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A WATER BASED MANUFACTURING METHOD FOR TWO PHASE MATRIX COMPOSITE MATERIALS

By

JAMES HECTOR FERNANDES

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

A WATER BASED MANUFACTURING METHOD FOR TWO PHASE MATRIX COMPOSITE MATERIALS

By

James Hector Fernandes

A novel processing technique for the manufacture of continuous fibers with a two phase matrix from a well-mixed aqueous colloidal dispersion bath was developed. In this study, carbon fibers were spread using acoustic energy and then coated with the two particles, i.e. an epoxy resin and an elastomer, by passing through a bath of the mixture. The prepreg tape was then consolidated into a uni-directional multi-layered part, under vacuum in an autoclave and under a specific consolidation cycle. Several composite parts were consolidated by preparing prepreg tape with different ratios of epoxy resin particles to elastomeric particles, by changing the concentration of the elastomer to the epoxy resin in the dispersion bath. The parts were subjected to mechanical testing and morphological study, and the results indicated two distinct phases in the composites. To my late Father, Mummy, Sweetie, Sana & Julie

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INTRODUCTION

A composite material may be defined as a substance comprised of two or more identifiable constituents. The individual constituents in a composite material are combined in such a way that the final composite part has superior properties than the individual components. Composites are both natural and man-made. These materials can be categorized into the following groups:

- a) fibrous composites consist of either short, long or continuous fibers in a matrix.
- b) laminated composites consist of layers of different materials.
- c) particulate composites consist of particles of one or more materials enveloped in a matrix.

In this dissertation we will confine our study to fibrous composites. Some of the more popular fiber types are carbon, glass, and Kevlar (aramid) fibers. Fiber diameters vary from 5 to 15 microns. The matrices associated with such composites are usually of two types:

a) Thermoplastics: They are one- or two-dimensional in molecular structure and show a discrete melting point. In these compounds the process of softening and regaining rigidity upon cooling is a reversible one^[1] e.g. polyethylene, polystyrene,

polypropylenes, polyamides, and nylon.

 b) Thermosets: They form a well-bonded three-dimensional molecular structure upon curing. Once cross-linked or hardened, these polymers will decompose rather than melt. e.g. epoxy, polyester, phenolic polyimide resins.

Table 1.1 compares the properties of thermoset and thermoplastic matrices for composites.

PROPERTY	THERMOSET	THERMOPLASTIC
Weight	+	+
Material Cost	+	+
Processing Cost-Reduction		+
Potential		
Simplicity of Chemistry		+
Melt Flow	+	
Prepreg Tack and Drape	+	
Long Prepreg Shelf Life		+
Low Processing Temperature	+	
Low Processing Pressure	+	
Low Processing Cycle		+
Low Cure Shrinkage		+
Quality Control Data Base	+	
Mechanical Property Data Base	+	
Ability to Translate Fiber Propertie	s +	+
Solvent Resistance	+	
Corrosion Resistance	+	+
Resilience	+	
Toughness		+
Lack of Time-Dependence	+	
Interfacial Adhesion	+	
Low Thermal Expansion	+	

Table 1.1 Comparison of matrices^[2]

Unidirectional prepreg tapes are generally the precursors for fibrous composite materials. Prepregs are fibers preimpregnated with a resin system (thermoplastic or thermosetting). The finished composite part is formed by consolidating unidirectional prepreg tapes that have been stacked in a predetermined sequence of orientation e.g. 0°, 45°, 90°. Consolidation cycles for thermoplastic or thermosetting prepregs are different. Thermosets undergo a chemical reaction and so have to be cured by the application of heat and/or pressure during processes such as vacuum bagging, autoclave molding, hot press molding, etc. Thermoplastics are usually in their final polymerized form and so their consolidation involves heating under pressure to achieve fusing between adjacent prepreg tapes. Hergenrother and Johnston^[3] proposed the following requirements for an ideal polymeric system to be used as a composite matrix :

- a) Easy prepreg preparation
- b) Good shelf life
- c) Acceptable tack (stickiness) and drape (shape relaxation)
- d) Acceptable quality control procedures
- e) Low processing temperature and pressure
- f) No volatile evolution
- g) Dense void-free matrix
- h) Good mechanical performance over the desired temperature range, time and environmental conditions
- i) Acceptable repairability and cost effectiveness

No currently available matrix conforms to all these properties and hence the choice of a matrix usually represents a compromise^[4].

The primary objective of this study is to investigate the manufacture of unidirectional prepreg tape on a continuous basis from aqueous colloidal dispersions of multiple resins in order to control the microstructure and morphology of the prepreg and composite. Such a process would offer complete control on the final coating of epoxy resin on the fiber surface and at the same time provide a tape of uniform dimensions and a high degree of drapability, so that it can be formed into any desired part. These tapes would then be consolidated within a prescribed curing cycle to give a void-free composite material. The combination of high-strength fibers with the adhesive properties of epoxy resin yields physical properties unsurpassed by other similar materials of construction.

It should be noted that epoxies are inherently brittle materials, only slightly tougher than inorganic glasses. Considering the fracture energy as a measure of toughness of materials, it can be seen than most thermosetting polymers have fracture energies ranging from 80 to 200 J/m², whereas certain thermoplastics have fracture energies of 1kJ/m². ^[5] An important aspect of this thesis, is to demonstrate that the same process can deposit two particles, an epoxy and an elastomer, from an aqueous colloidal dispersion. Prepreg tapes prepared from epoxy resin coating with elastomeric inclusions in the matrix, can be consolidated and optimized for toughness by controlling the size, density and nature of these elastomeric inclusions.

4

PROCESS DESCRIPTION

2.1 INTRODUCTION

Since prepreg tape is the prerequisite for most continuous unidirectional fibrous composite parts, it is exigent for developing a process for the manufacture of prepreg tape on a continuous basis. While several processes have been developed for the manufacture of prepreg tape, this thesis only encompasses coating from aqueous dispersions of resins, therefore only those processes that make use of slurries will be discussed.

2.1.1 Slurry Processing

In this slurry process, spread fibers are drawn through a liquid suspension of the polymer powder. The liquid carrier is removed by subsequent drying in the heating zones and the prepreg tape is wound onto a take-up winder. O'Connor^[6] developed a patented process for prepreg tape manufacture using a polymer slurry. Major drawbacks of the process were determination of right concentration of slurry, maintaining this concentration and removal of all liquid so that voids are not formed during the consolidation step. The minimum void content in the slurry processed tape were 2-4%. Dyksterhouse et al^[7] made use of a polymer gel to impregnate the fibers. See Figure 2.1



Figure 2.1 Production of Prepreg Tape using Polymer Slurry



Figure 2.2 Process Schematics for Foam Towpregging

for details on the process description using slurry processing techniques.

2.1.2 Aqueous Foam Processing

Chary et al^[8] developed a process wherein an aqueous foam is used as the carrier medium to deposit polymer onto the fiber tow. This technique has the advantages of controlled deposition of polymer onto the tow with considerable ease in process control and a reduction in drying times as compared to solution/slurry coating. The major problem with this method is that agglomeration of molten polymer takes place, due to high temperatures in the heating section being required for removal of surfactant, which leads to a stiff prepreg tape. Figure 2.2 is a schematic representation of this process.

2.2 PROPOSED PROCESS

In conceiving the proposed process, whereby an aqueous colloidal dispersion of a resin is the coating medium, all the currently available prepregging techniques were evaluated and the salient features of each process were adapted into the final process. Figure 2.3 shows the unit operations involved in the process.

2.2.1 General Description

A tow of continuous fiber is unwound from the feed spool by means of a DC motor. The fiber tow is then directed through a guide slot and passed through the first of the four sets of pinch rollers. The four sets of pinch rollers are driven by a single DC motor and are interconnected with chain links and sprockets. The fiber tow then passes over a spreader unit, where the tow is separated into individual filaments. The second set of pinch rollers helps maintain the spread and facilitates its passage through the dispersion bath. In the dispersion bath, the separated fiber filaments are coated with the dispersed solid particles. Once the fibers are coated, all the moisture is removed in the



Figure 2.3 Schematic of Aqueous Colloidal Dispersion Prepregging Process

heating section. The heating section comprises of a convection oven and two infra-red lamps. Most of the heat energy is expended in evaporating the moisture. The final two sets of pinch rollers facilitate the passage of the coated fibers through the bath and the heating section. The dry prepreg tape is then directed through another guide slot and is then wound on a take up drum, such that the winding is both in the rotary and traverse as given below:

2.2.2 Fiber Motion System

The fiber motion system performs the following functions:

- a. Unwind the unsized carbon tow from the feed spool.
- b. Facilitate the motion of the fibers through the various units in the process line.
- c. Provide rotary and lateral motion of the coated fibers on a take-up spool, so that the prepreg tape is wound over the entire surface of the spool.

The fiber motion system comprises two DC motors, an AC take-up winder, pinch rollers, guides and chain links. The two motors are 90VDC permanent magnet, ball bearing, continuous operation (10 hr/day, 40°C max), 1/10 HP type with gears for speed reduction. See Figure 2.4 for details. Both these motors are controlled by a variable speed controller. Incoming AC voltage is converted to an adjustable full wave rectified DC voltage to operate the DC motor. (Details of the circuitry will be given in the section on process automation).

The processing line is provided with four sets of pinch rollers. Dimensions and construction of rollers are shown in Figure 2.5. Two sets of pinch rollers are installed before and after the spreader unit, one after the dispersion bath and the other after the heating section. Each set of rollers is provided with a bleeder cloth wiper at the top and



Figure 2.4 DC Gearmotor



Figure 2.5 Pinch Rollers

the bottom. The function of these wipers are to gently remove any stray carbon fiber thus preventing entanglement of the tow. The bottom roller of each set of pinch roller is connected to the next set of rollers by means of a chain link and sprocket mounted on the protruding end of the roller. Fibers are unwound from the feed spool, as supplied by vendor, by utilizing the first of the two DC motors. Speed of this motor is adjusted so as to match it as closely as possible to the second motor. The second or drive motor controls the motion of all the four sets of pinch rollers. The speed of each roller is matched with the drive motor by the interconnected link chain. The unwound fiber then passes through a guide and taken up by the first of the four pinch rollers. The subsequent rollers assist the motion of the fibers through the spreader, dispersion bath and heating units. The line speed is adjusted via the speed controller located on the drive motor.

The prepreg tape is wound on an empty cardboard spool. This spool is mounted on a commercial take-up winder, Leesona #959. The take-up winder has been specifically retrofitted to match the process line speeds. It is provided with a three-phase 220V, AC, 0.5 HP motor. To the motor is linked a cam shaft and an expanding flange tube holder. (See Figure 2.6). An empty cardboard spool is placed on the flanged tube holder. Air or nitrogen is filled into a diaphragm located within the tube holder. The flanges expand and form a tight fit with the spool. Prepreg tape is passed through the guide and fixed to the spool. Speed of the motor is adjusted by a torque controller. It adjusts the tension between the final pinch roller and the take-up winder such that a winding similar to that of the feed spool is attained. The motor provides rotary winding, whereas the cam shaft provides for transverse winding.



Figure 2.6 Take-Up Winder

2.2.3 Spreader Unit

The spreader unit is a patented device developed at the Michigan State University^[9]. A schematic representation of this unit is as shown in Figure 2.7. It is necessary to spread the fibers to achieve uniform and maximum coating of polymer particles from colloidal bath. The spreader unit consists of a 10" dia woofer speaker mounted in a wooden housing with dimensions as shown above. The speaker has a frequency response to 4,500 Hz and an input power of 20 W nominal and 50 W maximum. The speaker is driven by a frequency generator and a power amplifier. A BK Precision 2MHz digital display function generator is used to generate a signal of specified frequency. This signal is amplified by a 5W Optimus STA-20 AM/FM stereo receiver and supplied to the speaker. The speaker vibrates at a constant predetermined frequency and amplitude. The acoustic energy thus delivered assists in the spreading of the narrow incoming fiber tow to any required width. For a particular fiber tow, there is a narrow band of operation at which the fibers absorb the most energy and give an optimum spread. The narrow fiber tow is passed through the 3/8" dia case hardened polished steel shafts arranged as shown in figure. The shafts are held in place by means of an aluminum block fitted with precision bearings. The function of the shafts is to hold the tow in its spread form as it is being conveyed forward. The speaker provides the acoustic energy for spreading the fibers. The fibers are maintained in a spread manner by ensuring zero tension between the ends of the spreader. This is achieved by the two by two pinch rollers at both ends of the speaker.



Figure 2.7 Spreader Unit

2.2.4 Dispersion Bath

A schematic representation of the dispersion bath is as shown in Figure 2.8. The dispersion bath comprises of a 6.5"x 6.5" x 12" plexiglass box in which is placed a 1.5" dia aluminum roller mounted on sealed bearings. The colloidal dispersion of a polymeric resin is diluted with deionized water to the desired level of pickup. Spread fibers pass through this bath and the suspended solid particles are coated onto the fiber surface. The roller within the bath facilitates the passage of the fibers. The volume of the dispersion and the line speed determine the residence time of fibers within the bath. With the passage of time, the concentration of the solid particles in the bath would decrease as it is being coated onto the fiber surface. However, the concentration of the bath is maintained by periodic replenishment of bath with fresh colloidal dispersion.

