HIGH TEMPLE *WORKSHOP 22*
21 – 24 JANUARY, 2002, Santa Fe, New Mexico

Presentation Title: "Evaluation of Graphite Fiber/Polyimide PMCs from Hot Melt vs Solution Prepreg"

Authors: E. Eugene Shin[1], James K. Sutter[2], Howard Eakin[2], Linda Inghram[1], Linda McCorkle[1], Dan Scheiman[3], Demetrios Papadopoulos[4], John Thesken[1] --- *NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH 44135*
[1] Contract via. OAI; [2] C/S NASA; [3] Contract via. QSS; [4] Contract via. U. of Akron;
Jeffrey E. Fink --- *Boeing-Rocketdyne Division, 6633 Canoga Park Av, MS AC-67, Canoga Park, CA 91309-7922*

Submitted by: E. Eugene Shin

Address: Ohio Aerospace Institute - NASA Glenn Research Center
21000 Brookpark Rd., MS 49-1
Cleveland, Oh 44135
Tel: 216-433-2544, Fax: 216-977-7132
E-mail: E.Eugene.Shin@grc.nasa.gov

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.

OAI

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

E. Eugene Shin[1], James K. Sutter[2], Howard Eakin[2], Linda Inghram[1], Linda McCorkle[1], Dan Scheiman[3], Demetrios Papadopoulos[4], John Thesken[1] --- *NASA Glenn Research Center, 21000 Brookpark Rd., MS49-1, Cleveland, OH 44135: [1] OAI; [2] NASA-GRC; [3] QSS; [4] U. of Akron;*

Jeffrey E. Fink --- *Boeing-Rocketdyne Division, Canoga Park, CA*

Tel: 216-433-2544, Fax: 216-977-7132, E-mail: E.Eugene.Shin@grc.nasa.gov

High Temple Workshop XXII

21 – 24 JANUARY, 2002, Santa Fe, New Mexico

* Sponsored by NASA-GRC HOTPC, Carol A. Ginty/James K. Sutter

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

Application of HTPMC for Acess to Space: Validations

Materials & Process Selection

Material Variables & Optimization ↔ **Process Variables & Optimization** ↔ **Design Variables & Optimization**

Matrix Resin
- PMR-II-50 vs Newer resin
- Nanoparticle Filled

Fiber Types & Sizing
- T650-35
- M40j vs. M60j
- Sized vs. De-sized

Prepreg Preparation
- Hot melt
- Solution Cast

Composite Fabrication
- Hand-Layup; Vacuum Bagging
- Resin Infusion/RTM

Reinforcement Architecture
- Woven Fabric Laminate;2D;3D
- Uni-Tape Laminate (0°/90°)
- **Stitched Fabric/Uni-Tape**
- **Hybrid/Honeycomb/C-Foam Sandwitch**

Test Structure
- Flat Panel in diff. thicknesses
- Subscale Component
- Actual Full Scale Component

STIFF; LIGHT; HIGH Tg

Performance-Durability Evaluation

Base Property Data ↔ **Potential Degadation Mechanisms** ↔ **In-Service Exposure Simulation Core Programs**

Constituents Property
- Neat Resin:
- Fiber:
- Sizing vs. Surface Treatment

Composite Property
- Physical: FVF, Void Vol., Resin wt%, Moist Diffusivity, Density, C-scan
- Thermal: T_g, T_B, TGA Wt loss, E' (DMA), Thermal Conductivity
- Mechanical: E, σ_f ε_f in Tensile, Comp, In-plane & Interlaminar Shear, and Fatigue as a fn of T

Exposure Conditions
- T_{max} (600°F)
- Heating/Cooling Rate (~200°F/s)
- RH%; - O_2, O_3 and other gas
- Pressure induced σ

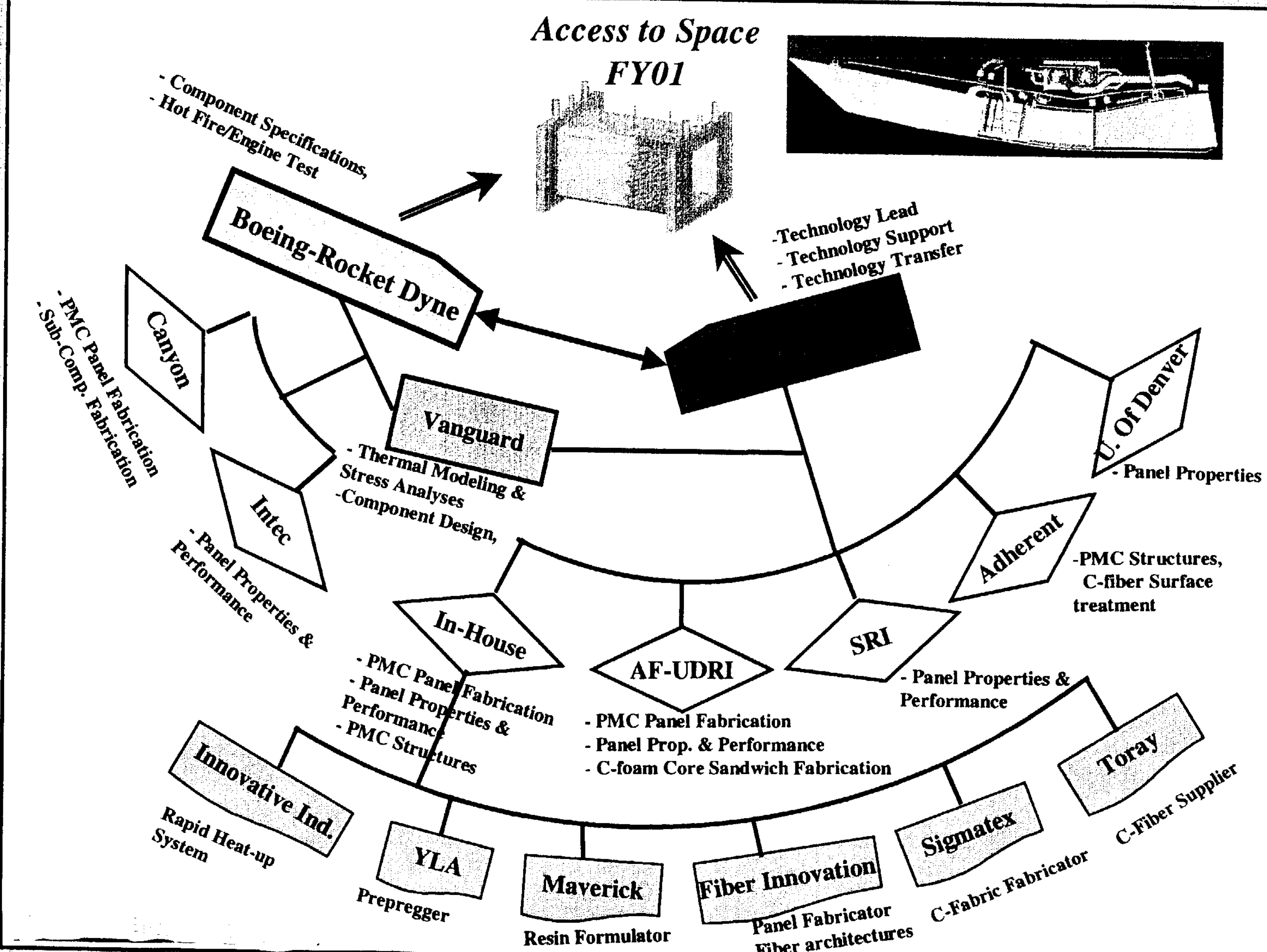
Potential Degradation
- Hygrothermal Induced Blistering
- Residual Solvent or Thermal Decomposition Induced Blistering
- Hydrolytic Chemical Degradation
- Thermo-Oxidative Degradation
- Residual Stress & CTE Mismatch Induced Cracking/Failure
- TMF-Induced Degradation
- Rapid Cooling Induced Ice Formation

Performance
- In-Service Realtime Tests
  - At-Temperature Tests as a fn of dT/dt, T, t_{dwell} in Tension, Compression, & Shear
- Property Retention Tests
  - Iso-Hygrothermal Exposures as a fn of T & RH%
  - Thermal Cycling as a fn of dT/dt, RH%, # of cycles
  - TMF as a fn of σ and dT/dt

Durability/Aging of Optimum Sys.
- Longer Term-Real Time Exposure
- Accelerated Tests

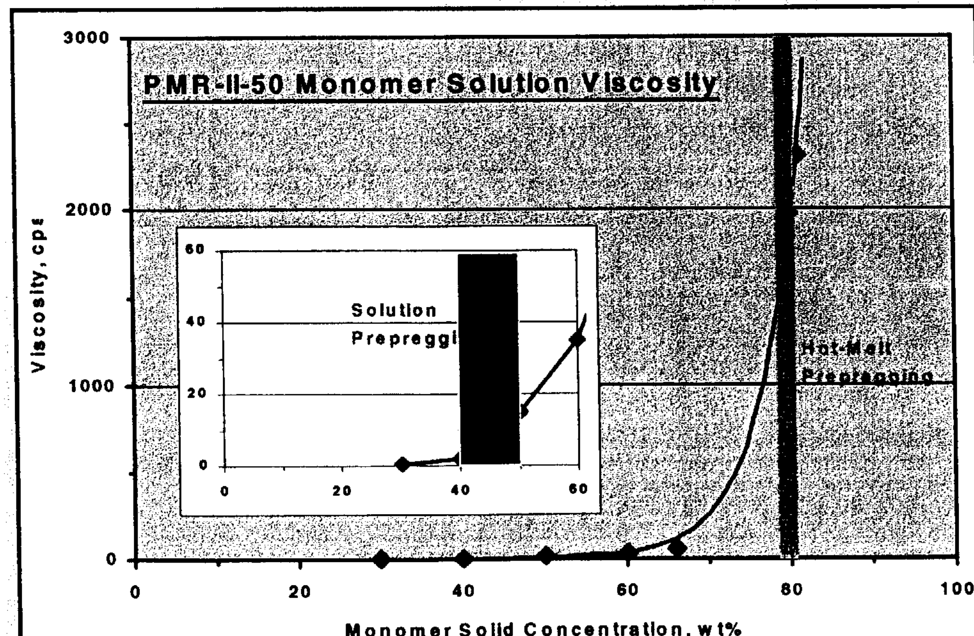
Sub and Full Scale In-Service Demonstration

