CHAPTER VII

DIELECTRIC MEASUREMENT
7.1 DIELECTRIC BEHAVIOUR

The dielectric constant and dissipation factor are the crucial quantities in the design of devices. The study of these parameters as a function of temperature and frequency reveal much information on the chemical and physical state of a polymer [1]. A knowledge of the dielectric loss behaviour of thin films is very important because of their possible technical application for insulation, isolation and passivation in microelectronic circuits. Some of the work reported in the literature is reviewed briefly below. Excellent reviews on dielectric properties appeared in the literature [2-5].

Tanaka [6] investigated dielectric relaxation in high polymers. It was shown that the dielectric properties can be interpreted phenomenologically in terms of a generalized Fröhlich's response absorption. Dielectric $\alpha$ and $\beta$ dispersions in polyvinyl butyral was studied by Takashi [7]. The higher temperature dispersion labelled as $\alpha$ and the low temperature dispersion was labelled $\beta$, dielectric relaxation of polyvinylidene fluoride was studied by Koizumi et al. [8]. The $\alpha$-relaxation was related to molecular motions in crystalline regions and the $\beta$ to the microbrownian motion in amorphous regions. Dielectric properties of impurity doped polyethylene was studied by Kosaki and Ieda [9]. Two peaks of dielectric absorption were observed. Dielectric relaxation of high polymers in the solid state was studied by Ishida [10]. Sasabe et al. [11] investigated the dielectric relaxations in PVF$_2$. Three distinct absorption peaks $\alpha_\text{c}$, $\alpha_\text{b}$ and $\beta$ were observed.
Dielectric characteristics of styrene formed by glow discharge was studied by Valentin and Carchano [12]. The results were explained in terms of dipolar and hopping process. Bahri and Singh [13] studied A.C. electrical properties of solution grown thin polyvinyl chloride films. Two high temperature loss peaks were observed and these were explained on the basis of a cluster model proposed by Ubblehode. Gupta et al. [14] studied anisotropy of dielectric relaxation in polyethylene terephthalate fibres. Considerable directional anisotropy was observed in the β relaxation process, which was independent of frequency. Gowrikrishna et al. [15] studied the dielectric behaviour of isocyanate terminated polymers. Activation energies were calculated. Maxwell-Wagner sillars interfacial polarization was proposed as the probable mechanism. Ribelles and Calleja [16] studied the β dielectric relaxation in some methacrylate polymers. Apparent activation energies and relaxation strengths were calculated.

Dielectric properties of bioriented polypropylene films were studied by Umemura et al. [17]. Ramu et al. [18] studied the dielectric properties of plasma polymerized hexamethyl disiloxane films. The observed dielectric properties were correlated with film structure and morphology. Basha et al. [19] studied the dielectric properties of pure and doped PVA films and the observed dielectric relaxation was attributed to the glass transition. Variation of dielectric loss of polyethylene terephthalate film with different parameters was reported by Prasad and Gupta [20].
The dielectric loss tan δ, and the capacitance C of plasma polymerized styrene films were measured between room temperature and 250°C at 1 kHz by Deok-Chool Lee and Kyoung-Si Jin [21]. The effects of the oxidation, heating and plasma treatment on tan δ and C were investigated. Contour maps of complex relative permittivity in the range -170°C to +175°C and 0.1 Hz to 3 MHz were presented for commercial polybutylene terephthalate by Pratt and Smith [22].

