polymer review

Dielectric properties of polymers at microwave frequencies: a review

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A review of the dielectric loss spectra of polymers at microwave frequencies has been carried out. While the main focus of attention is the frequency range from 100 MHz to 100 GHz, loss spectra outside this region are also reviewed because variations in temperature can cause a shift of dielectric loss into or out of the microwave range. A large volume of data for low loss polymers (polyethylene, polypropylene and poly(tetrafluoroethylene)), which are used in the communications industry, was available for review. Other polymers, for which data were available and which have significant loss at microwave frequencies are: polystyrene, poly(vinylchloride), poly(vinylidene chloride), poly(vinylidene fluoride), poly(methylmethacrylate), poly(methyl acrylate), poly(oxymethylene), poly(ethylene oxide), poly(propylene oxide), polyacetylene, and poly(sulphur nitride). Also, the microwave dielectric properties of engineering thermoplastics such as poly(phenylene oxide), polycarbonate and polysulphane have been reviewed. The origins of microwave dielectric loss in polymers are categorized as: (a) dipolar absorption dispersions in both crystalline and amorphous polymers; (b) dipolar losses due to impurities, additives or fillers in a polymer material; (c) microwave absorption in conducting polymers (polyacetylene and poly(sulphur nitride)) for which the current carriers are electrons; and (d) photon–phonon absorption spectra corresponding to the density of states in amorphous regions of a polymer material.

(Keywords: dielectric constant; dielectric loss; microwave absorption; microwave frequencies; polymers)

INTRODUCTION

In the past fifty years, measurements of complex dielectric constants have been used to study electrical properties and to elucidate the molecular dynamics of polar and nonpolar polymeric materials. Until recently most of these studies were carried out in the conveniently accessible audio frequency range with only a small fraction above 100 MHz. Today, the situation is changing because good microwave dielectric data is necessary in order to meet the demands of technological developments. Also, in the past decade, advances in instrumentation, particularly at mm wavelengths, have made measurements more accurate and more convenient.

The subject of this review is dielectric properties of polymers in the range of frequencies which is approximately bounded by 100 MHz to 100 GHz. Relaxation dispersions which occur in technologically important polymers and polymer composites usually appear at lower frequencies at room temperature. There are some exceptions to this such as poly(tetrafluoroethylene) which has a small dispersion at 10^9 Hz at room temperature. For most polymers the dielectric loss at microwave frequencies consists of background loss or the high and low frequency tails of losses which occur outside this region. For example, the low frequency tail of losses due to phonon absorption in the far infra-red can contribute to the loss, also, the high frequency tail of relaxation dispersions, which are associated with motion of polar segments of the polymer chain, extend into the microwave region. Since the losses which are observed at microwave frequencies often have their origins outside this region, we found that it was not possible to isolate our attention to the few decades of microwave frequencies.

The temperature of the material must also be considered because the loss spectra change in shape and position on the frequency scale with a change in temperature. Loss maxima can be displaced into or out of the microwave frequency range with a change in temperature. These effects are discussed below.

For the most part we will present the dielectric loss spectra as ε'' vs. frequency or tan δ vs. frequency where ε'' is the imaginary part of the complex dielectric constant, $\varepsilon^* = \varepsilon' - j\varepsilon''$ and $\tan\delta = \varepsilon''/\varepsilon'$. The real part ε' will not be the focus of our attention but, when appropriate, we will refer to it. In some cases, data will be presented with temperature as the independent variable.

SOURCES OF DATA

The appropriate bibliography was accumulated from various journals, books and reports. Computer searches of various abstracting services were helpful but these were not used exclusively. We found that the information was distributed over a large number of different journals and report sources and was not confined to the polymer literature. During our searches we focused our attention on data for polymers, copolymers and epoxies.

The largest single source of data has been reports from the MIT Insulation Laboratory. These data consist of dielectric measurements on commercially available polymer materials and composites as a function of frequency, temperature and (in some cases) humidity. The data, which extend in frequency up to 10 or 24 GHz, have

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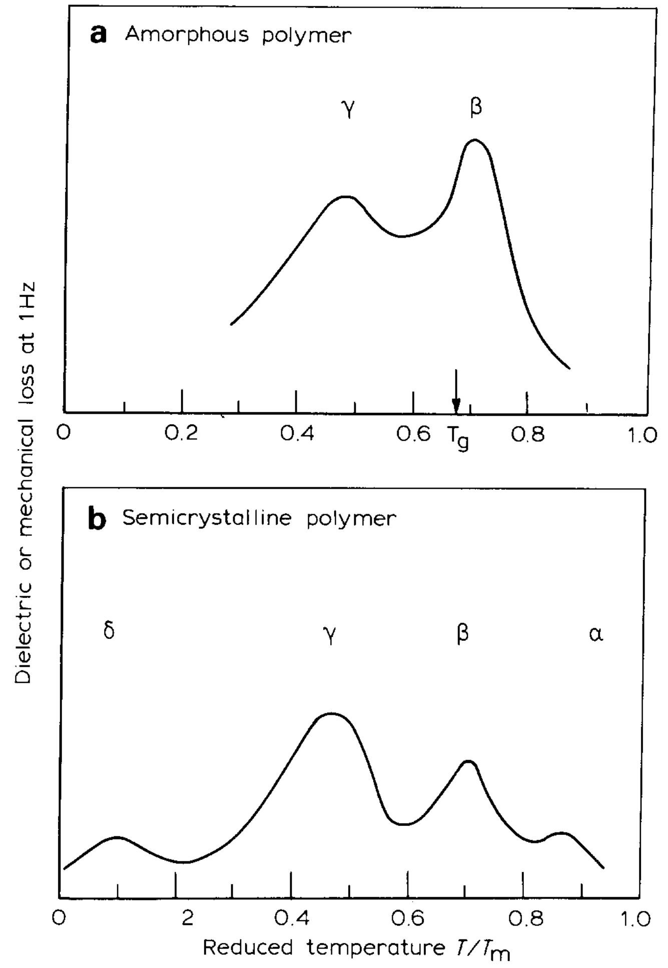


Figure 1 Approximate positions of dielectric or mechanical loss at 1 Hz are shown on a reduced temperature plot, T/T_m, where T_m is melting point temperature, for a linear polymer molecule. T_g is the glass transition temperature

been taken over a period of many years beginning in the 1940's up to the present under the direction of Von Hippel and Westphal[1–8]. Unfortunately, these data are presented without discussion or interpretation. In their reports, the preparation and characterization of the samples are not given although their commercial source is usually stated. The MIT reports are a good source of raw data which should be used together with data and interpretation from other sources if they are available.

The most useful and informative dielectric data are those which extend over a range of frequencies and/or temperatures. Interpretation of the data usually requires information from a wide frequency range along with other materials data such as melting point and glass transition temperature. Because of the experimental difficulties which are encountered working at microwave frequencies, much of the published microwave data consists of loss measurements at one or two frequencies. These data are not very useful unless they are taken together with other measurements.

Below, we present a review of data in two categories: first, for data in the range $f < 100$ GHz; and second, for $f > 100$ GHz. The first category will cover the microwave region and the second will cover the far infra-red frequencies for some technologically important polymers. A complementary bibliography of absorption data on polymers and other materials at millimetre and far infra-red frequencies has been compiled by Simonis[9].

DATA FOR $f < 100$ GHz

Before assembling the data for specific polymers we will present an overall spectral view of the dielectric loss which is observed in polar linear polymers. For both semi-crystalline and amorphous polymers the spectra are broadly outlined in *Figure 1* where tan δ vs. temperature at constant frequency is schematically drawn. In this plot, the spectra are displayed using temperature as the independent variable and the nomenclature is in accordance with Hoffman, Williams and Passaglia[10]. The relationship between temperature and frequency is such that the lowest temperature loss peak will occur at the highest frequency. For a semi-crystalline polymer the spectrum has an α peak close to T_m (the melting temperature), a β peak immediately above T_g (the glass transition temperature), and a γ peak below T_g. A δ peak at lower temperatures has also been observed. For an amphorous polymer, the α peak is absent, and the β and γ peaks occur above and below T_g. Designating the β peak as that which occurs above T_g aligns the nomenclature being used for both crystalline and noncrystalline polymers.

When the temperature and frequency data of the loss peaks are plotted on a $\log f_{max}$ vs. $1/T$ plot, a mapping of the position of the loss peaks is seen such as that for poly(vinylidene fluoride) shown in *Figure 2*. Such a plot can be used to ascertain the potential for a polymer to have a loss peak at microwave frequencies for a given range of temperatures. It should be noted that, for all dispersions, f_{max} moves to higher frequencies as the temperature increases.

An ongoing problem concerning polymer materials is the variation in materials properties and molecular conformations for the same polymer as it is processed by different manufacturers or even by the same manufacturer. Materials parameters such as molecular weight, crystallinity, branching, end group content, polar impurities and antioxidant additives can affect the dielectric loss. Usually, differences seen in the loss for the same polymer are differences in magnitude with the loss peaks occuring at approximately the same frequencies. However, it is also possible that a loss peak observed in one

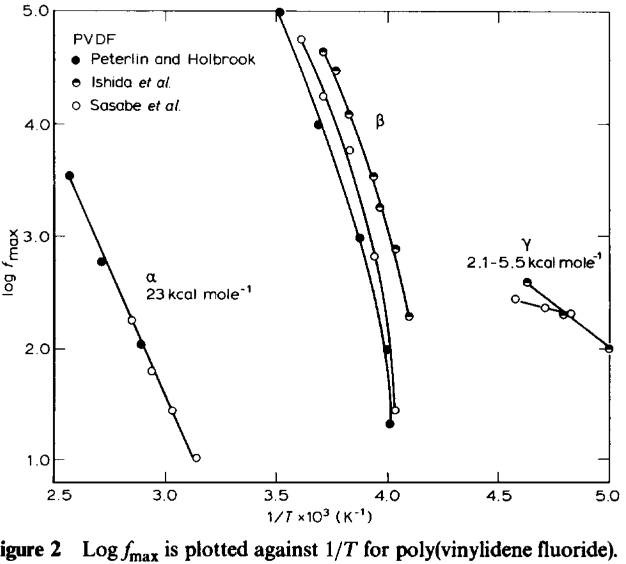


Figure 2 $\log f_{max}$ is plotted against $1/T$ for poly(vinylidene fluoride). Here, f_{max} is the frequency of maximum dielectric loss. The data are from Peterlin, A. and Holbrook, J. D. *Kolloid Z.* 1965, **203**, 68; Sasabe, H. *et al. J. Polym. Sci.* 1969, 7, 1405; and Ishida, Y. *et al. Kolloid Z.* 1964, **200**, 48. (Reproduced from Bur, A. J., ref. 46, by permission of John Wiley and Sons, New York, NY)

sample will not be present in a sample from another source because of the differences in polar impurities or the nature of the catalyst and/or antioxidant which were used. Whenever possible we will point out these differences and the source of the measured samples.

