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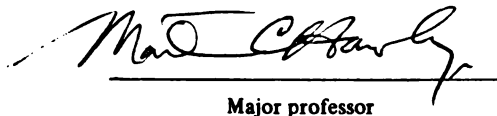
thesis entitled

Continuous Processing of Polymers and
Composites With Microwave Radiation

presented by
Min Lin

has been accepted towards fulfillment
of the requirements for

Masters degree in Chemical Engineering



Major professor

Date October 1, 1993

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**CONTINUOUS PROCESSING OF POLYMERS AND COMPOSITES
WITH MICROWAVE RADIATION**

By

Min Lin

AN ABSTRACT OF A THESIS

Submitted to
MICHIGAN STATE UNIVERSITY
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1993

Research Advisor
Dr. Martin C. Hawley

ABSTRACT

CONTINUOUS PROCESSING OF POLYMERS AND COMPOSITES WITH MICROWAVE RADIATION

By

Min Lin

Continuous microwave processing is a new approach for microwave processing applications to polymers and composites. This processing method has the potential to process long and large profile parts which are highly desired in industries. The continuous microwave processing technique was applied to curing of a heat cable and pultrusion of composites in this study.

A cylindrical tunable microwave cavity was modified to perform the continuous processing. The curing of the heat cable was studied at different cavity positions and cable orientations. The microwave leakage was within safety limits during processing even with conducting wires in the processed cable. Microwave transparent dies were designed to study the microwave pultrusion of glass/vinyl ester composites. The possibility of microwave pultrusion of composites was demonstrated. A process model for microwave pultrusion was also developed to study the curing of the composites. The model simulation agreed with experimental results very well.

To my parents
and my wife, Dong

ACKNOWLEDGEMENTS

I would like to thank Dr. Martin C. Hawley for his support and guidance throughout the completion of this thesis. I would also like to thank Dr. Jianghua Wei for his valuable discussions and suggestions, thank Larry A. Fellows for his proofreading of the thesis and valuable suggestions, and thank Richard Delgado, Valerie Adegbite and Dhulipala Ramakrishna for their help through the duration of this study.

The most important thanks goes to my wife, Dong, for her love, support and encouragement.

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CHAPTER 1

INTRODUCTION

1.1 Microwave Processing

Microwave heating is used as an alternative to conventional thermal heating for the processing of materials¹⁻¹⁴. Microwave heating process is achieved by placing a material in an electromagnetic field. This heating process has been widely used in various applications such as food heating, drying, material processing, and some biomedical researches^{15,16}. The materials being processed using microwave includes polymers, composites, and ceramic materials. The general advantages of microwave heating include: (1) fast, direct and outward heating, (2) better control of material temperature profile and input power to optimize the material processing, (3) selective heating based on the lossy magnitude of constituents in a material, and (4) improved mechanical properties for microwave processed parts.

1.2 Microwave Heating Mechanism

The microwave heating takes the advantage of dielectric properties of these materials. The frequency of a dipolar oscillation in a material is in the microwave range. This makes it possible for microwave energy to excite a dipole

group to its higher energy state. The heating mechanism can be described as follows. In microwave heating, the dipoles of molecules in a material align themselves with the applied electric field, and the relaxation of the dipoles causes a friction among molecules. This friction will cause a temperature rise of the material. As a result, microwave energy is converted into thermal energy of the material. Furthermore, the microwave heating is initiated from molecule-dipole interactions. In the processing of materials, this heating mechanism will lead to microwave heating advantages over conventional thermal heating which is achieved by conduction and convection.

The dielectric properties of a material are described by the dielectric constant ϵ' , and the dielectric loss factor ϵ'' . The dielectric constant ϵ' , which represents the electrical polarizability, is defined as the ratio between the capacitance of a condenser filled with dielectrics and the capacitance of the same condenser when empty. The dielectric constant also reflects the ability of a material to store electrical energy. The dielectric loss factor, ϵ'' , describes the molecular relaxation phenomenon which reflects the ability of a material to dissipate electrical energy. The conversion of microwave energy to thermal energy is characterized by the material's dielectric loss factor. Ku and Liepin¹⁷ reported the results of heating materials with different dielectric loss factors. The microwave power or the time required to heat a material increases as its

dielectric loss decreases.

The microwave power absorption rate for materials can be calculated using Poynting's Theorem¹⁸:

$$P = \frac{1}{2} \omega \epsilon_0 \vec{E} \cdot \vec{\epsilon}_{eff}'' \cdot \vec{E}^* \quad (1.1)$$

$$\vec{\epsilon}_{eff}'' = \vec{\epsilon}_d'' + \frac{\vec{\sigma}}{\epsilon_0 \omega} \quad (1.2)$$

where ω is the frequency of the electromagnetic waves in rad/sec,

$\vec{\epsilon}_{eff}''$ and $\vec{\epsilon}_d''$ are the effective dyadic loss factor

and relative dyadic loss factor of materials respectively,

σ is the dyadic conductivity in S/m, and

$\vec{E}$ and $\vec{E}^*$ are the electric field vector and its conjugation in V/m.

The electric field can be calculated theoretically for a empty cavity with boundary conditions of a given shape of cavity. However, when a cavity is loaded with dielectric lossy materials, the electric field inside the cavity will be disturbed. The calculation of microwave absorption by the material becomes very complicated.

1.3 Microwave Distributions Inside a Cavity

Microwave distributions inside a cavity are different for different resonant conditions. Figure 1.1 shows the microwave resonant modes at different cavity length at different microwave frequency. These resonant modes can be divided into two categories: Transverse Electric (TE) modes or Transverse Magnetic (TM) modes. In TE modes, the electric fields are aligned perpendicular to the axis of the cavity. In TM modes, they are aligned parallel to the axis of the cavity. As a result, the set-up of the material inside a cavity is very important for an effective microwave processing. For an optimum processing result, processing materials should be aligned along the electric field as much as possible. Figure 1.2 shows the alignment at both microwave resonant modes for the material inside a microwave cavity. The alignment of the material will give the maximum interactions between materials and microwave fields.

1.4 Microwave Heating Advantages

The difference in the energy dissipation into a material between microwave heating and conventional thermal heating lies in the different heating mechanisms. In conventional thermal heating, a material is heated by applying heat to the outer surface of the material, and the heat is transferred to the inner sections by conduction. This heating mechanism may result in temperature gradients inside the material. For the processing of polymers and polymer composites, the outer regions of the material will

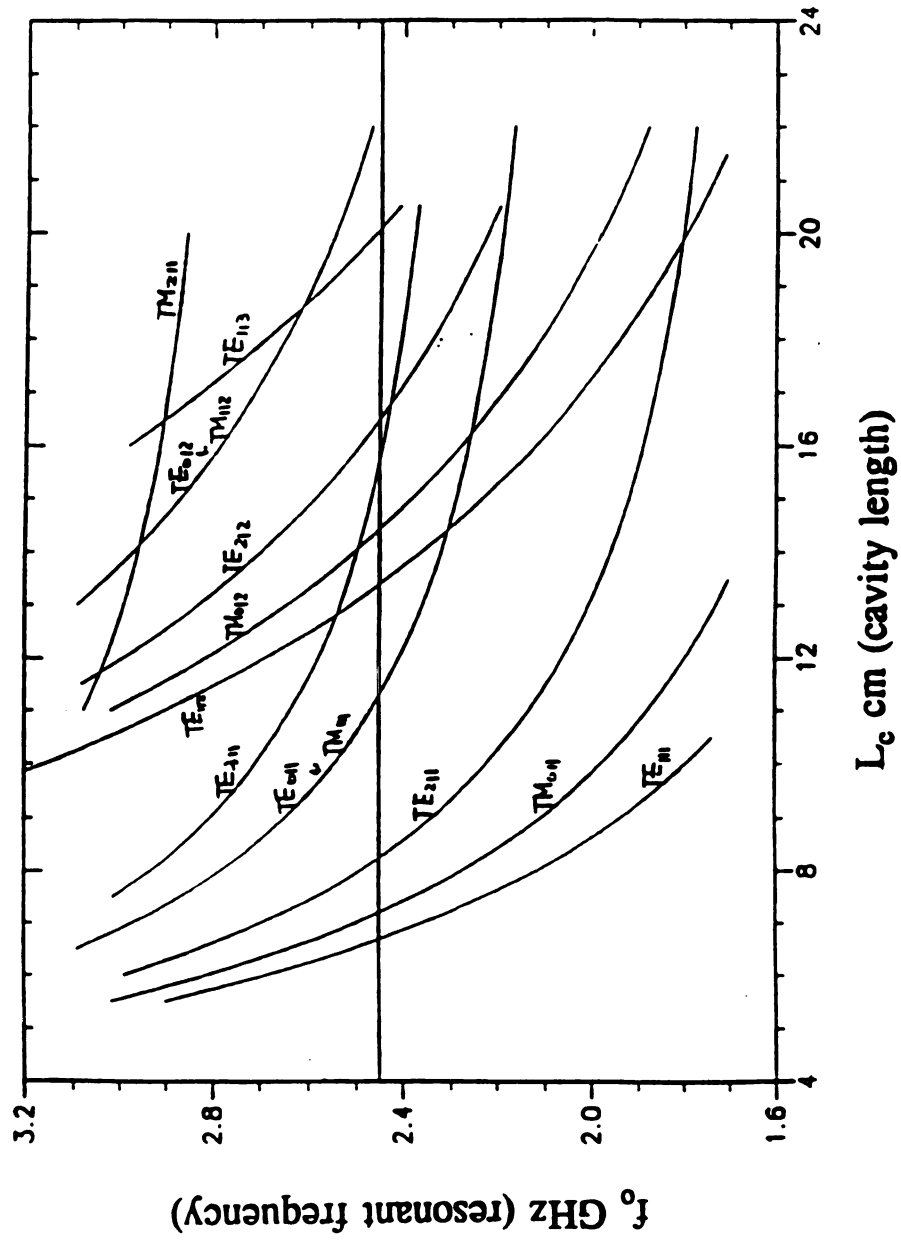


Figure 1.1 Resonant Mode Chart for 17.78 cm Diameter Microwave Cavity

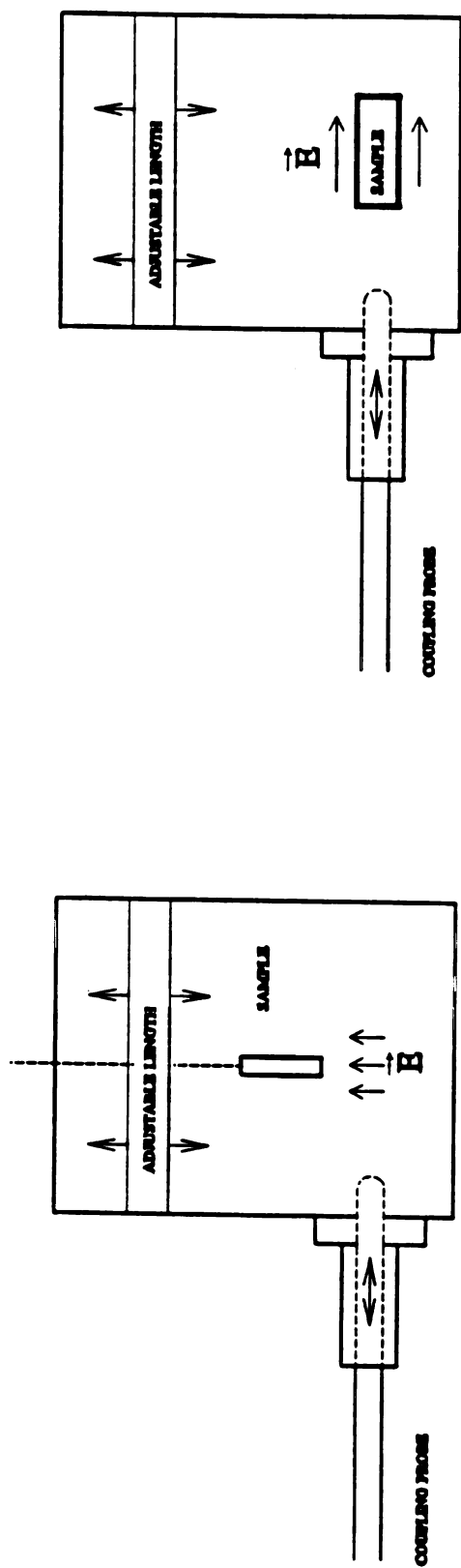


Figure 1.2 Material Alignments with the Electric Field Inside the Cavity

be cured faster, forming a skin seal on the material. This could cause problems during processing. Some polymer reactions have side products or require solvents. The cured outer skin on the material's surface can form a barrier and trap the undesired evolving products. This leads to the formation of voids inside the material. Voids decrease the mechanical properties of polymers and composites. Also, polymer cross-linking reactions are exothermic. The exotherm can cause temperature excursions during processing, which can lead to thermal degradation of the material.

Microwave heating, on the other hand, transfers energy directly to the material's molecules. The inside of the material can be heated selectively. The temperature gradient is therefore outward. This "inside-out" heating pattern may decrease the entrapment of the undesired ingredients. Because the outer regions of a microwave heated material are less reacted and less rigid than the inside, the mechanical properties of the material may be improved. Also, this heating mechanism may result in a better consolidation of the part, or require a lower processing pressure.

Another advantage of microwave heating is that it allows better control of the temperature profiles. The direct heating mechanism of the microwave heating has been shown to eliminate the temperature excursions for exothermic polymer reactions¹⁹. Jow demonstrated this by conduction thermal and microwave heating experiments. The microwave

system can be turned off and on instantaneously to better compensate for the reaction exotherm than the thermal system. This provides an opportunity to process a material at higher temperature without degrading it.

The polymers are sometimes not lossy enough to be promising materials for microwave processing. However, the addition of lossy materials can be added into the matrixes to make microwave processing of these composites possible. In a graphite composite, graphite fibers are good conductors and very lossy. The microwave will heat the fibers by inducing a current in them. The bindings between graphite fibers and polymer resin will be enhanced due to the concentrated reaction regions at fiber-resin interfaces. The mechanical properties of the composite will thus be improved. It has been shown²⁰ that microwave coupling could alter the interphase properties between fibers and matrix. Compared with thermally cured composites, it was found that not only the interfacial shear strength was different, but the failure mode at the interface was also altered.

Microwave heating also affects the extent of reaction for certain polymer reactions. It has been found that the extent of reaction is higher for microwave processing than thermal processing at a given temperature^{21,22}. The result could be due to the advantages of microwave heating in the area of reaction kinetics. Faster reaction rates have been reported by the directly applying microwave energy to the reactive sites of polymers. Wei, DeLong, and Hawley used

thin film technique to study the reaction kinetics of epoxy and found microwave processing to be faster²³. Also, enhanced reactions of polygamic acids in solutions have been reported by Virginia Polytechnic Institute^{24,25}. Molecular "hot spots" have also been reported where the reaction is much faster than the observed reaction rate for conventional thermal processing²⁶.

1.5 Microwave Applicators

Several microwave applicators, such as waveguides, commercial multimode microwave ovens, and single-mode tunable resonant cavities, are commonly used in the microwave processing of materials. Microwave curing of epoxy has been studied using waveguides^{27,28}, and multimode microwave ovens^{29,30}. However, the waveguides and multimode microwave ovens are usually energy inefficient devices. In a multimode microwave oven, the electromagnetic fields are standing waves. In a waveguide, the electromagnetic fields are travelling waves. Both microwave distributions inside the microwave device can not be efficiently controlled for the heating of materials.

In a single-mode tunable microwave cavity, however, electromagnetic waves are resonant inside the cavity. The microwave energy is well focused and distributed according to the cavity boundaries and materials being processed. The microwave energy being reflected and absorbed by the cavity walls can be minimized by tuning the cavity and by selecting a cavity wall material with lower electrical resistance.