2.2.5 Heating Section

The main purpose of the heating section is to remove moisture from the fiber and sinter the polymeric particles to the fiber surface. The heating section consists of a convection type laboratory oven and 375 W infra-red lamps. The oven is a Grieve, 120V, LW 201C convection type oven with a maximum operating temperature of 200°C. The oven has been retrofitted to meet these material and process requirements. (See Figure 2.9 for details). The temperature in the convection oven is controlled by a dedicated controller details of which will be covered in the section on process automation. This oven is not capable of providing all the energy required to remove all the moisture from the fiber surface at the given line speeds. Therefore, heating is supplemented by two infra-red lamps installed downstream of the oven. The first of the two lamps is a 375 watt infra-red lamp with intensity control range from 15% to 80%.



Figure 2.8 Dispersion Bath



Figure 2.9 Heater

The second lamp is also 375 watts, but is housed in an ordinary lamp holder. It is possible to adjust the height of the bulb from the prepreg tape, thus varying the intensity of heating. Both lamps can supply a maximum of 120°C to the fiber surface. Partial sintering of the solid particles is also achieved in this section.

2.3 PROCESS AUTOMATION

Process automation is achieved in the different sections of the processing line by different controllers. Each will be described separately.

2.3.1 Fiber Motion

As described earlier, the motion of the fibers through the processing unit is controlled by means of a drive motor, pinch rollers, chain links and sprockets. The motors are controlled by a variable speed controller, DART Controls 125K Series. This controller is a dedicated speed controller and adjusts the current to the motor according to the desired setting. (See Figure 2.10 for details on the circuit diagram). The controller was calibrated against the dial settings to ascertain the line speed. For this purpose the process line was run for one minute time periods with carbon fiber tow to calibrate the line speed. For e.g. if for a dial setting of 1, the resulting fiber length was 60 cm; then the line speed at 1 would be 1cm/sec. At least three sets of samples were taken for each dial setting. (See Figure 2.11 for calibration chart). The speed of the motor linked to the feed roller is adjusted manually such that there is very little tension or a slight slack between the feed roll and the first pinch roller. The take-up winder is controlled by a 2100 Series Fincor DC motor speed controller. This controller has been set for maintaining a constant tension between the last pinch roller and the take-up spool. The initial speed has to be dialed in and after this the torque controller takes over.



Figure 2.10 Circuit Diagram of Variable Speed Controller



Figure 2.11 Calibration Graph for Speed Controller

2.3.2 Oven Temperature

The temperature of the convection oven is controlled by a dedicated controller. See Figure 2.12 for details of the circuit diagram. The oven temperature is measured by a J-type thermocouple, which is converted to a millivolt signal and fed to a CN 300 Omega Temperature Controller. This temperature controller operates on an ON-OFF principle. As long as the temperature of the oven is below the set point, the controller keeps the heating circuit on; but as soon as the temperature exceeds the set point the controller switches off the heating circuit and does not restart it until the measured temperature goes below the set point. Temperature control of between $\pm 5^{\circ}$ C was obtained by by-passing the oven's original thermostat.

2.4 SUPPLEMENTARY EQUIPMENT

Additional equipment is required for consolidation of the prepreg tape into final composite parts. Besides this it is also necessary to identify equipment for characterization of prepreg tape, prepregging material and composite parts. Given below are brief descriptions of the various ancillary equipment required for this:

2.4.1 Prepreg Tape Winder

Prepreg tape produced from the process has to be wound onto a frame so that a multi-lamina composite part can be consolidated from it. A sketch with dimensions of the winding frame is given in Figure 2.13. The winding frame is fixed to a rotary winder. This winder has been specifically designed to wind prepreg tape or fiber tow. (See Figure 2.13 for details). The winder has an AC motor, which rotates the frame about its axis. The motor is also provided with a counter, which counts the number of revolution. The fiber guide is attached to a second motor. This motor moves the fiber



Figure 2.12 Circuit Diagram for Convection Oven Temperature Controller



Figure 2.13 Schematic for Frame

tow in a traverse motion. Both the motors are operated simultaneously. The speeds of these motors are based upon the width of the fiber tow. Detailed calculations for determining the speeds of the motors are provided in the following chapters. The prepreg tape is taken from the product spool and passed through the tow guide. The tape is fixed to the rotary frame. When both the motors are operated, the tape undergoes rotary and traverse motion, so that it is wound over the entire width and length of the frame.

2.4.2 Autoclave Consolidation

The multi-layered prepreg tape part must be consolidated into the final composite. Consolidation involves the curing of the resin under controlled conditions, i.e. according to a specific heating, pressurization cycle. This is usually done in an autoclave under vacuum. A United McGill autoclave is used to carry out the curing of the epoxy resin. The consolidation cycle has been programmed into the control loop of the autoclave. (See Figure 2.14 for details). The finally layed-up part is placed in an autoclave vacuum bag and then placed within the autoclave. In the autoclave, nitrogen is used as the pressurizing and heating gas. After the part has undergone the consolidation cycle it is removed from the autoclave. Details of the consolidation cycle and autoclave molding process are provided in later chapters.

2.4.3 Volume/Void Fraction Analysis

Consolidated composite parts have to be void free and have a certain volume fraction of fibers and material to ensure optimum mechanical properties. Volume fraction and voids within the composite part are determined by the volume fraction analyzer as shown in Figure 2.15. Samples are cut from the final plaque on a diamond


Figure 2.14 Autoclave



Figure 2.15 Equipment for Volume Fraction/Void Analysis

saw. These samples are then mounted in an acrylic mold and polished in successive steps using a 80 grit belt sander, Struers Abrahim Automated Polisher (240, 320, 1000, 2400 and 4000 grit), LECO GP20 Grinder/Polisher (5 microns and 1 micron) and a Buelher Vibromet (0.05 micron). Details of polishing and cleaning are provided in later chapters. The polished surface of the sample is placed on an Olympus microscope, which is viewed with a video camera. Images from the video camera are sent to a video monitor and to an Amiga personal computer in order to digitize random images of the sample surface. These images are then manipulated with brightness and contrast, so that the voids appear as dark regions. These dark regions are then analyzed as a void fraction of the total surface area by using the ONVFA (Optical Numeric Volume Fraction Analyzer). This analysis method uses the grey levels from a histogram to determine the void fraction. The same arrangement is also used to determine volume fraction of fibers except the digitized images need not be altered for brightness and contrast.

2.4.4 Mechanical Testing

Mechanical testing for the composite parts consists of short beam shear, 3-point flexure, and Mode II fracture analysis. For all three tests the United SFM Testing Machine is used. It is composed of two interconnected yet separate components :

- a) The Loadframe : The actual testing of a specimen takes place here.
- b) The Console : It contains the computer, which processes and stores data, and controls the loadframe.

The power source is a variable speed DC motor. Testing speed is controlled by two feedback loops. A DC tachometer provides instant feedback of motor speed to stabilize the servo loop and provide coarse control. The microcomputer senses and provides precise control of position and speed, strain, or load and load rate as required. Every testing methodology has a separate testing fixture, which is adaptable to the loadframe. Prior to the test, the fixture is attached to the loadframe along with an appropriate load cell.

MATERIAL PROPERTIES

3.1 INTRODUCTION

In this chapter, the different materials used for manufacture of water-based composites will be discussed. An in-depth presentation of the material properties and material selection procedure will be made. It is exigent to understand the various physical properties like particle size, fiber diameter, thermal properties, viscosity etc. for optimal operations of the prepregging, consolidation and characterization processes.

3.2 FIBER REINFORCEMENT

Various types of fiber reinforcements are available in the market today. Selection can be based upon processing, final properties of composite and compatibility with matrix. Commonly used fibers are glass, carbon, and Kevlar fibers. For our process, it is essential for the fibers to be free of sizing or have one applied at very low concentrations so as to be spreadable. Unsized carbon fibers meet this criterion most adequately. For this research Hercules Magnamite[•] Type IM7 12k tow carbon fibers were used.

3.2.1 Magnamite[•] Carbon Fiber Type IM7

Magnamite[•] Type IM7 12k tow carbon fiber is a continuous, high performance,

intermediate modulus, PAN-based fiber having 12,000 filament-count tows. The fibers are provided in an unsized state, so as to facilitate spreading. Presence of any sizing on the fiber surface will inhibit spreading by acoustic waves. This type of fiber is ideal for prepregging and filament-winding processes. It has a high tensile strength, shear strength and modulus, so can be used in stiffness-critical and strength-critical applications. Typical properties of the fiber are as given in Table 3.1

 Table 3.1 Typical Physical Properties of IM7 12k Carbon Fiber Tow

FIBER PROPERTIES	U.S. Units S.I. Units				
Tensile Strength	800,000 psi	5,518 MPa			
Tensile Modulus	44 x 10° psi	303 GPa			
Ultimate Elongation	1.86 %	1.86%			
Density	0.0643 lbs/in ³	1.78 gm/cm ³			
Typical Epoxy Composite Properties @ R.T. ¹					
Tensile Strength ²	630,000 psi	4,341 MPa			
Tensile Modulus ²	40.0 x 10° psi	276 GPa			
Ultimate Elongation	1.50%	1.50%			
Compression Strength	265,000	1,826 GPa			
Compression Modulus	23 x 10° psi	1,633 MPa			
Flexural Strength ³	237,000 psi	1,633 MPa			
Flexural Modulus ³	24.1 x 10° psi	166 GPa			
SBS Strength'	18,700 psi	129 MPa			
Yarn/Tow Characteristics					
Filament Diameter	0.197 mils	5 μ			
Filament Shape	Round	Round			
Twist	None	None			
Tow Cross-Sectional Area	3.90 x 10 ⁻⁴ in ²	0.25 mm ²			

1. All values are based on 3501-6 resin

2. Tensile values are normalized to 100% $V_{\rm f}$

3. Values are normalized to 62% V_f

3.3 MATRIX

In this thesis, emphasis is being placed on prepregging using water based epoxy resin systems. Prior to outlining the properties and features of the selected materials it is essential to have a brief knowledge of colloidal dispersions, which are the basis for water dispersed epoxy resins.

3.3.1 Colloids⁽¹⁰⁾

By definition colloids are liquids having dispersions of particles in the size range of $0.01-1\mu m$. The particles remain in suspension by two modes of stabilization, namely:

1. Electrical Double Layer Stabilization

2. Steric Stabilization

3.3.1.1 Electrical Double Layer Stabilization

Electrostatic repulsion arises from the presence of ionized moieties at the particle surface. In the region around the surface a charge cloud is formed, which is also known as the electrical double layer (EDL) and the charge cloud consists of evenly distributed opposite charges, known as counterions. See Figure 3.1 for a schematic representation of the model. The Stern Layer is a small space separating the ionic atmosphere around a surface, the actual double layer, from the "steric" wall of the charged plane just adjacent to the surface. The overlap of the counterion clouds leads to repulsion between ions of the same charge, and hence to a repulsion of the particles.



Figure 3.1 Model for Electrical Double Layer Stabilization





3.3.1.2 Steric Stabilization

Steric stabilization can be used in all liquid media. The basic requirements for steric stabilization are that the particle surface be covered by a contiguous layer of solvated chain molecules anchored to the surface either chemically or strongly physically absorbed. Steric stabilization agents are soluble macromolecules or non-ionic surfactants. A schematic representation of the steric stabilization model is give in Figure 3.2. When h < 2L, the layers interfere with each other and so have either to interpenetrate or indent, or undergo a combination of the two. This leads to a change in the local osmotic pressure and free energy. This may be attractive or repulsive in nature. When h < L, there is an additional contribution to the steric potential due to loss of configurational freedom experienced by anchored chains. This force is purely repulsive in nature and hence gives rise to steric stabilization.

3.3.2 Material Selection

Since this thesis encompasses prepregging via aqueous based resins, only those materials will be discussed that can be obtained as a water-based dispersion.

3.3.2.1 Waterborne Epoxy Dispersions

A variety of waterborne epoxy dispersions are currently available. They will adhere to a wide variety of substrates and when properly cured will develop high strength and resistance properties. Non-ionic reactive surfactants such as polyoxyethylene, polyols etc., are used to effect dispersion of epoxy resins in water. These dispersions are easily blended with other waterborne chemistries to produce hybrid systems. Rhône-Poulenc has developed a wide variety of such waterborne epoxy dispersions. The term epoxy or oxirane refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms which are also bonded in some way^[11]. The most widely used family of epoxy resins are known as "Bis A epoxies" based on the condensation reaction of bisphenol A and epichlorohydrin. A theoretical Bis A epoxy molecule is as shown in Figure 3.3.

BISPHENOL A BASED EPOXY



Figure 3.3 Theoretical Bis A Epoxy molecule

These resins come in different molecular weight series. As molecular weight increases, the epoxy equivalent weight and the number of hydroxyl groups available for reaction increases. Also polyfunctional epoxies are also available in which there are more than two epoxy groups per molecule. Advantages of these systems are as follows:

- Excellent volatile release.
- Adhesion to a wide range of substrates.
- Can be formulated to be formaldehyde free.

- Excellent electrical properties.
- Compatible with other resin types.
- Two phase for longer pot life.
- Shear stable.
- Can be used with conventional epoxy curatives.
- Uniform particle size.
- Low water sensitivity.

