Chapter-4

Dielectric properties
DIELECTRIC PROPERTIES

4.1 Introduction

The dielectric behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction through such films and their applications in capacitors for microelectronics. To obtain high values of capacitance, the dielectric constant should be high and the thickness be small. Due to the difficulty of obtaining structurally continuous and stable ultra thin films, capacitor applications are generally limited to thick films.

The evaluation of dielectric properties of insulator films (317-321) is carried out by measuring simultaneously the capacitance and the dissipation factor over a wide range of frequencies and temperatures. As all the other electrical parameters of dielectrics, the permittivity depends on the changeably external factors such as the frequency of voltage application, temperature, pressure, humidity etc. In a number of cases these dependences are of great practical importance.

Recently dielectric properties of several polymers (322-341) polar and non-polar have been investigated. Some general relations between dielectric properties have been
discussed, distinguishing between resonance phenomena that commonly occur in the optical region and relaxation phenomena which occur in polymers at the lower frequency regions. It has been shown how the real and imaginary parts of the complex constant depends primarily on the density, but little is known regarding the nature of the dielectric loss. Attention has also been paid to polar polymers. After some preliminary remarks on the nature of dielectric dispersions, some phenomenological notions of dielectric dispersions have been considered. Attempts have been made to relate theory and practice. The topics, such as phase transitions, anisotropy and inhomogeneity have been dealt with.

Dielectric relaxations in polyvinyladene fluoride were studied by Sasabe et al. They observed three distinct absorption peaks (α, β, γ) in the frequency range from 0.1 to 300Hz in the temperature range -66 to 100°C. The γ absorption is related to molecular motion in the crystalline region. The β absorption can be interpreted as due to the micro-Brownian motion of the amorphous main chains. The α absorption is attributed to local oscillations of the frozen main chains, Kakutani and Ashina (325) studied low-temperature absorption of polyvinyl chloride and concluded that, the γ and β processes are the result of molecular
motion in crystalline and amorphous regions of the polymer respectively. Low temperature dielectric relaxation in polyethylene and related hydrocarbon polymers was investigated by Phillips (342). He uses a simple quantum mechanical model of relaxation process to explain the experimental results. According to this process, a particle in a double potential well tunnels from one well to the other with emission or absorption of a phonon. Results of Kawamura et al. (322) on dielectric properties of co-polymer of methyl-methacrylate with n-bityl methacrylate lead to the following conclusions.

1. The loss peak temperature attributed to side chain relaxation varies with the comonomer ratio when the comonomer does not have a methyl group but remains almost unchanged for comonomer having methyl group.

2. In both cases, the β-peak (height) decrease with increasing ratio of comonomer. It is suggested on the basis of the above facts that the moving unit in the side chain relaxation consists of single side chain with a segment of the backbone chain and that the change in mobility of the side chain upon copolymerization results from the distortion of the helical structure of the backbone chain due to random distribution
of methyl groups.

Though there is a wide literature available on dielectric properties of polymers, yet a few reports (343-345) exist on impurity doped polymers. Kokasi and Ieda (343) have doped high and low density polyethylene. One of them has the loss maximum dependent on the amount of the impurity and is related to the relaxation of a dipole orientation of the impurity. Another shows an odd behavior named retrogressing phenomenon near the melting point of polyethylene and can not be detected in the amorphous polystyrene doped with the same impurity. An interfacial polarization is proposed assuming a model which is justified semi-quantitatively. The retrogressing phenomenon is explained by the change of the layer thickness that affects the dielectric relaxation time of the model. Kulshretha and Srivastava (344) doped polystyrene with chloranil and Srivastava et al (345) with copperphthalocyanine and observed interfacial polarization in the measurement of dielectric losses of the polymer.

Less has been reported on dielectric properties of doped PS (346) and it seems to carry out further investigations to understand the dielectric behaviour of the doped polymer. This
FIG 4.1 Capacitance Vs frequency at different temperatures for PS and I, it also shows effect of iodine concentration at 30°C
Fig. 4.2 Capacitance Vs Temperature for PS & For $I_1, I_2, I_3$
FIG 4.3 Capacitance Vs Iodine Concentration of various Temperatures
Fig. 4.4 Loss tangent Vs Temperature at various frequencies depicting for PS & For $I_1$, & $I_3$. 
chapter reports on capacitance and dielectric loss factor of iodine doped PS films as a function of temperature and frequency in audio frequency range.

