CHAPTER VI

DIELECTRIC BEHAVIOUR
CHAPTER VI: Dielectric behaviour

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Introduction:

Polymers are complex dielectric materials. The knowledge of dielectric properties of material is of vital importance to understand charge storage and their transportation. With this knowledge, some important activities, such as movement of dipoles, losses and energy, segmental motion, latent heat, conduction mechanism, could be easily classified. Investigation of dielectric properties is also one of the most convinient and sensitive methods for studying polymer structure. It is therefore important that their dielectric behaviour is fully understood. When solid polymeric materials are subjected to an electric field, polarization phenomena occur. The electric field may cause a small displacement of electrons, which produce an induced electric moment in the molecules during the whole time, the field is applied. In the case of molecules with permanent dipole moments, an electric field brings about their orientation and the polarization of materials. The displacement of polar groups requires some time and is thus dependent on frequency and temperature, which lead to different dispersion phenomena according to segmental motion of the chain or orientation of pendent dipoles. Actually, at frequencies and temperatures, where dispersion occur, only a part of entering electrical energy is stored, while some of it is dissipated as heat.
The electrical energy stored per cycle is proportional to true permittivity and the energy loss per cycle is proportional to imaginary permittivity. These losses in a dielectric are commonly known as dielectric losses. The loss tangent exhibits a maxima at frequencies \(^1\) at which dielectric permittivity shows dispersion. The maxima in dielectric loss occurs at temperatures \(^1\) at which motion of large segments of the chain or different polar side groups begins. Thus their temperatures are related to temperatures at which some transitions are observed in mechanical studies. Dielectric behaviour of polymers is generally characterized by the distribution of relaxation times. These distributions may be obtained by the procedure applied to obtain distributions of mechanical relaxation times.

Valuable informations could be obtained on the dielectric relaxation studies\(^2-9\) made in polar, non polar linear polymers using various techniques. Various mechanisms for the charge storage in polymers, could be easily classified as a result of these studies. It has been observed that total charge stored in a polymer electret\(^10\) and the different mechanisms which contribute to this charge are very sensitive to the structure of the forming material. It was also observed that charge can be produced by making some structural changes in the polymer matrix itself by doping with certain impurities\(^11-13\).
Structure of dielectrics could be easily determined and this information could be obtained by varying dielectric constant with temperature and frequency range. However, the measurements of dielectric constant of the electret forming material before and after polarization and the resulting values therefrom are capable of giving information regarding the orientation and the freezing in of the permanent dipoles in polar dielectrics.

6.2: Affecting Parameters:

The dielectric losses in polymers are convolution of two effects viz; the presence of dipoles which get coupled to the electric field and suitable thermal motion in the polymer to give rise to a dispersion. The polar group includes polymer like polymethyl methacrylate, polyvinyl acetate, polyvinyl chloride, polyacrylnitriles. The dielectric constant and losses get mainly affected by the parameters- temperature, field, frequency, humidity, impurity and nature of polymers etc.

(a) Temperature:

Temperature affects the dielectric properties by decreasing the number of polarized ions per unit volume due to thermal expansion. Expansion of lattice result in increase
of polarizability. At constant volume macroscopic polarizability depends upon the temperature. Debye's equation which relates the temperature of a substance to dielectric constant is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4 \pi N}{3} \left( \alpha_o + \frac{\mu^2}{3kT} \right) \quad (6.1)$$

where,

N = the number of molecules per c.c.

$\alpha_o$ = the polarizability of the molecule, i.e. the dipole moment induced per molecule by unit electric field.

$\mu$ = the permanent electric dipole moment of the molecule.

K = the molecular gas constant.

T = the absolute temperature.

The molecular polarizability ($\alpha_o$), is sum of a part independent of temperature and one inversely proportional to the absolute temperature -

$$\alpha = \alpha_o + \frac{P_{\text{perm}}^2}{3kT} \quad (6.2)$$

where,

$\alpha_o$ = the contribution to the polarizability of the electron shifting process, and

$P_{\text{perm}}$ = the permanent dipole moment of the molecule.

$\frac{P_{\text{perm}}^2}{3kT}$ is due to molecular rotation and a part which is clearly temperature dependent part.
The dielectric constant of simple elemental dielectric show relatively small temperature dependence. In semiconductors, temperature increase may raise the free carriers density to conduction band to introduce conduction losses and thus, develop a remarkable decrease in the values of dielectric constant.\textsuperscript{14,15} In ionic dielectrics, substantial increase in dielectric constant is brought about at high temperature because of the loosening of the bonds which hold the ions in place.\textsuperscript{16} In case of polar polymers dielectric constant is temperature dependent.\textsuperscript{17}

(b) Frequency :

Dielectric losses depend on a wide range of frequencies. In case of polar substances, dielectric constant changes at a characteristic frequency, when a substance is subjected to an alternating field.