Since a variety of waterborne epoxy resins are available, selection for the most suitable dispersions system was made based on comparing its utility for prepregging in terms of ease of coating, comparatively low viscosity, high mechanical properties, simplistic curing cycle and compatibility with elastomer latexes. Based upon this selection criterion Epi-Rez[•] W60-3515 epoxy resin dispersion was chosen.

3.3.3 Epi-Rez[•] W60-3515 Epoxy Resin Dispersion

Epi-Rez W60-3515^[11] is a non-ionic, aqueous dispersion of a bisphenol A epoxy resin with an equivalent weight of 220-260. It has a moderate viscosity and is mechanically stable. No organic solvents are present. It is completely water reducible, providing wide latitude for viscosity reduction.

3.3.3.1 Performance Highlights/Features

- High epoxy functionality
- High solids
- Completely water reducible
- Compatible with most latex resins and some waterborne phenolic resins
- Good water resistance

• Good chemical resistance

3.3.3.2 Uses

- Industrial textile binders or finishes
- Adhesives
- Fiberglass reinforced plastics
- Coating and electrical dip coatings and varnishes
- Performance modifiers for other waterborne resins

3.3.3.3 Typical Properties

- Viscosity at 25°C, cps 11,000
- Non-volatile, % 63
- Volatile portion Water
- Pounds/Gallon 9.2
- Particle size, average, microns <3
- pH 3.7
- Weight per Epoxide, on solids 250

When applied at room temperature, Epi-Rez W60-3515 coalesces to form a clear, continuous, tacky film after evaporation of water. A DSC and TGA analysis of the Epi-Rez W60-3515 dispersion are as shown in Figures 3.4 and 3.5, respectively.

3.3.3.4 Curing agents

Dicyandiamide is used as a curing agent with W60-3515 to provide extended pot life formulations which cure at 300-350°F to form highly crosslinked systems suitable for service at high temperature. Dicyandiamide is a high functionality (4-5) curing agent having a molecular weight of 84.08 and a molecular formula $HN-C-(NH_2)-NH-C-N$.



Figure 3.4 DSC Analysis of Epi-Rez W60-3515



Figure 3.5 TGA Analysis of Epi-Rez W60-3515

It is available as odorless, white rhombic leaflets or plates or monoclinic prisms. It has a melting point of 412-414°F, specific gravity of 1.404 @14°C and solubility in water 2.26%@ 13°C. 2-methyl imidazole catalyst is used as the dicy accelerator. It has a molecular formula of $C_4H_6N_2$, melting point of 142°C to 143°C and is available as a white crystalline solid. The formulation with the above mentioned curing agent and accelerator is ideal for prepregs. A typical formulation for the epoxy varnish is as given:

Material	Parts by Weight	
Epi-Rez W60-3515	100	
Dicyandiamide	3.50	
2-methyl imidazole	0.10	
Deionized Water	13	

3.3.4 Carboxylated Styrene Butadiene Rubber (CSBR) Latex

Selection of an appropriate elastomer as the second coating particle is based upon its compatibility, stability and cured state properties when added to the epoxy resin dispersions. Research work done at Rhône-Poulenc indicated that carboxylated styrenebutadiene rubber (CSBR) is fairly compatible with epoxy resin W60-3515. CSBR is available as a latex from Gencorp Polymer Products as Gen-Flo^{*} 3000 series latexes. Gen-Flo^{*} 3000 is a carboxy-modified, formaldehyde free, styrene/butadiene latex designed for non-woven and saturation application. It has a chemical formula : $[-(C_4H_6)_x-(C_8H_8)_y-(R-COOH)_z-]_n$. The recommended uses of this product are toweling, laminated fabrics and bedding fabrics. Typical properties of this material are as given in Table 3.2. DSC/TGA analysis of CSBR latex are as shown in Figures 3.6 and 3.7.

PHYSICAL PROPERTIES		CHEMICAL/	
		MECHANICAL PROPERTIES	
Solids, % by weight	50.7	Mechanical Stability	Excellent
Wet Weight/Gallon	8.3	Multivalent Ion Stability	Excellent
Dry Weight/Gallon	4.2	Shelf Life	Excellent
Specific Gravity	1.0	Foam	Low
рН	9.0	Odor	Low
Brookfield Viscosity	150	Emulsifier	Anionic
Surface Tension (dyn/cm)	46		
Glass Transition Temp, °C	-37		
Particle Size	0.18-0.19 μ		

Table 3.2 Typical Properties of CSBR



Figure 3.6 DSC Analysis of CSBR



Figure 3.7 TGA Analysis of CSBR

Epoxies are inherently brittle materials, only slightly tougher than inorganic glass. In order to mitigate the brittleness of epoxy materials, a soft rubbery inclusion is dispersed in the brittle epoxy matrix to create a multi-phase system. During crack propagation, the crack front requires a lot more energy to pass through the soft rubbery inclusions, than it would take in passing through the brittle epoxy matrix. Thus, as the concentration of the rubbery inclusions increases, the fracture energy for the material also increases and makes it a tougher part. Increase in fracture energy reaches a maximum with the increase of elastomeric particles, and then begin to decrease. This decrease is closely related to the resin morphology as it transfers from a "particulate" to a "blend" morphology. Other mechanical properties like flexural strength, flexural modulus and short beam shear strength all go down with the increase in the concentration of the elastomeric additives. This is all due to the increase in the quantity of the "softer" second phase^[5]. Typical morphological studies of the fracture surfaces of rubbermodified epoxy matrixes indicate gross plastic deformation in the matrix and a highly porous structure in the resin. These holes results from the cavitation of elastomer particles in response to the dilational stress field, as the crack propagates through the material. Figure 3.8 shows the typical morphology of the fracture surface of a rubber modified epoxy/carbon composite^[5].





Figure 3.8 Fractograph of F85/Graphite Composite Sample

Chapter 4

SAMPLE PREPARATION

4.1 INTRODUCTION

In this chapter, the complete set of experimental details for the process for manufacturing of multi-component water based composite materials will be discussed. The composite parts have varying concentrations of a second elastomer phase in the epoxy matrix. These multi-phase composite materials were mechanically and morphologically characterized.

4.2 DISPERSION BATH PREPARATION

Prior to manufacturing prepreg tape by using the continuous prepregger, a the epoxy resin dispersion has to be mixed with the catalyst and accelerator and then diluted with deionized water to give the right concentration of the dispersed solids.

4.2.1 Matrix Dispersion Preparation

Epi-Rez W60-3515 is supplied as a non-ionic, aqueous dispersion of a bisphenol "A" epoxy resin having approximately 63% by weight of solids. This colloidal solution does not have any catalyst to promote cross-linking reaction during the consolidation cycle of the prepreg tape. Therefore, catalyst and accelerator has to be added to it. The catalyst used is dicyandiamide and the catalyst accelerator is 2-methyl imidazole. The procedure is given below:

Materials

Parts by weight, as supplied:

- Epi-Rez W60-3515 : 100.0
- Dicyandiamide : 3.5
- 2-methyl imidazole : 0.1
- Deionized or distilled water : 13.0

Mixing Procedure

- Heat the deionized or distilled water to 70-80 °C.
- Add the dicyandiamide (dicy) to the warm water and agitate until completely dissolved. Additional heating will be required to maintain the required temperature of 70-80°C.
- When solution is complete, add the 2-methyl imidazole and dissolve.
- Add the warm dicy solution to the epoxy dispersion (W60-3515) and agitate slowly at room temperature until well mixed (30-60 min). If the dicy solution cools and begins to crystallize before it is added to the dispersion, it should be reheated to 70-80 °C.
- An induction period of at least one hour is required prior to use.

4.2.2 Dispersion Dilution

It has been observed that a good composite part having a V_f of 60-70% is obtained when the coating on the prepreg tape is around 25-30% by weight of epoxy matrix. Such levels of coating cannot be achieved with the existing concentration of the solution. To attain lower coating levels, the as-supplied epoxy resin dispersion has to be diluted with deionized water. The level of dilution was determined by a simple experimental procedure, which is described as below:

- Take 6-6.5" length of carbon fiber tow.
- Spread the to about an inch in width and weigh.
- Fill a flat pan (6" x 4" x 2") with the epoxy dispersion.
- Different levels of dilution are maintained in the pan by the addition of deionized water. Dilution is carried out per volume.
- Dip tape lengths in the dispersion for around 15 seconds.
- Remove water by drying in an oven and measure the coating pick-up by weighing.

A graphical representation of the results is as given in Figure 4.1. From the graph it is evident that at a volumetric dilution level of 6:1, a coating of around 30% by weight will be obtained. When the process was run, this dilution level did not give the desired level of coating. The main reason was that the residence time of the fibers in the bath was around 6-7 seconds in comparison to 15 seconds taken during the dipping step. Eventually it was found that a dilution level of 1:1 gave the optimum coating level of 25-30% by weight of epoxy resin in the prepreg tape.

The prepregging process was run with the diluted epoxy resin dispersion. In subsequent runs, CSBR latex was added to the diluted dispersion so that a coating medium containing 5, 10, 15 and 20% of CSBR by weight were obtained and prepreg tape were produced with each of these dispersion mixtures. Addition of CSBR latex to the dispersion to give the desired concentration is based upon the following formula:

$$V_{SL} = \frac{V_{ES} \rho_{ES} W_{ES} W_{SM}}{W_{EM} W_{SL} \rho_{SL}}$$

where V_{sL} is the volume of CSBR latex added to epoxy resin dispersion

 V_{ES} is the volume of epoxy resin dispersion



Figure 4.1 Coating of 12k IM7 Carbon Fibers with EpiRez W60-3515 at different Dilution Levels

 $\rho_{\rm ES}$ is the density of epoxy resin dispersion

 W_{ES} is the weight fraction of solid epoxy in dispersion

 W_{SM} is the weight fraction of CSBR particles in epoxy resin/CSBR mixture

 W_{EM} is the weight fraction of epoxy resin particles in epoxy resin/CSBR mixture

 W_{SL} is the weight fraction of CSBR particles in CSBR latex

 $\rho_{\rm SL}$ is the density of CSBR latex

4.3 PREPREG TAPE PREPARATION

The process is operated with the matrix dispersion as the coating medium to give prepreg tape with epoxy resin coated at a level of 25-30% by weight and CSBR coated at a concentration of 0, 5, 10, 15 and 20% by weight.

4.3.1 Processing

A spool of Hercules[•] IM7 12k unsized carbon fiber is located on the feed spool frame. The fiber tow is unwound, threaded through the first guide slot and then passed over a pinch roller. Refer to Figure 2.3 for details. The tow is then alternately passed through the guide shafts on the spreader. From the spreader the tow passes through another pinch roller. It is then passed under the support roller in the dispersion bath, through a set of pinch rollers and through the heating zone. From the heating section the tow passes though a final guide slot and is then taken up by a spool located on the rotating arm of the automatic torque controlled winder. Once the threading of the fiber tow is done through the continuous prepregging unit, the diluted epoxy resin dispersion, with CSBR if required, is added to the dispersion bath. The convection oven is switched on and the temperature is maintained at 190°C. The infra-red lamps are switched on and the temperature at the fiber surface due to these lamps are about 120°C.

unwinding motor and the main motor are switched on. The setting of the main motor is around 1.75 on the dial, which corresponds to around 1 inch/sec in terms of line speed. The speed of the feed spool motor is adjusted manually, so that there is a slight slack between the spool and the first pinch roller. The take-up winder is started and its speed is adjusted manually to match that of the main motor. The torque controller adjusts the speed of the winder so as to maintain a constant torque between the last pinch roller and the winder. Winding of the prepreg tape is done in such a way that the spool is rotating along its axis, whereas the prepreg tape is traversing the entire length of the spool. In this way the geometric configuration of the wound spool is similar to that of the feed spool. The speed of all the rollers are synchronized by inter-linking them with chains.

Once the fibers are set in motion, the spreader is switched on. The underlying principle of the spreader is that when the fibers pass over the vibrating speaker, acoustic energy assist the fibers in separating into individual filaments. Normal operating conditions of the speaker are 38Hz and 11.2-11.6V to spread the fiber tow by 3"-4". It is also important to maintain zero tension in the fiber tow through the spreader to achieve the desired effect. This is done by using two pinch rollers at either end of the speaker to control fiber tow tension.

Spread fibers then pass through the dispersion bath. Suspended epoxy resin particles and/or CSBR particles along with water adhere to the surface of the carbon fibers. The possible mechanism responsible for coating is as follows:

4.3.2 Mechanism for Coating

Coating of the carbon fibers can take place by any of the following factors:

- Binding by physical interactions.
- Mechanical binding, including anchor effect.
- Binding by chemical interactions.

Whenever a liquid is brought into contact with a solid material, the liquid is said to undergo a *wetting* or *non-wetting* phenomenon. Consider a drop of liquid on a solid surface as shown in the model Figure 4.2.



Figure 4.2 Schematic Illustration of the Various Degrees of Wetting

As seen in the model, when a drop of liquid is placed on a solid surface, the liquid will either spread across the surface to form a thin film or it will spread to a limited extent but remain as a discrete drop on the surface^[10]. The final condition of the applied liquid on the surface is taken as an indication of the wettability of the surface by

the liquid or the wetting ability of the liquid on the surface. The quantitative measure of the wetting process is taken to be the contact angle, θ , which the drop makes with the solid. In the case of a liquid that forms a uniform film, i.e. where $\theta = 0^{\circ}$, the solid is said to be completely wetted by the liquid. If a contact angle is formed that lies between $0^{\circ} < \theta < 89^{\circ}$ constitutes partial wetting and anything greater than 90° forms a non-wetting system. The contact angle forms the basic framework for the thermodynamics of wetting. This is represented as Young's equation.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

where γ_{sv} is the interfacial tension of the solid in contact with the liquid.

