Microwave Processing and Diagnosis of Chemically Reacting Materials in a Single-Mode Cavity Applicator

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Abstract—**On-line microwave processing and dielectric diagnosis of chemically reacting materials (epoxy/amine) have been successfully performed using a TM_{012}-mode cylindrical cavity at a frequency of 2.45 GHz in conjunction with fluoroptic temperature measurement. Complex permittivity measurements by this single-frequency technique are repeatable and consistent with those obtained by conventional swept frequency methods. The accuracy of complex permittivity measurements for both methods is within ±5 percent for permittivity (ϵ') and ±15 percent for loss (ϵ''). Both techniques are based on material–cavity perturbation theory. Perturbation equations for cylindrical shapes of the cavity and loaded material have been derived to account for volume variation of the sample due to thermal expansion. Complex permittivity of epoxy/amine as a function of the extent of cure and temperature was determined in order to monitor the chemical reaction progress during microwave processing.**

I. Introduction

THERMOSETTING resins are liquid materials that are converted to solids by the addition of heat. The conversion of liquid to solid is brought about by small chain polymer molecules reacting with curing agents or each other to form a cross-linked molecular network. Epoxy resins are one example of this class of materials. Epoxy resins contain epoxide groups which react via a ring-opening mechanism. A common epoxy/curing agent system is a DGEBA (diglycidyl ether of bisphenol A) /amine system. The materials in this study are a difunctional DGEBA resin (DER 332) and a tetrafunctional curing agent (diaminodiphenylsulfone, DDS). Functionality of resin or curing agent is determined by the number of reactive groups per molecule. The cross-linking occurs through reaction of terminal (chain ending) epoxy groups with amine groups, and subsequent reaction of epoxy groups with hydroxyl groups formed during the reaction. The progress of the reaction is defined in terms of the extent of cure or the percentage of available epoxide groups reacted.

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An alternative method of promoting reactions which require heat is to use microwave heating instead of conventional thermal heating. Many molecules contain polar groups which undergo molecular rotation due to thermal Brownian motion. Incident microwave radiation interacts with the polar groups in the molecules so that the normal random orientation of the dipoles becomes ordered. The molecules then relax to their normal random orientation. Since energy is required to hold the dipoles in place, the relaxation of the dipole is accompanied by transfer of thermal energy to the material. The relaxation is described by an exponential decay function with a characteristic relaxation time; when the frequency of the incident radiation is equal to the reciprocal of the relaxation time, the system is said to be in resonance. This resonant frequency, which is defined as the molecular resonant frequency, is a characteristic of the absorbing material and is independent of the resonant frequency of the microwave cavity. Molecular rotations tend to have relaxation times such that they resonate at microwave frequencies. Some of the advantages of microwave heating are: (1) selective and controlled heating due to absorption of microwave energy by polar groups, (2) decreased thermal degradation due to rapid uniform bulk heating, and (3) increased control of material temperature time profile and cure cycle. These advantages may cause microwave-cured materials to have superior mechanical characteristics when compared to conventionally cured materials. Some microwave experiments have been carried out in a TE_{01} waveguide [1], a TE_{10} waveguide [2], and multimode microwave ovens [3], [4]. Typically, temperature and power level were measured in these experiments. The results indicated that microwave heating initiated a rapid increase in temperature. Heat produced by the exothermic curing reaction significantly increased the temperature slope. The cure time using microwave heating was much less than that using thermal heating. The heat transfer mechanism was also different between microwave curing and thermal curing. The microwave energy directly heated the polymer; however, for the conventional thermal case, the mold was first heated and heat was subsequently transferred into the epoxy via conduction. These experiments showed that rapid cure and high efficiency of energy utilization can be

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obtained using microwave heating processes instead of thermal processes.

Nondestructive and on-line complex permittivity measurement techniques have been applied below microwave frequencies to monitor the epoxy polymerization reaction by several investigators. Delmonte [5] used aluminum foil electrodes to measure the complex permittivity as a function of time for three epoxy resins (DER 332, Epon 828, and Ciba Araldite 6020) with a curing agent (diethylenetriamine; DETA) at a frequency of 0.01 MHz and a temperature of 23.9 to 29.4°C. Uncured epoxy resins of lower molecular weight were found to have higher permittivity (ϵ') and loss (ϵ'') than those of higher molecular weight. It was concluded that the loss decreased before epoxy molecules approached an irreversible gel structure, abruptly increased around gelation, and then decreased due to continuous curing after gelation. They defined the time of maximum loss as the time of gelation. However, the permittivity slightly decreased before the gel structure formed and raidly decreased during reaction. Haran [6] has investigated the isothermal polymerization of DGEBA epoxy (Epon 828) with amine (DETA) as a curing agent by making complex permittivity measurements within the frequency interval from 330 Hz to 1 MHz and at constant temperatures of 30, 45, and 60°C using a specially designed electrode. The permittivity and loss showed the similar frequency dependence as described by Delmonte. The minima in the graphs of the loss as a function of time disappear and the maxima become flatter as frequency is increased. They found that the time of gelation and magnitude of the complex permittivity decreased with increasing temperature and frequency, which the authors conclude is due to molecular absorption phenomena.