4.2 Results

Dielectric properties of polymers are investigated by measuring simultaneously the capacitance and the losses at regularly varying temperature and frequency. Capacitance as a function of frequency for PS and I$_1$ at 30, 90 and 120$^0$C is shown in Fig 4.1. Fig. 4.2 also shows the effect of iodine concentration at 30$^0$C. There is no variation in capacitance with the frequency in the range (0-15 KHz). Due to increase in temperature capacitance increase. Similar results were also found for other concentrations of iodine incorporation. Due to doping capacitance is increased which is further increased due to increase in iodine loading. Fig.4.3 exhibits capacitance versus iodine concentration at 30, 60, 90 and 120$^0$C temperatures. Capacitance increases with the increase in iodine concentration as well as with the increase in temperature. Fig 4.4 illustrates the effect of concentration of iodine incorporation in PS on tan$\delta$ (loss tangent) versus temperature at 2kHz. For the sake of comparison the plot for pure
PS film has also been included in fig 4.4. For PS a loss maxima at 85°C is observed. Due to doping, this loss maxima is shifted to a lower temperature. For concentrations I₁ and I₃ the loss maxima occurs at 78, and 70°C respectively. Loss is increased due to doping which is further increased due to increase in dopant concentration. It is also clear from fig 4.4 that due to decrease in frequency dielectric loss is increased and the loss maxima shifts to a lower temperature. Fig 4.5 shows tanδ versus iodine concentration at 30°C and at a frequency of 2kHz. The plot is a straight line. In fig. 4.6 log $f_{\text{max}}$ versus $10^3/T$ has been plotted for PS and I₁. The plots are straight lines. The value of activation energy is calculated to be 0.72eV for pure PS and 1.12eV for doped PS. Due to doping activation energy is increased. Due to increase in iodine concentration there was no regular and significant difference in activation energy.

4.3 Discussion:

Permittivity is the basic parameter of a dielectric describing its properties from the view point of the process of its polarization or propagation of electromagnetic waves in it, or more generally from the point of view of the processes of its interaction with an electric field. Permittivity is a macroscopic
parameter of a dielectric which reflects the properties of a given substance in a sufficiently large volume but not the properties of the separate atoms and molecules in the substance. There are three well-known types of polarization: Electronic, ionic and dipole polarization.

Electronic polarization is the displacement of electrons with respect to the atomic nucleus, to be more precise the displacement under the action of an external field of the orbits in which negatively charge electrons move around a positively charged nucleus. This type of polarization occurs in all atoms or ions and can be observed in all dielectric irrespective of whether other types of polarization are displayed in the dielectrics. One specific feature of electronic polarization is the fact that when an external field is superposed, this type of polarization occurs in a very short interval of time (of the order of $10^{-15}$ seconds) i.e. the time of the period of oscillation of ultraviolet rays.

Ionic polarization is the mutual displacement of ions forming heteropolar (ionic) molecules. A shorter time is required for the process of ionic polarization to set in, but is longer than that of electronic polarization, i.e. $10^{-13}$ - $10^{-12}$ seconds. On the
whole the process of electronic and ionic polarization have much in common. Both phenomena may be regarded as the varieties of polarization caused by deformation which is a displacement of charges with respect to each other in the direction of the field. Apart from a very high velocity mentioned above with which the state of polarization sets in, it is important to bear in mind that the process of deformational polarization is practically unaffected by the temperature of the dielectric and is not connected with an irreversible dissipation of energy. The electric energy required to polarize a molecule is completely returned to the energy source after the voltage is removed. For this reason deformational polarization does not entail any dielectric losses.

Polar dielectrics (347-350) exhibit a tendency towards dipole or orientational polarization. The essence of this kind of polarization can be reduced in a simplified manner, as has been first suggested by Debye, to the rotation of the molecules of a polar dielectric having a constant dipole moment in the direction of field. If orientational polarization is considered more strictly, it must be understood as the introduction by an electric field of certain orderliness in the position of polar molecules being in uninterrupted chaotic ‘thermal’ motion, and not as a
direct rotation of polar molecules under the action of a field. For this reason, dipole polarization is connected by its nature with the thermal motion of molecules, and temperature must exert an appreciable effect on the phenomenon of dipole polarization.

