Dynamic Mechanical Analysis of Graphite/Epoxy

Composites with Varied Interphases

by

Jennifer Susan Elmore

Thesis submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

Master of Science

in

Engineering Mechanics

Kenneth L. Reifsnider, Co-Chair Wayne W. Stinchcomb, Co-Chair

Muhammed Hajj

July, 1994

Blacksburg, Virginia
Dynamic Mechanical Analysis of Graphite/Epoxy Composites with Varied Interphases

by

Jennifer Susan Elmore

Committee Co-Chairmen: Wayne W. Stinchcomb and Kenneth L. Reisneider
Engineering Science and Mechanics

(ABSTRACT)

Dynamic mechanical analysis (DMA) has been used extensively to characterize polymeric materials. This thesis investigates the use of this technique to characterize composite materials. Four material systems, all having the same fiber and the same matrix material, were systematically altered with different interphase regions. Initial run data indicates that the variation in fiber sizings create different interphase regions that are detectable by DMA. However, some post-cured specimens revealed that those differences are reduced with further heat treatment. Fiber sizing variation also affects the material response to thermal and mechanical cycling. Different fiber surface treatments have little effect on the dynamic mechanical response of the materials. It is shown that DMA is a test method that yields repeatable results and is capable of detecting small changes in composite constituents.
Dedication

This work is dedicated to the memory of Dr. Wayne Webster Stinchcomb, my teacher, mentor, and friend.
Acknowledgments

The author would like to thank the following people for their contribution to this work:

- Dr. Wayne Stinchcomb, for being there to listen whether the problem was academic or personal. Thank you for believing in me and guiding me through my masters work. Your presence is sorely missed.

- Dr. Kenneth Reifsnider, for taking the time to serve on my committee and fill in as a co-advisor. Thank you for your advice, time, and patience.

- Dr. Muhammad Hajj, for serving on my committee. I will always appreciate our conversations and your advice.

- Dr. Robert Swain, for having the patience to teach me to run an MTS, strain gauge, and other basic research principles, when he really didn't have to take the time. I'll forget about all the hours I spent tabbing.

- Scott Case, here's to the thick and the thin, the ins and the outs, the ups and the downs. We have been through it all together, and came out as quite different people than we were in the beginning. Love always...

- Jack Lesko, for the friendship, support, and insight you have given me.

- Dr. Suresh Subramanian, thank you for all your advice on my data, for letting me use some of your results in my thesis, and for not calling me one day ahead of time to go to Montreal. No Problem!

- Mehran Elahi and Kin Liao, part of the late night crowd at the MRG, thanks for all those interesting late night conversations.

- The fellow members of the MRG, more than a research group, more than friends, more like a family.

- Melba Morrozoff, Sheila Collins, Paula Lee, and Cindy Hopkins, for all their help.

- Virginia Institute for Material Systems and the National Science Foundation, for supporting me over the years.

- Samuel, Rilla, and Kristi Elmore - For all your support, financially and emotionally, you have given me over the years. I don't know what I would have done without all of you being there for me.
# Table of Contents

1.0 INTRODUCTION .................................................................................................................. 1  
  1.1 Introduction ...................................................................................................................... 1  
  1.2 Literature Review ............................................................................................................. 2  

2.0 EXPERIMENTAL TECHNIQUES ............................................................................................. 8  
  2.1 Material System .................................................................................................................. 8  
  2.2 Laminate Preparation and Configuration .......................................................................... 8  
    2.2.1 Laminate Preparation .................................................................................................... 8  
    2.2.2 Laminate Configuration ................................................................................................. 8  
    2.2.3 Test Specimens .............................................................................................................. 9  
  2.3 Experimental Procedure ..................................................................................................... 9  
    2.3.1 Scanning Electron Microscopy ...................................................................................... 9  
    2.3.2 Dynamic Mechanical Analysis ...................................................................................... 11  
    2.3.3 Thermogravimetric Analysis ......................................................................................... 13  
    2.3.4 Penetrant Enhanced X-ray Radiography ..................................................................... 13  

3.0 RESULTS AND DISCUSSION ............................................................................................... 15  
  3.1 Scanning Electron Microscopy .......................................................................................... 15  
  3.2 DMTA Results ................................................................................................................... 16  
    3.2.1 Unidirectional Specimens ............................................................................................ 16  
    3.2.2 Transverse Specimens ................................................................................................ 23  
    3.2.3 Cross-Ply Specimens ................................................................................................... 24  
    3.2.4 Statistical Analysis ...................................................................................................... 25  
  3.3 X-ray Radiography ............................................................................................................ 26  
  3.4 Thermogravimetric Analysis .............................................................................................. 28  
  3.5 Property Comparison ........................................................................................................ 33  

4.0 CONCLUSIONS .................................................................................................................. 35  
  4.1 Scanning Electron Microscopy ......................................................................................... 35  
  4.2 DMTA Results .................................................................................................................. 35  
    4.2.1 Unidirectional Specimens ............................................................................................ 35  
    4.2.2 Cross-Ply Specimens ................................................................................................... 38  
    4.2.3 Transverse Specimens ................................................................................................ 38  
  4.3 X-ray Radiography ............................................................................................................ 38  
  4.4 Thermogravimetric Analysis .............................................................................................. 38  
  4.5 Property Comparison ........................................................................................................ 39  
  4.6 Future Work ....................................................................................................................... 39  

REFERENCES ............................................................................................................................. 40  

APPENDIX A ............................................................................................................................. 43  

VITA ......................................................................................................................................... 90
List of Illustrations

Figure 1. Single cantilever type test configuration. ................................................. 48
Figure 2. SEM of 810A material at 8.0X. ................................................................. 49
Figure 3. SEM of 810A material at 10.0X. ................................................................. 49
Figure 4. SEM of 810O material at 8.0X. ................................................................. 50
Figure 5. SEM of 810O material at 10.0X ................................................................. 50
Figure 6. The first runs for all 82A unidirectional specimens. .............................. 51
Figure 7. The first runs for all 810A unidirectional specimens tested. ................. 52
Figure 8. The first runs for all 810O unidirectional specimens tested. .................. 53
Figure 9. The first runs for all 820A unidirectional specimens tested. ................. 54
Figure 10. Representative 82A unidirectional specimen at multiple frequencies... 55
Figure 11. Representative 810A unidirectional specimen at multiple frequencies.. 56
Figure 12. Representative 810O unidirectional specimen at multiple frequencies.. 57
Figure 13. Representative 820A unidirectional specimen at multiple frequencies.. 58
Figure 14. Shift in glass transition temperature with frequencies. ......................... 59
Figure 15. Comparison of representative curves for 82A, 810A, 810O, and 820A unidirectional specimens at 1 Hz. ......................................................... 60
Figure 16. Multiple run comparison of an 82A unidirectional specimen at 1 Hz.... 61
Figure 17. Multiple run comparison of an 810A unidirectional specimen at 1 Hz... 62
Figure 18. Multiple run comparison of an 810O unidirectional specimen at 1 Hz... 63
Figure 19. Multiple run comparison of an 820A unidirectional specimen at 1 Hz... 64
Figure 20. Second run comparison of representative curves for 82A, 810A, 810O, and 820A unidirectional specimens at 1 Hz. ........................................... 65
Figure 21. Third run comparison of representative curves for 82A, 810A, 810O, and 820A unidirectional specimens at 1 Hz. ................................. 66

Figure 22. First run comparison of representative curves for 82A, 810A, 810O, and 820A transverse specimens at 1 Hz. ........................................ 67

Figure 23. First run comparison of representative curves for 82A, 810A, 810O, and 820A cross-ply specimens at 1 Hz. ........................................ 68

Figure 24. First run comparison of representative curves for 82A unidirectional, cross-ply, and transverse specimens at 1 Hz. ................................. 69

Figure 25. First run comparison of representative curves for 810A unidirectional, cross-ply, and transverse specimens at 1 Hz. ................................. 70

Figure 26. First run comparison of representative curves for 810O unidirectional, cross-ply, and transverse specimens at 1 Hz. ........................................ 71

Figure 27. First run comparison of representative curves for 820A unidirectional, cross-ply, and transverse specimens at 1 Hz. ........................................ 72

Figure 28. Multiple run comparison of an 82A, post-cured, unidirectional specimen at 1 Hz. .......................................................... 73

Figure 29. Multiple run comparison of an 810A, post-cured, unidirectional specimen at 1 Hz. .......................................................... 74

Figure 30. Multiple run comparison of an 810O, post-cured, unidirectional specimen at 1 Hz. .......................................................... 75

Figure 31. Multiple run comparison of an 820A, post-cured, unidirectional specimen at 1 Hz. .......................................................... 76

