Effect of Sizings on the Durability of High Temperature Polymer 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. Sizings commercially supplied on most carbon fibers are not compatible with polyimides. In this study, the chemistry of sizings on two high modulus carbon fibers (M40J and M60J, Toray) was 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 after thermal aging show that the reactive finish produces a higher strength and more durable interface compared to the manufacturer's sizing. When exposed to moisture blistering tests, however, the better bonded composite displayed a tendency to delaminate, presumably due to trapping of volatiles.

KEYWORDS: sizings, reactive finish, thermal aging, mechanical properties, blistering

INTRODUCTION

High-temperature polymer matrix composites (PMCs) are desired for many aerospace and military applications. These aggressive environments have required new blends of materials properties in the composite fiber and matrix. In that endeavor, it is often found that the sizings routinely added to commercial carbon fibers are not compatible with the new high-temperature matrix resins. The result is that the thermo-oxidative stability (TOS) and mechanical properties of composites made with such fibers are compromised. Before high-temperature PMCs can routinely be used in demanding applications, their long-term TOS must be improved.

M40J and M60J carbon fibers available from Toray (Japan) have an unusual combination of stiffness and strength for use in high-temperature applications; however, the epoxy-compatible sizes available on these fibers may not be optimum for compatibility with high-temperature polymers. Prior work using single filament wetting has shown that the sized surfaces are energetically and topographically heterogeneous

[1]. Formamide wetting shows that M40J surfaces and M60J surfaces display similar acidity whether sized or desized. Ethylene glycol wetting suggests that the size covers basic functionality that is uncovered by desizing. PMR-II-50 polyimide resin is mildly amphoteric, since W^{a-b} is small but finite for both acidic and basic probe liquids. The Toray fibers are highly striated on the surface, and the surface is amphoteric with 12-15% oxygen moieties present.

The work described here was undertaken to further characterize the Toray size, develop a means to remove the commercial size and replace it with a high temperature finish, and to determine the thermomechanical properties of polyimide composites fabricated with the various fiber surface types. Our approach was to characterize the M40J and M60J sizings using scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and fourier transform infrared spectroscopy (FTIR). The Toray sizing was then removed using hot chloroform in a continous desizing process and a high temperature finish applied and characterized. Cross plied composites were fabricated with PMR-II-50 matrices and tested in the thermally aged and unaged conditions. Finally, moisture blistering tests were conducted on the various laminates.

Results show that the Toray sizing is very nonuniform on the fiber surface and that it contains predominantly hydroxyl groups. Desizing in hot chloroform with ultrasound leaves mostly clean fiber with a few small (tenths of microns) nodules of residual size. The desized Toray fibers are also highly striated, creating the possibility of improved interfacial adhesion by a mechanical interlocking mechanism. The reactive finish bonds well to the desized fiber and improves interfacial adhesion before and after high temperature aging; however, the well bonded laminates debonded in the moisture blistering tests, presumably due to internal trapping of volatiles.

EXPERIMENTAL PROCEDURES

Desizing Approach

Initial desizing studies showed that one, three, and five minutes in boiling chloroform dropped the surface oxygen content to a constant level of approximately 10%. [1]. These data were used to design a continuous desizing unit shown schematically in Figure 1. The desizing unit shown in Figure 1 consists of 20 feet of heated tubing feeding in and out of a bath that is irradiated with ultrasound. The entire system is filled with chloroform. For application of reactive finish, a dip bath followed by a tube furnace is placed between the desizing unit and the take-up winder. The desizing unit was operated at a speed of 10 feet/minute. Additional information on the desizing process is given in Reference 2.
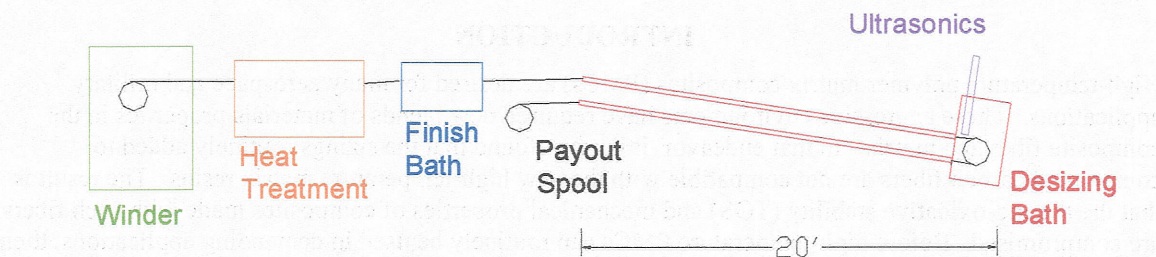