Kranbuehl [7] used a low-frequency impedance analyzer to monitor the polymerization of epoxy resin (Epon 828) cured with an unidentified curing agent between heating plates at three frequencies, 0.125 kHz, 5.0 kHz, and 0.5 MHz, and one temperature, 30°C. Complex permittivity–time graphs have the same profile as those obtained by other investigators, but minima in the loss curve disappear when the working frequency is decreased to 0.125 kHz. Day [8] used the dielectric sensor (microdielectrometry) in a preheated conventional oven by sweeping frequencies from 0.1 Hz to 0.01 MHz to study effects of stoichiometric mixing ratio on isothermal epoxy (Epon 828/DDS) cure by dielectric measurement at 177°C. Again, the complex permittivity profiles are the same as before and minima in the loss curve disappear when the frequency is decreased to 10 Hz. The tendency of the minima in the loss curve as the frequency changes is completely different between Haran's and Day's experiments. These phenomena are not fully understood, but might be due to interaction of complicated molecular relaxations at low frequencies.

An on-line sweeping frequency dielectric diagnostic technique using material–cavity perturbation has been applied to monitor a chemical reaction at microwave frequencies [9], [10]. Terselius [9] used a TM_{010} cylindrical cavity with a thermostat-controlled heating oven to make on-line measurements of the complex permittivity of rod-shaped vulcanizing rubber and polyethylene compounds at 2.8 GHz. TM_{010} cavity perturbation techniques were used to measure ϵ' (permittivity) from 2 to 10 and ϵ'' (loss) from 0.05 to 1.0. It was suggested that a TM_{012} cavity would be more suitable for higher loss materials. Martinelli [10] used a cylindrical TE_{011} cavity at 9.5 GHz to on-line measure dielectric properties of thermo- and photo-initiated polymerization of polymers heated by hot flowing nitrogen or UV light. The extent of polymerization reaction was related to the changes of dielectric properties.

New methods in microwave processing combined with on-line dielectric diagnostic technique have also been developed. Couderc [11] heated several materials up to 600°C using a heating mode of TM_{010} at 2.45 GHz, and simultaneously diagnosed dielectric properties of materials using measurement modes of TE_{11} at 3.1 GHz and TM_{012} at 3.7 GHz for spherical and rodlike materials, respectively. Temperature measurements were made using an IR radiation thermometer. The sample was placed at the position of the strongest and most uniform electric fields for both heating and measurement modes in the cylindrical cavity. The heating and measurement modes were individually coupled without any cross-coupling. The accuracy of dielectric measurements during microwave heating was ± 3 percent for ϵ' and ± 15 percent for ϵ''. Huang [12] used a TM_{010}-mode resonant cavity operated at 2.45 GHz to heat Nylon 66 in an overcoupled condition and used thermocouples for temperature measurement. On-line control of thermal runaway due to dielectric changes in Nylon 66 during microwave heating was successfully accompanied by matching impedance.

Conventional dielectric measurements at microwave frequencies using cavity perturbation usually employ sweeping frequencies along with a resonant cavity of fixed cavity dimensions to measure the changes in the resonant frequency and the Q-factor of the cavity with and without a loaded material. Application of on-line dielectric diagnosis during microwave curing of epoxy in a swept resonant cavity has been previously described [13]. However, most of the incident power supplied from the swept energy source is reflected and cannot be coupled to the material. Therefore, a single-frequency dielectric measurement technique is developed to improve the power efficiency during microwave processing of materials at the same diagnosis mode. This single-frequency technique has also been previously described [14]. The objective of this study is to process and to on-line diagnose dielectric properties of reacting polymers using a single-mode microwave resonant cavity at a single frequency. An early example of this heating and measurement technique using small nylon and water loads has been reported [14]. Here a chemically reacting load (epoxy/amine) is heated and diagnosed in a single electromagnetic mode at a single frequency of 2.45 GHz. The experimental conditions are selected so that a perturbation approximation is satisfied.

Since the relaxation time for an epoxy/amine mixture changes with temperature and extent of cure, it is not

possible to identify a single molecular resonant frequency for the system. This research is instead focused on determining how complex permittivity of DER 332/DDS mixtures depends upon temperature and extent of cure at a single frequency of 2.45 GHz. The frequency of 2.45 GHz is selected due to commercial availability of low-cost energy sources operating at this frequency for future industrial application. These experiments are carried out in the TM_{012} mode. The TM_{012} cavity loaded with materials can be continuously tuned to critically couple with a microwave external circuit by adjusting the cavity length and the field excitation probe depth. A fluoroptic temperature-sensing device, which does not interfere with fields in the microwave environment, is used to on-line measure material temperature. These temperature measurements are then used to modify the results of dielectric measurements due to volume changes caused by thermal expansion.

