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Microwave Processing of Polyimides and Polyimide Composites

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Larry Allen Fellows

has been accepted towards fulfillment of the requirements for

Master's degree in Chemical Engr.

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# MICROWAVE PROCESSING OF POLYIMIDES AND POLYIMIDE COMPOSITES

By

Larry Allen Fellows

### A THESIS

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

MASTER OF SCIENCE

Department of Chemical Engineering

#### ABSTRACT

# MICROWAVE PROCESSING OF POLYIMIDES AND POLYIMIDE COMPOSITES

By

## Larry Allen Fellows

Polyimides possess excellent mechanical and thermal properties, but their use is hindered by long, hightemperature processing cycles. The removal of volatiles such as solvents and side products is crucial to optimize polyimide properties. Microwave processing offers an alternative to conventional processing. Microwave processing techniques were applied to polyimide powders, polyamic acids in solution, and polyimide composites.

Cylindrical microwave cavities operating at 2.45 GHz were used to heat and process polyimides. The dielectric properties of the polyimides were too low to be heated by microwave without adding a material with a high dielectric loss factor. LARC-TPI varnish heated until the solvent evaporated. Unidirectional panels were fabricated by impregnating graphite fibers with LARC-TPI varnish (polyamic acid dissolved in diglyme). Composites were evenly heated using sets of electromagnetic modes (mode-switching). Flexural properties were greater for microwave-processed versus conventionally-processed panels.

To my wife, Cara

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#### CHAPTER 1

#### INTRODUCTION

Polyimides are a diverse class of materials which have demonstrated a great potential as high-temperature resins and matrix materials. Table 1-1 lists polyimides along with their thermal and mechanical properties. Aerospace applications have been proposed for polyimides, but their widespread use is limited by their inherently difficult processing cycles. Long, slow processing cycles have been developed to maximize the mechanical properties and quality of polyimides and polyimide composites. Thermoplastic and thermosetting polyimides have been examined as potential matrix materials for composites. Microwave processing may Provide an alternative to conventional heating methods that ill shorten heating times without sacrificing thermal and Chanical properties.

**I** - I POLYIMIDES

🔍 - 11 General Chemistry

Polyimides are formed by multiple reactions between Ctracarboxylic acids or their dianhydrides and diamines.<sup>1</sup> Cter or alcohols are formed as side products by these Cactions. The reactions are shown in a general form in Sigure 1-1. The diamine combines with a carboxylic group in

	POLYIMIDE	GLASS TRANSITION TEMPERATURE (°C)	FLEXURAL Strength (kpsi)	FLEXURAL MODULUS (Mpsi)
	PMR-15 <sup>2</sup> ( <u>8</u> )	340	25.5	0.58
	<b>Ultem 1000<sup>2</sup> (<u>P</u>)</b>	210	21.0	0.48
$\mathbb{L}$	UpJohn 2080 <sup>2</sup> ( <u>8</u> ) <sup>3</sup>	280	17.0	0.48
$\parallel$	LARC-TPI <sup>4</sup> ( <u>P</u> )	260	19.3	0.540
	<b>Thermid</b> IP-600 <sup>5</sup> ( <u>8</u> )	325		0.511
	<b>Thermid</b> MC-600 <sup>5</sup> ( <u>8</u> )	325		0.395
	<b>Thermid</b> FA-700 <sup>5</sup> ( <u>8</u> )	300		0.448
	Typical Polyimide at 20°C <sup>6</sup>		208	16.6
	Typical Polyimide at 232°C <sup>6</sup>		103	15.0

Table 1-1. Thermal and Mechanical Properties of Polyimides

 $(\underline{P})$  - thermoplastic  $(\underline{8})$  - thermoset



Figure 1-1. The general reaction forming a polyimide from starting materials.

t 00 0 ); I Í S 2 d • Ý I f Ţ :: 2 ea 1 К 1 00 ij the first step. This occurs at ambient temperature. The combination at the carboxylic site results in the formation of an intermediate product known as a polyamic acid. Dianhydrides and diamines are listed in Tables 1-2 and 1-3, respectively. In Table 1-2, the ester, anhydride and acid forms of 3,3',4,4'-benzophenone tetracarboxylic acid are shown. The end polymer resulting from these starting materials would be the same, but each would yield a different side product from the first step of the reaction, which forms the polyamic acid.

Polyamic acids are stable and useful to industry. Some Polyimides are sold as a varnish which is actually a 15-50% resin content polyamic acid in solution. Solvents frequently used in polyimide chemistry are presented in Table 1-4 with their properties. These varnishes are used form films and coatings. They are also used in Prepregging operations to coat fibers. The varnish is sier to handle with the solvent lowering the viscosity of polyamic acid.

Another intermediate form useful to industry is the yisoimide form.<sup>7</sup> National Starch and Chemical markets ermid IP-600, a polyisoimide powder.<sup>8</sup> This allows a eater availability of the reaction site for solubility in mon solvents. The structure of a polyisoimide is shown Figure 1-2. The specific chemistry of Thermid IP-600 il be discussed further in Section 1.14.

The polyamic acid undergoes further reaction with the

Ta
3
3
3
Py

Monomer	Structure
3,3',4,4' benzophenone- tetracarboxylic acid	
Dianhydride of 3,3',4,4' benzophenone- tetracarboxylic acid	
Diethyl ester of 3,3',4,4' benzophenone- tetracarboxylic acid (BTDE)	
₽yromellitic dianhydride (PMDA)	

# Table 1-2. Carboxylic Acids/Dianhydrides/Esters Used as Starting Materials in the Formation of Polyimides

Table	1-3.	Diamines	Used	in	the	Formation	of	Pol	yimid	les
-------	------	----------	------	----	-----	-----------	----	-----	-------	-----

DIAMINE	STRUCTURE
diamino benzophenone	
1,3 bis (3-amino- phenoxy) benzene (ABP)	<sup>4</sup> <sup>4</sup> O <sup>4</sup> O <sup>4</sup> O <sup>-#</sup>
4,4' -methylenedianiline (MDA)	H <sub>2</sub> N-()-CH <sub>2</sub> -()-NH <sub>2</sub>
p-phenylenediamine (PPDA)	H <sub>2</sub> N-()-NH <sub>2</sub>
3,3'-diaminophenyl- sulfone (3,3'-DDS)	H <sub>2</sub> N-0-50 <sub>2</sub> -0-WH <sub>2</sub>
 1,3-bis(4-amino-phenoxy- 4'benzoyl) benzene (1,3-BABB)	₩ <u></u> ₩
3,3'-diaminobenzidine	

Table 1-4. Common Solvents Used with Polyimides

Γ	SOLVENT AND PROPERTIES	STRUCTURE
	Diglyme FW 134.18 bp 162°C	Н Н Н Н Н               H-C-O-C-C-O-C-C-H               H Н Н Н Н
	1-Methyl-2-pyrrolidi- none (NMP) FW 99.13 bp 202°C	
	N,N-Dimethylacetamide FW 115.18 bp 164.5-166 <sup>0</sup> C	OCH3 III CH3-C-N-CH3
	Dimethyl sulfoxide FW 78.13 bp 189°C	0 II H <sub>3</sub> C-S-CH <sub>3</sub>
	N,N-dimethylformamide FW 73.09 bp 149-156 <sup>°</sup> C	о Н <sub>3</sub> С-N-СН <sub>3</sub> СН <sub>3</sub>
	Tetrahydrofuran FW 72.11 bp 67°C	





Figure 1-2. The structures of (A) polyimide and (B) polyisoimide.

remaining carboxylic group and the hydrogen on the primary amine to form the imide ring. This step of the process is called imidization. Higher than ambient temperatures are required for this reaction. The temperature range is dependent upon the polyimide formed. It is important to note that the imidization is also associated with the evolution of side-products such as water or alcohols for condensation polyimides. The temperatures attained also may cause the evaporation of solvents in the reaction systems as the imidization occurs.

Solution imidization is the most common form of reaction of the polyimides, but a melt imidization is also possible. The melt polymerization is possible only for crystalline materials and must occur within a temperature window. The reaction must be carried out above the melting temperature of the material and below the decomposition temperature. The presence of volatiles may also present a problem to this processing.

Cross-linking of the structures occurs at even higher temperatures than the imidization. Different polymers and their proposed cross-linking structures have been investigated.<sup>2</sup> Ring-opening occurs within the molecular chain around the nitrogen in the polyimide. The crosslinking of Thermid 600 was studied by magic angle NMR with proposed structures evaluated to determine which of the structures were most plausible.<sup>9</sup> High temperatures are required for the cross-linking of polyimides and pressure is

used to reduce microcracking. If side products or solvents are trapped within the polyimide, the volatile could cause stresses within the polyimide and lead to microcracking.

The processing of the materials is made very difficult by the required conditions of the reactions. The polyimides have a high thermal stability because of the aromatic structures within the backbones of their molecular chains. Temperatures above 300°C are typically required to process polyimides and achieve the desired high-temperature properties. The temperatures for processing are higher than the temperatures required for epoxy materials because the polyimides have higher glass transition temperatures and use temperatures. Special bagging and layup materials must be used since these temperatures exceed the capabilities of the materials used for epoxy curing.<sup>2</sup> The shrinkage of the polyimide during processing gives rise to internal stresses and microcracking. Some condensation polyimides require processing temperatures up to 371°C for their best properties, which exceed the capabilities of nonspecialized autoclaves that were designed for epoxy resins.<sup>6</sup>

The presence of solvents is by far the largest complication faced in the processing of polyimides. The high temperatures required for processing combines with the evolution of volatiles to increase the times of the processing of the materials. Processing cycles begin at lower temperatures and increase the temperature slowly to prevent the entrapment of the volatiles. Long holds at temperatures

allow for the minimization of stresses and voids within the material. Internal stresses are a severe problem for polyimides if the volatiles are not removed, and the long, slow process cycles were developed to reduce this.

The complicated processing cycles at high temperatures and pressure become a tradeoff between the application of polyimides' advantageous properties and the economics of the processing. Postcures greater than ten hours at high temperatures are common. The recommended processing cycles for a polyimide/graphite composite marketed by Ferro Corporation as CPI-2249 are shown in Figure 1-3 for processing at 15 psi and in Figure 1-4 for processing at 250 psi.<sup>10</sup> From Figure 1-3, the low-pressure cure and postcure cycle requires 8 hours of processing with the temperature "stepped up" in discrete intervillous. The high-pressure cure also requires the holds at intermediate temperature on the way up to the final cure temperature. The cure and postcure cycle require 17.5 hours of process time. A slow heating rate is used because the solvent must be given time to escape before the outer layers of the material are allowed to harden. The heating rates of the processing are crucial to the removal of the solvent from the material. Yang et al.<sup>11</sup> studied the removal of solvents from polyimide composites and found that solvent removal can be limited by the heating rate of the processing. If the heating rate is too great, the solvent may be trapped within the composite part.



Figure 1-3. The temperature cycle for the recommended cure and postcure of CPI-2249/glass composites at 15 psi.



Figure 1-4. The temperature cycle for the recommended cure and postcure of CPI-2249/glass composites at 250 psi.

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#### 1.12 Solvent Interaction

The presence of solvents in polymers during processing serves different purposes. The solvent aids in the handling of the material by lowering the viscosity for prepregging operations.<sup>12</sup> Solvents also play a role in the chemical interactions and transformations during the reactions in the polymer during processing.

The solvents form complexes with the polyamic acids in solution.<sup>13</sup> Hydrogen bonding within the materials has been offered as the explanation for the formation of these complexes. Amines also have been found to form precipitates with polyamic acids.<sup>14</sup> Precipitates of polyamic acids with water have been found to form. Feger<sup>15</sup> studied the curing of polyimide films and reported that solvent interactions precede the formation of the imide. Before imide formation begins, a 1/4 solvent/molecular unit complex decomplexes to a 1/2 complex which also decomplexes. The decomplexation is followed by plasticization of the polyimide before any imide formation is formed. By laser interferometry and TGA, Feger and Brekner<sup>16</sup> determined that polyimide films retain solvent even after the completion of imide formation.

Solvents act as plasticizers during processing. The solvent acts to soften the material during processing and allows more mobility for the molecules.<sup>17</sup> The TGA studies by Feger and Brekner concluded that solvent loss is impeded by the degree of cure during imidization.<sup>16</sup> Yang et al.

found that heating rates played a very important part in the removal of the solvent.<sup>11</sup> The heating rate has to be optimized to best influence the properties of the polyimide, which leads to the long, controlled processing cycles.

Feger studied the role of the solvent and the side products of the imidization reactions.<sup>15</sup> As the solvent is freed from the complexes, it plasticizes the polyimide and increases the mobility of the molecular chains. The imidization reaction is increased by the greater mobility, and a tradeoff arises from this. A fast heating rate may remove the solvent to quickly from the polymer, and the lack of chain mobility may slow down or inhibit the reaction. If the heating rate is too slow, the solvent and the side product are not freed to plasticize the polymer. The solvent provides an enhancement for the kinetics and the handling of the polyimides, but the presence of the solvent also give rise to complications in the processing.

## **1**-13 LARC-TPI

LARC-TPI is a linear, thermoplastic polyimide developed at NASA research center in Langley. The name itself is an acronym for Langley Research Center Thermoplastic PolyImide.<sup>18</sup> The material is formed from the reaction of 3.3' -benzophenone tetracarboxylic dianhydride (BTDA) and 3.3' -diamino benzophenone (DABP) to form the polyamic acid. The polyamic acid follows the reaction scheme detailed earlier for polyimides. Figure 1-5 shows the reaction Scheme for LARC-TPI formation beginning with BTDA and DABP.





3,3' -diamino benzophenone

H\_O



Polyamic Acid





LARC-TPI

Figure 1-5. The series of reactions forming LARC-TPI from starting materials.

LARC-TPI was developed as a candidate material for aerospace applications. Applications that have been tested by different researchers are as an adhesive, a thin film, a molding powder, and a composite matrix material.<sup>18,19</sup>

LARC-TPI exhibits high thermal stability while also possessing some characteristics of a thermoplastic due to the flexibility introduced by the meta-substituted diamines in its structure.<sup>18</sup> Mitsui Toatsu Chemicals, which markets LARC-TPI as a molding powder and a varnish, reported a glass transition temperature of  $260^{\circ}$ C and a decomposition temperature greater than  $500^{\circ}$ C  $^{20,21}$ . The polyamic acid is dissolved in a polar solvent, and Mitsui Toatsu sells a 30% resin solution of LARC-TPI polyamic acid in diglyme as its varnish. LARC-TPI has been studied in the form of thin films cast on potassium bromide plates by Frayer,<sup>22</sup> and a model was developed for the reaction rate of LARC-TPI. The model of the reaction is a first order model<sup>11,22</sup> with the rate constant calculated by Frayer's equations.

$$\frac{-dC_{\lambda}}{dt} = K_{r}C_{\lambda}$$
 (1-1)

where  $C_A$  = concentration of the active groups in the monomer and polymer

A model was proposed for the reaction rate constant  $K_R$  which is defined:

$$\ln K_r = A_0 + A_1 \ln t + A_2 / T$$
 (1-2)
where 
$$A_o = \ln (60 \text{ ekT/h}) = 31.2113$$
,  $\ln \min^{-1}$   
 $A_1 = \Delta S / R \ln t = -0.7555$ ,  $\ln \min^{-1}$   
 $A_2 = -E_a/R = -14.25 \times 10^3$ , K  
 $R = 8.3143 \text{ J/mol K} = \text{gas constant}$   
 $E_a = 118.5 \text{ kJ/mol} = \text{activation energy}$   
 $t = time$ , min  
 $\Delta S = \text{change of molar entropy of activation}$   
 $K_r = \text{reaction rate constant, min}^{-1}$   
 $T = \text{absolute temperature, K}$ 

The removal of the volatiles, mostly the solvent, affects the reaction and is affected by the reaction of the polyamic acid. Frayer found that hydrogen bonds and solvent interaction affected solvent loss as well as the formation rate of the imide rings.<sup>22</sup> Frayer found that the solvent diffusion activation energy was affected by different processes within the sample. Polymer-solvent interaction is the dominant factor just above  $T_g$  while polymer chain mobility is dominant just below  $T_g$ . The solvent-polymer relationship is very crucial to understanding the kinetics of LARC-TPI, and a full explanation of these interactions has yet to be determined.

