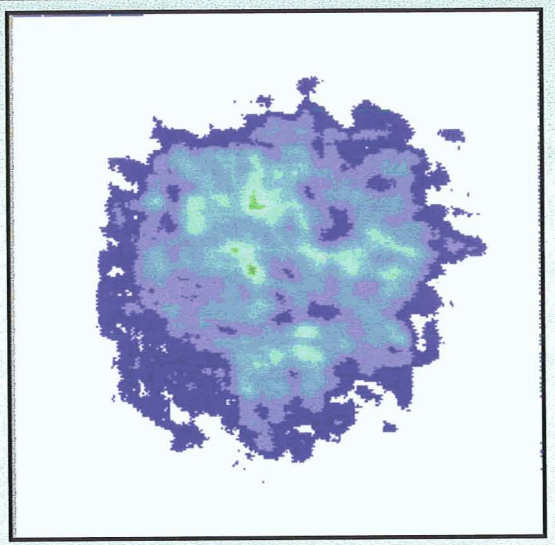
Solution Prepregs

Hot-melt Prepregs

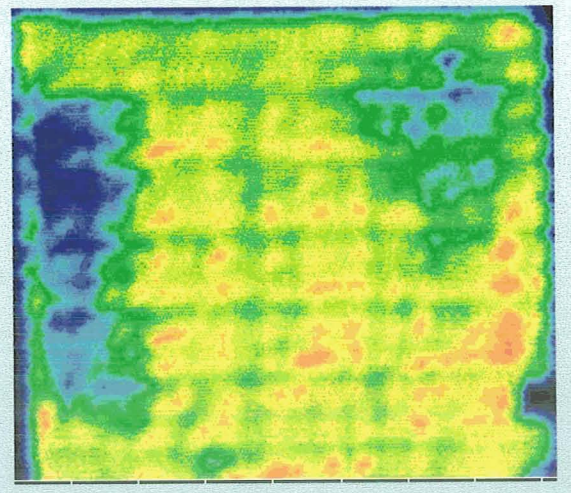
M40JB/ PMR-II-50

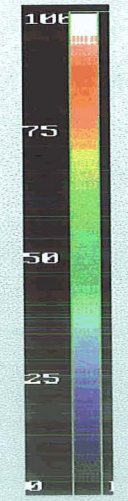


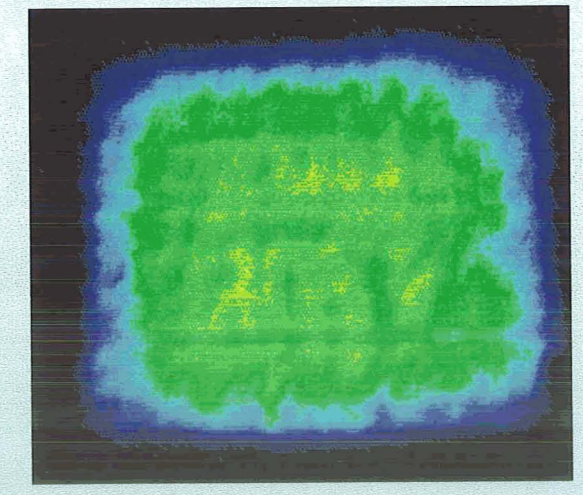




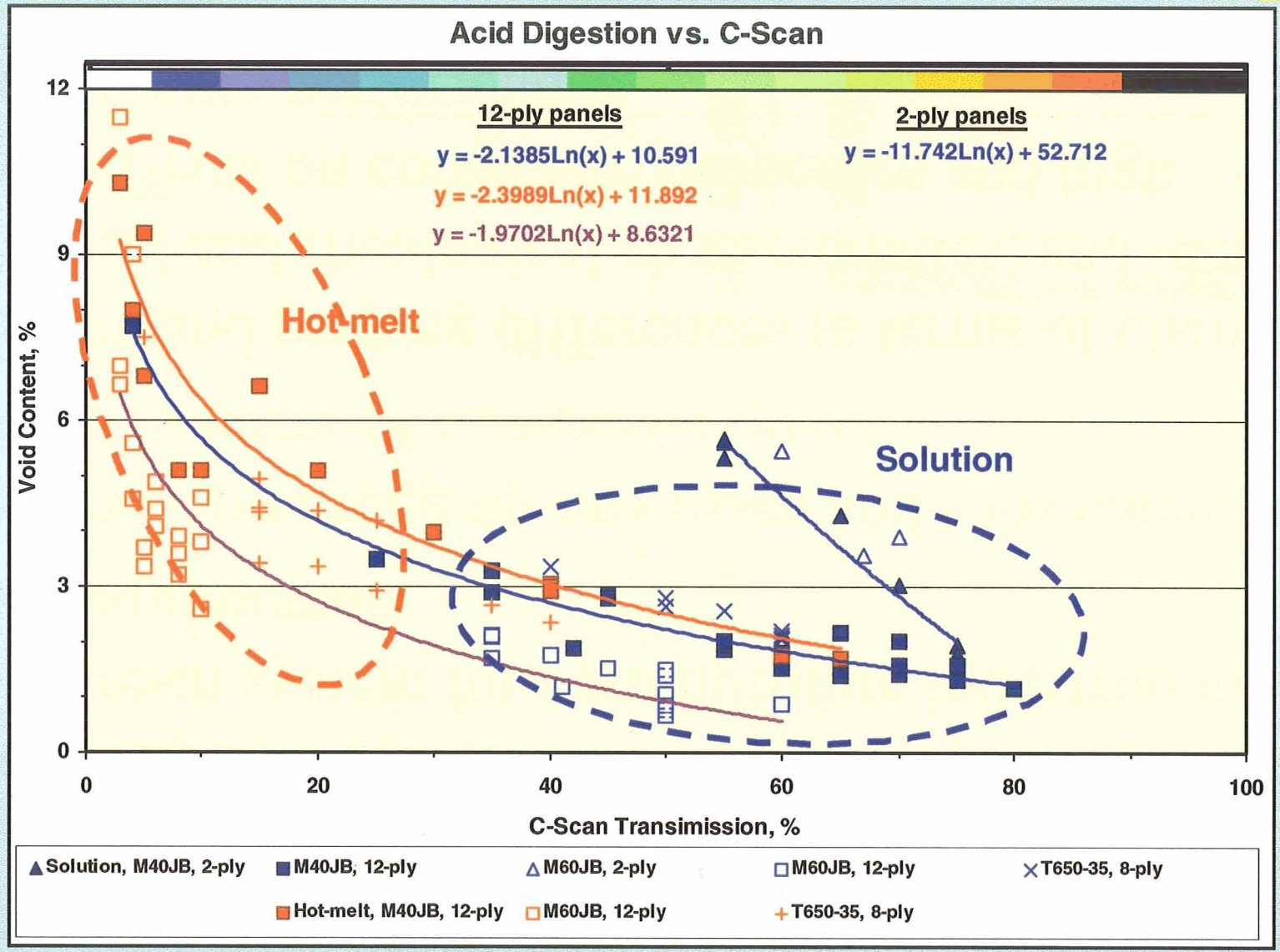
T650-35/ PMR-II-50







CHALLENGE


Acid Digestion vs. C-Scan
12-ply panels
y = -2.1385Ln(x) + 10.591
y = -2.3989Ln(x) + 11.892
y = -1.9702Ln(x) + 8.6321
2-ply panels
y = -11.742Ln(x) + 52.712
Hot-melt
Solution
Void Content, %
C-Scan Transimission, %
0
3
6
9
12
0
20
40
60
80
100
Solution, M40JB, 2-ply
M40JB, 12-ply
M60JB, 2-ply
M60JB, 12-ply
T650-35, 8-ply
Hot-melt, M40JB, 12-ply
M60JB, 12-ply
T650-35, 8-ply

OBJECTIVES

- Explore prepregging method alternatives for PMR-II-50 resin system for current/future industrial needs and requirements
- Optimize prepregging processes and subsequent cure cycles in terms of composite quality
- Understand prepreg differences in terms of chemical, physical and rheological characteristics, and identify their effects on composite properties and high temperature performance

Experimental Approaches

- Resin Chemical Characterization
  - HPLC
- Prepreg Evaluation
  - Rheometrics:
    - Torsion Rectangular; 4-ply, 1.25"×0.5"; 10 rad/sec, 1%γ
  - OM/SEM
- Composite Property/Performance
  - Panel evaluation and Process Optimization;
    - C-scan (5MHz), XRD, OM/SEM, Acid digestion, DMA
  - Isothermal Aging @ 650°F up to 400 hrs
    - Residual Properties: physical, thermal, mechanical

MATERIALS STUDIED

- Matrix Resin
  - PMR-II-50: Tg=~385°C (from G' of composites), Td=~530°C, ρ=1.44g/cm^3
- Carbon Fabric
  - M40JB (Toray): 6k-4HS, ρ=1.77g/cm^3, FAW=215g/m^2 E=377GPa (54.7Msi), ε_f=1.2%
  - M60JB (Toray): 6k-4HSρ=1.93g/cm^3, FAW=215g/m^2 E=588 (84.5Msi), ε_f=0.7%
  - T650-35 (Amoco): 3k-8HS, ρ=1.77g/cm^3, FAW=300g/m^2 E=241GPa (35Msi), ε_f=1.75%

