DIELECTRIC PROPERTIES OF POLYMERS AT MICROWAVE FREQUENCIES

by

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(ABSTRACT)

The measurement of the dielectric properties of a polymer system is an important physical characterization technique. With the ability to use microwave radiation for curing of polymer systems, the measurement of the dielectric properties at microwave frequencies is vital. Two polymer systems that have been investigated in this work are the epoxide system of EPON 828/ 4,4' DDS (diaminodiphenyl sulfone) and a series of well defined polystyrenes with varying end groups and end group concentrations. The Hewlett-Packard network analyzer has been used to measure both the real and imaginary parts of the dielectric in the frequency range of 1-18 GHz. Both coaxial airline and wavequide techniques were used.

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INTRODUCTION

The study of the dielectric properties of a polymer system is an important physical characterization technique. The dielectric behavior (permittivity) of a polymer system is a measure of the response of that system to an applied alternating electric field. The permittivty is a function of time, temperature, and frequency. Concurrent with the use of microwave radiation for curing of polymer systems, the measurement of the permittivity at microwave frequencies is important.

The permittivity is mathematically expressed as a complex number, where both the real and imaginary terms have physical interpetations. The permittivity or dielectric real constant (ϵ') is oftened referred to as the dielectric constant or the relative dielectric constant. It can be used to monitor the change of the electric field when a polymer is placed in a microwave cavity to be heated. The dielectric imaginary constant (ϵ'') often referred to as the dielectric loss or loss factor, reflects the ability of a polymer system to generate heat when placed in an electric field.

The permittivity at low frequencies (1Hz-10KHz) has been extensively studied for a range of polymer systems[1,2,3,4]. Studies at microwave frequencies have been difficult and time consuming. However the availability of automated network analyzers enables these measurements to be made quickly and precisely. The frequency range availiable with the Hewlett-Packard (HP) network analyzer is 45MHz-

26.5GHz.

The polymer systems that have been investigated include an epoxide system of EPON 828/4,4' DDS (diaminodiphenyl sulfone) and a series of well defined polystyrenes with varying end groups and end group concentrations. The epoxide system was studied for two reasons. 1) To measure the permittivity at microwave frequencies as a function of cure and 2) to use the dielectric data obtained to automate a microwave cavity so as to provide maximum power as the epoxy is cured by microwave radiation.

The polystyrene samples were very low molecular weight polymers, terminated with polar end groups. A series of the polystyrenes were hydroxyl terminated with varying molecular weights to provide different concentrations of the hydroxyl end group. All the samples had very narrow molecular weight distributions. These samples were measured to determine the effect of polar groups and polar group concentration on the permittivity.

LITERATURE REVIEW

The literature review is divided into three basic areas, dielectric behavior, polymers, and curing techniques. The first section is a review of fundamentals and provides mathematical equations and definitions. The other two sections outline theoretical concepts and provide references to the work that has been done in these areas.

A. Dielectric Behavior

A dielectric material is defined as any nonconducting material. When a dielectric material is placed in an electric field the response of that material is measured by the permittivity. A.R. Von Hippell (ed.) [5] and A.Chelkowski[6] provide excellent references for the review of dielectrics. When two parallel plates in a vacuum are seperated by a distance, d, the capacitance of the circuit is given as $C_o=q/V$. The subscript donates a vacuum, q is the charge, and V is the voltage. If a dielectric material is placed between the plates and the equivalent voltage applied the capacitance will increase and is given as $C=q/V$. It is the ratio of the two capacitances that provides a definition of the dielectric real constant, ϵ'. The equation is written as:

$$C/C_o = \epsilon / \epsilon_o = \epsilon_r = \epsilon' \qquad (1)$$

Therefore the relative dielectric is also a ratio of a materials dielectric permittivity to that of free space. The dielectric

susceptibility, χ', is a parameter that is often used instead of the dielectric constant. The real component of the dielectric susceptibility χ', is defined as

$$\chi' = \Delta C/C_o \qquad (2)$$

where C is the change in capacitance. The dielectric constant and dielectric susceptibility are related as follows:

$$\chi = \epsilon - 1 \qquad (3)$$

$$\chi' = \epsilon' - 1 \qquad (4)$$

When a voltage is applied in a vacuum capacitor the current, I_o, is 90^o out of phase with the voltage (Figure 1). If a completely loss-free or inelastic material is placed in the capacitor the current, Δ i, will again follow the voltage by 90^o. A capacitor filled with a completely elastic material will have a current, i_s, that flows in phase with the voltage. A lossy material is neither completely inelastic nor elastic, and the phase difference, or angle, between the current and voltage will be less than 90^o.

There are two parameters, δ and ψ, referred to as dielectric loss angles, that can be used to describe the behavior of a lossy material. The tangent of these two angles provides a relationship between the real and imaginary parts of the permittivity or the dielectric susceptibility.

$$\tan \delta = \epsilon'' / \epsilon' \qquad (5)$$

$$\tan \psi = \chi'' / \chi' \qquad (6)$$

The imaginary values of the dielectric constant and dielectric susceptibility are equal. The equivalent electrical circuit is shown in Figure 2.

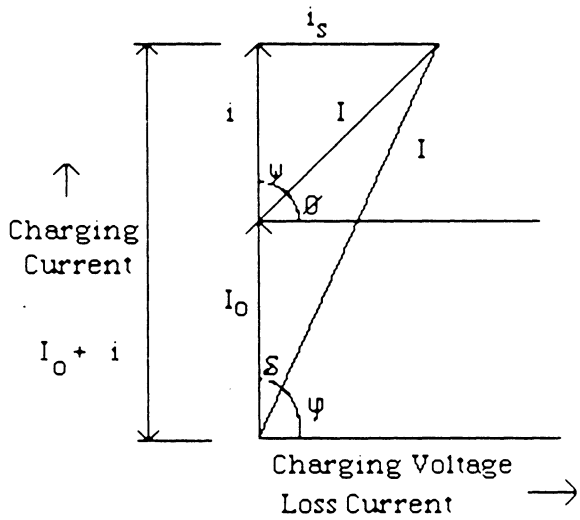


Figure 1. Voltage and Current in a Capacitor Filled With a Dielectric Material

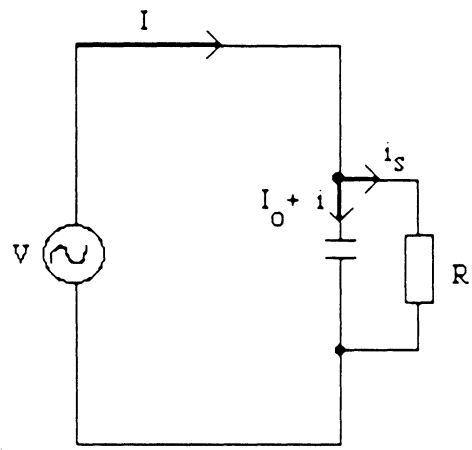


Figure 2. Eqiuvalent Electrical Circuit

All dielectric phenomena are due to the microscopic polarization of a material when an electric field is applied. There are three polarization mechanisms and they are generally given as induced, super conducting or nomadic, and orientation[7]. Induced polarization is comprised of an electronic and an atomic contribution. Electronic polarization is the displacement of the electronic distribution about the nuclei of the atoms. It is therefore a universal polarization response and is seen in all materials. Atomic polarization is the displacement of the atomic nuclei relative to one another. In most organic solids, where ions are absent, the contribution to the total polarization of a material by atomic displacement is small. The mechanisms that generate induced polarization resonate at frequencies greater than 10^{12} Hz. Thus these mechanisms are not a significant contribution to the total polarization in the microwave frequency range.

Superconducting or nomadic polarization is a mechanism present in certain highly aromatic polymeric solids. Two conditions must be present to allow this polarization mechanism to be effective. a) The structure inheriently dissociates to form active carriers and b) there are long domains of equivalent sites for free carriers to move about. Either protons or electrons can be the active carriers in the long domains. This polarization mechanism will only occur in highly conjugated polymers having giant molecular orbitals.

Orientation polarization depends upon the permanent dipole or dipolar groups in a material. When an electric field is applied the dipoles will realign to reduce the potential energy. The direction of

dipole realignment will oppose the direction of the applied field. In a polymer the permanent dipole groups can be along the main chain or in a side chain. Those groups that can shift or rotate in position will provide a greater contribution to the polarization than those that are hindered in motion. The orientation polarization mechanism is the dominate mechanism to the total polarization of a material in the microwave frequencies.

The microscopic polarization of a material can be related to three macroscopic vector quantites, E, D, and P[8]. E is the electric field. P, the dielectric polarization, is the charge per unit area on surface of the dielectric material. The dielectric displacement ,D, is the total electric density. In an alternating electric field these three quantities are complex numbers. They are defined, where w is frequency, as:

$$E = E_o e^{iwt} \tag{7}$$

$$D = D_o e^{i(wt + \delta)} \tag{8}$$

$$P = P_o e^{(wt + \Psi)} \tag{9}$$

The following equation relates the vector quanities:

$$\epsilon_o E + P = D \tag{10}$$

In free space, with no dielectric present, E and D will be equal. When a dielectric is introduced D will decrease by the amount P, because the orientation of the permanent dipoles of the material opposes the direction of the applied field thereby reducing the total electric field.

Although the dielectric values can be expressed mathematically for both single and multiple relaxation models[4], the physical

interpetation of the values is of greater importance in this work[9]. ϵ' is a measure of the amount of energy that can be stored in a material in the form of an electric field and ϵ'' is a measure of the amount of energy that can be dissipated in a material in the form of heat. The value of ϵ' will influence the electric field and can be used to monitor the change in electric field when a material is placed in a field. The magnitude of ϵ'' is direct measure of the heat generated when a material is placed in an electric field. It can be used to monitor the ability of a material to be heated with electromagnetic radiation.

B. Polymer Review

Dielectric behavior as a function of temperature at microwave frequencies is contrasted to low frequency behavior in Figure 3[10]. At microwave frequencies the dielectric values will normally have a characteristic linear behavior. A.Bur provides an excellent review of the conditions necessary for a dispersion (transitional peak) in the microwave frequencies[11]. The T_g of a polymer, characterized by a primary relaxation peak, is required to be less than $-10^{o}C$ to display the corresponding peak at room temperature in the microwave frequencies.

The formation of a master curve and asssociated shift factor plot, as well as the shift of a relaxation peak with either a change in temperature or frequency are important concepts in polymer chemistry[12]. A series of experimental curves may be measured as a function of time or frequency at a constant temperature. The master

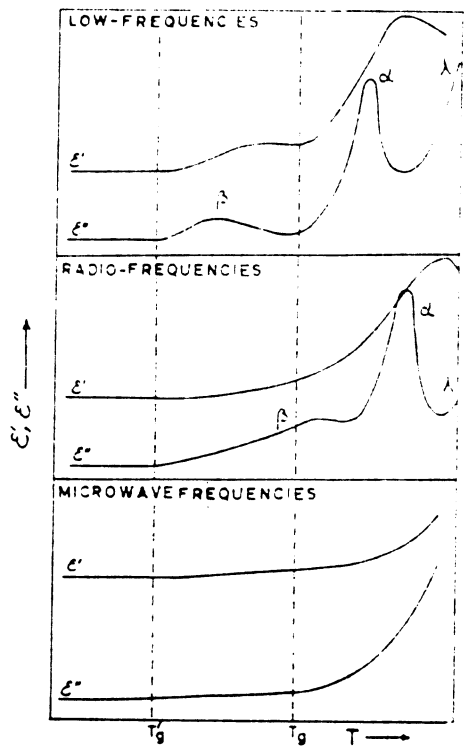


Figure 3. Comparison of Low and High Frequency Dielectric Behavior Ref. 10

curve is formed by shifting these curves relative to a desiginated reference curve. The amount that each curve is shifted from the reference curve is called the shift factor, and can be plotted versus reduced temperature to produce the shift factor plot.

The curve of the shift factor plot can be characterized by two equations and the type of relaxation determines which equation it will follow. Primary relaxation peaks, the T_g, follow the well known WLF equation. Secondary relaxation peaks, due to main chain or side chain movement, follow the Arrhenius equation. This difference can often be used to determine which relaxation peak has been observed. For many polymer systems, with peaks that shift into the microwave frequency range, the two shift curves often merge together, and a single relaxation peak results (Figure 4)[11].

Dielectric measurements are very sensitive to material factors such as molecular weight, branching, crosslinking, crystallinity, endgroup concentration, polar impurities and antioxidants. Aras and Baysal[13] have studied the dielectric properties of crosslinked and branched polymers at low frequencies. At microwave frequencies the conclusions of their results would be valid although the magnitude of the experimental results would be less. Branching can increase dielectric results by making the polymer chain more mobile. Crosslinking, which would restrict molecular motion, decreases the dielectric values.

The dielectric results in the microwave frequencies for LDPE (low density polyethylene) and HDPE (high density PE)[11] show the effect of crystallinity. HDPE, or high crystallinity, results in

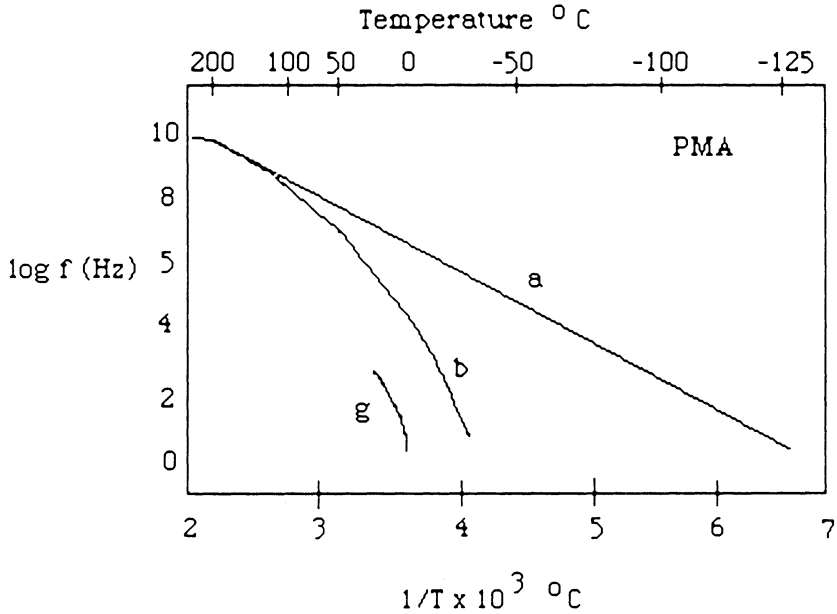


Figure 4. Shift Factor Plot for Poly(methylacrylate) a-primary, b & g-secondary relaxation peaks. Reproduced from Ref. 11

lower dielectric values than LDPE. In a related study, Bandyopadhyay (et.al)[14], measure dielectric properties as a function of foam density for a series of polystyrene foams. The results show that as the foam density increases the dielectric constant increases.

Water and other polar impurities can have a significant effect on dielectric properties. In an article by Suzuki, Adachi, and Kotaka[15] the rate of water absorption of several polymeric materials is given and the dielectric properties of dry and wet materials compared. Water has one of the highest dielectric constants of all liquids, 78 at 25°C. It is therefore a prerequisite that materials be dry to obtain accurate dielectric measurements.

Submramanyam and Khare[16] compare the dielectric data of a single polystyrene foam with infrared spectra to provide an explanation of the dielectric results obtained. The results showed a dissipation in the loss factor, which the authors speculated was trapped water. The IR showed a broad peak indicating water, although the water could have originated from the IR pellet formation. The authors concluded that a preliminary tests should be required for materials used as sample supports for microwave applications.

Bur[11], Forsini and Butta[10],A. VonHippell[5], and W.R. Tinga and S.O. Nelson[17] provide graphs and tables of dielectric measurements for many polymer systems. The review by Bur provides a comprehensive explanation of the dielectric results of many common and important polymers. The dielectric data are presented as master curves, at room temperature, of ϵ'' or tan δ versus frequency. The polymers are grouped into low loss, significant loss, and thermoset polymers.

Those reviewed as low loss are: polyethylene, polypropylene, and poly(tetraflouroethylene). The polymers reviewed as significant loss are: polystyrene, poly(vinylchloride), poly(vinylidene chloride), poly(vinylidene flouride),poly(methyl-methacrylate), poly(methyl acrylate), poly(oxymethylene), poly(ethylene oxide), poly(propylene oxide), polyacetylene, and poly(sulphur nitride). The thermosets reviewed are: poly(phenylene oxide), polycarbonate, and polysulphane.

Forsini and Butta reviewed the dielectric properties of polar polymers at one frequency, 9 GHz, over the temperature range of -150-200^{o}C. The polymers reviewed are: polyoxymethylene, polythiomethylene, poly(3,3' chloromethyl)oxetane, polycarbonate, poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl chloride), vinyl-chloride-vinyl acetate copolymer and two ABS plastics, type B (blend) and G (graft). The authors, based on their results, provide explanations for the comparison of dielectric behavior at low and high frequencies. When increasing from low frequencies to microwave frequencies all relaxation peaks, either primary or secondary, tend to dissappear. The corresponding relaxation effects are observed through a progressive increase in losses with increasing temperature.

C. Polymer Curing Review

The curing processes due to thermal energy and microwave radiation are conceptually different. Thermal heating is a conductive heating process where by the heat is transferred directly from the outer hot surface of a body into the inner cold layers[18]. Microwave energy is an alternating electric field that penetrates into a

material. The dipole groups of the material attempt to oscillate with the electric field, and as a result of the molecular motion, frictional heat developes. It is this frictional heat that cures the polymeric material. Polymeric materials, which generally have low thermal conductivities, are ideal materials for heating by microwave radiation.

N.S. Strand[9,18,19] provides a clear description of the microwave technologies and applications in industry. A review of the requirements for plastic molding materials is given and two low loss tooling systems are described. For heating with microwave radiation Strand presents an equation relating the temperature rise in a material to the power of the emitter and the dielectric loss value of the material. He concluded that the use of microwave radiation is a useful method for the plastic industry, but that a considerable amount of work needs to be done to truely optimize a microwave production system.

Much of the current research in the area of microwave curing of epoxies and polyurethanes is being done by Jullien and Valot[20,21], Gourdenne (et al)[22,23], and Karmazsin and Satre[24]. A large amount of the research has been directed towards the study of polymerization using either continuous or pulsed microwave sources at different power levels. The modulus and thermal properties are generally measured and used as a comparison for different heating methods. It was concluded that the energy transfer by pulsed microwaves was more efficient than by an equivalent continuous wave value.

Temperature versus time curves were generated by the above

authors and used to characterize three general modes of polymerization by microwave radiation; 1. heating of the epoxy resins 2. the initiation of the exothermic reaction and 3. completion of the network structure of the epoxy. These curves were further used to optimize experimental conditions. A smaller portion of the above research has been directed at studying the effect of fillers and solvents on the polymers heated by microwave radiation. The epoxy system of DGEBA (Diglycidil Ether of Bisphenol A) and 4,4' Diaminodiphenyl Methane was studied with glass fibers as the filler. It was found that at a certain level of filler the dielectric imaginary value was enhanced. This was explained by

> the fact that the dipolar activity of the resins is enhanced by the interactions between the epoxy resins and the glass fillers. When the amount of glass fiber is increased past an optimum level the velocity of heating decreases because large quantities of fiber promote thermal loss by convection from the sample to the external medium[22].

The solvents that were investigated[21] include dimethylformamide (DMF),methlyethylketone (MEK), and benzene. The solvents decrease in polarity, respectively. The polymers used in the study were poly(vinylacetate) (PVAC) and polystyrene (PS). The results obtained were explained by the following hypotheses:

> The nature of the polymer is the main factor which governs interactions between the microwave field and polymer solutions. Solvent polarity and its associated dilectric losses, as well as concentrations, were secondary factors which control the amplitude of interactions, but did not influence the general aspect of the phenomena.

The authors feel that further work needs to be carried out in this area.

The microwave curing of rubbers has been studied by several

research groups. Lee[25] and Ippen[26] have studied the modifacation of rubbers to increase their dielectric imaginary values. The methods used are: 1. incorporation of polar groups into the main chain of the polymer and 2. incorporation of high dielectric loss additives into the polymer mixture.