### 1.14 Thermid Materials

An approach to the problems of processing with volatiles present has been the development of addition polyimides. These materials do not react by the formation of a condensation product. Functional groups are attached to the end of the polymer chains which carry out crosslinking reactions without the formation of condensation side





longer-chain versions of the polyisoimide form. The materials have an increased solubility which can facilitate the casting of polyimide films. Thermid IP-600 is appropriate for use as a molding compound with processing cycles requiring high temperatures and pressures to form void-free parts. The structures are shown in Figure 1-6c.

Thermid MC-600 is a fully-imidized molding powder. The imide ring is already closed, which decreases the solubility of the material in solvent. Its structure is shown in Figure 1-6a. Thermid MC-600 is the tradename used by National Starch and Chemical, but Gulf Oil has also marketed it under the name Thermid 600. This form of the polyimide is also used as a molding powder requiring high temperatures and pressure for good mechanical parts. The cross-linking reactions were studied by Sefcik et al.<sup>9</sup>, and proposed mechanisms yielded the structures shown in Figure 1-7. They concluded that the cross-linking occurred during cure and post-cure heatings with addition reactions involving the acetylene group being the site of these reactions.

Thermid LR-600 is the polyamic acid precursor of Thermid MC-600 dissolved in N-methyl pyrrolidone.<sup>23</sup> The solution is supplied as a 50% by weight solids solution which may be used for the applications listed before for polyamic acids. Thermid AL-600 contains the monomer mixtures dissolved in ethanol.<sup>24</sup> The solution is 75% by weight solids. The varnishes are useful for making prepregs or coatings, but they lack the neatness of the powders due









Figure 1-7. The possible cross-linking structures for Thermid MC-600.

to the presence of the solvents.

## **1.2 MICROWAVE PROCESSING**

Microwave heating has been used for many applications such as heating food, paper drying, and biomedical research.<sup>25,26</sup> The heating process is initiated by the placement of a material in an electromagnetic field. In the case of polymer materials, the dipoles of the molecules align themselves with the electric field, and the rotation of the dipoles causes a molecular friction within the dipoles. The resulting friction causes heating by the conversion of power of the electric field to heat. The heating occurs within the molecules, which leads to advantages of microwave heating over conventional heating in the processing of materials.

The conversion of the microwave energy to heat is characterized by a material's dielectric loss factor. For materials with too low a dielectric loss factor value, microwave heating is not impossible, but the process is made more difficult. The power or the time required to heat a material is increased as the dielectric loss decreases. Ku and Liepin<sup>27</sup> compared the times required for heating different materials by ratios of their dielectric properties. Teflon is a good example of a material with a low dielectric loss. It has an  $\epsilon$ " of 0.0004, while epoxy materials have been used in past processing experiments had an  $\epsilon$ " of 0.03.<sup>28,29</sup> The values of  $\epsilon$ " are typically reported for frequencies lower than the frequency used for

Table	1-5.	The D	ielectri	ic Proper	ties (	of Poly	yimides
						_	

Polyimide	Т (°С)	f (Hz)	٤'	٤"	tan δ
Skygard 700 <sup>30</sup>	25	10 <sup>3</sup>	4.10	0.00445	
KAPTON H <sup>30</sup>	25 200	10 <sup>3</sup>	3.5 3.0	0.003	
LARC-TPI <sup>4</sup>		60 10 <sup>6</sup>	2.7	0.003	
<b>CPI-2249</b> <sup>10</sup>		1 mc	4.1	0.00445	
CPI-2214 <sup>31</sup>		10 <sup>6</sup>	4.64	0.0032	
Thermid MC-600 <sup>32</sup>		10 <sup>5</sup> 10 <sup>6</sup> 10 <sup>7</sup>	3.38 3.36 3.33		0.00654 0.00643 0.00493
<b>Ultem 1000<sup>33</sup></b>		10 <sup>3</sup>	3.15	0.001	
<b>Ultem 5000<sup>33</sup></b>		10 <sup>3</sup>	2.92	0.001	
<b>Ultem 6000<sup>33</sup></b>		10 <sup>3</sup>	3.00	0.001	
U-60 <sup>34</sup>		10 <sup>3</sup> 10 <sup>4</sup> 10 <sup>5</sup>	3.3 3.3 3.2	0.000 0.003 0.034	

microwave heating devices. The values are reported for different polyimide materials in Table 1-5.

Conductive materials interact strongly with the electromagnetic fields. The electric fields set up a surface current across the surface of the conductive materials. The ratio of  $\epsilon''$  to  $\epsilon'$  defines the loss tangent as:

$$\tan \delta = \frac{e''}{e'} = \frac{\sigma}{\omega e}$$
 (1-3)

where 
$$\sigma$$
 = conductivity of the material, (siemens/m)  
 $\omega$  = angular frequency =  $2\pi$ (frequency), (rad/sec)  
 $\epsilon$  = permittivity, (Farad/m)

A material is considered a good material if  $\sigma >> \omega \epsilon$ . If the material is a good conductor, the value of the dielectric loss factor can be seen to be large for conductors.<sup>35</sup>

The difference in the application of energy between microwave heating and conventional heating results from the method of the delivery of the heat to the material. A conventional oven heats a material by conduction and convection. Heat is applied to the outside of the material and is conducted to the inside. This could set up thermal gradients within the material. For polymer and composite processing, the outer skin of the material may cure faster, forming an outside seal on the material. If side products of the reaction or solvents are present in the material, the reaction of the outer regions of the material will form a barrier and trap the volatiles. This leads to the formation of voids within the material. The voids decrease the mechanical properties of polymers and composites.

Microwave heating, however, applies the energy directly to the material. The higher temperatures may therefore be on the inside of the material. The "inside-out" heating of the material may decrease the entrapment of volatiles. The mechanical properties of the material may also be enhanced by the outer boundary being less reacted and less rigid than the inside. A better consolidation of the part may result, or a reduced pressure for processing may be required.

A better-controlled temperature profile can also be attained by microwave heating. The direct application of microwave heating to the materials allows for the elimination of temperature excursions for exothermic reactions. Processing temperatures may therefore be pushed to the upper limits without degrading the material.  $Jow^{29}$  demonstrated this by reacting epoxy samples by both thermal and microwave methods. The microwave system compensated better for the reaction exotherm than the thermal system, so the temperature overshoot was greater for the thermal processing. The microwave supplies as much power as is necessary to heat the sample to its processing temperature. An endothermic reaction could also be compensated for by supplying more power to prevent a drop in temperature.

The polyimides shown in Table 1-5 are not lossy enough to be promising candidates for microwave processing in their

pure form. The processing of composites, however, can be made possible by the addition of fibers or powders which are lossy materials. Graphite is a conductor and very lossy in a microwave environment, so the addition of graphite fibers will provide a conduit for transferring the heat into the material. The composite may be pictured as adding heating coils within the material. The mechanical properties of the materials should be affected for two reasons. For a polyimide composite, the "inside-out" heating should be advantageous because it would prevent the formation of the outer skin. The second possible effect would be the concentration of the heat for the reaction at the fiber-matrix interface.

Work performed at Michigan State University has found significant changes in the interface region of polymers processed by microwave methods. The epoxy and amine constituents DGEBA and m-PDA were heated with AS4 graphite fiber separately by thermal and microwave methods. Oxygen content was measured by X-ray photoelectron spectroscopy on the fiber before and after heating by microwave and thermal methods. The microwaved samples were found to be more fully reacted by a significant amount.<sup>36</sup>

Not only may reaction pathways change, but also the extent of reaction is affected. Work with polyesters and polycarbonates at Michigan State University has found the extent of reactions to be higher for microwave processing than thermal processing at a given temperature.<sup>37,38</sup>

Microwave processing offers advantages in the area of

kinetics. Faster reactions have been reported by the direct application of the energy to the reactive sites of materials. Molecular "hot spots" have been reported where the reaction is many times faster than the observed reaction during conventional processing.<sup>39</sup> Wei, DeLong, and Hawley<sup>40</sup> studied thin film reactions of epoxy and found the microwave cure to be faster, but not to the extent as earlier reported at Virginia Polytechnic Institute. The reactions of polyamic acids in solutions have also been reported as enhanced by Virginia Polytechnic Institute.<sup>41,42</sup>

#### CHAPTER 2

#### DIELECTRIC MEASUREMENTS

The resonant microwave cavity may be used to measure the dielectric properties of materials placed within it. As stated before, the dielectric permittivity of a material may be expressed as :

$$\boldsymbol{\epsilon} = \boldsymbol{\epsilon}' - \boldsymbol{j} \boldsymbol{\epsilon}'' \tag{2-1}$$

where  $\epsilon$  is the complex dielectric permittivity expressed with a real part  $\epsilon'$  and an imaginary part  $\epsilon''$ . The real part quantifies the ability of the material to store microwaves. The positive portions of the molecules of the dielectric migrate in the direction of the electric field while the negative portions move against the field. Because the dielectric is nonconducting, these charges are fixed with the molecules. The charge carriers could move across molecules if the material were a conducting material. The imaginary part accounts for the failure of the dipoles of the material align themselves immediately to the electric field. The dipoles cannot keep up with the microwave energy, and as they continue to reorient themselves, there

is a lag and an associated power loss. The microwave energy is lost in the form of heat, and  $\epsilon''$  is therefore called the dielectric loss factor.<sup>27</sup>

Equations may be derived which, with the proper measurements, may be used to calculate the dielectric properties of a material in a microwave cavity. One method of measurement uses an oscilloscope and a sweeping frequency source. The disturbance of the resonant frequency is measured by a power absorption curve on the oscilloscope. The oscilloscope presents a picture of the mode by displaying the frequency of the signal as the x-axis and the power absorbed by the cavity as the y-axis. Jow outlined all of the necessary equations for the measurement of the dielectric properties of material in a cylinder in a  $TM_{012}$ mode.<sup>29</sup> The determination of the dielectric constants requires some approximations. One is that the volume of the sample is negligible when compared to the volume of the cavity. Another is that the disturbances within the cavity are not enough to disrupt the field patterns to the point that the field patterns no longer match those of the empty cavity.

An oscilloscope is used to display the microwave power versus the frequency in the cavity. A picture of the pattern is shown in Figure 2-1. The pattern resembles a parabolic curve, and the cavity is perfectly tuned when the height of the peak is maximized. As the peak reaches 100% absorption, the reflected power is minimized. The shape of



Figure 2-1. The oscilloscope pattern of the  $TM_{012}$  mode of a microwave cavity tuned to  $f_0$ .



Figure 2-2. The measurement of  $\Delta f$  for the calculation of Q factor from the oscilloscope pattern indicating the operating mode.

the curve is used to evaluate the cavity. The bandwidth of the curve at half the height of the peak, denoted  $\Delta f$  and shown in Figure 2-2, is used to calculate the Q factor of the cavity by the equation<sup>43</sup>:

$$Q = \frac{2f}{\Delta f} \tag{2-2}$$

The Q factor is the ratio of the power absorbed by the cavity to the power lost or dissipated by the cavity. This is directly affected by the cavity conditions and the frequency at which the cavity is operated.

The resonant frequency, also pictured in Figure 2-2, is the frequency at which the maximum amount of power is delivered to the cavity and the minimum amount of the power is lost. For heating in the  $TM_{012}$  mode, a cylindrical sample is suspended in the center of the microwave cavity. Figure 2-3 depicts the loaded cavity. The electric field of the cavity in cylindrical coordinates is found to be<sup>29</sup>:

$$E_{\rho} = \frac{1}{j\omega e} (X_{01}/R_c) (2\pi/L_c) J'_0 (X_{01}\rho/R_c) \sin(2\pi z/L_c)$$
(2-3a)

$$E_{\phi} = 0 \tag{2-3b}$$

$$E_{z} = \frac{1}{j\omega e} (X_{01}/R_{c})^{2} J_{0} (X_{01}\rho/R_{c}) \cos(2\pi z/L_{c})$$
(2-3c)

The cylindrical coordinates are  $\rho$ , z, and  $\phi$ . The cavity radius and length are R<sub>c</sub> and L<sub>c</sub>, respectively. The zero order Bessel function and its derivative are  $J_0$  and  $J_0'$ , and  $X_{01}$  is the solution to the Bessel function. The angular frequency is  $\omega$ .

The introduction of the sample to the empty cavity disrupts the electromagnetic fields. This results in a shift in the oscilloscope peak to a new frequency and a



Figure 2-3. The loading of a cylindrical sample into the microwave cavity for dielectric measurements in the  $TM_{012}$  mode.



Figure 2-4. The measurements  $f_0$  and  $\Delta f_c$  for the empty cavity peak, and  $f_L$ ,  $\Delta f_L$ , and df for the peak shifted by the loading of a sample.

different shape, as shown in Figure 2-4. This difference between the new frequency and the unloaded frequency is denoted df, and it is used in the calculation of the dielectric constant  $\epsilon'$ . The change in shape of the peak is also important because a new  $\Delta f$  is measured across the halfheight of the peak. This new  $\Delta f$  is used to calculate the loaded cavity  $Q_g$ . The empty cavity Q and the loaded cavity  $Q_g$  are used to calculate the dielectric loss factor  $\epsilon''$  by the equation:

$$\frac{1}{2Q_s} - \frac{1}{2Q_0} = e^{\prime\prime} ABG \frac{V_s}{V_c}$$
(2-4)

The dielectric constant  $\epsilon'$  may be calculated by the equation:

$$\frac{df}{f_0} = (e' - 1) ABG \frac{V_g}{V_c}$$
 (2-5)

#### where

 $Q_{g} = \text{the } Q \text{ factor of the loaded cavity}$   $Q_{0} = \text{the } Q \text{ factor of the empty cavity}$   $f_{0} = \text{the resonant frequency of the unloaded cavity}$   $f_{g} = \text{the frequency of the loaded cavity}$   $df = f_{0} - f_{g}$   $A = J_{0}(2.405R_{g}/R_{c})^{2} + J_{1}(2.405R_{g}/R_{c})^{2}$   $B = 1 + [L_{c}/2\pi L_{g}]\sin(2\pi L_{g}/L_{c})\cos(4\pi H/L_{c})$   $G = 0.2718 [v_{0}/(f_{0}R_{c})]^{2}$   $v_{0} = \text{the speed of light}$   $V_{c} = \text{the volume of the sample}$   $V_{c} = \text{the length of the sample}$   $L_{c} = \text{the length of the cavity}$   $R_{g} = \text{the radius of the cavity}$   $R_{c} = \text{the radius of the cavity}$ 

These equations also appear in Appendix A in an explanation of the calculations performed by a computer program in the measurement of the dielectric properties of powder samples. Jow<sup>29</sup> developed these equations for the measurement of the dielectric properties of samples by the perturbation method.