CURRENT ACTIVITIES

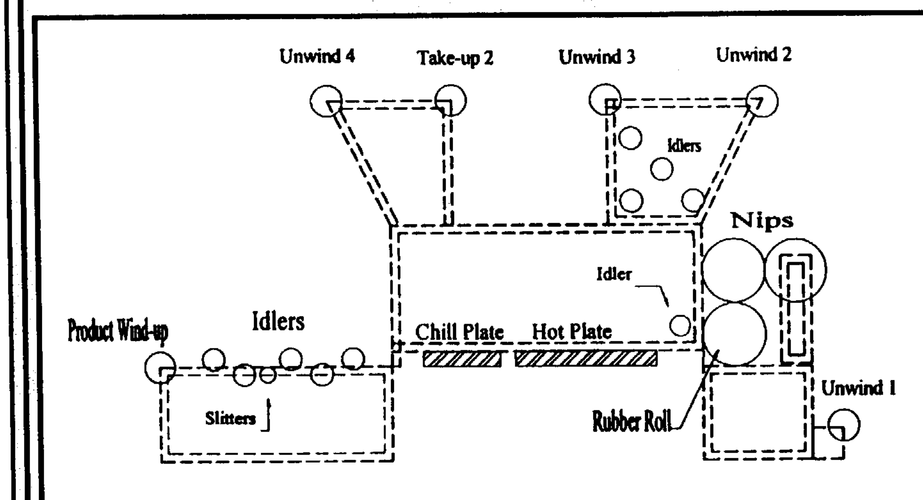


PREPREG STUDY: BACKGROUND

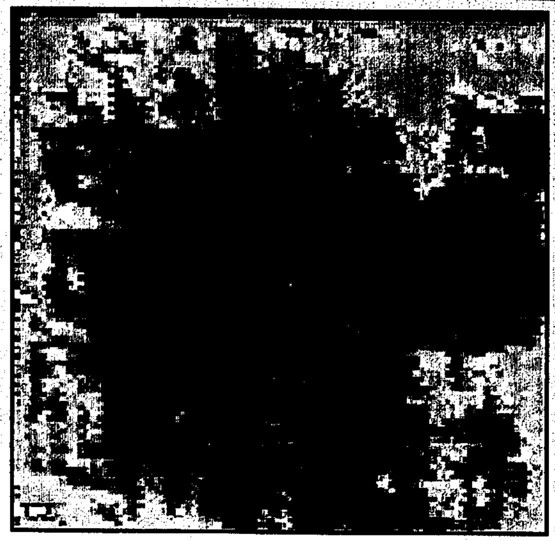
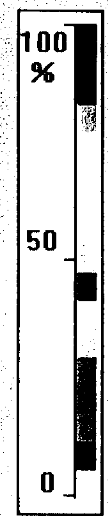
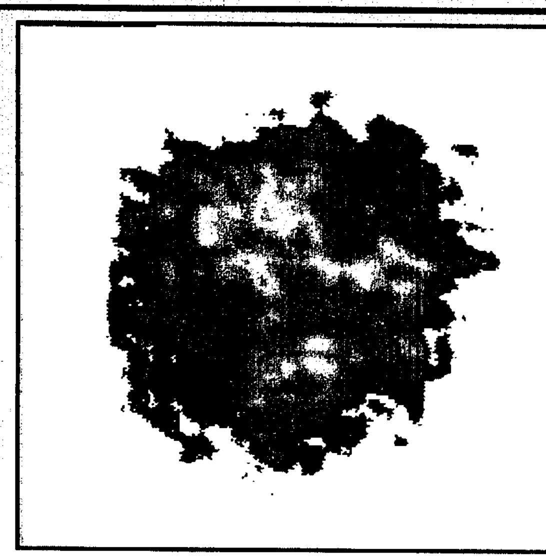
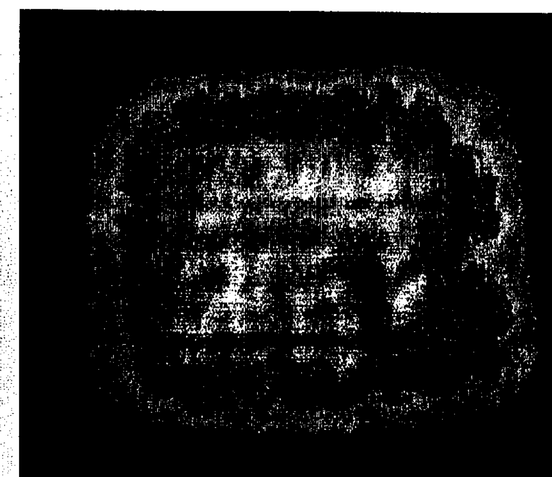
- Solution Prepregging
  - Conventional, available from lab scale to large production,
  - Easier process control



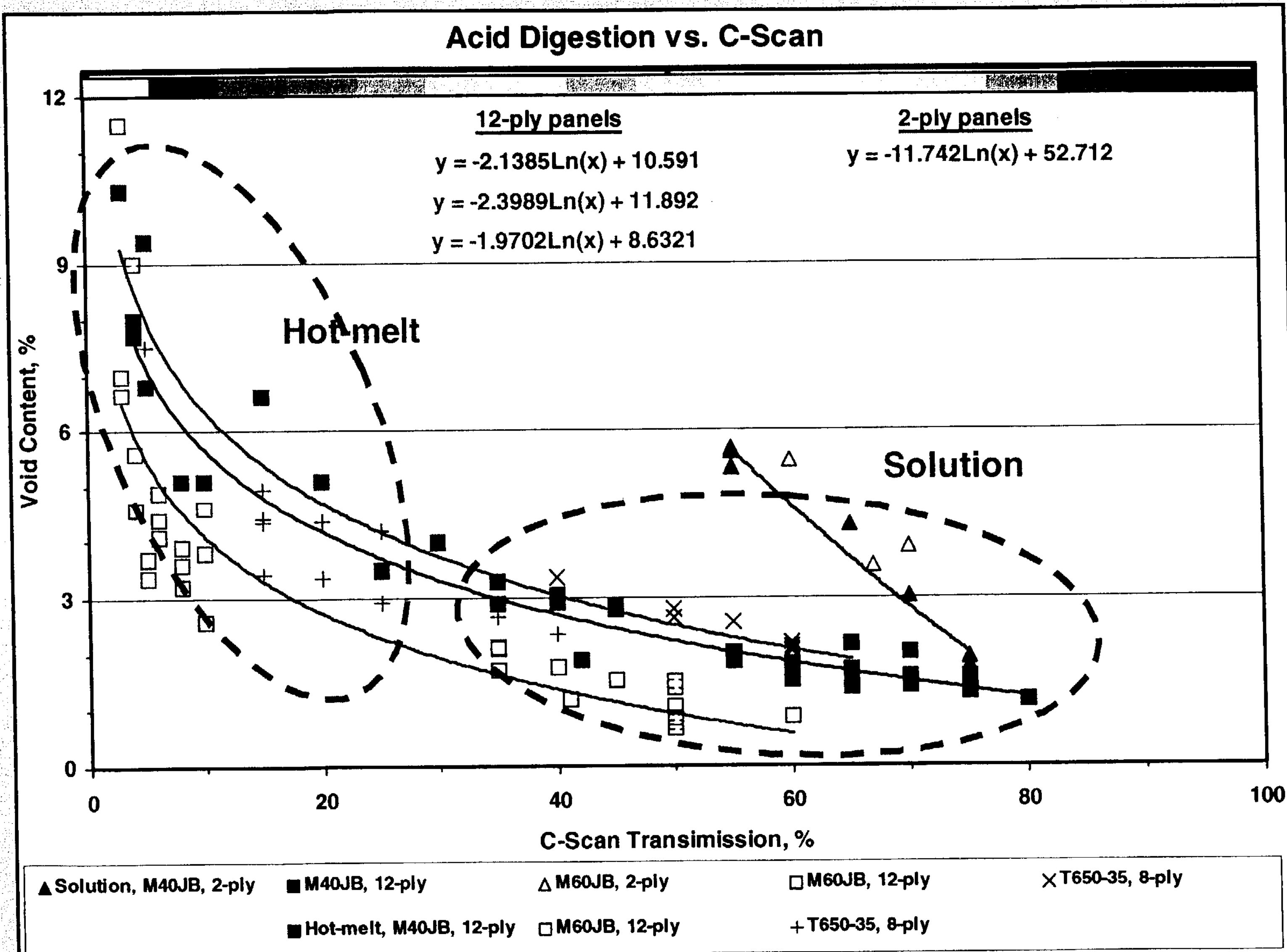
- Hot-Melt Prepregging
  - Environmentally friendlier,
  - Less residual solvent,
  - More uniform resin distribution



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
  - <u>M40JB (Toray):</u> 6k-4HS, ρ=1.77g/cm^3, FAW=215g/m^2 E=377GPa (54.7Msi), ε_f=1.2%
  - <u>M60JB (Toray):</u> 6k-4HSρ=1.93g/cm^3, FAW=215g/m^2 E=588 (84.5Msi), ε_f=0.7%
  - <u>T650-35 (Amoco):</u> 3k-8HS, ρ=1.77g/cm^3, FAW=300g/m^2 E=241GPa (35Msi), ε_f=1.75%

MATERIALS STUDIED: Composites

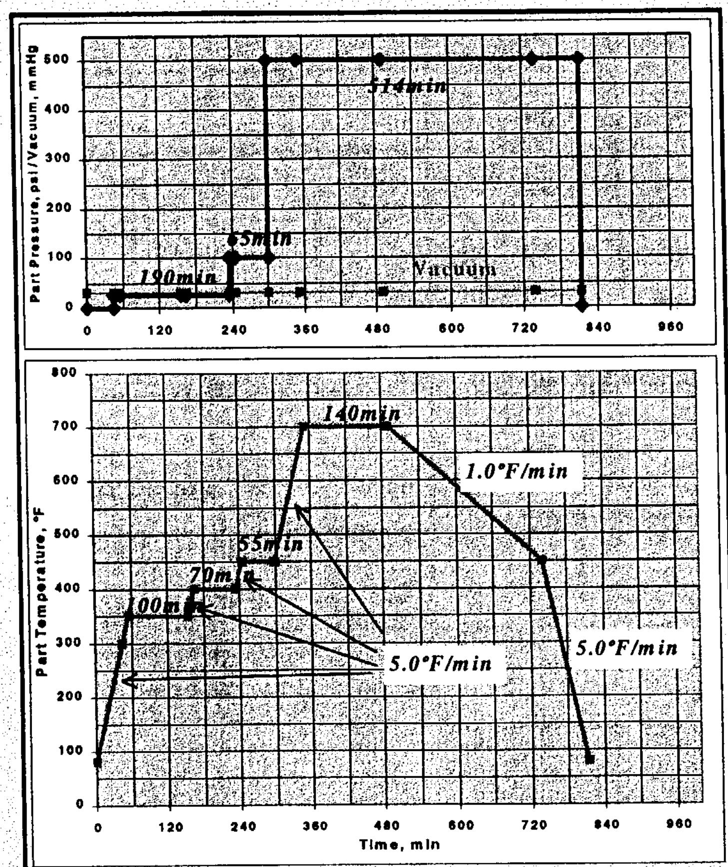
:[$0_f/90_f$] configurations; in compression-molding or Autoclave Cure