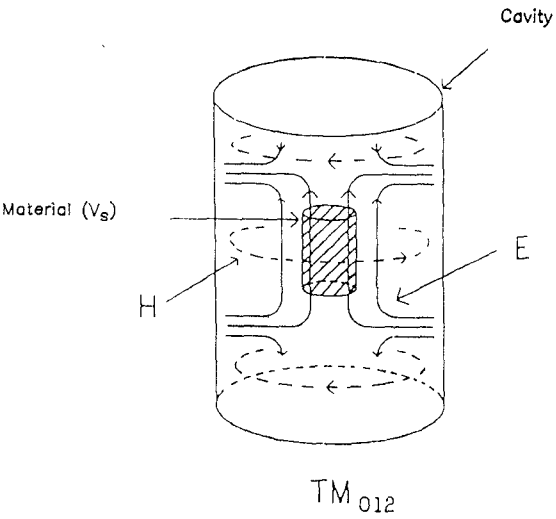

Fig. 1. *E*- and *H*-field patterns in the cylindrical TM_{012}-mode resonant cavity.

II. Material–Cavity Perturbation Method

Dielectric measurement by cavity perturbation techniques at microwave frequencies has been well developed and widely used to accurately determine the complex permittivity of materials from low loss to high loss (ϵ' up to 80 and ϵ'' up to 40) by many investigators [15]–[30]. Using standard material–cavity perturbation techniques, equations have been derived for a cylindrical TM_{012}-mode cavity. A diagram of the field patterns in the TM_{012}-mode loaded cavity is shown in Fig. 1 and perturbation equations are listed as follows:

$$df/f_0 = (\epsilon' - 1)ABGV_s/V_c \tag{1}$$

$$(1/Q_s - 1/Q_c) = 2\epsilon'' ABGV_s/V_c \tag{2}$$

where

$$A = J_0(2.405R_s/R_c)^2 + J_1(2.405R_s/R_c)^2$$

$$B = 1 + [L_c/(2\pi L_s)]\sin(2\pi L_s/L_c)\cos(4\pi H/L_c)$$

$$G = = 0.2718[v_0/(f_0 R_c)]^2$$

$$df = f_0 - f_s.$$

The permittivity of the sample is ϵ' and the loss of the sample is ϵ''. The lengths of the loaded sample and the cavity are L_s and L_c, respectively. The radius of the loaded sample is R_s and the radius of the cavity is R_c. The volumes of the loaded sample and the cavity are V_s and V_c, respectively. The resonant frequencies of the unloaded cavity and the loaded cavity are f_0 and f_s, respectively. The quality factors of the unloaded cavity and the loaded cavity are Q_c and Q_s, respectively. The speed of light is v_0. The height of the sample above the bottom of the cavity is H.

Assumptions used in deriving the above equations are (1) f_s is very close to f_0 (i.e., $df/f_0 < 1$ percent); (2) $1 \ll Q_c$ and $1 < Q_s$; (3) the loaded sample must be cylindrical and placed along the longitudinal axis of the cavity; (4) the diameter of the sample is less than the free-space wavelength so that the quasi-static approximation for the electric fields is valid inside and outside the sample; and (5) integration of radial electric fields over the entire sample is negligible compared to that of axial electric fields. Assumption (5) suggests that the sample is placed at a position of maximum axial electric fields and minimum radial fields, and has a length approximately one quarter of the free-space wavelength so that radial electric fields can be neglected compared to the axial electric fields integrated over the entire sample volume. Assumption (4) suggests that the radius of the sample should be less than one twentieth of the free-space wavelength. Assumption (3) suggests that the length-to-radius ratio of the sample should be greater than 4.5 to obtain a cylindrical shape. From experimental experience, the volume ratio of the sample to the cavity is usually much less than 0.1 percent for $\epsilon'' > 1$ and much greater than 0.1 percent for $\epsilon'' < 0.001$.

The accuracy of complex permittivity measurement of materials by cavity perturbation is related to the volume size of the sample and the cavity. In this study, the sample volume due to thermal expansion significantly increased, by 6 percent and 10 percent at temperatures of 170 and 260°C, respectively. Therefore, continuous monitoring of sample temperature is required to account for the volume change of the sample during microwave heating. However, errors caused by the cavity thermal expansion are negligible (about 0.02 percent of the original cavity volume) [31]. An air temperature change from 25°C to 170°C produces a cavity resonant frequency shift of 0.065 MHz due to the change in relative humidity [32]. The resonant frequency shift due to relative humidity change is also negligible compared to the resolution of the frequency marker.

