THERMOMECHANICAL PROPERTIES OF 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 are also discussed.

KEYWORDS: desize, carbon fibers, sizing, surface chemistry, surface energy, polyimide

1. INTRODUCTION

High-temperature polymer matrix composites (PMCs) are desired for many aerospace and military applications and the design and development of unique, robust high-temperature composite systems has been driven by NASA and the DoD. 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 are not optimum for compatibility with high-temperature polymers. This work was undertaken to develop a means to remove the commercial size and to characterize the desized fiber surface as the first step in developing composites with high-temperature stable interfaces and improved TOS.

The approach taken was to remove the sizing with a variety of hot solvents and characterize the extent of sizing removal to aid in selection of the best desizing process. We then compared sized and desized fibers for surface topography by scanning electron microscopy (SEM), for surface chemistry by x-ray photoelectron spectroscopy (XPS), and for surface energy by single filament wetting [1]. We also characterized a candidate high-temperature polyimide resin, PMR-II-50, for surface energy and surface chemistry. Our ultimate goal is to find empirical correlations between composite interfacial measurements and composite performance to develop high-temperature surface treatments.

Results show that the Toray sizing is very nonuniform on the fiber surface and that it contains predominantly hydroxyl groups and shows slightly acidic character. Desizing in hot chloroform with ultrasound leaves mostly clean fiber with a few small (tenths of microns) nodules of residual size. The desized fiber surface is amphoteric (has acidic and basic character) with 12-15% oxygen moieties. The PMR-II-50 polyimide resin is also amphoteric, which indicates that potentially good adhesion should be obtained between desized M40J or M60J and PMR-II-50. The 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.

2. EXPERIMENTAL PROCEDURES

2.1 Desizing Approach

Initial desizing studies were conducted in laboratory glassware and the ensuing fiber surfaces evaluated using SEM and XPS. The fiber sizings were extracted from 1 to 30 minutes in hot chloroform, acetone, and water. Boiling water did not remove the sizing to any measurable extent. Five minutes in boiling chloroform or acetone dropped the surface oxygen content to a

constant level of approximately 10%. One, three, and five minutes in boiling chloroform gave the same results [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 6.5 m of heated tube 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 3 m/minute.

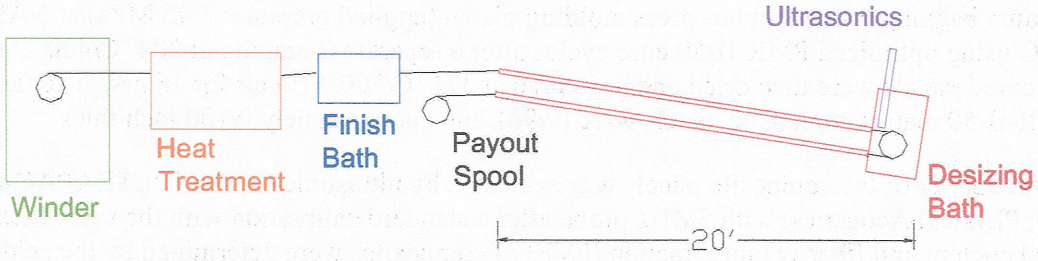
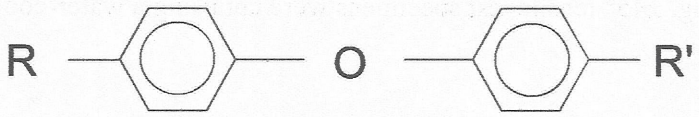


Figure 1. Schematic of continuous desizing unit

2.2 Reactive Finish Formulation

The reactive finishes were based on the work in Reference 2. That work and subsequent studies by the authors have shown that the reactive coupling agent chemically bonds to carbon fiber surfaces. Figure 2 depicts the structure of the proprietary 9307 coupling agent.



R, R' = proprietary functional groups

Figure 2. Chemical structure of 9307 coupling agent

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.

2.3 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 photoelectron peaks into components based on binding energy references from model compounds [3]. The spectra were not charge referenced.

