CHAPTER VII

DIELECTRIC RELAXATION
7.1 Introduction

Polymers are complex dielectric materials. Dielectric studies in polymers are of special interest, since they provide vital information\textsuperscript{1-12} on the molecular configuration of a system; for example - movement of dipoles, losses of energy, segmental motion, conduction mechanism etc. When solid polymeric materials are subjected to an electric field, an induced electric moment is produced. This induced electric moment persists, whenever the field is present. In case, when permanent dipoles are present, an electric field brings about their orientation and polarises the material. The displacement of polar groups require some time and is thus dependent on frequency and temperature, which lead to different dispersion phenomena. Actually at frequencies and temperatures where dispersion occurs, only a part of electrical energy is stored, while some of it is dissipated as heat.

The electrical energy stored per unit cycle is proportional to true permittivity and the energy loss per unit cycle in proportional to imaginary permittivity. The complex dielectric permittivity of a material is defined by the relation\textsuperscript{13}

\[
\varepsilon(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega) \quad \cdots \quad (7.1)
\]
where,

\( \varepsilon' \) - Permittivity and

\( \varepsilon'' \) - Dielectric loss factor

The loss tangent exhibits a maxima at frequencies at which dielectric permittivity shows dispersion. The maxima in dielectric loss occurs at temperatures at which motion of large segments of the chain or different polar side groups begins.

7.2 Theory

Debye gave the equations for the complex permittivity.

The Debye equations are -

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + \omega^2 \tau^2} \tag{7.2}
\]

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

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \tag{7.4}
\]

where,

\( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the complex dielectric constant respectively.

\( \varepsilon_S \) and \( \varepsilon_\infty \) are the static and infinite-frequency dielectric constants respectively. \( \omega \) is the angular frequency and \( \tau \) is the Debye relaxation time given by -
\[ T = \tau_0 \exp \left( -\frac{E}{kT} \right) \quad \ldots \quad (7.5) \]

where,

- \( E \) is the dipolar activation energy and
- \( T \) is the absolute temperature.

Debye derived these equations for a set of non-interacting dipoles free to rotate against some viscous resistance in a fluid-like medium. Polymers show much broader dispersion and low loss as compared to single relaxation processes given by Debye's theory. The broader dispersion nature was explained on the basis of distribution in relaxation times. Many models \(^{15-23}\) have been suggested for the distributed relaxation and losses in polymers, but until now it is far from clear. Cook \(^{24-27}\) et al. analyzed the dielectric behavior of amorphous polymer systems in macroscopic and molecular terms.

7.3 Parameters Affecting Dielectric Constant

(i) Structural changes

These develop into the polymer when it is subjected to an electrical field. \(^{53,54}\)

(ii) Temperature

Debye's \(^{28}\) equation relating to the dielectric constant with structure and temperature of a substance is -
\[ \frac{\varepsilon - 1}{\varepsilon - 2} = \frac{4\pi N}{3} \left( \alpha_0 + \frac{\mu^2}{3kT} \right) \quad (7.6) \]

where,

\[ N = \text{Number of molecules per c.c.} \]
\[ \alpha_0 = \text{Polarizability of the molecule.} \]
\[ \mu = \text{Permanent electric dipole moment of the molecule.} \]

This equation suggests that dielectric constant of polar substances is temperature dependent and that of non-polar substances temperature independent.

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.\(^{29}\)

(iii) Frequency

Polarizability is a function of the frequency of the applied field. Each type of polarization has a particular frequency range at which it responds quickly. Only in this range they show proper variations in dielectric constants and losses\(^{30,31}\) (Fig. 7.1).

Oriental polarization may be out of phase with the applied field, the dipolar motion can no longer follow the applied field. This complexity becomes the cause
FIG. 7.1 -
VARIATION OF PERMITTIVITY WITH FREQUENCY FOR SIMPLE DIELECTRICS.
of complex permittivity of polymers.\textsuperscript{32}

(iv) **Field**

An electric field orients the dipoles of the polar dielectric in all the possible directions parallel, antiparallel or others, depending upon the applied field strength. High dielectric constant and high dielectric losses appear when dipoles align parallel to the field. However, their perpendicular alignment with the field produces almost no dielectric constant.