The complex permittivity of the material itself is a function of material composition, material temperature, excitation frequency, and the electric field strength. It also depends on the time history of material structure response due to temperature, pressure, and the applied electric

fields. Modified perturbation equations for microwave processing and diagnosis of chemically reacting materials then can be expressed as follows:

$$df/f_0 = [\epsilon'(X,T,f_0)-1]ABGV_s(T)/V_c \quad (3)$$

$$(1/Q_s - 1/Q_c) = 2\epsilon''(X,T,f_0)ABGV_s(T)/V_c \quad (4)$$

$$V_s(T) = V_s(T_0)[1+\alpha(T-T_0)]^3. \quad (5)$$

The thermal expansion coefficient of the material is α. The original volume of the material at a temperature of T_0 is $V_s(T_0)$. The material temperature is T. The extent of cure is X. The working frequency is f_0.

III. Experiments

A. Experimental System

The experimental system for microwave processing and diagnosis is shown in Fig. 2. The microwave energy source is an HP 8350B sweep oscillator connected by an HP 11869A adapter with a 1.7–4.3-GHz HP 86235A RF plug-in. The resolution of the frequency markers in this sweep oscillator is 0.1 MHz. The source incorporates a Varian TWT amplifier (VA-1356S) which can amplify the signal from 0 to 27 W. An isolator (King KN-59-38) is used to protect the energy source. A circulator (Ferrite Control Co. Model 2620) is used to isolate the reflected power P_r from the input power P_i. Two 20-dB directional couplers (Narda Model 30020) are used to monitor the incident signal and the reflected signal. Both incident and reflected signals are attenuated and directly measured by power meters (HP435B). The reflected signal is rectified by a crystal detector and displayed on an $X-Y$ oscilloscope (Tektronix 485) whenever the swept frequency method is employed. The oscilloscope is used to display the resonance absorption curve which is used to determine the resonant frequency and the Q factor of the empty cavity. The measurement error is less than ± 0.06 percent for the resonant frequency and less than ± 5 percent for the Q factor.

A cylindrical brass cavity applicator was designed as reported earlier [14] for processing of rod-shaped material loads. The radius of this cavity was 7.62 cm. The optimum sample dimensions and volumes were determined experimentally for precise complex permittivity measurement to allow the use of cavity perturbation theory. The sample volumes of epoxy ranged from 1.5 to 3.5 cm^3. A cylindrical Teflon sample holder 0.476 cm in radius was found to be suitable for this application. The similarity in shapes of the applicator and loaded material was selected in order to facilitate diagnosis, modeling, and theoretical analysis. A diagram of this cylindrical cavity is shown in Fig. 3. The cavity was made of a cylindrical brass tube (15.25 cm ID, 25.40 cm long, and 0.318 cm thick) covered with three transverse circular brass short plates. One sliding short plate was built in the cavity so that the internal cavity lengths could be adjusted from 4.5 to 22.9 cm. The sample loads were placed in the cavity through 1.275-cm-radius holes located at the center of the two top plates. A

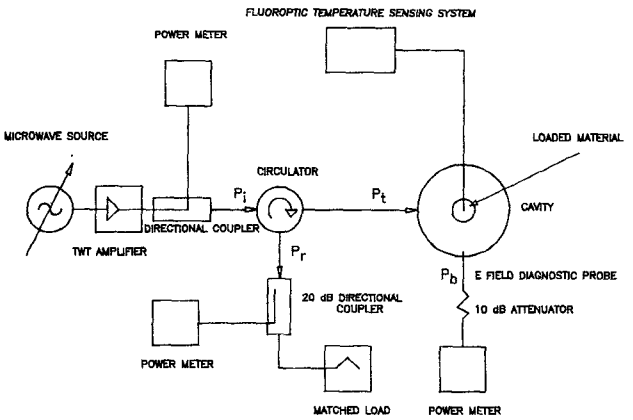

Fig. 2. Experimental microwave system circuit.

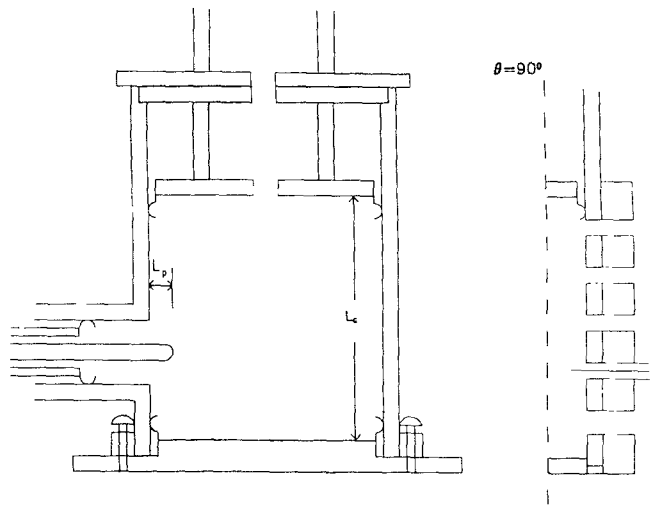

Fig. 3. Cross-sectional view of the cylindrical cavity (the $\theta = 0$ plane passes through the excitation probe).