2.4 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 4. The 30.5 cm x 30.5 cm" laminated composite panels were fabricated by typical vacuum bagging process in hot-press molding platen (applied pressure: 3.45 MPa) 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 composite panels were $[0/90]_s$ and approximately 0.100 inch thick.

Initial quality of the composite panels was evaluated by ultrasonic C-scan (ULTRAPAC-AD-500, Physical Acoustics) with 5MHz probe after a standard calibration with the same Plexiglas. Void content and fiber volume fraction (FVF) of composites were determined by the acid digestion method in 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). 1 Composite mechanical properties were measured using an Instron test frame with Series IX Automated Materials Testing System.

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

3. RESULTS AND DISCUSSION

3.1 Fiber Characterization

3.1.1 Surface Texture

The appearance of the sized Toray M40J fibers is shown in Figure 3 [1].

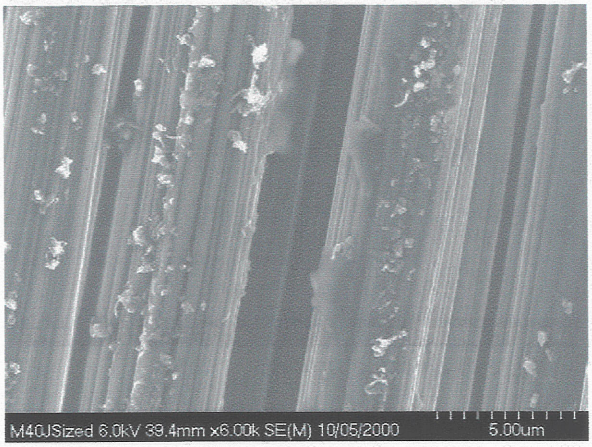
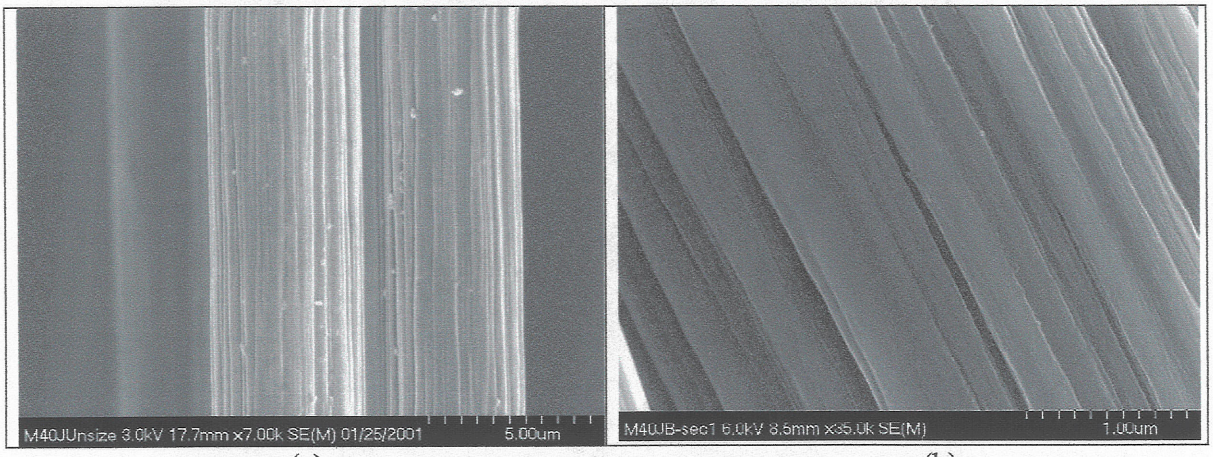


Figure 3. Appearance of sized M40J carbon fiber

Figure 3 shows that the Toray size is very non uniform in thickness and coverage on the as-produced fiber. The deep striations on the fiber surface are also seen in Figure 3. The appearance of M40J fibers after treatment in the desizing unit with and without ultrasound is shown in Figure 4.