MATERIALS STUDIED: Composites

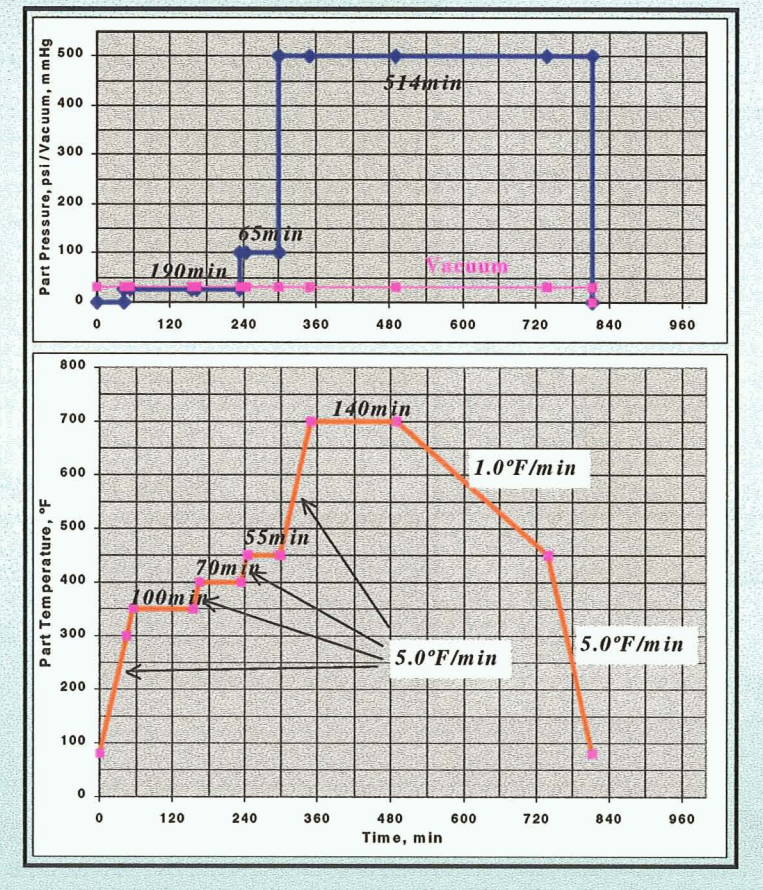
:[$0_f/90_f$] configurations; in compression-molding or Autoclave Cure

B-Staging and Conventional Cure

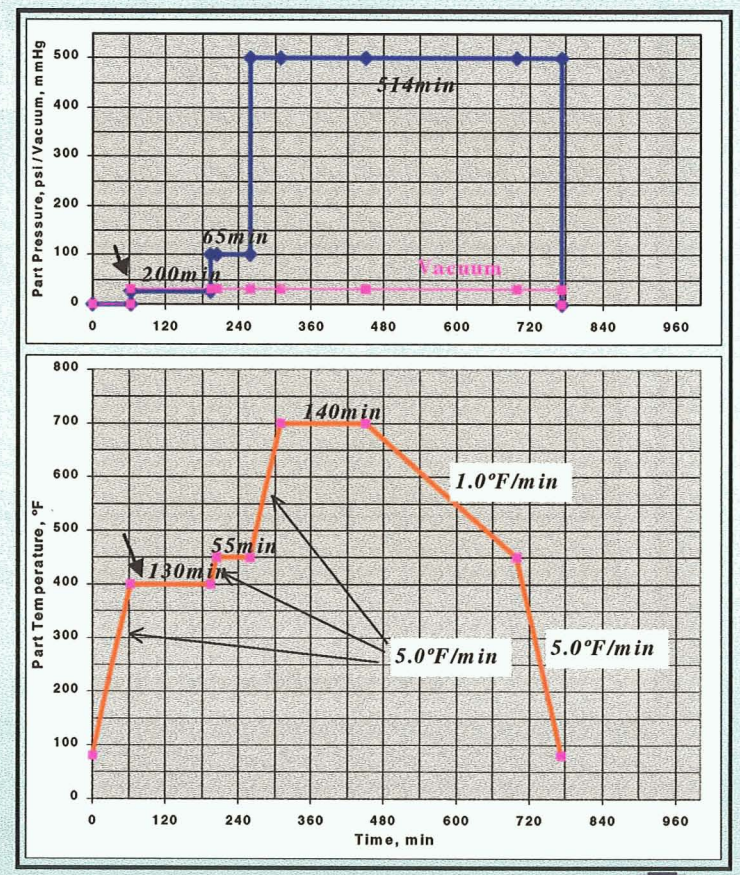
B--Staged @ 400°F for 1 hr in a metal mold

Post Cure Cycle

- ➢RT to 450°F in 2h, hold for 1 hr;
- ➢450 to 550°F in 2 h, hold for 1h;
- ➢550 to 600°F in 2 h, hold for 2;
- ➢600 to 700°F in 2h, hold for 16 h;
- ➢Cool to RT in Oven (for 4 hrs)

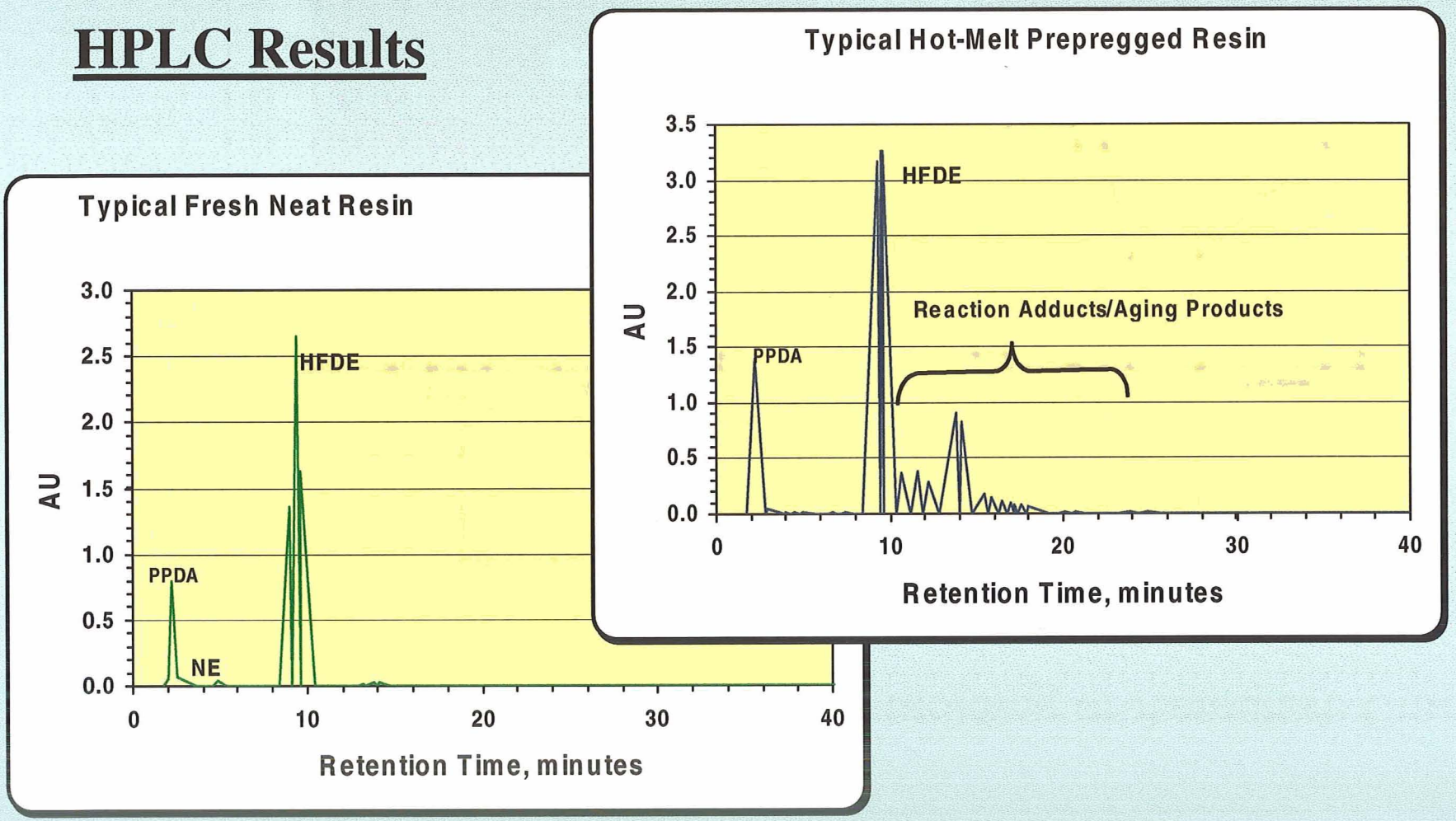


Combined B-Staging & Cure



RESIN CHEMICAL CHARACTERIZATION

HPLC Results



RESIN CHEMICAL CHARACTERIZATION

Summary of HPLC Analysis of Various PMR-II-50 Solutions

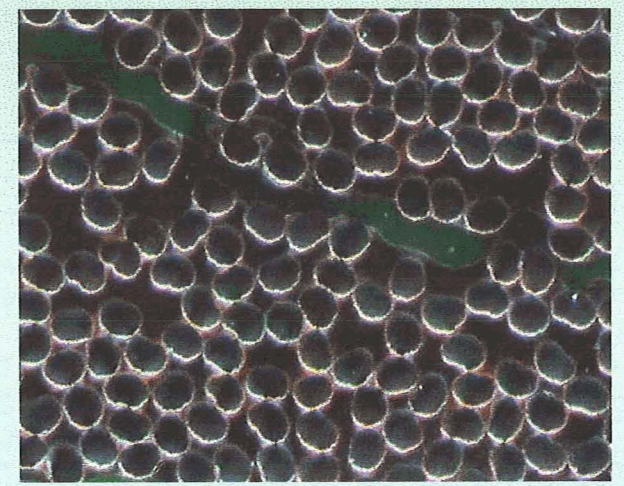
% Area (0.1% or higher only)				Normalized by HFDE, %			# of Aging Product/Adducts
PPDA	NE	HFDE	All Other Adducts	PPDA	NE	All Other Adducts	
1. Fresh Resin; Newly formulated w/ 50-60 wt% solid monomer content							
8.23	0.64	89.24	1.62	9.22	0.72	3.14	8
2. As-stored in Freezer (~1 year)							
6.57	0.67	85.31	7.1	7.70	0.78	8.51	11
3. Solvent-stripped resin for Hot-melt Prepregging to ~ 80wt% solid monomer content							
5.8	0.1	63.96	29.4	9.06	0.15	45.97	17
4. Solvent-stripped resin - aged in freezer for 2 months							
5	0.2	73.81	19.8	6.83	0.34	27.94	18
5. Solvent-stripped resin; thin film made by prepregging process							
4.51	0.09	71.36	23.67	6.33	0.13	33.17	19
6. Extracted Resin from Prepregs							
4	0.09	67.48	24.39	5.74	0.13	35.55	18