B-Staging and Conventional Cure

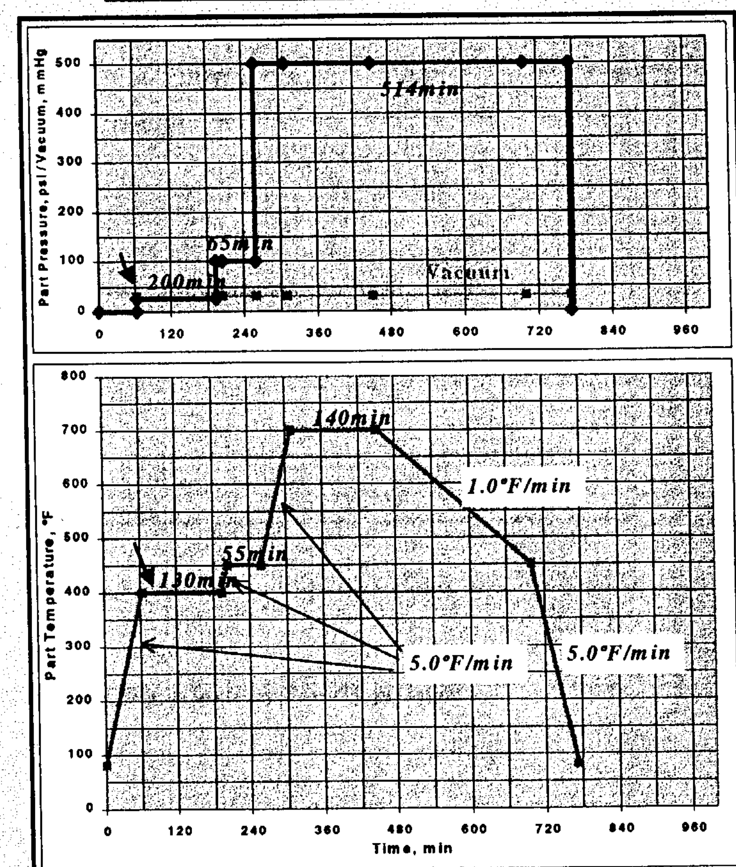
B--Staged @ 400°F for 1 hr in a metal mold

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)

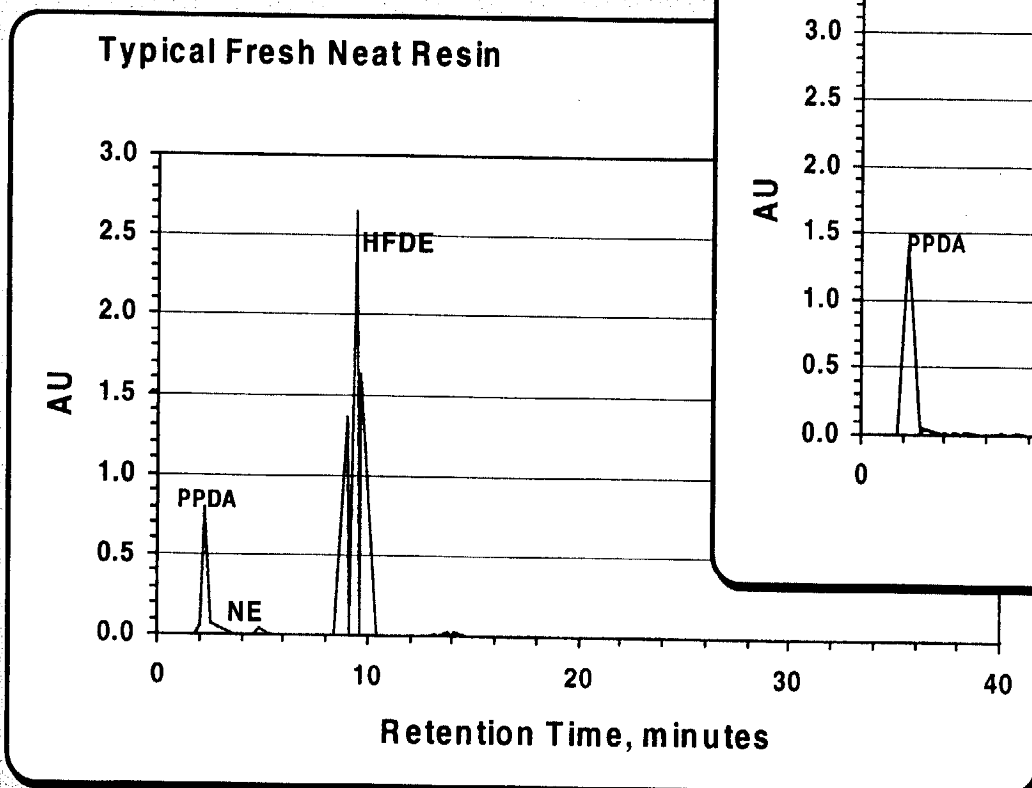


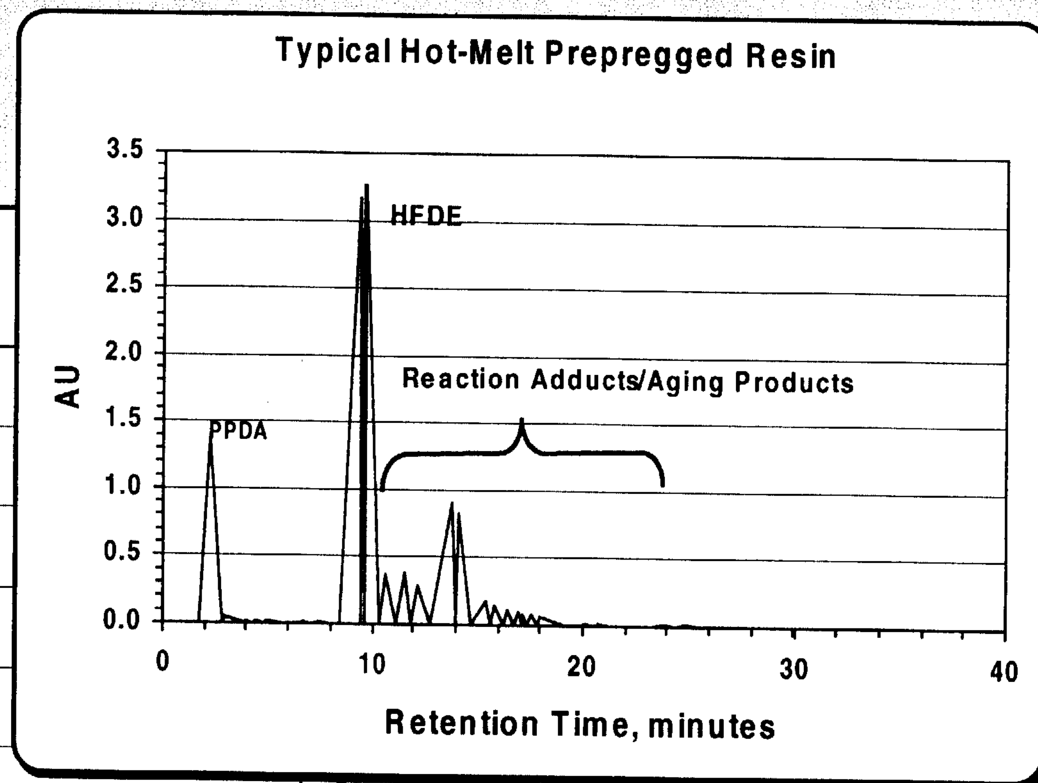
Combined B-Staging & Cure



RESIN CHEMICAL CHARACTERIZATION

HPLC Results





RESIN CHEMICAL CHARACTERIZATION

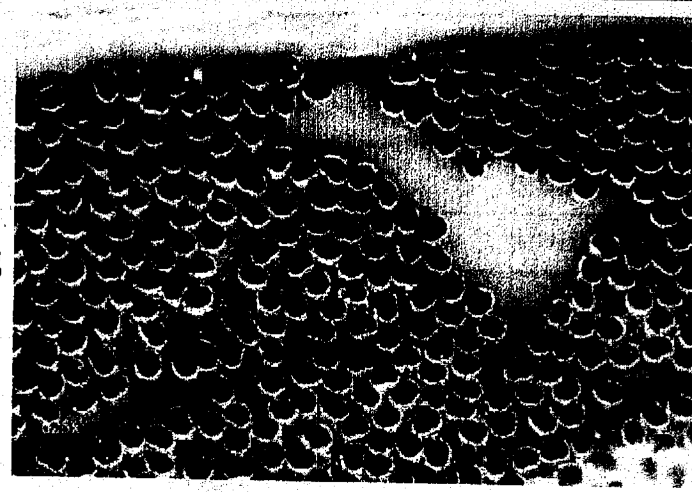
Summary of HPLC Analysis of Various PMR-II-50 Solutions

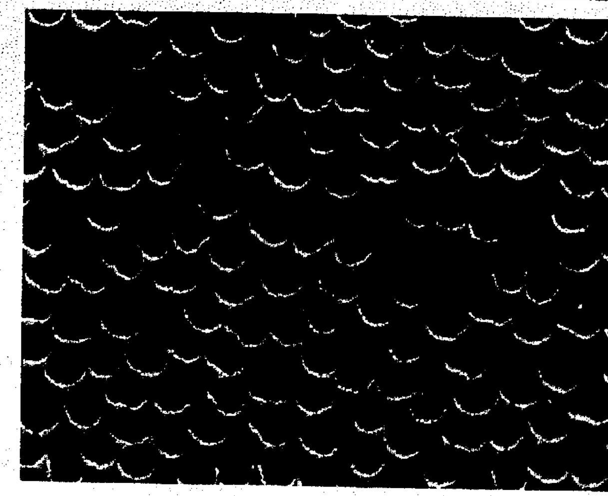
% Area (0.1% or higher only)				Normalized by HFDE, %			# of Aging Product/Adducts
PPDA	NE	HFDE	All Other Adducts	PPDA	NE	All Other Adducts	
1. Fresh Resin; Newly formulated w/ 50-60 wt% solid monomer content							
8.23	0.64	89.24	1.62	9.22	0.72	3.14	8
2. As-stored in Freezer (~1 year)							
6.57	0.67	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

