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ELECTROMAGNETIC PROCESSING OF MATERIALS

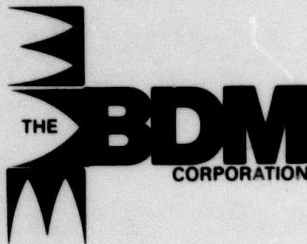
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August 17, 1984

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A review is made of the coupling of electromagnetic radiation to non-conductive solids. The mechanisms for coupling microwaves to these solids are identified and variables which can influence dielectric loss are reviewed. A survey of the literature on microwave processing of materials is given. Finally, a discussion is presented on modifying materials so as to enhance coupling.

Advantages of microwave processing of materials include:

- (1) Rapid bulk heating;
- (2) Selective heating in strong coupling regions;
- (3) Rapid switching and sensing yield potentials for intelligent processing;
- (4) Precise control of heating;
- (5) Low operating costs;
- (6) Improved throughput and quality
- (7) The potential for field repair applications.

The key to realizing these improvements in materials processing is to be able to improve the coupling of microwave to materials nearly transparent to microwave frequencies and understand how this is done so that processed materials can perform their desired functions.

Among the conclusions drawn from this work are:

- (1) Processing materials candidates probably can be modified to enhance microwave coupling and dielectric loss;
- (2) As adhesives and composite materials become increasingly utilized in the defense and commercial sectors, advantages of using microwave energy for processing and field repair will increase; and
- (3) Economic factors such as low energy costs and improved quality and output also make microwave processing attractive.

The report recommends that a program be initiated to investigate (1) coupling theories of microwaves to materials; (2) microwave coupling to adhesives; (3) microwave coupling to composites; (4) microwave couplers; (5) field repair possibilities; (6) microwave induced chemical reactions; and (7) integration of microwave processing into an intelligent materials processing system.

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CHAPTER I
EXECUTIVE SUMMARY

This report examines the potential for using electromagnetic radiation (microwaves) in the processing of materials. The feasibility of enhancing the coupling of incident microwave energy for materials processing is investigated with emphasis on ordinarily low-loss materials, e.g., polymers.

A review is made of the coupling of electromagnetic radiation to non-conductive solids. The mechanisms for coupling microwaves to these solids are identified and variables which can influence dielectric loss are reviewed. A survey of the literature on microwave processing of materials is given. Finally, a discussion is presented on modifying materials so as to enhance coupling.

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- (2) As adhesives and composite materials become increasingly utilized in the defense and commercial sectors, advantages of

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using microwave energy for processing and field repair will increase; and

- (3) Economic factors such as low energy costs and improved quality and output also make microwave processing attractive.

The report recommends that a program be initiated to investigate (1) coupling theories of microwaves to materials; (2) microwave coupling to adhesives; (3) microwave coupling to composites; (4) microwave couplers; (5) field repair possibilities; (6) microwave induced chemical reactions; and (7) integration of microwave processing into an intelligent materials processing system.

CHAPTER II INTRODUCTION

This study, and resulting report, is a consequence of DARPA/DSO interest in developing a program to investigate the use of microwaves in the processing of materials, particularly polymeric and ceramic materials. Activities in support of this effort were undertaken as part of a task on the Quick Response Contract between DARPA/DSO and The BDM Corporation.

BDM conducted an on-line literature search of the DIALOG data base and obtained copies of references to the microwave processing of materials. Also obtained were the NTIS¹ and Engineering Index² bibliographies on radiation curing of polymers. Additional sources on the dielectric properties and behavior of polymers and ceramics were also obtained. Most of this material is listed in the references at the end of this report and also discussed in Chapters IV and V.

As a result of the literature search, BDM assisted DARPA in preparing a briefing on "Electromagnetic Processing of Materials." BDM was subsequently asked to prepare this report on the same subject. In the next chapter we review the theories of microwave coupling to materials and introduce the relevant material parameters. In Chapter IV we present representative data and information on dielectric loss, mechanisms of dielectric loss and physical parameters which influence this loss. A review of previous work is presented in Chapter V and in Chapter VI we discuss the coupling of microwaves to designed materials. Conclusions are given in Chapter VII.

Advantages of microwave curing include the ability to heat a material almost instantaneously, avoiding thermal gradients from conduction. Thus, the entire body is heated uniformly. The heating process can be turned on or off instantaneously, and therefore curing is controlled more accurately than conventional methods. Little waste heat is generated, equipment is easily operated and selected regions of the material can be heated.

Possible objectives of a DARPA program on microwave processing of materials include:

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- (1) Understanding the mechanisms of selective coupling of microwave energy to materials; including polymers, ceramics and composites;
- (2) Assessment and demonstration of the use of selective coupling of microwaves in the processing of materials. Particularly relevant examples might be the curing of adhesives and polymers, the fabrication of fiber reinforced plastics, and the sintering of ceramics;
- (3) Identification of techniques to increase microwave absorption in intrinsically microwave transparent materials;
- (4) Determination of the feasibility for using microwave generated selective coupling in the development of new materials;
- (5) Assessment of using microwave processing for field repair;
- (6) Development of support microwave structures for use in a field environment and for use with materials having varying dielectric properties; and
- (7) Evaluation of the potential for novel chemical synthesis using selective heat coupling.

At the core of this list of possible objectives is a clear understanding of the mechanisms which couple electromagnetic radiation at microwave frequencies with various classes of materials and of what leverage can be applied both at the microscopic level (e.g., additives) and the macroscopic level (e.g., support structures and temperature) in order to enhance, control, and direct this coupling. Although no definitive answers are generated by the present report, a number of areas are identified for further investigation and possibly high payoff.

Preliminary conclusions drawn from this study include:

- (1) Many options are available to modify materials to enhance microwave heating. Parameters which influence coupling include temperature, pressure, frequency, composition, impurities, additives, phase, conductivity, dispersives and moisture;

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- (2) The macroscopic coupling of the microwave cavity to the material is extremely important. This coupling can be enhanced by multimode resonance to improve penetration depth, by preheating and by using high and low loss materials in combination;
- (3) Problems with high frequency cavities (cf. conduction furnaces) include cost, poor cavity-material coupling, and difficulty in maintaining uniform voltages; and
- (4) Problems with microwave curing include preferential heat absorption by volatiles leading to evaporation and voids, excess selective heating (hot spots) leading to regions of thermally induced stress, and inadvertent chemical changes during processing which in turn lead to non-uniform heating.

Obviously, the problems and benefits of selective microwave curing must be balanced for a given application, environment and material system. In the remainder of the report we will discuss some of these tradeoffs. We will also discuss the above general conclusions in more detail, as well as more specific conclusions. However, it appears that the modification and subsequent microwave processing of materials may be a viable alternative to conventional materials processing and, indeed, in some cases may be the only practical method.

CHAPTER III

MICROWAVE COUPLING TO MATERIALS

In this chapter we introduce the necessary parameters to describe the response of materials to electromagnetic radiation. We also discuss possible microscopic mechanisms for the coupling of this radiation to matter. Since metals respond instantaneously to incident electromagnetic waves and, with the exception of skin depth effects, reflect this radiation, we will concentrate primarily on dielectric materials. Likewise, since we are interested in the microwave region of the spectrum we will be looking at the high frequency (GHz) response of dielectrics.

Probably the simplest way of looking at the response of dielectrics to a time varying external field is to charge a dielectric in a parallel plate capacitor. Borrowing heavily from von Hippel (3-5), if we connect a sinusoidal voltage source to a capacitor we obtain the configuration in Figure III-1.

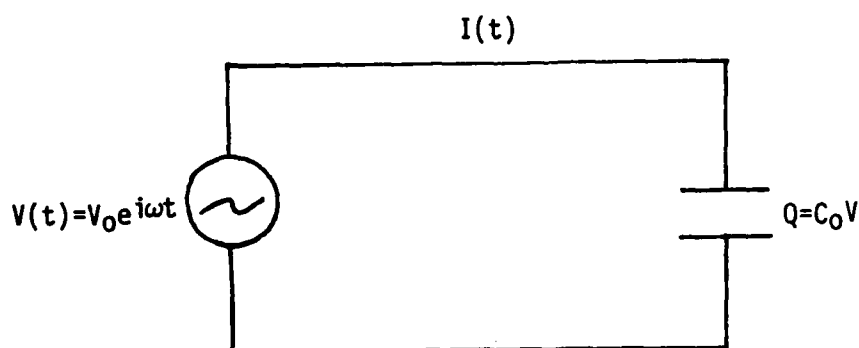


FIGURE III-1

The charging current is,

$$I_c = \frac{dQ}{dt} = C_0 \frac{dV}{dt} = i\omega C_0 V \quad (\text{III-1})$$

and leads the voltage by 90° .

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If the capacitor is filled with a dielectric, the capacitance increases to,

$$C = C_0 \frac{\epsilon'}{\epsilon_0} = C_0 \kappa' \quad (\text{III-2})$$

where ϵ' and ϵ_0 are the permittivities, or dielectric constants, of the dielectric and vacuum respectively. The relative dielectric constant is given by κ' .

If there are losses (heat) generated in the dielectric then a loss current can be defined by,

$$I_l = GV, \quad (\text{III-3})$$

and in phase with the voltage (G is the dielectric conductance). The total current is then,

$$I = I_C + I_l = (i\omega C + G)V. \quad (\text{III-4})$$

This is represented graphically in Figure III-2.

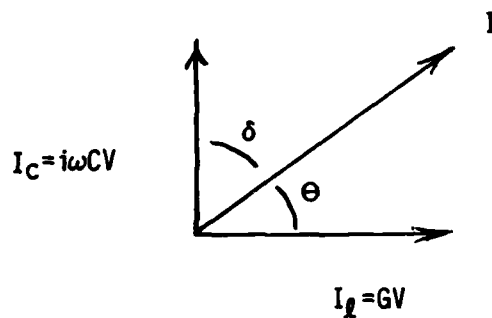


FIGURE III-2

The dissipation factor, D , or loss tangent, $\tan \delta$, is defined as the ratio of loss current to charging current, i.e.,

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$$D = \tan \delta = I_l / I_c = \frac{GV}{\omega CV} = \frac{1}{\omega RC} \quad (III-5)$$

The definition of D is general. However, the analogy to an RC-circuit does not necessarily generalize. We can generalize the loss current by introducing a complex dielectric constant,

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (III-6)$$

so that the current becomes

$$I = \frac{dQ}{dt} = \frac{CdV}{dt} = \frac{\epsilon^*}{\epsilon_0} C_0 \frac{dV}{dt} \quad ,$$

or

$$I = (\epsilon' - i\epsilon'') \frac{C_0}{\epsilon_0} i\omega V,$$

$$I = (i\omega\epsilon' + \omega\epsilon'') \frac{C_0 V}{\epsilon_0},$$

or,

$$I = i\omega\kappa^* C_0 V, \quad (III-7)$$

where κ^* is the complex relative permittivity and ϵ'' is the loss factor. The loss tangent now becomes,

$$\tan \delta = \frac{I_l}{I_c} = \frac{\epsilon''}{\epsilon'} = \frac{\kappa''}{\kappa'} \quad (III-8)$$

From the current,

$$I = (i\omega\epsilon' + \omega\epsilon'') \frac{C_0 V}{\epsilon_0},$$

we can substitute $C_0 = \epsilon_0 A/d$ and $E=V/d$ for a parallel plate capacitor to obtain the current density, J ,

$$J = \frac{I}{A} = (i\omega\epsilon' + \omega\epsilon'')E = \epsilon^* \frac{dE}{dt}, \quad (\text{III-9})$$

where $E=E_0 e^{i\omega t}$. Consequently we define a dielectric conductivity,

$$\sigma = \omega\epsilon'' \quad (\text{III-10})$$

to represent all dissipative effects, including charge migration.

The above analysis can be carried out for a magnetic material in an inductor. Such an analysis yields comparable, though slightly more complicated, equations to those for a dielectric. A complex permeability $\mu^* = \mu' - i\mu''$ is introduced along with the complex relative permeability, $\kappa_m^* = \kappa_m' - i\kappa_m''$.

With the exception of ferromagnetic materials, $\mu^* \approx \mu_0$, the vacuum permeability, and we consequently ignore energy loss mechanisms related to magnetism. Also, dissipative magnetic response of dielectrics tends to occur at low frequencies when it does become a factor. Thus, for the purposes of this report, we concentrate on the electric properties of dielectrics.

To understand the dynamics of dielectric response to incident electromagnetic waves we move to Maxwell's equations. Ampere's Law as modified by Maxwell is,

$$\vec{\nabla} \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \quad (\text{III-11})$$

By using the constitutive relations,

$$\vec{D} = \epsilon' \vec{E} \quad (\text{III-12})$$

and,

$$\vec{J} = \sigma \vec{E} = (\omega\epsilon'') \vec{E}, \quad (\text{III-13})$$

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[The use of (III-12) and (III-13) implies that we are considering homogeneous, isotropic and linear materials.] we can write

$$\vec{\nabla} \times \vec{H} = \omega \epsilon'' \vec{E} + \epsilon' \frac{\partial \vec{E}}{\partial t} . \quad (\text{III-14})$$

For sinusoidal fields,

$$\frac{\partial \vec{E}}{\partial t} = i\omega \vec{E} ,$$

and thus,

$$\vec{\nabla} \times \vec{H} = -i\epsilon'' \frac{\partial \vec{E}}{\partial t} + \epsilon' \frac{\partial \vec{E}}{\partial t} ,$$

or,

$$\vec{\nabla} \times \vec{H} = \epsilon^* \frac{\partial \vec{E}}{\partial t} . \quad (\text{III-15})$$

Likewise, starting with Faraday's Law,

$$\vec{\nabla} \times \vec{E} = - \frac{\partial \vec{B}}{\partial t} \quad (\text{III-16})$$

and the constitutive relation,

$$\vec{B} = \mu^* \vec{H} , \quad (\text{III-17})$$

we can write,

$$\vec{\nabla} \times \vec{E} = -\mu^* \frac{\partial \vec{H}}{\partial t} , \quad (\text{III-18})$$

As is well known, we can combine (III-15) and (III-18) (for one dimensional fields $E(x,t)$ and $B(x,t)$) to yield wave equations, i.e.,

$$\frac{\partial^2 \vec{E}}{\partial x^2} = \epsilon^* \mu^* \frac{\partial^2 \vec{E}}{\partial t^2} , \quad (\text{III-19a})$$

$$\frac{\partial^2 \vec{B}}{\partial x^2} = \epsilon^* \mu^* \frac{\partial^2 \vec{B}}{\partial t^2} . \quad (\text{III-19b})$$

Plane wave solutions of (III-19) are given by,

$$\vec{E} = \vec{E}_0 e^{i\omega t - \gamma x} , \quad (\text{III-20a})$$

$$\vec{B} = \vec{B}_0 e^{i\omega t - \gamma x} , \quad (\text{III-20b})$$

where,

$$\gamma = i\omega(\epsilon^* \mu^*)^{1/2} \equiv \alpha + i\beta \quad (\text{III-21})$$

is the complex propagation factor. Specifically,

$$\alpha = \frac{\lambda \omega^2}{4\pi} (\epsilon' \mu'' + \epsilon'' \mu') \quad (\text{III-22a})$$

and

$$\beta = \frac{2\pi}{\lambda} = \omega \left[\frac{(\epsilon' \mu' - \epsilon'' \mu'')}{2} \left| 1 + \sqrt{1 + \left(\frac{\epsilon' \mu'' + \epsilon'' \mu'}{\epsilon' \mu' + \epsilon'' \mu''} \right)^2} \right| \right]^{1/2} . \quad (\text{III-22b})$$

The phase velocity of the electromagnetic waves is,

$$v = \lambda \nu = \omega / \beta , \quad (\text{III-23})$$

which for a lossless medium ($\epsilon^* = \epsilon'$, $\mu^* = \mu'$) becomes,

$$v = (\mu' \epsilon')^{-1/2} . \quad (\text{III-24})$$

The intrinsic impedance of the dielectric is given by,

$$Z = \frac{E}{H} = \frac{\gamma}{i\omega\epsilon^*} = \sqrt{\frac{\mu^*}{\epsilon^*}} \quad (III-25)$$

For lossless magnetic materials ($\mu''=0$), the dielectric wavelength becomes,

$$\lambda = \frac{2\pi}{\beta} = \frac{1}{\nu} \left\{ \frac{1}{2} \epsilon' \mu' [\sqrt{1 + \tan^2 \delta} + 1] \right\}^{-\frac{1}{2}}, \quad (III-26)$$

and, for $\mu' = \mu_0$, we get for the index of refraction,

$$n = \frac{\lambda_0}{\lambda} = \left[\frac{1}{2} \epsilon' \left\{ \sqrt{1 + \tan^2 \delta} + 1 \right\} \right]^{\frac{1}{2}}, \quad (III-27)$$

the attenuation factor,

$$\alpha = \frac{2\pi}{\lambda_0} \left[\frac{1}{2} \epsilon' \left\{ \sqrt{1 + \tan^2 \delta} - 1 \right\} \right]^{\frac{1}{2}}, \quad (III-28)$$

and the index of absorption,

$$k = \frac{\alpha}{\beta} = \left[\frac{\sqrt{1 + \tan^2 \delta} - 1}{\sqrt{1 + \tan^2 \delta} + 1} \right]^{\frac{1}{2}}. \quad (III-29)$$

There are obviously three regimes of interest:

High Loss $\longrightarrow \tan^2 \delta \gg 1$
 Moderate Loss $\longrightarrow \tan^2 \delta \approx 1$
 Low Loss $\longrightarrow \tan^2 \delta \ll 1$.

We will discuss specific high, moderate and low loss materials in the next chapter.

The above equations present a macroscopic description of electromagnetic waves in dielectric media and introduce the relevant material parameters. Again, we have assumed isotropic and linear materials. This may not be the case for composite materials or for high

field heating of thin materials. In the remainder of this chapter we want to discuss three areas. First, a relationship between the energy deposited by microwaves and the corresponding temperature rise will be generated. Second, microscopic coupling mechanisms of microwaves to matter will be discussed and, finally, microscopic models for the dominant coupling mechanisms will be discussed. The effects of macroscopic boundary conditions on the field equations will form the subject of Chapter VI.

For ohmic (linear) materials the power density deposited by electromagnetic waves is,

$$\frac{P}{V_s} = \vec{J} \cdot \vec{E} = \sigma E^2 \quad (\text{III-30})$$

where V_s is the volume. If we average this over one cycle for an alternating field, we obtain,

$$P = \frac{1}{2} V_s \sigma E_0^2 = \frac{1}{2} V_s \omega \epsilon'' E_0^2 ,$$

or

$$P = \frac{1}{2} V_s \omega E_0^2 \epsilon' \tan \delta. \quad (\text{III-31})$$

Thus, the power is linearly proportional to the frequency and loss factor. Increasing fields are limited by dielectric breakdown.

We can relate the power dissipated by the sample volume, dU/dt , where U is the internal energy, to the corresponding temperature change as,

$$\frac{dT}{dt} = \frac{dT}{dU} \frac{dU}{dt} = \frac{1}{mC_v} \frac{dU}{dt}$$

where we have used the specific heat,

$$C_v = \frac{1}{m} \frac{dU}{dt} .$$

Now, the rate of energy dissipation in the sample is,

$$\frac{dU}{dt} = \left(\frac{P}{V_S} \right) V_S = \sigma E^2 V_S ,$$

or,

$$\frac{dT}{dt} = \frac{\sigma V_S}{mC_V} E^2 ,$$

and,

$$\Delta T = T - T_0 = \frac{V_S \sigma}{mC_V} \int_0^t E^2 dt ,$$

or

$$\Delta T = \frac{V_S \sigma E_0^2 t}{2mC_V} = \frac{V_S E_0^2 \omega \epsilon' \tan \delta}{2mC_V} t , \quad (\text{III-32})$$

for the increase in temperature. From (III-32), the heating rate becomes,

$$\frac{dT}{dt} = \frac{\omega V_S E_0^2}{2mC_V} \epsilon' \tan \delta . \quad (\text{III-33})$$

Note here that we have assumed a constant C_V and ϵ'' , when in fact both of these material parameters are functions of temperature. In addition, ϵ'' is also a function of the frequency. As the heating progresses chemical changes in the material may occur causing both C_V and ϵ'' to also be time dependent parameters.

The presence of an electric field in a dielectric material polarizes the material. This polarization can be related to the external field and to the underlying molecular structure. The polarization, \vec{P} , or dipole moment per unit volume, is given by

$$\begin{aligned} \vec{P} &= \vec{D} - \epsilon_0 \vec{E}, \\ \vec{P} &= (\epsilon' - \epsilon_0) \vec{E} \\ \vec{P} &\equiv \chi_e \epsilon_0 \vec{E} \end{aligned}$$

(III-34)

where,

$$\chi_e = \kappa' - 1 \quad , \quad (\text{III-35})$$

is the electric susceptibility. The polarization can also be written in terms of the polarizability α by,

$$\vec{P} = N\alpha\vec{E}' \quad , \quad (\text{III-36})$$

where N is the number of contributors per unit volume (dipoles, etc.) and \vec{E}' is the local electric field at the contribution site.