Homopolymers

In this section we will review published data for a number of homopolymers. Polyethylene, polypropylene, polystyrene, poly(tetrafluoroethylene and poly(vinyl chloride) have been examined thoroughly because of their potential use as low loss dielectrics for wiring and communication cables. Tan δ for these polymers is less than 10^{-3} at microwave frequencies, an exception being poly(vinyl chloride) for which it is less than 10^{-2}.

Polymers with high losses at microwaves such as polyacetylene, poly(vinylidene fluoride), poly(methylmethacrylate) and poly(oxymethylene), have received less attention because of the absence of a commercial application as dielectric materials at microwave frequencies. The available data for these polymers are reviewed below.

Polyethylene (*PE*). Ideally, polyethylene is a nonpolar polymer whose main chain is a simple hydrocarbon, $(\text{-}CH_2CH_2\text{-})_n$. It is a semicrystalline with a melting temperature of approximately 130°C. The origin of dielectric loss in PE is dipolar impurities, end groups, chain folds and branch points. The lower the concentration of these groups, the lower will be the dielectric loss.

Dielectric measurements, carried out over a reasonably wide frequency range, have been made by Buckingham and Reddish[11], Ayers[12], Buckingham and Belling[13], and by MIT[1]. Data of ref. 11 are shown in the graph of *Figure 3* where δ is plotted vs. log frequency at room temperature. The data show that a small dispersion is present at approximately 10^9 Hz. This is the γ peak, which, for 1 kHz dielectric measurements[16], is seen at -102°C and shifts to 7×10^8 Hz as the temperature increases to room temperature. It is also dependent on density with the higher density (or crystallinity) having the lower loss.

The use of polyethylene by the communications industry as the dielectric in submarine cables has encouraged investigations of the causes of losses at microwaves. In particular, the effects of water[12-14] oxidation[16-18] and polymerization synthesis[13] have been studied.

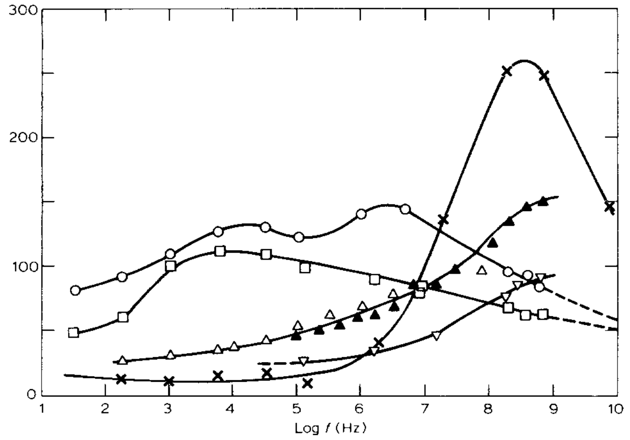


Figure 3 Loss angle vs. log f is plotted at room temperature for several polymers: □, polypropylene; △▲, polyethylene, $\rho=0.923$ g cm^{-3}; ▽, polyethylene, $\rho=0.934$ g cm^{-3}; ×, poly(tetrafluoroethylene); and ○, polyethylene/polypropylene copolymer. (Reproduced from Buckingham, K. A. and Reddish, W., ref. 11, by permission of the Institution of Electrical Engineers, Stevenage, England)

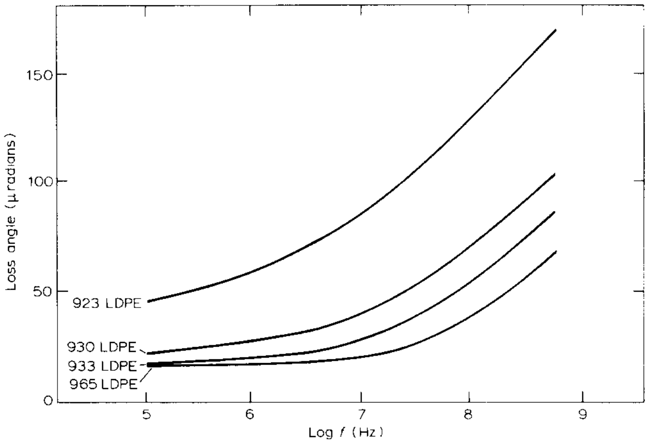


Figure 4 Loss angle vs. log f for low and high density polyethylene (LDPE and HDPE) at room temperature. Numbers refer to density, e.g. 923 is 0.923 g cm^{-3}. (Reproduced from Buckingham, K. A. and Belling, J. W., ref. 13, by permission of the Institution of Electrical Engineers, Stevenage, England)

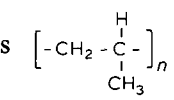
Microdroplets of water in PE cause an increase in the loss in proportion to the amount of water absorbed by the polymer[12-14]. A dispersion with $\tan\delta=1.50\times10^{-4}$ is observed at 10 MHz for water content of 192 ppm[12]. The origin of the loss is considered to be a Maxwell–Wagner dispersion which occurs because of the motion of impurity ions in microdroplets of water[14].

The effect of oxidation on the microwave behaviour of PE can be seen in the data of Jackson and Forsyth[18]. In their experiments, PE samples were subjected to milling and measured at various time intervals during the milling process. A loss peak at 10^8 Hz (room temperature) increased with time of milling and is presumably due to oxidation. Other dielectric measurements on oxidized PE have been carried out at audio frequencies and low temperature by Ashcraft and Boyd[16] and by Mikhailov and coworkers[17]. If the low temperature γ peak, seen in these data at -105°C (1 kHz), is extrapolated to room temperature using the activation energy of Ashcraft and Boyd[16], then the peak will occur near 10^9 Hz. Both the shifted data and the data of Buckingham and Reddish[11] show the γ dispersion at a somewhat higher frequency than the data of Jackson and Forsyth.

Buckingham and Belling[13] have contributed significantly to this field in an extensive examination of dielectric losses up to 660 MHz for several types of PE, polypropylene (PP) and copolymers of the two. Their study included samples of high and low density PE and samples polymerized by different techniques. The data are summarized in *Figure 4* which shows losses for low and high density PE increasing with frequency up to 660 MHz. We note that the level of loss in PE is lower in *Figure 4* than in *Figure 3*. The more recent data of Buckingham and Belling benefit from improvements in polymerization and processing techniques which have yielded PE with fewer dipolar impurities and lower background loss. The dispersion at 10^9 Hz is an inherent property of PE and is attributed to localized dipolar motion in the amorphous phase[16].

Other microwave data for PE, which are limited in spectral range, have been published in refs. 15 and 19 through 23.

Polypropylene (*PP*). Polypropylene is a slightly polar semicrystalline polymer with a melting temperature of 170°C. Its main chain can be represented as

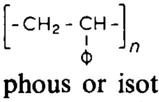


$[-CH_2-C(H)(CH_3)-]_n$

Dielectric measurements at microwave frequencies have been carried out by Buckingham and Reddish[11], by Buckingham and Belling[13] and by Sazhin and coworkers[24]. The data, presented in *Figures 3* and *5*, show that there is a low background loss at 10^8–10^9 Hz. This can be interpreted as a dispersion with a very broad distribution of relaxation times which merges with the 10^4 Hz dispersion, the latter being the β or glass transition loss peak in PP($T_g \approx 0$°C). Thus, this broad ill-defined loss at 10^8–10^9 Hz is probably the γ loss peak which has been observed in dynamic mechanical measurements at −90°C (1 Hz)[25]. The mechanical data, taken at constant frequency with temperature as the independent variable, also show a very broad distribution as reflected on the temperature scale. Dielectric data taken in this laboratory by Mopsik at audio frequencies as a function of temperature display such a broadly distributed character for this dispersion that it is not possible to obtain an activation energy and to carry out an extrapolation of the dispersion peak to microwave frequencies at a higher temperature[26].

Also, shown in *Figure 5* are the data for a copolymer of PE and PP containing only a few per cent of PE. The copolymer was made for the purpose of improving the processing characteristics as were required for extrusion into a submarine cable dielectric[13]. Its dielectric properties are nearly the same as the PP homopolymer with the loss tangent above 10^8 Hz being less than 10^{-4}.

Polystyrene (*PS*). This polymer, which is considered to be 'nonpolar', does in fact possess a small dipole moment (0.26D) due to the asymmetry at the phenyl side group[27],



$[-CH_2-CH(\Phi)-]_n$

. Polystyrene can be made as atactic amorphous or isotactic semicrystalline with $T_g = 110$°C. The microwave data in the literature have been obtained using atactic PS at temperatures less than T_g. Referring to *Figure 1*, we note that, for $T < T_g$, amorphous PS will have only γ and δ dispersions. β cannot occur for $T < T_g$, because the main chain of the polymer molecule will be locked into the glassy state.

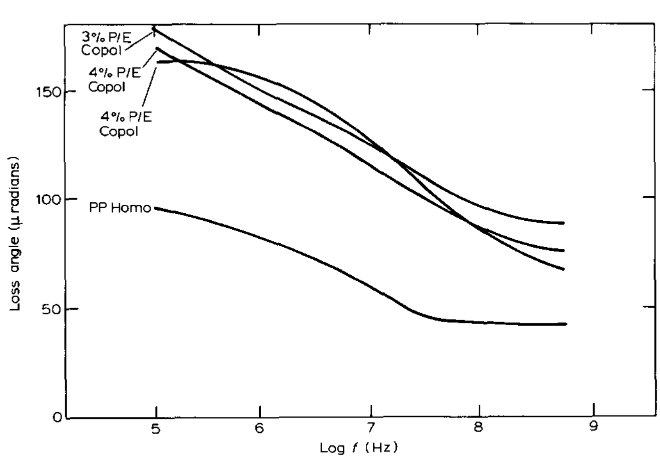


Figure 5 Loss angle vs. log *f* for polypropylene (PP Homo) and propylene/ethylene copolymers at room temperature, where the percentages indicate the amount of ethylene in the copolymer. (Reproduced from Buckingham, K. A. and Belling, J. W., ref. 13, by permission of the Institution of Electrical Engineers, Stevenage, England)

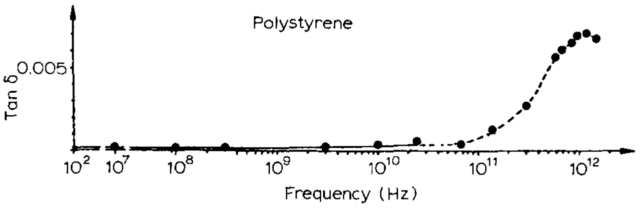


Figure 6 Loss tangent vs. log *f* is plotted for polystyrene at room temperature. (Reproduced from Amrhein, E. M., ref. 28, by permission of Dr Dietrich Steinkopff Verlag, Darmstadt, W. Germany)

In *Figure 6*, the dielectric frequency spectrum for PS at room temperature, as taken from Amrhein, is presented[28]. The loss tangent is seen to be constant and relatively small ($< 10^{-4}$) over a very broad frequency range from subaudio to 10^{10} Hz. A loss peak occurs at 10^{12} Hz, a very high frequency for a relaxation dispersion; it appears to be the γ peak which has been measured by McCammon *et al.* at −227°C (1 kHz) with an activation energy of 3.3 ± 1 kcal mole^{-1}.[29] Using 2.3 kcal mole^{-1}, this dispersion extrapolates to 10^{12} Hz at room temperature. McCammon and coworkers also measured the low temperature dielectric properties of chlorine substituted polystyrenes[29]. These have loss intensities which are 4 to 5 times higher than that for polystyrene and also extrapolate to microwave frequencies at room temperature.