Several microwave resonant modes can usually be found at different cavity dimensions for a tunable cavity loaded with processing materials. Jow used a single-mode resonant microwave cavity to study the curing of epoxy. Efficient microwave heating was found and materials were heated to higher temperature in less time. In addition, the single-mode resonant microwave cavity can be used to diagnose the dielectric properties of a material while processing it³¹.

1.6 Microwave Processing Techniques

Microwave processing of polymer materials is investigated extensively at Michigan State University. Current research issues for microwave processing are: (1) process scale-up; (2) processing of complex shapes of parts; (3) automation of processing control; and (4) continuous processing.

The scale-up of the microwave cavity was studied for the batch processing of larger part of materials³². The scale-up factors were found for 18'' diameter cavities to maintain the same heating patterns as 7'' diameter cavities. The effect of the orientation of graphite fibers in a composite was studied to determine the processing orientation of composites³³. It was found that the heating results were different for the composite for different fiber orientations.

Processing of complex shape of composite materials is also under study to extend tunable microwave processing to a more extensive application. In order to achieve uniform

microwave heating over the surface of a complex shape material, a mode-switching technique has been recommended by Larry³⁴. The goal is to achieve a uniform heating profile throughout the material by switching between microwave heating modes. Each heating mode may yield a different heating pattern for a sample, and the temperature gradients across the sample may be minimized by alternating between the different heating modes. A computer-based control system has been developed that implements this technique to automate and better control the processing of the simple and complex shape materials³⁵.

1.7 Research Scope and Goals

Microwave processing has been widely used in various aspects of industrial and commercial applications. Most of these applications are batch processing. In batch processing, the size of a processed part is limited by the size of the microwave batch applicator. Because materials with large or continuous geometries are highly desired in industrial and commercial applications, continuous microwave processing of materials exhibits a great potential for materials processing.

The idea of continuous microwave processing is to pass materials through the microwave applicator. The material is processed by the microwave environment inside the applicator and exits the applicator when the processing is completed. Many rubber materials, polar or non-polar, have been processed continuously using microwave processing

systems^{36,37}. One of the key points in continuous microwave processing is to control the microwave leakage from the entry and exit ports of the applicator. The safety threshold limit value (TLV) at 2.45 GHz is 10 mW/cm^2 ³⁸. The TLV presents the maximum radiation level to which workers may be repeatedly exposed without adverse health effects. For non-conductive materials, the microwave leakage is easier to control during continuous processing. Devices called double corrugated reactive chokes were studied and used for reducing microwave leakage during the continuous processing of polystyrene³⁹. Conductive graphite fiber with epoxy resin was also studied for continuous microwave processing⁴⁰. The microwave leakage control in this case is far more difficult due to the tremendous microwave leakage caused by the conductive graphite fibers.

The main goal of this research is to develop a low-cost, high-speed microwave processing technique. The research conducted in this study is to demonstrate the feasibility of continuous microwave processing. Several aspects of the continuous processing will be explored to evaluate the microwave processing methods.

The possibility of processing a heat cable will be tested. The heating and curing of the heat cable at different heat modes and different sample positions will be studied. Because the heat cable contains two electric wires, the microwave leaking during processing will also be studied. The continuous microwave application will also be

applied to pultrusion, a composite manufacturing process. A microwave transparent die will be designed to perform the microwave pultrusion. Heating and curing profiles of the pultruding material will be studied at different processing conditions. A process model, which includes reaction kinetics and microwave power absorption models, will also be developed to further study the microwave pultrusion process.

CHAPTER 2

CONTINUOUS MICROWAVE PROCESSING OF HEAT CABLE

2.1 Introduction

Continuous microwave processing of materials has been studied for decades for polymer and composite materials. Most microwave processing applications are with non-conductive materials, such as rubbers. Conductive materials such as graphite fibers have also been processed by continuous microwave techniques. Microwave leakage during the continuous microwave processing has been controlled within safety limit.

In the study of graphite fiber composites, Wei modified a batch tunable resonant microwave applicator for the continuous processing⁴⁰. As shown in Figure 2.1, two rectangular slots were opened at opposite sides of the cavity wall perpendicular to the coupling probe. A jacket box was attached to each opening slot to prevent microwave leakage. The entry and exit ports of the cavity were specially designed to reduce the microwave leakage due to the open space and conductive graphite fiber. A set of doubly corrugated reactive chokes have been used for reducing microwave leakage at the entry points during continuous microwave processing³⁹. In addition, Wei

suggested using conductive fins grounded to the cavity wall openings. As a result, the majority of the induced current in the conductive fibers is grounded by the fins. This design allows a small portion of the microwave radiation into the jacket box attached to the cavity wall. The dies on the jackets were designed to fit prepregs of varying thicknesses and widths. Finger stocks were used to further reduce microwave leakage by making contact with the composite material and grounding the induced current.

This project is a continuation of the continuous microwave processing studies using the modified tunable resonant microwave cavity described above. To extend the application of continuous microwave processing, materials containing conductive wires are under study for possible processing.

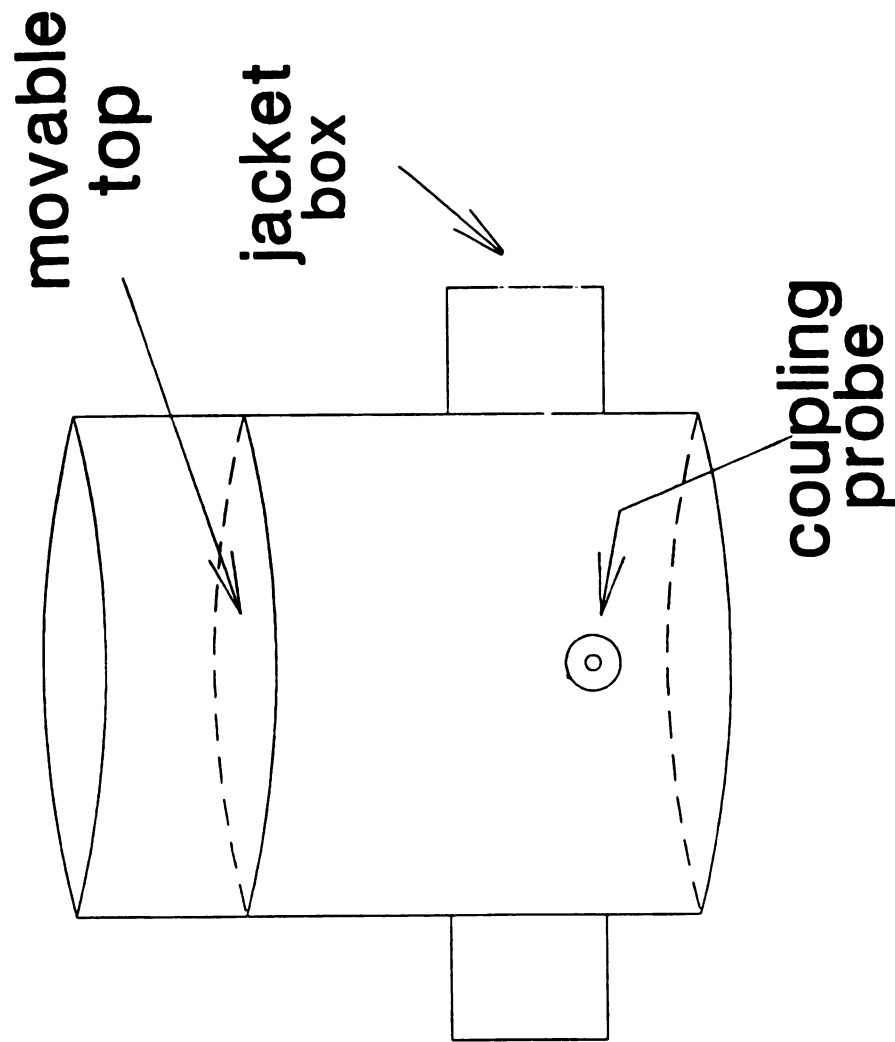


Figure 2.1 Microwave Cavity for Pultrusion Application

2.2 Experiments

The continuous microwave processing system is similar to that of batch processing systems. As shown in Figure 2.2, the system includes four basic units: a microwave source circuit, a modified tunable cylindrical cavity, a data acquisition unit, and a temperature measurement unit. The low-power, swept frequency microwave source is a HP 8350B Sweep Oscillator with the HP 86235A RF Plug-In (frequency range from 1.7 to 4.3 GHz). The high-power, single frequency microwave source is an Opthos MPG-4M microwave generator. The modified tunable cylindrical microwave cavity with a 17.78 cm inner diameter is the same as shown in Figure 2.1. The top plate of the cavity is movable to adjust cavity length. By adjusting the top plate, different microwave resonant modes can be found inside the cavity. The microwave energy is conducted into the cavity through the coupling probe. The data acquisition unit is a data collection board in a personal computer driven by a data processing software⁴¹. The temperature measurement is performed with a Luxtron 755 multichannel fluoroptic thermometer or an infrared thermometer.

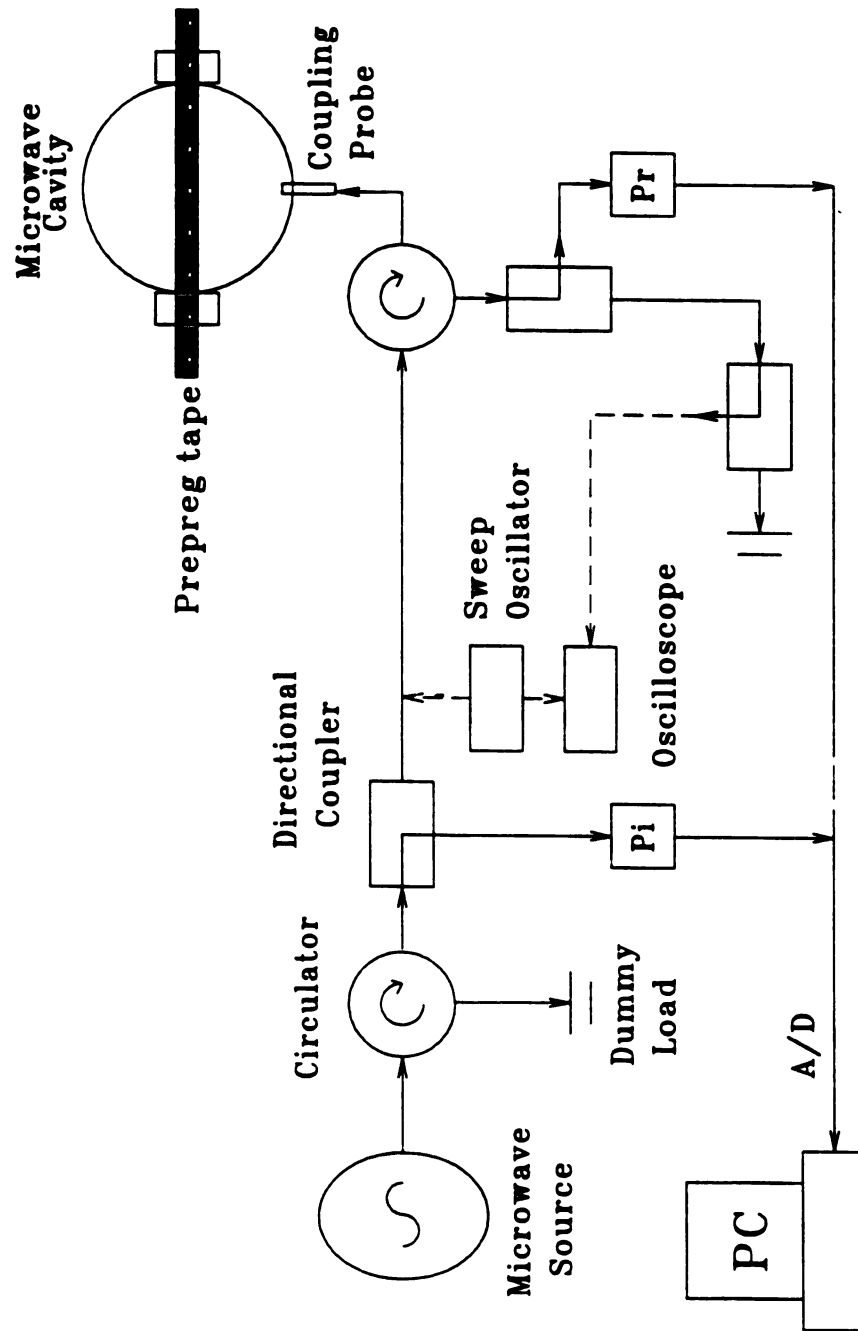


Figure 2.2 Microwave Circuit for Pultrusion Application

Some microwave radiation is reflected back into the microwave circuit from the cavity when the cavity is not well tuned to a certain resonant mode. The power reflection is monitored by an oscilloscope (Tektronix 2213) over the swept range of microwave frequencies. Resonant modes can be found at locations on the oscilloscope trace where the reflected power is zero. Once the resonant modes at 2.45 GHz are found, the single frequency microwave source is used for the processing of materials. The input power, P_i , and reflected power, P_r , are measured on-line during processing. By tuning the cavity, the reflected power can be minimized, and the microwave cavity is thus at a resonant condition.

The material in this study is a raw product of Chromalox Division, Emerson Electric. It is a 0.15 cm thick and 0.95 cm wide heat cable. The cable is made of two copper wires emerged in a base compound, with the shape of standard TV cable. The base compound is low density polyethylene with 20% highly conductive carbon black and zinc powder. This mold compound is also mixed with a cross-linking agent, di-cup peroxide(3% by weight). The processing of the material is to cure the raw product with the cross-linking agent, which initiates at 177°C.

An infrared thermometer (Omega OS1100) was used to measure the surface temperature on the center line of the cable material during processing. The temperature measurements were made through an opening at the center of the top plate of the cavity. The cable material was passed

through the cavity by a pulling roller. The pulling speed was controlled by a step motor which had a variable speed control. The cable material was processed at optimum resonant modes using a single frequency source at different input powers. Microwave distributions inside the cavity for samples at different cavity heights were also studied. The temperatures were taken at different sample positions using optical temperature probes attached directly onto the cable surface. As shown in Figure 2.3, position 1 was at center of the cavity, positions 2 and 3 were 15 mm off the center, and position 4 was 30 mm off the center.

The possibility of processing cable materials through the axial direction of the cavity was also tested. The microwave distribution across this sample orientation was measured by recording temperatures with optical temperature probes attached to the surface of the cable. Figure 2.4 shows the cable positions from which temperatures were taken. Positions 1 through 8 were along the axial direction of the cavity. The positions were 2 cm apart with position 1 at 1 cm from the bottom plate of the cavity.

The processing speeds of the cable material for the curing studies were 2.5 cm/s and 1.8 cm/s. The corresponding residence times for the material in the cavity were 7 and 10 seconds. The microwave input power was 70 W. The curing of the material was studied using DSC to determine the extent of cure.