On-line dielectric measurements can be made during processing. The calculations require the measurement of the electric field strength, preferably at its strongest point. The measured electric field strength is a power reading designated as  $P_b$ . This reading is used along with the measured input power  $P_I$  and the reflected power  $P_R$  to define a cavity constant K. The constant K is defined to be:

$$K = \frac{P_b}{P_I - P_R}$$
(2-6)

Any changes in the cavity constant are considered to be proportional to changes in the cavity's Q. By measuring the cavity's initial K and Q, the online measurement of the different powers may be used to calculate the Q of the cavity during processing. The ratio is

$$\frac{K}{K_0} = \frac{Q}{Q_0} \tag{2-7}$$

where the subscript 0 denotes the initial K and Q of the loaded cavity. An assumption of little volume change and small variations in the frequency and cavity tuning are necessary for these calculations to be valid. The dielectric loss factor may be calculated by this method. This is important because a measure of the dielectric loss factor not only reflects the microwavable nature of the material, but also the extent of reaction. As cross-linking and polymerization occur, the dipoles are not as free to rotate, so the dielectric loss factor decreases with increasing cure. On-line diagnosis of the extent of reaction has been used to monitor the cure of polymers.<sup>44</sup>

The dielectric properties of the polymers also vary with temperature. In general, the dielectric loss factor will go through peaks as the temperature is varied. The polymer structure itself goes through transitions due to increasing temperature, and the dielectric loss factor will also go through transitions. As the temperature is increased, the dielectric loss factor will also increase due to greater mobility of the molecules within the particular region (peak) of the dielectric loss. At some temperature, however, the dielectric loss factor will fall with temperature increase if the temperature lies on the downside of one of the transition peaks.<sup>27</sup>

#### CHAPTER 3

### DIELECTRIC PROPERTY MEASUREMENTS AND MICROWAVE HEATING CHARACTERISTICS OF POLYIMIDE POWDERS

## 3.1 EXPERIMENTS

The dielectric constants and loss factors of polyimide powders were measured with the method described by Chapter 2 and Appendix A. Microwave heating of the powders was also attempted using high power in the TM<sub>012</sub> mode. The characteristics of the microwave heating were compared the results of thermal analysis of the powders. Thermid IP-600, Thermid MC-600, Thermid IP-6010, Thermid IP-6015, and Thermid FA-7001 were received for testing from National Starch and Chemicals. LARC-TPI was received from Mitsui Toatsu.

The powders were loaded into Teflon cylinders with outer diameters of 0.51 inches and inner diameters of 0.375 inches and lengths of 1.62 inches. The cylinders were packed tightly to fill the holders. Dielectric measurements were made as described in Chapter 2. The 6-inch diameter microwave cavity was used in the  $TM_{012}$  mode at 2.45 GHz. The microwave setup is shown in Figure B-1 of Appendix B. The sweeping frequency generator provided the microwave fields in the cavity, and an oscilloscope displayed the

electric field patterns. Following the measurements of the field patterns, the data were input into the computer program DIEL.FOR to calculate the dielectric properties relative to the known values for Teflon ( $\epsilon' = 2.1$  and  $\epsilon'' = 0.00033$ ).

The equipment used for analysis is listed in Table B-3 of Appendix B. The powders were studied by differential scanning calorimetry (DSC) on a Dupont 910 Differential Scanning Calorimeter. THERMID IP-600 was studied to determine the temperatures at which the reactions would be initiated. The effect of varying the heating rate on the reaction exotherm was also studied. For reaction peak evaluations, samples were heated at 10°C/min to 450°C with a 50 cc/min stream of nitrogen as a purge. This method appeared often in literature.

Thermogravimetric analysis (TGA) was also run to determine the weight loss of the material due to solvent presence or side product evolution. The thermal degradation of the polyimide was also determined. A Dupont 951 Thermogravimetric Analyzer was used for these experiments. The sample was heated at  $10^{\circ}$ C/minute to  $600^{\circ}$ C with a 50 cc/min stream of nitrogen gas as a purge.

Microwave experiments were attempted to react the powders. The microwave system was powered by the Opthos source. The  $TM_{012}$  was selected to heat the powders in a cylindrical holder. The microwave system is displayed in Figure B-2 of Appendix B with the six-inch diameter

microwave cavity substituted for the seven-inch diameter microwave cavity. Attempts to heat different powders to sufficiently high temperatures were made. It was also attempted to heat the Thermid IP-600 by the addition of ground AS4 graphite fiber. The ground powder was added to the Thermid IP-600 powder in 10, 20 and 30% by weight mixtures and mixed in a mortar and pestle.

LARC-TPI molding powder was also received from Mitsui Toatsu. The powder was 99% imidized and 30% crystalline. Thermal analysis was performed to was performed to evaluate the properties of the powder. The dielectric properties were measured by the previously described methods.

# 3.2 RESULTS AND DISCUSSION

# 3.21 Thermid Materials

The results of the dielectric measurements for the powders is presented in Table 3-1. The dielectric loss factors measured for the powders were too low for them to be heated efficiently by the microwave method. The precision of the calculated values may not be reliable as absolute values, but the magnitudes are significant. The introduction of error into the absolute value of the materials begins with the method itself. A slight change in the bandwidth measurement with the oscilloscope and the sweeping frequency generator changed the value of the Q factor by over 10% in some cases. The precision of the sweeping frequency generator was within 0.01 MHz.

The values for the dielectric loss factors were lower

Polyimide Powder	Dielectric Constant $\epsilon'$	Dielectric Loss Factor $\epsilon''$
Thermid IP-600	1.7	0.00095
Thermid MC-600	1.7	0.00023
Thermid IP-6010	1.9	0.00100
Thermid IP-6015	1.8	0.00057
Thermid FA-7001	1.8	0.00022
LARC-TPI	1.9	0.00030

# Table 3-1. Measured Dielectric Properties of PolyimidePowders

for Thermid MC-600 and LARC-TPI (see Table 1-5) than the values reported in the literature. The dielectric loss constant of Thermid MC-600 was reported as approximately 0.0164 at 10 MHz. The dielectric loss constant of LARC-TPI was reported as 0.003 at 1 MHz. The calculated dielectric loss factors for Thermid MC-600 and LARC-TPI powders were 0.00023 and 0.00030. The lower values for the powdered samples were consistent with theory. The powdered samples contained both the polyimide molding powders and air. While tight packing of the sample was attempted, the presence of the air was a factor as far as the measurement of the dielectric properties of the materials.

Despite the attempts to tightly pack the materials, the densities of the powders were still lower than the densities of the solid materials. The literature values were reported for the solid materials (in the form of a film). The lower values for the powders are consistent with models developed to predict the dielectric properties of solids from measurements of the dielectric properties of granulated samples. Nelson<sup>45</sup> evaluated different models which relate the values of  $\epsilon'$  and  $\epsilon''$  to the density of the material. Linear regression and extrapolation were used to calculate the dielectric properties. The models listed predict that the less dense the materials, the lower the dielectric properties.

The numbers calculated for the materials should be designated as the properties of the powders, and not considered the values for the solid samples. As far as testing the feasibility of the microwave heating, however, the values are practical. The measured dielectric properties of the powdered samples are more indicative of the state of the material as it would appear during processing in the microwave applicator.

The long chains of the molecules are too rigid and lack dipoles to easily accommodate heating by microwaves. Despite the presence of oxygen atoms, the bonds in the Thermid materials hinder the rotation of the atoms to convert electromagnetic energy to heat by the realignment of the dipoles. The long structures of the chains may also sufficiently separate the possible dipole sites from the reaction sites to inhibit any beneficial effects of microwave heating from a kinetic standpoint.





The results of the DSC analysis of Thermid IP-600 appear in Figure 3-1. This sample was heated to 450°C at a rate of 10°C/min. The heat of reaction occurs at an elevated temperature across a broad range of temperatures starting at 130°C and ending at 340°C. Two peaks appear together because two reactions occur almost simultaneously in the DSC. The first peak is a rearrangement of the polyisoimide structure - possibly a ring closure to form the polyimide form. The second peak is the cross-linking reaction that was discussed earlier for Thermid MC-600.<sup>46</sup> The exotherm of the reaction varied with the heating rate. Table 3-2 summarizes the reaction exotherms of Thermid IP-600 at different heating rates. The peak temperature is the temperature at which the maximum of the reaction exotherm occurs in the DSC thermogram.

The exotherms of the Thermid IP-600 were used to extrapolate the reaction exotherm for a heating rate of  $0^{\circ}$ C/min. The data point at  $20^{\circ}$ C/min was not used in the calculation of the exotherm for a  $0^{\circ}$ C/min heating rate. The exotherm for  $20^{\circ}$ C/min appears to be greater than the actual value should be. The other three heating rates and exotherms formed a line with a linear regression constant of -0.99. Figure 3-2 shows the extrapolation of the  $0^{\circ}$ C/min heating rate from the data.

The DSC results for Thermid MC-600 were consistent with the results for Thermid IP-600. The first peak of the Thermid IP-600 scan, the "rearrangement" peak, was greatly

Heating Rate, (°C/min)	Peak Tempera- ture, ( <sup>o</sup> C)	Reaction Exotherm, (J/g)
0 (extrapolated)	-	403.6
2	204.78	384.5
5	236.91	368.4
10	242.86	321.5
20	253.50	320.2

Table 3-2. The Reaction Exotherm for Thermid IP-600 Measured by DSC At Different Heating Rates



Figure 3-2. The extrapolation of the exotherm for Thermid IP-600 at  $0^{\circ}$  C/min.





reduced. This left a much larger peak (relatively speaking) for the second reaction peak, the "cross-linking" peak. Some polyisoimide groups are present in the Thermid MC-600, but the polyimide group is the most abundant. A reduction in exotherm also accompanied the change in structure. The DSC thermogram is shown in Figure 3-3. The bulk of the reaction occurred over a temperature range of 200°C to 350°C with the exotherm peak at 259.92°C.

A Teflon holder containing Thermid IP-600 was placed in the microwave cavity. The microwave heating of these materials was not promising because Thermid IP-600 failed to heat. The temperature profile for the microwave heating of Thermid IP-600 appears in Figure 3-4. As can be seen, the Thermid IP-600 was not heated to temperatures anywhere near the level needed to initiate the reaction. The maximum temperature recorded was approximately 75°C, and this temperature did not correspond to any reaction peaks in the DSC thermograms. Heating the powder by the microwave cavity was not feasible with the microwave apparatus available. The material could heat if enough power were supplied to the system, but this experiment applied 60 Watts and no apparent reaction occurred within a reasonable time.

A repeat trial with the Thermid IP-600 was run, and the temperature profile was much different. The sample heated to a temperature of 220°C. The sample, however, was uncured except for the material in contact with the Pyrex temperature probe cover. The Pyrex tube was more lossy than

the polyisoimide material. This run further illustrated the lossless nature of the polyimide. A run to test the holder materials was performed. Figure 3-5 presents the heating of a Teflon cylinder without a temperature probe cover inserted, the heating of a Teflon cylinder with a Pyrex capillary tube inserted, and the heating of a Teflon cylinder with a quartz capillary tube inserted. Clearly, the quartz was better suited for experiments with polyimides.

Although the heating of the Pyrex tube was not desired for these experiments, the curing of the Thermid IP-600 in contact with the tube was useful. The processing of composites could be performed by selecting a lossy fiber in the center of the polyimide. The selectivity of the microwave energy was illustrated by the reaction of the Thermid IP-600 in contact with the Pyrex and the lack of reaction of the Thermid IP-600 in the outer portions of the holder. Composite processing for polymers should also proceed in the same manner if the fiber is a material more lossy than the polyimide. The diffusion of the solvent in a composite away from the fiber would be improved by this direction of the heating.

Since the polyimide materials would not heat by themselves in the microwave cavity, the microwave heating of Thermid IP-600 was attempted with ground AS4 fibers mixed with the Thermid IP-600. It was highly successful. Heating



Figure 3-4. The temperature profile for the microwave heating of unreacted Thermid IP-600.



Figure 3-5. Comparison of microwave heating of different holder materials and temperature probe covers.

was carried out with 10, 20 and 30% by weight AS4 fibers. The samples were easily maintained at 250°C. Figure 3-6 displays the temperature profiles of the heatings at 0, 10, 20, and 30 % by weight AS4 powder. The polyimide/graphite mixtures heated easily since the graphite acted as a conduit to focus the microwave energy into the samples. The processing of polyimide composites is possible, but only if the proper reinforcement material is used to absorb the microwave energy and heat the material.

The power curve for the experiments with the graphite powder mixtures with THERMID IP-600 is shown in Figure 3-7. The power needed to maintain the sample at the high temperature is very small except in the case of the neat Thermid IP-600. The power requirement for graphite powder mixtures was not greatly reduced from the level of input power used with the neat Thermid IP-600 powder.

The loss factor of the 20% AS4 sample was measured during the microwave heating and shown in Figure 3-8. As expected, the loss factor leveled off at an average value of 0.25 after 45 minutes. The curve was extremely uneven during the heating, but this was due to the reaction occurring in the sample. The reflected power fluctuated during this time because the tuning of the cavity could not be performed quickly enough to minimize the reflected power. The changing dielectric properties and the shrinkage of the sample during the reaction caused these fluctuations.

A compression molding operation with the proper



Figure 3-6. The temperature profiles for the microwave heatings of Thermid IP-600 powder with 0, 10, 20, and 30 weight percent ground AS4 fiber.



Figure 3-7. The input power required to heat the Thermid IP-600/AS4 samples in Figure 3-5 in the microwave cavity.



Figure 3-8. The dielectric loss factor for a 20% AS4/80% Thermid IP-600 powder during microwave processing.

reinforcement and pressure application would be an avenue to explore if the system were not limited by the lack of pressure application. A graphite core would heat from the inside-out even though the pressure would be applied to the outside of the system. Microcracking is a problem with molding powders, and polyimides are brittle materials. The inside-out effect could be a big influence on the microcracking, but whether it would help or hinder is a question for future work.

The analysis of the samples was greatly hindered by the presence of the graphite fibers. The fiber interferes with the DSC analysis by disrupting the baseline in such a way that peaks are not recognizable as the same peaks for the neat powder. The unreacted materials may be analyzed, but the reacted materials exhibit peaks which could be interpreted as exothermic or endothermic transitions. FTIR analysis of the samples was also disrupted by the presence of the graphite, which would shift the baseline of the spectrum too much for analysis.

### 3.22 LARC-TPI Powder

LARC-TPI powder was also tested for its properties and evaluated for its feasibility for the microwave processing. Figure 3-9 depicts the DSC thermogram of LARC-TPI powder. The material was listed as 99% imidized by Mitsui Toatsu and 30% crystalline. The thermogram clearly shows a melting exotherm occurring at 290°C. Figure 3-10 shows the TGA results for the LARC-TPI powder. The sample shows a high


The DSC Thermogram for LARC-TPI powder. Figure 3-9.





thermal stability. At 520°C, the sample still had over 99% of its weight remaining.

The dielectric measurements for LARC-TPI found that its dielectric loss factor was much lower than the given literature values. Table 3-1 lists the loss factor as 0.00030, which is roughly equivalent to Teflon. An attempt to heat LARC-TPI powder resulted in no change to the powder. Given the results of the Thermid powder experiments, LARC-TPI was deemed as unfeasible for processing without some conduit for the microwave energy. Since the powder was fully imidized, there was no reaction to monitor as there was for the Thermid IP-600. Heating experiments were continued with different forms of LARC-TPI - polyamic acid solutions and graphite fiber composites.

#### CHAPTER 4

## MICROWAVE HEATING OF POLYAMIC ACIDS

# 4.1 EXPERIMENTAL

The microwave heating characteristics of LARC-TPI and Thermid LR-600 polyamic acid solutions were studied. The polyamic acids were received in solution with solvents. The materials were marketed as varnishes. Thermid LR-600 was received from National Starch and Chemical. This solution contains the polyamic acid which imidizes to Thermid IP-600 and Thermid MC-600. The material was received as 50% resin dissolved in 1-methyl-2-pyrrolidinone (NMP). The other polyamic acid received was LARC-TPI varnish from Mitsui Toatsu Chemicals, or MTC America, Inc. The varnish consisted of 28% resin content dissolved in diglyme.