There are essentially four dominant mechanisms of polarization (Figure III-3): electronic, atomic, orientational and space charge. For the most part other mechanisms are either variations of these, or are due to interactions between these mechanisms. The electronic and atomic polarization mechanisms are due to induced charge displacement and vanish when the external field is removed. Generally, these mechanisms are not major contributors to microwave heating. First, the frequencies are usually in the IR to visible range of the spectrum, and second, energy dissipation will only occur when nonlinear interactions between the induced dipoles and the surrounding medium come into play.

Consequently, when plotting ϵ' versus frequency one sees normal dispersion for atomic and electronic polarization (Figure III-4) with small loss factors (ϵ''). The dispersion curve in the microwave regime is anomalous and characteristic of relaxation phenomena, versus the resonance phenomena for atomic and electronic polarization. The energy dissipated is significant and is characteristic of a model of dipole orientation. The final polarization mechanism shown in Figure III-3 is due to space charge separation (Maxwell-Wagner effects) and will be discussed in more detail later, particularly in Chapter VI.

The dipole orientation model for microwave absorption is completely analogous to the classical model for a paramagnet. Essentially one starts with a system of randomly directed non-interacting dipole moments.

COUPLING MICROWAVES TO MATERIALS

MOLECULAR PERSPECTIVE

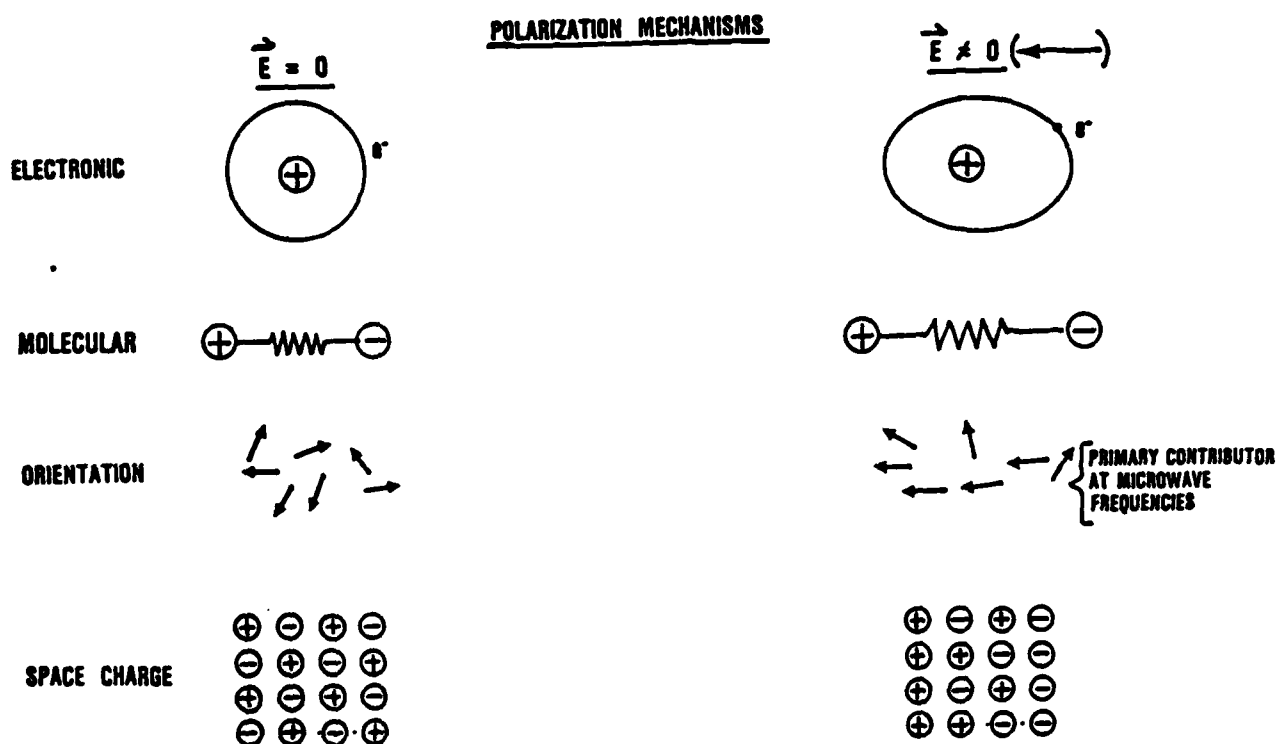


Figure III-3. Molecular Coupling Mechanisms

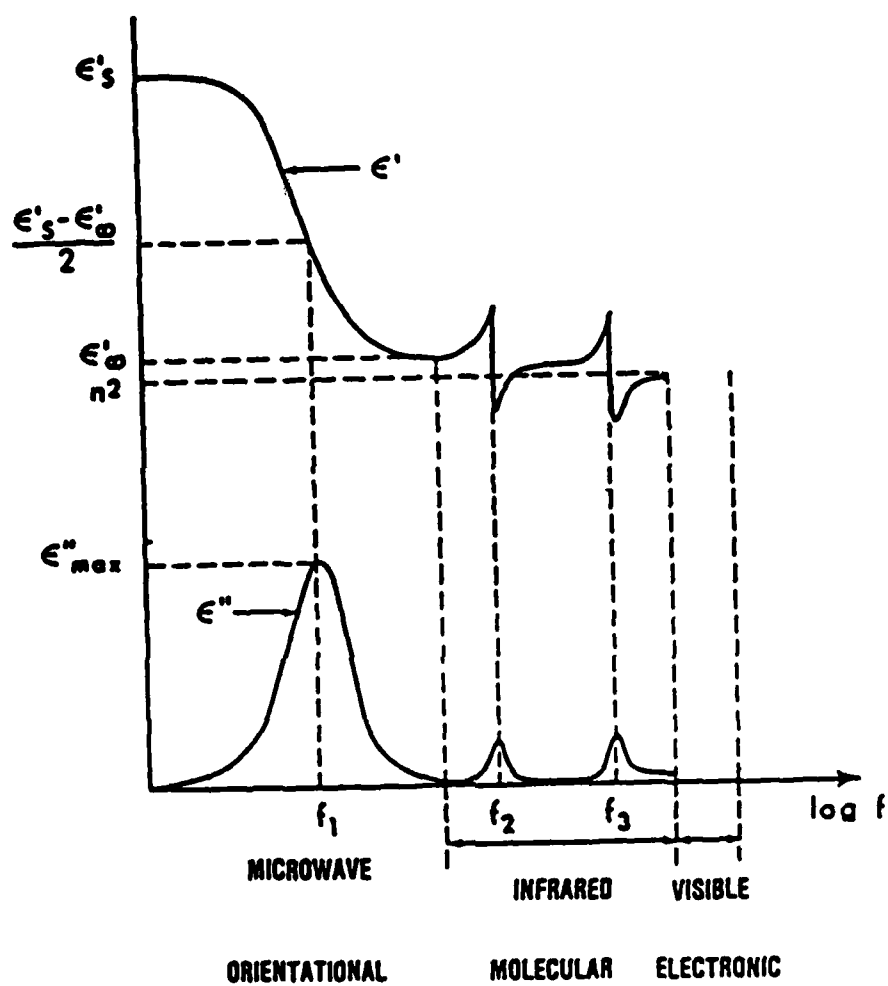


Figure III-4. Dispersion Relation, $\epsilon^*(\omega)$

Assuming that the dipoles are free to move (gas or liquid), they will line up in the presence of an external electric field. If the field changes direction, so will the dipoles. However, if the field begins to change direction more rapidly, there will be a point when the dipoles cannot stay in phase with the field due to inertia effects (mass and interactions). It is at this point that losses begin to occur.

In a solid, the physical dipoles are constrained and are unable to move freely as in gases or non-viscous liquids. Consequently, loss tangents in solids are significantly lower than fluids. However, the model described above still obtains. This model, originally introduced by Debye, simply assumes the existence of two states separated by some energy which, in our case, is characteristic of microwave frequencies. The limitations of the Debye model are in the neglect of interactions and in the use of a single relaxation time. Thus, the two states which are involved in the orientation flipping could be two spatial orientations of a molecule, two rotational states, two vibrational states, two tunneling states, etc. The key to microwave absorption is that the characteristic energies are in the microwave frequency range.

In order to get a quantitative feel for the Debye model we provide a quick derivation. Losses occur when the polarization acquires a component out of phase with the field and the displacement current acquires a conductance in phase with the field (Figure III-2). The optical limit of $\epsilon(\omega)$ is designated $\epsilon(\omega \rightarrow \infty) \equiv \epsilon_{\infty}$ and the static limit is $\epsilon(\omega \rightarrow 0) = \epsilon_s$. The displacement current can be written as,

$$D(t) = \epsilon_{\infty} E(t) + \int_{-\infty}^t E(t') f(t-t') dt' , \quad (\text{III-37})$$

where the first term is the instantaneous, high frequency (electronic) response and the second term represents dissipative processes. Assuming relaxational processes, the response function is given by,

$$f(t) \sim e^{-t/\tau}, \quad (\text{III-38})$$

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where τ is a characteristic relaxation time. Note that τ is generally a function of the temperature and interactions and that, in general, there should be a distribution of relaxation times. Substitution of (III-38) into (III-37), and differentiating, yields,

$$\tau \frac{dD(t)}{dt} = \epsilon_{\infty} \tau \frac{dE(t)}{dt} + \tau f(0)E(t) - \int_{-\infty}^t E(t')f(t-t')dt' \quad (III-39)$$

Combining (III-37) and (III-39) gives,

$$\tau \frac{d}{dt} (D(t) - \epsilon_{\infty} E(t)) + (D(t) - \epsilon_{\infty} E(t)) = \tau f(0)E(t) .$$

For constant field,

$$\frac{d}{dt} (D - \epsilon_{\infty} E) = 0 ,$$

and,

$$D = \epsilon_s E ,$$

yielding,

$$\tau f(0) = \epsilon_s - \epsilon_{\infty} , \quad (III-40)$$

Thus,

$$\tau \frac{d}{dt} (D(t) - \epsilon_{\infty} E(t)) + (D(t) - \epsilon_{\infty} E(t)) = (\epsilon_s - \epsilon_{\infty})E(t) . \quad (III-41)$$

Assuming,

$$E(t) = E_0 e^{i\omega t} ,$$

and

$$D = \epsilon * E$$

yields,

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$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_S - \epsilon_\infty}{1 + i\omega\tau} \quad (\text{III-42})$$

when substituted in (III-41).

Thus, for the Debye model of a non-interacting two level system with a single relaxation time,

$$\epsilon'(\omega) = \epsilon_\infty + \frac{(\epsilon_S - \epsilon_\infty)}{1 + \omega^2\tau^2} \quad (\text{III-43a})$$

$$\epsilon''(\omega) = \omega\tau \frac{(\epsilon_S - \epsilon_\infty)}{1 + \omega^2\tau^2} \quad (\text{III-43b})$$

Absorption is a maximum when,

$$\omega_m\tau = 1 \quad (\text{III-44a})$$

giving,

$$\epsilon''(\omega_m) = \frac{1}{2} (\epsilon_S - \epsilon_\infty) \quad (\text{III-44b})$$

and

$$\epsilon'(\omega_m) = \frac{1}{2} (\epsilon_S + \epsilon_\infty) \quad (\text{III-44c})$$

The Debye model can be made more realistic by applying the techniques of modern statistical mechanics and many-body analysis to account for interactions. Modifications to this model were introduced by Onsager (Reaction Field) and Kirkwood.⁶ More contemporary are the correlated effective field approximation of Lines⁷ and linear response theory.⁷⁻¹⁰

CHAPTER IV DIELECTRIC LOSS

In this chapter we present and discuss the dielectric properties for a variety of different materials and comment particularly on the microstructural factors which influence the dielectric loss ϵ'' . In Chapter VI we will discuss macroscopic coupling mechanisms, e.g., resonant cavities. We have been able to locate three useful but dated compendia on dielectric properties. These are the compilations by von Hippel,⁴ Tinga and Nelson,¹¹ and Young and Frederikse.¹² Dielectric properties can also be found in a variety of sources ranging from microwave journals to materials journals. Some of these are also mentioned in this chapter. A good reference is the series Progress in Dielectrics¹³ containing a variety of articles on dielectric properties of gases, liquids, and solids.

In Chapter II we commented on some of the factors which influence dielectric loss, i.e., temperature, frequency, etc. Here we discuss these factors in more detail based on the background of coupling theories and mechanisms presented in Chapter III. Preliminary investigations indicate that there is a great deal of leverage in controlling material properties so as to enhance selective heating effects through ϵ'' .

Generally, heating of materials can be described as,¹⁴

$\epsilon''/\epsilon_0 > 0.2$	—————>	good heating
$0.08 < \epsilon''/\epsilon_0 < 0.2$	—————>	fair heating
$0.01 < \epsilon''/\epsilon_0 < 0.08$	—————>	poor heating
$\epsilon''/\epsilon_0 < 0.01$	—————>	little or no response.

Most polymers, for instance polyethylene DE-3401 at 25°C and $f=3$ GHz, have ϵ'/ϵ_0 on the order of 2 and $\tan \delta$ approximately 3×10^{-4} , i.e., $\epsilon''/\epsilon_0 = 6 \times 10^{-4}$, or little or no response to microwaves by the above criteria. Thus, the obvious objective of this report and program: Are there ways of heating an intrinsically low loss material using microwaves?

**LOSS TANGENT
VS.
TEMPERATURE
FOR WATER
AT
 3×10^9 Hz**

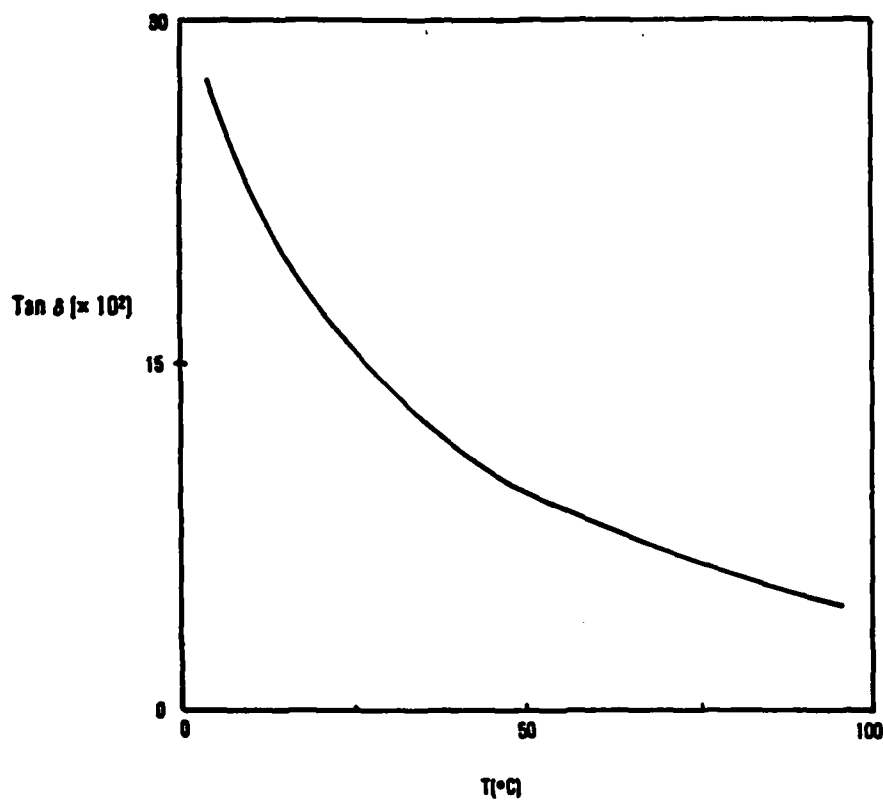


Figure IV-1a. Loss Tangent for Water (Reference 4)

**LOSS TANGENT
VS.
FREQUENCY
FOR WATER
AT
ROOM TEMPERATURE**

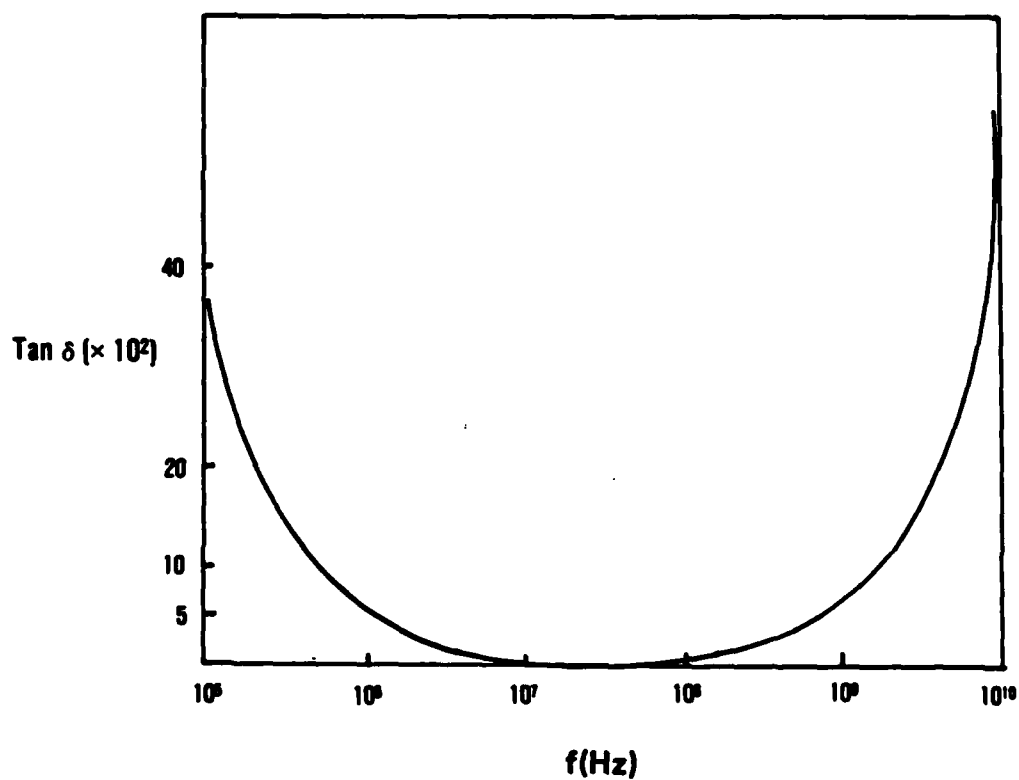


Figure IV-1b. Loss Tangent for Water (Reference 4)

To get a feel for the dielectric properties of different classes of materials Figures IV-1 through IV-12, taken from Reference 4 and Reference 12, give ϵ' and $\tan \delta$ as a function of temperature and frequency for a number of low loss materials. However, Figure IV-1 gives the loss tangent for water as a calibration for high loss materials. The reason for water's high loss value is that it is a polar molecule and is able to rotate in the liquid state in response to the external field.

Figures IV-2 through IV-4 give values for ϵ'/ϵ_0 and $\tan \delta$ versus temperature for various ceramics: steatite ($(\text{OH})_2 \cdot \text{Mg}_3 \cdot \text{Si}_4\text{O}_{10}$ based) (Centralab) a low loss ceramic used in electronic applications; zirconium porcelain ($\text{ZrO}_2 \cdot \text{SiO}_2$ based) Zi-4 (Coors); and, porous ceramic AF-497 (63% diatomaceous earth, 32% anthracite coal and 5.5% whiting (Stupakoff)). Notice in all cases that the loss tangent decreases significantly at microwave frequencies. Generally lower frequency losses are due to interfacial polarization of either the Maxwell-Wagner type due to random or layered inhomogeneities or of the defect type, i.e., grain boundaries, voids, dislocations, etc. Also, real charge migration comes into play as a loss mechanism at lower frequencies. Increases in loss at high temperature can be attributed to thermally assisted hopping between the Debye two-level states or to ionic charge migration.

In the case of polymers we have, in Figures IV-5 through IV-7, loss tangents for Nylon FM 10,001 (Polyamide), Laminac 4115 and PDL7-627 (Polyesters), and Araldite Casting Resin Type B (Epoxy). Polymers generally have low loss tangents. Polar macromolecules will have loss tangents with more variation with temperature than non-polar polymers. One mechanism, as will be discussed later, for increasing the loss in non-polar polymers is to add side groups to increase the dipole moment of the molecule.