(v) **Humidity**

Presence of water molecules in dielectric configuration increases the dielectric constant to a considerable amount.\textsuperscript{33} Chatterjee\textsuperscript{34} has done a detailed study about variation of dielectric constant with varying amount of moisture in ebonite and fiber specimens.

(vi) **Pressure**

The related increase per unit increase of pressure is given by -

\[
\frac{d\varepsilon}{dP} = \rho \varepsilon^2
\]  

--- (7.7)
where,
\[ P \] - Pressure,
\[ c \] - capacity,
\[ \varepsilon' \] - permittivity

As the number of molecules per unit volume increases the permittivity of dielectric increases. Smyth and Reihl,\textsuperscript{35} and Shrinivasan and Kay\textsuperscript{36} observed changes in permittivity of organic materials with pressure.

(vii) Impurity

Impurity in polymer produces changes in dielectric constant and dielectric losses of the polymers. Effect of chloronil on polystyren is observed by Shrivastava\textsuperscript{37} et al. Relaxation behaviour of doped poly-carbonate thin film has been studied by Mahendru and Agrawal.\textsuperscript{38}

7.4 Experimental Technique

At the start, temperature of the sample is increased with the help of variac. When it attained required temperature, the sample was allowed to reach the steady state. The oscillator was set at the required frequency and then the null detector tuned to obtain maximum deflection in the meter. This made the bridge very sensitive. The capacitance and dissipation factor levers were then alternately adjusted to get minimum deflection in the meter. Near null point the
sensitivity of the bridge was increased by a small amount and then perfect null was obtained. The capacitance is directly read out in scale while the loss is obtained by multiplying dissipation factor (D) reading with the frequency.

Dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$) of PMMA, PVAc and their Polyblends ($P_2$, $P_4$, $P_6$, $P_8$, $P_{10}$) are measured with temperature range (40 - 200°C) at various frequencies ($2 \times 10^2 - 2 \times 10^3$ Hz).

7.5 Results and Discussion of PMMA and PVAc Polymers

Dielectric relaxation behaviour of PMMA and PVAc has been studied by several works. To understand the effect of blending on the dielectric relaxation behaviour, relaxation behaviour of individual polymers are discussed in the light of reported work.

Figures 7.2 and 7.3 show the variation of dielectric constant and dielectric loss of PMMA with temperature. Increase in dielectric constant is found with increasing temperature (Fig. 7.2). This may be due to the increase in molecular mobility. At temperature below the glass transition temperature, molecules are immobile and, therefore, the number of dipoles which facilitate to orient with the field will be less. Increase in temperature, increases the molecular
FIG: 7.2 - VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR PMMA.
FIG: 7.3 -
VARIATION OF DIELECTRIC LOSS FACTOR $\varepsilon''$ WITH TEMPERATURE AT DIFFERENT FREQUENCIES FOR PMMA.
mobility, therefore, more number of dipoles orient themselves in the field direction, and hence dielectric constant increases.

Another possibility which may take part in increasing the dielectric constant with temperature is excitation of the charge carriers which are likely to be present inside the specimen at the imperfection sites. The amorphous crystalline interfaces may behave as trapping centres for carriers. The molecular chains with different mobilities for the amorphous crystalline regions try to adjust themselves in such a way as to add to the polarization of the system. This molecular alignment of chain may also contribute to the observed increase in capacitance with temperature.