The experiments consisted of heating the varnishes in the 6-inch diameter microwave cavity with the microwave system described in Appendix B. The  $TM_{012}$  mode was used for these applications. The holders were Teflon cylinders suspended in the center of the cavity by a string, as shown in Figure 2-3. A fluoroptic temperature probe was placed within a quartz capillary tube and inserted into the sample. Different temperatures and processing times were used for different experiments. Temperature and power profiles were

recorded by computer, and the data was saved by the DARPA software developed at Michigan State by Jow.<sup>47</sup>

For the LARC-TPI studies, thermal samples were prepared by heating LARC-TPI within the Blue M oven at the desired temperatures for the desired time intervals. LARC-TPI samples were studied by TGA to determine solvent content and thermal stability. Some samples were heated in bulk in the Teflon cylinders as described above, while others were heated in the  $TE_{111}$  mode by the thin film technique applied by Wei, DeLong, and Hawley.<sup>40</sup> FTIR analysis was attempted using the peaks appearing at 1780 and 715 cm<sup>-1</sup> as analyte peaks and the peak at 995 cm<sup>-1</sup> as a reference, as done in an earlier study by Frayer.<sup>22</sup>

### 4.2 RESULTS AND DISCUSSION

#### 4.21 Thermid LR-600

Thermid LR-600 was heated in the  $TM_{012}$  mode in the 6inch cavity. The sample heated easily, but the tuning of the cavity was difficult to maintain. The loss of solvent during the processing changed the dielectric properties and the volume of the sample. As the polyimide solidified, it expanded within the Teflon holder. Due to the failure of the microwave processing for the neat powders in Chapter 3, it was concluded that the heating occurred in the sample due to the presence of the solvent.

A second experiment was run with 1-methyl-2pyrrolidinone only in the Teflon holder. The NMP heated the same as the Thermid LR-600. The comparison of the tempera-

ture profiles is depicted in Figure 4-1. The heating curve of the NMP is the same as the curve for the Thermid LR-600 sample. The solvent was evaporating from the sample as the heating experiment progressed. At the beginning of the experiment, the Thermid LR-600 sample was a thick viscous liquid. After the microwave heating, it resembled a paste. The sample lost 35.4% of its weight during the experiment. Some of the solvent was visible on the bottom of the microwave cavity.

#### 4.22 LARC-TPI Heating in Bulk

LARC-TPI varnish was heated in the  $TM_{012}$  mode in cylindrical Teflon holders. Approximately 1 - 1.5 g samples were used to examine the heating characteristics of the samples. It was desired to reach temperatures above 250°C for evaluation of the reaction kinetics. The heating of the Thermid LR-600 demonstrated the loss of solvent by the polyamic acid solutions during the heating. The dielectric properties of the diglyme were measured, and  $\epsilon'$  and  $\epsilon''$  were found to be 5.5 and 0.18, respectively. As the cure proceeds, the sample is losing both volume and its "conduit" for focusing the microwave energy and converting it to heat.

A sample was heated for 30 minutes at  $100^{\circ}$ C and another half hour at  $150^{\circ}$ C, as shown in Figure 4-2. The loss factor during this heating is shown in Figure 4-3. As can be seen, the loss factor drops off significantly as the sample cures. The initial measurement of the loss factor by the swept frequency method found the dielectric loss factor to be



Figure 4-1. The temperature profiles for the microwave heatings of NMP for 10 minutes and Thermid LR-600 for 30 minutes.



Figure 4-2. The temperature profile for the microwave heating of a LARC-TPI varnish sample.



Figure 4-3. The loss factor of LARC-TPI varnish (polyamic acid) heated by the profile shown in Figure 4-2.

approximately 0.18 for the varnish. Fluctuation in the online processing measurement occurs because the cavity was detuned to maintain temperature control, but the trend is clearly shown.

Another sample was heated for an hour at 100°C followed by another 30 minutes at 200°C. The temperature profile is shown for this in Figure 4-4. The input power required to maintain the temperature is shown in Figure 4-5. The power required to maintain the sample at 200°C increased as solvent loss increased. An attempt to lower the power once the desired temperature was reached failed and resulted in a temperature drop. The heating could have continued until the sample was so deficient in solvent that the temperature could no longer be maintained. A fully cured sample of LARC-TPI requires heating at temperatures near 300°C, so a full cure was impossible under these constraints.

### 4.23 Analysis of Bulk LARC-TPI Samples

A TGA thermogram for unreacted LARC-TPI varnish is presented in Figure 4-6. The sample is thermally stable until approximately 550°C, which is consistent with the results for the fully imidized LARC-TPI powder. The analysis of samples after processing was made difficult by the tendency of the sample to absorb water from its surroundings. FTIR was attempted on the samples with the Diffuse Reflectance technique, but the results were inconsistent and contradictory. The presence of water in the samples or possible advancement of the reaction after processing were



Figure 4-4. The temperature profile for LARC-TPI varnish (polyamic acid) microwave heated for 1 hour at 100°C and 30 minutes at 200°C.



Figure 4-5. The input power for the LARC-TPI sample shown in Figure 4-4.





Heating Cycle	Microwave	Thermal
unreacted LARC-TPI		30.00
1 hr at 100°C 1/2 hr at 150°C	73.93	68.12
1 hr at 100°C 1/2 hr at 150°C 1/2 hr at 200°C	91.00	95.08
1 hr at 100°C 1/2 hr at 200°C	90.92	93.69

Table 4-1. Polyimide Content of LARC-TPI Polyamic Acid Heated in Thermal and Microwave Cycles

the reasons for these inconsistencies. TGA analysis was still performed, and the resulting comparisons of samples heated with different cycles are listed in Table 4-1. The polyimide content was the weight percent remaining at 520°C.

The samples were run on the TGA at  $10^{\circ}$ C/min with a 50 cc/min nitrogen gas purge. At the lower temperatures, the solvent content was greater for the thermal sample. At the higher processing temperatures, the thermal samples had a lower solvent content. There was a large removal of the solvent by the heating. The higher solvent content by the microwave sample was unexpected. The thermal samples were expected to exhibit the higher contents. An enhanced removal of the solvent was expected since the heating of the solvent was the key to the microwave heating occurring. It could be that the solvent was heated to the higher temperature, but the reaction of the polyamic acid leeched

off enough of the latent heat of vaporization to retain more solvent in the microwave samples. The thermal oven would heat the polyamic acid and the solvent together. Due to its high loss factor, the solvent would supply the heat for the microwave sample. The polyimide appeared to form the hardened skin described earlier in the literature<sup>7</sup>, but the skin was across the top of the Teflon cylinder and the test tube.

Longer heating times at the higher temperatures were limited by the removal of the solvent. The loss factor was lowered to a point where the microwave system could no longer supply enough power to heat the samples, as mentioned in section 4.22. The processing of composites would be possible if the fiber reinforcement was lossy enough to overcome this problem. Graphite fiber is a good candidate, but quartz fibers are not if the composites are to be fully cured and achieve the highest mechanical properties.

#### CHAPTER 5

# MICROWAVE PROCESSING OF POLYIMIDE COMPOSITES

#### 5.1 **EXPERIMENTAL**

Polyimide composites were processed in conventional thermal ovens and in the microwave cavity. The cavity used for processing was a 7-inch diameter cavity with the Opthos source used to supply power. The equipment diagram is shown in Appendix B. Polyimide composites with graphite fiber reinforcement were cut into 3-inch square plies and stacked to form panels for mechanical testing. The processing was performed without pressure since the microwave system was incapable of supplying sufficient pressure to use commercial cycles. The processing of the thermal samples was performed within Fisher Isotemp Ovens with WAHL RS210 programmable controllers. The samples were laid up and sealed within a vacuum bag. A tube sealed into the vacuum bag which extended through the top of the oven and a vacuum hose could Samples were run under vacuum, and a cold trap be attached. with liquid nitrogen coolant was used to protect the vacuum pump from solvent vapors.

Two different polyimide composites were processed for

the experiments. Their source and particular experiments will be described further below.

### 5.11 CPI-2249

Commercial prepreg was obtained from Ferro Corporation. The reinforcement was a Celion 3k graphite fiber weave. The processing of the material required no pressure application, so it was selected for preliminary studies. Panels were made by laying up 12-plies 3-inches square. A release film was placed on top and on bottom of the sample, and 3 layers of air weave were placed on top of the layup. A cork dam was placed about the sample, and it was sealed within a vacuum bag. One end of a metal tube was sealed within the vacuum bag for venting volatiles from thermal samples. The layup was placed on top of an aluminum plate, and a large circular block of Teflon 1.5 inches thick was placed on top of the composite layup. The use of the plate and the Teflon was to insure that the cure would go from the bottom layers up to the top layers. This sample was cured in a Precision Scientific Thelco Oven controlled by a Wahl RS210 Programmable Controller. The postcure was freestanding and carried out in a Blue M (general Signal) Oven.

The microwave samples were prepared by similar layup methods. Instead of the metal tube sealed within the vacuum bag, a piece of Teflon tubing was used. The metal plate was replaced by another 1.5-inch Teflon block for two reasons. The first reason was because metal could not be used in the microwave. The second reason was to insulate the sample.

Capillary tubes sealed at one end were inserted through the top Teflon block. Luxtron fluoroptic temperature probes were inserted into the capillary tubes. These probes were connected to the Luxtron 750 device. The capillary tubes were in contact with the top of the layup (the vacuum bag).

This setup was loaded through the bottom of the 7-inch microwave cavity. The bottom plate was lowered to put the sample in, and the vacuum tube was run through an opening in the side of the cavity. The bottom plate was raised and a good electrical seal about the cavity was obtained. A processing mode, or electromagnetic field pattern, was found by using the oscilloscope to determine the point at which the cavity was tuned to a minimum reflected power. Once the operating mode was chosen, the microwave cavity was connected to the Opthos power source. The processing conditions chosen were  $180^{\circ}$ C for 1 hour followed by a 1/2 hr at  $220^{\circ}$ C.

### 5.12 LARC-TPI

LARC-TPI prepreg was prepared by impregnating Hercules 12k AS4 fibers with the LARC-TPI varnish received from Mitsui Toatsu Chemicals. Early attempts at making a prepreg used the varnish diluted with N-methyl-pyrrolidinone. Different formulations were attempted. The first attempt used NMP and the LARC-TPI varnish in a 50% by weight solution with the NMP. This lowered the viscosity of the polymer to make the prepreg. A second attempt used a 75% by weight LARC-TPI varnish solution with the NMP. The lowered

viscosity allowed for tapes to be made, but their polymer content appeared too low. It was decided to use the varnish undiluted. The high viscosity of the material required that the spreading pins of the prepregger not be used in the resin pot. The roller apparatus from the other resin bath of the prepregger was clamped so that the fibers were passed over the rollers just before they entered the resin pot. This helped spread and flatten the fiber bundles. Also, the carriage guide was removed from the fiber path to reduce tension on the fiber. Figure 5-1 shows the path of the fiber for the prepregging operations.

Prepregs were successfully made. From the first prepregs, 3-inch square samples were prepared. Twelve-ply panels were fabricated for testing. The cork was removed from the layups. The number of layers of airweave was also reduced to allow for better heating by the microwave energy.

The samples made from the undiluted varnish were laid up in 3-inch square panels as before. For these samples, a frame was cut from 3/16-inch thick Teflon sheet. The frame was approximately 4 inches wide, and a 3-inch square was machined from the center of the Teflon sheet, as shown in Figure 5-2. The plies of the layup were laid into the frame. Release film was placed on the top and the bottom of the material, and one layer of airweave was placed across the top of the sample. Another square approximately 3 inches wide was cut from Teflon sheet and placed on top of the airweave. The small square of Teflon acted as a piston.





**(B)** 

Figure 5-1. The fiber path during (A) regular prepregging operations and (B) modified prepregging operations.





Figure 5-2. The dimensions of the teflon frame and plug used for the modified layup procedure.

The sample was placed in a Carver press, and 3000 lbs of force (333 psi) were applied to the sample at 110°C for 10 minutes under vacuum. This consolidated the plies and removed water complexes formed during prepregging operations when in contact with the atmosphere. As before, the thermal samples were placed in the oven with a metal plate on bottom and a Teflon block on top. A vacuum hose was attached to the metal tube sealed in the vacuum tube.

The microwave samples were again placed between two Teflon plates and capillary tubes were used to bring close contact of the fluoroptic temperature probes. Unlike the CPI-2249 layups, however, the temperature probes and the sample had only the vacuum bag and the release film between them. A much better measurement of the surface temperatures was achieved for these samples. A short piece of Teflon tubing with one end sealed in the vacuum bag was used to connect a vacuum hose outside the 7-inch cavity.

Twelve-ply LARC-TPI samples were prepared by these methods. After unsuccessful heating patterns were achieved, a fully-reacted panel was placed in the microwave cavity with no vacuum bagging. The Teflon frame and blocks were in place with the temperature probes.

Heating experiments were performed to try to find a mode to heat the panel evenly. The electrical field was measured using a probe through sample ports located along the radial positions on the cavity and along two axial positions. Figure 5-3 presents a picture of the cavity and the







Figure 5-4. The positions of the electric field measurement ports as viewed from the top of the cavity. location of these sampling ports. Table 5-1 lists the height of the sample ports along the edge of the cavity. Holes at axial positions 3,4, and 5 were used as sampling ports to measure the radial pattern of the electromagnetic field. The position of the coupling probe was designated as the  $0^{\circ}$  position in the cavity. The electric field strengths were recorded at these positions to form a picture of where the electric field was strongest. Figure 5-4 shows the positions of the sample ports for the radial field.

Different fiber orientations were tested to find the proper orientation of the sample. A 24-ply sample was prepared thermally to continue the field pattern testing. This sample was also placed in the cavity to search for a proper heating mode. Fiber orientation was designated by the direction parallel to the fibers with respect to the coupling probe. Figure 5-5 illustrates the direction of fiber orientation. This is the same system used for the designation of the radial port positions in Figure 5-4.

# 5.13 Presentation of Electric Field Data

The measurements of the electric fields were taken by measuring the power of the electric field along the cavity walls. These measurements were presented in two different plots to present a relative picture of the electric fields. This method of presentation was developed internally at Michigan State University by Wei, Chang, and Thomas.<sup>48</sup>

One plot presents the radial field data measured at different positions along the cavity at holes 3,4, and 5.



Figure 5-5. The directions indicated by the fiber orientation with respect to the coupling probe.

Hole Number	Height (cm)
1	1.527
2	2.449
3	3.371
4	4.293
5	5.215
6	6.137
7	7.059
8	7.981
9	8.903
10	9.825
11	10.747
12	11.669
13	12.591
14	13.513
15	14.435

Table 5-1. The Height of the Electric Field Sampling Ports for the 7-inch Cavity

Some positions were blocked by the coupling probe port and the side port used to accommodate the vacuum line. The readings were recorded in  $\mu W$ , and these were used to set the radius of the data point in the polar plot by the equation:

$$r_{B} = 4.1 - \frac{P_{b}}{100}$$
 (5-1)

where  $r_E$  is the radius of the plot,  $P_b$  is the reading of the power at the probe position in  $\mu W$ . The stronger electric fields are represented by the data point being closer to the center of the plot.

At 90° and 180°, the axial field can be measured by holes 1 through 15. These readings were also power readings recorded in  $\mu$ W, and a relative field strength representation was used to present the axial electric field. An X-Y plot was used with the cavity height plotted along the Y-axis and the electric field readings plotted along the X-axis. The 90° set of data point were plotted as:

$$x_{90} = \frac{P_b}{100}$$
 (5-2)

and the 180° data was presented as:

$$x_{180} = 3 - \frac{P_b}{100}$$
 (5-3)

where  $x_{90}$  is the dielectric field strength at 90° in units equal to 0.1 mW,  $x_{180}$  is the dielectric field strength at 180° in units equal to 0.1 mW, and P<sub>b</sub> is the power reading in  $\mu$ W.