Figure 1. Schematic of continuous desizing unit

Reactive Finish Formulation

The reactive finishes were based on the work in Reference 3. That work and subsequent studies by the authors have shown that the reactive coupling agent chemically bonds to carbon fiber surfaces. The finish formulations used 0.3% coupling agent and 3.0 wt.% PMR-II-50 polyimide resin in acetone. The tube furnace was set at a temperature of 250°C to initiate the bonding reaction with the desized M40J.

XPS Analysis

Sized, desized, and refinished M40J carbon fibers were analyzed by XPS. Survey spectra were taken to examine the as-received surface chemical stoichiometry. High-resolution spectra were taken of significant peaks seen in the survey scans to determine possible surface bonding states. The analyses were run at NASA Glenn Research Center using a Surface Sciences SSX-100 spectrometer with an Al Kα source. C_{1s} high-resolution peaks were averaged over 10 to 15 scans using a spot size of 300 μm^2 with no flood gun. O_{1s} peaks were averaged over 30 scans. A Gaussian curve fitting routine was used to resolve high-resolution photopeaks into components based on binding energy references from model compounds [4]. The spectra were not charge referenced.

FTIR Analysis

A Nicolet Magna 560 FT-IR spectrometer equipped with a Nic Plan microscope was used to acquire spectra. The microscope was operated in reflectance mode using a 32X objective (spot diameter 100 micron). Typically 100 scans were averaged at 4 cm-1 resolution vs. a gold microscope slide. Spectra were corrected for water and carbon dioxide.

Composite Fabrication

A new process called "tow plate-winding" was developed with a modified lathe for the fabrication of all unidirectional panels. The tow plate-winding process is described in detail in Reference 5. The 30 cm x 30 cm laminated composite panels were fabricated by typical vacuum bagging process in hot-press molding platen (applied pressure: 500 psi) at NASA GRC using optimized PMR-II-50 cure cycles after a separate B-staging at 204°C (400°F) for 1 hr. All cured panels were then dried and postcured at 371°C (700°F) in air for 16 hrs. The fabricated PMR-II-50 matrix panels were $[0,90,90,0,90,0,0,90,0,90,90,0]_s$ 24-ply composite laminates and approximately 0.25 cm thick.

Initial quality of the composite panels was evaluated by ultrasonic C-scan (ULTRAPAC-AD-500, Physical Acoustics) with a 5 MHz probe after a standard calibration with poly(methyl methacrylate). Void content and fiber volume fraction of composites were determined by acid digestion per ASTM D 3171. The glass transition temperatures, thermal degradation temperature, coefficient of thermal expansion, and dynamic mechanical properties of the cured and postcured composites were determined by standard thermo-analysis techniques including dynamic mechanical analysis (TA Instrument 2980 DMA), thermomechanical analysis (TA Instrument 2940 TMA), and thermogravimetric analysis (TA Instrument 2950 TGA HR). Composite mechanical properties were measured using an Instron universal testing machine with a Series IX Automated Materials Testing System.

Aging Tests

Quarter sections of the laminates were aged in an air circulating oven at 343°C (650°F) for various times. Following aging, ±45° tensile test specimens and short beam shear specimens were cut using a water-cooled diamond wheel.

Two inch square (5 cm square) blister specimens were sonicated in a cleaning agent and dried in a vacuum oven until constant weight was obtained. The specimens were then conditioned in a humidity cabinet at 60°C and 90% relative humidity. After the specimens maintained a constant weight, blister

testing was performed. The blister tests were performed on the saturated samples at 2 different conditions. The first condition was at a ramp rate of 50°C/min to a temperature of 400°C. The second blister condition was obtained at two ramp rates. The first ramp rate of 5°C/min was used up to a temperature of 250°C then it was increased to a ramp rate of 50°C/min to 400°C.