In Figure IV-8, the dielectric properties of silicone rubbers: Silastic 181 (45% siloxane elastomer, 55% SiO_2), Silastic 250 (70% siloxane, 30% SiO_2) and Silastic 6167 (33% siloxane, 67% TiO_2), are given. As will be discussed in Chapter V, there has been fairly extensive work done in the microwave curing of both natural and synthetic rubbers. In

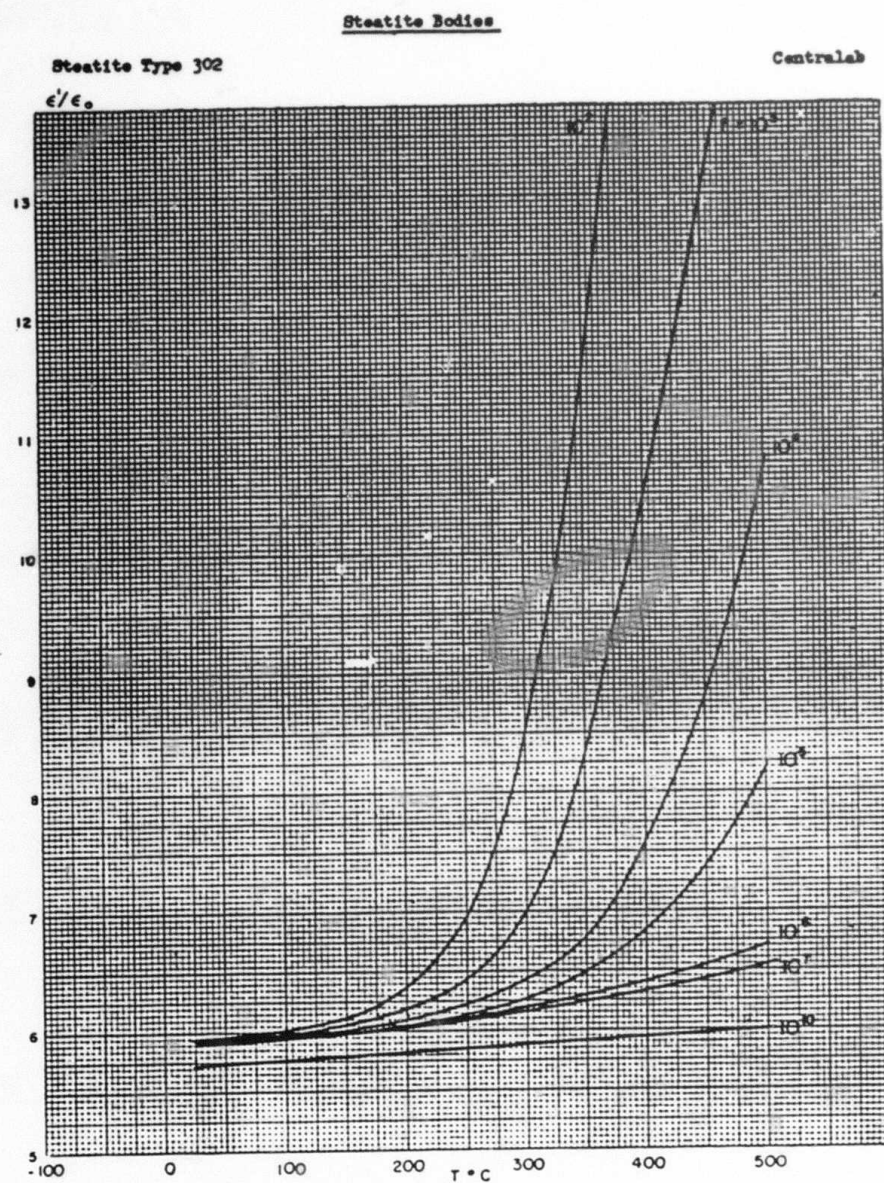


Figure IV-2a. Dielectric Constants for Steatite Type 302 (Reference 4)

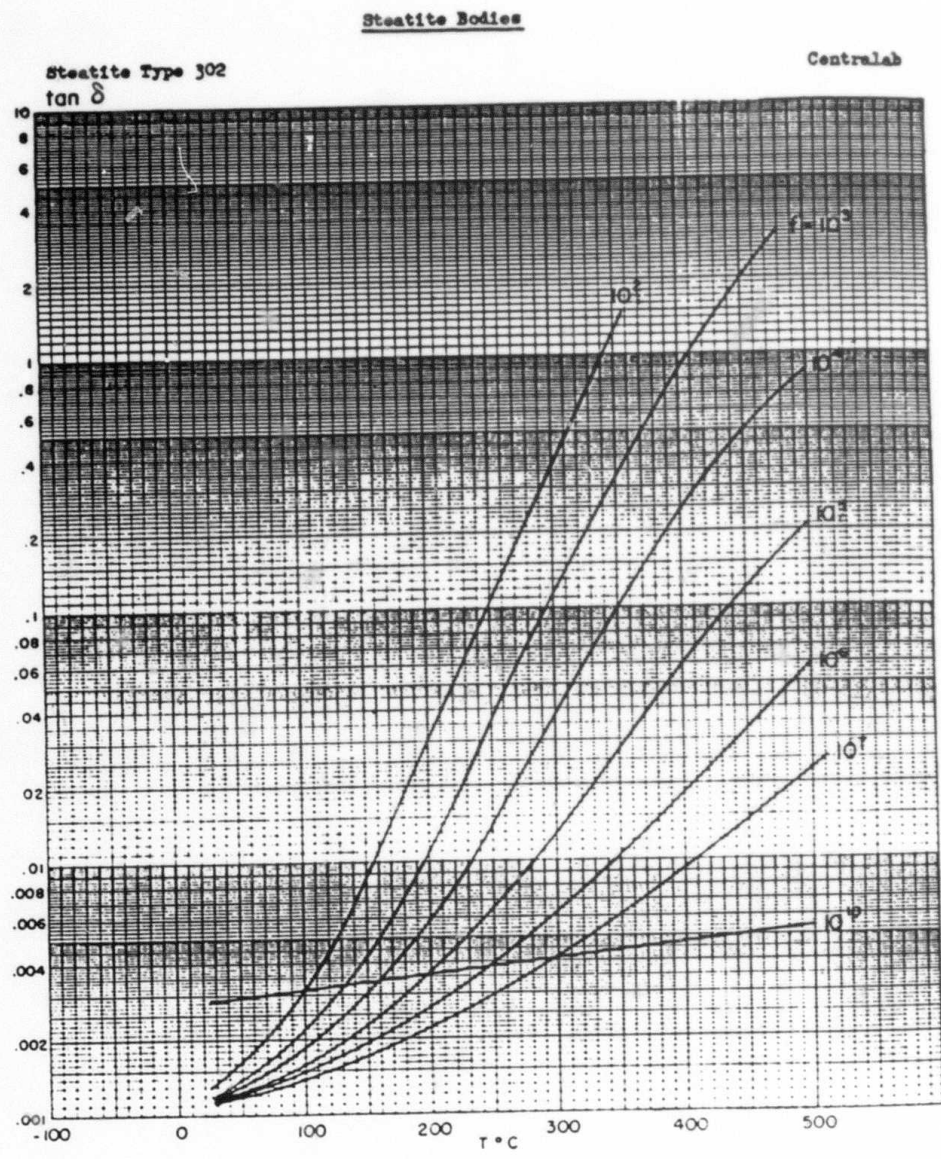


Figure IV-2b. Dielectric Constants for Steatite Type 302 (Reference 4)

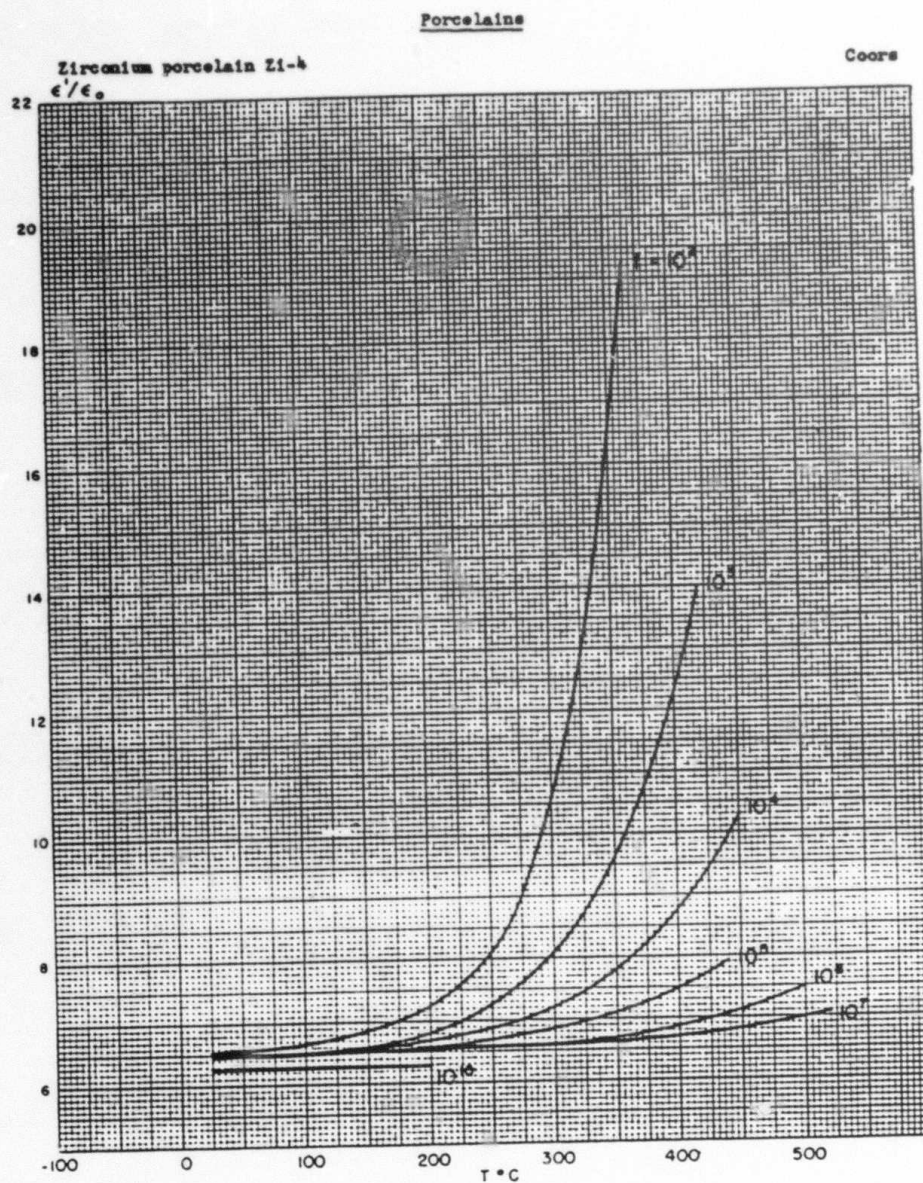


Figure IV-3a. Dielectric Constants for Zirconium Porcelain Zi-4
(Reference 4)

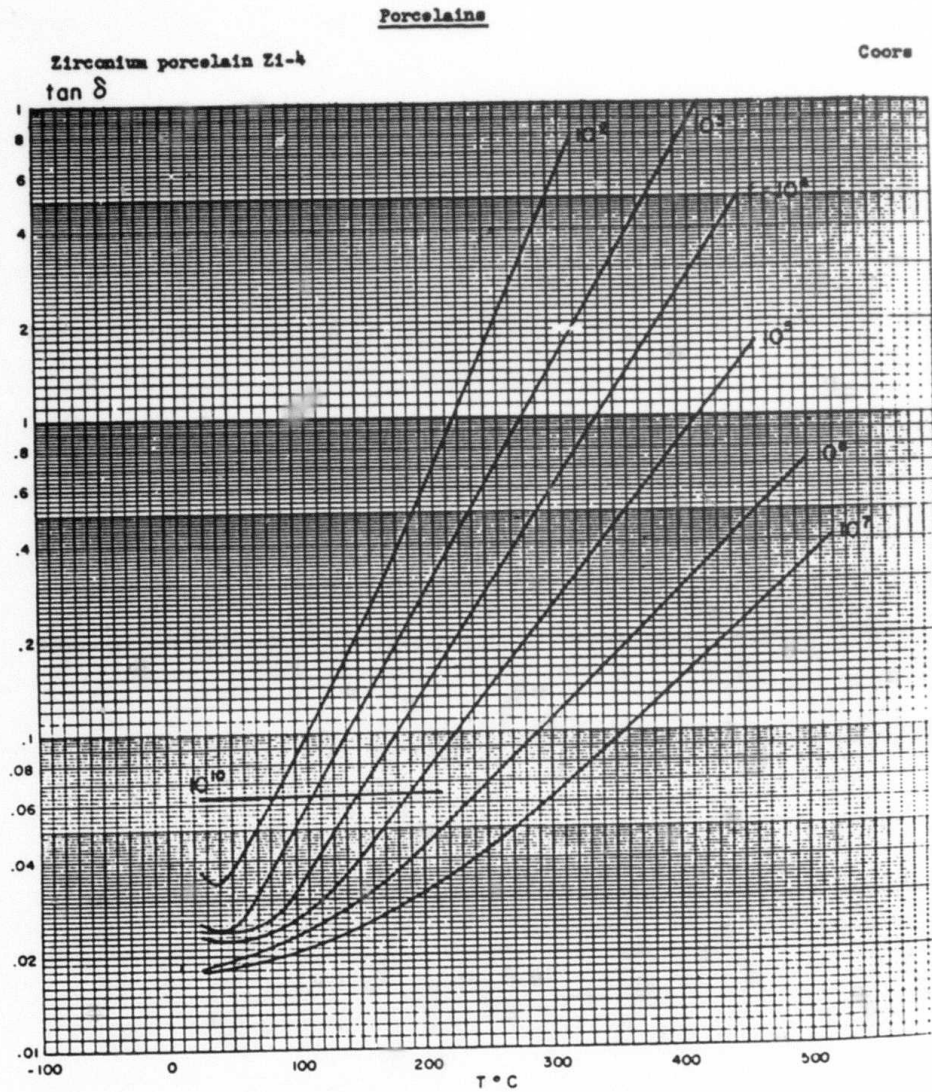


Figure IV-3b. Dielectric Constants for Zirconium Porcelain Zi-4
(Reference 4)

Miscellaneous Ceramics

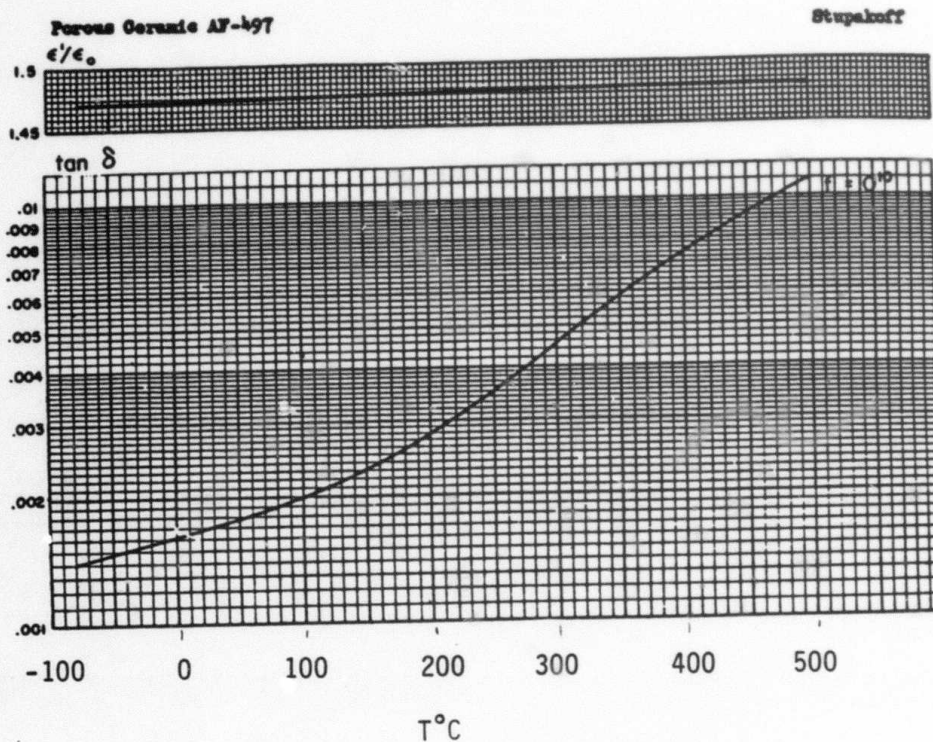


Figure IV-4. Dielectric Constants for Porous Ceramic AF-497 (Reference 4)

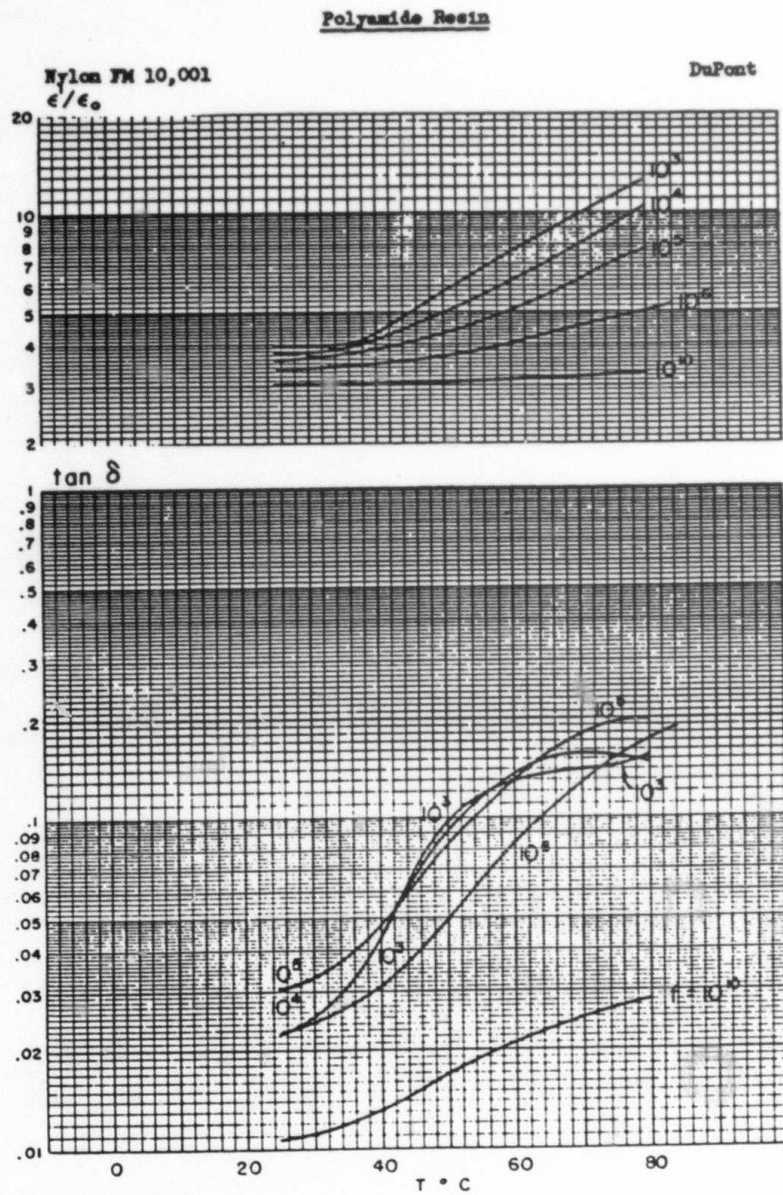


Figure IV-5. Dielectric Constants for Polyamide Resin (Reference 4)

