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MICROWAVE PULTRUSION OF UNIDIRECTIONAL REINFORCED EPOXY COMPOSITES USING SINGLE FREQUENCY AND VARIABLE FREQUENCY PROCESSING TECHNIQUES

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By

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ABSTRACT

MICROWAVE PULTRUSION OF UNIDIRECTIONAL REINFORCED EPOXY COMPOSITES USING SINGLE FREQUENCY AND VARIABLE FREQUENCY PROCESSING TECHNIQUES

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Aaron C. Smith

The pultrusion process is a continuous manufacturing method, which can be used to produce reinforced plastics with a constant cross-sectional area through the length of the product. The continuous microwave processing technique is highly desired for processing large composite materials, which need even and fast heating such as long pipes or panels. The general advantages of using microwave technology include: decreased processing times, better control of temperature profiles within the composite material, and enhanced mechanical properties.

The objective of this project was to obtain experimental data for microwave pultrusion processing. Heating and curing profiles of the pultruded material were studied at different processing conditions. The fixed frequency pultrusion tests were accomplished using the best heating mode for the prepreg system at a certain processing speed and input power. The relation between microwave processing rate, input power, and extent of cure was studied by finding the optimum operating conditions. Mechanical tests, such as flexural and tensile strength measurements, were conducted. A variable frequency power source was used to achieve a more even temperature distribution across the prepreg. The effects of fiber reinforcement on the efficiency of microwave heating were studied. Concepts for an on-line monitoring system were explored.

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TABLE OF CONTENTS

LIST OF TABLES viii

LIST OF FIGURES ix

KEY TO SYMBOLS xiii

INTRODUCTION 1

CHAPTER 1
BACKGROUND 2

1.1. Microwave Processing 2

1.2. Microwave Heating Mechanism 3

1.3. Microwave Heating Advantages 5

1.4. Microwave Applicators 6

1.5. Research Scope and Goals 8

CHAPTER 2
APPLICATION OF CONTINUOUS MICROWAVE PROCESSING 10

2.1. Introduction 10

2.2. Pultrusion 11

2.3. Experimental Setup 14

2.3.1. Cavity 15

2.3.2. Calibration of Rollers 17

2.4. Materials: Preparation and Discussion 17

2.5. Goals 19

CHAPTER 3
CAVITY CHARACTERIZATION ... 20

3.1. Finding Electromagnetic Modes ... 20

3.2. Temperature Measurement ... 22

3.3. Heating Studies At Various Modes ... 23

3.4. Preliminary Heating Studies in TE112 Mode ... 26

3.5. Conclusions ... 27

CHAPTER 4
FIXED FREQUENCY PULTRUSION EXPERIMENTS ... 29

4.1. Background ... 29

4.2. Experimental Setup ... 29

4.3. Variation in Pulling Speed ... 30

4.4. Variation in Input Power ... 31

4.5. Extent of Cure Measurement ... 31

4.6. Mechanical Properties Measurement ... 38

4.6.1. Tensile Strength ... 38

4.6.2. Flexural Strength ... 41

4.7. Conclusions ... 45

CHAPTER 5
VARIABLE FREQUENCY PULTRUSION EXPERIMENTS ... 46

5.1. Background On Variable Frequency Processing ... 46

5.2. Frequency Sweep Analysis ... 48

5.3. Input Power vs. Frequency ... 50

5.4. Temperature Measurement and Heating Studies Part I: 6-ply Graphite/Epoxy Prepreg, Four Frequencies For V.F. Processing ... 51

5.5. Heating Studies Part II: 18-ply Graphite/Epoxy Prepreg, Change In Cavity Dimension ... 52

5.6. Heating Studies Part III: 11-ply Graphite/Epoxy Prepreg, Four Frequencies and Time Intervals ... 56

5.7. Heating Studies Part IV: 11-ply Graphite/Epoxy Prepreg, Four Frequencies and Variation In The Time Interval ... 60

5.8. Extent of Cure Measurement ... 62

5.9. Conclusions ... 63

CHAPTER 6
FIBER REINFORCEMENT EFFECTS ON MICROWAVE PROCESSING EFFICIENCY ... 64

6.1. Material Identification and Purpose of Study ... 64

6.2. Experiments ... 65

6.3. Results and Discussion ... 67

6.4. Conclusions ... 70

CHAPTER 7
ON-LINE MONITORING ... 71

7.1. Possible On-line Monitoring Techniques ... 71

7.2. Pultrusion Model for On-Line Monitoring ... 73

7.3. Conclusions on On-Line Monitoring ... 79

CONCLUSIONS ... 80

RECOMMENDATIONS ... 82

BIBLIOGRAPHY ... 86

LIST OF TABLES

Table 1. Calibration of Rollers To Evaluate Possible Processing Speeds 17

Table 2. Heating Modes for the Cavity with Teflon Die 24

Table 3. Heating Modes for the Cavity with Teflon Die and Graphite/Epoxy Prepreg .. 24

Table 4. Heating Modes for the Cavity with Teflon Die and Glass/Epoxy Prepreg 24

Table 5. Extent of Cure Measurement For Preliminary Heating of Six-Ply Graphite/Epoxy Composite in TE_{112} Mode With Input Power Varied 27

Table 6. Extent of Cure of 11-ply Prepreg With Variable Frequency Processing 62

Table 7. Heating Modes for the Cavity with Teflon Die and Glass/Epoxy Prepreg 65

LIST OF FIGURES

Figure 1. Microwave Pultrusion Experimental Apparatus at MSU 15

Figure 2. Schematic of Microwave Applicator at MSU 16

Figure 3. Entrance To Microwave Cavity Through Teflon Die 16

Figure 4. Frequency vs. Cavity Length for 7.00" +/- 0.001" (TE modes) 21

Figure 5. Frequency vs. Cavity Length of 7.00" +/- 0.001" (TM modes) 22

Figure 6. Teflon Die Used for Heating Studies and Microwave Pultrusion Processing .. 23

Figure 7. Temperature Versus Time Results for Heating Studies of Six-Ply Hercules AS4/3501-6 Prepreg at 100 Watts and 0.787 ft/min 25

Figure 8. Temperature Versus Time Results for Heating Studies of Stationary Six-Ply DA409/E250 Prepreg At Approximately 50 Watts 25

Figure 9. Results For Preliminary Heating of Six-ply Graphite/Epoxy Composite In TE_{112} Mode At Various Input Powers 26

Figure 10. Effect of Input Power on Extent of Cure 34

Figure 11. Trendline for Extent of Cure as Function of Input Power (40-70 Watts) ... 34

Figure 12. Trendline for Extent of Cure as Function of Input Power (70-100 Watts) ...35

Figure 13. Effect of Pulling Speed on Extent of Cure 36

Figure 14. Trendline For Extent Of Cure As Function Of Pulling Speed (0.281-0.562 ft/min) 36

Figure 15. Trendline For Extent Of Cure As Function Of Pulling Speed (0.562-0.733 ft/min) 37

Figure 16. Trendline For Extent Of Cure As Function Of Pulling Speed (0.733-1.17 ft/min) 37

Figure 17. Tensile Strength of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power 39

Figure 18. Tensile Modulus of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power 39

Figure 19. Tensile Strength of Six-ply Graphite/Epoxy Prepreg Tape with An Input Power of 100 Watts and Variable Pulling Speed 40

Figure 20. Tensile Modulus of Six-ply Graphite/Epoxy Prepreg Tape with An Input Power of 100 Watts and Variable Pulling Speed 40

Figure 21. Flexural Strength of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power 42

Figure 22. Flexural Modulus of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power 42

Figure 23. Flexural Strength of Six-ply Graphite/Epoxy Prepreg Tape with An Input Power of 100 Watts and Variable Pulling Speed 43

Figure 24. Flexural Modulus of Six-ply Graphite/Epoxy Prepreg Tape with An Input Power of 100 Watts and Variable Pulling Speed 43

Figure 25. Six Ply Hercules AS4/3501-6 Heated in TE_{112} mode at 100 Watts and 0.281 ft/min 47

Figure 26. Six Ply Hercules AS4/3501-6 Heated in TE_{011} mode at 100 Watts and 0.281 ft/min 48

Figure 27. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 90 mm And d_p = 15.89 mm And Containing Six-ply Hercules AS4/3501-6 Prepreg 49

Figure 28. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 135 mm And d_p = 15.89 mm And Containing Six-ply Hercules AS4/3501-6 Prepreg 50

Figure 29. Incident Power Versus Processing Frequency for Lambda Variable Frequency Power Source (REF) 51

Figure 30. Six-Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4285 GHz, 2.444 GHz, 2.594 GHz, and 2.6140 GHz - 100 ms each) At An Average Of 70 Watts And A Pulling Speed of 0.281 ft/min 52

Figure 31. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 90 mm And d_p = 15.89 mm And Containing Eighteen-ply Hercules AS4/3501-6 Prepreg 53

Figure 32. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 90 mm And d_p = 22.90 mm And Containing Eighteen-ply Hercules AS4/3501-6 Prepreg 54

Figure 33. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 93 mm And d_p = 22.90 mm And Containing Eighteen-ply Hercules AS4/3501-6 Prepreg 55

Figure 34. Eighteen-Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.1173 GHz, 2.4162 GHz, and 2.7014 GHz - 1000ms each) and A Pulling Speed of 0.281 ft/min 56

Figure 35. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.1173 GHz - 1000ms, 2.4162 GHz - 10ms, 2.6328 GHz - 1000 ms, 2.6809 GHz - 1000ms) and Using A Pulling Speed Of 0.281 ft/min 57

Figure 36. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 1000 ms, 2.4281 GHz - 1000 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed Of 0.281 ft/min 58

Figure 37. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4281 GHz - 2000 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed Of 0.281 ft/min 59

Figure 38. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4287 GHz - 2000 ms, 2.6328 GHz - 7000 ms, 2.6809 GHz - 7000 ms) and Using A Pulling Speed of 0.281 ft/min 59

Figure 39. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4287 GHz - 1000 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed of 0.281 ft/min 61

Figure 40. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4287 GHz - 1500 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed of 0.281 ft/min 61

Figure 41. Temperature Versus Time Results for Heating Studies of Stationary Six-Ply DA490/250 Prepreg At Approximately 50 Watts 66

Figure 42. Stationary Six-ply Glass/Epoxy Prepreg Heated in TE_{112} Mode At 57 Watts for Two Minutes 67

Figure 43. Centerline Temperature for Six-ply Graphite/Epoxy Prepreg Heated in TE_{112} Mode At 50 Watts and 0.281 ft/min 68

Figure 44. Six-ply Glass/Epoxy Prepreg Heat in TE_{112} Mode At 50 Watts and 0.281 ft/min 68

Figure 45. Stationary Six-ply Glass/Epoxy Prepreg Heated in TE_{112} Mode At 85 Watts for Five Minutes 69

Figure 46. Centerline Temperature for Six-ply Graphite/Epoxy Prepreg Heated in TE_{112} Mode At 80 Watts and 0.281 ft/min 70

KEY TO SYMBOLS

α [=] extent of cure

β [=] ratio of initial hardener equivalents to epoxide equivalents

δ [=] penetration depth

∂ [=] partial derivative

ε_o [=] permitivity of free space (8.854×10^{-14} F/m)

ε' [=] dielectric constant

ε^* [=] effective complex permitivities

ε'' [=] effective dielectric loss factor

ε_d'' [=] loss factor due to the dielectric

f [=] frequency (Hz, MHz, or GHz)

λ [=] wavelength (cm)

μ_o [=] permeability of free space

μ' [=] permeability of material

ω [=] $2*\pi*f$ (Hz)

π [=] 3.14159

ρ [=] density (g/cm^3)

σ [=] electrical conductivity (S/m)

σ_{fu} [=] ultimate strength of fiber (MPa)

σ_{lu} [=] ultimate strength of composite (MPa)

σ_{mfu} [=] matrix stress at the onset of fiber cracking (MPa)

$\tan\delta_\varepsilon$ [=] dielectric loss tangent

θ [=] angular direction in cylindrical coordinate system

c [=] speed of light (3.00 x 10^8 m/s)

°C [=] Celsius, a unit of temperature

cm [=] centimeter, a unit of length

cos [=] trigonometric cosine function

C_{pf} [=] heat capacity of fiber (J/g_K)

C_{pm} [=] heat capacity of matrix (J/g_K)

D [=] diameter of brass cavity (cm or in)

d_p [=] coupling probe depth (mm)

DSC [=] Differential Scanning Calorimetry

E [=] electric field vector quantity

$|E_m|$ [=] magnitude of electric field inside the material

f_o [=] 2.45 x 10^9 Hz

ft [=] feet, a unit of length

g [=] gram, a unit of weight

GHz [=] Gigahertz (10^9 Hz)

H [=] magnetic field vector quantity

$|H_m|$ [=] magnitude of magnetic field

$\dot{H}$ [=] rate of heat generation per unit weight by the polymerization reaction (W/g)

H_r [=] heat of reaction

H_{rc} [=] heat of reaction for cured material (J/g)

H_{ru} [=] heat of reaction for uncured material (J/g)

Hz [=] hertz, a unit of frequency

in [=] inch, a unit of length

j [=] imaginary number

J [=] joule, a unit of energy

$J_1(x)$ [=] Bessel Function

$J'_1(x)$ [=] Henckel Function

k [=] thermal conductivity (W/cm_K), or kinetic rate constant

°K [=] Kelvin, a unit of temperature

l [=] number of full-period variations of E_r with respect to θ

lb_f [=] pound force

L_c [=] cavity length (cm)

L_p [=] coupling probe depth (mm)

m [=] meter, a unit of length, or
number of half-period variations of E_θ with respect to r

MHz [=] megahertz (10^6 Hz)

min [=] minute, a unit of time

mm [=] millimeter, a unit of length

MPa [=] megapascal, a unit of pressure or force

ms [=] millisecond, a unit of time

N [=] number of half-period variations of E_r with respect to z

P [=] microwave input power (W)

P_{abs} [=] power absorption per unit volume (W/cm^3)

P_m' [=] rate of heat generation per unit volume by absorbed microwave energy (W/cm^3)

r [=] radius, or radial direction

R [=] universal gas constant (8.314 J/mol_K)

R.P. [=] reflected power (W)

s [=] second, a unit of time

sec [=] second, a unit of time

sin [=] trigonometric sine function

t [=] time

T [=] temperature

T_a [=] ambient temperature

T_c [=] curing temperature

TE [=] transverse electric

TM [=] transverse magnetic

T.W.T. [=] traveling wave tube

V_z [=] pulling speed

W [=] watts, a unit of power, or energy per time

w_f [=] weight fraction of fiber in composite

w_m [=] weight fraction of matrix in composite

x [=] plane across width of prepreg

x_{lm} [=] mth root of Henckel Function for the TE-modes or
mth root of Bessel Function for TM-modes

z [=] axial distance or direction in brass cavity, or plane of pulling direction

INTRODUCTION

The pultrusion process is a continuous manufacturing method which can be used to produce reinforced plastics with a constant cross-sectional area through the length of the product. Pultruded samples are expected to exhibit good hydrolytic stability, improved mechanical strength, and electrical insulation properties. The continuous microwave processing technique is highly desired for processing large composite materials, which need even and fast heating such as long pipes or panels. The general advantages of using microwave technology include: decreased processing times, better control of temperature profiles within the composite material, and enhanced mechanical properties.

The objectives of this project are to obtain experimental data of microwave pultrusion processing and to compare variable frequency and single frequency processing methods. Temperature-time curves and extent of cure measurements will aid in finding the optimized microwave pultrusion variables of input power and pulling speed. Mechanical tests, such as flexural and tensile strength measurements, will be conducted. A variable frequency power source will be used to determine if mode-switching heating can provide more even heating in pultruded composites than with fixed frequency heating. By processing continuous, unidirectional glass and graphite reinforced epoxy prepregs, it is a goal to observe an effect of the reinforcement on the efficiency of microwave processing. Finally, the experimental data obtained will be applied to a pultrusion model to begin the formulation of a computer program that will assist in the future integration of on-line monitoring equipment for the microwave pultrusion apparatus.

Chapter 1. Background

1.1. Microwave Processing

Fiber reinforced polymer composites are widely used in the military, the aerospace industry, and the sporting goods world. The primary way of processing these composites is thermally. The autoclave process requires a relatively long time to perform. To increase processing speed and to treat thick thermosetting composites, industry has turned to microwave processing. Microwave heating is an alternative method to conventional thermal heating for the processing of materials. Compared to the thermal heating method, microwave curing of composite materials is a faster and more direct heating method that takes advantages of the dielectric properties of the material being processed.

An electromagnetic field interacting with a dielectric material, such as a composite, heats from the inside out. The temperature profiles inside the composite and the absorption of microwave energy are a strong function of the electromagnetic wave modes resonating inside the cavity. [1] By changing the length of the microwave cavity and/or the coupling probe depth, the waves are allowed to resonate inside the cavity, and the reflected power is minimized. The cavity length controls what mode is excited and the coupling probe, which attenuates the radio frequency signal, controls how much power is reflected back into the circuit from the cavity. The general advantages of microwave heating are rapid, inside-out heating, better control of the material's exotherm, selective heating based on the lossy magnitude of the constituents in a material, and improved mechanical properties of the composite.

1.2. Microwave Heating Mechanism

In conventional thermal heating, the surface of the material is heated and the heating of the interior occurs by thermal conduction and by the exotherm of the reaction if the polymer is thermosetting. On the other hand, microwaves heat the bulk of the material simultaneously and offer fast, selective, instantaneous, and relatively controllable heating. Microwaves can penetrate into the bulk of the material and cause heating by coupling with the material at the molecular level. Microwave energy excites dipole groups, which align themselves with the electric field. After the electric field is removed, there is relaxation of the dipoles, which causes heating at the molecular level. The dielectric constant is a measure of the material's ability to store electrical energy. The dielectric loss factor (Equation 1) corresponds to the material's ability to dissipate electrical energy as heat. The effective dielectric loss factor consists of two terms: the loss factor due to the dielectric and a term dependent on the conductivity and processing frequency. The electrical conductivity portion of Equation 1 is often large when a conductive material is present, so as to drown out the dielectric term.

$$\varepsilon'' = \varepsilon_d'' + \frac{\sigma}{\omega \varepsilon_o} \quad (1)$$

The materials' dielectric properties play an important role in determining how well radio frequency heating will work. The dielectric loss factor is a function of temperature and extent of cure. The dielectric constant and loss factor are both implicit functions of temperature by way of the relaxation time. The relaxation time is the time is takes for dipolar molecules to reorient themselves after they have been aligned with the electric field. The relaxation time is a function of temperature through an Arrhenius relationship.

The penetration depth, δ, in Equation 2, of the electromagnetic waves is a function of the dielectric properties. [2]

$$\delta = \frac{1}{2\omega}\left[\frac{2}{\mu_o \mu' \varepsilon_o \varepsilon'}\right]^{1/2}\left[\left(1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2\right)^{1/2} - 1\right]^{-1/2} \quad (2)$$

The penetration depth, which is traditionally known as the point in the thickness of the sample where the power has decreased to 37% of its incident value, is inversely proportional to the processing frequency. As frequency decreases, the skin depth increases, meaning the waves travel further into the tape than would be observed with higher frequencies.

The dielectric power absorption per unit volume of the material can be calculated using Equation 3, in which the power absorption is proportional to the dielectric loss factor.

$$P_{abs} = 2\pi f \varepsilon_o \varepsilon' \tan\delta_\varepsilon E \quad (3)$$

where
- P_{abs} = Power absorption per unit volume
- f = Frequency (Hz)
- ε_o = permitivity of free space (8.854×10^{-14} F/m)
- ε' = Dielectric constant
- E = Electric field strength
- $\tan\delta_\varepsilon$ = Dielectric loss tangent

The dielectric loss tangent is equal to the ratio of $\varepsilon''/\varepsilon'$, so it is apparent that the effects of microwave heating are predominant in materials where the dielectric loss factor is high relative to the dielectric constant. The dielectric loss factor is a function of the temperature and frequency. For reactive systems, it is also a function of the extent of cure. The absorbed power can be set into Equation 4 to generate basic theoretical temperature versus time curves. If the percentage of power absorbed is the same when all of the experimental conditions except input power level are kept the same, an increase in input

$$dT/dt = P_{abs} / (Cp*\rho) \qquad (4)$$

power would lead to an increase in power absorption per unit volume. The slope of the temperature-time curves would then be directly proportional to the input power level. In other words, increasing the microwave power will increase the slope of the temperature-time curve, which is synonymous with a more rapid heating rate. Preliminary heating studies on the composite material will attempt to prove this theory.