 γ_{LV} is the interfacial tension of the liquid in contact with vapor.

 γ_{sv} is the interfacial tension of the solid in contact with vapor.

There are three types of wetting phenomena of importance: *adhesional*, *spreading*, and *immersional* wetting. *Adhesional Wetting* refers to the situation in which a solid, previously in contact with a vapor, is brought into contact with a liquid phase. During the process, a specific area of solid-vapor interface, A, is replaced with an equal area of solid liquid interface. The free energy change of the process is given by the work of adhesion:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

where W_a is the thermodynamic work of adhesion.

From this equation it can be seen that any decrease in the solid-liquid interfacial energy will produce an increase in the work of adhesion, while an increase in solid-vapor or liquid-vapor interfacial energies will decrease the energy gain from the process. Spreading Wetting applies to the situation in which a liquid and the solid are already in contact and the liquid spreads to displace a second fluid, usually air. Here the spreading coefficient $S_{L/S(V)}$ is defined as

$$S_{LS(V)} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL}$$

If this term is positive then the spreading liquid will spontaneously displace the second fluid and spread completely over the surface. If it is negative, then spontaneous spreading will not occur.

Immersional Wetting results when a solid substrate not previously in contact with a liquid is completely immersed in it, displacing all of the second fluid with which it was in contact prior to immersion. The free energy change in this case is given as:

$$-\Delta G = A(\gamma_{SV} - \gamma_{SL})$$

where ΔG is the free energy change.

A is the total surface area of the solid

From these relationships it is quite clear that the interfacial energies between a solid and any contacting liquid and the interfacial energies between the solid and the second fluid (usually air), control the manner in which the liquid will spread and adhere to the solid surface.

This process involves the immersional wetting of carbon fibers when they pass through the dispersion bath. From the above discussions it can be seen that larger the work of adhesion better is the adhesiveness. To examine the effect of wettability on adhesion strength, Zosel et al.^[12] showed that when the surface free energy of the adherent is lower than that of the solid adherend (i.e. wetting is not complete), but approaching that of the adherend, the adhesive strength is large and adhesion is favored. In general the formulation should have surface tension less than or equal to the surface free energy of the solid adherend to wet its surface. The surface tension for the given epoxy resin formulation is around 40 dynes/cm and that for CSBR is 46 dynes/cm, whereas the surface free energy for unsized IM7 carbon fibers is around 45-50 dynes/cm. In this case there is a positive thermodynamic driving force, and so the epoxy resin and the CSBR latex partially wet the fiber surface giving good adhesion.

Another factor governing the adhesion of the coating mixture onto the fiber surface, is the penetration of the fluid into the cavities, which are characteristic of the inherent surface roughness of the fibers^{[13], [14]}, while passing through the bath. Capillary driving forces via penetration through surface features are governed by the capillary penetration pressure ΔP , which can be described by the Zisman equation^[15] as shown:

$$\Delta P = \left(\frac{\gamma_1}{2} + \frac{1}{2b}\right) \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

where ΔP is the capillary penetration pressure

 γ_1 is the liquid surface tension of a homologous series of liquids

 $r_1 \& r_2$ are the principal radii of curvature of the pore interstices

b is a so-called solid-liquid interaction constant

Also in the process the fibers are in a spread condition, causing a larger exposure of surface area to the epoxy/rubber particles. Without spreading the fiber tow a coating level of 23% by weight was obtained, whereas with spreading a coating level of 29% by weight was obtained with the same dilution of 1.4:1 by volume of epoxy resin formulation in deionized water. This shows that spreading is also important to coating.

In many cases a sizing is applied to the carbon surface, so as to protect it from damage. This provides sites on the carbon fibers for chemical interaction between the sizing and the epoxy matrix to give a complex interface structure, which may result in a strong and in many cases irreversible bonding. For this study, use of unsized fibers have been made, therefore bonding by chemical interactions is not taken into account.

As the solid epoxy resin and/or CSBR particles are coated onto the fiber surface the concentration of the particles within the bath decreases. This results in a decrease in the amount of particles coated. This can be seen graphically by plotting the quantity coated onto the bare fiber surface versus time (Figure 4.3). From the best fit line, it can be seen that the coating concentration decreases from 21% by weight to around 18.5% by weight in about 16 minutes. In order to maintain a constant coating level it is observed that over a period of about five minutes the decrease in coating level is not substantial. So 5cm³ of fresh solution was added to the system every ten minutes to keep the coating level steady.

4.3.3 Heating

The coated prepreg tape has a significant amount of moisture in it. Moisture is removed in two stages within the heating section. The first section consists of a convection oven in which the prepreg tape is heated to 190°C for a residence time of 18 seconds at a line speed of 1 inch/second. Here most of the heat is used up in the removal of water. At these process speeds, the oven is undersized and heating must be supplemented by use of an additional pair of infra-red lamps located in the second section of the heating unit. The IR lamps heat the fibers to 120°C for about 10 seconds. In this



Figure 4.3 Coating versus Time

section the moisture is removed and the epoxy resin particles melt onto the fiber surface, completely wetting the surface and forming an even coating on every individual fiber. Figure 4.4 contains SEM photographs of the coated prepreg tape after it has passed through the heating section. As is evident from the picture, the coating is very even and there is complete wetout of the fiber surfaces. Prepreg tape thus produced is very drapable and tacky. Despite this additional heating, moisture is not completely removed from the prepreg tape. Figure 4.5 is a TGA analysis of the prepreg tape. From the analysis of data for different samples, it can be seen that approximately 0.04-0.12% by weight water is still present in the prepreg tape. It is mandatory to remove this moisture prior to curing the epoxy resin, otherwise the moisture would vaporize creating excessive voids in the final part. Removal of this moisture will be touched upon later.

4.4 COMPOSITE MANUFACTURING PROCESS

This prepreg tape is now ready for consolidation into a multi-laminate composite. Several steps are involved in the composite part manufacturing operation.

4.4.1 Prepreg Tape Winding

Prepreg tape is unwound from the spool onto a specially fabricated aluminum frame. The dimensions and details of the frame and the winder are given in Figure 2.13. A 1.18" x 8" non-porous teflon tape is fixed to one end of the frame so that it traverses the entire width. The purpose of this strip is to act as the initial crack propagator in the ENF samples. Figure 4.6 is a photographic representation of the winding system. Winding onto the frame is done in the rotary direction and in the traverse direction. Adjustments to the speed of the two motors are made in such a way that there is no gap between adjacent strips of prepreg tape traversing the length of the frame. As mentioned



Figure 4.4 SEM Photographs of Prepreg Tape



Figure 4.5 TGA Analysis for Prepreg Tape





Figure 4.6 Photographic Representation of Winding System

previously, the prepreg tape is very tacky. Care has to be taken while unwinding the tape from the spool, so that the prepreg tape layers do not stick together, entangle and break. A low motor speed allows for flexibility in operations and any hard-to-handle tacky part of the tape can be manually guided onto the frame. From calculations a traverse speed setting of 32 and a rotary speed setting of 20 rpm were selected. Appendix A contains details of these calculations. At the completion of this procedure a prepreg plaque of 6" x 8" in dimensions is obtained. The plaque is then heated in the oven at 65° C for about an hour to remove all the residual moisture. On an average, about 1 gm of water is lost from each 63-70 gm plaque. The plaque is now ready for consolidation in the autoclave.

4.4.2 Autoclave Molding

The part is placed in a vacuum bag as per arrangement shown in Figure 4.7. Details of vacuum bagging are as given.

- Two clean flat steel plates of dimensions greater than that of the plaque are covered with release ply. Bleeder cloth is added on top and wrinkles are removed.
- Cut two pieces of porous teflon having dimensions equal to that of the plaque. Place one teflon sheet on the bleeder cloth of one steel plate.
- Place the unconsolidated prepreg tape on the teflon sheet.
- Build a cork-dam around all four edges of the part with 1/8" thick cork-dam tape.
- Place the second teflon sheet on the part and tape the ends.
- Place the second plate on top of the part.
- Make a hole in the vacuum bag having dimensions equal to that of the vacuum adaptor.



Figure 4.7 Vacuum Bag Molding Schematic

- Place the entire arrangement along with the adaptor within the vacuum bag.
- Seal the edges of the bagging with tacky tape, so that it is completely airtight.

Place this part in the autoclave as per the arrangement shown in Figure 4.8. The part is then subjected to a consolidation cycle graphically represented in Figure 4.9

and which is as given below:

- Pull vacuum on the part.
- Pressurize the part to 150# @20#/min.
- Heat the part to 212°F @20°F/min for about ten minutes.
- Heat the part to 340°F @20°F/min.
- Maintain part at 340°F and 150# for about an hour.
- Fifteen minutes into the cycle remove vacuum from the part.
- After an hour cool the part to 100°F @10°F/min.
- At about 150°F, reduce the pressure to atmospheric pressure 20#/min.
- Remove the part from the autoclave once the curing cycle has ended.

This cycle is controlled through a program in the controls of the autoclave and is given in Appendix B. The part is then removed from the autoclave and can now be subjected to mechanical testing and micro-graphical analysis.


Steel Plate

Figure 4.8 Vacuum Bagging Arrangement in Autoclave⁶



Figure 4.9 Consolidation Cycle

4.5 SAMPLE CUTTING

Composite parts were prepared from solutions containing 0, 5, 10, 15 and 20% by weight of CSBR particles in the epoxy resin dispersion. These parts were then cut into test coupons in accordance with ASTM standards. All the samples were cut on a diamond saw. See Figure 4.10. For 3-point flexural tests, dimensions of the samples conformed to that given in Table 4.1. Typical dimensions for the test coupons are given in Figure 4.11^[16]. For short beam shear the sample dimensions conformed to that given in Table 4.2. See Figure 4.11 for typical dimensional details. For End Notch Flexural (ENF) testing the dimensions conformed to those given in Figure 4.12. Samples for DMA, fiber volume fraction and void fraction do not have any standard specifications and were cut from residual parts. Both volume fraction and void fraction can be analyzed from the same sample but they have to be cast in a plastic mold.

4.5.1 Sample Preparation for Volume/Void Fraction Analysis

4.5.1.1 Casting of Samples in Plastic Mold

- Cut small rectangular specimen of the composite part.
- Place the specimen in the mounting cup, so that the fibers are oriented in a longitudinal manner.
- Prepare the mounting material, by mixing well 1 part by volume of hardener with 2 parts by volume of epoxy resin powder for 30-60 seconds. Place the mounting material in vacuum bell jar to remove air particles. Care must be taken that the mounting material does not harden prior to pouring it into the cup.
- Carefully pour the material into the cup, so that the composite sample does not move.



Figure 4.10 Diamond Saw¹⁶



Figure 4.11 Sample Dimensions for Three-Point Flexure and Short Beam Shear Test¹⁶

Table 4.1 Sample Dimensions for 3-Point Flexural Testing Method per ASTM D790

Test Method I (3-Point Loading)													
Nominal Specimen Depth, mm (in.)	Specimen Width mm (in.)	Support Span-to-Dapth Ratio (See Note 7)											
		L/d = 16 to 1			L/d = 32 to 1		L/d = 40 to 1		L/d = 60 to 1				
		Specimen Langih, mm (in.)	Support Span, mm (In.)	Rate of Cross-head Motion (Procs- durs A), mm (in.)/ min ⁴	Specimen Length, mm (in.)	Support Span, mm (in.)	Rate of Cross-head Motion (Procs- dure A), mm (in.)/ min ⁴	Specimen Length, mm (in.)	Support Span, mm (in.)	Rate of Cross-head Motion (Proce- dure A), min (in.)/ min^	Specimen Length, mm (in.)	Support Span, mm (in.)	Rate of Cross-head Motion (Proce- dure A) svm (Pr.)/ min ⁴
0.8 (V/m)	25 (1)	50 (2)	16 (%)*	0.5 (0.02)	50 (2)	25 (1)	1.3 (0.05)	60 (2%)	30 (1%)	2.0 (0.05)	80 (2%)	48 (1%)	4.8 (0.19)
1.8 (1/14)	25 (1)	50 (2)	25 (1)	0.8 (0.03)	80 (3)	50 (2)	2.8 (0.11)	90 (3%)	60 (2%)	4.3 (0.17)	124 (474)	96 (3%)	9.4 (0.37)
2.4 (+2)	25 (1)	60 (21/2)	40 (1%)	1.0 (0.04)	100 (4)	80 (3)	4.1 (0.16)	120 (4%)	95 (3%)	6.4 (0.25)	185 (7%)	143 (5%)	14.2 (0.58)
3.2 (%)	25 (1)	80 (3)	50 (2)	1.3 (0.05)	130 (5)	100 (4)	5.3 (0.21)	180 (7)	130 (5)	84 (0.33)	247 (9%)	190 (7%)	18.8 (0.74)
4.8 (1/10)	13 (1/2)	100 (4)	80 (3)	2.0 (0.08)	191 (7%)	150 (6)	8.1 (0.32)	240 (9%)	191 (7%)	12.7 (0.50)	372 (14%)	286 (11%)	20.4 (1.12)
6.4 (14)	13 (1/2)	130 (5)	100 (4)	2.8 (0.11)	250 (10)	200 (8)	10.9 (0.43)	330 (13)	250 (10)	17.0 (0.67)	495 (19%)	381 (15)	37.8 (1.40)
9.6 (%)	13 (14)	191 (7%)	150 (6)	4.1 (0.16)	380 (15)	300 (12)	16.3 (0.64)	480 (19)	380 (15)	25.4 (1.00)	744 (29Ym)	572 (22%)	56.1 (2.24)
12.7 (14)	13 (14)	250 (10)	200 (8)	5.3 (0.21)	495 (19%)	410 (16)	21.6 (0.85)	640 (25)	510 (20)	34.0 (1.34)	991 (39)	762 (30)	76.2 (8.00)
18.1 (%)	19 (%)	380 (15)	300 (12)	8.1 (0.32)	740 (29)	610 (24)	32.5 (1.28)	940 (37)	760 (30)	50.0 (2.00)	1486 (58%)	1143 (45)	114 (4.40)
25.4 (1)	25 (1)	495 (19%)	410 (16)	10.9 (0.43)	990 (39)	810 (32)	43.4 (1.71)	1240 (49)	1020 (40)	67.8 (2.67)	1981 (78)	1524 (80)	152 (5.99)

^A Rates indicated are for Procedure A where strain rate is 0.01 mm/mm/min (0.01 in./m./min). To obtain rates for Procedure B where strain rate is 0.10 mm/mm/min (0.10 in./m./min), multiply these values by 10. Procedure A is to be used for all specification purposes unless otherwise stated in the specifications. See 9.1.3 for the method of calculation.

