# Characterization of Cryogenic Microcracking in Carbon Fiber/Epoxy Composite Materials

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## Abstract

# Characterization of Cryogenic Microcracking in Carbon Fiber/Epoxy Composite Materials

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Polymeric composite materials have been widely utilized to take advantage of their large specific strength and stiffness. These characteristics have made them attractive for use in aerospace applications as containment structures for cryogenic fluids. However, the anisotropic, heterogeneous, and viscoelastic nature of polymeric composite materials creates a unique set of challenges for the storage of cryogenic fluids. Mismatches in thermal expansion between the fibers and the matrix in these materials result in the generation of thermal stresses at low temperatures that can ultimately cause failure in the form of microcracks that propagate throughout the material, degrading performance. This work examined the phenomenological and theoretical aspects of microcrack formation in carbon fiber/epoxy composite materials at low temperatures. Microcrack formation was initially investigated using an experimental approach. The role of the fiber and matrix type in microcracking was studied, along with the interaction between the fibers and the matrix and the effects of nanoparticle matrix modification. It was found that the fiber and matrix type had significant effects on microcrack formation, with decreased fiber moduli, decreased matrix coefficient of thermal expansion, nanoparticle modification, rubber toughening, and increased adhesion all corresponding to reduced microcracking. These improvements were achieved by reducing the thermal stresses in the materials studied and increasing the failure resistance of the laminates. It was found that the processing conditions of a laminate, namely the cure temperature, had a direct impact on microcracking by changing the stress free temperature of a material and the corresponding thermal stresses at cryogenic temperatures. The analysis of the variables that contributed to microcrack formation was used to develop a stress-based compound beam model to predict the onset temperature for microcracking in composite materials. This model was unique in that it accounted for the variation in material properties at low temperatures. Collectively, this work examined the phenomena behind the cryogenic microcracking of composite materials and applied this information to develop a predictive model for low temperature failure of composite materials from thermal stress generation.

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To mom and dad

# CHAPTER 1: INTRODUCTION

## 1.1 COMPOSITE MATERIALS

Composite materials are composed of two or more distinct materials, a matrix and a reinforcing phase, that are combined to create a material with improved properties and performance over the individual constituents. The matrix serves as a protecting and supporting medium that transfers any applied loads to the reinforcing phase. Typically, the matrix is ductile and tough, and the reinforcing phase is strong, stiff, and has a low density. When the matrix and reinforcing phase are combined it can result in a material that is both strong and tough [1]. Additional advantages of composite materials result from their anisotropy and heterogeneity. The components of a composite material can be combined in various volume and weight fractions as well as different orientations. This allows the properties of a material to be customized on a macroscopic and microscopic scale [1-3].

The matrix in composite materials can be metal, polymer, or ceramic. The reinforcing phase can also be metal, polymer, or ceramic-based and is commonly used in the form of particles, whiskers, or fibers. Most discussions of composites focus on mechanical properties, but materials with different properties can be combined to create composites with improved optical, thermal, electronic, magnetic, or chemical properties. Some examples that illustrate the variety of composite materials and their applications include wood, concrete, superconducting wires, boron-reinforced aluminum, silicon carbide-reinforced alumina, and fiber-reinforced plastics [1, 4, 5].

## 1.2 FIBER-REINFORCED POLYMERIC COMPOSITES

### 1.2.1 Fibers

Several different types of fibers are used as the reinforcing phase in fiber-reinforced polymeric composite materials. These fibers differ in their chemical structure as well as their microscopic structural character. The most commonly used fibers for structural applications are carbon, glass, and aramid fibers. These fibers are used in different applications depending on the desired final properties of the material. The important factors to be considered when choosing one of these fibers include density, tensile strength and modulus, compressive strength and modulus, coefficient of thermal expansion, thermal conductivity, electrical conductivity, toughness, compatibility with matrix, fatigue resistance, environmental durability, and cost [2].

Carbon fibers are a blend of amorphous and graphitic carbon and are used because of their large specific tensile strength and moduli, fatigue resistance, and low coefficient of thermal expansion. Disadvantages of carbon fibers include their high electrical and thermal conductivity and poor impact resistance [2].

Glass fibers are the most widely used reinforcing fibers in polymeric composites because of their low cost. Additional advantages include high tensile strength, high chemical resistance, and low electrical conductivity. The disadvantages of glass fibers are low tensile modulus, susceptibility to damage during processing, high density, and low fatigue resistance [2].

Aramid fibers are highly crystalline polymer-based materials. They have very low densities, high specific tensile strengths, and good resistance to impact and abrasion. They suffer from low compressive strengths, machining difficulties, and a poor-resistance to hot-wet environments [2, 6].

Reinforcing fibers in polymeric composite materials are used in continuous, chopped, woven, or braided forms. Continuous and woven forms are most commonly used because they produce the most efficient utilization of the fiber properties. The fibers are often coated with a polymer sizing or subjected to a chemical surface treatment to ensure good adhesion to the matrix [2].

### 1.2.2 Matrices

The polymeric matrix can be classified as either a thermoplastic or a thermoset [2, 7, 8]. The distinction between these two types of matrices results from differences in connectivity and structure on the molecular level. Thermoplastics are composed of long chains of atoms that are held together by intermolecular forces. This results in materials that can soften and flow under repeated applications of heat [7, 8]. Typical thermoplastics used in advanced composites include polyetheretherketone (PEEK), polyphenylene sulfide (PPS), polyetherimide, and polyamideimide [2, 9-12]. Thermosets are materials composed of small molecules that react irreversibly to form a network structure. In this case, the polymer chains are linked together by covalent bonds and once reacted, the material may soften but will not flow under the application of heat [7, 8]. Typical thermosets used in advanced composites include epoxies, cyanate esters, phenolics, bismaleimides, and vinyl esters [2, 13]. Thermosets are more widely used than thermoplastics, largely due to easier processing for thermosets and a much larger resistance to creep [2].

## 1.3 COMPOSITE PROCESSING TECHNOLOGIES

### 1.3.1 Prepregging

Prepregging is a fundamental operation in the production of fiber-reinforced composite materials. It is a process by which the fibers and the matrix are combined to form a continuous tape that can be used to produce larger composite structures [2, 14-16]. Most prepregs contain thermosetting matrices, although a few thermoplastic prepregs are used. Prepregging is widely used because of the large volume percentages (50 %) of fibers that can be achieved, the ease of working with the finished material, and the excellent properties of composites made using prepreg [2, 15, 16].

Two main types of prepregging operations are used: Hot melt and solution dip. A hot melt process is shown in Figure 1-1. The polymeric matrix is placed on a hot plate and formed into a film on release paper. The fibers are then impregnated with the matrix by a series of rollers. The material then passes over a cooled plate to increase the viscosity of the matrix and stop any reaction that may be occurring. The final properties of the prepreg are determined by the line speed, the pressure of the impregnation rollers, the temperature of the impregnation zone, and the thickness of the polymer film [16-18].

A solution dip process is used when a low matrix viscosity is necessary to properly impregnate the fibrous reinforcement. This situation usually occurs when woven fabric reinforcement is used. A solution dip process is shown in Figure 1-2. The fabric is pulled through a resin bath where capillary forces draw the polymer solution into the fabric. Nip rolls are then used to control the resin thickness and the solvent is removed in a drying tower. The material passes over a cooled roll to stop any reaction and raise the viscosity of the matrix before the product is wound onto a roll. Solution dip prepregging is not used as often as hot melt because of the increased processing necessary and the environmental implications of solvent use [16].

### 1.3.2 Autoclaving

Once the prepreg material has been produced, it is cut into the appropriate shapes and stacked to form a laminate. This stack of laminas is then subjected to heat and pressure in an autoclave to cure and consolidate the material into a composite laminate. The prepreg stack is subjected to vacuum pressure before being placed in the autoclave in order to begin consolidation of the plies and remove any air or entrapped volatiles. The stack is then placed in a vacuum bag on a tool that is used in the autoclave to provide uniform consolidation pressure and remove any gases that are evolved during cure. A schematic of a typical vacuum bag is shown in Figure 1-3. The release film ensures that the part does not stick to the mold or the vacuum bag, and the breather distributes vacuum evenly over the part. The vacuum bag itself separates the assembly from the environment of the autoclave so that vacuum can be drawn on the part [15, 19].

The cure cycle in the autoclave usually consists of a ramp to the desired pressure, a ramp to the cure temperature, a hold at the cure temperature, a ramp to room temperature, and a ramp to ambient pressure. These parameters can be varied to control the final properties of the composite laminate. In some cases a hold at a lower temperature than the cure temperature will be used to improve consolidation of the part or a post cure will be used to increase material performance while still utilizing a relatively low cure temperature. During the autoclave cycle vacuum is applied to the vacuum bag until the pressure in the autoclave has become large enough to consolidate the part on its own. At this point, the bag is vented so that any entrapped gases or volatiles produced during cure are eliminated [15, 19].

## 1.4 SCOPE OF RESEARCH

The primary objective of this work was to understand how the process-structure-property relationship of polymeric composite materials relates to the response of composite materials to cryogenic temperatures. The methodology developed by Seferis et al. combines the process-structure-property relationship of polymeric composite materials with performance, design, and manufacturing using scaling concepts. This approach to fiber-reinforced composite materials is shown in Figure 1-4 [3, 20]. The behavior of composite materials at cryogenic temperatures is uniquely suited to take advantage of this approach to composite analysis. The processing of composite materials has a strong influence on their structure and properties, especially internal stresses, which relate directly to failure mechanisms at cryogenic temperatures [21-23]. This then connects to material performance at cryogenic temperatures and the intelligent design of materials with improved performance during and after exposure to low temperatures.

The basis of this research was an exploration of the fundamental phenomena that determine the response of fiber-reinforced composite materials to thermal cycling between cryogenic and ambient temperatures. This analysis began with a phenomenological approach that investigated the role of the processing, structure, and properties of composite materials on their behavior at cryogenic temperatures. The components of a composite material, the fibers and the matrix, were investigated along with the interaction between the fibers and the matrix to determine the effects of composite structure and properties on performance. In addition, processing effects on internal stresses were also investigated. This approach provided an understanding of which variables influence composite behavior at cryogenic temperatures. Once this knowledge base had been established it could be extended to predict and model the performance of composite materials and develop design procedures to produce composite materials with optimized performance. Overall, this work investigated the performance of composite materials at cryogenic temperatures through a phenomenological and theoretical approach that established a fundamental understanding of the science and engineering of composite materials.

## 1.5 SUMMARY OF CHAPTERS

In chapter 2 the fundamentals of thermal cycling and its effect on composite materials are outlined. Thermal cycling results in the development of internal stresses that can cause material failure. Internal stresses are discussed and the failure mechanisms of composite materials during thermal cycling are explained. The implications of composite material failure and past work on the topic are presented. This chapter deals with the fundamental phenomena that occur during cryogenic cycling that will be investigated in later chapters.

In chapter 3 the effects of matrix and fiber variations on the cryogenic microcracking of carbon fiber/epoxy composites are investigated. The fibers and the matrix make up a composite material and a fundamental understanding of their role in the performance of composite materials at cryogenic temperatures is necessary to build a foundation for further analyses. The flexibility of the polymeric backbone, the curing agent used, the network structure of the matrix, and the presence of a rubber interpenetrating network were all examined to determine the role of the matrix. The effects of fiber type, which corresponded to the fiber strength, modulus, and longitudinal coefficient of thermal expansion, were investigated.

Chapter 4 builds off chapter 3 to analyze how adhesion between the fibers and the matrix influenced the behavior of carbon fiber/epoxy composites exposed to thermal cycling at cryogenic temperatures. The properties of a composite material are determined largely by the properties of their interfaces, and composite failure at cryogenic temperatures often propagates along the fiber-matrix interface. Effective adhesion between the fibers and the matrix was therefore expected to be an important variable in preventing microcracking at cryogenic temperatures.

Chapter 5 deals with the modification of the polymeric matrix using nanoparticles derived from layered silicate clays. This formed a nanocomposite matrix that was expected to improve the properties of the composite material through a reduction in internal stresses and an increase in matrix strength. The design of composite matrices to perform well at low temperatures is an important area to investigate, and the role of nanostructures in the performance of composite materials was determined.

The objective of chapter 6 was to determine how processing, in this case cure temperature, influenced the behavior of composite materials at low temperatures. A unique matrix resin was developed so that carbon fiber/epoxy composites could be cured at a variety of temperatures without any significant changes in network structure or degree of cure. The cryogenic microcracking of the laminates cured at different temperatures was determined, and the residual stresses in model laminates were calculated and compared with the experimental results. This chapter related processing to performance and presented a model of residual stress development in composite materials.

Chapter 7 expands on chapter 6 to develop a predictive model for microcracking in composite materials at cryogenic temperatures. This model accounted for the variation in material properties at low temperatures and used a stress-based failure analysis to determine what level of thermal stress would cause microcrack formation. This chapter showed that microcracking could be predicted based on the room temperature properties of a material, appropriately modified, using a straightforward modeling methodology.

Chapter 8 presents conclusions based on the presented work and describes research paths to be explored in the future.

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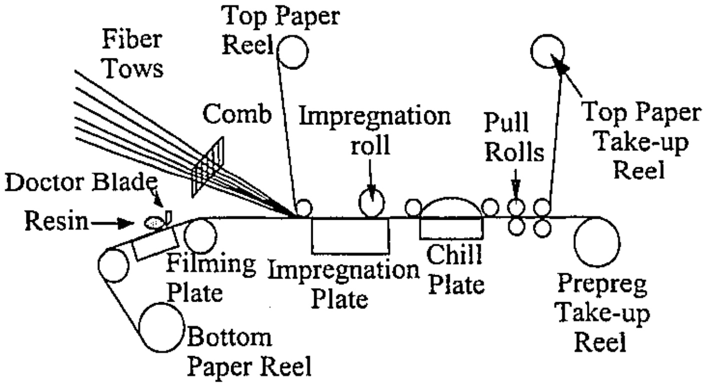

Figure 1-1. Hot melt prepregging operation

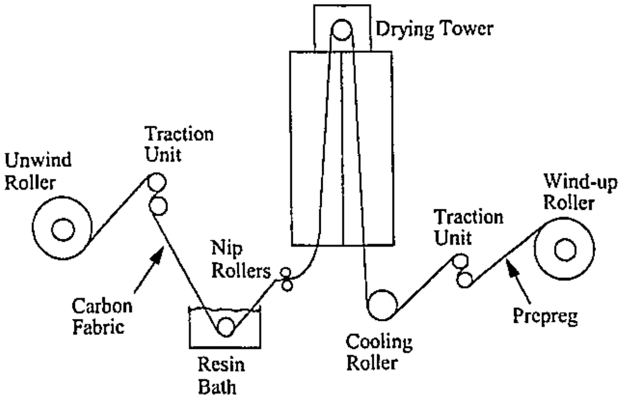

Figure 1-2. Solution dip prepregging operation

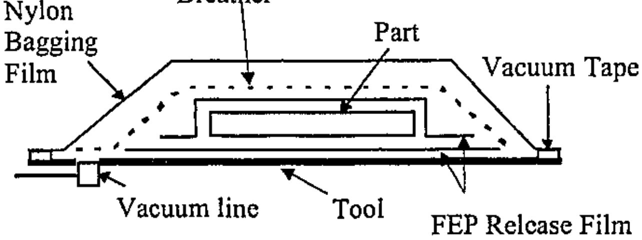

Figure 1-3. Typical vacuum bagging operation

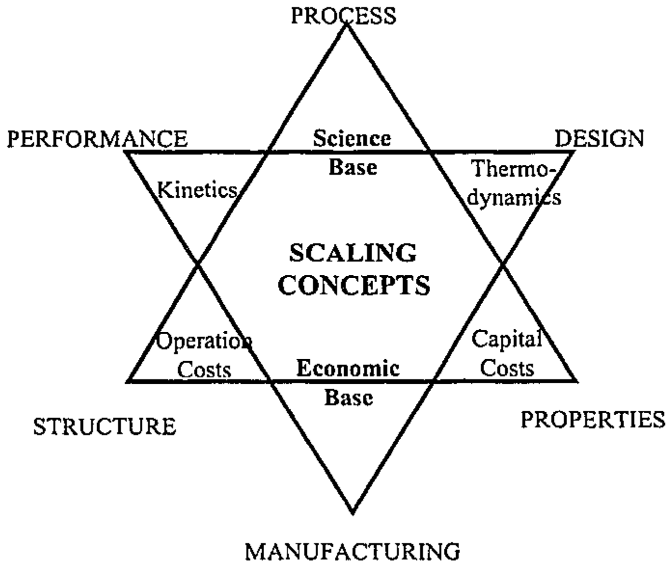

Figure 1-4. Double trinity of characterization of composite materials

# CHAPTER 2: THERMAL CYCLING INDUCED STRESSES IN FIBER-REINFORCED POLYMERIC COMPOSITES

## 2.1 INTRODUCTION

Fiber reinforced composites continue to be targeted for more applications in extreme environments. Work in the past focused on understanding high temperature exposure of composite materials and the mechanisms of degradation and deterioration at these conditions. While research is ongoing in this area and is still necessary, more recent uses for composites in low temperature and cryogenic applications demand increased attention [1]. Some specific uses for fiber-reinforced composites in these applications are for fuel containment of liquid oxygen and hydrogen or containment of liquid helium for cooling applications. When these tanks are filled or emptied the temperature of the composite material can change rapidly, which may damage the structure. The issue of thermal shock and rapid material cycling needs to be explored in detail to provide a fundamental understanding of composite failure caused by exposure to cryogenic temperatures.

Since designs for cryogenic fuel tanks are not specified, and the tanks are not likely to be monolithic structures, the effects of honeycomb materials and adhesives are important in the performance of composite materials used for cryogenic liquid storage. Past work by the Boeing Company identified the importance of film adhesives in these applications since rib stiffened structures may be desirable and the use of metallic bolts is not feasible [2]. In addition, as emphasized by the Boeing Company, the composite materials are never statically loaded, and therefore, should also be tested under vibration or dynamic loading for a realistic approach to investigating their utilization [3].

Over the past two decades, a significant but limited quantity of work has been performed in investigating materials that are subjected to cryogenic exposure [1]. NASA specifies that toughened thermosets are the most likely candidates for cryogenic applications in the future [4]. In their research they have focused mainly on toughened epoxy-based prepreg systems such as Hercules IM7/8551-7. Boeing/NASA has also focused on a similar material for their work on the DC-Y composite cryotank, namely Hercules 8552 [2]. Most, if not all research has been performed on commercial prepreg or composite materials and has been typically characterization studies. Of the research that has been conducted in this area, Markley et al. were one of the only investigators to use epoxy resins of known and described compositions [5]. This work was only done for resins, but a significant amount of data was generated on many model systems; however, no explanations were given as to the findings. They found a general trend that that the compressive modulus at –196°C was constant for the systems investigated and independent of the 27°C modulus. They also determined that flexiblizing agents that greatly reduced warm temperature modulus did not affect cold temperature modulus and caused slight increases in the –196°C modulus.

In a summary of past work presented by Nettles and Biss, it is reported that cryogenic temperatures have a significant effect on thermosetting and thermoplastic resins [4]. The important findings were that all the resins tested got more brittle when at cryogenic temperatures. An interesting finding in their work was that the fracture strain was found to increase with toughened thermosets and thermoplastic matrix composites at cryogenic temperatures but decreased if the thermoset was untoughened. Similarly, the ultimate tensile strength of the entire composite increased with decreasing temperature for thermoplastics and toughened thermoset matrices but decreased for untoughened thermosets. They observed a marginal increase in matrix strength with decreasing temperature but a modest increase in matrix stiffness with decreasing temperature. Other research has shown that the tensile strength can increase by as much as two fold when cooled to –196°C, but the moduli were much less temperature dependent, increasing usually only 10-20% when cooled from 27 to -196°C [6].

Clark et al. stated that the application of polymers at low temperatures is determined by their flexibility and toughness [1]. These properties are closely linked to molecular movements in their glassy state, which are shown as specific secondary relaxations in the mechanical vibration spectrum [1]. In this pursuit, some preliminary investigations have been conducted analyzing thermal conductivity in the –272.9 to 27°C temperature range, but how these thermal conductivities translate into thermal expansion and mechanical behavior has yet to be determined [7-9].

A number of investigators have also pursued work in the development of testing methods for composite materials at cryogenic temperatures [10, 11]. Sereining and Gross developed testing methods for determining the thermal expansion/contraction of epoxies at cryogenic temperatures [8]. In addition to laboratory type testing, methods have been established for analyzing and testing sub-component structures [12-14]. Others have focused on actual fuel storage tanks [15].

In meeting ease of fabrication issues, work has been performed on skin and stringer bond line analyses for rib stiffened structures. This work is critical in manufacturing adhesively bonded structures for streamlining the production process and ultimate weight reduction [2].

There has been some research on the microcracking behavior of composite materials when exposed to cryogenic temperatures. However, this usually has focused on the construction of the laminate with nothing mentioned about the mechanisms. For example, Epstein and Ruth specified that the problem of microcracking can be mitigated by selection of materials less prone to microcracking, such as materials with ply lay-ups with low-angle orientations, laminates made from thinner plies and fabrics, composites with minimized fiber twist, and post cured composite structures [16]. While this is useful information, there is a gap in the fundamental causes of microcracking based on the composite components. Additionally, while there has been some work on cryogenic cycling, little is directly applicable to the in-service conditions experienced by composite structures [17, 18].

## 2.2 BACKGROUND

### 2.2.1 Sources of internal stresses

Increased thermal stresses are the underlying cause of microcracking in composites at cryogenic temperatures. Residual stresses develop in composite materials during cure and after cure as the temperature of the material falls below its stress free temperature. The stress free temperature is the temperature at which no residual stresses exist in the laminate. Dimensional changes in the matrix during cure usually drive the stress free temperature above the maximum processing temperature. Residual stresses are the result of cure shrinkage of the matrix, Poisson's effects, differences in the coefficient of thermal expansion (CTE) between the fibers and the matrix, and anisotropy in the expansion of the individual plies [2, 19-22]. In a symmetric cross-ply laminate

($[0^\circ_n\ 90^\circ_n]_S$) the 0° and 90° ply groups behave differently as the temperature is reduced from the stress free temperature. When the temperature of the laminate decreases the carbon fibers that form the backbone of the composite expand in the longitudinal direction and contract in the axial direction. The resin behaves isotropically and contracts in all directions when the temperature decreases. Assuming that no slip between the matrix and the fibers occurs, a given ply will contract in the transverse direction and expand in the longitudinal direction [23]. Therefore, in a symmetric cross-ply laminate the plies are placed in a state of transverse tension and longitudinal compression when the temperature drops below the stress free temperature. Additional stresses are generated within each ply and at the fiber-matrix interface due to the mismatch in coefficient of themal expansion between the fibers and the matrix, Poisson's effects, and cure shrinkage. When a decrease in temperature occurs the matrix shrinks more than the fibers and generates a compressive hoop stress around the fiber, while the fibers expand axially and place the matrix in a state of tension. Lastly, the thickness of the laminate changes as the temperature is lowered due to contraction of the matrix and the fibers. The above factors combine to create a complex stress state in carbon fiber/epoxy composites as they are cooled to cryogenic temperatures. The ply groups in a laminate are least able to resist transverse tension and failure often occurs [24].