# 5.14 Mechanical Testing

The panels were cut into testing coupons 0.5 inches wide for mechanical testing. The device used to test the samples was a United UTS testing machine. The samples were tested with a three-point flex test procedure. The flexural strengths and moduli of the samples were calculated for the comparison of thermal samples to microwave samples. Due to the limited size of the samples, some coupons did not meet ASTM standards. For the 24-ply samples, a set span of 2.410 inches was used for all the samples since they were too thick or too short to meet the proper length-to-thickness ratio of 16.

The calculations of the flexural properties was performed according to ASTM D790<sup>49</sup>. The flexural strength was calculated by the equation;

$$FS = \frac{3UL}{2bd^2} \tag{5-4}$$

The flexural moduli of the samples were calculated by:

$$FM = \frac{L^3 m}{4 b d^3} \tag{5-5}$$

d = the thickness (depth) of the sample (inches)

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## 5.2 RESULTS AND DISCUSSION

# 5.21 CPI-2249

The thermal cycle used to process the CPI-2249 is shown in Figure 5-6. This cycle was slightly modified from the recommended cycle due to controller limitations. The sample was of good quality, but the processing cycle was on the order of hours to obtain a good part. The microwave cycle was a two-stage process with 60 W of power delivered to the sample. The temperature profile of this cycle is shown in Figure 5-7, and the power delivered to the system is shown in Figure 5-8. Microwave processing of this sample was carried out with the fibers of the graphite weave parallel and orthogonal to the coupling probe.

The samples were tested by TGA to determine the solvent and resin content. Figure 5-9 compares the TGA data obtained by heating the samples to 850°C at 10°C/min under a 50 cc/min nitrogen purge. One sample was a piece of the uncured prepreg. The other two samples were thermal- and microwave-cured samples. The thermal sample was reacted further in the ovens by the more complete cycle that included curing and postcuring. This cycle was on the order of hours, while the microwave sample was only processed for 2 hours at 180°C and 1 hour at 220°C. This 6 to 1 ratio in processing time is too great to ignore when comparing the samples. At 550°C, the thermal sample exhibited only a 3.2% weight loss while the microwave sample had lost 7.1%. The uncured sample, by comparison, had lost 16.2% of its weight.



Figure 5-6. The temperature profile of the cure and postcure cycle used to process 12-ply Celion 3k/CPI-2249 thermal samples.



Figure 5-7. The temperature profile for the two-stage microwave curing of 12-ply CPI-2249/Celion 3k woven composite.



Figure 5-8. The input power to the during the two-stage microwave processing of 12ply CPI-2249/Celion 3k woven composite.



Figure 5-9. The results of TGA analysis of CPI-2249 composites and prepreg.

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SAMPLE	Flexural Strength (psi)	Flexural Modulus (Mpsi)
Thermal	66700 ± 2100	87.43 ± 1.10
Microwave	62400 ± 2700	47.92 ± 3.61

# Table 5-2. Results of Flexural Testing of CPI-2249 Composites

All solvent would be gone from the samples at 520°C, and the polyimide would be beginning to degrade.

The mechanical testing of the samples also supported the TGA analyses. The long thermal cure had a greater advantage over the shorter microwave cycle. The results of the mechanical testing are presented in Table 5-2.

The target values for from Ferro Corporation<sup>50</sup> are 80 Mpsi and 9 Mpsi for Flexural strength and flexural moduli. The flexural strength of the thermal sample was slightly lower than the target value. The microwave sample was of the same order of magnitude as the thermal sample in flexural strength and moduli, but it was still less than the value for the thermal sample. The slight difference arose, however, after shortening the processing time from 16.5 hours to 3 hours.

Problems were also encountered during the processing. The layup materials used for the microwave processing of the samples was not suited for the temperatures and environments to which they were subjected. Burning of the materials occurred during the experiments. The cork dam was a primary source of burning, and the material was collected within the

va tr pr he 58 vi th of De WO Vo gr th . Li ар 5. ta CO lo in fr ٣h Un; taj eas vacuum tube.

Another problem was the proper selection of the electromagnetic mode. At the time of the experiments, this process had not been refined. It is assumed that a proper heating mode may increase the mechanical properties of the sample to match or exceed the thermal and literature values within a very short processing time. Vogel et al. found that the proper orientation of the sample and the selection of the electromagnetic mode had a significant effect on mechanical properties.<sup>51</sup> The CPI-2249 prepreg, however, would respond differently to changes in fiber orientation. Vogel et al. used unidirectional composites, but the graphite weave of the CPI-2249 prepreg was more similar to the cross-ply composites later studied by Wei.<sup>52</sup> The microwave processing showed promise, but a more careful application of the method was needed.

# 5.22 Prepregging Operations with LARC-TPI

Two early attempts at prepregging AS4 fiber resulted in tapes that appeared to be wetted properly. The high solvent content made for easy prepregging operation because of the low viscosity of the solution. The prepregger was operated in the standard settings and windings. The tapes obtained from these diluted solutions were not adequate, however, when preparing layups for processing experiments. The unidirectional tapes had gaps which made portions of the tape unusable. During cutting, the fibers pulled apart too easily, which also resulted in wasted material.
A 12-ply composite panel obtained from this prepreg was not of good quality. The center of the sample was flexible, and the carbon fibers were unconsolidated within the plies themselves. It was concluded that more polymer was needed within the prepreg tapes. A different prepregging strategy was needed to improve the tapes.

The undiluted LARC-TPI varnish was used for the next prepreg tapes. The viscosity of the solution was too high, and the tension caused the fibers to break when the spreading pins were inserted. A tape was obtained by removing the spreading pins and the carriage guide. This tape was better for layups, but more impregnation of the fibers was desired. A set of rollers was removed from the optional bath on the prepregger. This was mounted with clamps just above the resin pot. The fiber was passed over the rollers to spread the fibers more before they entered the resin pot, but the fiber tension was still not increased to the point that the fibers would break. The tapes obtained from this method were used for the composite processing and mechanical testing.

The prepreg tapes exhibited a low amount of tack during layup. At the completion of the prepregging operations, the top layer of release film placed over the tape for storage protection would not adhere to the sample. Since the bottom layer would adhere, it was concluded that the lack of tack was attributable to the formation of complexes between the polyamic acid and solvents with moisture from the air.

Other studies with polyimide materials have reported the formation of white precipitates when using polyamic acids, so this was consistent with the nature of the polyimides and polyamic acids.

The layup procedure was modified for the processing of the AS4/LARC-TPI samples to accommodate the problem of the low tack. The plies were stacked in a Teflon frame which served as a dam during processing. Earlier attempts at microwave processing (with the CPI-2249) had found that the traditional cork dams used for epoxy materials burned too easily within the microwave cavity at the processing temperatures. A layer of Wrightlease 5900 received from Airtech International, Inc. was placed across the top and bottom of the composite's surface. A layer of air weave was placed across the top of the sample, and a Teflon square was placed on top of the layup so that it could fit down within the frame. All of this was sealed within a vacuum bag with a tube placed in the vacuum bag to allow for the attachment of the vacuum lines. For thermal samples, this tube was a metal tube. For microwave samples, the tube was Teflon.

Once the layup was completed, the sample was "prestaged" to remove the problems introduced by the water complexes. The layup was placed within a Carver press with the platens heated to 110°C. A vacuum pump was connected to the tube, and 3000 pounds of force was applied to the samples for 10 minutes. The early pressure consolidated the samples and also helped to drive off some of the water and

solvents. The Teflon square on top of the Teflon frame acted as a piston to apply the force to the sample (approximately 333.33 psi). Once the sample was released from the press, it was ready for processing either by microwave or thermal ovens.

The sample was turned over for microwave processing, making the bottom surface during prestaging the top surface during microwave processing. This left only the release film and the vacuum bag between the composite surface and the temperature probes. The modified layup procedure served two purposes for the composite preparation. The Teflon frame and square made the consolidation of the sample possible with an easy ten minute process. After the prestaging, the sample was also ready to go into processing cycles with the surface of the sample readily available for the placement of temperature probes on the surface of the composite. There was minimum interference from layup materials in the temperature measurements. The Teflon also served as an insulator to hinder heat transfer from the sample to its surroundings.

Although more layers of bleeder cloth or air weave are recommended for industrial processing, less materials were used in the layups. The CPI-2249 studies showed that some layup materials heated too well within the microwave environment, resulting in hot spots and burning. The "slimmer" layup also allowed for better measurement of temperatures during processing. Discrepancies in material properties would result from inconsistent and inaccurate temperature measurements. The placement of the temperature probes in contact with the surface of the composite with a minimum of layers between them was attempted for these experiments.

## 5.23 12-ply AS4/LARC-TPI Composite Processing

The microwave heating of the 12-ply AS4/LARC-TPI materials produced panels for testing. The temperature profiles of the panels during processing indicated uneven heating. The temperature gradients were too large to consider the processing modes acceptable. Figure 5-10 presents the temperature profile for a 12-ply sample with a 315° fiber orientation with respect to the coupling probe. The panel was cured during this heating, and its mechanical properties are presented along with the results for all the 12-ply samples in Table 5-4. Two other panels were fabricated, but they too demonstrated too large a temperature gradient for the processing to be considered successful.

After the failure of the 12-ply processing, a search for better processing modes was undertaken by heating a previously-cured panel in the microwave with different electromagnetic modes. The goal of this study was to find a mode and fiber orientation that yielded a uniformly-heated sample. The temperature profiles are presented for



Figure 5-10. The temperature profile for the microwave processing of a 12-ply AS4/LARC-TPI unidirectional composite at 315° fiber orientation.

different modes used to heat the panel in Figures 5-11 and 5-12. These experiments failed to provide a uniform heating mode. It was decided to attempt further heating experiments with a thicker panel. This decision was based upon private communications with Wei.<sup>53</sup> He had found that more uniform heating profiles were achieved with thick-section graphite/epoxy composites.

## 5.24 Microwave Heating of 24-ply AS4/LARC-TPI Composites

A 24-ply unidirectional AS4/LARC-TPI panel was prepared and cured thermally to be used in heating experiments. The 24-ply sample was placed in the microwave cavity at a 315° fiber orientation. Figures 5-13, 5-14, and 5-15 are the oscilloscope patterns for the candidate processing modes. Figure 5-16 depicts the placement of the temperature probes across the top surface of the composite panel. The sample was heated in the mode appearing at a cavity length of approximately 11.4 cm. The temperature profile across the sample is presented in Figure 5-17. The radial dielectric field during the heating is presented in Figure 5-18, and the axial field appears in Figure 5-19. The shape of the radial field seems to follow the edge of the panel, and the axial field maximum was appropriate for processing. The temperature gradient across the sample's surface was too great to consider this a feasible mode. The chosen processing temperature of 180°C was easily achieved, and the temperature was maintained by cycling the input power between 60 and 20 Watts. After 25 minutes, the temperature



Figure 5-11. The temperature profile for the microwave heating of a 12-ply AS4/LARC-TPI panel at 315° with  $L_c = 12.507$  cm and  $L_p = 31.31$  mm.



Figure 5-12. The temperature profile for the microwave heating of a 12-ply AS4/LARC-TPI panel at 315° with  $L_c = 16.610$  cm and  $L_p = 30.425$  mm.



Figure 5-13. The oscilloscope pattern of the electromagnetic field about a 24-ply unidirectional composite at  $315^{\circ}$  with  $L_c = 9.115$  cm and  $L_p = 29.72$  mm.



Figure 5-14. The oscilloscope pattern of the electromagnetic field about a 24-ply unidirectional composite at  $315^{\circ}$  with  $L_c = 11.347$  cm and  $L_p = 30.30$  mm.

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Figure 5-15. The oscilloscope pattern for the electromagnetic field about a 24-ply AS4/LARC-TPI at 315° with  $L_c = 12.98$  cm and  $L_p = 23.10$  mm.



Figure 5-16. The location of the temperature probes across the surface of the 24-ply panel during heating experiments.



Figure 5-17. The temperature profile for the microwave heating of a 24-ply AS4/LARC-TPI composite at 315° with  $L_c = 11.347$  cm and  $L_p = 30.30$  mm.







Figure 5-19. The axial representation for the electric field pattern of the microwave heating of Figure 5-17.

profile was stable, and the experiment was discontinued.

The panel was not removed from the cavity after the first heating experiment, so the probe placement for the next experiment remained the same as shown in Figure 5-16. The mode appearing at 13.0 cm was used for to heat the sample. The temperature profile is presented in Figure 5-20. The dielectric fields are presented in Figures 5-21 and 5-22. This heating mode also resulted in an unacceptable temperature profile. The temperature of 180°C was easily maintained by power cycling, and the experiment was terminated at 25 minutes.

The comparison of the temperature profiles from these two experiments revealed an important result. The temperature profiles of Figure 5-17 is T4>T1>T2>T3. The temperature profile of Figure 5-20 is T3>T2>T1>T4. The complementary patterns of the two different modes and the closeness of the cavity lengths were amenable to attempting to heat the panel by switching between the modes to control the temperature profile. The same setup was used as the previous heating, and the temperature profile is shown in Figure 5-23. The resulting temperature profile shows all four surface temperatures maintained within a tight range. The "mode-switching" resulted not only in a tight temperature profile, but the probe with the highest temperature kept changing. As the different temperature traces intertwined, the maximum temperature difference was as low as 2°C between the highest and lowest temperatures.



Figure 5-20. The temperature profile for the microwave heating of a 24-ply AS4/LARC-TPI at  $315^{\circ}$  with  $L_c = 13.025$  cm and  $L_p = 23.96$  mm.



Figure 5-21. The radial representation of the electric field pattern for the microwave heating of Figure 5-20.



Figure 5-22. The axial representation of the electric field pattern for the microwave heating of Figure 5-20.

he th e] fi th ot fo th DOC the cla Wa þi 0 d 9 P.°0 The method of mode-switching was a success as far as heating was concerned. Manring and Asmussen<sup>54</sup> have shown that combinations of modes can be used to obtain a uniform electromagnetic field by superimposing one electromagnetic field pattern over another. A uniform field results from the matching the peaks of one field with the nodes of the other or others. More than two modes could be superimposed for this type of processing, which eventually develops into the conventional multimode microwave cavity as the number of modes is increased.

Uniform heating is attained from a uniform field, and their demonstration of heating profiles supported this claim. The processing of the AS4/LARC-TPI by mode-switching was achieved not only because of the complementary heating profiles, but also because the modes selected were close to one another with respect to the cavity geometry. A difference of 2 cm in the cavity length still resulted in approximately 30 seconds to switch from one mode to another with manual tuning. Figure 5-24 illustrates the switching of the modes during the processing.

Heating by mode-switching provides great potential for the application of microwave processing. While processing with a single mode would be preferable, the use of combinations of modes is more adaptable. In the case of the LARC-TPI composites, a single processing mode did not yield a satisfactory temperature pattern. Asmussen and Fritz<sup>55</sup> proposed that one mode would not be sufficient to process a



Figure 5-23. The temperature profile of the microwave heating of a 24-ply AS4/LARC-TPI composite at  $315^{\circ}$  with mode-switching between  $L_c = 11.35$  cm and 13.03 cm.



Figure 5-24. The selection of the modes during the microwave heating of Figure 5-23.

sa ch IC CC 01 tł 90 a a P S f V t P sample completely, and the proper processing mode could even change as the processing proceeds. A single processing mode would not yield good mechanical samples. The combination of modes, however, resulted in very good control of the temperature across the sample. The selectivity of the application of the microwave energy was a proposed advantage for microwave processing, and the mode-switching allows for a greater utilization of this advantage.

It is important to remember that these composite panels are of simple geometry. The samples are essentially one plane throughout the cavity. During the polymer property studies, smaller samples were matched with the electric field to select a mode for heating. Cylindrical samples were used for a  $TM_{012}$  mode, and a flat film was heated by the  $TE_{111}$  mode. These geometries were acceptable for property testing, but an actual composite part in an industrial application may not be so conveniently simple in its geometry. The processing of a complex geometry could not be easily achieved by the use of a single-mode operation.