(a) (b)

Figure 4. Appearance of desized M40J carbon fiber; (a) w/o ultrasound, (b) w/ultrasound

Most of the sizing except persistent nodules have been removed by the hot chloroform (Figure 4a). The residual nodules tenths of microns in size. They are nearly all removed with the addition of ultrasound as seen in Figure 4b.

An intermediate stage of the desizing process is shown in Figure 5.

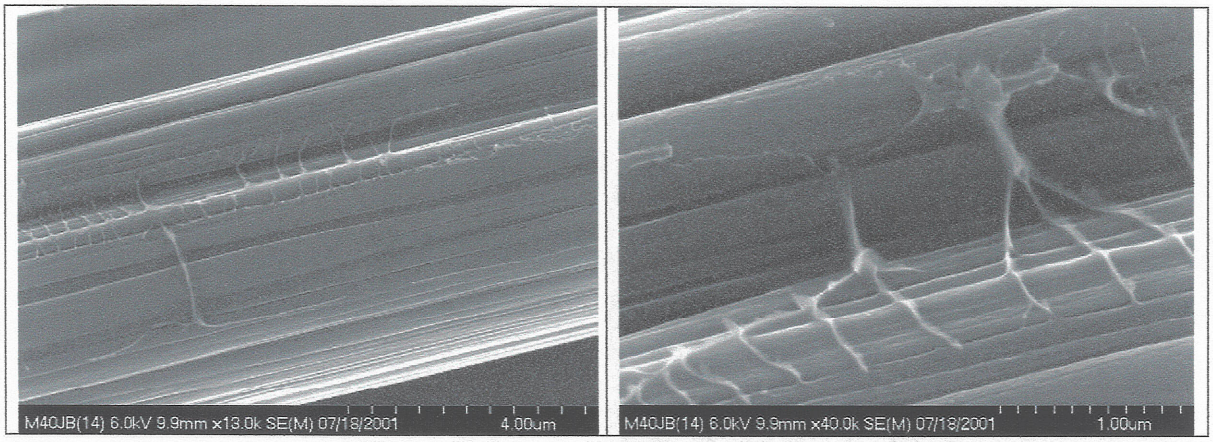


Figure 5. Intermediate stage of desizing process

The micrographs in Figure 5 show how the sizing has been removed initially except in the thickest places, which are slowly coming off. This shows that the underlying structure is the fiber surface that is heavily striated. A close up view of the desized fiber surface is shown in Figure 6.

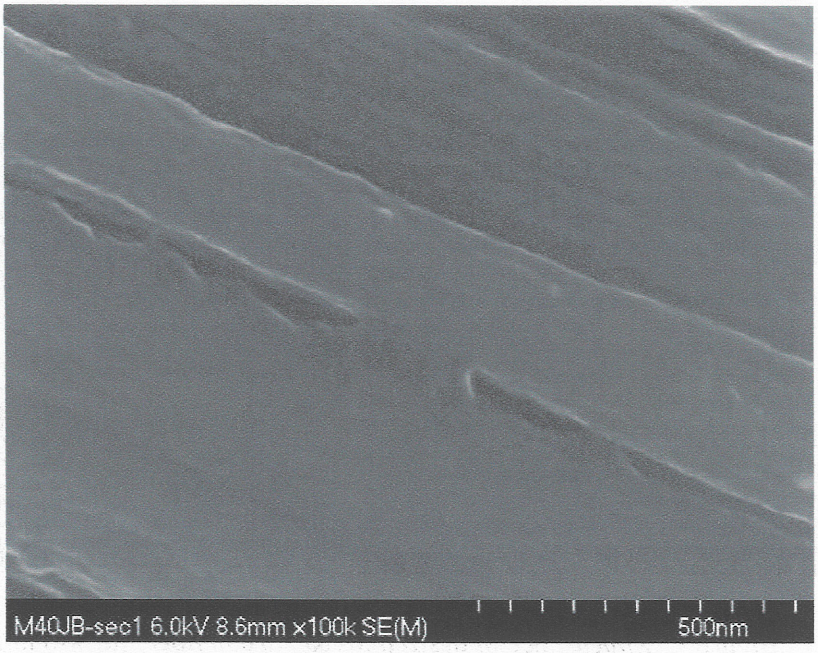


Figure 6. High magnification view of desized M40J surface

3.1.2 XPS Analysis

In order to check the consistency of the desizing process, a 1 kg roll of desized M40J carbon fiber was analyzed using XPS for surface chemistry. XPS results from the beginning (section 1), center (section 2), and end (section 3) of the roll are given in Table I.