### 2.2.2 Failure mechanisms

When the internal stresses in a carbon fiber/epoxy composite exposed to low temperatures become large enough they can cause failure of the composite material. In a transverse tensile loading mode the fibers do not act as reinforcing elements; rather they behave like inclusions and stress concentrators. The fibers cause the development of local radial stresses at the fiber-matrix interface that are 50 % larger than the applied stress. In the case of fiber-reinforced composites with large fiber volume fractions ($\geq 50$ %), the stress fields around the individual fibers can interact and cause stress concentrations of 75 % over the applied stress. These stresses eventually result in debonding or matrix failure that forms transverse cracks which propagate through the material [2, 25]. In some cases, other physical processes such as potholing and delamination occur as a result of internal stresses [2, 21, 22]. Chung et al. showed that the degradation of composite materials exposed to cryogenic temperatures is increased by thermal cycling between cryogenic and room temperature conditions [26].

Once a pathway for cryogenic liquids has been established in a storage tank structural failure can occur [13, 27]. Microcracking is particularly damaging for the storage of liquid hydrogen and helium as their small size allows them to diffuse through extremely small flaws. Once the escape of cryogenic liquids occurs a particularly damaging sequence of events is initiated. The released liquids can cause the condensation of liquid water and air on the tank or in the interior of sandwich tanks. Subsequent emptying and filling of the storage tank results in solid/liquid and solid/gas transformations that can ultimately result in failure of the entire structure.

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# CHAPTER 3: MATRIX AND FIBER INFLUENCES ON CRYOGENIC MICROCRACKING

## 3.1 INTRODUCTION

The need for high strength and low weight materials has made polymeric composites ideal for use in aerospace applications, which often require the storage and transportation of cryogenic liquids [1]. Dramatic changes in the structure and properties of composite materials can occur when they are exposed to cryogenic temperatures, particularly in a cyclical fashion [2-5]. Previous work has demonstrated the presence of structural changes and failure in composite materials after cryogenic cycling but has failed to elucidate the mechanism behind their occurrence [6-9].

Understanding the mechanisms behind thermal stress development and structural failure processes is key to preventing or controlling cryogenic microcracking. In this chapter, cryogenic cycling effects on symmetric carbon fiber/epoxy laminates were examined using model prepreg systems. The properties of the composite materials studied were altered through the introduction of variations in their structure and composition. Examination of the laminates after cycling provided insight into the mechanisms and origins of thermal stress-induced microcracking. The impact of fiber type and matrix composition on the cryogenic behavior of carbon fiber/epoxy composites was investigated. The influence of the matrix structure, morphology, and presence of an interpenetrating rubber network as well as the tensile modulus and CTE of the fibers on the low temperature behavior of model laminates was determined. It was shown that the tensile modulus and longitudinal CTE of the fibers, the curing agent chemistry, the presence of rubber toughening, the glass transition temperature of the matrix ($T_g$), and the flexibility of the backbone of the polymeric matrix had a direct and significant impact on the concentration, distribution, and morphology of microcracks created by thermal stresses.

## 3.2 EXPERIMENTAL

### 3.2.1 Materials

The model resins used as matrices were formulated using a mixture of commercial epoxy resins. The resins used were EPON® 828, 836, and 871 from Resolution Performance Products (formerly the Shell Chemical Company) and D.E.R. 661 from the Dow Chemical Company. The epoxy equivalent weights of these materials were 187, 315, 430, and 530 g/epoxy, respectively. D.E.R. 661 and EPON® 836 and 828 are based on diglycidyl ether of bisphenol-A and only differ in their backbone lengths. EPON® 871 is an aliphatic epoxy ester resin. Two curing agents that are common in commercial aerospace prepreg and adhesives were used. The first, 4,4'-diaminodiphenyl sulfone (DDS), HT976, was obtained from Ciba-Geigy. The second, 1-cyanoguanidine (dicy), Amicure® CG 1400 from Pacific Anchor Chemical Co., was accelerated with 3-(3,4-dichloro-phenyl)-1,1-dimethyl urea (diuron) from the Aldrich Chemical Company. Nipol 1472 from Zeon Chemicals Inc., a solid butadiene/acrylonitrile rubber with randomly distributed carboxyl functionality and 27 percent acrylonitrile content, was included in some of the formulations as a toughening agent. Chromium (2%) naphthenate, from OMG Americas Inc., was used as a catalyst for the epoxy/carboxyl esterification reaction [10].

Two resin series were prepared in this study. These series were designated 1 and 2 and their formulations can be found in Table 3-1. In series 1 EPON® 836:EPON® 871 ratios by weight of 62.5:37.5 and 50:50 were used to alter the backbone flexibility of the matrix and DDS and dicy/diuron were used as the curing agents. In series 2 a constant ratio of EPON® 828 to D.E.R 661 was used, while DDS and dicy/diuron were used as the curing agents and Nipol 1472 was used in some systems as a rubber modifier. In both series a stoichiometric amount of DDS was used. Dicy was incorporated at 5 parts per hundred resin (phr) and diuron was used at 2 phr due to their catalytic nature.

The components of each epoxy resin system were combined in an oil bath at 110°C and stirred until completely mixed. When DDS was used as the curing agent it was initially melted, added to the epoxy mixture in the oil bath, and stirred for one minute until the components were thoroughly mixed. When dicyandiamide and diuron were used as the curing agent, a paste was made using dicyandiamide, diuron, and half of the 871 or 828 and incorporated into the epoxy mixture at 80°C. The resin was then quenched to room temperature and stored at -10°C before prepregging. For the rubber-toughened systems, the Nipol 1472 was washed with methanol to remove any surface talc and dissolved in acetone to make a 17 wt. % solution. The epoxy mixture was added to the rubber solution and mixed until it became uniform. The combination was then spread over a large surface area where the acetone was removed under vacuum at 100°C. This rubber-epoxy combination was then combined with the curing agent as detailed previously for the untoughened systems.

The resin systems were poured into molds and cured in an autoclave. The autoclave cure cycle consisted of a 2.8°C/min ramp to 177°C followed by a 90 minute hold at 177°C and a ramp down to 27°C at a rate of 2.8°C/min. The total consolidation pressure used during cure was 551 kPa. These resin plaques were machined into 0.5 x 0.5 x 0.32 cm (length x width x thickness) samples for thermal mechanical analysis testing.

This study utilized three types of carbon fibers with low, intermediate, and high tensile moduli. The fibers used were Toray T300, T800H, and M35J. Epoxy sizing was present on all of the fibers, and the filament count in each case was 12,000 filaments per tow. The tensile moduli of these fibers were 230, 294, and 343 GPa, respectively. The corresponding linear longitudinal coefficients of thermal expansion of these fibers were -0.41, -0.56, and -0.73 μm/(m°C) [11].

Three unidirectional prepregs consisting of the resins discussed previously and the fiber types described above were developed, for a total of 24 systems. The fibers were impregnated with the epoxy resin using a hot-melt prepreg machine [12]. The prepreg areal weight was set to 145 g/m$^2$ and the nominal resin content was 35±2 weight percent for all of the experiments. The filming and impregnation temperatures were 75°C and 85°C, respectively. The impregnation pressure was 275 kPa and the line speed was 1.22 m/min.

The resin content of the prepregs was determined by weighing a 5.08 x 5.08 cm square of prepreg, dissolving the resin with acetone, and weighing the dried fibers. This technique is in accordance with ASTM D 3171-99 and Boeing Support Standard 7336 [13, 14]. Five samples from each batch of prepreg were used in the determination of resin content.

Symmetric cross-ply laminates were laid up using the above prepregs. The laminates consisted of 12 plies of prepreg in a $[0^{o}_{3}, 90^{o}_{3}]_{S}$ configuration. After every third ply the laminate was precompacted under vacuum pressure for two minutes during the lay-up before additional plies were positioned.

The autoclave cycle used to cure these laminates was the same as that described for the resin plaques, but the total consolidation pressure used during cure was 310 kPa. A larger pressure was used during the neat resin cure to prevent void formation. The vacuum bag was vented to the atmosphere when the autoclave pressure reached 104 kPa.

Once cured, the edges of the laminates were removed for consistency and the laminates were cut into 3.49 x 1.27 x 0.16 cm (length x width x thickness) samples for cycling studies. An additional 3.49 x 3.49 x 0.16 cm sample was prepared to compare the extent of microcracking in adjacent faces. These faces were designated 1 and 2 as demonstrated in Figure 3-1. The samples were sufficiently large to neglect edge effects. The edges of the laminates were polished prior to cycling to facilitate optical microscopy of the surfaces.

### 3.2.2 Analysis

Thermal mechanical analysis (TMA) was performed on the resins using a DuPont Instruments 2940 TMA controlled by thermal solutions 1.2J software. A macro-expansion probe was used with an applied force of 0.05 N. The samples were exposed to a ramp rate of 5°C/min from -150°C to 60°C in a nitrogen atmosphere.

Dynamic mechanical analysis (DMA) experiments were performed on the cured laminates with a TA instruments 2980 DMA in single cantilever mode controlled by Thermal Solutions 1.2 J software. A heating rate of 5°C/min to 300°C with a frequency of 1 Hz and an oscillation amplitude of 0.1 mm in nitrogen was used.

The cut and polished laminates were allowed to equilibrate in a desiccator at 22°C and were then placed in a liquid nitrogen bath (-195.8°C) for 10 minutes. After exposure to liquid nitrogen, the samples were placed in the desiccator and allowed to return to room temperature. Each sample was exposed to a minimum of five cycles, or until optical microscopy revealed no further microcracking.

Optical microscopy was used to observe and document the response of the samples to cryogenic exposure. Each sample was examined prior to cycling to ensure that there were no initial cracks or defects in the surface. The samples were examined after each cycle at 50x, 100x, and 200x magnification using an optical microscope after returning to thermal equilibrium at room temperature in the desiccator. Photomicrographs were taken to document the sample response and the number of microcracks on the polished surface was counted.

The extent of microcracking in each material was quantified by dividing the total number of microcracks on the sample face by the face area to give a crack density value. Unless otherwise specified, face 1 was used in the microcracking analysis.

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 Material influences on crack density

This chapter presents the results of an investigation into the trends and behaviors of composite materials when cycled between cryogenic and ambient temperatures. Optical microscopy revealed a variety of responses to cycling, such as potholing, delamination, and microcracking. Microcracking represented the majority of the structural changes in the samples, and as such, was the focus of this study.

The model resin formulations used in this analysis were chosen to provide a balance between strength and flexibility. The curing agents used were also selected to provide varying degrees of network regularity and different crosslink morphologies. These materials were selected to study the fundamental behavior of composites exposed to cryogenic cycling; however, they are not commercially viable for composite structures. EPON® 836 has an aromatic backbone that is relatively stiff and EPON® 871 has a more flexible aliphatic structure. As a result, in series 1 EPON® 836 imparts a higher modulus to the mixture while EPON® 871 provides increased backbone flexibility [15, 16]. The components of the resin in series 1 had similar epoxide equivalent weights, which allowed alterations in the proportion of EPON® 871 in the resin to change the flexibility of the matrix backbone while maintaining a similar molecular weight between crosslinks. The incorporation of Nipol 1472 into series 2 served to toughen the system through the formation of an interpenetrating network and is representative of typical epoxy resin toughening agents [17, 18].

It should be noted that matrix 1d only formed acceptable prepreg on T300 fibers and, as such, no data exists for this system on higher modulus fibers due to the inability to fabricate laminates with these materials. Similarly, matrix 1c could not be formed into the appropriate neat resin samples and was not tested. Matrix 2a was extremely brittle and any samples formed from this material fractured during preparation.

Figure 3-2 documents the changes in the microcracking behavior of the laminates as the matrix and fibers were altered. The following general observations can be drawn from this figure. Laminates in which dicy and diuron were used as the curing agent contained more microcracks after cycling than the laminates that were cured with DDS for series 1. Raising the proportion of EPON® 871 in the resin formulation corresponded to larger levels of microcracking. Resin series 2 exhibited no cracking when toughened with Nipol 1472 and the untoughened formulation exhibited microcracking only when system 2b was combined with M35J fibers. It was observed that the laminates with lower glass transition temperatures displayed greater microcrack densities. Increased delamination and potholing of the surfaces of the laminates corresponded to increased levels of microcracking for all laminates.

The increase in microcrack density in systems 1c and 1d resulted partly from a decrease in the laminate strength as the proportion of EPON® 836 was reduced. When less EPON® 871 was used in the resin formulation, the flexible aliphatic portion of the backbone increased the ability of the laminates to resist microcracking. When larger proportions of EPON® 871 were used the overall strength of the matrix could have been degraded, which may have increased the microcrack density in laminates containing these matrices. This may have decreased the level of thermal stress at which microcracking occurred.

Increased backbone flexibility altered the response of the matrix to temperature changes. Previous work has shown that flexible matrix segments are more mobile and occupy a greater effective volume, which raises the linear coefficient of thermal expansion (CTE) of the matrix [19]. Figure 3-3 shows the CTEs as determined by TMA for the resins studied. A small increase in the CTE at -125°C and a large increase in the CTE at 25°C between matrices 1b and 1d occurred as the proportion of 871 was increased from 37.5 to 50.0 wt.%. The disparity between the dimensional changes of the matrix and fibers, and therefore the difference between the expansion and contraction of the 0°

and 90° plies, at low temperatures was enhanced as the level of EPON® 871 was raised, which in turn increased the stresses in the materials and caused more microcracking. Resin system 1a showed the largest CTE value; however, laminates containing this matrix showed the lowest levels of crack density in series 1. Laminates made with this resin contained greater thermal stresses, but it is proposed that the matrix was able to withstand greater stresses before failing, preventing extensive microcracking. Series 2 showed lower CTE values than those observed for series 1. This is partly responsible for the small microcrack density in laminates that contained series 2 as the matrix. Variations in the matrix chemistry and the incorporation of a rubber toughening agent could have altered the degree of adhesion between the fibers and the matrix. Microcracks tend to propagate along the fiber/matrix interface, and any change in the strength of adhesion in this area could have significantly altered the response of the composite materials to cryogenic cycling.

The choice of curing agent had a significant effect on the final morphology of the polymeric matrix, and as such, played a role in how the laminates responded to cryogenic cycling. DDS is a tetrafunctional amine curing agent with a rigid aromatic composition that forms a relatively regular network structure [20]. Dicyandiamide reacts through a much more complicated mechanism that can produce di, tri, and tetrafunctional reactive and catalytic species. Evidence also suggests that difunctional species produced in the reaction can act as chain extenders for epoxy resins [21]. The more irregular and flexible network created when dicy/diuron was used as a curing agent may have decreased the ability of the matrix to accommodate thermal stresses and contributed to the increase in microcrack density of the laminates. Figure 3-3 demonstrates that the use of dicy/diuron as a curing agent caused a decrease in matrix CTE at 25°C and -125°C for series 1 and a negligible change for series 2. The fact that dicy/diuron reduced the matrix CTE and increased laminate microcracking would not be expected because lower thermal stresses were present in the laminate. The use of dicy/diuron probably weakened the matrix, reducing the level of thermal stress it could accommodate before microcracking.

The glass transition temperatures ($T_g$) of the laminates studied were obtained from the peak in loss modulus as determined by dynamic mechanical analysis. Increased microcracking with decreased Tg is shown in Figure 3-4. Larger EPON® 871 proportions and dicy/diuron cure increased backbone flexibility and epoxy chain length, which decreased the glass transition temperatures of the laminates [22, 23]. These same factors increased microcracking by decreasing the strength of the matrix and, in the case of EPON® 871 incorporation, increasing the CTE of the matrix.

Figure 3-2 shows the final crack density in the laminates studied as a function of the longitudinal CTE of the fiber used. The fiber tensile modulus increased by 27.8 percent from T300 to T800H and by 16.7 percent from T800H to M35J, which corresponded to a 36.6 percent increase in fiber longitudinal CTE from T300 to T800H and a 30.4 percent increase from T800H to M35J. Increasing the tensile modulus and negative longitudinal CTE of the fibers caused an increase in the crack density in all of the composite materials studied. No microcracking was observed when T300, a low modulus fiber, was used in conjunction with system 1a. The tensile modulus of the fibers influenced the microcrack morphology as well as the crack density. The microcracks typically became wider and more tortuous when higher modulus fibers were used.

Composites containing higher modulus fibers are more prone to microcracking. A higher tensile modulus corresponds to increasing crystallinity and orientation of the crystallographic basal planes parallel to the fiber axis [24]. This increases the negative longitudinal CTE of the fibers [24]. When the temperature was decreased the fibers contracted in the radial direction and expanded along the longitudinal axis while the matrix contracted in all directions [24]. Larger differences in the CTE between the fibers and the matrix increased the thermal stresses at low temperatures and caused a corresponding increase in microcracking. In addition, it has been shown for transverse tensile mechanical testing that as the ratio of the fiber modulus to the matrix modulus increases the stress concentration at a fiber increases [24]. More total crack surface needed to be created and more material displaced in order to relieve the larger thermal stresses that were created in laminates containing fibers with high tensile moduli and CTEs. The change in aspect ratio of the fibers at low temperatures could have altered the physical properties of the laminates and their ability to resist internal stresses. Differences in fiber diameter and surface irregularities could have played a role in the cryogenic behavior of the laminates studied. M35J fibers have a diameter of 5 μm while

T800H fibers have a diameter of 7-8 μm [24]. This difference could have changed the wetting and adhesion of the matrix to the fibers and altered the microcracking propensity of the materials studied.

### 3.3.2 Cryogenic microcracking

Microcracks propagated through the epoxy matrix transverse to the fibers in the x-direction as shown in Figure 3-1 and ended at the interface between the plies with different orientations. Figure 3-5 presents optical photomicrographs that document these phenomena in three representative laminates. Figure 3-5A presents a typical microcrack in face 1 of a model laminate. Delamination occurred in some cases when the microcracks encountered the interface between cross plies. This is illustrated well in Figure 3-5B. Examination of face 1 showed microcracks initiating at the laminate surface and propagating in the x-direction towards the interior of the specimen. For these laminates, the crack density was always larger on the bag side than the tool side. This can be attributed to the greater surface roughness on the bag side, which would provide more locations for crack initiation.

Investigation of faces 1 and 2 of a 3.49 x 3.49 x 0.16 cm laminate revealed that microcracking occurred in the central and outer plies of a $[0^{\circ}_3\ 90^{\circ}_3]_S$ laminate. In face 2 microcracks initiated at the interface between the 0° and 90° plies and propagated across the central plies of the laminate in the x-direction, transverse to the fibers. Figure 3-5C contains an example of microcracking in the central plies. However, the crack density in the central plies of face 2 was lower than the crack density observed in the outer plies of face 1. Microcracking in the central plies could provide a pathway for liquid to flow through the laminate. This could be disastrous for the storage of cryogenic liquids, particularly liquid hydrogen or helium [1].

All of the materials that microcracked in response to cryogenic cycling showed a large initial increase in the crack density, which generally leveled off after three or four cycles and reached a constant value. A representative example of this behavior is illustrated in Figure 3-6 for matrix 1a. Microcracking began soon after cyclic exposure to low temperatures was initiated, and once the stress was relieved to a level below the yield stress of the fiber/matrix interface, no more cracking occurred. This data indicated that the probability and severity of microcracking in a material can be determined after only a few cycles.

## 3.4 CONCLUSIONS

This chapter examined the propagation and distribution of microcracks in cryogenically cycled symmetric cross-ply carbon fiber/epoxy composites. Microcracks formed in some of the materials studied as a response to thermal stresses generated through cryogenic cycling. Cracking occurred in the polymeric matrix transverse to the fibers in both the inner and outer plies of autoclave cured $[0^{\circ}{}_3\ 90^{\circ}{}_3]_S$ laminates. The type of fibers and the polymeric matrix used in the composites played a large role in determining the propensity for microcracking as well as the microcrack morphology. Higher fiber tensile moduli resulted in increased microcrack density and larger cracks. Increased backbone flexibility caused an increase in microcrack density and decreased the glass transition temperatures of the laminates studied. The curing agent used in the matrix formulation also played a key role in the response of the resulting material to cryogenic cycling. The presence of a rubber interpenetrating network toughener prevented the formation of microcracks in all of the laminates studied. Collectively, it was shown that the fibers and the matrix used in a composite play an important role in determining the response to cryogenic cycling by altering the thermal stresses present in a material as well as the ability of the material to resist thermal stresses.