Polyesters

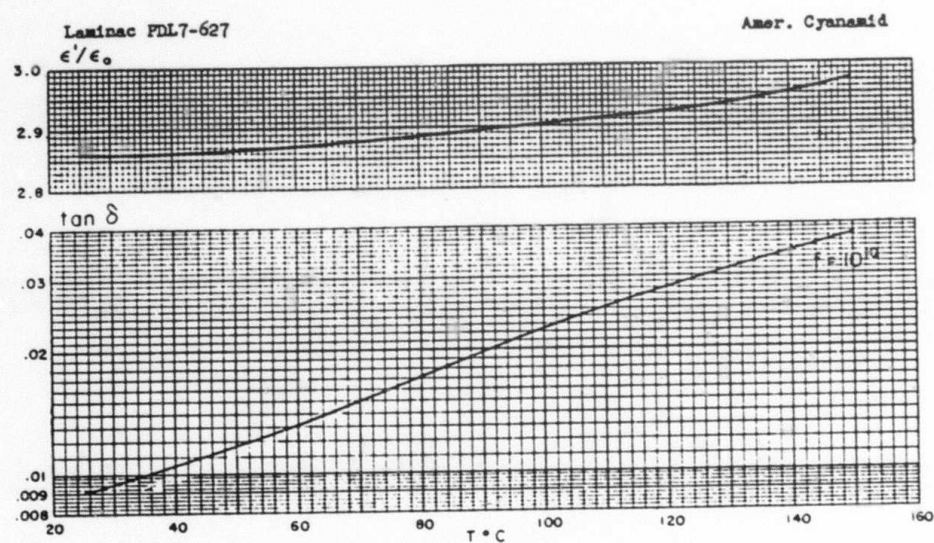
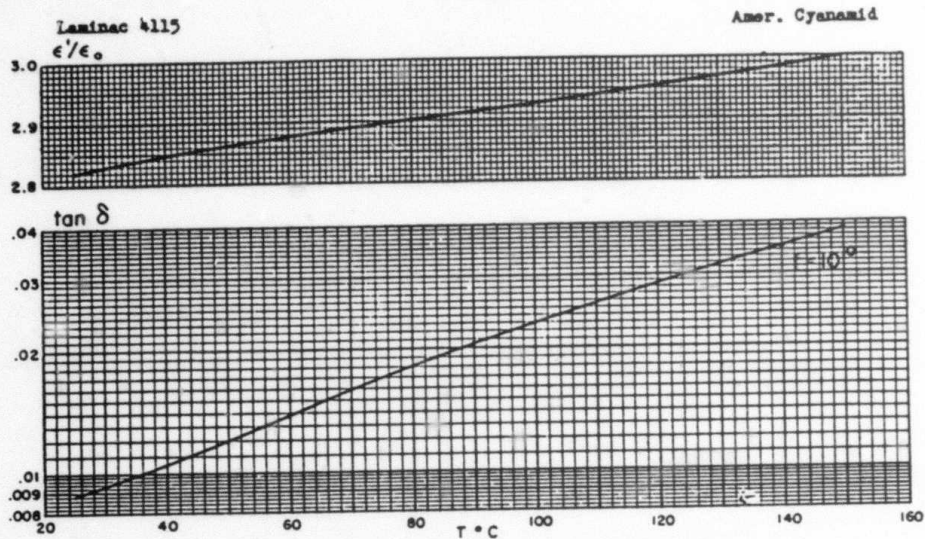


Figure IV-6. Dielectric Constants for Polyesters (Reference 4)

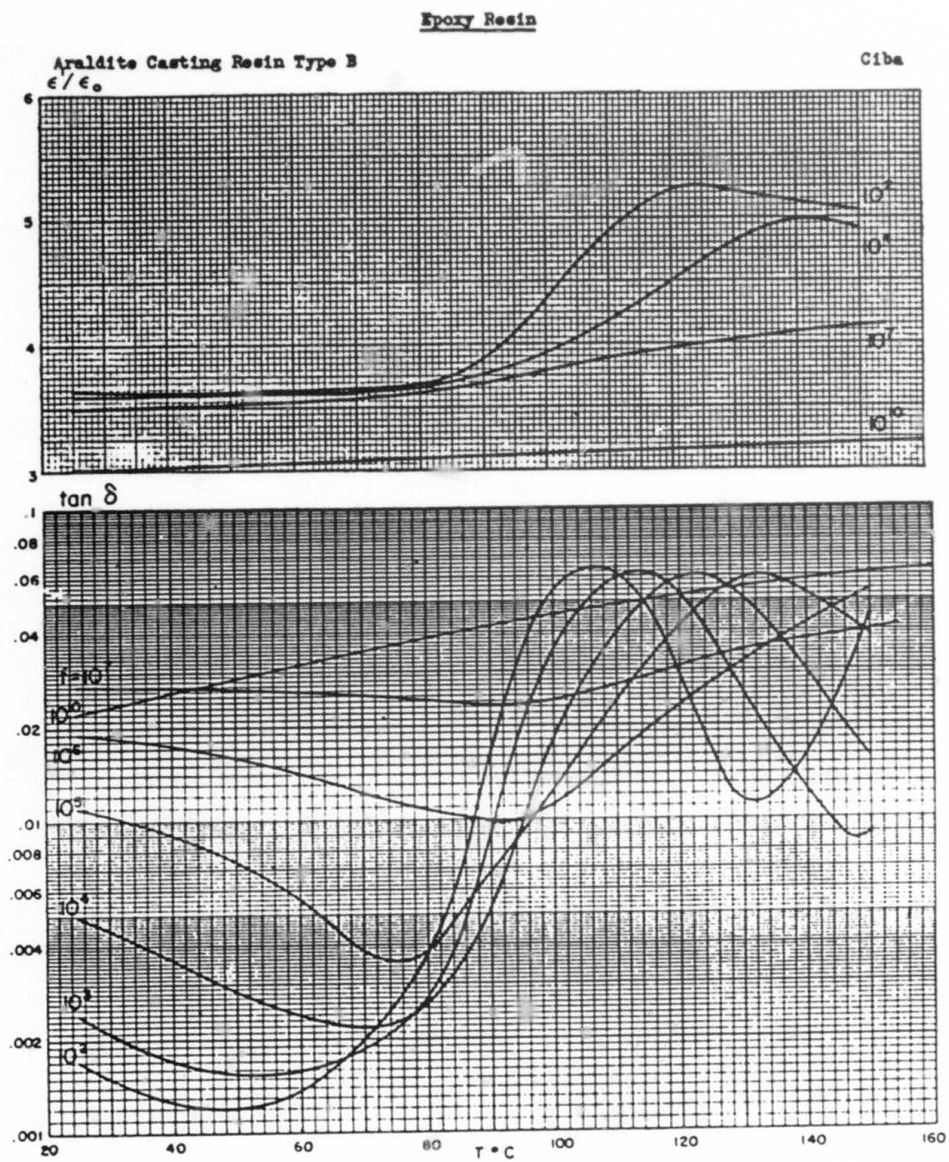


Figure IV-7. Dielectric Constants for Epoxy Resin (Reference 4)

Silicone Rubbers

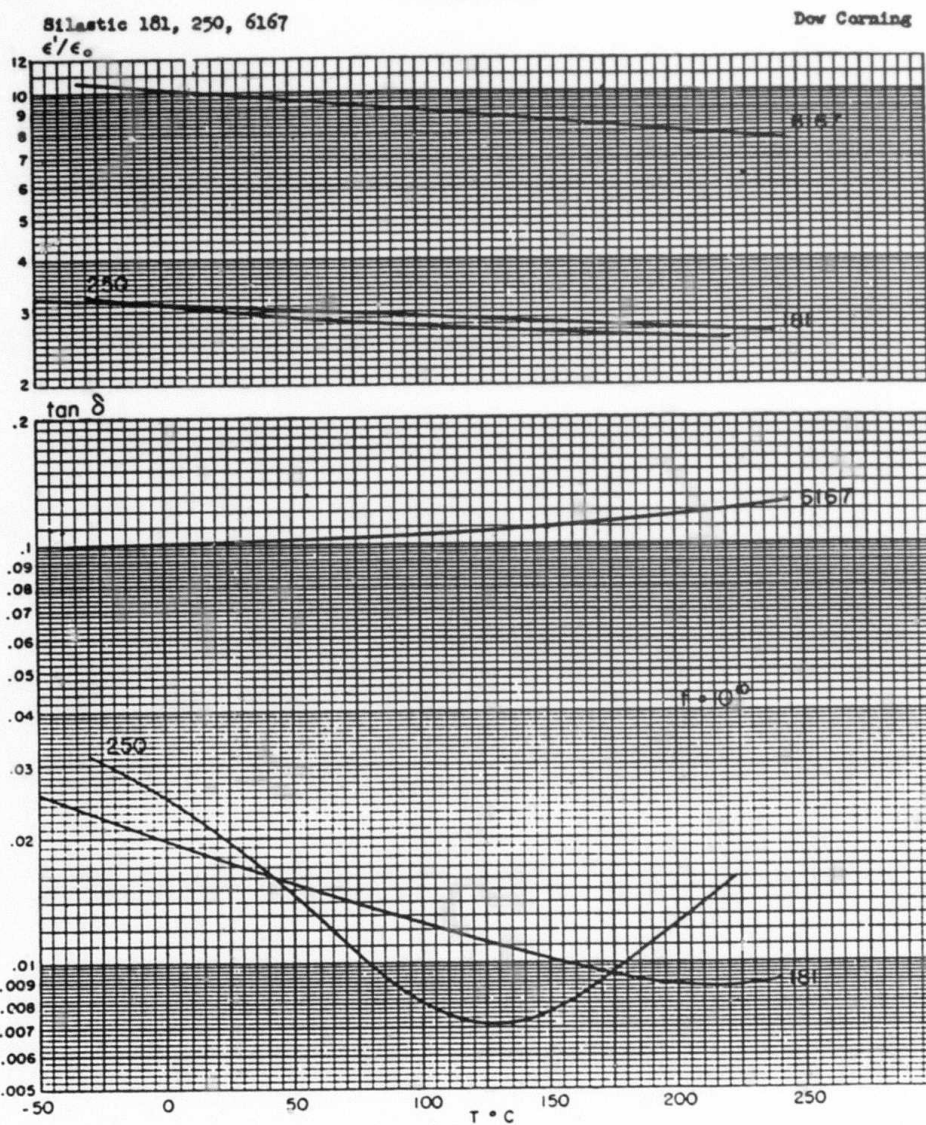


Figure IV-8. Dielectric Constants for Silicon Rubber (Reference 4)

Figure IV-8 the difference between the TiO_2 and SiO_2 modified rubbers is significant.

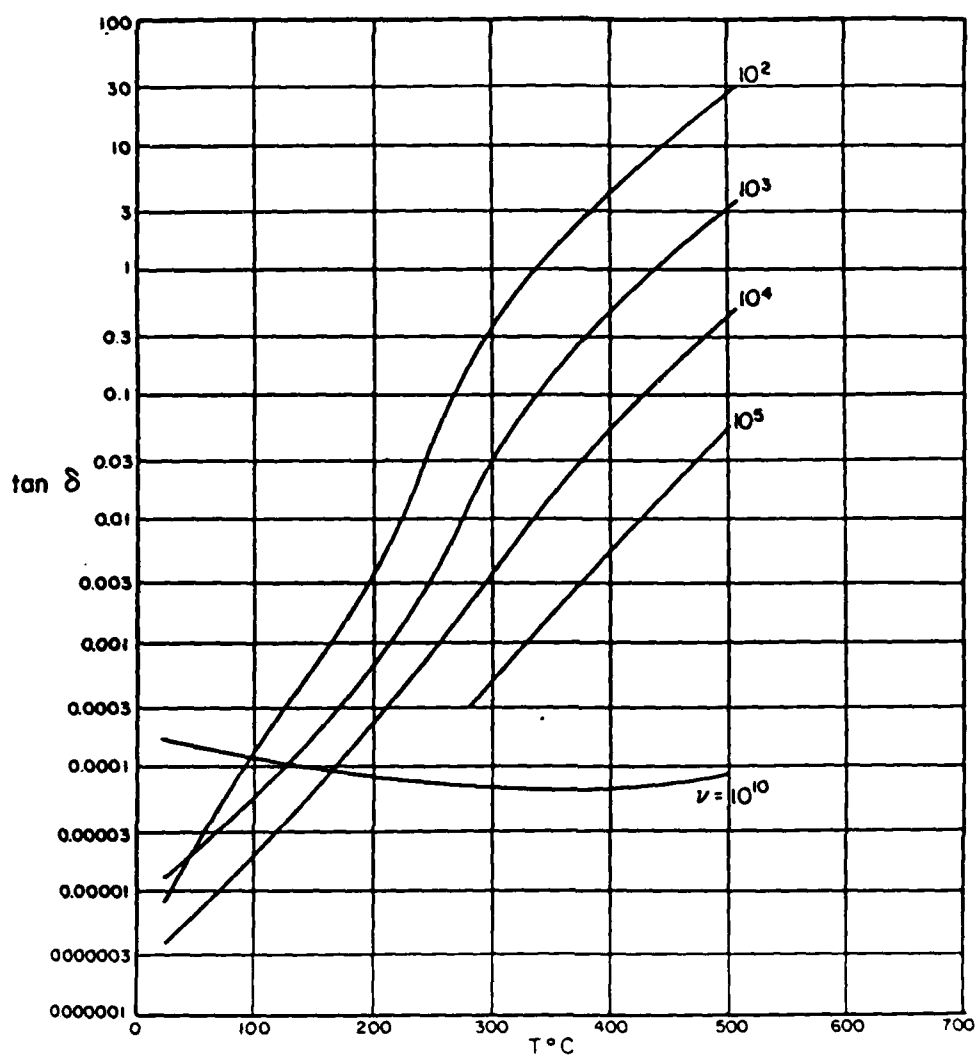
The temperature dependence of fused silica and borosilicate glasses is given in Figure IV-9 and IV-10. The loss tangent for the borosilicate glass is seen to be an order of magnitude greater than fused quartz at 10 GHz, while the dielectric constant is approximately the same. Finally, in Figure IV-11 and IV-12, we have the real and imaginary parts of ϵ^* for transition metal oxides. For NiO in particular a wide variation of ϵ'' is seen with frequency and temperature.

As discussed in Chapter III, the dominant mechanisms for microwave absorption is dipole orientation of the Debye type, i.e., relaxational. This relaxation between two states can be very general and complex. That is to say, the states can be any two low lying states, or a distribution of states. In addition, the states can interact among themselves to further modify the relaxation times or resonant frequency.

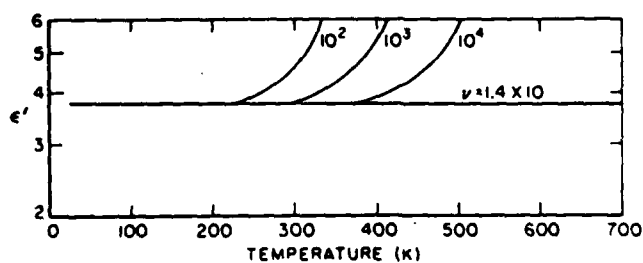
We have seen in the figures, i.e., Figure III-4, that ϵ'' is a function of the frequency. The key question here is, can we somehow enhance the absorption in the microwave regime by material modification without destroying the useful properties of the material. The information gathered in this chapter indicates that it is probable that this may be done.

First, ϵ'' generally increases with temperature, i.e., mobility between two-level states increases with increasing temperature. Consequently, preheating a low loss material by conventional methods before exposure to microwaves is a possibility. However, this technique is often not desirable from an energy viewpoint. Likewise, as a sample heats up in a microwave cavity it will absorb increasing energy due to its temperature enhanced loss tangent. If the heating is done in the vicinity of a phase transition, precursor effects due to anharmonicities (e.g., nonlinear phonon-phonon interactions) can enhance losses.

Applied pressure can also shift and increase the absorption of microwaves (Figure IV-13). We can see from previous figures that at constant pressure increasing temperature shifts ϵ'' to higher frequency.



SiO_2 (quartz). Temperature dependence of dielectric loss tangent of 915 C fused silica. SiO_2 .



SiO_2 (quartz). Temperature dependence of the dielectric constant of General Electric fused quartz. SiO_2 .

Figure IV-9. Dielectric Constants for Fused Silicon (Reference 12)

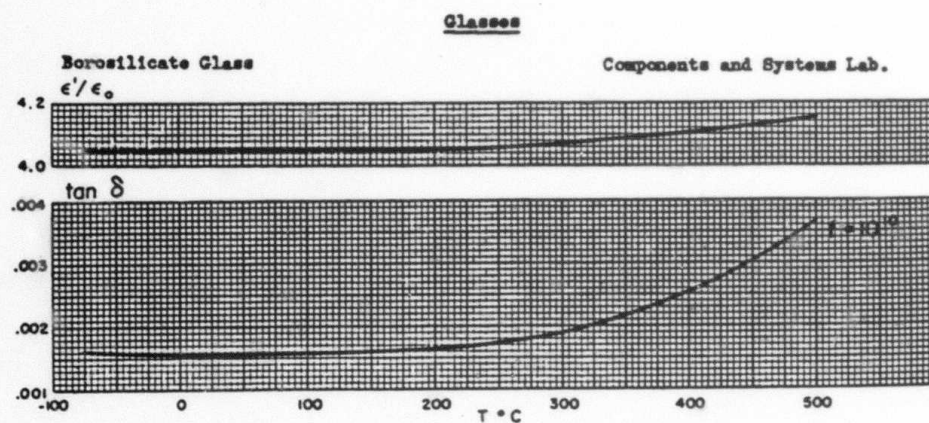
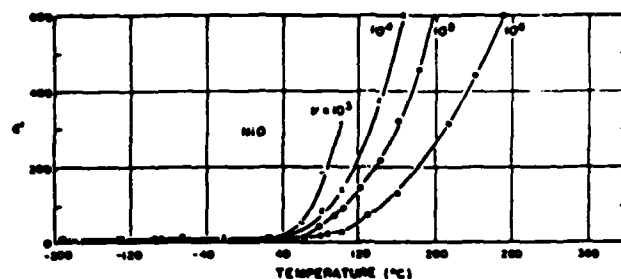
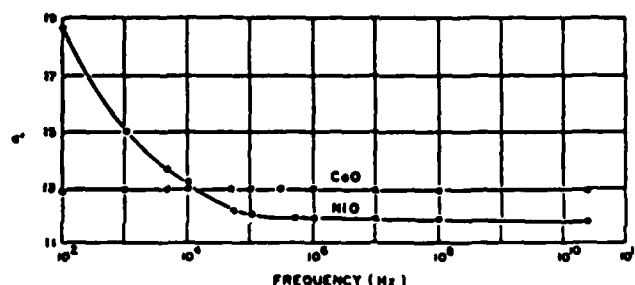


Figure IV-10. Dielectric Constants for Borosilicate Glass (Reference 4)

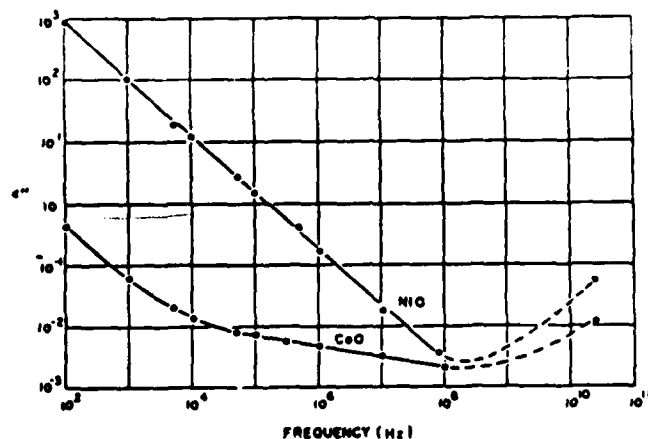


NiO. Temperature dependence of the dielectric constant of NiO

Remarks—Plotting the conductivity (as deduced from the dielectric loss ϵ'' : $\sigma = \omega \epsilon'' \epsilon'$) versus $\frac{1}{T}$ one finds the activation energy for intrinsic conduction to be 0.66 eV for NiO.