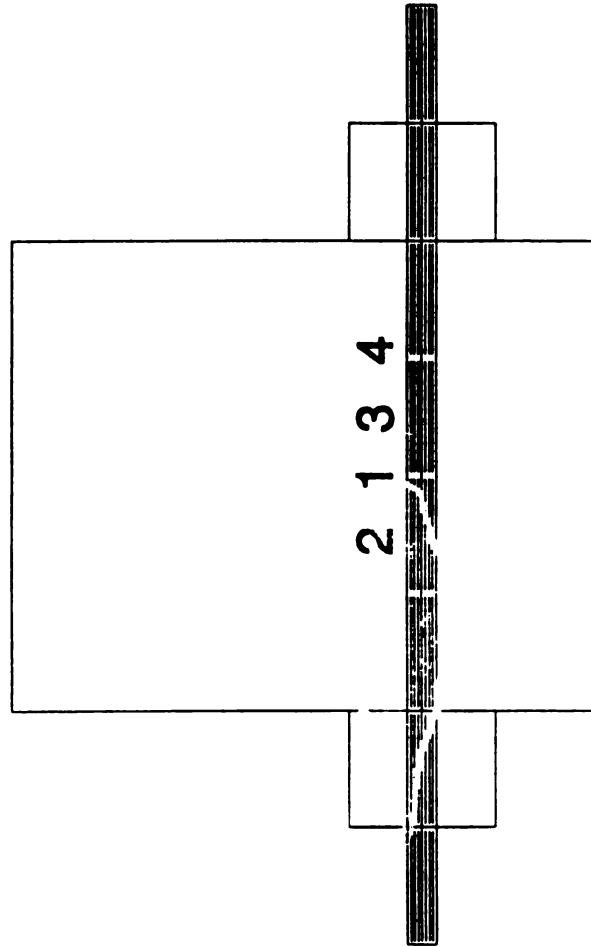


Figure 2.3 Sideview of Microwave Cavity with Positions for Temperature Measurement on Cable at Horizontal Direction

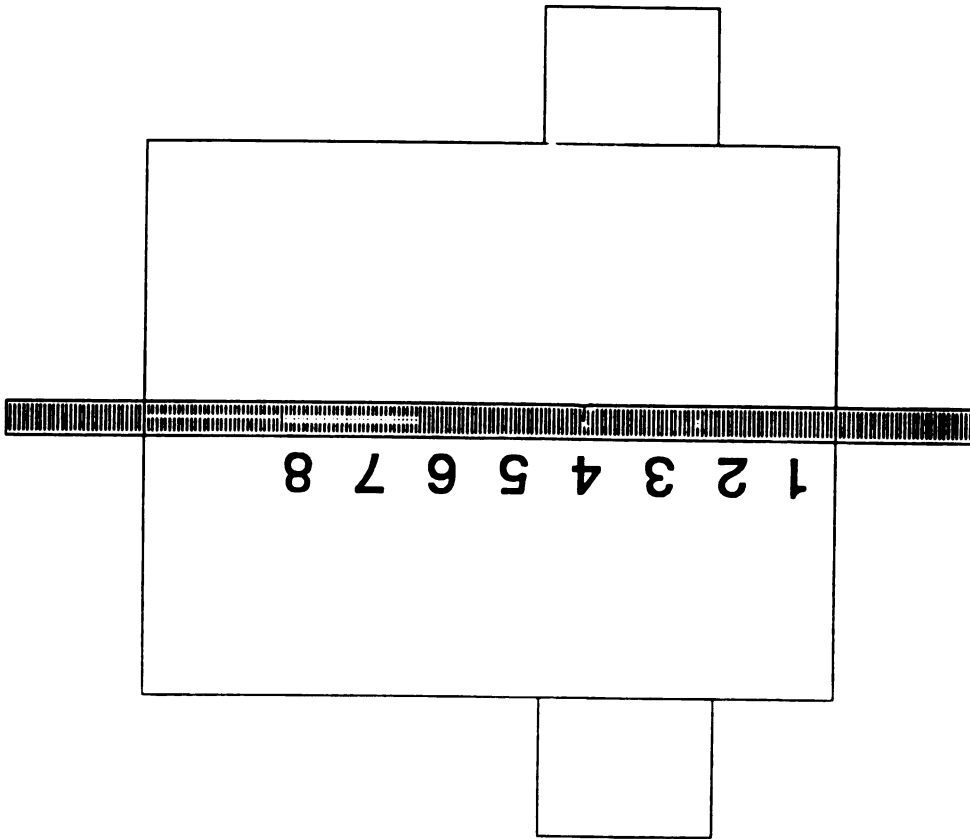


Figure 2.4 Sideview of Microwave Cavity with Positions for Temperature Measurement on Cable at Vertical Direction

2.3 Results and Discussions

There were eight resonant modes available for the horizontally loaded microwave cavity. The cavity dimensions and mode types for each resonant mode are listed in Table 2.1.

Table 2.1. Heating Modes for Cable in Horizontal Direction

Mode No.	Cavity Length(mm)	Mode Type	Max. Temperature (°C)
1	63.0	TE ₁₁₁	150
2	72.0	TM ₀₁₁	40
3	101.5	TE ₀₁₁	36
4	108.5	TM ₁₁₁	42
5	130.0	TE ₁₁₂	112
6	145.5	TM ₀₁₂	29
7	153.0	TE ₃₁₁	29
8	182.0	TE ₂₁₂	28

From the preliminary heating results above, mode 1 and 5 show the most promising results for further processing studies. Both resonant modes can heat the cable material over 100°C at only 30 W input. The heating of the cable material was studied at two cavity heights, 40 mm and 50 mm from the bottom of the cavity. The heating results are shown in Figure 2.5 using mode 1 and 5 at 30 W microwave input power. At both heating modes, the heating for the cable at height 50 mm was more effective than those at

height 40 mm. The microwave distribution patterns for both heating modes were basically the same. The center of the cable material was heated more efficiently than the rest of the cable. This indicates that the microwave energy may concentrate more in the center of the cavity. This finding led to the subsequent study in which the cable material was passed through the cavity in the axial direction.

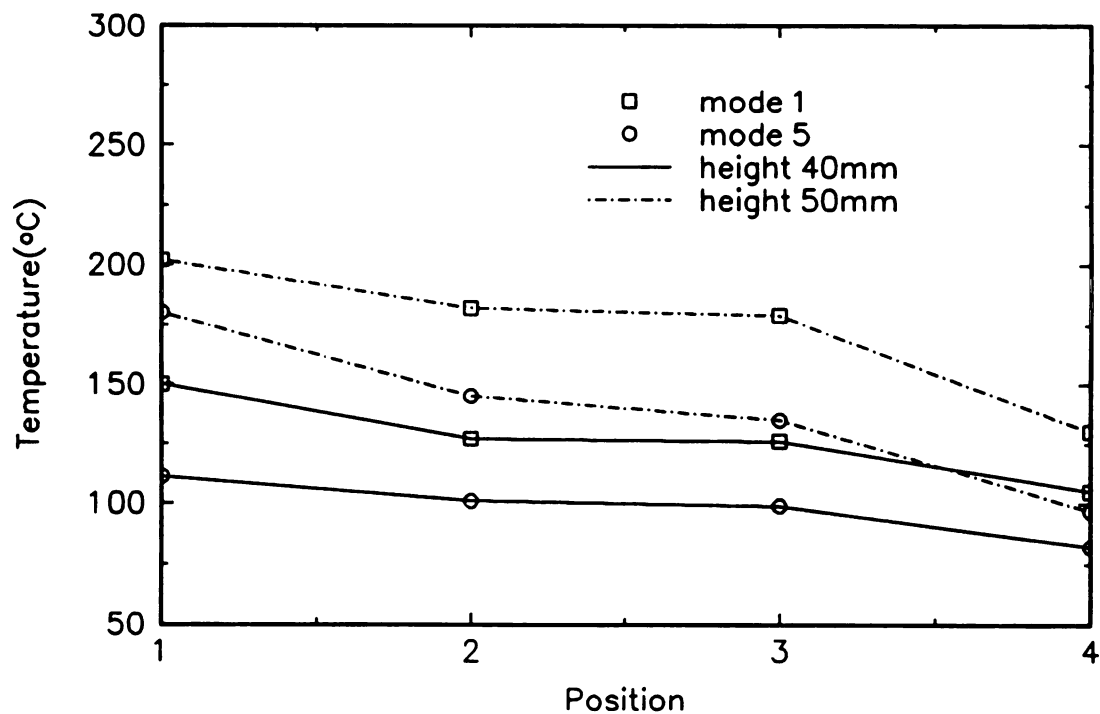


Figure 2.5 Heating Results for Cable at Horizontal Direction

The curing results of the material are shown in Table 2.2. The thermal curing result in the table is for the conventional manufacturing processing condition. Compared to the thermal curing, microwave processing is much more efficient. At different microwave processing speeds, the residence times for the cable material inside the microwave cavity are different. A longer residence time will result in a greater extent of curing for the same input power and pulling speed. At a processing speed of 1.8 cm/s, the cable material was 63% cured after being pulled through the cavity for a microwave input power 70 W. At a faster processing speed of 2.5 cm/s, the cable material was cured less even though the material was passed through the cavity twice. The reason is that the curing rate of the material is a strong function of temperature. At a faster pulling speed, the cable material is not heated to as high a temperature as it is at a slower pulling speed. To maintain the rate of curing at a faster processing speed, the microwave input power must be increased.

Table 2.2 Curing Results at Different Pulling Speeds

Curing Type	Residence Time(s)	Processing Speed(cm/s)	Curing Result
Thermal Curing	360	7.5	100%
Microwave Curing	10	1.8	65%
Microwave Curing	7	2.5	13%
Microwave Curing	14	2.5	45%

The heating modes available for processing cable material in vertical direction are shown in Table 2.3. The disturbance of the material to the microwave field is different for the processing material at different sample positions inside the cavity. As a result, the resonant conditions are changed for the cable material in the vertical direction compared with those at horizontal positions.

Table 2.3 Heating Modes for Cable in Vertical Direction

Mode No.	Cavity Length(mm)	Mode Type	Heating Results(°C)
1	63.0	TE ₁₁₁	120
2	80.0	TE ₂₁₁	45
3	111.0	TM ₁₁₁	42
4	129.5	TE ₁₁₂	67
5	153.0	TE ₃₁₁	82

As can be seen in Table 2.3, modes 1 and 5 are most effective for the processing system. The cable was heated over 80°C at both heating modes with an input of 30 W. The further heating results using these two modes are shown in Figure 2.6. As the cavity length varies with different resonant modes, the residence times at different resonant modes for the vertical processing orientation are different. By comparing with the heating results for the cable in the horizontal direction, it can be seen that the microwave heating for the cable in the vertical direction is less efficient. This could be attributed to the microwave energy distribution changing dramatically with the cable running through the axial direction of the cavity. The microwave energy does not concentrate along the axial line of the cavity for the vertical processing orientation.

In addition to the difficulties of designing the microwave leakage control device for the vertical processing, the heating of the cable material was less efficient than that of the horizontal processing direction. The processing of cable material along the axial direction is not as promising as in the horizontal direction.

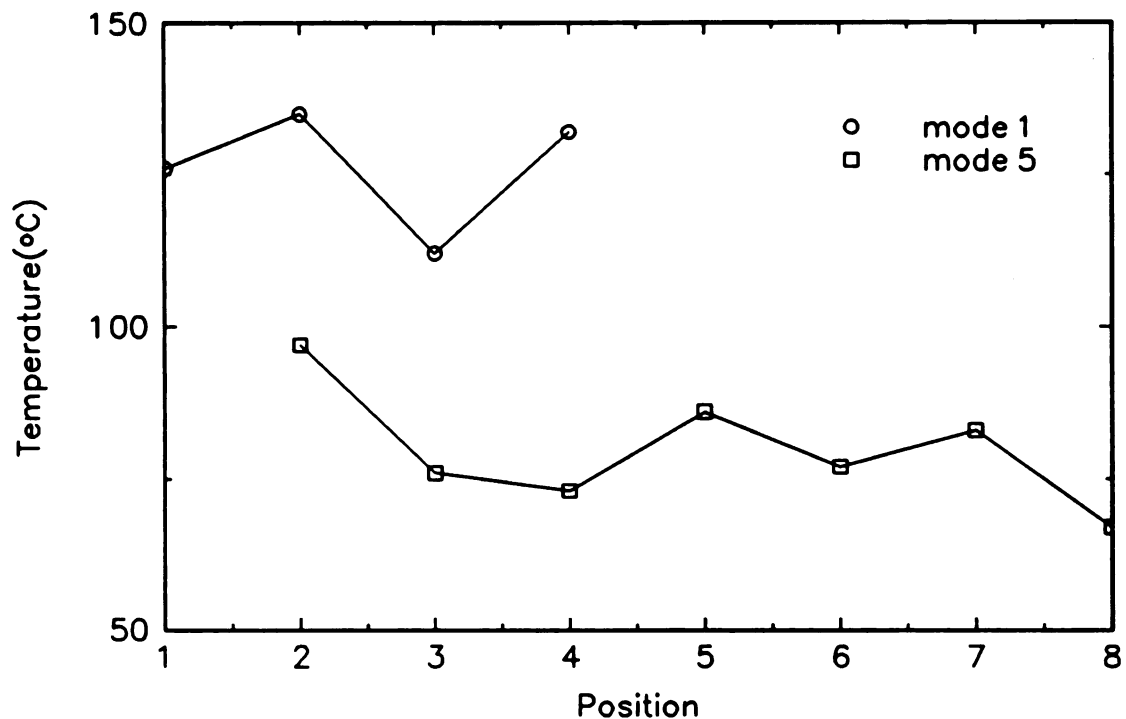


Figure 2.6 Heating Results for Cable at Vertical Axial Direction

One problem for the microwave curing of the cable material is the surface roughness after processing. This problem may be attributed to the fast heating rate of microwave processing. The sudden temperature rise might result in fast chemical reactions for the cable material. Another possibility is burning of the polymer material during intensive microwave processing. To address this issue, an inert gas processing environment is needed. In addition, a high pressure processing environment would help to produce a better performance cable product.

The microwave heating is not only a function of the electromagnetic resonant modes and the dielectric properties

of the material, but also a function of the location of the material load in the cavity. The processing positions for this study was confined by the openings on the cavity wall. To find an optimum processing condition for this cable material, the potential sample processing positions need to be fully explored. It might be possible to achieve a better processing result at a different microwave cavity position.

2.4 Conclusion

The potential of continuous microwave processing of cable material was explored. With the modified tunable microwave cavity, the feasibility of continuous microwave processing of heat cable was demonstrated.

The processing of the cable material at two cavity heights was studied. The processing at a height of 50 mm yielded better heating results and temperature profiles. The potential of processing the cable material along the vertical cavity axis was also studied. The microwave heating was less effective for the cable material along the vertical direction.

CHAPTER 3

APPLICATION OF CONTINUOUS MICROWAVE PROCESSING TO PULTRUSION

3.1 Introduction

3.1.1 Pultrusion

Pultrusion is a continuous manufacturing method used to produce fiber reinforced plastic profiles with a constant cross-sectional area through the length of the product. In pultrusion, the product's shape is determined by continuously pulling the composite material through a die. Pultruded composites consist of reinforcing materials, a resin, and often a mat material and other ancillary materials⁴². The reinforcing materials include mainly glass fibers and graphite fibers. The resin materials are usually thermosetting polymers which bind the fibers together. During processing, the polymers are transformed from their initial low viscosity liquid state to a rigid thermoset polymer state as a result of a thermally induced polymerization. The mat material is used to improve the appearance of the composite surface.

As a result of efforts and achievements by processors, material suppliers, universities, and research organizations, pultrusion technology is evolving rapidly. Pultrusion has become a key manufacturing method capable of

offering reliable and cost-effective products with specifically defined properties. Pultruded composites have been utilized over a broad spectrum of applications ranging from civil constructions to aircraft and space vehicles. Figure 3.1 shows the sketch of a typical pultrusion machine. Fibers coming from roving are impregnated with resin polymers. The preforming fixture brings fibers together and form a consolidated shape. The polymers start polymerization within the heated metal die and form a solid profile. The cured composite is then pulled through the die by the pulling mechanics at a constant rate. The product is cut into desired lengths with the cut-off saw at the end of the process.

One of the key steps in a pultrusion process is to control the interactions among fiber, resin, and additives. The conventional processing method is to heat the materials inside the pultrusion die via thermal convection or conduction. The pultrusion dies used for this processing method are made of steels which are characterized by their toughness and excellent heat conductivity. Both convection and conduction heating convey heat through the surface of the material. The heat is then conducted into the interior of the material. This heating mechanism often causes temperature excursions inside the processing materials especially for large parts.

