CHAPTER - V

DIELECTRIC BEHAVIOUR
5.1 Introduction

There are large number of reports on dielectric relaxation studies made on polar/nonpolar polymers listing various techniques (1-8). The evaluation of dielectric properties of films is carried out by measuring simultaneously the capacitance and the dissipation factor (9). Like all other electrical parameters of dielectrics, the permittivity, depends on the variable external factors such as frequency, voltage applied to the dielectric, temperature, pressure and humidity. These dependence is of great importance in understanding the dielectric relaxation. Dielectric relaxation can also be studied with the TSDC data of the samples. Previous chapter in the present thesis describes the results and there interpretation of the TSDC of PMMA samples mixed with PVP₂ in different percentage by weight. It has been suggested on the basis of the above studies that dipolar peak is made by peak because of migration of charges over microscopic distance and their subsequent trapping. Such an effect produces induced dipoles which are electronic as well ionic (10-13).

In order to confirm the results of TSDC studies capacitance measurements of different sample containing
varying proportion of PVF₂ ranging from 10% to 90% have been undertaken. Measurements have been done at different frequencies starting from 100 Hz to 1 MHz. The temperature was varied from 30°C to 140°C. The experimental set up and electrode assembly has been described in chapter II.

5.2 (1) Capacity Variation with Frequency

(1) Figure 5.1 shows variation of capacity with frequency for sample P₁ containing 90% of PMMA and 10% PVF₂ by weight in the frequency range from 100 Hz to 1 MHz for temperature 30°C, 40°C, 60°C, 80°C, 100°C and 120°C. The capacity decreases with frequency for all temperatures. The fall in the value of capacity for temperature 30°C and 40°C with frequency is a bit slower on the otherhand the fall in the capacity is faster for temperatures corresponding to 60°C, 80°C, 100°C and 120°C. Maximum change in capacity with frequency occurs at 60°C.

(2) Figure 5.2 shows the variation of capacity with frequency for sample P₂ containing 80% of PMMA and 20% PVF₂ by weight in the same frequency and temperature as in (P₁). Here the capacity decreases with frequency. For temperatures 30°C, 40°C and 60°C the decrease in capacity with frequency is smaller corresponding to that
which takes place for $100^\circ C$, $120^\circ C$ and $140^\circ C$. The rate at which capacity falls with frequency for temperature up to $60^\circ C$ is slower as compared to that which takes place for temperature greater than $60^\circ C$.

(3) Figure 5.3 represents variation of capacity with frequency for sample $P_3$ having 70% PMMA and 30% PVF$_2$ for the same range of frequency and at temperatures as mentioned above the fall in the capacity corresponding to all the temperatures is faster as compared to fall in the value of capacity with frequency for samples $P_1$ and $P_2$. The maximum charge corresponds to $140^\circ C$ temperature.

(4) Figure 5.4 (a), (b) gives the change in capacity with frequency for samples $P_4$ containing 50% PMMA and 50% PVF$_2$. The change in capacity corresponding to the temperature $40^\circ C$ and $60^\circ C$ is small and it shows a saturation with frequency and that for temperatures $80^\circ C$, $100^\circ C$, $120^\circ C$ and $140^\circ C$, the change in capacity is large and takes place at a faster rate.

(5) The same pattern in the change of capacity with frequency is found for samples $P_5$ with 30% PMMA and 70% PVF$_2$ as found for samples $P_4$ and described in (4) above. It is shown in figure (5.5).
(11) **Capacity Variation with Temperature**

(1) The temperature variation of capacity at different frequency is represented in figures 5.6. Figure shows temperature variation for frequencies 100 Hz to 1 MHz. The capacity first increases with temperature initially for temperature up to 40°C and then it decreases in the temperature range 40°C to 60°C and then again increases up to 100°C, showing a maxima at 100°C and then decreases and falls to a low value at 120°C. This feature is noted for the entire frequency range of 100 Hz to 1 MHz.

(2) For sample P₂ in which content of PVF₂ is increased by 10% and that of PMMA is decreased by 10%, the temperature variation of capacity is represented in figure 5.7 (a) (b). The capacity increases up to the temperature 80°C and then increases very fast up to 100°C and then increase becomes slower. This feature was noted for the entire frequency range.