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Table 3-1. Formulation of model resins

| Series 1 | Wt. Percent EPON® 836 | Wt. Percent EPON® 871 | phr[a] DDS | phr Dicyandiamide | phr Diuron |
|---|---|---|---|---|---|
| a | 62.5 | 37.5 | 17.5 | - | - |
| b | 62.5 | 37.5 | - | 5 | 2 |
| c | 50.0 | 50.0 | 16.6 | - | - |
| d | 50.0 | 50.0 | - | 5 | 2 |

| Series 2 | Wt. Percent EPON® 828 | Wt. Percent D.E.R. 661 | phr Nipol 1472 | phr DDS | phr Dicyandiamide | phr Diuron | phr Chromium Naphthenate |
|---|---|---|---|---|---|---|---|
| a | 45.0 | 50.0 | - | 16.9 | - | - | - |
| b | 45.0 | 50.0 | - | - | 5 | 2 | - |
| c | 45.0 | 50.0 | 5.3 | 16.9 | - | - | 0.1 |
| d | 45.0 | 50.0 | 5.3 | - | 5 | 2 | 0.1 |

---

[a] phr: parts per hundred resin

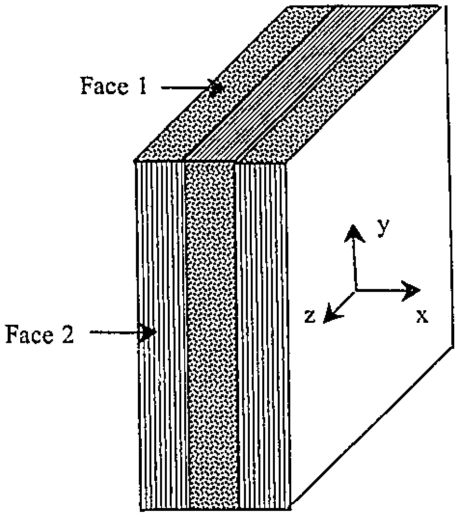

Figure 3-1. Polished faces of model laminates

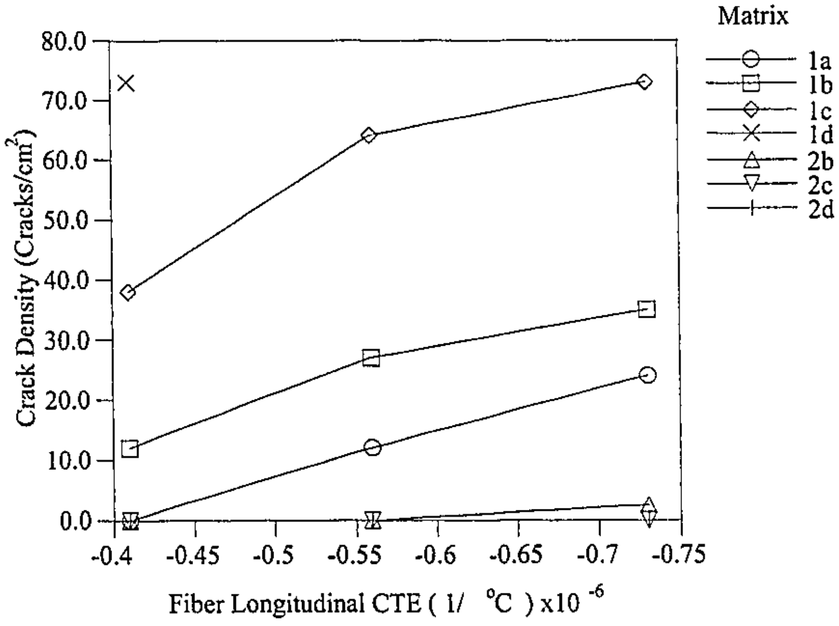

Figure 3-2. Crack density variation with fiber longitudinal CTE

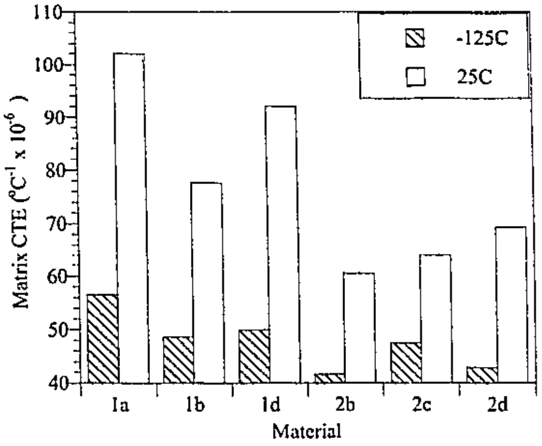

Figure 3-3. Matrix CTE variation with resin composition

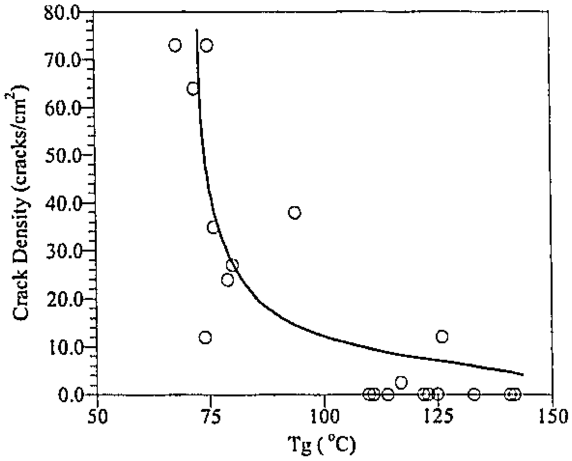

Figure 3-4. Crack density variation with laminate glass transition temperature as reported from the peak in dynamic loss modulus

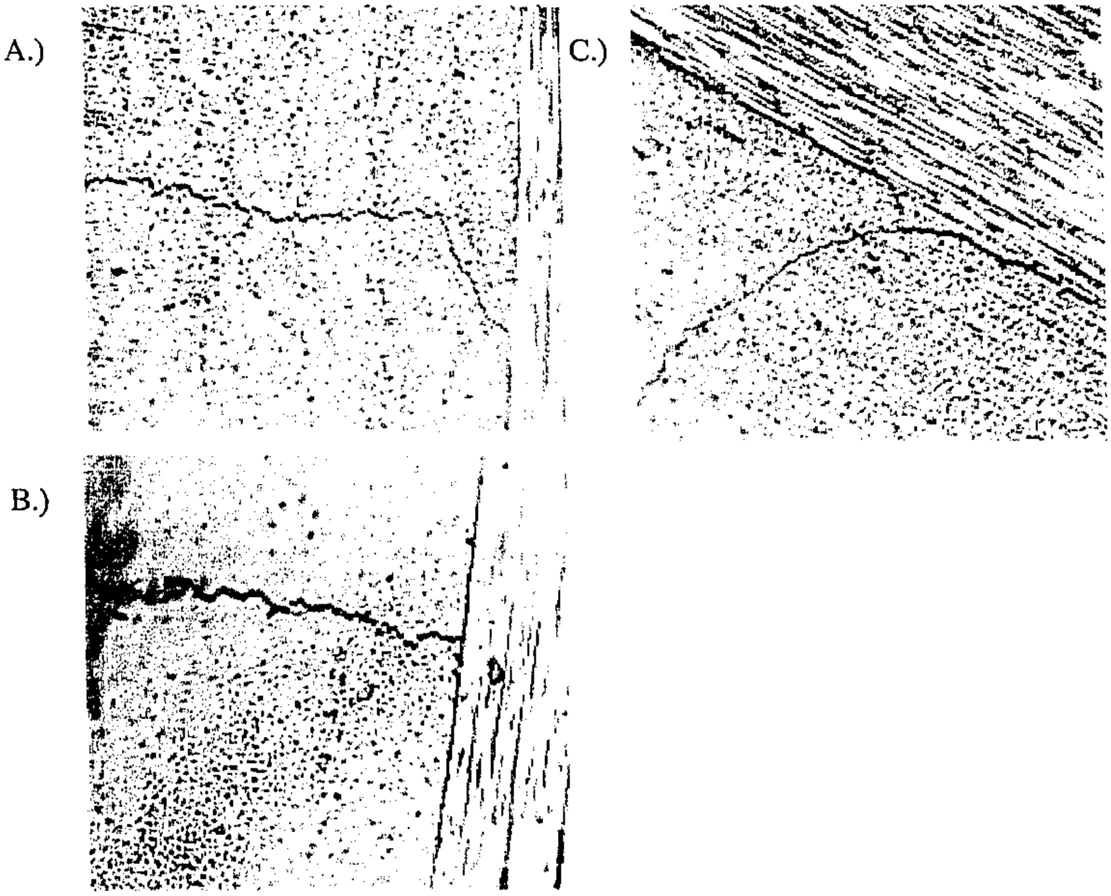

Figure 3-5. Optical photomicrographs of cryogenically cycled laminates containing M35J fibers. A: System 1c. B: System 1b. C: System 1a, central plies in face 2 of laminate. 200x magnification

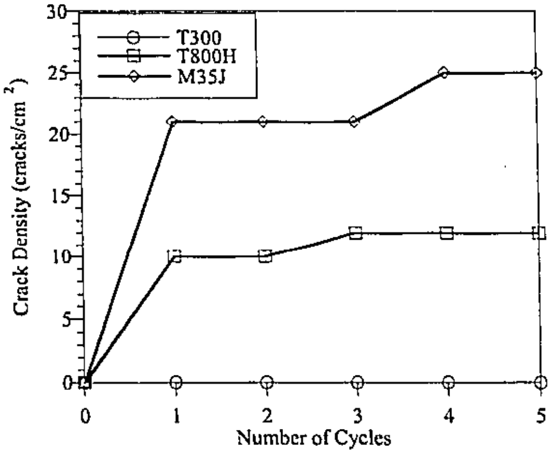

Figure 3-6. Microcracking progression with cryogenic cycling in system 1a

# CHAPTER 4: EFFECTS OF FIBER-MATRIX ADHESION ON CRYOGENIC MICROCRACKING

## 4.1 INTRODUCTION

Traditional composite materials combine a strong, stiff reinforcing phase with a second phase that serves to transfer loads to the reinforcing phase. In the case of fiber-reinforced polymeric composites, the polymeric matrix allows applied stresses to be transferred to the fibers [1]. In chapter 3, the effects of variations in the matrix and the fibers on cryogenic microcracking were investigated. This chapter extends the work in the last chapter to examine how interactions between the fibers and the matrix influence the behavior of carbon fiber/epoxy composites at low temperatures. Stress transfer between the matrix and the fibers plays a large role in determining the ability of a composite material to support applied loads, and the properties of the fiber-matrix interface control matrix-fiber stress transfer [1-5]. Therefore, the final mechanical properties of composite materials are determined, to a large extent, by the properties of the interface and the quality of adhesion between the fibers and the matrix.

Carbon fiber/epoxy composites are often used to store cryogenic liquids, and good thermal characteristics and mechanical properties are essential for these materials to perform effectively [6]. Carbon fiber/epoxy laminates, particularly symmetric cross-ply laminates, develop thermal stresses during cryogenic cycling that place the ply groups in a state of transverse tension. Repeated applications of these loads can cause structural failure [7, 8]. Debonding and matrix cracking occur in response to these stresses and eventually combine to form transverse cracks that propagate through the material [9]. Better fiber-matrix adhesion makes it more difficult to debond the fibers from the matrix; therefore, transverse microcracking should be reduced if the quality of adhesion in a laminate is increased [10].

In this chapter the impact of fiber/matrix adhesion on the transverse microcracking of fiber reinforced polymeric materials thermally cycled at cryogenic temperatures was investigated using symmetric cross-ply carbon fiber/epoxy laminates containing fibers with different surface treatments. Three fiber surfaces were used:

Unsized but exposed to an oxidative surface treatment, epoxy sized, and surfactant sized. Modifications of the fiber surfaces changed the adhesion of the matrix to the fibers as determined by interlaminar shear strength and dynamic mechanical analysis. The extent of microcracking in the laminates exhibited a dependence on fiber/matrix adhesion, with high levels of adhesion corresponding to decreased microcracking.

## 4.2 EXPERIMENTAL

### 4.2.1 Materials

A mixture of commercial epoxies was used as the base resin for the polymeric matrix. The resins used were EPON® 828 from Resolution Performance Products and Araldite MY 9512 from Vantico Inc. The structural details of EPON® 828 are given in chapter 3. Araldite MY 9512 is a tetraglycidyl methylene dianiline (TGMDA) derivative. HT 976, diaminodiphenyl sulfone (DDS), from Ciba was used as the curing agent.

The epoxy resins were combined in a 66:34 ratio by weight of MY 9512: EPON® 828 in an oil bath at 120°C and stirred until they were completely mixed. A stoichiometric amount of DDS was melted and added to the epoxy mixture in the oil bath. The epoxy/DDS mixture was blended for two minutes in the oil bath at 120°C after which the resin was quenched to room temperature and stored at –10°C until it was prepregged.

Unidirectional prepregs were developed consisting of the resin discussed above and Hexcel AS4C PAN-based carbon fibers. Fibers with three different proprietary surfaces were used. The first, referred to as U, was unsized but exposed to an oxidative surface treatment. The second, referred to as GP, was coated with 0.3 wt. % epoxy sizing. The third, referred to as S, was coated with 0.3 wt. % surfactant sizing. The filament count for all of the fibers was 12,000 per tow [11]. A laboratory-scale hot-melt prepreg machine was used to impregnate the fibers with the epoxy resin [12]. The prepreg fiber areal weight was set to 160 g/m$^2$ and the nominal resin content was 30±3 wt. % for all of the experiments. The filming and impregnation temperatures were 70°C and 85°C, respectively. Two rollers were used to apply the impregnation pressure. The pressure on the first roller was 69 kPa and the pressure on the second was 241 kPa. The line speed was 1.5 m/min and the gap height for resin filming was 0.25 mm.

The resin content of the prepregs was determined in accordance with ASTM D 3171-99 and Boeing Support Standard 7336 using the technique outlined in chapter 3 [13, 14].

Symmetric 15.24 x 15.24 cm and 20.32 x 15.24 cm unidirectional laminates were laid up using the above prepregs. The symmetric laminates consisted of 12 plies of prepreg in a $[0^\circ_3, 90^\circ_3]_S$ configuration, and the unidirectional laminates consisted of 20 plies. After every third ply for the symmetric laminates and every fourth ply for the unidirectional laminates the prepreg stack was precompacted under vacuum pressure for two minutes before additional plies were positioned.

The autoclave cure cycle consisted of a 2.8°C/min ramp to 177°C followed by a two hour hold at 177°C and a ramp down to 27°C at a rate of 2.8°C/min. The total consolidation pressure used during cure was 310 kPa. The vacuum bag was vented to the atmosphere when the autoclave pressure reached 104 kPa.

Once cured, the symmetric laminates were cut into 3.49 x 1.27 x 0.16 cm (length x width x thickness) samples for cycling studies and the unidirectional laminates were cut into 2.54 x 1.27 x 0.32 cm (length x width x thickness) samples for interlaminar shear strength testing and dynamic mechanical analysis. The edges of the symmetric laminates were polished prior to cycling to facilitate optical microscopy of the surfaces.

### 4.2.2 Analysis

X-ray photoelectron spectroscopy (XPS) was performed on the surfaces of the fibers to determine the differences in surface chemistries between the fibers. For each sample, survey spectra were taken from five different locations on the fiber to determine the surface composition. Once the surface composition was obtained, C 1s and O 1s spectra were acquired from the surface of each sample.

Inverse gas chromatography (IGC) was used to characterize the surface energies of the fibers. The experiments were conducted using a Varian Star 3400 gas chromatograph equipped with a 1 m stainless steel column and a flame ionization detector. The column temperature was 30°C and the detector temperature was 250°C for all runs. 3.2 g of fibers were packed in the column in all cases. Before each fiber was tested, the column was purged with nitrogen for 20 minutes at 30°C. A series of normal hydrocarbon probes (methane, n-hexane, n-heptane, n-octane, and n-nonane) were injected into the column at concentrations of $10^{-3}$ to $10^{-4}$ ppm to ensure practically zero surface coverage. A minimum of five retention time ($t_R$) data points was recorded for each probe and the mean values were used in all subsequent calculations. The retention times of the probes were then used to calculate the dispersive component of the surface energy for each of the fiber types using the following equations.

$$RT\ln(V_n) = 2a\sqrt{\sigma_S\sigma_L} + C \tag{4-1}$$

$$V_n = ft_N \tag{4-2}$$

$$t_N = t_R - t_{CH4} \tag{4-3}$$

Where R is the universal gas constant, T is the column temperature, $V_n$ is the net retention volume, a is the molar area of the probe, $\sigma_S$ is the surface energy of the fibers, $\sigma_L$ is the surface energy of the probe, and C is a constant. The net retention volume was calculated from the flow rate (f) and the net retention time ($t_N$), which was calculated from the observed retention time ($t_R$) and the retention time for methane ($t_{CH4}$).

Dynamic mechanical analysis (DMA) experiments were performed on the cured unidirectional laminates using the technique described in chapter 3 with an amplitude of 0.01 mm.

Interlaminar shear strength (ILSS) tests were conducted on the unidirectional laminates using the short beam shear (SBS) technique. An Instron 4505 screw-testing frame controlled by Instron series IX software was used in these experiments. Five samples of each material were tested and the average value reported. The interlaminar shear strength tests were performed in accordance with ASTM D2344-84 [15].

The cut and polished symmetric laminates were tested using the cryogenic cycling procedures described in chapter 3. Three samples of each material were tested and the average crack density value reported.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Fiber characterization

The fibers studied in this chapter were analyzed using XPS in order to determine if any differences in surface chemistry existed that may have influenced the cryogenic microcracking of laminates containing these fibers. XPS allows high-resolution analyses to be performed on the outer 25Å of a solid material and is widely used to determine the chemical composition of solid surfaces [16]. As expected, significant differences were found between the fibers, which were unsized (U), epoxy sized (GP), and surfactant sized (S). Table 4-1 summarizes the surface chemistry of the fibers studied. Values in parentheses represent one standard deviation. The atomic percentage of oxygen on the surface of the fibers increased from the unsized to the epoxy sized to the surfactant sized fibers. This was paralleled by a decrease in the atomic percentage of carbon and nitrogen on the fiber surfaces.

It was found that the oxygen on the surface of the fibers was located in hydroxyl or ether groups. The unsized fibers showed an almost equal distribution of oxygen between ether and hydroxyl functionalities, with slightly more C-O-C linkages than C-OH groups. In contrast to this, both the sized fibers showed significantly larger percentages of C-OH groups than C-O-C groups. No significant difference in the oxygen chemistry was observed between the two sized fibers. Carbon atoms on the surface of the fibers were found to be either graphitic carbon (C-C bonds) or carbon atoms bonded to oxygen atoms. The surface carbon of the unsized (U) fibers was mostly graphitic carbon, with a small percentage of C-O bonds. The epoxy (GP) sized fiber surfaces contained more than 50 % graphitic carbon, but a smaller percentage than in the unsized fibers. The surfactant (S) sized fibers exhibited a larger percentage of C-O bonds than C-C bonds, which was markedly different from the other fibers.

Figure 4-1 illustrates how the dispersive component of the surface energies of the fibers, as determined using IGC, changed with surface treatment. The surface energy decreased dramatically from the unsized to the sized fibers. It should be noted that this was only the dispersive component of the surface energy and reflected only van der

Waals interactions with the fibers. The surface energy of the surfactant sized fibers was slightly less than that for the epoxy sized fibers, paralleling the differences in surface chemistry of the fibers. A decrease in surface energy occurred as the percentage of carbon in C-C bonds decreased because it became more difficult for normal hydrocarbons to interact favorably with the fiber surface. The GP and S sized fibers showed increasing atomic percentages of oxygen on the fiber surface and increasing amounts of oxygen located in hydroxyl groups when compared with the unsized fibers. Larger amounts of oxygen on the fiber surfaces could have reduced the interaction of hydrocarbons with the fibers and lowered the observed dispersive component of the surface energies. While the dispersive component of the surface energy was seen to decrease with increasing atomic percentages of oxygen and hydroxyl groups, it was likely that the acid-base component of the surface energy increased with the greater concentration of polar groups on the fiber surface. An increase in the acid-base component of the surface energy could have resulted in an overall increase in the fiber surface energy that would have promoted good adhesion between the fibers and the matrix [2-4, 17]. It has been observed that the presence of groups that can participate in electron acceptor-donor relationships can decrease the observed dispersive component of surface energy, while increasing fiber-matrix adhesion [17].

### 4.3.2 Composite properties

Figure 4-2 displays how the interlaminar shear strength of unidirectional laminates varied with the sizing type. The error bars represent one standard deviation. The unsized and GP-sized fibers had ILSS values that were statistically the same, but a significant increase was observed for the S-sized fibers. This can be attributed to greater fiber-matrix adhesion in the laminates containing S-sized fibers [1, 2]. Poor adhesion, as evidenced by low ILSS values, was observed in the laminates containing the epoxy coated fibers. This could have been the result of the epoxy sizing dissolving into the matrix during prepregging and cure, which may have left behind a fiber surface that interacted poorly with the surrounding material. The GP sizing also often achieves less than complete coating of the fiber, which would significantly reduce fiber-matrix adhesion [18]. The S sized fibers had a larger percentage of C-O bonds on the surface than the other fibers and a larger percentage of C-OH groups than the unsized fibers. It has been shown that the presence of groups that can participate in acid-base or hydrogen bonding interactions, such as hydroxyl or carboxylic acid groups, will increase fiber-matrix adhesion and interlaminar shear strength [17, 19].

Scanning electron microscopy (SEM) was used to examine the failure surfaces of the SBS specimens. All SEM samples were gold sputtered and examined using a working distance of 48 mm with a 15 kV potential. Figure 4-3 presents scanning electron micrographs of representative failure surfaces from laminates containing different fibers. Failure was primarily adhesive for the laminates containing unsized and GP sized fibers, as seen in Figures 4-3 A and B, but Figure 4-3 C shows cohesive failure in the laminates fabricated using S sized fibers. This provided evidence for increased adhesion when the S sized fibers were used and was supported by the interlaminar shear strength results. When the fiber-matrix bond was sufficiently strong failure shifted from the fiber-matrix interface to the bulk matrix. Other researchers have observed this and correlated the switch from interfacial to matrix failure in short beam shear testing to direct measurements of increased fiber-matrix adhesion [2].

Dynamic mechanical analysis was performed to determine if different levels of adhesion and interfacial damping would manifest themselves as differences in the dynamic bulk properties of the laminates. Previous research has shown that dynamic mechanical analysis can be used to characterize interfacial adhesion in composite materials [20-22]. Larger amounts of energy can be dissipated by poor interfacial bonding than by good bonding, and this is observed as a change in the viscous response ($\tan(\delta)$) of a material [20]. Increased interfacial damping, which corresponds to poor adhesion, has been shown to correlate with a decrease in static transverse tensile strength [21].

As shown in Figure 4-4, the shapes and peak temperatures of the $\tan(\delta)$ peaks for the unsized and GP sized fibers were similar, but were significantly different from the peak for the laminates containing S sized fibers. This suggests that the unsized and GP sized fibers resulted in laminates that had different adhesion and interfacial properties than the laminates that contained S sized fibers. The surface energies and chemistries of the fibers as well as the observation of lower ILSS values for the systems that contained U and GP fibers supported this result.

### 4.3.3 Laminate microcracking

Microcracking occurred in all of the laminates studied and representative optical photomicrographs of the microcracks are shown in Figure 4-5. The microcracks propagated towards the interior of the samples normal to the fibers when the fibers were viewed along their length. Crack termination occurred when the interface between the 0° and 90° ply groups was reached. In some cases delamination occurred at the 0°/90° interface as shown in Figure 4-5 B. Generally, the microcracks propagated along the fiber-matrix interfaces, but in some cases fiber splitting was observed as is shown in Figure 4-5 B. No significant variation in individual crack morphology was observed as the fiber type was varied.

Significant variations in the crack density, shown in Figure 4-6, were observed as the fiber type was varied. The error bars indicate one standard deviation. There was no statistical variation in microcrack density between the laminates fabricated using U and GP fibers, but a significant decrease was observed for the laminates containing S sized fibers. When viewed in light of the adhesion results it can be concluded that as the fiber-matrix adhesion increased the microcrack density resulting from cryogenic cycling decreased. It is also interesting to note that the traditional epoxy sizing showed no improvement over the unsized material, while the surfactant sizing increased the microcrack resistance. Room temperature static tests have shown similar decreases in the transverse crack density in composite materials when increasing levels of surface treatment were used [10].

## 4.4 CONCLUSIONS

Fiber reinforced composite materials were prepared using fibers with different surface chemistries. Variations in the fiber surface chemistry changed the fiber-matrix adhesion in laminates containing these fibers. The fiber-matrix adhesion had a direct impact on the formation of transverse microcracks in symmetric, cross-ply carbon fiber/epoxy laminates as a response to cryogenic cycling. Reduced microcrack density relative to laminates with poor adhesion was seen in laminates with good adhesion, and it was observed that improved mechanical properties and microcrack resistance occurred when surfactant sized fibers were used instead of traditional epoxy sized fibers.

