Abstract: Microwave properties of conductive polymers is crucial because of their wide areas of applications such as coating in reflector antennas, coating in electronic equipments, frequency selective surfaces, EMI materials, satellite communication links, microchip antennas, medical applications etc. The present work involves a comparative study of dielectric properties of selected conducting polymers like Polyaniline, Poly (3, 4-ethylenedioxythiophene), Polythiophene, Polypyrrole, and Polyparaphenylene diazomethine (PPDA) in microwave frequencies (S band). DC conductivity of the polymer samples are also evaluated and compared. The microwave properties like dielectric constant, dielectric loss, absorption coefficient, heating coefficient, skin depth and conductivity in the microwave frequency (S band) and DC fields were compared. PEDOT and Polyaniline were found to exhibit excellent properties in DC field and microwave frequencies, which make them potential materials in many of the aforementioned applications.

Microwave properties of conductive polymers is crucial because of their wide areas of applications such as coating in reflector antennas, coating in electronic equipments, frequency selective surfaces, EMI materials, satellite communication links, microchip antennas etc[1-3]. Many microwave absorbing materials based on conducting polymers have been developed. Rimili and coworkers have developed
Chapter 6

Polyaniline (PANI/DEHEPSA) films of high conductivity (5000-6000 S/m) and permittivity of above 6000 over X and S bands [4]. This confirms the metallic character of PANI films and their efficient use in micro-electronic technology such as microwave integrated circuits (MMIC) and microwave devices.

Many microwave absorbing materials based on conducting polymers have been developed [5, 6]. A comparative study of dielectric properties of selected conducting polymers like Polyaniline, Poly (3, 4-ethylenedioxythiophene), Polythiophene, Polypyrrole, and Poly paraphenylene diazomethine (PPDA) in microwave and DC fields is proposed to be undertaken in this study. The microwave properties like dielectric constant, dielectric loss, absorption coefficient, heating coefficient, skin depth and conductivity in the microwave frequency (S band) and DC fields will be compared.

6.1 EXPERIMENTAL METHODS

Polythiophene was prepared by chemical oxidative polymerisation using FeCl₃ as oxidant in nitrobenzene solvent [7]. Poly (3, 4-ethylenedioxythiophene) was prepared in aqueous DBSA micellar solution using FeCl₃ as oxidising agent [8]. Chemical oxidative polymerization of aniline was carried out using FeCl₃ as oxidising agent in aqueous media [9]. Polyaniline (PANI) was doped with 1M solution of camphor sulfonic acid for 24 hrs. Polypyrrole was prepared by the polymerisation of pyrrole with ferric chloride in methanol solvent [10]. The polymer was then doped in IM FeCl₃ solution in nitromethane for 24 hrs. Poly paraphenylene diazomethine (PPDA) was prepared by solution polycondensation of para phenylene diamine and glyoxal trimeric hydrate in DMF at a molar ratio of 1:1 at 120 °C for 5 hrs. PPDA was doped with 1 M solution of HCl for 24 hrs.
The conductivity measurements were carried out on pellet samples using Keithley 2400 Sourcemeter and a Keithley 2182 Nanovoltmeter having a very low noise of 15 nV at 1s response time. The dielectric properties in microwave frequencies (S band 2-4 GHz) were evaluated by Cavity Perturbation Technique. The transmission type resonator used in this experiment was excited with TE\textsubscript{10p} mode by connecting it to an HP8510 C Network Analyzer. The rectangular wave guide cavity resonator was constructed from a section of standard WR-284 wave guide.

The resonant frequency \(f_0\) and the corresponding quality factor \(Q_0\) of each resonant peak of the empty cavity are first determined. Now after selecting a particular resonant frequency, the dielectric sample is introduced into the cavity and the position is adjusted for maximum perturbation (i.e. maximum shift of resonant frequency towards the low frequency region, with minimum amplitude for the peak) and the corresponding change in the frequency of the resonant peak is observed. The new resonant frequency \(f_s\) the corresponding 3 dB bandwidth and the quality factor \(Q\) are determined. The procedure is repeated for other resonant frequencies and the measurements are carried out for all the samples. Knowing the volumes of the sample and the cavity resonator the dielectric parameters can be evaluated [11-15].