Five locations on a sample were marked to measure the thickness change before and after blister testing. A micrometer was used to measure the thickness. The schematic depicting of the five locations is shown in Figure 2. Corner #4 was cut for photomicrograph, microcrack counts, and void calculation before exposure to humidity conditions.

Figure 2: Schematic illustrating 5 different location of a blister sample

RESULTS AND DISCUSSION

Sized Fiber Characterization

The appearance of the sized Toray M40J and M60J fibers is shown in Figure 3.

Figure 3. Appearance of sized M40J and M60J (right) carbon fibers

Figure 3 shows that the Toray size is very nonuniform in thickness and coverage on the as-produced fibers. The deep striations on the fiber surface are also seen in Figure 3.

High resolution XPS C_{1s} photopeaks for the sized Toray fibers are shown in Figure 4. Results show that the surface oxygen groups are predominately singly bound to carbon, presumably as hydroxyl moities.

Surface reflectance FTIR spectra for the Toray sized carbon fibers are shown in Figure 5. In addition to aliphatic and aromatic C-H stretching bands between 2800 and 3000 cm^{-1}, a broad peak between 3200 and 3600 cm^{-1} is seen that is indicative of hydroxyl groups. It is also evident in Figure 5 that the sizings on both fibers have the same chemistry. At this point, the balance of the study was conducted on M40J fibers only.
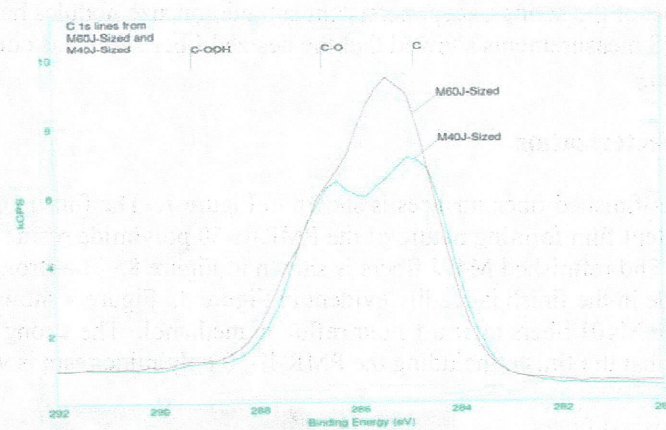
Figure 4. High resolution C_{1s} photopeak for M40J and M60J sized carbon fibers
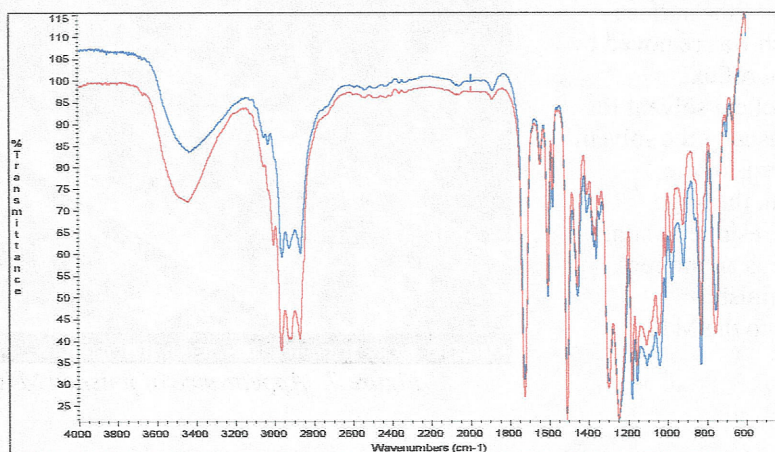

