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THERMOMECHANICAL PROPERTIES OF INTERFACE MODIFIED M40J CARBON/PMR-II-50 COMPOSITES

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ABSTRACT

To increase performance and durability of high-temperature composites for potential rocket engine components, it is necessary to optimize wetting and interfacial bonding between high modulus carbon fibers and high-temperature polyimide resins. It has been previously demonstrated that the electro-oxidative shear treatments used by fiber manufacturers are not effective on higher modulus fibers that have fewer edge and defect sites in the surface crystallites. In addition, sizings commercially supplied on most carbon fibers are not compatible with polyimides. In this study, the surface chemistry and energy of high modulus carbon fibers (M40J and M60J, Torray) and typical fluorinated polyimide resins, such as PMR-II-50 were characterized. A continuous desizing system that uses an environmentally friendly chemical-mechanical process was developed for tow level fiber. Composites were fabricated with fibers containing the manufacturer's sizing, desized, and further treated with a reactive finish. Results of room temperature tests show that desizing reduces interface sensitive properties compared to the manufacturer's sizing and that subsequent surface re-treatment with reactive finish increases interface sensitive properties. Properties of thermally aged composites and composites with varying finish concentrations will also be discussed.

KEY WORDS: Interphases and interface

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Thermomechanical Properties of Interface Modified M40J Carbon/PMR-II-50 Composites

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Presentation Outline

- Program Goals and Prior Year Results Summary
- Composite Fabrication and Characterization
- Aging and Mechanical Testing
- Conclusions and Future Work

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Problem Statement

- Toray M40J and M60J Carbon Fibers Have an Unusual Combination of Stiffness and Strength for Use in High-Temperature Applications
- Sizes on These Fibers are not Optimized for Compatibility with High-Temperature Polymers

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Purpose

Search for Empirical Correlations between Interfacial Measurements and Composite Performance to Develop Surface Treatments for High-Temperature Applications

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FY 00 Technical Approach

- Compare Sized and Chloroform Desized (5 min.) Fibers:
  - surface chemistry by XPS
  - surface energy by wetting
  - topography by SEM
- Characterize PMR-II-50 Resin:
  - surface energy by wetting
  - surface chemistry by XPS

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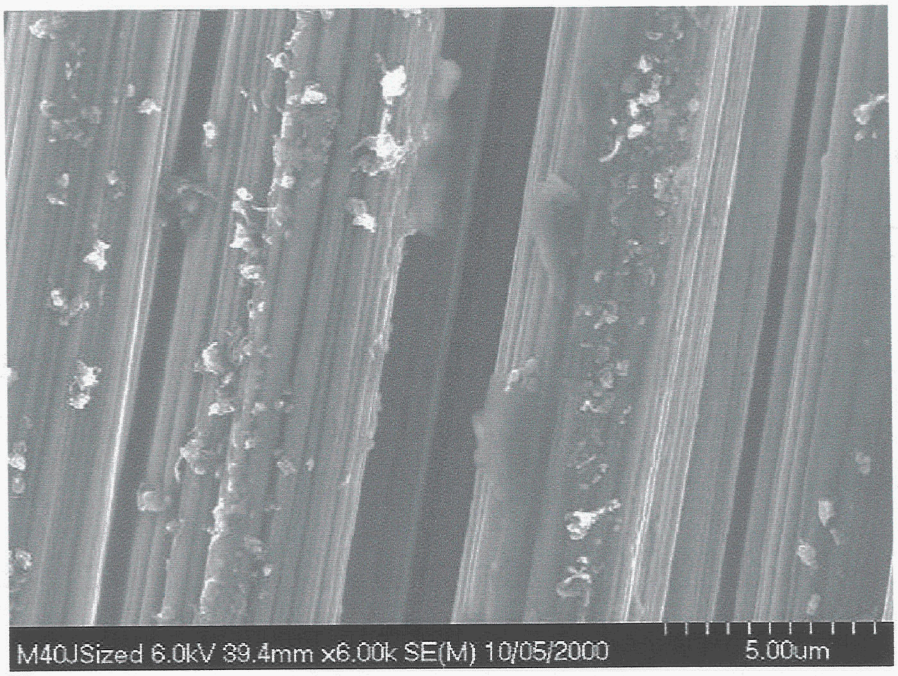
Toray Sized M40J