The success of processing by mode-switching lends itself well to developing specific processing protocol for complex geometries. Given a particular part to process, one could select the proper modes for processing by first mapping the different modes according to the temperature profiles that arise for each particular mode. The position of the samples and the relation of the temperatures from

fastest-heating to lowest-heating could be used to intelligently select the proper heating mode. A protocol for mode switching is presented in Section 5.25.

The mechanization of cavity tuning with computer control, which is a logical step in microwave processing, could enhance and be enhanced by the mode-switching method. Motor-driven tuning would decrease the response time between the decision to switch modes and the actual tuning to the new mode. The modes would not need to be as close to one another in cavity geometry to be used for processing. The temperature maps of different processing modes could be programmed into a computer with the algorithms for selecting a new mode according to the thermal responses of the part being processed. More modes could be applied to the processing because the computer could sort through the modes faster and determine which mode best fits the required criteria for continued processing.

## 5.25 Mode-switching Protocol

The following is an algorithm for processing by modeswitching, which should be considered during the development of computer control software:

1. The different temperature profiles for each of the possible processing modes should be determined and catalogued. The relation of temperatures at specific locations to temperatures at other locations are an important consideration.

2. A pair of modes are good candidates for use if they

result in "complementary temperature profiles", i.e. T4>T1>T2>T3 for mode A and T3>T2>T1>T4 for mode B. Complementary modes would be the best candidates for modeswitching.

3. A special consideration must be made if the differences in the temperatures for individual processing modes is large between different temperature probe sites. It is possible for one temperature measurement to be in the middle of the temperature profiles for the individual modes, but that site heats so well in both modes so that it becomes a runaway temperature (or hot spot) during mode-switching processing.

4. The time to switch modes may be selected for one of many reasons:

- a. One temperature is running away from the others.
- b. One temperature is falling too far behind the others.
- c. The temperature range across the sample is too large.
- d. The sample is heating too slowly.

5. Successful heating can be achieved by selecting the modes according to different criteria.

6. One method for heating is to heat in one mode until the difference between the highest and lowest temperatures is too great. The modes are switched until the temperatures even out. The first mode is again used until the temperature range is too large. Essentially one temperature pulls the rest along.

7. Another possible way to heat is for the temperatures to "chase" one another. One mode is used until the temperature it favors gets so far ahead of the other temperature. The modes are switched until another favored temperature is pushed highest. This would push the temperature profile to the desired processing pattern by sending the lowest temperature to the highest temperature.

8. For controlling runaway heating, it would be ideal if there existed a mode for each temperature measurement site where this site could be "parked" until the other temperatures catch up to it. In the single-mode temperature pattern, a site which is 20°C or more cooler than the other sites would be useful for this purpose.

9. Temperature gradients during the heat-up can be tolerated if they are not too large. Once the desired processing temperature is achieved, power cycling combined with mode-switching will tend to decrease the differences in the temperatures, especially when conduction helps to even out the temperatures. The temperature profile can level out as the sample is maintained at the particular temperature.

## 5.26 24-Ply AS4/LARC-TPI Composite Processing

A 24-ply unidirectional layup was made with AS4/LARC-TPI prepreg and prestaged. The unreacted panel was placed in the microwave cavity at a  $315^{\circ}$  fiber orientation and heated to  $180^{\circ}$ C for one hour. The temperature profile is



Figure 5-25. The temperature profile during the microwave processing of a 24-ply AS4/LARC-TPI composite at 315° at 180°C by mode-switching.



Figure 5-26. The temperature profile for the postcure of an AS4/LARC-TPI composite panel processed at  $315^{\circ}$  fiber orientation.

shown in the Figure 5-25. The sample was postcured with the temperature profile shown in Figure 5-26. The samples were processed with the same modes used for the mode-switching heating experiments. The mode selection is shown for the processing at  $180^{\circ}$ C in Figure 5-27. The placement of the temperature probes across the surface of the 24-ply samples is shown in Figure 5-28. The sample was to be heated at  $250^{\circ}$ C for 1 hour for the postcure, and a 30 minute heat-up time was allowed. The temperature  $250^{\circ}$ C was chosen because it was the limit of the Teflon which insulated the material. The power used to reach and maintain the higher temperature was 80 W.

A sample at a 45° fiber orientation was processed with the same processing cycles, but a different set of processing modes were used for the sample processing. The oscilloscope patterns are shown in Figures 5-29, 5-30, and 5-31. The change in the fiber orientation of the sample resulted in the different electromagnetic fields, so the original modes used for mode-switching were no longer available. The temperature profile of the sample during processing is shown in Figure 5-32, and the temperature was successfully maintained at approximately 180°C by cycling the power between 60 W and 20 W. The postcure of the sample is shown in Figure 5-33. The temperature was also maintained at 250°C due to the limits of the Teflon insulation. Figure 5-34 shows the mode selections during the processing.

Thermal samples were also prepared with the



Figure 5-27. The selection of the processing mode during the processing of Figure 5-25.



Figure 5-28. The position of the temperature measurements on the of 24-ply AS4/LARC-TPI composites during microwave processing.



Figure 5-29. The oscilloscope pattern for the electromagnetic field about a 24-ply unidirectional composite at 45° with  $L_c = 10.929$  cm and  $L_p = 26.44$  mm.



Figure 5-30. The oscilloscope pattern for the electromagnetic field about a 24-ply unidirectional composite at 45° with  $L_c = 11.417$  cm and  $L_p = 35.52$  mm.



Figure 5-31. The oscilloscope pattern for the electromagnetic field about a 24-ply unidirectional composite at 45° with  $L_c = 13.254$  cm and  $L_p = 16.68$  mm.



Figure 5-32. The temperature profile during the microwave processing of a 24-ply AS4/LARC-TPI composite at 45° at 180°C by modeswitching.



Figure 5-33. The temperature profile during the microwave postcure of a 24-ply AS4/LARC-TPIcomposite at 250°C and 45° fiber orientation.



Figure 5-34. The selection of the processing mode during the processing of Figure 5-32.

conventional ovens. One hour holds at 180°C under vacuum and 250°C freestanding postcures were used to obtain even comparisons between the processes. The heat-up of one of the thermal samples during the 180°C processing was measured by placing the thermocouple of the oven in contact with the aluminum plate under the sample. Though the temperature measurement was not made on the surface of the composite itself, this approximation was reasonable given the high thermal conductivity of the aluminum.

#### 5.27 Mechanical Testing of AS4/LARC-TPI Composites

The thermal and microwave samples were cut into 1/2inch wide coupons for mechanical testing. Both 12- and 24ply samples were tested, and a 12-ply sample which had undergone the prestaging process for 30 minutes was also tested. The processing cycles and conditions are listed for each of the different 12-ply samples in Table 5-3. The resulting dimensions of the test coupons are shown in Table 5-4. It should be noted that the width *b* of the samples is needed only for calculation of the flexural strength, and it is not different due to processing. The flexural strengths of the 12-ply samples are presented in Table 5-5 and the flexural moduli in Table 5-6.

The flexural strengths and moduli of the microwave samples were greater than those of the thermal samples. The microwave sample which had not undergone a postcure process exhibited the least of the flexural strengths. The postcure process was necessary to increase the sample's strength.

# Table 5-3.Processing Cycles and Conditions of 12-plyAS4/LARC-TPI Composites

Sample ID	Processing Cycle and Conditions		
LPS30	Prestaged for 30 minutes		
LT12-1	Prestaged 10 minutes; thermally heated at 180°C for 4 hours, then free-standing postcure thermally for 1 hour at 335°C.		
LP12-1	Prestaged 10 minutes; microwave cured at 180°C for 1 hour at 315° fiber orientation.		
LP12-2	Prestaged 10 minutes; microwave cured at 180°C for 1 hour at 315° fiber orientation, microwave postcured for 65 minutes at 250°C.		
LP12-3	Prestaged 10 minutes; microwave cured for 1 hour at 180°C at 90° fiber orientation, microwave postcured for 1 hour at 250°C.		

## Table 5-4. The Dimensions of Cured 12-ply AS4/LARC-TPI Composites

SAMPLE ID	d (in)	s <sub>x</sub> of d (in)	b (in)	s <sub>x</sub> of b (in)	L (in)
LPS30	0.137	± 0.002	0.520	± 0.014	2.198
LT12-1	0.106	± 0.001	0.511	± 0.010	1.694
LP12-1	0.098	± 0.002	0.509	± 0.005	1.580
LP12-2	0.108	± 0.002	0.538	± 0.019	1.727
LP12-3	0.096	± 0.003	0.510	± 0.021	1.529

SAMPLE ID	FLEXURAL STRENGTH (kpsi)	s <sub>x</sub>	s <sub>x</sub> /FS (%)
LPS30	18.4	± 1.0	± 5.7
LT12-1	25.2	± 2.7	± 10.7
LP12-1	18.9	± 1.1	± 5.8
LP12-2	31.4	± 2.6	± 8.2
LP12-3	28.0	± 5.6	± 20.1

Table 5-5. Flexural Strengths of 12-ply AS4/LARC-TPI Composites

Table 5-6. Flexural Moduli of 12-ply AS4/LARC-TPI Composites

SAMPLE ID	FLEXURAL MODULUS (Mpsi)	s <sub>x</sub>	s <sub>x</sub> /FM (%)
LPS30	1.8	± 0.1	± 6.0
LT12-1	3.7	± 0.2	± 6.6
LP12-1	1.7	± 0.1	± 4.6
LP12-2	4.9	± 0.3	± 6.8
LP12-3	4.3	± 1.6	± 38.2
The sample which was prestaged for 30 minutes had a flexural strength which was only slightly less than the sample cured for 1 hour at 180°C, and the flexural moduli was slightly greater for the unheated sample. The microwave samples that underwent the cure and postcure processes both exhibited greater flexural properties than the thermal sample, even though the thermal sample had been processed for a longer period of time at 180°C and at a higher postcure temperature. This is a significant reduction in the time of processing. The difference in the properties is not as great as the differences for the CPI-2249, but these favor the microwave process rather than the thermal process. One value reported in the literature for the flexural strength is 1600 MPa (232 kpsi) with a flexural modulus of 124 GPa (18000 kpsi)<sup>18</sup>, but another source lists values of 137 kpsi and 13 Mpsi for flexural strength and modulus, respectively.<sup>56</sup> The application of pressure during the cycle is required to achieve these properties. The prepregs for the studies in the literature were also fabricated with multiple resin coatings on the fibers and B-staged before layup. The available equipment did not allow for multiple coatings of LARC-TPI to be applied to the AS4 fibers in the laboratory.

The processing cycles for the 24-ply samples are summarized in Table 5-7 for each of the samples. The dimensions of the samples are listed in Table 5-8. As stated before, the dimension *b* was not a result of the

Table 5-7.	The	Processing	Cycles	and	Conditions	of	24-ply
AS4/LARC-TPI Composites							

SAMPLE ID	Processing Cycle and Conditions
LT24-1	Prestaged 10 minutes; thermally processed for 1 hour at 180°C, and postcured for 1 hour at 250 °C.
LT24-2	Prestaged 10 minutes; thermally processed for 1 hour at 180°C, and postcured for 1 hr at 250°C.
LP24-1	Prestaged for 10 minutes; microwave processed for 1 hr at 180°C and 315° fiber orientation by mode-switching, and postcured for 1 hour at 250°C at 315° fiber orientation by mode-switching.
LP24-2	Prestaged for 10 minutes; microwave processed for 1 hr at 180°C and 45° fiber orientation by mode-switching, and postcured for 1 hour at 250°C at 45° fiber orientation by mode-switching.

Table 5-8. Dimensions of 24-ply AS4/LARC-TPI Composites

SAMPLE ID	d (in)	s <sub>x</sub> of d (in)	b (in)	s <sub>x</sub> of b (in)	L (in)
LT24-1	0.251	± 0.003	0.519	± 0.019	2.410
LT24-2	0.228	± 0.005	0.558	± 0.017	2.410
LP24-1	0.241	± 0.006	0.554	± 0.021	2.410
LP24-2	0.168	± 0.005	0.536	± 0.037	2.410

SAMPLE ID	FLEXURAL STRENGTH (kpsi)	s <sub>x</sub> (kpsi)	s <sub>x</sub> /FS (१)
LT24-1	12.7	± 1.2	± 9.4
LT24-2	11.5	± 1.5	± 13.0
LP24-1	18.3	± 1.2	± 6.4
LP24-2	15.0	± 1.0	± 6.6

Table 5-9. Flexural Strengths of 24-ply AS4/LARC-TPI Composites

# Table 5-10. Flexural Moduli of 24-ply AS4/LARC-TPI Composites

SAMPLE ID	Flexural Modulus (Mpsi)	s <sub>x</sub> (kpsi)	s <sub>x</sub> /FM (%)
LT24-1	1.2	± 0.2	± 19.3
LT24-2	1.0	± 0.2	± 21.2
LP24-1	2.0	± 0.4	± 20.8
LP24-2	2.3	± 0.4	± 16.0

processing. It was listed because of its use in the calculation of the flexural properties. The calculated flexural strengths of the 24-ply samples are presented in Table 5-9, and the calculated flexural moduli are presented in Table 5-10.

The 24-ply LARC-TPI samples also demonstrated greater flexural properties for the microwave samples. Two thermal samples were prepared for this study, and a discrepancy between the flexural strengths of the thermal samples was due primarily to one coupon for the second thermal sample exhibiting a significantly lower flexural strength than the other coupons. If not for that low value, the sample would have had a flexural strength of  $12.05 \pm 1.36$  kpsi. There were four coupons cut from this thermal sample, and the inner samples exhibited higher flexural strengths than the outer ones. Edge effects may have been significant since the samples were so small. The presentation of the standard deviation divided by the average value for the set of coupons was made in an attempt to give some indication of the variation across the sample. From this standpoint, the microwave samples exhibited more uniformity than the thermal sample.

The flexural moduli of the samples were inconsistent across some of the samples, particularly for sample LP12-3. The samples exhibited such low values for the flexural properties that the success of the processing was questioned. The presence of solvent and water within the

prepregs was a complication which may not have been fully eliminated by prestaging. The water forming complexes may not have been properly purged by the prestaging. The prestaging appeared to be successful, however, since the samples were of good quality from the appearance of the final products. The uniformity of the 12-ply samples was better, which may indicate that the thickness of the 24-ply samples was a significant hindrance.

The thicker samples would have had a greater chance of entrapping solvents and water during processing. The short length of the samples made the mechanical tests fail to conform to ASTM standards. Conventional studies on composites typically fabricate composite parts 8 to 12 inches long to avoid edge effects. The small L/d ratio is important because this term is cubed in the calculation of the flexural moduli. A larger sample size would have been desired for testing, but the limitations of the microwave processing system prevented this.

The lack of pressure during processing also was a major limitation to the composite processing. The consolidation of the composites as the cure proceeds is not currently available during microwave processing. During conventional processing, the plies are pressed together as the resin reacts and the viscosity is minimized. A higher processing temperature would also be preferred for LARC-TPI. A higher postcure is recommended to increase the final properties of the composites.

The 12-ply samples showed a marked increase in the flexural properties after postcuring. Higher postcure temperatures can be reached by the microwave process, but the heat loss would need to be minimized by insulation. The Teflon dam and plates serve this purpose well, but the recommended continuous use temperature for Teflon is 205°C. The melting point and the glass transition temperature of LARC-TPI occur at temperatures higher than the temperatures applied during the microwave processing. These limitations contributed to the low values of the flexural properties, but trends were shown by comparing like processing conditions for the thermal and microwave processing methods.