removable bottom plate was designed to be able to place large-radius (greater than 1.275 cm) materials. Silver fingers (Varian CF 300) were soldered around both movable short plates to provide good electrical contact with the cavity wall. A semirigid 50-Ω copper coaxial probe served as a field excitation and coupling probe; it had an outer conductor 1.275 cm in diameter and an inner conductor 0.442 in diameter. This probe was located 3.81 cm above the cavity bottom plate and provided a variable inner-conductor depth of 0.0 to 40.00 mm to couple microwave power into the cavity. Adjustments of the cavity length and the coupling probe depth were made by manual rotation of the knobs and measured within 0.01 mm by the micrometer indicators. The TM_{012}-mode cavity with or without the sample was always tuned to critically couple with the external circuit by manual adjustments of the cavity length and the probe depth. The cavity length and the coupling probe depth for the entire microwave processing of epoxy in the TM_{012} mode at a selected frequency of 2.45 GHz ranged from 15.336 to 15.400 cm and from 1.520 to 1.726 cm, respectively.

A rectangular brass block soldered outside the cavity wall had 16 field diagnostic holes 2.26 mm in diameter,

equally spaced 0.922 cm apart. The diagnostic holes were drilled through the cavity wall and the lowest hole was located 0.635 cm above the cavity bottom plate. A 2-mm microcoaxial probe was inserted into the cavity applicator through the fifth diagnostic hole (4.32 cm above the bottom plate), where the probe could diagnose almost the maximum magnitude of the TM_{012} standing radial wave near the cavity wall at a frequency of 2.45 GHz. The penetration depth of the inner conductor of the diagnostic probe was about 1.5 mm where the probe did not disturb the field pattern and the resonant frequency. The diagnostic probe was connected through an attenuator to a power meter (HP432A). This probe served as a radial electric field diagnostic probe which directly measured the power P_b proportional to the square of the radial electric field near the wall ($P_b = K_b|E_r|^2$).

A fluoroptic thermometer (Luxtron Model 750) was used to continuously monitor the center temperature of the sample. The accuracy of temperature measurement was $\pm 0.1°C$. The fluoroptic probe was protected by a 3-mm-od Pyrex capillary tube and placed in the center of the Teflon holder. A Teflon holder was required to contain the unreacted liquid epoxy–amine mixture. The Teflon holder was suspended in the center of the cavity by a cotton thread. The Teflon holder was 3.5 cm long with a 0.476-cm inner radius and a 0.635-cm outer radius. Several advantages for using Teflon as a sample holder are a very low loss, temperature-independent complex permittivity, high temperature resistance (up to 260°C), and chemical inertness of reactants and products [13]. The cavity with the empty Teflon holder and a fluoroptic probe was considered as an unloaded cavity, while the cavity with the epoxy-filled Teflon holder was loaded. The Q value of this unloaded cavity was about 11000 at 2.45 GHz. The Q value of the loaded cavity varied from 100 to 3000 at the same frequency during processing.

B. Materials

The epoxy resin for this study was DER 332, manufactured by Dow Chemical Co. The epoxy resin was chemically stable before reaction with a curing agent. Diaminodiphenylsulfone (DDS) was chosen as a curing agent. DER 332 was heated up to 125°C and well mixed with equivalent moles of DDS. An equivalent molar mixture of DER 332 and DDS was prepared by mixing 100 parts resin with 36 parts curing agent by weight. In this study, the epoxy has been partially cured; the extent of cure using differential scanning calorimetry was determined to be 23 percent. The volumes of samples were 2.00 and 2.35 cm^3. The resonant frequency shifts were less than 1 percent of the resonant frequency of the unloaded cavity during the course of microwave processing for these epoxy–amine volumes.

C. Experimental Dielectric Diagnostic Technique

The experimental dielectric diagnostic technique is a single-frequency method which is to critically couple the cavity with the external microwave circuit at a selected resonant frequency and mode by adjusting the cavity length L_c and the excitation probe depth L_p to obtain a zero reflected power P_r compared to the input power P_t. Since experimental measurements of the axial variation of the radial electric field near the cavity wall show a similar standing wave for the cavity with and without different loaded materials, the quality factor Q of the loaded cavity can be determined by (6). Therefore, only measurements of the ratios of the square of the radial electric field at a fixed position, the quality factor of the unloaded cavity, and the total dissipated powers into the unloaded and the loaded cavity are required to calculate the quality factor of the loaded cavity. The measurements of L_c and L_p for the unloaded and the loaded cavity at the same frequency and mode are also required to determine the resonant frequency shift. The resonant frequency shift of the unloaded and the loaded cavity is equal to the resonant frequency difference of the empty cavity at different configurations of $L_c$and L_p corresponding to the unloaded and the loaded cavity.

$$Q/Q_0 = \left(|E_r|^2/|E_{r0}|^2\right)(P_{t0}/P_t) = (P_b/P_t)/(P_{b0}/P_{t0}) \tag{6}$$

where

$$P_{b0} = K_b|E_{r0}|^2 \quad \text{and} \quad P_b = K_b|E_r|^2$$
$$P_{t0} = P_{i0} - P_{r0} \quad \text{and} \quad P_t = P_i - P_r.$$

The dissipated power of the diagnostic probe at a fixed penetration depth of 1.5 mm away from the cavity wall is P_b for the loaded cavity and P_{b0} for the unloaded cavity. The effective coefficient of the diagnostic probe is K_b. The input and reflected powers of the loaded and the unloaded cavity are P_i, P_r, P_{i0}, and P_{r0}, respectively. The dissipated powers into the loaded cavity and the unloaded cavity are P_t and P_{t0}, respectively.