Complex form of dielectric constant $\varepsilon^*$ is represented by -

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \quad \text{(6.3)}$$

where $\varepsilon''$ is real part (observed dielectric constant) and $\varepsilon'$ is imaginary part, called dielectric loss. Both these constants have been lumped in-to a single complex dielectric constant.

The phase angle ($\delta$) between the displacement and the applied electric field is given by -
\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \ldots \ldots \quad (6.4)
\]

where \(\tan \delta\) is termed as loss tangent, \(\delta\) is frequency dependent, since \(\varepsilon'\) and \(\varepsilon''\) are frequency dependent.

The Debye equation for \(\varepsilon'\) and \(\varepsilon''\) in terms of frequency and relaxation time \(\tau\) are -

\[
\varepsilon' = \varepsilon_{ea} + \frac{\varepsilon_s - \varepsilon_{ea}}{1 + \frac{w^2 \tau^2}{1}} \quad \ldots \ldots \quad (6.5)
\]

and,

\[
\varepsilon'' = \left( \varepsilon_s - \varepsilon_{ea} \right) \frac{w \tau}{1 + \frac{w^2 \tau^2}{1}} \quad \ldots \ldots \quad (6.6)
\]

where, \(\varepsilon_s = \) static dielectric constant.

\(\varepsilon_{ea} = \) instantaneous dielectric constant.

For all the frequencies less than \(\frac{1}{\tau}\) the real part of the dielectric constant \(\varepsilon'\) approaches the static dielectric constant \(\varepsilon_s\). In this frequency range, therefore the losses vanish and dipole contribute their full scale to the polarization. On the other hand for frequencies greater then \(\frac{1}{\tau}\), the dipoles are no longer able to follow the field variations and the dielectric constant \(\varepsilon'\) approaches \(\varepsilon_{ea}\).

Therefore, as the frequency increases, the relaxation spectrum is characterized by a region of constant value followed by a slow fall of \(\varepsilon'\) to a lower value, the corresponding variation of \(\varepsilon''\) being a broad peak. On the other hand, the resonance spectrum show a rapid fall from constant value for \(\varepsilon'\) and a sharp peak for \(\varepsilon''\).
The polymers do not follow the Debye's equation. Cole-Cole\textsuperscript{18} pointed out that this anomaly arises due to the fact that the long chain molecular compounds do not have a relaxation time. On the contrary their relaxation times are distributed within certain minimum and maximum limits. The different bonds between the molecular chains are responsible for these relaxation limits and it is still possible for most purposes to consider that the practical situation is represented by a complete relaxation time. The convolution of dipoles to couple the electric field and thermal motions in the polymer may give rise to a dispersion.

\((\varepsilon)\): Field :

The permanent dipoles in the domain structure are aligned in direction of the applied field, when the dielectric is subjected to an external electric field. When dipoles align parallel to the field, high dielectric constant and large dielectric losses appear, and no dielectric constant were observed when their alignment is perpendicular to the field. The orientation of the dipoles is proportional to the applied field strength and therefore a greater increase in the value of dielectric constant is to be expected with increasing field strength.\textsuperscript{19}

The isotropic increase in dielectric constant suggests that direct coupling of electric dipoles with the field is not in itself sufficient. Anisotropy of the dielectric properties in case of carnuba wax\textsuperscript{20,21} and ferroelectric material has been observed.
Lal\textsuperscript{22} studied the variation of the static dielectric constant of some single crystals with DC field and observed that the dielectric constant first increases to a minimum and then decreases for higher fields. However the increase is not so large and the increase in dielectric constant has been explained in terms of trapped electrons.\textsuperscript{15} At higher fields, these trapped electrons are probably released from the potential well and are excited to the conduction bond, then they produce a conduction current in phase with the applied voltage, which results in the decrease in polarization and the dielectric constant. Dielectric constant variation with field, temperature and frequency has been reported by many workers.

(d) Humidity:

The presence of water vapour or water molecules inside the dielectric, increase the dielectric constant to a considerable amount.\textsuperscript{23} Bhargava\textsuperscript{24} has reported in PS, dielectric constant increase with humidity in low temperature region.