1.3. Microwave Heating Advantages

There are numerous advantages to using microwaves for the processing of polymers and composites: decreased processing times, "inside-out" and selective, molecular heating, control of the exotherm by turning off microwave power, and improved mechanical properties due to better resin/fiber interfacial bonding. Because thermal heating of composites heats from the outside-in, the material on the outside surface could degrade before the middle of a large-profiled part reaches the cross-linking temperature. If the thermal conductivity of the resin decreases during the cure cycle, it becomes more difficult to transfer the necessary heat to cure the inside of the part. Often, there is a post-cure step when using conventional techniques, which increases processing times. Radio frequency technology has been used in pultrusion lines for more than twenty years in the form of a preheater for the wetted fibers. Often a large frequency sweep is used for this preheating step. By installing a single-mode microwave applicator in the pultrusion line that operates at either a single frequency or a series of intelligently selected frequencies, it is believed that processing times will decrease. By knowing the dielectric properties of the materials and how each frequency will directly and instantaneously interact with the composite, microwaves can properly and efficiently heat the material from the inside-out and at the molecular level, thereby largely decreasing processing times.

For conventional processing, pultrusion dies have several temperature zones to control the temperature and viscosity of the material in the die. The zones also control the gelation point inside the die. As the resin begins to cure, crosslinking occurs which rids the molecules of their dipolar nature. The microwave energy becomes selective in what it heats in the resin/fiber mixture because only the monomer dipoles can align themselves with the electric field, not the crosslinked polymer molecules. If the reinforcement material has better electrical properties than the resin, the fibers will absorb the majority of the microwaves and help cure the resin at the interface through conduction. This transfer of heat at the resin/fiber interface [3] will improve the bonding, and subsequently, the mechanical properties.

1.4. Microwave Applicators

Four types of applicators are prevalent in the microwave industry: multimode, single-mode, waveguide, and specialized applicators. Multimode applicators are favorable because they can excite several electromagnetic modes at a single frequency, and they are able to process a wide range of materials. On the downside, they are not particularly energy efficient and can have trouble heating uniformly.

Single-mode applicators heat more efficiently than multimode applicators. The single electromagnetic mode excited in the applicator causes regions of the process material to be heated in a highly localized fashion. "The heating uniformity inside lossy materials is a strong function of the resonant mode." [4] If medium- to low-loss materials are processed in the applicator, there is no single mode that will heat the large sample uniformly. [4] The single-mode and multimode applicators are used to process low-loss and medium-loss materials.

Either single mode heating or mode switching heating can be used in the process. Proper mode switching heating provides a more uniform temperature profile and can help alleviate the problems of processing low-loss materials in single-mode applicators. In fixed frequency processing, adjusting the cavity length mechanically can change the modes. With the variable frequency power source, the modes can be changed by electronically tuning the frequency, which is a much better approach than mechanical tuning.

The third applicator that can be used to process materials with microwaves is a waveguide. It is a rectangular or cylindrical hollow pipe made of a conducting material. Materials are processed with a traveling wave, as opposed to a standing wave in the above microwave applicator examples. Because the traveling wave is partially absorbed by the material in the waveguide, the materials are often of high-loss so the waveguides are not inordinately long.

The final applicators used in industry are specialized applicators such as part-shaped cavities or horn applicators. Microwave energy is coupled into these units by way of an iris or a series of irises. Part-shaped cavities are built to have the same dimensions as the desired part, but the mold walls are the applicator by which the microwaves are attenuated. Horn applicators concentrate microwave energy before it is delivered into a larger chamber. Although the design aspect of the specialized applicators is more difficult, the customer will save money on tooling costs if various dies are normally inserted into the single- or multi-mode applicator.

1.5. Research Scope and Goals

The objectives of this project are to obtain experimental data of microwave pultrusion processing and to compare variable frequency and single frequency processing methods. There will be a fundamental study of the microwave pultrusion equipment, aimed at providing the data for a pultrusion system design. It is also a goal of this project to find the optimized microwave pultrusion variables of input power and pulling speed.

The beginning of this study includes system design and material selection. The materials to be used in this study are continuous, unidirectional prepregs consisting of glass fiber or graphite fiber and epoxy resin. The effect of the reinforcement on microwave processing efficiency will be investigated through heating studies and extent of cure measurements. The prepreg was purchased from suppliers. Hexcel provided samples of their AS4/3501-6 prepreg tape. It is an amine-cured epoxy resin with unidirectional graphite fiber reinforcements. [5] The glass reinforced epoxy prepreg, DA409/E250-6", was purchased from Adhesive Prepregs for Composites Manufacturers. [6] Several plies of the prepreg will be stacked together to form the composite prepreg tape for pultrusion. Differential Scanning Calorimetry (DSC) will be used to determine the extent of cure of the pultruded samples. The pultrusion tests will be accomplished using the best heating mode for the prepreg system at a certain processing speed and input power. The Teflon die will be used because of its transparency to microwaves. The relationship of microwave processing speed, input power, and extent of cure will be investigated to find the optimum operating conditions for microwave pultrusion processing. Pultruded samples are expected to exhibit good hydrolytic stability, improved mechanical strength, and electrical insulation properties. Mechanical tests, such as flexural and tensile strength measurements will be conducted. A variable frequency power source will be used to determine if mode-switching heating can provide more even heating in pultruded composites than with fixed frequency heating. Finally, the experimental data obtained will be applied to a pultrusion model to begin the formulation of a computer program that will assist in the integration of on-line monitoring equipment for the microwave pultrusion apparatus.

Chapter 2: Application of Continuous Microwave Processing

2.1. Introduction

Microwave heating is an alternative method to conventional thermal heating for the processing of materials. Compared to the thermal heating method, microwave curing of composite materials is a faster and more direct heating method that takes advantages of the dielectric properties of the material being processed. In conventional thermal heating, the surface of the material is heated and the heating of the interior is induced by thermal conduction. On the other hand, microwaves heat the bulk of the material simultaneously and offer fast, selective, instantaneous, and relatively controllable heating. Microwaves can penetrate into the bulk of the material and cause heating by coupling with the material at the molecular level. Microwave energy excites dipole groups and the relaxation of the dipole groups causes heating at the molecular level.

The continuous microwave processing technique is highly desired for processing large composite materials that need even and fast heating such as long pipes or panels. The shape of the product is determined by continuously pulling the composite material through a die to produce uniform profile parts. The idea of continuous microwave processing is to pass the material through the microwave applicator. The applications of continuous microwave processing in industry have been used to preheat materials or to post-cure parts. [7] Asmussen describes a general purpose microwave applicator that is commercially available. [8] The unique feature of this apparatus is that it allows for precise tuning for mode selection and fine tuning within a mode selected. The problem, which was not solved in using this apparatus, is how to seal the cavity when the material is being continuously processed through the microwave cavity. The control of the microwave leakage from the entry and exit ports of the applicator is one of the key points in continuous microwave processing. The microwave leakage during continuous processing of non-conductive materials has been controlled by attaching extended entry and exit ports to the microwave cavity. [9] A method for controlling microwave leakage in pultrusion of conductive materials has also been developed. [10]

One pultrusion application of processing materials continuously in a waveguide has been patented. [11] The idea of using a waveguide as part of a pultrusion die is excellent in terms of the simplicity of the system. However, the dimension of the waveguide has to be in accord with the dielectric properties of the materials being processed in order to create the suitable microwave field patterns. [12] This requirement has greatly limited the wide application of the technique in industry due to the large variety of materials being processed. A microwave transparent die will be used for the microwave pultrusion process. Heating and curing profiles of the pultruded material will be studied at different processing conditions. The current microwave pultrusion experimental apparatus [10,13] developed at MSU will be the basis of this pultrusion system study.

2.2. Pultrusion

The pultrusion process is a continuous manufacturing method, which can be used to produce reinforced plastics with a constant cross-sectional area through the length of the product. The shape of the product is determined by continuously pulling the composite material through a die to produce uniform profile parts. Pultruded composites consist of reinforcing materials, a resin that binds the fibers together, and often a mat material to improve the appearance of the composite's surface and other ancillary materials. [14] The key step in a pultrusion process is to control the interactions among fiber, resin, and additives.

The general pultrusion process involves pulling continuous strands of glass or graphite fiber from a creel station. To alleviate the build-up of static charge in the fibers, the creel station is often in the form of steel shelving to ground the fiber spools. A shelf can hold up to 20 roving packages. [15] The fibers can be passed through ceramic rings to prevent the fibers from crossing paths and causing entanglements in the resin bath. Fiber mats or woven rovings can be added to the outside of the part before the die to improve the transverse strength. There is approximately 500 feet of mat per roll. [15] Surface veils are also used to give a more finished look to the finished part. Fibers move through a set of rollers at the entrance and exit of a resin bath to ensure complete wetting out of the fibers. This is the most important step in establishing good mechanical properties. Slower line speeds and higher resin bath temperatures give better fiber wet-out results.

The resin bath is metal and contains a plug so it can be drained and cleaned. After the resin bath, the fibers pass through a set of rollers to rid the fibers of excess resin. Preformers before the die begin to align the wetted fibers into the desired profile. Cross sectional wall thickness of the part should help estimate the line speed needed to make a satisfactory product. If the wall thickness is 3/16", ¼-3/8", or ½-3/4", then the average line speed should be 32, 20, or 16 inches per minute, respectively. [15]

Platens or electrical strip heaters heat the metal die. Platens, although easy to assemble, are only able to heat the top and the bottom of the die. They are usually placed equidistantly down the die in the beginning, middle, and end. Platens are less efficient than strip heaters, which will raise energy costs. [15] Zoned, electrical strip heating controls temperatures along the width and the length of the die. The pultruder will have more control over the optimization of the process parameters such as pulling speed and die temperature. The conventional processing method is to heat the materials in the die through thermal convection/conduction. Thermal heating is slow and requires a long die, often causing uneven heating in large parts.

The preformers before the metal die are somewhat cool to prevent premature gelation of the resin/fiber system. The die is approximately three feet long. The resin viscosity initially decreases upon entering the heated die. As the fibers conform to the desired profile, the resin is allowed to further penetrate fibers. The die's temperature is increased to ensure that a resin skin does not form on the die walls, causing undue shear forces and poor finishes as the rollers pull the part through the die. [16] In the industrial pultrusion apparatus, the heating zones are monitored and controlled by an experienced operator. Pulling speed has a lot of influence on where the peak exotherm will be located in the die. Ideally, one would like the pultruded part to be nearly cured before exiting, thereby allowing it to transfer some of its heat to the die walls. If the exotherm peak occurs to close to the die exit, residual heat in the center of the part could cause fractures in the end product. [16]

The pulling section or mechanical pulling apparatus can be a set of rollers or a pair of continuous belts containing pads that grip the pultruded product. Terms used are hydraulic reciprocating (easy set up), electromechanical caterpillar (requires a large number of pulling blocks), and ballscrew (high maintenance). [15] In a commercial process, pulling speeds can range from 2-3 in/min to 10-15 ft/min. [16] If maximum pulling speeds are desired, it is best to have multiple dies in the line so as to avoid incomplete fiber wet-out and curing. [16] The pulling force must be greater than the frictional force of the fibers and the shear force of the resin layer against the die wall and the fibers dragging against the resin flowing back into the bath. [16]

A cut-off saw, wet or dry and automatic or manual, provides a method to produce the pultruded members at the customer's specified length requirements. A wet saw has water that cools and lubricates the blade at the same time it prevents harmful fiberglass dust to travel through the air. A dry saw needs a dust collection system. Automatic saws are programmed to cut at the appropriate lengths, while manual saws are run by the operators themselves. [15] Cut parts are then sorted and stacked for finishing, packaging, or shipping.

2.3. Experimental Setup

The experimental apparatus (Figure 1) at Michigan State University [10,13] includes a power source that is either a single frequency (2450 MHz) source with a magnetron or a variable frequency (1700-4300 MHz) power source with a microwave power generator and TWT (traveling wave tube) amplifier. Circuit components include directional couplers to send power to the cavity and to the incident and reflected power meters, circulators to prevent any reflected power of damaging the power source, coaxial connectors, coaxial cables, and resistors for dummy loads. Power meters were used to measure the incident and reflected power, and Luxtron temperature units were used to measure the surface temperature of the prepreg as it was pulled through the cavity.

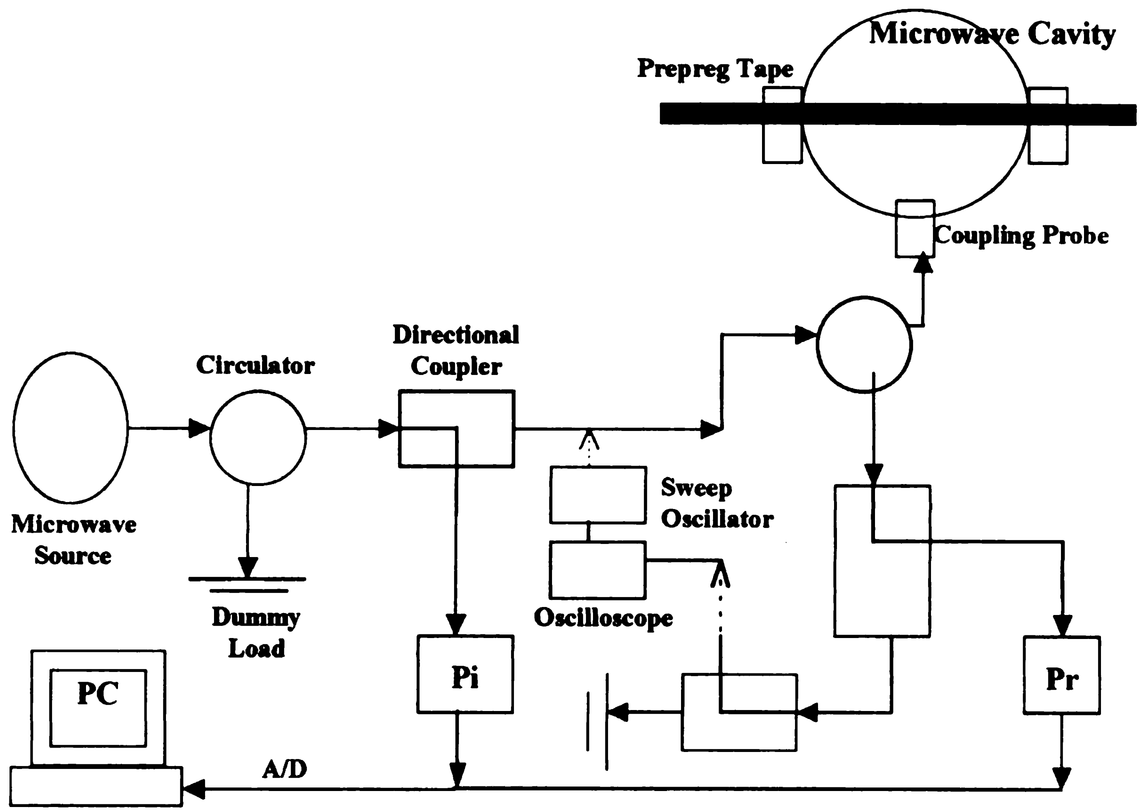

Figure 1. Microwave Pultrusion Experimental Apparatus at MSU

2.3.1. Microwave Cavity

A Teflon die, as shown in Figure 3, which is transparent to microwaves, producing a profile measuring 3.80 cm wide by 0.294 cm high was inserted into an opening in the side of the 17.78 cm inner diameter, tunable, cylindrical, batch, brass microwave cavity. The dies need to have sufficient dimensional stability and mechanical strength, just like the ones used in conventional pultrusion. Ceramic dies are also transparent to microwaves. Teflon dies have lower dielectric loss than the ceramic dies, but have less mechanical strength. The cavity can be tuned for mode selection and fine tuned to minimize reflected power by mechanically adjusting the sliding short height and coupling probe depth, respectively. The microwave cavity in Figure 2 is modified for pultrusion processing such that doubly corrugated chokes [9] are extended from the cavity to contain the electromagnetic radiation. Conductive fins [3] are grounded to the cavity opening and in turn, ground the induced current in the conductive graphite fibers when graphite/epoxy is processed. Finger stock placed in the opening out of the jacket boxes provides additional dampening of the induced current, thereby reducing microwave leakage.

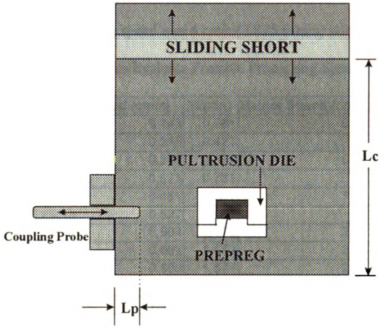

Figure 2. Schematic of Microwave Applicator at MSU

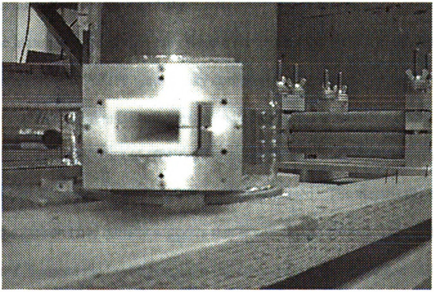

Figure 3. Entrance To Microwave Cavity through Teflon Die

2.3.2. Calibration of Rollers

A Penta Power motor and a Baldor motor were chosen to pull the prepreg tape through the system. The motors' dial settings were calibrated to calculate possible processing speeds (see Table 1). Past work at MSU suggested that the mechanical pulling system be improved to allow for increased product throughput. [17] It was found that the maximum obtainable processing speed was 4 cm/s (7.875 ft/min) with the Baldor motor.

Table 1. Calibration of Rollers to Evaluate Possible Processing Speeds

Dial Setting	Penta Power Speed (cm/s)	(ft/min)	Baldor Speed (cm/s)	(ft/min)
20	0.143	0.281	0.400	0.787
25	0.215	0.423		
30	0.286	0.562	0.870	1.712
35	0.373	0.733		
40	0.451	0.887	1.333	2.625
45	0.527	1.038		
50	0.594	1.170	2.143	4.218
60	0.667	1.312	2.857	5.624
70	0.800	1.575	2.857	5.624
80	1.000	1.969	4.000	7.874
90	1.333	2.625	4.000	7.874
100	1.333	2.625	4.000	7.874

2.4. Materials: Preparation and Discussion

The materials used in the study were a Hercules AS4/3501-6 graphite/epoxy composite and a DA409/E250 glass/epoxy composite. The reason for performing experiments on both systems is to compare and contrast the ability to process each material. Processing speeds and efficiency of microwave heating are important factors that are influenced by the type of reinforcement that is used. The electrically conductive nature of the carbon fiber initially suggests that it will absorb more of the electromagnetic radiation and dissipate the heat throughout the composite by conductance. Glass fibers are less electrically conductive, but are inherently denser than the carbon fibers, leading one to believe that they may provide better mechanical properties. An optimum product could involve a mixture of these two reinforcements.

As was discussed before, the dielectric constant is a measure of the material's ability to store electrical energy. The dielectric loss factor corresponds to the material's ability to spread electrical energy as heat. The effective dielectric loss factor consists of two terms: the loss factor due to the dielectric and a portion that deals with the conductivity. The materials' dielectric properties play an important role in determining how well radio frequency heating will work. The dielectric loss factor is a function of temperature and extent of cure. The dielectric constant and loss factor are both implicit functions of temperature by way of the relaxation time. The relaxation time is the time is takes for dipolar molecules to reorient themselves after they have been aligned with the electric field.

The University of Mississippi Pultrusion research group conducted pultrusion experiments on an epoxy system with glass fiber and carbon fiber reinforcements. [18] Using a thermally heated die, the temperature and extent of cure profiles across the die were very similar for both material systems. When pultruding a composite using thermal techniques, the resin's thermal conductivity is an important variable in determining the cure inside the composite. The cured material on the outside of the pultruded part continues to be heated for the sole purpose of making sure the exotherm in the center of the part is enough to meet cure specifications.

2.5. Goals

The objectives of this project are to obtain experimental data of microwave pultrusion processing and to compare variable frequency and single frequency processing. It is thought that variable frequency will provide a more even temperature distribution across the width of the prepreg tape. It is also a goal of this project to find the optimized microwave pultrusion variables of input power and pulling speed. Extent of cure and mechanical property (tensile and flexural strength and modulus) measurements will be made to support process design. Comparison and contrasting of the effect of fiber reinforcements on the efficiency of microwave processing will be made. Possible on-line monitoring techniques will be investigated for future study.