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Table 4-1. Characterization of fiber surface chemistry using XPS

| | U | GP | S |
|---|---|---|---|
| Atomic Percentage Oxygen (1s) | 8.05 (0.22) | 14.63 (1.05) | 27.94 (3.01) |
| Atomic Percentage Carbon (1s) | 87.46 (0.88) | 83.72 (1.96) | 71.11 (2.70) |
| Atomic Percentage Nitrogen (1s) | 3.28 (0.46) | 0.87 (0.80) | 0.82 (0.58) |
| Percentage of Total Carbon as C-C | 87.00 | 69.00 | 41.00 |
| Percentage of Total Carbon as C-O | 13.00 | 31.00 | 59.00 |
| Percentage of Total Oxygen as C-O-C | 54.00 | 35.00 | 33.00 |
| Percentage of Total Oxygen as C-OH | 46.00 | 65.00 | 67.00 |

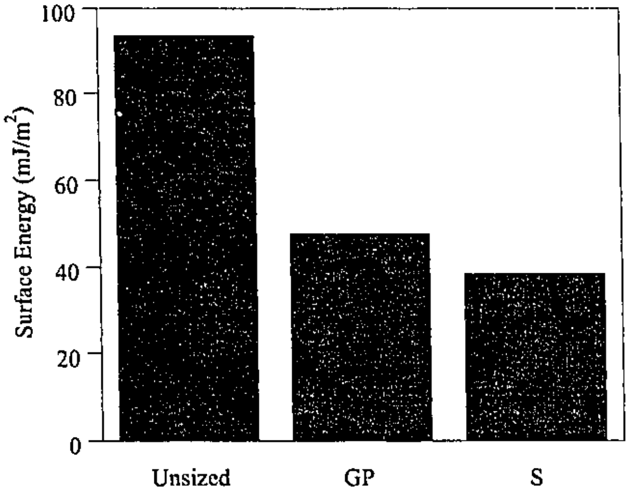

Figure 4-1. Surface energy variation with fiber type

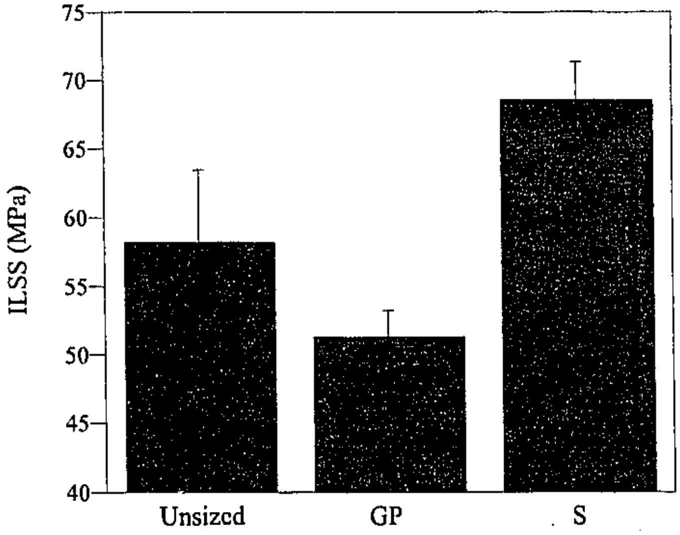

Figure 4-2. Interlaminar shear strength variation with fiber type

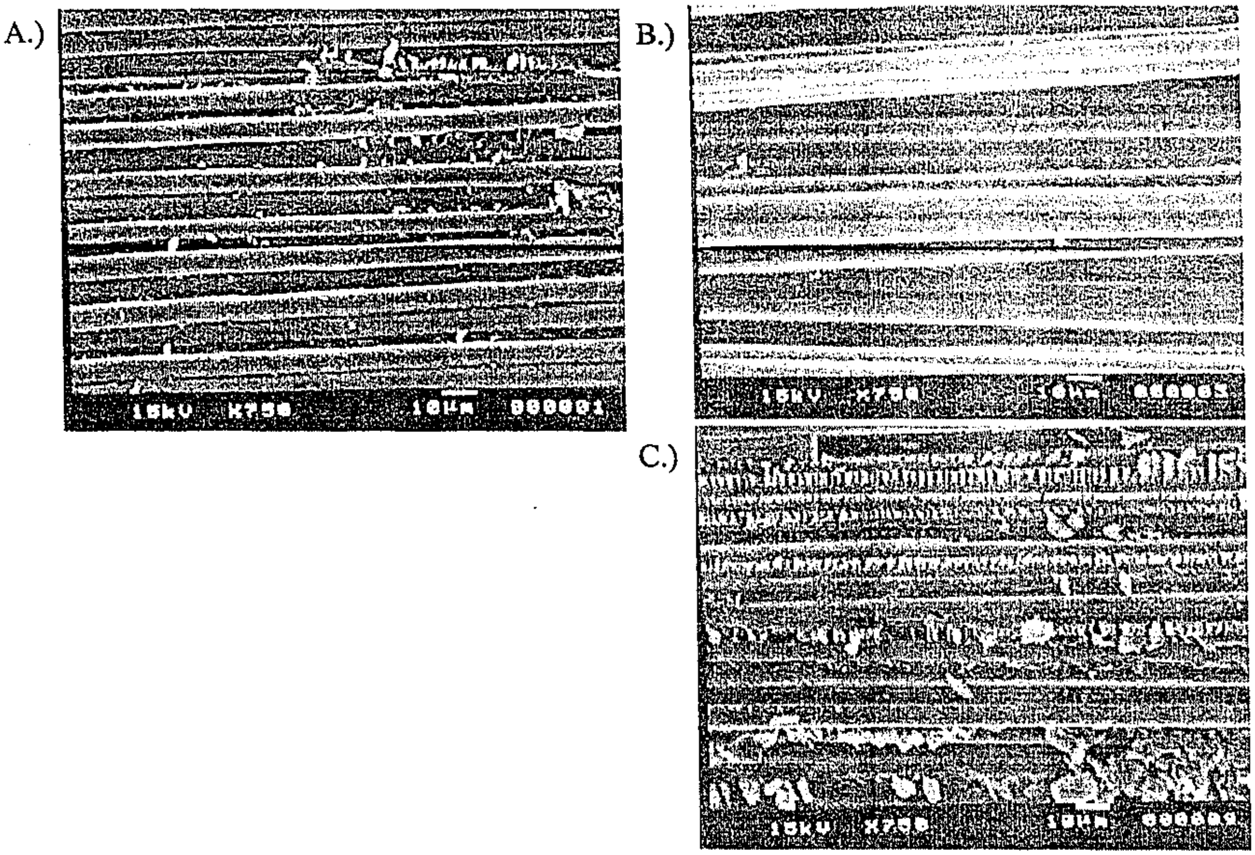

Figure 4-3. SEM images of SBS failure surfaces. A: Unsized and surface treated, B: GP sized, C: S sized. All images 750x

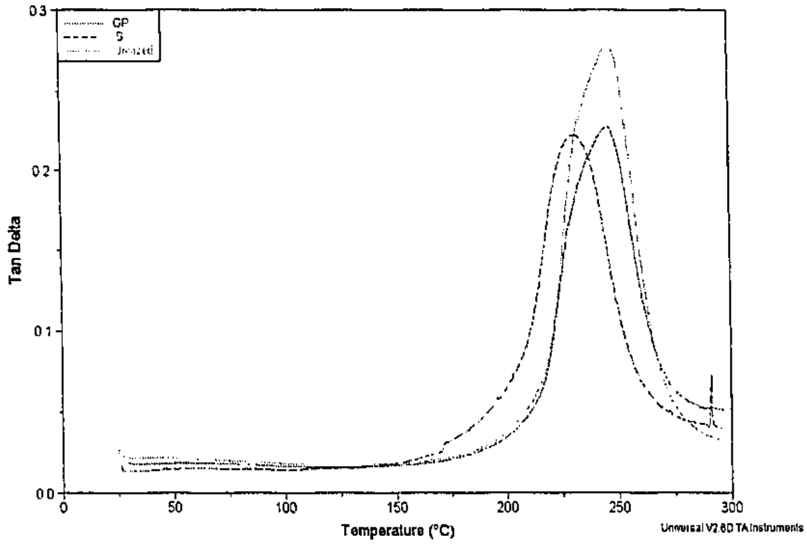

Figure 4-4. Tan(δ) variation with fiber type

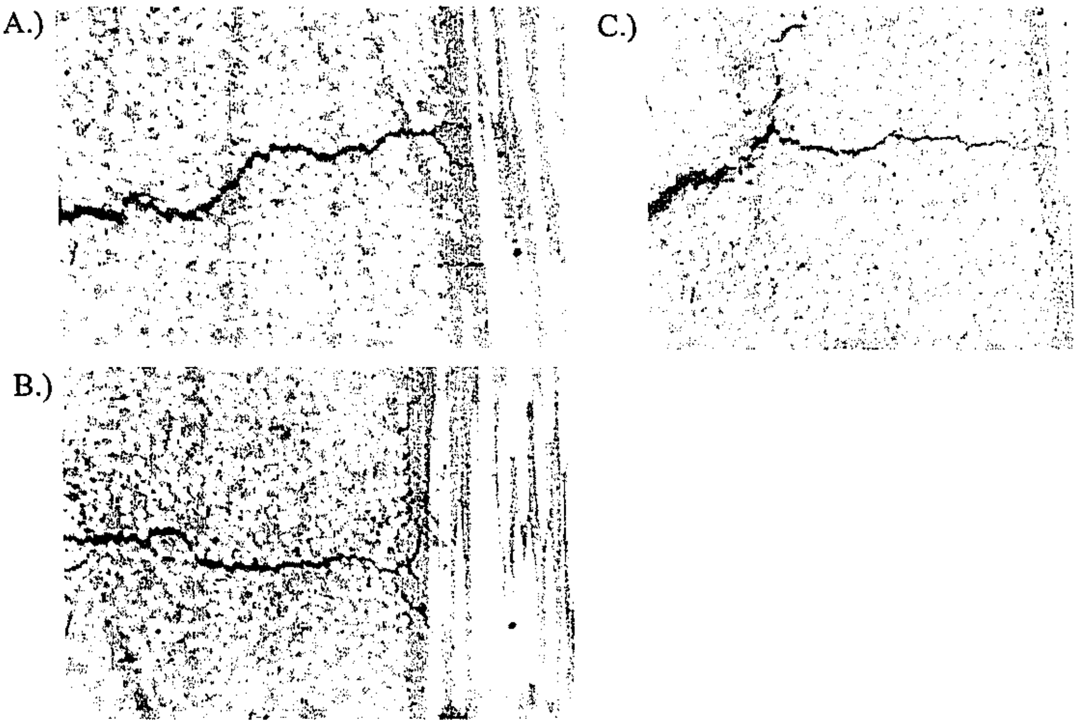

Figure 4-5. Optical photomicrographs of microcracks formed in response to cryogenic cycling. A: Unsized and surface treated, 200x, 2 cycles, B: GP sized, 200x, 5 cycles, C: S sized, 200x, 5 cycles

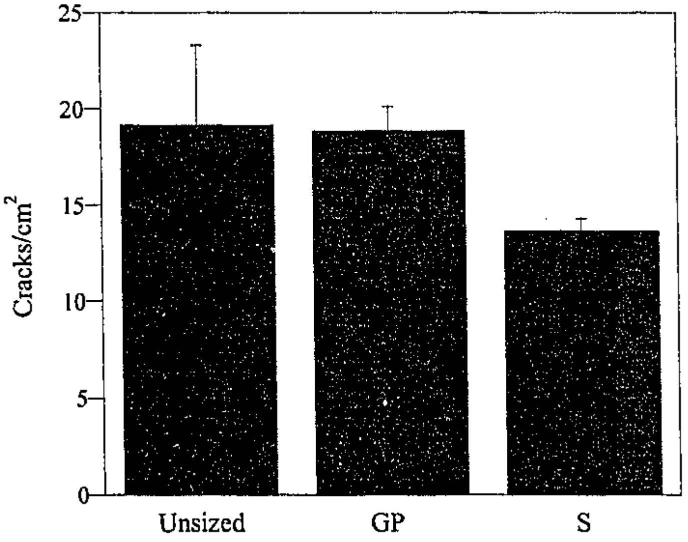

Figure 4-6. Crack density variation with fiber type

# CHAPTER 5: CRYOGENIC CYCLING BEHAVIOR OF NANOCLAY MODIFIED POLYMERIC COMPOSITE MATERIALS

## 5.1 INTRODUCTION AND BACKGROUND

The mechanical, thermal, and chemical properties of polymers and composites can be altered through the use of various kinds of fillers. The dimensions of these fillers typically fall on a macroscopic (1µm-1mm) length scale. Fillers of this type increase the stiffness and heat distortion temperature of a polymer, primarily because the filler makes up a significant proportion of the total mass. However, macroscopic fillers usually cause decreases in strength, impact resistance, and processability [1-3].

A new area of composites research has emerged in the last two decades that utilizes nanoparticle fillers to alter the properties of polymers. A widely studied class of nanoparticles is derived from layered aluminosilicate clays, such as montmorillonite, bentonite, and hectorite. These clays are composed of layers of an octahedral metal, usually aluminum or magnesium, complex sandwiched between two sheets of silicate tetrahedrons that are stacked to form the bulk clay [4-7]. Figure 5-1 shows a representation of the structure of montmorillonite. Each layer is approximately 1 nm thick and 500 nm in diameter. In the bulk state the layers are located roughly 1 nm apart. The surfaces of the clay layers develop a negative charge due to defects in the crystal structure and free hydroxyl groups located at the clay surface. Sodium ions in the interlayer region bond to the negative surfaces to create a net zero charge [6, 8, 9].

These layered structures can be dispersed in a polymeric matrix using a process called exfoliation to develop nanocomposite materials. The first step in this procedure involves modifying the interlayer, or gallery, region of the clay with alkyl ammonium compounds in order to create a hydrophobic environment for the polymer. Once this has been done, the polymer or polymer precursor can diffuse into the interlayer region to create what is known as an intercalated structure. Finally, polymerization and/or mechanical processing disperse the clay layers in the polymer, producing an exfoliated nanocomposite [5-8, 10, 11]. A diagram of this process is presented in Figure 5-2.

Definitive results have not yet been achieved for all nanoclay modified polymeric systems, but trends show that when processed properly small amounts (≤ 5 wt. %) of nanoparticle fillers can increase the modulus, strength, toughness, resistance to chemical attack, gas impermeability, resistance to thermal degradation, and dimensional stability of polymeric materials. However, the majority of this work has focused on neat thermoplastics and it is only recently that thermosets have begun to be examined as potential matrices for nanocomposites [5, 7, 12-16].

Inorganic layered nanoparticles have gained acceptance as possible reinforcing structures because of their low cost and ease of fabrication [5, 7]. Some of the earliest work on layered inorganic toughening was performed in 1987 at Toyota. Researchers demonstrated the possibility of functionalizing the surface of layered inorganic silicates to increase their affinity for a polymeric matrix [12]. Usuki et al. polymerized ε-caprolactam in the interlayer of an organoclay to form a nanocomposite. This material contained only 4.2 wt. % clay and had a 50 percent increase in strength, an increase in the heat distortion temperature (HDT) of 80°C, a 100 percent increase in tensile modulus, and a 20 percent increase in impact resistance [5]. Many researchers, using a variety of clays and polymeric matrices, have produced similar results to these [8, 14, 16-26].

Toughening using layered inorganic structures is achieved through the high specific surface area and aspect ratio of the filler [18]. These materials are also dominated by the properties of their interfaces as nearly all the polymer in the nanocomposite is near a clay surface. Inhibition of chain rotation by the presence of silicate platelets has also been shown to influence the properties of these materials [26]. Some researchers have suggested that these particles deform under stress to form microvoids that inhibit crack propagation, thus increasing toughness [18, 22, 27]. Zilg et al. demonstrated that exfoliation of the clay particles is central to achieving high performance. If this is not done, an intercalated structure will result that increases stiffness but has no other significant benefits [22, 23]. Pinnavaia et al. showed that manipulation of the surface functionality of the clay particles can tailor the clay surface chemistry to the polymer to maximize exfoliation. They also demonstrated that catalytic groups could be located in the gallery regions of layered clays to alter the reaction rate inside the clay tactoids [8, 10, 17].

Clays and inorganic reinforcements have been shown to be effective reinforcements in neat polymeric structures, but very little work has been done to examine advanced fiber-reinforced composites that utilize nanocomposite matrices [5, 7]. Hussain reported that matrix reinforcement with nanowhiskers can damage the fibers in composite materials. As such, he incorporated micro and nano-scale $Al_2O_3$ particles in filament-wound carbon fiber/epoxy composites. He observed an increase in modulus, flexural strength, interlaminar shear strength (ILSS), and fracture toughness when the matrix was filled at 10 vol. % with alumina particles (25 nm diameter). This effect stemmed largely from the large surface area of the filler and the ability of the particles to mechanically interlock with the fibers [28]. Work by Seferis et al. has shown the ability to incorporate nanosized alumina structures in the matrix and interlayer regions of prepreg-based carbon fiber/epoxy composites [29]. Rice et al. incorporated nanoclays in fiber-reinforced materials and found few improvements, but it should be noted that their work was preliminary and many variables were not explored [30].

## 5.2 RESEARCH MOTIVATION

Nanoparticle reinforcement of continuous fiber reinforced composites has been shown to be a possibility, but much work remains to be performed in order to understand how nanoreinforcement results in dramatic changes in material properties. The understanding of these phenomena will facilitate their extension to the reinforcement of more complicated anisotropic structures and advanced polymeric composite systems. The property and performance enhancements made possible by nanoparticle reinforcement may be of great utility for carbon fiber/epoxy composites that are used for the storage of cryogenic liquids. The structure and properties of these materials can change dramatically when they are exposed to cryogenic temperatures, especially in a cyclical fashion [31-33].

Therefore, the work presented in this chapter investigated the effects of nanoscale matrix modifications on the properties of macro-scale composite materials at low temperatures. The matrices of carbon fiber/epoxy composites were modified with layered inorganic clays and a traditional filler to determine the effects of particle reinforcement, both micro and nano scale, on the response of these materials to cryogenic cycling. The mechanical properties of the laminates studied were not significantly altered through nanoclay modification of the matrix. The incorporation of nanoclay reinforcement in the proper concentration resulted in cryogenically cycled laminates with microcrack densities lower than those seen in the unmodified or macro-reinforced systems. Lower nanoclay concentrations resulted in a relatively insignificant reduction in microcracking and higher concentrations displayed a traditional filler effect.

## 5.3 EXPERIMENTAL

### 5.3.1 Materials and processing

A mixture of commercial epoxy resins was used as the base resin for the polymeric matrix. The resins used were EPON® 828 from Resolution Performance Products and Araldite MY 9512 from Vantico Inc. The details of the chemical structure of these resins are given in chapters 3 and 4, respectively. HT 976, diaminodiphenyl sulfone (DDS), from Ciba was used as a curing agent.

Cloisite® 25A from Southern Clay Products Inc. and 5 μm alumina particles from Buehler Ltd. were used to modify the base matrix formulation. Cloisite® 25A is a layered montmorillonite clay that was treated with a quaternary alkyl ammonium salt to increase the layer spacing and the hydrophobic character of the interlayer region. This material had a cation exchange capacity of 125 meq/100g and a bulk density of 1.87 g/cm$^3$ [34]. The 25A material was incorporated into the base resin at concentrations of 2, 5, and 8 parts per hundred resin (phr). The alumina particles were used at a concentration of 5 phr. Only one modifier type was present in each resin formulation.

The epoxy resins were combined in a 60:40 ratio by weight of MY 9512: EPON® 828 in an oil bath at 120°C and stirred until they were completely mixed. At this point, the appropriate amount of modifier was added and the material was stirred for two hours. It should be noted that the unmodified resin was also stirred for two hours at 120°C even though no modifier was present. A stoichiometric amount of DDS was melted and added to the epoxy mixture in the oil bath. The epoxy/modifier/DDS mixture was blended for two minutes in the oil bath at 120°C after which the resin was quenched to room temperature and stored at –10°C until it was prepregged.

Plaques of the resin were cured in an autoclave using a 2.8°C/min ramp to 177°C followed by a two hour hold at 177°C and a ramp down to 27°C at a rate of 2.8°C/min. The total pressure used during cure was 310 kPa.

Unidirectional prepregs were developed consisting of the resins discussed above and Toray 50C T300YC carbon fibers. Epoxy sizing was present on all of the fibers, and the filament count was 12,000 per tow. A hot-melt prepreg machine was used to impregnate the fibers with the epoxy resin [35]. The prepreg fiber areal weight was set to 150 $g/m^2$ and the nominal resin content was 30±3 weight percent for all of the experiments. The filming and impregnation temperatures were 68°C and 85°C, respectively. Two rollers were used to apply the impregnation pressure. The pressure on the first roller was 69 kPa and the pressure on the second was 241 kPa. The line speed was 0.91 m/min and the doctor blade gap was 0.25 mm.

The resin content of the prepregs was determined in accordance with ASTM D 3171-99 and Boeing Support Standard 7336 using the technique described in chapter 3 [36, 37].

Symmetric cross-ply and unidirectional laminates were laid up using the above prepregs. The symmetric laminates consisted of 12 plies of prepreg in a $[0^{\circ}_{3}, 90^{\circ}_{3}]_{S}$ configuration, and the unidirectional laminates consisted of 20 plies. After every third ply for the symmetric laminates and every fourth ply for the unidirectional laminates the prepreg stack was precompacted under vacuum pressure for two minutes before additional plies were positioned.

The autoclave cure cycle consisted of a 2.8°C/min ramp to 177°C followed by a 2 hour hold at 177°C and a ramp down to 27°C at a rate of 2.8°C/min. The total consolidation pressure used during cure was 310 kPa. The vacuum bag was vented to the atmosphere when the autoclave pressure reached 104 kPa.

Once cured, the symmetric laminates were cut into 3.49 x 1.27 x 0.16 cm (length x width x thickness) samples for cycling studies and the unidirectional laminates were cut into 2.54 x 1.27 x 0.32 cm and 15.24 x 1.27 x 0.32 cm (length x width x thickness) samples for interlaminar shear strength and transverse flexure testing, respectively. The edges of the symmetric laminates were polished prior to cycling to facilitate optical microscopy of the surfaces.

### 5.3.2 Analysis

Differential scanning calorimetry (DSC) analyses were performed on the above resins to determine if the presence of nanoparticles altered the curing behavior of the polymer. A TA Instruments 2910 differential scanning calorimeter was used to perform these experiments. All samples were tested in a nitrogen atmosphere. Each sample was ramped at 5°C/min to 300°C and the peak temperature, onset temperature, and heat of reaction were recorded.

Samples of the unmodified clay, the Cloisite® 25A clay, and cured resin plaques with 2, 5, and 8 phr of nanoclay were subjected to x-ray diffraction experiments. A Siemens D5000 Diffraktometer with 2-15 $2\Theta$, 30 rpm, and a 0.008° step size was used to perform all of the experiments. All of the curves were background corrected and peak smoothed prior to analysis.

Dynamic mechanical analysis (DMA) experiments were performed on single cured symmetric laminates as described in chapter 3 with an amplitude of 0.05 mm.

Interlaminar shear strength (ILSS) and transverse flexural tests were conducted on the unidirectional laminates. An Instron 4505 screw-testing frame controlled by Instron series IX software was used in these experiments. The interlaminar shear strength tests were performed in accordance with ASTM D2344-84 and the transverse flexure tests were performed in accordance with ASTM D790-98. Five samples of each material were tested and the average value reported [38, 39].

The unidirectional samples from the flexural tests were used to fabricate 1 x 1 cm samples for the determination of the longitudinal and transverse coefficients of thermal expansion (CTE) of the laminates. Each sample was obtained from a portion of the flexural sample that was not damaged during testing. The coefficient of thermal expansion was determined using a TA instruments 2940 thermomechanical analyzer

(TMA) controlled by Thermal Solutions 1.2 J software. A heating rate of 5°C/min from 25°C to 100°C was used with a macro-expansion probe and a force of 0.05 N in a nitrogen environment. The coefficient of thermal expansion was calculated from the slope of the dimension change with temperature between 25°C and 75°C. Three samples of each material were tested and the average value reported. This technique was performed according to ASTM E 831-93 [40].

Three cut and polished symmetric laminates from each material were exposed to the cryogenic microcracking test procedures described in chapter 3 and the average crack density was recorded. Scanning electron microscopy (SEM) was used to examine the laminate surfaces after they exhibited no further microcracking. All SEM samples were gold sputtered and examined using a working distance of 48 mm with a 15 kV potential.

## 5.4 RESULTS AND DISCUSSION

### 5.4.1 Nanocomposite formation

The processing characteristics of the epoxy resins used in this study were not changed by the incorporation of small concentrations of clays or alumina particles. A slight viscosity increase was observed when the clays were blended with the epoxies, but the increase was not sufficient to alter the material processing parameters. DSC analysis showed no change in the heat of reaction, onset temperature, peak temperature, or peak shape when the particle modifiers were blended with epoxy/amine systems.