Figure 32. Comparison of curves for 82A, 810A, 810O, and 820A, post-cured, unidirectional specimens at 1 Hz. .......................................................... 77

Figure 33. First run comparison of 1 Hz curves for 82A, not post-cured versus post-cured. .......................................................... 78

Figure 34. First run comparison of 1 Hz curves for 810A, not post-cured versus post-cured. .......................................................... 79

Figure 35. First run comparison of 1 Hz curves for 810O, not post-cured versus post-cured. .......................................................... 80
Figure 36. First run comparison of 1 Hz curves for 820A, not post-cured versus post-cured. .......................................................... 81

Figure 37. X-ray radiograph of a [0], 810A composite specimen subjected to thermal and mechanical cycling. ......................................................... 82

Figure 38. X-ray radiograph of a [0], 810O composite specimen subjected to thermal and mechanical cycling. ......................................................... 82

Figure 39. X-ray radiograph of a [0], 82A composite specimen subjected to thermal and mechanical cycling. ......................................................... 83

Figure 40. X-ray radiograph of a [0], 820A composite specimen subjected to thermal and mechanical cycling. ......................................................... 83

Figure 41. X-ray radiograph of a [90], 810A composite specimen subjected to thermal and mechanical cycling. ......................................................... 84

Figure 42. X-ray radiograph of a [90], 810O composite specimen subjected to thermal and mechanical cycling. ......................................................... 84

Figure 43. X-ray radiograph of a [90], 82A composite specimen subjected to thermal and mechanical cycling. ......................................................... 85

Figure 44. X-ray radiograph of a [90], 820A composite specimen subjected to thermal and mechanical cycling. ......................................................... 85

Figure 45. X-ray radiograph of a [0,90], 810A composite specimen subjected to thermal and mechanical cycling. ......................................................... 86

Figure 46. X-ray radiograph of a [0,90], 810O composite specimen subjected to thermal and mechanical cycling. ......................................................... 86

Figure 47. X-ray radiograph of a [0,90], 82A composite specimen subjected to thermal and mechanical cycling. ......................................................... 87

Figure 48. X-ray radiograph of a [0,90], 820A composite specimen subjected to thermal and mechanical cycling. ......................................................... 87

Figure 49. X-ray radiograph of a [0,90], 810O composite specimen subjected to mechanical cycling only. ......................................................... 88

Figure 50. Results of initial TGA run. .......................................................... 89
List of Tables

Table 1. Representation of material system according to fiber sizing and fiber surface treatment. ................................................................. 10

Table 2. This table shows the standard deviations for several DMTA curve properties. .............................................................................. 27

Table 3. The Duncan grouping for the maximum $E'$ values for each material system. ........................................................................... 29

Table 4. The Duncan grouping for the maximum tan $\delta$ value for each material system. ................................................................. 30

Table 5. The Duncan grouping for the glass transition temperature for each material system. ........................................................................ 31

Table 6. The Duncan grouping for the area under the tan $\delta$ curve. ......................................................................................... 32

Table 7. Mechanical properties for 810A and 810O material systems. .................................................... 34
1.0 Introduction

1.1 Introduction

This work began with the idea that Dynamic Mechanical Analysis (DMA) could be used as a screening method to eliminate materials from further, more thorough and expensive testing when being considered for a specific application. If certain trends could be established between DMA properties and macro-level behavior, then perhaps this quick test could be used to screen composite materials. DMA is a technique that has been used to detect changes in dynamic mechanical properties of polymers for nearly 25 years. More recently it has been used as a method to detect changes in the properties of composite materials. Of these studies, there seems to be a lack of information on interphase characterization in systematically-altered graphite/epoxy composite materials. The interphase is the region around the fiber that has properties that are different from the properties of the fiber and the matrix. The interphase is thought to have properties that are some combination of the fiber properties and the fiber properties. While there is general agreement that this test method is able to detect interphase differences in polymeric composite materials, it is not clear which parameters best detect the differences in material interphases. Also, while interphase studies have been performed, in very few cases is there an effort made to relate these dynamic mechanical properties back to known macro-level properties.

This study proposes to determine what dynamic mechanical properties best detect interphase differences in a set of materials in which the nature of the interphase is known to be different, to determine how laminate geometry affects the dynamic
response, and to determine if there are any correlation's between dynamic mechanical properties and macro-level properties. Can the DMA detect interphase differences? Is there any correlation between storage modulus, \( E' \), and strength to failure? Is there any comparison to be made with energy dissipation and fatigue life? Although DMA is a bending type test, can any trends be established with fatigue, creep, or static material tests? These are the types of questions this study will explore.

1.2 Literature Review

The properties of fiber-reinforced polymer composites depend on the properties of the two main constituents, the fiber and the matrix. However, the performance of these materials is often controlled by the properties of the interphase between the fiber and the matrix. A fundamental understanding of this fiber-matrix interphase, which may have different characteristics than the bulk matrix, can contribute to an evaluation of the mechanical behavior and capabilities of composite materials. Dynamic mechanical analysis is a method that has been shown to be sensitive to the presence of an interphase in glass/epoxy and graphite/epoxy composites.

The first dynamic mechanical tests performed to detect an interphase region were in the area of polymer-filler interactions [1-5]. Ziegel, et al. [2] studied the effect of various inorganic fillers on the storage modulus of four elastomers in order to investigate the formation of an interphase. The effect of such an interphase on damping properties of composites was described by the following equation:

\[
\tan \delta_i = (1-B\Phi) \tan \delta_m
\]  
(1)
where $\phi$ is the volume fraction of the reinforcement and the subscripts c and m refer to the composite and the matrix. The parameter B is used to correct the volume fraction of reinforcement because of the formation of a layer of immobilized interphase resulting from strong interactions at the interfaces.

Another parameter was introduced by Kubat, et al. [4] in a study on high density polyethylene filled with 20% by volume of untreated glass spheres or glass spheres treated with a silane based coupling agent. It was assumed that an interphase region formed in the matrix around each filler particle with properties different than those of the bulk matrix. Parameter A can be estimated from the damping of the matrix and the composite by:

$$A = (1 - \phi_j)^3 \left( \tan \delta_j / \tan \delta_m \right) - 1 \quad (2)$$

where A is always positive and is due to the reduction of mobility of the molecular chains at the interfaces. For example, a low value of A indicates a high degree of interaction or adhesion between the phases. For an ideal composite, where "ideal" interfaces transfer load but do not contribute to damping, the rule of mixtures, as suggested by Nielsen [6], can be used to estimate the damping of an ideal composite.

For low damping reinforcement ($\tan \delta_j = 0$), this leads to:

$$\tan \delta_c = (1 - \phi_i) \tan \delta_m \quad (3)$$

where for an ideal composite, $A = 0$, indicating complete interaction between the phases, and B=1, the minimum correction for the volume fraction of reinforcement.
Several other studies on interfacial interactions of filled polymers include one by Boluk and Schreiver [3] where the dynamic mechanical response of rutile-filled chlorinated polyethylene was studied as a function of temperature, filler loading, and filler surface condition. By making the surfaces of the fillers either acidic or basic, the values of $B$ and $A$ were determined to be 1.84 and 1.03, respectively. Iisaka and Shibayama [1] investigated the dynamic mechanical properties of polymers filled with glass beads and mica flakes. In this case the glass transition temperature, $T_g$, increased with and increase of filler content in each system. The increase in $T_g$ was attributed to the polymer-filler interaction energy. Ibarra and Chamorro [5] investigated the mechanical and dynamic properties of composites with an EDPM matrix and short fibers at three different fiber concentrations. They found that properties such as green strength, tear strength, storage modulus, and stress at constant strain were dependent on fiber volume fraction and the type of fiber, either polyester or carbon.