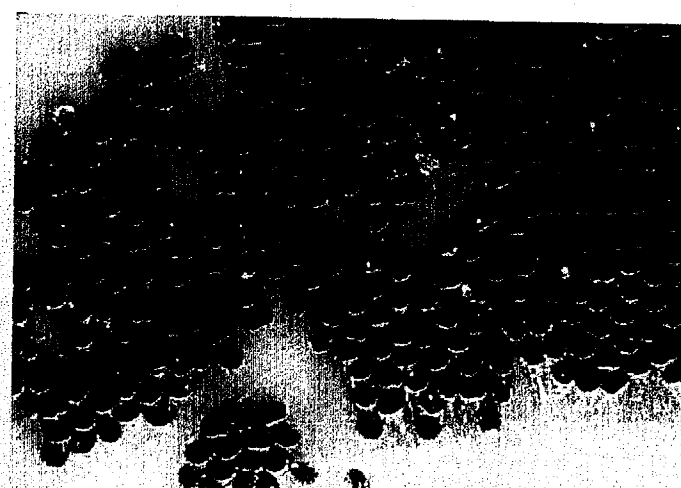
OM Cross-Sections of B-Staged M40JB Prepregs

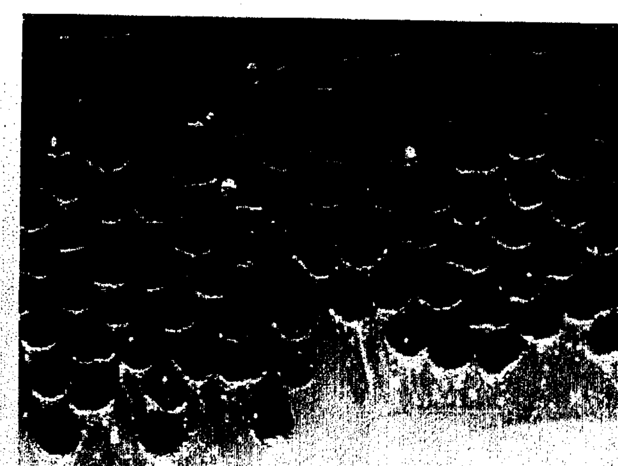
Solution Prepregs





Hot-melt Prepregs

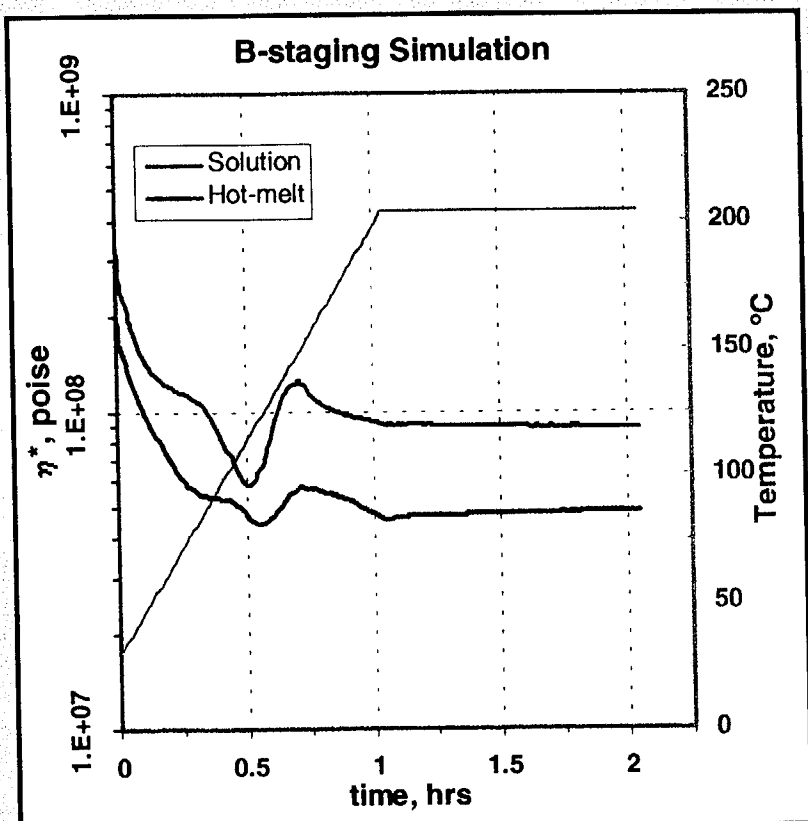


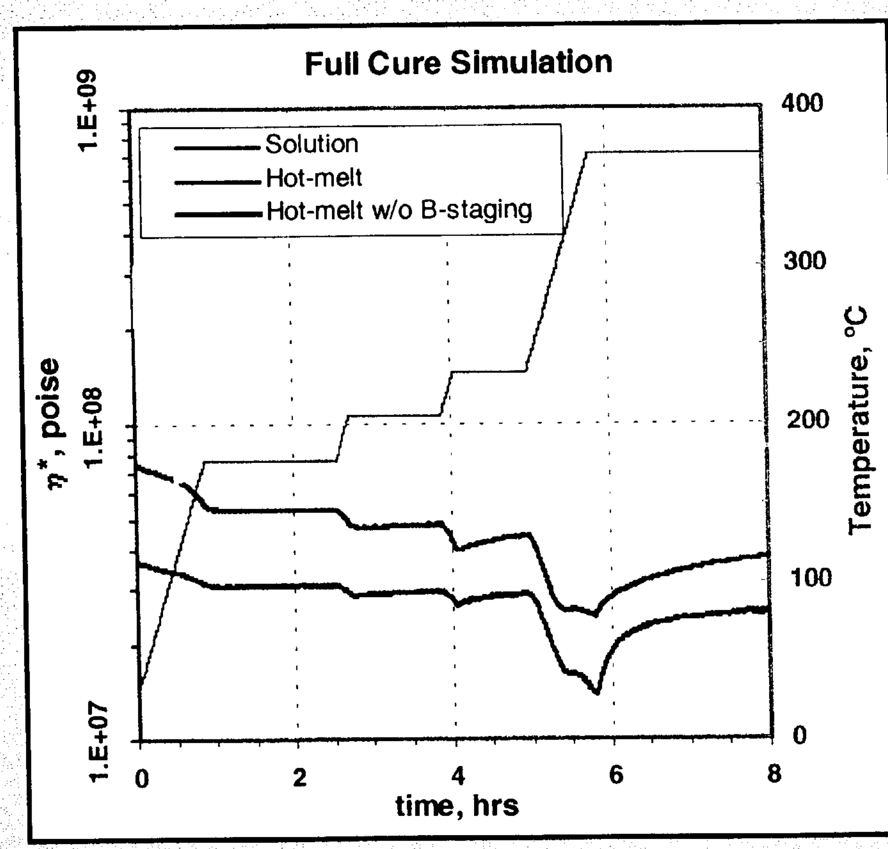


1250x

PREPREG EVALUATION

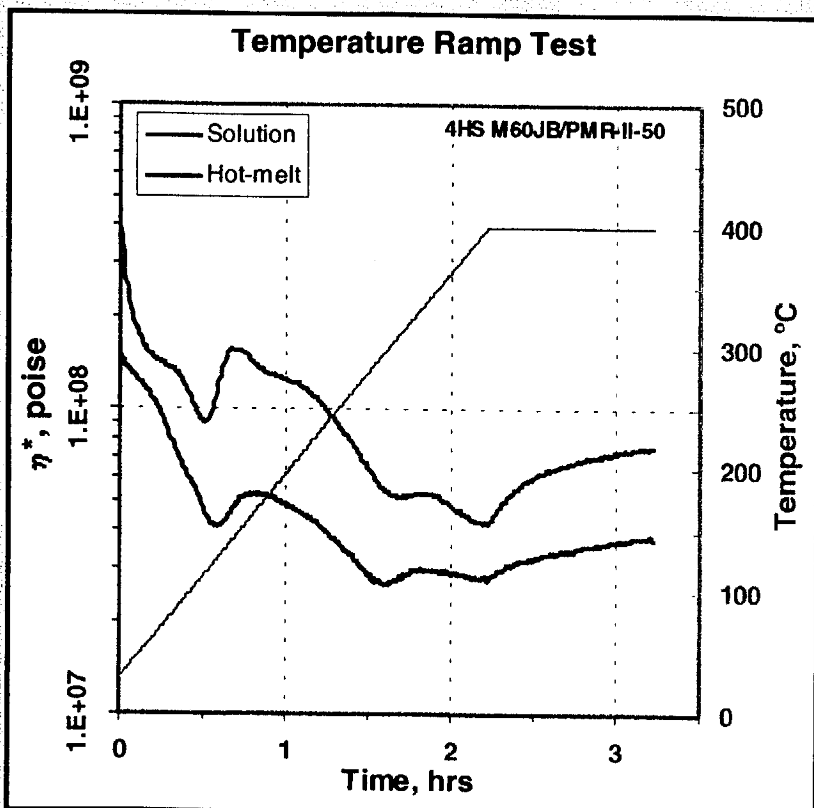
Dynamic Mechanical Analysis of 4HS M60JB/PMR-II-50 Prepreg Tape (Torsional rectangular Mode)