Figure 5. FTIR spectra comparing M40J (top) and M60J sized surfaces

Desized Fiber Characterization

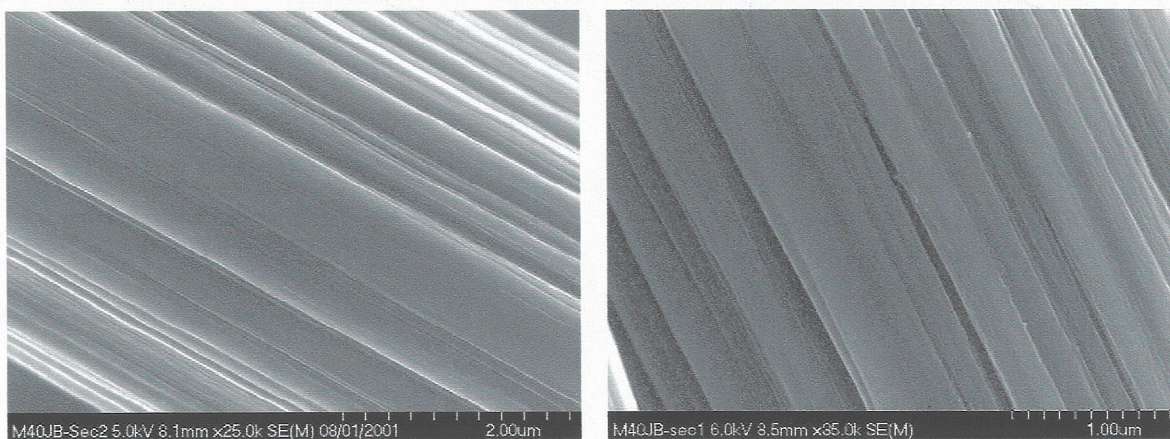The appearance of M40J fibers after treatment in the desizing unit with ultrasound is shown in Figure 6.

Figure 6. Appearance of continuously desized M40J carbon fiber

As seen in Figure 6, most of the sizing except persistent sub micron size nodules have been removed by the hot chloroform. XPS measurements showed that the desized fiber surface is composed of carbon with $11.7 \pm 1.65\%$ a/o oxygen.

Finished Fiber Characterization

The appearance of the as-finished fiber surfaces is shown in Figure 7. The finish goes on in a uniform coating due to the excellent film forming nature of the PMR-II-50 polyimide resin. An XPS survey spectrum of the desized and refinished M40J fibers is shown in Figure 8. The strong fluorine peak from the PMR-II-50 polyimide in the finish is readily evident in Figure 8. Figure 9 shows an XPS survey spectrum for the finished M40J fibers after a 1 hour reflux in methanol. The strong remaining fluorine peak in Figure 9 shows that the finish, including the PMR-II-50 polyimide resin is well bonded to the M40J fiber surface.

The XPS data on the finished fibers compared to PMR-II-50 polyimide resin is given in tabular form in Table I. Only 13% of the surface fluorine in the finish was removed by the 1 hour methanol reflux. Methanol is an excellent solvent for PMR-II-50 and is usually the solvent of choice for synthesis of the polyimide. As such, the large amount of residual resin remaining on the fiber surface is an indirect indication that the finish is chemically bonded to the M40J carbon fiber.
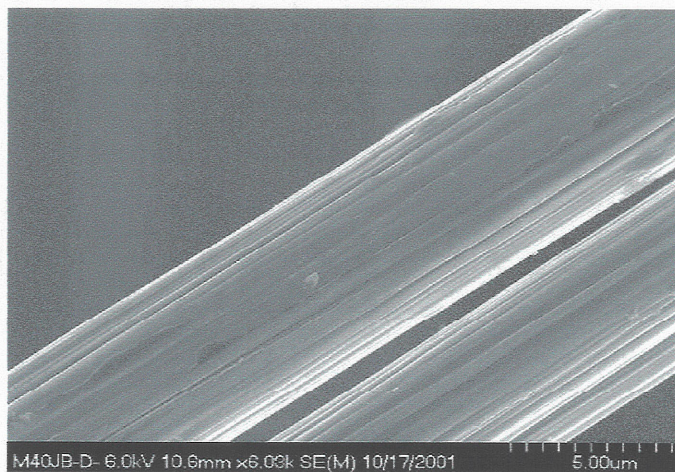