Several studies have been performed on the effects of fiber surface treatments on glass fiber reinforced matrices. Reed [7] studied a bisphenol-A based epoxy with silane coated E-glass fibers. The dynamic mechanical and thermal properties were determined for unidirectional epoxy/glass composites at various fiber orientation angles. The damping behavior, i.e. the tan $\delta$ curves, of the composites in flexural deformation becomes similar to the matrix when the fibers are oriented towards 90°. The contribution of the interfacial region becomes more significant when the fiber-dominated properties, 0°, are measured. Therefore, in flexural deformation, there is a more sensitive detection of the interphase in unidirectional specimens. Gerard, et al. [8-
performed fatigue experiments in a three point bend configuration and measured viscoelastic properties by DMA. It was concluded that glass/epoxy composite materials sustained permanent interphase damage during fatigue while carbon/epoxy composites sustained little damage to the interphase. It was found that damping depends strongly on the orientation of fibers with the direction of oscillation and concluded that damping is more interface sensitive because in the bending mode, more of the load is carried by the fibers. They also compared bending and torsion methods of dynamic mechanical analysis. Generally, good agreement was found between the two different test modes for dynamic mechanical measurements. The torsion mode was found to be more sensitive to the matrix while the bending mode was more sensitive to the fibers. Cinquin, et al. [10] studied unidirectional glass composites with a thermoplastic matrix with varied additives. Varied fiber surface treatments were also applied. A coupling agent introduced onto the fiber decreased the damping which is associated with an improvement in interface bonding. However, matrix additives were found to have a detrimental or negligible effect on the composite performance. Thomason [11] produced a study of seven glass fibers and one carbon fiber embedded in several different matrix types. The materials were investigated as a function of fiber type, fiber content, fiber orientation angle, and effect of heating rate. At heating rates above 2 °C/min. an artificial damping peak was observed above the Tg of the matrix material for the glass fiber reinforced composites. However, this artifact was not seen for the carbon fiber reinforced composites evaluated.

Some of the investigations into carbon/epoxy composites have investigated
similar trends. Chang [12] investigated the effects of varied fiber surface treatments on the dynamic mechanical response of thermoplastic matrix composites. Differences in the height of the tan δ curves were distinguishable for unidirectional composites, (0°), and matrix dominated composites, (90°). These differences were attributed to the differences in the interphase properties. No significant effect was noted for differences in Tg, the glass transition temperature. Ide, et al. [13] investigated graphite/epoxy composites and suggested that an interphase may consist of two kinds of phases with different properties and that one of them may be ascribed to a boundary layer with relatively weaker interaction. Edie, et al. [14] studied unidirectional carbon/epoxy composites in torsional DMA. Dynamic mechanical analysis was able to differentiate between the fiber/matrix bond strength of two different fiber types, based on the principle that composites with poor interface bonding tend to dissipate more energy than that with good interface bonding. Dong and Gauvin [15] studied carbon/epoxy composites and the effect of fiber volume fraction on experimental parameters such as oscillation mode, amplitude, frequency, and temperature. Detection of similar interface quality was found for the different fiber volume fractions. For unidirectional composites, the flexural deformation mode provides a more sensitive detection of the interfacial region than the torsional mode.

Some of the conclusions that can be drawn from the literature are:

- Unidirectional specimens, (0°), are more sensitive to the presence of the interphase. This is attributed to the measurement of fiber dominated properties as opposed to 90° specimens which exhibit matrix dominated properties.
• The flexural deformation mode is more sensitive to interphase detection than the torsional mode of dynamic mechanical analysis.

• Dynamic mechanical analysis is able to detect interphase differences, i.e. the changes in $E'$, $E''$ and $\tan \delta$ are detectable. Differences in fiber surface treatments and fiber surface states as well as different matrix materials producing different interfaces were detectable by this method.

• It is generally accepted that a heating rate of 2 °C/min. should be used to avoid producing an artificial damping peak. However, this phenomena was only observed in glass/epoxy composite systems.
2.0 Experimental Techniques

2.1 Material System

Four different material systems, obtained from McDonnell Aircraft Co. through Dexter Hysol, were investigated in this study. These four material systems contain the same 45 Msi tensile modulus, 850 ksi tensile strength carbon fiber in the HC9106-3 toughened epoxy matrix. Three of the systems have the fiber sized with an 'A' epoxy sizing. The other system has an 'O' organic fiber sizing. Lesko et al. [18] have identified these sizings with the manufacturers' permission. The 'A' sizing is an unreacted Bisphenol-A based epoxy and the 'O' sizing is a thermoplastic, Polyvinylpyrrolidone (PVP). The amount of surface treatment was varied, 20%, 100%, and 200% of the industry standard, for the three material systems with the 'A' epoxy sizing. Using the nomenclature of Swain [19] these materials are designated 82A, 810A, and 820A respectively. The 'O' PVP sized fiber only received 100% of the standard surface treatment. This material is designated 810O.

2.2 Laminate Preparation and Configuration

2.2.1 Laminate Preparation

The prepreg was laid into desired composite laminate configurations and shipped to Dexter-Hysol for autoclave preparation. For further information on processing HC9106-3 and thermosetting composites in general, see Appendix A.

2.2.2 Laminate Configuration

The pre-preg sent to Dexter-Hysol for processing was vacuum debulked into two configurations. All of the material systems were laid-up into an 8-ply
unidirectional, \([0]_\text{s}\), laminate and an 8-ply cross ply, \([0,90]_\text{s}\), laminate. The resulting 6” x 6” panels were ultrasonically C-scanned for imperfections after processing.

2.2.3 Test Specimens

Both laminate types, \([0]_\text{s}\), and \([0,90]_\text{s}\), were cut into Dynamic Mechanical Analysis (DMA) specimens. The unidirectional, \([0]_\text{s}\), specimens were also cut into \([90]_\text{s}\), specimens. These specimens had nominal dimensions of 12 x 35 x 1 mm. Although the specimens were ultrasonically C-scanned, there were visible surface flaws, made during processing, present in some of the specimens. It is assumed that these flaws do not significantly affect dynamic performance.

The laminates used in Scanning Electron Microscopy (SEM) were cut and placed, with surface of interest perpendicular to the free surface, in a cold-mount ring. The ring was then filled with Epoxide Resin from Buehler and allowed to cure overnight at room temperature. The potted specimens were then polished to create a smooth surface with minimal scratching so that microscopic inspection was possible.

The composites used in Thermogravimetric Analysis (TGA) were untested composite laminates that were cut into 10-30 mg pieces. These pieces were then placed in TGA pans and analyzed in air.

2.3 Experimental Procedure

2.3.1 Scanning Electron Microscopy

The characteristics of the fiber-matrix interphase were investigated using a permanganic etching technique. This method was used to investigate the influence of
Table 1. Representation of material system according to fiber sizing and fiber surface treatment.

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>Fiber Surface Treatment</th>
<th>Fiber Sizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>82A</td>
<td>20%</td>
<td>A-Epoxy Sizing</td>
</tr>
<tr>
<td>810A</td>
<td>100%</td>
<td>A-Epoxy Sizing</td>
</tr>
<tr>
<td>810O</td>
<td>100%</td>
<td>O-PVP Sizing</td>
</tr>
<tr>
<td>820A</td>
<td>200%</td>
<td>A-Epoxy Sizing</td>
</tr>
</tbody>
</table>
fiber sizing on the local cure chemistry of the matrix material near the fiber [20].

Polished edges of samples are etched using a prepared potassium permanganate solution. One gram of potassium permanganate was added to 40 ml of 85% Orthophosphoric acid and 10 ml of distilled water. The solution was stirred for 15 minutes and the liquid decanted from the remaining potassium permanganate crystals. The polished specimen was submerged and stirred in the etchant solution for 5 minutes. The specimens were then washed in water to prevent further etching. The etched specimen was then coated with gold and observed under a scanning electron microscope.

2.3.2 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis is a technique originally developed for testing the molecular weight, relaxations in the amorphous phase, motion in the crystalline phase, and other properties of polymers [21]. In recent years this method has been extended to include the testing of composite materials. For these experiments a Polymer Labs Dynamic Mechanical Thermal Analysis Unit was used [22]. The PL_DMTA consists of three parts, the mechanical measuring head, the microprocessor-controlled analyzer, and the temperature programmer.

The dynamic mechanical measuring head can hold a bar in a single or double cantilever type test. The sample is rigidly held at one or both ends by clamping to the steel frame supported on ceramic pillars as shown in Figure 1. It is then flexed by a central clamp driven sinusoidally by an electromagnetic vibrator coupled through a light ceramic drive shaft. The drive head for the PL_DMTA unit used is a Power head
with a flexing capability of approximately 12N for use with stiffer composite materials. Various sample thickness and lengths can be accommodated by the use of different sized steel frames attached around the drive shaft. The sample stiffness range measurable using the Power head is approximately 20,000 kN/m to 0.4 kN/m [23]. Motion of the drive shaft is sensed by a non-contacting, non-loading transducer. The furnace is situated inside a removable cover which fits around the drive shaft and the frame holding the specimen. The PL_DMTA unit used for testing has a temperature range of 0-800 °C. This frame, due to its ceramic parts, cannot be cooled by liquid nitrogen for subambient testing.