Chapter 3: Cavity Characterization

3.1. Finding Electromagnetic Modes

The brass cavity was characterized to obtain the resonant modes by mechanically changing the cavity length and the coupling probe depth. Normal modes in a right circular cylinder consist of transverse electric (TE) and transverse magnetic (TM) modes. Subscripts define which TE-mode is resonant in the cavity: l ≡ number of full-period variations of E_r with respect to θ, m ≡ number of half-period variations of E_θ with respect to r, n ≡ number of half-period variations of E_r with respect to z. The subscripts are defined equally for the TM-modes, but E is replaced by H, the magnetic field. Equation 6 shows the definition for the resonant frequencies inside the cavity. [19]

$$f = \sqrt{\left(\frac{cx_{lm}}{\pi D}\right)^2 + \left(\frac{cn}{2D}\right)^2\left(\frac{D}{L}\right)^2} \tag{6}$$

where c = speed of light = 3.00×10^8 m/s

x_{lm} = mth root of Henckel Function $J'_l(x) = 0$ for the TE-modes

x_{lm} = mth root of Bessel Function $J_l(x) = 0$ for the TM-modes

From the equation above, a mode chart was constructed for the 7" brass cavity in which the frequency in Hz was plotted versus the cavity length in centimeters. It was assumed that the mode charts were independent of coupling probe depth, which assists in minimizing reflected power. It was also assumed that the chokes on the entrance and exit ports of the cavity did not affect the electromagnetic waves inside the cylindrical cavity itself. The Teflon or ceramic die, albeit transparent to microwave radiation, was assumed not to interfere with the resonant conditions of the cavity. There was no material inserted into the cavity or the die. The x-axis is drawn from the 2.45×10^9 Hz point on the y-axis because that was the processing frequency used by the single frequency power source. As seen by Figures 4 and 5, one may obtain eight different modes in single frequency processing by changing the cavity length a range of 10.5 cm.

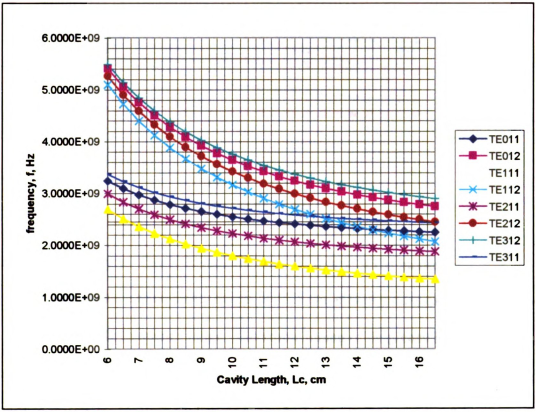

Figure 4. Frequency vs. Cavity Length for 7.00" +/- 0.001" (TE modes)

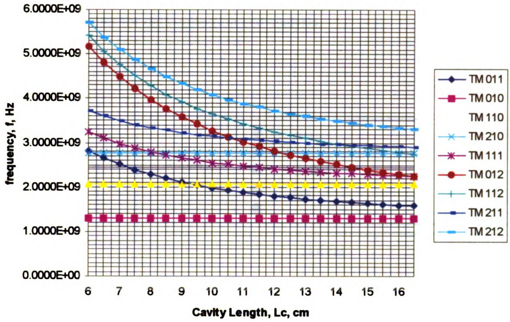

Figure 5. Frequency vs. Cavity Length of 7.00" +/- 0.001" (TM modes)

If one chooses a fixed cavity height of 15.5 cm, eleven modes can be excited over the 2.00 to 3.00 GHz frequency range. Electronic tuning of frequency is faster than the mechanical tuning of the cavity, giving rise to the idea of variable frequency processing of composite materials. Heating studies were conducted using a processing frequency of 2.45 GHz for each mode to find which electromagnetic mode most efficiently heated the material.

3.2. Temperature Measurement

Fluorotropic temperature probes, which are transparent to microwaves, were placed through holes in the die 8 mm apart across the width of the die and 21 mm apart along the length of the die (Figure 6). The probes rested against the surface of the prepreg. Temperature readings were sent from the Luxtron temperature meter to a personal computer for data collection and analysis.

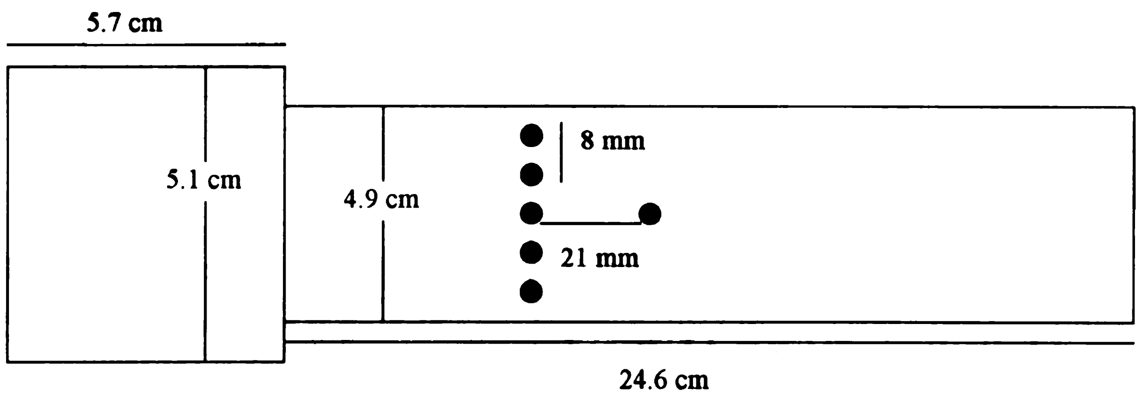

Figure 6. Teflon Die Used for Heating Studies and Microwave Pultrusion Processing

3.3. Heating Studies At Various Modes

Heating studies were conducted using a processing frequency of 2.45 GHz for each mode to find which electromagnetic mode most efficiently heated the material. Table 2 lists the cavity dimensions used for the characterization studies. The Teflon die was in place when the preliminary cavity dimensions were measured. Tables 3 and 4 list the heating modes for the 17.78 cm cavity with the six-ply graphite/epoxy and glass/epoxy prepreg inserted into the cavity, respectively.

Temperature versus time curves are shown in Figures 7 and 8 for the graphite/epoxy and glass/epoxy systems, respectively. The glass/epoxy system was not pultruded for the full range of process variables in the heating study because the temperature rise was small over time, and an elevated temperature value was desired to be able to choose the proper mode to continue studying.

Table 2. Heating Modes for the Cavity with Teflon Die

Mode #	Mode Type	Cavity Length, Lc, mm	Probe Depth, Lp, mm
1	TM 011	70.5	8.80
2	TE 011	100.5	25.29
3	TM 111	119	13.15
4	TE 112	131	6.95
5	TE 311	152	13.32

Table 3. Heating Modes for the Cavity with Teflon Die and Graphite/Epoxy Prepreg

Mode #	Mode Type	Cavity Length, Lc, mm	Probe Depth, Lp, mm
1	TM 011	70	8.80
2	TE 011	99	16.17
3	TM 111	115	21.57
4	TE 112	133.5	23.42
5	TE 311	151	13.49

Table 4. Heating Modes for the Cavity with Teflon Die and Glass/Epoxy Prepreg

Mode #	Mode Type	Cavity Length, Lc, mm	Probe Depth, Lp, mm
1	TM 011	70	11
2	TE 011	101	13.94
3	TM 111	117	15.75
4	TE 112	131	9.5
5	TE 311	152	16.33

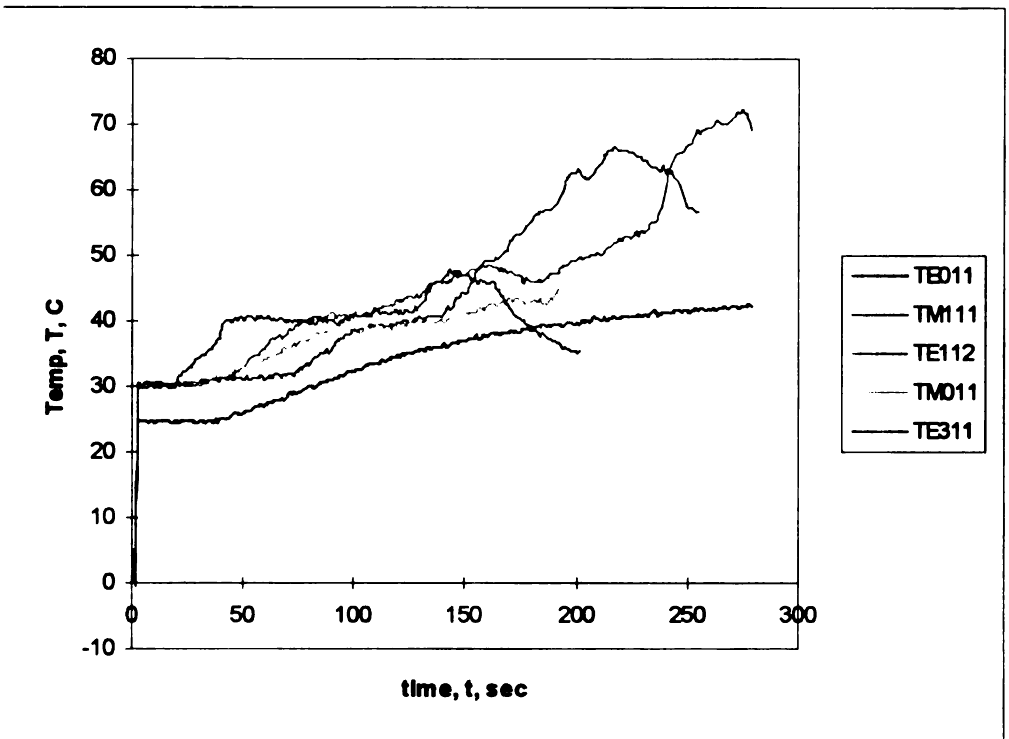

Figure 7. Temperature Versus Time Results for Heating Studies of Six-Ply Hercules AS4/3501-6 Prepreg at 100 Watts and 0.787 ft/min

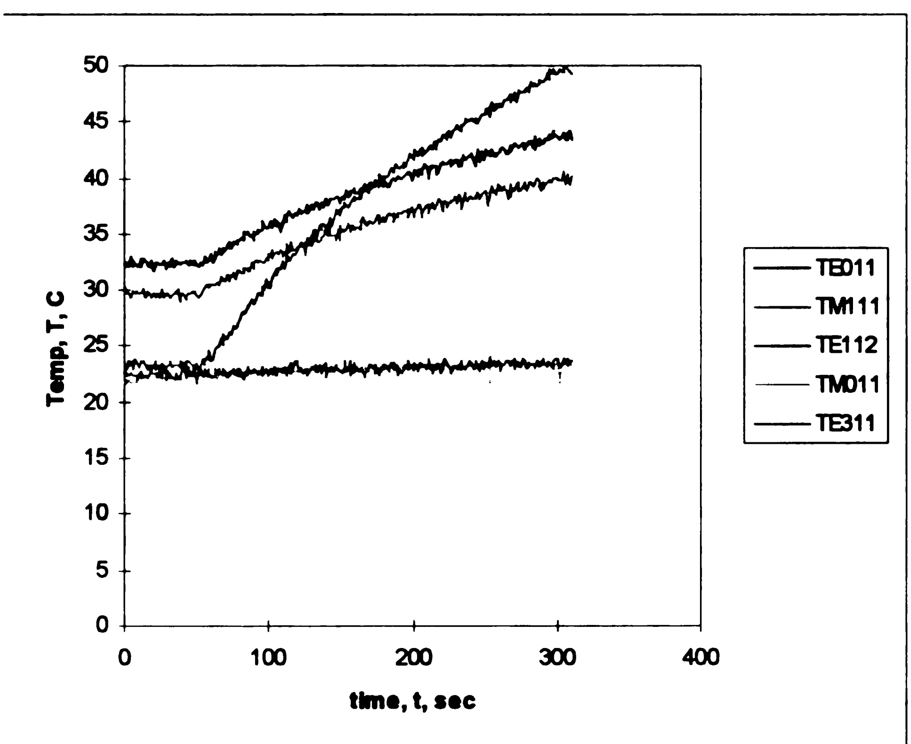

Figure 8. Temperature versus Time Results for Heating Studies of Stationary Six-Ply DA409/E250 Prepreg at Approximately 50 Watts

3.4. Preliminary Heating Studies In TE_{112} Mode

Three foot, six-ply Hercules AS4/3501-6 prepreg tape samples were processed in a TE_{112} mode cavity at 2450 MHz in the existing pultrusion apparatus with input powers of 50, 75, and 100 Watts and a pulling speed of 0.281 ft/min. From the results in Figure 9, it was observed that an increase in input power increased the steady state temperature value of the material. Also, the linear portion of the temperature vs. time curve has a larger slope for increasing input power, suggesting that higher power leads to decreased processing times. Table 5 lists the relative values from the extent of cure measurements conducted on DSC.

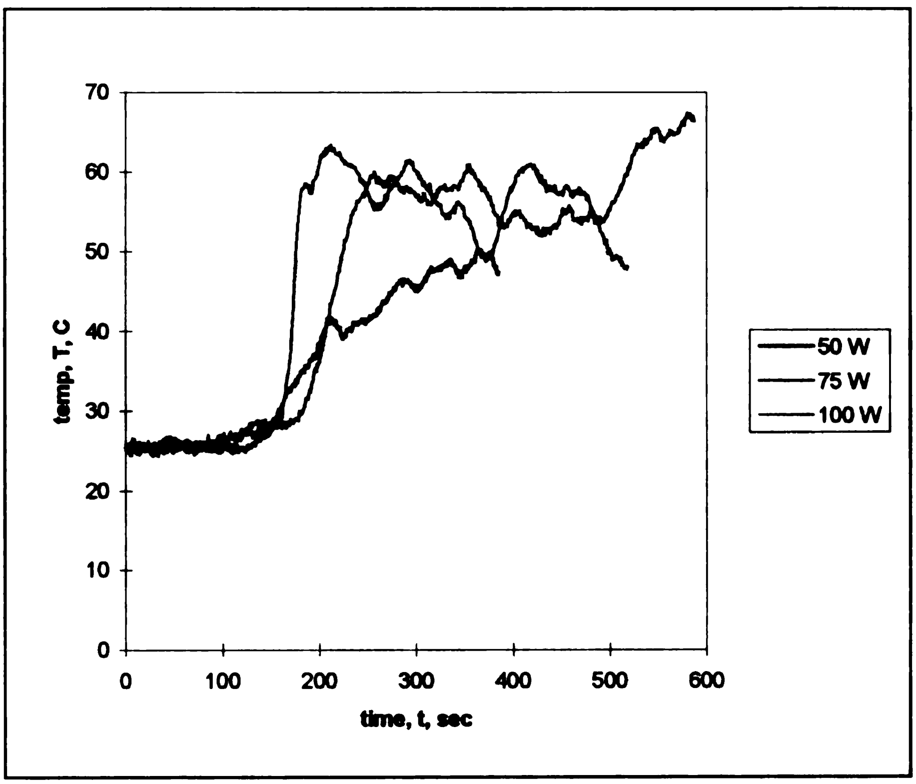

Figure 9. Results For Preliminary Heating of Six-ply Graphite/Epoxy Composite In TE_{112} Mode At Various Input Powers

Table 5. Extent of Cure Measurement for Preliminary Heating of Six-Ply Graphite/Epoxy Composite in TE_{112} Mode with Input Power Varied

Input Power (Watts)	Pulling Speed (ft/min)	Extent of Cure
50	0.281	21.97%
75	0.281	96.66%
100	0.281	97.74%

3.5. Conclusions

The continuous microwave applicator was characterized to find which electromagnetic modes could be excited during pultrusion. Mode charts for a 7" brass cavity gave promising prospects for variable frequency processing because eleven modes could be excited at a specified cavity height. Heating studies of the two prepreg materials gave insightful results in establishing what mode heated the material most efficiently. TE_{112} mode was chosen for the fixed frequency studies.

It appears that both the graphite/epoxy and glass/epoxy systems are able to be processed in the microwave environment. It is shown in Figures 7 and 8 that there is a more rapid temperature increase in the graphite/epoxy prepreg than the glass/epoxy prepreg for the same heating mode. Graphite fibers absorb more electromagnetic energy than the epoxy. In glass/epoxy systems, the matrix absorbs the majority of the energy. There was a slower rate in temperature rise for the glass/epoxy because there was more reflected power during processing. The energy was coupling efficiently with the composite. The microwave cavity must be finer tuned when processing the glass/epoxy system. Preliminary pultrusion experiments on the graphite/epoxy prepreg revealed that the surface temperature rises more rapidly and to a higher temperature with an increase in input power, supporting the hypothesis that higher microwave input power will lead to a decrease in processing time. Promising data collected in this series of experiments set the stage for more in-depth fixed frequency and variable frequency studies.

Chapter 4: Fixed Frequency Pultrusion Experiments

4.1. Background

Three foot long, 1 ¼" wide, six-ply Hercules AS4/3501-6 prepreg tape samples were processed in a TE_{112} mode cavity at 2450 MHz in the existing pultrusion apparatus. Input powers of 40, 45, 50, 55, 60, 65, 70, 80, and 100 Watts were used to heat the tape at a pulling speed of 0.281 ft/min. Pulling speeds with the corresponding dial settings of 20, 25, 30, 35, 40, 45, and 50 on the Penta Power motor (0.281 ft/min - 1.17 ft/min) were used to process the tape while an input power of 100 Watts was selected.

From the heating studies, the TE_{112} mode was established as a center heating mode where the electric field was the strongest along the central, axial (pulling direction) down the tape (Figure 23). Optimizing the pultrusion variables of pulling speed and input power is important in producing a high quality part. Even though high product throughput is desired, good resin/fiber adhesion is paramount in achieving the mechanical properties sought by the customer.

4.2. Experimental Setup

Six plies of three foot by 1 ¼" prepreg were cut parallel to the continuous fiber direction. Next, they were stacked and sent through a pressurized roller to rid the tape of any voids and air bubbles that were present from the stacking process. The tape was manually fed through the Teflon die in the side of the cavity until just before the pulling rollers. The circuit was closed by connecting the input coaxial line to the 100 Watt fixed frequency power source and the output line to the coupling probe. The Luxtron temperature probes were placed across the die width in four locations and calibrated to ambient conditions. The probe tips touched the surface of the prepreg for accurate temperature measurement. Temperature data was collected by electronic signals sent to a PC. Temperature measurements began for a 30 second period to establish a steady state reading. After the 30 second start-up, the pulling rollers and power source were simultaneously turned on to their pre-determined positions. The reflected power meter was monitored to insure that maximum power was being delivered to the composite. Temperature readings halted once the back end of the prepreg exited the cavity. At this time, the power source was turned off. Upon exiting the cavity, the tape traveled through a set of pressurized rollers. The pultruded product was left to cool before thermal and mechanical analysis samples were made and tested.

4.3. Variation in Pulling Speed

At a fixed pulling speed, the material's residence time in the cavity defines how long the microwave energy has to heat the product to its curing temperature. If the pulling speed is too fast for the power input level used, the material will exit the cavity partially cured and a post-curing step will be needed. On the other hand, too slow of a pulling speed may cause the resin to be overheated and degrade. "The location of the exothermic peak depends on the speed of pulling the fiber-resin stream through the die." [16] The exotherm peak will shift towards the die exit with an increase in pulling speed. This will also increase the pulling force needed by the mechanical systems. By combining temperature versus time curves and extent of cure measurements, one can determine the point where the exotherm has ended and continuing with the addition of microwaves could cause undue heating. The only chance for heat transfer when the tape has exited the cavity is from the heat conduction through the resin and fiber, which tends to be low, and by the remaining exotherm of the polymerization reaction. It is desired that the exotherm be completed before the die exit because if the interior of the pultruded part is still at an elevated temperature, interlaminar cracks may form within the product. [16]

4.4. Variation in Input Power

The issue of input power level must be considered. In the microwave pultrusion energy balance (see Chapter 7), input power is an implicit variable in the heat generation due to the power absorption term. In a published power absorption model [1], the five parameters of interest are all explicit functions of input power. Also, to shorten processing times and times for a material to reach a desired temperature, higher power input is required, as suggested by the preliminary heating studies on the graphite/epoxy prepreg. At a fixed pulling speed, too high of power may cause the resin to degrade and the mechanical properties may suffer. Not enough power will result in a low-cured product and the resin/fiber interfacial adhesion will be poor. Extent of cure and mechanical property measurements will be related to pulling speed and input power in order to find the optimum processing conditions.