PREPREG EVALUATION

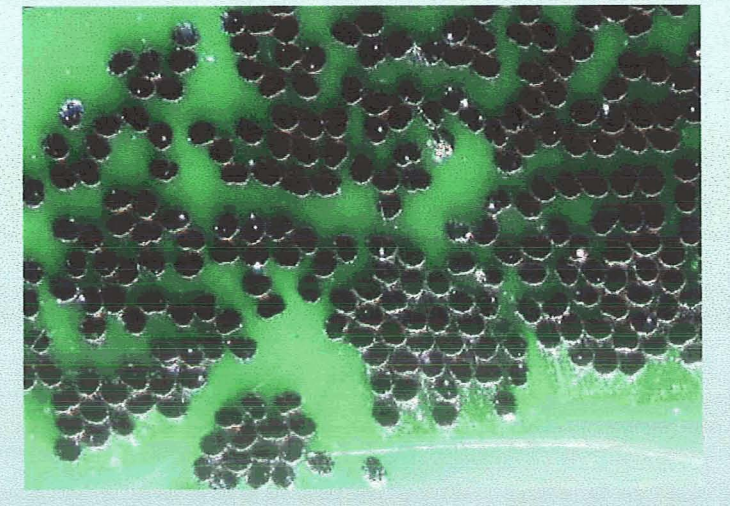
OM Cross-Sections of B-Staged M40JB Prepregs

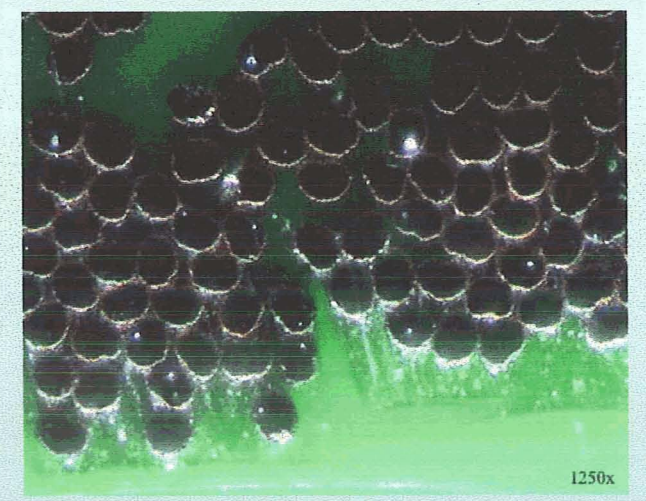
Solution Prepregs





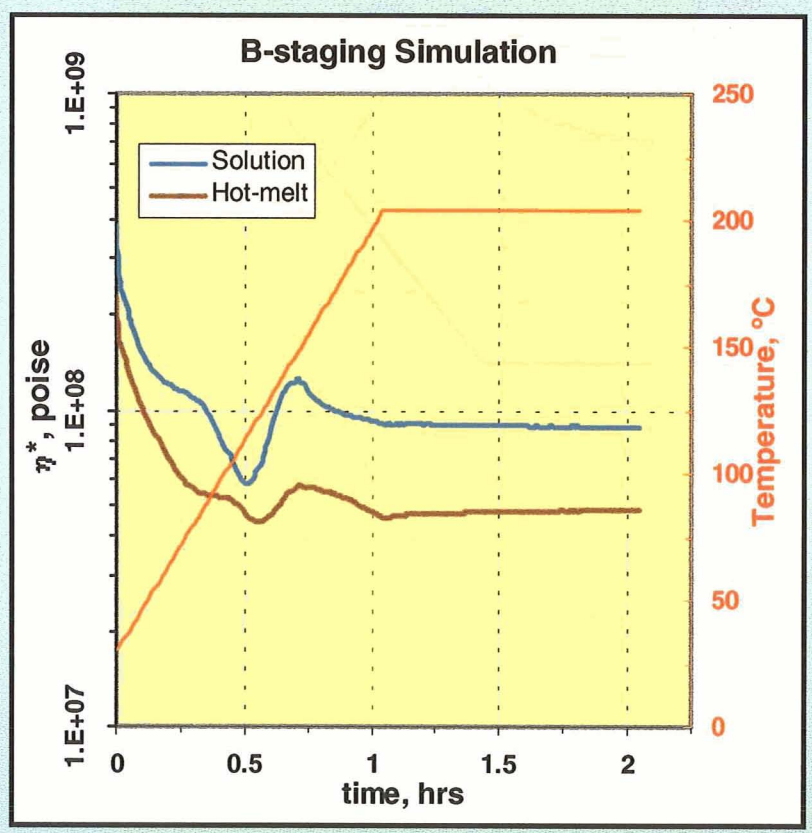
Hot-melt Prepregs

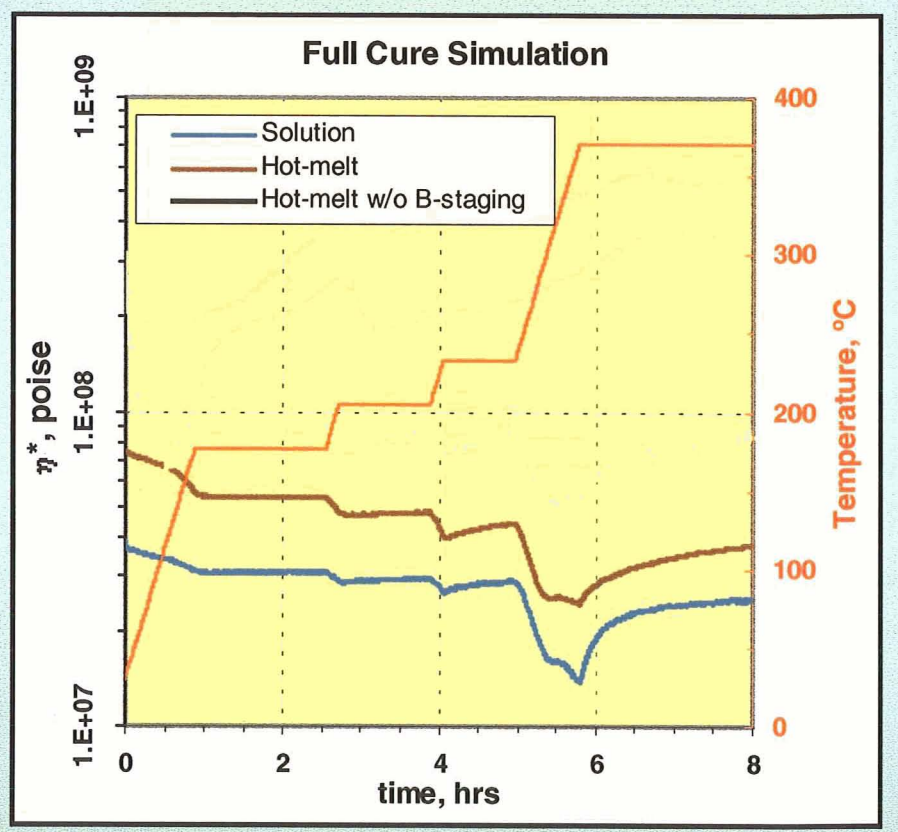




PREPREG EVALUATION

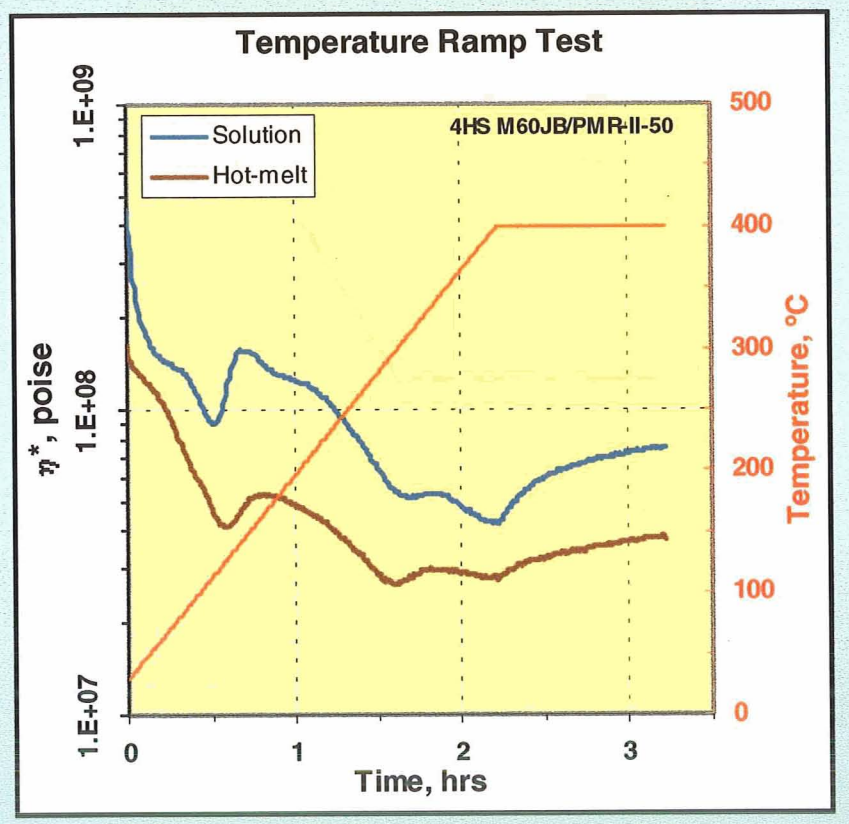
Dynamic Mechanical Analysis of 4HS M60JB/PMR-II-50 Prepreg Tape (Torsional rectangular Mode)