(e) Impurity:

Impregnating of polymer with impurity affects the dielectric constant and losses as well. Tiwari\textsuperscript{25} and Kulshrestha\textsuperscript{26} have reported considerable change in capacity and losses values.
(f) Nature of the Polymer:

Polymers can be divided as polar and non-polar materials. For non-polar substances containing no ionic impurities, the measured loss factor is very small but is not actually zero in the liquid state\textsuperscript{27,28} and rather it increases with frequency in microwave region.

The dielectric constant exhibits a sharp drop when transition from liquid to the solid state occurs in the polar substances. Dielectric losses are also approximately zero for such non rotating polar molecules.

6.3: Present and Last Decade's Work:

The response of matter to an electric field (either static or alternating) is one of the most general phenomena of nature. The investigation of dielectric properties has provided an important approach to an understanding of the electronic structure of matter, and without some understanding of the relation of these properties of matter, our extensive knowledge of dielectric behaviour loses is not much of significance.

Nearly all organic solids are dielectrics, consequently are more less good insulating materials.\textsuperscript{23} Organic solids are molecular crystals, mostly and can be grouped as polar and non-polar. Several workers\textsuperscript{4-10} have studied the dielectric constant of organic materials. On high polymers a good amount
of work has been done by Fuoss and coworkers\textsuperscript{11} and others\textsuperscript{12-14}. Dielectric relaxation behaviour of polyvinylidene fluoride (PVDF)\textsuperscript{29,30}, polyvinyl acetate\textsuperscript{31} has been reported. Reported work/papers are also available on polychlorotrifluoro ethylene\textsuperscript{32} and polyacrylonitrile\textsuperscript{33}. Reports are available on acrylonitrile\textsuperscript{33} acrylonitrile butadiene\textsuperscript{34} and poly methyl trifluoro propyl siloxane.

Chattergi and Bhadra\textsuperscript{20}, Mc Mohan\textsuperscript{35}, Elgard\textsuperscript{36} and others\textsuperscript{22,23} have observed isotropic increase in dielectric constant with field, but no satisfactory explanation has been given for this effect so far.

The dielectric behaviour of undoped, lithium-doped, and sodium-doped polycrystalline ZnO was reported by Seitz et al.\textsuperscript{37} as a function of frequency and field. They found that this dielectric behaviour is caused by barrier layer polarization. The barrier layer polarization was thought to be responsible for the observed dielectric behaviour of Ca-doped CeO\textsubscript{2}\textsuperscript{38} also.

In both cases, the effective dielectric constant for the doped specimen was raised exponentially with temperature.

In the literature the subject has been discussed in review\textsuperscript{39} and books\textsuperscript{40,41} by many authors.

6.4: Present Investigation:

It is evident from the proceeding review of the available
literature that there does not exist a universally accepted
time of conduction mechanism, thermo and photo electret states
in the field of organic solid state. The most widely used
explanation of the experimentally observed conduction
phenomenon in organic solids is in terms of modified electronic
energy band model. The dielectric constant and dielectric
loss are being interpreted in terms of charge carrier
mechanisms because a correlation between the response of
organic dielectrics under step tight and step field
excitation has been established. More experimental data on
new dielectric is needed to test the validity of electron
trapping in deep traps and or orientation of molecules with-in
the dielectric which are said to be responsible for formation
of heterocharge. Dielectric relaxation of several polymers,
at temperature below and above the glass transition
temperatures has been investigated. Almost no report seems to
be available on composite polymeric systems. The results of
dielectric bridge measurements carried out on PMMA, and
composite system (PMMA + Malachite Green) to understand, the
effect of doping on the dielectric relaxation behaviour under
the influence of alternating field. The permittivity and loss
variation of PMMA and composite (PMMA + Malachite Green)
samples, as a function of frequency and temperature are
discussed in this chapter.
6.5 : Various Methods :

A wide variety of methods\textsuperscript{42,43} exists for the measurement of dielectric constant. These techniques depend on the nature of specimen and limits of variation in capacity and losses at particular frequency range which decides the choice of the method. Accurate measurements demand care in the design of the measuring apparatus and types of measuring cell.

A simple method for determining the d.c. or initial relative permittivity is to measure the time constant for discharge of a condenser, through a standard resistor, with and without the dielectric present. The applicability of this method is limited in cases, for which the time constant can be made long enough to permit observation.