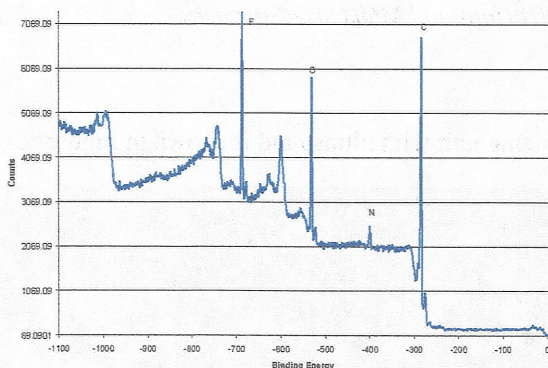Figure 7. Appearance of finished M40J carbon fiber

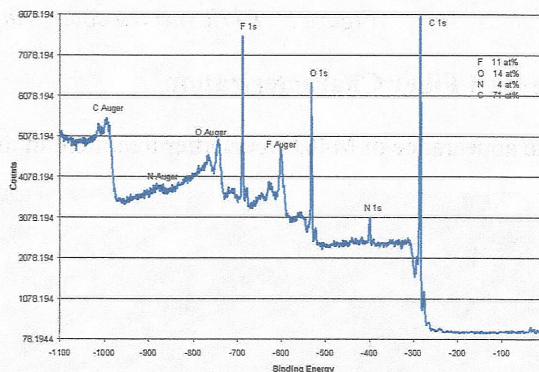*Figure 8. Survey XPS spectrum of finished M40J carbon fiber*

Figure 9. Finished fiber survey spectrum after 1 hour methanol wash

Table I. XPS Elemental Analysis of Finished M40J Carbon Fibers

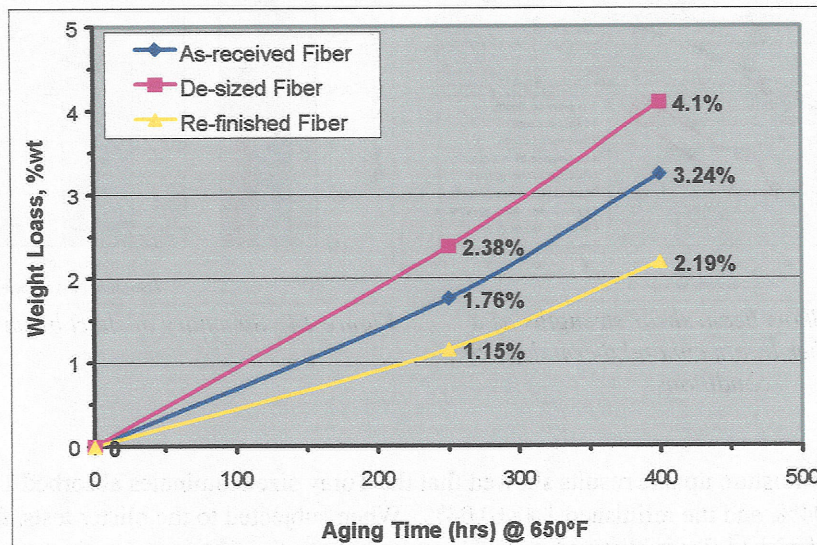| Element	% As Finished	% After MeOH Wash	% PMR-II-50 [1]
F	12.6	11.0	18.1
O	16.2	14.0	10.4
N	2.9	4.0	5.5
C	68.4	71.0	66.1

Composite Laminate Characterization and Aging

Thermomechanical characterization data for the three laminate types showed matrix Tg's at 390°C. Microcracks and void content of the as-fabricated laminates is given in Table II. The different fiber surfaces lead to a wide range of microcrack densities, with the low-temperature sizing being the highest. A range of void contents were also observed with the refinished laminates having more than twice the voids of the laminates with sized fibers.

Table II. Measured Microcracking and Void Content of As-Fabricated Laminates

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 3 measurements at 3 locations			

Thermal aging weight loss data given in Figure 10 shows the desized laminates to be the least stable while the laminates with refinished fibers exhibited the lowest weight loss.