The higher flexural properties of the samples processed by microwaves shows great promise. The application of the heat directly to the graphite fibers may result in a stronger matrix/fiber interface. The formation of the hard outer skin developed during conventional processing may be avoided, and this will also allow for faster heating cycles since the long slow cycles for polyimides were developed to facilitate solvent loss. Chapter 7 recommends further experiments and studies to investigate the solvent removal and fiber/matrix interface. These results would be useful for the comparison of thermal and microwave processing. Further improvements to microwave processing are needed to produce mechanical properties equal to current conventional technology, but the potential improvement of the microwave Processing over thermal processing was demonstrated.

#### CHAPTER 6

#### CONCLUSIONS

## 6.1 POWDERS

The dielectric properties of Thermid MC-600 and LARC-TPI were lower than those reported by the literature. The powders had a lower density than the solid materials, so a lower value should have been reported. The measured loss factors were too low for the microwave processing of the neat powders. DSC analysis found that the required temperatures for reaction of the polyimide powders were above 200°C. The addition of ground graphite powder to the polyimide powder enhanced the loss factor so that temperatures of 260°C and higher were used for processing Thermid IP-600. Preimidized LARC-TPI powder melted over a range of 270-300°C. The dielectric loss factor was too low to melt the powder by microwave heating.

#### 6.2 POLYAMIC ACIDS

Solvent removal was the controlling factor for the microwave processing of the polyamic acids. The loss of the solvent made typical processing temperatures for LARC-TPI processing unattainable as the dielectric loss factor was lowered with the solvent content. Differences were found in the solvent contents of thermal and microwave samples

processed by identical processing cycles. Improved methods for sampling are needed for the preparation of FTIR samples and analysis.

## 6.3 POLYIMIDE COMPOSITES

Modified layup techniques were used for processing AS4/LARC-TPI composites. The new layup had the benefits of less flammable materials and more insulation for the layups. Panels were successfully prepared for mechanical testing by microwave heating. A new technique of processing by modeswitching was applied since single modes did not evenly heat the panels. A mode-switching protocol was offered for future consideration in the development of process control, especially by computer-controlled, mechanized processes. The most significant application of mode-switching is the elimination of hot spots during microwave heating.

The flexural properties of the microwave samples were consistently higher than the properties of the thermal samples. Both methods fell short of literature values, but the lack of pressure and lower processing temperatures contributed to this. Microwave processing shows promise for the future, and as better techniques and materials are applied, the processing of high temperature composites may be facilitated with more efficiency and cost effectiveness.

#### **CHAPTER 7**

# FUTURE WORK

The polyimide studies have evaluated the feasibility of microwave processing. There are different directions which may be undertaken for future study that would greatly enhance the use of microwave processing. These studies could be divided into four different areas:

- 1.) Composite processing with thermoplastic powders
- 2.) Mass transfer/diffusion studies
- 3.) Mode-switching processing
- 4.) Evaluation of fiber/matrix interactions

## 7.1 Composite Processing with Thermoplastic Powders

The studies of the polyimide and polyisoimide powders demonstrated that the microwave processing of these powders could not be done without the presence of a microwave absorber or conduit. Lossy fibers could act as the conduit for microwave processing if the dielectric properties of the powder are too low to heat. By placing thermoplastic powders in contact with fibers within the microwave environment, the fibers could be impregnated by the melting powders. Studies of the surfaces of the fibers and the strengths of the resulting composites would evaluate the effectiveness of powder processing by microwave methods. It

would also be possible to study powder impregnation techniques. These techniques would be favorable because they lack the complications of solvents.

The impregnation of fibers by powders is currently being studied by different researchers. Modifications and improvements to powder impregnation have been developed and proposed.<sup>57</sup> Specific methods for prepregging with LARC-TPI thermoplastic powders have been studied.<sup>58,59</sup> St. Clair studied prepregging techniques that made a slurry of the preimidized powder and the polyamic acid for prepregging.<sup>56</sup>

### 7.2 Mass Transfer/Diffusion Studies

The processing of polyamic acid samples demonstrated the loss of solvent from the reacting polymer system. The final properties of the polymers and composites are greatly affected by this. The mass transfer coefficients could be better evaluated if the weight loss of the samples could be followed during microwave processing along with power and temperature profiles. The current method of suspending the sample from a stationary holder by a string into the cavity for heating in the  $TM_{012}$  or  $TE_{111}$  mode could be modified by replacing the stationary holder with a load cell, as shown in Figure 7-1. The load cell would be mounted on the middle platform on threaded rods. A knob and gear mechanism would permit the middle plate to move up and down. The sample



Figure 7-1. The proposed design of the load cell apparatus for measuring the weight loss of materials within the microwave cavity. suspended from the load cell would be raised and lowered in the cavity to find the proper location. The position of the sample with relation to the load cell would be fixed. The measurement of the weight would not change during the placement of the sample into the cavity.

The load cell readings can be read into the computer through an RS232 interface. The current data collection software could be easily modified to accept and record the information from the load cell. The load cell reading could be tared so that the weight change of the sample could be followed simultaneously with temperature, power, and dielectric loss factor profiles. This would, in effect, create a microwave version of a TGA, which would allow for the measurement of weight loss in the case of volatile contents or the degradation of a sample within the microwave environment. The relationship between weight loss and cure could be used as a possible monitor for the reaction of the polymer, particularly for a polymer undergoing a condensation reaction.

By fixing the sample geometry, the proper equations could evaluate the mass transfer of volatiles from the sample to the air. This would be a powerful tool for the comparison of thermal heating to microwave heating in terms of molecular effects. Neat solvents as well as resin solutions could be evaluated on-line, instead of by the current batch method of weighing the sample before and after the run. Polymer degradation within the microwave

environment could be studied. The experimental apparatus would not only establish comparisons between thermal and microwave processing in the area of mass transfer, but also establish a valuable diagnostic tool for polymer evaluation in the future.

An evaluation of a polymer could be performed with the dielectric property measured with the weight loss. The extent of cure could be found by the measurement of the dielectric cure, or by where the solvent or side product of a reaction has stopped being evolved from the resin. The degradation of polymers being processed could also be followed. If, for instance, a low-boiling constituent is present in the sample, the load cell would indicate the loss of the material. This is important for polymer systems where one component may heat much better by microwave energy than the other components.

Another important consideration for the load cell is safety. When testing new materials or working near the degradation temperature, side products may be dangerous. A preliminary run with the load cell may indicate possible hazards that must be considered. Differences in weight loss between thermal and microwave processing must also be considered. The entrapment of volatiles or degradation of a polymer are important considerations for processing, and a microwave version of TGA would be very useful in evaluating microwave processing.

### 7.3 Mode-switching Processing

The use of mode-switching for even temperature distributions was demonstrated during the processing of composites in Chapter 5. This technique must be better developed to take full advantage of the microwave environment for the processing of composites. The current composite panels could be studied to develop process control strategies, but the ultimate goal would be to process complex geometries.

A proposed shape would be the one pictured in Figure 7-2. This shape could be well-suited for the next generation of shapes for composite processing. It would essentially consist of three planes within the cavity. A transelectric mode (TE) would be suitable for each of the horizontal planes while a hybrid mode could be applied to the diagonal plane. This shape could be easily developed from current layup methods. The measurement of the surface temperatures would still be made by temperature probes placed on top of the sample. Another benefit would be that the fibers could be oriented so that samples for mechanical testing could be cut from each of the three planes of the geometry for evaluation.

The use of mode-switching to evenly heat composite and polymer parts could further advance the microwave processing technique. If the mode-switching could be done fast enough to evenly heat a sample, the process could be applied to replace thermal heating in other composite processing technologies. One envisioned application would be to create a



Figure 7-2. A proposed complex shape for composite curing by mode-switching.

teflon mold for resin transfer molding (RTM) or structural reaction injection molding (SRIM) and use microwave energy to heat the sample. With the quick application of microwave heating, thorough heating of the sample could be achieved while decreasing the residence time of the part. The microwave could heat the part more thoroughly than the traditional mold which places a hot surface in contact with the resin. A true test of the proposed "inside-out" thermal gradient would be combined with the fast heating of the microwave process.

# 7.4 Examination of Fiber/Matrix Interfaces

The composites cured by microwave processing exhibited greater flexural properties in Chapter 5. The samples may be stronger because of effects at the interface of the fiber and the polyimide matrix. Surface analysis to measure the presence of voids and pockets of solvent might explain these differences. The inside-out heating of microwave processing would be better understood by knowing whether there is a greater diffusion of solvent away from the fiber. If the solvent is removed more quickly from the fiber region during the early stages of processing, the avoidance of the hardened outer surface would be a significant enhancement to polyimide processing. A different rate of solvent removal would also affect the kinetics of the reactions for polyimides.

Void analysis and microcrack formation must also be considered when speaking of the fiber/matrix interface.

**Past** studies have seen different mechanisms between fiber and matrix due to microwave processing.<sup>36</sup> The processing **requirements** of the polyimides could be met by microwave **processing** if there are enhancements in these areas. A **better** coating of the fiber by the polymer could be achieved by microwave processing. These studies would be useful not only for composites fabricated from solutions, but also for **composites** processed from thermoplastic powders (as **described** in Section 7.1). The heating of the graphite **fiber** by the microwave energy should introduce different **properties**, and these studies could show reasons for the **improvement** or failure of composite processing while **defining** future criteria and standards for composite **evaluation**. APPENDIX A

DIELECTRIC PROPERTY CALCULATIONS

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#### APPENDIX A

#### DIELECTRIC PROPERTY CALCULATIONS

From Chapter 2, the following equations may be recalled for determining the values of  $\epsilon'$  and  $\epsilon''$  from oscilloscope patterns:

$$\frac{1}{2Q} - \frac{1}{2Q_0} = \epsilon'' ABG \frac{V_s}{V_c}$$
(2-4)

$$\frac{df}{f_0} = (e' - 1) ABG \frac{V_s}{V_c}$$
(2-5)

These two equations were considered valid for cylindrical **Samples** within a cylindrical microwave cavity operating in the  $TM_{012}$  mode. The following assumptions are made about the cavity and the sample:

The volume of the sample is negligible compared to the
 Volume of the cavity.

2. The perturbation of the electromagnetic field is not enough to destroy the resonant mode. The equations for its Pattern will still apply with the sample inside.

A method for measuring the dielectric properties of powdered samples was developed that did not require the evaluation of the constants A, B, and G. A solid Teflon rod was prepared with the same volume as the Teflon sample holders containing the powders. The six-inch microwave cavity was tuned to be resonant at 2.45 Ghz. The quantity  $\Delta f$ , the bandwidth at the half height of the Q curve, was measured and recorded. The solid Teflon rod was introduced to the cavity and the field patterns. The optimum position of the rod was determined by lowering the rod until the shift in the operating frequency was maximized. At this point, the shift in the frequency, df, and the power of the peak at half-height,  $\Delta f$ , were recorded.

The cavity was retuned to 2.45 GHz, and a holder containing the powder was lowered into the field. Once its position was determined, the same values were recorded from the oscilloscope pattern as for the Teflon. The information was now complete for the calculation of the dielectric properties by the developed method below.

Let the subscript t denote the properties and oscillo-SCOPE measurements referring to the Teflon and the oscillo-SCOPE measurements made while the Teflon cylinder was inside the cavity of the Teflon are:

$$\frac{1}{2Q_t} - \frac{1}{2Q_0} = e_t'' ABG \frac{V_t}{V_c}$$
 (A-1)

$$\frac{df_t}{f_0} = (e_t' - 1) ABG \frac{V_t}{V_c}$$
 (A-2)

Let the subscript s denote the Teflon holder loaded with the powder and the oscilloscope measurements made while the powder was inside the cavity. The resulting equations are:

$$\frac{1}{2Q_s} - \frac{1}{2Q_0} = \epsilon_s'' ABG \frac{V_s}{V_c}$$
 (A-3)

$$\frac{df_s}{f_0} = (e_s' - 1) ABG \frac{V_s}{V_c}$$
 (A-4)

By dividing the corresponding sample equations by the equations for the Teflon rod, the constants A, B, and G are dropped from the equations. This also removes the volume terms since the sample holders and the Teflon cylinder are assumed to have equal volumes ( $V_g = V_t$ ). The resulting equations for  $\epsilon'$  and  $\epsilon''$  become:

$$\frac{\frac{1}{Q_s} - \frac{1}{Q_0}}{\frac{1}{Q_t} - \frac{1}{Q_0}} = \frac{e_s''}{e_t''}$$
(A-5)

$$\frac{df_s}{df_t} = \frac{e_s^{\prime} - 1}{e_t^{\prime} - 1}$$
 (A-6)



Figure A-1. The teflon rod and the loaded sample holder used for comparative dielectric measurements.

This solution is not dependent upon the weight of the sample used. A slight error is introduced because of the lack of correction for the presence of air within the sample. The only difference introduced to the cavity from the loading of the powdered sample and the Teflon sample is the presence of the powdered sample in place of the solid Teflon center, as shown in Figure A-1. By substituting the known values for the dielectric properties of Teflon, the equations can be solved for the dielectric properties of the powder. For Teflon,  $\epsilon'$  is equal to 2.1 and  $\epsilon''$  is equal to 0.00033 at 2.45 GHz. The resulting equations are:

$$e_{g}^{\prime\prime} = 0.00033 \frac{\left[\frac{1}{Q_{g}} - \frac{1}{Q_{0}}\right]}{\left[\frac{1}{Q_{t}} - \frac{1}{Q_{0}}\right]}$$
 (A-7)

$$\boldsymbol{\varepsilon_g}' = 1 + 1.1 \left[ \frac{(df_g)}{(df_t)} \right]$$
 (A-8)

The program DIEL.FOR was written in FORTRAN to accept the values of the oscilloscope measurements from a data file and calculate the dielectric properties of the powdered samples.

The program also includes subroutines that perform statistical analysis upon repeated trials for the same material. The program listing is presented.