The microprocessor control unit is capable of generating a frequencies ranging from 0.03 Hz to 200 Hz. A displacement is then selected based on specimen geometry and stiffness. The minimum peak-to-peak displacement is 11 μm and the maximum peak to peak displacement is 256 μm. The unit determines the appropriate sinusoidal current, proportional to stress, to apply to the vibrator and compares this in-phase and amplitude with the return signal from the displacement transducer, which is proportional to strain. The specimen geometry factor, -log K, along with four machine constants, are dialed into the machine enabling the unit to compute continuously the storage modulus, E', and damping, tan δ. This data is usually plotted versus temperature.

The temperature programmer enables a specimen to be heated from 0 °C to 800 °C. Heating rates range from 0.2 °C/s to 60 °C/s. Three heating options are available, isotherm, step-isotherm, and ramp. The isotherm will hold the specimen at a desired
temperature for a specified time. A step isotherm will heat to a temperature range and hold for a specified time, ex. a hold at 10 °C for 5 minutes. A ramp will take the specimen to the maximum temperature at a controlled rate, ex. 3° C/minute. Only water cooling is available, and must be used for temperatures exceeding 300 °C.

The specimens in this study are heated from 50 to 250 °C at a rate of 3° C/min. The cycling frequencies are 0.1, 1, and 10 Hz. The peak-to-peak displacement is 64μm.

2.3.4 Thermogravimetric Analysis

Thermogravimetric analysis is a method by which mass loss of a material can be determined over a temperature range. The material to be tested is placed in a pan which is placed in a balance. This balance detects the deviation of the balance beam from its null position [24]. The specimen, in the balance pan, is then enclosed and the desired temperature profile activated from the computer control. For these experiments a heating rate of 3 °C/min. from 50 °C to 250 °C is employed. This heating rate and range match the rate used in the DMA experiments. Samples of 10-20 mg were tested using this cycle and run twice.

2.3.5 Penetrant Enhanced X-ray Radiography

X-ray radiography was used to detect damage in thermally and mechanically cycled DMA specimens. Penetrant-enhanced radiographs can detect matrix cracking and delaminations through the thickness of the laminated.

A tested specimen is first coated, and allowed to soak overnight, with a zinc iodide solution. This solution will soak into any damaged areas of the specimen. The penetrant is removed from the surface with acetone before X-raying to avoid damaging
the film. The specimens were X-rayed at 30 kVP for 30 seconds.
3.0 Results and Discussion

3.1 Scanning Electron Microscopy

It has been shown by Swain [19] that the scanning electron micrographs of etched 810A, 810O, and 820A materials reveal different interphase regions. At a magnification of 20,000X, distinctly different interphase regions appear for the 810A and 810O materials. This difference is attributed to the presence of the thermoplastic PVP sizing in the 810O material. The permanganate etchant used in this technique is believed to act only on linear material or uncross-linked material, i.e. thermoplastic or unreacted epoxy found in the composite material. The 810O material had a large band of material missing around the fiber, while the 810A and 820A materials did not exhibit this characteristic. It was concluded that the materials varied by fiber surface treatment do not show significantly different interphases. However, when different fiber sizings were applied, different interphase regions were shown.

Due to the differences found in the dynamic mechanical response of the 810A and 810O materials, the effect of temperature on the interphase was investigated. Specimens that had been cycled from 50 °C to 250 °C four times were etched. The scanning electron micrographs of these specimens can be seen in Figures 2-5. The 810A material is shown in Figures 2 and 3 at magnifications of 0.80kX and 10.1kX respectively. At the lower magnification it can be seen that there are no large areas where the etchant has removed material. On closer inspection, at the higher magnification, small pockets of material are missing in a random configuration. Figures 4 and 5 show the 810O material at 0.80kX and 10.1kX respectively. In contrast to the
810A material, large sections of linear material has been removed by the etchant in Figure 4. These dark regions occur irregularly, indicating the PVP is not distributed evenly on the fibers. At the higher magnifications, the dark bands around the fibers indicate a distinct interphase region, unlike the random pitted patterns found for the 810A material. Comparing these SEM’s to those obtained by Swain [19], there does not seem to be any effect on the interphase due to cycling at these temperatures.

3.2 DMTA Results

A Polymer Labs DMTA unit was used for all dynamic mechanical tests. Unless otherwise specified, all specimens were tested from 50 to 250 °C with a heating rate of 3 °C/min. Frequencies tested were 0.1, 1, and 10 Hz, representing three orders of magnitude difference, with a peak-to-peak displacement of 64 μm. Nominal specimen dimensions were 12 x 35 x 1 mm. Specimens were tested in a single cantilever type configuration.

3.2.1 Unidirectional Specimens

Several unidirectional, [0], specimens were tested for each material type. As stated in Chapter 1, it is generally believed that unidirectional specimens give the best dynamic response. These specimens give the dynamic response controlled by the fibers, with matrix properties having a small effect.

The first runs for each specimen tested of each material type, 82A, 810A, 810O, and 820A, are shown in Figures 6-9. The curves shown represent material response at 1 Hz. Figure 6 represents the initial runs for the four specimens tested for the 82A material system. Figure 7 represents the first runs for the five specimens tested for the
810A material system. Figure 8 represents the first runs of the three specimens tested in the 810O material system. The first runs of the six specimens tested in the 820A material system are represented in Figure 9. These figures show $E'$, storage modulus, versus temperature and $\tan \delta$ versus temperature. $\tan \delta$ is defined as

$$\tan \delta = \frac{E''}{E'}$$

(4)

where $E''$ is the loss modulus and $E'$ is the storage modulus. $\tan \delta$ is often called the loss tangent, and can be used as a measure of energy dissipation. [21] The peaks shown on the $\tan \delta$ curve represent the glass transition temperature, $T_g$. The glass transition temperature is defined as the temperature at which the material properties change from those of a plastic to those of a rubber. There are several techniques used for determining this value. Taking the maximum $\tan \delta$ value as the glass transition temperature is a generally accepted method.

Analysis of Figure 6, 82A, shows good correlation of the $\tan \delta$ curves, a less than 3 °C spread in $T_g$, and reasonably good correlation for the $E'$ curves. Figure 7, 810A, shows a 10 °C spread in glass transition temperatures and no outliers for the $E'$ curves. However, the $\tan \delta$ curves bunch into two groups, one group represented by peaks 1 and 2, the other by peaks 3, 4, and 5. The latter group shows a higher $T_g$, and higher maximum $\tan \delta$ values than the first group. Figure 8, 810O, shows an 8 °C spread between glass transition temperatures over the three tested specimens. Correlation of the maximum $E'$ values is good, however, there is a slight dip in $E'$, with a corresponding rise in $\tan \delta$, around 120 °C. Several attempts have been made to explain
this occurrence with little success. Due to the temperature range over which this phenomena occurs, the presence of water has been suggested, which may burn off at this point of the cycle. However, thermogravimetric analysis (TGA), discussed later, disproved this theory. Another suggestion was further curing, or cross-linking of the matrix. This would stiffen the composite, but as seen, $E'$ decreases, showing a softening at this point of the cycle. This phenomena is only seen in the 810O material, and then only two out of three times, suggesting an interphase reaction with one of the components of the matrix. No satisfactory conclusion can be reached as to the presence of this additional rise in the tan $\delta$ curve for the 810O material around 120 $^\circ$C. Figure 9, 820A, shows excellent correlation among the tan $\delta$ curves, and a 5 $^\circ$C spread among the $T_s$. There is a wider spread among the $E'$ curves than seen for the other material systems.

From the four curves representing all unidirectional specimens tested, a representative curve was chosen. This representative specimen will be used for all further analysis. The middle $E'$ curve was chosen as the representative curve for all four materials. Figures 10-13 show the response of these representative specimens at 0.1, 1, and 10 Hz. The corresponding increase in $T_s$ with an increase in frequency is expected. Figure 14 shows the shift in glass transition temperature with frequency. At higher frequencies the material has less time to respond to the deformation, indicating that the glass transition temperature is rate dependent. These four representative curves all follow similar trends. There is a shift to the right with the $E'$ curves with an increase in frequency, although the initial $E'$ value is virtually the same. The shift to the
right of the tan $\delta$ curves with the corresponding increase in $T_s$ with an increase in frequency also occurs for all of the material systems.

The 1 Hz curve from all of these representative curves is then compared in Figure 15. It can be seen that all of the curves follow a similar path, with a similar shape. All of the curves have a minimal decrease in slope until the temperature reaches approximately 150 °C. At this point the storage modulus starts to drop as the tan $\delta$ value starts to rise. This indicates the material is starting to soften. The slope between approximately 150 °C and 210 °C is constant and very similar for all the material systems. The 810A material has the highest $E'$ curve, with 82A following a similar path. At a slightly lower value, the 820A material responds in the same manner. The 810O material has the lowest initial storage modulus. Because these curves are from the representative samples, they represent the general trends for these material systems. The 810A system has the highest storage modulus, while 810O has the lowest initial storage modulus.