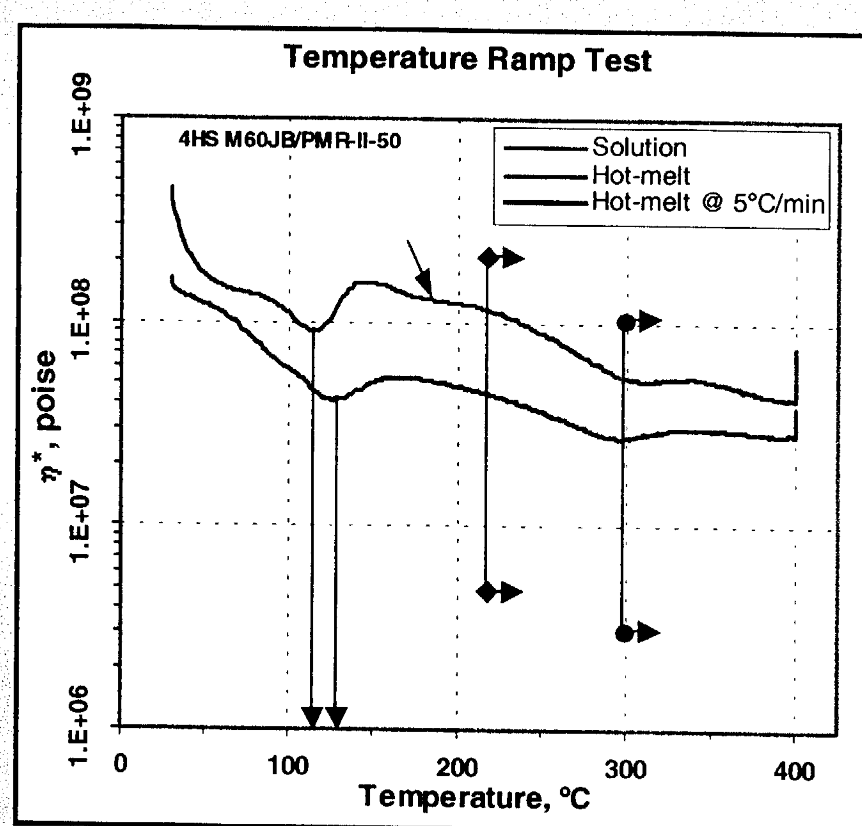




PREPREG EVALUATION

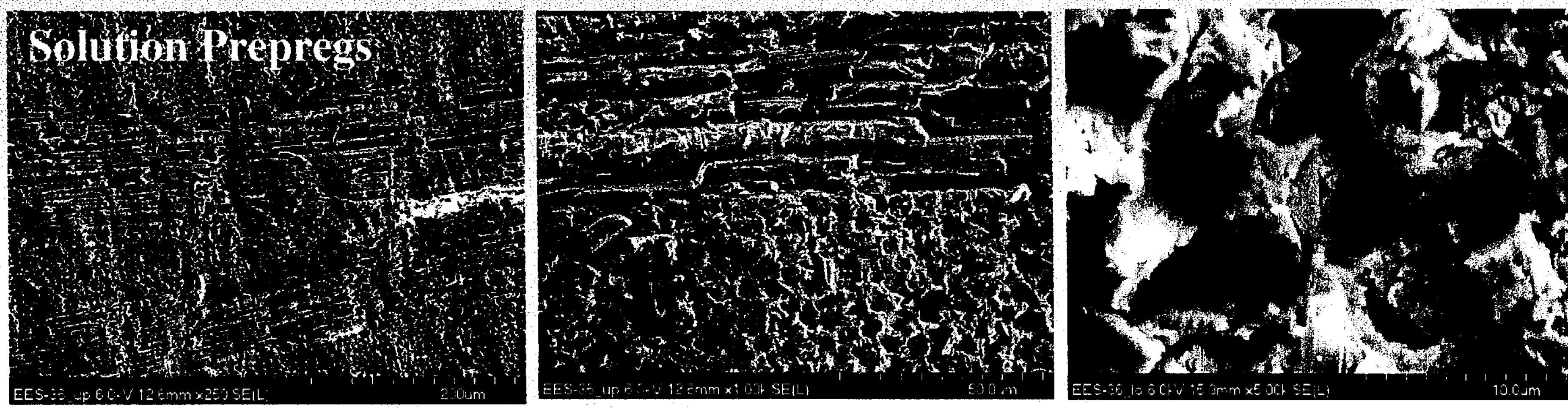
Dynamic Mechanical Analysis of 4HS M60JB/PMR-II-50 Prepreg Tape (Torsional rectangular Mode)

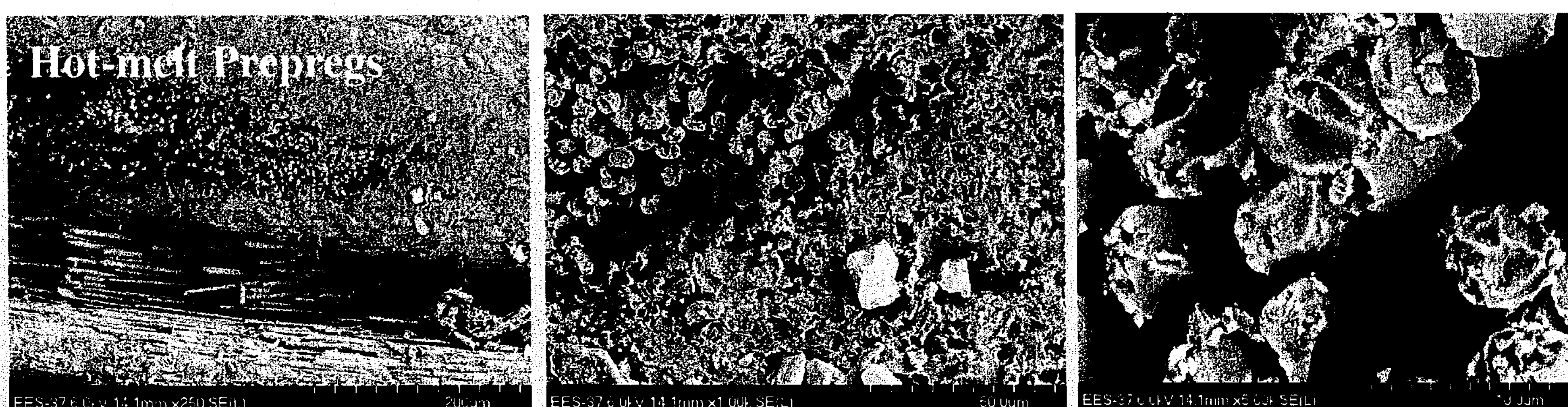




COMPOSITE FABRICATION/EVALUATION

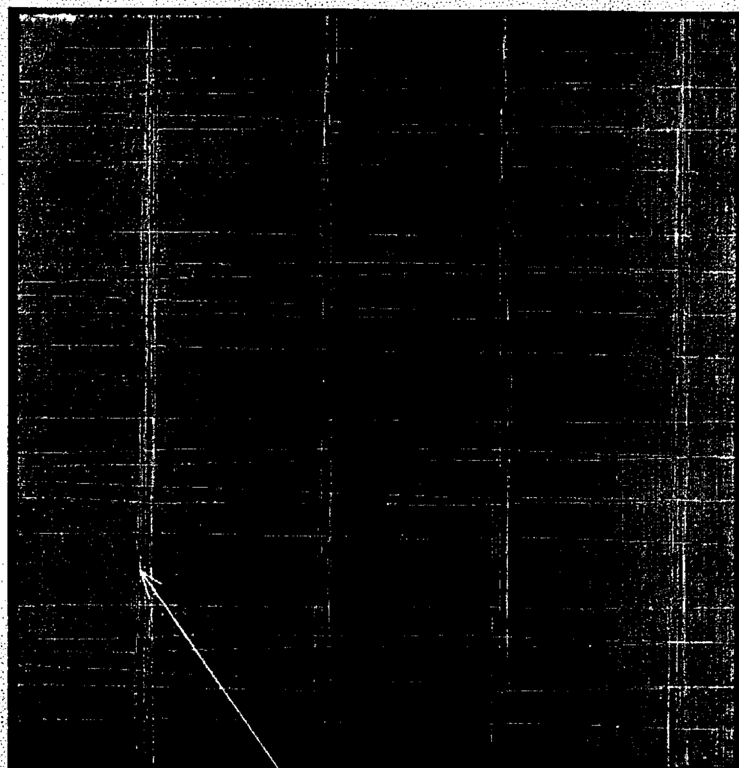
SEM Cross-Sections of M40JB Composites (Waterjet-Cut)