X-ray diffraction experiments were performed to determine the structural characteristics of the clays used as reinforcements and their distribution in epoxy matrices. It has been shown that this technique can be used to observe how layered nanoparticles are distributed in a polymer and characterize their degree of dispersion [4, 7, 26]. Table 5-1 summarizes the x-ray diffraction data obtained in this study. The modification of the neat clay with a quaternary ammonium salt resulted in an increase in d-spacing as the clay layers were separated. This functionalization of the interlayer region facilitated nanocomposite formation by increasing the gallery spacing and creating a more hydrophobic environment for the epoxy resin and curing agent. It can also be seen that as the concentration of the clay increased, more ordered structures were obtained. No peaks were seen at 2 phr of 25A, indicating an exfoliated or partially exfoliated structure, but as the concentration was increased to 5 and 8 phr smaller peaks appeared and the presence of long range order was observed. These trends can be observed more clearly in Figure 5-3. At 5 phr a small peak was observed. At 8 phr a similar peak was seen, but an additional shoulder at low 2Θ was also observed. Using the nomenclature of Vaia, these nanocomposites were characterized as disordered intercalated and ordered intercalated, respectively [26]. Intercalated indicates that polymer was located between the clay platelets but some long-range stacking order still remained. The ordered and disordered characterizations refer to the level of order present in the intercalated structures. These results showed that the morphology of the nanocomposites depended on the concentration of the nanoclay.

### 5.4.2 Composite properties

DMA analysis of the symmetric laminates prepared in this study showed no change in the laminate glass transition temperature (Tg), as determined by the peak in loss modulus, when any of the particle modifiers were present. Therefore, any changes in mechanical properties were due to the physical presence of the modifiers as opposed to changes in the polymeric network structure. Figures 5-4A and B show the results of dynamic mechanical analysis experiments performed on the symmetric laminates used in this study. Figure 5-4A illustrates that the dynamic storage modulus showed a dependence on the type and concentration of the modifier particles below the Tg, while no variation between the samples was seen above the Tg. The largest dynamic storage modulus increase was observed for the alumina modified system. A small dynamic storage modulus increase was seen at 5 phr 25A and no significant change when compared with the control for the 2 phr 25A system was observed. The 8 phr 25A laminate showed a slightly decreased dynamic storage modulus. The high modulus of the alumina particles increased the dynamic storage modulus of the laminates that contained these particles. The well dispersed nanoparticles in the laminate containing 5 phr 25A probably increased the modulus of the matrix. The dynamic storage modulus of the 5 phr 25A modified laminate also remained higher in the vicinity of the Tg than the control and the other clay-modified systems. This was also most likely due to a stiffening of the matrix caused by the well-dispersed nanoparticles. At 2 phr of 25A the nanoparticle concentration was too small to cause a noticeable change in the laminate properties. Figure 5-4B shows the variation in tan(δ) as different modifiers were used. The width of the tan(δ) peaks at Tg were the same for all the laminates studied, implying that no change in network structure occurred when particle modifiers were incorporated into the matrices of these materials.

Figure 5-5 presents the variation in interlaminar shear strength (ILSS) of the laminates as the concentration and type of particle modification of the matrix were varied. The error bars in this figure represent one standard deviation. A small increase in the ILSS was observed at 2 and 5 phr 25A. This was most likely due to reinforcement of the matrix by the nanoparticles. The largest increase in ILSS was seen when the laminates contained alumina particles. This increase may have resulted from the alumina particles reinforcing the interlayer region. When 8 phr 25A was used the ILSS decreased slightly. It is possible that the more ordered clay particles in this sample acted as flaws or crack initiators instead of reinforcements.

Figure 5-6 shows how the transverse flexural strength of the laminates changed as the concentration and type of particle were varied. One standard deviation is represented by the error bars. When 2 and 5 phr 25A were present in the laminates the flexural strength decreased slightly; however, at 8 phr 25A the strength was the same as the unmodified laminate. When alumina particles were present the strength increased when compared with the control. It has been shown that nanoclay particles will orient themselves preferentially so that the platelets are parallel to the longitudinal axis of the fibers [41]. This effect may have been more pronounced at 2 and 5 phr and could have resulted in orientation effects that caused increases in ILSS and decreases in transverse strength because of the different sample geometries and loading modes in these tests. In the ILSS test the load was applied with the loading nose perpendicular to the fibers, while the loading nose was parallel to the fibers in the transverse flexural testing. The more ordered structures in the laminates containing 8 phr of 25A and the larger, anisotropic particles in the alumina-containing laminates may have made fiber/particle orientation effects less significant. This may have allowed the inclusions to act differently from the more dispersed clay particles and changed their impact on the flexural strength.

Figure 5-7 shows how the transverse flexural modulus changed with the modifier concentration and type. The error bars indicate one standard deviation. The transverse modulus showed no statistical change when the nanoparticle modifiers were incorporated into the matrix at concentrations of 5 and 8 phr. Very slight decreases were observed when alumina and 2 phr 25A were used as modifiers; however, these changes were very small when compared with the variations in the other mechanical tests performed. The modulus was relatively unaffected because of the small concentrations of the modifier particles used. The particles made up a very small fraction of the matrix, and as such, did little to change its stiffness.

Figure 5-8 shows how the transverse CTE of a unidirectional laminate changed as different particle modifiers were used. The error bars in this figure represent one standard deviation. A small initial increase was seen at a nanoclay concentration of 2 phr 25A. After this increase the CTE decreased steadily with increasing nanoclay concentration. No change in CTE when compared with the control was observed when 5 phr alumina was used as a modifier. The increase in CTE at low nanoclay concentrations was unexpected and was most likely due to slight variations in resin content; however, it is possible that orientation of the nanoparticles or nonuniform particle morphologies may have affected the CTE values. Increasing the nanoclay concentration reduced the CTE and demonstrated the possibility that nanoclays could be used to increase the dimensional stability of composite materials. Figure 5-9 demonstrates the difference between the transverse and longitudinal CTEs of the unidirectional laminates tested, with the error bars indicating one standard deviation. The CTE difference values were essentially identical to the transverse CTE values, indicating that the longitudinal CTE was not affected by the presence of a modifier. This suggests that the nanoparticles were preferentially oriented and could be used to customize the thermal expansion properties of composite materials. At concentrations of 2 and 5 phr 25A the nanoparticles were more dispersed and it is possible that this increased the significance of any nanoparticle orientation effects. At a concentration of 8 phr 25A the nanoparticles were more ordered and less dispersed, possibly reducing the impact of any nanoparticle orientation.

### 5.4.3 Laminate microcracking

Microcracking occurred in all of the laminates studied, and representative optical photomicrographs of the microcracks are shown in Figure 5-10. Scanning electron photomicrographs of the crack surfaces are shown in Figure 5-11. The microcracks propagated towards the interior of the samples normal to the fibers when the fibers were viewed along their length and terminated when the interface between the 0° and 90° ply groups was reached. Figures 5-10B, C, and D along with Figures 5-11A and C show instances in which crack bifurcation was observed and delamination occurred at the 0°/90° interface. Most of the microcracks propagated along the fiber/matrix interface, as shown in Figure 5-11B, but in some cases fiber splitting, which indicates good fiber/matrix adhesion, was observed as shown in Figure 5-10B and indicated with arrows in Figure 5-11A. No significant variation in individual crack morphology was observed as the particle modifier type and concentration were varied.

Significant variations in the crack density were observed as the concentration and type of particle modification were changed. Figure 5-12 demonstrates these variations, with error bars indicating one standard deviation. At 2 phr of 25A the average crack density decreased slightly, but the change was not statistically significant. At 5 phr of 25A the crack density was reduced by 50 percent when compared with the unmodified laminate. When the concentration of 25A was increased to 8 phr the mean crack density increased slightly over the unmodified case, but the change was not statistically significant. Finally, when the micro alumina particles were incorporated into the laminate no change in the microcrack density was observed when compared with the unmodified system. At low nanoclay concentrations the nanoparticles were probably too dispersed to effectively reinforce the matrix and reduce the CTE of the matrix. 5 phr of 25A was a large enough concentration of nanoclay and was dispersed well enough, as shown in the x-ray diffraction data, that the nanoparticles were probably able to reinforce the matrix and lower the thermal stresses present in the laminate by reducing the matrix

CTE. When 8 phr of 25A was used the nanoparticles were not as well distributed as shown by the ordered intercalated structure of the nanocomposite matrix. This may have prevented the nanoparticles from providing effective reinforcement in spite of the fact that they reduced the thermal stresses in the laminates. They may have begun to act like larger structures by serving as flaws and crack initiation sites. The micro alumina particles most likely did not alter the microcrack density because any increase in matrix strength was offset by their ability to concentrate stresses and act as crack initiators.

## 5.5 CONCLUSIONS

Layered clays were used as nanoparticle fillers in fiber-reinforced polymeric materials. Transverse cracking in symmetric carbon fiber/epoxy laminates as a response to cryogenic cycling was significantly reduced when nanoparticle fillers were used at concentrations much lower than those used for traditional fillers. The concentration of the particles and their distribution in the matrix was observed to be very important in maximizing the benefits of nanoparticle reinforcement. Large concentrations exhibited a typical, macro-scale filler effect and low concentrations showed little or no effect. Exfoliated and disordered intercalated structures provided the best reinforcement, with more ordered intercalated structures offering little benefit. The mechanical properties and processing characteristics of the laminates studied were not adversely influenced by the presence of the nanoparticles and the thermal expansion characteristics were improved. Overall, the work in this chapter showed that nanoclays can be easily used to modify traditional fiber-reinforced composite materials and enhance their resistance to thermal cycling induced stresses.

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Table 5-1. X-ray diffraction data for nanoclays and nanocomposites

| Sample | 2Θ | d-spacing (Ang.) | Morphology |
|---|---|---|---|
| Unmodified clay | 8.74 | 10.1 | Clay tactoids |
| Alkylammonium modified clay (25A) | 4.65 | 19 | Swollen tactoids |
| 2 phr in resin | No Peak | No Peak | Exfoliated |
| 5 phr in resin | 2.51 | 35.16 | Disordered intercalated |
| 8 phr in resin | 2.738<br>5.597 | 32.23<br>15.77 | Ordered intercalated |

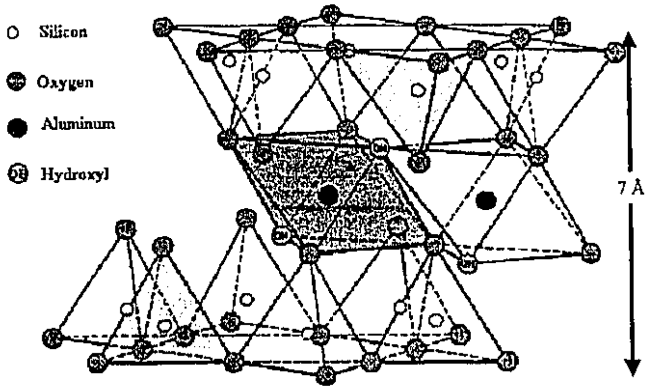

Figure 5-1. Structure of montmorillonite

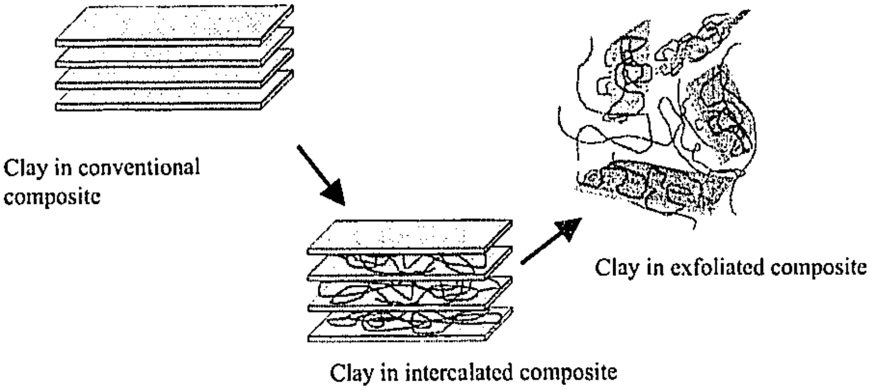

Figure 5-2. Exfoliation of layered clays

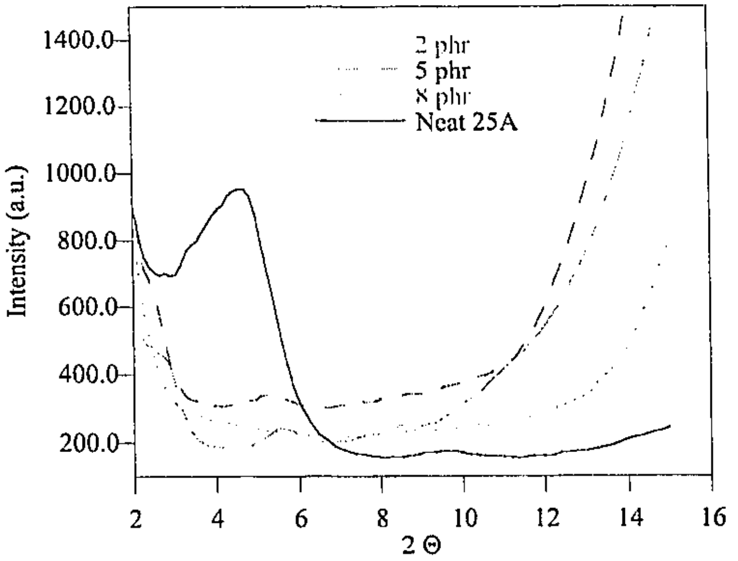

Figure 5-3. X-ray diffraction curves for nanocomposites

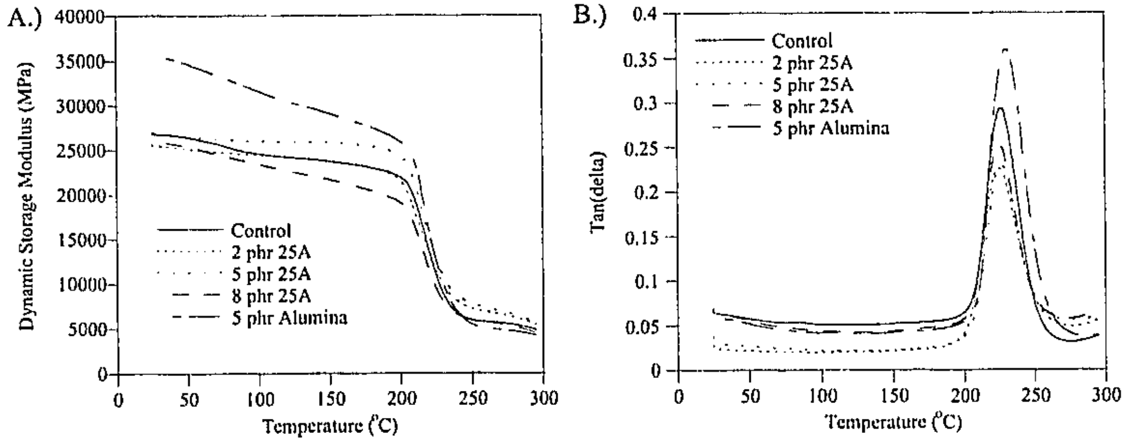

Figure 5-4. Dynamic mechanical property variation with temperature and particle modification. A: Dynamic storage modulus. B: tan(δ)

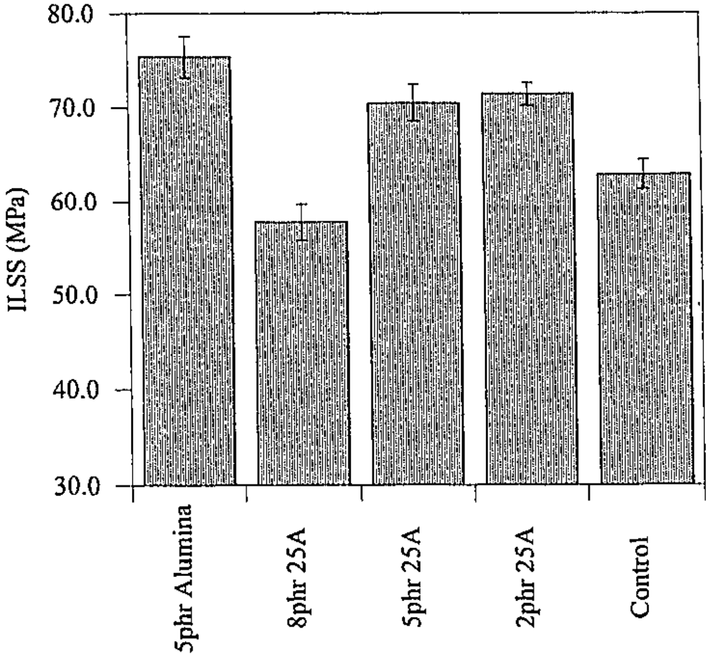

Figure 5-5. Interlaminar shear strength variation with particle modification

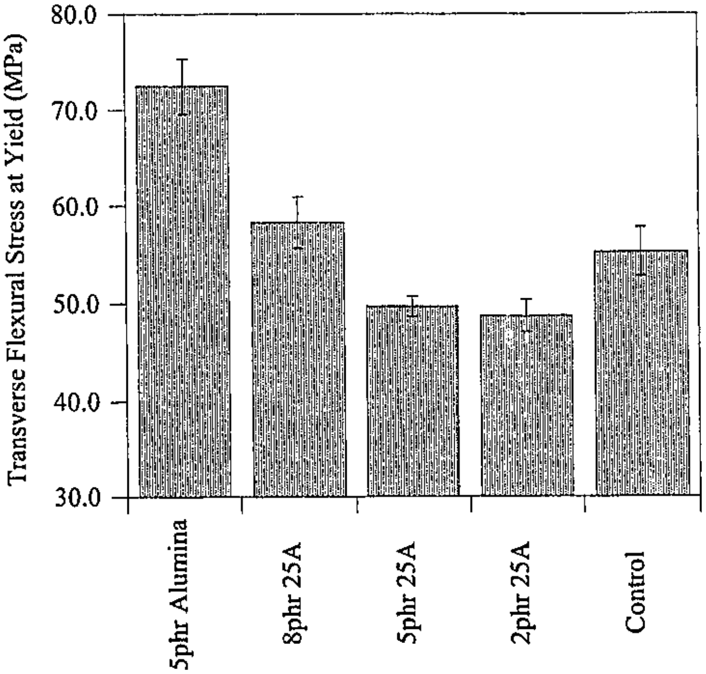

Figure 5-6. Transverse flexural strength variation with particle modification

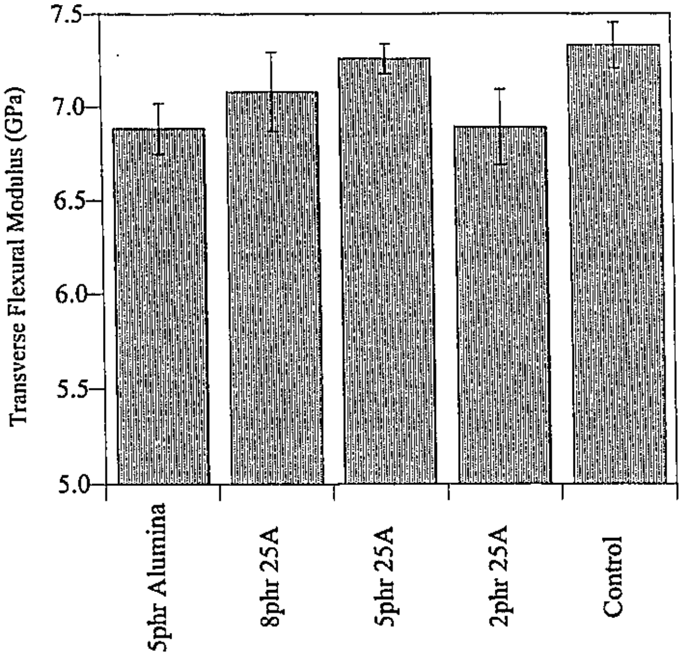

Figure 5-7. Transverse flexural modulus variation with particle modification

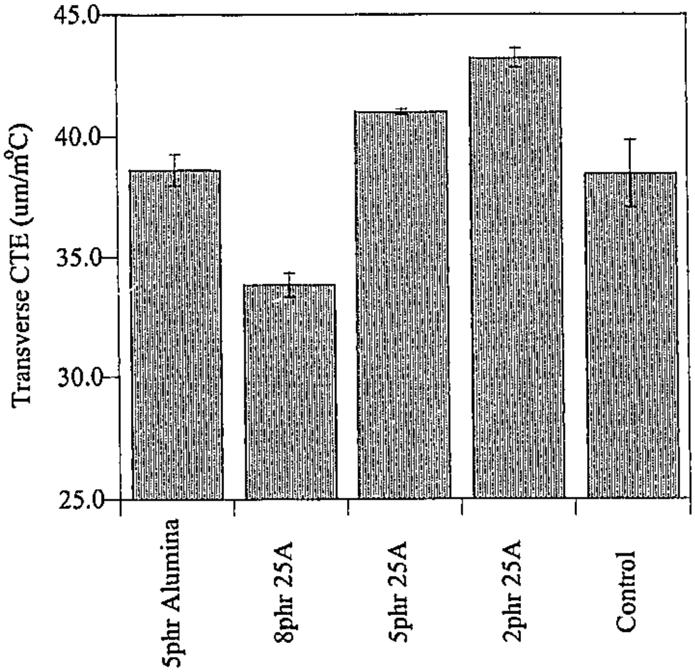

Figure 5-8. Transverse CTE variation with particle modification

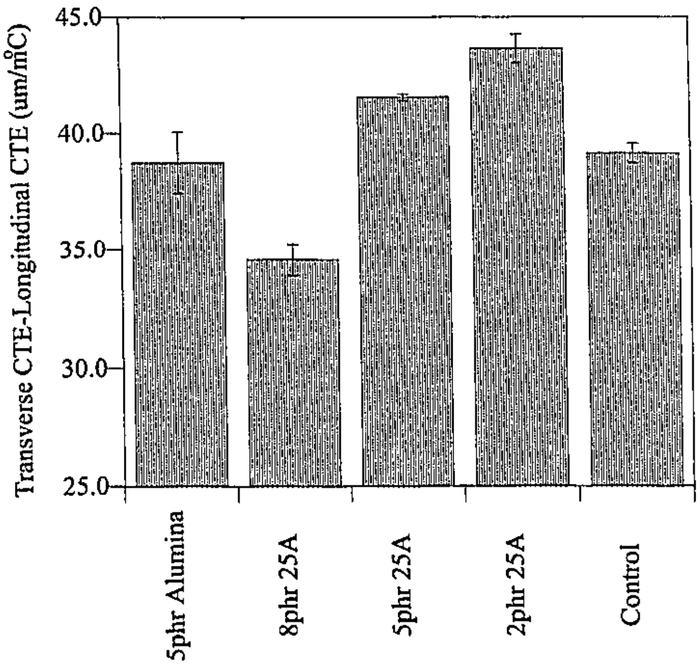

Figure 5-9. Transverse/longitudinal CTE difference variation with particle modification