After a dielectric is energized, the process of establishing a dipole polarization requires a relatively long time as compared with practically almost inertialess phenomena of deformational polarization. More or less time is needed in any individual case. As distinct from deformational polarization, dipole polarization and also other kinds of relaxation polarization dissipate electric energy which transforms into heat in a dielectri,

i.e. this energy causes dielectric losses.

In polymers dielectric loss behaviour may be attributed to the deformation of polymer chains (351-353). The molecular flexibility of chains are responsible for this characteristic property of the polymers. The other important mechanism for the dielectric losses in the polymers is considered to be the internal motions or the local movements of the molecular chains of the polymer. At high temperature, especially at the glass transition temperature of the polymer such segmental
motions are prominent. However, at low temperature these motions become less significant.

4.3 (a) Frequency Dependence of Capacitance:

The capacitance and hence the dielectric constant of (fig. 4.1) iodine doped PS remains constant with the change in frequency. This is so because the polarization settles itself during a very short period of time as compared with the time of voltage sign change. Dielectric constant of non polar polymers remains invariable with frequency. In case of polar polymers, the dielectric begins to drop at a certain critical frequency and at very high frequencies it approaches the values typical of non polar polymers. In amorphous polymers structural polarization (i.e. related to the loose structure of matter) is also possible. For this type of polarization, the capacitance falls with the increase in frequency (354).

4.3 (b) Temperature Dependence of Capacitance:-

The increase in capacitance above the room temperature (Fig. 4.2 & 4.3) may be partly due to the expansion of the lattice and partly due to an ionic mechanism of polarization. The molecules can not orient themselves in polar dielectric (355)
FIG 4.5 Loss tangent Vs iodine Concentration at 30°C and at a frequency of 2KHz.
in the low temperature region. When the temperature rises, the orientation of dipoles is facilitated and this increases dielectric constant. Addition of iodine may form charge transfer (CT) complexes with the polymer and so the increase in capacitance with temperature is enhanced.

4.3 (c) Variation in loss Tangent :-

Temperature transition corresponding to Alpha relaxation process has been observed near the glass transition temperature of PS (Fig. 4.4 & 4.5). The Alpha-relaxation process in polymer is observed at temperatures above the glass transition of the polymer. Though at glass transition temperature the segmental motion is expected but at the temperatures above the glass transition temperature some thing larger than segments and possibly the entire molecular chain motion is expected. Polymers are considered to be the mixtures of amorphous and crystalline regions. Above the glass transition temperature they seem to loose the intermolecular cohesive bondings and the association and dissociation processes involved are governed by thermodynamical equilibrium. Therefore, Alpha-relaxation process may be attributed to the motion of the more mobile molecular chains in which the intermolecular forces between the crystalline
FIG 4.6 Log Fmax Vs $10^3/T$ for PS and $I_1$
regions are weakened due to thermally activated process. This weakening of forces causes the motion of the entire molecular chain and hence the occurrence of Alpha-relaxation.

Incorporation of iodine in PS softens the viscosity of the system and causes the Alpha-relaxation to shift to the region of lower temperature. The view is further supported by the observation that the increase in iodine concentration has an effect of displacing the loss maxima to a lower temperature.

Logarithm of frequency at which loss maxima occurs, has been plotted against inverse absolute temperature in (fig 4.6) for pure and iodine doped PS films. The activation energy is calculated to be 0.72 eV for PS and 1.12 eV for $I_1$. Incorporation of iodine has an effect of increasing the activation energy. Besides molecular chain movements, the losses also occur due to electrical conduction which increase with the decrease of frequency. This is also what has been observed presently. Mixing of iodine in PS increases the conductivity of the film and so the doped films exhibit more pronounced increase in losses with the decrease of frequency.
4.4 Conclusions:

The present investigation on dielectric behaviour of pure and iodine doped PS films helps to conclude:

(1) Dipole polarization involving ionic motion is prominent in PS. Doping of the matrix with iodine enhances the process of polarization.

(2) The Alpha-relaxation in the polymer is due to the motion of polymer chains. Addition of iodine reduces the viscosity of the system shifting Alpha-relaxation peak to lower temperature.

(3) Doping causes conduction losses.

(4) Above the glass transition temperature of the polymer, main chains are mobilized and the mobilization is facilitated due to incorporation of iodine.

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