Lee determined that the following polar groups, incorparated into the backbone of a silicone elastomer, would increase the dielectric loss value substantially: $-CH_2CH_2CF_3-$, $-CH_2CH_2CH_2SH-$, $-CH_2CH_2CH_2Cl-$, and $-(CH_2CH_2O)_x-$. Ippen discovered that the addition of diethylene glycol and triethanol amine, in equal weight parts, to light colored nonpolar elastomers is sufficient to allow heating by microwave radiation. Both authors discuss the addition of various carbon blacks to polymeric solutions and provide dielectric data for those systems.

A comprehensive review of the curing of synthetic rubbers is given by Schwarz and co-workers[27,28]. Dielectric properties and results of measurements on both uncured and cured samples for several synthetic sytems are given. A comparison of mechanical properties is given for thermal and microwave cured systems. A conclusion from their work provides an excellent justifaction of the research presented in this thesis.

> The microwave curing of a given rubber composition- a polymeric material- under industrial production conditions can be predicted from simple laboratory tests; undoubtedly the most direct and meaningful type of experiment consists of measuring the dielectric properties ϵ', ϵ'' and $\tan\delta$, as these properties characterize the rate of microwave absorption by the material[28].

DIELECTRIC MEASUREMENT

A. Instrumentation

Historically the measurement of the permittivity of polymer systems in the microwave frequency range has been difficult and time consuming. The most common method of measurement has employed the use of tuned cavities, with the permittivity measurements being made at one frequency[29]. The use of automated network analyzers allows broad band measurements to be made rapidly and precisely.

A Hewlett-Packard 8510 network analyzer was used in this study to measure the permittivity of dielectric materials. The HP 8510 network analyzer system is composed of three parts: an HP 8510A network analyzer, an HP 8515A S test parameter test set, and an HP 8340A synthesized sweeper. In addition, a 9000 series 320 HP computer is interfaced to the network analyzer.

The network analyzer is a two port measurement system, where the stimulus can be applied or the responce measured at either port. The synthesized sweeper generates the radiation to be supplied to the specified port. The HP 8340A can generate frequencies between 30MHz-26.5GHz. Although this frequency range is available the sample measurement holder dictates the range of frequencies that can be used in any particular measurement. The measurments were made at ambient temperatures held constant to $\pm 2^{o}C$.

Figure 5 shows the schematic arrangement of the analyzer and measurement components. The network analyzer and S test parameter set

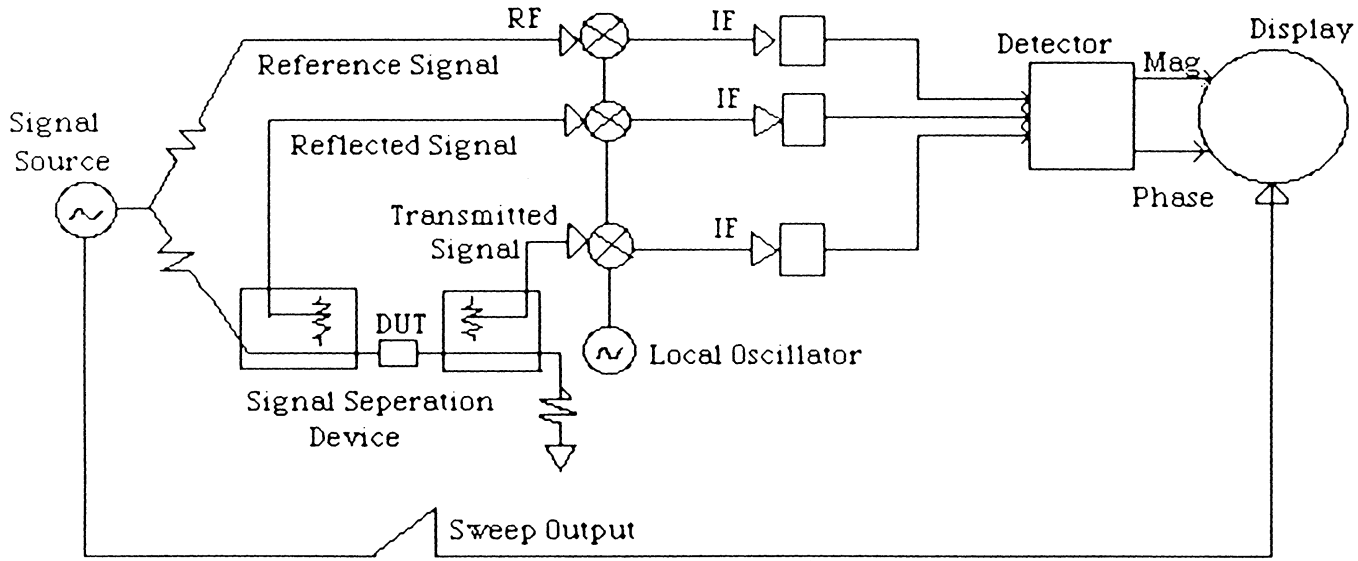


Figure 5. HP 8510 Network Analyzer

are the signal processing components. The attenuation and phase shift of an applied signal as it passes through a material, are the measured parameters. They are found by the comparison of the incident signal to the transmitted signal or to the reflected signal[30]. The results of a measurement are expressed as S parameters, which are related to the complex transmission amd attenuation coefficients. The notation for an S parameter is $S_{OUT,IN}$, where OUT designates the port at which the energy output from the sample is measured and IN specifies the port from which the applied signal is input to the sample.

There are four S parameters as shown in Figure 6. S_{11} is the measured response at port 1 when the stimulus or signal is sent from port 1 and S_{21} is the measured response at port 2 when the stimulus is applied from port 1. Therefore S_{11} is a measure of the ratio of the reflected signal to the incident signal and S_{21} the ratio of the transmitted signal to the incident signal. The two S parameters used for permittivity calculations are S_{11} and S_{21}. The S parameters, S_{22} and S_{12}, can be used in a similar manner.

Data within a specified frequency range can be measured at 401, 201, 101, or 51 frequency points. At each measurement point the values of the S parameters are stored in the computer and the calculations of ϵ' and ϵ'' are preformed at the end of each frequency sweep. S_{11} and$_{21}$, which are functions of frequency, are used to calculate the reflection coefficient, Γ , and transmission coefficient, T , through the following equations:

$$T = \frac{(S_{11}(w) + S_{21}(w)) - \Gamma}{1 - (S_{11}(w) + S_{21}(w))\,\Gamma} \qquad (11)$$

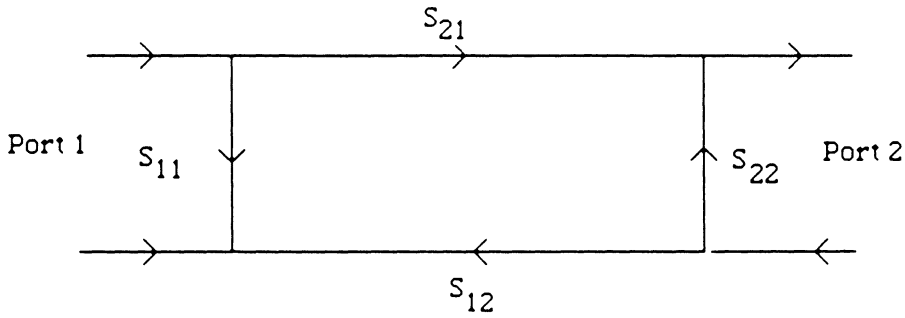


Figure 6. S Parameter Diagram

$$\Gamma = K \pm \sqrt{K^2 - 1} \tag{12}$$

where
$$K = \frac{(S_{11}^2(w) - S_{21}^2(w)) + 1}{2 S_{11}(w)} \tag{13}$$

Γ and T may also be defined by the following equations where Z_o is the intrinsic impedence of free space in the sample holder and Z_s is the intrinsic impedence in the sample.

$$\Gamma = (Z_s - Z_o)/(Z_s + Z_o) \tag{14}$$

$$T = 2Z_s/(Z_s + Z_o) \tag{15}$$

Γ and T are used to calculate μ, the permeability of the material. The permeability is a measure of the magnetic properties of a material and is calculated using the following equation:

$$\mu = \frac{1 + \Gamma}{\Lambda (1 - \Gamma) \sqrt{\frac{1}{\lambda_o^2} - \frac{1}{\lambda_c^2}}} \tag{16}$$

where
$$\frac{1}{\Lambda^2} = -\left[\frac{1}{2\pi d} \ln \frac{1}{T}\right]^2 \tag{17}$$

λ_o is the wavelength of free space, λ_c is the cutoff frequency, a constant for the measurement setup in use, and d is the sample length. The permittivity values are calculated from the equation:

$$\varepsilon = \frac{\left(\frac{1}{\Lambda^2} + \frac{1}{\lambda_c^2}\right) \lambda_o^2}{\mu} \tag{18}$$

The preceeding calculations were for the case of the stimulus being applied from port 1. If the radiation is applied from port 2, then the equations must be adjusted by substituting S_{22} and S_{12} for

S_{11} and S_{21}, respectively. This method of measuring permittivity is best suited for high-loss materials. For low-loss materials the uncertainty for ϵ" becomes high.

The HP network analyzer has an internal time domain gating capability. The gating increases the instrument accuracy by eliminating residual mismatch errors. The residual mismatch occurs at the connection of the sample holder to the ports and is due to imperfect system source and load match. The gating allows only the responce of the sample to be measured, providing greater accuracy. The effect of the gating is to decrease the noise that results because of the mismatch. For the measurement of data at 401 frequency points, using gating, the entire measurement procedure of the permittivity requires about five minutes.

B. Sample Measurement Parameters

There are two basic measurement holders, a coaxial airline or a rectangular waveguide. The dimensions of a particular component are the determining factor in what frequencies can be measured. The coaxial airline is a cylindrical sample holder with an outer and inner conductor. The sample must fit in the space between the two conductors. There are two coaxial airlines, 7mm or 3.5mm, where the size specifies the diameter of the outer conductor. The 7mm airline is used to study the frequency range of 45MHz to 18 GHz and the 3.5mm airline covers the range of 18 to 26.5GHz. Figure 7 shows a schematic drawing of the airline and Table 1 gives the airline and sample dimensions.

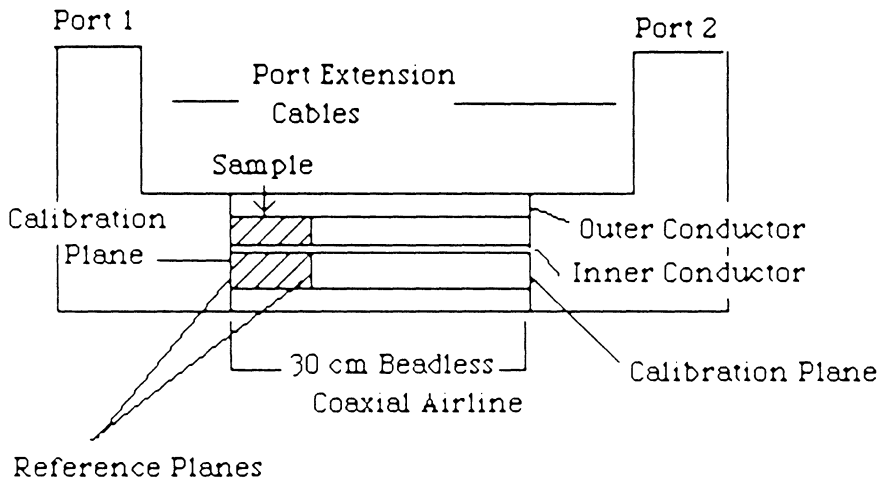


Figure 7. Coaxial Measurement Setup

Table 1. Coaxial Airline and Sample Dimensions

Coaxial Airline:

Length	Outside Diameter	Inside Diameter
30 cm. (11.811 in.)	7.000 mm. (.276 in.)	3.040 mm. (.120 in.)
10 cm. (3.937 in.)	3.500 mm. (.138 in.)	1.520 mm. (.0598 in.)

Sample:

Length	Outside Diameter	Inside Diameter
.317 - 1.270 cm. (.125 - .500 in.)	7.000 mm.	3.040 mm.
.317 - 1.270 cm. (.125 - .500 in.)	3.500 mm.	1.520 mm.

The microwave region of the electromagnetic spectrum is divided into specific frequency bands which are linked to the particular range of frequencies that can be transmitted by a rectangular waveguide of a particular size. The two frequency bands that have been used in this work are X and P (Ku). The X-band covers the frequency range of 8.2 to 12.4 GHz, and the P-band 12.4 to 18 GHz. The waveguide measurement setup and sample holder are shown in Figure 8. The waveguide and sample dimensions are listed in Table 2. It is noted that as the frequency range decreases the waveguide size increases. This inverse relation limits the practicality of studying low frequencies, as the sample dimensions would be very large.

It is important the samples have the correct dimensions. For coaxial measurements the sample must completely fill the area between the inner and outer conductor of the airline. For waveguide measurements the sample must completely fill the rectangular holder. The sample lengths can vary, but must be known to 10^{-4} inch. Each side of a sample is referred to as a reference plane. The reference plane should present a flat surface and be right angles to the sides of the sample holder.

For each measurement a calibration, using the same setup and frequency range, must be made. Calibrations use several standard terminations: fixed, sliding, short, and open. The calibration measurement is compared to the known values for each termination and the differences that exist are subtracted from the sample measurements. A two port calibration, where the terminations are measured at each port, is the preferred calibration method.

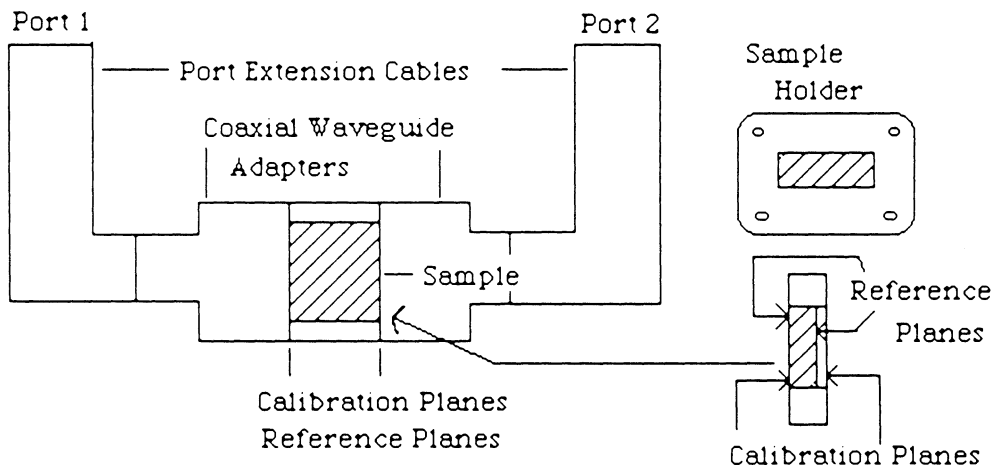


Figure 8. Waveguide Measurement Setup

Table 2. Waveguide and Sample Dimensions

Rectangular Waveguide:

Frequency Band	Inside	Outside	
X	.900 -.400	1.000 - .500	in.
	2.286 - 1.016	2.540 - 1.270	cm.
P	.622 - .311	.702 - .391	in.
	1.580 - .790	1.783 - .993	cm.

Waveguide Sample Holder:

Frequency Band	Inside	Outside	
X	.900 - .400	1.625 - 1.625	in.
P	.622 - .311	1.320 - 1.320	in.

Sample:

Frequency Band	Length	Width	Height	
X	.900	.400	.120 - .130	in.
	2.286	1.016	. 305 - .330	cm.
P	.622	.311	.115 - .125	in.
	1.580	.790	.292 - .318	cm.

The calibration can be made with or without the sample holder in place. It has generally been found that the results are more accurate when a calibration is made with the sample holder in place. Using this method any errors due to the sample holder can be calibrated out of the sample measurements. This method is not always practical and the calibration without the sample holder must be made. The calibration planes are shown in Figures 7 and 8.

When the reference plane for the measurement is different from the original calibration plane the measurement must be corrected for the corresponding phase shift. The phase shift occurs because the sample is shorter than the sample holder. This can occur with both the coaxial airline and waveguide setups. The HP 8510A network analyzer has an internal reference plane extension capability for the coaxial setup, and therefore no additional calculations are necessary. For the waveguide setup an additional calculation must be made. Appendix A gives the appropriate equations and definitions for the calculation.

There are several sources of error in each sample measurement. The number and magnitude of errors is dependent on each individual sample. The instrument error associated with the HP network analyzer is very small. For an ideal sample of a high loss material the error is less than 1%. As already stated for low loss materials the instrument error in ϵ'' is high due to the method of calculation although the results for ϵ' will be accurate.

Possible sources of sample error include:

1. Sample does not completely fill sample holder.

2. Sample thickness not measured exactly.
3. Sample reference plane not a flat surface.
4. Sample not exactly perpendicular to sides of sample holder.

The magnitude of the error associated with each of the above differs for each sample and can not be measured precisely.

There are three remaining possible errors. When the signal is applied from port 1 the calculations are set up such that the calibration plane and reference plane coincide at the end of the sample holder. During the connection of the sample holder to the cables, leading from the ports, it could be possible to shift the sample. The two planes would no longer be exactly at the same point. This shift in position would cause an error. All measurements should be made at a constant temperature held to $\pm 2^{o}C$. A fluctuation in the temperature could have an effect on the measurement accuracy. Finally as with any analytical technique the possibility of user error exists.

MATERIALS AND METHODS

A. Materials

The EPON 828 resin (Shell Company) was heated in an oil bath for one hour under vacuum, T= 90-100°C, to remove water and remaining volatile solvents. 4,4' DDS (Aldrich) was recrystallized in MEOH/H_2O and dried under vacuum for more than 36 hours at a temperature of 60-80 °C. The melting point of the recrystallized DDS was 177-179°C.

The polystyrene samples were synthesized by Jing-Jing Ma and Roderick P. Quirk at the Institute of Polymer Science, University of Akron. The polystyrene hydroxyl terminated samples (PSOH) were prepared as follows:

> Styrene, benzene and ethylene were purifed as described in the literature[31,32]. Solutions of sec-butyllithium initiator (Lithium Corporation, 12 wt% in cyclohexane) were analyzed by the double titration method[33]. Anionic polymerizations were carried out at 30°C using standard high vacuum techniques[34]. Ethylene oxide (4-fold excess) was added to benzene solutions of poly(styryl)lithium and the contents hydrolzed after 12 hours with acidic methanol. The concentrations of the hydroxol chain ends was determined by titration (ASTM E222-73). Vapor osmometry measurements were made in a solution of chloroform on a Knauer Type 11.00 VPO at 37°C. Size exclusion chromatography analyses were preformed in THF at 30°C using a Waters HPLC component system (RI detector) equipped with six ultra-Styragel columns (two- 500, two 10^3, 10^4, and 10^5 A).

The polystyrene samples were prepared as a fine powder. Table 3 gives the molecular structure and formula of the samples.

B. Sample Preparation- Epoxide System

The recrystallized 4,4' DDS was added to the EPON 828 in a stoichiometric ratio (1:3 by weight DDS:EPON). The mixture was heated

Table 3. Molecular Formula and Structure of Polystyrene Samples

Molecular Formula:

Sample	$\overline{M}n \times 10^{-3}$			$\overline{M}w/\overline{M}n$
	GPC	VPO	End Group Analysis	
PSOH	1.2	1.3	1.3	1.05
PSOH	3.6	3.8	3.7	1.08
PSOH	5.7	5.5	6.0	1.05
PSOH	9.4	9.9	9.7	1.08
PSMA	1.3	1.4	--	1.05
PSMT	9.4	--	--	1.08
PSU	3.6	--	--	1.08
PSB	3.6	--	--	1.08

Molecular Structure:

PSOH: Sec-Bu--(-CH_2-CH-)$_n$--CH_2-CH_2-OH

PSMA: Sec-Bu--(-CH_2-CH-)$_n$--CH_2-CH_2-O-C(=O)-C(CH_3)=CH_2

PSMT: Sec-Bu--(-CH_2-CH-)$_n$--CH_2-CH_2-O-C(=O)-C$_6$H$_4$-C(=O)-O-CH_3

PSU: Sec-Bu--(-CH_2-CH-)$_n$--CH_2-CH_2-O-C(=O)-N(H)-C$_6$H$_5$

PSB: Sec-Bu--(-CH_2-CH-)$_n$--CH_2-CH_2-O-C(=O)-C$_6$H$_5$

under vacuum in an oil bath to 135-140°C. The solution was mixed, for approximately 20 minutes, until the DDS was completely dissolved into the EPON. The samples to be thermally cured were poured directly into hot Dow Corning silicon RTV molds and placed in a convection oven at T=162-168°C. The molds were removed at recorded intervals and allowed to cool to room temperature. The samples for the waveguide measurements were molded to the correct dimensions while the coaxial samples were machined. Below 85% cure, the epoxy samples were too brittle to be machined.