In this single-frequency technique of monitoring a chemically reacting material, initial measurements of the dissipated power for the diagnostic probe P_{b0} and the empty cavity P_{t0} were made when this empty cavity was tuned to critically couple with the microwave external circuit at a specific cavity length (at a selected frequency of 2.45 GHz and TM_{012} mode). The critical coupling of the cavity was accomplished by adjusting the excitation probe depth L_p so that the reflected power P_{r0} was close to zero compared to the incident power P_{i0}. The quality factor Q_0 of this critically coupling empty cavity at the same position of L_c and L_p was then measured from the cavity resonance curve on the X–Y oscilloscope using a conventional swept frequency method.

After these initial measurements, a Teflon sample holder with a fluoroptic probe was suspended along the center axis of the cavity by a cotton thread. This cavity was called an unloaded cavity. The critically coupling tuning of this unloaded cavity was preceded by a manual adjustment of L_c and L_p at the same frequency and mode. The measurements of P_b, P_t, L_p, and L_c were then made. The value of the quality factor Q_c of this unloaded cavity was calculated by (6). The holder was removed and the resonant

frequency f_0 of the empty cavity was measured by the swept frequency method. The holder was then filled with the material to be processed and was placed at a position of the maximum axial electric fields (around the center axis of the cavity). This cavity is called the loaded cavity. L_p and L_c of the loaded cavity were manually readjusted to critically couple at the same selected frequency and low input power level (10 to 14 mW). Input power was then raised to the desired level and the loaded material was heated electromagnetically. As the material was heated, its complex permittivity changed so that the loaded cavity tended to become untuned. Therefore, the loaded cavity was continuously tuned to a critically coupled condition by manually adjusting L_c and L_p to maintain a zero reflected power compared to the incident power during the microwave heating process. At selected time intervals, the dissipated power of the loaded cavity and the diagnostic probe as well as the cavity length and probe depth were measured. The value of the quality factor Q_s of the loaded cavity was determined for each measurement using (6). After completing the heating process, the loaded material was removed and the resonant frequency f_s for each set of L_c and L_p measured during the processing was determined by the swept frequency method. The resonant frequency shift (df) was then calculated. On-line temperature measurement of the sample was made during the entire microwave heating process. The complex permittivity of the material was then determined for each data point using (3) and (4).

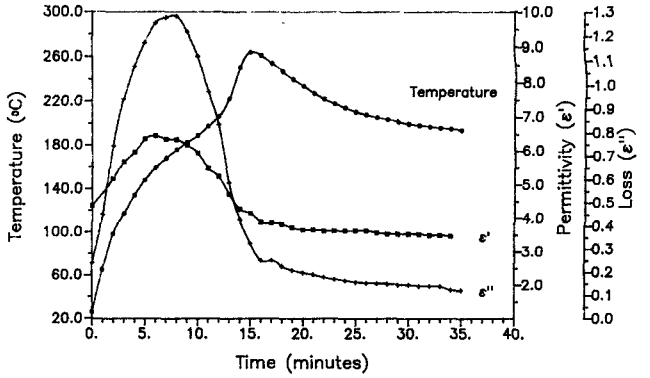

Fig. 4. Temperature and complex permittivity versus microwave cure time. Average P_i: 5.7 W, sample volume: 2.35 cm^3, f_0: 2.458 GHz.

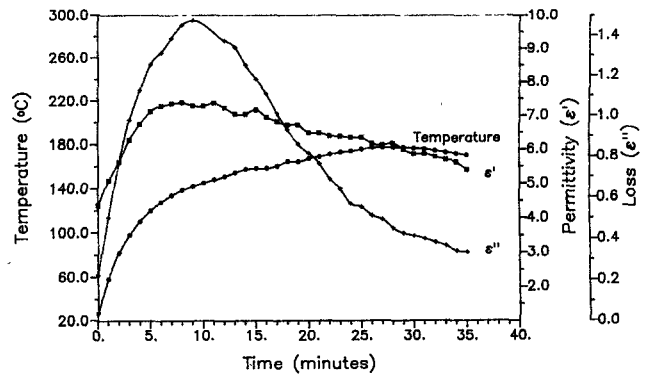

Fig. 5. Temperature and complex permittivity versus microwave cure time. Average P_i: 4.3 W, sample volume: 2.00 cm^3, f_0: 2.450 GHz.