Other dielectric measurements on PS at microwave frequencies have been made by MIT[1] and by Breeden and Sheppard[30].

Styrene copolymers. Styrene can be copolymerized with other monomers to produce commercially important materials such as styrene–butadiene rubber (SBR), acrylonitrile–butadiene–styrene terpolymer (ABS) and styrene–acrylonitrile copolymer (SAN). These polymers have desirable mechanical properties and are used extensively in the building, packaging and automotive industries. They have not been used in situations which place demands upon their microwave dielectric properties. Considering that the acrylonitrile monomer has a large dipole moment due to the CN bond, we would expect a correspondingly large dielectric loss. Measurements by MIT[1] on acrylonitrile–butadiene copolymer show a maximum tan δ of 0.016 at 10 MHz at 25°C which shifts to 100 MHz at 80°C.

Poly(tetrafluoroethylene) (*PTFE*). PTFE is a nonpolar polymer whose main chain is $[CF_2\text{–}CF_2\text{–}]_n$. Dielectric properties for a 60% crystalline sample, shown in *Figure 3*, have been measured by Buckingham and Reddish[11]. For $f < 10^4$ Hz, it has one of the lowest dielectric losses for any polymer, tan $\delta < 10 \times 10^{-6}$. For higher frequencies, PTFE has a dispersion which peaks at 200 MHz at room temperature with $\delta_{max} = 250 \times 10^{-6}$ radians, still a relatively low loss. This dispersion disappears for a sample of high crystallinity (93%) indicating that the dipole associated with this loss is either end groups or loosely packed crystal fold surfaces[11].

Poly(vinyl chloride) (*PVC*). PVC is a mostly amorphous, polar polymer whose main chain is $[\text{–}CH_2\text{–}CHCl\text{–}]_n$. Its properties, both mechanical and dielectric are dominated by the amorphous phase which has a glass transition at 95°C. The dielectric properties of PVC in both the rigid and plasticized forms have been studied by many workers. Audio frequency measurements on rigid PVC were measured many years ago by Fuoss[31], Dyson[32] and by Ishida[33]. Plasticized PVC, which has many commercial applications, has been measured often, notably by Fuoss[31,34], Fitzgerald and Miller[35] and by Saito[36]. Microwave measurements on rigid PVC are summarized by Amrhein[28]. Also, PVC and its plasticized derivatives have been measured at microwave frequencies by MIT[1].

These data show that, for rigid PVC at room temperature, the γ dispersion occurs at 10 kHz with tan $\delta = 0.028$; the loss falls off to tan $\delta = 0.005$ at 10^{10} Hz. According to Ishida[33], the γ peak would not move into the microwave range even if the temperature were increased to 90°C which is approximately the glass transition temperature. Above 10^{11} Hz Amrhein reports an increase in tan δ to 0.02. This loss, shown in *Figure 7*, has not been resolved into a peak and its molecular origin is not known.

Considerable latitude in the position of the β (glass) peak on the frequency scale can be achieved through the incorporation of plasticizer in PVC. For example, the addition of 20% diphenyl, which is nonpolar, will lower T_g to approximately 20°C[34]. There is a corresponding shift of the β dispersion to lower temperatures at constant frequency and a merger between the β and γ dispersions. Raising the temperature of PVC plasticized with nonpolar diphenyl will not yield large microwave absorption.

On the other hand, if a polar plasticizing molecule, such as tricresyl phosphate, is used, then the plasticizing molecule itself will display dielectric loss of its own, most likely at high frequencies and into the microwave region. In this case PVC is a matrix into which the microwave absorbing molecule is incorporated. Such effects have been observed by Wurstlin[37] and a review of the effects of plasticizer on the dielectric properties of PVC has been made by Curtis[38].

The spectrum for PVC at audio frequencies is shown in *Figure 8* where the data of Ishida are shown[33]. We note that the magnitude of the β dispersion is several times larger than that of the γ loss peak. This is typical of the case for which the principal dipole moment of the molecule is incorporated into the main chain. Such is the case for PVC whose main chain contains the CHCl group which is strongly dipolar because of the chlorine substituents on alternate carbon atoms. Since the β dispersion is associated with micro-Brownian motion of the main chain at temperatures above T_g, the main chain dipoles will absorb dielectrically in accordance with the relaxation time of the main chain motion if $T > T_g$.

Even though PVC does not appear to be a microwave absorber, we have presented these data in order to contrast the molecular and materials characteristics of PVC with other polymers which do absorb at microwave frequencies. PVC, with its high T_g (90°C) and perpendicular main chain dipole moment will have most of its polarization relaxation in the β dispersion above T_g. At lower temperatures the β peak is not seen and the loss peaks which do occur are relatively low in intensity. In order for the β dispersion to be seen at microwave frequencies at room temperature, the glass transition of a polymer should be 10°C or lower. For example, poly(vinylidene chloride) and poly(vinylidene fluoride) which have T_g at -18°C and -50°C respectively do absorb strongly at the low end of the microwave region.

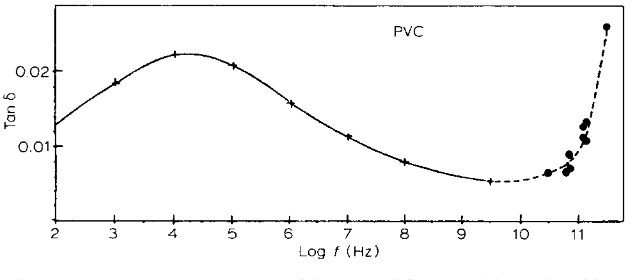


Figure 7 Loss tangent vs. log *f* is plotted for poly(vinyl chloride) at room temperature. (Reproduced from Amrhein, E. M., ref. 28, by permission of Dr Dietrich Steinkopff Verlag, Darmstadt, W. Germany)

Poly(vinylidene chloride). This polymer (PVDC) has two chlorine atoms at alternate carbon atoms along the main chain of the molecule, $[-CH_2CCl_2-]_n$. The change in atomic configuration compared to PVC significantly alters the dipole moment and interchain dynamics so that T_g for PVDC is -18°C compared to 90°C for PVC. At room temperature, dielectric absorption of the β peak occurs at 10^3 Hz and raising the temperature to 50°C moves the dispersion to 10^5 Hz[39]. The addition of 5 or 10% plasticizer significantly shifts the β dispersion to higher frequencies so that, at 50°C, the loss peak occurs at 10^6 Hz with a large loss ($\varepsilon'' = 0.1$) extending into the microwave region[39,40].

These data are presented in *Figures 9* and *10* where the observations of Saito and Nakajima[39] and Ishida *et al.*[40] are plotted. In *Figure 10*, which is a plot of the loci of the frequency at maximum loss *versus* $1/T$, data for plasticized PVDC (10% phenyl glycidyl) are compared with the results for an unplasticized sample. The effect of the plasticizer is to cause a lower T_g and an overall shift of the dielectric spectrum to higher frequencies by 1 or 2 decades.

Poly(vinylidene fluoride) (*PVDF*). PVDF is a semicrystalline polymer with a melting temperature of 171°C and $T_g \approx -50$°C. Its main chain, $[-CH_2CF_2-]_n$, has a large dipole moment which is reflected in a high dielectric constant ($\varepsilon' = 10$ at low frequency) and dispersions with relatively high values of ε''_{max}. Dielectric measurements at microwave frequencies have been published by MIT[5] and Wentink[41]. Other dielectric data, taken as a function of temperature and frequency in the audio range, have been published by many authors[42-45]. A review of some of these data has been published[46]. PVDF has also been the subject of many studies of its piezoelectric and pyroelectric activity. Piezoelectric thickness resonances of thin films (30 μm thick) have been observed by Schewe at approximately 41 MHz[47].

Wentink's room temperature data are shown in *Figure 11*. The loss peak at 10^7 Hz is the β dispersion whose molecular origin is micro-Brownian motion of the main chain in the amorphous regions of the polymer and is associated with glass transition. Rapid main chain dynamics with 10^{-8} s relaxation time are possible because T_g is well below room temperature. We note that the magnitude of $\varepsilon''_{max} = 1.1$ and $\tan\delta_{max} = 0.22$. This is a relatively high value of loss when compared to polymeric dispersions of other polymers. Increasing the amount of amorphous phase in the polymer will result in a larger β dispersion loss[43].

In *Figure 2*, the dispersion loci are shown on a log *f* vs. $1/T$ plot. The α, β and γ dispersions occur in accordance with the pattern observed for other semicrystalline polar polymers. PVDF, having a large dipole moment perpendicular to the main chain and having a T_g well below

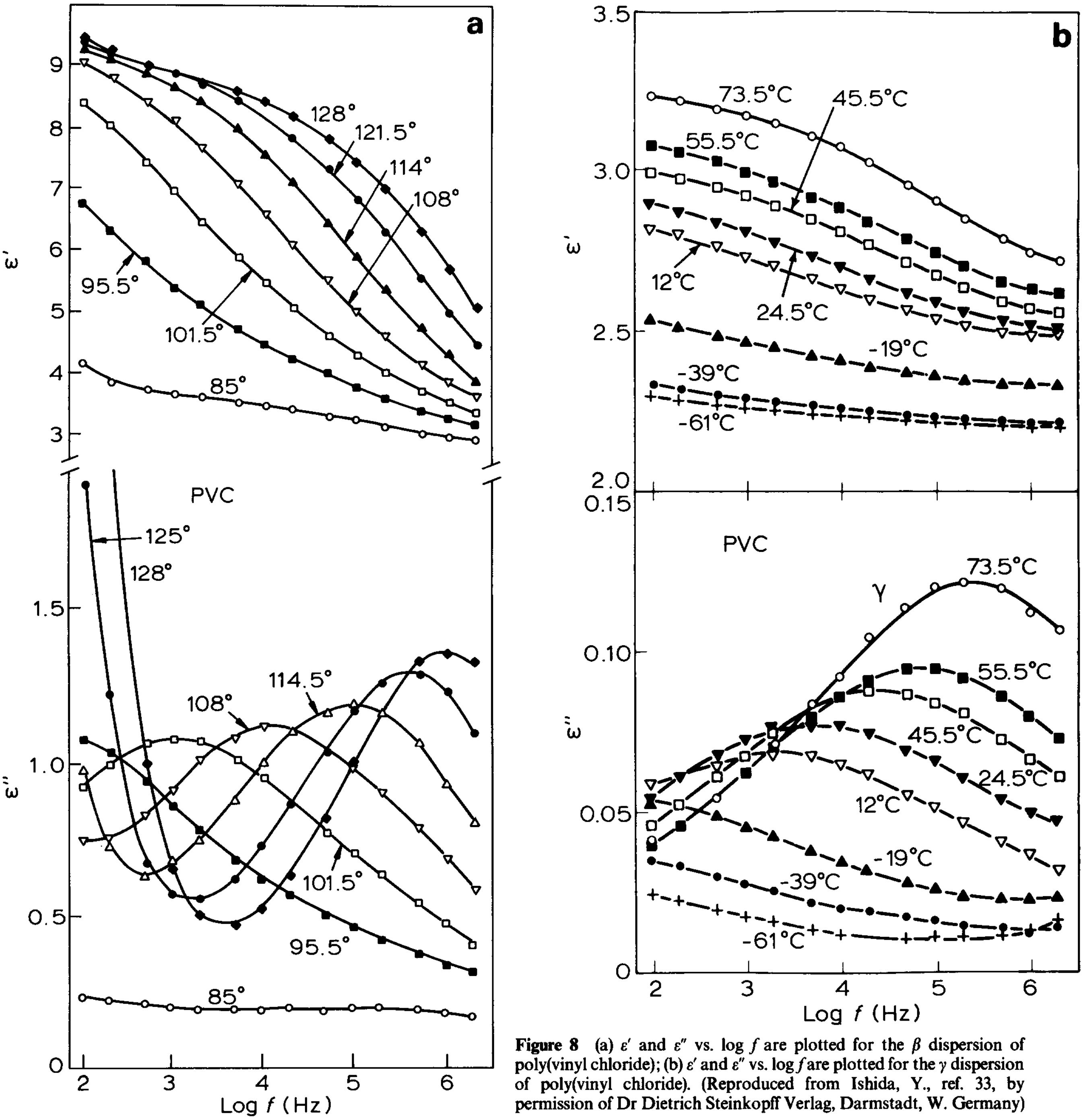
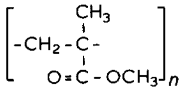