The tan $\delta$ curves in Figure 15 reveal some significant differences in material behavior, specifically, the differences in the curve shapes for the 810A and 810O systems. The tan $\delta$ response for the 810A and 82A systems are similar, while the 820A system has a slightly lower glass transition temperature and a lower amount of energy dissipated. The 810O system not only has the lowest $T_s$ and the lowest amount of energy dissipated, but also has a broader transition with a more emphasized secondary plateau between 170 °C and 190°C. This plateau is present in all material systems, but is broader for the 810O system. This plateau is possibly the glass transition region for
the thermoplastic toughener in the matrix system and is emphasized more in the 810O system due to the PVP fiber sizing also being a thermoplastic. However, since the glass transition region for the toughener or the PVP is not known, this is only a hypothesis. The biggest conclusion to be drawn from the tan δ curves is that the fiber sizing does make a difference in the energy dissipation behavior. This is seen in the differences between the 810A and 810O curves.

The next part of the analysis deals with multiple runs. Figures 16-19 represent three consecutive DMA runs on the same specimen. There are several characteristics all of these materials share when the multiple run case is examined. The first characteristic is the jump in the maximum E' values between runs 1 and 2. With the exception of the 82A specimen, this jump is approximately 0.1 Pa. The 82A material does not exhibit this increase in E' until the third run. This jump is consistent and happens for nearly all tested specimens between runs 1 and 2. The jump between runs 2 and 3 is small in all materials except for the 82A material. The second characteristic is the increase in Tₓ between runs 1 and 2, and again between runs 2 and 3. The glass transition generally increases at least 20 °C between runs 1 and 2, and then another 5 °C between runs 2 and 3. This behavior could indicate two possibilities. First, physical aging may be taking place in the specimens. This does not seem probable because the total cycling time, heating and cooling, for three runs is less than ten hours. It does not seem feasible that physical aging would occur in such a short period of time. The other possibility is that the matrix material is curing further. This possibility poses another set of problems. If the matrix is not fully cured, is the initial run data of any value, or should the data for
the second and third runs be considered closer to the actual material behavior?

Figures 20 and 21 represent the second and third run comparisons of all four material systems. As can be seen, for the second run comparison, the tan δ curves collapse on each other and the glass transition temperatures are within 3 °C of each other. The only significant difference is that the 8100 material still has a wider transition region. The E' curves still show some separation. Examination of Figure 21 shows the third run comparisons of the four material systems. Again it can be seen that the curves collapse further, nearly identical to each other. Neither the tan δ curves nor the storage modulus curves show any distinguishing characteristics.

In order to determine whether the effects shown in Figures 20 and 21 are due to post curing, one unidirectional specimen of each material type was post-cured. The specimens were post-cured at 150 °C for 4 hours in a vacuum. Figures 22 through 25 show the results of multiple, consecutive runs for all material types. Figure 22 shows runs 1, 2, and 3 for 82A. These results show the same increase in the storage modulus, E' as can be seen in Figure 15. However, the differences in the glass transition temperatures are reduced. For the post-cured specimen, the Tg differences are only approximately 4 °C between runs 1 and 2, and approximately 3 °C between runs 2 and 3. This is a lot different than the initial 20 °C increase between runs 1 and 2 seen in Figure 15. Another characteristic to be noted is that the bump seen on the tan δ curve around 200 °C disappears with additional runs. This trend is also seen in the non post-cured specimens. Inspection of the curves for the 810A, 8100, and 820A specimens reveal the same trends. In general, the increase in E' is still present, with the same
magnitude increase found in the non post-cured specimens. The $T_c$ still increases for all materials on the second and third runs, but to a much lesser degree than seen in the non post-cured specimens. This change in the $T_c$ suggests that some curing effects are taking place. Since these effects are significant the next step would be to vary post-cure temperatures and times to establish complete cure of the composite. This, however, is beyond the scope of this study. Figure 26 shows the comparison of the first runs of all four post-cured materials. This figure shows a much closer comparison of storage modulus curves, with no material system having any distinguishing characteristics. The tan $\delta$ curves are also very similar, again with no significant differences. This is a different response than the data shown in Figure 15 representing the non post-cured specimens.

Next, a comparison of post-cured specimens and non post-cured specimens was made for the initial specimen run. These comparisons are shown in Figures 27-30. The general trends established in these figures are that the storage modulus for the non post-cured specimens is consistently higher and that the tan $\delta$ curve for the post-cured specimens is shifted to the right with the glass transition temperature being 8-10 °C higher. The maximum amount of energy dissipated is also greater for the post cured specimens. The post-cured specimen having a lower initial $E'$ value is puzzling. If the specimens are curing further with the post-cure, it would be expected for the material to get stiffer with further cross linking. This is not the case. The shift in the tan $\delta$ curve, and corresponding increase in $T_c$, is expected with further cure. If the specimen has cured further, or been otherwise changed by the 4 hours at 150 °C, it should dissipate
more energy due to the higher cross link density or other effects. Upon closer inspection of these curves, it is shown that the secondary transition on the tan δ curves, around 200 °C, is broader for the post cured curves. If this bump is the phase separation of the thermoplastic, its effect is more pronounced for the post-cured specimens.

3.2.2 Transverse Specimens

Two specimens from each material type were cut into [0], specimens. These specimens were cut from the same panel as the unidirectional specimens. They were cycled under the same test conditions as the unidirectional specimens. The response of these specimens should closely resemble matrix properties, with the fibers having little effect on the response. These specimens were only run once, the combination of the thermal cycle and the bending deformation warped the specimens. It is speculated that the 64µm peak-to-peak displacement was too large and that a smaller displacement should have been used to avoid permanently deforming the specimen. The specimens had cracking damage along the fiber direction.

The results of these tests can be seen in Figure 31. This is a comparison of all four material types, 82A, 810A, 810O, and 820A, at a frequency of 1 Hz for the initial and only run. The storage modulus curves have similar initial values and slope until around 180 °C where the curvature begins to deviate. The tan δ curves show similar behavior. The most interesting result is the closeness of the glass transition temperatures, only a 1.5 °C variation is shown. The Tg for the matrix material could be approximated at 172 °C based on these results. However, the from DMA results on the
matrix material, the $T_s$ was shown to be 180 °C. [28] This temperature discrepancy could be due to the presence of the fibers, or due to a need for further curing. It was shown for the unidirectional specimens that the glass transition temperature increased after further heat treatment. It is a reasonable assumption that the same increase in $T_s$ would occur for the transverse specimens.

3.2.3 Cross-Ply Specimens

Several specimens were cut from $[0,90,\ldots]$ laminates. This was done for two reasons, comparison with other material properties gathered from the same laminate layup, and to see how unidirectional (fiber) properties interact with transverse (matrix) properties.

Figure 32 shows the dynamic mechanical response of the cross-ply materials. The maximum $E'$ values are much closer together than those seen for the unidirectional materials. Additionally the maximum tan $\delta$ values are closer together and the glass transition temperatures show a spread of about 3 °C. There are no significant differences in the shapes of the tan $\delta$ curves. Cross-ply specimens are not good for detecting material system differences.

A comparison of material responses based on laminate geometries are shown in Figures 33-36. These are comparisons based on the curves shown in Figures 15, 31, and 32. All of these graphs are first run comparisons. Figure 33 shows the geometry comparison for the 82A material system. The $E'$ curves follow what is expected with the unidirectional specimens having the highest initial storage modulus. The cross-ply specimens have a slightly lower storage modulus, which is expected due to the
presence of the six 90° plies. The $E'$ curve for the transverse specimens is substantially lower than the unidirectional specimen initial modulus value. This is expected because the reinforcement plays little part in the response of the transverse specimens. However, the tan $\delta$ curves show some interesting effects. For the 82A specimens, peak 2 represents the response of the unidirectional specimen. The maximum amount of energy is dissipated by the unidirectional specimen, followed by peak 1 which represents the transverse specimen. The cross-ply specimen dissipates the least amount of energy. On first inspection, this does not seem to make any sense. Shouldn't the cross-ply specimen dissipate nearly as much energy as the unidirectional specimen? This lower energy dissipation can be attributed to inter-laminar effects. The 0° plies constrict the movement of the 90° plies. This frictional effect reduces the loss modulus and consequently reduces the tan $\delta$ curves. This effect also contributes to the consistently higher $T_g$ for the cross-ply specimens. The glass transition temperatures are not significantly different for the unidirectional and transverse specimens. The other material systems show similar trends with the maximum energy dissipation values for the $[0]_4$ and $[90]_4$ specimens being very similar. The $T_g$ for the cross-ply specimens is consistently higher.