IV. Experimental Results and Discussion

The temperature, permittivity, and loss are plotted as a function of time during microwave diagnosis and processing of epoxy in Figs. 4 and 5. The permittivity and loss as functions of temperature are shown in Figs. 6 and 7. As previously mentioned, the initial extent of cure for this epoxy mixture was 23 percent. The final extent of cure was 75 percent for an average input microwave power level of 5.7 W and 64 percent for an average input power level of 4.3 W for a total processing time of 35 minutes at a frequency of 2.45 GHz. The purpose of these reported experimental results is to document the methodology of simultaneous measurement of the complex permittivity and temperature profiles during a reaction in which the complex permittivity of the products differs from that of the reactants. Therefore, these results do not represent an optimal cure cycle.

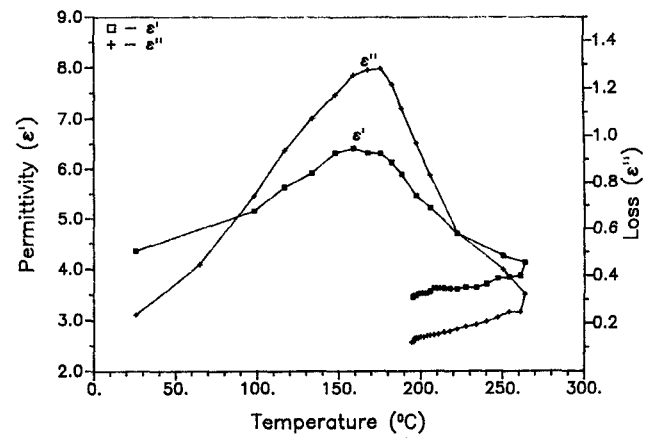

Fig 6. Complex permittivity versus temperature during microwave heating. Average P_i: 5.7 W, sample volume: 2.35 cm^3, f_0: 2.458 GHz.

The dielectric properties increased with increasing temperature until a temperature of about 160°C was reached. The dielectric properties subsequently decreased after this point due to the curing reaction. After the reaction was completed, it was shown that the dielectric properties of the cured epoxy decreased with decreasing temperature. This once again demonstrates [13] that the dielectric properties increase with increasing temperature and decrease with increasing extent of cure. The dielectric measurements during the heating cycle were carried out using a single-frequency method while the dielectric measurements during the cooling cycle were conducted using a swept frequency method. Results of both techniques are presented in Fig. 7. The continuity between the heating and cooling curves is apparent. The error associated with dielectric measurements for both single and swept frequency methods is less than ± 5 percent for permittivity and less than ± 15 percent for loss. This clearly demonstrates the consistency of the two methods.

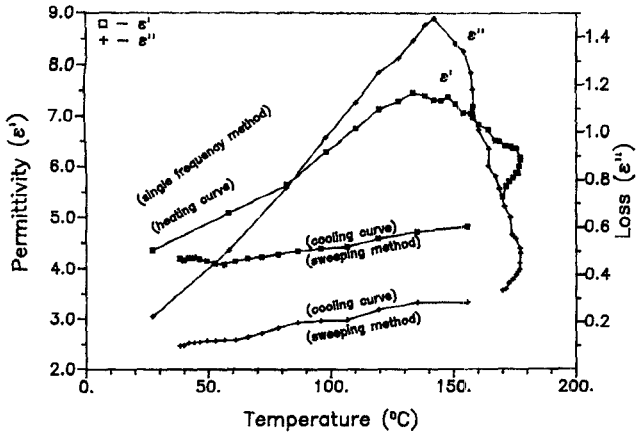

Fig. 7. Complex permittivity versus temperature for microwave heating and convective cooling. Average P_i: 4.3W, sample volume: 2.00 cm^3, f_0: 2.450 GHz.

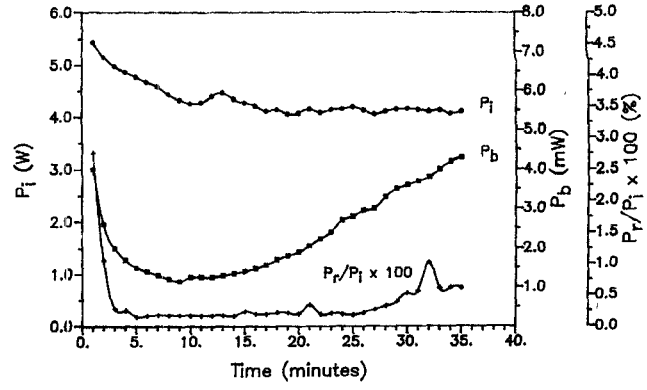

Fig. 8. Power measurements versus microwave cure time at 2.450 GHz.