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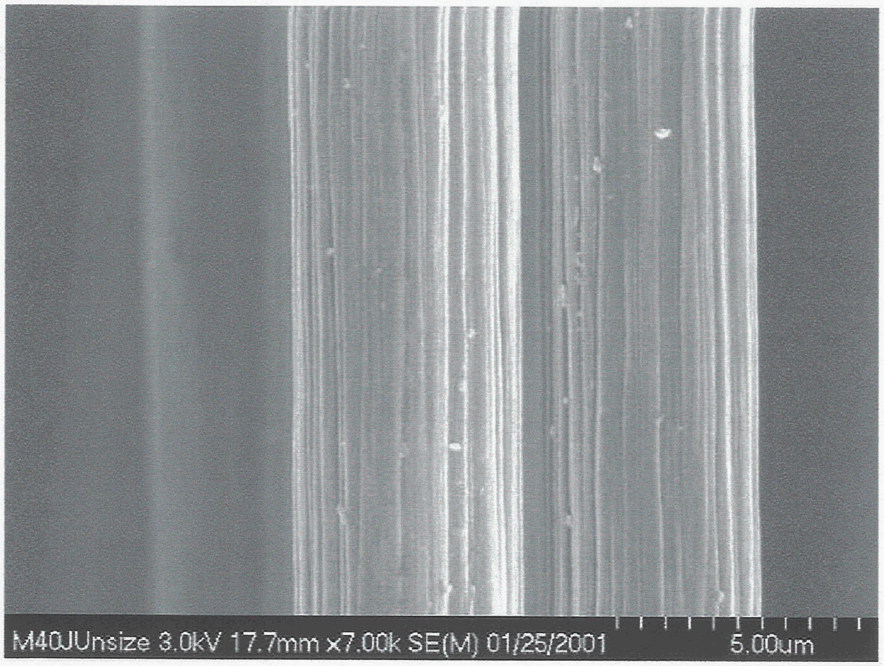
Toray M40J Desized



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FY 00 Conclusions

- Toray Size Coverage is very Nonuniform
- Size Contains Predominantly Hydroxyl Groups and Shows Slightly Acidic Character
- Desizing in Hot Chloroform Leaves Mostly Clean Fiber with Small Nodules of Residual Size
- Desized Fiber Surface is Amphoteric with 12-15% Oxygen Moieties

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FY 00 Conclusions (concluded)

- PMR-II-50 Resin also Amphoteric
- Toray Fibers Highly Striated
- High-Temperature Applications will Require Better Sizing Removal and/or Surface Treatment to Remove Residual Size
- Previous Work on Unsized Fiber Indicates that the Desized Toray Fiber Surface Should be Receptive to Surface Treatments and Finishes

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FY 01 Technical Approach

- Fabricate Continuous Desizing Apparatus
- Characterize Continuous Desized Fiber Surfaces
- Develop High-Temperature Finish for Desized Fiber

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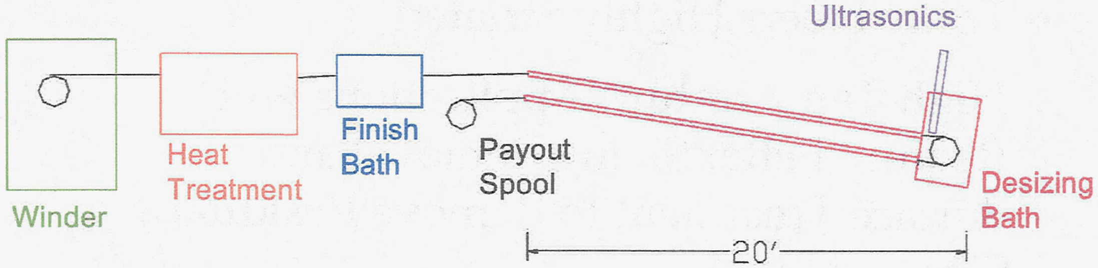
Schematic of Desizing System