3.2.4 Statistical Analysis

To demonstrate repeatability, for the 1 Hz curves, statistical analysis was done on the maximum $E'$ value, $T_g$, the area under the tan $\delta$ curve, and the maximum tan $\delta$ value. The area under the tan $\delta$ curve is a way to quantitatively measure the amount of energy dissipated by each material type. If the area under the tan $\delta$ curves is calculated,
beginning where the slope of the curve reaches a slope of 5E-4/°C and ending at 250 °C or where the slope of the curve becomes positive after going through the glass transition temperature, it can be shown that the areas under the curves are different [27]. The standard deviations were calculated and the results are in Table 2. The data being compared in this study has small but consistent differences between the material systems. In order to determine which parameters are significant a Duncan’s multiple-range test is used. This test is based on a one-way analysis of variance (ANOVA) to disprove the null hypothesis. The null hypothesis for this case is that all means are statistically equal, i.e., all of the averages for the maximum E' values, the T_g, the maximum tan δ values, and the areas under the tan δ curves are statistically the same. To disprove this hypothesis, the Duncan’s test for comparisonwise error rate was used to test for significance between means. A 95% confidence level was used as a criteria for determining significance. [26] Tables 3-6 show the results of this analysis.

3.3 X-ray Radiography

Penetrant enhanced X-ray radiography was used as a tool to evaluate the laminate composites. This method was used to detect matrix cracking and delaminations. All three composite laminate configurations, [0,90], [0], and [90], were evaluated. Figures 37-40 show unidirectional, [0], specimens that were run once at 0.1, 1, and 10 Hz, from 50 to 250 °C with a 64 μm peak-to-peak displacement. From these x-rays some small matrix cracks can be seen in the fiber direction. The majority of these cracks are located in the grip region of the specimen. For the 82A, 810A, and
Table 2. This table shows the means and standard deviations for several DMTA curve properties. The small standard deviations indicate that the data is consistent and repeatable.

<table>
<thead>
<tr>
<th></th>
<th>82A</th>
<th>810A</th>
<th>810O</th>
<th>820A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean, std dev</td>
<td>mean, std dev</td>
<td>mean, std dev</td>
<td>mean, std dev</td>
</tr>
<tr>
<td>Max E' (log Pa)</td>
<td>10.81, 0.070</td>
<td>10.86, 0.036</td>
<td>10.74, 0.036</td>
<td>10.81, 0.064</td>
</tr>
<tr>
<td>T_g (°C)</td>
<td>172.8, 0.985</td>
<td>173.9, 4.24</td>
<td>170.2, 3.68</td>
<td>170.4, 1.73</td>
</tr>
<tr>
<td>Max. Tan δ</td>
<td>0.221, 0.061</td>
<td>0.226, 0.012</td>
<td>0.194, 0.0090</td>
<td>0.213, 0.0061</td>
</tr>
<tr>
<td>Area Under the Tan δ Curve</td>
<td>10.55, 0.14</td>
<td>10.47, 0.24</td>
<td>11.4, 0.44</td>
<td>10.69, 0.32</td>
</tr>
</tbody>
</table>
820A specimens only one split can be seen. However, matrix cracking is more prevalent in the 810O specimen.

The [90], specimens reveal the same trends. Figures 41-44 show radiographs of specimens cycled with the same specifications as described above. Again, the 810O specimen has many more matrix cracks in the fiber directions. The 82A specimen has some splits in the left grip area, while 810A and 820A show no matrix cracking.

Most dramatically, the [0,90], specimens, Figures 45-48 demonstrate the difference in fiber sizings on matrix cracking. From these radiographs the 810O specimen stands out with an edge delamination and numerous longitudinal and transverse cracks. In contrast, the 810A specimen shows an edge delamination in the grip region while the 820A specimen demonstrates no cracking or delamination. The 82A specimen also shows some cracking in the grip region. While the amount of surface treatment applied to the fiber seems to have little effect on the occurrence of matrix splitting, the type of fiber sizing does. The 810O, PVP sizing, material seems to be more prone to matrix splitting. To further investigate this, a 810O specimen was tested in an isotherm, 50 °C, for 67 minutes with the same displacements and test frequencies as stated above. Shown in Figure 49, this specimen was tested three times. Very few matrix cracks are present. This leads to the conclusion that the matrix cracking that is more prevalent in the 810O specimen is due to thermal effects rather than mechanical cycling effects.

3.4 Thermogravimetric Analyses

TGA was done on all material types to investigate the possibility of water or
Table 3. The Duncan grouping for the maximum $E'$ values for each material system. This shows that only 810O and 810A are statistically significantly different from each other.

<table>
<thead>
<tr>
<th>Statistical Grouping</th>
<th>Material Type</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>810A</td>
<td>10.86</td>
</tr>
<tr>
<td>B A</td>
<td>82A</td>
<td>10.81</td>
</tr>
<tr>
<td>B A</td>
<td>820A</td>
<td>10.81</td>
</tr>
<tr>
<td>B</td>
<td>810O</td>
<td>10.74</td>
</tr>
</tbody>
</table>
Table 4. The Duncan grouping for the maximum tan $\delta$ value for each material system. This shows only the 810O material system is significantly different from the others.

<table>
<thead>
<tr>
<th>Statistical Grouping</th>
<th>Material Type</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>810A</td>
<td>0.225</td>
</tr>
<tr>
<td>A</td>
<td>82A</td>
<td>0.221</td>
</tr>
<tr>
<td>A</td>
<td>820A</td>
<td>0.213</td>
</tr>
<tr>
<td>B</td>
<td>810O</td>
<td>0.194</td>
</tr>
</tbody>
</table>
Table 5. The Duncan grouping for the glass transition temperature for each material system. This shows there is no significant difference between the glass transition temperatures for each material system.

<table>
<thead>
<tr>
<th>Statistical Grouping</th>
<th>Material Type</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>810A</td>
<td>172.65</td>
</tr>
<tr>
<td>A</td>
<td>82A</td>
<td>173.92</td>
</tr>
<tr>
<td>A</td>
<td>820A</td>
<td>170.88</td>
</tr>
<tr>
<td>A</td>
<td>810O</td>
<td>170.4</td>
</tr>
</tbody>
</table>
Table 6. The Duncan grouping for the area under the tan δ curve. This shows the 8100 material has a significantly larger area under the tan δ curve compared to the other material systems.

<table>
<thead>
<tr>
<th>Statistical Grouping</th>
<th>Material Type</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>810A</td>
<td>10.47</td>
</tr>
<tr>
<td>A</td>
<td>82A</td>
<td>10.55</td>
</tr>
<tr>
<td>A</td>
<td>820A</td>
<td>10.71</td>
</tr>
<tr>
<td>B</td>
<td>810O</td>
<td>11.40</td>
</tr>
</tbody>
</table>
some other volatile material burning off of the specimen, attributing to the stiffening of the material between runs 1 and 2. Figure 37 show that the result was a 0.5% weight loss for each material type for the first thermal cycle from 50 to 250 °C. The second thermal cycling yielded no weight loss, indicating some volatiles did burn off during the first cycling. However, the weight loss was constant, i.e. no significant loss at any particular temperature. This negates the theory that water was burning off of the 810O unidirectional specimens around 110 °C.

3.5 Property Comparison

A list of material properties for cross-ply laminates for the 810A and 810O material systems is available largely from the work of Subramanian []. Some of these properties are shown in Table 7. Although these properties are for cross-ply laminates, they will be compared to the first run unidirectional DMTA results. The cross-ply laminates do not give a good dynamic mechanical response, for comparison purposes, mostly due to ply interaction effects. Therefore, since the 90° plies in a cross-ply laminate have little effect on properties such as tensile strength and fatigue life, this comparison is somewhat justified.

From the statistical analysis above, the only differences detected in the dynamic mechanical response of the material systems was for the 810A and 810O materials. The 810O material is generally more compliant, this correlates to the lower stiffness of the 810O material. Another good correlation is the prevalent cracking in the 810O cross-ply specimens with the lower onset crack stress found for the 810O material.
Table 7. Some mechanical properties of 810A and 810O cross-ply specimens.