Figure 10. Weight loss vs time for 343°C (650°F) aging as a function of fiber treatment

Composite Mechanical Properties

Tensile shear and short beam shear tests were run on specimens from each of the laminates as-fabricated and after thermal aging for 250 and 400 hours at 343°C (650°F). The ±45° tensile shear strengths as a function of percent return from the C-scans are plotted in Figure 11. The data given in Figure 11 are summarized in Figure 12. These results show that the refinished fibers have a stronger and more thermally stable interface, whereas the desized fibers have the weakest and least thermally stable interface. The laminates made with fibers treated with the manufacturer's sizing are in between the other two treatments.

Figure 11. ±45° tensile shear strengths as a function of fiber treatment and thermal aging conditions

Figure 12. Summary of ±45° tensile shear strengths

Similar trends are seen in the short beam shear data given in Figures 13 and 14; however, the laminates with refinished fibers show a larger than expected drop after thermal aging (Figure 14).
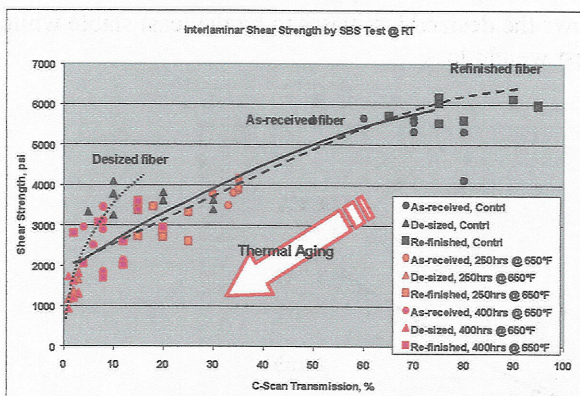

Figure 13. Short beam shear strengths as a function of fiber treatment and thermal aging conditions
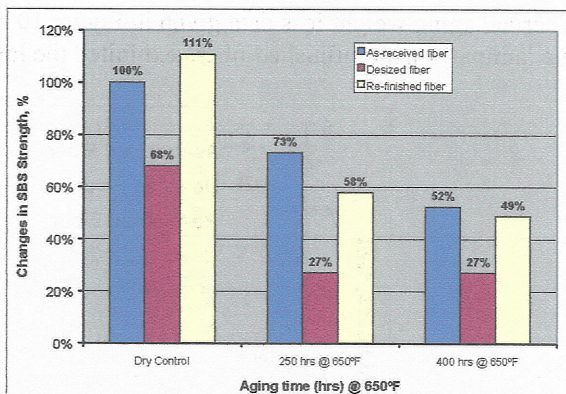

Figure 14. Summary of short beam shear strengths

Blister Tests

The equilibrium moisture uptake results showed that the Toray sized laminates absorbed 1.62±0.11%, the desized 1.51±0.04%, and the refinished 1.48±0.04%. When subjected to the blister tests, the laminates containing the refinished fibers blistered at 260°C under both test conditions. Laminates containing

desized fibers did not blister under any conditions, whereas the laminates with the Toray sizing only blistered under condition 1. The blister results are shown graphically in Figures 15 and 16.
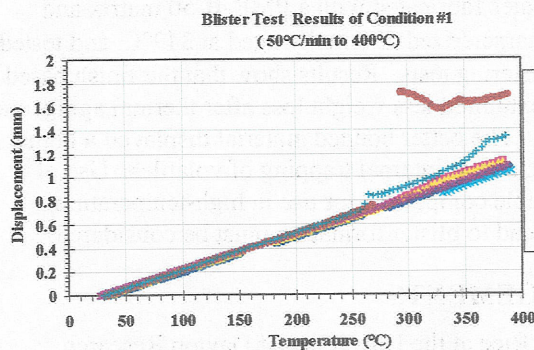

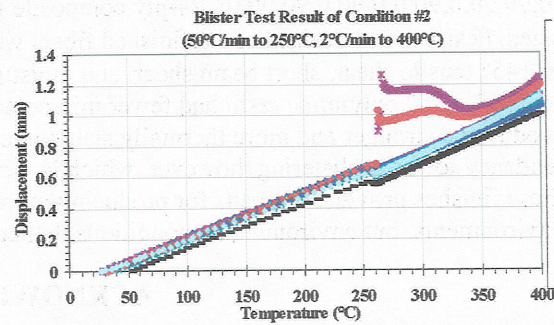Figure 15. Blister test response for condition 1