The microwave cured samples were poured into hot Dow Corning silicon 664 RTV molds. This molding material contains no metal fillers, in contrast to the above molding material, and has a very low dielectric loss factor. The samples were placed 13.5 cm from the short at the end of the microwave cavity and irradiated at a frquency of 2.45 GHz. At this point, a power maximum was measured using a slotted line. The samples were heated for recorded time intervals and power, and allowed to cool to room temperature.

C. Sample Preparation- Polystyrene

The polystyrene samples were compression molded directly into waveguide holders. The samples were heated 30-50°C above the glass transition temperatures. The T_g of the samples are between 55-85°C, the exact value dependent on the molecular weight of the polymer. After reaching set temperature 315-890 psi pressure was applied for 10-20 minutes. The pressure was reduced and the sample cooled slowly between the press plates.

The P-band waveguide samples were prepared first. The samples were generally heated and compressed several times to produce a satisfactory mold. The X-band molds were heated to 100°C in a vacuum oven prior to molding. This melted the polymer before molding and decreased the number of times each sample had to be reheated and compressed.

Many polymer properties, including tensile strength, T_g, and density, follow a relation given by[35]:

$$\text{Property} = \text{Property}_{\infty} - (\text{constant})/ M_n$$

At low values of $\overline{M}_n$ the polymer property has a low value and at high values of $\overline{M}_n$ the property reaches its infinite value. As a result, the polystyrene samples, with very low molecular weights, were very brittle. As the samples cooled several large cracks developed through the polymer. Although the surfaces (reference planes) remained smooth and flat.

Several of the samples had bubbles dispersed in the polymer. These bubbles resulted because solvent or water was present in the polymer powder. As the sample was heated the solvent or moisture was trapped in the polymer. It was for this reason the samples were reheated and compressed several times, to try to release the trapped bubbles. Further heating and compression did not significantly reduce the bubbles in several samples. The effect of the bubbles is to increase the apparent sample length to be used in the calculations.

D. Dielectric Measurements

The 8510 HP network analyzer was used to measure the

permittivities. In all measurements gating was used and the data collected at 401 frequency points. Teflon samples were run as standards to varify each calibration procedure.

E. Thermal Analysis

The degree of cure and T_g were determined using the DuPont 9900 DSC. The sample weights were between 9-12 mg, and the scan rate was $10^{o}C$/min. To determine the percent cure the enthalpy of the exothermic peak area was compared to the enthalpy of the polymerization reaction for the complete epoxide cure.

RESULTS

A. Teflon

Teflon, $(CF_2CF_2)_n$, was used as a reference material because it has well characterized permittivity. The dielectric constant is 2.0, in the microwave region, and with no resultant dipole moment, the loss factor is very close to 0. Figures 9 and 10 show the dielectric values using the coaxial airline over the frequency range of 1-18 GHz. To provide greater accuracy four frequency intervals were used to cover the entire frequency range. The dielectric constant is $2.0 \pm .01$ and the dielectric loss is $0 \pm .01$. The greatest source of error associated with the dielctric loss measurement is due to the instrument uncertainty.

The effect of gating, using teflon in the P-band region, is shown in Figures 11 , 12 , and 13 . Figure 11 is the dielectric loss values without gating. A significant amount of noise is seen, although the baseline appears to be 0. Figure 12 shows the loss curve for the same sample with gating. The values appear to be very close to 0. Figure 13 shows the effect of gating with the Y axis scale decreased ten fold from the previous plots. The dielectric loss measured using a waveguide sample holder is seen to be comparable to the values measured using the coaxial airline over the same frequency range. An artifact that often results due to gating is the distortion at the ends of the experimental curves. This distortion results in shifting either downwards or upwards the last part of the curve.

B. Epoxide System

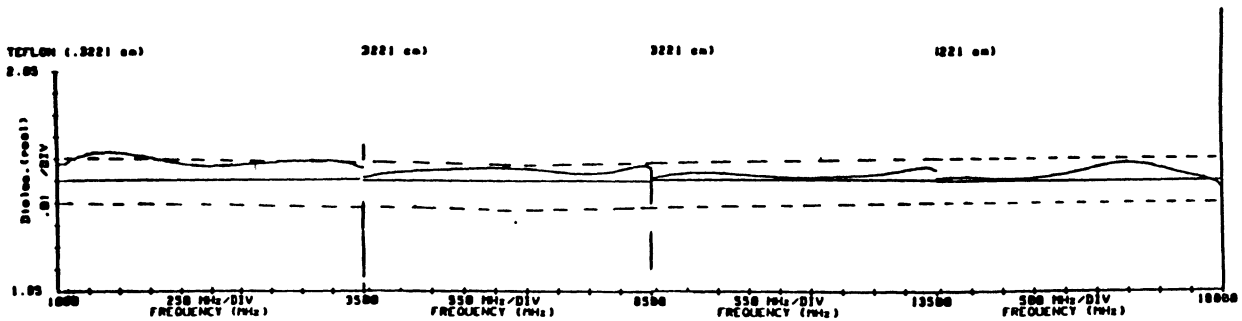


Figure 9. Dielectric Constant of Teflon 1-18 GHz

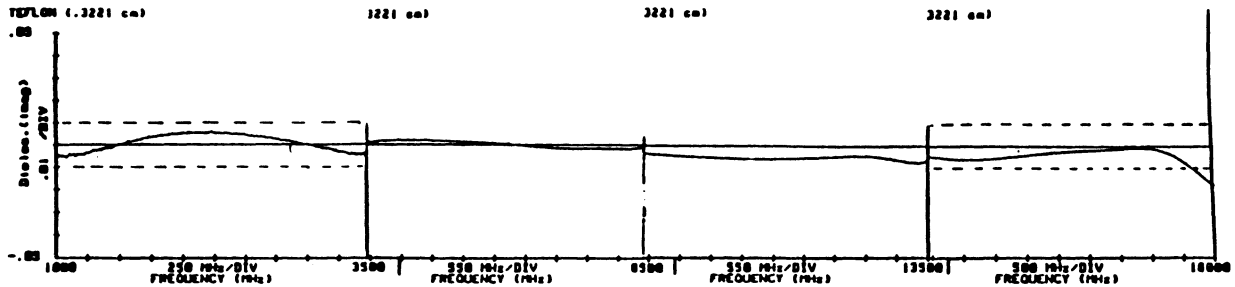


Figure 10. Dielectric Loss Factor of Teflon 1-18 GHz

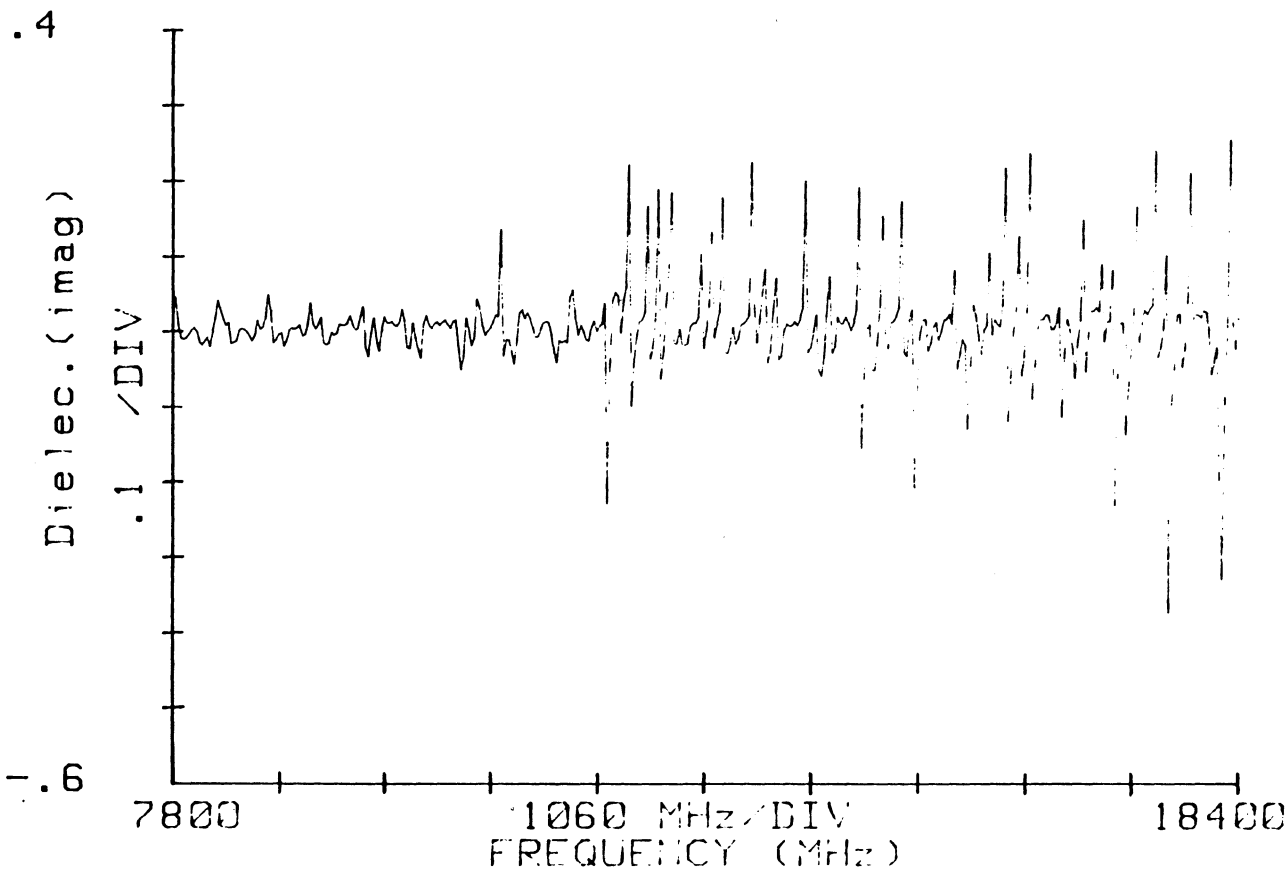


Figure 11. Dielectric Loss Factor of Teflon Without Gating

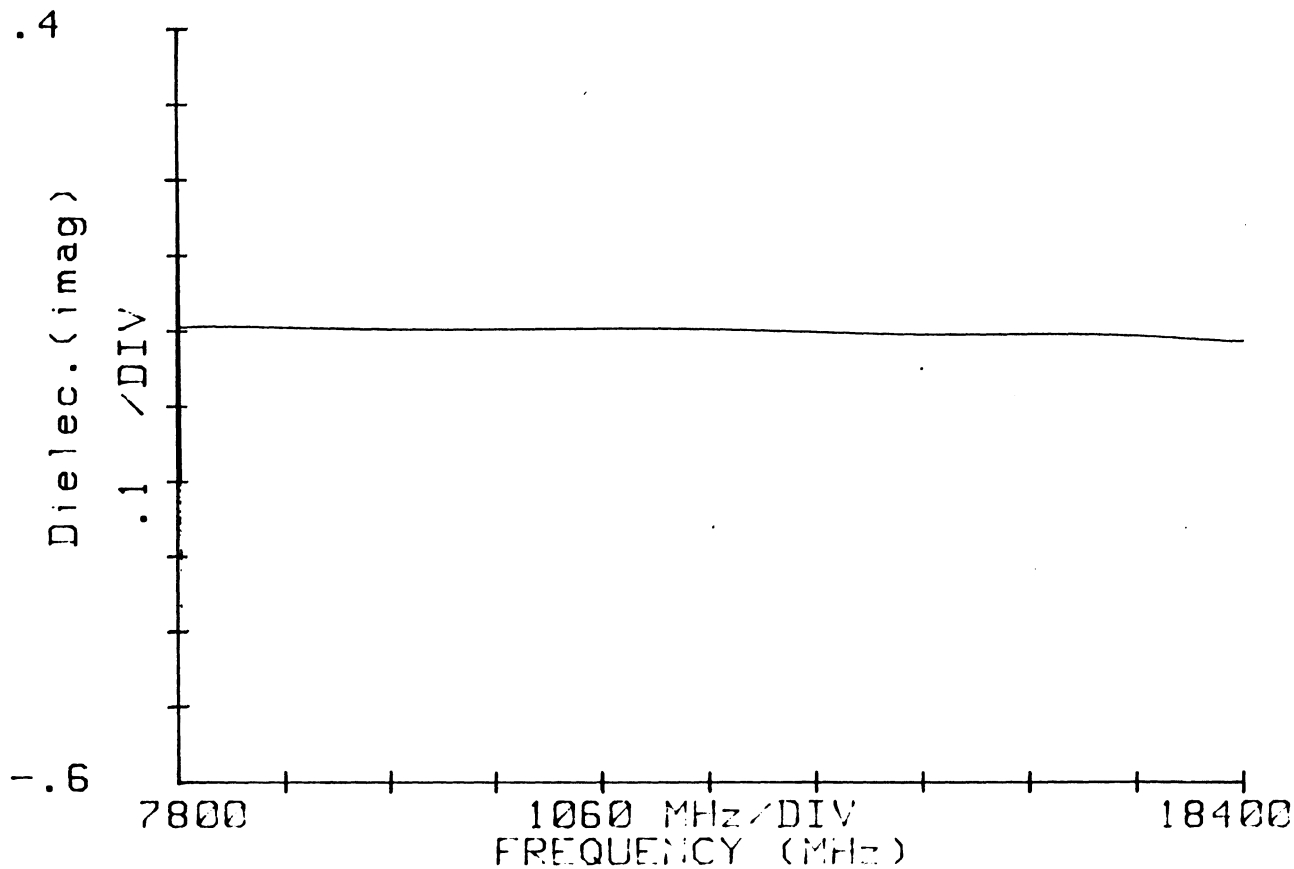


Figure 12. Dielectric Loss Factor of Teflon With Gating

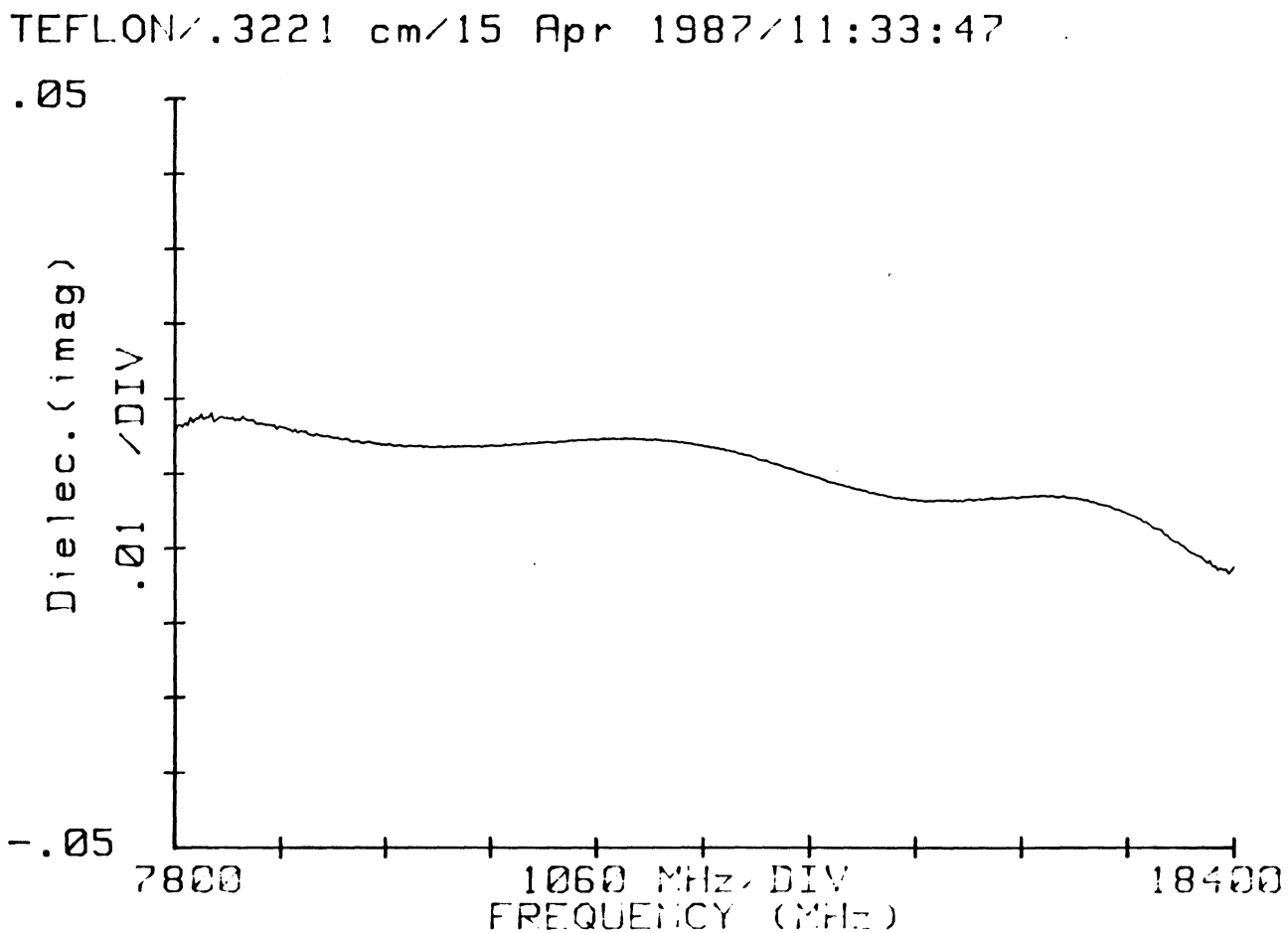
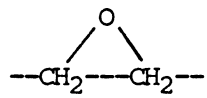


Figure 13. Dielectric Loss Factor of Teflon With Gating and Different Y-Axis Scale

The behavior of the dielectric parameters of a 98% thermally cured sample over the frequency range of 1-18GHz is shown in Figure 14. The data was collected over four frequency intervals and uses the same calibration as used for Figures 9 and 10. The dielectric constant decreases initially and then levels off with increasing frequency. The dielectric loss shows no appreciable change throughout the entire frequency range. At this percent cure the network formation is approximately complete and the main contribution to the dielectric parameters will originate from the motion of the hyroxyl groups. The mismatch at the ends of the ajoining curves is a result of the gating.

The structure and chemical reactions in the epoxy system can be correlated with dielectric properties. The epoxy resin, characterized by the epoxide ring,



is a thermosetting material. When reacted with a curing agent, an insoluble, infusible network system developes. The network is three dimensional and is held together by physical crosslink points. The cure of the epoxy resins differs from other thermosetting materials in that no by products result since the cure is accomplished by direct addition of bridging molecules[36].