⁹ This support span-to-depth ratio is greater than 16 to 1 in order to give clearance between moving head and specimen support.

Table 4.2 Sample Dimensions for Short Beam Show Testing Method on per ASTM D2344

NOTE I-Reinforcements may be in the form of single fibers.

Note 1 — Reinforcements may be in the form of single fibers, strands, yarn, tows, woven cloth, nonwoven cloth, etc. Note 2 — The following are recommended support span to thickness and specimen lengths to thickness ratios; however, there are many specifications in existence with different required specimen thicknesses and span to thickness ratios which take precedence. The report should clearly specify the specimen nominal thickness and support span to thickness ratio used and the specification with which it complies. Specifications with span to thickness ratios from 3 to 1 up to 6 to 1 have been identified.

Reinforcements	Span/Thickness*	Length/ Thickness		
Glass fibers	5	7		
Graphile fibers	4	6		
Carbon fibers	4	6		
Stael Wire	4	6		
Boron filaments	4	6		
High modulus organic strands (aramid, ctc.)	4	6		

⁴ Span length equals specimen length for ring specimens. See

Fig. 1. Total length for flat specimens.



All dimensions are in mm

Figure 4.12 Sample Dimensions for ENF Testing^[16]

- Cure the material at room temperature for about 60-90 minutes.
- Remove the mounted sample from the cup.

4.5.1.2 Polishing of Sample Surface

- The base of the cast samples are sanded down to a flat smooth surface using an 80 grit belt sander. Also one of the edges of each sample is bevelled with this sander.
- The samples are placed in a rotary sample holder, such that the bevelled end is exposed.
- The holder is fixed to the rotary arm of a Struers Abrahim Automated Polisher. Polishing of the sample surfaces are successively done using 320, 600, 1000, 2400 and 4000 grit paper at 150 and 300 rpm, respectively, for about 2 minutes at each cycle. Each polishing cycle should remove scratches from the previous cycle.
- The samples are then polished in a LECO GP20 polisher using 5 microns and 1 micron aluminum oxide dispersions.
- These samples are then mounted in heavy steel holders and polished for about 12 hours in a Buelher Vibromet, which uses 0.05 micron dispersion for polishing the sample surface.
- Samples are then placed in an ultrasonic bath and cleaned using deionized water. At the end of the entire process the sample surface get a mirror like finish. See Figure 4.13 for a photograph of a typical sample.



Figure 4.13 Polished Sample for Volume/Void Fraction Analysis. Composite Part Embedded in Plastic Mold.

4.6 SUMMARY

The process was run with coating medium containing 0, 5, 10, 15 and 20% by weight CSBR in epoxy dispersion. The prepreg tape produced at the end of each run was then consolidated into composite plaques, as per procedure outlined in the previous paragraphs. These plaques were then cut into samples for void/volume fraction analysis, mechanical testing and morphological studies. These tests would establish the validity of the process to coat two particles from an aqueous dispersion mixture, with the final composite having two distinct phases and the second phase being well dispersed in the matrix.

PROCESS MODELLING

5.1 INTRODUCTION

The water-based continuous prepregger is dependent upon a number of physical parameters. These parameters can be incorporated into process models to define the characteristics and dynamics of the unit operations involved. The entire process can be defined in terms of discrete operations : fiber motion, fiber spreading, coating and heating. The heating, aerosolization for coating and spreading phenomenon have been discussed in detail by Iyer^[4] and Padaki^[17] for dry powder prepregging processes. The aim of this chapter is to develop a process model for the heating unit and discuss the removal of moisture from the coated tape in light of heating bottleneck in the convection oven.

5.2 PROCESS MODEL DEVELOPMENT

Prepreg tape coated with epoxy resin and/or CSBR particles and a thin film of water enter the heating section. The purpose of the heating unit is to remove moisture from the prepreg tape. The tape passes as a very thin flat sheet through the convection oven, where the temperature of the fiber tow is raised to the boiling point of water by both convection and radiation. (Figure 5.1). The presence of water is very detrimental



Front View in x-Direction

Figure 5.1 Heating Arrangement in Convection Oven

in the consolidation step, since water vaporizes at the high consolidation temperatures causing excessive void formation in the final composite part.

The composition of the prepreg tape based upon a material balance carried out on the tape at the exit of the dispersion bath and prior to entering the heater is given in Table 5.1:

Material	Weight Percent	Volume Percent		
Carbon Fiber	42.42	30.14		
Epoxy Resin	17.42	19.14		
Water	40.16	50.72		

 Table 5.1 Composition of Prepreg Tape Prior to Heating

5.2.1 Process Data

Line speed	1 inch/sec		
Coating of solid, by weight	29.0%		
Dilution of solution in bath	1:1 by volume		
Weight of bare fiber	0.3583 gm/32"		
Density of epoxy resin solids	1.137 gm/cm ³		
Density of carbon fibers	1.783 gm/cm ³		
Oven Temperature	190°C		
Emissivity of IR lamp	0.39		
Emissivity of water	0.96		
Emissivity of aluminum	0.18		
Thickness of dry coated tape	0.252 mm		
Width of dry coated tape	2.30 mm		
Length of tape travel in oven	18"		
Thermal conductivity of air	0.02195 Btu-ft/hr -ft ² -°F		
Thermal conductivity of water	0.353 Btu-ft/hr-ft ² -°F		
Thermal conductivity of resin	0.35 W/m-°K		
Thermal conductivity of fibers	4.5 Btu-ft/hr-ft ² -°F		

5.2.2 Development of Equation

Consider the prepreg tape, shown in Figure 5.1, moving as a thin flat sheet through the convection oven at constant line speed. Individual fiber strands are all moving at the same speed. The temperature is constant in the y-direction. This tape is being heated with hot air over the entire surface of the fiber. It is also assumed that the bulk temperature of air, T_b , is constant. At any time, t, from the start of the heating operation i.e. when the prepreg tape enters the oven, the quantity of heat, dQ, transferred in a short time, dt, depends upon the surface area of the tape, the difference in temperature between the air and the surface of the tape and the heat transfer coefficient of air, h_c , such that^[19] :

$$\frac{dQ}{dt} = h_c A(T_b - T)$$
(5.1)

where T is the surface temperature of tape after time dt.

A is the surface area of tape after time dt.

The heat of conduction in the slab is given as:

$$dQ = mc_{d} dT \tag{5.2}$$

Equating equations 5.1 and 5.2 results in:

$$dQ = mc_n dT = h_A (T_h - T) dt$$
(5.3)

As explained earlier, part of the heat transfer in the oven is convective in nature. This can be either forced or natural. As the tape is moving within the oven some forced convective currents are also produced, which can result in heating of the tape. If the forced-convection effects are very large, the influence of natural-convection currents may be negligible, and similarly, when the natural-convection forces are very strong, the forced-convection effects may be negligible. The ratio of the Grashof's number to the square of the Reynold's number establishes the dominance of one mode of heating over the other^[18]. If the ratio is much larger than one, then natural convection is dominant and vice versa. In this case, the ratio was much greater than one indicating that the mode of heat transfer in the oven is predominantly natural convection.

In equation 5.3, the value for heat transfer coefficient is difficult to determine as it depends upon the units employed, physical properties of the fluids, dimensions of the apparatus, velocity of the fluid past the surface and often even on the temperature difference, ΔT ^[19]. For an accurate estimation of heat transfer by convection it is essential to employ point or local surface coefficients. However, for most engineering applications, it is quite safe to use average heat transfer coefficient values based upon the average of the local heat transfer coefficients over the entire surface area. For this model the average heat transfer coefficient will be used. Even when average heat transfer coefficients are used, its absolute value can fluctuate tremendously. For air, in case of heating or cooling, the average heat transfer coefficient can range from 1.2 to 57 Watt/m²-K. Thus the importance of a fairly accurate estimate of the average heat transfer coefficient is essential.

5.2.3 Experimental Evaluation of Heat Transfer Coefficient

The average heat transfer coefficient can be estimated experimentally by heating an aluminum slab in the oven from a certain inlet temperature to the set temperature of the oven. The experimental set up is as shown in Figure 5.2. Two aluminum slabs are taken having the dimensions L x w x h. A k-type thermocouple is placed between the



Flow of Air from Convection Oven

Figure 5.2 Experimental Set-Up for Evaluation of Heat Transfer Coefficient

two slabs, such that the sensing tip is in the center of the slab, far away from the edges. The convection oven is heated to a certain set temperature, such that the bulk temperature of air is T_b . The slabs are held tightly together with insulating tape stuck around the edges. It is assumed that heat transfer from the sides of the slabs is negligible, as the slabs are fairly thin. There is continuity of heat flow at the faces of the slabs that are in contact with the flowing air. It is also assumed that temperature remains constant in the yz-plane. The energy equation reduces to :

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$
 (5.4)

where α is the thermal diffusivity of the material

The following initial and boundary conditions hold true:

Initial Condition
$$t = 0$$
 $0 \le x \le h$ $T = T_i$ Boundary Condition 1For $t > 0$ $x = 0$ $\frac{\partial T}{\partial x}\Big|_{x=0} = 0$ Boundary Condition 2For $t > 0$ $x = \pm h$ $-k \frac{dT}{dx}\Big|_{x=\pm h} = h_c(T-T_b)$

where \mathbf{k} is the thermal conductivity of the aluminum slab.

 h_c is the heat transfer coefficient.

Equation 5.4 can be converted into dimensionless form by substituting the dimensionless variables $\xi = x/h$, $\tau = t\alpha/h^2$ and $\Theta = (T_b - T)/(T_b - T_i)$, such that the equation now becomes:

$$\frac{\partial \Theta}{\partial \tau} = \frac{\partial^2 \Theta}{\partial \xi^2}$$
(5.5)

and the initial and boundary conditions now become:

I.C. $\tau = 0$ $0 \le \xi \le 1$ $\theta = 1$

- B.C. 1 For $\tau > 0$ $\xi = 0$ $\frac{\partial \Theta}{\partial \xi}\Big|_{\xi=0} = 0$
- B.C. 2 For $\tau > 0$ $\xi = \pm 1$ $\frac{\partial \Theta}{\partial \xi}\Big|_{\xi=\pm 1} = -Bi\Theta$

By separation of variables and only considering the transient part of the equation, the solution of Equation 5.5 with the given conditions is as given below:

$$\frac{T_b - T}{T_b - T_i} = \sum_{n=1}^{\infty} B_n \exp\left(-\frac{\lambda_n^2 \alpha t}{h^2}\right) \cos\left(\frac{\lambda_n x}{h}\right)$$
(5.6)

where B_n are the Eigen Coefficients and has the form $2\sin \lambda_n/(\lambda_n + \sin 2\lambda_n/2)$

 λ_n are the Eigen Values and solutions lie in $\lambda_n tan \; \lambda_n$ = Bi

x is the Slab Location

A program to solve equation 5.6 using Fortran is given in Appendix C. The program solves the given equation for an inputed value of the heat transfer coefficient and generates the temperature at x = 0 versus time. The eigen values of the above equation are calculated in a sub-routine in the program using the Newton Raphson

Iteration method and the values are converged to a difference of less than $1 \ge 10^{-8}$.