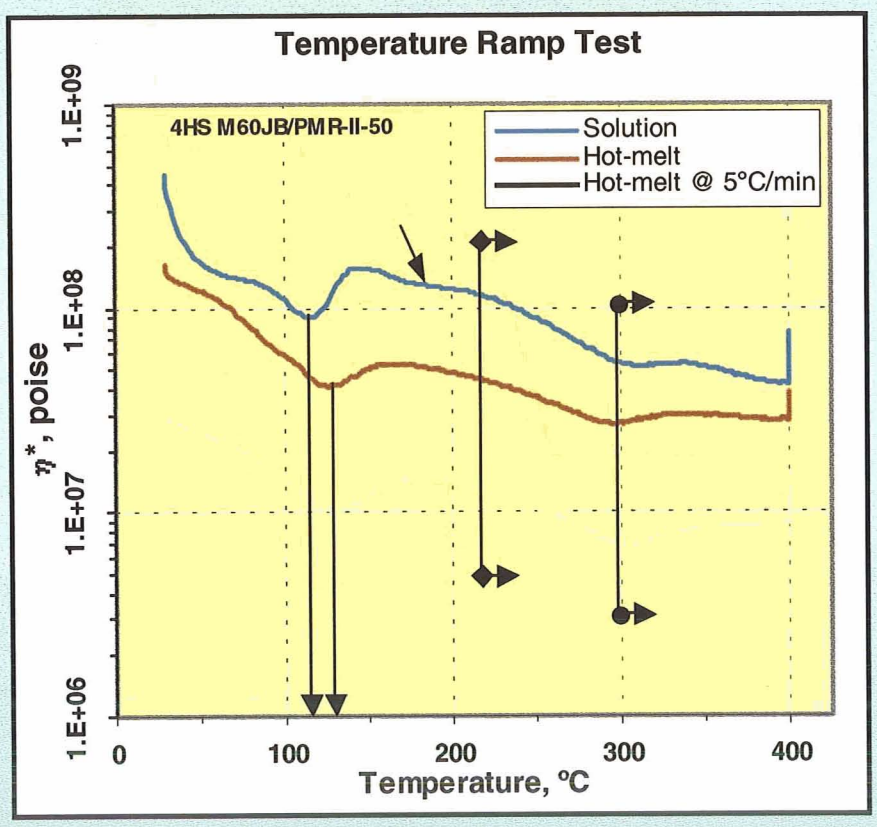




PREPREG EVALUATION

Dynamic Mechanical Analysis of 4HS M60JB/PMR-II-50 Prepreg Tape (Torsional rectangular Mode)

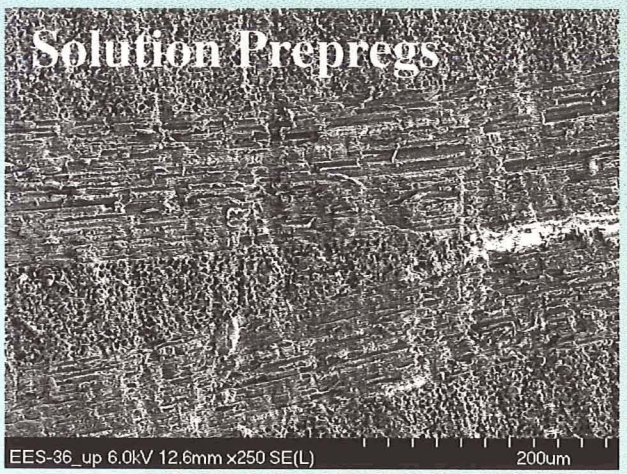


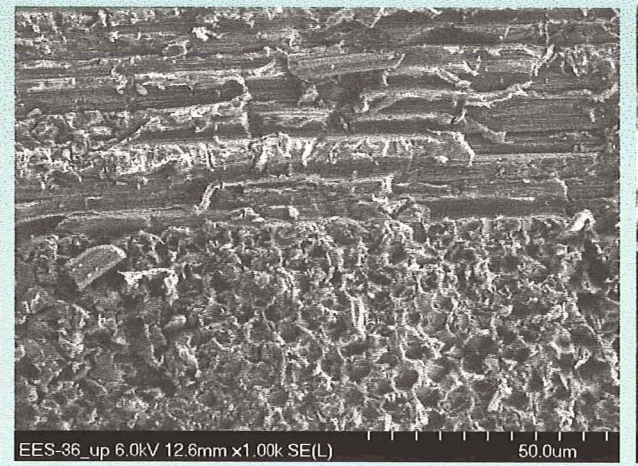


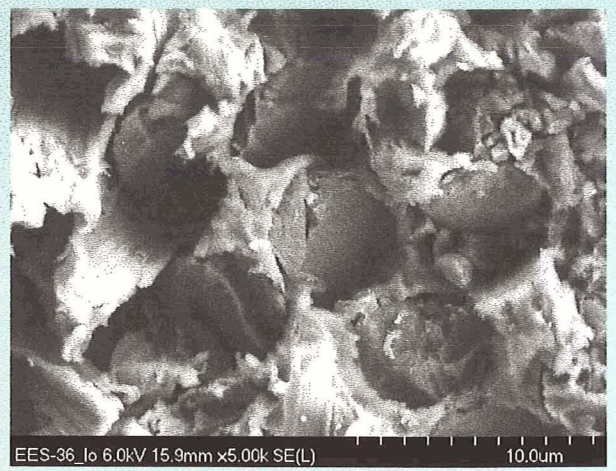
COMPOSITE FABRICATION/EVALUATION

SEM Cross-Sections of M40JB Composites (Waterjet-Cut)