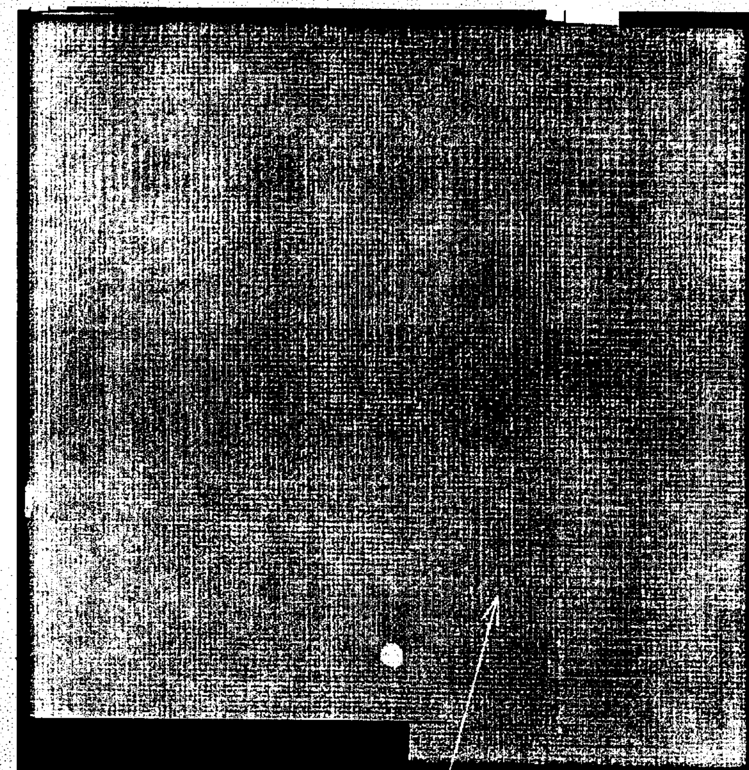
COMPOSITE FABRICATION/EVALUATION

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



M40JB Panel w/ Solution Prepregs

Glass fiber tracers



w/ Hot-melt Prepregs

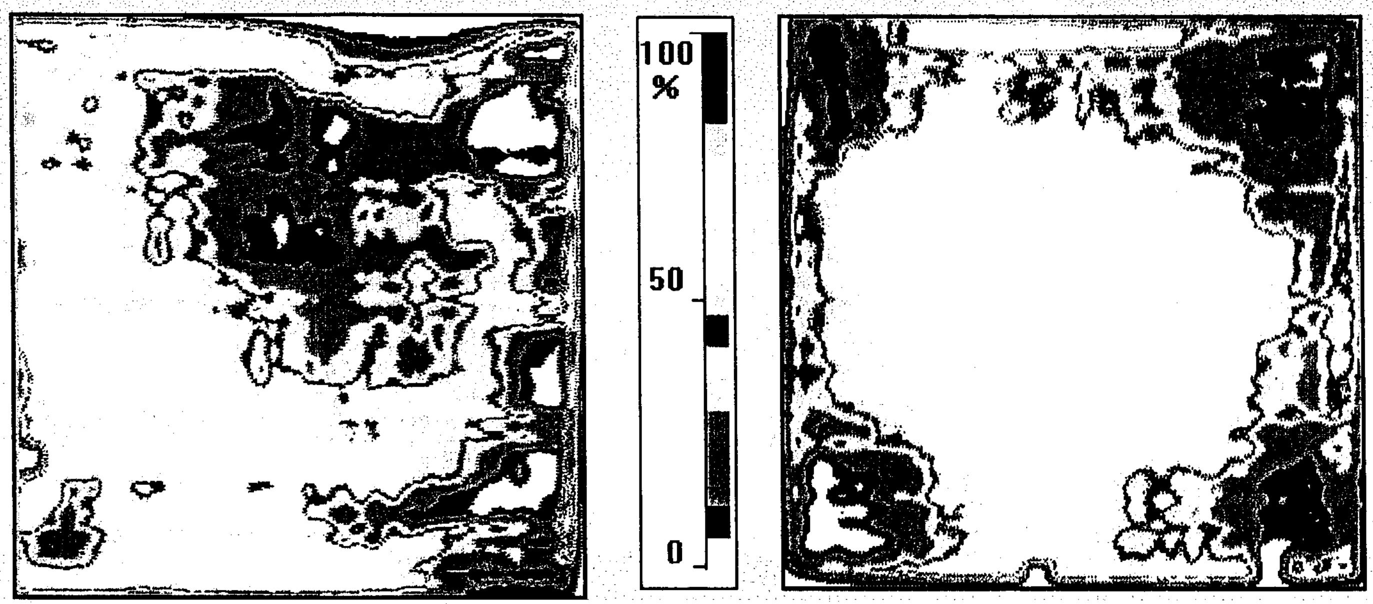
Carbon fibers

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, % / Composite	Solution Avg	Solution S.D	Hot-melt Avg	Hot-melt S.D	Hot-melt, Wet Treated Avg	Hot-melt, Wet Treated 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

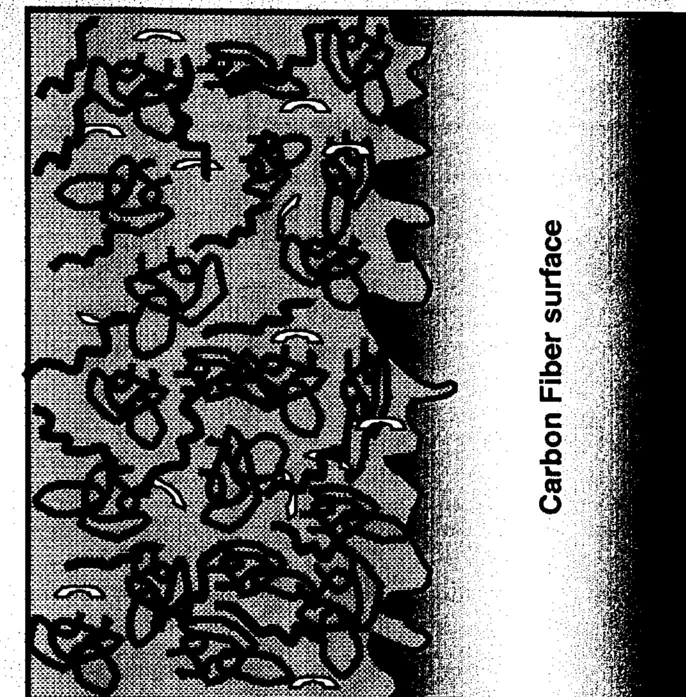
Thickness, in / Composite	Solution Avg	Solution S.D	Hot-melt Avg	Hot-melt S.D	Hot-melt, Wet Treated Avg	Hot-melt, Wet Treated S.D
M40JB, 12-ply	0.099	0.001	0.105	0.003		
M60JB, 12-ply	0.091	0.001	0.097	0.003		
T650-35, 8-ply	0.107	0.000	0.111	0.000	0.111**	0.000

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

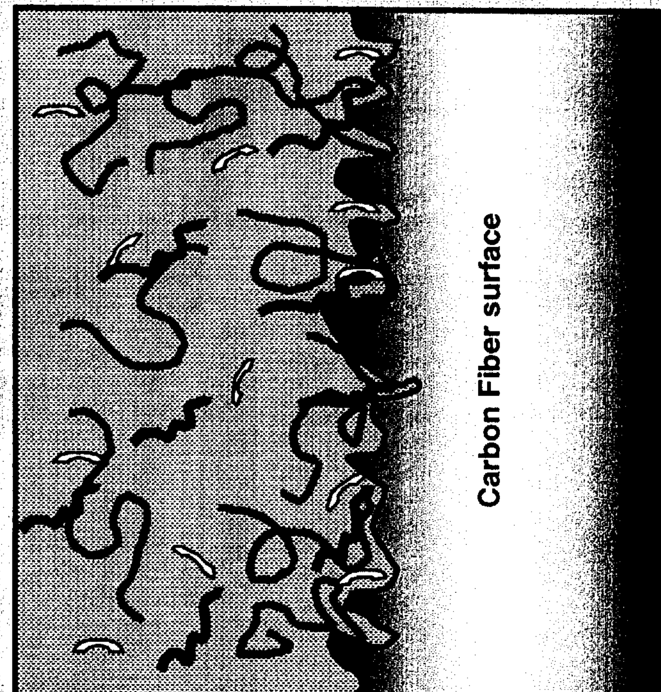
** higher FVF, 61% vs. 58%

OAI

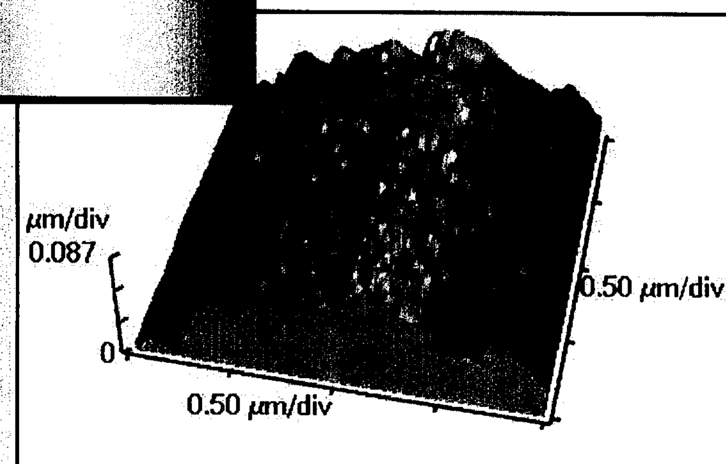
MOLECULAR LEVEL WETTING



High Mononer Solid Concentration in Hot-melt Prepregging



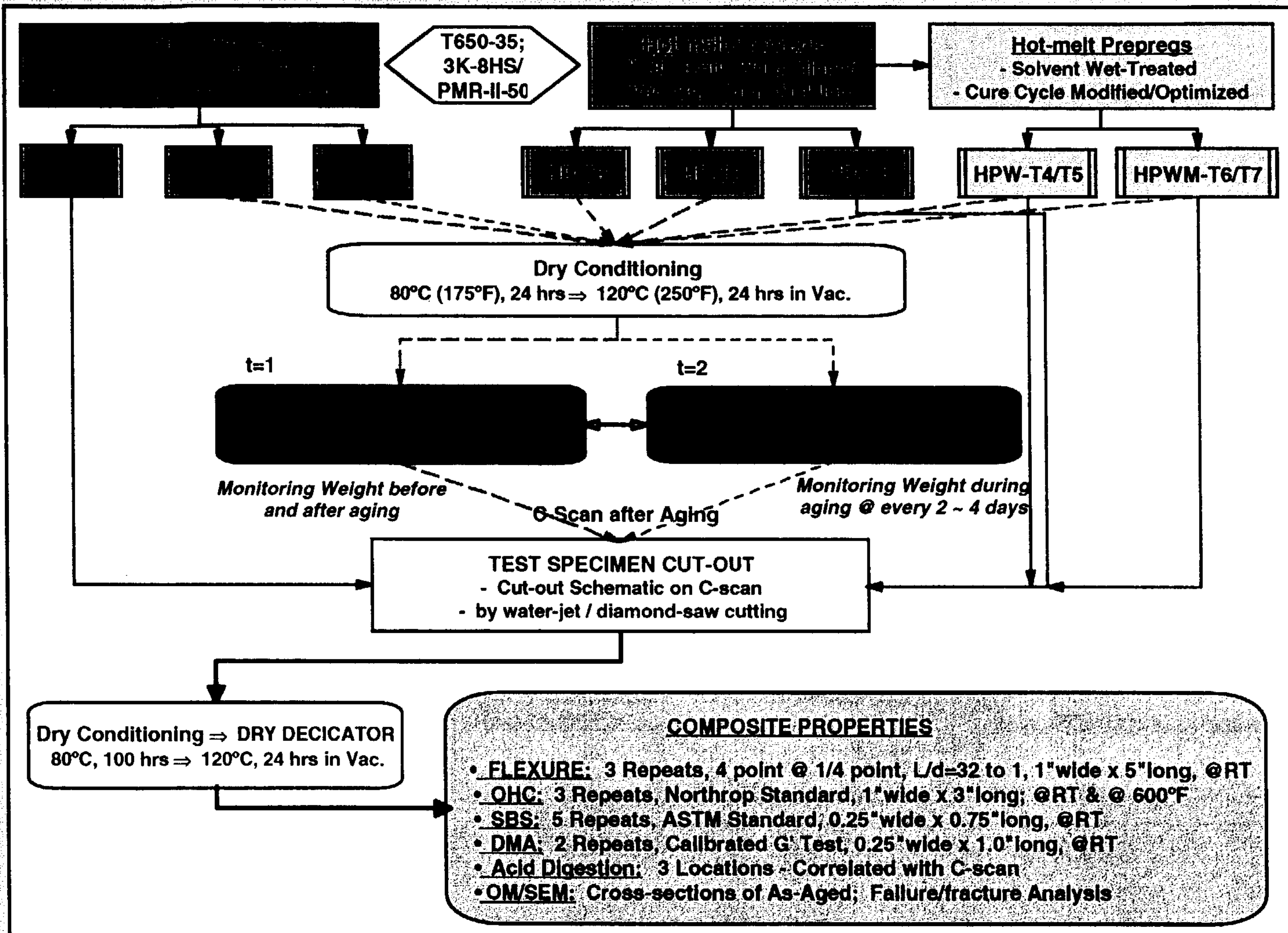
Low Mononer Solid Concentration in Solution Prepregging