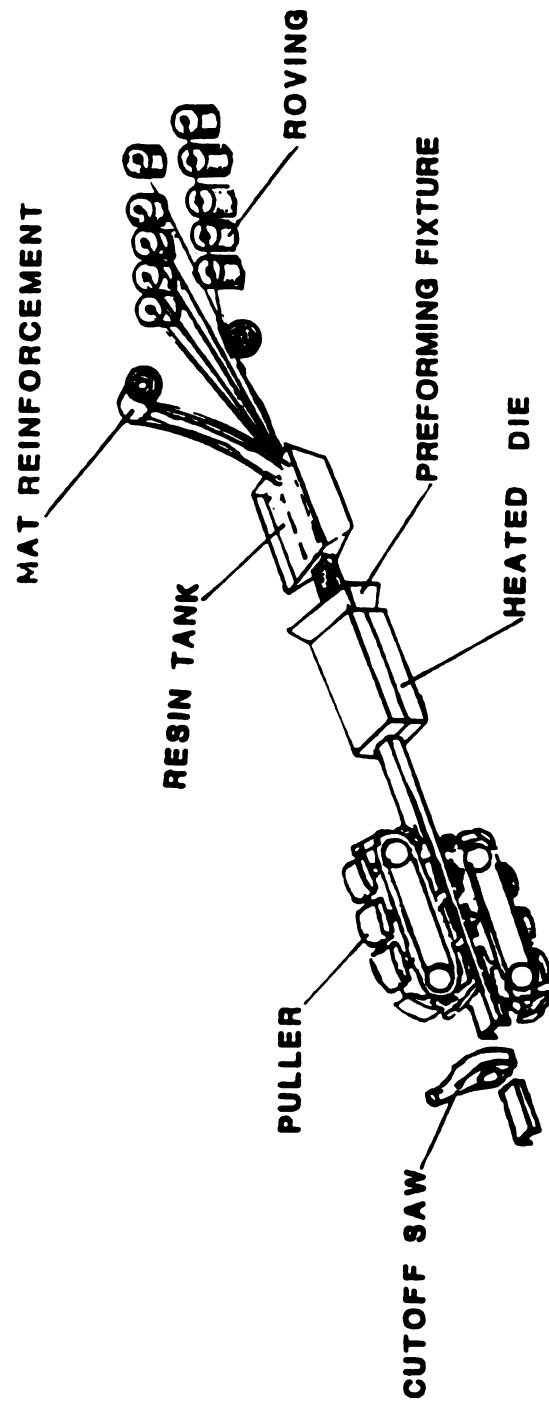


Figure 3.1 A Sketch of Typical Pultrusion Machine

3.1.2 Microwave Processing

Compared to the thermal heating method, microwave curing of composite materials is a faster and more direct heating method that takes advantage of the dielectric properties of the material being processed. The general advantages of using microwave technology include: shorter processing time, better control of temperature profiles within the composite material, and improved mechanical properties of the final part⁴³. As a result, microwave heating devices such as commercial microwave ovens⁴⁴ and waveguides⁴⁵ are widely used in industry. Meanwhile, the continuous microwave processing technique is highly desired for processing large composite parts, such as long pipes or panels. The critical problem of microwave leakage during continuous processing can be controlled by using special designed jackets attached to the entry and exit ports of the microwave cavity⁴⁶.

The applications of continuous microwave technique in industries has been under investigation for decades. Most of these applications use microwave energy to preheat or to postcure materials after parts are made⁴⁷. One pultrusion application of processing materials continuously in a waveguide has been patented⁴⁸. 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 have to be in accord with the dielectric properties of the materials being processed in order to

create the suitable microwave field patterns⁴⁹. This requirement has greatly limited the wide application of the technique in industry due to the large variety of materials being processed.

In this study, a batch resonant microwave cavity was modified to perform continuous pultrusion processing⁵⁰. Unlike a waveguide, a resonant microwave cavity can be tuned to the optimum heating mode for different processing materials. The microwave pultrusion process proposed here is fundamentally different from the preheating and postcuring applications described above. A microwave transparent die was specially designed to fit into the microwave cavity. The microwave energy will heat materials directly through the die as they are pultruded through the microwave cavity.

3.2 Experimental

3.2.1 Microwave pultrusion setup

The microwave circuit system for the microwave pultrusion process is similar to that of a batch microwave processing system described in chapter 2. The microwave resonant modes were located using a swept frequency oscillator. A single frequency (2.45 GHz) power source was used for heating and curing tests. The input and reflected power were measured on-line during processing. As is seen in Figure 2.2, the microwave cavity was kept tuned by adjusting the cavity length(L_c) and coupling probe depth(L_p) so that the reflected power is minimized. A 17.78 cm inner diameter tunable cylindrical batch microwave cavity was modified for the microwave pultrusion processing.

Two dies were used in this study. A Teflon die was used for heating studies, and a ceramic die was used for pultrusion tests. Figure 3.2 shows the design of the die. The opening shape of the die is an 0.294 cm high, 2.45 cm wide rectangular. The top and bottom pieces of the die are bonded together with nylon screws along both edges of the die. The rectangular shape at one end of the die is to hold the die in place during pultrusion. Figure 3.3 shows the microwave cavity loaded with the pultrusion die. The die is inserted inside the cavity through the openings on the cavity wall.

The inner surface of the ceramic die was treated with a mold release agent to prevent it from scratching as the

processing material is pulled through. The release agents are mono-coat multi-release agents from Chem-Trend Incorporated. The first layer of the agents, model number E304, is used to seal the micro-holes in the die surface. The second layer of the agents is applied to further smooth the die surface. Both layers of release agents have to be treated at processing temperature. The treatment will improve the durability of the Mono-coat release film and provide maximum number of releases. In the heating tests, the temperatures were measured with optical temperature probes attached directly to the surface of the prepreg. The data were collected with a Luxtron temperature measurement system. The system was connected to the computer and the data were processed with data processing software.

In the pultrusion tests, the prepreg was pulled through the cavity using a variable speed step motor which drove the rollers. The input power for pultrusion tests was 100 W. The prepreg was pultruded at different pulling speeds and different input powers. The maximum microwave leakage during processing was under the safety limit⁵¹.

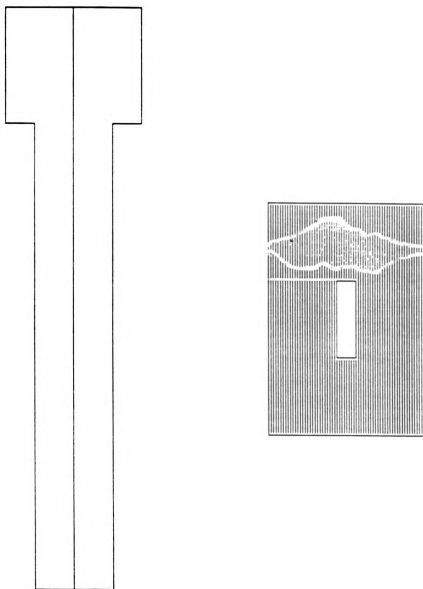


Figure 3.2 Sideview and Cross-Section of the Microwave Pultrusion Die

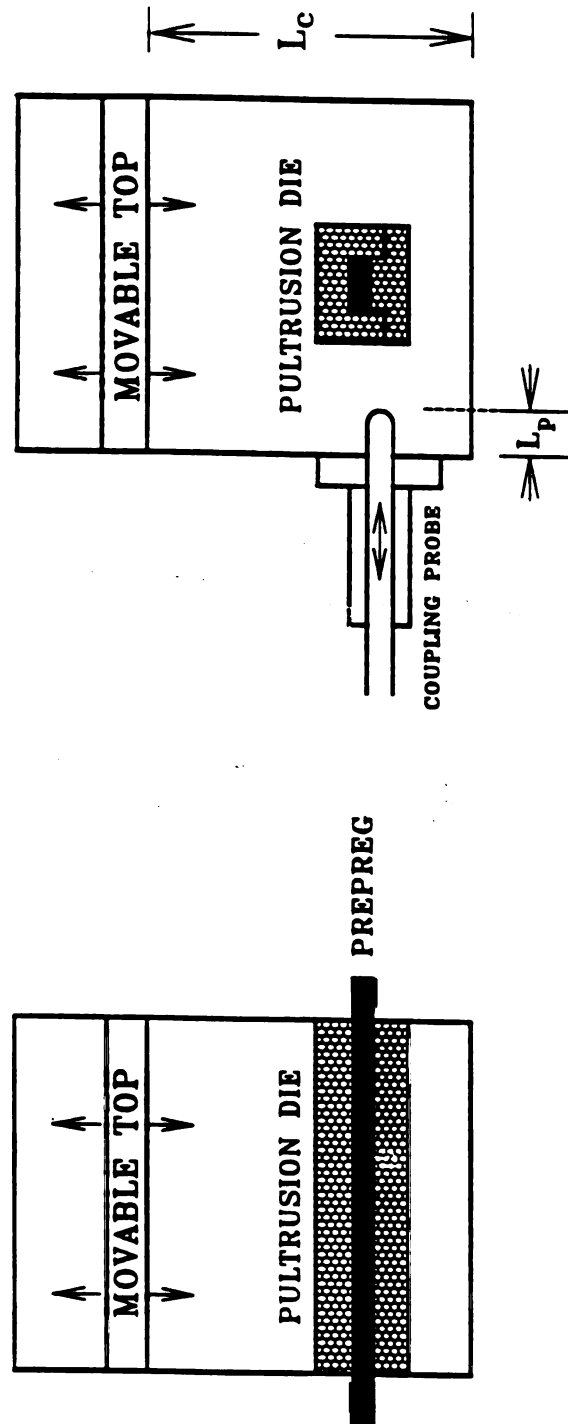


Figure 3.3 Sideviews of Microwave Cavity with Pultrusion Die

3.2.2 Material Preparation

The material used in this study was a continuous prepreg consisting of glass fiber/vinyl ester and vinyl toluene resin. The resin contained 1 wt% of cross-linking initiator Benzoyl Peroxide(BPO). The prepreg was prepared separately in a fiber/resin prepregging machine. As shown in Figure 3.4, the glass fiber tow is unrolled from the roving and passed through the guiding wheels. The fiber tow then passes through the resin pot which contains vinyl ester polymers. After the fibers are impregnated with the polymers, they are wound on the take-up drum. The drum moves horizontally while rotating and taking up the fiber tow. The fiber tow forms a sheet of prepreg on the drum. By adjusting the drum rotating speed, various thickness of prepreg can be obtained. The prepreg sheet is then cut into widths of 2.45 cm plies. Several plies of the prepreg is stacked together to form the composite prepreg tape with a cross-section dimension of 2.45 cm by 0.3 cm for the processing.

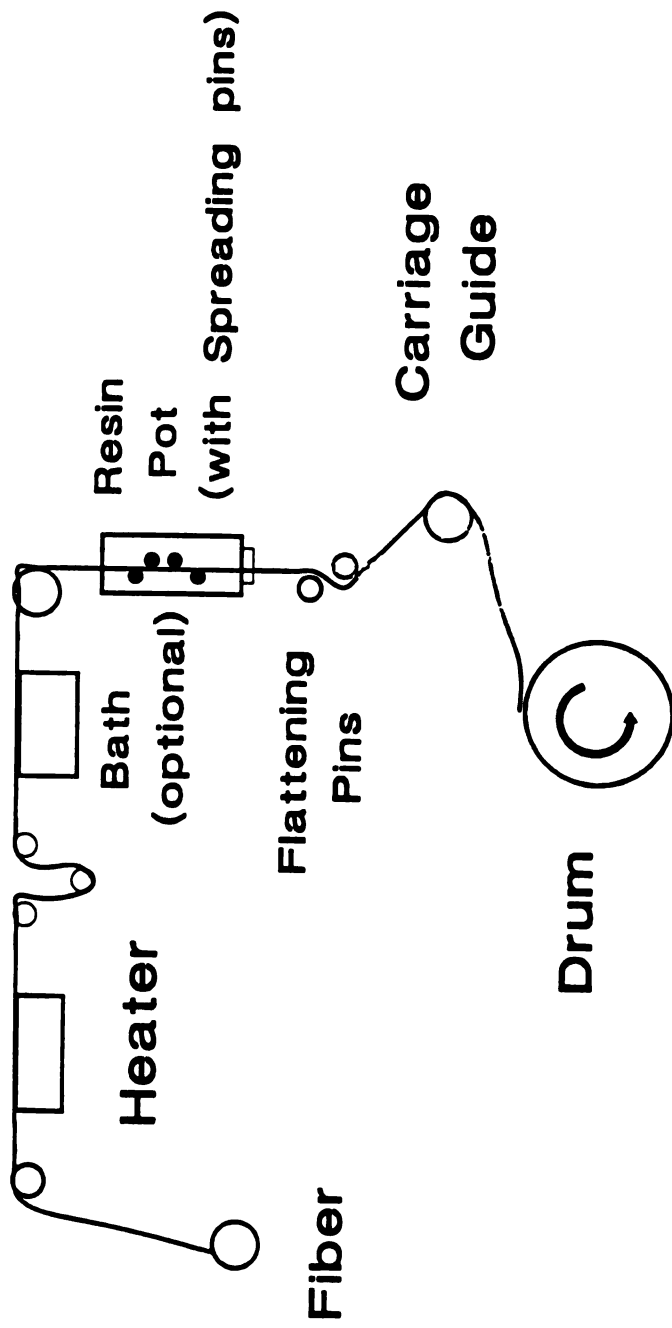


Figure 3.4 Prepregging Process

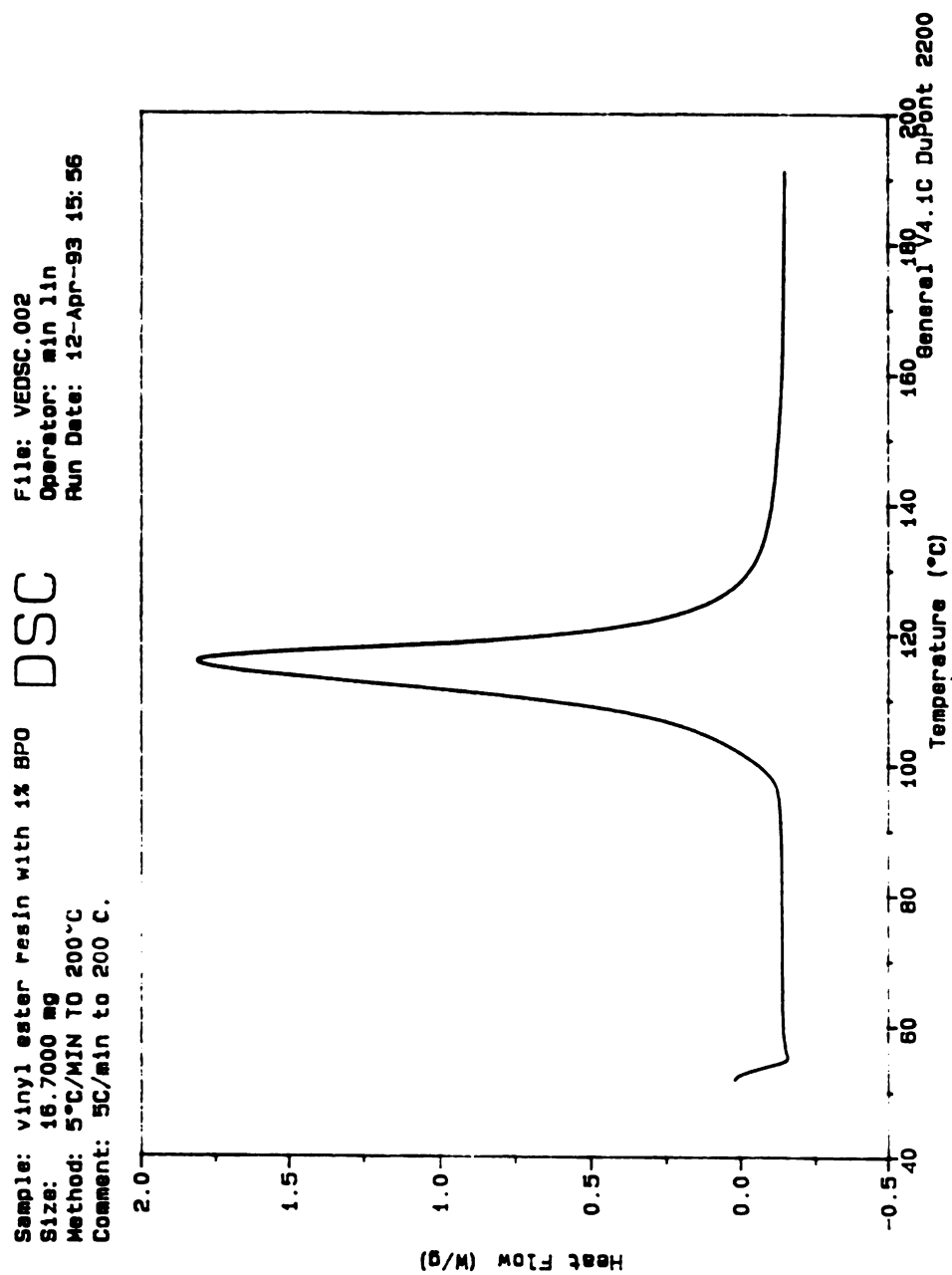


Figure 3.5 DSC Measurement for Vinyl Ester Resin

3.2.3 Reaction Conditions

Polymer samples were taken for DSC measurements. The results shown in Figure 3.5 give the information about the polymer cross-linking reactions. The reaction starts at about 80°C. The exothermic heat from the reaction is studied by heating resin samples at different heating rates for DSC measurements. From the DSC results in Figure 3.6, the exothermic heat for the resin polymerization reaction is found to be 272.5 J/g.