The structure of EPON 828, a DGEBA type material, and 4,4' DDS is shown in Figure 15. The specific value of n ranges between 4-8 for the EPON. The epoxy system cures by the reaction of the amine with the CH_2 of the epoxide ring forming a secondary amine and hydroxyl group. After the reaction of the primary amines, the secondary amines

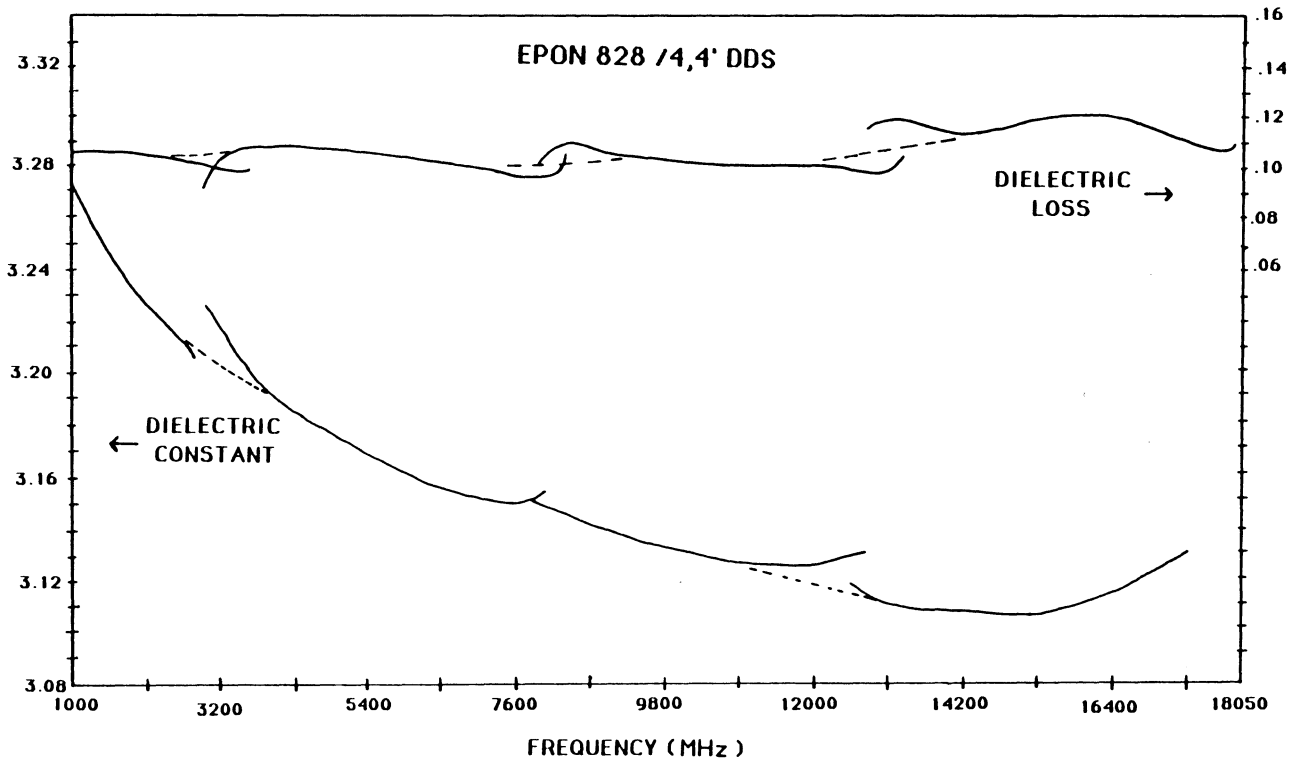
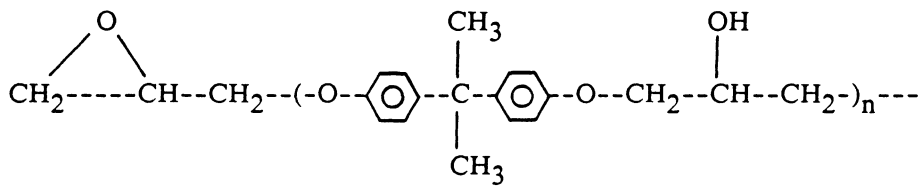
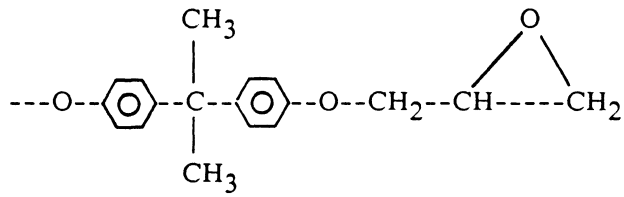


Figure 14. Permittivity of 98% Cured Epoxy Sample

EPON 828





4,4' DDS (diaminodiphenyl sulfone)

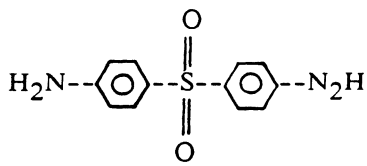


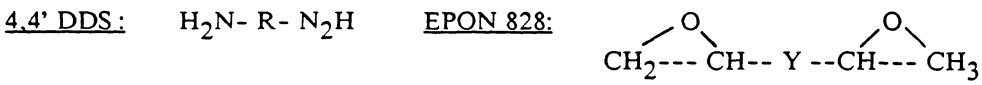
Figure 15. Structure of EPON 828 and 4,4' DDS

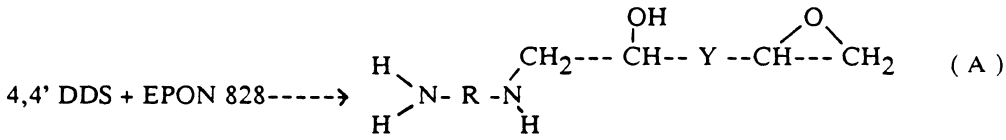
will react at the epoxide bridge to produce a tertiary amine and another hydroxyl group. The reaction mechanism is outlined in Figure 16.

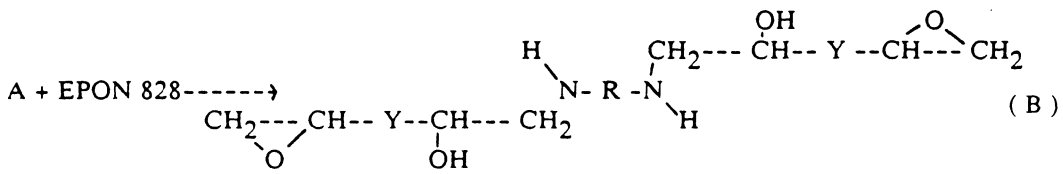
The reaction mechanism can effect the dielectric properties for two reasons. As the cure proceeds the number and type of permanent dipole groups changes. Initially the groups with the greatest dipole moments are the amine groups of the DDS and the hyroxyl groups initially present on the EPON backbone. As the reaction proceeds the concentration of the primary amine groups decrease while the concentration of the secondary amine and hyroxyl groups increase. With further cure the concentration of the secondary amine group decreases and the hyroxyl group concentration increases. At complete cure the hydroxyl groups are the primary dipole groups attributing to the dielectric values.

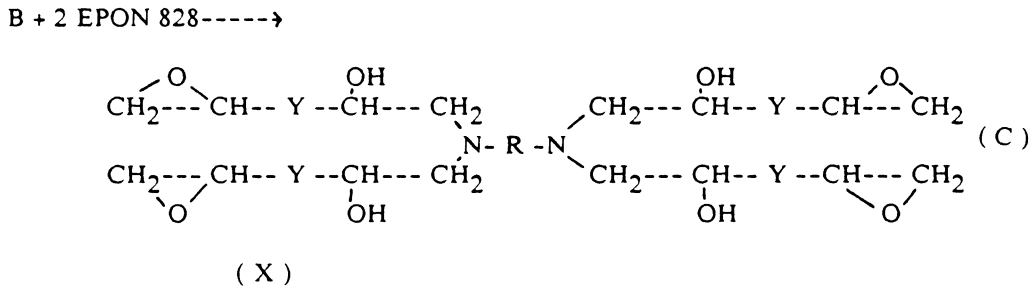
Concurrent with the change in dipole groups and concentrations, the epoxy system cures to form a network structure. The mobility of the active dipole groups will decrease as the network structure forms. Therefore the measured dielectric properties reflect a change in dipole groups and concentration, as well as a decrease in movement of those groups.

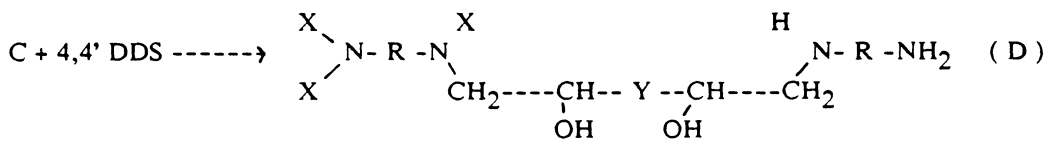
The dielectric constants at different levels of cure and at five different frequencies, are shown in Figures 17-21. The samples below 85% cure were measured using the waveguide sample holders and above 85% cure were measured using the coaxial airline. The values decrease rapidly to about 30% cure after which the decrease is much less rapid. The change in slope occurs at a level of cure where the T_g passes through the measurement temperature. The decrease in dielectric











D + 4,4' DDS + EPON 828-------> Network Formation

Figure 16. Epoxy Reaction Mechanism

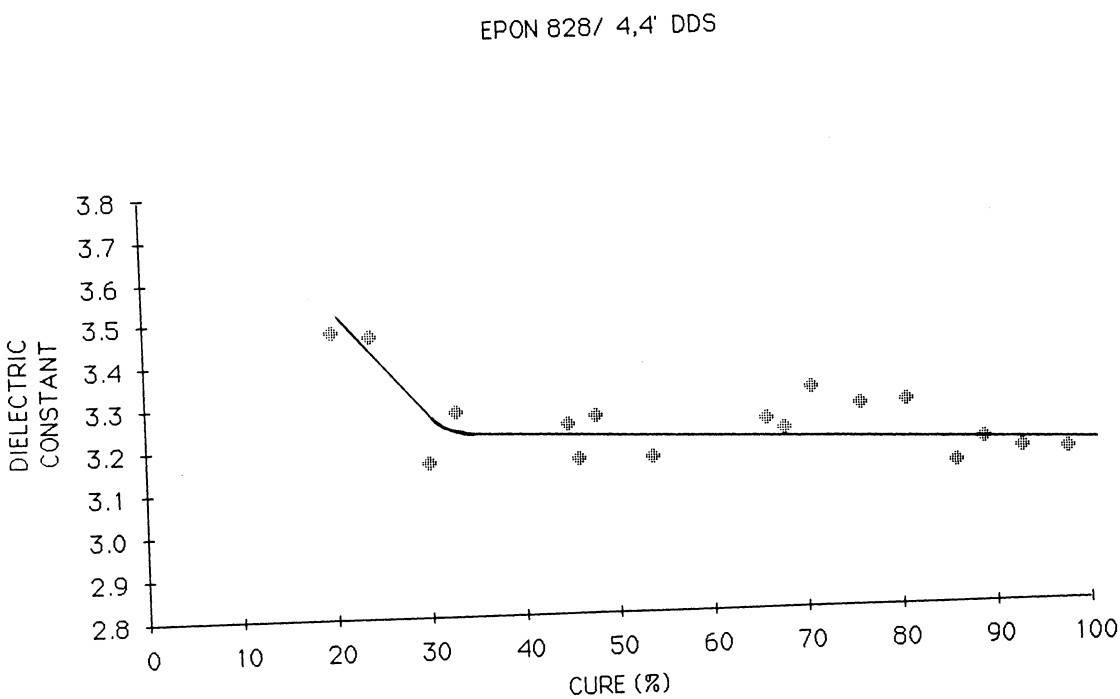


Figure 17. Dielectric Constant Versus % Cure for X-Band Epoxy Samples at 8.625 GHz

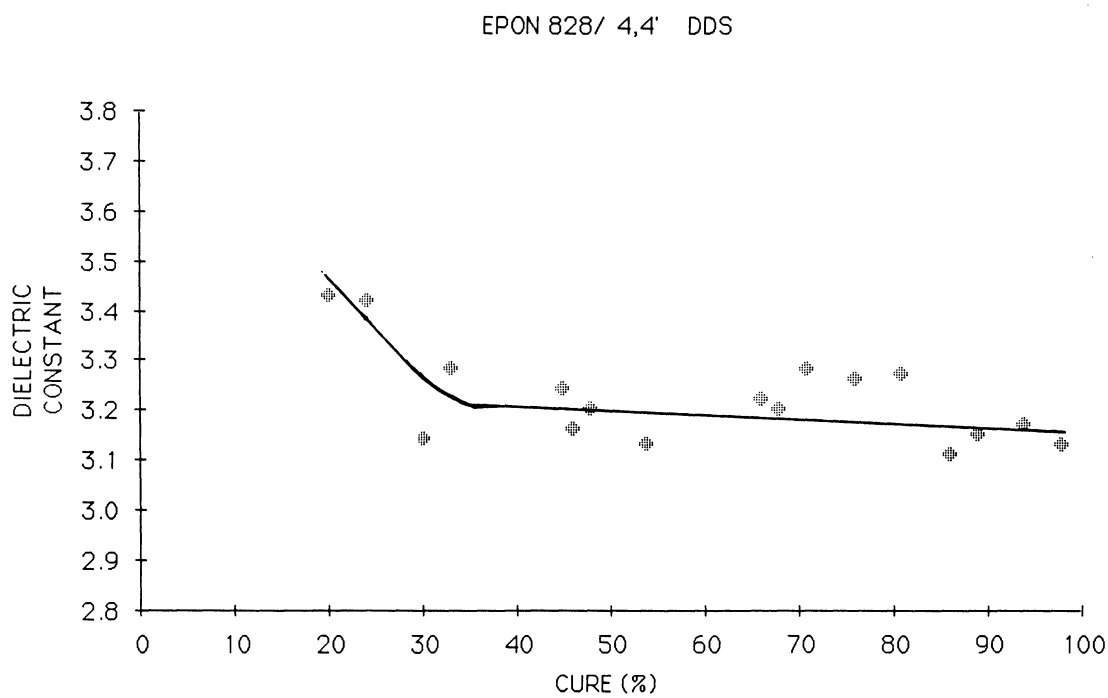


Figure 18. Dielectric Constant Versus % Cure for X-Band Epoxy Samples at 10.3 GHz

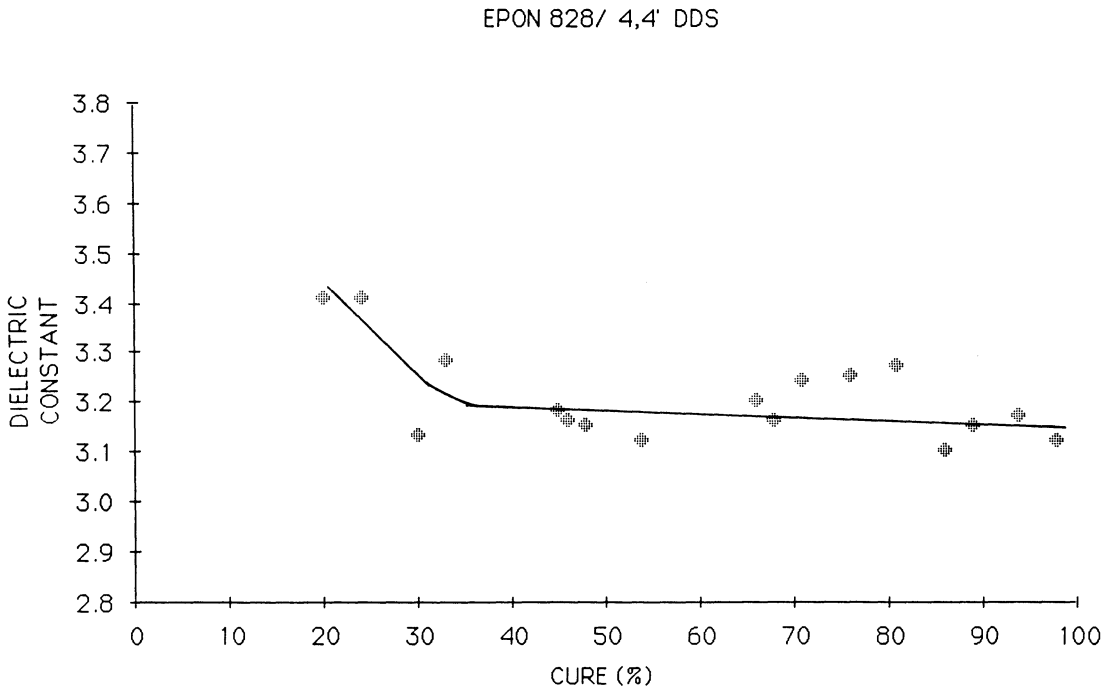


Figure 19. Dielectric Constant Versus % Cure for X-Band Epoxy Samples at 11.8 GHz

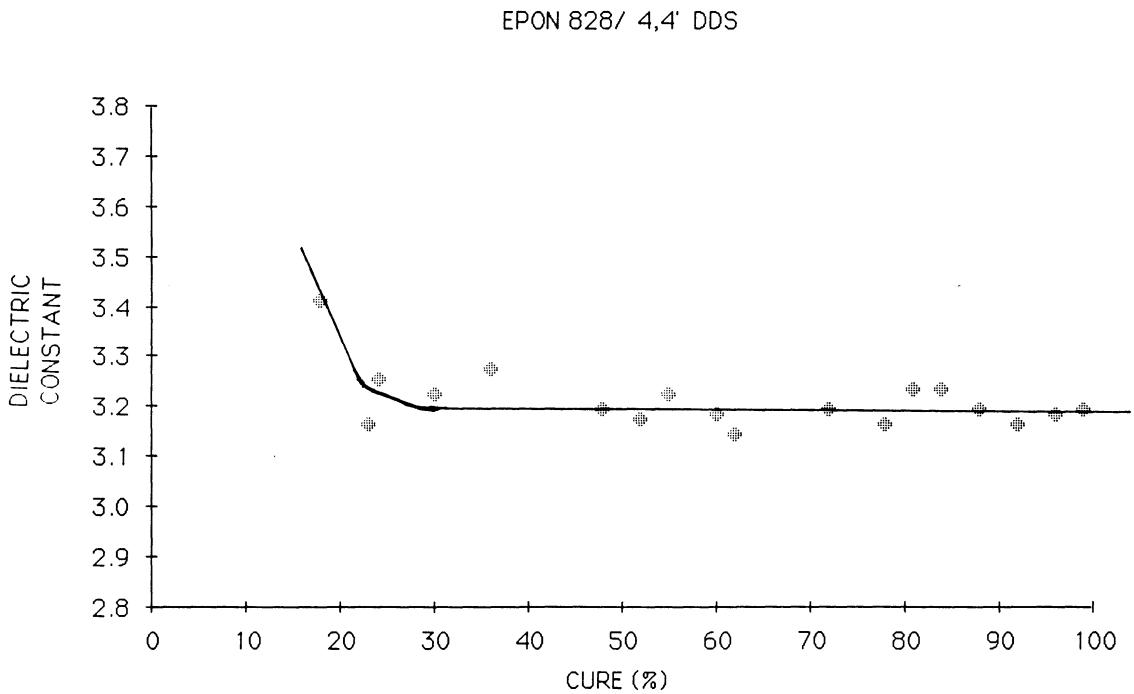


Figure 20. Dielectric Constant Versus % Cure for P-Band Epoxy Samples ay 13 GHz

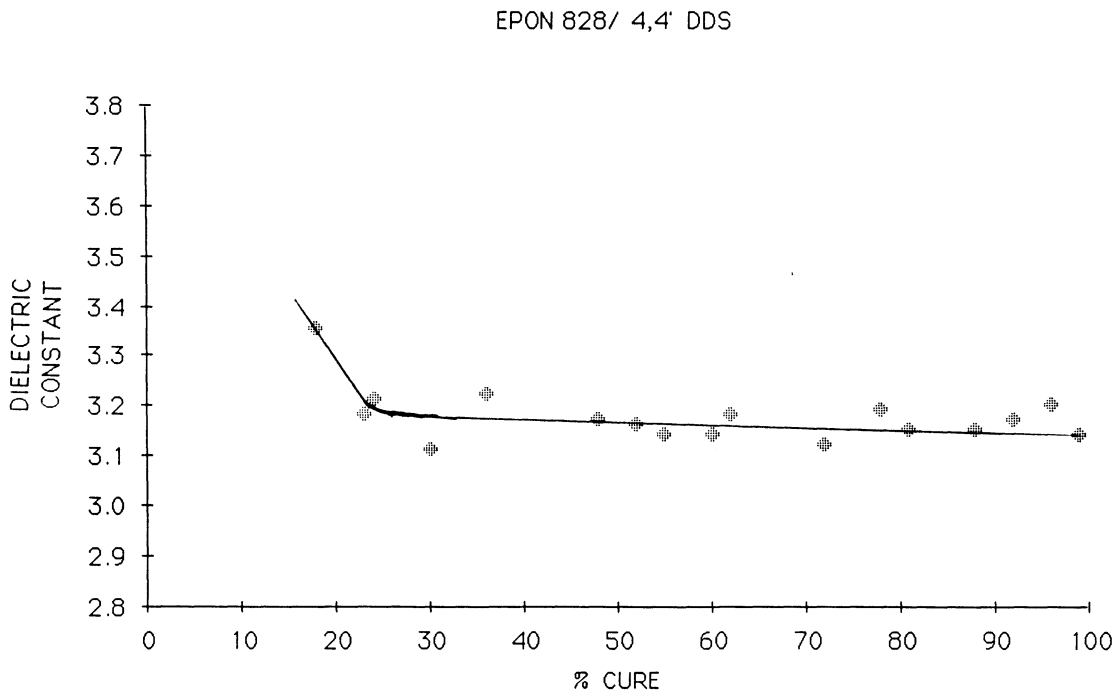


Figure 21. Dielectric Constant Versus % Cure for P-Band Epoxy Samples ay 16 GHz

constant is due to increasing network formation and and the resultant decrease in molecular motion as well as reduced functionality.