The parameters are calculated using the following formulae (1-7)

\[
\varepsilon' = 1 + \frac{f_0 - f_s}{2 f_s} \left[ \frac{V_c}{V_s} \right] \quad \text{(1)} \\
\varepsilon'' = \frac{V_c}{4V_s} \left[ \frac{Q_0 - Q_s}{Q_0 Q_s} \right] \quad \text{(2)}
\]

\[
J = \frac{1}{\varepsilon \tan \delta} \quad \text{(3)} \\
\alpha = \frac{\varepsilon'' f}{n \cdot c} \quad \text{(4)}
\]
\[ \sigma = 2\pi f \varepsilon_0 \varepsilon'' \] \hspace{1cm} (5) \hspace{1cm} \tan \delta = \frac{\varepsilon''}{\varepsilon} \hspace{1cm} (6)

\[ d = \frac{1}{\alpha} \] \hspace{1cm} (7)

Where,

\[ \varepsilon' = \text{Dielectric constant} \hspace{2cm} \varepsilon'' = \text{Loss factor} \]

\[ \varepsilon_0 = \text{Permittivity of free space} \hspace{2cm} \alpha = \text{Absorption Coefficient} \]

\[ d = \text{Penetration depth} \hspace{2cm} \sigma = \text{Conductivity} \]

\[ J = \text{Efficiency of heating} \hspace{2cm} c = \text{Velocity of light} \]

\[ V_c = \text{Volume of cavity} \hspace{2cm} V_s = \text{Volume of sample} \]
6.2 RESULTS AND DISCUSSION

6.2.1 Microwave properties

6.2.1.1 Dielectric constant ($\varepsilon'$)

The dielectric constant of different conducting polymers at S band frequency is compared in Figure 6.1. When an electric field is applied to a material, an induced dipole moment connected to the polarizability appears. This dipole moment comes from a non-homogeneous repartition of the electrical charges in the material. That repartition corresponds to several types of polarization:

- The electronic cloud displacement around the atom called electronic polarization.
- Electric field can modify the electron repartition and consequently the equilibrium location of the atoms in the molecule, called as the atomic polarization.
- Orientation of permanent dipoles causing dipolar polarization

The higher the polarizability of the material the greater will be the dielectric constant.

Figure 6.1 shows that dielectric constant decrease with increase in frequency. This is due to the orientation polarization in the microwave field. The polarization is caused by the alternating accumulation of charges at interfaces between different phases of the material. This dipole polarization may be related to the frictional losses caused by the rotational displacement of molecular dipoles under the influence of the alternating electrical field. As the frequency of the applied field is increased the polarization has no time to reach its steady field value and the orientation polarization is the first that falls. Due to the orientation polarization of
the dipoles, the possibility of dielectric relaxation (so also dielectric loss) cannot be ruled out at higher frequencies. This might result in the decrease of ‘\( \varepsilon' \)’ with frequency [16-17]. It can be seen that the dielectric constant is highest for PEDOT, and lowest for PPDA.

![Figure 6.1 Variation of dielectric constant (\( \varepsilon' \)) with frequency for various conducting polymers.](image)

In conducting polymers conductivity is not constant along the conducting paths and that several relaxation times may coexist. The distribution of conductivity leads to a dispersion of ‘\( \varepsilon' \)’ and ‘\( \sigma \)’ without any polarization phenomenon. So the large dielectric constants measured at low frequency in conducting polymers may be linked to the heterogeneity of materials in the form of a conductivity variation along the conducting path. At low frequencies, the different polarizations (electronic, atomic and dipolar polarizations) contribute to a high permittivity ‘\( \varepsilon' \)’ value, beyond that each kind of polarization will create one resonance or one
relaxation process and \( \varepsilon' \) decreases. The same trend in variation of dielectric constant with frequency has been reported by Chandrasekhar and Naishadham [18]. The decrease of permittivity with increase in frequency reveals that the systems exhibit strong interfacial polarization at low frequency [19].