4.5. Extent of Cure Measurement (Differential Scanning Calorimetry)

Because TE_{112} mode was used, the magnitude of the electric field was greater at the center of the cavity and parallel to the pulling direction. Further examination of the prepreg revealed it to be preferentially heated down the center of the tape. Relative values of extent of cure were found using DSC. A sample from an uncured piece of graphite/epoxy composite was heated 10°C/min to 350°C to establish a theoretical maximum heat of reaction. When an epoxy matrix is heated, 100% of the possible reactive sites do not react, so 100% extent of cure is not theoretically possible. Extent of cure values reported below and in plots in Figures 10 and 13 are relative values and not absolute. Samples were taken from the center of the prepreg tape. Samples were heated 10°C/min to 350°C to find the heat of reaction, which was compared to the heat of reaction for the uncured composite. Equation 7 shows how the extent of cure was calculated.

$$\alpha = 1 - \frac{H_{RC}}{H_{RU}} \tag{7}$$

where α=extent of cure
H_{RC}=heat of reaction of cured sample (J/g)
H_{RU}=heat of reaction of uncured sample (J/g)

The heat of reaction for the uncured composite sample was found to be 197.5 J/g. Extent of cure increased with microwave power input up to 70 Watts and then leveled off to approximately 98%. At these high levels of power input, the resin may have degraded, resulting in what looks to be a "well-cured" product. There was negligible change in extent of cure with powers above 70 Watts. Powers below 40 Watts, which gave 18% extent of cure, had low heating potential and were neglected. Equation 8 simply reveals why increasing input microwave power at the same pulling speed results in a higher extent of cure.

$$t = \frac{\left(C_{pf} * w_f + C_{pm} * \left(1 - w_f\right)\right) * \left(T_c - T_a\right) * \left(w_m + w_f\right)}{P} \tag{8}$$

Above, the time, t, for the temperature to rise to a curing temperature, T_c, from the ambient temperature, T_a, is dependent on the weight fractions, w_m and w_f, and heat capacities, C_{pm} and C_{pf}, of the matrix and fiber, respectively. The microwave power, P, is inversely proportional to time so an increase in power leads to a decrease in time. If the material's residence time is the same for varying input power, the exiting temperature of the prepreg will be greater with increasing input power. The extent of cure is indirectly related to the temperature through the kinetic parameters in the kinetic model. Equation 8 is a basic energy balance, which assumes that all the incident power delivered to the microwave cavity is absorbed by the composite, causing heat generation within the material from dipole relaxation.

Extent of cure increased somewhat linearly with increasing microwave power up to 70 Watts and then leveled off to approximately 98%. The increase in power increases the amount of heat generation inside the composite. Heat conduction is low perpendicular to the fiber direction, resulting in a low-cured outer region of the product. There was negligible change in extent of cure with powers above 70 Watts. At a pulling speed of 0.281 ft/min, power levels below 40 Watts had low heating potential and were neglected. Figures 11 and 12 show trendlines with equations for extent of cure as a function of input power at a constant pulling speed.

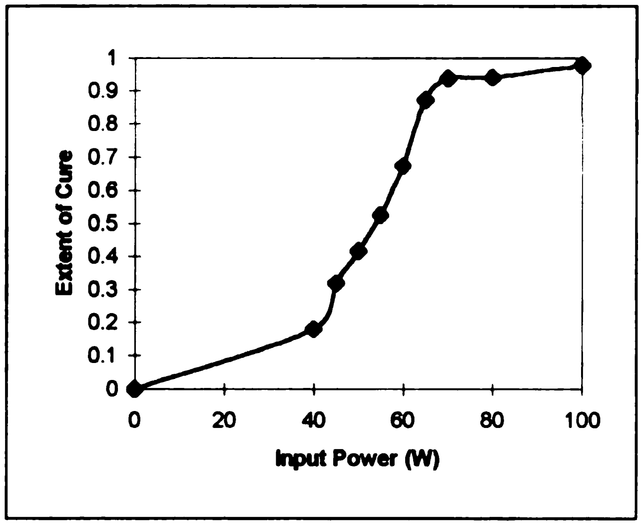

Figure 10. Effect of Input Power on Extent of Cure

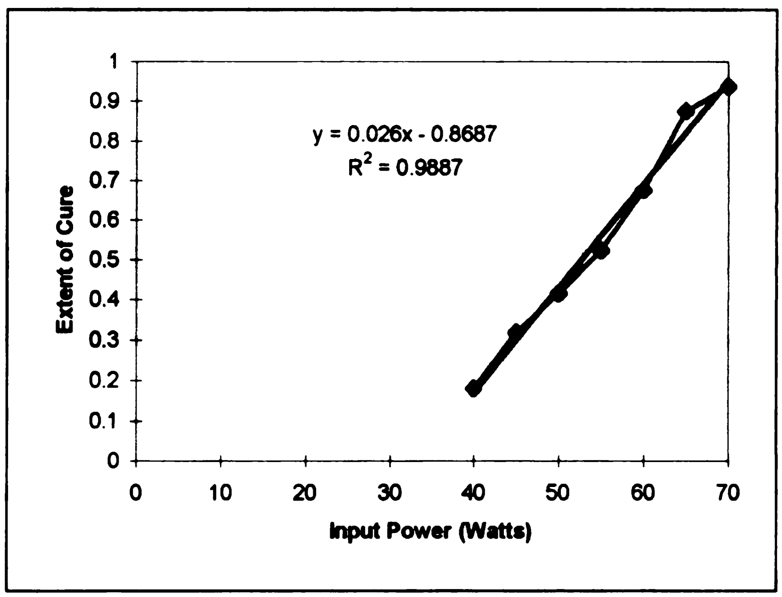

Figure 11. Trendline for Extent of Cure as Function of Input Power (40-70 Watts)

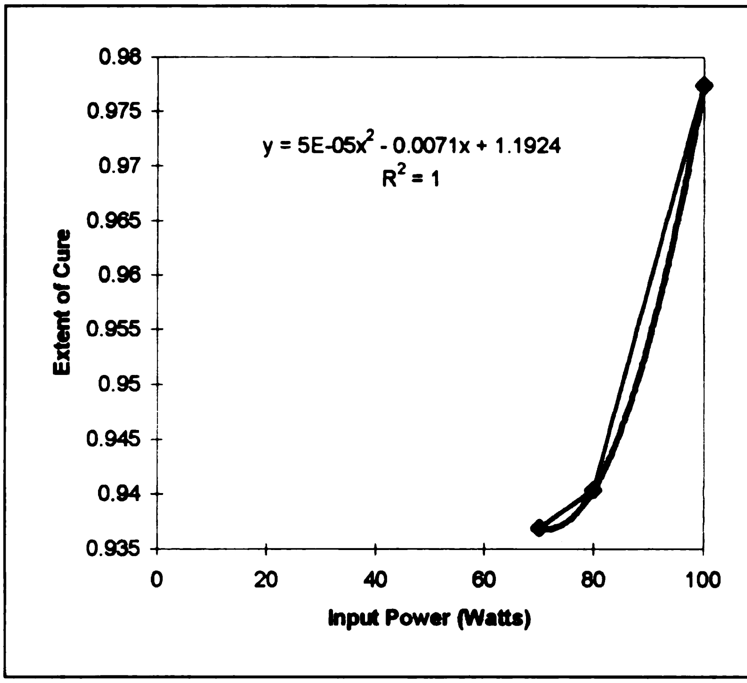

Figure 12. Trendline for Extent of Cure as Function of Input Power (70-100 Watts)

For pulling speeds between 0.5 ft/min and 0.7 ft/min, the extent of cure decreases rapidly. For pulling speed ranges of 0.3-0.5 ft/min and 0.7-1.2 ft/min, the extent of cure changed only 15% in each range. It is suggested to operate within these ranges for greater control of extent of cure and better quality of product. It should be noted that line speeds would increase with higher input power. The extent of cure dependence on pulling speed is justified by the "residence time" of a differential slice of prepreg inside the cavity. Figures 14, 15, and 16 show the extent of cure as a function of the pulling speed and give trendlines for each of the three regions of interest: the high cure section of slow processing speeds, the linear region of moderate pulling speeds for a low input power, and high pulling speed region below the gel conversion point. Longer residence times will allow the electromagnetic energy to interact with the composite for a longer period of time. For slower processing speeds, the prepreg was cured across a greater width of the tape. For processing conditions that produce a product with an extent of cure of 30% (gel conversion for epoxy resin) or below, the microwave applicator could act as a preheating device in a pultrusion line. If maximum extent of cure is desired, the microwave pultrusion apparatus could be the sole heating element in the pultrusion line.

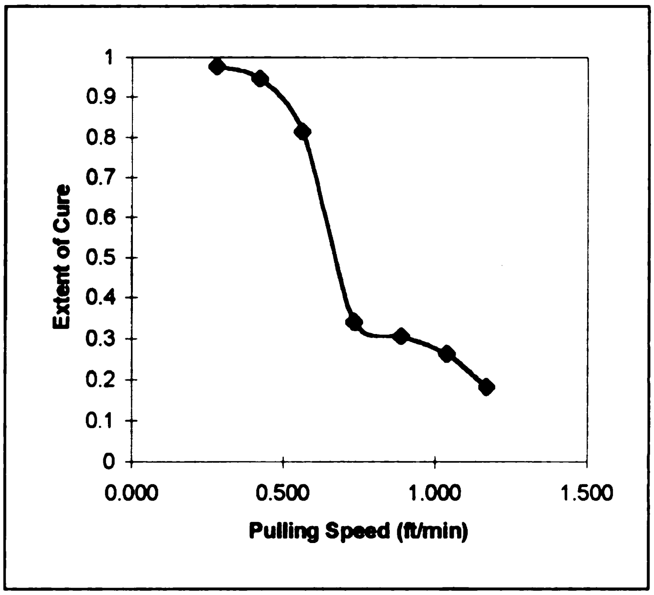

Figure 13. Effect of Pulling Speed on Extent of Cure

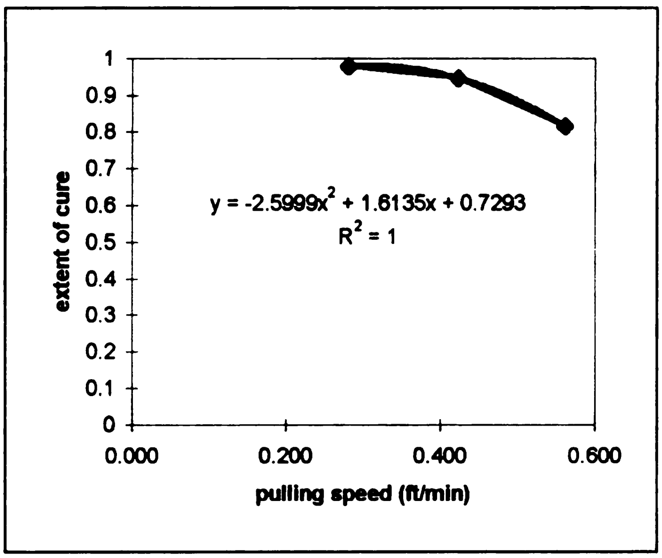

Figure 14. Trendline for Extent of Cure as Function of Pulling Speed (0.281-0.562 ft/min)

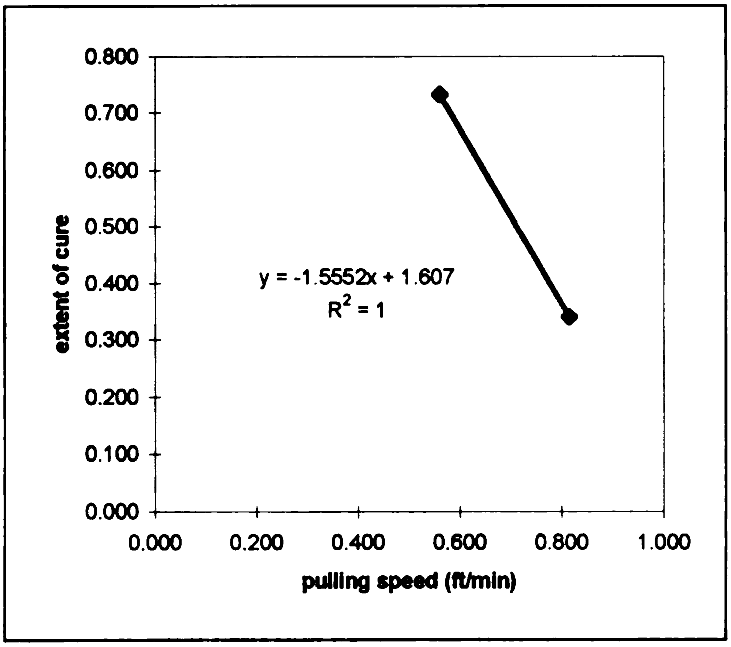

Figure 15. Trendline for Extent of Cure as Function of Pulling Speed (0.562-0.733 ft/min)

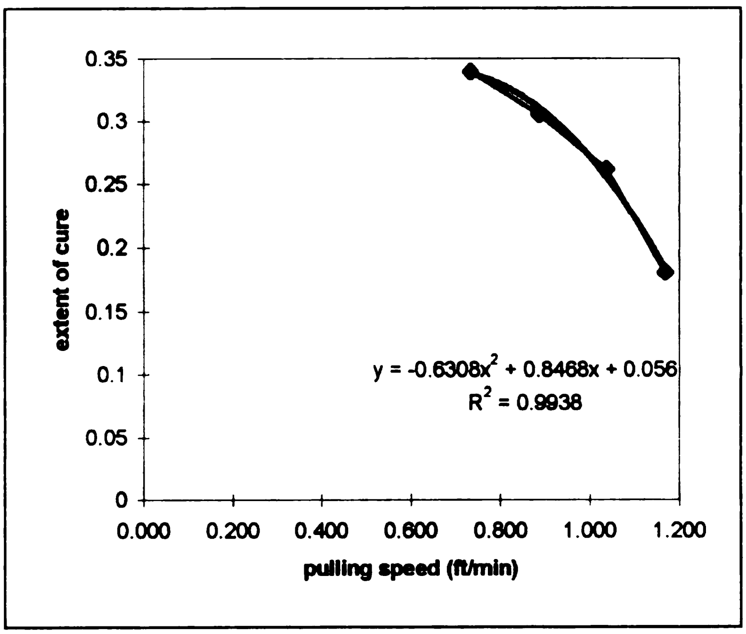

Figure 16. Trendline for Extent of Cure as Function of Pulling Speed (0.733-1.17 ft/min)

4.6. Mechanical Properties Measurements

4.6.1. Tensile Strength

Tensile coupons measuring approximately 17.78 cm (7") long and 0.9525 cm (0.375") wide at the middle were cut from the cured, unidirectional graphite/epoxy product. Three samples were tested for each set of processing conditions. The coupon was shaped to specifications with a router while the sample was in a tensile bar metal clamp. Tensile strength measurements were made using a pulling rate of 1.27 cm/min (0.5"/min), and the samples were pulled parallel to the fiber direction. A 1000 lb_f load cell was used, in which the grips each held one inch of the tensile bar's ends. The load was plotted against the strain to help calculate the tensile modulus. Three samples were made for each processing condition. Coupon thickness and width in the middle were measured at three points and averaged. Maximum tensile strength and load were measured and tensile modulus was calculated through analysis of stress versus strain curves.

The results for the tensile tests were averaged for the three samples, and those values are shown in Figures 17 through 20. Measurements typically varied from the average by no more +/- 10%. Values for the tensile strength ranged from 138 to 188 MPa. The tensile strength was not affected by pulling speed or input power variations because the samples were tested by pulling in the fiber direction. The tensile modulus was calculated by performing a linear regression on the initial portion of the stress versus strain curve. Average tensile modulus values ranged from 1100 to 1500 MPa, with values varying +/- 15% from the average. Any anomalies in the curves were from experimental error, such as the sample slipping in the tensile bar grips.

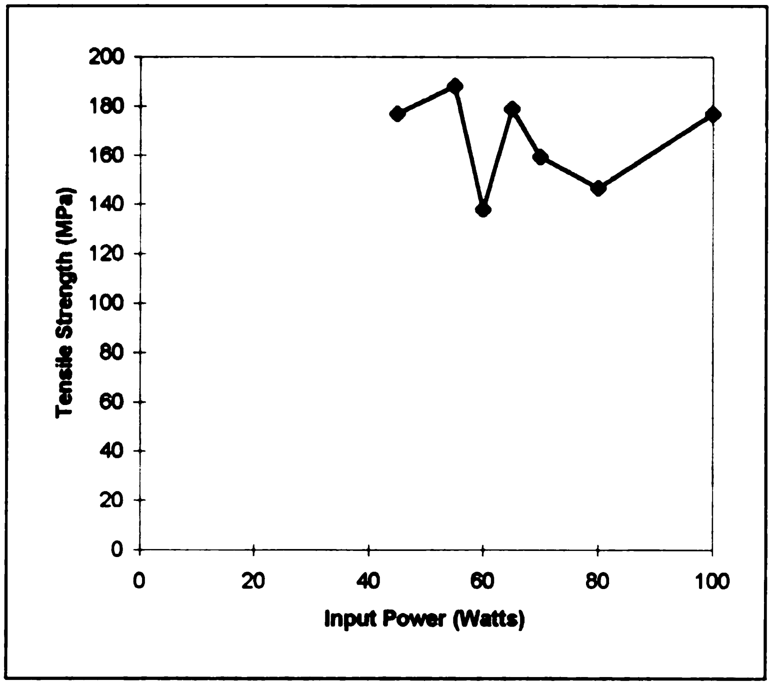

Figure 17. Tensile Strength of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power

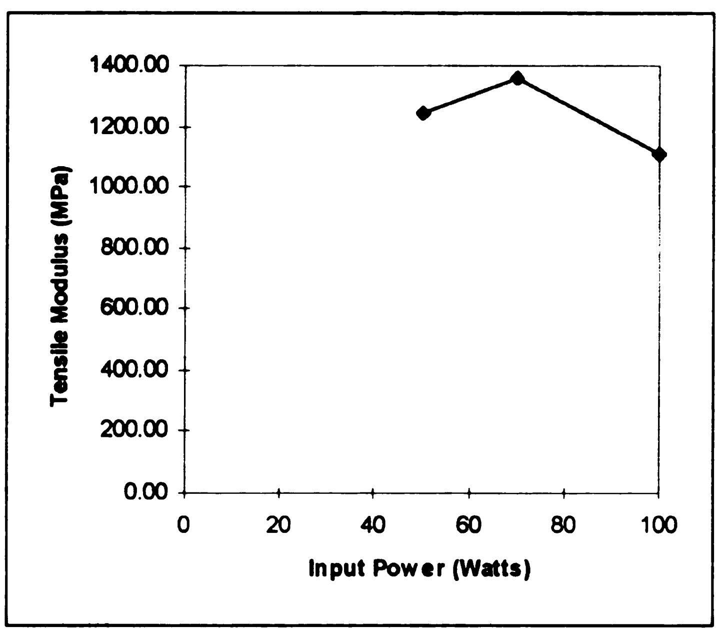

Figure 18. Tensile Modulus of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power

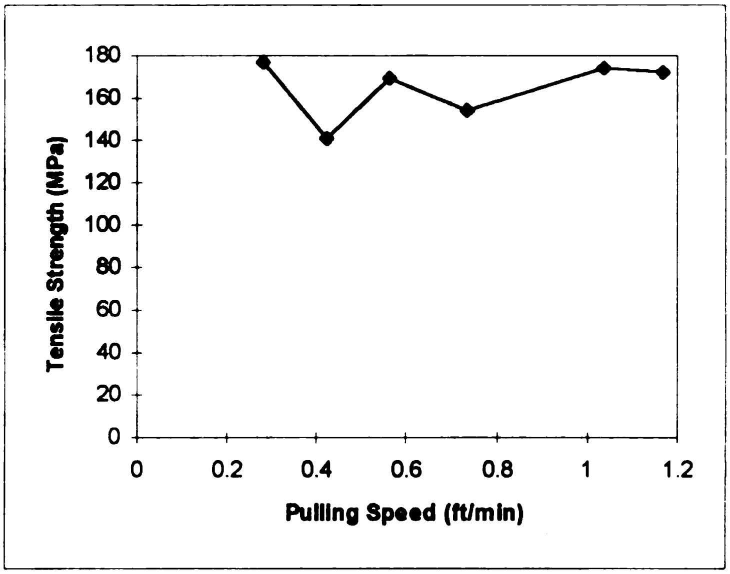

Figure 19. Tensile Strength of Six-ply Graphite/Epoxy Prepreg Tape with an Input Power of 100 Watts and Variable Pulling Speed

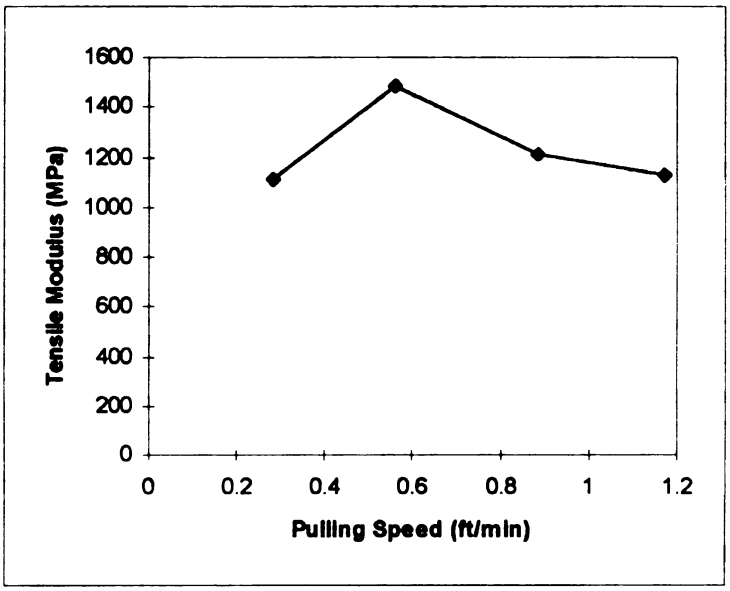

Figure 20. Tensile Modulus of Six-ply Graphite/Epoxy Prepreg Tape with an Input Power of 100 Watts and Variable Pulling Speed

For unidirectional composites containing fibers parallel to the pulling direction, the samples fail by tensile rupture of the fibers. [16] This is followed or accompanied by the debonding of the fiber/matrix interface parallel to the fibers. [16] Any final failures in the composite are equal to $(1-f)\sigma_{mu}$, where f is the volume fraction of fibers in the composite, and σ_{mu} is the ultimate strength of the matrix. If the matrix begins to fail while the fibers are still bearing a portion of the load, then the composite's ultimate tensile strength can be calculated from Equation 9. [20]

$$\sigma_{lu} = f\sigma_{fu} + (1-f)\sigma_{mfu} \qquad (9)$$

where σ_{fu} = ultimate strength of the fiber

σ_{lu} = ultimate strength of the composite

σ_{mfu} = matrix stress at the onset of fiber cracking

4.6.2. Flexural Strength

Flexural strength tests were conducted on the Universal Testing System in compliance with ASTM Standard D 790 - 84a. [21] The flexural strength and flexural modulus were obtained for the tests. The support span-to-depth ratio was 16 to 1 for the three-point loading machine. The pultruded composite samples were approximately 3.2 mm thick. Again, three samples were cut for each processing condition. The recommended dimensions for test specimens were 25 mm wide and 80 mm long. The support span was 50 mm, and the rate of cross-head motion was 1.3 mm per minute.