Table I. XPS Analysis of Large Batch M40J Desized 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

The % oxygen results from Table I show that the fiber surface contains 11.7 ±1.65 percent oxygen. The standard deviation is near the normal error expected for XPS measurements, which shows that the desizing process is consistent over time.

The appearance of the 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.

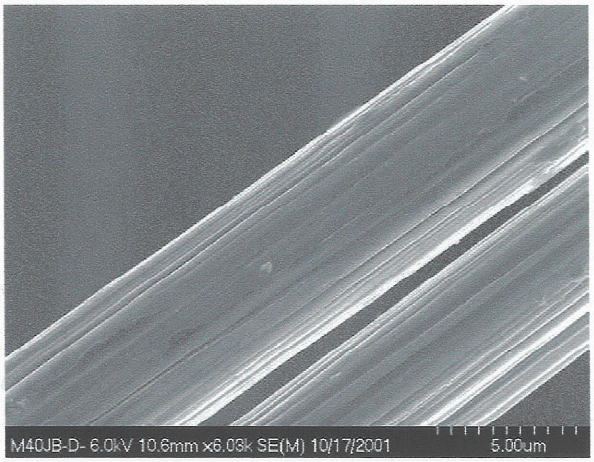


Figure 7. Appearance of Finished M40J Carbon Fiber

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 II. Only 13 percent 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.