The dielectric losses plotted as a function of percent cure, at five different frequencies, are shown in Figures 22- 26. The data appears to be linear with very little change. The experimental uncertainty in ϵ'' is highest at low values of ϵ''. Changes in the dielectric parameters can be attributed to the disapearance of the 4,4' DDS free N-H groups and the subsequent appearance of the hydroxyl groups on the EPON chain. The general results of the data at each different frequency appear similar. At increased frequencies the experimental points deviate further from the interpolated curve.

A typical DSC plot for a very low cured sample, 23%, is shown in Figure 27. The area under the exotherm is measured to be 295.51 J/gm (70.70 cal/gm). The exothermic enthalpy value for the complete polymerization reaction is 384.56 J/gm (92 cal/gm) and a ratio of the two enthalpy values allows the calculation of the percent cure. Figure 28 shows the DSC plot of a 94% thermally cured epoxy sample. At this percent cure the exotherm has almost disappeared and there is a transition temperature of 136^{o}C corresponding to the T_g. Figure 29 shows the conversion of the X-band epoxy samples as a function of time.

Table 4 gives the results the DSC for the series of epoxy samples, molded to X-band dimensions. As the percent cure increases the area under the exotherm decreases and the exotherm peak shifts to higher temperatures. The T_g's of the partially cured epoxy samples also shift to increasing temperature. The T_g of the completely cured epoxy sample is measured by running a second DSC. The DSC results are

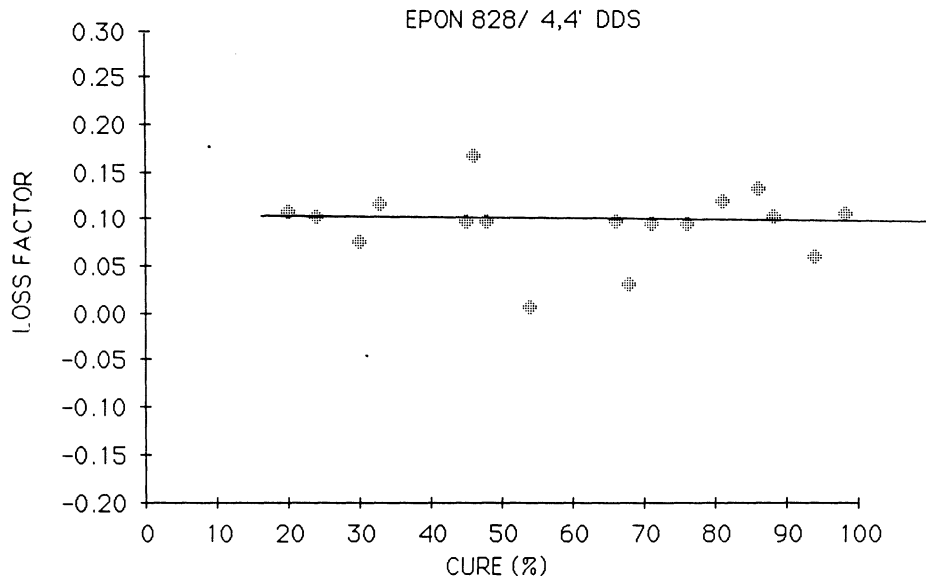


Figure 22. Dielectric Loss Factor Versus % Cure for X-Band Epoxy Samples at 8.625 GHz

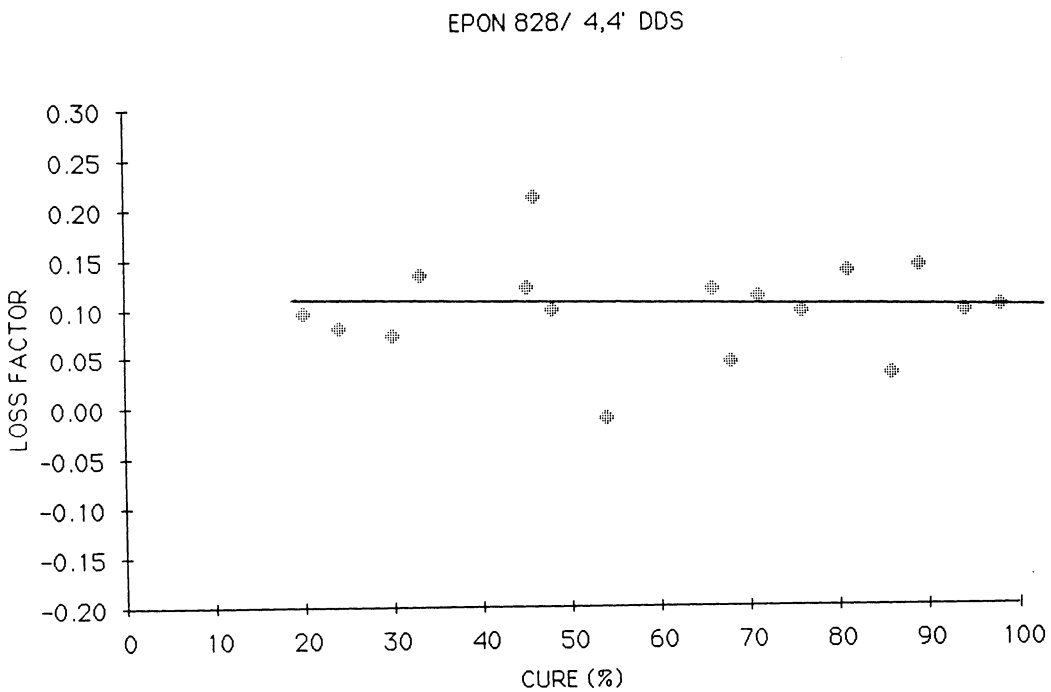


Figure 23. Dielectric Loss Factor Versus % Cure for X-Band Epoxy Samples at 10.3 GHz

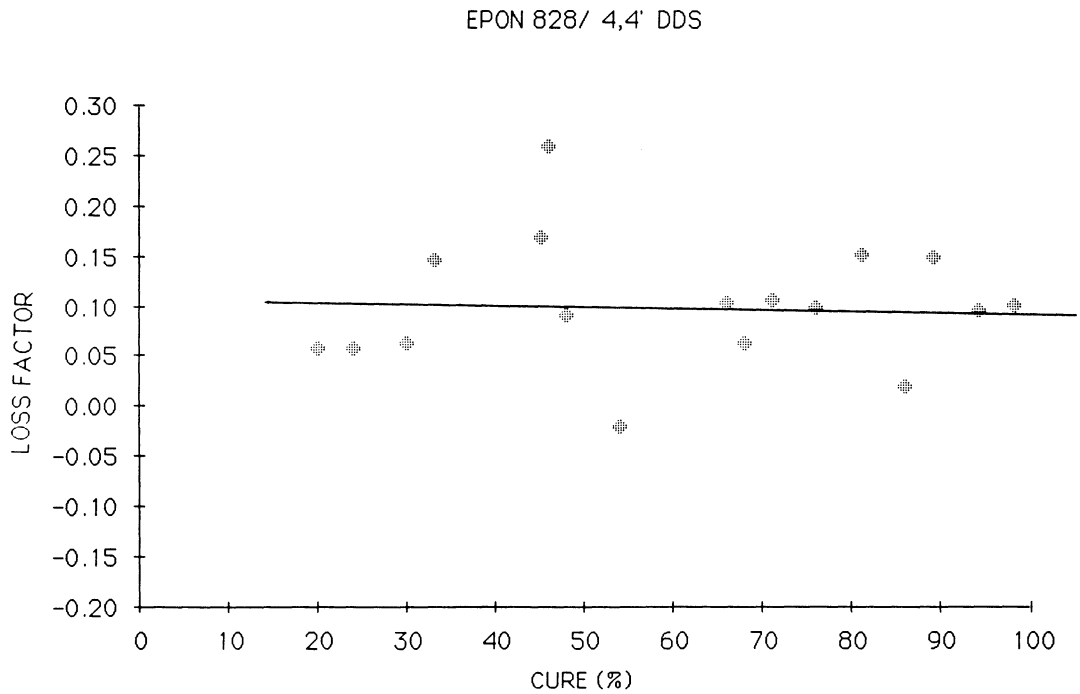


Figure 24. Dielectric Loss Factor Versus % Cure for X-Band Epoxy Samples at 11.8 GHz