Figures 21 through 24 show the averaged results for the flexural test measurements. Values were averaged for the flexural strength and ranged from 25 to 120 MPa. Measurements typically varied from the average by no more +/- 10%. The flexural strength of the material is thought to be the maximum fiber stress at failure on the tension side of a flexural sample. [16] The flexural strength increased with increasing input power and reached a maximum at approximately 60 Watts. At input powers greater than 60 Watts, the flexural strength decreased due to the brittleness of the specimens. Flexural strength increased with increasing pulling speed up to a maximum of about 0.42 ft/min. For faster pulling speeds, the specimens bent much more because the resin/fiber interfacial strength was low and the resin was undercured. The flexural strength values for these higher pulling speed experiments were a reflection of the non-homogeneity of cure across the width of the prepreg.

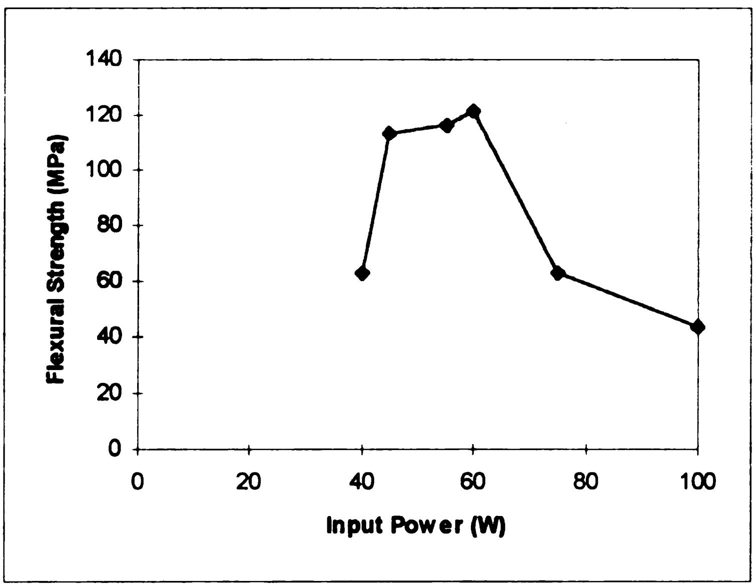

Figure 21. Flexural Strength of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power

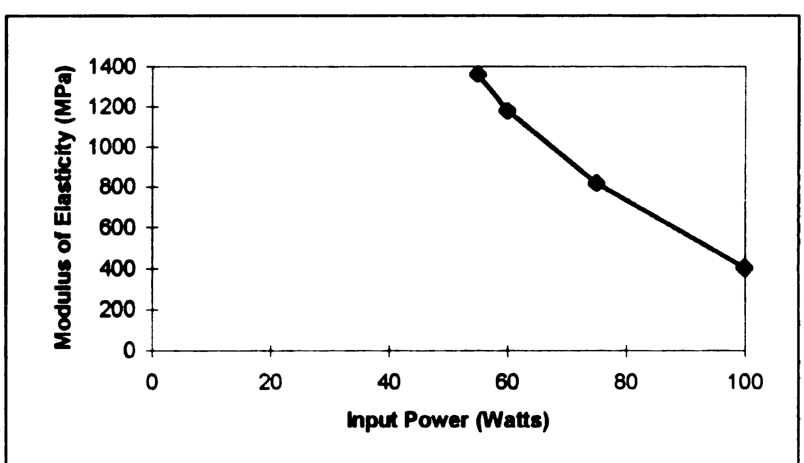

Figure 22. Flexural Modulus of Six-ply Graphite/Epoxy Prepreg Tape with A Pulling Speed of 0.281 ft/min and Variable Input Power

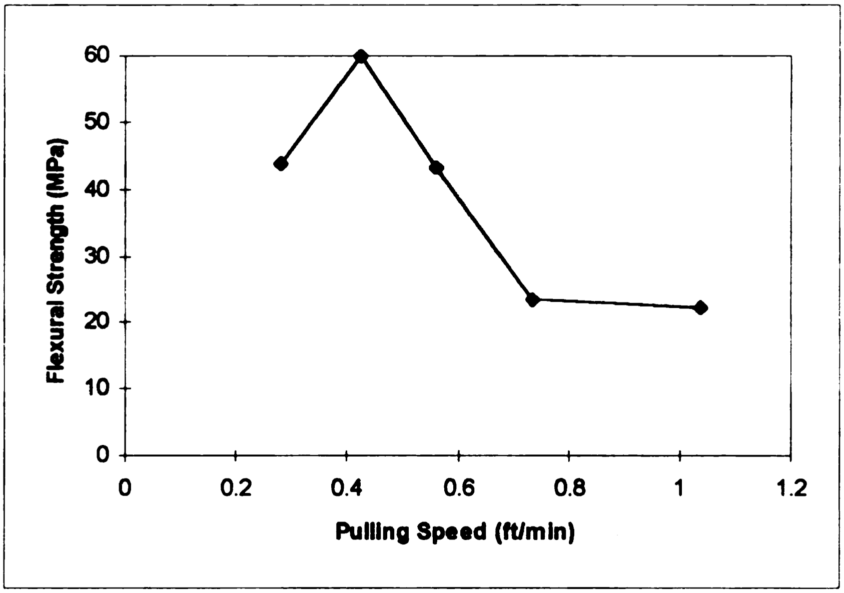

Figure 23. Flexural Strength of Six-ply Graphite/Epoxy Prepreg Tape with An Input Power of 100 Watts and Variable Pulling Speed

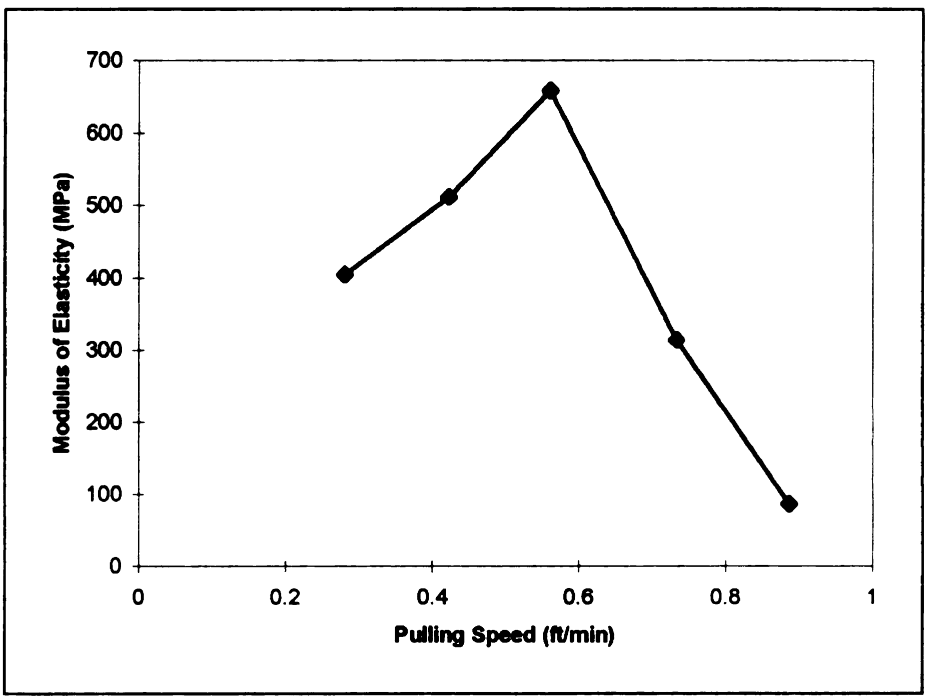

Figure 24. Flexural Modulus of Six-ply Graphite/Epoxy Prepreg Tape with An Input Power of 100 Watts and Variable Pulling Speed

Average flexural modulus measurements ranged from approximately 300 MPa to 1400 MPa, with values varying +/- 15% from the average. The modulus suffered from a low-cured product at low input power levels or too high pulling speeds and from a brittle product with a partially degraded matrix. When fibers are long and continuous, there is larger statistical chance that there will be flaws in the fibers which could allow for failure in the composite. [22] The resin acts like glue between the sensitive, dry fiber bundles. When a load is applied, the resin increases the fibers' ability to carry that load by holding together the surface imperfections in the fibers. [22] If the resin degrades with overheating, the resin/fiber interfacial bond strength is at risk. The resin will not fill its role of being glue and may become brittle just like the dry fiber bundles. It is important to balance the processing conditions to ensure that the resin/fiber interface is strong, so the resin can help improve the composite's strengths and moduli.

4.7. Conclusions

Extent of cure of the graphite/epoxy composite was established as a function of input power and pulling speed for a microwave pultrusion apparatus. Extent of cure increased with an increase in microwave power input and decreased with an increase in pulling speed. At 100 Watts input power and a pulling speed of 0.281 ft/min, the center of the six-ply graphite/epoxy prepreg was 98% cured.

Tensile strength and modulus were relatively unaffected by the change in process variables. There was variability in the flexural strength and modulus with respect to input power and pulling speed. Too high of power or too slow of pulling speed resulted in a brittle matrix. Low input power and fast pulling speeds gave a product that had a relatively uncured matrix and low interfacial bond strength.

Chapter 5: Variable Frequency Pultrusion Experiments

5.1. Background

Either a fixed frequency or variable frequency microwave power source can be used to obtain uniform and fast microwave heating. When applying fixed frequency heating, one must rely on the thermal properties of the materials to dissipate heat throughout the composite for a more even distribution of cure. During the single mode heating studies, the prepreg tape was not heated evenly over the width. Some transverse electromagnetic modes revealed that the tape was heated more in the center (Figure 25), while others heated preferentially on the outside edges (Figure 26). Temperature gradients for the single mode experiments reached as much as 40-45°C. Past results have shown that an even cure distribution occurred after 15 minutes of single mode heating. [17] These results and the need to increase process throughput led to the idea of variable frequency processing of the prepreg, such that the cavity length would be kept constant and processing frequencies would be intelligently selected.

Either single mode heating or mode switching heating can be used in the process. Proper mode switching heating provides a more uniform temperature profile. In fixed frequency processing, the modes can only be changed by adjusting the cavity length mechanically. With the variable frequency power source, the modes can be changed by electronically tuning the frequency, which is a much better approach than mechanical tuning.

In the variable frequency study, the 17.78 cm cylindrical brass cavity was characterized, with a Teflon die and processing material inserted, for a frequency range of 2.00 to 3.00 GHz. Heating studies for selected frequencies helped to intelligently select those used in further processing studies. Prepreg thickness was varied to investigate if sample size affected microwave power absorption efficiency. Time intervals for each processing frequency were varied to establish an optimum set of processing conditions for a particular prepreg thickness.

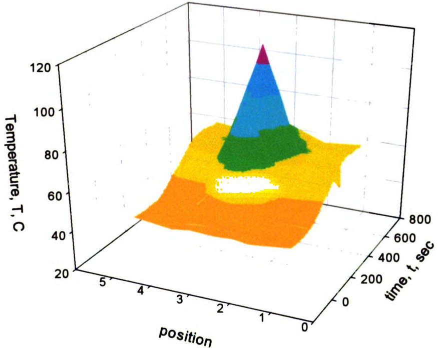

Figure 25. Six Ply Hercules AS4/3501-6 Heated in TE_{112} mode at 100 Watts and 0.281 ft/min

Position 3 corresponds to the middle of the die, while positions 1 and 5 correspond to the outer edges of the die. Each position is 8mm apart. The y-coordinate is the processing time in seconds and can be compared to die length in conventional pultrusion processing by considering a differential slice of prepreg and monitoring its temperature as it passes through the heater. Then, by multiplying the processing time by the pulling speed, die length would vary from two to three feet for the cases below.

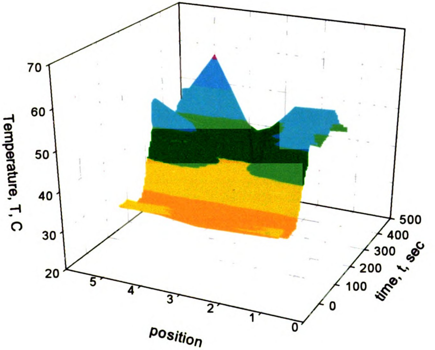

Figure 26. Six Ply Hercules AS4/3501-6 Heated in TE_{011} mode at 100 Watts and 0.281 ft/min

5.2. Frequency Sweep Analysis

For an initial set of cavity dimensions, the coupling probe was set at a depth of 15.89 mm and the cavity length (L_c) was varied from 160 mm to 70 mm by 10 mm increments. A Lambda variable frequency power source acted as an amplifier to a HP Sweep Oscillator to enable the microwave input power to be increased to approximately 150 Watts. A process control program written by Qiu [23] measured the reflected power for a frequency sweep of 2.00 to 3.00 GHz. Figure 27 is presented as an example of a poor selection of cavity dimensions such that there are only a couple of frequencies that have below 10% reflected power. When high input power is desired, there is a greater risk of the source shutting down due to the reflected power, even at 10-15% reflection.

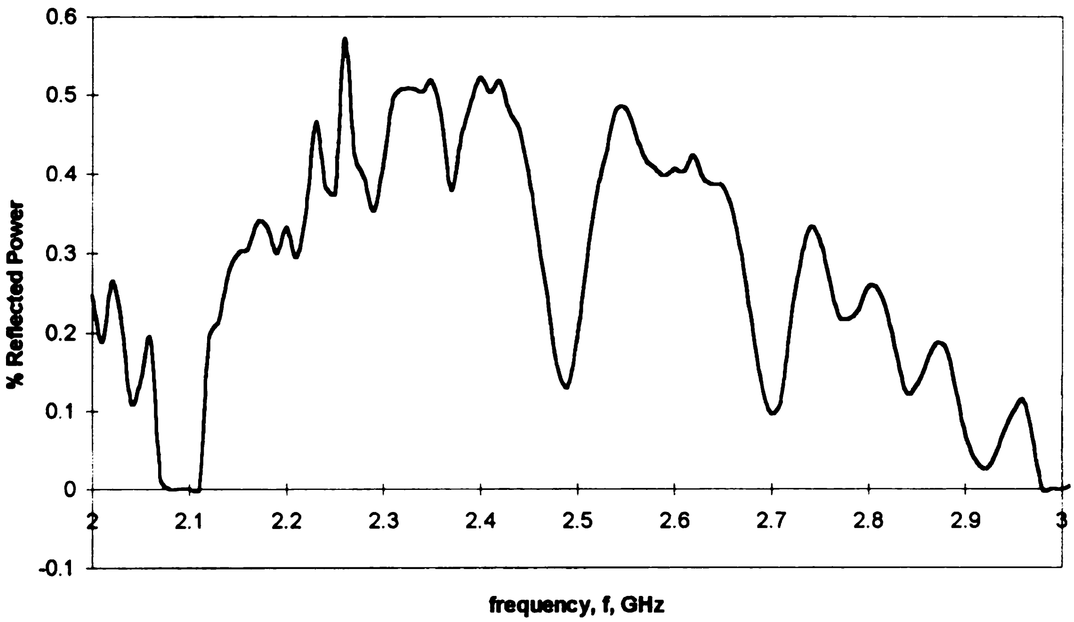

Figure 27. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 90 mm And d_p = 15.89 mm And Containing Six-ply Hercules AS4/3501-6 Prepreg

Frequencies with minimum reflected power were individually selected to determine their heating potential (Figure 28). A cavity length of 135mm and a coupling probe depth of 15.89mm were used in the first study of variable frequency processing of a six-ply Hercules AS4/3501-6 prepreg tape. A mode-switching control program was used to intelligently select the appropriate frequencies. The process control program allowed the operator to specify the time interval each frequency would heat the material. The time intervals could be the same, or they could vary by simply changing the value before the next experimental run. Initially, each frequency was given the same time interval value.

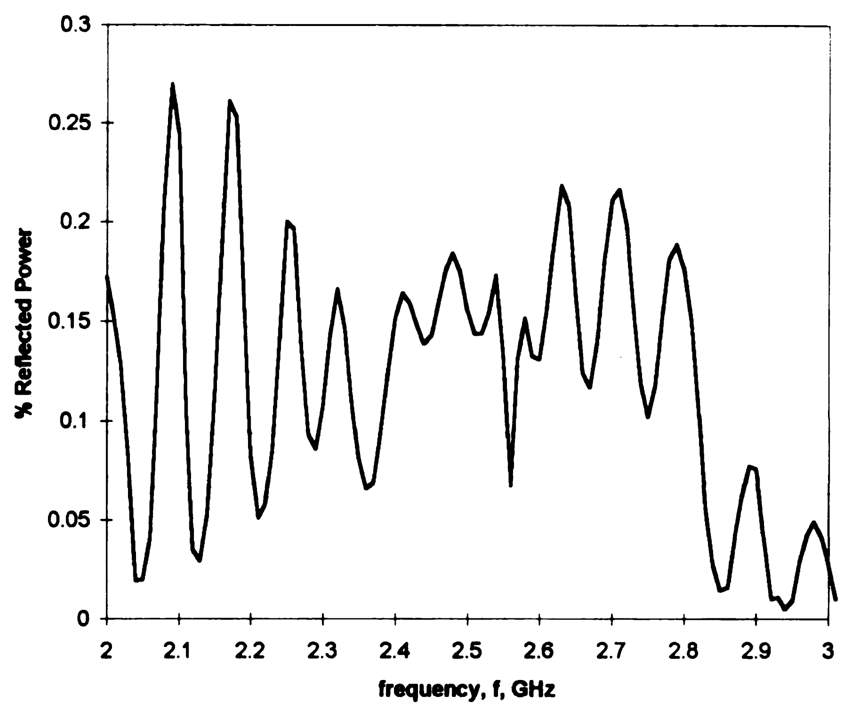

Figure 28. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 135 mm And d_p = 15.89 mm And Containing Six-ply Hercules AS4/3501-6 Prepreg

5.3. Input Power vs. Frequency

For the variable frequency power source, power output varies with frequency (Figure 29). For example, if the input power was set to 100 Watts, the frequencies with low power output make the average input power less than 100 Watts. Also, when the time interval is on the order of milliseconds, the frequencies are changing very quickly, and there is a relatively high proportion of time spent not heating the composite. Higher input power is needed overall if the composite is to be cured in a short time scale.