Figure 8 (a) ε' and ε'' vs. log f are plotted for the β dispersion of poly(vinyl chloride); (b) ε' and ε'' vs. log f are plotted for the γ dispersion of poly(vinyl chloride). (Reproduced from Ishida, Y., ref. 33, by permission of Dr Dietrich Steinkopff Verlag, Darmstadt, W. Germany)

room temperature, possess two criteria for displaying large dielectric loss at high frequencies at room temperature.

Poly(methyl methacrylate) (PMMA). Atactic PMMA is an amorphous polymer with $T_g = 105°C$. It can be prepared in syndiotactic or isotactic forms which are crystallizable but the commercial product is the atactic form whose properties we will review. The main chain of the molecule is represented as



$$\left[-CH_2-\overset{CH_3}{\underset{O=C-OCH_3}{C}}- \right]_n$$

The dielectric properties are determined mostly by the strongly dipolar side group, $-COOCH_3$.

Dielectric measurements over a spectrum of frequencies have been made by Broadhurst and Bur[48] and by MIT[1]. Other data, limited in spectral range, have also been published[49–52]. These data, which are shown in *Figure 12*, display two loss regions at room temperature, the γ dispersion at 30 Hz and the δ dispersion at 10^6 Hz. The δ dispersion appears as a shoulder on the larger γ peak and extends into the microwave region. The β dispersion is absent from this room temperature spectrum because $T < T_g$.

The origin of the δ peak has been established by Wada and Yamamoto[53] and by Hendus *et al.*[54] to be caused by absorbed water. PMMA, having hydrophilic ester groups, can absorb up to 2% water. Raising the temperature to 50°C has little effect on the level of microwave loss.

In contrast to poly(vinyl chloride), PMMA has its dominant dipolar group on the side chain rather than on the main chain. In the dielectric loss spectrum, this is reflected in the relative magnitude of the β and γ loss peaks. For PMMA the intensity of the β peak is much less than that of the γ peak and *vice versa* for PVC. The γ dispersion in PMMA, which is associated with local chain motion involving the side chain, is large in intensity but far removed from microwave frequencies at room temperature. Although a direct application of this observation to microwave absorption cannot be achieved with PMMA and PVC, we use this opportunity to point out that, for most polymers, only the β and γ dispersion have the potential for occurring at microwave frequencies if T_g is low enough. Thus, if one desired to have a polymer material with large microwave absorption, then an amorphous polymer with low T_g and with a molecular dipole moment perpendicular to the main chain would probably suffice. In such a polymer the dipole moment would relax with the rubber-to-glass transition of the main chain.

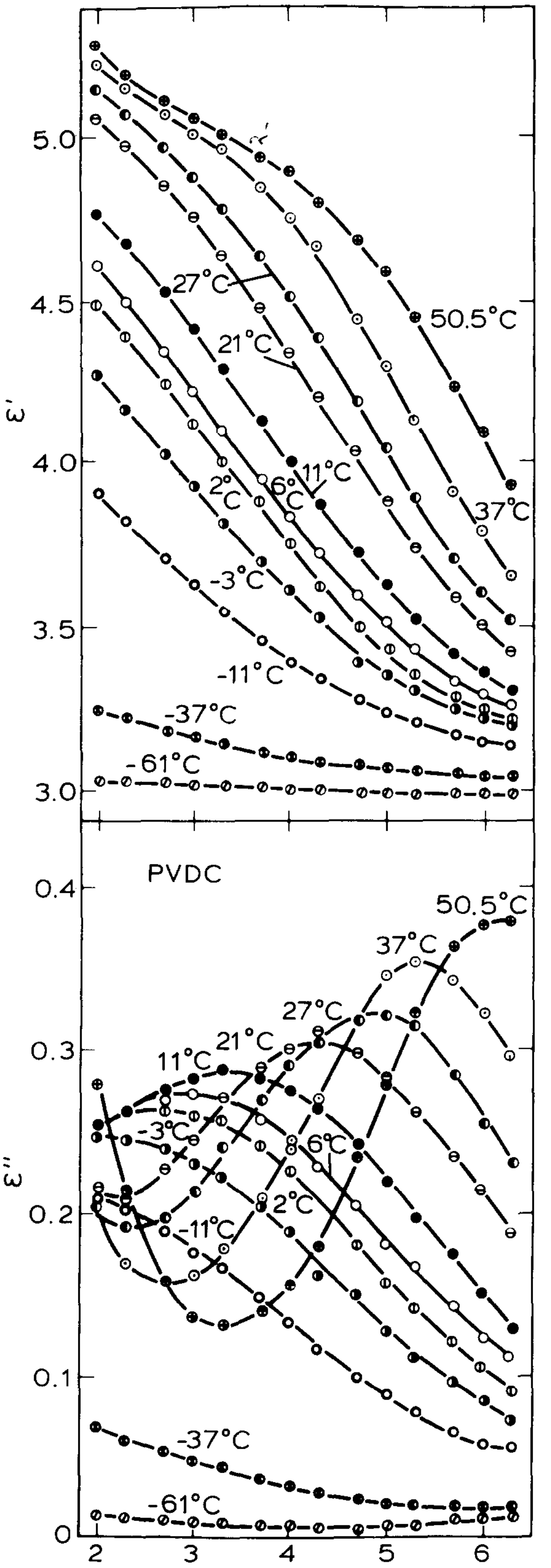


Figure 9 ε' and ε'' vs. $\log f$ are plotted for poly(vinylidene chloride) plasticized with 10% phenyl glycidyl ether. (Reproduced from Ishida, Y. *et al.*, ref. 40, by permission of Dr Dietrich Steinkopff Verlag, Darmstadt, W. Germany)

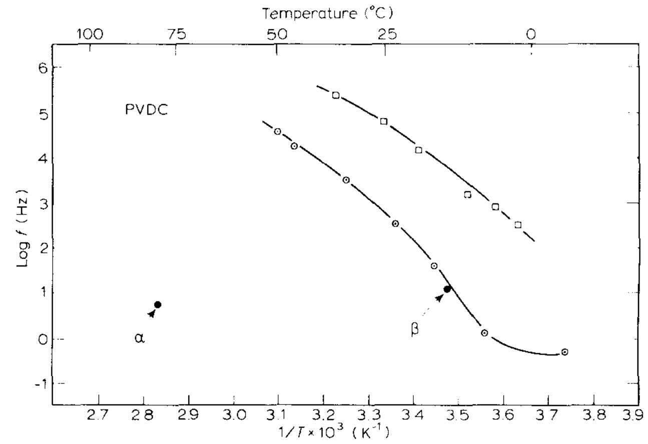


Figure 10 Log f_{max} vs. $1/T$ is plotted for dielectric data (open points) and mehcanical data (closed points) on poly(vinylidene chloride): □, plasticized; ○, ●, unplasticized. (Reproduced from McCrum, N. G., Read, B. and Williams, G., ref. 57, p. 441, by permission of John Wiley and Sons, Chichester, England)

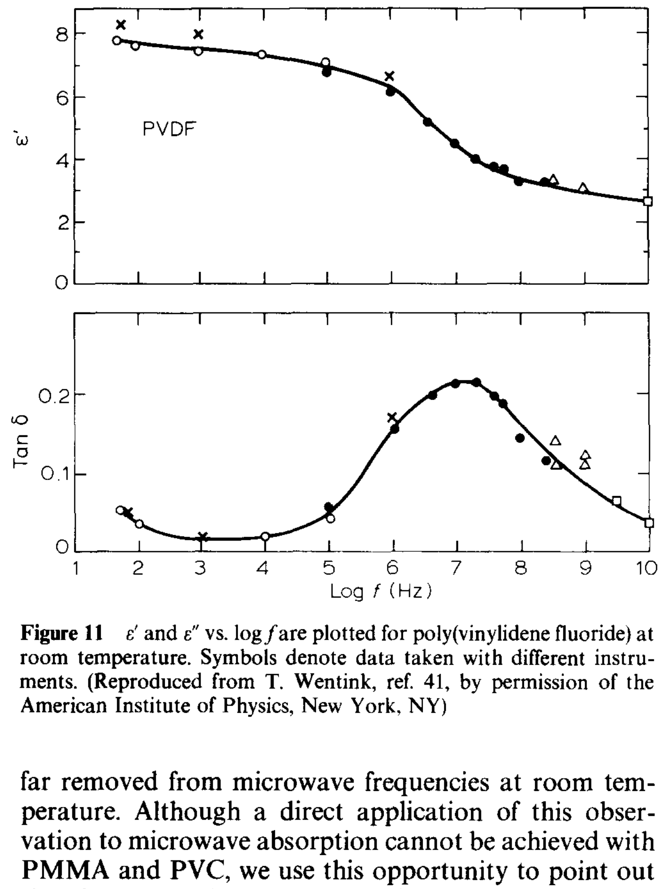
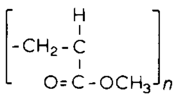


Figure 11 ε' and ε'' vs. $\log f$ are plotted for poly(vinylidene fluoride) at room temperature. Symbols denote data taken with different instruments. (Reproduced from T. Wentink, ref. 41, by permission of the American Institute of Physics, New York, NY)

The relaxation time τ of the PMMA side group is determined by the energy barriers to rotation at the side group site. It is independent of molecular weight and the value of T_g; the later point having been demonstrated by Mihailav *et al.*[55] who plasticized PMMA thereby lowering T_g and observed that the relaxation time of the γ peak remains unchanged. A shorter τ for the local side group motion can be achieved by lowering the energy barrier to rotation. A rearrangement of the atomic grouping in the side chain could accomplish this.