Figure 7.3 shows the variation of loss factor of PEMA with temperature at different frequencies. The magnitude of loss factor maxima ($\epsilon''_{\text{max}}$) increases with frequency and shifts towards the higher temperature side. Tonscher\textsuperscript{50} characterised it as a relaxation process. It was found that\textsuperscript{51,52} a single relaxation peak splits into two peaks with increasing pressure and decreasing temperature (Fig. 7.4). This fact was elucidated to the decoupling of the micro Brownian motion of the main chain and the side chain. At increasing temperature and decreasing pressure, these motions decoupled into segmental motion of the main chain and the side
FIG: 7.4 - VARIATION OF DIELECTRIC LOSS $\varepsilon''$ WITH TEMPERATURE AT HIGH PRESSURE.
FIG. 7.5 - VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR PVAc.
FIG. 7.6 – 
VARIATION OF DIELECTRIC LOSS FACTOR $\varepsilon''$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR PVAc.
chain motions. The pressure of metal ions in the methacrylate side chain causes retardation of the orientation of the segmental dipoles. The valency of the glass transition temperature increases with the increase in the valency of the metal. It might be of interest that independent of $\alpha$ and $\beta$ peaks, at higher temperatures, another absorption appears, which may be related to the D.C. conduction (ionic charge transfer).

Figures 7.5 and 7.6 show dielectric constant and dielectric loss behaviour of PVAc. Dielectric constant initially increases with temperature, but at higher temperature it decreases (Fig. 7.5). Increase in dielectric constant with temperature may have the same cause as that of PMA. Decrease at higher temperature may be attributed to the thermal agitation.

The loss factor maxima of PVAc (Fig. 7.6) does not show any regular variation with temperature or frequency. The independent nature of $\varepsilon''_{\text{max}}$ is suggestive of $\alpha$-relaxation in PVAc.

7.6 Results and Discussion of Polyblends

7.6.1 Results

Figures 7.7 to 7.11 show the variation of dielectric
FIG: 7.7 –
VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR $P_2$. 
FIG. 7.8 - VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR $P_4$. 
FIG. 7.9 - VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR $P_6$. 
FIG. 7.10 -
VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR P$_8$. 

- $2 \times 10^2$ Hz
- $5 \times 10^2$ Hz
- $1 \times 10^3$ Hz
- $2 \times 10^3$ Hz
FIG. 7.11 -
VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR P$_{10}$. 
FIG. 7.12 -
VARIATION OF DIELECTRIC CONSTANT $\varepsilon'$ WITH TEMPERATURE AT $10^3$ Hz FREQUENCY FOR DIFFERENT POLYBLENDS.
constant \( \varepsilon \) with temperature at various frequencies for polyblends. These figures show that the dielectric constant initially increases with temperature, after producing a peak approximately at 70°C - 120°C, it decreases. It has also been found that dielectric constant decreases, when the observations have been taken at higher frequencies.

For the comparison of different polyblends, variation of dielectric constant with temperature is plotted in figure 7.12. This figure shows that below the peak temperature, magnitude of dielectric constant increases with increasing percentage of PVAc in polyblends. Peak temperature is also shifted towards the higher temperature side with decrease in percentage of PVAc in polyblends.