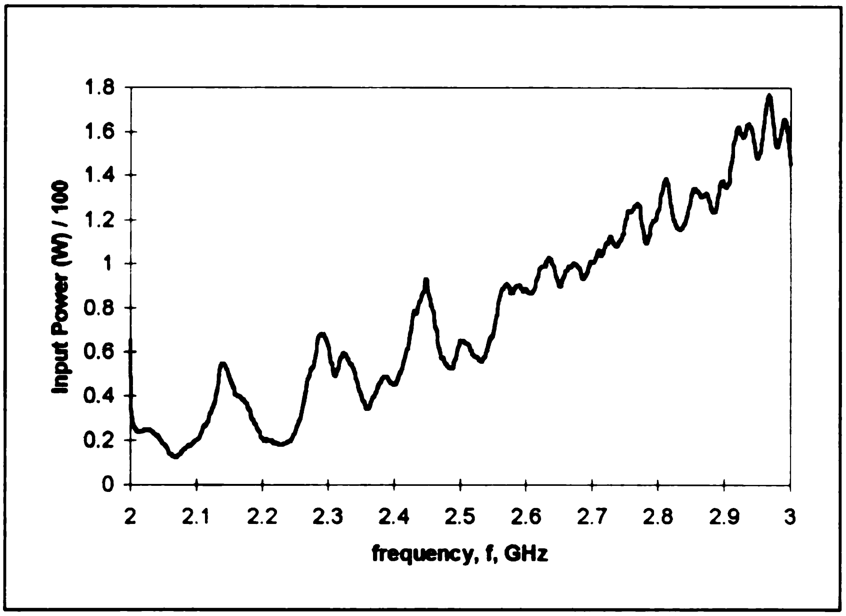

Figure 29. Incident Power Versus Processing Frequency for Lambda Variable Frequency Power Source [23]

5.4. Temperature Measurement and Heating Studies Part I: 6-ply Prepreg, Four Frequencies For V.F. Processing

By placing fluorotropic temperature probes across the Teflon die inside the microwave cavity, it was found that temperature varied by less than 15 degrees across the 1 ¼" prepreg tape. The tape was only heated to 42°C using 65 to 73 Watts input power and a time interval of 100ms for each frequency (Figure 30). The frequencies with low reflected power were judged by measuring their heating capabilities. This was done by heating a stationary prepreg sample in the cavity and recording data from the temperature meter. The frequencies that had provided efficient heating were compared for their power output potential from Figure 27. The frequencies with similar power outputs were chosen out of this second set of characterization studies and were used for additional variable frequency studies.

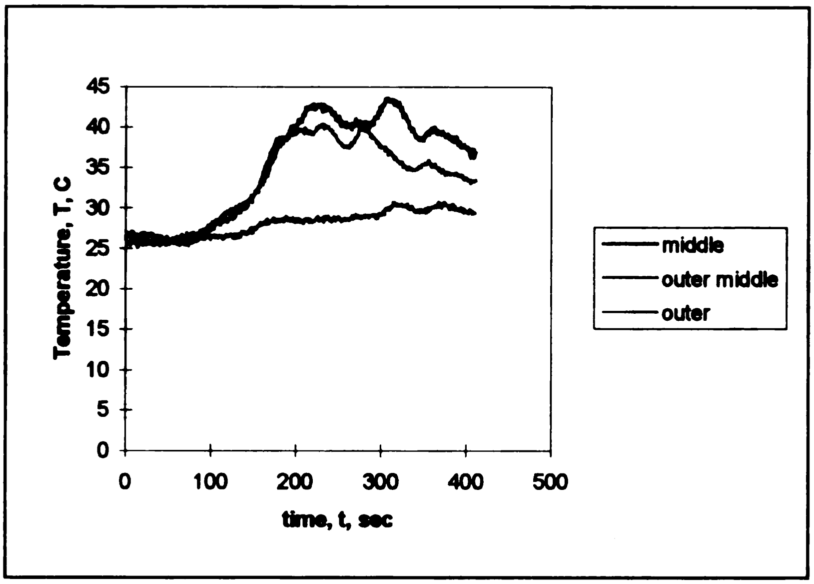

Figure 30. Six-Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4285 GHz, 2.444 GHz, 2.594 GHz, and 2.6140 GHz - 100 ms each) At An Average Of 70 Watts And A Pulling Speed of 0.281 ft/min

5.5. Heating Studies Part II: 18-ply Prepreg, Change In Cavity Dimension

A new set of experiments was conducted in which an 18-ply piece of prepreg tape was processed in the cylindrical brass cavity. It was thought that the thickness of the six-ply tape was not efficiently interacting with the electromagnetic radiation put out by the power source. The coupling probe depth (d_p) was changed, and the cavity length was again varied. At a cavity length of 93 mm and a coupling probe depth of 22.90 mm, it was found that several modes could be excited. Figure 33 shows there were thirteen frequencies having below 10% reflected power.

Figures 27, 31, 32 and 33 will show the natural selection of the final set of cavity dimensions that was used for many of the variable frequency experiments. Cavity length, coupling probe depth, and prepreg thickness affected the frequency sweep charts. By changing the prepreg thickness from 6-ply to 18-ply, more of the incident power was absorbed by the material, resulting in more possible modes that could be excited with minimal reflected power (R.P. < 10%). Increasing the coupling probe depth seven millimeters decreased the reflected power for the possible modes and the peaks were tighter, giving a better idea of the processing frequency needed. Finally, the cavity height was increased three millimeters. The reflected power was decreased slightly, and there was a tighter range of possible modes around the center frequency of 2.45 GHz, which was theoretically the most efficient processing frequency in the swept range.

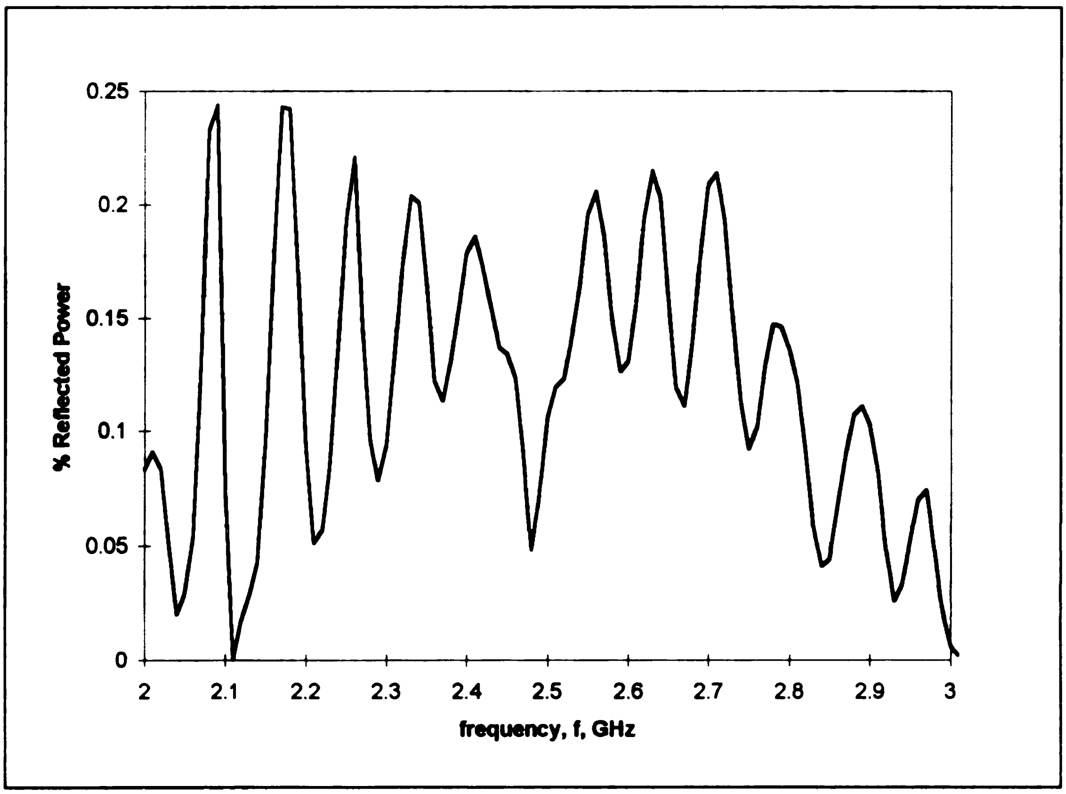

Figure 31. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 90 mm And d_p = 15.89 mm And Containing Eighteen-ply Hercules AS4/3501-6 Prepreg

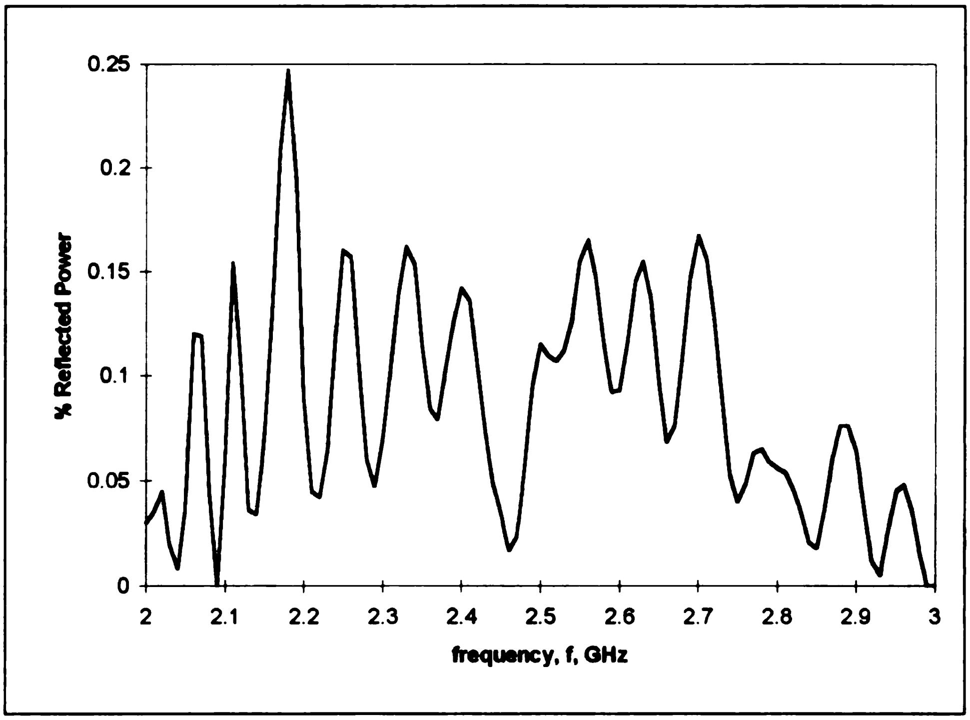

Figure 32. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 90 mm And d_p = 22.90 mm And Containing Eighteen-ply Hercules AS4/3501-6 Prepreg

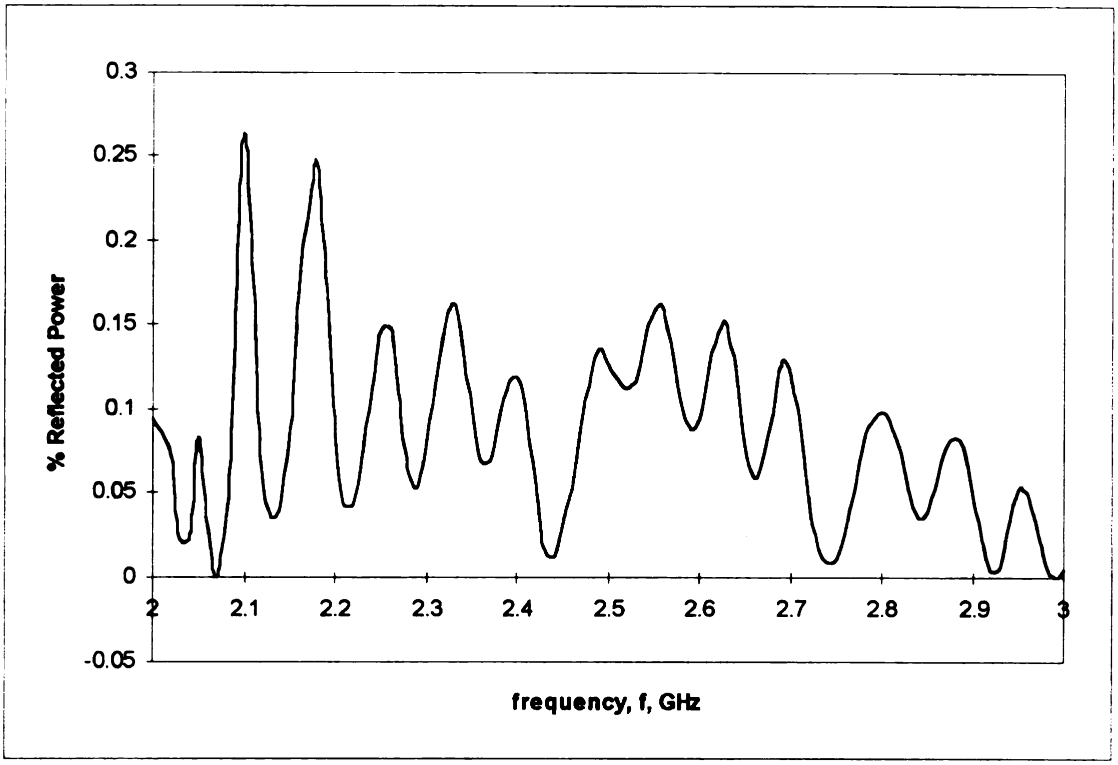

Figure 33. Percentage of Reflected Power At 2.00 to 3.00 GHz Processing Frequencies For A Cylindrical Brass Cavity With L_c = 93 mm And d_p = 22.90 mm And Containing Eighteen-ply Hercules AS4/3501-6 Prepreg

Input power was raised to approximately 100 Watts, and the time interval was set to 1000ms for each frequency. Each of the three frequencies heated the composite for approximately one second before switching to the next one selected. Temperature versus time profiles (Figure 34) revealed that again the center temperature was higher than the outside of the tape. The tape was too thick to exhibit large heating rates with the small input power used, so the tape thickness was decreased to 11 plies. It was then suggested that the time interval used to switch among the frequencies not be constant, but that the time in which the outside heating frequencies are attenuated be increased. This would allow the outside edges to be heated to a temperature closer to that in the center of tape, resulting in a more even distribution of cure.

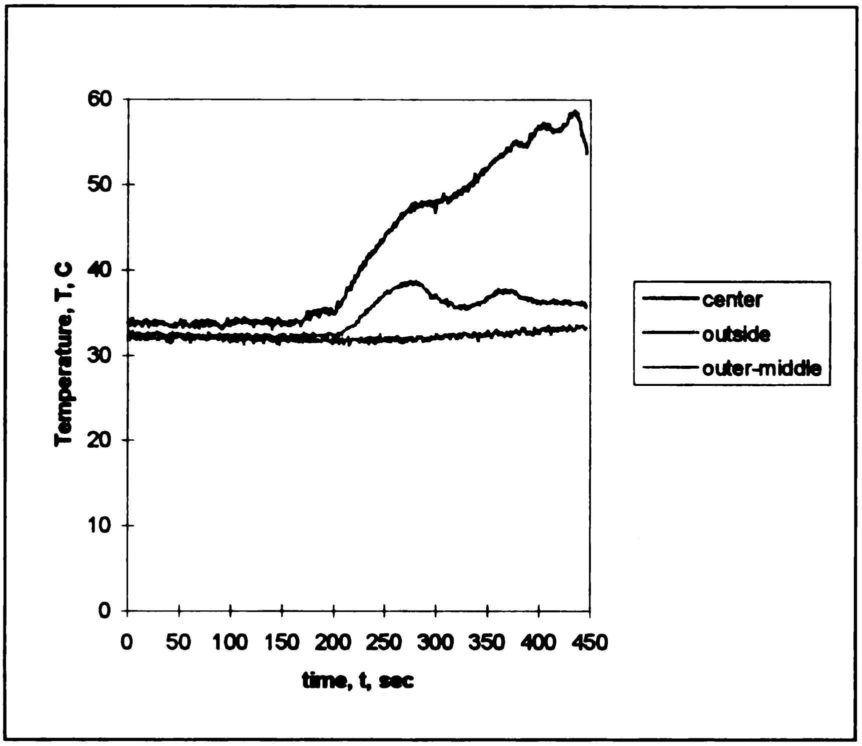

Figure 34. Eighteen-Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.1173 GHz, 2.4162 GHz, and 2.7014 GHz - 1000ms each) and A Pulling Speed of 0.281 ft/min

5.6. Heating Studies Part III: 11-ply Prepreg, Four Frequencies and Time Intervals

The third set of experiments involved heating eleven-ply Hercules AS4/3501-6 prepreg tape. Four frequencies (2.1173 GHz, 2.4162 GHz, 2.6328 GHz, and 2.6809 GHz) were used to process the tape at 0.281 ft/min and 50 Watts input power. 2.1173, 2.6328, and 2.6809 GHz were deemed as outside heating frequencies from previous heating studies. 2.4162 GHz had the highest heating potential out of the four frequencies; therefore, the time interval was set to 10ms, while the other three were set at 1000 ms. Figure 35 shows the heating profiles for this set of processing conditions. The composite did not heat at a rapid rate or to high temperature. 2.1173 GHz in TE_{211} mode was deemed to be a poor heating frequency by running single frequency heating experiments on static prepregs. It was replaced by 2.4267 GHz in TE_{112} mode for the remainder of the variable frequency heating studies. This change established two center heating frequencies and two outside heating frequencies. Another modification made was the input power being raised to approximately 100 Watts. Ideally, the goals were to obtain rapid heating to a high temperature and an even temperature distribution across the composite prepreg.

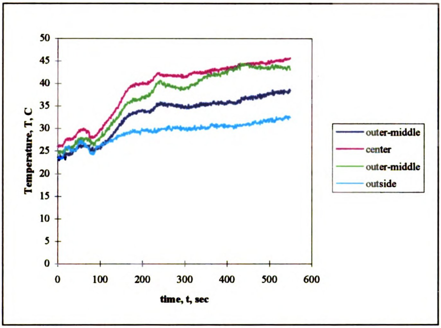

Figure 35. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.1173 GHz - 1000ms, 2.4162 GHz - 10ms, 2.6328 GHz - 1000 ms, 2.6809 GHz - 1000ms) and Using A Pulling Speed Of 0.281 ft/min

Runs were conducted in which the center heating frequencies (2.4162 GHz and 2.4267 GHz) were set at equal time intervals (1000ms and 2000ms) and the outside heating frequencies (2.6328 GHz and 2.6809 GHz) were set at time intervals of 5000ms and 7000ms.

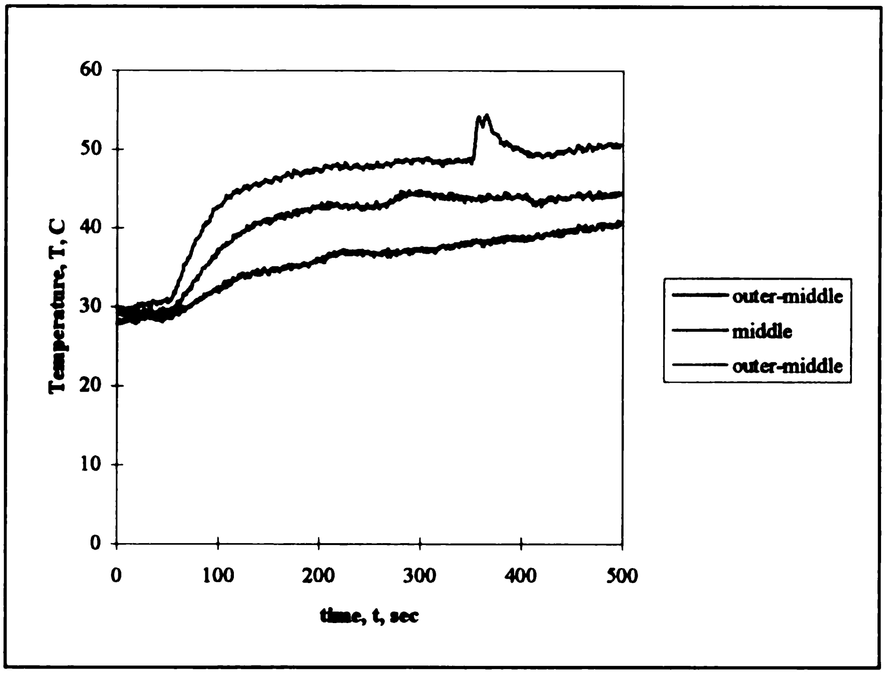

Figure 36. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 1000 ms, 2.4281 GHz - 1000 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed Of 0.281 ft/min

By increasing the center frequency time interval, the heating rate of the tape increased, but the temperature distribution was not uniform. This can be seen by comparing Figures 36 and 37. Increasing the outside heating frequency time interval was detrimental to heating and was discontinued. The temperature gradient across the width of the prepreg increased. Figure 38 shows the results of for an increase in time interval for the outside heating frequencies.