<table>
<thead>
<tr>
<th>Property</th>
<th>810A</th>
<th>810O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stiffness (Msi)</td>
<td>7.78</td>
<td>7.71</td>
</tr>
<tr>
<td>Tensile Strength (ksi)</td>
<td>107</td>
<td>111</td>
</tr>
<tr>
<td>Failure Strain (%)</td>
<td>1.36</td>
<td>1.6</td>
</tr>
<tr>
<td>Fatigue Life (R=0.1, 85% UTS)</td>
<td>5 k</td>
<td>50 k</td>
</tr>
<tr>
<td>Transverse Crack Onset Stress (ksi)</td>
<td>41</td>
<td>26</td>
</tr>
</tbody>
</table>
4.0 Conclusions

4.1 Scanning Electron Microscopy

The results of the permanganate etching on the materials that had been thermally cycled from 50 to 250 °C, revealed differences in the interphase region for the materials varied by fiber sizing, i.e. 810A and 810O. There was no significant differences in the interphase regions for the materials varied by fiber surface treatment. These interphase regions are the same as those found by Swain [19]. Therefore, it can be concluded that the interphase region is not affected by these temperatures.

4.2 DMTA Results

The DMTA results reveal several trends in the unidirectional specimens. All comparisons made are at the 1 Hz frequency. All other frequencies show similar results. Several generalization can also be made about cross-ply and transverse specimens.

4.2.1 Unidirectional Specimens

The tests for the unidirectional specimens reveal several trends. These trends are summarized as follows:

- Unidirectional specimens give the best dynamic mechanical response. This orientation is more sensitive to the fiber variations due to the fiber properties dominating the test response. The coupling of the fiber and the matrix at the interphase region also attributes to the sensitivity of this orientation. It could be concluded that since this orientation is most sensitive to fiber variations, it should be most sensitive to interphase differences.
• The results and trends from multiple DMTA runs on various specimens and material types are repeatable and consistent. This is shown in Figures 6-9 and Figures 16-19. See Table 2 for standard deviations.

• For first run data, a difference can be seen in the behaviors of the 810O and 810A materials. The maximum tan δ value is much higher for the 810A material than the 810O material. The 810O material has a distinctive bump around 100 °C, as well as a broader transition region on the tan δ curve. The broader transition region for the 810O material leads to a larger area under the tan δ curve than the area under the 810A material.

• The 810A material has a higher maximum tan δ value than the 810O material. However, the 810O material dissipates approximately 10% more energy than the 810A material.

• There seems to be no significant difference in the dynamic response of the materials varied only by extent of fiber surface treatment, i.e. 82A, 810A and 820A. This is shown in figure 15.

• The storage modulus, E', increases between runs 1 and 2. A smaller increase in stiffness is observed between runs 2 and 3. This trend always occurs and seems to indicate further curing.

• A comparison of the second and third DMTA runs show the curves for all four material types collapsing on each other. There is little difference between the 810A and 810O materials in the second run comparison and even less for the third run comparison. This effect could be due to further curing of the matrix material.
• The increase in similarity of the curves in runs two and three could be due to cracking of the materials as shown in the radiographs. The cracks seem to form in the grip region for the A-epoxy sized materials and are more prevalent for the 810O system. The cracking could account for the similarity in stiffnesses for the third run.

• Post cured specimens show a smaller increase in the glass transition temperature between runs 1 and 2. However, the increase in E' is still present for all material types. This is shown in Figures 22 - 25.

• A comparison of post-cured, unidirectional, specimens in Figure 26, show little difference in dynamic response between the material systems.

Statistical analysis was performed on first run, unidirectional data to determine which DMTA parameters were significant. For these materials three parameters detected a difference in interphase. The results are as follows:

• The maximum E' values show that 810A and 810O are statistically significantly different from each other. However, this parameter is affected by gripping orientation and specimen to specimen variation.

• A comparison of the maximum tan δ values will show only the 810O material falls out. The 82A, 810A, and 820A have similar maximum tan δ values.

• The glass transition temperature reveals no statistically significant results. The Tg for all materials is similar.

• The area under the tan δ curve calculations show that the 810O material is statistically significantly different from the other material systems.

It can be concluded from these results that the 810O material gives a significantly
different dynamic response than the other material systems.

4.2.2 Cross-Ply Specimens

The dynamic mechanical response of the cross-ply specimens was not good due to the interaction between the 0° and 90° plies. Therefore, it is not recommended that this orientation be used to make any kind of material system comparison. However, the response of the materials in this lay-up is very good for determining how, or if, materials will crack or delaminate under specific deformations and temperature ranges.

4.2.3 Transverse Specimens

The transverse mechanical response is the matrix dominated response. The results from these specimens show little variation in the glass transition temperature between the material systems.

4.3 X-ray Radiography

The penetrant enhanced X-ray radiographs revealed that the materials varied only by amount of fiber surface treatment, 82A, 810A, and 820A, were prone to cracking in the grip region for the unidirectional and cross-ply specimens. The material varied by fiber sizing, 810O, shows a large network of cracks in all material orientations, unidirectional, cross-ply, and transverse. Of particular note is the difference in the 810A and 810O material response for the cross-ply specimens. The 810O material delaminated and cracked both axially and transversely, while the 810A material had only a small delamination in one grip region.

4.4 Thermogravimetric Analysis

The TGA results show that approximately 0.5 weight percent of the specimen
was lost when heating to 250 °C. This small loss occurred gradually over the entire
temperature range, with no significant loss at any particular temperature.

4.5 Property Comparison

There is evidence from this work that Dynamic Mechanical Analysis can be used as a screening test. The dynamic mechanical response of these materials can be related back to compliance, onset crack stress, and modulus. Further characterization of other materials could lead to a better understanding of how the storage modulus, loss modulus, and tan δ response relates to creep, fatigue, and other material behaviors.

4.6 Future Work

This author believes that the effects of temperature on these materials need to be investigated more thoroughly. Some important questions have been raised by the post-curing phenomena seen in the dynamic mechanical response of these materials. If these materials had been aged, would some of the differences seen in the creep results and fatigue lives been seen? What effects would various degrees of post-curing have on the behavior of these materials? While it can be shown from these results that the response of the 810O material does differ from the response of the 810A material, there is evidence that further curing would lessen those differences.
References


Appendix A

The cure cycle for HC9106-3 for the autoclave is as follows:

1) Apply 966 Mpa (140 psig) autoclave pressure.

2) Apply full vacuum to the vacuum bag.

3) Heat up from 25 °C (77 °F) to 110 °C (230 °F) in 60 minutes.

4) Hold at 110 °C (230 °F) for 120 minutes.

5) Vent vacuum after 1 hour of the hold at 110 °C (230 °F), then apply 483 Mpa (70 psig) pressure into the bag.

6) Heat up from 110 °C (230 °F) to 177 °C (350 °F) in 30 minutes.

7) Hold at 177 °C (350 °F) for 4 hours.

8) Vent bag pressure after 1 hour at 177 °C (350 °F).

9) Cool down from 177 °C (350 °F) to 25 °C (77 °F) in 60 minutes.

Two important features of this schedule are the implementation of an intermediate-temperature dwell period and the pressurization of the bag during part of this dwell period. [28]

This autoclave procedure can also be adapted for the hot press. The following hot press schedule was found to produce 6" x 6" panels of acceptable quality.

The adapted hot press cure cycle for HC9106-3 is as follows:

1) Pull vacuum on properly bagged composite panel at beginning of cycle.

2) Apply contact pressure (200-300 pounds).

3) Heat at 2 °C/minute to 110 °C.
4) At 1 hour and 15 minutes into the cycle, ramp pressure to 3600 pounds (100 psi) in 500 pound increments every four minutes.

5) After ramping pressure, disconnect vacuum.

6) After holding at 100 °C for 2 1/2 hours, including pressure ramping time, increase temperature to 177 °C at 2 °C/minute.

7) Hold at 177 °C for 4 hours, turn off heat, loosen bolts on two sides of the mold by 2 turns for each bolt. The bolts must be loosened to allow for mismatches in thermal expansion/contraction between the mold and the panel.

8) Put on cooling system, leave at 3600 pounds (100 psi) until cool.

**Preparing a Thermosetting Composite Panel for Hot Press Curing**

**Vacuum Debulking**

Thermosetting composite pre-preg must be vacuum debulked in the desired laminate configuration before processing. Most of this pre-preg comes in rolls and is backed by a white or tan release paper. The pre-preg must first be cut into the desired orientation and size. After this, the panel must be assembled layer by layer. The first layer must be placed, paper side up, on a non stick surface. Porous teflon sheeting is a good choice. Then a vacuum must be pulled on this layer, the release paper removed, the next layer applied in its proper orientation, a vacuum pulled, the release layer removed, etc., until the entire panel has been assembled. Make sure any large pieces of dust or other contamination are removed before applying the next layer.