Effect of temperature on the dielectric constant of vinylidene fluoride trifluoroethylene was studied by Eatah and Tawlik [23]. There was a marked change in dielectric constant (ε') at 70°C. The maximum value of (ε') at 70°C was attributed to the phase transition. The poling field reduced ε' and shifted ε'max towards higher temperature. Dielectric properties of a one dimensional polymer PTS were measured along the chain direction in the temperature range 77-273 K by Ruan Yao Zhong et al. [24]. A second order phase transition from a high temperature nonpolar state to a low temperature polar state accompanied by an anomaly in dielectric constant was observed at 195 K. Two peaks in the dielectric loss were found at 150 and 100 K. These results were explained by a model which involves modes of side group motion. The variation of dielectric constant (ε') of polyethylene terephthalate (PET) film was studied as a function of temperature and frequency ranging from 0.3 to 15.0 MHz, by Prasad et al. [25]. The study of ε vs T plots showed a transient temperature at 349 K, independent of frequency. Thus, below the transition temperature the
sample behaved as ferro-electric and above it as para-electric. The plot \(1/\varepsilon'\) vs T also confirmed the transition and the Curie temperature \(T_C\). From the positive slopes of this curve, calculated value of Curie constant was found to be nearly \(1.4 \times 10^{-2}\).

A.C. conductivity \(\sigma(\omega)m\) and the dielectric constant \(\varepsilon'\) of vinyl chloride vinyl acetate (VC:VAc) copolymers having 3, 10 and 17% VAc content (by weight) was measured in the temperature range 77-410 K and in the frequency range 50-100 kHz by Mahendru et al. [26]. At temperatures up to 250 K the dielectric constant showed a very weak frequency and temperature dependence, whereas at temperatures above 300 K, showed a strong frequency dispersion. The mechanism of conduction in low and high temperature regions was discussed in the light of an existing theoretical model.

Composites of PZT with polymethyl methacrylate (PZT/PMMA); polystyrene (PZT/PS); polyvinyl chloride (PZT/PVC); and PZT/PVDF in the weight ratio 90:10 were prepared by the solvent casting technique and their dielectric properties were studied by Sinha and Pillai [27]. From these results it was concluded that the absolute value of the dielectric constant of the composite depends on the dielectric constant of the polymer phase.

The dielectric permittivity and loss of bisphenol-A polycarbonate (PC) was measured over the frequency range 100 Hz to 200 kHz and temperature 77-383 K by Pathmanathan et al. [28]. One sub-\(Tg\) relaxation
peak was observed which rapidly broadened with decrease in temperature. This was attributed to a progressive separation of the $\gamma$ and $\beta$ peaks, which at high temperatures merged to form one peak of high strength.

Measurements of the complex permittivity of cross linked polyurethanes at different temperatures in the frequency range $1-10^5$ Hz were studied by Schlosser and Schonhals [29]. Using a new model, the shape parameters were related to small and large scale interaction.

High frequency dielectric measurements in the range 10 MHz to 10 GHz were performed on poly(ethylene oxide) PEO and its complexes with lithium perchololate using time domain spectroscopy by Gray and Vincent [30]. Measurements were made over a wide polymer to salt composition and in the temperature range 50-75°C. All the samples were amorphous. A relaxation was observed for PEO and its complexes with LiClO$_4$ in the GHz region and was attributed to the (\(\beta\)) relaxation arising from long range segmental motion of the polymer or the ion polymer complex.

Plasticization of poly(ethyl methacrylate) (PEMA) by CO$_2$ was investigated by Kamiya et al. [31] by dielectric relaxation spectroscopy. The dissipation factor was measured as a function of frequency (1-10000 kHz) and CO$_2$ pressure (-60 atm) over the temperature range 35-115°C. A maximum in the frequency dependence of the dissipation factor was
attributed to the relaxation of PEMA, which shifted to higher frequency with increasing temperature, pressure or concentration.

7.2 BASIC THEORY

Debye [32] gave the classical picture of relaxation of polarization with a single relaxation time. In this model he considered a set of non interacting dipoles free to rotate against some viscous resistance in a fluid like medium.

Equation for complex permittivity given by Debye is

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega \tau} \]  \hspace{1cm} (7.1)

where \( \varepsilon_0 \) - dielectric constant at low frequency

\( \varepsilon_\infty \) - dielectric constant at high frequency

\( \omega \) - angular frequency

\( \tau \) - relaxation time.