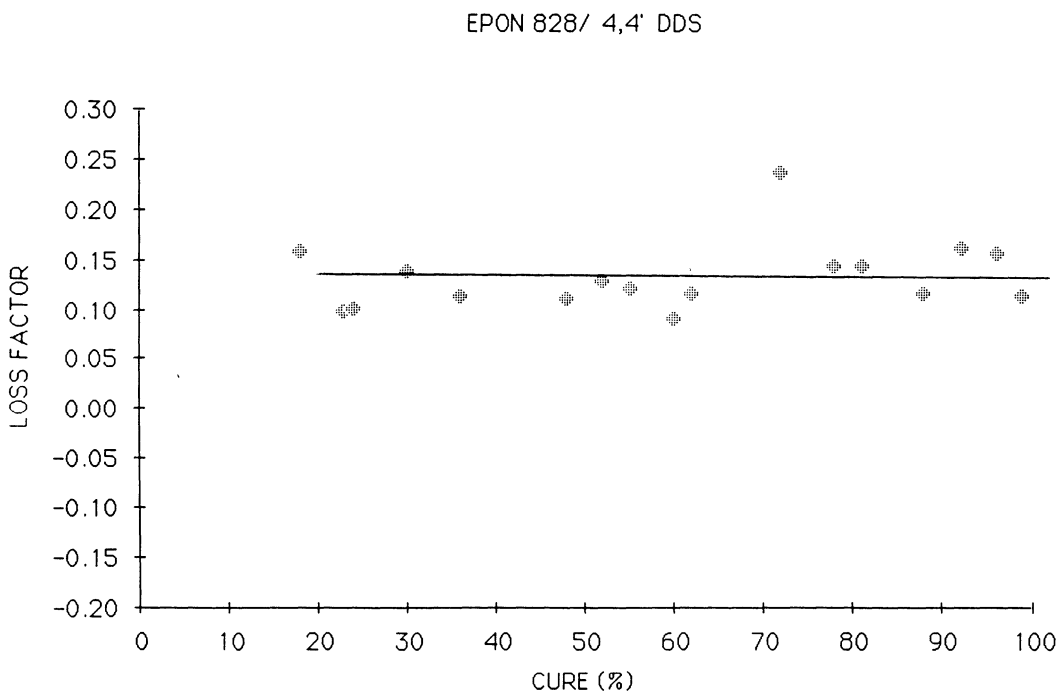


Figure 25. Loss Factor Vesus % Cure for P-Band Epoxy Samples at 13 GHz

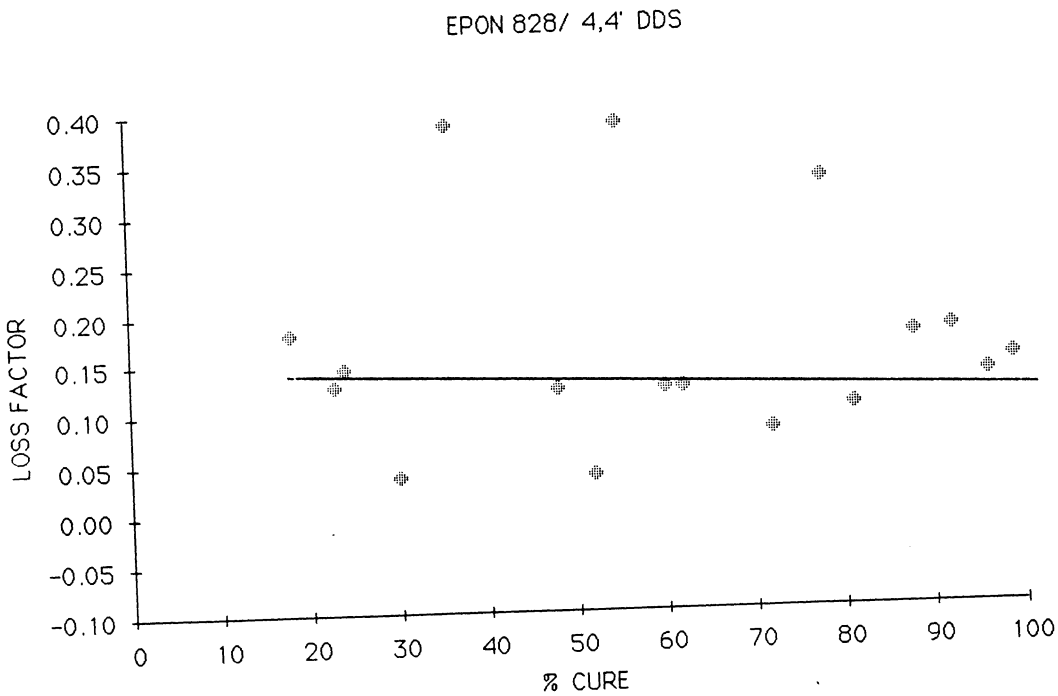


Figure 26. Loss Factor Vesus % Cure for P-Band Epoxy Samples at 16 GHz

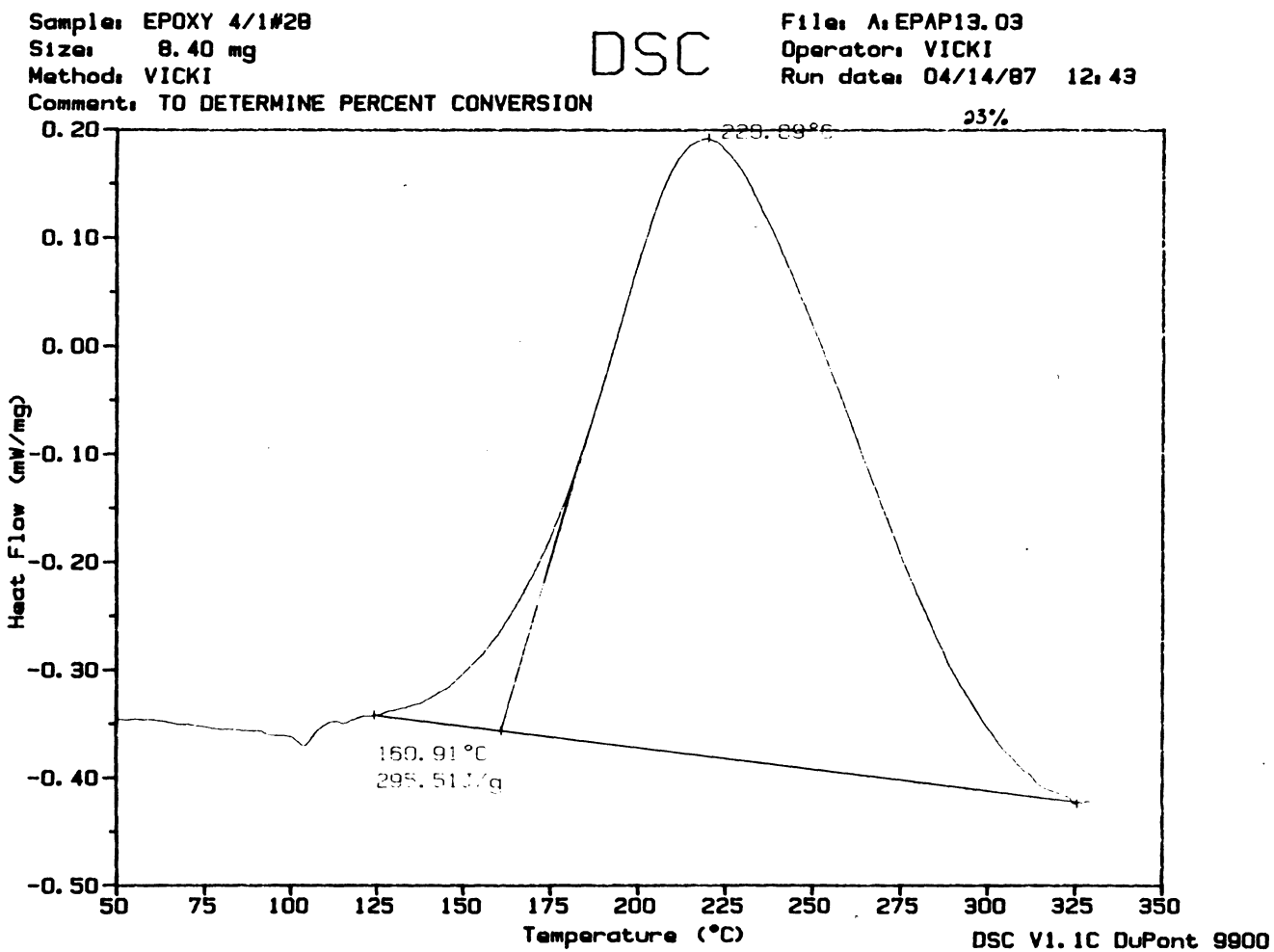


Figure 27. DSC Plot of 23% Cured Epoxy Sample

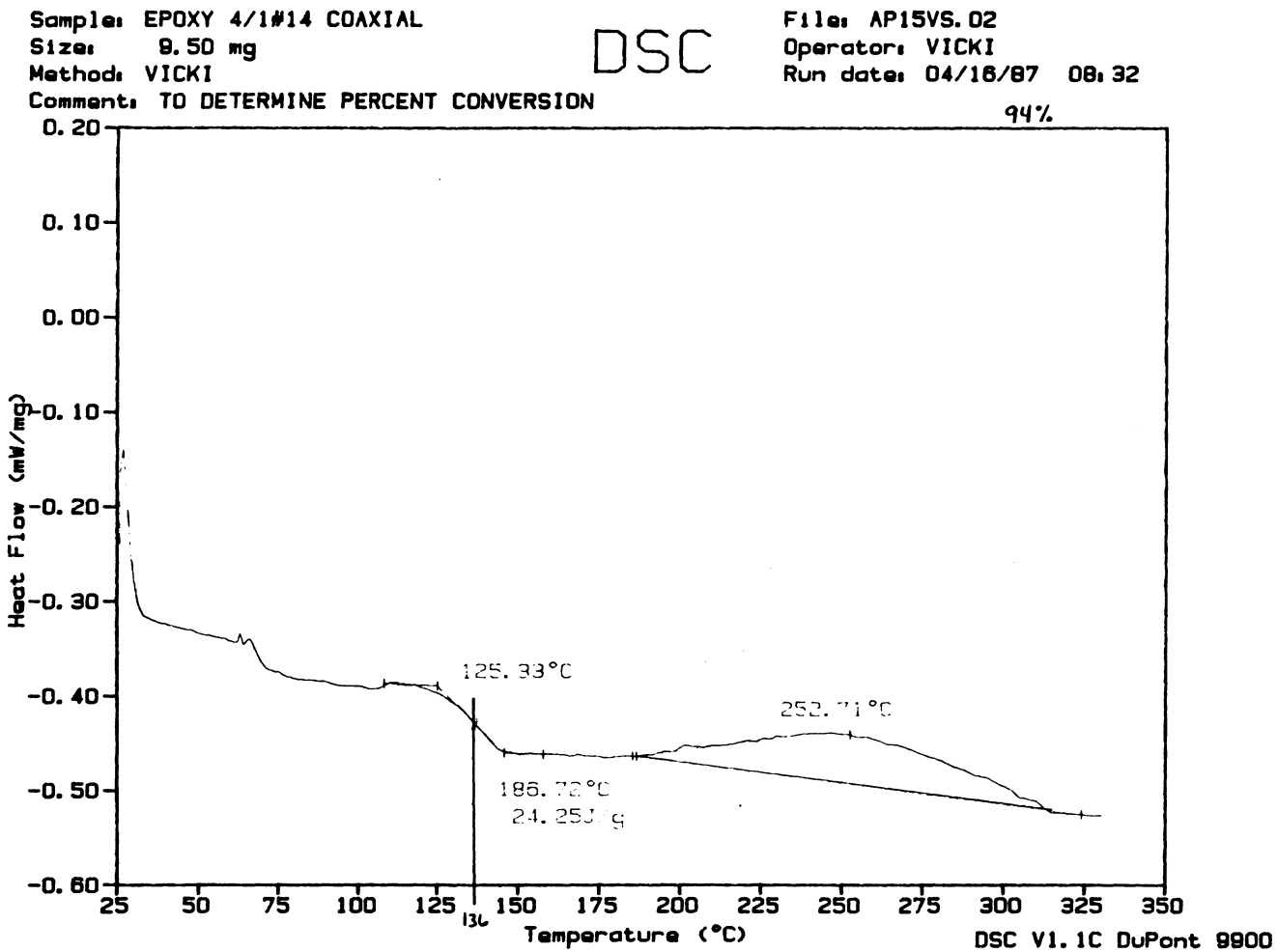


Figure 28. DSC Plot of 94% Cured Epoxy Sample

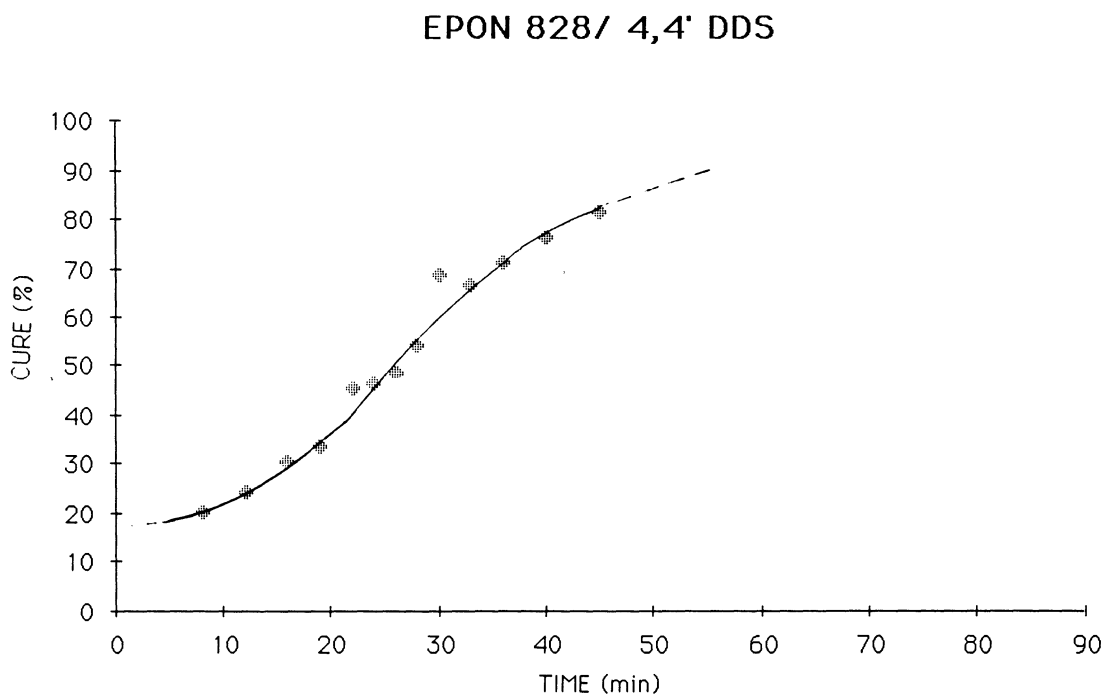


Figure 29. % Conversion Versus Time for X-Band Epoxy Samples

Table 4. DSC Results for Epoxy System - X-Band Samples
EPON 828/ 4,4' DDS

% Cure	Exotherm (J/g)	Peak T (°C)	Onset T (°C)	Tg(°C)		
				Onset	Mid-Point	
98	6	247	209	103	116	*
94	24	246	184	95	105	*
94	24	253	186	125	136	
91	35	250	185	116	125	
87	50	246	167	86	97	*
86	53	246	174	96	107	
81	74	242	170	79	96	
76	91	241	167	59	73	
71	112	241	162	47	67	
68	125	240	157			#
66	130	240	156	47	63	
54	175	236	153			#
48	199	229	152			#
46	207	231	149			#
45	211	233	154			#
33	258	221	151			#
30	271	219	154	> RT		
24	293	220	157	>RT		
20	304	220	166	>RT		

* Different DSC calibrations.

Endothermic peaks mask Tg. Endotherm due to Melting and/or Physical Ageing effects.

recorded to 340°C and this temperature increase will complete the cure of the epoxy sample. Figure 30 is the second measured DSC plot for the epoxy sample shown in Figure 27. The plot shows only the T_g for the completely cured sample. The T_g of the cured samples was 194-199°C, and this value was used as a measure to varify the epoxy samples. A measured T_g below or above the expected value would indicate that an error was made in the epoxy preperation.

A series of DSC plots is shown in Figures 31-32, the percent cures of the epoxy samples are between 33-68 %. The series shows an endothermic peak which increases in size to a maximum and then decreases, while shifting towards increased temperatures. This behavior has been attributed to two different causes. Brett[36] describes the endotherms to be a melting process of the polymer mixture. Wilkes et.al.[37] explains the endotherms to be a result of a physical ageing process. These same general results were obtained for the P-band samples.

The dielectric results obtained for the microwave cured epoxy samples are given in Table 5. The results obtained were a preliminary study to determine if any appreciable differences were found between microwave and thermal cured samples. The maximum power available with the Raytheon Microwave Generator is 80 watts. The power output to the samples was 30-80% of the total power and the samples were irradiated for 240-1200 seconds. The results obtained show no appreciable difference in permittivity between the two methods of curing. Further there appeared to be no noticeable difference between samples cured with different percent power or different lengths of time.

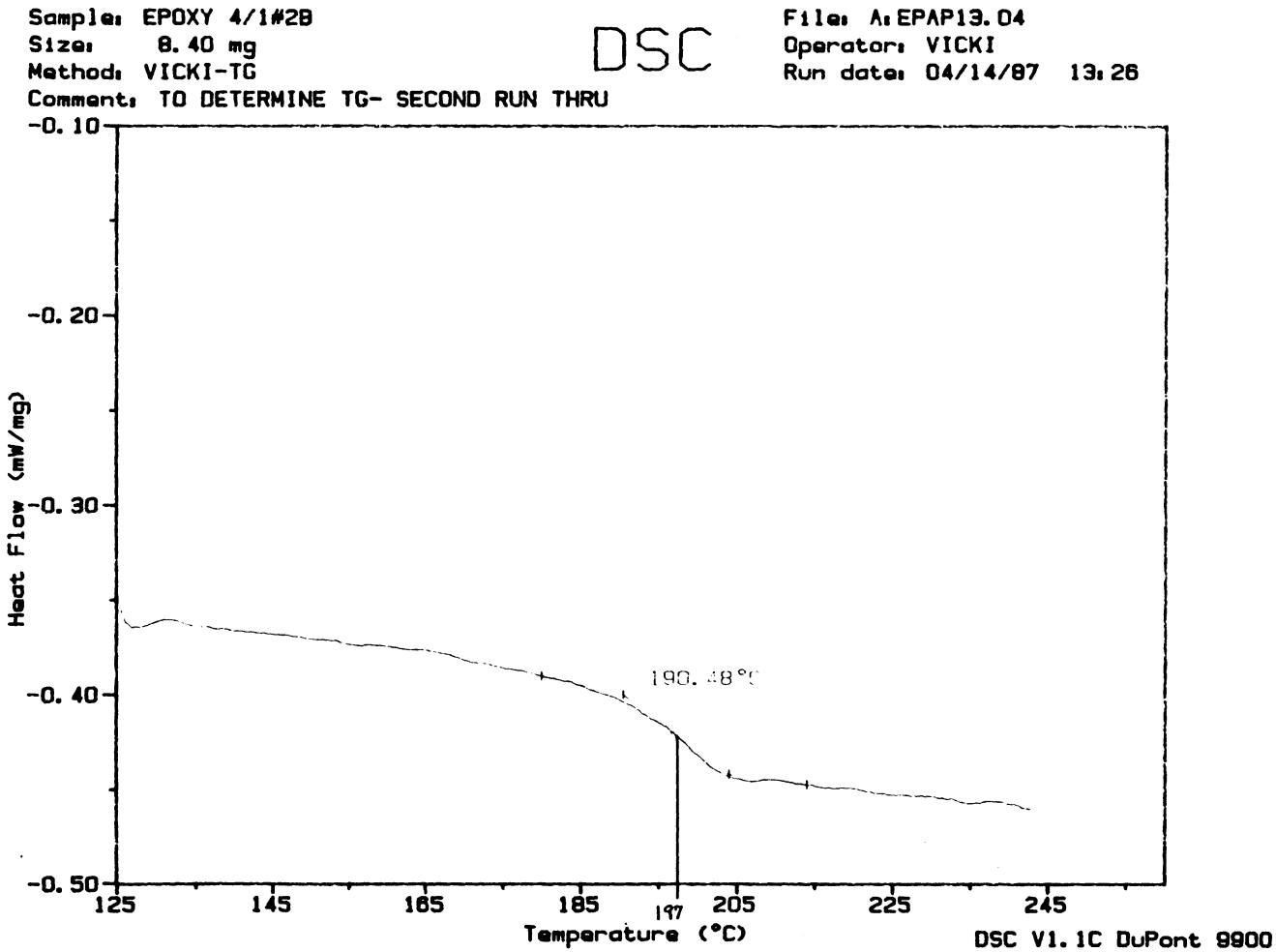


Figure 30. Second Measured DSC Plot of 23% Cured Epoxy Sample

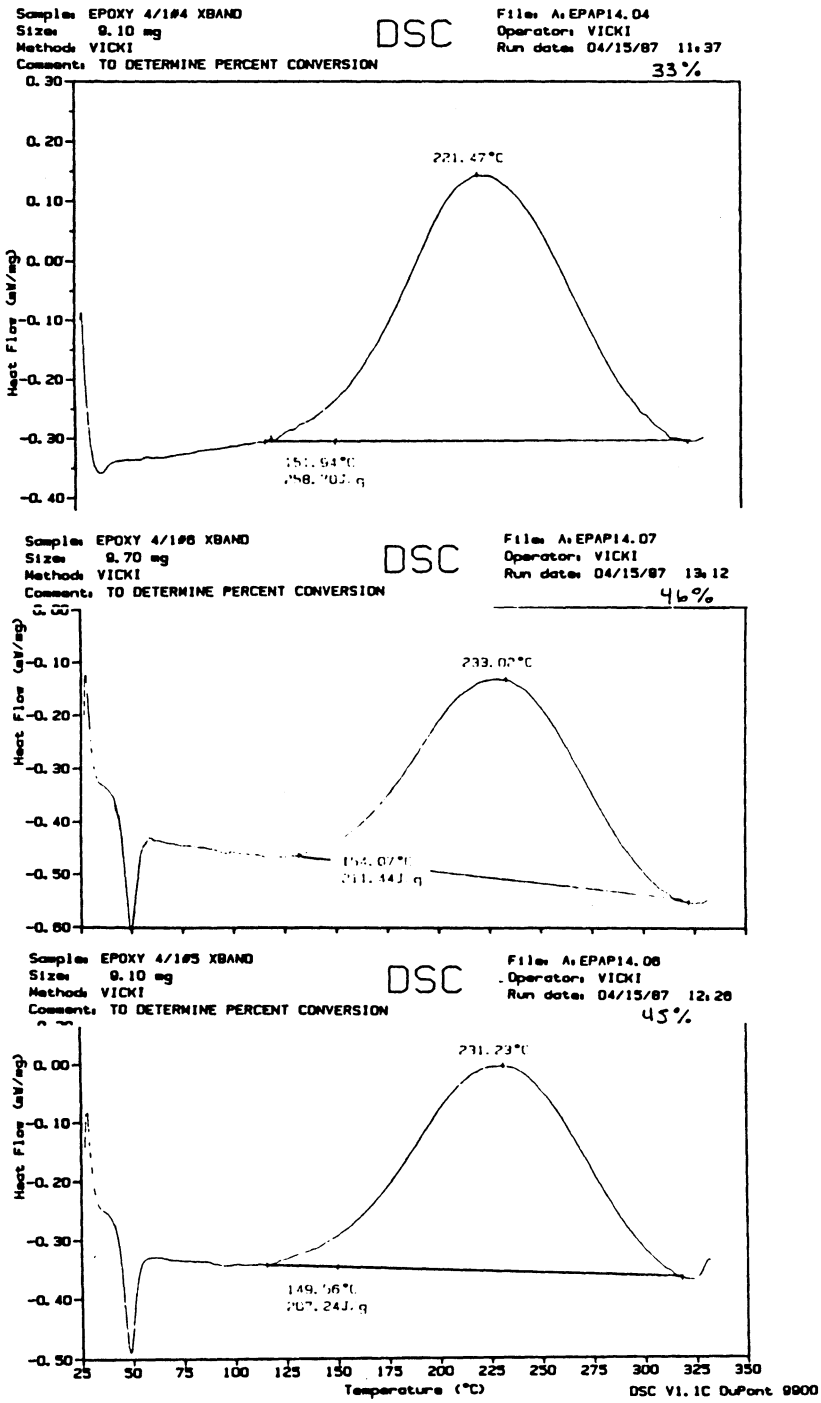


Figure 31. DSC Plots of Epoxy Samples 33- 45% Cure

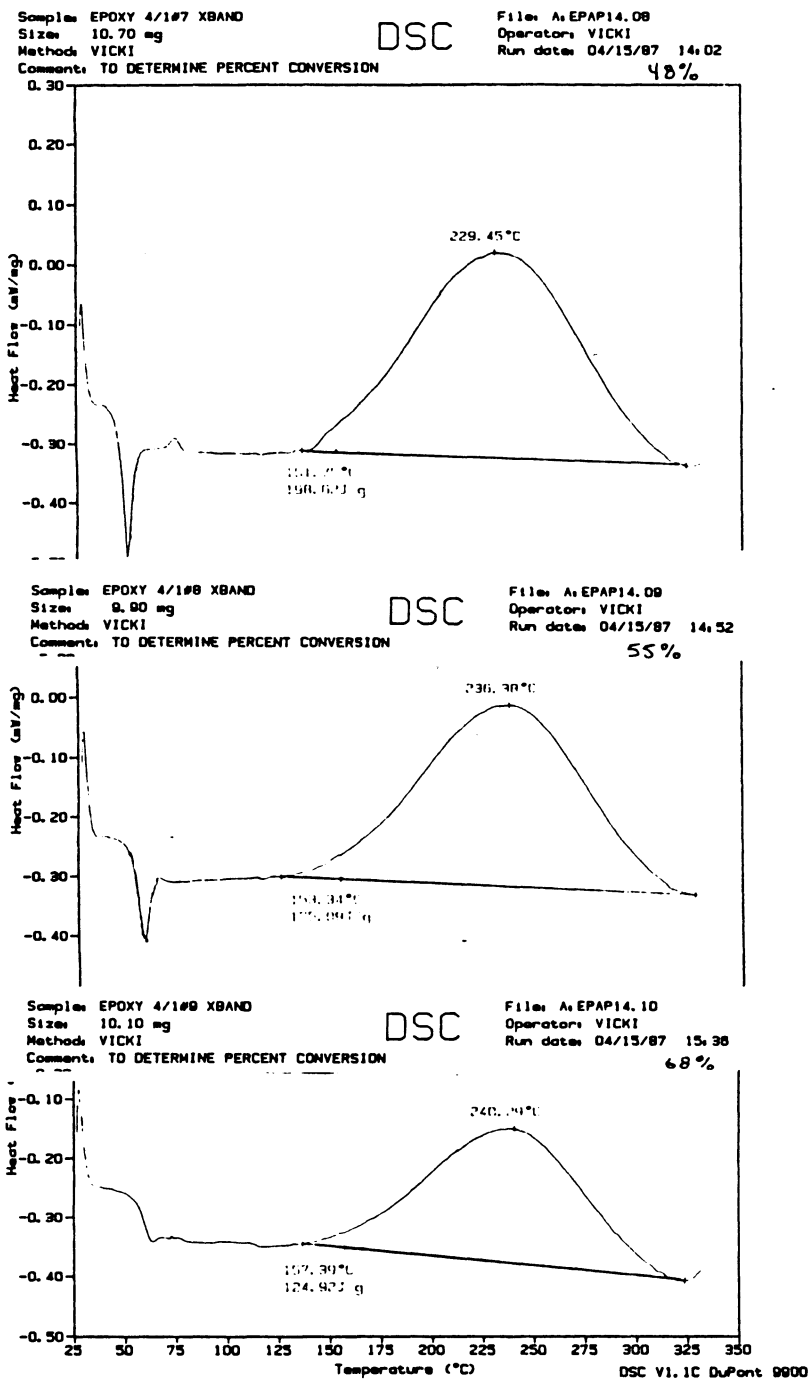


Figure 32. DSC Plots of Epoxy Samples 48- 68% Cure

Table 5. Permittivity of Microwave Cured Epoxy Samples - X-Band (8.2-12.4 GHz)

Sample Number	% Power	Time of Irradiation (seconds)	Dielectric Constant	Loss Factor
1	30	1000	3.22 - 3.28	.06 - .12
2	30	700		
	70	1032	3.20 - 3.26	.10 - .16
3	50	452.6	3.20- 3.28	.12 - .18
4	50	1200	3.10 - 3.20	.02 - .06
5	53	700.2	3.23 - 3.31	.12 - .20
6	55	700	3.22 - 3.26	.14 - .18
7	80	240.1	3.18 - 3.28	.06 - .14
8	80	300.3	3.10 - 3.20	.06 - .14

C. Polystyrene

An increase in dielectric constant with increasing frequency is seen in all the experimental data. A list of the measured permittivities for the polystyrene samples at X- and P-band are given in Table 6. With the exception of PSOH 9.4K and PSOH 3.6K, the dielectric constants overlap reasonable well between the two frequency bands. These two PSOH samples contained a significant amount of bubbles and this could account for the differences. The loss factors measured were $0\pm.05$, and because the values are close to 0 the experimental error is too great to allow any significant conclusions to be made. Where trends appear in the loss factor the data will be presented.

The molecular structures and formulas of the polystyrene have been given in Table 3. To accurately compare the measured results, the data must be presented to keep molecular factors constant. As such, the hydroxyl terminated samples and samples with equivalent molecular weight and molecular weight distribution will be compared. The measured dipole moments of molecules equivalent to the end groups of the polystyrene are listed in Table 7 and will be used to correlate the measured permittivity results[38]. These values were obtained at ambient temperatures with benzene as the solvent.

The P-band dielectric constants for the hydroxyl terminated polystyrene samples are shown in Figure 33. The results show an increase in dielectric constant with a decrease in chain length, corresponding to an increase in hydroxyl concentration. The curves for the PSOH 3.6 and PSOH 5.7 overlap. The difference in molecular weights between those two samples is less than the difference between

Table 6. Permittivity of Polystyrene Samples

Dielectric Constant:

Polystyrene	$\bar{M}n$	X-Band	P-Band
PSOH	1.2	2.54 - 2.58	2.55 - 2.57
PSOH	3.6	2.40 - 2.43	2.51 - 2.54
PSOH	5.7	2.45 - 2.49	2.52 - 2.54
PSOH	9.4	2.50 - 2.54	2.47 - 2.50
PSMA	1.3	2.47 - 2.50	2.50 - 2.60
PSMT	9.4	2.52 - 2.54	2.54 - 2.62
PSU	3.6	2.40 - 2.44	2.46 - 2.56
PSB	3.6	2.45 - 2.50	2.52 - 2.58

Loss Factor:

Polystyrene	$\bar{M}n$	X-Band	P-Band
PSOH	1.2	.03 - .05	.02 - .04
PSOH	3.6	0 - .03	-.03 - -.02
PSOH	5.7	.02 - .04 / -.04 - -.02 *	-.01 - .02
PSOH	9.4	-.02 - .01	0 - .015
PSMA	1.3	-.01 - 0	-.04 - -.01
PSMT	9.4	-.04 - 0 / 0 - .02*	-.04 - .05
PSU	5.7	-.05 - -.04 / .02 - .06 *	0 - .03
PSB	5.7	-.05 - -.03 / .01 - .08 *	-.05 - .05

* Measured Twice Changing Orientation of Sample Holder

Table 7. Dipole Moments of Molecules Corresponding to End Groups of Polystyrene Samples*

Polystyrene	Molecule	Formula	Dipole Moment	Temperature ^{o}C
PSOH	methanol	CH_4O	1.63 - 1.78	10 - 60
PSMA	methyl methacrylate	$C_5H_8O_2$	1.60	na.
			1.97	18
PSMT	dimethyl p-phthalate	$C_{10}H_{10}O_4$	2.2	25
PSU	methyl n-phenyl carbamate	$C_8H_9O_2N$	3.69	25
			4.11	25
PSB	methyl benzoate	$C_8H_8O_2$	1.8	20 - 50
			$1.9 \pm .05$	26
			2.53	25

* Solvent- Benzene

* Data taken from reference 38.