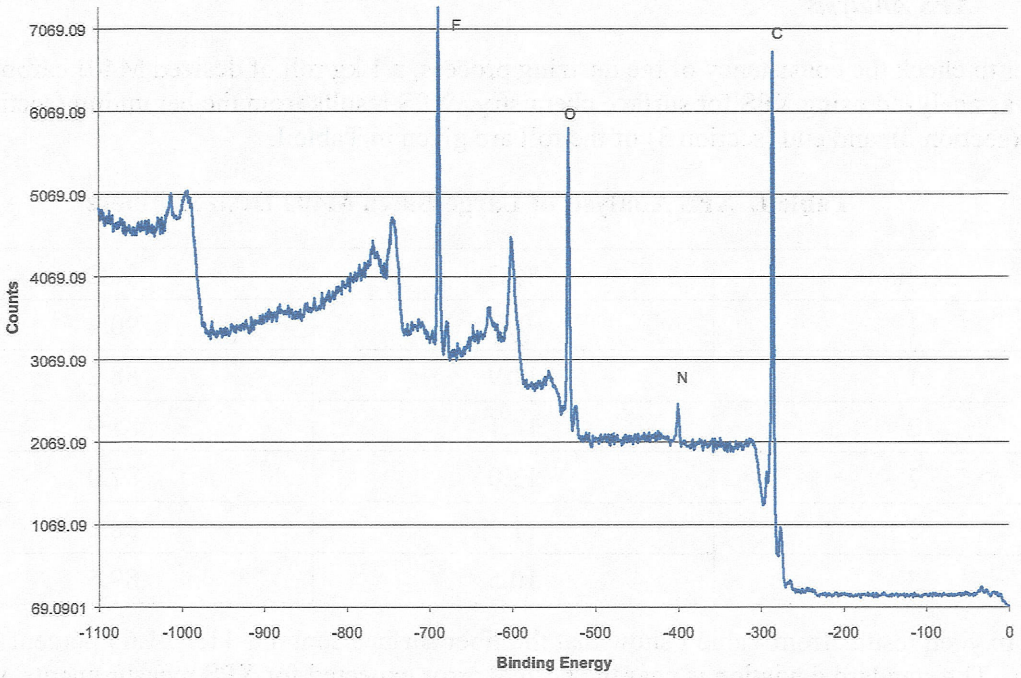


Figure 8. Survey XPS Spectrum of Finished M40J Carbon Fiber

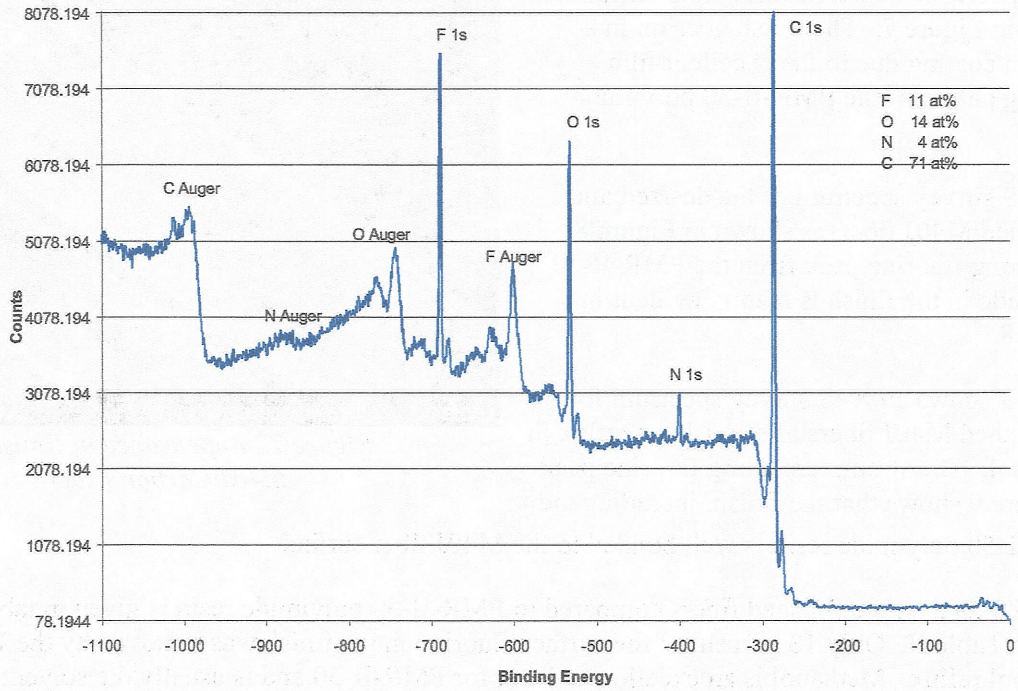


Figure 9. Finished Fiber Survey Spectrum after 1 Hour Methanol Wash

Table II. 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

3.1.3 Dry Tow Tensile Strength

The dry tows with the various surface treatments were then tested for tensile strength according to method ASTM D885. The dry tows were tested at a 25.4 cm nip to nip gage length, untwisted with a cross head speed of 30.5 cm/minute. Ten specimens were tested at each condition. Dry tow tensile results are summarized in Table III.

Table III. Mechanical Properties of M40J Tows

	Dry Tow Tensile Testing*			
	Tenacity/Tensile Strength			Strain-to Failure %
	g/d	ksi	% drop	
As-received Control	12.8 ± 1.4	290 ± 32		0.7 ± 0.1
Desized	10.2 ± 0.7	231 ± 16	20%	0.6 ± 0.0
Desized and Refinished	10.6 ± 1.1	240 ± 25	17%	0.7 ± 0.1

The tensile data in Table III indicate that the desizing operation is degrading the tow strength by 20 percent compared to the as-received tows. Clearly, some damage is being inflected on the fibers during the desizing process; however, a dry tow test may be misleading in terms of the amount of damage. In a dry tow test, any broken fibers are unable to carry any load for the balance of the test. In contrast, in an impregnated tow test, broken fibers are able to reload through interfacial shear at the broken ends and contribute to the overall failure load. As such, the performance of the desized tows may be better in composites than indicated by the 20 percent

strength loss in the dry tow data. Additional testing is needed to determine the actual amount of damage to the desized fibers.