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Desizing/Finishing System

- Seven-meter long, 2-cm Diameter Steel Tube In and Out of Tank Containing 25-cm Diameter Wheel
- Filled with Heated Chloroform
- Tension-Controlled Feed and Take Up at 1.6 meters/minute
- In-line Drying Furnace and Finishing Bath
- Ultrasonic Transducer Added to Return Tank

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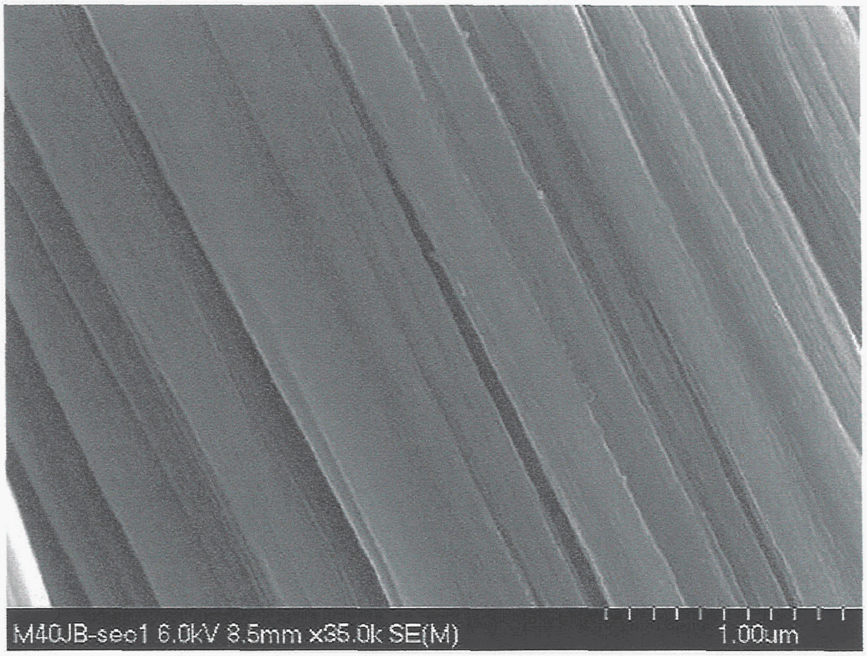
Appearance of M40J Carbon Continuously Desized with Ultrasound



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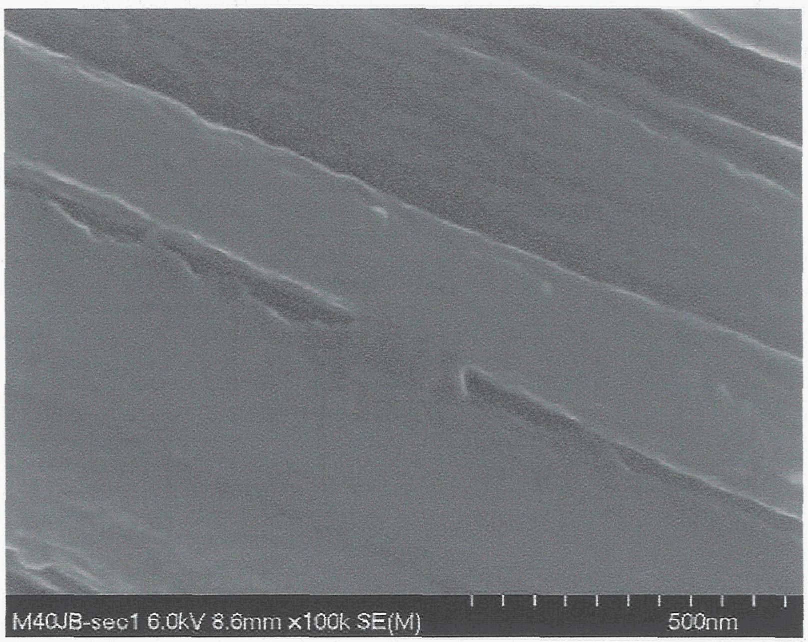
High Magnification Appearance of M40J Carbon Continuously Desized with Ultrasound