Cole and Cole\textsuperscript{18} has devised an alternative method, in which the charging current of the condenser containing the dielectric, is observed. This method is capable of being slightly better than that described first.

For frequencies, in the range audio to high range (\(10^2\) to \(10^7\) c/s) in the measurement of dielectric constant, though there are many bridges used, but due to capability of giving direct calibrated reading of "\(\tan \delta\)" up to higher frequency ranges, "shearing bridge" is used commonly. For reducing the stray capacitances from earth, a standard capacitor
is also used with it, to ensure Wagner earth. This avoids earth currents, which would otherwise arise in an actual connection. For frequencies, in the range of 10 Mc/s to 100 Mc/s bridge methods are generally difficult to the increasing importance of the effects of stray capacitance.

In the very high frequency range 100-1000 Mc/s, the tuned-circuit technique can not be employed, because of the impossibility of realizing a lumped resonant circuit and therefore, distributed circuits are used, the common form of these are transmission lines and wave guides. The transmission line methods are generally used for the measurement of permittivity or dielectric constant, as the wave guides are inconveniently bulky in the very high frequency range. In the frequency range above 100 Mc/s, it becomes desirable to use waveguide or "cavity resonator technique".

There are also other methods for measuring dielectric constant at microwave frequencies.

6.6 : Present Method :

In the present investigation, the experimental technique used, has been undertaken to measure permittivity and dielectric loss as a function of frequency and temperature. Attention has been paid to lower frequencies and temperature range, (323 - 453 K). The method is quite simple and consists of following parts -
(a) Film Preparation:

The sample in the form of thin films (20 μm thick) of PMMA (2.1 gms) + Malachite Green (100 mg) has been prepared as described earlier in chapter II. They were sandwiched between vacuum deposited electrodes.

(b) Apparatus Used:

A suitable two terminal assembly made of brass and rectangular holder, employing the principle of embedded electrodes, has been used for the measurement, in the present investigation.

Dielectric constant of any substance depends on the temperature, hence it becomes necessary to obtain the stability of temperature during the course of measurements. This was attained by the use of a thermostat. In the present work the method of thermoelectrets preparation was similar to that one adopted previously for other studies.

The dielectric measurements were performed using a "Radart Impedence Bridge". For variation of frequency of measurement a "Radart Frequency Generator" was used.

Capacitance measurements were carried out by putting a sample in an assembly, the temperature of which was controlled by an auto-transformer.
6.7: Procedure:

The following procedure was adopted to measure the complex dielectric constant as a function of frequency and temperature. Two terminal binding post connections have been used for all the measurements. The capacitance and dissipation factor of the sample PMMA and composite (PMMA + Malachite Green) have been observed as follows -

The two main electrode of the cell are connected across the two large terminals. The connecting leads should be kept as short as possible in order to avoid introducing stray capacitance and hum pick-up will obscure the balance indication. All the connections are made by grounded and shielded leads. The body of the cell and the ground terminal of bridge are also earthed. These connections were grounded to avoid the noise voltage further. Now selecting range, full scale, appropriate to the expected value of capacitance, with the function and range multiplier switches and the sensitivity control is set to give a meter deflection of less then full scale. The bridge is balanced with the main balance and loss balance controls. The capacitance value "C" is obtained on the bridge for the capacitance assembly in-directly.

The bridge is set to measure loss simultaneously with the capacitance measurements at particular frequencies. The
oscillator was set for the desired frequency and the null
detector was tuned to it. The bridge balance was done by
repeated adjustment of capacity selector, capacity and
dissipation knobs till the null detector indicated the least
deflection. The oscillator was then set for the next
frequency and the bridge was balanced in a similar manner.
Temperature effect has also been taken in-to consideration.
After covering the entire frequency range, the temperature
was changed and the measurements were repeated over the entire
frequency range and so on.

Experiment was not started until required temperature
was obtained. The cell was allowed sufficient time to reach
the steady state. Capacity and loss readings of the cell were
noted at different temperature and frequencies.

6.8: Details of Measurement:

Variation of complex dielectric constant and loss are
measured with temperature and frequency. Temperature is used
in the range 323-453K and frequency in the range 200 Hz to
3000 Hz. The frequency is set at a desired temperature and the
steady capacitance is measured. Also at the same frequency,
loss has been observed which is to be multiplied by the
frequency to yield "tan δ " value, where " δ " is the loss
angle. The temperature is raised in steps for whole range and
at each temperature, the thermostat is allowed to attain
thermal equilibrium of sample in about 45 minutes. At each
temperature, the steady value of dielectric loss is measured.
When the whole temperature range is applied, other frequencies
are set on the bridge and the same process is repeated by
varying different temperatures at different frequencies.
At each frequency, fresh sample is used.