3.1.4 Composite Laminate Characterization and Aging

Microcracks and void content of the as-fabricated laminates is given in Table IV. 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 IV. 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			

Thermomechanical characterization data for the 3 laminate types is given in Table VI. A trend is seen in Table V toward lower Tg's for the desized and refinished fibers. It is not evident why the fiber surface would have that great an affect on the bulk Tg or whether another phenomenon is occurring, such as small variations in processing.

Table V. Thermomechanical Analysis of As-Fabricated Laminates

Fiber Treatment	T_g, °C G' onset	T_g, °C Tan d	T_β°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

After thermal aging, all of the laminates showed a Tg (G') around 390°C, which shows that the as-fabricated refinished laminate T_g was artificially depressed for some reason.

Thermal aging weight loss data given in Table VI shows the desized laminates to be the least stable with the laminates with refinished fibers exhibit the lowest weight loss.

Table VI. Weight Loss from Thermal Aging at 343 °C

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

3.1.5 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. The ±45° tensile shear strengths as a function of percent return from the C-scans are plotted in Figure 10. The data given in Figure 10 are summarized in Figure 11. 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.

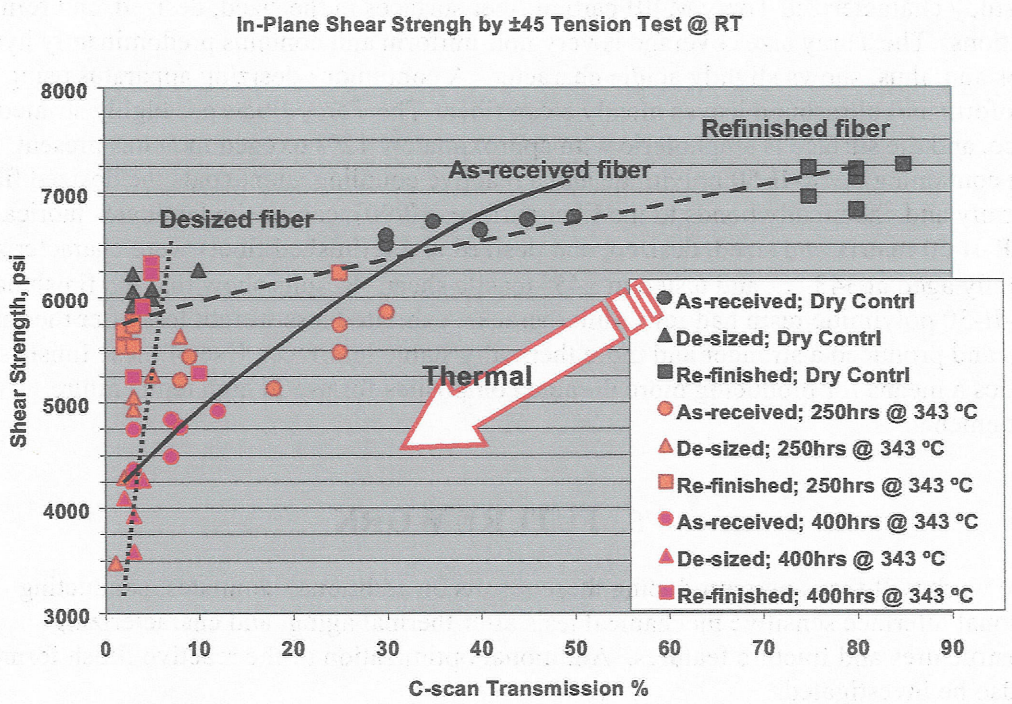


Figure 10. ±45° tensile shear strengths as a function of fiber treatment and thermal aging conditions