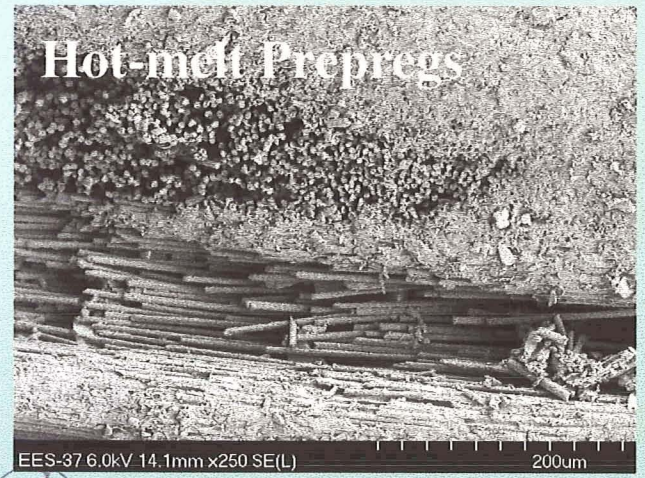
Solution Prepregs

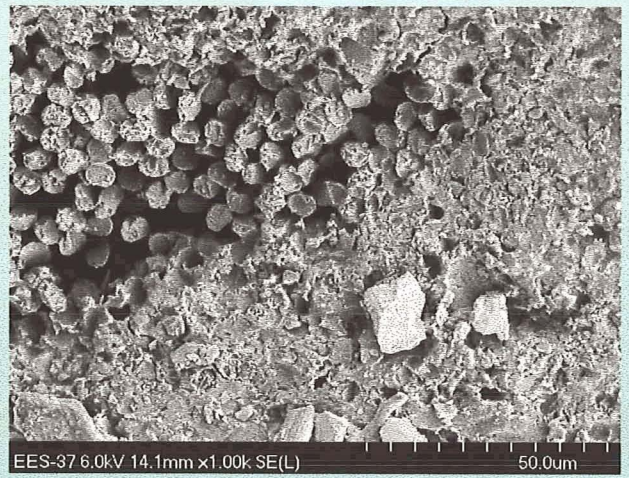


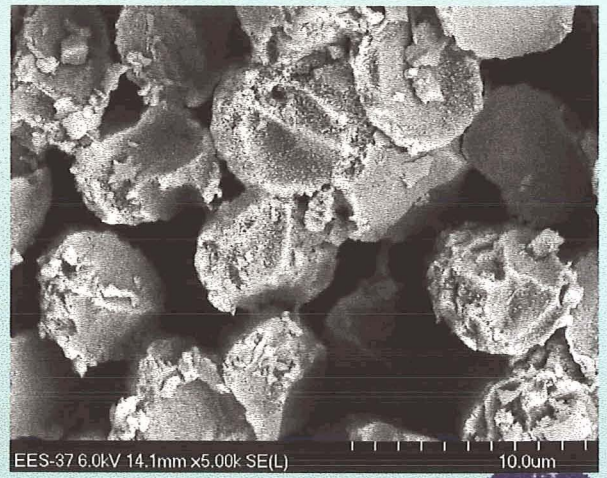




Hot-melt Prepregs

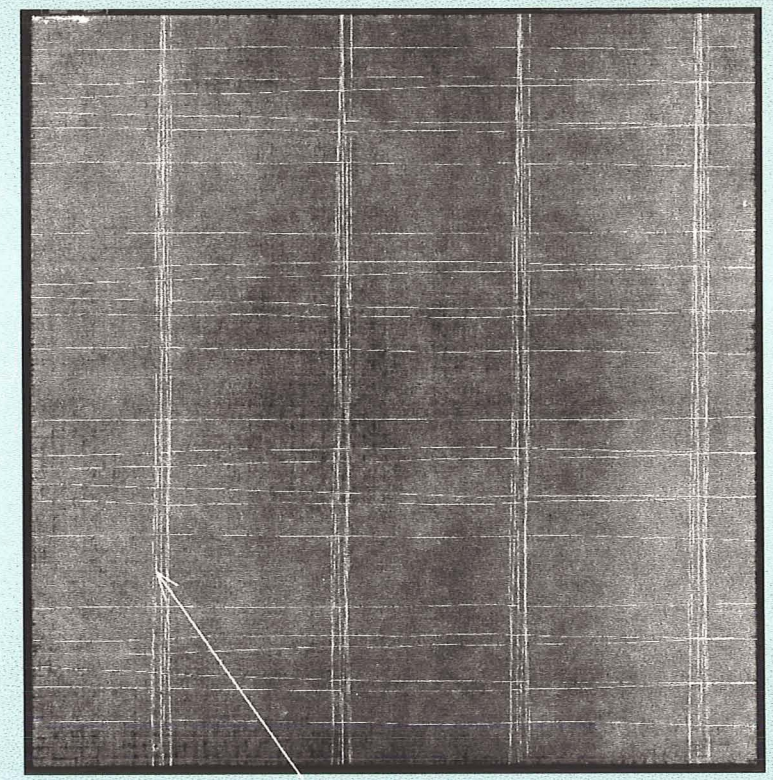






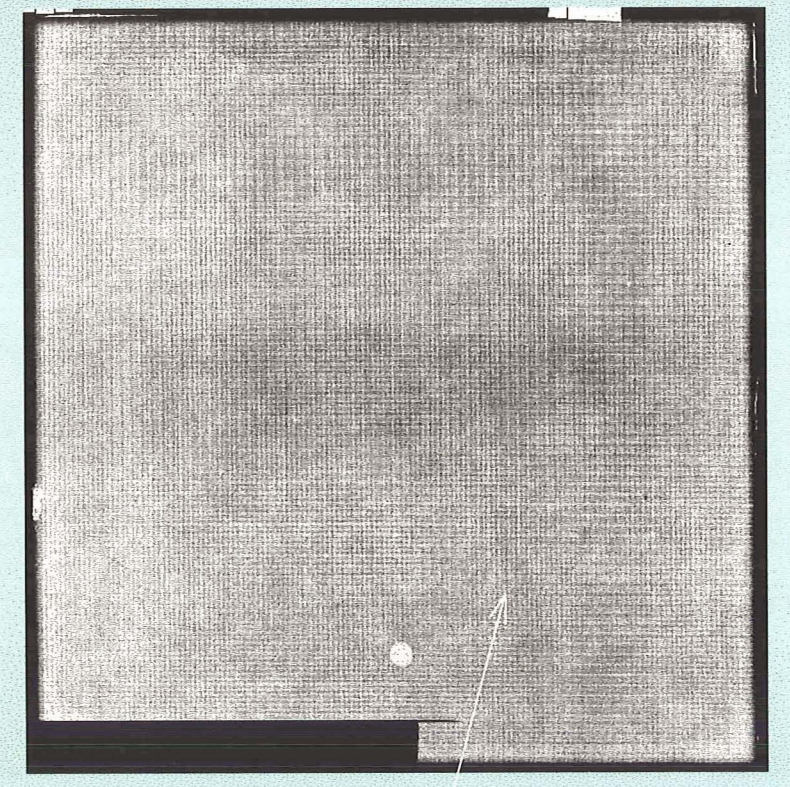
COMPOSITE FABRICATION/EVALUATION

X-ray (25kV) Image vs. Degree of Wetting



M40JB Panel w/ Solution Prepregs

Glass fiber tracers



w/ Hot-melt Prepregs

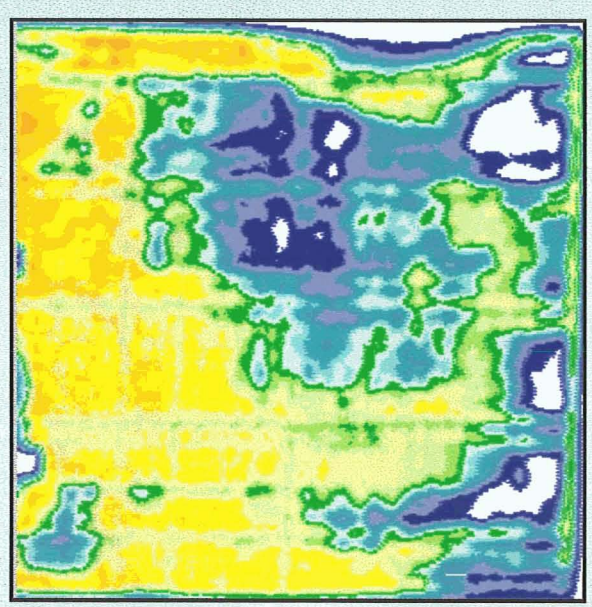
Carbon fibers

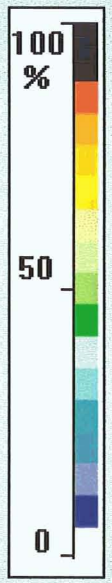
COMPOSITE FABRICATION/EVALUATION

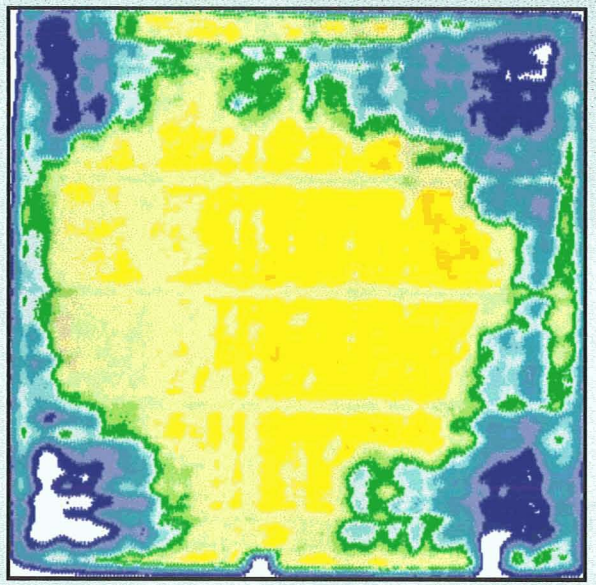
T650-35 Panels w/ Solvent Wet-Treated Prepregs

(Methanol sprayed @ 0.1 oz/m^2)

B-Staging and Cure







B-Staging Incorporated In Cure

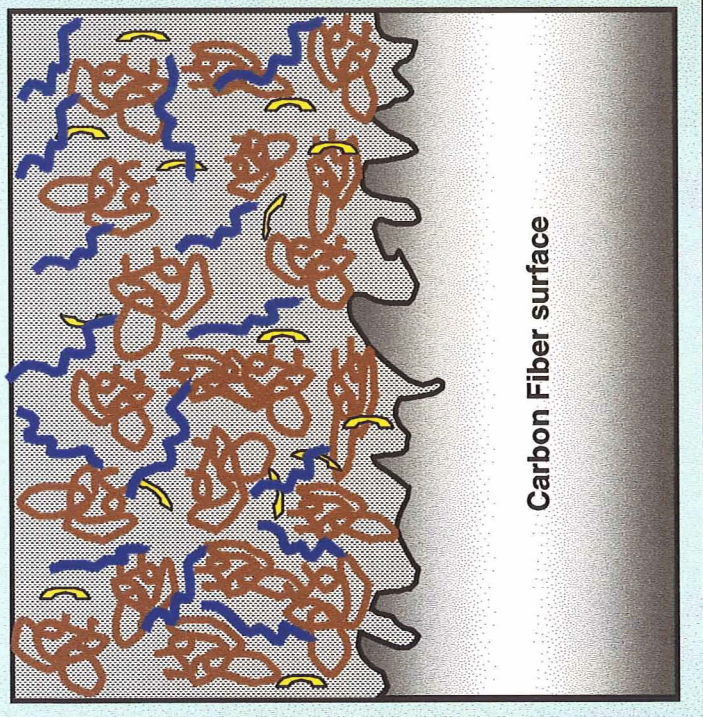
Void Content, %	Solution		Hot-melt		Hot-melt, Wet Treated	
Composite	Avg	S.D	Avg	S.D	Avg	S.D
M40JB, 12-ply	2.5	1.7	5.3	2.6		
M60JB, 12-ply	1.3	0.5	5.1	2.3		
T650-35, 8-ply	2.3	0.5	5.1	1.4	2.9	1.0

Thickness, in	Solution		Hot-melt		Hot-melt, Wet Treated	
Composite	Avg	S.D	Avg	S.D	Avg	S.D
M40JB, 12-ply	0.099	0.001	0.105	0.003		
M60JB, 12-ply	0.091	0.001	0.097	0.003		
T650-35, 8-ply	0.107	0.000	0.111	0.000	0.111**	0.000

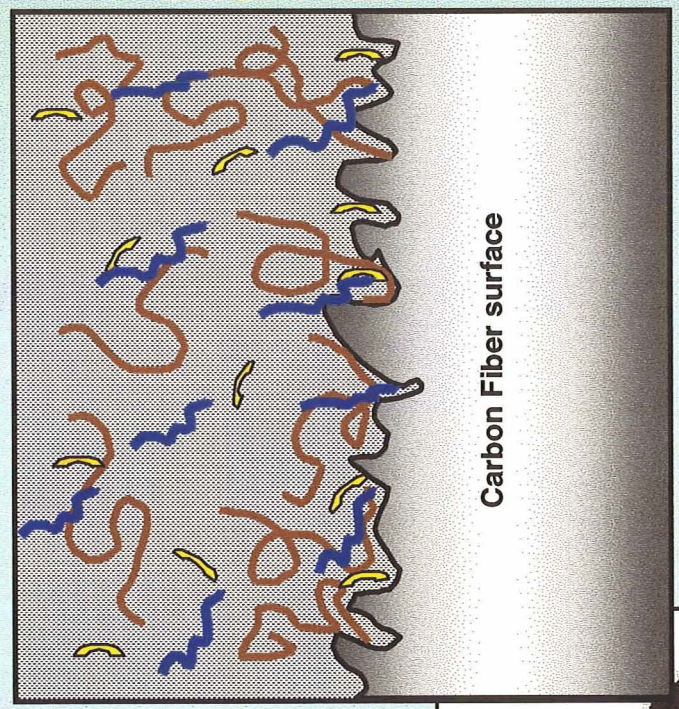
* All panels by same or similar T-P-t cure/postcure cycles