Frohlich modified Debye theory. According to him real and imaginary part of the dielectric constants are given by -

\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 + \varepsilon_\infty}{1 + \omega^2 \tau^2} \]  \hspace{1cm} (7.2)

\[ \varepsilon'' = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau \]  \hspace{1cm} (7.3)

The maximum value of \( \varepsilon' \) and \( \varepsilon'' \) is

\[ \varepsilon' = \frac{\varepsilon_0 + \varepsilon_\infty}{2} \]  \hspace{1cm} (7.4)
\[ \varepsilon'' = \frac{\varepsilon_0 - \varepsilon_\infty}{2} \] ...

(7.5)

The magnitude of dielectric dispersion is given by -

\[ \varepsilon_0 - \varepsilon_\infty = \left( \frac{3}{2} \varepsilon_\infty \right) \left( \frac{\varepsilon_0 + 2}{3} \right) \frac{4}{3} \frac{\pi n g \mu^2}{kT} \] ...

(7.6)

where
- \( n \) = number of dipoles
- \( \mu \) = dipole moment
- \( g \) = parameter related to dipole interaction
- \( \Gamma \) = temperature

Polymers rarely follow the Debye theory and they show much broader dispersion and low loss as compared to single relaxation process.

Cole [33] pointed out that this anomaly arises due to the fact that the long chain molecular compounds do not have a single relaxation time. On the contrary their relaxation times are distributed within certain minimum and maximum limits.

Every molecular dipole in a given chain is coupled to neighbouring dipoles of the same chain by primary valence bands so that the motion of any dipole affects the motion of its neighbours and they in turn influence its response to a torque. Furthermore, in various configurations which a chain molecule can assume, we can find one or another segment of chain acting effectively as a co-operative electrical unit and these segments will of course vary in length between the improbable extremes of a single monomeric unit and the whole extended chain. Such a state of affair leads to distribution of relaxation time.
On eliminating the parameter $\omega \tau$ between the two equations and rearranging the two parameters ($\varepsilon'$ and $\varepsilon''$) we get -

$$
\left[ \varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2} \right] + \varepsilon''^2 = \left[ \frac{\varepsilon_0 - \varepsilon_\infty}{2} \right]^2 \quad \cdots (7.7)
$$

The above equation represents a circle with center \([(\varepsilon_0 + \varepsilon_\infty)/2, 0]\) and radius \((\varepsilon_0 - \varepsilon_\infty)/2\). Only the semicircle over which $\varepsilon''$ is positive has physical significance. Materials with single relaxation time yield a semicircle in $\varepsilon'$ and $\varepsilon''$ plane. Polymers do not yield such a semi circle and the $\varepsilon'$-$\varepsilon''$ plane falls within the Debye semicircle (Fig. 7.1). Cole Cole [33] modified the Debye equation by an empirical equation for the complex permittivity

$$
\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega \tau)^{1-\alpha}} \quad \cdots (7.8)
$$

where $\alpha$ is an empirical parameter. It lies between 0 and 1 and it denotes the angle of tilt of the circular arc from the real axis.

Though the modified expression measures the small deviation from the ideal Debye behaviour, but there are materials which deviate very much from the Debye behaviour.

Havriliak and Negami [34] gave an expression which is of the form -

$$
\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{\left[1 + (j\omega \tau)^{1-\alpha}\right]^{1-\beta}} \quad \cdots (7.9)
$$

where $\beta$ is an empirical parameters which lies between 0 and 1 and represents the angle of tilt.
7.3 EXPERIMENTAL

Dielectric studies were carried out on all the sample to study dielectric constant and dielectric loss. The instrument used was HP 4192A impedance analyzer which gives a direct display of capacitance and tan $\delta$ in the frequency range 10 Hz to 13 MHz.