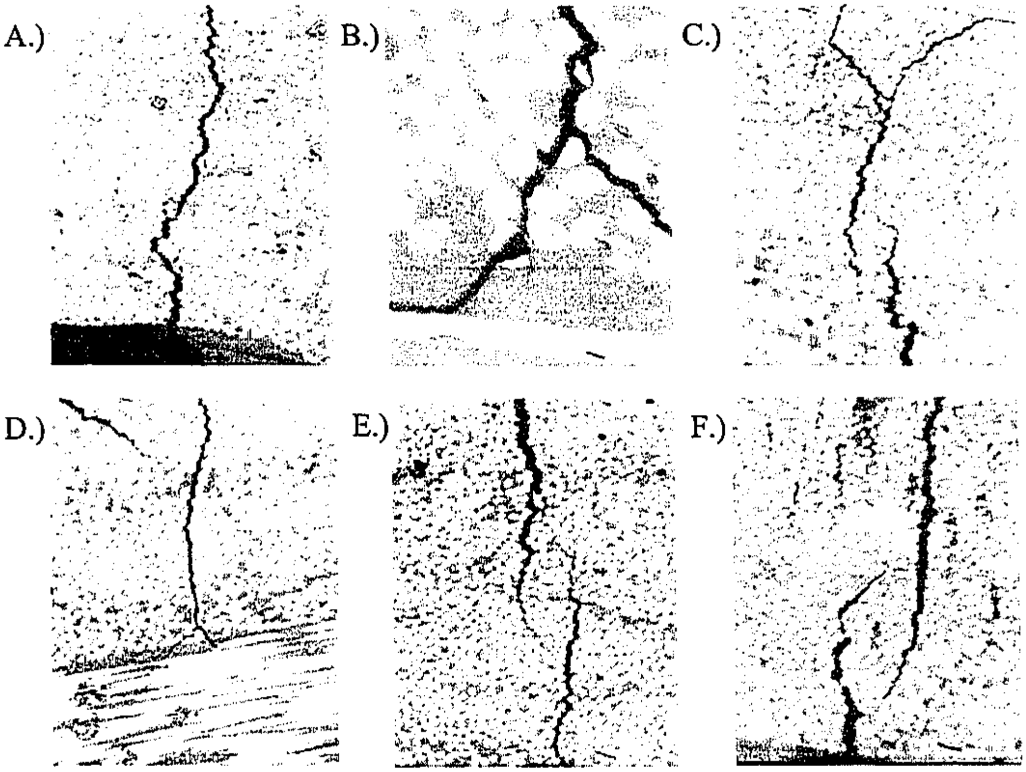

Figure 5-10. Optical photomicrographs of microcracks formed in response to cryogenic cycling. A: Unmodified, 200x, 2cycles. B: Unmodified, 1000x, 1 cycle. C: 2 phr 25A, 200x, 5 cycles. D: 5 phr 25A, 200x, 2 cycles. E: 8 phr 25A, 200x, 2 cycles. F: 5 phr 5μm alumina, 200x, 2 cycles

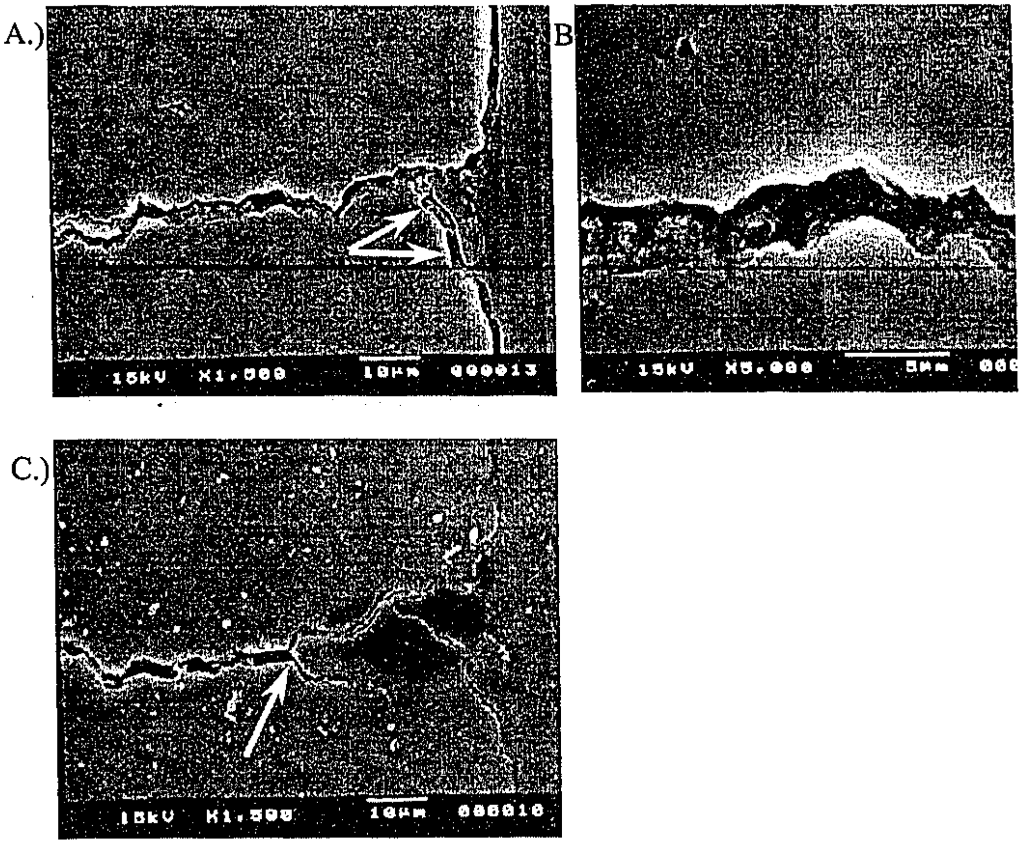

Figure 5-11. Scanning electron micrographs of microcracks formed as a response to cryogenic cycling. A: 8 phr 25A, 1500x. B: 8 phr 25A, 5000x. C: Unmodified, 1500x

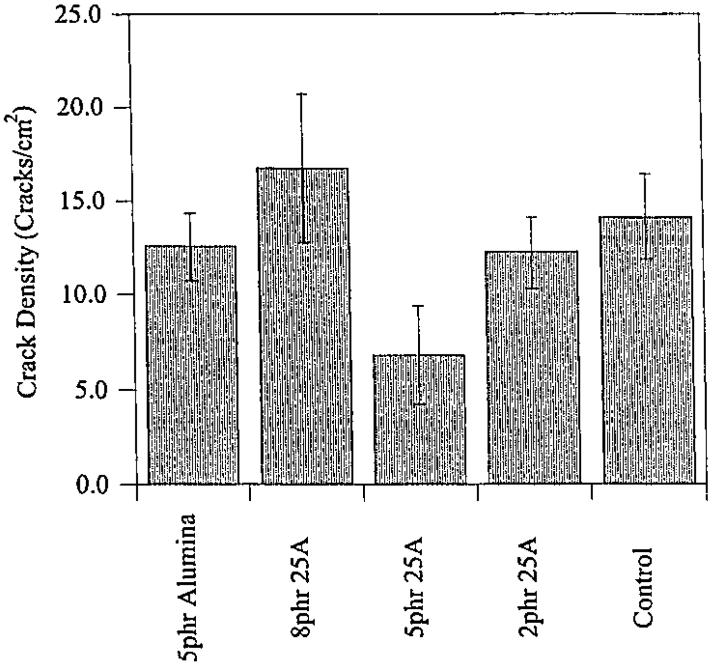

Figure 5-12. Crack density variation with particle modification

# CHAPTER 6: CURE TEMPERATURE EFFECTS ON MICROCRACKING AND INTERNAL STRESS DEVELOPMENT

## 6.1 INTRODUCTION

Increased thermal stresses are the underlying cause of microcracking in composites at cryogenic temperatures. Residual stresses develop in composite materials during and after cure as the temperature of the material falls below its stress free temperature. Residual stresses are the result of cure shrinkage of the matrix, Poisson's effects, differences in the coefficient of thermal expansion between the fibers and the matrix, and anisotropy in the expansion of the individual plies [1-5]. The amount of thermal stress in a laminate increases as the temperature deviates from the stress free temperature. When the residual stresses in the material become large enough they are relieved through physical processes such as potholing, delamination, and/or microcracking [3-5]. Chung et al. showed that the degradation of composite materials exposed to cryogenic temperatures is increased by thermal cycling between cryogenic and room temperature conditions [6]. Work in the past has shown that the residual stresses in a laminate depend directly on the processing conditions during laminate fabrication. Higher curing temperatures have been shown to cause an increase in the residual stress in a laminate by increasing the stress free temperature [1, 7-9]. However, these studies have not been performed for composite materials used in cryogenic applications.

Understanding the mechanisms behind the generation of residual stresses is key to preventing microcracking and the degradation of composite materials when exposed to cryogenic cycling. The previous chapters focused on a phenomenological approach that evaluated the effects of variations in the components of a composite material on cryogenic microcracking. In this chapter, the effects of processing were evaluated on an experimental and a theoretical level, and a simple model was developed to gain a better understanding of the internal stresses in composite materials at cryogenic temperatures.

A model prepreg system was used to evaluate the effect of cure temperature on microcracking in polymeric composite materials exposed to cryogenic cycling. Symmetric and unsymmetric carbon fiber/epoxy laminates were fabricated to examine the development of thermal stresses and microcracks at cryogenic temperatures. The residual strains and theoretical curvatures of the laminates were calculated from the composite properties and correlated with the microcrack density and experimentally observed curvatures. Higher cure temperatures resulted in higher stress free temperatures and residual strains in the laminates, which corresponded directly to increased levels of microcracking.

## 6.2 EXPERIMENTAL

### 6.2.1 Materials and processing

A mixture of commercial epoxy resins was used as the model resin for the polymeric matrix. The resins used were EPON® 828 and EPON® 1031 from Resolution Performance Products and D.E.N. 438 from the Dow Chemical Company. EPON® 828 is described in chapter 3. EPON® 1031 is a tetrafunctional epoxy resin with an aromatic backbone (tetraphenyloethane glycidyl ether). D.E.N. 438 is a multifunctional epoxy novolac resin. Ancamine 2049, 4,4'-methylenebis(2-methyl-cyclohexanamine), a liquid tetrafunctional cycloaliphatic amine from Air Products, was used as a curing agent.

The epoxy resins were combined in a 50:40:10 ratio by weight of D.E.N. 438: EPON® 1031: EPON® 828 in an oil bath at 120°C and stirred until they were completely mixed. The mixture was allowed to cool to 40°C at which point a stoichiometric amount of Ancamine 2049 was added. The resin was then mixed until uniform and immediately prepregged.

Unidirectional prepregs consisting of the resin discussed above and Toray 50C T300YC carbon fibers were developed. Epoxy sizing was present on all of the fibers, and the filament count was 12,000 per tow. A hot-melt prepreg machine was used to impregnate the fibers with the epoxy resin [10]. The prepreg fiber areal weight was set to 150 g/m$^2$ and the nominal resin content was 30±2 weight percent for all of the experiments. The filming and impregnation temperatures were 55°C and 65°C, respectively. Two rollers were used to apply the impregnation pressure. The pressure on the first roller was 69 kPa and the pressure on the second was 276 kPa. The line speed was 1.53 m/min. The resin content of the prepregs was determined in accordance with ASTM D 3171-99 and Boeing Support Standard 7336 using the technique described in chapter 3.

Symmetric, unsymmetric, and unidirectional 15.24 x 15.24 cm laminates were laid up using the above prepregs. The symmetric laminates consisted of 12 plies of prepreg in a $[0^{\circ}_3, 90^{\circ}_3]_S$ configuration, the unsymmetric laminates consisted of 4 plies in a $[0^{\circ}_2, 90^{\circ}_2]$ configuration, and the unidirectional laminates contained 20 plies of prepreg. After every third ply for the symmetric and unidirectional laminates and every ply for the unsymmetric laminates the prepreg stack was precompacted under vacuum pressure for two minutes before additional plies were positioned.

The autoclave cure cycle consisted of a 2.8°C/min ramp to the cure temperature followed by a hold at the cure temperature and a ramp down to 27°C at a rate of 2.8°C/min. The total consolidation pressure used during cure was 310 kPa. The vacuum bag was vented to the atmosphere when the autoclave pressure reached 104 kPa. Several curing temperatures were investigated, and the different curing temperatures necessitated different curing times to achieve a high degree of cure. Table 6-1 shows the curing times and temperatures used in this study.

Once cured, the symmetric laminates were cut into 3.49 x 1.27 x 0.16 cm (length x width x thickness) samples for cycling studies. The edges of the symmetric laminates were polished prior to cycling to facilitate optical microscopy of the surfaces. Geometric considerations were used to measure the curvature of the unsymmetric laminates, and the unsymmetric laminates were then cut into 1 x 20 cm (width x length) samples for three point bend testing. The unidirectional laminates were cut into 11 x 1.2 x 0.3 cm (length x width x thickness) samples for flexural tests.

### 6.2.2 Analysis

Differential scanning calorimetry (DSC) was performed on the matrix resin to determine the amount of residual cure present when different curing times and temperatures were used. The same instrument described in chapter 5 was used for this investigation. All samples were tested in a nitrogen atmosphere. Each sample was ramped at 2.8°C/min to a cure temperature (70, 80, 100, 120, 140, 160, or 180°C), held for a specified time, and cooled to room temperature at 2.8°C/min before being subjected to a 5°C/min ramp to 350°C. The percentage cure was found by comparing the heat evolved during the cure cycle to the exotherm when an untested sample was ramped at 5°C/min to 350°C.

The resin content of the prepregs was determined in accordance with ASTM D 3171-99 and Boeing Support Standard 7336 [11, 12] using the technique described in chapter 3.

Dynamic mechanical analysis (DMA) experiments were performed on the cured symmetric laminates using the same instrument and experimental techniques outlined in chapter 3. The cured unsymmetric laminates were tested with the DMA described in chapter 3 using a three point bending apparatus in a controlled force mode. The samples were exposed to a 2°C/min ramp to 250°C with an applied force of 0.005 N. The stress free temperature of each sample was reported as the temperature at which each laminate displayed zero curvature.

The flexural modulus and strength of the unidirectional laminates in the transverse and longitudinal directions were determined through three point bend testing. The samples were tested using an Instron 4505 test frame and all samples were tested in accordance with ASTM D 790-98 [13]. Five samples from each material were tested and the average value reported

The unidirectional samples from the flexural tests were used to fabricate 1 x 1 cm samples for the determination of the longitudinal and transverse coefficients of thermal expansion of these materials. Each sample was obtained from a portion of the flexural sample that was not damaged during testing. The coefficient of thermal expansion was determined using a TA instruments 2940 thermomechanical analyzer (TMA) with subambient temperature capability controlled by Thermal Solutions 1.2 J software. A heating rate of 5°C/min from 0°C to 100°C was used with a macro-expansion probe and a force of 0.1 N in a nitrogen environment. The coefficient of thermal expansion was calculated from the slope of the dimension change with temperature between 10°C and 60°C. This technique was performed according to ASTM E 831-93 [14]. Three samples from each material were tested and the average value reported.

Three cut and polished symmetric laminates from each material were exposed to the cryogenic microcracking test procedures described in chapter 3 and the average crack density was recorded.

### 6.2.3 Modeling approach

Bailey et al. used the model developed by Brand and Backer to show that the longitudinal strain, $\varepsilon_{tl}^{th}$, that develops in the transverse plies of a 0°/90°/0° composite upon cooling to a temperature $T_2$ below the stress-free temperature $T_1$ is given in the following equation [8, 15].

$$\varepsilon_{tl}^{th} = \frac{E_l b(\alpha_t - \alpha_l)(T_1 - T_2)}{E_l b + E_t d} \tag{6-1}$$

$E_l$ and $E_t$ are the Young's moduli of the unidirectional plies parallel to the fibers and perpendicular to the fibers, respectively. Similarly, $\alpha_l$ and $\alpha_t$ are the longitudinal and transverse linear coefficients of thermal expansion of the unidirectional plies. *b* and *2d* are the 0° and 90° ply group thicknesses. An extension of the above analysis showed that the radius of curvature, ρ, of a $[0^{\circ}_{b}\ 90^{\circ}_{d}]$ laminate can be calculated using the following equation [8, 9, 15].

$$(\alpha_t - \alpha_l)(T_1 - T_2) = \frac{b+d}{2\rho} + \frac{E_l b^3 + E_t d^3}{6\rho(b+d)}\left(\frac{1}{E_l b} + \frac{1}{E_t d}\right) \tag{6-2}$$

This model is based on compound beam theory and assumes that the materials obey Hooke's law of elasticity, the number of 0° and 90° plies in the unsymmetric laminate are the same, the laminate cross-section is rectangular, and the radius of curvature of the unsymmetric laminate is much greater than the thickness of the laminate [15].

The above equations were used to calculate the longitudinal thermal strains in the transverse plies of $[0^{\circ}_{3}\ 90^{\circ}_{3}]_S$ laminates and the curvature of $[0^{\circ}_{2}\ 90^{\circ}_{2}]$ laminates cured at different temperatures. When the number of 90° plies equals the number of 0° plies in this geometry, as is the case in this study, it can be shown that the strains are of the same magnitude in the 0° and 90° plies [8, 15].

## 6.3 RESULTS AND DISCUSSION

### 6.3.1 Internal stress observation and prediction

In this study carbon fiber/epoxy laminates were cured at 70, 80, 100, 120, 140, 160, and 180°C. Curing times were adjusted so that all of the laminates showed approximately 5% residual cure as determined by differential scanning calorimetry. The anisotropy in expansion between the 0° and 90° plies in an unsymmetric laminate resulted in stresses that manifested themselves as curvature in the laminate [2]. Higher curing temperatures caused increased residual stresses in the laminates that were observed as larger curvatures of the unsymmetric laminates. Figure 6-1 shows the variation in curvature with cure temperature. Theoretical curvature values were determined from the mechanical properties of the laminates using Equation 6-2. These predicted curvatures are compared with the experimentally determined values in Figure 6-2. The error bars on the predicted curvatures represent one standard deviation. In nearly all of the cases, the predicted curvature was larger than the experimental curvature. This was probably due to the fact that the model approximated the laminates as being perfectly elastic, when they actually acted viscoelastically.

Controlled force dynamic mechanical analysis was used to determine the temperature at which the curvature of the unsymmetric laminates became zero. This method of determining the stress free temperature of a laminate has been shown to be an effective technique, taking into account both thermal and cure shrinkage effects [1, 16]. Figure 6-3 shows how the stress free temperatures of the laminates varied with cure temperature.

At lower cure temperatures the stress free temperature was significantly higher than the cure temperature, but as the cure temperature was increased the stress free temperature began to approach a constant value. This may have been the result of an increase in the temperature of the laminate above the autoclave temperature because of an exotherm. It is also possible that at higher cure temperatures the ultimate glass transition temperature of the resin system was approached. At this point free volume changes would become smaller and a reduced dependence of the laminate properties on cure temperature would be seen.

Equation 6-1 was used to calculate the residual thermal strains in the symmetric laminates at cryogenic temperatures. Figure 6-4 shows how the predicted residual strains changed with cure temperature. The error bars represent one standard deviation. The residual strains increased with cure temperature and leveled off at the high and low end of the temperature range studied. This paralleled the increase in stress free temperature shown in Figure 6-3.

### 6.3.2 Composite properties

Crasto et al. showed that the ratio of the difference between the stress free temperature (SFT) and the cure temperature (Tcure) to the difference between the stress free temperature and the use temperature ($TLN_2$) is a measure of the percent of the total stresses that may be attributed to cure shrinkage [1]. The use temperature was considered to be that of liquid nitrogen (-195.6°C) in this study as it was primarily concerned with thermal stresses at cryogenic temperatures. Figure 6-5 shows the percentage of shrinkage stress in the laminates at cryogenic temperatures.

Some small variations in the percent of stress resulting from cure shrinkage were present at low cure temperatures and were most likely due to the longer curing times and slightly lower degree of cure when the laminates were cured at 70 and 80°C. When cure temperatures above 100°C were used the percent shrinkage stress decreased regularly with increasing cure temperatures.

The cure temperature affected the glass transition temperature ($T_g$) of the laminates as obtained by the peak in the loss modulus from dynamic mechanical analysis. Figure 6-6 demonstrates the effect of cure temperature on the laminate glass transition temperature. The $T_g$s of the laminates increased with cure temperature. When higher cure temperatures were used the polymeric network was formed at a higher temperature, and as such, the glass transition temperatures were higher.

### 6.3.3 Laminate microcracking

All of the laminates in this study formed microcracks as a response to cryogenic cycling. The density, distribution, and morphology of the microcracks varied with the cure temperature. Figure 6-7 is an optical photomicrograph of a representative microcrack in one of the laminates after thermal cycling at cryogenic temperatures.

Microcracks began at the outer edge of the sample and propagated towards the interior, transverse to the fibers as shown in Figure 6-7. Higher cure temperatures caused the formation of microcracks that were more tortuous and wider than those in the laminates cured at lower temperatures. The laminates with cure temperatures above 140°C exhibited some delamination at the 0°/90° ply interface, which can be seen in Figure 6-7. This phenomenon became more widespread as the cure temperature increased. Laminates with higher cure temperatures were also more prone to the formation of networks of cracks rather than individual cracks as shown in Figure 6-8. Larger thermal stresses were generated in the laminates when cured at higher temperatures. Fracture processes relieved these stresses in the laminates and manifested themselves as more delamination, wider microcracks, and greater crack network formation during thermal cycling relative to laminates cured at lower temperatures.

The microcrack density in the ambient/cryogenic thermally cycled laminates, shown in Figure 6-9, exhibited a dependence on the cure temperature. The error bars represent one standard deviation. It should be noted that no statistical difference in the flexural modulus, flexural stress at yield, or coefficient of thermal expansion was observed in the unidirectional laminates cured at different temperatures. This suggested that any dependence of microcrack density on cure temperature was due to different levels of stress and not a variation in the mechanical properties of the laminates. Higher curing temperatures caused an increase in the microcrack density by elevating the level of thermal stress present in the laminates. There was no statistical difference in the microcrack density between the laminates cured at 140, 160, and 180°C. However, within this series of cure temperatures the microcrack tortuosity, width, and presence of crack networks increased. These phenomena could have increased the amount of stress relieved without increasing the microcrack density. The microcrack density was also shown to be affected by the stress free temperature of the laminate. When the stress free temperature became larger the level of thermal stress in the laminate increased and the release of more energy was necessary to relieve the stresses [2]. Figure 6-10 presents the relationship between the microcrack density and the stress free temperature of the laminates, with the error bars representing one standard deviation. Predicted values of residual strain in the laminates parallel the stress free temperature and correlate with the microcrack density. Figure 6-11 shows how the microcrack density varied with the calculated thermal strains in the laminates, with the error bars representing one standard deviation. The microcrack density increased with higher stress free temperatures and the resulting larger thermal strains but reached a constant value as differences in microcrack distribution and morphology began to outweigh the formation of more microcracks.

## 6.4 CONCLUSIONS

The research presented in this chapter examined the effects of cure temperature on the response of carbon fiber/epoxy composite materials to cryogenic cycling. Theoretical predictions of the development of thermal strains in composite materials were shown to correlate with experimental observations. Microcracking occurred in all of the laminates tested, but significant variations in the number and morphology of the microcracks existed between the laminates cured at different temperatures. Higher curing temperatures resulted in higher stress free temperatures, residual thermal strains, and glass transition temperatures of the laminates. The larger stress free temperatures corresponded to increased microcrack densities and larger levels of residual thermal strain. Laminates cured at high temperatures also showed a greater propensity to delaminate, contain wider and more tortuous cracks, and form networks of cracks. Collectively, this work showed that the development of thermal stresses in composite materials at cryogenic temperatures could be modeled and was enhanced by higher cure temperatures.