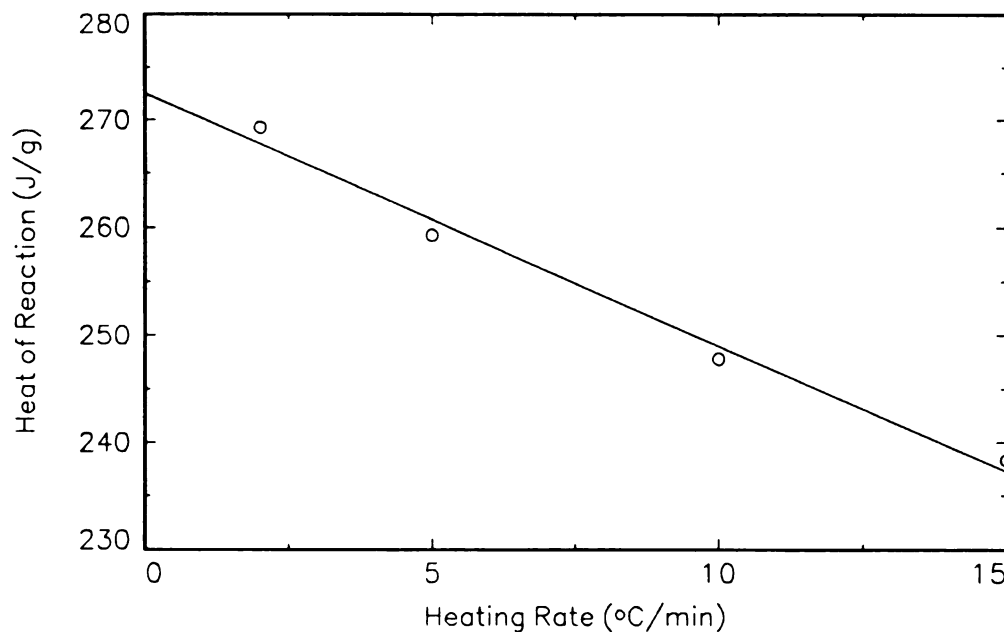


Figure 3.6 Heat of Reaction Measurements Using DSC for Vinyl Ester Resin

3.2.4 Temperature Measurement

The temperature measurements for the heating experiment were made by attaching optical temperature probes on the surface of the prepreg. The temperatures on the positions through the prepreg inside the cavity were recorded at different heating modes. Figure 3.7 shows the top view of the cavity with processing prerpeg. Positions 0 through 7 are along the pultrusion direction, while positions a, b, and c are across the prepreg width. Position 0 is at the entry port of the cavity and position 7 is at the exit port. Since the cavity diameter is 17.78 cm, the positions along the length of the prepreg are approximately 2.5 cm apart.

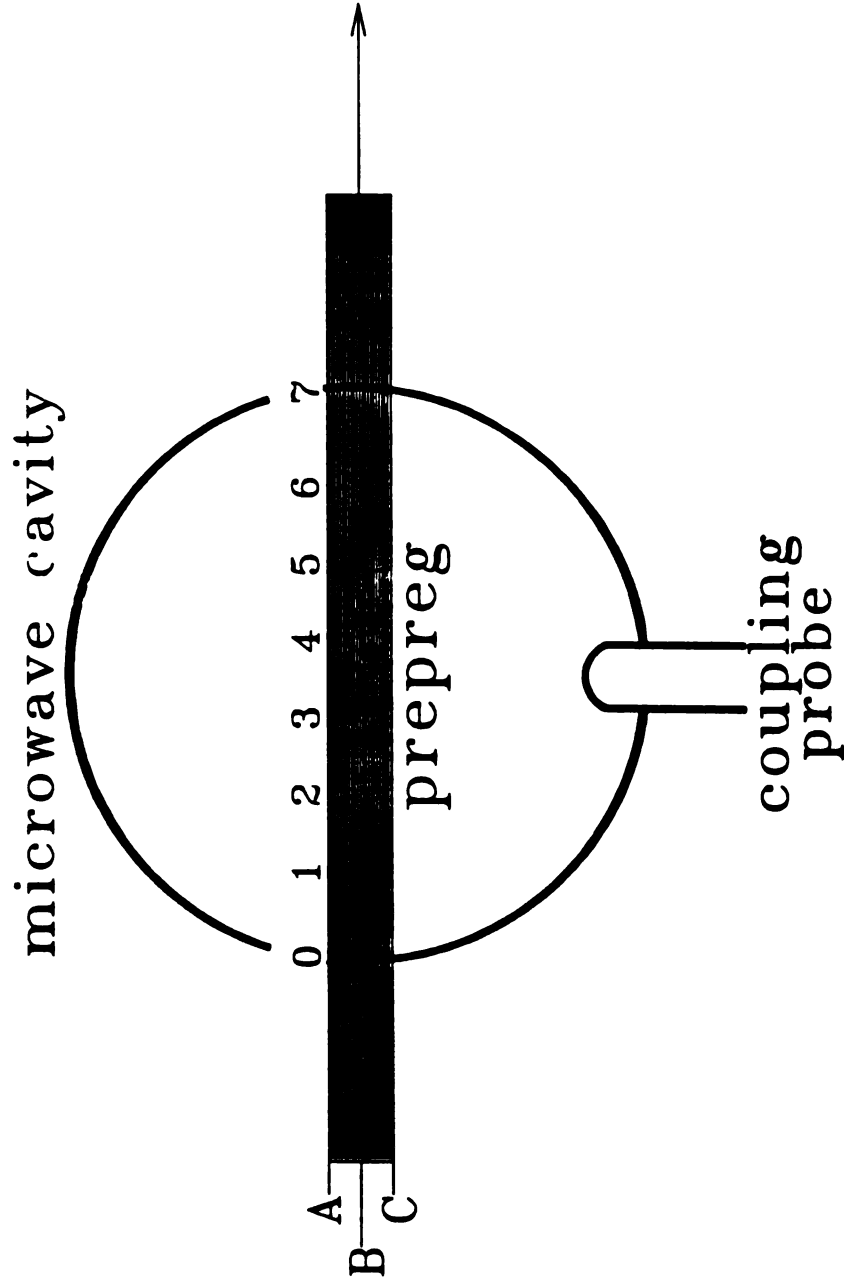


Figure 3.7 Top View of the Microwave Cavity with Positions for Temperature Measurement on Composite

3.2.5 Extent of Cure Measurement

A Differential Scanning Calorimetry(DSC) technique was used to determine the extent of cure for the microwave pultruded samples. The measurements were performed by comparing the exothermic peaks of uncured and cured samples. The extent of cure α is then calculated using the following equation

$$\alpha = 1 - \frac{[\text{peak area}]}{[\text{peak area}]_0} \quad (3.1)$$

where $[\text{peak area}]$ and $[\text{peak area}]_0$ are the exothermic peak integrations from the DSC results. They correspond to the exothermic heat of the cured and uncured samples, respectively.

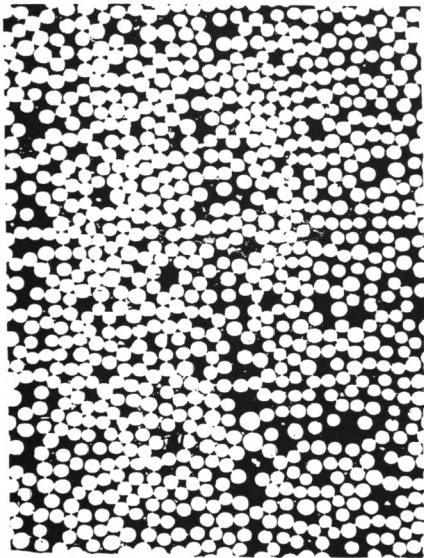
The samples for DSC measurements were taken from the positions on the prepreg where the temperatures were measured: positions 0 through 7 and positions a, b and c.

3.2.6 Fiber Fraction Measurement

The microwave pultruded samples were also measured for fiber volume fraction and void fraction. The measurements were performed in a microscopic instrument with a data processing software called Optical Numerical Volume Fraction Analysis (ONVFA).

Samples were prepared through several steps of fine grinding to make sure the measured surface is smooth. The sample cross-section was analyzed through microscopic images. The average fiber diameter was measured by marking

the fibers with electronic counting. The total fiber area was then calculated by multiplying the number of fibers with the average fiber diameter. The fiber volume fraction for this analysis was found by comparing the total fiber area with the cross-section area under analysis. After analyzing fifteen cross-section areas at arbitrary spots of three samples, the average fiber volume fraction was found.



Fiber diameter: 10 - 15 microns.

Figure 3.8 Microscopic Image of the Microwave Pultruded Glass/Vinyl Ester Composite Sample

3.3 Results and Discussions

There were four resonant heating modes available in the prepreg loaded tunable microwave cavity with Teflon die. Table 3.1 lists the cavity length and coupling probe depth parameters for each mode.

Table 3.1 Heating Modes for the Cavity with Teflon Die

Mode No.	Mode Type	Cavity Length L_c (mm)	Cavity Length L_{c^*} (mm)	Probe Depth L_p (mm)
1	TE_{011}	113	109.85	12.79
2*	TE_{112}	134	130.51	9.74
3	TM_{012}	143	137.08	22.99
4	TE_{311}	158	154.45	11.54

- L_c is the theoretical cavity length for empty microwave cavity.
- L_{c^*} is the cavity length with Teflon die and processing material.

In order to find the optimum heating mode for the prepreg system, further tests were conducted by heating the prepreg at each heating mode with an input power of 30 W. Temperatures were taken along the centerline of the prepreg at a time interval of 5 seconds. As shown in Figure 3.9, mode 4 is the heating mode with greatest heating rate for the prepreg system and die geometry. The prepreg was heated to 40°C in approximately 2 minutes at an input power of 30 W.

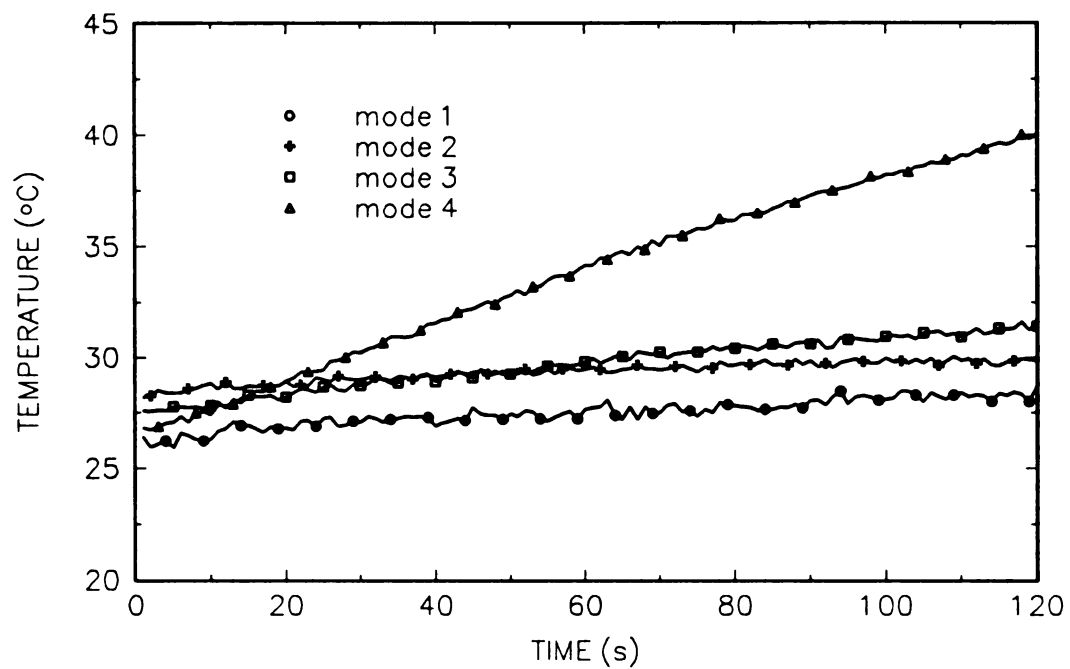


Figure 3.9 Heating Tests at Different Modes for Glass/Vinyl Ester Composite with Microwave Input of 30 W

More heating experiments were conducted to study the absorption of microwave energy by the prepreg material inside the cavity. The prepreg was tested at mode 4 and temperatures were taken along the length of the prepreg at the center and on the edges. Figure 3.10 shows the temperature measurements at different positions on the prepreg tape. Positions a and c refer to the edges of the prepreg, while position b refers to the centerline of the prepreg. The temperatures were taken along the length of the prepreg from position 1 through 8 and the average of these temperatures is presented in the graph. It can be seen that the prepreg was heated to 80°C (the cross-linking temperature) within 5 minutes. The temperature gradient across the prepreg is small, with less than 10°C difference between the center and edges of the prepreg.

When dielectric materials were loaded inside a microwave cavity, the microwave resonant modes will be disturbed. The extent of disturbance depends mainly on the dielectric properties of the materials. Ceramic materials are less transparent to the microwave than Teflon materials. As a result, the resonant mode disturbance for the ceramic die is greater than that for the Teflon die. By inspecting Table 3.1 and 3.2, we can see that the cavity length L_c for the cavity with the ceramic die loaded is shifted more than for the cavity with Teflon die. The basic heating patterns for the corresponding modes, however, remain unchanged.