÷ DIELECTRIC CONSTANT CALCULATION AUTHOR: LARRY A. FELLOWS 11/17/88 This program will read experimental data generated by perturbation method in a microwave ÷ cavity and calculate the dielectric constants \* \* of the sample material. The method used calculates the material's constants using the ratio of the materials constants to Teflon's \* known constants. ÷ MATRIX NAMES: \* ÷ ID = a number assigned to identify the material tested \* DATE = the date the data was collected × TRIAL = number of the measurement\* = calculated value for the loss factor EP × EDP = calculated value for the dielectric × constant \* FC = frequency of resonance of empty \* cavity (GHz) \* DFC = width of frequency peak at half \* height (MHz) \* = frequency of resonance with Teflon FT × cylinder (GHz) × = width of peak at half power with DFT \* Teflon coupon (MHz) \* FTSH = difference in resonant frequency with \* the Teflon cylinder loaded (MHz) \* FS = frequency of resonance with \* \* powder sample loaded (GHz) \* \* = width of peak at half height with DFS \* powder sample loaded (MHz) \* FSSH = difference in resonant frequency with \* powder sample loaded (MHz) \* QC = empty cavity value for Q \* \* QT = value for Q with Teflon ÷ \* QS = value for Q with sample ÷ 

*	*		*
*	* SPECIAL MATRICES:		*
*	*		*
*	<pre>* DCIP6 = dielectri</pre>	ic constant of THERMID IP-600	*
*	<pre>* LFIP6 = loss fact</pre>	cor of THERMID IP-600	*
*	<pre>* DC610 = dielectri</pre>	ic constant of THERMID IP-6010	*
*	* LF610 = loss fact	cor of THERMID IP-6010	*
*	* DC615 = dielectri	ic constant of THERMID IP-6015	*
*	LF615 = loss fact	cor of THERMID IP-6015	*
*	* DC630 = dielectri	ic constant of THERMID IP-6030	*
*	LF630 = loss fact	cor of THERMID IP-6030	*
*	DCMC6 = dielectri	ic constant of THERMID MC-600	*
*	LFMC6 = loss fact	tor of THERMID MC-600	*
×	DCTH2 = dielectri	ic constant of THERMCON 2000	*
*	LFTH2 = loss fact	tor of THERMCON 2000	*
*	DCFA7 = dielectri	ic constant of THERMID FA-7001	*
*	LFFA7 = loss fact	tor of THERMID FA-7001	*
*	DC710 = dielectri	ic constant of THERMID FA-7010	*
*	LF710 = loss fact	tor of THERMID FA-7010	*
*	DC715 = dielectri	ic constant of THERMID FA-7015	*
*	LF715 = loss fact	tor of THERMID FA-7015	*
*	DCLR6 = dielectri	ic constant of THERMID LR-600	*
*	LFLR6 = loss fact	tor of THERMID LR-600	*
*	DCAL6 = dielectri	ic constant of THERMID AL-600	*
*	LFAL6 = loss fact	tor of THERMID AL-600	*
*	DCTPI = dielectri	ic constant of LARC-TPI	*
*	LFTPI = loss fact	tor of LARC-TPI	*
* 1	* * * * * * * * * * * * * * * * * * * *	*************************	**
	CHARACTER*15 NAME(1	L2),HEAD(7)	
	REAL EP(1000), EDP(1	L000),QC(1000),QT(1000),QS(1000)	
	PEAT ECTIONS DECT	1000\ FT (1000\ DFT (1000\ FTGH (10	000

CHARACIER\*15 NAME(12), HEAD(7)
REAL EP(1000), EDP(1000), QC(1000), QT(1000), QS(1000)
REAL FC(1000), DFC(1000), FT(1000), DFT(1000), FTSH(1000)
REAL FS(1000), DFS(1000), FSSH(1000)
REAL DCIP6(100), DC615(100), REF(12), DATE(1000)
REAL DCMC6(100), DC715(100)
REAL DCFA7(100), DC710(100), DC715(100)
REAL DCLR6(100), DC711(100)
REAL DCAL6(100), LF615(100), LF630(100)
REAL LFIP6(100), LF615(100), LF630(100)
REAL LFFA7(100), LF710(100), LF715(100)
REAL LFFA7(100), LF710(100), LF715(100)
REAL LFLR6(100), LF610(100)
REAL LFAL6(100), LF7110(100)

\* The input data is read from the file DIEL.DAT

open(unit=47,file='DIEL.DAT',status='OLD',form= &'FORMATTED',access= 'SEQUENTIAL',READ ONLY)

TRIAL(1) = 1

```
I=1
      READ (47, \star, END=20) ID(I), DATE(I), FC(I), DFC(I),
10
     \&FT(I),DFT(I),FTSH(I),FS(I),DFS(I),FSSH(I)
      TRIAL(I) = I
      I = I + 1
      IF (I.LE.1000) THEN
           GO TO 10
      ENDIF
20
      NUM = I-1
      DO 100 I = 1.NUM
           QC(I) = FC(I) * 2000/DFC(I)
           QT(I) = FT(I) * 2000/DFT(I)
           QS(I) = FS(I) * 2000/DFS(I)
           A = 1/QC(I)
           B = 1/QT(I)
           C = 1/QS(I)
           EDP(I) = 0.0003 * (C-A)/(B-A)
           EP(I) = 1 + (FSSH(I)/FTSH(I)) *1.1
100
      CONTINUE
      NAME(1) = 'THERMID IP-600'
      REF(1) = 600
      NAME(2) = 'THERMCON 2000'
      REF(2) = 2000
      NAME(3) = 'THERMID FA-7001'
      REF(3) = 7001
      NAME(4) = 'THERMID FA-7010'
      REF(4) = 7010
      NAME(5) = 'THERMID FA-7015'
             = 7015
      REF(5)
      NAME(6) = 'THERMID LR-600'
      REF(6) = 6003
      NAME(7) = 'THERMID AL-600'
      REF(7) = 6004
      NAME(8) = 'LARC-TPI'
      REF(8) = 160
      NAME(9) = 'THERMID MC-600'
      REF(9)
             = 6002
      NAME(10) = 'THERMID IP-6010'
      REF(10) = 6010
      NAME(11) = 'THERMID IP-6015'
      REF(11) = 6015
      NAME(12) = 'THERMID IP-6030'
      REF(12) = 6030
 500
         FORMAT(' ',A15,2x,I6,3x,F7.0,3x,F7.0,3x,
     &F7.0,3x,F6.3,4x,F8.6/) 400
 FORMAT('1',A8,10x,A4,6x,A2,8x,A2,8x,A2,5x,A8,2X,A10/)
 HEAD(1) = 'MATERIAL'
     HEAD(2) = 'DATE'
     HEAD(3) = 'Qc'
```

HEAD(4) = 'Qt'HEAD(5) = 'Qs'HEAD(6) = 'CONSTANT'HEAD(7) = 'LOSSFACTOR'**PRINT400, HEAD(1), HEAD(2), HEAD(3), HEAD(4), HEAD(5), HEAD(6),** &HEAD(7) DO 150 J=1,NUM IPR=0 DO 160 M=1,12 IF (ID(J).EQ.REF(M)) THEN PRINT 5OO, NAME(M), DATE(J), QC(J), QT(J), QS(J), EP(J), EDP(J) IPR = 99ENDIF 160 CONTINUE IF (IPR.EQ.0) THEN **PRINT\*** PRINT\*, 'ERROR. UNIDENTIFIED COMPOUND AT 160.' PRINT\* ENDIF 150 CONTINUE PRINT\* PRINT\* \* THE FOLLOWING WILL BREAK DOWN THE RESULTS AND SEND THEM \* THROUGH A STATISTICAL ANALYSIS PROGRAM TO COMPUTE THE \* AVERAGES FOR THE DATA. print 137 137 format('1'///) I1 = 0I2 = 0I3 = 0I4 = 0I5 = 0I6 = 0I7 = 0I8 = 0I9 = 0I10 = 0

> I11 = 0I12 = 0

```
DO 800 M=1,NUM
IF (REF(1).EQ.ID(M)) THEN
     I1 = I1 + 1
     DCIP6(I1) = EP(M)
     LFIP6(I1) = EDP(M)
ELSE IF (REF(2).EQ.ID(M)) THEN
     I2 = I2 + 1
     DCTH2(I2) = EP(M)
     LFTH2(I2) = EDP(M)
ELSE IF (REF(3).EQ.ID(M)) THEN
     I3 = I3 + 1
     DCFA7(I3) = EP(M)
     LFFA7(I3) = EDP(M)
ELSE IF (REF(4).EQ.ID(M)) THEN
     I4 = I4 + 1
     DC710(I4) = EP(M)
     LF710(I4) = EDP(M)
ELSE IF (REF(5).EQ.ID(M)) THEN
     I5 = I5 + 1
     DC715(I5) = EP(M)
     LF715(I5) = EDP(M)
ELSE IF (REF(6).EQ.ID(M)) THEN
     I6 = I6 + 1
     DCLR6(I6) = EP(M)
     LFLR6(16) = EDP(M)
ELSE IF (REF(7).EQ.ID(M)) THEN
     I7 = I7 + 1
     DCAL6(I7) = EP(M)
     LFAL6(I7) = EDP(M)
ELSE IF (REF(8).EQ.ID(M)) THEN
     I8 = I8 + 1
     DCTPI(I8) = EP(M)
     LFTPI(I8) = EDP(M)
ELSE IF (REF(9).EQ.ID(M)) THEN
     I9 = I9 + 1
     DCMC6(I9) = EP(M)
     LFMC6(I9) = EDP(M)
ELSE IF (REF(10).EQ.ID(M)) THEN
     I10 = I10 + 1
     DC610(I10) = EP(M)
     LF610(I10) = EDP(M)
ELSE IF (REF(11).EQ.ID(M)) THEN
     I11 = I11 + 1
     DC615(I11) = EP(M)
     LF615(I11) = EDP(M)
ELSE IF (REF(12).EQ.ID(M)) THEN
     I12 = I12 + 1
     DC630(I12) = EP(M)
     LF630(I12) = EDP(M)
ELSE
     PRINT*, 'UNIDENTIFIED COMPOUND IN TRIAL ', M
ENDIF
```

800 CONTINUE

IF (I1.NE.O) THEN CALL STAT(NAME(1), DCIP6, LFIP6, I1, HEAD(6), HEAD(7)) ENDIF IF (I2.NE.O) THEN CALL STAT (NAME(2), DCTH2, LFTH2, I2, HEAD(6), HEAD(7)) ENDIF IF (I3.NE.O) THEN CALL STAT (NAME(3), DCFA7, LFFA7, I3, HEAD(6), HEAD(7)) ENDIF IF (I4.NE.O) THEN CALL STAT (NAME (4), DC710, LF710, I4, HEAD (6), HEAD (7)) ENDIF IF (15.NE.O) THEN CALL STAT(NAME(5), DC715, LF715, I5, HEAD(6), HEAD(7)) ENDIF IF (I6.NE.O) THEN CALL STAT(NAME(6), DCLR6, LFLR6, I6, HEAD(6), HEAD(7)) ENDIF IF (I7.NE.O) THEN CALL STAT(NAME(7), DCAL6, LFAL6, I6, HEAD(6), HEAD(7)) ENDIF IF (I8.NE.O) THEN CALL STAT (NAME (8), DCTPI, LFTPI, 18, HEAD (6), HEAD (7)) ENDIF IF (I9.NE.O) THEN CALL STAT(NAME(9), DCMC6, LFMC6, I9, HEAD(6), HEAD(7)) ENDIF IF (I10.NE.O) THEN CALL **STAT(NAME(10)**, DC610, LF610, I10, HEAD(6), HEAD(7)) ENDIF IF (I11.NE.O) THEN CALL **STAT(NAME(11), DC615, LF615, I11, HEAD(6), HEAD(7))** ENDIF IF (I12.NE.O) THEN CALL STAT(NAME(12), DC630, LF630, I12, HEAD(6), HEAD(7))ENDIF END SUBROUTINE STAT (NAME, X, Y, N, XNAM, YNAM)

```
+
        NAME = The name of the material or experiment
+
             = The first set of values for statistical *
        X
          analysis
*
             = The second set of values for statistical *
        Y
          analysis
*
             = The number of trials for set X and Y
        N
        CHARACTER*15 NAME, XNAM, YNAM, HED(3)
        REAL X(100), Y(100)
        XSUM = 0
```

YSUM = 0XAVG = 0YAVG = 0IF ((N.EQ.0).OR.(N.GT.100)) THEN print\*,'Number of trials 0 or greater than 100.' print\*,'EXPERIMENT: ',NAME GO TO 5350 ELSE IF ((N.LT.20).AND.(N.NE.1)) THEN NTR = N-1ELSE IF (N.EQ.1) THEN XAVG = X(1)YAVG = Y(1)SDX = 0SDY = 0SXE = 0SYE = 0NTR = 1GO TO 5300 ELSE NTR = NENDIF DO 5000 I=1,N XSUM = XSUM + X(I)YSUM = YSUM + Y(I)5000 CONTINUE XAVG = XSUM/NYAVG = YSUM/NXWGH = 0YWGH = 0DO 5100 J=1,N XWGH = XWGH + (XAVG-X(J)) \* (XAVG-X(J))YWGH = YWGH + (YAVG-Y(J)) \* (YAVG-Y(J))5100 CONTINUE XVAR = XWGH/NTRYVAR = YWGH/NTRSDX = SQRT(XVAR)SDY = SQRT(YVAR)B = 1.0 \* NA = SQRT(B)SXE = SDX/ASYE = SDY/A5300 HED(1) = 'AVERAGE' HED(2) = 'STND DEVIATION'HED(3) = 'STND ERROR'

5555 FORMAT (//)

- PRINT 5555
- 5200 FORMAT(5X,A15,4X,A10,2X,A10,3X,A10,3X,I3,1X,'TRIALS'/) PRINT 5200,NAME,HED(1),HED(2),HED(3),N
- 5400 FORMAT(5X,A15,3X,F10.8,3X,E10.4,3X,E10.4/) PRINT 5400,XNAM,XAVG,SDX,SXE PRINT 5400,YNAM,YAVG,SDY,SYE
- 5350 PRINT 5555

RETURN END

LIST OF EQUIPMENT

APPENDIX B

# APPENDIX B

# LIST OF EQUIPMENT

Two different microwave sources were used for the microwave processing system. The setup presented in Figure B-1 and Table B-1 was the setup used for the microwave processing and measurements of powders and polyamic acids in either the  $TM_{012}$  or the  $TE_{111}$  modes. The six-inch cavity was used for the microwave processing of cylindrical samples and thin films. This setup was also used for finding and selecting modes for the processing of composites in the seven-inch diameter microwave cavity.

Figure B-2 and Table B-2 show the microwave setup for The processing of 3-inch square panels at a single frequency (2.45 GHz). The processing of powders and polyamic acids at high power were also performed with this setup, but the sixinch cavity was substituted for the seven-inch cavity.

Table B-3 lists other equipment used for thermal **Processing and analysis of the polyimides and polyimide Comp**osites.



Figure B-1. The microwave apparatus used for selecting modes and for diagnostic testing with the components listed in Table B-1.
able B-1. Microwave Setup for Sweeping Frequency Operation		
Component from Figure B-1	Description of Equipment	Model
(A)	Hewlett Packard Sweep Oscillator (with HP RF Plug-in)	8350B (8623A)
(B)	Marconi S/N 817 Isolator	<b>F6217-47</b>
(C)	Narda Coaxial Directional Coupler (-20 DB)	3043-20
(D)	Ferrite Control Co. Circulator	2620
(E)	Six-inch diameter microwave cavity developed at Michigan State University	
(F)	Hewlett Packard Power Sensor Power Meter	8482H 435B
(G)	Luxtron Fluoroptic Thermometry System	750

Luxtron Fluroptic Probes

Hewlett Packard

Power Sensor

Power Meter

Termaline Coaxial Resistor

Tektronix 485 Oscilloscope

NIW MIH ASC MIWR

8482**a** 

435B

8201

485

•

(H)

**(I)** 

(J) (X)

Table tion



Figure B-2. The microwave apparatus for operation at high power with equipment listed in Table B-2.

Component from Figure B-2	Description of Equipment	Model
(A)	Opthos Instruments Inc. Microwave Generator	MPG-4M- 297
(B)	Ferrite Control Co. Circulator	2620
(C)	Narda Coaxial Directional Coupler (-20 DB)	3043-20
(D)	Seven-inch diameter microwave cavity developed at Michigan State University	
(E)	Termaline Coaxial Resistor	8201
(F)	Hewlett Packard Power Sensor Power Meter	8482H 435B
(G)	Luxtron Fluoroptic Thermometry System	750
(H)	Luxtron Fluroptic Probes	MIW Mih Asc Miwr
(I)	Hewlett Packard Power Sensor Power Meter	8482 <b>X</b> 435B

Table B-2. Microwave Setup for Single Frequency Operation

## Table B-3. Equipment Used for the Processing and Analysis of Polyimide Naterials

DESCRIPTION OF EQUIPMENT	MODEL NUMBER
DuPont Instruments 910 Differential Scanning Calorimeter	910
DuPont Instruments 951 Thermogravimetric Analyzer	951
DuPont Instruments 9900 Computer/Thermal Analyzer	9900
Perkin Elmer Fourier Transform Infrared Spectrophotometer	1800
United Calibrations Corp. Mechanical Property Tester	<b>SFM-</b> 20
Carver Laboratory Press	30-12-4T
Carver Hydraulic Equipment "Time and Pressure" Motorization Package	
Blue M (General Signal) Oven	OV-490A-3
Blue M (General Signal) Programmable Oven	CW-6680F
Precision Scientific Thelco Oven	29
Fisher Isotemp Oven	230F
Sartorius Analytic Balance	A2008
Wahl RS210 Programmable Controller	R8-210
Research Tool Corporation Prepregger	30

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