(3) Sample P₃ which contains still larger percentage of PVF₂ than that for P₂ sample. Here the capacity increases with the temperature up to 120°C for the entire frequency range (Figure 5.8 (a), (b)). The rate of increase falls as the frequency is increased. At 1 MHz the capacity remains almost constant showing a very small increase with temperature.
(4) For sample containing 50% PMMA and 50% PVF₂ i.e. sample P₄, the capacity decreases with temperature for frequency beyond 1 KHz. At lower frequency i.e. 100 Hz, the capacity instead of decrease, shows an increase with temperature after showing tendency of decrement at 40°C.

(5) The maximum percentage of PVF₂ was increased upto 70% and samples prepared thus contained 30% PMMA. These samples (P₅) show an increase in the value of capacity for the entire range of frequency. The increase noted was highest for 100 Hz and as the frequency is increased, the rate of increase is decreased. The variation of capacity for these sample is shown in figure 5.9(a),(b).

(iii) Dielectric Loss Variation with Frequency

(1) The dielectric loss variation of sample number P₁ recorded with frequency is shown in Figure 5.10 for different temperatures. The dielectric loss increases with frequency and attains a maximum value at 3.16 KHz for temperature 30°C and 40°C. The position of maxima of the dielectric loss changes corresponding to temperatures 60°C, 80°C and 100°C and occurs at 5.62 KHz. For 120°C the position of maxima shift to 10 KHz.
(2) For sample number P₂, the dielectric loss increases with frequency as for sample number P₁. The position of maxima occurs at frequency 56.2 KHz for temperature 30° C. The dielectric loss increases with frequency and attains a maximum value at frequency 31.6 KHz and then decreases with frequency upto 100 KHz and again starts increasing with frequency for temperature 40 and 60° C. This maxima shifts to lower frequency corresponding to temperature 80, 100 and 120° C. An increase in loss with frequency is noticed for these temperatures beyond 100 KHz (Figure 5.11).

(3) Sample P₃ which contained 30% PVF₂ and 70% PMMA shows a maxima in dielectric loss at frequency 3.16 KHz for temperature 30, 40, 60 and 80° C and again shows an increase with frequency with a minima which varies for each temperature i.e. for 30° C the minima occurs at 20 KHz for 40° C, 60° C and 80° C it shifts to 10 KHz (Figure 14). For 100° C and 120° C no clear maxima is seen but a shoulder occurring at 2 KHz and 1 KHz respectively is seen. The minima shifts to 1 KHz for 140° C temperature. The dielectric loss shows an increase with frequency with a minima at 100 KHz for 80° C and 140° C. No minima is seen corresponding to temperature 100 and 120° C (Figure 5.12).
(4) A similar behaviour is seen for sample number $P_4$ in dielectric loss variation with frequency. For $40^\circ C$ the maxima occurs at 18 KHz and that for $30^\circ C$ and $60^\circ C$, the maxima is seen at frequency 51 KHz, while the position for maximum is found at 6 KHz for $140^\circ C$. The dielectric loss decreases with frequency for temperature 30, 40, 60 and $140^\circ C$ beyond the respective maxima position of the frequency. A similar pattern frequency variation of dielectric loss is seen corresponding to the temperature $80^\circ C$, $100^\circ C$ and $120^\circ C$ except that the position of maxima for temperature $80^\circ C$ is 30 KHz and that for $100^\circ C$ and $125^\circ C$ its is found at 20 KHz (Figure 5.13).

(5) The dielectric loss variation with frequency for sample $P_5$ corresponding to temperature $30^\circ C$, $40^\circ C$, $60^\circ C$ and $80^\circ C$ shows an increase in the region of frequency 100 KHz to 3.16 KHz and then decrement in the dielectric loss occurs with frequency for sample $P_5$. The position of minima for $30^\circ C$ occurs at 8 KHz and for $40^\circ C$ its occurs at 16 KHz and for $60^\circ C$ it is found at 30 KHz and that for $80^\circ C$ it is found at 50 KHz. Another peak is found at frequency at 550 KHz for temperature $30^\circ C$. Similar pattern in dielectric loss variation is seen at $100^\circ C$, $120^\circ C$ and $140^\circ C$. The position of maxima for $100^\circ C$ occurs at 30 KHz and that for $120^\circ C$ and $140^\circ C$ it is found at 1 KHz. The
dielectric loss shows a decrement with frequency beyond the frequency at which maxima occurs and attains a minimum value at frequency at 100 kHz for temperature 100°C, 120°C and 140°C (Figure 5.14).