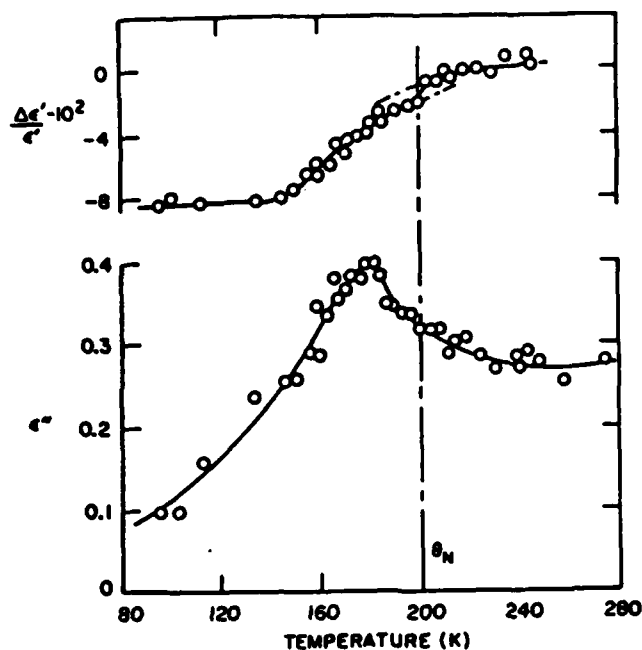


CoO, NiO. Frequency dependence of dielectric constant ϵ' of CoO and NiO at 298 K

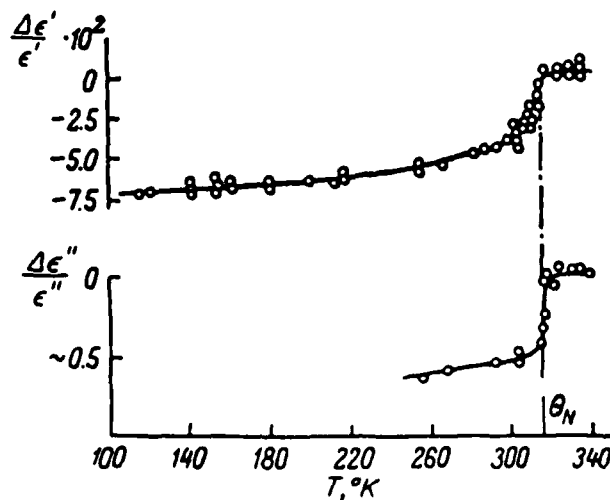


CoO, NiO. Frequency dependence of the dielectric loss ϵ'' of CoO and NiO at 298 K

Figure IV-11. Dielectric Constants for NiO and CoO (Reference 12)

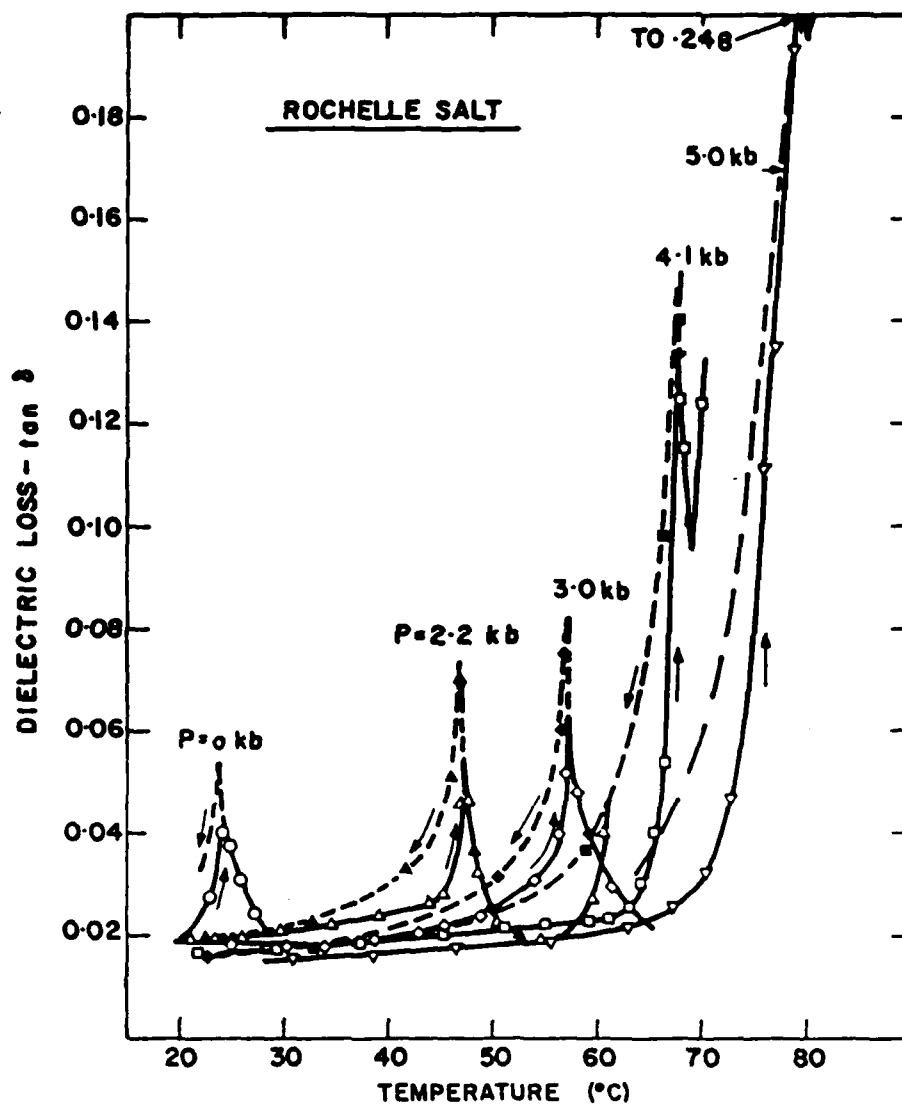


FeO. Temperature dependence of the percentage change of dielectric constant ϵ' and dielectric loss ϵ'' relative to their values at 240 K for FeO



Cr₂O₃. Temperature dependence of the percentage change in dielectric constant ϵ' and dielectric loss ϵ'' relative to their values at the Néel temperature, θ_N , of Cr₂O₃

Figure IV-12. Dielectric Constants for FeO and Cr₂O₃ (Reference 12)



NaKC₄H₄O₆ · 4H₂O (Rochelle salt). Temperature dependence of the dielectric loss of Rochelle salt near the upper Curie point at different pressures

Figure IV-13. Dielectric Constants for Rochelle Salt (Reference 12)

At fixed temperature, increasing pressure broadens the peak in $\epsilon''(\omega)$ and shifts it to lower frequency. This effect is probably not dissimilar from strain induced hopping in two-level states in glasses.

Mixing of additional components in materials can either increase or decrease the loss tangent. By mixing of additional components we mean solutions with finite amounts of the added material. This is to be distinguished from impurity related (small concentration) phenomena. Thus, in this solution model as the concentration of one component (B) increases the solution changes from material A to material B with a corresponding change in loss tangent, i.e.,

$$\tan \delta_{AB} = c_A \tan \delta_A + c_B \tan \delta_B$$

where $c_A(c_B)$ is the concentration of component A(B). Figure IV-14 gives the peak permittivity temperature for barium titanate with various additional components.

The addition of additives can also create a great deal of leverage in modifying the loss tangent. By additives we mean generally small amounts of material having a specific objective. For instance, adding water or hydroxyl groups would have the effect of increasing losses dramatically. The addition of curing agents in polymers can increase the intrinsic heat loss and consequently enhance coupling (sometimes through the production of intermediate hydroxyl groups).

Polar impurities can also enhance the coupling. Figure IV-15 shows the dielectric constant for polar hexasubstituted chloromethylbenzenes as the number of substituted chlorines is changed. Generally the dielectric constant and loss factor decrease as the molecule becomes more symmetric. This is evident from Figure IV-16 for chlorinated diphenyl. In Figure IV-17 the dielectric constant for camphor is given for different substituting radicals. Again, one can see a fair amount of leverage is possible.

In the impurity limit, ionic impurities can increase low frequency loss due to migration. Vacancies, impurities and complex defects (e.g., vacancy-impurity pairs) can all enhance intrinsically low loss materials. Chemical reactions can also add to losses. As mentioned above, if a

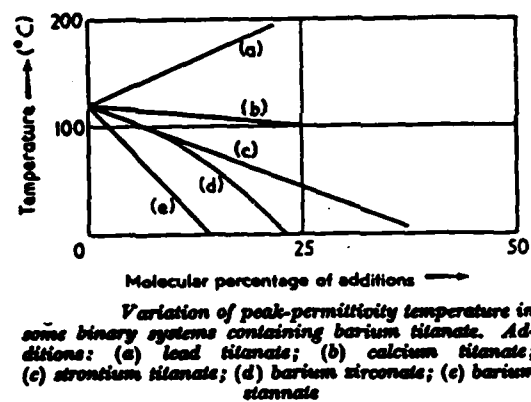
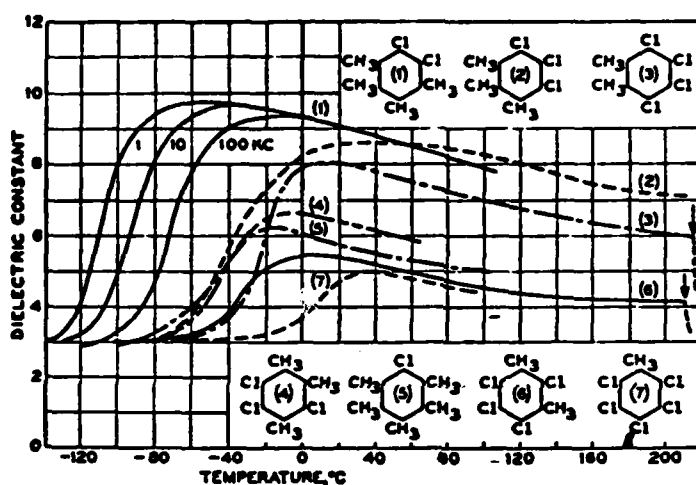
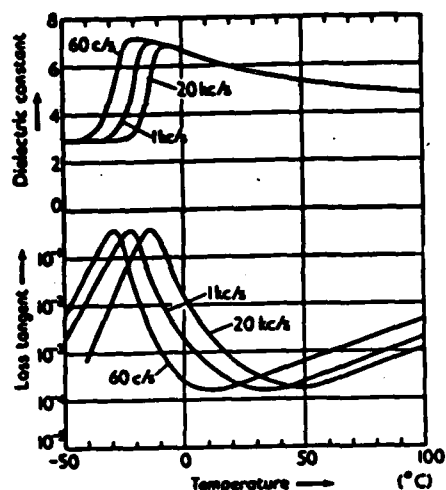


Figure IV-14. Variation of Peak Permittivity Temperature of Binary Systems of Barium Titanate (Reference 15)

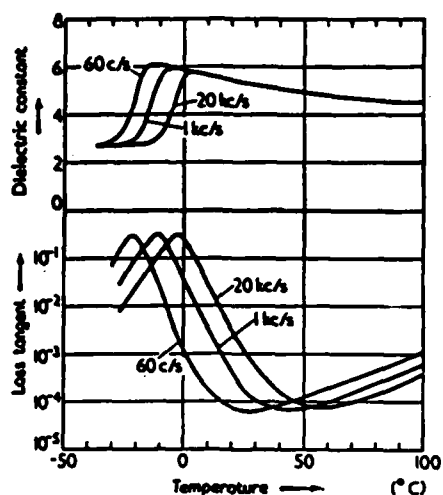


Dielectric constant of polar hexasubstituted chloromethylbenzenes at 100 kHz:
 (1) dichlorophrenitene, (2) trichlorohemimellitene, (3) tetrachloro-o-xylene, (4) trichloropseudocumene, (5) pentamethylchlorobenzene, (6) tetrachloro-m-xylene, (7) pentachlorotoluene. [From A. H. White and S. O. Morgan: *J. Am. Chem. Soc.* 57, 2078 (1935).]

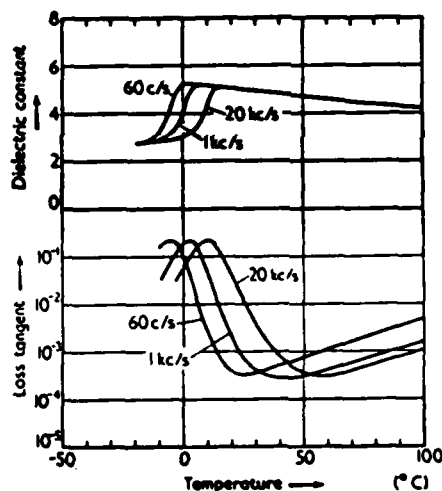
Figure IV-15. Dielectric Constants of Polar Hexasubstituted Chloromethylbenzenes (Reference 15)



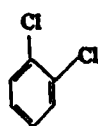
Dielectric properties of trichlorodiphenyl^a
(^aAroclor[®] 1242)



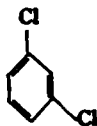
Dielectric properties of tetrachlorodiphenyl^a
(^aAroclor[®] 1246)



Dielectric properties of pentachlorodiphenyl^a
(^aAroclor[®] 1254)



Ortho-
 $\mu = 2.83$

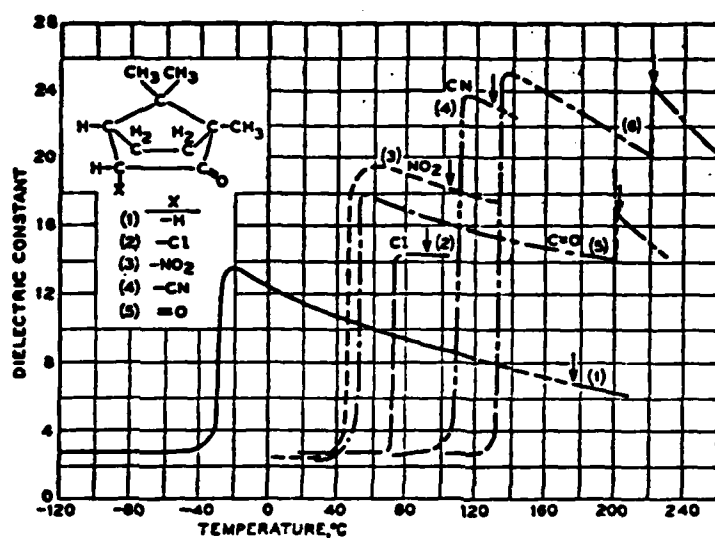


Meta-
 $\mu = 1.48$



Para-
 $\mu = 0$

Figure IV-16. Dielectric Constants of Various Chlorodiphenyls
(Reference 15)



Dielectric constant of camphor (1), chlorocamphor (2), nitrocamphor (3), cyanocamphor (4), camphor quinone (5), and camphoric anhydride (6). Heavy arrow indicates the melting point; values are independent of frequency below 100 kHz. [From Moryan and Louny, *J. Phys. Chem.* 34, 2385 (1930).]

Figure IV-17. Dielectric Constants for Camphor (Reference 16)

curing agent produces intermediate hydroxyl groups, then losses are increased. Also, radiation can induce defects of either a temporary or permanent nature. In polymers, this produces semiconducting behavior (states in the band gap) which can influence loss mechanisms.

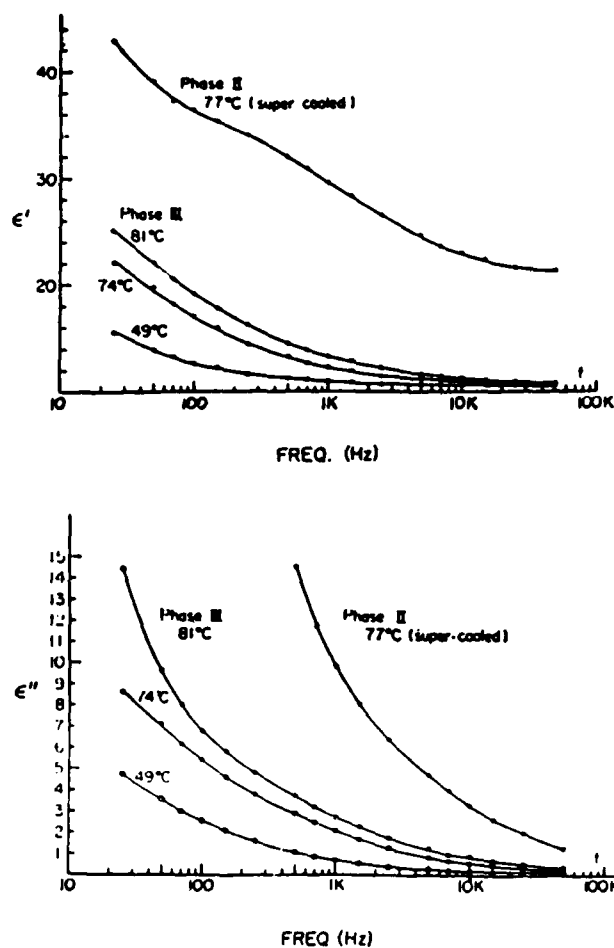
Another factor which influences dielectric loss is phase. From what we discussed so far, we would expect that losses would be greater (for non-polar materials) in a disordered, or amorphous, phase. Again, in analogy to a glass, this would be attributable to a multitude of ground states. Figure IV-18 gives ϵ' and ϵ'' for NH_4NO_3 . Note that the supercooled phase has the higher values.

Another factor influencing losses is processing. (Though in this case processing losses are due to other factors, i.e., impurities, particle size, water, etc.) Figure IV-19 shows the dielectric constants for porcelain produced by wet and dry processes. The wet process has higher values of ϵ' and ϵ'' , more than likely due to increased amounts of waters of hydration. Anisotropy can also influence losses. We indicate in Figure IV-20 the anisotropic loss tangent in ferroelectrics. Moreover, anisotropy may be a critical factor in enhanced coupling to composite materials.

One final mechanism, which will be discussed in more detail in Chapter VI, is interfacial, or Maxwell-Wagner, losses. Even though this factor tends to diminish at higher (microwave) frequencies it still contributes, and after orientational effects, is generally the next major contributor to losses.

In summary, we have reviewed the dielectric properties of representative materials. We have also discussed some of the underlying physical mechanisms which contribute to dielectric loss. There are a number of intrinsic physical parameters which can be maximized to ensure optimum coupling of microwaves to materials.

In the next chapter we will review previous work in this area and in Chapter VI we discuss ways to design materials and microwave structures so as to maximize coupling of microwaves to materials.



NH_4NO_3 . Frequency dependences of the real and imaginary parts of the dielectric constant ϵ' , ϵ'' of NH_4NO_3 pressed powder sample measured at different temperatures

Figure IV-18. Dielectric Constants of NH_4NO_3 (Reference 12)

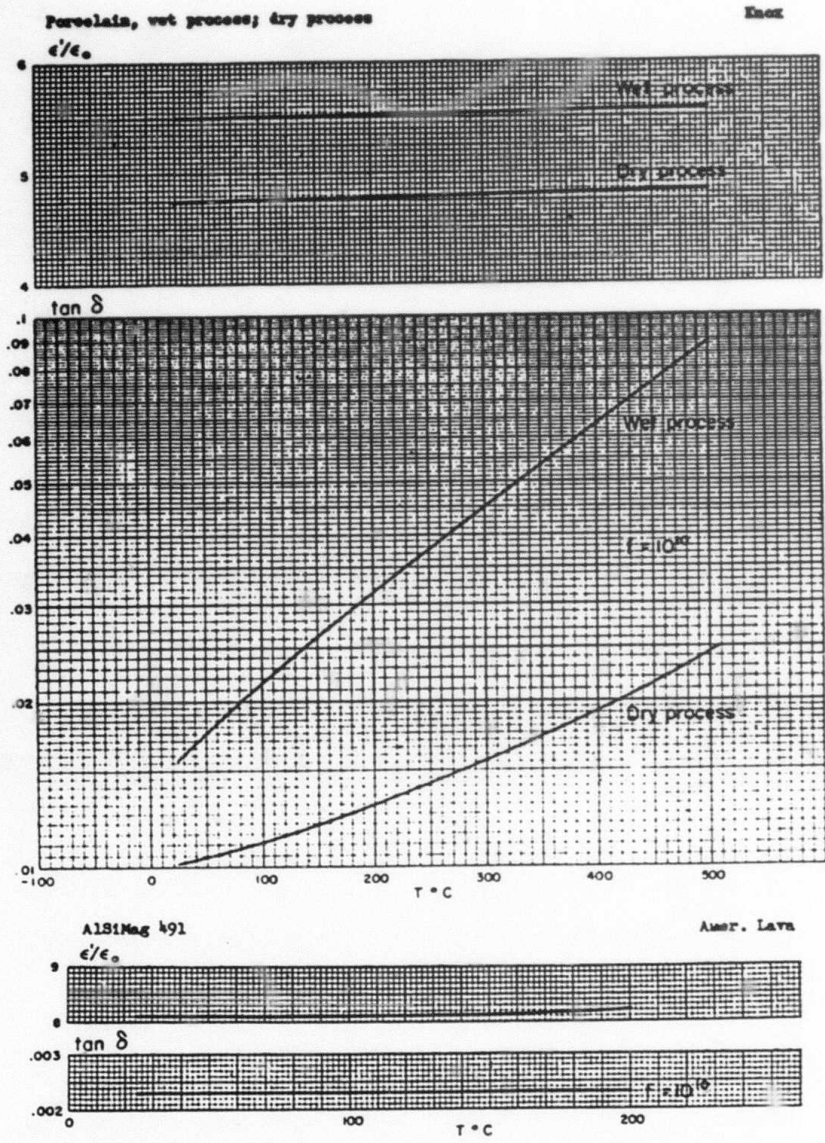
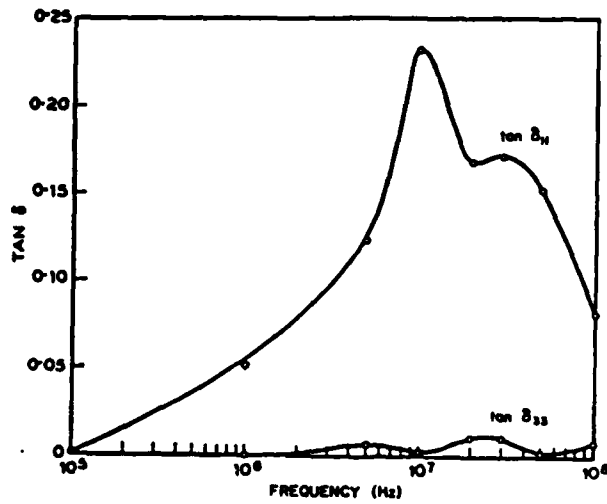
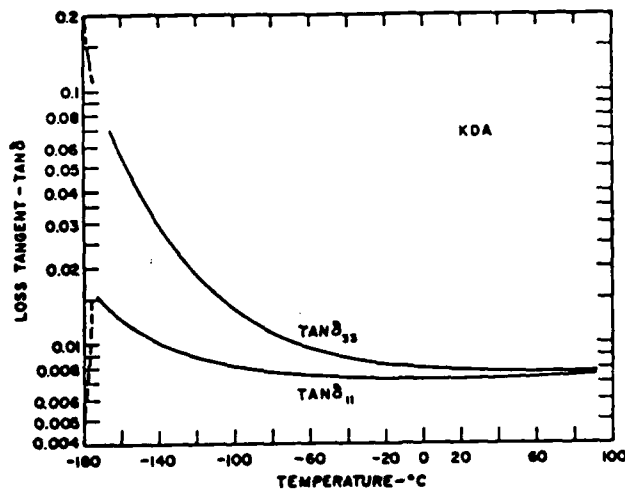


Figure IV-19. Dielectric Constants of Porcelain (Reference 4)



LiNbO₃. Frequency dependences of the dielectric loss tangents $\tan \delta_{11}$ and $\tan \delta_{33}$ of LiNbO₃



KH₂AsO₄ (KDA). Temperature dependences of the dielectric loss tangents $\tan \delta_{11}$, $\tan \delta_{33}$ for KDA

Figure IV-20. Dielectric Constants of LiNbO₃ and KH₂AsO₄ (Reference 12)

CHAPTER V

REVIEW OF PREVIOUS WORK

In reviewing previous work on the coupling of microwaves to materials we will be looking at a number of different areas. First we will be looking at a variety of applications ranging from drying inks to food processing. Second, we will be looking specifically at work, which we have identified, which relates directly to the interaction of microwaves with materials. Third, we will comment on the use of microwaves in field repair, and finally, we will discuss the measurement of dielectric properties.