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XPS Elemental Analysis Large Batch M40J Carbon Fibers

Section	% O	% C
1	9.6	90.4
1	11.9	88.2
2	14.1	85.9
2	13.0	87.0
3	11.2	88.8
3	10.5	89.5

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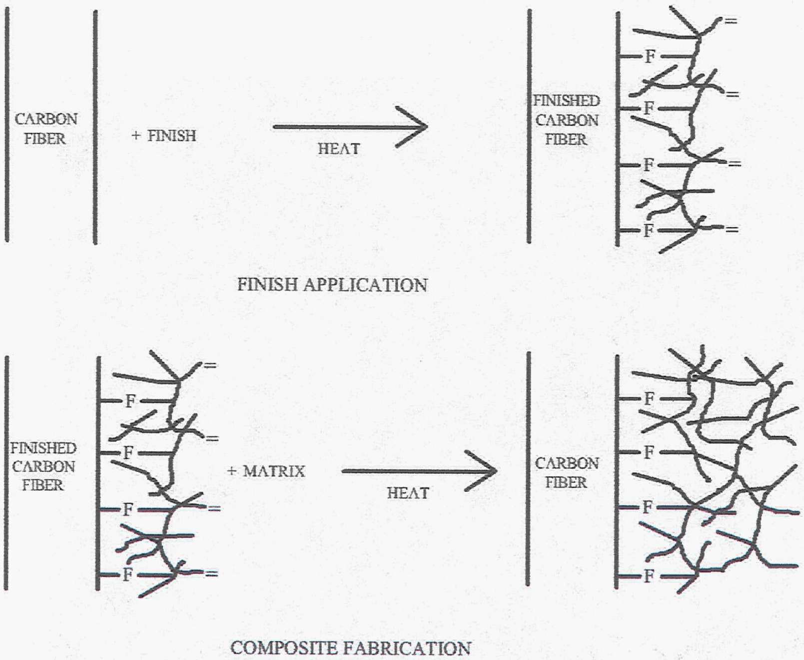
Reactive Finish Schematic



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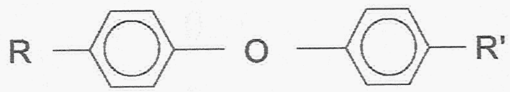
Reactive Finish Formulation

1. ATI 9307 Reactive Coupling Agent (0.3%)



R, R' = proprietary functional groups

2. PMR-II-50 Polyimide (3.0%)

3. Acetone

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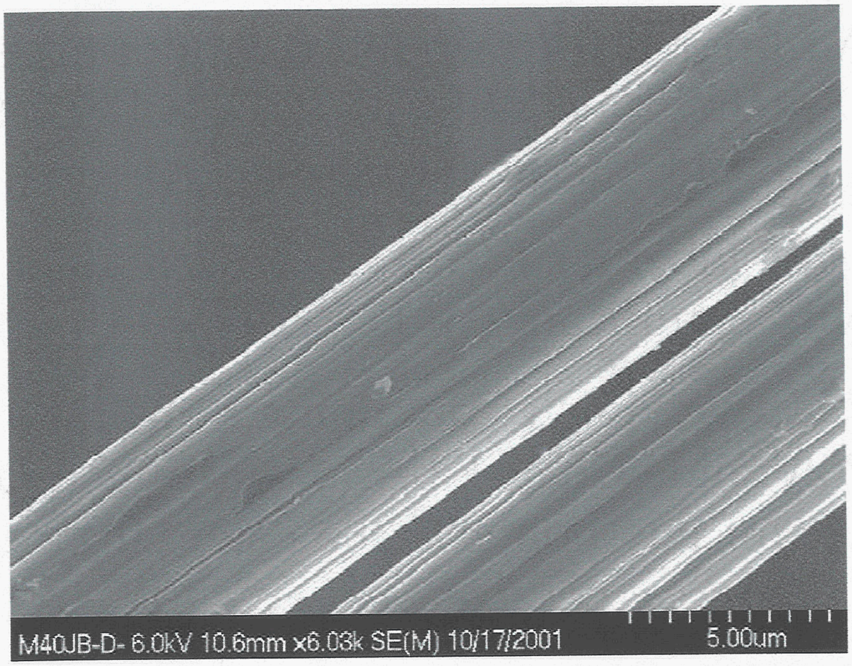
Appearance of Finished M40J Carbon Fiber