The oven is heated to a preset temperature and allowed to stabilize for some time at this temperature. The two slabs, conforming to the arrangement as shown in Figure 5.2, are placed in the oven and the temperature at the center of the slab ,i.e. at x = 0, is noted after short intervals of time (after every 5 seconds). This process is continued until the temperature at the center is near that of the oven set point. Data is plotted for the experimental results of temperature versus time. (Figure 5.3). The program generates theoretical values of center line temperature versus time at different values of heat transfer coefficient, with all the other physical parameters like thermal diffusivity and thermal conductivity of aluminum, initial temperature, bulk temperature and half thickness are constant. A heat transfer coefficient of 25 Watts/m².^oK was found to give the best fit with experimental data, with the conductivity and thermal diffusivity of aluminum as 201 Watts/m-^oK and 8.5 x 10⁻⁵ m²/sec, respectively, half thickness as 0.00635 m, bulk temperature as 129°C and initial temperature as 22°C. (Figure 5.3).

It was discussed earlier that in the convection oven, some heating also takes place due to radiation. So it is important to evaluate the heat transfer coefficient due to radiation and see if there is an overall impact on prepreg tape heating due to radiation. The heat transfer coefficient due to radiation in a grey body is evaluated by the given formula¹⁸:

$$\mathbf{h}_{\mathrm{r}} = \mathscr{F}_{1-2} F_{\mathrm{T}} \tag{5.7}$$

where h_r is the radiative heat transfer coefficient

 \mathcal{F}_{1-2} is the gray-body shape factor

 $F_{\rm T}$ is the temperature factor



Figure 5.3 Experimental Evaluation of Average Heat Transfer Coefficient: Temperature versus Time

The value of h_r based upon Equation 5.7 is only 6% of the heat transfer coefficient due to convection, therefore heating due to radiation is very minimal and so can be neglected.

5.2.4 Moisture Removal in Convection Heater

Prior to using Equation 5.3 for the evaluation of time taken to raise the prepreg tape to 100°C and amount of water removed after that, it is essential to ascertain the mode that limits heat transfer to the tape. For this the Biot number has to be evaluated. The Biot number^[18] measures the significance of internal (heat conduction within the solid) to external (heat convection to the surface of the solid) heat transfer resistances and is given by :

$$Bi = \frac{hL}{k_s}$$
(5.8)

- where h is the heat transfer coefficient which includes contribution from convection and radiation.
 - k_s is the thermal conductivity of the solid.
 - L is the significant length dimension obtained by dividing the volume of the body by its surface area.

If the Bi \lt 0.1 then the resistance to heat transfer is due to external heat transfer i.e. convection. The thermal conductivity of the solid for the prepreg tape is a combination of the conductivities of water, resin and carbon fibers. It is assumed that the resistance to heat flow in the water/resin system is parallel in nature, whereas that of the fibers is in series with the two. The thermal conductivity of the water/resin system was evaluated using a parallel resistance analysis and this came out to be 0.534 Watts/m-°K. Relationships for conductivity through two-phase materials have been discussed as Generalized Rayleigh-Maxwell Relationships^[20]. In the case of parallel fibers and transverse heat transfer, the Rayleigh form of the relationship is as follows:

$$k_{c} = 1 + \frac{2\left(\frac{k_{f}}{k_{m}} - 1\right)V_{f}}{\left(\frac{k_{f}}{k_{m}} + 1\right) - \left(\frac{k_{f}}{k_{m}} - 1\right)V_{f}}$$
(5.9)

where k_c is the thermal conductivity of the composite.

 k_f is the thermal conductivity of the fiber.

 k_m is the thermal conductivity of the matrix (water/resin system in this case).

Equation 5.9 was used to evaluate the thermal conductivity of the prepreg tape and this was 2.03 Watts/m- $^{\circ}$ K. Based upon the evaluated values of heat transfer coefficient and thermal conductivity, the Biot number was calculated to be 0.0019 which is much lesser than 0.1. This implies that external heat transfer resistances are rate controlling and conduction across the thickness of the tape is not significant. In this case a lumped model for heat transfer gives a fairly accurate representation of the physical situation existing within the oven. Therefore, integrating Equation 5.3 from zero time, when the temperature of the prepreg tape is T_i , to any time t, when the temperature of the prepreg tape is T, gives the following equation:

$$t = \frac{mc_p}{h_c A} \ln \left(\frac{T_b - T_i}{T_b - T} \right)$$
(5.10)

where m is the mass of the material in lb/sec.

 c_p is the specific heat capacity in Btu/lb-°F.

A is the surface area of the material in ft^2/sec .

From Equation 5.10, the time taken for the tape to reach 100°C is around 13.5 seconds. After the tape has reached this temperature, all of the heat transferred is used up in evaporating water from the tape surface. For the remaining time approximately 5-6% by weight moisture is removed from the convection oven. Hence, the convection oven does not have the capacity to remove the moisture content from the prepreg tape. This phenomenon was also observed physically, since the tape produced with this configuration had a lot of moisture on it.

5.2.5 Moisture Removal by IR Lamps

Since the convection oven is too small in size to remove water from the prepreg tape completely, heating is supplemented by two IR lamps. Each lamp is provided with a 375-watt IR bulb. The mathematical formula used to evaluate the heat transfer due to radiation for each of these bulbs is as given in Equation 5.11^[21].

$$Q = \frac{F_A A_1 \sigma}{\left(\frac{1}{\epsilon_1}\right) + \left(\frac{1}{\epsilon_2}\right) - 1} (T_1^4 - T_2^4)$$
(5.11)

where Q is the heat flow or net heat exchange

 ϵ_1, ϵ_2 are the emissivities of surfaces 1 & 2, respectively

- F_A is the geometric factor
- A_1 is the surface area of the emitting surface

 T_1, T_2 are the absolute temperatures of surfaces 1 & 2, respectively

 σ is the Stefan-Boltzmann constant

Based upon Equation 5.11, each of these lamps is capable of supplying a

maximum quantity of 73.35 Btu/hr heat to the prepreg tape, when the lamp bulb is about 2.5" above the surface of the tape. The first of the two lamps, which is located 2.5" above the surface of the tape, removes around 95% by weight moisture. The second lamp is adjusted in such a way that some moisture is removed, but the resin is not effected. It was physically observed that if the second lamp was placed very near the surface of the tape the resin would begin to smoke and smell, indicating some reaction or burning of the resin. It was therefore decided to place the second lamp well above the tape, so as to remove maximum moisture and at the same time maintain the integrity of the matrix material. As will be discussed in the later chapter, the final prepreg tape has some moisture, which is removed by heating in the convection oven at a lower temperature prior to consolidation of laid up part.

RESULTS AND DISCUSSIONS

6.1 INTRODUCTION

The primary objective of this study was to develop a continuous prepregging process for the manufacture of two-phased composite materials using a two mixture aqueous dispersion as the coating medium. Chapters prior to this deal with the development of the process, consolidation of the prepreg tape into composite parts and preparing samples for characterization of the parts to see if the two coated particles exist as distinct phases in the composite part. As mentioned earlier, the composite part is manufactured of two materials in the matrix, i.e. the epoxy resin and styrene/butadiene rubber (CSBR). Epoxies are inherently brittle materials and so have very low fracture energies. Addition of CSBR particles to create a multi-phase system, may result in a soft rubbery inclusion dispersed in the brittle epoxy matrix, which if properly bonded to the epoxy, increases its fracture energy. Forthcoming topics will deal with the different experimental techniques used to identify the two phases, evaluate the effect of CSBR on the epoxy matrix and discuss these results in the light of earlier work done around rubber-toughened epoxy matrixes.

6.2 VOLUME/VOID FRACTION ANALYSIS

The stiffness and strength parameters of fiber composites are determined by the internal packing geometry of the fibers and the constitutive behavior of the fiber and the matrix^[16]. The geometry of the composite part is generally defined by a transverse plane, in which the fibers appear as circles embedded within the matrix. The volume fraction of the constituents of a composite may be determined by chemical matrix digestion or by photomicrographic techniques. Emphasis will be placed on the latter of the two techniques, as it is the preferred method of analysis in this study. This technique also can be used to determine the void content within the part. It is imperative that an adequate number of samples are taken randomly throughout the composite part and enough surface should be examined under the microscope to make a definitive analysis of the voids and fiber content. For a good composite part it is necessary for it to have a void content of less than $\sim 1\%$ to carry out mechanical testing on it. Also for the mechanical analysis to be consistent from part to part, the fiber volume fraction for most plaques must be fairly consistent. Details for preparation of samples for volume/void fraction analysis are given in section 4.5.1 and the equipment set-up/operations is given in section 2.4.3.

Thirty images of the polished surface for each sample were scanned by the digitizer and the images were then analyzed by the Optical Numeric Volume Fraction Analyzer (ONVFA). Results of this analysis are given in Table 6.1. It can be seen that the void fractions of all the composite parts are well within the prescribed limit of less than $\sim 1\%$. A typical micrographic image at a magnification of 65 is as shown in Figure 6.1.

CSBR Content (%)	Void Fraction (%)	Vol Fraction (%)
0	0.41	65.57
5	0.70	65.48
10	0.64	67.92
15	1.08	63.56
20	0.52	61.57

 Table 6.1
 Volume/Void
 Fraction
 Analysis

6.3 MECHANICAL TESTING

Mechanical testing for the composite parts consists of three-point flexure, short beam shear and Mode II fracture analysis. All these tests are carried out on the United SFM Testing Machine. Details of this equipment are given in Chapter 2.4.4.

6.3.1 Three-Point Flexure Test

The primary objective of the three-point flexure test as shown in Figure 6.2 is to determine the stress-strain response of the laminated composite part in bending^[16]. In this test, the central load, applied by the central loading pin, is monitored versus strain, which is measured by a deflectometer located on the tension side of the beam (bottom surface). Commonly, a unidirectional laminate with the fiber direction along the beam axis is loaded in bending to determine the *flexural modulus* in the fiber direction, the *flexural strength* in the fiber direction and the *ultimate flexural stress and strain*. The flexural modulus and strength is a combination of the tensile and compressive properties of the material.



Figure 6.1 Micrograph of Polished Composite Surface at Magnification of 65X



Figure 6.2 Arrangement for Three-Point Flexure Testing

All the testing was done as per ASTM D790-86. Five sample coupons were tested from each composite plaque containing 0, 5, 10, 15 and 20% by weight CSBR particles in the epoxy matrix. Consolidated results of this test for the different samples are given in Table 6.2. A graphical representation of the flexural strength and flexural modulus with varying concentration of CSBR particles are given in Figures 6.3 and 6.4, respectively. Data output in graphical form for load versus extension as generated by the UTS software is given in Appendix D.

 Table 6.2 Flexural Properties of Composites with varying CSBR Concentration

CSBR Content (% by wt)	Flexural Strength (MPa)	Standard Deviation (MPa)	Flexural Modulus (GPa)	Standard Deviation (GPa)
0	1,210	87	124	6
5	1,175	20	122	3
10	965	31	118	3
15	848	103	104	21
20	788	113	85	19



CSBR Content (by weight %)

Figure 6.3 Flexural Strength of Composite with varying CSBR Concentration



Figure 6.4 Flexural Modulus of Composite with varying CSBR Concentration

6.3.2 Short Beam Shear Test

Short beam shear testing methodology is described in ASTM D2344-84. The testing equipment is similar to that used in three-point flexure test, the only difference being the loading nose and the distance between supports. (See Figure 6.5 for details). This test determines the inter-ply strength, with failure occurring in horizontal shear. The apparent shear strength for each sample is calculated by the following formula:

$$S_H = 0.75 \frac{P_B}{bd} \tag{6.1}$$

where S_H is the short beam shear strength in N/m² or psi.

- P_B is the breaking load in N or lbf.
- b is the width of specimen in m or in.
- d is the thickness of specimen in m or in.

Samples cut as per guidelines set in section 4.5, were tested for short beam shear strength. The load at break for each of these samples was noted and the shear strength was then calculated as per equation 6.1. These results have been tabulated in Figure 6.6.



Figure 6.5 Arrangement for Short Beam Shear Strength Analysis



CSBR Content (by weight %)

Figure 6.6 Short Beam Shear Strength for varying CSBR Concentrations in Composite Samples

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6.3.3 Fracture Energy Analysis

The failure mode of epoxy resins is generally characterized by flaw growth and progressive crack propagation. Fracture mechanics deals with the presence of flaws and crack propagation, fracture analysis of the tested coupon is generally used to understand the failure mechanism in epoxy matrixes. Fracture occurs when sufficient energy is released from the applied stress field to generate new fracture surfaces at the instant of crack propagation. This strain energy release rate provides a measure of the energy required to extend a crack over a unit area and is termed the *fracture energy* (kJ/m^2) ^[5]. Several tests exist for the evaluation of the delamination failure mode. Most of them are limited to unidirectional laminates where the crack propagates between the plies along the fiber direction. In this study, the End-Notched Flexure (ENF) test was chosen to determine the fracture energy of the material. Details of the ENF test are given in Appendix E. From the elastic beam theory an expression to evaluate the fracture energy in pure Mode II loading is given as^[72]:

$$G_{II_c} = \frac{9P^2Ca^2}{2w(2L^3 + 3a^2)}$$
(6.2)

where G_{IIc} is the fracture energy at critical load during pure Mode II loading in kJ/m².

- P_c is the critical load in N.
- C is the compliance of the material in mm/N.
- a is the crack length in mm.
- w is the specimen width in mm.
- L is the span between the central loading pin and the outer support pins in mm.

The compliance may be calculated from the following formula based on the beam theory^[22]:

$$C = \frac{2L^3 + 3a^3}{8Ewh^3}$$

where E is the flexural modulus in the axial direction of the beam in GPa.

h is the semi thickness of the beam in mm.