We have identified four useful reviews of the application of microwaves to industry, science and medicine. The Encyclopedia of Polymer Science and Technology article on Dielectric Heating¹⁴ gives a general introduction and discusses applications involving preheating, foam curing, drying, wood gluing, sealing and microwave heating. Though somewhat dated (1966), this article is a good overview. The HEW report entitled "Survey of Selected Industrial Applications of Microwave Energy"¹⁷ discusses microwave processing and equipment. Applications identified are in microwave drying, the food industry, the forest products industry, and plastics industry, the mining industry, the chemical industry, and in miscellaneous other areas.

The January 1974 issue of the Proceedings of the IEEE¹⁸ is dedicated to microwave applications. Articles cover the application of microwaves to such areas as remote sensing, measurement of dielectric properties, detection of moisture content in crude oil, measurement of soil properties and chemistry of microwave plasmas. We discuss some of these articles in more detail later. Finally, the recent report "Research Opportunities in Industrial Applications of Electromagnetic Heating Technology"¹⁹ covers work through 1982. This report surveys existing applications and discusses areas for possible future development.

References to be found in the above four reviews should give a broad overview of the basis and applications of microwave coupling to matter.

References generated for this report in most cases do not overlap significantly with these previous reviews. This is, of course, due to the emphasis here on the use of microwaves in the processing of materials (particularly polymers).

Microwaves have been used in the drying of inks²⁰ and coated films.²¹ The microwaves couple preferentially to the water molecules (high loss) causing immediate vaporization. Advantages of these on-line drying capabilities are increased throughput, better products and improved cost.

In the area of materials processing, microwaves have been used most extensively in the rubber industry. In addition to the general references, References 22 to 27 deal with microwave vulcanization of synthetic and natural rubbers. Even though most rubbers absorb weakly in the microwave region, their loss tangents can be increased by mixing in compounds such as carbon black to increase absorption. In fact variables which influence microwave energy absorption in synthetic rubbers include:

- (1) The dielectric behavior of different base polymers;
- (2) Adding small amounts of polar substances (e.g., polar polymers) to non-polar polymers;
- (3) Adding various carbon blacks to different polymers;
- (4) Adding light-colored fillers to various polymers; and
- (5) The effects of various plasticizers on nitrile butadiene rubbers.

Note that these variables were mentioned, for the most part, in the last chapter when we discussed physical parameters which influence dielectric loss.

The use of microwave processing with polymers (including plastics, adhesives, and composites) has been limited by the extremely low loss factors for these materials. In addition to the general references already mentioned, References 28 to 34 treat the microwave processing of polymeric materials. Basically, one is going to have to take advantage of the mechanisms discussed in the last chapter to enhance microwave coupling. Alternatively, either the material or the microwave support

structure need to be designed in such a way as to enhance coupling. This latter approach will be discussed in the next chapter.

For the microwave curing of silicone elastomers and foams²⁸ the intrinsically low loss tangent of polydimethylsiloxane was increased by changing the structure of the silicone polymer (adding polar molecules) and by introducing additives with high loss tangents (carbon black). The polar group increases the orientational coupling by increasing the molecular dipole moment. The carbon black, as it is also used in the vulcanization of rubber, is a high loss material and absorbs microwave energy readily. This energy is then transferred to the low loss silicone.

An interesting study²⁹ was done on the curing of epoxy resins as used in fiberglass/epoxy laminate structures. Best agreement between theory and experiment occur when the real part of the dielectric constant (ϵ') is assumed to be that of the epoxy, while the loss tangent is that of water. This discrepancy is attributable to hydroxyl groups in the uncured and curing material which cause high loss factors. Anomalies in the rate of heating are believed due to exothermic chemical reactions caused by the curing.

Reference 30 gives a quantitative approach to the microwave induced cross-linking of thermosetting resins including epoxy, polyester and styrene. In Reference 31 a general overview is given of fast microwave curing of thermoset parts (epoxy casting resin, polyurethane elastomer and polyester resin). The epoxy casting resin has iron oxide filler to increase the loss tangent. The polyester resin consisted of a polyester woven-glass laminate containing lossy fillers and a latent peroxide catalyst. Conclusions drawn from this work on microwave curing in the plastics industry are:

- (1) Microwave curing is broadly applicable to all types of glass fiber reinforced plastics;
- (2) Thick cross-sections cure significantly faster in a microwave field than do thin-section materials;
- (3) Tooling costs for product manufacture can be cut in half with inexpensive glass-fiber tools; and

- (4) Energy consumption in production can be reduced by one-third or more.

Reference 32 gives an overview of new plastics processing methods based on microwave heating. Additives are used to increase coupling. Also crosslinking is aided by UHF-sensitive initiators.

In Reference 33 the use of microwave curing of photoresist-coated substrates in the processing of LSI circuits is discussed. Advantages of this technique in photoresist applications include:

- (1) Resist thickness through the developing stage is comparable to standard baking methods, with more efficient solvent removal;
- (2) Undercutting is reduced;
- (3) Reduced critical dimension sensitivity to exposure and bake time; and
- (4) A yield improvement in lots processed was also evident.

An interesting possible application of microwave curing can be seen in Reference 35. Here materials composed of metallic particles (Ni, C, and Cu) and polymer particles (PVC, PMMA, Nylon, PE) were compacted to form a random network of fused crosslinked large polymer particles and a fine network of small metallic particles. In this case curing was done by gamma irradiation. A system of this type, i.e., a low loss polymer interspersed with metallic particles is an ideal candidate for microwave curing. This should also be the case for metallic particles in a ceramic matrix (cermets).

The dielectric properties of ceramic materials have been investigated for some time now. Some recent work³⁶ has centered on understanding microwave coupling to strong-coupling materials such as UO_x ($2 \leq x \leq 3$), B_4C and B_6O which absorb more energy per mole than water. Also, work has been reported on the mechanisms for coupling microwaves to nepheline³⁷ glass-ceramics. Microwave sintering of ceramics has been shown to be feasible.

The use of microwave induced plasmas to facilitate chemical reactions was reviewed by Wightman.¹⁸ The literature is surveyed from 1965-1973. Microwave plasmas can induce chemical reactions which might not otherwise proceed. This can be caused by either the formation of new radicals by

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the plasma, or excited state chemical reactions. Most of the work done prior to the writing of Ref. 18 was on gas-atom interactions. For materials processing the more interesting interactions are of the solid-atom type.

In Reference 19 it is pointed out that microwave plasmas are used in materials processing for etching, junction formation and surface modification. However, many of these processes are proprietary. Because of the coupling of microwaves to molecules, it is possible for ordinarily non-flammable mixtures to be combustible when exposed to microwaves. This can be important in the detoxification of hazardous materials.

The idea behind the use of microwave processing for field repair is to be able to readily patch and cure damage to a composite structure. This would necessitate the identification of a compatible patching material (adhesive, composite, etc.) for the adherends and the means of executing a fast, dependable cure. References 38 and 39 describe work done at Syracuse University on the use of microwave heating in road maintenance and rapid runway repair. A polymeric concrete was used as the patching material. The dispersed concrete filler material caused sufficient heating to cure the usually transparent polymer matrix. The portable microwave unit was also used to preheat the surrounding pothole to improve bonding. This unit was scaled up for the rapid runway repair. In this case a truck mounted microwave unit was used to cure the patched runway.

References 4 and 12 give a thorough overview of dielectric measurements techniques. The basic idea is to compare an empty capacitor with the same capacitor filled with the dielectric of interest (ϵ^*). In the low frequency range ($10^2 - 10^7$ Hz) the capacitance (Schering) bridge is used to measure ϵ^* . At higher frequencies (10-100 MHz), as the bridge technique becomes inaccurate, resonant circuits are used. A capacitor is placed in an LC-circuit and tuned while empty, and then tuned with a dielectric. In the 100 MHz-1GHz range, transmission line techniques are used to measure ϵ^* . The transmission line has a terminating impedance constructed from the dielectric. The variation in the resultant standing

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wave measures ϵ^* . Finally, for frequencies above 1 GHz (microwaves) either the transmission line technique or the cavity perturbation method is used.

In both the high and low frequency regimes one has to be careful of conduction effects. In the low frequency regime there is a conductive loss term,

$$\tan \delta_c = \frac{\sigma}{\epsilon' \omega},$$

where σ is frequency independent (the dc conductivity). These effects are large for $\omega \ll \omega_m$, where $\omega_m \tau = 1$. For $\omega \gg \omega_m$, there are again conduction effects, but this time from the migration of ionic (dipolar) charge carriers. Since we are primarily interested in microwave coupling near ω_m we have largely ignored these conduction effects.

Impurities, inhomogeneities, defects, etc. primarily influence the loss tangent, and not the real part of ϵ^* . For measuring ϵ^* one consequently wants a very pure sample. On the other hand, if one wants to increase coupling then, as we said in Chapter III, defects and impurities should be increased. ϵ' is usually measured no better than 1% while for materials with $\tan \delta > 0.1$ a value of 5-10% from the true value usually obtains. Single crystal measurements are preferred over polycrystalline and powdered samples. One also has to be careful of interfacial polarization when electrodes are used.

A dynamic measurement technique for ϵ^* is presented in Reference 40. Here two microwave modes are used. One mode is used to heat the sample and the other to measure ϵ^* for spheres or rods using cavity perturbation methods. Present methods of measuring $\epsilon^* = \epsilon^*(T)$ use conventional heating techniques. The results are consistent with von Hippel's measurements⁴ and yield ϵ' within $\pm 3\%$ and $\tan \delta$ within $\pm 15\%$. An interesting variation on this dual use of microwaves is given in Reference 41 which discusses, and gives a bibliography on, microwave instrumentation for materials control. Microwave signals have been used to monitor moisture content, surface roughness, degree of cure and wire diameters. Thus, dual mode processing units could conceivably process and monitor materials

simultaneously. The dielectric spectroscopy of soft modes in ferroelectrics is reviewed in Reference 42. Two techniques for measuring $\epsilon^*(\omega)$ are discussed: (1) rapid-scan Fourier transform spectroscopy (10 - 10^4 cm^{-1}), and (2) Backward Wave Oscillator (BWO) spectroscopy (3 - 30 cm^{-1}). The latter technique, developed in Russia, is not commercially available.

Having now reviewed the available literature, in the next chapter we will discuss ways in which materials and microwave systems can be designed to enhance microwave coupling and control selective heating.

CHAPTER VI

COUPLING TO DESIGNED MATERIALS

We have reviewed the mechanisms for coupling microwaves to materials in Chapter III and have seen that the dominant mechanism in the microwave regime is orientational flipping of the elemental dipoles. However, this dipole orientation is general in the sense that we are dealing with transitions between two-level states. Consequently, from a microscopic perspective a material with strong dielectric properties would either have two-level ground states compatible with microwave energies, or be amenable to modification so as to generate these types of ground states.

In Chapter IV we discussed the dielectric properties of a variety of materials and commented on the physical parameters which influence dielectric behavior. The number of these physical variables appears to be quite large. In fact, in reviewing previous work on dielectric heating and microwave curing in Chapter V we have seen that many of the parameters which we have identified have been used in enhancing microwave coupling and loss factors. These have included additives, impurities, pre-heating, disorder, etc.

In this chapter we want to look for leverage which may exist with designed materials. For designed materials we have two approaches in mind. First, how can the material of interest be modified so as to enhance microwave coupling in a predetermined manner. An example of this approach might be to add a particular dopant, of a particular particle size, in a particular phase and distributed in such a manner to enhance microwave coupling in a selected region of the host material. Second, and related to the first, how can the macroscopic configuration (i.e., thickness, layers, etc.) of the targeted material and the support microwave structures be varied so as to enhance microwave coupling in a predetermined controlled manner. A simple example of this approach would be to use layers of materials of different dielectric impedances as quarter-wave plates. Likewise, the modes in the microwave cavity can be tuned so that maximum power is transferred to the targeted material.

Before describing the effects of inhomogeneities in materials we discuss polarization due to space charge effects, or interfacial polarization. These Maxwell-Wagner effects will be important in leveraging the coupling of microwaves to materials due to dispersants. Assuming that one has the "best" materials for coupling microwaves, these materials can be geometrically combined in ways which increase or decrease their cumulative loss properties.

The dipole reorientation coupling (two-level states) is due to charge which is bound. Space charge polarization is due to migrating charge carriers and produces large field distortions. Figure IV-1 shows the standard example of interfacial polarization, the Maxwell-Wagner two-layer capacitor. Generally, in treating dispersed materials the component materials are assumed to be loss free. More realistic treatments would, of course, include loss terms. In spite of this, the combined materials have a loss term. In this case the dielectrics are characterized by dielectric constants, conductivities and thicknesses, $(\epsilon'_i, \sigma_i, d_i)$, $i = 1, 2$.

For an applied dc-field to the capacitor of Figure VI-1, the initial field distribution is determined by the requirement of constant flux density,

$$D_1 = D_2 , \quad (VI-1a)$$

or

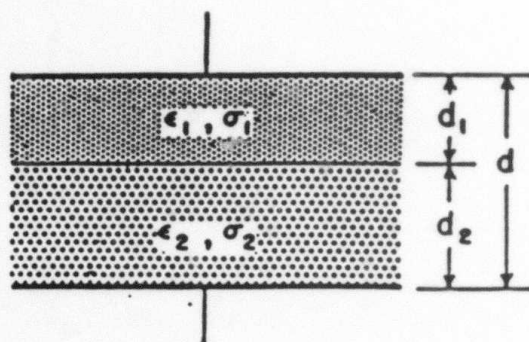
$$\frac{E_2}{E_1} = \frac{\epsilon'_1}{\epsilon'_2} . \quad (VI-1b)$$

The final field distribution is determined by the requirement of current continuity,

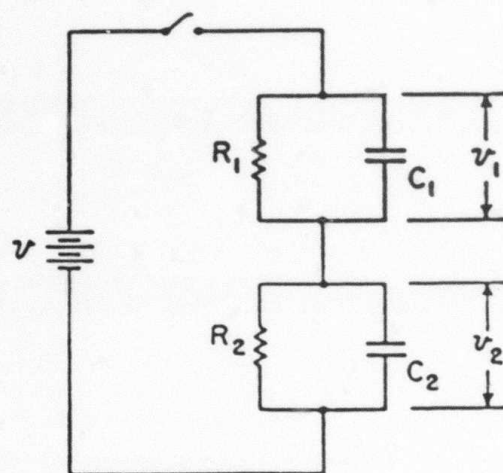
$$J_1 = J_2 , \quad (VI-2a)$$

or

$$\frac{E_1}{E_2} = \frac{\sigma_2}{\sigma_1} . \quad (VI-2b)$$



Maxwell-Wagner two-layer capacitor.



Equivalent circuit of two-layer capacitor.

Figure VI-1. Maxwell-Wagner Two-Layer Capacitor and Equivalent Circuit (Reference 5)

Thus, from the equivalent circuit diagram in Figure VI-1, the change from one condition to the other takes place exponentially with time constant,

$$\tau = \frac{R_1\tau_2 + R_2\tau_1}{R_1 + R_2}, \quad (\text{VI-3})$$

where $\tau_i (i=1,2)$ are the time constants for the individual RC-circuits.

For an ac-field, the two-layer capacitor yields a relaxation spectrum which is indistinguishable from that of the two-level state dipole reorientation. The complex permittivity becomes,

$$\kappa^* = \kappa_\infty' + \frac{\kappa_s' - \kappa_\infty'}{1 + i\omega\tau} - \frac{i\sigma}{\omega\epsilon_0} \quad (\text{VI-4})$$

where,

$$\kappa_s' = \frac{\tau_1 + \tau_2 - \tau}{C_0(R_1 + R_2)}, \quad (\text{VI-5a})$$

$$\kappa_\infty' = \frac{\tau_1 \tau_2}{C_0(R_1 + R_2)}, \quad (\text{VI-5b})$$

$$\sigma = \frac{\epsilon_0}{C_0(R_1 + R_2)}. \quad (\text{VI-5c})$$

The only difference between Equations (VI-4) and (III-42) is the presence of the conduction term, $\sigma/\omega\epsilon_0$. The optical and static permittivities can be written as

$$\kappa_\infty' = \frac{d/\epsilon_0}{d_1/\epsilon_1' + d_2/\epsilon_2'}, \quad (\text{VI-6})$$

and,

$$\kappa_s' = \kappa_\infty' \left\{ 1 + d_1 d_2 \left[\frac{(1/\sigma_1)\sqrt{\epsilon_1'/\epsilon_2'} - (1/\sigma_2)\sqrt{\epsilon_2'/\epsilon_1'}}{d_1/\sigma_1 + d_2/\sigma_2} \right]^2 \right\} \quad (\text{VI-7})$$

The static permittivity is larger than the optical permittivity due to charge migration to the interface, resulting in charge accumulation and a new field distribution. The field changes until the dc-conductivity,

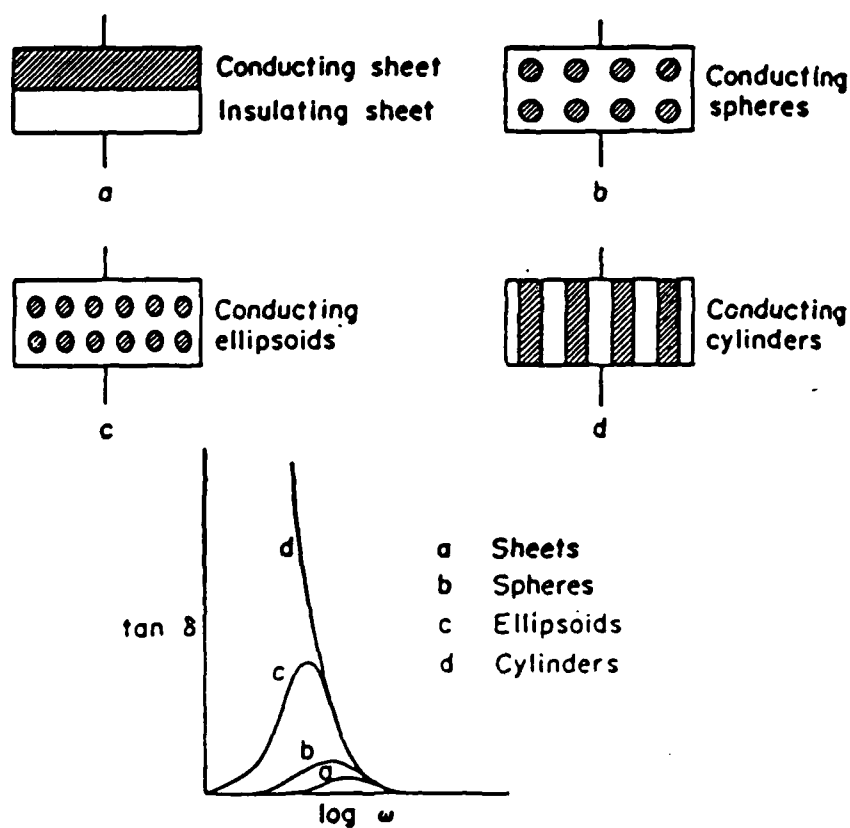
$$\sigma = \frac{d}{d_1/\sigma_1 + d_2/\sigma_2} \quad , \quad (VI-8)$$

is established.