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XPS Elemental Analysis
Finished M40J Carbon Fibers

Element	% As Finished	% After MeOH Wash	PMR-II-50
F	12.6	11.0	18.1
O	16.2	14.0	10.4
N	2.9	4.0	5.5
C	68.4	71.0	66.1

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FY 01 Conclusions

- Addition of Ultrasound to Continuous Desizing Line Reduced Residual Size to a few Submicron Particles
- M40J Fiber Structure Highly Irregular with Significant (10-15%) Oxygen
- Reactive Finish Containing PMR-II-50 Polyimide Coats Fibers Uniformly and Chemically Bonds to the Fiber Surface

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FY 02 Technical Approach

- Produce Significant Quantities of Desized and Desized/Refinished M40J
- Fabricate and Characterize 0/90 PMR-II-50 Matrix Composites with Three Fiber Surface Treatments
- Thermally Age Composites and Determine Residual Interface-Sensitive Mechanical Properties

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Composite Fabrication

- Preparation of Unitape Using Drum Winding and Resin Impregnation
- PMR-II-50 Cure Cycles: B-staging 204°C/ 400°F for 1 hr, Dry and Postcure 371°C/ 700°f in Air for 16 hr
- Panels were [0/90]s and Approximately 0.100 inch thick

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Composite Characterization

- Panel Quality Evaluated by Ultrasonic C-scan with a 5-MHz probe
- Void Content and V_f Determined by Acid Digestion (ASTM D 3171)
- T_g, $T_{degradation}$, α, and Dynamic Mechanical Properties Determined by DMA, TMA, and TGA Techniques
- Mechanical Properties Measured using an Instron Universal Testing System

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Composite Microstructure

Fiber Treatment	Microcracks/ Cross-Section*	Void Content, %*	Fiber Volume Fraction
As-Received Size	291 ± 16	2.1 ± 0.2	58.5 ± 0.7
Desized	63 ± 29	3.5 ± 1.4	59.3 ± 1.2
Desized, Refinished	120 ± 6	4.4 ± 1.7	54.7 ± 2.9

* Average of three measurements at three locations.

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Thermomechanical Analysis of Composite Laminates

Fiber Treatment	Tg, °C G' Onset	Tg, °C Tan d	Tg, °C G" Peak	G' @ 100°C, MPa
As-Received Size	418.0	445.0	140.5	12555.0
Desized	382.5	423.0	146.0	9510.5
Desized, Refinished	364.0	388.0	143.0	10387.0

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Weight Loss from Thermal Aging at 650°F

Fiber Treatment	24 hour % wt. Loss	250 hour % wt. Loss	400 hour % wt. Loss
As-Received Size	0.81	1.76	3.24
Desized	1.00	2.38	4.10
Desized, Refinished	0.85	1.15	2.19