**Vacuum Bagging for Hot Press Curing**

Thermosetting composite panels must be placed in a bagging system due to the
epoxy bleeding under heat and pressure. The following method was designed to contain epoxy bleeding, pull a vacuum to remove air from the debulked panel, and provide a smooth finished surface texture. This process was developed for a 6" x 6" panel in a steel mold, smaller sizes adapt well, but a 12" x 12" mold can be difficult to assemble.

1) Spray Kapton film, or other suitably smooth material, on both sides with Frekote release agent in a fume hood. Let dry for at least 30 minutes. After dry, cut into 6" x 6" pieces, or desired size. This coated film will allow the panel to be easily removed from the mold as well as provide a smooth surface on the finished panel.

2) Clean the mold with a new razor blade to remove any excess substances. Do not use sandpaper or solvents, these will damage the mold. Spray the mold with Frekote every 6 uses to insure easy assembly and disassembly.

3) Place the debulked panel in the mold and tighten all the bolts ensure the edges do not have to be trimmed. If too large, trim to size. A little bit of overhang on one side turns into a big problem when trying to align the sides of the mold.

4) Remove the panel from the mold and remove all sides of the mold.

5) Cut a 1.5' x 1.5' piece of porous teflon, or other porous material, and cut a 6" x 6" hole in the middle of the teflon.

6) Bagging...

   a) Cut a piece of mylar, or other smooth high temperature material, about 3' long and seal all but one edge with vacuum sealant.

   b) Put Kapton film on both sides of debulked composite panel.
c) Place panel in the 6” x 6” hole in the porous teflon cloth, this will absorb the epoxy that is pulled off.

d) Place panel and cloth inside of the mylar bag.

7) Prepare the mold by placing one layer of high temperature tape on two opposing sides of the bottom of the mold, and two layers of high temperature tape on the other two opposing sides.

8) Place panel, in the bag, on the bottom of the mold. The tape allows for the thickness of the bag when the sides of the mold are attached.

9) Put the top of the mold on the panel and align the edges.

10) Make the first fold of the bag on a side with just one layer of tape applied. Put the two mold sides on where there is just one layer of tape on the sides. Fold the corners and attach the other two sides of the mold.

11) Check that the bottom edges of the side pieces are not below the bottom mold plate. There should not be any force applied to the side pieces. The sides of the mold should be perpendicular to the mold top and bottom. Any angle could shear the bolts when pressure is applied.

12) The bag should not come above the corners of the mold, they will puncture causing a leak.

13) Now that the panel and bag are in the mold, tape a piece of breather cloth to the non-porous teflon layer. Cut a small hole in the front of the bag, near the unsealed edge, and attach the vacuum nozzle. Seal the bag.

14) Center the mold in the hot press and attach vacuum hose to the nozzle.

This procedure has been used effectively for various material systems. A small
amount of bleeding usually indicates most of the air bubbles have been pulled from the panel. If the material system bleeds excessively, pull the vacuum for shorter amounts of time to reduce the bleeding.
Figure 1. Single cantilever type test configuration.
Figure 2. SEM of 810A material at a magnification of 0.8 kX.

Figure 3. SEM of 810A material at 10.1 kX.
Figure 4. SEM of 810O material at 0.8 kX.

Figure 5. SEM of 810O material at 10 kX.
Figure 6. The first runs for all 82A unidirectional specimens tested.
Figure 7. The first runs for all 810A unidirectional specimens tested.
Figure 8. The first runs for all 8100 unidirectional specimens tested.
Figure 9. The first runs for all 820A unidirectional specimens tested.
Figure 10. Representative 82A unidirectional specimen at multiple frequencies.
Figure 11. Representative 810A unidirectional specimen at multiple frequencies.
Figure 12. Representative 8100 unidirectional specimen at multiple frequencies.
DMTA
Head: Power 800°C

Representative 820A Unidirectional Specimen
0.1, 1, and 10 Hz

Legend
+
0 Hz
x
1 Hz
0 0.1 Hz

Figure 13. Representative 820A unidirectional specimen at multiple frequencies.
Figure 14. Shift in glass transition temperature with frequency change.
Figure 15. Comparison of representative curves for 82A, 810A, 810O, and 820A unidirectional specimens at 1 Hz.
Figure 16. Multiple run comparison of an 82A unidirectional specimen at 1 Hz.
Figure 17. Multiple run comparison of an 810A unidirectional specimen at 1 Hz.
Figure 18. Multiple run comparison of an 8100 unidirectional specimen at 1 Hz.
Figure 19. Multiple run comparison of an 820A unidirectional specimen at 1 Hz.
Figure 20. Second run comparison of representative curves for 82A, 810A, 810O, and 820A unidirectional specimens at 1 Hz.
Figure 21. Third run comparison of representative curves for 82A, 810A, 810D, and 820A unidirectional specimens at 1 Hz.
Figure 22. First run comparison of representative curves for 82A, 810A, 810O, and 820A transverse specimens at 1 Hz.
Figure 23. First run comparison of representative curves for 82A, 810A, 810O, and 820A cross-ply specimens at 1 Hz.
Figure 24. First run comparison of representative curves for 82A unidirectional, cross-ply, and transverse specimens at 1 Hz.
Figure 25. First run comparison of representative curves for 810A unidirectional, cross-ply, and transverse specimens at 1 Hz.
Figure 26. First run comparison of representative curves for 810O unidirectional, cross-ply, and transverse specimens at 1 Hz.
Figure 27. First run comparison of representative curves for 820A unidirectional, cross-ply, and transverse specimens at 1 Hz.
Figure 28. Multiple run comparison of an 82A, post-cured, unidirectional specimen at 1 Hz.
Figure 29. Multiple run comparison of an 810A, post-cured, unidirectional specimen at 1 Hz.
Figure 30. Multiple run comparison of an 8100, post-cured, unidirectional specimen at 1 Hz.
Figure 31. Multiple run comparison of an 820A, post-cured, unidirectional specimen at 1 Hz.
Figure 33. First run comparison of 1 Hz curves for 82A, not post-cured versus post-cured.
Figure 34. First-run comparison of 1 Hz curves for 810A, non-post-cured versus post-cured.
Figure 35. First run comparison of 1 Hz curves for 810O, not post-cured versus post-cured.
Comparison of Unidirectional 820A Specimens
Post Cured versus non Post Cured
First Run
1 Hz

Legend
not Post-Cured
Post-Cured

Figure 36. First run comparison of 1 Hz curves for 820A, not post-cured versus post-cured.
Figure 37. X-ray radiograph of a [0]₀, 810A composite specimen subjected to thermal and mechanical cycling.

Figure 38. X-ray radiograph of a [0]₀, 810O composite specimen subjected to thermal and mechanical cycling.
Figure 39. X-ray radiograph of a [0]_8, 82A composite specimen subjected to thermal and mechanical cycling.

Figure 40. X-ray radiograph of a [0]_8, 820A composite specimen subjected to thermal and mechanical cycling.
Figure 41. X-ray radiograph of a [90]₀, 810A composite specimen subjected to thermal and mechanical cycling.

Figure 42. X-ray radiograph of a [90]₀, 810O composite specimen subjected to thermal and mechanical cycling.
Figure 43. X-ray radiograph of a [90]₀, 82A composite specimen subjected to thermal and mechanical cycling.

Figure 44. X-ray radiograph of a [90]₀, 820A composite specimen subjected to thermal and mechanical cycling.
Figure 45. X-ray radiograph of a [0,90], , 810A composite specimen subjected to thermal and mechanical cycling.

Figure 46. X-ray radiograph of a [0/90], , 810O composite specimen subjected to thermal and mechanical cycling.
Figure 47. X-ray radiograph of a [0/90], 82A composite specimen subjected to thermal and mechanical cycling.

Figure 48. X-ray radiograph of a [0/90], 820A composite specimen subjected to thermal and mechanical cycling.
Figure 49. X-ray radiograph of a [0]_r, 810O composite specimen subjected to mechanical cycling only.
Figure 50. Results of initial TGA run.
Vita

Jennifer Susan Elmore was born on October 13, 1970, to Samuel and Rilla Elmore in Charleston, West Virginia. She grew up in Beckley, West Virginia and attended Woodrow Wilson High School from where she graduated with honors in 1988. In the fall of 1988 she entered Virginia Tech to pursue an engineering degree. Ms. Elmore graduated with a Bachelor of Science in Industrial and Systems Engineering in 1992. At that time she chose to enter graduate school in the Department of Engineering Science and Mechanics under the direction of Dr. W. W. Stinchcomb. She completed her Master of Science in Engineering Mechanics in July, 1994 and has accepted a position with the Naval Aviation Depot in Cherry Point, North Carolina, as a materials engineer.