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Table 6-1. Laminate cure times and temperatures

| Cure Temperature (°C) | Cure Time (hr) |
|---|---|
| 70 | 18 |
| 80 | 5 |
| 100 | 3 |
| 120 | 2 |
| 140 | 2 |
| 160 | 2 |
| 180 | 2 |

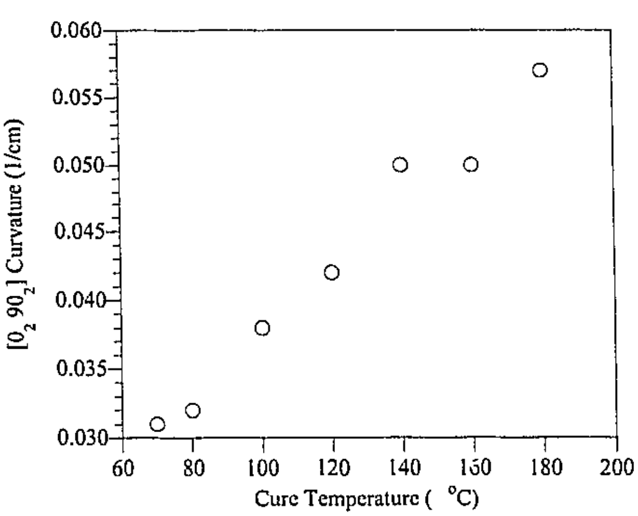

Figure 6-1. Variation in laminate curvature with cure temperature

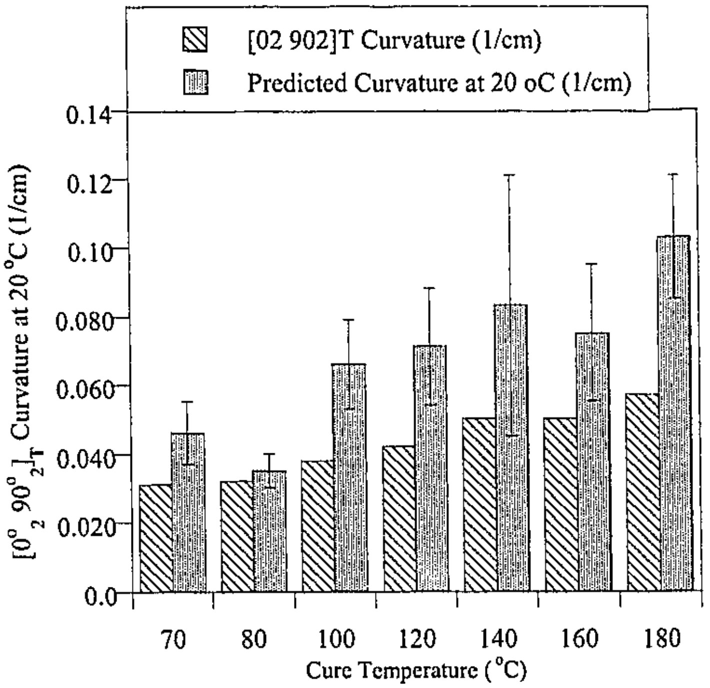

Figure 6-2. Predicted and experimental laminate curvatures at 20°C

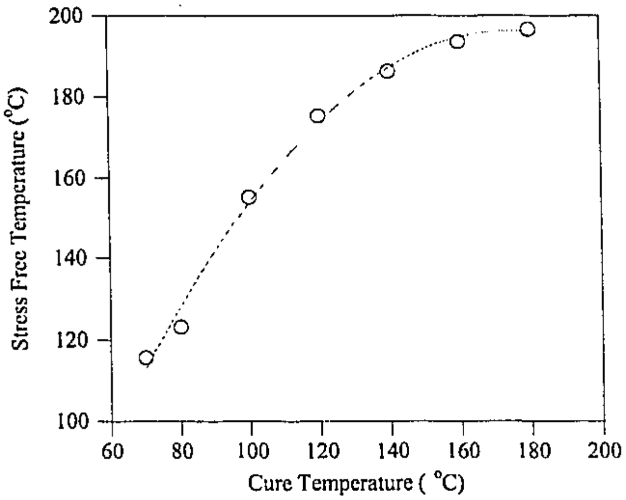

Figure 6-3. Variation in stress free temperature with cure temperature

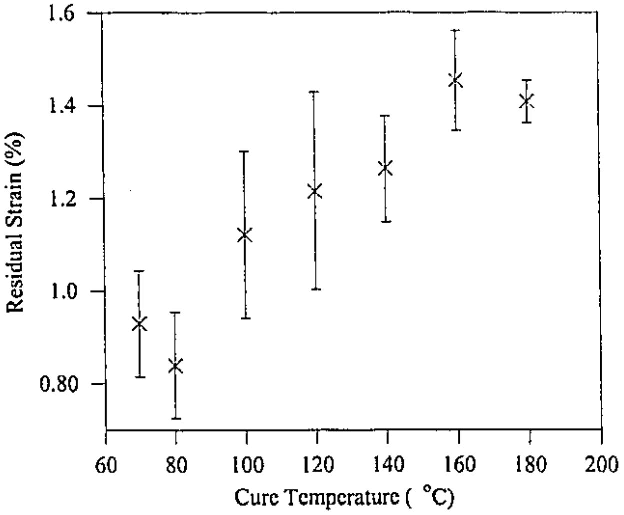

Figure 6-4. Variation in predicted residual thermal strains transverse to the plies in a $[0^\circ_b\ 90^\circ_{2d}\ 0^\circ_b]$ laminate with cure temperature at −195.6°C

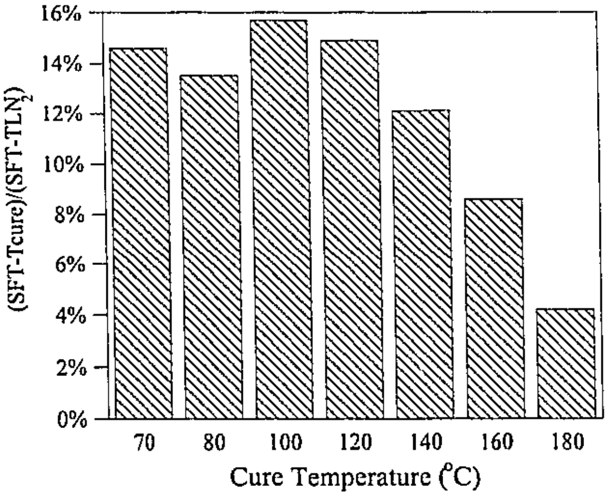

Figure 6-5. Variation in percent shrinkage stress with cure temperature

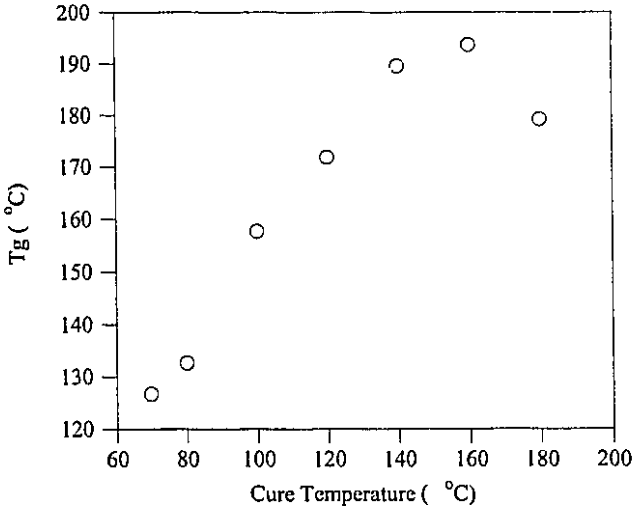

Figure 6-6. Variation in laminate glass transition temperature (from dynamic loss modulus) with cure temperature

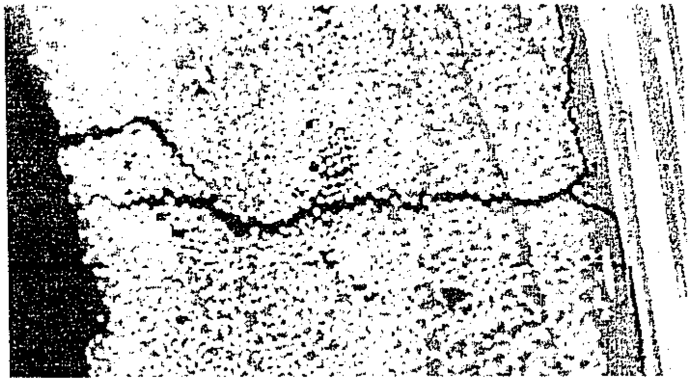

Figure 6-7. Optical photomicrograph of microcrack in a cured laminate (160°C) after 2 cycles in liquid nitrogen. 200x magnification

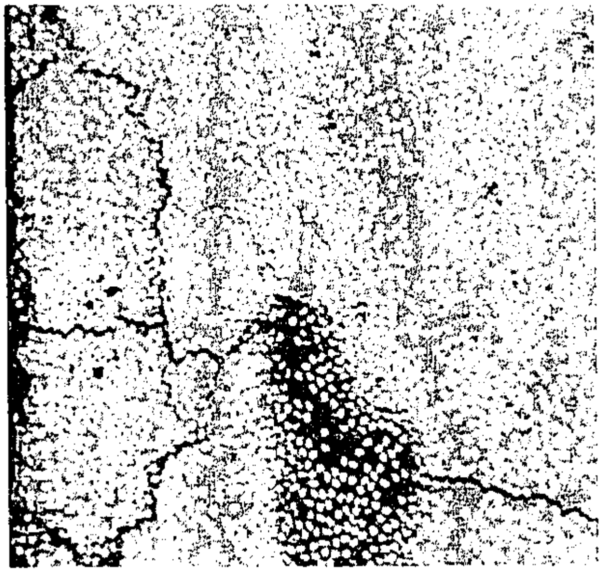

Figure 6-8. Optical photomicrograph of crack network in a cured laminate (180°C ) after 3 cycles in liquid nitrogen. 200x magnification

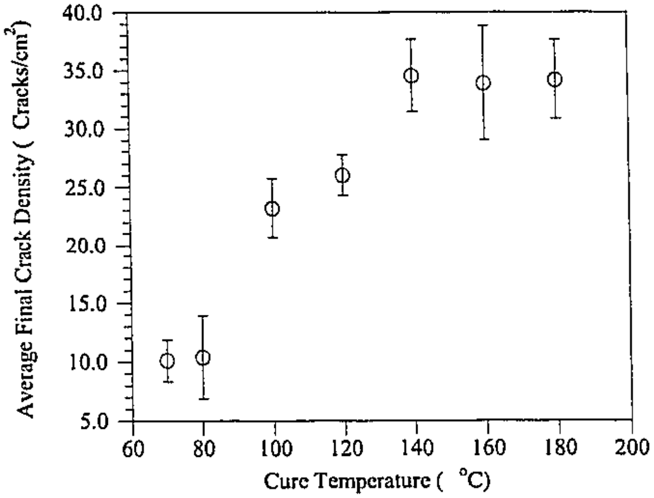

Figure 6-9. Variation in microcrack density with cure temperature

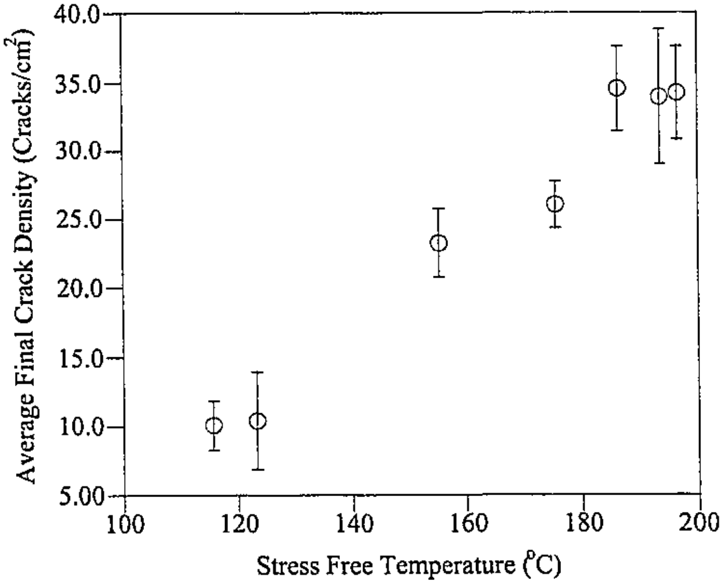

Figure 6-10. Variation in microcrack density with stress free temperature

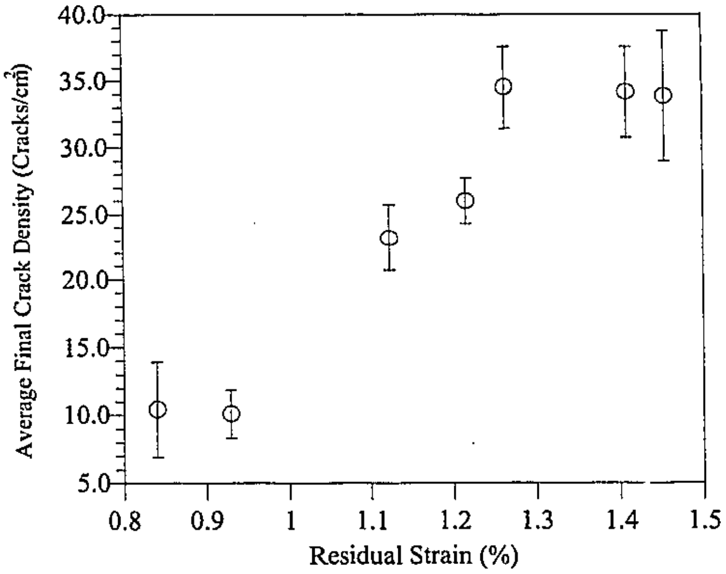

Figure 6-11. Variation in microcrack density with predicted residual thermal strains transverse to the plies in a $[0°_b\, 90°_{2d}\, 0°_b]$ laminate at –195.6°C

# CHAPTER 7: PREDICTIVE MODELING OF MICROCRACKING IN CARBON FIBER/EPOXY COMPOSITES AT CRYOGENIC TEMPERATURES

## 7.1 INTRODUCTION

### 7.1.1 Background

As discussed in the previous chapters, the failure of composite cryogenic liquid storage structures is serious concern [1-8]. Because of this issue, many attempts have been made to predict the generation of thermal stresses in composite materials, the onset of microcracking, and the distribution and origination of microcracks during failure. Shear lag analyses, variational and strain energy release rate approaches, Monte-Carlo simulations, and *in situ* strength analyses are among the approaches that have been used to address this problem [9-14]. Varying degrees of success have been achieved by these analyses, but they are often unnecessarily complex and fail to account for the change in material properties with temperature. The strength and modulus of the laminate and its components, particularly the viscoelastic polymeric matrix, will be altered when exposed to significant decreases in temperature, resulting in stress generation and failure criteria that are different from those at room temperature [1, 15-19].

In this chapter, the temperature at which microcracking occurred in symmetric cross-ply carbon fiber/epoxy composite materials was predicted using a yield stress-based failure model. A fracture mechanics analysis of the *in situ* strength of the ply groups in a composite material was combined with a compound beam determination of thermal stress development to create the predictive model. This approach, unlike many other models, incorporated the change in material properties with temperature by using the room temperature properties of the laminate to predict the low temperature behavior of the ply groups. Dynamic mechanical analysis was used to assess microcracking at cryogenic temperatures through the observation of discontinuities in material properties during failure. Four different material systems were studied, and the model accurately predicted the onset temperature for microcracking in three of the four cases. It was shown that the room-temperature properties of a fiber reinforced polymeric composite laminate, appropriately modified to account for property variation at low temperatures, could be used to predict transverse microcracking as a response to thermal stresses at cryogenic temperatures.

### 7.1.2 Model Development

Brand and Backer developed a compound beam analysis that can be adapted to describe the generation of thermal stresses in laminated materials. The advantage of this approach is that it takes into account stress relaxation during curing and cooling. The foundation of the compound beam analysis involves considering the ply groups as individual elastic entities and calculating the stresses that result from thermal expansion and contraction [20, 21]. The transverse tensile thermal stress in the central plies of a symmetric cross-ply laminate ($\sigma_{tl}^{th}$) was derived using compound beam theory and can be described by the following equation. It should be noted that Equation 7-1 was modified from Equation 6-1 to account for the change in material properties with temperature.

$$\sigma_{tl}^{th} = \frac{-E_t(T)E_l(T)\int_{T_{SFT}}^{T_{Use}}\left[(\alpha_t(T)-\alpha_l(T))dT\right]}{E_l(T)+E_t(T)} \qquad (7\text{-}1)$$

$T_{Use}$ is the use temperature of the laminate (°C), $T_{SFT}$ is the stress free temperature (°C), $E_l$ and $E_t$, are the longitudinal and transverse Young's moduli (Pa) of a unidirectional laminate with the same thickness as the central ply group expressed as a function of temperature, and $\alpha_l$ and $\alpha_t$ are the longitudinal and transverse linear coefficients of thermal expansion expressed as a function of temperature ($^{o}C^{-1}$). It is proposed that microcracking will occur at the temperature that sets the thermal transverse tensile stress in the central ply group equal to the *in situ* yield strength. Past work by Wang et al. and Laws et al. showed that the yield strength of this ply group ($Y_t$) can be expressed as follows [12, 22].

$$Y_t = \frac{\sqrt{G_{IC}(T)E_t(T)}}{F_l\sqrt{a}} \qquad (7\text{-}2)$$

Note that the original expression has been modified to account for the variation in material properties with temperature. $G_{IC}$ is the critical strain energy release rate (N/m), $E_t$ is the transverse modulus of the ply group in a plane stress condition, $F_I$ is a factor derived from fracture mechanics, and a is the initial half crack length (m). The $F_I(a)^{1/2}$ term can be expressed as a constant, C ($m^{1/2}$). The following expression was produced from the combination of Equations 7-1 and 7-2 and can be solved to obtain the temperature at which failure will first occur.

$$\frac{\sqrt{G_{IC}(T)E_t(T)}}{C} = \frac{-E_t(T)E_l(T)\int_{T_{SFT}}^{T_{Use}}[(\alpha_t(T)-\alpha_l(T))dT]}{E_l(T)+E_t(T)} \tag{7-3}$$

A model laminate system was developed to determine the constant C and describe the temperature dependence of the material properties. The thermal stress in the laminate at the first failure event was calculated from the observed material parameters and the experimentally determined microcracking onset temperature. The thermal stress at failure was then set equal to the yield stress and Equation 7-3 was solved to determine C. This value of C was used in the model prediction for all subsequent materials.

## 7.2 EXPERIMENTAL

### 7.2.1 Material development

Four different unidirectional, prepreg-based carbon fiber/epoxy composite systems were used to determine the model parameters and validate its effectiveness. Three of these prepregs (referred to as prepregs 1 to 3) were prepared in the laboratory and one (prepreg 4) was supplied from an outside industrial source. The industrial material was used to assess the performance of the model in relation to a material with a less well known composition and processing history. The four prepregs are outlined in Table 7-1. The numbers in parentheses in Table 7-1 indicate standard deviations.

A mixture of commercially available epoxy resins formed the base of the polymeric matrix for the prepregs prepared in the laboratory. The resins used were EPON® 828 and 1031 from Resolution Performance Products and D.E.R. 661 from the Dow Chemical Company. EPON® 828 and D.E.R. 661 are described in more detail in chapter 3, and the structure of EPON® 1031 is discussed in chapter 6. HT 976, 4,4'-diaminodiphenyl sulfone (DDS), from Ciba and 1-cyanoguanidine (dicy), Amicure® CG 1400 from Pacific Anchor Chemical Co., accelerated with 3-(3,4-dichloro-phenyl)-1,1-dimethyl urea (diuron) from Aldrich Chemical Co. were used as the curing agents.

The epoxy resins were combined in the weight ratios shown in Table 7-1 in an oil bath at 120°C and stirred until they were completely mixed. For prepreg systems 1 and 2, a stoichiometric amount of DDS was melted and added to the epoxy mixture in the oil bath. The epoxy/DDS mixture was blended for two minutes in the oil bath at 120°C after which the resin was cooled to 80°C and prepregged. For prepreg system 3, half of the 828 was set aside and blended with 5 parts per hundred resin (phr) dicy and 2 phr diuron in a high shear mixer to form a curing paste. The epoxy mixture was blended and allowed to cool to 80°C, at which point the curing paste was added. After blending the paste with the epoxies, the mixture was prepregged.

Unidirectional prepregs were developed consisting of the resins discussed above and epoxy sized Toray 50C T300YC carbon fibers. The filament count for all of the fibers was 12,000 per tow. A hot-melt prepreg machine was used to impregnate the fibers with the epoxy resin [23]. The prepreg fiber areal weight and the nominal resin content for the different prepregs are shown in Table 7-1. The filming and impregnation temperatures were 82°C and 93°C, respectively. Two rollers were used to apply the impregnation pressure. The pressure on the first roller was 69 kPa and the pressure on the second was 138 kPa. The line speed was 1.5 m/min and the gap height for resin filming was 0.30 mm.

The resin content of the prepregs was determined in accordance with ASTM D 3171-99 and Boeing Support Standard 7336 using the technique described in chapter 3 [24, 25].

Symmetric, unsymmetric, and unidirectional 10.16 x 10.16 cm laminates and unidirectional 33.02 x 12.7 cm laminates were laid up using the above prepregs. The symmetric laminates consisted of 12 plies of prepreg in a $[0^{\circ}_{3}, 90^{\circ}_{3}]_{S}$ configuration. The unsymmetric laminates consisted of four plies in a $[0^{\circ}_{2}, 90^{\circ}_{2}]$ configuration. The 10.16 x 10.16 cm unidirectional laminates consisted of 6 plies and the 33.02 x 12.7 cm unidirectional laminates consisted of 16 plies with a 5.08 cm fluorinated ethylene propylene copolymer (FEP) crack starter placed in the midplane.

The laminates described above were exposed to an autoclave cure cycle that consisted of a 2.8°C/min ramp to 93°C, a one hour hold at 93°C, a ramp at 2.8°C/min to 177°C, a two hour hold at 177°C, and a ramp to 25°C at 2.77°C/min. The total consolidation pressure used during cure was 310 kPa. The vacuum bag was vented to the atmosphere when the autoclave pressure reached 104 kPa.

Once cured, the symmetric laminates were cut with a diamond saw into 3.49 x 1.27 cm (length x width) samples for cycling studies and the 6-ply unidirectional laminates were cut into 5.08 x 1.27 cm (length x width) transverse and longitudinal samples for modulus determination. The unsymmetric laminates were cut into 20.0 x 1.27 cm (length x width) samples for the determination of the stress free temperature and the 16-ply unidirectional laminates were cut into 33.02 x 1.27 cm (length x width) samples for fracture toughness testing. The edges of the cycling and modulus samples were polished prior to testing to facilitate optical microscopy of the surfaces.

### 7.2.2 Testing and analysis

Mode I interlaminar fracture toughness, $G_{IC}$, was measured using the double cantilever beam (DCB) method [26]. For each laminate, five samples were tested. Each sample was precracked before testing to create a sharp crack tip. The specimens were pulled apart at a rate of 25.4 mm/min using an Instron 4505 screw testing frame controlled by Instron Series IX software.

The longitudinal and transverse tensile moduli of the 6-ply unidirectional samples were determined using a Seiko SII 6100 dynamic mechanical spectrometer (DMS) controlled by Exstar 6000 version 6.0 software. The samples were exposed to a 2.5 N load for 10 seconds and then held at zero load for 10 seconds. This process was repeated as the samples were heated at 5°C/min from –120°C to 170°C. From the resulting position/load data, modified to account for thermally induced dimension changes in the samples, the modulus during each loading cycle could be determined. The dependence of the modulus on temperature was quantified using these data. The samples were examined using optical microscopy before and after testing to ensure that no cracks or failure sites were formed during testing.