Figure 16. Blister test response for condition 2

The specimens showing large displacements in Figures 15 and 16 are from laminates with refinished fibers. The microstructures of the laminates with Toray size and the reactive finish as-fabricated and after blister testing are shown in Figures 17-20.
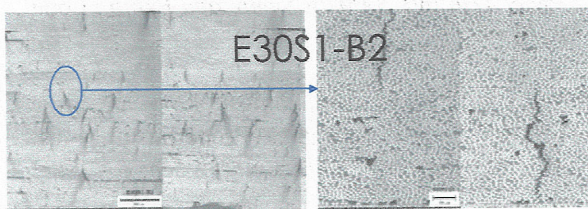

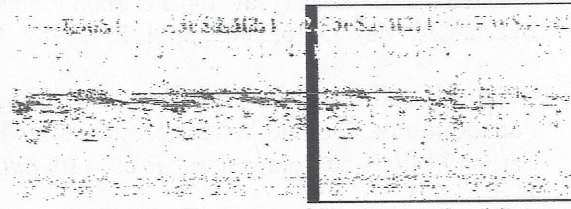Figure 17. As-fabricated cross-section of laminate with Toray-sized fibers

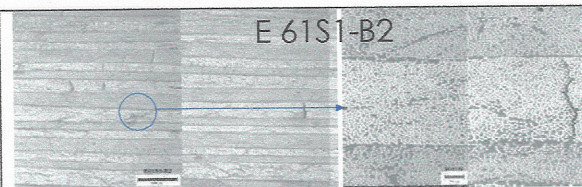Figure 18. Toray-sized laminate after blister testing

Figure 19. As-fabricated cross-section of laminate with reactive finished fibers
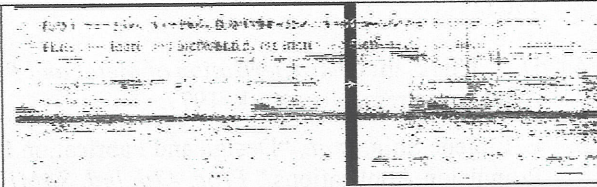

Figure 20. Reactive finished laminate after blister testing

Examination of the microcrack density data in Table II and the as-fabricated cross-sections in Figures 17 and 19 leads to the hypothesis that the better bonded laminate with the refinished fibers traps volatiles from moisture and matrix thermal degradation internally, causing the eventual blister formation (Figure 20). Where a network of microcracks exist that can provide diffusion paths out of the laminate as in the Toray-sized material, blisters do not form (Figure 18). This observation may also explain the large drop in short beam shear strength after thermal aging for the laminates with refinished fibers if internal delaminations were caused by trapping of matrix thermal degradation products.

CONCLUSIONS

This study characterized Toray M40J and M60J carbon fiber sizings and desized and refinished fibers and laminates fabricated with them. The Toray size coverage is very non-uniform and contains predominantly hydroxyl groups. A continuous desizing apparatus using hot chloroform and ultrasound

produced clean fiber. The Toray fibers are highly striated on the surface and the surface is amphoteric with approximately 12% oxygen moieties present. A finish containing PMR-II-50 polyimide and a reactive coupling agent coats the desized fibers uniformly and chemically bonds to the fiber surface. [0,90,90,0,90,0,0,90,0,90,90,0]$_s$ 24-ply composite laminates fabricated with a PMR-II-50 matrix and sized, desized, and desized and refinished fibers were characterized, thermally aged at 343°C, and tested in ±45° tensile shear, short beam shear, and moisture blistering tests. Results show that the finish based on PMR-II-50 polyimide resin had fewer microcracks, exhibited less weight loss after thermal aging, and produced a stronger and more thermally stable interface. The better bonded material displayed a higher tendency towards blistering, however, which is, perhaps, due to internal trapping of volatiles. Use of these finishes provides a means for producing more durable composites for use in high-temperature environments, but environmental conditions that could lead to blister formation must be considered.

ACKNOWLEDGEMENTS

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