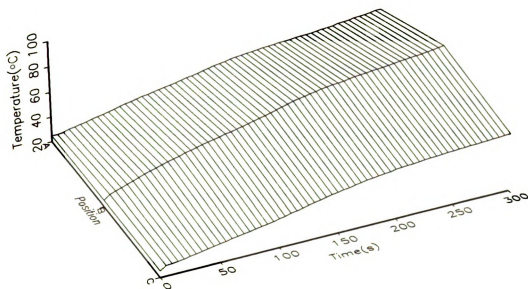


Figure 3.10 Heating Results at Mode 4 for Glass/Vinyl Ester Composite with Microwave Input of 60 W

Table 3.2 Heating Modes for the Cavity with Ceramic Die

Mode No.	Mode Type	Cavity Length Lc (mm)	Cavity Length Lc** (mm)	Probe Depth Lp (mm)
1	TE ₀₁₁	113	97.35	12.79
2	TE ₁₁₂	134	114.92	9.74
3	TM ₀₁₂	143	120.64	22.99
4	TE ₃₁₁	158	146.76	11.54

--Lc is the theoretical cavity length for empty microwave cavity.

--Lc** is the cavity length with ceramic die and processing material.

The pultrusion tests were accomplished using the best heating mode(mode 4) for the prepreg system at a certain processing speed and 100 W input power. The ceramic die was used because of its superior mechanical properties. However, the input power had to be increased due to its reduced microwave transparency as compared to that of the Teflon die. As is seen in Figure 3.11, the extents of cure were measured for pultruded prepreg samples cured at different residence times. At short residence times, the extent of cure is greater at the center than at the edges. But as the residence time increases, the extent of cure is consistent and complete across the width of the prepreg. To increase the microwave processing speed, the input power has to be increased. A higher microwave power source is required for faster continuous microwave pultrusion processing.

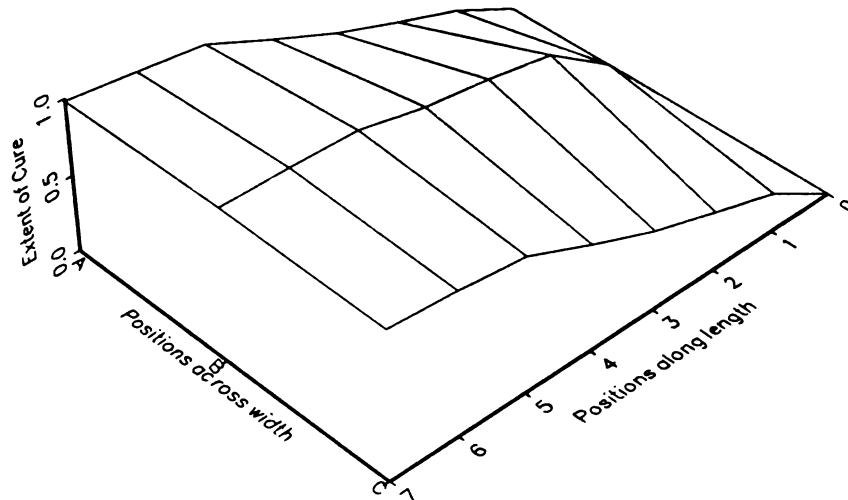


Figure 3.11 Curing Results at Mode 4 for Glass/Vinyl Ester Composite with Microwave Input of 100 W

To find the optimum operating conditions for the microwave pultrusion processing, the relation between processing rate and extent of cure was studied at an input power of 100 W. The prepreg tape was processed at pultruding rates of 1, 2, and 3 cm/min. The curing results are shown in Figure 3.12. From the curing results, at pultrusion speed of 1 cm/min, the composite prepreg was fully cured at the beginning of the process. At 2 cm/min, it was fully cured at the 2/3 of the cavity length(position 5). And at 3 cm/min, it was only cured 80% at the exit port

of the cavity(position 7). These results showed that the optimum pultruding speed for this pultrusion system at an input of 100 W is approximately 2.5 cm/min.

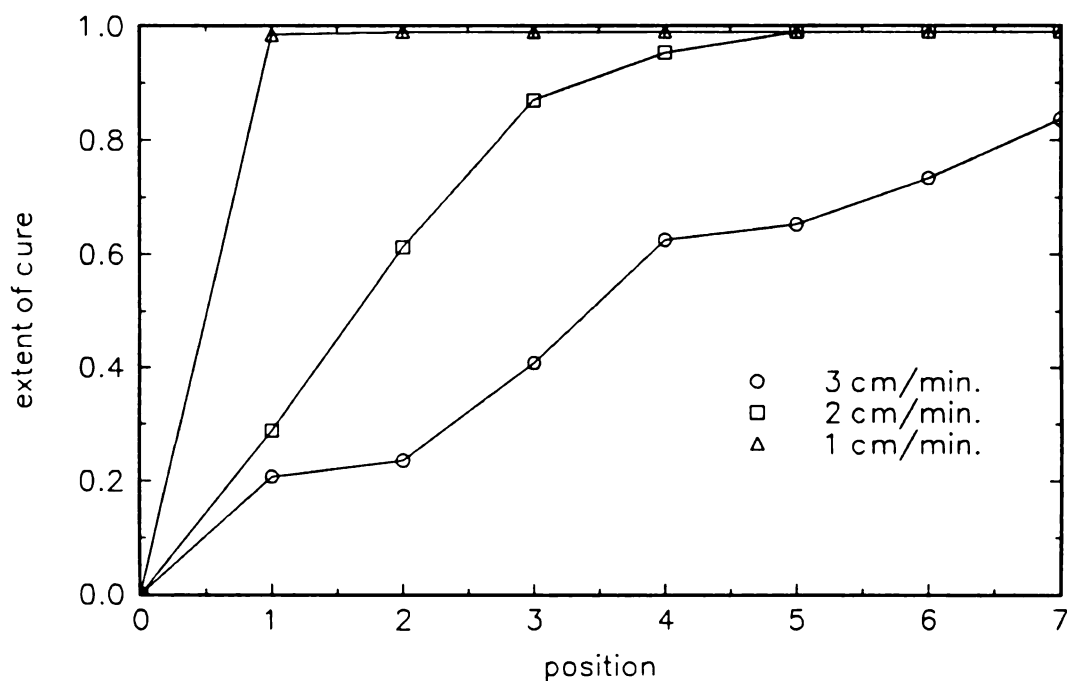


Figure 3.12 Curing Results for Glass/Vinyl Ester Composite at Different Pultruding Speeds

The curing rate of a composite material is determined by the heating efficiency which, in turn, is dependent upon the efficiency of microwave energy coupling into the material. The coupling of microwave energy with the material will mainly depend on the dielectric properties of the material. Other factors include the efficiency of the

microwave cavity and the location of the pultrusion die inside the cavity. Other heating modes might be able to heat the material as efficiently at different die locations. Therefore, more detailed studies on die locations are necessary for an optimized microwave pultrusion process.

3.4 Conclusions

It has been illustrated that continuous microwave pultrusion is feasible in a modified tunable microwave cavity with a microwave-transparent die fitted inside. The absorption of the microwave energy is a strong function of the resonant heating mode. The distribution of the microwave energy is uniform across the width of the prepreg. The prepreg is heated directly through the die while being pultruded through the microwave cavity. The fast heating rate shows the capability of coupling microwave energy into the prepreg through the die. Also, the uniform curing of the prepreg will be found the basis for producing high performance microwave pultruded composites.

CHAPTER 4

PROCESS MODEL FOR THE MICROWAVE PULTRUSION

4.1 Introduction

The feasibility of microwave pultrusion has been explored in Chapter 3. To better understand the microwave pultrusion process, a processing model is developed in this chapter. The model focuses on the prediction of the curing and temperature profiles at various pultrusion rates. The limitation of pultrusion rate is also studied for the optimum microwave pultrusion conditions.

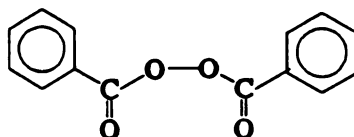
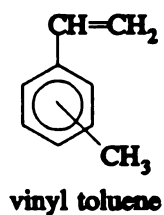
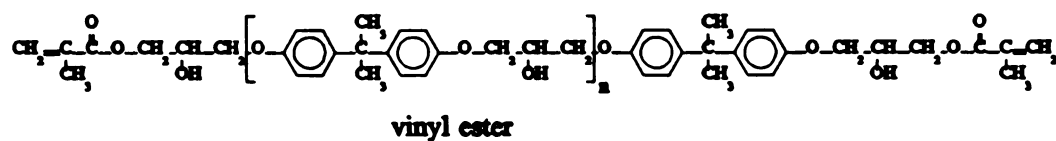
Optimum material properties and reliable processing conditions are necessary for the processing of high performance thermoset composites. These data are usually obtained through extensive testing of various designed materials at different processing conditions. However, this kind of testing is time consuming, and the tested results are often limited to a certain extent. Sometimes the experimental testing is limited by laboratory set-up and instrumental conditions available. Also, the procedure of finding the optimum operating conditions could be costly. A fast and cost-effective way to achieve this objective is through the numerical simulation of the processing. The simulation usually uses a processing model which includes

chemical, physical and mechanical properties of the material during processing. The model should include the information of chemical changes and energy transfer of the material.

In this study, a kinetics model for free radical polymerization is used for the vinyl ester's cross-linking reaction. An empirical microwave absorption model is developed to describe the microwave heating process. A FORTRAN computer code was written to simulate the processing at various operating conditions. The simulation can be used to predict the curing and temperature profiles at various processing conditions. It can also provide an optimum processing condition based on the required properties of the products.

4.2 Kinetics of resin polymerization

The resin used in this study is a methacrylic ester of Diglycidyl Ether of Bisphenol-A (DGEBA) vinyl ester mixed with 45 wt% vinyl toluene monomers. Benzoyl peroxide(BPO) is added to the mixture at an amount of 1 wt% as the initiator. The chemical structures of these chemicals are shown below:

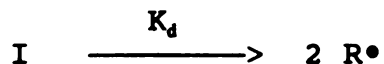


BPO

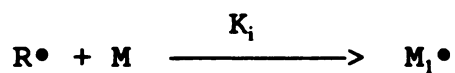
Figure 4.1 Chemical Structures of the Resin

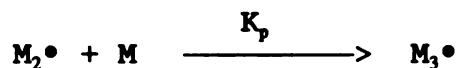
As can be seen in the chemical structure of vinyl ester, the cross-linking of polymers achieves via the two vinyl groups at the both ends of the structure. The polymerization of the resin is through a free radical mechanism. The reaction procedure is as follows⁵²:

Initiation

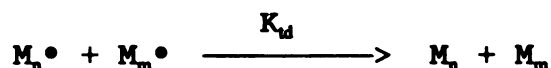
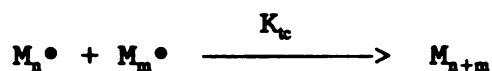


Propagation





Termination



The curing kinetics for the polymeric mixture containing monovinyl and divinyl monomers can be described by the following equations⁵³:

$$\frac{dX}{dt} = K_p \left(\frac{2fK_d[I]}{K_t} \right)^{\frac{1}{2}} \left[\frac{(1-X)(1+sX)}{(1-s+2sX)} \right] \quad (4.1)$$

$$[I] = [I]_0 \frac{\exp(-K_d t)}{(1-sX)} \quad (4.2)$$

$$s = \frac{d_p}{d_m} - 1 \quad (4.3)$$

where X is the fraction conversion of the vinyl groups; t is the reaction time; f is the initiator efficiency; k_d is the initiator decomposition rate constant; $[I]$ and $[I]_0$ are the initiator concentration at reaction times t and zero, respectively; s is the volume shrinkage factor; d_p is the density of the thermosetting polymer formed; and d_m is the density of the monomer mixture.

In this kinetics model, it is assumed that the termination reaction is diffusion controlled at the beginning of the polymerization. The model also assumes that the vinyl groups of the monovinyl and divinyl monomers have the same reactivity. The polymerization of methyl methacrylate/ethylene glycol dimethacrylate system has been reported using this model with a good correlation to experimental results⁵².

The polymerization of DGEBA vinyl ester/vinyl toluene system has also been studied using this model⁵⁴. The system was thermally cured at different processing temperatures. The modelling prediction provided a good fit with the experiment results. The following adjustable parameters of the model in Table 4.1 were obtained through the fitting of the experiment data with the prediction.

Table 4.1 Kinetics parameters for vinyl ester/vinyl toluene polymerization

d_m	1.04 g/cm ³
d_p	1.11 g/cm ³
k_d	$8.02e7 \exp(-8795.4/T) \text{ sec}^{-1}$
k_e	$2.18e6 \exp(-6776/T) (\text{L/mole-s})^{1/2}$
B_t	2.89
$B_{t,c}$	0.58

* T is the temperature in °K

The curing rate equation using these parameters becomes:

$$\frac{dX}{dt} = \frac{K_e (2K_d[I])^{\frac{1}{2}}}{(\exp[B_i(\frac{1}{V_{j0}} - \frac{1}{V_f})] + \frac{B_{i,p}}{K_{i,0}} K_p)^{\frac{1}{2}}} \frac{(1 - X)(1 + sX)}{(1 - s + 2sX)} \quad (4.4)$$

where

$$K_e = K_p \sqrt{\frac{f}{K_i}} \quad (4.5)$$

$$K_i = K_{i,0} + K_{i,p} \quad (4.6)$$

$$K_{i,0} = \frac{K_{i,p}}{\exp[B_i(\frac{1}{V_{j0}} - \frac{1}{V_f})]} \quad (4.7)$$

$$K_{i,p} = B_{i,p} K_p \quad (4.8)$$

$$V_{j0} = [0.025 + 0.001 * (T - T_{gm})] \quad (4.9)$$

$$V_f = V_{j0} + [0.00048 * (T - T_{gp}) - 0.001 * (T - T_{gm})] * \phi_p \quad (4.10)$$

$$\phi_p = \frac{X(1 + \varepsilon)}{(1 + \varepsilon X)} \quad (4.11)$$

$$\varepsilon = \left(\frac{d_m}{d_p}\right) - 1 \quad (4.12)$$

The microwave pultrusion in this study used the kinetics model and its parameters above except for the activation energies in k_d and k_c . The reason for this change is that in microwave heating, the curing process may be a little different due to the different energy dissipating mechanism of the microwave heating. The activation energies were obtained by minimizing the square of the error between the experimental data points and the model prediction.

4.3 Composite Material Properties

4.3.1 Literature Data

From the optical fiber fraction analysis of the pultruded composite in Chapter 3, the fiber fraction in the composite is about 0.7. The composite density was obtained from the reported densities of fibers and polymers. The heat of the polymerization reaction was studied in Chapter 3 and should be approximately the same for the microwave induced polymerization.

Other properties of the material include the dielectric properties of the materials inside the microwave cavity: composite material and pultrusion die material. Table 4.2 lists the dielectric constant and loss factor of these materials.

Table 4.2 Dielectric Properties of the Materials

Material	Dielectric Constant	Loss Factor
Resin	19.2	2×10^{-1}
Macor Ceramic	5.67	4×10^{-2}

As can be seen from the table, the dielectric loss factor of polymers is much greater than those of glass fibers and ceramic material. As discussed in Chapter 1, the dielectric loss factor is an important criterion for materials to absorb microwave energy. Therefore, the microwave pultrusion processing of the composite material will be modelled as if the die is transparent to microwave and the polymers are heated selectively.

The gel point is an important parameter for the processing of polymer composites, especially for the microwave processing. The reason is that the dielectric properties of polymers change dramatically after gel point. The gel point is defined as the critical conversion in thermosetting polymerization at which a three-dimensional cross-linked network is formed. Walling⁵⁵ derived a theoretical expression for the critical conversion in a chain polymerization containing monovinyl and divinyl monomers. The results showed a very low conversion (5%) when the reaction mixture formed a gel. This is the reason for the assumption of diffusion controlled termination reaction in the kinetics model.