Poly(methyl acrylate) (PMA). PMA has the same side chain but a slightly different main chain as PMMA. For PMA we have



$$\left[-CH_2-\overset{H}{\underset{O=C-OCH_3}{C}}\right]_n$$

where the methyl group on the alternate carbon atoms of the PMMA main chain has been changed to a single H atom. This change greatly alters the steric hindrance to rotation in the main chain allowing a wider conformational range of motion which results in a lower glass transition temperature; $T_g \approx 5°C$ for PMA.

At room temperature the β peak is seen at 10 Hz and the γ relaxation is seen at 10^8 Hz[56]. The loci of these dispersions are shown in the log frequency vs. $1/T$ plot of *Figure 13*. We note that the γ dispersion occurs almost exclusively in the microwave region for the temperature range from 0° to 100°C. Above 100°C, the β and γ processes merge into a single relaxation time indicating that side and main chain motion cooperate as one in order to randomize the orientation of the dipole vector. Another interpretation of this is that the larger motion of the main chain (β process) entirely encompasses that of the local side chain motion. On this plot of log f vs. $1/T$, lines of different slope will not cross but, rather, if they meet, they will merge.

Other methacrylate polymers. An extensive review of the dielectric and mechanical properties of the methacrylates and other polymers has been carried out by McCrum, Read and Williams[57]. Many different polymers have been synthesized by varying the nature of the alkyl group on the side chain. One effect of these chemical alterations is to change the glass transition temperature and correspondingly change the dielectric loss spectrum. Microwave data on these polymers have not been obtained, however.

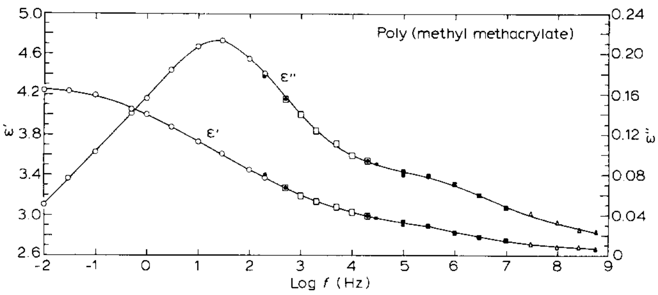


Figure 12 ε' and ε'' vs. log f are plotted for poly(methyl methacrylate) at room temperature. Symbols denote data taken with different instruments. Data of M. G. Broadhurst and A. J. Bur, ref. 48

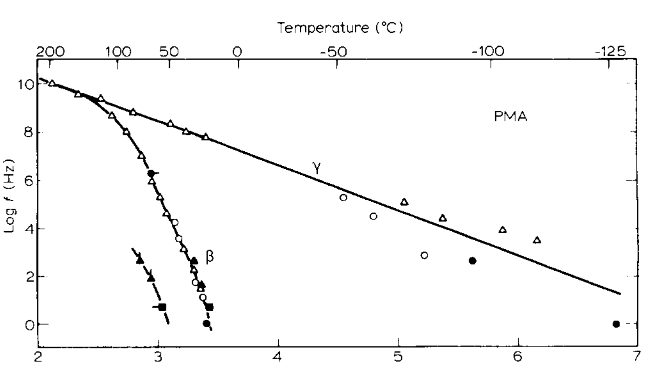


Figure 32 Log f_{max} vs. $1/T$ is plotted for poly(methylacrylate). Open data points are from dielectric data and closed points from mechanical data. (Reproduced from N. G. McCrum *et al.*, ref. 57, p. 289, by permission of John Wiley and Sons, Chichester, England)

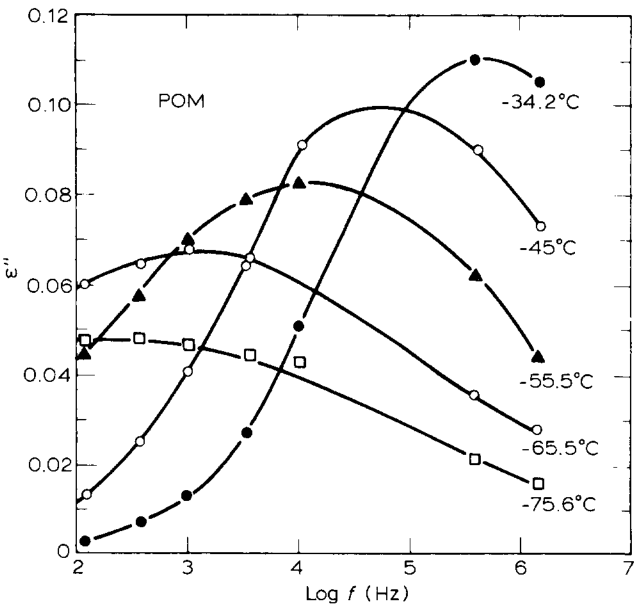


Figure 14 ε'' vs. log f is plotted for polyoxymethylene. (Reproduced from B. Read and G. Williams, ref. 58, by permission of Butterworth Scientific Ltd., Guildford, England)

We note that in the McCrum, Read and William's book[57], the designated α and β dispersions in methacrylate polymers are called β and γ here.

Oxide polymers. These polymers contain an oxygen atom in the main chain along with one or two carbon atoms. Polyoxymethylene, poly(ethylene oxide) and poly(propylene oxide) have been the subject of dielectric experiments at or near microwave frequencies.

Polyoxymethylene (POM). The main chain of this polymer consists of alternating carbon and oxygen atoms, $[-CH_2-O-]_n$. It is a semicrystalline polymer with a melting temperature of 183°C. T_g has been reported to be at $-90°C$[58] and $-25°C$[59]. Such reported differences of the value of T_g for crystalline polymers is not unusual because T_g is difficult to measure when the crystalline phase is dominant. Since most of the macroscopic behaviour of POM is determined by its crystallinity, it is not critical for our purposes that we know the precise value of T_g.

Microwave dielectric measurements on POM have been carried out by Read and Williams[58] and by Thurn[60]. These data are shown in *Figures 14* and *15*, where we note the γ peak is strongly absorbing at microwave frequencies over the temperature range 0° to 100°C. The position of its loss peak, as presented on the log f vs. $1/T$ plot of *Figure 15*, displays a very weak dependence on temperature. In order for this to occur, the activation nergy associated with the dispersion mechanism must be very low.

The γ peak has been shown by McCrum[61] and by Read and Williams[58] to be proportional to the amount of disordered or amorphous phase present in the material. Because POM has no side chain, this dispersion obviously involves a mode of main chain motion. The simplicity of

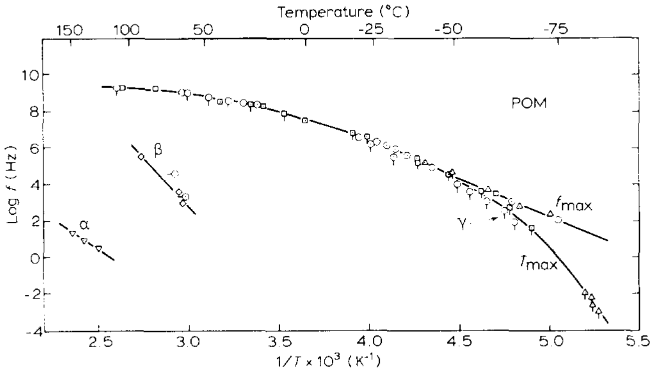


Figure 15 Log f vs. $1/T$ is plotted for polyoxymethylene. (Reproduced from N. G. McCrum *et al.*, ref. 57, p. 543, by permission of John Wiley and Sons, Chichester, England)

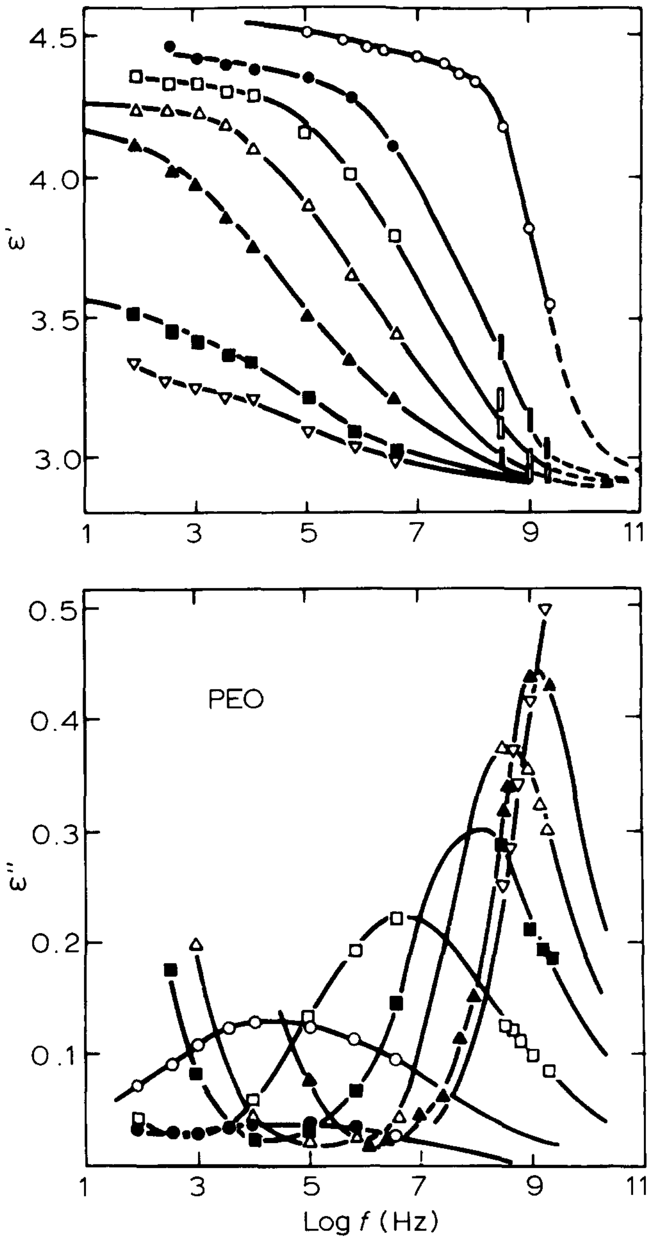


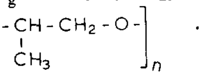
Figure 16 ε' and ε'' vs. log f are plotted for poly(ethylene oxide). For ε', the point symbols refer to temperatures of measurements, ○, 20°C; ▽, −75°C; other symbols for intervening temperatures, −15°C, −30°C, −40°C, −50°C and −60°C. For ε'', the extreme measurement temperatures are: ▽, 35°C and ●, −75°C and the intervening temperatures are: 20°C, 1°C, −16°C, −35°C and −50°C. (Reproduced from T. M. Connor *et al.*, ref. 64, by permission of the Society of Chemical Industry, London, England)

the main chain having only bonded hydrogen atoms at each carbon, minimizes steric hindrance and permits a wide dynamic range of motion. Takayanagi has ascribed the γ dispersion to a localized mode of motion in the main chain[62].