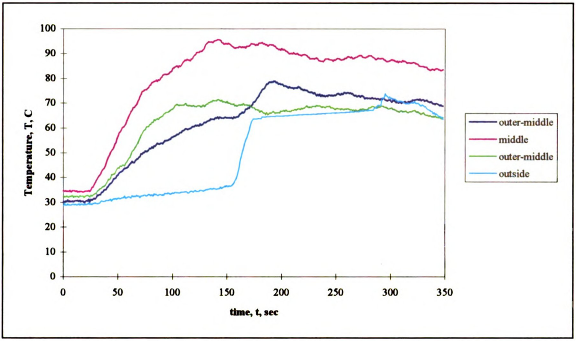

Figure 37. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4281 GHz - 2000 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed Of 0.281 ft/min

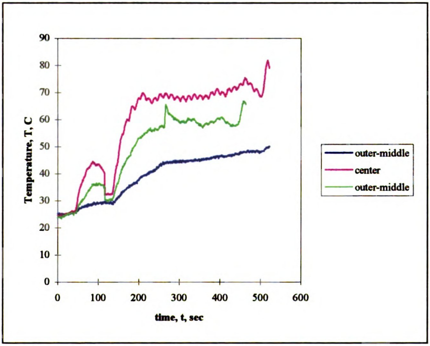

Figure 38. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4287 GHz - 2000 ms, 2.6328 GHz - 7000 ms, 2.6809 GHz - 7000 ms) and Using A Pulling Speed of 0.281 ft/min

5.7. Heating Studies Part IV: 11-ply Prepreg, Four Frequencies and Variation In The Time Interval

The final three experiments involved setting the following time intervals for the appropriate frequencies: 2000ms for 2.4162 GHz, 1000, 1250, and 1500 ms for 2.4267 GHz, and 5000 ms for 2.6328 and 2.6809 GHz. Since 2.4267 GHz supplied the most efficient heating, it was paired with the lowest time interval in hopes of better controlling the heating rate and temperature distribution of the composite prepreg. Microwave input power was approximately 100 Watts for the three trials. Figures 39 and 40 show the two heating profiles for a change in the time interval for the frequency 2.4267 GHz from 1000 ms to 1500ms.

When the time interval was changed from 1000 ms to 1500 ms, the heating of the composite was more rapid - approximately half the time to reach steady state. The temperature gradient across the prepreg was less pronounced. The increase in the time interval also allowed the composite to be heated an additional 10°C. The temperature distribution across the pultruded part varied from a few degrees to 20°C, which is much improved from the 40°C temperature gradient on the prepreg from center to edge with single frequency processing at 100 Watts input power.

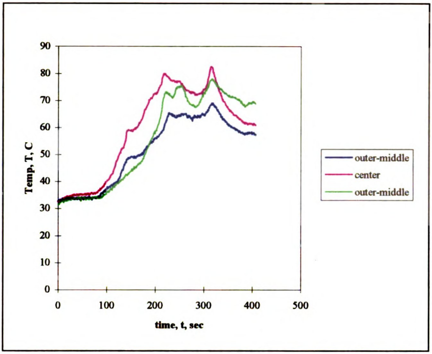

Figure 39. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4287 GHz - 1000 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed of 0.281 ft/min

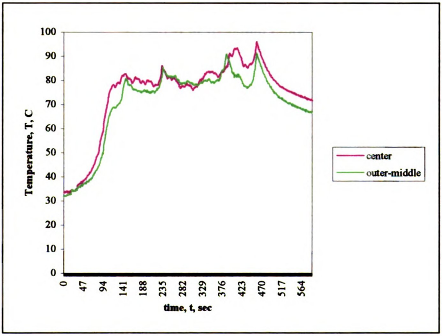

Figure 40. Eleven Ply Hercules AS4/3501-6 Heated With Variable Frequency Processing (2.4162 GHz - 2000 ms, 2.4287 GHz - 1500 ms, 2.6328 GHz - 5000 ms, 2.6809 GHz - 5000 ms) and Using A Pulling Speed of 0.281 ft/min

5.8. Extent of Cure Measurement

Extent of cure was measured for the product from the pultrusion of an 11-ply prepreg heated with the variable frequency power source. Temperature versus time curves are displayed in Figure 37. The processing frequencies and their corresponding time intervals and input powers used were 2.4162 GHz (2000 ms and 90 Watts), 2.4281 GHz (2000 ms and 87 Watts), 2.6328 GHz (5000 ms and 88 Watts), 2.6809 GHz (5000 ms and 74 Watts). DSC samples were taken from five points across the width of the prepreg to investigate the distribution of cure. The processing speed for the experiment was 0.281 ft/min. The heat of reaction of the uncured sample Hercules AS4/3501-6 was 197.5 J/g from DSC. Table 6 lists the results of the extent of cure study for variable frequency processing.

Table 6. Extent of Cure of 11-ply Prepreg With Variable Frequency Processing

Position	Heat of Reaction (J/g)	Extent of Cure (%)
Outside - Left	158.3	19.85
Middle/Outside - Left	142.2	28.0
Center	125.0	36.71
Middle/Outside - Right	130.5	33.92
Outside - Right	153.6	22.23

The graphite/epoxy composite prepreg was successfully heated using variable frequency processing technology by setting individual time intervals for the processing frequencies as opposed to having the same time interval for all four frequencies. Pulling speed was kept constant at 0.281 ft/min for all experimental runs. Higher microwave input power will allow more rapid heating, heating to a higher temperature, and ultimately, faster processing speeds.

5.9. Conclusions

Variable frequency processing provided an even temperature distribution across the prepreg. Thicker samples provided more efficient heating in the variable frequency study. The cavity was characterized by measuring reflected power versus frequency for various cavity lengths and coupling probe depths. Frequencies with the highest heating potential and similar power output were selected to perform curing studies. Time intervals were increased for the outer edge heating frequencies to allow for even temperature distribution across the tape. Better control of microwave heating was obtained by varying the time interval for the frequency with the highest heating potential. Variable frequency microwave pultrusion processing of composite materials looks to be promising in providing an even cure distribution across the profile.

Chapter 6. Fiber Reinforcement Effects On Microwave Processing Efficiency

6.1. Material Identification and Purpose of Study

The reinforcing of composites has benefits, which are two-fold. One is that the fibers absorb the majority of the load when the composite undergoes some kind of tensile or flexural stress. The second benefit is that the thermal conductivity of the fibers is typically different than that of the resin, allowing the energy to couple preferentially into the fiber or resin. The materials used in the study were a Hercules AS4/3501-6 graphite/epoxy composite and a DA409/E250 glass/epoxy composite. The reason for performing experiments on both systems is to compare and contrast the ability, or efficiency, of microwaves to process each material.

As was discussed before, the dielectric constant is a measure of the material's ability to store electrical energy. The dielectric loss factor corresponds to the material's ability to dissipate electrical energy as heat. The effective dielectric loss factor consists of two terms: the loss factor due to the dielectric and a portion that deals with the conductivity. The materials' dielectric properties play an important role in determining how well radio frequency heating will work. The dielectric loss factor is a function of temperature and extent of cure. Jow, et al. document that the dielectric loss factor increased with increasing temperature until the gelation point was reached. The dielectric loss factor decreased suddenly during the gel and then continued to decrease as the matrix fully cured. [24] Springer and Lee examined the microwave interaction with both glass and graphite fiber reinforced epoxy composites. [25] They listed the dielectric properties of both material systems, and the graphite/epoxy composite was far superior over the glass/epoxy - both uncured and cured. [25] If the graphite/epoxy system has a higher dielectric constant, it is expected that it will absorb microwave energy more efficiently than the glass/epoxy system. For the electrical energy the material system does absorb, the graphite/epoxy system, with a much higher loss factor, is expected to take that electrical energy and dissipate it as heat more efficiently. Carbon fibers have a thermal conductivity value an order of magnitude higher than glass fibers [26], suggesting that thermal heat transfer will be better than a composite with glass fiber from the inside to the outside of the composite part. It is then predicted that the graphite/epoxy system will heat more rapidly than the glass/epoxy system.

6.2. Experiments

The glass/epoxy system was processed in a single-mode microwave applicator. Three foot, six-ply DA409/E250 prepreg tape samples were prepared. The cavity was characterized with the material inserted into the Teflon die to find what electromagnetic modes could be excited (Table 7), followed by heating studies for each mode (Figure 41). The most efficient heating mode, namely TE_{112}, was chosen to further conduct tests on the 6-ply glass/epoxy prepreg tape samples.

Table 7. Heating Modes for the Cavity with Teflon Die and Glass/Epoxy Prepreg

Mode #	Mode Type	Cavity Length, Lc, mm	Probe Depth, Lp, mm
1	TM 011	70	11
2	TE 011	101	13.94
3	TM 111	117	15.75
4	TE 112	131	9.5
5	TE 311	152	16.33

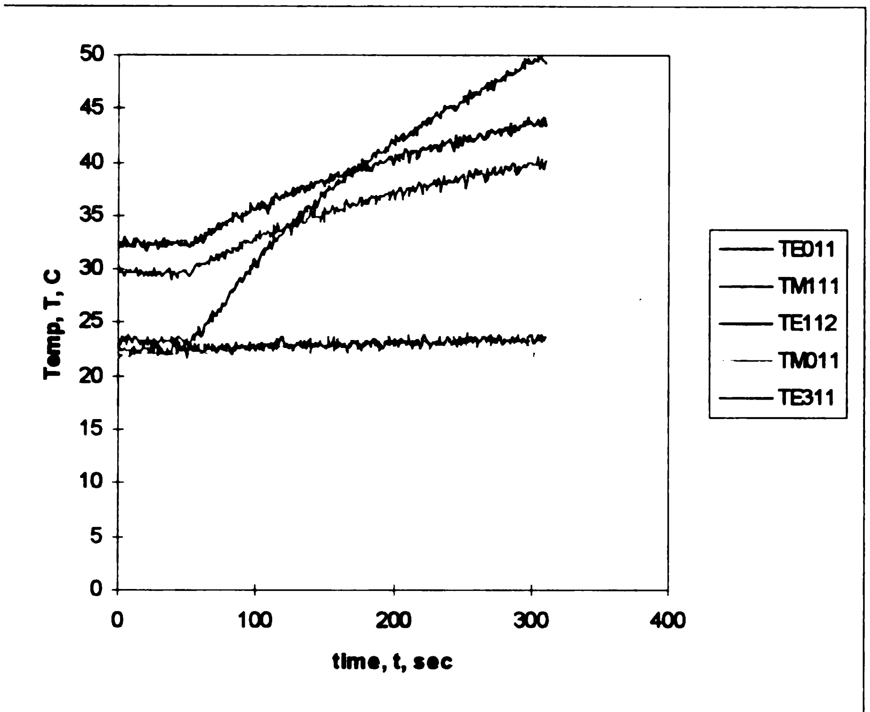

Figure 41. Temperature versus Time Results for Heating Studies of Stationary Six-Ply DA490/250 Prepreg at Approximately 50 Watts

The glass/epoxy prepreg was processed in a TE_{112} mode cavity at 2450 MHz in the existing pultrusion apparatus. The tape was not pulled through the cavity to see just how well the material would heat in the microwave environment. The processing time was varied from one minute to 15 minutes. For the 7" cavity, the processing time was assumed to correspond to the residence time of a differential slice of prepreg. In the fixed frequency experiments for graphite/epoxy samples (see Chapter 4), the fixed pulling speed for variable input power experiments was 0.281 ft/min. When the glass/epoxy was heated for two minutes, the equivalent pulling speed to give the same residence time was 0.292 ft/min.

6.3. Results and Discussion

Figures 42 and 43 show the heating results for a six-ply glass/epoxy and graphite/epoxy prepreg, respectively, at approximately 50 Watts. The centerline temperature at 120 seconds after the power was turned on was 31.38°C for the glass/epoxy system and 41.29°C for the graphite/epoxy system. The extent of cure was measured on DSC for the glass/epoxy samples. For the sample heated in TE_{112} mode at 57 Watts for two minutes, the material had below 10% cure. With an idea of how well the glass/epoxy heated with microwaves, an attempt was made to pultrude a six-ply sample at 50 Watts and 0.281 ft/min. Figure 44 shows that there was only a 5°C temperature increase over the tape.

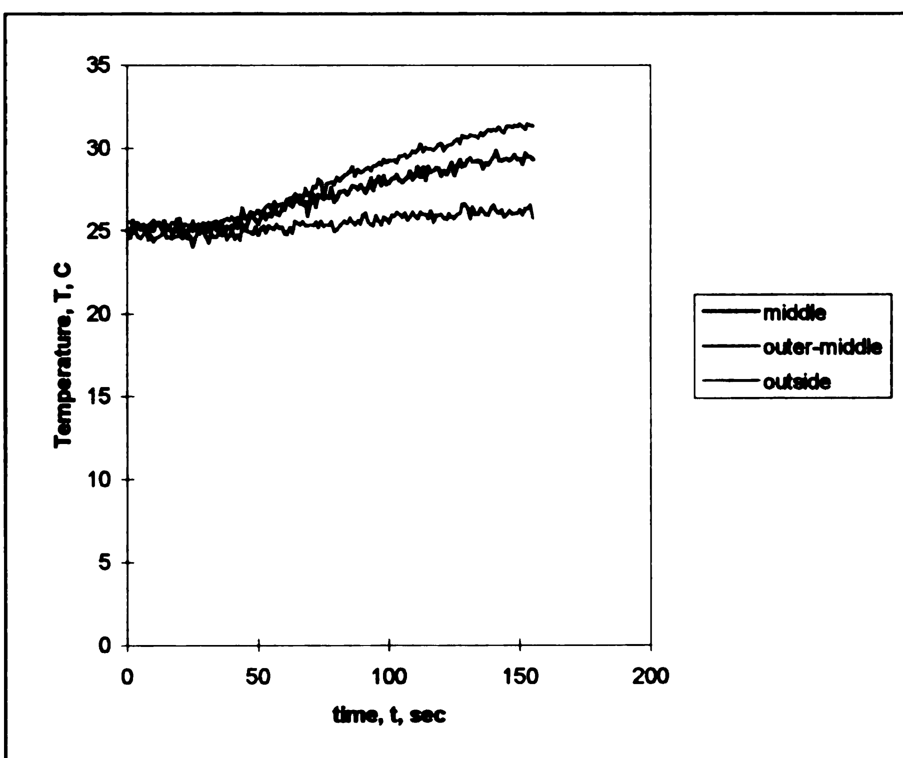

Figure 42. Stationary Six-ply Glass/Epoxy Prepreg Heated in TE_{112} Mode at 57 Watts for Two Minutes

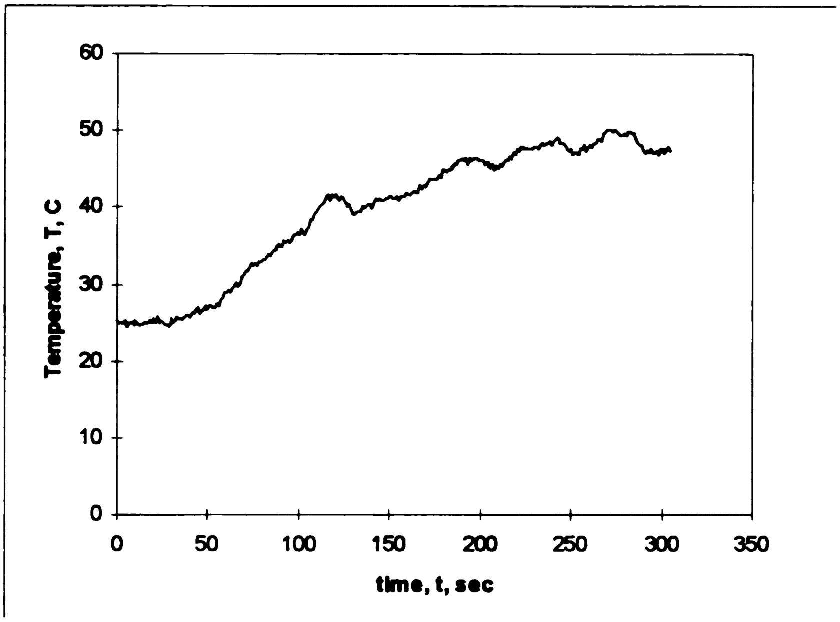

Figure 43. Centerline Temperature for Six-ply Graphite/Epoxy Prepreg Heated in TE_{112} Mode at 50 Watts and 0.281 ft/min

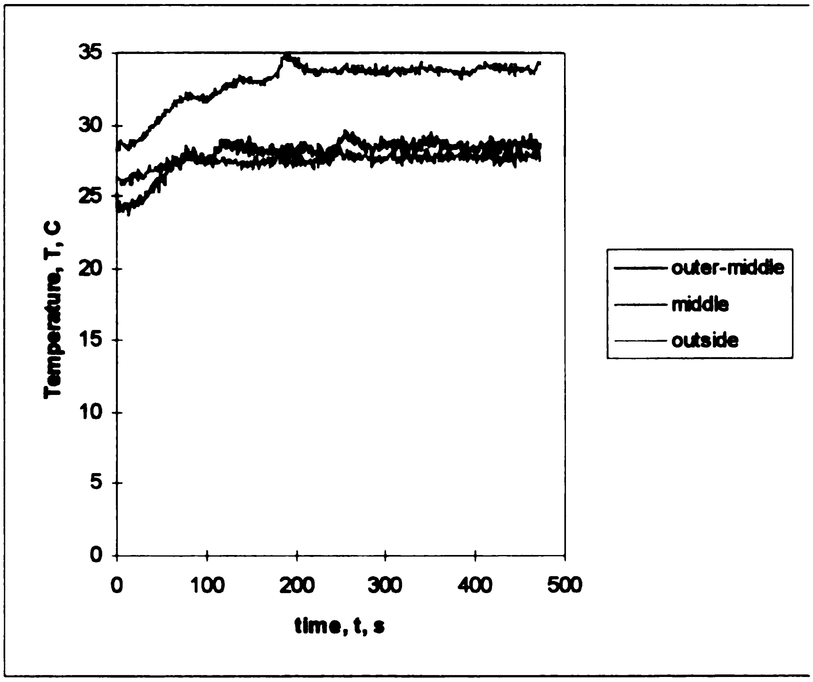

Figure 44. Six-ply Glass/Epoxy Prepreg Heat in TE_{112} Mode at 50 Watts and 0.281 ft/min

Power was increased to 85 Watts for processing the glass/epoxy samples because power absorption was low. The residence time was also increased in attempt to identify a point in time where the exotherm of the polymerization reaction would make the temperature rise more rapidly with time. Figure 45 shows the temperature versus time curves for points across the tape. The temperature did continue to rise for the span of five minutes, but the slope of the temperature-time curve did not increase even with the increase in power. This could be due to poor tuning of the cavity, which would lead to more reflected power and inefficient coupling with the material. Extent of cure of the above prepreg was measured to be approximately 70%. Figure 46 reveals that for similar power levels, the centerline temperature of graphite/epoxy is 40°C greater than that of the glass/epoxy sample.