6.9 : Results :

Fig. 6.1 to 6.3 represent the capacity (permittivity)
and loss factor ($\varepsilon''$ ) as a function of temperature at a
fixed frequency (200 Hz) for pure PMMA and composite samples
(PMMA + Malachite Green). The capacity (permittivity) of
composites as well as pure PMMA, was found to increase with
temperature from 323 to 433 K at frequency 200 Hz. The
variation with temperature of loss tangents is shown in
figure 6.1(b) and 6.2(b). Loss tangents have two maxima,
i.e. at the temperatures 373 and 423 K losses are maximum.

Fig. 6.2(a) and (b) represent the variation of
capacity and loss tangents with temperature, for different
concentration of Malachite Green (50 mg, 70mg, 100mg by
weight). It is observed that permittivity and loss factor
show slight increase in values as concentration of
Malachite Green is increased. The peak position is shifted
towards the higher temperature side with increase in
concentration.
CAPACITY (PERMITTIVITY) AND LOSS FACTOR VS. TEMPERATURE FOR POLYMETHYL METHACRYLATE FILMS.

FIG: 6.1
CAPACITY AND LOSS FACTOR VS. TEMPERATURE FOR PMMA: MALACHITE GREEN, MATRICES. CURVES 1, 2 & 3 CORRESPOND TO 50 mg, 70 mg, 100 mg MALACHITE GREEN RESPECTIVELY.

FIG: 6.2
CAPACITY AND LOSS FACTOR VS. TEMPERATURE WITH DIFFERENT ELECTRODE SYSTEM FOR COMPOSITE (PMMA + MALACHITE GREEN, 100 mg.) FILMS.

FIG: 6.3
VARIATION OF LOSS FACTOR WITH TEMPERATURE AT DIFFERENT FREQUENCIES FOR COMPOSITE (PMMA + MALACHITE GREEN, 100 mg) FILM.

FIG: 6.4
Fig. (6.3) shows the variation of loss tangents and permittivity with temperature at constant frequency 200 Hz for dissimilar electrode system. Loss tangents show two maxima for similar electrode system (Al-composite-Al) and single loss maxima for dissimilar electrode system (Al-composite/Cu/Ag). It is also observed that magnitude of loss peaks and capacitance values are high in case of different electrodes than in the similar electrode system. Fig. (6.4) exhibits the variation of loss tangents with temperature at different constant frequencies. The magnitude of both the loss peaks was found decreasing as frequency increases.

6.10 : Discussion :

Dielectric measurements have proved to be important techniques in understanding the change in the environment of the molecules, intra molecular interactions and relaxation behaviour in polymeric materials. The addition of impurities, plasticizers, change the dielectric relaxation behaviour of the polymer to a great extent. The dielectric loss measurements are also useful in understanding the phase transition behaviour, relaxation behaviour in polymers.

The polarization of a dielectric material may take place by various processes, and depending upon the process involved, we can categories the polarization in the following
states-orientational polarization, atomic polarization, electronic polarization and the interfacial polarization. The sum of all these components is the total polarization of the dielectric i.e. the dielectric constant.

Electronic polarization is the displacement of electrons with respect to atomic nucleus, to be more precise the displacement under the action of an external electric field of the orbits in which negatively charged electrons move around a positively charged atomic nucleus. Electronic polarization occurs in all atoms or ions and can be observed in all dielectrics irrespective of whether other types of polarization are displayed in the dielectric. One specific feature of electronic polarization is the fact that when an external field is superposed this type of polarization occurs during a very brief interval of time. Ionic polarization is the mutual displacement of ions forming a heteropolar (ionic) molecule. A short time is required for the process of ionic polarization to set in, but longer than for electronic polarization. Both phenomena may be regarded as the varieties of polarization caused by deformation. Polar dielectrics exhibit a tendency towards dipole or orientational polarization. Dipole polarization can appear in a pure form in amorphous viscous bodies. Interfacial polarization is the accumulation of electric charges on the interfaces of inhomogeneities. Migrational polarization setting processes are comparatively slow and can take minutes or even hours.
Dipole polarization requires a relatively long time as compared with that of practically almost inertialess phenomenon of deformational polarization. Therefore the dielectric constant of non-polar polymers remains invariable with frequency. In case of polar polymers, the dielectric constant begins to drop at a certain critical frequency and at high frequencies, it approaches the values typical of non-polar dielectrics.