Poly(ethylene oxide) (*PEO*). PEO is a crystalline polymer with a helical main chain whose melting point is 60°C. Its glass transition, as determined from dilatometric studies, is −67°C[63]. The main chain molecule can be represented as $[\text{-CH}_2\text{-CH}_2\text{-O-}]_n$, whose similarity to POM is apparent.

Figures 16 and *17* show dielectric data of Connor, Read and Williams[64]. The loss data of *Figure 16* are for the β dispersion which is attributed to micro-Brownian motion of the main chain at temperatures above T_g. Microwave absorption is seen to occur over the temperature range 0°C to 30°C.

Poly(propylene oxide) (*PPrO*). PPrO is also a crystalline polymer with a melting point at 73°C and $T_g = -75$°C. The main chain sequence is represented as



$$\left[\begin{array}{c}\text{-CH-CH}_2\text{-O-}\\ \text{|}\\ \text{CH}_3\end{array}\right]_n$$

. Dielectric studies of Williams are presented in *Figures 18* and *19* where the β dispersion associated with the glass transition is emphasized[65]. If the log f–$1/T$ curve for the β dispersion is extrapolated to room temperature, the dispersion will occur at microwave frequencies and from *Figure 18* it can be seen that the magnitude of the loss, $\varepsilon''_{max} = 0.7$ or $\tan \delta_{max} = 0.12$, is relatively high.

Other commercial polymers. Dielectric data on commercial polymeric materials, such as nylon, poly(vinyl esters), synthetic rubber, polyurethanes and polyesters were reviewed[1–8,57]. Also, their potential as microwave absorbers was considered by examining their log f vs. $1/T$ plots[57]. We have found that, either the dielectric loss at microwaves was low, or the frequency location plots did not extrapolate loss dispersions to microwave frequencies at room temperature. A widely used polyester, poly(ethylene terephthalate), has $\tan \delta = 0.003$ at 1 GHz at 25°C[66].

Engineering thermoplastics, an important class of

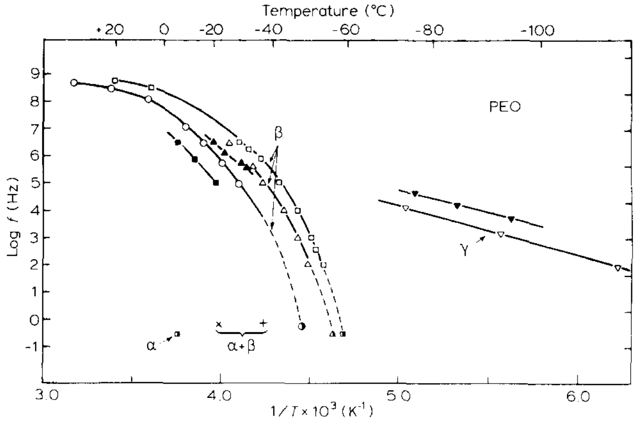


Figure 17 Log f vs. $1/T$ is plotted for poly(ethylene oxide). Data for the β dispersion is from T. M. Connor *et al.*, ref. 64; point symbols refer to sample of different molecular weight: ▲, 4×10^3; □, 3×10^4; ○, 2.8×10^5; △, 8.4×10^5; □, 2.8×10^6. Data for the γ dispersion is from Y. Ishida *et al.*, *J. Polym. Sci. B* 1965, 3, 321, ▼, single crystal mat; ▽, melt crystallized PEO. (Reproduced from N. G. McCrum *et al.*, ref. 57, by permission of John Wiley and Sons, Chichester, England)

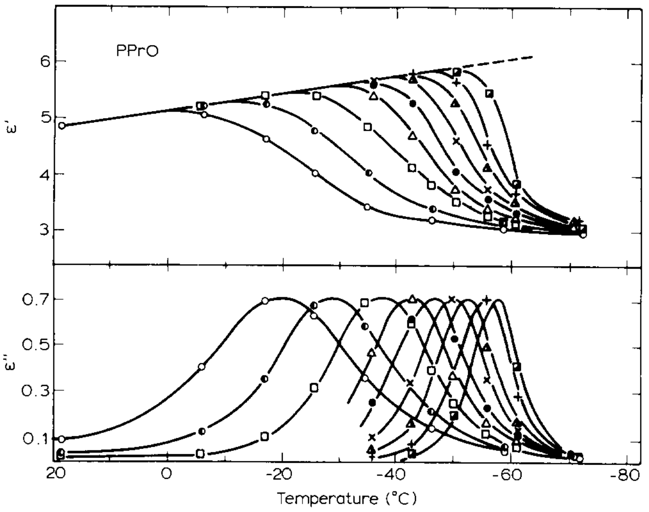


Figure 18 ε′ and ε″ vs. temperature is plotted for poly(propylene oxide) ○, 3.3×10⁶ Hz; ◪, 100 Hz; all other symbols are for intervening frequencies. (Reproduced from G. Williams, ref. 65, by permission of the Royal Society of Chemistry, London, England)

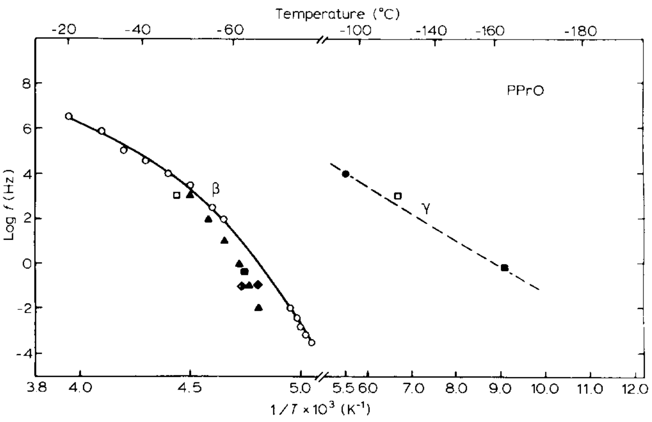


Figure 19 Log f_{max} vs. $1/T$ is plotted for poly(propylene oxide). Open data points are dielectric data and closed data points are mechanical data. (Reproduced from N. G. McCrum *et al.*, ref. 57, p. 573, by permission of John Wiley and Sons, Chichester, England)

commercial materials, are characterized by a glass transition which is much greater than room temperature. In the glassy state, $T < T_g$, they have both desirable mechanical properties, i.e. high modulus and ductile fracture behaviour, and also low dielectric loss. At room temperature (the glassy state), the potential dielectric dispersions are the γ and δ loss regions. Examples of these polymers are: poly(phenylene oxide), $T_g \approx 210°C$; polycarbonate, $T_g \approx 130°C$; polysulphone, $T_g \approx 225°C$; poly(ethersulphone), $T_g \approx 225°C$; and poly(etherimide), $T_g \approx 220°C$. In *Figure 20*, tan δ vs. frequency at 23°C is shown for these five polymers[8,67,68]. The loss peak at 1 MHz, common to four of the polymers, is probably due to a local dipolar motion. The real part of the dielectric constant at 10^9 Hz and 23°C is 2.63 for poly(phenylene oxide)[8], 2.78 for polycarbonate[5], 2.99 for polysulphones[5], and 3.05 for poly(etherimide)[67].

Epoxy resin. The dielectric properties of a common epoxy resin, bisphenol A, have been measured by Westphal and Sils[5]. Their sample consisted of 100 parts by weight of bisphenol A cured with 31 parts by weight of pyromellitic dianhydride. At room temperature and at 10^9 Hz, ε″ = 3.0 and tan δ = 0.015.

Conducting polymers

In this section we will summarize the data taken at microwave frequencies on two polymers: polyacetylene and poly(sulphur nitride). The electrical conductivity of these polymers is high, approaching that of a metal, and it has been shown that the current carriers are electrons.

Polyacetylene $(CH)_x$. Polyacetylene has been the focus of much attention and experimentation for the past several years because it has been demonstrated that doped $(CH)_x$ can have conductivities ranging from insulator to metal depending on the amount and nature of the dopant. The molecule is represented as $[-CH{=}CH-]_n$ where the double bond alternates along the chain. It is presumed that the dynamics of the double bond, switching from one side to the other of the carbon atom, are a feature of the electron conduction.

One characteristic of the conductivity of iodine doped $(CH)_x$ is that it remains constant, independent of frequency from d.c. to microwave frequencies[69], unlike the insulating polymers of the previous section whose conductivity depended on dipolar orientation with very specific temperature dependent relaxation times. For dopant levels higher than 1% the conductivity is independent of temperature over a wide temperature range from liquid nitrogen to room temperature.

Feldblum *et al.* carried out measurements of conductivity at d.c. and microwave frequencies on foamed $(CH)_x$ doped up to 3% with iodine[70]. Their results are shown in *Figure 21* where conductivity for d.c. and microwave frequencies are plotted against the fractional amount of iodine dopant. Also, their measurement of dielectric constant at microwave frequencies is shown in *Figure 22*. It is seen that d.c. and microwave conductivities are the same within experimental error; this same result was obtained by Epstein *et al.*[69]. ε′ is less than 2 as would be expected for a foam material.

Feldblum *et al.* also considered the microwave absorbing properties of this material. With low dielectric constant, reflection would be minimized and absorption is maximized by the high conductivity[70]. They calculated that 90% of microwave radiation could be absorbed by foamed $(CH)_x$ at 35 GHz.