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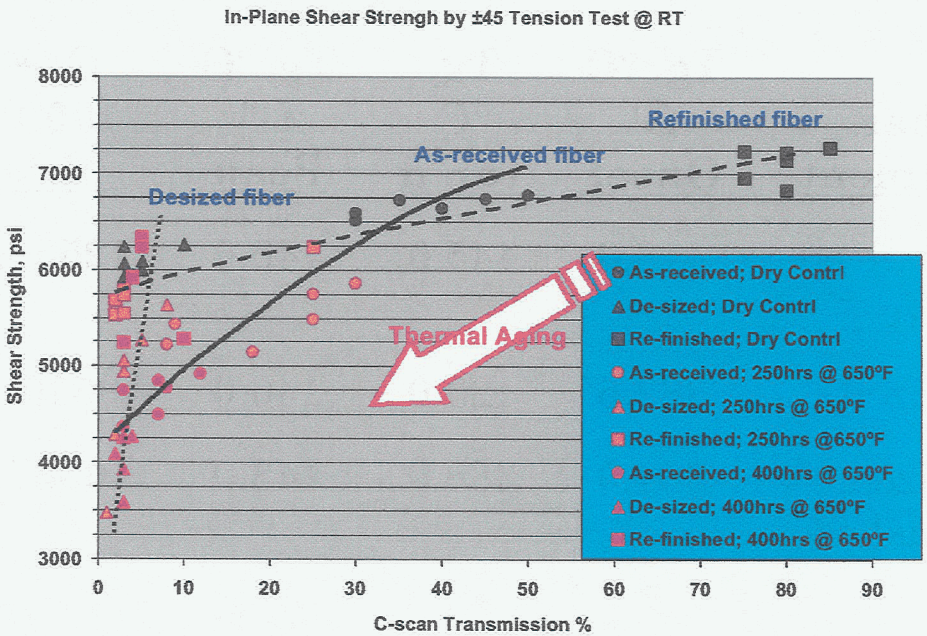
Tensile Shear Strengths as f(Fiber Treatment and Laminate Quality



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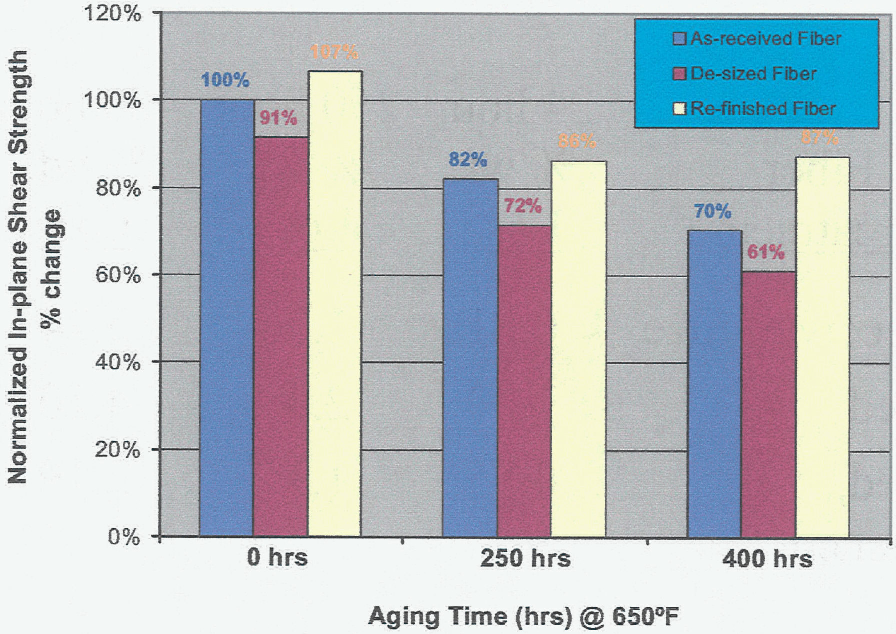
±45° Tensile Shear Summary