The cured unsymmetric laminates were tested as described in chapter 6 to determine the stress free temperature.

The unidirectional samples from the $G_{IC}$ tests were used to fabricate 1.0 x 1.0 cm samples for the determination of the longitudinal and transverse coefficients of thermal expansion of the laminates. Each sample was obtained from a portion of the fracture toughness specimen that was not damaged during testing. The coefficient of thermal expansion was determined using the instrument and technique described in chapter 6. The dependence of the coefficient of thermal expansion on temperature was determined from the slope of the dimension change with temperature between -100°C and 170°C.

The cut and polished symmetric laminates were allowed to equilibrate at 22°C and were then cooled to a specified temperature and held for 10 minutes in the DMS 6100 described earlier. The microcracking onset temperature was determined by lowering the hold temperature in 5°C increments between runs until microcrack formation was observed. During cycling the laminates were deformed at a frequency of 1 Hz with an oscillation amplitude of 10 μm to identify changes in dynamic mechanical behavior at low temperatures and as microcracking occurred. It should be noted that previous experiments showed that deformation of this type and duration did not change the microcracking behavior of these samples.

Optical microscopy was used to observe and document the microcracking onset temperature and the response of the samples to cryogenic exposure as described in chapter 3. Five samples from each laminate were tested to determine the onset temperature for microcracking.

## 7.3 RESULTS AND DISCUSSION

### 7.3.1 Microcracking

Dynamic mechanical analysis of the symmetric laminates at cryogenic temperatures revealed information about the low temperature properties of composite materials and the effects of microcracking on their response to dynamic loads. The storage modulus (E′) and tan(δ) during exposure to sub-ambient temperatures are shown in Figure 7-1 for a symmetric cross ply laminate made from prepreg 2. Figure 7-1A demonstrates that the storage modulus of the laminate increased as the temperature decreased, establishing that the properties of the laminates studied changed significantly at low temperatures. Therefore, the temperature dependence of material properties must be accounted for in a predictive model of microcracking at cryogenic temperatures.

The sharp, discontinuous decrease in the storage modulus seen in Figure 7-1A and the spike in tan(δ) shown in Figure 7-1B corresponded with the onset of microcracking in the laminate. Examination of the laminate after cycling revealed the formation of a microcrack spanning the interior ply group of face 2 of the laminate as defined in Figure 3-1. It should be noted that a similar E′ and tan(δ) response appeared in all of the laminates where microcracking was observed. It was seen that microcrack formation decreased the stiffness of the laminate and caused a momentary increase in the phase lag. Microcracking debonded the fibers from the matrix and prevented efficient load transfer, reducing the modulus of the sample and increasing the ability of the laminate to dissipate energy at the fiber/matrix interface, causing an increase in tan(δ) [27, 28].

Microcracking was observed in the laminates made from prepregs 1, 2, and 4 as a response to cryogenic cycling. The majority of the microcracks spread across the entire width of the central plies in face 2 and propagated through the laminate. When the microcracks reached the interface between the 0° and 90° ply groups delamination was observed in some cases. Figure 7-2 presents optical photomicrographs of representative microcracks formed during cryogenic cycling. Figure 7-2A shows the microcrack formed during the thermal cycle in Figure 7-1. Figures 7-2B and 7-2C illustrate the formation and extension of a small crack during exposure to progressively lower temperatures. In some cases, as seen in Figure 7-2A, microcracks formed effectively instantaneously and propagated through the sample, at other times, demonstrated in Figures 7-2B and 7-2C, small cracks formed initially and gradually extended through the sample.

The microcracks propagated along the fiber-matrix interface and demonstrated considerable variation in width and morphology. Irregularities in crack size and shape introduced significant error into the prediction of the number and distribution of microcracks as one large, tortuous crack may have dissipated as much energy as the formation of two smaller cracks. It is for this reason that the objective of this study was to predict the onset of microcracking and not the specific number or distribution of failure events.

### 7.3.2 Model predictions

The important material properties, specifically the coefficients of thermal expansion and the longitudinal and transverse tensile moduli, varied with temperature to different extents, ranging from effectively constant to depending strongly on temperature. The linear and transverse coefficients of thermal expansion did not exhibit temperature dependence between –100°C and 170°C for the carbon fiber/epoxy laminates studied. The longitudinal tensile modulus showed a small linear increase with decreasing temperature, with a typical increase of 0.08% after cooling from 25°C to -120°C. The transverse tensile modulus, which played a key role in the development of transverse tensile stresses, showed a significant linear increase with decreasing temperature, increasing on average 25% from 25°C to –120°C. The fracture toughness ($G_{IC}$) as a function of temperature was unknown and unable to be determined; therefore, an additional factor to account for changes in fracture behavior at low temperature was grouped into the constant C in Equation 7-3.

The average onset temperature for microcracking ($T_{Usc}$), $T_{SFT}$, $E_l(T)$, $E_t(T)$, $\alpha_l(T)$, $\alpha_t(T)$, and $G_{IC}$ for the laminates made from prepreg 1 were used to solve Equation 7-3 for the constant C. C was calculated to be 0.036 $m^{1/2} \pm 0.0062$. Once C was determined, the model could be applied to other material systems.

Figure 7-3 illustrates the effectiveness of the model in predicting the microcracking onset temperature, with the error bars indicating one standard deviation. It should be noted that the error bars are relatively large due to the variation in microcrack size and shape between each failure event. Error bars are not present on the observed microcracking temperature for prepregs 3 and 4 because less than 3 out of 5 samples formed microcracks and a standard deviation could not be calculated. The microcracking temperatures were essentially the same for prepregs 1 and 2, which was consistent with their similar composition. The use of dicy/diuron as the curing agent in prepreg 3 increased the microcracking temperature, which was consistent with the results in chapter 3. The model correctly predicted the onset of microcracking for laminates made from prepregs 1-3. In the case of prepreg 4, the model predicted microcracking between –140°C and -60°C, while microcracking actually occurred at –190°C.

The microcracking temperature may have been underpredicted for prepreg 4 due to the fact that it was supplied by an industrial source. The properties of this material were known less accurately than those of the prepregs that were produced in the laboratory. It was also possible that the longitudinal and transverse coefficients of thermal expansion were no longer temperature-independent or the dependence of the tensile moduli on temperature deviated from linearity as the temperature approached the microcracking temperature (≈-200°C). Instrumental limitations prevented the recording of data below –120°C; therefore, the property variation with temperature trends in the –100°C to 0°C temperature range were extended to lower temperatures.

## 7.4 CONCLUSIONS

Symmetric, cross-ply carbon fiber/epoxy laminates were produced and exposed to sub-ambient temperatures to determine the microcracking onset temperature. These data were then compared with the predictions of a stress-based compound beam model in which fracture mechanics was used to determine the *in situ* yield strength of the ply groups in the laminates and the variation in material properties at low temperatures was accounted for. The model correctly predicted the failure temperature for most of the materials tested. In addition, it showed that accurate predictions of thermal stress-induced failure can be made using the room temperature properties of a laminate, appropriately modified to account for low temperature property variation. Microcracking changed the dynamic mechanical properties of the composite materials studied, and it was shown that dynamic mechanical analysis could be used to assess the formation of microcracks.

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Table 7-1. Prepreg characteristics

| Prepreg | Carbon Fiber Type | Epoxy Formulation | Curing Agent | Prepreg Resin Content (wt. %) | Prepreg Fiber Areal Weight (g/m$^2$) |
|---|---|---|---|---|---|
| 1 | T300 YC | 3:1 1031:828 | DDS | 54.7 (0.77) | 124.0 (2.26) |
| 2 | T300 YC | 3:2 1031:828 | DDS | 45.3 (0.65) | 129.9 (1.60) |
| 3 | T300 YC | 2.4:2:1 828:661:1031 | Dicy/Diuron | 47.0 (1.00) | 144.5 (2.40) |
| 4 | T-50S | - | - | 47.7 (0.021) | 100.0 |

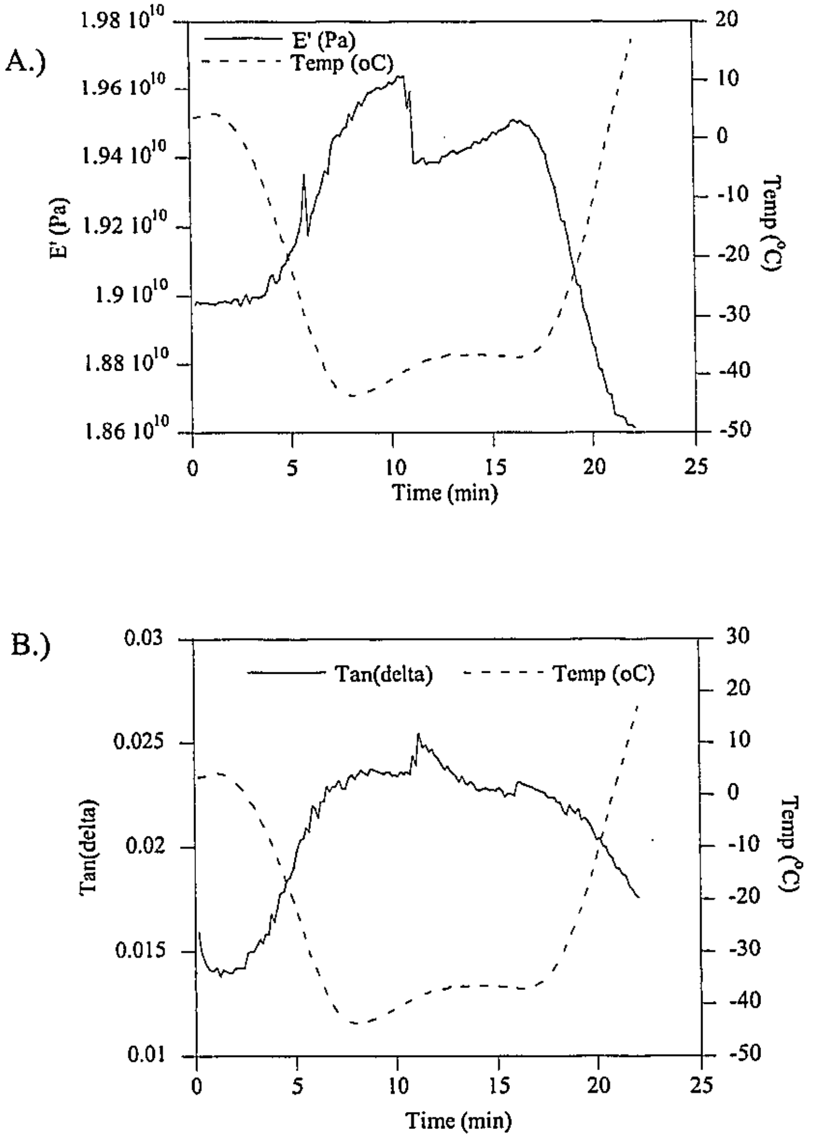

Figure 7-1. Effects of cryogenic temperatures and microcracking on the dynamic mechanical properties of symmetric laminates. A.) Storage modulus B.) tan(δ)

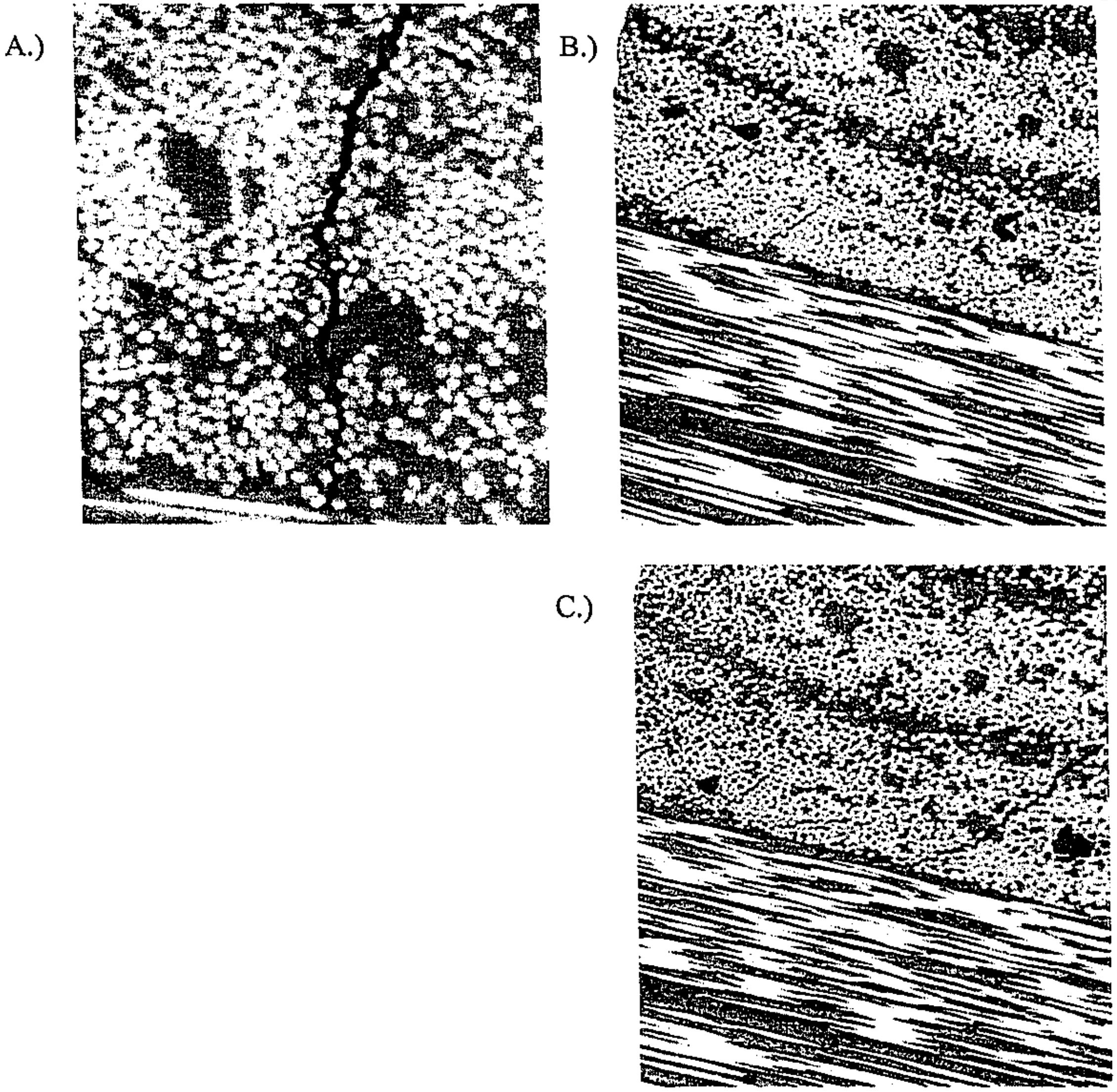

Figure 7-2. Optical photomicrographs of microcracks. A.) Prepreg 2, 200x, -40°C, B.) Prepreg 1, 100x, -40°C, C.) Prepreg 1, 100x, -60°C, extension of crack in B

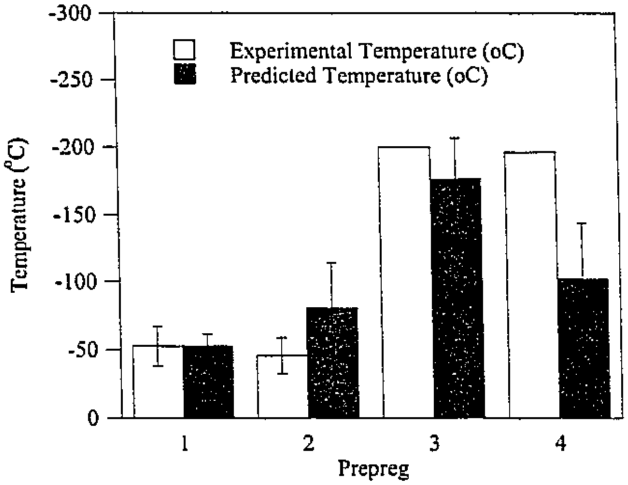

Figure 7-3. Comparison of predicted and experimental microcracking onset temperatures

# CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

## 8.1 CONCLUSIONS

In this work the behavior of carbon fiber/epoxy composites at low temperatures was investigated. Of particular interest was the generation of internal stresses during thermal cycling between cryogenic and ambient temperatures. These stresses reached a level at which failure of the composite occurred through the formation of transverse microcracks and delamination between ply groups. These phenomena were analyzed using a process-structure-property methodology. This approach allowed the effects of the components of a composite material, the fibers and the matrix, to be investigated along with the interface between the matrix and the fibers and the processing conditions during laminate fabrication. Understanding the links between the processing and structure of a composite material facilitated the development of a fundamental knowledge base on how these parameters influenced the performance of composite materials at low temperatures. The majority of this work used a phenomenological approach to identify the important variables in matrix microcracking during cryogenic cycling. Once these variables had been identified, a model was developed to predict the thermal strains generated in composite materials at low temperatures and the temperature at which microcrack formation occurred.

The first set of variables to be explored was the structure of the matrix and fibers used in the composite materials studied. It was found that the type of fibers and the polymeric matrix used in the composites played a large role in determining the propensity for microcracking as well as the microcrack morphology in symmetric cross-ply carbon fiber/epoxy composites. The microcrack density increased and larger cracks were formed when fibers with larger tensile moduli and longitudinal coefficients of thermal expansion were used. Increased flexibility of the polymeric matrix decreased the glass transition temperatures of the laminates studied and caused an increase in the microcrack density. The response of composite materials to cryogenic cycling was found to be influenced by the type of curing agent used. A curing agent that led to stiffer and more regular network structures resulted in a decrease in microcrack density. The presence of a rubber interpenetrating network toughener prevented the formation of microcracks in all of the laminates studied. It was shown that the fibers and the matrix used in a composite altered the thermal stresses present in a material as well as the ability of the material to resist thermal stresses, and therefore, had a direct influence on matrix microcracking at cryogenic temperatures.

The second set of variables to be investigated was the interaction between the fibers and the matrix in the interfacial region. Symmetric cross-ply carbon fiber-reinforced polymeric composite materials were prepared using fibers with different surface chemistries. Variations in the fiber surface chemistry changed the fiber-matrix adhesion in laminates containing these fibers. The fiber-matrix adhesion had a direct impact on the microcrack density in composite materials after cryogenic cycling. The laminates with good adhesion exhibited lower microcrack densities than the laminates with poor adhesion. Surfactant sized fibers outperformed traditional epoxy sized fibers by yielding composites with improved mechanical properties and resistance to microcracking.

Modification of the polymeric matrix on the nano and micro scale and its effects on microcracking was studied using layered clays as nanoparticle fillers and alumina particles as microfillers in fiber-reinforced polymeric materials. When nanoparticle fillers were used at concentrations much lower than those used for traditional fillers a significant reduction in cryogenic microcracking was observed. The concentration of the particles and their distribution in the matrix were important parameters in the optimization of the benefits of nanoparticle reinforcement. A typical, macro-scale filler effect was seen at large concentrations of nanoclay, and low concentrations showed little or no effect. The best reinforcement was provided by exfoliated and disordered intercalated structures, with more ordered intercalated structures, which were seen at large clay concentrations, offering little benefit. The mechanical properties and processing characteristics of the laminates studied were not adversely influenced by the presence of the nanoparticles and the thermal expansion characteristics were improved. It was shown that the resistance of traditional fiber-reinforced composite materials to microcracking during cryogenic cycling could be enhanced using nanoparticle modification.

The last variable explored was the processing conditions, namely the cure temperature, of a composite material. A theoretical and experimental analysis was performed on carbon fiber/epoxy symmetric cross-ply laminates to investigate microcracking and the development of thermal stresses at low temperatures. Experimental results correlated with the theoretical predictions of the development of thermal strains in composite materials. Microcracking occurred in all of the laminates tested, but the number and morphology of the microcracks was strongly dependent on the cure temperature. Higher stress free temperatures, residual thermal strains, and glass transition temperatures of the laminates were all the results of elevated cure temperatures. The larger stress free temperatures corresponded to increased microcrack densities and larger levels of residual thermal strain. Larger cure temperatures resulted in laminates with a greater propensity to delaminate, contain wider and more tortuous cracks, and form networks of cracks when cycled between ambient and cryogenic temperatures. The development of thermal stresses in composite materials at cryogenic temperatures was modeled and the levels of these stresses were enhanced by higher cure temperatures.

The investigation of the role of the cure temperature in thermal stress generation was extended to develop a model that predicted the onset temperature for microcracking in symmetric cross-ply carbon fiber/epoxy laminates based on the thermal stresses in a laminate and the yield strengths of the ply groups in a laminate at sub-ambient temperatures. The fact that the model accounted for the change in material properties at cryogenic temperatures by predicting the low temperature behavior of the ply groups in a laminate based on the room temperature properties of the plies made it unique. It was also found that microcrack formation caused a discontinuity in material properties that could be detected using dynamic mechanical analysis. Four different material systems were studied, and the model was found to accurately predict the onset temperature for microcracking in three of the four cases. It was shown that microcracking resulting from thermal cycling and thermal stresses could be predicted based on the room-temperature properties of a laminate, with appropriate modifications for property variation at low temperatures.

Taken as a whole, this work comprised a phenomenological and theoretical investigation of cryogenic microcracking in composite materials. The results presented here furthered the understanding of the causes and mechanisms of cryogenic microcracking and will be of utility in the development of composite materials and structures that operate at low temperatures.

## 8.2 RECOMMENDATIONS FOR FUTURE WORK

The studies that have been performed so far have characterized microcracking in fiber-reinforced composites at cryogenic temperatures and predicted the onset temperature for crack formation. However, the distribution and number of microcracks and the formation of microcracks in an already cracked material have not been satisfactorily predicted. It is proposed that a model that could predict how the low temperature properties of a composite material changed with microcrack formation would be very useful for the design of composite structures and would facilitate a deeper understanding of cryogenic microcracking [1-3]. If the variation in properties with microcracking was known, it could be incorporated into a model similar to the one presented in this work and used to predict additional microcracking after the first failure event. An understanding of the changes in the local stress state of a composite material with microcracking could be used to gain a deeper knowledge of how thermal stresses develop in a microcracked material and how microcracks are distributed during failure.

Composite structures that are used for the storage and transportation of cryogenic liquids are exposed to a dynamic environment that was not accounted for in previous studies of microcracking. Future work will investigate the effects of the frequency and amplitude of loads applied to a composite specimen during cryogenic cycling. These loads will alter the stress state in a material and have the potential to change the microcracking behavior of cryogenically cycled materials.

Recent work on the modification of the matrix in fiber-reinforced composite materials has shown that microcracking can be reduced by the incorporation of toughening agents into the matrix. Second phase liquid rubber tougheners have been used to reduce microcracking, as have nanoclay particles [4]. It has been shown that rubber/clay nanocomposites can be formulated and that they can exhibit improved properties over the neat rubber [5, 6]. It is proposed that modifying the dispersed rubber phase with nanoclay structures could improve the properties of a traditionally toughened composite material. Stiffening of the second phase may prevent the decrease in glass transition temperature and matrix stiffness that is often associated with rubber tougheners. Alignment or preferential orientation of the nanoparticles at the interface between the phases could also result in improved properties of the bulk composite. Much work remains to be done to understand how toughening agents reduce microcracking and how nanoparticles interact with larger, macro-sized structures in composite materials.

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# Vita

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