The sample of polyvinylidene fluoride was placed inside the temperature controlled measurement cell and the test leads of the impedance analyzer were connected to it. The sample capacitance and dielectric loss tangent of the samples were measured at fixed temperature and the frequency was varied from 500 Hz to 1000 kHz in steps. These observations were repeated for different temperatures ranging from 40 to 70°C. A fixed voltage of 1 V was applied to the sample.

The dielectric constant and losses were calculated from $C$ and tan $\delta$ using the equation valid for parallel plate capacitor.

$$
\varepsilon' = \frac{C_X}{\varepsilon_0 A} \quad \text{and} \quad \varepsilon'' = \varepsilon' \tan \delta 
$$

where $C_X$ is the sample capacitance in Farad, $A$ is the area of the sample, $d$ is the thickness of the sample and $\varepsilon_0$ is a constant representing permittivity of free space.

7.4 RESULTS AND DISCUSSION

The dielectric constant and dielectric losses of polyvinylidene fluoride samples are observed in the temperature 40-70°C and frequency (500 Hz to 1000 kHz) range. The result are interpreted in terms of existing theories.
(A) Dielectric Constant

(i) Effect of Temperatures

To observe an effect of temperature on dielectric constant, its variation as a function of temperatures is plotted at different frequencies (i.e. 500 Hz, 2, 10, 100, 500 and 1000 kHz) are shown in the Figs. 7.1-7.7 for similar (Al-Al, Cu-Cu, Ag-Ag and Sn-Sn) and dissimilar electrode (Al-Cu, Al-Ag and Al-Sn) combinations. It is clear from the figures that the value of dielectric constant decreases with increasing frequencies. For higher frequencies (i.e. 500 kHz and 100 kHz) the value of dielectric constant increases attaining a maxima at 70°C and then decreasing. This nature is not observed for other frequencies.

(ii) Effect of Frequencies

The frequency dependence of dielectric constant of the sample at different temperatures (i.e. 40, 50, 60 and 70°C) are shown in Figs. 7.8-7.14 for similar (Al-Al, Cu-Cu, Ag-Ag and Sn-Sn) electrode system and dissimilar electrodes (Al-Cu, Al-Ag and Al-Sn) combinations. It is found that with increasing temperature dielectric constant increases. As per nature of the curve is concern, it is clear that the value of dielectric constant decreases up to $10^4$ Hz and beyond this it increases. The rate of decrease and increase of dielectric constant is sharp.

(B) Dielectric Losses

(i) Effect of Temperatures

The effect of temperatures on PVDF samples of 20 μm thickness for similar (Al-Al, Cu-Cu, Ag-Ag and Sn-Sn) and dissimilar (Al-Cu, Al-Ag and
Dielectric constant versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Cu - Cu system

Dielectric constant versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Ag - Ag system
Fig. No. - 7.5

Dielectric constant versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Ag system

Fig. No. - 7.6

Dielectric constant versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Sn system
Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Cu system
Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Al system.
Fig. No. - 7.9

Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Cu - Cu system.
Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Ag - Ag system.
Fig. No. - 7.11

Dielectric constant versus frequency for polyvinylidene fluoride samples at different temperature (i.e. 40, 50, 60, 70 and 80 °C) for Sn - Sn system.
Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Cu system.
Fig. No. - 7.13

Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Ag system.
Fig. No. - 7.14
Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Sn system.
Al-Sn) are shown in Figs. 7.15 to 7.21. It is clear from dielectric loss versus frequency curves that dielectric loss value sharply decays attaining a minima and again it sharply increases. It is very interesting to note that with increasing temperature (i) the value of dielectric losses are less for higher temperature in the first half and after attaining a minimum value, dielectric losses are more for higher temperatures, and (ii) the minima position shifts towards lower frequency range. The nature of all the curves are similar.