If the dielectric layers in Figure VI-1 are further divided and rearranged the complex permittivity of the composite system does not change from (VI-4). However, if the geometry is changed, then the dielectric properties change. This is illustrated in Figure VI-2 and will be discussed later in more detail. We now comment on the effects of various types of inhomogeneities.

When we discussed mechanisms in Chapter IV we pointed out that the dielectric loss tangent is affected by a variety of additives and fillers. Here we are not so much interested in the effect of a particular additive or filler as in how the additive and the host material can be arranged to control dielectric loss. We have just seen that for loss free materials, i.e., $\text{Im}(\epsilon^*)=0$, loss can occur if there are conduction processes and interfacial regions. There should be leverage then in utilizing the Maxwell-Wagner effect by varying the conductivity and interfacial regions of the component materials.

The parameters to be varied are the type, concentration, and distribution of dispersed particles (ϵ_i, σ_i), and the size and shape of the dispersed particles (d_i). One can see from (VI-6) and (VI-7) that it is the trade-off between dielectric properties (ϵ_i'), conduction (σ_i) and particle size (d_i) that determines loss terms. In addition, if there is a designed distribution of particles, or if there are shape dependent effects, or if there is interaction between the particles, then averages must be taken over the simple Maxwell-Wagner equations or more powerful



Dependence of dielectric response on shape and orientation of particles of medium 2.

Figure VI-2. Dependence of Dielectric Response on Shape and Orientation (Reference 5)

many-body techniques applied. This is much like accounting for the effects of a distribution of relaxation times in the Debye model.

Obviously the conductivity is affected by the available charge carriers. Thus, metal and semiconducting dispersants may provide more leverage than, say, ceramic dispersants in a polymeric matrix. In addition, the particles can be distributed, or graded, in such a way as to maximize coupling to a particular mode in a specified location in the material (selective heating). The interfacial area and charge traps can be affected by the phase of the material (e.g., crystalline or amorphous) and the mixing of phase (grain boundaries). There should also be an optimum particle size and shape for the component materials with the application of microwave processing.

With composite materials there should be a great deal of leverage with the use of fillers and additives in the matrix material. We have seen some of this in discussing polymeric materials in Chapter IV and V. The fiber materials can be chopped and random, or in one-, two-, or three-dimensional weaves. Thus, there is a great deal of interfacial and geometric leverage. However, a common problem in composite curing is the natural tendency for impurities to migrate to phase boundaries, i.e., the matrix-fiber interface, and attack the fiber. Ways should be investigated to utilize selective microwave heating to control this fiber/matrix bond.

In the case of great many particles compacted together, i.e., sintering, the Maxwell-Wagner double-layer capacitor (or its multilayer extension) is a good approximation. We will be discussing these dispersed systems further in the next few paragraphs. Also, for a given dispersant losses are increased if there is a wide distribution of particle size.⁴³

We have not commented at all on molecular states, i.e., molecular spectroscopy. Microwave absorption by molecules⁴⁴ is a resonance mechanism and generally occurs in the far microwave or infrared region of the spectrum. There are loss terms but, as with other resonance mechanisms, these tend to be small. It may be possible, for macromolecules, to push these molecular transitions into the microwave

region of interest. This, perhaps, could be done by varying the effective moment of inertia of the molecule, applying pressure or changing the phase (e.g., glassy). It is not clear that the pay-off would be great.

Reference 45 by Meakins gives an overview of microwave absorption in solids. Based on a Debye model, the loss term for low concentrations of conducting particles in a non-conducting host becomes,

$$\epsilon'' = \frac{9v(\epsilon_1')^2}{2\epsilon_1' + \epsilon_2'} \frac{\omega\tau}{1+\omega^2\tau^2}, \quad (\text{VI-9})$$

where v is the volume fraction of conductors, and ϵ_1' (ϵ_2') is the dielectric constant of the non-conductor (conductor). Note that the absorption does not depend on the size of the dispersants in this low concentration limit. The maximum absorption frequency is given by,

$$\nu_{\max}(\text{cps}) = 1.8 \times 10^{12} \frac{\sigma_2}{2\epsilon_1' + \epsilon_2'}, \quad (\text{VI-10})$$

where σ_2 is the specific conductivity of the conducting dispersants. Note that the frequency maximum can be shifted by varying the conductivity. For higher concentrations of dispersants these expressions (VI-9,10) fail due to dispersant-dispersant interactions.

Van Beek⁴⁶ treats the dielectric behavior of heterogeneous systems. Assuming loss-free dielectrics and a Debye model, tables of equations and references are given for various forms of dispersants including spheroids, cylinders, porous dielectrics and colloidal suspensions. For the Debye model (Equations III-43) the loss tangent can be written as,

$$\tan \delta = \frac{\epsilon_s' - \epsilon_\infty'}{(\epsilon_s' \epsilon_\infty')^{1/2}} \frac{\omega\tau_\delta}{1+\omega^2\tau_\delta^2} \quad (\text{VI-11a})$$

where

$$\tau_\delta = \left(\frac{\epsilon_\infty'}{\epsilon_s'} \right)^{1/2} \tau \quad (\text{VI-11b})$$

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Van Beek goes on to give ϵ_s' , ϵ_∞' , τ and σ for various configurations of dispersants.

The Maxwell-Wagner double-layer equations (VI-4 to VI-8) can be generalized to many layers⁴⁷ where

$$\epsilon_s' = d \left(\sum_i d_i \epsilon_i' / \sigma_0^2 \right) / \left(\sum_i d_i / \sigma_i \right)^2 \quad (\text{VI-12a})$$

and

$$\epsilon_\infty' = d / \left(\sum_i d_i / \epsilon_i' \right) . \quad (\text{VI-12b})$$

These two- or many-layer dielectrics, as has been mentioned, are often good approximations to compressed or sintered polycrystalline materials. Note also from (VI-11) that there are no Maxwell-Wagner losses if,

$$\epsilon_s' = \epsilon_\infty' \quad (\text{VI-13a})$$

or

$$\frac{\epsilon_1'}{\epsilon_2'} = \frac{\sigma_1}{\sigma_2} . \quad (\text{VI-13b})$$

As an example of the complexity of the equations used for dispersed loss-free particles we present the parameters for the Debye equations for dispersed spheres. Complications arise when the Debye model is not applicable; if there is a distribution of relaxation times, or if there are interactions between dispersants. We obtain,

$$\tau = \frac{\epsilon_0 [2\epsilon_1' + \epsilon_2' + v_2(\epsilon_2' - \epsilon_1')]}{2\sigma_1 + \sigma_2 - v_2(\sigma_2 - \sigma_1)} , \quad (\text{VI-14a})$$

$$\epsilon_s' = \epsilon_1' \frac{2\sigma_1 + \sigma_2 + v_2(\sigma_2 - \sigma_1)}{2\sigma_1 + \sigma_2 - v_2(\sigma_2 - \sigma_1)} + 3v_2\sigma_1 \frac{(2\sigma_1 + \sigma_2)(\epsilon_2' - \epsilon_1') - (2\epsilon_1' + \epsilon_2')(\sigma_2 - \sigma_1)}{[2\sigma_1 + \sigma_2 - v_2(\sigma_2 - \sigma_1)]^2} \quad (\text{VI-14b})$$

and

$$\epsilon_\infty' = \epsilon_1' \frac{2\epsilon_1' + \epsilon_2' + 2v_2(\epsilon_2' - \epsilon_1')}{2\epsilon_1' + \epsilon_2' - v_2(\epsilon_2' - \epsilon_1')} \quad (\text{VI-14c})$$

These expressions can be substituted in (VI-11) to obtain $\tan \delta$ for the system. Considerable loss occurs for $\epsilon_1' = \epsilon_2'$, but $\sigma_1 \neq \sigma_2$.

Having seen above how materials can be modified, or designed, to enhance their dielectric loss, we want to look in more detail at the incident microwaves. Basically, as the microwave impinges on the surface of the target material part will be reflected and part will be transmitted. The transmitted part will be attenuated (Equation III-20) and power may be transferred to the material. A standing wave pattern is set up in the microwave coupler, so that a system of nodes and anti-nodes are created. However, this system is a highly multimode one.

Because of the attenuation, or penetration depth, for lossy materials, material modification can affect where the power deposited (anti-nodes) is located. Generally, for disordered, heterogeneous materials multimode couplers would be superior to single mode couplers to ensure uniform heating. In the multimode phase a distribution of anti-nodes will be set up in the heterogeneous material for uniform heating throughout the sample. In pure materials, on the other hand, a single mode can be carefully focused by either varying the position of the material and coupler, or by modifying the material using additives to maximize coupling at specified locations. Using graded particle distributions may enable strong coupling over a broader region of the material.

In Figures VI-3 through VI-9 we show graphs for the attenuation of various dielectric media. Consequently, from these figures one can obtain the rate at which power is damped in the material, and the power available

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at a given anti-node. For instance, at room temperature (25°C), a microwave of frequency 3×10^9 Hz and free space wavelength (λ_0) of 0.1 m striking an epoxy adhesive with a loss tangent of 0.023 and permittivity of $\kappa' = 3.14$, would attenuate at the rate of 12 decibels/meter, where,

$$\text{Decibels} = 10 \log \frac{P(0)}{P(x)} = 8.686 \alpha x, \quad (\text{VI-15a})$$

or

$$8.686 \alpha = 8.686 \frac{2}{\lambda_0} \left[\frac{1}{2} \kappa' \left\{ \sqrt{1 + \tan^2 \delta} - 1 \right\} \right]^{\frac{1}{2}} \text{ db/m.} \quad (\text{VI-15b})$$

This attenuation rate is readily obtained graphically from Figure VI-5 using the above information.

In many applications incident microwaves impinge upon layered materials, i.e., the thin adhesive bond between two adherends. On the other hand, in materials processing additional layers of material are sometimes necessary (platens) or useful (indirect microwave heating). The analysis of electromagnetic waves impinging on a layered system is given in von Hippel.⁴ At normal incidence, the reflection and transmission coefficients for a boundary between dielectrics 1 and 2, with intrinsic impedances Z_1 and Z_2 (Equation III-25), are given by,

$$r_o = r_E = \frac{Z_2 - Z_1}{Z_2 + Z_1} = -r_H \quad (\text{VI-16})$$

$$t_E = \frac{2Z_2}{Z_2 + Z_1} = \frac{Z_2}{Z_1} t_H \quad (\text{VI-17})$$

The reflected and incident waves combine to form standing waves. We note from (VI-16) the condition of zero reflection,

$$Z_1 = Z_2, \quad (\text{VI-18a})$$

Dielectric Parameters

1. ϵ'/ϵ_0 , the dielectric constant or permittivity relative to vacuum, also designated in the literature as K , ϵ , ϵ , D.C., etc.
2. $\tan \delta$ or $\tan \delta_d$, the dielectric-loss tangent or dissipation factor, also designated in the literature as D.F., $1/Q$, and, when losses are low, as power factor or $\cos \delta$.
3. μ'/μ_0 , the magnetic permeability relative to vacuum, also given in the literature as μ' or μ_0 .
4. $\tan \delta_m$, the magnetic-loss tangent.
5. ρ , the a-c volume resistivity in ohm-cm. This parameter is used in these tables only for very high-loss materials.

Transformation to Other Parameters. The dielectric-loss factor relative to vacuum, ϵ''/ϵ_0 , is the product of the dielectric loss tangent and ϵ'/ϵ_0 . Alternating-current volume conductivity, σ , is given by

$$\sigma = \frac{1}{\rho} = \frac{f(\epsilon'/\epsilon_0) \tan \delta}{1.8 \times 10^{12}} \text{ [mho-cm]} \quad (f \text{ in cps}).$$

A chart is given (page 295) for approximate calculations of σ or ρ from the data given in the tables.

The magnetic-loss factor relative to vacuum, μ''/μ_0 , is the product of the magnetic-loss tangent and μ'/μ_0 (in analogy to the dielectric-loss factor). In the literature, the loss factor is sometimes given as $1/\mu_0'Q$ or, in our notation, $\tan \delta_m/(\mu'/\mu_0)$.

The attenuation constant, α , for propagation in free space is

$$\frac{2\pi}{\lambda_0} \left[\frac{\mu' \epsilon' - 1 - \tan \delta_d \cdot \tan \delta_m}{2} \left((1 + \tan^2 (\delta_d + \delta_m))^{1/2} - 1 \right) \right]^{1/2},$$

which for nonmagnetic dielectrics reduces to

$$\frac{2\pi}{\lambda_0} \left(\frac{\epsilon'}{\epsilon_0} \right)^{1/2} \left[\frac{(1 + \tan^2 \delta_d)^{1/2} - 1}{2} \right]^{1/2}.$$

Charts for finding α in terms of ϵ'/ϵ_0 and $\tan \delta_d$ are included in this section (pages 296-298). They apply also to magnetic dielectrics when the product $(\mu'/\mu)(\epsilon'/\epsilon_0)$ is substituted for ϵ'/ϵ_0 and an equivalent combined loss tangent $\tan \delta_c$ is used instead of $\tan \delta_d$. A graph on page 299 gives $\tan \delta_c$ for values of $\tan \delta_d$ and $\tan \delta_m$ in the range 0.1 to 10. For smaller values, $\tan \delta_c$ is the sum of $\tan \delta_d$ and $\tan \delta_m$.

The phase constant β for propagation in free space is

$$\frac{2\pi}{\lambda_0} \left[\frac{\mu' \epsilon' - 1 - \tan \delta_d \cdot \tan \delta_m}{2} \left((1 + \tan^2 (\delta_d + \delta_m))^{1/2} + 1 \right) \right]^{1/2},$$

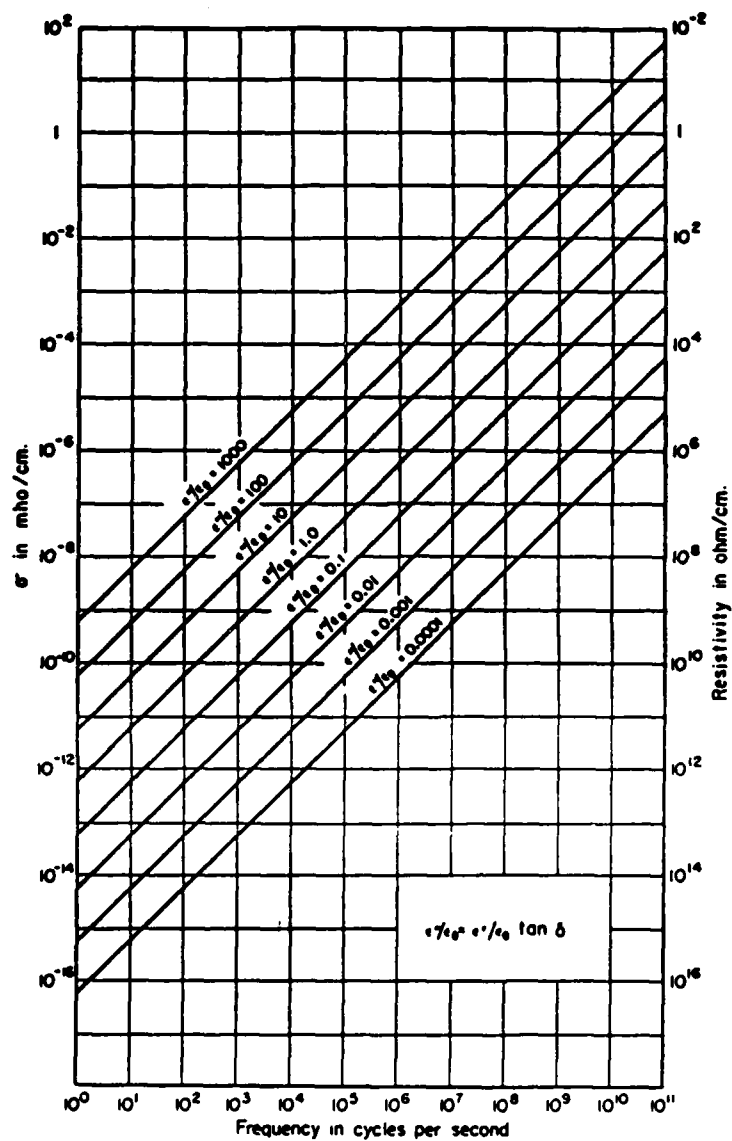
which reduces for nonmagnetic materials to

$$\frac{2\pi}{\lambda_0} \left(\frac{\epsilon'}{\epsilon_0} \right)^{1/2} \left[\frac{(1 + \tan^2 \delta_d)^{1/2} + 1}{2} \right]^{1/2}.$$

The intrinsic impedance Z of the material is

$$377 \left(\frac{\mu' \epsilon_0}{\epsilon_0 \epsilon'} \right)^{1/2}.$$

Figure VI-3. Dielectric Parameters (Reference 4)



Conductivity-Resistivity as Function of ϵ''/ϵ_0 and Frequency

Figure VI-4. Conductivity-Resistivity vs κ_e'' and ν (Reference 4)