(6) It is very difficult to find out the dielectric loss behaviour for sample P1 with temperature in the low frequency region because experimental setup did not respond correctly at low frequencies. There is tendency of dielectric loss to increase with temperature, attaining a maximum value at 100°C in the frequency region 100 Hz to 5.62 KHz and then full to a low value beyond this temperature (Graphs not shown).

(7) Figure (5.15) represents temperature variation for sample number P1. A clear maxima occurring at 100°C is seen for frequencies above 10 KHz and upto 562 KHz. It is only at 1 MHz that two maxima are seen, one occurring at 40°C and the other at 80°C.

(8) For sample number P2, the temperature variation of dielectric loss shows a remarkable change from that found for P1. For the entire range of frequency i.e. from 31.6 KHz to 1 MHz, one distinct maxima was found occurring at 40°C was found. The loss was found to be minimum at 80°C for entire range of frequency (Figure 5.16 (a),(b)).
Fig. 5.1: Shows variation of capacity with frequency for sample $P_1$ (PMMA 90%, PVF$_2$ 10%).
Fig. 5.2: Shows variation of capacity with frequency for sample $P_2$ (PMMA 80%, PVF$_2$ 20%).
Fig. 5.3: Shows variation of capacity with frequency for sample P_3 (PMMA 70%, PVF_2 30%).
Fig. 5.4 (a): Shows variation of capacity with frequency for sample $P_4$ (PMMA 50%, PVF$_2$ 50%).
Fig. 5.4 (b): Shows variation of capacity with frequency for sample $P_4$ (PMMA 50%, PVF$_2$ 50%).
Fig. 5.5: Shows variation of capacity with frequency for sample $P_5$ (PMMA 30%, PVF$_2$ 70%).
Fig. 5.6: Shows variation of capacity with temperature for sample $P_1$ (PMMA 90%, PVF$_2$ 10%).
Fig. 5.7(a): Shows variation of capacity with temperature for sample $P_2$ (PMMA 80%, PVF$_2$ 20%).
Fig. 5.7(b): Shows variation of capacity with temperature for sample P₂ (PMMA 80%, PVF₂ 20%).
Fig. 5.8(a) shows variation of capacity with temperature for sample P₃ (PMMA 70%, PVF₂ 30%).
Fig. 5.8(b): Shows variation of capacity with temperature for sample $P_3$ (PMMA 70%, PVF$_2$ 30%).
Fig. 5.9(a): Shows variation of capacity with temperature for sample $P_5$ (PMMA 30%, PVF$_2$ 70%).
Fig. 5.9(b): Shows variation of capacity with temperature for sample P₅ (PMMA 30%, PVF₂ 70%).
Fig. 5.10: Shows variation of dielectric loss with frequency for sample $P_1$ (PMMA 90%, PVF$_2$ 10%).
Fig. 5.11: Shows variation of dielectric loss with frequency for sample $P_2$ (PMMA 80%, PVF$_2$ 20%).
Fig. 5.12: Shows variation of dielectric loss with frequency for sample $P_3$ (PMMA 70%, PVF$_2$ 30%).
Fig. 5.13: Shows variation of dielectric loss with frequency for sample P₄ (PMMA 50%, PVP₂ 50%).
Fig. 5.14: Shows variation of dielectric loss with frequency for sample $P_5$ (PMMA 30%, PVF$_2$ 70%).
Fig. 5.15: Shows variation of dielectric loss with temperature for sample $P_1$ (PMMA 90%, $PVP_2$ 10%).
Fig. 5.16(a): Shows variation of dielectric loss with temperature for sample P₂ (PMMA 80%, PVF₂ 20%).
Fig. 5.16(b) : Shows variation of dielectric loss with temperature for sample $P_2$ (PMMA 80%, PVP 20%).
Fig. 5.17(a): Shows variation of dielectric loss with temperature for sample P₃ (PMMA 70%, PVF₂ 30%).
Fig. 5.17(b): Shows variation of dielectric loss with temperature for sample P₃ (PMMA 70%, PVF₂ 30%).
(9) Dielectric loss vs temperature graph for sample P3 is represented in Figure 5.17 (a), (b). At lower frequencies i.e. from 100 Hz to 1 KHz, the loss rises very fast attaining a maximum value at 140°C. The loss behaviour curve is also seen to rise up to 100°C and very fast and thin rise is showed down for remaining range of frequency i.e. from 1 KHz to 17.8 KHz. For higher ranges of frequency (31.6 - 178 KHz) the rise noticed is very fast up to 45°C and then it shows down. The variation in dielectric loss with temperature for frequencies 316 KHz, and 1 MHz is almost linear and increases with temperature.