(ii) Effect of Frequencies

Figures 7.22 to 7.28 represent the dielectric losses versus temperature curves at constant frequencies (i.e. 500 Hz, 2, 10, 100, 500 and 1000 kHz) for similar (Al-Al, Cu-Cu, Ag-Ag and Sn-Sn) and dissimilar (Al-Cu, Al-Ag and Al-Sn) electrode combinations. The nature of the curves are approximately similar. In general, losses decreases with increase in frequency. In certain cases the curve show slight decrease in the value of dielectric losses and then continuous increasing character is found. The value of losses are found higher, when Al-Al electrode system are replaced by Cu-Cu and Ag-Ag electrode combination.

We have observed a pronounced effect of electrode materials on dielectric constant as well as dielectric losses of the sample when dielectric parameters, i.e. temperature and frequency are changed.

The dielectric behaviour of the polymer is determined by the charge distribution and also by statistical thermal motion of its polar groups. The
Fig. No. - 7.15

Dielectric losses versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Al system.
Fig. No. - 7.16

Dielectric losses versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Cu - Cu system.
Fig. No. - 7.17

Dielectric losses versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Ag - Ag system.
Fig. No. - 7.18

Dielectric losses versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Sn - Sn system.
Fig. No. - 7.19

Dielectric losses versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Cu system.
Fig. No. - 7.20

Dielectric losses versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Ag system.
Fig. No. 7.21

Dielectric constant versus frequency for polyvinylidene fluoride samples at different Temperature (i.e. 40, 50, 60, 70 and 80 °C) for Al - Sn system.
Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Cu - Cu system.

Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Al system.
Fig. No. - 7.24
Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Ag - Ag system

Fig. No. - 7.25
Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Sn - Sn system
Fig. No. - 7.26
Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Cu system

Fig. No. - 7.27
Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Ag system
Fig. No. - 7.28

Dielectric losses versus Temperature for polyvinylidene fluoride samples with various frequency (i.e. 500 Hz, 2 KHz, 10 KHz, 100 KHz, 500 KHz and 1000 KHz) for Al - Sn system
polarization. The electronic polarization occurs during a very short interval of time (of the order of $10^{-15}$ sec), but longer than for electronic polarization, i.e. $10^{-13}-10^{-12}$ sec required for the process of ionic polarization to set in. Dipole polarization requires a relatively long time compared with that of practically almost inertialess phenomena of deformational polarization so dielectric constant of non-polar polymer remains invariable with frequency. In case of polar polymers, the dielectric constant begins to drop at a certain critical frequency. The dipole molecules cannot orient themselves in the lower temperature region. However, owing to thermal expansion, the ratio of the number of molecules to the effective length of the dielectric decreases when the temperature increases. As the temperature increases, the orientation of dipoles is facilitated and this increase the dielectric constant. This behaviour is apparent from the upward trend of the slopes of dielectric constant curves in the neighbourhood of glass transition temperature (Tg). As the temperature increases further, the chaotic thermal oscillations of molecules are intensified and the degree of order of orientation is diminished.

The dielectric dispersion appearing at high temperature is generally admitted to be due to the rotatory diffusional motion of the molecules from one quasi-stable position to another around the skeletal bond involving large-scale conformational rearrangement of the main chain, and is known is primary dispersion region or the $\alpha$-relaxation. The low temperature
groups which are considered to be more mobile or the small displacement of the dipoles near the frozen-in position and known as the secondary dispersion region or β-relaxation.

Thin polymer films are known to be a mixture of amorphous and crystalline regions. The amorphous regions are the areas in which the chains are irregular and entangled, whereas, in crystalline regions the chains are regularly folded or orderly arranged. In the crystalline areas, because of the presence of hindering structural units (due to greater density of these regions) the polymeric chains move with a greater difficulty than in the amorphous regions. The hinderance can be assumed to possess a certain potential energy. When the polymer is heated the movements of the main chain sets in, becoming maximum at Tg, at which maximum losses occur corresponding to the α-relaxation peak. This relaxation peak, corresponding to Tg, may also be understood by the free volume theory [35] according to which the molecular mobility (and consequently the relaxation time) near Tg depends mainly on the free volume. In the glassy state below Tg, the free volume will be frozen in and will remain fixed. As the temperature increases, the glassy state will expand due to normal expansion of all the molecules, which results from the changing vibrational amplitudes of bound distances [36]. As Tg is reached, in addition to the normal expansion process, there will be an expansion of free volume itself, which results in a larger expansion of the
polymer. This yields room for rotational or translational motion of the molecules to occur at Tg, accounting for the maximum dielectric loss at Tg [37].