It is, however, recommended that the compliance be measure experimentally. Test specimen for ENF testing are so prepared that an initial crack having length equal to "a", such that $a \approx L/2$. At this condition the crack growth is unstable even under fixed grip conditions. (Details of this derivation are given in Appendix E). A three-point flexure fixture with a total span of 100 mm is used to test the ENF specimen. Consequently, the initial crack length is 25 mm for the crack growth to be unstable. Prior to testing, the crack should be carefully wedged open and extended about 2 mm beyond the insert to achieve a natural starter crack.

ENF samples for 0, 5, 10, 15 and 20% by weight CSBR in epoxy matrix were tested as per guidelines of Appendix E. Compliance was evaluated by linearly regressing twenty random data points of each test sample, as shown by a sample spreadsheet in Appendix F. The equation^[4] used for compliance calculation was:

$$b = \frac{(n\Sigma XY - \Sigma X\Sigma Y)}{n\Sigma X^2 - (\Sigma X)^2}$$

where b is the material compliance in mm/N.

X is the load on the test specimen in N.

Y is the extension in mm.

The spreadsheet also incorporates equation 6.2 for calculation of the material fracture energy. Appendix G gives the graphical output of the ENF test data plotted as

load versus extension. (See Figure 6.7 for a graphical representation of the fracture energy as a function of increase in CSBR concentration in epoxy matrix).

6.3.4 Discussion of Mechanical Testing Results

From Figures 6.3, 6.4, 6.5, and 6.7 it can be seen that the flexural strength, modulus, the short beam shear strength and the fracture toughness all decrease with the increase in the CSBR concentration in the epoxy matrix. These results are to be expected as the increase in the volumetric amount of the "soft" rubbery inclusions proportionally lowers the mechanical properties of the matrix like flexural strength, modulus and short beam shear strength. Work done by Ting et. al.,^{[23], [24]} show similar results for a graphite epoxy system modified by a CTBN elastomer except that the fracture toughness increases with increasing elastomer concentration. As the concentration increases, the softer rubber particles present in the second phase begin to dominate the properties of the epoxy matrix by a simple rule of mixtures phenomenon. As mentioned earlier, epoxy materials in itself are very brittle and are highly susceptible to rapid crack propagation upon application of load. On the other hand rubbers are very tough and resilient materials and are capable of withstanding large loads before complete failure occurs. When these rubber particles are dispersed within the epoxy matrix, they act as crack arresters in case of a crack propagation. The softer rubber particle requires a lot more energy for the crack to propagate through it, therefore as the concentration of the rubber particles increases in the epoxy matrix the fracture energy should increase, i.e. the amount of energy required for the crack to propagate throughout the epoxy matrix. As seen in Figure 6.7, the fracture energy of the composite samples decrease with the increase in CSBR concentration. This behavior is quite contrary to what should have



Figure 6.7 Fracture Energy of Composite Parts with varyings CSBR Concentration

been expected from the above discussion.

An important aspect to consider for the propagation of the crack through a rubbertoughened epoxy matrix is the interfacial adhesion between the epoxy matrix and the rubber particles. Work done by Kinloch et. al.^{[25], [26]}, Mülhaupt et. al.^[27], Qian et. al.^[28] and other relevant literature place a strong emphasis on the interfacial bonding of the rubber particle and the epoxy matrix for improvement in the toughening characteristics. In toughened resins, as the crack propagates through the matrix a dilational stress field is formed causing cavitation of rubber particles^[29]. The cavitation is initiated by interfacial debonding around the particles. In case of a strong interfacial bonding, the epoxy matrix will get tougher. A possible explanation for a decrease in the fracture energy of CSBR toughened epoxy/carbon composites with the increase in CSBR concentration, is the weak interfacial bonding between CSBR particles and epoxy matrix. This study is beyond the scope of the current work being done as the primary thrust of this thesis is to develop a continuous prepregging process for coating two particles from a water-based mixture of the two particles and consolidating them to form two phase composites.

6.4 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical instruments measure the deformation of a material in response to vibrational forces^[30]. This equipment measures the dynamic modulii over a wide range of temperatures. These dynamic parameters are used to determine the glass transition region, relaxation spectra, degree of crystallinity, molecular orientation, crosslinking, phase separation, structural or morphological changes resulting from processing, and chemical compositions. For this study the DMA will be used to see if

two materials, i.e. the epoxy and the rubber particles, exist as two distinct phases within the composite matrix. While running the DMA over a range of temperature, it is seen that there is a distinct peak in the loss modulus of the material at its glass transition temperature. In case of the presence of a second phase in the material, there will be another peak corresponding to the glass transition temperature of the second material^[31].

The samples for the DMA are cut as long rectangular strips, with the fibers aligned along or traverse to the axis of the samples. For consistency in results the fiber orientation of all the samples should be same, as the absolute values of the modulli are very sensitive to the fiber orientation. Since sufficient material was not available from each individual plaque, the fibers are not aligned in the same direction for all the samples. But in this study, as only the presence of two phases is of significant importance, consistency in the alignment of the fibers is not important.

Figure 6.8 through Figure 6.12 show the results of the DMA analysis. Analysis results for the 10, 15 and 20% by weight CSBR samples show two distinct peaks occurring at or around the glass transition temperatures of the two materials. This clearly indicates that the CSBR particles exist as a distinct phase in the epoxy matrix. DMA analysis for the 0 and 5% by weight CSBR samples show only one peak. This is expected for the 0% part, but not for the 5% part. One possible explanation for this could be that the instrument is not able to detect CSBR particles at such low concentration levels. Phase separation occurs during the reaction because the increase in the molecular weight of the epoxy resin diminishes the entropy of the blend^[32]. The chemical reaction drives the change in free energy, so this entire process is kind of a "chemical quench". The morphology formed (diameters, number and volume fraction


Figure 6.8 DMA Analysis of 0% CSBR Composite Part



Figure 6.9 DMA Analysis of 5% CSBR Composite Part



Figure 6.10 DMA Analysis of 10% CSBR Composite Part



Figure 6.11 DMA Analysis of 15% CSBR Composite Part



Figure 6.12 DMA Analysis of 20% CSBR Composite Part

of the dispersed spherical particles) is determined by the competing effects between phase separation and polymerization rates. Shift in the glass transition temperature could be attributed to the possibility to chemical reactions at interface during the sample's high temperature cure cycle.

6.5 MORPHOLOGICAL STUDY

Crack surfaces obtained after ENF testing, were studied under the SEM to identify the morphology of the rubber-toughened epoxy matrix. Figures 6.13 through 6.22 show the photomicrographs of the morphology of the cracked surfaces of the ENF composite samples with varying concentration of CSBR particles taken at a magnification of 5,400 and 10,000. Figure 6.13 and 6.14 shows the fracture surface of 0%CSBR composite part. Features of the surface are typical of a pure epoxy matrix failure. There are well defined ridges and planes. Figure 6.15 and Figure 6.16 shows the fracture surface of 5% CSBR composite part. The features are very similar to that of the 0% CSBR part, except that there are small cavities evenly dispersed all over the These cavities are an identifying feature of a rubber toughened epoxy surface. composite. This porous structure results from the cavitation of rubber particles in response to the dilational stress field, as a crack propagates through the material^[29]. Figures 6.17 through 6.22 show the fracture surface of 10, 15, and 20% CSBR composite parts. The porous structure in all these cases is more pronounced and the cavities are dispersed all over the epoxy matrix indicating a larger concentration of CSBR particles in the epoxy matrix. Also the morphology has a spongy texture indicating gross plastic deformation. The morphology of all the fracture surfaces are typical to that cited in literature.



Figure 6.13 ENF Fracture Surface for 0% CSBR Composite Sample at 5,400X



Figure 6.14 ENF Fracture Surface for 0% CSBR Composite Sample at 10,000X



Figure 6.15 ENF Fracture Surface for 5% CSBR Composite Sample at 5,400X



Figure 6.16 ENF Fracture Surface for 5% CSBR Composite Sample at 10,000X



Figure 6.17 ENF Fracture Surface for 10% CSBR Composite Sample at 5,400X



Figure 6.18 ENF Fracture Surface for 10% CSBR Composite Sample at 10,000X



Figure 6.19 ENF Fracture Surface for 15% CSBR Composite Sample at 5,400X



Figure 6.20 ENF Fracture Surface for 15% CSBR Composite Sample at 10,000X



Figure 6.21 ENF Fracture Surface for 20% CSBR Composite Sample at 5,400X



Figure 6.22 ENF Fracture Surface for 20% CSBR Composite Sample at 10,000X

6.6 SUMMARY

Results of mechanical testing indicate that as the concentration of the "soft" rubber inclusions in the epoxy matrix increases the mechanical properties like flexural strength, flexural modulus and short beam shear strength, decrease. Including a rubber phase should increase the fracture energy of the composite material, but in this study the fracture energy decrease with increasing concentration of CSBR particles. A possible explanation could be a weak interfacial adhesion between the epoxy matrix and the rubber particles. DMA analysis show two distinct phases in the final composite parts. Morphological studies show an even distribution of the CSBR particles in the epoxy matrix and the features are similar to other rubber-toughened epoxy matrix systems.

CONCLUSIONS AND FUTURE WORK

The primary objective of this study was to develop a continuous prepregging process for coating fibers with at least two polymers suspended in an aqueous mixture. Based upon this study a number of conclusions can be drawn and a variety of recommendations can be made for future work.

7.1 CONCLUSIONS

- 1. The developed water-based prepregging unit was successfully used to manufacture quality prepreg tape coated with two different polymer particles from a colloidal aqueous mixture of each. SEM study of the tape indicated an even coating spread over the entire surface of the carbon fibers. This process is independent of solvents. Small colloidal particles improve wetting of fibers, prevent agglomeration and coating is more even. Water, as a dispersing medium, is environmentally friendly. The prepreg tapes produced were fairly tacky, but despite this fact they wind off quite easily from the spool during composite part lay-up.
- 2. The prepreg tapes were consolidated to give void-free composite parts having varying concentrations of CSBR particles dispersed all through the matrix. These multiple phase matrix composites were fabricated independent of the compatibility of the matrix components.
- 3. As the concentration of the CSBR particles was increased in the epoxy matrix, mechanical properties like flexural strength, flexural modulus and short beam shear

strength all went down. This is because increasing the concentration of the "softer" CSBR particles causes the mechanical properties of these particles to dominate the properties of the epoxy/carbon composite. These results are consistent with other research work done in the area of rubber-toughened epoxy matrixes.

- 4. A secondary objective was to study the improvement in the fracture behavior of the epoxy matrix by the increase in concentration of the elastomer. In this study it was observed that the fracture energy decreased with the increase in concentration of the rubber particles. A possible explanation could be the poor interfacial adhesion between the rubber particles and the epoxy matrix, causing the crack to propagate through the interface with relative ease.
- 5. Morphological study of the fractured surface indicated distinct cavitation in the epoxy matrix due to propagation of the crack. These results are consistent with that seen in literature. The rubber particles are well dispersed through the entire volume of the matrix. Also a lot of plastic deformation was noticed in the fracture surfaces that had a higher concentration of the rubber particles.

7.2 FUTURE WORK

The ease with which two particles can be coated from an aqueous dispersion onto the fiber surface independent of the compatibility of the two particles in suspension, as long as they remain in suspension, leaves several avenues open for modifications in the current set-up, developing appropriate mathematical models and application to other processes. These are as given below:

1. Mechanisms of coating should be studied in more depth and a model should be developed to understand the coating phenomenon.

- 2. The process should be run with suspensions of modified rubber particles and the effect of the interfacial adhesion should be studied on the epoxy matrix.
- 3. The convection oven should be replaced with an IR heater. This will also help if a scale-up and high speed version of the process is to be developed.
- 4. Coating on fibers is currently done in a dispersion bath. Other means of coating should also be looked into. Some prospective coating methods would be spraying with micron spray-heads and humidification of suspension.
- 5. The fiber motion system will have to be improved by incorporating proper controllers and motors at each pinch roller. It is imperative to synchronize all of the motors to produce motion in the fibers such that there is no tension in them. Zero tension helps during the spreading process.
- 6. The current study was carried out by using an aqueous dispersion of epoxy resins. The process should also be run using aqueous dispersions of other thermoplastic and thermoset resins. It could also be envisaged that more than two materials could be used during the coating process.
- 7. The current study was carried out by using 12k tows. Another possibility would be to use tows having a much larger quantity of fiber filaments and maybe other fiber materials like glass, Kevlar etc..
- 8. Look into the possibility of impregnating chopped fiber preforms with aqueously dispersed resins.
- 9. Develop a high speed version of the current set up. For this it would be imperative to make modification in the fiber motion, heating and coating set-ups. These have been discussed above.

APPENDIX A

METHOD FOR WINDER SPEED EVALUATION

Given below is a table of the speed versus the dial setting for traverse motor.

Where	F denotes	forward	motion	of motor.
	R denotes	reverse	motion	of motor

Width of prepreg tape w = 1/8"

Width of composite plaque W = 6"

Number of prepreg strips in entire width N = W/w = 48

Therefore, the rotary winding motor will have to rotate 48 times to fill the entire width of the frame with prepreg tape.

Choose a conservative rotary speed of $\omega = 20$ rev/min.

Time taken to make up one layer $t = N/\omega = 2.4$ min.