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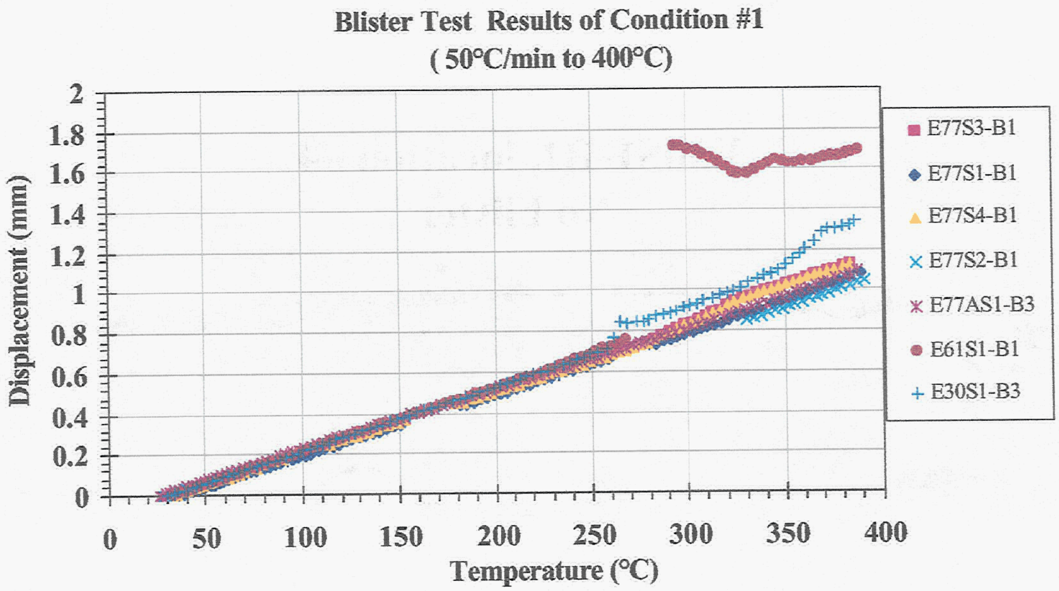
Blister Tests after Conditioning at 60°C and 90% Relative Humidity



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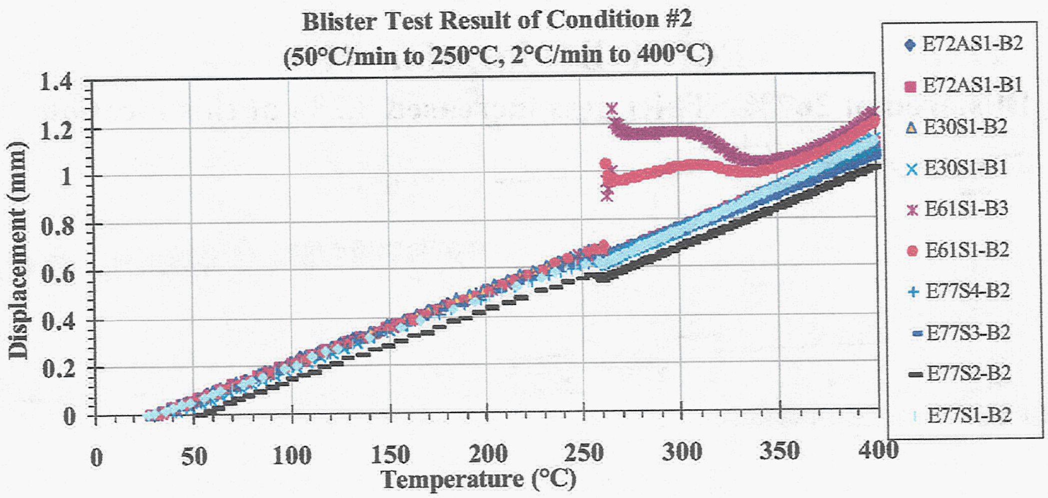