The presence of dipolar molecules may also contribute in the process. The dipoles associated with the backbone of a segment of polymer chain will orient with a certain frequency governed by the elastic restoring force which binds the dipoles to their equilibrium positions and the rotational frictional forces exerted by the neighbouring dipoles [38]. In the crystalline or ordered polymers, the forces which hold the structural unit together are of a homopolar chemical binding nature and are much stronger than the vander Wall's forces between the molecules in the amorphous phase which vary from region to region. Moreover, the dipolar molecules in the crystalline phase will make discontinuous jumps from one equilibrium position to another and hence contribute to the absorption at the same temperature or frequency, whereas, in the amorphous phase, dipolar molecules should be able to orient from one equilibrium position to another relatively more easily and will contribute to the absorption over a wide frequency or temperature range since each dipole in the later case would have slightly different environments and hence would have different intermolecular interaction.
net effect of some internal field within the polymer along with the external ac field. The dipole-dipole interactions between the different groups or many body interactions suggest the lower losses with higher frequency range. The dependence of the dielectric constant on frequency can be determined from the equation

\[ C = C_g + \frac{S \tau}{1 + \frac{\tau^2}{\omega^2}} \] ... (7.11)

where \( C_g \) is the geometrical capacitance, \( S \) the conductance corresponding to the absorption current, \( \tau \) the dipole relaxation time and \( \omega \) the angular frequency. Above equation show that \( C \) should diminish with increasing frequency. The increase in losses at low frequency could be associated with the polarization of the trapped charge carriers. With the increase in frequency, polarization decreases and becomes vanishingly small at high frequencies. The decrease in losses with frequency also seems to show the decrease in the number of charges and delay in settling of dipoles due to availability of very short time in one half cycle of alternating voltage. The general expression for dielectric loss is given by the equation -

\[ \tan \delta = \frac{\omega^2 \tau^2 (G_{in} + S) + G_{in}}{\omega \left\{ S \tau + C_g \left( \omega^2 \tau^2 + 1 \right) \right\}} \] ... (7.12)

where \( G_{in} \) is the conductance for the residual current. Obviously, from eqn. (7.12),

\[ \omega \xrightarrow{\lim} 0 \quad \tan \delta = \infty \] ... (7.13)
\[
\omega \xrightarrow{\text{lim}} \infty \quad \tan \delta = 0
\]  

...(7.14)

Differentiating eqn. (7.12) with respect to \( \omega \) and equating the derivative to zero, it is possible to obtain the value of \( \omega' \) of the frequency, corresponding to maximum loss.

Figures 7.1-7.28 exhibit the variation of dielectric constant and losses versus temperature and frequency curves for different electrode materials. Values of dielectric constant and losses seems to be controlled by the effective work function of metal-insulator-metal interfaces, i.e. the difference in energy between the Fermi level in metal and the bottom of the conduction band in the insulator. The difference between the work function of metal (1) and metal (2) will control the magnitude of loss but for similar electrode system the characteristic of the polymer may prevail as the net contribution of charges injected from the electrode would then be zero [39]. The various thermograms represent the distributed relaxation. The reason for distributed relaxations may be due to the combined effect of space charge injected from electrodes and dipolar relaxations in the polymer. In these results, we suggest that the internal field of polymer may get modified by the difference in the work function of various electrode metals [40].

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24. Zhong, Ruan Yao, Li-Ping Li, You-Jun Chen and He Ping Sheng Chin, Phys. (U.S.A.), 8, 4, 937 (1988).