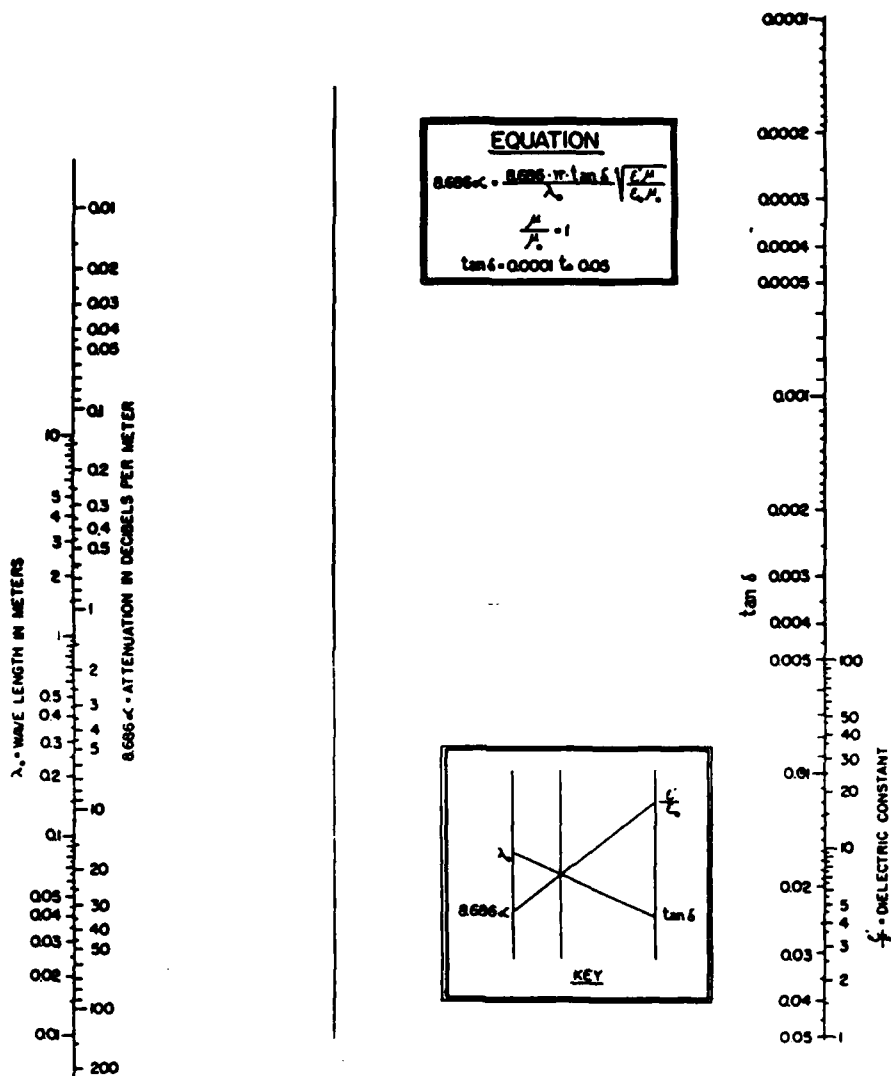
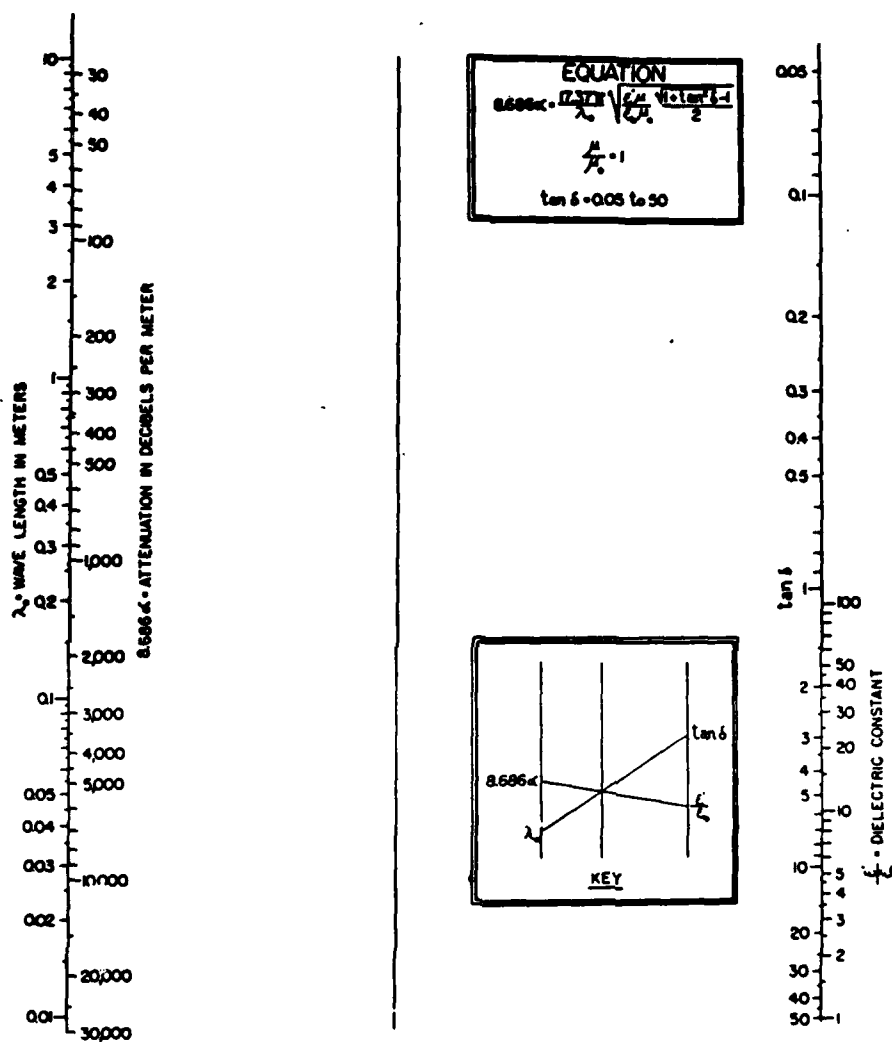
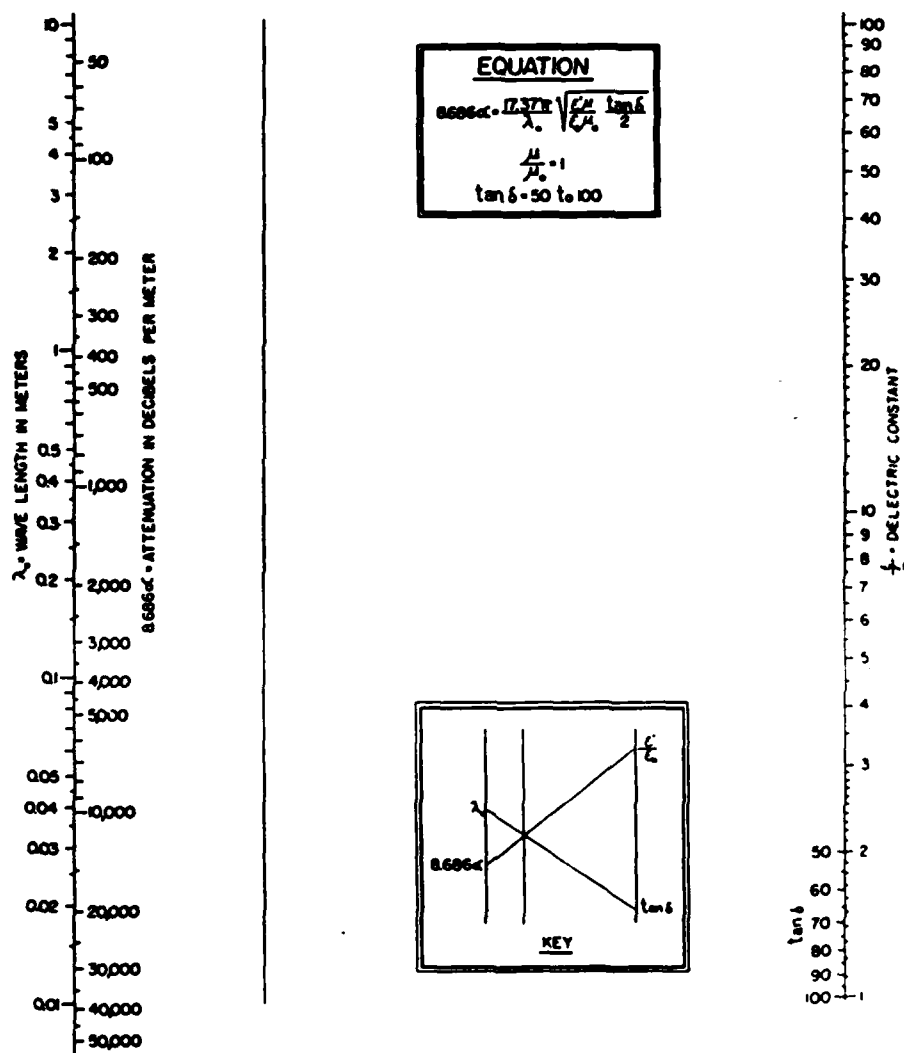


Figure VI-5. Decibel Loss per Meter for Low-Loss Dielectrics (Reference 4)



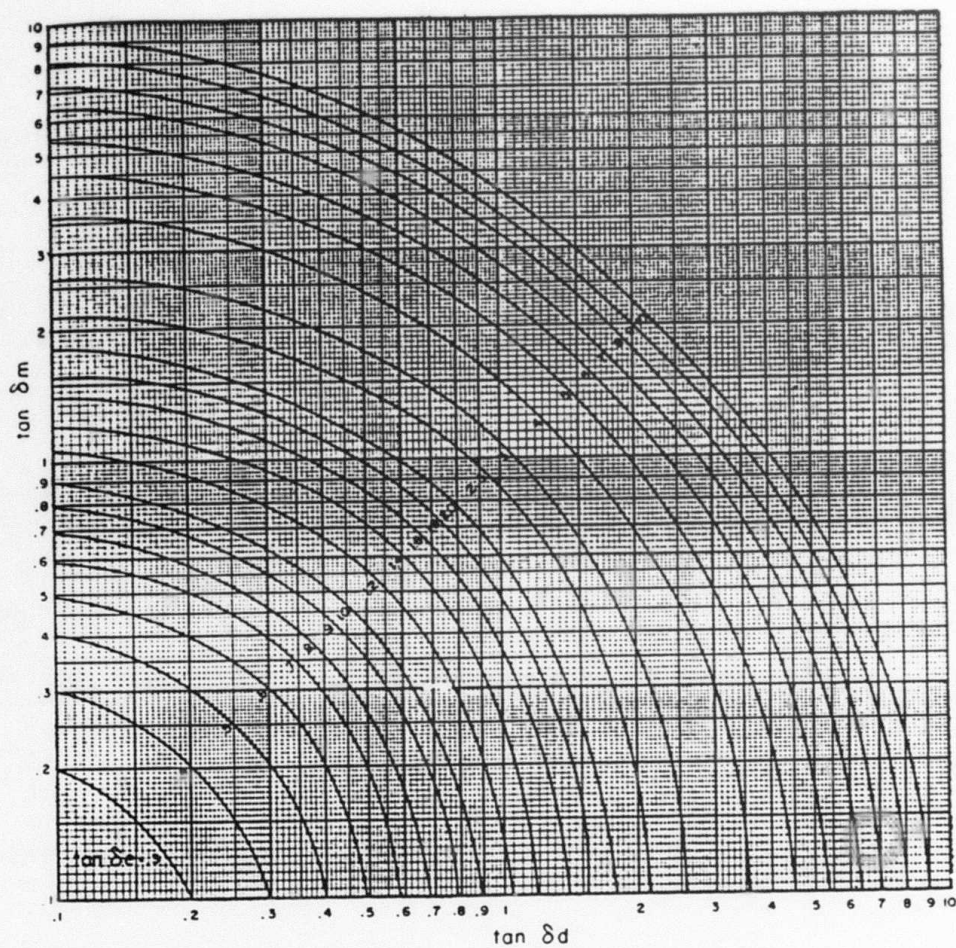
Decibel Loss per Meter for Medium-Loss Dielectrics ($\tan \delta$ comparable to 1)

Figure VI-6. Decibel Loss per Meter for Medium-Loss Dielectrics (Reference 4)



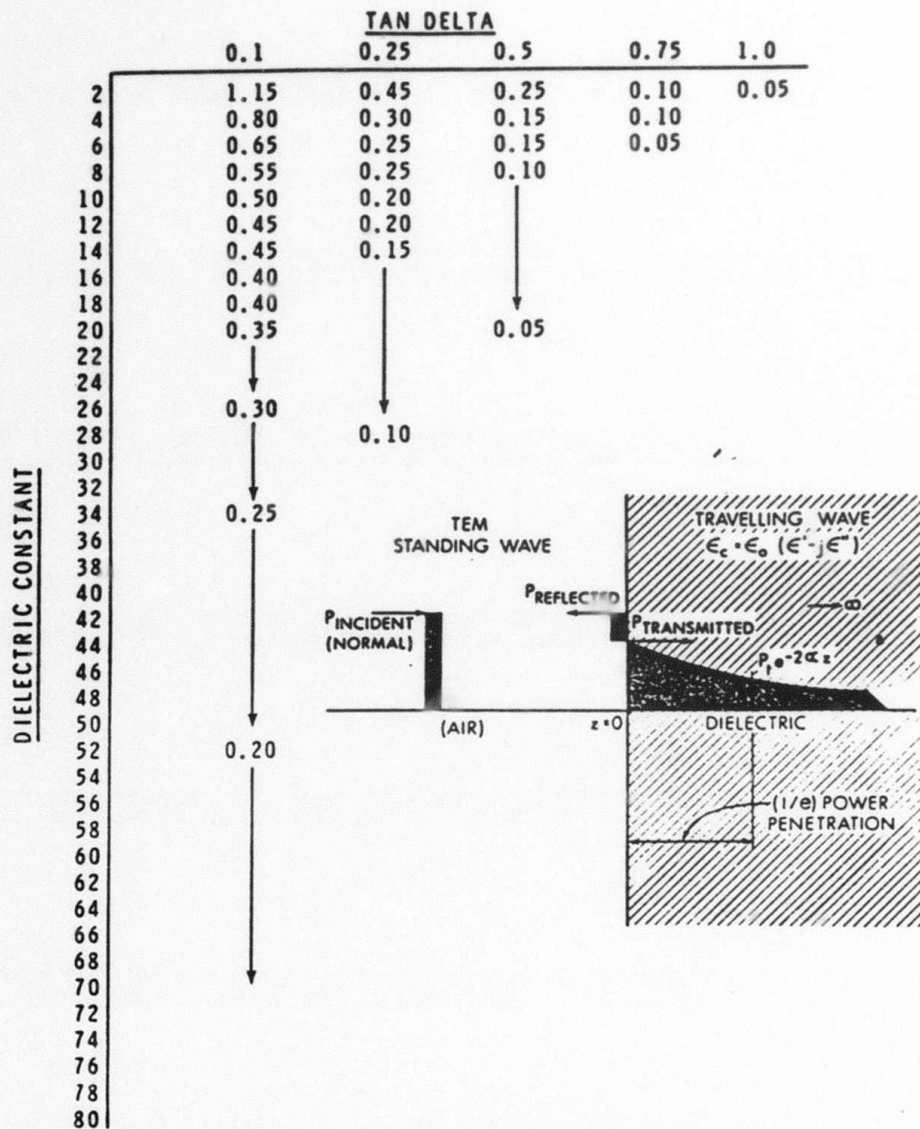
Decibel Loss per Meter for High-Loss Dielectrics ($\tan \delta \gg 1$)

Figure VI-7. Decibel Loss per Meter for High-Loss Dielectrics (Reference 4)



Equivalent Combined Loss Tangent for Magnetic Materials

Figure VI-8. Equivalent Combined Loss Tangent for Magnetic Materials
(Reference 4)



The power penetration depth $D = 1/\alpha$ = depth at which the *transmitted* power is reduced to 36.8% ($1/e$) of its surface ($z = 0+$) value, as illustrated in the inset figure. $\alpha = R\{j\omega \sqrt{\mu_0 \epsilon_0 \epsilon_c}\}$ and D is expressed in the table in terms of free-space wavelengths. Thus the penetration depths is $0.1\lambda_0$ for $\epsilon' = 28$ and $\tan \delta = 0.25$. (Part of a set of tables produced by APL/360 computer, University of Alberta)

Figure VI-9. Power Penetration Depth vs Dielectric Constant and Loss Tangent (Reference 41)

or

$$\frac{\epsilon_1^*}{\epsilon_2^*} = \frac{\mu_1^*}{\mu_2^*} \quad (VI-18b)$$

Total reflection occurs by a complete mismatch between the two media, i.e., media with very high and very low permittivity or permeability or with a loss mismatch (ceramic to metal). For metal, conduction dominates and $Z(\text{metal}) \ll Z(\text{dielectric})$, or,

$$r_E = \frac{Z(\text{metal}) - Z(\text{dielectric})}{Z(\text{metal}) + Z(\text{dielectric})}$$

and,

$$r_E \cong -1$$

In medium 1 for partial reflection,

$$E_y = E_0 e^{i\omega t - \gamma_1 x} (1 + r_0 e^{2\gamma_1 x}) \quad (VI-19)$$

or

$$P_E \sim E_y^2 = E_0^2 e^{-2\gamma_1 x} (1 + r_0 e^{2\gamma_1 x})^2 \quad (VI-20)$$

At the boundary, the terminating impedance of medium 1 is given by,

$$Z(x=0) = \frac{E_1(0)}{H_1(0)} = Z_1 \frac{1+r_0}{1-r_0} \quad (VI-21)$$

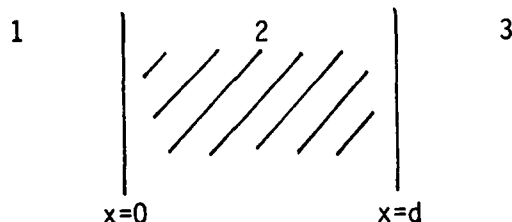
Measuring r_0 yields $Z(x=0)$ if Z is known. If there is no reflection in medium 2, boundary conditions give,

$$Z(x=0) = \frac{E_1(0)}{H_1(0)} = \frac{E_2(0)}{H_2(0)} \quad (VI-22)$$

or we have $Z_2 = Z(x=0)$.

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If there is an additional boundary between medium 2 and another medium 3, i.e.,



then a reflection at $x=d$ yields a standing wave in medium 2, in addition to that in 1. The field in medium 2 is given by,

$$E_{y2} = E_2 e^{i\omega t} \{ e^{-\gamma_2(x-d)} + r_{23} e^{\gamma_2(x-d)} \}, \quad (\text{VI-23})$$

and the power by,

$$P_2 \sim E_{y2}^2 = E_2^2 [e^{-\gamma_2(x-d)} + r_{23} e^{\gamma_2(x-d)}]^2. \quad (\text{VI-24})$$

The terminating impedance at $x=0$, as seen in medium 2 is now,

$$Z(x=0) = \frac{E_2(0)}{H_2(0)} = Z_2 \frac{e^{\gamma_2 d} + r_{23} e^{-\gamma_2 d}}{e^{\gamma_2 d} - r_{23} e^{-\gamma_2 d}}. \quad (\text{VI-25})$$

If the wave continues in medium 3 without reflecting,

$$r_{23} = \frac{Z_3 - Z_2}{Z_3 + Z_2}. \quad (\text{VI-26})$$

However, if medium 3 is a metal, $r_{23} \cong -1$, and from (VI-25),

$$Z(x=0) = Z_2 \tanh \gamma_2 d. \quad (\text{VI-27})$$

Standing waves such as the above are used to measure dielectric properties.

CHAPTER VII
CONCLUSIONS AND RECOMMENDATIONS

From the material which has been presented in the previous six chapters, it is apparent that a great deal of work has gone into analyzing the coupling of microwaves to materials. However, with few exceptions this work has not been focused on the microwave processing of materials. The exceptions have been in the rubber industry, the wood industry for drying and processing particle board, etc., and in industries which use microwaves to dry inks and films. Of course, there is the ubiquitous microwave oven in which organic matter is processed by the strong coupling of microwaves to waters and hydroxyl groups. Also, questions remain with respect to the quality of microwave measurements, since field strengths are difficult to measure.

The lack of interest in materials processing by microwaves is partly due to high capital equipment costs and by the low loss factors for most materials of interest. We believe that one result of this study is that a coherent, directed program in this area can have a high payoff, and more than likely will have such a payoff.

The reasons for this optimistic assessment can be derived from the conclusions which we have drawn from this report. These include:

- (1) Modern techniques of materials preparation have created a number of ways in which loss mechanisms can be systematically enhanced. These methods include the substitution of polar for non-polar compounds, controlling the degree of disorder, controlling the pressure and temperature, using fillers, additives, inhibitors, or catalysts, and selectively doping (e.g., ion implantation).
- (2) The use of microprocessor controlled processing is particularly amenable to microwave materials processing. Consequently, as industry progresses further into robotics and intelligent processing, and energy costs continue to grow, microwave processing of materials will become more attractive to those industries in which the materials coupling problems have been overcome.

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- (3) Likewise, even in industries where microwave processing is presently used, e.g., wood processing, microwave use should increase due to the economic advantages.
- (4) The use of dual mode microwave couplers in which one mode processes the material and the other mode acts as a control device presents interesting possibilities.
- (5) Another driving force for utilizing microwave processing of materials is the increasing use of composite materials and adhesives in the defense and commercial sectors. Microwave processing will increase the quality of the finished product and, as in (3) above, increase throughput, etc.. With this increasing use of adhesives and composites, goes the requirement of effectively repairing these materials in the field environment.

In summary, it would appear as if the time is right to conduct a coherent, directed program to study and demonstrate the feasibility of processing materials using microwaves. In support of such a program and consistent with the results and conclusions of this report, the following recommendations are made:

- (1) An analysis should be made of the various coupling theories of electromagnetic radiation to solids. Even though a great deal of work was done in this area through the 1950's, a new effort is appropriate. The rationale for this effort is twofold. First, on the experimental side, the preparation of materials and the measurement of their dielectric properties has reached a level unavailable in the 1950's. Thus, it should be possible to produce measurements on designed materials to verify theories and to provide accurate dielectric properties. Second, solid state theory has grown dramatically in the past twenty years. Significant work has been done on disordered materials, polymers, and ferroelectrics. The techniques of many-body physics have been applied to these materials, and the use of renormalization group theory and high speed computers has gained

new insight into materials properties. There has also been a great deal of work done on electromagnetic scattering and absorption by particulates, and the classified RAM work. In addition, only recently have well characterized field measurements been done in conjunction with coupling experiments.

- (2) An experimental and modeling study should be made of parameters which enhance microwave coupling to adhesives. A common adhesive which is used in fiber reinforced plastics (FRP) should be chosen, say a polyester. Controlled studies should be undertaken and analyzed to determine how changing parameters affects microwave coupling and the subsequent adhesive cure. Levels and varieties of dopants should be varied, pressure and temperature varied, degree of disorder varied, etc.
- (3) An experimental and modeling study should be made of parameters which enhance microwave coupling to FRP using the inputs gained from adhesive curing, and using the same polymer for the matrix material. In this case chopped fiber, and 1-, 2-, and 3-dimensional lay-ups can be used for a chosen fiber. The effect of the fiber can be sorted out from the matrix, and leverage determined for enhancing coupling.
- (4) An analysis should be made of microwave structures to enhance the coupling of microwaves to materials. Efforts should be made to minimize microwave leakage for safety and efficiency reasons. Studies and experiments should be undertaken to determine the optimum coupling structure for the materials used in (2) and (3) above. The possibility of using the microwave structure simultaneously as a control device and a processing device should be looked into.
- (5) Underlying the work of (2)-(4) should be the eventual possibility of using this process in a field environment. Thus studies of adhesives, composites and microwave structures should consider problems of portability, reproducibility, simplicity and adverse environments.

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- (6) An experimental and modeling study should be made of leveraging which may arise from microwave induced chemical reactions. Can harmful reactions be avoided in materials processing, and can helpful reactions be utilized.
- (7) Finally, an effort should be made to integrate microwave processing of materials, say FRP, into a unified intelligent materials processing system. This would be a demonstration study to facilitate the application of the knowledge gained from this program.

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