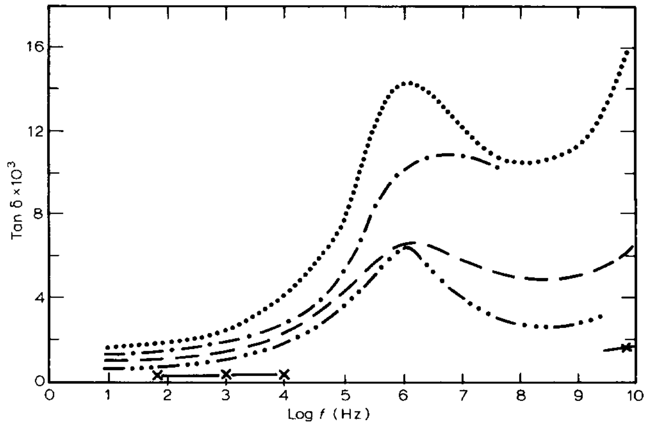


Figure 20 Tan δ vs. log f at 23°C is plotted for five engineering thermoplastics: poly(ether sulphone), polycarbonate, polysulphone, polyetherimide and poly(phenylene oxide). The polyetherimide is Ultem 1000. Ultem is a trademark of the General Electric Co. Data are from refs. 8, 67 and 68. (Reproduced by permission from the General Electric Co., Pittsfield, Mass.). (·····) poly(ethersulphone); (–·–·–) polycarbonate; (–––) polysulphone; (–···–) polyethermide; (×—×) poly(phenylene oxide)

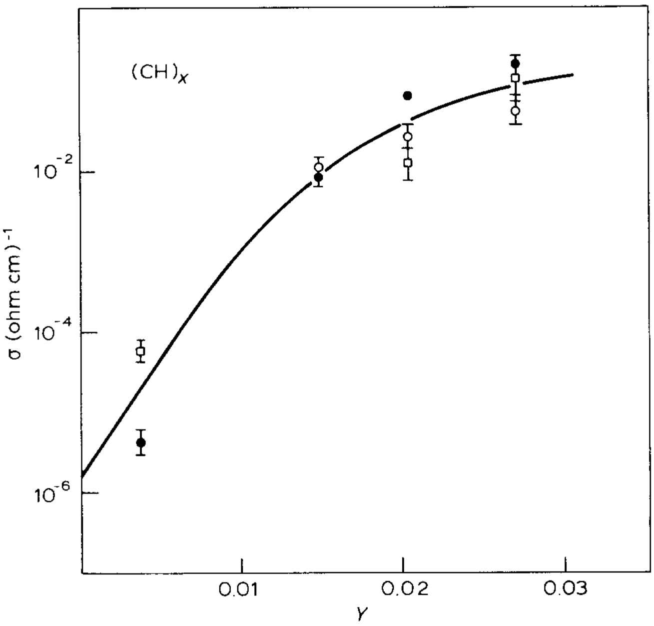


Figure 21 Electrical conductivity σ at room temperature vs. fraction of iodine doping (Y) in polyacetylene is plotted. ○, d.c. four-probe; □, 10 GHz; △, 30 GHz. (Reproduced from A. Feldblum *et al.*, ref. 70, by permission of John Wiley and Sons, New York, NY)

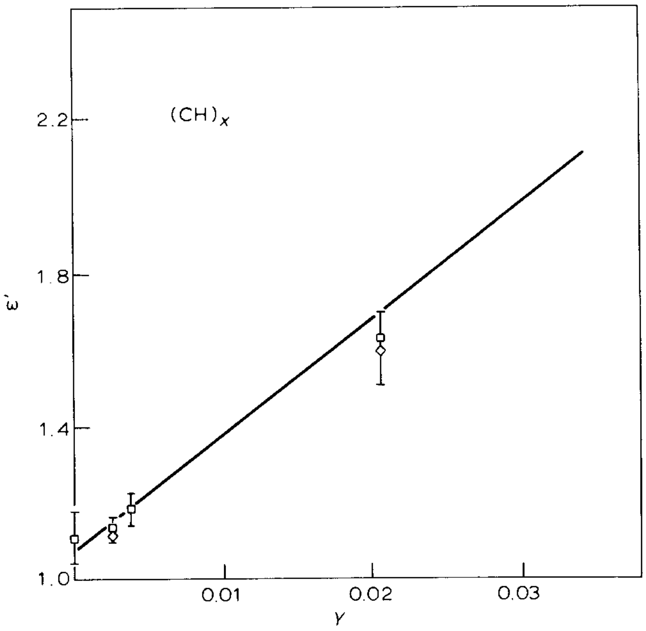


Figure 22 ε' at room temperature vs. fraction of iodine doping (Y) in polyacetylene is plotted. □, 10 GHz; △, 30 GHz. (Reproduced from A. Feldblum *et al.*, ref. 70, by permission of John Wiley and Sons, New York, NY)

Poly(sulphur nitride) $(SN)_x$. As indicated this polymer molecule has a main chain containing alternating sulphur and nitrogen atoms. At low temperatures ($2.5\,K < T < 10\,K$), its conductivity is nearly 10^6 (ohm cm)$^{-1}$ but decreases as $1/T^2$ from 10 K to 300 K[71]. Microwave and d.c. conductivity measurements, carried out by Gill and Harker[71], show that within experimental error these conductivities are the same.

DATA FOR $f > 100$ GHz

We now focus our attention on the frequency range from the upper end of the microwave region to the far infra-red frequencies, i.e. millimetre and submillimetre wavelengths. At these frequencies, polymers usually have dielectric loss which appears as a continuum background with little structure. Two exceptions to this are: polystyrene which has a distinct dielectric relaxation associated with the motion of the phenyl side chain at 10^{12} Hz at room temperature[28]; and high pressure crystallized polyethylene which has a sharp absorption peak at 1.2×10^{12} Hz[72]. These dispersions are in the frequency range 10^{11}–10^{13} Hz which is normally too high for dipolar relaxation loss to occur and too low for isolated single phonon absorption processes.

We distinguish between the behaviour of amorphous and semicrystalline polymers.

Amorphous polymers

Measurements of loss in amorphous polymers at mm wavelengths have been published in a series of papers by Amrhein and coworkers[73–76] and by Strom *et al.*[49]. The main feature of these data is that amorphous polymers (and low molecular weight glasses also) display a continuum of loss in the frequency range 10^{11} to 10^{13} Hz which is an order of magnitude or more higher than losses observed for highly crystalline polymers or low molecular weight inorganic crystals. These losses were observed to be independent of temperature over a wide temperature range.

Both Amrhein and Strom have attributed the loss in amorphous polymers to a continuum of single phonon absorptions which reflects the density of phonon states in this frequency region. In the crystalline state, symmetry at the molecular level would forbid phonon absorption for all but a few optically active modes, but, for the amorphous state, because of the lack of long range translational symmetry, the selection rules cannot be applied. Transition dipoles, created by virtue of the amorphous disorder, permit the absorption of electromagnetic energy. Amrhein views the glass as having 'quasi-lattice modes' which reflect the short range order. These modes of vibration or density of states have been observed in neutron scattering experiments[77,78]. Amrhein has shown the similarity of dielectric loss spectra and the density of state curves for polyoxymethylene[73] and polyethylene[75,76], from which she has concluded that a nearly one-to-one correspondence between density of states and dielectric loss exists. The mechanism of absorption is called 'disorder-induced absorption' which is similar but not identical to 'defect induced absorption' in crystals. Loss data and density of states data are shown in *Figure 23*.

Strom[49] noted the similarity which exists in the loss spectra of nearly all glasses in frequency region 10^{11} to 10^{13} Hz, namely that the conductivity is proportional to ω^2 where ω is the radial frequency. Strom's interpretation of these data is that the absorption is caused by very low frequency Debye modes. For $\omega \ll \omega_{\mathrm{Debye}}$, the Debye phonon density of states is proportional to ω^2 as reflected in the data. This interpretation is essentially in agreement with Amrhein.

The presence of these low frequency phonon modes has been observed in low temperature specific heat[79,80], dielectric[81], and Brillouin scattering measurements[82]. The dielectric loss measurements at low temperature also demonstrate the effect of phonon absorption in glasses in comparison with the much lower loss for the corresponding crystal.

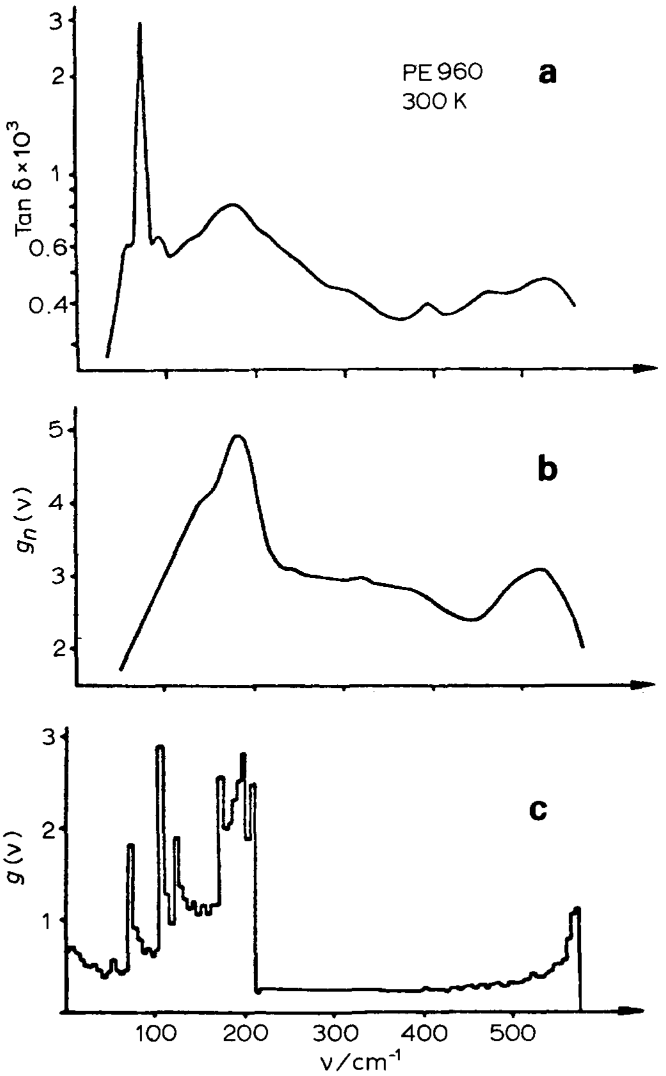


Figure 23 (a) Tan δ vs. wave number (ν) for polyethylene ($\rho = 0.960\,\mathrm{g\,cm^{-3}}$) is shown; (b) neutron inelastic scattering data from W. Meyers *et al.*, ref. 73; (c) a calculated density of states from M. Tascomi and S. Krimm, *J. Chem. Phys.* 1967, **46**, 45. (Reproduced from E. M. Amrhein, ref. 76, by permission of Dr Dietrich Steinkopff Verlag, Darmstadt, W. Germany)

Amrhein also made extensive dielectric measurements on polyethylene as a function of temperature at 75 and 32 GHz[73,83]. Single phonon absorptions are not seen at these frequencies but multiphonon processes, which are temperature dependent, do contribute to the loss.

Semicrystalline polymers

For semicrystalline polymers, far infra-red measurements have been made on polyethylene[73,83-86], polypropylene[84,85] and poly(tetrafluoroethylene)[87,88]. Since these polymers are used in the communication industry, the objective has been to find a low loss dielectric at the upper end of the microwave spectrum. The observed losses have been attributed to several causes: (1) to single phonon absorption reflecting the phonon density of states in the amorphous regions; (2) to absorption due to impurities and degradation products; and (3) to absorption due to microdroplets of water which is usually present in these polymers. *Figure 24* shows data for polyethylene samples of different density. It is seen that the losses are proportional the the amorphous content or inversely proportional to density.