6.2.1.2 Dielectric loss \((\varepsilon'')\)

The dielectric loss of different conducting polymers at S band frequency is compared in Figure 6.2.

![Graph](image)

Figure 6.2 Variation of dielectric loss \((\varepsilon'')\) with frequency for various conducting polymers.

The reorientation of the unassociated groups, because of their high dipole moment, is believed to be a major contributor to the dielectric loss \((\varepsilon'')\). At higher
frequency, the rotatory motion of the molecules may not be sufficiently rapid for the attainment of equilibrium with the field. The polarization then acquires a component out of phase with the field, and the displacement current acquires a conductance component in phase with the field, resulting in thermal dissipation of energy. When this occurs, dielectric losses will be generated.

Dielectric loss tends to increase with increase in frequency within the range 2.4 to 2.9 GHz. As the frequency is increased the inertia of the molecule and the binding forces become dominant and it is the basis for high dielectric loss at higher frequencies. The dielectric loss factor leads to so called conductivity relaxation. From the Figure 6.2 it is clear that PEDOT is showing higher dielectric loss followed by PANI, PTH, PPY and PPDA.

The loss factor must be regarded as the contribution of three distinct effects, due to DC conductance, interfacial polarization, and dipole orientation or Debye loss factor, i.e. [20]

\[ \varepsilon'' = \varepsilon''_{\text{conduction}} + \varepsilon''_{\text{polarization}} + \varepsilon''_{\text{dipolar orientation}} \]

At lower frequencies, the loss factor decreases linearly with the increasing of frequency. This result suggests that dc conductivity process is more significant than interfacial polarization in these materials. The interfacial polarization equation does not follow a linear behavior at lower frequencies. Generally it is believed in dielectric analysis that the high frequency permittivity (dielectric constant) is mainly associated to dipolar relaxation, whereas at lower frequency and higher temperature, the contributions of interfacial polarization and DC conductivity become more significant in both \( \varepsilon' \) and \( \varepsilon'' \). Interfacial polarization arises
mainly from the existence of polar and conductive regions dispersed in relatively less polar and insulating matrix. This phenomenon is particularly important in conjugated polymers and may interfere on the relaxation process analysis [21]. The value of $\varepsilon''$ polarization is related to the molecular polarization phenomena such as dipole rotation (Debye model), space charge relaxation (Maxwell-Wagner model) and hopping of confined charges [22-24].

6.2.1.3 Loss tangent (tan $\delta$)

The tan $\delta$ is commonly employed as a direct measure of the dielectric loss, which in turn provides a measure of the conductivity. Angle $\delta$ is the angle between the vector for the amplitude of the total current and that for the amplitude of charging current and the tangent of this angle is the loss tangent [25]. Since it is directly related to the dielectric loss, it shows the same behavior as that of dielectric loss. Figure 6.3 shows that the loss tangent of conducting polymers increases with frequency.
Figure 6.3 Variation of loss tangent (tanδ) with frequency for various conducting polymers.

6.2.1.4 Absorption coefficient (α)

Materials can be classified in terms of their transparency of wave through it, which in turn specify the absorption of electromagnetic waves when it passes through the medium [25]. The transparency is defined by the parameter, absorption coefficient. Absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behavior as dielectric loss. Figure 6.4 shows that PEDOT has highest absorption coefficient followed by PANI, PTH, PPY and PPDA respectively.
Microwave and electrical properties of selected conducting polymers

6.2.1.5 Conductivity ($\sigma$)

The microwave conductivity is a direct function of dielectric loss and so it shows a similar variation with frequency as the dielectric loss factor. Figure 6.5 shows that conductivity increases with frequency. Here also the trend continues with PEDOT showing the best conductivity followed by PANI, PTH, PPY and PPDA successively.

Figure 6.4 Variation of absorption coefficient ($\alpha$) with frequency for various conducting polymers.
Figure 6.5 Variation of conductivity ($\sigma$) with frequency for various conducting polymers.