Heating of a dielectric material causes the expansion of the lattice\(^\text{51}\) and therefore, the ratio of the number of molecules to the effective length of the dielectric decreases and this in turn should decrease the dielectric constant with temperature, but in case of polymers because of the presence of dipoles, the permittivity changes the behaviour and the dielectric constant increases with temperature. In the present study also the dielectric constant of pure PMMA and composite increases with increasing temperature. This can be explained on the basis of increase in molecular mobility. At low temperature the mobility of the molecules is less and the number of dipoles orienting with the field will also be less but as the temperature increases the molecular mobility also increases and causes more and more dipoles to orient in the direction of the field and therefore, the dielectric constant also increases with increasing temperature.
The nature of dependence of capacitance on temperature may be different in case of ionic mechanism. In most cases, an ionic mechanism of polarization results in increased capacitance when the temperature grows. Rise of permittivity (and hence the dielectric constant) is due to maximum orientation of dipoles.

In the polar polymers the deformation of the polar chains is responsible for dielectric loss behaviour. The internal movement of the molecular chains is also responsible for the dielectric loss of the material. At higher temperature specially at glass transition temperature, the segmental motions become prominent, whereas, at low temperatures these are less significant.

In the present dielectric loss studies, two peaks are observed at two different temperature for various frequencies. The first loss peak is obtained near about the glass transition temperature while the second peak is obtained at temperature 423K. This loss peak seems to be associated with the orientational rotation of the polar units of macromolecule, where segmental motion is possible, i.e. rubber like state (above Tg) of the polymer, and the first low temperature loss peak might be due to the orientation of the polar groups themselves or in other words, we can call peak as a dipolar one. It is also possible that the relaxation may take place due to
the rotation of backbone chain segments. This is termed as local mode relaxation by Okano.\textsuperscript{52}

Large amplitude rotational vibrations of the backbone segments become incoherent among neighbourhood chains. When the polymer is strained the distance between the chains is changed and distribution of the rotational displacement goes to a new equilibrium with a corresponding relaxation time. In composite the dielectric constant increases with increasing temperature which can be explained on the basis of increase in dipolar orientation due to the increase in molecular mobility.

There are two peaks observed in TSDC thermograms. The location is comparable with peaks of thermally stimulated discharge current.

A polymer may posses crystalline and amorphour phases. In the crystalline region,\textsuperscript{42} the molecules are found with equilibrium position with each other. In the amorphous region, the dipoles can orient rather easily from one equilibrium to the other equilibrium position. In the present study the composite films grown by solution technique might also be a mixture of crystalline and amorphous region. Because of the amorphous nature of films, the Vander Wall's force is weak and binding force will also be weak. This may cause the movement of the segments more easy.
As in present investigation second peak is observed near the temperature 423°K in the frequency range 500 to 2000 Hz. Andrews and Kimmel\textsuperscript{53,54} also observed a high temperature transition in polyacrylenitrile, which lies above glass transition temperature.

Addition of Malachite Green in PMMA enhances the conductivity. The continuous rise in dielectric loss magnitude with Malachite Green may be attributed to the progressively increasing conduction losses of the system. The polar group attached to a side chain, hence the mobility of the chains increases with adding Malachite Green. The polymer chains become more loosely packed and the backbone mobility is increased. The presence of guest molecules enhances the conductivity of the host matrix and so the doped film exhibits pronounced increase in losses. This effect is greatly magnified when Malachite Green is used as the dopant and consequently the conductivity of the polymer is improved considerably. This explains the low losses at high frequencies observed in the present investigation.

Conclusion:

Permittivity variation with temperature may be assigned to - thermal expansion of matter in lower temperature region, orientation of dipolar molecules in the neighbourhood of Tg., random disorriented motion of molecules at higher temperature
and release of charge carriers from deep traps at high temperature. Loss tangents have two maxima (at 373 and 423 K) for various frequencies. Second loss peak seems to be associated with the orientation rotation of the polar units of macromolecule where segmental motion is possible, i.e., rubber-like state (above Tg) of the polymer. Addition of Malachite Green in PMMA: Malachite Green matrices enhances the conductivity. The continuous rise in dielectric parameters may be attributed to the progressively increasing conduction losses of the system. The presence of guest molecules enhances the conductivity of the host matrix and so the doped film exhibits pronounced increase in parameters.
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