MOLECULAR MECHANISMS OF DIELECTRIC LOSS

Frequencies less than 100 GHz

In order to isolate and describe those modes of molecular and dipole motion which contribute to loss in the microwave region, it is necessary to consider the full spectrum of losses and the models which have been suggested to describe dielectric behaviour in polymers. A broad outline of the experimental observations of dielectric loss spectra of semicrystalline and amorphous polymers has been presented in schematic diagrams of *Figures 1* and *2*. As we discussed above, the α peak is associated with molecular motion in the crystalline phase of a semicrystalline polymer; the β peak with the rubber-to-glass transition; and the γ peak with local or side chain motion. Generally, the α peak occurs at low frequencies and it is considered unlikely that it will be seen as a loss mechanism at microwave frequencies. Depending on the temperature, the β, γ and δ peaks are potential microwave dispersions.

The β dispersion. The β dispersion is associated with the rubber-to-glass transition which occurs in the temperature region above T_g. It is characterized by a nonlinear curve on the $\log f_{\max}$ vs. $1/T$ plot, by an activation energy and relaxation times which become large as T approaches T_g, by a broad and unsymmetrical distribution of relaxation times, and by a temperature dependence of relaxation times which correlates with the macroscopic viscosity. For $T < T_g$, the β dispersion will not occur. Usually, the rubber-to-glass transition is associated with long relaxation times ($\tau \approx 10\,\mathrm{s}$) in the vicinity of T_g. However, when $T \gg T_g$ it is possible for the dispersion to move into the microwave region. The shift of the dispersion from low to high frequencies is seen to be continuous as temperature increases. The γ dispersion also shifts during the temperature change, but, since its activation energy is different, the shift constant is different and a merger of the β and γ transitions can occur.

Molecular theories of the dielectric β dispersion fall into two categories: those which are based on a calculation of the normal modes of motion of a polymer chain in a viscous neighbourhood and those which consider the motion of the coordinates of the atoms in the polymer

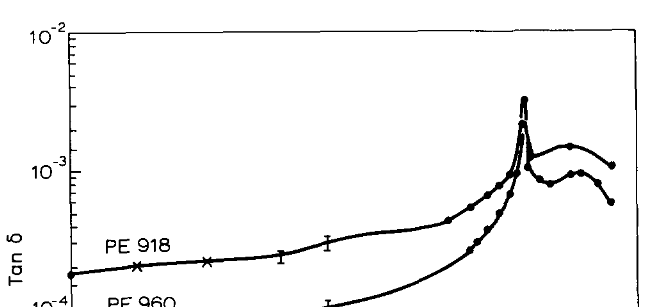


Figure 24 Dielectric loss tangent vs. log f for high and low density polyethylene at room temperature is shown. (Reproduced from E. M. Amrhein, ref. 73, by permission of the New York Academy of Sciences, New York, NY)

chain in a more detailed manner. The normal mode theories for dielectric dispersion are based on the Rouse model for mechanical relaxation of a polymer chain in solution[89].

The temperature dependence of relaxation times of the normal modes are dominated by the temperature dependence of a friction term, ξ, which, although it is a molecular constant, is usually related to the macroscopic viscosity of the medium. Here, the free volume model of the macroscopic viscosity[90], which decreases rapidly with temperature, is used. The Rouse model as extended to polar molecules and dielectric relaxation by Zimm[91] and by Stockmayer and Baur[92]. These models considered only the case of the dipole moment parallel to chain, i.e. a total dipole moment proportional to the end-to-end distance of the chain. Polymer molecules containing dissimilar atoms in the chain such as poly(propylene oxide) and poly(alkylisocyanates) are examples of polymers with dipole moments along the chain axis[93,94].

The model of Yamafuji and Ishida[95] applies to the case of the dipole moment perpendicular to the polymer chain. Polymers such as poly(vinyl chloride) and polystyrene possess a perpendicular dipole moment. The dipolar motion is described by the angle of rotation from an equilibrium position and damped torsional oscillation about equilibrium; translation of the dipole is neglected. In this model rotational motion gives rise to the β relaxation and the damped torsional motion is associated with the short relaxation times of the γ and δ dispersions. Yamafuji and Ishida solved the diffusion equation for micro-Brownian motion with the angle of rotation as the coordinate. This yielded a distribution of relaxation times which are functions of the rotational energy potential well parameters and the rotational friction coefficient. It has been difficult to assess this model quantitatively because the parameters of the energy well and the friction constant have not been calculated in an *a priori* manner. The merit of the model is the concept that both β and γ processes are described by different modes of the same motion.

The observed temperature dependence of the relaxation times of the β dispersion do not follow the simple Arrhenius temperature dependence, but rather the WLF equation[96]. This equation and Doolittle's free volume model for viscosity of liquids above their glass temperature have the same temperature dependence[86]. Thus, the β dispersion is viewed as micro-Brownian motion of the whole polymer chain. At T_g the motion of the whole chain becomes frozen so that molecular dynamics below T_g are associated with short segments of the main chain or pendant side groups.

The γ and δ dispersions. The γ and δ dispersions are characterized by short relaxation times (relative to β and α) which do not correlate with the mcaroscopic liquid viscosity, by a temperature dependence of relaxation times according to the Arrhenius equation, and by a loss peak which can be observed above or below T_g.

Mechanisms which have been proposed for the γ and δ losses are: (1) rotation of a polar group about a chemical bond in a side chain; (2) motion of a short segment of the main chain, e.g. the crankshaft motion[97]; and (3) a damped oscillation or local mode of a dipolar group.

The barrier models of Debye[98], Frohlich[99] and Hoffman[100], were developed for the case of dipoles rotating in a crystalline lattice. These models have been appropriately extended and applied to mechanisms (1) and (2) (above) of the γ and δ dispersions by Ishida and Yamafuji[101], by Boyd and Breiting[102], and by Hoffman, Williams and Passaglia[10].

The local mode mechanism has been developed in the Japanese school by Yamafuji and Ishida[95], and Saito *et al.*[103]. The idea is that the vibrations of the molecule are a superposition of normal modes. Those modes associated with torsional movement would have the lowest force constant, compared to bond stretching and valence angle deformation, and therefore would be the lowest frequency modes. If the amplitude of these modes is large, they will be highly damped by the viscous glassy neighbourhood. The relaxation time is given by the force constant divided by the friction constant.

A valuable tool for evaluating molecular models is the dipole time correlation function. This function can be used to describe the time decay of correlated motion which exists between dipole vectors in a polar material. An application involves the description of a hypothetical molecular model in the time domain either by an analytical or numerical time correlation function followed by the Fourier transform of this function to the frequency domain for comparison with experimental data. A review of dipole correlation functions in dielectric relaxation has been published by Williams[104].

These are the molecular models which have been developed for the β, γ and δ dispersions in dipolar polymer materials. Depending on the temperature and the dynamics of the molecule, these dispersions have the potential for occurring at microwave frequencies. For dipole moment parallel to the polymer chain, the β dispersion is attributed to micro-Brownian motion of the normal modes. For dipole moment perpendicular to the polymer chain, micro-Brownian rotation of the dipole in a potential well is the model presented by Yamafuji and Ishida. For the γ and δ dispersion, models have focused on the motion of pendant side groups, on the motion of small segments of the main chain and on damped vibrations of local modes.

Frequencies greater than 100 GHz

The dominant experimental effect observed in this frequency range is that the dielectric loss for amorphous polymers is much higher than that for the equivalent crystalline material[48,69-72]. Both Amrhein[69] and Strom[49] have suggested that this loss is due to the absorption of electromagnetic energy by the phonon density of states. Amrhein pointed out the near equivalence between the spectra of dielectric loss and the spectrum of the density of phonon states.

The experimental data do, indeed, suggest photon–phonon interaction, but a working model describing the mechanism of interaction has not been developed. Amrhein suggests that the absorption is caused by transitions between low frequency vibrational states of energy that are forbidden by the selection rules in a crystalline material, but, in an amorphous material, the selection rules do not apply because of the lack of long range order.

SUMMARY AND CONCLUSIONS

A review of the high frequency and microwave dielectric data for polymers has revealed several different types of absorption phenomena: (a) dipolar absorption dispersions in both crystalline and amorphous polymers; (b) dipolar losses due to impurities and/or additives in a polymer material; (c) microwave absorption in conducting polymers where the current carriers are electrons; and (d) photon–phonon absorption spectra corresponding to the density of states in an amorphous polymer. Losses due to (a) and (b) are temperature and frequency dependent, whereas for (c), they are independent of frequency.

The dipolar dispersions which occur at microwave frequencies or have the potential for occurring there are those which have been designated as the β, γ and δ dispersions. These will occur with varying intensity in all polar polymers. Since the β dispersion is associated with the glass transition, it will be observed only for $T > T_g$, and, in a semicrystalline polymer, the intensity of the β peak will be proportional to the amount of amorphous phase in the material. The γ and δ dispersions can occur above or below T_g and therefore are attributed to localized modes of dipolar motion such as crankshaft motion of a few monomers in the main chain and torsional or rotational motion of dipoles in a side chain.

Those dipolar polymers for which microwave data exist and for which the loss is relatively high (tan $\delta > 0.01$) were found to be: poly(vinyl chloride), poly(vinylidene fluoride), poly(methyl methacrylate), poly(methylacrylate), poly(oxymethylene), poly(ethylene oxide), and poly(propylene oxide). Of these polymers, only poly(methyl methacrylate) and poly(methylacrylate) have a dipole in the side chain. The other polymers are dipolar by virtue of their substituents on the main chain. Regarding their glass transition temperature, only poly(vinyl chloride) and poly(methyl methacrylate) have T_g above room temperature; for the other polymers, the room temperature loss is due to the β dispersion or a combination of β and γ. From these observations, we have concluded that a relatively intense relaxation dispersion will be observed for a dipolar, linear polymer molecule which has no side chain and whose glass transition temperature is below the temperature of observation. The intensity of the loss will be proportional to amount of material in the amorphous phase.

Polymers with low dielectric loss at microwave frequencies (tan $\delta < 0.01$) are those which have been studied by the communications industry such as polyethylene, polypropylene and polystyrene. Also, engineering thermoplastics such as polycarbonate, poly(phenylene oxide) and polysulphone fall into the category of low loss dielectrics.

At the high end of the microwave region, $f > 100$ GHz, absorption of electromagnetic energy is achieved via a photon–phonon interaction. The data reveal that this absorption is proportional to the amount of amorphous phase in the polymer also. Thus, for the entire microwave region, above and below 100 GHz, high losses can be observed in an amorphous polymer whose β or γ dispersion occurs at microwave frequencies.

Losses due to impurities have been observed at microwave frequencies. A dispersion in poly(methyl methacrylate) and in polyethylene near 10^7 Hz is attributed to water. Its magnitude is small as are the microwave losses due to impurities in other polymers.

Polyacetylene and poly(sulphur nitride) belong to a class of electrically conducting polymers with electron carriers. Their dielectric behaviour is distinctly different from the dipole dominated effects in nonconducting polymers. The loss for $(SN)_x$ and doped $(CH)_x$ is independent of frequency, i.e. their d.c. conductivities are the same as those measured at microwave frequencies. For polyacetylene, the conductivity is temperature independent and for poly(sulphur nitride) the conductivity has a $1/T^2$ dependence. Since their conductivities are high (10^3 ohm^{-1} cm^{-1}), they have the potential for being highly absorbing at microwave frequencies.

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