** higher FVF, 61% vs. 58%

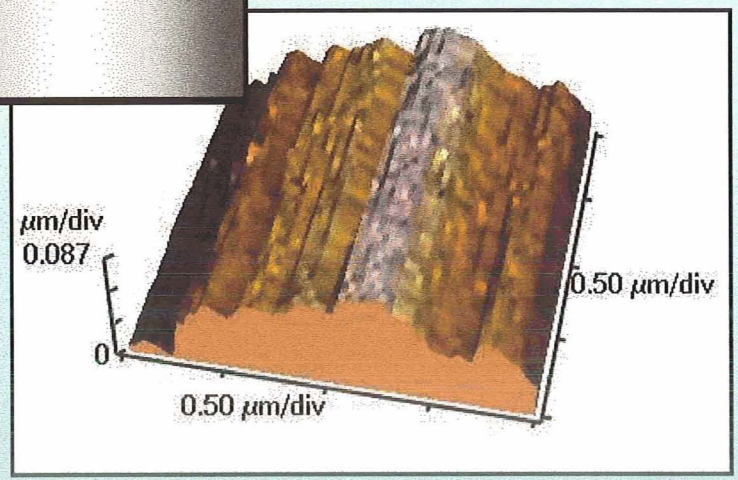
MOLECULAR LEVEL WETTING



High Mononer Solid Concentration in Hot-melt Prepregging



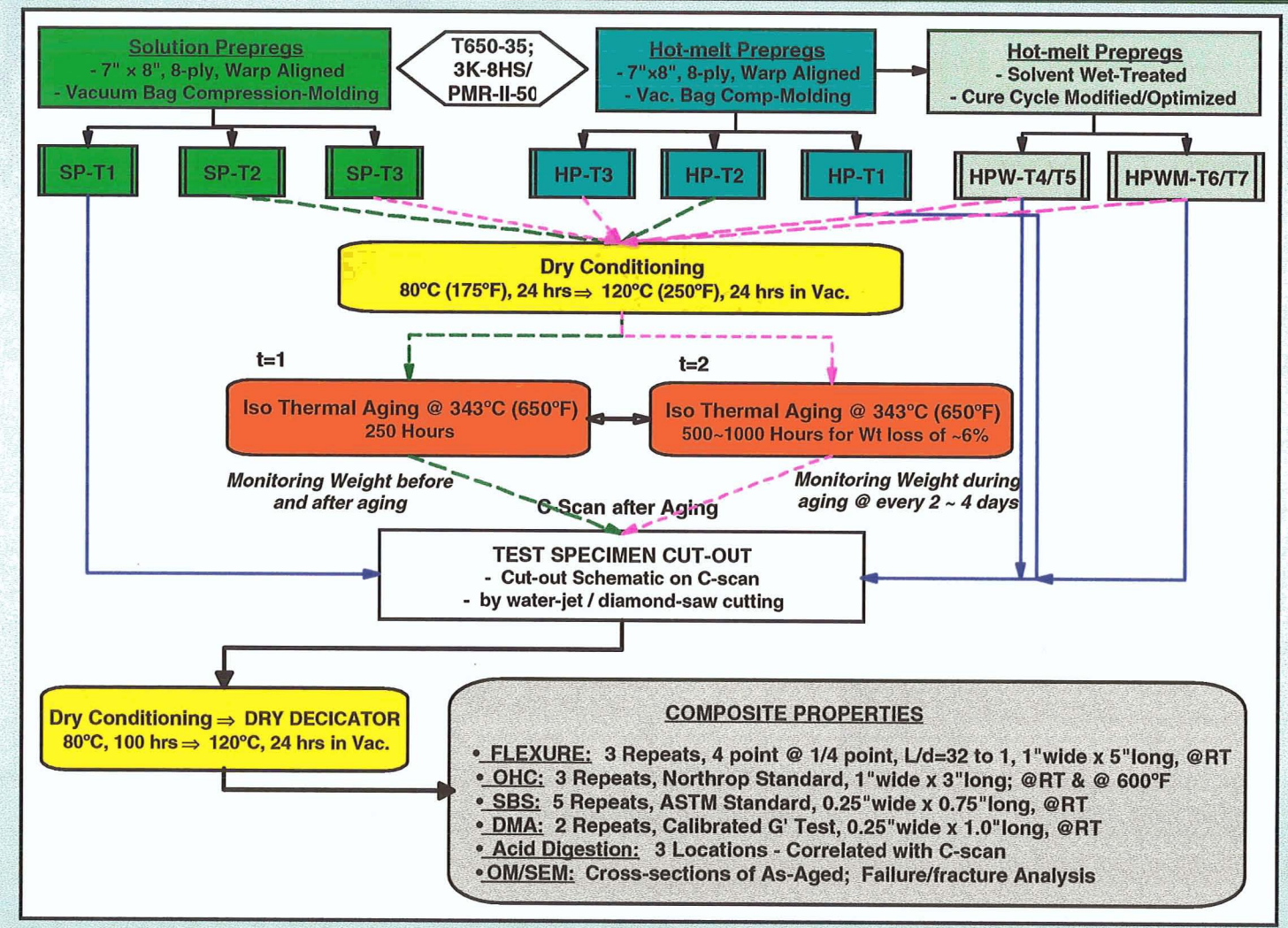
Low Mononer Solid Concentration in Solution Prepregging



M Carbon Fiber Surface by AFM

COMPOSITE PROPERTY/PERFORMANCE

Overall Program Plan: the Effects of Interface Wetting on Composite Properties & High Temperature Durability