Traverse speed s = W/t = 6/2.4 = 2.5

From table dial setting for traverse motor is around 32.

Therefore, rotary motor is set at 20 and traverse motor is set at 32.

APPENDIX B

Autoc	lave	Program	#	7
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For James Fernandes

CH :	1				CH2		
SOAK PVEVT DEVEVT	0 1 3	0.00 700 3	0 1600	SOAK1 PVEVT PVEVT	0 2 6	0.00 330 400	1 1
RAMPT TMEVT	20.0 4	0.00	0.00	rampt Tmevt	20.0 9	0.01	0.04
gsoak Tmevt	212 4	10.00 0.00	1 0.00	gsoak Tmevt Tmevt	150 [°] 8 12	1.00 0.01 0.05	1 0.04 0.08
RAMPT TMEVT	20.0 4	0.00	0.00	RAMPT	20.0		
gsoak Tmevt	340 4	60.00 0.00	1 0.00	SOAK	0	1.00	
RAMPT TMEVT TMEVT	10.0 4 5	0.00 0.00	0.00				
SOAK TMEVT TMEVT	100 5 11	60.00 0.00 30.00	0.00 30.04	4			

This program ramps pressure at 20psi/min to 150psi, holds, and ramps temperature at 20°F/min to 212°F, holds for 10 minutes, ramps temperature at 20°F/min to 340°F, holds for 1 hour, ramps temperature at 10°F/min to 100°F, holds for 30 minutes, then ramps pressure 20psi/min to 0psi.

Brian Rook Sept 13, 1993 Updated Jan 14, 1993

APPENDIX C

Program to Evaluate Temperature Profile in Slab Due Conduction

c c	PROGRAM FOR ONE DIMENSIONAL HEAT CONDUCTION THROUGH AN INFINITE SLAB CONVECTIVELY HEATED FROM BOTH
с с с	SURFACES WRITTEN BY SANJAY PADAKI
	<pre>real lambda(50),bn(50),bi,k,h character*80 infile,outfile common lambda,bn,bi write(*,*)'INPUT FILE NAME :' read(*.2)infile</pre>
2	<pre>format(a80) write(*,*)'OUTPUT FILENAME :' read(*,2)outfile open(unit=1,file=infile,status='old') open(unit=2,file=outfile,status='new') read(1,*)k,h,alpha,b,y,t0,tinf write(2,*)'THERMAL CONDUCTIVITY :',k write(2,*)'TRANSFER COEFFICIENT :',h write(2,*)'ALPHA :',alpha write(2,*)'SLAB HALF THICKNESS :',b write(2,*)'LOCATION OF INTEREST :',y write(2,*)'INITIAL AND FINAL TEMPERATURES :',t0,tinf bi=h*b/k</pre>
с	GENERATE EIGEN VALUES and COEFFICIENTS call eigen do 16 j=1,1000 t=(j-1)*5. sum=0.0 do 15 n=1,30 sum1=bn(n)*exp(-1.*lambda(n)**2.*alpha*t/b**2.) sum2=cos(y*lambda(n)/b) sum=sum1*sum2
15	<pre>sum=sum+sum1*sum2 continue temp=tinf+(t0-tinf)*sum write(*,*)t,temp</pre>

write(2,*)t,temp tempdiff=abs(temp-tinf) if (tempdiff.lt.1.e-1) then goto 17 endif 16 continue 17 stop end С С SUBROUTINE FOR EIGEN VALUE GENERATION subroutine eigen common lambda, bn, bi real lambda(50), bn(50), bi pi = acos(0.0) * 2.do 10 i=1,30 x0=lambda(i-1)+piif (i.eq.1.0) then x0=pi/4. endif 5 f0=0. fprime0=0. **x**1=0. if (bi.ge.(pi/2.)) then f0=(x0/bi)-(1./tan(x0))fprime0 = (1./(sin(x0) * sin(x0))) + (1./bi)qoto 6 endif f0=x0*tan(x0)-bifprime0 = (x0/(cos(x0) * cos(x0))) + tan(x0)6 x1=x0-(f0/fprime0) diff=abs(x1-x0) if (diff.lt.1.e-8) then qoto 7 endif x0=x1goto 5 7 lambda(i) = x1bnum=2.*sin(lambda(i)) bden=lambda(i)+sin(lambda(i))*cos(lambda(i)) bn(i) = bnum/bden 10 continue return end

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APPENDIX D

FLEXURE TEST DATA



Figure D.1 Three-Point Flexural Test Data for 5% CSBR Composite Samples



Figure D.2 Three-Point Flexural Test Data for 10% CSBR Composite Samples



Figure D.3 Three-Point Flexural Test Data for 15% CSBR Composite Samples



Figure D.4 Three-Point Flexural Test Data for 20% CSBR Composite Samples

APPENDIX E

ENF TESTING METHOD

13.2 ANALYSIS OF THE ENF SPECIMEN

The End Notched Flexure (ENF) specimen and the test principle are shown in Fig. 13-7. The purpose of this specimen is to determine the critical strain energy release rate in pure Mode II loading [6]. This specimen has been found to produce shear loading at the crack tip without introducing excessive friction between the crack surfaces.

From elastic beam theory an expression for the strain energy release rate can be derived [6],

$$G_{\rm H} = \frac{9P^2Ca^2}{2w(2L^3 + 3a^3)}$$
(13)

where P is the applied load, C is the compliance, a is the crack length, w is the specimen width, and L is the span between the central loading pin and the outer support pins (see Fig. 13-7).

The compliance may be calculated from the following formula, based on beam theory [6],

$$C = \frac{2L^3 + 3a^3}{8Ewh^3}$$
(14)



Figure 13-7. ENF specimen.

where E is the flexural modulus in the axial direction of the beam, and h is the semi thickness of the beam. It is, however, recommended that the compliance be measured experimentally.

In the derivation of eqs. (13) and (14), deformations due to the action of interlaminar shear stress and the influence of friction between the crack surfaces were neglected. These effects may influence the results in some cases as shown by Carlsson et al. [7] and Gillespie et al. [8]. The localized high shear stress and strain in the vicinity of the crack front especially appear to influence the strain energy release rate computation [8]. However, as a conservative estimate, the beam theory expression, eq. (13) appears satisfactory.

13.2.1 Stability of Crack Growth

The stability of crack growth may be judged from the sign of dG_{II}/da analogous to the treatment for the DCB specimen in Sec. 13.1.1 (see also [7]).

For fixed load conditions, eqs. (13) and (14) give

$$\frac{\mathrm{dG}_{\mathrm{II}}}{\mathrm{da}} = \frac{9\mathrm{a}\mathrm{P}^2}{8\mathrm{E}\mathrm{w}^2\mathrm{h}^3} \tag{15}$$

This quantity is positive, hence the crack growth is unstable.

For fixed grip conditions, eqs. (13) and (14) give

$$\frac{dG_{II}}{da} = \frac{9\delta^2 a}{8Ew^2h^3C} \left[1 - \frac{9a^3}{(2L^3 + 3a^3)}\right]$$
(16)

For stable crack growth dG_{II}/da has to be less than or equal to zero. This gives

$$a \ge L/\sqrt[3]{3} \approx 0.7L \tag{17}$$

Consequently, for the commonly used a $\approx L/2$, the crack growth is unstable even under fixed grip conditions.

13.2.2 ENF Testing

A three-point flexure fixture with a total span of 100 mm (Fig. 13-8) should be mounted in a properly aligned and calibrated test machine (Fig. 13-9). The crack should be carefully wedged open and extended about 2 mm beyond the insert in order to achieve a natural starter crack. The specimen shall then be placed in the loading fixture so that the initial crack length is about 25 mm (see Fig. 13-8). The



Figure 13-8. ENF specimen geometry and loading. All dimensions are in mm.



Figure 13-9. ENF est setup.

crosshead rate should be approximately 5 mm/min and the displacement under the central loading pin may be recorded by an extensometer or LVDT. If correction is made for the machine compliance, the beam compliance may be evaluated from the crosshead travel. In either case, a real time plot of the load versus displacement should be made on an x-y recorder. It has been observed that the crack generally propagates to the central loading point in an unstable manner (see Sec. 13.2.1). This means that only one value of $G_{\rm HC}$ is obtained for each specimen.

13.2.3 ENF Data Reduction

Figure 13-10 shows a typical load-deflection curve for an ENF specimen. The actual dimensions of the specimen were: L = 50.8 mm, a = 27.9 mm, 2h = 3.5 mm, and w = 25.3 mm. The critical load was 762 N, and the specimen compliance was $2.3 \times 10^{-3} \text{ mm/N}$. These data in eq. (13) give: $G_{IIC} = 0.56 \text{ kJ/m}^2$.

The compliance calculated from eq. (14) with E = 140 GPa is: $C = 2.2 \times 10^{-3}$ mm/N. The small difference between the measured and calculated compliances may be due to scatter in the material properties or influence of interlaminar shear deformation [7].

The initial crack length, a, can best be evaluated by opening the specimen in two parts after completion of the fracture test, and measuring the distance between



Figure 13-10. Typical load-deflection curve for an ENF specimen made from AS4/3501-6 graphite/epoxy.



Figure 13-11. CLS specimen.

the end of the precrack and the imprint of the outer loading pin on the specimen surface. In cases where the compliance is evaluated from the crosshead travel, it may be important to correct for the machine compliance.

13.3 ANALYSIS OF THE CLS SPECIMEN

The Cracked Lap Shear (CLS) specimen was developed by Wilkins et al. [2] as a Mode II specimen for composites (see Fig. 13-11). This specimen was originally designed for shear dominated fracture investigations of adhesive joints [3]. However, this specimen does not produce a pure Mode II loading at the crack tip [2]. The unbalanced configuration of the CLS specimen results in peel stress (Mode I). Consequently, the CLS specimen is a mixed-mode specimen.

The compliance of the specimen, obtained from simple strength of materials analysis with the notations given in Fig. 13-11 is

$$C = \frac{L}{wEh_1} + \frac{a(h_1 - h_2)}{wEh_1h_2}$$
(18)

From this equation and eq. (2) the strain energy release rate is

$$G = \frac{P^2(h_1 - h_2)}{2w^2 E h_1 h_2}$$
(19)

APPENDIX F

COMPLIANCE CALCULATION DATA SHEET

ENFOS3.XLS

Linear Regression of ENF Data for Compliance Calculations 0% SBR

o o u de u de un	

Width (mm) =	25.11	
Half Span L (mm) =	48.09	
Crack Length a (mm) =	25.64	
Thickness (mm) =	2.63	
Helf Thickness (mm) =	1.315	
Breek Load P =	151.099 lbf =	672.1186 N

No.	X (lbf)	Y (%)	Y (in)	X (N)	Y (mm)	X*Y	X~2	¥-5
1	5.0366	0.663919	0.006639	22.4038	0.168635	3.778075	501.9304	0.028438
2	10.3785	1.0302	0.010302	46.16564	0.261671	12.0802	2131.267	0.068472
3	17.2466	1.6102	0.016102	76.71633	0.408991	31.37627	5885.395	0.167273
4	24.7253	2.2283	0.022283	109.9831	0.565988	62.24913	12096.28	0.320343
5	31.5934	2.7472	0.027472	140.5338	0.697789	98.06289	19749.74	0.486909
6	47.619	3.9911	0.039911	211.8188	1.013739	214.7291	44867.22	1.027668
7	59.8291	4.9603	0.049603	266.1318	1.259916	335.3038	70826.14	1.587389
8	65.1709	5.38	0.0538	289.8932	1.36652	396.1449	84038.07	1.867377
9	74.949	6.1966	0.061966	333.3881	1.573936	524.7317	111147.7	2.477276
10	81.1966	6.6239	0.066239	361.1787	1.682471	607.6726	130450.1	2.830707
11	91.2698	7.4557	0.074557	405.9863	1.893748	768.8357	164824.9	3.586281
12	99.5116	8.1349	0.081349	442.6475	2.066265	914.6269	195936.8	4.269449
13	107.448	8.7301	0.087301	477.9502	2.217445	1059.828	228436.4	4.917064
14	113.553	9.264	0.09264	505.1065	2.353056	1188.544	255132.5	5.536873
15	122.1	9.89	0.0989	543.1252	2.51206	1364.363	294985	6.310445
16	130.9524	10.638	0.10638	582.5025	2.702052	1573.952	339309.1	7.301085
17	133.852	10.8822	0.108822	595.4005	2.764079	1645.734	354501.7	7.640132
18	136.752	11.157	0.11157	608.3002	2.833878	1723.849	370029.2	8.030865
19	140.873	11.538	0.11538	626.6313	2.930652	1836.438	392666.8	8.588721
20	150.183	12.546	0.12546	668.044	3.186684	2128.845	446282.8	10.15495
				7313.907	34.45958	16491.14	3523799	77.19772

Compliance C =	0.00458 mm/N
Error r=	0.999742
Glic -	0.892982 kJ/m ² 2

APPENDIX G

ENF TEST DATA



Figure G.1 ENF Data for 0%CSBR Composite Samples



Figure G.2 ENF Data for 5% CSBR Composite Samples



Fiugre G.3 ENF Data for 10% CSBR Composite Samples



Figure G.4 ENF Data for 15% CSBR Composite Samples



Figure G.5 ENF Data for 20% CSBR Composite Samples

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