M Carbon Fiber Surface by AFM

COMPOSITE PROPERTY/PERFORMANCE

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

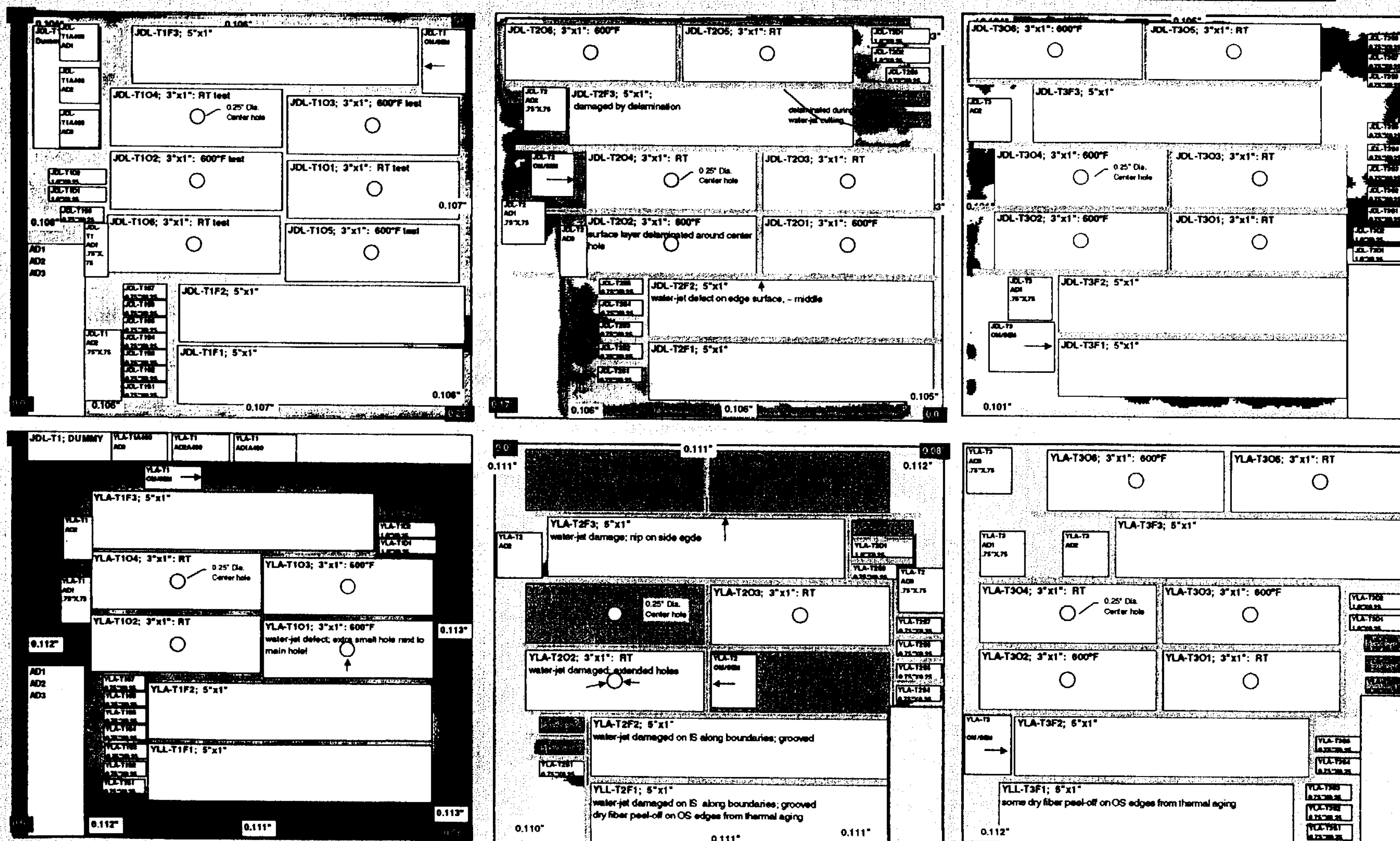


COMPOSITE PROPERTY/PERFORMANCE

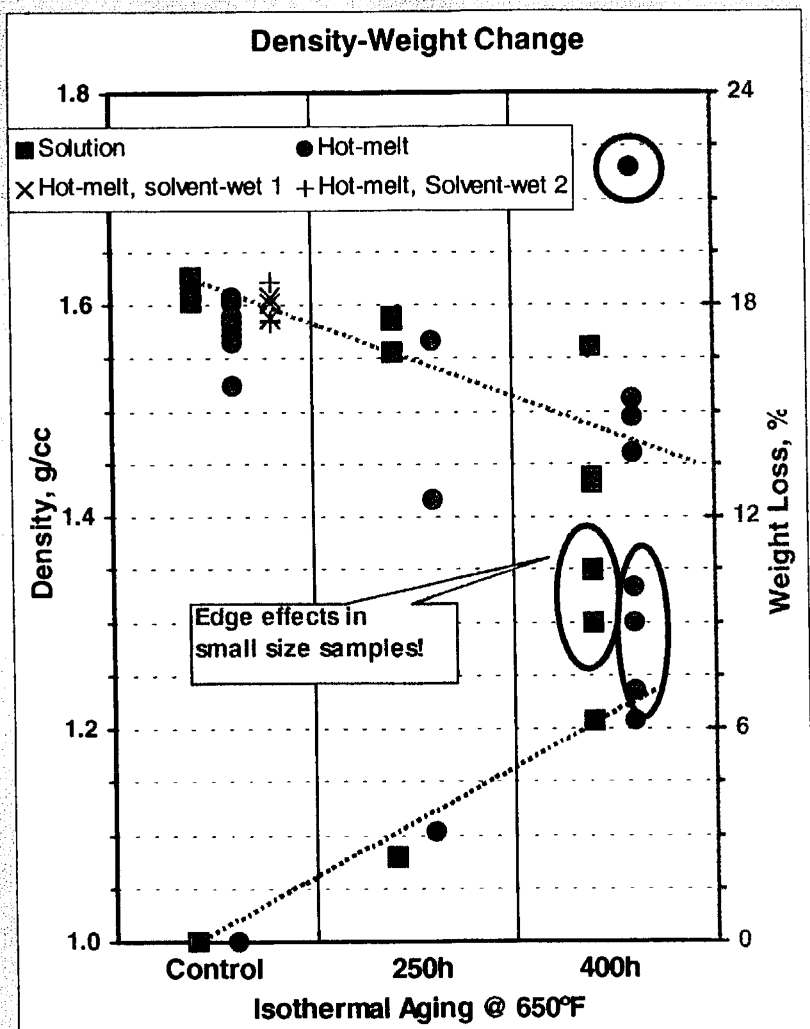
Un-aged Control | After 250 h @ 650°F | After 400 h @ 650°F