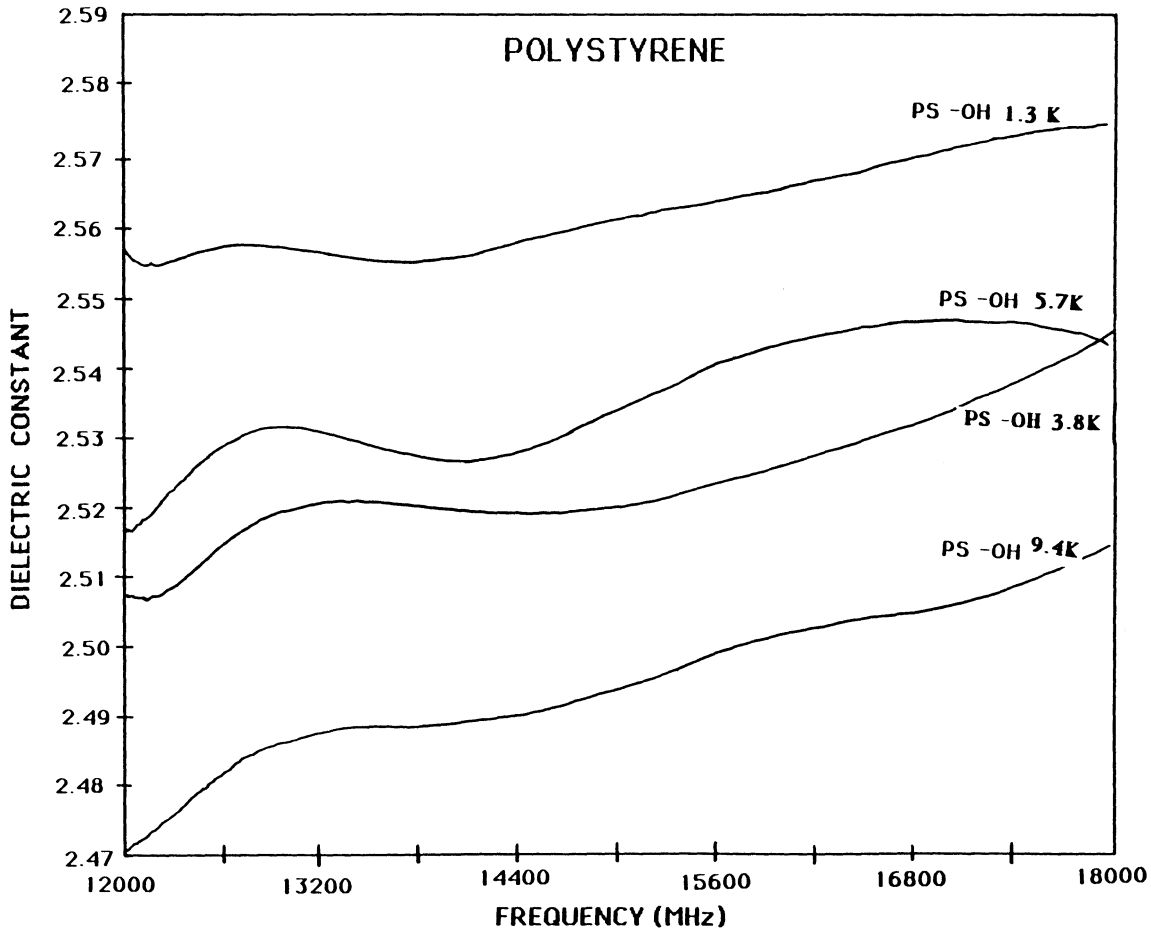


Figure 33. Dielectric Constant of PS-OH Samples
Number Indicates $\overline{M}_n$, P-Band Measurement

the PSOH 3.6 and 1.2 and the PSOH 5.7 and 9.4, and as such the values would be expected to be very close. The sample of the PSOH 3.6 contained bubbles and was the poorest of the series. If the sample length were decreased by 2%, to account for the increase in sample length caused by the bubbles, the values obtained would increase and be in the expected range of ϵ' for the corresponding $\overline{M}_n$.

Figure 34 shows the measured results for the X-band PSOH samples. The PSOH 1.3 and 5.7 samples were very good with flat surfaces, few cracks and no bubbles in the polymer matrix. It is assumed that the values for these samples have less experimental error associated with the dielectric measurements, and the results obtained are an accurate reflection of the permittivity. Between those two samples an increase is seen with increasing hydroxyl concentration and molecular motion, resulting from decreased chain length. The PSOH 3.6 and 9.4 samples were of poor quality and a number of errors could be associated with the measured results, accounting for the descrepency in the expected results.

The loss factors for hydroxyl terminated polystyrene samples in the X- and P-bands are shown in Figures 35 and 36. The PSOH 1.2 sample shows the highest loss factor in both frequency bands. The results may show an increase in the loss factor with increasing hydroxyl concentration, but because of the large error associated with these results no conclusive interpetation can be made.

The dielectric constants of the three polystyrenes with, $\overline{M}_n$ 3.6 and distribution 1.08, are shown in Figures 37 and 38. The results, for both the X- and P-band, show the dielectric constant increase with frequency. The dielectric constant decrease as the end group is

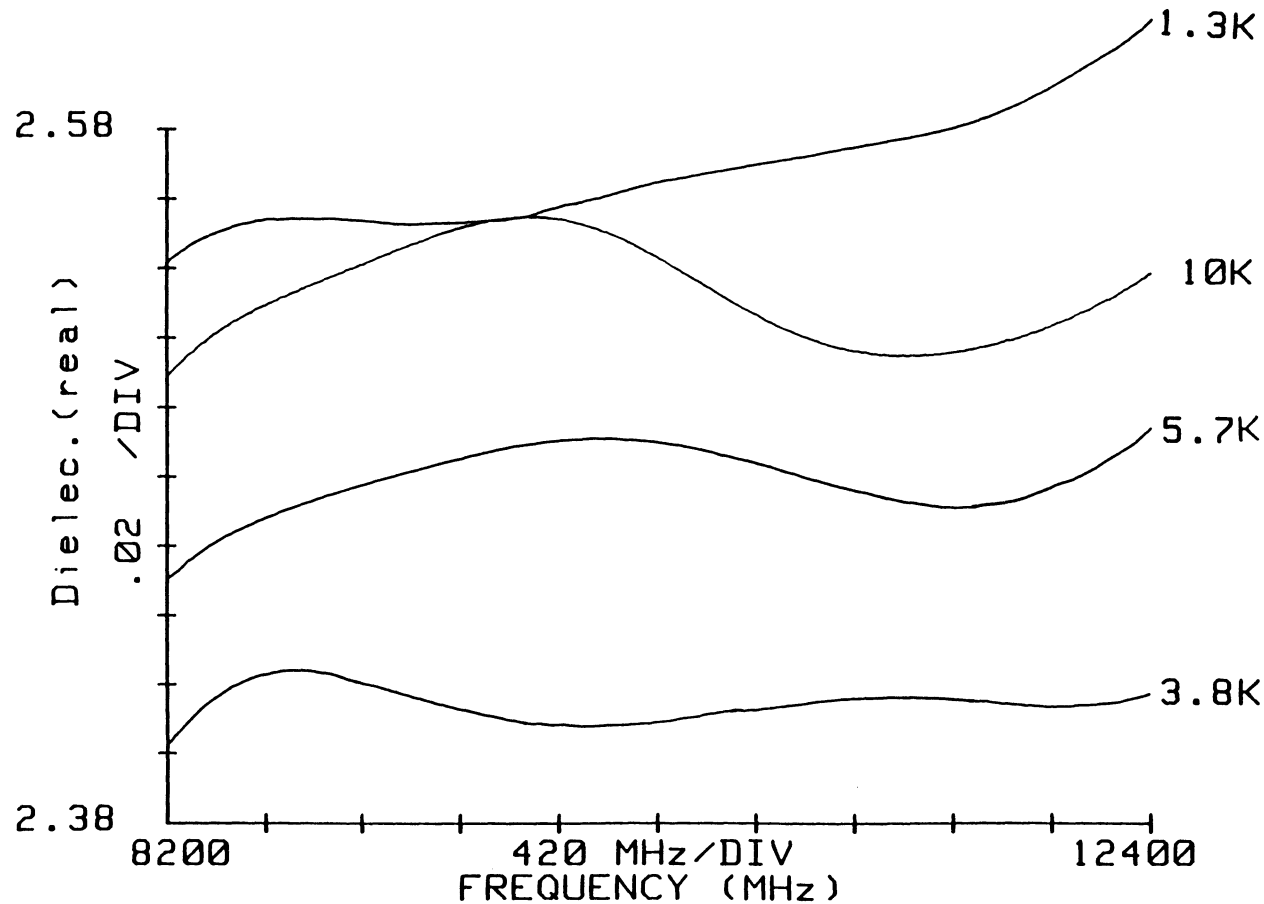


Figure 34. Dielectric Constant of PS-OH Samples
Number Indicates $\overline{M}_n$, X-Band Measurement

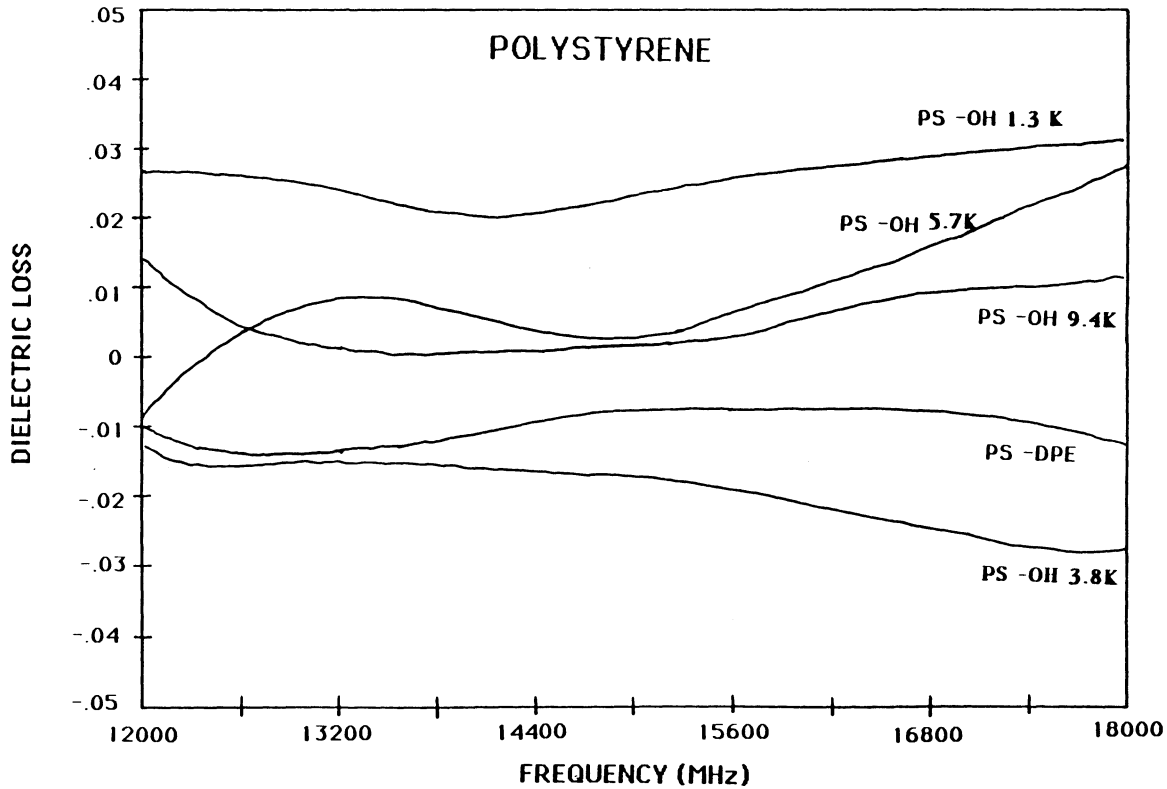


Figure 35. Loss Factor of PS-OH Samples
Number Indicates $\overline{M}_n$, P-Band Measurement

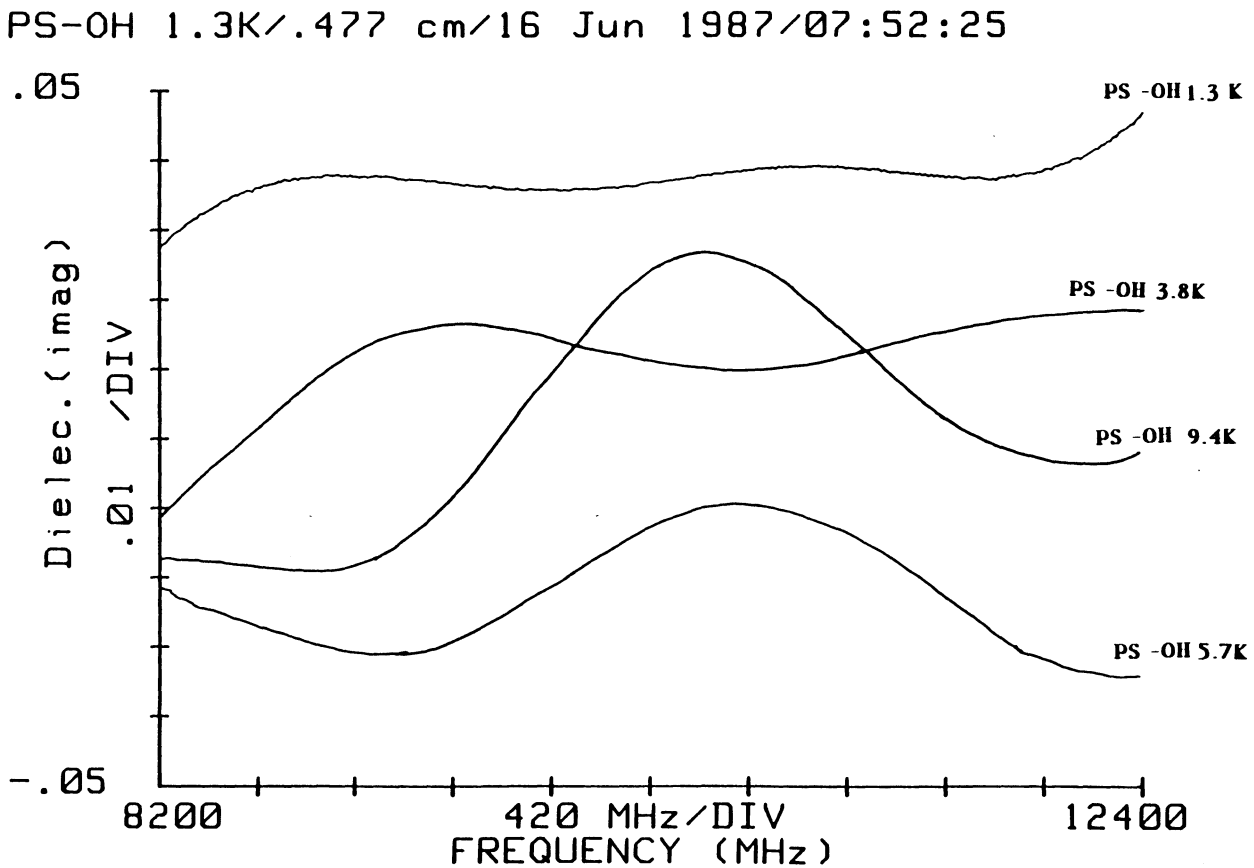


Figure 36. Loss Factor of PS-OH Samples
Number Indicates $\bar{M}_n$, X-Band Measurement

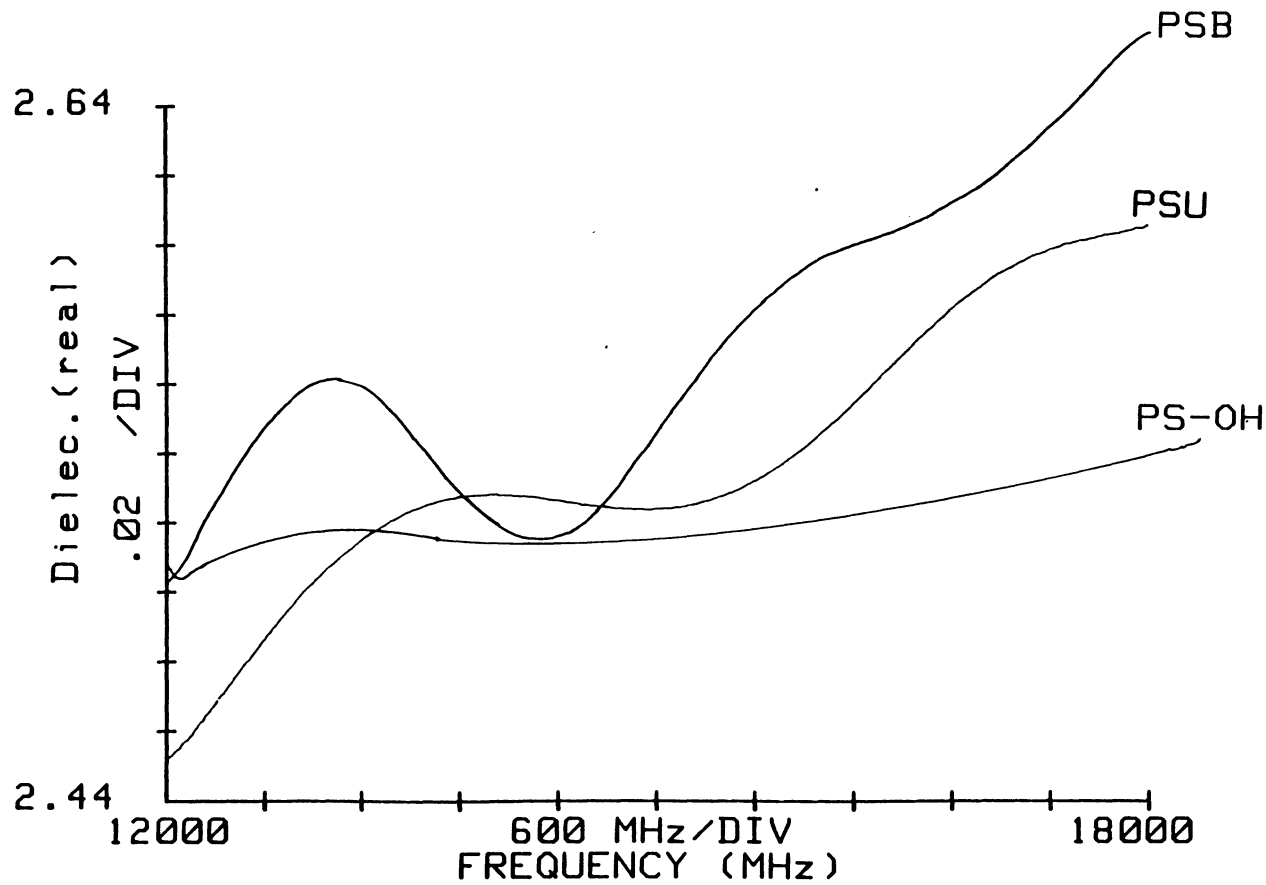


Figure 37. Dielectric Constant of P-Band PSB, PSU, and PSOH
$\overline{M}_n$ = 3.6