Variation of dielectric loss factor \( \varepsilon'' \) with temperature at various frequencies for different polyblends is shown in Figs. 7.13 to 7.17. Dielectric loss factor \( \varepsilon'' \) initially increases with temperature and after giving a peak it decreases. Below the peak its magnitude is higher for lower frequencies, but after the peak its magnitude is higher for higher frequencies. The magnitude of \( \varepsilon''_{\text{max}} \) is independent of frequency. Figure 7.18 shows this variation for different polyblends at 10 \(^3\) Hz. It has been found that the magnitude of dielectric loss factor decreases and temperature of \( \varepsilon''_{\text{max}} \) increases with decrease in percentage of PVAc in polyblend.
FIG. 7.13 -
VARIATION OF DIELECTRIC LOSS FACTOR $\varepsilon''$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR $P_2$. 
FIG: 7.14 -
VARIATION OF DIELECTRIC LOSS FACTOR ε'' WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR P₄.
FIG: 7.15 -
VARIATION OF DIELECTRIC LOSS FACTOR ε'' WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR P₆.
FIG: 7.16 -
VARIATION OF DIELECTRIC LOSS FACTOR $\varepsilon''$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR P$_8$. 
FIG: 7.17 -
VARIATION OF DIELECTRIC LOSS FACTOR $\varepsilon''$ WITH TEMPERATURE AT VARIOUS FREQUENCIES FOR $P_{10}$. 
FIG. 7.18—
VARIATION OF DIELECTRIC LOSS FACTOR $\varepsilon''$ WITH TEMPERATURE AT $10^3$ Hz FREQUENCY FOR DIFFERENT POLYBLENDS.
Table 7.1: Values of $\varepsilon^', \varepsilon'^{\text{max}}$ and $T^\text{max}$ for PiMA, PVAc and their blends at $10^3$ Hz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon^'$ (at 70°C)</th>
<th>$\varepsilon'^{\text{max}}$</th>
<th>$T^\text{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PiMA</td>
<td>2.4</td>
<td>5.6</td>
<td>130°C</td>
</tr>
<tr>
<td>P2</td>
<td>7.4</td>
<td>6.7</td>
<td>80°C</td>
</tr>
<tr>
<td>P4</td>
<td>6.4</td>
<td>7.0</td>
<td>90°C</td>
</tr>
<tr>
<td>P6</td>
<td>4.5</td>
<td>5.8</td>
<td>110°C</td>
</tr>
<tr>
<td>P8</td>
<td>4.4</td>
<td>5.7</td>
<td>110°C</td>
</tr>
<tr>
<td>P10</td>
<td>3.8</td>
<td>5.0</td>
<td>120°C</td>
</tr>
<tr>
<td>PVAc</td>
<td>6.8</td>
<td>1.9</td>
<td>70°C</td>
</tr>
</tbody>
</table>
7.6.2 Discussion

In polyblends below the peak temperature, dielectric constant increases with temperature. It has the same explanation as that of its constituent polymers, i.e., PMMA and PVAc (§7.5). Increase in the molecular mobility increases the polarization, which is observed as increase in the dielectric constant. The decrease in the dielectric constant with decreasing percentage of PVAc shows that the contribution towards the total polarization decreases with the decrease in the percentage of PVAc.

At higher temperature, drop in dielectric constant is found, as in the case of one of its constituent PVAc. This may be attributed to the thermal agitation (which decreases the polarization), thermal expansion (which decreases the ratio of the number of molecules to the effective length of the dielectric) and to the vigorous motion of the polymer chain. This decrease is higher for the samples having higher weight ratio of PVAc. This suggests that the blending influences greatly the polymer chain motions. Value of dielectric loss (\(\varepsilon\)) in polyblends is higher than that of PMMA and lower than that of PVAc (Table 7.1). Its value decreases as the percentage of PVAc decreases. Dielectric loss behaviour is attributed to the deformation of polymer chains. The molecular flexibility of the chains are responsible for this characteristic property of polymers. The other important
mechanism for dielectric losses in polymers is considered to be the internal motions or the local movements of the molecular chains of the polymer. These segmental motions are prominent, especially at the glass transition temperature of the polymer. The maxima of dielectric loss is shifted towards the higher temperature side with decrease in PVAc percentage. This suggests that the glass transition temperature increases with decrease in PVAc percentage. The magnitude of $\varepsilon''_{\text{max}}$ is independent of frequency. It indicates that $\alpha$-relaxation process is dominated in polyblends $\beta$-relaxation which is observed in case of MMA is completely masked by the $\alpha$-relaxation process operative in PVAc.

7.7 Conclusions

(i) Dielectric constant decreases as percentage of PVAc in polyblend decreases. This decrease may be due to the increase in molecular interaction.

(ii) Dielectric loss is higher for the samples having higher weight ratio of PVAc.

(iii) Glass transition temperature is shifted towards the higher temperature side as percentage of PVAc in polyblend decreases.
(iv) Observed relaxation peak in polyblends is attributed to the \( \alpha \)-relaxation process.

(v) Compatibility of the two polymers is confirmed by the single relaxation peak.
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