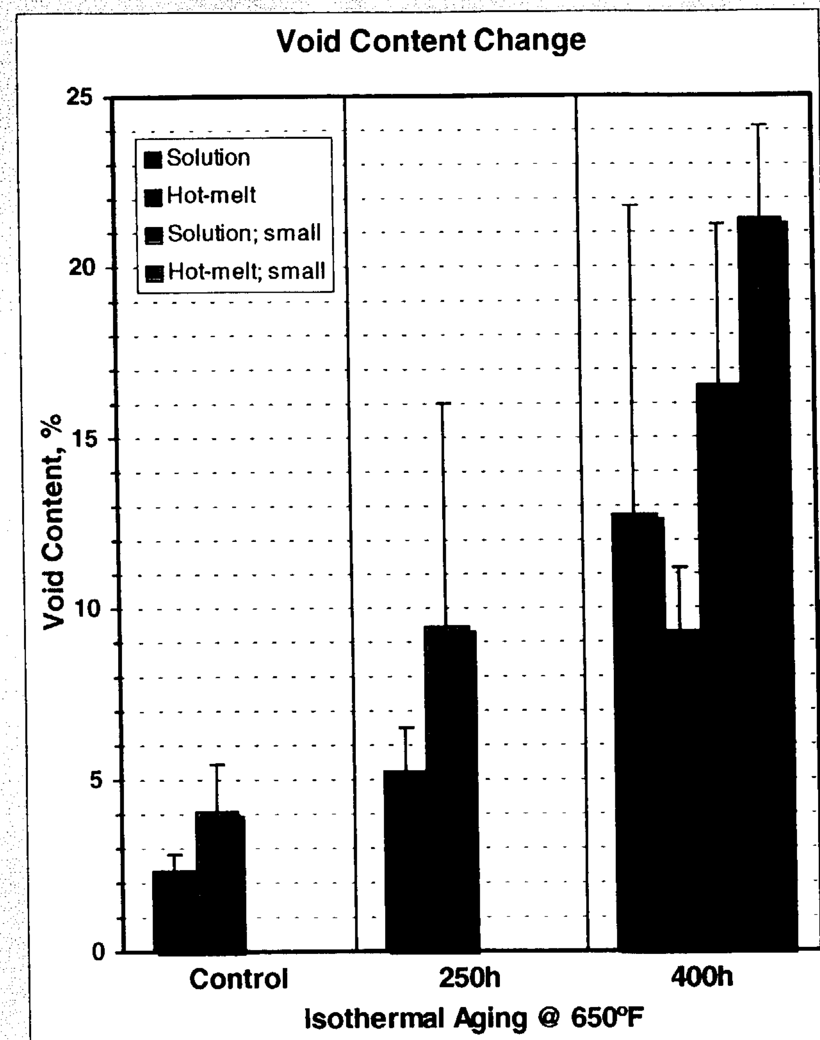
Solution

Hot - melt

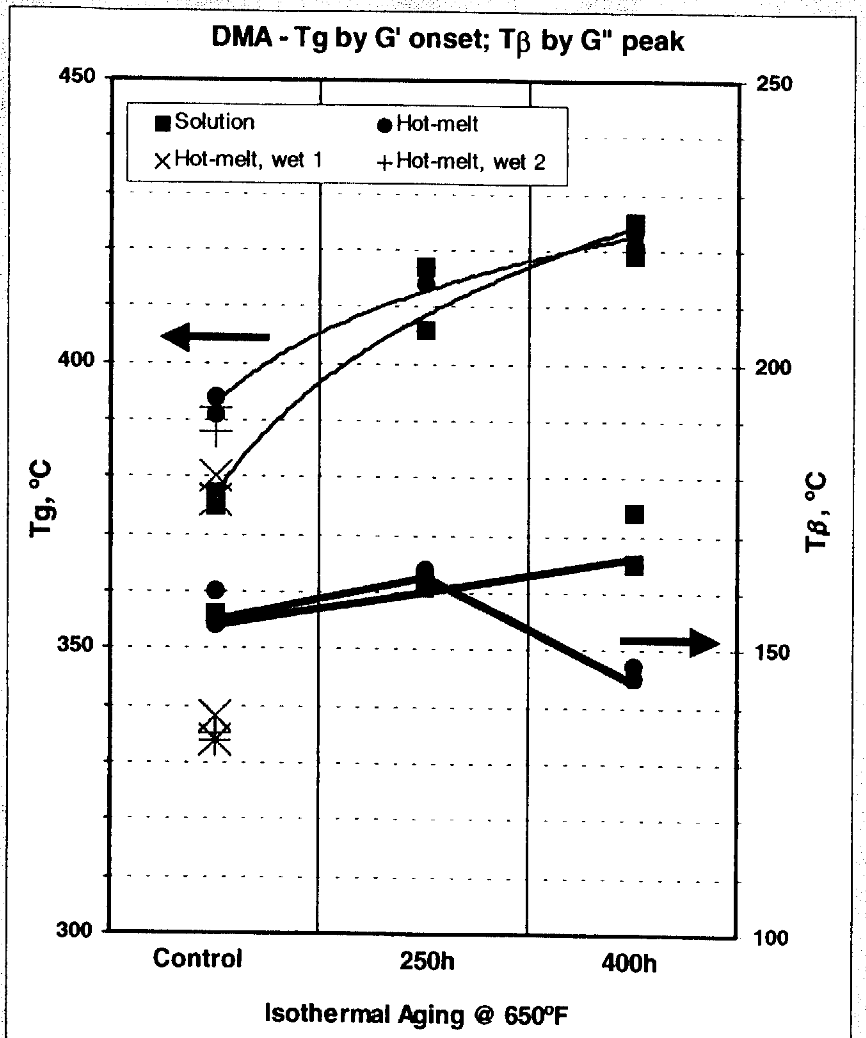


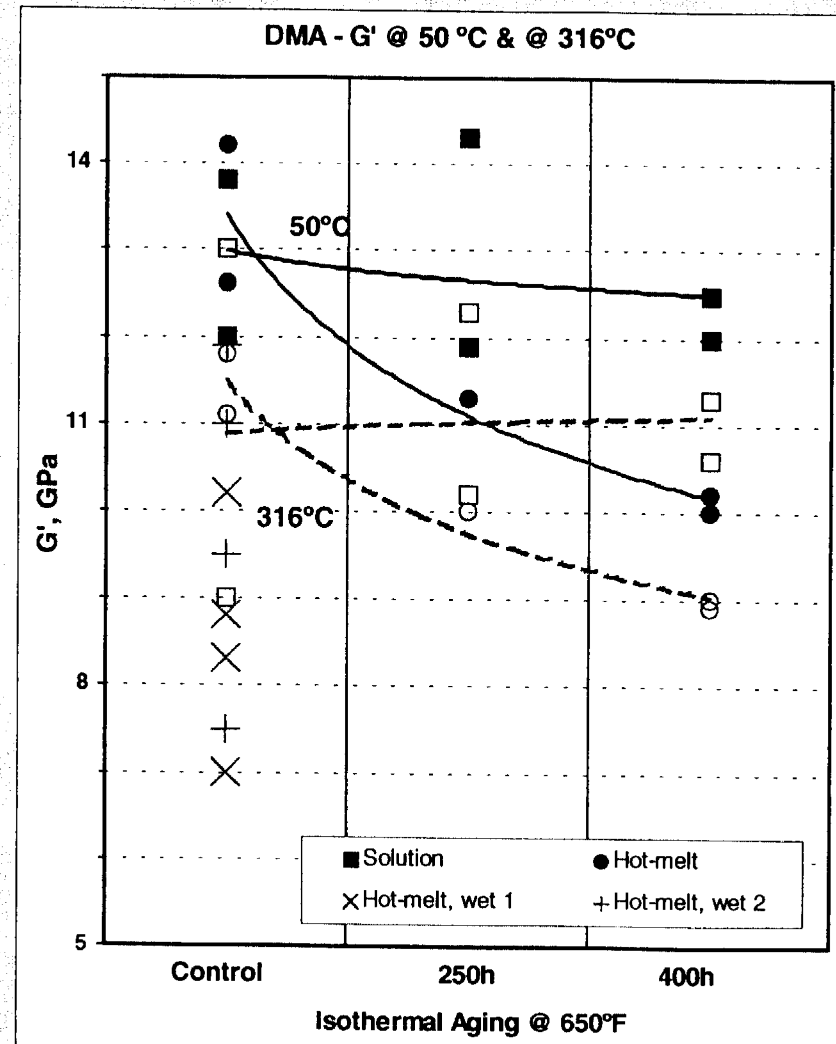
COMPOSITE PROPERTY/PERFORMANCE



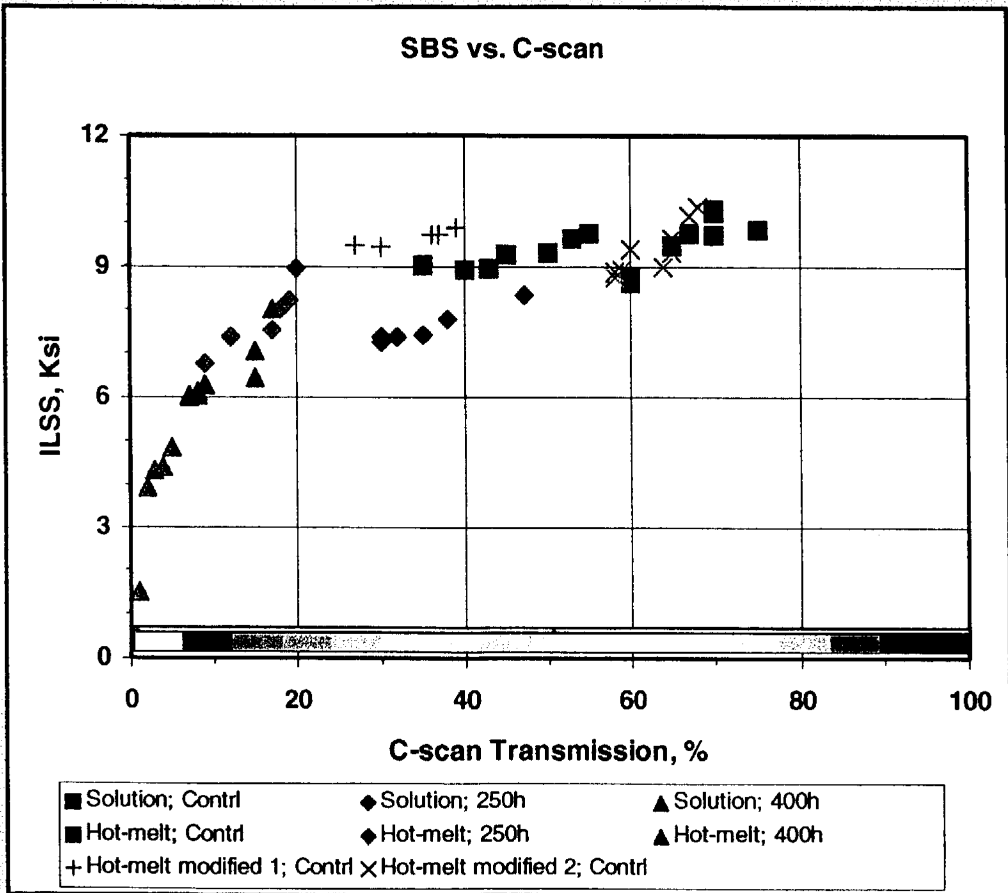


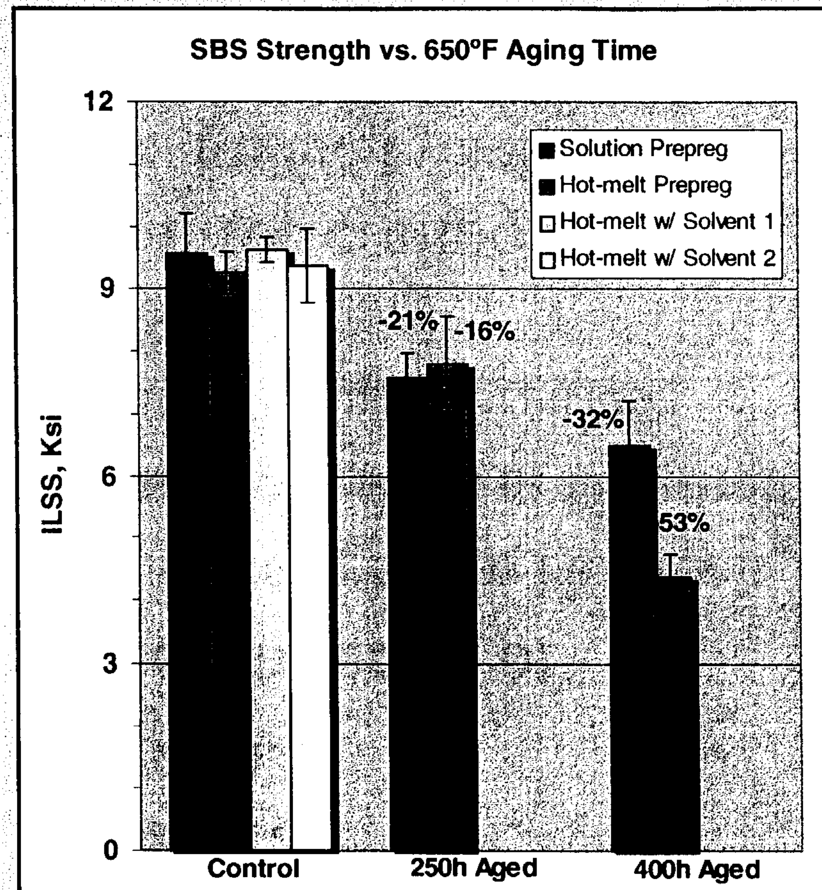
COMPOSITE PROPERTY/PERFORMANCE





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

ACKNOWLEDGEMENT

- YLA, Inc.
- JD Lincoln, Inc.
- Canyon Composites
- Rich Martin & G.Y. Baaklini, GRC
  : X-ray imaging
- Terry McCue, QSS: SEM
- Joe Lavelle & Tim Ubienski, AKAC;
  V. Ojars Klans, GRC;
  Myles McQuater, QSS
  : Test specimen preparation