Discussion

As can be seen from the results described above that the capacitance i.e. dielectric constant, for all the sample decreases with frequency. The slow decrease of capacity for samples containing smaller percentage of PVF2 in the lower temperature region and a faster decrease in dielectric constant in the higher temperature region, is indicative of the fact that process of polarisation follows Debye relaxation patterns (14). The same behaviour has been seen in all the samples except the value of dielectric constants is highest for samples containing 70% PVF2 and 30% PMMA.
One of the striking features of dielectrics is the relationship between dielectric constant and dielectric losses with frequency. Each type of polarisation has a particular frequency range at which it responds quickly. Only in this range of frequency they show proper variations in dielectric constants and losses \((15,16)\). When a dielectric is subjected to an alternating field, the polarisation and displacement vectors vary periodically but due to absorption, they lag behind in phase with the applied field resulting in complex form of dielectric constant. This complex dielectric constant \(\varepsilon^*\) is made of real and an imaginary parts as

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]  

(1)

where \(\varepsilon'\) is the real dielectric constant, which is observed as change in the value of capacitance and \(\varepsilon''\) is the dielectric loss related with the real part by a relation

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(2)

According to classical equations of Debye (14)

\[
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\gamma}
\]  

(3)

Comparing equations (1) and (3) and separating real and imaginary parts we have

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\gamma^2}
\]  

(4)
\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty) \omega \gamma}{1 + \omega^2 \gamma^2}
\]

where \(\varepsilon_0\) is the static dielectric constant and \(\varepsilon_\infty\) is the optical dielectric constant \(\gamma\) is the relaxation time for phenomenon responsible for polarisation. If \(\omega < \frac{1}{\gamma}\), then \(\varepsilon'\) approaches \(\varepsilon_0\) and for \(\omega > \frac{1}{\gamma}\) approaches which follows that dipoles are no longer able to follow the field. Thus with increase in frequency the relaxation spectrum is characterised by a constant valued followed by a slow fall of dielectric constant (capacitance) to a low value and shows a broad peak.

As can be seen from variation of dielectric loss with frequency for all the samples, a dielectric loss peak is seen at some frequency. No correlation is seen between the frequency and dielectric loss with percentage variation of 1PFP. Thus it is inferred that dielectric loss peak is not related to structural relaxation of the sample. For sample containing highest percentage of PMMA i.e. sample 1P loss peak is found at lowest frequency of 3.16 KHz for 30°C and 40°C and it shifts to higher frequency for higher temperature. This behaviour corresponds to conduction losses connected with charges which are trapped at the crystalline amorphous interface of the material. Maximum dielectric loss was found for sample containing highest percentage of
PVF$_2$ at 120° C. This may be because of decrease of concentration of charge carriers in traps and barrier layers (17). Mahendru et al. (18) has observed that strong temperature dependence of dielectric constant and dielectric loss starts at high temperature of high frequencies. They have shown that when there is strong temperature dependence of capacity i.e. dielectric constant $\varepsilon'$ at a given frequency, the A.C. electrical conductivity approaches the d.c. electrical conductivity. This again leads as to conclude that the polarisation behaviour is because of induced dipoles which originates from trapping of charge carriers. This polarisation gets weakened as the trapped charge carriers are released from their traps at higher temperature.

From figure 5 showing variation of capacitance with frequency at different fixed temperature it is seen that for some samples P$_1$, P$_2$ and P$_4$ the value of capacitance approaches a saturation region. For samples P$_3$ and P$_5$ through the capacitance does not show saturation but the value of capacitance shows a tendency to attain the same value, at higher frequency. This value of capacitance corresponds to static dielectric constant.

It is seen from dielectric loss variation with temperature that some samples P$_1$, P$_2$ show two peaks, one in the neighbourhood of 60° C and the other in the neighbour-
hood of $110^\circ C$. These two peaks may correspond to the position of two relaxations reported for $PVF_2$. For other samples $P_3$, $P_4$ and $P_5$, these relaxations are completely masked by d.c. conductivity. Similar results have also been reported by Kihira et al. (19). Das Gupta et al. (20) have noted that their results on polymer films of $PVF_2$ are in agreement with trapped charge mechanism for explanation of pyroelectric behaviour of the polymer.