6.2.1.6 Dielectric heating coefficient ($J$)

Practically all applications of polymers in electrical and electronic engineering require materials with a low tan $\delta$. However, one application that takes advantage of a high value of loss tangent is high frequency dielectric heating. As the heat generation in polymers is due to relaxation loss, the efficiency of heating of a polymer is compared by means of a heating coefficient [26] $J'$. Higher the $J'$ value, poorer will be the polymer for dielectric heating purposes. Of course, the heat generated in the polymeric material comes from the loss tangent, but that loss may not come entirely from the relaxation loss. Rather, conductivity of the polymeric material may also contribute to the tan $\delta$. This situation may be compared with ohmic heating of metals [13].

The heating coefficient is inversely related to the loss tangent and hence it decreases with increase in frequency.
Microwave and electrical properties of selected conducting polymers

6.2.1.7 Skin depth (d)

Figure 6.7 shows that skin depth decreases with increase in frequency. It is the effective distance of penetration of an electromagnetic wave into the material. It can be applied to a conductor carrying high frequency signals. The self inductance of the conductor effectively limits the conduction of the signal to its outer shell and the shell thickness is the skin depth, which decreases with increase in frequency. PPDA shows highest skin depth followed by PPY, PTH, PANI and PEDOT.
Figure 6.7 Variation of Skin depth ($d$) with frequency for various conducting polymers.

6.2.2 DC conductivity

DC conductivity of the polymer samples are tabulated in Table 6.1. From the Table 6.1 it can be seen that the DC conductivity of the conducting polymers follows the order PEDOT > PANI > PTH > PPY > PPDA.

PANI and PEDOT are reported to show very good DC conductivity. In the case of PEDOT synthesized in dodecyl benzene sulfonic acid (DBSA) micellar solutions, DBSA–FeCl$_3$ complex is expected to be formed. The anchoring efficiency of dodecylbenzene sulfonate anion with iron (III) on the PEDOT particles seems to increase the doping of the bulky anionic surfactant and gives good conductivity [8].
Table 6.1 DC conductivity of the polymer samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Dopant</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PEDOT</td>
<td>FeCl₃ &amp; DBSA</td>
<td>26.41</td>
</tr>
<tr>
<td>2</td>
<td>PANI</td>
<td>CSA</td>
<td>2.45</td>
</tr>
<tr>
<td>3</td>
<td>PTH</td>
<td>FeCl₃</td>
<td>4.76 x 10⁻¹</td>
</tr>
<tr>
<td>4</td>
<td>PPY</td>
<td>FeCl₃</td>
<td>1.25 x 10⁻¹</td>
</tr>
<tr>
<td>5</td>
<td>PPDA</td>
<td>HCl</td>
<td>1.36 x 10⁻⁴</td>
</tr>
</tbody>
</table>

6.3 CONCLUSIONS

Dielectric constant, dielectric loss, conductivity, absorption coefficient, heating coefficient, loss tangent and skin depth of conducting polymers like PEDOT, PTH, PANI and PPDA were studied and compared at S band frequency. The important conclusions are

- Dielectric constant, Dielectric loss, tan δ, conductivity and absorption coefficient of the conducting polymers are highest for PEDOT and PANI
- Heating coefficient and skin depth are lower for PEDOT and PANI
- Comparing the different polymers, better microwave properties are shown by PEDOT and PANI
Dielectric constant, heating coefficient and skin depth tend to decrease with increase in frequency and dielectric loss, conductivity, loss tangent and absorption coefficient increases with increase in frequency in S band. PEDOT doped with DBSA and FeCl₃ was found to have very good DC conductivity of 26.41 S/m. PANI also offered very good conductivity, 2.45 S/m. DC conductivity of the conducting polymers are in the order PEDOT > PANI > PTH > PPY > PPDA

The microwave and electrical properties of some important conducting polymers were successfully evaluated. PANI and PEDOT showed good microwave and electrical properties and hence have potential applications in EMI shielding, microwave absorption etc.
6.4 REFERENCES