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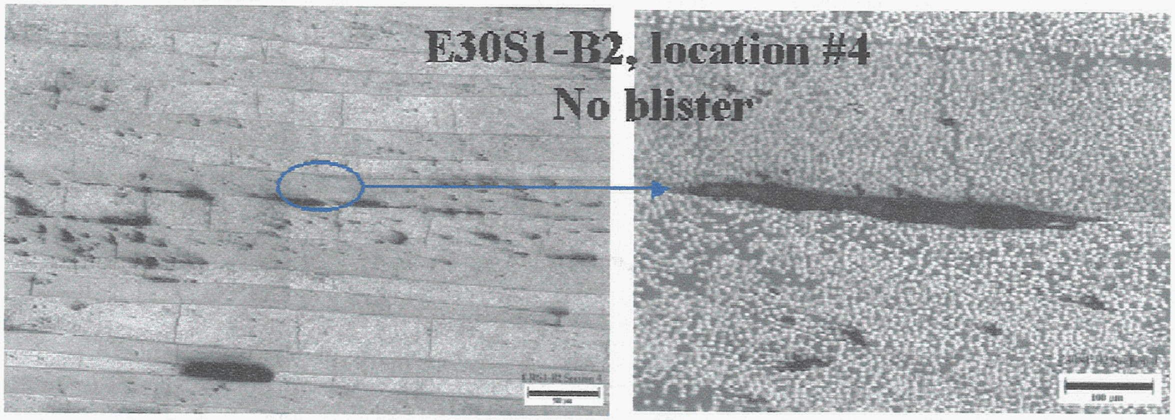
Blister Results for Laminates with As-Received M40J Fibers



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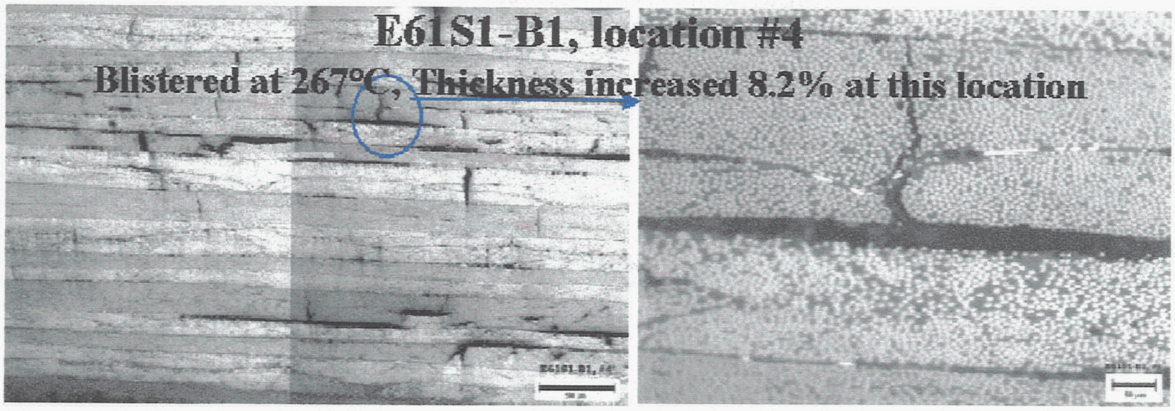
Blister Results for Laminates with Refinished M40J Fibers



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Conclusions

- Toray Size Coverage Nonuniform and Contains Predominantly Hydroxyl Groups with Slightly Acidic Character
- A Continuous Desizing Apparatus using Hot Chloroform and Ultrasound Leaves mostly Clean Fiber
- M40J Fibers are Highly Striated and Amphoteric with Approximately 12% Oxygen Moieties Present

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Conclusions (continued)

- A Finish Containing PMR-II-50 Poly-imide and a Reactive Coupling Agent Coats the Desized Fibers Uniformly and Chemically Bonds to the Fiber Surface
- Composites with Reactive Finish Had Fewer Microcracks, Less Weight Loss after Thermal Aging, and Produced a Stronger and More Thermally Stable Interface

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Conclusions (concluded)

- Composites with Reactive Finish Blistered at 260°C after Moisture Exposure and Rapid Heating
- A Better Interface and Fewer Microcracks May Restrict Diffusion Out of the Laminate Eventually Resulting in Blister Formation

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Program Status and Future Work

- Additional Unidirectional Composite Laminates Produced with Various Finish Formulations
- Will be Thermally Aged and Tested in 0° and 90° Flexure and Short Beam Shear
- Results Expected to Show Means to Optimize the Finish Formulation to Produce Composites with Improved Thermo-Mechanical Properties