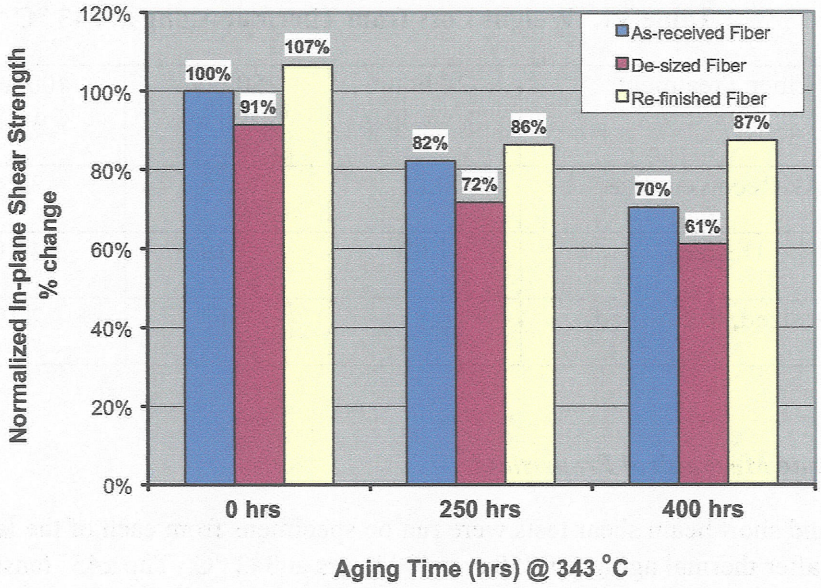


Figure 11. Summary of ±45° tensile shear strengths

4. CONCLUSIONS

This study characterized Toray M40J carbon fiber surfaces in the sized, desized, and refinished conditions. The Toray size coverage is very non-uniform and contains predominantly hydroxyl groups and, thus, shows slightly acidic character. A continuous desizing apparatus using hot chloroform and ultrasound leaves mostly 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. $[0/90]_s$ 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. 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. Use of these finishes provides a means for producing more durable composites for use in high temperature environments.

5. FUTURE WORK

Future work will focus on reproducing these results on additional laminates, conducting additional interface sensitive mechanical tests after thermal aging, and characterizing microstructures and fracture features. Additional optimization of the reactive finish formulation will also be investigated.

6. REFERENCES

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7. BIOGRAPHIES

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Dr. Allred earned his Sc.D. in the Polymerics Panel of the Department of Materials Science and Engineering at MIT under a Doctoral Study Fellowship from Sandia National Laboratories. He has a B.S. in Chemistry and an M.S. in Nuclear Engineering Materials, both from the University of New Mexico. Dr. Allred is president and owner/founder of Adherent Technologies, Inc., a company that provides contract research and development services to government and industry. He has research experience at Sandia National Labs, MIT, and PDA Engineering. Dr. Allred's research has included radiation curing materials, plasma surface modification of materials, plasma/surface spectroscopy, environmental effects on polymers/composite materials, composite and adhesive test development, materials for electronic packaging, acoustic wave and fiber optic microsensors, tertiary recycling of complex polymer mixtures, and the development of specialty polymers, adhesives, coatings, and foams. Dr. Allred has published over 100 papers in technical journals and conference proceedings. He has 20 patent disclosures and over 250 company reports. The vast majority of those publications are in the fields of composites, polymers, recycling, and sensors.

Dr. James K. Sutter

Dr. Sutter earned his DSc in Chemistry at Case Western Reserve University. He has a BS in chemistry from SUNY College of Environmental Sciences Forestry in Syracuse. Since graduating from Case Western, Dr. Sutter has been a member of the technical staff at NASA Glenn Research Center in Cleveland, OH. His research is focused on applications requiring high-temperature polymers for advanced aircraft engines. Dr. Sutter's research has included coatings for erosion and oxidation protection on polymer composites. Dr Sutter has published over 100 publications in technical journals and conference proceedings. Dr. Sutter also co-chairs a joint DoD-NASA workshop on high temperature polymer composites.