4.3.2 Cp Measurement

Heat capacity measurements were made using a TA Instruments Differential Scanning Calorimeter mode 910. Heat flow of an empty pan is first measured, then the heat flow of sample material in the same pan is measured. Sample material is heated to the desired temperature range to measure the heat capacity.

The heat capacity is given by the equation

$$C_p = \frac{60E\Delta P}{H_r m} \quad (4.13)$$

Where C_p is the heat capacity in J/g°C; E is the cell calibration coefficient at the temperature of interest; ΔP is the difference in heat flow between the sample and blank curves at the temperature of interest, in mW; H_r is the heating rate in °C/min; and m is sample mass in mg.

Values of E are calculated by measuring C_p of a standard Al_2O_3 sample⁵⁶. Using the calculated set of E values, the heat capacity of the sample material is obtained using equation 4.13. The DSC results of the sample material are listed in the following table.

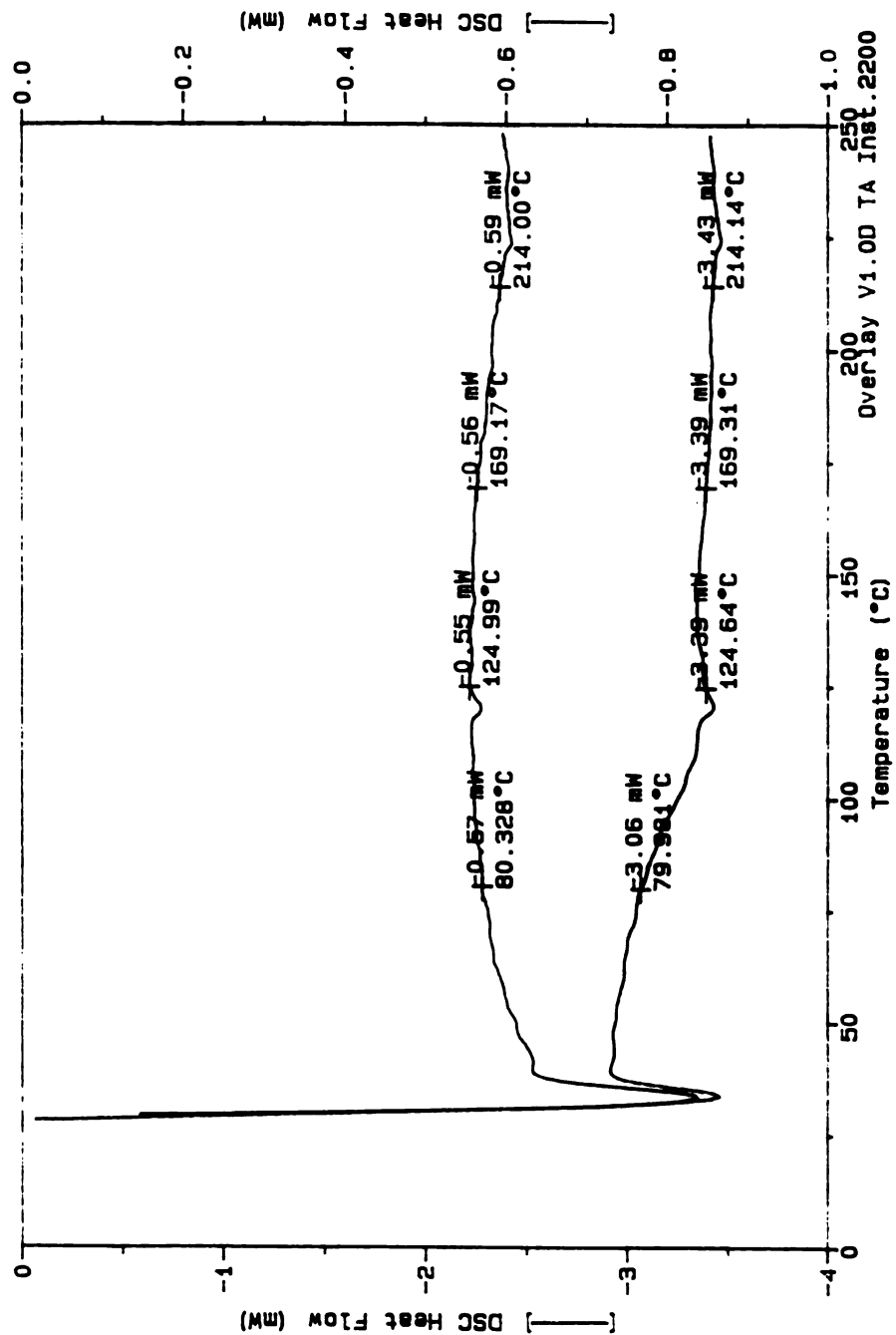


Figure 4.2 Heat Capacity Measurement Using DSC for Microwave Pultruded Glass/Vinyl Ester Composite Sample

Figure 4.2 shows the DSC results of the heat capacity measurements. The calculated values are listed in Table 4.3. From these results, the average heat capacity of the composite in the processing temperature range was found. The value was used in the energy balance for the process model.

Table 4.3 Heat Capacity Measurement

Temperature of Interest (°C)	Standard Cp for Al ₂ O ₃ (cal/g°K)	Coefficient E	Calculated Cp of Samples (cal/g°K)
80	0.2090	1.378	0.241
126	0.2200	1.335	0.266
169	0.2362	1.344	0.267
214	0.2460	1.338	0.267

4.4 Microwave Power Absorption

A power absorption model is critical for the development of a processing model. The temperature profiles and curing rates are strong functions of the interaction of microwave radiation with processing materials. In addition to the dielectric properties of the material, the power absorption is also controlled by the microwave distribution pattern and electric field strength. Poynting's theorem can be used to calculate the power dissipation into a material as described in equation 4.1.

$$P_2 = \frac{1}{2} \omega \vec{E} \cdot \vec{\epsilon}_e'' \cdot \vec{E}^* \quad (4.14)$$

where P_2 is the time average power dissipated in the composite due to electric field of the incident transverse electromagnetic (TEM) waves from top and bottom of the material. $\vec{E}$ and $\vec{E}^*$ are the electric field vector and its conjugate respectively, and $\vec{\epsilon}_e''$ is the effective dyadic loss factor of the material. Since the composite prepreg tape of microwave pultrusion has very small edges (0.3 cm in thickness), P_2 can be approximated as the power absorbed by the material.

For an empty microwave cavity, the electric field inside the cavity can be calculated based on Maxwell's electromagnetic equations and boundary conditions. For a

cavity loaded with small objects which only perturb the resonant condition by a few percent, the electric field can be calculated using a cavity perturbation theory⁵⁷. For the cavity loaded coaxially with a homogeneous, isotropic rod, a mode-matching technique could be used. However, the electric field for a cavity loaded with anisotropic material becomes very complicated. The power absorption models developed are only for specific type of materials and processing situations, such as a five-parameter model for the processing of a graphite composite plate⁵⁸.

The microwave energy absorbed by polymers during pultrusion processing is modelled by an empirical power absorption model. The model describes the microwave absorption ability according to the dielectric properties of the material.

$$P_a = P_i \exp\left(-\frac{1}{\sqrt{A\epsilon''}}\right) \quad (4.15)$$

In equation 4.2, two adjustable parameters are used for different processing conditions, such as different heating modes and pultrusion positions on the cavity wall.

4.5 Simulation of Microwave Pultrusion Process

The configuration of pultrusion processing of composite prepreg tape is sketched in Figure 4.3. The prepreg tape is enclosed in the ceramic pultrusion die. The microwave energy dissipates into the prepreg material through the microwave transparent die. The exothermic heat from the resin polymerization reaction is conducted through the die material into the environment.

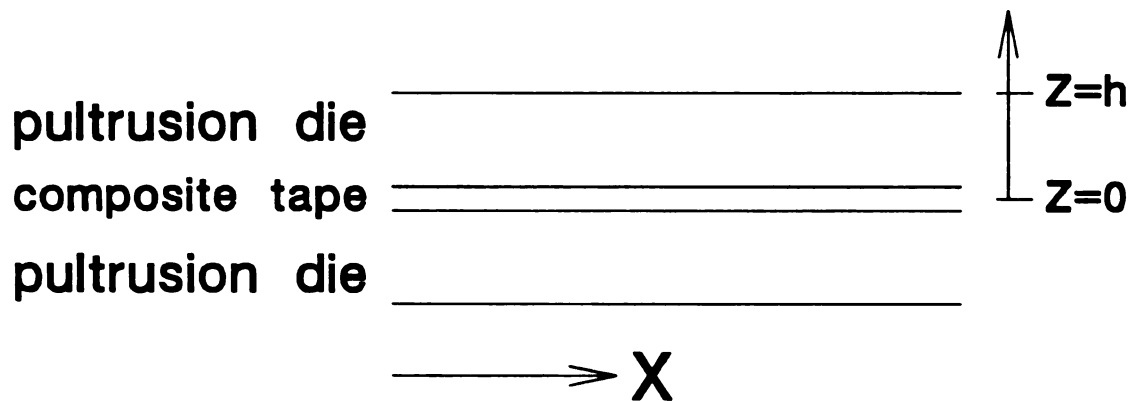


Figure 4.3 Modeling Configuration for Microwave Pultrusion Process

To simplify the computation process, following assumptions are used in the simulation:

1. the microwave pultrusion is at steady state for a defined input power and pultruding rate.
2. the temperature distribution is uniform along the thickness and across the width of the prepreg tape.
3. the heat transfer is only through the top and bottom surface of the pultrusion die.
4. the die material and glass fibers in the prepreg are transparent to microwave.
5. the temperature profile is uniform on the outer surface of pultrusion die.

From an energy balance, a one-dimensional heat transfer equation was derived as follows

$$\rho C_p v \frac{dT}{dx} = P_m + \rho \dot{H} + \frac{d}{dZ} \left(k \frac{dT}{dZ} \right) \quad (4.16)$$

with temperature boundary conditions

$$\left(\frac{dT}{dZ} \right) \Big|_{z=0} = 0 \quad (4.17)$$

$$k \left(\frac{dT}{dZ} \right) \Big|_{z=h} = h_a (T_s - T_a) \quad (4.18)$$

where ρ and C_p are the density and specific heat of the composite, k is the thermal conductivity of pultrusion die material, H is the heat generation rate per unit rate by the

polymerization reaction, and P_a is the heat generation rate per unit volume by the absorbed microwave energy.

To solve for $T(x)$ on the prepreg tape during microwave processing, the reaction kinetics and microwave power absorption models in chapter 4.2 and 4.3 are required. To simulate the temperature and extent of cure profiles along the length of the prepreg tape, implicit method of Lee's⁵⁹ was used to numerically code the equations. The Lee's method is based on the forward-difference approximation. The finite-difference expressions for the partial derivatives are:

$$\frac{\partial T}{\partial x} = \frac{T_{i+1,j} - T_{i,j}}{\delta x} \quad (4.19)$$

$$\frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) = \frac{k [(T_{i,\frac{1}{2},j}) (T_{i+1,j} - T_{i,j}) - (T_{i-\frac{1}{2},j}) (T_{i,j} - T_{i-1,j})]}{\delta z^2} \quad (4.20)$$

where i represents nodes in x direction, j represents nodes in z direction.

With the models for P_a and H , the temperature and extent of cure profiles of the prepreg tape were computed. The computer simulation was programmed in FORTRAN code and presented in Appendix I. The microwave pultrusion processing was studied at different input powers and pultruding rates. A processing temperature limit was set in the program to prevent the degradation of composite due to temperature excursion.

4.6 Results and Discussions

The fitting of experiment data with the model prediction is shown in Figure 4.4. The pultruding rates under this study were 1 and 2 cm/min, and microwave input power was 100 W. The pultrusion processing for this study is at microwave resonant mode 4 ($L_c=146.76$ mm) for the composite system.

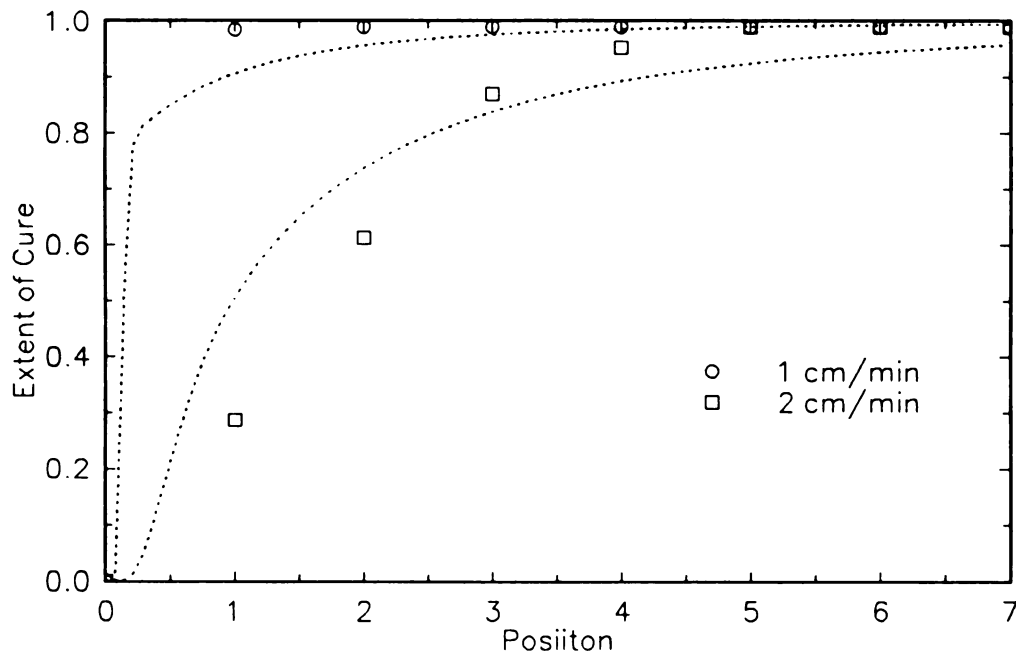


Figure 4.4 Modeling of the Microwave Pultrusion Processing of Glass/Vinyl Ester Composite

As can be seen from the graph, the computer simulation curves agree with the experimental results quite well. The predicted temperature profiles at each processing condition were also shown in Figure 4.5 and 4.6. The simulation predicted a temperature excursion occurring at beginning of the process if the pultruding speed is too slow (at 1 cm/min).