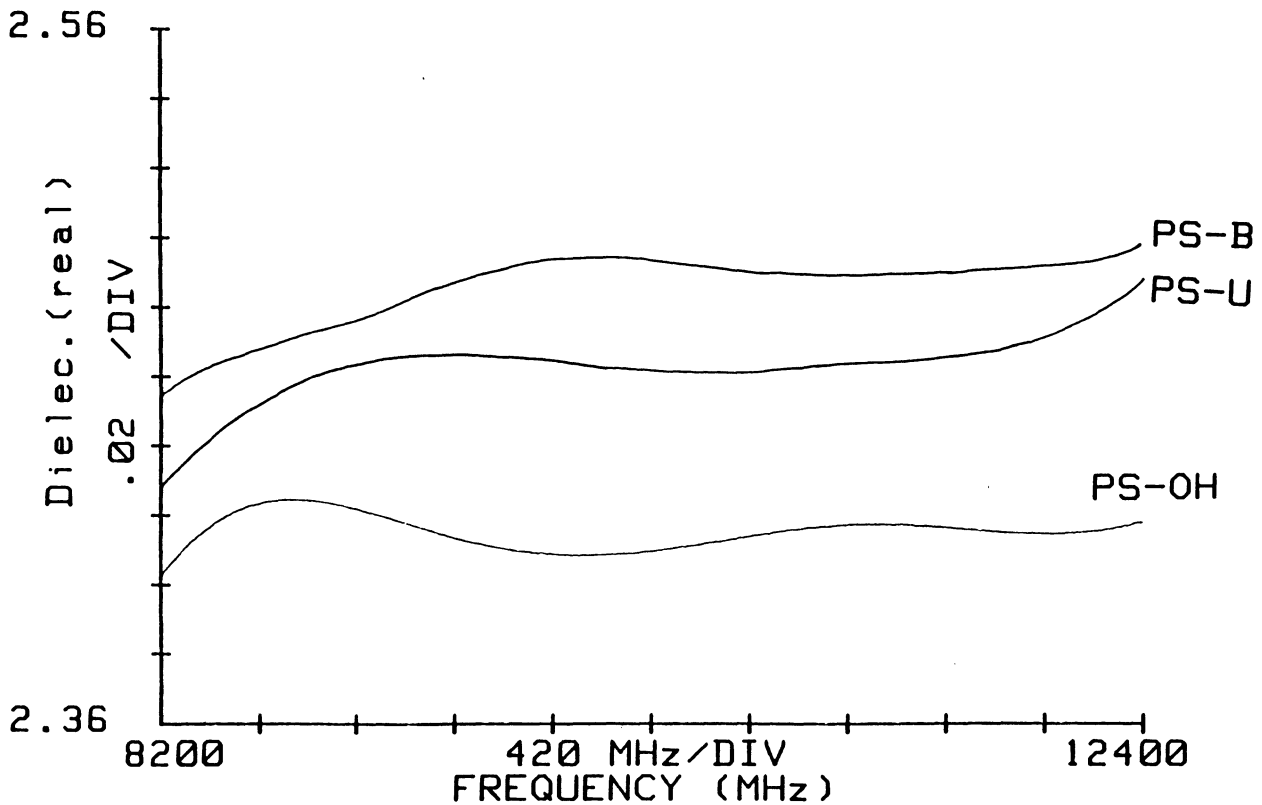


Figure 38. Dielectric Constant of X-Band PSB, PSU, and PSOH
$\overline{M}_n$ = 3.6

changed from methyl benzoate (B) to methyl n-phenyl carbomate (U) to OH, respectively. The value of the dipole moments of the corresponding end group molecules would indicate the order decreasing U to B to OH, respectively. The reversal of the the U and B groups may possibly be due to the fact that the amine with a polymer attached would be more restrictive in the motion of the dipole or the amine dipole in the polymer may be significantly different than that of the corresponding end group molecule.

Figures 39 and 40 show the dielectric constants of dimethyl p-phthalate terminated polystyrene (PSMT) and PSOH, both having $\overline{M}_n$= 9.4 and $\overline{M}_w/\overline{M}_n$= 1.08. The X-band results show no apparent difference between the two polystyrene samples. The results of the P-band show a large difference in values. From the dipole moments measurements of MT and OH it would be expected that the dielectric constant of PSMT would be greater than PSOH. The X-band sample of PSOH, as previously discussed, was of poor quality and as such had a significant amount of error associated with the measured results.

The dipole moments of methanol and methyl methacrylate (MA) are approximately equal and as such the dielectric constants of PSOH and PSMA (1.3 $\overline{M}_n$, 1.05 $\overline{M}_w/\overline{M}_n$) would be expected to be equivalent. The results in Figures 41 and 42, show the dielectric constants to be approximately equal, within experimental error. However, the dielectric constants of the PSMA increase more rapidly than the PSOH.

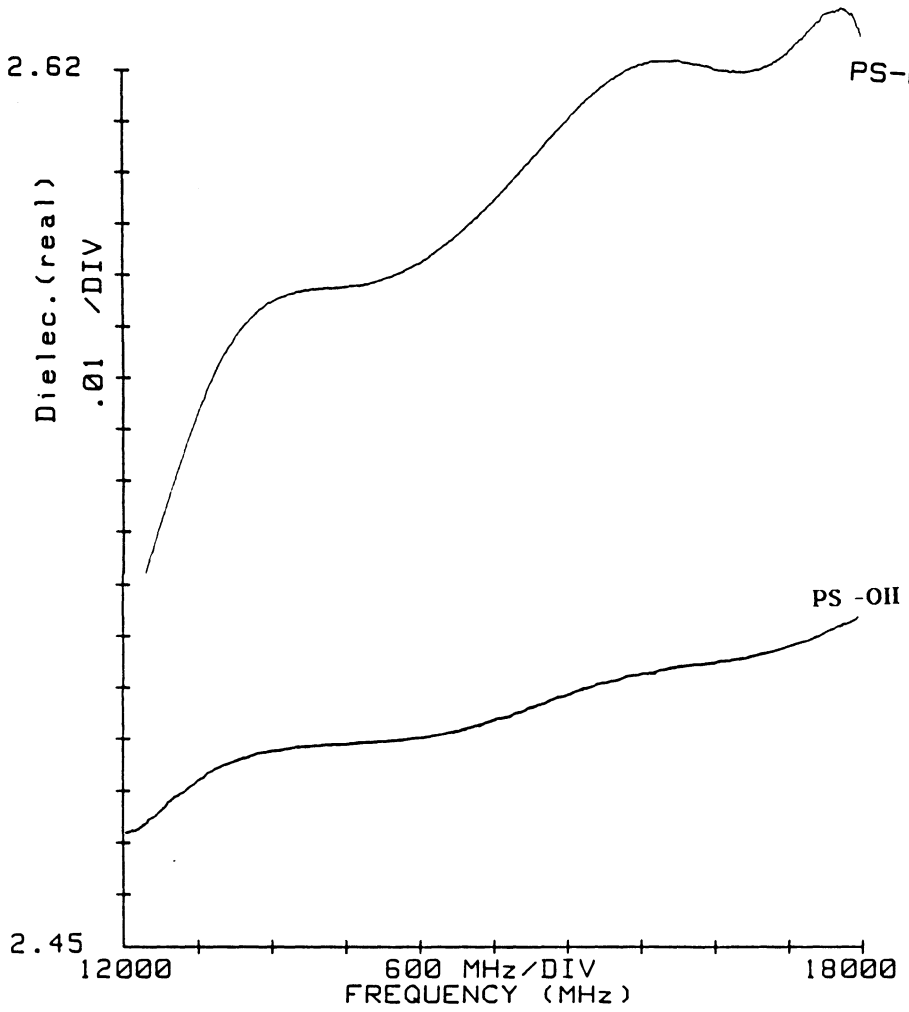


Figure 39. Dielectric Constant of P-Band PSMT and PSOH
$M_n = 9.4$

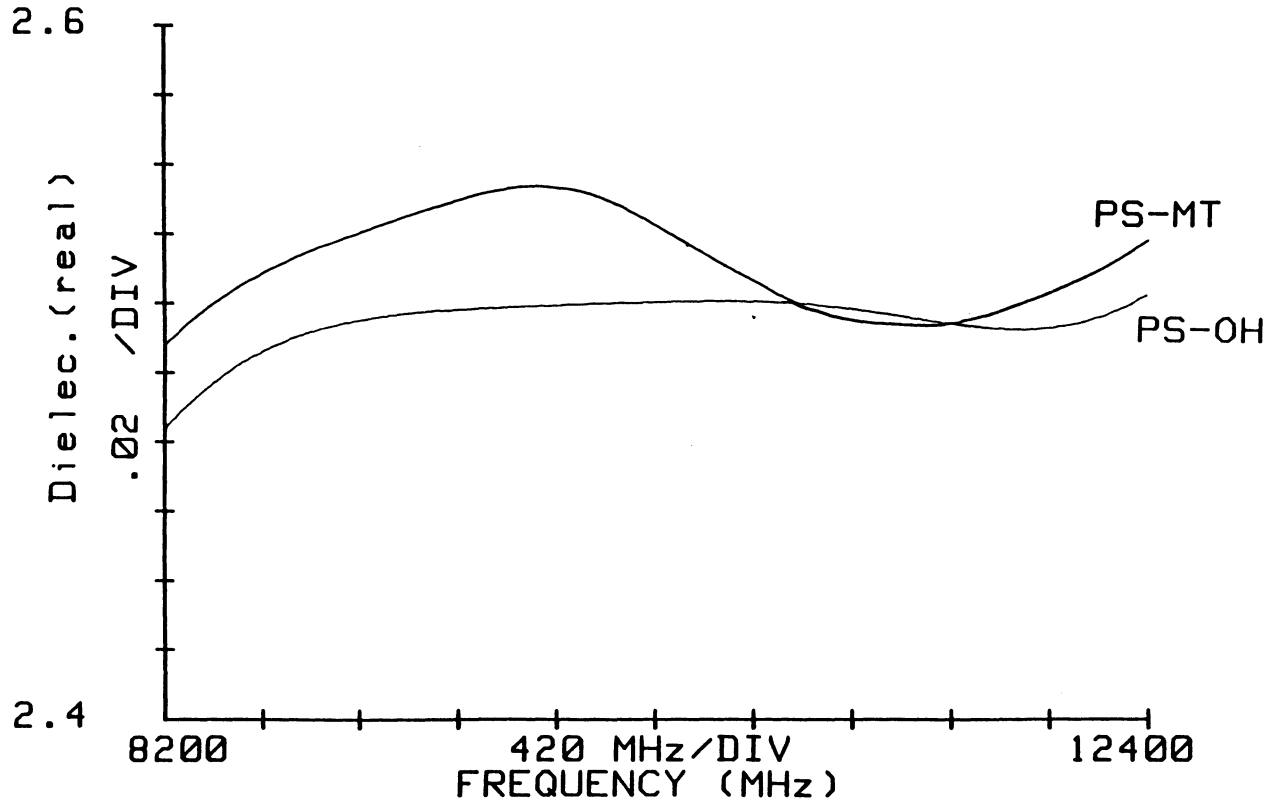


Figure 40. Dielectric Constant of X-Band PSMT and PSOH
$\overline{M}_n$ = 9.4

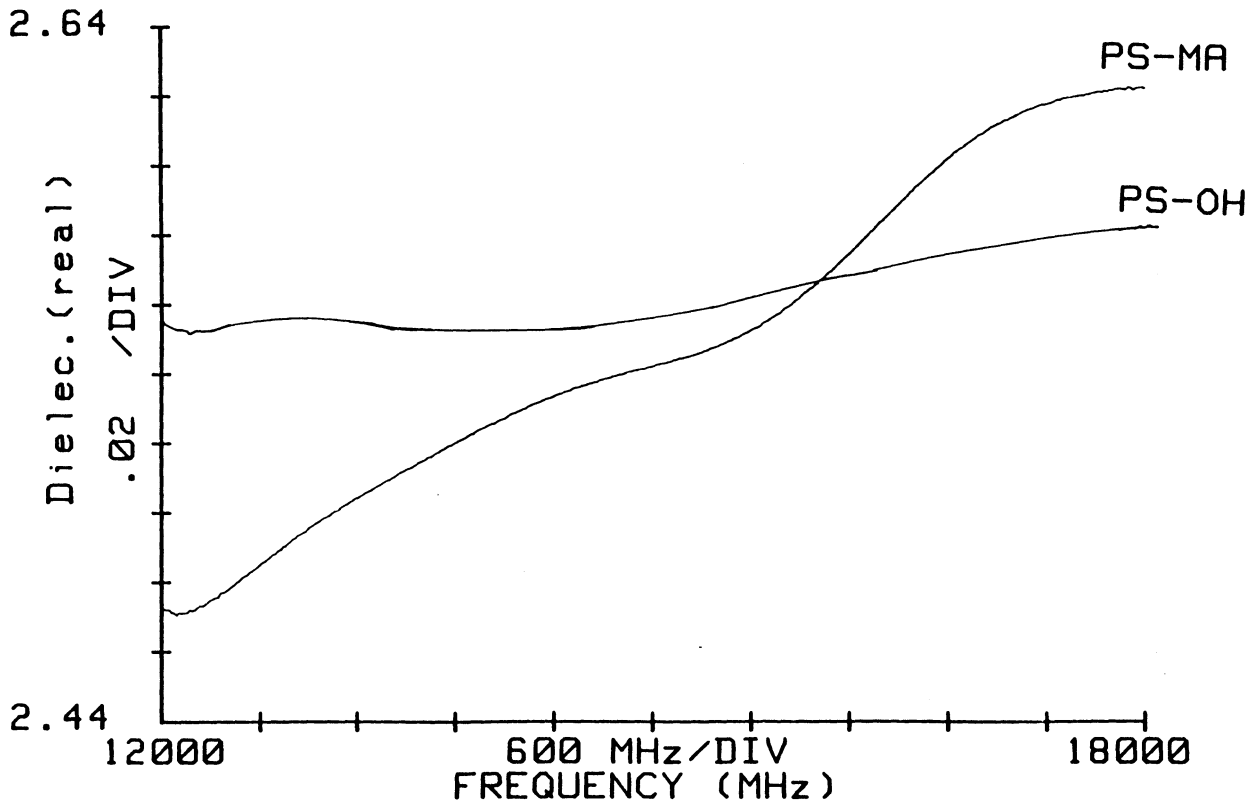


Figure 41. Dielectric Constant of P-Band PSMA and PSOH
$\overline{M}_n$ = 1.3

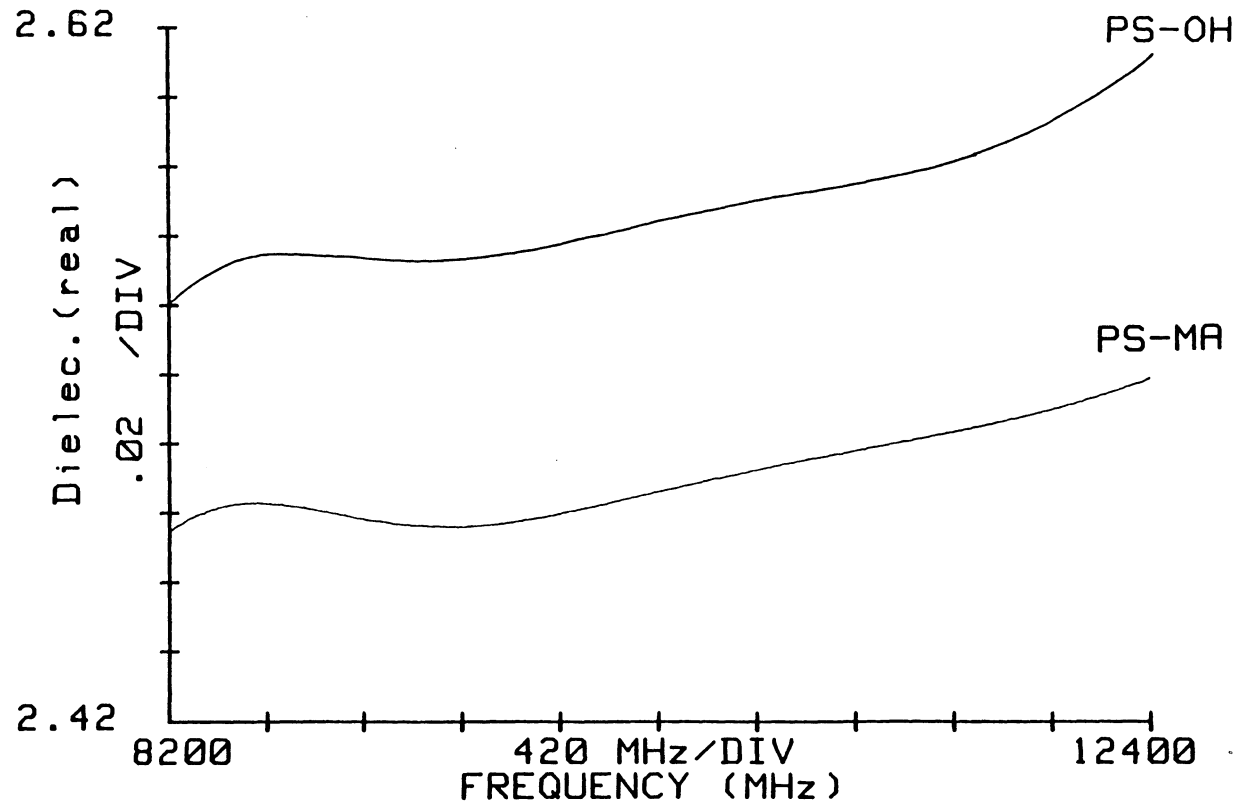


Figure 42. Dielectric Constant of X-Band PSMA and PSOH
$\overline{M}_n$ = 1.3

CONCLUSIONS/SUMMARY

The permittivity results obtained for both the epoxy system and polystyrene samples lead to several important conclusions. The dielectric constant for the 98% cured epoxy sample showed a slight dependency on the frequency and the loss factor showed no dependence. The dielectric constants measured for the epoxy samples as a function of percent cure were sensitive to the T_g. As the T_g passed through the measurement temperature the dielectric constant decreased. The loss factors appeared to decrease monotomically with increasing cure. The dielectric constant appears to influenced by changes in molecular motion, where as the loss factor appears to be more influenced by changes in dipole groups and dipole concentration.

The low loss factor of the epoxy system indicates that it is not an ideal epoxy for microwave applications. Materials with ϵ'' of 0.2 or more results in good heatability, 0.08 -0.02 fairly good heatibility, 0.01 -0.08 poor heatability, and under 0.01 there is little or no heating[11]. To improve the epoxy system for applications of microwave curing the value of ϵ'' must be increased. This could be obtained by several different methods including: 1) Add more permanent dipole groups in the epoxy backbone, 2) modify with a polar side chain, and 3) dope with high loss impurities.

The results of the loss factors of the PSOH samples showed no conclusive results. The increase in the hydroxyl concentration was not large enough to produce a significant change. The molar ratio of

the hydroxyl groups in the PSOH samples was between 0.0131 and 0.0018, and as such the polar group concentration is very small compared to the overall concentration of polymer molecules. To significantly increase the loss factor of a material a large concentration of polar groups must be introduced.

Research relating the concentration of dipole groups on the permittivity of a polymer system needs to be continued. To achieve the precision possible with the network analyzer, a system with high a larger loss factor needs to be studied. Additionally permittivity measurements at increased temperature in the microwave frequencies would allow more significant conclusion to be made .

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Appendix A

Phase shift for $S_{11}(w)$ and $S_{21}(w)$ using waveguide measurement setup.

For $S_{11}(w)$:

$$\text{Phase Shift} = \frac{360^{o} \times f_{o}\sqrt{1 - \left(\frac{f_c}{f_o}\right)^2}}{c} \times 2 \times a$$

For $S_{21}(w)$:

$$\text{Phase Shift} = \frac{360^{o} \times f_{o}\sqrt{1 - \frac{f_c}{f_o}^2}}{c} \times (a + b)$$

where f_o = measurement frequency

f_c = cutoff frequency of the waveguide

c = velocity of light

a = physical distance between calibration plane and measurement plane of port 1

b = physical distance between calibration plane and measurement plane of port 2

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