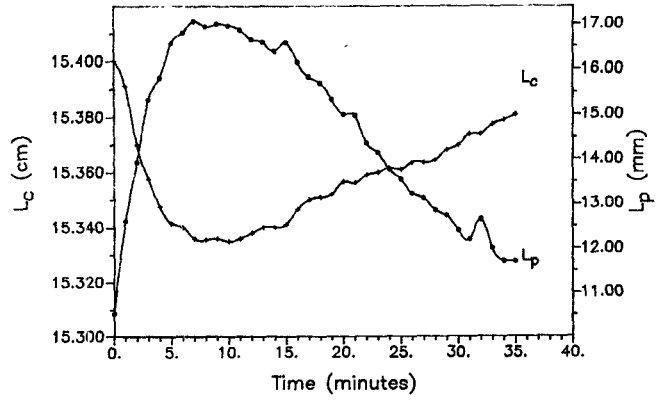

Fig. 9. Cavity length and excitation probe depth versus microwave cure time at 2.450 GHz.

Epoxy systems approach molecular resonance as they are heated so that absorption tends to increase with temperature. However, once the reaction has progressed to a significant extent, the dipoles can no longer rotate freely due to the formation of a cross-linked molecular network. This moves the molecular resonant frequency of the absorbing material away from the microwave region with a consequent loss of microwave absorption. The net result is that epoxy/amine systems tend to adsorb increasing amounts of microwave power initially as the system heats followed by decreased absorption as the system cross-links. These systems would therefore be expected to have complex permittivity which increases during the initial heating and which decreases as the reaction progresses.

Comparison of Figs. 4 and 5 shows that this is indeed the case for the epoxy/amine systems studied. The parameter (ϵ'') which governs the energy absorption increases initially and then decreases as the reaction progresses. Quantitative knowledge of how the complex permittivity changes with temperature and reaction extent is necessary so that absorption phenomena can be predicted. This in turn would allow optimal cure cycles to be properly selected. Constant temperature in the sample could be achieved by varying the input power level during the course of the reaction. Critical coupling of the TM_{012}-mode loaded cavity at a selected resonant frequency of 2.45 GHz is always accomplished by adjusting the cavity length and the coupling probe depth so that the reflected power is negligible compared to the incident power. An example of on-line measurements of P_b, P_i, P_r, L_c, and L_p during microwave curing of epoxy in a TM_{012}-mode cavity at a single frequency of 2.450 GHz is shown in Figs. 8 and 9. These results indicate that this microwave processing and diagnostic technique can efficiently transfer most of the input power into the loaded cavity and can be used to diagnose the complex permittivity of the loaded material. Also, this technique can be adaptable to intelligent, automatic processing during microwave heating in a single-mode resonant cavity at a single frequency.

V. Conclusions

This work successfully demonstrates the use of a microwave single-mode resonant cavity applicator at a single frequency in conjunction with fluoroptic temperature measurement to process and to on-line diagnose curing of epoxy resin. Consistent results were obtained for both single-frequency and conventional swept methods as previously reported [13]. A limitation of using perturbation is that the method requires a small material volume related to the cavity. Further research will be focused on determination of the energy absorption by materials and determination of fields in the cavity to diagnose the complex permittivity of materials for a wider range of sample shapes and volumes.

Future research will be directed towards development of intelligent, automatically controlled microwave processing with feedback diagnostic measurements to select optimal cure cycles for epoxy which can provide rapid, uniform bulk heating to reduce thermal degradation which usually occurs in conventional thermal curing processes. These microwave processing and diagnostic techniques can be applied to the heating of foods, and semiconducting and biological materials, the processing of thermoplastics, and the curing of polymers and composite materials. Curing of composite materials is complicated by the inclusion of conducting (graphite) or nonconducting (glass) fibers in

the bulk matrix. The effect of the presence of such materials has yet to be completely assessed.

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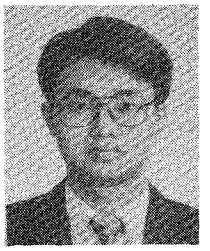

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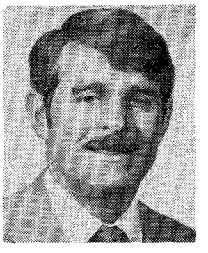

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Dr. Asmussen has authored numerous technical papers, holds several U.S. patents, and has served as a consultant to private industry and government agencies in both the wind energy and plasma technology areas. He is a member of Eta Kappa Nu, Tau Beta Pi, and Sigma Xi. Dr. Asmussen is a member of the Executive Committee of IEEE Plasma Science and Applications and a member of the AIAA Technical Committee on Electrical Propulsion.

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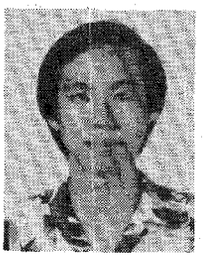

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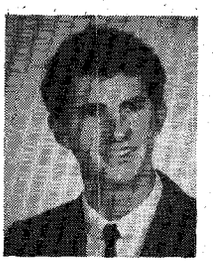

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