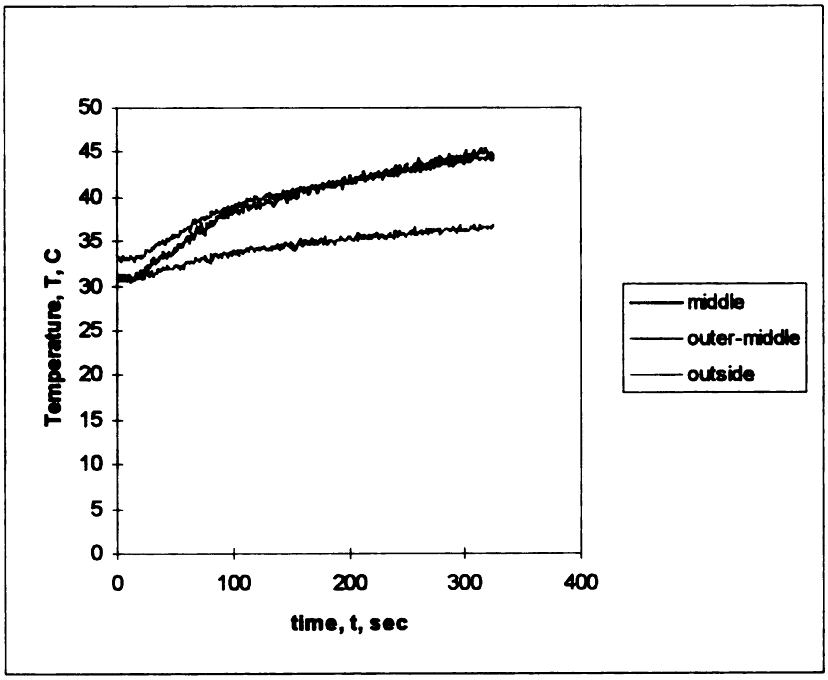

Figure 45. Stationary Six-ply Glass/Epoxy Prepreg Heated in TE_{112} Mode at 85 Watts for Five Minutes

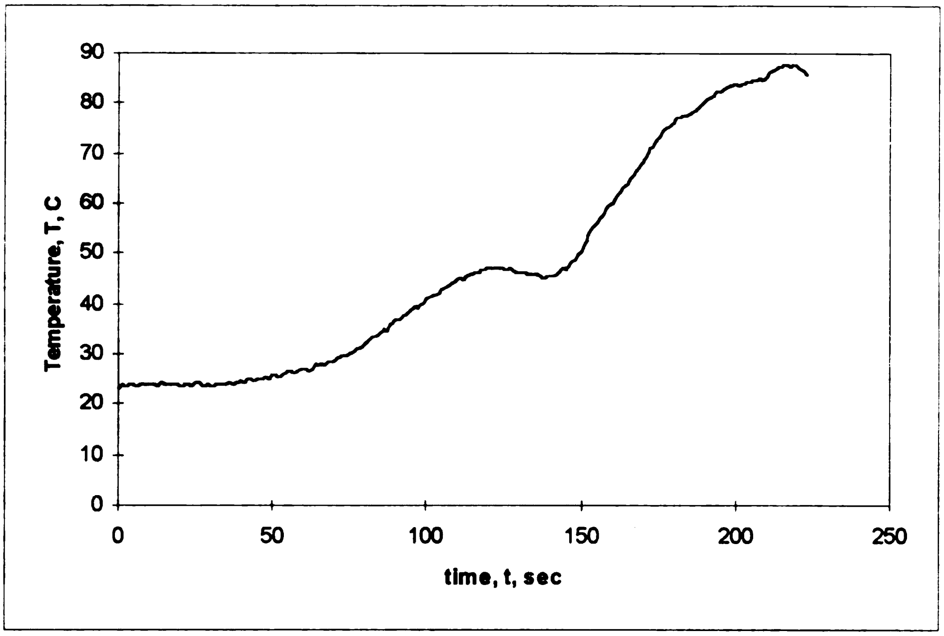

Figure 46. Centerline Temperature for Six-ply Graphite/Epoxy Prepreg Heated in TE_{112} Mode at 80 Watts and 0.281 ft/min

6.4. Conclusions

Glass/epoxy and graphite/epoxy prepregs were evaluated as to their reinforcement's effect on the efficiency of microwave heating. The graphite/epoxy system had a higher dielectric constant, suggesting it would absorb microwave energy more efficiently than the glass/epoxy system. For the electrical energy that it did absorb, the graphite/epoxy system, with a much higher loss factor, seemed to dissipate the electrical energy as heat more efficiently with evidence from the temperature-time curves. The glass/epoxy will heat to similar temperatures as the graphite/epoxy, but it will require a longer processing time. It is concluded that the graphite fiber / epoxy heats more efficiently in a microwave environment and heats more rapidly than the glass fiber / epoxy system.

Chapter 7: On-Line Monitoring

7.1. Possible On-line Monitoring Techniques

Possibilities for an on-line monitoring system are being explored. Possible variables to be monitored are temperature, dielectric constant, dielectric loss factor, and extent of cure. Extent of cure cannot be monitored directly. It would be deduced based on the properties of heat capacity, dielectric constant, and dielectric loss. It would be possible to correlate these properties with the temperature as long as the chemical reaction taking place in this process is exothermic. At the completion of the reaction, the exotherm subsides, indicating completion of cure. However, measuring the temperature of the material that is moving through the die is difficult. The degree of cure is related through the temperature profile of the material with respect to time and the dielectric loss, dielectric constant, and heat capacity in the batch study. Then, one can position a probe at the die exit location where values for the dielectric constant and dielectric loss can be achieved.

The other on-line monitoring method can be the measurement of surface temperature to ensure complete cure. The assumption is that the material would be heated from the inside to the surface. If the surface temperature of the exiting material is predefined as the criteria to denote complete curing, (which incidentally is possible to arrive at from the batch curing studies with appropriate assumptions and calculations) one can use simple probes to monitor the temperature of the exiting material. By being able to observe certain characteristics of the composite during processing, one can get a better idea on how to control gelation before the material enters the die. Based upon the outcome of the examination of a possible on-line monitoring system, a strategy will be developed to implement the desired on-line monitoring and control system into the pultrusion apparatus.

Previous work by Dr. Jinder Jow, et al. [24], included a monitoring method in a batch microwave process. The brass cavity dimensions were adjusted to allow resonation of the 2450 MHz wave. Initial dielectric measurements were taken for the uncured epoxy sample. The sample was heated with a specified input power, and microwave transparent fluorotropic probes were used to monitor the internal temperature of the sample. Upon completion of the cure cycle, the circuit was reconfigured to include the low-power sweep oscillator in place of the 100 W source in order to begin diagnostic measurements using the sweep frequency method. Temperature, dielectric constant, and dielectric loss were monitored during convective cooling. Then DSC tests were run to find the extent of cure. From the results of the batch studies, various curves can be generated:

- Dielectric loss versus temperature at different extents of cure
- Dielectric constant versus temperature at different extents of cure
- Dielectric loss versus extent of cure
- Extent of cure versus microwave processing time

It is known that both the dielectric constant and the dielectric loss will increase with increasing temperature. The dipole relaxation time is related to temperature through an Arrhenius relationship. If temperature increases, the relaxation time decreases and subsequently increases the dielectric loss factor. Also, the dielectric properties will decrease with increasing extent of cure. This is because the dipoles become less mobile as crosslinking increases. Jow found that at approximately 40% cure, the dielectric properties became less dependent on temperature and more dependent on extent of cure. [24]

If extent of cure is related through the temperature profile of the material with respect to time and the dielectric loss, dielectric constant, and heat capacity in the batch study, a fluorotropic temperature probe can be positioned at the die exit. It can be initially assumed that if the surface temperature is approximately equal to the consolidation temperature, then complete cure has occurred. The monitored temperature can give values for the dielectric constant and dielectric loss factor by interpolating the curves from the batch study. DSC will again evaluate the extent of cure.

7.2. Pultrusion Model for On-Line Monitoring

A pultrusion model is proposed that will relate the necessary variables to establish an on-line monitoring system. It begins with a two-dimensional energy balance for a rectangular profile part in Equation 10, [27] where ρ, Cp, and k are the density, heat capacity, and thermal conductivity of the composite, respectively.

$$\rho C_p V_z \frac{\partial T}{\partial z} = \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z}\right) + \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) + \rho \dot{H} + P_m' \qquad (10)$$

$\dot{H}$ is the rate of heat generation per unit weight by the polymerization reaction.

P_m' is the rate of heat generation per unit volume by the absorbed microwave energy.

$$\dot{H} = \frac{\partial \alpha}{\partial t} H_r \qquad (11)$$

where H_r is the heat of reaction = 197.5 J/g from DSC.

The Cartesian coordinate plane for the rectangular profile is such that z is in the pulling direction and x is across the width of the prepreg. Note that in Equation 10, V_z is the pulling speed of the prepreg through the die. It can be assumed that the heat transfer in the axial direction is negligible relative to the heat transfer across the prepreg, therefore making the energy balance one-dimensional ($\frac{\partial T}{\partial z} = 0$). The microwave power absorption term in the energy balance is dependent on the processing frequency, dielectric loss factor, and the electric field strength inside the material.

$$P_m' = \pi f_o \varepsilon_o \varepsilon'' |E_m|^2 \qquad (12)$$

where $f_o = 2.45 \times 10^9$ Hz and $\varepsilon_o = 8.854 \times 10^{-12}$ F/m (permittivity of free space). The loss factor is broken up into two terms, one for the loss factor due to the dielectric, and one for the electrical conductivity.

$$\varepsilon'' = \varepsilon_d'' + \frac{\sigma}{\omega \varepsilon_o} \qquad (13)$$

The magnitude of the electric field inside the material is a complex calculation, and the power absorption model by Wei [1] gives an accurate account of the power dissipation of microwave energy inside a composite. If it is assumed that all of the microwave incident power is absorbed into the composite, then the electric field strength inside the material will be similar to the electric field strength inside the cavity. The electric field strength inside the cavity for the transverse electric (TE) and transverse magnetic (TM) modes can be calculated by taking the cross product of the vector equations given in Equations 14-19 for the TE modes and Equations 20-25 for the TM modes below. [19] The modes in a cylindrical cavity can be modeled by a computer program in order to establish the magnitude of the electric field at a specified cavity height. This can help by finding the optimum sample height in the cavity and by being able to visualize where the "hot spots" will be in the cavity as it heats the pultruded part.

For the TE-modes,

$$E_r = -l\frac{J_l(k_1 r)}{k_1 r}\sin(l\theta)\sin(k_3 z) \tag{14}$$

$$E_\theta = -J'_l(k_1 r)\cos(l\theta)\sin(k_3 z) \tag{15}$$

$$E_z = 0 \tag{16}$$

$$H_r = \frac{k_3}{k}J'_l(k_1 r)\cos(l\theta)\cos(k_3 z) \tag{17}$$

$$H_\theta = -l\frac{k_3}{k}\frac{J_l(k_1 r)}{k_1 r}\sin(l\theta)\cos(k_3 z) \tag{18}$$

$$H_z = \frac{k_1}{k}J_l(k_1 r)\cos(l\theta)\sin(k_3 z) \tag{19}$$

For the TM-modes,

$$E_r = -\frac{k_3}{k} J'_l(k_1 r)\cos(l\theta)\sin(k_3 z) \tag{20}$$

$$E_\theta = l\frac{k_3}{k}\frac{J_l(k_1 r)}{k_1 r}\sin(l\theta)\sin(k_3 z) \tag{21}$$

$$E_z = \frac{k_1}{k} J_l(k_1 r)\cos(l\theta)\cos(k_3 z) \tag{22}$$

$$H_r = -l\frac{J_l(k_1 r)}{k_1 r}\sin(l\theta)\cos(k_3 z) \tag{23}$$

$$H_\theta = -J'_l(k_1 r)\cos(l\theta)\cos(k_3 z) \tag{24}$$

$$H_z = 0 \tag{25}$$

where $k_1 = 2x_{lm}/D$, $k_3 = n\pi/L$, $k^2 = k_1^2 + k_3^2$, and $\lambda = 2\pi/k$.

The documented kinetics [28] for the Hercules AS4/3501-6 composite will serve as a basis for this section. The gel point for the graphite/epoxy system occurs at an extent of cure of 30% and separates the two prevalent kinetic expressions. When the conversion is less than 30%, Equation 26 defines the kinetics. Equation 27 gives the kinetics for the conversion when it is greater than the gel point.

$$\frac{\partial\alpha}{\partial t} = (k_1 + k_2\alpha)(1-\alpha)(\beta-\alpha) \tag{26}$$

$$\frac{\partial\alpha}{\partial t} = k_3(1-\alpha) \tag{27}$$

$$k_1 = 2.101\times10^9 \exp\left(-8.07\times10^4/RT\right) \tag{28}$$

$$k_2 = -2.104\times10^9 \exp\left(-7.78\times10^4/RT\right) \tag{29}$$

$$k_3 = 1.960 \times 10^5 \exp\left(-5.66 \times 10^4 / RT\right) \tag{30}$$

where R = 8.314 J/mol K

β = 0.47 = ratio of initial hardener equivalents to epoxide equivalents.

The dielectric properties of the Hercules AS4/3501-6 composite have been reported in the literature [25]. The effective complex permitivities of the uncured material along and perpendicular to the fiber direction are ε^* = 1-j25000 and ε^* = 33.0 - j53.3, respectively. The real part of the complex permittivity equation is the dielectric constant, while the imaginary part is the loss factor.

The electrical properties also come into play in the energy balance for the material system. A proposed energy balance to model the microwave processing of composite materials [27] can be modified into a pultrusion model. One must take the pulling speed, Vz, as small incremental steps in the pulling direction, z. Then the chain rule can be utilized to establish an energy balance equation that is time dependent for temperature and time dependent for extent of cure. Originally, the derivative of temperature with respect to time was equated with a two-dimensional dependence of temperature on location in the composite and a reaction term. Substituting the pulling speed on the left side, the temperature-time curves are now dependent on the processing speed.

The reaction term is broken down into two terms. The first is the heat of reaction, which is multiplied by the derivative of the extent of cure with respect to time. This is the heat generated inside the composite by the polymerization reaction. The second term takes into account the electromagnetic interaction of the microwaves with the material system. Pm' is equivalent to the rate of heat generation per unit volume by the absorbed microwave energy. A power absorption model must be employed here to accurately calculate the amount of heat generated. Pm' is a function of the processing frequency, permittivity of free space, which is a constant, the square of the electric field strength inside the material, and the effective dielectric loss factor. A five-parameter power absorption model was proposed by Wei, et. al in order to simulate the "power dissipation inside a fiber reinforced composite during microwave processing in a tunable resonant cavity." [1] The five parameters involved in the model are the power dissipation due to the electromagnetic (EM) waves from the side and the magnitudes and the polarization angles with respect to the fiber direction of the incident TEM waves at the top and bottom of the composite.

7.3. Conclusions on On-Line Monitoring

It is possible to integrate an on-line monitoring system and process control equipment to a microwave pultrusion line. First, the curves from the batch studies, i.e., dielectric data and temperature-time curves, will be obtained. Then, a two-dimensional energy balance with heat transfer, polymerization reaction, and microwave power absorption terms will be employed to find the temperature dependence on the profile size, dielectric properties, and pulling speed. Next, electric and magnetic fields should be modeled by computer software to calculate where the "hot spots" will be inside the cavity for the various transverse electromagnetic modes that can be excited. Finally, a previous microwave power absorption model [1] will be used to define the electric field magnitude inside the composite. Computer simulations could then model what would happen in a microwave pultrusion apparatus with a chosen set of processing variables. The on-line monitoring system would allow the operator to easily control the process variables to optimize the pultruded product characteristics.

CONCLUSIONS

The microwave pultrusion apparatus was assembled. The 17.78 cm inner diameter, tunable, cylindrical, batch, brass microwave cavity was characterized by finding the different electromagnetic modes for different cavity dimensions. Heating studies were conducted for each of the modes to find how rapidly each could heat the prepreg and where the electric field magnitude was large. Fixed-frequency experiments at 2450 MHz were run in TE_{112} mode. The microwave input power was varied from 40 to 100 Watts, and the pulling speed was varied from 0.281 to 1.17 ft/min. Extent of cure of the graphite/epoxy composite was established as a function of input power and pulling speed for a microwave pultrusion apparatus. Extent of cure increased with an increase in microwave power input and decreased with an increase in pulling speed. At 100 Watts input power and a pulling speed of 0.281 ft/min, the center of the six-ply graphite/epoxy prepreg was 98% cured.

Tensile strength and modulus were relatively unaffected by the change in process variables. Flexural strength measurements revealed there to be maxima in strength and modulus for certain processing conditions. Too high of power or too slow of pulling speed resulted in a brittle matrix. Low input power or fast pulling speeds gave a product that had a relatively uncured matrix and low interfacial bond strength.

Variable frequency processing provided an even temperature distribution across the prepreg. The cavity was characterized by measuring reflected power versus frequency for various cavity lengths and coupling probe depths. Frequencies with the highest heating potential and similar power output were selected to perform curing studies. Thicker samples provided more efficient heating in the variable frequency study by absorbing a greater percentage of the incident power. Time intervals were increased for the outer edge heating frequencies to allow for even temperature distribution across the tape. Better control of microwave heating was obtained by varying the time interval for the frequency with the highest heating potential. Variable frequency microwave pultrusion processing of composite materials looks to be promising in providing an even temperature distribution across the profile.

Glass/epoxy and graphite/epoxy prepregs were compared and contrasted as to their effect on the efficiency of microwave heating. The graphite/epoxy system had a larger dielectric constant, suggesting it would absorb microwave energy more efficiently than the glass/epoxy system. The graphite/epoxy system, with the larger loss factor, converted dissipated the electrical energy as heat more efficiently with evidence from the temperature-time curves. It is concluded that the graphite/epoxy would heat more rapidly than the glass/epoxy system.

Possibilities for an on-line monitoring system were explored. Possible variables to be monitored are temperature, dielectric constant, dielectric loss factor, and extent of cure. The degree of cure is related through the temperature profile of the material with respect to time and the dielectric loss, dielectric constant, and heat capacity in the batch study. Then, one can then position a probe at the die exit location where values for the dielectric constant and dielectric loss can be achieved. A pultrusion energy balance in conjunction with a five-parameter power absorption model could help provide a basis for an on-line monitoring system and/or a process control program for microwave pultrusion processing.

RECOMMENDATIONS

Microwave processing was applied to a continuous manufacturing process for composite materials. After studying glass fiber/vinyl ester composites, Min Lin suggested that in future microwave pultrusion research, one should include other resin/fiber systems so the technology can branch out to new applications. He also recommended improving the system for high-speed pultrusion by modifying the cavity design, installing a new pulling mechanism, and integrating a high power source. Finally, he suggested researching new microwave transparent die materials and combining a part-shaped cavity and pultrusion die, where the walls of the die would be the microwave applicator. [29]

Experimental data on the microwave pultrusion of graphite/epoxy and glass/epoxy systems was collected. Higher RPM pulling rollers were placed in the line to increase the maximum pulling speed to 240 cm/s from 3 cm/s. Heating and curing profiles of the pultruded material were studied at different processing conditions. To find the optimum operating conditions for microwave pultrusion processing, the relation between processing rate, power, and extent of cure was examined. A variable frequency power source capable of 150 Watts input power was used to achieve a more even temperature and cure distribution across the prepreg.

It is recommended that the following issues concerning the pultrusion project be addressed in future work:

- A higher microwave power source is needed to process larger-profiled parts and to increase processing speeds.

- New mechanical pulling equipment capable of the higher line speeds.

- New die material that has a longer life and is more transparent to microwaves than both Teflon and ceramic.

- Thermally heated die at die exit of microwave cavity to see if single-mode applicator is a viable alternative to a radio frequency preheater.

- Parallel plate dielectric analysis machine at die-exit to assist in on-line monitoring of material properties.

- Combine part-shaped cavity ideas with a pultrusion die to make the die walls the actual microwave applicator.

- Computer program relating all process variables and material properties for inclusion in a process control program and/or on-line monitoring system.

- Modification of an existing larger single-mode applicator to operate at 915 MHz for the continuous processing of materials. The larger cavity will be useful in the high power experiments.

It is proposed that the existing microwave technology available at Michigan State University be integrated into a Vermont Pultrusion Test System available from Vermont Instrument Company, Inc. The laboratory set-up would provide a means by which to compare and contrast conventional and microwave pultrusion processing, or to study the two techniques in conjunction. By selecting a resin system, one may study the optimum cure conditions, microwave input power, die oven temperature, and pulling speeds. A polyester or vinyl ester resin would be mixed with the appropriate catalysts and additives in the disposable container. The glass rovings would be led through the pultrusion line to ensure proper alignment of the fibers during processing. The rollers would be controlled electronically and have a maximum pulling speed of 75 cm/min (2.46 ft/min). The VICO bench pultruder would produce 3 mm rods. The experiment station would include glass rovings that pass through a ceramic ring, a resin fiber-wetting system complete with disposable resin bath containers and roller bars, an aluminum oxide ring which would act as the preformer, and a VICO preheater, bench pultruder, and postcure oven. A VICO mechanical torsion tester would be available to measure the product's shear modulus and its fracture energy in shear.

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