Lovingier et al. (21) have examined the dielectric behaviour of vinylidene fluoride and trifluoroethylene copolymer. They found a disordered structure of the copolymer from the X-ray study. A paraelectric transition occurs from ferroelectric one at high temperature. Alexandrovich et al. (22) have studied the dielectric properties of the blends of polystyrene and poly-2 chlorostyrene. Their results have demonstrated that dielectric relaxation studies are sensitive to the intimacy of mixing and can be used to investigate compatible blends. They found that blends of high molecular weight polymers are heterogeneous while that of low molecular weights polymer are homogeneous.

A normalised dielectric loss curves for the composite samples investigated in the present studies have been drawn (Figure 18-20). As can be seen that the half and three quarter width of normalised curves varies from sample to sample.
The increased breadth of dielectric loss curves of blends has been taken by Wetton et al. (23) and Bank et al. (24) as evidence of for distribution of molecular environment. Other authors have also reported the observation of broadened loss curves for compatible blends (25, 26). Similar phenomenon occur in dynamic mechanical measurements. Nelson observed damping curves to widen with increased chemical heterogeneity of random copolymers (27) and with decreased compatibility of plasticizers (28).

The increase in capacitance with temperature at lower region frequencies observed in the present study may again be attributed to interfacial polarisation. Similar observations have been made by various authors (29-31). Miyamoto (32) analysed his data on pressure dependence study of dielectric constant and dielectric losses of \( \text{PVF}_2 \) and observed that the increase in \( \varepsilon' \) and \( \varepsilon'' \) with temperature in two frequency region can be attributed to interfacial polarisation. Narayana et al. (33) also reported similar results on mixed oxide films and explained them on the basis of interfacial polarisation.

The loss factor is the sum of various dielectric loss processes which includes the loss due to series resistance and capacitance of the electrode. The later contribution perhaps is responsible for the frequency dependent loss.
This is greatly affected by the accumulation of charge layer near the electrode which is very much dependent on the temperature of the specimen and its conductivity.

Two loss peaks have been observed by us in sample $P_1$ at higher frequencies i.e. from 562 Hz. The first peak occurs at 60°C and the other at 100°C. For sample number $P_2$ the first peak shifts to lower temperature and occurs at 40°C while the second peak shifts to higher temperature i.e. 120°C. For sample $P_3$ only one peak is observed at 100°C and there is a tendency for the occurrence of second peak not recorded here. Again for sample number $P_4$ only the second peak occurring at 100°C is seen. For sample number $P_5$, no peak is observed but there is a tendency of the second peak occurring at still higher temperature.

No systematic effect is seen of increasing content of PVF$_2$ in PMMA. Two peaks have also been seen in TSDC around 60°C and 100°C. It seems that addition of PVF$_2$ in PMMA matrix results only in heterogeneous mixture. The mixture presents an easier phase for the transport of charge carriers as such peak shift to lower temperature only the charges trapped in deep traps remained immobile and emptied when the temperature is raised to 120°C. Further addition of PVF$_2$ results in disappearance of first peak which points out to the fact that traps responsible for first peak are destroyed and deep traps
remained intact. The same feature is seen for other samples having high content of the PVF$_2$. The effect of addition of PVF$_2$ is also responsible for increasing the charge density and destruction of shallow traps.

Das Gupta et al. (34) reported well defined peaks in PVF$_2$ occurring at different frequencies corresponding to different temperature varying from 60°C to 120°C as observed by us in sample F$_5$, containing highest percentage of PVF$_2$. They assigned higher temperature peak at low frequencies due to conduction (35). Such dispersions have been observed in low frequency range in nylon (36) polymethyl methacrylate (37) and PET (38), which have been attributed to interfacial or electrode polarisation. Since no electrode dependence has been reported for the absorption currents in PVF$_2$ (39) and because space charge effects have been reported (40,41), then the process involved in dielectric loss behaviour may be due to the motions of space charge trapped at the crystalline/amorphous boundaries.
Fig. 5.18: Shows a variation of frequency with dielectric loss for sample P₅ (PMMA 30%, PVF₂ 70%).
Fig. 5.19: Shows a variation of dielectric loss with frequency $f/f_{\text{max}}$ for sample P₁.
Fig. 5.20: Shows a variation of dielectric loss with temperature $T_{max}^oC/T^oC$ for sample $P_5$. 
REFERENCES