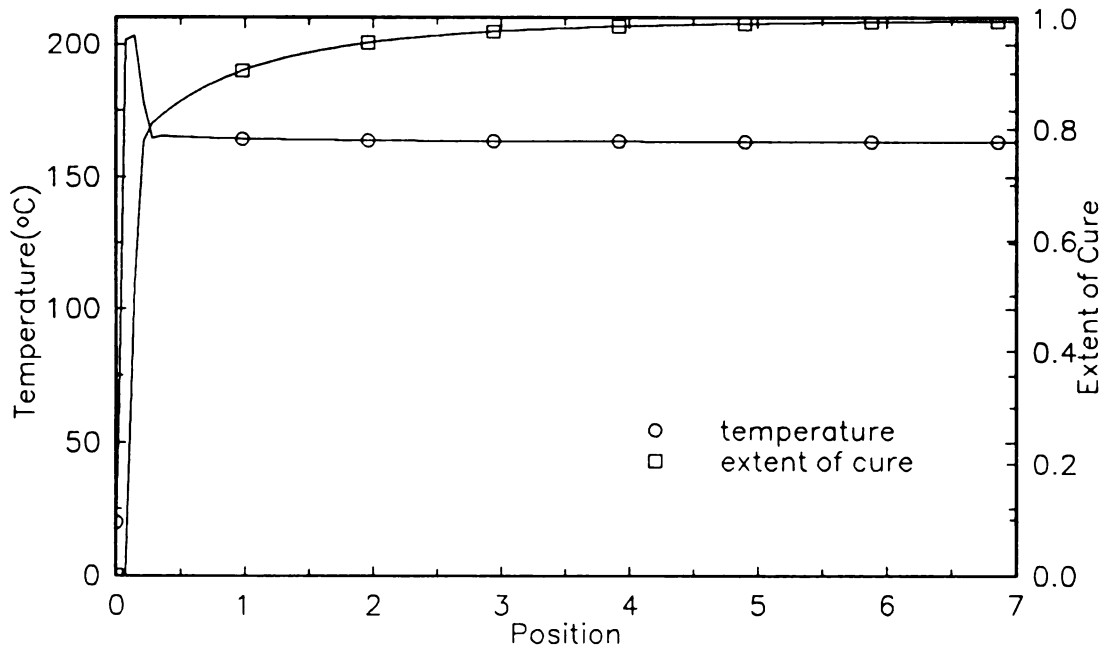


Figure 4.5 Simulation of Curing and Temperature Profiles of Glass/Vinyl Ester Composite at the Pultruding Speed of 1 cm/min

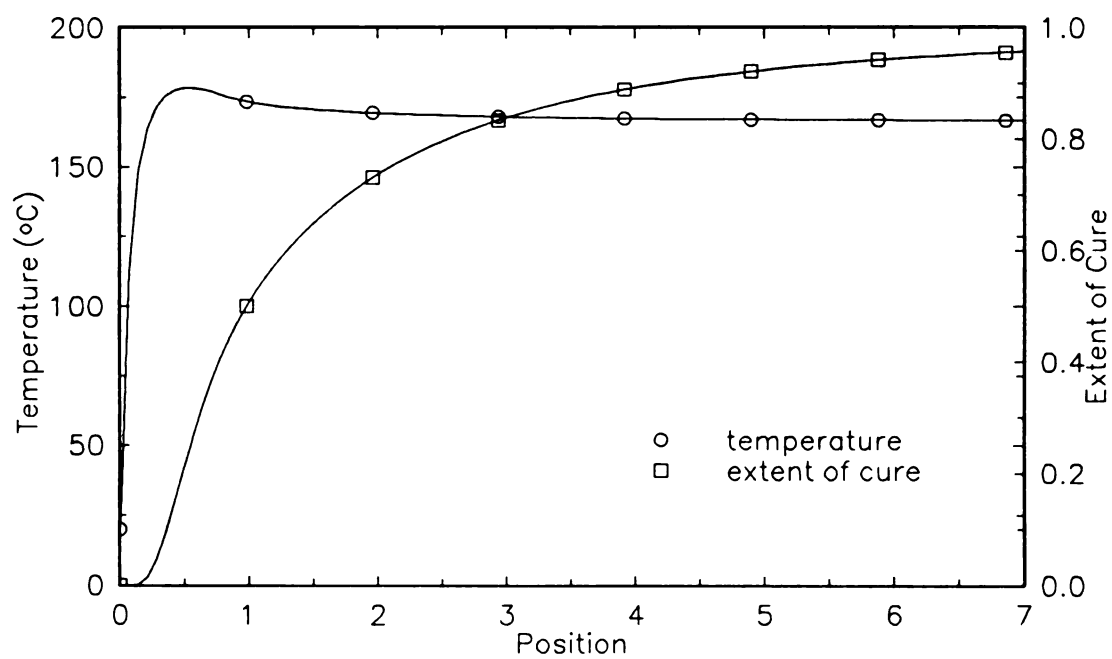


Figure 4.6 Simulation of Curing and Temperature Profiles of Glass/Vinyl Ester Composite at the Pultruding Speed of 2 cm/min

The adjustable parameters, A and B, in the power absorption model and activation energies, E_a and E_c , in the kinetics model were obtained by optimizing the fit of predicted values to experiment data in Figure 4.4. A general least square method was used to minimize the errors. The optimization scheme is

$$S = \sum (\alpha_i - Y_i(a_j)) \quad (4.20)$$

Where i presents for the measuring points along the tape, α_i is the measured extent of cure at point i, and $Y_i(a_j)$ is the predicted value at point i using the processing model. The parameters were obtained in Table 4.4.

Table 4.4 Parameters for the Process Model

A = 8
B = 0.5
$E_a = 7.963$ KJ/mol
$E_c = 5.446$ KJ/mol

Applying these parameters for the process model, curing and temperature profiles at higher pultruding rates are predicted. The simulation results are shown in Figure 4.7 and 4.8. The microwave pultrusion at pultruding rates of 6, 12 and 24 cm/min were studied. At pultrusion rates of 6 and 12 cm/min, the composite tape would be fully cured at the exit port of the cavity(position 7). The corresponding microwave input power would be 136 and 164 W, respectively.

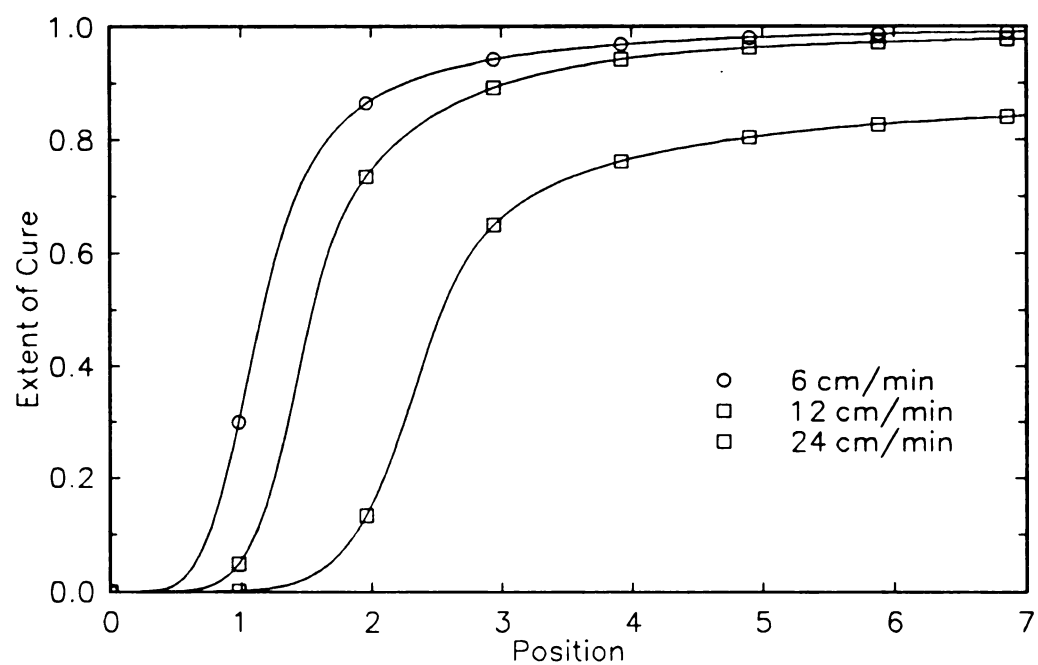


Figure 4.7 Simulation of Curing Profiles of Glass/Vinyl Ester Composite at Higher Pultruding Speeds

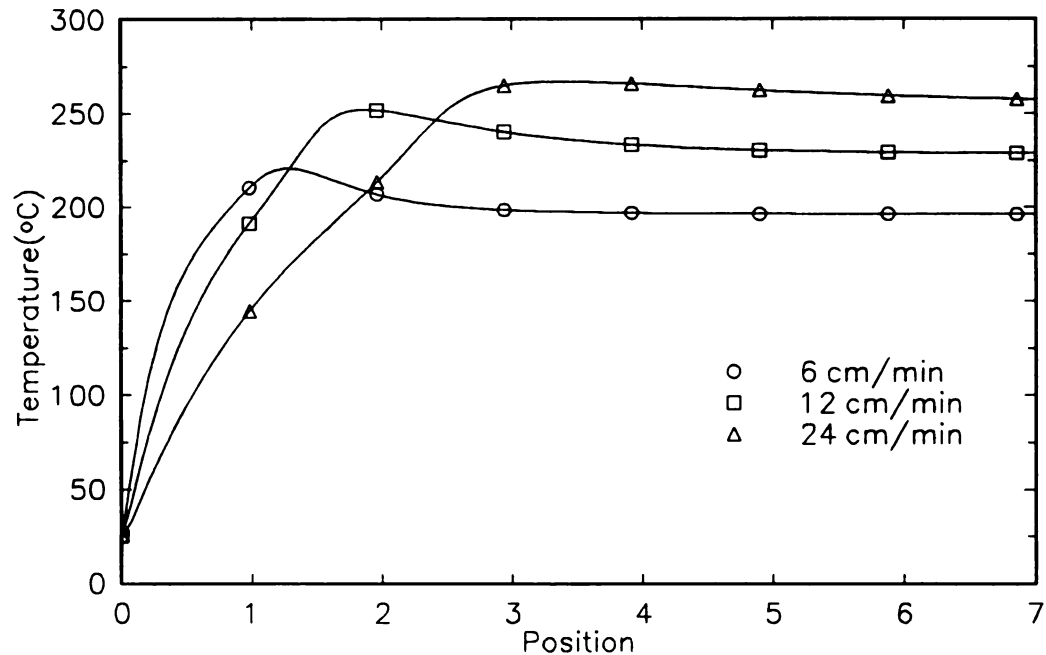


Figure 4.8 Simulation of Temperature Profiles of Glass/Vinyl Ester Composite at Higher Pultruding Speeds

The pultrusion speed limit for the microwave pultrusion system was also studied. A processing temperature limit was set at 275°C to prevent the pultruded composite from degrading. At pultrusion rate of 24 cm/min, as shown in Figure 4.7, the composite was only 80% cured at the exit of the cavity. The reason is that for a defined microwave cavity, fully cure of a composite material at a faster pultruding rate requires higher microwave input power. But

higher microwave input causes a temperature rise in the processing composite. The processing temperature would exceed the temperature limit set in the simulation program if a higher extent of cure is desirable at this pultruding rate. To maintain the processing temperature under the degradation temperature limit, the pultrusion rate for the microwave processing is thus limited to a certain degree to eliminate the degradation of the composite.

The temperature profile simulation in Figure 4.8 shows a uniform processing temperature after composite material reaches processing temperature. A uniform processing temperature will provides a better control of cross-linking reaction of the polymers. The cross-linking of polymers is important for composite to achieve a high quality mechanical properties.

The microwave processing simulation model provides a good direction for further microwave pultrusion studies. It also predicts the possible experimental results for a better design of the microwave processing system. The model is confined to the specific defined process. The simulation results could be different for different processing situations.

4.7 Conclusions

A one-dimensional processing model was developed for microwave pultrusion processing of composites. An empirical microwave power absorption model was proposed to describe the interaction between microwave radiation and polymers in composites. A free radical reaction mechanism was used to model the polymerization of resin during microwave processing. The activation energies for the microwave curing are obtained by optimizing the fit of the model to experimental data. The agreement between the model simulation and the experimental data is quite good. The optimized parameters are used to predict temperature and extent of cure profiles during the microwave pultrusion. The curing results provide the processing conditions for microwave pultrusion at higher pultruding rates and higher microwave input power.

The modelling results also provide a pultrusion rate limit for the microwave pultrusion system by setting a processing temperature limit in the simulation program. The processing temperature limit prevents degradation of the processing composite material. The temperature profile prediction shows a uniform processing temperature along the length of the material during microwave pultrusion. The uniform processing temperature is important for producing a high quality composite.

CHAPTER 5

SUMMARY OF RESULTS

The feasibility of continuous microwave processing of polymers and composites has been explored. The application of continuous microwave processing has been studied by processing heat cable with conductive wires. The microwave pultrusion process has also been studied as an extensive application of continuous microwave processing. A process model has been developed to describe the microwave pultrusion process. These studies have illustrated that continuous microwave processing offers a potential opportunity for various aspects of polymer and composite processing.

In the study of the processing of heat cable, the main results are summarized as follows:

- * Microwave heating was very effective for the heat cable. The cable material was heated over 100°C with only 30 W of microwave input power.
- * Microwave processing efficiency was a strong function of the processing position in the cavity. It was found that processing the cable at a cavity height of 50 mm results in better heating than at height of 40 mm.
- * The curing of the heat cable was much faster using

microwave processing compared to the thermal processing.

- * The microwave processing of heat cable was less effective for the vertical cable position than that for the horizontal position.

In the study of the pultrusion application of continuous microwave processing, the following results were obtained.

- * The microwave processing of glass fiber/vinyl ester composite was quite effective considering the dielectric properties of the material.
- * Microwave distribution during processing was relatively uniform across the width of composite prepreg. The maximum temperature difference between the center and edge of the prepreg was less than 10 °C.
- * The microwave distributions for the cavity loaded with Teflon and ceramic dies were basically the same. Although the cavity lengths for the heating modes shifted, the basic resonant modes were maintained.
- * The curing of the composite prepreg was uniform across the width after being pulled through the pultrusion die.
- * At pultrusion rate of 2 cm/min and 100 W microwave input power, the composite was fully cured at the exit port of the cavity.

In the simulation study of the microwave pultrusion process, a process model containing kinetics and power

absorption models was developed. The following results were obtained:

- * The power absorption model worked well for the simulation of the microwave pultrusion process.
- * The modified kinetics model offers a good description of the cross-linking reactions of the polymers.
- * The results of the simulation model fit well with the experimental data.
- * The model described the temperature profiles for the higher microwave processing rates, which provided information to prevent thermal degradation.
- * The model predicted a processing rate limit for the microwave pultrusion system.

CHAPTER 6

FUTURE WORK

The continuous microwave application on the processing of heat cable has been studied. The feasibility of microwave pultrusion has been explored. The advantages of microwave heating as an alternative to conventional heating methods have been demonstrated in these applications. In order to apply these processing techniques to practical industrial applications, some fundamental and technical issues need to be further investigated.

For the processing of heat cable, the following aspects need further study:

- * Processing of the cable material in an inert gas environment to eliminate the burning of the cable material during microwave processing.
- * Design of a microwave cavity capable of maintaining high processing pressures to improve the quality of the processed materials.

For the microwave pultrusion study, some application and fundamental areas need to be further explored.

- * Microwave pultrusion with other composite systems to extend the microwave pultrusion technique to a greater variety of applications.

- * Improvement of the existing microwave processing system for high-speed microwave pultrusion by improving the microwave cavity design, introducing high power microwave source, and constructing new pulling mechanics.
- * Improvement of the microwave pultrusion die by developing a more microwave transparent die to better exploit the advantages of microwave heating.
- * Use of the microwave cavity wall as the pultrusion die itself eliminate the processing difficulties caused by introducing the pultrusion die into the microwave cavity. A preliminary approach to the idea of using microwave cavity as the pultrusion die is shown in Figure 6.1.

The pultrusion die between two tunable microwave cavities is attachable. Different pultrusion dies could be attached to the system for different shapes. Since the pultrusion die is part of the microwave cavity, this application would require the design of a suitable microwave resonant cavity to provide a suitable heating mode.

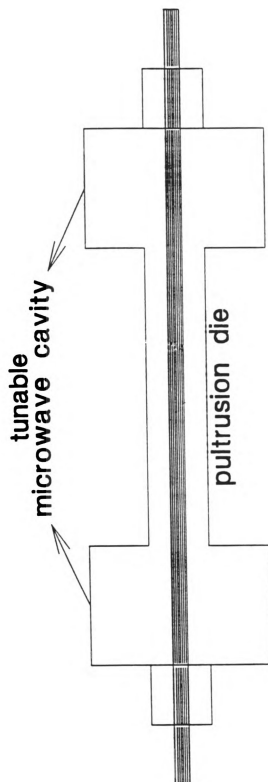


Figure 6.1 A Sketch of Novel Microwave Pultrusion System
With Part of the Cavity Wall Served as Pultrusion Die

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