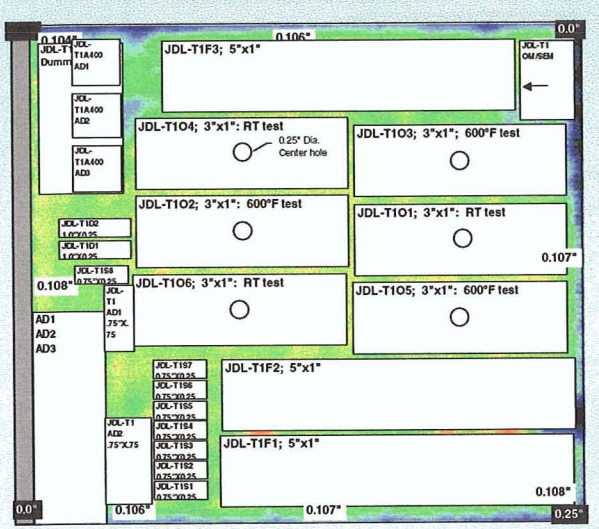
COMPOSITE PROPERTY/PERFORMANCE

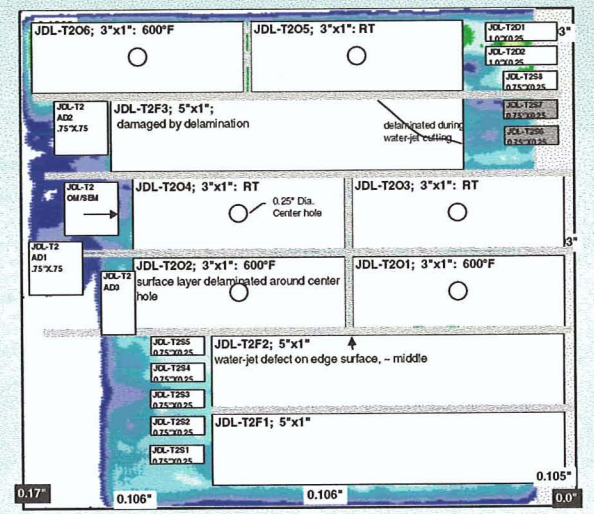
Un-aged Control

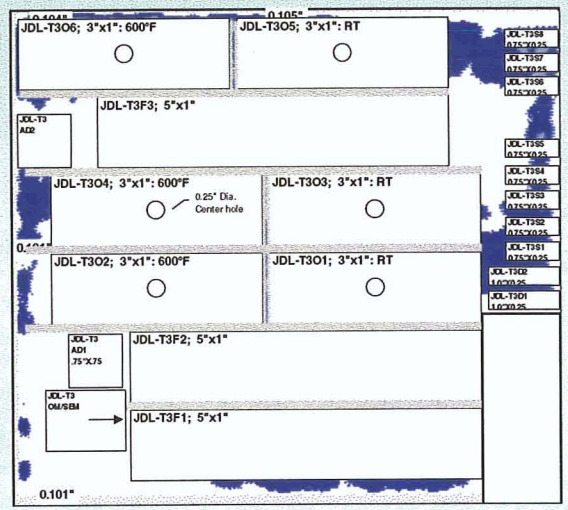
After 250 h @ 650°F

After 400 h @ 650°F

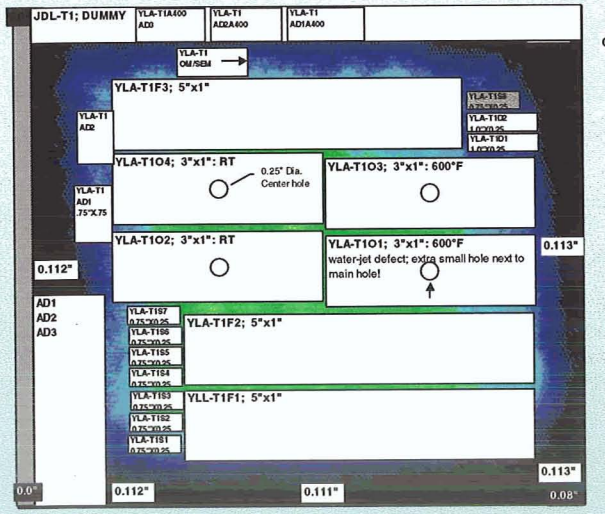
Solution

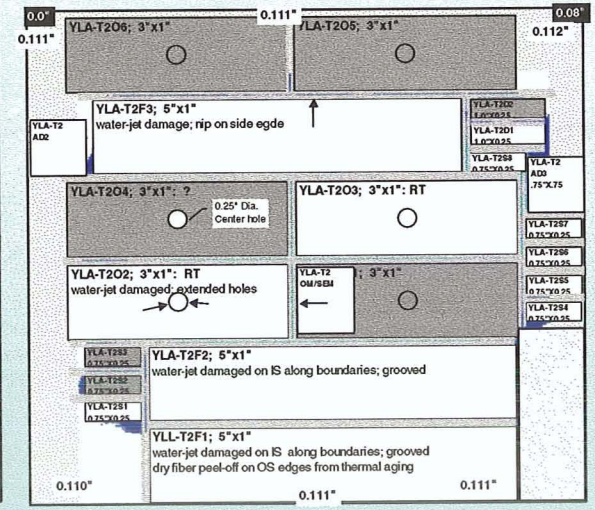


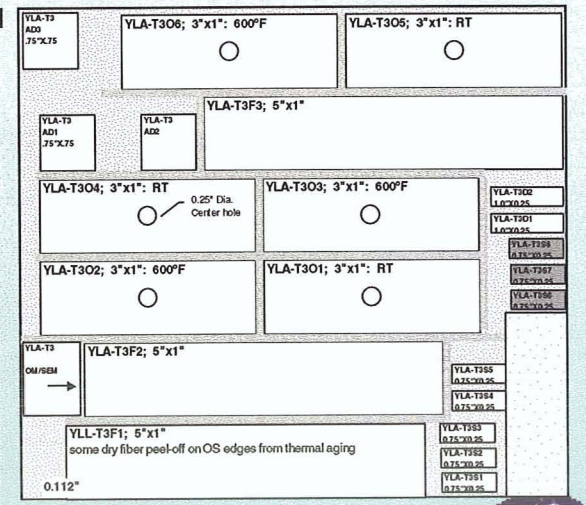




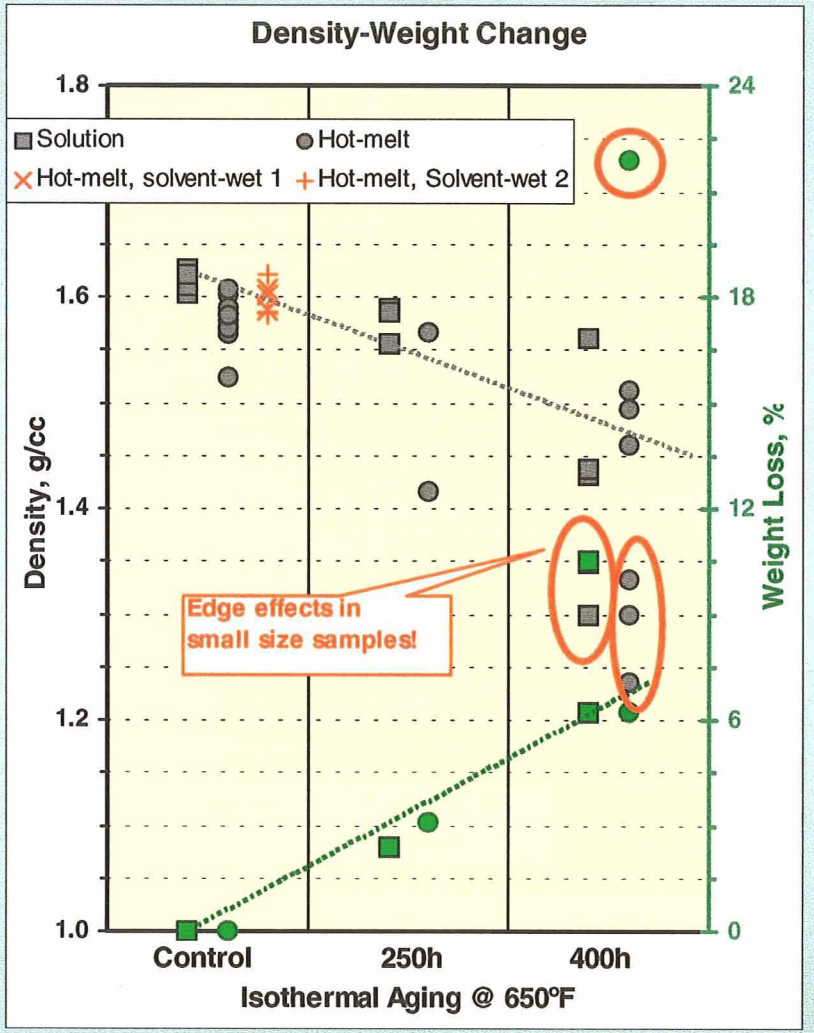
Hot - melt

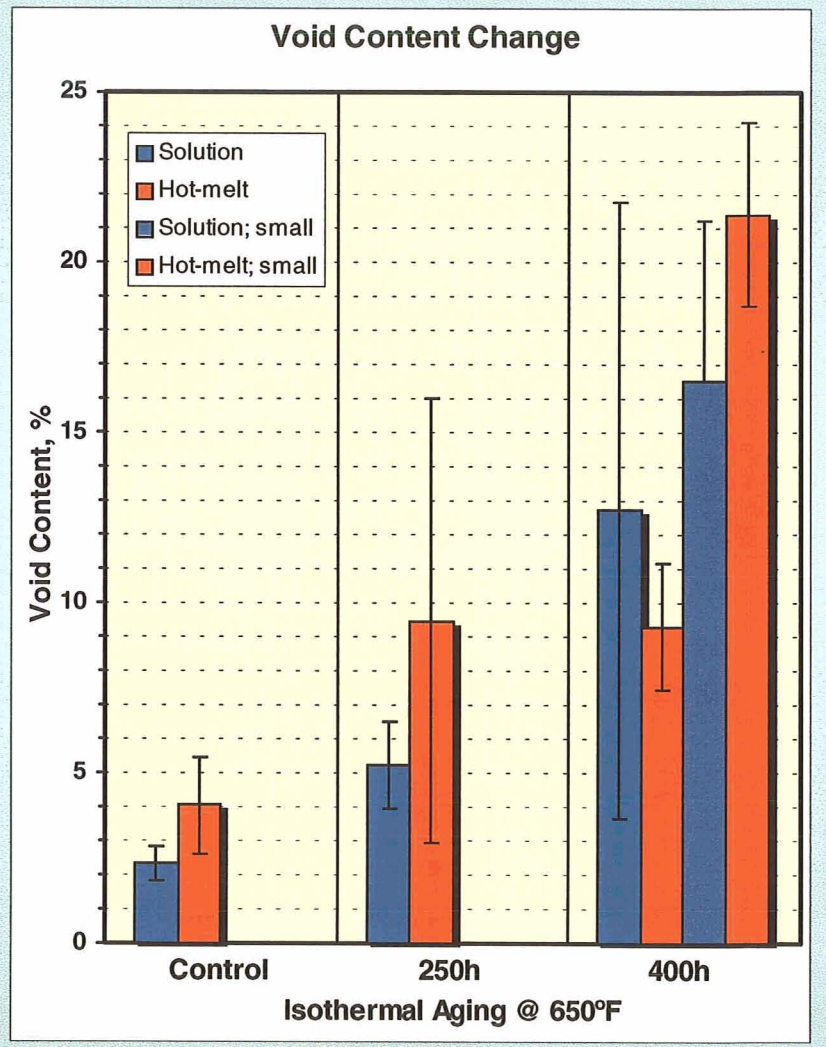




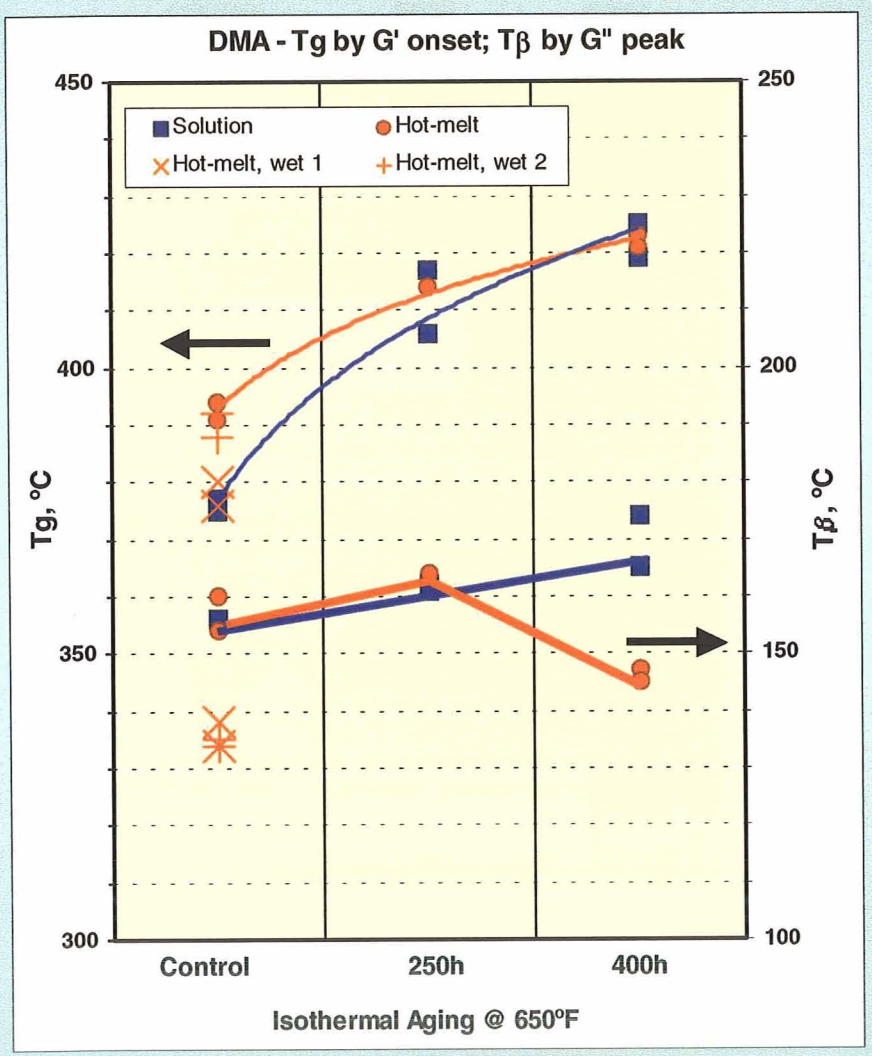


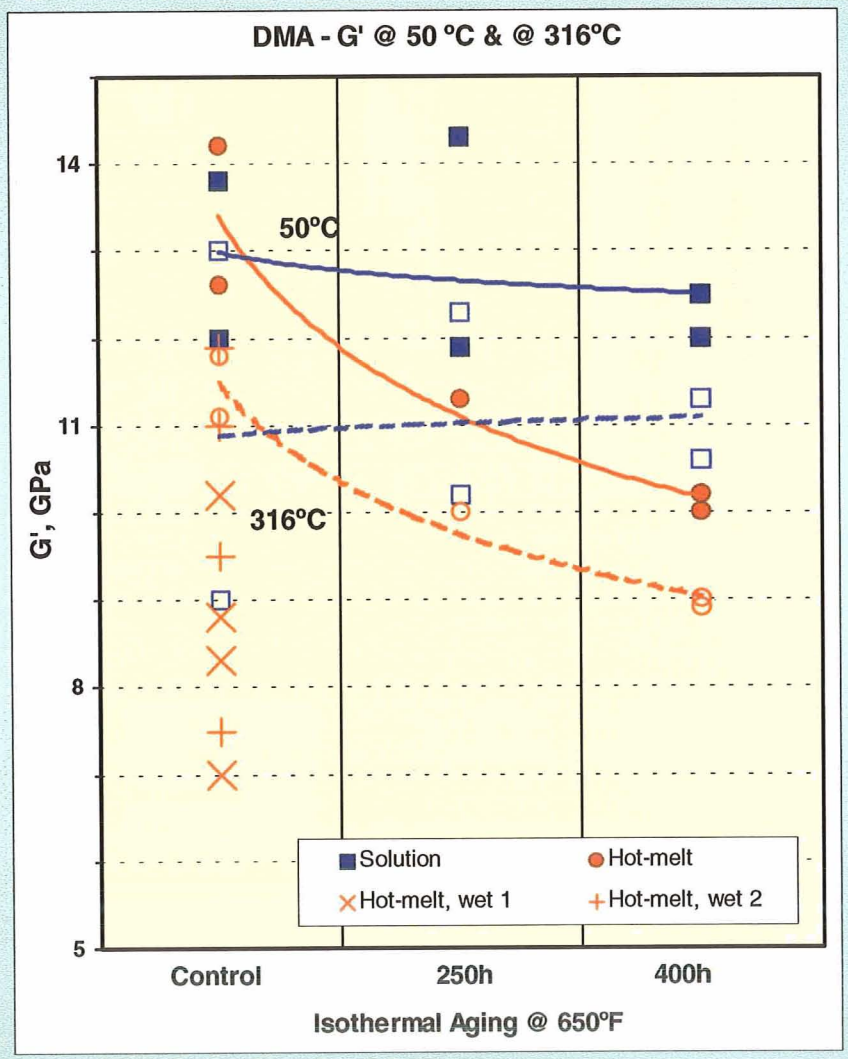
COMPOSITE PROPERTY/PERFORMANCE



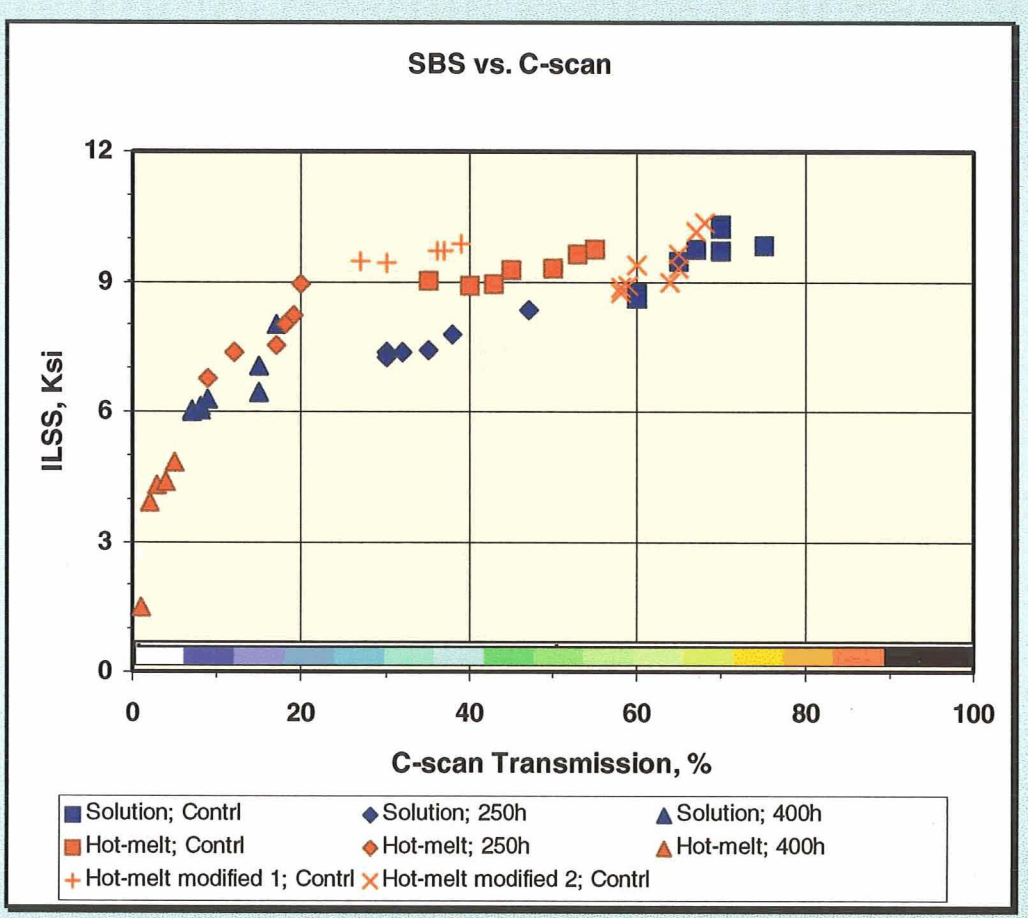


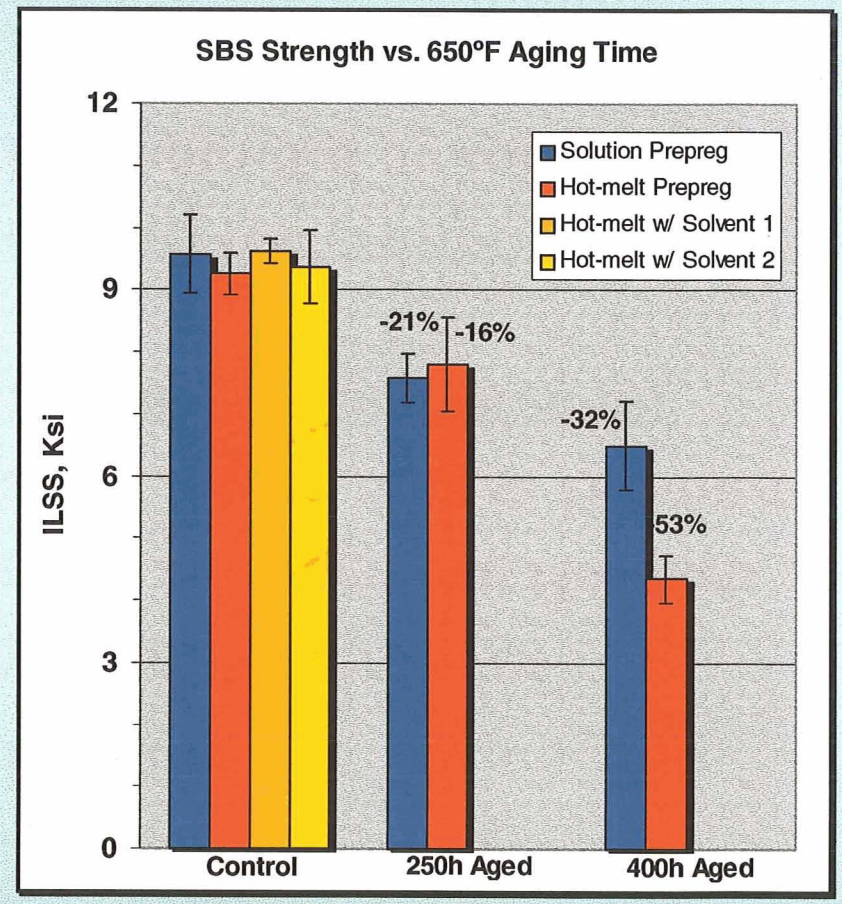
COMPOSITE PROPERTY/PERFORMANCE





COMPOSITE PROPERTY/PERFORMANCE





SUMMARY & CONCLUSIONS

- Developed a systematic, multi-team effort… in HTPMCs for Access to Space Program.
- Characterized the prepreg differences in terms of
  - Resin chemical aging characteristics: more aging in Hot-melt
  - Prepreg physical, rheological characteristics: drier in Hot-melt
  - Composite physical, structural/mechanical characteristics: inferior in Hot-melt
- Identified the controlling mechanism for composite quality: Fiber-resin interface wetting controlled by solution viscosity
- Poor wetting resulted in severer property degradation.

Future Studies

- Optimization of Hot-melt prepregging process
  - Quantifying the degree of wetting as a function of solution viscosity (solid monomer conc.) and process time-temperature,
  - Modifying prepregging processes, e.g., gap of nip rolls, roll pressure and/or Temperature, or other mechanical modifications
  - Alternative solvent system, e.g., isopropanol for possibly wider viscosity window and aging resistance
- Optimization of cure cycle based on η-T-t-P modification

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